SOURCE APPORTIONMENT OF POLYCHLORINATED BIPHENYLS IN NEW JERSEY AIR AND DELAWARE RIVER SEDIMENTS

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ABSTRACT OF THE DISSERTATION

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Polychlorinated Biphenyls (PCBs) are chlorinated organic compounds that are classified as toxic, bioaccumulative, and persistent in the environment. Although the commercial production and use of PCBs was banned in the late 1970s, PCBs are ubiquitous in the environment as they cycle through air, water, soil, and sediment at levels that often exceed applicable environmental standards. The purpose of this dissertation was to identify PCB sources to the sediments of the Delaware River and the air of the New Jersey/Delaware River basin region. This was accomplished in part by analyzed existing data sets via a source apportionment tool called positive matrix factorization (PMF). In Delaware River sediment (Chapter 2), PMF resolved seven factors. Three were unweathered Aroclors, two were non-Aroclor sources related to pigment use and production, and the remaining two were probably originally related to Aroclors but were highly weathered.

PMF was also applied to data from the Delaware Atmospheric Deposition Network (DADN) collected in Camden (1999-2011) and New Brunswick (1997-2011)

(Chapter 3). PMF resolved four factors at each site. The factors that dominate PCB burden in the atmosphere at both sites resemble unaltered Aroclor 1242 and vaporized Aroclor 1248. During 2004-2011, only one of the eight factors was declining. All others were unchanged or increasing. This suggests natural attenuation alone will not control atmospheric PCB concentrations, and additional efforts are needed to control PCB emissions. Moreover, the Total Maximum Daily Loads promulgated for PCBs in the tidal Delaware River are not achievable in the foreseeable future due to continuing atmospheric deposition.

In Chapter 4, PCBs 4 and PCB 11 were measured by reanalyzing the original gas-phase DADN samples from Camden, New Brunswick, and Lums Pond. To ensure that these dichlorobiphenyl congeners can be accurately quantified in these samples, a careful study of the breakthrough of PCBs when using polyurethane foam (PUF) as a sorbent for high-volume air sampling was performed. Gas-phase concentrations of PCB 11 ranged from non-detect to 146 pg m^{-3} and did not display a strong urban to rural gradient. PCB 4 concentrations ranged from 0.18 to 168 pg m^{-3} and were highest at Camden.

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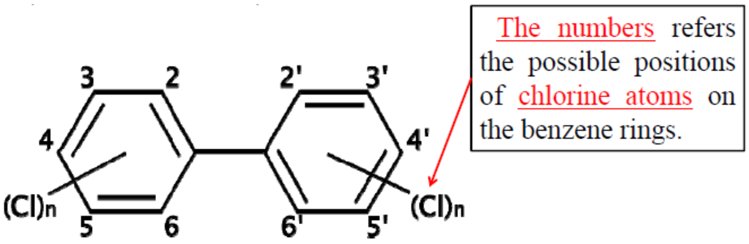
Chapter 1: Introduction

1.1 Background of Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are one of the original dozen persistent organic pollutants (POPs) addressed by the United Nations Environment Program's Stockholm Convention.[1] PCBs have 209 congeners, and they were sold in the United State as the mixture of various PCBs congeners called Aroclors. In the Aroclor naming scheme, the first two digits referred to the number of carbon atoms (12) and the percentage of chlorines by mass in the mixture are referred in the last two digits.[2] Although many Aroclors were produced before 1970, the most commonly used Aroclors were 1016, 1221, 1232, 1242, 1248, 1254, and 1260.[3] (Aroclor 1016 is the exception to the numbering convention, and the number 1016 has no relevant meaning). The peak of Aroclors production in the United State was in 1970 when about 43,000 tons were produced.[4] The total of PCBs production in the United States before manufacture was banned in 1979[5] was about 650,000 tons.[6] The structure of PCBs is shown in figure 1-1 which the numbers represents the positions of chlorine atoms substitution in the biphenyl rings.[7]



The numbers refers the possible positions of chlorine atoms on the benzene rings.

Figure 1-1. Structure of polychlorinated biphenyl (PCB).

Before 1970, because of useful physical and chemical properties of PCBs such as high boiling point, electric insulating, non-flammability, chemical stability, etc, PCBs were produced and used in hundreds of industrial and commercial applications such as coolants, insulation fluids for transformer and capacitors, plasticizers in paints, pesticides, pigments and dyes, carbonless copy papers, etc.[5] However, during many of these uses, humans can be exposed to PCBs via pathways such as breathing contaminated air, consuming contaminated food, touching contaminated soils, and contacting via skin to equipment that contains PCBs, etc. These exposures may lead to a variety of adverse human health effects on the immune system, reproductive system, nervous system, etc.[8] In addition, PCBs can cause cancer, so PCBs were banned for production and applications in the late 1970s.[5]

Before 1979, the main PCB sources were the production and use of PCB Aroclors that released into the environment into air, water, and soil. PCBs can also be introduced into the environment from non-Aroclor sources. For example, PCB congeners such as PCB 11 and 206, 208, and 209 are produced from an inadvertent production of some pigments. PCB 11 is found in diarylide yellow pigments which may accidentally release PCB 11 through using customer products that are printing with inks containing these pigments.[1] In addition, PCB 11 is also found in the currently commercial paint pigments.[9] PCBs 206, 208, and 209 are produced during titanium tetrachloride ($TiCl_4$) production, and these heavy PCB congeners tend to accumulate in river sediments.[10]

Currently, PCBs are continuously released in the environment from many sources such as poorly managed municipal and industrial wastes, illegal and improper dumping of PCB wastes, disposal of PCB wastes in the landfills, poorly designed landfills for hazardous waste, accidentals leaking of PCBs from old electric equipment, and poorly maintained hazardous waste sites.[11] In addition, PCBs cycling through air, water, soil, and sediment.[11]

1.2 Environmental Cycling of PCBs

PCBs persist and accumulate in the environment through air, water, sediment, and soil circulation by chemical and biological processes such as volatilization, dry or wet deposition, and biodegradation (Figure 1-2).[12] PCBs can be released from the water column and soil surface to the atmosphere through volatilization, and they may recycle back to the water and soil by dry or wet deposition from the atmosphere. In addition, the biodegradation of heavy chlorinated PCB congers to the lower chlorinated PCB congeners may slowly occur in the soil and river sediments through reductive dechlorination under anaerobic conditions.[13]

All of these processes are considered to be “weathering” processes, and some of these will remove high molecular weight PCBs or low molecular weight PCBs that will alter the congener fingerprints. For example, the primary Aroclor released into the Upper Hudson River was Aroclor 1242. Weathering, primarily via bacterial dechlorination, has produced a distinct congener pattern in the Upper Hudson River that resembles Aroclor 1242 but has higher proportions of dechlorination products such as PCBs 4 and 19.[14]

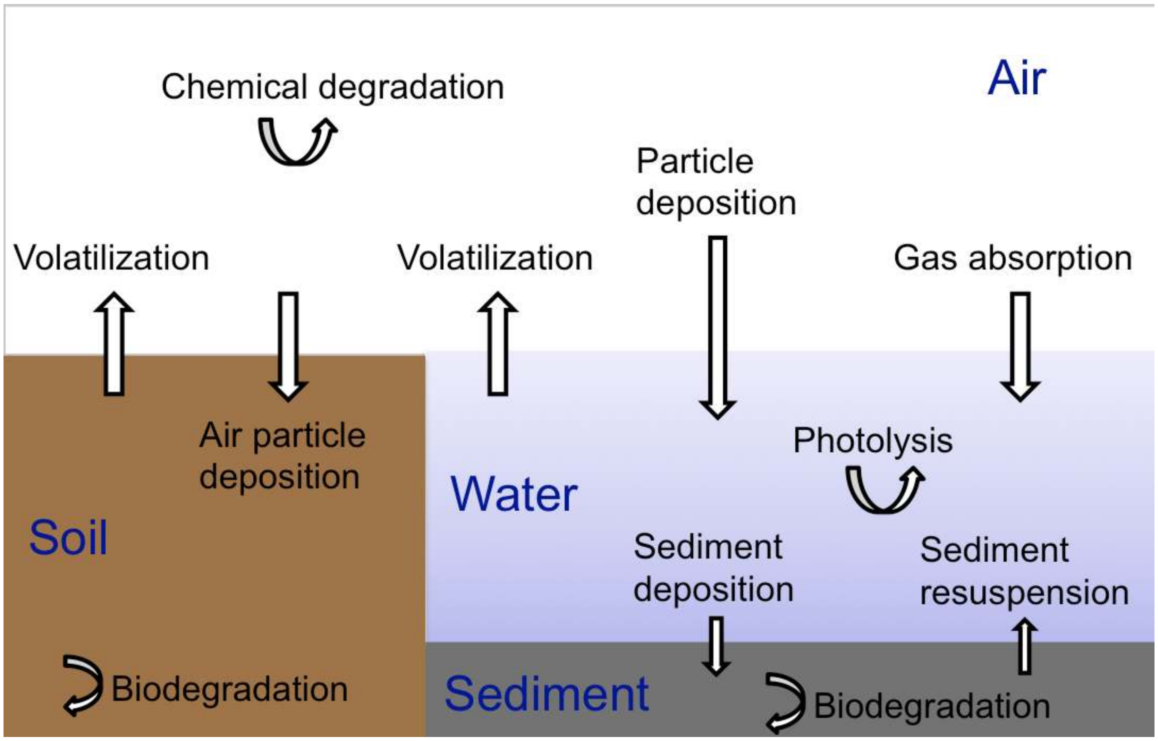


Figure 1-2. PCBs cycling in the environment through air, water, sediment, and soil.[12]

PCBs widely disperse in the atmosphere though two phases which are gaseous and particle phases. The highly chlorinated congeners tend to accumulate in the particle phase whereas the low molecular weight PCBs remain in the gaseous phase in the atmosphere due to their higher vapor pressures. In the atmosphere, PCBs may react with the hydroxyl (OH) radical with half-lives that vary depending on the structure of the PCB molecule and range from 3 days for trichlorobiphenyls to 500 days for heptachlorobiphenyls.[15]

The dominant sources of PCBs in the water column come from the atmospheric deposition and accumulated river sediments.[16] PCB losses in the water column may occur from the air-water exchange through volatilization as well as the accumulation of heavy PCB congeners in river sediments. Since the higher chlorinated PCBs are less soluble in water, they tend to accumulate in the river sediments whereas the lower chlorinated PCBs are more soluble in water and tend to accumulate in the water as well volatilizing into the atmosphere. Two degradation processes of PCBs can happen in the water column. The dominant process is reductive dechlorination in which higher chlorinated PCBs are transformed into lower PCBs, which occurs slowly in anaerobic river sediments.[13] The second less important process is photolysis.[17]

Although the accidental leaking from the old PCB-containing equipments such as capacitors, transformers, etc. through landfills and hazardous waste sites may spill PCBS into the soil, the main source of PCBs in the soil is often atmospheric deposition.[18] Again, the heavy chlorinated PCBs tend to accumulate in the soil whereas the lower chlorinated PCBs may volatile to the atmosphere. PCBs are slowly degraded in soil as well as in sediments.[7] These are additional examples of weathering processes that may remove high or low molecular weight of PCBs and alter congener fingerprints.

1.3 The Delaware River

A Total Maximum Daily Load (TMDL) is the maximum amount of pollutant that can enter to the water body without exceeding the federal water quality standard (WQS).[19] Because the high PCB concentrations in the Delaware River exceed the WQS by two or three orders of magnitude, this river received TMDL for PCBs promulgated by the Delaware River Basin Commission (DRBC) in 2003 for zone 2-5 and in 2006 for zone 6.[19, 20] The TMDL for PCBs was required by the Clean Water Act (CWA) to minimize PCB concentration and improve water quality for safe human consumption in this estuary.[19] All PCBs loads from both point sources and non-point sources are included in a TMDL to meet the water quality standard. To calculate the TMDL, DRBC undertook a massive data collection effort to monitor PCBs in the air, water, discharges, sediment, and biota of the Delaware River. The municipal and industrial dischargers along Delaware River with National Pollutant Discharge Elimination System (NPDES) permits are also required by DRBC to measure all 209 PCB concentrations in their effluents using EPA method 1668A once or twice a year.[21] This long data history has helped to accurately estimate PCB loadings to the tidal Delaware River in order to develop, promulgate, and implement the PCB TMDLs.

Many studies of our group have helped to increase our understanding of PCB cycling in an urban estuary through air, water, dischargers, and sediments. Four Ph.D students (Amy Rowe, Songyan Du, Jia Guo, and I) have studied different aspects of PCB cycling in the river. The understanding of the interaction of PCBs in air, water, and sediment was studied by Amy Rowe.[22] Her studies helped to understand more about the air-water exchange in the Delaware River as well as the understanding of atmospheric deposition of PCBs.[23, 24] Songyan Du's studies helped to understand PCB sources in the air and water by using an efficient source apportionment tool called positive matrix factorization (PMF).[25-27] Jia Guo studied the fate and transport of PCBs in the air, water, and sewers in Delaware River basin.[12] She revealed evidence that PCB 11 is a contaminant in many customer products that may lead to human exposure, and she also investigated the dechlorination of PCBs sewers of cities on the Delaware River.[12] Our group also has already published the evidence of an inadvertent PCB source of PCB 11[1], and the evidence of dechlorination signal in the groundwater, landfills, and wastewater systems.[28]

1.4 Positive Matrix Factorization (PMF)

Positive matrix factorization (PMF) is an advanced factor analysis method that was developed by Paatero and Tapper.[29] The PMF2 software (YP-Tekniika KY Co., Helsinki, Finland) was used for this study in order to help to identify PCBs sources in the Delaware River sediments in Chapter 2 and in Camden and New Brunswick Air in Chapter 3. The details of PMF modeling[29] are briefly summarized here and described in more detail in Du et al.[25] PMF defines the sample matrix (X) as the product of two unknown factor matrices (F and G) with a residue matrix (E):

$$X = GF + E \qquad ; X = m \times n,\ G = m \times p, \text{ and } F = p \times n \qquad \text{(Eqn. 1-1)}$$

X is the sample matrix that is composed of m observed samples and n chemical species. The G matrix is the source contribution matrix that is composed of m observed samples and the p factor or strength (concentration) of each source. F is the source profile matrix (fingerprint) that is composed of p factors or sources and n chemical species, and E is a residue matrix. The solution of the PMF model comes from the minimize of the sum of square of the difference (e_{ij}) between the observation (X) and model (GF) weight by the measurement of uncertainty (s_{ij}):[25]

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(e_{ij}/s_{ij}\right)^2 \qquad \text{(Eqn. 1-2)}$$

The ability to include and account for measurement uncertainty is one of the main advantages of PMF. For the present work, the measurement uncertainty is associated with the extraction efficiency of each analyte, and is calculated as the variability in the recovery of the surrogate associated with that PCB congener. The PMF model also accounts for changes in the limits of detection (LOD). Therefore the input to the PMF model consists of three matrices, each with the dimensions m x n: the concentration matrix, the uncertainty matrix, and the LOD matrix.

1.5 Outline of Dissertation

Besides PCB sources in the waterways, other PCB sources in the air and river sediments cannot be ignored. PCB contamination in the atmosphere can contribute the PCB loads to the river through atmospheric deposition.[30, 31] As a result, finding PCBs sources in the air can help to control PCB loads to both air and rivers. The PCB sources that contaminate river sediments also are of concern. To identify PCB sources in the environment, PMF was chosen since this tool has been shown to be effective in many studies.[14, 25-27, 32-34] As a result, this dissertation relies on this tool to identify PCB sources in the sediments in the chapter 2 and in the air in the chapter 3. The ambient concentrations and temperature dependence of PCBs 4 and 11 in the atmosphere of New Jersey were studied in chapter 4. Therefore, this dissertation is includes three separated parts, which are described below.

Chapter 2 attempts to determine the sources of PCB to the Delaware River sediments. In previous work, our research group successfully identified PCB sources in the atmosphere, water, and the dischargers.[14, 25, 26, 28, 35] Adding sediment to list of compartments investigated helps us to understand in the big picture of PCB cycling in the environment. The sediment data for PMF analysis was conducted by the Partnership for the Delaware River Estuary (PDE) in July 2008, August 2008, September 2008, and September 2010.

Although PCB sources in the air have already been studied,[26, 27, 35] more studies in different areas allow us to determine whether PCB sources in the air differ by location. To achieve this purpose, in Chapter 3 atmospheric PCB sources in two New Jersey cities were investigated using PMF: Camden (urban) and New Brunswick (suburban). These two areas are chosen because they have long data histories that allow us determine whether the PCB sources are declining over time. The air samples of these two sites were collected by the Delaware Atmospheric Deposition Network (DADN) at Camden (1999-2011) and New Brunswick (1997-2011). This chapter attempted to apportion the major sources of PCBs to the air in New Jersey and the Delaware River Basin, to investigate the relationship between atmospheric PCB sources and sources to the water column, dischargers, and sediment of Delaware River, and to compare the PCB sources in Camden (Philadelphia)[26] to another major US city, Chicago.[35]

Because the DADN did not measure low molecular weight PCB congeners such as PCBs 4 and 11, in Chapter 4, I conducted the first careful study of breakthrough of PCBs during sample collection using polyurethane foam as a sorbent in order to determine whether the DADN samples could be reanalyzed to provide accurate measurements of these congeners. This study determined that the DADN samples were useful for this purpose, so PCBs 4 and 11 were quantified in samples from the Camden, New Brunswick, and Lums Pond DADN sites. The temperature dependencies of atmospheric concentrations of PCBs 4 and 11 in these locations were investigated, since a strong correlation with temperature can indicate that PCBs arise from passive volatilization from surfaces such as soil and water. PCBs 4 and PCB 11 are of interest because they arise from non-Aroclor sources.

These three chapters were designed to increase our understanding of PCB sources in the region as well as showing the picture of PCB cycling in an urbanized estuary, to determine whether different locations are dominated by different PCB sources, and to determine concentrations of PCBs 4 and 11 in the atmosphere of the region.

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Chapter 2: Source Apportionment of Polychlorinated Biphenyls in the sediments of the Delaware River

Praipipat, P., Rodenburg, L.A., and Cavallo, G.J., 2013. Source Apportionment of Polychlorinated Biphenyls in the Sediments of the Delaware River. *Environ. Sci. Technol.* 47:4277-4283.

Abstract

Polychlorinated biphenyls (PCBs) are toxic, persistent, bioaccumulative compounds that threaten water quality in many areas, including the Delaware River. In 2003, Total Maximum Daily Loads for PCBs were promulgated for tidal portion of the river, requiring the collection of a massive and unprecedented data set on PCBs in an urban estuary using state of the art, high-resolution high mass spectrometry (EPA method 1668 revision A). In previous publications, this data set has been examined using positive matrix factorization (PMF) to apportion PCB sources in the air, water, and permitted discharges to the river. Here, the same technique is used to apportion PCB sources in the sediment. This holistic approach allows the comparison of source types and magnitudes to the air, water, and sediment, and allows conclusions to be drawn about the cycling of PCBs in a typical urbanized estuary. A data set containing 87 chromatographic peaks representing 132 PCB congeners in 81 samples and 6 duplicated samples was analyzed. Seven factors were resolved. Three represent relatively unweathered Aroclors. Two were related to the non-Aroclor sources of diarylide yellow pigments and titanium tetrachloride production. The two remaining factors were probably originally related to Aroclors, but they are so highly weathered as to be unrecognizable as Aroclors, and thus have probably resided in the river for a long time.

Comparing the abundance of the resolved PCB factors in the air, water, discharges, and sediment demonstrates that high molecular weight formulations such as Aroclor 1260 and PCBs 206, 208, and 209 produced during titanium tetrachloride synthesis accumulate preferentially in the sediment, in keeping with their greater hydrophobicity. In contrast, lower molecular weight formulations, including the products of PCB dechlorination occurring in sewers, do not accumulate appreciably. PCB 11 from pigment use does accumulate in sediments and also seems to be distributed throughout the estuary via the atmosphere.

2.1 Introduction

Polychlorinated biphenyls (PCBs) are chlorinated organic compounds that are classified as hydrophobic, bioaccumulative, and persistent in the environment. Many water bodies in US are impacted by PCB contamination including the tidal Delaware River (see Appendix A, Figure A-1), where PCB concentrations in many areas exceed the stream quality objectives by 2-3 orders of magnitude in the Estuary.[1] In 2003, a total maximum daily load (TMDL) for PCBs was promulgated by the Delaware Basin Commission (DRBC) for Zones 2 through 5 of the Delaware River as required under the Clean Water Act to minimize the PCB contamination and improve water quality.[1] Development of these TMDLs required a massive data collection effort. PCBs were measured by the newest methods (EPA method 1668 Revision A) in water, sediment, biota, and National Pollution Discharge Elimination System (NPDES) permitted discharges. In addition, the Delaware Atmospheric Deposition Network (DADN) measured PCBs in the gas and aerosol phases by active sampling and electron capture detection[2, 3] as well as by passive sampling and tandem quadrupole mass spectrometry

(MS/MS).[4] The resulting data sets have been used for source identification using positive matrix factorization (PMF) to identify sources and develop management strategies to limit PCB contamination in the Delaware River.[5-7] These studies have demonstrated the importance of non-Aroclor PCB sources in this river basin[5, 8] and have demonstrated that extensive dechlorination of PCBs occurs in sewers, landfills, and contaminated groundwater.[7]

In this study, source apportionment of PCBs in the sediment of the Delaware River was conducted in order to complete the picture of PCB cycling in an urbanized estuary. Specifically, this analysis investigated the extent to which PCBs from sources such as the atmosphere and specific discharges accumulate in the sediments. The compilation of such an extensive data set on PCBs in many environmental compartments provides a unique opportunity to examine the cycling of PCBs through the river and to match PCB emissions with accumulation in the sediments.

2.2 Methodology

2.2.1 Sampling and Chemical Analysis

Sediment sampling was conducted by the Partnership for the Delaware River Estuary (PDE) in July, August, and September of 2008 as part of their Delaware Estuary Benthic Inventory (DEBI) Program primarily in the lower Estuary from Zone 6 to the lower portion of Zone 4. The Commission augmented PDEs efforts with sediment sample collection in Zone 2-4 in September of 2010 (Appendix A, Figure A-1).

Surficial bottom sediments were targeted (< 7 cm) and were collected using a Young stainless steel grab or a Ponar stainless steel grab samplers, and placed in pre-cleaned amber glass jars and stored on ice. Samples were shipped to a contract lab for analysis via EPA method 1668 Revision A. The initial data set consisted of 81 samples and 6 duplicated samples in which all 209 PCB congeners were quantified in 152 peaks using the SPB-Octyl gas chromatography column and high-resolution mass spectrometry. The surface sediment sampled may represent erosion bottoms, transport bottoms, or accumulation bottom and may be of various ages. In general, the main stem of the Delaware River is erosional, with sediment deposition highly localized within the estuarine turbidity maximum, located in lower zone 4 and upper zone 5 (Appendix A, Figure A-1).

2.2.2 PMF Data Matrix

In general, data sets submitted for factor analysis should have at least as many samples as analytes. Thus the 209 PCB congeners (152 peaks) were pared down to 87 peaks representing 132 congeners in the original 87 samples, and concentrations were used without normalization. The PMF 2.0 software (YP-Tekniika KY Co., Helsinki, Finland) was used in this study. Uncertainty was assigned to be 15% for all data points except those below detection limit. For data points below the detection limit, a value of one-half the detection limit was applied and an uncertainty of 166% was assigned.[9] The median detection limit was 0.2 pg/g of sediment. As a result of these low detection limits, just 56 out of the 7569 points in the data matrix were below detection limit.

2.3 Results and Discussion

Seven factors were resolved from the data set. Criteria used to determine the correct number of factors is detailed in the Appendix A.

2.3.1 Identification of the resolved source profiles

We identified factors by weight of evidence based on their spatial distribution as well as their congener patterns in comparison with those of the Aroclors. The seven resolved source profiles (factors) generated by the PMF model are shown in Figure 2-1. Of the seven factors, three resembled Aroclors, two represented non-Aroclor sources, and two were weathered PCB sources.

Non-Aroclor Factors

Previous work has demonstrated that a significant portion of the PCBs entering the Delaware River are from non-Aroclor sources,[10] so it is not surprising that these non-Aroclor PCB fingerprints are detectable in the sediment. Factor 3 contains a high proportion of PCB 11 and constitutes 1.4 % of the total PCBs in the data set. Previous work has demonstrated the PCB 11 is associated with diarylide yellow pigments. Since there are no manufacturers of these pigments on the Delaware River,[8] the main source of PCB11 to the Delaware River is probably via indirect emissions of PCB 11 from the use of diarylide yellow pigments in customer products such as printed paper. PCB 11 in these products can enter the river via treated wastewater effluents, storm water, and combined sewer overflows (CSOs).[7] Thus we have sometimes used PCB 11 as a tracer for these types of sources[5, 7, 8] However, Factor 3 (PCB 11) is evenly distributed in concentration across the estuary (Figure 2-2). This is somewhat surprising, since most of the treated wastewater, urban stormwater, and CSO inputs enter the river around the urban areas of Philadelphia, PA, Camden, NJ, and Wilmington, DE. In contrast, PCB 11 is evenly distributed in the air of the Delaware valley.[4] This suggests that atmospheric deposition may be an important source of PCB 11. Factor 3 is the dominant source of

PCBs in the sediment in the southern-most portion of the river (Delaware Bay, zone 6). Since it is thought that pigments are the main source of PCB11in the environment, this presence of a PCB 11-dominated factor suggests that the inadvertent production of PCBs during pigment manufacture has an impact on the sediment as well as the water column.

Factor 7 is dominated by PCBs 206, 208, and 209. For convenience, we refer to this as the ‘deca’ signal. This factor accounted for the largest share of PCBs in the data set at 61.3%. It represents inadvertent PCB production during the carbochlorination process used to produce $TiCl_4$ at a plant near Wilmington, DE. Most of the $TiCl_4$ produced is then converted to TiO_2 and used as a white pigment.[5, 11] Ferric chloride is a by-product of this process, and was reportedly sold to water treatment plants in the Philadelphia area as a coagulant. Thus the ‘deca’ signal is found throughout the Delaware River, but is most prevalent near Wilmington, DE, and Philadelphia, PA[5] Factor 7 is highly localized, suggesting that these heavy PCB congeners do not move substantially. Most likely, they are so strongly sorbed to the sediment that they move only when the sediment moves. These heavy PCB congeners are relatively immobile in the environment, and accumulate in the sediment near their sources.

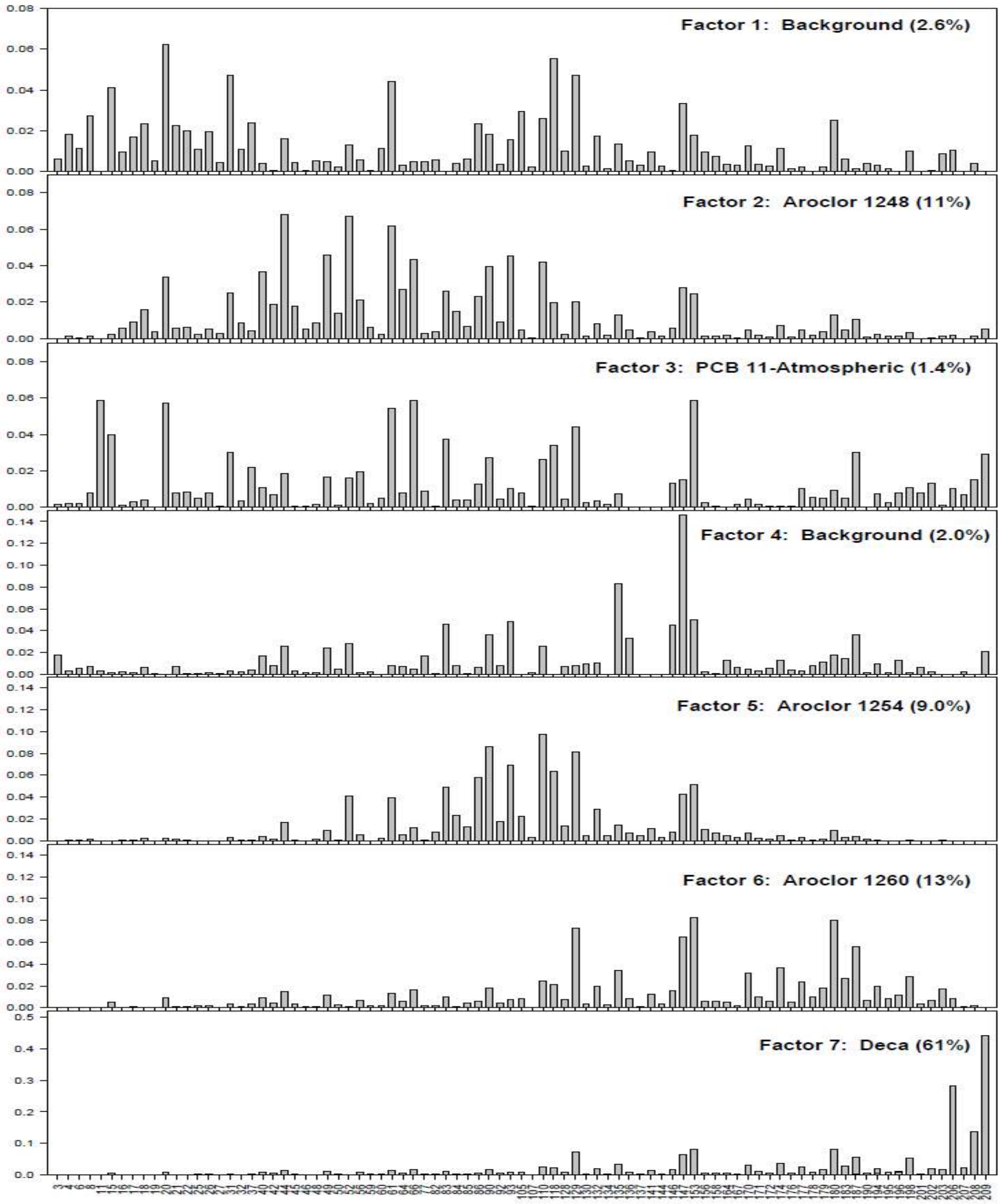

Figure 2-1. Normalized congener patterns of the seven source profiles (factors). PCB congener numbers on the x-axis are plotted versus their fractional contribution to the sum of PCBs on the y-axis. Numbers in parenthesis refer to the percent of the total mass in the data set comprised by each factor.

Aroclor Factors

For Aroclor comparisons, we used the PCB congener patterns measured by Rushneck et al.[12] for the nine commercial Aroclors (1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262, and 1268). Factors 2, 5, and 6 resemble Aroclors 1248, 1254, and 1260, respectively. The correlation coefficients (R^2) for these comparisons are 0.75 for factor 2/Aroclor 1248, 0.91 for factor 5/Aroclor 1254, and 0.98 to factor 6/Aroclor 1260. Factors 2, 5, and 6 constitute 11%, 9%, and 13% of the total PCB mass in the data set, respectively. Thus relatively unweathered Aroclors represent about a third of the PCBs in the sediment. These three Aroclor factors are most prevalent in the industrial and urban areas of Philadelphia and Camden (Figure 2-2). This distribution is in keeping with their use and subsequent discharge in the urban/industrial region and suggests that they did not travel far from where they were discharged, or that they were discharged more recently. During the time required for extensive transport, their congener patterns would undergo weathering and come to resemble factors 1 and/or 4 (see below).

It is somewhat surprising that none of the factors strongly resembled Aroclor 1242 or 1016, which together accounted for about 64% of PCB production in the United States.[13] Factor 1 somewhat resembles Aroclor 1242 ($R^2 = 0.34$). However, factor 1 contains far more high molecular weight congeners, many of which are virtually absent in Aroclor 1242 and 1016. Thus it is unlikely that factor 1 represents unweathered Aroclor 1242. Instead, it appears to represent a weathered combination of several Aroclors, including 1242. When we attempted to describe factor 1 as a linear combination of the four main Aroclors (1242, 1248, 1254, and 1260, keeping in mind that Aroclor 1242 is very similar to Aroclor 1016), the best fit ($R^2 = 0.61$) was a combination of 50% Aroclor 1242, 22% Aroclor 1254, and 21% Aroclor 1260.

Using the same approach, factor 4 was best described as a mixture of 1% Aroclor 1242, 14% Aroclor 1248, 17% Aroclor 1254, and 55% Aroclor 1260, but the R^2 for this mixture vs. the factor profile was just 0.38. This suggests that these two factors originally came from Aroclor sources, but are so heavily weathered that they are no longer recognizable as an Aroclors. Factors 1 and 4 account for 2.6% and 2.0% of the PCBs in the data set, respectively. Their advanced stage of weathering may suggest that they arise from older sources and have resided in the river longer than some of the other factors. Factors 1and 4 are evenly distributed along the Delaware River (Figure 2-2). Thus we hypothesize that these factors represent PCB background.

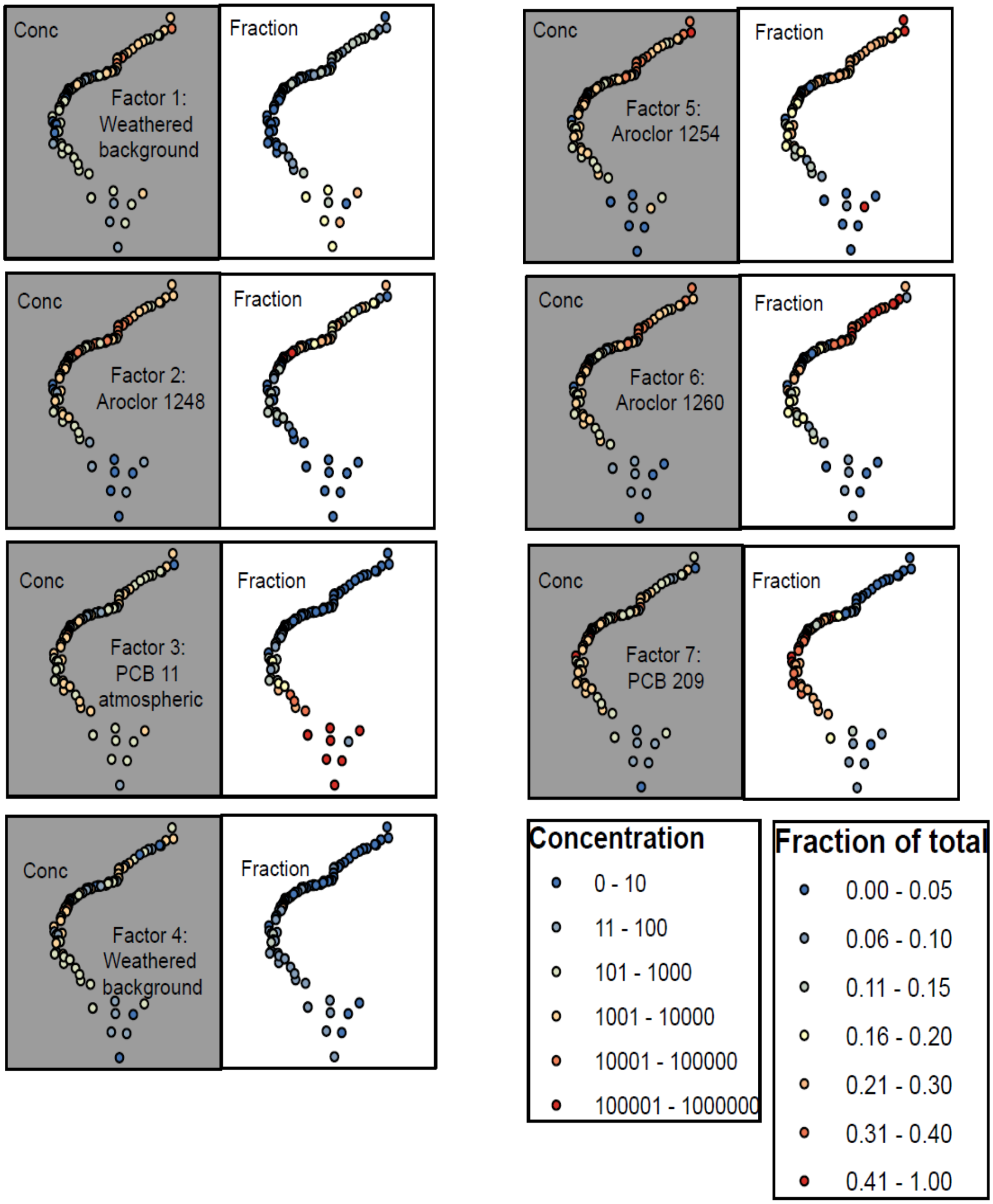

Figure 2-2. Spatial distribution of the resolved factors in terms of concentrations in picograms per gram (pg/g) (gray panels) and fraction of total PCBs (white panels).

2.3.2 Comparison to other studies

In most systems where PCBs have been measured and studied extensively, such as the Fox River in Wisconsin or the Hudson River in New York, the major source of PCBs is known. In contrast, when the TMDL process began, there were no obvious major sources of PCBs to the Delaware River. For this reason, the Delaware River was thought to be representative of urban waterways throughout the U.S. in terms of PCB sources. On the basis of the present work, however, it may fairly be argued that the carbochlorination process is the obvious major source of PCBs, especially high molecular weight congeners, to the sediment, if not the water column. Ironically, this source was not identified until after the TMDL process began, largely because older methods for measuring PCBs did not usually quantify PCB 209. The Delaware River is not unique in containing high concentrations of PCB 209. PCB 209 has been detected as a major congener in the water, sediment, and biota of the Houston Ship Channel,[14] although it is not known whether its presence there is related to titanium tetrachloride production.

Many studies have used factor analysis to identify PCB sources and dechlorination signals in aquatic sediment. Factor analysis has also been used to investigate PCBs in aquatic sediments of Lake Hartwell[15] and the Fox River[16], but these investigations were focused on detecting evidence of microbial dechlorination, not to apportion sources, since the main sources were already known. Positive Matrix Factorization (PMF) in particular has been used to identify PCB sources in the Great Lakes, Sheboygan River (Wisconsin, USA), and Nakdong River (Korea). All of these studies utilized much smaller data sets. For the Great Lakes study, Soonthornnonda et al.[17] compiled data sets containing between 28 and 37 PCB peaks (each representing one or more congeners) in sediment cores from 10 locations. They resolved three or four factors in the data sets from the individual lakes (Erie, Huron, Michigan, and Ontario), whereas the single data set of all four lakes yielded five factors. They found that all four lakes are dominated by Aroclors 1248, 1254, and 1260. Like us, they did not identify a factor associated with Aroclor 1242/1016. They did detect evidence of microbial dechlorination in sediment cores from Lakes Ontario, Michigan, and Huron. In the Sheboygan River, Bzdusek et al.[18] collected 9 sediment cores and measured 39 PCB congeners in 34 peaks in a total of 132 sediment samples. Two factors were resolved from the PMF model. One represented a 50:50 combination of Aroclors 1248 and A1254, and the other represented microbial dechlorination. Subsequently, Henry and Christensen[19] analyzed 32 congeners in 106 sediment samples from the Sheboygan River and found 5 factors. One was again associated with a 50:50 combination of Aroclors 1248 and A1254, and the other 4 represented various pathways of microbial dechlorination. Again, no factor resembling Aroclor 1242/1016 was observed. Jin et al.[20] used three different models to identify PCB sources in the sediment of the Nakdong River: principal component analysis/absolute principal component scores (PCA/APCS), positive matrix factorization (PMF), and multiple linear regressions. The three models gave similar results. However, they reported that PMF showed more stable results than PCA/APCS. They found the highest amounts of Aroclor 1260 in the samples that had the highest PCB concentrations, which were collected near landfills, leachate-treatment facilities and industrial facilities. This is in agreement with our observation that the highest proportions of Aroclor 1260 are found in the urban/industrial areas of the Delaware River.

2.4 Implications

The data sets collected by the DRBC for the PCB TMDL are extensive and unparalleled. They allow us to compare PCB signals across air, water, sediment, and NPDES-permitted dischargers. There are some shortcomings of the various data sets, however. The water column, discharger, and sediment data sets all utilized EPA method 1668 Revision A and measured all 209 PCB congeners in hundreds of samples. In contrast, PCBs were measured in the atmosphere in two ways. Active air sampling was conducted under the Delaware Atmospheric Deposition Network (DADN) using high-volume air samplers and electron capture detection (ECD).[2] The use of a different detector (ECD instead of mass spectrometry) limits our ability to compare the DADN data and the factors derived from it via PMF analysis[6] with the factors derived from the water column, discharger, and sediment data sets. Gas-phase PCBs were also measured in 32 passive air samples from the Philadelphia/Camden area using tandem-quadrupole mass spectrometry (MS/MS).[4] However, PMF analysis of that data set isolated just two factors representing Aroclors 1248 and 1254.

In comparing the different data sets, it should be remembered that PCBs were measured in NPDES-permitted dischargers, but loads from these dischargers are estimated to represent only about 15% of the *total* loads of PCBs to the river, which also include loads from atmospheric deposition, tributaries, combined sewer overflows, stormwater runoff, and runoff from contaminated sites. Stormwater runoff is thought to be the largest single source of PCBs to the Delaware River.

Keeping these shortcomings in mind, we find that the congener profiles of PCBs in the air, water, discharges, and sediments to the Delaware River follow some expected trends. The relative contributions of the PMF-resolved factors to PCB burdens in the NPDES-permitted discharges, the water column, and the sediment are detailed in figure 2-3. Note that in this figure, some factors have been combined to enhance the comparison. For example, factors 1 and 4 from the sediment analysis are lumped together in this figure under the category of "other" since they are difficult to identify. The "other" category refers to weathered, integrated, or dechlorinated PCB fingerprints. This category thus refers to the extent of alteration of PCBs in each compartment, whereas the other categories refer to PCB fingerprints that are generally recognizable in comparison to Aroclors or other source terms and, as such, have probably resided in their compartments for a relatively short amount of time. This figure demonstrates that some sources of PCBs, such as PCB 209 from $TiCl_4$ production, may be insignificant in the water column but dominant in the sediment. In contrast, Aroclor 1254 is an important contributor to PCB loads in the NPDES-permitted discharges, and is important in the water column, but is a lesser contributor to sediment contamination.

Factor 6 and 7, which contain highly chlorinated congeners, are not very mobile in the river. In contrast, factor 3, which contains some higher MW congeners but is dominated by PCB 11, appears throughout the river and is the dominant source to the sediment in Zone 6, probably due to atmospheric transport and deposition.

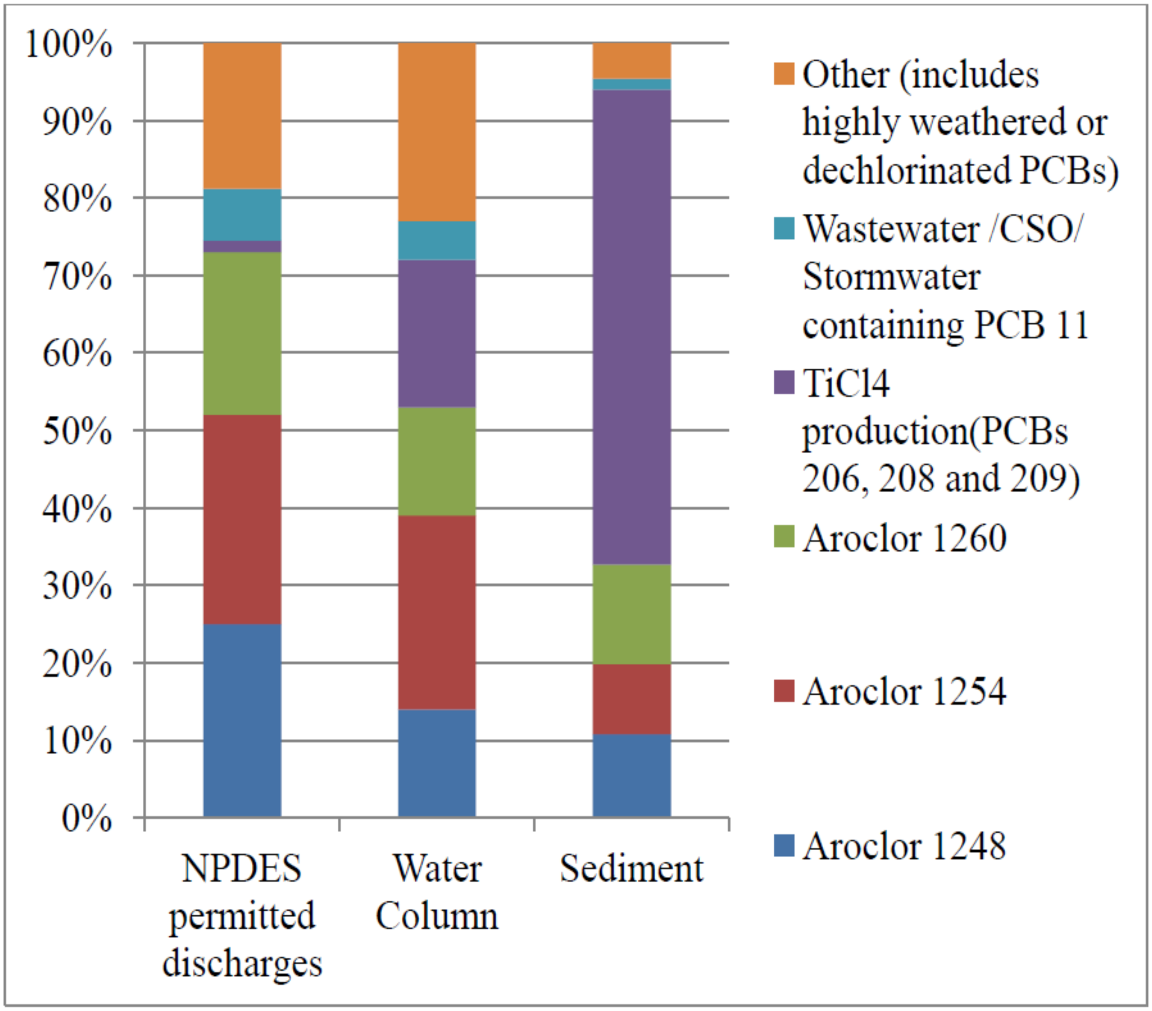

Figure 2-3. Relative contributions of the factors resolved by PMF analysis.[6, 8, 21] For water column and sediments, contributions are based on the total mass in the data set, which is assumed to be representative of the compartment as a whole. For the NPDES-permitted discharges, the contribution is based on the total *loads* of PCBs to the river (i.e., concentrations multiplied by the flow of each discharger). Note that in some cases, factors were combined into the "other" category to facilitate comparison.

Unlike Bzdusek et al.[18] and Soonthornnonda et al.[17], we did not observe a factor associated with microbial dechlorination in the sediments. Our finding is in keeping with the fact that the TMDL model did not include parameters for degradation of PCBs in either the sediment or the water column. However, dechlorination does happen in the sewers, landfills, and contaminated groundwater in the region, and the dechlorination products represent about 19% of the NPDES-permitted discharges to the River.[7] The main dechlorination product is PCB 4. Upon closer examination of the factors resolved from the ambient water column data set,[5] factor 1 from that analysis contains a relatively high proportion (6.7%) of PCB 4. This factor was well described as a combination of Aroclors 1242, 1248, and 1254, none of which contain more than about 5% PCB 4. We originally hypothesized that this factor represented the ambient dissolved phase PCB background. Upon further review, we hypothesize that this factor contains traces of the dechlorination signal from the wastewater treatment plant discharges to the River. In contrast to the water column, none of the factors resolved from the sediment data set contained a high proportion of PCB 4. The highest proportion of PCB 4 lies in factor 1 (1.8% PCB 4) and this factor contains just 0.5% of the other major dechlorination product, PCB 19. This suggests that even if the loads of dechlorinated PCBs are large enough to support a measurable PCB 4 concentration in the water column, they are not large enough to allow a discernable PCB dechlorination signal to accumulate in the sediment, especially given that PCB 4, as a dichlorobiphenyl, is less hydrophobic than more chlorinated congeners and less likely to partition to the sediment but more liked to volatize to the atmosphere, where is it rapidly destroyed by reactions with hydroxyl radical.[22] This is yet another benefit of dechlorination in sewers, landfills, and contaminated groundwater.

The factors dominated by PCB 11 in the water column, dischargers, and sediment display very different congener patterns. The correlation of the congener patterns of the PCB 11-dominated factors between the dischargers and the water column yields an R^2 of just 0.14. Similarly, the PCB 11-dominated factors in the dischargers and sediment are not similar ($R^2 = 0.03$). The best correlation is between the PCB 11-dominated factors in the sediment and the water column ($R^2 = 0.58$). Thus it appears that there is some relatively weak linkage between the sediments and the water column for the PCB 11 factors, but the dischargers display a very different PCB 11 pattern. This is in agreement with our hypothesis that atmospheric deposition is the main source of PCB 11 to the sediment. In comparison, PCB 11 from dischargers is less important and hence the discharger congener pattern does not match the PCB 11-dominated pattern in the water column or sediment. If our interpretation is correct, then factor 3, which accounts for 1.4% of the PCB mass in the sediment data set, represents atmospheric deposition. This low percentage is consistent with our previous assessment that atmospheric deposition is a minor source of ΣPCBs to the Delaware River.[2] The congener patterns of the PCB 11-dominated sediment factor do not resemble the average atmospheric congener pattern observed in this area from either active or passive air sampling, but this could be due to differences in the detection methods between the different data sets, as noted above, or due to partitioning on the basis of Henry's law, octanol-water, or octanol-air partition coefficients, which would alter the congener patterns between air, water, and sediment. In the present work, the PCB 11-dominated factor in the sediments represents 1.4% of the PCB mass in the data set, versus 5% in the water column, suggesting that while PCB 11 does accumulate in the sediments, its accumulation is less efficient than that of other, heavier congeners. This lower efficiency may be due to volatilization, aerobic degradation, or other weathering processes.

Why is a PCB 11-dominated factor recognizable in the sediment but not a factor associated with dechlorination and dominated by PCB 4? The difference is not due to differences in loads. In a previous work we calculated that in 2001-2003, twice as much PCB 4 (1600 mg/d) as PCB 11 (740 mg/d) was discharged to the Delaware River from NPDES-permitted dischargers.[8] These loads do not account for stormwater or atmospheric deposition. PCB 11 and PCB 4 were both detected via passive air sampling at similar concentrations in the atmosphere of the Delaware River basin.[4] Thus both congeners are likely to be transported and deposited to the Delaware River via the atmosphere, and to the extent that stormwater contains atmospherically deposited PCBs, the loads of these two congeners via stormwater and atmospheric deposition should be similar. Aerobic degradation cannot account for the difference, since PCBs with double *ortho* substitions such as PCB 4 (2,2'-dichlorobiphenyl) are poorly degraded under aerobic conditions.[23, 24] In contrast, aerobic bacteria are capable of cometabolizing other dichlorobiphenyl congeners, and some strains can even use PCB 11 (3,3'-dichlorobiphenyl) as a sole carbon source.[25] Although they have similar physicochemical properties, PCB 11 does have a slightly higher octanol-water partition coefficient (log $K_{ow} = 5.21$) versus PCB 4 (log $K_{ow} = 4.84$). [26] Also, PCB 11 has a slightly lower vapor pressure (log p = -1.06 in Pa) versus PCB 4 (log p = -0.48 in Pa).[27] These two factors would tend to drive more PCB 4 into the water column and atmosphere, while proportionately more PCB 11 partitions onto the sediments. We therefore conclude that the greater accumulation of PCB 11 in sediments is driven by its physicochemical properties, rather than by differences in loads or aerobic degradation. If correct, this conclusion further highlights the need to limit the releases of PCB 11 to the environment from the use of pigments in printing inks.

Our previous work suggested that the ‘deca’ signal constitutes just 1.5% of the NPDES loads to the river, but 19% of the PCBs in the water column. Other sources, such as atmospheric deposition and stormwater, are not likely to be important sources of the deca signal because of the extremely low vapor pressure and high hydrophobicity exhibited by the nona- and deca-chlorobiphenyls. The dominance of the deca factor in the sediment may therefore be due to more efficient accumulation in the sediment or to changes in the emissions profiles over time. As noted above, the surficial sediment samples used in this analysis probably represent a broad range of sediment age due to the complex dynamics of this tidal system. The company responsible for the deca contamination in the Delaware River has modified the $TiCl_4$ production process to produce substantially less PCBs. It is possible that deca emissions were greater in the past (i.e., prior to the TMDL data collection, which started in about 2002), accounting for the large contribution of these congeners to the sediment PCB burden. Concentrations of PCB 209 in a sediment core collected by DRBC in a marsh on the banks of Woodbury Creek near Philadelphia in 2002[28] increase with depth to a maximum concentration of 21 ng/g dry weight around 1982.[21] The upper slices of the core show that PCB 209 concentrations have dropped by about 50% since then. PCB 209 was detected at a level of 3 ng/g dry weight in the deepest part of the core, which was deposited around 1944. Thus the carbochlorination process has had a significant impact on sediment quality in the Delaware River.

The deca factors in water, sediment, and dischargers are all dominated by PCBs 206, 208, and 209. When these three congeners are removed, the remainder of the congener fingerprints of the deca factors in the dischargers and the water column are quite similar ($R^2 = 0.85$), but they are not similar to the congener pattern in sediments ($R^2 < 0.3$). This may suggest that the deca deposited to sediments was discharged long ago, such that the congener pattern is not similar to more recent discharges. The deca signal in the water column is very similar to that in the dischargers because many of samples in the discharger database were actually river water masquerading as "non-contact cooling water".

Thus our analysis of PCB congener patterns in the sediment of the Delaware River suggests that historical production of $TiCl_4$ is the largest source of PCB sediment contamination in this urbanized waterway. This deca PCB signal shows no sign of degradation and the localized nature of the deca signal suggests that its transport is minimal, despite the usual processes of dredging, resuspension, and sediment transport that remove some contaminated sediment from the system. The persistently high concentrations of the deca signal in the Woodbury core are testament to the fact that the Delaware River has been impacted by the deca signal for decades. Lack of degradation and minimal transport mean that the Delaware River will continue to be impacted by this industrial legacy for decades to come. The historical use of Aroclors is the second largest culprit in sediment contamination. PCB 11 from the use of diarylide pigments is also important, and is delivered to the river primarily via the atmosphere.

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Chapter 3: Source Apportionment of Polychlorinated Biphenyls in Camden Air (1999-2011) and New Brunswick Air (1997- 2011)

Abstract

Even though the intentional production of PCBs has been banned in the US since the 1970s, PCB concentrations in the environment, including in the atmosphere, persist at levels that are problematic. The purpose of this work was to use a sophisticated source apportionment tool called Positive Matrix Factorization (PMF) to identify the atmospheric PCB sources in New Jersey. The data set was compiled by the Delaware Atmospheric Deposition Network (DADN) from samples taken in Camden from 1999 to 2011 and New Brunswick from 1997 to 2011. The PMF analysis revealed four resolved factors each in Camden and New Brunswick. The factors that dominate the PCB burden the atmosphere at both Camden and New Brunswick resemble unaltered Aroclor 1242 and vaporized Aroclor 1248. These factors declined in concentration over the entire monitoring period, but this decline ceased during 2004-2011. During 2004-2011, only one factor representing 17% of the PCB mass in the atmosphere at New Brunswick was declining. All others were unchanged or increasing. This suggests natural attenuation alone will not control atmospheric PCB concentrations, and additional efforts are needed to control PCB emissions. This analysis also suggests that without human intervention, the Total Maximum Daily Loads promulgated for PCBs in the tidal Delaware River are not achievable in the foreseeable future due to continuing atmospheric deposition.

3.1 Introduction

Polychlorinated biphenyls (PCBs) are toxic, persistent, and bioaccumulative chemicals that are targeted for phase out under the Stockholm Convention on Persistent Organic Pollutants.[1] The intentional production of PCBs has been banned in the US since the 1970s. PCB levels in most environmental compartments have declined dramatically since the ban.[2-5] However, PCB concentrations in the environment, including in the atmosphere, persist at levels that are problematic. The sources of atmospheric PCBs are not clear. They may include old PCB-containing equipment, joint sealants, caulks, waste incineration, storage and disposal facilities, superfund sites and accidental releases.[6-16] PCBs are a concern in the atmosphere because they deposit to water bodies, and atmospheric deposition alone can often cause the water to exceed the water quality standard for the sum of PCBs.[10, 17-20]

Such is the case in the Delaware River, which forms the border between New Jersey and Pennsylvania and Delaware. The major urban areas of Trenton, NJ; Philadelphia, PA; Camden, NJ; and Wilmington, DE all lie along the Delaware River. More than 15 million people use the waters of the Delaware River for drinking, agriculture, and industry. Concentrations of PCBs in the Delaware River exceed the prevailing water quality standards from Trenton downstream to the Atlantic Ocean.[21] In response, the Delaware River Basin Commission (DRBC) has promulgated Total Maximum Daily Loads (TMDLs) for PCBs across the entire tidal portion of the river. In support of the TMDLs, the DRBC commissioned Rutgers to operate the Delaware Atmospheric Deposition Network (DADN)[22] to measure PCBs in the atmosphere (gas and aerosol phases) at several sites along the river. In order to investigate the sources of atmospheric PCBs, data from two of these sites were analyzed using Positive Matrix Factorization (PMF). New Brunswick and Camden were chosen for this investigation because they have the longest data history, and they represent an urban (Camden) and a suburban (New Brunswick) location.

Positive Matrix Factorization (PMF) is an advanced source apportionment tool developed by Paatero and Tapper.[23] PMF has been used to identify PCBs sources in water, sediment, and air.[9-11, 17, 24-27] The present work builds on previous studies in which PMF was used to apportion PCB sources to the water column[17], dischargers[28], and sediment[27] of the Delaware River Basin. The present work also builds on our previous effort to apportion PCB sources in Chicago air.[12] Therefore, the goals of this work were to apportion the major sources of PCBs to the air in New Jersey and the Delaware River Basin and to determine whether atmospheric PCB sources are declining over time in order to predict when (if ever) the concentrations of PCBs in the Delaware River might drop below the water quality standard, achieving the TMDL. Another goal was to compare the PCB sources in Camden (Philadelphia) to another major US city, Chicago.[10, 12]

3.2 Methodology

3.2.1 Study Sites

Data from two sites of the DADN were analyzed using PMF. Camden, NJ is located across the river from Philadelphia, PA which is currently the fifth largest city in the US, and was 4th largest in 1970[29] during the years of peak PCB usage.[30] In a previous work, PCB sources in the Camden DADN samples from 1999 to 2002 were investigated using PMF.[10] The present study updates the previous one and includes data gathered from

1999 to 2011, allowing an evaluation of time trends. New Brunswick is a suburban city in New Jersey with a population of about 55,000 in the 2010 census.[31] New Brunswick hosts the main campus of Rutgers, the State University of New Jersey, which is host to about 40,000 students across New Brunswick and the adjacent town of Piscataway.

3.2.2 Sample Collection and Analysis

The methods used to measure PCBs in the DADN samples have been described previously and will be briefly summarized here.[18, 22, 32]

Sampling collection

24-hour integrated air samples were collected by using a modified high-volume air sampler (Tisch Environmental, Village of Cleves, OH) with a calibrated air flow of about 0.5 m^3 min^{-1}. The particular phase was collected on quartz fiber filters (Whatman), but this data was not used in the PMF model. The gas phase PCBs were collected on a polyurethane foam plug (PUF). Samples were collected on a 12-day cycle until January 2009 at Camden and New Brunswick sites, after which they were collected every 24th day. The DADN network did not operate in Camden from August 2002 to March 2004 due to lack of funding.

Analytical methods

Samples were injected PCB surrogate standards that included PCB 23, 65, and 166 before extraction, and then PUF samples were extracted in a Soxhlet apparatus for 24 hours in the petroleum ether. Samples were cleaned up on a column of 3% water-deactivated alumina. Samples were injected the internal standards containing PCB 30 and 204 before analysis.[22] PCBs were analyzed on HP 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector using a 60 m, 0.25 mm i.d. DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25 µm. A total of 60 peaks representing 93 congeners were quantified using the 610 ng/L PCB standard originally developed for the Lake Michigan Mass Balance study.[33] This standard was made by mixing the various Aroclors, and therefore did not contain non-Aroclor congeners such as PCB 11. The re-analysis of some of the DADN samples for non-Aroclor congeners is described in Chapter 4.

Quality Assurance

Details of quality assurance can be found in the DADN final report. [22] Field and lab blanks and matrix spikes were analyzed for quality control. Both field and lab PUF blanks contained less than 5% of the PCB mass found in the PUF samples, so blank correction was not performed. Detection limits for individual PCB congeners (or co-eluting groups) ranged from 0.013 to 1468 pg m^{-3} at Camden and from 0.002 to 612 pg m^{-3} at New Brunswick for PUFs.

PCB concentrations were corrected for surrogate recoveries. Recoveries of PCBs in PUF matrix spikes ranged from 84% to 300% with a median of 106% and an average of 114%.[22] When surrogate recoveries were >100%, surrogate correction was not performed.

3.3 PMF Data Matrix

For this study, we used the positive matrix factorization (PMF) version 2.0 software (Yp-Tekniika Ky Co., Helsinki, Finland) to identify PCBs sources. PMF analysis was performed on the gas phase PCB concentrations only (particle phase concentrations were ignored). In contrast, our previous PMF analysis of PCBs in Camden utilized the gas plus particle phase concentrations, however, that analysis isolated a factor that represented particle phase PCBs. Therefore the inclusion of particle-phase PCB concentrations in the PMF model is not helpful. In addition, the gas phase typically contains about ten times higher PCB concentrations that the particle phase, so excluding the particle phase excludes only a small fraction of the total atmospheric PCB mass. Data from the two DADN sites was analyzed in separate PMF runs. The relative standard deviation of the recoveries of the applicable surrogate was used as the uncertainty for the detected concentrations of PCBs. Non-detects were substituted with a random number between zero and the detection limits, and assigned three times the uncertainty of the detected concentrations (i.e. we used an (x, 3x) uncertainty matrix).

PMF analysis is an iterative process in which analysis is performed on several subsets of the data until a robust model can be generated. The first step was to remove congeners and samples in which a majority of measurements were below detection limit. This yielded 54 PCB congeners in 234 samples at Camden and 48 PCB congeners in 307 samples at New Brunswick. After initial data analysis (see below) and preliminary PMF runs, five PCB congeners were removed from the Camden data set (PCBs 83, 97, 105, 178+129, and 128) and two congeners (PCB 137+176+130 and 178+129) were removed from the New Brunswick data set because they displayed anomalous temperature dependence (see below). Thus the final data matrices consisted of 49 congeners in 234 samples at Camden, and 46 PCB congeners in 307 samples at New Brunswick.

3.4 Results and Discussion

Before doing the PMF analysis, it is important to investigate the raw data for trends. In particular, the measured gas-phase concentrations of each congener were investigated as a function of both temperature and time via widely-used approach[3, 12, 34-37] of fitting the natural log of concentration (ln C_{gas}) versus time (t in days) and inverse temperature (1/T in Kelvin):

$$\ln C_{gas} = a_0 + a_1\left(\frac{1}{T}\right) + a_2 t \qquad \text{(Eqn. 3-1)}$$

where a_0, a_1 and a_2 represent the coefficients for the intercept, temperature, and time parameters, respectively (Figure 3-1 and 3-2). As is typical of gas-phase PCB concentrations, all PCB congeners displayed a significant correlation with temperature, with higher PCB concentrations at higher temperatures. As observed in other studies, lower molecular weight congeners displayed weaker temperature dependence[37], in keeping with their lower enthalpies of vaporization.[38] Figure 3-3 demonstrates that the temperature dependence of most PCB congener concentrations was greater and a stronger function of vapor pressure at Camden than New Brunswick. A stronger temperature dependence of gas-phase PCB concentrations in urban versus rural areas has been observed in other studies.[37, 39, 40]

Most congeners displayed significant negative values of a_2, implying that their concentrations are decreasing over time. At Camden, PCBs 40, 83, 97, 85+136, 153+132, 105, 137+176+130, 163+138, 158, 187+182, 183, 128, 185, 202+171+156, 199, 170+190, 201, 203+196, and 194 displayed no significant correlation with time (i.e. neither increasing or decreasing). At Camden, PCBs 195+208 and 206 were increasing over time (i.e. a_2 was positive and significant $p < 0.05$). At New Brunswick, PCBs 178+129, 202+171+156, 199, and 170+190 were neither increasing nor decreasing, and PCBs 137+176+130, 195+205, 194, and 206 were increasing over time. This information helps to justify the decision to remove from the PMF data matrix PCBs 83, 97, 105, 178+129, and 128 at Camden and PCBs 137+176+130 and 178+129 at New Brunswick.

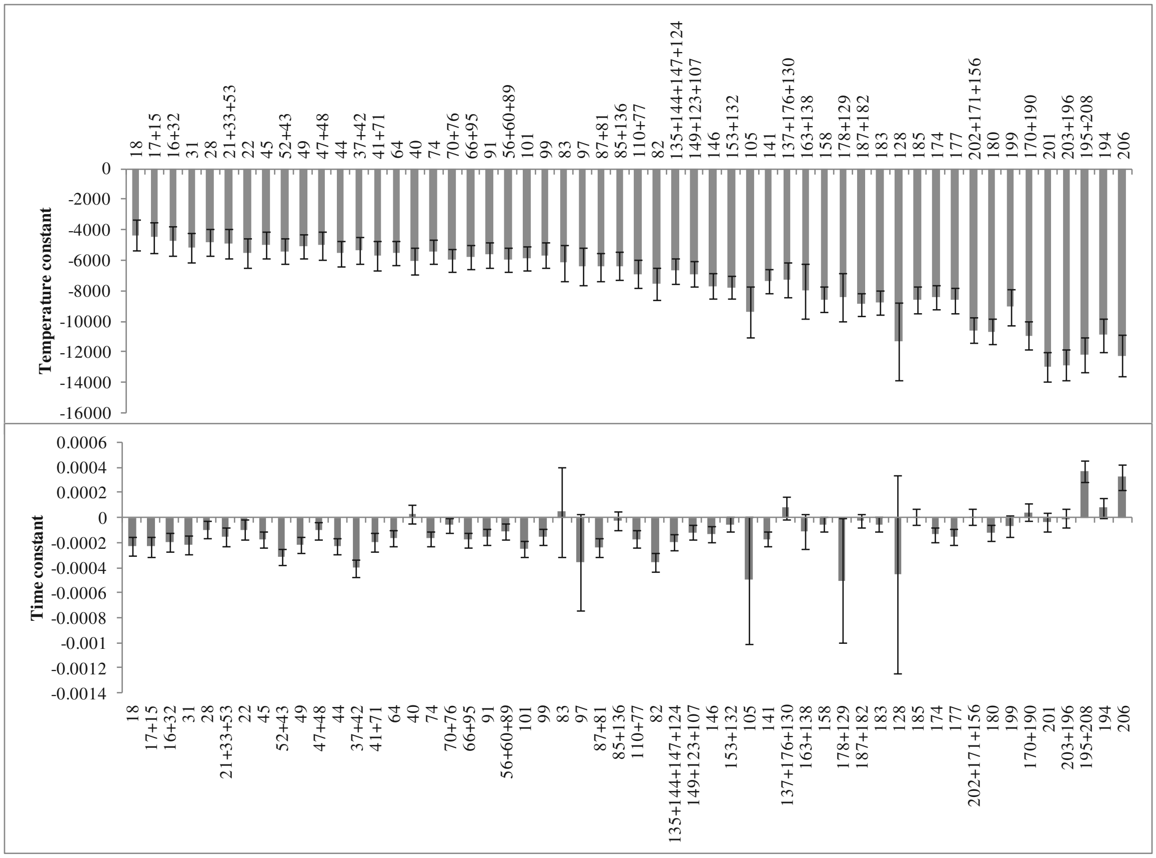


Figure 3-1. Temperature and Time dependence of individual PCB congeners in Camden (1999-2011) from equation 1. Top panel represents the temperature coefficient (a_1 of equation 1). Bottom Panel represents the time constant (a_2 from equation 1 in 1/d). Error bars represent 95% confidence limits.

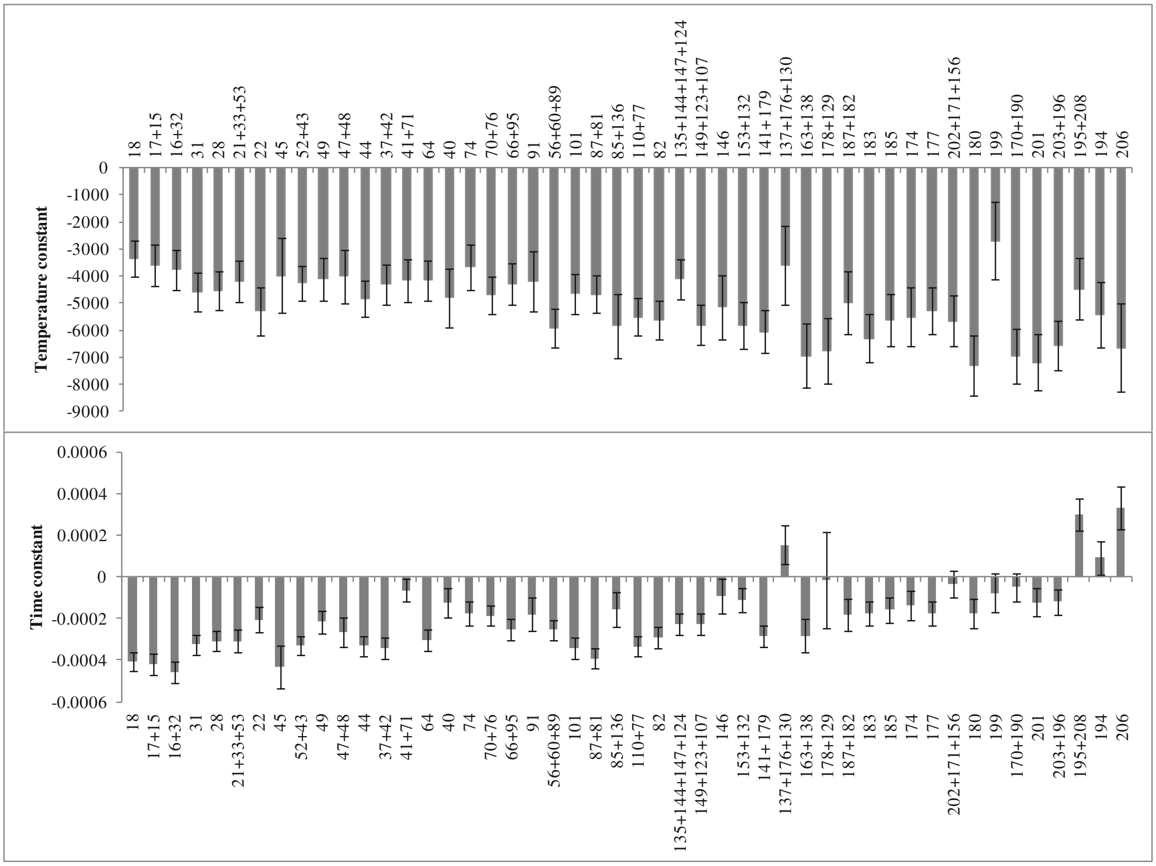


Figure 3-2. Temperature and Time dependence of individual PCB congeners in the air of New Brunswick 1997-2011 from equation 1. Top panel represents the temperature coefficient (a_1 of equation 1). Bottom Panel represents the time constant (a_2 from equation 1 in 1/d). Error bars represent 95% confidence limits.

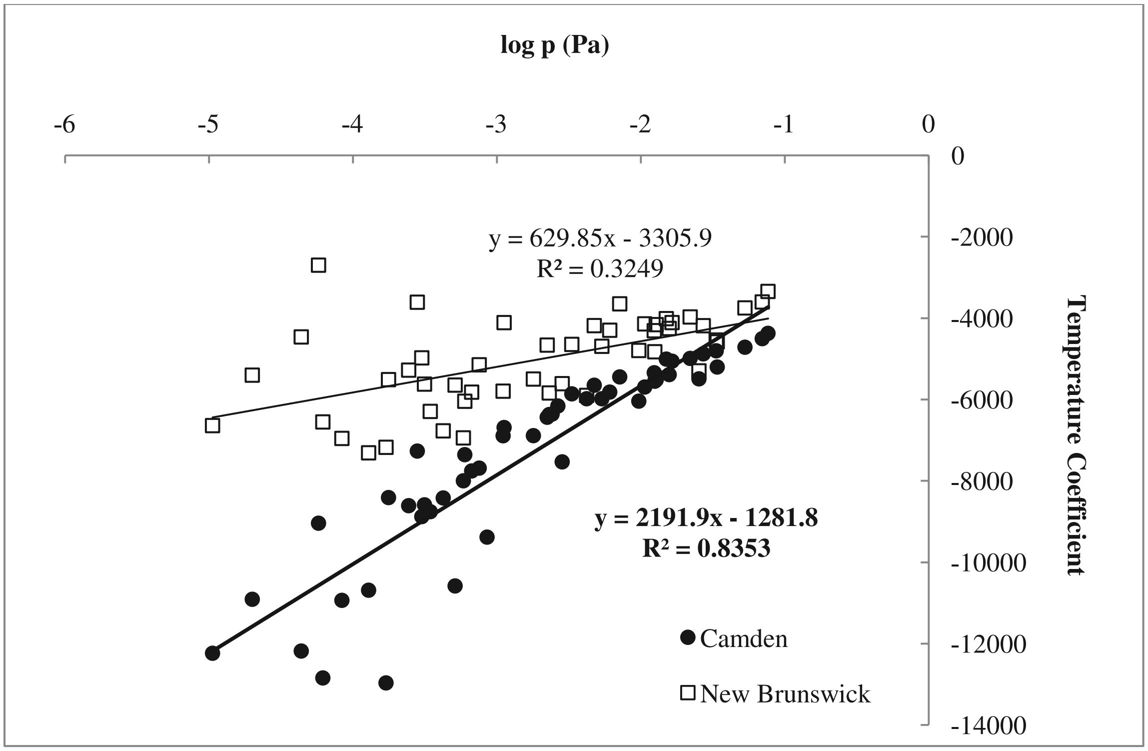


Figure 3-3. Temperature coefficients for individual PCB congeners versus their liquid vapor pressures at 25C.[38]

3.4.1 PMF Analysis

Determining the correct number of factors is a major difficulty in factor analysis. The correct number of factors was determined to be four each for Camden and New Brunswick. For clarity, these are hereafter referred to as factors 1C, 2C, 3C, and 4C (from Camden) and factors 1NB, 2NB, 3NB, and 4NB (from New Brunswick). The criteria used to determine the correct number of factors were the same as in Chapter 2.[27]

First, the relative standard deviation (RSD) of G-matrix in 9 model runs with different seed values can give a rough idea of the correct number of factors, which is the highest number of factors providing a stable model result. For New Brunswick, the four-factor model yielded an RSD 0.76%, versus 3.46% for the five-factor model and 63% for the six-factor model. For Camden, after three seeds were removed, the four-factor model yielded an RSD 0.21% (including all seeds yielded an RSD 48%), versus 0.71% for five-factor model and 38% for the six-factor model.

Second, the G-space plots (plots of the G matrix of one factor versus the G matrix of another) were examined to ensure that all factors were independent of each other (Figures 3-4 and 3-5). When factors are independent, these plots should show wide scatter with most of the space occupied and little or no correlation. The RSD values suggested that five might have been the correct number of factors at Camden; however, the G space plots revealed that one of the five factors was not independent of the others.

Third, to ensure that all factors contributed positively and significantly to the measured sum of PCBs, the four factor G matrix was regressed against the sum of PCBs. The regression coefficients of all factors were positive and significant ($p < 0.05$; See Appendix B).

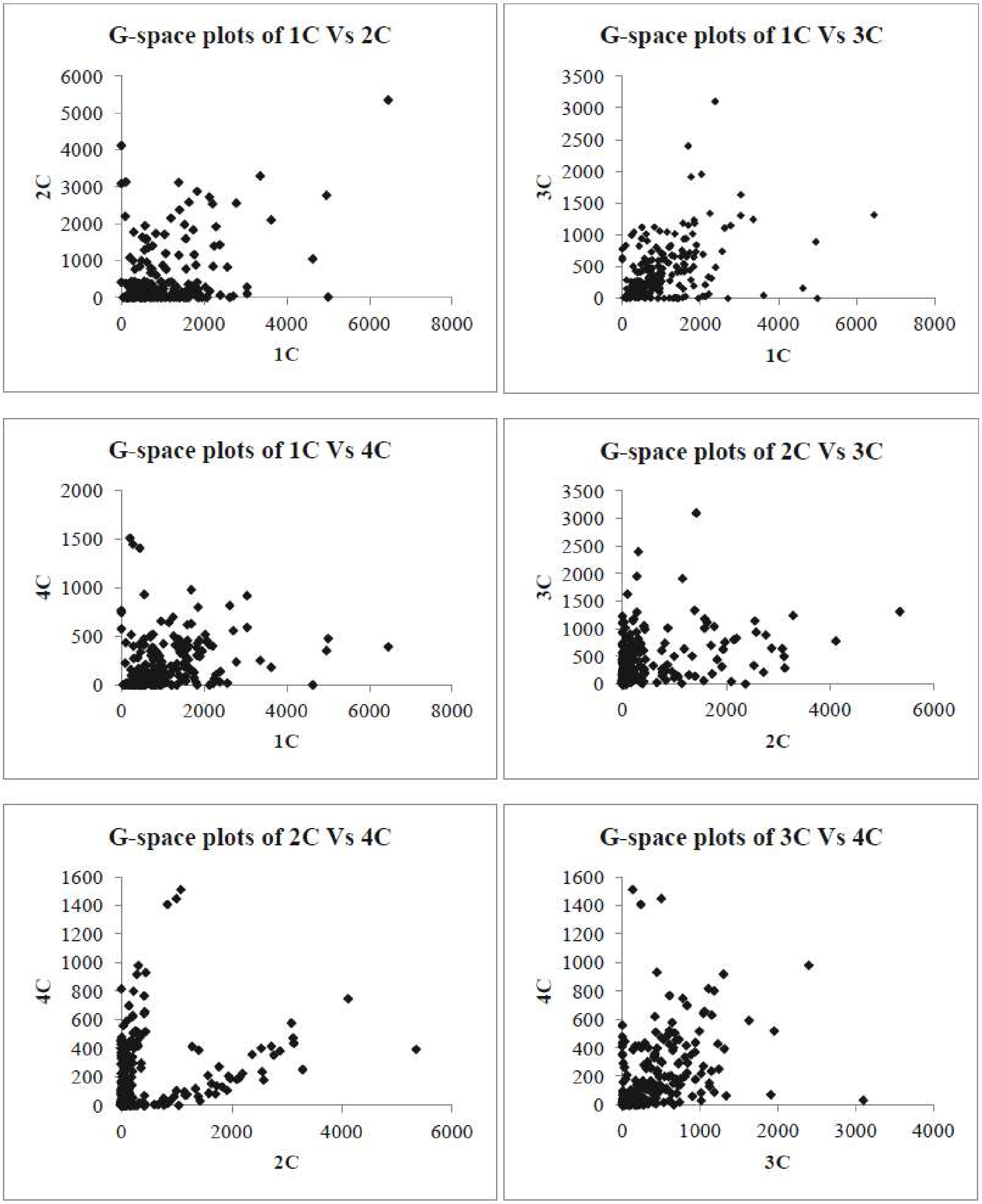


Figure 3-4. G-space plots (plots of G matrix of one factor versus the G matrix another) of the four factor model at Camden.

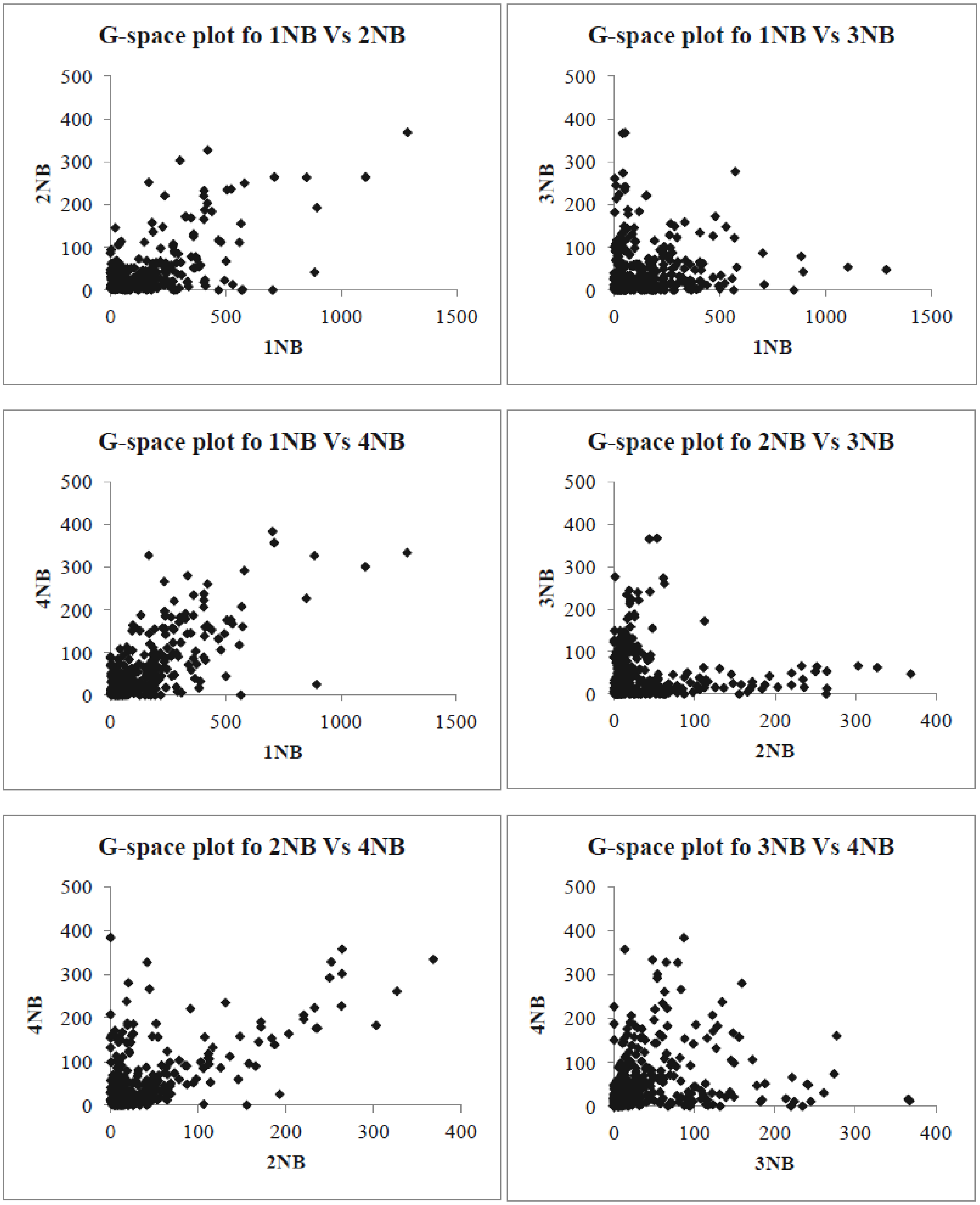


Figure 3-5. G-space plots (plots of G matrix of one factor versus the G matrix another) of the four factor model at New Brunswick.

Fourth, the chosen number of factors provided good correlation (high R^2) between the measured and modeled PCB concentrations. For Camden, the four-factor model yielded an R^2 between the measured and modeled concentrations better than 0.70 for 37 of 49 congeners. For the remaining twelve PCB congeners, the R^2 improved to greater than 0.7 after removal of outlier data points (See Appendix C). For New Brunswick data, the four-factor model yielded an R^2 between the measured and modeled concentrations better than 0.7 for 23 of 46 congeners. The R^2 improved to greater than 0.7 after removal of outlier data points (See Appendix C) for the remaining twenty three congeners (45, 49, 47+48, 74, 87+81, 85+136, 82, 135+144+147+124, 146, 187+182, 183, 185, 174, 177, 202+171+156, 180, 199, 170+190, 201, 203+196, 195+208, 194, and 206). Outliers are usually a result of either very low (below detection limit (BDL)) concentrations or very high measured concentrations. Low concentrations are sometimes outliers because of the way they are handled in the data matrix (i.e. replaced with a random value between zero and the detection limit). High concentrations may be outliers due to the application of the robust mode in PMF, which downweights very high concentrations.

The final criterion for determining the correct number of factors is that the factors should be physically meaningful and interpretable. The fact that many of them resemble Aroclors (see below) is a good indicator that they are physically meaningful.

3.4.2 Source profiles

The factors generated by the PMF model are shown in Figures 3-6 and 3-7 along with their percent contribution to the sum of PCBs. The factors from Camden and New Brunswick (Figure 3-6 and 3-7) were compared with each other (Table 3-1) to determine whether there is a PCB source type that dominates throughout the region. The highest correlation coefficient was for factors 1C and 1NB (r^2 at 0.78). Similarity was also observed between factors 1C and 3NB ($r^2 = 0.67$) and 3C and 4NB ($r^2 = 0.63$). These similarities suggest that similar PCB sources affect both New Brunswick and Camden.

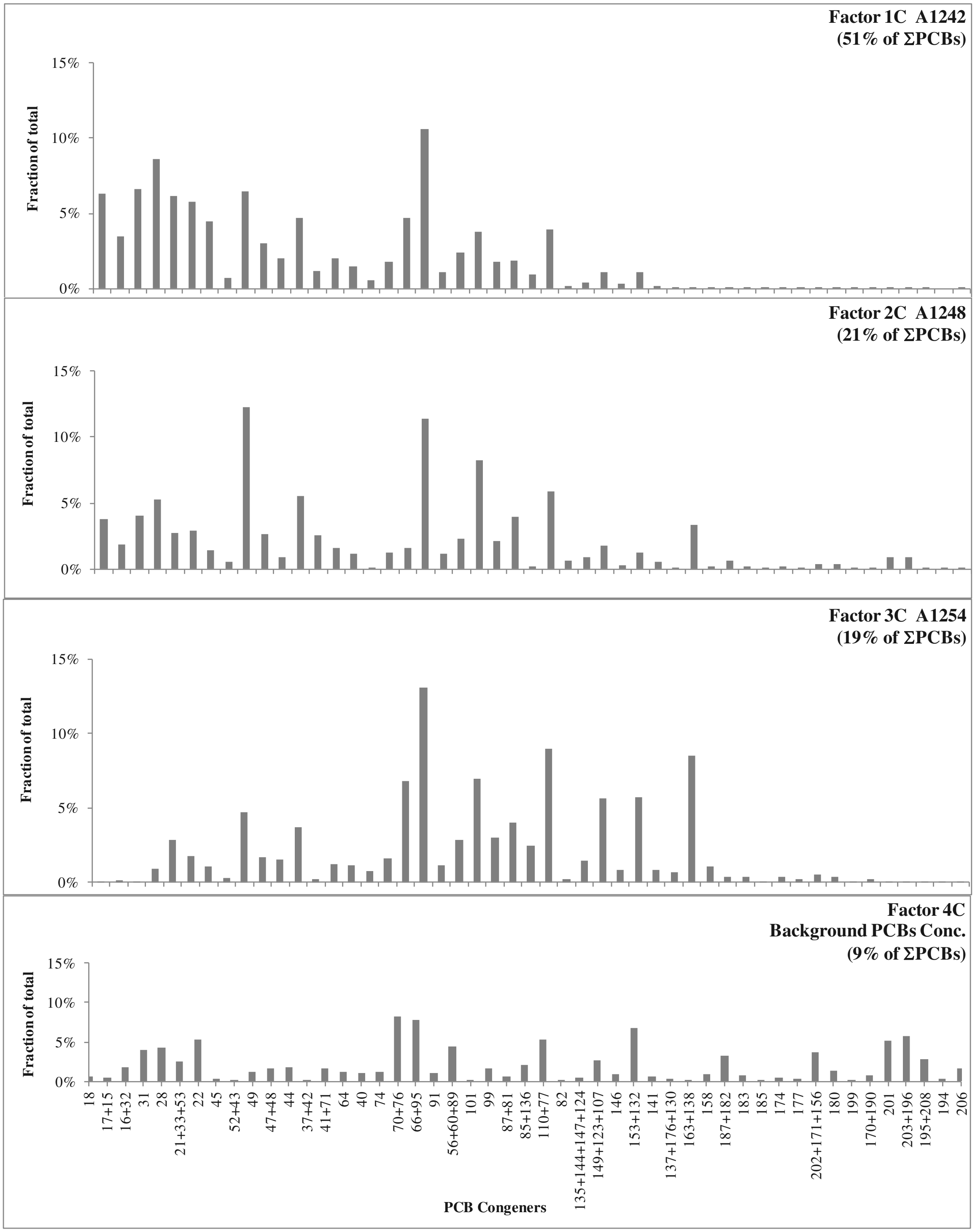


Figure 3-6. Congener patterns of the resolved factors of Camden data. Numbers in parentheses refer to the percent of the mass in each data set that this factor represents for the PMF2 model.

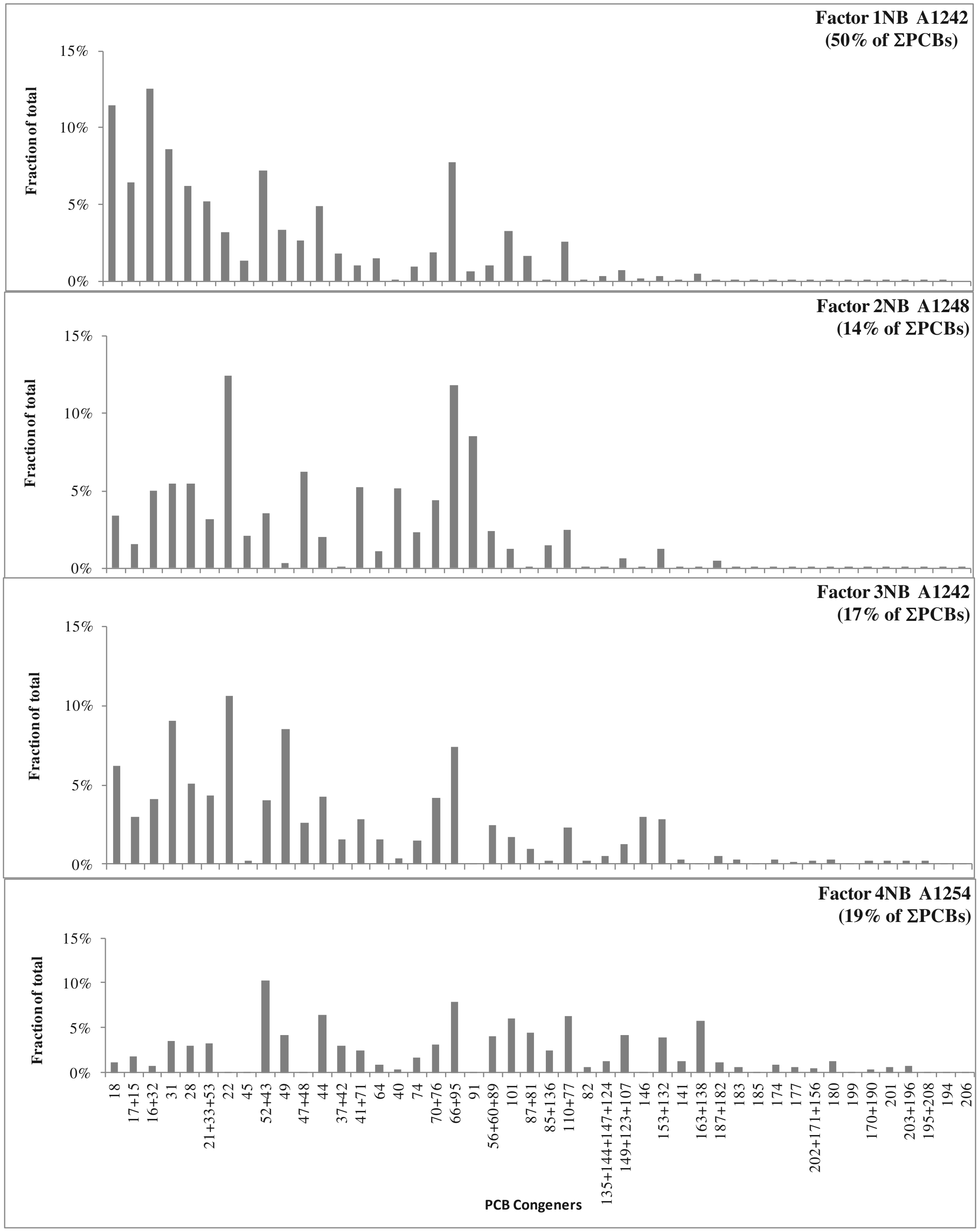


Figure 3-7. Congener patterns of the resolved factors of New Brunswick data. Numbers in parentheses refer to the percent of the mass in each data set that this factor represents for the PMF2 model.

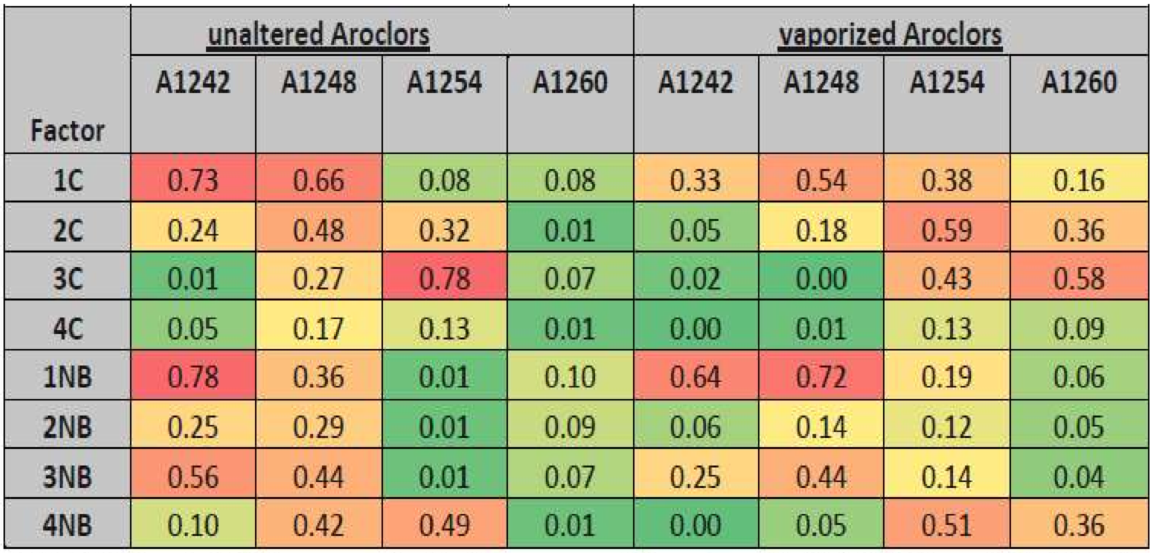
Table 3-1. Correlation coefficient (R^2) for the congener patterns (F matrix) of the factors resolved from PMF analysis for Camden and New Brunswick. Numbers in parentheses indicate the contribution of each factor to the sum of PCBs at each site.

R^2	1NB (50%)	2NB (14%)	3NB (17%)	4NB (19%)
1C (51%)	0.78	0.46	0.67	0.34
2C (21%)	0.44	0.17	0.26	0.75
3C (19%)	0.04	0.10	0.07	0.63
4C (9%)	0.01	0.17	0.14	0.04

3.4.3 Comparison with Aroclors

The resolved factors were compared with the four main Aroclors (1242, 1248, 1254, and 1260, keeping in mind that Aroclor 1242 strongly resembles Aroclor 1016) using the congener patterns of Frame et al.[41] In previous work,[10, 12] the factors were compared to both unaltered Aroclors and vaporized Aroclors (Table 3-2). The congener pattern of the vaporized Aroclor was determined by multiplying of the liquid vapor pressure of each congener with its abundance in the Aroclor, and then renormalizing the result such that the sum of PCBs equaled 100%. Factors 1C, 3C, and 1NB bore the most resemblance to Aroclors (both unaltered and vaporized). Factors 1C and 1NB most closely resembled unaltered Aroclor 1242 (which itself resembles Aroclor 1016), and somewhat resembled vaporized Aroclor 1248. As noted above, these factors are similar to each other and dominate the overall mass of PCBs in the gas phase, suggesting that Aroclors 1242/1016 and 1248 are major contributors to the atmospheric PCB signal across the region. Factors 2C and 4NB resemble each other as well as unaltered Aroclor 1248 and vaporized Aroclor 1254, suggesting (not surprisingly) that higher molecular weight Aroclors also contribute significantly to the urban/suburban PCB burden. Factors 4C and 2NB displayed little resemblance to unaltered or vaporized Aroclors.

Table 3-2. Coefficients of determination (R^2) for the congener patterns of resolved factors versus those of the most popular Aroclors from Frame et al.[41]



Factor	unaltered Aroclors				vaporized Aroclors			
	A1242	A1248	A1254	A1260	A1242	A1248	A1254	A1260
1C	0.73	0.66	0.08	0.08	0.33	0.54	0.38	0.16
2C	0.24	0.48	0.32	0.01	0.05	0.18	0.59	0.36
3C	0.01	0.27	0.78	0.07	0.02	0.00	0.43	0.58
4C	0.05	0.17	0.13	0.01	0.00	0.01	0.13	0.09
1NB	0.78	0.36	0.01	0.10	0.64	0.72	0.19	0.06
2NB	0.25	0.29	0.01	0.09	0.06	0.14	0.12	0.05
3NB	0.56	0.44	0.01	0.07	0.25	0.44	0.14	0.04
4NB	0.10	0.42	0.49	0.01	0.00	0.05	0.51	0.36

*** A1248 and A1254 are reported in the average of Type A and B. (A1248A,B , and A1254A, B)

To determine whether any of the factors represented mixtures of Aroclors, a multiple linear regression was performed in which a congener pattern was calculated that represented a linear combination of the four main Aroclors:

$$C_f = aC_{1242} + bC_{1248} + cC_{1254} + dC_{1260} \qquad \text{(Eqn. 3-2)}$$

where C is concentration of the resolved factor (f) or individual Aroclor and a, b, c, and d are partial regression coefficients. Coefficients were constrained to be positive, and R^2 values for this best-fit congener pattern vs. the factor congener pattern were calculated (Table 3-3). The results of this approach generally agreed with the comparisons to single Aroclors. Factors 3C, 4C, and 2NB cannot be adequately described as a combination of individual Aroclors, suggesting that they are highly weathered sources. This may indicate that they represent some kind of PCB background. In general, the PCB signal in Camden is more similar to Aroclors than the PCB signal in New Brunswick, which may be a consequence of Camden's more urban character (and thus closer proximity to primary PCB sources).

Table 3-3. Best-fit composition of each resolved factor as a combination of either unaltered or vaporized Aroclor. R^2 is the correlation coefficient between the best-fit prediction and the congener pattern of the factor.

Unaltered	**1242**	**1248**	**1254**	**1260**	**R^2**
1C	52%	24%	5%	0%	0.55
2C	9%	59%	14%	0%	0.48
3C	0%	35%	31%	0%	0.21
4C	11%	27%	3%	20%	0.02
Vaporized	**1242**	**1248**	**1254**	**1260**	**R^2**
1C	0%	47%	16%	0%	0.43
2C	0%	22%	40%	0%	0.46
3C	0%	0%	26%	15%	0.07
4C	0%	9%	3%	20%	0.0009
Unaltered	**1242**	**1248**	**1254**	**1260**	**R^2**
1NB	96%	0%	2%	3%	0.79
2NB	36%	41%	5%	3%	0.30
3NB	55%	31%	0%	9%	0.60
4NB	0%	63%	20%	19%	0.68
Vaporized	**1242**	**1248**	**1254**	**1260**	**R^2**
1NB	15%	50%	13%	14%	0.79
2NB	0%	30%	31%	11%	0.23
3NB	0%	47%	21%	9%	0.47
4NB	0%	15%	32%	31%	0.51

The results from Camden and New Brunswick generally agree with those observed in Chicago.[12] In all three locations, the dominant PCB sources resemble unaltered Aroclor 1242 and/or vaporized Aroclor 1248. In New Brunswick and Camden, the dominant factors (1C and 1NB) each comprise about half of the sum of PCBs in the gas phase. In Chicago, two dominant factors (the A and B factors) resembled unaltered Aroclor 1242 and vaporized Aroclor 1248. Together they comprised about 39% of the sum of PCBs.

It is difficult to surmise the source of these dominant PCB signal without determining whether they in fact represent Aroclor 1242 (which was used primarily in electrical equipment) and Aroclor 1016 (used in capacitors) versus Aroclor 1248 (which tended to be used more in hydraulic fluid and vacuum pumps). Aroclor 1242 represented about 51% of the total US Aroclor production between 1957 and 1977.[42] Aroclors 1016, 1248, 1254, and 1260 comprised 13%, 7%, 16%, and 11% respectively of total US production during that period.[42] Despite their large share of US production, previous source apportionment of PCBs in the Delaware River water, sediment, and dischargers failed to isolate a factor that was similar to Aroclors 1242 and/or 1016.[9, 10, 12, 17, 27, 28] The difference between the atmospheric source apportionment results and those for the other Delaware River compartments may be partially explained by methodology: in all other compartments, PCB were quantified by EPA method 1668A via high resolution mass spectrometry versus the ECD method used for the air samples in all three cities. Assuming that the difference in methods alone cannot explain the discrepancy, we can offer two possible explanations. The first is that the source responsible for the dominant atmospheric PCB signal in these three cities is in fact Aroclor 1248, not 1242/1016. This would imply that Aroclors 1242 and 1016 are 'missing' from all compartments: air, water, sediment, and discharges. This seems unlikely for two Aroclors that together comprised 64% of US PCB production. However, since these have the lowest molecular weight (MW) and smallest chlorine content of any of the popular Aroclors, it is possible that they were sufficiently labile that they have been degraded and/or transported out of urban centers, dispersing across the globe. It is possible that the 'background' signals observed in all three locations represent the highly weathered Aroclor 1242/1016 residual, which would imply that Aroclor 1242/1016 is more labile and prone to weathering than the higher MW Aroclors. The second explanation is that the dominant PCB signals in these three cities do in fact arise from Aroclors 1242 and 1016, but these two Aroclors are not found in the water column, sediment, and dischargers due to the higher volatility of these lower MW Aroclors and/or their usage patterns. For example, it is possible that Aroclor 1242's primary use in transformers[30] (a closed application) means that this Aroclor does not wash off into water and thence sediment, but instead volatilizes when transformers fail or slowly leak. Aroclor 1016 was used exclusively in capacitors, a close application.[30]

3.4.4 Time and Temperature Trends of Resolved Factors

Visual inspection of plots of concentration versus time for the resolved factors (Figures 3-8 and 3-9) suggest that some factors (notably 1C, 1NB, and 4NB) declined in concentration over the monitoring period. These plots also suggest that 4C may have increased in concentration over this period. Factor 2C was low before the network hiatus (1999-2002) and high afterward (2004-2011). Factor 2NB was high in 1997-1998 and again in 2010, but relatively constant in between. These plots also suggest that the time trends before 2004 might be different from those after 2004. Time constants for any significant decline or increase over the entire period of monitoring and from 2004-2011 were determined using equation 1 (Figure 3-10). The plots of the natural log of PCB concentrations and 1/T of Camden and New Brunswick data are shown in Appendix D.

These plots show that in the regressions, several data points were outliers (shown in red). In all this case, all outliers were very low concentrations caused by the model trying to zero out these factors on these days. These points were excluded from the regression results show in Figure 3-10.

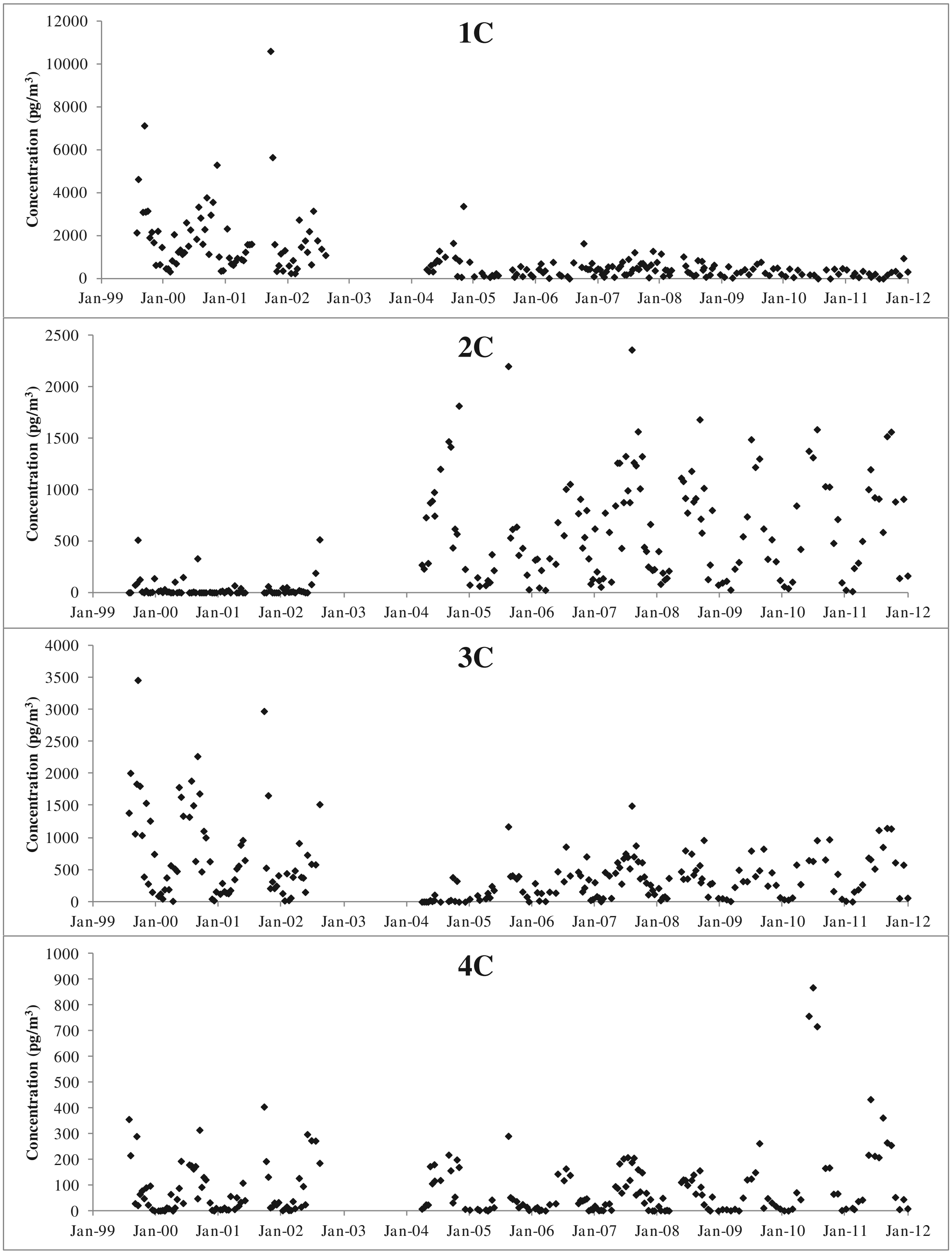


Figure 3-8. Concentration versus time for the resolved factors of Camden data.

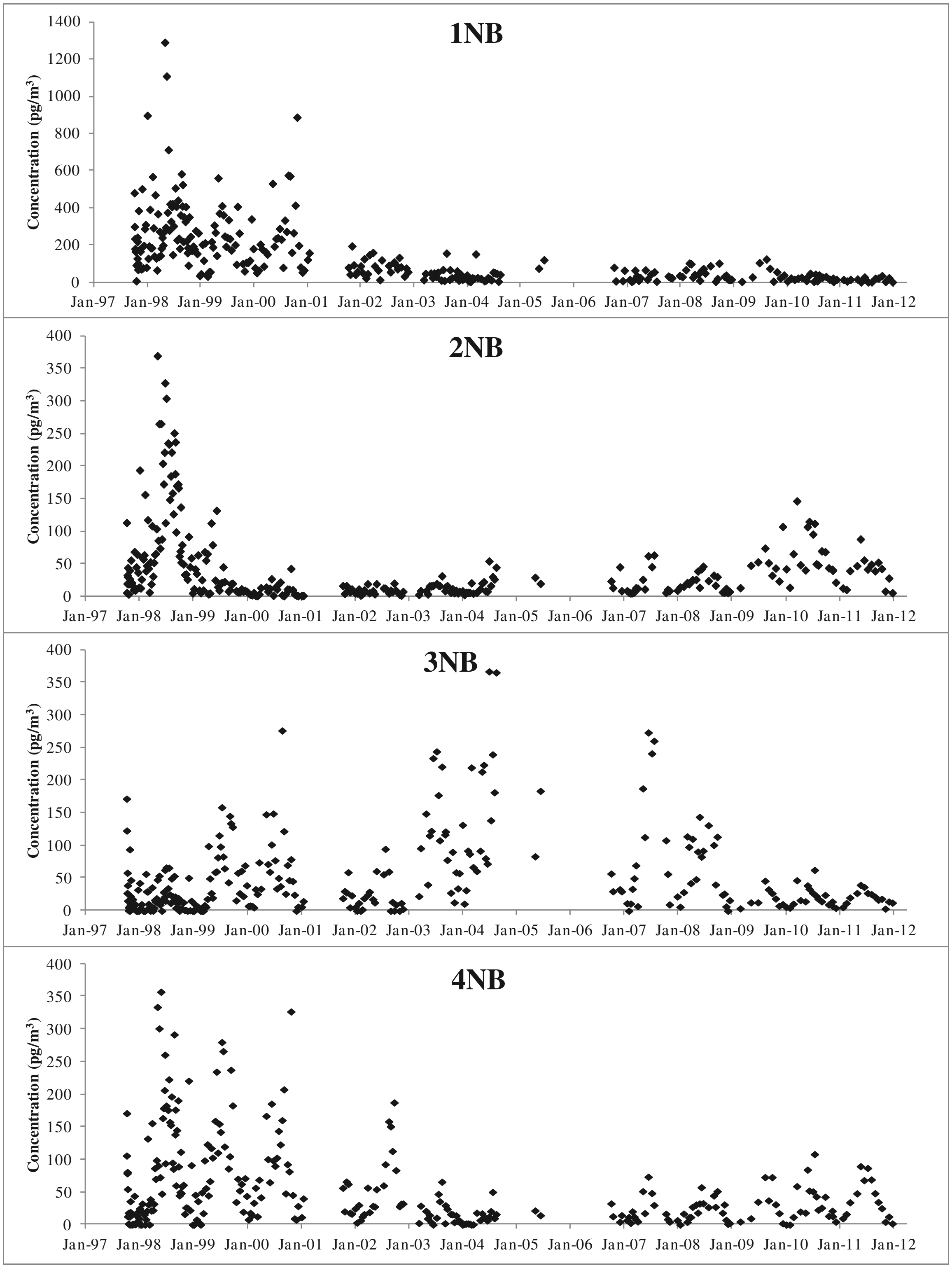


Figure 3-9. Concentration versus time for the resolved factors of New Brunswick data.

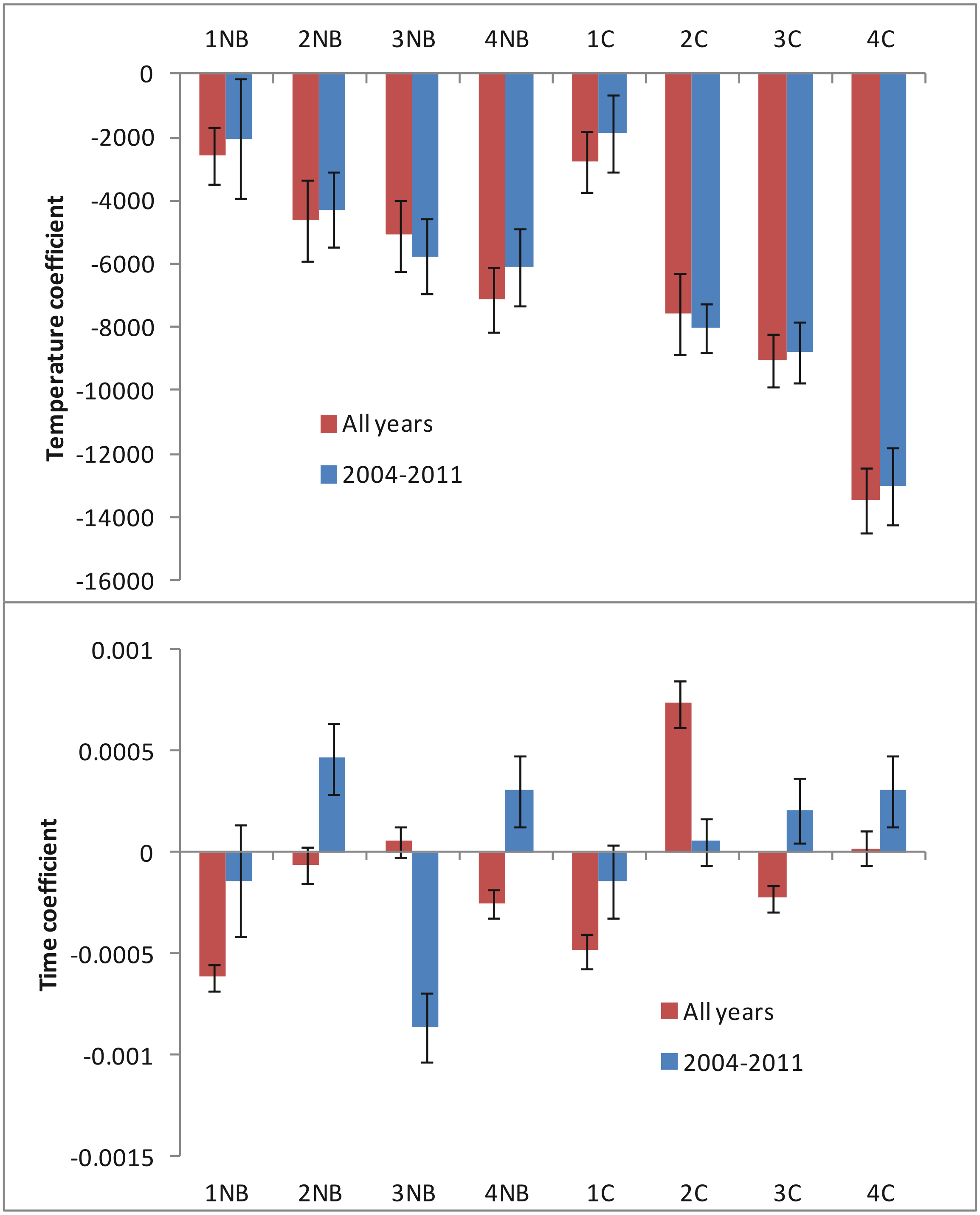


Figure 3-10. Time and Temperature dependence of the resolved factors in the air of Camden (1999 - 2011) and New Brunswick (1997 – 2011) from eq 1. Top panel represents the temperature coefficient (a_1 of eq 1.) Bottom panel represents the time constant (a_2 from eq 1. in 1/*d*). Error bar represents 95% confidence limits.

All factors displayed the expected temperature dependence, with higher PCB concentrations at higher temperatures. The temperature coefficients were not significantly different during the two time periods. As with the congener specific results above, factors with higher average molecular weight generally displayed stronger temperature dependence. A similar trend was observed for Chicago, where five factors were derived that had similar temperature dependencies of between -1600 and -10000.[12] In Chicago, the C factors displayed relatively strong temperature dependence and were not similar to any of the Aroclors, so it was surmised that they represented volatilization of PCBs from secondary sources such as soil, water, or vegetation. Factors 3NB and 4NB are not similar to any Aroclors and display relatively strong temperature dependence, suggesting that they too may represent volatilization of secondary PCB sources.

The time trends for the entire monitoring period were very different from those for 2004-2011. All of the factors that displayed significant declines during the entire monitoring period displayed either no trend or were actually increased from 2004-2011. This may indicate that in the atmosphere of New Jersey (as in many other environmental compartments[2-5]) the fast decline in PCB concentrations observed after the PCB ban of the 1970s has stalled. The only factor that shows a statistically significant decline from 2004-2011 is factor 3NB. Factors 2NB, 4NB, 3C, and 4C are all increasing in concentration during 2004-2011. At Chicago as well, some PCB signals were declining, others were increasing, and some were unchanged. The C factors, which were thought to represent volatilization of secondary PCB sources, were declining with a half life of about 4-8 years. Factor 3NB is the only factor at the two New Jersey sites that declined from 2004-2011, and it also seems to represent volatilization of secondary PCB sources. The decline of these factors (Chicago C factors and 3NB) probably results from natural attenuation. However, the failure of other PCB sources to decline suggests that natural attenuation alone will not control atmospheric PCB concentrations, and additional efforts are needed to control PCB emissions.

At each site, the factor (1NB and 1C) that dominated the mass and resembled unaltered Aroclor 1242 and vaporized Aroclor 1248 was decreasing with a half-life of 3-4 years over the full monitoring period, but was unchanged from 2004-2011. As noted above, the congener patterns of these two factors strongly resemble each other (R^2 = 0.78). Their similar time trends are further evidence that 1NB and 1C represent the same PCB source type. In Chicago, the B factors, which also resembled Aroclors 1242 and 1248, were declining with a half life of 4-7 years.[12] We speculated that the decline of the B factors in Chicago may be due to efforts under the Great Lakes Binational Toxics Strategy (GLBTS) to remove PCB-containing electrical equipment. The declines observed for factors 1NB and 1C in earlier years (roughly 1997-2002) may similarly result from efforts to control PCB-containing electrical equipment. Even if they are credited with the earlier decline, these efforts ceased to be effective by about 2003.

3.5 Interpretation

The results of this analysis generally agree with the results from the Chicago study. In all three locations, the atmospheric PCB signal is comprised of several source types with distinct congener patterns. Concentrations of some of these sources are decreasing over time (1C, 1NB, and 4NB). However, some are not declining and some are actually increasing over time. As noted above, this suggests natural attenuation alone will not control atmospheric PCB concentrations, and additional efforts are needed to control PCB emissions. The long term increase in PCB concentrations is particularly problematic at Camden, where none of the factors declined significantly from 2004-2011. The Delaware River cannot achieve the TMDL for PCBs unless atmospheric PCB concentrations in this region decline.[18] This analysis suggests that without human intervention, the TMDL is not achievable in the foreseeable future.

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Chapter 4: Atmospheric concentrations of PCBs 4 and 11 in the Delaware Atmospheric Deposition Network (DADN)

Abstract

The Delaware Atmospheric Deposition Network (DADN) measured PCB concentrations in the gas and aerosol phases at several sites in order to estimate atmospheric deposition of PCBs to the Delaware River. The DADN sampled gas phase PCBs using polyurethane foam (PUF) as an absorbent, an approach which is known to suffer from breakthrough of low molecular weight PCBs, possibly leading to inaccurate quantification. PCBs 4 and 11, both dichlorobiphenyls, are of particular interest due to their non-Aroclor sources but were not measured in the original DADN project. To quantify these congeners, air samples from Camden, NJ; New Brunswick, NJ; and Lums Pond, DE were reanalyzed via gas chromatography with tandem quadrupole mass spectrometry (GC/MS/MS). To determine the extent to which breakthrough impacted the measured concentrations, side-by-side samples were collected using both PUFs and a method with no breakthrough (sandwich of XAD-2 resin between PUF layers). The results suggested that the DADN measurements using PUF do not require correction for breakthrough. The gas-phase concentrations of PCB 11 measured at the DADN sites ranged from non-detect to146 pg m^{-3}, similar to concentrations measured in the Great Lakes region. Gas-phase PCB 11 concentrations did not display a strong urban to rural gradient. PCB 4 concentrations ranged from 0.18 to 168 pg m^{-3} and were highest at Camden.

4.1 Introduction

Atmospheric deposition is a large enough source of polychlorinated biphenyls (PCBs) that it alone can cause water bodies to exceed their Total Maximum Daily Loads.[1] Atmospheric monitoring of PCB concentrations is therefore necessary to determine the magnitude of atmospheric deposition and to identify sources of PCBs. The Delaware Atmospheric Deposition Network (DADN)[1-4] measured PCB concentration in the gas and aerosol phases at several sites including Camden, NJ; New Brunswick, NJ; and Lums Pond, DE. The DADN network sampled gas phase PCBs using polyurethane foam (PUF) as an absorbent, an approach which is known to suffer from breakthrough of low molecular weight (MW) PCBs[5, 6], possibly leading to inaccurate quantification. Breakthrough occurs when the leading edge of the analyte mass, which travels through the PUF as though it were a chromatography column, reaches the end of the column and is 'blown off' the column, resulting in loss of mass in the sample. Breakthrough depends strongly on the sorption capacity of sorbent. PUF is a popular choice for sampling gas phase organic compounds such as organochlorines, polycyclic aromatic hydrocarbons (PAHs), PCBs, etc. Due to possible breakthrough of volatile or low molecular weight compounds, however, adding solid absorbents such as XAD-2 resin in the middle of two separate PUFs has been used as a strategy to reduce breakthrough.[6]

The DADN methodology measured PCBs via gas chromatography with electron capture detection (GC/ECD). By this method, a variety of interfering compounds elute in the early part of the chromatogram and are detected by ECD, leading to problems with quantifying the low MW PCBs. For these reasons, the DADN project did not quantify any mono- and dichlorobiphenyls congeners.

PCBs 4 and 11, both dichlorobiphenyls, are of particular interest due to their non-Aroclor sources. PCB 11 is thought to arise primarily from the use of pigments,[7-9] while PCB 4 is a main product of the microbial dechlorination of PCBs.[10-14] In order to quantify these congeners in the gas phase at the DADN sites, air samples were reanalyzed via gas chromatography with tandem quadrupole mass spectrometry. In order to determine the extent to which breakthrough impacted the measured concentrations, breakthrough was measured by collecting side-by-side samples using both PUFs and a sandwich of XAD-2 resin between PUF layers that captures all PCBs with little or no breakthrough.[15, 16] This represents the first comprehensive study of breakthrough of PCBs on PUF as a function of temperature. The purposes of this investigation were to report accurate concentrations of PCBs 4 and 11 in the gas phase in the DADN region and to quantify breakthrough of these congeners when using the PUF high volume air sampler.

4.2 Methodology

This investigation involved the re-analysis of air samples previously collected by the DADN, as well as the collection of some new samples used to assess the breakthrough of PCBs on the polyurethane foam plugs used to collect the samples. DADN samples were collected by using a high-volume air sampler (Tisch Environmental, Village of Cleves, OH) integrated over 24 hours using polyurethane foam plug (PUFs) to capture the gaseous phase of PCBs. The particle phase was collected on a Quartz fiber filters (Whatman). Air flow was calibrated before and after each sample to about 0.5 m^3 min^{-1}.

4.2.1 Breakthrough samples

Air samples for the breakthrough study were collected using similar methods with the following modifications. Two side-by-side simultaneous 24-hour air samples were collected. One of the samples utilized the standard PUF plug as an absorbent, but the PUF was cut in half before sample collected so that the top and bottom could be analyzed separately. The second utilized the PUF/XAD sandwich system.[5, 6, 15] The "sandwich" prepared by cutting the PUF plug into two equal pieces and adding 30 g of XAD-2 resin in the middle. The XAD-2 resin was pre-cleaned and stored in milli-Q water in amber jars before sampling.[15]

The air samples were collected both inside the ENR building (room 336) to achieve higher sampling temperatures ($T > 15°C$) and outside the building to achieve lower sampling temperatures ($T < 15°C$). The ENR building was built in two stages, the first in the 1950s and the second in 1988. The samples were collected in the new wing of the building. The outside temperature was calculated using meteorological data continuously recorded by the Rutgers Weather Center at the New Brunswick DADN site.[17] The inside temperature was recorded using a temperature logger. PUF and PUF/XAD samples for measurement of breakthrough were spiked with deuterated PCBs (d_5 PCB 65 and d_3 PCB 159) as surrogates prior to extraction and deuterated PCBs (d_5 PCB 30 and d_5 PCB 116) as internal standards prior to analysis by GC/MS/MS. All deuterated PCBs were obtained from CDN Isotopes, Pointe-Claire, Quebec, Canada. Measured PCB concentrations were corrected for surrogate recoveries, which are detailed in Table 4-1. Lab blanks were used for quality control. The results showed no significant PCB masses in the blanks, so blank correction was not required.

Table 4-1. Surrogate recoveries of deuterated surrogates used in the breakthrough study.

	d_5 PCB 65	**d_5 PCB 159**
Minimum (%)	26%	25%
Maximum (%)	94%	61%
Average (%)	43%	42%
Standard deviation (%)	14%	9%

4.2.2 Reanalysis of DADN samples

The DADN samples were collected at three sites: New Brunswick (suburban), Camden (urban), and Lums Pond (rural) from 2008 to 2011. Two of these sites (Camden and New Brunswick) were described in more detail in Chapter 2. Camden, NJ is located across the Delaware River from Philadelphia, PA which is the fifth largest city in the US. The Lums Pond site is located inside Lums Pond State Park near the Chesapeake and Delaware Canal.[1] The New Brunswick site is located within Rutgers Gardens on the campus of Rutgers, the State University of New Jersey in New Brunswick. The new samples were collected on the Rutgers University campus inside and outside of the Environmental and Natural Resource (ENR) building at 14 College Farm Road, approximately 1.3 kilometers from the New Brunswick DADN site.

Because dichlorobiphenyls are expected to exist primarily in the gas phase in the atmosphere, the particle phase samples were not reanalyzed. The PUF sample analysis has been described previously, and it is briefly summarized here.[1, 2, 18, 19] Samples were spiked with a surrogate solution containing PCBs 23, 65, and 166 and extracted by Soxhlet for 24 hours. Samples were cleaned up on a 3% water deactivated alumina column, and reduced to a volume of about 0.5 ml by N_2 blown-down. Next, samples were injected with internal standards (PCBs 30 and 204) and analyzed by an HP 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector using a 60 m, 0.25 mm i.d. DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25 µm. A total of 60 peaks representing 93 congeners were quantified using the 610 ng/L PCB standard originally developed for the Lake Michigan Mass Balance study.[19] The samples were re-analyzed using a water Quattro Micro GC/MS/MS in order to detect additional PCB congeners by the method of Du et al, 2009,[3] using standards containing all 209 PCB congeners (Accustandard, New Haven, CT). The details of chromatographic conditions are found in Brunciak et al, 20001b.[20] Measured concentrations were corrected for surrogate recovery using the recovery of PCB 23 measured at the time the samples were originally quantified.

In order to ensure that there was no loss of PCBs from the extracts during years of storage, the surrogate PCB 23 was quantified during MS/MS reanalysis and the new surrogate recoveries were compared with those measured during the original ECD analysis (Table 4-2). Because of differences in the quantification methods, surrogate recoveries from the MS/MS reanalysis were often >100% and were almost always greater in the reanalysis than in the original analysis. Thus surrogate correction of the measured PCB 4 and 11 congeners was performed using the original (ECD) surrogate recoveries in order to be consistent with the rest of the DADN data. Lab blanks were used for quality control. The results showed no significant PCB masses in the blanks, so blank correction was not required.

Table 4-2. The minimum, maximum, average, standard deviation (sd) of the surrogate recoveries of PCB 23 for DADN samples. The original analysis used ECD; the re-analysis used MS/MS.

	PCB 23	
	ECD	**MS/MS**
New Brunswick		
minimum	35%	46%
maximum	94%	135%
average	69%	99%
sd	10%	18%
Camden		
minimum	17%	24%
maximum	96%	196%
average	66%	101%
sd	16%	28%
Lums Pond		
minimum	50%	50%
maximum	94%	146%
average	70%	105%
sd	10%	23%

4.3 Results and Discussion

4.3.1 Breakthrough curve results

Seven sets of side-by-side samples were collected over a temperature range of 0 to 25 °C. Each set included three samples: the top half of the PUF (T), the bottom half of the PUF (B), and the XAD/PUF sandwich (X).

In order to ensure that the two side-by-side samples were sampling the same air mass, the congener pattern of each top plus bottom PUF sample was compared to its paired PUF/XAD sample (Table 4-3). The congener patterns were strongly correlated in six out of seven sample sets when non-detects were excluded ($R^2 > 0.80$). The one exception is the sample set collected on 11/12/2013 when the average temperature (0°C) and the ΣPCB concentrations (about 50 pg m^{-3}) were the lowest of all sample sets. In these samples, only 17 congeners were detected in both the PUF and XAD samples, and the correlation coefficient (R^2) was 0.59. Thus for most of the sample sets, breakthrough or loss of low molecular weight congeners from the PUF sample was not extensive enough to affect the correlation between congener patterns.

Table 4-3. Correlations of congener patterns measured in side-by-side sample sets.

Sample set	**Slope**	**R^2**
11/17/2013	0.92	0.94
11/12/2013	0.60	0.59
11/5/2013	0.69	0.82
11/4/2013	0.75	0.80
10/29/2013	0.88	0.88
10/28/2013	1.07	0.96
10/21/2013	0.92	0.83

Measured ΣPCBs were similar between side-by-side sample pairs (Table 4-4). The measured ΣPCBs was also similar to those measured at the nearby New Brunswick DADN site. There was little difference between the indoor and outdoor samples, suggesting that the ENR building is not significantly contaminated with PCBs.

Table 4-4. Concentration of ΣPCB congeners in samples used to calculate breakthrough collected at New Brunswick.

Date	Average Temperature (°C)	C_T PUF top (pg/m^3)	C_B PUF bottom (pg/m^3)	C_X PUF/XAD (pg/m^3)
10/21/2013 (Indoor)	23.5	530	38	464
10/28/2013 (Outdoor)	9.44	379	31	353
10/29/2013 (Outdoor)	8.88	400	34	515
11/4/2013 (Outdoor)	4.44	294	16	373
11/5/2013 (Outdoor)	8.33	226	24	314
11/12/2013 (Outdoor)	0.0	41	7.2	50
11/17/2013 (Outdoor)	14.4	378	57	447

Previous investigations in our laboratory[16] demonstrated that no measurable breakthrough of low MW PCBs occurs when using the PUF/XAD sandwich system. In contrast, PCBs 4 and 11 were detectable in the bottom half of the PUF in all samples, indicating possible breakthrough (Table 4-5). PCBs with three or four chlorines were occasionally detectable in the bottom half of the PUF. The fraction of PCBs recovered on the PUF was calculated by dividing the measured concentrations in the PUF sample (C_T plus C_B) by the measured concentration on the simultaneously collected PUF/XAD sample (C_X):

$$Recovery = \frac{C_T + C_B}{C_X} \qquad \text{(Eqn 4-1)}$$

In addition to recovery, breakthrough was calculated using the top (C_T) and bottom (C_B) PUF concentrations:

$$Breakthrough = \frac{C_B}{C_T+C_B} \qquad \text{(Eqn 4-2)}$$

Recovery and breakthrough were calculated for PCBs 4 and 11 as well as PCB 28 (trichloro) and PCB 49 (tetra) and PCB 93+95 (penta) for comparison.

Breakthrough (i.e. low recovery) of semivolatile compounds is expected to be a function of vapor pressure. For example, in the side-by-side samples, only the lowest MW PCBs are detectable in the bottom half of the PUF (Table 4-3). Thus it was expected that less breakthrough (higher recovery) would be observed at low temperature and vice versa. This trend is observed when breakthrough on the PUF is calculated (Figure 4-1), but not when recovery is calculated by comparing the concentration captured by the whole PUF vs. that captured on the PUF/XAD sandwich (Figure 4-2). Thus although increased temperature does cause the PCBs to migrate further into the PUF, it does not appear that they actually break through, i.e. they do not exit the PUF, in significant quantities.

Table 4-5. Concentrations and Breakthrough of PCBs in side-by-side PUF and PUF/XAD samples.

Date	PCB congeners	C_T Top PUF (pg/m^3)	C_B Bottom PUF (pg/m^3)	C_X PUF/XAD (pg/m^3)	% Breakthrough	% Recovery
10/21/2013	4	0.7	0.7	3.1	49%	46%
Indoor	11	28	9.3	36	25%	105%
T_{av} = 296.65K	28	15	2.2	16	13%	107%
	49	4.3	0.0	5.7	0%	76%
	93+95	35	0.0	35	0%	99%
10/28/2013	4	4.7	2.0	5.3	30%	127%
Outdoor	11	7.8	0.8	11	10%	76%
T_{av} = 282.59K	28	8.2	0.1	8.7	1%	96%
	49	4.1	0.0	3.7	0%	111%
	93+95	32	0.0	29	0%	112%
10/29/2013	4	3.6	6.9	9.0	66%	116%
Outdoor	11	8.7	0.6	17	6%	56%
T_{av} = 282.03K	28	9.4	0.3	17	4%	57%
	49	3.7	0.0	6.0	0%	62%
	93+95	31	0.0	34	0%	92%
11/4/2013	4	7.5	2.4	11	24%	94%
Outdoor	11	7.9	0.6	11	7%	78%
T_{av} = 277.59K	28	12	0.0	12	0%	100%
	49	4.4	0.0	4.9	0%	91%
	93+95	13	0.0	24	0%	54%
11/5/2013	4	1.0	2.1	2.8	68%	108%
Outdoor	11	7.1	1.8	11	20%	79%
T_{av} = 281.48K	28	9.1	0.9	11	9%	89%
	49	2.9	0.3	3.3	9%	96%
	93+95	12	0.0	18	0%	65%
11/12/2013	4	0.8	0.3	1.0	25%	109%
Outdoor	11	2.2	0.2	5.1	8%	47%
T_{av} = 272.6K	28	1.2	0.0	2.7	0%	44%
	49	0.4	0.0	1.1	0%	34%
	93+95	4.0	0.0	3.4	0%	115%
11/17/2013	4	2.0	2.3	4.9	53%	88%
Outdoor	11	14	3.6	19	21%	93%
T_{av} = 287.59K	28	12	1.5	14	12%	95%
	49	5.5	0.7	5.4	11%	113%
	93+95	22	3.0	29	12%	88%

The recovery of the PCB congeners ranged from 35% to 130% with the average (± standard deviation) recoveries ranging from 76±20% for PCB 11 to 98±26% for PCB 4. There was no trend of congeners with higher vapor pressures displaying lower recoveries. Based on the results of the breakthrough experiments, it was decided not to correct the measured concentrations of PCBs 4 and 11 for breakthrough. This decision was based on three observations. First, the lack of clear temperature dependence of recovery suggests that any correction for breakthrough would not be a function of temperature, but rather a constant factor applied to all samples. As a result, seasonal patterns and temperature dependence would not be affected by the correction. Second, there was no clear trend of congeners with higher vapor pressures displaying higher breakthroughs. It seems arbitrary to assign a correction factor based on the empirical results of the breakthrough study with no underlying mechanistic principle. Third, because the variation in the breakthrough measurements does not appear to be function of temperature or vapor pressure, it is probable that the variation is random. Basing a correction factor on random variability will only serve to increase, not decrease, the uncertainty in the reported concentrations. No correction factor would be applied to PCB 4 in any case, since the average recovery of PCB 4 was not different from 100%. Sandy et al.[16] collected 4 side-by-side high volume air samples all using the same PUF/XAD sandwich and GC/MS/MS method employed in the breakthrough study. They found that the relative standard deviations (RSDs) of the measure concentrations of individual PCB congeners ranged from 2% to 42%, with an average of 17% and a geometric mean of 15%. The RSDs for PCBs 4 and 11 were 7% and 22%, respectively. Based on the average recovery of PCB 11 in the breakthrough experiments, the implied correction factor would be 24%, which is similar to the 22% uncertainty measured by Sandy et al.[16] Thus the uncertainty associated with breakthrough is likely to arise from the uncertainty in the measurement of PCB 11, not from breakthrough itself. Therefore the results of the breakthrough study do not justify the application of a correction factor to the gas-phase PCB concentrations measured from the re-analysis of the DADN samples.

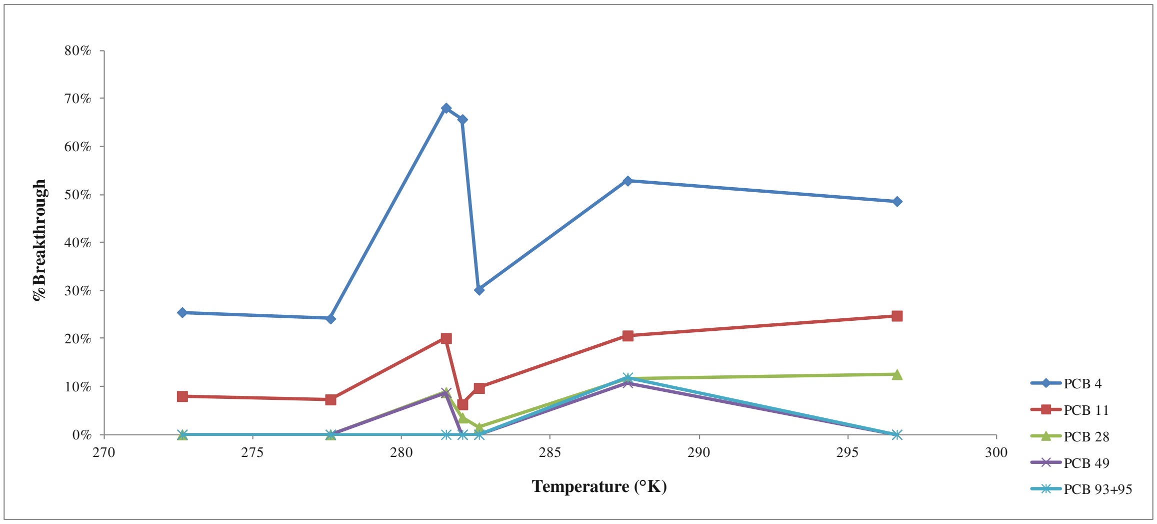

Figure 4-1. Breakthrough of PCBs 4, 11, 28, 49, and 93+95 as a function of temperature.

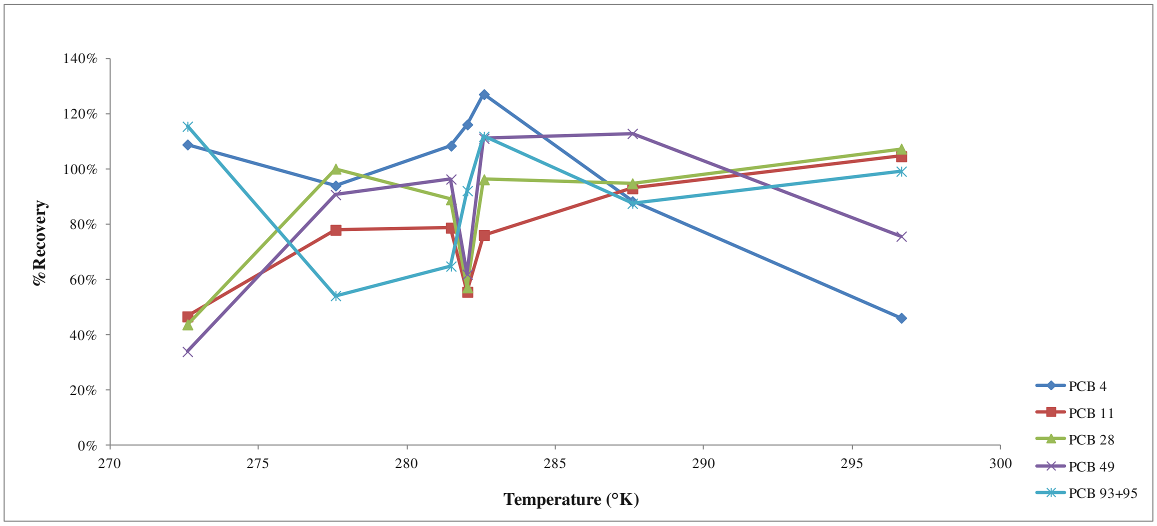

Figure 4-2. Recovery of PCBs 4, 11, 28, 49, and 93+95 as a function of temperature.

4.3.2 Concentrations of PCBs 4 and 11 in DADN samples

Concentrations of PCBs 4 and 11 measured at the three sites ranged from 0.18 to 168 pg m^{-3} for PCB 4, and from non-detect to 146 pg m^{-3} for PCB 11, respectively (Table 4-6; Figure 4-3 through 4-5). Concentrations of PCB 11 were higher than concentrations of PCB 4 in 28 out of 35 samples from New Brunswick, and in 31 of 38 samples from Lums Pond. At Camden, PCB 11 was greater than PCB 4 in only 9 of 46 samples.

Relatively few studies have quantified PCBs 4 and 11 in the atmosphere. The few studies that have measured PCB 11 in the gas phase found levels similar to those encountered at the three DADN sites. Choi et al.[21] reported the first measurements of PCB 11 in the air by passive sampling in Antarctica, and the highest concentrations was found at 60 pgm^{-3}. Hu et al.[9] reported PCB 11 concentrations via active sampling ranging from non-detect to 72 pg m^{-3} in Chicago. Basu et al.[22] measured PCB 11 in samples from the Integrated Atmospheric Deposition Network (IADN) from 5 sites surrounding the Great Lakes. They reported PCB 11 concentrations ranging from non-detect to 144 pg m^{-3}. Du et al.[3] reported PCB 11 concentrations via passive air sampling in Philadelphia metropolitan area (including the DADN Camden site) ranging from 4 to 44 pg m^{-3}. Sandy[15] reported PCB 11 concentrations ranging from 25 to 110 pg m^{-3} in Piermont, NY.

Measurements of PCB 4 in the atmosphere are even rarer. Using active high-volume air sampling and the PUF/XAD sandwich system, Sandy[15] reported PCB 4 concentrations ranging from non-detect to 181 pg m^{-3} in Piermont, NY. Du et al.[3] measured PCB 4 via passive sampling and found that concentrations in the Philadelphia region ranged from non-detect to 64 pg m^{-3} with a median of 11 pg m^{-3}, in good agreement with the DADN measurements presented here.

For most PCB congeners, gas-phase concentrations are highest at Camden and lowest at Lums Pond, where they are lower by a factor of about 20.[1-4] PCB 11 did not follow this pattern. PCB 11 concentrations were similar across all three sites (Table 4-6). For PCB 4, the concentrations were generally highest at Camden, but concentrations were lower by only a factor of about 5-10 at both New Brunswick and Lums Pond. This suggests that PCB 4 and PCB 11 come from different sources than other PCB congeners. In contrast, Basu et al.[22] reported higher gas-phase PCB 11 concentrations at the more urban sites (Chicago and Cleveland).

PCBs 4 and 11 were some of the most abundant congeners in the DADN samples. At New Brunswick, PCB 11 was the most abundant congener in 19 of 35 samples, accounting for between 3% and 44% of the sum of PCBs. At Lums Ponds, PCB 11 concentrations are about the same as in New Brunswick, but because the sum of PCBs is lower at Lums Pond, PCB 11 is proportionately more important there. PCB 11 is the most abundant congener in 19 of 37 samples from Lums Pond and comprises up to 46% of the sum of PCBs. PCB 11 is proportionately less important at Camden, where it accounts for up to 6% of the sum of PCBs.

PCB 4 concentrations were highest at Camden, where it was the most abundant congener in 6 out of 46 samples, accounting for between 0.1% and 16% of the sum of PCBs. This is particularly surprising since the sum of PCBs is so much higher at Camden than at the other DADN sites. At New Brunswick, PCB 4 was the most abundant congener in 5 of the 35 samples and accounted for between up to 13% of the sum of PCBs. At Lums Pond, PCB 4 comprised up to 16% of the sum of PCBs.

Table 4-6. Minimum, maximum, and percentile concentration (pg m^{-3}) of PCBs 4 and 11 at the three DADN sites. ND = not detected.

	New Brunswick	Camden	Lums Pond
	PCB 4		
Minimum	0.27	3.5	0.9
10%	1.6	12	2.0
25%	2.1	16	2.9
50%	3.4	29	4.4
75%	6.6	54	6.2
90%	8.6	123	13
Maximum	20	197	42
	PCB 11		
Minimum	1.7	ND	ND
10%	4.0	5.6	2.7
25%	5.7	11	8.5
50%	12	16	13
75%	64	23	21
90%	81	35	67
Maximum	195	120	243

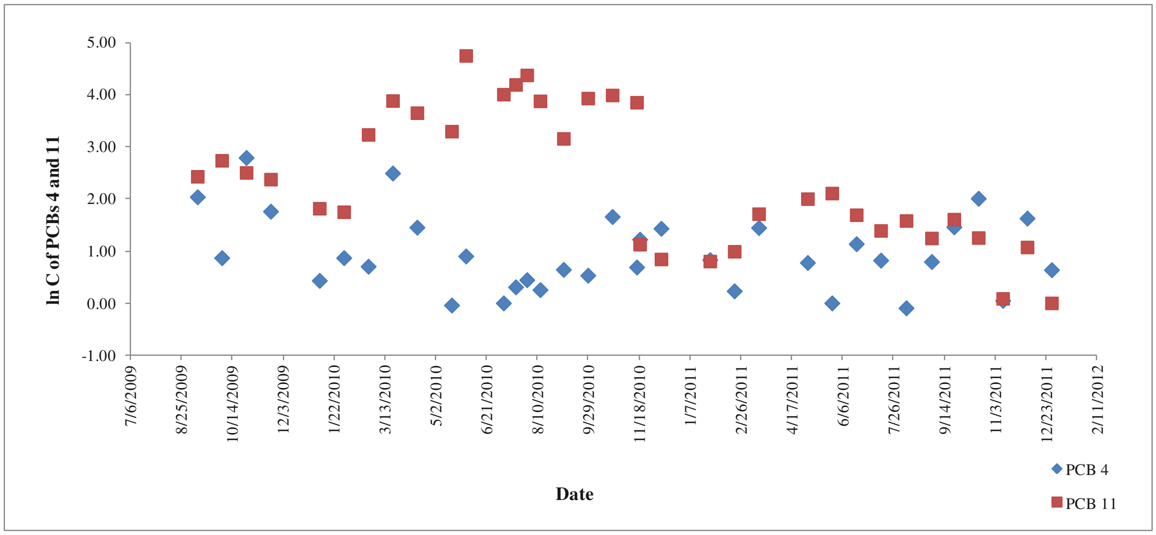

Figure 4-3. Natural log concentration of PCBs 4 and PCB 11 by date at New Brunswick.

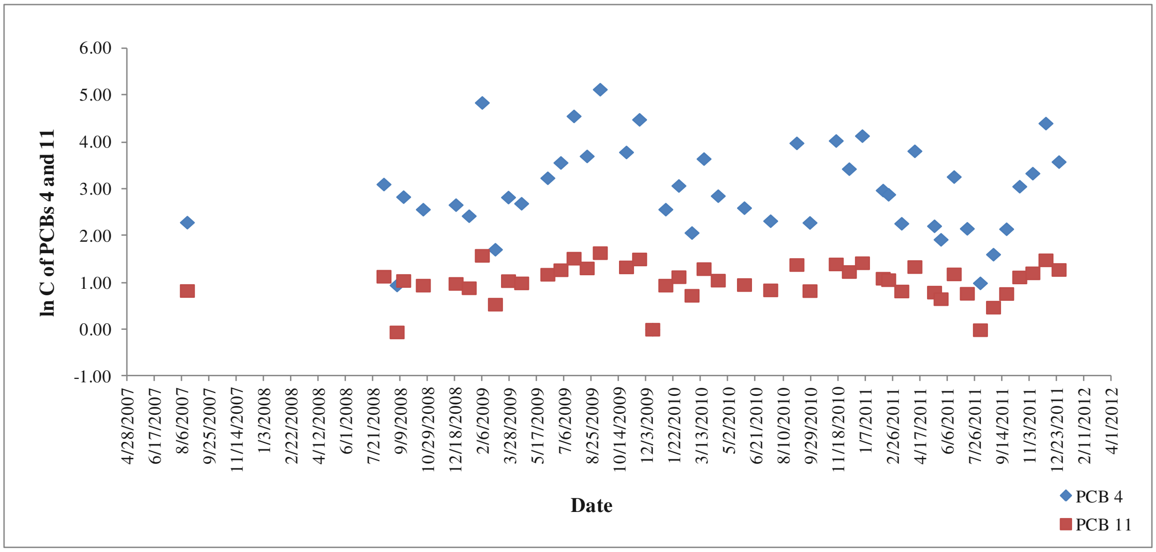

Figure 4-4. Natural log concentration of PCBs 4 and PCB 11 by date at Camden.

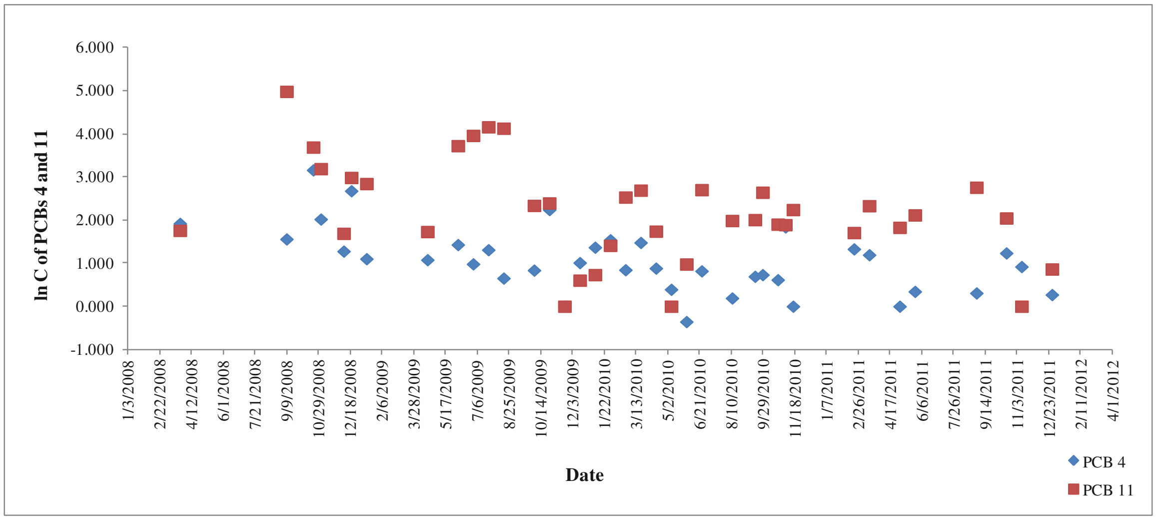

Figure 4-5. Natural log concentration of PCBs 4 and PCB 11 by date at Lums Pond.

There is no obvious seasonal trend in gas-phase PCB 4 and PCB 11 concentrations (Figures 4-3 through 4-5). This is surprising, since gas-phase atmospheric PCB concentrations are often a function of temperature[1, 23-29] according to the Clausius-Clapeyron equation:

$$\ln C_{gas} = a_0 + a_1\left(\frac{1}{T}\right) \qquad \text{(Eq. 4.3)}$$

where C_{gas} is the gas-phase PCB concentration, T is temperature (K), and a_0 and b_1 are fitting constants. Application of equation 4.3 reveals that PCB 4 concentrations are a function of temperature at only at Lums Pond, but the slope is positive indicating lower concentrations at higher temperatures (Table 4-7; Figures 4-6 through 4-8). Similarly, PCB 11 concentrations were significantly correlated with temperature at Lums Pond, but the slope is positive. Only for PCB 11 at New Brunswick is the relationship between concentration and temperature significant with a negative slope of -5213, which is typical for low MW PCB congeners at New Brunswick (see Chapter 3). The other PCB congeners generally display much stronger correlations with temperature at the DADN sites, with R^2 values generally in the range of 0.30 to 0.79 and slopes of -4000 to -12000 (see Chapter 2). In contrast, Basu et al. [22] observed that PCB 11 concentrations were strongly correlated with temperature in Chicago with a slope of -7377 and an R^2 of 0.697. They did not report the results of the temperature regression for the other IADN sites. It must be remembered, however, that these regressions were performed for a relatively small number of samples. Carlson and Hites[23] suggest that calculations based on less than 30 samples collected over the course of one year were not a reliable indicator of the temperature dependence of gas-phase PCB concentrations. Here between 35 and 46 samples collected over the course of 3 to 5 years were used.

Table 4-7. The results of regression of concentrations versus temperature via equation 4-3 at the three sites.

		R^2	a_1 (1/T)	P-Value of slope (sig < 0.05)
New Brunswick (n = 35)	PCB 4	0.06	1515 ± 2117	0.15
	PCB 11	**0.22**	**-5213 ± 3485**	**0.005**
Camden (n = 46)	PCB 4	0.02	1154 ± 2368	0.33
	PCB 11	0.04	554± 879	0.21
Lums Pond (n = 38)	PCB 4	**0.40**	**1839± 766**	**2E-05**
	PCB 11	**0.12**	**1597± 1439**	**0.03**

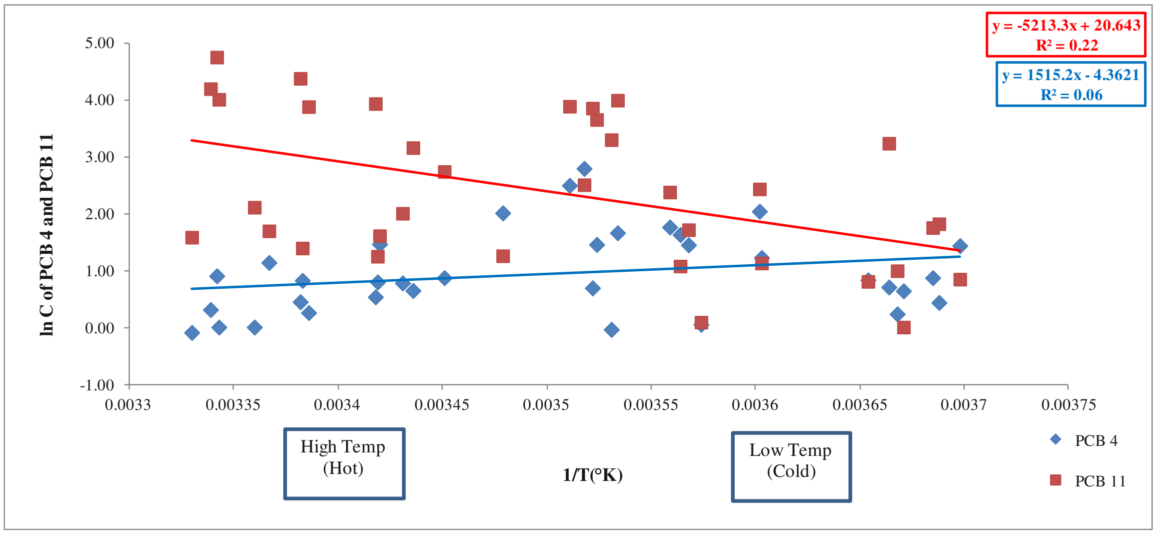

Figure 4-6. The results of the natural log concentration of PCBs 4 and PCB 11 versus one over temperature at New Brunswick.

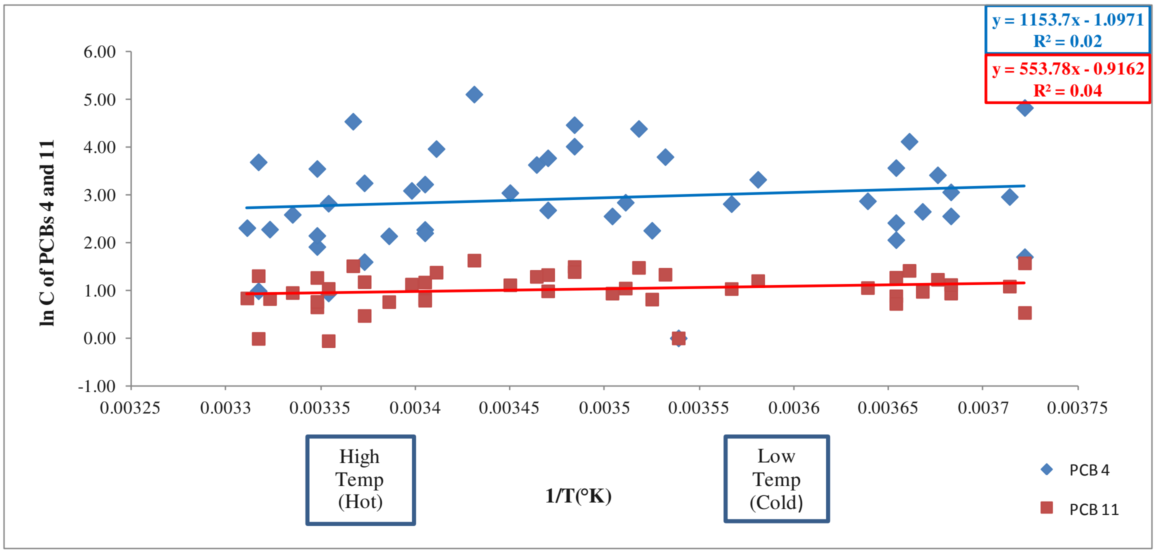

Figure 4-7. The results of the natural log concentration of PCBs 4 and PCB 11 versus one over temperature at Camden.

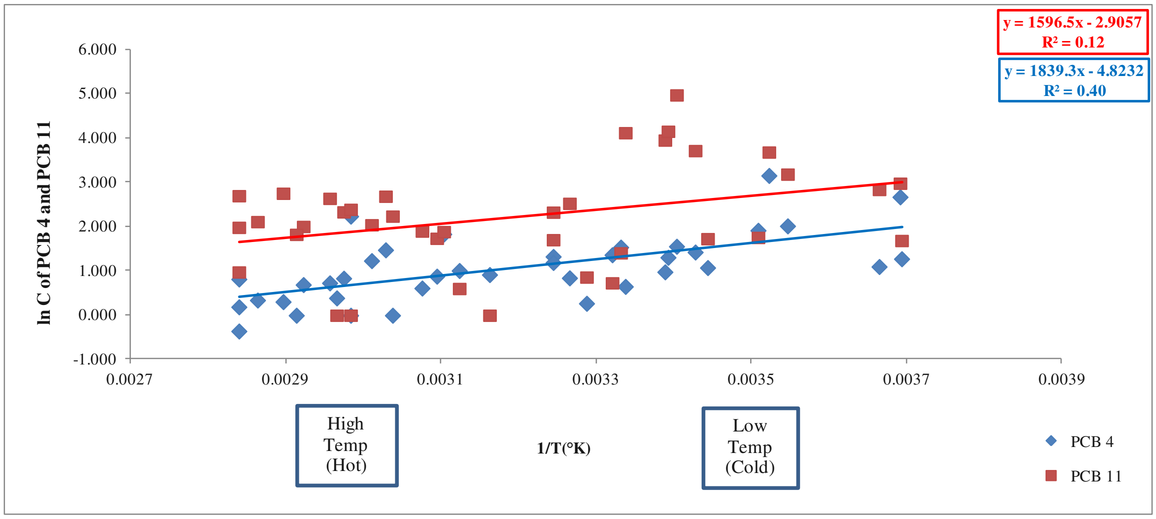

Figure 4-8. The results of the natural log concentration of PCBs 4 and PCB 11 versus one over temperature at Lums Pond.

4.4 Discussion

This study represents the first examination of the problem of breakthrough of PCB congeners when collecting air samples using PUF as a sorbent as a function of temperature. The results showed that while low MW PCB congeners do migrate into the bottom half of the PUF, under normal sampling conditions (24 hours at a flow of about 0.5 m^3 min^{-1}) they do not blow off the PUF. Therefore, PUF can be used to accurately quantify concentrations of low MW PCBs in the gas phase. Based on the breakthrough study, the DADN measurements of PCB concentrations using PUF were judged to be accurate and did not require correction for breakthrough.

The reanalysis of the DADN samples suggests that PCBs 4 and 11 constitute a significant proportion of the atmospheric PCB burden. Guo[30] developed a one-box model for the Delaware River Basin. Using her model and the median concentrations of PCBs 4 and 11 measured at Lums Pond and New Brunswick suggests that on the order of 120 kg y^{-1} of PCB 4 and 370 kg y^{-1} of PCB 11 are emitted into the air of the Delaware River Basin.

PCB 11 is thought to enter the environment via the use of certain pigments in printing inks.[7] Guo[30] calculated that the production of PCB 11 via this route is large enough to account for the levels of PCB 11 measured in the air, water, and sediment of the Delaware River Basin. This usage pattern implies that PCB 11 concentrations should be higher in areas with greater population density (i.e. greater pigment use). Basu et al.[31] observed higher PCB 11 concentrations in the urban areas of Chicago and Cleveland than at the more remote IADN sites. In the present work, however, PCB 11 concentrations were similar across all three sites representing urban, suburban, and rural locations. This may indicate that long-range transport contributes significantly to the PCB 11 concentrations measured in the DADN. Alternatively, it could suggest that pigment use in printed material does not drive the atmospheric distribution of PCB 11. Perhaps the presence of recycled paper mills or large print shops may drive PCB 11 concentration dynamics in the New Jersey/Delaware region. A search of the Toxics Release Inventory (http://iaspub.epa.gov/triexplorer/tri_release.chemical) for facilities that are listed under textiles, apparel, paper, printing and publishing, and furniture revealed some facilities that might use or process materials that contain pigments that contain PCB 11. Three facilities were located in Middlesex County near the New Brunswick site: ITWCOVID Security Group, Covalence Adhesives, and Schweitzer-Mauduit International. Near the Camden site, six facilities were located in Chester, Delaware, Philadelphia and Montgomery counties, including the Kimberly-Clark plant in Chester, PA, about 30 km from the Camden DADN site. This plant is noteworthy because stormwater from this site had extremely high concentrations of PCB 11 of up to 20 ng/L.[7] Near the Lums Pond site, Rohm & Hass has a large facility in New Castle county, DE.

The fact that gas-phase concentrations of PCBs 4 and 11 were generally not driven by temperature in these samples suggests that passive volatilization (as from printed material or painted surfaces) was not the dominant source of these congeners.

PCB 4 concentrations were about a factor of 8 higher in Camden than at New Brunswick or Lums Pond. A similar gradient was observed in PCB 4 concentrations in the passive sampling campaigns of Du et al.[3] and Guo.[30] PCB 4 is a main product of PCB dechlorination by anaerobic bacteria. PCB dechlorination can occur in the sediment of lakes and river, and is known to be prevalent in the Upper Hudson River.[32-34] Some of the dechlorination products travel downstream to the New York/New Jersey Harbor.[35] New Brunswick is about 39 km from Raritan Bay, which is part of the NY/NJ Harbor. It is possible that volatilization of PCB 4 from the Bay contributes to PCB 4 concentrations in New Brunswick. The analysis presented in Chapter 2 suggests that dechlorination of PCBs is not important in the sediment of the Delaware River, so it is unlikely to contribute to the PCB 4 concentrations measured at Camden and Lums Pond. Recently it has been recognized that PCBs are dechlorinated by bacteria in sewers.[36] This dechlorination is most extensive in the sewers of Philadelphia and Chester, PA; Camden, NJ; and Wilmington, DE. The Philadelphia, Chester, and Camden are all part of the metropolitan Philadelphia area. Camden County Municipal Utilities Authority lies approximately 3 km from the Camden DADN site. The Philadelphia Water Department operates three treatment plants called the Northeast, Southeast, and Southwest plants. They lie about 6 km, 5 km, and 10 km from the Camden DADN site, respectively. Thus we speculate that the high concentrations of PCB 4 measured at the Camden DADN site are largely driven by volatilization of PCB 4 directly from sewers or indirectly from sewage treatment plants during aeration and aerobic digestion of sewage and/or from the water column of the Delaware River, where PCB 4 volatilizes after being discharged to the river via treated effluents or combined sewer overflows. In contrast, the effluents of sewage treatment plants in New Jersey and the remainder of the Delaware River basin suggest that dechlorination is not particularly prevalent in the areas surrounding the Lums Pond and New Brunswick DADN sites.[36, 37]

This study has demonstrated that PCBs 4 and 11 are important contributors to atmospheric PCB concentrations and can be accurately quantified by PUF high-volume air sampling. We recommend the routine detection and reporting of these congeners as part of atmospheric PCB sampling in all future investigations.

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Chapter 5: Conclusions and Future Work

5.1 Summary of findings

This dissertation presented source apportionment of polychlorinated biphenyls in New Jersey Air and Delaware River Sediments. Chapter 2 attempted to identify PCB sources in Delaware River sediments. In our previous work, we identified PCB sources from other environmental compartments such as the air, water column, and the discharges from permitted facilities on the tidal Delaware River.[1-4] The main goal of this study was to complete the picture of PCB cycling in an urbanized estuary. Positive matrix factorization (PMF) was used to identify PCB sources in this study because this method has been used successfully to identify PCB sources in many studies.[1-9] Seven factors were resolved in the sediments. These were related to sources including PCB 209 ($TiCl_4$ production), three Aroclors (A1248, A1254, and A1260), and PCB 11 from pigments. The other two sources were thought to represent highly weathered Aroclors. The results of this study allowed us to compare the PCB sources to sediment with the sources to the other compartment.[1, 4, 6-9] This study did not find a dechlorination signal (characterized by high proportions of PCB 4) in the Delaware River sediments.

Although PCB sources in the air have already been investigated by our research group[2, 3, 5], this dissertation extended these investigations by examining PCB concentrations trends for a long period of time (1997-2011). Source apportionment using PMF was used to identify PCB sources to New Jersey air (Camden and New Brunswick) in Chapter 3. PMF analysis revealed four resolved factor each in Camden and New Brunswick. The dominant PCB source to the atmosphere in both locations resembled unaltered Aroclor 1242 and vaporized Aroclor 1248. A similar congener pattern was the dominant PCB source to Chicago air.[5] The correlations between PCB concentrations versus time and temperature at these two sites suggested that natural attenuation alone will not control atmospheric PCB concentrations, and additional efforts are needed to control PCB emissions. In addition, the total maximum daily loads (TMDLs) for the Delaware River cannot be achieved without human intervention because of the continuing atmospheric deposition of PCBs.

Besides PCB Aroclor sources, we found that non-Aroclor sources also contaminate the environment with PCBs. Our previous studies reported the evidence of non-Aroclor sources in the tidal Delaware River.[1, 2, 4, 10, 11] Both PCBs 4 and 11 are dichlorobiphenyls and are characteristic of non-Aroclor sources such as pigment use in consumer products (PCB 11)[12] and dechlorination of higher molecular weight PCBs (PCB 4). Since atmospheric deposition may be a significant source of PCBs to water bodies, possibly causing them to exceed their total maximum daily loads (TMDLs), monitoring of atmospheric PCB concentrations is necessary to identify their sources and to quantify atmospheric deposition. However, the original DADN project did not quantify PCBs 4 and 11 due to possible problems with breakthrough when using polyurethane foam (PUF) as an sorbent.[13] Therefore PCBs 4 and 11 were quantified in the gas phase by reanalyzing a subset of the DADN samples in Chapter 4. First it was necessary to quantify the extent of breakthrough of these congeners on the PUF sampling media; however the results showed little or no breakthrough of PCBs 4 and 11. This suggests that DADN measurements using PUF are accurate and do not require correction for breakthrough. The reanalysis of the DADN samples showed that the gas-phase concentrations measured at the DADN sites ranged from non-detect to146 pg m^{-3} for PCB 11 and ranged from 0.18 to 168 pg m^{-3} for PCB 4, and gas-phase PCB 11 concentrations did not display a strong urban to rural gradient.

Taken together, my results demonstrate that, due to their persistence, PCBs continue to cycle through the environment via air, water, sediment, and soils, even though PCB manufacture and use were banned in the late 1970s. Emissions of "legacy" or Aroclor-type PCBs were studied to reveal concentration trends and identify sources. This dissertation further developed the use of statistical tools (such as PMF) to help us to identify PCB sources, and also determined that air sampling using PUF is an acceptable method of measuring low molecular weight PCBs in the gas phase.

5.2 Implications

The results of these three chapters increased our understanding of PCB sources in the air and sediment in terms of their magnitude and their accumulation removal. For PCB sources in the Delaware River sediments, the result showed the largest single source of PCB was the production of $TiCl_4$ resulting in the accumulation of heavy PCB congeners (PCB 206/208/209) in sediment. No dechlorination signal was observed in sediments. Therefore these high molecular weight PCB congeners will persist and continue to effect the sediment and (via resuspension of sediment) water quality of the Delaware River.

In Camden and New Brunswick air, the dominant PCB sources were low molecular weight Aroclors such as Aroclors 1242 and 1016, and these factors were not decreasing from 2004-2011. In fact only one factor out of eight at both sites declined from 2004-2011. Therefore the dominant atmospheric PCB source will continue to effect air in Camden and New Brunswick. Since PCB concentrations are a function of temperature, urban areas might have higher PCB concentrations than suburban or rural areas due to their generally higher temperatures. As a result, it is not surprising that we found a stronger temperature effect in Camden (urban) than New Brunswick (suburban). It is possible that global warming might lead to increased PCB concentrations in the atmosphere due to increasing average temperatures.

The breakthrough study showed that PUF can be used to accurately sample low molecular weight PCBs in the gas phase. Thus I recommend that PCBs 4 and 11 should be measured in all future investigation since these two congeners are important and represent non-Arolcor PCB sources. Since PCB 4 concentration was highest at Camden, the sources of this PCB congener should be clarified. Future work should also study the breakthrough of PCBs when using PUF sampling media in other areas (urban and rural) to be sure the results obtained in New Brunswick can be applied to all areas.

5.3 Future Work

Even though this dissertation have successfully studied PCB sources in the air and the river sediments including temperature dependence and breakthrough studies of low molecular weight of PCBs, some new questions also need and allow the future thesis work to continuously find the answers The following directions below might be helpful to investigate more PCB sources in the air and the river sediments:

1) Source apportionment of PCBs in the Delaware River sediment revealed that PCBs 206, 208, and 209 from $TiCl_4$ manufacture are responsible for the largest share of the

PCB mass in the sediment. These congeners are very hydrophobic and are not likely to be transported out of the estuary. At the same time, dechlorination was not found to be measurable in the sediment. How will the concentrations of PCBs 206, 208, and 209 ever be reduced in the Delaware River sediment? I recommend more study of dechlorination in Delaware River sediments to determine whether any dechlorination is taking place and/or whether dechlorination can be stimulated in the sediment. Since some studies found evidence of microbial dechlorination in river or lake sediments[6, 9], so we expect that the dechlorination of the dominated PCB source (PCB 209) might occur in the Delaware River sediment as well. To investigate this issue, Delaware River sediments might be collected to study the degradation of PCBs under aerobic or anaerobic conditions.

2) Since the average concentrations of PCB 4 were highest at Camden Air (Chapter 4), we speculated that this PCB congener might come from the dechlorination of PCBs in the sewer, and might be volatized to Camden Air. To determine whether our speculation is correct, future work should identify how high PCB 4 concentrations are in dischargers near the Camden site, and use PMF modeling to identify PCB sources in these dischargers.

3) Since this study was the first time to investigate breakthrough of PCBs in air samples using PUF as an sorbent, to confirm that this study can be applied to all atmospheric PCB samples in all areas, additional PCB atmospheric samples should be collected at other locations and over a broader range of temperature. Samples should be collected at Camden and Lums Ponds to further study the breakthrough of PCBs since these two sites represent urban and rural areas and can be compared to New Brunswick (suburban).

Taking PCB air samples at Camden and Lums Ponds over a wider range of temperatures would help to determine whether the results observed in New Brunswick apply to all types of locations.

Although this dissertation revealed a lot of information, PCBs should continue to be studied to solve the complex problems associated with PCB occurrence in the environment. The information in this dissertation will support future work on PCB source identification and monitoring to further out understanding of PCB cycling in the environment.

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Appendix A

A) Supporting Information of Source Apportionment of Polychlorinated Biphenyls in the sediments of the Delaware River.

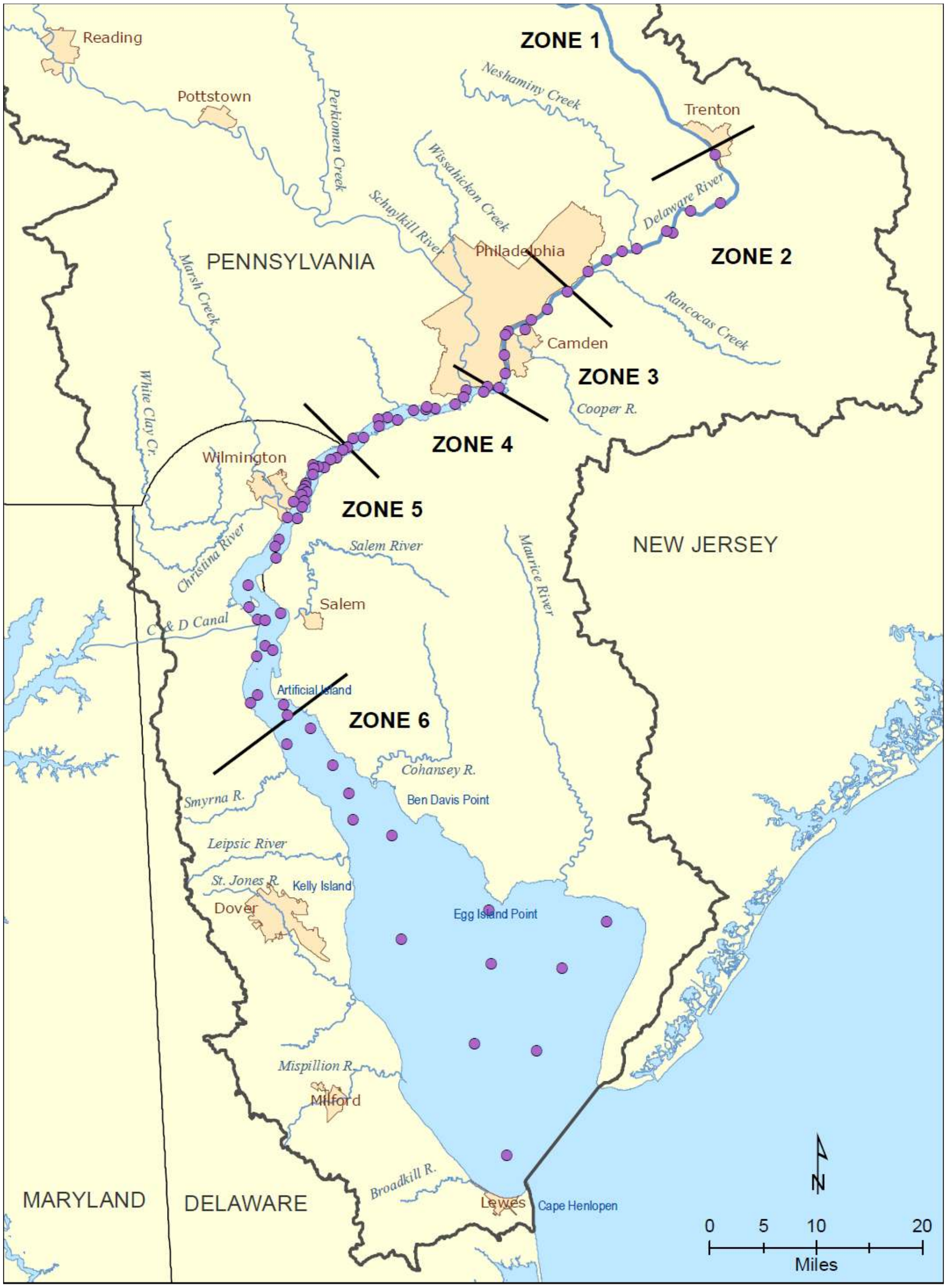


Figure A-1. Delaware River Stdudy area. Circles indicate locations where sediment samples were collected. The boundary of the watershed is outlined in back.

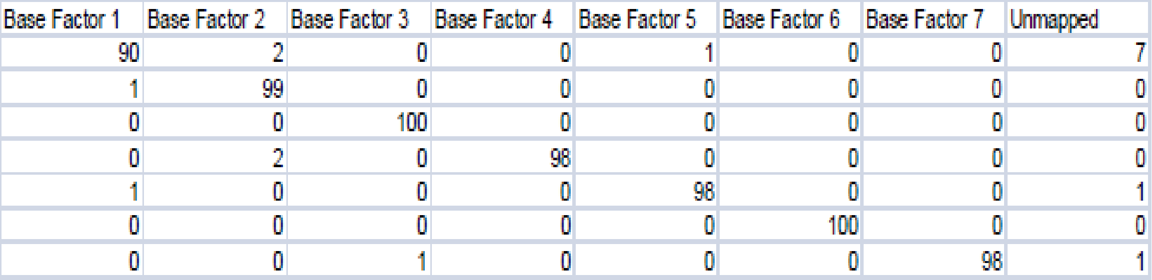
Analytical

Sediment samples were prepared and analyzed as per EPA method 1668A. Specifically, 10 grams of wet sediment were extracted in toluene using a Soxhlet/Dean Stark apparatus. The extracts in toluene were cleaned up on columns of acid, neutral, and basic silica gel and Florisil. Quantification was performed with a high-resolution gas chromatograph/high resolution mass spectrometer.

Determination of the number of factors

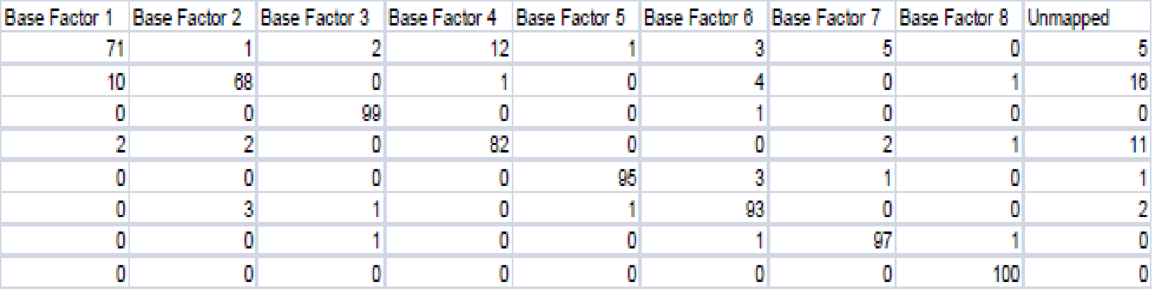
Determining the correct number of factors is an important step in any factor analysis. We used four criteria to determine that the correct number of factors was seven. First, we chose highest number of factors that provided a stable model result. This was determined by examining the relative standard deviation (RSD) of the G-matrix across 9 model runs using different seed values. The seven-factor model yielded an RSD of 0.5%, versus 41.5% for the eight-factor model. Second, the chosen number of factors must provide a good fit (correlation) between the measured concentrations and the model PCB concentrations. The seven factor model yielded an R^2 between the measured and modeled concentrations better than 0.95 for 85 of the 87 congeners. For the remaining two congeners (PCBs 60 and 77), the R^2 was better than 0.7. Third, the resolved factors must be interpretable. The seven resolved factors resembled the Aroclors and some non-Aroclor sources, as described below. Fourth, we used the EPA's PMF 3.0 software (http://www.epa.gov/heasd/products/pmf/pmf.html) and conducted a bootstrapping analysis of the 7 and 8 factors solutions. The results are presented in Table A-1 and A-2. Table A-1 demonstrates that all 7 factors are correctly mapped in at least 90% of all bootstrap runs. In contrast, Table A-2 reveals that some factors, especially factor 1 and 2, map correctly in as little as 68% of runs when 8 factors are requested. This is a clear indicator that 7 is the correct number of factors. Finally, we note that the PMF analysis of the PMF analysis of the DRBC discharger database also yielded seven factors[7], and the PMF analysis of the water column database yielded six factors.[5]

Table A-1. Bootstrapping analysis of the 7-factor solution using the EPA PMF 3.0 software.



Base Factor 1	Base Factor 2	Base Factor 3	Base Factor 4	Base Factor 5	Base Factor 6	Base Factor 7	Unmapped
90	2	0	0	1	0	0	7
1	99	0	0	0	0	0	0
0	0	100	0	0	0	0	0
0	2	0	98	0	0	0	0
1	0	0	0	98	0	0	1
0	0	0	0	0	100	0	0
0	0	1	0	0	0	98	1

Table A-2. **Bootstrapping analysis of the 8-factor solution using the EPA PMF 3.0 software.**



Base Factor 1	Base Factor 2	Base Factor 3	Base Factor 4	Base Factor 5	Base Factor 6	Base Factor 7	Base Factor 8	Unmapped
71	1	2	12	1	3	5	0	5
10	68	0	1	0	4	0	1	16
0	0	99	0	0	1	0	0	0
2	2	0	82	0	0	2	1	11
0	0	0	0	95	3	1	0	1
0	3	1	0	1	93	0	0	2
0	0	1	0	0	1	97	1	0
0	0	0	0	0	0	0	100	0

Appendix B

B) Multiple Linear Regressions (MLR) between G matrix and the sum of PCBs of Camden and New Brunswick.

B-1. Multiple Linear Regression between G matrix and the sum of PCBs of Camden data.

Regression Statistics	
Multiple R	0.986505596
R Square	0.973193291
Adjusted R Square	0.972725052
Standard Error	329.5352308
Observations	234

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	902806756.2	225701689	2078.409434	1.2155E-178
Residual	229	24867904.25	108593.4683		
Total	233	927674660.4			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-106.2277525	35.20457961	-3.0174413	0.002837381	-175.5940546	-36.86145042
1C	1.291140732	0.027515045	46.92489995	1.8738E-119	1.236925714	1.34535575
2C	1.02653827	0.028759582	35.6937833	1.56652E-95	0.969871046	1.083205495
3C	0.851213908	0.057844481	14.71555957	6.01214E-35	0.73723846	0.965189357
4C	1.095732651	0.092805133	11.8068108	1.93642E-25	0.912871529	1.278593773

B-2. Multiple Linear Regression between G matrix and the sum of PCBs of New Brunswick data.

Regression Statistics	
Multiple R	0.977789128
R Square	0.95607158
Adjusted R Square	0.955489746
Standard Error	64.95783354
Observations	307

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	27734147.93	6933536.983	1643.205094	1.6483E-203
Residual	302	1274295.082	4219.520138		
Total	306	29008443.01			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	40.39464711	5.886911786	6.861772111	3.85942E-11	28.8100868	51.97920743
NB1	1.02857667	0.030776818	33.42050119	1.7705E-103	0.968012505	1.089140836
NB2	1.076937985	0.080283577	13.41417538	1.66817E-32	0.918951935	1.234924036
NB3	1.016931872	0.061701219	16.48155241	5.60584E-44	0.895513118	1.138350625
NB4	1.027192251	0.076893293	13.35867153	2.66603E-32	0.875877771	1.178506731

Appendix C

C) New R^2 of Mass Vs Model without outliers for PCB congeners had low R^2

C-1. Camden

No	PCB Congener	R^2	R^2 excluded outliers	Outliers
1	17+15	0.433	0.701	10/9/1999, 11/2/1999, 3/1/2000, 5/12/2000, 6/5/2000, 8/7/2000, 8/8/2000, 8/9/2000, 8/9/2000, 8/10/2000, 8/10/2000, 9/20/2001, 8/15/02 8am, 8/31/2004, 8/4/2007
2	85+136	0.504	0.706	9/27/1999, 8/10/2000, 8/16/2000, 9/20/2001, 10/2/2001, 6/8/2004, 10/30/2004
3	82	0.457	0.703	8/16/2000, 9/9/2000, 8/10/2002
4	135+144+147+124	0.488	0.937	8/31/2004, 10/18/2004, 10/30/2004
5	137+176+130	0.349	0.707	2/18/2000, 3/1/2000, 3/25/2000, 4/30/2000, 8/4/2000, 8/16/2000, 8/28/2000, 9/21/2000, 10/3/2000, 11/20/2000, 12/2/2000, 8/13/2002 (10am), 10/18/2004, 10/20/2006, 12/13/2007
6	183	0.358	0.856	10/18/2004
7	185	0.002	0.827	10/21/1999, 8/12/2003, 8/13/2003, 10/18/2004, 4/28/2005, 10/13/2005, 12/12/2005, 2/10/2006, 5/17/2006, 7/4/2006, 10/8/2006, 11/25/2006, 12/7/2006, 12/19/2006, 4/6/2007, 11/8/2007, 11/20/2007, 1/19/2008, 1/31/2008, 2/12/2008, 2/24/2008, 2/10/2011
8	177	0.167	0.714	10/21/1999, 10/18/2004, 12/7/2006, 12/13/2007, 1/31/2008
9	199	0.030	0.702	10/21/1999, 12/20/1999, 10/18/2004, 2/27/2005, 3/18/2006, 12/19/2006, 2/17/2007, 11/8/2007, 12/13/2007, 1/31/2008, 2/12/2008, 3/2/2009
10	170+190	0.240	0.719	10/18/2004, 11/25/2006, 12/7/2006, 12/19/2006, 4/6/2007, 11/8/2007, 12/13/2007, 1/19/2008, 1/31/2008, 2/12/2008, 2/24/2008, 3/2/2009, 12/10/2010, 1/3/2011
11	194	0.213	0.707	10/18/2004, 3/18/2006, 2/17/2007, 12/13/2007, 1/19/2008, 1/31/2008, 2/12/2008,
12	206	0.576	0.682	6/25/2010

C-2. New Brunswick

No	PCB Congener	R^2	R^2 excluded outliers	Outliers
1	45	0.368	0.706	10/9/1997, 10/12/1997, 10/13/1997, 11/6/1997, 11/30/1997, 2/10/1998, 2/28/1998, 6/10/1998, 6/16/1998, 6/25/1998, 6/26/1998, 7/16/1998, 7/22/1998, 8/3/1998, 8/21/1998, 8/27/1998, 9/2/1998, 9/13/1998, 9/22/1998, 9/25/1998, 12/3/1998, 5/5/1999, 6/10/1999, 5/12/2000, 8/10/2000, 8/11/2000, 8/28/2000, 9/9/2000, 10/27/2000, 12/6/2006, 12/15/2009, 1/8/2010, 3/21/2010
2	49	0.344	0.721	3/25/2000, 8/7/2000, 8/9/2000, 8/9/2000, 4/12/2002, 5/6/2002, 5/30/2002, 7/17/2002, 5/1/2003,
3	47+48	0.480	0.718	8/3/1999, 4/6/2007, 1/8/2010
4	74	0.074	0.704	6/25/1998, 6/19/1999, 11/7/2001, 3/1/2007, 12/15/2009, 3/21/2010
5	87+81	0.082	0.702	10/21/1997, 1/5/1998, 2/22/1998, 2/6/1998, 5/5/1998, 6/22/1998, 6/25/1998, 6/26/1998, 7/28/1998, 8/9/1998,7/16/1999, 10/21/1999, 8/28/2000, 8/22/2002, 8/7/2004, 12/15/2009, 2/1/2010, 11/11/2011
6	85+136	0.039	0.727	6/10/1999, 8/3/1999, 3/31/2008, 9/15/2008, 9/27/2008, 11/14/2008
7	82	0.591	0.723	10/21/1997, 2/22/1999, 11/8/2007, 5/18/2008
8	135+144+147+124	0.005	0.759	10/21/1997, 6/26/1998, 10/13/1998, 10/28/1998, 11/15/1998, 12/30/1998, 1/8/1999, 2/22/1999, 8/8/2000, 8/9/2000, 1/16/2004, 8/7/2004, 8/19/2004, 2/1/2010, 11/11/2011
9	146	0.597	0.710	10/8/1997, 10/9/1997, 3/3/1999, 8/8/2000, 8/28/2000, 6/18/2003, 7/24/2003, 8/17/2003, 7/26/2004
10	187+182	0.0002	0.712	10/15/1997, 10/21/1997, 12/6/1997, 12/30/1997, 1/17/1998, 3/12/1998, 6/26/1998, 12/30/1998, 9/21/2000, 11/8/2000, 11/20/2000, 12/2/2000, 5/18/2002, 11/9/2003, 12/3/2003, 12/13/2003, 1/16/2004, 1/28/2004, 2/9/2004, 2/21/2004, 5/10/2005, 1/24/2007, 3/1/2007, 3/13/2007, 4/6/2007, 10/15,2007, 10/27/2007, 12/31/2007, 3/7/2008, 5/6/2008, 5/18/2008, 9/3/2008, 11/2/2008, 11/14/2008, 11/26/2008, 12/20/2008, 3/2/2009, 2/1/2010, 12/10/2010, 1/27/2011, 2/20/2011, 11/11/2011
11	183	0.054	0.707	10/8/1997, 10/21/1997, 10/29/1997, 1/5/1998, 1/23/1998, 2/10/1998, 4/23/1998, 5/5/1998, 6/25/1998, 6/26/1998, 8/3/1998, 8/15/1998, 12/30/1998, 2/4/1999, 6/10/1999, 7/16/1999, 3/13/2000, 6/17/2000, 2/23/2002, 1/16/2004, 12/6/2006, 8/17/2009, 12/10/2010, 11/11/2011, 12/29/2011

12	185	0.189	0.702	10/16/1997, 10/21/1997, 10/29/1997, 11/12/1997, 11/18/1997, 11/24/1997, 12/30/1997, 1/11/1998, 1/29/1998, 2/10/1998, 3/12/1998, 6/26/1998, 12/30/1998, 1/8/1999, 1/26/1999, 2/22/1999,3/21/1999, 3/30/1999,1/13/2000, 2/6/2000, 8/8/2000, 12/2/2000, 3/14/2003, 9/7/2003,10/16/2003, 11/9/2003, 12/13/2003,1/4/2004, 1/16/2004, 1/28/2004, 2/9/2004, 4/9/2004,8/7/2004, 10/20/2006, 12/6/2006, 1/24/2007, 2/5/2007, 2/17/2007, 3/25/2007, 4/6/2007,5/24/2007, 12/31/2007, 2/12/2008, 5/6/2008, 5/30/2008, 9/27/2008, 11/2/2008, 11/14/2008,11/26/2008, 12/20/2008, 12/15/2009, 1/8/2010, 2/1/2010,8/13/2010, 12/10/2010, 7/14/2011,12/5/2011
13	174	0.0001	0.701	11/24/1997, 5/5/1998, 5/17/1998, 5/29/1998, 6/25/1998, 6/26/1998, 7/22/1998, 8/27/1998, 12/3/1998, 6/10/1999, 7/16/1999, 7/25/1999, 9/15/1999, 7/11/2000, 8/11/2000, 8/28/2000, 9/9/2000, 10/27/2000, 4/23/2002, 7/29/2002, 1/28/2004, 8/7/2004, 10/20/2006, 6/17/2007, 7/11/2007, 7/26/2007, 5/30/2008, 12/8/2008, 8/17/2009, 12/10/2010,6/20/2011, 9/24/2011, 11/11/2011
14	177	1.10E-07	0.704	10/8/1997, 10/9/1997, 10/15/1997, 10/21/1997, 10/29/1997, 1/5/1998, 2/4/1998, 4/29/1998, 5/5/1998, 6/22/1998, 6/25/1998, 6/26/1998, 7/22/1998, 7/28/1998, 8/9/1998, 12/21/1998, 12/30/1998, 1/8/1999, 3/3/1999, 3/21/1999, 7/7/1999, 7/16/1999, 10/21/1999, 1/1/2000, 3/3/2000, 6/5/2000, 8/11/2000, 8/28/2000, 5/15/2004, 5/27/2004, 7/2/2004, 8/7/2004, 3/7/2008, 8/17/2009, 10/18/2011
15	202+171+156	9.75E-05	0.709	10/21/1997, 10/28/1997, 10/29/1997, 12/6/1997, 12/24/1997, 1/5/1998, 2/4/1998, 2/10/1998, 5/5/1998, 5/29/1998, 6/25/1998, 6/26/1998, 8/9/1998/8/15/1998, 10/10/1998, 12/12/1998, 12/21/1998, 3/12/1999, 5/5/1999, 6/28/1999, 7/7/1999, 7/25/1999, 10/21/1999, 2/6/2000, 3/1/2000, 3/25/2000, 8/8/2000, 8/9/2000, 8/11/2000, 1/8/2002, 2/11/2002, 2/23/2002, 5/6/2002, 5/30/2002, 3/26/2003, 6/18/2003, 7/12/2003, 1/4/2004, 1/16/2004, 8/7/2004, 7/26/2007, 3/7/2008, 10/18/2011, 11/11/2011, 12/5/2011

16	180	0.024	0.706	10/9/1997, 10/15/1997, 10/21/1997, 10/29/1997, 11/24/1997, 1/5/1998, 2/10/1998, 3/24/1998, 5/5/1998, 5/29/1998, 6/25/1998, 5/17/1998, 7/22/1998, 2/22/1999, 2/24/1999, 8/8/2000, 8/11/2000, 8/28/2000, 4/12/2002, 1/16/2004, 8/7/2004, 8/19/2004, 7/11/2007, 7/26/2007, 2/1/2010, 12/5/2011, 12/29/2011
17	199	0.055	0.711	10/8/1997, 10/12/1997, 10/13/1997, 11/6/1997, 11/18/1997, 12/18/1997, 1/5/1998, 1/23/1998, 2/10/1998, 3/12/1998, 3/30/1998, 5/5/1998, 5/17/1998, 5/29/1998, 6/4/1998, 6/22/1998, 6/25/1998, 6/26/1998, 7/16/1998, 7/22/1998, 8/27/1998, 9/22/1998, 10/1/1998, 10/7/1998, 10/10/1998, 10/13/1998, 12/3/1998, 1/17/1999, 6/10/1999, 7/16/1999, 7/25/1999, 9/15/1999, 5/12/2000, 6/5/2000, 7/23/2000, 8/11/2000, 8/28/2000, 9/9/2000, 10/3/2000, 10/27/2000, 8/7/2004, 8/19/2004, 6/17/2007, 7/11/2007, 5/30/2008, 9/3/2008
18	179+190	0.004	0.708	10/15/1997, 10/21/1997, 10/29/1997, 11/24/1997, 12/30/1997, 1/11/1998, 2/10/1998, 3/24/1998, 4/11/1998, 4/29/1998, 5/29/1998, 6/25/1998, 6/26/1998, 12/30/1998, 3/12/1999, 6/10/1999, 7/25/1999, 3/13/2000, 5/12/2000, 5/24/2000, 10/26/2001, 1/18/2002, 8/7/2004, 7/26/2007, 3/31/2008, 8/17/2009, 2/1/2010, 5/27/2011
19	201	0.180	0.710	11/12/1997, 11/18/1997, 11/24/1997, 12/30/1997, 1/11/1998, 1/29/1998, 2/10/1998, 6/26/1998, 12/30/1998, 1/17/1999, 2/13/1999, 2/22/1999, 11/9/2003, 12/3/1003, 12/13/2003, 1/28/2004, 3/16/2004, 10/20/2006, 2/17/2007, 4/6/2007, 11/8/2007, 12/31/2007, 1/19/2008, 12/8/2008, 10/4/2009, 1/8/2010, 2/1/2010, 3/21/2010, 7/14/2011, 8/8/2011, 11/11/2011

20	203+196	0.006	0.703	10/21/1997, 10/29/1997, 11/30/1997, 12/24/1997, 1/11/1998, 2/4/1998, 2/10/1998, 3/12/1998, 5/17/1998, 6/25/1998, 6/26/1998, 8/9/1998, 1/8/1999, 10/21/1999, 1/25/2000, 3/13/2000, 8/8/2000, 3/25/2000, 8/11/2000, 2/11/2002, 2/23/2002, 5/25/2003, 1/16/2004, 6/20/2004, 7/2/2004,8/7/2004, 3/25/2007, 2/25/2010, 8/8/2011, 10/18/2011, 11/11/2011, 12/29/2011
21	195+208	0.037	0.722	5/29/1998, 6/25/1998, 6/26/1998, 7/22/1998, 8/9/1998, 8/27/1998, 10/10/1998, 11/15/1998, 11/24/199812/30/1998, 3/12/1999, 7/16/1999, 9/27/1999, 10/21/1999, 12/8/1999, 1/13/2000, 1/25/2000, 2/6/20003/13/2000, 8/11/2000, 8/28/2000, 10/26/2001, 1/18/2002, 2/11/2002, 2/23/2002, 7/12/2003, 1/16/20047/2/2004, 8/7/2004, 8/19/2004, 6/17/2007, 7/26/2007, 3/7/2008, 8/17/2009
22	194	0.025	0.715	10/8/1997, 10/15/1997, 10/21/1997, 10/29/1997, 1/5/1998, 2/10/1998, 4/29/1998, 5/5/1998, 5/17/1998, 5/29/1998, 6/25/1998, 6/26/1998, 7/22/1998, 8/9/1998, 8/27/1998, 10/10/1998, 11/15/1998, 11/24/1998, 12/30/1998, 3/12/1999, 7/16/1999, 9/27/1999, 10/21/1999, 12/8/1999, 1/13/2000, 1/25/2000, 2/6/2000, 3/13/2000, 8/11/2000, 8/28/2000, 10/26/2001, 1/18/2002, 2/11/2002, 2/23/2002, 7/12/2003, 1/16/2004, 7/2/2004, 8/7/2004, 8/19/2004, 6/17/2007, 7/26/2007, 3/7/2008, 8/17/2009
23	206	0.006	0.702	10/15/1997, 10/29/1997, 1/11/1998, 4/17/1998, 5/11/1998, 6/16/1998, 6/26/1998, 10/10/1998, 11/24/1998, 12/30/1998, 6/10/1999, 10/21/1999, 12/8/1999, 1/25/2000, 2/6/2000, 2/18/2000, 8/11/2000, 8/28/2000, 12/1/2001, 1/6/2002/1/18/2002, 2/11/2002, 2/23/2002, 11/2/2002, 11/14/2002, 11/26/2002, 7/12/03, 7/24/2003, 8/17/2003, 1/4/2004, 2/9/2004, 2/5/2007, 7/11/2007, 7/26/2007, 10/15/2007, 5/18/2008, 3/21/2010, 6/1/2010, 6/13/2010, 7/8/2010, 7/19/2010, 5/27/2011, 11/11/2011

Appendix D

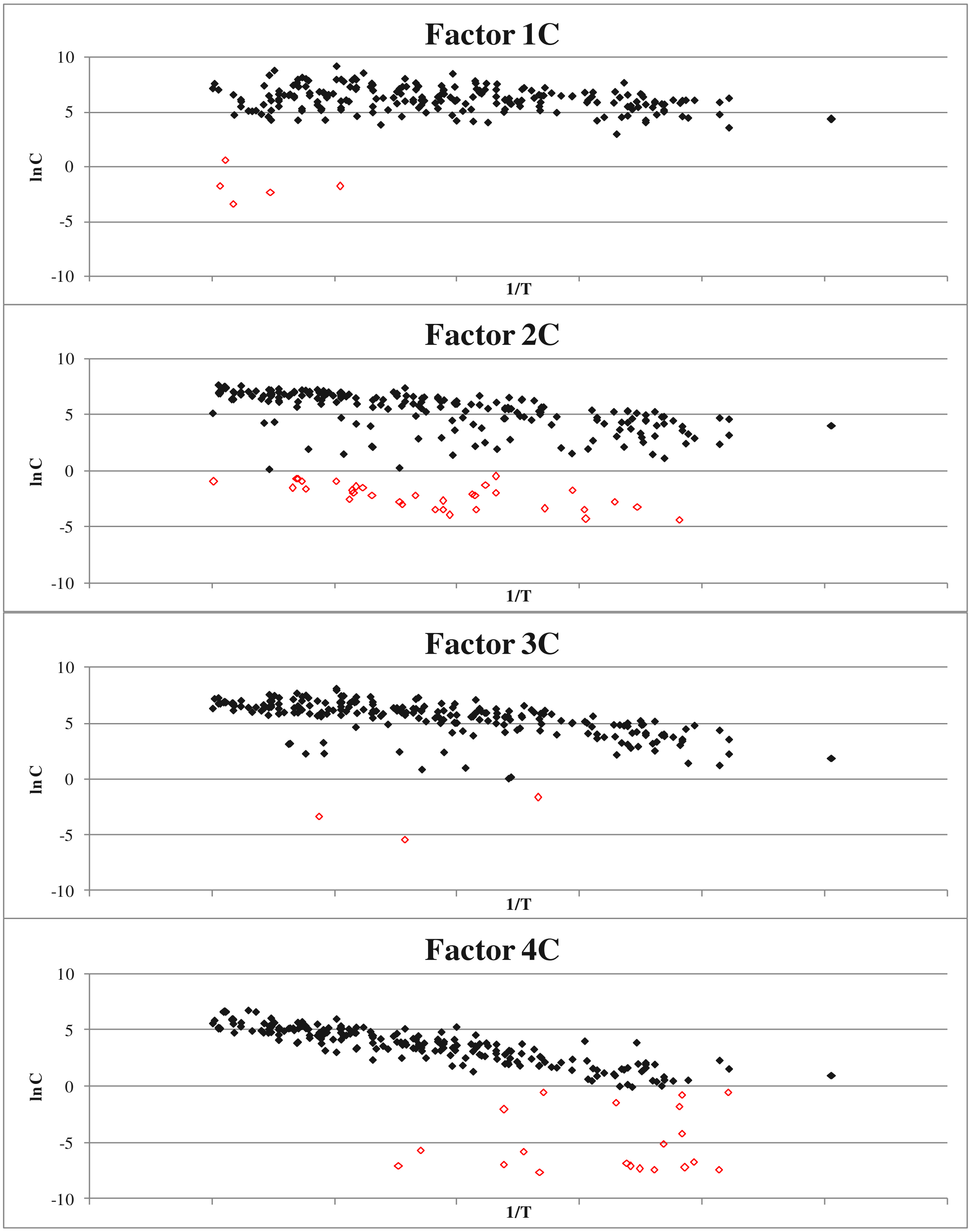


Figure D-1. The plot of the natural logarithm of PCB concentrations Vs 1/T of Camden.

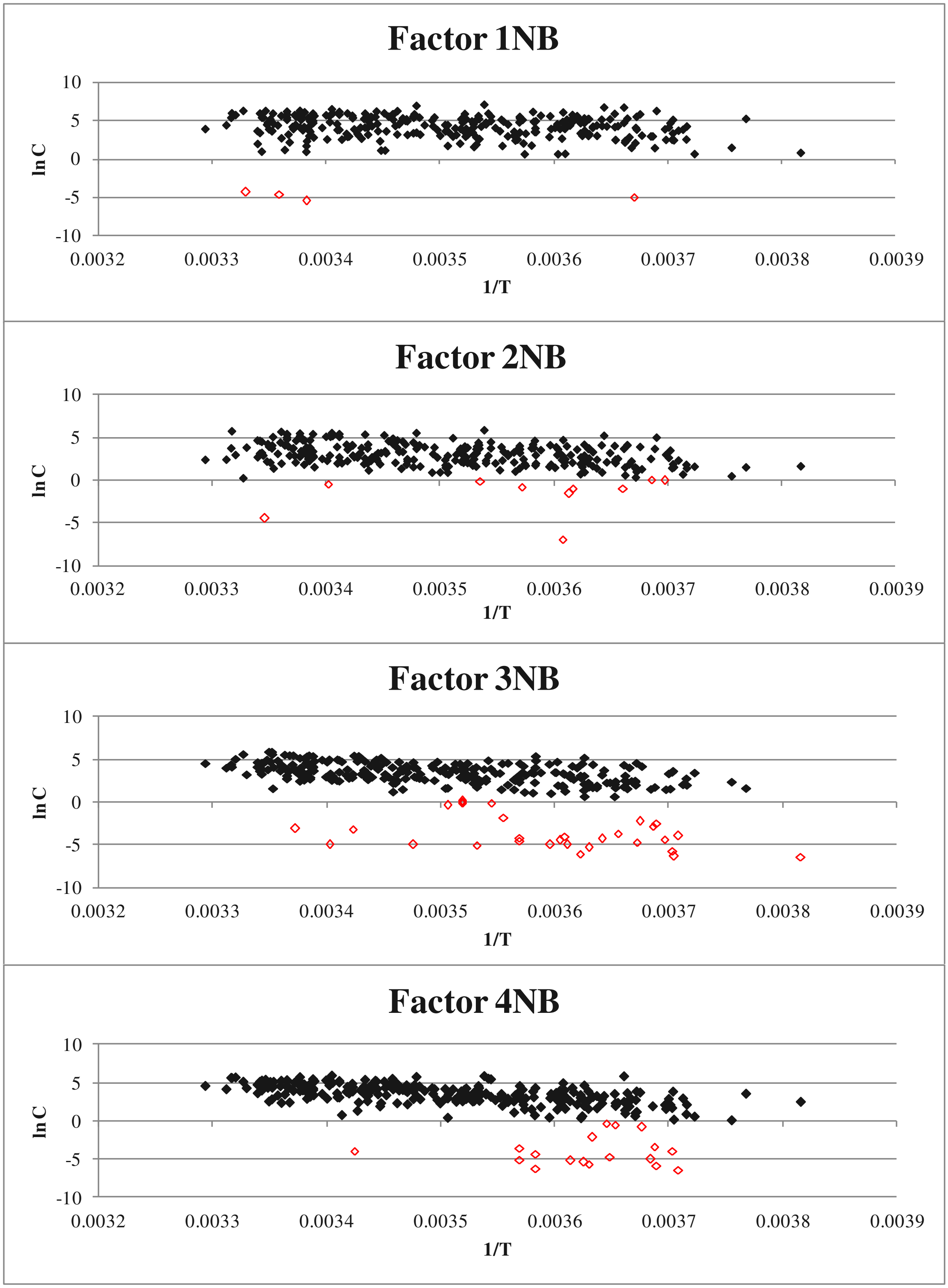


Figure D-2. The plot of the natural logarithm of PCB concentrations VS 1/T of New Brunswick.