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Innovative Technology Verification Report

Technologies for Monitoring and Measurement of Dioxin and Dioxin-like Compounds in Soil and Sediment

CAPE Technologies LLC
DF1 Dioxin/Furan Immunoassay Kit
PCB TEQ Immunoassay Kit

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DF1 Dioxin/Furan Immunoassay Kit
PCB TEQ Immunoassay Kit

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. Under the mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development (ORD) provides data and scientific support that can be used to solve environmental problems, build the scientific knowledge base needed to manage ecological resources wisely, understand how pollutants affect public health, and prevent or reduce environmental risks.

The National Exposure Research Laboratory is the Agency's center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. Goals of the Laboratory's research program are to (1) develop and evaluate methods and technologies for characterizing and monitoring air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies designed for characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act (RCRA) sites. The SITE Program was created to provide reliable cost and performance data in order to speed the acceptance and use of innovative remediation, characterization, and monitoring technologies by the regulatory and user community.

Effective monitoring and measurement technologies are needed to assess the degree of contamination at a site, provide data that can be used to determine the risk to public health or the environment, and monitor the success or failure of a remediation process. One component of the EPA SITE Program, the Monitoring and Measurement Technology (MMT) Program, demonstrates and evaluates innovative technologies to meet these needs.

Candidate technologies can originate within the federal government or the private sector. Through the SITE Program, developers are given the opportunity to conduct a rigorous demonstration of their technologies under actual field conditions. By completing the demonstration and distributing the results, the Agency establishes a baseline for acceptance and use of these technologies. The MMT Program is managed by the ORD's Environmental Sciences Division in Las Vegas, Nevada.

Gary Foley, Ph.D.
Director
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Abstract

A demonstration of technologies for determining the presence of dioxin and dioxin-like compounds in soil and sediment was conducted under the U.S. Environmental Protection Agency's (EPA's) Superfund Innovative Technology Evaluation Program in Saginaw, Michigan, at Green Point Environmental Learning Center from April 26 to May 5, 2004. This innovative technology verification report describes the objectives and the results of that demonstration, and serves to verify the performance and cost of the CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits. Four other technologies were evaluated as part of this demonstration, and separate reports have been prepared for each technology. The objectives of the demonstration included evaluating each technology's accuracy, precision, sensitivity, sample throughput, tendency for matrix effects, and cost. The test also included an assessment of how well the technology's results compared to those generated by established laboratory methods using high-resolution mass spectrometry (HRMS). The demonstration objectives were accomplished by evaluating the results generated by the technology from 209 soil, sediment, and extract samples. The test samples included performance evaluation (PE) samples (i.e., contaminant concentrations were certified or the samples were spiked with known contaminants) and environmental samples collected from 10 different sampling locations.

The CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits are immunoassay techniques that report the total toxicity equivalents (TEQ) of dioxin/furans and polychlorinated biphenyls (PCBs), respectively. As part of the performance evaluation, the technology results were compared to TEQ results generated by a reference laboratory, AXYS Analytical Services, using EPA Methods 1613B and 1668A, which involve the use of HRMS. It should be noted that the results generated by the CAPE Technologies kits may not directly correlate to HRMS TEQ in all cases because it is known that the congener responses and cross-reactivities of the kits are not identical to the toxicity equivalency factors that are used to convert congener HRMS concentration values to TEQ. The effect of cross-reactivities may contribute to this technology's reporting results that are biased high or low compared to HRMS TEQ results. Therefore, these kits should not be viewed as producing an equivalent measurement value to HRMS TEQ, but as a screening value to approximate HRMS TEQ. As described in CAPE Technologies literature, the best results for immunoassay screening are obtained on a single site basis. The ideal approach involves partially characterizing a site by HRMS, using those results to develop a site specific immunoassay calibration, and refining that calibration over time, based on an ongoing stream of confirmatory HRMS samples. This approach was not evaluated during this demonstration; samples from multiple sites were pooled and a single calibration was used.

A summary of the performance of the CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits is as follows: The CAPE Technologies kits generally reported data higher than the certified PE and reference laboratory values. The technology's estimated method detection limit [12 to 35 picogram per gram (pg/g)] was higher than what was reported by the developer (1 pg/g TEQ). The CAPE Technologies $TEQ_{D/F}$ results that were generated in the laboratory and in the field for replicate samples were statistically different for 19% of the samples, and of these samples, CAPE Technologies laboratory results were more comparable to the reference laboratory results. No significant effect was observed for the reproducibility of CAPE Technologies results by matrix type (soil vs. sediment vs. extract) or by sample type (PE vs. environmental vs extract). A slight effect was observed for total TEQ values by PAH concentration, but the effect was not statistically significant for $TEQ_{D/F}$ or TEQ_{PCB}. The technology had a rate of false negative results of 3 to 5% around 20 pg/g TEQ, with false positive rates ranging from 11 to 14%. However, CAPE Technologies's false positive and false negative rates around 50 pg/g were generally lower for all three TEQ types, ranging from 4 to 10%. These data suggest the CAPE Technologies kits could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for samples above and below 50 pg/g TEQ, particularly considering that both the cost ($59,234 vs. $398,029) and the time (three weeks vs. eight months) to analyze the 209 demonstration samples were significantly less than those of the reference laboratory.

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Abbreviations, Acronyms, and Symbols

Ah	aryl hydrocarbon
ANOVA	analysis of variance
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CIL	Cambridge Isotope Laboratories
cm	centimeter
CoA	Certificate of Analysis
COC	chain of custody
CRM	certified reference material
DER	data evaluation report
D/F	dioxin/furan
DNR	Department of Natural Resources
D/QAPP	demonstration and quality assurance project plan
EIA	enzyme immunoassay
ELC	Environmental Learning Center
ELISA	enzyme-linked immunosorbent assay
EMDL	estimated method detection limit
EMPC	estimated maximum possible concentration
EPA	Environmental Protection Agency
ERA	Environmental Resource Associates
FDA	Food and Drug Administration
g	gram
GC	gas chromatography
HPLC/GPC	high-performance liquid chromatography/gel permeation chromatography
HRP	horseradish peroxidase
HRGC	high-resolution capillary gas chromatography
HRMS	high-resolution mass spectrometry
i.d.	internal diameter
IDW	investigation-derived waste
ITVR	innovative technology verification report
kg	kilogram
L	liter
LRMS	low-resolution mass spectrometry

Abbreviations, Acronyms, and Symbols (Continued)

µL	microliter
µm	micrometer
m	meter
MDEQ	Michigan Department of Environmental Quality
mg	milligram
mL	milliliter
mm	millimeter
MDL	method detection limit
MMT	Monitoring and Measurement Technology
MS	mass spectrometry
NERL	National Exposure Research Laboratory
ng	nanogram
NIST	National Institute for Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
OD	optical density
ORD	Office of Research and Development
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCDD/F	polychlorinated dibenzo-p-dioxin/dibenzofuran
PCP	pentachlorophenol
PE	performance evaluation
pg	picogram
ppb	parts per billion; nanogram/g; ng/g
ppm	parts per million; microgram/g; µg/g
ppt	parts per trillion; picogram/g; pg/g
psi	pound per square inch
QA/QC	quality assurance/quality control
RM	reference material
RPD	relative percent difference
RSD	relative standard deviation
SDL	sample-specific detection limit
SIM	selected ion monitoring
SITE	Superfund Innovative Technology Evaluation
SOP	standard operating procedure
SRM	Standard Reference Material®
TCDD	tetrachlorodibenzo-*p*-dioxin
TEF	toxicity equivalency factor

Abbreviations, Acronyms, and Symbols (Continued)

TEG	tetraethylene glycol
TEQ	toxicity equivalent
$TEQ_{D/F}$	total toxicity equivalents of dioxins/furans
TEQ_{PCB}	total toxicity equivalents of World Health Organization dioxin-like polychlorinated biphenyls
TOC	total organic carbon
total TEQ	total toxicity equivalents including the sum of the dioxin/furan and World Health Organization dioxin-like polychlorinated biphenyls
WHO	World Health Organization

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Chapter 1
Introduction

The U.S. Environmental Protection Agency (EPA), Office of Research and Development (ORD), National Exposure Research Laboratory (NERL) contracted with Battelle (Columbus, Ohio) to conduct a demonstration of monitoring and measurement technologies for dioxin and dioxin-like compounds in soil and sediment. A field demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program. The purpose of this demonstration was to obtain reliable performance and cost data on the technologies to provide (1) potential users with a better understanding of the technologies' performance and operating costs under well-defined field conditions and (2) the technology developers with documented results that will help promote the acceptance and use of their technologies.

This innovative technology verification report (ITVR) describes the SITE MMT Program and the scope of this demonstration (Chapter 1); the CAPE Technologies LLC DF1 Dioxin/Furan and polychlorinated biphenyl (PCB) toxicity equivalent (TEQ) Immunoassay kits (Chapter 2); the demonstration site and the sampling locations (Chapter 3); the demonstration approach (Chapter 4); the confirmatory process (Chapter 5); the assessment of reference method data quality (Chapter 6); the performance of the technology (Chapter 7); the economic analysis for the technology and reference method (Chapter 8); the demonstration results in summary form (Chapter 9); and the references used to prepare this report (Chapter 10). Appendix A contains a verification statement; Appendix B contains supplemental information provided by the developer; Appendix C is a summary of method blank and batch duplicate data by the reference laboratory; and Appendix D contains a one-to-one matching of the developer and reference laboratory data.

1.1 Description of the SITE MMT Program

Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the EPA. The SITE Program was established by the EPA Office of Solid Waste and Emergency Response and ORD under the Superfund Amendments and Reauthorization Act of 1986. The overall goal of the Program is to conduct performance verification studies and to promote the acceptance of innovative technologies that may be used to achieve long-term protection of human health and the environment. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies, (2) demonstrate promising technologies and gather reliable performance and cost information to support site characterization and remediation activities, and (3) develop procedures and policies that encourage use of innovative technologies at Superfund sites as well as at other waste sites or commercial facilities. The SITE Program includes the following elements:

- MMT Program—Evaluates technologies that sample, detect, monitor, or measure hazardous and toxic substances. These technologies are expected to provide better, faster, or more cost-effective methods for producing real-time data during site characterization and remediation efforts than conventional laboratory technologies.

- Remediation Technology Program—Conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.

- Technology Transfer Program—Provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and participating

technologies. It also supports the technologies by offering technical assistance, training, and workshops.

The MMT Program's technology verification process is designed to conduct demonstrations that will generate high-quality data so that potential users have reliable information regarding the technology performance and cost. Four steps are inherent in the process: (1) needs identification and technology selection, (2) demonstration planning and implementation, (3) report preparation, and (4) information distribution. The first step of the technology verification process begins with identifying technology needs of the EPA and regulated community. The EPA Regional offices, the U.S. Department of Energy, the U.S. Department of Defense, industry, and state environmental regulatory agencies are asked to identify technology needs for sampling, measurement, and monitoring of environmental media. Once a need is identified, a search is conducted to identify suitable technologies that will address the need. The technology search and identification process consists of examining industry and trade publications, attending related conferences, and exploring leads from technology developers and industry experts. Selection of technologies for field testing includes evaluation of the candidate technologies based on several criteria. A suitable technology for field testing

- is designed for use in the field or in a mobile laboratory,
- is applicable to a variety of environmentally contaminated sites,
- has potential for solving problems that current methods cannot satisfactorily address,
- has estimated costs that are lower than those of conventional methods,
- is likely to achieve equivalent or better results than current methods in areas such as data quality and turnaround time,
- uses techniques that are easier or safer than current methods, and
- is commercially available.

Once candidate technologies are identified, developers are asked to participate in a developer conference. This conference gives the developers an opportunity to describe their technologies' performance and to learn about the MMT Program.

The second step of the technology verification process is to plan and implement a demonstration that will generate representative, high-quality data to assist potential users in selecting a technology. Demonstration planning activities include a pre-demonstration sampling and analysis investigation that assesses existing conditions at the proposed demonstration site or sites. The objectives of the pre-demonstration investigation are to (1) confirm available information on applicable physical, chemical, and biological characteristics of contaminated media at the sites to justify selection of site areas for the demonstration; (2) provide the technology developers with an opportunity to evaluate the areas, analyze representative samples, and identify logistical requirements; (3) assess the overall logistical and quality assurance requirements for conducting the demonstration; and (4) select and provide the reference laboratory with an opportunity to identify any matrix-specific analytical problems associated with the contaminated media and to propose appropriate solutions. Information generated through the pre-demonstration investigation is used to develop the final demonstration design and to confirm the nature and source of samples that will be used in the demonstration.

Demonstration planning activities also include preparation of a demonstration plan that describes the procedures to verify the performance and cost of each technology. The demonstration plan incorporates information generated during the pre-demonstration investigation as well as input from technology developers, demonstration site representatives, and technical peer reviewers. The demonstration plan also incorporates the quality assurance (QA)/quality control (QC) elements needed to produce data of sufficient quality to document the performance and cost of each technology.

During the demonstration, each technology is evaluated independently and, when possible and appropriate, is compared to a reference technology. The performance and cost of one technology are not compared to those of another technology evaluated in the demonstration. Rather, demonstration data are used to evaluate the individual performance, cost, advantages, limitations, and field applicability of each technology.

As part of the third step of the technology verification process, the EPA publishes a verification statement (Appendix A) and a detailed evaluation of each technology in an ITVR. To ensure its quality, the ITVR is published only after comments from the technology developer and external peer reviewers are satisfactorily addressed. All demonstration data used to evaluate each technology are summarized in a data evaluation report (DER) that constitutes a complete record of the demonstration. The DER includes audit reports, observer reports, completed data validation checklists, certificates of analysis, and the data packages (i.e., raw data) from the reference laboratory. The DER is not published as an EPA document, but a copy may be obtained from the EPA project manager.

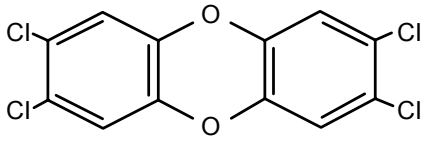
The fourth step of the verification process is to distribute demonstration information. To benefit technology developers and potential technology users, the EPA makes presentations, publishes and distributes fact sheets, newsletters, bulletins and ITVRs through direct mailings and on the Internet. Information on the SITE Program is available on the EPA ORD Web site (http://www.epa.gov/ORD/SITE). Additionally, a Visitor's Day, which is held in conjunction with the demonstration, allows the developers to showcase their technologies, and gives potential users the opportunity to have a firsthand look at the technologies in operation.

1.2 Scope of This Demonstration

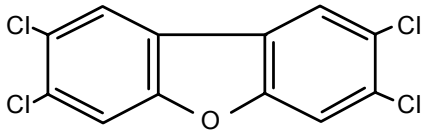
Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, commonly referred to collectively as "dioxins," are of significant concern in site remediation projects and human health assessments because they are highly toxic. Dioxins and furans are halogenated aromatic hydrocarbons and are similar in structure as shown in Figure 1-1. They have similar chemical and physical properties. Chlorinated dioxins and furans are technically referred to as polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). For the purposes of this document, they will be referred to simply as "dioxins," "PCDD/F," or "D/F." Dioxins and furans are not intentionally produced in most chemical processes. However, they can be synthesized directly and are commonly generated as by-products of various combustion and chemical processes.[1] They are colorless crystals or solids with high melting points, very low water solubility, high fat solubility, and low volatility. Dioxins and furans are extremely stable under most environmental conditions, making them persistent once released in the environment. Because they are fat soluble, they also tend to bioaccumulate.

There are 75 individual chlorinated dioxins and 135 individual chlorinated furans. Each individual dioxin and furan is referred to as a congener. The properties of each congener vary according to the number of chlorine atoms present and the position where the chlorines are attached. The congeners with chlorines attached at a minimum in the 2, 3, 7, and 8 positions are considered most toxic. A total of seven dioxin and 10 furan congeners contain chlorines in the 2, 3, 7, 8 positions and, of these, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is one of the most toxic and serves as the marker compound for this class.

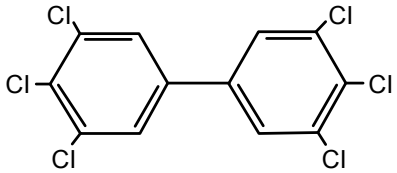
Certain polychlorinated biphenyls (PCBs) have structural and conformational similarities to dioxin compounds (Figure 1-1) and are therefore expected to exhibit toxicological similarities to dioxins as well. Currently only 12 of the total 209 PCB congeners are thought to have "dioxin-like" toxicity. These 12 are PCBs with four or more chlorines with just one or no substitution in the ortho position, and which assume a flat configuration with rings in the same plane. These



2,3,7,8-Tetrachlorodibenzo-p-dioxin



2,3,7,8-Tetrachlorodibenzofuran



3,3',4,4',5,5'-Hexachlorobiphenyl

Figure 1-1. Representative dioxin, furan, and polychlorinated biphenyl structure.

"dioxin-like" PCBs are often refered to as non-ortho and mono-ortho substituted coplanar PCBs.

Conventional analytical methods for determining concentrations of dioxin and dioxin-like compounds are time-consuming and costly. For example, EPA standard methods require solvent extraction of the sample, processing the extract through multiple cleanup columns, and analyzing the cleaned fraction by gas chromatography (GC)/high-resolution mass spectrometry (HRMS). The use of a simple, rapid, cost-effective analytical method would allow field personnel to quickly assess the extent of contamination at a site and could be used to direct or monitor remediation or risk assessment activities.

This data could be used to provide immediate feedback on potential health risks associated with the site and permit the development of a more focused and cost-effective sampling strategy. At this time, more affordable and quicker analytical techniques will not replace HRMS. However, before adopting an alternative to traditional laboratory-based methods, a thorough assessment of how commercially available technologies compare to conventional laboratory-based analytical methods using certified, spiked, and environmental samples is warranted. A summary of the demonstration activities to evaluate measurement technologies for dioxin and dioxin-like compounds in soil and sediment is provided below. The experimental design and demonstration approach are described in greater detail in Chapter 4 and was published in the Demonstration and Quality Assurance Project Plan (D/QAPP).[2]

1.2.1 Organization of Demonstration

The key organizations and personnel involved in the demonstration, including the roles and responsibilities of each, are fully described in the D/QAPP.[2] The EPA/ NERL had overall responsibility for this project. The EPA reviewed and concurred with all project deliverables including the D/QAPP and the ITVRs, provided oversight during the demonstration, and participated in the Visitor's Day. Battelle served as the verification testing organization for EPA/NERL. Battelle's responsibilities included developing and implementing all elements of the D/QAPP; scheduling and coordinating the activities of all demonstration participants; coordinating the collection of environmental samples; serving as the characterization laboratory by performing the homogenization of the environmental samples and confirming the efficacy of the homogenization and approximate sample concentrations; conducting the demonstration by implementing the D/QAPP; summarizing, evaluating, interpreting, and documenting demonstration data for inclusion in this report; and preparing draft and final versions of each developer's ITVR. The developers were five companies who submitted technologies for evaluation during this demonstration. The responsibilities of the developers included providing input to, reviewing, and concurring with the D/QAPP; providing personnel and supplies as needed for the demonstration; operating their technology during the demonstration; and reviewing and commenting on their technology's ITVR. AXYS Analytical Services, Ltd. was selected to serve as the reference analytical laboratory. AXYS analyzed each demonstration sample by EPA Method 1613B[3] and EPA Method 1668A[4] according to the statement of work provided in the D/QAPP. The Michigan Department of Environmental Quality (MDEQ) hosted the demonstration, coordinated the activities of and participated in Visitor's Day, and collected and provided some of the environmental samples that were used in the demonstration. The Dioxin SITE Demonstration Panel served as technical advisors and observers of the demonstration activities. Panel membership, which is outlined in the D/QAPP, included representation from EPA Regions 1, 2, 3, 4, 5, 7, and 9; EPA Program Offices; the MDEQ; and the U.S. Fish and Wildlife Services. Members of the panel participated in five conference calls with the EPA, Battelle, AXYS, and the developers. The panel contributed to the experimental design and D/QAPP development; logistics for the demonstration, including site selection, sample collection, reference laboratory selection, and data analysis; and technology evaluation procedures. As an example of the significant impact the panel had on the demonstration, it was the EPA members of the panel who suggested expanding the scope of the project from focusing exclusively on dioxins and furans, to also include PCBs and the generation of characterization data for polynuclear aromatic hydrocarbons (PAHs).

1.2.2 Sample Descriptions and Experimental Design

Soil and sediment samples with a variety of distinguishing characteristics such as high levels of PCBs and PAHs were analyzed by each participant. Samples were collected from a variety of dioxin-contaminated soil and sediment sampling locations around the country. Samples were identified and supplied through EPA Regions 2, 3, 4, 5, and 7 and the MDEQ. The samples were homogenized and characterized by the characterization laboratory prior to use in the demonstration to ensure a variety of homogeneous, environmentally derived samples with concentrations over a large dynamic range (< 50 to > 10,000 picogram/gram [pg/g]) were included. The environmental samples comprised 128 of the 209 samples included in the demonstration (61%). Performance evaluation (PE) samples were obtained from five commercial sources. PE samples consisted of known quantities of dioxin and dioxin-like compounds. Fifty-eight of the 209 demonstration samples (28%) were PE samples. A suite of solvent extracts was included in the demonstration to minimize the impact of sample homogenization and to provide a uniform matrix for evaluation. A total of 23 extracts (11% of the total number of samples) was included in the demonstration. The demonstration samples are described in greater detail in Section 4.3.

1.2.3 Overview of Field Demonstration

All technology developers participated in a pre-demonstration study where a representative subset of the demonstration samples was analyzed. The pre-demonstration results indicated that the CAPE Technologies technology was suitable for participation in the demonstration. The demonstration of technologies for the measurement of dioxin and dioxin-like compounds was conducted at the Green Point Environmental Learning Center in Saginaw, Michigan, from April 26 to May 5, 2004. Five technologies, including immunoassay test kits and aryl hydrocarbon (Ah)-receptor binding technologies, participated in the demonstration. The operating procedures for the participating technologies are described in the D/QAPP.

The technologies were operated by the developers. Because the sample throughput of the technologies varied widely, it was at the discretion of the developers how many of the 209 demonstration samples were analyzed in the field. Results from the demonstration samples, in comparison with results generated by AXYS using standard analytical methods, were used to evaluate the analytical performance of the technologies, including the parameters of accuracy, precision, and comparability. Observations from the field demonstration were used to assess sample throughput, ease of use, health and safety aspects, and the field portability of each technology. The performance evaluation of the CAPE Technologies LLC DF1 Dioxin/Furan and PCB TEQ Immunoassay kits is presented in this ITVR. Separate ITVRs have been published for the other four participating technologies.

Chapter 2
Description of CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay Kits

This technology description is based on information provided by CAPE Technologies and only editorial changes were made to ensure document consistency. Actual cost and performance data, as reported and observed during the demonstration, will be provided later in this document. The DF1 Dioxin/Furan Immunoassay Kit from CAPE Technologies is an enzyme immunoassay (EIA) test kit containing a polyclonal antibody specific for PCDD/Fs. The company's PCB TEQ Immunoassay Kit from CAPE Technologies is an EIA test kit containing a polyclonal antibody specific for dioxin-like PCBs. Both semi-quantitative screening and quantitative analysis are possible with these kits, but this evaluation focused only on quantitative analysis. Samples can be prepared for analysis by EIA using a variety of methods. Extracts of soil, sediment, food, water, fly ash, stack gas, tissue, or other samples that have been prepared by conventional extraction methods can be exchanged to a water-miscible solvent system for analysis using the CAPE Technologies immunoassay kits. More commonly, immunoassay specific sample preparation methods are used to reduce the time, effort, and cost of sample preparation. Design and operation of the two kits are nearly identical except for the combination of antibody and enzyme conjugate that is responsible for the specificity of each kit. One sample preparation method can be used for both kits, providing separate dioxin/furan and PCB fractions. These fractions can be analyzed by the respective kits, giving separate TEQ results for both dioxin/furan and PCB.

2.1 Company History

CAPE Technologies was founded in 1996 by Robert Carlson and Robert Harrison to develop and market immunoassay test kits and support technology for analysis of dioxins and related compounds. Its headquarters are in South Portland, Maine. Primary products are immunoassay kits and sample preparation kits for analysis of dioxin and related compounds; analytical services are also offered.

The principals of CAPE Technologies have more than 40 years combined experience in the design, development, validation, marketing, and technical support of immunoassays for environmental analysis, including five EPA 4000 series methods. In 2000, CAPE Technologies was selected by EPA Region 1 as an Environmental Technology Innovator of the Year.

2.2 Product History

The CAPE Technologies DF1 Dioxin/Furan Immunoassay Kit was first developed in 1996. Optimization and validation of the immunoassay as a TEQ predictor were pursued over the next two years in collaboration with several established dioxin laboratories around the world. During the same time period, the first immunoassay-specific sample processing methods were developed. Commercial sales of the DF1 kit began in late 1998. Concurrent refinement of sample preparation methods resulted in a simple extraction and one step oxidative cleanup for high pg/g levels in soil. This combination of sample preparation method and DF1 immunoassay was applied to rapid soil screening using field samples from two well known U.S. dioxin sites. The resulting data were reviewed by the U.S. EPA, leading to the acceptance in June 2001 of SW-846 Method 4025 based on the DF1 kit. During this validation process a more rigorous cleanup method was developed for soils, based on portions of the SW-846 Method 8290 cleanup. This method, when used with the DF1 kit, is referred to as modified Method 4025, or 4025m. Method 4025m allows for low pg/g analysis in solid samples using a 5-g sample and easily removes

high levels of aliphatic oils which occur commonly in dioxin contaminated soils. Commercial sale of this kit based sample preparation system began in 2002. The CAPE Technologies portion of the current study used this system exclusively.

An early PCB TEQ kit was developed and partially validated by CAPE Technologies before 1998, but was not released to market because of unacceptably high cross-reactivity for PCB 77. After various studies suggested changes in congener recognition profiles, the CAPE Technologies PCB TEQ kit was developed in 1998 based on a new antibody with improved specificity. In 2000, the sample cleanup of Method 4025m was modified to provide a separate PCB fraction for immunoassay analysis. The resulting single cleanup and fractionation were used by CAPE Technologies in the current study. In 2002, a validation study was started for the purpose of obtaining EPA acceptance of this method as SW-846 Method 4026. Partly because of the delay in EPA's dioxin reassessment, the validation study was put on indefinite hold. Commercial sales of the PCB TEQ Kit began in 2004 and are expected to spur reopening of the Method 4026 validation study.

2.3 Technology Description

The DF1 Dioxin/Furan Immunoassay Kit (Figure 2-1) and the PCB TEQ Immunoassay Kit are nearly identical in design and operation. They differ primarily in the antibody and competitor-horseradish peroxidase (HRP) conjugate used, and in the specificity resulting from these specially developed reagents. Both kits are designed to provide results as TEQ concentrations by responding to the toxic dioxin/furan or PCB congeners in approximate correlation with their toxic equivalency factors (TEFs). Both tests recognize multiple congeners, preferentially targeting congeners with high TEF values, i.e., those with the highest toxicity relative to 2,3,7,8-TCDD. The specificity of the dioxin/furan test is predominantly for dioxins and furans that contain 3 to 6 chlorines, with a strong preference for the 2,3,7,8 chlorinated congeners. This specificity roughly parallels the TEF values of the individual dioxin and furan congeners. The specificity of the PCB TEQ test is predominantly for non-ortho and mono-ortho chlorinated congeners, with a strong preference for PCBs 126 and 169. This specificity roughly parallels the TEF values of the individual PCB congeners. Both tests have only minimal recognition of the target compounds of the other test.

The immunoassay specific sample preparation begins with an organic solvent extraction. The extracts are then processed through an immunoassay specific cleanup. In the case of this evaluation, the cleanup combines two familiar parts of the Method 8290 cleanup, but in a way that allows for rapid batch processing using inexpensive disposable columns and no specialized equipment. Since the cleanup is performed in solvents incompatible with the immunoassays, a solvent exchange is required

Figure 2-1. CAPE Technologies DF1 Dioxin/Furan Immunoassay kit.

after the cleanup. Dioxins, furans, and dioxin-like PCBs have very low volatility and are retained during this solvent exchange in a small volume of a keeper solution (Triton X-100 detergent in tetraethylene glycol [TEG]) after evaporation of the original solvent. Methanol is added to dilute this solution, and the methanol-TEG-Triton mixture is added directly to the immunoassay tubes. During the first immunoassay incubation, analyte molecules are specifically bound by the analyte-specific antibodies, which have been immobilized on the immunoassay tube surface. After washing away the unbound material, the bound analyte molecules remain, and a competitor-HRP conjugate is added. Bound analyte molecules occupy the binding sites of the antibodies in proportion to the dioxin/furan or dioxin-like PCB content of the sample, reducing the binding of the competitor-HRP conjugate. After an incubation period, unbound conjugate is removed, and the test tubes are washed thoroughly. The incubation period can be 2 to 24 hours; for convenience, during the field demonstration, the samples were incubated overnight (~12 hours). The amount of conjugate bound by the anti-analyte antibody is inversely related to the amount of analyte originally present in the sample. Finally, a solution of chromogenic HRP substrate and hydrogen peroxide is added to the test tubes. Color development is directly proportional to enzyme concentration and inversely related to the dioxin/furan or dioxin-like PCB concentration in the original sample. The test tubes are analyzed using a tube reader or spectrophotometer to measure the optical density (OD). The OD values of unknown samples are compared to the OD values of standards to determine the level of dioxin/furan or dioxin-like PCB in the samples.

The final measured EIA response is the sum of the individual congener responses. Both the dioxin/furan kit and the PCB TEQ kit correlate with TEQ because the cross-reaction profile of each kit roughly correlates with the TEF values of its respective target congeners.

Accuracy may vary solely because of the variability of congener composition. To maximize accuracy, the variability of congener composition in the target sample population should be known. The best performance is achieved when all samples are from a single group that share as many properties as possible (common source of contamination, similar congener composition, similar sample matrix, etc.).

The limit of detection for the CAPE Technologies Dioxin/Furan Immunoassay Kit is approximately 4 pg of 2,3,7,8-TCDD, equivalent to 4 pg of dioxin/furan TEQ. The limit of detection for CAPE Technologies' PCB TEQ Immunoassay Kit is approximately 10 pg of PCB 126, equivalent to 1 pg of PCB TEQ. These detection limits make both tests sufficiently sensitive for analysis at levels below 10 pg/g TEQ using a 5-g sample. Less sensitive performance is possible by decreasing the amount of sample extract added to the cleanup procedure.

Regardless of sample load, the manufacturer's recommendations for extract cleanup must be followed closely in order to obtain acceptable results. Raw pg/tube results must be converted to raw pg/g in the original sample by use of the proper dilution and volume factors. For accurate absolute quantitation, raw pg/g results must be adjusted by a calibration adjustment factor. This factor is empirically determined by the user based on a variety of QA samples. Calibration adjustment factors can be estimated before analysis, but they are best refined on an ongoing basis by use of appropriate QA samples (see Appendix B).

During the demonstration, the dilution protocol used was designed to provide approximate quantitation of samples that were high relative to the primary target level, while using a minimum of resources (i.e., the residue of the sample already processed and analyzed). The protocol was not designed for maximum accuracy and may indeed have problems related only to potential overloading of cleanup columns. Most applications of the kits would not require a more refined result than this, but if such a result were required, the first result would be used to select a lower sample load and another (smaller) aliquot would be processed.

Matrix detection limits will vary according to matrix, sample size, and dilution factor. A single experienced analyst can process approximately 20 samples per day using the procedure evaluated in this study.

The following kits are available from CAPE Technologies (all DF1 kits have parallel PCB TEQ kits):

- DF1-ST-A, a small starter package containing two DF1-12 kits (40 antibody-coated tubes and matching liquid reagents), one Grip-Rack, and one set of dioxin standards, plus two check samples of dioxin in toluene made by Wellington Labs.

- DF1-ST-B, a large starter package containing one DF1-60 kit (100 antibody-coated tubes and matching liquid reagents), one Grip-Rack, and one set of dioxin standards, plus two check samples of dioxin in toluene made by Wellington Labs.

After the purchase of one starter package, subsequent purchases are either the DF1-12 or the DF1-60. These kits do not include dioxin standards and check samples, which must be ordered separately. The DF1-12 kit for screening analysis of 12 samples includes 20 antibody-coated tubes and matching liquid reagents. The DF1-60 kit for screening analysis of 60 samples includes 100 antibody-coated tubes and matching liquid reagents.

Tables 2-1 and 2-2 describe the cross-reactivity of the DF1 and PCB TEQ immunoassay kits, respectively.

This is the method that CAPE Technologies implemented during the field demonstration. A photo of the technology in operation during the demonstration is presented in Figure 2-2. CAPE Technologies provided supplemental information about the performance of their technology during the demonstration and it is presented in Appendix B.

2.4 Developer Contact Information

Additional information about the DF1 and PCB TEQ Immunoassay kits can be obtained by contacting:

CAPE Technologies LLC
Bob Harrison
3 Adams Street
South Portland, Maine 04106-1604
Telephone: (207) 741-2995
E-mail: cape-tech@ceemaine.org
Web site: www.cape-tech.com

Figure 2-2. CAPE Technologies DF1 Immunoassay kit in operation during the field demonstration.

Table 2-1. Cross-Reactivity of the DF1 Immunoassay Kit

Toxic Dioxin Congeners	% Crossreactivity[a]
2,3,7,8-TCDD	100
1,2,3,7,8-PeCDD	105
1,2,3,4,7,8-HxCDD	1.6
1,2,3,6,7,8-HxCDD	7.9
1,2,3,7,8,9-HxCDD	39
1,2,3,4,6,7,8-HpCDD	0.7
OCDD	<0.001
Toxic Furan Congeners	
2,3,7,8-TCDF	20
1,2,3,7,8-PeCDF	4.6
2,3,4,7,8-PeCDF	17
1,2,3,4,7,8-HxCDF	0.4
1,2,3,6,7,8-HxCDF	1.0
1,2,3,7,8,9-HxCDF	3.3
2,3,4,6,7,8-HxCDF	4.9
1,2,3,4,6,7,8-HpCDF	0.02
1,2,3,4,7,8,9-HpCDF	0.9
OCDF	<0.001
Other PCDD/F Congeners	
2,3-dichlorodibenzo-p-dioxin	0.13
2,7-dichlorodibenzo-p-dioxin	0.003
2,3-dichlorodibenzofuran	0.02
2,7-dichlorodibenzofuran	<0.002
2,3,7-trichlorodibenzo-p-dioxin	24
2,3,8-trichlorodibenzofuran	0.26
1,2,3,4-TCDD	<0.001
1,2,3,4-TCDF	<0.001
1,3,6,8-TCDD	0.05
1,3,6,8-TCDF	0.007
Polychlorinated Biphenyls	
3,3',4,4' (PCB 77)	0.4
3,3',4,4',5 (PCB 126)	0.5
2,2',4,4',5 (PCB 153)	<0.1
3,3',4,4',5,5' (PCB 169)	<0.1
Aroclor 1254	<0.1

[a] Response curves were prepared for each congener as noted. The percent cross-reactivity = (((2,3,7,8-TCDD I_{50}) ÷ (congener I_{50})) x 100). Values are typically based on two to four independent curves, each containing at least four concentrations.

Table 2-2. Cross-Reactivity of the PCB TEQ Immunoassay Kit

Category	PCB No.	Chlorination Pattern	TEF[a]	% Cross-Reactivity[b]
Non-Ortho	77	3,4 / 3',4'	0.0001	0.90
	81	3,4,5 / 4'	0.0001	0.54
	126	3,4,5 / 3',4'	0.1	100
	169	3,4,5 / 3',4',5'	0.01	232
Mono-Ortho	105	2,3,4 / 3',4'	0.0001	0.017
	114	2,3,4,5 / 4'	0.0005	0.0063
	118	2,4,5 / 3',4'	0.0001	0.0064
	123	3,4,5 / 2',4'	0.0001	0.11
	156	2,3,4,5 / 3',4'	0.0005	0.43
	157	2,3,4 / 3',4',5'	0.0005	1.1
	167	2,4,5 / 3',4',5'	0.00001	0.93
	189	2,3,4,5 / 3',4',5'	0.0001	9.2
Di-Ortho	170	2,3,4,5 / 3',4',5'	0.0001[c]	0.0083
	180	2,3,4,5 / 2',4',5'	0.00001[c]	0.0023

Aroclor 1254 Common Congeners (no assigned TEF values)

PCB No.	Chlorination Pattern	% Cross-Reactivity
44	2,3 / 2',5'	0.0002
49	2,4 / 2',5'	0.0002
52	2,5 / 2',5'	0.0002
66	2,4 / 3',4'	0.0058
70	2,5 / 3',4'	0.013
82	2,3,4 / 2',3'	0.0009
84	2,3,6 / 2',3'	0.0002
85	2,3,4 / 2',4'	0.0005
87	2,3,4 / 2',5'	0.0009
92	2,3,5 / 2',5'	0.0005
95	2,3,6 / 2',5'	0.0005
97	2,4,5 / 2',3'	0.0005
PCB No.	**Chlorination Pattern**	**% Cross-Reactivity**
99	2,4,5 / 2',4'	0.0002
101	2,4,5 / 2',5'	0.0002
110	2,3,6 / 3',4'	0.0005
128	2,3,4 / 2',3',4'	0.0035
132	2,3,4 / 2',3',6'	0.0005
138	2,3,4 / 2',4',5'	0.0002
141	2,3,4,5 / 2',5'	0.0005
149	2,3,6 / 2',4',5'	0.0018
153	2,4,5 / 2',4',5'	0.0023
158	2,3,4,6 / 3',4'	0.0005
163	2,3,5,6 / 3',4'	0.0021
168	2,4,6 / 3',4',5'	0.0028

[a] TEF values are from Van den Berg et al.[5]

[b] Response curves were prepared for each congener as noted. The percent cross-reactivity = (((congener I_{50}) ÷ (PCB 126 I_{50})) x 100). Values are typically based on two to four independent curves, each containing at least four concentrations.

[c] No TEF assigned by WHO.

Chapter 3
Demonstration and Environmental Site Descriptions

This chapter describes the demonstration site, the sampling locations, and why each was selected.

3.1 Demonstration Site Description and Selection Process

This section describes the site selected for hosting the demonstration, along with the selection rationale and criteria. Several candidate host sites were considered. The candidate sites were required to meet certain selection criteria, including necessary approvals, support, and access to the demonstration site; enough space and power to host the technology developers, the technical support team, and other participants; and various levels of dioxin-contaminated soil and/or sediment that could be analyzed as part of the demonstration. Historically, these demonstrations are conducted at sites known to be contaminated with the analytes of interest. The visibility afforded the sites is a valuable way of keeping the local community informed of new technologies and to help promote the EPA's commitment to promote and advance science and communication.

After review of the information available, the site selected for the demonstration was the Green Point Environmental Learning Center (ELC) site, located within the city of Saginaw, Michigan. The Saginaw city-owned, 76-acre Green Point ELC, formerly known as the Green Point Nature Center, is managed by the Shiawassee National Wildlife Refuge. The Green Point ELC is situated within the Tittabawassee River flood plain. The MDEQ found higher than normal levels of dioxins in soil and sediment samples taken from the flood plain of the Tittabawassee River. The flood plain is not heavily laden with PCBs; however, low levels of PCBs have been detected in some areas. Soil samples taken from areas outside the flood plain were at typical background levels. The source of the contamination was speculated to be attributed to legacy contamination from chemical manufacturing.

To summarize, Green Point ELC was selected as the demonstration site based on the following criteria:

- Access and Cooperation of the State and Local Community—Representatives from the MDEQ, EPA Region 5, and the local U.S. Fish and Wildlife Services supported the demonstration by providing site access for the demonstration, logistical support for the demonstration, and supported a Visitor's Day during the demonstration.

- Space Requirements and Feasibility—The demonstration took place in the parking lot adjacent to the Green Point ELC, not directly on an area of contamination. The site had electrical power and adequate space to house the trailers and mobile labs that were used for the demonstration. Furthermore, the site was close to an international airport. The weather in Michigan at the time of the demonstration was unpredictable; however, all participants were provided heated containment (a mobile laboratory or construction trailer).

- Site Diversity—The area encompassing the Green Point site had different levels and types of dioxin contamination in both the soil and sediment that were used to evaluate the performance of the technologies.

The demonstration was conducted at the Green Point ELC over a 10-day period from April 26 to May 5, 2004. All technologies were operated inside trailers equipped with fume hoods or inside mobile laboratories. As such, the ambient weather conditions during the demonstration had little impact on the operation of the technologies,

since all of the work spaces were climate-controlled with heat and air conditioning. The outdoor weather conditions were generally cool and rainy, but the developers kept their working environment at comfortable temperatures (16 to 18°C). The low temperature over the 10-day demonstration period was 2°C, the high temperature was 26°C, and the average temperature was 9°C. Precipitation fell on eight of the 10 days, usually in the form of rain, but occasionally as sleet or snow flurries, depending on the temperature. The largest amount of precipitation on a given demonstration day was 0.50 inches.

3.2 Description of Sampling Locations

This section provides an overview of the 10 sampling sites and methods of selection. Table 3-1 summarizes each of the locations, what type of sample (soil or sediment) was provided, the number of samples submitted from each location, and the number of samples included in the demonstration from each location. Samples were collected from multiple sampling sites so that a wide variety of matrix conditions could be used to evaluate the performance of the technologies in addressing monitoring needs at a diverse range of Superfund sites.

Samples consisted of either soil or sediment and are described below based on this distinction. It should be noted that it was not an objective of the demonstration to accurately characterize the concentration of dioxins, furans, and PCBs from a specific sampling site. It was, however, an objective to ensure comparability between technology samples and the reference laboratory samples. This was accomplished by homogenizing each matrix, such that all sub-samples of a given matrix had consistent contaminant concentrations. As a result, homogenized samples were not necessarily representative of original concentrations at the site.

3.2.1 Soil Sampling Locations

This section provides descriptions of each of the soil sampling locations, including how the sites became contaminated and approximate dioxin concentrations, as well as the type and concentrations of other major constituents, where known [such as PCBs, pentachlorophenol (PCP), and PAHs]. This information was provided by the site owners/sample providers (e.g., the EPA, EPA contractors, and the MDEQ).

3.2.1.1 Warren County, North Carolina

Five areas of the Warren County PCB Landfill in North Carolina, a site with both PCB and dioxin contamination, were sampled. Dioxin concentrations in the landfill soils range approximately from 475 to 700 pg/g, and PCB concentrations are greater than 100 parts per million (ppm). The Warren County PCB Landfill contains soil that was contaminated by the illegal spraying of waste transformer oil containing PCBs from over 210 miles of highway shoulders. Over 30,000 gallons of contaminated oil were disposed of in 14 North Carolina counties. The landfill is located on a 142-acre tract of land. The EPA permitted the landfill under the Toxic Substances Control Act. Between September and November 1982, approximately 40,000 cubic yards (equivalent to 60,000 tons) of PCB-contaminated soil were removed and hauled to the newly constructed landfill located in Warren County, North Carolina. The landfill is equipped with both polyvinyl chloride and clay caps and liners. It also has a dual leachate collection system. The material in the landfill is solely from the contaminated roadsides. The landfill was never operated as a commercial facility. The remedial action was funded by the EPA and the State of North Carolina. The site was deleted from the National Priorities List on March 7, 1986.

3.2.1.2 Tittabawassee River Flood Plain

The MDEQ sampled the Tittabawassee River flood plain soils from three sites in the flood plain. The source of the contamination was speculated to be attributed to legacy contamination from chemical manufacturing. Two samples were collected from two locations at Imerman Park in Saginaw Township. The first sample was taken near the boat launch, and the second sample was taken in a grassy area near the river bank. Previous analysis from these areas of this park indicated a range of PCDD/F concentrations from 600 to 2,500 pg/g. Total PCBs from these previous measurements were in the low part-per-trillion (ppt) range. Two samples were collected from two locations at Freeland Festival Park in Freeland, MI. The first sample was taken above the river bank, and the second sample was taken near a brushy forested area within the park complex. Previous PCDD/F concentrations were from 300 to 3,400 pg/g, and total PCBs were in the low ppt range. The final two samples were collected from Department of Natural Resources

Table 3-1. Summary of Environmental Sampling Locations

Sample Type	Sampling Location	Number of Samples	
		Submitted for Consideration	Included in Demonstration
Soil	Warren County, North Carolina	5	3
	Tittabawassee River, Michigan	6	3
	Midland, Michigan	6	4
	Winona Post, Missouri	6	3
	Solutia, West Virginia	6	3
Sediment	Newark Bay, New Jersey	6	4
	Raritan Bay, New Jersey	6	3
	Tittabawassee River, Michigan	6	3
	Saginaw River, Michigan	6	3
	Brunswick, Georgia	5	3
Total		***58***	***32***

(DNR)-owned property in Saginaw, which was formerly a farming area located almost at the end of the Tittabawassee River where it meets the Shiawassee River to form the Saginaw River. Previous PCDD/F concentrations ranged from 450 to 1,150 pg/g. Total PCBs were not previously analyzed, but concentrations were expected to be less than 1 ppm. The DNR property is approximately a 10-minute walk from where the demonstration was conducted at the Green Point ELC.

3.2.1.3 Midland, Michigan

Soil samples were collected by the MDEQ from various locations in Midland, Michigan. The soil type and nature of dioxin contamination are different in the Midland residential area than it is on the Tittabawassee River flood plain, but it is from the same suspected source (legacy contamination from chemical manufacturing). Samples were collected in various locations around Midland. Estimated TEQ concentrations ranged from 10 pg/g to 1,000 pg/g.

3.2.1.4 Winona Post

The Winona Post site in Winona, Missouri, was a Superfund cleanup of a wood treatment facility. Contaminants at the site included PCP, dioxin, diesel fuel, and PAHs. Over a period of at least 40 years, these contaminants were deposited into an on-site drainage ditch and sinkhole. Areas of contaminant deposition (approximately 8,500 cubic yards of soils/sludge) were excavated in late 2001/early 2002. This material was placed into an approximate 2½-acre treatment cell located on facility property. During 2002/2003, material at the treatment cell was treated through addition of amendments (high-ammonia fertilizer and manure) and tilling. Final concentrations achieved in the treatment cell averaged 26 milligrams/kilogram (mg/kg) for pentachlorophenol and from 8,000 to 10,000 for pg/g dioxin equivalents. Samples obtained for this study from this site were obtained from the treatment cell after these concentrations had been achieved.

3.2.1.5 Solutia

The chemical production facility at the Solutia site in Nitro, West Virginia, is located along the eastern bank of the Kanawha River, in Putnam County, West Virginia. The site has been used for chemical production since the early 1910s. The initial production facility was developed by the U.S. government for the production of military munitions during the World War I era between 1918 and 1921. The facility was then purchased by a small private chemical company, which began manufacturing chloride, phosphate, and phenol compounds at the site. A major chemical manufacturer purchased the facility in 1929 from Rubber Services Company. The company continued to expand operations and accelerated its growth in the 1940s. A variety of raw materials has been used at the facility over the years, including inorganic compounds, organic solvents, and other organic compounds, including Agent Orange. Agent Orange is a mixture of chemicals containing equal amounts of two herbicides: 2,4-D (2,4 dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5 trichlorophenoxyacetic acid). Manufacture of the chemical herbicide began at the site in 1948 and ceased

in 1969. The source of the dioxin contamination in the site soils was associated with the manufacture of 2,4,5-T, where dioxins are an unintentional by-product. The site has a dioxin profile from ppt to low parts per billion (ppb) range. No PCBs or PAHs were identified in the soil.

3.2.2 Sediment Sampling Sites

This section provides descriptions of each of the sediment sites that includes how the sites became contaminated and approximate dioxin concentrations, as well as the type and concentrations of other major constituents (such as PCBs, PCP, and PAHs). This information was provided from site owners/samples providers (e.g., the EPA, EPA contractors, and the MDEQ).

3.2.2.1 New York/New Jersey Harbors

Dredged materials from the New York and New Jersey harbors were provided as samples for the demonstration. The U.S. Army Corps of Engineers, New York District, and EPA Region 2 are responsible for managing dredged materials from the New York and New Jersey harbors. Dioxin levels affect the disposal options for dredged material. Dredged materials are naturally occurring bottom sediments, but some in this area have been contaminated with dioxins and other compounds by municipal or industrial wastes or by runoff from terrestrial sources such as urban areas or agricultural lands.

3.2.2.1.1 Newark Bay

Surrounded by manufacturing industries, Newark Bay is a highly contaminated area with numerous sources (sewage treatment plants, National Pollutant Discharge Elimination System discharges, and nonpoint sources). This bay is downstream from a dioxin Superfund site that contains some of the highest dioxin concentrations in the United States and also is downstream from a mercury Superfund site. The dioxin concentration in the area sampled for this demonstration was approximately 450 pg/g. Average PCB concentrations ranged from 300 to 740 ppb. Fine-grained sediments make up 50% to 90% of the dredged material. Average total organic carbon (TOC) was about 4%.

3.2.2.1.2 Raritan Bay

Surrounded by industry and residential discharges, Raritan Bay has dioxin contamination in the area, but it is not to the degree of Newark Bay. No major Superfund sites are located in the vicinity. Dioxin concentration should be significantly less than in Newark Bay. PCB concentrations are around 250 ppb. The fine-grained sediment and TOC values were similar to percentages in Newark Bay.

3.2.2.2 Tittabawassee River

The first Tittabawassee River location was approximately ¼-mile upstream of the Bob Caldwell Boat Launch in Midland, Michigan. The sediments are dark gray, fine sand with some silt. The estimated TEQ concentration was 260 pg/g; however, concentrations as high as 2,100 pg/g TEQ have been found in this area. The second site was on the Tittabawassee River approximately 100 yards downstream from old Smith's Crossing Bridge in Midland, Michigan. The sediment was brown and sandy with organic material. The estimated TEQ concentration was 870 pg/g; but, again, concentrations as high as 2,100 pg/g TEQ are possible in the area. The third site was on Tittabawassee River at the Emerson Park Golfside Boat Launch. The sediment was gray black silty sand, with many leaves and high organic matter. The estimated TEQ concentration was < 5 pg/g. The fourth site was on the Tittabawassee River adjacent to Imerman Park in Saginaw County across from the fishing dock. The sediment was sand with some silt. The estimated TEQ concentration was between 100 and 2,000 pg/g TEQ. The fifth site was on the Tittabawassee River approximately 1 mile downstream of Center Road Boat Launch in Saginaw Township. The sediment consisted of sand and gravel with some shells and not much organic matter. The estimated TEQ concentration was between 100 and 1,000 pg/g TEQ. The sixth site also was on the Tittabawassee River across from the Center Road Boat Launch. The sediment was fine sand with high organic matter. The estimated TEQ concentration was 1,000 pg/g TEQ. The source of the contamination was speculated to be attributed to legacy contamination from chemical manufacturing.

3.2.2.3 Saginaw River

Saginaw River were collected at six locations. The first sampling location was in the Saginaw River just downstream of Green Point Island. Samples were collected near the middle of the river in about 21 feet of water. The sample was granular with some organic material. The estimated TEQ concentration was 100 ppt. Another Saginaw River sample was taken upstream of Genesee Bridge on the right side of the river. The sample was a brown fine sand from about 15 feet of water. The estimated TEQ concentration was 100 ppt. The third location was in the Saginaw River downstream of the Saginaw wastewater treatment plant in about eight feet of water. The sample was gray silty clay with an unknown TEQ concentration. The fourth location was in the Saginaw River in about eight feet of water. The sample was a black sandy material. The estimated TEQ concentration for this location was unknown. The fifth location was downstream of a petroleum pipeline crossing upstream of the Detroit and Mackinaw railroad bridge crossing. This location was selected because of its proximity to a former PCB dredging location. The sediment sample consisted of dark black silt with some sand. The estimated TEQ concentration was unknown, but PCB concentrations are expected to be high. The sixth and final sampling location was near the mouth of the Saginaw River in about five feet of water. The sediment was a mix of fine black silt and layers of sand and shells. The estimated TEQ concentration for this location was also unknown.

3.2.2.4 Brunswick Wood Preserving Site

The Brunswick Wood Preserving Superfund site is located in Glynn County, Georgia, north of the city of Brunswick. The site was originally located in the city of Brunswick, but moved to its present location around 1958. The site is approximately 84 acres and is about two-thirds of a mile long. Burnett Creek, a tidally influenced stream, is located at the western corner of the site. At several points, most, if not all, of the drainage from the site flows into Burnett Creek. The site was first operated by American Creosote Company, which constructed the facility sometime between 1958 and 1960. The site was acquired by Escambia Treating Company in 1969 from Georgia Creosoting Company and the Brunswick Creosoting Company. In 1985, a corporate reorganization resulted in the purchase of the facility by the Brunswick Wood Preserving Company, which operated the site until it closed in early 1991. Each of the three major wood-treating operations was carried out at the facility: PCP, creosote, and chromium-copper-arsenic (CCA). The site was listed on the EPA's National Priorities List on April 1, 1997.

Sediment samples from the Brunswick Wood Preserving site in Brunswick, Georgia, were collected from six locations on the site, including areas thought to have lower (< 300 pg/g TEQ) and higher (> 10,000 pg/g TEQ) dioxin/furan concentrations. Due to the processes that occurred on this site, the samples also contain varying levels of PAHs and PCP, but they were not expected to contain PCBs.

Chapter 4
Demonstration Approach

This chapter discusses the demonstration objectives, sample collection, sample homogenization, and demonstration design.

4.1 Demonstration Objectives

The primary goal of the SITE MMT Program is to develop reliable performance and cost data on innovative, commercial-ready technologies. A SITE demonstration must provide detailed and reliable performance and cost data so that technology users have adequate information to make sound decisions regarding comparability to conventional methods. The demonstration had both primary and secondary objectives. Primary objectives were critical to the technology evaluation and required the use of quantitative results to draw conclusions regarding a technology's performance. Secondary objectives pertained to information that is useful to know about the technology but did not require the use of quantitative results to draw conclusions regarding a technology's performance.

The primary objectives for the demonstration of the participating technologies were as follows:

P1. Determine the accuracy.
P2. Determine the precision.
P3. Determine the comparability of the technology to EPA standard methods.
P4. Determine the estimated method detection limit (EMDL).
P5. Determine the frequency of false positive and false negative results.
P6. Evaluate the impact of matrix effects on technology performance.
P7. Estimate costs associated with the operation of the technology.

The secondary objectives for the demonstration of the participating technologies were as follows:

S1. Assess the skills and training required to properly operate the technology.
S2. Document health and safety aspects associated with the technology.
S3. Evaluate the portability of the technology.
S4. Determine the sample throughput.

Application of these objectives to the demonstration was addressed based on input from the Dioxin SITE Demonstration Panel members,[(2)] general user expectations of field measurement technologies, the time available to complete the demonstration, technology capabilities that the developers participating in the demonstration intend to highlight, and the historical experimental components of former SITE Program demonstrations to maintain consistency.

Note that this demonstration does not assess all parameters that can affect performance of the technologies in comparison to the reference methods (i.e., not all compounds have been characterized in the test samples, calibration of technologies results to HRMS results on site-by-site basis was not evaluated, etc.). However, the demonstration as outlined below was agreed upon by the Dioxin SITE Demonstration Panel members to provide a reasonable evaluation of the technologies.

4.2 Toxicity Equivalents

For risk assessment purposes, estimates of the toxicity of samples that contain a mixture of dioxin, furan, and PCB congeners are often expressed as TEQs. TEQs are calculated by multiplying the concentration of each congener with a TEF, according to the equation:

$$TEQ = C_C * TEF$$

where C_C is the concentration of the congener. The TEF (see Table 4-1) provides an equivalency factor for each congener's toxicity relative to the toxicity of 2,3,7,8-TCDD. The TEFs used in this demonstration were determined by the World Health Organization (WHO) for mammalian species.[5] The total TEQ from dioxin and furans ($TEQ_{D/F}$) in a sample is calculated by adding up all of the TEQ values from the individual dioxin and furan congeners. The total TEQ contribution from PCBs (referred to as TEQ_{PCB}) is calculated by summing up the individual PCB TEQ values. The total TEQ in a sample is the sum of the $TEQ_{D/F}$ and TEQ_{PCB} values. TEQ concentrations for soils and sediments are typically reported in pg/g, which is equivalent to ppt.

Concentrations of dioxins, furans, and PCBs, represented as total TEQ concentration, provide a quantitative estimate of toxicity for all congeners expressed as if the mixture were a TEQ mass of 2,3,7,8-TCDD only. While the TEQ concept provides a way to estimate potential health or ecological effects, the limitations of this approach should be understood. The WHO report noted that the TEF indicates an order of magnitude estimate of the toxicity of a compound relative to 2,3,7,8-TCDD.[5] Therefore, the accuracy of the TEF factors could be affected by differences in species, in the functional responses elicited by the compounds, and in additive and nonadditive effects when the congeners are present in complex mixtures. The WHO report[5] concluded, however, that it is unlikely that a significant error would be observed due to these differences. The larger impact to the TEF concept is the presence of Ah-receptor binding compounds, such as PAHS (including naphthalenes, anthracenes, and fluorenes) and brominated and chloro/bromo-substituted analogues of PCDD/Fs that have not been assigned TEF values but

Table 4-1. World Health Organization Toxicity Equivalency Factor Values

Compound[a]	WHO TEF	Compound	WHO TEF
PCDDs		**PCDFs**	
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	1	1,2,3,7,8-PeCDF	0.05
		2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDD	0.1	1,2,3,7,8,9-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
		2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
OCDD	0.0001	OCDF	0.0001
Dioxin-like PCBs			
Coplanar		**mono-*ortho***	
3,3',4,4'-TCB (PCB 77)	0.0001	2,3,3',4,4'-PeCB (PCB 105)	0.0001
3,4,4',5-TCB (PCB 81)	0.0001	2,3,4,4',5-PeCB (PCB 114)	0.0005
3,3',4,4',5-PeCB (PCB 126)	0.1	2,3',4,4',5-PeCB (PCB 118)	0.0001
3,3',4,4',5,5'-HxCB (PCB 169)	0.01	2,3,4,4',5-PeCB (PCB 123)	0.0001
		2,3,3',4,4',5-HxCB (PCB 156)	0.0005
		2,3,3',4,4',5-HxCB (PCB 157)	0.0005
		2,3',4,4',5,5'-HxCB (PCB 167)	0.00001
		2,3,3',4,4'5,5'-HpCB (PCB 189)	0.0001

[a] T = Tetra, Pe = Penta, Hx = Hexa, Hp = Hepta, O = Octa, CDD = chlorinated dibenzo-*p*-dioxin, CDF = chlorinated dibenzofuran, CB = chlorinated biphenyl

which may contribute to the total TEQ. This potentially can result in an underestimation of TEQs in environmental samples using the TEF approach.[5]

This demonstration was designed with these limitations of the TEQ concept in mind. The samples chosen contained a variety of combinations of dioxins, furans, and PCBs and at a wide range of concentration levels. Some samples were high in analytes with better understood TEFs, while others were high in analytes with TEFs that have more uncertainty. Some were high in other Ah-receptor binding compounds such as PAHs, while still others were free of these possible TEQ contributing compounds. The purpose was to evaluate each of the technologies under a variety of conditions and assess the comparability of the $TEQ_{D/F}$ and TEQ_{PCB} values determined by the reference laboratory.

4.3 Overview of Demonstration Samples

The goal of the demonstration was to perform a detailed evaluation of the overall performance of each technology for use in the field or mobile environment. The demonstration objectives were centered around providing performance data that support action levels for dioxin at contaminated sites. The Centers for Disease Control's Agency for Toxic Substances and Disease Registry (ATSDR) has established a decision framework for sites that are contaminated with dioxin and dioxin-like compounds.[6] If samples are determined to have dioxin TEQ levels between 50 and 1,000 pg/g, the site should be further evaluated; action is recommended for levels above 1,000 pg/g (i.e., 1 ppb) TEQ. A mix of PE samples, environmentally contaminated ("real-world") samples, and extracts were evaluated that bracket the ATSDR guidance levels. Table 4-2 lists the primary and secondary performance objectives for this demonstration and which sample types were used in each evaluation. The PE samples were used primarily to determine the accuracy of the technology and consisted of purchased soil and sediment standard reference materials with certified concentrations of known contaminants and newly prepared spiked samples. The PE samples also were used to evaluate precision, comparability, EMDL, false positive/negative results, and matrix effects. Environmentally contaminated samples were collected from dioxin-contaminated sites around the country and were used to evaluate the precision, comparability, false positive/negative results, and matrix effects. Extracts, prepared in toluene, which was the solvent used by the reference laboratory, were used to evaluate precision, EMDL, and matrix effects. All samples were used to evaluate qualitative performance objectives such as technology cost, the required skill level of the operator, health and safety aspects, portability, and sample throughput. Table 4-3 shows the number of each sample type included in the experimental design. The following sections describe each sample type in greater detail.

4.3.1 PE Samples

PE standard reference materials are available through Cambridge Isotope Laboratories (CIL) (Andover, Massachusetts), LGC Promochem (United Kingdom), Wellington Laboratories (U.S. distributor TerraChem, Shawnee Mission, Kansas), the National Institute of Standards and Technology (NIST), (Gaithersburg, Maryland), and Environmental Resource Associates (ERA, Arvada, Colorado). All of these sources were utilized to obtain PE samples for use in this demonstration, and Table 4-4 summarizes the PE samples that were included. PE samples consisted of three types of samples: (1) reference materials (RMs) or certified samples, which included soil and/or sediment samples with certified concentrations of dioxin, furan, and/or PCBs; (2) spiked samples, which included a certified dioxin, furan, PCB, and PAH-clean matrix spiked with known levels of dioxin and/or other contaminants; and (3) blank samples that were certified to have levels of dioxins, furans, WHO PCBs, and PAHs that were non-detectable or were considerably lower than the detection capabilities of developer technologies. The PE samples were selected based on availability and on the correlation of the PE composition as it related to the environmental samples that were chosen for the demonstration (e.g., the PE sample had a similar congener pattern to one or more of the environmental sites).

Table 4-2. Distribution of Samples for the Evaluation of Performance Objectives

Performance Objective	Sample Type Used in Evaluation
P1: Accuracy	PE
P2: Precision	PE, environmental, extracts
P3: Comparability	PE, environmental, extracts
P4: EMDL	PE, extracts
P5: False positive/negative results	PE, environmental, extracts
P6: Matrix effects	PE, environmental, extracts
P7: Cost	PE, environmental, extracts
S1: Skill level of operator	PE, environmental, extracts
S2: Health and safety	PE, environmental, extracts
S3: Portability	PE, environmental, extracts
S4: Sample throughput	PE, environmental, extracts

Table 4-3. Number and Type of Samples Analyzed in the Demonstration

Sample Type	No. of Samples
PE	58
Environmental	128
Extracts	23
Total number of samples per technology	209

Table 4-4 indicates a correlation between the composition of the PE sample and the samples from the environmental sites, where applicable. The certified samples only required transfer from the original jar to the demonstration sample jar. The spiked samples were shipped to the characterization laboratory in bulk quantities so each had to be aliquoted in 50-g quantities. Additional details about each source of PE sample are provided in this section.

4.3.1.1 Cambridge Isotopes Laboratories

Two RMs were obtained from CIL for use in this demonstration. RM 5183 is a soil sample that was collected from a location in Texas with the intended purpose of serving as an uncontaminated soil for use as a spiking material. The soil was sieved to achieve uniform particle size and homogenized to within 5% using a disodium fluorescein indicator. Samples were then sterilized three times for two hours at 121°C and 15 pounds per square inch (psi). Analytical results indicated that the soil had low levels of D/F and PCBs.

RM 5184 is a heavily contaminated soil sample with relatively high levels of D/F and PCBs. According to the Certificate of Analysis (CoA), approximately 75 kg of contaminated sediment was obtained from an EPA Superfund site in Massachusetts that was known to contain considerable contamination from PCBs and other chemical pollutants. The sediment was sieved to achieve uniform particle size and homogenized to within

Table 4-4. Summary of Performance Evaluation Samples

Sample Type ID	Source	PE Type	Product No.	Certified Concentration			Correlation to Environ. Sample Type ID[a]	No. of Replicates Per Sample
				$TEQ_{D/F}$ (pg/g)	TEQ_{PCB} (pg/g)	PAH (mg/kg)		
PE #1	CIL	Certified	RM 5183	3.9	5.0	0.18	6	7[b]
PE #2	LGC Promochem	Certified	CRM 529	6583	424[c]	NA[d]	5	4
PE #3	Wellington	Certified	WMS-01	62	10.5	NA	6	7[b]
PE #4	CIL	Certified	RM 5184	171	941	27	2, 8, 9	4
PE #5	NIST	Certified	SRM 1944	251	41[c]	2.4[e]	3, 4	4
PE #6	ERA	Spiked	custom	11	NS[f]	<0.33	10	4
PE #7	ERA	Spiked	custom	33	NS	< 0.33	10	4
PE #8	ERA	Spiked	custom	NS	NS	61[g]	5, 7	4
PE #9	ERA	Spiked	custom	NS	11	< 0.33	1	4
PE #10	ERA	Spiked	custom	NS	1121	< 0.33	1	4
PE #11	ERA	Spiked	custom	11	3,760[c]	< 0.33	1	4
PE #12	ERA	Organic, Semivolatile, Blank Soil	056 (lot 56011)	0.046	0.01	< 0.33	not applicable	8
Total Number of PE samples								***58***

[a] Environmental Sample IDs are provided in Table 4-5.
[b] Seven replicates were analyzed for EMDL evaluation.
[c] Little or no certified PCB data were available; mean of reference laboratory measurements was used.
[d] NA = no data available.
[e] Approximate concentration of 2-methyl naphthalene, acenaphthene, and fluorene, which were the only PAHs that were included in the analysis.
[f] NS = not spiked.
[g] Each of the 18 target PAHs was spiked at levels that ranged from 1 to 10 mg/kg. (See Section 5.2.3 for the list of 18 PAHs.)

5% using a disodium fluorescein indicator. Samples were then sterilized three times for two hours at 121°C and 15 psi.

RM 5183 and RM 5184 are newly available from CIL. For both RM 5183 and RM 5184, certified analytical values are provided for the D/F and the 12 WHO PCB congeners. The samples were included in an international interlaboratory study conducted by CIL and Cerilliant Corporation. More than 20 laboratories participated in analysis of the D/Fs; up to 20 laboratories participated in the analysis of the PCBs. Participating laboratories used a variety of sample preparation and analytical techniques.

4.3.1.2 LGC Promochem

Certified reference material (CRM) 529 was obtained from LGC Promochem. The following description is taken from the reference material report that accompanied CRM 529. The soil for CRM 529 was collected in Europe from a site where chloro-organic and other compounds had been in large-scale production for several decades, but where production had ceased more than five years before sampling. The site had been contaminated during long-term production of trichlorophenoxyacetic acid. An area of sandy soil was excavated to a depth of several meters. Several hundred kgs+ of this mixed soil were air-dried at about 15 °C for three months. After removal of stones and other foreign matter by sieving, the remaining material was sterilized in air at 120°C for 2 hours, thoroughly mixed, and ground in an Alpine air jet mill to a particle size of < 63 micrometers (μm). The material was homogenized once more in a Turbula mixer and packaged in 50-g quantities. The final mean moisture content at the time of bottling was found to be 1.5%. According to the CoA, certified values are provided for five dioxin congeners, seven furan congeners, three chlorobenzene compounds, and three chlorophenol compounds. No PCBs were

reported with certified values on the CoA, so the mean concentration determined by the reference laboratory was used as the certified value.

4.3.1.3 Wellington

PE sample WMS-01 was obtained from TerraChem, the U.S. distributor for Wellington, an Ontario-based company. As described in the CoA, WMS-01 is a homogeneous lake sediment that was naturally contaminated (and not fortified). The crude, untreated sediment used to prepare WMS-01 was collected from Lake Ontario. The sediment obtained was subsequently air-dried; crushed to break up agglomerates; air-dried again, and then sieved, milled, and re-sieved (100% < 75 µm). The sediment was then subsampled into 25-g aliquots. The demonstration samples for only the Wellington PE samples were 25 g rather than 50 g based on the package size available from Wellington. Certified values for the 17 D/F congeners and the 12 WHO PCB congeners are provided on the CoA.

4.3.1.4 National Institute for Standards and Technology

Standard Reference Material® (SRM) 1944 was purchased through NIST. As described in the CoA, SRM 1944 is a mixture of marine sediment collected from six sites in the vicinity of New York Bay and Newark Bay in October 1994. Site selection was based on contaminant levels measured in previous samples from these sites and was intended to provide relatively high concentrations for a variety of chemical classes of contaminants. The sediment was collected using an epoxy-coated modified Van Veen-type grab sampler designed to sample the sediment to a depth of 10 centimeters (cm). A total of approximately 2,100 kg of wet sediment was collected from the six sites. The sediment was freeze-dried, sieved (nominally 61 to 250 µm), homogenized in a cone blender, radiation sterilized, then packaged in 50-g quantities. Certified values are provided on the CoA for the 17 D/F congeners, 30 PCB congeners, 24 PAHs, four chlorinated pesticides, 36 metals, and TOC. Since only three WHO PCBs were reported out of the 30 PCB congeners, the mean concentration of the reference laboratory measurements was used as the certified value so that the TEQ_{PCB} concentration would not be underestimated when compared to the developer technologies.

4.3.1.5 Environmental Resource Associates

ERA synthesized PE samples for this demonstration. ERA spiked blank, uncontaminated soil to pre-determined levels of D/Fs, PCBs, and/or PAHs. Spiked PE samples were prepared to include additional concentration ranges and compositions that were not covered with the commercially available certified materials. The organic semivolatile soil blank (ERA Product #056, Lot 56011) is a topsoil that was obtained from a nursery and processed according to ERA specifications by a geochemical laboratory. The particle size distribution of the soil was -20/+60 mesh. The soil was processed and blended with a sandy loam soil to create a blank soil with the following make-up: 4.1% clay, 4.5% silt, 91.2% sand, and 0.2% organic material. Initially, ERA was required to certify that the blank soil matrix to be used as the blank and for the preparation of the spiked PE samples was "clean" relative to the list of required target analytes. This was accomplished through a combination of ERA-conducted analyses (PAHs, pesticides, semivolatile organic compounds, Aroclors which are trade mixtures of PCB congeners) and subcontracted analytical verification (D/F and PCBs). The subcontracted analyses were performed by Alta Analytical Perspectives, LLC, in Wilmington, North Carolina. The Alta Analytical Certificate of Results and the ERA Certification sheets for the organic semivolatile soil blank indicated that trace levels of the octa-dioxins and several WHO PCB congeners were detected, but the total TEQ (combined D/F and PCBs) was less than 0.06 pg/g. The level of PAHs, pesticides, Aroclors, and semivolatile organic compounds in the soil was determined to be < 0.33 pg/g. The TEQ level was considerably below the detection capabilities of the participating technologies, so the organic semivolatile soil blank was considered adequately clean for use in this demonstration.

The manufacturing techniques that ERA used to prepare the PE samples for this demonstration were consistent with those used for typical semivolatile soil products by ERA. These techniques have been validated through hundreds of round robin performance test studies over ERA's more than 25 years in business. The D/F stock solutions used in the manufacture of these PE samples were purchases from CIL. The PCB and PAH stock solutions were purchased from ChemService. For each PE sample, a spiking concentrate was prepared by combining appropriate weight/volume aliquots of stock

materials required for that PE sample. Typically, additional solvent was added to this concentrate to yield sufficient volume of solution, appropriate for the mass of soil to be spiked. Based on a soil mass of 1,600 g, the volume of spike concentrate was approximately 10 to 30 milliliters (mL). For each PE sample, the blank soil matrix was weighed into a two-liter (L) wide mouth glass jar, the spike concentrate was distributed onto the soil, and the soil was allowed to air-dry for 30 to 60 minutes. The PE samples were then capped and mixed in a rotary tumbler for 30 minutes. Each PE sample was certified as the concentration of target analytes present in the blank matrix, plus the amount added during manufacture, based on volumetric and gravimetric measurements. CoAs were provided by ERA for all six ERA-provided PE samples. The certified values provided by ERA were different from the commercially available certified samples since the data were not based on analytically derived results. Further confirmation of the concentrations was conducted by the reference laboratory.

4.3.2 Environmental Samples

Handling of the environmental samples is described in this section. Note that once the environmental samples were collected, they were dried and homogenized as best as possible to eliminate variability introduced by sample homogeneity. As such, the effect of moisture on the sample analysis was not investigated.

4.3.2.1 Environmental Sample Collection

Samples were collected by the EPA, an EPA contractor, or the MDEQ and shipped to the characterization laboratory. When determining whether a soil or sediment site had appropriate dioxin contamination, a guideline concentration range of < 50 pg/g to 5,000 pg/g was used.

Once necessary approvals and sampling locations had been secured, sample containers were shipped to site personnel. Each site providing samples received one-gallon containers [Environmental Sampling Supply, Oakland, California, Part number 3785-1051, wide-mouth, 128-ounce high-density polyethylene round packer] for collecting five or six samples.

Instructions for sample collection, as well as how the containers were to be labeled and returned, were included in a cover letter with the sample containers that were shipped to each site. Personnel collecting the samples were instructed to label two containers containing the same sample as "1 of 2" and "2 of 2" and to attach a description or label to each container with a description of the sample, including where the sample was collected and the estimated concentrations of dioxin and any other anticipated contamination (e.g., PCBs, PAHs, PCP). Final instructions to sample providers indicated that collected samples were to be shipped back to the characterization laboratory using the provided coolers. Federal Express labels that included an account number and the shipping address were enclosed in each shipment.

Sample providers also were asked to provide any information about the possible source of contamination or any historical data and other information, such as descriptions of the sites, for inclusion in the demonstration and quality assurance project plan (D/QAPP).[2]

4.3.2.2 Homogenization of Environmental Samples

If the material had very high moisture content, the jar contents were allowed to settle, and the water was poured off. Extremely wet material was poured through fine mesh nylon material to remove water. After water removal, the material was transferred to a Pyrex™ pan and mixed. After thorough mixing, an aliquot was stored in a pre-cleaned jar as a sample of "unhomogenized" material and was frozen.[1] The remaining bulk sample was mixed and folded bottom to top three times. This material was split equally among multiple pans. In each pan, the material was spread out to cover the entire bottom of the pan to an equal depth of approximately 0.5 inches. The pans were placed in an oven at 35ºC and held there until the samples were visibly dry. This process took from 24 to 72 hours, depending on the sample moisture. The trays were removed from the oven and allowed to rise to room temperature by sitting in a fume hood for approximately two hours. Approximately 500 g of material were put in a blender and blended for two minutes. The blender sides were scraped with a spatula, and the sample was blended for a second two-

[1] Ideally, the samples would have been stored at 4° ± 2°C; but, due to the large volume of buckets and jars that needed to be stored, the most adequate available storage at the characterization laboratory was a walk-in freezer that was at approximately minus 20°C.

minute period. The sample was sieved [USA Standard testing, No. 10, 2.00-millimeter (mm) opening] and the fine material placed in a tray. Rocks and particles that were retained on the sieve were placed in a pan. This process was repeated until all of the sediment or soil was blended and sieved. The blended and sieved sediment or soil in the tray was mixed well, and four aliquots of 100 to 300 g each were put into clean jars (short, wide-mouth 4-ounce, Environmental Sampling Supply, Oakland, California, Part number 0125-0055) to be used for the characterization analyses. The remaining sediment or soil was placed in a clean jar, and the particles that were retained on the sieve were disposed of. The jars of homogenized sediment and soil were stored frozen (approximately -20°C), unless the samples were being used over a period of several days, at which time they were temporarily stored at room temperature.

4.3.2.3 Selection of Environmental Samples

Once homogenized, the environmental samples were characterized for dioxin/furans (EPA Method 1613B[3]), PCBs, low-resolution mass spectrometry (LRMS) modified EPA Method 1668A[4], and 18 target PAHs (National Oceanic and Atmospheric Administration [(NOAA)] method[7]] to establish the basic composition of the samples. (Characterization analyses are described in Chapter 5.) Because the soil and sediment samples were dried and homogenized, they were indistinguishable. As such, the soil and sediment samples were jointly referred to as "environmental" samples, with no distinction made between soil or sediment other than during the matrix effects evaluations, as described in Section 4.7.6. Environmental samples were selected for inclusion in the demonstration based on the preliminary characterization data. The number and type of samples from each sampling location included in the demonstration are presented in Table 4-5.

Four aliquots of the homogenized material and one aliquot of unhomogenized material were analyzed. Two criteria had to be met for the environmental sample to be considered for inclusion in the demonstration. The first criterion was that the relative standard deviation (RSD) of the total D/F TEQ values from the four aliquots had to be less than 20% for samples with total TEQ values > 50 pg/g; RSD values up to 30% were considered acceptable if the concentration was < 50 pg/g TEQ. The second criterion was that no single RSD for an individual congener could be greater than 30%. If both of these criteria were met, the sample met the homogenization criteria and was considered for inclusion in the demonstration. If either of these criteria was not met, options for the sample included (a) discarding it and not considering it for use in the demonstration, (b) reanalyzing it to determine if the data outside the homogenization criteria were due to analytical issues, or (c) rehomogenizing and reanalyzing it. Of these options, (a) and (b) were utilized, but (c) was not because an adequate number of environmental samples were selected using criteria (a) and (b). The average D/F concentration and RSDs for the homogenization analyses of environmental samples are shown in Table 4-5. The composition of two particular Saginaw River samples was of interest for inclusion in the demonstration because of their concentration and unique congener pattern, but the homogenization criteria were slightly exceeded (i.e., 28% and 34% RSD, for Saginaw River Sample #2 and Saginaw River Sample #3, respectively). Since multiple replicates of every sample were analyzed, those samples were included in the study because of their unique nature but are flagged as slightly exceeding the homogenization criteria. A correlation of environmental samples to PE samples, similar to that presented in Table 4-4, is presented in Table 4-5.

Table 4-5. Characterization and Homogenization Analysis Results for Environmental Samples

Sample Type ID	Environmental Site Location	Soil or Sediment	Sample No.	Average Total $TEQ_{D/F}$ Concentration (pg/g)	RSD (%)	No. of Replicates Per Sample	Correlation with PE Sample Type ID[a]
Env Site #1	Warren County, North Carolina	soil	1	274	11	4	9, 10, 11
			2	5,065	7	4	
			3	11,789	3	4	
Env Site #2	Tittabawassee River, Michigan	soil	1	42	23[b]	4	4
			2	435	5	4	
			3	808	10	4	
Env Site #3	Newark Bay, New Jersey	sediment	1	16	26[b]	4	5
			2	62	14	4	
			3	45	26[b]	4	
			4	32	6	4	
Env Site #4	Raritan Bay, New Jersey	sediment	1	12	2	4	5
			2	14	3	4	
			3	13	7	4	
Env Site #5	Winona Post, Missouri	soil	1	3,831	1	4	2, 8
			2	11,071	2	4	
			3	11,739	1	4	
Env Site #6	Tittabawassee River, Michigan	sediment	1	1	23[b]	4	1, 3
			2	55	7	4	
			3	16	26[b]	4	
Env Site #7	Brunswick, Georgia	sediment	1	69	8	4	8
			2	65	1	4	
			3	14,500	2	4	
Env Site #8	Saginaw River, Michigan	sediment	1	921	9	4	4
			2	1,083	28[c]	4	
			3	204	34[c]	4	
Env Site #9	Midland, Michigan	soil	1	239	5	4	4
			2	184	5	4	
			3	149	7	4	
			4	25	10	4	
Env Site #10	Solutia, West Virginia	soil	1	48	10	4	6, 7
			2	1,833	19	4	
			3	3,257	11	4	
Average RSD for all environmental samples used in demonstration						***11%***	
Total number of environmental samples						***128***	

[a] PE Sample IDs are provided in Table 4-4.

[b] RSD values up to 30% were allowed for samples where the characterization analyses determined concentration to be <50 pg/g total $TEQ_{D/F}$.

[c] RSD value slightly exceeded the homogeneity criteria, but samples were included in the demonstration because they were samples of interest.

4.3.3 Extracts

A summary of the extract samples is provided in Table 4-6. The purpose of the extract samples was to evaluate detection and measurement performance independent of the sample extraction method. As shown in Table 4-6, two environmental samples (both sediments) were extracted using Soxhlet extraction with toluene. These extractions were performed by AXYS Analytical Services consistent with the procedures to extract the demonstration samples for reference analyses.[2] The environmental sample extracts represented a 10-g sediment sample extraction and were reported in pg/mL, which was calculated by the following equation:

$$\text{pg/mL} = \frac{(\text{pg/g samples}) \times (10\,\text{g aliquot})}{(300\,\text{mL extraction volume})} \times (30\ \text{DF})$$

where DF = dilution factor.Total extract volume per 10-g aliquot was 300 mL, but the sample extracts were concentrated and provided to the developers as 10-mL extracts, so a 30x dilution factor is included. The extracts were not processed through any cleanup steps, but they were derived from sediment samples that also were included in the suite of environmental samples. All environmental sample extractions were prepared in the same solvent (toluene). The extract samples also included three toluene-spiked solutions that were not extractions of actual environmental samples. Because adequate homogenization at trace quantities was difficult to achieve, one set of extract samples was spiked at low levels (approximately 0.5 pg/mL of 2,3,7,8-TCDD) and used as part of the EMDL evaluation.

4.4 Sample Handling

In preparation for the demonstration, the bulk homogenized samples were split into jars for distribution. Each 4-ounce, amber, wide-mouth glass sample jar (Environmental Sampling Supply, Oakland, California, Part number 0125-0055) contained approximately 50 g of sample. Seven sets of samples were prepared for five developers, the reference laboratory, and one archived set. A minimum of four replicate splits of each sample was prepared for each participant, for a total of at least 28 aliquots prepared for each sample. The purchased PE samples (i.e., standard reference materials and spiked materials) were transferred from their original packaging to the jars to be used in the demonstration for the environmental samples, making the environmental and PE samples visually indistinguishable.

Table 4-6. Distribution of Extract Samples

Sample Type ID	Sample ID	Sample Description	No. of replicates per sample
Extract #1	Environmental #6, Sample #2	Soxhlet extraction in toluene; no cleanup	4
Extract #2	Environmental #7, Sample #1	Soxhlet extraction in toluene; no cleanup	4
Extract #3	Spike #1[a]	0.5 pg/mL 2,3,7,8-TCDD	7[b]
Extract #4	Spike #2[a]	100 pg/mL 2,3,7,8-TCDD 1,000 pg/mL each WHO PCB (TEQ ~ 11)	4
Extract #5	Spike #3[a]	10,000 pg/mL each WHO PCB (TEQ ~ 1,000) [c]	4
Total number of extracts			***23***

[a] Prepared in toluene.

[b] Seven replicates were analyzed for EMDL evaluation.

[c] This extract was spiked with PCBs only but a low-level (approximately 0.3 pg/mL) 2,3,7,8-TCDD contamination was confirmed by the reference laboratory.

The samples were randomized in two ways. First, the order in which the filled jars were distributed was randomized. All jars had two labels. The label on the top of the jar was the analysis order and contained sample numbers 1 through 209. A second label placed on the side of the jar contained a coded identifier including a series of 10 numbers coded to include the site, replicate, developer, and matrix. All samples believed to have at least one D/F or PCB congener greater than 10,000 pg/g were marked with an asterisk for safety purposes. This was consistent for both the developer and reference laboratory samples. The developer was given the option of knowing which environmental site the samples came from and whether the sample was a soil or sediment. CAPE Technologies elected to have soil and sediment samples identified. As described in the D/QAPP, AXYS was informed of which environmental site that the samples came from so it could use congener profiles and dilution schemes determined during the pre-demonstration phase as a guide, along with the concentration range data that was provided in the D/QAPP. This information was supplied to the reference laboratory with the samples, along with which samples contained high (i.e., a sample with at least one congener with concentration > 120,000 pg/g) or ultrahigh (i.e., a sample with at least one congener with concentration > 1,200,000 pg/g) PCB levels. Using this information, AXYS regrouped the samples in batches so that, to the extent possible, samples from the same site would be analyzed within the same analytical batch. Because an analytical laboratory might know at least what site samples came from, and because it is reasonable from an analytical standpoint to group samples that might require similar dilution schemes and which have similar congener patterns in an analytical batch, this approach was an acceptable deviation from the original intention of having the samples run by the reference laboratory completely blind and in the prescribed analytical order. CAPE Technologies analyzed the samples in the prescribed order. The extracts were the first 23 samples in the analysis order. The randomization was generated so that, to the extent possible, an equal split of the sample replicates were analyzed in the field and in the laboratory. For example, when four replicates of a particular sample were included in the suite of demonstration samples, two replicates were analyzed among the first half of the samples and two replicates were among the second half of the samples. In the field, the samples were only analyzed by CAPE Technologies for total $TEQ_{D/F}$. A 40-mL fraction of each D/F extract that was generated in the field during the demonstration was archived for analysis in the developer's laboratories using the PCB TEQ Immunoassay Kit.

The environmental samples were stored at room temperature until homogenized. After homogenization and prior to distribution during the demonstration, the samples were stored in a walk-in freezer (approximately -20 °C) at the characterization laboratory. At the demonstration site, the samples were stored at ambient temperature. After the demonstration analyses were completed, the samples were stored at the characterization laboratory in the walk-in freezer until the conclusion of the project.

4.5 Pre-Demonstration Study

Prior to the demonstration, pre-demonstration samples were sent to CAPE Technologies for evaluation in its laboratory. The pre-demonstration study comprised 15 samples, including PE samples, environmental samples, and extracts. The samples selected for the pre-demonstration study covered a wide range of concentrations and included a representative of each environmental site analyzed during the demonstration.

The pre-demonstration study was conducted in two phases. In Phase 1, CAPE Technologies was sent six soil/sediment samples with the corresponding D/F, PCB, and PAH characterization data to perform a self-evaluation of their kits. In Phase 2, seven additional soil/sediment samples and two extracts were sent to CAPE Technologies for blind evaluation. AXYS analyzed all 15 pre-demonstration samples blindly. The CAPE Technologies pre-demonstration results were paired with the AXYS results and returned to CAPE Technologies so they could use the HRMS pre-demonstration sample data to refine the performance of their kits prior to participating in the field demonstration. Results for the pre-demonstration study can be found in the data evaluation report, which can be obtained by contacting the EPA program manager for this demonstration. The results confirmed that CAPE Technologies was a viable candidate to continue in the demonstration process.

4.6 Execution of Field Demonstration

CAPE Technologies arrived on-site on Sunday, April 25, and spent several hours that day setting up its trailer. The demonstration officially commenced on Monday, April 26 after 1.5 hours of safety and logistical training. During this meeting, the health and safety plan was reviewed to ensure that participants understood the safety requirements for the demonstration. Logistics, such as how samples would be distributed and results reported, were also reviewed during this meeting. After the safety and site-specific training meeting and prior to samples being received by the developers, each trailer and mobile laboratory was surface wipe sampled on the floor to the entrance of the developer work area to establish the background level of D/F and PCB contamination. The wipe sampling procedure was followed as described in the D/QAPP. Following demobilization by the developers, all of the trailers and mobile laboratories were cleaned and surface-wipe-sampled. Analysis of the pre- and post-deployment wipe samples indicated that all trailers and mobile laboratories met the acceptable clearance criteria that were outlined in the D/QAPP. Only one fume hood had to be re-cleaned and re-sampled before receiving final clearance.

Ideally, all 209 demonstration samples would have been analyzed on-site, but sample throughput of some of the technologies participating in the demonstration would require three weeks or more in the field to analyze 209 samples. Consequently, it was decided, as reported in the D/QAPP, that the number of samples to be analyzed in the field by each developer would be determined at the discretion of the developer.

CAPE Technologies received its first batch of samples by midmorning on April 26. CAPE Technologies completed analysis of 95 samples for D/F only in 5 working days (on April 30). It should be noted that the morning of April 28 was dedicated to a Visitor's Day, so minimal work on sample analyses was performed. The remaining analyses (95 samples for TEQ_{PCB} and 114 samples for both $TEQ_{D/F}$ and TEQ_{PCB}) were completed by CAPE Technologies in their laboratories and reported on August 27. CAPE Technologies reported that it took them two weeks of analytical time to complete the 114 sample analyses in their laboratories. CAPE Technologies was also offered the opportunity to reanalyze any samples before reporting final results. CAPE Technologies reanalyzed and reported new results for two samples that were analyzed for D/Fs in the field.

4.7 Assessment of Primary and Secondary Objectives

The purpose of this section is to describe how the CAPE Technologies reported its results $TEQ_{D/F}$, TEQ_{PCB} and total TEQ (all in pg/g). The CAPE Technologies results were compared to the certified values and reference laboratory results for $TEQ_{D/F}$, TEQ_{PCB}, and total TEQ. The reference laboratory total TEQ values were calculated by summing the $TEQ_{D/F}$ and TEQ_{PCB} data. Total TEQs value could not be calculated for two reference laboratory samples that were excluded due to sample preparation issues (see Section 6.4).

4.7.1 Primary Objective P1: Accuracy

The determination of accuracy was based on agreement with certified or spiked levels of PE samples. PE samples containing concentrations from across the analytical range of interest were analyzed. Percent recovery values relative to the certified or spiked concentrations were calculated. To evaluate accuracy, the average of replicate results from the field technology measurement was compared to the certified or spiked value of the PE samples to calculate percent recovery. The equation used was:

$$R = \overline{C} / C_R \times 100\%$$

where $\overline{C}$ is the mean concentration value calculated from the technology replicate measurements (reported in pg/g TEQ) and C_R is the certified value (in pg/g TEQ). Nondetects and values reported as "> (value)" were not included in the accuracy assessment. Mean concentration values were determined when at least three of four replicates were reported as actual values [i.e., were not reported as, "< (value)" or "> (value)"]. The mean, median, minimum, and maximum R values are reported as an assessment of overall accuracy. An ideal R value would be 100%.

4.7.2 Primary Objective P2: Precision

To evaluate precision, all samples (including PE, environmental, and extract samples) were analyzed in at least quadruplicate. Seven replicates of three different samples were analyzed to evaluate EMDLs.

Precision was evaluated at both low and high concentration levels and across different matrices. The statistic used to evaluate precision was RSD. The equation used to calculate standard deviation (*SD*) between replicate measurements was:

$$SD = \left[\frac{1}{n-1} \sum_{k-1}^{n} \left(\overline{C}_k - \overline{C} \right)^2 \right]^{1/2}$$

where *SD* is the standard deviation and $\overline{C}$ is the average measurement. Both values are in pg/g TEQ.

The equation used to calculate RSD between replicate measurements was:

$$RSD = \left| \frac{SD}{\overline{C}} \right| \times 100\%$$

RSD was calculated if detectable concentrations were reported for at least three replicates. The mean, median, minimum, and maximum RSD values, in percent, are reported as an assessment of overall precision.

Low RSD values (< 20%) indicated high precision. For a given set of replicate samples, the RSD of results was compared with that of the laboratory reference method's results to determine whether the reference method is more precise than the technology or vice versa for a particular sample set. The mean RSD for all samples was calculated to determine an overall precision estimate.

4.7.3 Primary Objective P3: Comparability

Data comparability was maximized by using the homogenization procedures and applying criteria for acceptable results prior to a sample being included in the demonstration. (See Section 4.3.2.3 for additional information.)

Technology results reported by CAPE Technologies were compared to the corresponding reference laboratory results by calculating a relative percent difference (RPD). The equation for RPD, reported in percent, is as follows:

$$\text{RPD} = \frac{\left(\text{M}_\text{R} - \text{M}_\text{D} \right)}{\text{average}\left(\text{M}_\text{R}, \text{M}_\text{D} \right)} \times 100\%$$

where M_R is the reference laboratory measurement (in pg/g TEQ) and M_D is the developer measurement (in pg/g TEQ). Nondetects were not included in this evaluation. The CAPE Technologies results were compared to the reference laboratory for $TEQ_{D/F}$, $TEQ_{PCB,}$ and total TEQ. For PE samples, $TEQ_{D/F}$ and TEQ_{PCB} RPD calculations were only performed for the analyte classes that the PE sample contained. For example, PE sample #6 was only spiked with 2,3,7,8-TCDD. Consequently, RPD calculations were only performed for $TEQ_{D/F}$ and not TEQ_{PCB} or total TEQ.

The absolute value of the difference between the reference and developer measurements in the equation above was not taken so that the RPD would indicate whether the technology measurements were greater than the reference laboratory measurements (negative RPD values) or less than the reference laboratory measurements (positive RPD). Because negative values for RPD could be obtained with this approach, the median RPD of all individual RPDs was calculated rather than the average RPD in calculation of comparability between the CAPE Technologies results and reference laboratory measurements. The median, minimum, and maximum RPD values were reported as an assessment of overall comparability. RPD values between positive and negative 25% indicated good agreement between the two measurements.

As another measure of comparability, the developer and reference data were grouped into four TEQ concentration ranges. The ranges were ≤ 50 pg/g, 50 to 500 pg/g, 500 to 5,000 pg/g, and ≥ 5,000 pg/g. The intervals were determined by the Demonstration Panel and were based on current guidance for cleanup levels. The percentage of developer results that agreed with those ranges of values was reported.

The accuracy of reporting blank samples was assessed. The blanks included eight replicate samples that contained levels of D/Fs and PCBs that were below the reporting limits of the developer technology but contained levels that could be detected by the reference methods (see Table 4-4). If the reference laboratory result was in the nondetect interval reported by the developer technology reporting limit, this result was considered accurately reported by the developer. The accuracy of the blank samples was reported in terms of % agreement. Ideal % agreement values would be 100%.

4.7.4 Primary Objective P4: Estimated Method Detection Limit

The method detection limit (MDL) calculation procedure described in the demonstration plan was 40 CFR Part 136, Appendix B, Revision 1.11. This procedure is based on an assumption that the replicates are homogeneous enough to allow proper measurement of the analytical precision and that the concentration is in the appropriate range for evaluation of the technology's sensitivity. For this evaluation, CAPE Technologies analyzed seven aliquots each of a low-level PE soil, PE sediment, and a toluene-spiked extract. MDL-designated samples are indicated in Tables 4-4 and 4-6. The developer reported nondetect values for some of the replicates, so provisions had to be made for the treatment of nondetects. As such, the results from these samples were used to calculate an estimated MDL (EMDL) for the technology.

A Student's t-value and the standard deviation of seven replicates were used to calculate the EMDL in pg/g TEQ is shown in the following equation:

$$EMDL = t_{(n-1,\,1-\infty=0.99)}(SD)$$

where $t_{(n-1,1-\infty=0.99)}$ = Student's t-value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom. Nondetect values were assigned the reported value (i.e., "< 1" was assigned as value of 1), half of the reported value (i.e., "< 1" was assigned 0.5), or zero. The various treatments of nondetect values were performed to see the impact that reduced statistical power (i.e., lower degrees of freedom) had on the EMDL calculation. The lower the EMDL value, the more sensitive the technology is at detecting contamination.

4.7.5 Primary Objective P5: False Positive/False Negative Results

The tendency for the CAPE Technologies kits to return false positive results (e.g., results reported above a specified level for the field technology but below a specified level by the reference laboratory) was evaluated. The frequency of false positive results was reported as a fraction of results available for false positive analysis. Similarly, the frequency of false negatives results was examined. For this purpose, the results were evaluated for samples reported as having concentrations above and below 20 pg/g TEQ and above and below 50 pg/g TEQ. As such, the samples that were reported as $\leq$ 20 (or 50) pg/g TEQ by the reference laboratory but > 20 (or 50) pg/g TEQ by CAPE Technologies were considered false positive. Conversely, those samples that were reported as $\leq$ 20 (or 50) pg/g TEQ by CAPE Technologies, but reported as > 20 (or 50) pg/g TEQ by the reference laboratory, were considered false negatives. In the case of semiquantitative results (reported as < or >), if the laboratory result was within the interval reported by the developer, it was not considered a false positive or false negative result. Ideal false positive and negative percentages would be equal to zero.

4.7.6 Primary Objective P6: Matrix Effects

The likelihood of matrix-dependent effects on performance was investigated by grouping the data by matrix type (i.e., soil, sediment, extract), sample type (i.e., PE, environmental, and extract), varying levels of PAHs, environmental site, and known interferences. Precision (RSD) data were summarized by soil, sediment, and extract (matrix type); by environmental, PE, and extract (sample type); and by PAH concentration. Analysis of variance (ANOVA) tests were performed to determine if there was a dependence on matrix type or sample type. Only the environmental samples were included in the matrix effect assessment based on PAH concentration, because only the environmental samples were analyzed for PAHs during the characterization analysis (described in Section 5.2.3). Some PAH data were available for the PE samples, but data were not available for all of the same analytes that were determined during the characterization analysis. The environmental samples were segregated into four ranges of total PAH concentrations: < 1,000 nanogram/g (ng/g), 1,000 to 10,000 ng/g, 10,000 to 100,000 ng/g, and > 100,000 ng/g. The precision (RSD) data were summarized for samples within these PAH concentration ranges. ANOVA tests were used to determine if the summary values for RSD were statistically different, indicating performance dependent upon PAH concentration. For the environmental site evaluation, the comparability (RPD) values from each of the 10 environmental sites were compared to see if the developer results were more or less comparable to the reference laboratory for a particular site. For known interferences, the developer's reported results for PE samples were

summarized for samples where the PE samples did not contain the target analyte (e.g., did the developer report D/F detections for a sample only spiked with PCBs).

This objective also evaluated whether performance was affected by measurement location (i.e., in-field versus laboratory conducted measurements), although this is not a traditional matrix effect. To evaluate the effect of measurement location, ANOVA tests were performed for sample results within a replicate set that were generated both in the laboratory and in the field. For these analyses, p-values < 0.05 indicated statistically different results between the laboratory and field measurements and therefore a significant effect of the measurement location on reported results. The percentage of replicate sets having p-values < 0.05 was reported.

4.7.7 Primary Objective P7: Technology Costs

The full cost of each technology was documented and compared to typical and actual costs for D/F and PCB reference analytical methods. Cost inputs included equipment, consumable materials, mobilization and demobilization, and labor. The evaluation of this objective is described in Chapter 8, Economic Analysis.

4.7.8 Secondary Objective S1: Skills Level of Operator

Based on observations during the field demonstration, the type of background and training required to properly operate the DF1 Dioxin/Furan Immunoassay Kit was assessed and documented. The skill required of an operator was also evaluated. The evaluation of this secondary objective also included user-friendliness of the technology.

4.7.9 Secondary Objective S2: Health and Safety Aspects

Health and safety issues, as well as the amount and type of hazardous and nonhazardous waste generated, were evaluated based on observer notes during the field demonstration. This also included an assessment of the personal protective equipment required to operate the technology.

4.7.10 Secondary Objective S3: Portability

Observers documented whether the DF1 Dioxin/Furan Immunoassay Kit could be readily transported to the field and how easy it was to operate in the field. This included an assessment of what infrastructure requirements were provided to CAPE Technologies (e.g., a trailer and fume hood), and an assessment of whether the infrastructure was adequate (or more than adequate) for the technology's operation. Limitations of operating the technology in the field are also discussed.

4.7.11 Secondary Objective S4: Sample Throughput

Sample throughput was measured based on the observer notes, which focused on the time-limiting steps of the procedures, as well as the documentation of sample custody. The number of hours CAPE Technologies worked in the field was documented using attendance log sheets where CAPE Technologies recorded the time they arrived and departed from the demonstration site. Time was removed for training and Visitor's Day activities. The number of operators involved in the sample analyses also was noted. Throughput of the developer technology was compared to that of the reference laboratory.

Chapter 5
Confirmatory Process

This chapter describes the characterization analyses and the process for selecting the reference methods and the reference laboratory.

5.1 Traditional Methods for Measurement of Dioxin and Dioxin-Like Compounds in Soil and Sediment

Traditional methods for analysis of dioxin and dioxin-like compounds involve extensive sample preparation and analysis using expensive instrumentation resulting in very accurate and high-quality, but costly, information. The ability to use traditional methods for high-volume sampling programs or screening of a contaminated site often is limited by budgetary constraints. The cost of these analyses can range approximately from $500 to $1,100 per sample per method, depending on the method selected, the level of QA/QC incorporated into the analyses, and the reporting requirements.

5.1.1 High-Resolution Mass Spectrometry

EPA Method 1613B[3] and SW-846 Method 8290[8] are both appropriate for low and trace-level analysis of dioxins and furans in a variety of matrices. They involve matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary GC (HRGC)/HRMS analysis. The main differences between the two methods are that EPA Method 1613B has an expanded calibration range and requires use of additional $^{13}C_{12}$-labeled internal standards resulting in more accurate identifications and quantitations. The calibration ranges for the HRMS methods based on a typical 10-g sample and 20-microliter (µL) final sample volume are presented in Table 5-1.

Table 5-1. Calibration Range of HRMS Dioxin/Furan Method

Compound	EPA Method 1613B	SW-846 Method 8290
Tetra Compounds	1–400 pg/g	2–400 pg/g
Penta-Hepta Compounds	5–2,000 pg/g	5–1,000 pg/g
Octa Compounds	10–4,000 pg/g	10–2,000 pg/g

5.1.2 Low-Resolution Mass Spectrometry

SW-846 Method 8280 is appropriate for determining dioxins and furans in samples with relatively high concentrations, such as still bottoms, fuel oils, sludges, fly ash, and contaminated soils and waters. This method involves matrix specific extraction, analyte-specific cleanup, and HRGC/LRMS analysis. The calibration ranges in Table 5-2 are based on a typical 10-g sample size and 100-µL final volume.

Table 5-2. Calibration Range of LRMS Dioxin/Furan Method

Compound	SW-846 Method 8280
Tetra-Penta Compounds	1,000–20,000 pg/g
Hexa-Hepta Compounds	2,500–50,000 pg/g
Octa Compounds	5,000–100,000 pg/g

5.1.3 PCB Methods

There are more options for analysis of dioxin-like compounds such as PCBs. EPA Method 1668A[4] is for low- and trace-level analysis of PCBs. It involves matrix-specific extraction, analyte-specific cleanup, and HRGC/HRMS analysis. This method provides very accurate determination of the WHO-designated

dioxin-like PCBs and can be used to determine all 209 PCB congeners. Not all PCBs are determined individually with this method because some are determined as sets of coeluting congeners. The calibration range for PCBs based on a typical 10-g sample and 20-µL final sample volume is from 0.4 to 4,000 pg/g. PCBs also can be determined as specific congeners by GC/LRMS or as Aroclors[1] by GC/electron capture detection.

5.1.4 Reference Method Selection

Three EPA analytical methods for the quantification of dioxins and furans were available: Method 1613B, Method 8290, and Method 8280. Method 8280 is a LRMS method that does not have adequate sensitivity (i.e., the detection limits reported by the developers are less than that of the LRMS method). Methods 1613B and 8290 are HRMS methods with lower detection limits. Method 1613B includes more labeled internal standards than Method 8290, which affords more accurate congener quantification. Therefore, it was determined that Method 1613B best met the needs of the demonstration, and it was selected as the dioxin/furan reference method. Reference data of equal quality needed to be generated to determine the PCB contribution to the TEQ, since risk assessment is often based on TEQ values that are not class-specific. As such, the complementary HRMS method for PCB TEQ determinations, Method 1668A,[4] was selected as the reference method for PCBs. Total $TEQ_{D/F}$ concentrations were generated by Method 1613B, and total TEQ_{PCB} concentrations were generated by Method 1668A. These data were summed to derive a total TEQ value for each sample.

5.2 Characterization of Environmental Samples

All of the homogenized environmental samples were analyzed by the Battelle characterization laboratory to determine which would be included in the demonstration. The environmental samples were characterized for the 17 D/Fs by Method 1613B, the 12 WHO PCBs by LRMS-modified Method 1668A, and 18 target PAHs by the NOAA Status and Trends GC/Mass Spectrometry (MS) method.[7]

5.2.1 Dioxins and Furans

Four aliquots of homogenized material and one unhomogenized (i.e., "as received") aliquot were prepared and analyzed for seventeen 2,3,7,8-substituted dioxins and furans following procedures in EPA Method 1613B. The homogenized and unhomogenized aliquots were each approximately 200 g. Depending on the anticipated levels of dioxins from preliminary information received from each sampling location, approximately 1 to 10 g of material were taken for analysis from each aliquot, spiked with $^{13}C_{12}$-labeled internal standards, and extracted with methylene chloride using accelerated solvent extraction techniques. One method blank and one laboratory control spike were processed with the batch of material from each site. The sample extracts were processed through various cleanup techniques, which included gel permeation chromatography or acid/base washes, as well as acid/base silica and carbon cleanup columns. As warranted, based on sample compositions, some samples were put through additional acid silica cleanup prior to the carbon column cleanup. Extracts were spiked with $^{13}C_{12}$-labeled recovery standards and concentrated to a final volume of 20 to 50 µL. Dilution and reanalysis of the extracts were performed if high levels of a particular congener were observed in the initial analysis; however, extracts were not rigorously evaluated to ensure that all peaks were below the peak area of the highest calibration standard.

Each extract was analyzed by high-resolution gas chromatography/HRMS in the selected ion monitoring (SIM) mode at a resolution of 10,000 or greater. A DB-5 column was used for analysis of the seventeen 2,3,7,8-PCDD/F congeners. The instrument was calibrated for PCDD/F at levels specified in Method 1613B with one additional calibration standard at concentrations equivalent to one-half the level of Method 1613B's lowest calibration point. Using a DB5 column, 2,3,7,8-TCDF is not separated from other non2,3,7,8-TCDF isomers. However, since the primary objective was to determine adequacy of homogenization and not congener quantification, it was determined that sufficient information on precision could be obtained with the DB5 analysis of 2,3,7,8-TCDF and no second column confirmation of 2,3,7,8-TCDF was performed. PCDD/F data were reported as both concentration (pg/g dry) and TEQs (pg TEQ/g dry).

5.2.2 PCBs

One aliquot of material from each sampling location was prepared and analyzed for the 12 WHO-designated dioxin-like PCBs by GC/LRMS. The LRMS PCB analysis method is based on key components of the PCB congener analysis approach described in EPA Method 1668A and the PCB homologue approach described in EPA Method 680. Up to 30 g of sample were spiked with surrogates and extracted with methylene chloride using shaker table techniques. The mass of sample extracted was determined based on information supplied to the laboratory regarding possible contaminant concentrations. The extract was dried over anhydrous sodium sulfate and concentrated. Extracts were processed through alumina column cleanup, followed by high-performance liquid chromatography/gel permeation chromatography (HPLC/GPC). Additionally, sulfur was removed using activated granular copper. The post-HPLC extract was concentrated and fortified with recovery internal standards. Extracts were concentrated to a final volume between 500 µL and 1 mL, depending on the anticipated concentration of PCBs in the sample, as reported by the sample providers. PCB congeners and PCB homologues were separated via capillary gas chromatography on a DB5-XLB column and identified and quantified using electron ionization MS. This method provides specific procedures for the identification and measurement of the selected PCBs in SIM mode.

5.2.3 PAHs

One aliquot of material from each sampling location was analyzed for PAHs. The 18 target PAHs included:

- naphthalene
- 2-methylnaphthalene,
- 2-chloronaphthalene
- acenaphthylene
- acenaphthene
- fluorene
- phenanthrene
- anthracene
- fluoranthene
- pyrene
- benzo(a)anthracene
- chrysene
- benzo(b)fluoranthene
- benzo(k)fluoranthene
- benzo(a)pyrene
- indeno(1,2,3-cd)pyrene
- dibenzo(a,h)anthracene
- benzo(g,h,i)perylene.

The method for the identification and quantification of PAH in sediment and soil extracts by GC/MS was based on the NOAA Status and Trends method[7] and, therefore, certain criteria (i.e., initial calibrations and daily verifications) are different from those defined in traditional EPA methods 625 and 8270C. Up to 30 g of sample were spiked with surrogates and extracted using methylene chloride using shaker table techniques. The mass of sample extracted was determined based on information supplied to the characterization laboratory regarding possible contaminant concentrations. The extract was dried over anhydrous sodium sulfate and concentrated. The extract was processed through an alumina cleanup column followed by HPLC/GPC. The post-HPLC extract was concentrated and fortified with recovery internal standards. Extracts were concentrated between 500 µL and 1 mL, depending on the anticipated concentration of PCBs in the sample, as reported by the sample providers. PAHs were separated by capillary gas chromatography on a DB-5, 60-m column and were identified and quantified using electron impact mass spectrometry. Extracts were analyzed in the SIM mode to achieve the lowest possible detection limits.

5.3 Reference Laboratory Selection

Based on a preliminary evaluation of performance and credibility, 10 laboratories were contacted and were sent a questionnaire geared toward understanding the capabilities of the laboratories, their experience with analyzing dioxin samples for EPA, and their ability to meet the needs of this demonstration. Two laboratories were selected for the next phase of the selection process and were sent three blind audit samples. Each laboratory went through a daylong audit that included a technical systems audit and a quality systems audit. At each laboratory, the audit consisted of a short opening conference; a full day of observation of laboratory procedures, records, interviews with laboratory staff; and a brief closing meeting. Auditors submitted followup questions to each laboratory to address gaps in the observations.

Criteria for final selection were based on the observations of the auditors, the performance on the audit samples, and cost. From this process, it was determined that AXYS Analytical Services (Sidney, British Columbia, Canada) would best meet the needs of this demonstration.

5.4 Reference Laboratory Sample Preparation and Analytical Methods

AXYS Analytical Services received all 209 samples on April 27, 2004. To report final data, AXYS submitted 14 D/F and 14 PCB data packages from June 11 to December 20, 2004. The following sections briefly describe the reference methods performed by AXYS.

5.4.1 Dioxin/Furan Analysis

All procedures were carried out according to protocols as described in AXYS Summary Method Doc MSU-018 Rev 2 18-Mar-2004 [AXYS detailed Standard Operating Procedure (SOP) MLA-017 Rev 9 May-2004], which is based on EPA Method 1613B. AXYS modifications to the method are summarized in the D/QAPP.[2] Briefly, samples were spiked with a suite of isotopically labeled surrogate standards prior to extraction, solvent extracted, and cleaned up through a series of chromatographic columns that included silica, Florisil, carbon/Celite, and alumina columns. The extract was concentrated and spiked with an isotopically labeled recovery (internal) standard. Analysis was performed using an HRMS coupled to an HRGC equipped with a DB-5 capillary chromatography column [60 meters (m), 0.25-mm internal diameter (i.d.), 0.1-µm film thickness]. A second column, DB-225 (30 m, 0.25-mm i.d., 0.15-µm film thickness), was used for confirmation of 2,3,7,8-TCDF identification. Samples that were known to contain extremely high levels of PCDD/F were extracted without the addition of the surrogate standard, split, then spiked with the isotopically labeled surrogate standard prior to cleanup. This approach allowed extraction of the method-specified 10-g sample volume, and subsequent sufficient dilution that high level analytes were brought within the instrument calibrated linear range. While this approach induces some uncertainty because the actual recovery of analytes from the extraction process is unknown, it was decided by the demonstration panel that in general analyte recovery through the extraction procedures are known to be quite good and that the uncertainty introduced by this approach would be less than the uncertainty introduced by other approaches such as extracting a significantly smaller sample size.

5.4.2 PCB Analysis

The method was carried out in accordance with the protocols described in AXYS Summary Method Doc MSU-020 Rev 3 24-Mar-2004 (AXYS detailed SOP MLA-010 Rev 5 Sep-2003), which is based on EPA Method 1668A, with changes through August 20, 2003. AXYS modifications to the method are summarized in the D/QAPP. Briefly, samples were spiked with isotopically labeled surrogate standards, solvent extracted, and cleaned up on a series of chromatographic columns that included silica, Florisil, alumina, and carbon/Celite columns. The final extract was spiked with isotopically labeled recovery (internal) standards prior to instrumental analysis. The extract was analyzed by HRMS coupled to an HRGC equipped with a DB-1 chromatography column (30 m, 0.25-mm i.d., 0.25-µm film thickness). Because only the WHO-designated dioxin-like PCBs were being analyzed for this program and in order to better eliminate interferences, all samples were analyzed using the DB-1 column, which is an optional confirmatory column in Method 1668A rather than the standard SPB Octyl column. Samples that were known to contain extremely high levels of PCBs were extracted without the addition of the surrogate standard, split, then spiked with the isotopically labeled surrogate standard prior to cleanup. This approach allowed extraction of the method-specified 10-g sample volume, and subsequent sufficient dilution that high level analytes were brought within the instrument calibrated linear range. While this approach induces some uncertainty because the actual recovery of analytes from the extraction process is unknown, it was decided by the demonstration panel that in general analyte recovery through the extraction procedures are known to be quite good and that the uncertainty introduced by this approach would be less than the uncertainty introduced by other approaches such as extracting a significantly smaller sample size.

5.4.3 TEQ Calculations

For the reference laboratory data, D/F and PCB congener concentrations were converted to TEQ and subsequently summed to determine total TEQ, using the TEFs established by WHO in 1998 (see Table 4-1).[5]

Detection limits were reported as sample-specific detection limits (SDLs). SDLs were determined from 2.5 times the noise in the chromatogram for D/F and 3.0 times the noise for PCBs, converted to an area, and then converted to a concentration using the same calculation procedure as for detected peaks. Any value that met all quantification criteria (> SDL and isotope ratio) were reported as a concentration. A "J" flag was applied to any reported value between the SDL and the lowest level calibration. The concentration of any detected congener that did not meet all quantification criteria (such as isotope ratio or peak shape) was reported but given a "K" flag to indicate estimated maximum possible concentration (EMPC).[8] TEQs were reported in two ways to cover the range of possible TEQ values:

(1) All nondetect and EMPC values were assigned a zero concentration in the TEQ calculation.

(2) Nondetects were assigned a concentration of one-half the SDL. EMPCs were assigned a value equal to the EMPC.

In both cases, any total TEQ value that had 10% contribution or more from J-flagged or K-flagged data was flagged as J or K (or both) as appropriate.

TEQs were calculated both ways for all samples. For $TEQ_{D/F}$, 63% of the samples had the same TEQ value based on the two different calculation methods, and the average RPD was 8% (median = 0%). For TEQ_{PCB}, 65% of the samples had the same TEQ value based on the two different calculation methods, and the average RPD was 9% (median = 0%). Because overall there were little differences between the two calculation methods, as presented in Appendix D, TEQ values calculated by option #1 were used in comparison with the developer technologies. On a case-by-case basis, developer results were compared to TEQs calculated by option #2 above, but no significant differences in comparability results were observed so no additional data analysis results using these TEQ values were presented.

Chapter 6
Assessment of Reference Method Data Quality

Ensuring reference method data quality is of paramount importance to accurately assessing and evaluating each of the innovative technologies. To ensure that the reference method has generated accurate, defensible data, a quality systems/technical audit of the reference laboratory was performed during analysis of demonstration samples after the first batch of demonstration sample analyses was complete. The quality systems/technical audit evaluated implementation of the demonstration plan. In addition, a full data package was prepared by the reference laboratory for each sample batch for both dioxin and dioxin-like PCB analyses. Each data package was reviewed by both a QA specialist and technical personnel with expertise in the reference methods for agreement with the reference method as described in the demonstration plan. Any issues identified during the quality systems/technical audit and the data package reviews were addressed by the reference laboratory prior to acceptance of the data. In this section, the reference laboratory performance on the QC parameters is evaluated. In addition, the reference data were statistically evaluated for the demonstration primary objectives of accuracy and precision.

6.1 QA Audits

A quality systems/technical audit was conducted at the reference laboratory, AXYS Analytical Services, Ltd., by Battelle auditors on May 26, 2004, during the analysis of demonstration samples. The purpose of the audit was to verify AXYS compliance with its internal quality system and the D/QAPP.[2] The scope specifically included a review of dioxin and PCB congener sample processing, analysis, and data reduction; sample receipt, handling, and tracking; supporting laboratory systems; and followup to observations and findings identified during the independent laboratory assessment conducted by Battelle on February 11, 2004, prior to contract award. Checklists were prepared to guide the audit, which consisted of a review of laboratory records and documents, staff interviews, and direct observation.

The AXYS quality system is documented in a comprehensive QA/QC manual and detailed SOPs. No major problems or issues were noted during the audit. Two findings were identified, one related to a backlog of unfiled custody records and the other related to the need for performance criteria for the DB-1 column used for the analysis of PCB congeners by HRMS. Both issues were addressed satisfactorily by AXYS after the audit. One laboratory practice that required procedural modification was identified: the laboratory did not subject all QC samples to the most rigorous cleanup procedures that might be required for individual samples within a batch. The AXYS management team agreed that this procedure was incorrect. As corrective action, the QA manager provided written instructions regarding cleanup of the quality control samples to the staff, and the laboratory manager conducted follow up discussion with the staff. Other isolated issues noted by the auditors did not reflect systemic problems and were typical of analytical laboratories (e.g., occasional documentation lapses or an untrackable balance weight).

The audit confirmed that the laboratory procedures conformed to the SOPs and D/QAPP and that the quality system was implemented effectively. Samples were processed and analyzed according to the laboratory SOPs and D/QAPP using the Soxhlet Dean Stark extraction method. No substantial deviations were noted. The audit verified the traceability of samples within the laboratory, as well as the traceability of standards, reagents, and solvents used in preparation, and that the purity and reliability of the latter materials were demonstrated through documented quality checks. In addition, the audit confirmed that analytical

instruments and equipment were maintained and calibrated according to manufacturers' specifications and laboratory SOPs. Analytical staff members were knowledgeable in their areas of expertise. QC samples were processed and analyzed with each batch of authentic samples as specified by the D/QAPP. QA/QC procedures were implemented effectively, and corrective action was taken to address specific QC failures. Data verification, reporting, and validation procedures were found to be rigorous and sufficient to ensure the accuracy of the reported data. The auditors concluded that AXYS is in compliance with the D/QAPP and its SOPs, and that the data generated at the laboratory are of sufficient and known quality to be used as a reference method for this project.

In addition, each data package was reviewed by both a QA specialist and technical personnel with expertise in the reference methods for agreement with the reference method as described in the demonstration plan. Checklists were prepared to guide the data package review. This review included an evaluation of data package documentation such as chain-of-custody (COC) and record completeness, adherence to method prescribed holding times and storage conditions, standard spiking concentrations, initial and continuing calibrations meeting established criteria, GC column performance, HRMS instrument resolution, method blanks, lab control spikes (ongoing precision and recovery samples), sample duplicates, internal standard recovery, transcription of raw data into the final data spreadsheets, calculation of TEQs, and data flag accuracy. Any issues identified during the data package reviews were addressed by the reference laboratory prior to acceptance of the data. All of the audit reports and responses are included in the DER.

6.2 QC Results

Each data package was reviewed for agreement with the reference method as described in the demonstration plan. This section summarizes the evaluation of the reference method quality control data.

6.2.1 Holding Times and Storage Conditions

All demonstration samples were stored frozen (<-10°C) upon receipt and were analyzed within the method holding time of one year.

6.2.2 Chain of Custody

All sample identifications were tracked from sample login to preparation of record sheets, to instrument analysis sheets, to the final report summary sheets and found to be consistent throughout. One COC with an incomplete signature and one discrepancy in date of receipt between the COC and sample login were identified during the Battelle audit and were corrected before the data packages with these affected items were accepted as final.

6.2.3 Standard Concentrations

The concentration of all calibration and spiking standards was verified.

6.2.4 Initial and Continuing Calibration

All initial calibrations met the criteria for response factor RSD and minimal signal-to-noise ratio requirements for the lowest calibration point.

Continuing calibrations were performed at the beginning and end of every 12-hour analysis period with one minor exception for dioxin/furan sample batch WG13551, which contained five samples from Environmental Site #1 (North Carolina) and 12 samples from Environmental Site #5 (Winona Post). On one analysis day, a high-level sample analyzed just prior to the ending calibration verification caused the verification to fail. In this instance, the verification was repeated just outside of the 12-hour period. The repeat calibration verification met the acceptance criteria and was considered to show acceptable instrument performance in the preceding analytical period; therefore, the data were accepted.

Continuing calibration results were within the criteria stated in Table 9-2 (D/F) and Table 9-4 (PCB) of the D/QAPP, with one exception. For PCB sample batch WG12108, which contained nine samples from Environmental Site #3 (Newark Bay) and 12 samples from Environmental Site #4 (Raritan Bay), isotopically labeled PCB 169 was above the acceptable range during one calibration verification on May 15, 2004. The acceptance range included in the D/QAPP is tighter than the acceptance range in Method 1668A Table 6. Because the result for labeled PCB 169 was within the Method 1668A acceptance limits, the data were accepted.

The minimum signal-to-noise criteria for analytes in the calibration verification solution were met in all instances.

6.2.5 Column Performance and Instrument Resolution

Column performance was checked at the beginning of each 12-hour analytical period and met method criteria.

Instrument resolution was documented at the beginning and end of each 12-hour period with one exception. In PCB sample batch WG13554, which contained five performance evaluation samples and 15 extract samples, on one analysis day (September 17, 2004), the ending resolution documentation was conducted at 12 hours and 54 minutes. However, as this resolution documentation met all criteria, it was considered representative of acceptable instrument performance during the analytical period, and the data were accepted.

6.2.6 Method Blanks

Method blanks were analyzed with each sample batch to verify that laboratory procedures did not introduce significant contamination. A summary of the method blank data is presented in Appendix C. There were many instances for both D/F and PCB data where analyte concentrations in the method blank exceeded the target criteria in the D/QAPP. Samples from this demonstration, which had very high D/F and PCB concentrations, contributed to the difficulty in achieving method blank criteria in spite of steps the reference laboratory took to minimize contamination (such as proofing the glassware before use in each analytical batch). In many instances, the concentrations of D/F and PCBs in the samples exceeded 20 times the concentrations in the blanks. For all instances, the sample results were unaffected because the method blank TEQ concentration was compared to the sample TEQ concentrations to ensure that background contamination did not significantly impact sample results.

6.2.7 Internal Standard Recovery

Internal standard recoveries were generally within the D/QAPP criteria. D/QAPP criteria were tighter than the standard EPA method criteria; in instances where internal standard recoveries were outside of the D/QAPP criteria, but within the standard EPA method criteria, results were accepted. In several instances, the dioxin cleanup standard recoveries were affected by interferences. As the cleanup standard is not used for quantification of native analytes, these data were accepted. Any samples affected by internal standard recoveries outside of the D/QAPP and outside of the EPA method criteria were evaluated for possible impact on total TEQ and for comparability with replicates processed during the program before being accepted.

6.2.8 Laboratory Control Spikes

One laboratory control spike (ongoing precision and recovery sample), which consisted of native analytes spiked into a reference matrix (sand), was processed with each analytical batch to assess accuracy. Recovery of spiked analytes was within the D/QAPP criteria in Table 9-2 for all analytes in all laboratory control spike samples.

6.2.9 Sample Batch Duplicates

A summary of the duplicate data is presented in Appendix C. One sample was prepared in duplicate in most sample batches; four batches were reported without a duplicate. Three of 14 dioxin sample batches and 5 of 14 PCB sample batches did not meet criteria of <20% RPD between duplicates. Data where duplicates did not meet D/QAPP criteria were evaluated on an individual basis.

6.3 Evaluation of Primary Objective P1: Accuracy

Accuracy was assessed through the analysis of PE samples consisting of certified standard reference materials, certified spikes, and certified blanks. A summary of reference method percent recovery (R) values is presented in Table 6-3. The R values are presented for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ. The minimum, maximum, mean, and median R values are presented for each set of TEQ results. The reference method values were in best agreement with the certified values for the TEQ_{PCB} results, with a mean R value of 96%. The mean R values for $TEQ_{D/F}$ and total TEQ were 125% and 94%, respectively. The mean and median R values for the TEQ_{PCB} and total TEQ were identical. The mean and median R values for $TEQ_{D/F}$ were not similar and were largely influenced by the $TEQ_{D/F}$ recovery for ERA Aroclor of 324%. The ERA Aroclor-certified $TEQ_{D/F}$ values were based on TCDD and TCDF only, whereas the reference method $TEQ_{D/F}$ values were based

on contributions from all 2,3,7,8-substituted D/F analytes. The R values presented in Table 6-1 indicate that the reference method reported data that were on average between 94 and 125% of the certified values of the PE samples.

The effect of known interferences on reference method TEQs is listed in Table 6-2. D/F and PCB TEQs were not affected by PAH as evidenced through the analysis of ERA PAH standard reference material. D/F and PCB TEQs were not affected by each other as evidenced by spikes that contained only one set of analytes having negligible influence on the TEQ of the other analyte set.

6.4 Evaluation of Primary Objective P2: Precision

The 209 samples included in the demonstration consisted of replicates of 49 discrete samples. There were four replicates of each sample except for PE sample Cambridge 5183 (7 replicates), ERA blank reference material (8 replicates), Wellington WMS-01 standard reference material (7 replicates), and 0.5 pg/mL 2,3,7,8-TCDD extract (7 replicates). Reference method data were obtained for all 209 samples; however, $TEQ_{D/F}$ and total TEQ data for samples Ref 197 (ERA PCB 100) and Ref 202 (LCG CRM-529) were omitted as outliers as it appeared that these two samples were switched during preparation after observing results of the replicates and evaluating the congener profiles of these two samples.

A summary of the reference method replicate RSD values is presented in Tables 6-3a and 6-3b. The RSD values are presented for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ in Table 6-3a, and a summary by sample type is presented in Table 6-3b, along with the minimum R

Table 6-1. Objective P1 Accuracy - Percent Recovery

PE Sample ID	PE Sample Description	% Recovery					
		TEQ_{PCB}		$TEQ_{D/F}$		Total TEQ	
1	Cambridge 5183	81		111		94	
2	LCG CRM-529	100		106		106	
3	Wellington WMS–01	93		106		105	
4	Cambridge 5184	120		106		118	
5	NIST 1944	102		91		93	
6	ERA TCDD 10	NA		79		79	
7	ERA TCDD 30	NA		77		77	
8	ERA PAH	NA		NA		NA	
9	ERA PCB 100	96		NA		95	
10	ERA PCB 10000	95		NA		95	
11	ERA Aroclor	82		324		83	
12	ERA Blank	NA		NA		NA	
All Performance Evaluation Samples		NUMBER	8	NUMBER	8	NUMBER	10
		MIN	81	MIN	77	MIN	77
		MAX	120	MAX	324	MAX	118
		MEDIAN	96	MEDIAN	106	MEDIAN	94
		MEAN	96	MEAN	125	MEAN	94

NA = not applicable.

Table 6-2. Evaluation of Interferences

PE Material with Known Interference	Mean TEQ (pg/g)
ERA PAH	0.195 (D/F + PCB)
ERA PCB 100	0.073 (D/F)
ERA PCB 10000	0.220 (D/F)
ERA TCDD 10	0.025 (PCB)
ERA TCDD 30	0.036 (PCB)

Table 6-3a. Objective P2 Precision - Relative Standard Deviation

Sample Type	Sample ID	RSD for TEQ_{PCB} (%)	RSD for $TEQ_{D/F}$ (%)	RSD for Total TEQ (%)
Environmental	Brunswick #1	8	6	6
	Brunswick #2	3	16	16
	Brunswick #3	5	8	8
	Midland #1	4	9	9
	Midland #2	10	6	6
	Midland #3	4	6	6
	Midland #4	77	9	10
	NC PCB Site #1	21	15	20
	NC PCB Site #2	21	2	21
	NC PCB Site #3	25	12	24
	Newark Bay #1	7	28	25
	Newark Bay #2	2	22	20
	Newark Bay #3	6	6	6
	Newark Bay #4	1	12	11
	Raritan Bay #1	6	5	4
	Raritan Bay #2	3	2	1
	Raritan Bay #3	3	5	4
	Saginaw River #1	8	25	23
	Saginaw River #2	7	19	18
	Saginaw River #3	60	19	19
	Solutia #1	36	13	13
	Solutia #2	4	7	7
	Solutia #3	11	5	5
	Titta. River Soil #1	7	6	5
	Titta. River Soil #2	9	10	10
	Titta. River Soil #3	12	26	26
	Titta. River Sed #1	19	27	26
	Titta. River Sed #2	14	37	37
	Titta. River Sed #3	13	9	8
	Winona Post #1	13	2	2
	Winona Post #2	4	9	9
	Winona Post #3	9	4	4
Extract	Envir Extract #1	71	50	50
	Envir Extract #2	83	2	2
	Spike #1	119	6	9
	Spike #2	1	5	3
	Spike #3	4	13	4
Performance Evaluation	Cambridge 5183	7	19	9
	Cambridge 5184	3	4	2
	ERA Aroclor	44	6	43
	ERA Blank	62	65	61
	ERA PAH	83	27	30
	ERA PCB 100	4	65 [a]	3
	ERA PCB 10000	7	91	7
	ERA TCDD 10	60	5	5
	ERA TCDD 30	39	6	6
	LCG CRM-529	14	2[a]	1
	NIST 1944	4	9	7
	Wellington WMS-01	5	3	3

[a] Does not include sample excluded due to sample preparation error.

Table 6-3b. Objective P2 Precision - Relative Standard Deviation (By Sample Type)

Sample Type	RSD for TEQ_{PCB} (%)					RSD for $TEQ_{D/F}$ (%)					RSD for Total TEQ (%)				
	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN
Environmental	32	1	77	8	13	32	2	37	9	12	32	1	37	10	13
Extract	5	1	119	71	56	5	2	50	6	15	5	2	50	4	14
PE	12	3	83	11	28	12	2	91	7	25	12	1	61	7	15
Overall	49	1	119	8	21	49	2	91	9	16	49	1	61	8	13

value, the maximum R value, and the mean R value for each set of TEQ results and sample types. In terms of sample type, the reference method had the most precise data for the environmental sample $TEQ_{D/F}$ results, with a mean RSD value of 12%. This was followed closely by environmental sample TEQ_{PCB} and total TEQ results, which both had mean RSDs of 13%. In terms of TEQ values, the reference method had the most precise data for the total TEQ values, with a mean overall RSD of 13%. Overall RSD values ranged from 1% to 119%. Precision was significantly worse for certified blanks and blank samples (e.g., samples that contained spikes of only one analyte set and were blank for the other analytes) as might be expected due to the very low levels detected in these samples.

6.5 Comparability to Characterization Data

To assess comparability, reference laboratory D/F data for environmental samples were plotted against the characterization data that was generated by Battelle prior to the demonstration. Characterization data were obtained as part of the process to verify homogenization of candidate soil and sediment samples as described in Chapter 5 and reported in Table 4-5. It should be noted that second column confirmations of 2,3,7,8-TCDF results were not performed during characterization analyses; therefore, characterization TEQs are biased high for samples where a large concentrations of non-2,3,7,8-TCDF coeluted with 2,3,7,8-TCDF on the DB-5 column. Characterization samples also were not rigorously evaluated to ensure that high concentration extracts were diluted sufficiently so that all peak areas were less than the peak areas of the highest calibration standard. In spite of these differences between reference and characterization analyses, the results had fairly high correlation ($R^2 = 0.9899$) as demonstrated in Figure 6-1.

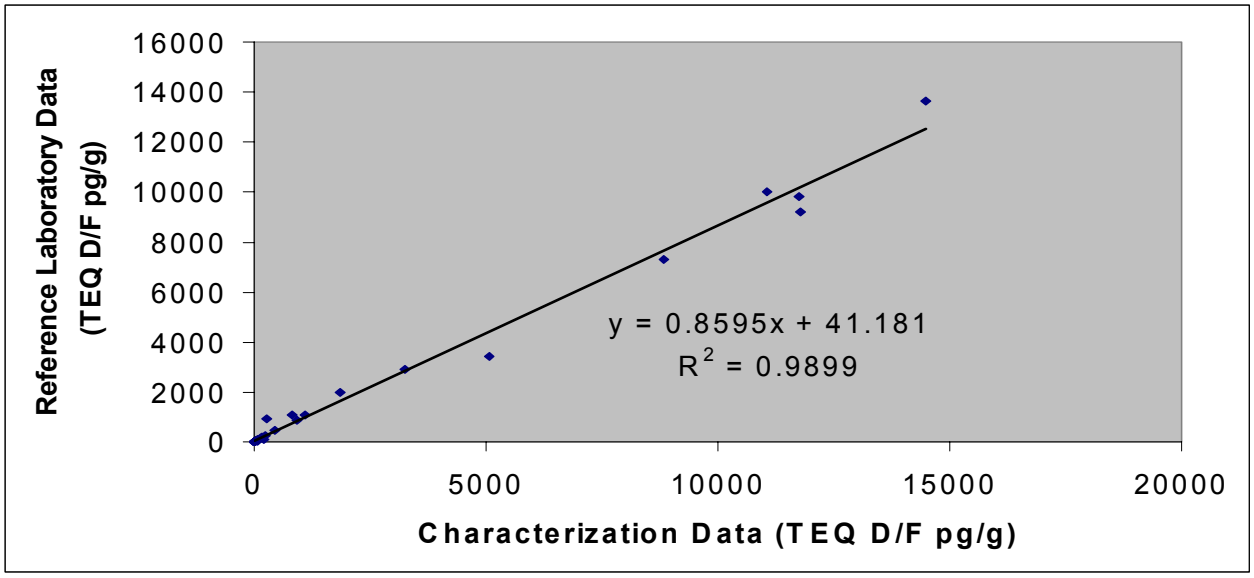


Figure 6-1. Comparison of reference laboratory and characterization D/F data for environmental samples.

6.6 Performance Summary

This section provides a performance summary of the reference method by summarizing the evaluation of the applicable primary objectives of this demonstration (accuracy, precision, and cost) in Table 6-4. A total of 209 samples was analyzed for seventeen 2,3,7,8-substituted D/F and 12 PCBs over an eight-month time frame (April 27 to December 20, 2004). Valid results were obtained for all 209 PCB analyses, while 207 valid results were obtained for D/F. The D/F and total TEQ results for samples Ref 197 (ERA PCB 100) and Ref 202 (LCG CRM-529) were omitted as outliers because it appeared that these two samples were switched during preparation after observing results of the replicates and evaluating the congener profiles of these two samples. The demonstration sample set provided particular challenges to the reference laboratory in that there was a considerable range of sample concentrations for D/F and PCB. This caused some difficulty in striving for low MDLs in the presence of high-level samples. The range of concentrations in the demonstration sample set also required the laboratory to modify standard procedures, which contributed to increased cost and turnaround time delay. For example, an automated sample cleanup system could not be used due to carryover from high-level samples; instead, more labor-intensive manual cleanup procedures were used; glassware required extra cleaning and proofing before being reused; cleanup columns sometimes became overloaded from interferences and high-level samples, causing low recoveries so that samples had to be re-extracted or cleanup fractions had to be analyzed for the lost analytes; and method blanks often showed trace levels of contamination, triggering the repeat of low-level samples.

Because the reference method was not to be altered significantly for this demonstration, the reference laboratory was limited in its ability to adapt the trace-level analysis to higher level samples. In spite of these challenges, the quality of the data generated met the project goals. The main effect of the difficulties associated with these samples was on schedule and cost.

Table 6-4. Reference Method Performance Summary - Primary Objectives

Objective	Performance			
	Statistic	TEQ_{PCB}	$TEQ_{D/F}$	Total TEQ
P1: Accuracy	Number of data points	8	8	10
	Median Recovery (%)	96	106	94
	Mean Recovery (%)	96	125	94
P2: Precision	Number of data points	49	49	49
	Median RSD (%)	8	9	8
	Mean RSD (%)	21	16	13
P7: Cost	209 samples were analyzed for 17 D/F and 12 PCBs. Total cost was $398,029. D/F cost was $213,580 ($1,022 per sample) and PCB cost was $184,449 ($883 per sample).			

Chapter 7
Performance of CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay Kits

7.1 Evaluation of DF1 Dioxin/Furan and PCB TEQ Immunoassay Kits Performance

The CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits are immunoassay techniques that report TEQ of dioxin/furans and PCBs, respectively. It should be noted that the results generated by the CAPE Technologies kits may not directly correlate to HRMS TEQ in all cases because it is known that the congener responses and cross-reactivities of the kits are not identical to the TEFs that are used to convert congener HRMS concentration values to TEQ. The effect of cross-reactivities may contribute to this technology's reporting results that are biased high or low compared to HRMS TEQ results. Therefore, these kits should not be viewed as producing an equivalent measurement value to HRMS TEQ but as a screening value to approximate HRMS TEQ. As described in Appendix B and CAPE Technologies literature, the best results for immunoassay screening are obtained on a single site basis. The ideal approach involves partially characterizing a site by HRMS, using those results to develop a site specific immunoassay calibration, and refining that calibration over time, based on an ongoing stream of confirmatory HRMS samples. This approach was not evaluated during this demonstration; samples from multiple sites were pooled and a single calibration was used.

The following sections describe the performance of the DF1 Dioxin/Furan Immunoassay Kit and the PCB TEQ Immunoassay Kit, according to the primary objectives for this demonstration. The developer and reference laboratory data are presented in Appendix D. The statistical methods used to evaluate the primary objectives are described in Section 4.7. Detailed data evaluation records can be found in the DER.

7.1.1 Evaluation of Primary Objective P1: Accuracy

A summary of the percent recovery (R) values for the CAPE Technologies D/F and PCB kits is presented in Table 7-1. The description of how R values were calculated is presented in Section 4.7.1. The R values are presented for $TEQ_{PCB,}$ $TEQ_{D/F,}$ and total TEQ values. The minimum R value, the maximum R value, median R value, and the mean R value are presented for each set of TEQ results. The mean R values for the $TEQ_{PCB,}$ $TEQ_{D/F,}$ and total TEQ results were 195%, 236%, and 160%, respectively. The R values presented in Table 7-1 indicate that the CAPE Technologies kits generally reported data that were biased high relative to the certified values of the PE samples, although the bias for one PE sample (NIST 1944) was consistently low (R values between 30% and 49%) for all TEQ values.

7.1.2 Evaluation of Primary Objective P2: Precision

Summaries of the RSD values for the CAPE Technologies D/F Immunoassay Kit and PCB TEQ Immunoassay Kit are presented in Tables 7-2a and 7-2b. The description of how RSD values were calculated is presented in Section 4.7.2. The RSD values are presented for TEQ_{PCB},$TEQ_{D/F}$, and total TEQ in Table 7-2a, and a summary by sample type is presented in Table 7-2b, along with the minimum RSD value, the maximum RSD value, the median RSD value, and the mean RSD value for each set of TEQ results and sample types. Low RSD values (< 20%) would indicate high precision. In terms of sample type, the CAPE Technologies D/F and PCB kits had the most precise data for the PE $TEQ_{D/F}$ results, with a mean RSD value of 64%. In terms of TEQ values, the CAPE Technologies kits had the most precise data for the $TEQ_{D/F}$ values with an

Table 7-1. Objective P1 Accuracy - Percent Recovery

PE Sample ID	PE Sample Description	% Recovery					
		TEQ_{PCB}		$TEQ_{D/F}$		Total TEQ	
1	Cambridge 5183	171		436		296	
2	LCG CRM-529	26		NA		105	
3	Wellington WMS-01	302		182		199	
4	Cambridge 5184	131		68		121	
5	NIST 1944	49		30		33	
6	ERA TCDD 10	NA		182		268	
7	ERA TCDD 30	NA		157		158	
8	ERA PAH	NA		NA		NA	
9	ERA PCB 100	523		NA		NA	
10	ERA PCB 10000	257		NA		NA	
11	ERA Aroclor	99		595		101	
12	ERA Blank	NA		NA		NA	
All Performance Evaluation Samples		NUMBER	8	NUMBER	7	NUMBER	8
		MIN	26	MIN	30	MIN	33
		MAX	523	MAX	595	MAX	296
		MEDIAN	151	MEDIAN	182	MEDIAN	139
		MEAN	195	MEAN	236	MEAN	160

NA = not applicable.

Table 7-2a. Objective P2 - RSD as a Description of Precision by Sample

Sample	Relative Standard Deviation (%)[a]		
	TEQ_{PCB}	$TEQ_{D/F}$	Total TEQ
Brunswick #1	117	71	68
Brunswick #2	141	51	49
Brunswick #3	38	187	174
Midland #1	163	96	95
Midland #2	187	23	31
Midland #3	136	36	41
Midland #4	172	46	46
NC PCB Site #1	93	92	42
NC PCB Site #2	82	23	17
NC PCB Site #3	145	34	52
Newark Bay #1	77	29	19
Newark Bay #2	96	21	19
Newark Bay #3	62	62	61
Newark Bay #4	120	46	68
Raritan Bay #1	181	40	43
Raritan Bay #2	79	17	20
Raritan Bay #3	65	59	53
Saginaw River #1	46	89	87
Saginaw River #2	145	70	72
Saginaw River #3	199	165	128
Solutia #1	132	65	63
Solutia #2	162	58	64
Solutia #3	96	27	27
Titta. River Soil #1	95	56	57
Titta. River Soil #2	177	87	88

Sample	Relative Standard Deviation (%)[a]		
	TEQ_{PCB}	$TEQ_{D/F}$	Total TEQ
Titta. River Soil #3	86	NA	67
Titta. River Sed #1	135	166	128
Titta. River Sed #2	200	86	85
Titta. River Sed #3	188	104	119
Winona Post #1	125	91	91
Winona Post #2	88	116	114
Winona Post #3	102	93	86
Envir Extract #1	50	155	154
Envir Extract #2	141	40	51
Spike #1	153	86	99
Spike #2	99	136	98
Spike #3	118	0	117
Cambridge 5183	74	29	18
Cambridge 5184	118	99	105
ERA Aroclor	173	98	169
ERA Blank	116	68	61
ERA PAH	110	NA	NA
ERA PCB 100	117	NA	NA
ERA PCB 10000	93	NA	NA
ERA TCDD 10	172	55	90
ERA TCDD 30	200	51	50
LCG CRM-529	99	NA	81
NIST 1944	53	66	54
Wellington WMS - 01	198	48	77

NA = not applicable (i.e., one or more of the replicates were reported as a nondetect value).

[a] Three or four replicate results were used to calculate the RSD values.

Table 7-2b. Objective P2 - RSD as a Description of Precision by Sample Type

Sample Type	RSD (%) for TEQ_{PCB}					RSD (%) for $TEQ_{D/F}$					RSD (%) for Total TEQ				
	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN
Env	32	38	200	122	123	31	17	187	62	71	32	17	174	63	68
Ex	5	50	153	118	112	5	0	155	86	83	5	51	154	99	104
PE	12	53	200	117	127	8	29	99	60	64	9	18	169	77	78
All	49	38	200	118	123	44	0	187	63	71	46	17	174	67	74

overall RSD of 71%. Overall RSD values ranged from 0% to 200%. Note that the vendor reported several TEQ_{PCB} results as "0" pg/g TEQ (see Appendix D), so zero was used in the calculation of RSD. This is different than the treatment of nondetects (reported as "< reporting limits"), which were not included in the analysis.

7.1.3 Evaluation of Primary Objective P3: Comparability

The description of the statistical analyses used in the comparability evaluations are described in Section 4.7.3. The comparability of the CAPE Technologies and reference laboratory data was assessed by calculating RPD values for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ, as presented in Table 7-3. The summary statistics presented in Table 7-3 provide an overall assessment of the RPD values that is reported by TEQ value and sample type. The CAPE Technologies values agreed best with the reference laboratory D/F measurements for extract samples, with a median RPD values of -4%. The median RPD value for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ were -13%, -26%, and -5%, respectively, with minimum and maximum values around minus 200% and positive 200%, respectively. RPD values between positive and negative 25% indicate good agreement between the reference laboratory and developer values. Of the TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ values, 22 (12%), 28 (17%), and 21 (13%) of the samples, respectively, had RPD values between positive and negative 25%. This evaluation indicates that the CAPE Technologies results were generally higher than the reference laboratory (as evidenced by all median values being negative).

Comparability was also assessed using the interval approach discussed in Section 4.7.3. The agreement when sorting the developer and reference laboratory results for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ data into four intervals $\leq$ 50 pg/g, 50 to 500 pg/g, 500 to 5,000 pg/g, and $\geq$ 5,000 pg/g) is described in Table 7-4. The agreement between the developer and reference laboratory was 82% for TEQ_{PCB}, 71% for $TEQ_{D/F}$, and 64% for total TEQ. Interval reporting addresses the question whether a value reported by the technology would result in the same decision of what to do next with the sample if it was analyzed by the reference method. This interval assessment table indicates that from 18 to 36% of the time, the CAPE Technologies result would have indicated a different interval (and therefore a different decision to be made about the sample) than if it was analyzed by the reference laboratory, depending on which TEQ value was being determined and the concentrations chosen for the intervals.

The ERA blank samples contained levels of D/Fs and PCBs that were below the reporting limits of the developer technologies (see Table 4-4 certified values: 0.046 pg/g $TEQ_{D/F}$ and 0.01 pg/g TEQ_{PCB}). The CAPE Technologies reported concentrations were compared with the reference laboratory reported data for these samples in Table 7-5. CAPE Technologies reported four of the eight TEQ_{PCB} values as detections (ranging from 2 to 4 pg/g), so the four results that were reported as nondetects (i.e., zero) agreed with the reference laboratory results. For $TEQ_{D/F}$, five of the results were reported as detections (13 to 46 pg/g), so three of eight results agreed with the reference laboratory's reporting of blank samples. For total TEQ values, two of the CAPE Technologies results were reported as nondetects and agreed with the reference laboratory results. It should be noted that the reference laboratory data presented in Table 7-5 were calculated with nondetect values assigned a zero concentration. When applying the TEQ calculation method of assigning nondetects with a concentration of one-half the SDL, the reference data increased, but the conclusions regarding agreement with the developer data remained the same.

Table 7-3. Objective P3 - Comparability Summary Statistics of RPD

Sample Type	TEQ_{PCB} RPD (%)				$TEQ_{D/F}$ RPD (%)				Total TEQ RPD (%)			
	N	MIN	MAX	MEDIAN	N	MIN	MAX	MEDIAN	N	MIN	MAX	MEDIAN
Env	128	-200	200	-10	120	-199	198	-26	122	-199	198	-8
Ex	16	-198	189	-115	16	-189	179	-4	12	-134	145	18
PE	38	-179	189	15	31	-129	169	-30	25	-138	171	-5
All	182	-200	200	-13	167	-199	198	-26	159	-199	198	-5

Table 7-4. Objective P3 - Comparability Using Interval Assessment

Agreement	TEQ_{PCB}	$TEQ_{D/F}$	Total TEQ
Number Agree	172	148	132
% Agree	82	71	64
Number Disagree	37	60	75
% Disagree	18	29	36

Table 7-5. Objective P3 - Comparability for Blank Samples

	TEQ_{PCB}			$TEQ_{D/F}$			Total TEQ		
Rep	CAPE Technologies (pg/g)	Ref Lab[a] (pg/g)	Agree?	CAPE Technologies (pg/g)	Ref Lab[a] (pg/g)	Agree?	CAPE Technologies (pg/g)	Ref Lab[a] (pg/g)	Agree?
1	0	J0.0243[b]	Yes	< 14	0.0942	Yes	14	J0.12	No
2	0	0.00385	Yes	15	0.0728	No	15	J0.08	No
3	2	0.00277	No	< 50	0.237	Yes	< 52	J0.24	Yes
4	2	J0.042	No	17	0.307	No	19	J0.35	No
5	0	J0.0229	Yes	46	0.113	No	46	J0.14	No
6	4	J0.0191	No	13	0.0524	No	17	J0.07	No
7	3	J0.0325	No	< 11	0.211	Yes	< 14	J0.24	Yes
8	0	J0.0225	Yes	13	0.0692	No	13	J0.09	No
% agree	50% (4 of 8)			38% (3 of 8)			25% (2 of 8)		

[a] All nondetect and EMPC values were assigned a zero concentration for the reference laboratory TEQ calculation.
[b] J flag was applied to any reported value between the SDL and the lowest level calibration.

7.1.4 Evaluation of Primary Objective P4: Estimated Method Detection Limit

It should be noted that these calculations did not strictly follow the definition in the *Code of Federal Regulations* (i.e., t value with 6 degrees of freedom). Since detections were not reported for all seven replicate samples, the degrees of freedom and statistical power of the analysis were reduced accordingly. The only approach that led to the use of the definitional calculation with 6 degrees of freedom required special treatment of the nondetect values (i.e., assigning values that were one-half or equal to the nondetect value). However, these calculations are provided as estimated method detection limits (EMDLs) to give the reader a sense of the detection capabilities of the technology.

The EMDLs of the CAPE Technologies D/F and PCB kits were determined for $TEQ_{D/F}$, TEQ_{PCB}, and total TEQ values using the Extract Spike #1 and Cambridge 5183 sample results in Tables 7-6a and b. Since 2,3,7,8-TCDD was the only congener in Extract Spike #1, only an EMDL for $TEQ_{D/F}$ could be determined. As shown in Tables 7-6a and 7-6b, because some of the results were nondetects, the EMDLs were calculated in three ways for nondetect values: by setting nondetect values to zero, by setting nondetect values to half of the reporting limit value, and by setting nondetect values to the reporting limit value itself. While the number of degrees of freedom was reduced from 6 to 2 or 3 for the Cambridge 5183 and Extract Spike #1 samples because of the nondetect values, the EMDLs for all calculations were in the range of 12 to 35 pg/g $TEQ_{D/F}$. The detection limit reported by CAPE Technologies in the demonstration plan was 1 pg/g TEQ. The EMDLs determined using the Wellington samples were significantly higher (200 to 300 pg/g TEQ) than for the other two samples. Since the D/F and PCB concentrations were much higher than the projected reporting limit, the Wellington samples did not seem appropriate for calculating EMDLs, so the MDLs for this sample were not included in the calculations.

Table 7-6a. Objective P4 - Estimated MDL for $TEQ_{D/F}$ and TEQ_{PCB}

Statistic	$TEQ_{D/F}$						TEQ_{PCB}
	Cambridge 5183			Extract Spike #1			
	Nondetect values set to zero	Nondetect values set to ½ value	Nondetect set to reported value	Nondetect values set to zero	Nondetect values set to ½ value	Nondetect set to reported value	Cambridge 5183
Degrees of Freedom	2	6	6	3	6	6	6
Standard Deviation (pg/g)	5	6	4	7	6	6	6
EMDL (pg/g)	35	20	12	33	20	18	20

Table 7-6b. Objective P4 - Estimated MDL for Total TEQ

Statistic	Cambridge 5183		
	Nondetect values set to zero	Nondetect values set to ½ value	Nondetect values set to reported value
Degrees of Freedom	2	6	6
Standard Deviation (pg/g, Total TEQ)	4.73	9.83	8.52
EMDL (pg/g, Total TEQ)	33	30	25

7.1.5 Evaluation of Primary Objective P5: False Positive/False Negative Results

The summary of false positive/false negative results is presented in Table 7-7. CAPE Technologies reported 14% false positive and 5% false negative results, relative to the reference laboratory's reporting of samples above and below 20 pg/g TEQ, for the TEQ_{PCB} results. For $TEQ_{D/F}$, the percentage of false positive/negative results were slightly less (11% and 4%, respectively) than for TEQ_{PCB}. CAPE Technologies reported 14% false positives and 3% false negatives around 20 pg/g for total TEQ. CAPE Technologies's false positive and false negative rates around 50 pg/g were generally lower for all three TEQ types, ranging from 4% to 10%.

These data suggest the CAPE Technologies kits as processed in the demonstration could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for sample above and below 50 pg/g TEQ. CAPE Technologies notes that the user can optimize performance of the kit at other desired screening levels by changing the size of sample extracted so that the desired screening level concentration falls at the optimum point on the kit response curve.

Table 7-7. Objective P5 - False Positive/False Negative Results

Rate	TEQ_{PCB}		$TEQ_{D/F}$		Total TEQ	
	20 pg/g	50 pg/g	20 pg/g	50 pg/g	20 pg/g	50 pg/g
False Positive	14% (29 of 209)	8% (17 of 209)	11% (22 of 207)	8% (17 of 207)	14% (28 of 207)	10% (20 of 207)
False Negative	5% (11 of 209)	4% (9 of 209)	4% (9 of 207)	8% (16 of 207)	3% (6 of 207)	5% (11 of 207)

7.1.6 Evaluation of Primary Objective P6: Matrix Effects

Six types of potential matrix effects were investigated: (1) measurement analysis location (field vs. laboratory), (2) matrix type (soil vs. sediment vs. extract), (3) sample type (PE vs. environmental vs. extract), (4) PAH concentration, (5) environmental site, and (6) known interferences. A summary of the matrix effects is provided in the bullets below, followed by a detailed discussion:

- Measurement location: 19% statistically different
- Matrix type: none
- Sample type: none
- PAH concentration: slight effect on total TEQ
- Environmental site: none
- Known interferences: slight

A one-way ANOVA was performed on samples that had at least one detected replicate analyzed in the field and in the laboratory to determine if performance was affected by the samples being analyzed in the field. A p-value less than 0.05 in Table 7-8 indicates that the mean of samples analyzed in the field was significantly different from the mean of those analyzed in the laboratory. Only $TEQ_{D/F}$ values were included in this evaluation because all TEQ_{PCB} and total TEQ values were generated by CAPE Technologies in its laboratories. Seven of 37 sets of $TEQ_{D/F}$ values (19% overall) showed statistically significant location effects, and of these samples, CAPE Technologies generally reported the laboratory result more comparably to the reference laboratory result. In Table 7-9, precision summary values are presented by matrix type. A one-way ANOVA model was used to test the effect of soil vs. sediment vs. extract on RSD. These tests showed no significant effect on RSD for TEQ_{PCB}, $TEQ_{D/F}$, or total TEQ. In Table 7-10, precision summary values are presented by PAH concentrations for environmental samples only. A one-way ANOVA model was used to test the effect of PAH concentration on RSD. These tests showed a slight effect ($p = 0.0327$) on total TEQ, but the effects for $TEQ_{D/F}$ ($p = 0.0526$) or TEQ_{PCB} ($p = 0.0771$) were not statistically significant. The summary of RSD values segregated by sample type is presented in Table 7-2b. A one-way ANOVA model was used to test the effect of sample type (PE vs. environmental vs. extract) on RSD. These tests showed no significant effect on RSD for $TEQ_{PCB,}$ $TEQ_{D/F,}$ or total TEQ. Based on the comparability results (RPD), CAPE Technologies's results were not more or less comparable for one particular environmental site, suggesting that matrix effects were not dependent on environmental site.

The effect of known interferences was also assessed by evaluating the results of PE materials that contained one type of contaminant (D/F, PCBs, or PAHs) but not another. Table 7-11 summarizes the detection of analytes not spiked in the PE samples along with the percent recovery values (from Table 7-1) for the spiked analytes. For the ERA PAH sample that contained no spike D/Fs or PCBs, CAPE Technologies reported a mean total TEQ value of 17 pg/g. The PCB-only spiked samples were reported with only one D/F detection. CAPE Technologies reported only one sample as a slight PCB detection for the ERA TCDD 30 D/F-only spiked PE samples, but three TEQ_{PCB} detections (mean = 9.5 pg/g TEQ_{PCB}) for the ERA TCDD 10 D/F only spiked PE sample.

7.1.7 Evaluation of Primary Objective P7: Technology Costs

Evaluation of this objective is fully described in Chapter 8, Economic Analysis.

7.2 Observer Report: Evaluation of Secondary Objectives

The secondary objectives described in this section were assessed only for the DF1 kit because the PCB TEQ Immunoassay Kit was not deployed during the field demonstration. Because of the similar principles and procedures for the two kits, it is likely that similar conclusions could be drawn, but this was not confirmed by observation.

The technology used by CAPE Technologies at the demonstration was composed of two kits, the SP-3 sample preparation kit and the DF1 dioxin/furan immunoassay. All steps of these procedures were observed during the field demonstration. The sample preparation consisted of first adding sodium sulfate to the sample to make it free flowing, and then extracting the samples for 2 to 4 hours using a 1:1 mixture of hexane-to-acetone. After extraction, samples were centrifuged at 1,000 x g or less for 10 to 15 minutes. A portion of the supernatant was removed and evaporated onto 0.25 mL of tetradecane. Hexane was added to dilute the residue. The acid silica-activated carbon coupled column system was prewashed with hexane.

Table 7-8. Objective P6 - Matrix Effects Using Descriptive Statistics and ANOVA Results Comparing $TEQ_{D/F}$ Replicate Analysis Conducted During the Field Demonstration and in the Laboratory

Sample Type	Sample	Location	$TEQ_{D/F}$ N	$TEQ_{D/F}$ Mean (SD) (pg/g)	$TEQ_{D/F}$ p-Value Comparing Field to Laboratory
Environmental	Brunswick #1	field	1	59.0	0.5292
		lab	3	137.3 (89.9)	
	Brunswick #3	field	2	5,025.0 (6696.3)	0.4084
		lab	2	111.5 (38.9)	
	Midland #1	field	2	471.0 (482.2)	0.6121
		lab	2	240.5 (259.5)	
	Midland #2	field	1	64.0	0.8466
		lab	3	59.7 (17.1)	
	Midland #3	field	1	119.0	0.3017
		lab	3	215.0 (60.3)	
	Midland #4	field	1	37.0	0.7780
		lab	2	28.5 (19.1)	
	NC PCB Site #1	field	2	13,800.0 (3535.5)	0.0582
		lab	2	1,949.0 (2320.7)	
	NC PCB Site #2	field	2	25,550.0 (1484.9)	0.8265
		lab	2	27,350.0 (10111.6)	
	NC PCB Site #3	field	1	33700.0	0.4931
		lab	2	53,700.0 (15980.6)	
	Newark Bay #1	field	1	31.0	0.4374
		lab	2	21.5 (6.4)	
	Newark Bay #2	field	1	75.0	0.5252
		lab	2	59.0 (14.1)	
	Newark Bay #3	field	1	11.0	0.1836
		lab	3	57.0 (19.9)	
	Newark Bay #4	field	1	63.0	0.5212
		lab	3	42.0 (23.6)	
	Raritan Bay #1	field	2	58.5 (23.3)	0.7519
		lab	2	69.5 (36.1)	
	Raritan Bay #2	field	2	42.5 (6.4)	0.8852
		lab	2	44.0 (11.3)	
	Raritan Bay #3	field	1	56.0	0.9221
		lab	2	49.5 (43.1)	
	Saginaw River #1	field	2	1,114.0 (503.5)	0.1601
		lab	2	239.5 (256.7)	
	Saginaw River #2	field	1	1690.0	0.8450
		lab	3	1,373.0 (1237.6)	
	Saginaw River #3	field	2	1,485.5 (1760.0)	0.3779
		lab	2	86.5 (50.2)	
	Solutia #1	field	2	109.0 (41.0)	0.1326
		lab	2	37.5 (0.7)	
	Solutia #2	field	2	712.5 (221.3)	**0.0466**[a]
		lab	2	2,030.0 (353.6)	
	Solutia #3	field	2	2,840.0 (1343.5)	0.7224
		lab	2	3,230.0 (127.3)	
	Titta. River Soil #1	field	2	118.0 (97.6)	0.1376
		lab	2	286.5 (16.3)	

Sample Type	Sample	Location	$TEQ_{D/F}$		
			N	Mean (SD) (pg/g)	p-Value Comparing Field to Laboratory
	Titta. River Soil #2	field	2	1,251.5 (68.6)	**0.0023**
		lab	2	174.5 (24.7)	
	Titta. River Sed #1	field	2	355.0 (468.1)	0.4401
		lab	2	38.0 (31.1)	
	Titta. River Sed #2	field	2	190.5 (95.5)	0.1765
		lab	2	46.0 (28.3)	
	Titta. River Sed #3	field	1	184.0	**0.0166**
		lab	3	35.7 (16.7)	
	Winona Post #1	field	2	1,945.0 (742.5)	0.2872
		lab	1	68.0	
	Winona Post #2	field	2	3,970.0 (1018.2)	**0.0321**
		lab	2	51.0 (12.7)	
	Winona Post #3	field	2	987.0 (748.1)	0.3669
		lab	2	319.5 (326.0)	
PE	Cambridge 5183	field	1	17.0	1.0000
		lab	2	17.0 (7.1)	
	Cambridge 5184	field	1	280.0	0.0589
		lab	3	62.7 (47.8)	
	ERA Aroclor	field	1	161.0	**0.0129**
		lab	3	33.7 (12.7)	
	ERA TCDD 10	field	2	15.0 (9.9)	0.4730
		lab	2	25.0 (12.7)	
	ERA TCDD 30	field	1	82.0	**0.0121**
		lab	2	36.5 (0.7)	
	NIST 1944	field	2	119.0 (8.5)	**0.0272**
		lab	2	34.0 (18.4)	
	Wellington WMS -01	field	4	121.3 (62.6)	0.6782
		lab	3	101.7 (51.1)	

[a] **Bold** signifies in-field measurement statistically different from the laboratory measurement at the $p<0.05$ significance level.

Table 7-9. Objective P6 - Matrix Effects Using RSD as a Description of Precision by Soil, Sediment, and Extract

Matrix Type	RSD for TEQ_{PCB} (%)					RSD for $TEQ_{D/F}$ (%)					RSD for Total TEQ (%)				
	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN
Soil	26	74	200	118	127	21	23	116	58	64	23	17	169	63	68
Sediment	18	38	200	119	119	18	17	187	64	77	18	19	174	68	74
Extract	5	50	153	118	112	5	0	155	86	83	5	51	154	99	104
Overall	49	38	200	118	123	44	0	187	63	71	46	17	174	67	74

Table 7-10. Objective P6 - Matrix Effects Using RSD as a Description of Precision by PAH Concentration Levels (Environmental Samples Only)

PAH Concentration Level (ng/g)	RSD for TEQ_{PCB} (%)					RSD for $TEQ_{D/F}$ (%)					RSD for Total TEQ (%)				
	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN	N	MIN	MAX	MED	MEAN
> 100,000	3	38	145	82	88	3	23	187	34	81	3	17	174	52	81
10,000-100,000	4	88	125	110	108	4	71	116	92	93	4	68	114	89	90
1,000-10,000	16	46	187	108	115	16	17	96	49	51	16	19	95	46	49
< 1,000	9	86	200	172	154	8	46	166	87	97	9	46	128	85	87
Overall (Environmental Samples Only)	32	38	200	122	123	31	17	187	62	71	32	17	174	63	68

Table 7-11. Objective P6 - Matrix Effects of Known Interferences Using PE Materials

PE Sample	% Recovery for Spiked Analytes [a]	Mean TEQ (pg/g) Reported by CAPE Technologies for Analytes that were not Spiked in the PE Sample
ERA PAH	NA[b]	17 (total)
ERA PCB 100	523% (PCB)	23 (D/F)[c]
ERA PCB 10000	257% (PCB)	all nondetects for D/F
ERA TCDD 10	182% (D/F)	9.5 (PCB)
ERA TCDD 30	157 (D/F)	1 (PCB)[c]

[a] Percent recovery values taken from Table 7-1.

[b] NA = not applicable because R value could not be calculated.

[C] Three replicates were reported as nondetects.

At this point a slight change was made in the method described in the demonstration plan by including a pretreatment for samples that had significant color. For such samples, a small amount of bulk fine acid silica was added to the sample tube, mixed briefly, and the sample loaded onto the acid silica column as a slurry of acid silica in hexane. Samples with no pretreatment were loaded as hexane solutions. The columns were washed with hexane. The carbon column was removed, washed with a small amount of hexane, then eluted with 1:1 toluene/hexane to give the PCB fraction, which was stored for later analysis. The column was flipped and the dioxin/furan fraction eluted with toluene. A keeper solution was added to the eluted dioxin/furan fraction (TEG-methanol-Triton X-100) and the solvent was evaporated and centrifuged at 1-2000 x g to concentrate all of the keeper solution at the bottom of the tube. The samples were then diluted with methanol and continued forward with the analysis.

The immunoassay was performed by first rinsing the tubes with American Society for Testing and Materials(ASTM)-grade distilled water. The rinse was dumped and the tubes were inverted and tapped to remove the excess water. After the rinse, 500 µL of reagent grade water was added along with 50 µL of the Triton X-100 in methanol. The tubes were then mixed for 10 seconds. To this, 10 µL of control, standard, or sample was added and the tubes were mixed. Tubes were then covered and allowed to incubate. Product literature indicates that incubation should occur for two hours (acceptable results) to 12 to 24 hours (best results). In the demonstration, the tubes were incubated overnight. After incubation, the tube contents were dumped and the tubes were washed four times with ASTM-grade distilled water. Competitor conjugate (HRP conjugate, 500 µL) was added and allowed to incubate for 15 minutes. The tubes were then emptied and washed an additional four times. A 500-µL aliquot of the substrate solution was added to each tube and allowed to incubate for an additional 30 minutes. After incubation, 500 µL of stop solution was added and the samples were analyzed with a differential photometer.

7.2.1 Evaluation of Secondary Objective S1: Skill Level of Operator

In the field demonstration, samples were processed with the CAPE Technologies kit by Dr. Bob Harrison,who has a Ph.D. in environmental toxicology, 23 years experience with environmental immunochemistry, and eight years with this specific technology. The developer recommends that users have at least a bachelor's degree in the sciences, and experience with both dioxin cleanup methods and enzyme-linked immunosorbent assay (ELISA) would be helpful. From observation, the education level may not be strictly necessary, but the experience with dioxin cleanup methods seemed very important in the use of the kit.

The instructions contained with the kits are detailed, but at times they seemed difficult to understand. The kits are supplied with basic instructions, procedural notes, and application notes. The addition of these notes, which may have conflicting instructions, seemed somewhat confusing and did not always seem clear as to what procedural changes should be followed without first seeking input from the developer. However, once the appropriate sample processing procedures are established and the supplies are in place, the equipment contained in the kit seemed straightforward and easy to use. All cleanup columns are premade and prepacked, and the assay itself is uncomplicated. CAPE Technologies provides an Excel file to aid in data analysis. This spreadsheet automatically processes the raw data into a useful form after data entry by the user. Accurate sample weights are necessary for later calculations. Accurate volumes are especially important when using the immunoassay tubes, since variations in volume can cause differences in results. The kit requires some safety precautions when dealing with the solvents. Because the fine acid silica for cleanup columns is prepacked, mask precautions are not necessary.

7.2.2 Evaluation of Secondary Objective S2: Health and Safety Aspects

It can be expected that around 60 mL of hexane will be used for each sample. Not all of this becomes waste, but a portion does. The disposable columns as well as the disposable glassware create solid waste. The solvent waste itself is not inherently more hazardous than would be expected, unless the samples are very contaminated.

A complete inventory of the waste generated was performed after the demonstration for processing of 95 samples by CAPE Technologies and the following was recorded. None of the containers was verified as full. Note that this summary does not include the samples that were analyzed in the CAPE Technologies laboratories:

(1) One 1-gallon container filled with aqueous waste
(2) One used broken glass container
(3) One box of 40 mL vials containing sample/solvent mixture.

Based on observation, the amount of waste recorded seemed low in comparison to what should have been generated, but portions of the hexane rinses of the columns were lost to volatilization and 6 mL of the column eluate was saved for later PCB analysis. The reader should be advised that, although no difficulties were encountered during this project, difficulties could arise with disposal of dioxin-contaminated waste.

7.2.3 Evaluation of Secondary Objective S3: Portability

A trailer was used by CAPE Technologies during the demonstration. The need for power, nitrogen tanks, a fume hood, shakers, vacuums, and other equipment requires a trailer at the very least for successful operation of this technology. While the assay itself is very easy to use in the field, the extraction and cleanup methods require level work space and could create some difficulty in the field unless there was a mobile lab or trailer available. The cleanup method requires a large amount of space within a hood. The space issue can be mitigated by the use of racks that have been designed by CAPE Technologies and are available for purchase. During the demonstration, the individual using the technology was able to easily overcome the hood space constraints and work quite efficiently. The photometer recommended by CAPE Technologies is also very easy to use and is designed with field portability in mind. In all, while this technology does require a mobile lab or trailer, it did not seem difficult to use in the field. The trailer used for this demonstration took approximately half of a day to set up before samples could be processed. Differences in reported results due to measurement location (in field vs. laboratory) are described in Section 7.1.6.

7.2.4 Evaluation of Secondary Objective S4: Throughput

During the demonstration, 95 samples were processed by CAPE Technologies, including sample extraction, extract cleanup, dioxin/furan immunoassay, and capture of the PCB fraction for later analysis. This was done entirely by one person over the full five-day field period, with a total work time of approximately 55 hours. The developer stated that, with one experienced user, 20 to 25 samples that are dry and relatively clean could be finished per day. The developer gives a range of acceptable times for the first sample incubation of both immunoassays, from 2 hours to overnight (12 to 24 hours). The shorter time gives a slight reduction in sensitivity (less than twofold), and the longer time eliminates the possibility of variable incubation time effects due to the time required for sample addition. Otherwise the two options provide equivalent results and the choice between the two is made based on ease of use and turnaround time requirements. Sample turnaround time is affected by this protocol choice, but overall sample throughput is not. During the entire project, except for the final day of the field phase, the longer incubation time was used because of flexibility and ease of use. On that last day, samples extracted in the morning were processed to completion that day.

The number of samples processed in a day could be higher with two experienced users, but would be far less for novice users. The first data would be available after about 8 hours using the shorter incubation time, but not until the next morning using the longer incubation time. The developer reports that shorter run times have been used in certain cases, but at the cost of decreased sensitivity. For the fastest results, it is possible to compress the entire immunoassay portion of the procedure into 1.5 hours. This could give first results in less than 8 hours. Smaller batch sizes will also give faster turnaround, but throughput would decrease because of the lesser efficiency of small batches. Based on observation, it seemed far more efficient to extract a large number of samples first, and then allow a large batch to incubate overnight, with the immunoassay completed the morning of the second day.

Because the sample preparation method provides both dioxin/furan and PCB fractions from a single procedure, the additional time required for completion of the PCB test for a set of samples would be limited to the time needed for solvent exchange, immunoassay set up, and later immunoassay manipulations (the developer estimates an extra 2 hours per day per batch of 20 samples). If the dioxin/furan and PCB tests for a single set of samples were run concurrently and incubated overnight, both dioxin/furan and PCB results would be available by the middle of the next morning.

7.2.5 Miscellaneous Observer Notes

CAPE Technologies is a U.S.-based company. The developer offers a training class that lasts a minimum of 1½ days that can be held either at the developer's laboratory or at the user's site. Training is completely flexible and tailored to the needs of the customer. CAPE Technologies also offers extensive phone support for customers and encourages users to discuss their projects so that CAPE Technologies can help guide the user's choices of sample preparation and assay procedures.

The materials that come with the DF1 kit are the coated antibody tubes (amount varies by kit purchased), the competitor conjugate, the HRP substrate, stop solution, a vial of the Triton X-100, a test tube rack, and a bag of uncoated tubes. The kit will also include a set of standards and controls. For the analysis alone, the user must supply methanol, a nitrogen evaporator, glass tubes, a differential photometer (or any photometer capable of reading at 450 nm), a timer, marking pens, a tray for waste disposal, and reagent grade water. The extraction and clean-up kit comes with disposable carbon minicolumns, disposable acid silica columns, containers for sample extraction, and steel bearings used for mixing. The user must supply anhydrous sodium sulfate, hexane, acetone, toluene, a balance, an orbital platform shaker, a centrifuge, fume hood, small vacuum pump (optional), luer ports, computer with Microsoft Excel 97 or higher, glass pipettes, glass vials, a repeater pipettor, a variable volume pipettor, and catch basins for column waste.

The developer assumes that there will be approximately 40% QC samples processed per kit. The developer leaves QC choices to the individual user, but it would recommend method blanks, method spikes, duplicates, and evaporation controls (solvent spikes that undergo the evaporation step to determine loss). All of the above QC samples were used during the demonstration, along with matrix spikes and known samples (RMs or previously analyzed samples). See Appendix B for developer HRMS calibration recommendations.

Chapter 8
Economic Analysis

During the demonstration, the CAPE Technologies kits and the reference laboratory analytical methods were each used to perform more than 200 sample analyses, including samples with a variety of distinguishing characteristics such as high levels of polychlorinated biphenyls and PAHs. Collectively, the samples provided different levels and types of contamination necessary to properly evaluate the technologies and to perform a comprehensive economic analysis of each technology. The purpose of the economic analysis was to estimate the total cost of generating results by using the CAPE Technologies kits and then comparing this cost to the reference method. This cost estimate also is provided so that potential users can understand the costs involved with using this technology.

This chapter provides information on the issues and assumptions involved in the economic analysis (Section 8.1), discusses the costs associated with using the DF1 Dioxin/Furan and PCB TEQ Immunoassay kits (Section 8.2), discusses the costs associated with using the reference methods (Section 8.3), and presents a comparison of the economic analysis results for the CAPE Technologies kits and the reference laboratory (Section 8.4).

8.1 Issues and Assumptions

Several factors affect sample measurement costs. Wherever possible in this chapter, these factors are identified in such a way that decision-makers can independently complete a project-specific economic analysis. The following five cost categories were included in the economic analysis for the demonstration: capital equipment, supplies, support equipment, labor, and investigation-derived waste (IDW) disposal. The issues and assumptions associated with these categories and the costs not included in the analysis are briefly discussed below. The issues and assumptions discussed below only apply to the DF1 Dioxin/Furan and PCB TEQ Immunoassay kits unless otherwise stated.

8.1.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the purchase of the CAPE Technologies kits. Components of the kits are presented in detail in Chapters 2 and 7. The purchase price information was obtained from a standard price list provided by CAPE Technologies.

8.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze all demonstration samples using the DF1 Dioxin/Furan and PCB TEQ Immunoassay kits that were not included in the capital equipment cost category. Examples of such supplies include filters, cleanup columns, gas cylinders, solvents, and distilled water. Only one sample preparation kit is required for assay using both the DF1 and PCB TEQ kits. The supplies that CAPE Technologies used during the demonstration fall into two general categories: consumable (or expendable) and reusable. Examples of expendable supplies utilized by CAPE Technologies during the demonstration include hexane, acetone, distilled water, toluene, methanol, tetradecane, nitrogen cylinders, sodium sulfate, Pasteur pipets, and glass disposable extraction tubes. Examples of reusable supplies include a top loading balance, orbital platform shaker, tabletop centrifuge, hot plate, and sample evaporation system. It should be noted that this type of equipment may or may not be already owned by a potential immunoassay kit user; however, for this economic analysis, an assumption was made that the user does not possess these items.

The purchase price of these supplies was either obtained from a standard price list provided by CAPE Technologies, or it was estimated based on price quotes from independent sources.

8.1.3 Support Equipment Cost

This section details the equipment used at the demonstration such as the construction trailer, fume hood, and laptop computer required by the technology. Costs for these items will be reported per actual costs for the demonstration.

8.1.4 Labor Cost

The labor cost was estimated based on the time required for work space setup, sample preparation, sample analysis, and reporting. For the demonstration, developers reported results by submitting a chain-of-custody (COC)/results form. The measurement of the time required for CAPE Technologies to complete 95 sample analyses during the field demonstration (55 labor-hours) was estimated by the sign-in log sheets that recorded the time the CAPE Technologies operator was on-site. Time was removed for site-specific training activities and Visitor's Day. Time estimates were rounded to the nearest hour.

During the demonstration, the skill level required for the operator to complete analyses and report results was evaluated. As stated in Section 7.2.1, based on the field observations, the education level may not be strictly necessary, but the experience with dioxin cleanup methods seemed very important in the use of the CAPE Technologies kits. A technician with at least a bachelor's degree in the sciences, and experience with both dioxin cleanup methods and ELISA would be helpful. Nonscientists with significant analytical experience should be able to perform the method without undue difficulty. Method-specific training could be obtained in as little as two days. This information was corroborated by CAPE Technologies.

The education level of the actual field operator includes a Ph.D. degree for the primary operator. For the economic analysis, costs were estimated using both actual and projected necessary skill levels for the operator.

8.1.5 Investigation-Derived Waste Disposal Cost

During the demonstration, CAPE Technologies was provided with 5-gallon containers for collecting wastes generated during the demonstration. Sample by-products such as used samples, aqueous and solvent-based effluents generated from analytical processes, used glassware, and personal protective equipment were disposed of in the containers. The total cost to dispose of these wastes generated during the demonstration is included in the economic analysis. Items such as coffee cups, food waste, and office waste were disposed of in regular public refuse containers and were not included as IDW and therefore not discussed in this economic analysis.

8.1.6 Costs Not Included

Items whose costs were not included in the economic analysis are identified below along with a rationale for the exclusion of each.

Electricity. During the demonstration, some of the capital equipment was operated using AC power. The costs associated with providing the power supply were not included in the economic analysis as it is difficult to estimate the electricity used solely by CAPE Technologies. The total cost for electricity usage over the 10-day demonstration was $288. With seven mobile labs/trailers and miscellaneous equipment being operated continuously during the course of the demonstration, the cost of CAPE Technologies electricity usage would be no more than $41. There was significantly more cost (approximately $13,000) to install an electrical board and additional power at the demonstration site, but this was a function of the demonstration site and not the responsibility of the individual developers, so this cost was not included in the economic analysis.

Oversight of Demonstration Activities. A typical user of the CAPE Technologies kits would not be required to pay for customer oversight of sample analysis. The EPA, the MDEQ, and Battelle representatives were present during the field demonstration, but costs for oversight were not included in the economic analysis because these activities were project-specific. For these same reasons, cost for auditing activities (i.e., technical systems audits at the reference laboratory and during the field demonstration) were also not included.

Travel and Per Diem for Operators. Operators may be available locally. Because the availability of operators is primarily a function of the location of the

project site, travel and per diem costs for operators were not included in the economic analysis.

Sample Collection and Management. Costs for sample collection and management activities, including sample homogenization and labeling, were not included in the economic analysis because these activities were project-specific and were not dependent upon the selected reference method or developer technology. Additionally, sample shipping, COC activities, preservation of samples, and distribution of samples were specific requirements of this project that applied to all developer technologies and may vary from site to site. None of these costs were included in the economic analysis.

Shipping. Costs for (1) shipping equipment and supplies to the demonstration site and (2) sample coolers to the reference laboratory were not included in the economic analysis because such costs vary depending on the shipping distance and the service used (for example, a courier or overnight shipping versus economy shipping).

Items Costing Less Than $10. The cost of inexpensive items was not included in the economic analysis when the estimated cost was less than $10. Items where it is estimated that the cost was less than $10 included:

- Distilled water
- Personal protective equipment
- Waste containers
- Lab stools

8.2 DF1 Dioxin/Furan and PCB TEQ Immunoassay Kit Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the DF1 Dioxin/Furan Immunoassay kit as well as a summary of these costs. Additionally, Table 8-1 summarizes the DF1 Dioxin/ Furan Immunoassay kit and PCB TEQ Immunoassay kit costs. As described in Section 4.6, CAPE Technologies analyzed 95 samples during the field demonstration using the DF1 kit, 114 samples in their laboratory using the DF1 kit, and all 209 demonstration samples using the PCB TEQ kit in its laboratory. It is important to note that costs estimated in this section are based on actual costs to analyze the 95 samples for D/Fs during the field demonstration. Cost estimates for analyzing the entire set of 209 demonstration samples for both D/F and PCBs were then determined based on the field demonstration costs.

8.2.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the purchase of the technology to perform sample preparation and analysis. The DF1 Dioxin/Furan Immunoassay kit can be purchased from CAPE Technologies for approximately $60 per sample. Two sizes of immunoassay kits are offered and contain enough supplies for 12 or 60 samples to be analyzed respectively. In conjunction with the immunoassay kits, CAPE Technologies offers sample preparation kits for extraction and cleanup of samples in preparation of immunoassay analysis. The sample preparation kit can be purchased from CAPE Technologies for approximately $15 per sample. Sample preparation kits are sold for 12 or 60 samples corresponding to the immunoassay kit sizes. All CAPE Technologies kits assume that 40% of the resources in each kit will be used for various quality control samples, including standards, reference samples, replicates, and matrix blanks. Because the kit is consumable, CAPE Technologies does not rent the immunoassay kits. During the demonstration, CAPE Technologies utilized two DF1 Dioxin/Furan Immunoassay kits (assuming the larger sized kit) over five days to analyze 95 samples and a total of four DF1 kits for the entire 209 samples. CAPE Technologies also used four PCB TEQ kits for the 209 samples.

8.2.2 Cost of Supplies

The supplies that CAPE Technologies used during the demonstration fall into two general categories: expendable or reusable. Table 8-1 lists all the expendable and reusable supplies that CAPE Technologies used during the demonstration and their corresponding costs. The cost of each item was rounded to the nearest $1. Expendable supplies are ones that are consumed during the preparation or analysis. Reusable costs are items that must be used during the analysis but ones that can be repeatedly reused. The estimated life of reusable supplies could not be assessed during this economic analysis.

The total cost of the supplies employed by CAPE Technologies during the demonstration was $7,143. Supplies have to be purchased from a retail vendor of

Table 8-1. Cost Summary

Item	Quantity Used During Field Demo		Unit Cost ($)	Itemized Cost[a] ($) 95 samples	Itemized Cost[a] ($) 209 samples
Capital Equipment					
Purchase of DF1 Dioxin/Furan Immunoassay Kit	2	kits	3,600	7,200	15,840
Purchase of PCB TEQ Immunoassay Kit	2	kits	3,600	7,200	15,840
Purchase of Sample Preparation Kit	2	kits	900	1,800	3,960
Supplies					
Expendable[b]					
Hexane (4-L bottle)	2	unit	65	130	286
Acetone (1-L bottle)	1	unit	27	27	59
Toluene (1-L bottle, 99.9%)	2	unit	28	28	62
Nitrogen Cylinder	1	unit	31	31	68
Cylinder Regulator	1	unit	182	182	182
Methanol (1-L bottle)	1	unit	30	30	30
Tetradecane (25 mL)	1	unit	8	8	18
Glass Tubes (16x125 mm; case of 1,000)	1	unit	84	84	84
Sodium Sulfate (anhydrous, granular, 500 g)	1	unit	40	40	40
Pasteur Pipets (package of 250; 2-mL size)	1	unit	10	10	20
Reusable					
Top Loading 0.1-g Balance	1	unit	550	550	550
Orbital Platform Shaker	1	unit	1,521	1,521	1,521
Tabletop Centrifuge	1	unit	1,613	1,613	1,613
Sample Evaporation System	1	unit	750	750	750
Hot Plate	1	unit	135	135	135
Photometer[d]	1	unit	1,200	1,200	1,200
Positive Displacement Pipettor	1	unit	100	100	100
Repeator Pipettor	1	unit	425	425	425
Support Equipment					
Construction Trailer	1	unit	1,919	1,919	1,919
Fume Hood	1	unit	1,100	1,100	1,100
Laptop Computer	1	unit	1,000	1,000	1,000
Labor					
Operator	55	labor hours	80[c]	4,414	12,139
IDW Disposal[e]	1	unit	133	133	293
Total Cost				**31,630**	**59,234**

[a] Itemized costs were rounded to the nearest $1.
[b] All reagents are HPLC grade, unless otherwise noted.
[c] Labor rate for field technicians to operate technology rather than research scientists was $50.75 an hour, $2,791 for 95 samples, and $7,675 for 209 samples.
[d] A photometer can be rented from CAPE Technologies for $120 per month.
[e] Further discussion about waste generated during demonstration can be found in Chapter 7.

laboratory supplies. Reusable items listed in Table 8-1 can be substituted with other models that operate under the same specifications, thereby modifying the cost of supplies to the potential kit user.

8.2.3 Support Equipment Cost

CAPE Technologies analyzed demonstration samples in a 32-foot construction trailer equipped with a fume hood. As determined by the observers, a construction trailer with fume hood would be necessary for operation of this technology. The rental cost for the construction trailer for use during sample extraction and sample analysis was $1,919. The minimum rental rate for the construction trailer was one month. CAPE Technologies only used the construction trailer for five days. Since weekly or daily rental rates for the construction trailer were not an option, the entire cost is reported. The fume hood rental and installation was $1,100.

A laptop computer is a necessary for the efficient operation of this technology. This is a one-time purchase that is reusable.

8.2.4 Labor Cost

As described in Section 8.1.4, 55 labor-hours were spent in the field to analyze 95 samples for D/F only. An hourly rate of $32.10 was used for a research scientist performing sample extractions and sample analysis, and a multiplication factor of 2.5 was applied to labor costs in order to account for overhead costs.[9] Based on this hourly rate and multiplication factor, a labor rate of $4,414 was determined for the analysis of the 95 samples during the field demonstration. It was estimated that the labor cost for the total 209 samples (for both D/F and PCBs) was $12,139.

Based on observation, it is anticipated that lower-cost field technicians, with proper training and skill levels, could have analyzed the samples in a similar amount of time. As such, the labor rate for the analysis of 95 samples during the field demonstration could have been as low as $2,791 (hourly rate of $20.30 with 2.5 multiplication factor for 55 labor-hours), and $7,675 for all 209 demonstration samples (for both D/F and PCBs).

8.2.5 Investigation-Derived Waste Disposal Cost

As discussed in Chapter 7, CAPE Technologies was provided with 5-gallon containers for collecting wastes generated during the demonstration. Chapter 7 discusses the type and amount of waste generated by the technology during the field demonstration in more detail.

During the demonstration, CAPE Technologies analyzed 95 samples. The total cost to dispose of the waste generated for these samples was $133. The cost to dispose of waste for all 209 samples is estimated at $293.

8.2.6 Summary of DF1 Dioxin/Furan and PCB TEQ Immunoassay Kit Costs

The total cost for performing dioxin and PCB analyses using the DF1 Dioxin/Furan Immunoassay Kit and PCB TEQ Immunoassay Kit was $59,234. The analyses were performed for 58 soil and sediment PE samples, 128 soil and sediment environmental samples, and 23 extracts. When CAPE Technologies performed multiple dilutions or reanalyses for a sample, these were not included in the number of samples analyzed.

The total cost of $59,234 for analyzing the 209 demonstration samples using the DF1 Dioxin/Furan and PCB TEQ Immunoassay kits included $35,640 for capital equipment; $7,143 for supplies; $4,019 for support equipment; $12,139 for labor; and $293 for IDW disposal. Of these five costs, the largest cost was for the purchase of the kits (60% of the total cost).

8.3 Reference Method Costs

This section presents the costs associated with the reference method used to analyze the 209 demonstration samples for dioxin and dioxin-like PCBs. Typical costs of these analyses can range from $800 to $1,100 per sample, depending on the method selected, the level of quality assurance/quality control incorporated into the analyses, and reporting requirements. The reference laboratory utilized EPA Method 1613B for dioxin/furan analysis and EPA Method 1668A for coplanar PCB analysis for all soil and sediment samples for comparison with the CAPE Technologies kits. The reference method costs were calculated using cost information from the reference laboratory invoices.

Table 8-2 summarizes the projected and actual reference method costs. At the start of the demonstration, the reference laboratory's projected cost per sample was $785 for dioxin/furan analysis and $885 for PCB analysis. This cost covered the preparation and analysis

Table 8-2. Reference Method Cost Summary

Analyses Performed	Number of Samples Analyzed	Cost per sample Quotation ($)	Itemized Cost ($)	
			Quotation[a]	Actual
Dioxin/Furans, EPA Method 1613B, GC/HRMS	23 extracts	735	16,905	213,580
	186 soil/sediment	785	146,010	
WHO PCBs EPA Method 1668A, GC/HRMS	23 extracts	685	15,755	184,449
	186 soil/sediment	735	136,710	
1668 Optional Carbon Column DB1	40	150	6,000	
Total Cost	209 samples		**321,380**	**398,029**

[a] Price includes up to 30% of samples requiring additional work of some kind (dilutions or extra cleanup). Greater than that would require additional work with further charges associated with them ($150 to $180 per sample per procedure).

of the demonstration samples, required method QC samples, electronic data deliverable, and the data package for each. The actual cost for the 209 demonstration analyses was $213,580 for D/F and $184,449 for PCBs, and a total of $398,029. This was higher than the projected ($321,380) due to reanalysis, re-extractions, dilutions and additional cleanups that were above the 30% repeats allowable by the original quote. The turnaround time by the reference laboratory for reporting all 209 samples was approximately eight months (171 business days). The quoted turnaround time was three months.

8.4 Comparison of Economic Analysis Results

The total costs for the DF1 Dioxin/Furan Immunoassay kit and PCB TEQ Immunoassay Kit analyses ($59,234) and the reference method ($398,029) are listed in Tables 8-1 and 8-2, respectively. The total cost for the CAPE Technologies kits was $338,795 less than the reference method. It should be noted that CAPE Technologies analyzed 95 samples for D/F in five days on-site during the field demonstration and it completed the remaining samples off-site in its laboratory. CAPE Technologies reported that the total analysis time to analyze the remaining 114 samples for D/F and all 209 samples for PCBs was two weeks. For comparison, the reference laboratory took 8 months to report all 209 samples.

In addition, use of the immunoassay kits in the field will likely produce additional cost savings because the results will be available within a few hours of sample collection; therefore, critical decisions regarding sampling and analysis can be made in the field, resulting in a more complete data set. Additional possible advantages to using field technologies include reduction of multiple crew and equipment mobilization-demobilization cycles to a single cycle, dramatically increased spatial resolution mapping for higher statistical confidence, leading to reduced insurance costs and reduced disposal costs, and compression of total project time to reduce administrative overhead. However, these savings cannot be accurately estimated and thus were not included in the economic analysis. Project-specific costs associated with the use of the technology, such as the cost for HRMS confirmation analyses and training costs to be proficient in the use of the technology, were also not accounted for in this analysis.

The CAPE Technologies immunoassay kits are screening methods that report TEQ values, unlike the reference method, which reports concentrations for individual congeners. Although the CAPE Technologies kit analytical results did not have the same level of detail as the reference method analytical results (or comparable QA/QC data), the DF1 Dioxin/Furan and PCB TEQ Immunoassay kits provided analytical results that could be generated on site at significant cost and time savings compared to the reference laboratory.

Chapter 9
Technology Performance Summary

The purpose of this chapter is to provide a performance summary of the CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits by summarizing the evaluation of the primary and secondary objectives of this demonstration in Tables 9-1 and 9-2, respectively. Detailed information about these evaluations, including a complete evaluation of the reference laboratory data, can be found in previous sections of this report.

The data generated and evaluated during this demonstration showed that the CAPE Technologies kits in many cases did not directly correlate with HRMS TEQ values, but that the kits could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for sample above and below 50 pg/g TEQ, particularly considering that both the cost ($59,234 vs. $398,029) and the time (three weeks vs. eight months) to analyze the 209 demonstration samples were significantly less than those of the reference laboratory. Because the CAPE Technologies kits are not expected to directly correlate to HRMS TEQ in all cases, the technology should not be viewed as producing an equivalent measurement value to HRMS TEQ but as a screening value to approximate HRMS TEQ. As described in CAPE Technologies literature, the best results for immunoassay screening are obtained on a single site basis. The ideal approach involves partially characterizing a site by HRMS, using those results to develop a site specific immunoassay calibration, and refining that calibration over time, based on an ongoing stream of confirmatory HRMS samples. This approach was not evaluated during this demonstration; samples from multiple sites were pooled and a single calibration was used.

Table 9-1. CAPE Technologies LLC DF1 Dioxin/Furan and PCB TEQ Immunoassay Kits Performance Summary - Primary Objectives

Objective	Performance			
	Statistic	TEQ_{PCB}	$TEQ_{D/F}$	Total TEQ
P1: Accuracy	Number of data points	8	7	8
	Median Recovery (%)	151	182	139
	Mean Recovery (%)	195	236	160
P2: Precision	Number of data points	49	44	46
	Median RSD (%)	118	63	67
	Mean RSD (%)	123	71	74
P3: Comparability	Number of data points	182	167	159
	Median RPD (%)	-13	-26	-5
	Interval agreement (%)	82	71	64
	Blank agreement (%)	50	38	25
P4: Estimated Method Detection Limit	EMDL (pg/g)	20	12–35	25–33
P5: False Positive/False Negative Rate[a]	False positive rate at 20 pg/g TEQ (%)	14	11	14
	False positive rate at 50 pg/g TEQ (%)	8	8	10
	False negative rate at 20 pg/g TEQ (%)	5	4	3
	False negative rate at 50 pg/g TEQ (%)	4	8	5
P6: Matrix Effects	• Measurement location: 19% statistically different • Matrix type: none • Sample type: none • PAH concentration: slight effect on total TEQ • Environmental site: none • Known interferences: slight			
P7: Cost	Cost for the analysis of 95 samples for D/F only during field demonstration: $31,630 Cost for the analysis of all 209 samples for both D/F and PCBs: $59,234			

[a] CAPE Technologies notes that the user can optimize performance of the kit at other desired screening levels by changing the size of sample extracted so that the desired screening level concentration falls at the optimum point on the kit response curve.

Table 9-2. CAPE Technologies LLC DF1 Dioxin/Furan and PCB TEQ Immunoassay Kits Performance Summary – Secondary Objectives[a]

Objective	Performance
S1: Skill level of Operator	The developer recommends that users have at least a bachelor degree in the sciences, and experience with both dioxin cleanup methods and ELISA would be helpful. From observation, the education level may not be strictly necessary, but the experience with dioxin clean-up methods seemed very important in the use of the kit. During the field demonstration, 95 samples were processed by CAPE Technologies equating to a sample throughput rate of 19 samples per day. This was accomplished in about 5 full working days (55 labor-hours), with a single operator performing all aspects of the technology operation.
S2: Health and Safety Aspects	Approximately 60 mL of hexane will be used for each sample. Not all of this becomes solvent waste, but a portion does. The disposable columns as well as the disposable glassware create solid waste. The solvent waste itself is not inherently more hazardous than would be expected, unless the samples are very contaminated. A fume hood is necessary for use during solvent extraction.
S3: Portability	This technology is readily deployable in a field or mobile environment. The need for power, nitrogen tanks, a fume hood, shakers, vacuums, and other equipment requires a trailer at the very least for successful operation of this technology. While the assay itself is very easy to use in the field, the extraction and cleanup methods require level work space and could create some difficulty in the field unless there was a mobile lab or trailer available.
S4: Sample Throughput	During the field demonstration, 95 samples were processed by CAPE Technologies equating to a sample throughput rate of 19 samples per day. This was accomplished in about five full working days (55 labor-hours), with a single operator performing all aspects of the technology operation. CAPE Technologies reports that the analysis time for the remaining 114 samples for D/F and all 209 samples for PCBs was approximately two weeks in its laboratory.

[a] The secondary objectives were assessed only for the DF1 kit because the PCB TEQ Immunoassay Kit was not deployed during the field demonstration. Because of the similar principles and procedures for the two kits, it is likely that similar conclusions could be drawn, but this was not confirmed by observation.

Chapter 10
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Appendix A
SITE Monitoring and Measurement Technology Program
Verification Statement

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, DC 20460

SITE Monitoring and Measurement Technology Program Verification Statement

TECHNOLOGY TYPE:	**Enzyme-Linked Immunosorbent Assay**
APPLICATION:	**MEASUREMENT OF DIOXIN AND DIOXIN-LIKE COMPOUNDS**
TECHNOLOGY NAME:	**DF1 Dioxin/Furan Immunoassay Kit and PCB TEQ Immunoassay Kit**
COMPANY:	**CAPE Technologies LLC**
ADDRESS:	**3 Adams Street** **South Portland, Maine 04106-1604**
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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of this program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The program assists and informs those involved in designing, distributing, permitting, and purchasing environmental technologies. This document summarizes results of a demonstration of the CAPE Technologies DF1 Dioxin/Furan and polychlorinated biphenyl (PCB) toxicity equivalent (TEQ) immunoassay kits.

PROGRAM OPERATION

Under the SITE MMT Program, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance protocols to produce well-documented data of known quality. The EPA's National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Battelle as the verification organization to assist in field testing technologies for measuring dioxin and dioxin-like compounds in soil and sediment.

DEMONSTRATION DESCRIPTION

The demonstration of technologies for the measurement of dioxin and dioxin-like compounds was conducted at the Green Point Environmental Learning Center in Saginaw, Michigan, from April 26 to May 5, 2004. The primary objectives for the demonstration were as follows:

P1. Determine the accuracy.
P2. Determine the precision.

P3. Determine the comparability of the technology to EPA standard methods.
P4. Determine the estimated method detection limit (EMDL).
P5. Determine the frequency of false positive and false negative results.
P6. Evaluate the impact of matrix effects on technology performance.
P7. Estimate costs associated with the operation of the technology.

The secondary objectives for the demonstration were as follows:
S1. Assess the skills and training required to properly operate the technology.
S2. Document health and safety aspects associated with the technology.
S3. Evaluate the portability of the technology.
S4. Determine the sample throughput.

A total of 209 samples was analyzed by each technology, including a mix of performance evaluation (PE) samples, environmentally contaminated samples, and extracts. CAPE Technologies analyzed 95 samples for D/F only during the field demonstration; the remaining 114 samples for D/F and all 209 samples for PCBs were analyzed in its laboratory. The PE samples were used primarily to determine the accuracy of the technology and consisted of purchased reference materials with certified concentrations. The PE samples also were used to evaluate precision, comparability, EMDL, false positive/negative results, and matrix effects. Dioxin-contaminated samples from Warren County, North Carolina; the Saginaw River, Michigan; Tittabawassee River, Michigan; Midland, Michigan; Winona Post, Missouri; Nitro, West Virginia; Newark Bay, New Jersey; Raritan Bay, New Jersey; and Brunswick, Georgia were used to evaluate precision, comparability, false positive/negative results, and matrix effects. Extracts prepared in toluene were used to evaluate precision, EMDL, and matrix effects. All samples were used to evaluate qualitative performance objectives such as technology cost, the required skill level of the operator, health and safety aspects, portability, and sample throughput. AXYS Analytical Services (Sidney, British Columbia) was contracted to perform the reference analyses by high-resolution mass spectrometry (HRMS) (EPA Method 1613B and EPA Method 1668A). The purpose of the verification statement is to provide a summary of the demonstration and its results; detailed information is available in *Technologies for Monitoring and Measurement of Dioxin and Dioxin-like Compounds in Soil and Sediment—CAPE Technologies DF1 and TEQ PCB Immunoassay kits* (EPA/540/R-05/004).

TECHNOLOGY DESCRIPTION

The technology description and operating procedure below are based on information provided by CAPE Technologies. The DF1 Dioxin/Furan Immunoassay Kit and the PCB TEQ Immunoassay Kit are nearly identical in design and operation. They differ primarily in the antibody and competitor-horseradish peroxidase (HRP) conjugate used, and in the specificity resulting from these specially developed reagents. Both kits are designed to provide results as TEQ concentrations by responding to the toxic dioxin/furan or PCB congeners in approximate correlation with their toxic equivalency factors (TEFs). Both tests recognize multiple congeners, preferentially targeting congeners with high TEF values, i.e., those with the highest toxicity relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The specificity of the dioxin/furan test is predominantly for dioxins and furans that contain from 3 to 6 chlorines, with a strong preference for the 2,3,7,8 chlorinated congeners. This specificity roughly parallels the TEF values of the individual dioxin and furan congeners. The specificity of the PCB TEQ test is predominantly for non-ortho and mono-ortho chlorinated congeners, with a strong preference for PCBs 126 and 169. This specificity roughly parallels the TEF values of the individual PCB congeners. Both tests have only minimal recognition of the target compounds of the other test. The immunoassay specific sample preparation begins with an organic solvent extraction. The extracts are then processed through an immunoassay specific cleanup. In the case of this evaluation, the cleanup combines two familiar parts of the EPA Method 8290 cleanup, but in a way that allows for rapid batch processing using inexpensive disposable columns and no specialized equipment. Since the cleanup is performed in solvents incompatible with the immunoassays, a solvent exchange is required after the cleanup. Dioxins, furans, and dioxin-like PCBs have very low volatility and are retained during this solvent exchange in a small volume of a keeper solution (Triton X-100 detergent in tetraethylene glycol [TEG]) after evaporation of the original solvent. Methanol is added to dilute this solution, and the methanol-TEG-Triton X mixture is added directly to the immunoassay tubes. During the first immunoassay incubation, analyte molecules are specifically bound by the analyte-specific antibodies, which have been immobilized on the immunoassay tube surface. After washing away the unbound material, the bound analyte molecules remain, and a competitor-HRP conjugate is added. Bound analyte molecules occupy the binding sites of the antibodies in proportion to the dioxin/furan or dioxin-like PCB content of the sample, reducing the binding of the competitor-HRP

conjugate. After a short incubation, unbound conjugate is removed, and the test tubes are washed thoroughly. Finally, a solution of chromogenic HRP substrate and hydrogen peroxide is added to the test tubes. Color development is directly proportional to enzyme concentration and inversely related to the dioxin/furan or dioxin-like PCB concentration in the original sample. The test tubes are analyzed using a tube reader or spectrophotometer to measure the optical density (OD). The OD values of unknown samples are compared to the OD values of standards to determine the level of dioxin/furan or dioxin-like PCB in the samples.

VERIFICATION OF PERFORMANCE

The CAPE Technologies kits are immunoassay technologies that report total dioxin/furan TEQ ($TEQ_{D/F}$) and total coplanar PCB TEQ (TEQ_{PCB}) in the sample in picogram/gram (pg/g). It should be noted that the results generated by the CAPE Technologies kits may not directly correlate to HRMS TEQ in all cases because it is known that the congener responses and cross-reactivities of the kits are not identical to the TEFs that are used to convert congener HRMS concentration values to TEQ. Therefore, these kits should not be viewed as producing an equivalent measurement value to HRMS TEQ but as a screening value to approximate HRMS TEQ. As described in CAPE Technologies literature, the best results for immunoassay screening are obtained on a single site basis. The ideal approach involves partially characterizing a site by HRMS, using those results to develop a site specific immunoassay calibration, and refining that calibration over time, based on an ongoing stream of confirmatory HRMS samples. This approach was not evaluated during this demonstration; samples from multiple sites were pooled and a single calibration was used.

Accuracy: The determination of accuracy was based on the agreement of the CAPE Technologies results with the certified levels of the PE samples that were obtained from commercial sources. Accuracy was assessed by percent recovery (R), which is the average of the replicate results from the kits divided by the certified or spiked value of the PE sample, multiplied by 100%. Ideal R values are near 100%. The overall R values were 195% (mean), 151% (median), 26% (minimum), and 523% (maximum) for TEQ_{PCB}; 236% (mean), 182% (median), 30% (minimum), and 595% (maximum) for $TEQ_{D/F}$, and 160% (mean), 139% (median), 33% (minimum), and 296% (maximum) for total TEQ.

Precision: Replicates were incorporated for all samples (PE, environmental, and extracts) included in the 209 samples analyzed in the demonstration. Replicates were incorporated for all samples (PE, environmental, and extracts) included in the 209 samples analyzed in the demonstration. Three samples had seven replicates in the experimental design, one sample had eight replicates, and all other samples had four replicates. Precision was determined by calculating the standard deviation of the replicates, dividing by the average concentration of the replicates, and multiplying by 100%. Ideal RSD values are less than 20%. The overall RSD values were 123% (mean), 118% (median), 38% (minimum), and 200% (maximum) for $TEQ_{PCB;}$ 71% (mean), 63% (median), 0% (minimum), and 187% (maximum) for $TEQ_{D/F}$; and 74% (mean), 67% (median), 17% (minimum), and 174% (maximum) for total TEQ.

Comparability: The CAPE Technologies DF1 and PCB TEQ kit results were compared to EPA Method 1613B and EPA Method 1668A results for TEQ_{PCB}, $TEQ_{D/F}$, and total TEQ. The results were compared by determining the relative percent difference (RPD) by dividing the difference of the two numbers by the average of the two numbers and multiplying by 100%. Ideal RPD values are between positive and negative 25%. The overall RPD values were -13% (median), -200% (minimum), and 200% (maximum) for TEQ_{PCB}; -26% (median), -199% (minimum), and 198% (maximum) for $TEQ_{D/F}$; and -5% (median), -199% (minimum), and 198% (maximum) for total TEQ. The CAPE Technologies results were also compared to the reference laboratory results using an interval approach to determine if the CAPE Technologies results and the reference laboratory results would place the samples in the same action-level interval, thereby resulting in the same action-oriented decision. The developer and reference data were grouped into four TEQ concentration ranges. The ranges were $\leq$ 50 pg/g, 50 to 500 pg/g, 500 to 5,000 pg/g, and $\geq$ 5,000 pg/g. The intervals were determined based on current guidance for cleanup levels. The percentage of developer results that agreed with reference laboratory results 82% for $TEQ_{PCB,}$71% for $TEQ_{D/F,}$ and 64% for total TEQ.

Estimated method detection limit: EMDL was calculated for the for the technology generally according to the procedure described in 40 CRF Part 136, Appendix B, Revision 1.11. Lower EMDL values indicate better sensitivity. The calculated EMDLs ranged from 12 to 35 pg/g TEQ, depending on whether nondetect values were assigned values

of zero, one-half the reporting limit value, or the reporting limit value itself. The detection limit reported by CAPE Technologies in the demonstration plan was 1 pg/g TEQ.

False positive/negative results: Samples that were reported as less than a specified level by the reference laboratory but above that level by CAPE Technologies were considered false positive. Conversely, those samples that were reported as less than a specified level by CAPE Technologies but reported as greater than the specified level by the reference laboratory were considered false negatives. Ideal false positive and negative percentages were zero. The CAPE Technologies kits had a false positive rate of 14% and a false negative rate of 5% for TEQ_{PCB}; 11% and 6%, respectively, for $TEQ_{D/F}$; and 14% and 3%, respectively, for total TEQ for reporting data above and below 20 pg/g TEQ relative to the reference laboratory data. CAPE Technologies's false positive and false negative rates around 50 pg/g were generally lower for all three TEQ types, ranging from 4 to 10%. These data suggest the CAPE Technologies kits as processed in the demonstration could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for sample above and below 50 pg/g TEQ. CAPE Technologies notes that the user can optimize performance of the kit at other desired screening levels by changing the size of sample extracted so that the desired screening level concentration falls at the optimum point on the kit response curve.

Matrix effects: The likelihood of matrix-dependent effects on performance was investigated by evaluating results in a variety of ways. The CAPE Technologies $TEQ_{D/F}$ results that were generated in the laboratory and in the field for replicate samples were statistically different for 19% of the samples, and of these samples, CAPE Technologies results were most comparable to the reference laboratory results. No significant effect was observed for the reproducibility of CAPE Technologies results by matrix type (soil, sediment, and extract) or by sample type (PE vs. environmental vs. extract). A slight effect was observed for total TEQ values by PAH concentration, but the effect was not statistically significant for $TEQ_{D/F}$ or TEQ_{PCB}. PE samples spiked for a particular contaminant (e.g., D/Fs) were sometimes reported as detections for other analytes that were not spiked in the sample (e.g., PCBs). The CAPE Technologies results were not more or less comparable to the reference laboratory results based on environmental site.

Cost: The full cost of using the CAPE Technologies kits was documented and compared to the cost of the reference analyses. As demonstrated, the total cost for the CAPE Technologies kits to analyze all 209 samples was $59,234. The cost for the reference laboratory to analyze all 209 samples by Method 1613B and Method 1668A was $398,029. The total cost for the CAPE Technologies kits was $338,795 less than the reference method.

Skills and training required: The developer recommends that users have at least a bachelor degree in the sciences, and experience with both dioxin cleanup methods and enzyme-linked immunosorbent assay would be helpful. From observation, the education level may not be strictly necessary, but the experience with dioxin cleanup methods seemed very important in the use of the kit.

Health and safety aspects: Approximately 60 mL of hexane will be used for each sample. Not all of this becomes solvent waste, but a portion does. The disposable columns as well as the disposable glassware create solid waste. The solvent waste itself is not inherently more hazardous than would be expected, unless the samples are very contaminated. A fume hood is necessary for use during solvent extraction.

Portability: This technology is readily deployable in a field or mobile environment. The need for power, nitrogen tanks, a fume hood, shakers, vacuums, and other equipment requires a trailer at the very least for successful operation of this technology. While the assay itself is very easy to use in the field, the extraction and cleanup methods require level work space and could create some difficulty in the field unless there was a mobile lab or trailer available.

Sample throughput: During the field demonstration, 95 samples were processed by CAPE Technologies equating to a sample throughput rate of 19 samples per day. This was accomplished in about five full working days (55 labor-hours), with a single operator performing all aspects of the technology operation. CAPE Technologies reported that the analytical time to complete the remaining 114 samples for D/F and all 209 sample analyses for PCBs was two weeks. For comparison, the reference laboratory took eight months to report all 209 samples.

Appendix B
Supplemental Information Supplied by the Developer

The purpose of this section is for the developer to provide additional information about the technology. This can include updates/changes/modifications planned for the technology or which have occurred since the technology was tested. The developers can also use this section to comment and expand on the findings of the report.

CAPE Comments

General Comments

CAPE Technologies wishes to express its gratitude to both EPA andBattelle for the skillful and professional manner in which this studywas designed and conducted. This task was obviously massive and probably seemed thankless. However, we understand the value of the effort that was made, and we sincerely appreciate the consideration andflexibility shown during all phases of the study.

The purpose of this appendix is to provide CAPE Technologies, as a technology developer, the opportunity to comment on the study and its results. Additionally, this is the place for information that the developer may deem to be relevant to the technology and its use but outside the scope of the main part of the report. Thus, the comments offered below are a critical part of the study and should be read carefully by any potential user of this technology. Additionally, much information beyond what is presented here can be found on the CAPE Technologies Web site (www.cape-tech.com). This Web site covers topics from the principles of immunoassay technology to the practical issues of quality assurance and data interpretation, and many important things in between. The CAPE site also includes links to EPA sites in two key areas: (1) SW-846 solid waste methods, including Method 4025, which uses the CAPE Technologies DF1 kit; and (2) the Technology Innovation Program(TIP), which seeks to educate the environmental community about new technologies, such as field analytical methods, and how to use them effectively.

Any research on Method 4025 or on CAPE Technologies products in general must refer first to the company Web site, since this is the single most important source of up-to-date information about the products themselves and the methods for which they are used.

Comments on the Reported Economic Value of the Kits Evaluated vs. the True Value of Field Analytical Methods

The primary conclusion regarding the two CAPE Technologies immunoassay kits studied was expressed in several places in the report. This evaluation project has demonstrated that CAPE Technologies kits "...could be an effective screening tool..." at low- to mid-pg/g levels in soil and sediment. Secondarily, the report notes that "... the DF-1Dioxin/Furan and PCB TEQ Immunoassay Kits provided analytical results that could be generated on-site at significant cost and time savings compared to the reference laboratory." In summary, the data on cost, turnaround time, and the ability of the method to work in the field demonstrate profound advantages over conventional methods.

These attributes are certain to be attractive to many who simply see analternative analytical method. However, the most significant advantage to using CAPE Technologies kits is that they offer the site manager a completely new tool to address a set of very old and familiar problems. The advantages of Method 4025 for site assessment and remediation are very similar to what was demonstrated by other EPA SW-846 4000 series methods in the early 1990s (such as 4020 for total PCB). These include (a) potential for reduction of multiple crew and equipment mobilization-demobilization cycles to a single cycle, (b) dramatically increased spatial resolution mapping for higher statistical confidence, leading to reduced insurance costs and reduced disposal costs, (c) compression of total project time to reduce administrative overhead, and (d) better defensibility of site actions for reduced legal costs.

Field analytical technologies, especially for dioxin and dioxin-likePCBs, represent a paradigm shift in site assessment and remediation. Quite simply, the speed, simplicity, and low cost of the 4000 series methods provide site managers the ability to generate site characterization maps and to guide remediation with speed and statistical confidence that are literally impossible with conventional lab-based methods.

As shown clearly by the EPA materials linked to from CAPE's site, the true cost savings from the use of field analytical technologies come from these points, rather than just the six-fold cost differential between two "competing" analytical methods. In fact, an important lesson to be learned from TIP's efforts is that field analytical methods and lab-based methods are complementary rather than competing, and the value of using the two methods in concert is much greater than the value of using either method alone.

Technical Issues in the Study Design and Interpretation of Results-Pooled Calibration and FP/FN Rates
Readers of this report likely know that analysis of dioxin and dioxin-like PCBs is expensive, time-consuming, technically difficult,and applied to an extremely wide variety of sample types and congener profiles. Because of these factors, the design of this evaluation study necessarily represents a balancing act between comprehensiveness on the one hand and cost control on the other. Some important ramifications of this compromise are discussed in more detail below.

Users of field analytical methods such as the two immunoassay kits evaluated in this report will almost always be seeking data from a single site or a group of related sites. In such cases, CAPE Technologies makes specific recommendations on how to apply the kits, especially including quality assurance samples and quantitative data interpretation. A key part of this recommendation is to use prior GC-MS data, if available, to perform an initial site-specific calibration adjustment, then to generate an ongoing stream of confirmatory GC-MS samples to for continuing support refinement of this calibration. A draft CAPE Technologies document that addresses these concerns, Technical Note TN-004, is included as part of this appendix.

Virtually no one uses the Dioxin/Furan or PCB-TEQ immunoassays as theyare presented in the report: a single large data set with many sample types from multiple unrelated locations, pooled and using a single calibration adjustment from samples that may or may not be from the same site as the unknowns. Because of this and the blind nature of the study (i.e., not knowing which samples came from one site), the blanket calibration adjustment applied is necessarily a compromise. It serves the nominal statistical purposes of the study, but in no way represents how individual kit users apply the raw data to decision making in the field. Differences among sites may arise for many reasons and can contribute to significant errors unless the differences are controlled. Site-specific calibration does this.

An important ramification of this issue is that in a single site, application with site-specific calibration based on selected GC-MS results, false negative and false positive rates at a predetermined level should decrease from the present study, with its pooled and and nonspecific calibration. Because of the study design, as dictated primarily by cost constraints, retrospectively imposing such a calibration is impossible, as that would require a set of known samplesfor calibration of each sample type/location subset.

An example of quantitative results from a blind, single-site study is given in CAPE Technologies Application Note AN-008. The methodology is nearly identical to that used here, except that none of the samples were analyzed in a field lab situation. The data summary page of AN-008 is included as part of this appendix. The full document is available on CAPE's Web site. An extreme case of the need for site-specific calibration can be found in Finland, where the primary wood preservative (with use patterns parallel to pentachlorophenol in the US) contains a dioxin/furan congener profile unlike any other sample type. Because these samples get about 70% of their TEQ from one heptachlorodibenzofuran, which is poorly recognized by the DF1 kit, a calibration adjustment of approximately sevenfold is required, due solely to the congenerprofile. However, because the DF1 kit results still correlate with TEQ and calibration is a separate issue, once the calibration adjustment is made, the adjusted results can be used effectively for screening at apreselected level. The use of the DF1 kit for this type of sample is heading into its second field season in Finland.

Technical Issues in the Study Design and Interpretation of Results-Curve Slope, Dilutions, and High End Quantitation
Both kits evaluated in this study are competitive immunoassays having anegative slope response curve, which is intrinsically sigmoid in shape. Thus the theoretical precision and the working range trade off againsteach other. As the curve slope increases, the precision improves, butthe working range shrinks. As the curve slope decreases, the workingrange increases, but the precision deteriorates. The Dioxin/Furan testand the PCB TEQ test have slightly different curves, but both representreasonable compromises between working range and precision.

Because of the very wide range of concentrations in the study samples, an amount of sample was chosen that would give the best results for low concentration samples. Many of the study samples were therefore off the high end of the standard curve in their first run and required dilution to give a quantitative result. There are two ways of doing this; and, because of the time and fiscal constraints of the study, the faster and less expensive of these methods was used. The approach used is also the less accurate of the two, but the effect of this on decision making should be nearly nil.

The reason is simple. Even though dilution and retesting of an off-scale high sample may give a result with a greater proportional error than a sample not requiring dilution, the first result of off-scale high remains unchanged.

Proper use of the Dioxin/Furan and PCB-TEQ kits for a single decision level is simple. Choose an amount of sample that would place your result in the steepest part of the curve if the sample were at the decision level. This approach is required if the best possible false positive/false negative rates at that decision level are to be obtained. Use of the kits for a second decision level would require either the dilution protocol used in the study or, more accurately, repeat cleanup of another aliquot of sample extract that would allow the analyst to also make the second decision in the steepest part of the response curve. This is generally not done because it increases the sample preparation resources required.

CAPE Technologies

DRAFT

High Performance Dioxin/Furan Immunoassay Kit

Technical Note TN-004

Quantitation, Calibration, and Quality Assurance for Method 4025m

Quantitation: Dioxin/furan analysis by US EPA Method 4025m using the CAPE Technologies DF1 Immunoassay Kit gives quantitative results which correlate with TEQ (per Application Note AN-008). However, just as with conventional chemical analysis, proper calibration and quality assurance are required for maximum reliability.

The DF1 immunoassay is inherently quantitative. Each immunoassay run should include 2378-TCDD standards to define a standard curve as described in Section D (Table 1) of the kit insert IN-DF1. This curve is applied to unknowns using Calculation Module C, a special purpose Microsoft Excel file available from the CAPE Technologies web site (www.cape-tech.com). Module C uses an iterative non-linear curve fitting procedure based on the same four parameter equation which is the basis for a variety of commercial immunoassay data analysis software. Module C calculates the best fit standard curve and the concentrations of unknowns based on that curve. Background information and instructions are included with Calculation Module C.

The process described above produces raw quantitative results based on the standard curve, which may or may not be an acceptable endpoint. If the analyst's goal is relative quantitation (i.e. looking for hot spots- finding deviations from a certain baseline and estimating their concentration relative to that baseline), then no calibration adjustment is required. However, if the goal is absolute quantitation (as for virtually all dioxin analysis by GC-MS), then a calibration adjustment must be applied to the raw quantitative results. Calculation Module C has this calibration adjustment calculation built in, but the analyst must determine the actual calibration adjustment factor (CAF) and provide the QA data supporting its use.

Calibration of other 4000 series methods: In order to articulate the rationale supporting this calibration adjustment, it is helpful to first describe the approach to calibration for the other 4000 series immunoassay methods approved by the US EPA (www.epa.gov/epaoswer/hazwaste/test/4_series.htm). These methods, such as Method 4020 for PCBs, have a calibration adjustment built into the method. This adjustment is determined by the kit manufacturer and is applied on the front end, through the use of immunoassay calibrators instead of standards. These calibrators are designed to let the analyst make semi-quantitative decisions at pre-selected levels, such as 1, 5, 10, or 50 µg/g. Once the kit user compares the sample to a calibrator in the same run and makes a decision, no further data interpretation is required. The calibration rationale assumes that the samples to be analyzed and the decision levels to be used are the same as those used for the validation study.

The actual concentrations of these calibrators may differ from the decision level by a factor of two or more. For example, users of one of the Method 4020 PCB kits would make a decision on whether the sample PCB level is less than 10 µg/g by comparing it to a calibrator in the same run that actually contains 5 µg/g PCB. This difference between decision level and actual concentration used for the calibrator is determined by splitting samples and analyzing by both the conventional method and the immunoassay, in quantitative mode and with no adjustment of the data. The resulting quantitative relationship between the two data sets is used to set the calibrator level so that a minimum false negative rate is achieved in the semi-quantitative decision making process.

There are several good reasons why these quantitative results from the two methods might not follow a 1:1 relationship (regression line slope of 1), even if the correlation is excellent. These include, but are not limited to, reduced efficiency of the rapid extraction method, effects of differences in congener profile between the PCB in the sample and standard, and random variation. The front end calibration procedure described above allows compensation for all such factors together, without explicitly determining their individual contributions. The calibration adjustment described above is effectively the same as obtaining unadjusted quantivative results, then multiplying them by a uniform adjustment factor. The approach to calibration for Method 4025m is similar and accomplishes the same goal, but with some very important differences. The rationale for this approach is described below.

Calibration rationale and procedure for Method 4025m: The same factors noted above which can cause the regression line slope to be less than 1 must also be dealt with when calibrating Method 4025m. However, there are more potential factors because of the increased complexity of the procedure (e.g. recovery through cleanup and solvent exchange as well as extraction) and because of the greater variability of the analyte composition (congener profile) among the population of possible samples. For these and other reasons, the front end calibration approach described above for other 4000 series immunoassays is not viable for Method 4025m. Therefore Method 4025m analysis uses standards rather than calibrators, and the analyst applies a back end calibration adjustment to the raw quantitative results.

The calibration procedure supported by the above rationale is straightforward. A set of split samples is analyzed by the reference method (GC-MS) and also by Method 4025m. The comparison data set will likely have some deviation from the ideal 1:1 relationship noted above (regression line slope other than 1). A new data set of adjusted 4025m results is created by multiplying each raw 4025m result by the CAF (starting at 1). The CAF is then changed and the regression line slope is calculated for the adjusted 4025m data. The final CAF value is that which gives a regression line slope of 1 for the adjusted 4025m data. This CAF is then uniformly applied to all raw 4025m results. Once a CAF is determined, it should be checked and refined continuously using the stream of GC-MS data from ongoing quality assurance samples. On a larger project, from 5 to 20 percent of samples screened by Method 4025m should be split for conventional analysis. These are the most important quality assurance samples, but are by no means the only ones that should be run.

Notes on calibration quality: For best results, calibration adjustment should be done on a site specific basis if possible. Differences in dioxin source, sample matrix, and congener profile will all increase the variability of quantitative results and decrease the probability of success. The effect of congener profile on calibration can be estimated in advance using Calculation Module A. More samples will obviously give better results. It is theoretically possible to base a CAF on a single sample, but statistically unwise. Likewise, it is statistically best for the samples on which the CAF is based to cover as wide a concentration range as possible.

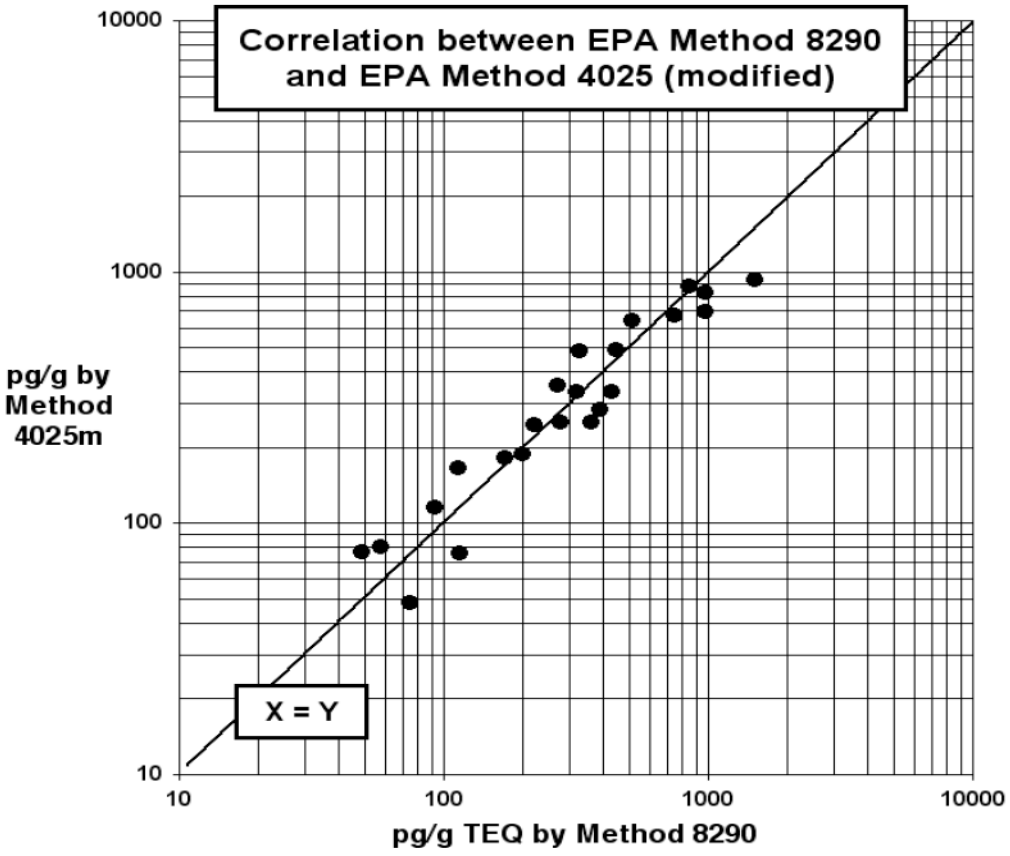
The closer the calibration samples are to the target sample population, the better the calibration adjustment will be. It is possible to use other reference samples for calibration, but the results will not be as good as when using samples from the same set as the unknowns. For example, calibration based solely on spiked samples can be used, but is less than ideal, since it will not account for extraction differences between spikes and incurred residues. Likewise, calibration based solely on unrelated samples, such as standard reference materials, will not account for matrix differences between the reference sample and the unknown samples.

Table 1. Quality assurance data within modified EPA Method 4025

QA sample	n	mean±SD	units (comment)
Solvent exchange negative controls	24	1.9±1.0	pg (lowest standard = 3.2 pg)
Unspiked method blanks	22	2.9±1.7	pg (lowest standard = 3.2 pg)
Solvent exchange positive controls	22	102±20	% of nominal pg (generally 50 pg)
Spikes into method blank extracts	14	79±27	% of nominal pg/g (30 to 195 pg/g)
Spikes into sample extracts	32	67±28	% of nominal pg/g (30 to 390 pg/g)
Duplicate precision (two aliquots of one extract cleaned and analyzed in parallel)			
	23	13±14	% cv (range 5 to 750 pg/g)

Figure 1. Correlation between modified EPA Method 4025 and EPA Method 8290

A set of 23 soil samples from a sewage treatment facility were prepared and analyzed as described in Sections F and G above. Each EIA tube received prepared extract equivalent to 500 to 640 mg of original sample. Samples which gave off-scale high results were diluted and the EIA was repeated so that each EIA tube received the equivalent of 50 to 100 mg of prepared sample. Subsamples of each sample were analyzed separately by HRGC-HRMS. The TEQ values were calculated from TEF values and individual congener concentrations as measured by Method 8290. The line represents x = y. The correlation coefficient was 0.95. The mean relative percent difference value for the samples plotted below was 24±15% (±SD), with a maximum of 47%.



Appendix C
Reference Laboratory Method Blank and Duplicate Results Summary

Table C-1. Summary of Method Blank Performance

Sample Batch Number	Criteria Met	Method Blank TEQ[a] (pg/g)	Sample TEQ Range[a] (pg/g)	Comments
D/F WG12107	Y	0.000812	26.1–74.1 (Newark Bay) 9.93–13.3 (Raritan Bay)	
D/F WG12148	N	0.133	13.5–50.4 (Newark Bay) 49.5–15,200 (Brunswick)	Many samples had concentrations >20x blank. Few that didn't were not significantly affected on a total TEQ basis.
D/F WG12264	N	0.0437	1.0–94.1 (Titta. River sediment) 0.237–6900 (PE)	Most samples had concentrations >20x blank. Low level Tittabawassee River sediment samples L6749-2 (Ref 48[b]), -9 (Ref 130), -10 (Ref 183), and -12 (Ref 207) were evaluated based on their replication within the demonstration analyses and comparison to characterization results and considered unaffected by method blank exceedances. Low-level PE samples L6760-1 (Ref 25), –3 (Ref 28), and -4 (Ref 29) were D/F blanks with resulting TEQs sufficiently low enough to still be distinguished as blank samples.
D/F WG12534	N	0.610	25.3–7,100 (PE)	Sample concentrations > 20x blank.
D/F WG12641	N	0.0475	31–269 (Midland) 72.8 (Brunswick) 123 (Titta. River sediment) 0.159–7690 (PE)	All but PE sample Ref 177 (0.159 TEQ) had significantly higher total TEQ than blank. Ref 177 was confirmed by running in another batch and results, which agreed within 18%. Additionally, Ref 177 was compared to its replicates within the program and considered acceptable.
D/F WG12737	N	0.348	25.7–192 (Midland) 35.2– 1,300 (Titta. River soil)	Sample concentrations >20x blank.
D/F WG12804	N	0.0153	3.89–188 (PE)	A few analytes higher than criteria but no significant contribution to total TEQ.
D/F WG13547	N	0.0553	57.5– 3,000 (Nitro) 37.9 (North Carolina) 122 (Saginaw River) 26.4– 222 (Midland)	Several analytes exceeded criteria, but blank total TEQ contribution to sample is relatively small.

Sample Batch Number	Criteria Met	Method Blank TEQ[a] (pg/g)	Sample TEQ Range[a] (pg/g)	Comments
D/F WG13548	N	0.0114	99.6–99.7 (Saginaw River) 32.9–36.4 (North Carolina) 0.268–100 (Extracts)	Several analytes exceeded criteria. In general, the blank contribution to total TEQ was negligible and in those cases results were accepted. Several low-level extract samples were evaluated as follows: Extract Spike #1 samples L6754-4 (Ref 4), -8 (Ref 8), -10 (Ref 10), -14 (Ref 14), -19 (Ref 19), -22 (Ref 22), and -23 (Ref 23) were known TCDD spikes at 0.5 pg/mL. Results were compared to the known spiked TEQ and considered unaffected by blank contribution to TEQ. Extract Spike #3 samples L6754-1 (Ref 1), -7 (Ref 7), -12 (Ref 12), and -15 (Ref 15) were PCB spikes and not expected to contain D/F. These spikes consistently contained a D/F TEQ of ~0.3. However, this came from a consistent ~0.3 pg/mL of TCDD detected in these extracts that was confirmed as a low-level TCDD contamination by AXYS. Since TCDD was not present in the lab blank, these results were accepted as unaffected by any blank contribution to TEQ.
D/F WG13549	N	0.0925	2,160–3,080 (Nitro) 146–1,320 (Saginaw River) 788–8,410 (North Carolina)	Many analytes exceeded limits, but the blank contribution to total TEQ is small relative to sample TEQs.
D/F WG13551	N	2.40	1,100–10,800 (North Carolina) 7,160–11,300 (Winona Post)	Many analytes exceeded limits, but the blank contribution to total TEQ is small relative to sample TEQs.
D/F WG13552	Y	0.000969	0.0386–9.28 (PE) 25.8 (Midland)	
D/F WG13984	N	0.0154	0.524–24.8 (PE) 10.4 (Raritan Bay) 53.1–444 (Extracts)	Blank contribution to total TEQ was negligible except for PE samples L7179-7 (Ref 94), -8 (Ref 96), -11 (Ref 108), -12 (Ref 109), -17 (Ref 132), and L7182-6 (Ref 150). All but L7179-8 were certified blanks. L7179-8 was a PAH spike with no D/F TEQ expected. The TEQs of these samples were considered sufficiently low enough to still be distinguished as blank samples and were accepted.
D/F WG14274	N	0.0434	2800 (Nitro) 35.5–8,320 (North Carolina) 0.0530–5.93 (PE)	Sample TEQs were large enough to be unaffected by the blank TEQ except for four PE samples L7179-4 (Ref 85), -16 (Ref 124) and L7182-12 (Ref 169) and -14 (Ref 184). These PE samples were either certified blanks or PCB spikes with no expected D/F TEQ. Resulting TEQs for these samples were considered low enough to be distinguished as blank samples and were accepted.

Sample Batch Number	Criteria Met	Method Blank TEQ[a] (pg/g)	Sample TEQ Range[a] (pg/g)	Comments
PCB WG12108	N	0.000137	2.63–5.19 (Newark Bay) 2.04–2.82 (Raritan Bay)	PCB 77 slightly high, but all samples >20x blank levels.
PCB WG12147	Y	0.000	1.21–5.06 (Newark Bay) 0.104–0.330 (Brunswick)	
PCB WG12265	Y	0.0000584	0.132–0.369 (Brunswick) 0.034–0.649 (Titta. River sediment) 0.00277–1030 (PE)	
PCB WG12457	N	0.000208	4.20–1,020 (PE)	PCB 77 slightly high. Did not report any samples where PCB 77 was <10x blank. No significant effect on total TEQ.
PCB WG12687	N	0.0183	0.974–2.73 (Midland) 10.3–1,180 (PE)	PCB 77 and 156 high, but all samples >20x blank levels.
PCB WG12834	N	0.000405	0.0157–62.4 (Saginaw River) 0.181–0.203 (Brunswick) 0.986–7.57 (Titta. River Soil)	PCB 77 slightly high. Does not affect total TEQ.
PCB WG12835	N	0.000125	0.822–2.06 (Winona Post)	PCB 77 slightly high. Sample TEQs much greater than blank TEQ.
PCB WG12836	N	0.0499	1,060–904,000 (North Carolina)	PCBs 77, 123, 126, 156, 167, and 118 high, but most samples significantly > 20x blank levels.
PCB WG13008	N	0.0221	2.38–3.15 (Midland) 1.03–8.37 (Titta. River soil) 41.0–1,140 (PE)	PCBs 77 and 118 high, but all samples >20x blank levels.
PCB WG13256	Y	0.000102	0.00385–0.051 (PE)	
PCB WG13257	Y	0.000251	0.253–0.318 (Midland) 0.135–2.08 (Extracts) 3.53–9.62 (PE) 1.14–1.33 (Titta. River Soil)	
PCB WG13258	Y	0.000301	0.163–37.0 (Nitro) 29.8–73.6 (Saginaw River) 40.1–42.1 (PE)	
PCB WG13554	N	0.0000900	0.000103–1,080 (Extracts) 435–1,160 (PE)	PCB 77 slightly high. Does not affect total TEQ.
PCB WG14109	N	0.000288	0.388–0.452 (Nitro) 0.0467 (Saginaw River) 0.654–1.87 (Winona Post) 0.00300–0.0420 (PE)	PCB 77 high. PE certified blanks Ref 85, Ref 85 duplicate, and Ref 108 were the only samples where PCB 77 was not >20x blank. TEQs for these certified blanks were considered low enough to be distinguished as blank samples and were accepted.

[a] All nondetect and EMPC values were assigned a zero concentration for the TEQ calculation.
[b] "Ref XX" is a reference laboratory sample ID number.

Table C-2. Sample Batch Duplicate Summary

Sample Batch Number	Criteria Met	Duplicate RPD[a] (%)	Comments
D/F WG12107	N	23	L6744-5, Ref 100 Newark Bay Because this was above the 20% criteria, an additional aliquot of this sample was prepared. Results for the additional aliquot were within 11% RPD from the original results; therefore, this duplicate result was accepted.
D/F WG12148	Y	2.1	L6744-9, Ref 122 Newark Bay
D/F WG12264	Y	1.2	L6760-2, Ref 27 PE
D/F WG12534	Y	5.7	L6760-14, Ref 55 PE
D/F WG12641	Y	4.6	L6747-1, Ref 32 Midland
D/F WG12737	Y	14	L6750-3, Ref 78 Tittabawassee River Soil
D/F WG12804	N	none	The duplicate processed with this batch was to be repeated due to some analytes being <20x blank level. However, it was reprocessed as a single sample and not a duplicate. Samples in this set were accepted based on their agreement with other replicates within the demonstration program.
D/F WG13547	Y	16	L7163-1, Ref 26 Nitro
D/F WG13548	Y	5.9	L6751-14, Ref 83 North Carolina
D/F WG13549	Y	3.6	L6751-7, Ref 135 North Carolina
D/F WG13551	Y	0.0	L6751-1, Ref 42 North Carolina
D/F WG13552	Y	20 (on U=1/2 DL basis[b])	L7179-3, Ref 74 PE. Fails on a U=0 DL basis due to presence of "K" flagged analytes in one replicate. When compared on U-1/2 DL basis where "K" concentrations are included in the TEQ calculation, the duplicate passed.
D/F WG13984	Y	3.4	L7179-14, Ref 113 PE
D/F WG14274	N	54	L7179-16, Ref 124 PE This was a PCB PE sample and contained only trace levels of D/F. Replicate precision is affected because D/F content is so low. This is not expected to indicate any problems with precision within this sample set. Samples in this set were accepted based on their agreement with other replicates within the demonstration program.
PCB WG12108	N	22	L6744-2, Ref 49 Newark Bay This result is only slightly above the acceptance criteria of 20%. The variability was influenced by 25% RPD for PCB126 (which has the highest TEF of the PCBs and, therefore, a larger influence on total TEQ). The slight exceedance in duplicate criteria was not considered to have any significant impact on the data reported in this sample batch. All samples in this set were also evaluated based on their agreement with other replicates within the demonstration program and deemed to be acceptable.

Sample Batch Number	Criteria Met	Duplicate RPD[a] (%)	Comments
PCB WG12147	N	none	L6748-9, Ref 129 Brunswick The duplicate sample for this batch required reprocessing. When reprocessed, it was not prepared in duplicate. Samples in this set were accepted based on the RPD of site replicates that were processed within the batch (RPDs <10%).
PCB WG12265	Y	2.5	L6760-5, Ref 35 PE
PCB WG12457	N	none	L6760-16, Ref 62 PE This duplicate set was to be repeated due to low internal standard recovery. When repeated, it was not prepared in duplicate. Data for this set was accepted because all samples in the set were PE samples. These PE samples met accuracy criteria and reproducibility criteria to other replicates of the same PE material processed within the demonstration.
PCB WG12687	Y	4.3	L6762-12, Ref 169 PE
PCB WG12834	Y	4.2	L6750-8, Ref 164 Tittabawassee River Soil
PCB WG12835	N	none	Duplicate sample repeated in WG13258. Results reported with that sample set. Three sets of sample replicates within this batch were also compared and found to have <13.5% RPD showing acceptable precision with this sample set.
PCB WG12836	Y	2.6	L6751-6, Ref 126 North Carolina
PCB WG13008	Y	5.1	L6750-6, Ref 121 Tittabawassee River Soil
PCB WG13256	Y	1.7 (on U=1/2 DL basis)	L6761-3, Ref 74 PE. Fails on a U=0 DL basis due to presence of "K" flagged analytes in one replicate. When compared on U=1/2 DL basis where "K" concentrations are included in the TEQ calculation, the duplicate passed.
PCB WG13257	Y	15	L7187-5, Ref 92 Tittabawassee River Soil
PCB WG13258	Y	19	L6743-2, Ref 36 Nitro
PCB WG13554	Y	12	L6762-1, Ref 202 PE
PCB WG14109	N	85 (on U=1/2 DL basis)	L7179-4, PE. Fails based on both U=0 and U=1/2 DL. This was a blank PE sample and contained only trace levels of PCBs. Replicate precision is affected because the PCB content is so low. This is not expected to indicate any problems with precision within this sample set. Samples in this set were accepted based on their agreement with other replicates within the demonstration program.

[a] Nondetects were assigned a concentration of zero unless otherwise noted and are referred to as U=0 DL values.
[b] U=1/2 DL indicates that non-detects were assigned a concentration equal to one-half the SDL and EMPC concentrations were assigned a value equal to the EMPC.

Appendix D
Summary of Developer and Reference Laboratory Data

Appendix D. CAPE Technologies and Reference Laboratory One-to-One Matching

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Environmental	CAPE 105	Laboratory	Brunswick #1	1	12	0.314	81	67.2	93	67.51
Environmental	CAPE 139	Laboratory	Brunswick #1	2	2	0.342	90	71.6	92	71.94
Environmental	CAPE 130	Laboratory	Brunswick #1	3	4	0.369	241	61.7	245	62.07
Environmental	CAPE 76	Field	Brunswick #1	4	0	0.313	59	67.8	59	68.11
Environmental	CAPE 158	Laboratory	Brunswick #2	1	2	0.127	24	49.5	26	49.63
Environmental	CAPE 115	Laboratory	Brunswick #2	2	10	0.128	79	72.8	89	72.93
Environmental	CAPE 136	Laboratory	Brunswick #2	3	1	0.132	116	56	117	56.13
Environmental	CAPE 84	Field	Brunswick #2	4	0	0.123	79	60.4	79	60.52
Environmental	CAPE 195	Laboratory	Brunswick #3	1	153	0.19	84	12600	237	12600.19
Environmental	CAPE 25	Field	Brunswick #3	2	77	0.181	9760	15200	9837	15200.18
Environmental	CAPE 83	Field	Brunswick #3	3	212	0.203	290	13100	502	13100.20
Environmental	CAPE 117	Laboratory	Brunswick #3	4	194	0.182	139	13600	333	13600.18
Environmental	CAPE 49	Field	Midland #1	1	1	2.59	130	222	131	224.59
Environmental	CAPE 56	Field	Midland #1	2	3	2.73	812	241	815	243.73
Environmental	CAPE 172	Laboratory	Midland #1	3	24	2.5	424	269	448	271.50
Environmental	CAPE 209	Laboratory	Midland #1	4	0	2.53	57	268	57	270.53
Environmental	CAPE 197	Laboratory	Midland #2	1	0	2.7	40	208	40	210.70
Environmental	CAPE 113	Laboratory	Midland #2	2	19	2.81	71	179	90	181.81
Environmental	CAPE 164	Laboratory	Midland #2	3	1	2.48	68	197	69	199.48
Environmental	CAPE 94	Field	Midland #2	4	0	3.15	64	192	64	195.15
Environmental	CAPE 173	Laboratory	Midland #3	1	33	2.28	269	185	302	187.28
Environmental	CAPE 98	Laboratory	Midland #3	2	1	2.17	150	174	151	176.17
Environmental	CAPE 27	Field	Midland #3	3	0	2.23	119	176	119	178.23
Environmental	CAPE 122	Laboratory	Midland #3	4	11	2.38	226	161	237	163.38
Environmental	CAPE 166	Laboratory	Midland #4	1	8	0.253	<13	25.7	<21	25.95
Environmental	CAPE 96	Laboratory	Midland #4	2	0	0.318	42	26.4	42	26.72
Environmental	CAPE 71	Field	Midland #4	3	1	0.974	37	31	38	31.97
Environmental	CAPE 191	Laboratory	Midland #4	4	0	0.263	15	25.8	15	26.06
Environmental	CAPE 38	Field	NC PCB Site #1	1	6506	53000	16300	788	22806	53788.00
Environmental	CAPE 148	Laboratory	NC PCB Site #1	2	3714	65300	3590	1100	7304	66400.00
Environmental	CAPE 170	Laboratory	NC PCB Site #1	3	22756	80500	308	852	23064	81352.00
Environmental	CAPE 40	Field	NC PCB Site #1	4	5217	85100	11300	906	16517	86006.00
Environmental	CAPE 31	Field	NC PCB Site #2	1	7766	311000	26600	3400	34366	314400.00
Environmental	CAPE 155	Laboratory	NC PCB Site #2	2	7564	305000	20200	3300	27764	308300.00
Environmental	CAPE 121	Laboratory	NC PCB Site #2	3	1092	210000	34500	3430	35592	213430.00

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Environmental	CAPE 81	Field	NC PCB Site #2	4	18250	361000	24500	3490	42750	364490.00
Environmental	CAPE 154	Laboratory	NC PCB Site #3	1	2550	848000	>8300	8320	>10850	856320.00
Environmental	CAPE 102	Laboratory	NC PCB Site #3	2	27180	618000	65000	8410	92180	626410.00
Environmental	CAPE 41	Field	NC PCB Site #3	3	3714	533000	33700	9360	37414	542360.00
Environmental	CAPE 134	Laboratory	NC PCB Site #3	4	847	904000	42400	10800	43247	914800.00
Environmental	CAPE 36	Field	Newark Bay #1	1	1	1.22	31	23	32	24.22
Environmental	CAPE 109	Laboratory	Newark Bay #1	2	5	1.44	17	14	22	15.44
Environmental	CAPE 137	Laboratory	Newark Bay #1	3	5	1.39	26	14.5	31	15.89
Environmental	CAPE 145	Laboratory	Newark Bay #1	4	1	1.34	<23	13.5	<24	14.84
Environmental	CAPE 99	Laboratory	Newark Bay #2	1	9	5.01	69	50.6	78	55.61
Environmental	CAPE 193	Laboratory	Newark Bay #2	2	5	5.19	49	47.4	54	52.59
Environmental	CAPE 204	Laboratory	Newark Bay #2	3	1	5.14	<11	74.1	<12	79.24
Environmental	CAPE 61	Field	Newark Bay #2	4	1	5.09	75	50.4	76	55.49
Environmental	CAPE 138	Laboratory	Newark Bay #3	1	8	4.61	80	38.9	88	43.51
Environmental	CAPE 110	Laboratory	Newark Bay #3	2	4	5.04	46	44.9	50	49.94
Environmental	CAPE 66	Field	Newark Bay #3	3	3	4.5	11	40.2	14	44.70
Environmental	CAPE 142	Laboratory	Newark Bay #3	4	2	5.03	45	41.9	47	46.93
Environmental	CAPE 82	Field	Newark Bay #4	1	8	2.73	63	33.6	71	36.33
Environmental	CAPE 108	Laboratory	Newark Bay #4	2	5	2.65	22	26.1	27	28.75
Environmental	CAPE 175	Laboratory	Newark Bay #4	3	82	2.72	68	27.6	150	30.32
Environmental	CAPE 167	Laboratory	Newark Bay #4	4	24	2.7	36	26.8	60	29.50
Environmental	CAPE 34	Field	Raritan Bay #1	1	2	2.33	42	10.2	44	12.53
Environmental	CAPE 131	Laboratory	Raritan Bay #1	2	3	2.06	95	10.3	98	12.36
Environmental	CAPE 55	Field	Raritan Bay #1	3	2	2.35	75	10.4	77	12.75
Environmental	CAPE 179	Laboratory	Raritan Bay #1	4	90	2.25	44	11.4	134	13.65
Environmental	CAPE 128	Laboratory	Raritan Bay #2	1	8	2.7	52	13.3	60	16.00
Environmental	CAPE 146	Laboratory	Raritan Bay #2	2	5	2.67	36	13.1	41	15.77
Environmental	CAPE 73	Field	Raritan Bay #2	3	1	2.68	38	12.8	39	15.48
Environmental	CAPE 58	Field	Raritan Bay #2	4	2	2.85	47	13	49	15.85
Environmental	CAPE 107	Laboratory	Raritan Bay #3	1	5	2.43	19	10.4	24	12.83
Environmental	CAPE 64	Field	Raritan Bay #3	2	3	2.43	56	11.1	59	13.53
Environmental	CAPE 162	Laboratory	Raritan Bay #3	3	1	2.3	80	10.6	81	12.90
Environmental	CAPE 147	Laboratory	Raritan Bay #3	4	7	2.33	<23	9.93	<30	12.26
Environmental	CAPE 89	Field	Saginaw River #1	1	22	62.4	1470	1050	1492	1112.40
Environmental	CAPE 78	Field	Saginaw River #1	2	25	73.6	758	683	783	756.60
Environmental	CAPE 123	Laboratory	Saginaw River #1	3	32	69.9	421	1070	453	1139.90
Environmental	CAPE 150	Laboratory	Saginaw River #1	4	8	63.7	58	694	66	757.70
Environmental	CAPE 29	Field	Saginaw River #2	1	14	30.6	1690	1110	1704	1140.60

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Environmental	CAPE 106	Laboratory	Saginaw River #2	2	26	31	1290	953	1316	984.00
Environmental	CAPE 178	Laboratory	Saginaw River #2	3	189	26.7	2650	1320	2839	1346.70
Environmental	CAPE 201	Laboratory	Saginaw River #2	4	10	29.8	179	864	189	893.80
Environmental	CAPE 68	Field	Saginaw River #3	1	6119	0.0202	241	99.7	6360	99.72
Environmental	CAPE 198	Laboratory	Saginaw River #3	2	0	0.0164	51	146	51	146.02
Environmental	CAPE 119	Laboratory	Saginaw River #3	3	14	0.0467	122	122	136	122.05
Environmental	CAPE 53	Field	Saginaw River #3	4	2	0.0157	2730	99.6	2732	99.62
Environmental	CAPE 153	Laboratory	Solutia #1	1	3	0.452	37	57.5	40	57.95
Environmental	CAPE 165	Laboratory	Solutia #1	2	0	0.163	38	76.9	38	77.06
Environmental	CAPE 59	Field	Solutia #1	3	2	0.388	138	62	140	62.39
Environmental	CAPE 45	Field	Solutia #1	4	14	0.391	80	61.6	94	61.99
Environmental	CAPE 177	Laboratory	Solutia #2	1	55	17.6	1780	2090	1835	2107.60
Environmental	CAPE 176	Laboratory	Solutia #2	2	364	18.8	2280	1950	2644	1968.80
Environmental	CAPE 50	Field	Solutia #2	3	5	19.2	556	1860	561	1879.20
Environmental	CAPE 30	Field	Solutia #2	4	4	18.5	869	2160	873	2178.50
Environmental	CAPE 77	Field	Solutia #3	1	7	29.7	3790	2810	3797	2839.70
Environmental	CAPE 127	Laboratory	Solutia #3	2	17	36.9	3320	2800	3337	2836.90
Environmental	CAPE 192	Laboratory	Solutia #3	3	48	37	3140	3000	3188	3037.00
Environmental	CAPE 51	Field	Solutia #3	4	8	31.5	1890	3080	1898	3111.50
Environmental	CAPE 174	Laboratory	Titta. River Soil #1	1	38	7.32	298	35	336	42.32
Environmental	CAPE 143	Laboratory	Titta. River Soil #1	2	24	8.26	275	35.2	299	43.46
Environmental	CAPE 87	Field	Titta. River Soil #1	3	6	7.57	49	40	55	47.57
Environmental	CAPE 85	Field	Titta. River Soil #1	4	2	8.37	187	35.8	189	44.17
Environmental	CAPE 163	Laboratory	Titta. River Soil #2	1	1	0.986	192	420	193	420.99
Environmental	CAPE 199	Laboratory	Titta. River Soil #2	2	0	1.2	157	450	157	451.20
Environmental	CAPE 39	Field	Titta. River Soil #2	3	21	1.03	1300	523	1321	524.03
Environmental	CAPE 62	Field	Titta. River Soil #2	4	1	1.06	1203	506	1204	507.06
Environmental	CAPE 161	Laboratory	Titta. River Soil #3	1	0	1.26	1220	1050	1220	1051.26
Environmental	CAPE 92	Field	Titta. River Soil #3	2	1	1.16	>330	676	331	677.16
Environmental	CAPE 135	Laboratory	Titta. River Soil #3	3	3	1.54	820	1220	823	1221.54
Environmental	CAPE 79	Field	Titta. River Soil #3	4	2	1.33	<280	1300	282	1301.33
Environmental	CAPE 182	Laboratory	Titta. River Sed #1	1	219	0.0527	60	1.05	279	1.10
Environmental	CAPE 46	Field	Titta. River Sed #1	2	74	0.034	686	1.11	760	1.14
Environmental	CAPE 156	Laboratory	Titta. River Sed #1	3	1	0.0407	16	1	17	1.04
Environmental	CAPE 33	Field	Titta. River Sed #1	4	6	0.0403	24	1.7	30	1.74
Environmental	CAPE 63	Field	Titta. River Sed #2	1	0	0.649	123	52.8	123	53.45
Environmental	CAPE 120	Laboratory	Titta. River Sed #2	2	1	0.71	66	123	67	123.71
Environmental	CAPE 88	Field	Titta. River Sed #2	3	0	0.566	258	66.1	258	66.67

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Environmental	CAPE 208	Laboratory	Titta. River Sed #2	4	0	0.515	26	94.1	26	94.62
Environmental	CAPE 43	Field	Titta. River Sed #3	1	65	0.0719	184	13	249	13.07
Environmental	CAPE 111	Laboratory	Titta. River Sed #3	2	2	0.0973	26	11.2	28	11.30
Environmental	CAPE 203	Laboratory	Titta. River Sed #3	3	0	0.083	26	12.7	26	12.78
Environmental	CAPE 132	Laboratory	Titta. River Sed #3	4	1	0.09	55	13.8	56	13.89
Environmental	CAPE 65	Field	Winona Post #1	1	2	0.654	1420	7290	1422	7290.65
Environmental	CAPE 160	Laboratory	Winona Post #1	2	1	0.904	68	7370	69	7370.90
Environmental	CAPE 74	Field	Winona Post #1	3	1	0.829	2470	7450	2471	7450.83
Environmental	CAPE 124	Laboratory	Winona Post #1	4	10	0.822	>1800	7160	>1810	7160.82
Environmental	CAPE 159	Laboratory	Winona Post #2	1	14	1.2	42	9720	56	9721.20
Environmental	CAPE 48	Field	Winona Post #2	2	23	1.3	3250	9770	3273	9771.30
Environmental	CAPE 189	Laboratory	Winona Post #2	3	66	1.32	60	9200	126	9201.32
Environmental	CAPE 26	Field	Winona Post #2	4	12	1.28	4690	11300	4702	11301.28
Environmental	CAPE 32	Field	Winona Post #3	1	10	1.68	458	10300	468	10301.68
Environmental	CAPE 144	Laboratory	Winona Post #3	2	73	1.87	550	9770	623	9771.87
Environmental	CAPE 194	Laboratory	Winona Post #3	3	42	1.8	89	9320	131	9321.80
Environmental	CAPE 72	Field	Winona Post #3	4	2	2.06	1516	9870	1518	9872.06
Extract	CAPE 3	Field	Envir. Extract #1	1	6	0.629	154	175	160	175.63
Extract	CAPE 2	Field	Envir. Extract #1	2	6	0.673	2240	444	2246	444.67
Extract	CAPE 9	Field	Envir. Extract #1	3	2	0.64	134	176	136	176.64
Extract	CAPE 5	Field	Envir. Extract #1	4	9	2.08	168	439	177	441.08
Extract	CAPE 11	Field	Envir. Extract #2	1	2	0.742	31	55.3	33	56.04
Extract	CAPE 13	Field	Envir. Extract #2	2	28	0.135	67	53.3	95	53.44
Extract	CAPE 8	Field	Envir. Extract #2	3	3	0.297	33	53.1	36	53.40
Extract	CAPE 10	Field	Envir. Extract #2	4	3	0.17	66	53.6	69	53.77
Extract	CAPE 17	Field	Spike #1	1	<50	0.0638	<6	0.504	<56	0.57
Extract	CAPE 14	Field	Spike #1	2	2	0.00013	4	0.509	6	0.51
Extract	CAPE 12	Field	Spike #1	3	0	0.0001	<3	0.537	<3	0.54
Extract	CAPE 20	Field	Spike #1	4	15	0.0275	19	0.524	34	0.55
Extract	CAPE 7	Field	Spike #1	5	2	0.0562	3	0.585	5	0.64
Extract	CAPE 21	Field	Spike #1	6	2	0.00724	8	0.576	10	0.58
Extract	CAPE 4	Field	Spike #1	7	1	0.139	<3	0.52	<4	0.66
Extract	CAPE 23	Field	Spike #2	1	623	113	143	91.6	766	204.60
Extract	CAPE 1	Field	Spike #2	2	92	113	5	91.8	97	204.80
Extract	CAPE 18	Field	Spike #2	3	3	111	29	89.1	32	200.10
Extract	CAPE 6	Field	Spike #2	4	548	113	13	100	561	213.00
Extract	CAPE 22	Field	Spike #3	1	2174	1060	6	0.324	2180	1060.32
Extract	CAPE 15	Field	Spike #3	2	42	1080	6	0.348	48	1080.35

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Extract	CAPE 19	Field	Spike #3	3	3392	1060	6	0.363	3398	1060.36
Extract	CAPE 16	Field	Spike #3	4	36	990	6	0.268	42	990.27
Performance	CAPE 126	Laboratory	Cambridge 5183	1	8	3.81	22	4.78	30	8.59
Performance	CAPE 116	Laboratory	Cambridge 5183	2	9	4.33	12	4.08	21	8.41
Performance	CAPE 112	Laboratory	Cambridge 5183	3	21	4.2	<14	4.06	<35	8.26
Performance	CAPE 157	Laboratory	Cambridge 5183	4	2	4.24	<13	3.56	<15	7.80
Performance	CAPE 205	Laboratory	Cambridge 5183	5	3	4.25	<11	3.89	<14	8.14
Performance	CAPE 42	Field	Cambridge 5183	6	11	3.86	17	5.93	28	9.79
Performance	CAPE 152	Laboratory	Cambridge 5183	7	6	3.53	<13	3.89	<19	7.42
Performance	CAPE 151	Laboratory	Cambridge 5184	1	160	1080	44	187	204	1267.00
Performance	CAPE 101	Laboratory	Cambridge 5184	2	520	1120	117	188	637	1308.00
Performance	CAPE 202	Laboratory	Cambridge 5184	3	3372	1140	27	173	3399	1313.00
Performance	CAPE 69	Field	Cambridge 5184	4	874	1160	280	180	1154	1340.00
Performance	CAPE 100	Laboratory	ERA Aroclor	1	588	1060	45	36.4	633	1096.40
Performance	CAPE 171	Laboratory	ERA Aroclor	2	258	3690	36	32.9	294	3722.90
Performance	CAPE 207	Laboratory	ERA Aroclor	3	13400	3790	20	37.9	13420	3827.90
Performance	CAPE 57	Field	ERA Aroclor	4	695	3800	161	35.5	856	3835.50
Performance	CAPE 90	Field	ERA Blank	1	0	0.0243	<14	0.0942	14	0.12
Performance	CAPE 86	Field	ERA Blank	2	0	0.00385	15	0.0728	15	0.08
Performance	CAPE 149	Laboratory	ERA Blank	3	2	0.00277	<50	0.237	<52	0.24
Performance	CAPE 104	Laboratory	ERA Blank	4	2	0.042	17	0.307	19	0.35
Performance	CAPE 133	Laboratory	ERA Blank	5	0	0.0229	46	0.113	46	0.14
Performance	CAPE 103	Laboratory	ERA Blank	6	4	0.0191	13	0.0524	17	0.07
Performance	CAPE 180	Laboratory	ERA Blank	7	3	0.0325	<11	0.211	<14	0.24
Performance	CAPE 184	Laboratory	ERA Blank	8	0	0.0225	13	0.0692	13	0.09
Performance	CAPE 28	Field	ERA PAH	1	0	0.0254	<14	0.159	<14	0.18
Performance	CAPE 125	Laboratory	ERA PAH	2	5	0.00429	14	0.141	19	0.15
Performance	CAPE 141	Laboratory	ERA PAH	3	9	0.00423	<12	0.161	<21	0.17
Performance	CAPE 60	Field	ERA PAH	4	1	0.026	<13	0.248	14	0.27
Performance	CAPE 185	Laboratory	ERA PCB 100	1	34	10.6	<12	0.0386	<46	10.64
Performance	CAPE 168	Laboratory	ERA PCB 100	2	158	11.1	23	NA[e]	181	NA[e]
Performance	CAPE 47	Field	ERA PCB 100	3	22	10.6	<12	0.053	<34	10.65
Performance	CAPE 75	Field	ERA PCB 100	4	16	9.95	<16	0.127	32	10.08
Performance	CAPE 37	Field	ERA PCB 10000	1	880	1030	<12	0.204	<892	1030.20
Performance	CAPE 67	Field	ERA PCB 10000	2	2634	1030	<16	0.507	2650	1030.51
Performance	CAPE 200	Laboratory	ERA PCB 10000	3	1258	1180	<11	0.105	<1269	1180.11
Performance	CAPE 169	Laboratory	ERA PCB 10000	4	6748	1020	<11	0.0628	<6760	1020.06
Performance	CAPE 70	Field	ERA TCDD 10	1	1	0.0147	22	8.69	23	8.70

Sample Type	Sample Number	Measurement Location[a]	Sample Description	REP	TEQ_{PCB} (pg/g)		$TEQ_{D/F}$ (pg/g)		Total TEQ (pg/g)	
					Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c]	Developer[b]	Reference Laboratory[c,d]
Performance	CAPE 24	Field	ERA TCDD 10	2	0	0.0123	8	9.28	8	9.29
Performance	CAPE 181	Laboratory	ERA TCDD 10	3	34	0.0299	34	8.44	68	8.47
Performance	CAPE 183	Laboratory	ERA TCDD 10	4	3	0.045	16	8.2	19	8.25
Performance	CAPE 52	Field	ERA TCDD 30	1	0	0.0451	82	27.4	82	27.45
Performance	CAPE 206	Laboratory	ERA TCDD 30	2	0	0.0153	<11	25.3	<11	25.32
Performance	CAPE 97	Laboratory	ERA TCDD 30	3	1	0.0436	36	24.8	37	24.84
Performance	CAPE 140	Laboratory	ERA TCDD 30	4	0	0.04	37	23.9	37	23.94
Performance	CAPE 114	Laboratory	LCG CRM-529	1	133	435	>350	NA[e]	>483	NA[e]
Performance	CAPE 91	Field	LCG CRM-529	2	254	405	>330	6930	584	7335.00
Performance	CAPE 129	Laboratory	LCG CRM-529	3	44	498	11600	6900	11644	7398.00
Performance	CAPE 187	Laboratory	LCG CRM-529	4	10	356	9760	7190	9770	7546.00
Performance	CAPE 186	Laboratory	NIST 1944	1	35	40.1	47	237	82	277.10
Performance	CAPE 54	Field	NIST 1944	2	19	43.7	113	206	132	249.70
Performance	CAPE 196	Laboratory	NIST 1944	3	9	42.1	21	252	30	294.10
Performance	CAPE 93	Field	NIST 1944	4	18	41	125	219	143	260.00
Performance	CAPE 188	Laboratory	Wellington WMS -01	1	11	10.6	65	68	76	78.60
Performance	CAPE 190	Laboratory	Wellington WMS -01	2	11	9.4	80	65.7	91	75.10
Performance	CAPE 44	Field	Wellington WMS -01	3	174	9.62	213	61.9	387	71.52
Performance	CAPE 118	Laboratory	Wellington WMS -01	4	12	9.07	160	66.1	172	75.17
Performance	CAPE 35	Field	Wellington WMS -01	5	4	10.3	108	68	112	78.30
Performance	CAPE 95	Laboratory	Wellington WMS -01	6	3	9.62	76	65.7	79	75.32
Performance	CAPE 80	Field	Wellington WMS -01	7	7	9.68	88	65.4	95	75.08

[a] All PCBs results were generated in the laboratory.

[b] Data listed exactly as reported by the developer.

[c] Qualifier flags (e.g., J and K flags) included in the raw data have been removed for the purposes of statistical analysis.

[d] Data calculated by the developer by summing TEQ_{PCB} and $TEQ_{D/F}$.

[e] Reference laboratory data was discarded due to laboratory sample preparation error.