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FATE AND TRANSPORT OF POLYCHLORINATED BIPHENYLS IN THE AIR,  
WATER, AND SEWERS OF THE DELAWARE RIVER BASIN

by

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Written under the direction of

Lisa A. Rodenburg

And approved by

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## ABSTRACT OF THE DISSERTATION

### FATE AND TRANSPORT OF POLYCHLORINATED BIPHENYLS IN THE AIR, WATER, AND SEWERS OF THE DELAWARE RIVER BASIN

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Passive air samplers were deployed at 45 sites across the Delaware River Basin to evaluate the spatial distribution of atmospheric polychlorinated biphenyls (PCBs). This study revealed strong spatial gradients in  $\Sigma$ PCB concentrations, a significant urban fractionation effect, and a distinct congener pattern arising from the area around Swarthmore, PA. Five factors were resolved by positive matrix factorization (PMF) analysis with three of them being interpreted as volatilized or weathered Aroclors. The other two factors were strongly correlated to the congener profiles observed at the Swarthmore site on a building roof and an urban site near rail yards, respectively. These findings suggest that volatilization of Aroclors from building materials and historical release in rail yards could represent significant sources of ambient atmospheric PCB concentrations.

In the passive air sampling, the concentrations of a non-Aroclor congener, PCB 11, were detected with small spatial variation in the airshed of the Delaware River Basin. PCB 11 was measured from non-detect to 79 ng g<sup>-1</sup> in consumer products containing pigments and dyes. The leaching potential of PCB 11 from these materials was confirmed by experimental tests. The inputs of PCB 11 to the Delaware River Basin were estimated between 0.025 and 42 kg y<sup>-1</sup>, while the outflows were between 8.4 and 260 kg y<sup>-1</sup>. These mass flows indicate that PCB 11 is present in pigments at levels close to or even exceeding the federal limits and/or that the degradation of these pigments releases PCB 11 into the basin.

Reductive dechlorination of PCBs was investigated in anaerobic microcosms of sewer sediments amended with Aroclor 1260 under methanogenic conditions. Spatial heterogeneity of the sediments resulted in differences in the extent of dechlorination activity. The most active microcosm showed dechlorination evidence after 35 days of incubation with significant accumulation of documented dechlorination products and molar dechlorination product ratio (MDPR). Total chlorines per biphenyl decreased by up to 10% with short or no lag time. This suggests that rapid dechlorination is at least possible to account for the dechlorination products comprising 10~30% of the total PCBs, which were found in many of the sewers in the Delaware River Basin.

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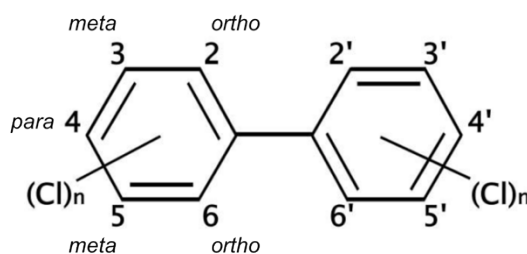


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## Chapter 1 : Introduction

### 1.1 Background on PCBs

Polychlorinated biphenyls (PCBs) are a class of synthetic organic chemicals consisting of 209 individual compounds (known as congeners) based on the numbers and positions of chlorine substitution on the biphenyl rings (Figure 1-1).<sup>1</sup> PCBs were produced and marketed as complex mixtures under the trade name of Aroclor in the United States from 1929 to 1977. Aroclors were widely used as dielectric and heat-transfer fluids in various applications including transformers and capacitors. The most commonly used Aroclors were: 1016, 1221, 1232, 1242, 1248, 1254, and 1260,<sup>2</sup> with the last two digits representing the percent content of chlorine. It is estimated that 650,000 tons of PCBs were produced in the United States<sup>3</sup> before the USEPA banned the manufacturing, processing and distribution in commerce of PCBs in 1979.<sup>4</sup> The manufacture and release of PCBs have led to extensive and persistent contamination in the environment and growing concerns over their toxic effects on human health. As a result, PCBs were listed among the initial 12 persistent organic pollutants (POPs) targeted for elimination and restriction under the Stockholm Convention.<sup>5</sup>



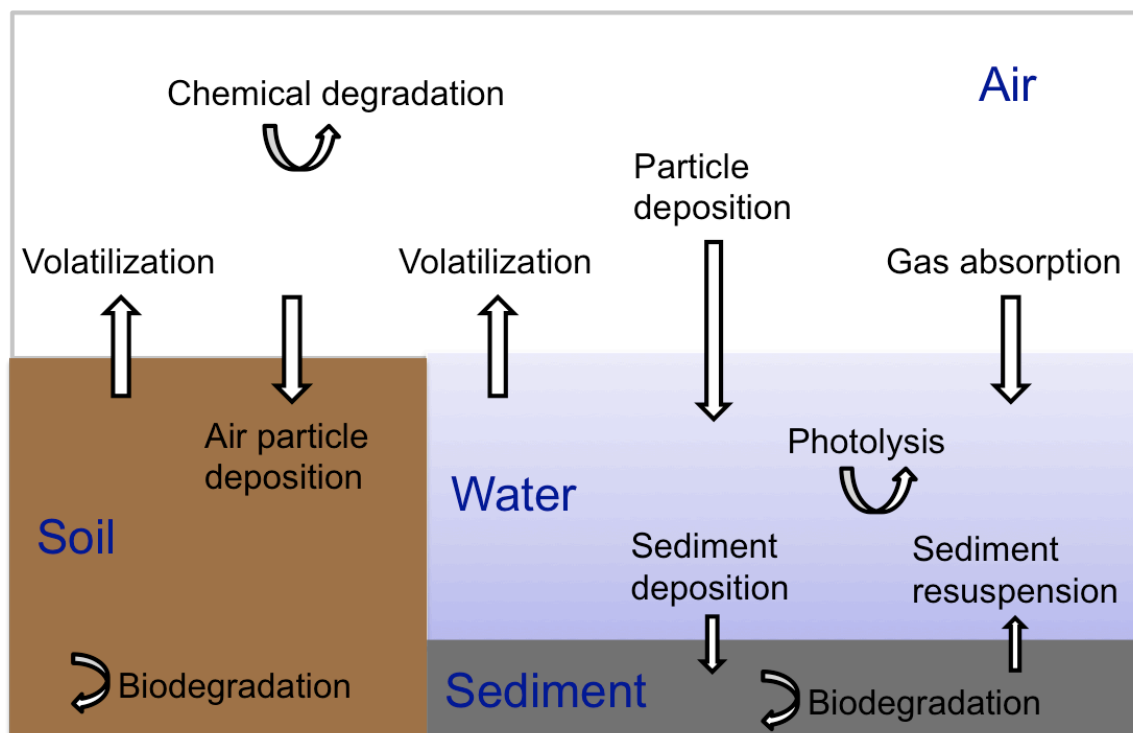
**Figure 1-1. Structure of polychlorinated biphenyl (PCB).**

In addition to mass production for industrial usage, PCBs can be inadvertently generated as by-products in a wide range of chemical processes that contain chlorines and hydrocarbons. These processes include, but are not limited to, manufacture of chlorinated solvents, chlorinated alkanes, chlorinated benzenes, organic intermediates such as 3,3'-dichlorobenzidine salts and synthetic organic pigments including diarylide yellow and phthalocyanine green.<sup>1</sup> The inadvertent production of non-Aroclor PCBs is regulated under the Toxic Substance Control Act (TSCA) administered by the USEPA.<sup>6</sup>

There are no known natural sources of PCBs in the environment. Prior to the ban in 1979, PCBs were released both intentionally and inadvertently into the air, water, and soil. Nowadays the major source of PCBs is associated with the environmental cycling process of PCBs previously introduced into the environment.<sup>7</sup> PCBs are also currently released to the environment from municipal and industrial incineration of organic wastes; poorly maintained hazardous waste sites; disposal of PCB-containing products in landfills; leaks or fugitive emissions from electrical transformers; and improper or illegal dumping of PCB wastes to open area.<sup>7</sup>

## **1.2 Environmental Cycling**

Because of their resistance to chemical and biological break-down, PCBs tend to persist in the environment as they circulate freely among air, water and soil (Figure 1-2). PCBs are widely dispersed in the atmosphere due to release from water and surface soil via volatilization. Airborne PCBs can be transported back to water and soil through dry and/or wet deposition in both gaseous and particulate phases.



**Figure 1-2. Environmental cycling of PCBs in the air, water and soil.**

The atmosphere is a net recipient of PCB fluxes volatilizing from both water and soil surfaces. PCBs in the atmosphere primarily exist in the gaseous phase although the highly chlorinated congeners are more likely to partition into the particulate phase. Atmospheric PCBs are subject to global long-range transport and physical removal through dry and wet deposition to surface waters and terrestrial surfaces.<sup>8</sup> The atmospheric transformation of PCBs is dominated by the reaction with hydroxyl (OH) radicals in the gaseous phase with estimated half-lives ranging from 3 days for trichlorobiphenyls to 500 days for heptachlorobiphenyls.<sup>9</sup>

The sources of PCBs in surface water are predominantly associated with input from atmospheric deposition and dissolution of sediment-sorbed PCBs into the water column.<sup>10</sup> Aquatic PCBs are distributed among dissolved, particulate and colloid-associated phases.<sup>11</sup> Exchange at the air-water and water-sediment interfaces could result in PCB losses in the water column due to volatilization to the atmosphere and sorption to the sediment. The direction of PCB flux at these interfaces is largely determined by the degree of PCB chlorination. The lower chlorinated PCBs are more soluble in the water column and ready to partition into the air as a result of higher vapor pressure. The highly chlorinated PCBs have a greater tendency to be sequestered in sediments due to lower water solubility and higher octanol-water partition coefficient ( $K_{ow}$ ). PCBs can also leave the water column by accumulation into biota.<sup>12</sup> Photolysis appears to be the only significant chemical degradation process in water although the rate is relatively slow.<sup>13</sup> Biodegradation is the major degradation process for PCBs in aquatic sediments. Highly chlorinated PCBs typically undergo reductive dechlorination under anaerobic conditions to form less chlorinated congeners that are more likely to degrade aerobically.<sup>14</sup>

Atmospheric deposition is the major contributor of PCB contamination in surface soil<sup>15</sup> although accidental leaks and spills from old transformers and capacitors or from PCB-containing wastes in landfills and hazardous waste sites can release PCBs into soil systems as well. PCBs, particularly the highly chlorinated ones, are strongly sorbed by solid particles in soil and hence remain significantly immobile against leaching into groundwater or being taken up by plants.<sup>13</sup> Volatilization from soil appears to be an

important loss mechanism, especially for the lower chlorinated PCBs with moderate vapor pressure. Biodegradation of PCBs could also occur slowly in soils.<sup>1</sup>

### **1.3 The Delaware River**

The Delaware River has a long history of PCB contamination that exceeds the water quality standard (WQS) by two to three orders of magnitude. As required by the Clean Water Act (CWA), the Delaware River Estuary was the one of the first waterways in the United States to receive a Total Maximum Daily Load (TMDL) for PCBs.<sup>16, 17</sup> The TMDL set the maximum amount of PCBs that may enter the receiving water body without violating applicable WQS. This amount was then allocated among point dischargers and non-point sources in the watershed to achieve reduction in PCB loads for implementation of the TMDLs. The development of TMDLs required extensive scientific investigation and data collection for hydrodynamic and water quality modeling under the leading effort of the Delaware River Basin Commission (DRBC).<sup>18-20</sup> Long-term monitoring of PCB levels has been undertaken in the atmosphere, ambient waters, aquatic sediment and fish tissues to identify and evaluate the extent and loadings of PCB contamination into the estuary. The DRBC also required all industrial and municipal dischargers with the National Pollutant Discharge Elimination System (NPDES) permits to measure 209 PCB congeners in their effluents and stormwater discharges by EPA method 1668A.<sup>21</sup> Notably, the congener specific analysis used for source identification and quantification has allowed more accurate estimation of loadings and more effective prioritization of source reduction plans. The comprehensive data available for a typical

urban watershed like the Delaware Estuary were unique and have made the investigations in this dissertation (particularly the mass flow analysis in Chapter 3) possible.

In our research group alone, the Delaware River TMDL project has spawned three PhD dissertations (including this one as well as Amy Rowe in 2006 and Songyan Du in 2008). A fourth PhD student, Pornsawai Praipipat, is working with DRBC data for her dissertation, and has already published one paper that relies on the measurements of PCBs in the sediments of the river by DRBC.<sup>22</sup> Our research group has so far published eight papers arising from the TMDL process. This data set has greatly expanded our understanding of the cycling of PCBs in an urban estuary, often in ways that were never intended. For example, the Delaware Atmospheric Deposition Network (DADN) data were collected to calculate the flux of PCBs deposition from the atmosphere directly into the river. However, these data were also subsequently used to track down atmospheric PCBs sources<sup>23</sup> including Chapter 2 and to understand how atmospheric deposition to land surfaces was processed within watersheds.<sup>24, 25</sup> The data on PCBs in the ambient water column were collected in order to calibrate the TMDL model, but were subsequently used for source apportionment and allowed the identification of some hitherto unknown sources.<sup>26</sup> This source apportionment study highlighted the unique sources of PCB 11 and PCBs 206, 208, and 209, and sparked subsequent studies into the sources and fate of PCBs from inadvertent production,<sup>27</sup> including Chapter 3. In attempting to demonstrate that PCB 11 is not a product of the dechlorination of heavier congeners, Rodenburg *et al.*<sup>27</sup> compared its concentrations with those of PCB 4, which is a known and characteristic product of dechlorination. This led to the surprising discovery

that a large proportion of the PCBs in effluents from sewage treatment plants were products of dechlorination. Based on this discovery, factor analysis was conducted on the discharger data set from DRBC and demonstrated that PCBs are dechlorinated in sewers, landfills and contaminated groundwater.<sup>28</sup> This discovery in turn led to examination on other data sets that provided evidence that polychlorinated dibenzo-p-dioxins and -furans were also dechlorinated in sewers,<sup>29</sup> and led to the microcosm work in Chapter 4. Thus the initial investment in data collection for the TMDL project has spawned rich and unexpected rewards.

#### **1.4 Outline of Dissertation**

As part of the effort to refine atmospheric deposition input in TMDL models, the DADN, formerly known as the New Jersey Atmospheric Deposition Network (NJADN)<sup>30</sup>, was established to study the temporal trends of atmospheric PCB concentrations at seven active air monitoring sites over the region. A distinct gradient was observed from urban to remote sites and thus interpolation of PCB concentrations among the limited number of monitoring sites could lead to inaccurate estimation of atmospheric deposition for TMDL model inputs. Therefore, the first passive air sampling campaign was conducted in 2005 at 32 sites across the Philadelphia metropolitan area to characterize the spatial variation of atmospheric PCBs and to improve the modeling of atmospheric inputs into the estuary.<sup>23</sup> This study revealed two hot spots in PCB concentrations: one in the center city of Philadelphia, PA, representing urban sources and the other near Swarthmore, PA, indicating industrial sources. However, sources for the unique pattern observed in the Swarthmore area could not be pinpointed. For this reason, the second passive air



sampling campaign (Chapter 2) was constructed in 2008 at 45 sites in the Delaware River Basin with a focus on the Swarthmore area. This chapter attempted to identify the sources and distribution of atmospheric PCBs by employing the passive air sampling technique and positive matrix factorization (PMF) analysis.

In Chapter 2, a unique non-Aroclor congener, 3,3'-dichlorobiphenyl (PCB 11), was discovered to be widespread at consistent atmospheric concentrations over the region.

PCB 11 loads from tributaries and point dischargers into the Delaware River were calculated using the DRBC data and found to exceed the TMDL for the sum of all PCBs,<sup>27</sup> suggesting a significant obstacle to achieving water quality standards.

Inadvertent production of PCB 11 was found to be associated with pigment manufacture<sup>27, 31</sup> and it was used as a tracer for wastewater and combined sewer overflows (CSOs).<sup>26</sup> In order to determine the source emissions of PCB 11, the study detailed in Chapter 3 was initiated to investigate the sources of PCB 11 from inadvertent production to its end fate in different environmental compartments. A mass flow analysis was constructed for PCB 11 in the Delaware River Basin. The estimated input from inadvertent production was compared with calculated outflows of PCB 11 exiting the basin to obtain insights on the magnitude of known emissions and additional sources in the environment.

In a previous work using PMF to identify the main components of PCB sources from the NPDES-permitted dischargers,<sup>28</sup> two unique signals representing PCB dechlorination were identified in wastewater influents in addition to Aroclor and non-Aroclor signals

including PCB 11. This observation for widespread dechlorination in wastewater collection systems has led to the research in Chapter 4 that evaluated the potential of PCB dechlorination in sewer sediments through microcosm experiment. To our knowledge, this was the first study using sediments from an environment other than aquatic systems as an inoculum. This chapter aimed to look for experimental evidence of PCB dechlorination in wastewater collection systems, which corroborated the findings from the fingerprinting analysis with in-depth knowledge on *in-situ* transformation of PCBs in built waste treatment environments.

Taken together, these three chapters represented a truly comprehensive approach to investigate the fate and transport of PCBs in the Delaware River Basin and provided useful information on characterization of PCB sources in support of developing load reduction strategies to meet the TMDLs. The findings from this dissertation also suggest that continuing research of PCBs from both Aroclor and non-Aroclor sources is worthwhile, as opposed to the belief that further investigation on these legacy contaminants would provide no new information to the science community.

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## **Chapter 2 : Source Apportionment of Atmospheric Polychlorinated Biphenyls in the Delaware River Basin**

### **Abstract**

Passive air samplers were deployed at 45 sites across the Delaware River Basin in 2008 to evaluate the spatial distribution of atmospheric polychlorinated biphenyls (PCBs). This study was a follow-up investigation with the 2005 passive air sampling campaign in the Philadelphia metropolitan area. The 2008 study covered more sampling sites around the area of Swarthmore, PA, that was identified as a hot spot of high  $\Sigma$ PCB concentrations in the 2005 study. Depuration compounds were applied to the sampler media to assess site-specific sampling rates. Similar to the earlier campaign, the 2008 study revealed strong spatial gradients in  $\Sigma$ PCB concentrations, a significant urban fractionation effect, and a distinct congener pattern arising from the Swarthmore area. Positive matrix factorization (PMF) analysis was performed to investigate the PCB source profiles and contributions. Five factors were resolved with three of them being interpreted as volatilized or weathered Aroclors. The other two factors were strongly correlated to the unique congener profiles observed on a building roof at Swarthmore and an urban site near rail yards, respectively. These findings suggest that volatilization of Aroclors from building materials and historical release in rail yards could represent significant sources of ambient atmospheric PCB concentrations.

## 2.1 Introduction

The Delaware Atmospheric Deposition Network (DADN, formerly known as the New Jersey Atmospheric Deposition Network or NJADN) had been collecting data between 2002 and 2011 to characterize the atmospheric deposition of polychlorinated biphenyls (PCBs) into the Delaware River. The results of the DADN have demonstrated that atmospheric PCB concentrations at three sites of the network (Camden, NJ; Swarthmore, PA; Northeast Philadelphia Airport, PA) exhibited atmospheric PCB levels that were about 20 times higher than the regional background,<sup>1, 2</sup> leading to PCB deposition fluxes to the Delaware River that exceeded the Total Maximum Daily Load (TMDL) by more than an order of magnitude.<sup>1</sup> Moreover, the congener patterns measured at the Swarthmore site were unusual and rich in high molecular weight (MW) congeners.

Although the DADN/NJADN had included as many as seven sites located on or near the Delaware River, even this relatively high number of sites was not sufficient to characterize the spatial variations in PCBs concentrations in this region. It is especially important to understand how the high PCB concentrations measured at the urban sites decline with distance from the urban centers. In order to more fully characterize the spatial variations in atmospheric PCB concentrations, a first passive air sampling campaign was performed in 2005 at 32 sites across the Philadelphia/Camden area.<sup>3</sup> This 2005 study identified two regions with high PCB levels: the center city of Philadelphia, PA, and the area surrounding Swarthmore, PA. The hot spot in Philadelphia was characterized as an urban source, while Swarthmore was speculated to be an industrial source. However, the sources of the high MW PCBs measured near Swarthmore could

not be pinpointed. Therefore, a follow-up passive air sampling campaign was performed in 2008 in the same region but covered a greater area in the Delaware River Basin and focused even more on the Swarthmore area.

Compared to the 2005 study using a polyurethane foam (PUF) plug enclosed in a cylindrical canister, the passive air sampler (PAS) used in the 2008 study consisted of a PUF disk as the sampling medium housed in a chamber made from two stainless steel domes. This “flying saucer” shaped design was widely used in many PAS studies<sup>4-7</sup> and showed a small wind dependency on sampling rates at low wind speeds ( $< 5 \text{ m s}^{-1}$ ).<sup>8</sup> These wind conditions were applicable for most field deployments including the 2008 study. Therefore, the sampler housing adequately reduced the wind effect and yielded time-weighted air concentrations. The PUF disk provided a greater surface area ( $365 \text{ cm}^2$ ) than the PUF plug ( $290 \text{ cm}^2$ ). In addition, depuration compounds were spiked into the PUF disks to access site-specific sampling rates. A larger suite of PCB congeners was quantified using the same analytical technique. The purpose of the 2008 study was to evaluate the spatial distribution of atmospheric PCBs in the Delaware River Basin and to identify PCB source types and contributions, especially in the Swarthmore area.

## **2.2 Materials and Methods**

### **2.2.1 Theory of Passive Air Samplers**

The principles of passive air sampling have been described elsewhere<sup>9-11</sup> and are summarized here. The accumulation of chemicals by the passive sampler is primarily controlled by the air-side mass transfer coefficient ( $k_A$ ), especially for chemicals with

large octanol-air partition coefficients (i.e.  $K_{OA} > 10^7$ )<sup>9</sup> such as PCBs.<sup>12, 13</sup> The uptake profile of a chemical is characterized by:

$$C_{PSM} = K_{PSM-A} C_A (1 - \exp[-(A_{PSM} / V_{PSM})(k_A / K_{PSM-A})t]) \quad (\text{Eq. 2-1})$$

where  $C_{PSM}$  and  $C_A$  are concentrations (mass  $\text{cm}^{-3}$ ) of the chemical in the passive sampler medium (PSM) and air, respectively;  $K_{PSM-A}$  is the PSM-air partition coefficient, which is similar in magnitude to  $K_{OA}$  for non-polar organic chemicals such as PCBs;  $A_{PSM}$  and  $V_{PSM}$  are the planar surface area ( $\text{cm}^2$ ) and volume ( $\text{cm}^3$ ) of the sampler medium;  $k_A$  is in  $\text{cm d}^{-1}$ ; and  $t$  is the deployment time in days.<sup>9</sup>

Eq. 2-1 can be viewed as a first-order rate expression in the form of  $C = C_0 \exp(-k_U t)$  or  $\ln(C/C_0) = -k_U t$ , where  $k_U$  is the uptake rate constant (in  $\text{day}^{-1}$ ) solved as:

$$k_U = (A_{PSM} / V_{PSM})(k_A / K_{PSM-A}) = 1 / \delta_{FILM} (k_A / K_{PSM-A}) \quad (\text{Eq. 2-2})$$

where  $\delta_{FILM} = V_{PSM} / A_{PSM}$  is the “effective” thickness of the sampler medium.<sup>9</sup>

Air sampling rates can be estimated by spiking depuration compounds (DCs) into PSM prior to deployment. DCs are semi-volatile compounds with negligible concentrations in the atmosphere<sup>14</sup> and should cover a range of volatility.<sup>10</sup> Because both uptake and loss of chemicals are air-side controlled, the depuration rate constant of a DC is equal to the uptake rate constant of a given chemical and can be expressed by Eq. 2-2 as well.

Therefore, the air-side mass transfer coefficient of a DC is solved by

$$k_A = \ln(C / C_0)(V_{PSM} / A_{PSM})K_{PSM-A} / t \quad (\text{Eq. 2-3})$$

where  $C/C_0$  can be interpreted as the recovery of DCs initially spiked into the sampler medium. Recoveries between 20% and 80% of the DCs are desirable to assess the

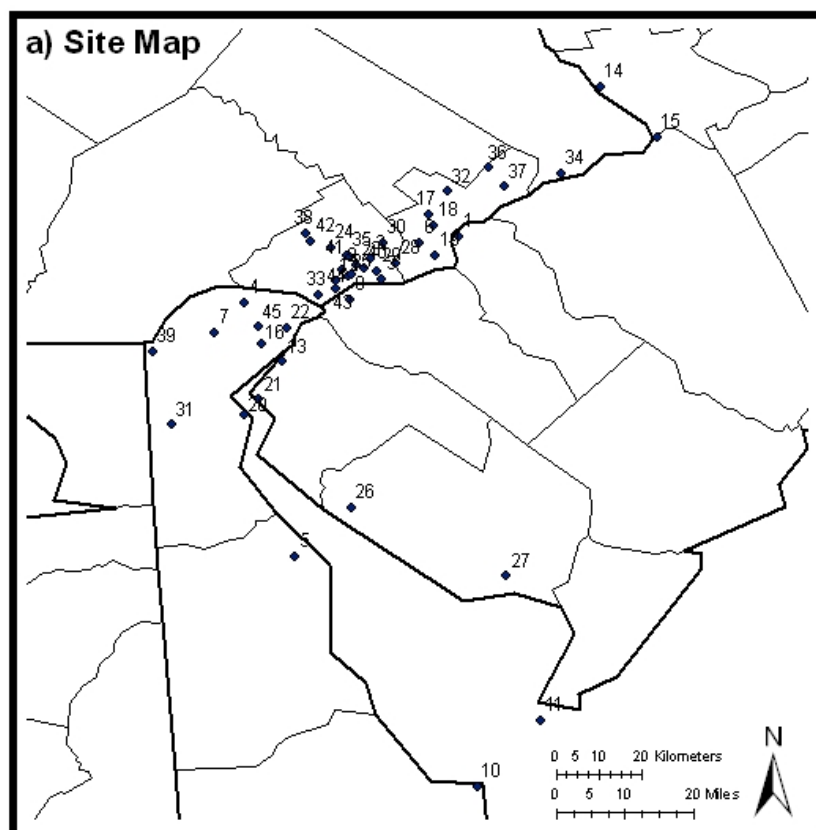


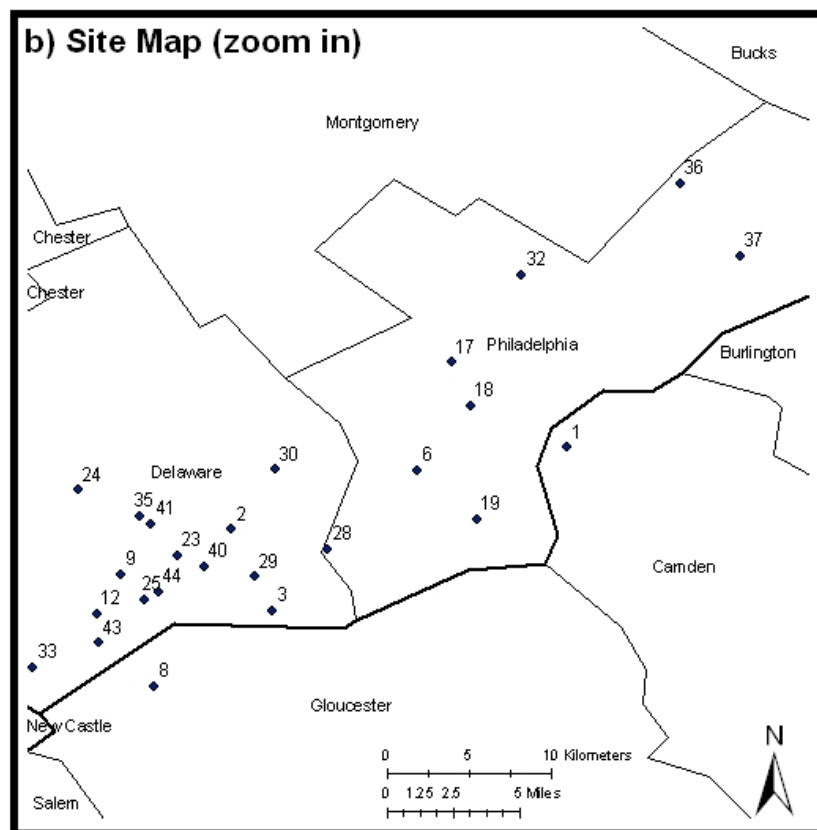
sampling rate within a linear calibration range.<sup>11, 15</sup> The sampling rate  $R$  in unit of  $\text{m}^3 \text{d}^{-1}$  is then calculated from  $k_A$  in  $\text{cm d}^{-1}$  by

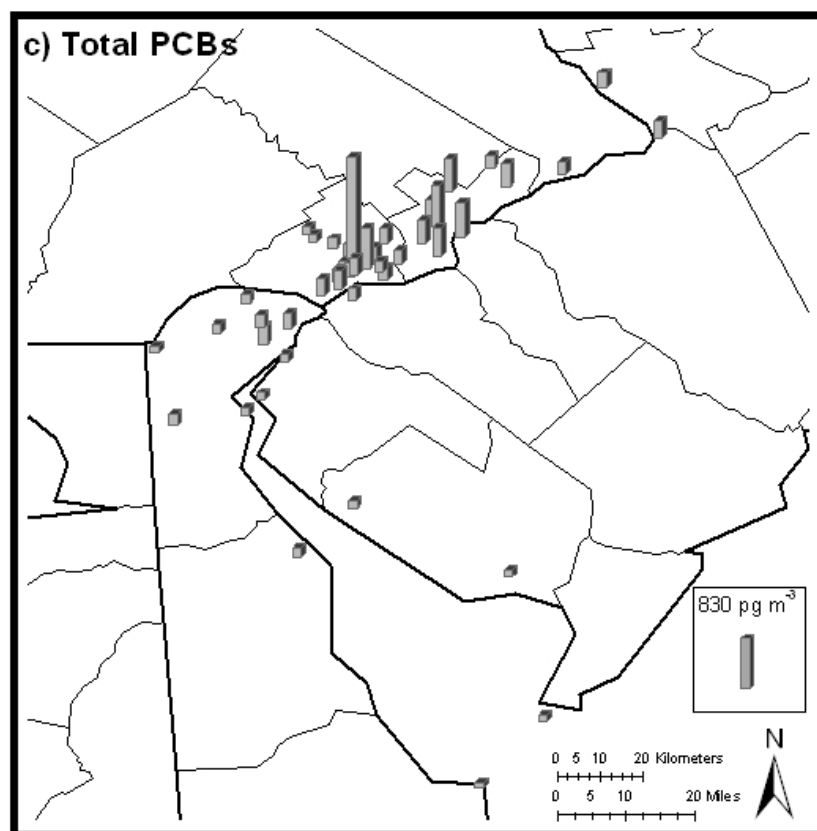
$$R = 10^6 k_A A_{PSM} \quad (\text{Eq. 2-4})$$

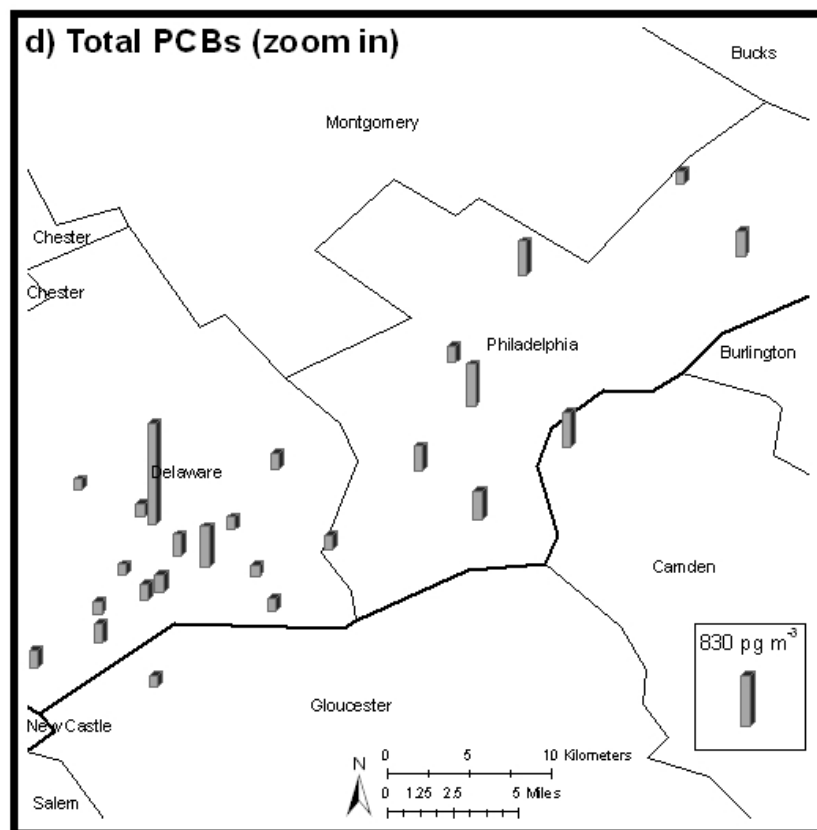
### 2.2.2 Sample Collection

Passive air samplers were deployed at 45 sites to investigate atmospheric PCB congener profiles throughout the Delaware River Basin (Figure 2-1a, b) during March 17~21, 2008. The samplers were retrieved during June 16~18, 2008. Details of site information are provided in Table 2-1.



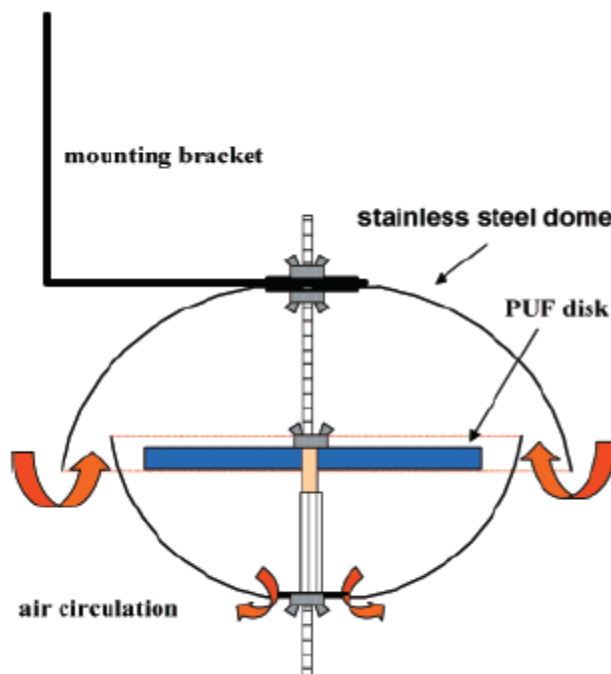






**Figure 2-1. Sampling sites (a-full view, b-zoom-in view) and distributions of the total PCB concentrations (c-full view, d-zoom-in view) in the 2008 passive air sampling study.**

The sampler design and depuration compounds replicated as closely as possible the approach of Shoeib and Harner.<sup>9</sup> The sampler consisted of a PUF disk (14 cm diameter × 1.35 cm thickness, 365 cm<sup>2</sup> surface area, from PacWill Environmental, Stoney Creek, Ontario) enclosed in a stainless steel chamber with two domes in different diameters (Figure 2-2, upper: 30 cm, lower: 20 cm). This “flying-saucer” sampler design protects the PUF disk from sunlight, direct precipitation, coarse particle deposition and minimizes the wind effect on sampling rates<sup>9, 16</sup> while still allowing air to flow through a ~2.5 cm gap between the domes and holes drilled in the bottom of the lower dome.



**Figure 2-2. Schematic of passive air sampler (PAS).**<sup>10, 17</sup>

Before exposure, all PUF disks were pre-cleaned by Soxhlet extraction for 24 h in acetone followed by 24 h in petroleum ether, dried in vacuum desiccators, and spiked with a mixture of DCs (250 ng each of PCBs 30, 107, 198, and 500 ng of  $\gamma$ -hexachlorocyclohexane from Cambridge Isotope Laboratories, Andover, MA) to evaluate site-specific air sampling rates. Sampling chambers were prewashed with soap (Alconox) and water, and air dried prior to installation of the PUF disks. Exposed PUF disks were stored frozen in pre-combusted glass jars until being processed.

### 2.2.3 Sample Analysis

The analytical procedures used to measure PCBs in the PUFs were similar to those described in detail in previous studies.<sup>3, 18</sup> In brief, all PUF disk samples were injected with surrogates (52.5 ng each of PCBs 14, 23, 65, and 166 from Cambridge Isotope

Laboratories, Andover, MA) prior to extraction. Each sample was extracted in a Soxhlet apparatus for 24 h in petroleum ether. The extract was reduced in volume by rotary evaporation and split with 50% of the extract archived and the other 50% being used for PCB analysis. The samples were then concentrated via nitrogen evaporation and fractionated on a column of 3% water-deactivated alumina. The PCB fraction was eluted with hexane, concentrated to ~0.5 mL under a gentle stream of nitrogen gas, injected with internal standard (21 ng of PCB 204 from Cambridge Isotope Laboratories, Andover, MA) and finally concentrated to ~0.1 mL prior to analysis. All samples were analyzed for PCBs on an Agilent 6890 gas chromatograph (GC) equipped with a tandem quadrupole mass spectrometer (Waters Quattro Micro GC) using DB-5 (5% diphenyl dimethyl polysiloxane) capillary column (60m × 0.25mm i.d. × 0.25µm film thickness). Details of instrument parameters were reported previously.<sup>3</sup> A total of 159 PCB congeners including three depuration compounds, four surrogates, and one internal standard were identified and quantified in the samples with this method. Details of retention time and relative response factor (RRF) for these congeners on the DB-5 capillary column are given in Table I-1 of the Appendix.

#### **2.2.4 Quality Assurance/Quality Control**

Six lab blanks and three matrix spikes were processed in the same way as the samples. Surrogate recoveries in lab blanks and matrix spikes ranged from 90% to 100%. PCB masses in the blanks were less than 5% of the masses in samples; therefore, data were not corrected for blank values. The instrument detection limit (IDL) was below 3.0 pg for all PCB congeners. Surrogate recoveries of PCBs 14, 23, 65, and 166 in the samples were 78

$\pm 10\%$ ,  $80 \pm 9\%$ ,  $81 \pm 7\%$ , and  $101 \pm 6\%$ , respectively. These recoveries were used to correct PCB masses directly measured in samples: PCB 14 for mono- and di- homologs, PCB 23 for tri- homolog, PCB 65 for tetra- homolog, the average recoveries of PCBs 65 and 166 for penta- homolog, and PCB 166 for hexa- through nona- homologs.

## 2.3 Results and Discussion

### 2.3.1 Air Sampling Rates

The recoveries of the DCs were  $25 \pm 8\%$ ,  $82 \pm 7\%$ , and  $85 \pm 7\%$  for PCBs 30, 107 and 198, respectively. Previous studies using the same PAS design and DCs have noted that these DCs are useful for the calculation of sampling rates when their recoveries are between 20% and 80%.<sup>10, 11</sup> The recoveries of PCB 198 in all samples and PCB 107 in most samples were above 80%; therefore, these compounds were not used to calculate sampling rates (R). Thus sampling rates for each individual site were derived from the recoveries of PCB 30 with 39 of the 45 recoveries (20~45%) in the desired range using Eq. 2-3 and 2-4.

R values ranged from 2.5 to 5.1  $\text{m}^3 \text{d}^{-1}$ , with a mean of 4.2  $\text{m}^3 \text{d}^{-1}$ . These sampling rates were comparable with those of passive sampling studies in other regions.<sup>10, 11, 19</sup> Site-specific R value was converted to sampled air volume based on deployment time. The average R value, corresponding to a sampled volume of  $382 \pm 56 \text{ m}^3$ , was assigned to the six samples with PCB 30 recoveries below 20%. The low recovery of PCB 30 probably indicated a very high sampling rate. Therefore, the highest measured sampling rate was also used to calculate the concentrations of PCBs in these six samples, but this caused

PCB concentrations to decrease by only 18%. Because the congener pattern in each sample was independent of sampling volumes, the choice of R value would not alter the results of source apportionment discussed later. Therefore, the average R value was applied to those six samples for calculation of PCB concentrations and subsequent factor analysis.

### **2.3.2 PCB Concentrations in Air**

Atmospheric PCB concentrations were calculated from masses corrected by surrogate recoveries and site-specific sampled volumes (Table 2-1).  $\Sigma$ PCB concentrations ranged from 83 to 1651  $\text{pg m}^{-3}$  (Figure 2-1c, d). In comparison, the 2005 study measured  $\Sigma$ PCB concentrations from 200 to 3000  $\text{pg m}^{-3}$ . The difference in PCB concentrations between the two studies was mainly associated with the uncertainty in the estimates of sampling volumes. Sampled air volumes in the 2005 study were derived through comparison with PCB concentrations measured by the NJADN and represented 60% of the average sampled volume in the 2008 study. When the variation in air volumes was excluded, PCB masses measured in these two studies were in good agreement. The PCB concentrations were also comparable with the range of PCB concentrations measured by the NJADN during the spring months.<sup>2</sup>



**Table 2-1. Sampling site information,  $\Sigma$ PCB masses (ng) and atmospheric concentrations ( $\text{pg m}^{-3}$ ). The 5 highest concentrations are highlighted in bold.**

Site	Site Name	Abrv	Lat °N	Long °W	$\Sigma_{151}\text{PCB}$ (ng)	$\Sigma_{151}\text{PCB}$ ( $\text{pg m}^{-3}$ )
<b>1</b>	<b>Adventure Aquarium Camden</b>	<b>ADAQ</b>	<b>39.94498</b>	<b>75.131108</b>	<b>247</b>	<b>568</b>
2	Amosland Elementary School	AMES	39.89992	75.31532	92	204
3	Amosland Park Norwood BB Fields	APNF	39.85563	75.29289	94	204
4	Brandywine Creek State Park	BCSP	39.80715	75.58054	55	144*
5	Bombay Hook NWR	BHWR	39.27517	75.47391	63	165*
6	Bartrams Park	BRTP	39.93250	75.21271	172	393
7	Brandywine Springs Park	BRWP	39.74506	75.64198	51	139
8	Vicinity of Comm. Barry Bridge	CBB	39.81382	75.35757	65	190
9	Chester Park	CHEP	39.87519	75.37506	54	167
10	Cape Henlopen State Park	CHSP	38.79413	75.09162	28	83
11	Cape May Point State Park	CMSP	38.93358	74.95923	43	106
12	Camp Upland Park	CUPP	39.85350	75.38855	84	204
13	Delaware Memorial Bridge	DMEB	39.68355	75.50013	60	146
14	Delaware River Basin Commission	DRBC	40.25983	74.83413	80	235
15	Rt. 295 Overlook Eastside	E295	40.15379	74.71731	79	270
16	Eden Park	EDEP	39.72216	75.54414	117	310
17	Fairmount Park One (Laurel Hill Mansion)	FAP1	39.99150	75.19430	104	264
<b>18</b>	<b>Fairmount Park Two</b>	<b>FAP2</b>	<b>39.96774</b>	<b>75.18365</b>	<b>286</b>	<b>684</b>
19	Franklin Delano Roosevelt Park	FDRP	39.90575	75.18007	142	466
20	Fort Dupont State Park	FDSP	39.57327	75.58057	51	121
21	Fort Mott State Park	FMSP	39.60467	75.54920	44	122
22	Fox Point State Park	FPSP	39.75536	75.49188	112	243
23	Grace Park Elementary School	GPES	39.88589	75.34454	129	337*
24	Glen Providence Park	GPRP	39.92162	75.39902	51	174
25	Gov. Printz Park	GVPP	39.86122	75.36284	107	253
26	Hancock Harbor Marina	HHMR	39.37900	75.35585	59	131
27	Haskin Shellfish Research Lab	HSRL	39.23431	75.03118	48	109
28	John Heinz NWR 1	JHN1	39.88911	75.26183	106	235
29	John Heinz NWR 2	JHN2	39.87409	75.30200	79	179
30	Kent Park	KENP	39.93278	75.29118	91	258
31	Lums Pond State Park	LPSP	39.55127	75.73203	71	185*
<b>32</b>	<b>LaSalle University</b>	<b>LSUN</b>	<b>40.03960</b>	<b>75.15548</b>	<b>247</b>	<b>549</b>
33	Linwood Elementary School	LWES	39.82430	75.42367	101	274
34	Neshaminy State Park	NSSP	40.07858	74.91875	84	198
35	Pendle Hill School	PEHS	39.90700	75.36509	51	202
36	Pennypack Park 1	PNP1	40.08957	75.06896	71	208
37	Pennypack Park 2	PNP2	40.04995	75.03585	153	401*
38	Ridley Creek State Park	RCSP	39.95157	75.45221	30	130

39	Rick Greens Estate	RICG	39.70552	75.77113	41	101
<b>40</b>	<b>Ridley Middle School</b>	<b>RIMS</b>	<b>39.87940</b>	<b>75.32963</b>	<b>265</b>	<b>661</b>
<b>41</b>	<b>Swarthmore Science Center Roof</b>	<b>SCSC</b>	<b>39.90268</b>	<b>75.3587</b>	<b>631</b>	<b>1651*</b>
42	Tyler Arboretum	TYAB	39.93473	75.44065	49	131
43	Veterans Memorial Park	VEMP	39.83765	75.38788	125	311
44	Washington Park	WHSP	39.86579	75.35473	81	285
45	Wilmington Park/Brandywine Zoo	WZOO	39.75560	75.55066	79	228

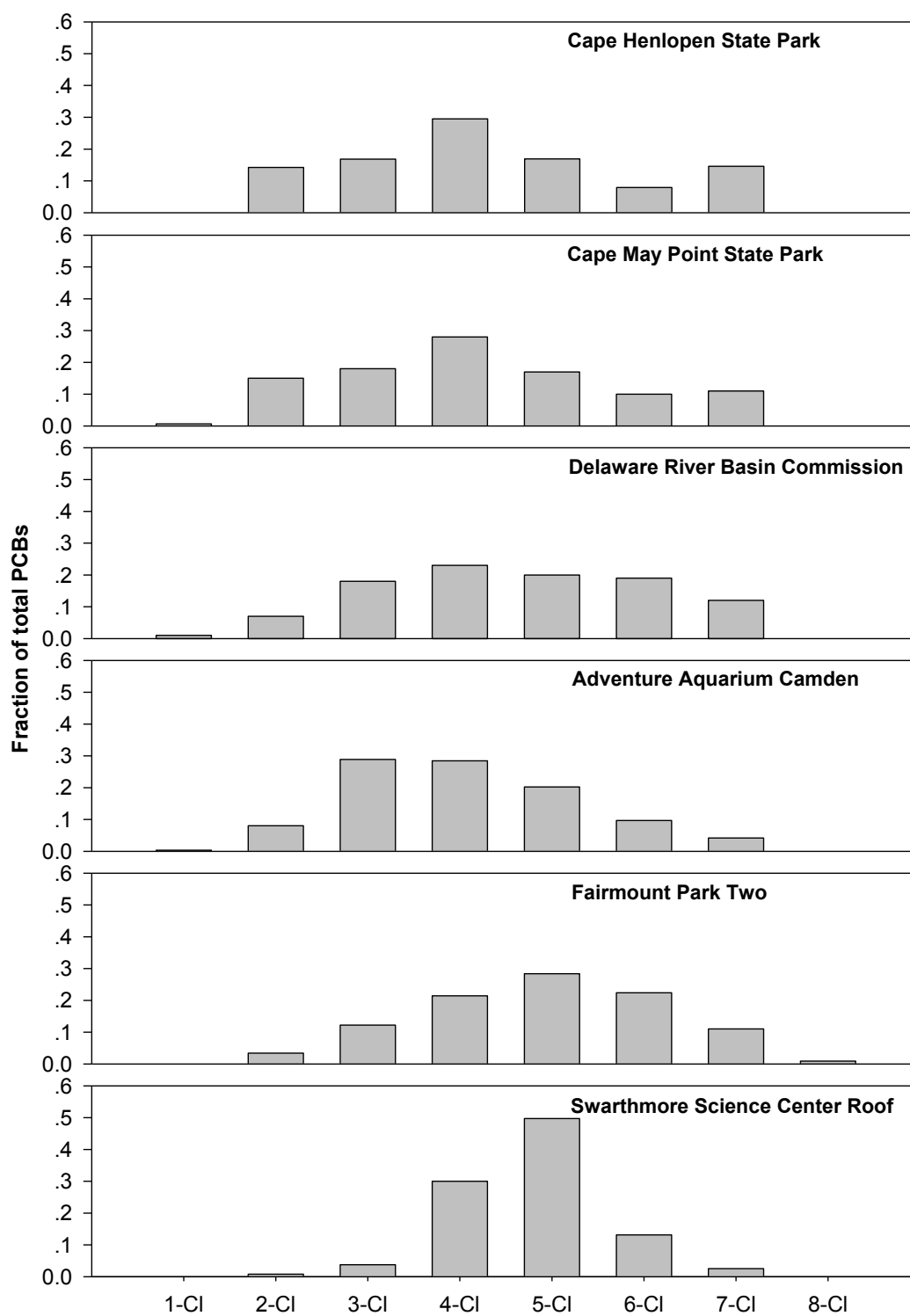
\* Numbers with an asterisk indicate an average sampling rate of  $4.2 \text{ m}^3 \text{ d}^{-1}$  was applied to calculate concentrations at these sites where the recovery of depuration compound PCB 30 was less than 20%.

As expected, the  $\Sigma\text{PCB}$  concentrations at two urban sites of Camden (Adventure Aquarium Camden, site 1) and Philadelphia (LaSalle University, site 32) were among the highest measured concentrations. Two sites near Swarthmore (Ridley Middle School, site 40 and Swarthmore Science Center Roof, site 41) also showed elevated PCB levels, in agreement with the 2005 study, with site 41 exhibiting the highest PCB concentration in the data set.

### 2.3.3 Homolog Distribution

The homolog distribution of PCBs at representative sampling sites is illustrated in Figure 2-3. PCBs at background sites such as Cape Henlopen State Park (site 10) and Cape May Point State Park (site 11) were dominated by low MW congeners. The suburban Delaware River Basin Commission (site 14) and urban Adventure Aquarium Camden (site 1) locations were enriched in high MW PCBs. Because heavier PCBs have greater affinity for the particle phase, they are likely to be removed from the atmosphere through particle deposition, which is fast relative to gaseous deposition.<sup>20</sup> Thus as the distance from the urban/suburban center increases, the lighter PCBs which are more volatile and less associated with particles will be enriched in the atmosphere. A similar urban-rural gradient described previously as the “urban fractionation effect” were also observed in

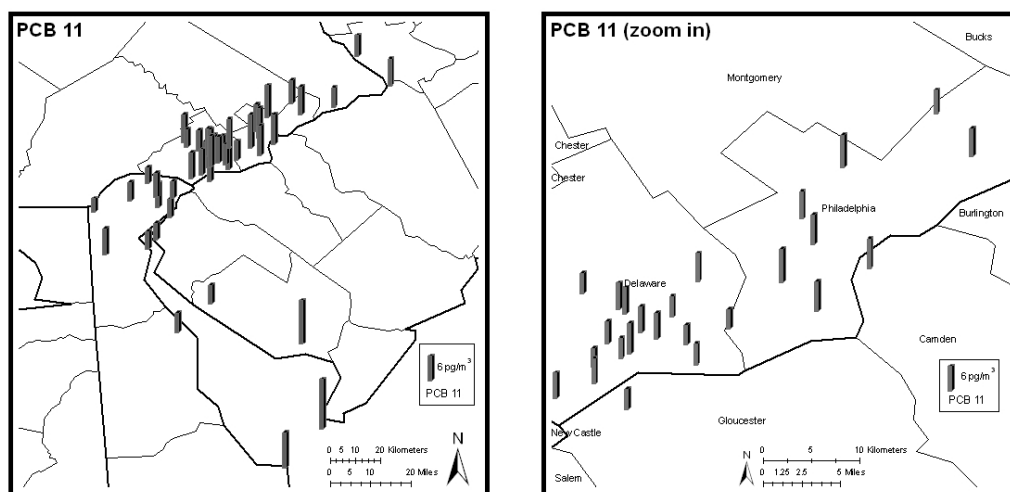
other studies.<sup>21, 22</sup>



**Figure 2-3. Homolog distribution of PCBs at representative sampling sites.**

#### 2.3.4 PCB 11 (3,3'-dichlorobiphenyl)

The non-Aroclor congener PCB 11 (3,3'-dichlorobiphenyl) was detected in all samples, at concentrations ranging from 3.2 to 12  $\text{pg m}^{-3}$  with a relative standard deviation (RSD) of 29% (Figure 2-4). In the 2005 passive sampling campaign,<sup>3</sup> PCB 11 was similarly detected in every sample ranging from 4 to 44  $\text{pg m}^{-3}$  with a RSD of about 85%. The larger variation of PCB 11 concentrations in the 2005 study may be due to uncertainty in the estimation of air volumes, since no depuration compounds were employed to determine sampled volumes.<sup>3</sup> Atmospheric PCB 11 concentrations observed in other urban areas varied from non-detect to 72  $\text{pg m}^{-3}$  (temperature normalized to 15 °C) in Chicago,<sup>23</sup> from non-detect to 307  $\text{pg m}^{-3}$  in the Great Lakes region<sup>24</sup> and from 11 to 92  $\text{pg m}^{-3}$  near an iron and steel plant in South Korea.<sup>25</sup> PCB 11 was also detected in the atmosphere of remote regions such as the Arctic (0.78~11.4  $\text{pg m}^{-3}$ ), the Antarctic (22.8~87.1  $\text{pg m}^{-3}$ ), and South Pacific (14.2~134  $\text{pg m}^{-3}$ ).<sup>26</sup>



**Figure 2-4. PCB 11 concentration and distribution (left: all sites; right: sites zoomed in Philadelphia/Camden and Swarthmore area)**

### 2.3.5 Positive Matrix Factorization (PMF)

Positive matrix factorization (PMF) was applied to identify co-varying PCB congener pattern or source profiles in the data set. Details of this method were presented elsewhere.<sup>27-29</sup> Briefly, the PMF model resolves the sample matrix ( $X$ ) as product of two factor matrices ( $G$  and  $F$ ) and a residual matrix ( $E$ ):

$$X = G \cdot F + E \quad (\text{Eq. 2-5})$$

The sample data set is viewed as a matrix  $X$  of  $m$  by  $n$  dimensions, in which  $m$  is the number of chemical species and  $n$  is the number of samples. The  $F$  matrix of  $m$  by  $p$  dimensions describes the chemical profiles of a number of  $p$  factors or sources. The  $G$  matrix of  $p$  by  $n$  dimensions describes the contribution of each factor to a given sample. The goal of PMF is to identify the number of factors  $p$ , the source profile matrix  $F$  and the source contribution matrix  $G$ .

The solution of PMF analysis is obtained by minimizing the sum of the weighed squared residuals that is the Q value as described in Eq. 2-6.

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left( \frac{e_{ij}}{s_{ij}} \right)^2 \quad (\text{Eq. 2-6})$$

where  $e_{ij}$  is the residual of the  $i^{\text{th}}$  chemical species measured in the  $j^{\text{th}}$  sample; and  $s_{ij}$  is an estimate of the uncertainty in the  $i^{\text{th}}$  chemical species measured in the  $j^{\text{th}}$  sample.

Because a total of 45 samples were collected and analyzed in the 2008 study, a maximum of 45 congeners/coeluting congener groups (Table 2-2) were selected for the PMF model input. The data list of 151 PCB congeners was reduced to 45 groups following the criteria as described below. First, congeners with non-detect in >10% of all samples were removed. Second, the contributions (%) of each congener group to the sum of PCBs measured in a sample were calculated and the relative standard deviations (RSDs) of these contributions in all samples were also determined for each group. Congener groups with large contributions and high RSDs were expected to yield more information about differences among samples. Third, a range of high and low MW homologs was desired for a representative congener pattern in the data list. Therefore, congener groups that had small % contributions, low RSDs, and whose homologs were already well represented, were removed from the list.

The PMF model input comprised three 45×45 matrices: the concentration matrix, the limit of detection matrix, and the uncertainty matrix. The model was run requesting three to six factors, changing the seed value from one to ten for each factor. Thus, the PMF

model output obtained ten matrices for each of  $G$  and  $F$  per factor. The optimal number of factors was determined to be five by evaluating the following rules. First, the RSD of the  $G$  matrices at the correct number of factors should be low, typically below 1%, and then increasing to 10% or more at a higher number of factors. Second, the  $Q$  value obtained in the model output as a function of the number of factors should be equal or close to the theoretical  $Q$  value at the correct number of factors. Finally, the PMF model at the correct number of factors should give a good agreement between the modeled results and measured data for the sum of congeners and for most of the individual congeners. The average RSD of the  $G$  matrices remained  $\leq 0.012\%$  from three to five factors and increased to 1.35% when requesting six factors. The five-factor model obtained a reasonable  $Q$  value of 1470, compared to the theoretical  $Q$  value of 1575. The Miesch coefficient of determination (CD) was observed  $> 0.9$  for 42 out of 45 congeners/coeluting congener groups, indicating an excellent fit between the modeled and measured sample matrices.<sup>30</sup> Additionally, in the five-factor model, four of the resolved factors each found a matching factor in the four-factor model ( $r^2 > 0.9$ ). The  $F$  and  $G$  matrices from the five-factor model output are provided in Table 2-2 and 2-3, respectively.

**Table 2-2. PCB congener list for the positive matrix factorization (PMF) model and composition of the five resolved factors ( $F$  matrix from model output).**

PCB Congeners	F matrix				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
4+10	5.2%	0.7%	0.1%	1.7%	0.6%
7+9	1.2%	0.3%	0.0%	0.4%	0.6%
6	2.1%	0.4%	0.1%	0.7%	0.3%
5+8	5.4%	0.9%	0.2%	1.8%	1.0%

<b>18</b>	14.9%	6.3%	1.0%	5.4%	4.6%
<b>17</b>	3.4%	1.6%	0.2%	1.3%	1.0%
<b>24+27</b>	0.9%	1.1%	0.1%	0.4%	0.4%
<b>16+32</b>	5.7%	3.4%	0.4%	2.2%	1.9%
<b>26</b>	1.8%	1.3%	0.2%	0.8%	0.9%
<b>25</b>	0.8%	0.7%	0.1%	0.3%	0.2%
<b>31</b>	9.4%	5.4%	1.1%	3.6%	4.2%
<b>20+21+33</b>	6.7%	2.7%	0.7%	2.6%	2.7%
<b>22</b>	3.6%	1.9%	0.4%	1.4%	1.7%
<b>54</b>	1.1%	2.2%	0.4%	0.6%	0.6%
<b>45</b>	1.3%	1.6%	0.2%	0.6%	0.6%
<b>43+49</b>	4.0%	7.1%	3.4%	2.0%	2.9%
<b>47+48+73</b>	2.6%	5.5%	0.8%	1.5%	1.8%
<b>44</b>	5.2%	6.8%	6.5%	2.5%	3.5%
<b>42</b>	1.4%	2.4%	0.5%	0.6%	0.8%
<b>41+64+68</b>	3.6%	5.7%	2.4%	2.0%	2.4%
<b>40</b>	0.6%	0.9%	0.3%	0.4%	0.2%
<b>66</b>	2.2%	4.4%	2.8%	1.9%	1.8%
<b>56+60</b>	2.1%	3.0%	1.6%	1.5%	2.1%
<b>93+95</b>	2.2%	4.3%	13.5%	7.2%	5.6%
<b>92</b>	0.4%	1.1%	2.5%	0.8%	1.0%
<b>84</b>	0.6%	1.3%	3.7%	0.8%	1.3%
<b>89+90+101</b>	2.7%	5.1%	16.6%	7.4%	6.6%
<b>85+120</b>	0.3%	1.1%	1.9%	0.5%	0.4%
<b>110</b>	2.0%	4.2%	12.8%	4.5%	4.0%
<b>106+118</b>	1.4%	1.1%	7.5%	2.8%	2.1%
<b>105+127</b>	0.7%	0.2%	2.3%	1.0%	0.6%
<b>136</b>	0.3%	1.0%	1.6%	2.6%	1.3%
<b>135+144</b>	0.2%	0.6%	1.1%	2.0%	1.8%
<b>146</b>	0.2%	0.7%	0.7%	1.2%	1.3%
<b>153</b>	0.9%	2.4%	3.7%	8.4%	3.3%
<b>132</b>	0.4%	0.6%	1.9%	2.2%	1.1%
<b>141</b>	0.2%	0.2%	0.7%	1.9%	0.7%
<b>138+163+164</b>	1.3%	1.1%	4.7%	7.1%	3.0%
<b>159</b>	0.1%	2.9%	0.0%	0.2%	0.7%
<b>179</b>	0.1%	0.8%	0.2%	3.0%	1.1%
<b>178</b>	0.1%	0.2%	0.2%	0.3%	11.8%
<b>182+187</b>	0.1%	1.8%	0.4%	3.4%	0.7%
<b>174+181</b>	0.2%	0.1%	0.2%	2.4%	0.5%
<b>172+192</b>	0.2%	1.7%	0.2%	0.4%	13.1%
<b>180</b>	0.3%	1.1%	0.3%	3.7%	0.8%

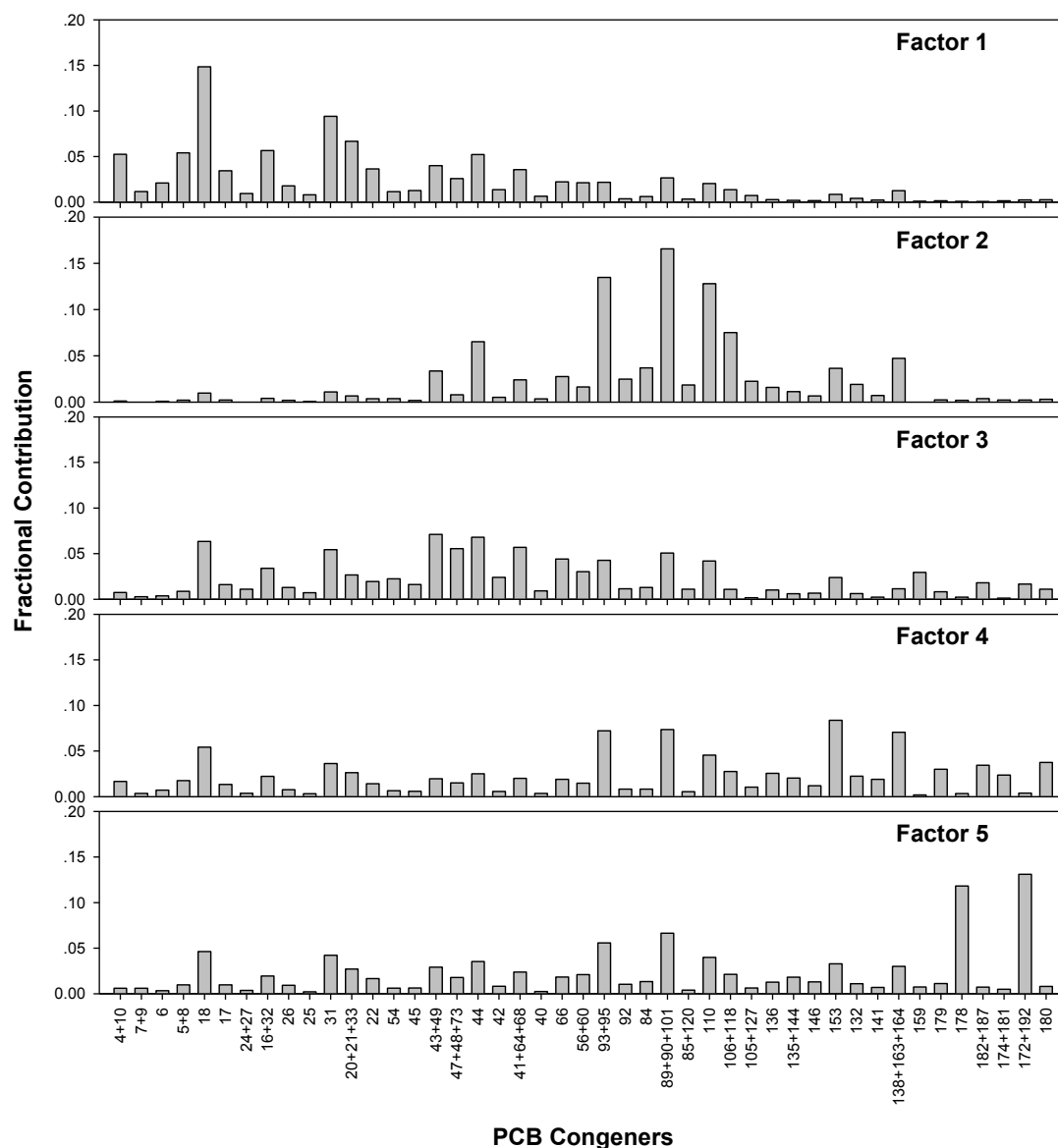


**Table 2-3. Contribution of each PMF factor to each sample (*G* matrix from model output)**

Site Number	Sampling Site Code	G matrix				
		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
1	ADAQ	64%	4%	18%	12%	2%
2	AMES	19%	18%	22%	25%	16%
3	APNF	35%	22%	18%	18%	6%
4	BCSP	20%	28%	27%	15%	10%
5	BHWR	1%	28%	10%	8%	53%
6	BRTP	35%	8%	40%	14%	3%
7	BRWP	26%	25%	22%	14%	13%
8	CBB	36%	10%	33%	11%	10%
9	CHEP	49%	17%	23%	7%	4%
10	CHSP	24%	40%	3%	7%	26%
11	CMSP	23%	31%	8%	17%	20%
12	CUPP	37%	20%	19%	18%	6%
13	DMEB	18%	30%	10%	29%	13%
14	DRBC	21%	8%	7%	50%	13%
15	E295	61%	17%	14%	1%	7%
16	EDEP	54%	17%	14%	12%	2%
17	FAP1	33%	14%	24%	23%	5%
18	FAP2	2%	3%	26%	64%	5%
19	FDRP	74%	10%	7%	8%	1%
20	FDSP	18%	36%	17%	13%	15%
21	FMSP	25%	39%	12%	11%	14%
22	FPSP	20%	28%	25%	24%	3%
23	GPES	24%	10%	20%	10%	36%
24	GPRP	34%	18%	19%	20%	10%
25	GVPP	36%	27%	19%	14%	4%
26	HHMR	11%	34%	19%	6%	29%
27	HSRL	23%	26%	23%	16%	11%
28	JHN1	52%	17%	14%	13%	4%
29	JHN2	45%	17%	16%	9%	13%
30	KENP	48%	10%	22%	14%	6%
31	LPSP	5%	27%	10%	13%	46%
32	LSUN	17%	1%	51%	10%	21%
33	LWES	41%	21%	19%	17%	2%
34	NSSP	42%	23%	15%	7%	12%
35	PEHS	41%	23%	22%	10%	5%
36	PNP1	34%	18%	15%	6%	27%
37	PNP2	36%	6%	17%	9%	32%
38	RCSP	59%	13%	4%	5%	20%
39	RICG	22%	30%	17%	11%	20%
40	RIMS	9%	3%	79%	7%	1%
41	SCSC	0%	2%	95%	1%	2%
42	TYAB	36%	19%	20%	6%	18%
43	VEMP	46%	12%	16%	22%	4%

44	WHSP	34%	16%	32%	11%	8%
45	WZOO	23%	18%	37%	13%	9%

The source profiles (Figure 2-5) were identified via comparison of their congener patterns with those of Aroclors<sup>31</sup> and sample profiles from suspected locations. The comparison with the Aroclors was performed in two ways: first the unaltered Aroclor congener pattern was compared with the source profile. Second, to simulate the volatilization process, the congener pattern of the Aroclor was multiplied by the vapor pressure of each congener and re-normalized. The cosine theta similarity metric ( $\cos \theta$ ) was used to measure the similarity between two multivariate vectors. The cosine measure assigns a high similarity to points that are in the same direction from the origin ( $\cos \theta = 1$ ), while assigning zero similarity to points that are perpendicular to one another ( $\cos \theta = 0$ ). The cosine theta values for each factor were calculated versus the nine Aroclors and mixtures of the four most abundant Aroclors 1242, 1248, 1254 and 1260.



**Figure 2-5. PCB congener patterns of the five resolved source profiles (factors). PCB congener numbers on the x-axis plotted versus their fractional contribution to the sum of PCBs on the y-axis.**

Factor 1 resembled volatilized Aroclor 1248 ( $\cos \theta = 0.97$ ) or unaltered Aroclor 1242 ( $\cos \theta = 0.93$ ), and therefore, represented a combination of low MW Aroclors. Factor 1 contributed to 29% of the  $\Sigma$ PCB concentration in the data set. Referring to Figure 2-6,

Factor 1 was most prevalent at both urban sites such as Adventure Aquarium Camden (site 1) and rural sites such as Ridley Creek State Park (site 38). At these two sites, Factor 1 constituted 64% and 59% of  $\Sigma$ PCBs respectively.

Factor 2 was similar to unaltered Aroclor 1248 ( $\cos \theta = 0.86$ ) or a volatilized mixture of Aroclors 1248:1254 (0.48:0.52) ( $\cos \theta = 0.81$ ) and contributed to 13% of the total PCBs. The contribution of Factor 2 displayed little spatial variation among all sites, indicating that a universal source of volatilized Aroclors affected the whole region.

Factor 3 comprised 33% of the  $\Sigma$ PCB concentration with a congener profile virtually identical to that observed at Swarthmore Science Center Roof (site 41) ( $\cos \theta = 0.99$ ) and volatilized Aroclor 1254 ( $\cos \theta = 0.84$ ). Factor 3 was the dominant source at Swarthmore Science Center Roof (site 41), accounting for 95% of  $\Sigma$ PCBs. This finding agreed well with the 2005 study.<sup>3</sup> This factor was also prevalent at the nearby Ridley Middle School (site 40), where it comprised 79% of  $\Sigma$ PCBs at this site. In contrast, this factor exhibited a relatively small fraction of  $\Sigma$ PCBs at most of the other sampling sites. This fact again reinforced the conclusion that there was a source of PCBs with a unique high MW congener profile near Swarthmore.

Factor 4 resembled the congener pattern at Fairmount Park Two (site 18) ( $\cos \theta = 0.97$ ). This site was immediately across the Schuylkill River from the Amtrak Race Street rail yards, where Aroclors 1254 and 1260 were frequently utilized as dielectric fluids in large transformers. This source profile was also correlated with unaltered Aroclor 1254 ( $\cos \theta$

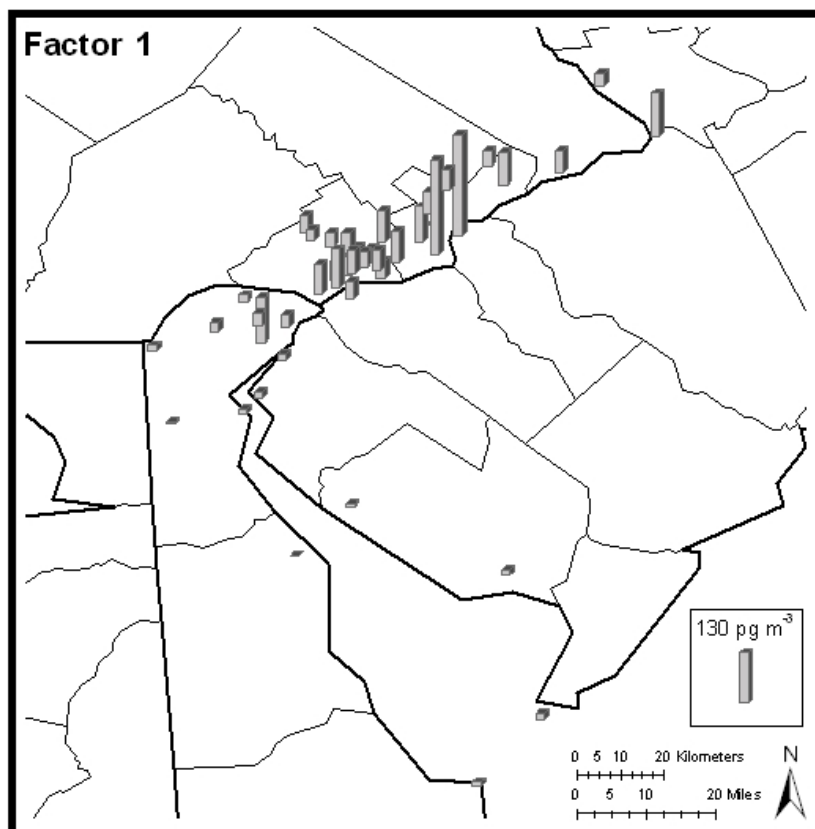
= 0.70) or volatilized Aroclor 1260 ( $\cos \theta = 0.72$ ). Using the Solver feature of Excel, the optimum mixture of Aroclors that best explained the congener pattern was a mixture of both low and high MW Aroclors such as original Aroclors 1242:1248:1254:1260 (0.35:0.03:0.29:0.33) ( $\cos \theta = 0.90$ ) or volatilized Aroclors 1248:1254:1260 (0.29:0.3:0.41) ( $\cos \theta = 0.74$ ). This factor accounted for 14% of the total PCBs in the data set.

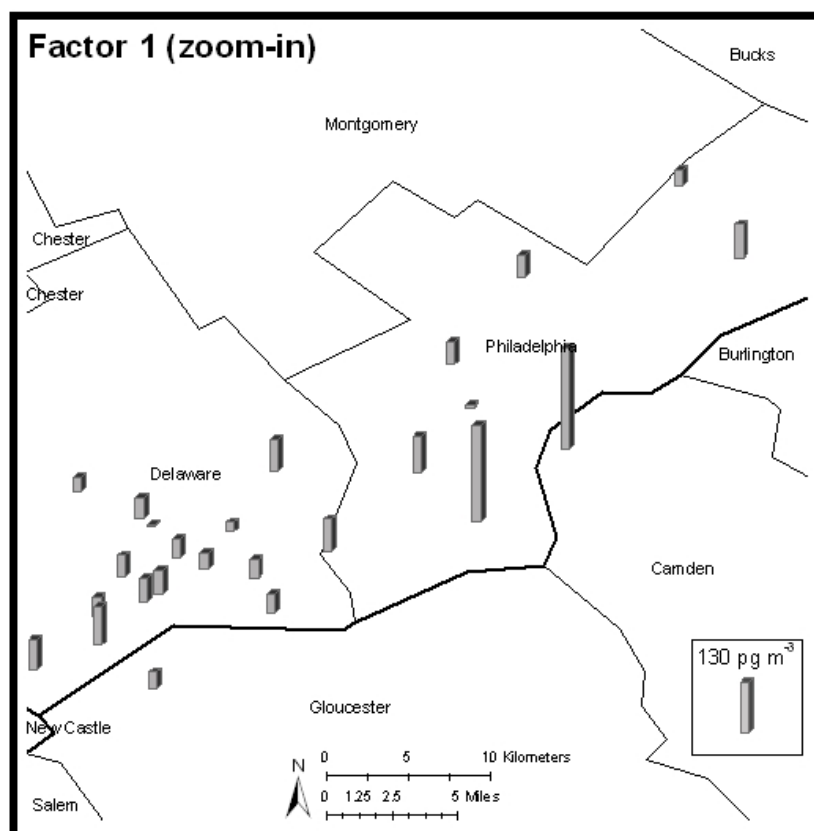
Factor 5 comprised only 9% of the  $\Sigma$ PCB concentration and was not well correlated with any of the Aroclors or mixtures, suggesting that it had undergone substantial weathering. It had the highest average molecular weight of the factors. Therefore, it may represent particle phase PCBs. Even though the design of the PAS prevented the deposition of coarse particles, some fine and ultra fine suspended particulates may still be collected.<sup>32</sup> Uptake rates appeared to be high at sites with large contributions from Factor 5 (such as 53% for site 5 and 46% for site 31) since their PCB 30 recoveries were  $< 20\%$ . It is possible that some fine particulates were sampled unintentionally under high flow rates.

Factor 4 mainly contributed to 64% of  $\Sigma$ PCBs at Fairmount Park Two (site 18) and 50% of  $\Sigma$ PCBs at Delaware River Basin Commission (site 14). Congener patterns at these two sites were well correlated ( $r^2 = 0.82$ ) although they were 44 km apart. This factor was found to be less significant in contribution to other sites. Factor 5 accounted for 53% of  $\Sigma$ PCBs at Bombay Hook NWR (site 5) and 29% of  $\Sigma$ PCBs at Hancock Harbor Marina (site 26), two sites 15 km away from each other across Delaware Bay that were observed with similar congener profiles ( $r^2 = 0.93$ ). The contribution of Factor 5 was also sparsely

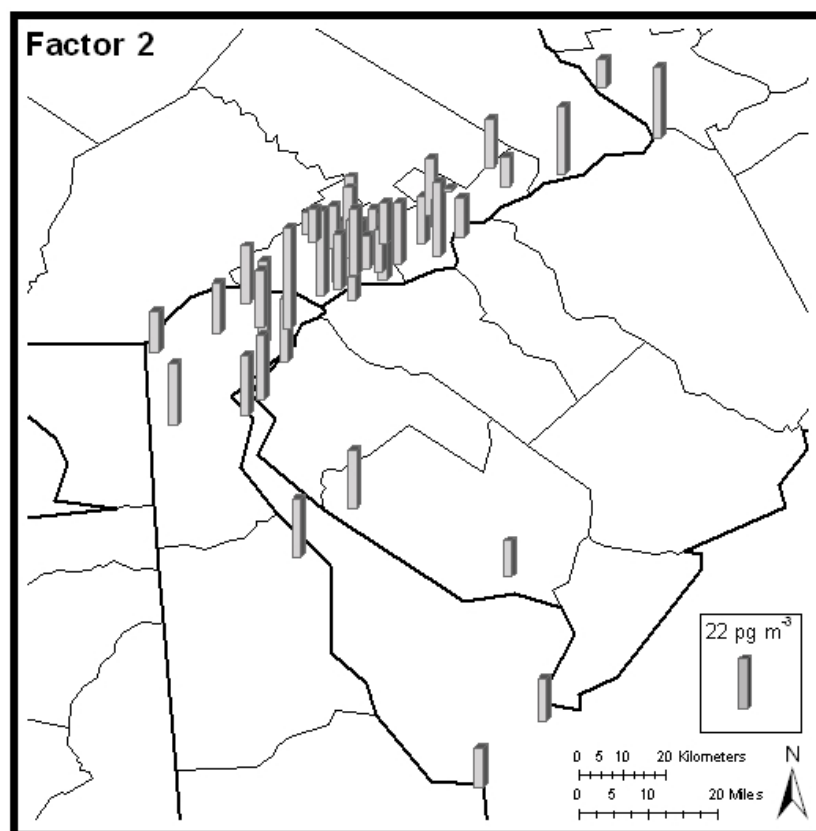
enhanced at some other sites such as Lums Pond State Park (site 31, 46% of  $\Sigma$ PCBs) and Grace Park Elementary School (site 23, 36% of  $\Sigma$ PCBs).

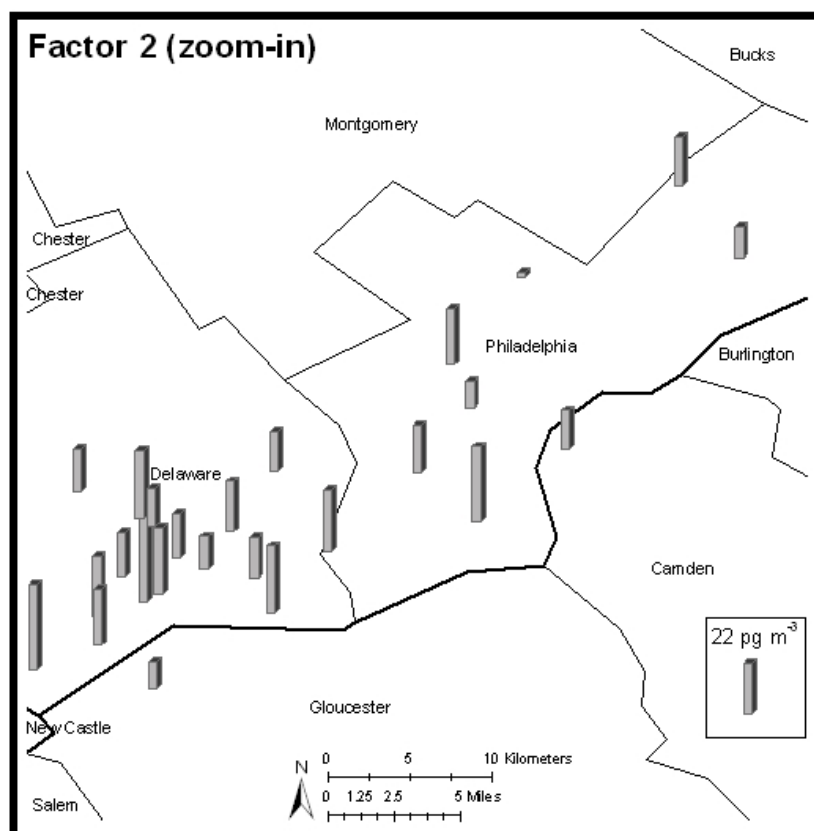
To investigate whether factor 5 could be related to ventilation of PCBs from inside contaminated buildings, factor 5 was compared to active air samples taken at the headquarter of the DRBC, which was known to be contaminated with PCBs. Indoor  $\Sigma$ PCB concentrations in the two samples were 62 and 73 ng m<sup>-3</sup>, about 300 times higher than outdoor concentrations. The indoor PCB congener pattern resembled a combination of volatilized Aroclor mixtures ( $r^2 = 0.59$ ). However, the congener patterns of the indoor and outdoor samplers were not correlated.

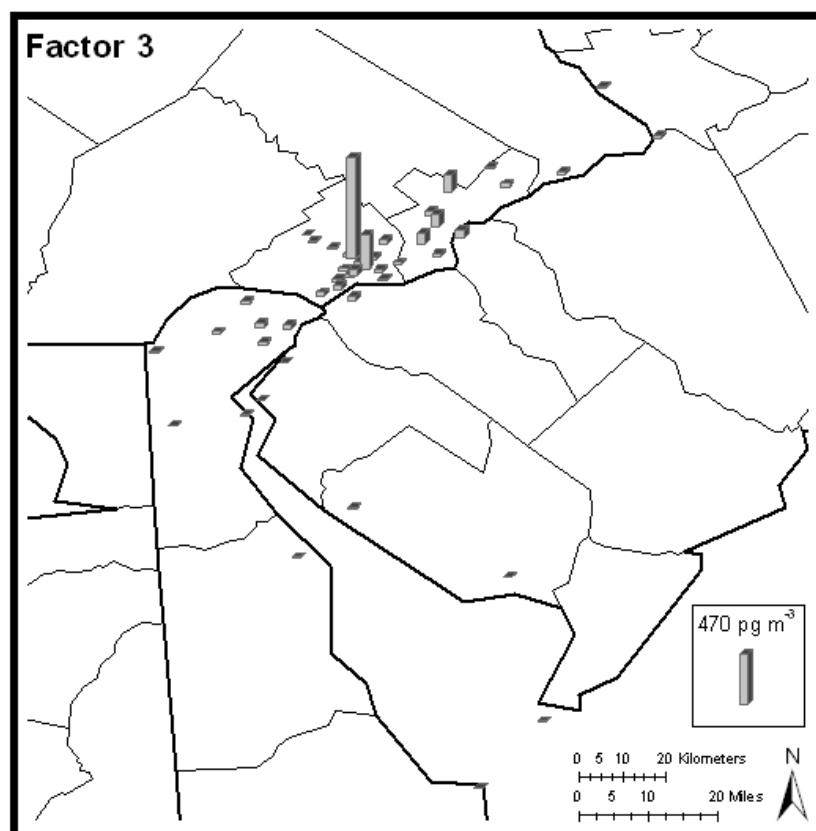


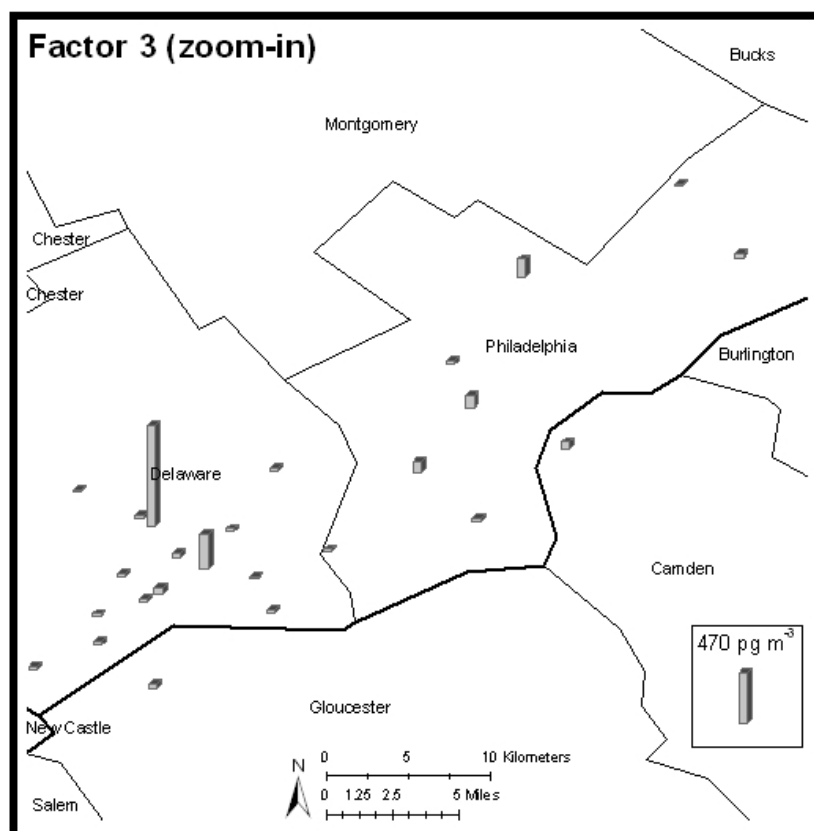


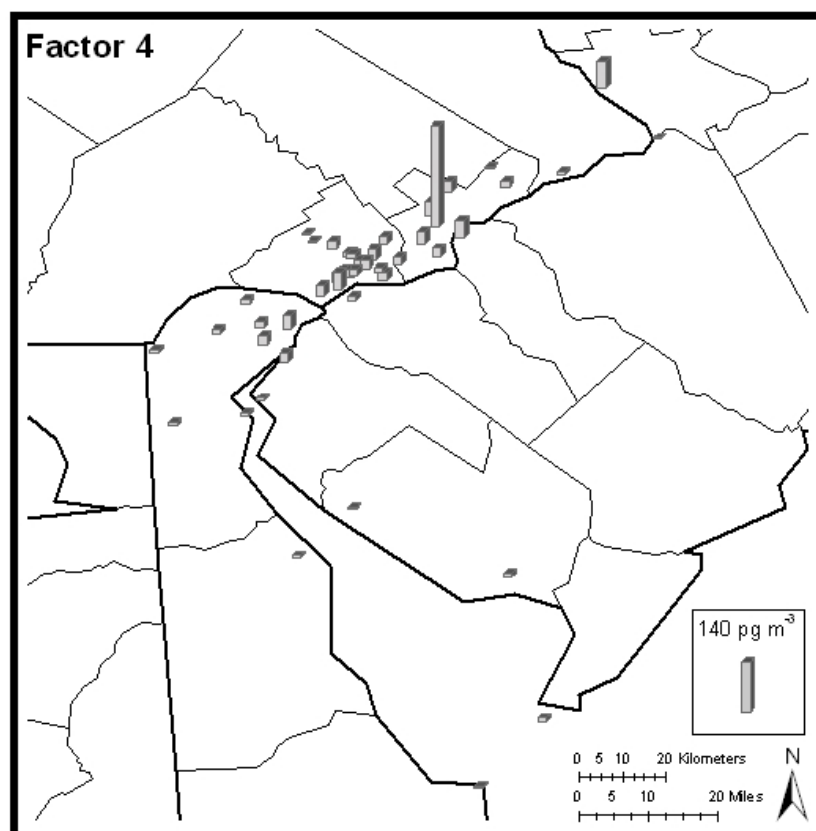


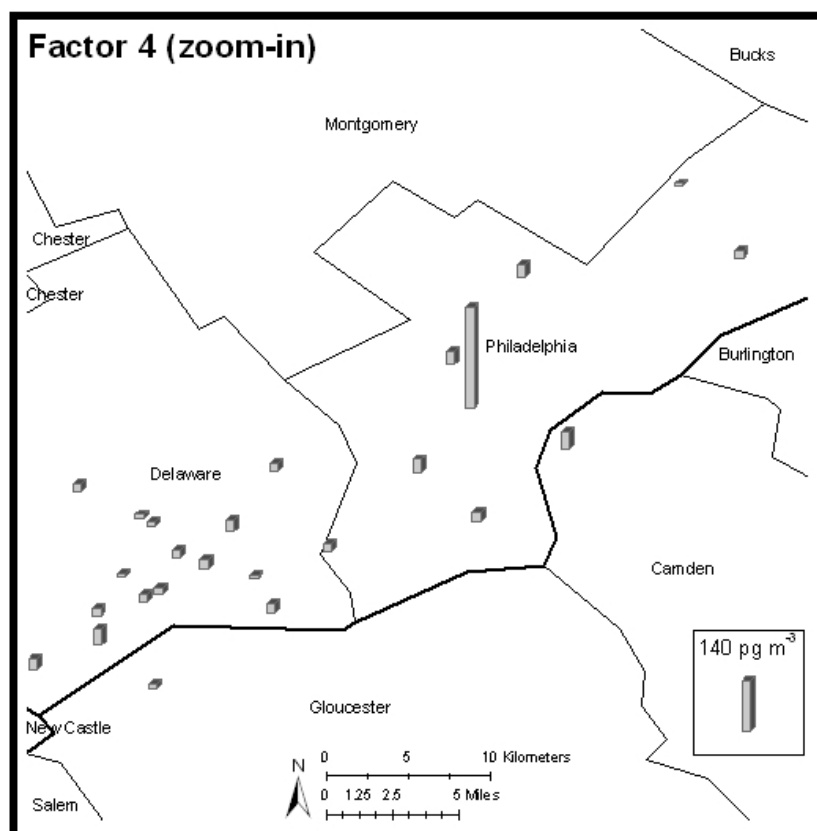


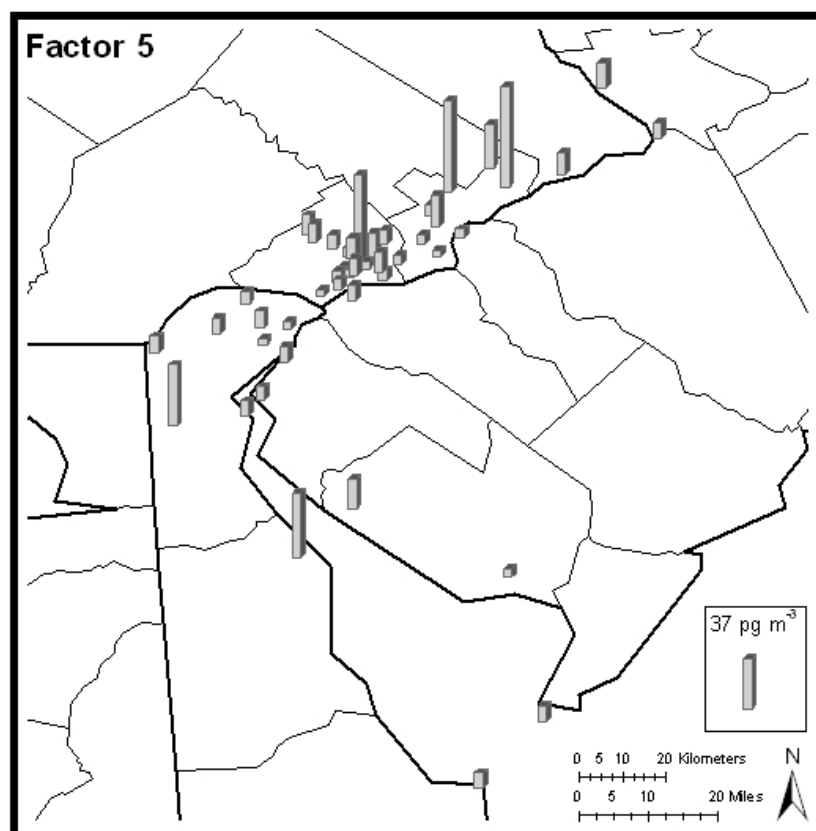


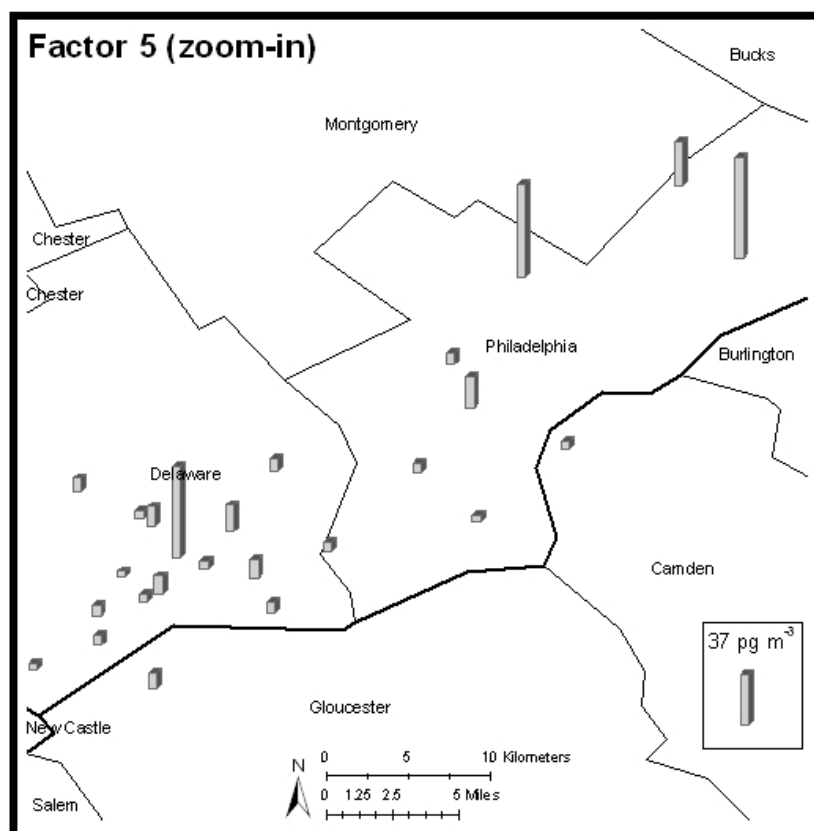












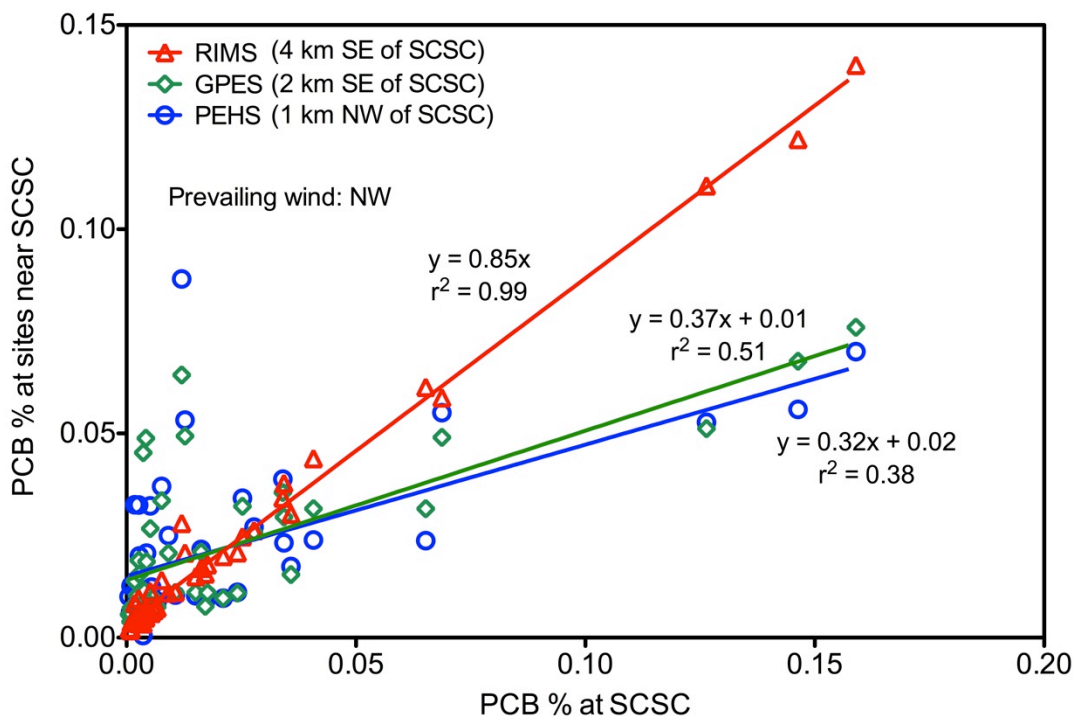
**Figure 2-6. Contributions of factors 1~5 to the sum of PCBs at all sites (full view and zoom-in view).**

### 2.3.6 The Swarthmore Source

The congener pattern at Swarthmore Science Center Roof (site 41) displayed a unique profile enriched in high MW PCBs. To investigate the source of PCBs at Swarthmore, several sites surrounding the Swarthmore area were compared in congener patterns that were expressed as fractional contribution to the sum of PCBs. The congener pattern at site 40 was strongly correlated to the Swarthmore profile ( $r^2 = 0.99$ ), despite a 66% decrease in  $\Sigma$ PCB concentration over a distance of 4 km along the direction of prevailing



wind (Figure 2-7). However, the congener pattern at site 23 (Grace Park Elementary School), which was located between site 41 and 40, showed a much weaker correlation with the Swarthmore profile due to enrichment in low MW congeners (Figure 2-7).  $\Sigma$ PCB concentration dropped by a factor of five from site 41 to site 23 that was 2 km away. The sharpest decline observed in the data set occurred between site 41 and site 35 (Pendle Hill School), where  $\Sigma$ PCB concentration decreased by a factor of eight. Site 35 was located 1 km upwind of site 41 and displayed a less chlorinated congener profile.



**Figure 2-7. Comparison of PCB congener patterns (expressed as % contribution to  $\Sigma$ PCB concentrations) surrounding the Swarthmore area. SCSC - Swarthmore Science Center Roof (site 41), RIMS - Ridley Middle School (site 40), PEHS - Pendle Hill School (site 35), GPES - Grace Park Elementary School (site 23).**

Therefore, the Swarthmore source is highly localized with 95% contribution from Factor 3 resembling volatilized Aroclor 1254. The source was speculated to be building materials such as PCB-containing sealants and caulks. PCBs were measured in currently in-use sealants from 0.56 to 550,000 mg kg<sup>-1</sup> with a congener pattern similar to Aroclors 1254 or 1260.<sup>33</sup> They were most frequently detected in buildings that were constructed or renovated between the 1950s and the 1970s when PCB usage was unrestricted. The Swarthmore Science Center was renovated around 2002 from old buildings. For example, DuPont building was constructed in 1959 and a wing of Martin Hall was added in 1963. By contrast, several buildings in Pendle Hill School (site 35) were also built or remodeled during 1950~1970, but these buildings may contain no or less PCBs because  $\Sigma$ PCB concentration at this site was measured low and showed only 10% contribution from Factor 3. Nevertheless, building materials were estimated to represent 10~18% of the remaining PCB stocks and considered as open sources of PCBs with release potential into the ambient environment.<sup>33</sup>

## 2.4 Conclusions

The 2008 passive air sampling study has largely confirmed the conclusions of the 2005 study.  $\Sigma$ PCB concentrations displayed strong spatial gradients with a factor of ~20 between the highest and lowest levels. Two PCB maxima were observed at Swarthmore and the center city of Philadelphia. Congener profiles at background locations were dominated by low MW homologs and enriched in heavier PCBs at urban/suburban sites (urban fractionation effect). The Swarthmore sample once again displayed a unique congener pattern. PMF analysis of the 32 samples collected in the 2005 study resolved

only two factors. The 2008 study collected more samples (45 samples); and therefore, the PMF analysis was able to resolve more factors (5 factors). A regional background signal was found to represent Aroclors 1248 and/or 1254. A combination of low MW Aroclors 1242 and/or 1248 contributed to  $\sim 1/3$  of  $\Sigma$ PCBs in the data set and was intensified at some urban and remote sites, similar to one of the two factors interpreted in the 2005 study.

Two unique factors were resolved centered on Swarthmore and Fairmont Park. We speculate that the source at Fairmont Park was volatilization of PCBs from the Amtrak Penn Coach Yard, since its congener profile matched the Aroclors 1254 and 1260 that were used at this rail yard. The stormwater discharge from this rail yard also showed elevated levels of PCBs around  $1000 \text{ ng L}^{-1}$ .<sup>34</sup> Railroad locomotive transformers were documented as containing PCBs at a concentration of 1000 ppm or less.<sup>35</sup> Historic maintenance of transformers and electric rail equipment released PCBs into the surrounding environment such as soil and groundwater.

One of the main goals of this study was to identify the source of PCBs near Swarthmore. In support of this goal, a large number of the samplers were placed near Swarthmore. The results revealed that the Swarthmore Science Center sample (site 41) contained the highest concentration of PCBs in the data set and displayed the by now familiar heavy congener pattern associated with Swarthmore. The PMF analysis suggested that this congener pattern was indeed unique and affected only a few other sites. Therefore, the source of PCBs was somewhere on or very near the Swarthmore campus and could be

related to the use of PCBs in building materials. Either active or passive air sampling of indoor air is recommended in some of the nearby buildings that were built or extensively renovated in the 1970s, including Hick's Hall. Our recent experience at Rutgers suggested that university buildings from this era could represent a significant source of PCBs to the surrounding atmosphere. For example, virtually identical PCB congener patterns were observed in paired indoor and outdoor air samples collected at a building on the New Brunswick campus of Rutgers, even though the indoor concentration was about 40 times higher than the outdoor concentration. Similar indoor/outdoor PCB concentration gradients have been observed in other studies.<sup>36-38</sup> Indoor PCB sources included building materials such as sealants and fluorescent light ballasts.<sup>39, 40</sup> The highest  $\Sigma$ PCB concentrations were measured in buildings constructed between the 1950s and the 1970s.<sup>40, 41</sup> We also recommend more sampling around rail tracks such as the Amtrak rail yards in Wilmington between sites 22 and 16 to further identify the source of the unique PCB congener pattern observed at Fairmont Park.

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## **Chapter 3 : Sources and Fate of 3,3'-dichlorobiphenyl (PCB 11) in the Delaware River Basin**

### **Abstract**

The non-Aroclor congener 3,3'-dichlorobiphenyl (PCB 11) has been recently detected in air, water, sediment, and biota. It has been known since at least the 1970s that this congener is produced inadvertently during the production of diarylide yellow pigments. In this work, we examine whether the known sources of PCB 11 are large enough to account for the levels of PCB 11 measured in the air, water, and sediment of the Delaware River Basin. PCB 11 is measured from non-detect to 79 ng g<sup>-1</sup> in consumer goods including newspapers, magazines, cardboard boxes used for food packaging, plastic bags, napkins, and garments that were collected from the United States and several other countries. Additionally, the leaching potential of PCB 11 from these materials is confirmed by experimental tests, suggesting that PCB 11 is released to wastewater via disposal of paper and washing of clothing. The printed materials are likely to be discarded in ways that allow PCB 11 to enter wastewater treatment plants and combined sewer overflows. Also in this work, PCB 11 is detected in wastewater collection systems and its removal from wastewater influents is calculated to average 80%. Based on these and other sources of information, we estimate that the inputs of PCB 11 to the Delaware River Basin are between the orders of 0.025 and 42 kg y<sup>-1</sup>, while the outflows from the basin are between the orders of 8.4 and 260 kg y<sup>-1</sup>. This estimate of outflows is biased low due to our inability to estimate sequestration in landfills and soils. Despite the large



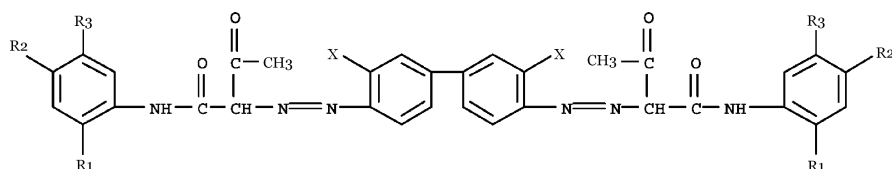
uncertainty in these numbers, the clear impossibility of the lower estimate of PCB 11 inputs into the Delaware Watershed suggests that PCB 11 is present in pigments at levels close to or even exceeding the federal limits and/or that degradation of these pigments releases PCB 11 into the environment. In addition, the mass flows indicate that a substantial fraction of the PCB 11 in these consumer goods is released to the environment, despite the assertions of pigment industry representatives. Both of these scenarios are problematic and suggest that further regulation of color organic pigments is necessary to protect water quality.

### 3.1 Introduction

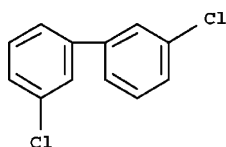
Efforts in the United States to control polychlorinated biphenyl (PCB) contamination have generally focused on legacy PCB sources, such as Aroclors that were banned from production in the 1970s.<sup>1, 2</sup> PCBs are regulated as the sum of all 209 congeners, however, regardless of source. Recently, PCBs from non-Aroclor sources have received much attention. Among these non-Aroclor congeners is 3,3'-dichlorobiphenyl (PCB 11) that has been recently detected in a variety of environmental media thanks to method development in congener-specific analysis of the entire PCB list.<sup>3</sup> Several studies reported the ubiquitous presence of PCB 11 in the atmosphere of U.S. cities such as Chicago and Philadelphia and in Polar Regions,<sup>4-6</sup> even though the actual sources were not identified. PCB 11 has been detected at levels sometimes exceeding the federal water quality standard for the sum of PCBs ( $64 \text{ pg L}^{-1}$ ) in surface waters across the US, including the New York/New Jersey Harbor, the Delaware River, the Houston Ship Channel, San Francisco Bay, Portland Harbor, and the Rio Grande and Santa Fe Rivers.<sup>7-12</sup> PCB 11 has also been detected as a dominant component in water, suspended particles and mussel tissues in Halifax Harbour, Canada.<sup>13</sup> It was accumulated in grey seals from Sable Island, Nova Scotia,<sup>14</sup> and in striped bass from Long Island Sound.<sup>15</sup>

The main source of PCB 11 is thought to be pigments. PCB 11 is produced inadvertently from synthesis of azo pigments that constitute 50~55% of color organic pigments and cover a wide range of colors including reds, oranges, and yellows.<sup>16</sup> The formation of azo pigments involves the reaction of diazotized aromatic amines with an appropriate coupling component.<sup>17</sup> During this coupling process, starting substances such as

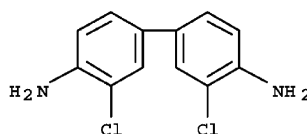
chlorinated aniline and common intermediates such as chlorinated benzidines can potentially produce PCB 11 by side reactions. PCB 11 has mostly been associated with the manufacture of diarylide yellows, a group of disazo-based pigments that contribute the majority of classical organic yellow pigments.<sup>7</sup> Diarylide yellow pigments are a series of disazoacetoacetanilides, synthesized by azo coupling of a tetrazotised benzidine derivative, most commonly 3,3'-dichlorobenzidine, with an acetoacetanilide coupling component.<sup>18</sup> The molecular structure and functional group substitutions of the most important commercial products of diarylide yellows are shown in Figure 3-1a and Table 3-1. These dichlorobenzidine pigments might contain PCB 11 (Figure 3-1b) as a result of deamination during the coupling reaction,<sup>19</sup> or undergo thermal cleavage at temperatures above 200 °C to form the intermediate 3,3'-dichlorobenzidine (Figure 3-1c),<sup>20</sup> which is itself listed as a probable human carcinogen.<sup>21</sup> For example, a pigment manufacturer noticed that particular combinations of Pigment Black 7 with Pigment Orange 13 or Pigment Orange 34 released 3,3'-dichlorobenzidine during the process of textile printing.<sup>22</sup>



a. Diarylide Yellow



b. PCB11



c. 3, 3'-dichlorobenzidine

**Figure 3-1. Molecular structures of diarylide yellow (a), PCB 11 (b), and 3,3'-dichlorobenzidine (c). (refer to Table 3-1 for examples of R1, R2, R3 and X groups in diarylide yellow)**

**Table 3-1. The substituent pattern of commercially important diarylide yellows (R1, R2, R3, X as positioned in Figure 3-1a)<sup>18, 23</sup>**

Color Index	R1	R2	R3	X	Shade
Yellow 12	H	H	H	Cl	Yellow
Yellow 13	CH <sub>3</sub>	CH <sub>3</sub>	H	Cl	Yellow
Yellow 14	CH <sub>3</sub>	H	H	Cl	Yellow
Yellow 17	OCH <sub>3</sub>	H	H	Cl	Greenish yellow
Yellow 55	H	CH <sub>3</sub>	H	Cl	Reddish yellow
Yellow 63	Cl	H	H	Cl	Yellow
Yellow 83	OCH <sub>3</sub>	Cl	OCH <sub>3</sub>	Cl	Reddish yellow
Orange 16	H	H	H	OCH <sub>3</sub>	Yellowish orange

The same azo compound can form both azo dyes and azo pigments, representing 60% to 80% of all organic colorants.<sup>24</sup> The major difference between dyes and pigments is that dyes are soluble in the substrate of application but pigments are not.<sup>25</sup> Some organic dyes can be converted to pigments through precipitation with an inert salt.<sup>26</sup> Azo dyes are widely used for the coloring process of textiles and leather materials.<sup>24</sup> It has long been

known that azo dyes may release carcinogenic aromatic amines including 3,3'-dichlorobenzidine by reductive cleavage of the azo groups.<sup>27</sup> The European Union enforced Directive 2002/61/EC to prohibit the manufacture and marketing of certain textile and leather products containing toxic amines produced from azo dyes.<sup>28</sup> A threshold limit was set for each restricted amine at 30 mg kg<sup>-1</sup> in the finished articles or in the dyed parts thereof. Even though certain azo pigments were also found to release these amines at levels up to over 30 mg kg<sup>-1</sup>,<sup>22</sup> they were exempted from prohibition because the regulatory agencies believe that the presence of pigments in consumer products such as printing inks and paints is unlikely to cause exposure concern to humans due to their extremely low solubility.<sup>22, 29</sup>

The levels of PCB 11 that have been found in pigments vary widely. Traces of PCB 11 were found in a dichlorobenzidine type azo pigment<sup>30</sup> and in sediments downstream of a dichlorobenzidine production plant located in northern France.<sup>31</sup> For wastewater treatment plants with high PCB 11 concentrations in their effluents, the source of PCB 11 has been tracked back to pigment manufacture including diarylide yellows.<sup>32</sup> According to a report from the USEPA, the Dry Color Manufacturing Association (DCMA) reported a PCB 11 level in diarylide yellow pigment at approximately 70 µg g<sup>-1</sup> (or ppm) in 1981 when the maximum concentration of inadvertently produced PCBs was regulated at an average of 50 ppm with exemptions up to 500 ppm.<sup>33, 34</sup> Dichlorobiphenyl was measured at 15.5 ng g<sup>-1</sup> (or ppb) in printing inks with yellow pigments in a study from 1992.<sup>35</sup> More recently, dichlorobiphenyl was reported at 3.7 µg g<sup>-1</sup> in Norwegian paints containing azo and phthalocyanin pigments produced in Finland.<sup>36</sup> Researchers in the United States have measured PCB 11 in consumer products of printed materials from non-detect to 38 ng g<sup>-1</sup>

and in commercial paint pigments with concentrations up to  $16 \text{ ng g}^{-1}$ , although the type of pigment was not known.<sup>7,37</sup> The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) stated in 2011 that "...there are minute traces of inadvertently generated PCBs in some pigments (usually less than 5 ppm), and values up to 20 ppm have occasionally been measured...".<sup>38</sup> In 2012, the Japanese ministries investigated by-product PCBs in dozens of different organic pigments and found nearly 32% of tested items, mostly pigment reds and yellows, contained PCBs from 0.5 to 1500 ppm.<sup>39</sup>

Worldwide production of color organic pigments was estimated to be about 250,000 metric tons (t) in 2006, with about 25%, or 62,500 t, being diarylide yellows.<sup>40</sup> The maximum concentration of PCBs allowed in these pigments under the Toxic Substances Control Act (TSCA) in the US is an average of 25 ppm, not to exceed 50 ppm at any time.<sup>41</sup> However, the concentrations of mono and dichlorobiphenyls are discounted in the calculation of the sum of PCBs. The Code of Federal Regulations (CFR 40 761.3 from 2011) states: "For any purposes under this part, inadvertently generated non-Aroclor PCBs are defined as the total PCBs calculated following division of the quantity of monochlorinated biphenyls by 50 and dichlorinated biphenyls by 5." In other words, pigments could contain an average of 125 ppm and a maximum of 250 ppm PCB 11 without exceeding the federal limit. In the European Union, Council Directive 89/677/EEC set a limit of 50 ppm for the sum of PCBs in pigments.<sup>42</sup> These regulations cover not only the manufacture, but also the processing and commercial distribution of PCB-containing products.

How much PCB 11 is produced inadvertently due to pigment production? Assuming the average concentration of PCB 11 in diarylide yellow pigments is the maximum of 125 ppm, the maximum amount of PCB 11 produced by this route is about  $7,800 \text{ kg y}^{-1}$  as of 2006. The actual amount produced could be much smaller than this. Di-CB concentration in printing inks with yellow pigments was measured around  $15 \text{ ng g}^{-1}$ .<sup>43</sup> Given that an average of 20% composition in printing inks are pigments,<sup>44</sup> PCB 11 concentration in diarylide yellow pigment would be roughly  $75 \text{ ng g}^{-1}$ . Using this lower number, we estimate that worldwide production of PCB 11 via the manufacture of diarylide yellow pigments would have been about  $5 \text{ kg y}^{-1}$  in 2006. It should be noted that in an earlier publication, we calculated that the global production of PCB 11 from pigments would be about 1.5 t in 2006.<sup>7</sup> This estimate was incorrect, and comes from a report in *Ink World* that stated the worldwide production of color organic pigments was 250 Mt.<sup>40</sup> We mistakenly interpreted the M to signify Mega ( $10^6$ ). We were recently notified by the author of that article that the M instead referred to the Latin milli ( $10^3$ ). Thus our estimate of the annual production of PCB 11 from pigments is now drastically lower. This begs the question, is this relatively small amount, 5 kg, of PCB 11 produced worldwide each year enough to account for all of the PCB 11 measured in the environment?

Even a cursory examination indicates that the answer is no. Litten *et al.* measured PCB 11 at about  $100 \text{ ng L}^{-1}$  in the effluent of the largest wastewater treatment plant in the New York metropolitan region, which received wastewater from a pigment manufacturer.<sup>32</sup> (This process was reportedly moved overseas. The Toxics Release Inventory (TRI)<sup>45</sup> shows that the last year for which a facility in this region reported releases of 3,3'-dichlorobenzidine was 2006.) The flow of this plant is about 260 MGD or  $3.6 \times 10^{11} \text{ L y}^{-1}$ , which means that the load of PCB 11 to the New York/New Jersey Harbor was about 40

kg y<sup>-1</sup> from this one plant alone in 2000. In addition, the majority of the PCB 11 entering the plant would have been sequestered in the sludge, so the amount of PCB 11 entering the plant was much higher (see below). Thus it is important to distinguish between PCB 11 present in the pigment product vs. PCB 11 present in the process waste, which appears to be much higher. Wastes from the manufacturing of certain azo dyes and pigments are listed as hazardous waste due to constituents of concern including anilines and amines.<sup>46</sup> Waste generated from off-site use, formulation and/or packaging of dyes and pigments are excluded from the listing as hazardous waste.

What are the emissions of PCB 11 to the environment? More importantly, is there any evidence that the amount of PCB 11 in the environment exceeds the estimated production such that PCB 11 must be generated in the environment, perhaps from breakdown of the pigment? If these popular pigments break down to form PCB 11 once they enter the environment, then there are no process controls that can limit the dispersal of PCB 11 throughout the environment, and these pigments will have to be banned. Thus it is of vital importance that we determine whether this process occurs.

To answer these questions, we have constructed a mass flow analysis for the Delaware River. Like many urban waterways in the United States, the Delaware River has been found to contain PCB 11 contamination even though no diarylide yellow pigment manufacturers were reported in this area (i.e. no facilities in the TRI report releases of 3,3'-dichlorobenzidine or related compounds).<sup>47</sup> Therefore, the objectives of this study are: (1) to provide evidence that the source of PCB 11 in urban waterways is associated with the applications of diarylide yellow pigments and dyes; (2) to examine the fate and transport processes of PCB 11 from pigment and dye use to receiving waters; (3) to



assess the magnitude of emissions required to reach PCB 11 levels measured in the watershed and airshed of the Delaware River Basin and determine whether the known sources are adequate to produce the measured concentrations.

## **3.2 Materials and Methods**

### **3.2.1 Measurement of PCB 11 in Consumer Goods**

PCB 11 was measured in samples of printed materials and other consumer goods collected from the United States and five other countries. Paper from color magazines and newspapers, cardboard from food packaging for breakfast cereal, yellow plastic grocery bags made of high-density polyethylene, and a variety of clothing were analyzed. The printed materials were stored for one day up to several months until being processed. The clothing was bought a few days before analysis and was not washed before extraction. Details of the clothing materials and colors are provided in Table 3-4.

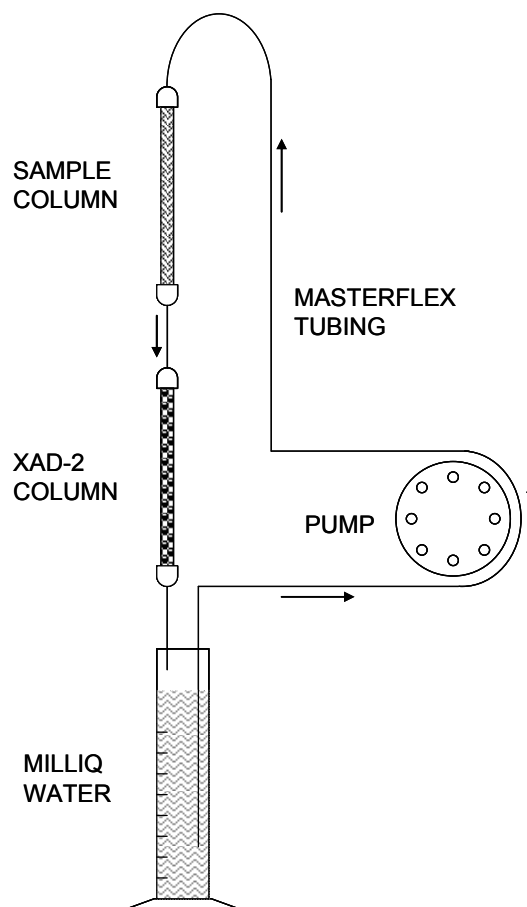
Paper and plastic bag samples were processed as described previously.<sup>7</sup> In brief, each sample (~5 g) was spiked with PCBs 14, 23, 65, and 166 (Cambridge Isotope Laboratories, Andover, MA) as surrogates and extracted by Soxhlet in dichloromethane for 24 h. The maximum temperature achieved during Soxhlet extraction was the boiling point of dichloromethane, 40 °C. Since diarylide yellow is reported to be able to withstand temperatures of up to 180 to 200 °C, breakdown of diarylide yellow to form PCB 11 during the extraction process is unlikely.<sup>23</sup> Extracts were then reduced in volume by rotary evaporation and fractionated on a column of 3% water-deactivated alumina (60-325 mesh, Fisher Scientific, Pittsburgh, PA). The PCB fraction was eluted with hexane,

concentrated under a gentle stream of nitrogen gas to about 0.5 mL, and injected with internal standards containing PCBs 30 and 204 (Cambridge Isotope Laboratories, Andover, MA) prior to instrumental analysis.

Samples of clothing were extracted either in ~5 g using a Soxhlet as described above or in 1~2 g using an accelerated solvent extraction system (ASE 200, Dionex, Sunnyvale, CA). The ASE was operated at 100 °C and 1500 psi using hexane/dichloromethane (3:1, v/v) as the extraction solvent. Deuterated PCBs 65 and 159 (C/D/N Isotopes, Inc., Quebec, Canada) were added as surrogates for both extractions. Soxhlet extracts were split into halves with one of them being processed for further analysis. Samples were cleaned up with either 3% water-deactivated alumina or 2.5% water-deactivated florisil (60-100 mesh, Fisher Scientific, Pittsburgh, PA). PCBs were eluted with petroleum ether on the florisil column. All PCB fractions were concentrated to 0.5 mL and spiked with deuterated PCBs 30 and 116 (C/D/N Isotopes, Inc., Quebec, Canada) as internal standards. Some clothing samples were analyzed with both methods (ASE with alumina cleanup and Soxhlet with florisil cleanup). The levels of PCB 11 measured in the same materials did not vary significantly between the two methods, indicating that the elevated temperature and pressure in the ASE does not cause breakdown of the pigment or additional release of PCB 11,<sup>48</sup> and that both cleanup methods are acceptable for clothing samples.

### 3.2.2 Leach Test of PCB 11 in Printed Materials

A simple column leach test (Figure 3-2) was developed to evaluate leaching potential of PCB 11 from printed materials and other consumer goods with pigment use. Test materials included color newspaper and commercial flyers, food and beverage packaging boxes collected in the United States. Two Teflon columns were prepared before the test: one packed with ~15 g of shredded paper samples and the other filled with clean XAD-2 resin (Amberlite, Dow Chemical, Midland, MI). MilliQ water was pumped from a plastic reservoir first through the sample column and then the XAD-2 column at a constant rate using a peristaltic pump (Masterflex L/S Easy Load II Pump, Cole-Parmer, Vernon Hills, IL). The test duration lasted approximately 48 h. All PCBs leached from the sample column were captured by XAD-2 resin and thus leachate coming out of the XAD-2 column is free of PCBs. This was confirmed because no PCBs were detected in the leachate from the XAD-2 column; therefore, 2 L of MilliQ water was continuously pumped and reused throughout the test duration. A total of 22 leach tests were performed. Loaded XAD-2 resin was stored in acetone at 4 °C until extraction.



**Figure 3-2. Schematic of leach test set-up**

PCB analysis for XAD-2 resin resembled the procedure described previously<sup>49</sup>. Prior to extraction, all samples were injected with surrogate standards including either PCBs 14, 23, 65, and 166 in six samples or deuterated PCBs 65 and 159 in 16 samples. Samples were Soxhlet extracted for 24 h in hexane/acetone (1:1, v/v) and then liquid-liquid extracted with 60 mL of Milli-Q water to separate the aqueous fraction from the organic fraction. The aqueous fraction was back-extracted three times with 50 mL of hexane and 1 g of NaCl in a separatory funnel. The extracts were then concentrated to ~ 1 mL and cleaned up on a 3% water-deactivated alumina column to collect the PCB fraction eluted with hexane. Finally the fraction was reduced in volume and injected with an internal

standards containing either PCBs 30 and 204 or deuterated PCBs 30 and 116 for quantification.

### **3.2.3 Measurement of PCB 11 in Sewer Sediments**

Grab samples were collected from interceptors that provided manhole access points for sampling sewer sediments in two industrialized cities (denoted as City A and B) of the Delaware River Basin. Samples from City A were collected at four locations (Site A1~A4) in 2010. Samples from City B were collected at three locations (Site B1~B3) in 2011. One sample from each site of City A and duplicate samples from each site of City B were analyzed. First, wet sediments (5~20 g) were air dried in a slowly vented fume hood. Dried sediments were spiked with surrogate standards including deuterated PCBs 65 and 159 and extracted with hexane/dichloromethane (3:1, v:v) at 100 °C and 1500 psi using ASE. The extract was then concentrated under nitrogen flow and cleaned up on a 2.5% water-deactivated florisil column. The PCB fraction was eluted with petroleum ether and concentrated by rotary evaporation and subsequently nitrogen evaporation. The final extract was injected with internal standards containing deuterated PCBs 30 and 116 prior to instrumental analysis.

### **3.2.4 Chemical Analysis**

Analysis of PCBs was performed by a gas chromatograph (6890N, Agilent, Santa Clara, CA) with a tandem quadrupole mass spectrometer (Quattro Micro GC, Waters, Milford, MA) by a modified EPA method 1668A as described previously.<sup>5</sup> It should be noted that A DB-5 capillary column (60m×0.25mm× 0.25µm, Agilent Technologies, Santa Clara,

CA) was used for PCB analysis for all paper extracts and XAD-2 resin extracts from the first six leach tests that were spiked with native PCB surrogates and internal standards. XAD-2 resin extracts from the other 16 leach tests and all extracts of sewer sediments and clothing samples were analyzed on an SPB-Octyl capillary column (30m×0.25 mm×0.25µm, Sigma-Aldrich, St Louis, MO).

Temperature programs for both columns are specified as follows. For the DB-5 column, the initial oven temperature 70°C was increased at a rate of 7°C min<sup>-1</sup> to 180°C, followed by 1.05°C min<sup>-1</sup> to 225°C, then 5.75°C min<sup>-1</sup> to 285°C, and 11.5°C min<sup>-1</sup> to a final temperature of 300°C, holding for 20 min. For the SPB-Octyl column, the initial oven temperature was held at 75°C for 5 min, then increased at a rate of 15°C min<sup>-1</sup> to 150°C, holding for 1 min, followed by 2.5°C min<sup>-1</sup> to a final temperature of 280°C, holding for 3 min. The instrument was operated with an electron impact (EI) source under multiple reaction monitoring (MRM) mode. Ion transitions for each PCB homologue group are identical on both columns. PCB 11 was identified by monitoring the transition from precursor ion at m/z 222+224 to product ion at m/z 152 using authentic PCB 11 standard (Ultra Scientific, N. Kingstown, RI). The Frame solutions (Accustandard, Inc., New Haven, CT) containing all 209 PCB congeners were analyzed on both columns to confirm that no other di-CB congeners coeluted with PCB 11 in the chromatographic system. Internal standards PCB 30 or deuterated PCB 30 were used for quantification of PCB 11. Recoveries of surrogate standards PCB 23 or deuterated PCB 65 were reported for quality assurance.

### **3.2.5 Quality Assurance/Quality Control**

Glass fiber filters (GFFs) or quartz fiber filters (QFFs), pre-cleaned XAD-2 resins and sea sand were analyzed as laboratory blanks for PCB 11 measurement in consumer goods. XAD-2 resin was used as the blank for leach tests and sewer sediments. GFFs and sea sand were baked at 450°C for 4 h prior to extraction. XAD-2 resins were Soxhlet extracted sequentially with methanol, acetone, hexane, acetone, and methanol for 24 h each and stored in MilliQ water before use. Teflon columns, tubings and cylinders were rinsed with methanol and MilliQ water prior to leach tests. PCB 11 was below the detection limit in all laboratory blanks. Recoveries of surrogate PCB 23 spiked onto paper samples averaged 103% and ranged from 70% to 127%. Surrogate recoveries of deuterated PCB 65 spiked onto clothing samples ranged from 22% to 122%. Recoveries of surrogate PCB 23 spiked onto selected XAD-2 resins ranged from 44% to 126%. Recoveries of the deuterated PCB 65 surrogate spiked onto XAD-2 resins ranged from 31% to 73%. Recoveries of the deuterated PCB 65 surrogate spiked onto sewer sediments ranged from 41% to 105%. PCB 11 concentrations reported below were corrected by surrogate recoveries except for sewer sediments.

## **3.3 Results and Discussion**

### **3.3.1 PCB 11 in Printed Materials**

PCB 11 concentrations in consumer goods sampled in the U.S. have been previously reported and ranged from non-detect to 38 ng g<sup>-1</sup> (Table 3-2).<sup>7</sup> Two samples of each product were extracted, but they were not duplicates. For example, the newspaper and magazine samples were different mastheads printed on different days. The cereal boxes

were from the same brand of cereal with a distinctive yellow box, but the boxes were obtained about three months apart. The plastic bags were obtained from a local grocery store several months apart. PCB 11 levels in these products are many orders of magnitude lower than the levels of  $\Sigma$ PCBs found in carbonless copy paper in 1972, when PCB concentrations were reported as high as  $64.7 \text{ mg g}^{-1}$ .<sup>50</sup> Recycled paper may contain PCBs from recovery of carbonless copy paper although the concentration has decreased due to volume reduction. Recycled PCB-containing paper has historically been used for food packaging with a tolerance limit of 10 ppm unless an impermeable barrier is present between the packaging material and food product (21CFR 109.30).



**Table 3-2. Concentrations of PCB 11 in consumer goods collected from the United States (ND = not detected, LOD = 0.10 ng g<sup>-1</sup>)**

Material	PCB 11 Concentration (ng g <sup>-1</sup> )
Black and white printed newspaper (A)	0.85
Black and white printed newspaper (B)	0.45
Brown (unprinted) cardboard (A)	3.0
Brown (unprinted) cardboard (B)	2.8
Color glossy magazine (A)	4.5
Color glossy magazine (B)	3.3
Color newspaper (A)	6.6
Color newspaper (B)	5.7
Plain white copy paper (A)	ND
Plain white copy paper (B)	ND
Manila envelope (A)	ND
Manila envelope (B)	0.11
Yellow cereal box (A)	3.0
Yellow cereal box (B)	2.9
Yellow plastic bag (A)	3.4
Yellow plastic bag (B)	38
Yellow sticky note (A)	0.82
Yellow sticky note (B)	0.11
Lab blank (GFF) (A)	ND
Lab blank (GFF) (B)	ND

Similarly, PCB 11 was detected from 1.6 to 16 ng g<sup>-1</sup> in printed materials that were collected from five other countries including Georgia, Moldova, China, Czech Republic, and Ukraine (Table 3-3). These findings indicate a common source of PCB 11 in printed materials from all over the world. PCB 11 was below the limit of detection (LOD = 0.10 ng g<sup>-1</sup>) in the GFF blanks and in samples of white copy paper and one of the manila envelopes. This suggests that the presence of PCB 11 in the printed materials is due to the ink, not passive absorption from the atmosphere. Hence PCB 11 is primarily associated with color, especially yellow, printing. It was by far the dominant PCB congener detected

in the color samples. Most other PCB congeners were below detection limit. Several non-Aroclor PCBs including PCB 11 were also found to be inadvertently formed during the production of paint pigments.<sup>37</sup> Therefore, we conclude that PCB 11 is ubiquitously present as a by-product in commercial pigment applications, particularly in printed materials.

**Table 3-3. Concentrations of PCB 11 in printed materials collected from worldwide locations**

Printed Material (Country)	PCB 11 concentration (ng g <sup>-1</sup> )
Black and white printed newspaper (Georgia)	1.6
Black and white printed newspaper (Moldova)	9.7
Black and white printed newspaper (China)	15
Color newspaper (Georgia)	6.5
Color newspaper (Moldova)	16
Food packaging box (Czech Republic)	6.8
Food packaging box (Ukraine)	5.0

### 3.3.2 PCB 11 in Fabric Materials

To assess the presence of PCB 11 in dyes (as opposed to pigments), we measured PCB 11 in a variety of clothing including knit shirts, pajamas, handkerchiefs and socks mainly for kids. PCB 11 concentrations in color fabrics ranged from 0.27 to 79 ng g<sup>-1</sup> (Table 3-4). Measured concentrations varied within a factor of two for the same fabric processed by both ASE-alumina and Soxhlet-florisil methods. This variation may be due in part to the natural variation in concentration in different parts of the garment. A few tri- through hexa-CBs are detected in some samples including high levels of PCB 52 (2,2',5,5'-tetrachlorobipheny) that may also form from azo pigment.<sup>37</sup> PCB 11 was not detected in

GFF and QFF blanks ( $\text{LOD} = 0.10 \text{ ng g}^{-1}$ ). However, the concentration of PCB 11 in white clothing was around  $1\sim 2 \text{ ng g}^{-1}$ , with most other PCB congeners below detection limit. As noted above, this indicates that the fabric material is not acquiring PCB 11 through passive uptake from the air, because this process would allow a wide variety of congeners to accumulate in the fabric. Instead PCB 11 may be entering the cloth via cross contamination, probably during the production or dyeing of the cloth or the sewing and processing of the garment. Concentrations of PCB 11 in many of the other dyed materials were similar to those in the white clothing, indicating that they, too, may acquire PCB 11 as a cross-contaminant. Several types of garments contained levels of PCB 11 well above  $2 \text{ ng g}^{-1}$ : the pajamas, handkerchief towels and luncheon napkins. All of these items contained a printed design that did not penetrate through the fabric, known as textile printing of which 80% in the US uses pigments.<sup>51</sup> This design could have contained diarylide yellow or other pigments containing PCB 11. In particular, the front and back pieces from the same pajama top was extracted separately and PCB 11 level in the front piece printed in yellow was about 20 times more than that of the back piece dyed in red. Thus PCB 11 in clothing could be a result of pigment, not dye, use. Nevertheless, the presence of PCB 11 in this clothing suggests that a primary route of entry of PCB 11 into wastewater is the washing of clothing. Future studies should assess the extent to which PCB 11 leaches out of clothing under conditions that simulate clothes washing (i.e. elevated water temperatures, presence of detergent and/or bleach).

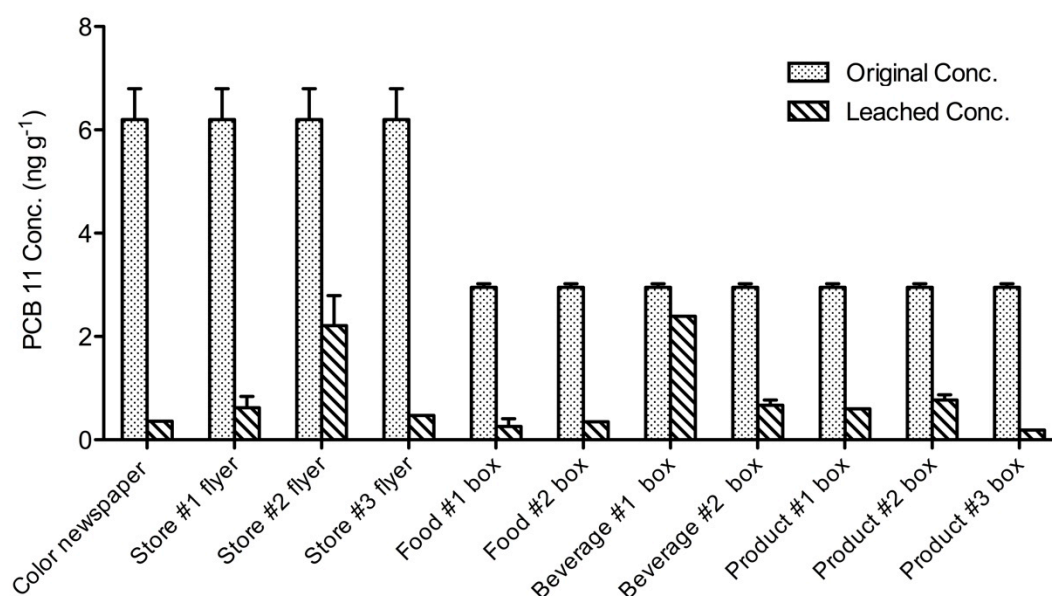
**Table 3-4. PCB 11 concentrations in fabric materials measured by different extraction-cleanup methods (ND = not detected, LOD = 0.10 ng g<sup>-1</sup>)**

Fabric Sample	Material	Color	Type of Coloring	PCB 11 (ng g <sup>-1</sup> )		
				ASE-Alumina	Soxhlet-Florisil	ASE-Florisil
Lab blank (GFF)	glass fiber filter	white		ND		
Lab blank (QFF)	quartz fiber filter	white			ND	
Kid's White Sock (A)	cotton/polyester/spandex	white	dyed			1.1
Kid's White Sock (B)	cotton/polyester/spandex	white	dyed			2.2
Woman's White Tank	cotton/ polyester	white	dyed	1.6		
Girl's White Sweatshirt	cotton/ polyester	white	dyed	0.41		
Girl's Knit Shirt	cotton/ polyester	dark pink	dyed	1.0	0.45	
Girl's Pink Sock	acrylic/polyester/spandex	dark pink	dyed	3.0	2.2	
Girl's Yellow Sock	acrylic/polyester/spandex	yellow	dyed	1.7	3.1	
Girl's Green Sock	acrylic/polyester/spandex	green	dyed	1.9		
Dish Wash Cloth	cotton	light yellow	dyed	0.27		
Luncheon Napkins #1	cellulose	yellow/red	printed	79		
Luncheon Napkins #2	cellulose	pink/white	printed	4.6		
Kid's Pajamas #1	polyester	yellow	printed	4.7	2.5	
Kid's Pajamas #2 Front	cotton	yellow	printed	14		
Kid's Pajamas #2 Back	cotton	red	dyed	0.62		
Kid's Handkerchief	cotton	yellow	printed	57	72	
Kid's Magic Towel	cotton	yellow/orange	printed	15		

### 3.3.3 Leaching of PCB 11 from Printed Materials

All leach tests resulted in measurable PCB 11 masses sorbed by the XAD-2 resin. Figure 3-3 shows that PCB 11 that leached from printed materials over the 48-hour tests ranged

from 6% in color newspaper and product packaging box to 81% in a beverage packaging box using Milli-Q water as leachant. Because surfactant-like substances such as humic acid in leachants would increase the leaching quantity of PCBs,<sup>52</sup> it is safe to assume that PCB 11 has a greater potential to leach out of printed materials in the actual environment where these surfactants are commonly found in industrial site leachate and sewage sludge. In addition, these materials could be exposed to leachant for longer than 48 hours, again potentially increasing the fraction of PCB 11 released to the water column. The tendency of leaching can impact the transport of PCB 11 into surface water and groundwater, thus affecting quality of receiving waters. In addition, given that paper and cardboard are easily shredded, especially when wet, it is certain that PCB 11 from these types of materials can contribute to particle-phase PCB concentrations in ambient waters.



**Figure 3-3. PCB 11 concentrations (ng g<sup>-1</sup>) that leached out of printed materials. Original concentrations are estimated from Table 3-2. Error bar represents one standard deviation of measurements from multiple samples or leach tests.**

A simple calculation illustrates the potential of these PCB 11-containing materials to affect surface water quality. An average cereal box such as those measured in Table 3-2 weighs about 90 g, and therefore, contains about 0.27  $\mu\text{g}$  of PCB 11. If the cardboard of the box is assumed to be similar to the type of organic carbon usually encountered in the environment (an assumption which is debatable<sup>53-55</sup>), then the organic carbon-water partition coefficient ( $K_{oc}$ ) can be used to estimate the volume of water that one cereal box can contaminate. Hansen *et al.* reported a log  $K_{oc}$  value for PCB 11 of 4.84.<sup>56</sup> Using this value, one cereal box can contaminate nearly 7,000 L of water at a level of 20  $\text{pg L}^{-1}$ , the average PCB 11 concentration in the ambient waters of the Delaware River.

### 3.3.4 PCB 11 in Sewer Sediments

PCB 11 concentrations varied from 0.27 to 3.3  $\text{ng g}^{-1}$  on a dry weight basis in sewer sediments collected from two major industrial cities in the Delaware River Basin (Table 3-5). Sediments from City A mainly consisted of sands and gravels. Sediments from City B were mostly fine-grained deposits. Despite the difference in physical properties of these sediments that may indicate different organic matter content, PCB 11 has been accumulated at similar levels in sewer sediments from both cities. Composite wastewater samples collected from sewer systems in City B showed an average PCB 11 concentration of 890  $\text{pg L}^{-1}$ .<sup>57</sup> The wastewater collection systems in the major cities of Delaware River Basin (Philadelphia, PA; Camden and Trenton, NJ; and Wilmington, DE) largely consist of combined sewers that contribute significant PCB loads from non-point sources and contaminated sites due to storm water runoff. It is reasonable to assume that

a large portion of PCB 11 detected in the sewer sediments comes from street runoff, which is likely to wash off discarded printed materials containing PCB 11. Therefore, it is not surprising to find PCB 11 in receiving influents of wastewater treatment plants (WWTPs) from these sewers. In our previous investigation of PCB 11 sources, we noted that the storm water runoff from a paper mill on the south site of Philadelphia contained high concentrations of PCB 11 (5.4 to 20 ng L<sup>-1</sup>), suggesting that PCB 11 may be released to the atmosphere during the paper recycling process.

**Table 3-5. Concentrations of PCB 11 in sewer sediments collected from two major industrialized cities (Site A1~A4 from City A and Site B1~B3 from City B) in the Delaware River Basin**

Location	PCB 11 concentration (ng g <sup>-1</sup> d.w.)
Site A1	0.27
Site A2	0.37
Site A3	1.5
Site A4	1.3
Site B1	0.84~0.88
Site B2	1.1~1.2
Site B3	3.1~3.3

### 3.4 Mass Flows of PCB 11 in the Delaware River Basin

Import of PCB 11 into the Delaware River Basin was estimated in order to determine whether it is adequate to account for the measured and estimated stocks and flows of PCB 11 within and exiting the basin.

### 3.4.1 Mass Inflow into the Basin

The worldwide PCB 11 production from diarylide yellow pigments was estimated between  $5 \text{ kg y}^{-1}$  and  $7,800 \text{ kg y}^{-1}$  in 2006. The US market consumes 20% of color organic pigments produced worldwide.<sup>16</sup> Assuming that regional pigment use is proportional to population (Delaware River Basin comprises 2.7% of US population<sup>58</sup>), PCB 11 imported into the basin via use of diarylide yellows is estimated to be between  $0.025 \text{ kg y}^{-1}$  ( $70 \text{ mg d}^{-1}$ ) and  $42 \text{ kg y}^{-1}$  ( $115,000 \text{ mg d}^{-1}$ ) in 2006. This is comparable to the Total Maximum Daily Loads (TMDLs) for  $\Sigma$ PCBs in Zones 2 through 6 of the Delaware River, which is  $2,256 \text{ mg d}^{-1}$ .<sup>59,60</sup> As noted earlier, the process waste from diarylide yellow manufacture may contain higher levels of PCB 11. However, since there are no facilities in the TRI that report use of 3,3'-dichlorobenzidine and its related compounds in this area, we assume that the only imports of PCB 11 into the Delaware River basin are from pigment use. Our investigation of PCB 11 in clothing suggests that it, too, could arise from pigments instead of dyes. Therefore, we assume that the input of PCB 11 to the watershed from dyes is negligible.

### 3.4.2 Mass Outflow/Storage

The necessary data are available to calculate flows of PCB 11 exiting the watershed via flow of the Delaware River to the Atlantic Ocean and via volatilization from the land or water surface to the atmosphere. It is also possible to estimate the mass of PCB 11 stored in the basin each year via sequestration in the sludge from municipal wastewater treatment and via sedimentation in the Delaware River. Other processes certainly occur that would export or sequester PCB 11 in the watershed, but they cannot be calculated and/or can be assumed to be negligible (see below). Significant among these is sequestration in soil. A simple fugacity model indicates that the largest fraction of PCB



11 mass would reside in soil under typical conditions. Although we could estimate the mass of PCB 11 stored in soil in the Delaware River Basin, we are unable to estimate the flow ( $\text{kg y}^{-1}$ ) of PCB 11 that would be sequestered in this way, other than to say that it is likely to be large. Another important process that we cannot accurately estimate is sequestration, along with paper that is not recycled, in landfills. This is likely to be large. In a survey of azo-colorants in Denmark, the final disposal of azo pigments associated with printing inks is distributed among landfill (24%), soil (7%), and incineration (69%).<sup>61</sup> Assuming these ratios are the same for PCB 11 in the Delaware River Basin, maximum sequestration of PCB 11 in landfill is estimated around  $10 \text{ kg y}^{-1}$  based on the high-end estimate on PCB 11 production. We did not include this in our mass flow analysis, because it is unclear whether the final disposal of pigments is similar in the US, and because PCB 11 may leach out before or after reaching the landfills. Given that these two processes are likely to be significant but cannot be estimated accurately, our estimates of outflow and storage of PCB 11 in the Delaware River Basin are biased low.

Although all of these mass flows are estimates with varying degrees of uncertainty, they can help us to determine whether additional sources of PCB 11 must be present in the watershed to explain the discrepancy between the inflows and outflows. Underpinning our analysis of mass flows is the assumption that the watershed is either at steady state with respect to PCB 11 flows or that PCB 11 flows and concentrations are increasing over time. This assumption is explored in more detail below.

### ***3.4.2.1 Advection to the Atlantic Ocean***

The average concentration of PCB 11 in Delaware River is about  $20 \text{ pg L}^{-1}$ . Based on 48

years of records collected by the USGS at Port Jervis, NY, the average flow of the Delaware River is  $4,800 \text{ ft}^3 \text{ s}^{-1}$  or  $1.2 \times 10^{10} \text{ L d}^{-1}$ .<sup>62</sup> Therefore, the mass flow of PCB 11 in the river under steady state is estimated to be  $240 \text{ mg d}^{-1}$ , and this estimate is associated with a high degree of certainty, i.e. it is probably accurate to within a factor of two. This is well in excess of our low-end estimate of the inputs of PCB 11 to the Delaware River Basin of  $0.025 \text{ kg y}^{-1}$  or  $70 \text{ mg d}^{-1}$  and immediately suggests that this lower bound is not reasonable.

#### ***3.4.2.2 Volatilization to the Atmosphere***

The average concentration of atmospheric PCB 11 in the Delaware River Basin is about  $6 \text{ pg m}^{-3}$  with a small relative standard deviation (RSD) of 29% via passive air sampling conducted during March to June 2008 (see Chapter 2). PCB 11 concentrations were mostly well above  $6 \text{ pg m}^{-3}$  from long-term monitoring of atmospheric PCBs by high-volume sampling in this area. Concentrations of PCB 11 averaged  $14 \text{ pg m}^{-3}$  at Camden, NJ,  $22 \text{ pg m}^{-3}$  at New Brunswick, NJ, and  $20 \text{ pg m}^{-3}$  at Lums Pond, DE (Pornsawai Praipipat, unpublished data). Notably, these concentrations were not temperature dependent at any of these sites except for a weak correlation at the New Brunswick site. In agreement with the results of the passive sampling, the spatial distribution of PCB 11 did not display higher concentrations in urban areas that are typical of other PCB congeners.<sup>63-65</sup>

A simple box model was constructed to calculate the emission required to maintain the average PCB 11 concentration in the airshed of the basin. Since the basin area is about 13,500 square miles, or  $35,000 \text{ km}^2$ , the airshed is assumed as a box with a square bottom

in the same width (W) and length (L) of 187,000 m. The multimedia urban model (MUM), developed by Diamond *et al.*<sup>66</sup>, divides the air compartment into low air from 0 to 50 m that is in contact with impervious surfaces, and upper air from 50 to 500 m that is above most building heights. Therefore, two model scenarios were considered with atmospheric mixing heights ( $H_a$ ) of 50 m and 500 m, respectively. Since the variation in PCB 11 concentrations measured in the air at the earth's surface is low, it is reasonable to assume that the box is well mixed.

The steady-state mass (M, g) of PCB 11 in the air box is calculated by Eq. 3-1.

$$M = C_a \cdot W \cdot L \cdot H_a \cdot 10^{-12} \quad (\text{Eq. 3-1})$$

where  $C_a$  is the average concentration in the atmosphere ( $\text{pg m}^{-3}$ ).

Major removal processes of PCB 11 from the atmosphere include advection and reaction with hydroxyl (OH) radical. The advective loss is calculated as a flushing rate ( $k_w, \text{s}^{-1}$ ) by Eq. 3-2.

$$k_w = u/W \quad (\text{Eq. 3-2})$$

where  $u$  is the wind speed ( $\text{m s}^{-1}$ );  $W$  is the width of the air box (m). The average wind speed in the watershed was around  $4 \text{ m s}^{-1}$ .<sup>67</sup>

The removal rate by reaction with OH radicals ( $k_{OH}, \text{s}^{-1}$ ) is calculated by Eq. 3-3.

$$k_{OH} = k \cdot C_{OH} \quad (\text{Eq. 3-3})$$

where  $k$  is the OH reaction rate constant ( $2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) obtained from that of a

similar dichlorobiphenyl, i.e. PCB 4, and  $C_{OH}$  is the global average concentration of OH radicals ( $9.7 \times 10^5$  molecules  $\text{cm}^{-3}$ ).<sup>68</sup>

Finally, the emission rate ( $I$ ,  $\text{mg d}^{-1}$ ) is calculated as the product of steady-state mass of PCB 11 in the air box and the sum of all rate constants using Eq. 3-4.

$$I = M \cdot (k_w + k_{OH}) \cdot 1000/86400 \quad (\text{Eq. 3-4})$$

With an atmospheric mixing height of 50 m, an emission of 21,000  $\text{mg d}^{-1}$ , or 7.8  $\text{kg y}^{-1}$  is required to meet the most conservative estimate of average atmospheric PCB 11 concentration of 6  $\text{pg m}^{-3}$  in the basin. This is about 300 times greater than our low- end estimate of the PCB 11 inflow (0.025  $\text{kg y}^{-1}$ ) to the basin, although it is within the maximum estimate of 42  $\text{kg y}^{-1}$ . With an atmospheric mixing height of 500 m, an emission of 210,000  $\text{mg d}^{-1}$ , or 78  $\text{kg y}^{-1}$  is required to produce an average concentration of 6  $\text{pg m}^{-3}$ , which even exceeds the maximum estimate of 42  $\text{kg y}^{-1}$ . To achieve an average concentration of 20  $\text{pg m}^{-3}$ , which is observed from active air sampling at Lum's Pond, an input of 26  $\text{kg y}^{-1}$  is needed if the mixing height is 50 m, and 260  $\text{kg y}^{-1}$  if the mixing height is 500 m. A typical height of 1~2 km vertical mixing is observed during daytime driven by convection from heated land surface and a stable boundary layer of 50~200 m is formed during the night.<sup>69</sup> Therefore, both scenarios have their own merit in describing the actual environmental conditions. However, the uncertainty in the mixing height renders the uncertainty in the estimated emissions very high.

It should be noted that PCB 11 inflow from upwind is assumed to be negligible because the background concentration is considered low surrounding the Delaware River Basin. If

this is not true, we can get an estimate for the entire continental US with a justified assumption that PCB 11 concentration of inflow from air above the ocean is zero. The lower 48 states have an area around  $8,000,000 \text{ km}^2$ , which is converted to a square with a side length of 2828 km. Using the same box model calculations by Eq. 1~4, an emission of  $270 \text{ kg y}^{-1}$  is required to maintain an atmospheric concentration of  $6 \text{ pg m}^{-3}$  for the whole US if the mixing height is 50 m. The estimated emission is scaled down to  $1.2 \text{ kg y}^{-1}$  for the Delaware River Basin. Likewise, an input of  $12 \text{ kg y}^{-1}$  is needed in the watershed for a mixing height at 500 m. To achieve an atmospheric concentration of  $20 \text{ pg m}^{-3}$ , an emission of  $3.9 \text{ kg y}^{-1}$  is required at 50 m mixing height and  $39 \text{ kg y}^{-1}$  for 500 m mixing height in the Delaware River Basin. These estimates are generally on the same order of magnitude with the emissions calculated earlier.

#### ***3.4.2.3 Sedimentation via Particulate Matter***

Sedimentation functions as a loss mechanism for PCB 11 in the Delaware River through burial into deeper layers of the sediment bed. Distinctive differences were noted in sediment types of the Delaware River ranging from sands and gravels to silt and clay. Generally the composition is dominated by coarse-grained particulate matter in the upstream and becomes progressively finer grained in the downstream. The sediment-water exchange preferentially occurs in sediments with high content of silt and clay.<sup>70</sup> In the Delaware River TMDL model, two types of organic carbon were considered: biotic carbon (BIC) and particulate detrital carbon (PDC). Sedimentation of PCB 11 is expected to be primarily associated with PDC because its settling rate is much faster than that of BIC. The mass flow of PCB 11 via settling of PDC into sediments ( $L_s, \text{mg d}^{-1}$ ) is

estimated by Eq. 3-5.

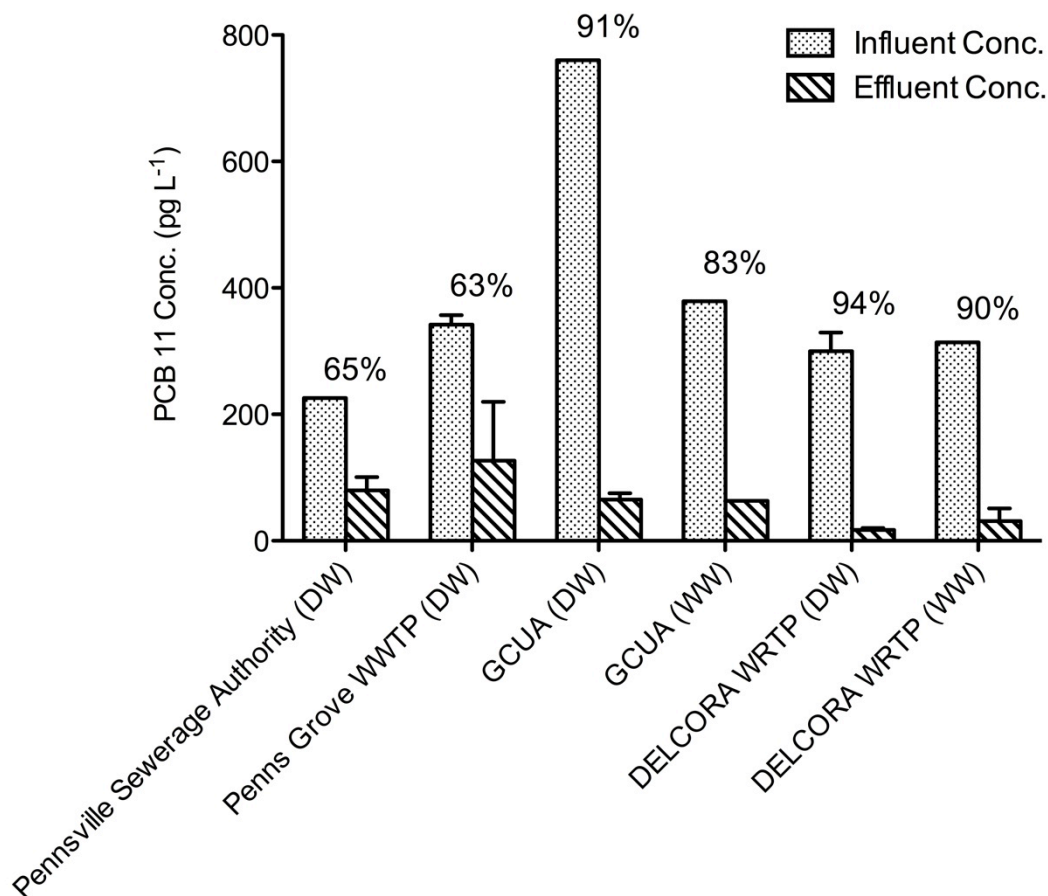
$$L_s = C_s \cdot A_s \cdot v_{PDC} \cdot C_{PDC,w} / 1000 \quad (\text{Eq. 3-5})$$

where  $C_s$  is PCB 11 concentration in the sediments with an average of  $100 \text{ pg g}^{-1}$ ;  $A_s$  is the water surface area around  $2,000 \text{ km}^2$ ;  $v_{PDC}$  is the gross settling velocity of PDC that was assigned at  $1 \text{ m d}^{-1}$  in the water quality model developed by DRBC;<sup>71</sup> and  $C_{PDC,w}$  is PDC concentration in the water column ranging from 0 to  $3.5 \text{ mg L}^{-1}$ .<sup>71</sup> Therefore, the loss of PCB 11 via sedimentation was estimated to be from zero up to  $700 \text{ mg d}^{-1}$  or about  $0.25 \text{ kg y}^{-1}$ . Again, this is well in excess of the low-end estimate of PCB 11 flows in to the watershed.

#### ***3.4.2.4 Removal via Sewage Sludge***

The mass flow of PCB 11 sequestered in sewage sludge can be calculated from the removal efficiency of WWTPs. Among the 20 NPDES-permitted dischargers for which both influents and effluents were sampled, four were WWTPs: Pennsville Sewerage Authority, Penn's Grove WWTP, Gloucester County Utilities Authority (GCUA), and Delaware County Regional Water Quality Control Authority (DELCORA). Removal rate was calculated by comparing influent and effluent concentrations of PCB 11 under either dry or wet weather conditions (Figure 3-4). These four plants removed from 63% to 94% of PCB 11 in their wastewater influents. Assuming an average removal efficiency of 80% for all WWTPs, the mass flow of PCB 11 in sewage sludge is estimated as four times the effluent load of PCB 11 from the top 12 dischargers that were all WWTPs, around  $760 \text{ mg d}^{-1}$  or about  $0.28 \text{ kg y}^{-1}$ . Because the effluent load was calculated from geometric mean concentration and average daily flow rate, both measured by the dischargers, the

uncertainty associated with this load estimate is relatively small and has been discussed earlier.<sup>7</sup> Once again, this flow is well above the low-end estimate of PCB 11 import into the watershed.



**Figure 3-4. PCB 11 concentrations ( $\text{pg L}^{-1}$ ) measured in influent and effluent samples from four WWTPs in the Delaware River Basin under dry (DW) or wet (WW) weather conditions. Error bar represents one standard deviation from multiple samples collected on different dates. Removal rate (%) is displayed above each sample group.**

#### ***3.4.2.5. Processes Assumed to Be Negligible***

Reductive dechlorination of higher molecular weight PCBs (PCBs 77, 118, 126, 156 and 169) could lead to elevated concentration of PCB 11 under anaerobic conditions in

sediments.<sup>72-75</sup> However, none of these potential precursors to PCB 11 are primary constituents in any Aroclor mixtures or in the environment. In addition, our previous study examined the concentration ratios of PCB 11 to PCB 4, a characteristic dechlorination end product, in the Delaware River and concluded that the source of PCB 11 is different from that of PCB 4.<sup>7</sup> Furthermore, we examined the congener patterns of PCBs that are formed from dechlorination in this watershed and found that PCB 11 was not a significant product.<sup>76</sup> Therefore, it is unlikely that reductive dechlorination of heavier PCBs is responsible for the prevalence of PCB 11 found in the environment.

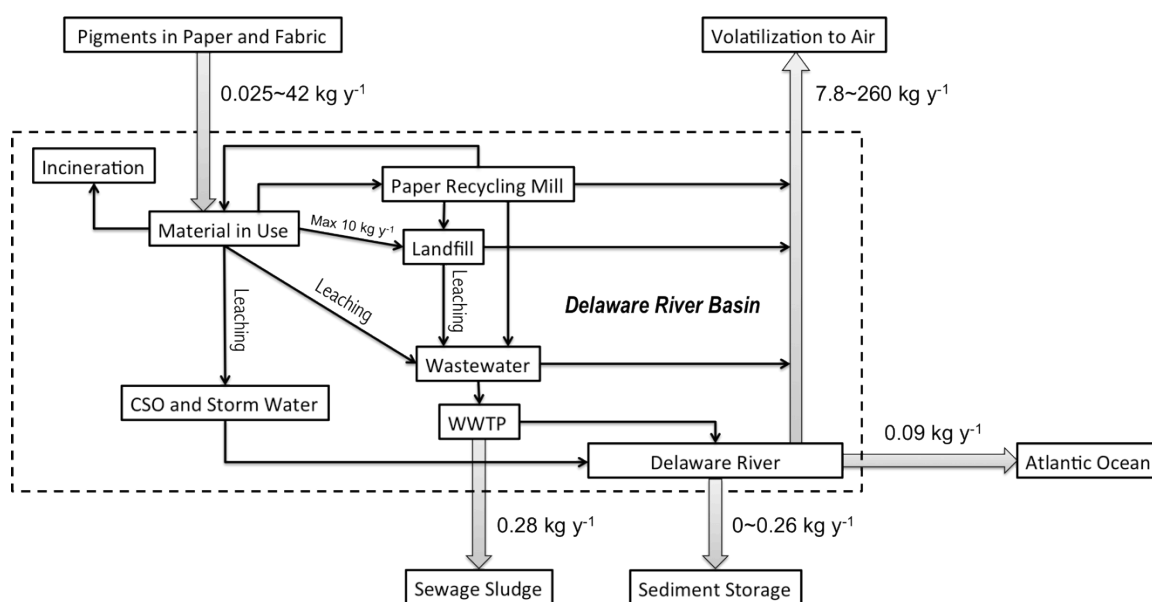
PCB 11 may be susceptible to aerobic degradation. Although some recent studies have isolated certain bacterial strains capable of growing on dichlorobiphenyls including PCB 11,<sup>77</sup> most microorganisms characterized in aerobic degradation of PCBs are mostly associated with monochlorobiphenyls and their growth frequently requires support from additional carbon sources such as biphenyl. There is no convincing data that demonstrate substantial degradation of PCB 11 in the environment. If such degradation did occur, it would only widen the discrepancy between the calculated inflow and outflow+storage of PCB 11 in the Delaware River Basin.

### **3.4.3 Conclusions on Mass Flow Estimates**

Estimated mass flows of PCB 11 from production to distribution in the environment are summarized in Figure 3-5. Our study provides evidence that sources of PCB 11 are primarily associated with diarylide yellow pigments that are mostly applied in printing inks. The mass flow analysis of PCB 11 in the Delaware River Basin suggests that total inflows may range from 0.025 to 42 kg y<sup>-1</sup>. Total outflows range from about 8.4 to 260 kg



$\text{y}^{-1}$  and are biased low due to our inability to estimate sequestration in landfills and soil. Landfilling could sequester as much as  $10 \text{ kg y}^{-1}$  of PCB 11. The most important loss process for PCB 11 from the watershed is volatilization. Even though this process is the most uncertain of the processes examined, the range of estimated losses ( $8.4$  to  $260 \text{ kg y}^{-1}$ ) far exceeds the low-end input and may even exceed the highest reasonable estimate of inflows.



**Figure 3-5. Mass flows of PCB 11 in the Delaware River Basin. External input from pigment use is shown with both low-end and high-end estimates. Estimated losses through advection, volatilization, sedimentation, and sludge removal are also given.**

There are several implications to this mass flow analysis. First, it suggests that a substantial fraction of the PCB 11 contained within the products imported into the Delaware River Basin is released to the environment and can be measured in air, water, and sediment. This is in stark contrast to the assertions of the ETAD, which has stated,

“...PCBs are present both on the surface and in the solid pigment matrix. This incorporated PCB is unlikely to lead either to human or environmental exposure. Additionally pigments are used to colour paints, inks and plastics and are themselves incorporated into a further matrix making release improbable – until both polymeric matrix and the pigments degrade.”<sup>38</sup>

Secondly, this estimate suggests that there could be additional sources of PCB 11 in the watershed. As noted above, we have assumed that the system is at or near steady state with respect to PCB 11 concentrations. This is not the case for Aroclor PCB congeners. For them, the sediments act as an internal load to the system, because they accumulated a PCB burden when concentrations were higher before the PCB ban of the 1970s and are releasing some of this reservoir now that concentrations have declined. The DRBC estimates that the sediments of the Delaware River contribute about 40% of the PCB burden in the water column.<sup>47</sup> We find it unlikely that this is the case for PCB 11, however, for several reasons. First, the production and use of diarylide yellow pigments has been increasing steadily over time,<sup>78</sup> as opposed to the drastic reduction in Aroclor emissions following implementation of the TSCA. Second, Hu *et al.*<sup>79</sup> measured the sedimentary PCB 11 profile in the Great Lakes and found that it matches the history of pigment production in the US. Assuming this is true in the Delaware, there is no gradient that would drive PCB 11 out of the sediments and into the water column. Third, we attempted to measure PCBs in a sediment core collected in Woodbury Creek near Philadelphia.<sup>80</sup> Most PCB congeners that are associated with Aroclors were detectable and displayed maximum concentrations at about 1975, with a decrease of a factor of 5

since then. In contrast, PCB 11 was not detectable in any of the core slices ( $\text{LOD} = 0.10 \text{ ng g}^{-1}$ ). This suggests that historical PCB 11 concentrations in the sediments of the Delaware River are relatively low and have stayed low for at least 50 years. Our measurements are in agreement with those of the DRBC, who measured an average concentration of PCB 11 in surface sediments of the Delaware of  $0.11 \text{ ng g}^{-1}$ , and a median concentration of  $0.03 \text{ ng g}^{-1}$ .<sup>81</sup> Fourth, PCB 11 is much less hydrophobic and has a higher vapor pressure than most of the Aroclor congeners, such that it is primarily removed from the system via volatilization, and the sediment cannot retain a large enough reservoir to account for all of this volatilization. The top 10 cm of sediment in the Delaware River (about  $2000 \text{ km}^2$ ) contains a median PCB 11 concentration of about  $30 \text{ pg g}^{-1}$ , which means this reservoir holds only about 3 kg of PCB 11 (assuming a solids concentration of  $500 \text{ g L}^{-1}$  in surface sediment). For these reasons, our assumption that PCB 11 is at or close to steady state in the Delaware River Basin is justified, and the sediments are not an important source of PCB 11.

Could the “extra” PCB 11 come from processes that are not related to pigment use? Dichlorobenzidine-based dyes (as opposed to pigments) could theoretically be a source of PCB 11, however, 3,3'-dichlorobenzidine is no longer used to manufacture soluble dyes since 1986 in the US.<sup>82</sup> This compound is now mostly manufactured outside the US and imported for on-site processing or for use in pigment production.<sup>82</sup> Our investigation of PCB 11 levels in clothing suggests that they may come from pigments, rather than dyes. At present, we have no evidence to indicate that dyes are an important source of PCB 11. We know of no processes other than pigment use that could be responsible for

the dispersion of PCB 11 in the environment. All of the source apportionment studies conducted for the New York/New Jersey Harbor and the Delaware River<sup>47, 83</sup> suggest that PCB 11 is not associated with Aroclors or microbial dechlorination, but is instead correlated with stormwater and wastewater. Furthermore, PCB 11 concentrations in the air (Chapter 2) and sediment<sup>84</sup> of the Delaware River are evenly distributed throughout the watershed, suggesting the sources are diffuse, as opposed to being associated with a small number of manufacturing facilities. Thus whatever the source of PCB 11, it is related to some kind of human activity that is dispersed across the Delaware River Basin.

Could pigments break down during use, recycling and disposal of consumer products, generating PCB 11? Even though azo colorants are designed to possess a high degree of stability in the environment, they are susceptible to abiotic transformation<sup>85-87</sup> and biodegradation under both aerobic and anaerobic conditions.<sup>88-90</sup> The rate of atmospheric photooxidation for diarylide yellow is considered moderate, however, it is not expected to exist in the vapor phase in the atmosphere.<sup>91</sup> The majority of diarylide yellow pigments are targeted for use in printing inks due to their high tinctorial strength and good fastness properties.<sup>23</sup> The manufacturing process of printing inks generally involves two steps. First a varnish is made by heating resins, solvents and additives to form a homogeneous mixture as the base of any ink. Then the pigment is dispersed thoroughly into the varnish by grinding and mixing.<sup>92</sup> The temperature during the mixing process of printing ink varnishes could reach as high as 315 °C,<sup>93</sup> and ETAD has warned about the probability of pigment decomposition under higher temperatures in the printing process.<sup>94</sup> According to a 2003 report by Norwegian Food Control Authority, it was informed by the printing ink

manufacturer that diarylide yellow pigments might decompose at temperatures well below 200 °C.<sup>94</sup> Therefore, it is possible that diarylide yellows could undergo thermal cleavage to form pigment monomer 3,3'-dichlorobenzidine that finally results in the release of PCB 11 during manufacture, application, or even during normal use in consumer products.

This investigation has demonstrated that the PCB 11 contained in consumer goods can leach into the environment, where humans and animals can be exposed. We have demonstrated that this release is not only possible, but appears to be extensive, such that most of the PCB 11 incorporated into consumer goods does escape the polymer matrix. Finally, our inventory of mass flows of PCB 11 in the Delaware River Basin raises the possibility that PCB 11 may be generated from the decomposition of diarylide yellow pigments during manufacturing and printing processes and/or during use, recycle and disposal of consumer goods. This scenario would mean that diarylide yellow pigments cannot be used safely, and should be banned. Further study is needed to determine the actual levels of PCB 11 in pigments, and to determine whether the decomposition of these pigments in the environment generates PCB 11 or other toxic products such as 3,3'-dichlorobenzidine.

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## **Chapter 4 : Microbial Reductive Dechlorination of Polychlorinated Biphenyls in Sewer Sediment Microcosms**

### **Abstract**

Reductive dechlorination of polychlorinated biphenyls (PCBs) was investigated in anaerobic microcosms of sewer sediments obtained from three locations in an industrial city in the Delaware River Basin. The sediment slurries were prepared in anaerobic minimal salts medium, amended with 10 ppm Aroclor 1260 and incubated in triplicate at 20°C for 370 days. Dechlorination activity varied among sediments from different locations, indicating spatial heterogeneity of *in-situ* dechlorination. In a single most active microcosm, significant evidence of dechlorination was observed after 35 days of incubation as determined by homolog distribution, congener pattern, and molar dechlorination product ratio (MDPR) consisting of five *ortho*-substituted congeners including PCBs 1, 4, 8, 10, and 19. A good mass balance was observed in homolog change, where tri- and tetra- homologs each increased by 5~6% in mole fraction, and hexa- and hepta- homologs each decreased by 6%. Both intermediate and end dechlorination products such as PCBs 47 and 8 were found in good agreement with the dechlorination signals in wastewater influents from a previous study. Total chlorines per biphenyl decreased by up to 10% with short or no lag time. This suggests that rapid dechlorination is at least possible in sewers and the rate is fast enough to account for the dechlorination products comprising 10~30% of the total PCBs found in many of the sewer systems in the Delaware River Basin.

## 4.1 Introduction

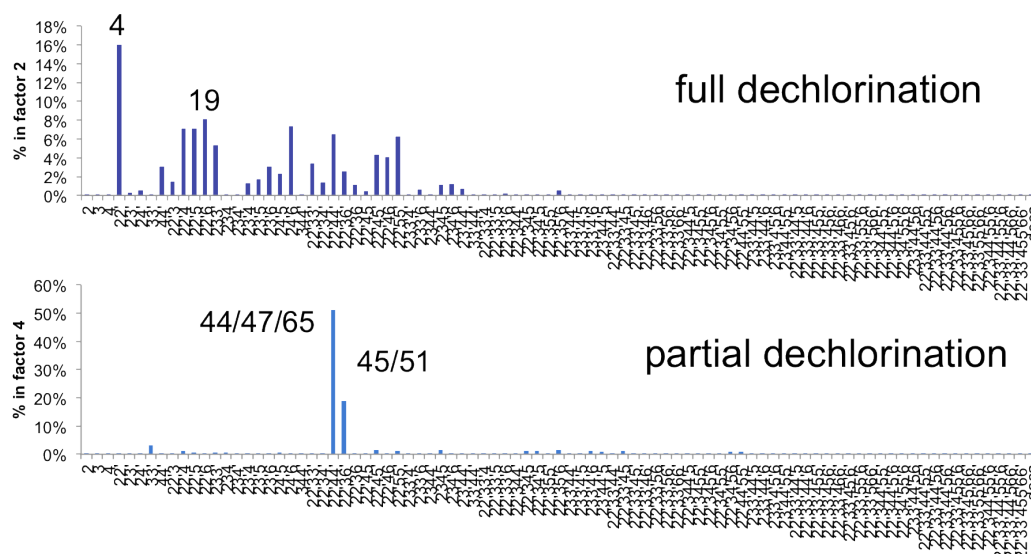
Polychlorinated biphenyls (PCBs) are listed among the 12 initial persistent organic pollutants (POPs) targeted for elimination and restriction under the Stockholm Convention.<sup>1</sup> Despite their resistance to chemical and biological breakdown, PCBs can undergo aerobic and anaerobic biodegradation in the environment.<sup>2-4</sup> Reductive dechlorination of PCBs has been extensively studied under anaerobic conditions in aquatic sediments and laboratory microcosms.<sup>5-9</sup> PCB-reducing bacteria were previously identified as belonging to *Dehalococcoides* spp., *Dehalobacter* spp. or *Dehalobium* spp. within a deep branch of the phylum *Chloroflexi*.<sup>2, 10</sup> Chlorines are removed from the biphenyl rings and replaced with hydrogen, transforming the highly chlorinated PCBs to less chlorinated congeners.<sup>2</sup> In general, chlorine removal from PCBs favors the order of *meta*, *para*, and *ortho* positioned chlorines.<sup>11</sup> This process reduces the potential exposure and risk of PCBs because the dechlorination products are less toxic and more susceptible to volatilization and aerobic biodegradation.<sup>2, 12</sup> Reductive dechlorination of PCBs usually occurs at a slow rate in the environment although it can be enhanced in laboratory with culture enrichment<sup>13</sup> or amendment of electron donor<sup>14</sup>, haloprimer<sup>15</sup> or surfactant<sup>16</sup>.

Organic pollutants may enter wastewater collection systems in urban areas from a wide range of sources including domestic sewage, street runoff and industrial effluents.<sup>17, 18</sup> In combined sewers, sanitary sewage and stormwater runoff are carried in a single pipe before entering wastewater treatment plants (WWTPs). PCBs are frequently detected with many other hydrophobic organic pollutants in WWTP influents from combined sewers.<sup>19, 20</sup> Partitioning of these pollutants between the dissolved and sorbed phases

plays an important role on their fate and transport in sewers and successive wastewater treatment processes. Highly chlorinated PCBs with larger  $K_{oc}$  values have stronger affinity to solids and sludge and the less chlorinated congeners are more likely to travel with wastewater. Although up to 90% of PCBs in the waste streams can be removed in WWTPs,<sup>21-23</sup> discharges of treated sewage effluents and combined sewer overflows (CSO) might still have significant impacts on the quality of receiving waters.<sup>24</sup> For example, an estimated total of 88 kg PCBs was released annually into the New York/New Jersey Harbor Estuary from WWTP effluent discharges and plant bypass through CSOs during high flows.<sup>25</sup>

A recent study has first demonstrated PCB dechlorination in a variety of built waste treatment environments including sewers and landfills.<sup>23</sup> Analysis was performed on a large database of PCB concentrations in effluents and some influents of dischargers on the Delaware River. Positive matrix factorization (PMF) was used to identify the sources of PCBs and to look for evidence of dechlorination in these data. Two of the seven resolved factors represented dechlorination signals (Figure 4-1). One of them was dominated by PCB 4 (2-2; numbers before the dash refer to the chlorine positions on one ring, and numbers after the dash refer to the chlorine positions on the other ring) and 19 (26-2) and indicated an advanced stage of dechlorination of highly chlorinated PCBs to di- and tri-chlorinated congeners. The other dechlorination signal appeared to represent an intermediate stage of dechlorination, dominated by two co-eluting groups of tetra-chlorinated congeners: PCB 44/47/65 (23-25, 24-24, 2356-) and PCB 45/51 (236-2, 24-26). A subsequent study using the same analytical method revealed additional evidence

on dechlorination of PCBs as well as polychlorinated dibenzo-pdioxins and dibenzofurans (PCDD/Fs) in sewers of the New York/New Jersey Harbor.<sup>22</sup>



**Figure 4-1. Dechlorination signals from PMF analysis of PCBs in wastewater.**<sup>23</sup>

It was hypothesized that PCB dechlorination in sewage collection systems probably occurred in sewer sediments.<sup>22, 23</sup> An investigation of contaminant distribution in different sewer deposits showed that 87% to 98% of hydrocarbons were stored in the gross bed sediment with the remaining settled in the organic layer or biofilm.<sup>26</sup> The largest load of solids in combined sewers is associated with sanitary wastewater input which contributes typically 97% of organic solids during low flow.<sup>27</sup> Sanitary wastewater solids settled in sewers can generate hydrogen sulfide and methane gas under anaerobic conditions during dry weather periods.<sup>27</sup> Therefore, sewers can serve as chemical and biological reactors to support sulfidogenic and methanogenic activities, and could therefore also support PCB-dechlorinating bacteria under these conditions. It is also

speculated that combined sewers are more likely to develop methanogenic zones than separate sewers, resulting in the highest contribution from the advanced dechlorination signal being observed in dischargers with combined sewer systems.<sup>23</sup>

The objective of this study is to investigate experimental evidence of PCB dechlorination in sewer sediment microcosms supplied with a commercial PCB mixture of Aroclor 1260 and other halogenated compounds under anaerobic conditions. Aroclor 1260 contains high chlorine content with predominantly penta-, hexa-, hepta- and octa- PCB homologs and provides a good means to assess potential for reductive dechlorination. This PCB mixture has been reported to be reductively dechlorinated in different contaminated sediments of rivers, lakes, and harbors.<sup>28-31</sup> However, only inconclusive results of PCB dechlorination were reported in non-aquatic systems such as compost,<sup>32</sup> landfills,<sup>33, 34</sup> and soils.<sup>35, 36</sup>

## **4.2 Materials and Methods**

### **4.2.1 Sediment Collection**

Grab samples were collected from interceptors that provide manhole access points for sampling sewer sediments in two industrialized cities (denoted as City A and B) of the Delaware River Basin. Samples from City A were collected at four locations (Site A1~A4) in 2010. Samples from City B were collected at three locations (Site B1~B3) in 2011. The wastewater collection systems in major cities of the Delaware River Basin largely consist of combined sewers. A legacy of PCB contamination is present in these heavily industrialized areas due to historical discharges and ongoing approved uses.

Sewers in the Delaware River basin are known to receive PCB loads from both point sources such as known contaminated sites and non-point sources from diffuse contamination via runoffs.<sup>37</sup> Sediments samples were transported to the laboratory immediately. A small portion from each site was archived at -20 °C for initial chemical characterization while the remainder was kept in sealed containers at room temperature for subsequent microcosm setup.

Sewer sediment is inherently heterogeneous. Some sediment has a very large grain size and gravelly texture, suggesting that it may consist primarily of abraded asphalt or concrete. Sediment of this type is difficult to handle (large particles clogged syringes, for example), and has low PCB concentrations, presumably due to low organic carbon content. Therefore, upon receipt, sewer sediments were visually examined, and only those exhibiting a relatively fine grain size were selected for use in microcosms.

Sediments from City A were primarily comprised of sands and gravels that might not support PCB dechlorination activity. The fine grained deposits from Site B1 and B2 appeared rich in oil and grease and could act as an excellent organic bed for PCBs. Sewer sediments from Site B3 exhibited a clayish texture due to dry weather. Testing for sediment composition, nutrient content and other characteristics was not performed in this study, but will be implemented in future work.

#### **4.2.2 Medium Preparation**

Anaerobic minimal salts medium was prepared by dissolving the following chemicals in 1 L of deionized water: 1.17 g of NaCl, 0.18 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.2 g of  $\text{KH}_2\text{PO}_4$ , 0.5 g of



$\text{NH}_4\text{Cl}$ , 1.3 g of  $\text{KCl}$ , 0.1 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . Resazurin was added to the medium as a redox indicator. The medium flask was capped and purged with  $\text{N}_2$  for 40 min followed by a gas mixture of  $\text{N}_2/\text{CO}_2$  (70/30, v/v). Adjustment to pH 7~7.5 was achieved by adding  $\text{NaHCO}_3$  to a final concentration of  $2.5 \text{ g L}^{-1}$ . Headspace of the capped medium was vacuumed using a syringe before the medium was autoclaved and then cooled to room temperature. Stock solutions of vitamins (5 mL) and trace salts I (1 mL) and II (0.1 mL) were added to medium. Vitamin solution contained ( $\text{g L}^{-1}$ ): 0.02,  $\text{D}$ -biotin; 0.02, folic acid; 0.1, pyridoxine hydrochloride; 0.05, thiamine hydrochloride; 0.05, riboflavin; 0.05, nicotinic acid; 0.05,  $\text{DL}$ -calcium pantothenate; 0.01, vitamin  $\text{B}_{12}$ ; 0.05, *p*-aminobenzoic acid; 0.05, lipoic acid; 0.04, 4-naphthoquinone; 0.1, nicotinamide; and 0.01, hemin. Trace Salts I stock solution contained ( $\text{g L}^{-1}$ ): 5,  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.5,  $\text{H}_3\text{BO}_4$ ; 0.5,  $\text{ZnCl}_2$ ; 0.5,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.46,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.3,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; 0.1,  $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ ; and 1.49,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . Trace Salts II stock solution contained ( $\text{g L}^{-1}$ ): 0.03,  $\text{NaSeO}_3$ ; and 0.08,  $\text{Na}_2\text{WO}_4$ . Finally 1 mL of  $500 \text{ g L}^{-1}$   $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  stock solution was injected into the medium as a reductant.

#### 4.2.3 Microcosm Set-up

Highly concentrated stock solutions of organohalogenated compounds were separately prepared in toluene at approximately  $5000 \text{ mg L}^{-1}$  each for Aroclor 1260 (neat chemical from AccuStandard, Inc., New Haven, CT), decabromodiphenyl ether (BDE 209, neat chemical from Sigma Aldrich, St. Louis, MO), and hexabromocyclododecane (HBCD, neat chemical from Sigma Aldrich, St. Louis, MO), and  $2000 \text{ mg L}^{-1}$  for dechlorane plus (DP, neat chemical from AccuStandard, Inc., New Haven, CT). Sediment from each site

was air dried, ground, and added to a 125 mL serum bottle as carrier material for spiking chemicals. Stock solutions in 200 to 400  $\mu\text{L}$  were spiked evenly onto dried sediments to obtain chemical masses from 0.8 to 1 mg. Toluene was allowed to evaporate leaving the chemicals in the carrier sediments. Wet sediments were stirred thoroughly with a stainless steel spatula prior to microcosm set-up.

Anaerobic microcosms were constructed by adding a slurry of 30 mL wet sediment and 60 mL medium to the 125-mL serum bottle containing the spiked carrier sediment inside a glove bag purged with  $\text{N}_2$ . Bottles were capped with grey PTFE coated butyl rubber septa and crimped with aluminum caps. For sediment from each site, triplicate microcosms (R1, R2, R3) were prepared and the nominal concentration of Aroclor 1260 in the sediment slurry was  $\sim 10 \text{ mg L}^{-1}$ . No electron donors were added because the sediments were expected to contain sufficient organic substances from wastewater input. Triplicate controls were prepared in the same way as the treatments and sterilized by sequential autoclaving for 40 min at  $121^\circ\text{C}$  on three consecutive days. All live cultures and sterile controls were incubated at  $20^\circ\text{C}$  in the dark. Serum bottles were vented periodically throughout the test period using a syringe needle inserted through the rubber septum to release gas production from microcosms.

Sediment slurries were sampled on Day 0, 35, 152 and 370 with 0.5 mL for biological analysis and 5 mL for chemical analysis in a  $\text{N}_2$ -purged glove bag. Control sediments were sampled in the same way except for Day 35. Slurries for biological analysis were centrifuged at 15,000 rpm and  $-20^\circ\text{C}$  for 5 min. The supernatant was discarded and the

sediment was stored at -80 °C for future analysis. Sampled sediment slurries from chemical analysis were either frozen or processed immediately.

#### **4.2.4 Chemical Analysis**

Chemical analysis was conducted for PCBs only and the results are presented in this chapter. The other spiked halogenated organic compounds will be analyzed in future work. Initial characterization of PCBs in sewer sediments was performed for each site. The analytical method for determination of PCBs in sewer sediments and microcosm samples is described as follows. Wet sediment was allowed to air dry in a slowly vented fume hood for 24~48 hrs. Dried sediment was spiked with surrogate standard including deuterated PCBs 65 and 159 (C/D/N Isotopes Inc., Quebec, Canada) and extracted with hexane and dichloromethane (75/25, v/v) at 100 °C and 1500 psi using an accelerated solvent extraction system (ASE 200, Dionex, Sunnyvale, CA). The extract was then concentrated under nitrogen flow and cleaned up on a 2.5% water-deactivated florisil column (Fisher Scientific, Pittsburgh, PA). The PCB fraction was eluted with 35 mL of petroleum ether and concentrated to 0.5 mL by rotary evaporation and subsequently nitrogen evaporation. The final extract was injected with an internal standard containing deuterated PCBs 30 and 116 (C/D/N Isotopes Inc., Quebec, Canada).

Analysis of PCBs was performed on a gas chromatograph (6890N, Agilent, Santa Clara, CA) with a tandem quadrupole mass spectrometer (Quattro Micro GC, Waters, Milford, MA) by a modified EPA method 1668A.<sup>38</sup> PCB congeners were separated on a Supelco SPB-Octyl capillary column (30 m× 0.25 mm× 0.25 µm) with helium at a constant flow

rate of  $0.8 \text{ mL min}^{-1}$ . Samples in  $3 \text{ }\mu\text{L}$  were injected in splitless mode at  $270 \text{ }^{\circ}\text{C}$ . The interface temperature was held at  $250 \text{ }^{\circ}\text{C}$ . The initial oven temperature was held at  $75^{\circ}\text{C}$  for 5 min, then increased at a rate of  $15^{\circ}\text{C min}^{-1}$  to  $150^{\circ}\text{C}$ , holding for 1 min, followed by  $2.5^{\circ}\text{C min}^{-1}$  to a final temperature of  $280^{\circ}\text{C}$ , holding for 3 min. The instrument was operated with an electron impact (EI) source at 70 eV under multiple reaction monitoring (MRM) mode using argon as the collision gas. The precursor/product ion transitions for each homolog group of PCBs were given in a method described previously.<sup>39</sup> Deuterated standards including PCBs 30, 65, 116, and 159 were monitored in independent retention windows by ion transition pairs of 261+263/191, 294.9+296.9/224.9, 328.9+330.9/258.9, 363+365/293, respectively.

The Frame solutions (AccuStandard, Inc., New Haven, CT) containing all 209 PCB congeners were analyzed to determine eluting orders and co-elutions in the chromatographic system and to generate different levels of calibration standards. This method allows identification and quantification of all 209 PCB congeners against a four-point calibration curve. Details of retention time and relative response factor (RRF) for each PCB congener/coeluting congener group are given in Table I-2 of the Appendix.

#### **4.2.5 Quality Assurance/Quality Control**

Clean sea sand (Fisher Scientific, Pittsburgh, PA) was baked at  $450 \text{ }^{\circ}\text{C}$  for over 4 hrs and extracted as laboratory blanks for each extraction sequence of up to nine sediment samples. All PCB congeners were quantified using deuterated PCB 30 as the internal standard, which was proved valid from an earlier analysis of triplicate PCB matrix spikes

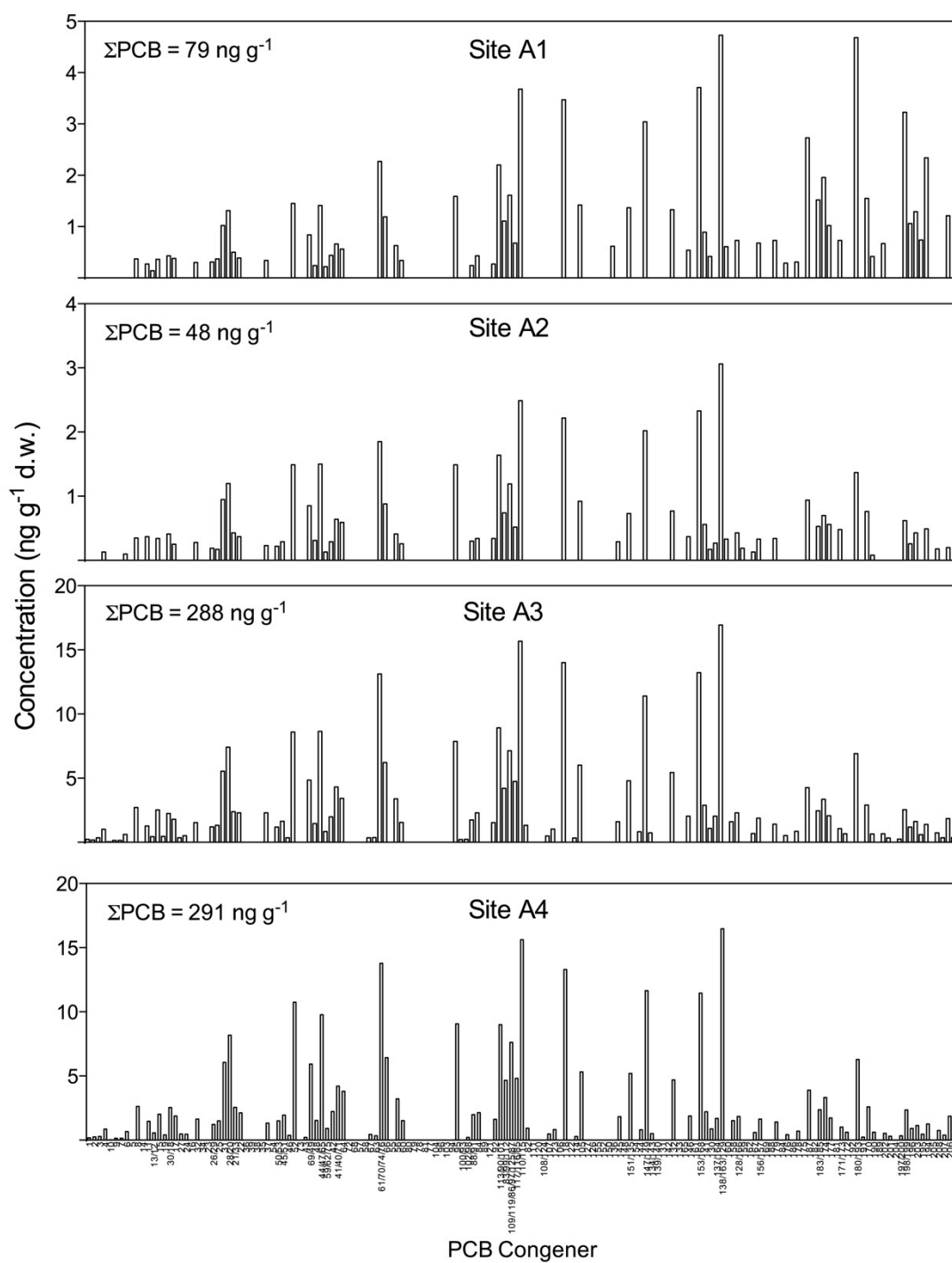
in sea sand. Deuterated PCB 116 was not used for quantification because it skewed the concentrations in the matrix spikes. Surrogate recoveries were reported for deuterated PCBs 65 and 159. PCBs detected in blanks were less than 0.5% of total PCBs detected in sediment samples with an average surrogate recovery of  $57\% \pm 9\%$  for deuterated PCB 65 and  $68\% \pm 20\%$  for deuterated PCB 159. Surrogate recoveries in all sediment samples ranged from 46% to 111% for deuterated PCB 65 and from 29% to 184% for deuterated PCB 159. PCB concentrations were reported on a dry weight basis ( $\mu\text{g g}^{-1}$  d.w. of sediment) without correction for blanks or surrogate recoveries. Mass concentrations were converted to molar concentrations and the mole fraction (%) of each congener/coeluting congener group with respect to the sum of PCBs was calculated.

## **4.3 Results and Discussion**

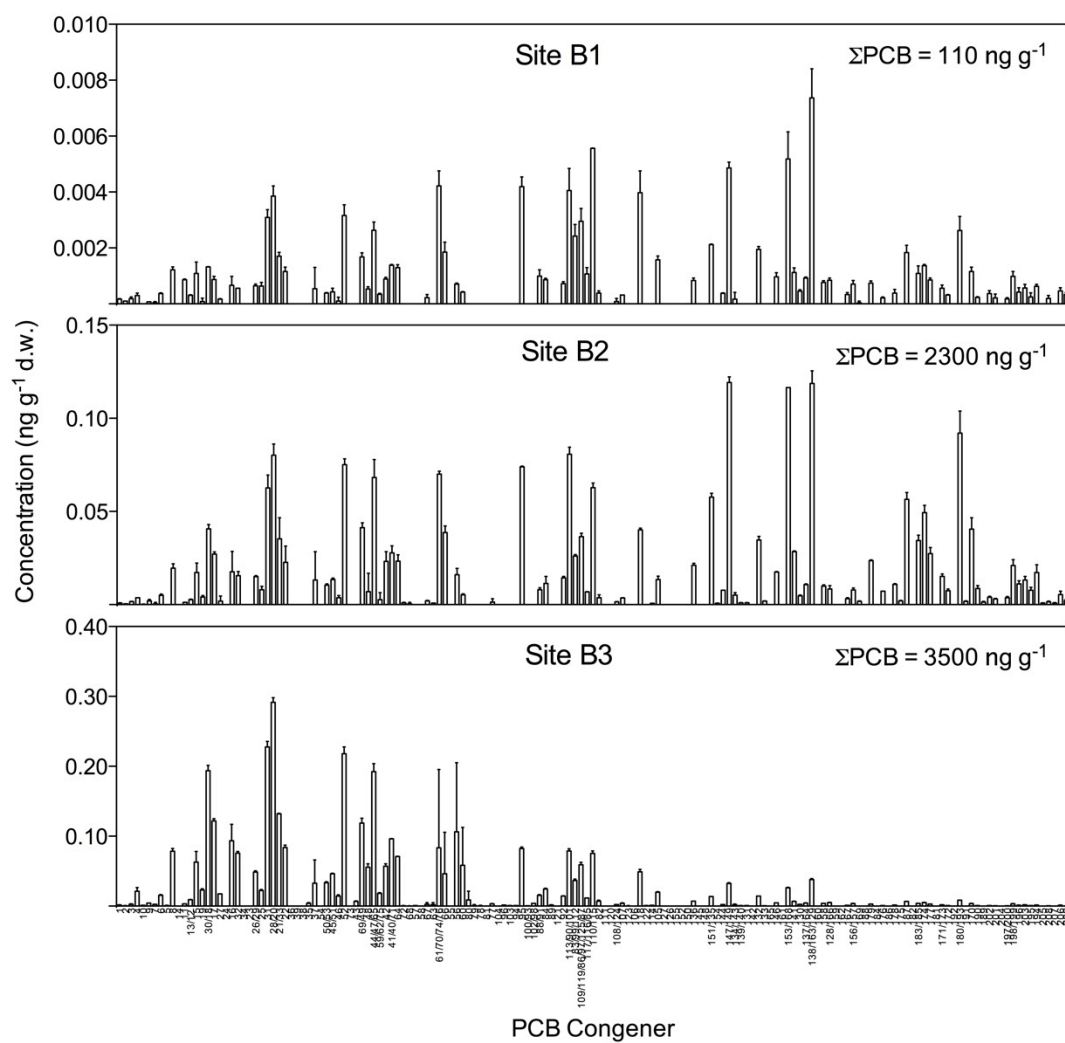
### **4.3.1 Characterization of PCBs in Sewer Sediments**

PCB concentrations were measured in the sewer sediment before construction of microcosms to investigate whether the congener patterns reveal evidence of dechlorination occurring in the sewer, and to determine which sediments were the best candidates for microcosms.  $\Sigma\text{PCB}$  concentration ranged from 48 to 291  $\text{ng g}^{-1}$  d.w. in sediments from City A (Figure 4-2) and from 110 to 3500  $\text{ng g}^{-1}$  d.w. in sediments from City B (Figure 4-3). All sewer sediments displayed a mixture of both low and high molecular weight (MW) PCBs except for the sediment from Site B3 that was dominated by the less chlorinated congeners.

Few other studies of PCB content in sewer sediment have been performed. Sediment PCBs in a storm sewer system in Canada varied from  $<0.005$  to  $0.53$  ppm (or  $\mu\text{g g}^{-1}$ ) in total concentration and moderately matched patterns of Aroclor 1254 in most samples.<sup>40</sup> However, the PCB congener pattern in the most contaminated Canadian sample did not align with the patterns of the other samples. It was enriched with highly chlorinated congeners that were believed to originate from Aroclor 1260, a major product known to be used by a former manufacturer near the sampling site. These findings suggested that PCBs in sewer sediments could show different congener patterns depending on the sources.



**Figure 4-2. PCB congener distributions in sewer sediments collected from four locations (A1~A4) in City A.**



**Figure 4-3. PCB congener distributions in sewer sediments collected from three locations (B1~B3) in City B. Error bar represents standard deviation from duplicate samples.**



A PCB congener pattern ( $S_i$ ) was generated using Eq. 4-1, described as a linear combination of the four most common Aroclors 1242, 1248, 1254 and 1260, and compared to the congener pattern of the sediment sample. The sum of the squared residuals between the generated congener pattern and the sample congener pattern was calculated. This sum of square residuals was then minimized by adjusting the coefficients  $a$ ,  $b$ ,  $c$ , and  $d$  using the Solver feature of Microsoft Excel, subject to the constraint that the coefficients  $a$ ,  $b$ ,  $c$ , and  $d$  could not be negative. The  $r^2$  value between this best-fit congener pattern and the sample congener pattern was then calculated.

$$S_i = a \cdot [A1242] + b \cdot [A1248] + c \cdot [A1254] + d \cdot [A1260] \quad (\text{Eq. 4-1})$$

The coefficients determined by the best-fit solution, representing fractional contributions from each Aroclor to each sediment sample, are shown in Table 4-1. PCB congener patterns in all sewer sediments were highly correlated ( $r^2 > 0.80$ ) to linear combinations of the four Aroclors when the non-Aroclor congeners containing PCBs 11, 206, 208 and 209 were excluded. Most of the sediments contained both highly chlorinated congeners from Aroclors 1254 or 1260 and less chlorinated congeners from Aroclors 1242 or 1248 except the one from Site B3. Site B3 sediment was predominantly enriched in the less chlorinated congeners with 72% contribution from Aroclor 1242. The unique congener pattern observed at Site B3 may be explained by the fact that this location received a known loading of PCBs from a nearby metal reclamation facility. Wastewater collected near scrap yards and metal reclamation shops, known to discharge to the sewer system in this city, also showed an intermediate PCB profile between Aroclor 1242 and 1248.<sup>41</sup> The strong resemblance to Aroclor mixtures may indicate that there was not much weathering

of PCBs including *in-situ* dechlorination in the sewers. This could be due to the fact that solids and debris are routinely cleaned out of wastewater interceptors and the newest sediments are likely to build up at these locations in the sewer system.

**Table 4-1. Fractional contributions of each of the four common Aroclors to PCB congener patterns measured in sewer sediments from City A and City B.  $r^2$  is the coefficient of determination of the linear regression between the sediment congener pattern and respective Aroclor mixture.**

Site	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	$r^2$
A1	0.05	0.17	0.21	0.50	0.82
A2	0.12	0.19	0.36	0.34	0.92
A3	0.12	0.21	0.36	0.28	0.91
A4	0.11	0.26	0.36	0.25	0.93
B1	0.24	0.06	0.37	0.29	0.92
B2	0.23	0.17	0.15	0.47	0.97
B3	0.72	0.11	0.12	0.03	0.84

#### 4.3.2 Reductive Dechlorination of Aroclor 1260

##### 4.3.2.1 Homolog Distribution

After spiking Aroclor 1260, total PCB concentrations in all sediments increased to 21~83  $\mu\text{g g}^{-1}$  d.w. and the congener patterns matched well with that of Aroclor 1260 (Figure 4-4).  $\Sigma\text{PCB}$  concentrations in sediment microcosms from the same site varied on day 0

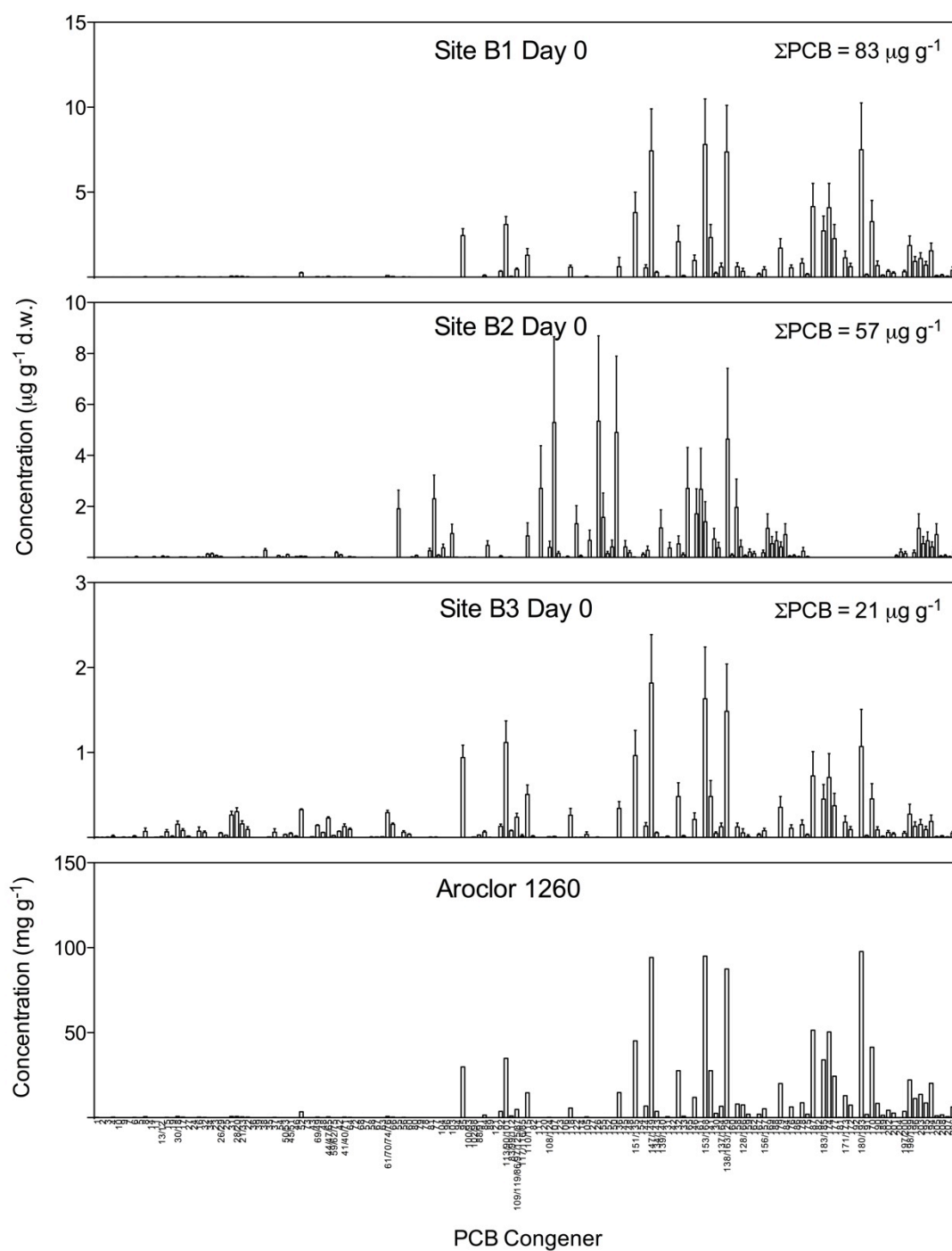
probably due to variability in spiking efficiency. Therefore, data from replicate microcosms of each site were treated individually instead of being grouped as an average.

Distributions of PCB homologs and individual congeners were examined in sediment microcosms over time to look for evidence of Aroclor 1260 dechlorination. Figure 4-5, 4-6 and 4-7 present the mole fractions (%) of all PCB homologs from mono- through deca- after 0, 35, 152, and 370 days of incubation in microcosm triplicate from each site.

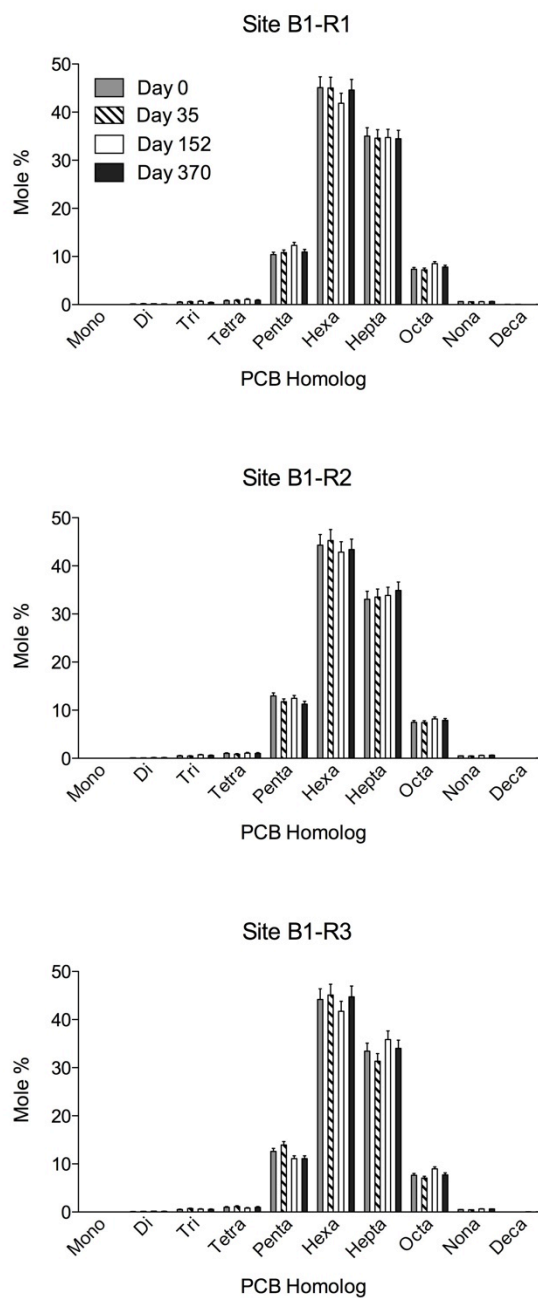
Because only one sample was withdrawn from each microcosm for PCB analysis at a given sampling time point, the standard deviation was estimated for each homolog group based on relative standard deviation (RSD) from measured triplicates of controls.

Generally the RSD was around 5% for penta- through deca- homologs and went up to 10~20% for the lighter homologs.

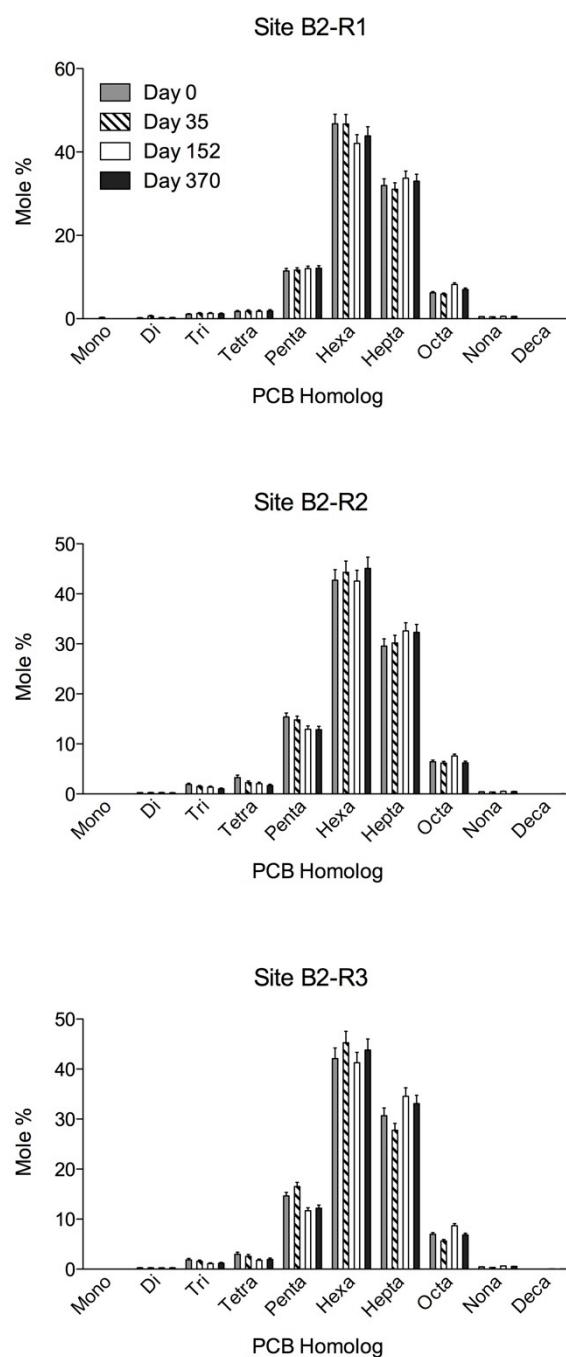
The homolog distribution from microcosm Site B3-R3 displayed obvious signs of dechlorination after 35 days of incubation, however, after day 35, the pattern remained largely the same through day 370. Overall, hexa- and hepta-chlorinated homologs each decreased by 6% in mole fraction, which is equivalent to 14% and 25% total dechlorination of each homolog, respectively. Mole fractions of tri- and tetra-chlorinated homologs increased by 5~6% each, which correspond to 106% and 65% increase from day 0, respectively. These findings also suggest an excellent mass balance between the increases of tri- and tetra- homologs and the decreases of hexa- and hepta- homologs. In the other treatments and sterile controls (Figure 4-8), evidence of dechlorination was either absent or more subtle.



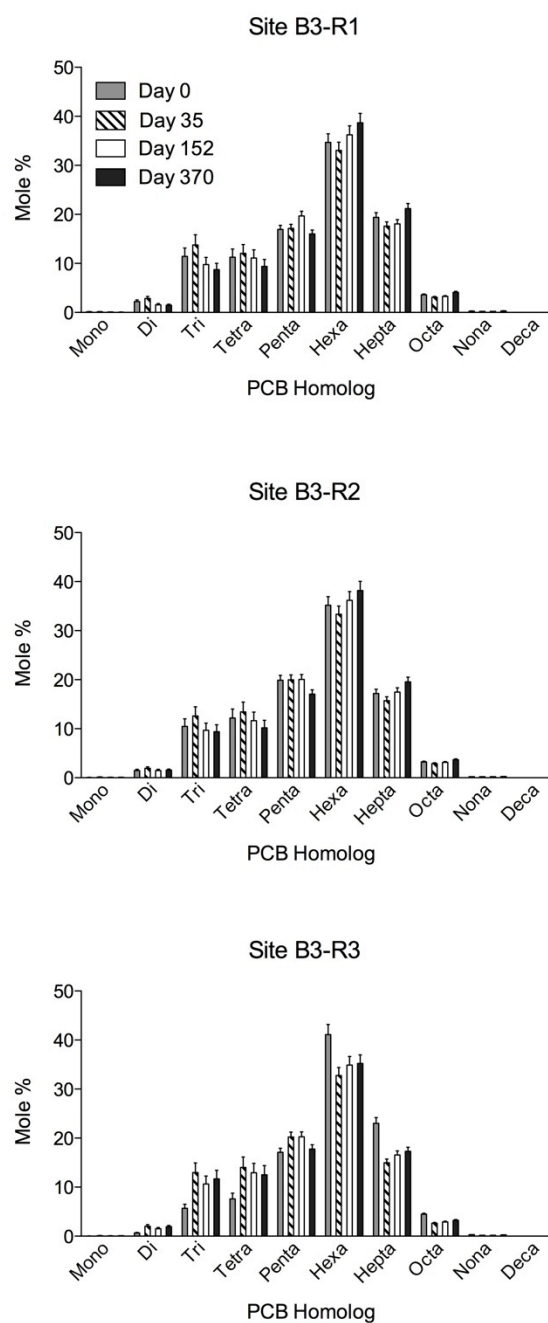
**Figure 4-4. PCB congener concentrations ( $\mu\text{g g}^{-1}$  d.w.) in City B sewer sediments after spiking with Aroclor 1260 for microcosm study. Sediment data from day 0 microcosms; error bar represents standard deviation from triplicate treatments. Aroclor 1260 data from Rushneck *et al.*<sup>42</sup>**



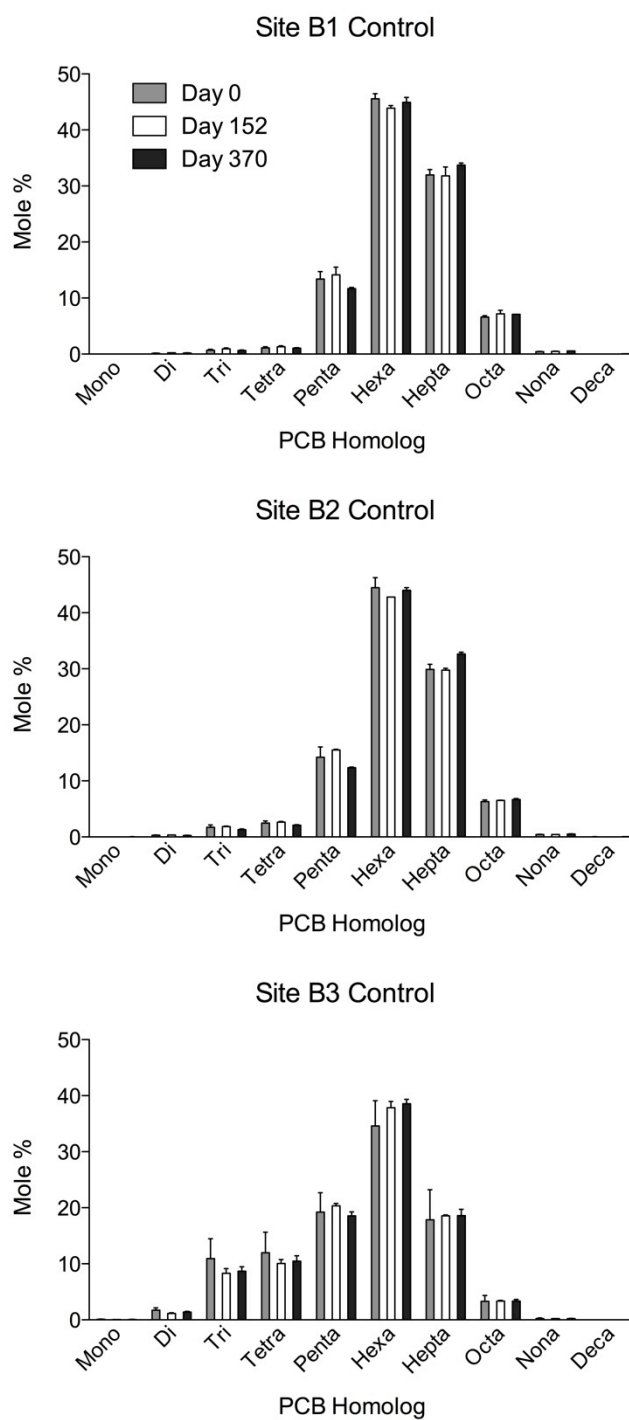
**Figure 4-5. PCB homolog distribution on days 0, 35, 152 and 370 in triplicate microcosms with Site B1 sediments. Error bar represents standard deviation estimated from relative standard deviation (RSD) of control measurements for respective homolog.**



**Figure 4-6. PCB homolog distribution on days 0, 35, 152 and 370 in triplicate microcosms with Site B2 sediments. Error bar represents standard deviation estimated from relative standard deviation (RSD) of control measurements for respective homolog.**



**Figure 4-7. PCB homolog distribution on days 0, 35, 152 and 370 in triplicate microcosms with Site B3 sediments. Error bar represents standard deviation estimated from relative standard deviation (RSD) of control measurements for respective homolog.**



**Figure 4-8. PCB homolog distribution on days 0, 152 and 370 in sterile controls. Error bar represents standard deviation of triplicates from each site.**

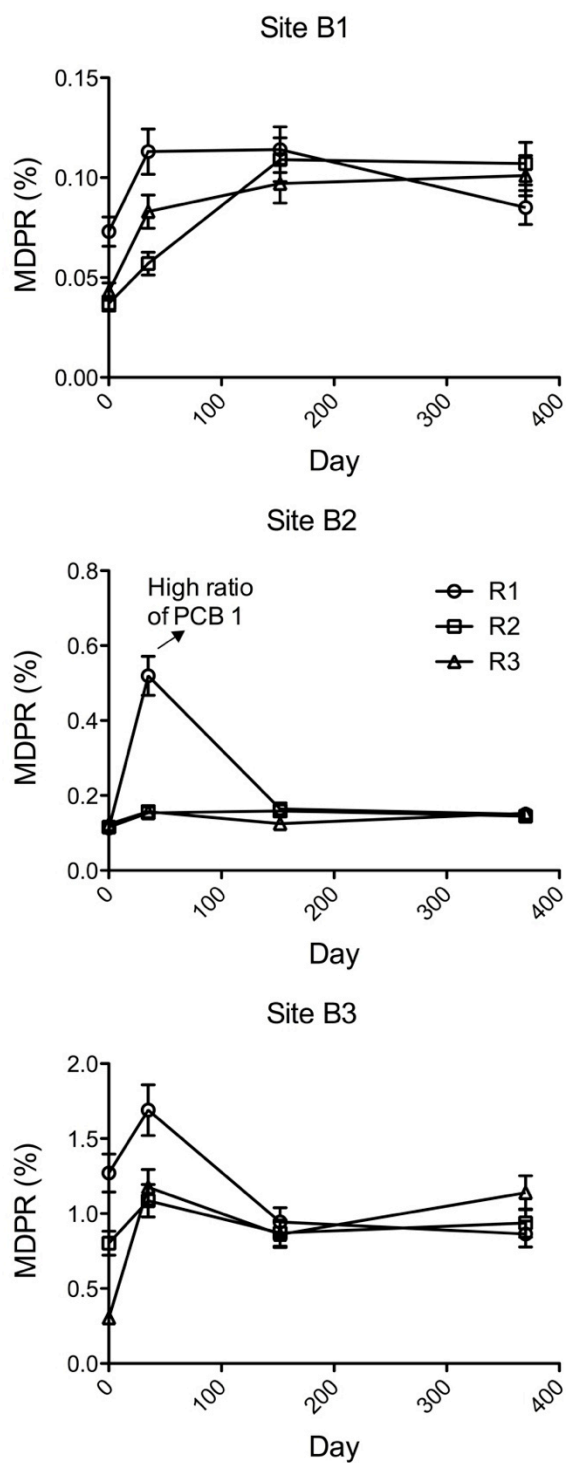


#### 4.3.2.2 Molar Dechlorination Product Ratio (MDPR)

Because reductive dechlorination does not destroy the biphenyl ring of a PCB molecule, and the *ortho* chlorines are usually difficult to remove,<sup>2</sup> the total molar concentration of *ortho*-substituted PCB congeners would be conserved assuming reductive dechlorination is the only possible pathway of PCB transformation. Therefore, the molar dechlorination product ratio (MDPR), described as the combined mole fractions (%) of *ortho*-substituted dechlorination products, has been used in several reports to evaluate the reductive dechlorination extent of PCBs.<sup>43, 44</sup> Five congeners were selected as representative dechlorination products with four of them being exclusively *ortho*-substituted, i.e. PCBs 1 (2-), 4 (2-2), 10 (26-), 19 (26-2), and PCB 8 (2-4) with an *ortho* and a *para* chlorine.<sup>44</sup> PCB 8 was included because it was observed to accumulate in Hudson sediments when MDPR was first developed by the USEPA.

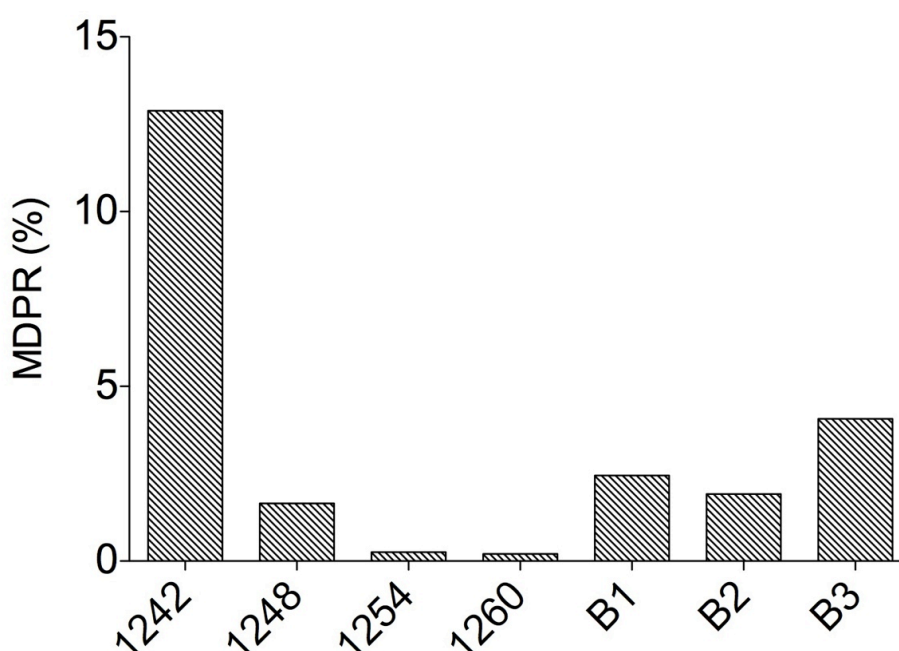
MDPR was calculated in each treatment microcosm at each sampling time point and plotted in Figure 4-9. While sediment microcosms from Site B2 displayed little change in MDPR over time, several microcosms from both Site B1 and B3 showed a gradual increase in MDPR from day 0 through day 370. Significant accumulation of MDPR ( $p < 0.05$ ) was found for Site B1-R3 and Site B3-R3 microcosms after 35 days of incubation, suggesting little or no lag time before the onset of dechlorination. This might support our expectation that PCB dechlorination happens routinely in sewers and PCB-dechlorinating bacterial communities have been well developed in the sediments. In contrast, many other studies waited longer (from one to several months) to see dechlorination in aquatic sediments.<sup>45</sup> Interestingly, the final MDPRs in this study after 370 days of incubation

were very similar among microcosms using the same sewer sediments, even though their MDPRs started out at different levels at time zero.



**Figure 4-9. Molar dechlorination product ratio (MDPR), calculated as the sum of mole fractions of PCBs 1, 4, 8, 10, and 19, in microcosm treatments at each time point of days 0, 35, 152, and 370. Error bars are estimated from RSD of mole % of each congener.**

The initial MDPRs in sewer sediments before spiking Aroclor 1260 were compared to those of Aroclors including 1242, 1248, 1254, and 1260 (Figure 4-10). Aroclor 1242 contained a high MDPR around 0.14 and the other Aroclors showed much lower MDPRs such as 0.002 in Aroclor 1260. Sewer sediments displayed an intermediate level of initial MDPRs around 0.02 to 0.04. A greater MDPR in the sample than that of the respective Aroclor source may indicate the likelihood of *in-situ* reductive dechlorination. Higher MDPR values ( $> 0.30$ ) were found in aquatic sediment cores from other studies,<sup>43, 44</sup> suggesting substantial dechlorination of Aroclors. It should be emphasized that MDPR measures the number of affected PCB molecules rather than mass losses.<sup>43</sup> Since the lighter PCB molecules from reductive dechlorination are more soluble and susceptible to other degradation processes, the extent of dechlorination determined by MDPR probably underestimates the actual potential of dechlorination.<sup>43</sup> Evaluation of reductive dechlorination through homolog or congener-specific changes and variation in MDPR are always subject to uncertainty because additional physical and chemical processes may affect these factors.



**Figure 4-10. Initial MDPRs in Aroclors 1242, 1248, 1254, and 1260, and in sewer sediments from Site B1, B2, and B3 before spiking Aroclor 1260.**

The most active microcosm, Site B3-R3, showed clear evidence of dechlorination by day 35, but the activity ceased subsequently as witnessed by consistent homolog distribution and MDPR from day 35 through day 370. In the previous study, the dechlorination factors including PCBs 4, 19, 47, and 52 contributed 11% to  $\Sigma$ PCBs in the effluent of a WWTP that served combined sewers in City B.<sup>23</sup> The proportion of dechlorination products would be lower in the influent because these lightly chlorinated PCBs are not as efficiently sequestered by the activated sludge in WWTPs. Assuming dechlorination products comprised 10% of  $\Sigma$ PCBs entering WWTP influent from the sewer system, the results from this study would suggest that this scenario could happen in about a month if the PCBs are in the right and active location. Because the most settleable sediments were largely retained in sewer beds and only removed by regular maintenance of sewer pipes,<sup>46</sup>

the microbial communities were likely to develop and maintain PCB-dechlorinating activity on a continuing basis in portions of the sewer system without physical disturbance. Since our sewer sediments were recovered from interceptors, we may have sampled the least “aged” or active portions of the system.

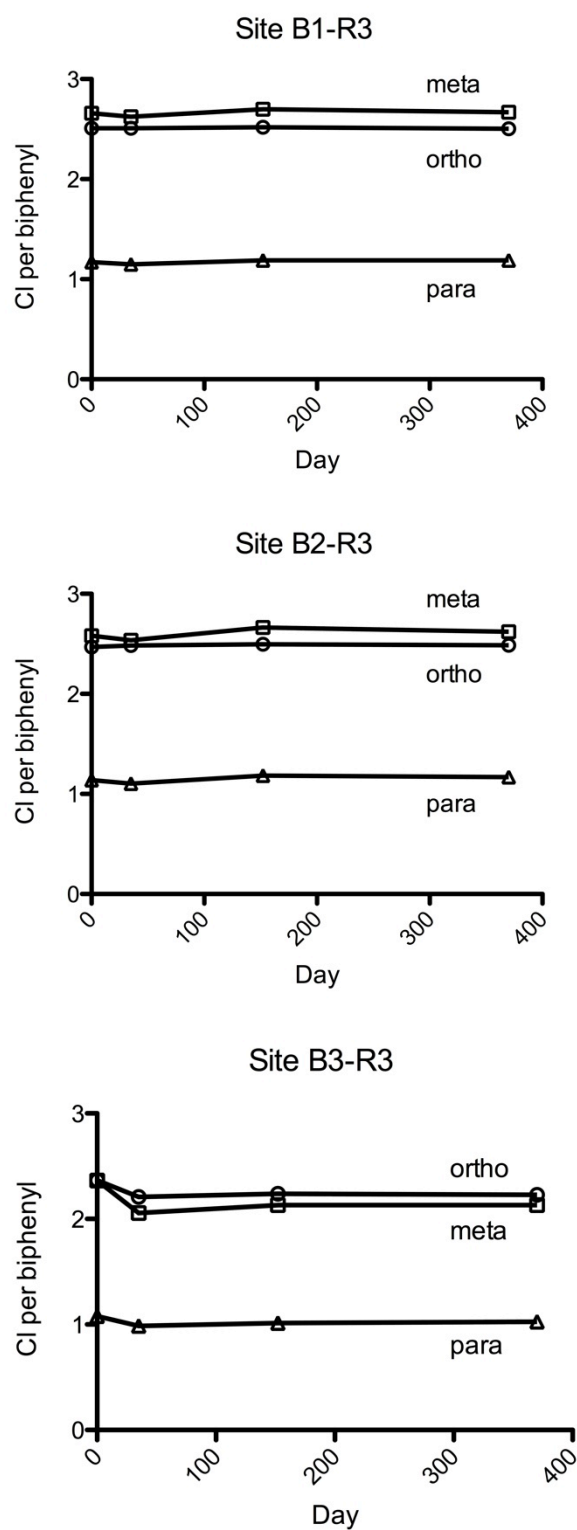
#### **4.3.2.3 Chlorine Removal**

Distribution of chlorine over time (Figure 4-11) indicates both *meta* and *ortho* dechlorination have occurred to a slight extent in the most active microcosm, i.e. Site B3-R3. Chlorines per biphenyl decreased from  $2.36 \pm 0.02$  on day 0 to  $2.06 \pm 0.02$  on day 35 for the *meta* position and from  $2.37 \pm 0.03$  on day 0 to  $2.21 \pm 0.02$  on day 35 for the *ortho* position. Dechlorination on the *para* position was insignificant. Total chlorines per biphenyl decreased by 10% after 35 days of incubation, which is equivalent to a removal rate of 0.11 chlorine per biphenyl per week, however, the overall rate was diminished as the dechlorination activity discontinued from day 35 through day 370.

The removal of *ortho* chlorines was unusual because *ortho* dechlorination does not constitute a significant component of microbial dechlorination of PCBs and *ortho* chlorines are frequently conserved over time during dechlorination processes.<sup>2</sup> Nevertheless, moderate *ortho* dechlorination was reported for Aroclor 1260 in a microbial enrichment culture in addition to significant *meta* dechlorination.<sup>47</sup> The rarely observed dechlorinating pattern might suggest that previously undescribed microorganisms in the sewer sediments are capable of removing *ortho* chlorines or that the environmental conditions support this unique biological activity. It should be noted

that the occurrence of *ortho* dechlorination might alter the interpretation of MDPR that was calculated under the assumption of conserved *ortho*-substituted congeners; however, this observation was likely to result in an underestimation of MDPR, which would indicate a greater extent of dechlorination activity in the microcosms.<sup>48</sup>

The removal of chlorines in this study is not as extensive as those observed in other studies where dechlorination was stimulated by addition of primers or by enrichment of cultures.<sup>47, 49</sup> Further, we did not amend additional electron/hydrogen donor to our microcosms. We assumed that the sediment itself contained sufficient organic matter to fuel dechlorination. It is possible that the systems became donor limited, because the gas production (e.g. methane formed by methanogens) indicative of bacterial activity did not sustain throughout the experiment.



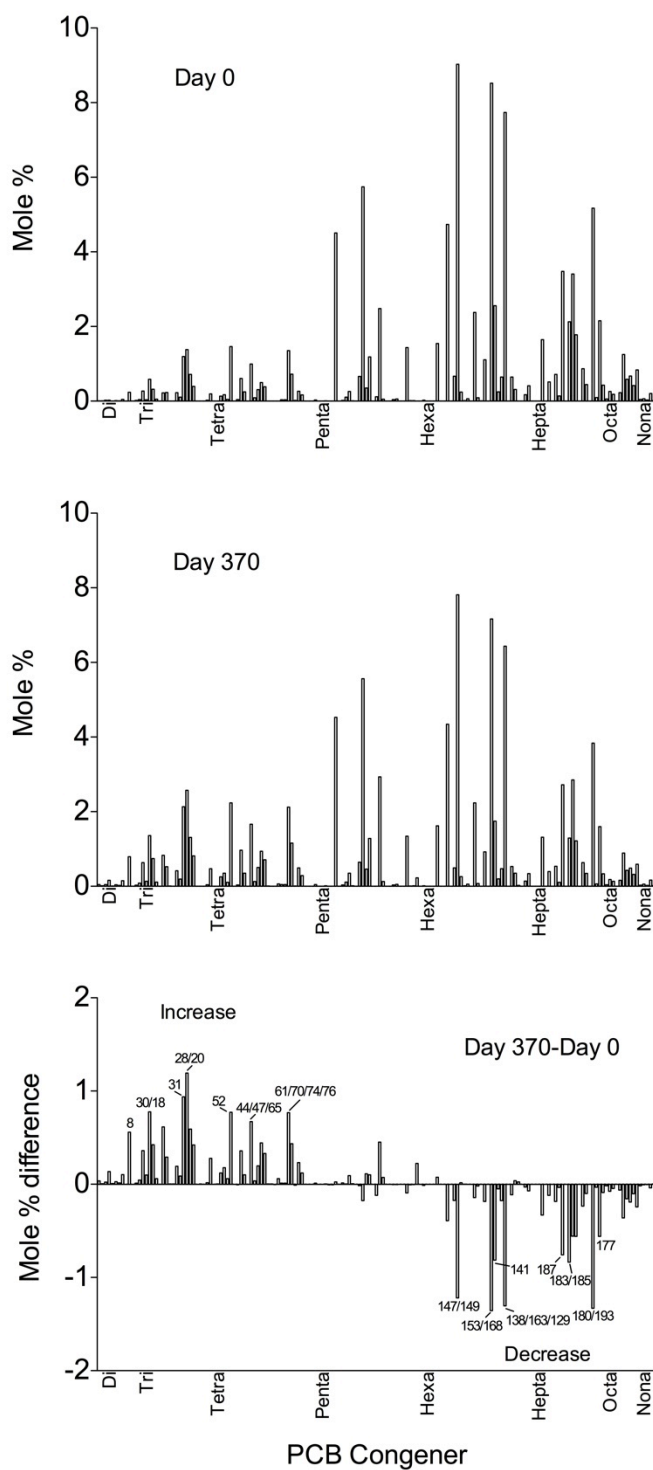
**Figure 4-11. Chlorine removal over time at *ortho*, *meta* and *para* positions in selected microcosms. Error bars are estimated from RSD of mole % of each congener and mostly masked by the symbols.**



#### 4.3.2.4 Dechlorination Pattern

A closer evaluation of the change in congener distributions from Site B3-R3 microcosm allows an assessment of dechlorination pathways. Figure 4-12 shows the congener profiles on days 0 and 370 as well as the distribution of mole % difference between these two profiles. Positive change was observed for di- through tetra- homologs, indicating an increase in mole % of these congeners. Large decrease in mole % was found for several congeners in hexa- through nona- homologs. The highly chlorinated congener PCB 180 (2345-245) decreased by over 1 mole % from day 0 to day 370, which is equivalent to 26% total dechlorination of this congener. Some other congeners in the hepta- and octa- homologs such as PCB 170 (2345-234) and 194 (2345-2345) were also dechlorinated by more than 25%. Similarly, PCB 180 (2345-245) and PCB 170 (2345-234) were documented for the *in-situ* dechlorination of Aroclor 1260 in the sediments of Woods Pond.<sup>28</sup> Small changes in the mole % of penta-chlorinated congeners may indicate an intermediary role for this homolog.

Some of the precursor congeners were identified as PCBs 147/149 (2356-24, 236-245), PCBs 153/168 (245-245, 246-345), PCB 141 (2345-25), PCBs 138/163/129 (234-245, 2356-34, 2345-23), PCB 187 (2356-245), PCBs 183/185 (2346-245, 23456-25), PCBs 180/193 (2345-245, 2356-345), PCB 177 (2356-234), and PCB 194 (2345-2345). Some of the major dechlorination products included PCB 8 (2-4), PCBs 30/18 (246-, 25-2), PCB 31 (25-4), PCBs 28/20 (24-4, 23-3), PCB 52 (25-25), PCBs 44/47/65 (23-25, 24-24, 2356-), and PCBs 61/70/74/76 (2345-, 25-34, 245-4, 2-345).



**Figure 4-12. PCB congener distribution in Site B3-R3 microcosm after 0 and 370 days of incubation. Difference between the two profiles is also plotted.**

A few dechlorination pathways were proposed. For example, PCB 180 (2345-245) could be dechlorinated to PCB 47 (24-24) via intermediate congeners PCB 153 (245-245) and then PCB 99 (24-245), or via intermediates PCB 138 (234-245) or PCB 137 (2345-24) and then PCB 99 (24-245) or PCB 85 (234-24), by removal of flanked *meta* chlorines. Similarly, PCB 170 (2345-234) could also be dechlorinated to PCB 47 (24-24) via sequential removal of flanked *meta* chlorines in the following pathways: via PCB 138 (234-245) or PCB 137 (2345-24) to PCB 99 (24-245) or PCB 85 (234-24) to PCB 47 (24-24); or via PCB 128 (234-234) to PCB 85 (234-24) to PCB 47 (24-24). These dechlorination pathways were specifically reported in Process N, which is described as exclusive dechlorination in the flanked and doubly flanked *meta* position, with a characteristically high accumulation of PCB 47 (24-24).<sup>50</sup> Process N has been frequently observed with Aroclor 1260 dechlorination in sediment microcosms from Silver Lake<sup>51</sup>, Woods Pond<sup>28</sup>, Hudson River<sup>52</sup>, and in sediment-free microcosms developed from the Housatonic River.<sup>53</sup> PCB 47 (24-24) was also identified as one of the two dominant congeners representing an intermediate stage of dechlorination in WWTP effluents and influents from previous research.<sup>22, 23</sup>

In the present study, dechlorination pathways may not be limited to Process N because some other processes may exist. For example, the dechlorination pathway of precursor congener PCB 153 (245-245) via PCB 101 (245-25) to product congener PCB 52 (25-25) is reported in Process P by removal of flanked *para* chlorines.<sup>50</sup> This transformation was also observed in an extensive manner with 65 mole % of PCB 153 (245-245) dechlorinated after 66 days when this hexa- congener was incubated separately with a

bacterial strain in pure cultures.<sup>54</sup> The di-chlorinated congener PCB 8 (2-4) showed a 2-fold increase in mole %, which may be attributed to dechlorination of the tetra congener PCB 47 (2,4-4,7) as specified in Process Q.<sup>50</sup> While PCB 8 is not an expected endpoint of reductive dechlorination, it appears to accumulate in Hudson River sediment microcosms,<sup>52</sup> suggesting it is resistant to further dechlorination and can be used as an indicator of dechlorination potential. The yield of di-chlorinated congeners in the Site B3-R3 microcosm indicates an advanced stage of Aroclor 1260 dechlorination. Most of the major dechlorination products contain unflanked chlorines, which could be subsequently oxidized by aerobic PCB-degrading bacteria.<sup>4</sup>

#### 4.3.3 Implications for PCB-dechlorinating Bacteria

Previous studies have shown that Aroclor 1260 is reductively dechlorinated in aquatic sediment microcosms, and PCB-dechlorinating microorganisms have been identified through individual congener enrichments. To date, several anaerobic bacteria have been confirmed to show PCB-dechlorinating activity including *Dehalococcoides ethenogenes* strain 195<sup>55</sup>, *Dehalococcoides* sp. CBDB1<sup>54</sup>, *Dehalobium chlorocoercia* DF-1<sup>56</sup>, bacterium o-17<sup>57</sup>, and *Chloroflexi* phylotypes SF1, SF2 and DEH10<sup>31</sup>. Many of the dechlorinated congeners observed in this study were found to degrade significantly in Aroclor 1260 microcosms with *Dehalococcoides* spp. strain CBDB1 in pure culture.<sup>54</sup> In another study,<sup>35</sup> anaerobic PCB-dechlorinating bacteria were detected in Aroclor 1260-contaminated soils from a storm water drainage ditch. The identified phylotypes clustered within either the clade of known *Dehalococcoides* spp. or the broader o-17/DF-1 *Chloroflexi* group. Dechlorination activity of indigenous microbial communities was

detected in some of the soil microcosms amended with a single PCB congener. Significant dechlorination was observed in soil microcosms with weathered PCBs as low as 5 ppm in a bioaugmentation test with pure cultures of DF-1. These findings demonstrated the occurrence and activity of existing PCB-reducing bacteria outside the aquatic environment, and the potential of PCB dechlorination under low substrate concentrations with enriched cultures.

Members of the *Dehalococcoides* group are widely distributed in nature including contaminated soils<sup>58</sup> and groundwater aquifers<sup>59-61</sup>, and in engineered habitats such as anaerobic digester sludge.<sup>62-64</sup> Members of the *Dehalobacter* spp. and *Desulfitobacterium* spp. were also detected in unsaturated subsurface soils<sup>65</sup> and a nondehalogenating strain of *Desulfitobacterium* was isolated from human feces.<sup>66</sup> Another study reported that *Chloroflexi* made up around 9% of the bacterial communities in sediments from an infiltration basin receiving highway runoffs.<sup>67</sup> Therefore, it is possible that diverse dehalogenating microbial communities could be developed in sewer sediments either directly from waste inputs, from eroded soils transported by storm water runoff into combined sewers, or by introduction of soil particles and infiltration of groundwater from aquifers.

The wastewater collection and treatment system may be considered as an ideal scheme for complete microbial degradation of PCBs.<sup>23</sup> The anaerobic “pretreatment” zone in the sewer reduces highly chlorinated PCBs to lighter congeners. The subsequent aerobic zone in treatment plant (e.g. activated sludge) supports cleavage of the biphenyl ring and

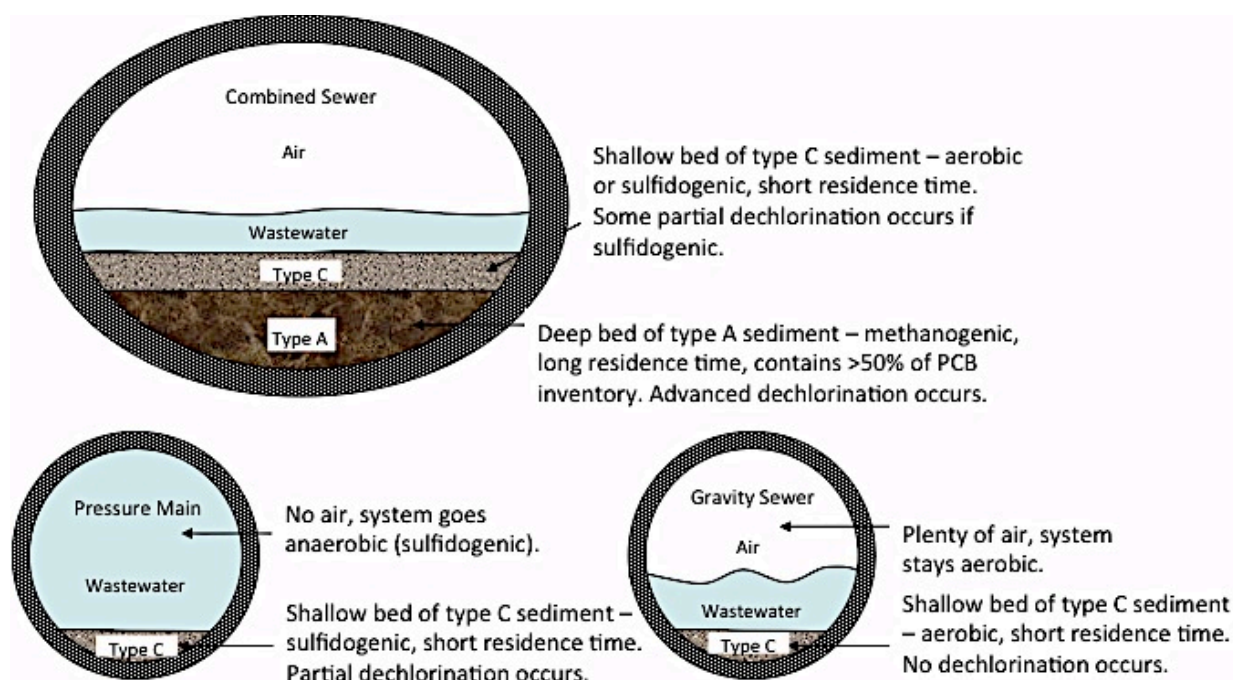
mineralization of the less chlorinated congeners. Because microbial reductive dechlorination is the rate-limiting step for complete PCB degradation, the presence of anaerobic dechlorinating bacteria combined with evidence of reductive dechlorination activity not only confirms microbial dehalorespiration of PCBs in sewers, but also provides useful insights into the sequential degradation process. It should be emphasized that mass reduction of PCBs due to dechlorination is sometimes insignificant with less efficient removal during the wastewater treatment process. However, the reduction in overall toxicity for dioxin-like PCB congeners could be substantial in treated effluents, resulting in decreased toxic load into receiving waters.<sup>22</sup>

The spatial heterogeneity inherent in sewer sediments had a profound effect on the ability of PCB dechlorination as only some of the microcosms showed evidence of dechlorination with varying rate and extent. Similar heterogeneity has been reported in studies on dechlorination activities in aquatic sediments and soils. The spatial variability of bacterial population and inhibitory metal or organic co-contaminants might have caused heterogeneity of PCB dechlorination activity in microcosms with soils collected at different locations within a distance of 730 m.<sup>35</sup> The particle size fraction and distance from sources could lead to microscale heterogeneities of contaminant concentrations and availability as well.<sup>68</sup> Another study demonstrated that the highly heterogeneous distribution of microbial degraders and their specific requirements for carbon and electrons played an important role in the degradation of chlorinated compounds in contaminated sites.<sup>69</sup> Diverse microorganisms form complex microbial communities varying among the water phase, biofilms and sediments of the sewage collection system.

Therefore, it is speculated that anaerobic dechlorination of PCBs is affected by the active microbial communities under different redox conditions and the availability of suitable electron donors and acceptors within the sewers.

#### **4.3.4 Implications on *in-situ* Dechlorination**

Reductive dechlorination of PCBs is speculated to take place in the anaerobic zones established in sewer systems. The two main anaerobic processes that occur in the sewers are sulfidogenesis and methanogenesis. Sulfidogenesis produces  $H_2S$  gas from reduction of sulfate and methanogenesis produces methane, which is also called sewer gas, from  $CO_2$  reduction or acetate utilization. The two processes are similarly favored from an energetic point of view and expected to exist simultaneously during fermentation of organic compounds in wastewater.<sup>70</sup> Nevertheless, different types of sewers, such as combined sewers and separate sewers, are likely to develop different characteristics in sediments and thus environmental conditions that preferably support one process over the other. One classification of sewer sediments divides them into different categories based on origin, nature and location of deposits.<sup>71</sup> As illustrated in Figure 4-13, type A sediments consisting of coarse and loose granular materials were usually found in the invert of sewer pipes. Type C sediments in the form of fine-grained organics are commonly deposited alone or above type A sediments.



**Figure 4-13. Sewer types and sediment characteristics for microbial dechlorination of PCBs.** <sup>23</sup>

Separate sanitary sewers are designed to carry wastewater only to treatment plants by either gravity flow or pressurized pipe systems. Both types of sewers are likely to accumulate type C sediments due to input of sanitary wastewater solids. Conventional gravity collection systems are usually aerobic due to the presence of air and thus no dechlorination is expected to occur. Pressure sewers may develop anoxic zones when thick biofilms are established below the water level and prevent penetration of dissolved oxygen. These shallow beds of type C sediments can easily go sulfidogenic because sulfate is a common and abundant component in domestic wastewater.<sup>72</sup> Under favorable conditions, sulfate-reducing bacteria within the fully productive biofilms could utilize sulfate as electron acceptor for the assimilation of organic matter. Partial dechlorination



of PCBs is expected to occur in these anaerobic sediments that have a relatively short residence time in sewers.

In contrast, the combined sewer system collects storm water runoff in addition to domestic sewage and industrial wastewater. Therefore, storm water runoff occasionally carries grits and gravels (in sizes of 8~10 mm) that will settle to the bottom of the sewer pipes.<sup>73</sup> Combined sewers may also have some fine-grained type C deposits, which could stay aerobic or become sulfidogenic under certain conditions, above type A sediment bed. The buried bacteria in the deep sediment bed are not exposed to a continuous supply of sulfate from wastewater.<sup>72</sup> Anaerobic microbes may turn to alternative electron acceptors and methanogenesis is likely to occur because of the plentiful carbon and nutrient source in the sewer bed. The majority of PCB inventory in sewer deposits is also stored in the sediment bed and expected to degrade extensively by PCB-dechlorinating bacteria during the extended residence time.

Together with the findings from previous studies,<sup>22, 23</sup> it is suggested that intermediate PCB dechlorination is likely to prevail in separate sanitary sewers where sulfidogenic conditions are frequently developed in the shallow layer of type C sediments (Figure 4-13). The advanced dechlorination signal dominant in WWTP effluents serving combined sewers may be associated with methanogenic activities in deeply buried type A sediment bed. Microbially mediated *in-situ* dechlorination of PCBs has occurred inadvertently and extensively in sewage collection systems of several urban areas. It offers a promising

approach for engineered bioremediation towards natural attenuation of halogenated contaminant mixtures in sewer systems prior to wastewater treatment.

A threshold concentration of 40 ppm was suggested for PCB dechlorination to occur and the rate of dechlorination was enhanced at higher concentrations.<sup>74, 75</sup> Nevertheless, many studies have shown evidence of PCB dechlorination with an enriched culture under lower substrate concentrations such as 1~5 ppm.<sup>35, 45, 76</sup> Although the highest PCB concentration in our sewer sediments obtained from interceptors was only around 4 ppm, the substrate concentrations were likely to be higher at other locations of the sewer system that were less susceptible to sewer pipe cleaning, especially when the other halogenated co-contaminants such as polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs) were also taken into account as electron acceptors for dehalogenating bacteria.

Many sewer systems may already have the favorable conditions for reductive dechlorination of PCBs: anaerobic environment, microbial communities with dechlorinating potential, elevated PCB concentrations in waste streams, and sufficient inputs of carbon and nutrients.<sup>23</sup> However, the large spatial heterogeneity with PCB transformation together with the difficulty in elucidating metabolic roles of active microorganisms within complex bacterial communities remains a challenge for development of site-specific strategies to enhance microbial dechlorination activities. Significant dechlorination of PCBs in sewers will not only decrease mass and toxicity contribution into treatment plants and receiving waters, but also reduce pollutant load

carried in sewer system overflows during storm events. Effective removal of less chlorinated congeners in WWTPs needs to be addressed as well since these dechlorination products are more soluble and mobile in wastewater than their parent congeners. The integration of sewer system and WWTP design will achieve a more sustainable and cost-effective urban wastewater management.

#### **4.4 Conclusions**

Our microcosm study with sewer sediment showed signs of reductive dechlorination activity with no lag phase. In one replicate, this dechlorination was extremely fast with apparent evidence after 35 days of incubation, suggesting that rapid dechlorination was at least possible in sewers. The rate was fast enough to mean that the 10~30% dechlorination products found in many of the sewer systems in the Delaware River Basin could plausibly have been produced in the sewers. The degree of dechlorination was moderate with accumulation of intermediate dechlorination products in the tri- and tetra-homologs as well as some di-chlorinated congeners. The site with the highest dechlorination activity was near an industrial site that leached PCBs to the sewer. It helped to explain the 10~30% of dechlorination products — dechlorination is fastest in regions where a larger proportion of the total PCB burden is entering the sewer. The results also indicate that the sewer is incredibly diverse in site-specific dechlorination activity, with some zones that may have great activity and some zones with virtually none. The most actively dechlorinating sewer sediment is likely to develop in sewers where PCB-dechlorinating bacterial communities have been well established and enriched by receiving high input of legacy PCB loads.

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## Chapter 5 : Conclusions and Future Work

This dissertation covered various aspects of fate and transport including source apportionment, emission and transport, and fate characterization of polychlorinated biphenyls (PCBs) in the Delaware River Basin. Chapter 2 achieved to identify the PCB sources at Swarthmore, PA, as a follow-up study of the first passive air sampling in 2005.<sup>1</sup> Both studies observed strong spatial gradients of  $\Sigma$ PCB concentrations with hot spots identified at Swarthmore and around Philadelphia-Camden area, an urban fractionation effect with low molecular weight (MW) PCBs enriched at remote locations, and a distinct congener pattern dominated by high MW PCBs at the Swarthmore Science Center. The current study covered a larger area in the Delaware River Basin with a focus in the Swarthmore area. Atmospheric PCB concentrations were measured with greater analytical capacity because more PCB congeners were included for quantification and the sampling rate was determined through use of depuration compounds. Three more factors indicative of PCB source types were resolved by PMF analysis compared to the 2005 study. Environmental cycling of historical release of Aroclor mixtures appeared to dominate the current emissions of PCBs to the environment. Rail yards with PCB-containing equipment could represent significant sources of atmospheric PCBs. The Swarthmore source that was unclear in the 2005 study has been pinpointed to building materials such as sealants. Recent discovery of PCBs in caulks of old buildings including schools received much attention with respect to possible human exposure especially among young children.<sup>2</sup> Future work is recommended on paired indoor and outdoor air sampling of buildings constructed between the 1950s and the 1970s when PCB usage was unrestricted. The relationship between PCB concentrations in building materials and

ambient levels in air and dust also needs to be addressed to assess the magnitude of the problem and to develop viable long-term solutions for remediation.

In addition to identification of the Aroclor sources, we have provided the first evidence that inadvertent production from color organic pigments has resulted in wide dispersion of the non-Aroclor congener PCB 11 throughout the environment.<sup>3</sup> PCB 11 was consistently detected at concentrations up to  $79 \text{ ng g}^{-1}$  in consumer products containing pigments and dyes, especially diarylide yellows. The use, recycle, and disposal of these products not only caused impaired surface water quality via mobilization of PCB 11 from the pigment matrix, but also raised concerns over oral and dermal exposure in humans through handling of common merchandise such as napkins and printed materials. Several other PCB congeners were also found to be by-products of pigment manufacture. For example, PCB 209 was detected in paint pigments including phthalocyanine blue and phthalocyanine green.<sup>4</sup> The mass flow analysis in Chapter 3 determined that PCB 11 inflow into the Delaware River basin was between  $0.025$  and  $42 \text{ kg y}^{-1}$ , and the outflows from the watershed and the airshed were estimated between  $8.4$  and  $260 \text{ kg y}^{-1}$ . These results indicated that PCB 11 might be present in pigments at levels close to or even exceeding the federal limits, although pigment industry representatives reported much lower PCB concentrations in pigments and claimed that environmental or human exposure from pigment use was implausible.<sup>5</sup> The other speculation that pigments may decompose in the environment to release PCB 11 is more worrisome, since this process is unlikely to be controlled or regulated due to widespread applications of pigments in consumer goods. Further study is needed to determine the actual PCB 11 levels in

different pigments and to investigate the favorable conditions for pigment breakdown.

Additionally, there is still much to learn about the toxicity and metabolism of PCB 11 in humans and other organisms.

Chapter 4 attempted to provide experimental evidence for the prevalent PCB dechlorination signals that were identified through PMF analysis in the wastewater collection systems of two urban watersheds.<sup>6,7</sup> To our knowledge, this is the first microcosm experiment inoculated with sewer sediments, as opposed to aquatic sediments in most microcosm studies. Spatial heterogeneity in PCB dechlorination activity was observed among sewer sediments from different locations. Even though the overall dechlorination was not extensive in most microcosms, the evidence from the most active microcosm suggested that dechlorination of PCBs in sewers could be fast enough to account for the extent of dechlorination observed in wastewater influents. This study also implied that interceptors might not be the ideal location for microbial dechlorination to occur in sewers, because the dechlorinating microbial communities might be wiped out with frequent removal of sediments through manhole cleaning. It is possible that the microcosms in this study did not receive adequate feeding of nutrients or suitable electron donors that would have promoted faster dechlorination. Additional studies are required to determine the optimal conditions for incubation of the microcosms. Instead of setting up microcosm study that usually runs for excessive time, analysis of perchloroethylene (PCE) in sewer sediments is suggested as a fast screen of dechlorinating activity. Finally, chemical analysis of the other spiked chemicals including decabrominated diphenyl ether (BDE 209), dechlorane plus (DP) and hexabromocyclododecane (HBCD) of the sampled

microcosm sediments will be useful for a more complete picture of dehalogenating potential in sewers. Correspondingly, molecular analysis is also recommended to identify the bacterial communities associated with dechlorination activity in the consortia.

Taken together, although the production of PCBs in the form of Aroclors has been banned since the 1970s, their persisting environmental presence is still a major problem and past research has been mostly concentrated on these historical emissions of PCBs. The development of analytical technology has enabled detection of non-Aroclor PCB congeners that led to the discovery of inadvertent production of PCBs from sources beyond the Aroclor mixtures. This dissertation has applied this technical advancement in research for a better understanding of PCB sources from both legacy and emerging emissions. Even though PCBs are currently regulated in products from manufacturing process and unintentional production,<sup>8</sup> this dissertation has demonstrated that PCBs are continuously released to the environment at unexpected high levels through PCB-laden materials like building sealants and through inadvertent production from pigment use. The dechlorination evidence observed in the microcosm study also benefited from congener-specific analysis for 209 PCBs and shed some light on inadvertent destruction of PCBs in built waste environments. The PCB problem has always been complex, but the ongoing development in knowledge and technology has allowed us to articulate the complexity in a way that will lead us to equally complex solutions. The information provided in this dissertation would greatly promote future work on identification, monitoring, and remediation of PCB contamination in the natural and engineered environments.

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<http://www.epa.gov/history/topics/pcbs/01.html>

## Appendix

**Table I-1. Retention time and relative response factor (RRF) for 151 PCB congeners resolved on a DB-5 GC capillary column. SS = surrogate; DC = depuration compound; IS = internal standard.**

PCB Homolog	PCB Congener	Retention Time (min)	Relative Response Factor (RRF)
<b>Mono</b>	1	19.00	1.01
	2	20.84	1.01
	3	21.06	1.01
<b>Di</b>	4/10	22.27	1.65
	7/9	23.79	2.59
	6	24.47	2.72
	5/8	24.89	4.84
<b>SS [1]</b>	14	25.82	2.29
	11	27.28	2.22
	12/13	27.76	2.72
	15	28.20	2.72
<b>Tri</b>	19	26.32	1.15
<b>DC [1]</b>	30	26.93	1.33
	18	28.01	0.70
	17	28.19	1.15
	24/27	28.88	1.15
	16/32	29.60	1.15
<b>SS [2]</b>	23	30.43	1.55
	26	31.14	1.15
	25	31.39	1.15
	31	31.90	1.15
	28	32.04	1.03
	20/21/33	32.96	1.15
	22	33.71	1.15
	36	34.19	1.15
	35	37.19	1.15
	37	38.02	1.15
<b>Tetra</b>	54	33.03	1.10
	53	33.51	1.10
	45	34.22	1.10
	46	35.00	1.10
	51/52	35.40	1.11
	43/49	35.88	1.07
	47/48/73	36.19	1.10
<b>SS [3]</b>	65	36.63	1.14

	44	37.62	0.92
	59	37.88	1.10
	42	38.01	1.10
	71	38.86	1.10
	41/64/68	39.00	1.10
	40	39.91	1.10
	57	40.05	1.10
	67	40.56	1.10
	63	41.23	1.10
	61/74	41.69	1.21
	76	42.12	1.10
	66	42.57	1.18
	56/60	44.63	1.10
	79	46.33	1.10
	81	48.96	1.11
	77	50.27	1.09
<b>Penta</b>	96	39.54	1.66
	100	40.58	1.66
	94	41.53	1.66
	98/102	42.39	1.66
	93/95	42.65	1.52
	91	43.43	1.66
	92	44.79	1.66
	84	45.26	1.66
	89/90/101	45.51	1.55
	99	46.18	1.62
	119	47.00	1.66
	83/109	47.59	1.66
	97	48.27	1.66
	87/111/115	48.95	1.34
	85/120	49.52	1.66
	110	50.27	1.77
	82	51.78	1.66
	124	52.68	1.66
<b>DC [2]</b>	107/108	53.18	2.05
	123	53.53	1.74
	106/118	53.86	1.75
	114	55.41	1.68
	122	55.73	1.66
	105/127	57.58	1.60
	126	61.72	1.61
<b>Hexa</b>	136	49.87	1.54
	154	50.41	1.54
	151	51.95	1.37

	135/144	52.55	1.54
	147	53.06	1.54
	139+149	53.61	1.45
	134	55.05	1.54
	146	56.24	1.45
	153	57.08	1.64
	132	57.41	1.54
	141	58.88	1.54
	137	59.79	1.54
	130	60.12	1.54
	138/163/164	60.76	1.51
	158	61.04	1.73
	129	61.61	1.54
<b>SS [4]</b>	166	62.29	1.57
	159	63.09	1.54
	128/167	63.48	1.85
	156	65.50	1.44
	157	65.92	1.66
	169	68.11	1.28
<b>Hepta</b>	179	59.09	1.00
	176	60.04	1.00
	178	61.71	0.95
	175	62.27	1.00
	182/187	62.55	1.15
	183	63.03	1.19
	185	63.98	1.00
	174/181	64.61	1.00
	177	65.06	0.86
	171	65.42	1.00
	172/192	66.28	0.88
	180	66.73	1.12
	170/190	68.65	0.83
	189	70.23	1.04
<b>Octa</b>	202	65.33	0.86
<b>IS</b>	204	66.05	1.00
	200	67.55	0.86
<b>DC [3]</b>	198	68.97	0.84
	199	69.17	0.75
	196/203	69.48	1.40
	195	71.00	0.56
	194	71.98	0.62
<b>Nona</b>	208	70.90	0.70
	206	73.89	0.70



**Table I-2. Retention time and relative response factor (RRF) for all 209 PCB congeners resolved on an SPB-Octyl GC capillary column. d-SS = deuterated surrogate; d-IS = deuterated internal standard. All RRFs were calculated using d-IS [1].**

<b>PCB Homolog</b>	<b>PCB Congener</b>	<b>Retention Time (min)</b>	<b>Relative Response Factor (RRF)</b>
<b>Mono</b>	1	16.79	0.50
	2	19.30	0.40
	3	19.53	0.37
<b>Di</b>	4	19.83	0.91
	10	20.05	1.60
	9	22.22	1.54
	7	22.40	1.52
	6	22.67	1.40
	5	23.03	1.37
	8	23.19	1.33
	14	25.05	1.23
	11	26.01	1.06
	13/12	26.33	1.04
	15	26.69	1.02
	19	23.52	0.62
<b>Tri</b>	30/18	25.64	0.89
	17	26.14	0.70
	27	26.35	1.17
	24	26.51	1.19
	16	26.62	0.36
	32	27.21	1.10
	34	28.59	1.04
	23	28.79	1.01
	26/29	29.11	1.02
	25	29.36	0.96
	31	29.69	0.97
	28/20	30.03	0.96
	21/33	30.25	0.93
	22	30.68	0.96
	36	32.38	0.93
	39	32.75	0.89
	38	33.39	1.00
	35	33.88	0.73
	37	34.29	0.73
<b>d-IS [1]</b>	d-30	25.55	1.00
<b>Tetra</b>	54	27.02	0.67
	50/53	29.39	0.50
	45/51	30.18-30.26	0.47
	46	30.45	0.39

<b>d-SS [1]</b>	52	31.97	0.49
	73	32.14	0.66
	43	32.25	0.35
	69/49	32.48	0.54
	48	32.82	0.47
	d-65	32.99	0.62
	44/47/65	33.07	0.50
	59/62/75	33.40	0.60
	42	33.61	0.43
	41/40/71	34.06-34.18	0.44
	64	34.35	0.58
	72	35.23	0.61
	68	35.55	0.64
	57	35.99	0.56
	58	36.22	0.57
	67	36.40	0.59
	63	36.68	0.57
	61/70/74/76	37.02	0.56
	66	37.37	0.51
	55	37.53	0.52
	56	38.06	0.53
	60	38.29	0.53
	80	38.71	0.60
	79	40.29	0.56
	78	40.87	0.49
<b>Penta</b>	81	41.34	0.49
	77	41.91	0.48
	104	33.00	0.43
	96	33.39	0.42
	103	35.43	0.37
	94	35.65	0.31
	95	36.11	0.32
	100/93	36.37	0.32
	102/98	36.55-36.64	0.33
	88/91	37.02	0.33
	84	37.23	0.27
	89	37.74	0.28
	121	38.20	0.45
	92	38.56	0.31
<b>d-IS [2]</b>	113/90/101	39.15	0.35
	83/99/112	39.71-39.95	0.35
	109/119/86/97/125/87	40.28	0.36
	d-116	40.95	1.00
	117/116/85	41.05-41.10	0.36
	110/115	41.26-41.36	0.38
	82	41.53	0.23
	111	41.93	0.43
	120	42.42	0.41
	108/124	43.56	0.37
	107	43.82	0.41
	123	43.95	0.37

<b>Hexa</b>	106	44.08	0.35
	118	44.26	0.37
	122	44.61	0.34
	114	44.83	0.40
	105	45.47	0.33
	127	46.98	0.34
	126	48.60	0.37
	155	38.95	0.52
	152	39.13	0.47
	150	39.3	0.49
	136	39.67	0.47
	145	39.99	0.48
	148	41.53	0.34
	151/135	42.17	0.33
	154	42.40	0.42
	144	42.74	0.37
	147/149	43.09	0.38
	134/143	43.36-43.45	0.28
	139/140	43.71	0.37
	131	43.91	0.29
	142	44.07	0.29
	132	44.38	0.31
	133	44.88	0.31
	165	45.28	0.42
	146	45.56	0.38
	161	45.68	0.41
	153/168	46.21	0.41
	141	46.38	0.34
	130	46.78	0.27
	137/164	47.10-47.18	0.38
	138/163/129	47.46	0.33
	160	47.63	0.42
	158	47.85	0.43
	128/166	48.72	0.34
	159	49.70	0.37
	162	50.01	0.40
	167	50.51	0.37
	156/157	51.68	0.37
<b>d-SS [2] Hepta</b>	169	54.96	0.49
	d-159	49.65	0.44
	188	44.81	0.45
	179	45.14	0.43
	184	45.67	0.48
	176	46.05	0.43
	186	46.52	0.44
	178	47.88	0.25
	175	48.54	0.30
	187	48.83	0.33
	182	49.01	0.32
	183/185	49.49-49.61	0.32
	174	49.67	0.28

	177	50.11	0.26
	181	50.52	0.30
	171/173	50.77	0.26
	172	52.37	0.24
	192	52.69	0.37
	180/193	53.00	0.34
	191	53.41	0.37
	170	54.32	0.25
	190	54.89	0.33
	189	57.45	0.31
<b>Octa</b>	202	50.24	0.28
	201	51.17	0.28
	204	51.87	0.27
	197/200	51.16-51.26	0.28
	198/199	54.98	0.17
	196	55.69	0.18
	203	55.90	0.20
	195	57.23	0.15
	194	59.56	0.18
	205	60.06	0.23
<b>Nona</b>	208	56.99	0.26
	207	57.91	0.23
	206	61.79	0.16
<b>Deca</b>	209	63.41	0.14

# Curriculum Vitae

**Jia Guo**

## EDUCATION

- 2013 Ph.D., Environmental Science  
**Rutgers, the State University of New Jersey**, New Brunswick, NJ.
- 2006 B.S., Environmental Science  
**Peking University**, Beijing, China.

## RESEARCH EXPERIENCE

- 2006-2013 Graduate Assistant, **Rutgers, the State University of New Jersey**.  
 2005-2006 Research Assistant, **Peking University**.

## TEACHING EXPERIENCE

- 2007-2012 Teaching Assistant, **Rutgers, the State University of New Jersey**.

## PROFESSIONAL EXPERIENCE

- 2010-2012 Summer Intern, **ExxonMobil Biomedical Sciences, Inc.**, Annandale, NJ.

## PUBLICATIONS

- Sandy, A.L.; **Guo, J.**; Miskewitz, R.J.; McGillis, W.R.; Rodenburg L.A. Mass transfer coefficients for volatilization of polychlorinated biphenyls from the Hudson River, New York measured using micrometeorological approaches. *Chemosphere* 2013, 90 (5): pp 1637-1643.
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- Sandy, A.L.; **Guo, J.**; Miskewitz, R.J.; McGillis, W.R.; Rodenburg, L.A. Fluxes of polychlorinated biphenyls volatilizing from the Hudson River, New York measured using micrometeorological approaches. *Environ. Sci. Technol.* 2012, 46 (2), pp 885-891.
- Rodenburg, L.A.; **Guo, J.**; Du, S.; Cavallo, G.J. Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl (PCB 11). *Environ. Sci. Technol.* 2010, 44 (8), pp 2816-2821.