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Interlaboratory Validation Study of Environmental Protection Agency Method 1668A for Analysis of PCB Congeners in Water

Volume 1

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PRODUCT DESCRIPTION

Polychlorinated biphenyls (PCBs) are a group of 209 chemicals with a common chemical structure. Historically, PCBs have been measured in environmental media as commercial mixtures of many PCB species. The U.S. Environmental Protection Agency (EPA) developed a highly sensitive analytical method, EPA Method 1668, that can be used to measure individual PCBs in water and other matrices. The EPA has proposed adding Method 1668 to the compilation of test methods that can be required to be used for monitoring compliance with water discharge permits. The Electric Power Research Institute (EPRI) undertook a multi-laboratory validation study to determine the performance of this method in clean water, as well as in a single-laboratory study with power-plant ash pond wastewater.

This report (1016277) is Volume 1 of a two-volume series. The other report is 1021505, *Interlaboratory Validation Study of Environmental Protection Agency Method 1668A for Analysis of PCB Congeners in Water: Volume 2.*

Results and Findings

The results of this investigation indicate that the sensitivity of Method 1668A is limited by the presence of the target chemicals as contaminants in the laboratory environment. Background contamination varies significantly from one laboratory to another, implying that an appropriate basis for method detection limits would be a laboratory-specific, long-term average of method blanks. When Method 1668A was applied to reagent (clean) water, quality control criteria specified in the method were met for most PCB compounds. Results for two ash pond wastewater samples were not significantly different from those for reagent water.

Challenges and Objectives

Method 1668A is a complex method that demands a high degree of laboratory expertise and outstanding quality control to produce acceptable results. Because the method is so sensitive that it will likely detect PCBs in the cleanest water samples, including the "clean" reagent water used by laboratories, distinguishing background levels from low-level concentrations in a sample is challenging. This report provides information that may assist permitting staff at power companies and other entities that need to monitor for PCBs or evaluate PCB data to assess the quality of results delivered by their laboratory.

Applications, Value, and Use

The EPRI study provides a baseline for evaluating the capabilities of Method 1668A as applied to reagent water and ash pond wastewater. However, neither of these matrices presents the challenges of more complex water samples such as surface waters and high-strength industrial

wastewaters, which are more likely to contain interfering substances. The results of the EPRI study should be compared with results in the matrix of interest. Future research is needed to evaluate the performance of the method outside the context of a controlled validation study.

EPRI Perspective

EPRI has been involved in the evaluation of analytical method performance for water methods since the early 1990s. This report is one of a series of reports evaluating method detection limits and other performance indicators.

Approach

A multi-laboratory study was conducted using reagent water samples fortified with different concentrations of 209 PCB compounds. Samples were sent to eight laboratories for analysis. Statistical approaches were applied to evaluate the performance of the method. A single-laboratory study was also conducted using ash pond wastewater fortified with different concentrations of PCB compounds.

Keywords

EPA methods
PCBs
Polychlorinated biphenyls
Wastewater
Water analysis

ABSTRACT

Polychlorinated biphenyls (PCBs) are a group of 209 chemicals with a common chemical structure. Historically, PCBs have been measured in environmental media as Aroclor mixtures, commercial mixtures of many PCB species. Recently, the U.S. Environmental Protection Agency (EPA) developed an analytical method, EPA Method 1668, which can be used to measure individual PCB congeners in water and other matrices. This method can detect far lower concentrations in water than previous methods: parts per quadrillion or picograms/liter, compared to parts per billion or micrograms per liter for earlier methods.

The EPA has proposed adding Method 1668 to the compilation of water test methods that can be required to be used for monitoring compliance with water discharge permits. When a method is used for this purpose, EPA typically first performs a study in multiple test laboratories to demonstrate the precision and accuracy of the method, as well as the sensitivity of the method in various types of samples. EPA conducted such a study in 2003-2004; however, it addressed only one type of wastewater and did not supply sufficient information to fully evaluate the ability of the method to measure PCBs accurately at very low concentrations.

PCBs are ubiquitous in the environment and are present at detectable levels in laboratory method blanks. Experience with Method 1668 has shown that most, if not all, water samples will contain detectable PCBs at levels exceeding instrument detection limits. Distinguishing sample-derived PCBs from ambient and laboratory contamination is a critical part of obtaining an accurate measurement of the actual concentrations in a sample, particularly for industrial facilities that have a "zero discharge" limit for PCBs in their permits. Due to concerns about background contamination, the EPA has based the detection limits in Method 1668 not on the sensitivity of the analytical instrument, as in most EPA methods, but on the levels of each PCB species that can be detected in the presence of background contamination.

To supplement the EPA interlaboratory study, EPRI undertook a validation study of Method 1668A (the version in place at the inception of this project) that included analysis of spiked reagent water samples by eight laboratories. The results of this study were used to derive statistically-based detection and quantitation limits for all PCB species. The study also evaluated the ability of laboratories to achieve these detection and quantitation levels in the presence of laboratory background contamination. The performance of Method 1668A was evaluated for two samples of a matrix of interest (ash pond discharge from coal-fired power plants). The wastewater evaluation was based on a single-laboratory study.

EXECUTIVE SUMMARY

This report is one in a series of method validation studies sponsored by the Electric Power Research Institute (EPRI). The purpose of the EPRI studies is to characterize the performance of analytical methods for chemical substances in water and to develop scientifically based detection and quantification levels for those substances.

Background

Federal and state permits require electric power generating facilities and other industries to monitor for Polychlorinated Biphenyls (PCBs) in their discharge wastewater. Historically, PCBs have been measured as Aroclor mixtures, with detection limits of about 1 part per billion (ppb). In December 1999, the U.S. Environmental Protection Agency (EPA) published an analytical method for measuring individual PCB compounds (congeners) and announced its intent to promulgate this method in *40 CFR, Part 136,* as EPA Method 1668, Revision A, "*Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS).*" This method is intended for the analysis of PCB congeners at trace level concentrations, as low as a few parts-per-quadrillion (ppq) in water. On September, 23, 2010, the EPA issued a proposal in the Federal Register to promulgate Method 1668C. The proposed method revision was published after the completion of the EPRI study, and is not evaluated in this report.

PCBs are ubiquitous in the environment due to their chemical properties and widespread historical usage as dielectric fluids and in a wide variety of commercial products. PCBs are also commonly found as contaminants in the laboratory environment. Due to these factors and the high sensitivity of the method, Method 1668A will likely detect trace levels of PCBs in most, if not all, water samples. The PCBs found in samples may be unrelated to the sample source and background concentrations can vary for each PCB congener. For these reasons, understanding the levels of PCBs contributed by the analytical process is essential to obtaining accurate measurements of environmental samples.

The preferred approach to establishing method performance characteristics is to perform an interlaboratory validation study, in which samples of identical composition are analyzed by multiple laboratories. The multilaboratory approach accounts for measurement variability associated with instrument and operator performance within a single laboratory, as well as variability among a population of laboratories.

Method 1668A was initially validated in a single laboratory study. In 2003-2004, EPA conducted a multi-laboratory validation study that included the analysis of PCB-spiked wastewater from a

publicly owned treatment works (POTW) and several solid matrices. The EPA study started with 14 laboratories, but only 11 submitted data. For the POTW water, only six laboratory data sets were deemed usable. The results were published in the *Method 1668A Interlaboratory Validation Study Report* in November 2008, reissued in April 2010 (EPA-820-R-10-004).

EPRI identified a need to better characterize analytical performance of Method 1668A in a clean water matrix, and evaluate the method in wastewaters characteristic of the electrical power industry. This report presents the results of the EPRI study.

Objectives

The objectives of this study were to:

- Validate method performance across multiple laboratories using a clean water matrix.
- Evaluate potential matrix effects of a range of power industry wastewaters on method performance.
- Determine method sensitivity using reagent water as a pure matrix.
- Assess the presence of PCB background contamination across qualified laboratories that perform this method and the impact on method detection and quantitation levels.
- Evaluate the application of this method in producing high-quality, defensible data for use in permitting and regulatory decisions.

Approach

A detailed work plan for the study was developed and provided to external reviewers, including the EPA Office of Water. Changes to the study design were made in response to reviewer comments.

Laboratories were selected for participation in the study based on their level of experience and ability to comply with detailed reporting and quality control requirements. Therefore, the data produced by the study are representative of a group of qualified laboratories that are currently using this method, but may not be representative of the entire population of commercial laboratories performing Method 1668.

The study design included three main components:

- *A comprehensive round-robin study*. Eight laboratories analyzed a set of PCB-spiked reagent water samples. The results provide the basis of descriptive statistics for all 209 PCB congeners, including percent recovery and precision, interlaboratory detection and quantification estimates (IDE/IQE), PCB background levels across multiple laboratories, and confidence limits for detection of PCBs.
- *A focused single-laboratory study.* Two representative power plant wastewater samples were analyzed using Method 1668A. The two wastewaters were composites of ash pond effluent from coal-fired power plants. These data were used to assess matrix effects on method performance.

- *An evaluation of PCB background levels*. Data were generated using blanks from the interlaboratory study as well as historical method blank data provided by seven of the participating laboratories.

The EPRI Study Plan originally proposed to subject a subset of 44 of the 209 PCB congeners to detailed statistical evaluation. These "target" PCBs (which actually comprised 54 congeners due to coelution with other PCBs) were selected based on chemical properties, toxicity, regulatory significance, and known association with laboratory background contamination. However the statistical evaluation was later extended to all 209 PCB congeners.

Results and Conclusions

The interlaboratory study results indicate that qualified laboratories are capable of achieving the quality control criteria established by EPA Method 1668A in reagent water. Laboratories were able to meet criteria for spike recovery and precision identified in the method, analyzing high-purity reagent water spiked with 209 PCBs at concentrations ranging from 25 picograms per liter (pg/L) to 5,000 pg/L.

Results from a single-laboratory evaluation of two ash pond wastewaters demonstrate that the accuracy and precision limits cited in the method are also achievable for this specific test matrix. Although some differences were observed between reagent water and wastewater data, the ash pond wastewater did not affect the overall performance in meeting the method control limits.

The study did not meet the objective of testing multiple types of power plant wastewaters; therefore, the results of this study can only be directly compared to reagent water and ash pond wastewaters with characteristics similar to those in the study.

Interlaboratory detection estimates (IDE) and interlaboratory quantitation estimates (IQE) are calculated from the study data. The IDE and IQE are statistically based measures of method sensitivity developed by the American Society for Testing and Standards (ASTM). The IDE calculates the lowest concentration at which a single measurement by a qualified laboratory in a population of laboratories will distinguish a true detection from a blank with a 99% level of confidence. The IQE calculates the lowest concentration at which an analyte can be measured by a qualified laboratory, with a specific level of interlaboratory variability. For example, the IQE20% is the quantitation estimate at a relative standard deviation of 20%.

For this study, the IDE/IQE values were developed using high-purity, reagent grade water as the test matrix. The use of this test matrix was intended to demonstrate performance of the method under ideal conditions. The study results did not evaluate method performance using "real world" samples. Real world samples would be expected to differ from reagent water in chemical properties (pH, alkalinity, matrix complexity, presence of interferents), biological activity, and in the number and type of modifiers present, such as suspended and dissolved solids, dissolved organic matter, organic carbon, and surfactants. These added components would most likely degrade method performance and produce higher detection and quantitation limits.

Other features of the EPRI study that may not be present for real world samples include the quality of the participating laboratories and the restriction of certain method modifications. A

subset of eight test laboratories was selected that was considered to be well qualified in conducting the method. The results may therefore compare favorably versus laboratories with less expertise. The laboratories were required to use the same chromatographic column and to report all method modifications (as they also were required to do in EPA's validation study). As the method is performance-based, a wider range of modifications will likely be encountered in practice and could be considered to be compliant. As with the EPA study, EPRI's restrictions on laboratory procedures are likely to have produced more consistent results (lower interlaboratory variability) than would be found in practice.

The IDEs and IQE20% concentrations calculated from EPRI's data were compared to the Estimated Minimum Detection Limits (EMDLs) and Estimated Minimum Levels (EMLs) listed in EPA Method 1668A. EMDLs are defined as the lowest concentration of a PCB that can be detected with laboratory interferences present, and are calculated as the mean plus two standard deviations of the concentrations measured in method blanks over an extended time period. EMLs are defined as the minimum PCB concentration that can be measured reliably with laboratory interferences present, and are calculated by applying a multiplier to the EMDL.

The IDEs are lower than the Method 1668A EMDL concentrations in nearly all cases and up to 50 times lower for some PCB congeners. Similarly, the IQE20% and IQE30% values are generally much lower than the Method 1668A EMLs. However, the IDEs are consistently higher (ranging up to 158 pg/L) than the Method 1668A EMDL of 5 pg/L for samples without laboratory interferences. The EMDLs and EMLs in Method 1668A are based on historical method blank data (prior to March, 2000)[1] , and these results may indicate that PCB laboratories have succeeded in reducing laboratory contamination over time.

Method 1668A allows laboratories to develop their own minimum levels of quantitation (MLs) based on their method blank data for a particular sample medium, but the limits must be lower than the EMLs listed in the method. MLs are defined by EPA as the lowest concentrations at which quantitative results are reported. Lower concentrations would be reported as "<ML". However, EPA also notes in the method that regulatory authorities or permits may require reporting quantitative results below the ML.

Method 1668A specifies that a laboratory may modify the method to improve performance or lower costs. However, each time the method is modified, the laboratory is required to repeat an Initial Precision and Accuracy procedure to demonstrate that the change in performance is equivalent or superior to the method as written. If the detection limit of the method is affected by the change, the laboratory is required to demonstrate that the resultant MDLs (as determined by 40CFR Part 136, Appendix B) are lower than one-third the regulatory compliance level or one-third the EMDLs of Method 1668A. The EPRI study results show that the IDE20% values in reagent water for the majority of PCBs (40 of the 44 target PCB congeners/congener groups), or 91% were below the corresponding one-third EMDL value. This comparison suggests that a qualified laboratory should be able to achieve IDEs that are below the threshold of one-third the EMDL for most but not all of the representative PCB congeners or congener groupings in reagent water.

Laboratory background contamination was evaluated from three types of data: clean (unspiked) reagent water samples from the EPRI interlaboratory study which were submitted blind to the laboratory, the laboratories' internal method blanks from the interlaboratory study, and longer-term historical method blank data obtained from seven laboratories. Unspiked reagent water (provided by EPRI) and method blanks from the same laboratory (using their own sources of clean water) show a similar pattern of PCB background contamination, indicating that the source of these detections is the laboratory environment rather than the water source used for the samples.

One approach used to evaluate the impact of laboratory background on the interlaboratory study data was to model the relationship between the true sample concentration and the recovered (measured) concentration. Confidence intervals were calculated for the zero-intercept of the linear relationship, which represents a true concentration at a "zero" spiked concentration (i.e., the reagent water without any PCB added). If the lower 95% confidence limit (95% LCL) of the intercept exceeded zero, this indicated that the average laboratory background across all laboratories was statistically significant.

By this analysis, only one of 44 target PCB congeners and seven of all PCB congeners (or coeluting congener groups) were shown to have a significant laboratory background, on average, across laboratories. All other PCB congeners did not exhibit, on average, statistically-significant PCB background across laboratories. However, 16 of 44 representative PCBs that did not meet the test for significance exhibited upper 95% confidence limits (95% UCL) greater than 10 pg/L with some significantly higher (up to 153 pg/L for PCB 11). Therefore, these data do not exclude the possibility that an average background contamination may exist.

A second approach used in this study to evaluate background contamination was to calculate EMDLs from historical method blank data supplied by the test laboratories. However, most of the seven laboratories that submitted blank data did not provide enough blanks (10 or more) or were not collected over a long enough time period to calculate a valid EMDL. In addition, the historical blanks were reported without associated detection limits or were censored at the laboratory reporting limit. Consequently, these "historical" EMDLs were calculated as the average plus two standard deviations of detected values only, producing a conservatively high estimate of background. Due to these limitations on data received from the laboratories, the study objective to evaluate long-term background PCB levels across multiple laboratories was not met.

Given the limitations of the historical blank data, it is still possible to compare these data to the results of the interlaboratory study. EMDLs exceeded the IDE and/or the IQE20% in at least one laboratory for more than half of the congeners reported. This result indicates that qualified laboratories, over the course of many analytical batches, will experience PCB detections that are not related to the sample composition and that would not be screened out by censoring reported results at a statistically based interlaboratory detection or quantitation limit. Virtually all samples analyzed by Method 1668A will have PCBs present at levels above noise-based, instrumental detection limits. This will pose a problem to facilities that have wastewater discharge limits that are set at "zero discharge" of PCBs.

One solution to this problem is to report blank-corrected concentrations in addition to uncorrected concentrations, as allowed by Method 1668A. This approach requires the testing laboratory to supply valid EMLs based on a sufficient number of method blanks, and also would require the agency using the data to agree to use and track the background-corrected values rather than the uncorrected values. However, because the method permits blank correction only when the blank concentration is significantly lower than the EML, there will still be false positive detections. Likewise, the use of a laboratory-specific ML will reduce the number of false positive detections for laboratories with low background levels, but will not have the same effect for laboratories with backgrounds close to the EML.

Even with blank-correction, a sample containing PCBs at levels equivalent to the long-term average blank concentration would be expected to have some congeners above detection due to normal measurement variability. For this reason, selection of an appropriate quantitation level for Method 1668A is critical for the use of this method in environmental compliance monitoring. The IQE20%s or IQE30%s calculated in this study may be suitable for this purpose. To determine whether laboratories can achieve background levels below the IQE on a consistent basis will require a more representative set of laboratory-specific EMDLs, calculated from the requisite number of method blanks over a longer time period. Only then will it be clear what proportion of qualified laboratories will be able to keep their background levels below statistically based quantitation levels.

Due to the large number of congeners measured by this method, there will sometimes be sporadic detections of congeners that appear with a low frequency and so are not accounted for by the long-term background averages. These detections underline the importance of analyzing method blanks along with each analytical batch. A statistical approach such as the IDE/IQE could be used to evaluate whether sporadic detections are present at a level that should be reported quantitatively. However, all detections should first be investigated by the laboratory, and should not be removed from the data set as outliers unless there is an indication that they are present due to laboratory error (e.g., obvious contamination or instrument carryover).

The results of this study are applicable to reagent water and to ash pond wastewater from coal-fired power plants with characteristics similar to those in the study. Further research will be required to extend the results of this study to other wastewater types. It will also be important to determine whether comparable method performance can be achieved across the entire community of PCB laboratories and with more complex, real-world environmental samples.

ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CASN	Chemical Abstract Number
DRBC	Delaware River Basin Commission
EDL	Estimated Detection Limit
EMDL	Estimated Maximum Detection Limit
EML	Estimated Minimum Level
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
GC/MS	Gas chromatography / mass spectrometry
HRGC/HRMS	High resolution gas chromatography / high resolution mass spectrometry
IDE	Interlaboratory Detection Estimate
IIAG	Inter-Industry Analytical Group
ILSD	Interlaboratory standard deviation
IQE	Interlaboratory Quantitation Estimate
IQR	Interquartile Range
LCL	Lower confidence limit
MDL	Method Detection Limit
ML	Minimum Level
MRI	Midwest Research Institute
NOAA	U.S. National Oceanic and Atmospheric Administration
PCB(s)	Polychlorinated biphenyl(s)
RSD	Relative standard deviation
UCL	Upper confidence limit
WHO	World Health Organization

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

The purpose of this report is to provide a better understanding of the analytical performance characteristics of EPA Method 1668A, *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS).*

1.1 Background and Objectives

In 1995, the EPA developed a sensitive analytical method (EPA Method 1668) for measuring 13 PCBs identified as toxic in water and other environmental media. This high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) method measures individual PCBs compounds (congeners) at parts-per-quadrillion levels (e.g., pg/L in water) compared to methods such as SW-846 Method 8081, a gas chromatographic electron-capture detector (GC/ECD) technique that measures Aroclor mixtures or total PCBs (e.g., summed concentration of Aroclor mixtures) to low parts-per-billion levels (e.g., µg/L).

The EPA in 1999 expanded Method 1668 to apply to all 209 congeners. Draft Method 1668A was validated in a single-laboratory study. The results of this study were published in March 2000 [1]. Based on peer review comments, the EPA revised and published the final Method 1668A in December 1999 and announced their intent to promulgate the method in 40 CFR, Part 136 [2]. In 2003-2004, EPA developed and conducted a multiple laboratory validation study involving three matrices: wastewater from Publicly Owned Treatment Works (POTW), biosolids (sewage sludge), and biota (fish tissue). The results were subsequently published in the Method 1668A Interlaboratory Validation Study Report, initially published in November 2008, updated in March 2010, and released to the public in August 2010 [3]. On September 23, 2010, the EPA proposed Method 1668C [4], which has significant differences from earlier versions of the method. EPRI's study does not include an evaluation of results against the criteria proposed in Method 1668C.

EPRI initiated the current study in 2005 to supplement the EPA's efforts. The EPRI study is intended to address data gaps identified in the EPA's 2003 study plan, including:

- The POTW wastewater that EPA included in their study is expected to be a challenging matrix, due to the presence of potentially interfering organic compounds. In the past, EPA method validation studies have been conducted using a clean (reagent) water matrix, supplemented by alternative matrices such as natural waters or wastewaters. It is important to know the method's best case performance as well as its performance with challenging matrices. The EPA multilaboratory study only addressed the latter.

- POTW wastewater is quite unlike most wastewaters produced by coal-fired power plants. Ash pond wastewaters, the highest volume discharge (other than cooling water) at coal-fired plants with wet ash handling, are high in solids but low in organic compounds. EPRI's plan included testing wastewaters characteristic of the electric power industry.
- EPA's precision and bias determination included only two concentration levels for each matrix. Procedures defined by the American Society for Testing and Materials (ASTM) for evaluation of method precision and bias (D2777-03) require at least five distinct concentrations that encompass the entire working range of the method.
- The EPA's approach to evaluating detection and quantitation levels for Method 1668A does not fully characterize the method's sensitivity. Detection limits for PCB congeners are influenced by the presence of PCBs in laboratory and outdoor air [5]. The congeners and levels present can vary significantly from one laboratory to the next. The Estimated Method Detection Limits (EMDLs) and Estimated Minimum Levels (EMLs) in Method 1668A are based on background contamination found in a single laboratory. Assessment of long term background levels was not part of the EPA multilaboratory study, while the EPRI study attempted to obtain this information from laboratory-provided, historical blank data.

The EPRI study was designed to:

- Validate method performance across multiple laboratories using a clean water matrix.
- Evaluate potential matrix effects of a range of power industry wastewaters on method performance.
- Determine method sensitivity using reagent water as a pure matrix.
- Assess the presence of PCB background contamination across qualified laboratories that perform this method and the impact on method detection and quantitation levels.
- Evaluate the application of this method in producing high-quality, defensible data for use in permitting and regulatory decisions.

1.2 Organization of This Report

The report covers three main study areas: a comprehensive interlaboratory study of EPA Method 1668A in which reagent water was used as the sample matrix, a focused single laboratory study of wastewaters from coal-fired power plants, and an evaluation of background PCB levels. This report is organized as follows:

- Section 1 discusses the background and objectives of the study.
- Section 2 describes the study design and implementation.
- Section 3 presents data validation and exploration procedures.
- Section 4 presents the statistical methodologies used to analyze the data.
- Section 5 presents the results of the study.
- Section 6 summarizes the findings and conclusions from this study.

- Section 7 lists references used in the report.

The Appendices provide detailed summaries and statistics for all reported data. The Appendices are provided as Volume II of this report.

2
STUDY DESIGN AND IMPLEMENTATION

This study was performed in accordance with the EPRI Study Plan, dated July 28, 2005. The Study Plan was reviewed by senior members of the EPA Office of Water (William Telliard and Richard Reding), and modifications to the Plan were made in response to EPA comments. This section presents an overview of the study design and activities associated with preparing the test samples.

2.1 Study Design Objectives

This section outlines the objectives that guided the selection of types, numbers, and concentrations of samples used in the study.

2.1.1 Interlaboratory Study Design Objectives

The interlaboratory study was performed using reagent water. The results therefore represent a best case for method performance. The interlaboratory study was designed to collect data to fulfill the requirements of the following ASTM Standard Practices:

- ASTM D2777-03: Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water [6]
- ASTM D6091-03: Standard Practice for 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error [7]
- ASTM D6512-03: Standard Practice for Interlaboratory Quantitation Estimate (IQE) [8]

The IDE is defined as "the lowest concentration at which there is 90% confidence that a single measurement from a laboratory selected from the population of qualified laboratories represented in an interlaboratory study will have a true detection probability of a least 95% and a true nondetection probability of at least 99%." A measured critical level as defined by Currie is computed from the standard deviation data and corrected to a true concentration using a recovery equation [9]. A detection level is then computed. The key feature of the IDE is that it is based on interlaboratory standard deviation models, and it uses tolerance limits to address the issue of estimating performance of multiple laboratories in the future.

The $IQE_{Z\%}$ is defined as "the lowest concentration for which a single measurement from a laboratory selected from the population of qualified laboratories represented in an interlaboratory study will have an estimated Z% relative standard deviation (Z% RSD, based on interlaboratory standard deviation), where Z is typically an integer multiple of 10, such as 10, 20 or 30."

The numbers and concentrations of samples were selected to meet the requirements of the ASTM Standard Practices:

- D2777-03 (Precision and Bias) requires a minimum of three Youden pairs, with concentrations spanning the range of the method. Youden pairs may differ by up to 20% in concentration. A replicate pair may be substituted for one of the Youden pairs.
- D6091-03 (IDE) requires five or more true concentrations, including a blank. Spike concentrations must be targeted to bracket the anticipated IDE (the IDE_0). At least one nonzero concentration must be below the IDE_0, and one spike must be approximately two times the IDE_0. For this study, the IDE_0 values were estimated from the EPA's reported EMDLs, which were calculated from 30 single-laboratory method blanks by the method recommended by Ferrario [5].
- D6512-03 (IQE) requires five or more true concentrations, including a blank. Spike concentrations must be targeted to bracket the anticipated IQE (the IQE_0). At least one nonzero concentration must be below the IQE_0 and one spike must be approximately two times the IQE_0. The IQE_0 at a standard deviation of 10% was estimated at twice the IDE_0, based on results of previous EPRI studies.

EPRI also requested data from participating laboratories to support calculation of the following alternative measures of method sensitivity:

- Estimated Method Detection Limit (EMDL)—participating laboratories were requested to supply at least 10 historical method blanks, in order to calculate EMDLs using the Ferrario procedure.
- Estimated Detection Limits (EDL)—sample-specific instrumental detection limits were reported by all labs, following the calculation procedure specified by the Delaware Basin River Commission (DRBC). These limits are based on the signal-to-noise ratio of the analytical instrument. Reporting to EDLs is common laboratory practice for isotope dilution mass spectrometry methods; however, EDLs are not defined or used in Method 1668A.

EPRI's study did not include the 7 replicate spiked samples needed to calculate method detection limits (MDLs) and minimum levels (ML) according to the 40 *CFR* Part 136, Appendix B procedure. The EPA's multilaboratory study plan included samples to determine these limits in the study matrices; however, the MDL portion of the EPA study was not completed and was not included in the EPA November 2008 study report. EPA subsequently gathered MDL data from three laboratories and used these data sets to develop pooled MDLs which were incorporated into Method 1668C (dated April 2010, released to the public in August 2010).

The decision to omit MDLs and MLs from the EPRI study design was due to technical concerns related to the statistical properties of the MDL. Detailed discussion of these issues is outside the scope of this report; however, the issues are discussed at length in the final report of the EPA's Federal Advisory Committee (FACA) on Detection and Quantitation [10]**.**

The EPRI Study Plan originally proposed to subject a subset of 44 of the 209 PCB congeners to detailed statistical evaluation. These "target" congeners were selected based on chemical properties, toxicity, regulatory significance, and known association with laboratory background

contamination. As some of the 44 target congeners coeluted with other PCBs, the 44 target peaks actually include 54 individual congeners. The congeners selected include:

- First and last eluting congener for each of the 10 homolog series.
- Common background PCBs found in the environment.
- PCBs listed by the World Health Organization (WHO) and U.S. National Oceanic and Atmospheric Administration (NOAA) as chemicals of toxic or environmental concern.
- PCBs that are calculated by isotope dilution and PCBs that are calculated by internal standard method.
- Congeners that coelute, as well as congeners that are resolved, on the SPB-Octyl column specified in the Method.

Subsequently, EPRI decided to evaluate all 209 congeners to the extent possible. Some congeners coelute with other PCBs and cannot be adequately quantified as single congeners; therefore, coeluting congeners were evaluated in groups. These groups were not always consistent among laboratories, due to differences in coelution patterns. The evaluation for the 44 target congeners (as a single PCB or as part of a PCB group) is presented in the body of this report; results for all congeners are presented in Volume II.

Eight participant laboratories were included in the interlaboratory study. The number of laboratories was selected to meet the requirements of ASTM D2777-03.

2.1.2 Wastewater Matrix Study Design Objectives

This component of EPRI's study was designed to detect impacts on method performance of wastewater matrices characteristic of the electric power industry. The study was conducted in a single laboratory; thus, interlaboratory detection or quantitation estimates could not be calculated. However, the data were used to compare the single-laboratory precision and bias with results obtained in the multi-laboratory study. If the method were to give a significantly worse performance than with reagent water, this would indicate the need for further studies in that specific matrix.

The Study Plan proposed to base the spike concentrations in the wastewater on the background levels detected in the wastewater. However, very few PCB congeners were detected in the samples, so the spiking levels were instead based on the average EPA EMDLs for the 44 target congeners, which ranged from 20 pg/L (PCB-9) to 455 pg/L (PCB-208).

2.2 Laboratory Qualification and Selection

At the onset of the study, 12 laboratories were identified and interviewed as possible candidates for participation. Of these, eight laboratories were selected for the round-robin reagent water study and one laboratory was selected to prepare the study samples. Each of the participating laboratories was selected based on:

- Familiarity with EPA Method 1668A and current use of the method for regulatory programs.
- Experience (5 years minimum) with HRGC/HRMS analysis for PCBs in environmental samples.
- Ability to provide comprehensive data packages for third-party validation and sample results in an electronic data deliverable (EDD) format.
- Willingness to share laboratory operational information and to comply with study protocol specifications.

The eight laboratories selected for the interlaboratory study were: Alta Analytical Laboratory, Inc. (El Dorado Hills, California), Analytical Perspectives (Wilmington, North Carolina), Axys Analytical Services Ltd. (Sidney, British Columbia, Canada) Analytical Group, Battelle (Columbus, Ohio), Columbia Analytical Services (Houston, Texas), Maxxam Analytics Inc. (Burlington, Ontario, Canada), Paradigm Analytical Laboratories (Wilmington, North Carolina), and Severn-Trent Laboratories (West Sacramento, California).

Severn-Trent Laboratories (Knoxville, Tennessee) was selected as the sample preparation laboratory because of their qualifications and previous experience in a similar role for the EPA PCB interlaboratory study. The sample preparation laboratory was responsible for characterizing and screening the study matrices, preparing standard solutions and spiking the study samples, performing quality control analyses using EPA Method 1668A, and shipping the study samples to participating laboratories.

2.3 Sample Preparation

This section describes how the reagent water and wastewater study samples were prepared and shipped. Sample preparation, spiking solution preparation, and confirmation analyses by Method 1668A were performed by Severn-Trent Laboratory under the direction of MRI.

2.3.1 Preparation of Interlaboratory Study Samples

The interlaboratory study was performed using a clean reagent water matrix. Fisher Scientific Environmental Grade Water (Catalog No. W11) was selected because it was:

- Produced as reagent quality material under controlled manufacturing conditions.
- Provided with a certificate of analysis, lot number, and expiration date spanning the duration of the study.
- Available in adequate quantity so that a single lot could be used for preparation of all the reagent water study samples.
- Distributed in individual 4-L amber glass jugs, allowing excess reagent to be archived in original form.

For quality control, a sample of the reagent water was analyzed for background PCBs using EPA Method 1668A prior to preparing the study samples. The same reagent water was also used as a

control sample for characterization tests on the wastewater composite samples, as presented in Section 2.3.2.

Sample containers (1-L amber glass jars) were purchased precleaned from a commercial source (Environmental Sampling Supply) and certified to be in compliance with EPA cleaning procedures for low-level chemical analysis.

PCB spiking solutions were prepared from certified standards obtained from AccuStandard, Inc. (New Haven, Connecticut) and from Cambridge Isotope Laboratories, Inc. (Andover, Massachusetts). For quality control, the intermediate mixed spiking solution used to prepare the individual spiking solutions was analyzed in duplicate against an independent standard solution prepared from a second source or from a different lot of the commercial standard. The accuracy of the PCB concentrations in the mixed intermediate standard solution was verified to be within method tolerances of 70% to 130% accuracy. Table 2-1 presents accuracy results of this quality control check for the 44 target congeners.

The spiking scheme used for the interlaboratory study was based on guidelines listed in ASTM D2777-03, D6091-03, and D6512-03. Table 2-2 presents the spiked PCB concentrations and associated ASTM designated spike levels for the reagent water study samples. Table 2-3 presents the spike level code (e.g., "RW-A," etc.), and number of samples distributed to each of the participating laboratories. For quality control, one sample each from the lowest and highest spiking levels was randomly selected and analyzed by the preparation laboratory. The measured concentrations were calculated to be within method tolerances prior to shipping the sample sets to participating laboratories.

The PCB-spiked concentrations ranged from about 25 to 15,000 pg/L. The reported dynamic range of the method is about 4 to 40,000 pg/L. Concentrations higher than 4,000 pg/L were not used for most congeners, to avoid saturation of the detector from coeluting PCBs. The minimum spike level of 25 pg/L was based on the statistical design and potential effect of background PCB. Each sample set was comprised of 11 samples at nine concentration levels, plus one reagent water blank sample. Within each sample set, there were three Youden pairs at low, mid, and high levels. Three of the eight participating laboratories received two additional samples as blind duplicates.

An initial interlaboratory detection estimate (IDE) of about 200 pg/L was based on the average EPA single-laboratory estimated minimum detection limit (EMDL) listed in Method 1668A for a representative subset of 44 PCBs. The EMDL is defined in the method as the lowest concentration at which a PCB can be detected in the presence of common laboratory interferences. The initial estimate of the interlaboratory quantitation estimate (IQE_0) was set at twice the IDE_0 based on the ASTM Standard Practice guidance. Spike levels of approximately 25 pg/L and 50 pg/L were added to assure that a majority of PCB congeners would meet the requirements of the statistical analysis (minimum of five concentration levels) and because most of the commercial laboratories report achievable estimated detection limits at or below 50 pg/L.

Table 2-1
Precision and Accuracy Results for Intermediate Spiking Standard Solution of Target PCBs

PCB No.	Measured concentration (ng/mL)			Nominal or added concentration (ng/mL)	Relative percent bias (%) [b]	Percent recovery (%)[c]
	First analysis	Second analysis	Average			
1	34.2	34.7	34.5	32.0	7.8	108
3	34.0	34.8	34.4	32.0	7.6	108
4	49.7	51.8	50.8	56.9	–10.9	89
8	53.4	53.2	53.3	56.9	–6.4	94
9	28.6	30.1	29.4	32.0	–8.2	92
15	20.2	20.9	20.6	22.0	–6.5	93
18 + 30 [a]	70.8	71.4	71.1	85.9	–17.2	83
19	29.6	29.9	29.8	32.0	–6.9	93
20 + 28	53.5	52.5	53.0	54.0	–1.9	98
37	25.2	25.8	25.5	25.0	2.1	102
52	48.6	50.8	49.7	56.9	–12.7	87
54	23.5	24.6	24.1	28.0	–14.0	86
66	29.4	29.4	29.4	32.0	–8.0	92
77	20.4	21.0	20.7	23.0	–9.9	90
81	23.9	24.7	24.3	28.0	–13.1	87
90 + 101 + 113	63.4	64.9	64.2	74.0	–13.3	87
104	19.5	20.2	19.9	23.0	–13.6	86
105	21.7	21.5	21.6	22.0	–1.7	98
111	23.1	23.5	23.3	26.0	–10.3	90
114	20.7	21.3	21.0	23.0	–8.6	91
118	45.8	46.4	46.1	47.0	–1.8	98
123	18.6	21.7	20.2	23.0	–12.3	88
126	23.4	24.5	24.0	24.0	–0.1	100
128 + 166	43.9	45.1	44.5	49.0	–9.2	91
129 + 138 + 160 + 163	94.5	96.5	95.5	109.0	–12.4	88
153 + 168	116.0	120.0	118.0	101.9	15.8	116
155	23.2	23.8	23.5	26.0	–9.5	90
156 + 157	40.2	41.8	41.0	45.0	–8.9	91
167	19.4	20.2	19.8	23.0	–13.8	86

Table 2-1 (continued)
Precision and Accuracy Results for Intermediate Spiking Standard Solution of Representative PCBs

PCB No.	Measured concentration (ng/mL)			Nominal or added concentration (ng/mL)	Relative percent bias (%) [b]	Percent recovery (%)[c]
	First analysis	Second analysis	Average			
169	21.1	21.8	21.5	24.0	–10.5	89
170	23.1	23.4	23.3	25.0	–6.9	93
178	22.7	22.7	22.7	25.0	–9.1	91
180 + 193	54.6	54.0	54.3	57.0	–4.7	95
187	30.2	29.5	29.9	32.0	–6.6	93
188	23.4	23.3	23.4	26.0	–10.1	90
189	20.5	20.8	20.7	23.0	–10.1	90
194	29.9	30.2	30.1	32.0	–6.0	94
195	30.3	30.8	30.6	32.0	–4.4	95
202	23.9	24.5	24.2	28.0	–13.5	86
205	23.0	23.8	23.4	25.0	–6.3	94
206	28.8	30.7	29.8	32.0	–6.9	93
208	18.9	19.3	19.1	22.0	–13.1	87
209	19.0	19.3	19.2	22.0	–12.9	87

[a] Multiple PCB numbers indicate that values represent coeluting or combined PCB concentrations.
[b] Relative percent bias = $(C_{avg.\ measured} - C_{nominal}) / C_{nominal} \times 100$.

[c] Percent accuracy = $C_{avg.\ measured} / C_{nominal} \times 100$.

Table 2-2
PCB Concentrations and ASTM Spike Level Designations for Interlaboratory Study Samples

PCB concentration (pg/L)													
Source Standards		Group code:	RW-A	RW-B	RW-C	RW-D	RW-E		RW-F	RW-G	RW-H	RW-I	RW-J
Accu-Standard	No. of PCBs	ASTM spike level:	blank	IQE 10‰/16 IDE_o/8	IQE 10‰/8 IDE_o/4	IQE 10‰/2 IDE_o	Low-range Youden pair (duplicate pair) IQE 10‰ IDE_o x 2		IQE 10‰ x 2 IDE_o x 4	Mid-range Youden pair (< 20% difference) IQE 10‰ x 5 IDE_o x 10		Hi-range Youden pair (< 20% difference) IQE10‰ x10 IDE_o x 20	
PCB Mix #1	39		0	32	64	240	480	480	959	1,918	2,238	4,156	4,795
PCB Mix #2	36		0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB Mix #3	27		0	22	44	165	330	330	659	1,319	1,538	2,857	3,297
PCB Mix #4	22		0	28	56	210	420	420	839	1,678	1,958	3,636	4,196
PCB Mix #5	20		0	23	46	172	345	345	689	1,379	1,608	2,987	3,447
PCB Mix #6	18		0	24	48	180	360	360	719	1,439	1,678	3,117	3,596
PCB Mix #7	14		0	27	54	202	405	405	809	1,618	1,888	3,506	4,046
PCB Mix #8	12		0	29	58	217	435	435	869	1,738	2,028	3,766	4,346
PCB Mix #9	21		0	26	52	195	390	390	779	1,558	1,818	3,377	3,896
Total PCBs	209												
Cambridge Isotope Standard		Also added from:											
PCB 4	1	PCB Mix #1	0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB 8	1	PCB Mix #1	0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB 18	1	PCB Mix #1	0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB 52	1	PCB Mix #1	0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB 118	1	PCB Mix #3	0	25	50	187	375	375	749	1,499	1,748	3,247	3,746
PCB 153	1	PCB Mix #1	0	70	140	524	1,049	1,049	2,098	4,196	4,895	9,091	10,490
Combined PCB 4, 8, 18 & 52 =			0	57	114	427	854	854	1,708	3,417	3,986	7,403	8,541
Combined PCB 118 =			0	47	94	352	704	704	1,409	2,817	,287	6,104	7,043
Combined PCB 153 =			0	102	204	764	1,528	1,528	3,057	6,114	7,133	13,247	15,285

Table 2-3
Number and Concentration Levels of Samples Distributed to Laboratories for the Interlaboratory Study

Group code (spike level)	RW-A	RW-B	RW-C	RW-D	RW-E Low-range Youden pair (duplicate pair)	RW-F	RW-G / RW-H Mid-range Youden pair (< 20% difference)		RW-I / RW-J High-range Youden pair (< 20% difference)		Total distributed, by laboratory
							RW-G	RW-H	RW-I	RW-J	
Lab 1	1	1	1	1	2	1	1	1	1	1	11
Lab 2	1	1	1	1	2	1	2	1	2	1	13
Lab 3	1	1	1	1	2	1	1	1	1	1	11
Lab 4	1	1	1	1	2	1	1	1	1	1	11
Lab 5	1	1	1	1	2	1	1	1	1	1	11
Lab 6	1	1	1	1	2	1	2	1	2	1	13
Lab 7	1	1	1	1	2	1	2	1	2	1	13
Lab 8	1	1	1	1	2	1	1	1	1	1	11
Total distributed, by concentration:	8	8	8	8	16	8	11	8	11	8	96

The reagent water study samples were prepared by transferring 1 L of reagent water (using a Class A volumetric flask) into amber glass jars. Each sample was individually spiked by adding 1-mL of a standard solution prepared in acetone at the appropriate concentration. Zero-concentration (i.e., no PCB added) study samples were prepared by adding 1 mL of reagent acetone to 1 L of water. Each sample was uniquely identified by spike level and number, stored at refrigerated temperatures (< 6°C), and protected from light after preparation.

2.3.2 Preparation of Wastewater Study Samples

A separate single-laboratory study was conducted to evaluate the performance of Method 1668A with wastewater from coal-fired power plants. The Study Plan proposed to evaluate three samples of different wastewaters; however, due to the intermittent nature of many low-volume wastewater streams at power plants, and practical considerations of obtaining samples, two samples of the same wastewater matrix, ash pond wastewater, were used in the study.

Representative ash pond wastewaters were provided by several power generation facilities and homogenized to form two different composite matrices (designated Wastewater A and Wastewater B).

The wastewater samples were collected in individual 1-gallon amber glass jugs and shipped to the sample preparation laboratory. The individual grab samples received from the field were manually mixed for 1 minute and then transferred and combined into a large polypropylene carboy for dispersing the homogenized sample into individual 1-liter glass volumetric flasks before transferring the composited sample into individual 1-liter amber glass containers.

The study samples were created by placing the carboy on a large stirring plate with a 5-inch stir bar inside. After 1 hour stirring, portions of the blended mixture were drawn via the carboy spigot into a 1-liter (1-L) Class A volumetric flask for measurement, while the content of the carboy continued to stir on the stir plate. The content of the 1-L volumetric flask was then transferred to a certified precleaned 1-L amber glass container and immediately sealed with a Teflon® lined cap. The 1-L amber containers were sequentially numbered, including the wastewater identifier (i.e., A or B) and order in which each sample was taken, then the samples were stored under refrigerated conditions (< 6°C). Figure 2-1 shows photographs of the equipment and procedures used during preparation of the wastewater composite samples.

Three bottles from each wastewater composite (A and B), along with the reagent water, were randomly selected for PCB analysis (1668A), semivolatile organic chemical screen, and other general chemistry tests. Table 2-4 presents the characterization data for both composite wastewater matrices and for the reagent water used for the interlaboratory study.

Wastewater samples collected from field

Composite sample in carboy

Dispensing homogenized sample into 1-L flask

Transfer of sample to 1-L container for spiking

Figure 2-1
Preparation of Wastewater Study Samples

Table 2-4
Characterization Data for Wastewaters and Reagent Water (Control Sample)

Parameter[a]	Analytical method	Reagent water	Wastewater A composite	Wastewater B composite
pH Aqueous	SW-846[b] 9040B	pH = 5.5	pH = 6.8	pH = 7.6
Filterable residue (total dissolved solids, TDS)	MCAWW[c] 160.1	TDS < 10.0 mg/L	TDS = 166 mg/L	TDS = 213 mg/L
Non-filterable residue (total suspended solids, TSS)	MCAWW 160.2	TSS < 4 mg/L	TSS < 4 mg/L	TSS < 4 mg/L
Total organic carbon (TOC)	MCAWW 415.1	TOC = 0.26 mg/L (est.)	TOC = 2.9 mg/L	TOC = 2.4 mg/L
Semivolatile organic compounds (SVOCs) by GC/MS	SW846 8270C	All SVOCs were less than the method reporting limits of 10 to 50 µg/L		
Residual chlorine[d]	Colorimetric Test Kit (SLA-73)	Negative	Negative	Negative
Native PCBs	EPA Method 1668A	No PCBs detected at or above the minimum reporting level of the laboratory (40 to 60 pg/L)		

[a] The general chemistry analyses were performed by Severn-Trent Laboratories (STL) in North Canton, OH. The Method 1668A analyses were performed by STL-Knoxville Laboratories.

[b] SW846 “Test Method for Evaluating Solid Waste, Physical/Chemical Methods,” Third Edition, November 1986 and updates.

[c] MCAWW “Method for Chemical Analysis of Water and Wastes,” EPA-600/4-79-020, March 1983 and subsequent revisions.

[d] All samples were checked for residual chlorine by the analysis laboratory.

The spiking scheme used for the wastewater samples is presented in Table 2-5. Five samples were prepared from each composite wastewater. One of the five was a blank (no PCBs added). The remaining four samples had approximately half of the 209 PCBs spiked in duplicate (two samples at a low-range concentration and two at a high-range concentration) and the other half of the PCBs increasing in concentration throughout the series. This dual spiking approach allowed the study measure precision for a subset of PCBs while also using the same four samples to evaluate the impact of increasing congener concentration.

The wastewater study samples were individually prepared by spiking 1 L of wastewater sample with mixed PCB standard solutions in a total spiking volume of 1 mL acetone. The standard solutions used for PCB spiking mixtures were prepared from the same certified standard solutions used to prepare the reagent water samples. For quality control, the intermediate spiking standard solutions were analyzed against a second source standard, and were determined to be within method tolerances for calibration (i.e. 70% to 130% of the theoretical concentration). The wastewater samples were fortified at PCB concentrations equivalent to about 100 to 2000 pg/L of water. The minimum spiking level for the PCBs was set at about one-half the average Method 1668A EMDL for a representative list of 44 target PCBs.

Table 2-5
Spiking Scheme for Wastewater Study

INTERMEDIATE MIXED STANDARD A		**Sample Spike Concentrations (pg/L)**				
		Gradient concentrations for PCB congeners				
	Spike level =	**blank**	**1X**	**4X**	**8X**	**16X**
Certified stock standard	No. of PCBs					
PCB Mix #1 (C-CS-01)	39	0	100	400	800	1,600
PCB Mix #3 (C-CS-03)	27	0	150	600	1,200	2,400
PCB Mix #5 (C-CS-05)	20	0	125	500	1,000	2,000
PCB Mix #7 (C-CS-07)	14	0	140	560	1,120	2,240
PCB Mix #9 (C-CS-09)	21	0	115	460	920	1,840
INTERMEDIATE MIXED STANDARD B		**Duplicate concentrations for PCB congeners**				
			Duplicate low range		Duplicate high-range	
	Spike level =	**blank**	**4X**	**4X**	**16X**	**16X**
Certified stock standard	No. of PCBs					
PCB Mix #2 (C-CS-02)	36	0	500	500	2,000	2,000
PCB Mix #4 (C-CS-04)	22	0	520	520	2,080	2,080
PCB Mix #6 (C-CS-06)	18	0	580	580	2,320	2,320
PCB Mix #8 (C-CS-08)	12	0	440	440	1,760	1,760
Total PCB congeners	209					

2.3.3 Labeling and Shipment of Study Samples

During preparation, all study samples were assigned and labeled with a unique identification number that included a descriptor of the type of sample (i.e., reagent water, wastewater A or B), spiked concentration level, and a number corresponding to the preparation order. Before shipping, the samples were also labeled using a random number generator program.

Individual sample sets were created by selecting one or more of the spiked samples from each spike-level group as appropriate. Sample containers within groups (i.e., spike level) were randomized so that a laboratory did not receive sequentially prepared samples. The sample sets were then prepared for shipment to the participating laboratories by removing the original descriptive labels and completing a chain-of-custody/traceability form. The sample sets were shipped by overnight delivery to the laboratories with analysis and reporting instructions. Sample preservation and storage complied with method specifications (i.e., $< 6^{o}$C, protected from light) during shipment, and was documented by the receiving laboratory on the chain-of-custody forms.

2.3.4 Sample Analysis

For both the reagent water and wastewater sample series, each laboratory received a set of samples with an undisclosed and random order of PCB concentrations. The laboratories were contracted to analyze the samples per the following specifications:

- Document sample receipt and store the samples at < 6°C, protected from light, until preparation.
- Prepare and analyze the samples in accordance with EPA Method 1668A, Revision A [with corrections and changes through 8/20/03]. This unpublished draft of the method was obtained from EPA, and was the version used in EPA's interlaboratory study.
- Analyze the sample extracts using a SPB-Octyl chromatographic column, indicated in the EPA method as the primary column.
- Verify that EPA method calibration and instrument tune criteria were met prior to analyzing the samples.
- Report all results on a noncensored basis; that is, report all measurable responses above an instrument signal-to-noise ratio of 2.5.
- Report all quality-control results associated with the sample batch.

For this study, the laboratories were not required to resolve co-eluting PCBs or to reanalyze the sample extracts on a different column. Resolution of all 209 PCB congeners is not possible on any commercially available chromatography column.

3
DATA VALIDATION AND DATA EXPLORATION

This section describes the data review process that was performed prior to statistical analysis of the results.

3.1 Data Compilation

Each laboratory submitted an electronic data deliverable (EDD) of their results, a written report, and a supporting data package. The EDD was archived in original form and a copy was formatted for input into a statistical database.

Each laboratory used its own unique codes to qualify specific data points. These qualifiers were included in the statistical database and the frequency at which these occurred was examined by concentration level and by individual laboratory during the data exploration process. For the final data set, these qualifiers were decoded so that a consistent convention for retaining or omitting data was applied throughout the data set, as shown in Table 3-1.

3.2 Data Exploration

After the data were compiled and sorted for review, data exploration (comparative reviews) and quality checks were performed to identify any suspected outliers or anomalies. This process included:

- Verifying that the EDD value was consistent with the written report and supporting data package (e.g., no transcription errors).
- Checking for correct assignment and consistency of the reported PCB value relative to PCB name (or abbreviation), Ballschmiter ("BZ number"), IUPAC number, and the corresponding Chemistry Abstracts Service (CAS) Registry Number. The CAS number was used as a primary field in the database structure.
- Confirming that co-eluting PCBs were consistent with the written report, supporting data package, and CAS number identifications.
- Checking for potential outliers by sorting and comparing data between laboratories, congener groups, and concentration levels.
- Examining associated quality control results (e.g., internal standard recoveries, control spikes, and laboratory method blanks.)

Table 3-1
Data Qualifiers and Use in Statistical Analysis

Qualification description	Meaning or usual cause	Typical flag(s) used by laboratories	Data used in statistical analysis?
Nonqualified PCB	All qualitative and quantitative method criteria met.	None	Yes[a]
Blank or zero data points	No PCB is detected at or above the noise-threshold of the instrument.[a]	ND (not detected), U (undetected), blank field, zero (0) value. A sample-specific, noise-based EDL is reported for undetected PCBs.	No[b]
Reportable PCB that was also detected in the laboratory method blank	Laboratory background or contamination	B	Yes
Reportable PCB that was detected at a concentration less than the lowest calibration standard.	Low determined concentration of PCB in sample. This value would normally be excluded for censored data.	J	Yes
Qualified data point that does not meet one or more qualitative method criteria for a PCB	Typically caused by a chromatographic interference.	K or EMPC (estimated maximum possible concentration)	No
PCBs that coelute with one or more other PCB congeners, otherwise qualitative criteria are met	Unresolved peaks for the chromatographic system.	C	Yes[c]

Table 3-1 (continued)
Data Qualifiers and Use in Statistical Analysis

Qualification description	Meaning or usual cause	Typical flag(s) used by laboratories	Data used in statistical analysis?
Multiple flags (one or more of those described above).	Combination of qualifiers indicated above, e.g., a specific data point may be below the calibration curve and the PCB may also be detected in the laboratory method blank.	Combination of those described above.	Yes (as long as all method qualitative criteria were met)
Data that were associated with an internal standard outside method criteria for recovery	Low recovery may indicate poor extraction recovery. High values may indicate that there is an interference or that the internal standard solution may be compromised.	Typically, the internal standard recoveries are flagged as being outside of method criteria.	No[d]

[a] EPA Method 1668 defines a PCB based on the mass ions and ratios (*m/z)*, retention times, and signal-to-noise response greater than or equal to a 2.5 ratio.

[b] ASTM D2777-03, Section 9.4.3, states that reporting of “less-than” or “greater-than” negates the objectivity of subsequent statistical calculations and should be avoided.

[c] Co-eluting PCBs are treated as a single data set for statistical analysis as long as there is consistency in reporting between laboratories. The reported value represents the combined concentrations of all possible co-eluting PCBs.

[d] These data points were not used as per Method 1668A.

3.3 Independent Data Validation

Data packages submitted by each participating laboratory were independently validated by Environmental Chemistry Consultants, Inc., of Gorham, ME. Data validation reports provided a summary of data qualification actions based on quality control specifications in Method 1668A, Revision A and consistent with EPA procedures [11]. Validation included review of the quality control results and administrative forms, all qualifications affecting data usability; and an overall assessment of each individual data set.

3.4 Resolution of Outlying Data Points

Section 10.3 of ASTM Standard Practice D2777-03, *Evaluation of Outliers*, suggests the use of data exploration techniques for identification and subsequent testing of outliers rather than the use of statistical methods for removing entire laboratories, results, or individual data points. The following procedure was used to determine data usability or removal:

- Suspect outliers or anomalies in the data were identified through summary statistics tables.
- Supporting data packages (including original data) and written reports were examined, and/or the laboratory was contacted to investigate any unusual results.
- Individual data points were retained or removed from the database as a result of the investigation.

This approach is considered to be consistent with EPA's approach and with Section 10.3 of D2777-03. In no cases were laboratories or data points removed from the statistical analysis without reasonable cause. Based on these reviews and actions, the data used in the statistical analysis were fully compliant with Method 1668A validation requirements. The data set listed in Appendix B identifies those points that did not meet method criteria and therefore were excluded from the statistical analysis.

4
STATISTICAL METHODOLOGY

This section provides details of the statistical methodology used in this report, for evaluating method performance in reagent water and wastewater, and for assessing PCB background levels.

4.1 Methodology for Statistical Analysis of Reagent Water Results

This section describes the summary statistics and statistical methodologies used in the interlaboratory study. The code for all computations of descriptive statistics, detection estimates, and quantitation estimates was written using SAS®, a commercially available software program [12, 13, 14]. All figures and tables shown in Section 5 and in most of the appendices were generated using SAS®.

The interlaboratory study met the requirements of ASTM Standard Practice D 2777-03:

- The recommended minimum number of eight qualified laboratories was used.
- The required minimum number of three Youden pairs was used (two pairs with less than 20% difference in concentration and one pair with equal concentration).
- Additional concentration levels at or near the detection limit were added to satisfy IDE calculation requirements.

Samples beyond those required in D2777-03 included:

- Duplicate samples for the lower concentration level of the two non-equal Youden pair concentrations were provided to three of the eight laboratories for further evaluation of precision.
- Unspiked, water samples were provided to each laboratory to evaluate laboratory background PCB concentrations.

The study layout describing the sample distribution across labs was provided previously in Section 2 (Table 2-3).

4.1.1 Descriptive Summaries

4.1.1.1 Data Validity

As described in Section 3, laboratory results may be qualified for various reasons. The laboratories were requested not to censor their results to a reporting limit, but rather to report a

numerical value for all congeners for which an instrument signal was received that met the following criteria:

- Detection based on instrument signal-to-noise ratio > 2.5 (i.e., above the EDL).
- Met qualitative criteria established in the method for identification as a PCB.

Data points reported as zero or blank for one of the above reasons, those identified by the laboratory as EMPC (estimated maximum possible concentration), those associated with an internal standard outside of the Method 1668A criteria, and those determined to be outliers as described in Section 3.4 were excluded from statistical analysis. The number and percent of qualified data points were tabulated by spike level across all PCB congeners.

Unspiked samples (i.e., study samples in which no PCBs were added) were also excluded from the statistical analyses. Section 7.2.6.1 of ASTM D2777-03 states that study samples at or near the detection limit of a test method are likely to produce nonquantitative results, and that conducting the specified statistical analysis on whatever quantitative data are available for those samples can produce misleading precision-and-bias estimates. Evaluation of outliers was performed in accordance with Section 10.3 of D2777-03. Results appearing to be "out of line" based on percent recovery determinations were noted. The program manager attempted to resolve data issues by contacting the laboratories as suggested in the Standard, and/or by examining the raw data. Formal statistical outlier tests were not conducted for exclusion of data points, as the laboratories were all considered to be qualified and the data sets were independently validated.

Contamination in blanks can be distributed normally, but it is common to observe occasional spikes from abnormally high contamination events. Statistical outlier tests can help prevent these events from skewing the variance to the high side. Identifying and investigating these outliers can help the laboratory and the user identify the real background population, and can help distinguish contamination events from random variation. However, for this study, which did not include measurements collected over a long period of time, it was assumed that all PCBs detected in the blanks were representative of the lab's normal background concentrations.

The participating laboratories did not always report the same PCB congeners as coelutions. Coeluting PCBs were treated as a single chemical for statistical analysis as long as there was consistency in reporting between laboratories. If six or more of the eight possible laboratories reported the same congener group, this group met the ASTM D2777-03 minimum standard and was processed as normal. If fewer than six but at least three laboratories reported consistently, those data were processed for informational purposes, and are identified in the results tables as not meeting the ASTM Standard Practice criteria. If only one or two laboratories reported consistently, those data were excluded from the statistical summaries as having too few data points.

4.1.1.2 ASTM Standard Practice D2777-03 Statistics

ASTM D2777-03 provided the basis for the computation of summary statistics. However, as written, this standard is only applicable to a balanced interlaboratory study design, that is, one in

which the number of samples at a given concentration level is the same for all laboratories. This was not the case in the present study, where duplicate samples were submitted to some laboratories and not to others. The unbalanced replication across laboratories can produce biased estimates. A more general version of the D2777-03 statistical method was used to account for unbalanced replication in the sample design and to appropriately apportion measurement variability.

The descriptive statistics in D2777-03 were modified using generalizations of the calculations to produce unbiased estimates of mean recovery, overall variability, and single-operator variability. Modifications were made primarily to Equations (1), (3), and (4) of the Standard Practice to address the unbalanced design with respect to spiking levels across laboratories. The equations were modified as described below to eliminate bias introduced by laboratories that analyzed additional duplicate samples. For each congener (or coeluted congeners) and spike level, the number of nonqualified values, number of laboratories reporting, theoretical concentration (spike level), mean recovery across laboratories, percent recovery, overall standard deviation, overall relative standard deviation, and single-operator standard deviation as computed from the Youden pairs are reported in Section 5-1 and in Appendix C of this report. The study design included three Youden pairs: a low-, mid-, and high-range pair corresponding to ~ 2, 10, and 20 times the IDE_0.

Statistical calculations from D2777-03 were performed for each matrix, analyte, and concentration, including:

- *Single-Operator Standard Deviation Estimates*. For the mid-range and high-range Youden pairs, Equation (1) required modification to account for the duplicate samples at three of the eight labs for the lower concentration in the non-equal Youden pairs. Equation (2) was used as presented for the low-range Youden pair with blind duplicates.
- *Calculation of Mean and Overall Standard Deviation*. The mean, Equation (3), was used as provided for lab groups RW-B, RW-C, RW-D, RW-F, RW-H, RW-J but was adjusted for spiking group RW-E, RW-G, and RW-I to account for replication of samples. Averaging results across all data points for a specific concentration level, as indicated in the standard, will lead to estimates that are biased toward results from laboratories with replication. The percent recovery used in this equation is the average percent recovery.
- The overall standard deviation as provided in Equation (4) was used for spiking groups RW-B, RW-C, RW-D, RW-F, RW-H, and RW-J. Equation (5) was used for spiking group RW-E. An adjusted standard deviation estimate, similar to the adjustment in Equation (5), was used for groups RW-G and RW-I. Modified equations were used for these groups to account for the additional blind duplicates provided to a subset of the participating laboratories. The standard deviation estimates so calculated are the square root of an unbiased estimator of the variance, but are not themselves unbiased, similar to the estimators provided in the Standard Practice.

4.1.1.3 Graphical Representation

Box plots were generated using SAS® to graphically display percent recovery results for each individual congener and for coeluting congener groups. These plots show the distribution of percent recoveries across all laboratories and thus provide a sense of the variability between laboratories. Information included in the box plots includes the mean and median, 25th and 75th percentile values, as well as extreme values of the distribution.

4.1.2 Statistical Inference

The main objective of this interlaboratory study was to estimate the IDE and the IQE for PCB congeners according to the following ASTM Standard Practices:

- ASTM D6091-03 "Standard Practice for 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error"
- ASTM D6512-03 "Standard Practice for Interlaboratory Quantitation Estimate"

The methodology to obtain these estimates is described below. Equations are provided within the referenced documents.

4.1.2.1 Regression and ILSD Model

Computation of the IDE and IQE require knowledge of the interlaboratory variability of recoveries. ASTM D6091-03 and D6512-03 rely on the computation of a mean recovery model and an interlaboratory standard deviation (ILSD) model. The mean recovery model is a linear model in which recovery is assumed to be linearly related to concentration. The ILSD model accounts for increasing variability in measurements as concentration increases. The Standard Practice proposes producing an ILSD model by fitting a curve to the sample standard deviations at each of the study concentrations.

In this study, a model was used that accounts for the correlation in measurement errors within a laboratory and assumes that the error variability within a laboratory across concentrations is a function of the concentration. A maximum likelihood estimation technique was used to estimate the mean recovery model parameters as well as the between laboratory variance and the within laboratory variance model parameters. Parameter estimates were calculated using PROC NLMIXED in SAS®9.1. The ILSD for a concentration is the square root of the sum of the between-laboratory variability and the within-laboratory variability at the concentration level. An R^2 "goodness-of-fit" value is reported based on the likelihood ratio test [15].

As a visual indicator of the fit of the mean recovery model and the variance model, two types of plots were developed: (a) scatter plots of the measured versus spiked concentrations, plotted together with the fitted regression lines for each laboratory individually and overall, and (b) scatter plots of the absolute residuals versus spiked concentrations, plotted along with the overall fitted standard deviation model.

4.1.2.2 Estimation of Background Levels

The statistical analysis assumes that the PCB congener levels in the reagent water samples are zero. The intercept of the regression model can be considered a point estimate of the background level, i.e., an estimate at the zero spike level. Using the mean and variance model, 95% confidence intervals were calculated for the estimated background PCB levels of each congener or coeluting congener group.

4.1.2.3 IDE and IQE Estimation

The IDE is based on the description provided in ASTM D6091-03. Section 6.3.3 of that Standard Practice describes the identification and fitting of the ILSD model. Three ILSD models were proposed based on fitting a curve (constant, linear, and exponential) to the sample standard deviations computed at each concentration level. Standard deviations were adjusted for bias, by multiplying the sample standard deviations by a bias-correction factor.

D6091-03 is written to accommodate a range of interlaboratory studies. When applied to this study, several limitations of the modeling approach were noted, specifically:

- Correlation between observations from the same laboratory is ignored, so that standard deviations are not independent across concentrations.
- The suggested models do not ensure a positive value for the standard deviation across all concentrations.
- An ILSD model is selected based on best fit to a data set, and can therefore vary among chemically similar analytes, e.g., some PCB congeners may have standard deviation increasing proportional to concentration, and others may have standard deviation increasing exponentially with concentration. This difference between best fit models could be due to scatter in the data, rather than representing a real difference in response by the method to the different analytes.
- The procedure does not iteratively fit the regression and standard deviation models to provide a best fit for both.

Section 6.3.3.2 (*h)* allows for the selection of more complex models than those listed in D 6091-03, including that of Rocke and Lorenzato (1995) and quadratic or cubic models. The use of maximum likelihood estimation (rather than ordinary least squares, weighted least squares, or nonlinear least squares estimation) to fit a model is also allowed.

To account for all of the aspects listed in the above bullets, this study used a model that allows for increasing variability between laboratories and increasing variability within laboratories. The model used was similar to the Rocke and Lorenzato (Hybrid) model but separating the two variance components.

$$Y = a + b \times T + \lambda + \delta \times T + \varepsilon$$
$$\lambda \sim N(0, c^2)$$
$$\delta \sim N(0, d^2)$$
$$\varepsilon \sim N(0, (g + h \times T)^2)$$

The parameters *a* and *b* are fixed parameters in the mean recovery model; λ is a random intercept coefficient for labs; δ is a random slope for labs; and ε is a random within-lab error. As opposed to directly fitting a model to the standard deviations, maximum likelihood is used to estimate simultaneously the two parameters of the mean recovery model (*a* and *b*) and the four parameters of the variance model (*c*, *d*, *g*, and *h*). This model ensures that the variance estimate is always a positive number and thus the standard deviation estimate is also a positive number.

The IDE was computed according to Section 6.4 of D6091-03. The tolerance limit factors were computed based on the study design rather than using the values provided in Table 3 of the Standard Practice, as the latter were created from estimating a tolerance bound for a random sample from a population rather than applying it to a linear model. Graybill (1976) described the application of tolerance bounds to a linear model [16].

The IDE was computed as described in Section 1.2 of D6091-03 and is based on the mean and variance model described in Section 4.1.2.1. An approximation of the 90% upper confidence bounds for the 99th and 95th percentiles was used based on the unequal variance across concentrations and random laboratory effects [16, 17].

The IQE is based on the description provided in ASTM Standard Practice D6512-03, however, using the estimated standard deviation model discussed above. The IQE was estimated at the 10%, 20%, and 30% relative standard deviation levels using the mean and variance model described in Section 4.1.2.1 of the Standard Practice.

4.2 Methodology for Statistical Analysis of Wastewater Results

This section describes the approach used to summarize basic information from the single laboratory study results and the statistical methodologies used in the estimation of relevant statistics for wastewater.

4.2.1 Descriptive Summaries

4.2.1.1 Data Validity

As described in Section 3, laboratory results may be qualified for various reasons. Results that are below detection limit, i.e., reported as a blank or zero, or do not meet one or more qualitative criteria for a congener or coeluted congeners or were associated with an internal standard outside of the Method 1668A criteria, or were determined to be outliers as described in Section 3.4, were not used in the analysis of the wastewater results. However, these occurrences were tabulated by

spike level and the percent of qualified results for the spike levels across all PCBs is presented in Section 5.2.

4.2.1.2 Precision and Accuracy

Approximately half of the PCBs were spiked at duplicate concentrations and the other PCBs were spiked at increasing concentrations within the same sample set. The duplicated PCB values were used to calculate precision as relative percent difference (RPD) separately for each composite wastewater.

Percent recovery for spiked wastewater samples was computed by using the reported concentration divided by the spike level, separately for each composite wastewater, PCB congener or group, and spike level. This assumes that the PCB congener levels in the wastewater samples are zero. Generally, the unspiked wastewater results are comparable to method blanks but this is not always the case. The impact on percent recovery due to background in the wastewater is expected to be minimal

4.2.2 Statistical Inference

The spiking scheme used for the wastewater samples facilitates estimation of PCB background levels in each composite wastewater via regression analysis. The statistical methodology and assumptions are discussed below.

4.2.2.1 Regression Model

A regression model was estimated based on the spiked wastewater results. The assumption of constant variance across spike levels is made due to the small number of observations available for a congener. The estimated regression model, error variance, and R^2 goodness-of-fit value were estimated for each congener.

4.2.2.2 Estimation of Background Levels

For each congener, a 95% confidence interval for the baseline level was estimated based on the regression model in Section 4.2.2.1.

4.2.2.3 Matrix Effect

One objective of this study was to assess method performance in the presence of a wastewater matrix. The matrix effect on PCB recovery was investigated by means of analysis of covariance based on reagent water and wastewaters A and B sample results. Separate slopes were estimated for reagent water and combined waste waters, and then compared. Statistical significance at the 5% level was reported for each PCB congener or congener group.

4.3 Methodology for Evaluation of PCB Background Levels

Laboratory background data for PCB were obtained from several sources, including: individual laboratory sample results for method blanks and unspiked reagent water from the interlaboratory study, statistical analysis of interlaboratory study results across all laboratories, and historical method blank results provided by participating laboratories. The methodology used to compare these data is discussed below.

4.3.1 Interlaboratory Study Sample Results

As part of the interlaboratory study, eight separate laboratories reported a minimum of one method blank and one nonspiked reagent water (as a blind sample). These data were entered into the statistical database, qualified data points were identified, and the results tabulated for review. PCBs that were detected for method blanks (both internal and blind study samples) and included in this report represent true and valid concentrations of PCBs that are greater than two and one-half times the instrumental signal-to-noise (i.e., the estimated detection limit of the laboratory) and meet all qualitative criteria specified by the EPA method.

4.3.2 Estimates from Interlaboratory Study Regression Model

The statistical methodology for the interlaboratory study results provided estimates of laboratory background. These estimates include the upper 95% confidence limit for the intercept and the interlaboratory detection estimate (IDE), which defines a concentration at which the probability of false positive or false negative results is low.

4.3.3 Historical Laboratory Background PCB Levels

Historical background PCB levels for method blanks were obtained from seven of the laboratories participating in this study. The EPRI Study Plan had proposed to require 6 months of blank data from each participating laboratory, or a minimum of 10 blanks, but many of the laboratories did not have or were not able to provide that much data. The method blanks that were provided were from batches analyzed over a period of several months and varied in number from 3 to 12 individual analytical batches. In addition, the laboratories did not always report all PCB congeners. Only detected PCBs were reported, with no indication of the detection or reporting limits that were used to censor data for each analysis.

Because of the significant variability of method blank results within and between reporting laboratories, the mean plus two standard deviations (EMDL) of values reported by each laboratory was calculated and tabulated for review, excluding any qualified data points. These individual lab EMDLs were plotted and compared to calculated IDE and IQE values.

EPRI did not calculate EML concentrations from the historical background data. In Method 1668A, EPA has derived EMLs by multiplying each EMDL by three, and rounding the resulting value to the nearest of the following values: 10, 20, 50, 100, 200, 500, 1000 ng/L. The technical

justification for these values is not provided in the method: these values are not equidistant on either an arithmetic or a logarithmic scale.

5
RESULTS

This section is divided into three parts: the interlaboratory reagent water study, the wastewater focus study, and laboratory background comparisons.

In the EPRI Study Plan, 44 of the 209 PCB congeners were initially selected for detailed statistical evaluation. As some of the 44 target congeners coelute with other PCBs, the 44 target peaks actually include 54 individual congeners. These 44 congeners or groups are referred to in this report as the "target" PCBs. EPRI's evaluation was later expanded to encompass all 209 congeners. However, to keep Volume I to a manageable length, only the results for the target PCBs are presented in this section and form the basis of discussion. The statistical results for all PCBs are presented in Volume II.

The target PCBs were selected to include:

- First and last eluting congeners for each of the 10 homolog series.
- Common background PCBs found in the environment (PCB-77, PCB-105, PCB-126 and PCB-169).
- PCBs listed by the World Health Organization (WHO) and the National Oceanic and Atmospheric Association (NOAA) as chemicals of toxic or environmental concern.
- PCBs that are calculated by isotope dilution and PCBs that are calculated by the internal standard method.
- Congeners that either coelute on the SPB-Octyl chromatographic column specified in the method, or are susceptible to chromatographic interference.

5.1 Interlaboratory Study Results for Reagent Water

5.1.1 Descriptive Summaries

5.1.1.1 Data Validity

Table 5-1 shows the percentages of disqualified or excluded data points by increasing concentration level (e.g., RW-A is the unspiked reagent water; RW-J is the reagent water samples with the highest spiked PCB concentrations). Data points were disqualified primarily for reasons that the chemical response did not meet method 1668A identification criteria (e.g., ion ratio did not meet validation requirements). In a few cases, a statistically invalid measurement (e.g., a "0" concentration) for a specific PCB was reported by the laboratory for one of the spiked

samples. For unspiked samples, where the true value is expected to be zero (in the absence of contamination) the zero values were not disqualified but were also not used in the statistical evaluation. Table 5-1 shows that the number of excluded values increases as the sample spike concentration decreases. The range of EDLs reported by the laboratories generally ranged from about 0.5 to 40 pg/L; the majority of PCBs detected in the method blanks fell within this concentration range. The high percentage of excluded values for RW-A (unspiked water) may be attributed, in part, to a higher number of nondetected PCBs. However, this table also shows that a significant number of PCBs (26% of all potential data points) were detected in an unspiked reagent water sample.

Table 5-1
Reagent Water Qualified Results

Spiking Group	Nominal PCB concentration (pg/L)	Number of disqualified[a] values	Total number of potential values [b]	Percent of disqualified values (%)	Percent disqualified due to non-detect value (%)
RW-A	0	942	1,268	74.3	NA
RW-B	25	167	1,268	13.2	5.7
RW-C	50	55	1,268	4.3	2.6
RW-D	200	15	1,268	1.2	0
RW-E	400	31	2,536	1.2	0
RW-F	800	9	1,268	0.7	0
RW-G	1,900	19	1,771	1.1	0
RW-H	2,200	11	1,268	0.9	0
RW-I	4,100	9	1,771	0.5	0
RW-J	4,800	26	1,268	2.1	0

[a] Results that did not meet Method 1668A qualitative criteria or were undetected, i.e., less than a 2.5 times signal-to-noise response.
[b] These results represent potential data points for all 209 PCB congeners (as individual or coeluting groups).
NA Not applicable

Appendix B presents the entire data set for the reagent water study, arranged by sample. Values that do not meet one or more qualitative criteria are identified with an asterisk (*). Results are listed for each PCB as either a single congener or as combined PCBs (coelution) for each spiked concentration level (pg/L). Blank cells indicate that the PCB is reported in a different coelution group by that laboratory. Coeluting PCBs are treated as a single data point.

The 13.2% of disqualified values at the RW-B spike level should not have a large impact on the statistical analysis of the data if the method is truly linear over the range of spike concentrations.

In some cases, laboratories report different PCB coelution patterns. This produced a smaller data set for a particular PCB or coelution group, and sometimes resulted in fewer than the six data sets required by ASTM D2777-03. For the statistical analysis, PCB data sets with three or more, but less than six laboratories reporting were processed and identified in the results tables as estimated values. Data sets with less than three laboratories reporting values were not processed.

5.1.1.2 ASTM Standard Practice D2777-03 Statistics

ASTM D2777-03 was used as the basis for determining precision and accuracy for the interlaboratory study. Table 5-2 presents an example of the final statistical summary for PCB 1 (IUPAC assigned number). Appendix C presents the statistical summaries for all PCBs at all spike levels.

Each summary table consists of two portions. The top portion shows the number of usable values, the number of participant laboratories reporting that PCB, the true concentration (spike) level, the mean recovery, the percent recovery, the overall standard deviation (includes within- and between-lab variability), and overall relative standard deviation. The number of potential values prior to disqualification are listed in Table 2-3 as "Total Distributed by Laboratory" and ranged from 11 to 13 potential values for each spike level. The bottom portion shows estimates of the single-operator standard deviation (within-lab variability) based on the three Youden pairs.

Table 5-2
ASTM D 2777-03 Final Statistical Summary for PCB 1

Statistic	RW-B	RW-C	RW-D	RW-E	RW-F	RW-G	RW-H	RW-I	RW-J
Number of usable values	7.00	7.00	7.00	15.0	8.00	9.00	7.00	10.0	7.00
Number of laboratories	7.00	7.00	7.00	8.00	8.00	7.00	7.00	8.00	7.00
True concentration (pg/L)	32.0	63.9	240	480	959	1918	2238	4156	4795
Mean recovery (pg/L)	36.8	68.6	236	500	1017	2049	2365	4243	5244
Percent recovery (%)	115	107	98.5	104	106	107	106	102	109
Overall standard deviation (pg/L)	13.4	15.2	42.5	65.1	100	182	321	811	442
Overall relative standard deviation (%)	36.5	22.2	18.0	13.0	9.86	8.88	13.6	19.1	8.42

Statistic	Low	Mid	High
Number of usable pairs	7.00	7.00	7.00
Single-operator standard deviation (pg/L)	56.57	132.32	556.64

The ASTM D2777-03 precision and bias statements provide the basis for generic limits that can be used in the quality control section of a method. With few exceptions, recovery values (bias) across all spiked PCB levels were within Method 1668A on-going acceptance criteria of 50% to 150% and precision values were within the initial demonstration criteria of 40% RSD.

The precision and bias values reported here represent best case values, in that the study was performed using a reagent water matrix. The fundamental assumption of an interlaboratory study is that the matrix, concentrations, and participating laboratories provide a representative and fair evaluation of the scope and applicability of the test method as written. To the extent that these assumptions are valid, the results of this study will be representative of method performance in actual practice. However, many real world samples would be expected to differ from reagent water in chemical properties (pH, alkalinity, matrix complexity, presence of interferents), biological activity, and in the number and type of modifiers present, such as suspended /

dissolved solids, dissolved organic matter, organic and soot carbon, and surfactants. These added components would most likely degrade method performance and produce higher detection and quantitation limits.

5.1.1.3 Graphical Representation

Percent recoveries for all congeners are shown in Appendix C and are summarized by PCB across all concentration levels in the form of box plots in Appendix D. Figure 5-1 below presents an explanation of a box plot. Note that extreme values indicated by a square are those outside 1.5 times the Interquartile Range (IQR). The values beyond 1.5 times the IQR are not considered outliers and are included in the statistical analyses.

Figures 5-2 through 5-7 present the box plots of the 44 target PCBs, where the number(s) directly below each box plot indicates the PCB congener(s) in that plot, the number of data points, and minimum/maximum values. The side-by-side box plots show the distribution of the percent recovery for each PCB and allow for comparison of mean percent recovery across PCBs. For example, mean percent recovery for PCB 104 is higher than that of PCB 105, and in turn, that of PCB 105 is higher than that of PCB 111. The plots also highlight maximum percent recovery values along with the identification of the reporting laboratory. For example, laboratory Nos. 2 and 7 reported extreme percent recoveries for PCB 52. Some of the observed higher recoveries are reported for the least-concentrated spiked study samples in which PCB concentrations are likely enhanced due to corresponding background contamination. For example, method blank results are elevated for Lab 5 (PCB 1) and Lab 7 (PCB 52) resulting in higher recoveries for corresponding samples from RW Lab Group Code B (lowest spiked sample set).

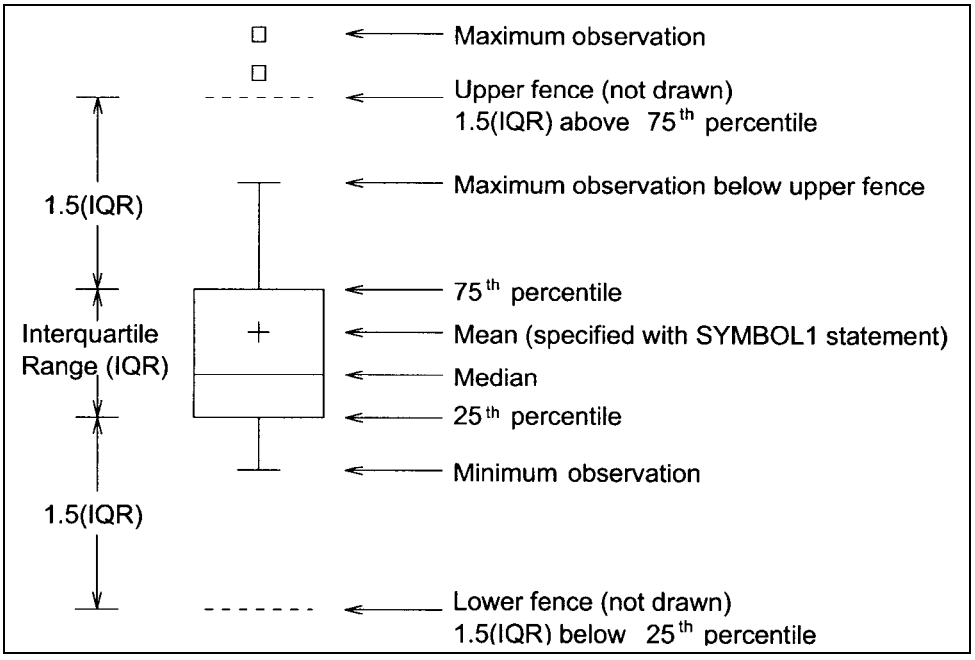
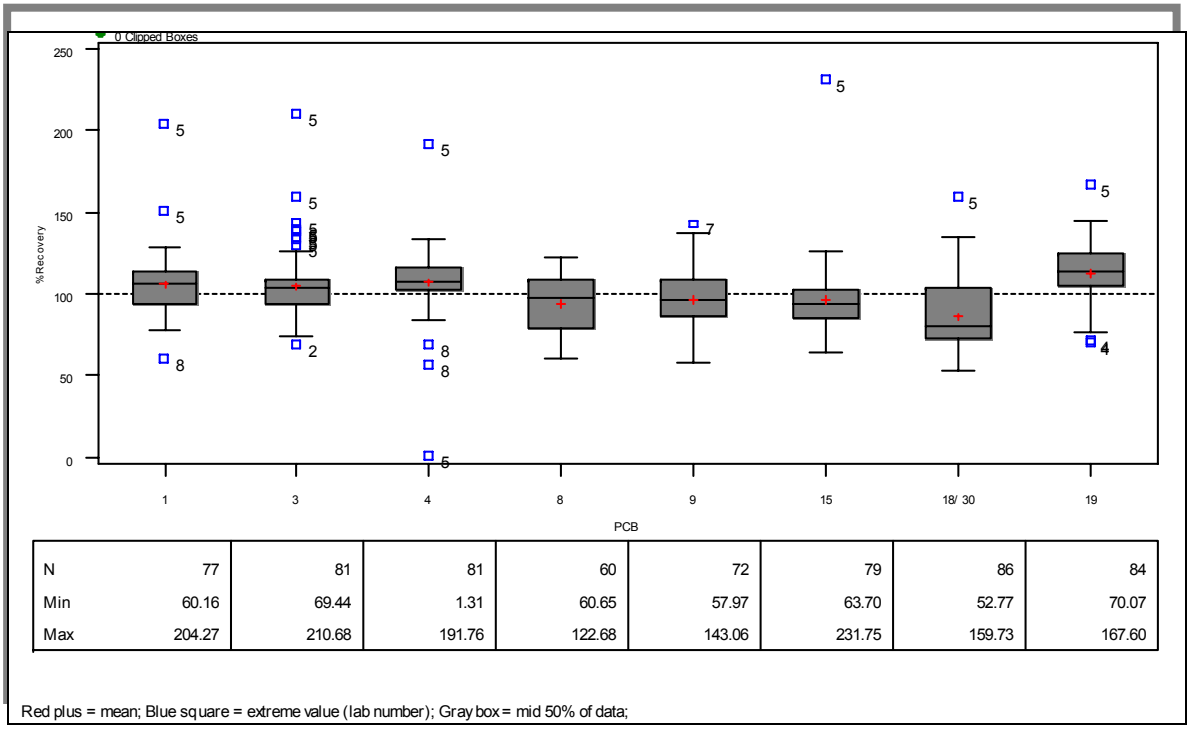


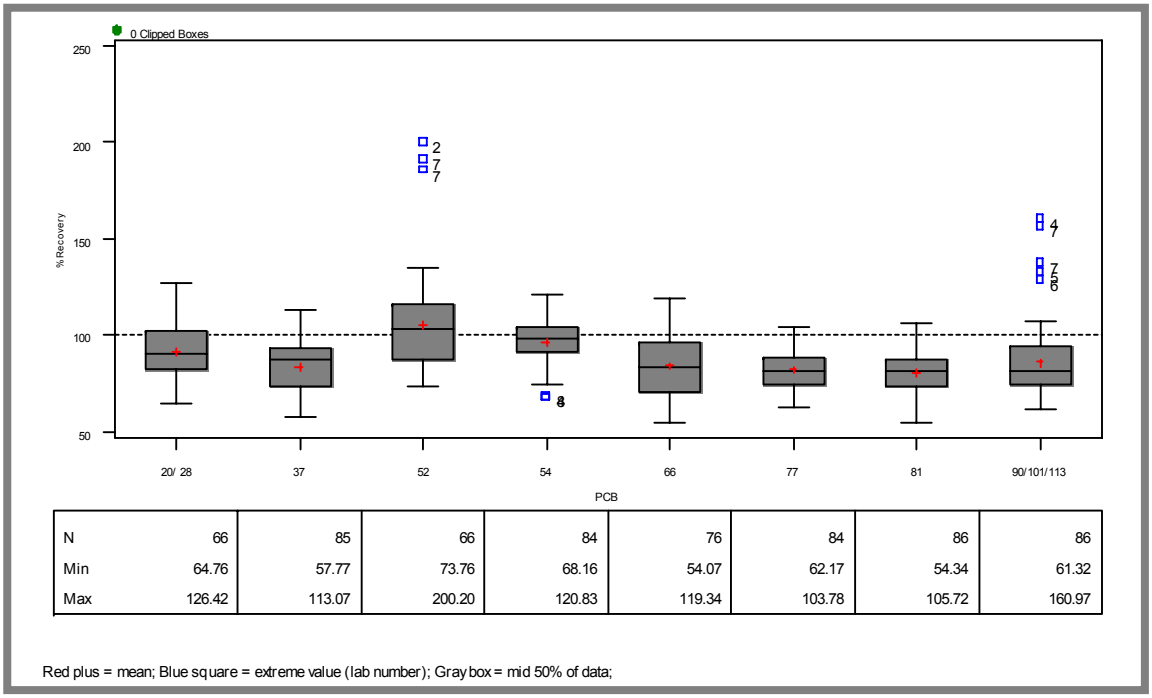
Figure 5-1
Description of a Generic Box Plot (Source: SAS, 2004)

Results for the unspiked reagent water (RW-A) were not reported in this statistical summary, but are discussed in the evaluation of background PCB levels (Section 5.3). The unspiked reagent water results are in effect a method blank that is unknown to the laboratory. Results of all laboratory method blanks and the unspiked reagent waters are presented in Appendix E.



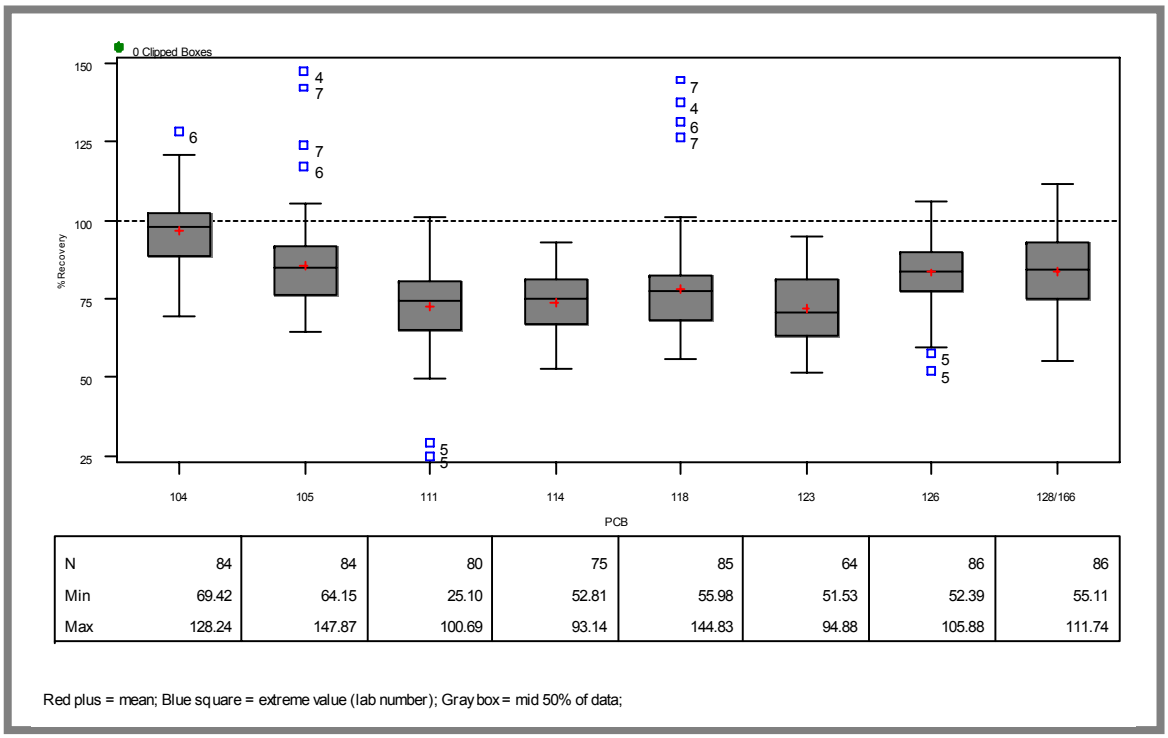
	1	3	4	8	9	15	18/ 30	19
N	77	81	81	60	72	79	86	84
Min	60.16	69.44	1.31	60.65	57.97	63.70	52.77	70.07
Max	204.27	210.68	191.76	122.68	143.06	231.75	159.73	167.60

Figure 5-2
Percent Recovery Box Plots for PCBs in Reagent Water (1, 3, 4, 8, 9, 15, 18/30 and 19)



N	66	85	66	84	76	84	86	86
Min	64.76	57.77	73.76	68.16	54.07	62.17	54.34	61.32
Max	126.42	113.07	200.20	120.83	119.34	103.78	105.72	160.97

Figure 5-3
Percent Recovery Box Plots for PCBs in Reagent Water (20/28, 37, 52, 54, 66, 77, 81 and 90/101/113)



N	84	84	80	75	85	64	86	86
Min	69.42	64.15	25.10	52.81	55.98	51.53	52.39	55.11
Max	128.24	147.87	100.69	93.14	144.83	94.88	105.88	111.74

Figure 5-4
Percent Recovery Box Plots for PCBs in Reagent Water (104, 105, 111, 114, 118, 123, 126, and 128/166)

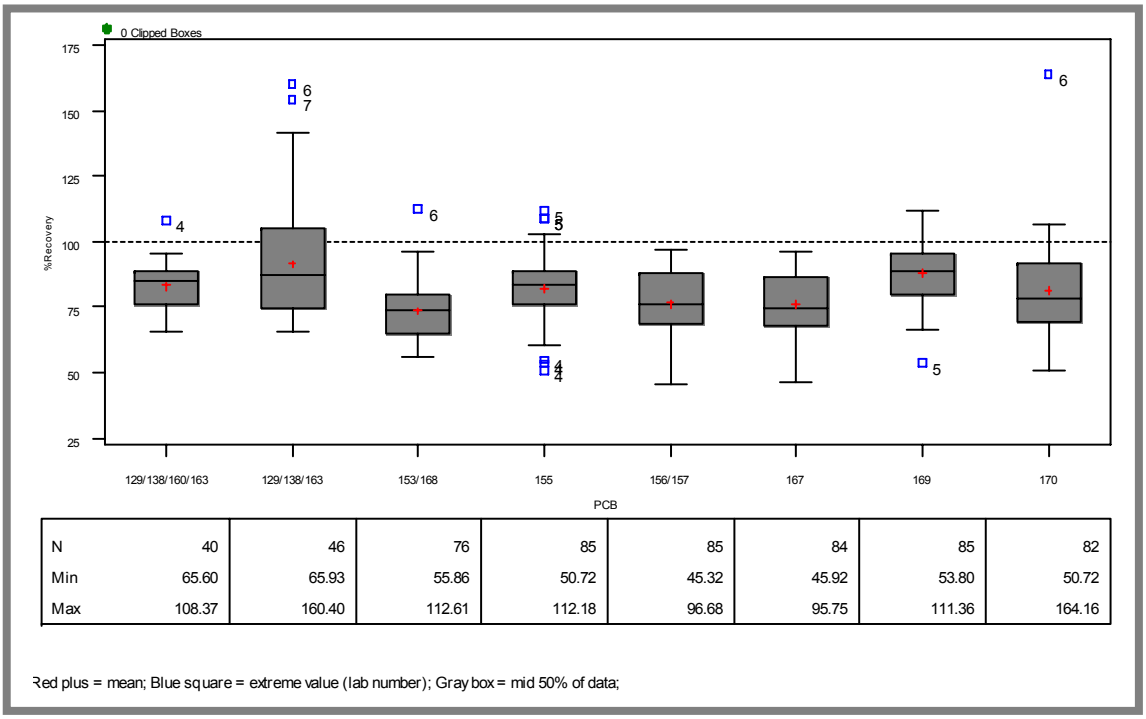
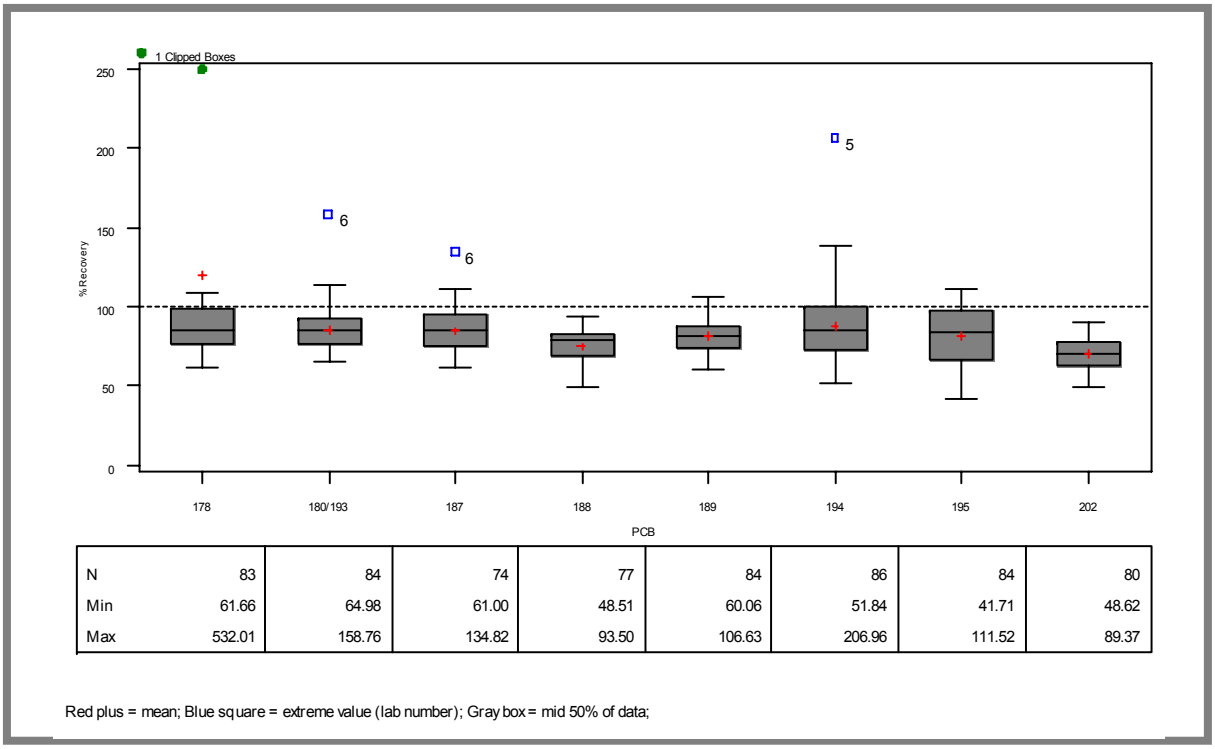


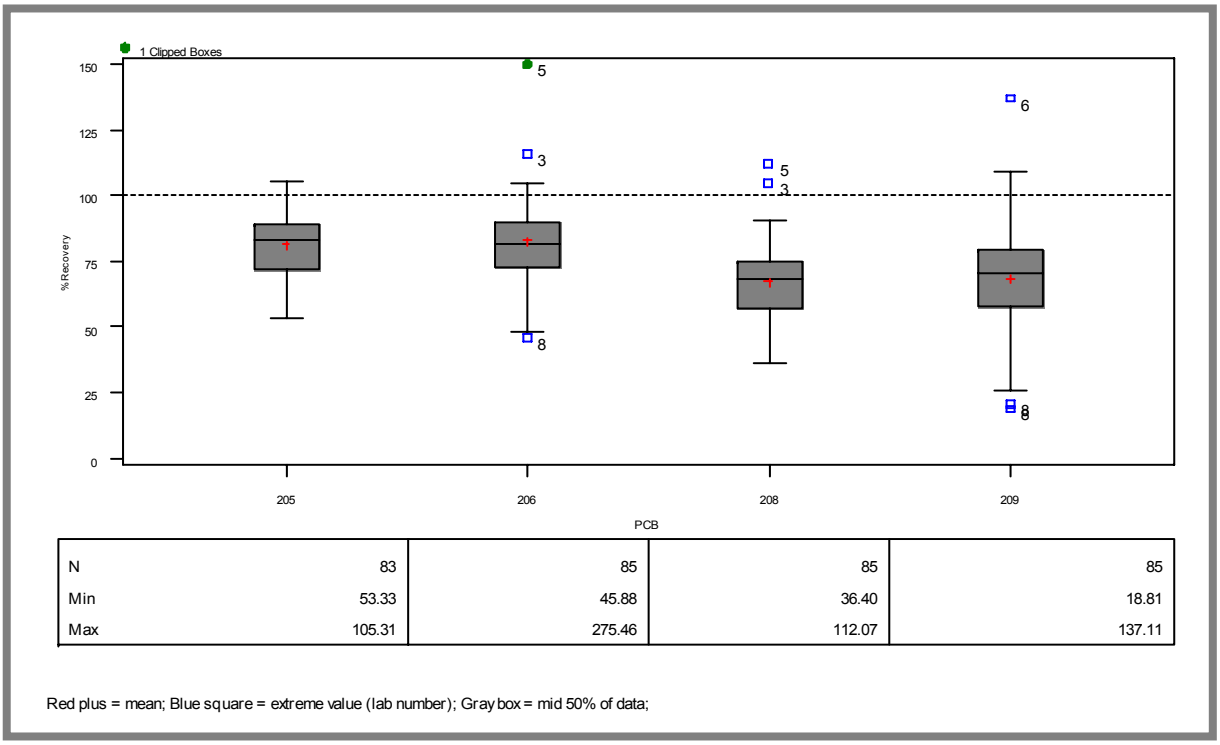
Figure 5-5
Percent Recovery Box Plots for PCBs in Reagent Water (129/138/160/163, 129/138/163, 153/168, 155, 156/157, 167, 169, and 170)



	178	180/193	187	188	189	194	195	202
N	83	84	74	77	84	86	84	80
Min	61.66	64.98	61.00	48.51	60.06	51.84	41.71	48.62
Max	532.01	158.76	134.82	93.50	106.63	206.96	111.52	89.37

Red plus = mean; Blue square = extreme value (lab number); Gray box = mid 50% of data;

Figure 5-6
Percent Recovery Box Plots for PCBs in Reagent Water (178, 180/183, 187, 188, 189, 194, 195, and 202)



	205	206	208	209
N	83	85	85	85
Min	53.33	45.88	36.40	18.81
Max	105.31	275.46	112.07	137.11

Red plus = mean; Blue square = extreme value (lab number); Gray box = mid 50% of data;

Figure 5-7
Percent Recovery Box Plots for PCBs in Reagent Water (205, 206, 208 and 209)

5.1.2 Statistical Inference

5.1.2.1 Regression and ILSD Models

Estimated models for mean recovery between- and within-laboratory variance are shown in Appendix F for each PCB congener or group reported by at least three laboratories. The seventh column in Appendix F provides an overall goodness-of-fit measure (i.e., the extent that the statistical model fits the set of observations) for regression and variance models. Table 5-3 highlights these results for the 44 target PCBs. As noted in Section 4.1.2, the same ILSD model form was applied to all congeners. This model accounts for both within laboratory and between laboratory variability.

The between-laboratory variance estimate is an indicator of the replicability of results between laboratories. PCBs with high between-laboratory variance, such as PCBs 4 and 178, are not reported consistently across laboratories. Low between-laboratory variance indicates that the PCB was reproducibly measured across laboratories, for example PCBs 37 and 77. Although there is no established criterion for an acceptable interlaboratory variance, these results show that reproducibility of results between laboratories varies by the individual PCB or coeluting PCB group.

5.1.2.2 Scatter Plots

Appendix F presents scatter plots for each PCB of the measured versus spiked concentrations, with fitted regression curves for each individual laboratory individually and overall. Also shown are scatter plots of the absolute residuals (i.e., absolute difference between observed and predicted concentrations) versus spiked concentrations, plotted against the overall fitted standard deviation model. An example pair of scatter plots (for PCB 1) is shown in Figures 5-8 and 5-9. Data points and regression lines are color-coded by laboratory in both figures. Figure 5-8 indicates the overall fitted regression equation of measured versus spiked concentrations. Figure 5-9 shows the variance model used in the estimation of IQE and IDE for that PCB; note that the fitted ILSD estimate is the square root of the variance model.

5.1.2.3 Estimates of Background Levels

Estimates of background (blank) contamination were derived from the mean recovery model and the variance model, in the form of a 95% confidence interval for the y-intercept. The y-intercept of the model represents an estimate of the average PCB concentration at the zero spike level (i.e., the background PCB concentration) across the entire EPRI data set. The upper 95% confidence limit (95%UCL) provides an upper bound for the average PCB background concentrations across all laboratories. Confidence intervals for the 44 target PCBs are shown in the last column of Table 5-3, and are shown graphically in Figure 5-10. PCBs with particularly high 95%UCL values are labeled in the figure.

Table 5-3
Reagent Water Mean Model and ILSD Estimates for Target PCB List

PCB	ASTM D 2777-03 criteria met?	Mean recovery model	Between-lab variance model	Within-lab variance model	Degrees of freedom	Likelihood ratio test R^2	95% confidence interval for the intercept (pg/L)
1	Y	3.37+1.04T	(10.82)**2+(0.08T)**2	(–2.09+0.10T)**2	6	0.9980	(–6.75, 13.48)
3	Y	0.41+1.04T	(9.13)**2+(–0.13T)**2	(1.42+0.06T)**2	6	0.9988	(–8.51, 9.33)
4	Y	3.77+1.06T	(0.11)**2+(0.06T)**2	(1.26–0.19T)**2	6	0.9925	(–7.39, 14.94)
8	Y	2.03+0.94T	(0.08)**2+(0.16T)**2	(0.06–0.05T)**2	4	0.9990	(–3.37, 7.42)
9	Y	1.95+0.97T	(4.76)**2+(–0.15T)**2	(–4.23+0.10T)**2	6	0.9975	(–3.27, 7.16)
15	Y	4.73+0.95T	(17.40)**2+(–0.12T)**2	(–2.17–0.05T)**2	6	0.9980	(–11.38, 20.83)
18/ 30	Y	16.40+0.81T	(29.80)**2+(–0.16T)**2	(18.57–0.06T)**2	6	0.9985	(–10.38, 43.17)
19	Y	3.41+1.11T	(4.56)**2+(0.13T)**2	(–0.94+0.11T)**2	6	0.9977	(–1.56, 8.39)
20/ 28	Y	0.88+0.90T	(3.28)**2+(0.10T)**2	(7.18+0.03T)**2	4	0.9994	(–8.70, 10.46)
37	Y	–0.34+0.84T	(1.60)**2+(0.11T)**2	(–2.37–0.05T)**2	6	0.9988	(–4.32, 3.64)
52	Y	19.02+0.99T	(19.81)**2+(–0.13T)**2	(9.41+0.07T)**2	4	0.9977	(–6.77, 44.80)
54	Y	–0.52+0.96T	(0.07)**2+(0.07T)**2	(–0.87+0.08T)**2	6	0.9987	(–1.99, 0.95)
66	Y	3.57+0.81T	(5.07)**2+(0.14T)**2	(1.57+0.05T)**2	5	0.9988	(–2.30, 9.45)
77	Y	–1.22+0.83T	(2.11)**2+(0.09T)**2	(–1.35–0.04T)**2	6	0.9990	(–3.90, 1.46)
81	Y	–2.77+0.82T	(–0.00)**2+(0.09T)**2	(–1.20–0.05T)**2	6	0.9989	(–5.10, –0.44)
90/101/113	Y	21.95+0.80T	(23.11)**2+(0.09T)**2	(–6.74–0.04T)**2	6	0.9989	(0.54, 43.36)
104	Y	–1.34+0.98T	(2.90)**2+(0.08T)**2	(–1.63+0.08T)**2	6	0.9986	(–3.93, 1.24)
105	Y	2.62+0.83T	(7.20)**2+(0.08T)**2	(3.04+0.05T)**2	6	0.9984	(–4.69, 9.94)
111	Y	–0.72+0.73T	(1.01)**2+(0.11T)**2	(2.12–0.07T)**2	6	0.9980	(–1.98, 0.53)
114	Y	–0.90+0.74T	(1.62)**2+(0.09T)**2	(–0.88–0.04T)**2	5	0.9989	(–3.50, 1.69)
118	Y	9.33+0.74T	(14.75)**2+(–0.07T)**2	(–6.25–0.04T)**2	6	0.9982	(–5.22, 23.87)
123	Y	–0.00+0.72T	(0.00)**2+(–0.09T)**2	(–0.61–0.06T)**2	4	0.9975	(–2.61, 2.60)
126	Y	–1.98+0.85T	(2.91)**2+(0.07T)**2	(–0.60–0.05T)**2	6	0.9989	(–5.26, 1.29)
128/166	Y	–2.26+0.84T	(6.61)**2+(0.10T)**2	(0.08+0.06T)**2	6	0.9987	(–8.81, 4.30)
129/138/160/163	N	3.77+0.82T	(0.24)**2+(0.02T)**2	(6.38+0.07T)**2	2	0.9986	(–25.91, 33.45)

Table 5-3 (continued)
Reagent Water Mean Model and ILSD Estimates for Target PCB List

PCB	ASTM D 2777-03 criteria met?	Mean recovery model	Between-lab variance model	Within-lab variance model	Degrees of freedom	Likelihood ratio test R2	95% confidence interval for the intercept (pg/L)
129/138/163	N	27.05+0.86T	(29.48)**2+(–0.15T)**2	(–6.20–0.03T)**2	2	0.9991	(–38.30, 92.40)
153/168	Y	8.26+0.72T	(18.44)**2+(–0.08T)**2	(6.53+0.05T)**2	5	0.9986	(–12.86, 29.38)
155	Y	–2.20+0.83T	(1.20)**2+(0.10T)**2	(1.53–0.07T)**2	6	0.9987	(–3.52, –0.88)
156/157	Y	–0.76+0.76T	(5.66)**2+(0.10T)**2	(–1.17–0.04T)**2	6	0.9991	(–6.55, 5.03)
167	Y	–1.75+0.77T	(3.06)**2+(0.09T)**2	(–1.13–0.06T)**2	6	0.9982	(–5.37, 1.87)
169	Y	–0.44+0.88T	(1.53)**2+(0.09T)**2	(–1.32–0.05T)**2	6	0.9988	(–3.14, 2.25)
170	Y	3.27+0.79T	(7.26)**2+(0.12T)**2	(2.24+0.05T)**2	6	0.9981	(–3.74, 10.27)
178	Y	0.73+1.20T	(–0.00)**2+(0.96T)**2	(9.19+0.10T)**2	6	0.9979	(–7.88, 9.33)
180/193	Y	9.10+0.83T	(12.43)**2+(0.10T)**2	(4.93+0.05T)**2	6	0.9985	(–3.35, 21.55)
187	Y	5.93+0.82T	(7.06)**2+(–0.10T)**2	(0.21+0.07T)**2	5	0.9978	(–1.63, 13.49)
188	Y	–1.85+0.76T	(–0.00)**2+(0.08T)**2	(–1.12–0.05T)**2	6	0.9986	(–4.18, 0.49)
189	Y	–0.53+0.82T	(2.20)**2+(0.08T)**2	(–1.03–0.06T)**2	6	0.9984	(–3.56, 2.50)
194	Y	5.72+0.83T	(7.23)**2+(–0.14T)**2	(–7.39–0.05T)**2	6	0.9982	(–2.96, 14.41)
195	Y	–0.83+0.81T	(0.17)**2+(0.16T)**2	(–2.48–0.06T)**2	6	0.9983	(–4.55, 2.90)
202	Y	–0.30+0.70T	(2.04)**2+(–0.08T)**2	(0.89–0.05T)**2	6	0.9989	(–2.29, 1.68)
205	Y	–2.15+0.82T	(1.02)**2+(0.09T)**2	(–3.17–0.04T)**2	6	0.9988	(–6.14, 1.84)
206	Y	2.78+0.79T	(7.78)**2+(–0.12T)**2	(12.72+0.04T)**2	6	0.9975	(–8.63, 14.19)
208	Y	0.24+0.66T	(–0.00)**2+(–0.12T)**2	(2.74+0.05T)**2	6	0.9976	(–2.82, 3.30)
209	Y	1.20+0.67T	(–0.00)**2+(0.15T)**2	(0.05+0.12T)**2	6	0.9941	(–1.31, 3.71)

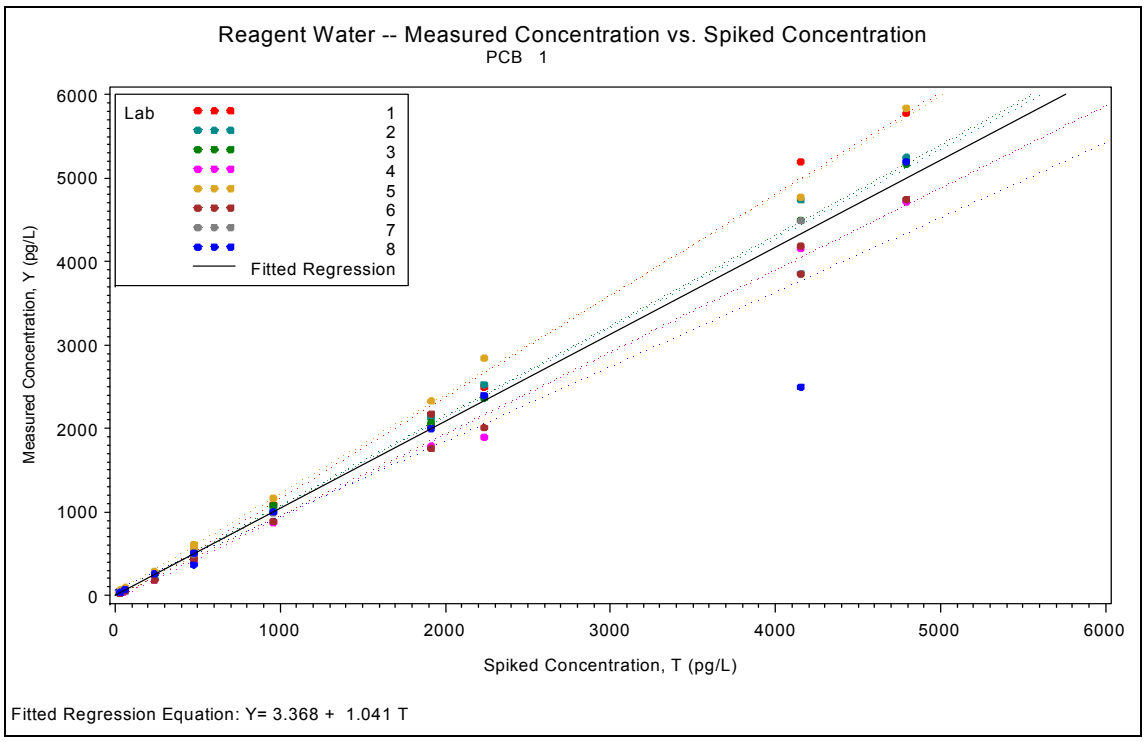


Figure 5-8
Measured versus Spiked Concentrations and Fitted Regression Lines for PCB 1

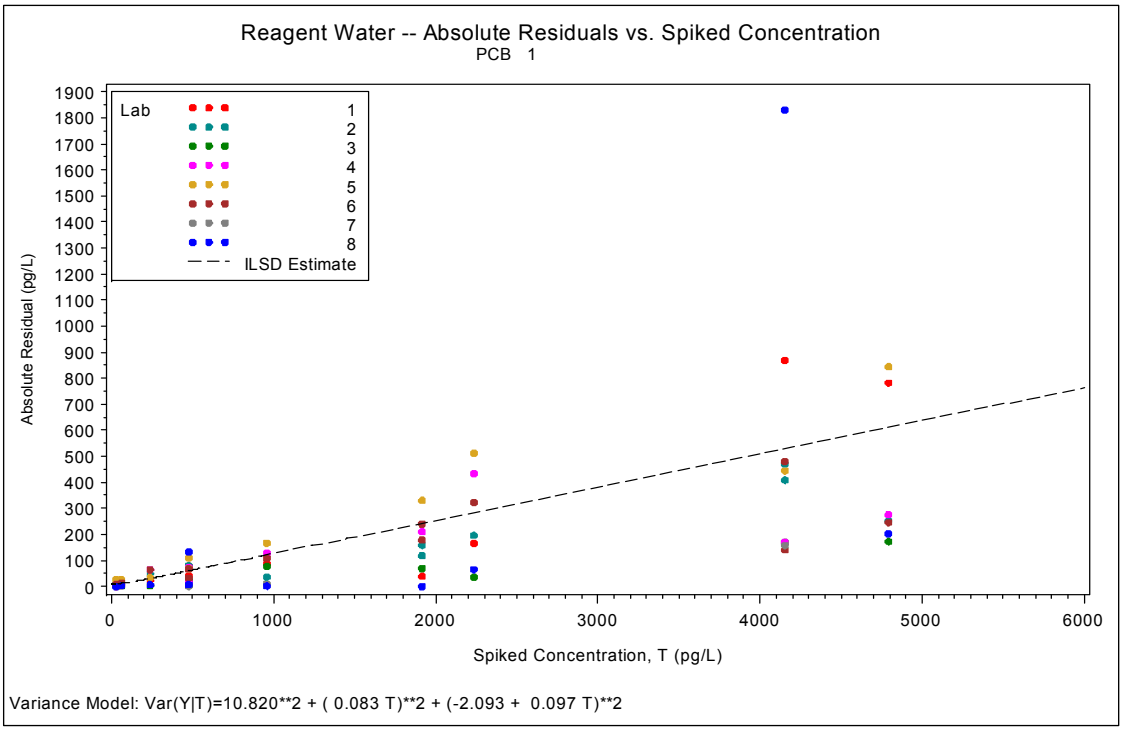


Figure 5-9
Absolute Residuals versus Spiked Concentrations for PCB 1

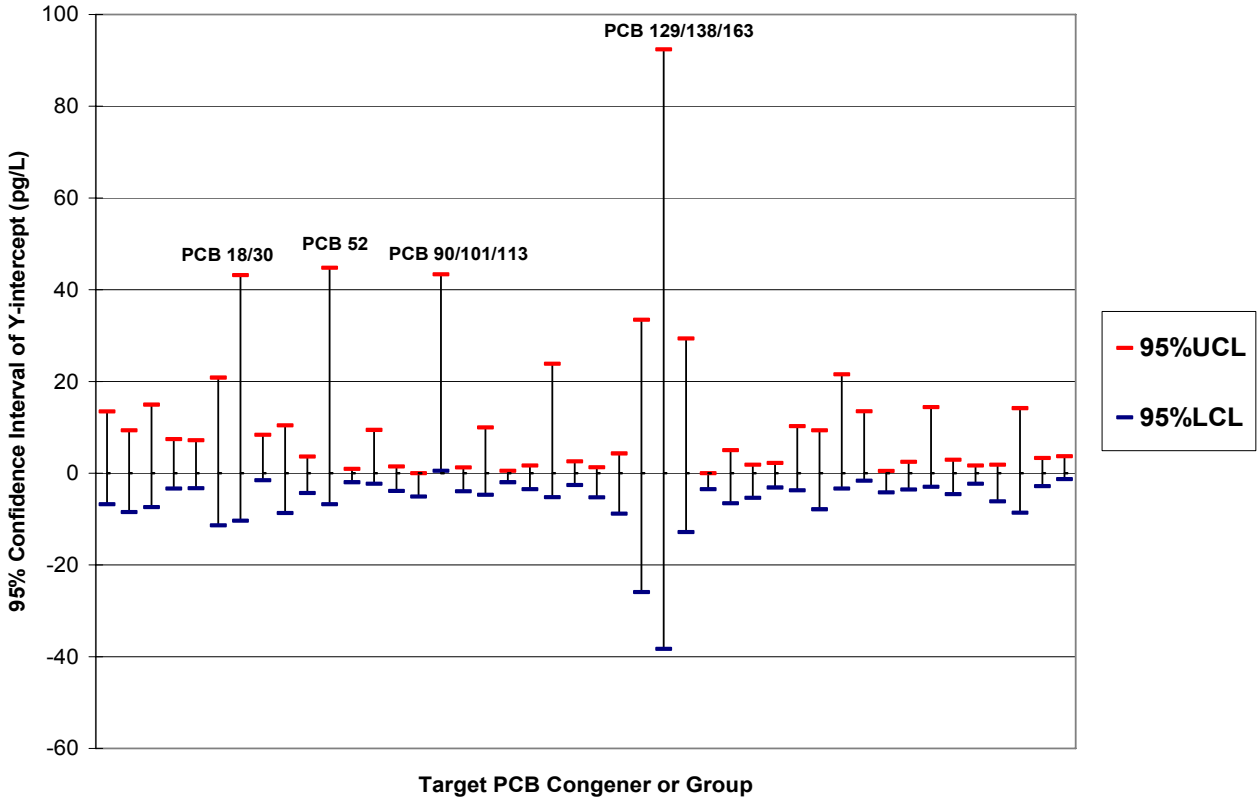


Figure 5-10
Confidence Intervals on Y-Intercept of Spike Recovery Plot (44 Target PCBs)

If the lower 95% confidence limit (95% LCL) of the measured concentration exceeded zero, the presence of an average laboratory background was confirmed. By this analysis, 19 of 209 congeners (10 of 172 peaks) or congener groups were shown to have a significant laboratory background across laboratories. Of the 44 target PCBs, only the congener group 90/101/113 had a 95% LCL greater than zero. The other 43 target congeners (or coeluting congener groups) did not exhibit, on average, statistically-significant PCB background across laboratories. However, many of the PCBs exhibited a 95% UCL significantly above zero (up to 153 pg/L for PCB 11). Therefore, this statistical analysis does not exclude the possibility that an average background contamination may exist. PCB background contamination may also appear as a random event at a laboratory; therefore, it is good laboratory practice to prepare and analyze method blanks with each analytical batch.

5.1.2.4 IDE and IQE Estimates

IDE and IQE estimates for the 44 target PCBs are presented in Table 5-4. The IDE and the IQE estimates for all PCBs are listed in Appendix G. YC and LC values, as defined in ASTM Standard D6091-03, are included in Appendix G. YC is defined as the measurement value that with ~90% confidence will be exceeded no more than 1% of the time when a blank sample is measured. LC is defined as the true concentration that has an expected recovery that, with ~90%

confidence, will be exceeded no more than 1% of the time when a blank sample is measured. In both of these summary tables, an empty cell indicates that the IQE value at that level of precision could not be calculated according to ASTM procedures. For most PCBs, only IQE20% and IQE30% values could be calculated. The fact that most IQE10% values could not be calculated indicates that the method cannot measure PCB congeners with a 10 percent relative standard deviation at the trace levels included in this study.

The second column in Table 5-4 and Appendix G indicates whether the D 2777-03 criterion of six or more laboratories reporting was met for that congener or congener group. If this criterion was not met, the resulting IQE value is not valid and should not be used, but is shown for information purposes.

Method 1668A EMDLs and EMLs are included in Table 5-4 for comparison. The Method 1668A EMDLs are higher than the corresponding IDE values in all cases. The ratios between the Method 1668A EMDLs and the IDEs ranged from 1 to 300; the average ratio was 26. The Method 1668A EMLs are likewise higher than the calculated IQE20% values, with ratios ranging from 1 to > 500, with an average ratio of 35.

Table 5-4
Reagent Water IDE and IQE Estimates for the PCB Target List

PCB	ASTM D2777-03 criteria met?	IDE (pg/L)	IQE10% (pg/L)	IQE20% (pg/L)	IQE30% (pg/L)	EPA EMDL (pg/L)	EPA EML (pg/L)
1[a]	Y	36.7	.	59.9	36.2	82	200
3[a]	Y	32.3	.	63.3	34.1	88	200
4[a]	Y	3.03	11.6	3.21	2.51	172	500
8[c]	Y	0.39	.	0.93	0.41	121	500
9	Y	22.1	.	37.9	21.0	20	50
15[a]	Y	67.3	.	136.1	71.6	183	500
18/30[c]	Y	158	.	.	168	175	500
19[a]	Y	14.9	.	27.5	15.0	42	100
20/28[c]	Y	31.9	.	65.3	35.4	192	500
37[a]	Y	13.2	.	33.3	15.4	132	500
52	Y	82.5	.	204	95.5	191	500
54[a]	Y	2.8	44.2	3.4	2.4	118	500
66[c]	Y	24.8	.	97.2	29.4	162	500
77[a,b,c,d]	Y	11.2	.	22.8	12.2	169	500
81[e]	Y	5.66	.	14.0	6.7	177	500
90/101/113[c]	Y	110	.	212	116	241	1000
104[a]	Y	11.4	.	16.1	10.5	228	500
105[b,c,d,e]	Y	34.7	.	65.9	36.9	109	200
111	Y	10.5	.	14.6	9.2	243	1000
114[e]	Y	9.24	.	20.0	10.3	120	500
118[c,d,e]	Y	79.4	.	150.8	84.5	193	500
123[a]	Y	3.40	.	13.0	4.68	150	500
126[a,b,c,d]	Y	12.7	.	22.5	13.1	136	500
128/166[c]	Y	28.4	.	53.1	29.4	124	500
129/138/160 /163[c]	N	28.4	693	68.9	36.4	211	500
129/138/163	N	125	.	392	149	130	500
153/168[c]	Y	99.5	.	204	108	339	1000

Table 5-4 (continued)
Reagent Water IDE and IQE Estimates for the PCB Target List

PCB	ASTM D2777-03 criteria met?	IDE (pg/L)	IQE10% (pg/L)	IQE20% (pg/L)	IQE30% (pg/L)	EPA EMDL (pg/L)	EPA EML (pg/L)
155[a]	Y	7.71	.	10.7	6.95	132	500
156/157[d,e]	Y	27.9	.	58.6	29.9	115	500
167[d,e]	Y	15.8	.	33.9	17.4	161	500
169[a,b,c,d]	Y	8.63	.	17.9	9.56	162	500
170[c]	Y	36.5	.	102	41.7	221	500
178	Y	31.2	.	.	.	136	500
180/193[c]	Y	60.1	.	130	65.7	191	500
187[c]	Y	31.0	.	64.9	33.2	235	500
188[a]	Y	5.69	.	14.3	6.83	177	500
189[a,d]	Y	11.1	.	22.7	12.1	170	500
194	Y	49.1	.	229	61.3	427	1000
195[c]	Y	12.6	.	.	19.9	442	1000
202[a]	Y	10.9	.	17.7	10.7	449	1000
205[a]	Y	15.5	.	34.9	17.7	451	1000
206[a,c]	Y	74.1	.	254	90.8	455	1000
208[a]	Y	17.0	.	716	26.1	153	500
209[a,c]	Y	0.28	.	.	3.08	82	200

.": Not calculated by the statistical model.

[a] First or last eluting PCB of a homolog series on SPB–octyl column; these PCBs are measured by isotope dilution.

[b] Commonly reported background PCB.

[c] NOAA–listed PCB of toxic or environmental concern.

[d] WHO–listed PCB (as congener as part of coelution) of toxic concern.

[e] PCB calculated using isotope dilution method.

IDE = Calculated 99%/95% interlaboratory detection estimate (ASTM D 6091–03).

IQE = Calculated interlaboratory quantitation estimate (ASTM D 6512–03).

EMDL = Estimated method detection limit, defined as the concentration of a PCB that can be detected with common laboratory interferences present (Method 1668A).

EML = Estimated minimum level of a PCB that can be reliably measured with common laboratory interferences present (Method 1668A).

5.2 Single–Laboratory Study Results for Wastewater

5.2.1 Descriptive Summaries

5.2.1.1 Data Validity

Table 5-5 shows the percentages of flagged or excluded data points (i.e., qualified values) for method blanks (MB), and by increasing concentration level for the wastewater study. Measurements in the zero spike samples that were below instrument detection limits were not disqualified, as the expected concentration in those samples was zero. However, those values were also not used in the statistical analysis.

Table 5-5
Method Blank and Wastewater Qualified Results

Nominal concentration (pg/L)	Spiking group	Number of disqualified values [a]	Total number of potential data points[b]	Percent disqualified values (%)
0	MB	275	318	86.5
0	WW–A	238	318	74.8
100–500	WW–B	0	318	0
500	WW–C	0	318	0
1,000–2,000	WW–D	0	318	0
2,000	WW–E	0	318	0

[a] Results that did not meet Method 1668A qualitative criteria or were undetected, i.e., less than a 2.5 times signal–to–noise response.
[b]: These results represent potential data points for all 209 PCB congeners (as individual or coeluting groups).

Appendix H presents the entire data set for the wastewater study. Values that do not meet one or more qualitative criteria are identified with an asterisk (*). Blank cells indicate that the PCB is reported as a coelution by the laboratory. Results are listed for each PCB as either a single congener or as coeluting group, by spike concentration (pg/L). Coeluting PCBs were treated as a single data set.

The numbers of nonmeasurable data points for the unspiked wastewaters were similar to, but slightly less than, for the method blanks. This is likely the result of the single laboratory determination rather than a matrix effect. The nonusable data include nondetected values (i.e., less than the EDL) and measurable responses that did not meet method 1668A qualitative identification criteria. In the spiked wastewater samples, all PCB congeners were detected and no values were disqualified.

5.2.1.2 Precision and Accuracy

Precision, expressed as relative percent difference (RPD) is presented in Appendix I for the duplicated PCBs. These results show that for both wastewater composite samples tested, the variability at the lower PCB concentrations was generally larger than that at the higher

concentrations. It is expected for imprecision to increase as the concentration decreases and approaches the lower limit of detection.

Figure 5-11 through 5-16 present the box plots of percent recovery for the 44 target PCBs. Box plots for all PCBs are included in Appendix J. The side-by-side box plots allow for direct comparison of the percent recovery of composite samples within and across PCBs. It is interesting to note that for PCBs numbered 100 or above, composite A has consistently higher percent recovery than composite B. The reason for this observed difference between wastewater composite study samples could not be determined. In general, spike recoveries range from about 70% to 110%, within the ongoing accuracy and precision sample (OPR) control limits of the method (i.e., 50% to 150%). PCB recovery tolerances and actual PCB spike recoveries may be greater than 100% due to calibration variances and other experimental factors of the method.

5.2.2 Statistical Inference

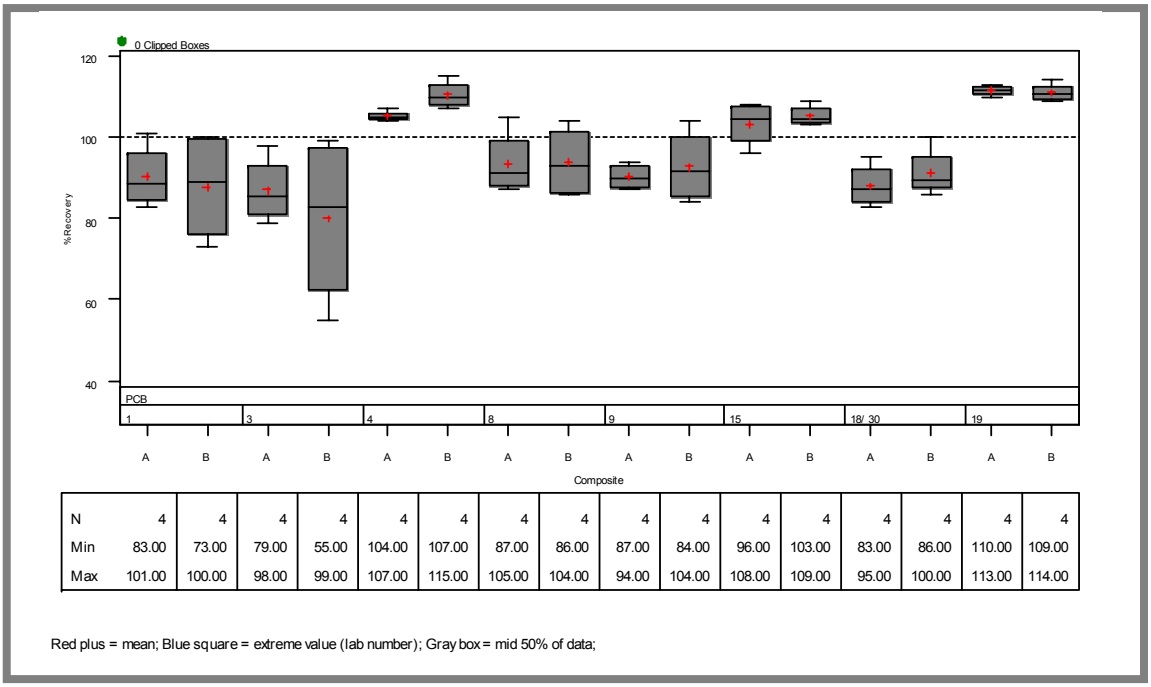
5.2.2.1 Regression Model

The estimated mean recovery model for each composite wastewater and the error variance estimate are shown in Appendix K for each PCB. The sixth column in Appendix K provides an overall goodness-of-fit measure for the two regressions. The higher that measure and the closer to 1, the better the model fits. Table 5-6 highlights the results for the 44 target PCBs.

5.2.2.2 Background Level Estimates

Background level estimates were derived from the mean recovery models in the form of 95% confidence intervals for each y-intercept. These estimates are shown separately for each wastewater in the last two columns of Appendix K. Table 5-6 includes these results for the 44 target PCBs. The statistical results for the wastewater samples and the reagent water data are not equivalent or statistically comparable. As noted earlier, the precision and accuracy determination for the wastewater samples were consistent with Method 1668A criteria.

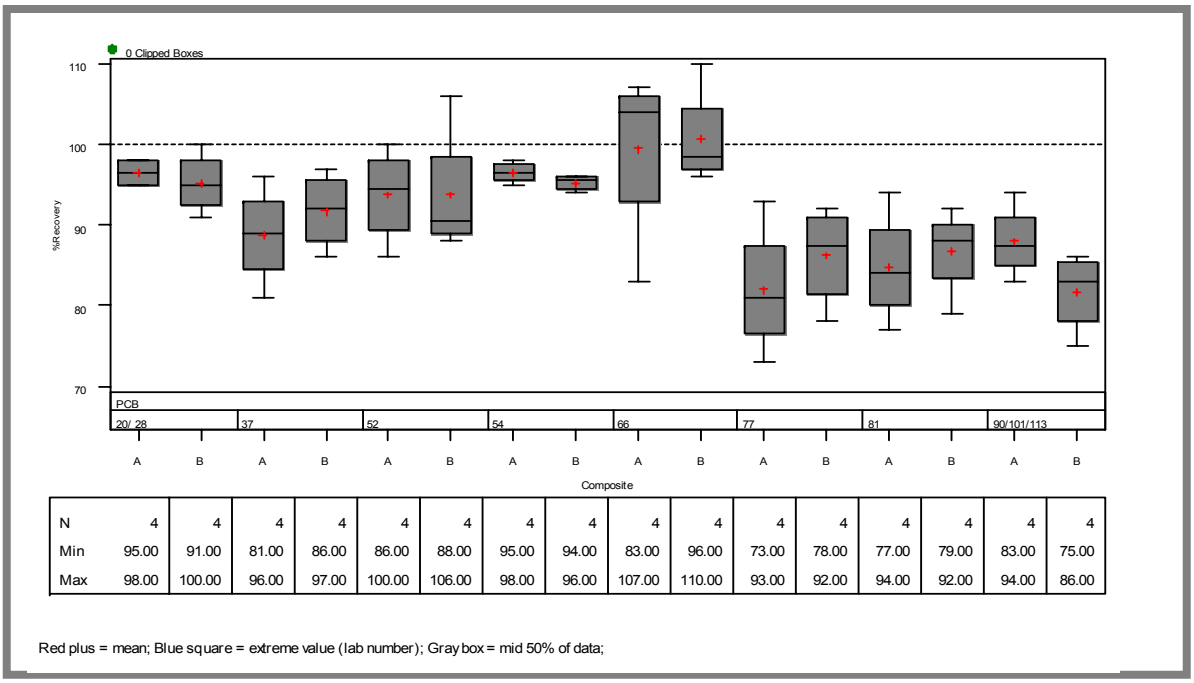
Results of the unspiked composite wastewater samples are also compared to the IDE values in Table 5-7. This table shows that all PCB results for the wastewater samples are below the calculated IDE values except for PCBs 8, 118 and 209. For these three congeners, the laboratory detected the PCB in the method blank at concentrations near the values reported for the corresponding wastewater samples. Values listed as less than ("<") in Table 5-7 correspond to an estimated maximum possible concentration (EMPC) due to an interference, indicating that the listed PCB could be present at or below this concentration.



N	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Min	83.00	73.00	79.00	55.00	104.00	107.00	87.00	86.00	87.00	84.00	96.00	103.00	83.00	86.00	110.00	109.00
Max	101.00	100.00	98.00	99.00	107.00	115.00	105.00	104.00	94.00	104.00	108.00	109.00	95.00	100.00	113.00	114.00

Red plus = mean; Blue square = extreme value (lab number); Gray box = mid 50% of data;

Figure 5-11
Percent Recovery Box Plots for PCBs in Wastewater (1, 3, 4, 8, 9, 15, 18/30 and 19)



N	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Min	95.00	91.00	81.00	86.00	86.00	88.00	95.00	94.00	83.00	96.00	73.00	78.00	77.00	79.00	83.00	75.00
Max	98.00	100.00	96.00	97.00	100.00	106.00	98.00	96.00	107.00	110.00	93.00	92.00	94.00	92.00	94.00	86.00

Red plus = mean; Blue square = extreme value (lab number); Gray box = mid 50% of data;

Figure 5-12
Percent Recovery Box Plots of PCBs in Wastewater (20/28, 37, 52, 54, 66, 77, 81, and 90/101/113)

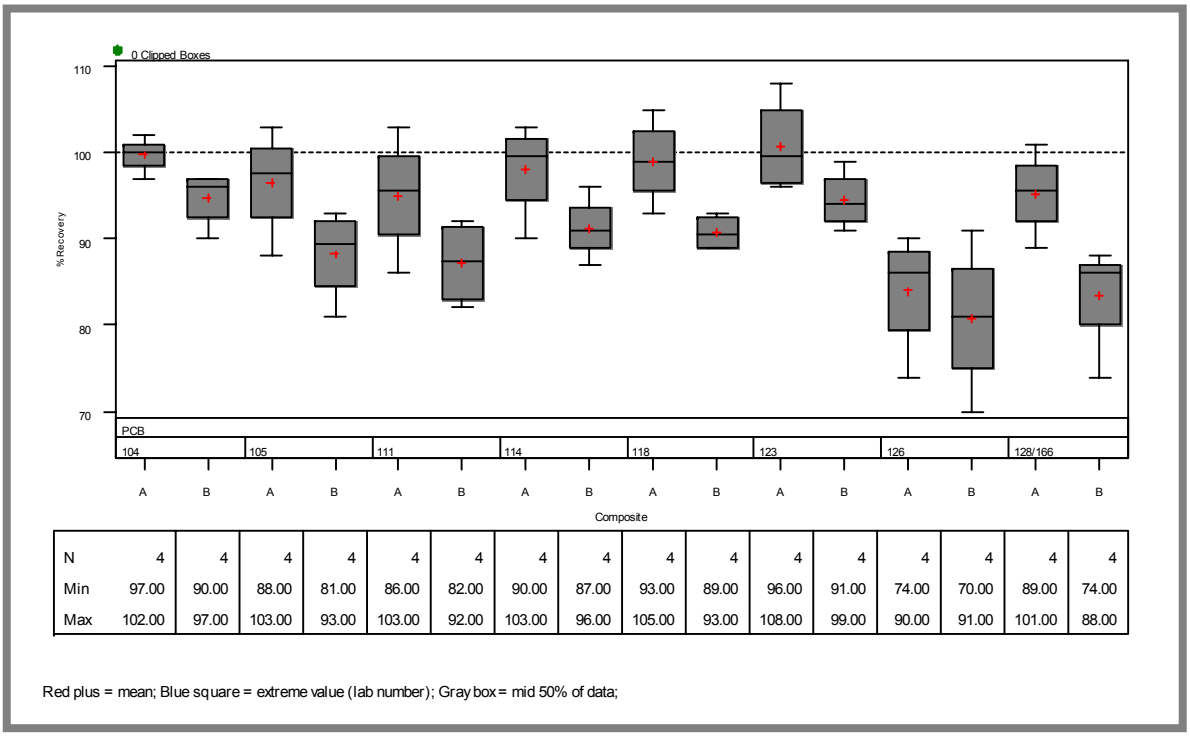


Figure 5-13
Percent Recovery Box Plots of PCBs in Wastewater (104, 105, 111, 114, 118, 123, 126, and 128/166)

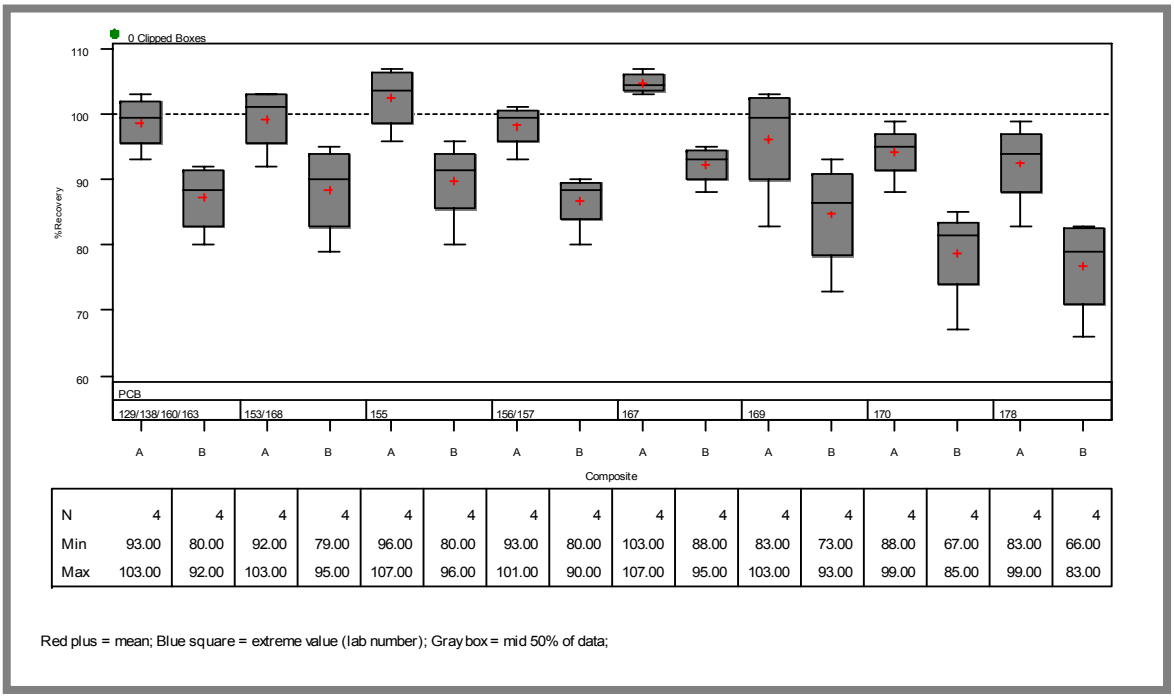


Figure 5-14
Percent Recovery Box Plots of PCBs in Wastewater (129/138/160/163/, 153/168, 155, 156/157, 167, 169, 170 and 178)

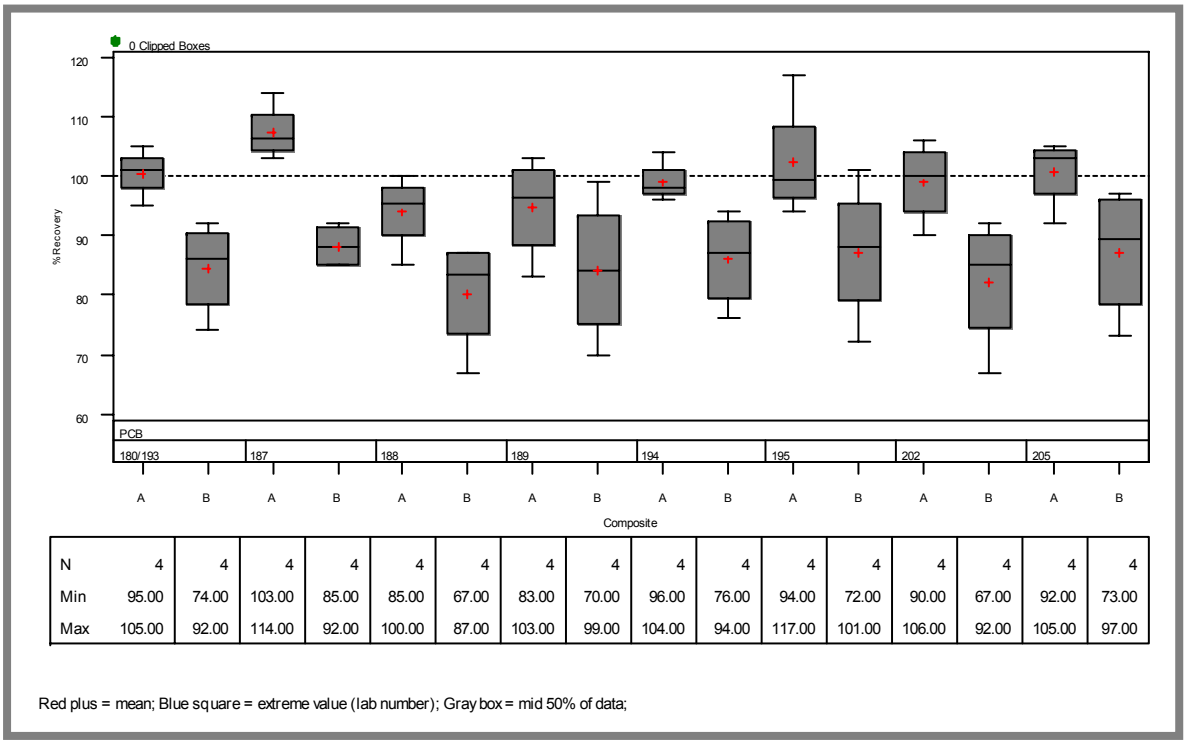


Figure 5-15
Percent Recovery Box Plots of PCBs in Wastewater (180/193, 187, 188, 189, 194, 195, 202, and 205)

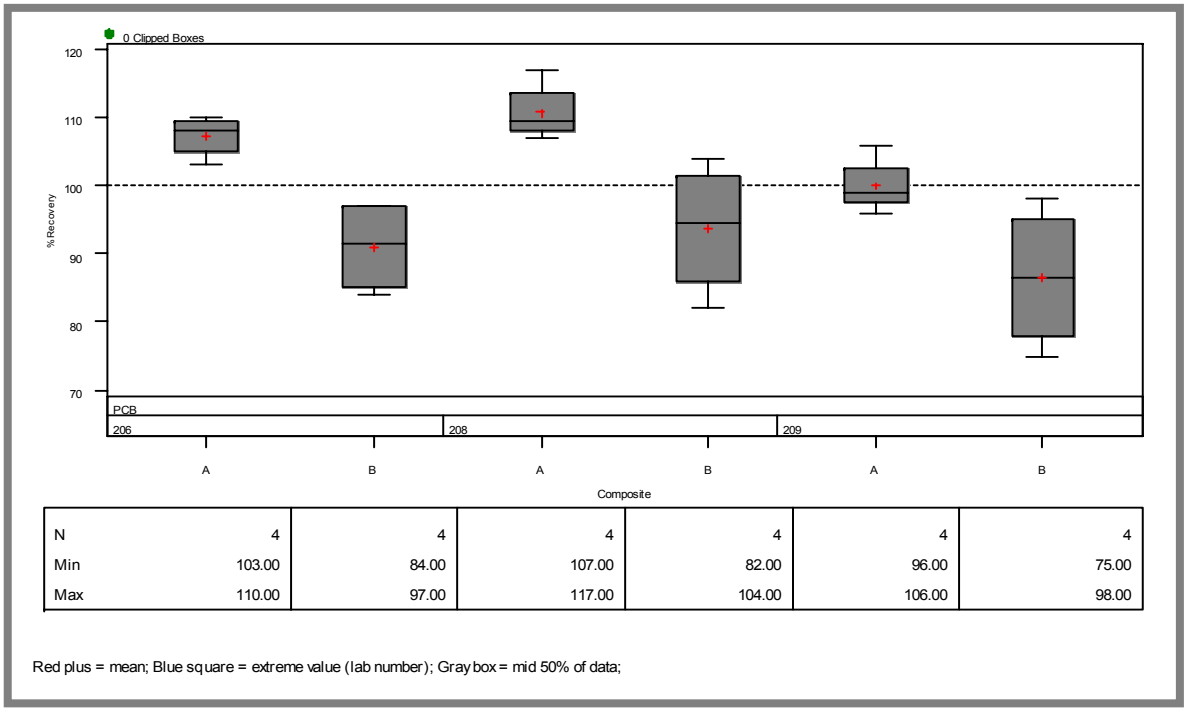


Figure 5-16
Percent Recovery Box Plots of PCBs in Wastewater (206, 208, and 209)

Table 5-6
Wastewater Mean Model Estimates for Target PCB List

PCB	Degrees of freedom	Likelihood ratio test R–squared	Wastewater A		Wastewater B	
			Mean recovery model	95% CL of the intercept	Mean recovery model	95% CL of the intercept
1	6	0.9579	24.18+0.85x	(–84, 132)	57.35+0.74x	(–51, 166)
3	6	0.9260	26.64+0.81x	(–128, 181)	94.49+0.57x	(–60, 249)
4	4	0.9998	5.40+1.04x	(–13, 24)	2.98+1.09x	(–16, 22)
8	6	0.9957	10.06+0.89x	(–42, 62)	34.49+0.86x	(–17, 86)
9	4	0.9949	17.88+0.87x	(–59, 95)	58.17+0.82x	(–19, 136)
15	6	0.9981	38.80+0.96x	(–21, 98)	11.59+1.04x	(–48, 71)
18/30	6	0.9913	23.82+0.86x	(–113, 161)	19.98+0.89x	(–117, 157)
19	5	0.9993	4.67+1.11x	(–19, 28)	6.54+1.10x	(–12, 25)
20/28	6	0.9987	13.11+0.95x	(–41, 67)	42.25+0.91x	(–11, 96)
37	6	0.9949	–19.82+0.93x	(–92, 53)	–1.10+0.92x	(–74, 71)
52	6	0.9941	30.81+0.86x	(–15, 77)	27.35+0.87x	(–19, 73)
54	5	0.9999	6.33+0.96x	(–14, 27)	–5.16+0.96x	(–20, 10)
66	5	0.9982	–0.89+1.03x	(–37, 35)	13.85+0.98x	(–14, 42)
77	5	0.9925	25.98+0.81x	(–57, 109)	11.77+0.85x	(–53, 76)
81	4	0.9925	–51.67+0.91x	(–216, 113)	–16.33+0.89x	(–181, 148)
90/101/113	6	0.9973	–21.31+0.90x	(–222, 179)	3.33+0.82x	(–197, 204)
104	4	0.9998	5.09+1.00x	(–19, 29)	5.88+0.95x	(–18, 30)
105	4	0.9962	2.03+0.98x	(–54, 58)	–15.09+0.91x	(–71, 40)
111	4	0.9975	4.86+0.97x	(–62, 72)	27.14+0.84x	(–40, 94)
114	4	0.9995	–1.19+1.00x	(–35, 33)	11.18+0.90x	(–23, 45)
118	5	0.9980	13.61+0.99x	(–29, 56)	–6.33+0.92x	(–61, 49)
123	4	0.9968	34.66+0.96x	(–52, 121)	4.65+0.94x	(–82, 91)
126	4	0.9960	–55.33+0.90x	(–184, 73)	–2.00+0.81x	(–130, 126)

Table 5-6 (continued)
Wastewater Mean Model Estimates for Target PCB List

			Wastewater A		Wastewater B	
PCB	Degrees of freedom	Likelihood ratio test R–squared	Mean recovery model	95% CL of the intercept	Mean recovery model	95% CL of the intercept
128/166	5	0.9991	10.60+0.96x	(–63, 84)	–9.54+0.87x	(–104, 85)
129/138/160/163	6	0.9976	11.26+0.99x	(–141, 163)	23.97+0.88x	(–128, 176)
153/168	6	0.9988	15.90+0.99x	(–46, 78)	26.84+0.87x	(–35, 89)
155	4	0.9987	15.71+1.01x	(–35, 67)	6.17+0.91x	(–45, 57)
156/157	5	0.9999	–28.86+1.02x	(–55, –3)	–15.89+0.90x	(–36, 4)
167	4	0.9997	12.97+1.03x	(–14, 40)	–11.88+0.95x	(–38, 15)
169	4	0.9950	–61.00+1.03x	(–221, 99)	–30.00+0.88x	(–190, 130)
170	5	0.9988	–4.47+0.95x	(–50, 41)	–30.67+0.83x	(–94, 33)
178	4	0.9950	–42.00+0.98x	(–172, 88)	–26.33+0.80x	(–156, 104)
180/193	6	0.9943	–2.86+1.01x	(–100, 94)	8.08+0.85x	(–89, 105)
187	6	0.9969	8.99+1.06x	(–27, 45)	14.26+0.85x	(–22, 51)
188	4	0.9983	3.87+0.96x	(–51, 58)	16.02+0.81x	(–39, 71)
189	4	0.9947	21.77+0.94x	(–80, 123)	53.99+0.78x	(–47, 155)
194	4	0.9961	16.46+0.96x	(–56, 89)	26.93+0.83x	(–45, 99)
195	4	0.9892	22.86+1.01x	(–103, 149)	23.83+0.87x	(–102, 150)
202	4	0.9930	–41.00+1.04x	(–212, 130)	–38.67+0.86x	(–210, 132)
205	4	0.9932	–48.67+1.06x	(–216, 118)	–28.33+0.91x	(–195, 139)
206	4	0.9963	26.68+1.02x	(–47, 100)	37.43+0.85x	(–36, 111)
208	4	0.9969	18.10+1.10x	(–88, 124)	54.18+0.89x	(–52, 161)
209	6	0.9852	21.01+0.97x	(–76, 118)	39.18+0.82x	(–58, 137)

CL = confidence limit

Table 5-7
Comparison of Results for the Two Unspiked Wastewater Samples to the IDE and IQE

PCB	Waste-water A (pg/L)	Waste-water B (pg/L)	Lab method blank (pg/L)	IDE (pg/L)	IQE10% (pg/L)	IQE20% (pg/L)	IQE30% (pg/L)
1	2.6	2.7	3.3	36.7	.	59.9	36.2
3	2.4	2.4	4.1	32.3	.	63.3	34.1
4	U	U	U	3.03	11.6	3.21	2.51
8	8.7	2.8	3.9	0.39	.	0.93	0.41
9	U	U	U	22.1	.	37.9	21.0
15	18.6	4.0	U	67.3	.	136.1	71.6
18/ 30	4.5	3.9	3.5	158	.	.	168
19	0.56	1.6	1.0	14.9	.	27.5	15.0
20/ 28	12.2	5.7	4.7	31.9	.	65.3	35.4
37	4.0	1.3	1.7	13.2	.	33.3	15.4
52	8.5	8.3	5.7	82.5	.	204	95.5
54	U	0.67	U	2.8	44.2	3.4	2.4
66	<2.8	2.5	3.0	24.8	.	97.2	29.4
77	<1.1	0.78	1.1	11.2	.	22.8	12.2
81	U	U	U	5.66	.	14.0	6.7
90/101/113	6.3	4.2	2.3	110	.	212	116
104	U	U	U	11.4	.	16.1	10.5
105	<3.0	<1.3	1.2	34.7	.	65.9	36.9
106	U	U	U	10.5	.	14.6	9.2
111	U	U	U	9.24	.	20.0	10.3
114	U	U	U	79.4	.	150.8	84.5
118	7.3	<4.1	2.3	3.40	.	13.0	4.68
123	U	U	0.63	12.7	.	22.5	13.1
126	U	U	U	28.4	.	53.1	29.4
128/166	1.0	U	U	28.4	693	68.9	36.4
129/138/160/163	8.0	4.7	2.1	125	.	392	149
153/168	5.9	3.9	2.1	99.5	.	204	108
155	U	U	U	7.71	.	10.7	6.95
156/157	<1.5	0.82	0.82	27.9	.	58.6	29.9
167	U	U	U	15.8	.	33.9	17.4

Table 5-7 (continued)
Comparison of Results for the Two Unspiked Wastewater Samples to the IDE and IQE

PCB	Waste-water A (pg/L)	Waste-water B (pg/L)	Lab method blank (pg/L)	IDE (pg/L)	IQE10% (pg/L)	IQE20% (pg/L)	IQE30% (pg/L)
169	U	U	0.54	8.63	.	17.9	9.56
170	1.7	<1.2	0.66	36.5	.	102	41.7
178	U	<0.85	U	31.2	.	.	.
180/193	4.7	1.8	1.4	60.1	.	130	65.7
187	2.3	1.5	0.62	31.0	.	64.9	33.2
188	U	U	U	5.69	.	14.3	6.83
189	U	<0.76	U	11.1	.	22.7	12.1
194	<1.3	<0.71	U	49.1	.	229	61.3
195	U	U	U	12.6	.	.	19.9
202	U	U	U	10.9	.	17.7	10.7
205	U	U	0.54	15.5	.	34.9	17.7
206	<1.9	<1.2	1.3	74.1	.	254	90.8
208	U	U	U	17.0	.	716	26.1
209	2.0	1.4	1.1	0.28	.	.	3.08

U = No PCB detected at or above 2.5 times signal to noise ratio.
" . " = Not calculated by statistical model.
"< " = PCB concentration cannot be confirmed at or below this concentration due to matrix interference or other data qualifier (EMPC).

Method blank values are the average concentration found for two batches in which the wastewaters were analyzed, except in a few cases where only one of the two method blanks had a reportable PCB, then the single value is listed.

5.2.2.3 Matrix Effect

The results of the analysis of covariance to assess matrix effect on PCB recovery are shown for the 44 target PCB peaks in Table 5-8 and for all congeners in Appendix L. Scatter plots of measured versus spiked concentrations with separate regression lines for reagent water and combined wastewater, are also shown in Appendix L. The matrix effect comparison was based on reagent water and wastewater results from the same laboratory, but the analyses were performed on different dates.

Table 5-8
Matrix Effect Evaluation for 44 Target PCBs

PCB	Slope of Spike Recovery		P-value[a]	Significantly different slopes
	Reagent water	Waste water		
1	1.08	0.773	<.0001	*
3	1.07	0.655	<.0001	*
4	1.06	1.066	0.9024	
8	0.955	0.867	0.1835	
9	0.928	0.847	0.0032	*
15	1.09	0.998	0.0019	*
18/ 30	0.742	0.871	0.0165	*
19	1.17	1.101	0.0213	*
20/ 28	0.926	0.926	1	
37	0.869	0.93	0.0122	*
52	0.829	0.849	0.7912	
54	0.997	0.96	0.0132	*
66	0.910	1.001	0.0016	*
77	0.875	0.828	0.0423	*
81	0.852	0.899	0.1018	
90/101/113	0.818	0.865	0.0903	
104	1.03	0.974	0.0066	*
105	0.891	0.949	0.0501	
111	0.752	0.903	<.0001	*
114	0.822	0.951	<.0001	*
118	0.801	0.95	<.0001	*
123	0.825	0.948	0.0006	*
126	0.917	0.855	0.0374	*
128/166	0.910	0.914	0.8926	
129/138/160/163	0.881	0.934	0.0734	
153/168	0.738	0.927	<.0001	*
155	0.857	0.963	0.0002	*
156/157	0.900	0.962	0.0077	*
167	0.870	0.99	<.0001	*
169	1.02	0.954	0.0906	
170	0.952	0.889	0.151	
178	0.877	0.888	0.8008	
180/193	0.936	0.931	0.9222	
187	0.918	0.954	0.5873	
188	0.864	0.882	0.5206	
189	0.904	0.864	0.2514	
194	0.937	0.898	0.2281	
195	0.918	0.939	0.7567	
202	0.847	0.951	0.0152	*
205	0.903	0.985	0.0535	
206	0.919	0.936	0.7516	
208	0.871	0.993	0.0231	*
209	0.924	0.885	0.5093	

[a] Significance level of difference in slopes.
[b] The "*" indicates that the two slopes are statistically different at the 5% significance level.

Figure 5-17 illustrates this approach for PCB 1. The smaller slope for the wastewater samples in this plot indicates that this congener was not recovered as completely from wastewater as from reagent water, particularly at higher spike levels. For this congener, the two slopes of 1.079 (reagent water) and 0.773 (wastewaters), are statistically different at the 5% significance level (p-value < 0.0001). Table 5-8 shows the calculated slopes and p-values for the 44 target PCBs. The last column in Table 5-8 indicates whether the slopes are statistically different at the 5% significance level (as indicated by the '*'). Twenty-two of the 44 target PCBs had significantly different slopes in wastewater and reagent water. Of these, 13 PCBs had higher slopes in the wastewater matrix and 9 PCBs had higher slopes in the reagent water. Thus, there does not appear to be a consistent difference in performance for the two matrices. The differences that were observed appear to have no practical significance because the method calibration criteria allow a variance of 70% to 130%.

Matrix effect was also evaluated based on internal standard recoveries. In Method 1668A, isotopically-labeled internal standards for a representative group of PCBs are added to each sample prior to extraction. These internal standards are chemically identical to the corresponding native PCB, except for a slight difference in mass number. The internal standard is used to calculate the concentration of the associated unlabeled or native PCB, and to serve as a quality control check on method performance. Internal standard recoveries are required to fall within specific data quality objectives specified in the method.

Table 5-9 presents a summary of the internal standard recoveries for all samples within the wastewater and reagent water sample sets. Both sample sets were analyzed by the same laboratory. These results show that both sets of data were within method specifications for internal standard recovery (25% to 150%), comparable in precision (expressed as relative standard deviation), and showed good agreement between mean values (generally within 20% difference of one another). Of the 31 labeled congeners, 14 had better average recovery in wastewater while 17 had better average recovery in reagent water. There was no discernable pattern of increased or decreased recovery with chlorination level.

Lower recovery for PCBs of lesser molecular weight (e.g., monochlorinated PCBs) may be attributed to higher vapor pressures for these chemicals and subsequent loss during evaporative steps of the procedure or possibly other causes. Method 1668A allows recoveries as low as 15% for mono-chlorinated labeled compounds in samples.

Based on these analyses, the two ash pond water composites tested in this study do not appear to have any significant matrix effect on the performance of Method 1668A that would cause results to be outside control limits specified in the method. However, as shown by the test results in Table 2-4, these two ash pond wastewaters do not represent a complex matrix that would be expected to interfere in this analysis. Specifically, the samples had low levels of total organics and dissolved solids. Ash ponds that receive inputs from flue gas desulfurization systems or other higher-strength sources would likely pose a greater challenge to the method.

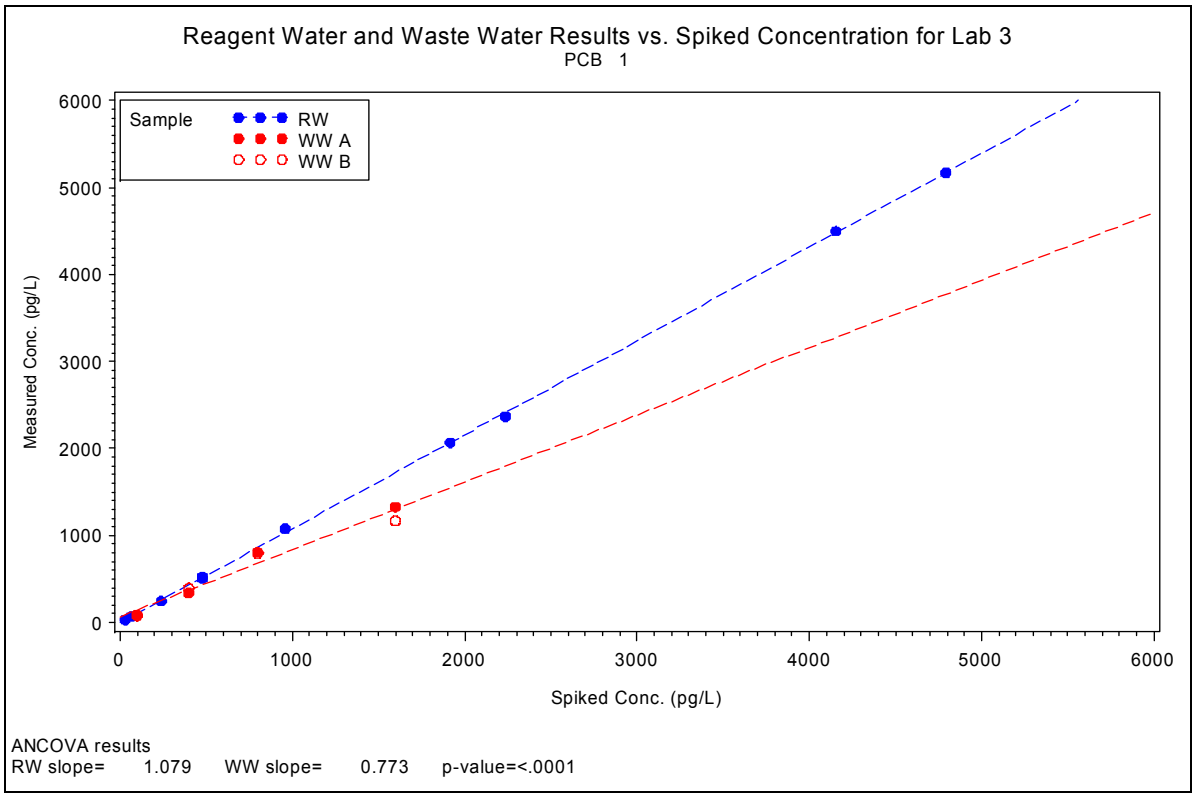


Figure 5-17
Measured Versus Spiked Concentrations for PCB 1 in Reagent Water and Wastewater Samples

Table 5-9
Comparison of Internal Standard Recoveries: Reagent Water and Wastewater

IUPAC No.	Wastewater (WW) % recovery (n=11)			Reagent water (RW) % recovery (n=11)			Difference Avg.(RW) - Avg.(WW)
	Avg.[b]	Std. dev.[c]	RSD[d]	Avg.[b]	Std. dev.[c]	RSD[d]	
1L[a]	39	8.2	21%	36	4.5	13%	-3
3L	38	7.1	19%	34	4.6	13%	-4
4L	41	8.4	20%	36	4.6	13%	-5
15L	47	6.9	14%	40	4.6	12%	-7
19L	51	8.1	16%	41	6.4	15%	-10
28L	57	8.7	15%	53	7.3	14%	-4
37L	58	5.1	9%	54	4.8	9%	-4
54L	47	6.5	14%	49	5.2	11%	2
77L	76	6.1	8%	63	4.6	7%	-13
81L	75	5.6	7%	59	4.8	8%	-16
104L	55	5.0	9%	63	8.1	13%	8
105L	83	5.4	7%	72	3.5	5%	-11
111L	79	5.1	7%	75	7.0	9%	-4
114L	80	5.3	7%	67	3.8	6%	-13
118L	82	5.2	6%	70	3.2	5%	-12
123L	82	5.3	6%	69	3.5	5%	-13
126L	84	7.0	8%	69	4.8	7%	-15
155L	58	4.7	8%	71	7.2	10%	13
156L / 157L	77	4.6	6%	79	2.6	3%	2
167L	78	4.6	6%	80	2.5	3%	2
169L	77	5.9	8%	76	3.4	5%	-1
170L	81	5.1	6%	84	7.3	9%	3
178L	86	3.9	5%	87	9.3	11%	1
180L	79	5.0	6%	82	6.5	8%	3
188L	64	4.0	6%	83	5.3	6%	19
189L	82	5.3	6%	79	4.6	6%	-3
202L	73	2.8	4%	93	11.6	12%	20
205L	76	3.7	5%	83	1.9	2%	7
206L	74	2.5	3%	83	5.3	6%	9
208L	76	2.8	4%	83	6.6	8%	7
209L	71	3.6	5%	90	10.4	11%	19

a. L = Isotopically labeled PCB.
b. Average recovery of all wastewater or reagent water samples.
c. Standard deviation of mean.
d. Precision, expressed as relative standard deviation (RSD).

5.3 Background PCB Levels

Historical blank data were provided by seven of the nine laboratories participating in the study. The laboratories were requested to provide the last 10 method blanks or those completed over the previous 6 months; however, the number of blank analyses reported per laboratory ranged from 3 to 12, while the number of actual data points per PCB varied greatly; only a single detection was reported for some congeners. If a specific PCB congener was not detected in the method blank, the laboratory did not report a value for that congener. Therefore, the EMDL values listed in Table 5-10 vary significantly in number of actual values reported and only include reportable

numbers provided by the laboratory. Because the historical data submittals provided to EPRI were not well documented with quality control/quality assurance data, these results were not independently validated. For example, one laboratory (Laboratory No. 5) had markedly higher blank contamination levels than the others, but only provided three method blanks representing samples analyzed over about a 3-year period.

For each of the 44 target PCBs, Table 5-10 lists the mean concentration plus two standard deviations and number of historical blanks reported by each laboratory. These data represent PCB concentrations recorded over an extended period by each laboratory, but may not reflect long-term background variability. Appendix M provides EMDL values for all PCBs historical data provided by the laboratories. The calculated EMDLs for the interlaboratory study method blanks and unspiked reagent water samples are shown for comparison, along with the 95% upper confidence limit of the statistically-derived intercept and the IDE concentration.

EMDLs calculated from the historical method blanks exceeded IDE and IQE values in many instances:

- Thirty-one (31) of the 44 target PCBs had one or more lab-specific EMDLs greater than the IDE. If Laboratory 5 is excluded from the data set, 21 of the 44 congeners exceeded the IDE.
- Twenty-one (21) of the 44 target congeners had one or more lab-specific EMDLs greater than the IQE20%. If Laboratory 5 is excluded from the data set, 10 of the 44 congeners exceeded the IQE20%.

These data comparisons suggest that:

- A positive method blank result produced by a laboratory may be related to PCB background rather than indicative of PCB native to the sample.
- Statistically based interlaboratory quantitation and detection limits cannot be achieved routinely for all 209 congeners by a population of well-performing laboratories, due to frequent detections of congeners in method blanks at levels exceeding the IDE and IQE. PCB background contamination represents a significant limitation to the use of this method.
- Background levels vary by laboratory and by PCB. Some laboratories are capable of maintaining very low blank levels (under 10 pg/L), while others have much higher background levels for specific congeners.

Table 5-10
Summary of PCB Background Estimates (pg/L)

	Historical blank data EMDL (mean + 2s)							EPRI Interlaboratory study EMDL (mean + 2s)		Statistically-derived values	
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Laboratory reported method blanks	Unspiked reagent water		
No. analyses reported:	12	12	10	10	3	6	6	10	8		
PCB IUPAC#										Upper 95% CL of intercept	IDE
1	7	13	10	44	•	5	3	45	35	13.5	36.7
3	6	10	8	•	1048	12	4	20	28	9.33	32.3
4	161 *	63	25	• *	35	•	3	51	•	14.9	3.03
8	34 *	54	51	• *	71	•	3	146 *	97	7.42	0.39
9	• *	37	•	• *	•	•	•	•	3	7.16	22.1
15	186	27	25	•	33	•	3	•	2	20.8	67.3
18	25	45 *	32 *	35	71 *	6	4 *	63 *	91 *	43.2 *	158 *
19	•	•	4	•	9	2	3	12	17	8.39	14.9
28	18	34 *	79 *	•	218 *	9 *	4 *	107 *	135 *	10.5 *	31.9 *
37	10	•	21	•	37	3	1	11 *	28 *	3.64	13.2
52	41 *	17	63	28 *	489	14	5	69	87	44.8	82.5
54	11	•	•	•	•	•	2	•	11	0.95	2.8
66	9 *	17	42	• *	125	7	3	31	39	9.45	24.8
77	2	•	5	9	16	5	1	18	19	1.46	11.2
81	1	•	•	3	•	•	2	4	9	< 0.00	5.66
101	20 *	27 *	134 *	• *	451 *	100 *	5 *	67 *	131 *	43.4 *	110 *
104	2	•	•	•	•	•	3	•	17	1.24	11.4
105	5 *	•	17	6	106	45	2	48	49	9.94	34.7
111	5 *	•	•	• *	•	•	•	•	10	0.53	10.5
114	2	•	•	•	•	2	2	•	9 *	1.69	9.24
118	14 *	21	54	11 *	256	69	4	62	87	23.9	79.4

Table 5-10 (continued)
Summary of PCB Background Estimates (pg/L)

	Historical blank data EMDL (mean + 2s)							EPRI Interlaboratory study EMDL (mean + 2s)		Statistically-derived values	
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Laboratory reported method blanks	Unspiked reagent water		
No. analyses reported:	12	12	10	10	3	6	6	10	8		
PCB IUPAC#										Upper 95% CL of intercept	IDE
123	1	•	•	•	30 *	•	1	• *	22 *	2.60	3.40
126	1	•	•	5	•	3	1	1	10	1.29	12.7
128	5	•	17 *	• *	49 *	27 *	• *	10 *	43 *	4.30 *	28.4 *
138	15 *	36 *	163 *	• *	322 *	135 *	4 *	70 *	145 *	33.5 *	28.4 *
153	26	8 *	278 *	•	294 *	64 *	4 *	42 *	101 *	92.4	99.5
155	1	•	•	•	•	•	5	•	7	29.4	7.71
156	1	•	11 *	5	45 *	10 *	2 *	15 *	22 *	5.03 *	27.9 *
157	1	•	11 *	5	45 *	10 *	2 *	15 *	22 *	5.03 *	27.9 *
167	3	•	6	•	20	5	1	5	9	1.87	15.8
169	3	•	•	10	20	•	1	38	20	2.25	8.63
170	10 *	•	103	•	27	8	2	85	23	10.3	36.5
178	•	•	15	•	11	•	•	48	12	9.33	31.2
180	44	10 *	325 *	•	69 *	10 *	2 *	576 *	112 *	21.6 *	60.1 *
187	23 *	11	65	• *	65	11	2	367 *	29	13.5	31.0
188	•	•	•	•	•	•	3	•	8	0.49	5.69
189	1	•	8	3	38	•	1	15	8	2.50	11.1
194	29	•	76	•	18	•	1	354	134	14.4	49.1
195	2	•	7	•	4	•	•	121	7	2.90	12.6
202	3	•	30	•	•	•	2	29	13	1.68	10.9
205	2	•	1	•	46	•	•	22	11	1.84	15.5
206	11	•	16	•	62	•	•	629	145	14.2	74.1
208	2	•	•	•	15	•	6	43	20	3.30	17.0
209	4	•	60	•	49	3	2	32	13	3.71	0.28

• No PCB detected or reported by laboratory; actual reportable values may vary between one and total number of analyses.
* Reported as highest value within a group of coeluting PCBs that includes the listed PCB. The individual PCB value is not reported.
* CL = confidence limit

Method 1668A specifies in Section 9.1.2.1 that a laboratory may modify the method to improve performance or lower costs. However, each time the method is modified, the laboratory is required to repeat the Initial Precision and Accuracy procedure (in Section 9.2 of the method) to demonstrate that the change in performance is equivalent or superior to the method as written. If the detection limit of the Method is affected by the change, the laboratory is required to demonstrate that the resultant MDLs (as determined by the 40CFR Part 136, Appendix B process) are lower than one-third the regulatory compliance level or one-third the EMDLs of Method 1668A, whichever is greater. Figure 6-1 below shows a direct comparison of the Method 1668A EMDLs, the calculated one-third EMDLs, and the IDEs determined from the EPRI study for the target PCB congeners or congener groups. This chart shows that 40 of the 44 target PCB congeners/congener groups (~91%) were below the corresponding one-third EMDL value.

This comparison suggests that a qualified laboratory should be able to achieve IDEs that are one-third of the EMDL for a majority of representative PCB congeners or congener groupings, but a few congeners may not achieve IDEs at the one-third of the EMDL level.

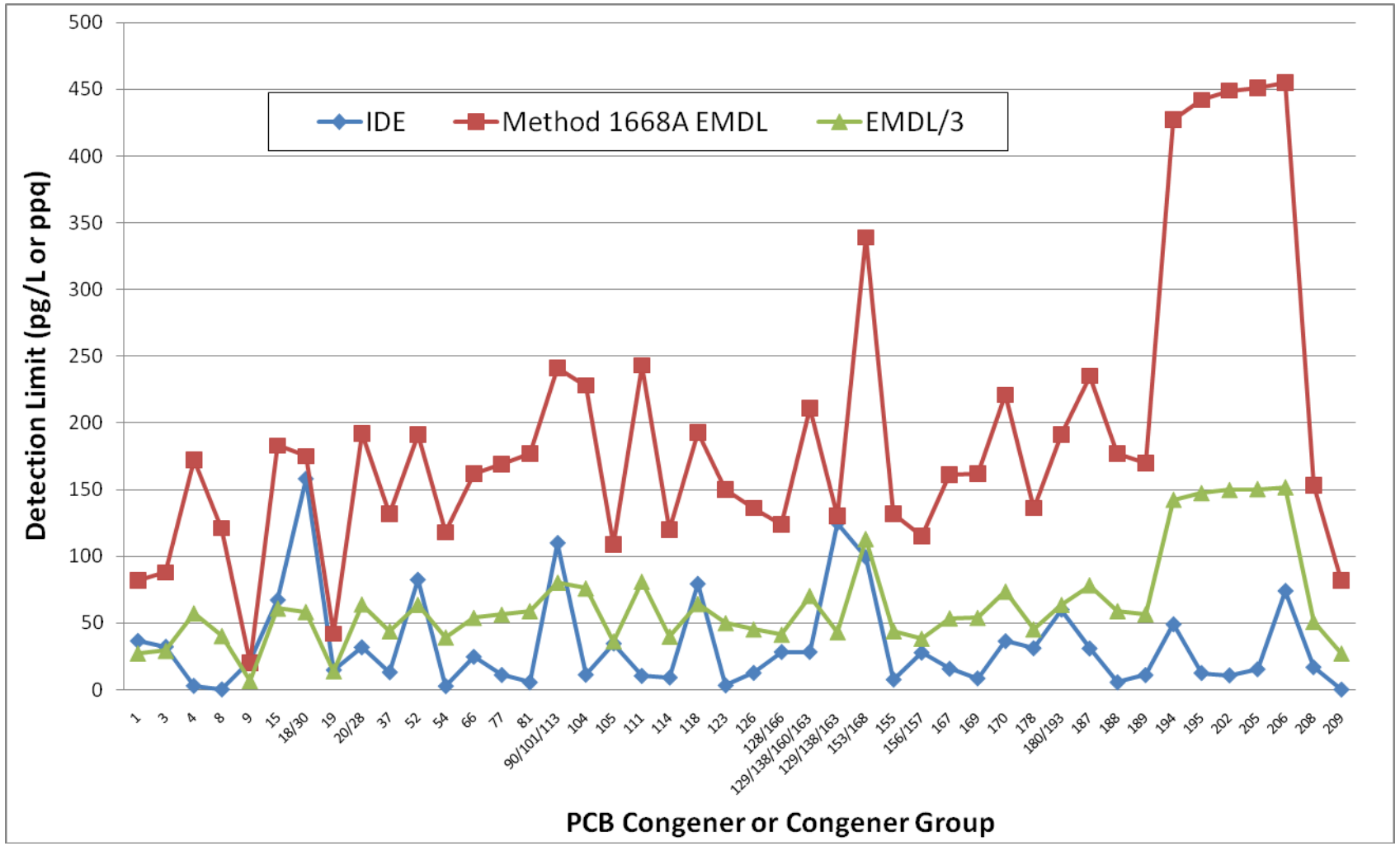


Figure 5-18
Comparison between Method 1668A EMDL Concentrations, One-third EMDL, and EPRI Study IDE Values

6
SUMMARY AND CONCLUSIONS

This section summarizes the findings of the study pertaining to the study objectives and significant findings and conclusions derived from the study data.

Due to the large amount of test data generated from this study, the discussion of results is focused on 44 of the 209 PCBs, either as a individual PCB or as part of a congener group. These "target" PCBs were selected for technical reasons (e.g., first and last eluting congeners of each homolog series) or because the specific PCB was listed by the WHO or NOAA as chemicals of toxic or environmental concern. Detailed sample results and statistics for the 209 PCBs are provided in Volume II.

6.1 Validation of Method Performance

EPA Method 1668A achieved the method performance criteria for accuracy and precision within the parameters of this study for both the reagent water and the two ash pond wastewater composite samples.

The Method requires a laboratory to perform an initial precision and accuracy demonstration with at least four PCB spiked water samples to establish that the laboratory can meet an acceptance criterion of 40% relative standard deviation (RSD) for precision. With few exceptions, the overall relative standard deviation for PCB spiked reagent water in this study also achieved a precision of 40% RSD or better at concentrations ranging from about 25 pg/L to 15,000 pg/L.

The Method was tested on two composite wastewater samples, consisting of ash pond wastewater from coal-fired power plants. From a single-laboratory test, method recovery, precision, and detection were evaluated relative to the interlaboratory statistics. Over a spiked PCB concentration range of about 100 pg/L to 2,000 pg/L, accuracy results were within the method objective (50% to 150%). Precision, as measured by duplicate spiked PCBs at concentrations of 500 pg/L and 2,000 pg/L, were all within 30% relative percent difference (RPD) at the lower concentration, and less than 22% RPD at the higher concentration. These results met the Method 1668A precision objective of 40% RSD.

Matrix effects resulting in significantly different spike/recovery slopes were observed for 22 of the 44 target PCBs. However, the direction of the slope difference was not consistent among these PCBs, and there is no indication that, across all of the 209 congeners, that the method performed more poorly in the wastewater matrix.

These findings show that Method 1668A can achieve the quality control limits in the method for both clean reagent water and chemically un-complex ash pond water matrices, within the range of concentrations tested. The study samples did not extend to the maximum working range of the method.

Statistically based interlaboratory quantitation and detection limits cannot be achieved consistently for all 209 congeners by a population of well-performing laboratories, due to frequent detections of congeners in method blanks at levels exceeding the IDE and IQE. The presence of background contamination poses a significant limitation on use of the method.

6.2 Applicability and Limitations of Study Results

For this study, the IDE/IQE values were developed using high-purity reagent grade water as the test matrix. The use of this test matrix was intended to demonstrate performance of the method under ideal conditions. The interlaboratory study design did not address method performance in "real world" samples. Real world samples, such as surface water and many industrial wastewaters, would be expected to differ from reagent water in chemical properties (pH, alkalinity, matrix complexity, presence of interferents), biological activity, and in the number and type of modifiers present, such as suspended / dissolved solids, dissolved organic matter, organic and soot carbon, and surfactants. These added components would most likely degrade method performance and produce higher detection and quantitation limits.

The evaluation of method performance on the ash pond wastewaters was performed using two composite samples that may not be representative of other ash ponds. In particular, the levels of potentially interfering substances in the samples (dissolved solids, organic compounds) were very low. In applying the results of this study to other power plant ash pond wastewaters, it would be prudent to examine the water characteristics to see if they are similar in composition.

Other differences between this study and "real world" conditions may have influenced the results and conclusions of the study:

- The majority of the 44 target PCBs or groups (27 or 61%) are quantified by the isotope dilution technique, compared to 13% of all congeners (27 of 209). In general, the use of isotope dilution technique provides more precise data and helps correct for any matrix effect. Therefore, the relative accuracy of the 44-PCB subset is likely to be better than that of the remaining congeners.
- The process used to select the laboratories used in the study was designed to obtain labs with a high level of expertise. The eight test laboratories selected were considered to be well qualified in conducting the method. The results of this study would be expected to compare more favorably versus results produced by laboratories with less expertise.
- The laboratories were required to use the same chromatographic column and to report all method modifications. As this method is performance-based, a wider range of practices would be acceptable in practice. The restrictions imposed in this study result in more consistent results (lower interlaboratory variability) than would be found in actual monitoring applications.

6.3 Evaluation of Detection and Quantitation Levels

Numerous approaches have been used and suggested for determining detection and quantitation levels for analytical methods. This study evaluated results from two approaches: the ASTM IDE and IQE, and the EMDL and EML.

The IDE is designed to determine analyte concentrations associated with a set probability of false positive and false negative reporting. The IQE determines concentrations associated with a specific level of interlaboratory variability. The EMDL constitutes a practical limit on detection in the presence of laboratory interferences from background levels of PCBs. The EML is the practical level of reliability in the presence of laboratory background contamination.

Data from eight test laboratories were used to calculate IDEs and IQEs. IQEs were calculated for most PCB congeners and congener groups at the 20% and 30% RSD level; IQEs corresponding to a 10% RSD could not be calculated for most PCBs, indicating that this level of interlaboratory precision was not achievable by the method.

Comparing the calculated IDEs and IQEs with the Method 1668A requirements, the IDEs are significantly lower than the Method 1668A EMDL concentrations. Similarly, the IQE20% and IQE30% values are generally much lower than the Method 1668A EMLs. However, the IDEs were consistently higher (up to 158 pg/L) than the Method 1668A estimated detection values of 5 and 10 pg/L for samples without laboratory interferences.

Environmental and laboratory PCB background levels present a known difficulty for trace level analytical methods such as Method 1668A. This study provided an opportunity to measure PCB background concentrations across eight qualified laboratories using blind control samples (unspiked reagent water) and the laboratories' internal method blanks. The method blanks from the interlaboratory study (both known and blind to the laboratories) exhibited a significant number of detected PCBs. There were 326 PCBs detected out of 1,268 total possible reportable PCBs. These data identify a relatively high percentage (26%) of detected PCBs for a reagent water matrix—PCBs that either originated in the reagent water or were introduced during sample processing and analysis. The PCB congeners detected in the unspiked reagent water were generally the same as those detected in the method blanks, supporting a source in the laboratory environment. This finding supports the conclusion that false positive results may be reported in samples even under the best of conditions.

The EPRI study results are consistent with those reported in the EPA Interlaboratory Validation Report [3], in which the six reporting laboratories detected 231 PCBs out of 1136 reportable PCBs (a ~ 20% detection rate for PCBs) in a clean water matrix.

One approach used to evaluate the impact of laboratory background on the interlaboratory study data was to plot the linear relationship between the true sample concentration and the recovered (measured) concentration. Confidence intervals were calculated for the zero-intercept of the relationship, representing a true concentration (spike) of zero. If the lower 95% confidence limit (95% LCL) of the measured concentration exceeded zero, the presence of laboratory background was confirmed. By this analysis, only one of 44 PCB "target" congeners (and seven

of the full PCB congener list) was shown to have significant laboratory background across the complete interlaboratory study data set. However, the statistical analysis does not exclude the possibility that an average background contamination may exist.

Finally, historical method blank data obtained from seven laboratories were used to calculate laboratory-specific EMDLs, which represent upper bound estimates of background levels over three to twelve analytical batches and various time periods. The laboratory-specific EMDLs range from well below the IDE to well above the IQE. Of the 44 target congeners or congener groups, 31 had EMDLs above the IDE in one or more of the laboratories and 21 also had EMDLs above the IQE20% in one or more laboratories.

Several caveats must be made to the above comparison of the historical blanks and the EPRI study data. The laboratory EMDLs were calculated from the average of detected PCBs only (because detection limits were not provided by the laboratories), and are thus high estimates. The historical data were not validated by MRI or EPRI, were not equal in the number of blanks submitted across laboratories, and the labs generally did not submit ten or more blanks from different analytical batches, as specified in the EMDL procedure.

By contrast, the EPRI study data were collected under strictly controlled conditions, were subjected to validation to confirm their reliability, and were uncensored (i.e., labs were instructed to report any numerical value that complied with identification criteria set by Method 1668A). The laboratories were aware that they were participating in a large multilaboratory study, and thus may have taken steps to lower their blank levels for this study. The EPRI data represent a single analytical batch, and thus do not incorporate long-term variability. EMDLs based on the EPRI study data would therefore be expected to be much lower than those based on the historical blank data.

Background contamination varies significantly by laboratory. This is evident in the wide ranges of concentrations and frequencies of PCB detections in historical method blanks provided by the test laboratories. Background contamination can also be demonstrated by comparing method blank results with unspiked reagent water results from the same laboratory. In general, there were comparable detections and concentrations in the method blank (which the lab expects to be clean) and the reagent water blank (concentration blind to the laboratory). This trend shows that the detected low-level PCBs come from the laboratory environment rather than from the sample itself.

PCB laboratory background can vary over time due to changes in laboratory expertise, contamination of reagents or equipment, and other factors such as cross-contamination from highly contaminated samples. Therefore, EMDLs should be updated frequently from recent method blanks. A laboratory should demonstrate control of PCB background using both long-term quality control data and batch-specific blanks reported with the sample set. A qualified laboratory should reveal to their client if blank results indicate unacceptable contamination. Field blanks should be analyzed with each sample to help distinguish laboratory from sampling sources of contamination.

Results from this study indicate that, with current levels of laboratory background contamination, all samples analyzed by Method 1668A will have PCBs present at levels above noise-based, instrumental detection limits. This will pose a problem to facilities that have wastewater discharge limits that are set at "zero discharge of PCBs".

One approach to addressing this problem is to report blank-corrected concentrations in addition to uncorrected concentrations, as allowed by Section 17.6.1.4.4 of Method 1668A. However, the procedure specified in that subsection is of limited help when sample PCB concentrations are very low or blanks contamination is high. The procedure as stated in the Method allows laboratories to subtract blanks, but only when the sample concentration is "significantly above the blank level", and only if the resulting corrected concentration is greater than the corresponding EMDL. As blank contamination can often be a significant contributor to the total detected concentration, the provision as written will produce many false positive detections.

Method 1668A specifies (in Section 9.1.2.1) that a laboratory may modify the method to improve performance or lower costs. However, each time the method is modified, the laboratory is required to repeat the Initial Precision and Accuracy procedure (Section 9.2 of Method 1668A) to demonstrate that the change in performance is equivalent or superior to the method as written. If the detection limit of the Method is affected by the change, the laboratory is required to demonstrate that the resultant MDLs (as determined by 40CFR Part 136, Appendix B) are lower than one-third the regulatory compliance level or one-third the EMDLs of Method 1668A, whichever is greater. Results of this study showed that 40 of the 44 target PCB congeners/congener groups, or 89%, were below the one-third EMDL value. This suggests that a qualified laboratory should be able to achieve IDEs in clean water that are one-third the EMDL for a majority, but not all, of the representative PCB congeners or congener groupings.

The selection of a quantitation level for Method 1668A is critical for the use of this method in environmental compliance monitoring. The IQEs calculated in this study may be suitable for this purpose. To determine whether laboratories can achieve background levels below the IQE on a consistent basis will require developing a more adequate set of laboratory-specific EMDLs, calculated from the requisite number of method blanks over a longer time period, and analyzed under controlled conditions comparable to the EPRI study. This information is critical to the end user of the data in order to distinguish between typical background PCB and residual PCB from the test sample.

6.4 Data Defensibility

The following procedures were used to assure the accuracy and defensibility of the study data:

- Using reference methods and ASTM standards for development of the study design.
- Generating an appropriate number of data from representative qualified laboratories to ensure that the statistical analysis requirements were met.
- Incorporating quality control checks and verification analyses to ensure accuracy in preparation of the study samples.

- Conducting the study with many sources of random variability that would be expected to occur under normal testing conditions, such as different preparation days, different personnel, different reagents and preparatory equipment, and different analytical instrumentation.
- Utilizing technical review, validation, and data exploration techniques to identify outliers or excludable data points.
- Having external subject matter experts participate in the technical review of the study design and findings.

6.5 Recommended Future Work

This study evaluated method performance in reagent water using eight well qualified laboratories. The study also included a limited evaluation of method performance for coal-fired power plant ash pond wastewater. Further research would is needed to better understand the performance of the method when applied to environmental samples and across a larger pool of laboratories. Although it is not feasible to conduct a multilaboratory study on every environmental sample type of interest, the results of this study should provide a baseline against which a more limited test program can be measured. In particular, EPRI recommends the following additional research to more fully characterize method performance:

- Characterize PCB background concentrations by a larger set of individual laboratories, to provide more current and complete information on achievable background across the entire laboratory community.
- Evaluate method performance in a wider range of power plant wastewater types, as well as in ash pond waters with differing characteristics.
- Compare method performance obtained with environmental samples to those reported in this study. In particular, for samples with similar concentrations of PCBs to those in our study but higher levels of interfering non-PCB substances, determine the impact on the detection limits, congener co-elution patterns, and other factors that affect method performance.
- Evaluate method performance based on total PCBs, the parameter typically used for wastewater compliance monitoring, rather than only on a congener basis. The latter approach would provide information on method performance relevant to the use of the method for discharge compliance monitoring.
- Establish an improved methodology for blank correction of test results to assure with high probability that any PCB detected is or is not above background levels.

7
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8
VOLUME II - TABLE OF CONTENTS

Volume II contains the following Appendices:

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