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A Handbook for Determining the Sources of PCB Contamination in Sediments

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14. ABSTRACT

This handbook provides information on conducting environmental forensic investigations for polychlorinated biphenyls (PCBs) at sediment sites. The document includes a discussion of: 1) the general forensic approach including relevant background information and benefits to Department of Defense (DoD); (2) a general summary of the technical methods that are used in a PCB environmental forensics investigation; and (3) a summary of the application of the described procedures in two demonstration case studies.

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ACRONYMS AND ABBREVIATIONS

2D	two-dimensional
3D	three-dimensional
ACF	advanced chemical fingerprinting
ALS	alternating least square
CD	coefficient of determination
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
COPC	contaminant of potential concern
CSIA	compound specific isotopic analysis
CSM	conceptual site model
CSO	combined sewer overflow
DoD	United States Department of Defense
DQO	data quality objective
ECD	electron capture detection
EDA	exploratory data analysis
ELISA	enzyme-linked immunosorbent assay
EM	end-member
ER	environmental restoration
ESTCP	Environmental Security Technology Certification Program
FA	factor analysis
FCM	fuzzy-c-means
FS	feasibility study
GC	gas chromatography
GIS	geographic information system
GLLA	Great Lakes Legacy Act
GLNPO	Great Lakes National Program Office
GPS	global positioning system
HCA	hierarchical cluster analysis
HOC	hydrophobic organic contaminant
HPS	Hunters Point Shipyard
HRGC	high-resolution gas chromatography
HRMS	high-resolution mass spectrometer
IA	immunoassay
IC	instrument check
ID	identification
IUPAC	International Union of Pure and Applied Chemistry

LCS	laboratory control sample
LRMS-SIM	low resolution mass spectrometry-selected ion monitoring
LRMS	low-resolution mass spectrometer
MCR-ALS	multivariate curve resolution/alternating least square
MDL	method detection limit
ML	minimum level
MS	mass spectrometry
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NRMRL	National Risk Management Research Laboratory
ORD	Office of Research and Development
PAH	polycyclic aromatic hydrocarbon
PB	procedural blank
PBMS	performance based measurement system
PCA	principal component analysis
PCB	polychlorinated biphenyl
PCT	polychlorinated terphenyl
PMF	positive matrix factorization
ppb	parts per billion
ppm	parts per million
PVA	polytopic vector analysis
QA	quality assurance
QC	quality control
RI	remedial investigation
RL	reporting limit
RPD	relative percent difference
RPM	Remedial Project Manager
RSC	rapid sediment characterization
RSD	relative standard deviation
SFPUC	San Francisco Public Utilities Commission
SIS	surrogate internal standard
SRM	standard reference material
TMDL	total maximum daily load
TOC	total organic carbon
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plan
U.S. EPA	United States Environmental Protection Agency

WCSD	Watershed Contaminated Source Document
WHO	World Health Organization

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1.0 GENERAL FORENSICS APPROACH

1.1 Introduction

Defining the source of anthropogenic contamination from military facilities into sediments can be a difficult task. This is particularly true in waterways and coastal settings where multiple point sources are present along with persistent non-point sources such as urban background. This situation often results in complex mixtures of contaminants in sediments.

For sediment sites under the Environmental Restoration (ER) Program, Navy Remedial Project Managers (RPMs) are required to implement cleanup programs that include identifying the sources of contaminants at their sites; thus, there is a need for technical guidance on the application of techniques that can be used to determine these sources. Environmental forensics is a methodology to unambiguously identify the contamination and its source or sources.

This handbook provides information on conducting environmental forensic investigations for polychlorinated biphenyls (PCBs) at sediment sites and should give RPMs and their contractor's useful guidance to perform such studies. This document provides an overview of the site-specific information that is needed and the type of technical activities to be conducted. The approach described in this handbook includes the combined use of rapid screening technologies to characterize the distribution of sediment contamination and advanced chemical fingerprinting (ACF) on a subset of samples to more definitively identify sources. This provides a cost-effective, technically advanced, and defensible approach to characterizing the PCB contamination and its sources at a given site.

Handbook Roadmap

This handbook is intended to be a useful guide for determining when a forensics investigation of a PCB contaminated sediment site may be considered and is comprised of the following sections:

- **Section 1:** Summarizes the requirements of Navy policy for source identification at sediment sites and provides background information on PCBs and their analysis. It reviews a step-wise process for implementing environmental forensics as part of a contaminant source study. This section will be of interest to RPMs and contractors wanting to familiarize themselves with the use of environmental forensics for PCBs.

- **Section 2:** Provides more information on PCB chemistry and a summary of the techniques that are used in a PCB environmental forensics investigation. This section covers sample design, sample collection, analysis methods, data analysis, and reporting. While the site-specific information and technical resources required are discussed in detail, this handbook is not intended as a "how to" manual for the actual conduct of a forensics investigation.

- **Section 3:** Summarizes the application of two case study examples to demonstrate the methodology. Discusses both a remedial cleanup and a dredging project case study to provide RPMs with example case studies that may be useful for their sites.

1.1.1 Navy Policy for Source Identification

Determining the original source of contamination is a requirement for cleanup programs within the military. Understanding the source(s) of contaminants to a contaminated sediment site is a prerequisite to implementing any proposed sediment remedial options under cleanup programs [1]. This is because sources must be controlled prior to remedial efforts to ensure that recontamination can be avoided.

It is Navy policy on sediment site investigations and response actions to determine all sources of sediment contamination prior to the start of remediation efforts in order to eliminate ongoing sources that could re-contaminate a closed site and to ensure that government funding is directed towards cleaning up contamination from Navy sources [2]. Under Navy policy, sediment investigations and response actions performed under the ER Program must be directly linked to Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) contaminant releases. The term "directly linked" means that the sediment contamination is scientifically connected to a Navy ER site. Therefore, all potential sources of Navy and non-Navy contamination at a site should be identified. At complex sediment sites, it may be appropriate to apply ACF techniques to support this source determination.

It should also be noted that, consistent with Navy policy, ER Program funding can only be used to perform forensic studies for the purpose of identifying the presence of other sources and/or to verify if the Navy is a contributor. The forensic study can only identify sources as non-Navy or Navy and cannot name a potentially-responsible party. RPMs should consult with the appropriate legal representatives regarding this matter.

1.1.2 PCB Chemistry and Fate Overview

PCBs are not a single compound, but a class of chlorinated organic compounds comprised of a biphenyl backbone with substitutions of from one to 10 chlorine atoms. Although there are 209 possible unique patterns in which these chlorines can be substituted onto the biphenyl rings, in practice there are about 100 to 150 individual compounds (termed congeners) that are present in the PCB formulations that have been in use and found in environmental samples. This is because PCBs are generally released into the environment as a limited set of a few distinct mixtures of congeners, termed Aroclors. It should be noted that while the term "Aroclor" is often thought of as synonymous with "PCB," Monsanto manufactured non-PCB products that also carried their Aroclor trade name. Aroclor 5460 for example was a polychlorinated terphenyl (PCT) product. PCB Aroclors did, however, account for the majority of Monsanto Aroclor production, and the term Aroclor refers to PCB Aroclors throughout this handbook. Less than 10 PCB Aroclor formulations were widely used. They were manufactured for specific industrial uses in the US from the 1930s through the 1970s when production was banned. Old equipment containing PCBs are still in use today, and therefore releases to the environment are still occurring. In addition, contaminated upland sites and runoff from many industrial environments continue to contribute PCBs to aquatic systems. PCBs were also used in caulk, paint, sealants, gasket materials, and numerous other industrial applications, a few of which did not use Aroclor formulations but relied on individual PCB congeners or non-Aroclor mixtures.

Because of their stable and persistent nature, historic PCB contamination can be widely found. In addition, certain PCBs accumulate in fatty biological tissue and the food web. Bioaccumulating contaminants such as PCBs are a concern because past contamination in sediments may represent a continuing source to aquatic food webs, and PCBs are frequently a driver in contaminated sediment management. Human and ecological health risks due to consumption of fish and shellfish are an issue at many Department of Defense (DoD) sites contaminated with PCBs. Because of the wide use of PCBs, many PCB-contaminated sediments near DoD sites may have been contaminated from multiple sources. Delineating the PCB sources is therefore an important concern where the DoD site may represent only one of many potential sources.

Definitions

This section presents a brief overview of PCB chemistry and its fate in the environment. More detailed information on PCB chemistry can be found in Section 2.

- A **PCB congener** is any individual chemical compound in the PCB category. The name of the congener is based on the total number of chlorine substituents and the position of each chlorine. Click here for a complete list of all PCB congeners.
- **PCB homologues** are subcategories of PCB congeners with equal numbers of chlorine substituents. Click here for a list of all PCB homologues.
- **PCB Aroclors** are mixtures of PCB congeners. These PCB mixtures were what was most commonly sold and used for a variety of commercial applications.

1.1.3 PCB Analysis and Environmental Forensics

PCBs can be measured by a number of different techniques depending on the intended use of the data. These techniques range from simple, rapid methods such as immunoassays that can provide total PCB estimates (including near real-time data in the field) to comprehensive PCB congener methods using laboratory gas chromatography (GC) separations with mass spectrometry (MS) detection. In between are laboratory methods that measure total Aroclor, PCB homologues, and limited sets of PCB congeners. Aroclor analysis has been widely used, and the identification of Aroclors is based on using only five to 10 key "representative" congeners selected from an unaltered single Aroclor standard. However, in environmental samples, multiple Aroclor sources with overlapping congeners are often present, and/or the PCB pattern may be altered by a number of natural processes once released into the environment. Aroclor analysis is thus often highly unreliable for identifying the type and amount of PCBs in environmental samples. In order to characterize and more fully understand the PCB contamination, and determine the PCB sources, it may be necessary to generate more detailed PCB data and unravel the alterations that may be "hiding" the original source patterns. Forensic studies may use a combination of sample and data analysis methods to achieve their goals, ranging from identifying sources for initial source control to later use for remedial cost apportionment. Often, forensic investigations are successfully used to eliminate a suspected

source (e.g., a DoD source) as the primary source rather than quantitatively allocate attribution of each source component, which can be much more difficult.

Environmental forensic studies are fairly mature for petroleum contaminated sites [3], but less common for other contaminants. Work on PCB fingerprinting is developing and there is clearly a need for reliable PCB forensics because of the abundance of this contaminant; it is often a decision driver at contaminated sediment sites. PCB forensics is particularly challenging because PCBs do not "weather" (i.e., change in chemical composition) merely in accordance with molecular weight, solubility, or other predictable factors. Some of the diagnostic principles used for polycyclic aromatic hydrocarbon (PAH) fingerprinting can be applied to PCB fingerprinting, but PCB mixtures are vastly different from PAH/petroleum mixtures; many factors need to be considered in addition to the most common weathering factors and interpretation methods need to be modified and new data interpretation and analysis considerations developed [4]. In addition to the mainly physically-based environmental processes (e.g., selective dissolution, adsorption, and volatilization), other environmental transformation and degradation processes (including microbial dechlorination) are also important and must be considered. Emerging PCB fingerprinting techniques have successfully been applied at a few sites in the US [5-9], but there is a need to more fully develop, demonstrate, and validate the utility of fingerprinting PCB contamination. More detailed information on PCB analysis and environmental forensic techniques can be found in Section 2.4.

1.2 General Approach

This section of the handbook presents the general approach (much of which will be discussed in more detail in Section 2.0 and applied to the case study sites in Section 3.0). The case studies provide examples of how to apply the approach described here at a range of sites. The case studies in this document should be viewed as examples and a start in defining the overall usefulness of forensics studies at Navy sediment sites.

Integrated Forensic Approach

This handbook demonstrates an integrated forensic approach to identify sources of sediment PCB contamination that combines sediment screening technologies on a large number of field samples, detailed PCB congener analysis on a subset of samples, followed by environmental forensic data interpretation to identify sources. The sample analysis and contaminant characterization is comprised of two major components:

- **Rapid sediment characterization (RSC)** technologies which provide for wide spatial coverage to delineate sediment contaminant heterogeneity and semi-quantitative characterization in a cost-effective manner; and
- **Advanced chemical fingerprinting (ACF)** on a selected subset of samples to delineate sources. ACF includes both advanced laboratory chemical analysis of samples, along with the application of sophisticated data analysis and interpretation methods.

The objective of combining RSC with ACF is to maximize the benefits of each method and control costs. For example, RSC provides a cost-effective technique for obtaining spatial

concentration information (and perhaps temporal with sediment core age dating), allowing chemical gradients to be determined for initial assessment of the significance of the contamination and preliminary indications of potential sources. However, individual PCB congener data (a component of the ACF) are usually required for actually fingerprinting sources unless the sources are composed of different Aroclor signatures. ACF may require specialty analyses that are beyond the scope of most regulatory requirements and beyond the capabilities of many commercial laboratories. For example, in the case of PCBs, many regulatory programs only require PCB concentrations be determined as total Aroclors, or possibly a limited set of PCB congeners (e.g., the 18 National Oceanic and Atmospheric Administration [NOAA] Status and Trend congeners), while ACF often requires that up to 100 PCB congeners be determined, at a higher cost. Therefore, this integrated approach is a cost-effective and technically defensible methodology to identify PCB sources in sediments at DoD sites.

This combination of relatively inexpensive RSC analyses to map contaminant gradients combined with a subset of ACF analyses with advanced statistical analyses can tease out source compositions. The relative contributions of each source to the impacted sediments can also be estimated depending upon the nature of the co-mingled sources and the degree of weathering. RSC can help cost effectively answer the question of "where" there are sediments with contamination issues, the general distribution of the contamination, and generally where possible sources may be located, while ACF can confirm "what" those potential source fingerprints are, and more definitively link them to physical sources. Contaminant "fingerprinting" using RSC and ACF methods can also have many applications within the regulatory process relative to sediment investigations and response actions. Fingerprinting techniques applied early in the remedial investigation (RI) can be effectively used for source identification to augment the Watershed Contaminated Source Document (WCSD) and/or verification of background locations and concentrations. Fingerprinting methods can also be employed in the later stages of the feasibility study (FS) to evaluate baseline conditions and the potential for natural attenuation in remedy selection and/or setting appropriate cleanup goals. Both source fingerprints, as well as weathering patterns (due to differences in solubility, dechlorination, etc.), can often be discerned using these advanced chemical and statistical analyses [8, 10]. Although it is difficult to isolate all possible changes in PCB congener patterns, the selection of Hunters Point Shipyard (HPS) and Ashtabula River as case studies provides two examples to demonstrate the methodology. Providing both a remedial cleanup (HPS) and a dredging project (Ashtabula River) example will provide the RPMs with example case studies that may be useful for their sites.

1.2.1 Six Step Integrated Forensics Approach

This handbook demonstrates how to apply the techniques used in RSC and ACF to a variety of PCB sites. This handbook follows the approach outlined in Stout et al. [3] for developing a PAH forensics study, but applies this approach to case study sites with PCB contamination. The combined use of RSC and ACF, however, is only one step in the overall integrated forensics approach described in this document. The six steps that are important to follow for conducting a contaminant source study are summarized in Figure 1-1.

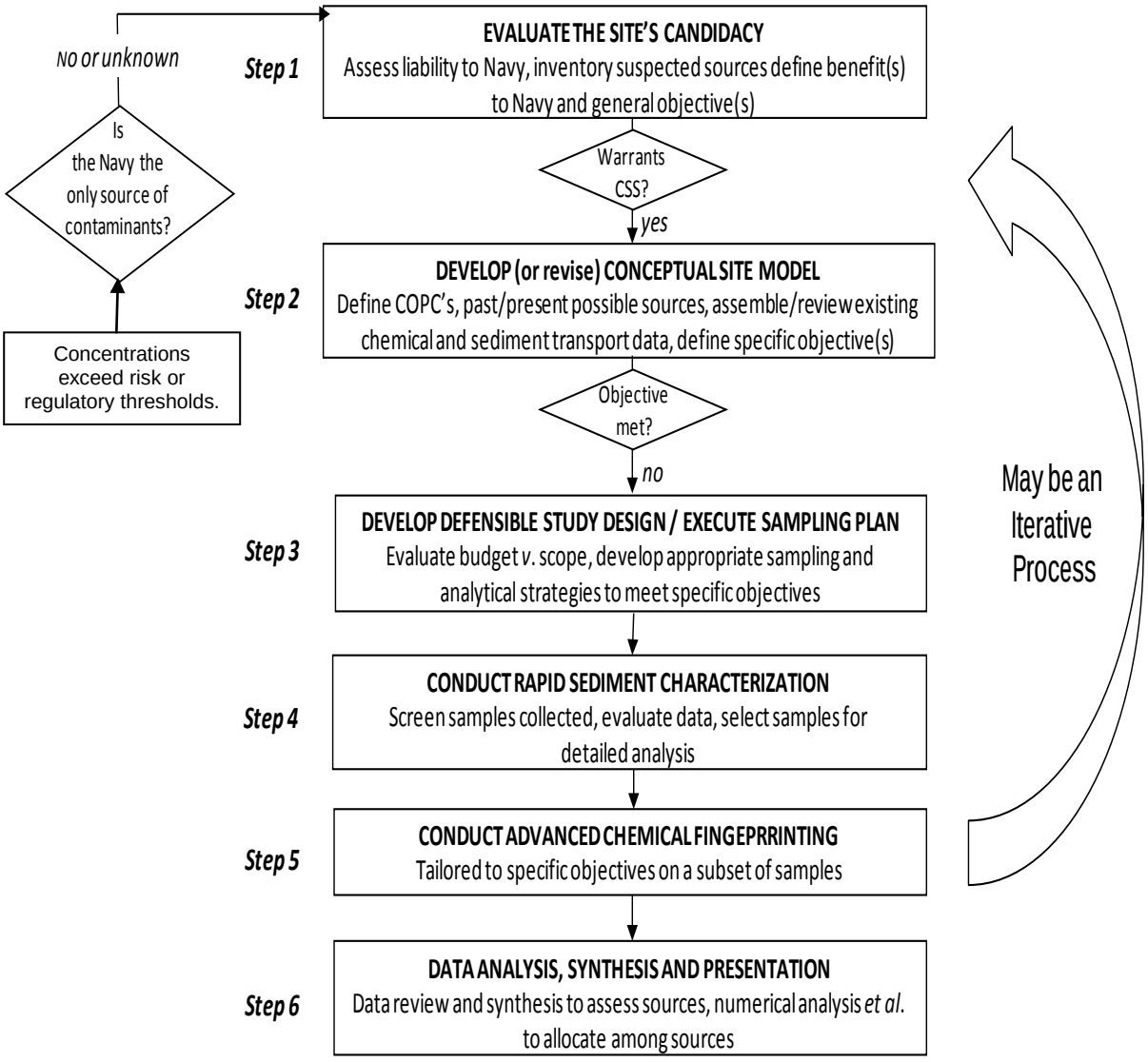


Figure 1-1. Flowchart Showing Considerations, Steps, and Decision Points for Conducting a Contaminant Source Study

1.2.1.1 Step 1: Evaluate Site for Forensic Study

The most obvious and common consideration when evaluating a site's potential for a forensics study is whether or not it is possible that non-site sources may have contributed to the known or suspected contamination at the site. Other questions that may be posed are summarized below. Each question must be considered and weighed in determining if the site will serve as a good candidate to apply forensic techniques.

Step 1: Evaluate Site for Forensic Study

1) Has it been determined that background cannot be established and/or concentrations exceed risk or regulatory thresholds?

2) Is it possible that non-site sources may have contributed to the known or suspected contamination at the site?

3) What known or suspected PCB contaminant sources existed on the site property (now or in the past)?

4) What known or suspected industries and potential sources are (or were) located on nearby properties?

5) What are (or were) the known typical contaminants associated with those industries?

6) What are the general sediment transport dynamics of the area (i.e., could contamination get from "here to there")?

1.2.1.2 Step 2: Develop Conceptual Site Model

The conceptual site model (CSM) is a mental "picture" of the site. It typically includes graphical representations of the contamination (e.g., contaminant contour maps) and fate and transport processes at the site. Once a site's candidacy has been established, a CSM for the ensuing contaminant source study should be developed to help understand how a source, or multiple sources, may have contributed to the contamination. At the completion of a CSM, it should be possible to accomplish the following:

1) Identify (or confirm the identity of) the known or suspected contaminants of potential concern (COPCs) for the site;
2) Identify all of the known or suspected sources or source areas of the COPCs within the study area; and
3) Develop specific objectives (hypotheses or forensic questions) to be evaluated by the study that address the potential PCB sources.

There is obvious overlap with some of the questions in Step 1, but those will be explored in more detail in Step 2. The forensic questions developed under Step 2 will then guide the development

of the sampling design in Step 3 (Sampling and Analysis Plan [SAP]). Specific samples will need to be collected to answer the CSM questions, so this will focus the scope of the forensic study. This does not preclude unforeseen findings, and it is likely that some surprises will occur at most sites. However, this directed development of the forensics study will ensure a cost-effective and well defined study.

An important step in the identification of COPCs is a review of the pre-existing information for the study area, including environmental data. The pre-existing data from past work typically only represent a start in providing defensible interpretations surrounding the source(s) of contamination within the study area. Thoroughly researching existing data, including the history of industries and potential sources in the area, changes over time that could impact contaminant transport (e.g., runoff/drainage, combined sewer outfall/overflow [CSO] activity, site/source cleanup, etc.) are all key components of the records research phase of any forensics investigation. Comprehensive records research is a crucial part of any environmental forensics investigation and is often overlooked or not given the priority it should have.

The case study examples used for this handbook had pre-existing data that were determined to be of sufficient quantity and quality for use in developing the forensics approach in this document, without needing to collect or analyze additional samples. It is rare to be able to conduct a forensics investigation solely using available data, but these case studies were selected, in large part, because of the availability of such data. For instance, all of the PCB data were generated by the same laboratory using consistent procedures, ensuring data comparability and reliable use.

Step 2: Develop a CSM

The CSM is a mental "picture" of the site. It includes graphical representations of the contamination (e.g., contaminant contour maps) and fate and transport processes at the site. CSM development should include the following elements:

- It should provide an understanding of contaminant fate and sediment transport processes at the given site (such as sediment dynamics, identifying areas of net accretion or loss, prop scour, review of dredging records, and more).
- It should include a review of pre-existing information and environmental data to identify COPCs and all of the known or suspected sources or source areas.
- It should support the development of specific objectives (hypotheses or forensic questions) to be evaluated by the study that address the potential PCB sources.

1.2.1.3 Step 3: Develop and Execute a Technically Defensible Sampling Plan

The development of a technically defensible sampling strategy requires a balance between meeting project objectives and data quality objectives (DQOs) within the budget of the project. This often leads to the practical question of how many samples will be used in the study and the type of analyses to be performed. Ultimately, it is the number of samples and analytical costs that will largely determine the cost of the project. By using a tiered study design that allows

RSC data to first characterize the PCB concentrations, the study can be designed to more cost-effectively produce and use the more costly ACF data.

Since forensic investigations are not part of the standard investigation processes, RPMs should contact their Quality Assurance Officer to ensure adherence to Navy policy on the development of SAPs under the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPPs). Forensic specialists should also be involved in the DQO and SAP development process as early as possible to ensure proper data collection and analysis.

At some sites, it may be beneficial to include the collection of sediment cores to capture a record of the historic PCB contributions to the sediments. Some of the cores should be age dated to determine sediment chronology (i.e., the rate of sediment deposition and the dates the sediments at different depths were deposited). If only surface sediments are collected, only recent contamination can be assessed and only recent sources can be determined. This may be sufficient if the only objective is to identify and contain current sources prior to a remedial effort to control recontamination, but these are the types of issues that must be considered during the development of a study design. Many of these types of considerations are addressed in outside references (e.g., [11]), to assist with study design.

Step 3: Develop and Execute and Defensible Sampling Plan

- Develop defensible DQOs and SAPs that follow Navy and UFP-QAPP policies.
- Determine how many samples will be used and the type of analyses to be performed.
- Plan for a tiered study approach that implements RSC first to characterize the PCB extent followed by ACF techniques for source determination.

1.2.1.4 Step 4: Conduct Rapid Sediment Characterization

RSC of semi-volatile organics can be conducted using various immunoassay techniques. The techniques for the RSC of PCBs in sediments have been adapted from methods developed for use in soils (U.S. Environmental Protection Agency [U.S. EPA] Method 4020). Total PCB analysis by the standard laboratory Aroclor method (U.S. EPA Method 8082) may not qualify as a *rapid* sediment characterization method, but is a widely available analytical method that provides general PCB concentration information without the information detail of ACF, and such data can be used similarly to RSC data. More detailed information on the use of RSC methods can be found in the *Navy Guide for Using Rapid Sediment Characterization Methods in Ecological Risk Assessments* [12]. Some limitations in the sensitivity and specificity of RSC methods are also discussed in Section 2.4.1.

The PCB concentration data and variations are plotted using geographic contour plots, or other suitable graphical representation of the concentration distribution at the site. RSC data interpretation can benefit from additional physicochemical information for the sediments, such as the grain size distribution and total organic carbon (TOC) content, as PCBs tend to be preferentially associated with fine-grained and higher TOC content sediment. Grain size and

TOC information also may assist in interpretation of sediment transport and sources of the sediment at sample locations. PCBs can be normalized to TOC in order to better visualize the correlation behavior. With additional sediment transport information, the chemical gradients (PCBs sorbed on sediments generally move from high concentration source areas to lower concentration depositional zones) can be used to suggest various PCB sources. The contour maps (both surface and subsurface) thus can, if properly interpreted, display chemical gradients that indicate potential sources, and additional three-dimensional (3D) plumes (i.e., contoured subsurface information) may be defined because a higher number of samples can cost effectively be analyzed. These spatial presentations of the data allow different source areas to be proposed for validation by the more detailed laboratory analysis (ACF). The benefit of using a tiered approach (using RSC to select ACF samples) is a cost-effective study design in a heterogeneous matrix such as sediment. If only higher cost ACF samples are used, fewer locations would be sampled and source areas may be overlooked due to heterogeneity.

Regardless of the approach used in the generation and evaluation of RSC data, it is important to remember that the goal of the RSC analysis is to develop a sufficient set of visual or conceptual displays to aid in the selection of samples for ACF (and not to alone achieve the objectives of the study).

Step 4: Conduct RSC

- RSC of PCBs in sediment is conducted primarily using immunoassay techniques, but total PCB analytical methods may also be employed for site wide screening of PCB levels.
- The benefit of a tiered approach (e.g., using RSC to select ACF sample locations) is a cost-effective study design for a heterogeneous matrix such as sediment.
- The goal of the RSC analysis is ultimately to develop a sufficient set of visual or conceptual displays to aid in the selection of samples for ACF.
- Physicochemical data, such as the grain size distribution and TOC for sediment, may assist in interpretation of sediment transport and provide useful correlations to PCB concentrations.

1.2.1.5 Step 5: Conduct Advanced Chemical Fingerprinting

This section discusses how to select the location of ACF samples and provides an overview of the types of PCB analyses and statistical techniques to be applied to interpret results. More detailed information can be found in Section 2.4.2.

Determining the Number and Location of ACF Samples. The analytical strategy and budget will largely determine the number of samples that will be selected for ACF. It is not possible to define a fixed percent value of RSC samples to be used for ACF because this depends upon the level of detail in the RSC characterization, the heterogeneity of the sediment, and the overall complexity of the site. Therefore, the task of selecting samples for ACF is largely a matter of selecting a reasonable and justified subset from the complete set of RSC samples. Some guiding principles for the selection of samples for ACF are as follows:

1) Select samples that provide ample spatial coverage of the entire study area (try to represent all areas of the study and do not completely ignore any area on the basis of RSC alone),
2) Select a sufficient number of samples from specific location(s) within the study area that address a specific project objective(s) (i.e., select sufficient samples in areas of specific concern or interest [source areas and mixing zones], potentially including accessible upland sites of interest), and
3) Select samples that represent the range of RSC concentrations observed, including those that are (apparently) representative of the ambient/background conditions (i.e., do not exclude all the low concentration samples as they may provide important information on "background" conditions).

The selection of samples for ACF to meet these guidelines is in large part driven by cost. Thus, a degree of professional judgment is needed in the selection of samples for ACF.

Selecting Analytical Method(s) for the ACF Study. The need for an ACF methodology rests with the limitations of standard U.S. EPA methods (SW-846) to meet the objectives of a contaminant source study [3]. The fundamental shortcoming with virtually every conventional U.S. EPA SW-846 method of analysis, when used for measuring contaminants, particularly organic contaminants in sediment and other media, is a lack of detailed measurements of those diagnostic chemicals known to comprise these complex mixtures. Instead, the standard methods are focused on compounds identified as "priority pollutants," which are quite pervasive in contaminant mixtures, and are generally inadequate to distinguish different sources of otherwise similar contaminants [13]. In addition, standard PCB methods are primarily intended to generate bulk PCB concentration information (i.e., total PCB), and not information for identifying compositional and source differences.

Because of these limitations, standard U.S. EPA methods have been modified at some laboratories to yield the data necessary to support detailed contaminant source investigations. With respect to these modified methods, note that U.S. EPA SW-846 guidelines allow flexibility in the deployment of the 'standard' analytical methods, including modification of the list of target compounds. While most commercial laboratories apply unmodified standard methods, some laboratories have the experience and flexibility to optimize methods to meet project goals without violating method guidelines and project DQOs. When properly planned, most data generated by ACF methods can support contaminant source studies, as well as conventional regulatory assessment requirements. In other words, the ACF data can be considered defensible and accepted by regulatory agencies if the DQOs are clearly defined and met. While RSC and most ACF analyses do not require validation or accreditation review/oversight, it is emphasized that any data that will also be used for definitive purposes (e.g., risk assessment or site close out) must be from a laboratory accredited by the DoD-Environmental Laboratory Accreditation Program. RPMs should consult with their Quality Assurance Officer for an evaluation of accreditation requirements.

Aroclor analysis may, in a few rare circumstances, provide sufficient fingerprinting information to indentify sources. However, because many of the Aroclor formulations consist of overlapping congeners and weathering processes further complicate forensic resolution, more advanced ACF

methods are usually needed. The ACF techniques available for the assessment of semi-volatile organic contaminants in sediments (e.g., PCBs) are based on high-resolution GC (HRGC), usually operated in conjunction with compound-specific detectors (e.g., electron capture detection [ECD] or MS). Some laboratories have developed state-of-the-art PCB analytical methods using HRGC with low-resolution MS operating in selected ion monitoring mode (HRGC/LRMS-SIM), which are both highly cost-effective and provide detailed, high-quality data [14, 15]. The method employs components of U.S. EPA Method 680 (HRGC/LRMS PCB homologue and total PCB method) and Method 1668 (HRGC/HRMS PCB congener method). The base methods have been modified to include a large number of non-standard environmentally important and diagnostic PCB congeners that permit data analysis for differentiating potential sources and environmental processes.

Interpreting ACF Results. Once a subset of samples has been selected for ACF, a forensic analysis for PCBs will typically include the characterization of more than 100 discrete PCB congeners (congeners that comprise >98% of the total and possible PCB contamination), which enables scientists to apply a variety of powerful data interpretation methods. In some cases, a smaller set of 50 to 75 congeners may suffice, but the incremental increase in the cost is fairly small relative to the benefit of having the longer analyte list. PCB forensics data reduction and analysis include:

- Various types of statistical and other numerical analyses,
- Forensics graphing/plotting/mapping,
- Cross plotting,
- Cluster and principal component analysis (PCA) for similarity and dissimilarity analysis,
- Analysis for determining the age of the contamination, and
- Determination of degradation and dechlorination activity.

More detailed descriptions of these forensics methods, including specifically for PCBs, have been presented and documented elsewhere [5-10, 14], and some are further described and applied in this document.

PCA is one commonly used multivariate classification data analysis technique for identifying PCB compositional similarities and dissimilarities among samples and source materials. Receptor modeling (e.g., polytopic vector analysis [PVA]) is another often useful chemometric technique that was applied for the HPS and Ashtabula River case studies, in accordance with methodologies outlined by Johnson et al. [9]. For PCA, PVA, and most chemometric data analyses, the data are first carefully reviewed to assess their quality and usefulness, and the potential impact of low concentration samples, non-detects, and the presence of outliers. Data screening is summarized in Section 2 and also outlined by Johnson et al. [9] and may include: (1) data correction; (2) removal of samples from the data set; and (3) removal of congeners/peaks from the data set. After the data are prepared, the resultant data matrix is analyzed using the multivariate receptor modeling method. The first step in this process is the determination of the number of 'fingerprints' in the system. The next step in the receptor modeling process is to resolve the end member compositions (source profiles) and mixing proportions (source contributions) within each sample. The final step in the process is to: (1) compare the resolved end-member congener profiles with known or suspected source patterns (i.e., Aroclors) and

alteration mechanisms (e.g., literature reported dechlorination methods [16]) and (2) map the end-member mixing proportions both temporally and geographically.

PVA can be a useful component of the ACF data analysis because it is a well-established method that has been applied extensively in PCB forensics applications [5, 8, 9, 17]. Other receptor modeling methods (alternating least squares [ALS], positive matrix factorization [PMF], and Unmix [9]) should also be considered for individual studies. Recent receptor modeling method comparisons [9, 18, 19] indicate that results of these various methods are usually comparable, assuming the use of high quality and diligently screened data sets. The more important consideration is experience of the analyst, and their sensitivity to the scientific/chemical context of the problem.

Step 5: Conduct ACF

- The number of ACF samples depends upon the level of detail in the RSC characterization, the heterogeneity of the sediment, and the complexity of the site.
- ACF techniques typically include the characterization of over 100 PCB congeners.
- The PCB analytical methods employ HRGC usually operated in conjunction with compound-specific detectors (e.g., ECD or MS).
- Some laboratories have developed state-of-the-art PCB analytical methods using HRGC with low-resolution MS operating in selected ion monitoring mode (HRGC/LRM-SIM).
- Statistical techniques such as PCA, PVA, and others are then used to determine the number of "fingerprints" in the system, the source profiles, and the mixing proportions within each sample.
- This information is compared to known or suspected source patterns (i.e., Aroclors) and degradation mechanisms.

1.2.1.6 Step 6: Data Analysis, Synthesis, and Presentation of Results

The data analysis, synthesis, and information interpretation is most effective when multiple lines of evidence are used to develop the findings and draw the final conclusions. If multiple lines of evidence support the findings, it provides confidence and lends credibility to the conclusions. If multiple methods to evaluate the data provide confounding or inconsistent results, then that may mean that additional investigations may be warranted, or that there is no strong evidence of discrete and clearly identifiable sources. The multiple approaches to data analysis include:

1) A site history and records research component,
2) Incorporating contaminant/sediment transport and hydrodynamic information,
3) Evaluating the PCB concentrations across a site,
4) Evaluating the PCB composition of samples from across a site and possible sources,
5) Applying one or several available chemometric statistical methods to the PCB data, and
6) Integrated data analysis and interpretation incorporating these multiple approaches to draw conclusions related to potential sources of the contamination.

Section 2.5 provides examples of figures for the synthesis and presentation of ACF data. The manner by which the results and conclusions of a contaminant source study are conveyed needs to consider the audience, particularly whether they are highly technical or non-technical decision-makers and stakeholders. The target audience will dictate the level of technical detail conveyed in a report or presentation. Chemical 'fingerprinting' data in graphical and/or tabular form can be very confusing to all but an experienced chemist. Their interpretation is easier (and thereby useful) when the results of a contaminant source study are reported using different visual displays that either convey the data spatially or by some other easily interpreted visual (e.g., contour maps, bubble plots, histograms, etc.). Such visuals can be readily explained to and interpreted by most audiences. This is important since the value of any contaminant source study will be undermined if the audience cannot understand the results and conclusions.

Step 6: Data Analysis, Synthesis, and Presentation of Results

- Using RSC, it is possible to have the data density to support two-dimensional (2D) and 3D contour mapping, which provides a good visual display of the concentration gradients.
- Other visual displays (such as bubble plots, transect charts, or histograms) can be used with the RSC data. Bubble plots are often used as visual displays of the lower density ACF data when there is not enough data for support contour mapping.
- PCB compositional histograms are useful for illustrating and describing the contaminant composition, relationships among the samples and to potential sources, and link the field samples to source material (e.g., Aroclor formulations or mixtures).
- Single horizon pie chart or multi-horizon core diagram inserts on a map view of sample locations can be used to show the distribution of end members around the site.

The ACF data by themselves only provide information of compositional similarity and dissimilarity in the data set, and must be viewed along with other information (e.g., site history, sediment and contaminant transport, etc.) to determine where sources can be found. In addition, the PCB information and linkages to potential sources must make sense from a chemical reasonableness perspective, and it must be possible for a PCB chemist to understand and justify the observations and source identifications; statistical software packages and graphical representations by themselves are insufficient for explaining sources. The previously mentioned RSC contour maps provide a first impression of where sources are located. By combining this data with other site information (including site contaminant use history, other upland and upstream contaminant studies, sediment transport studies, contaminant deposition history with dated cores, etc.), it may be possible to tell not only what sources are present, but where they are located and when they contaminated the sediments.

2.0 GENERAL SUMMARY OF TECHNICAL METHODS

2.1 Introduction to PCBs and PCB Chemistry

Environmental forensics methodologies are well developed for petroleum-originating contamination, and less so for PCB contamination. PCBs were intentionally produced through chlorination of the biphenyl molecule, unlike petroleum and one of their primary constituent PAHs, which are naturally produced and introduced into the environment both by man and through natural processes. This chemical process that produces PCBs places from one to 10 chlorines on available substitution locations on the six-sided biphenyl molecule (Figure 2-1). Multiple naming conventions have been developed to differentiate the 209 possible congeners (a term given to distinguish different PCB compounds with unique combinations of attached chlorines). Early naming conventions relied on substituted chlorine positions to differentiate congeners. These early methods numbered the six "corners" of each ring in the biphenyl structure, and referred to the individual congener by the numbers where substituted chlorines resided (for example see Figure 2-1 where ortho "corners" are at positions labeled 2,6,2',6'; meta "corners" are at 3,5,3',5'; and para is at 4 and 4'). The International Union of Pure and Applied Chemistry (IUPAC) naming conventions later simplified things by sequentially numbering all congeners by increasing chlorine content, from PCB 1 through PCB 209. PCBs can also be simply divided into homolog groups based on the number of chlorine substitutions on the biphenyl rings (mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, or deca-chlorobiphenyl). These naming conventions are all shown in Table 2-1. Information on the 10 homologs, including the number of possible PCB congeners for each level of chlorination (i.e., each homolog), is also summarized in Table 2-2.

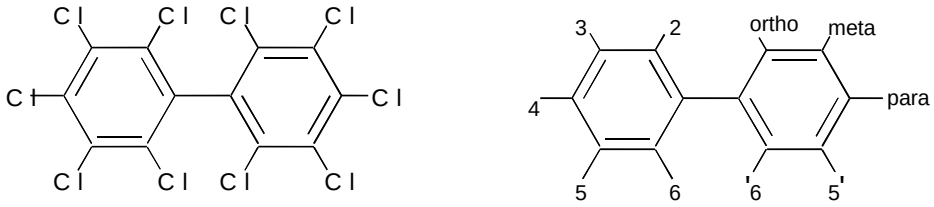


Figure 2-1. PCB Molecule Showing Possible Chlorine Positions

PCBs were produced commercially in the US from 1929 through 1977 by Monsanto Chemical Company. They were produced in specific PCB congener mixtures (termed Aroclors) to obtain chemical properties that were desired for specific industrial applications. PCBs have increasing density, boiling point, and hydrophobicity with increasing levels of chlorination. High molecular weights and boiling points lead to a viscous fluid with low flammability that can tolerate high temperatures without substantial chemical degradation. Most of the PCBs were produced for use in transformers and capacitors, with other uses including hydraulic fluids, carbonless copy paper, printing inks, and other applications [20]. When manufactured in the US by Monsanto, these mixtures were termed Aroclors; those manufactured outside the US by others had trade names such as Clophen (Germany), Prodolec (France), and Phenoclor (Japan). Monsanto reportedly produced from 500,000 to 600,000 metric tons of PCBs (about half the world-wide total) during its almost 50 years of production [21], although most PCBs are no longer being used, some are still held in older equipment and materials (e.g., in landfills) and potentially available for release to the environment.

Table 2-1. The 209 Possible PCB Congeners (IUPAC and Structural Nomenclature)

IUPAC#	Chl Pos	IUPAC#	Chl Pos	IUPAC#	Chl Pos	IUPAC#	Chl Pos
Mono-Chlorobiphenyls		**Tetra-Chlorobiphenyls (cont.)**		**Penta-Chlorobiphenyls (cont.)**		**Hexa-Chlorobiphenyls (cont.)**	
1	2	53	25-2'6'	107	234-3'5'	160	23456-3'
2	3	54	26-2'6'	108	2346-3'	161	2346-3'5'
3	4	55	234-3'	109	235-3'4'	162	235-3'4'5'
Di-Chlorobiphenyls		56	23-3'4'	110	236-3'4'	163	2356-3'4'
4	2-2'	57	235-3'	111	235-3'5'	164	236-3'4'5'
5	23	58	23-3'5'	112	2356-3'	165	2356-3'5'
6	2-3'	59	236-3'	113	236-3'5'	166	23456-4'
7	24	60	234-4'	114	2345-4'	167	245-3'4'5'
8	2-4'	61	2345	115	2346-4'	168	246-3'4'5'
9	25	62	2346	116	23456	169	345-3'4'5'
10	26	63	235-4'	117	2356-4'	**Hepta-chlorobiphenyls**	
11	3-3'	64	236-4'	118	245-3'4'	170	2345-2'3'4'
12	34	65	2356	119	246-3'4'	171	2346-2'3'4'
13	3-4'	66	24-3'4'	120	245-3'5'	172	2345-2'3'5'
14	35	67	245-3'	121	246-3'5'	173	23456-2'3'
15	4-4'	68	24-3'5'	122	345-2'3'	174	2345-2'3'6'
Tri-chlorobiphenyls		69	246-3'	123	345-2'4'	175	2345-2'3'5'
16	23-2'	70	25-34'	124	345-2'5'	176	2346-2'3'6'
17	24-2'	71	26-3'4'	125	345-2'6'	177	2356-2'3'4'
18	25-2'	72	25-3'5'	126	345-3'4'	178	2356-2'3'5'
19	26-2'	73	26-35	127	345-3'5'	179	2356-236
20	23-3'	74	245-4'	**Hexa-chlorobiphenyls**		180	2345-2'4'5'
21	234	75	246-4'	128	234-2'3'4'	181	23456-2'4'
22	23-4'	76	345-2'	129	2345-2'3'	182	2345-2'4'6'
23	235	77	34-3'4'	130	234-2'3'5'	183	2346-2'4'5'
24	236	78	345-3'	131	2346-2'3'	184	2346-2'4'6'
25	24-3'	79	34-3'5'	132	234-2'3'6'	185	23456-2'5'
26	25-3'	80	35-3'5'	133	235-2'3'5'	186	23456-2'6'
27	26-3'	81	345-4'	134	2356-2'3'	187	2356-2'4'5'
28	24-4'	**Penta-chlorobiphenyls**		135	235-2'3'6'	188	2356-2'4'6'
29	245	82	234-2'3'	136	236-2'3'6'	189	2345-3'4'5'
30	246	83	235-2'3'	137	2345-2'4'	190	23456-3'4'
31	25-4'	84	236-2'3'	138	234-2'4'5'	191	2346-3'4'5'
32	26-4'	85	234-2'4'	139	2346-2'4'	192	23456-3'5'
33	34-2	86	2345-2'	140	234-2'4'6'	193	2356-3'4'5'
34	35-2'	87	234-2'5'	141	2345-2'5'	**Octa-chlorobiphenyls**	
35	34-3'	88	2346-2'	142	23456-2'	194	2345-2'3'4'5'
36	35-3'	89	234-2'6'	143	2345-2'6'	195	23456-2'3'4'
37	34-4'	90	235-2'4'	144	2346-2'5'	196	2345-2'3'4'6'
38	345	91	236-2'4'	145	2346-2'6'	197	2346-2'3'4'6'
39	35-4'	92	235-2'5'	146	235-2'4'5'	198	23456-2'3'5'
Tetra-chlorobiphenyls		93	2356-2'	147	2356-2'4'	199	2345-2'3'5'6'
40	23-2'3'	94	235-2'6'	148	235-2'4'6'	200	23456-2'3'6'
41	234-2'	95	236-2'5'	149	236-2'4'5'	201	2346-2'3'5'6'
42	23-2'4'	96	236-2'6'	150	236-2'4'6'	202	2356-2'3'5'6'

Table 2-1. The 209 Possible PCB Congeners (IUPAC and Structural Nomenclature) [Continued]

IUPAC#	Chl Pos	IUPAC#	Chl Pos	IUPAC#	Chl Pos	IUPAC#	Chl Pos
Mono-Chlorobiphenyls		**Tetra-Chlorobiphenyls (cont.)**		**Penta-Chlorobiphenyls (cont.)**		**Hexa-Chlorobiphenyls (cont.)**	
43	235-2'	97	245-2'3'	151	2356-2'5'	203	23456-2'4'5'
44	23-2'5'	98	246-2'3'	152	2356-2'6'	204	23456-2'4'6'
45	236-2'	99	245-2'4'	153	245-2'4'5'	205	23456-3'4'5'
46	23-2'6'	100	246-2'4'	154	245-2'4'6'	**Nona-chlorobiphenyls**	
47	24-2'4'	101	245-2'5'	155	246-2'4'6'	206	23456-2'3'4'5'
48	245-2'	102	245-2'6'	156	2345-3'4'	207	23456-2'3'4'6'
49	24-2'5'	103	246-2'5'	157	234-3'4'5'	208	23456-2'3'5'6'
50	246-2'	104	246-2'6'	158	2346-3'4'	**Deca-chlorobiphenyl**	
51	24-2'6'	105	234-3'4'	159	2345-3'5'	209	23456-2'3'4'5'6'
52	25-2'5'	106	2345-3'				

Table 2-2. PCB Homologs and Number of Congeners within Each Homolog Group

Homolog	Chemical Formula	Number of Chlorines	Number of Congeners in Homolog Group
Mono-chlorobiphenyl	$C_{12}H_9Cl$	1	3
Di-chlorobiphenyl	$C_{12}H_8Cl_2$	2	12
Tri-chlorobiphenyl	$C_{12}H_7Cl_3$	3	24
Tetra-chlorobiphenyl	$C_{12}H_6Cl_4$	4	42
Penta-chlorobiphenyl	$C_{12}H_5Cl_5$	5	46
Hexa-chlorobiphenyl	$C_{12}H_4Cl_6$	6	42
Hepta-chlorobiphenyl	$C_{12}H_3Cl_7$	7	24
Octa-chlorobiphenyl	$C_{12}H_2Cl_8$	8	12
Nona-chlorobiphenyl	$C_{12}H_1Cl_9$	9	3
Deca-chlorobiphenyl	$C_{12}Cl_{10}$	10	1

Only a limited number of Aroclor mixtures were produced in the US, each with a distinct homolog and congener fingerprint. Table 2-3 lists the nine major Aroclors produced in the US, and their PCB homolog composition; Aroclors 1016, 1242, 1254, and 1260 together comprised more than 90% of the PCBs that were produced in the US. A few additional Aroclors were produced, but only in small quantities. Aroclors carried a four digit numbering convention. For many years it was reported/repeated in the literature, and often taken as fact that the first two digits in the Aroclor naming convention represented the number of carbon atoms on the molecule and the last two digits represented the average weight percent chlorine in the formulation. The latter half of that explanation is true: the "60" in Aroclor 1260 indicates that is has a mixture of PCB congeners that result in 60% chlorine by weight. A recent paper by Erickson and Kaley [22] suggest that the 12-carbon part of that common explanation may be incorrect. While PCB congeners do indeed contain 12 carbons, the "12" indicates only that the product is refined PCB.

Hence, nearly all PCB Aroclors follow the naming convention "12xx" (Aroclor 1016 which was produced as a replacement for Aroclor 1242 being the sole exception). Erickson and Kaley [22] point out that if the "12=12 carbon atoms" myth was true, the first two digits of Monsanto's line of PCT products would have been "18," since there are 18 carbon atoms in the terphenyl molecule, assuming the same naming rules were used for PCT as for PCB. But PCT products were named using a 5000 series convention (such as Aroclor 5460 – a PCT product with 60% chlorine).

Table 2-3. PCB Homolog Composition of the Nine Major Aroclors Produced in the US

	Level of Chlorination/Homolog % Composition									
Aroclor	**Mono**	**Di**	**Tri**	**Tetra**	**Penta**	**Hexa**	**Hepta**	**Octa**	**Nona**	**Deca**
A1221	60.1	33.4	4.2	1.2	1.1	0	0	0	0	0
A1232	27.5	26.8	25.5	10.6	9.4	0.2	<0.1	0	0	0
A1016*	0.7	17.5	54.6	22.1	5.1	0	0	0	0	0
A1242*	0.7	15.0	44.9	20.3	18.8	0.3	0	0	0	0
A1248	<0.1	1.1	21.4	32.9	42.9	1.6	<0.1	0	0	0
A1254*	<0.1	0.2	1.3	10.2	59.1	26.8	2.7	<0.1	<0.1	0
A1260*	<0.1	<0.1	0.2	0.4	8.7	43.2	38.4	8.3	0.7	0
A1262	<0.1	0.2	0.4	0.5	3.4	26.4	48.5	19.7	1.6	0
A1268	0	0	<0.1	0.1	0.2	4.4	10.1	45.0	35.0	4.8

From Frame et al., 1996 [23] and Kannan et al., 1997 [24].

*Aroclors 1016, 1242, 1254, and 1260 accounted for >90% of the PCB production.

Each Aroclor mixture was a unique combination of up to approximately 50 individual congeners of significant relative concentration, formulated to provide specific chemical properties. A total of a little more than 100 of the possible 209 PCB congeners were included in the different Aroclor formulations at easily detectable levels, and a few additional congeners may be detected in environmental samples as a result of environmental transformation processes. A set of about 120 PCB congeners can describe more than 99% of the total PCB in all Aroclor formulations and environmental samples, and most of the rest of the possible congeners were never produced or are rarely detected above ultra-trace levels. Information on the PCB congener composition of Aroclors is presented in Appendix A (based on Rushneck et al. [25]), including a series of plots showing the concentrations of a set of 80 major PCB congeners.

Given that only a few distinct Aroclors were produced, and their generally stable chemical characteristic, one might assume fingerprinting the distinct Aroclor sources should be a relatively easy exercise. Figure 2-2 shows the composition of 18 major PCB congeners in fresh Aroclor 1248 and 1260 PCB material, illustrating that one can easily discriminate individual Aroclors even with this relatively small subset of 18 NOAA Status and Trends Program congeners. However, environmental PCB contamination is rarely from a single Aroclor and environmental PCB contamination rarely resembles a fresh Aroclor material; environmental processes and comingling from multiple sources significantly complicate PCB environmental forensics. Furthermore, the changes due to environmental processes (i.e., "weathering" processes) can be difficult to predict (i.e., they are not simply correlated to molecular weight or solubility).

PCB Materials

This section presents an overview of PCB chemistry and its behavior in the environment. PCBs are typically described as:

- **PCB Congeners.** The individual PCB compounds. There are 209 PCB congeners, a subset of which were present in commercial PCB formulations and found in PCB contamination.
- **PCB homologues.** The categories of PCB congeners with equal numbers of chlorine substitutions, or levels of chlorination. There are 10 PCB homologues.
- **PCB Aroclors.** Mixtures of PCB congener mixtures that were most commonly sold and used in the US. A total of nine Aroclors are most commonly described, but a few other rare Aroclors also existed.

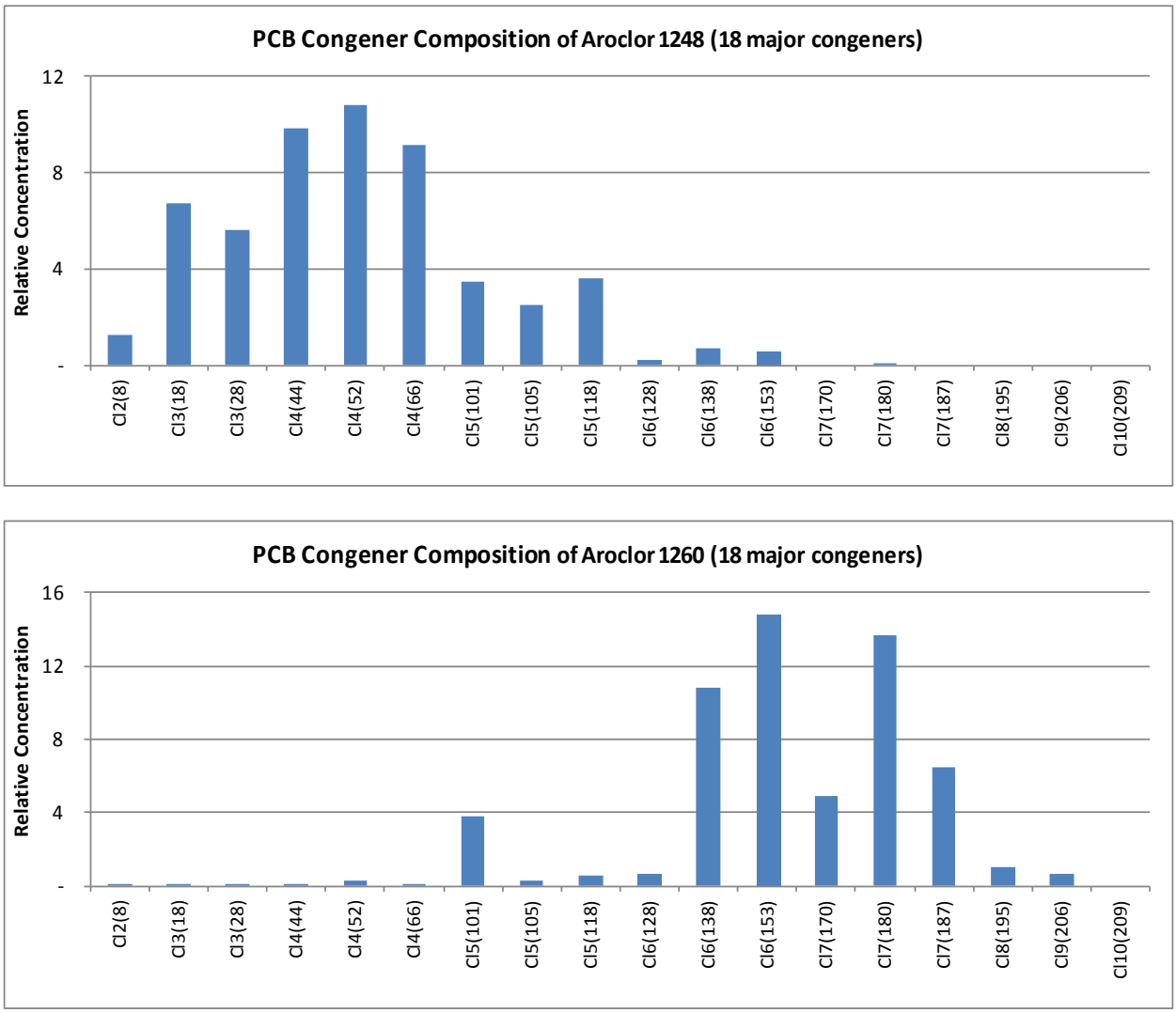


Figure 2-2. PCB Congener Composition of Aroclors 1248 (top) and 1260 (bottom)

The same properties that led to their usefulness for industrial applications also led to PCBs becoming an environmental problem. PCBs resist thermal and other degradation processes; they are stable and thus persist in the environment. The chemical characteristics of PCB also mean that they have low water solubility and adhere to solid soil and sediment particles rather than freely dissolving in water or volatilizing to air; they have high octanol/water partitioning coefficients (k_{ow}) and are therefore lipophilic ("fat loving" rather than hydrophilic or "water loving") and tend to partition into organic phases.

Their hydrophobic nature means that PCBs are usually associated with the organic carbon fractions of soils and sediments (i.e., they concentrate in organic rich sediment, as opposed to sandy sediment); they also accumulate in fatty biological tissue. When organisms consume PCB-containing material (e.g., organic matter or other organisms) some become associated with the lipid fraction of the organism, and some may not be readily metabolized or excreted. This process results in some of the PCBs biomagnifying, or increasing in concentration as PCBs are consumed by higher trophic level organisms, rather than being lost from the organism. Although PCBs may be persistent in the environment because they are recalcitrant, they can still undergo some degradation and alteration in the environment, as well as within the tissue of organism. PCBs as a group are considered very stable and persistent, but they are in fact a diverse mixture of molecules (PCB congeners) with varying chemical properties, including large congener-to-congener differences in the rates of and susceptibility to degradation and alteration. In general, the less chlorinated congeners will be more soluble and volatile. More chlorinated congeners are more hydrophobic and tend to accumulate in organic rich sediments, bioaccumulate up the food chain, and fractionated into the fatty tissues in organisms to a higher degree. Within organisms, different congeners will bioaccumulate and metabolize at different rates, so additional biological fractionation can occur. PCB congeners can also undergo microbial dechlorination, particularly in anaerobic sediments, and the susceptibility to dechlorination is highly dependent on the structure of the PCB molecule (i.e., the degree of chlorination and position of the chlorines on the biphenyl molecule); the environmental PCB composition can thus also be altered by dechlorination processes.

PCB dechlorination can be a particularly confounding PCB transformation process that complicates PCB source identification and PCB analytical chemistry. In anaerobic sediments, certain bacterial groups have been found to be able to dechlorinate PCBs given the right conditions. Long-term studies of contaminated sediments [26, 27] have shown specific bacterial groups have distinctive dechlorination patterns, transforming certain PCB congeners to less chlorinated congeners as chlorines are removed. Specific dechlorination pathways have been documented, and can be predicted [16]. Figure 2-3 illustrates a few examples of potential dechlorination pathways. The dechlorination potential is rather complicated, and depends on factors such as the position of the chlorine subject to dechlorination as well as the number and positions of other chlorines on the molecule, and the overall level of chlorination.

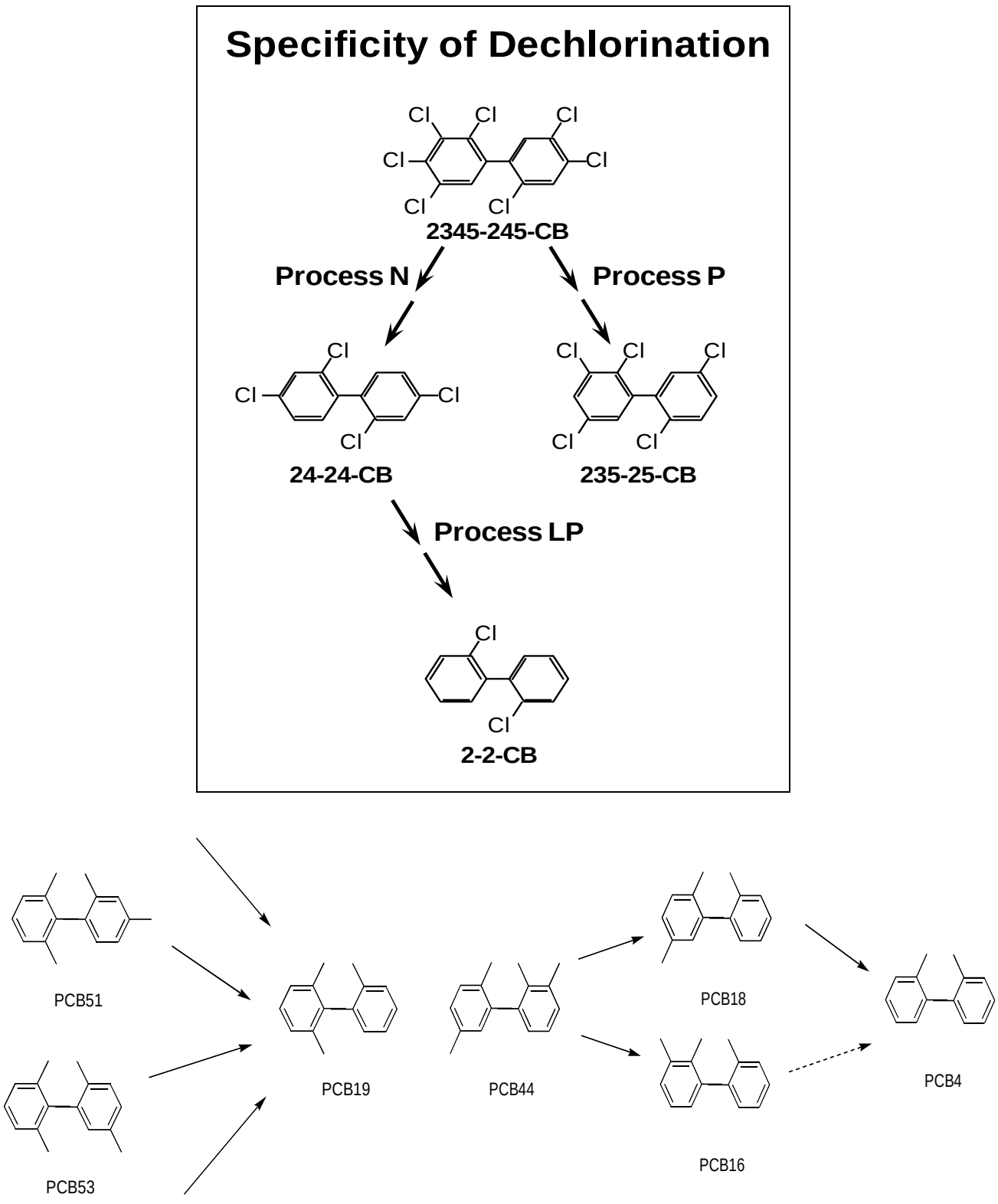


Figure 2-3. Example of Documented PCB Dechlorination Processes and Pathways, Including Pathways Resulting in an Increase in PCB19 and PCB4 Concentrations

Table 2-4. PCB Congeners Susceptible to and Resistant to Dechlorination Mono- to hexa-chlorobiphenyls [28]

Congeners with High *Potential* for Dechlorination (possible dechlorination product congener are listed in parenthesis for major PCB congeners)			**Congeners with High *Resistance* to Dechlorination**
Double Flanked m/p-substitution	Single Flanked m/p-substitution	Unflanked m/p-substitution on di- or tri-substituted ring	All o-substitutions, mono-substituted, or non-para mono-substituted rings
21	5	7	1
38	12	***9*** (1)	2
41 (17)	***16*** (4)	14	3
55	***20*** (6)	***17*** (4)	4
60 (28)	***22*** (8)	***18*** (4)	6
61	23	***25*** (6)	10
62	24	***26*** (6)	11
76	29	***28*** (8)	19
78	***33*** (8, 6)	30	27
81	35	***31*** (8)	32
82 (42)	***37*** (15, 13)	34	54
85 (47)	***40*** (16)	36	
87 (49)	***42*** (17)	39	
88	43	***47*** (17)	
89	***44*** (18)	***49*** (17, 18)	
105 (66)	***45*** (19)	50	
106	***46*** (19)	51	
108	***48*** (17, 18)	***52*** (18)	
109	***56*** (33, 22, 20)	53	
114	57	***66*** (28, 25)	
115	58	69	
116	59	72	
122	63	75	
123	***64*** (32)	80	
124	65	86	
125	67	100	
126	68	103	
127	***70*** (31, 26)	104	
128 (85)	***71*** (32, 27)	121	
129	73	155	
130 (90)	***74*** (28, 31)		
131	77		
132 (91)	79		
137 (99, 90)	***83*** (44, 43)		
138 (99)	***84*** (46, 45)		
139	86		
140	90 (49)		
141 (101, 92)	***91*** (51)		
142	***92*** (52)		
143	93		
144 (103)	94		
145	***95*** (53)		
156 (118, 107)	96		
157	***97*** (48, 42, 44)		
158 (119)	98		

Table 2-4. PCB Congeners Susceptible to and Resistant to Dechlorination. Mono- to hexa-chlorobiphenyls [28] (Continued)

Congeners with High *Potential* for Dechlorination (possible dechlorination product congener are listed in parenthesis for major PCB congeners)			**Congeners with High *Resistance* to Dechlorination**
Double Flanked m/p-substitution	Single Flanked m/p-substitution	Unflanked m/p-substitution on di- or tri-substituted ring	All o-substitutions, mono-substituted, or non-para mono-substituted rings
159	***99*** (47, 49)		
160	***101*** (49, 52)		
161	102 (51)		
162	***107*** (70, 63, 56, 57)		
164 (110, 113)	***110*** (71, 64, 59)		
166	111		
167	112		
168	113		
169	117		
	118 (66, 74, 70)		
	119		
	120		
	133		
	134		
	135 (95, 94)		
	136 (96)		
	146 (101, 90, 92)		
	147 (91)		
	148		
	149 (102, 90, 92)		
	150		
	151 (95)		
	152		
	153 (99, 101)		
	154 (100)		
	163 (117, 110)		
	165		

Bolded and italicized congeners are present at ~0.25% or more in Aroclors 1016/1242, 1248, 1254, and/or 1260.
Only congeners with up to six chlorines are listed; more chlorinated congeners are less susceptible to dechlorination.

In general, meta-substituted chlorines are dechlorinated most readily (process N in Figure 2-3), followed by para-substituted chlorines (process P in Figure 2-3). The presence of adjacent chlorines (i.e., "flanked" meta- and para-substituted chlorine) increases the susceptibility to dechlorination. A double-flanked meta-substituted congener (i.e., with also a chlorine in the adjacent para- and ortho-positions) is particularly susceptible to dechlorination of the chlorine in the meta position [28, 29]. Ortho-substituted chlorines are significantly less likely to be removed through dechlorination and, over time, the primarily ortho-substituted PCB congeners therefore increase in relative concentration if a significant amount of anaerobic dechlorination is occurring in the sediment. The most heavily chlorinated PCB congeners (e.g., hepta-, octa-, nona- and deca-chlorobiphenyls; Table 2-1) tend to be less susceptible to dechlorination than the less chlorinated congeners (e.g., tri-, tetra-, penta-, and hexa-chlorobiphenyls). Table 2-4 presents a summary of congeners (by IUPAC congener number) that are particularly susceptible to dechlorination because of the described chlorine substitution on their molecules, as well as congeners that are relatively resistant to dechlorination. Congeners with high relative concentrations in common Aroclor formulations and much environmental contamination are indicated in bold. PCB dechlorination, in and of itself, does not remove PCBs; it only alters the composition of the PCB congeners. However, dechlorination does transform the PCB into forms that are more amenable to mineralization processes that can occur.

Dechlorination pathways have been used in fingerprinting studies to follow the changes in PCB composition to reconstruct the original source fingerprints [8]. Figure 2-4 (top) illustrates the PCB composition in surface sediment samples from a site in Lake Hartwell, NC, which closely resembles that of the known contamination source (a mixture of Aroclors 1242 and 1254). The bottom portion of Figure 2-4 illustrates the PCB composition in buried sediment which has been significantly dechlorinated and no longer resembles the known source material.

Figure 2-5 illustrates the difference in the PCB congener composition of the deeper and the surface sediment. The dechlorinated sediments have an increase in and very high relative proportion of PCB congeners with primarily ortho substitution (e.g., PCB4 [chlorines in the 2,2' positions], PCB10 [2,6], and PCB19 [2,6,2']), and a decrease in concentration of congeners with meta-substituted chlorines highly susceptible to dechlorination (e.g., PCB22, PCB28, PCB33, PCB44); see Tables 2-1 and 2-4, and Figures 2-1 and 2-3. The deeper, "older", sediments had no PCB compositional resemblance to Aroclors 1242 and 1254, or any other Aroclor, but could be linked to Aroclors 1242 and 1254 as the source material by understanding the chemical processes and through dechlorination pathway and deconvolution analysis [8]. Another important result of significant dechlorination is that PCB-as-Aroclor analysis, which remains the most widely used laboratory PCB analytical method, often results in large errors in the reported PCB concentration of such samples, and may even miss the presence of PCBs altogether. It would not be surprising, for instance, if the sample illustrated in Figure 2-4 (bottom) would be reported as "no PCB detected", even though the sample had very high PCB concentrations, simply because the PCB composition no longer resembles Aroclor material.

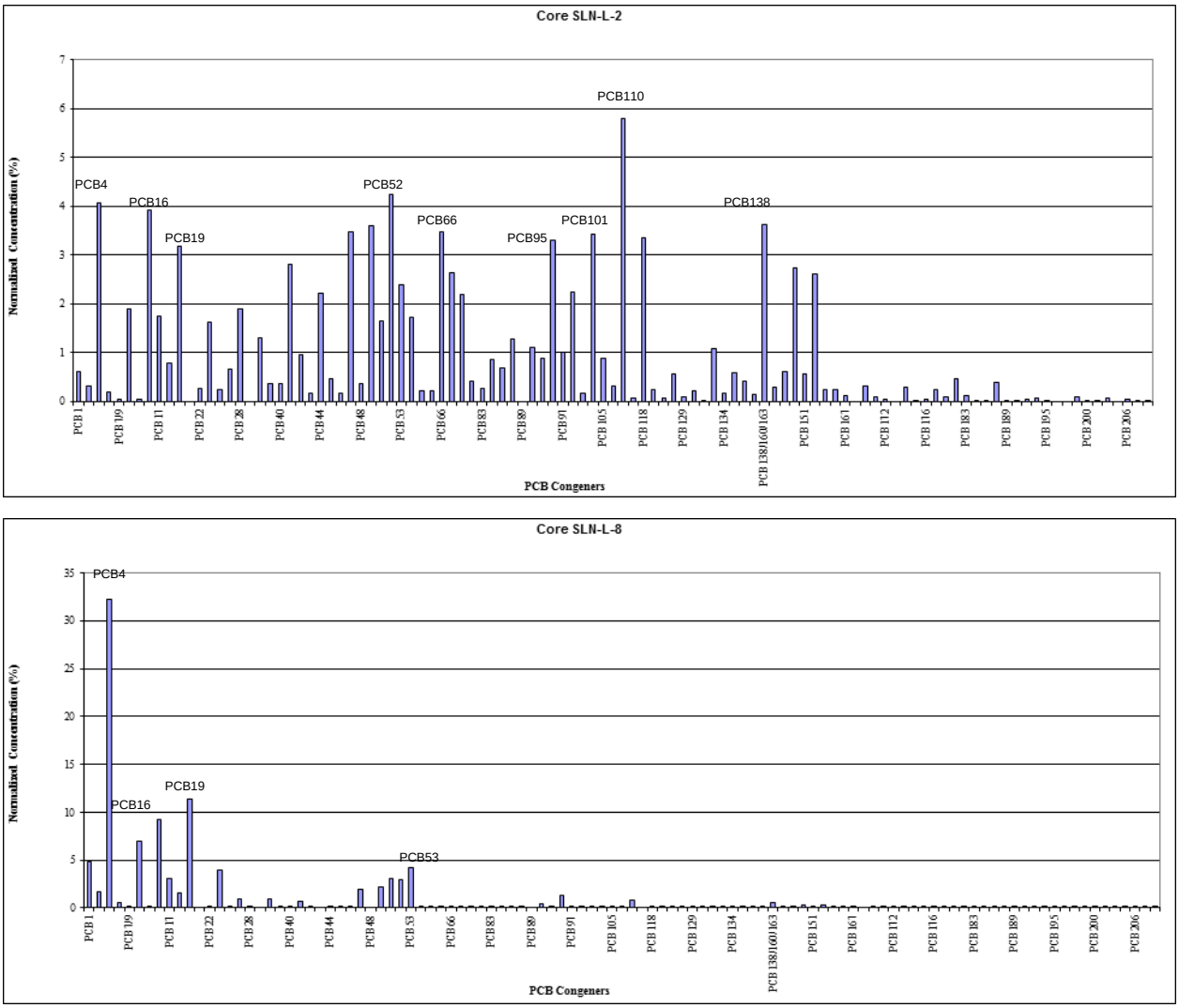


Figure 2-4. PCB Congener Distribution in a Surface (top) and Deep (bottom) Sediment Sample Collected at Location L at Lake Hartwell [6]

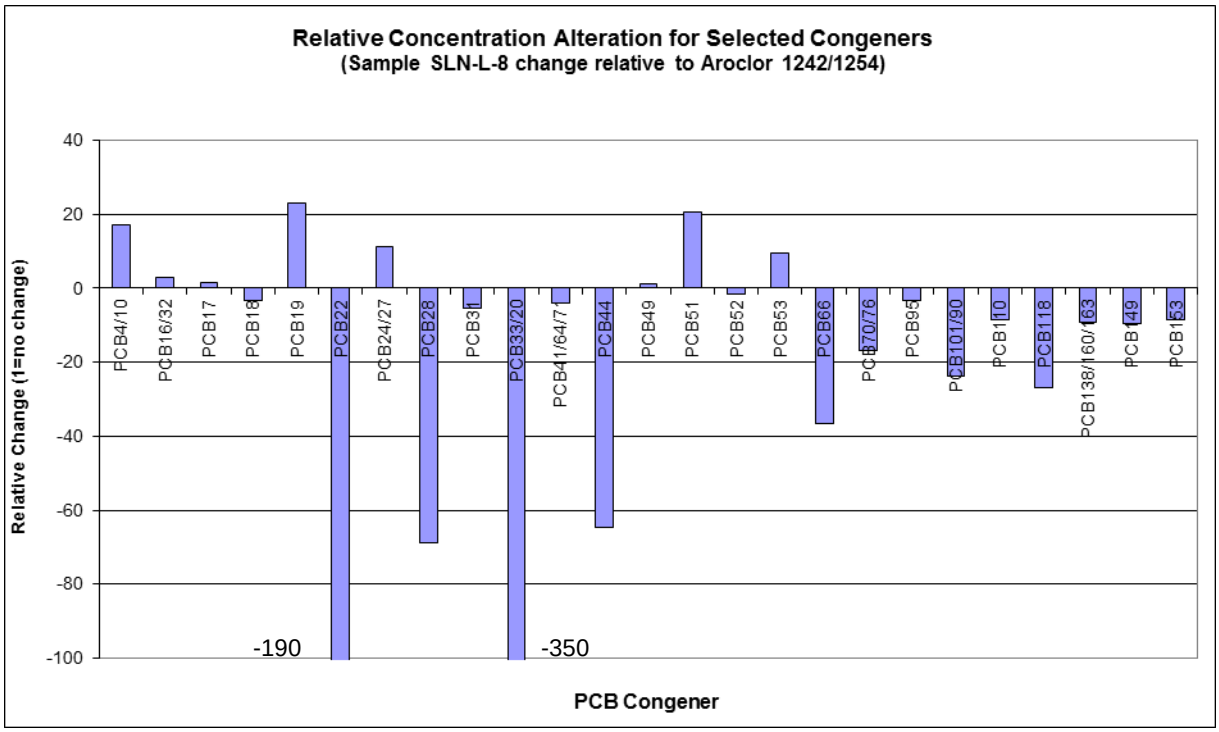


Figure 2-5. Change in Relative PCB Congener Concentrations in a Deep Sediment Sample from Location L at Lake Hartwell Compared to Aroclor 1242/1254

Linking PCB contamination in biological tissue to sources is particularly challenging since one must consider not only the alterations in the environment prior to animal exposure (e.g., selective dissolution, adsorption, and dechlorination processes), but also the biological fractionation in PCB patterns due to differences in uptake and loss of different PCB congeners. The more chlorinated congeners are more lipophilic and have a greater affinity for bioaccumulation, but some congeners also may pass across cell membranes differently from other congeners due to the chlorine substitution pattern on the molecule; different types of biological fractionation occur.

Planar congeners (those with no chlorines in the ortho positions, allowing the molecule to be "flat") are more likely to pass through cell membranes than PCB molecules with ortho-substituted chlorines across from each other (i.e., in the 2,2' and 6,6' positions; Figure 2-1). The World Health Organization (WHO) has identified a set of 13 planar, or mono-ortho substituted, congeners that are of particular concern for human health (Table 2-5). Likewise during metabolism different congeners may show preferential losses, so again biological fractionation can occur. For these and other reasons, it becomes increasingly difficult to trace PCB patterns from tissues back to original sources. But linking PCB tissue data to sediment sources has been done, and some studies [4] have even attempted to fingerprint human blood samples to match ingested fish as likely exposure sources for PCBs in human health studies. This short review demonstrates the need to understand the very complex PCB fate and transport processes in the environment since they impact the observed PCB congener composition in the different environmental matrices, and the ability to associate with sources. If exposure pathways are

going to be traced back to original sources, these types of physical, chemical and biological processes must be better understood (see [4]; and references therein).

Table 2-5. World Health Organization (WHO) List of Toxic PCB Congeners and Their 2,3,7,8-TCDD Toxic Equivalency Factors for Mammals

PCB Congener		Toxic Equivalency Factor (relative to 2,3,7,8-TCDD[a])
Congener Number (IUPAC)	Congener "Type" (chlorine substitution characteristics)	
PCB77	Non-ortho substituted (coplanar)	0.00010
PCB81	Non-ortho substituted (coplanar)	0.00030
PCB105	Mono-ortho substituted	0.00003
PCB114	Mono-ortho substituted	0.00003
PCB118	Mono-ortho substituted	0.00003
PCB123	Mono-ortho substituted	0.00003
PCB126	Non-ortho substituted (coplanar)	0.10000
PCB156	Mono-ortho substituted	0.00003
PCB157	Mono-ortho substituted	0.00003
PCB167	Mono-ortho substituted	0.00003
PCB169	Non-ortho substituted (coplanar)	0.03000
PCB189	Mono-ortho substituted	0.00003

[a] 2,3,7,8-TCDD toxicity is commonly used as a reference for the toxicity of "dioxin like" PCB congeners.

Although PCBs were produced as specific Aroclor mixtures of congeners because of the physical/chemical (solubility, adsorption, volatility, etc.) and biological (bacterial dechlorination, organism metabolism, etc.) processes described, environmental samples are often found with different mixtures and with very different PCB congener composition, and confound the PCB fingerprinting [4, 16, 30]. These various processes alter the congener patterns once the PCB is released into the environment. The impact of weathering and degradation on source patterns is always a concern in environmental forensics; given a situation of multiple sources, and patterns modified by one or more alteration processes, source apportionment can be difficult. For instance, one can easily imagine an onshore spill or source of PCB oil that results in a soil contaminated with PCBs. Subsequent erosion can bring soil particles into surface water bodies where they can deposit out as PCB-contaminated sediments. In aqueous settings, lower weight congeners are more easily dissolved and transported away, and higher molecular weight congeners are more strongly adsorbed to organic matter, so the remaining sediment PCB composition possesses a greater proportion of high molecular weight congeners than that found in the original mixture. If the sediments are anaerobic, microbial dechlorination may occur, and more so for congeners with specific molecular structure. The PCB in the sediments would have a very different composition than the original PCB release due to these environmental processes, and the compositional alteration continues as long as the PCB is exposed to the natural environment.

Taken together, the potential alteration processes demonstrate that the "simple" exercise in fingerprinting environmental samples using a few possible PCB source signatures (i.e., Aroclor patterns, or even a set of PCB congeners) may in fact become a substantially more difficult problem. The compositional analysis and interpretation often require knowledge of the potential

alteration mechanisms to "back out" their effects before identifying the actual original source fingerprints, and associating field samples and sources. In addition, the fact that the PCB congener composition changes in the environment limits the use of Aroclor analyses for identifying contamination sources to only fresh samples (for example, PCB oils or soils with freshly spilled PCB); typical environmental samples require more extensive congener analysis in conjunction with data analysis methods and an understanding of PCB chemistry to be able to determine sources. However, even given the complex PCB compositional alteration scenarios, the data analysis methods discussed in this document are valuable tools to identify sources and estimate both the original source profiles and alteration patterns [8, 31-35].

2.2 Establishing a General Understanding of the Site

It is important to establish an understanding of the site that goes well beyond the PCB contamination characteristics to fully understand the contaminant situation and establish the relationship between the sediment contamination and potential sources. Two key components are: (1) establishing the site history through records and other information research, and (2) establishing the hydrodynamics and sediment transport characteristics of the site.

2.2.1 Site History and Records Research

A crucial aspect of a PCB forensics investigation is determining a relationship between the contamination observed in the sediments and historical activities at or near the site, including recent and historical operations and releases. This requires an understanding of site history, and the history of the area around the site that could have impacted the site. If one cannot identify historical industrial activities, processes, material handling, and possible release and transport scenarios that can explain the sediment contamination, the forensic investigation would be missing an important puzzle piece.

The availability of records can vary widely from project to project, but it is important to devote significant effort to the site history and records research as part of the forensic investigation, and preferably early in the process during the planning phase. In terms of determining potential sources of PCBs in sediments, the types of information that are usually the focus of a records search include:

1. Identifying current and historical production/operations for the properties that could have contaminated the sediments through intentional or unintentional discharge/runoff.
2. Identifying PCB-related activities (e.g., transformer/capacitor use, carbonless copy paper, hydraulic fluid, marine paints) by the potential contributors of sediment contamination, and the timeframe of their use.
3. Identifying historical waste handling and disposal for PCB containing materials/waste.
4. Identifying possible migration pathways to sediment (e.g., waste disposal, landfills, drainage ditches and creeks receiving runoff), and how those have changed over time.
5. Reviewing historical environmental investigation reports and data.
6. Reviewing historical remedial activities, and summarizing their implications on the history of the contamination.

7. Summarizing the activities and site characteristics that may have involved PCBs, the possible history (years) of releases, and possible migration pathways to the sediments.

Conducting a comprehensive site history investigation can be difficult and time consuming, depending on how readily available the information is. The challenges include:

- The nature, volume, and availability of relevant documents vary greatly from project to project.
- Unlike when generating new data, the existence of useful historical information cannot be guaranteed.
- Even information that exists may be forgotten or inaccessible in archived files.
- Identifying the specific information that is relevant to a PCB forensics study, as it may be a small percentage of the available material. Historical document review can become a time-consuming search for a few relevant needles in a very large haystack.
- Obtaining historical information may be particularly challenging if it is perceived that it may implicate them as a PCB source.
- It is often difficult to develop a plan or scope of work for conducting historical records research because the types, locations, and availability of information may be unknown.

However, the potential importance of a thorough historical investigation often far outweighs the challenges, and should be pursued. The following is a summary of possible sources of potentially important historical information, which are described in more detail in Section 2.5.3.

- **Internal Corporate/Facility Documents**. Internal communications and other records of their operations over time, and maybe also study reports of prior site investigations.
- **State and Federal Regulatory Files**. If environmental investigations have been conducted at a site under regulatory authority, then data and reports should be publically available.
- **Publications**. Published literature may provide general information on industrial/commercial use of PCBs, but site-specific studies may also be in the published literature.
- **Interviews**. Interviews with current and past workers and residents can be very useful.
- **Aerial Photographs/Remote Sensing**. Aerial photographs and other remote imaging and sensing information can be purchased, and can be very useful to document the characteristics and changes at a site.

2.2.2 Sediment Transport and Hydrodynamics

It is critical to understand the water and sediment dynamics of a system to be able to understand how contaminants may move from their sources to where they were sampled and measured. This includes drainage, runoff, and discharge from a potential source location, to the movement of waters and sediment in the receiving environment which usually is the primary study site.

Contaminant fate and transport in aquatic systems are influenced by a range of physical, chemical, and biological processes. Physical processes significantly affect the fate and transport of hydrophobic organic contaminants (HOCs), such as PCBs, as well as many inorganic contaminants such as lead and mercury, because they are naturally adsorbed to particles in the sediment bed or suspended in the water column. Often, sediment resuspension, transport, and deposition are the largest components of contaminant transport at a given site. Moreover, the success of many remediation approaches such as in situ capping, dredging, and natural recovery is directly affected by physical sediment transport processes. The effects of physical processes must be evaluated in conjunction with the effects of chemical and biological processes to assess overall fate and transport at a site.

Many Navy sediment sites are located in areas of relatively low hydrodynamic energy such as rivers, bays, and estuaries, where sediments and contaminants tend to accumulate over time. In some cases, the original source(s) of contamination have been eliminated, reduced, or controlled as environmental management practices improved over the past 50 years. At some sites, the deposition of newer, relatively clean sediment on top of more contaminated sediment has resulted in burial of contamination. The most common sediment management questions associated with these sites are as follows:

- Could erosion of the sediment bed lead to the exposure of buried contamination?
- Will sediment transport lead to the redistribution of contamination within the site, or movement of contamination off site?
- Will natural processes lead to the burial and isolation of contamination by relatively clean sediment?
- If a site is actively remediated, could sediment transport lead to the recontamination of the site?

Blake et al. [36] developed a user's guide to address these sediment transport issues. It focuses on the collection and analysis of data needed to address these primary questions. A combination of regional and historical data, site-specific measurements, empirical data evaluation methods, and numerical modeling techniques can be used to characterize sediment transport at a given site. Empirical approaches are particularly useful for characterizing the past and present effects of sediment transport; however, numerical models are more useful for predicting the effects of future events and sediment deposition patterns. The appropriate method(s) and tool(s) should be selected and used on a site-specific basis to qualitatively and/or quantitatively characterize sediment transport, and assess the viability of various remedial options. The approach for a given site will depend upon the size and complexity of the site, the CSM, the specific site objectives, and the available resources.

Information on sediment stability, sediment transport, and other hydrodynamic information (e.g., circulation, currents, tides) are not only important for sediment management considerations, but are essential to help understand the distribution of contamination in a system, and link the contamination to potential sources. An understanding of contaminant transport is essential in any environmental forensic investigation to explain how contamination from a source can be

found where it is ultimately detected in the environment. Sometimes, these locations are not simply immediately downstream from the release.

2.3 Sampling Design and Sample Collection

As noted in the previous section, PCBs tend to be particle bound and selectively associated with such environmental matrices. Even in studies of PCBs in water samples [17], the majority of the PCBs tend to be associated with the suspended solids in the water. By studying suspended material in water samples, recent source information may be determined, possibly identifying active sources that can be targeted in compliance programs such as total maximum daily loads (TMDLs). Surface sediments obtained with surface grab samples similarly provide data on recently deposited sediments and potentially active sources, and often provide similar information as the suspended material in water samples. Deeper, buried sediment samples (ideally with the aid of a sediment age dating technique) may provide a historical record of source contributions to a water body. Depending on the temporal and spatial information needs developed in the study design, a combination of sample matrices and sampling types may be required. Some forensics studies have sampled both sediment and biological tissue (e.g., fish) at the same locations to also follow PCB pathways through the food web. If fish consumption is a risk driver at a site, it may be important to identify the source of the PCBs. Regardless of the management driver (e.g., a sediment or tissue PCB concentration), it is important that the source(s) is identified to ensure it is controlled before considering any remediation.

The sampling design is typically based on some sort of a statistical based sampling (e.g., random, systematic, stratified, cluster, etc.) or professional judgment that can be justified technically, based upon the information assembled in the CSM. Sampling designs are often site-specific and require consideration of many aspects of the study design. These types of considerations are addressed in many references (e.g., [12], and references herein). The extent and density of sampling (i.e., spatial coverage) is usually the issue requiring the greatest consideration in developing a sampling design strategy. It is the number of samples that will largely determine the cost of the project and the confidence in the data analysis. By using a tiered study design that allows RSC data to first characterize the overall PCB concentration (e.g., through geographic information system [GIS]-based concentration contouring), it can be designed to more cost effectively generate the ACF data.

Sediments can be collected with either surface grabs or subsurface coring systems, depending on the objectives of the particular study. Surface grabs (such as Van Veen grabs; Figure 2-6) recover only the surface sediments and therefore are used to recover sediments that represent more recent conditions. Subsurface sediment cores (such as Vibracores or piston cores; Figure 2-7) are used to recover subsurface sediments which cover a longer time period and therefore may provide a historical record of sediment deposition. Sediment cores can also be collected and analyzed for age dating, using lead and cesium isotope (Pb-210 and Cs-137) techniques, to determine the age (approximate year of deposition) of the sediment deposition at different depths, by determining the rate of sediment deposition (usually in cm/yr). Such information on specific years that subsurface sediment was deposited can be extremely useful for associating the contamination at different depths with site and other historical activities, and, generally, helps to better understand the contamination history.

Figure 2-6. Van Veen Sediment Grab Sampler and Sediment from Inside the Grab

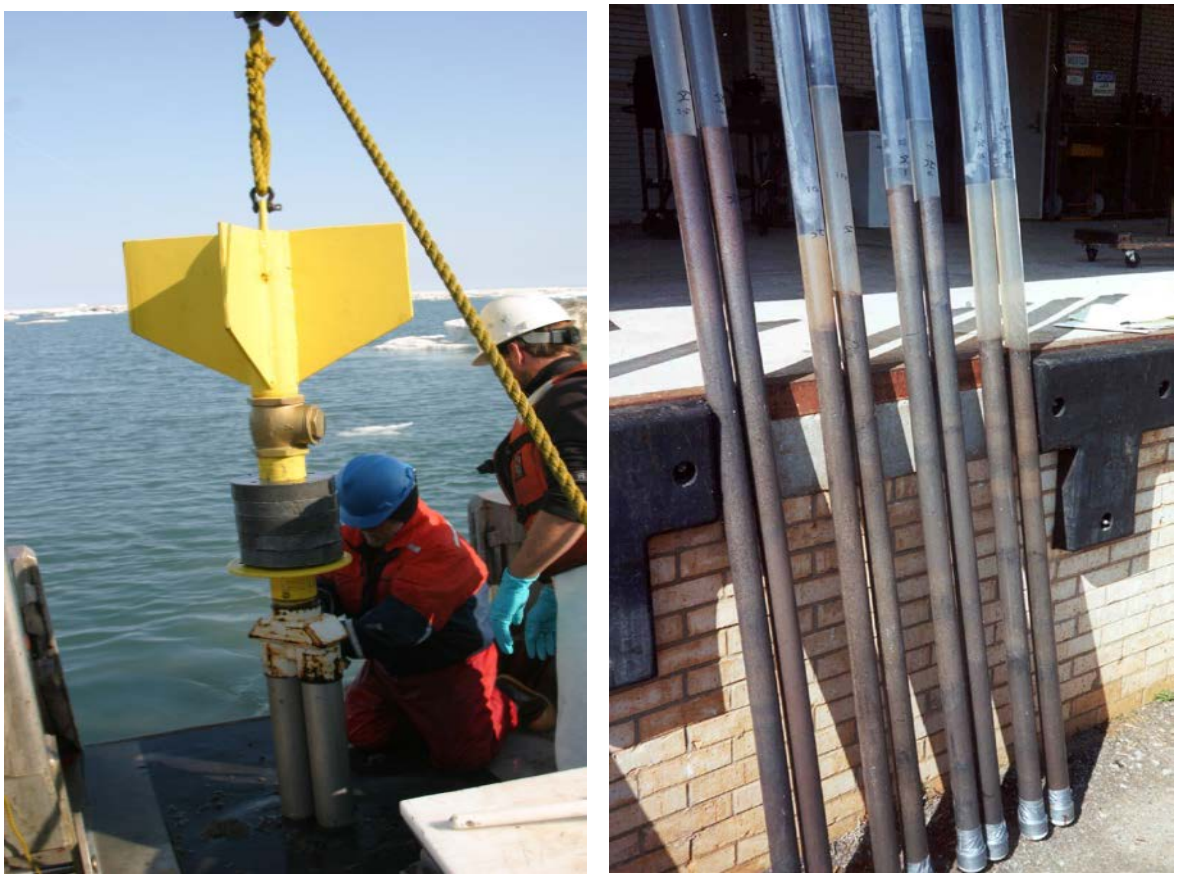


Figure 2-7. Sediment Corer and Collected Sediment Cores in Core Liners

2.4 Sample Analysis

A variety of options are available to determine PCB concentrations in environmental samples. There is also a significant amount of confusion about the benefits and drawbacks of the different methods, and for what purposes one method may be suitable while it is unsuitable for a different purpose. Many of the standard PCB analytical methods that were developed for regulatory programs may not be appropriate for forensic studies, similarly to analysis of samples for petroleum and PAH forensics [3]. For instance, U.S. EPA analytical methods developed for regulatory programs (such as the Superfund Program) require strict adherence to procedures outlined in U.S. EPA's SW-846 Methods [37]. The goal of many of these regulatory programs is to determine the "nature and extent" of the contamination, often of highly contaminated samples, which is not always sufficient to determine the sources of contamination in a forensics study. Forensics studies may require modifications of standard methods, including lower limits of detection and the analysis of additional diagnostic analytical parameters, to obtain the necessary data. U.S. EPA has recognized this for a variety of environmental investigations and is moving towards performance based measurement systems (PBMSs) rather than strict adherence to SW-846 methods. The types of analyses discussed in this document for forensic applications meet the PBMS requirements and, with adequate planning, the data can be used for both forensic and regulatory purposes. There may also be a need to use a combination of analytical methods to most effectively meet the goals of a well-developed forensics study.

Before choosing a PCB analytical method, it must be determined whether all that is needed is a measure of the total PCB concentration, or if more detailed PCB information is needed. For forensic investigations it is often useful to obtain two sets of information, and thus implement the project in a tiered manner – an initial set of Total PCB analysis using RSC or other Total PCB analysis approach, followed by a detailed congener-specific ACF analytical method on a sub-set of the samples to obtain more detailed information for more comprehensive forensic data interpretation.

Total PCB analysis can be conducted using (1) a semi-quantitative enzyme-linked immunosorbent assay (ELISA) screening method, (2) a widely used total PCB as Aroclor laboratory method, (3) a less widely used total PCB as homologs method, or (4) using a method that quantifies individual congeners which are then summed to represent the total PCB, either with or without the application of a Total PCB correction factor.[1] Individual PCB congener analysis can also be performed in a few different ways, the primary differences being the

[1] Total PCB concentrations can be estimated by summing the individual PCB congener concentrations, if those congeners are expected to capture a sufficiently large proportion of the total PCB. The PCB Aroclor compositional information in Appendix A can be useful for estimating the total PCB in a given PCB contamination, recognizing that environmental processes, including dechlorination (Table 2-4), can alter the actual environmental concentrations, as described in this document. A well selected set of a little over 100 PCB congeners, such as the 117 PCB congeners used in the Ashtabula River case study (Appendix B), can capture 97-98% of the total PCB in most environmental samples, and summing the concentrations of those congeners provides a good estimate of the Total PCB. It has been shown that the 18 NOAA National Status and Trends Monitoring Project PCB congeners capture about 50% of the Total PCB in most US coastal sediment environments, and summing the concentrations of those congeners and then multiplying that by 2 has been widely used to estimate the Total PCB concentration in such sediments. Other corrections factors can be developed for other sets of congeners using the information in Appendix A, once the type of contamination is understood.

analytical instrument that is used and the number of PCB congeners that are quantified. These analytical methods are discussed further below.

2.4.1 Total PCB Sample Analysis Techniques (including RSC)

This section describes three analytical methods, based on U.S. EPA Methods 4020, 8082, and 680, that are available for determining the Total PCB concentration in environmental samples. These methods can all be considered for RSC, and the first analytical step in gaining a general understanding of the PCB contamination at a site.

Total PCB Immunoassay Methods

ELISA analysis is a simple and relatively inexpensive immunoassay (IA) option for Total PCB analysis. Recent advances in the environmental field have followed the medical field in the application of ELISA methods for environmental contaminants. The ELISA PCB method is captured with U.S. EPA Method 4020. This is also the method recommended in this handbook for the Tier I, rapid RSC analysis of sediment samples for most situations.

The immunoassay method includes a simple extraction step followed by a reaction step for a competitive reaction between unknown sample PCBs and kit-provided PCB conjugates (PCBs with added color indictors that are activated in later reaction steps). A modification to U.S. EPA Method 4020, which is required for sediment analysis, is the dewatering of the sediment to below about 30% moisture by placing on filter paper to remove excess water. Antibody sites where this competitive reaction occurs have traditionally been on the "frosted" sides of test tubes, but more recent advances have led to antibody sites on free floating particles within the test tube solutions to provide better precision and accuracy. Contaminant concentrations are related to a color change that is either visually observed or quantified using a calibrated spectrometer, and compared to that of PCB calibration solutions with known PCB concentrations. Samples tend to be analyzed in large batches (20 to 50 samples) along with a series of Aroclor calibration standards.

These ELISA methods can be employed in the field as a near real-time method, or in the laboratory with often higher level of control of environmental factors (e.g., temperature) and quality control (QC) (e.g., replicates and calibration standards). ELISA methods are highly specific, and the PCB ELISA method has been developed to be particularly responsive to a limited set of PCB congeners. Although the immunoassay detects individual PCB congeners, individual congener quantities are not determined and total quantities are reported in Aroclor equivalents relative to the standard Aroclor series that was run along with the particular batch. This specificity can provide an advantage in that it is not sensitive to analytical interferences (i.e., it primarily responds to what it was developed to respond to), but this can also be a limitation if the concentrations of the method-specific PCB congeners is low or if the relative composition of those method-specific PCB congeners in the environmental samples and the calibrant differ. For instance, PCB101 is one of the major congeners the PCB ELISA was developed to respond to, and this congener comprises about 10% of the Total PCB in Aroclor 1254, about 4% in Aroclor 1260, and about 1% in Aroclor 1242 (see Appendix A), which impact the response to the PCB ELISA method. The PCB ELISA kit is provided with Aroclor 1254 as the calibrant, even though different Aroclors respond differently in the PCB ELISA method (Table 2-6). The PCB ELISA kit calibrated with Aroclor 1254 as supplied would determine a 10

parts per million (ppm) concentration of Aroclor 1254 to indeed be 10 ppm. However, a 10 ppm concentration of Aroclor 1260 would be reported as 16 ppm Total PCB and a 10 ppm concentration of Aroclor 1242 would be reported as 4 ppm Total PCB. Another way to describe this would be that a Total PCB concentration determined to be 10 ppm could be the result of 52 ppm Aroclor 1232, 24 ppm of Aroclor 1242, 10 ppm of Aroclor 1254, or 6 ppm of Aroclor 1260. Mixtures of Aroclors and environmental transformation would further confound the analysis. However, two simple methods can improve the accuracy of the PCB ELISA IA test results; two techniques that are, unfortunately, not always used or well communicated.

Table 2-6. Sensitivity and Selectivity of PCB ELISA IA Method to Different Aroclors

Compound	PCB Kit Sensitivity	
	Limit of Detection (ppb)	Relative Response
Aroclor	22.6	0.022
Aroclor	2.61	0.19
Aroclor	1.22	0.41
Aroclor	3.56	0.14
Aroclor	0.59	0.85
Aroclor	0.5	1
Aroclor	0.32	1.6
Aroclor	0.66	0.76
Aroclor	3.03	0.17

- Analyze a set of representative site samples using both the PCB ELISA method and a recognized accurate laboratory instrument method, correlate the results, and determine a "correction factor" if the correlation is acceptable. For instance, the ELISA immunoassay results were compared to highly reliable fixed laboratory results for a set of HPS samples (Figure 2-8), and the immunoassay results were determined to be about 1.12 times the laboratory results with a correlation coefficient (r^2 value) of 0.95; the immunoassay results were 12% higher than the "true" concentration. A correction factor could thus be generated; if the immunoassay results were divided by 1.12, the "true" concentration would be obtained. However, this approach is highly site specific and it is important to demonstrate that it applies across the site, or identify subsets of samples that may have different composition and correction factors.
- Analyze a set of representative site samples using a recognized accurate laboratory instrument method, and determine the Aroclor(s) present in the samples, and their relative composition. Prepare a site-specific Aroclor, or mixed Aroclor, calibration solution that represents the Aroclor(s) at the site, rather than simply relying on the Aroclor 1254

standard assumed to be used with the PCB ELISA kit, and measure the field sample concentrations using this site-specific Aroclor standard.

The PCB ELISA method has some analytical limitations, most of which can be avoided as described above. However, it is an excellent semi-quantitative screening method for relatively cost effectively and rapidly obtaining approximate Total PCB concentrations to characterize the PCB distribution within a set of samples and across a site and develop a general understanding of the PCB contamination at a site. A plan for more detailed sampling and analysis can then be developed, as needed.

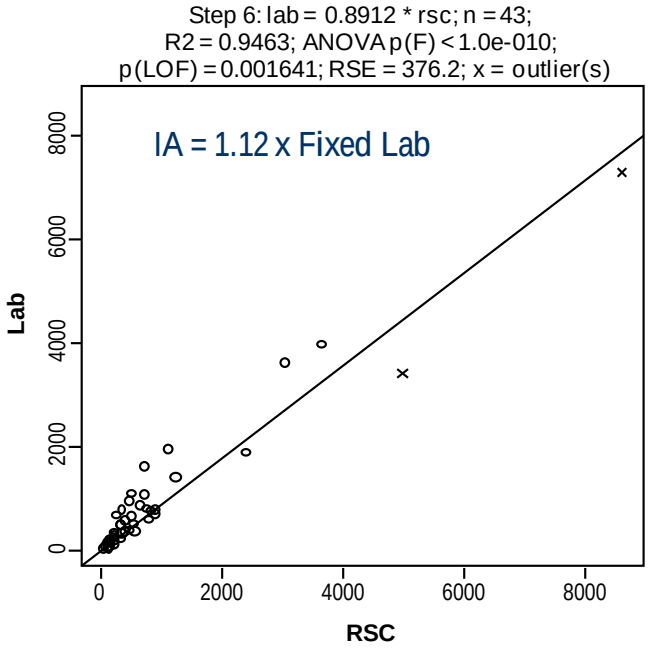


Figure 2-8. Correlation between Laboratory-based and ELISA-based Total PCB Measurements of Hunters Point Shipyard Sediment Samples

Total PCB as Aroclor Methods

U.S. EPA Methods 608 and 8082 have historically been the most widely used analytical methods for providing Total PCB data; Method 608 is for the analysis of water samples and Method 8082 for solid samples (e.g., sediment). The methods are based on identifying and quantifying the predominant Aroclor(s) in the samples. The methods assume a standard extraction technique is used, which is then followed by the method described instrumental analysis which is GC separation and ECD detection. GC columns ensure that the PCB congeners move through the GC column and reach the ECD at different rates generally based on the volatility and molecular weight of the PCB congeners (i.e., the mono- and di-chlorobiphenyls are detected first, and the nona- and deca-chlorobiphenyls last).

The ECD provides a rather unsophisticated detection capability, sensing electro-negative constituents including chlorinated PCBs and chlorinated pesticides. It is considered relatively specific to halogenated organic compounds, but, in fact, can respond to a variety of compounds

and is, thus, quite susceptible to matrix interferences and false positives. GC/ECD instrument output consists of a chromatogram showing a series of peaks, with the PCB congeners spread out by elution time in the x-direction and the peak height/area in the y-direction related to the congener concentration. Identification is made through comparison of the chromatogram to Aroclor standards that are analyzed under the same conditions as the field samples. Quantification is based on the peak area counts of a set of (generally four to eight) representative peaks, or peak clusters, and comparing to the same in the Aroclor standards. Multiple Aroclors may be identified in a sample, and the Total PCBs would be determined by summing the individual Aroclor concentrations. However, multiple Aroclor quantitation is not only complicated by environmental weathering, but mixtures of Aroclors can significantly confound the identification and quantitation of the Aroclors due to the limitations of this method. The relatively non-selective nature of the ECD can result in non-PCB contributions from other sample constituents to the targeted peaks, possibly resulting in erroneous quantitation; this is particularly common with complex environmental matrices, such as sediment or tissue samples. As discussed earlier, the PCB composition undergoes a variety of compositional changes once released to the environment, so it may not closely resemble the Aroclor standards the samples are compared to and quantified against; the Aroclor determination is a "best fit" to the peaks from the Aroclor standards even when they may not be present in the environmental samples, or present at dramatically altered relative composition. This can result in inaccurate quantification or, even worse, identifying a sample as not having any PCBs when there may be significant concentrations of a highly altered PCB. For instance, the PCB composition of the sample illustrated in the bottom of Figure 2-4 does not resemble any Aroclor, and using U.S. EPA Method 608 or 8082 may easily be identified as a "non detect" for PCBs, even though it contained high concentrations of significantly weathered/dechlorinated PCBs.

The standard Total PCB as Aroclor methods (U.S. EPA Methods 608 and 8082) are susceptible to significant identification and quantitation problems due to Aroclor mixing, environmental weathering of PCB, and complex sample matrices, as described above. The method should not be used by itself identifying the type and source of the PCB contamination, unless it is a recent release and there is certainty that the environmental samples have not been subjected to environmental weathering. This may be the case with some soil samples collected near a recent spill, but is otherwise rarely the case. However, assuming the samples have not been weathered to the point where PCB can no longer be identified, the Total PCB as Aroclor methods may be a useful semi-quantitative method for obtaining approximate Total PCB concentrations, and some limited additional compositional information (Figure 2-9) to characterize the PCB distribution within a set of samples and develop a general understanding of the PCB contamination at a site. A plan for more detailed sampling and analysis can then be developed, as needed.

Total PCB Homologue Methods

U.S. EPA Method 680 is available for providing reliable Total PCB data, along with concentration data for each of the 10 levels of chlorination (the Total PCB value is the sum of the 10 levels of chlorination data). The methods are based on identifying and quantifying the concentrations of the 10 levels of chlorination (Tables 2-2 and 2-3) by summing all the "peaks" that represent each level of chlorination separately. The method assumes a standard extraction technique is used, which is then followed by the method described instrumental analysis (GC separation and MS detection).

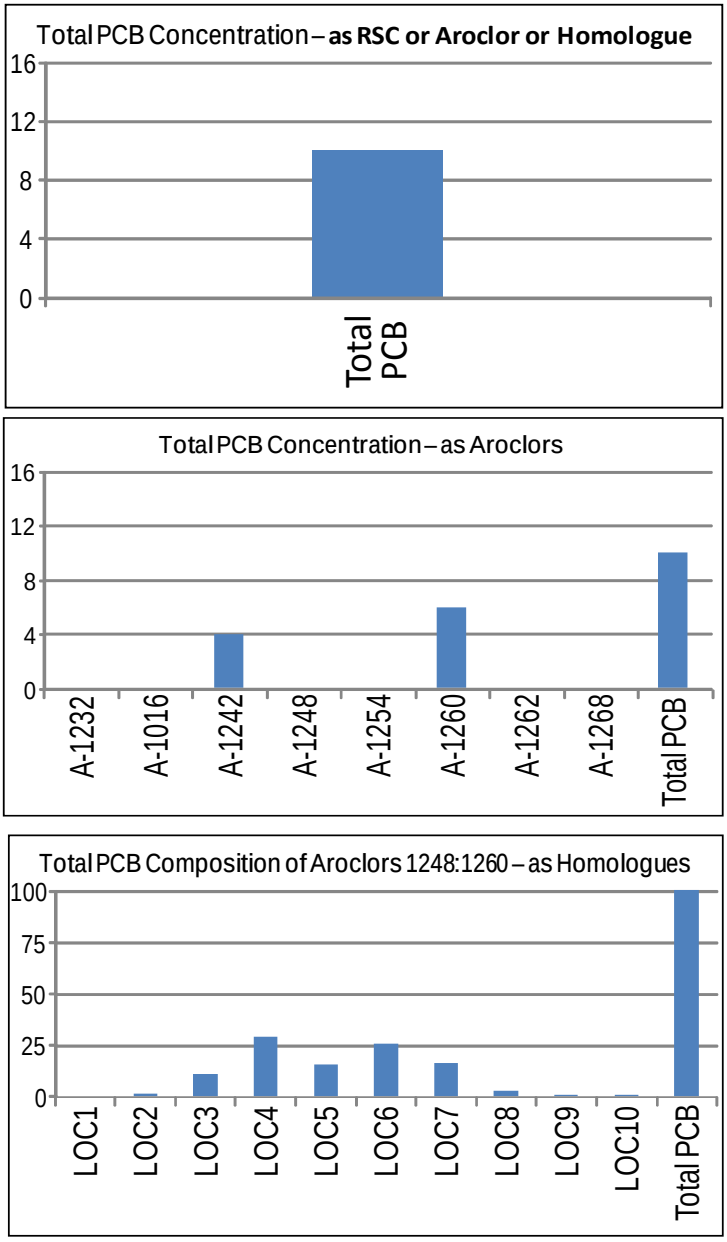


Figure 2-9. The Amount of PCB Information That May Be Available with ELISA (Method 4020), PCB as Aroclor (Method 8082), and PCB as Homologue (Method 680) Total PCB Analytical Methods

The instrument is calibrated by using the first and last eluting PCB congener for each level of chlorination (which has been well established), to obtain information on the chromatographic region for each level of chlorination and the response factor for each level of chlorination (for quantitation; by averaging the response factor for the two congeners). The MS detector provides a significant advantage over the previously described ECD detector. The MS detector is set to within a certain time window in each analysis to detect certain molecule and mass fragments based on their particular mass weight to unit charge, all of which are unique to the originating

molecule. For instance, all tri-chlorobiphenyls will produce two to three unique molecules and mass fragments, the tetra-chlorobiphenyls will produce two to three other molecules and mass fragments, and so on. The MS detector is programmed to detect the molecules and masses that are typical to PCBs. This means that the analysis is highly specific to PCBs and not as prone to interfering compounds and matrix components. Mass spectral detection is not affected by weathering/alteration of the PCB; the PCB composition of an environmental sample may no longer closely resemble an Aroclor, but this is irrelevant in the MS analysis as it reliably quantifies PCBs by level of chlorination regardless of the composition. Another possible advantage with Method 680 is that the MS analysis method can be set up so that PCB congener methods are acquired and stored, for cost-effective reduction of those data at a later time to generate PCB congener results.

The primary drawback of the Total PCB as homologues (level of chlorination) method (U.S. EPA Method 680) is that it is not an analysis that is widely offered by analytical laboratories. The method is an excellent choice for obtaining reliable Total PCB data, regardless of the composition of the PCB (i.e., it is not affected by environmental transformation or Aroclor mixtures), and also provides some level of compositional information by also generating concentration data for each of the 10 levels of chlorination. The method provides accurate Total PCB concentrations, some additional compositional information (Figure 2-9), and can be useful for characterizing the PCB contamination at a site. A plan for more detailed sampling and analysis can then be developed, as needed.

2.4.2 Congener-specific Sample Analysis Techniques (including ACF)

This section summarizes three analytical methods that are available for determining PCB congener concentration in environmental samples; a GC/ECD-based method suitable for approximately 20 PCB congeners (Method 8082), a GC/low-resolution mass spectrometer (LRMS)-based method suitable for 40 to 120 congeners (modified Method 680/1668), and a GC/high-resolution mass spectrometer (HRMS)-based method suitable for more than 100 PCB congeners (Method 1668a).

Congener-specific Methods

U.S. EPA Method 8082, the previously described Total PCB as Aroclor GC/ECD method, can be applied to PCB congener analysis and can provide data for a limited set of congeners (usually about 20 congeners). The NOAA National Status and Trends Project 18-22 PCB congeners are often monitored using this method. However, many of the limitations discussed for GC/ECD and Method 8082 in Section 2.4.1 also apply to its application to PCB congener analysis. The GC/ECD is highly susceptible to interferences from other compounds or sample matrix components, which can, at times, make it difficult to accurately resolve and quantify discrete PCB congeners in the analysis, and can result in inaccurate quantitation (both incorrectly elevated *and* reduced concentrations may be observed, depending on how and to what interferences contribute in the chromatogram). Because of the interference and resolution limitations of conducting PCB congener analysis using a GC/ECD instrument, PCB congener analysis by Method 8082 is generally limited to no more than about 25 PCB congeners.

The previously described method for analyzing PCB homologues using GC/MS and Method 680 can be modified for identifying and quantifying a large set of individual PCB congeners. The

method, as widely used by a number of high-quality analytical laboratories, is generally referred to as a modification and combination of U.S. EPA Methods 680, 8270, and 1668, and can reliably be used to quantify more than 100 PCB congeners (or about 99% of the PCBs in most environmental samples). It is a LRMS method, like Methods 680 and 8270; the "low resolution" refers to the accuracy in the identification of masses that the detector is capable of (to +/- 1 mass unit). The method operated the MS in SIM mode, unlike the base full-scan mode described in Method 8270, but like Method 1668, to obtain a higher degree of specificity and more sensitivity. The method uses individual congener calibration for a very extensive set of PCB congeners, like Method 1668, and many of the QC guidelines from Methods 8270 and 1668. Although this is considered a modified method, it does fall within the general guidelines permitted under Method 8270, adapted for PCB congeners, and is like the widely applied high-quality methods for PAH analysis [3], just adapted to PCB rather than PAH compounds. This PCB analysis method has been available for more than 10 years [6, 14, 15], and is increasingly being used in high quality environmental analytical laboratories.

U.S. EPA Method 1668 is also a GC method but uses a HRMS as the detector, also operating in SIM mode. The "high resolution" refers to the accuracy in the identification of masses that the detector is capable of, which may be to within 0.001 mass units (or better), compared to within 1 mass unit for a LRMS detector. For instance, the molecular mass of trichlorobiphenyl is 255.9613. A HRMS with a 0.001 mass unit resolution would be set to detect this compound with a mass of 255.961 +/- 0.001, while a LRMS would be set to detect it with a mass of 256. This higher mass resolution of the HRMS provides additional compound specificity. However, this additional resolution is rarely needed for most PCB analyses. A benefit to using HRMS is that it can accurately resolve and detect a few of the 12 WHO toxic congeners when other methods may not be able to. Some of the WHO congeners are only present at very low concentrations in PCB contamination (see Appendix A), and the added specificity and sensitivity of HRMS is a benefit for detecting those congeners (e.g., PCB77, PCB81, PCB126). These congeners are often important in human health risk assessment investigations, but are of no significant value for a PCB forensics investigation. Method 1668a can also discretely separate slightly more PCB congeners than a LRMS analysis, but the additional congeners are ultra-trace level congeners that generally do not provide important additional information for PCB forensics.

Recent Analytical Advances in Fingerprinting Techniques

Recent advances in fingerprinting analysis include isotope ratio MS analysis, which allows for the use of isotopic variations between different molecules that are otherwise the same to assist in fingerprinting PCBs and potentially differentiate sources. The use of this technique began in the mid 1990s with carbon isotopic variations in primarily single-compound organic contaminants, such as organic solvents (e.g., trichloroethylene). In recent years isotope ratio MS has been evaluated for use for multi-component contaminants, such as PAHs [3] and PCBs [17]. One of the most important recent advances in the technology has been compound specific isotopic analysis (CSIA) to allow for individual PCB congeners to be analyzed separately, rather than all congeners together producing a bulk isotopic signal. So for carbon isotopic analysis the GC is used to separate the congeners, then each is combusted separately to form carbon dioxide gas which is analyzed by isotope ratio MS. For forensic studies this allows selection of specific PCB congeners that are more resistant to alteration to be used for analysis to avoid changes in source patterns that might be related to environmental alteration rather than differences in original

source signatures. Although the CSIA techniques show great promise, continued work is required to lower detection limits and reduce interference from coeluting components; isotope-ratio mass spectrometry and CSIA are methods that may be considered for a PCB forensics investigation, but are not further discussed in this document.

2.4.3 Selecting Analysis Methods for Forensics Investigations

When selecting the most appropriate analytical method, it is most important to determine what types of data are needed to answer the questions at hand, and then select the method accordingly. Data quality and cost are also important considerations, and it usually becomes a matter of balancing the information needs with the data quality and analytical costs (Figure 2-10).

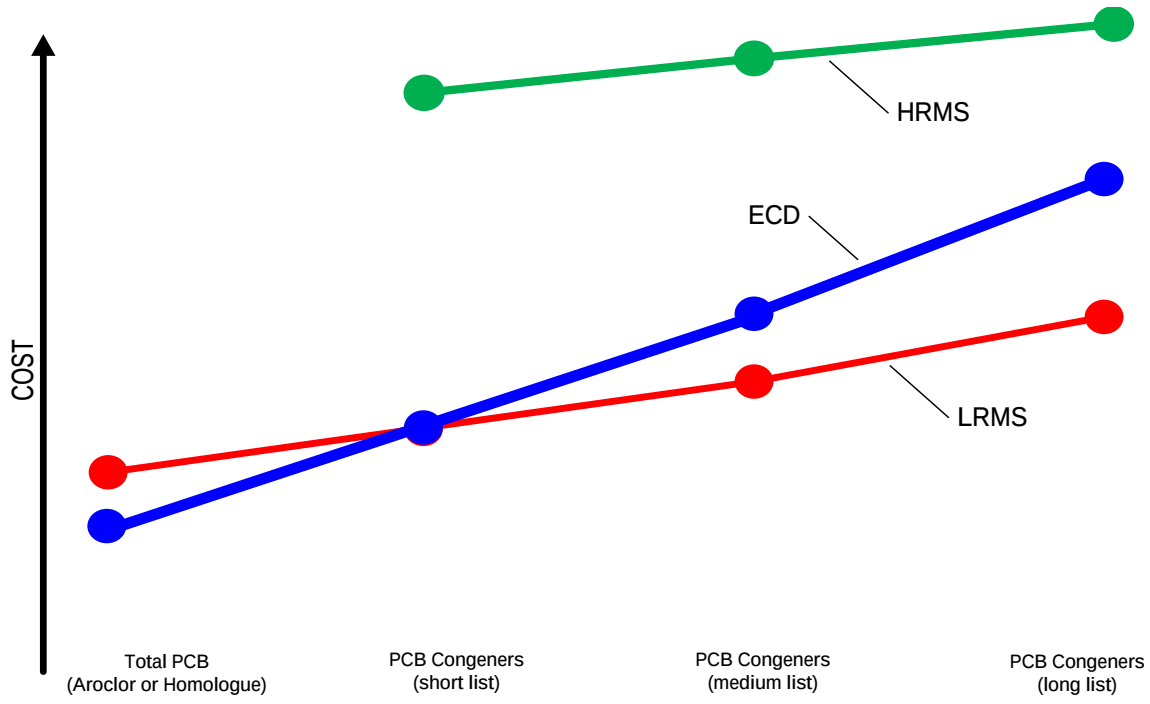


Figure 2-10. General Evaluation of Analytical Costs for Different PCB Analytical Instrument Methods, by the Type (Total PCB or Congeners) and Amount of Data (Number of Congeners) Produced

Total PCB analytical method options (i.e., RSC) were summarized in Section 2.4.1, and some key aspects of the three method options (including relative cost) are also summarized in Table 2-7. As discussed, the ELISA IA technique (Method 4020) is a rapid and cost-effective method for conducting Total PCB analysis, and is usually suitable for RSC (Tier I) analyses. This is also what was used for the two case studies described in this document. The Total PCB as Aroclor (Method 8082) method is an alternative for generating screening-level Total PCB data, as long as the PCB composition has a relatively close resemblance to Aroclors (see discussion in Section 2.4.1). Because Method 8082 is the most widely used Total PCB method, PCB data may have been generated for regulatory or other purposes for the site using this method, and may be available for use in a Tier I assessment. The Total PCB as homologue method (Method 680)

produces the most reliable and highest quality Total PCB data, and additional useful information by producing results for each of the 10 PCB homologues; this is the method of choice, if the slightly higher cost can be justified. However, Method 4020 (ELISA IA analysis) is the most suitable RSC method for most purposes, and can often provide Total PCB analysis for about $100/sample, with sensitivity and data quality that meet most RSC needs. The speed of the ELISA IA analysis is also a significant advantage, with the potential benefit of being able to map out PCB concentration gradients while still in the field and adjust subsequent sampling in a timely manner; the two other Total PCB methods are both laboratory-based and require several days, at best, to obtain the results.

Table 2-7. Comparison of Total PCB Analytical Methods

Method	Approximate Unit Analytical Cost ($)	Approximate Sediment Detection Limit (ppb)	Key Technical Advantages and Disadvantages
ELISA IA Method (Method 4020)	75-150	50	Advantage: Rapid Disadvantage: Potential calibration issues (can be avoided, as discussed)
PCB-as-Aroclor Method (Method 8082)	150-225	10	Advantage: Widely available; slightly more information than IA Disadvantage: Susceptible to interferences and misidentification
PCB-as-Homologue Method (Method 680)	250-325	1	Advantage: Accurate; not impacted by PCB alteration; more information than both IA and PCB-as-Aroclor Disadvantage: Not widely available

PCB congener analytical method options (i.e., ACF) were summarized in Section 2.4.2, and some key aspects of the three method options (including relative cost) are also summarized in Table 2-8. When selecting the detailed PCB congener ACF analytical method (Tier II), balancing the information needs with data quality and cost generally becomes an even more involved consideration than when selecting the RSC method. It is important to select enough PCB congeners and an appropriate set of diagnostic PCB congeners to be able to identify and differentiate potential PCB sources. Using information such as the PCB congener composition of Aroclor formulations (Appendix A and Table 2-3), and possible PCB dechlorination pathways (Table 2-4), it is possible to select a set of congeners that represent common environmental PCB contamination, including possible degradation products that may be of interest. A total of 80 to 120 well-selected PCB congeners are typically sufficient to provide the necessary PCB analytical data. For instance, the 117 PCB congeners reported for the Ashtabula River case study (Appendix B) represent 97 to 98% of the Total PCB in all Aroclor formulations and most environmental samples; the 92 additional possible PCB congeners are either not present in Aroclor formulations or environmental samples, or present at such ultra-trace levels that they would not be detected and/or useful for forensic purposes. Aroclor mixtures are generally the most appropriate PCB source material for assessing potential environmental PCB contamination, but a few non-Aroclor unique PCB source materials are possible. A few individual congeners, including PCB11 and PCB209, have been identified as being used for some industrial applications (e.g., PCB11, as part of some industrial pigment process [38]), and a process

involving the production of titanium tetrachloride has been identified to generate a small set of highly-chlorinated PCB congeners (in the octa- to deca-chlorobiphenyl range [39]). It is usually possible to conduct a high quality PCB forensic investigation with less than 100 PCB congeners. A smaller set of 44 PCB congeners was used in the HPS work (Appendix B), and this did provide solid information for general PCB characterization, but was somewhat limiting for forensic purposes. It can be difficult to predict which congeners will be important for the data analyses, and it is a fairly small increase in analytical cost to analyze 100 to 120 PCB congeners versus, for instance, 60 to 80 PCB congeners.

Table 2-8. Comparison of PCB Congener Analytical Methods

Method	Approximate Unit Analytical Cost ($)	Approximate Sediment Detection Limit (ppb)	Key Technical Advantages and Disadvantages
GC/ECD Congener Method (Method 8082) ~20 PCB congeners	250-400	0.25	Advantage: Widely available Disadvantage: Susceptible to interferences and misidentification
GC/LRMS Congener Method (Modified Method 680/1668) ~40-120 PCB congeners	450-650	0.05	Advantage: Accurate; not significantly impacted by interferences; can determine more congeners than GC/ECD method Disadvantage: Not suitable for a few WHO congeners
GC/HRMS Method (Method1668a) >100 PCB congeners (including WHO congeners)	800-1,200	0.01	Advantage: Accurate and sensitive; not impacted by interferences; can quantify all 12 WHO congeners Disadvantage: Costly

The three different PCB congener analytical instrument options that are available (Section 2.4.2) are suitable for somewhat different sets of information, provide different data quality, and have different costs (Table 2-9 and Figure 2-10). The information in Table 2-9 and Figure 2-10 is quite general, and different scientists may arrive at slightly different conclusions for Table 2-9, for instance. However, they are a general relative assessment, and illustrate a method consideration process that is useful when selecting an analytical method for an investigation.

Table 2-9. General Evaluation of PCB Congener Analytical Method for Method Selection (5="good"; 1="bad")

Performance Measure	ECD	LRMS	HRMS
Data Quality			
Sensitivity/detection limit	3	4	5
Accuracy	2	4	5
Precision/reproducibility	2	4	5
Matrix interference	2	4	5
Lab/field contamination interference	2	5	4
Analyte confirmation	2	4	5
Calibration performance	2	5	5
PCB Information			
Data generation: total PCB	3	5	4
Data generation: PCB homologues	1	5	3
Data generation: PCB congeners (short list)	3	5	5
Data generation: PCB congeners (long list)	2	5	5
Data generation: PCB congeners (WHO list)	1	3	5
Cost			
Cost – initial lab investment	4	3	1
Cost – maintenance/operation	3	4	2
Cost – sample analysis (project price)	3	4	1

As mentioned earlier, Method 8082 is generally considered inadequate for generating PCB congener data for a PCB forensic investigation. The GC/HRMS method (Method 1668a) is widely considered the ultimate PCB congener method for forensics studies, providing the highest quality data; it is, however, a costly analysis (often in excess of $1000 per sample). The GC/LRMS method (modified Method 680/1668) generally provides data of almost equal quality to GC/HRMS, often for about half the analysis cost of GC/HRMS analysis. The number of PCB congeners, sensitivity, and data quality in general that can be obtained with a GC/LRMS is generally adequate for the Tier II ACF analyses. GC/LRMS most often provides the optimum balance between information needs, data quality, and cost for most ACF projects.

A tiered analytical approach is recommended for a PCB forensic investigation, as was also described for PAH forensics [3]. By combining a larger numbers of less expensive RSC immunoassay Total PCB analyses with fewer more costly ACF PCB congener analyses, a high quality, yet cost effective, study design can be developed. The larger number of RSC samples allow for sufficient spatial coverage to map out the contamination and gain a general understanding of the situation, including the possibility of one or more potential sources. The PCB information from the RSC can be used to select a subset of samples for ACF analysis to provide the unique PCB congener diagnostic data needed to match the site samples to potential sources. The initial contour mapping provides an initial understanding of the site to better formulate a conceptual model that makes optimum use of the subsequent ACF analyses. In this manner, the more costly PCB congener analyses are not wasted by analyzing samples with no detectable PCB or generating redundant PCB information. In summary, combining the ELISA IA method (Method 4020) for the RSC Total PCB analysis with the GC/LRMS method (modified Method 680/1668) for the ACF congener-specific analysis generally provides an

effective analytical plan, although the other described methods can also generate useful information, assuming their listed strengths and weaknesses are recognized and accommodated.

Common PCB Analytical Options

This section presents an overview of common available PCB analysis methods, and their advantages and limitations

- **Total PCB Methods.**
  - PCB Immunoassay Method (e.g., RSC)
  - PCB-as-Aroclor Method
  - PCB Homologue Method
- **Individual PCB Congeners Methods**
  - Limited Congener Set Analysis using GC/ECD
  - Extensive Congener Set Analysis using GC/LRMS
  - Extensive Congener Set Analysis using GC/HRMS

2.4.4 Laboratory Data Quality Control

There are several components to a program to ensure that reliable and high quality data are generated, so that such data can be used with confidence, including the analysis of a series of laboratory QC samples and the subsequent evaluation of the resulting data. QC is an integral part of the laboratory activities. It demonstrates the quality of operations and analyses, provides analysts with metrics about method performance, and aids project managers in identifying and correcting systematic and random problems that can plague the laboratory operations.

The laboratory PCB analysis QC measures should allow for an assessment of processing effectiveness, potential laboratory contamination/interference, accuracy, and precision. A routine set of QC samples should accompany every batch of samples processed and analyzed at the laboratory; the following is a description of types of QC samples that are suitable for analysis with each batch of samples; suitable types of performance objectives are summarized in Table 2-10. The exact criteria used should be designated by the PM to ensure the results are suitable for site- and project-specific data needs and decision making. This laboratory QC program is suitable for the ACF analysis, but samples that demonstrate that contamination is controlled and analytical accuracy and precision should also be incorporated with the RSC analyses.

Table 2-10. Example Laboratory Performance Objectives (additional field QC samples may also be included in a project QA Program)

QC Sample Type	Example Performance Objective[a]	Corrective Action
Procedural blank (PB)	< 5× method detection limit (MDL), or field sample concentration >10×blank value	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Laboratory control sample (LCS)	40 – 120% recovery	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Matrix spike (MS)	40 – 120% recovery Spike levels >5× unspiked field sample concentration for DQO to apply	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Matrix spike duplicate precision	Relative percent difference (RPD) < 30% Spike levels >5× unspiked field sample concentration for DQO to apply	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Duplicate Precision	RPD < 30% Field sample concentration >5× MDL for DQO to apply	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Standard reference material (SRM)	Values to be within 30% of designated certified value on average for all compounds. Target concentration > 5× MDL for DQO to apply	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Surrogate internal standard (SIS) recovery	40 – 120% recovery	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Initial calibration	< 25% relative standard deviation (RSD) in relative response factors (RRFs), or correlation coefficient $r \geq 0.99$	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented
Continuing calibration	< 25% percent difference (PD) from expected concentration	Re-extraction, re-analysis, and/or document and justify per PM; all corrective actions documented

[a] These are ***example*** performance objectives that may be considered for PCB instrumental analysis. Actual performance objectives or criteria should be set on a project-specific basis to meet project-specific objectives.

- Procedural Blank (PB) - A PB is a combination of solvents, surrogate internal standard (SIS) compounds, and all reagents used during sample processing, processed concurrently with the field samples. It is intended to monitor purity of reagents and potential laboratory contamination and interferences.
- Laboratory Control Sample (LCS) - An LCS is a contaminant-free matrix-specific sample (e.g., Ottawa sand or sodium sulfate). It is spiked with the analytes of interest and processed identically to the field samples to assess analyte recoveries and effectiveness of the method with no influence by the sample matrix.
- Matrix spike - A matrix spike is a field sample spiked with the analytes of interest at approximately 10 × the method detection limit (MDL), processed concurrently with the field samples. It is intended to monitor the recoveries and effectiveness of the method in the presence of the sample matrix.
- Sample duplicate - A duplicate is a second aliquot of a field sample processed and analyzed to monitor precision. The duplicate may be a second matrix spike sample.

- Standard reference material (SRM) – An SRM is prepared like a field sample to assess the accuracy of the analytical procedures. This is natural sediment that has been certified by the National Institute of Standards and Technology (NIST) to contain certified concentrations of the target compounds.
- Instrument Check (IC) – An IC sample is prepared by spiking a small amount of solvent with target compounds obtained from a vendor that is different from that used for the calibration standards, and then analyzing the IC as a sample. The IC sample is used as an independent measure of accuracy in the absence of sample processing.

In addition, a suite of SIS compounds are added to all field and QC ACF samples prior to sample preparation. These compounds are added to determine the efficiency of the sample extraction and analysis procedures, and to aid in the accurate quantification of native concentrations of the target analytes in the field sediment samples. A set of at least three SIS compounds with varying molecular size should be used to represent the range of target analytes (e.g., a trichlorobiphenyl, a pentachlorobiphenyl, and a heptachlorobiphenyl, at a minimum). It is also important that the SIS compounds are representative of the target compounds in the analytical procedure (i.e., have similar behavior). PCB congeners that are not expected to be in environmental samples (i.e., not present in Aroclor formulations and not expected to be generated through environmental processes), and well resolved analytically from PCB congeners that are present, are particularly suitable for use as SIS compounds. Isotopically labeled PCB congeners are also an excellent choice. A PCB chemist should be involved to assist in the selection of these SIS compounds.

Method Detection Limit

The MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is generally determined by the method outlined in the U.S. Federal Register [37]. However, MDLs are not always the best measure of analytical sensitivity, and are one of several ways to evaluate the sensitivity of an analytical method. Reporting limits (RLs, sometimes referred to as minimum levels [MLs]) are defined by the sample concentration of a compound that is equivalent to the final extract concentration based on the low calibration standard concentration, and is often used to qualify data. However, uncensored data are most useful and should be reported for most environmental forensics studies based on a careful review of the analytical chromatogram by an experienced analytical chemist. Target compounds *confidently* detected below the RL (typically to a concentration with a signal-to-noise ratio criterion of 3:1, and identified with confidence by an experienced PCB analytical chemist) should be reported and qualified appropriately, regardless of how it compares to the calculated MDL. Target compounds detected between the RL and MDL are reported and typically also qualified, with a unique qualifier.

2.5 Data Analysis and Interpretation

Environmental forensics and statistics/data analysis often intersect because forensics projects typically depend on the analysis of large amounts of chemical data that need to be interpreted. PCB environmental forensics investigations often involve the collection of hundreds, if not thousands, of samples. If such data are analyzed by congener-specific methods, each sample will have associated with it 50 to more than 100 chemical measurements. Such large chemical data sets translate to major data management and data analysis challenges. As such, it often makes

sense that multivariate statistical methods are one important tool used to analyze such data. Unfortunately, there are very large sets of different data analysis methods that can be and have been used in environmental forensics investigations. The majority of these have been borrowed from scientific disciplines that predate by decades the current practice of environmental forensics (e.g., diagnostic ratio analysis in petroleum geochemistry, PCA in psychometrics, geology, and countless other disciplines). The methods discussed herein are based on the authors' collective experience. A comprehensive discussion of methods available to PCB forensics investigations goes beyond the scope of this document.

Given the wide range of potentially useful methods, it is best to begin in terms of general data analysis objectives and philosophy. The major objective of a PCB forensics investigation is generally the identification and delineation of multiple sources in an impacted system. Given data from a well-designed sampling plan that spans the desired geographical and temporal range of the study, three things should be determined:

1. The number of chemical patterns contributing to a chemical system. Ideally, different sources produce different chemical patterns, but this is not always the case.
2. The unique chemical composition ("fingerprint") of each chemical pattern.
3. The relative contribution of each fingerprint in each sample.

The systems under study (sites with historical contamination) are not well-designed experiments. Rather, they are the results of inadvertent releases ("accidental experiments") that generally occurred long before any detailed environmental investigations were undertaken. The contamination is often decades old, and records associated with the chemical releases are often sparse or nonexistent. This makes for an extremely complex system with many unknowns: site history, source chemistry, timing of release, and the presence of additional, unsuspected sources. A priori knowledge of all contaminant sources that have impacted a system is rare. A philosophy of exploratory data analysis (EDA) must be adopted, rather than classical hypothesis testing. The objective of EDA is to allow patterns and correlations to be derived directly from the analysis of ambient data, with minimal a priori hypotheses. A number of proven methods are discussed below (e.g., PCA, receptor models, ratio methods, simple graphics), but any number of methods that meet the above listed objectives, and conform to EDA philosophy, are potentially applicable to PCB forensics investigations.

2.5.1 Background and History of Data Analysis

While the term environmental forensics began seeing widespread use in the late 1990s, the data analysis methods most often used (and discussed herein) predate their application to environmental forensic by years, if not decades. The following sections discuss the history of some of the more commonly used methods.

2.5.1.1 Chromatograms and Simple Compositional Analysis

A forensic investigation includes several key steps of information and data analysis, including (1) review of site history and records research, (2) analysis of sediment/contaminant transport and hydrodynamic data, (3) review of the PCB concentrations, (4) initial review of the PCB composition, and (5) comprehensive chemometric analysis of the PCB data. The most basic

assessment of the PCB data and its potential association with sources is to review how the PCB concentration is distributed across a site; attempts to link PCB contamination with potential sources through PCB concentration contours and geographic distribution is the simplest and oldest approach to PCB forensics. Although not statistically rigorous, it has always been a useful first use of the PCB data to develop an image of the source association.

PCB composition (i.e., relative concentrations of PCB homologues and PCB congeners) is generally the next step in the initial PCB characterization of a site to develop ideas of potential sources. This can be done by carefully reviewing analytical chromatograms, or using bar graphs which are, in essence, recreated chromatograms with only the PCB data (e.g., Figure 2-2). Again, although not statistically rigorous, samples that have similar PCB composition may have a contaminant source relationship and understanding which sub-sets of samples have similar PCB compositional characteristics is useful initial information.

Analyzing PCB congener ratios is another type of PCB compositional analysis. Compound ratios have been used to infer sources of contaminants (e.g., [40, 41]) and to identify PCB transformation, including dechlorination [8, 10]. The idea is that if one can identify pairs of source-diagnostic congeners, then ratios between those compounds will retain the initial source signature. Conversely, if one can identify compounds that are susceptible to dechlorination and those that are resistant to dechlorination (Table 2-4), one can monitor the degree of dechlorination, assuming the original type of PCB contamination was a constant. Figure 2-11 illustrates active dechlorination, with the increase in the relative amount of PCB4/10 (dechlorination products) and the simultaneous decrease in PCB118 (a congener susceptible to dechlorination) with depth (time) in the sediment. Active dechlorination was confirmed multiple ways for the Lake Hartwell sediments, including with PCA analysis (Figure 2-12); deeper sediments with “old” PCB contamination exhibited a significant dechlorination, with a unique PCB composition that did not resemble any Aroclor (Figures 2-4 and 2-12). A potential drawback of ratio analysis is that the data analyst must make a decision regarding which chemical pairs are diagnostic of source, and have similar affinities to weathering. This requires a priori knowledge and/or assumption, and generally an uncommon depth of understanding PCB chemistry. As for most (if not all) of the PCB forensics methods discussed herein, diagnostic ratio-based methods were widely used in geochemistry applications prior to being adopted for forensics, most notably in fingerprinting of oil and source rocks in petroleum geochemistry applications [41, 42]. In the HPS demonstration study (Section 3.1), the ratio of PCB28 to PCB153 was used to evaluate the hypothesis of a source of less chlorinated PCB material in Yosemite Creek (a tributary that outfalls near HPS).

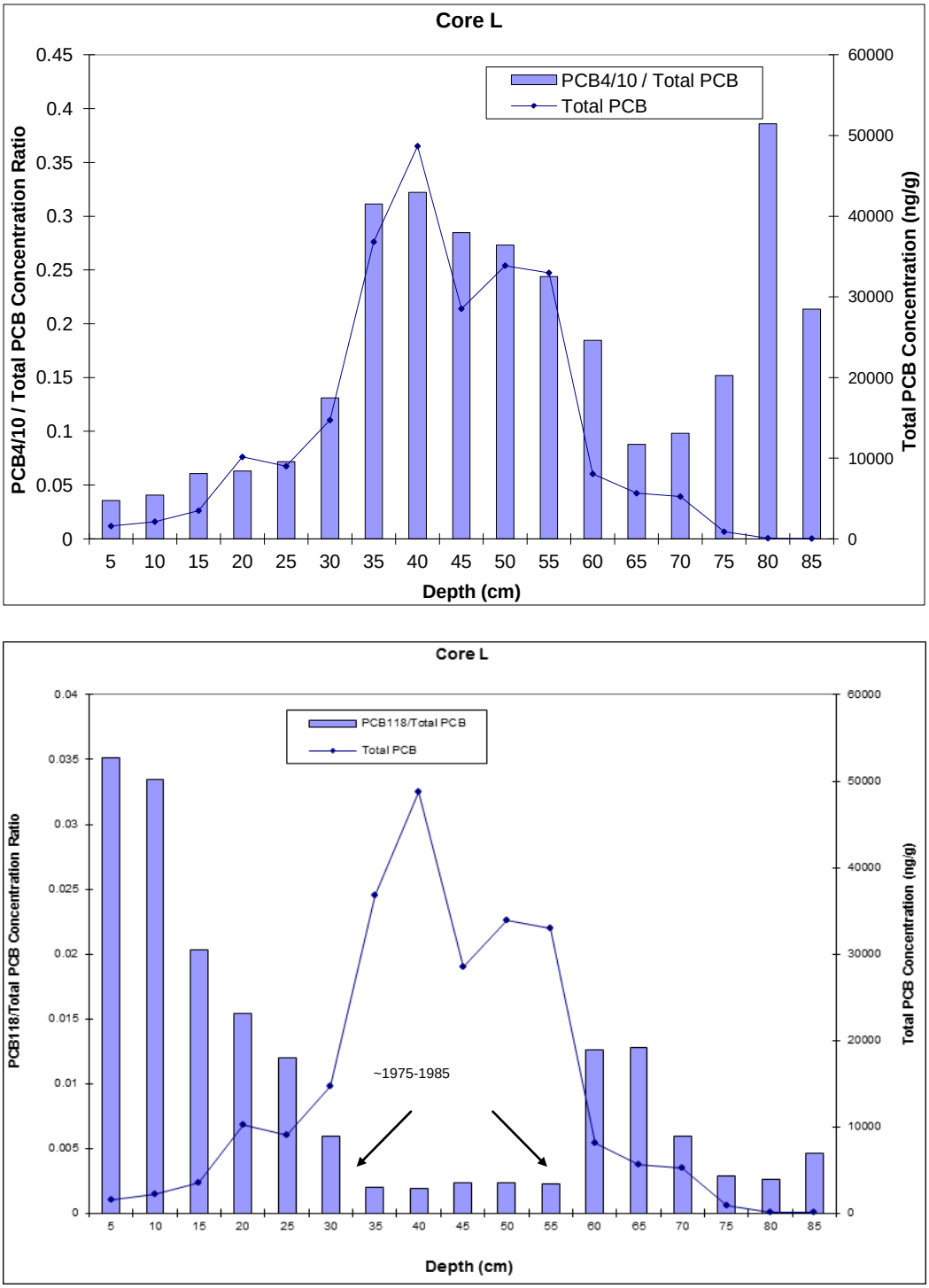


Figure 2-11. PCB4/10 (top) and PCB118 (bottom) to Total PCB Concentration Ratio Bar Graph along with the Total PCB Concentration (line chart) for a Core from Lake Hartwell

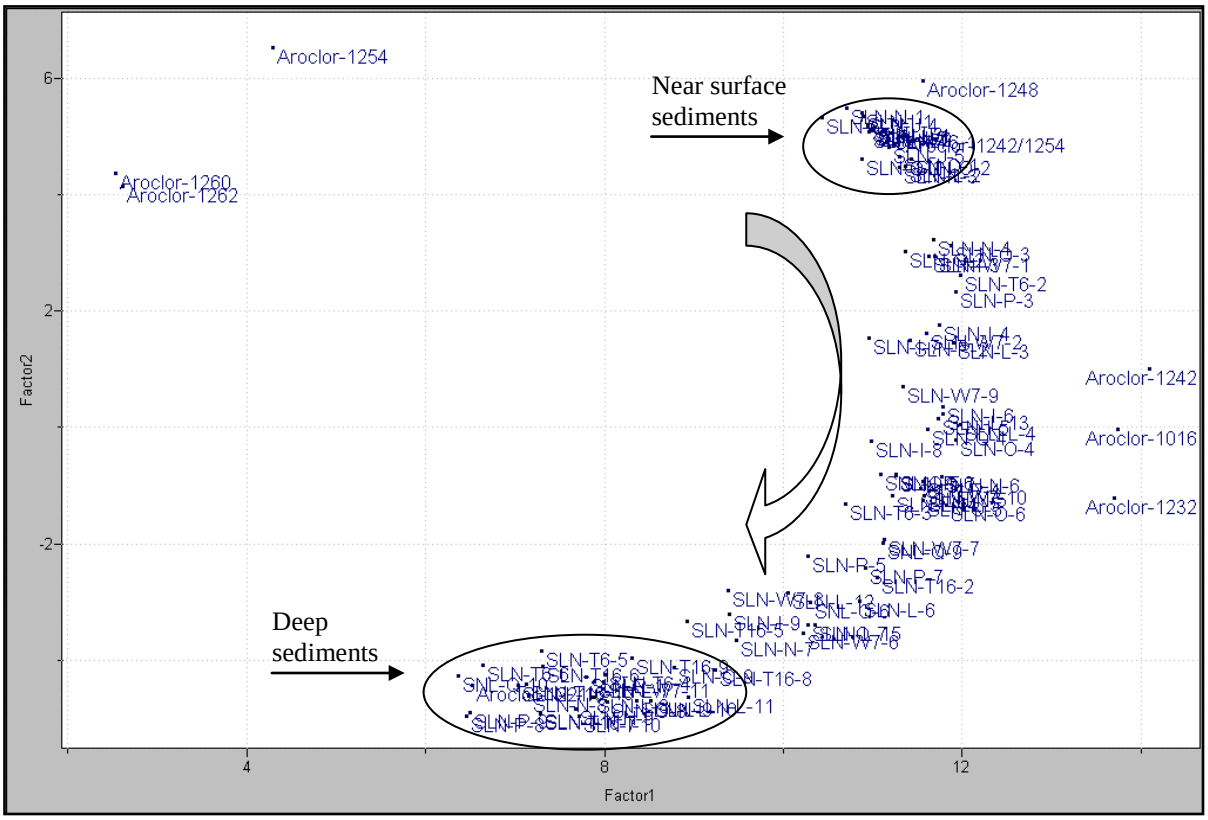


Figure 2-12. Principal Component Analysis Plot Using PCB Congener Data from Lake Hartwell Surface and Subsurface Sediment Samples
(Subsurface samples exhibit dechlorination and have no resemblance to Aroclors.)

2.5.1.2 Multivariate Analysis (Classification Analysis)

Several different classification multivariate analysis methods are available, of which PCA is the most widely used in PCB forensics. PCA is widely used for environmental forensics as a whole and in many scientific disciplines far removed from environmental chemistry. It is used both as an exploratory data analysis method on its own, and as an intermediate step in receptor modeling. PCA was used in many scientific disciplines long before the terms *environmental forensics* or *chemical fingerprinting* were ever coined, and long before the development of quantitative congener-specific PCB analysis. The roots of PCA go back to at least 1904 and psychologist/statistician Charles Spearman [43]. PCA methods began seeing widespread use in the earth sciences in the early 1960s [44]. In those early days, the method was generally referred to by geologists as *factor analysis* (FA) – a term borrowed from the psychologists that followed Spearman. There is considerable confusion on the relationship between PCA and FA. Much of this is due to the fact that there is little agreement on terminology across scientific disciplines (e.g., chemometrics, psychometrics, engineering, mathematical geology, etc.). The confusion still remains. However, *PCA* is generally the term of choice in environmental forensics, and *scores* and *loadings* are generally used for the chemometric definitions.

2.5.1.3 Receptor, Chemical Mass Balance, and Mixing Models

An increasingly common method used in environmental forensic investigations involves the use of receptor models. These methods are designed to resolve three parameters of concern in a multivariate mixed system: (1) the number of components in the mixture, (2) the identity (i.e., chemical composition) of each component, and (3) the relative proportions of each component in each sample.

Receptor methods often (but not always) use PCA as an intermediate step to (1) determine the number of "significant" principal components (i.e., the number of potential sources), and (2) provide a reduced dimensional reference space for resolution of the model. If source compositions are known a priori, then those compositions may be used as a training data set in the receptor model, and source contributions may be found via regression methods such as chemical mass balance [45, 46]. However, in environmental forensics, one typically does not know and/or wishes not to assume knowledge of sources. For such situations, it usually is preferable to use a self-training receptor model method: a class of algorithms designed to resolve the number of sources, and provide feasible estimates of the multivariate source patterns and source contributions, without a priori assumption of sources. Methods in common use in environmental forensics include PVA, multivariate curve resolution/alternating least squares (MCR-ALS), PMF and Unmix.

Based strictly on the environmental forensics literature, it might appear that there was an evolution of methods from less sophisticated PCA applications in the mid to late 1990s to the development and implementation of more sophisticated algorithms in the new millennium. However, once again, all of these methods actually existed long before the term environmental forensics was in widespread use, and certainly well before being applied to PCB congener data. The PVA method used in recent PCB applications (e.g., [8]), and for the HPS and Ashtabula River case studies in this research (Sections 3.1 and 3.2) is essentially the same algorithm published 30 years ago by Full et al. [47, 48]. Similarly, PMF was first published in 1994 [49] and MCR-ALS in 1993 [50]. While not called Unmix at the time, the development of that algorithm can be traced back to the early 1990s [51, 52], and was an extension of self-modeling curve resolution work from the 1970s [53]. These methods have been modified and new options published since they were originally introduced, but the algorithms remain largely unchanged since the early 1990s.

There are a number of likely reasons why it may appear that the receptor model methods came along later than they did. Firstly, there is a big difference in accessibility and user friendliness of receptor model software as compared to more common data analysis techniques such as PCA. In the mid-1980s one needed to use Fortran software running on a main-frame computer to apply PVA. In the 1990s, if one wanted to use PVA, ALS, or PMF one had to contact the academician that had developed it and determine how to apply it. The software was primarily developed for academic research purposes, and as such was neither intuitive nor particularly user friendly. Today, one can download a much improved version of Unmix or PMF from the U.S. EPA Web site (http://www.epa.gov/ttnamti1/unmixmtg.html), and commercial data exploration and analysis software products (e.g., Pirouette from Infometrix) include an ALS module.

The application and comparison of these methods has been presented in the literature [9, 19, 54]. Given high quality chemical data (and data that have undergone rigorous quality assurance [QA]/QC to identify and address any problems with non-detects, interferences, and other analytical issues), each of these methods perform well and resolve similar source patterns and apportionment. However, like PCA, these methods require that the user has a certain level of experience and familiarity with environmental data structures.

2.5.2 Data Review and Preparation

2.5.2.1 Laboratory Data Quality Review

The laboratory QC sample data should be reviewed against the DQO to assess the key QC measures for potential contamination, accuracy, and precision, to ensure that the analytical data represent the PCB concentrations in the samples. The DQOs for the laboratory QC samples included with the ACF analyses from the HPS and Ashtabula River case studies are presented in Table 2-11. A summary of the QC sample results are summarized in Table 2-12. As can be seen, the vast majority of the QC samples prepared and analyzed along with the PCB samples produced QC results that met the DQOs for these sample sets. For instance, 96% of the SIS recoveries and 100% of the LCS recoveries determined with the HPS samples met the DQOs. In general, the QC sample results were of uncommonly high quality for both case studies.

Table 2-11. Comparison of Project Results to Data Quality Objectives – PCB Congener Analysis of Hunters Point Shipyard Sediment Samples

QC Sample or Measurement Type	Data Quality Objective	Total Number of QC Measure Data Points[a]	Number of QC Data Points that Met the DQO	% of QC Data Points that Met the DQO
SIS Recovery	40 to 120% recovery	560	540	96.4
Method/Procedural Blank	No compound to exceed 5 times the RL, unless sample is >10 times blank amount	308	308	100
LCS Recovery	40 to 120% recovery for spiked compounds	308	308	100
Matrix Spike/Duplicate Recovery	40-120% recovery for spiked compounds. Applies to analytes with spiked concentration >5 times the native sample concentration.	616	609	98.6
Matrix Spike/Duplicate Precision	RPD <30%. Applies to analytes with spiked concentration >5 times the native sample concentration.	308	236	76.6
Instrument Check Accuracy/Precision	PD <20%.	308	308	100

[a] Total number of data points of the indicated QC measure. For instance, for surrogate recovery it would be the number of surrogate compounds in each sample multiplied by the total number of samples. For the method blank it would be the numbers of method blank samples analyzed with the sample set, multiplied by the number of target analytes measured.

Table 2-12. Comparison of Project Results to Data Quality Objectives – Ashtabula Sediment Samples (EPA-ORD and GLNPO Project Combined)

QC Sample or Measurement Type	Data Quality Objective	Total # of QC Measure Data Points[a]	# of QC Data Points that Met the DQO	% of QC Data Points that Met the DQO
SIS Recovery	40 to 120% recovery	992	987	99.5
Method/Procedural Blank	No compound to exceed 5 times the MDL, unless sample amount is >10 times blank amount	1,902	1,902	100
LCS Recovery	40 to 120% recovery for spiked compounds	1,902	1,899	99.8
Matrix Spike Recovery	40 to 120% recovery for spiked compounds Applies to analytes with spiked concentration >5 times the native sample concentration.	1,902	1,900	99.9
Sample Duplicate Precision	RPD <30%. Applies to analytes with concentration >5 times the MDL.	1,902	1,899	99.8

[a] Total number of data points of the indicated QC measure. For instance, for surrogate recovery it would be the number of surrogate compounds in each sample multiplied by the total number of samples. For the method blank it would be the numbers of method blank samples analyzed with the sample set, multiplied by the number of target analytes measured.

Some DQO exceedances can be expected with challenging sample matrices and when applying ultra-trace level analytical methods. Analytical results that do not meet the listed DQOs should always be reviewed by a senior analytical chemist for assessment of the potential impact of the results. Affected samples may be reanalyzed if needed to ensure high quality data. QC sample data that are accepted outside the DQOs should be indicated with the appropriate data qualifier, and the rationale for accepting the analysis should be documented, so that subsequent data users can assess if there was any potential impact on the data quality. Overall, the QA program, including the analysis of laboratory QC samples processed and analyzed with the field samples, produced data that demonstrate that the methods were appropriate and that the analyses were under control, generating high quality and reliable data that can be used with confidence.

2.5.2.2 Data Preparation

Typical data assessment and preparation are summarized below, using examples from the Ashtabula River data set for illustration. The laboratory ensures that the data have met the analytical data quality expectations (Section 2.5.2.1), and deliver the data to end users. Additional preparation (Section 2.5.2.2) and quality/usability review and screening (Section 2.5.2.3) are then performed before the final data (and potentially reduced data set) are interpreted for forensic purposes.

Data are typically received in a variety of formats (e.g., spreadsheets, databases, GIS files). Regardless of the format, the first step is to put all data into a format that is readily useable for review and data analysis. A common format is Excel spreadsheets, with samples as rows in the spreadsheet, variables (PCB congeners or homologs) as columns, or vice versa. It is important to compile as much information about the data and samples as possible in the data preparation stage. Additional important sample information to capture in the spreadsheet or data transmission includes:

- **Unambiguous Sample Identification (ID).** Often, the same sample will carry different sample names/numbers, and it is important to be able to cross reference. A common example is a field station ID, field sample ID (the sample name assigned by field personnel) and the lab sample ID (the analytical laboratory's internal tracking number).
- **Laboratory Analytical Batch ID.** It is often valuable to know what analytical batch the sample was analyzed with to be able to associate field samples to laboratory QC sample results (which tend to be analytical batch specific), and should there be a need to discuss the data with the analytical laboratory.
- **Sampling Date.** It is critical to know when the sample was collected to understand what period in time the data represent. This is particularly important if data are available from different time periods for the site, but is important for any sample since putting contamination into a historical perspective is important in any forensic investigation.
- **Sample Sediment Depth.** It is important to know sediment depth interval below surface that the sample represents to understand how samples can be compared with each other, and to link the data to source input history, among other things. The top and bottom depth of the sample (e.g., 5 cm to 10 cm) is important to know. If the sample is a surface sediment sample, it is critical to know to what depth the sample was collected, as surface sediments are collected differently in different projects (it may be just the top 1 cm representing very recent contamination, or as deep as the top 1 ft potentially representing decades of contamination). Samples that represent a wide range of sediment depth (e.g., from the surface to 1 ft deep) are often less useful for a forensics investigation than samples representing smaller depth intervals.
- **Concentration Information.** Having information on the concentration units (e.g., ng/g,), and whether the data are on a dry or wet weight basis, is important to be able to put the contamination into perspective, and to support a variety of data analyses. It is best to avoid the ppm and parts per billion (ppb) nomenclature, and instead use units in a format such as mg/kg and µg/kg. Although some data analysis (e.g., pattern recognition methods) use data normalization and transformations to optimize the analysis, it is important to also maintain a data set with concentration information.
- **Sampling Location.** It is critical to be able to link a sample with a specific sampling location. Manually indicated "dots on a map" showing the approximate locations will not suffice for a forensics investigation; accurate global positioning system (GPS)-based location information (latitude-longitude, northing-easting) are needed. Although some chemometric analysis may be performed with less detailed location information, a high degree of accuracy and location certainty may prove crucial to evaluating the

fingerprinting data, and supporting the results. Location-specific geochronology data (e.g., ^{210}Pb or ^{137}Cs data; Section 2.5.3.2) are extremely valuable, and often critical, for understanding the history of the contamination and support rigorous statistical and other data analysis.

ACF PCB congener analysis requires the application of high QA/QC standards to produce data of sufficiently high quality to support a forensic interpretation. Experienced PCB analysts should be overseeing and conducting the laboratory analyses and reviewing the analytical results. The analyst should have a familiarity with PCB chemistry and sensitivity to common as well as PCB-specific analytical QA/QC issues. The data should be accompanied by information related to the QC sample results and the overall data quality (a QC narrative; Section 2.5.2.1). Data qualifiers should be applied as appropriate to help data users understand potential laboratory data quality limitations, or other important sample or value-specific issues (see below). Additional data quality, reasonableness and usability assessment should be performed separately and independently following the laboratory's delivery of the data, and is discussed in Section 2.5.2.3.

The application of laboratory data qualifiers (sometimes referred to as data "flags") can vary from project to project depending on the project-specific DQOs, but widely applicable DQOs and an example laboratory QC sample program were described in Section 2.4.4. Chemical data reporting conventions and the use of data qualifiers may vary from lab to lab, but such information should accompany the data delivery and QC narrative to be able to understand and use the analytical data.

The "value" reported for non-detects is particularly important to understand for data assessment purposes. Some laboratories will report an empty/blank field if not detected, some laboratories will report a zero, and some laboratories will insert a value based on the laboratory's separately determined detection level (e.g., the MDL, half the MDL, or the RL or ML). Whatever the reporting convention for non-detects, it should be well documented with the data delivery and, ideally, also accompanied by a qualifier in the data set that identifies it as being non-detect. The data qualifier "U" is most commonly used to indicate a non-detect. Additional common laboratory data qualifiers are summarized below, but different qualifying conventions can be used as long as they are appropriately documented.

- **U** – Analyte not detected based on the careful review of the chromatogram by an experienced PCB analyst. A criterion of a signal-to-noise ratio of approximately 3 to 5:1 for the analyte peak in the chromatogram, and acceptable peak shape, is often used, and preferably manually assessed and confirmed.
- **J** – Most laboratories use this qualifier to indicate the identification of an analyte (using the criteria listed for the "U" qualifier), and reporting of a concentration that is below a common reference point; sometimes referred to as an estimated concentration. It is often assigned when a data value is near the detection limit, and below some commonly calculated reference value (e.g., the RL or ML, which is the field sample concentration that produces a final sample extract with a concentration that is equivalent to the low calibration standard). The RL/ML are generally more useful sensitivity and detestability reference values than the MDL, which is a periodically calculated performance measure

that incorporates precision and method performance, but may not be the best measure to represent analytical sensitivity.

- **ME** – This is a common qualifier to use to indicate that there was matrix interference (i.e., not a "clean," well resolved analytical peak in the chromatogram) and that the value should be considered an estimate.
- **N** – This is a common qualifier to use to indicate a value that did not meet the recovery, precision, or accuracy DQO, but is deemed by the laboratory to not impact the overall quality of the field sample results (as discussed in the QC narrative). This qualifier may be used for surrogate compound recoveries of field samples, or recovery, accuracy, and precision results for various QC samples.
- **R** – Rejected. The reported value for this data point was rejected by some laboratory criterion and/or through review by the laboratory, determining that the laboratory could not produce a reliable value or even an estimate. The "reject" assessment may apply to an individual compound, or an entire sample, as indicated, and should be discussed in the QC narrative.
- **D** – Diluted. Sample had to be diluted, usually due to a high concentration of the analyte (i.e., the concentration was above the calibration curve in the initial analysis).
- **C** – Coelution. For PCB congener analysis, some laboratories will report this flag for PCB congeners that coelute with some other congener, usually indicating which congener it coelutes with using the IUPAC number (e.g., C4 for PCB10). Other labs will not report "C" but will identify the analyte as the coeluting set of congeners (e.g., PCB4/PCB10).

If the laboratory qualifying system (i.e., lab-flag scheme) and non-detect reporting method are not clear from the deliverable provided, it is important to contact the laboratory to obtain clarification before proceeding with the data analysis. Such information is extremely useful in deciding which samples/analytes to include in an analysis, determining the proper course of action in handling outliers, and evaluating the validity of a chemometric model's interpretation.

Standard graphics resulting from statistical data analysis (e.g., PCA scores plots) are useful, but are by themselves often insufficient. In any environmental forensics investigation, one must be able to put results in a spatial context, creating maps or other geographical representations. It is often very useful to incorporate the data into a GIS, and producing GIS files of the site; sampling locations are ideally part of the project planning or, at a minimum, an early part of the information analysis. If the primary data interpreter is not proficient in GIS mapping, they should solicit the help of somebody who is. In the case of the Ashtabula data set, GIS information was available in the form of GIS shapefiles, which were used to construct a simple base map, showing key geographic features of the study area (Figure 2-13). The HPS site also had good GIS information available, as will be shown in Section 3. The objective initially is not necessarily to generate report-ready graphics, but to have the ability to quickly put data and analysis results in geographic context.

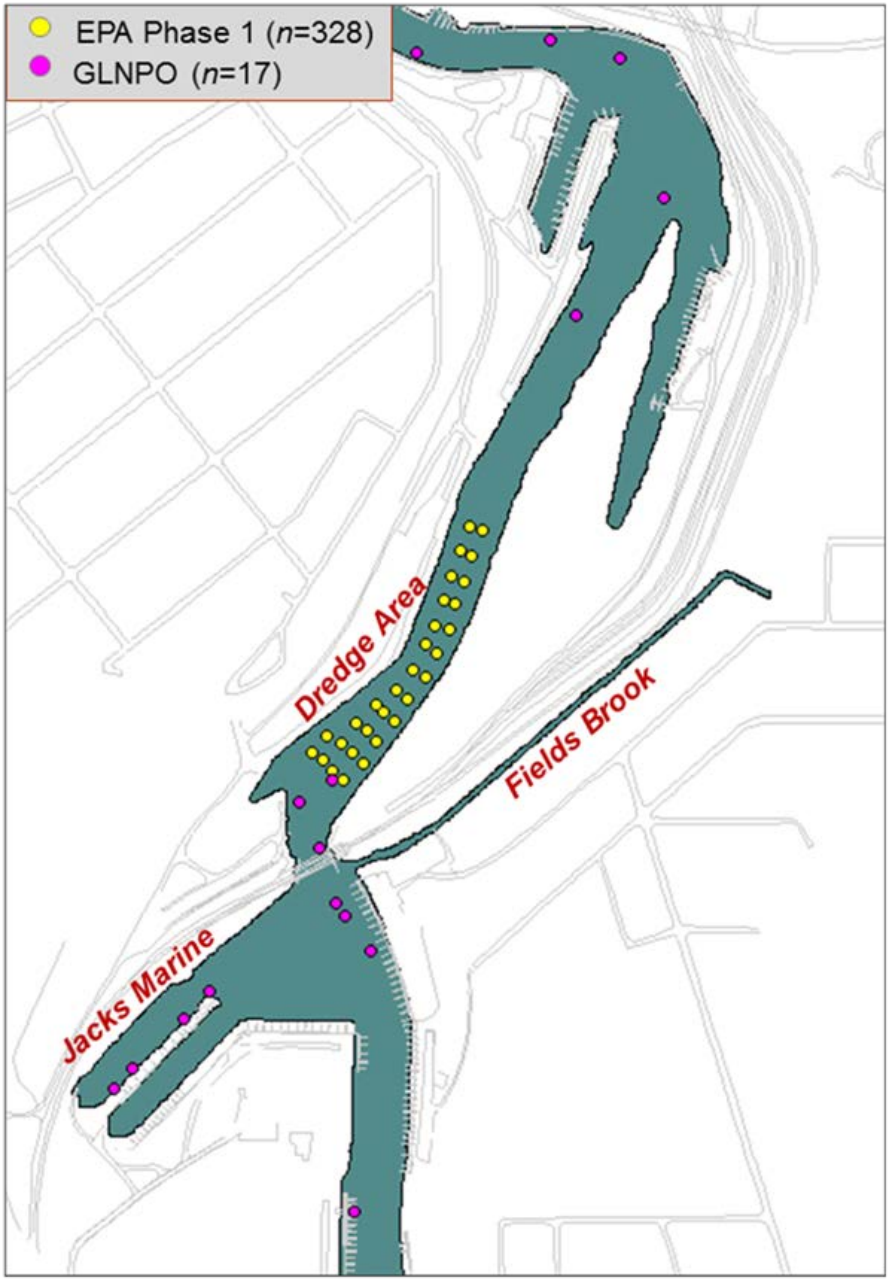


Figure 2-13. Simple Base Map of the Ashtabula River Study Site Showing Sampler/Core Locations

Historical PCB data from a site are commonly available only as hardcopy in old reports. In such cases, a time-consuming first step may be a hand-entry of data into spreadsheets, or the application of a scanning-to-digital information translation software (which, if used, needs to be carefully verified), and digitization of sample locations off of hard-copy maps such that the data can be analyzed in geographic context.

Using PCB congener data from multiple laboratories is another common challenge. Often, when historical PCB data are available for a site, samples may have been analyzed by different laboratories and perhaps using different analytical methods (often with different coelutions characteristics and different PCB congener analyte lists). The ability to perform PCB congener pattern comparisons between samples analyzed by different labs is dependent on (1) determining which reported analytes are most comparable between data sets and (2) reducing both data sets to a PCB congener list that is most comparable.

The solution to such a challenge with merging data from multiple laboratories and/or methods is usually project specific, taking into account the different analytical methods that were used, considering the reported quality of the QC sample results, the age of the data, etc. (for example, PCB153 coelutes with different congeners in different laboratory method systems). On a GC/ECD system using a DB1 column, PCB153 often coelutes with PCB184. In contrast, on a GC/MS system using a DB5 column, PCB153 may coelute with PCBs 168 and 132 [55]. Fortunately, when comparing data from these two analytical systems, it is not unreasonable to compare these two peaks as "PCB153", because PCB153 is more abundant of these potentially coeluting congeners in Aroclors and most environmental compartments. The key to compiling comparable analyte lists is a peak-by-peak comparison between the two data sets, done in context of (1) analytical method comparability considerations, (2) known or suspected sources and potential alteration processes, and (3) the media sampled (e.g., keeping sediment data together, but separate from biota). Most aspects of the data preparation, review, and screening are best performed by a highly experienced PCB environmental chemist.

2.5.2.3 Data Review and Screening

Prior to detailed data analysis and interpretation, the investigator or his/her PCB environmental chemist team member, should conduct a data review focused on assessing data quality and overall usability for forensic purposes, which goes beyond what the laboratory performed when generating the data. This step is an evaluation data quality assessment, but from the data analyst/statistician's perspective rather than that of the laboratory chemist (Section 2.5.2.1).

It is important to point out that in a step-wise framework, as in this handbook, this task has been positioned as a discrete step in a linear process (between data generation, preparation and data analysis). Ideally, data screening should take place before data analysis. However, in practice, that is not always possible. Or it may become an iterative process. Data outliers, for instance, may not be clearly evident during the conduct of the data analysis itself. The outlier issue(s) should then be addressed and the data analysis process repeated. Data quality assessment is an ongoing process, starting with the analytical chemist (long before the end user ever receives the data) and continuing to final analysis and report preparation (as the project team seeks to explain the subtlest bits of variation in the data set). Regardless of specific approach, a key component of this process is outlier detection and sample screening. Johnson et al. [9] discusses statistical and graphical methods for sample screening. A brief overview is provided here.

In environmental forensics investigations, detection and evaluation of outliers is a crucial part of the process. As such, the data analyst should develop a systematic approach for summarizing and reviewing PCB congener data to determine data reliability and usability, with a goal of obtaining a robust data matrix for subsequent chemical fingerprinting. Beyond this general

guidance, the specific approach is often a function of one's training and preferred workflow, and generally an experienced chemist's "chemical reasonableness" assessment that cannot easily be described in a written step-wise fashion.

A common data preprocessing challenge is how one deals with low concentration samples and/or samples with numerous congeners reported at or below the limit of reliable detection. Clearly, such samples will be of limited utility when it comes to congener pattern comparisons, as they either have no concentration reported, tend to have higher uncertainty in the reported value than the rest of the data, and are, simply, of low relative significance in the data set. As such, it is usually advisable to review total PCB concentrations for each sample, as well as a tabulating the number of non-detects in each sample. In the experience of these authors, there are no hard-and-fast rules on what total PCB concentration is acceptable, or what percentage of non-detects is considered too high. These decisions are usually project specific, with logic and analytical accuracy being the key considerations.

Similarly, the analyst should screen the data set for problematic variables (congeners). This typically includes identifying congeners with a high percentage of non-detects, which may have to be omitted from the analysis. One may also want to determine congener concentration as percent of total PCB and the variability in the contribution (as percent relative standard deviation [%RSD]), to identify congeners with significant variability and uncertainty, but ensuring that it cannot be attributed to source or other "real" differences. Any number of approaches can be employed, but the ultimate objective is to determine if variability within a variable is due to "real" composition differences (e.g., different sources or dechlorination) or a function of noise or censored data (i.e., non-detects).

Finally, when outlier samples or congeners are identified, it is important to understand that causes for each may differ, so the appropriate action required to address outliers may vary. For example, if the outlier is the result of data entry error, the appropriate action would be to correct the error and rerun the analysis. If, however, the cause is uncorrectable matrix interference or other analytical issues, the only reasonable course of action might be to delete the sample from the data analysis. Another possible explanation of an apparent outlier may be that the reported concentrations are completely reliable and accurate, but the sample is truly unique. An example of such an outlier might be a single or limited set of samples with significant dechlorination in an otherwise unaltered suite of samples. In this case, the outlier represents a true fingerprint observed in the field, should be possible to identify using PCB chemistry knowledge and sample investigation, and should not be omitted from the analysis solely because it is unique.

Most chemometric studies will include some criterion for handling data points where an analyte was not identified and reported below laboratory detection limits (non-detects). Common reporting and data qualifying of non-detects was discussed in Section 2.5.2.2. If, as part of the data reporting, an artificially inserted value was inserted for the non-detect (e.g., half the MDL), and qualified with a "U", then such values are typically best replaced with a zero in the data screening process, prior to data analysis. Non-detects with an empty value cell often need to be populated with a zero, as many data analysis software cannot handle empty cells. The handling of non-detects is an important project decision, and should be discussed within the project team and the agreed on approach justified and documented.

It is important to conduct a rigorous review and pre-screening of the data before conducting any statistical, chemometric, or other key data presentation and analysis so only the most reliable data are used in subsequent analysis; only data for which there is a high degree of confidence. All samples and all parameters (PCB congeners) are generally not needed to conduct a solid forensics interpretation, and the quality of and confidence in the data analysis is greater if data of low reliability are removed. As discussed, it is difficult to develop strict quantitative screening methods for when to include and when to reject a sample or parameter, and it is important to include an experienced PCB chemist in the data evaluation process to ensure that a solid "chemical reasonable" assessment is part of the data review and screening process. The following are some considerations that may be included in such a data screening process.

***Samples** Inclusion/Removal Assessment*

- Identify the overall PCB concentration below which it is unlikely that reliable results are consistently generated for the sample, and remove those samples from the data set. The following are example guidelines, but project-specific, sample-specific, and analyte-specific decisions are often most appropriate, with accompanying documentation.
  - If >50% of the PCB congeners are non-detect, those samples may be removed.
  - If the sum of the PCB concentrations is low compared to most samples in the data set, and/or low concentrations are contributing to unusually high variability and overall data uncertainty; the congener composition does not appear to be technically reasonable. The PCB concentration is near the limit of detection. This sum of the PCB congener's screening level was in the 80 to 100 ppb range for the Ashtabula River sediment samples; samples with a sum of congener concentrations below that were not used. Most samples had much higher PCB concentrations.
  - If the relative concentration of PCB congeners is unusual for a large number of congeners in the sample (Figure 2-14), and cannot be explained by expected sources or weathering differences, that sample can be removed from the data set (once it has been assured that it cannot be explained by sampling or laboratory error, or the presence of another source).

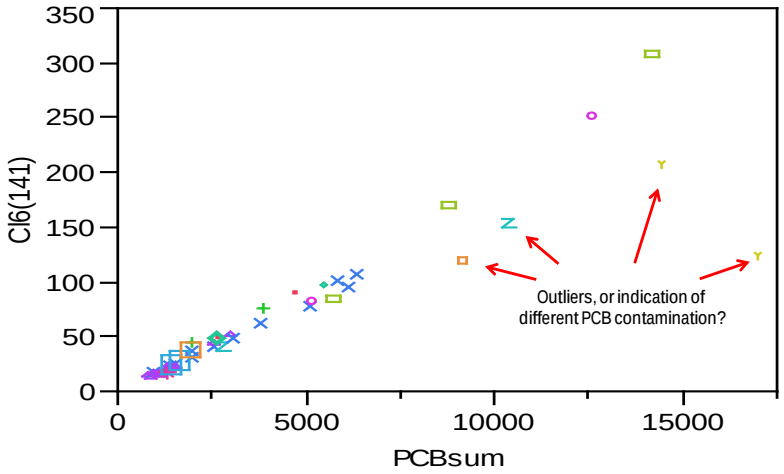


Figure 2-14. PCB Congener Ratio Analysis to Determine Potential Outliers

***PCB Congeners** Inclusion/Removal Assessment*

Considerations for whether to include or exclude specific congeners from a data-set are similar to deciding whether to include or exclude samples (see above), but there are some differences.

- Identify the PCB congeners with inconsistent, unexplainable, or otherwise unreliable results, and remove those congeners from the data set. It is important that the congener is removed altogether from the data set (not only for the samples with low congener data reliability), as it is important that the same set of congeners be used for all samples. The following are example guidelines, but project-specific, sample-specific, and analyte-specific decisions are often most appropriate, with accompanying documentation.
    - If the congener concentration is consistently near the limit of detection in the data set, that PCB congener can be removed from the data set. For the Ashtabula River sediment samples, for example, a congener was removed from the data set if >50% of the samples had a concentration of <1 ppb for that congener.
    - If, after removal of unreliable samples, >50% of the samples have non-detects for a PCB congener, that PCB congener may be removed from the data set.
    - If the relative concentration of a PCB congener is uncommonly low or high for a large proportion of the samples, and cannot be explained by possible source or other weathering differences, that PCB congener can be removed from the data set. For instance, calculating the percent contribution to the total PCB for the congeners in each sample is a useful component of the data assessment. If the percent relative standard deviation (% RSD) in the percent contribution to the total PCB is >100 %RSD, and that high variability cannot be explained by different sources or weathering in the data set, that PCB congener can be removed from the data set. This assessment can also be performed with ratio plots (Figure 2-14).
    - If, using PCB chemical reasonableness evaluation, the results for a congener are frequently anomalous and cannot be reasonably explained by its composition in Aroclor formulations or by degradation or other weathering/transformation processes, that PCB congener can be removed from the data set. For instance, if a PCB congener concentration is relatively constant and does not co-vary with the overall PCB concentration, or if a PCB is detected at high frequency in some analytical batches and not in other analytical batches of samples from the same site, such anomalies can likely be assumed to be due to analytical issues, and the PCB congener should not be used.

The values indicated above are *not* strict criteria, and should only be used as general guidelines (e.g., 50% non-detects for excluding a sample from the data set). The actual assessment cutoff will likely be different from data set to data set, and may also vary from sample to sample and congener to congener, and needs to be determined on a project-specific basis by an experienced PCB chemist. In addition, it is critical that it be determined if any data outliers and apparent anomalies may be the result of different sources, or dechlorination or other weathering processes, before data are removed from the data set; if the variability or anomaly can be explained using an understanding of PCB chemistry, or if there is any doubt about it being a “real” PCB signature, then it may be best to kept such data in the data set. For the Ashtabula River data set, for

instance, there were 345 sediment samples with available data, and 53 of those were removed during the data screening process. In addition, 38 of the 120 PCB congeners were removed, providing a final data set of 292 samples and 82 PCB congeners for the data analysis and interpretation exercises.

2.5.3 Data Analysis and Interpretation

This section describes several common data analysis approaches. This discussion will move from relatively simple graphics through to more sophisticated statistical methods. However, the simpler methods should not be considered less helpful. Often, the most effective method of gaining an intuitive understanding of data is through use of simple graphs or maps.

The primary information analysis components in an environmental forensics investigation are:

- Determine the site history and history of the surrounding area
- Determine the contaminant/sediment transport characteristics and hydrodynamics
- Determine the PCB concentrations across the site, and in relation to potential sources
- Determine the PCB composition across the site, and in relation to potential sources
- Conduct chemometric data analysis, ideally using multiple techniques
- Integrate the data analyses and findings through multiple lines of evidence to identify potential sources, and, if multiple sources, their relative significance.

It is absolutely critical that these components are addressed in an integrated manner. These types of studies are often conducted with the interpretation being limited to basic chemical "fingerprinting" of analytical chromatograms and/or a single statistical analysis method, with other potentially critical information not being used, and conclusions drawn with insufficient knowledge and a low degree of confidence.

Even for more sophisticated data analysis methods, lucid, well-conceived graphics are important. An ideal graphic must, first and foremost, be faithful to the data. But it should also be lucid and simple to understand. These general guidelines provide constraints, but also leave room for considerable creativity.

2.5.3.1 Site History and Record Research

The components of conducting a record research were discussed in Section 2.2.1. This is an important, and often overlooked, component of a forensics investigation, and is conducted to help determine a relationship between the observed contamination and historical activities at or near the site. This requires an understanding of the history of the site and area surrounding the site that could have impacted the site. If one cannot identify historical industrial activities, processes, material handling, and possible release and transport scenarios that can explain the sediment contamination, the forensics investigation would be missing an important puzzle piece.

As discussed in Section 2.2.1, the availability of records can vary widely from project to project, but it is important to devote significant effort to the site history and records research as part of the forensics investigation, and preferably early in the process during the planning phase. In

terms of determining potential sources of PCBs in sediments, the types of information that are usually the focus of records search include:

1. Identifying current and historical production/operations for the properties that through intentional or unintentional discharge/runoff could have contaminated the sediments.
2. Identifying PCB-related activities (e.g., transformer/capacitor use, carbonless copy paper, hydraulic fluid, marine paints) by the potential contributors of sediment contamination, and the timeframe of their use.
3. Identifying historical waste handling and disposal for PCB containing materials/waste.
4. Identifying possible migration pathways to sediment (e.g., waste disposal, landfills, drainage ditches and creeks receiving runoff), and how those have changed over time.
5. Reviewing historical environmental investigation reports and data.
6. Reviewing historical remedial activities, and summarizing their implications on the history of the contamination.
7. Summarizing the activities and site characteristics that may have involved PCBs, the possible history (years) of releases, and possible migration pathways to the sediments.

Obtaining historical information can be challenging because it is rarely readily available and can require creative and atypical research techniques. The elements of a record research investigation were described in Section 2.2.1, and the following summarizes possible sources of potentially important historical information.

- **Internal Corporate/Facility Documents**. Available internal communications and other records that document the operations that may have used PCBs. Documentation of remediation that may have been conducted at the site, as well as past environmental studies and related data and reports. Such information is sometimes publicly available, and at other times may not be made available.
- **State and Federal Regulatory Files**. If environmental investigations have been conducted at a site under regulatory authority, then a case file should exist, and all information should be available in the public domain. Access to such files varies greatly, depending on the regulatory agency. In some instances, many or all case files are available online, and can be searched and downloaded. In other cases, a formal request may be required under the Freedom of Information Act. It may take weeks or months before access is approved, and the agency may require that files be reviewed on their premises. In yet another scenario, regulatory programs may require that a local library or other public facility serve as a document repository, and key documents can then be accessed at that location with no pre-arrangements.
- **Publications**. Published reports and other literature may provide general information on industrial/commercial use of PCBs (e.g., [5, 20, 22, 56]). Such papers are useful, but generally provide information on an industry-wide basis (not a specific facility or site). If one can find specific case study papers or presentations or reports that focus on the specific site, or a similar site, that may provide useful historical information. If such a

document includes citations for such information, it will usually be well worth the effort to track down the original source.

- **Interviews**. Interviews with current and past residents of the area, and workers at the facilities potentially responsible for the contamination or nearby facilities, can often produce a wealth of useful information about past activities. This is a particularly valuable way to obtain information on important activities and site matters that are not well documented.
- **Aerial Photographs/Remote Sensing**. Aerial photographs and other remote imaging and sensing information are publically available from commercial sources and sometimes also from public sources. A wide range of such imagery and information can be purchased if it is not part of the readily available information. Such information can be obtained from many past decades to help reconstruct physical and industrial changes over time to better understand the PCB contamination.

2.5.3.2 Sediment Transport and Hydrodynamics

As discussed in Section 2.2.2, a general approach for a sediment transport evaluation is presented in Blake et al. [36]. Initially, the project team will collect all available data, conduct a site inspection, and develop a site-specific CSM for sediment transport. The team also will formulate the preliminary sediment management questions, define the overall study objectives, and identify the most critical data gaps. After this initial evaluation, the team can conduct a Tier 1 sediment transport evaluation. The goal of the Tier 1 evaluation is to address the most common sediment management questions, using readily available data from the RI and relatively uncomplicated data analysis methods. The Tier 1 evaluation has relatively simple data needs, a lower cost, a shorter timeframe, and a higher level of uncertainty than a Tier 2 evaluation. The Tier 1 results can be used to refine the sediment transport CSM and address the relevant site-specific sediment management questions. Depending on the questions asked at a specific site, this level of analysis may be sufficient.

For large or complex sites, a higher degree of certainty may be needed to characterize sediment transport processes and address sediment management questions. In this case, collection of additional site-specific data may be necessary and more detailed and complex data analysis methods may be warranted, including the possible development and use of predictive models. These activities comprise the Tier 2 evaluation. The scope of data collection and analysis for the Tier 2 evaluation will depend on the complexity of the site, the type of data needed to address the most critical data gaps, and the available project budget. Tier 2 results will be used to refine the CSM until the uncertainty associated with the sediment management decision(s) is reduced to an acceptable level.

The sediment transport and hydrodynamic studies, and associated data generation, conducted as part of a forensics investigation are intended to help determine how contaminants move and deposit at the site. This means understanding runoff and discharge characteristics at potential sources, input characteristics to the study site (e.g., creeks, drainage ditches, discharge pipes, CSOs), and the hydrodynamic and sediment transport conditions that impact how the contaminants are distributed in the aquatic system, and eventually settled to the sediments. It is therefore important to understand and obtain the appropriate data to explain factors including:

- All water and sediment input sources to the study site, including their history and activity
- Water circulation (currents) and their consistency and fluctuation
- Tides and their potential impact on currents and sediment movement
- Suspended sediment transport, suspension, resuspension, transport, and depositional characteristics
- Areas of erosion and deposition
- Sediment deposition rate in areas of demonstrated deposition
- Sediment stability and susceptibility to erosion under different conditions (e.g., storms).

Understanding the hydrodynamic conditions, and particularly the transport and fate of sediments, is crucial to explaining the movement of contaminants, and how the identified sediment contamination may be related to a distant source.

2.5.3.3 PCB Concentrations

One of the first steps in assessing the PCB contamination at a site, and to begin to get an understanding of the contaminant situation in terms of source association, is to review the overall (total) PCB concentration information for the site. Surface sediment data provide information on recent contamination, and subsurface sediment data provide information on historical contamination and needs to incorporate the sediment depth and the rate of sediment deposition. Factors to consider include how high, in general, the PCB concentrations are across the site, how variable the PCB concentrations are across the site, and determining if there are any PCB concentration "hot spots" and spatial gradients that could help understand potential sources. The PCB concentration information is then considered together with the historical site information (Section 2.5.3.1) and hydrology and contaminant transport for the site (Sections 2.5.3.2), to develop a preliminary understanding of the contaminant distribution and how it may relate to potential sources.

In environmental contaminant studies, the highest concentrations of contaminants are, more often than not, found in close proximity to their source. The hydrodynamics of the site and sediment stability and transport (e.g., areas of erosion where sediments do not settle or are resuspended and moved, and areas of deposition where suspended sediment settle) must be considered to support the contaminant distribution interpretation, and to ensure that there are no surprising contaminant transport characteristics that are not being considered. PCB concentration contouring is a widely used, and very useful, technique for understanding the approximate PCB concentration distribution to obtain an initial understanding of the contamination situation, and potential source areas. Thus, a simple map showing concentrations of contaminants in the sediment is a powerful and useful initial analysis, and may be more insightful than some sophisticated statistical technique. Figure 2-15, for instance, illustrates the surface contaminant concentration in a lake with two significant locations where run-off and other input to the lake occur. One of those (the northern one), appears to be associated with contaminating the sediment, while the other does not appear to be, assuming there are no unusual contaminant transport characteristics in the lake. In addition, given that the ultimate audience for

an environmental forensics investigation is not often scientists (an arbitrator, community representatives, a court of law), a map is familiar and easier to explain to a layman. Maps and aerial photos that include data can be simple and powerful tools in environmental forensics. If GIS capabilities are not readily available, then simple histograms can be used to illustrate the concentration changes in sampling stations away from a potential source location (e.g., with stations represented along the x-axis), accompanied by a map or aerial photograph for illustration purposes.

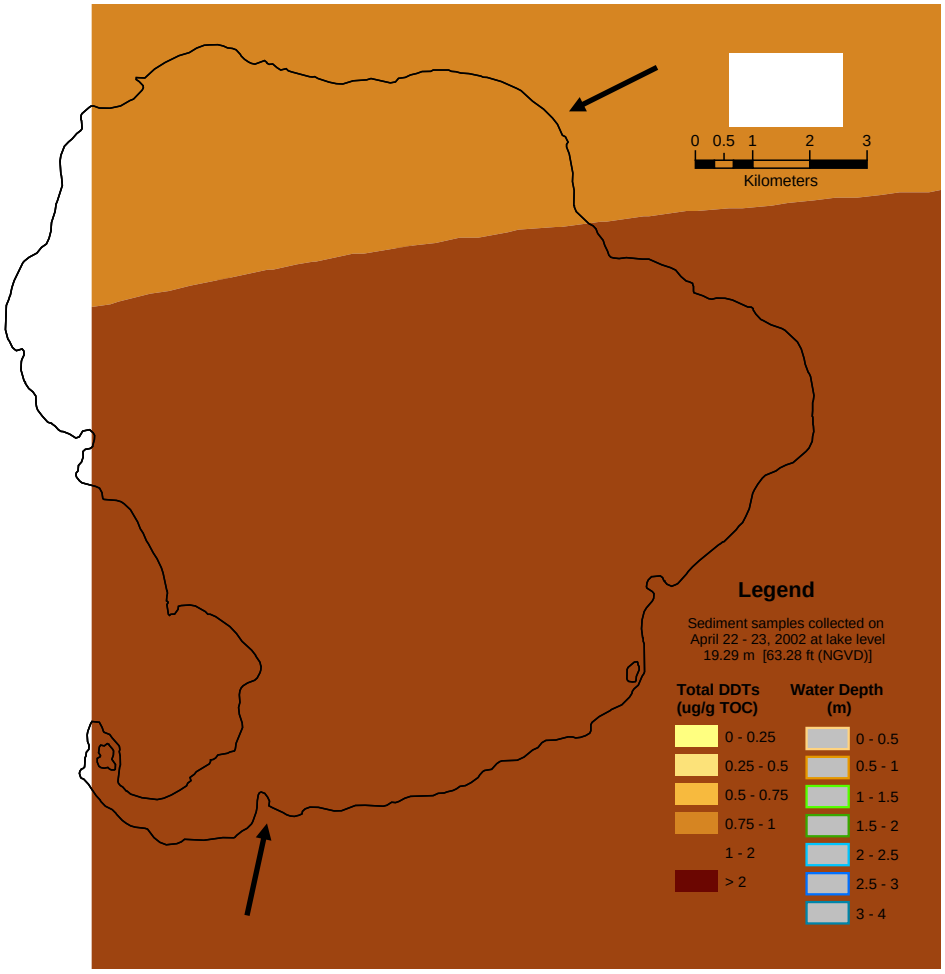


Figure 2-15. Florida Lake with Two Sources of Runoff/Input and Potential Sources of Contamination Indicated
(Contours indicate surface sediment DDT concentrations.)

It is usually important to understand the PCB concentrations both horizontally (i.e., surface sediment concentrations) and vertically (using sediment core data) to understand the history of the contamination. Histograms of sediment core concentrations, ideally linked to a year of contamination by incorporating sedimentation rate information (i.e., sediment dating data), are very useful (Figure 2-16). 3D extrapolations and contouring of sediment core data can further help in developing an understanding of the contamination (Figure 2-17).

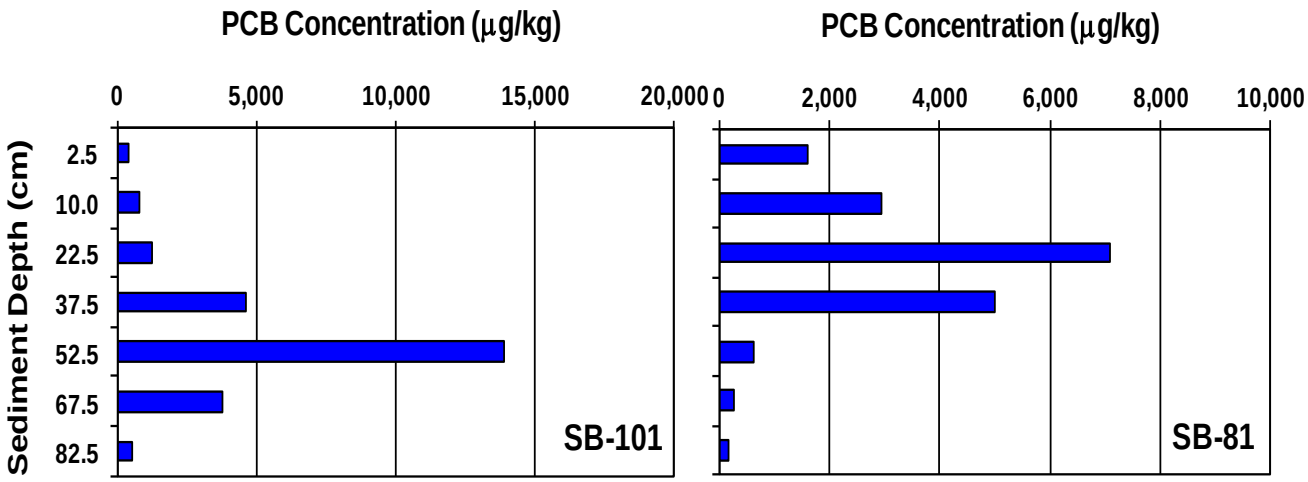


Figure 2-16. Total PCB Concentrations in a Sediment Core Collected on the West (SB-101) and East (SB-81) Side of Hunters Point Shipyard South Basin

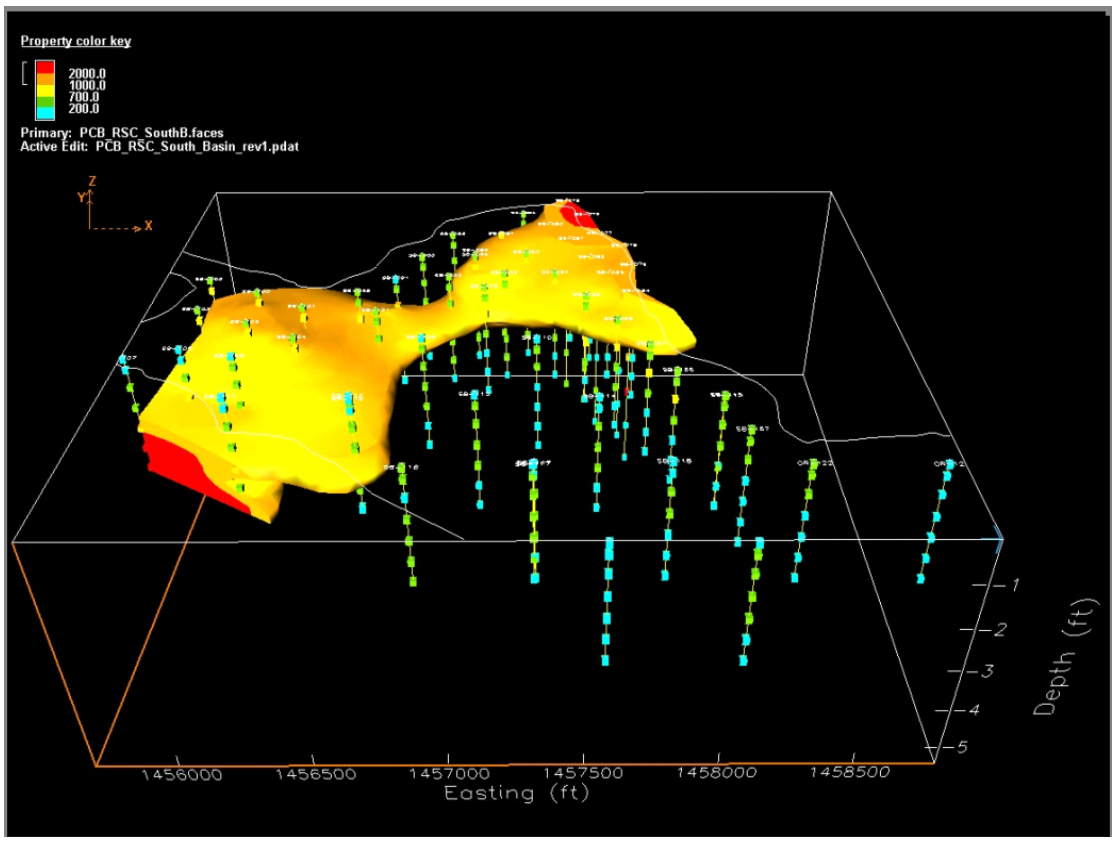


Figure 2-17. Illustration of Subsurface Sediment Total PCB Concentrations and Sediment Coring Locations in the Hunters Point Shipyard Study Area

2.5.3.4 PCB Composition

Once there is a good understanding of the overall PCB concentration distribution and characteristics of a site, the next level of detail in the analysis of the data usually comes with studying the *composition* of the PCB contaminating the sediment – the relative concentrations of the PCB congeners or homologues. One might assume that the PCB composition correlates with concentration gradients and this should then be confirmed as it would provide support to the initial assumptions about sources. If PCB concentrations and PCB composition do not appear to be closely related, then the compositional characteristics need to be more carefully studied and explained.

It is usually important to understand the PCB composition, like the concentrations, both horizontally (i.e., surface sediment concentrations) and vertically (using sediment core data) to understand the history of the contamination. If there is only one source, and that source has been the only source for a long time, the surface PCB composition is likely similar across the site. The subsurface PCB concentrations may be similar to the surface sediment composition if the source has been constant, or it can be altered depending on if dechlorination and other weathering factors have affected the composition. In sandy, aerobic sediment, there may be little alteration of the PCB composition over time (i.e., with sediment depth), although some reduction of congeners with a low level of chlorination has been shown to occur in some environments. However, in some highly organic and anaerobic sediment, with the appropriate microbial conditions, the PCB composition may change significantly over time (Figures 2-4 and 2-5), even if the source and PCB type (e.g., a specific Aroclor) have remained the same.

As with concentrations, it is important to consider what the PCB composition is, in general, across the site, how the PCB composition changes and how variable it is across the site, and determining if there are any PCB composition "hot spots" where the composition is particularly similar to a fresh Aroclor or Aroclor mixture, suggesting proximity to a source and recent contamination. The PCB composition information is then considered together with the PCB concentration information, the historical site information, and hydrology and contaminant transport, to further develop the understanding of the contamination and how it may relate to potential sources.

Compositional information is generally presented using simple bar graphs, and can be done using PCB homologue data presenting the relative concentrations of the 10 levels of chlorination (Figure 2-9), but is most often done using a larger set of PCB congeners (e.g., Figures 2-2 and 2-4). Analytical chromatograms can also be useful for compositional illustrations, but they are often more difficult to compare and decipher than "recreated" chromatograms using simple histogram plots. Comparing the sample compositional information to the composition of Aroclor formulations (see figures in Appendix A), or mixtures of Aroclors, can be useful to help better understand the contamination. Figure 2-18 shows the composition of 18 PCB congeners in sediment samples collected from the west and east sides of HPS South Basin, together with the composition for a mixture of Aroclor 1254/1260 and only Aroclor 1260. The PCB congener composition of the sample from the west side resembles that of the mixed Aroclor, but the sample from the east side resembles that of just Aroclor 1260.

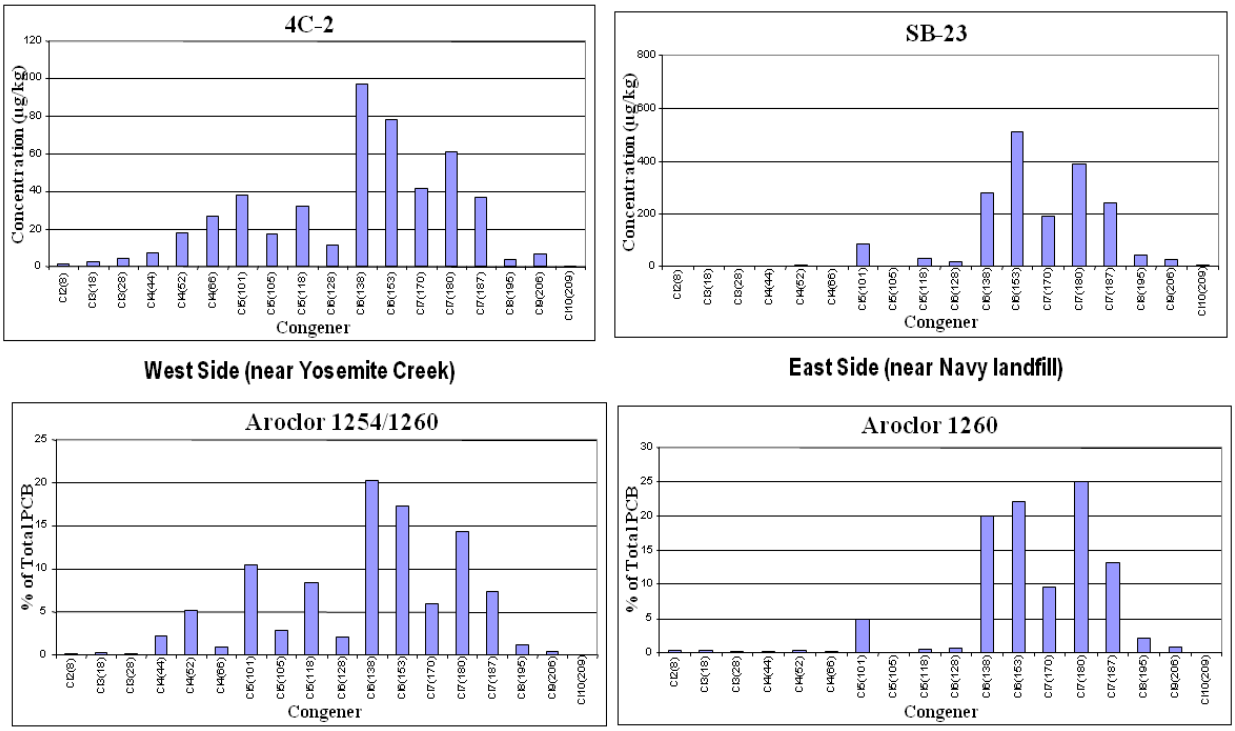


Figure 2-18. PCB Congener Composition in a Sediment Sample Collected on the West (4C-2) and East (SB-23) Side of Hunters Point Shipyard South Basin, and the PCB Composition in a Mixture of Aroclors 1254/1260 and Only Aroclor 1260

Another technique for illustrating compositional characteristics is to plot simple or double ratios of key diagnostic congeners – congeners with a concentration relationship that are resistant to change (i.e., stable congeners; Table 2-4) and unique to a source (e.g., an Aroclor), or that illustrate an active process (e.g., dechlorination/weather) but still can be associated with a source, or a combination of both. Diagnostic ratio analysis requires an in-depth understanding of the PCB chemistry and behavior of different PCB congeners, but when applied correctly can be a powerful technique (Figure 2-19). PCB compositional information can also be integrated with maps to further enhance the power of the information presentation. This can be done using a GIS system and illustrating diagnostic ratios (Figure 2-19) or PCB composition bar graphs for different locations directly on the map, or by presenting the compositional graphics accompanied by maps or aerial photographs.

While direct visual inspection of PCB composition and congener patterns is extremely useful and is often a valuable tool for gaining an intuitive insight into the source of PCBs in samples, it is often also useful to employ some statistical chemometric method, and generate some semi-quantitative similarity metric (Section 2.5.3.5). A similarity metric may assign a value to the degree of similarity between patterns, but no scalar measure will provide information on why or how two patterns differ. Visual pattern analysis allows the user to take qualitative information into account, and explain the observation from a PCB chemistry and environmental processes perspective, which ultimately is critical to the interpretation. Thus, regardless of the numerical methods used for pattern recognition and comparison, the data analyst is well advised to devote

significant effort to direct, visual inspection of congener patterns, and simple graphical presentation analyses. While there may be some comfort in reliance on an objective, quantitative similarity metric, it does not replace qualitative visual pattern analysis and the application of PCB chemical reasonableness considerations.

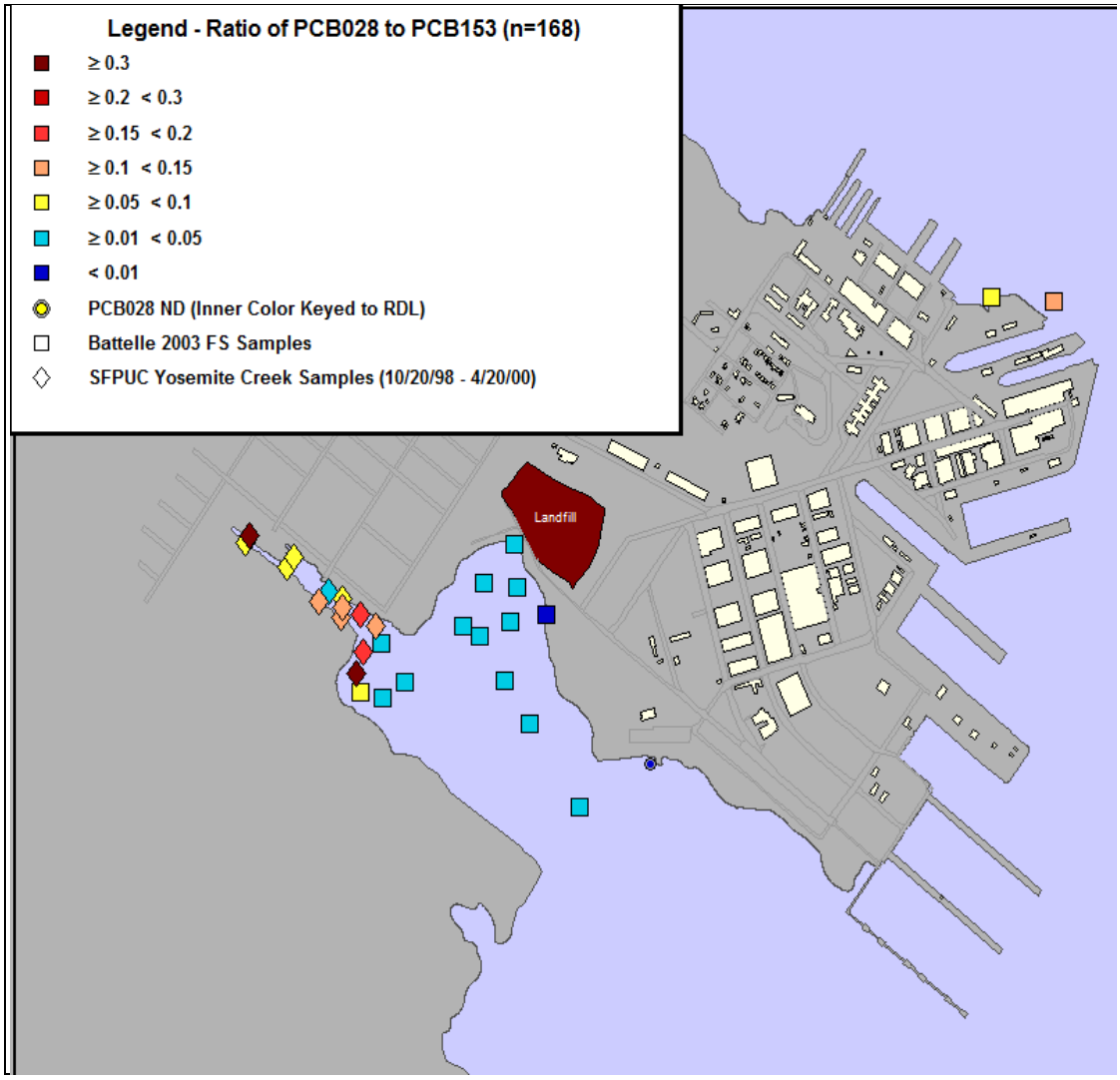


Figure 2-19. Ratio of PCB28 to PCB153 in Sediments near HPS South Basin

2.5.3.5 Chemometric Statistical Methods

Environmental forensics projects typically involve large chemical data sets with many samples and variables. This presents a data management and analysis problem: an inherently multivariate problem. There are numerous multivariate methods in the literature that are potentially applicable, a complete description of which is beyond the scope of this handbook. Three such approaches are presented: (1) cluster analysis, (2) PCA, and (3) mixing model analysis. Cluster analysis and PCA are perhaps the most widespread of these, primarily because of their ease of

use, and the fact that there are cluster analysis and PCA modules available in many different commercial statistical software packages. Mixing models can provide a more detailed insight into a PCB data set, but require more extensive experience, and are often available only as specialty software packages.

Cluster/Classification Analysis

Cluster analysis/classification refers to a general category of algorithms designed to classify samples into discrete groups or clusters. A PCB-related example of a cluster might be all samples in a data set with an Aroclor 1254 congener pattern. Samples that exhibited a different pattern (e.g., Aroclor 1242) would hopefully be grouped in a different cluster.

The most common of these methods is hierarchical cluster analysis (HCA). HCA is an exploratory method that operates on calculation of similarity between samples. Different mathematical criteria are used to group similar samples into clusters. The most common similarity metrics are based on distances calculated in multivariate space. In HCA, distances between individual samples are calculated. When distances between samples are relatively small, this implies that the samples are similar, at least with respect to PCB composition. The most similar samples are linked as a single cluster, and the process is repeated. Numerous linkage criteria/options are usually available in commercial software packages. Dissimilar samples will be separated by larger distances. HCA can be performed on either samples or variables (PCB congeners). The example that follows is HCA conducted in sample space.

The standard graphical method used for visualization of HCA results is the dendrogram. Figure 2-20 shows a dendrogram for HCA of PCB congener data from Lake Hartwell, South Carolina [8, 10]. This data set is composed of 237 samples (211 sediment samples, and 26 pure Aroclor standards), and 54 PCB congeners. HCA was run on samples. While difficult to read, each of the 237 sample names are listed down the left side of the dendrogram. The red lines link samples based on their distance (x-axis) from each other. Samples shown at the bottom of the dendrogram are very different from those at the top.

A hierarchical cluster approach will work well, provided that a data set is “hard-clustered.” In other words, HCA works well if one can safely assume that each sample belongs in one, and only one, cluster. In Lake Hartwell, this was not the case. Most samples were mixtures of two or three Aroclors, and/or were dechlorinated to some degree. As such, numerous samples that were mixtures of Aroclor 1242 and Aroclor 1254 did not cluster with either of the two Aroclor sources that contribute to it. The Lake Hartwell example is not at all unusual. More often than not, PCB forensics studies involve mixing multiple sources and/or weathering. As such, it is recommended to use hard cluster algorithms only in those instances where one can safely preclude mixing and weathering. HCA is readily available in many commercial statistical software packages, including Pirouette, Statistica, and SAS among others. Other classification methods have been described in the literature, which while not considered cluster analysis, are somewhat similar in that they seek to classify samples into discrete groups. One of these methods is SIMCA, which is available as a module in many software packages, primarily those that are focused on general chemometrics applications (e.g., Pirouette and Unscrambler).

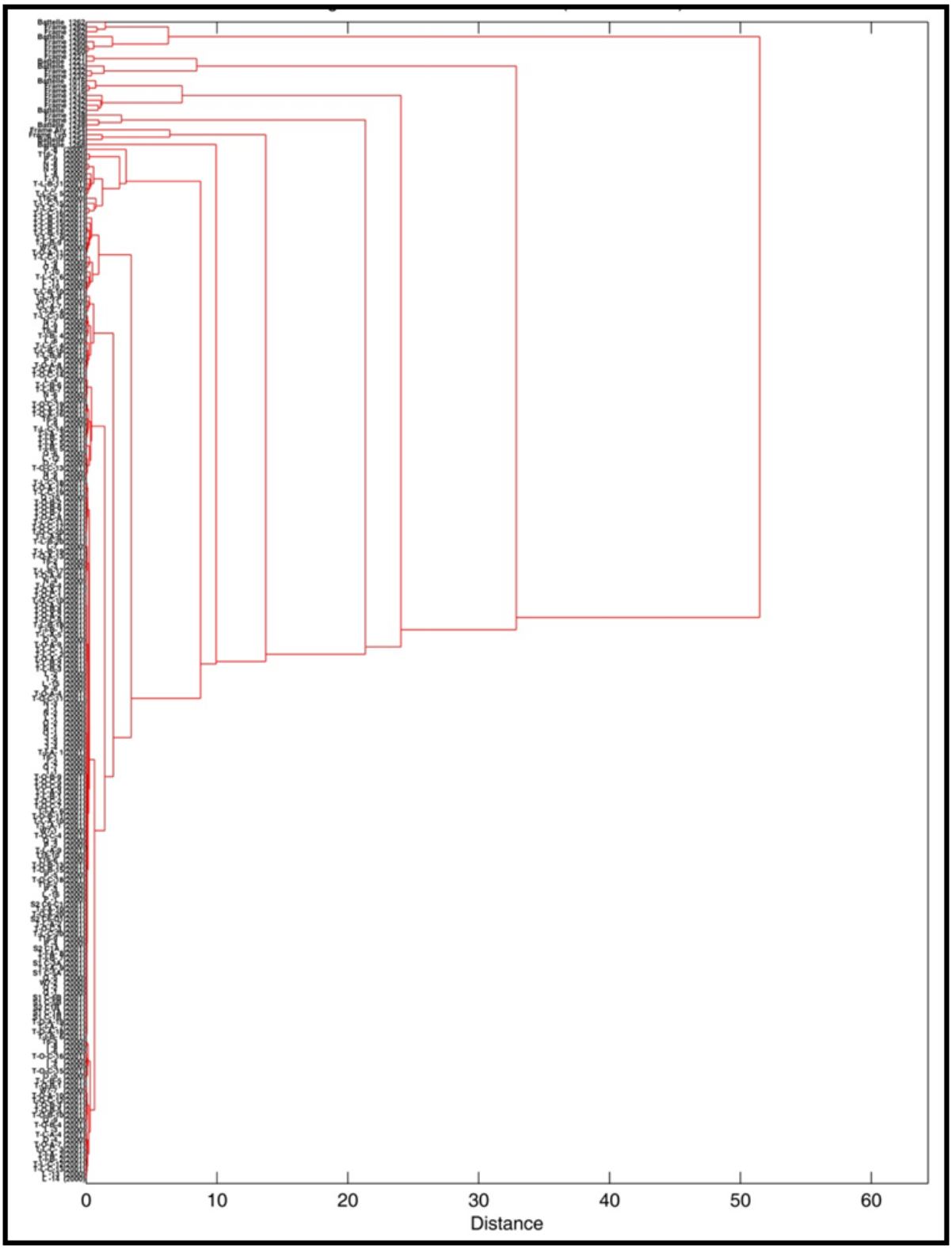


Figure 2-20. HCA Dendrogram of 211 Sediment Samples and 26 Aroclor Standards, Using Ward's Clustering and Euclidean Distance

Another alternative to HCA (especially if one is dealing with gradational data structures such as mixing and dechlorination) is fuzzy-c-means clustering (FCM [57, 58]). FCM is an exploratory data analysis method similar to HCA in that it operates on similarity between samples by calculation of Euclidean distance between samples. It differs in that it allows for a conceptual model of gradations between clusters. Thus, a sample that is a mixture of two Aroclors could be classified as having membership in two different clusters (e.g., a 0.50 membership in the Aroclor 1242 cluster and a 0.50 membership in the Aroclor 1254 cluster). FCM is not as widely used, and therefore is often not included as a module in general purpose statistical software packages. It is, however, available within the fuzzy logic toolbox for use with the software package Matlab.

Principal Component Analysis

PCA is commonly used in environmental forensics as a stand-alone exploratory data analysis method, and as an intermediate step in other chemometric methods (including SIMCA and receptor modeling methods). PCA reduces the dimensionality of a data set so that the similarities and differences between samples can be assessed by direct inspection of 2D or 3D graphs called "score plots" (Figures 2-21 and 2-22). These simple plots carry the advantage of being a single graphic that quickly provides the analyst a genuinely deeper insight into the PCB compositional characteristics of the samples in the system. An advantage of PCA over HCA is that the algorithm does not carry with it the implicit assumption of discrete classes or clusters. Rather, it offers a more objective visualization of the data. If the data are indeed hard clustered, that will be evident on a scores plot (Figure 2-21).

If, however, the data are not hard clustered, but are gradational/mixed, that will also be evident. It will not be hidden on an ambiguous dendrogram or confounded by inherent cluster assumptions. Figure 2-22 shows a scores plot for the same Lake Hartwell data shown on the dendrogram in Figure 2-20. It is now apparent that the vast majority of Lake Hartwell samples are gradational intermediates between pure Aroclor patterns or dechlorination end-products.

There is a natural appeal to being able to reduce such a large multivariate data to a simple 2D plot. However, to the inexperienced practitioner, there are a number of potential pitfalls. Contaminant sources and alteration mechanisms may be inferred from these simple 2D plots, but a more rigorous evaluation of the number of principal components that carry source-relevant information actually show even more. A typical PCA implementation may be limited by graphical limitations of two or three axis score plots. Potential pitfalls for PCA in forensics applications are discussed in detail by Johnson et al. [9]. Like HCA, PCA is readily available in many commercial statistical software packages, including Pirouette, Statistica, SAS, and Matlab.

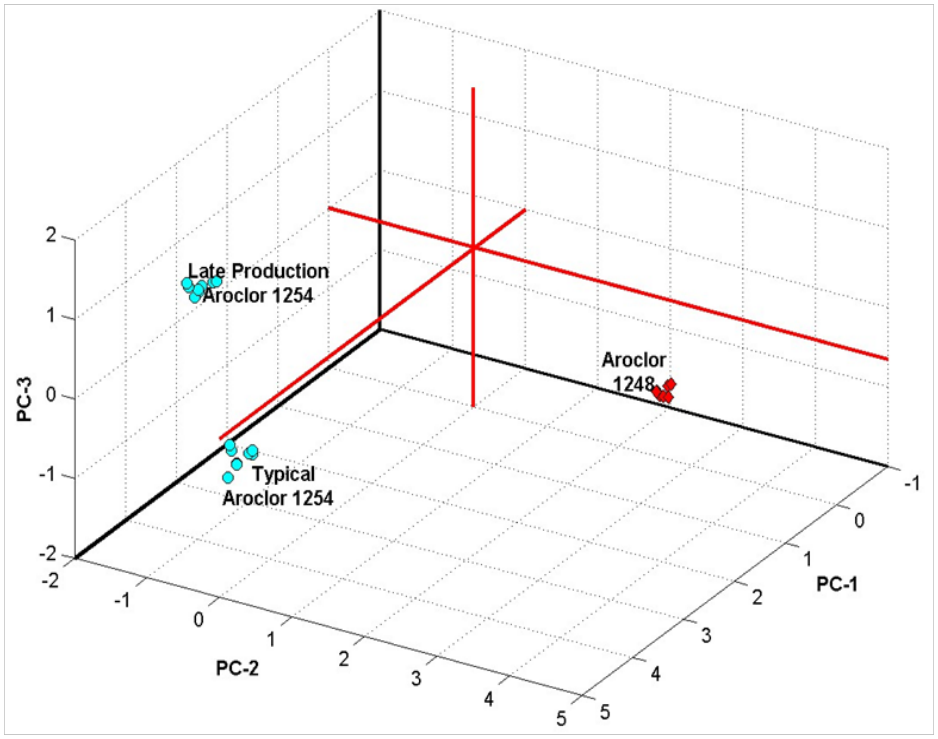


Figure 2-21. A Hard Clustered Three Source Data Set as Observed on a PCA Scores Plot (from Johnson et al., 2007 [9])

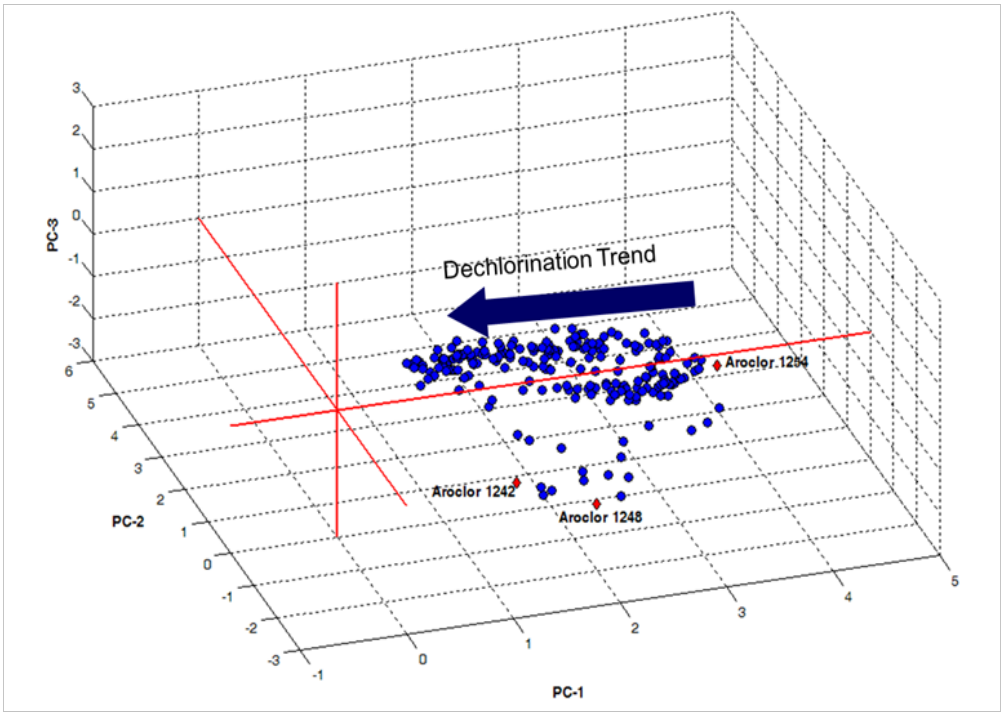


Figure 2-22. Lake Hartwell Data (from Magar, et al., 2005 [8]) Plotted on a Three-dimensional PCA Scores Plot

Receptor/Mixing Model Analysis

An increasingly common method used in environmental forensics investigations involves the use of receptor models. These methods are designed to resolve three parameters of concern in a multivariate mixed system: (1) the number of components in the mixture, (2) the identity (i.e., chemical composition) of each component, and (3) the relative proportions of each component in each sample. Stated mathematically, given a matrix X of m samples and n variables, and the unknown number of components k, one wishes to find a feasible solution to the following equation:

	X	=	A	F
Dimensions	(*m* x *n*)		(*m* x *k*)	(*k* x *n*)

Receptor methods often use PCA as an intermediate step to (1) determine the number of "significant" principal components (i.e., the number of sources), and (2) provide a reduced dimensional reference space for resolution of the model. The number of sources (*k*) essentially reduces the problem of choosing the number of significant principal components.

Within *k* dimensional space, receptor models then resolve the chemical compositions of the sources (F) and the contributions of the sources in each of the samples (**A**). If source compositions are known a priori, then those compositions may be used as the row vectors of **F** or as a training data set. Source contributions can be found via regression methods such as chemical mass balance.

However, in environmental forensics, one typically does not know and/or wishes not to assume such a priori knowledge of sources. For such situations, it is usually preferable to use a self-training receptor model method: a class of algorithms designed to resolve the number of sources, and feasible estimates of the multivariate source patterns and source contributions, without a priori assumption of sources. Receptor model methods in common use in environmental forensics include PVA [48, 49], MCR-ALS [51], PMF [50] and Unmix [59]. Application and comparison of these methods have been presented in the literature [9, 19]. These methods have some differences in the mathematics of their implementation, but all will provide estimates of contributing source fingerprints in a mixed system, without a priori knowledge or assumption of the number or chemical composition of those sources.

In addition to method comparisons cited in the literature above, the DoD Environmental Security Technology Certification Program (ESTCP) research that preceded development of this handbook [19] included a comparison of these four receptor model methods, as part of project performance objectives. That comparison included running these four algorithms on each of three data sets: (1) an artificial data recently published in the peer-reviewed literature [54]; (2) an artificial PCB data set originally published by [9]; and (3) the HPS data set. All four methods have since been analyzed on the second demonstration site data as well (Ashtabula), and reproduced the method comparison of the Henry data set below. The reader is referred to Johnson, et al. [9] for the method comparison applied to the Johnson data. The results of these methods applied to the two demonstration sites (HPS and Ashtabula River) will be included in the case-study discussions (Sections 3.1.7.5 and 3.2.7.5).

The Henry data set offered the advantage that it was created by two researchers that have published extensively on receptor model development and deployment, but who are not involved

in this particular project (the ESTCP research or the development of this handbook). Henry and Christensen [54] proposed a statistical performance criterion to measure the success of the methods that they tested: the standard deviation of the true source composition subtracted from the receptor-model estimated composition ($\sigma_{Est-True}$). This was adopted as one of the performance criterion for the method comparison exercise. Their published results were used for Unmix (the method Henry developed and has used extensively: [51, 56]) and PMF (a method Christensen has published on [34, 35]). For PVA, Dr. Glenn Johnson (co-investigator on this research) ran the Henry data set using Matlab code that he wrote and which he has used in many studies [5, 8, 10]. For ALS [51, 60] Dr. Scott Ramos (Chief Scientist at Infometrix, Inc., Bothell, WA) implemented the ALS. Dr. Ramos is also an experienced ALS practitioner [60]. The Henry data set is an artificial data set with 200 samples and eight chemical compounds, with 1% multiplicative error in the concentrations and three sources. The data set was included in the supporting information on the publishing journal's Web site (http://pubs.acs.org/journal/esthag).

Table 2-13 shows a comparison of true values of source compositions to those estimated by Unmix, three versions of PMF, PVA and ALS. As noted by Henry and Christensen, $\sigma_{Est-True}$ indicates that results from Unmix and the U.S. EPA PMF3 (with fpeak = -0.1) yielded estimated source compositions that were very close to true compositions ($\sigma_{Est-True} < 1$). PMF with other options chosen did not fare as well. The performance evaluation metric ($\sigma_{Est-True}$) was much larger. This observation is confirmed using the two similarity metrics from Johnson et al. [4]: $\cos\theta$ and $\boldsymbol{r}$. Similarity was low for B-PMF and U.S. EPA's PMF without f-peak. The estimated source compositions from PVA and ALS solutions (run by Johnson and Ramos) were added to this table. These methods also performed very well with low $\sigma_{Est-True}$ values, and $\cos\theta$ and $\boldsymbol{r}$ values ≥ 0.99 for all three source compositions.

Before concluding that any of these is the "best" method, note that one could argue that PMF performed among the best (see results for PMF3 with fpeak = -0.01) or that PMF performed the worst (see results for PMF NNLS; Table 2-13. There are many similarities between these methods, and "best performance" is not necessarily a function of the acronym one uses to label their method. Rather, it is often a function of options chosen, the expertise of the analyst, and their sensitivity to the data structure. The results of this method comparison were presented at the Society of Environmental Toxicology and Chemistry North America 31st Annual Meeting in Portland, OR [61].

This receptor model method comparison shows that given good quality chemical data (or data that have undergone rigorous QA/QC to identify and address any issues) these receptor model methods usually perform well and resolve similar source patterns and apportionment estimates. But like PCA, these methods require a certain level of experience and sensitivity to common environmental data structures. When faced with bad data, any or all of these methods can produce spurious results. One of the most crucial steps in the data analysis process is vigilant outlier detection and data cleaning. Even with good data, these methods can be problematic in the hands of an inexperienced user and/or a user without sensitivity to chemistry and environmental science. In the hands of an experienced practitioner, these methods should result in source patterns and contributions that are consistent.

Table 2-13. Comparison of True Source Compositions for Data Set 1 (Henry Data Set) with Values Determined from Unmix, PMF (four versions), PVA, and ALS

	compd #	True value	UNMIX	B-PMF NNLS	B-PMF penalty functions	EPA PMF3	EPA PMF3 fpeak=-0.1	Johnson Matlab PVA	Pirouette MCR-ALS
Source 1	1	11.44	11.31	10.9	10.45	11.07	11.72	11.20	11.40
	2	12.83	13.3	15.24	15.15	15.45	12.67	13.29	12.91
	3	11.9	12.17	12.74	13.26	12.54	11.61	12.25	12.00
	4	15.34	16.01	18.46	18.66	18.57	15.01	16.06	15.50
	5	14.79	15.04	16.18	15.76	16.49	14.9	14.97	14.82
	6	12.27	12.08	10.41	11.51	9.73	11.97	12.20	12.32
	7	11.76	11.29	10.15	9.56	10.3	12.07	11.22	11.59
	8	9.66	8.8	5.91	5.65	5.86	10.04	8.81	9.47
	$\sigma_{Est.-True}$		**0.51**	**2.35**	**2.44**	**2.5**	**0.3**	**0.53**	**0.13**
	Corr Coef (*r*)		**0.992**	**0.947**	**0.941**	**0.939**	**0.989**	**0.990**	**0.999**
	Cos θ		**0.999**	**0.986**	**0.985**	**0.984**	**1.000**	**0.999**	**1.000**
Source 2	1	12.54	12.47	11.13	11.72	12.59	12.6	12.58	12.56
	2	8.85	7.86	6.22	7.16	7.18	9	8.39	8.52
	3	10.46	10.43	11.87	11.24	10.26	10.36	10.36	10.39
	4	10.11	9.08	8.08	8.8	8.24	10.29	9.62	9.77
	5	12.63	11.85	9.58	10.72	11.44	12.82	12.33	12.43
	6	15.29	16.61	21.6	19.12	17.29	14.89	15.74	15.62
	7	14.38	14.71	13.56	14	15.06	14.45	14.63	14.55
	8	15.75	16.99	17.96	17.26	17.95	15.59	16.35	16.17
	$\sigma_{Est.-True}$		**0.93**	**3.16**	**1.95**	**1.56**	**0.21**	**0.41**	**0.29**
	Corr Coef (*r*)		**0.991**	**0.873**	**0.931**	**0.985**	**0.998**	**0.998**	**0.999**
	Cos θ		**0.998**	**0.976**	**0.990**	**0.994**	**1.000**	**1.000**	**1.000**
Source 3	1	13.64	13.7	15.77	15.36	13.87	13.48	13.53	13.49
	2	12.12	12.55	12.24	11.66	11.19	11.76	12.11	12.16
	3	9.43	9.33	6.84	7.36	9.03	9.52	9.47	9.53
	4	13.25	13.61	11.92	11.5	11.94	12.84	13.19	13.26
	5	15.96	16.35	17.76	17.02	15.45	15.58	15.89	15.90
	6	8.77	7.99	3.84	5.57	9.38	9.46	8.93	8.93
	7	14.53	14.57	17.39	17.02	15.3	14.6	14.54	14.49
	8	12.31	11.9	14.18	14.52	13.85	12.76	12.33	12.25
	$\sigma_{Est.-True}$		**0.42**	**2.73**	**2.17**	**0.95**	**0.41**	**0.08**	**0.10**
	Corr Coef (*r*)		**0.994**	**0.956**	**0.941**	**0.926**	**0.990**	**1.000**	**1.000**
	Cos θ		**1.000**	**0.982**	**0.988**	**0.998**	**1.000**	**1.000**	**1.000**

The use of receptor model methods are not as widespread as PCA and HCA, and are therefore not as commonly included in general purpose chemometrics software. Pirouette does, however, include an ALS module. A free Matlab version of ALS is available at the Web site of its developer (Roma Tauler http://www.ub.edu/mcr/ndownload.htm). A free version of PMF is available at http://www.epa.gov/heasd/products/pmf/pmf.html. The developer of PMF (Pentii Paatero offers a commercial version of the software with more features and options than the free version. Unmix is available free at www.epa.gov/heasd/products/unmix/unmix.html. A commercial version of PVA software was available for many years through one of its

developers, Dr. Robert Ehrlich. Current availability of the software is unknown. A Matlab version of PVA can be obtained from the authors of this handbook.

2.5.3.6 Integrated Data Analysis and Interpretation

Integrated data analysis and interpretation is the process of synthesizing information and interpretations from multiple lines of evidence to arrive at scientific interpretations that answer the key questions of a forensics investigation. Various lines of evidence are combined, compared, inconsistencies analyzed, and the "full story" developed. Lines of evidence typically considered include the site history, contaminant transport, PCB concentration distribution, PCB composition considerations, and chemometric statistical analyses, as described in Sections 2.5.3.1 through 2.5.3.5, in addition to conducting the chemical reasonableness assessment and incorporating less easily identifiable pieces and linking the information into one cohesive understanding of the sources of contamination.

Common lines of evidence based on the data that to be integrated and compared include:

- Typically congener patterns will have been analyzed in several different ways, including simple chromatogram inspection (Section 2.5.1.1) and one or more chemometric analysis methods. The inferred congener patterns identified by each of these methods should be compared for consistency across methods. In addition, the geographic distribution of the observed congener patterns should be compared. As an example, if an Aroclor 1242 fingerprint is observed in one specific area of the field by one method, is that in agreement with the geographic distribution for that pattern observed by another method.
- If congener pattern analyses result in inference of a source, determine if that conclusion is supported by concentration gradient mapping. One key tenant of environmental forensics investigations is that the highest concentrations are typically observed near sources or outfalls, but this should be supported by hydrodynamic and sediment transport data.
- Are the locations of sources as inferred through data analysis consistent with known site history? For example, if an Aroclor 1260 congener pattern was observed in high concentrations near a former electrical transformer manufacturing facility, all three independent lines of evidence (concentrations, congener patterns and site history) would support a transformer source interpretation because Aroclor 1260 was often used in transformers.
- If a congener pattern does not match any known Aroclor source patterns, it is often useful to review literature that describes alteration processes. Reference data for common PCB alteration mechanisms such as dechlorination and volatilization may be found in the literature [4, 16].

Ideally, this process leads to an internally consistent and lucid interpretation of contaminant sources and environmental history. However, this is not always the case. Often, there will be one or more ambiguous lines of evidence, and (hopefully) another line of evidence will shed light on that ambiguity confirming that it may not be of value in the overall analysis, and move the final interpretation in the right direction. There may occasionally even be independent lines of evidence that seemingly contradict each other. In such a case, integrated data analysis is

equally important, because in the process of evaluating multiple lines of evidence, an investigator may better decide which lines of evidence deserve more weight and why. The decisions need to be justifiable using sound science, with an understanding of PCB chemistry and reasoning related to the behavior of PCB in the environment often the most critical component. As with other aspects of this workflow, there are no prescribed steps for this task. In fact, the investigator will likely have most success if they are resourceful and creative in finding new lines of evidence that might help shed light on such questions.

Example of a multiple lines of evidence approach to integration of interpretations is provided with the two case studies conducted as part of developing this handbook: HPS (Section 3.1.7.6) and Ashtabula River (Section 3.2.7.6). The summary presented below in this section is from Lake Hartwell, South Carolina. The summary describes aspects of that study integrating multiple lines of evidence to arrive at a conclusion that might not otherwise be apparent. Specifically, aspects of the study where an integrated data analysis approach helped clear up an ambiguous story, or resolve seemingly conflicting lines of evidence are focused on.

A receptor model method (PVA) was used to resolve contributing PCB fingerprints [8]. Dechlorination pathway analyses were performed as part of that study to associate dramatically varying PCB composition across the site to a single source, and the elevated PCB concentrations could be associated with known high historic releases. One of the resolved source patterns in that analysis was consistent with published Aroclor 1248 congener patterns. When this information was compared to historical information, it was learned that the primary suspected source to the lake (a former capacitor manufacture) had not used Aroclor 1248, but had used Aroclor 1242. While these two pieces of evidence apparently conflict, a third line of evidence resulted in a simple, lucid and consistent story. Previously published empirical experimental data [30] had shown that weathering (volatilization) of Aroclor 1242 could result in a residual pattern in sediments that more closely resembles Aroclor 1248 than the original Aroclor 1242. As a result, the apparent Aroclor 1248 fingerprint was entirely consistent with an Aroclor 1242 source. The PCB pattern in buried highly dechlorinated samples, which did not resemble any Aroclor, was also linked to Aroclor 1242 and the primary source through dechlorination pathway analysis.

Data Analysis and Interpretation

This section presents an overview of the data analysis and interpretation, including the inclusion of information other than PCB data, data preparation, and PCB data interpretation.

- **Site History and Records Research**
- **Sediment Transport and Hydrodynamics**
- **Preliminary PCB Concentration Assessment**
- **Preliminary PCB Composition Assessment**
- **Chemometric Statistical Analysis,** such as
    - Cluster analysis
    - Principal component analysis
    - Mixing model analysis
- **Integrated Multiple Lines-of-Evidence Interpretation**

2.6 Presentation and Reporting

The presentation of results of a PCB forensics investigation will vary greatly, depending on the purpose and the venue. For example, given two projects that involve identical technical issues, the context of one might require verbal reporting, where the other might require a detailed technical report. In terms of presentation of results, there are a few guidelines that apply and can be used for most purposes. It is important to find an effective means of data visualization. Standard graphical presentations (e.g., histograms) of concentration and composition information can be useful, and any GIS-based illustration of the contamination and unique signatures are especially useful (e.g., Figures 2-15 and 2-17). Most statistical software packages include standard graphical output for data analysis results (e.g., cross-plots, score plots, loadings plots, etc.) but these graphics may mean little to the non-user and may require simplification; it is important to produce graphics that are intuitive to a non-scientist. The primary objectives of a PCB forensic investigation are identification of contributing chemical patterns (i.e., Aroclor sources and/or alteration patterns) and their geographic and temporal distribution. Summarizing historical industrial practices and local activities that can explain the observations, and using hydrological information to describe how sediments and potential contaminants move around in the system, can also be important to support the PCB chemistry. When describing the findings, it is useful to do so in a step-wise fashion, clearly lining up multiple lines of evidence, showing how they point towards the same findings and support each other.

As discussed in the beginning of this section, the format for presentation of results depend largely on project context and target audience/reader. The following scenarios may involve the exact same technical approach and forensic investigations, but the context of the project dictates different presentation formats.

If the audience does not have extensive technical knowledge (e.g., the public, managers, lawyers), it is likely that they are not intimately familiar with environmental chemistry, statistics, or PCB industrial history. Therefore, a presentation to this audience may require an element of introductory chemistry, statistics, and/or industrial history. In addition, the first communication of results is then often verbal, rather than written. Therefore, the presentation format is less formal than a report (e.g., a conference call, or a face-to-face meeting, perhaps with PowerPoint slides).

A second common context is a presentation to other scientists. This is likely a more formal context than the first example. However, the approach to the presentation will also be different in other ways. In a more technical context (among peers), it is assumed the audience knows much of the prerequisite science. A paper or presentation will then include a great deal of technical short-hand. In this venue, one may summarize important foundational material with no more than a citation at the end of a single sentence summary.

A third, and again, completely different example is a venue where contributions from multiple sources are not widely understood or agreed-on, and is common for forensics investigations. This may include what could be considered expert opinion, and to support that the expert is more likely to produce a report that errs on the side of completeness, even if it means a pedantic narrative and extensive appendices.

3.0 DEMONSTRATION CASE STUDIES

3.1 Site I: Hunters Point Shipyard

3.1.1 Site Description

The HPS site is located in the San Francisco Bay as shown in Figure 3-1. HPS is a former Navy installation located on a peninsula in the southeast corner of San Francisco, CA. The peninsula is bounded on the north, east, and south by San Francisco Bay and on the west by the Bayview Hunters Point district. HPS comprises about 955 acres, with approximately 457 acres of offshore sediment (Parcel F). From 1945 to 1974, the Navy maintained and repaired ships at HPS. The facility was deactivated in 1974 and remained relatively unused until 1976, when it was leased to Triple A Machine Shop, a private ship repair company. In 1986, the Navy resumed occupancy of HPS. The facility was closed in 1991 under the Defense Base Realignment and Closure Act of 1990 and is in the process of conversion to non-military use.

The shipyard is divided into several parcels with the offshore sediments designated as Parcel F. The specific area of interest for a PCB forensics investigation is the Parcel F (offshore) sediments near Parcel E and E-2 in the South Basin (Figure 3-1). This area is shown in more detail in Figure 3-2, where it is labeled Area X. South Basin's current configuration reflects filling activities that took place from the 1940s to the 1970s (Figure 3-3). Previous studies have shown potential PCB source areas associated with the former Navy landfill and multiple CSOs in nearby Yosemite Creek. Of particular concern is whether these different sources have contributed PCBs to sediments in the South Basin area, and to what degree. This site has been under regulatory study and RI/FS has been completed as part of the CERCLA program. The data used in this case study example were collected as part of the RI/FS study, most of it from a comprehensive data gaps investigation [62].

South Basin is a shallow embayment on the south side of HPS, with water depths ranging from 6 ft to less than 2 ft. No streams or rivers enter South Basin except for Yosemite Creek, a shallow, tidally-influenced channel with no permanent flow. Circulation in South Basin is restricted and tidal currents are very weak. The basin is open to the southeast, which is the direction of the maximum winds during winter storms. Although the prevailing winds in the area are westerly, the acute storm waves responsible for sediment resuspension are generated by southeast storm winds. Yosemite Creek enters South Basin at the southwest corner of HPS. Yosemite Creek is listed as a site of concern under the Bay Protection and Toxic Cleanup Program in 1997. Prior to 1965, three CSOs discharged to this area: one at the head of Yosemite Creek (Figure 3-2), one on the north side of the creek near Griffith Street, and one on the south side near Fitch Street. All wet weather overflows were directed to the CSO at the head of Yosemite Creek after 1965. Contaminants identified during investigations of Yosemite Creek by the City and County of San Francisco included PCBs, PAHs, pesticides and metals.

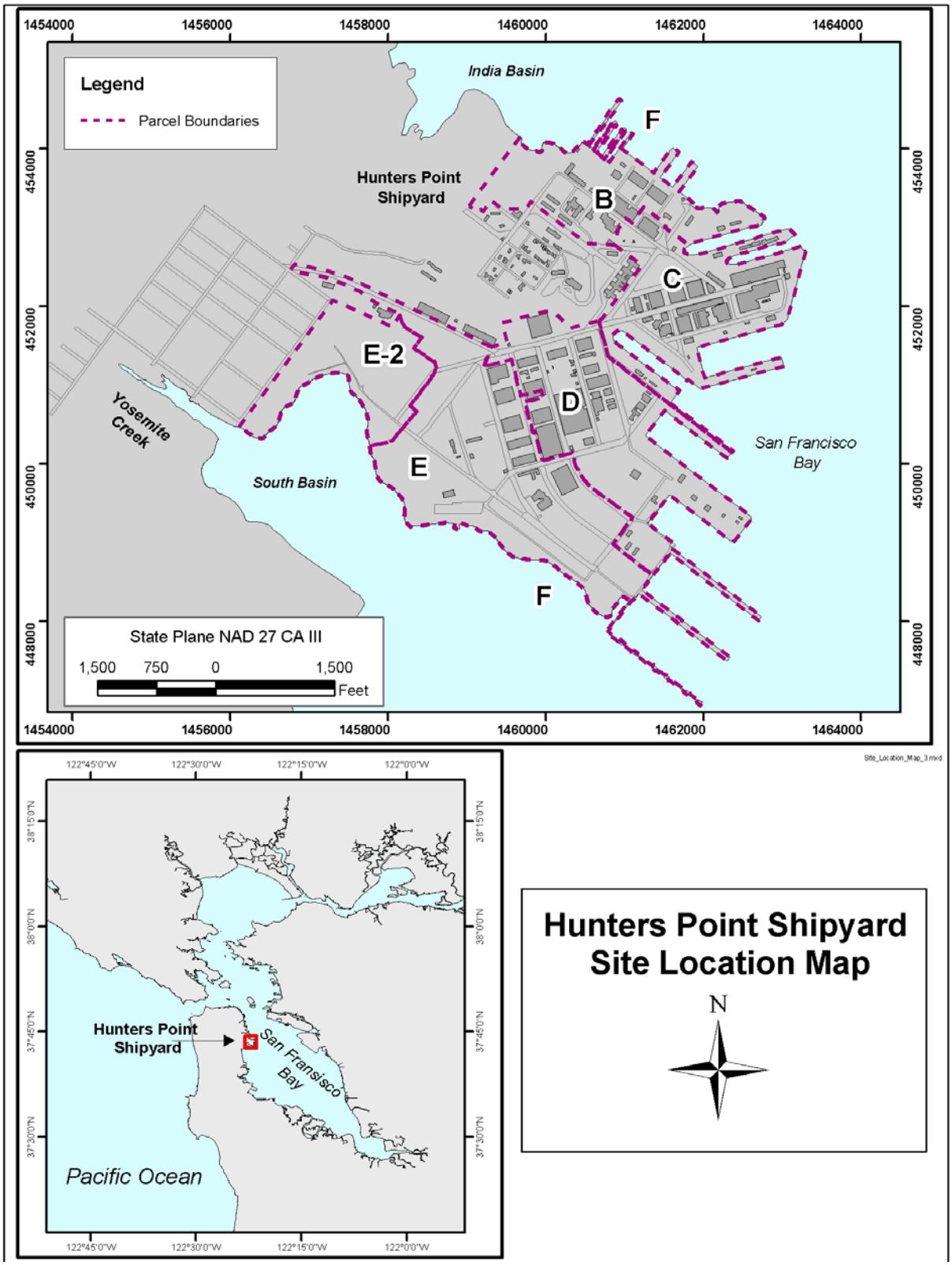


Figure 3-1. Hunters Point Shipyard Location Map Showing South Basin Area

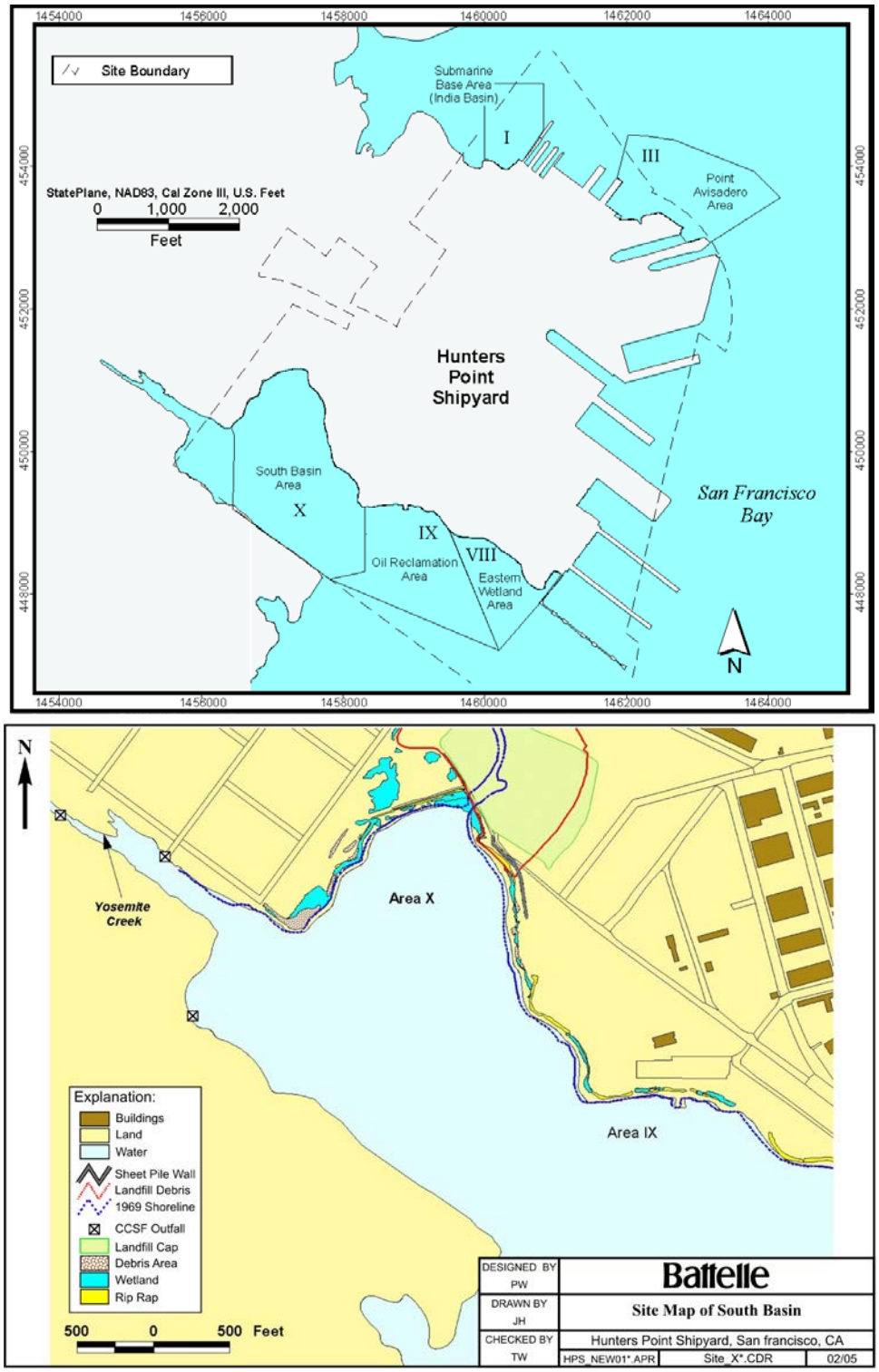


Figure 3-2. Study Areas and Shoreline Features in South Basin (Areas IX-X) of Parcel F Offshore Sediments

(Note Former Landfill to the north and City Outfalls to the west.)

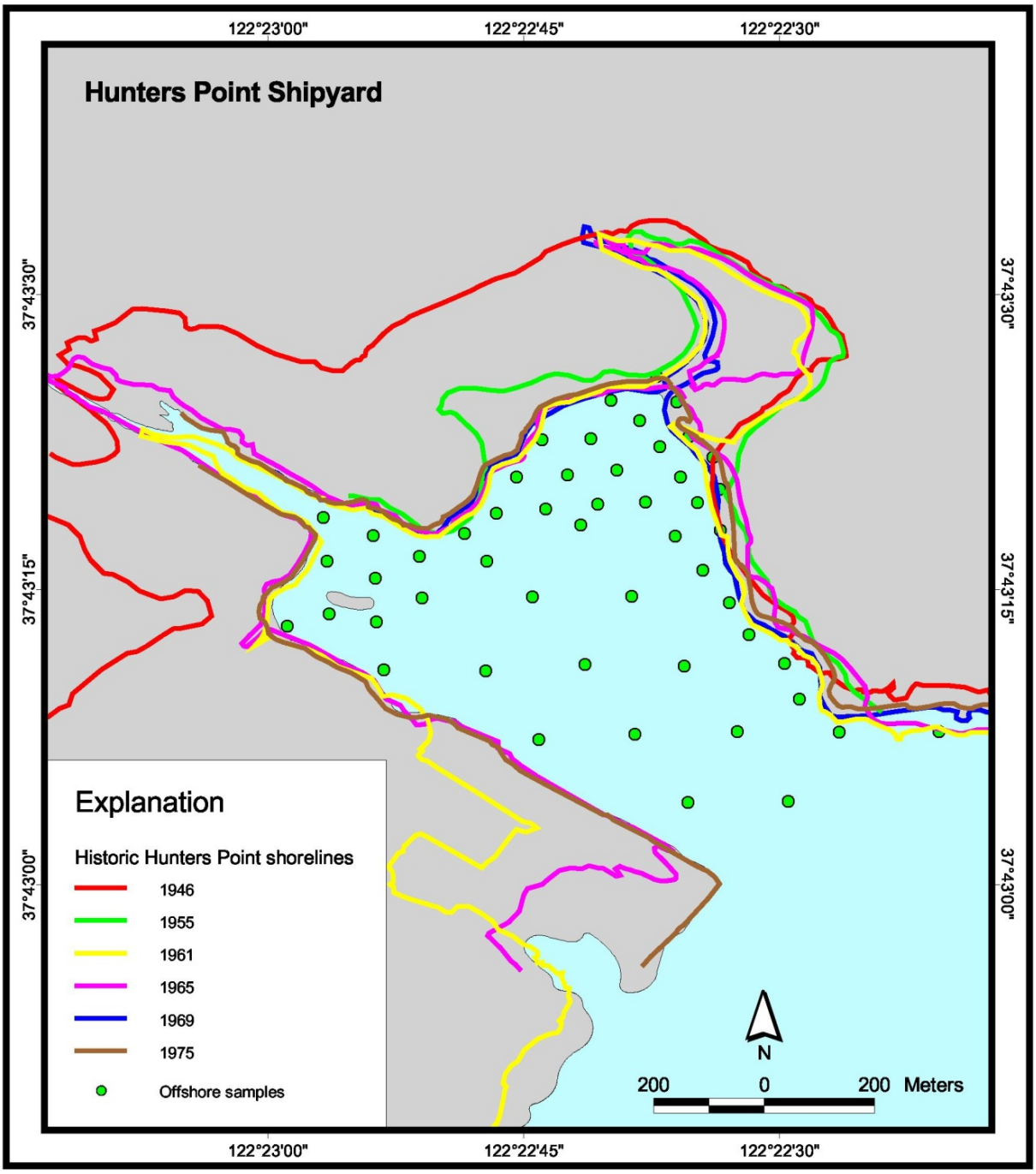


Figure 3-3. Shoreline Evolution in HPS South Basin and 2003 Offshore Sample Locations

3.1.2 Evaluate Site for Forensic Study

To evaluate whether the site is a candidate for a forensic study, the questions posed in Section 1.2.1.1 should be answered. The HPS site has a former landfill in Parcel E-2 (near the northeastern shore of South Basin; Figure 3-2) with records showing wastes (including transformers with PCB oils) deposited at the site from the 1950s through the 1970s. Other records indicate that PCBs with an Aroclor 1260 composition have been detected in some groundwater wells near the shoreline. Related to Questions 2 and 3, there have been known discharges from CSOs in and near Yosemite Creek, and previous studies by the City of San Francisco [63] have shown sediments upstream in Yosemite Creek contain PCBs with both Aroclor 1254 and 1260 contamination. Addressing Question 4, there was a sediment transport study conducted as part of the RI/FS [31, 62] that shows South Basin to be a relatively quiet depositional basin with occasional wind derived local resuspension and local redeposition. This conclusion is further supported by the persistent PCB concentration gradients shown in the sediment contour maps in later sections of this handbook. For Question 5 (i.e., how amenable regulators would be to the use of forensic information), the answer varies depending on when in the process such information would be used. There was a consensus early in the RI/FS process that a forensics study would be useful, and there were plans to incorporate such a study in the RI/FS. Later, there were questions from both the regulators and the Navy about whether they could use such a forensics study at HPS. After the samples for the RI/FS were collected, it was decided not to complete the forensics study as part of the RI/FS. The information from the HPS site was available for use in this handbook to help promote the use of forensics studies at Navy sites, but a dedicated PCB contaminant forensics investigation has not been conducted at HPS. The data generated in the RI/FS, and used in this handbook, support the contention that there appear to be at least two potential sources for PCBs to the offshore sediments in South Basin (one from the former Navy landfill area and one possibly from CSOs in the Yosemite Creek area) and a forensics study could defensibly document this and better understand the relative contributions from the multiple source to the offshore sediments.

3.1.3 Develop Conceptual Site Model

Figure 3-4 shows a contour map of surface PCB concentrations, based on ELISA IA RSC analysis, that assisted in early CSM development at HPS. These data were collected early in the regulatory RI/FS project, and they suggest a potential PCB source in the northeast along the Navy shoreline near the former landfill. An additional source is also suggested at the creek on the west side of the site where PCB concentrations are also elevated. Other data from CSOs in and near this creek have shown PCB levels similar to those along the Navy shoreline. The sampling design for a forensics investigation should therefore be placed strategically to confirm that these two areas represent sources and also in other areas (for example along the south shore of South Basin where construction of Candlestick Park Stadium may have contributed contamination) to ensure that there are no additional unidentified sources to the offshore sediments in the area. Samples should also be placed in all areas of comingling sources and where it is appropriate to determine source contribution and apportioned, for the Navy to share or recover any remedial costs.

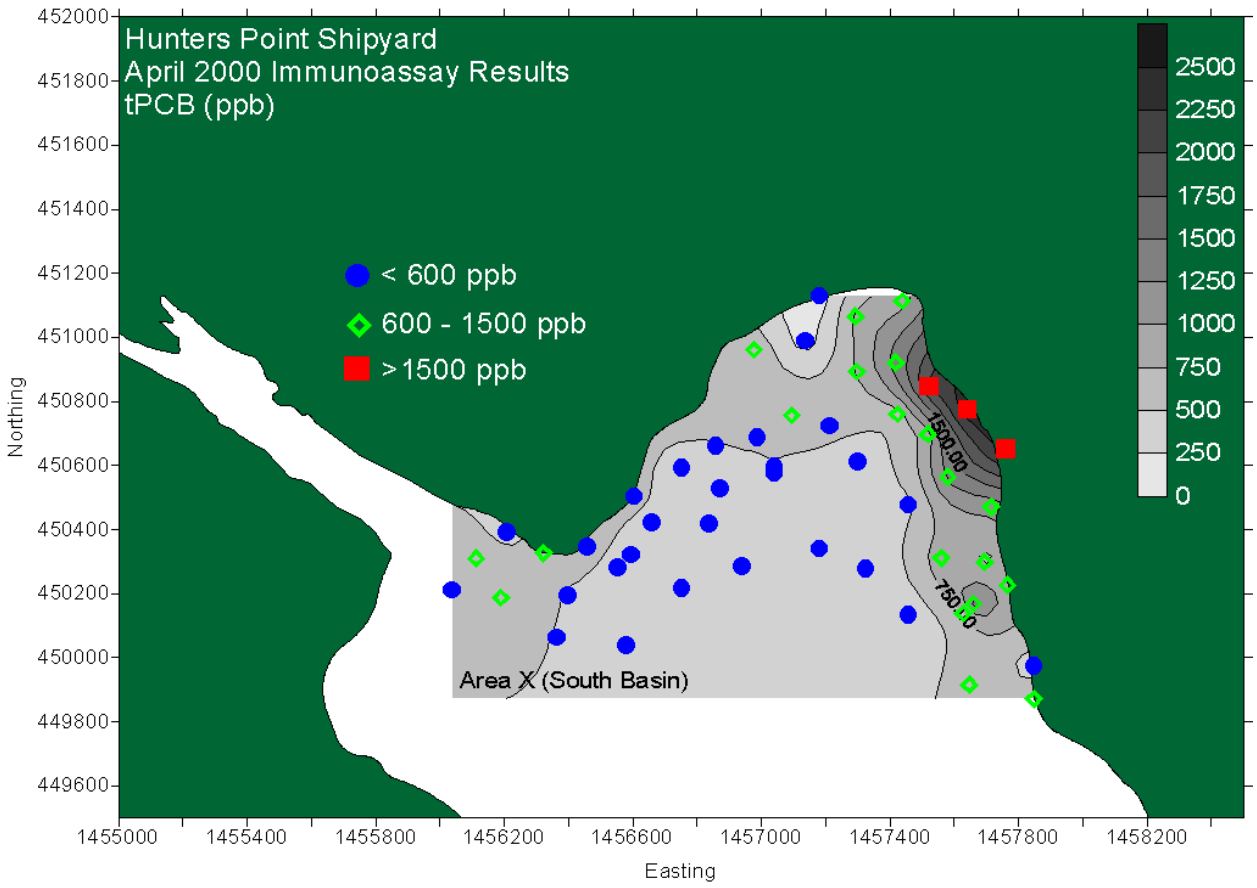


Figure 3-4. Contour Map of PCB Concentrations in Surface Sediments in South Basin at HPS

Since this case study was not a stand-alone project, there were no resources to conduct extensive records research and build a separate CSM. However, a CSM was developed by the regulatory RI/FS program (Figure 3-5) and could be used for some project considerations. The major pathways for PCB contaminant transport to the South Basin sediments are indicated as originating from: (1) historic filling and disposal practices associated with the landfill area, which allowed PCBs to be transported via the historic slough, or channel, out into the South Basin sediments; (2) releases from CSO outfalls in Yosemite Creek area (shown as active red arrows) transports PCBs out into sediments; and (3) erosion of contaminated fill that was used around Yosemite Creek releases PCBs into the sediments. One might consider making the minor active pathway arrow from the "Shoreline Erosion/Runoff" box to the "Sediment" box into a bolder major pathway arrow, indicating the potential for PCB releases from erosion of the fill material along the beach in front of the former landfill. This may be the major continuing active source (although current plans include a removal action to remove this contaminated beach material and stabilize the shoreline) based on the high surface sediment concentrations observed in this area (Figure 3-4). This CSM serves to focus the SAP in the next section, by identifying the locations where samples should be taken to answer the forensic questions raised during development of the CSM.

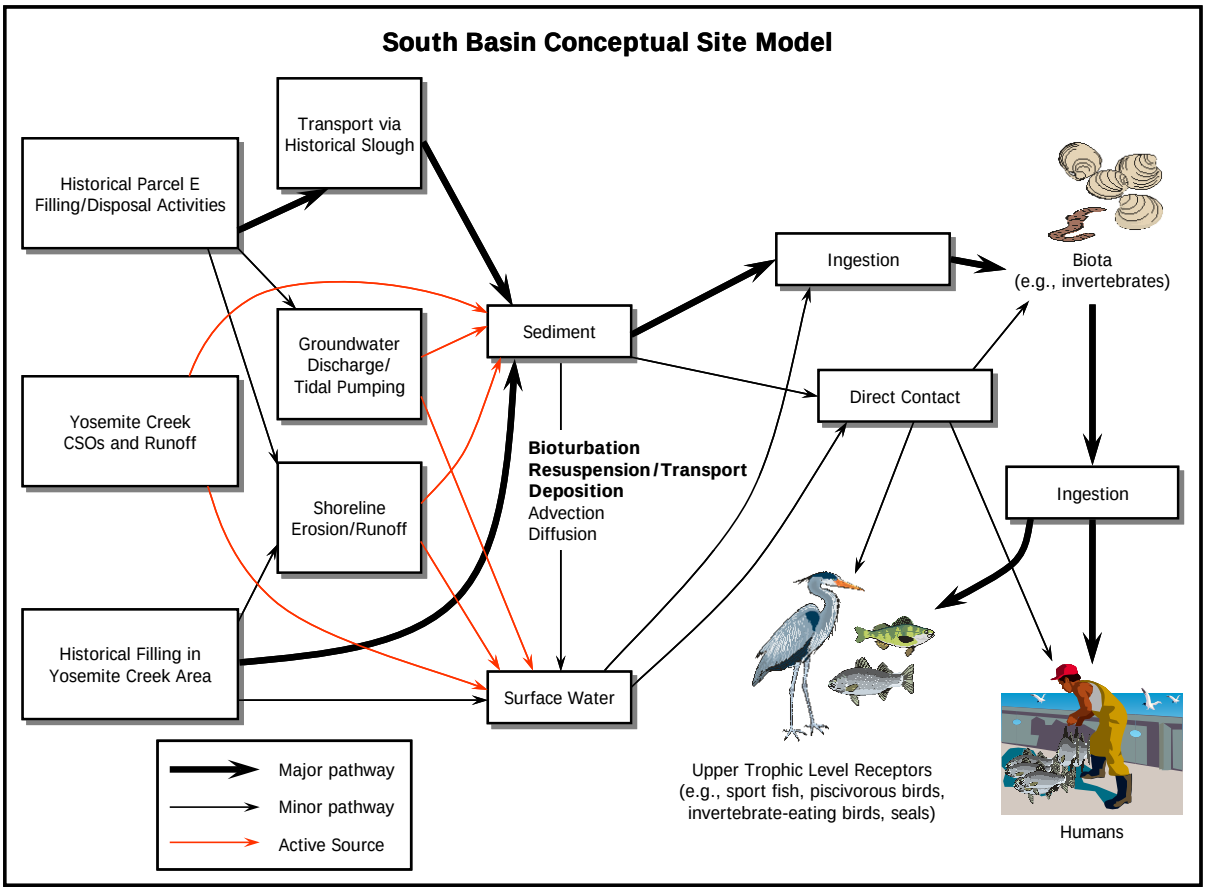


Figure 3-5. HPS South Basin CSM from Regulatory Program RI/FS

3.1.4 Develop and Execute a Technically Defensible Sampling Plan

In the HPS case, the regulatory RI/FS project included a grid design for samples with spacing that would allow for the detection of hotspots larger than a predetermined size. This grid sampling design is shown in Figure 3-6. Higher density sampling is seen in the potential source areas with lower density in the farther offshore sediments. Figure 3-6 also shows the core intervals that would be composited for initial RSC analysis, with only a subset of these samples being later analyzed for ACF. This resulted in about 400 samples being analyzed for RSC and about 100 samples for ACF. Unfortunately, the regulatory project was restricted to sampling primarily on Navy property, so no samples were collected further upstream in Yosemite Creek near several CSOs that were additional potential sources. In addition, additional samples in the zone where the PCB sources are well mixed would have benefitted a forensics investigation.

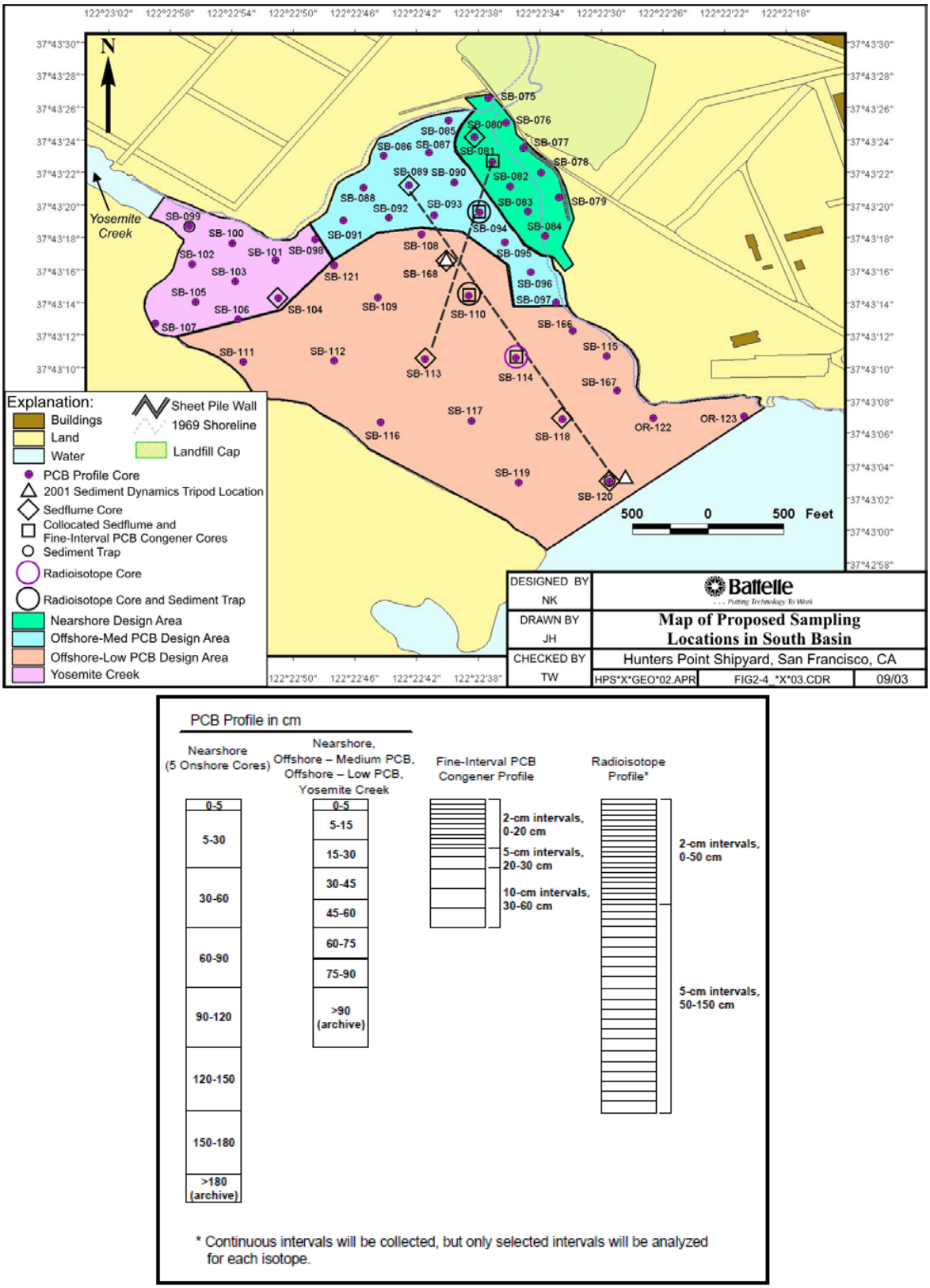


Figure 3-6. Sampling Design Map for the HPS Feasibility Study [62]
(This includes the cores that provided the data used in the forensics demonstration at HPS.)

The HPS case study is based on using existing data from study designs that had not been optimized for a forensics investigation. There are clearly advantages and limitations of designing a forensics study with only pre-existing data. Although using pre-existing data provides a large cost savings, the shortcomings of not being able to design a sampling plan to collect all the samples desired must be accepted. As stated earlier, even in the best designed forensics study, there are likely to be surprises, such as those seen with this case study using only pre-existing data. For example, if additional sources are indicated by some of the study samples (e.g., Yosemite Creek), then there is a need to conduct additional sampling and analysis to identify such sources. That has not been conducted for the HPS site. So although it may be easier to grasp a forensics study that follows a linear process (Figure 1-1), it may be more realistic to assume the process will be iterative with a need to obtain information on additional unknown sources, and fill in additional information gaps.

While it is cost-effective to use pre-existing data (no additional field or analytical costs), the limitations are that the study design may not meet all of the objectives of a well executed forensics study. Fortunately, in the HPS case, the study plans, although not intended to satisfy a forensics study, did include relatively detailed sediment sampling and rather comprehensive PCB congener analysis; significantly more useful information was produced than would be typical in a standard RI. However, detailed sampling and analysis in proximity to a potential second source is missing.

3.1.5 Conduct Rapid Sediment Characterization

For HPS, the ELISA IA technique was used to obtain the RSC data, generating a comprehensive data-set of Total PCB concentrations. The HPS study was tiered, as described earlier, with the 450 RSC analyses followed by a smaller subset of 120 ACF analyses of frozen archived splits. The RSC data were used to generate the contour maps that aided in selecting the ACF samples. The HPS RSC data are summarized in Appendix C. The HPS RSC Total PCB data compared well with Total PCB based on laboratory congener analysis; the laboratory-based Total PCB determination was made by the widely used approach of summing the concentrations of the 18 NOAA National Status and Trend monitoring project congeners, and multiplying that by two [62-63]. On average, the RSC results provided a Total PCB concentration approximately 12% higher than the laboratory congener-based Total PCB analysis (Figure 2-8). This is as can be expected, since the RSC analysis kit "as received" uses Aroclor 1254 as the calibrant, and the HPS samples contained significant amounts of Aroclor 1260 type contamination, which has a greater response than Aroclor 1254 (Table 2-6). This response difference can be corrected for, as discussed in Section 2.4.1, by either calibrating with an Aroclor standard that better represents the Aroclor composition of the field samples or by using a correction factor that represents the response correlation (Figure 2-8). However, these adjustments to the RSC data are not needed as long as the data are mainly to be used to gain a general understanding of the Total PCB concentrations across the site (Figures 2-16 and 2-17).

3.1.6 Conduct Advanced Chemical Fingerprinting

The ACF analysis of the HPS sediment samples consisted of determining the concentrations of 44 PCB congeners using modified Method 680/1668 (a HRGC/LRMS analysis technique), as described in Sections 2.4.2 and 2.4.3. Again, the HPS study was not conducted as a forensics investigation, but the ACF analyses were conducted on a subset of the RSC samples following

review of the full RSC dataset. In addition, the 44 PCB congeners were selected primarily to generate data that were comparable to historical data for San Francisco Bay, and not for forensic purposes. The HPS ACF data are summarized in Appendix B.

During the data review and screening (Section 2.5.2.3) about 14 of the 120 samples were identified as candidates for potentially excluding from the data analysis because of lower data reliability (e.g., low overall PCB concentration [e.g., sum of congeners less than ~50 to 100 ppb] and a high percentage of the 44 PCB congeners with non-detects). Six PCB congeners were also identified as potential candidates for exclusion from the data set prior to detailed data analysis because of possible reliability issues (e.g., high percent non-detect of the congener, low congener concentration, a high %RSD in the percent contribution of the congener to the Total PCB, or other data outlier issues).

3.1.7 Data Analysis, Synthesis, and Presentation of Results

3.1.7.1 Site History and Records Research

The specific area of interest for the PCB forensics investigation was the Parcel F (offshore) sediments near Parcel E and E-2 in the South Basin; the area labeled Area X in Figure 3-2. Previous studies have shown potential PCB source areas associated with the former Navy landfill and multiple CSOs in nearby Yosemite Creek. Historical activities in adjacent upland Parcel E-2 that may have contributed to contamination of sediments in South Basin include filling and disposal activities, residual onshore contamination, and surface runoff. Groundwater discharge was also evaluated as a potential transport pathway of PCBs to South Basin from Parcel E-2, however, the magnitude of PCB release via this pathway is not likely to be significant given the limited extent of PCBs detected in groundwater and their low solubility. A former landfill at Site IR-01/21 in Parcel E-2 (Figures 3-1 and 3-2) was used from 1958 to 1974 for the disposal of materials such as construction and industrial debris and waste, domestic refuse, sandblast waste, paint sludge, solvents, waste oils, transformers and electrical equipment and other potentially contaminating materials. No records that document landfill contents or disposal practices are available. In the mid-1970s, the Navy placed 2 feet of compacted imported fill on top of the landfill and graded the entire site to facilitate storm water drainage. In the 1990s, a sheet pile wall was installed and riprap was placed along the Parcel E-2 shoreline to control the movement of contaminants into South Basin. In 2001, an interim landfill cap was constructed and placed over most of the landfill. The cap consists of a multilayer system of sub-base soil, high density polyethylene membrane, synthetic drainage layer, and topsoil.

South Basin was originally a marshy wetland area. Its current configuration reflects filling activities that took place from the 1940s to the 1970s. Figure 3-3 shows the South Basin shoreline in 1946, 1955, 1961, 1965, 1969, and 1975. The shoreline positions were mapped by digitizing historical aerial photographs. The greatest period of land expansion was between 1946 and 1955, in which the northern, western, and southern portions of the basin were filled, forming the areas now occupied by Parcel E-2, Yosemite Creek, and Candlestick Point, respectively. The second largest period of land expansion occurred between 1965 and 1969, in the northern part of South Basin. This fill event formed a slough, apparent in the 1969 (blue) shoreline contour, through the middle of the waste disposal area now known as the Parcel E-2 landfill. This slough, or channel, drained an unmarked outfall located at the north end of this channel up behind the marked landfill boundary. By 1975 (brown color), this outfall was closed off and the slough had

been filled; today's shoreline is virtually the same as the 1975 contour, and therefore is not shown. Between each recorded shoreline, it is uncertain when each fill event occurred. The sources of material used to fill these areas are not documented. The Navy operated the shipyard during the periods of the major filling events. The property was leased to the Triple A Machine Shop after the current shoreline was established (ca. 1975).

The historical information suggests that there could be sources of PCB from activities at the Navy facility, contributing PCBs to the northeastern side of Area X in South Basin (Figure 3-2), particularly from the landfill near that shoreline and the historical slough that discharged to that area. Historical information also suggests that there could be sources of PCBs associated with runoff to Yosemite Creek, and historical CSOs that discharge into Yosemite Creek and to the west just outside the mouth of Yosemite Creek (Figure 3-2). Review of historical records shows that there were commercial and industrial activities along city streets just north of Yosemite Creek, including a drum recycling facility. The Consent Decree shows that drum recycling activities at the site from 1948 to 1988 likely resulted in releases of PCBs that may have served as a source for PCB contamination to surrounding areas.

3.1.7.2 Sediment Transport and Hydrodynamics

At HPS, a leveraged sediment transport study was conducted as part of the RI/FS, and is reported as a case study in Appendix B of Blake et al. [36]. Sediment stability and transport studies were also conducted as part of the RI/FS data gaps investigation [62]. Blake at al. reported that "PCBs tend to adsorb to fine-grained sediment particles and organic matter, so sediment transport processes (i.e., resuspension, transport, and deposition) are important contaminant transport pathways in South Basin. Because of its restricted circulation, tidal currents in South Basin are very weak. Waves are likely to be the dominant sediment resuspension mechanism because the basin is shallow and open to the southeast, which is the direction of the prevailing winds during winter storms. The primary source of sediment to the basin appears to be suspended sediment from San Francisco Bay; shoreline erosion may contribute some sediment. The basin appears to be a net depositional environment with a net accumulation rate of about 1 cm/yr. The dispersal pattern of PCBs, with higher concentrations near shore and decreasing concentrations offshore, is consistent with wave-influenced and tidally influenced sediment transport. Storm waves breaking along the shoreline suspend fine, low-density sediments in the near shore region. A return flow near the bottom of the water column (balancing the shoreward flow due to waves at the surface of the water column) transports the sediments away from the shoreline and into South Basin. Tidally induced currents may facilitate additional transport across the mudflats and extend the influence of waves further offshore during low tide, potentially carrying material further offshore into South Basin. The deposition of cleaner background sediments transported in from San Francisco Bay and deposited in South Basin results in the dilution and burial of the nearshore and offshore sediments. As new sediments are deposited, mixing processes (physical and biological) act to mix surface and subsurface sediments, resulting in the gradual decrease in surface PCB concentrations over time. The smooth vertical PCB profiles in sediment cores (i.e., gradual increase and then decrease in concentration with increasing depth) indicate that overall, the sediment bed in South Basin appears to be relatively stable and undisturbed."

Sediment stability work conducted in South Basin is also reported in Battelle et al. [62]. The primary purpose of this work was to determine the erosion and deposition characteristics of the South Basin to estimate the fate of the contamination in the sediments, assuming sources were controlled and background level sediments were depositing. The average net deposition was determined to be approximately 1 cm/yr, and the most contaminated zone was expected to, over time, progressively become deeper and deeper in the sediment (Figure 3-7), and surface sediment PCB concentrations would eventually reach background levels (Figure 3-8). The current sediment deposition information in this study was also useful for understanding contaminant transport. The findings indicated that South Basin is a relatively quiet depositional basin with occasional wind derived local resuspension and local redeposition. The information did not indicate any unusual transport characteristics, and suggested that the contamination would be expected to show a gradual decline away from sources. This conclusion is further supported by the PCB concentration gradients shown in the sediment contour maps (Section 3.1.7.3).

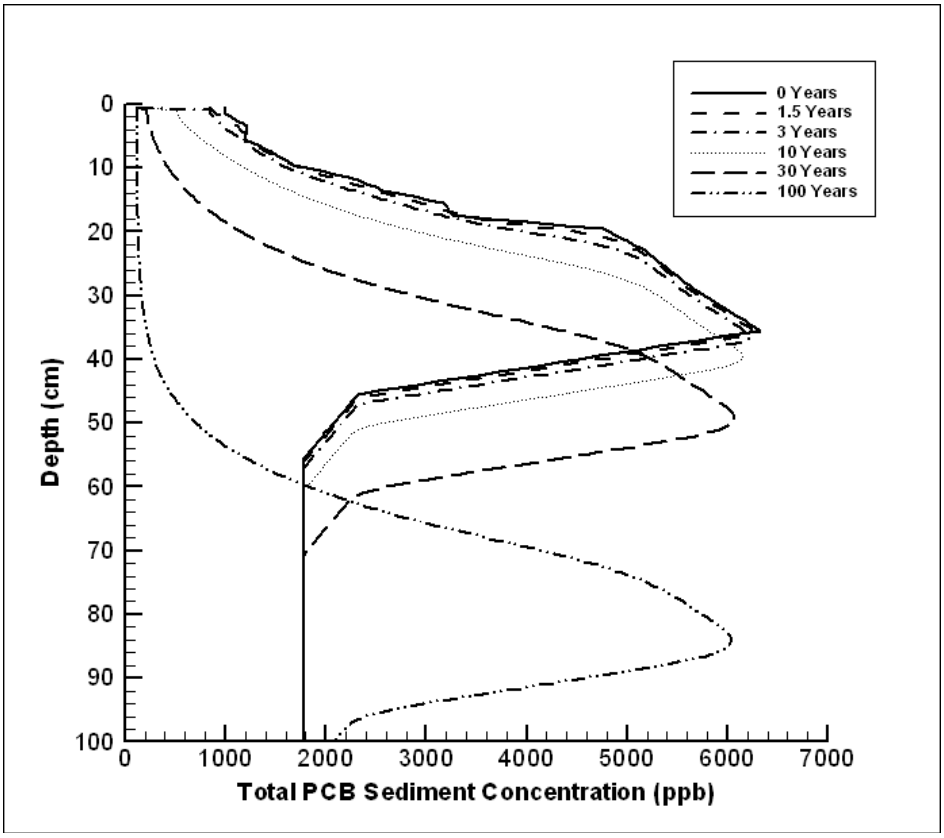


Figure 3-7. Predicted Total PCB Profiles over Time at HPS Station SB-081

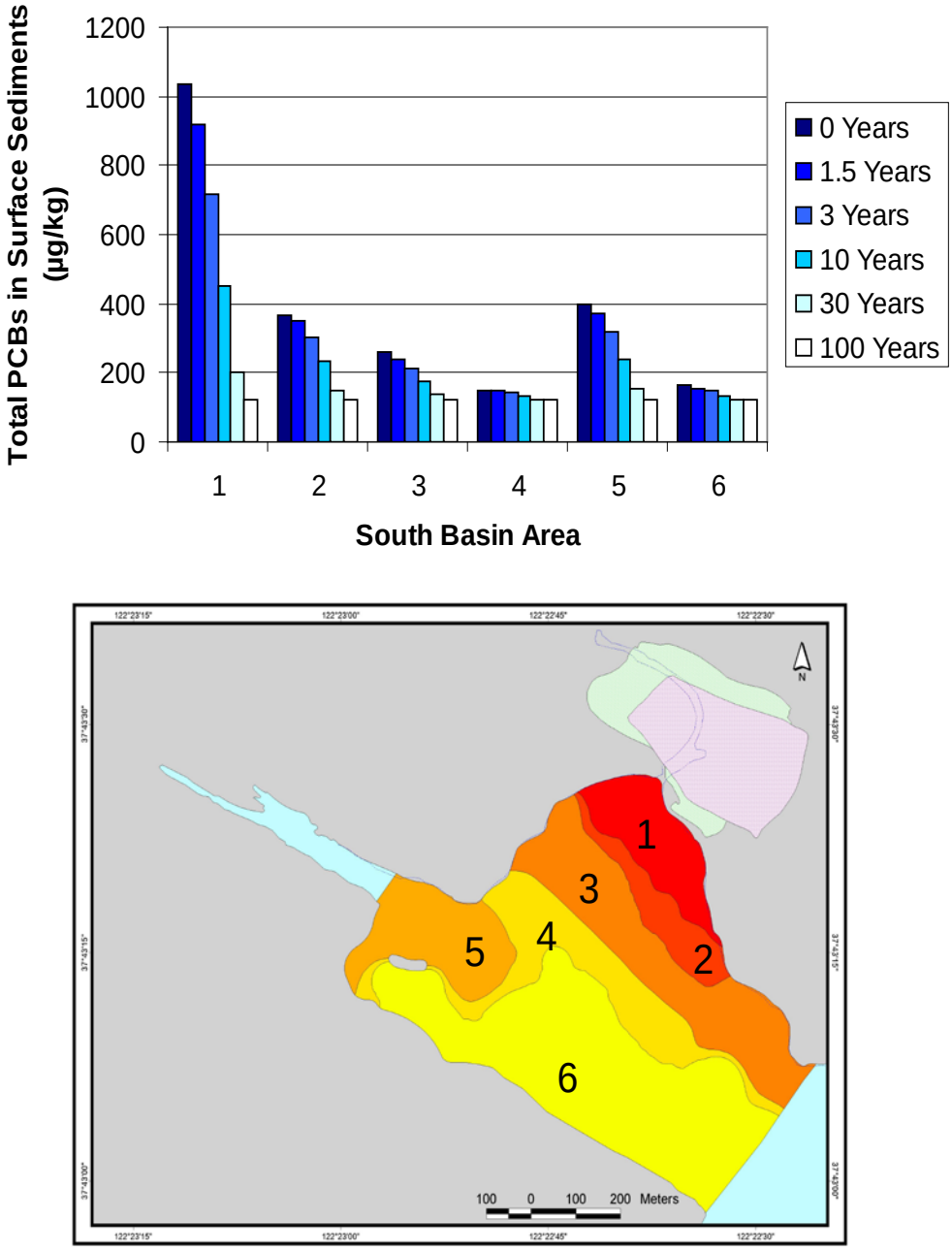


Figure 3-8. Areas Evaluated for PCB flux (top), and Predicted Surface PCB Concentrations over Time (bottom)

3.1.7.3 PCB Concentrations

Elevated PCB concentrations were measured in the northern portions of HPS South Basin; particularly in the northeastern parts near Parcel E-2 and the northwestern parts near the mouth of Yosemite Creek (Figure 3-1). The South Basin sediments with elevated PCB concentrations near Parcel E-2 are also near shoreline locations where high PCB concentrations have been measured (Figure 3-9; [62]).

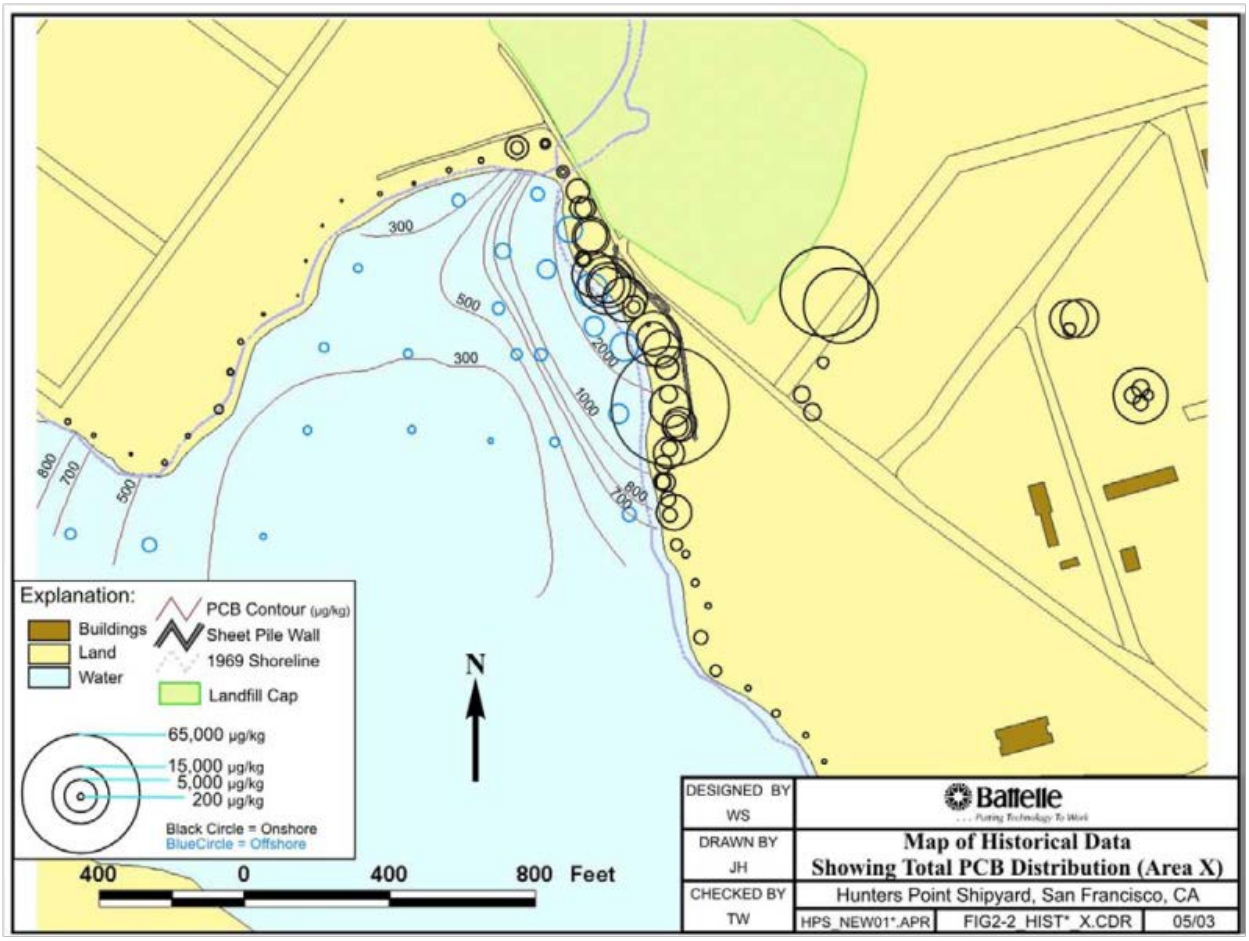


Figure 3-9. Upland Shoreline PCB Concentrations along South Basin

Figures 3-10 and 3-11 show examples of contour maps produced with the HPS RSC data, which can be useful to aid in selection of ACF samples. These contour maps show different PCB concentrations, with the standard red, for instance, representing 2,000 ppb and higher and the deep red representing above 5,000 ppb. It should be noted, and cautioned, that these represent extrapolations using data points spaced well apart, and the actual concentration at a specific location is not known except for where samples were collected (see core and sample locations in top of Figure 3-11). Contouring is, however, a widely used technique for understanding the approximate PCB concentration distribution.

The 3D visualization (Figure 3-11) makes it easy to assess the mass of PCB-contaminated sediment, and its distribution, while the 2D maps (Figure 3-10) are easier to use for directly comparing concentrations at different locations for samples from the same depth. Figure 3-10 features plan view maps of PCB concentrations with increasing depth below the mudline based on the 2003 FS Data Gaps Investigation data [62]. The plan view maps represent horizontal slices at 0.5-ft intervals. Observations based on these maps include the following:

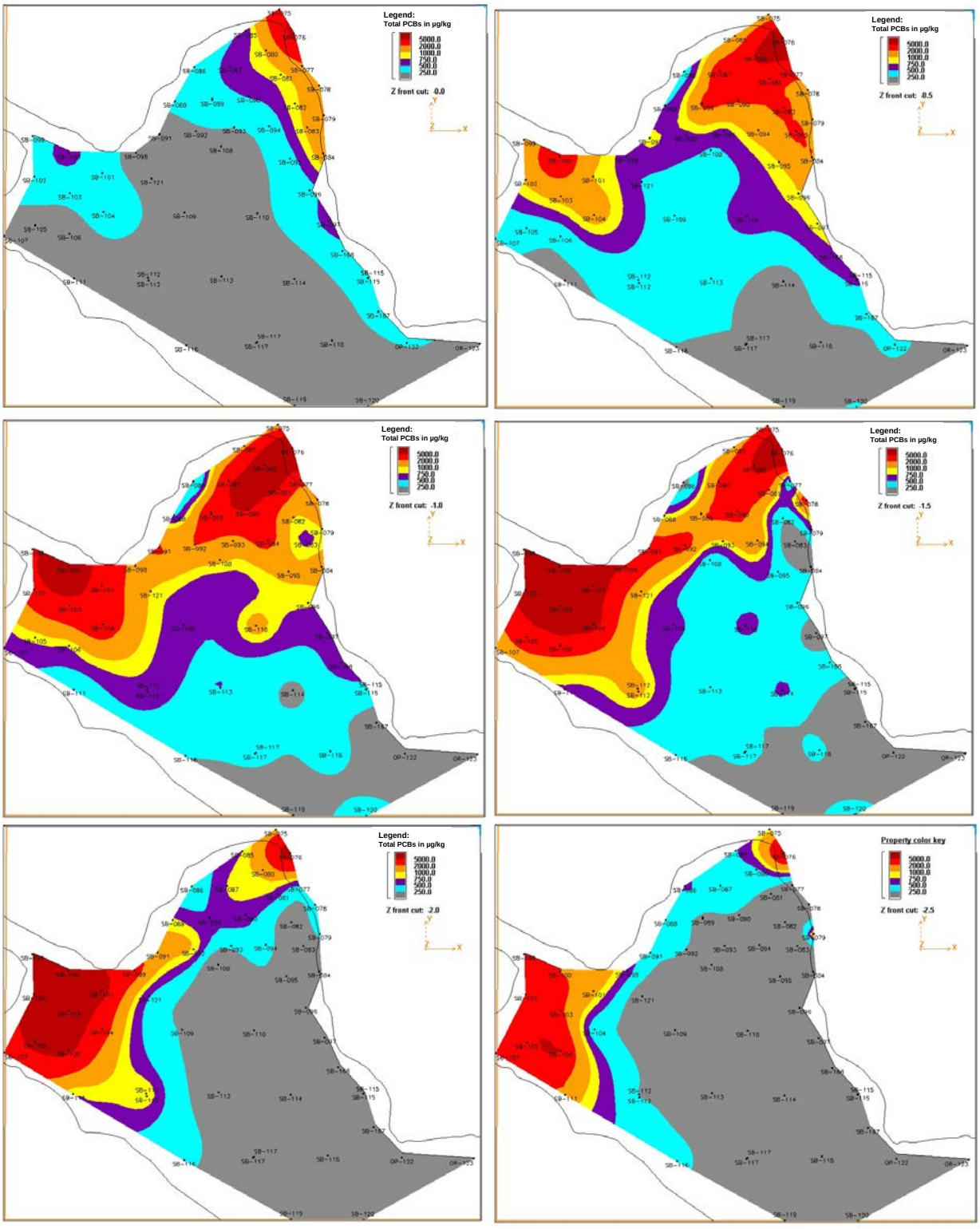


Figure 3-10. HPS Total PCB Concentration in Sediments from Surface, 0.5 ft Depth, 1 ft Depth, 1.5 ft Depth, 2 ft Depth, and 2.5 ft Depth, Respectively, from Top Left to Right

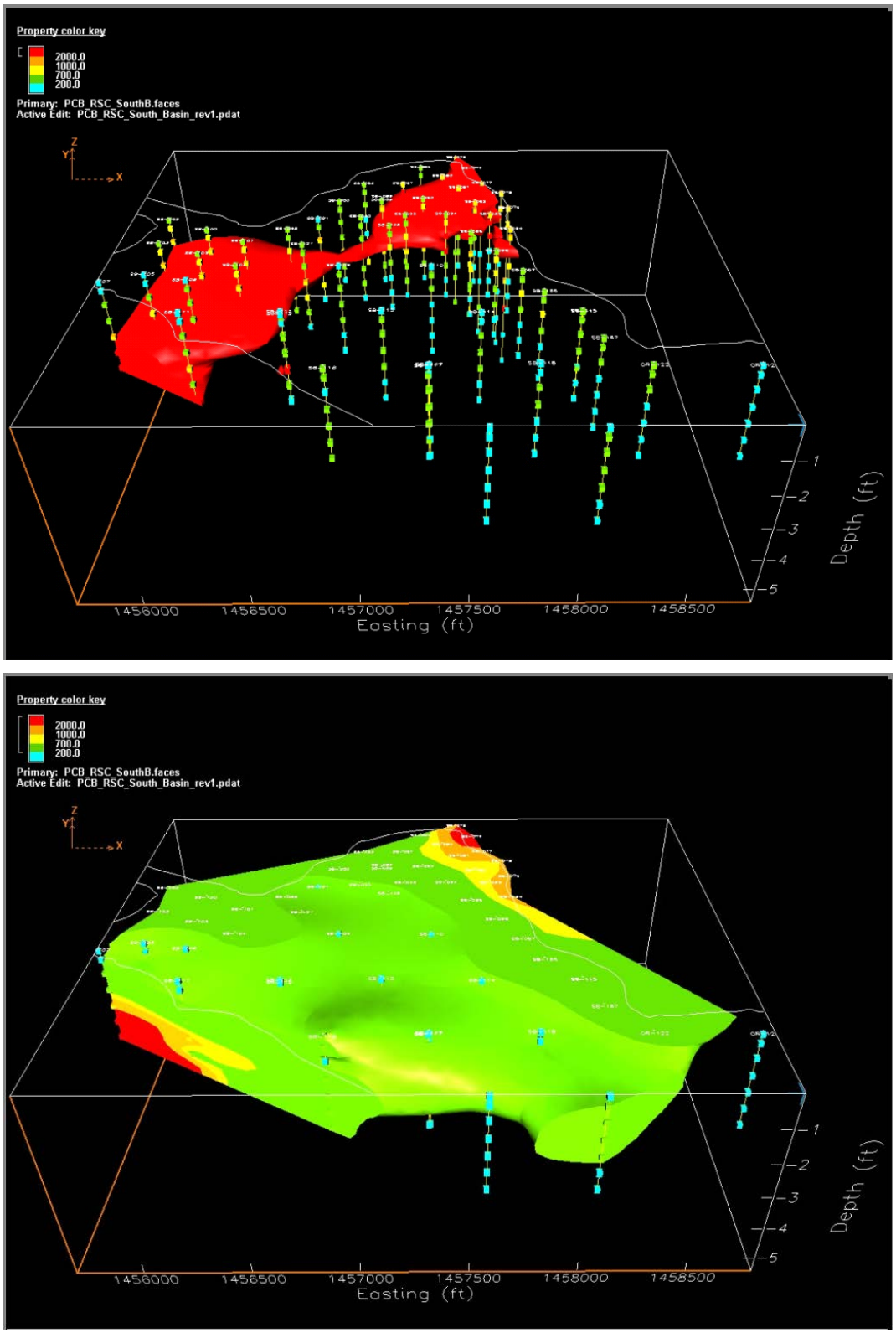


Figure 3-11. 3D Contour Maps from HPS Showing Total PCB Concentrations and Color Coded Core Horizons

(Upper map shows concentrations >2000 ppb in red [62].)

- PCB concentrations in surface sediment are highest (>2,000 µg/kg) at the north end of South Basin, near the area where the former slough connected with South Basin. Surface PCB concentrations decrease with increasing distance from the Parcel E-2 shoreline on the northeast side of South Basin. An area of slightly elevated surface concentrations (i.e., greater than 250 µg/kg) is also apparent near the mouth of Yosemite Creek.
- At a depth of 1-ft below the mudline, the area with PCB concentrations >2,000 µg/kg is more extensive, both at the north end of South Basin and at the mouth of Yosemite Creek. Overall, concentrations are higher 1-ft below the surface than at the surface, and the mass of highly contaminated sediment is greater in the 1 to 2 ft depth zone.
- At 1.5-ft below the mudline, the area of highest PCB concentrations decreases in extent at the north end of South Basin, and increases in extent at the mouth of Yosemite Creek. At 2.5-ft below the mudline, PCB concentrations of >2,000 µg/kg at the north end of South Basin are limited, whereas the affected area at the head of Yosemite Creek has not diminished substantially.

Figure 3-12 shows the surface sediment Total PCB concentrations at each sample station in South Basin and Yosemite Creek, and along the shoreline, based on combined data sets from multiple years (i.e., from 1999-2003). This map uses older historical data for the Yosemite Creek site; Yosemite Creek was not included in the detailed 2003 investigations of HPS. Three regions with the most highly-elevated PCB concentrations can be identified on this map: (1) the Parcel E-2 shoreline south of the Parcel E-2 landfill (shown as blue boxes along the shoreline); (2) the outlet of the former slough at the north end of South Basin; and (3) near the mouth of Yosemite Creek. The highest shoreline PCB concentrations are found to the south of the Parcel E-2 landfill, whereas the highest offshore PCB concentrations are found at the outlet of the former slough and at the mouth of Yosemite Creek.

These PCB data indicate that the South Basin sediment areas with the highest PCB concentrations adjacent to the Parcel E-2 shoreline, and particularly areas in close proximity to the former landfill and slough, and at the mouth of Yosemite Creek, do not appear to be continuous or linked (Figure 3-9), and the elevated PCB near the mouth of Yosemite Creek is at a greater depth than near Parcel E-2. These PCB concentration data suggest that there may be two separate sources of PCBs in South Basin: one associate with Parcel E-2 shoreline and the other with Yosemite Creek. The data also indicate that the contamination near Yosemite Creek is primarily historic and that this source has, for the most part, been controlled, and that the source of most of the contamination near Parcel E-2 is more recent and may still be contributing to the surface sediments (when these samples were collected, in 2003).

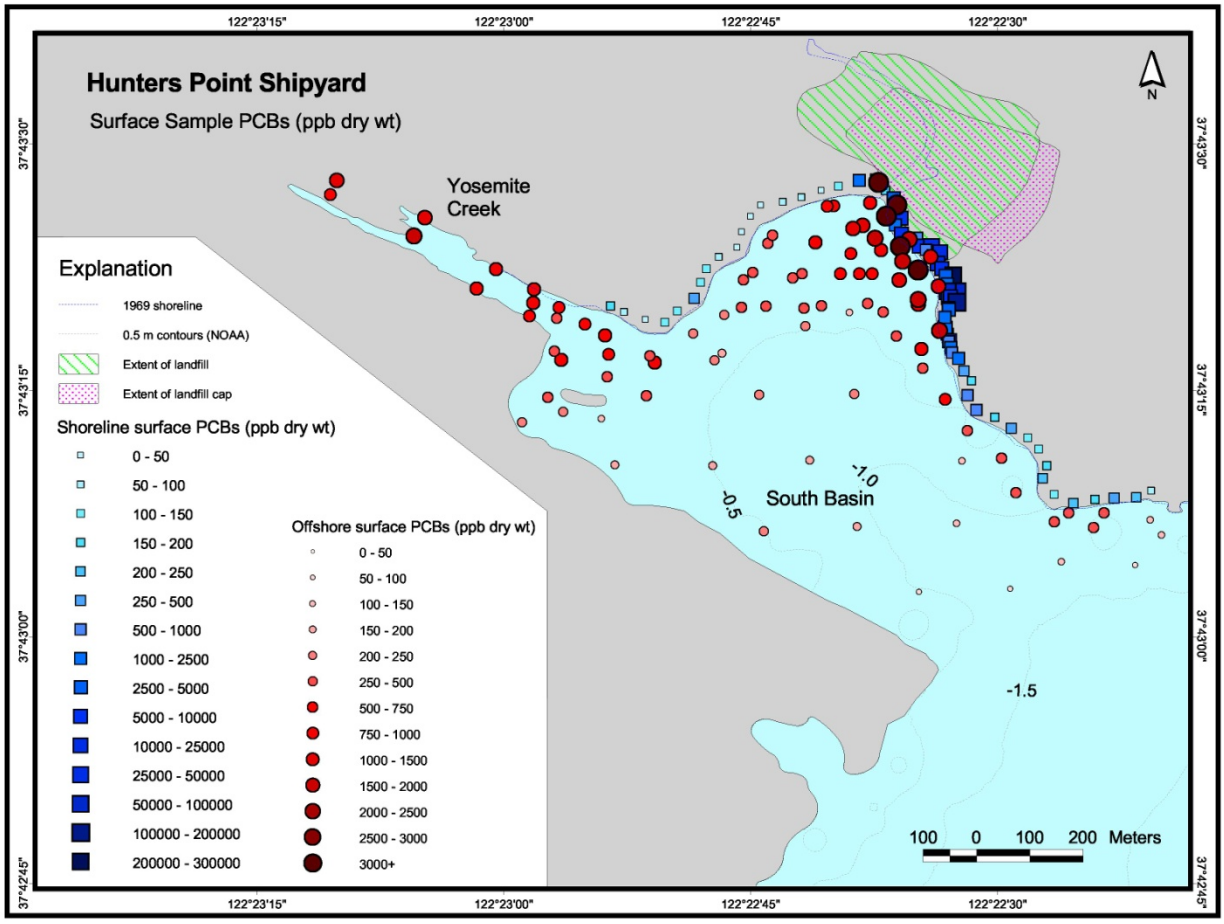


Figure 3-12. Surface Soil and Sediment Total PCB Concentrations
(Sampled 1999-2003)

3.1.7.4 PCB Composition

Comparisons of the PCB patterns of samples and Aroclors are often part of PCB contamination assessments. The similarity of a samples' PCB composition to that of an Aroclor formulation can provide information related to potential source(s) and changes that may have occurred since the contaminant was released to the environment. It is rare that one finds a perfect match in the PCB composition of a sediment field sample and an Aroclor formulation. A close match may be observed for samples that represent a recent release to the environment and are also near the source. However, the PCB composition begins to change as soon as the material enters the environment, and selective PCB congener alterations occur due to different weathering processes, as discussed earlier. Similarities and dissimilarities in the PCB composition were assessed using exploratory data analysis techniques, as described in Section 3.1.7.5.

General PCB composition is usually best studied using simple bar graphs (bar chart "fingerprints"), with the PCB congeners from low to high molecular weight along the x-axis and normalized (percent of Total PCB) concentration along the y-axis. Given the environmental

transformation considerations, it is particularly notable that the PCB compositions of most of the surface sediment field samples were similar to that of one Aroclor formulation – Aroclor 1260.

The PCB composition data suggest that there may also have been partial contributions from Aroclor 1254 source(s), particularly in the Yosemite Creek area and in deeper sediments also on both sides of South Basin, but the majority of the recent PCB clearly appears to be from an Aroclor 1260 source in most of South Basin. The resemblance to Aroclor 1260 was particularly good in surface and near-surface samples collected near the shore of Parcel E-2, in proximity to the historic landfill and slough (Figure 3-13).

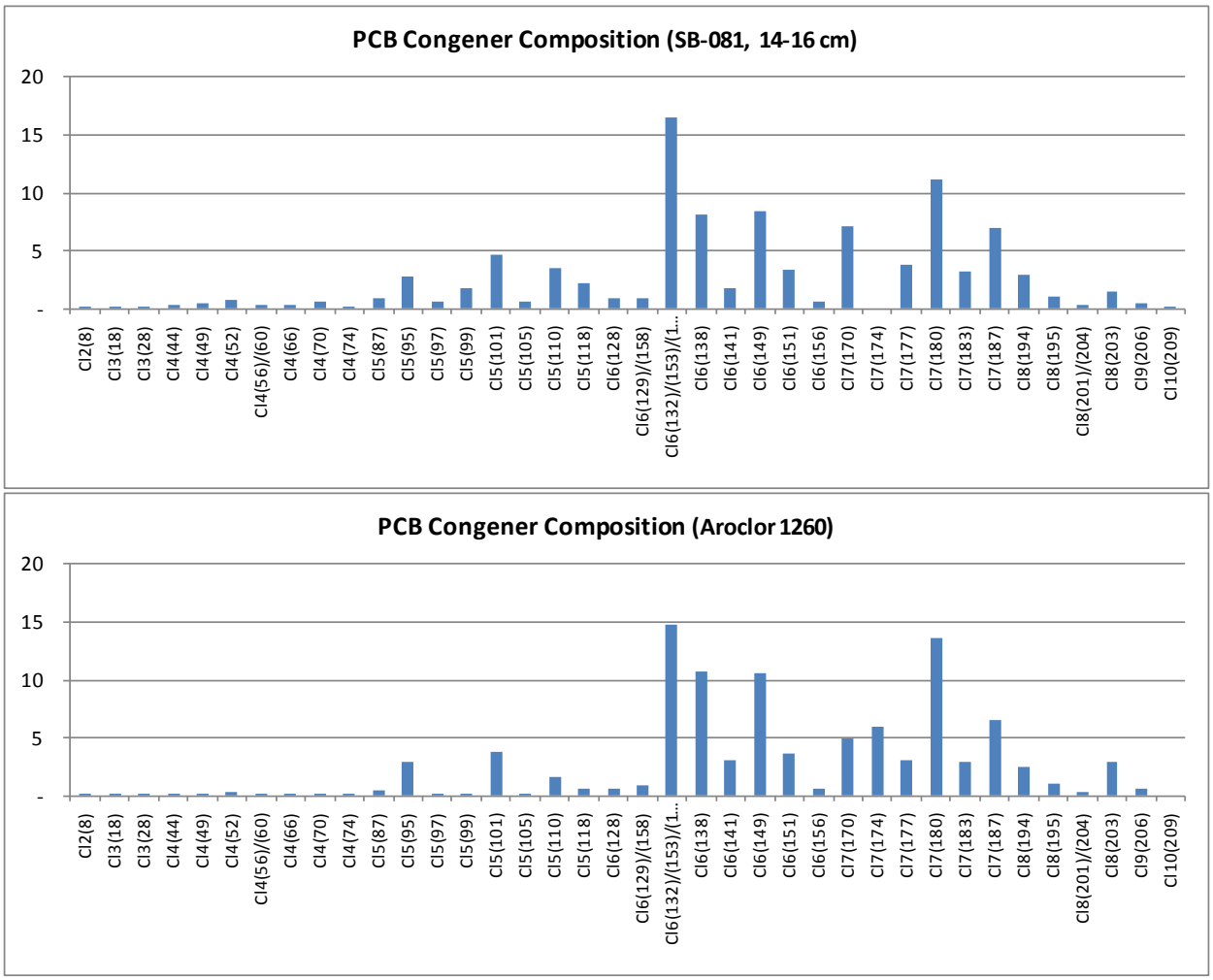


Figure 3-13. PCB Fingerprint of Surface Sediment Samples from the East Side of Hunters Point South Basin Compared to Reference Aroclor 1260

Samples from Yosemite Creek and the westernmost part of the basin, and some of the deeper sediments from the east, showed evidence of PCBs other than Aroclor 1260 contributing to the dominant Aroclor 1260 signature. Lower molecular weight PCB congeners, such as from Aroclor 1254 and possibly also 1242/1248, were evident. This inclusion of lower molecular

weight PCB became increasingly evident in the deeper, more contaminated, sediments from the west side of South Basin (Figure 3-14). The influence of Aroclor 1254 was evident in all samples from and near Yosemite Creek, and the PCB composition was similar throughout the Creek [62]. In contrast, the Aroclor 1260 signature dominated the PCB composition in the surface sediments throughout the basin, including the western parts. There were, proportionately higher concentrations of less chlorinated PCB congeners in the subsurface sediments than in the surface sediments, including in deep sediments from the east side. Slightly higher levels of Aroclor 1254 and/or other less chlorinated Aroclors in historic loadings to the basin may partly explain the subtle difference.

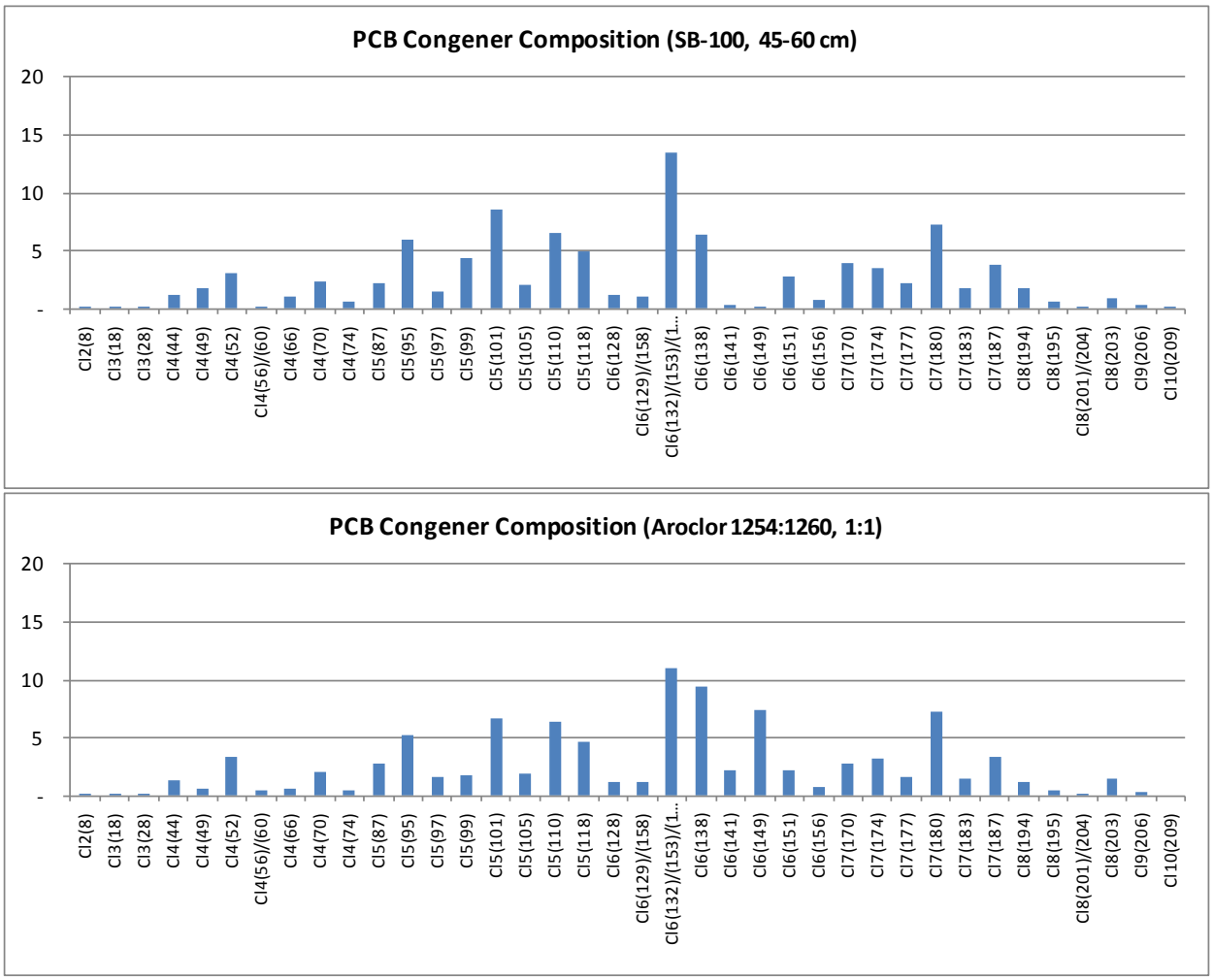


Figure 3-14. PCB Fingerprint of Deeper Sediment Samples from the West Side of Hunters Point South Basin Compared to a Mixture of Reference Aroclors 1254 and 1260 in a 1:1 Proportion

It can sometimes also be useful to examine ratios of key diagnostic PCB congeners (see Tables 2-1 and 2-4) to assess compositional characteristics. For instance, a change in composition (i.e., PCB congener ratios) may represent a change in source composition, and may be linked with

such data for other Aroclors or source material. Changes may also be due to alteration from environmental processes, and the distinction would need to be determined if changes are observed.

After comparing the bar chart fingerprints, one may use techniques such as congener-to-congener cross plots to assess compositional variations in the data. Figure 3-15 shows a cross plot of congeners PCB187 and PCB52 in segments of a core collected at Station SB94, an age-dated core located just offshore from the former landfill. If all depths in the core had similar congener composition, data would fall along a single trend (slope or ratio) which could be interpreted to represent a single source of PCBs over time. However, a change in composition with depth is noted where the ratio of these congeners in the shallow segments (0-20 cm) is about 7.2 and in the deeper/older sediments (30-60 cm) it falls to 1.8. This change may represent a change in source composition (or a change due to compositional alteration, such as dechlorination), so rather than having contamination from one PCB type (e.g., Aroclor 1260) there appears to be two distinct PCB signatures (e.g., Aroclor 1260 as well as another Aroclor), representing different time periods, with intermediate depth samples showing a progression from one ratio to the other. The more recent (shallow) sediments from 0-20 cm show a bar chart fingerprint similar to Figure 3-13 indicating an Aroclor 1260 source. The deeper sediments (30-60 cm) show bar chart fingerprints similar to Figure 3-14, indicating deeper sediments on both sides of the embayment show a mixed Aroclor 1254/1260 pattern. The difference in PCB composition does not necessarily reflect contamination from two different *physical* PCB sources, but indicates that the type of PCB that contaminated the sediments at this location changed over time, which may or may not originate from different locations. This dated core shows the change in composition at about 30 cm (the two highest concentration samples are duplicates of 30-40 cm interval) occurs in sediment deposited around 1965-1970. The timing of this basin-wide compositional shift will be discussed later, but this shows the importance of identifying PCB congener compositional differences to interpret potential source information. It would be tedious to view each possible individual congener cross plots if data for up to 100 different PCB congeners are available, but Aroclor compositional and congener behavioral information (Appendix A and Table 2-4) are available to help focus such an analysis on Aroclor/source-specific diagnostic ratios. Multivariate techniques (Section 3.1.7.5) are more suitable for analyzing comprehensive PCB compositional patterns with large data sets at one time.

In summary, the observed PCB compositional match to Aroclor 1260 in the northeastern part of South Basin suggests that there may be a current (2003) or recent, and possibly also historic, source of PCB in the vicinity of Parcel E-2. It is possible that the type of PCBs entering South Basin from the northeast was slightly different in the past. There is also PCB compositional evidence that there may have been a second source of a slightly different type of PCB (e.g., Aroclors 1254/1260, possibly also with some other Aroclor contribution) in the vicinity of Yosemite Creek, and that this source was more significant historically than recently. This source may have also contributed to the PCB contamination historically throughout South Basin, and not only near Yosemite Creek. The relative contribution of these sources has changed over time, with an apparent decline in the loadings from both sources in the past decades. The combined Aroclor 1254/1260 loadings have declined the most; Aroclor 1260 is dominating the Aroclor composition in the more recently deposited sediments throughout South Basin.

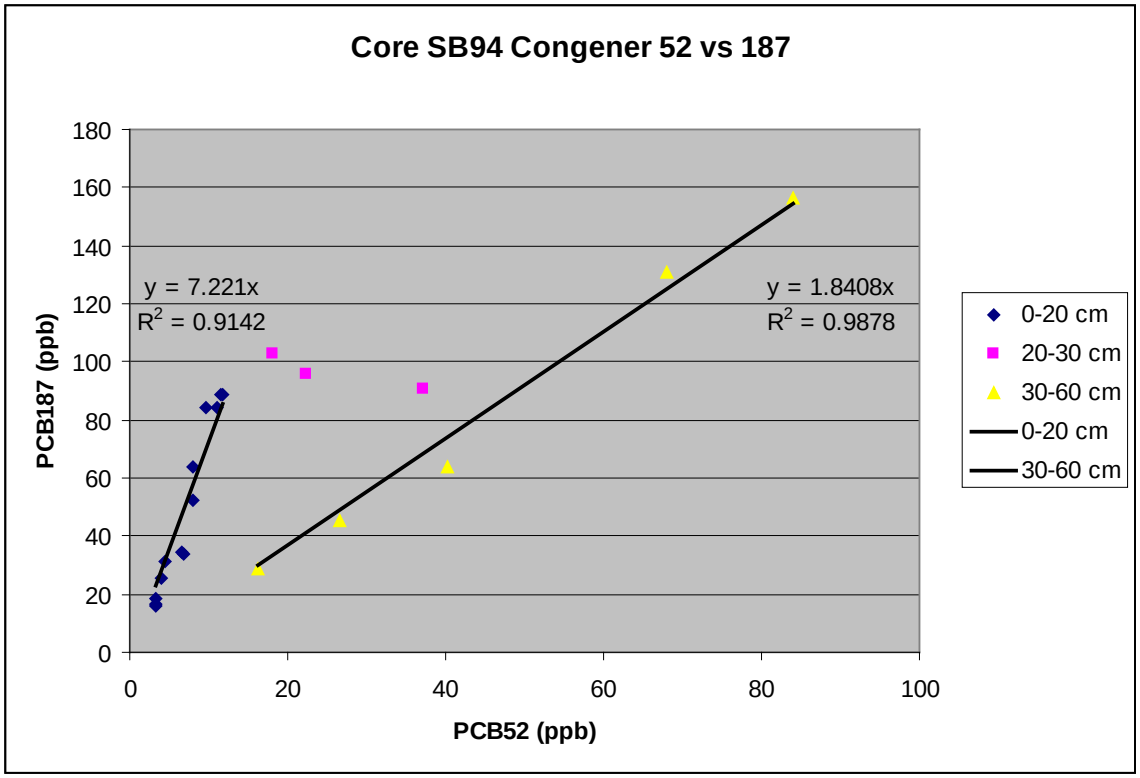


Figure 3-15. HPS Congener Cross Plot Showing Relationship between PCB187 and PCB52

3.1.7.5 Chemometric Statistical Analysis

As per Section 2.5.2.2, the data were reviewed and processed prior to statistical analysis. For the HPS project, PCB congener data had already been compiled and delivered as part of the Hunters Point FS data gaps investigation deliverable [62]. This data spreadsheet contained all of the information listed in Section 2.5.2.2, including: sample ID, sample coordinates, sample depths, analyte identifiers (i.e., congener names), laboratory results, and laboratory qualifiers (e.g., non-detect flags). A digital base map was received in the form of a GIS shapefile, which was used to construct a simple base map (Figure 3-16) showing key geographic features of the study area and sample/core locations. The data set initially considered for statistical analysis was comprised of 120 samples and 44 congeners. As per Sections 2.5.2.2 and 2.5.2.3, the data were assessed and run through an initial multivariate analysis to assess data usability. This process resulted in the removal of 35 samples and eight congeners from the chemometric analysis. For the sake of brevity, every individual decision point that led to these data screening decisions will not be recounted here. However, some of these are discussed below, to provide an idea of the types of considerations in this process. Refer to Johnson et al. [9] for discussions on data screening, outlier identification and general considerations that the data analyst should consider when screening a data set prior to statistical analysis.

Eight samples from two cores (PA-139 and PA-162) were omitted from the analysis because they were not located in or near the South Basin; they were located on the north side of HPS, in the Port Avisadero area (Area III on Figure 3-2). In addition, only those samples with a total

PCB concentration > 100 µg/kg, and samples with fewer than nine non-detects were retained for statistical analysis. It should be noted, and as discussed in Section 2.5.2.2, that these or other thresholds are not solid numbers that can be applied generally to any data set. It is typically an iterative and data set-specific process whereby the user balances a need to keep as much data in the analysis as possible with the desire for a robust data set, where chemical fingerprints are not influenced by less reliable data, such as low concentration samples with multiple non-detects.

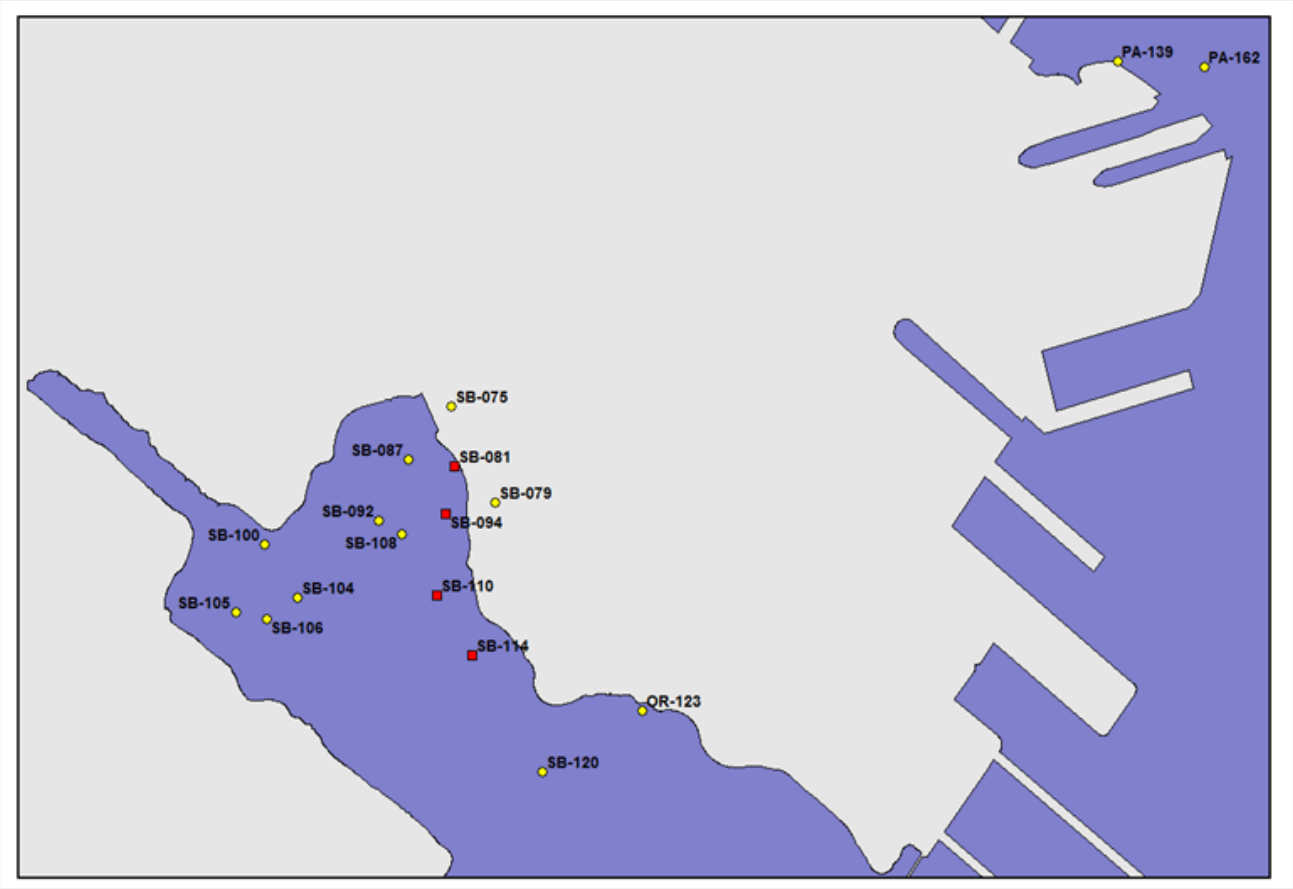


Figure 3-16. Simple Base Map Showing Sample/Core Locations
(Red squares are fine interval cores collected as part of a separate phase of sampling and analysis.)

Criteria used to screen congeners varied. PCB77 and PCB126 were both omitted because they were reported as non-detect in more than 98% of the samples. PCB141 was removed from the analysis for a very different reason. Initial data screening showed a strong bias in the proportion of PB141 as a function of the phase of investigation. Samples from four cores all showed systematically higher concentrations of PCB141, when expressed as percent of total PCBs (Figure 3-17). All other samples from other cores showed systematically lower concentrations.

These cores are not geographically separated from each other. As such, the team concluded that this bias was probably due to an issue such as matrix interference or analytical method bias between investigation phases, rather than a true compositional difference between these two sets

of samples. As such, PCB141 was removed from the analysis. The final data set submitted for analysis using receptor models was 85 samples and 36 congeners.

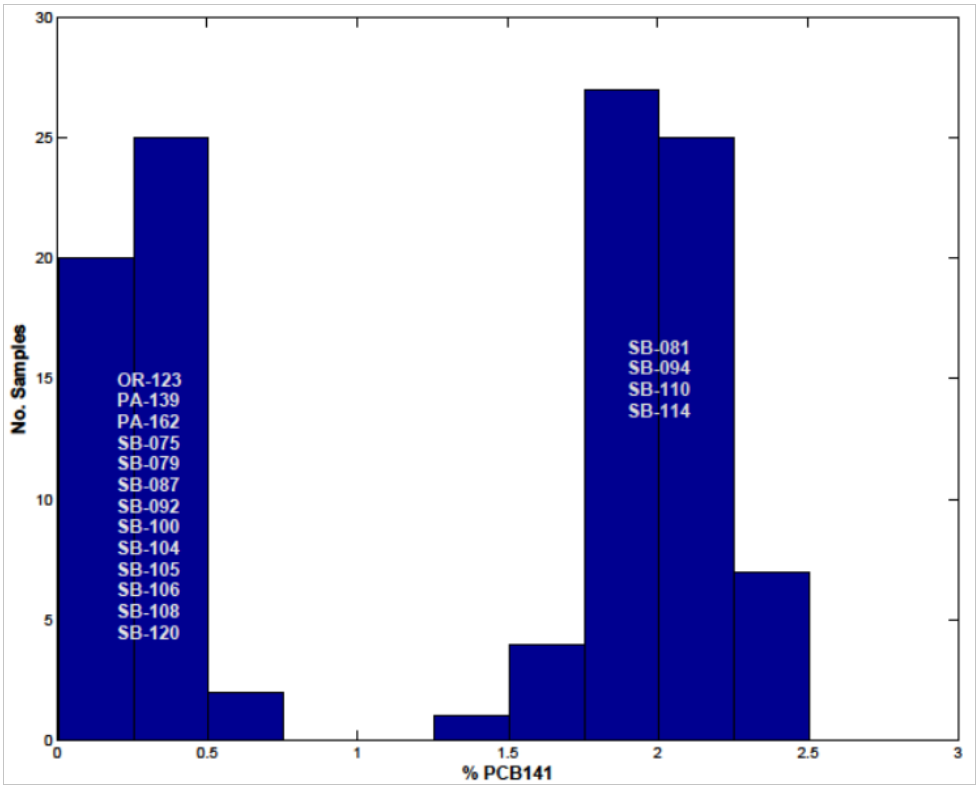


Figure 3-17. Histogram Showing Systematic Bias in PCB141 (as percent of total PCB) between Primary HPS Cores and Subsequent Fine-interval Cores SB-081, SB-094, SB-110 and SB-114

A review/summary of a number of chemometric/statistical analysis methods was presented in Section 2.5.3.5. For analysis of HPS congener data, PCA was applied as an initial exploratory data analysis method, followed by four different receptor model methods (PVA, ALS, Unmix, and PMF). Implementation of four different receptor models is not necessary. Most published applications use one [8-9, 34, 35, 64]. However, as all four have been applied as part of the method comparison, those results will be presented below.

A number of goodness of fit diagnostics were examined to determine the number of end-members (see [9]). One of these methods is shown in Figure 3-18, which is a coefficient of determination (CD) scatter plot array showing the fit of each of the 36 variables for a three end-member model. Each square graph on the array represents a PCB congener (or coeluting peak comprised of two or more congeners). The x-axis of each graph shows the measured amount of that congener/peak. The y-axis shows the amount as back-calculated from a three source model. A perfect fit would show all samples plotting on the 45 degree line that bisects each graph (a 1:1 fit). In PCA based receptor models, the number of principal components retained equals the number end-members. Fit always improves as additional principal components are added, so

one needs to decide at what point the fit is sufficient, without over-fitting and modeling noise. In the case shown on Figure 3-18 (three principal components/end-members), most of the congeners show a fairly good fit between the modeled values on the y-axis and the measured values on the x-axis, indicating that three end-members is a reasonable solution and that no more are needed. Scatter plots and other goodness of fit diagnostics are discussed in more detail by Johnson et al. [9].

Note, however, that some congeners exhibit at best a fair fit (e.g., PCB49 exhibits a wide scatter about the 1:1 fit line [Figure 3-18]). This may suggest the presence of another fingerprint in the system, and/or that this congener is particularly susceptible to environmental alteration or analytical issues (which is, ideally, identified during data screening). The feasibility of a fourth end-member was evaluated and will be discussed later in this section.

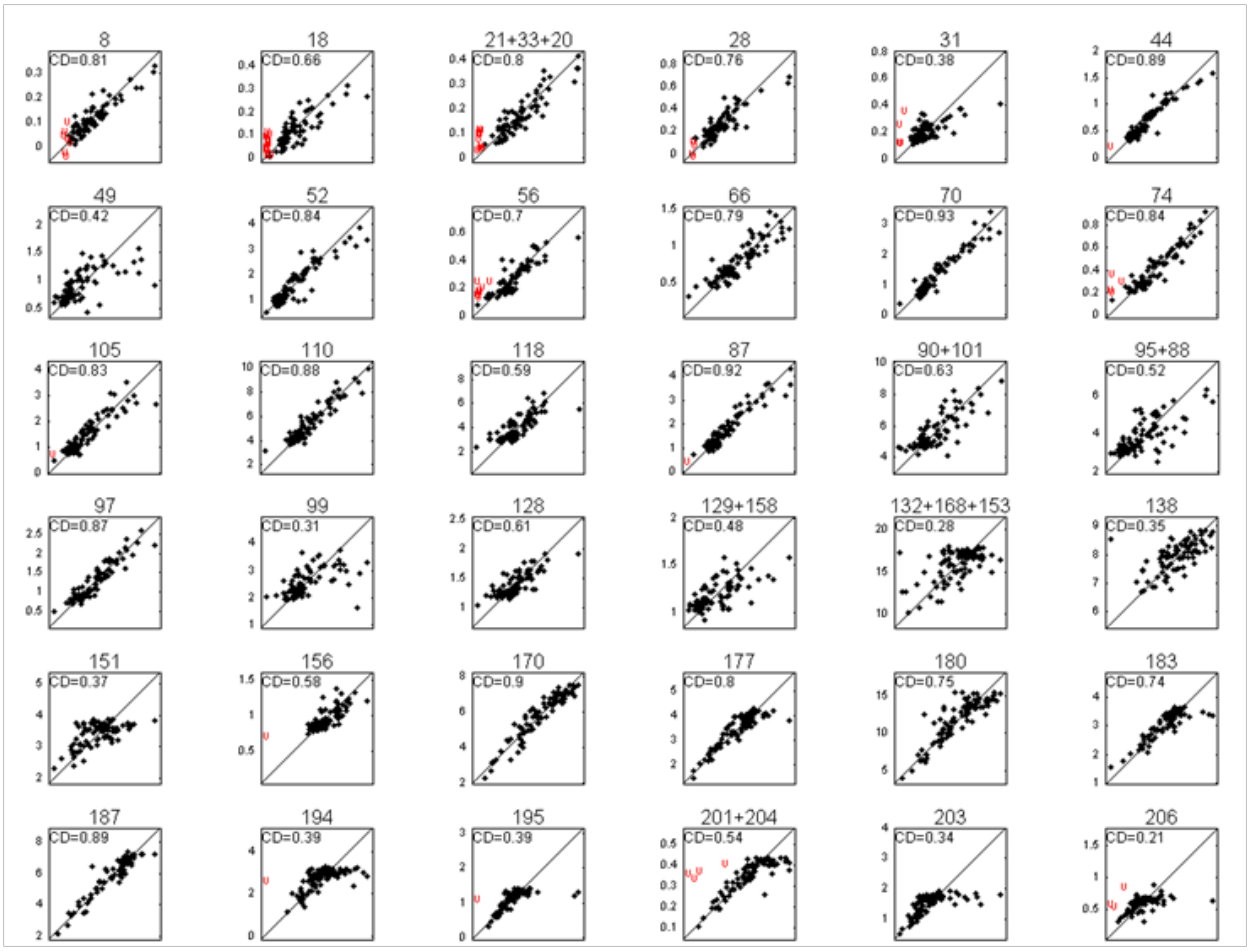


Figure 3-18. CD Scatter-plot Array for 85 Sample, 36 Analyte PCB Data Set from South Basin, Hunters Point Shipyard
(Non-detect samples are indicated as "U".)

This data set was analyzed using the four receptor model methods, each for a three source system. The congener patterns resolved by each of these four methods are shown in Figure 3-19 as blue bar graphs. At the top of each column of bar graphs, the congener pattern of an Aroclor (or a mixture of Aroclors) is shown. Each of the four receptor model methods resolved very similar profiles, and each matched known Aroclor profiles.

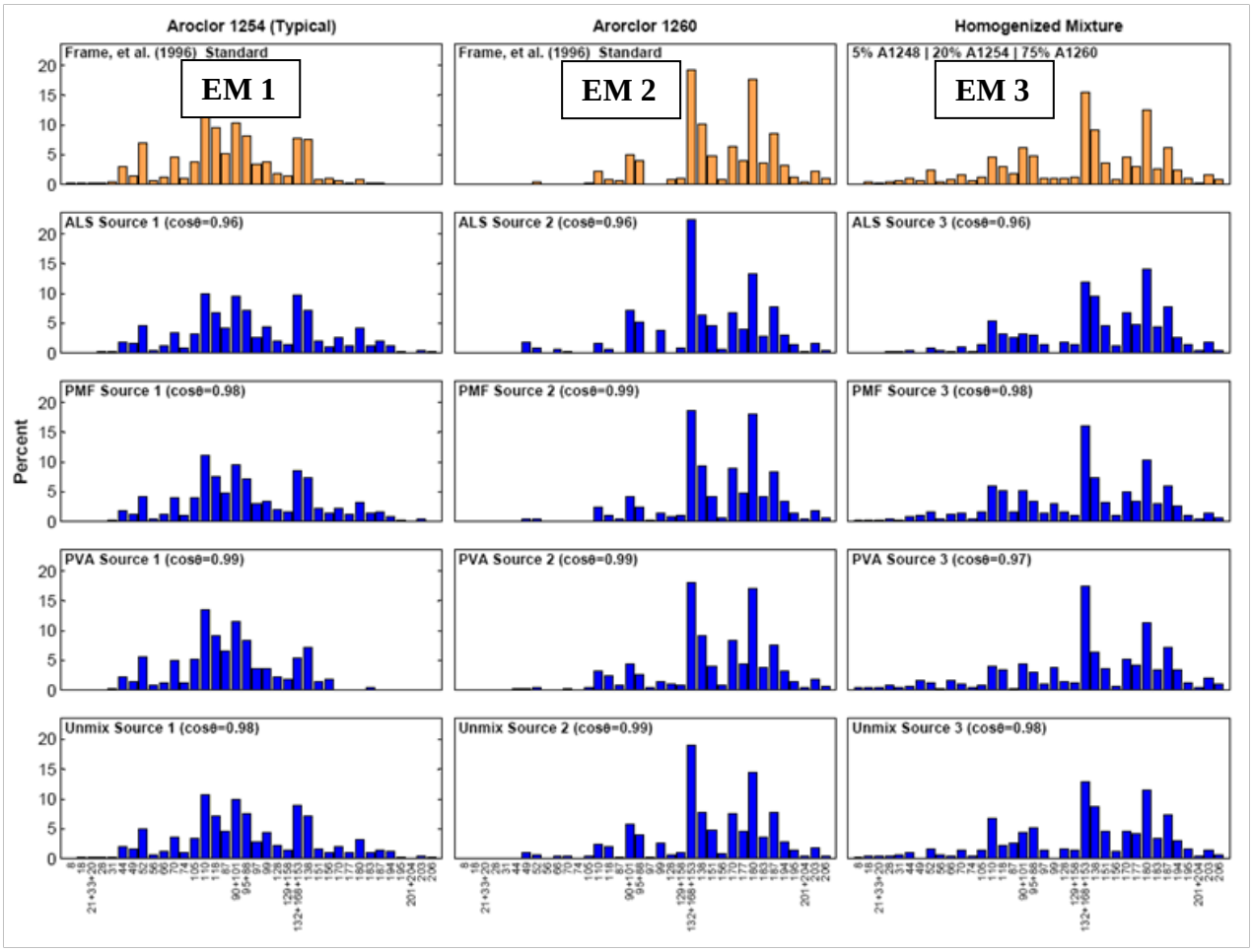


Figure 3-19. Congener Profiles (end-members, source profiles) Derived from Four Receptor Model Methods

Note that the congener patterns of the middle panel (Aroclor 1260) and the right panel (homogenized mixture) are very similar. Both are heavier congener patterns dominated by Aroclor 1260 congeners. The difference is that the "homogenized mixture" also has secondary amounts of congeners in the lighter Aroclors 1248 and 1254 molecular weight range. The discussions that follow evaluate whether these slightly different congener patterns represent real differences in the field.

Figure 3-20 shows the geographic distribution of each source as resolved by each of the four methods. Again, the geographic distribution of the three congener patterns is similar for each of the four receptor model methods. Note also that the slightly lower molecular weight Source 3 pattern is generally higher in proportion to the southwest, near the mouth of Yosemite Creek. This geographic distance suggests that a real PCB compositional pattern difference is being observed in the field.

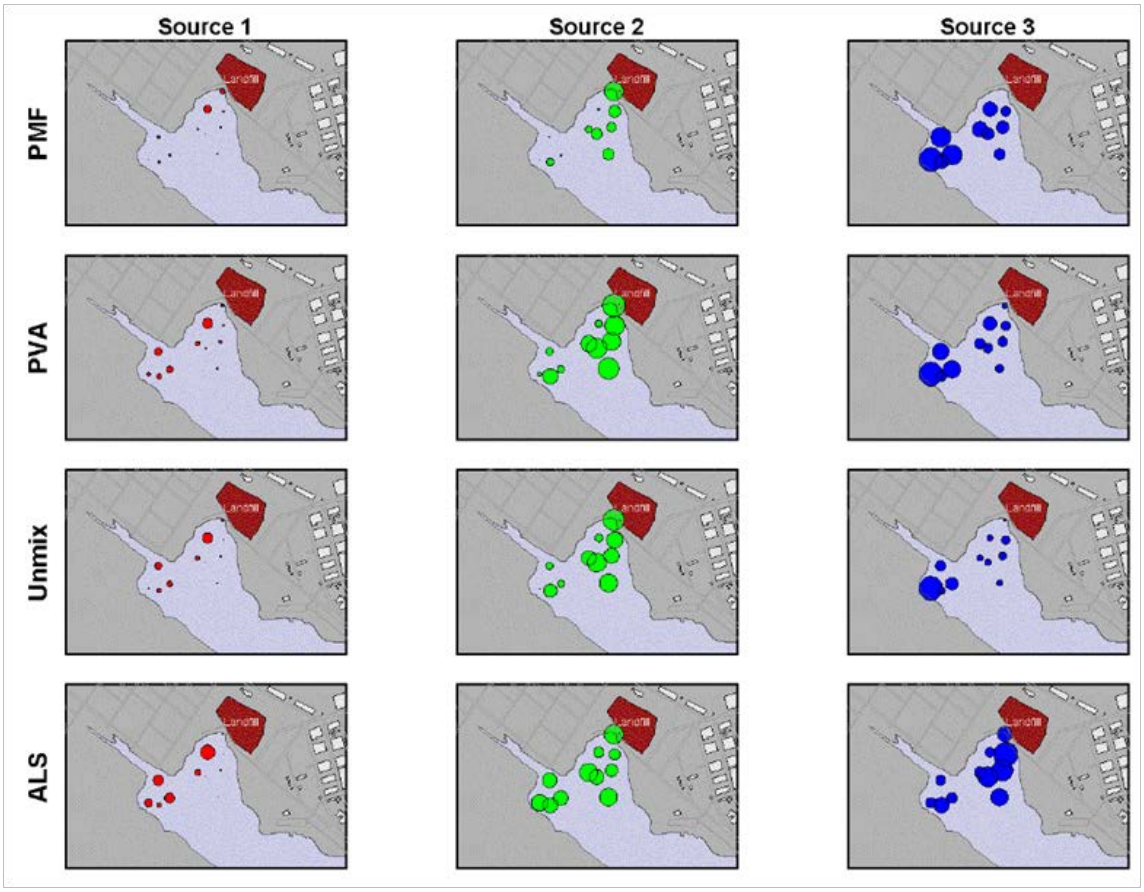


Figure 3-20. Maps of Three Receptor Model Derived End Members (potential sources) in Surface Sediments of the South Basin at Hunters Point Shipyard

Note on Figure 3-20 also that Source 1 (Aroclor 1254) is not present in high proportions in surface sediments. This is because it is much more abundant at depth, as is apparent on the cross section through cores (Figure 3-21). Also note that the terminology "source" in Figure 3-21 may be misleading, as it refers to the differentiation of different PCB compositional characteristics in the sample set (i.e., "end-members", in Figure 3-19), and not necessarily geographically different sources of the PCB. For instance, the three different PCB characteristics identified may be originating with just two different sources.

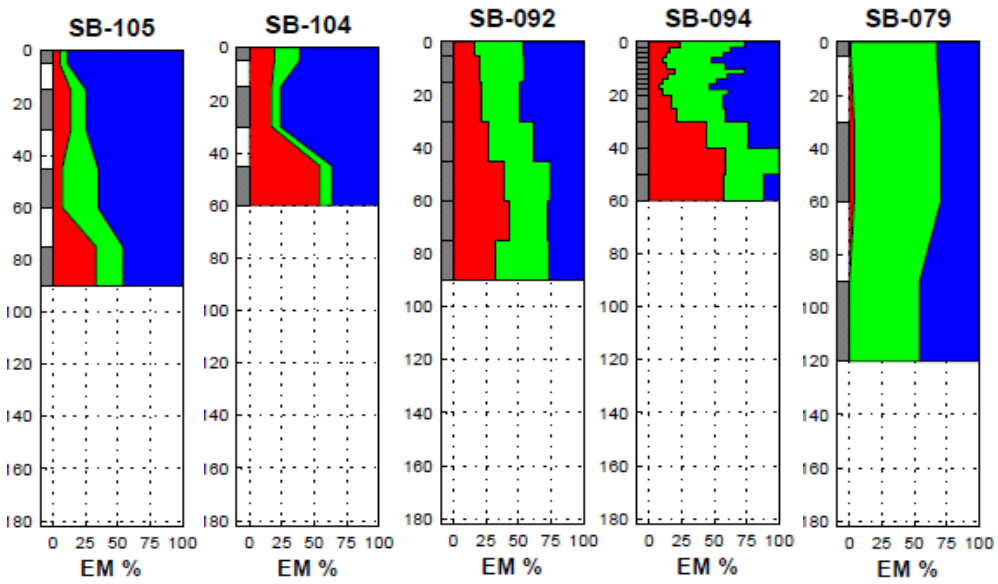


Figure 3-21. HPS EM Compositions in Selected Cores
(Red=EM-1; Green=EM-2; Blue=EM-3)

This three-composition interpretation was confirmed using another chemometric method, PCA (Figure 3-22), which can be used to summarize much of the information in this section. This PCA figure shows the HPS sediment sample PCB data plotted in 3D PCA space. The data cloud exhibits a generally triangular shape (indicative of mixtures, not clusters). This PCA scores plot has also been annotated to show the locations of these three source end-members as vertices of a triangle (i.e., a mixing diagram or, more specifically, a ternary mixing diagram).

Each sample point in the PCA illustration in Figure 3-22 represents the PCB congener data from a separate sample (see Appendix D for sample numbers) that could, for instance, be represented by separate bar chart fingerprints. The closer together samples plot in the PCA graphic the more similarity their bar chart fingerprints would be. A sample point located at the corner of the triangle marked EM1 has a bar chart fingerprint that closely matches Aroclor 1254. A sample point at the corner of the triangle marked EM2 has a fingerprint that matches Aroclor 1260. The third corner of the triangle at EM3 does not appear to match any single Aroclor, and since no evidence of dechlorination was observed, this pattern was intended to match the mixtures of Aroclors. The best fit was obtained with the mixture shown at the bottom of Figure 3-22 (a mixture of 80/15/5 of Aroclors 1260/1254/1248, in this case), which showed a cosine theta (cos θ) value of 0.97 (1.0 represents a perfect match). In summary, the PCA scores plot in Figure 3-22 shows the surface sediments to the east near the former landfill plot (e.g., sample point 5 is the surface sample from core SB79 in front of landfill) closer to the bottom left corner marked EM2 (with a Aroclor 1260 source pattern) and surface samples from near Yosemite Creek (e.g., sample 26 from core SB105) closer to the top corner of the triangle marked EM3 (representing a mixture of Aroclors 1260/1254/1248). Deeper samples from both sides of South Basin plot further to the right near EM1 (e.g., sample point 25 is 45-60 cm in core SB104 and sample point 55 is 30-40 cm in core SB81), which indicates approximately a 50/50 mix of Aroclors 1260 and 1254. One can easily see this change in composition with depth in core SB81, where deeper

samples from 30-60 cm (e.g., sample points 54, 55, 56, 57) all plot close together with the same 50/50 mixture of Aroclors 1260 and 1254. Shallower samples (0-20 cm) plot to the left close to EM2 (e.g., sample points 45 to 51), with a few intermediate depths (e.g., sample points 52 and 53) showing the transition in patterns.

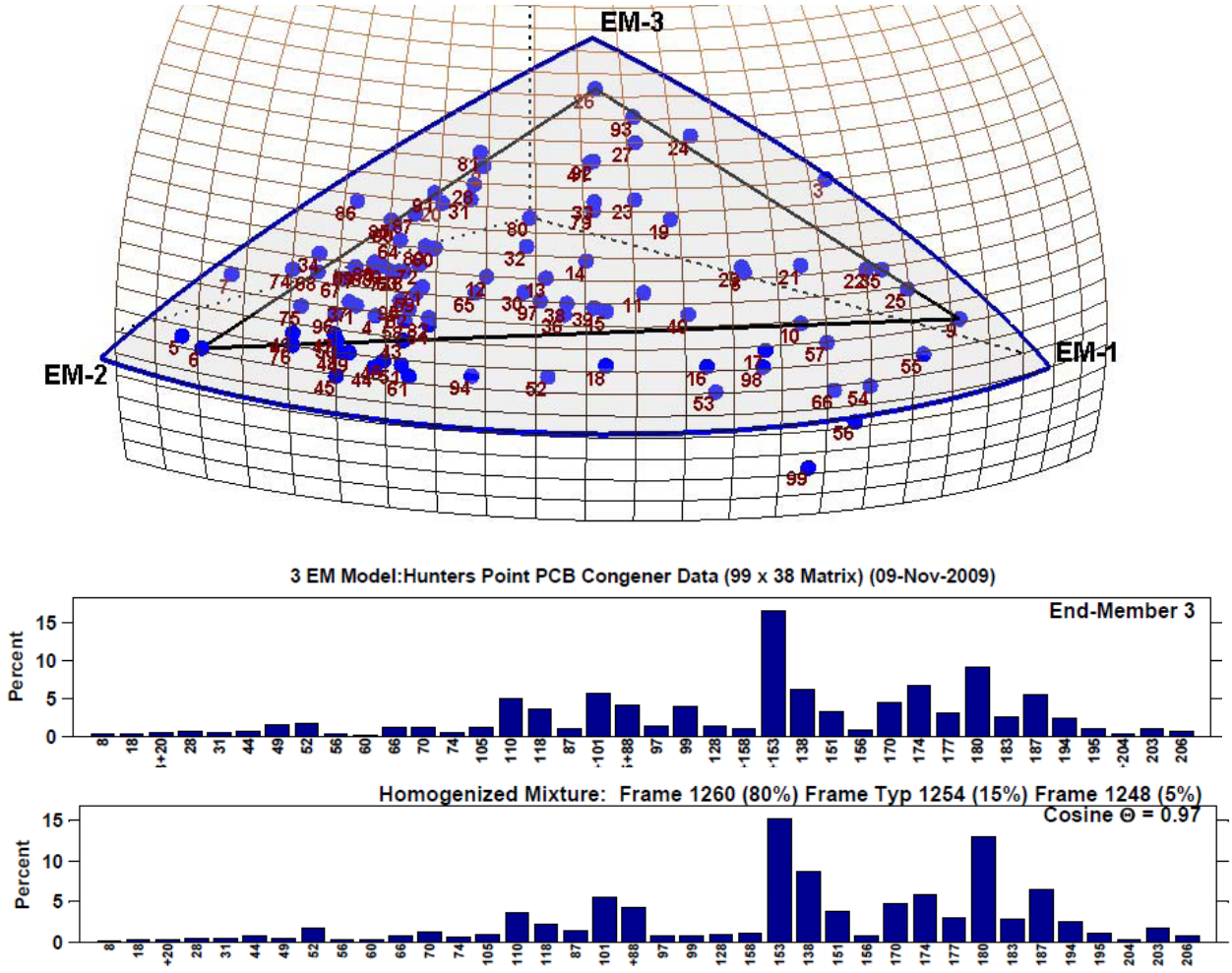


Figure 3-22. Conceptual PCA Model for PVA at HPS
(Each dot represents a sample. Samples plotting close together have similar PCB compositions.)

This is similar to the previous discussions of Figure 3-15 for core SB94, which was a dated core that showed this same transition in PCB composition at depths in the sediment from around 1965 to 1970. There appears to be similar historic PCB composition at depth on both sides of South Basin represented by samples on the right side of the triangle in Figure 3-22, with a composition similar to a 50/50 mix of Aroclors 1260 and 1254. As discussed earlier, the compositional similarities do not necessarily mean they are from one and the same physical source of PCB; this information needs to be combined with other forensic lines of evidence to better understand potential source implications. We might speculate that around 1970 when the CSOs in South Basin were all realigned to the head of Yosemite Creek, some Aroclor 1260 contaminated fill

material was used to close off the former channel that ran through the landfill on the east side (see high concentrations onshore in Figure 3-9). This contaminated fill material along the beach in this area may have become the EM2 source to the east side sediments after about 1970 through continuing erosion along the beach in front of the landfill. On the west side by Yosemite Creek, when the CSOs were realigned and the sewer capacity expanded, overflows were dramatically reduced so PCB loadings (and surface sediment PCB concentrations) were reduced and in recent years appear to have a mixed composition of Aroclor 1260/1254/1248. The remaining questions are whether this third composition pattern (EM3) represents a real and distinctly different pattern, and a different source physically and in time, rather than a mixture of the other two patterns (EM1 and EM2), and whether there is any evidence of an alteration or dechlorination pattern, both of which are addressed in the next few paragraphs.

Confirmation of a Third Source Pattern

All four receptor models resolved a third PCB congener profile that differed subtly from one of the other two. Two PCB congener profiles were consistent with a predominant Aroclor 1260 congener pattern (EM-2 and EM-3; Figure 3-19). End-member 3, however, also included some less chlorinated congeners within the Aroclor 1254 and Aroclor 1248 range (Figure 3-19). These two patterns were somewhat separated geographically (Figure 3-20), although this should be interpreted with care as the relative contribution of the end members can have a fairly substantial amount of uncertainty associated with it. Much of the pure Aroclor 1260 congener pattern appears to be associated with the Navy facility. The PCB composition of Aroclor 1260 together with less chlorinated congeners was observed in higher proportions in the western parts of the study area, near Yosemite Creek. Given the subtle difference in these two congener patterns, it was important to independently confirm the compositional differences to understand if it was possible that there was a different source of Aroclor 1260-like PCB also in Yosemite Creek, based only on the congener pattern information. There was no way to do this purely within the realm of this chemometric analysis so another independent line of evidence was investigated.

Several years before the collection of the congener data used in the chemometric analysis described above (Section 3.1.7.5), the San Francisco Public Utilities Commission (SFPUC) had sampled sediments from Yosemite Creek. Only surface sediment samples had been collected, and the number of congeners reported was much smaller than that available in the South Basin. However, knowing which congeners were important in the distinction between the two PCB patterns discussed above, a simple ratio analysis approach (Section 2.5.1.1) was used to see if the SFPUC data supported the hypothesis of a slightly less chlorinated PCB source up Yosemite Creek. The ratio of two congeners included in both the FS and the SFPUC data sets was calculated: PCB28 and PCB153. PCB28 is a tri-chlorinated congener typical of an Aroclor 1248 source. PCB153 (a hexachlorinated congener) is prominent in both Aroclors 1254 and 1260, but present in low proportions in Aroclors 1242 and 1248. The PCB28/PCB153 ratio was calculated for samples from both data sets and plotted on a map (Figure 3-23); the ratio is approximately 76, 17, 0.03, and 0.003 for Aroclors 1242, 1248, 1254, and 1260, respectively (Appendix A). The combined data set clearly shows a higher ratio (i.e., lower chlorinated pattern) in Yosemite Creek sediments – a ratio that is higher than can be explained by combinations of only Aroclors 1254 and 1260. The augmentation of the main data set with useable data from a completely independent investigation helped confirm (1) the subtle difference in PCB patterns observed in surface sediments in the South Basin (near the landfill and near Yosemite Creek) likely reflects

different sources; and (2) there is/was indeed a lower molecular weight PCB source in Yosemite Creek that contributes some to the PCBs in the South Basin.

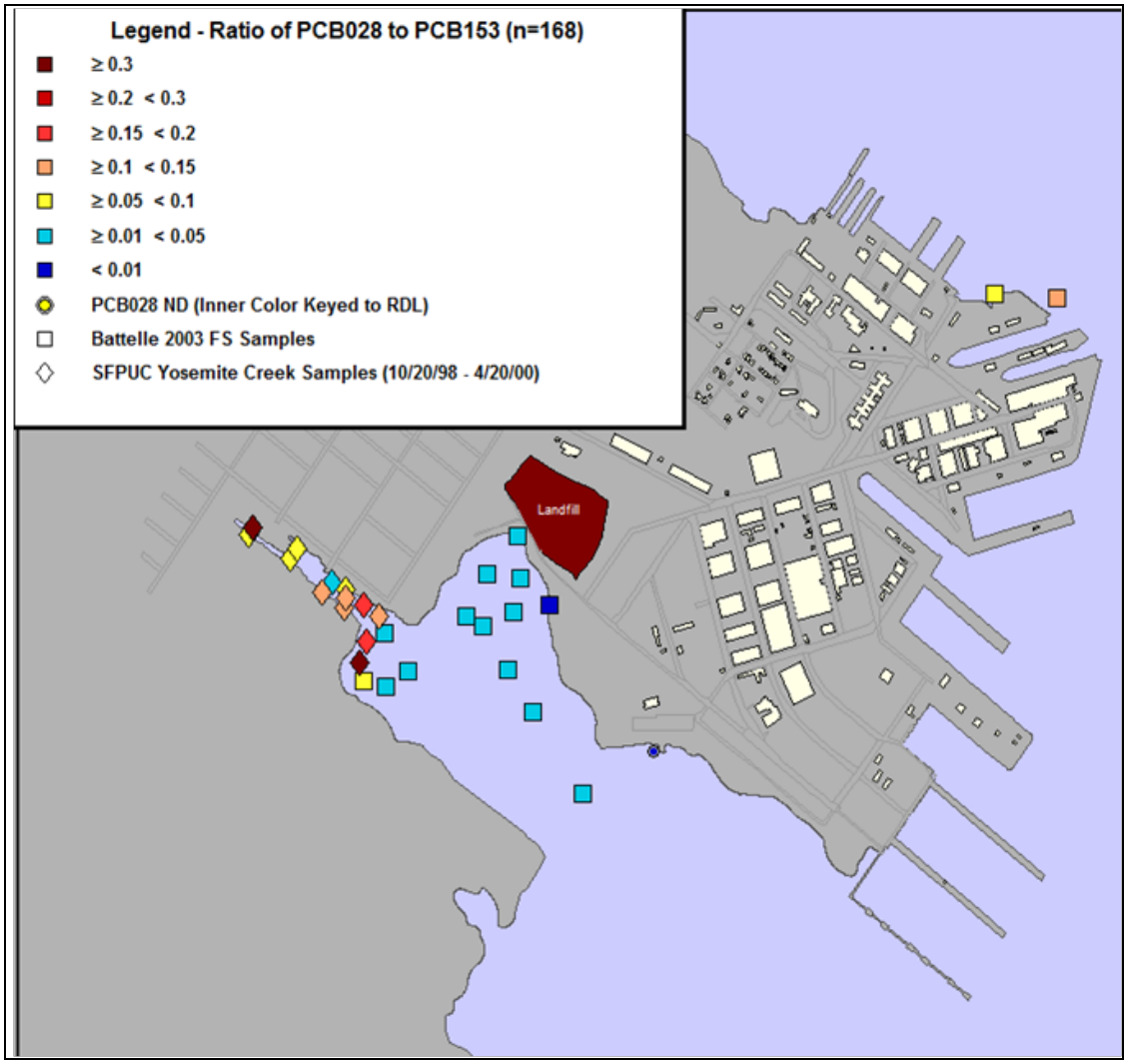


Figure 3-23. Ratio of PCB28 to PCB153 in Sediments Near Hunters Point Shipyard and Yosemite Creek, San Francisco, CA

Consideration of a Possible Fourth Source Pattern

As indicated in Section 3.1.7.5, through the statistical goodness of fit diagnostics, in conjunction with the receptor models (Figure 3-18), a minimum of three PCB compositional patterns were indicated for this data set, likely from at least two different physical sources, but some congeners still exhibited a noisy fit (see for example the PCB49 scatterplot on Figure 3-18). Therefore, the possibility of a fourth end member pattern was evaluated by applying one of the receptor model methods (PVA) to four end-members. The result was a resolution of three end-members very similar to the previous three, plus a fourth that was similar to Aroclor 1254, but with slightly higher proportions of PCB49. PCB49 is a known dechlorination product [65]. A fourth pattern

is plausible but, if present, it is not important to the source apportionment study because (1) it is a slight variant of an Aroclor 1254 weight range pattern; (2) Aroclor 1254 is already represented in the three source model; (3) to the extent that it represents a true congener pattern, there is independent evidence from the literature that suggests that is related to alteration and not a source; and (4) if this pattern does represent dechlorination, it is very subtle.

3.1.7.6 Integrated Data Analysis and Interpretation

As discussed in Section 2.5.3.6, integrated data analysis and interpretation is the process of synthesizing information from multiple lines of evidence to arrive at scientific interpretations that answer the key questions of a forensics investigation (i.e., PCB sources, alteration mechanisms, timing/history of releases). Lines of evidence typically considered include site history, published scientific literature, sediment transport/hydrodynamics, analytical chemistry which is then used to interpret total PCB concentration gradients and inspection of sample chromatograms/compositions, and chemometric analysis.

At HPS, such lines of evidence consistently support the key conclusion – that there appear to be two general physical source areas that have contributed the majority of the PCBs in the South Basin sediments – one of the source areas being the general vicinity of the landfill near the north-east shore of South Basin and the other being Yosemite Creek and, possibly also, old outfalls southwest of the mouth of Yosemite Creek (lower Figure 3-2). The PCB concentrations and compositions from these two source areas have shifted over time. In the past, sediments from deeper than 30 cm, or pre-1970s on both sides of South Basin show a similar 50/50 mix of Aroclors 1254 and 1260, but the concentrations are higher on the west side at greater depth. More recent surface sediments to the west by Yosemite Creek show much lower concentrations (indicating the source has been significantly reduced) and an increase in the relative proportion of Aroclor 1260, with smaller contributions of lower weight Aroclors (1254 and 1248). Surface and more recently deposited subsurface sediments to the east by the former landfill still have elevated concentrations, suggesting a continuing source (as of the 2003 sample collection date), with a composition that is almost entirely Aroclor 1260.

This observation is consistent with and supported by site history (Section 3.1.7.1), which indicates that PCB-contaminated material went into the landfill from 1958 to 1974, and that, in addition to leaching and erosion from the landfill, a former slough/ditch/channel in the area (which was later filled by landfill expansion) could have contributed PCBs to South Basin through runoff from other parts of the Navy property and from the landfill (Figure 3-3). Figures 3-9 through 3-12 show elevated PCB levels along the shoreline in front of the landfill, possibly from contaminated fill used to close off the former slough/channel around 1970 or illegal dumping activities noted by DTSC when HPS operated as a commercial shipyard from 1976 to 1986. The offshore sediment PCB concentration gradients (Figure 3-10) line up with the onshore elevated shoreline PCB levels (Figures 3-9 and 3-12), indicating that erosion of these shoreline materials have represented a source of PCBs to the South Basin.

The presence of numerous commercial/industrial facilities that could contribute PCBs were located up and around Yosemite Creek and could have contributed PCBs through runoff and CSO discharge. For instance, a facility operated as a 55-gallon drum recycling operation from 1948 to 1988 with noted releases of PCBs as well as other contaminants. CSO releases of mixed

stormwater/sewage were more common in the past, but after about 1970 when all CSOs were realigned into Yosemite Creek and the sewer storage capacity was increased, these releases were reduced to about one per year.

The sediment transport and hydrodynamic information for South Basin (Section 3.1.7.2) indicates that contamination entering the Basin would be expected to be relatively predictably deposited and distributed away from sources (i.e., that the geographical distribution of the PCB contamination would radiate and decline away from sources). This implies that the contour maps such as Figure 3-10 can be viewed to show two high concentration areas where PCB sources are likely to have been located. Sedimentation rates derived from the dated cores indicate a constant, steady 1 cm/yr depositional rate, so events that occurred around 1970 should be seen in these cores at about 30 cm depth. The various PCB data analyses further support the initial findings of potential sources, adding additional lines of evidence.

The PCB concentration gradients in the South Basin showed two areas of high concentration: one near the shoreline adjacent to the former landfill and another near the mouth of Yosemite Creek (Section 3.1.7.3 and Figures 3-10, 3-11, and 3-12). The preliminary PCB composition information (Section 3.1.7.4 and Figures 3-13 and 3-14) indicates at least two PCB compositional characteristics of the PCB in the sediments – one closely resembling Aroclor 1260 in the surface and near surface sediments near the former landfill, and another resembling a combination of Aroclors 1254 and 1260 in the deeper sediments near Yosemite Creek. Figures 3-15 and 3-21 show PCB data from core SB94 collected near the landfill, and illustrates a compositional shift in the PCB composition at 30 cm, which was dated at about 1970. This was the time period when the slough/channel was closed off by the landfill, the sewer capacity was increased to reduce CSO events, and the CSOs were realigned within Yosemite Creek. This suggests that the common PCB compositional signature (50/50 mix of Aroclor 1260/1254) seen deeper than 30 cm across South Basin may have been from one source or similar sources, possibly CSO outfalls located both in Yosemite Creek and at the north end of the slough/channel that was being filled by the landfill. Another possibility was that the same contaminated fill was used on both sides of the embayment and this fill served as a common source of PCBs for these deeper sediments. After the slough/channel was filled in the 1970s, the PCB composition in the sediments near the landfill shifted to closely resemble Aroclor 1260, possibly from continued erosion of the contaminated beach in front of the landfill (Figure 3-9). Sediments shallower than 30 cm in the Yosemite Creek area have much lower PCB concentrations because the CSOs (the local source of the PCB) were realigned and the sewer capacity was increased to reduce the overflow events. These PCB composition in the sediments on the west side of South Basin also show a compositional shift from the deeper sediments (Aroclor 1260 [50%]/1254 [50%]) to the shallower sediments (Aroclor 1260 [75%]/1254 [20%]/1248 [5%]).

The various chemometric analyses, which are described in more detail in Section 3.1.7.5, further support the initial findings of potential sources, adding additional lines of evidence. Much of the information from that section can be summarized in the PCA scores plot (Figure 3-22), and accompanying discussion (Section 3.1.7.5). In summary, the PCA scores plot shows the data cloud of sample points that can be enclosed by a geometric shape (triangle) with the corners (vertices) representing end-member (EM) PCB congener compositions that can be linearly mixed to provide the congener composition of all the samples at the site. The surface and near surface

sediments from the east near the former landfill plot closer to the bottom left corner marked EM2 (an Aroclor 1260 source pattern) and the surface sediment samples from Yosemite Creek plot closer to the top corner of the triangle marked EM3 (a mix of Aroclors 1260/1254/1248). Deeper samples from both sides of South Basin, and the most contaminated deep sediments from the west plot near EM1 represent a mix of Aroclors 1260 and 1254. One can easily see the change in composition with depth, where deeper samples from below 30 cm throughout South Basin generally plot close to the same 50/50 mix of Aroclors 1260 and 1254, while shallower samples have a stronger influence of Aroclor 1260.

Another way to visualize these compositional variations in a spatial representation is shown in Figure 3-21. This figure shows an east to west transect of cores to show the vertical and horizontal variations in the end member compositions across the site. On the left of each core are the depth (cm) and darkened sediment horizons that were homogenized and used for ACF congener analysis (undarkened intervals only had RSC total PCB measurements, so there is less data accuracy and the results were interpolated over these horizons). On average, there is more green (EM2) to the east (see core SB079) and more blue (EM3) to the west (see core SB105). The one fine interval dated core in this transect (SB094) shows a sharp transition at 30 cm depth (around 1970) with more red (EM1) at deeper depths. It should be noted that the error bars associated with this type of display in this case study are larger than in typical cases (usually estimated to be about 10 to 20%) because of the similarity in composition between EM2 and EM3. In fact, because Aroclor 1260 is notably present in all samples, the uncertainty in allocation among the end members is greater than in a more desirable candidate site where the different end member compositions are more unique and easy to separate.

Combining multiple lines of evidence, it appears that there are three different PCB contaminant characteristics in the sediments of the South Basin at HPS, which could have originated at two or more general areas at different times. Considering only individual lines of evidence, this might not have been at all apparent. For example, the raw concentration maps show two distinct areas of high concentration (Yosemite Creek and the HPS landfill – Section 3.1.7.3). Analyzed in isolation, this suggests two sources. It is only when one analyzes congener patterns (through direct inspection of sample composition or through chemometric analysis) that it becomes clear that there was a historical shift in congener patterns near the landfill. This suggests a change in source material emanating from the landfill area overt time. An Aroclor 1254 pattern is more dominant at depth, while an Aroclor 1260 pattern is more recent in shallow sediments. Alternatively, it is possible that sources in and around Yosemite Creek also contributed to the PCBs in the deeper, historic, South Basin sediments also closer to the Navy landfill area. However, it should be noted that the amount of PCBs (i.e., the PCB concentrations) are much lower in the deep sediments on the east side of South Basin, and, therefore, accurately identifying the origin of that contamination may be of less importance, from a sediment management perspective.

The HPS case study here has shown that these multiple lines of evidence present a consistent story. Since this case study was done with pre-existing data, it presents both advantages and limitations compared to a typical forensics study planned from the start. The obvious advantage is the cost savings, since the regulatory RI/FS project paid all the planning, sample collection, and sample analytical costs. Ideally, from a technical and defensibility perspective, it would

have been preferable to have additional samples to validate the proposed end member source compositions and sample from physical locations where the sources may have been present. This was possible for EM2, where the composition matched an Aroclor 1260 pattern and samples onshore along the beach on the east side showed the same pattern. The physical source for EM1 and EM2 seen in the deeper sediments (before 1970) is more problematic since these past sources are no longer present and contributing to recent sediments. Additional work upstream in Yosemite Creek might help to find the physical source of EM3, possibly in upstream sewer sumps. However, even without this complete validation of source locations, this case study has shown how forensics studies can be used to identify PCB sources in sediments.

3.2 Site II: Ashtabula River

3.2.1 Site Description

The second case study site is on the Ashtabula River, where the river flows into Lake Erie, east of Cleveland, Ohio (Figure 3-24). A maintenance and contaminated sediment management project was conducted at the site, in conjunction with a U.S. EPA research project of environmental dredging (e.g., investigation of dredging residuals [66]). The detailed study location is highlighted in Figure 3-24 (lower figure).

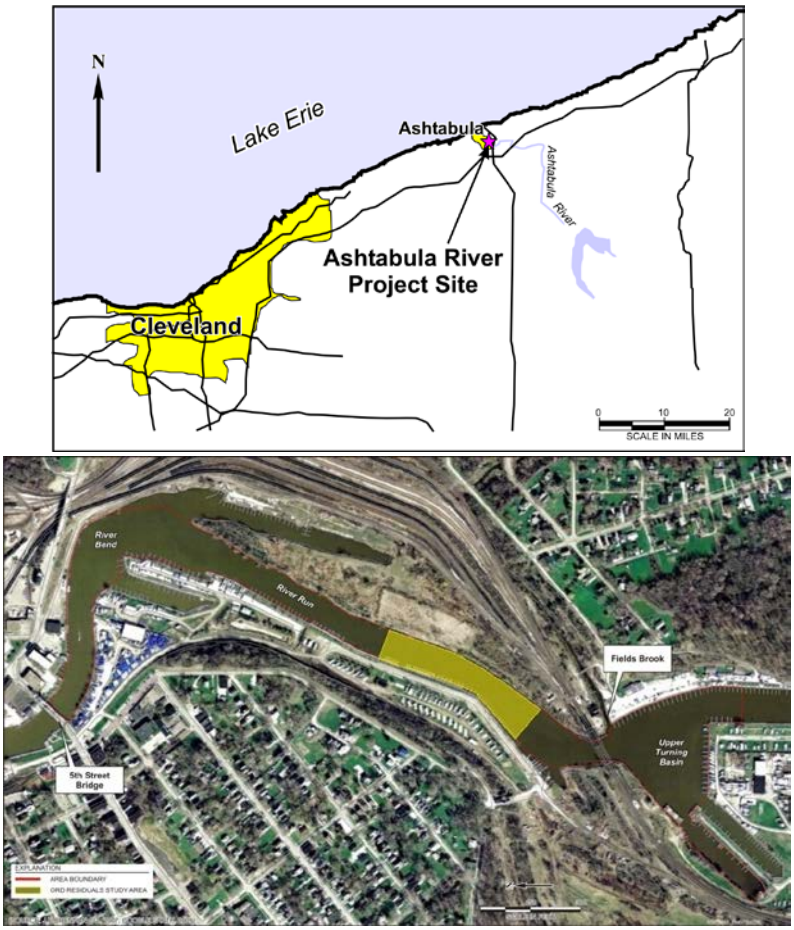


Figure 3-24. Ashtabula River with Dredge Site Study Area Highlighted

A joint partnership project was initiated in 2006 between U.S. EPA's Chicago-based Great Lakes National Program Office (GLNPO) and the U.S. EPA's Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL), and the National Exposure Research Laboratory. GLNPO, via its Great Lakes Legacy Act (GLLA) mandate, and ORD, through its research mission, had mutual interests in evaluating the efficacy of environmental dredging. The organizations jointly initiated a monitoring effort on the Ashtabula River Dredging Project. Extensive sampling and analysis were completed before, during, and after dredging operations to measure sediment residuals and the impact of remediation.

The remediation of contamination in rivers and other water bodies often involves dredging bed sediment. Dredging, whether used alone or in conjunction with other treatment technologies like in situ capping or natural recovery, can result in the release of contaminated sediments. These residual sediments ('residuals') can be transported within dredged areas (near-field) and downstream or offsite (far-field). A number of factors can influence residual levels including: dredging equipment; operator technique; debris; dredging to bedrock; over dredging; cut lines, slopes, and depths; sediment characteristics; contaminant characteristics and distribution; and the accuracy and resolution of contaminant characterization. Residuals can be categorized as either undredged or dredge-generated. Undredged residuals are the result of missed areas and incomplete characterization. Dredge-generated residuals are released via resuspension, transport and downstream deposition; dredge mixing and immediate deposition; and sloughing.

The Ashtabula River in extreme northeast Ohio flows into Lake Erie's central basin at the City of Ashtabula (Figure 3-24). Its drainage basin covers an area of 137 square miles, with 8.9 square miles in western Pennsylvania. Major tributaries include Fields Brook, Hubbard Run, and Ashtabula Creek. The City of Ashtabula, with an estimated population of approximately 21,000 (2000 census), is the only significant urban center in the watershed, with the rest of the drainage basin being predominantly rural and agricultural. There is concentrated industrial development around Fields Brook (east of the Ashtabula River) and east of the mouth of the Ashtabula River. Sediments in portions of the Ashtabula River are contaminated with a variety of chemicals, including PCBs, the primary chemical of potential concern for this project.

Approximately 550,000 yd^3 of contaminated sediments were dredged between the Turning Basin at the mouth of Fields Brook and the Fifth Street Bridge. COPCs in this stretch of the river include PCBs, PAHs, hexachlorobenzene, hexachlorobutadiene, metals, and the radionuclides uranium, radium, and thorium. The radionuclides are above background levels but below regulatory criteria. In Phase 1 of the research project, GLNPO conducted a baseline characterization of the river that included these COPCs, while ORD focused only on the PCBs in selected areas of the river. In Phases 2 and 3 of this dredge residuals research project, ORD continued to focus on the PCB inventory in the test reach and selected areas of the river.

Historically, the PCBs are thought to have originated primarily from Fields Brook, a stream that drains into the Ashtabula River in the area of the upper Turning Basin. The Fields Brook source has been controlled and eliminated as a source of contamination (or re-contamination) of the Ashtabula River. A CERCLA cleanup of Fields Brook was completed in 2003. A post-cleanup monitoring program is in place to protect against recontamination of Fields Brook as well as the Ashtabula River.

3.2.2 Evaluate Site for Forensic Study

Potential PCB source areas at the Ashtabula River study site have been associated with upstream locations in Fields Brook (on the east side of river at Transects 185 and 186; Figures 3-25 through 3-27). Subsequent studies suggested a second much smaller source from Strong Brook where it meets the river near Jacks Marine (on the west side of the river across from Transects 187 and 188). The U.S. EPA ORD dredge study focused on identifying techniques to characterize dredge residuals and understand their sources. One technique that was evaluated was using PCB compositional information to characterize dredge residuals (the amount of sediment material that is unintentionally left behind after dredging). To support this part of the research, a large number of sediment core samples were analyzed for a detailed list of more than 100 PCB congeners. These cores were subsectioned based on elevation and sediment characteristics (sand lenses, organic matter layers, etc.). These sections were analyzed for PCB congeners and compared to the dredging information (dredge position, production, sediment slopes, etc.) to evaluate potential mechanisms for contributing to dredge residuals.

For the purposes of a case study for this document, this site resembles a typical Navy dredge site (similar dredge technology, similar deposition of contaminants, similar COPCs, etc.) and the chemical forensics data that were generated can be used to demonstrate the approach used in this document to identify multiple upstream sources of contamination. As was demonstrated in the first case study example in this document, the site history and suspected sources for Ashtabula River justify the need for a forensics study to differentiate potential contributions to the river. There appear to be at least two potential historic and/or current sources of PCBs upstream of the dredge area that may become mixed into the sediments in the downstream dredge area. If this was a Navy dredge project, it would be desirable to develop a technically defensible allocation scheme to apportion dredge costs among the upstream sources. A quantitative forensics analysis to apportion the source contributions from the Navy and other sources would be necessary. A forensics investigation would also be warranted to identify if any potential active sources continue to contaminate the river if it is unclear if all sources have been controlled. Environmental dredging or other sediment management actions should only be implemented once it has been demonstrated that all sources are controlled.

3.2.3 Develop Conceptual Site Model

Figure 3-25 shows a contour map of surface sediment PCB concentrations for the Ashtabula River dredge area to support CSM considerations at this site. Additional historic data show potential source areas up the industrial waterway, Fields Brook. The source area has had significant remediation under Superfund that was completed in the 1990s. These actions include source control to eliminate PCB discharge to Fields Brook and subsequently reduce the contaminant migration off site to Ashtabula River. As a result, the Ashtabula River recently deposited surface sediments no longer show high concentrations of PCB contamination, but the older, deeper sediments in the downstream dredge area still show contamination from these historic Fields Brook sources (Figure 3-26). However, the surface sediment contours suggest increasing concentrations across the river from Fields Brook toward Jacks Marine (and Strong Brook). As a result, additional sediment cores (JAM1-3) were later collected in this area and showed total PCB concentrations well above 1000 ppb. Therefore, this area is considered a second source area for PCBs that has more recently contributed to PCBs transported downstream to the dredge area. A forensics investigation for this area included collecting samples near the

source areas and in the comingled dredge area to compare to the two known source areas. This could be used to allocate relative contribution and apportion costs for the dredge project. Additionally, this forensic analysis provided information to ensure that all sources have been controlled before initiating sediment management activities.

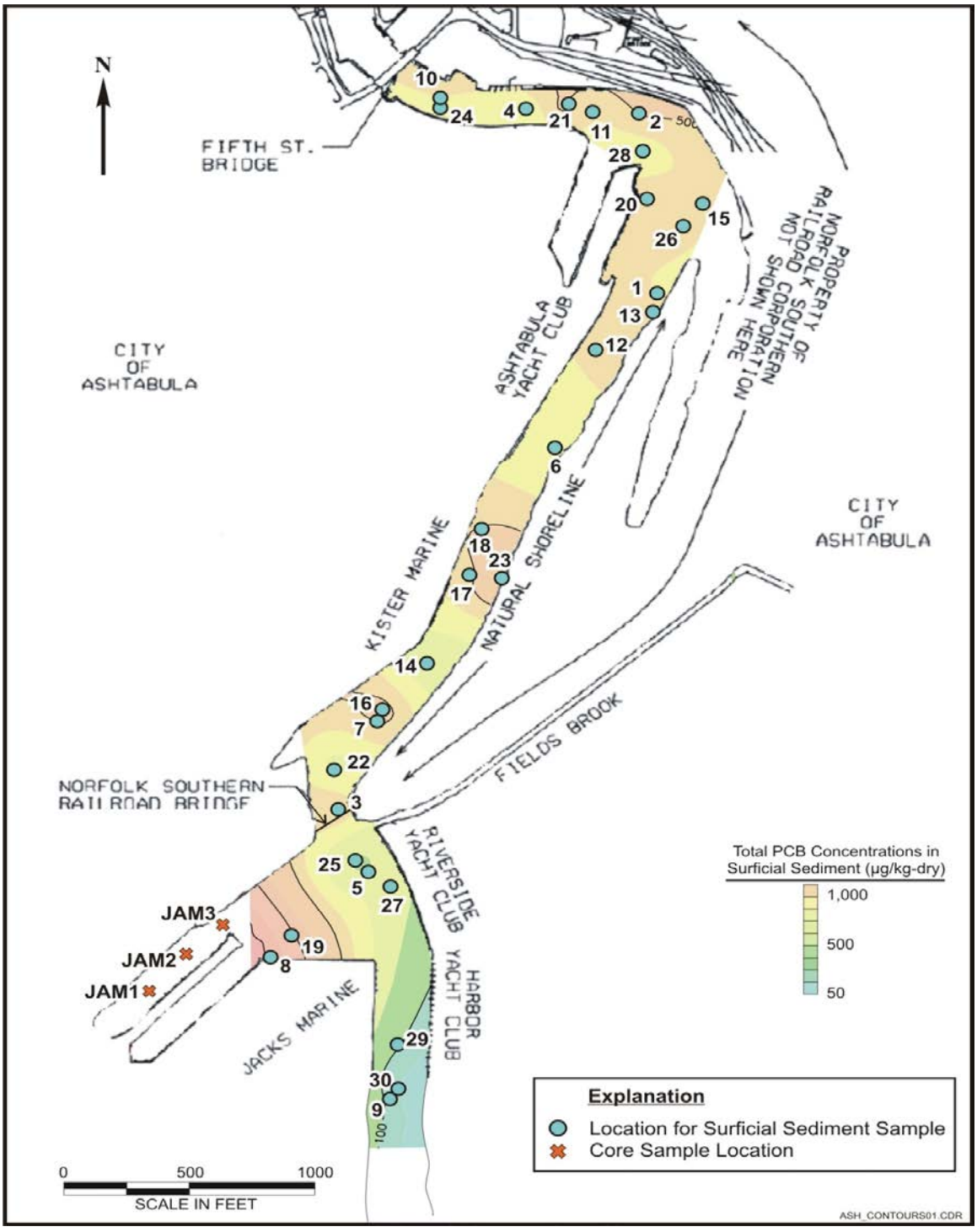


Figure 3-25. Pre-Dredge Contour Map of PCB Concentrations in Surface Sediments in the Ashtabula River Study Area

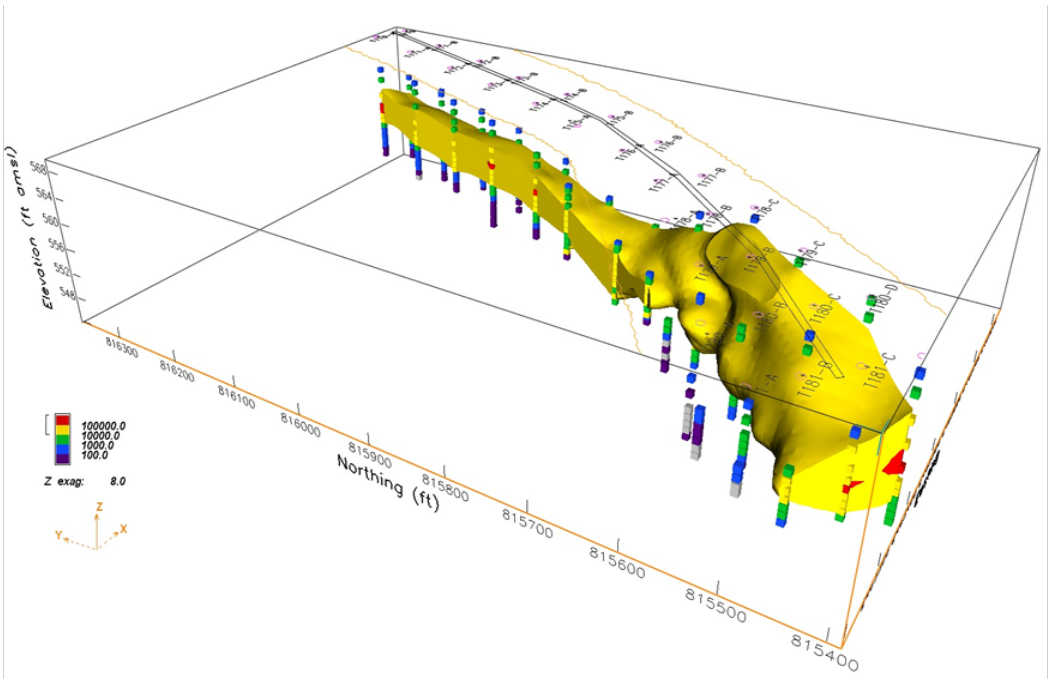


Figure 3-26. Pre-dredge Sub-surface Sediment Concentration Profiles in the Ashtabula River Study Area Indicating Sediment with Total PCB Concentration > 10,000 ppb

3.2.4 Develop and Execute a Technically Defensible Sampling Plan

Though the ORD project on Ashtabula River had significant amounts of data that were used for this case study, there were limitations to the data in terms of use for an environmental forensics investigation. The purpose of the ORD study was not to demonstrate the ACF; however, the study did provide a large portion of the data needs (at a significant cost savings) for the case study for this document. The environmental forensics demonstration made use of available data as best as possible. Figure 3-27 shows a portion of the dredge area where 30 cores were collected and segmented to produce more than 350 subsamples for both RSC and ACF analysis. Additionally, three cores (JAM1-3 in Figure 3-25) were collected in the Jacks Marine area near the confluence of Strong Brook and analyzed to identify another potential source.

To utilize these data as a case study, a data gap analysis was completed. Inconsistent sampling and analysis techniques were used for the two sets of in-river core samples (30 original cores and the JAM cores). One significant problem was the different depths of surface sediment sampling and sediment core segmenting between the two coring events. Secondly, samples were not collected at the mouth of Fields Brook, an historic source. Therefore, older and incomplete information must be relied upon to define this source. In addition, samples were not collected upstream of the confluences of the two brooks discharging to the river to ensure there were no additional sources and to identify the background PCB concentrations and composition of the river sediment. The surface sediments were generally 15 cm or more in depth in the original core samples. This depth may represent many years and even decades, depending on the rate of deposition. For ACF analysis, surface sediment samples should be no more than a few cm deep to obtain information on current or recent sources.

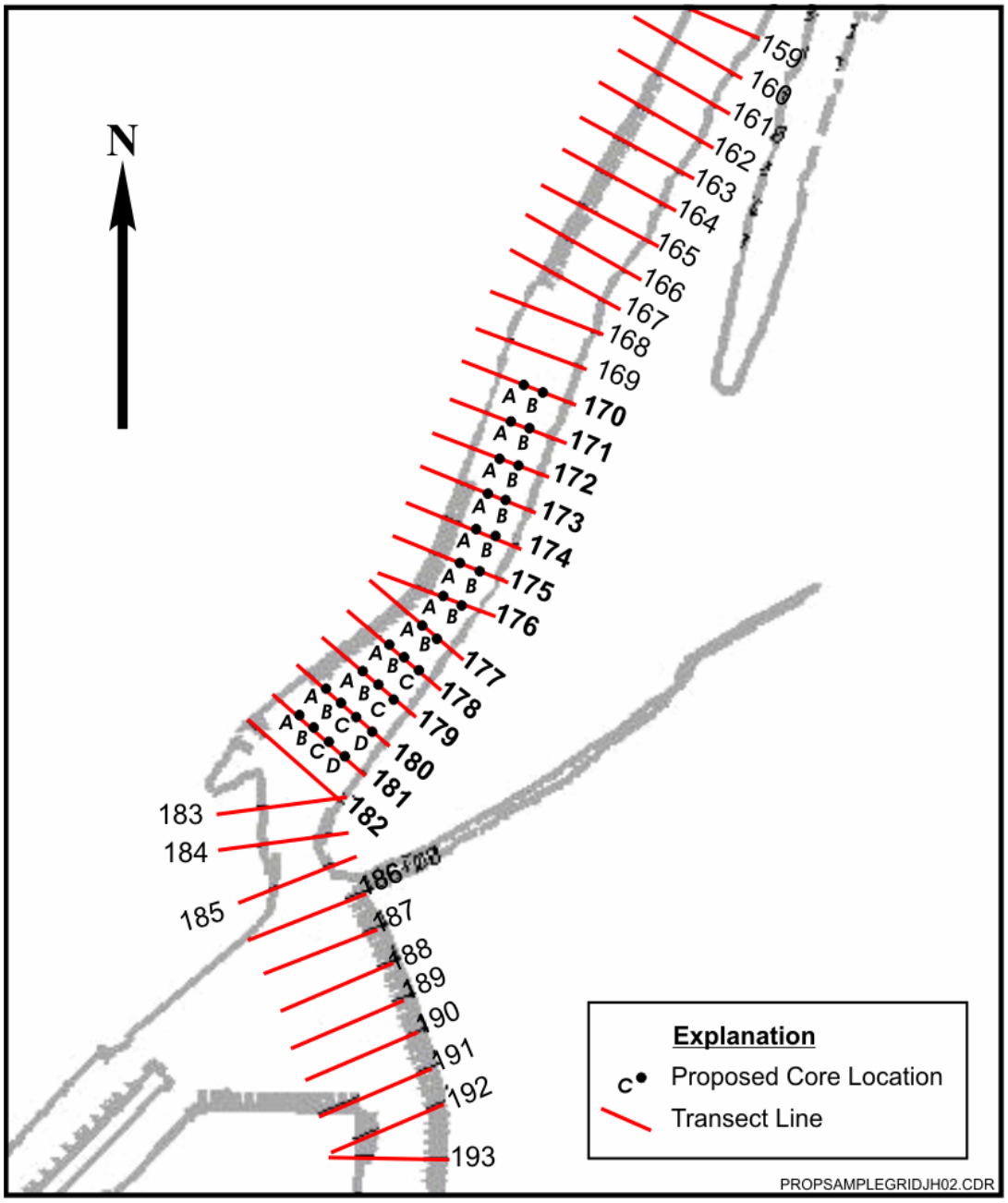


Figure 3-27. Sampling Design Map for ORD Dredge Residuals Study at Ashtabula River Transect Cores
(U.S. EPA, 2010 [67]) (These cores provided the pre-existing data used in this forensics demonstration.)

The Ashtabula River case study, like the HPS study, is based on using existing data from study designs not optimized for a forensics investigation. Clearly, there are advantages and limitations to a forensics study using only pre-existing data. Though pre-existing data provides a large cost savings, the shortcomings of a sampling design to provide information for another purpose must be accepted. As stated earlier, unexpected results are likely to occur even in the best designed forensics study. In the case of the Ashtabula study, this is why the additional JAM1-3 cores

were collected and analyzed. Initial data for this segment of the river showed surprisingly elevated concentrations with a strong Aroclor 1260 signature. This signature was different from the Aroclor 1248-dominated Fields Brook contamination. Originally, Fields Brook had been assumed to be the only source to the Ashtabula River that needed to be managed. The additional sampling in the Jacks Marine/Strong Brook confluence area identified an active source of Aroclor 1260, which subsequently was controlled shortly before dredging began. Although it may be easier to grasp a forensics study that follows a linear process (Figure 1-1), it may be more realistic to assume the process will be iterative with a need to obtain information on additional unknown sources and fill in additional information gaps as the project proceeds.

While it is cost effective and faster to use pre-existing data (no additional field or analytical costs), the limitations are that the study design may not meet all of the objectives of a well-designed forensics study. Fortunately, the study plans in the Ashtabula River case, although not intended to satisfy a forensics study, did include relatively detailed sediment sampling and rather comprehensive PCB congener analysis. Significantly more useful information was produced in the ORD research study than would be typical in a standard RI.

3.2.5 Conduct Rapid Sediment Characterization

The ELISA IA technique was also used to obtain RSC data on Ashtabula River sediment samples and the RSC data are summarized in Appendix C. The Ashtabula River research study was, like the HPS study and as described earlier, not conducted as a forensics investigation. As a result, the analyses were not tiered with the RSC analysis followed by a smaller set of ACF analyses. The PCB congener analyses were also conducted on all RSC samples.

For the Ashtabula River research study, the ELISA RSC data were not used in a tiered approach to select additional analyses. The research question was to compare the RCS to the PCB homologue data. These homologue data were also generated on the samples and provide more reliable and useful Total PCB data (Sections 2.4.1 and 2.4.3). The laboratory-based Total PCB concentrations were determined both using Method 680 to quantify individual homologues and summing those to generate the total PCB (Section 2.4.1) and by summing the 117 PCB congeners quantified during the ACF analysis; the results compared very well. The Total PCB concentrations based on the sum of the 117 PCB congeners are presented along with the individual congener data in Appendix B. As discussed earlier, those 117 congeners represent approximately 97 to 98% of the Total PCB in most environmental samples and are a good representation of the Total PCBs.

3.2.6 Conduct Advanced Chemical Fingerprinting

The ACF analysis of the Ashtabula River sediment samples consisted of determining the concentrations of 123 PCB congeners using modified Method 680/1668 (a HRGC/LRMS technique), as described in Sections 2.4.2 and 2.4.3. As for the HPS study, this work was not conducted as a forensics investigation and the ACF analysis was performed on the majority of the samples, not a subset selected by first reviewing the RSC results. However, the congeners were carefully selected to represent what could reasonably be expected in environmental PCB contamination, considering potential source material (Aroclor formulations) and environmental processes (Section 2.4.3). The Ashtabula River ACF data are summarized in Appendix B.

During the initial data review, the PCB congener set was reduced to 120 PCB congeners, because three of the congeners were consistently not detected (PCB11, PCB30, and PCB50). Those are the 120 PCB congeners reported in Appendix B. During the subsequent more detailed data review and screening (Section 2.5.2.3), about 53 of the 345 sediment samples were identified as candidates for potentially excluding from the data analysis because of lower data reliability (e.g., low overall PCB concentration [e.g., sum of congeners less that ~50 ppb], a high percentage of the PCB congeners with non-detects, or anomalous composition that cannot be explained by PCB chemistry or weathering factors). Thirty-eight of the 120 PCB congeners were also identified as potential candidates for exclusion from the data set prior to detailed data analysis because of possible lower reliability (e.g., high percent non-detect of the congener, low congener concentration, a high %RSD in the percent contribution of the congener to the Total PCB, or other data outlier issues). As discussed earlier, a stronger and more reliable data interpretation can be obtained with a high quality data for a pared down set of 80 PCB congeners than from a larger set that also includes congeners with lower reliability.

3.2.7 Data Analysis, Synthesis, and Presentation of Results

3.2.7.1 Site History and Records Research

Historical source information was lacking for the Ashtabula River case study, posing a limitation that would need to be rectified if a comprehensive forensics investigation was performed. A major tributary to the study area includes Fields Brook, a U.S. EPA Superfund site which had a high concentration of industry around it with significant runoff and drainage to Fields Brook (Figure 3-28). The site had been historically identified as a source of PCBs to the Ashtabula River; this source had been controlled (Section 3.2.1). Other locations of runoff and input to the river but with less information on historical activities include Hubbard Run, Ashtabula Creek, and Strong Brook (which flows into Jacks Marine).

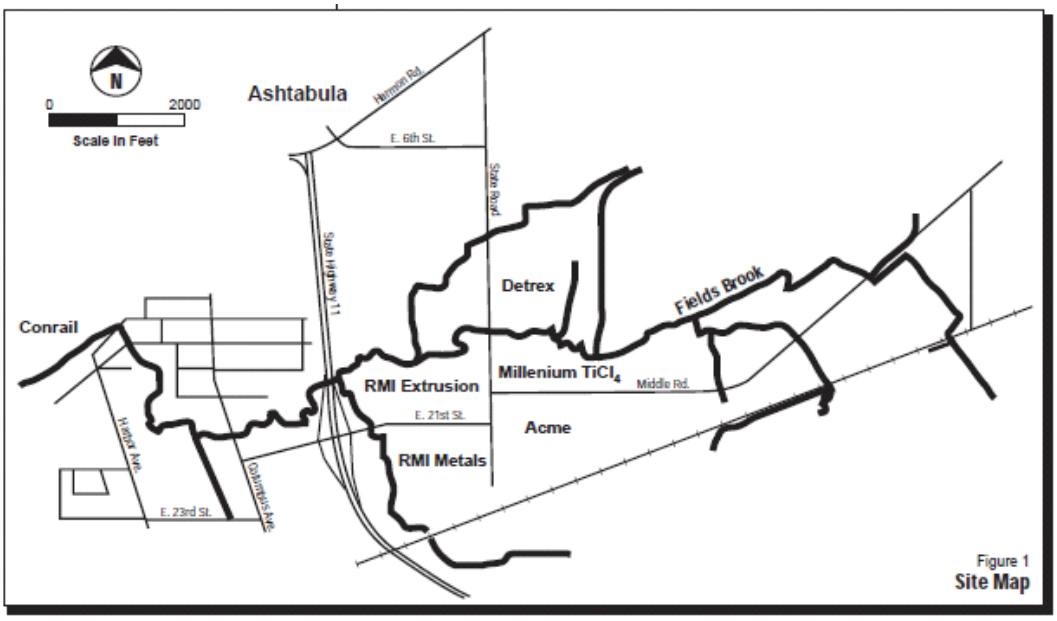


Figure 3-28. Fields Brook Drainage Showing Industrial Activities East of Ashtabula River
(Ashtabula River is located on the left side of this figure.)

3.2.7.2 Sediment Transport and Hydrodynamics

As part of the GLNPO GLLA remediation activities, sediment transport and deposition studies were conducted at Ashtabula River, but the results are not readily available. These studies indicated that an estimated 4 cm of sediment will be deposited annually. These newly deposited sediments are anticipated to be clean materials from upstream of the project area. There were no dedicated studies of hydrology or sediment stability/transport available for this Ashtabula River case study, and this was clearly a limitation that would need to be rectified if a comprehensive forensics investigation was performed. The segment of the river that was studied is upstream of tidal influence, and standard river flow considerations are all the transport information that was available.

3.2.7.3 PCB Concentrations

The PCB concentrations were relatively uniform in the Ashtabula River surface sediments for most of the ORD research study area (Figure 3-25). Figures 3-26 and 3-29 illustrate a 3D model of the sediment PCB concentration profile in the study area. Each color in the 3D figure shows a distinct isoconcentration profile that varies both horizontally and vertically. The surface sediment Total PCB concentration was between 500 and 1,000 ppb in most of the ORD research study area (Figure 3-25 and 3-27). The subsurface sediment PCB concentrations were more variable and were generally much higher than the surface concentrations. The total PCB concentration was above 10,000 ppb in much of the subsurface sediment (Figure 3-26; [66]). The most contaminated sediments were generally found at 5 to 10 ft depth, but highly contaminated sediments were found at less depth at some locations. The sediments at greater depth (below the most contaminated zone) had variable PCB concentrations that were more comparable to the surface sediment PCB concentrations. The subsurface PCB concentrations were somewhat variable within the relatively small ORD study area, but no obvious pattern of increasing or decreasing concentrations geographically was evident with the exception of the highest concentrations being measured at depth close to and immediately downstream of the mouth of Fields Brook (top, Figure 3-29).

On more careful review of the surface sediment data from the Ashtabula River, it appeared that the PCB concentrations might be elevated just outside the ORD research study area (Stations 8 and 19 in Figure 3-25), and near Jacks Marine and the confluence of Strong Brook (Figure 2-13). The PCB composition of downstream surface sediment samples indicated a composition that was slightly different from that of the primary known source (Fields Brook) and these two facts prompted additional sampling near Strong Brook's confluence area to further investigate the elevated concentrations. This was important since the area was to be dredged and it was critical that all known sources of PCBs were controlled to avoid recontamination.

The additional sampling at the confluence of Strong Brook demonstrated that the surface sediment PCB concentrations were significantly elevated (Figure 3-30); surface sediment concentrations in Jacks Marine were around 10,000 ppb (more than 10 times higher than the GLLA project area) and elevated concentrations were also measured in shallow subsurface sediment from this area.

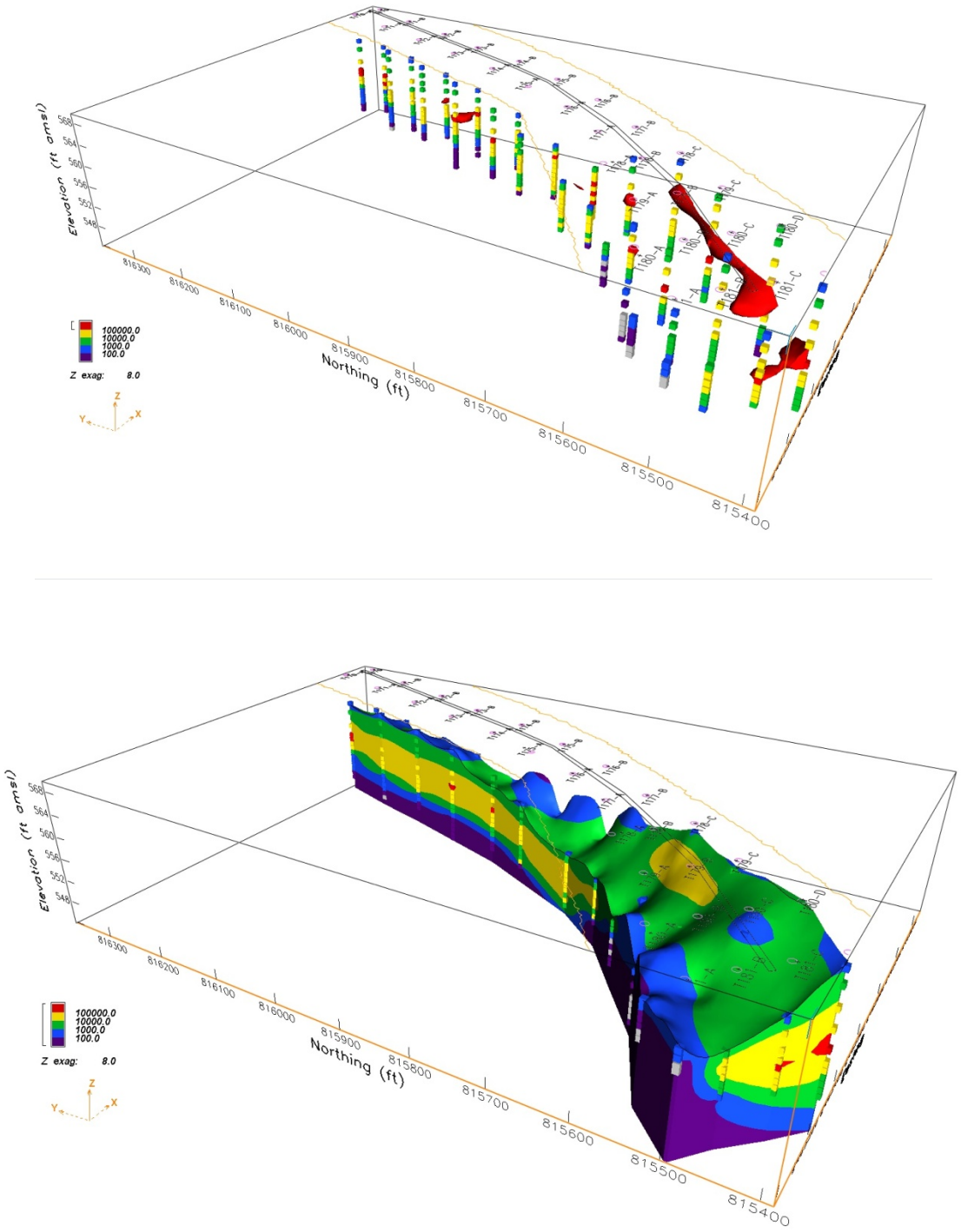


Figure 3-29. Example Ashtabula 3D Contour Maps (µg/kg or ppb total PCB): (a) >100,000 ppb Contoured Volume; (b) all contours including >100, >1000, >10,000, >100,000 ppb
(from U.S. EPA, 2010 [66])

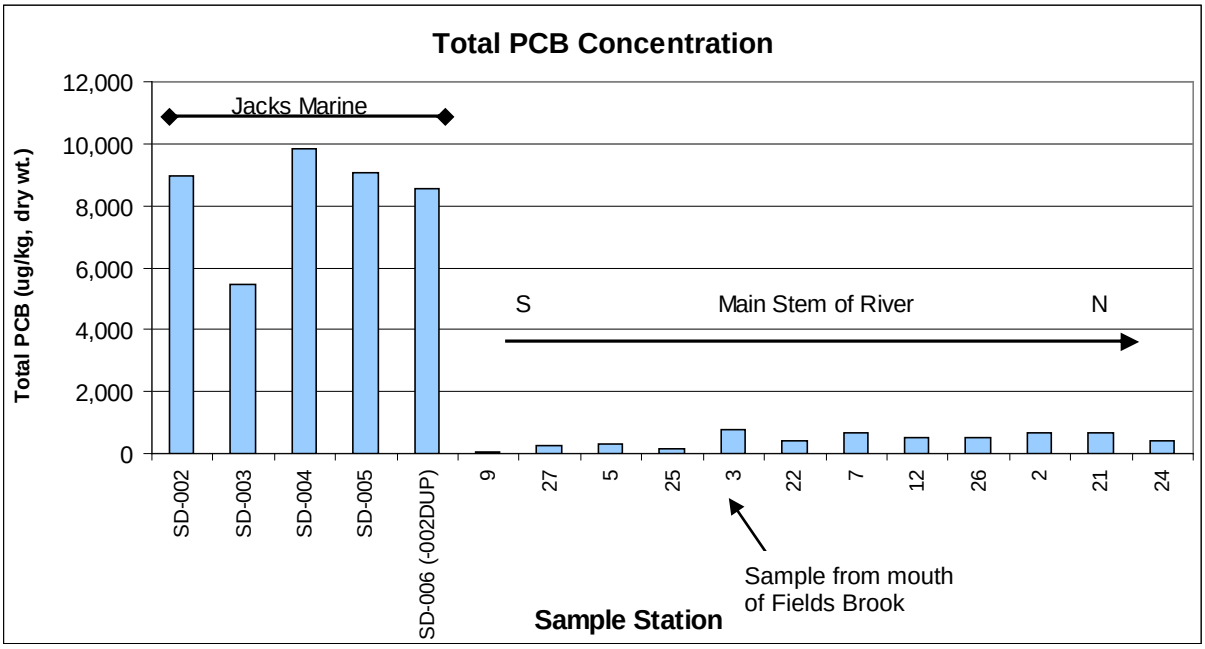
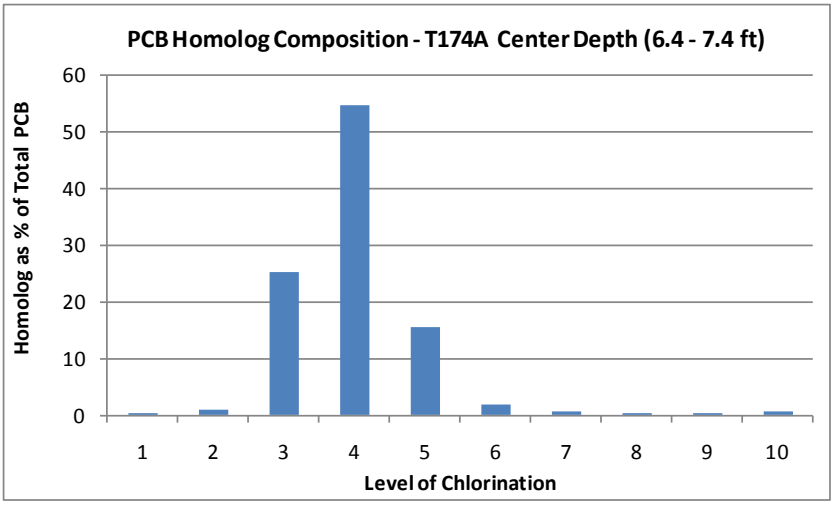


Figure 3-30. Total PCB Concentrations for Selected Ashtabula River Surface Sediment Samples, Including from Jacks Marine and the Main ORD Study Area (µg/kg, dry weight)

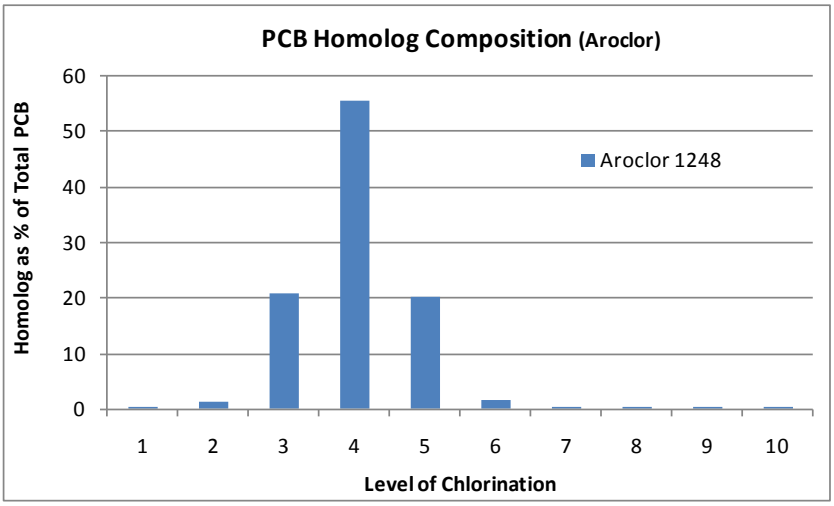
The Ashtabula River PCB concentration data indicate that most of the PCB contamination is historic and originated with the controlled Fields Brook Superfund source. This is apparent by comparing the high subsurface PCB concentrations in the main stem of the river downstream from the mouth of Fields Brook and the substantially lower surface sediment concentrations. The surface sediment PCB concentrations suggest that low levels of PCB may still be discharging from Fields Brook. This is indicated by the slightly higher PCB concentration at Station 3 (at the mouth of Fields Brook) compared to the rest of the study area, but the magnitude of elevation is small. The surface and near-surface data do, however, indicate a recent and active source of PCB to Jacks Marine (i.e., Strong Brook), likely a source of PCBs to the Ashtabula River.

3.2.7.4 PCB Composition

The Ashtabula sediment PCB composition was evaluated using both homolog and congener-specific data. Most samples from the most contaminated zone (at 5 to 10 ft depth) had a PCB composition that closely resembled Aroclor 1248-type contamination consistent with information regarding the historic Fields Brook source. This was demonstrated using both PCB homolog and PCB congener data (Figures 3-31 and 3-32); PCB homologue data can often also be very useful for compositional analysis including for multivariate analysis. This close match with Aroclor 1248 was observed throughout the ORD study area in most sediment below 1 ft in depth and in all of the most contaminated sediment. Sediment samples with a total PCB concentration above 10,000 ppb all showed a very close compositional match with Aroclor 1248.

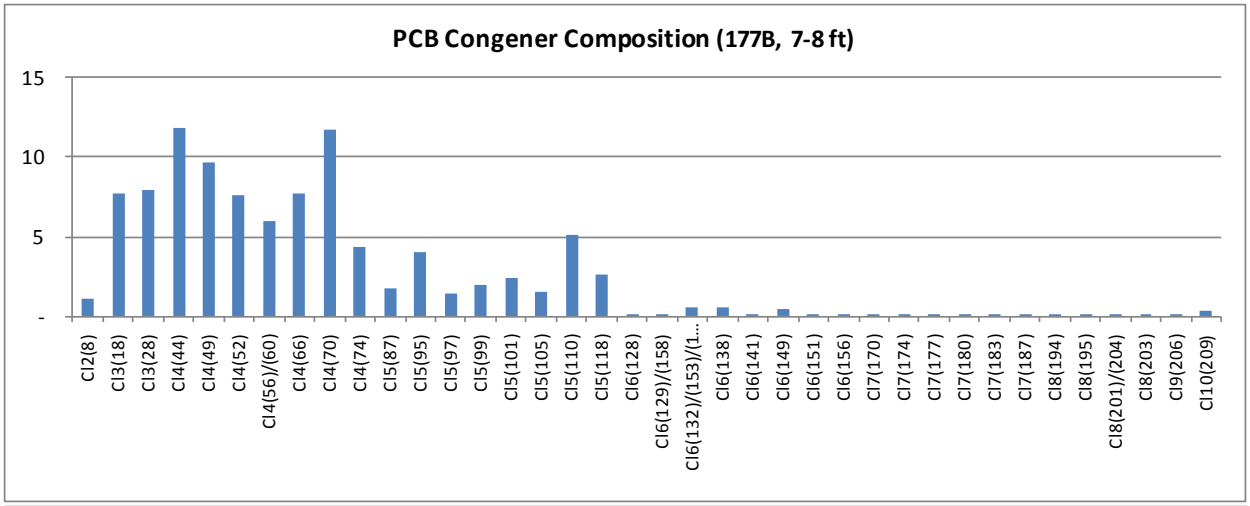


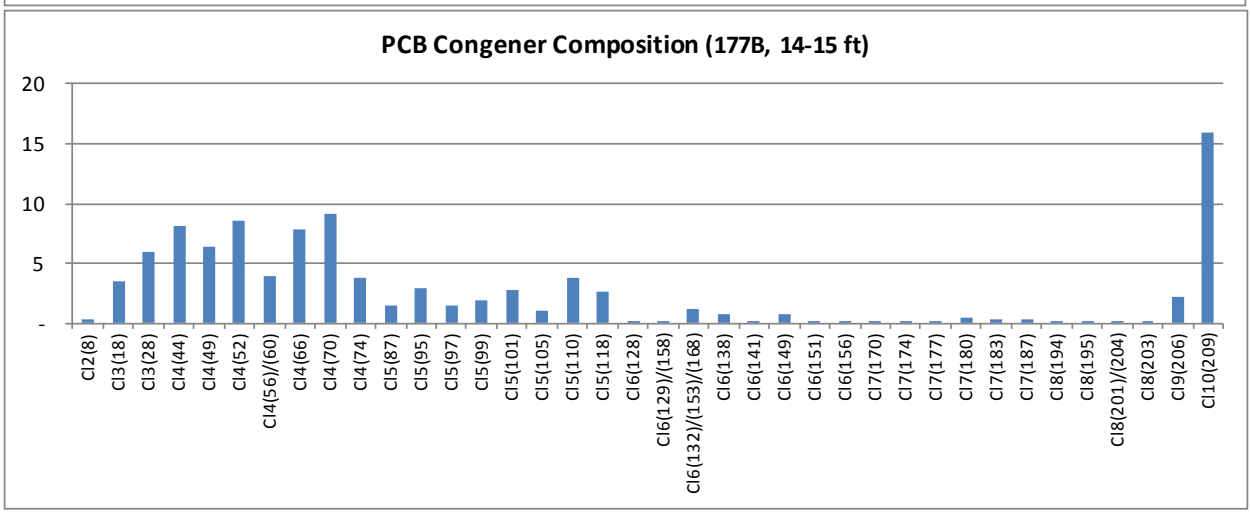
a) Pre-Dredge Core Sample T174A (from 6.4–7.4 ft sediment depth)



b) PCB Aroclor 1248

Figure 3-31. Composition Analysis Showing the Similarity in the PCB Homologue Composition of Ashtabula River: (a) Sediment Core T174A from a Depth of 6.4–7.4 ft; (b) and Aroclor 1248





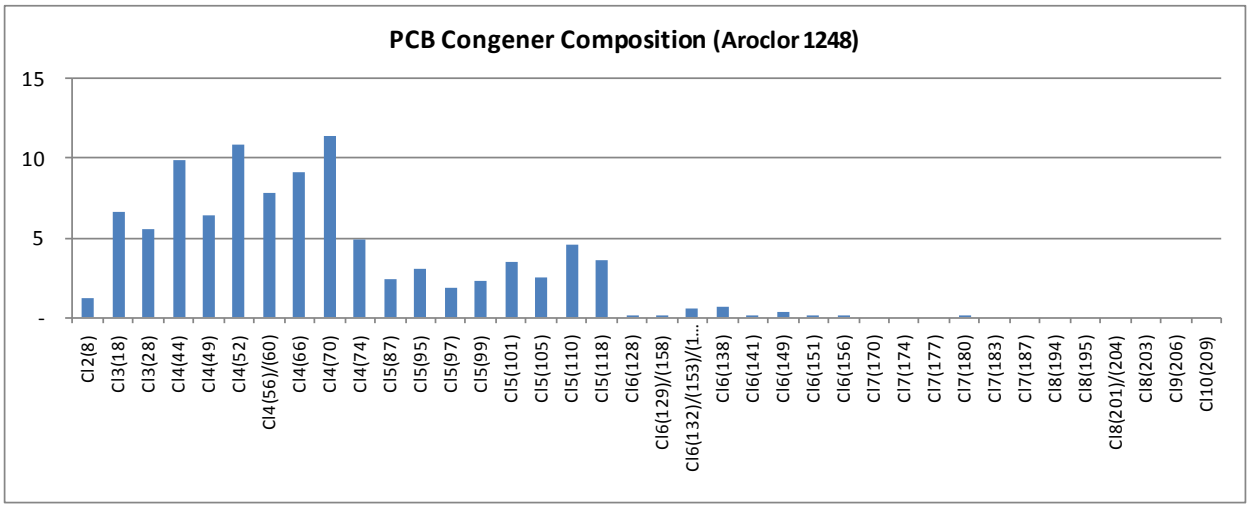


Figure 3-32. PCB Fingerprint of Sediment Samples from 7-8 ft and 14-15 ft Depth in the Center of the Ashtabula Study Area Compared to a Reference Aroclor 1248
(The primary source of the PCB was assumed to be the Fields Brook Aroclor 1248 source.)

The sediments collected from the greatest sediment depth (the lowest elevation) that were below the most contaminated zone exhibited a PCB composition that also was dominated by an Aroclor 1248 signature. However, these deeper sediments (e.g., as illustrated by the 14 to 15 ft segment in Figure 3-32), often also had a contribution by a few chlorinated PCB congeners (e.g., a few octa-, nona-, and deca-chlorobiphenyls) that do not have a clear relationship to any particular Aroclor formulation. The high relative amounts of PCB209 (deca-chlorobiphenyl) compared to the octa- and nona-chlorobiphenyls, for instance, were greater than in the highly-chlorinated Aroclor formulations (e.g., Aroclor 1268, and the rare Aroclors 1269-1271). The distribution cannot be explained by common environmental alteration processes. There are industrial processes (e.g., titanium tetrachloride production) that may selectively produce these highly-chlorinated congeners and this would warrant further investigation in a comprehensive forensics investigation. However, the sediments with this unique composition generally had low PCB concentrations compared to most samples ranging from less than 1,000 to about 3,000 ppb.

The surface and near-surface samples from the Strong Brook and Jacks Marine area did not have an Aroclor 1248-type PCB composition, but instead closely resembled Aroclor 1260 (Figure 3-33) with minor contributions from also a lower molecular weight Aroclor (possibly Aroclor 1248). The downstream surface sediment for the ORD research study area had a PCB composition that indicated contamination from both an Aroclor 1248 and Aroclor 1260 source (Figure 3-32). This was confirmed using data sets with both 38 and 80 PCB congeners (Figures 3-34 and 3-35). The Aroclor 1248 predominance was strongest near Fields Brook even in the surface sediments and the Aroclor 1260 predominance was strongest in the Strong Brook confluence. Figure 3-36 is a PCA analysis of the surface sediment PCB data (homologs and congeners) that demonstrates the association of the sample from the mouth of Fields Brook to Aroclor 1248, the association of the samples from Strong Brook confluence to Aroclor 1260 and the samples from the main study area are influenced by both the Aroclor 1248 and Aroclor 1260 source.

The observed PCB compositional match to Aroclor 1248 near Fields Brook and the sediments that were highly contaminated before the Fields Brook source was controlled. This analysis indicates that this was the source of the majority of the PCB in the ORD research study area and that, for the most part, it has been controlled. The strong Aroclor 1260 signature in the Jacks Marine sediment was evident in the surface sediments, indicating a recent and active source of PCB in this area, most likely Strong Brook which flows into Jacks Marine. The Aroclor 1260 signature and the PCB concentrations declined with depth near the confluence of Strong Brook, indicating that a source may have been active only recently.

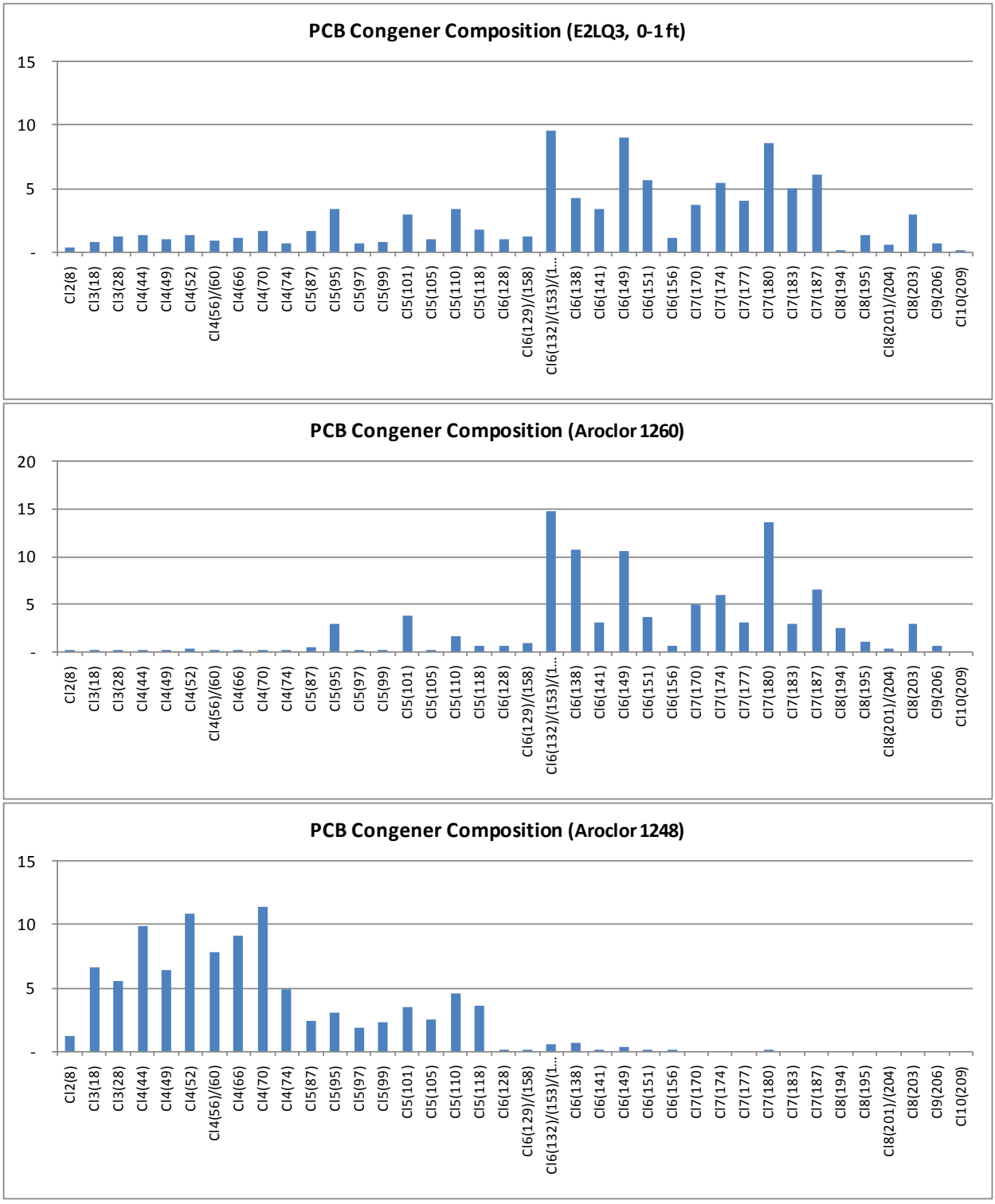


Figure 3-33. PCB Fingerprint of a Sediment Sample from a 0-1 ft Depth in the Jacks Marine Part of the Ashtabula Study Area Compared to a Reference Aroclor 1248 and Aroclor 1260

(Sample is primarily influenced by a local source of Aroclor 1260 as well as smaller proportions of Aroclor 1248.)

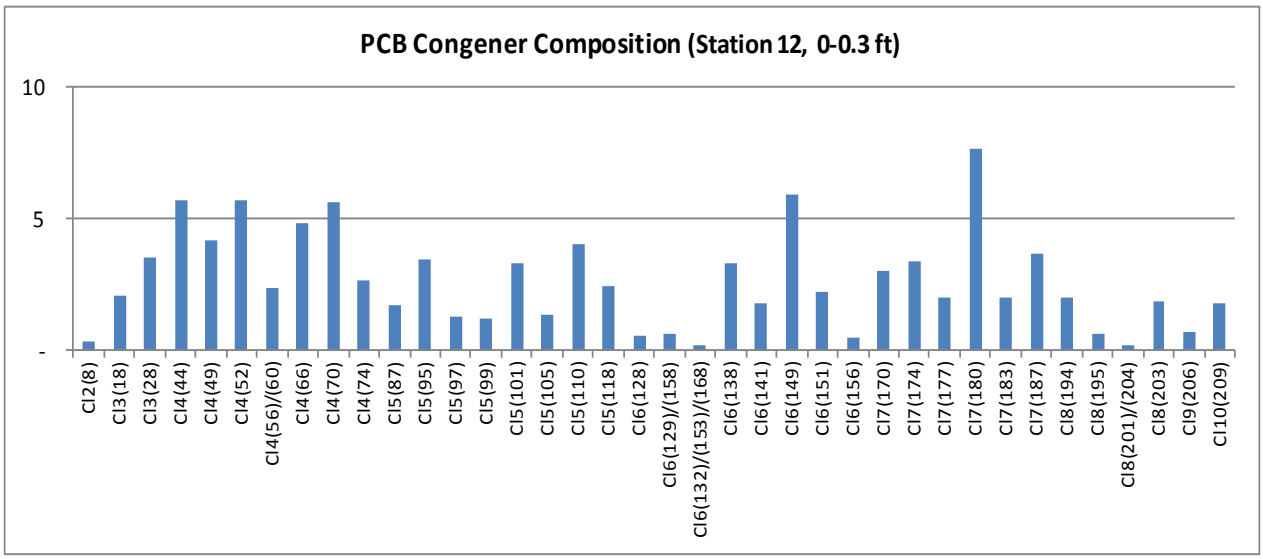


Figure 3-34. PCB Fingerprint of a Surface Sediment Sample from 0-0.3 ft Depth in the Center of the Ashtabula Study Area

(PCB composition indicates contributions from both the Strong Brook Aroclor 1260 source and the Fields Brook Aroclor 1248 Source; see Figure 3-33.)

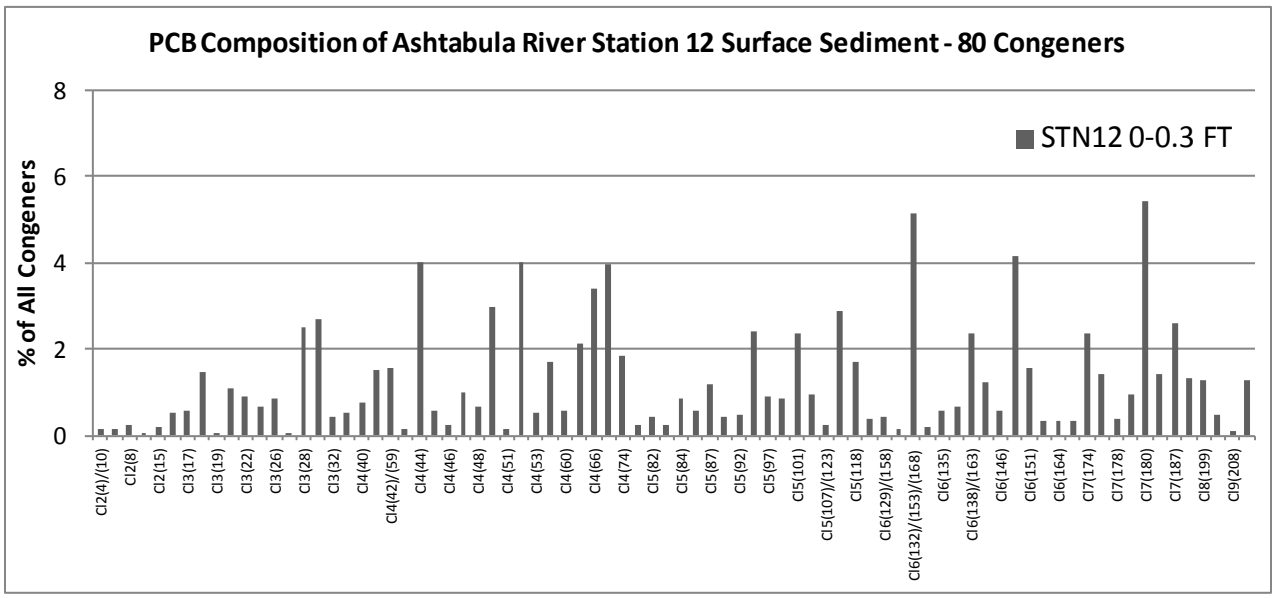


Figure 3-35. PCB Fingerprint of a Surface Sediment Sample from 0-0.3 ft Depth in the Center of the Ashtabula Study Area Using 80 Key Congeners

(A set of 38 congeners are plotted in Figure 3-34.)

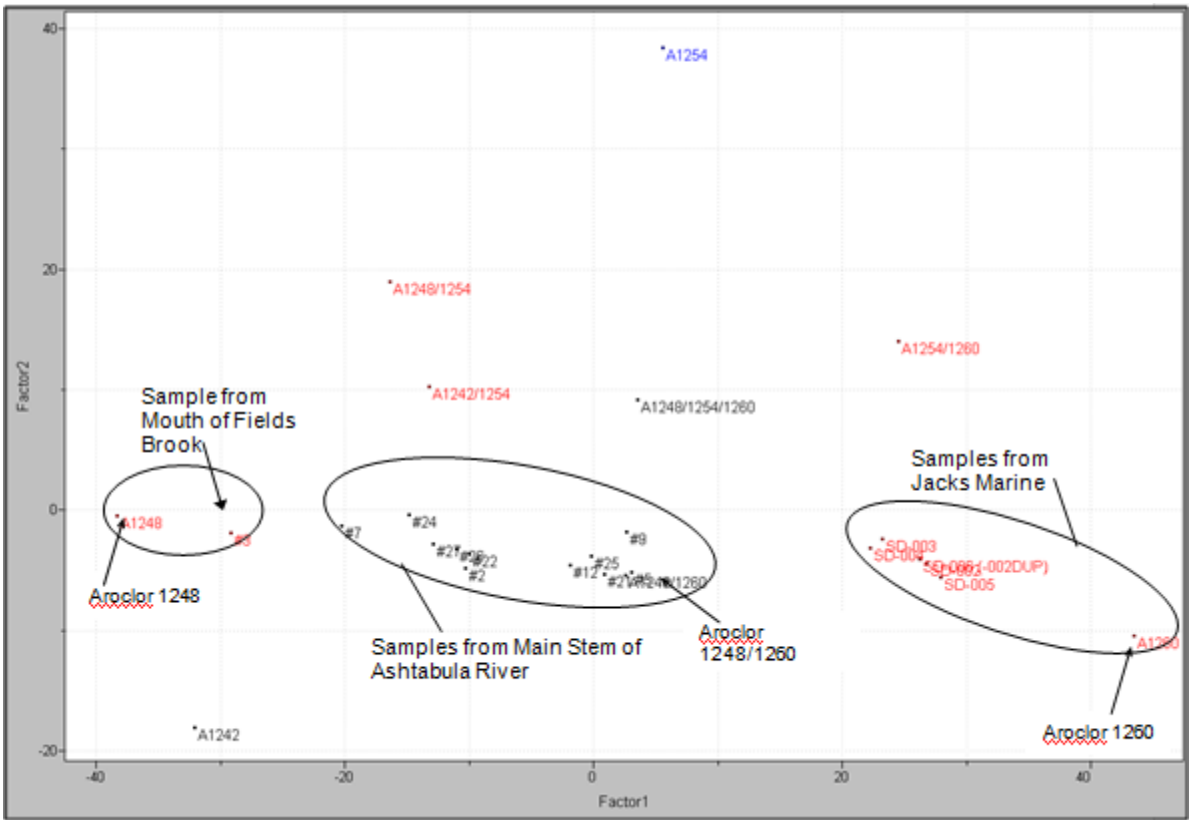


Figure 3-36. Principal Component Analysis Using PCB Data for Selected Ashtabula River Surface Sediment Samples and Aroclor Formulations
(Those illustrated in Figure 3-30; see sample IDs in above figure and x-axis of Figure 3-30.)

3.2.7.5 Chemometric Statistical Analysis

As discussed in Section 2.5.2.3, the data screening process is presented in this handbook as a discrete step between data preparation (2.5.2.2) and data analysis (Section 2.5.3). In reality, it is usually an iterative process with preliminary data interpretations on numerous analyses of the data and finally arriving at data interpretation that are both robust and spatially/temporally representative of a study area. This process is well illustrated with the Ashtabula ORD research data set.

For the Ashtabula project, the PCB congener data were from two separate pre-dredge investigations: (1) the Summer 2006 GLNPO baseline surface sediment sampling (17 samples); and (2) the Fall 2006 EPA ORD Phase 1 core sampling within the proposed dredge area (328 samples). Congener-specific analyses were conducted on both data sets by the same laboratory (Battelle) using the same preparation and analytical methods. Therefore, the data from the two events could be considered comparable and subsequently combined for greater spatial representation.

The combined data were delivered in spreadsheet tables which contained the information listed in Section 2.5.2.2, including: sample ID, sample coordinates, sample depths, analyte identifiers (i.e., congener names), and laboratory results. A digital base map was received in the form of a GIS shapefile, which was used to construct a simple base map (Figure 2-13) showing key geographic features of the study area and sample/core locations.

The data set initially considered for statistical analysis was comprised of 345 samples and 123 congeners. While this represents many more samples and congeners than were available at HPS (Section 3.1), it is clear that this data set still had limitations. The vast majority of samples were a very small area (the ORD research area within the larger GLNPO GLLA project area). GLNPO collected samples across a much wider geographic area but only 17 of surface samples were collected and none at depth. In addition, samples were not collected from Fields Brook (where PCB sources are known to be located). The contribution from Strong Brook was not initially considered and samples were not collected at its confluence. This is understandable given the sampling objectives of the EPA ORD (to establish baseline conditions for evaluating dredge residuals) and EPA GLNPO programs (to evaluate pre-remediation conditions). These two sampling campaigns were designed with a PCB forensics investigation in mind for source identification and allocation.

While not ideal for purposes of source identification and apportionment, the Ashtabula case study makes for a useful and instructive example. If there are limited or no resources available for additional sampling and analysis (as is often the case), existing data may be used to effectively conduct an ACF study. An adaptation of the ideal six-step integrated forensics approach process (Section 1.2.1) that includes development of a detailed sampling plan focused on specific forensic objectives (Section 1.2.1.3) may need to be developed to use existing data with budget or time limitations.

As per Section 2.5.2.1, the Ashtabula ORD research data set underwent laboratory data quality review. Based on that review, the congener data were accompanied by recommendations for exclusion of samples and congeners. These included (1) exclusion of samples with total PCB concentrations less than 100 µg/kg; (2) exclusion of samples with greater than 20% of congeners non-detect and total PCB less than 250 µg/kg; (3) exclusion of congeners with non-detects in more than 25% of samples; and (4) exclusion of congeners that were consistently reported at low concentrations (<0.2% of total sum of all congeners). This data QA review resulted in a recommended reduced data set composed of 293 samples (down from 345) and 83 congeners (down from 123).

As was the case for the HPS case study (Section 3.1.7.5), all individual data screening decision points will not be recounted here. However, one is instructive and provides an idea of the types of considerations typically taken into account in this process. The reduced data set (based on the criteria above) considered a 293 sample/83 congener subset of the full 345 sample/123 congener data set. As per Section 2.5.2.3, these data were processed through initial multivariate analyses to assess data usability for chemometric analysis. As a result of this review, it was found that the initial 100 µg/kg sample cut off resulted in a poor fit for some key congeners, and a receptor model would not converge. As is the iterative nature of this ACF approach, it was necessary to increase the concentration cut off to 500 µg/kg. This new threshold resulted in a 252 sample 83

congener matrix and subsequently, a cleaner, better fit model was developed with more interpretable end-members.

As a means of demonstrating the data evaluation process for ACF, another data screening option is described below. The data set was also evaluated with a higher concentration threshold by increasing the total PCB concentration cut off to 1,000 µg/kg (1 ppm). This resulted in a 222 sample data matrix and an even cleaner model. However, by adopting such an aggressive concentration threshold, many GLNPO surface samples were removed from the analysis (all except those collected near Strong Brook). In addition, many of the lower concentration, deeper, samples were eliminated by the 1,000 µg/kg cut off criterion. Given this, the data set used for chemometric analyses of the Ashtabula ORD and GLNPO data set (Section 3.2.7.5) was based on the 500 µg/kg cut off. This decision was made, not because it was ideal in all respects, but because it was a good compromise between (1) a relatively clean, well fit model and (2) good spatial coverage across the study area. This example is instructive as a lesson for data screening prior to statistical analysis because the best solution is often a compromise that attempts to balance different project objectives.

The 252 sample × 83 congener matrix was analyzed using PCA as an initial exploratory tool, and was then run using all four receptor models. Goodness-of-fit diagnostics were again examined [9]. These indicated the presence of at least four congener patterns contributing to the system. The CD scatter plot array from the PVA analysis is shown in Figure 3-37. Most of the congeners show a fairly good fit, indicating that a four end-member model is a reasonable solution. Those showing a systematic lack of fit (e.g., PCB4/10 and PCB8) may provide evidence for additional source/congener patterns contributing to the system and such possibilities will be discussed in more detail in Section 3.2.7.6.

A PCA was run on these data and the resulting three component scores plot is shown in Figure 3-38. Colored symbols are used to indicate different groups of samples to illustrate the variations in PCB congener composition in the data set. Note that the data are generally not widely distributed, with the majority of the samples (around 200 of the 252) concentrated on the left side of the plot. These mid-depth core samples (green circles) show a range of chemical compositions between two distinct patterns, an Aroclor 1248 (lower left) pattern and a slightly altered Aroclor 1248 (upper left) pattern. A third distinct congener composition is shown in the deeper core samples (red circles) that plot toward the back right of the data cloud.

There is also one small group of five samples on the front right side of the plot (light blue square symbols – the one to the right labeled E2LQ3). These five samples were all collected in Jacks Marine near the confluence of Strong Brook, indicating that samples are very different from the rest of the data set. Direct inspection of chromatograms from these samples (Section 3.2.7.4) indicated that the Strong Brook area sediment samples exhibit a strong Aroclor 1260 pattern. Other surface sediment samples show a progression in congener composition from this Aroclor 1260 pattern back to more of an Aroclor 1248 pattern (bottom left samples in the data cloud). The general shape of the data cloud roughly outlines a tetrahedron in principal component space which has been drawn here using the four most mutually extreme samples as vertices. Each of these four samples are labeled with different symbols and colors on Figure 3-38.

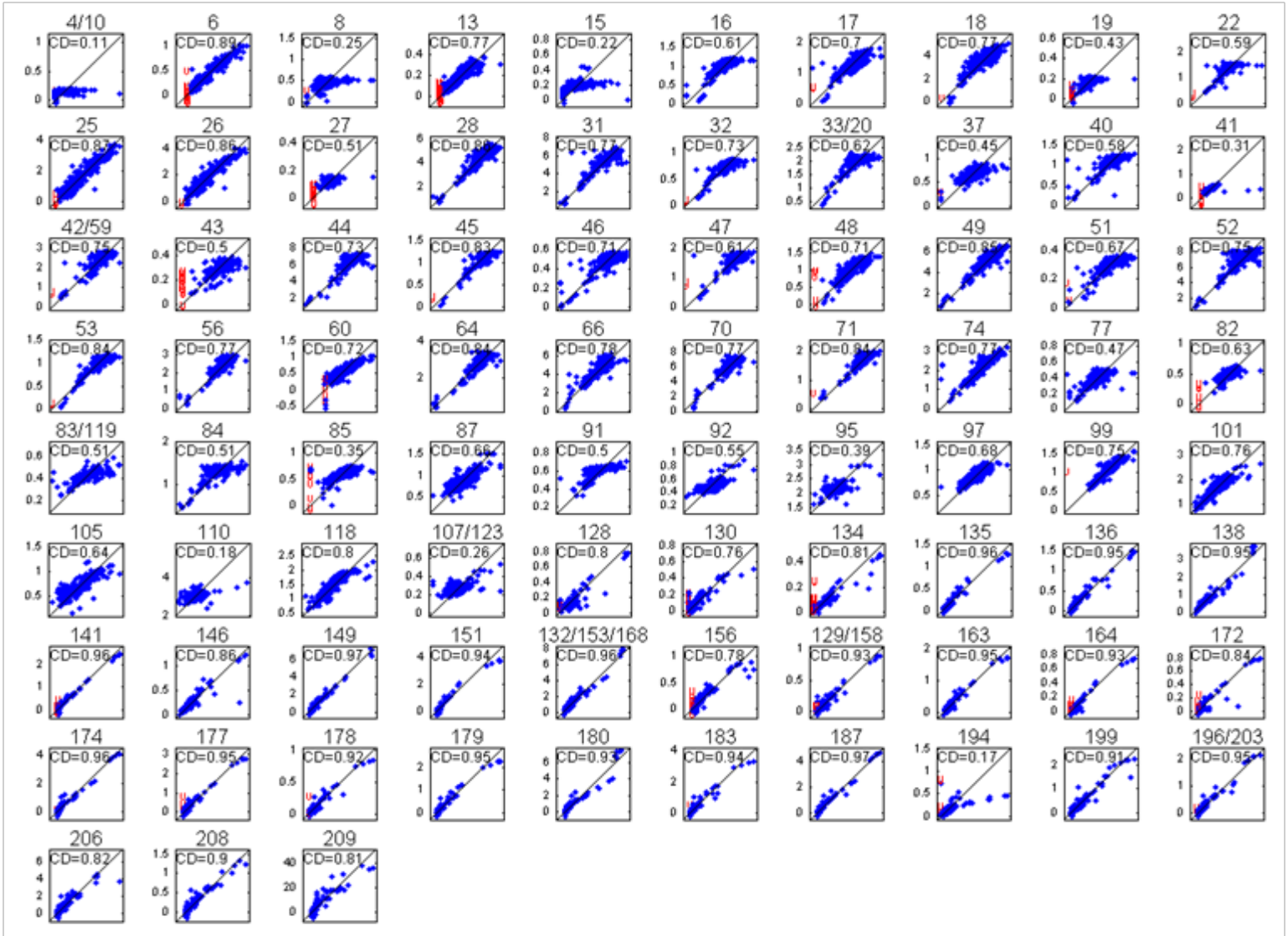


Figure 3-37. CD Scatter-plot Array for a Four Sources System, for 252 Sample 83 Analyte PCB Data Set from Ashtabula River, Ohio

(Non-detect samples are indicated as red "U".)

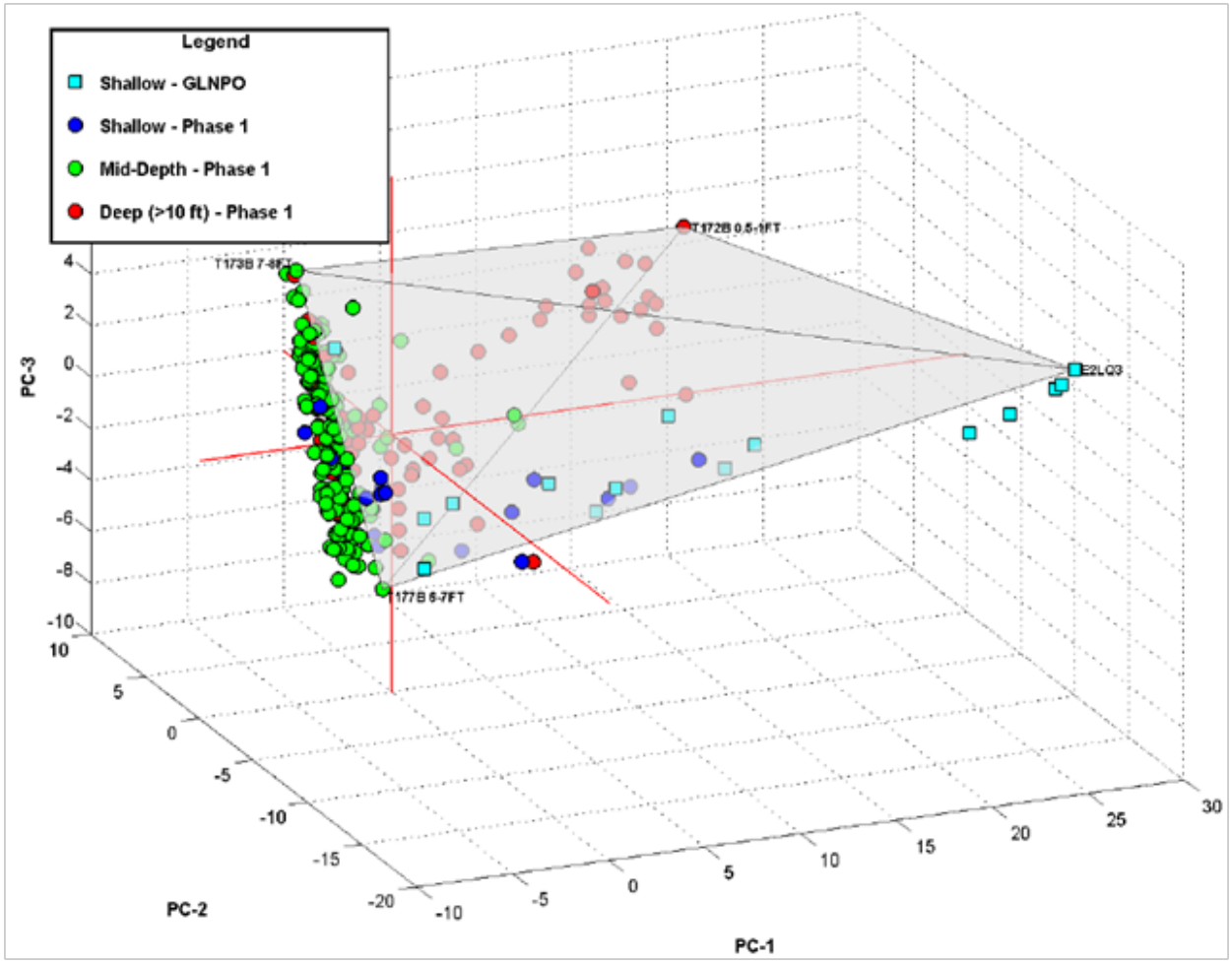


Figure 3-38. PCA Scores Plot for 252 Samples, 83 Analyte PCB Data Set from Ashtabula River

Bar graphs of these four extreme samples are shown on Figure 3-39. The tetrahedron can be thought of as a four end member mixing diagram (as opposed to the three end member triangular mixing diagram from the HPS case study), where each sample congener composition can therefore be represented by a linear mixture of these four distinct end member compositions.

The top pattern of Figure 3-39 (T177B 6-7 feet) is a high concentration sample (∑PCB = 162 ppm) and is a close pattern match to Aroclor 1248 (a source previously identified as the primary Aroclor found in Ashtabula sediments [26]). The second pattern on this figure (T173B 7-8 feet) exhibits a pattern in a similar chlorinated higher range but slightly lighter. This pattern was consistent with a PCB dechlorination pattern reported previously for the Ashtabula River [26].

The third sample (T172B 0.5-1 ft) is a low concentration sample dominated by a single congener; PCB209 (deca-chlorobiphenyl), with additional contributions from a few other highly chlorinated congeners. The bottom sample in Figure 3-39 is E2LQ3, one of the Strong Brook area surface sediment samples. This PCB pattern is primarily composed of highly chlorinated

congeners and is consistent with Aroclor 1260. It would be expected in the receptor modeling that resolved end members (congener source profiles) might be similar to these extreme samples.

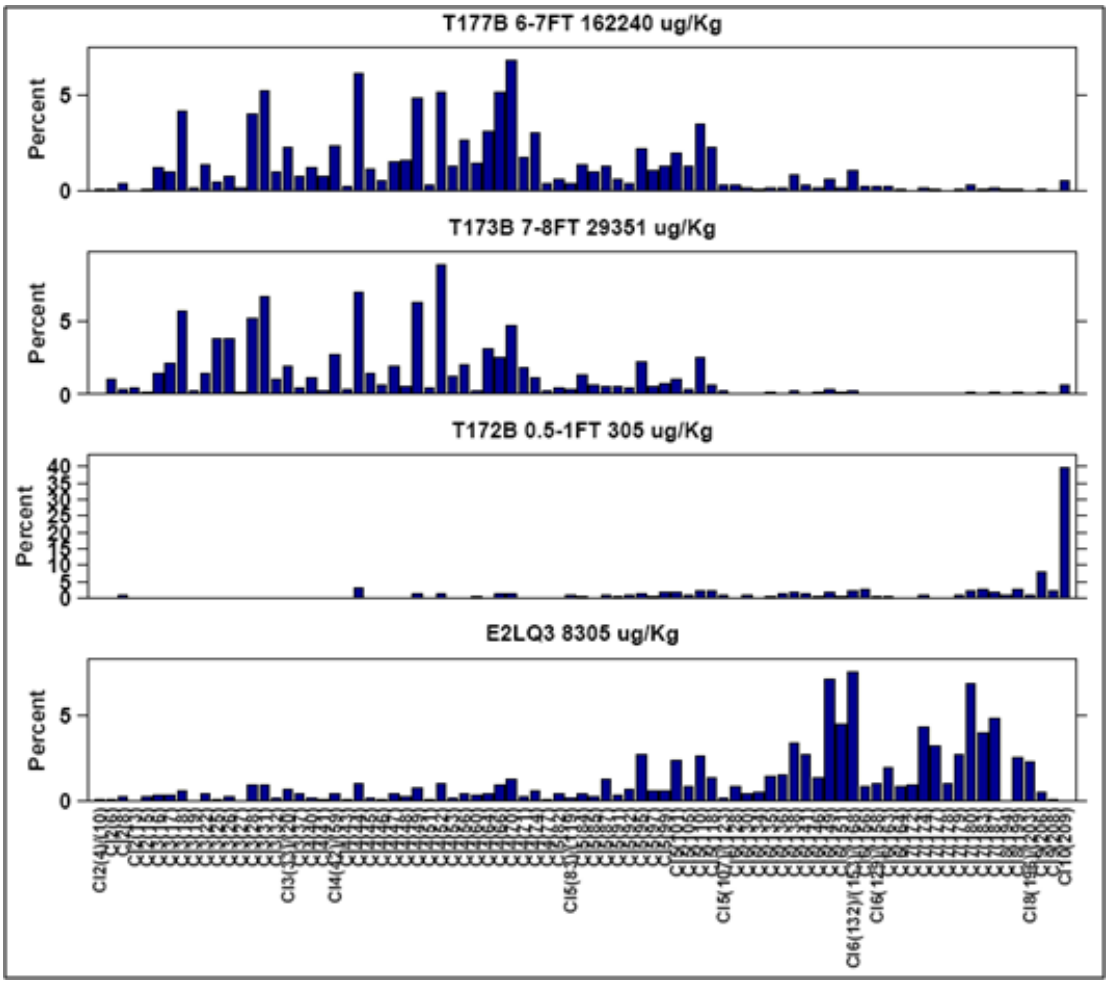


Figure 3-39. Bar Graphs of Four Extreme Samples Labeled on Figure 3-38

This data set was analyzed using the four receptor model methods described in Section 2.5.3.5. Three of the four methods were able to resolve a four compositional solution for this data set. The fourth method (Unmix) was unable to find a feasible solution. The congener profiles resolved by PVA, ALS and PMF are shown in Figure 3-40. All three methods resolved similar congener patterns as "source profiles" and those profiles generally matched those observed in the four extreme samples identified in Figures 3-38 and 3-39. Of these three models, ALS and PVA provided the best estimates. PMF resolved patterns similar to the deca-PCB and Aroclor 1260 patterns, but with notably higher proportions of lower chlorinated congeners not observed in the actual source and/or the most extreme samples in the data set.

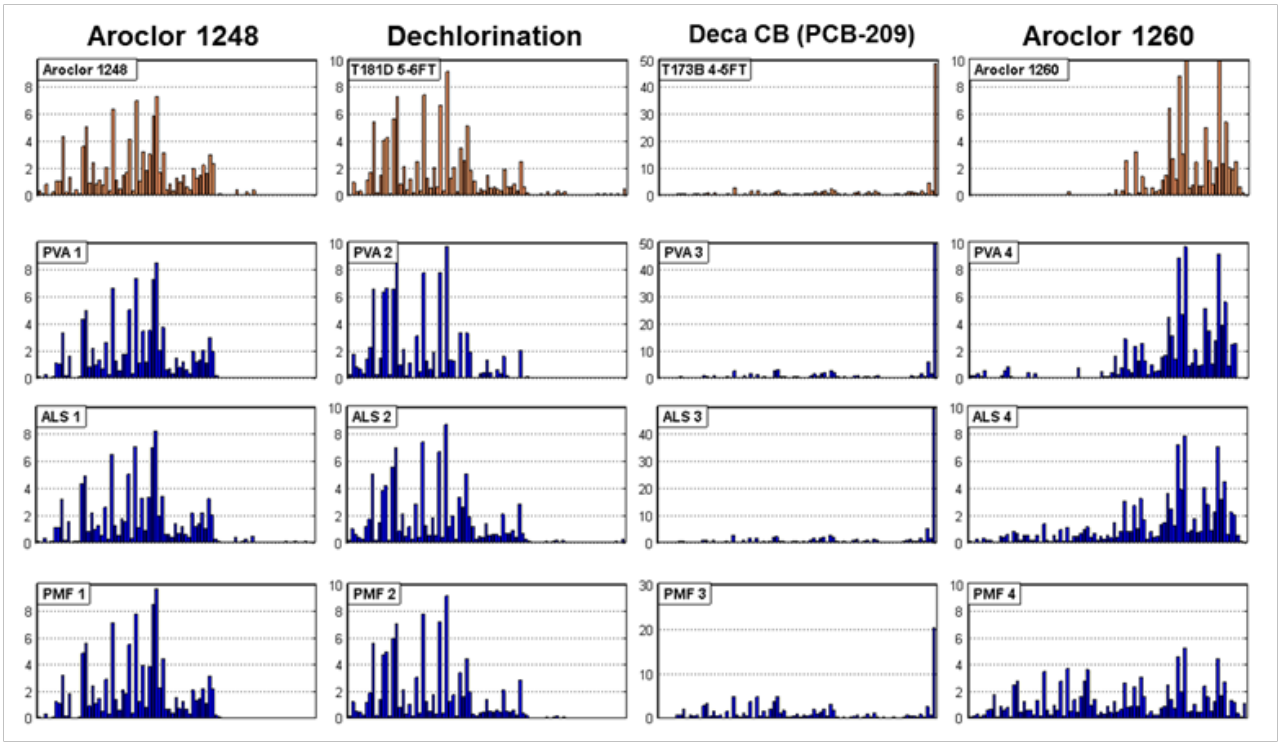


Figure 3-40. Four Congener Profiles (End Members, Source Profiles) Derived from Three Receptor Model Methods (PVA, ALS and PMF), as well as Their Reference Source Composition (e.g., Aroclors 1248 and 1260)

Unmix could not find a feasible solution for this data set. It is suspected that the Unmix method is a mathematical method of finding "edges" in multivariate space. In terms of a four source system, this process involves finding faces of a tetrahedron, which in turn requires a data set with good sample representation along faces of the tetrahedron. As is evident in the PCA scores plot (Figure 3-38), this is not the case for this data set. The data cloud is sparsely populated in the area of the Strong Brook area samples. This is a function of the sampling plan designed for other purposes and not explicitly for ACF (extremely dense sampling in the dredge area; extremely sparse sampling elsewhere) as discussed earlier in this section. Given sampling density inherited for this project, the recommendation is that the data analyst opt for PVA, ALS or PMF as preferred methods over Unmix.

Figure 3-41 shows the spatial distribution of each of the four end members as resolved from the PVA model along a north-south cross section through the dredge area. The predominance of dark and light blue patched areas confirms the observations on the PCA scores plot (Figures 3-38 and 3-39) that the predominant patterns in these cores are the Aroclor 1248 (light blue) and 1248 dechlorination patterns (dark blue). The deca/PCB209 pattern (yellow), when present, is generally observed in deeper samples in the core. Aroclor 1260 (red) is never a predominant pattern within dredge area sediments. However, when it is present, the Aroclor 1260 pattern tends to be in shallower samples. Samples that were omitted as a result of the data screening process are shown as gray patched rectangles and tend to be lower concentration samples (total PCB concentrations [mg/kg] are shown to the right of each sample).

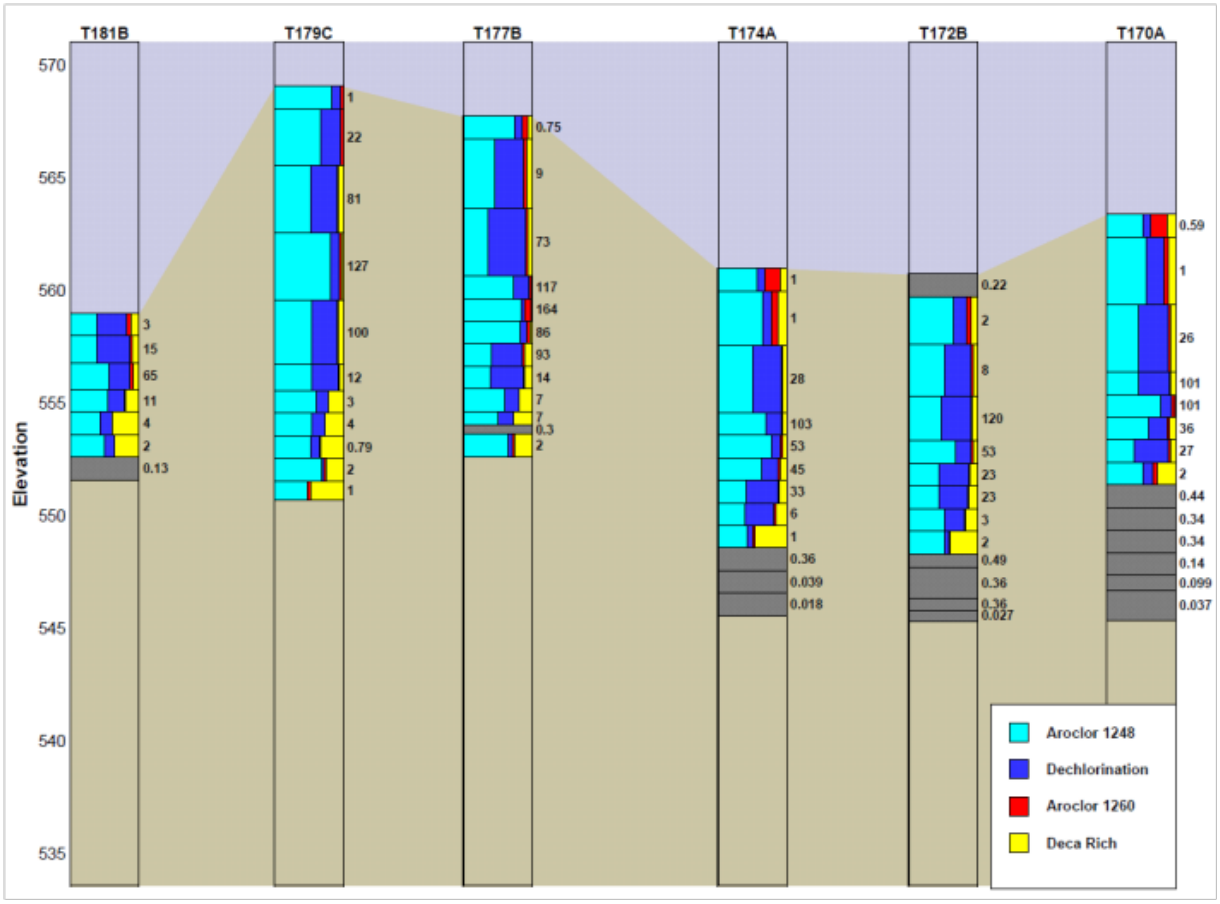


Figure 3-41. South-North Cross Section Showing Percent End-member Compositions and Total PCB Levels (ppm) in Dredge Area Sediments

Aroclor 1260 is not well represented on the sediment/depth profiles (Figure 3-41) because all cores were collected from the dredge area (Figure 2-13). As was evident in the PCA, Aroclor 1260 is predominant in the surface samples collected from the Strong Brook area (south of the dredge area and represented by surface sediment samples only). The absence of an Aroclor 1260 match in the surface sediments is likely because the top 6 inches were sampled in the dredge area, which represents not only relatively recent contamination (e.g., the top 2 cm) but also older deposition. Other work suggests that the Aroclor 1260 source may only have been active in recent years. The spatial distribution of these four patterns in surface sediments is shown on Figure 3-42. As compared to the core profile view (Figure 3-41), this surface sediment map clearly shows that the Aroclor 1260 pattern (right panel – red) is dominant in the Strong Brook area.

As was discussed in relation to HPS, one hopes to find internal consistency across all lines of evidence. However, integrated data analysis often proves most valuable when addressing lingering questions or ambiguities. The remainder of this section provides examples where further chemometric interpretation and separate lines of evidence helped answer such questions.

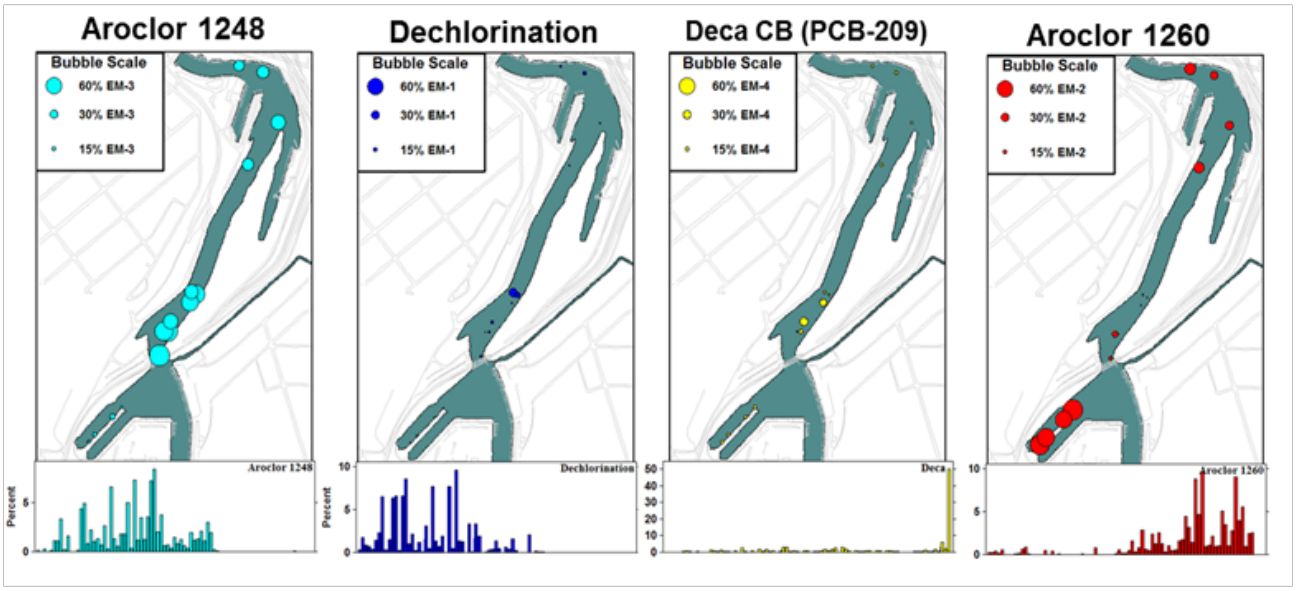


Figure 3-42. Maps of Four PVA Derived Sources in Surface Sediments of Ashtabula River

Source Explanation for Deca Source Pattern

One of the congener patterns resolved in this analysis was dominated by a single congener (deca-chlorobiphenyl; PCB209) which was preferentially observed in deeper (older) sediment taken from cores in the dredge area. This suggests an older historic source, but the specific source, industrial process and/or alteration process, could not be identified. A deca-dominated pattern is not consistent with any known, published Aroclor standard, although it had some resemblance to rarely used PCB products in the Aroclors 1269 to 1271 range. Another possibility could be the production of these highly-chlorinated congeners as part of the titanium tetrachloride manufacturing process [39]. The literature was reviewed, and several publications revealed where a similar, deca-dominated congener had been identified in other study areas [35, 39, 67]. These studies offered some possible interpretations of their version of this pattern, but nothing that could be clearly tied to known sources or alteration processes in Ashtabula. Ultimately, the choice was made to describe and map this congener pattern, but refrain from offering any speculative interpretations. The reason was that when observed in sediments, the deca pattern is usually in older samples (at great depth in sediment cores) and in samples with low relative total PCB concentration (Figure 3-41). Shallower sediment samples often exhibited total PCB concentrations that were two orders of magnitude, or more, higher. In terms of PCB mass that would require remediation, this unusual, highly chlorinated PCB pattern was not a major contributor. Given remediation/dredging concerns as the primary driver in this study, solving the mystery of this fingerprint's origin was not a priority given overall project objectives.

Consideration of a Possible Fifth Source Pattern

As indicated in Section 3.2.7.5, the statistical goodness-of-fit diagnostics performed in conjunction with PVA (Figure 3-37) indicated a minimum of four end members in this system. Some congeners, however, still exhibited a noisy fit (see for example the PCB4/10 and PCB8 scatter plots on Figure 3-37). Therefore, the efficacy of a fifth source pattern was evaluated by

running one PVA for five end members. The result was resolution of four end members very similar to the previous four, and a fifth that was similar to Aroclor 1242 (Figure 3-43).

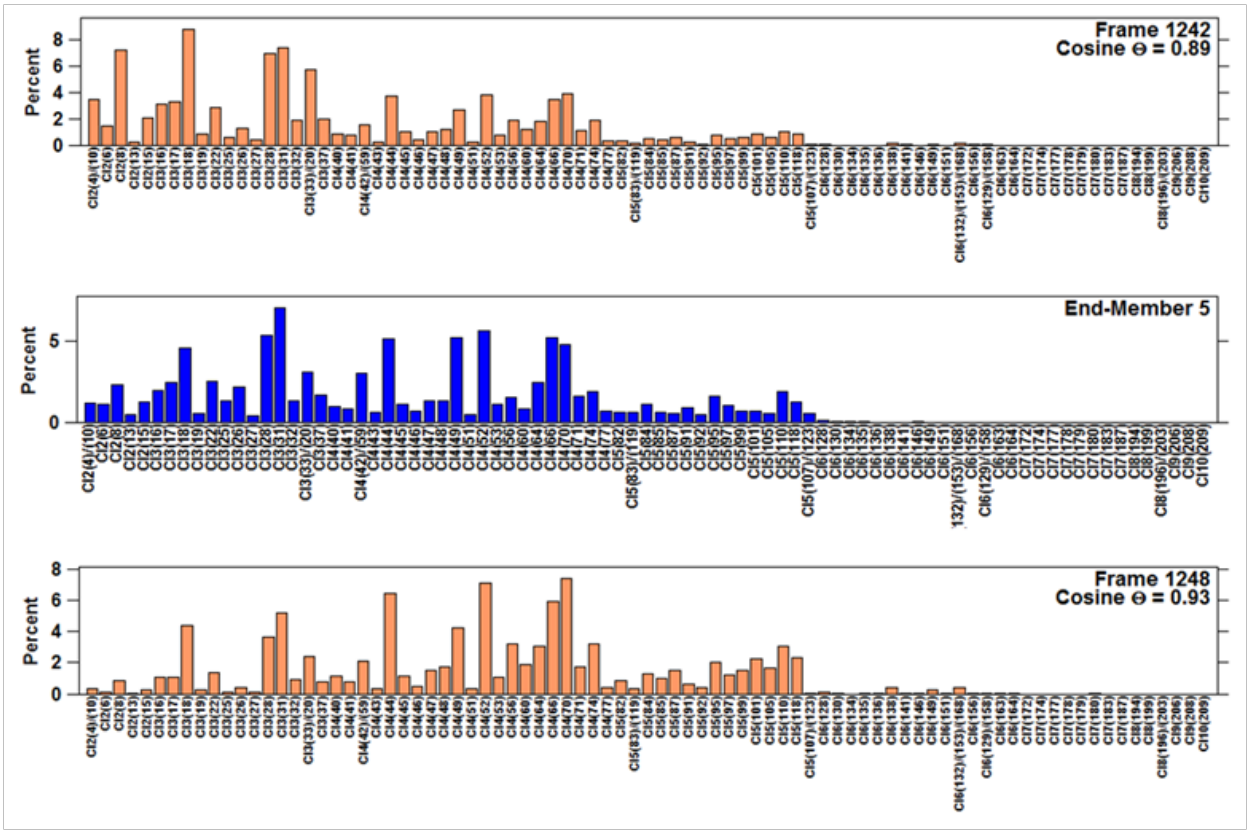


Figure 3-43. Congener Pattern Resolved as a Fifth End Member (blue bar graph) Using PVA Applied to Ashtabula Sediment Data Set
(Two Aroclors with patterns that showed similarity are plotted above and below EM-5.)

The fifth congener pattern is similar (bottom panel of Figure 3-43: cos θ = 0.93) to one of the source patterns already seen in the four end member model (Aroclor 1248). The primary difference is that this new pattern exhibits slightly higher proportions of two congeners that are more characteristic of an Aroclor with very similar chemical pattern: Aroclor 1242 (top panel of Figure 3-43 cos θ = 0.89). The new EM-5 pattern is actually intermediate in composition between Aroclors 1242 and 1248, with more lighter congeners (such as PCB4/10 and PCB8) than is present in Aroclor 1248, but not as much as is observed in Aroclor 1242. The relative contribution of this pattern is shown in Figure 3-44.

The Aroclor 1248 and the new EM-5 (altered Aroclor 1242) are very similar (cos θ = 0.89). This is an issue called "colinearity." When two resolved source patterns have very similar compositions, it increases the uncertainty of reported mixing proportions between these two end members. Ultimately, it seemed best to report the four end member model. By doing this additional exploration of a five end-member model, it is clear that Aroclor 1242 may be a more

important contributor to Ashtabula River than thought. There is clear evidence of an Aroclor 1242 source that has weathered to the point that now looks more like Aroclor 1248. This has been described elsewhere in the literature [4, 8, 30] and was discussed earlier in Section 2.5.2.3.

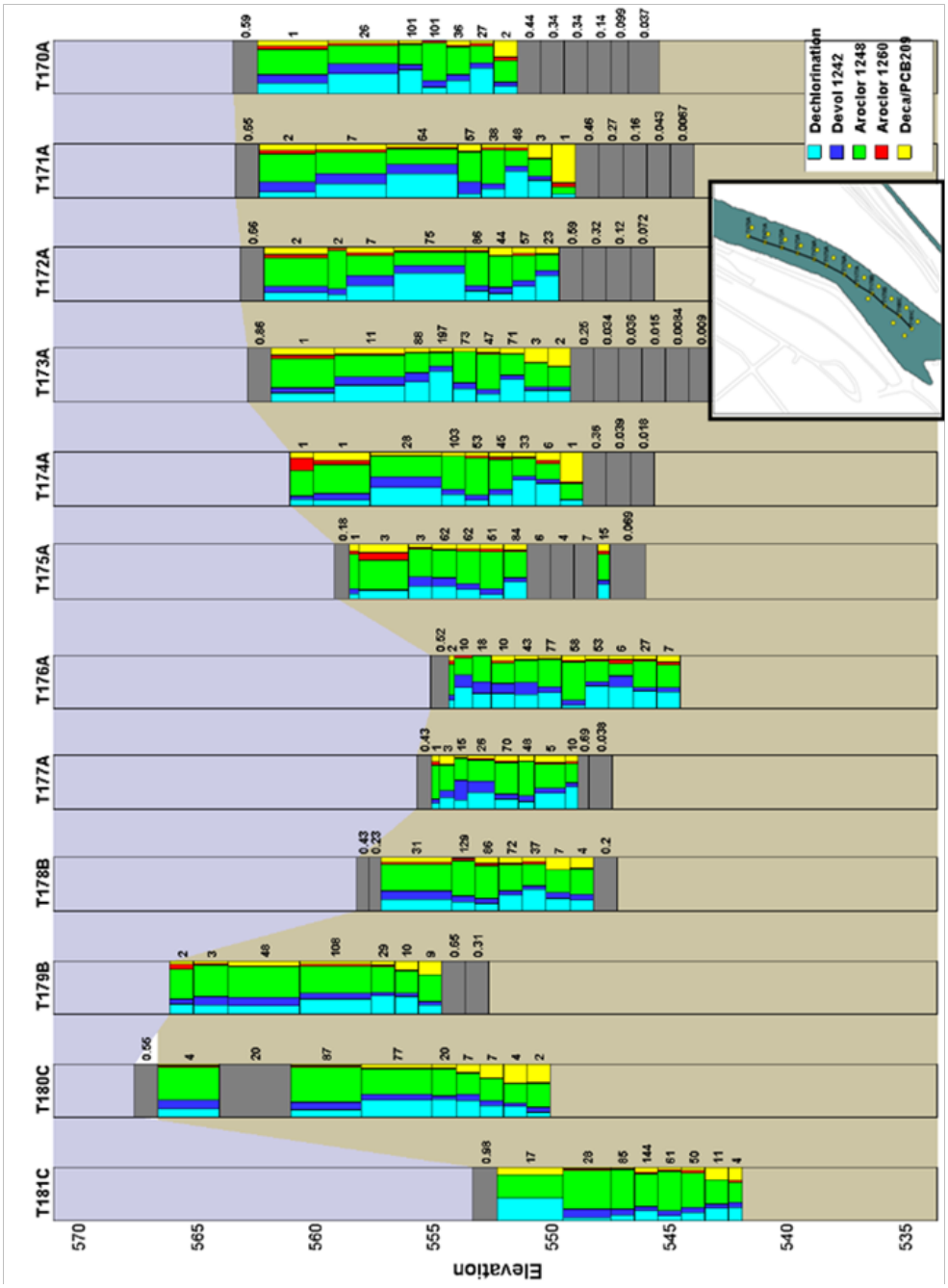


Figure 3-44. Cross-section Showing Percent Contribution of Five Chemical Fingerprints Resolved through PVA of Ashtabula Sediment Data Set

(Each pattern is color-coded. The "new" EM-5 [intermediate between A1242 and A1248] contributions are dark blue. Total PCB concentration [ppm] for each sample is indicated to the right of each sample. Gray shaded samples were omitted from the analysis because they were determined to be outliers [low concentration, or many non-detects].)

3.2.7.6 Integrated Data Analysis and Interpretation

As discussed in Section 2.5.3.6, integrated data analysis and interpretation is the process of synthesizing information from multiple lines of evidence to arrive at scientific interpretations that answer the key questions of a forensics investigation (i.e., PCB sources, alteration mechanisms, timing/history of releases). Lines of evidence typically considered include site history, published scientific literature, sediment transport/hydrodynamics, analytical chemistry which is then used to interpret total PCB concentration gradients and inspection of sample chromatograms/compositions, and chemometric analysis.

At Ashtabula, although we do not have as much data for some lines of evidence as we did for HPS (especially for site history and sediment transport), the lines of evidence consistently support several key conclusions. The analytical chemistry line of evidence may, in fact, be stronger at Ashtabula compared to HPS because of the larger number of congeners (83 versus 38) and samples (252 versus 85) for the chemometric analyses. The primary congener pattern contributing to sediments in the dredge area was consistent with an Aroclor 1248 source, and assumed to be associated with controlled sources within Fields Brook. This was confirmed by direct inspection of PCB compositions (Section 3.2.74) by four separate chemometric analyses (PCA, PVA, ALS and PMF – Section 3.2.7.5). An Aroclor 1260 source in the vicinity of Strong Brook was found to be important to the surface sediments in the study area.

This source observation is consistent with and supported by site history (Section 3.2.7.1). The sediment transport and hydrodynamic information (Section 3.2.7.2) indicates that contamination would be expected to be relatively predictably deposited and distributed away from sources (i.e., that the spatial distribution of the PCB contamination would decline downstream from sources). The PCB concentration distribution showed two general contamination profiles, one associated with historic contamination from Fields Brook and another associated with recent contamination from Strong Brook (Section 3.2.7.3 and Figures 3-25, 3-29, and 3-30). The preliminary PCB composition information (Section 3.2.7.4 and Figures 3-31 through 3-36) indicates two PCB compositional characteristics of the PCB in the sediments: one closely resembling Aroclor 1260 in the sediments near Strong Brook and another resembling Aroclor 1248 in the sediments near Fields Brook, and finally the historic, deeper sediments. The various chemometric analyses further support the initial findings of potential sources adding additional lines of evidence.

There is considerable PCB compositional alteration (e.g., through dechlorination) in some Ashtabula river sediments, suggesting dechlorination of primarily Aroclor 1248; the dechlorination compositional signature was distributed much like the Aroclor 1248 contamination. PCA, receptor models and direction inspection of raw sample compositions all identified a similar dechlorination pattern with key non-Aroclor, less chlorinated, congeners indicating dechlorination. This interpretation was further confirmed by published literature. Dechlorination had previously been reported in Ashtabula sediments [31] by looking at a completely different data set, and using two chemometric methods not used here. The Imamoglu data set [31] had far fewer congeners (24 congeners as opposed to 83). Two congeners that they did have (PCB25 and PCB26) were their primary evidence of dechlorination, and are the same two primary dechlorination indicator congeners in the current data set.

The Aroclor 1260 pattern was confirmed through direct inspection of sample compositions (Section 3.2.7.4) and by four chemometric methods (PCA, PVA, ALS, and PMF). The Aroclor 1260 was associated with sediments in and near Strong Brook, and in combination with Aroclor 1248 in downstream surface sediment. Imamoglu et al. [31] did not report an Aroclor 1260 pattern, but their study included only four cores, none of which were taken near Strong Brook. Another possibility for not observing the Aroclor 1260 pattern could be that their cores were collected in 1998, and this 1260 source appears to be relatively recent and may therefore only be observed in these 2007 cores.

The final congener patterns resolved in this analysis were dominated by a single congener (deca-chlorobiphenyl; PCB209) with lower, secondary contributions from other "heavy" congeners (e.g., PCB199 and PCB206). The deca-chlorinated PCB congener (PCB209) pattern was evident in the data set, whether the data were analyzed by direct inspection of sample congener profiles, or by chemometric analysis. This pattern was observed in deeper sections of cores collected from the dredge area. As with the Aroclor 1260 pattern, Imamoglu et al. [31] did not see the deca pattern in their analysis because PCB209 was not analyzed as part of their study and their cores were much shallower (with a maximum PCB concentration of 10 mg/kg) and never reached the deeper horizons seen in these cores. The high relative amounts of PCB209 were greater than in the highly-chlorinated Aroclor formulations (e.g., Aroclor 1268, and the rare Aroclors 1269 to 1271), and can also not be explained by common environmental alteration processes. There are industrial processes (e.g., titanium tetrachloride production) that may selectively produce these highly chlorinated congeners, and this would warrant further investigation in a comprehensive forensic investigation. This unusual PCB compositional pattern was associated with deep and less contaminated sediment, and was of limited interest from a contaminant source perspective.

Most of this information can be summarized by viewing Figures 3-38, 3-39, and 3-41. The congener compositional information is summarized in Figures 3-38 and 3-39. Most of the samples in Figure 3-38 (around 200 of the 252 samples) are from the middle of the cores and show a congener composition with a mix of Aroclor 1248 (represented at bottom left corner of tetrahedron shape) and slightly dechlorinated Aroclor 1248 (represented at the top left corner of tetrahedron shape). These two congener compositions are shown as the top two bar chart fingerprints in Figure 3-39, and appear similar since they represent the same primary Fields Brook source. The surface samples show more of the Aroclor 1260 pattern (represented at the front right of the tetrahedron) and the deeper samples show a forth compositional pattern characterized by higher levels of congener 209 and other highly chlorinated congeners (represented at the back right of the tetrahedron). The compositions of these two corners of the tetrahedron are shown by the bottom two bar chart fingerprints in Figure 3-39.

The proportion of these four compositional patterns can be better viewed in spatial displays such as the core transect diagram shown in Figure 3-41. These cores were chosen to show the general relationships between end member compositions from south (left) to north (right) in the dredge area, but multiple other transects could be constructed from other cores at the site. Core diagrams are plotted in elevation above sea level on the left, and percent end member composition along the bottom color coded to the legend. The numbers to the right of each core horizon are Total PCB concentrations in parts per million (mg/Kg). The most obvious feature of

these core diagrams is that most of the cores show (>90%) have a source of Aroclor 1248 (although some show dechlorination). Deeper sections of the cores show increasing amounts of the more chlorinated end member composition, but the majority is still Aroclor 1248 and these have lower PCB concentrations. There are only sporadic indications of the very recent additions of Aroclor 1260 in the surface sediments of some cores, ignoring the slight indications of Aroclor 1260 at depth (which is within the margin for error). Error bars on the percent end member contributions are difficult to estimate, but are likely on the order of 10 to 20% in this type of analysis. Compared to the previous HPS case, this allocation of end member compositions at Ashtabula should be more quantitative because of the more unique patterns present in the end member compositions.

In summary, it appears there was a significant source associated with Fields Brook that contributed primarily Aroclor 1248 contamination to the Ashtabula River. The majority of this contamination is several feet down in the Ashtabula River. Deeper sediments also show relatively low amount of a more chlorinated PCB pattern, which may also be from a Fields Brook source. The Fields Brook source(s) appear to have been, for the most part, controlled. It also appears that in recent years, and at the time these samples were collected, there was also a source of primarily Aroclor 1260, in the vicinity of the confluence of Strong Brook. These appear to be the two primary sources of the PCB in the Ashtabula River study area, contributing the four distinct PCB congener compositions that were observed in the Ashtabula River sediment.

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