

SOURCE APPORTIONMENT AND MEASUREMENT OF PCBs AND POPs IN NY/NJ AREA

by

Songyan Du

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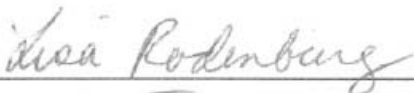
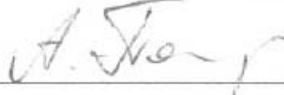
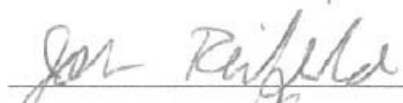

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written under the direction of

Lisa A Rodenburg

and approved by

  
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## **Abstract of the Dissertation**

SOURCE APPORTIONMENT AND MEASUREMENT OF PCBs AND POPs IN  
NY/NJ AREA

By Songyan Du

Dissertation Director:

Lisa Ann Rodenburg

Investigating the source of Persistent Organic Pollutants in ambient air and water is imperative in the development and implementation of Total Maximum Daily Load (TMDL) process for the impaired water bodies. Atmospheric deposition is an important process involved in the TMDL modeling, therefore one objective of this thesis aims to achieve is how to identify PCB source types and regions in air. The coupling of Positive matrix factorization (PMF) model, which is use to apportion the contributing sources, with potential source contribution function (PSCF) model, which is used to locate the source regions, allowed the identification of PCB sources in urban air in Camden, US. Four factors are identified which are thought to represent sources such as volatilized Aroclors and particle-phase PCBs. The PSCF model output for  $\Sigma$ PCBs and the resolved factors suggests that the urban PCB signal is comprised of multiple signals, some of which may come from discrete sources that can be identified and remediated.

As an attempt to refine the atmospheric deposition modeling input, passive sampling study is conducted to investigate the spatial extent of the urban-impacted elevated atmospheric persistent organic pollutants (POPs) including PCBs, PAHs, OCPs and BDEs by deploying passive samplers at 32 sites across the Philadelphia –Camden area. This study revealed two maxima for PCBs representative of urban (population density driven) sources vs. industrial sources, highlighting the potential role of densely populated urban centers as well as industrial areas as sources of PCBs to the regional environment. PAHs and BDEs all showed urban-rural gradients with maximum concentrations found in the urban center. Some of OCPs showed urban-rural gradient, while others exhibited either a relatively uniform concentration level across the sampling area or a relatively random spatial distribution.

In order to corroborate the loading estimate used in the development of TMDL, PMF model is also used to apportion the source of PCBs in Delaware River and NY/NJ Harbor Estuary. The analysis of ambient water either generally corroborates the PCB loading estimate used in the water quality model or identified factors associated with top loading categories in previous mass balance study.

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## Chapter 1

### General Introduction

Throughout the US, many surface water bodies are impaired due to polychlorinated biphenyl (PCB) concentrations that exceed the federal water quality standard (WQS). The Clean Water Act requires that total maximum daily loads (TMDLs) be developed for these systems. PCB TMDLs are constructed based on detailed water quality models that rely upon estimated PCB loadings from multiple sources. The TMDL indicates the amount of a pollutant that can enter the water body and have it still meet the applicable WQS. Substantial reductions in PCB discharges to these waters must be made in order to implement the TMDLs. This dissertation is targeting two aquatic systems for which PCB TMDLs have been or are being developed: the Delaware River and the NY/NJ Harbor estuary.

Currently, PCB concentrations in the Delaware River and NY/NJ Harbor exceed the WQS established by the Delaware River Basin Commission (DRBC) of  $7.9 \text{ pg L}^{-1}$  and NY State WQS of  $1 \text{ pg L}^{-1}$  respectively by several orders of magnitude (Ref). In 2003, the DRBC promulgated a Stage 1 TMDL for PCBs in the tidal Delaware River of  $380 \text{ mg d}^{-1}$  (Fikslin and Suk 2003). The TMDL for PCBs in the NY/NJ Harbor is still under development. Developing TMDLs for complex aquatic systems such as the Delaware River and the NY/NJ Harbor that are heavily impacted by urban and industrial sites is challenging given limited data on current and historical PCB loadings. The Delaware River is probably typical of most urbanized rivers/estuaries in the United States where a single major source of PCBs is absent. The PCB sources to the NY/NJ Harbor

are dominated by a single input from the Upper Hudson that is relatively well characterized (Farley et al. 1999; Totten 2005b), however, other sources of PCBs to the Harbor are less well understood and are being addressed primarily through the Contaminant Assessment Reduction Project (CARP), which is designed to find source of POPs in Harbor collecting various samples including ambient water, point discharges, storm water, sediment, etc in areas extending from the Upper Hudson near Fort Edward and out to the Bight Apex during 1998-2001. Therefore, it is essential to identify and prioritize sources of PCBs in both systems in order to clarify the relative importance of various loading categories and aid in the implementation of the TMDLs. Additionally, the validation of the loading estimates used in the construction of the TMDLs will bolster their scientific defensibility, especially in the face of any potential litigation that could challenge the implementation of the TMDLs.

This dissertation will attempt to validate the loadings used in the development of the Delaware River and NY/NJ Harbor TMDLs by applying source apportionment modeling to untangle the various loadings to these aquatic systems.

One important source of PCBs to both of these systems is atmospheric deposition. Previous studies have demonstrated that atmospheric deposition of urban atmospheric PCBs emissions can contaminate adjacent water bodies (Offenberg et al. 2005a; Zhang et al. 1999a). Urban atmospheric PCB emissions are likely to lead to unacceptable levels of contamination in adjacent water bodies wherever PCBs were used extensively. This is the case happening in Delaware and NY/NJ Harbor estuary. The measured high level of  $\Sigma$ PCBs in both the gas and particle phases in the atmosphere of Camden, NJ, as measured by the New Jersey Atmospheric Deposition Network (NJADN) (Totten et al. 2004;

Totten et al. 2006b) lead to estimated atmospheric deposition loadings of PCBs to the tidal Delaware River that exceed the entire stage 1 TMDL (Fikslin and Suk 2003) by a factor of 20. In order to implement the current TMDL, atmospheric deposition of PCBs cannot be ignored, and therefore atmospheric emissions must be investigated. This dissertation furthers our understanding of the sources of PCBs to a typical US city (Camden/Philadelphia) by resolving the types of sources contributing to the high measured PCB concentrations at Camden and by investigating the source locations through the combination of two receptor models, which attribute pollution to sources through statistical and/or meteorological interpretation of data. In this way, PCB source regions and processes are identified.

Since atmospheric deposition is an important and sometimes dominant source of POPs to aquatic system, estimation of atmospheric deposition parameters for water quality models is imperative. Usually, modeling input of atmospheric deposition is performed using data on atmospheric POP concentrations from a limited number of active monitoring sites (Hillery et al. 1998; Offenberg and Baker 1997b; Simcik et al. 1997; Sun et al. 2006). Data collected by the NJADN has been used to calculate atmospheric deposition fluxes and loads to the NY/NJ Harbor and the Delaware River (Totten et al. 2004; Totten et al. 2006b) in the TMDL models. The NJADN data indicates that strong gradients in atmospheric PCB concentrations exist in urban areas. Because of these gradients, interpolation of PCB concentrations between a small number of active monitoring sites is difficult and can result in highly inaccurate estimates of local atmospheric PCB concentrations, which can have significant consequences on the TMDL models. Therefore it is important to characterize the spatial distribution of atmospheric



PCBs in order to accurately model atmospheric deposition inputs to adjacent aquatic systems. In this dissertation, passive air sampling was conducted at 32 sites across the Philadelphia –Camden area in order to improve the modeling of atmospheric deposition of PCBs to the Delaware River. Other persistent organic pollutants were measured in the passive samples as well.

Therefore this dissertation work uses three main tools to investigate PCB sources to the water and atmosphere. The first one is a source apportionment tool called positive matrix factorization (PMF), which is an advanced factor analysis method and can be used to extract source information. The second is the Potential Source Contribution Function (PSCF), which is a conditional probability describing the spatial distribution of probable geographic source locations inferred by using trajectories arriving the sampling sites. The coupling of PMF with PSCF allows the investigation not only what types of PCB sources are important in a typical city such as Philadelphia, but also provides a crude indication of where those PCB sources originate. The third tool is passive air sampling, which is cost-effective and can provide integrated atmospheric POP concentrations over a period of months and assess concentrations in air simultaneously at multiple sites at far lower cost.

This dissertation is composed of four parts addressing the issues related to developing PCB loads for the TMDL models: Chapters 2 and 3 focus on atmospheric PCB sources, in which, Chapter 2 attempts to identify the type and location of PCB sources in a typical urban area by applying PMF and PSCF to the database of atmospheric PCB measurements acquired at Camden by the NJADN, Chapter 3 presents the results of the passive air sampling campaign which reveal the spatial distribution of

PCBs in the Philadelphia area, and are examined in the context of the predictions arising from the PSCF study in Chapter 2. Additional categories of POPs were measured in the passive air samplers, and their spatial distributions are also described in Chapter 3 (PCBs, OCPs, PAHs and BDEs). The results of this study were used to refine the atmospheric input functions of PCBs for the TMDL model of the Delaware River; Chapters 4 and 5 focus on sources of PCBs to the water column. In these chapters, PMF is used to analyze PCB concentrations in ambient water samples to apportion PCB sources in the Delaware River (Chapter 4) and the NY/NJ Harbor (Chapter 5).

This dissertation represents an innovative approach to the investigation of POP sources in urban systems. Chapter 2 represents the first time the PMF and PSCF models have been combined to investigate POP sources. Chapter 3 presents what is, to date, the largest passive air study focused on a single urban area. Chapter 4 and 5 represent POP source apportionment studies that are far more successful than their predecessors due to the use of a more sophisticated statistical tool (PMF) and much larger and more robust data sets. Taken together, these four chapters represent a truly comprehensive attempt to understand POP sources in urban systems.

The author would like to acknowledge the provider of the PCB data without whom the dissertation would have never been possible. The author participated in the passive air sampling and subsequent analysis and quantification. The author was generously provided PCB data for PCB modeling work in Chapter 2, 4 and 5 from NJADN study, DRBC and NYDEP respectively.

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## Chapter 2

### **Source Identification of Atmospheric PCBs in Philadelphia/Camden Using Positive Matrix Factorization Followed by the Potential Source Contribution Function**

Du, S. and Rodenberg, L. 2007. Source and identification of atmospheric PCBs in Philadelphia/Camden using positive matrix factorization followed by the potential source contribution function. *Atmospheric Environment* 41: 8596-8608

#### **Abstract**

The concentrations of gas-phase polychlorinated biphenyls (PCBs) in the atmosphere of the Camden, NJ, USA are elevated by as much as 20 times over regional background. These high PCB levels are a concern because they lead to atmospheric deposition loadings of PCBs to the tidal Delaware River that exceed the entire total maximum daily load (TMDL). Two models were applied to the atmospheric PCB concentration data from Camden in an attempt to identify the PCB source types and regions. Positive matrix factorization (PMF) was used to identify source types. Four factors were identified which are thought to represent sources such as volatilized Aroclors and particle-phase PCBs. The potential source contribution function (PSCF) model was then used to identify the geographic source regions by examining the origination points for air parcels that result in high PCB concentrations at the Camden receptor site. The PSCF model for  $\Sigma$ PCBs indicates PCB source regions throughout the Philadelphia-Camden metro area, including portions of both Pennsylvania and New Jersey. The PSCF plots for the resolved PMF factors suggest that factors 1 and 4 show fewer distinct source regions, indicating that their sources are diffuse and/or lie very close to the receptor site. The PSCF plots for factors 2 and 3 reveal very different source

regions. Factor 2 primarily arises from the city of Philadelphia, whereas factor 3 originates in southern New Jersey and south of Philadelphia. This study demonstrates the utility of the combined PMF/PSCF approach in identifying atmospheric PCB source types and regions.

## **Introduction**

Atmospheric concentrations of persistent organic pollutants such as polychlorinated biphenyls (PCBs) tend to be higher in urban areas, such that cities act as sources of these pollutants to their surrounding environments. Atmospheric deposition of urban atmospheric PCBs emissions can contaminate adjacent water bodies. Perhaps the most famous example of this is Chicago, IL, USA, where atmospheric PCB concentrations are elevated, and atmospheric deposition of these PCBs into the adjacent Lake Michigan is thought to be one of the largest sources of PCBs to the Lake (Offenberg et al. 2005b; Zhang et al. 1999b). Urban atmospheric PCB emissions are likely to lead to unacceptable levels of contamination in adjacent water bodies wherever PCBs were used extensively, including North America and Europe. This is the case in the Delaware River, where atmospheric deposition, although small compared to inputs from sewage treatment plant effluents, stormwater, and contaminated sites, still exceeds the total maximum daily load (TMDL) of  $380 \text{ mg d}^{-1}$  (Fikslin and Suk 2003). PCB sources in urban areas may include waste combustion and other incinerators, landfills, storage and disposal facilities, Superfund sites, accidental releases, joint sealants and caulks, and municipal wastewater sludge drying beds (Epa 1998; Herrick et al. 2004b; Hsu et al.

2003b; Kohler et al. 2005a). The relative importance of these sources is not known, and other unidentified sources may be significant (Epa 1998).

This study uses a database of atmospheric PCB concentrations collected at Camden, NJ, USA to attempt to identify urban atmospheric PCB sources. Camden is part of the Philadelphia, PA, USA megalopolis, and lies immediately across the Delaware River from Philadelphia (Fig. 2.1). Philadelphia is the fifth largest city in the US by population, home to about 1.5 million people (factfinder.census.gov). It is one of the oldest cities in the US; the first development in the Philadelphia area occurred around 1650. Daily and average concentrations of  $\Sigma$ PCBs in both the gas and particle phases of the Camden atmosphere, as measured by the New Jersey Atmospheric Deposition Network (NJADN), are elevated by as much as 20 times over the regional background prevailing at nearby suburban sites (Totten et al. 2004; Totten et al. 2006b). These high PCB levels are a concern because they lead to atmospheric deposition loadings of PCBs to the tidal Delaware River that exceed the entire TMDL recently established for PCBs (Fikslin and Suk 2003). Other sources of PCBs, such as resuspension of contaminated sediments, wastewater effluents, and non-point sources, are more significant than atmospheric deposition (Fikslin and Suk 2003), but they are also easier to track down. Identification of the sources of these atmospheric PCBs is therefore crucial to the implementation of the TMDL. The PCB congener fingerprint at Camden is distinct from that at other NJADN sites, which may indicate that Camden is affected by discrete PCB sources (Totten et al. 2004). Nearby at Swarthmore, PA, the congener pattern is also different from the other NJADN sites but similar to Camden, suggesting significant PCB sources may lie to the southeast of Camden (Totten et al. 2006b).

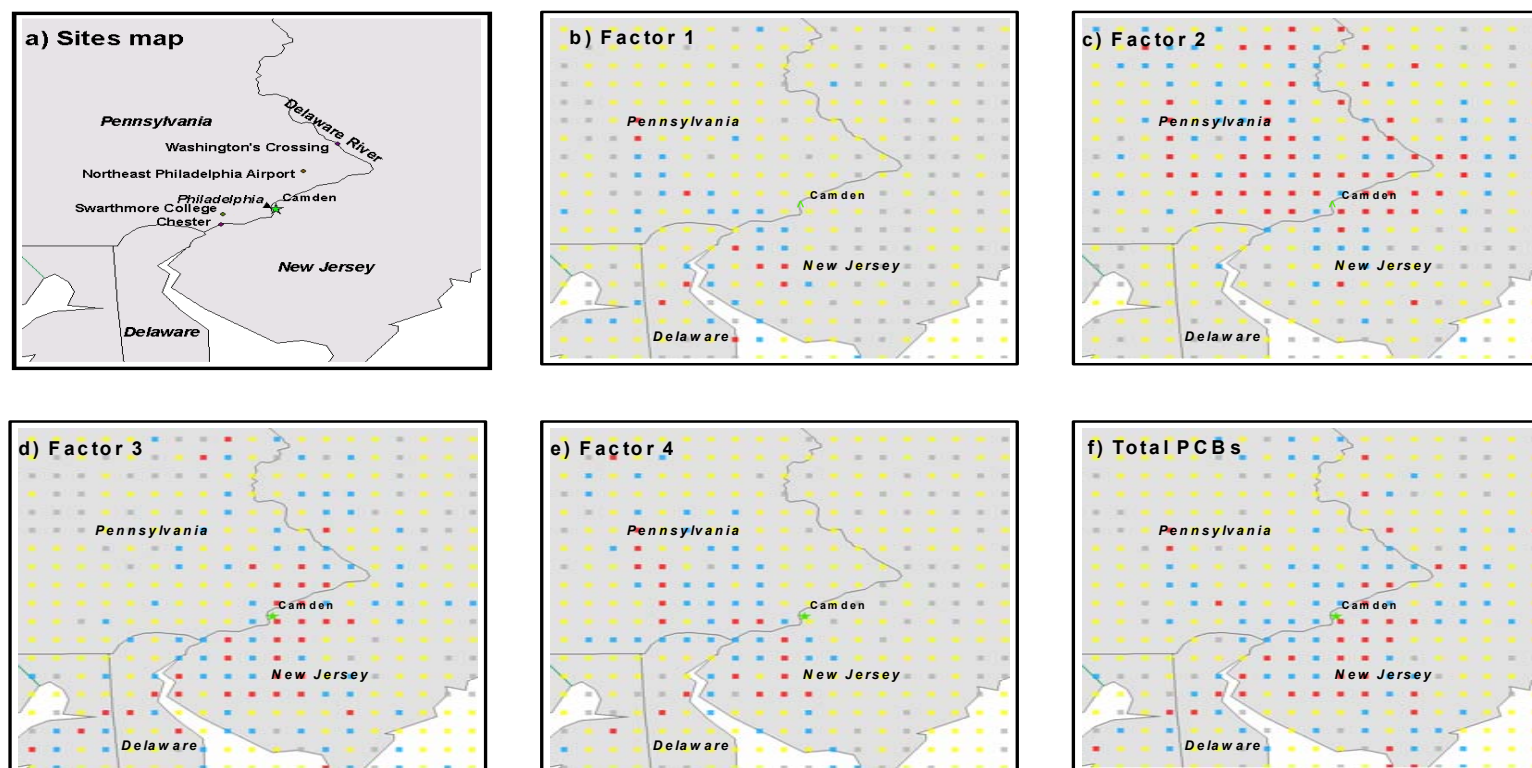


Figure. 2.1. Panel a) map of the area indicating NJADN sampling sites (circles). PSCF plots were constructed using the NJADN data from Camden, NJ (green star). Panels b through f depict the PSCF plots for each resolved factor (panels b through e) and total measured gas phase  $\Sigma$ PCB (panel f). Red squares represent PSCF values from 0.5 to 1.0, blue squares represent PSCF values from 0.3 to 0.5, and yellow squares represent PSCF values from 0 to 0.3. Grey squares indicate regions where a PSCF score could not be calculated. PSCF scores were calculated using 500-meter starting elevations and concentrations normalized to constant temperature.

In order to estimate atmospheric PCB source regions affecting the Camden site, a probabilistic model called the potential source contribution function (PSCF) was used. PSCF has been used to identify source regions of particles (Ashbaugh et al. 1985; Malm et al. 1994), pollutants in precipitation (Zeng and Hopke 1989), and persistent organic pollutants (Hafner and Hites 2003; Hsu et al. 2003b). PSCF can only reveal the potential source location, but cannot give a quantitative indication of the source strength (Hafner and Hites 2005). Previous studies demonstrated that the combination of PSCF with an advanced factor analysis model called positive matrix factorization (PMF) is an effective tool for identification of atmospheric aerosol sources and locations (Liu et al. 2003; Polissar and Hopke 2001). The goal of this work was to determine whether the combined PMF/PSCF approach was useful for identification of PCB sources.

PMF has been successfully implemented in many source apportionment studies, including identification of sources of PM<sub>2.5</sub> (Kim et al. 2004; Paatero and Hopke 2003), volatile organics (Anderson et al. 2001; Jorquera and Pappengluck 2004), and semivolatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (Gao et al. 2002; Larsen and Baker 2003) in the atmosphere. PMF has also been used for congener fingerprinting of PCBs in sediment ((Bzdusek and Christensen 2006; Bzdusek et al. 2006a; Bzdusek et al. 2006d) and water (Gigliotti 2003). In this study, PMF is used for the first time for source identification of atmospheric PCBs. The purpose of this study was to resolve the *types* of sources contributing to the high measured PCB concentrations at Camden and to investigate the source locations by combining these two receptor models, which attribute pollution to sources through statistical and/or meteorological interpretation of data.



## Experiment section

### *Sampling and Analytical Procedure*

The PCB data were collected as part of the NJADN study during 1999- 2002 at Camden, NJ. They consist of 74 measurements each in the gas and particle phase. Full details of sample collection, preparation, extraction and analysis can be found elsewhere (Totten et al. 2001). Air samples were typically collected at 12 d frequencies using a modified high-volume air sampler (Tisch Environmental, Village of Cleves, OH) with a calibrated airflow of  $\sim 0.5 \text{ m}^3 \text{ min}^{-1}$ . Quartz fiber filters (QFFs) were used to capture the particle phase, and polyurethane foam plugs (PUFs) were used to capture the gas phase PCBs.

Samples were injected with surrogated standards (PCBs 14, 23, 65, and 166) before extraction. Because an interference with PCB 14 was observed in most samples, PCB 23 was used as a surrogate after mid-2000. Each sample was extracted in a Soxhlet apparatus for 24 h in petroleum ether (PUFs) or dichloromethane (QFFs). These extracts were then reduced in volume by rotary evaporation and fractionated on a column of 3% water-deactivated alumina. The PCB fraction was eluted with hexane, concentrated under a gentle stream of nitrogen gas, and injected with internal standard containing PCBs 30 and 204 prior to analysis. PCBs were analyzed on an HP6890 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector using a 60m, 0.25mm i.d. DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25  $\mu\text{m}$ . A total of 63 peaks representing 93 congeners were quantified.

**PMF**

PMF is an advanced factor analysis method, described in detail by Paatero and Tapper (Paatero and Tapper 1994) and briefly summarized here. PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix  $X$  is composed of  $n$  observed samples and  $m$  chemical species.  $F$  is a matrix of chemical profiles of  $p$  factors or sources. The  $G$  matrix describes the contribution of each factor to any given sample, while  $E$  is the matrix of residuals. The PMF solution, i.e.  $G$  and  $F$  matrices, are obtained by minimizing the objective function  $Q$  through the iterative algorithm:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (2)$$

$Q$  is the sum of the squares of the difference (i.e.  $e_{ij}$ ) between the observations ( $X$ ) and the model ( $GF$ ), weighted by the measurement uncertainties ( $s_{ij}$ ). The higher the residue matrix  $E$ , the higher the  $Q$  value.

Some special features inherent in the PMF technique distinguish it from conventional factor analysis methods, such as principal components analysis (PCA). For instance, the built-in non-negativity constraints in PMF minimize the ambiguity caused by rotating the factors. PMF also utilizes the estimated error in each measurement to provide the optimum data point weighting. Another important advantage of the PMF method is the ability to handle missing and below detection limit data by adjusting the corresponding error estimates of these data points.

### *PMF Data Matrix*

The tendency of PCB congeners to partition between gas and particle phases raises concerns regarding the use of PCBs in source apportionment studies. Therefore, only paired measurements of PCBs in gas and particle phases were included into the data matrix for PMF analysis, and the gas and particle phase concentrations were summed for entry into the model. Prior research demonstrates that PCBs react with OH radical on a time scale of days (Anderson and Hites 1996; Mandalakis et al. 2003; Totten et al. 2003). Since we are examining transport of PCBs within a small geographic area, the transport times are on the order of hours, and therefore OH radical reactions are not important. Although one of the advantages associated with PMF is the ability to handle data that is below the detection limit by assigning higher error estimate, it was found that the resolved source profiles was improved after removing the PCB congeners that were below the method detection limit in more than half of the samples. These congeners include PCBs 17+15, 21+33+53, 40, 87+81, 118 (+ indicates congeners that co-elute and are quantified as the sum). PCB 8+5 was also excluded due to concerns that it co-elutes with an unidentified interference. Accordingly, 52 PCB peaks were submitted for modeling analysis. If either the gas or particle value was below the detection limit, then one -half the limit of detection was used as a proxy. There was no missing data.

### *PMF Uncertainty Estimate*

PMF requires the input of individual uncertainty estimates for each measurement. To derive the estimated uncertainties, we assumed the analytical uncertainties associated with the PCB concentrations can be attributed to the following factors: laboratory

extraction efficiency, sampling precision, and method detection limits. In this study, error model EM=14 was used because it is recommended for general purpose environmental work (Paatero 2003b). The uncertainty values  $S_{ij}$  are computed according to the following equation:

$$S_{ij} = t_{ij} + u_{ij} \sqrt{\max(|x_{ij}|, |y_{ij}|)} + v_{ij} \max(|x_{ij}|, |y_{ij}|) \quad (3)$$

Where  $t$  is the congener- and sample-specific detection limit,  $u$  is the Poisson distribution (here designated as 0),  $v$  the measurement precision,  $x$  the observed data value, and  $y$  the modeled value. For each element, the computation is based on the larger value of  $x_{ij}$  or  $y_{ij}$ . This is done iteratively.

The array  $t$  represents the method detection limits, calculated as three times the standard deviation of the PCB mass in all field blanks divided by the average volume of air sampled, resulting in units of  $\text{pg m}^{-3}$ . The array  $v$  represents measurement precision. This uncertainty estimate consisted of the propagated error estimate of both the gas and particle phase PCB concentrations. The uncertainty associated with the extraction efficiency was calculated as the variability in the recovery of the surrogate associated with that congener over time. Thus the overall uncertainty in laboratory extraction efficiency is calculated as the square root of the sum of the squares of the standard deviations of the surrogate recoveries for the gas phase and particle phase PCBs. The standard deviations for the gas-phase surrogates were 22%, 16%, and 16% for PCBs 23, 65, and 166, respectively. The standard deviations for the particle-phase surrogates were 16%, 16%, and 20% for PCBs 23, 65, and 166, respectively. The uncertainty in sampling precision is caused by the variation of sampling volume because of the fluctuation of the

atmospheric temperature and pressure. The uncertainty in sample volume (%) is calculated as:

$$\text{sampling precision} = \frac{\Delta \text{flowrate}_{(\text{min temp} - \text{max temp})}}{\text{average flowrate}_{(\text{min} + \text{max})}} \quad (4)$$

The overall uncertainty estimate for each PCB congener was calculated using a pooled coefficient of variation ( $CV_{\text{pooled}}$ ) by the equation:

$$CV_{\text{pooled}}(\%) = \sqrt{(\text{Sampling precision})^2 + (\text{Extraction efficiency})^2} \quad (5)$$

Total error estimates were in the range of 15 to 22% for the PCB congeners.

### ***PSCF***

PSCF can be interpreted as a conditional probability describing the spatial distribution of probable geographical source locations inferred by using trajectories arriving the sampling site (Polissar and Hopke 2001). The construction of the PSCF model is based on the idea that once PCBs are emitted and incorporated into the air parcel, they can be transported along the air trajectories to the receptor site. The trajectories are composed of a series of end points that are presented as paired latitude and longitude values for each specific time interval being modeled. The PSCF value for a single grid cell was calculated as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (6)$$

Where  $m_{ij}$  is the number of trajectories resulting in high concentrations, and  $n_{ij}$  the total number of trajectories passing through that grid cell.

### *PSCF Data Matrix*

In contrast to the input data matrix of PMF, only gas phase PCB data were included in the PSCF model of  $\Sigma$ PCBs. Approximately 90% of the airborne  $\Sigma$ PCBs are in the gas phase. Thus, using gas phase or total (gas+particle) concentration should yield the same results. A total of 63 PCB peaks, some of which consist of co-eluting congeners, were measured. The concentration of each PCB congener was converted to the partial pressure by the ideal gas law and summed to give the partial pressure of the sum of PCBs ( $\Sigma$ PCBs). Atmospheric PCB concentrations have been found to be driven by temperature via the Clausius-Clapeyron equation (Carlson and Hites 2005; Hillery et al. 1997; Panshin and Hites 1994; Panshin and Hites 1994; Totten et al. 2004; Totten et al. 2006b; Wania 1998). In some cases, atmospheric PCB concentrations have also been found to be a function of wind speed (Brunciak et al. 2001a). Thus in order to reduce the variation caused by the ambient temperature and wind speed, multiple linear regressions were applied to normalize the partial pressure of  $\Sigma$ PCBs to 25°C and average wind speed. The multiple linear regression calculates fitting parameters (Herrick et al. ), which describe the natural logarithms of partial pressure ( $\ln P$ ) of  $\Sigma$ PCBs as a function of the reciprocal atmospheric temperature ( $1/T$  in degrees Kelvin) and wind speed ( $W$  in  $\text{m s}^{-1}$ ):

$$\ln P = a_0 + a_1 \left( \frac{1}{T} \right) + a_2 W \quad (7)$$

The daily observations were then divided into two groups: those greater than and those less than the criterion value. As in previous studies (Biegalski and Hopke 2005; Hafner and Hites 2005; Hafner and Hites 2003; Hopke 2004; Hsu et al. 2003b), we designated

the mean partial pressure as the criterion value. Some studies used other criterion values, such as the 60th percentile value, based on trial and error (Polissar and Hopke 2001).

### *Trajectory generation*

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model available on the website of the National Oceanic and Atmospheric Administration's (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/ready/hysplit4.html>) was used to generate 36-h back trajectories, a collection of trajectory end points each representing 1-h time intervals. Longer back trajectories were not used because they generated end points well outside of the 50-km radius around the receptor site in which the PCB sources are presumed to reside. Because wind direction can vary significantly during the 24-hour sampling period, eight different start times at 3 hour intervals (0900, 1200, 1500, 1800, 2100, 2400, 0300 and 0600 hours) were chosen for the calculation of the back trajectories to better approximate the pathway of the air sample. Since the air parcels did not maintain the same height for the duration of the back trajectory due to vertical motion, each back trajectory was calculated at three different starting altitudes: 10m, 100m and 500m above local ground level. Therefore, for each chemical measurement, 24 trajectories were generated. A total of 84 measurements were taken at Camden, but some of the meteorological data are missing from NOAA's database, such that only 71 of the 84 were used in the PSCF model. This resulted in a total of 63,048 hourly points (37 hours x 8 starting times x 71 samples x 3 altitudes), which approximate the position of a particle in the modeled air mass at a given hour.

### *Grid cell size*

Hourly points from the HYSPLIT back trajectories are imposed onto a geographical  $0.1^\circ$  latitude  $\times$   $0.1^\circ$  longitude grid, which correspond to an average area of about  $64 \text{ km}^2$ . This grid covers a geographical region of  $5^\circ$  latitude  $\times$   $5^\circ$  longitude with 2500 cells. This is the smallest grid size possible given the constraints of the data set. The most important constraint was the number of samples\_collected. Each grid cell must contain enough back-trajectory end points to give a reasonable PSCF score. For example, a grid that is too small will yield many cells with no trajectory end points. The smallest possible grid size was used because it is evident from the spatial variations in atmospheric PCB concentrations measured in urban areas such as Camden and more rural areas that atmospheric PCBs arise from highly localized, urban sources which influence atmospheric concentrations over a distance of a few tens of kilometers (Totten et al. 2004). Through trial and error, it was found that the  $0.1^\circ \times 0.1^\circ$  grid size was the smallest grid that resulted in interpretable PSCF maps in which most grid cells contained multiple trajectory end points.

### *Weight function*

Because the PSCF score is computed as the ratio of the counts of selected events ( $m$ ) to the counts of all of the events ( $n$ ) in Eq. (6), it is likely that at small values of  $n$ , the PSCF score may become unreliable. To reduce the effect of small values of trajectory end points, an arbitrary weight function  $W$  is multiplied into the PSCF value to better reflect the uncertainties in the values for these cells. The weight function is very important in applying PSCF to measurement of organic pollutants due to the relatively



small number of sample. In this study, the weight function was applied to about 97% of all the data, because most grid cells contained less than 10 trajectory and end points. The  $W$  function used is as follows:

$$W(n_{ij}) = n \begin{bmatrix} 1.00 & n_{ij} \geq 10 \\ 0.90 & n_{ij} = 9 \\ 0.80 & n_{ij} = 8 \\ 0.70 & n_{ij} = 7 \\ 0.60 & n_{ij} = 6 \\ 0.50 & n_{ij} = 5 \\ 0.40 & n_{ij} = 4 \\ 0.30 & n_{ij} = 3 \\ 0.20 & n_{ij} = 2 \\ 0.10 & n_{ij} = 1 \end{bmatrix}$$

## Results and Discussion

### *PMF Results*

#### *PMF - Determination of Number of Factors*

Determination of the number of factors is a critical step in PMF analysis. We applied two major rules to determine the optimal number of factors. First, it is important to choose the number of factors that provide clear, physically meaningful results while reducing matrix dimensionality as much as possible (Paterson et al. 1999). Second, by examining the Q value as a function of the number of factors, the point where the curve flattens is considered the proper number of factors. The theoretical Q value is equal to the number of the elements in data matrix, as this represents the situation where the specified uncertainty equals the residuals of the factor analysis. The dimension of the

input data matrix is 74x52, so the theoretically optimum value of Q equal to 3848. The PMF model was run requesting 3 to 9 factors, and each run was initialized with different starting points, i.e. changing the seed value from 1 to 10, in order to ensure that the program identified a global (not local) minimum. The Q vs. number of factors curve started to flatten out at about 4 factors. Furthermore, the four factors generated were independent of each other and fell into distinct molecular weight ranges. Thus, the optimal number of factors contributing to the measured PCB signal at Camden was determined to be four. Compared with the theoretical Q value, the obtained Q value of 2730 is relatively low, which is indicative of the higher input uncertainty estimate. The discrepancy between the obtained Q value and the theoretical Q value is caused by the fact that constructing the V matrix is rather subjective, and is based on the understanding of the measurement involved.

To further validate the choice of the selected factors for the current PMF model, we examined the fit between the modeled total PCB concentrations and the measured concentration. Assuming that all of the sources contributing to the PCB samples have been identified, the sum of the mass contributions should add to the measured PCB concentration. Thus, a regression of the measured mass concentration of PCB against the source contribution values permits the estimation of those scaling factors. This comparison gives an  $r^2$  of 0.995, a slope that is not statistically different from 1, and no significant intercept, which suggests a close match between the modeling result and the measured data. This result validates the number of factors used.

### *PMF - Resolved Congener Profiles*

The contribution of each congener to the  $\Sigma$ PCBs was normalized to 1 for the four resolved factors (Fig. 2.2). PMF modeling also generates a breakdown of the contribution of each factor to the total  $\Sigma$ PCB concentration (Fig. 2.3). Factor 1, which contributes about 27% of the measured  $\Sigma$ PCBs in the Camden area, is dominated by low molecular weight PCBs. Factors 2 and 3 consist predominantly of tetra- and penta-PCB congeners, and account for about 41% and 25% of  $\Sigma$ PCBs, respectively. Factor 4 is characterized by the presence of high molecular weight PCB congeners, comprising a minor percentage of about 6.5% of measured  $\Sigma$ PCBs.

### *PMF - Identification of Resolved Factors*

We attempted to identify these resolved source profiles via comparison of the congener patterns of the factors with congener patterns from suspected sources, including Aroclors, atmospheric samples, obtained source profiles from nearby locations, etc.

First we attempted to match the resolved source patterns (factors) with the published PCB profiles for the Aroclors. Implicit in the comparison of the resolved source profile and PCB Aroclor profile is the assumption that if no significant alteration processes or environmental weathering has occurred, the congener composition of the resolved PCB sources in atmospheric and the composition of the Aroclor or their mixture will match closely. It is believed that there is often enough stability in the compositions to determine probable source Aroclors though the congener compositions of environmental samples differ to varying extent from the original Aroclor sources.

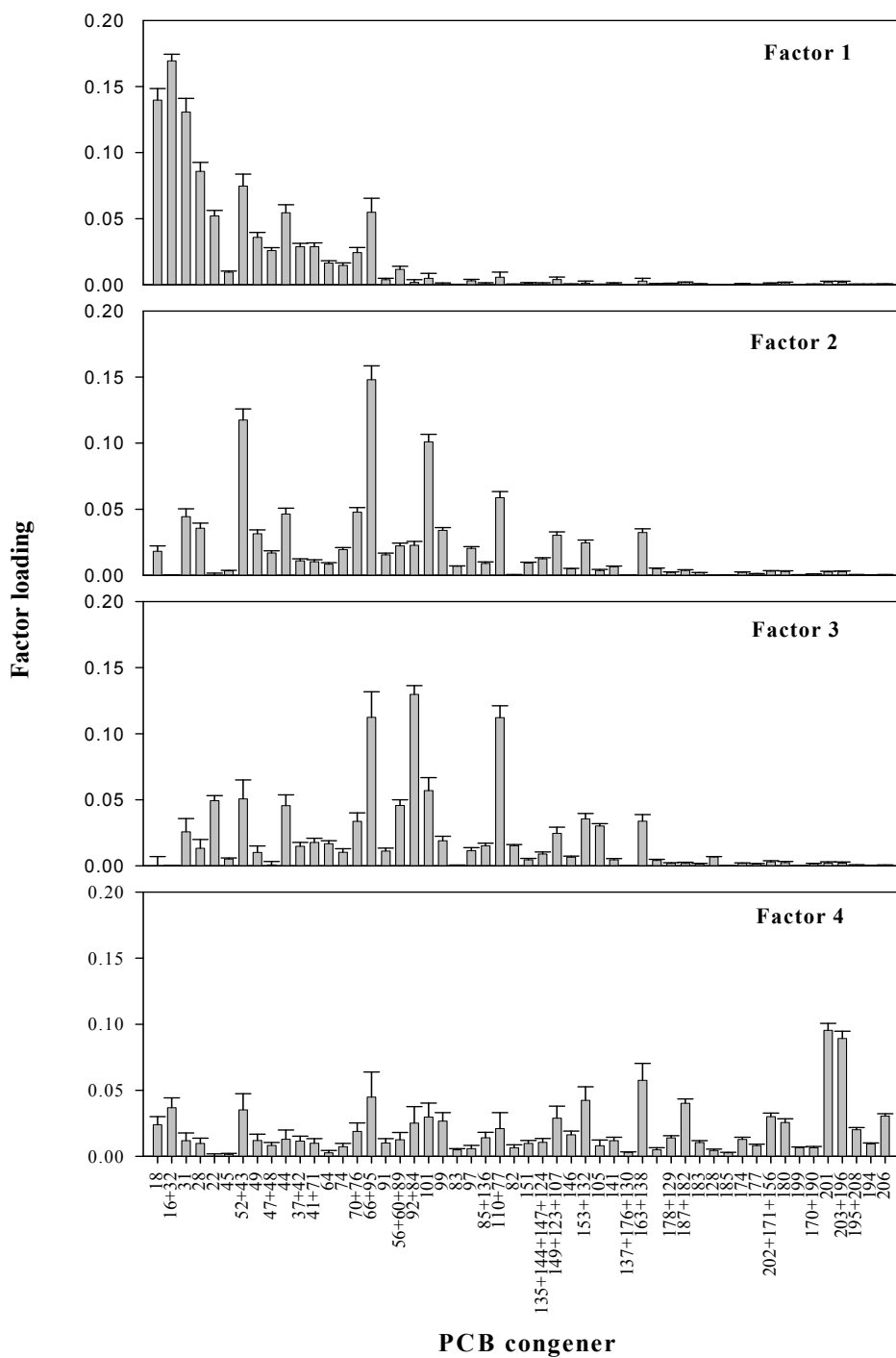


Figure 2.2. Normalized congener patterns of the four resolved source profiles (factors). Error bars stand for the standard deviation of calculated factor loading.

Aroclor composition values were taken from high resolution GC/MS analysis as published by Rushneck et al. (Rushneck et al. 2004). In order to facilitate the comparison, data for individual congeners from the Rushneck study were composited to approximate the co-eluting congener groups in the NJADN data set. As a result, 42 resolved peaks that include 65 PCB congeners were included into the comparison. Ten peaks could not be matched with the Rushneck data. These congener concentrations were then multiplied by their liquid vapor pressures from Falconer and Bidleman (Falconer and Bidleman 1994) to simulate the volatilization process. Then the Aroclor congener pattern (adjusted for volatilization) was compared to the factor profiles.

Because the Aroclor mixtures were all manufactured by a similar process, some overlap in congener composition between many of the Aroclors occurs, especially in those with similar overall chlorine content. Other studies have considered the similarity of the different Aroclors and concluded that Aroclors 1242, 1254, and 1260 are “sufficiently” independent, while the other Aroclors can be explained as a linear combination of the three independent Aroclors (Sather et al. 2001). These three were the major Aroclors produced in North America (Brown 1994).

The identification of each resolved factor profile was conducted by using the  $\cos\theta$  measurement. The cosine theta similarity metric ( $\cos\theta$ ) is a very important similarity measure for multivariate vectors (Davis 1986), which calculates the cosine of the angle between two multivariate vectors, in this case the two  $1 \times 42$  matrixes formed by the 65 congeners used in the PMF model for each factor and the corresponding source to which the factor is compared. 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 versus each factor were calculated for the 9 Aroclors as well as mixtures of Aroclors 1242, 1248, 1254 and 1260. The best similarity (highest  $\cos\theta$ ) are presented here.

Factor 1 resembles volatilized Aroclor 1242 ( $\cos\theta = 0.98$ ). As mentioned above, because of the overlap in congener composition between Aroclors, Factor 1 is also highly related to Aroclor 1016. Weathered Aroclor 1242 can also sometimes resemble unaltered Aroclor 1248 (Chiarenzelli et al. 1997). Therefore, we hypothesize that Factor 1 represents a combination of volatilized low molecular weight Aroclors, including Aroclors 1016, 1242, and 1248. Factor 2 is significantly correlated ( $p < 0.05$ ) with the congener profile of volatilized Aroclor 1254 ( $\cos\theta = 0.88$ ), and a volatilized 50/50 mixture of Aroclors 1248 and 1254 ( $\cos\theta = 0.93$ ). Factors 3 and 4 were not well correlated with any of the volatilized Aroclors ( $\cos\theta < 0.70$ ). Factor 3 is, however, similar to the PCB congener profile observed at Swarthmore ( $\cos\theta = 0.87$ ). This could indicate a significant PCB source near Swarthmore that affects Camden. Factor 4 is correlated with the average particle phase PCB profile at Camden ( $\cos\theta = 0.90$ ). Factor 4 accounts for about 6.5% of the total PCBs measured at Camden, which is similar to the fraction of PCBs typically present in the particle phase (~10%). To confirm our assignment of factor 4 as particle phase PCBs, we reran the PMF model using gas phase PCB concentrations only. This modeling exercise reproduced factors 1-3, but not 4. Factors 1-3 each matched ( $\cos\theta > 0.9$ ) one of the factors resolved from the gas-phase only data. In contrast, factor 4 (particle phase) was not similar to any of the gas-phase only factors.

### *PMF - Temperature Dependence of the Factors*

Just as ambient atmospheric PCB concentrations are typically temperature driven (Hillery et al. 1997; Simcik et al. 1999; Wania 1998), the factors also appear to be correlated with temperature (Fig. 2.3). Application of the Clausius-Clapeyron equation demonstrates that all four factors are significantly temperature dependent ( $p < 0.001$ ) after removing at most 2 outliers, although their correlation coefficients are not as strong as that for  $\Sigma$ PCBs. The Clausius-Clapeyron equation yields the following slopes and  $r^2$  values, respectively:  $\Sigma$ PCBs, -5833, 0.56; factor 1, -4883, 0.28; factor 2, -5367, 0.47; factor 3, -6398, 0.48; factor 4, -6317, 0.32. Slopes therefore increase with the average molecular weight of the factor. This dependence of the Clausius-Clapeyron slope on PCB molecular weight has been observed in other studies (Carlson and Hites 2005; Hornbuckle and Eisenreich 1996). The  $r^2$  values describe the fraction of the variation in atmospheric PCB concentration that can be described by changes in temperature.  $\Sigma$ PCBs display similar temperature dependence at the NJADN sites, with  $r^2$  values in the range of 0.3-0.8 and slopes between -3570 and -6920 (Carlson and Hites 2005).

### *PSCF Results*

In our previous work (Totten et al. 2004), we noted that sites near Camden, including Washington Crossing, NJ and the NJ Pinelands (both about 40 km from the Camden site) display atmospheric PCB concentrations that are typical of the regional

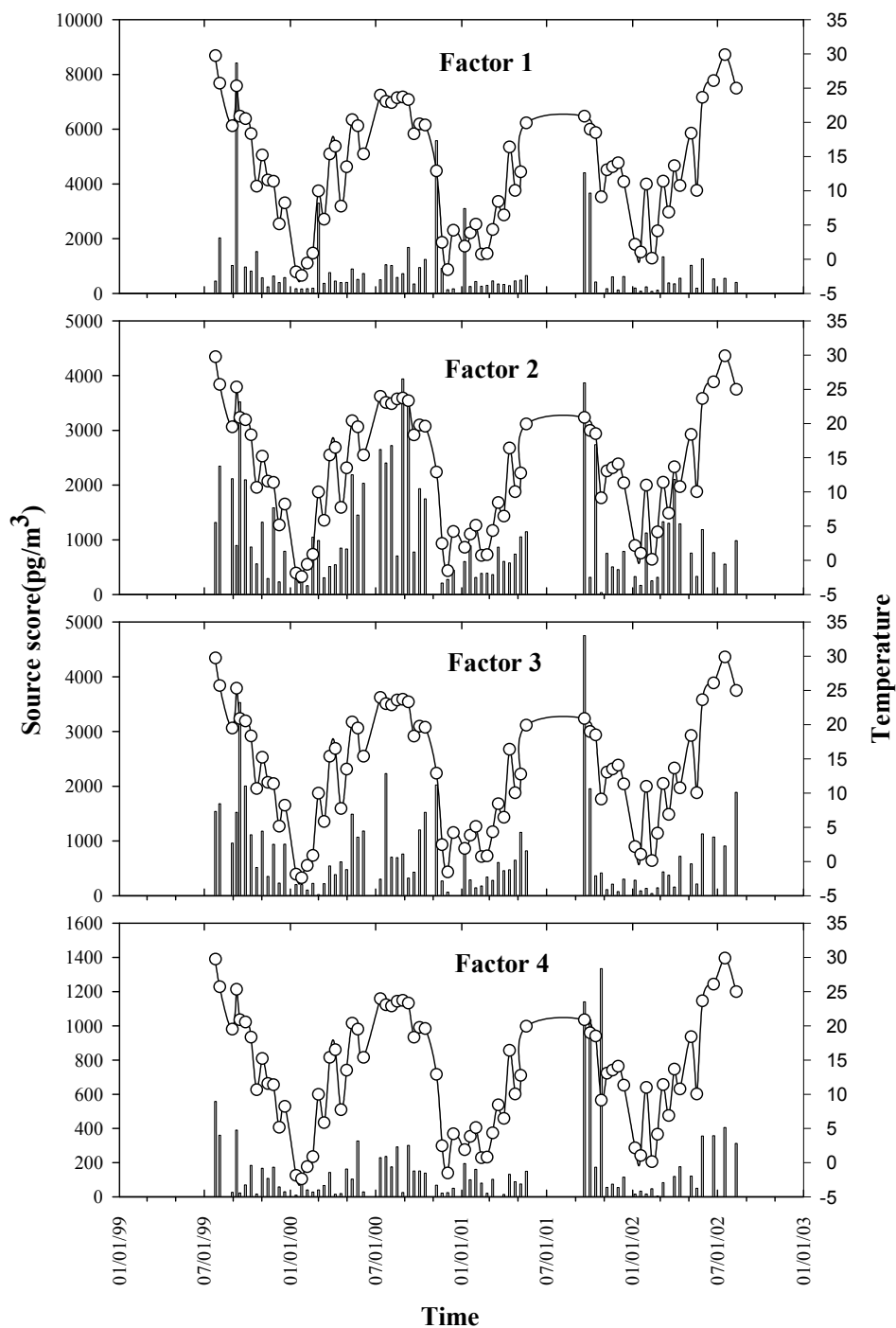


Figure. 2.3. Daily source contribution of the resolved factors (bars, left scale) and daily temperature (circles, right scale).



background. This strong gradient in PCB concentrations suggests that the atmospheric PCBs at Camden arise from highly localized, urban sources which influence atmospheric concentrations and deposition fluxes over a distance of a few tens of km (Totten et al. 2004). Thus the sources of PCBs to Camden lie within about 50 km of the receptor site, and high probability points in the PSCF plots that lie more than 50 km from Camden are not likely to represent source regions, and instead probably represent the projection of local sources outward, a problem inherent in the PSCF model. This problem is exacerbated by the use of 24-hour composite air samples. Because meteorological conditions, including wind direction, change significantly over this time frame, the use of 24-hour samples limits the utility of the PSCF model. Thus the PSCF maps should be viewed with caution.

The PSCF maps for  $\Sigma$ PCBs and the resolved potential source factors are shown in Fig. 1. In the same way that  $\Sigma$ PCBs were normalized for temperature in order to determine which samples were above the criterion value, the factors were also normalized to a constant temperature (25°C) in constructing their PSCF plots, although this normalization had only a minor effect on the resulting PSCF plots. After removing the  $\leq 2$  outliers from these temperature regressions, 63 samples were included in the PSCF maps for factors 1-4 (Fig. 2.1). Back trajectories generated at 10, 100, and 500 m showed little variation in the generated PSCF plots. Others have noted that for short range atmospheric transport, the PSCF results were the same regardless of the starting height of the back trajectory (Hsu et al. 2003a). Representative plots utilizing 500 m back trajectories are shown here.

In interpreting these maps it is important to remember that a single high probability grid cell is not very significant, but a cluster of high probability grid cells does indicate a probable source region. Additionally, the PSCF maps do not provide an emission inventory of PCBs but rather show those source areas whose emissions can be transported to the measurement site. A low PSCF score does not necessarily indicate low emissions from the region, rather it may mean that any emissions there are not transported to the receptor site (Hsu et al. 2003b).

The PSCF map for  $\Sigma$ PCBs (Fig. 2.1f) shows high probability points ( $> 0.5$ ) immediately around the receptor site, indicating a strong local source influence from the Philadelphia metropolitan area. The PSCF plots for  $\Sigma$ PCBs also indicate that there are significant sources within NJ contributing to the PCBs measured at Camden, in addition to sources in the city of Philadelphia.

The PSCF plots for the different factors reveal significant differences in source regions. The PSCF plots for factors 1 shows relatively few high probability regions, suggesting that these factors either originate from a high number of low intensity sources (generating a uniformly low PSCF score across the region), or that their sources lie very close to the receptor (Hsu et al. 2003). Factor 1 resembles low molecular weight Aroclors 1016, 1242, and 1248, comprises about 27% of the total PCB burden at Camden, and displays few high probability cells in the PSCF map. We hypothesize that this factor represents the ubiquitous PCB background of any urban area. Since these Aroclors were used in transformers and capacitors (the largest categories of PCB use) as well as a variety of other applications, including heat transfer fluids, carbonless copy paper, and adhesives (Nisbet and Sarofim), it is not surprising that this is factor is a

diffuse source with no obvious source regions. Aroclors 1016, 1242, and 1248 comprised 13%, 51%, and 7% of US Aroclor production between 1957 and 1977 (Brown 1994). Thus combined these Aroclors represent more than 70% of all the PCBs produced in the US, yet only comprise about 27% of the PCB burden at Camden according to this analysis. The reasons for this discrepancy are not immediately apparent.

The PSCF plot for factor 2 indicates sources arise mainly from the urban zone of Philadelphia and Camden. Factor 2 resembles higher molecular weight Aroclors such as 1248 and 1254, and comprises about 41% of the total PCB burden at Camden. Aroclor 1254 was used in caulks and sealants, which are thought to be significant sources of atmospheric PCBs in buildings (Kohler et al. 2005; Herrick et al. 2004). Aroclor 1254 was also used extensively in transformers and capacitors (Nisbet and Sarofim). We hypothesize that this factor represents volatilization of PCBs out of “open” applications such as caulks, adhesives, and plasticizers that were used in the buildings in the Philadelphia/Camden area. This factor probably includes some contribution from “closed” applications, such as transformers and capacitors, which may leak small quantities of PCBs. Aroclors 1254 and 1260 comprised 16%, and 11%, respectively, of total US production between 1957 and 1977 (Brown 1994). Thus it is somewhat surprising that this factor comprises about 41% of the total PCB burden at Camden, especially since factor 3, which comprises another 25%, also contains PCB congeners in the medium molecular weight range. As with the discrepancy between factor 1 and Aroclor 1016+1242+1248 production, the reasons for this discrepancy are not immediately apparent.

In contrast, the PSCF plot for factor 3 shows almost no high probability points within the Philadelphia city limits. The major source areas for factor 3 lie within New Jersey and include the city of Camden and its east and south sides. The string of high probability points extending toward the Chesapeake Bay could be indicative of a source somewhere along this trajectory, which would include the Swarthmore area. This is not surprising considering that the congener pattern of factor 3 is similar to the congener pattern observed at Swarthmore. It is important to note that the PSCF model indicates that the source of factor 3, which comprises 25% of the total atmospheric PCB burden at Camden, probably lies outside of the city limits of Philadelphia and Camden. If the source is indeed near Swarthmore, then the source lies in the Philadelphia suburbs, not the urban center. Although the south side of Philadelphia is not a population center, it is an industrial center, home to several oil refineries and chemical plants, the Philadelphia International Airport, and the Philadelphia Naval Shipyard (closed in 1996). Chester, PA lies south of Philadelphia on the Delaware River and is infamous for housing four hazardous and municipal waste facilities, the fourth largest garbage incinerator in the US, the largest medical waste autoclave in the US, and a sewage treatment plant and sludge incinerator.

Factor 3 does not strongly resemble any single Aroclor. It is most similar to the PCB congener pattern measured at Swarthmore, PA. In a previous publication (Totten et al. 2006), we hypothesized that the PCB signal measured at Swarthmore may be a sampling artifact from the building on which the sampler was placed (Hick's Hall on the Swarthmore College campus). The PMF/PSCF results, as well as results from passive air sampling conducted at multiple locations in the area, indicate that the PCB signal

measured at Swarthmore is not an artifact. Instead, the available information suggests that there is a significant atmospheric PCB source near Swarthmore. The PSCF results indicate that factor 3 originates somewhere SSW of Camden, a trajectory which could, in theory, encompass the “Swarthmore source”. If factor 3 does in fact represent this source, then the source is large enough to contribute 25% of the total PCB burden measured at Camden, 20 km away.

The PSCF plot for factor 4 also shows relatively few high probability cells in the PSCF map as in factor 1. Factor 4 also does not resemble any single Aroclor and comprises about 6.5% of the total PCB burden at Camden and is relatively high in molecular weight. We hypothesize that it represents the particle phase PCB burden, which averages 5% at Camden. If factor 4 does indeed represent the particle phase, this conclusion would make sense, since particles are rapidly scavenged from the atmosphere and are therefore not expected to travel as far as gases.

The general conclusions of this study therefore are: (1) The urban PCB signal at Camden is composed of at least four independent PCB sources or source types that have different congener patterns, temperature functions, and source regions; (2) The major PCB source at Camden appears to be factor 2, which resembles Aroclors 1248 and 1254, and arises primarily from the urban area of Philadelphia/Camden; (3) A secondary source of PCBs at Camden is factor 3, which resembles the PCB pattern observed at Swarthmore and may originate from that general area. The source regions for factors 2 and 3 are very different. Source regions for factor 3 lie primarily in New Jersey and to the southwest of the receptor site; (4) Other sources of PCBs to Camden are more difficult to locate via the

PSCF model, which may indicate that they consist of multiple low intensity sources and/or lie close to the receptor site.

Inasmuch as Philadelphia/Camden can be considered a typical US city, this study suggests that the urban PCB signal is comprised of multiple signals, some of which may come from discrete sources that can be identified and remediated. PMF is a useful tool for source apportionment of the urban PCB signal, but PSCF is of less utility in identifying urban PCB sources due to the mismatch between the proximity of the sources (within ~50 km) and the resolution of the PSCF model. The availability of more samples and samples collected for shorter time periods would increase the utility of the PSCF model, but because PCB analysis is difficult and expensive, this may not be a viable option for many cities.

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## Chapter 3

### **Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia, USA Metropolitan Area**

Du, S., Wall, S.J., Casia, Dawn and Rodenburg, L.A. Passive air sampling for polychlorinated biphenyls in the Philadelphia, USA metropolitan area. *Environmental Science & Technology*. In press.

#### **Abstract**

Passive air samplers were deployed at 32 sites across the Philadelphia metropolitan area to investigate the types and locations of atmospheric polychlorinated biphenyl (PCB) sources in a typical US city. PCB levels varied over a factor of ~30 and displayed strong spatial gradients. Two regions of high PCB levels were observed, one in the center of Philadelphia and another on the city's south side. These two maxima are thought to represent urban vs. industrial sources. A Gaussian diffusion model was found to adequately describe the spatial gradients for the primary (center city) concentration maximum. Higher molecular weight PCBs were more prevalent at the more urban locations, in agreement with other urban gradient studies and suggesting that re-emission (i.e. secondary sources) of PCBs are important. Positive Matrix Factorization (PMF) analysis resolved two factors that are interpreted to represent light Aroclors and a heavier industrial source concentrated at the secondary maximum on the city's south side. The results generally corroborate an earlier study in which data from the NJADN site in Camden, NJ was used to investigate source types and locations. Additionally, the non-Aroclor congener PCB 11 (3,3'-dichlorobiphenyl) was detected in all samples.

## Introduction

Although the production and new use of polychlorinated biphenyls (PCBs) have been prohibited in industrialized regions, they continue to be detected in the atmosphere as a result of emissions from remaining PCB usage (Meijer et al. 2003a; Robson and Harrad 2004) and from environmental surfaces such as soil (Harner et al. 1995). The relative importance of “fresh” versus “recycled” PCB sources is the matter of much debate (Harner et al. 1995; Robson and Harrad 2004). Previous source apportionment studies have attempted to identify atmospheric PCB source types and locations (Du and Rodenburg 2007; Hafner and Hites 2003) but they have not been able to pinpoint source locations and have generally only identified the Aroclors responsible for atmospheric PCB emissions, not the usage categories. Pinpointing source locations has proven difficult because these studies have relied on data from a small number of sampling locations. In the present study we attempt to differentiate between “urban” and “industrial” PCB sources. We define urban sources as those that are primarily a function of population density, which would include transformers and capacitors as well as PCBs in building materials (caulks, paints, insulators, fluorescent light ballasts, etc.) (Herrick et al. 2004a; Kohler et al. 2005b). In contrast, we define industrial sources as those that are related to a specific industrial process and therefore are not necessarily present in all urban areas and whose use was not necessarily related to population density. An example of an industrial source could be the use of Aroclor 1242 in the manufacture of capacitors that occurred at the General Electric plants in northern New York state. This process resulted in huge releases of PCBs (U.S. Epa 2002), despite the fact that this area of New York is relatively sparsely populated.

High atmospheric PCB concentrations lead to large atmospheric deposition fluxes that can be important and sometimes dominant sources of PCBs to aquatic systems (Offenberg and Baker 1997a; Totten et al. 2004; Totten et al. 2006b). Estimation of atmospheric deposition parameters for water quality models is usually performed using data on atmospheric POP concentrations from a limited number of active monitoring sites. For example, data collected at twelve New Jersey Atmospheric Deposition Network (NJADN) sites has been used to characterize atmospheric deposition to the NY/NJ Harbor and the Delaware River (Fikslin and Suk 2003; Totten et al. 2004; Totten et al. 2006b). This data demonstrated that PCB concentrations at the urban site of Camden are ~20 times higher than regional background concentrations measured about 45 km away (Totten et al. 2004). It is not clear how such strong gradients should be interpolated between sites within water quality models. This spatial heterogeneity is also of concern for predicting human exposure (Sioutas et al. 2005) and for tracking down atmospheric sources.

Passive air sampling (PAS) is a cost-effective tool that can provide integrated atmospheric contaminant concentrations over a period of months and assess concentrations in air simultaneously at multiple sites at low cost. PAS has been used to investigate the atmospheric concentration of organic pollutants not only at the local scale (Harner et al. 2004; Harrad and Hunter 2006) but also at continental (Jaward et al. 2004) and global scale (Pozo et al. 2006).

In this study, PAS were deployed at 32 sites across the Philadelphia/Camden area including 5 sites operated under the NJADN. In a recent publication (Du and Rodenburg 2007), we examined atmospheric PCB sources to the Camden NJADN site from the

active air sampling data by using Positive Matrix Factorization (PMF) to identify source types followed by the Potential Source Contribution Function (PSCF) to identify source locations. The passive air sampling described here is a complementary study, designed to overcome some of the limitations associated with identifying local PCB sources using the PSCF approach. The objectives were as follows: (a) to measure and model the spatial variations in atmospheric PCB concentrations in a typical US city, (b) to identify potential source regions, (c) to investigate the relative importance of primary versus secondary and urban versus industrial PCB sources, and (d) to compare the PAS approach to the previous PSCF+PMF approach for identifying PCB source types and locations. In addition, PCBs were quantified using gas chromatography with tandem quadrupole mass spectrometry (GC/MS/MS), which allowed the measurement of non-Aroclor PCB congeners. Specifically, PCB 11 was targeted as an analyte because it was detected in the water column throughout the tidal Delaware River (Du et al. 2008b).

## **Methodology**

**Sample Collection** Passive samples were deployed at 32 sites across the Philadelphia-Camden area (Figure 1a) during April 4-8, 2005 and retrieved during July 11-13, 2005. Table 1 gives detailed site information including coordinates and population density. Two samplers were placed at Swarthmore College, one on the roof of Hicks Hall (site 26), where active air sampling was conducted during 2002, and one nearby on the roof of the newly constructed Science Center (site 27). These two samples should indicate whether the roof of Hicks Hall is a significant PCB source (Totten et al. 2004; Totten et al. 2006b). Most samplers were placed in parks, away from obvious PCB sources. To

dissuade vandals, samplers were usually hung from trees at least 3 meters above street level. Passive samplers were also installed at 5 NJADN sites (Lum's Pond (site 17), Swarthmore (site 26), Northeast Philadelphia Airport (site 22), Camden (site 3), and New Brunswick (site 21)) so that the active NJADN PCB measurements could be used to calibrate the passive measurements, allowing the conversion of the mass of PCBs measured in the passive samplers to approximate concentrations.

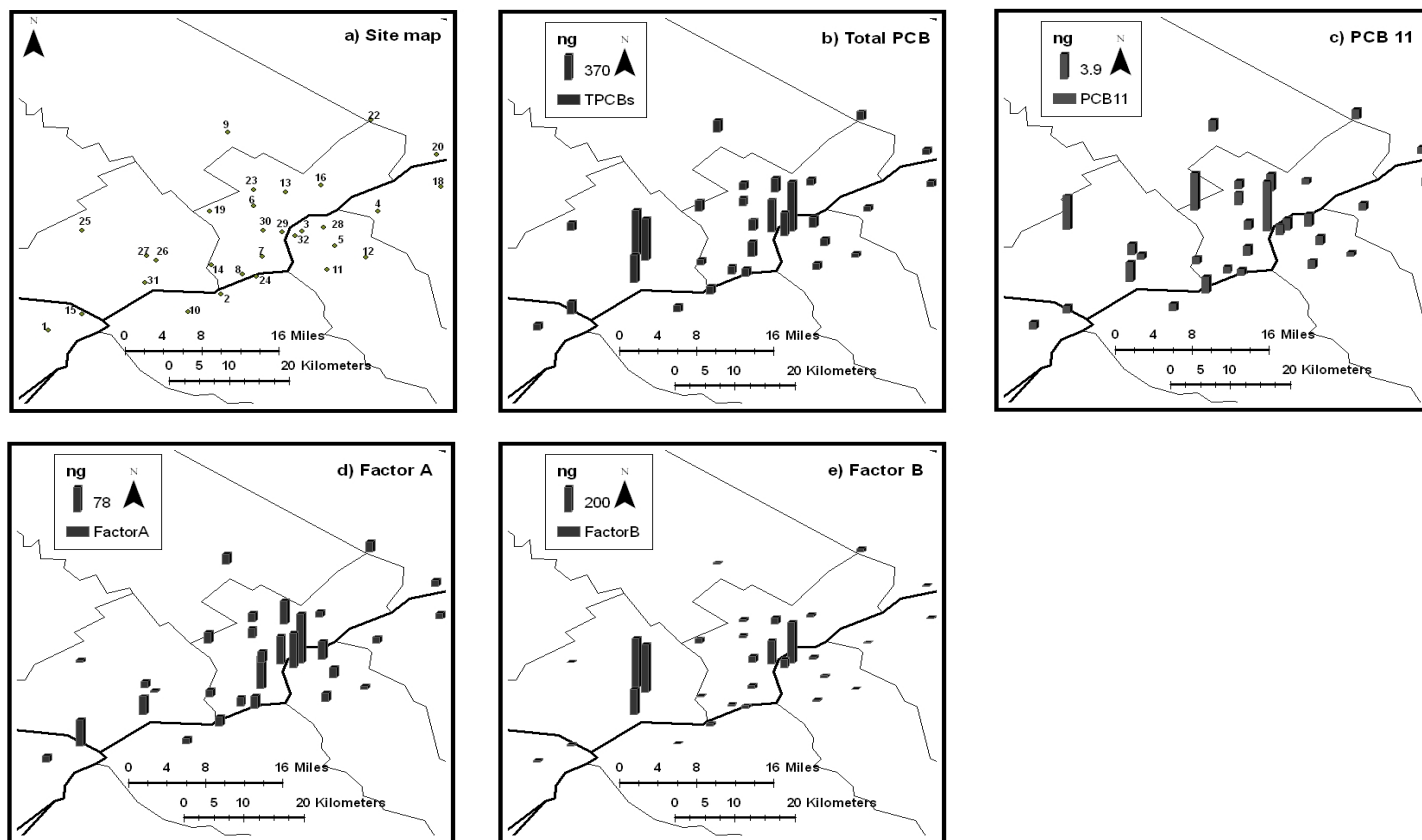


Figure 3.1. Map of the study area. Panel a: map showing sampling sites, with numbers keyed to Table 1. Panels b through e: the spatial distribution of PCBs (ng per sample): total PCBs in panel b, PCB 11 in panel c, and factors resolved from PMF modeling of the congener patterns in panels d and e.



Table 3.1. Information on sampling sites and PCBs (ng) measured at each site.

Site	Site location	Longitude	Latitude	Pop density (people/km <sup>2</sup> )	Σ <sub>97</sub> PCBs (ng)
1	Bellevue State Park	-75.5022	39.7811	709	51
2	Billingsport elementary school	-75.2426	39.8425	1213	75
3	Camden	-75.1212	39.9486	2073	700
4	Cinnaminson	-75.0069	39.9824	952	31
5	Cooper River	-75.0713	39.9244	2347	65
6	Fairmont Park	-75.1945	39.9918	11547	72
7	FDR Park	-75.1807	39.9056	3069	181
8	Fort Mifflin	-75.2112	39.8760	251	61
9	Fort Washington	-75.2327	40.1161	154	68
10	Greenwich Park	-75.2928	39.8121	202	35
11	Hadden Lake Park	-75.0837	39.8842	1959	57
12	Hopkins Pond Park	-75.0255	39.9045	1695	24
13	Hunting Park	-75.1460	40.0154	5988	165
14	John Heinz NWR	-75.2569	39.8915	706	48
15	Knollwood Park	-75.4518	39.8084	1561	152
16	La Salle University	-75.0922	40.0273	2504	65
17	Lum's Pond	-75.7321	39.5514	448	24
18	Mill Creek Park	-74.9123	40.0237	1830	42
19	Morris Park	-75.2595	39.9826	1848	63
20	Neshaminy State Park	-74.9189	40.0785	1779	86
21	New Brunswick (Rutgers Gardens)	-74.4226	40.4728	1960	41
22	Northeast Philadelphia Airport	-75.0176	40.1366	679	60
23	Philadelphia University	-75.1935	40.0194	2126	61
24	Red Bank Battlefield	-75.1895	39.8720	1243	84
25	Ridley Creek State Park	-75.4523	39.9496	155	21
26	Swarthmore (Hicks)	-75.3400	39.9000	1722	586
27	Swarthmore (Science Center)	-75.3552	39.9072	1722	645
28	Von Neida Park	-75.0884	39.9560	3847	103
29	Washington Square Park	-75.1516	39.9474	8230	390
30	Welty house	-75.1790	39.9499	21168	120
31	Widener University	-75.3578	39.8625	4767	373
32	Wiggins Park Marina	-75.1322	39.9413	674	246

The passive air sampling canisters were constructed of two aluminum duct end caps. The top cap was 6" in diameter and fit over the lower 5" diameter cap (Figure 2). The larger upper cap prevents rainwater from getting inside the canister. A cylinder of metal bug screen was placed between the two caps to act as a spacer, to allow good airflow through the canister and to prevent insects from building nests inside. The clean PUFs were prepared as described previously (Brunciak et al. 2001b) and stored in sealed glass jars until deployment. Passive air sampling canisters were washed with soap and water prior to assembly. Immediately before the PUF was placed in the canister, the interior of the canister was rinsed with hexane and allowed to air dry. For most locations, PUFs were placed in the sampling canisters in the field immediately before deployment. For a few locations (Philadelphia University, Northeast Philadelphia Airport, Welty house, and Swarthmore), samplers were assembled in the lab and sent via FedEx overnight to a contact person who deployed the sampler, typically within 48 hours. This approach was used for Northeast Philadelphia Airport due to security restrictions. For this location the canister was stored in a refrigerator for nearly two weeks until deployment. Two trip blanks were sent via FedEx to the Academy of Natural Sciences at Philadelphia, and were returned via FedEx immediately upon arrival. A third trip blank was transported to the field and back during deployment. No PCBs were detected in these blanks, and therefore correction of samples for blank masses was not necessary. The PUFs were ~10 cm tall and ~7.5 cm in diameter with a surface area of 290 cm<sup>2</sup>, similar to the surface area of the PUFs used by Shoeib and Harner (Shoeib and Harner 2002) of 365 cm<sup>2</sup>.



Figure 3.2 . The interior of a disassembled passive sampling canister (top) and the assembled canister (bottom). This design uses no bolts that can rust or come unscrewed, and consists entirely of two aluminum duct end caps, metal bug screen, heavy gage wire, and tie-wraps.

**Analysis** Passive samples were processed as described previously (Brunciak et al. 2001b). They were spiked with PCBs 14, 23, 65, and 166 as surrogates. Each sample was Soxhlet extracted in petroleum ether for 24 h. Extracts were then reduced in volume by rotary evaporation and separated into two fractions on a column of 3% water-deactivated alumina. The fraction containing PCB was concentrated under a gentle stream of nitrogen gas to about 0.5 ml, and injected with internal standards PCBs 30 and 204 prior to analysis.

Analysis of PCBs was performed by a tandem quadrupole GC/MS/MS system (Waters Quattro Micro GC). All chromatographic conditions were as described previously (Brunciak et al. 2001b) for GC analysis with electron capture detection (ECD). Our strategy was to use the same analytical techniques as used previously in our laboratory for ECD analysis, similar to EPA method 8082 (Usepa 2000), but substitute the MS/MS as the detector. This approach has several advantages over EPA method 1668A(Usepa 1999), which uses a high-resolution MS. First, it is much less expensive because the instrument is cheaper and because it does not require  $^{13}\text{C}$ -labeled PCB standards. Second, our method, like 1668A, allows unequivocal detection of all 209 PCB congeners, although some coelute. Third, samples may still be analyzed by GC/ECD as a screening tool before or after GC/MS/MS analysis, because  $^{13}\text{C}$ -labeled PCB standards have not been added to them which would co-elute and interfere with analysis of native (unlabelled) PCBs via ECD. The disadvantages of this method are higher detection limits than method 1668A (but lower than ECD methods). Also, because far fewer surrogates are used, this method may not achieve all quality assurance data objectives. The MS/MS operating parameters for the determination of PCBs are summarized in Table 2. In order

to achieve maximum sensitivity, the two most abundant isotope ions,  $M^+$  and  $[M + 2]^+$ , were monitored and the total ion current (TIC) was used for quantification with the aim of achieving maximum sensitivity.

**Quality assurance** Average percent recoveries ( $\pm$ SD) determined by GC/MS/MS for PCBs 14, 23, 85, 166 were as follows:  $77 \pm 6\%$ ,  $85 \pm 6\%$ ,  $82 \pm 6\%$ ,  $92 \pm 9\%$ . Lab blanks were run with every batch of extraction to check for the contamination from the laboratory or equipment. PCB masses in the three trip blanks and in the lab blanks were less than 5% of the masses in samples, so data were not blank corrected.

**Detection limits** The instrument limits of detection (LOD) for GC/MS/MS were estimated by sequential dilutions of the standard. The lowest concentration giving a peak with a minimum signal-to-noise ratio (S/N) of 3 was defined as the LOD. The LODs were generally higher for the lower molecular weight congeners, and ranged from 0.4 to 0.8 pg. These instrument LODs translated to method detection limits (MDL) of about 80 to 160 pg per passive sampler, which are comparable to those recently obtained by ion trap MS/MS (Malavia et al. 2004; Verenitch et al. 2007). Detector response was linear ( $R^2 > 0.999$ ) over the calibration range (0.4-16  $\text{ng ml}^{-1}$ ).

Table 3.2. GC-MS-MS operating parameters for the determination of PCBs. The MS operating conditions were the following: the temperature of the transfer line was held at 250°C during the chromatographic run. EI source is operated at 200°C with an electron energy of 70 eV and a trap current of 100 A. The MRM mode was operated at an argon collision gas pressure of  $3.0 \times 10^{-3}$  mBar.

Functions	PCBs	Start time (min)	End time (min)	Parent Ion (m/z)	Daughter Ion (m/z)	Dwell (secs)	Collision Energy (ev)
1	Mono-PCB	15	32	188+190	153	0.05	15
2	Di-PCB	15	32	222+224	152	0.05	15
3	Tri-PCB	23	42	256+258	186	0.05	15
4	Tetra-PCB	32	55	289.9+291.9	220	0.05	23
5	Penta-PCB	34	65	323.9+325.9	254	0.05	25
6	Hex-PCB	49	75	359.8+361.8	289.90	0.05	25
7	Hepta-PCB	58	75	393.8+395.8	323.90	0.05	22
8	Octa-PCB	64	76	429.8+431.8	360.0	0.05	22
9	None-PCB	69	77	463.7+465.7	394.0	0.05	22
10	Deca-PCB	77	90	497.7+499.7	428	0.05	22

## Results and Discussion

Masses of  $\Sigma$ PCBs ranged from 21 to 700 ng (Figure 3.1b). Congener specific data is presented in Table 3. The sampled air volume can be derived by plotting the mass of each homologue in the passive samples versus concentrations measured at the 5 NJADN sites (Totten et al. 2004; Totten et al. 2006b). These plots are linear with  $r^2 > 0.89$  (Figure 3). The sampled air volumes ranged from 160 m<sup>3</sup> for tri-PCB to 175, 262, 341, and 349 m<sup>3</sup> for tetra, penta, hexa, hepta-PCB respectively and 224 m<sup>3</sup> for total PCBs (Figure 3). When normalized to the surface area of the PUF media, these sampling rates agree to within 15% of others reported elsewhere (Harner et al. 2004; Shoeib and Harner 2002). Active air monitoring data from the NJADN indicates that average gas-phase PCB concentrations in this region range from about  $\sim 3000$  pg m<sup>-3</sup> at Camden to  $\sim 200$  pg m<sup>-3</sup> at remote sites such as Lum's Pond. Since the highest PCB mass in the passive samplers was measured at the Camden site and the lowest was similar to that measured at Lum's Pond, these concentrations appear to characterize the entire range of PCB levels in this region. Thus although the mass measured in the passive sample is linearly related to atmospheric concentration, in this work we will focus on mass to exclude the uncertainty in the sampled volume from the discussion.

Table 3.3. Measured mass (ng) of the 20 most predominant PCB congeners in passive air samples and PCB 11.

Site	Site location	8+5	11	18	32+16	31	28	21+33
1	Bellevue State Park	1.3	1.1	2.8	1.4	2.0	2.0	1.4
2	Billingsport elementary school	2.0	2.6	3.8	2.0	2.8	2.7	1.8
3	Camden	14.8	1.8	24.6	11.8	20.8	18.5	15.1
4	Cinnaminson	1.4	1.1	2.8	1.4	1.8	2.0	1.2
5	Cooper River	2.2	1.3	4.2	2.0	3.3	3.0	2.1
6	Fairmont Park	1.9	1.9	3.8	1.8	3.0	2.6	1.7
7	FDR Park	9.1	1.5	14.3	6.4	10.1	9.4	7.2
8	Fort Mifflin	1.9	1.0	3.7	1.9	2.7	2.4	1.5
9	Fort Washington	2.5	1.7	4.7	2.0	2.9	2.8	1.8
10	Greenwich Park	1.5	1.1	2.8	1.4	1.8	2.1	1.2
11	Hadden Lake Park	2.3	1.3	4.1	1.9	3.0	2.8	2.1
12	Hopkins Pond Park	0.9	0.6	1.4	0.7	1.0	1.0	0.7
13	Hunting Park	4.9	2.6	9.5	4.7	7.9	7.0	5.3
14	John Heinz NWR	2.1	1.1	3.7	1.8	2.6	2.5	1.6
15	Knollwood Park	7.8	1.1	14.5	6.7	10.3	9.0	6.8
16	La Salle University	1.0	0.8	1.8	0.9	1.5	1.4	0.9
17	Lum's Pond	0.6	1.1	1.4	0.6	1.1	1.0	0.6
18	Mill Creek Park	1.3	1.2	2.6	1.3	1.9	1.9	1.2
19	Morris Park	1.0	6.1	4.5	1.7	4.3	4.1	3.0
20	Neshaminy Park	1.4	1.0	2.9	1.3	2.4	2.0	1.3
21	New Brunswick (Rutgers Gardens)	2.0	1.2	4.0	1.9	3.1	2.9	1.9
22	Northeast Philadelphia Airport	2.0	1.5	3.9	2.2	3.2	3.1	2.1
23	Philadelphia University	2.0	1.2	3.6	1.8	2.8	2.5	1.6
24	Red Bank Battlefield	1.9	1.0	4.7	2.8	3.1	3.4	1.7
25	Ridley Creek State Park	0.8	5.3	1.2	0.5	0.9	0.9	0.6
26	Swarthmore (Hicks)	2.0	0.8	3.8	1.9	3.9	3.4	2.5
27	Swarthmore (Science Center)	2.2	1.7	5.5	2.8	6.2	5.0	3.8
28	Von Neida Park	5.2	1.9	8.6	4.1	6.1	5.6	4.2
29	Washington Square Park	8.2	7.8	14.4	6.6	12.4	10.8	8.3
30	Welty house	3.3	1.4	5.1	2.2	3.7	3.3	2.5
31	Widener university	3.3	3.0	7.8	4.1	8.9	7.3	5.2
32	Wiggins Park Marina	6.6	1.5	15.0	7.5	11.8	11.6	7.6



Table 3.3, continued. Measured mass (ng) of the 20 most predominant PCB congeners in passive air samples and PCB 11.

Site	Site location	52+43	49	44	64	70+76	95	101+90
1	Bellevue State Park	3.2	1.4	1.7	1.1	1.6	2.5	2.5
2	Billingsport elementary school	4.0	1.9	2.4	1.4	2.3	4.2	4.5
3	Camden	41.1	14.6	24.9	12.2	31.6	44.7	51.1
4	Cinnaminson	2.0	1.1	1.3	0.9	1.1	1.4	1.6
5	Cooper River	3.5	1.7	2.4	1.4	2.1	3.1	3.1
6	Fairmont Park	3.9	1.7	2.6	1.5	2.2	3.4	3.7
7	FDR Park	8.2	4.7	6.3	4.0	5.4	5.7	5.8
8	Fort Mifflin	3.6	1.8	2.3	1.5	1.8	3.1	3.0
9	Fort Washington	4.3	1.7	3.1	1.6	1.9	3.2	3.3
10	Greenwich Park	2.0	1.1	1.3	0.9	1.1	1.4	1.6
11	Hadden Lake Park	3.2	1.4	2.2	1.3	1.7	2.5	2.3
12	Hopkins Pond Park	1.4	0.6	0.8	0.4	0.6	1.1	1.1
13	Hunting Park	8.8	4.2	6.0	3.7	5.9	7.9	8.2
14	John Heinz NWR	2.7	1.4	2.0	1.0	1.4	2.4	2.3
15	Knollwood Park	7.7	4.4	6.1	3.7	4.2	4.3	4.3
16	La Salle University	2.3	1.1	1.3	0.7	1.5	2.1	2.8
17	Lum's Pond	1.4	0.8	0.9	0.8	0.7	1.1	1.3
18	Mill Creek Park	2.5	1.1	1.6	0.8	1.4	1.9	2.1
19	Morris Park	7.4	3.4	4.7	3.9	5.7	8.7	7.1
20	Neshaminy Park	2.4	1.4	1.6	1.1	1.5	1.9	1.8
21	New Brunswick (Rutgers Gardens)	3.5	1.9	2.5	1.5	2.0	2.8	2.8
22	Northeast Philadelphia Airport	4.8	2.1	3.2	1.6	3.1	4.6	5.0
23	Philadelphia University	3.6	1.8	2.2	1.3	2.3	3.2	3.1
24	Red Bank Battlefield	5.5	3.0	3.3	2.2	2.4	4.2	4.1
25	Ridley Creek State Park	1.1	0.7	0.7	0.5	0.6	0.8	0.7
26	Swarthmore (Hicks)	28.1	7.2	15.3	5.6	26.6	46.6	58.5
27	Swarthmore (Science Center)	55.0	12.5	26.3	9.6	35.7	61.8	63.7
28	Von Neida Park	5.4	2.7	3.9	2.3	2.9	3.7	3.7
29	Washington Square Park	22.7	8.6	13.9	6.8	16.9	24.7	26.8
30	Welty house	7.0	2.7	4.0	2.0	4.5	7.6	7.5
31	Widener university	26.7	9.8	16.8	9.0	22.2	25.7	26.9
32	Wiggins Park Marina	14.0	7.5	9.8	5.3	8.8	11.4	12.0

Table 3.3, continued. Measured mass (ng) of the 20 most predominant PCB congeners in passive air samples and PCB 11.

Site	Site location	99	87	110	118	149	153	138+163
1	Bellevue State Park	1.1	1.5	2.1	1.4	1.9	1.3	1.4
2	Billingsport elementary school	1.7	2.5	3.6	2.5	2.5	2.1	2.2
3	Camden	17.6	25.5	43.5	31.6	24.8	17.8	21.6
4	Cinnaminson	0.6	0.9	1.2	0.7	0.0	0.0	0.0
5	Cooper River	1.1	2.0	2.6	1.5	1.7	1.4	1.4
6	Fairmont Park	1.3	1.9	2.8	1.9	2.4	1.7	1.6
7	FDR Park	2.2	3.2	4.9	3.5	3.8	3.8	3.6
8	Fort Mifflin	1.0	1.4	2.3	1.3	2.0	1.3	1.4
9	Fort Washington	0.9	1.9	2.4	1.2	0.0	0.0	1.5
10	Greenwich Park	0.6	0.9	1.2	0.8	0.9	0.7	0.7
11	Hadden Lake Park	0.9	1.3	2.1	1.3	1.5	1.1	1.3
12	Hopkins Pond Park	0.3	0.7	0.7	0.6	0.6	0.6	0.4
13	Hunting Park	2.8	4.1	6.9	4.3	5.0	4.0	3.9
14	John Heinz NWR	0.8	1.3	1.9	0.9	1.1	0.9	0.9
15	Knollwood Park	1.6	2.7	3.7	3.2	2.3	1.9	2.9
16	La Salle University	1.0	1.2	2.0	1.6	1.8	1.3	1.6
17	Lum's Pond	0.4	0.4	1.1	0.6	0.9	0.8	0.6
18	Mill Creek Park	0.8	0.8	1.4	1.1	1.4	0.9	0.9
19	Morris Park	2.8	6.8	7.2	0.0	2.1	1.7	1.8
20	Neshaminy Park	0.6	0.9	1.4	1.0	0.8	0.8	1.0
21	New Brunswick (Rutgers Gardens)	1.1	1.4	2.0	1.5	1.8	1.4	1.5
22	Northeast Philadelphia Airport	1.8	2.9	4.5	2.7	2.8	2.2	2.6
23	Philadelphia University	1.2	1.9	2.3	1.5	1.6	1.4	1.5
24	Red Bank Battlefield	1.5	1.8	3.2	1.8	2.2	1.9	1.6
25	Ridley Creek State Park	0.3	0.5	0.5	0.0	0.5	0.5	0.2
26	Swarthmore (Hicks)	19.9	31.4	56.7	42.2	29.0	23.5	27.2
27	Swarthmore (Science Center)	22.5	31.5	54.5	35.7	24.1	17.5	21.0
28	Von Neida Park	1.3	1.7	2.9	1.8	2.1	1.9	1.7
29	Washington Square Park	9.4	13.4	21.9	15.3	13.8	10.8	11.6
30	Welty house	2.6	3.4	5.7	4.5	4.6	3.4	3.8
31	Widener university	10.7	13.8	22.7	15.8	11.4	8.3	9.7
32	Wiggins Park Marina	4.5	5.7	9.9	7.3	7.4	5.9	6.2

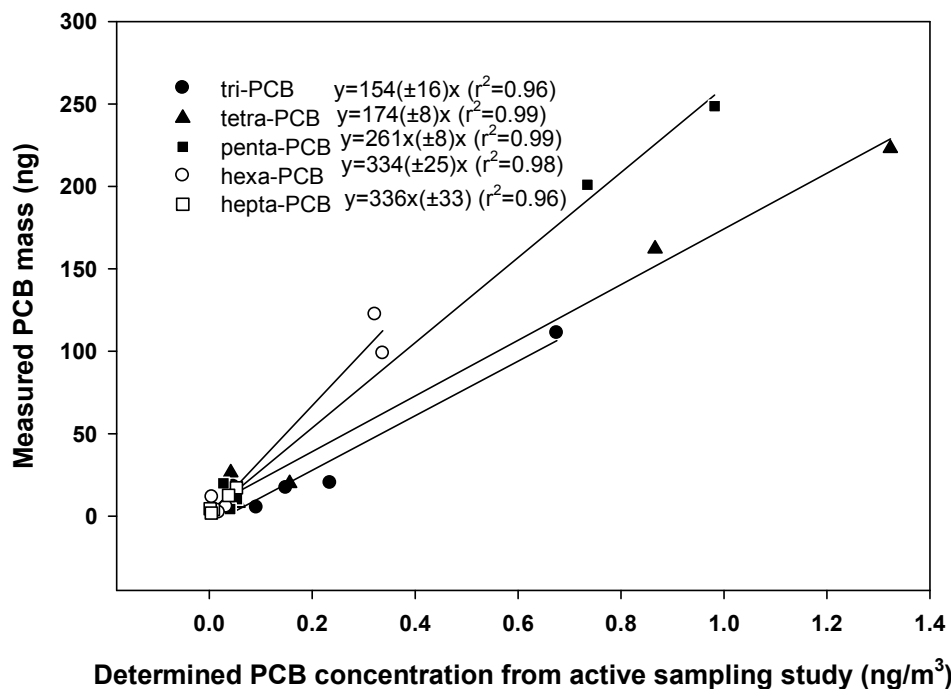


Figure 3.3. Linear regression of measured PCB mass of each homologue group versus the corresponding average PCB concentration determined from NJADN active air sampling. NJADN samples were collected at a 12-day sampling frequency during April – July of 1999-2002. Uncertainties represent 95% confidence limits.

As expected, the samples from downtown Camden (site 3) and Philadelphia (Washington Square Park; site 29) have some of the highest  $\Sigma$ PCB masses of 700 and 390 ng, respectively. Unexpectedly, a secondary PCB maximum was observed south of Philadelphia at Swarthmore (sites 26 and 27) and Widener (site 31), where masses ranged from 586 to 373 ng. The two samples from Swarthmore and the one from Widener University were similar to each other in their  $\Sigma$ PCB masses as well as their congener patterns. In a previous publication (Totten et al. 2006b), we hypothesized that the high PCB signal measured via active air monitoring at Swarthmore may be a result of volatilization of PCBs from the building on which the sampler was placed (Hick's Hall on the Swarthmore College campus). This hypothesis was based on the unique congener pattern and strong temperature dependence of the PCB signal at Swarthmore, as well as the fact that Hick's Hall was extensively renovated in the 1970's, when PCB usage was at its peak. The second passive sampler at Swarthmore College was placed on the roof of their new Science Center, which was constructed in 2002 and therefore should not contain PCB-laden building materials. The sampler at Widener University was also placed on a building constructed after the PCB ban took effect in the mid-1970's. These passive sampling results, as well as results from a recent study of congener patterns and back trajectories in Camden NJADN data (Du and Rodenburg 2007), indicate that the PCB signal measured at Swarthmore does not represent volatilization from the Hick's Hall building material. Instead, the available information suggests that there is a significant atmospheric PCB source near Swarthmore.

We speculate that this "Swarthmore source" is industrial in nature, because the south side of Philadelphia is not heavily populated but is an industrial center. It is home

to several oil refineries and chemical plants, the Philadelphia International Airport, and the Philadelphia Naval Shipyard (closed in 1996). Widener University is located in Chester, PA, a city that is infamous for housing four hazardous and municipal waste facilities, the fourth largest garbage incinerator in the US, the largest medical waste autoclave in the US, and a sewage treatment plant and sludge incinerator (Du and Rodenburg 2007). The elevated PCB levels in the Swarthmore and Widener samples suggest that such industrial sources could be important contributors to the local (within 5-10 km) atmospheric PCB signal.

It is interesting to note that, by sheer coincidence, the two highest PCB masses were measured at two of the NJADN active air monitoring sites (Camden site 3 and Swarthmore site 26). This demonstrates one of the pitfalls of applying air monitoring data from a limited number of sites to calculate atmospheric deposition parameters for nearby waterways. The passive air sampling results suggest that the application of Camden and Swarthmore data over large areas of the nearby Delaware River within the TMDL model (Fikslin and Suk 2003; Totten et al. 2004; Totten et al. 2006b) resulted in significant overestimation of both atmospheric concentrations and deposition fluxes in this region.

**PCB 11** PCB 11 is produced inadvertently during the manufacture of diarylide yellow dye (Litten et al. 2002), which is the primary yellow dye used in printing applications (Barrow et al. 2002). PCB 11 has been detected in water samples throughout the tidal Delaware River (Du et al. 2008b) as well as in the NY/NJ Harbor (Litten 2003). PCB 11 was detected in every passive air sample with masses ranging from 0.64 to 7.04 ng. The

highest mass was detected at Washington Square Park (site 29). Because the NJADN did not measure dichloro PCBs, the sampled air volume of  $160 \text{ m}^3$  for trichloro PCBs was used to calculate that concentrations of PCB 11 ranged from 4 to  $44 \text{ pg m}^{-3}$ . PCB 11 represents 0.14% to 25% of  $\Sigma\text{PCBs}$ , with the highest fraction found at Ridley Creek State Park (site 25). The spatial variation of PCB 11 is not correlated ( $p > 0.05$ ) with any of the other congeners (Figure 1c), as opposed to most other congeners which were correlated with each other and with  $\Sigma\text{PCBs}$ . To our knowledge, only two other studies have reported PCB 11 in the atmosphere. The first measured PCB 11 via passive sampling in Antarctica at concentrations that are relatively high ( $60 \text{ pg m}^{-3}$ ) considering the remoteness of the site and the low temperatures at which samples were collected (Choi et al. 2008). The second study reported PCB 11 in Chicago (Hu et al. 2008), where it was measured by active sampling of the gas phase at concentrations ranging from non-detectable to  $72 \text{ pg m}^{-3}$  (normalized to  $25^\circ\text{C}$ ), in good agreement with the concentrations in the present study.

**Variation of Spatial concentration of PCBs** The spatial concentration pattern is very localized and patchy (Figure 1b). The urban/industrial area of Camden (site 3) displays high gas phase PCB levels which are typical of an urban/industrial area (Miller et al. 2001; Simcik et al. 1997). This local signal is diminished to about half at Washington Square (site 29) and Wiggins Park Marina (site 32) which are 1.3 and 2.6 km from Camden (site 3) respectively. The sharpest decline observed occurred between Camden and Cooper River Park. Over this distance of about 5 km, the PCB masses dropped by a factor of 10.

A similar urban-rural gradient has been observed in other studies. Harner et al. (Harner et al. 2004) observed a 5- to 10-fold decrease in PCB concentrations, ranging from  $\sim 500 \text{ pg m}^{-3}$  in downtown Toronto, Canada to  $\sim 50\text{-}100 \text{ pg m}^{-3}$  at the rural end of the transect about 75 km away (Harner et al. 2004). Similarly, Jamshidi et al. (Jamshidi et al. 2007) deployed passive samplers at 10 locations on a 79 km transect across the West Midland conurbation, at the heart of which is Birmingham, UK. They reported an “urban pulse” in the city center that decreased by nearly a factor of 4 with distance (Jamshidi et al. 2007). None of these studies identified the kind of secondary PCB maximum observed at Swarthmore.

**Spatial distribution of congener patterns** The homologue distributions of PCBs at some representative locations are illustrated in Figure 3.4. PCBs at background sites such as Lum’s Pond (site 17) were dominated by lower molecular weight (MW) congeners. The suburban (New Brunswick site 21) and urban (Camden site 3 and Washington Square site 29) locations are comparatively enriched in higher MW PCBs. Higher abundance of heavier congeners at urban sites has been observed in other studies (Harner et al. 2004; Pozo et al. 2004), indicating potential primary sources at these sites. The lower MW PCBs, which are more volatile, were enriched at the more remote locations. This is consistent with the “urban fractionation” effect observed for the Toronto urban-rural gradient study (Gingrich et al. 2001; Harner et al. 2004), and has been interpreted to mean that fresh sources dominate in the urban zone and aged sources dominate further out.

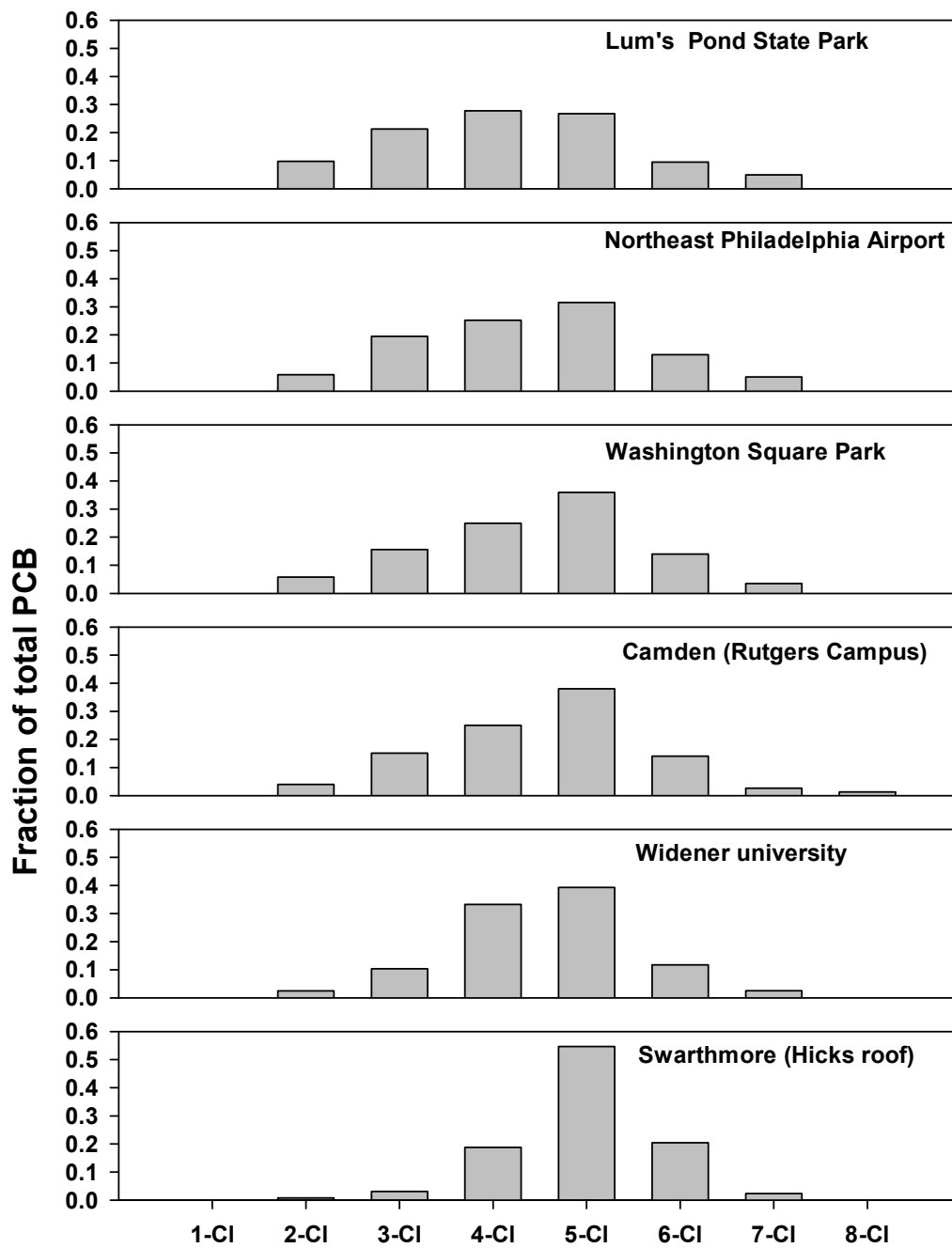


Figure 3.4. Homologue composition of PCBs in passive air samples collected at representative sites.



Hereafter,  $\cos\theta$  is used as a measurement of similarity. A very important similarity measure for multivariate vectors (Davis 1986),  $\cos\theta$  calculates the cosine of the angle between two multivariate vectors, in this case the two  $1 \times 42$  matrixes formed by the 65 congeners used in the PMF model for each factor and the corresponding source to which the factor is compared. 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 PCB congener pattern at Swarthmore (sites 26 and 27) is most similar ( $\cos\theta = \sim 0.92$ ) to Camden (site 3) and Widener University (site 31). Because of the proximity of Swarthmore to Widener, these two sites are presumably influenced by a common source or sources. Data from the NJADN (Totten et al. 2004) also revealed a distinct and heavier congener pattern at Swarthmore.

**Gaussian diffusion model** Previous studies have shown that the variations of the spatial concentration of the inert organic pollutants as a function of distance from the source can be modeled either with a simple radial dilution model (McDonald and Hites 2003; Zhu and Hites 2006) or Gaussian diffusion model (Qiu and Hites 2008), both of which assume a point source and no degradation of the chemical during transport. This model has been used to successfully explain the spatial distribution of toxaphene, brominated diphenyl ethers (BDEs), and dechlorane in North America. We chose to apply this model on the smaller spatial scale investigated here, following the example of Qiu and Hites (Qiu and Hites 2008), where the concentration of the pollutant at location  $i$  ( $C_i$ ) is given by

$$C_i = a_0 d_i^{-(a_1+a_2)} \quad (1)$$

Where  $a_0$  is the fitted constant,  $d_i$  is the spherical Euclidian distance of each sample relative to the source location. The exponent variable ( $a_1+a_2$ ) in theory depends mainly on atmospheric stability and ranges from 1.1 to 2.3 (Klug 1969). Equation 1 is linearized by taking the logarithms of both sides:

$$\log(C_i) = -(a_1 + a_2) \log(d_i) + \log(a_0) \quad (2)$$

The source location and the value of the exponent can be determined by varying the latitude ( $\text{lat}_{\text{sor}}$ ) and longitude ( $\text{lon}_{\text{sor}}$ ) of the source, the constant ( $a_0$ ), and the exponent ( $a_1+a_2$ ) simultaneously such that the following function is minimized (using the Solver feature of Microsoft Excel):

$$\xi_d = \sum [a_0 d_i^{-(a_1+a_2)} - C_i]^2 \quad (3)$$

Modeling mass instead of concentration makes the tacit assumption that the sample volume is constant for all samplers and is included in the fitting parameter  $a_0$ . The input data were limited to sites within 20 km of Camden to exclude the influence of the secondary maximum at Swarthmore. Applying equation 3 to the sum of PCBs results in a source location 1.3 km northeast of the Camden sampling site (39.95466 N, 75.12594 W;  $r^2 = 0.71$ ; Fig.3.5). Using this as the source location, the spatial distribution of each congener was fit to equation 2. The regression was significant ( $P < 0.05$ ) for 37 of 44 congeners (or co-eluting groups). The slopes ( $a_1+a_2$ ) ranged from 0.39 to 0.66 and displayed a significant ( $P < 10^{-4}$ ) correlation with the log of the liquid vapor pressure (Falconer and Bidleman 1994), such that congeners with higher vapor pressures had

shallower slopes. In other words, low MW PCBs are more prevalent in more remote locations, a manifestation of the “urban fractionation effect.”

In all cases, the slopes ( $a_1+a_2$ ) were lower than the suggested range of 1.1 to 2.3 that ideally reflects the typical stability of the atmosphere in the study area during the deployment period (Klug 1969). The lower exponents probably indicate that the major assumptions of the Gaussian model are not met in this data set. We hypothesize that there are two possible reasons for the shallow slopes. First, they may represent multiple primary sources distributed throughout the urban zone (i.e. “sprawl” of sources). Second, the shallow slopes may represent secondary PCB sources, i.e. deposition and revolatilization of PCBs, which serves to lessen spatial gradients. If the low slopes were due solely to sprawl of sources, then all PCB congeners would have similar slopes and/or their slopes would not be a function of the physical-chemical properties of the congeners. The dependence of the slopes on the vapor pressure suggests that secondary PCB sources contribute significantly to PCB levels even within 20 km of the city center. Sprawl of primary sources probably also contributes to the low slopes, but this factor alone cannot explain the observed urban fractionation effect. Even though some of the basic assumptions of the Gaussian Diffusion model are not met in this data set, the model still explains 71% of the variation in the data set for  $\Sigma$ PCBs and therefore is a reasonable empirical method of interpolating atmospheric PCB concentrations in small (~20 km) spatial scales, for example between monitoring sites.

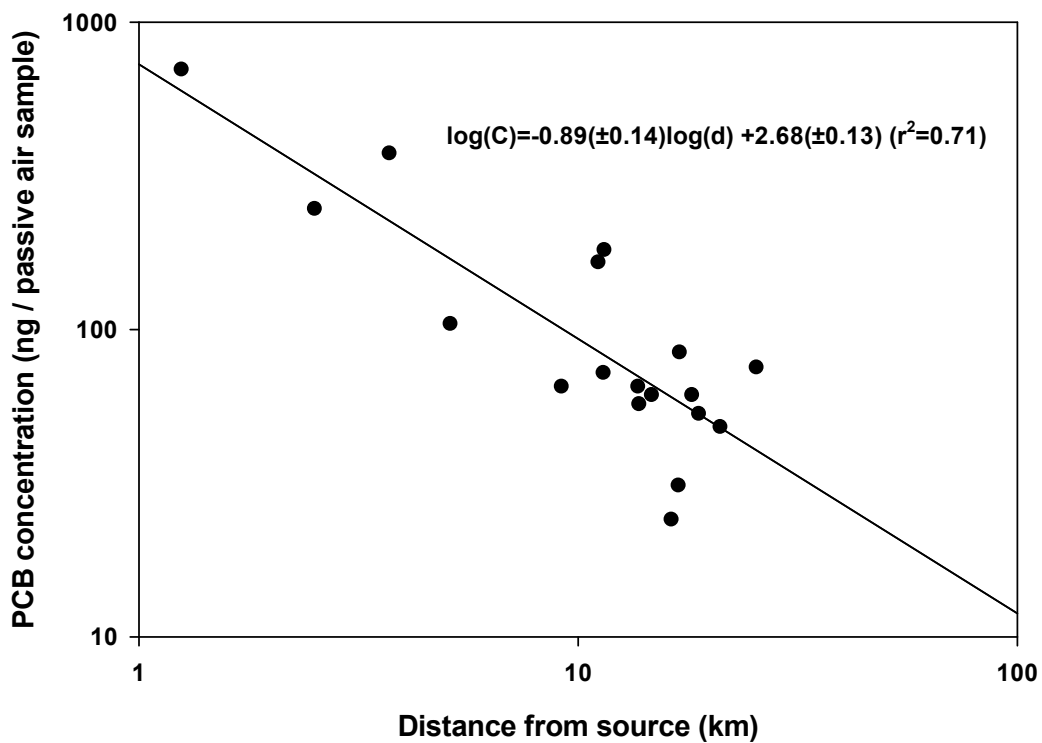


Figure 3.5. Masses of  $\Sigma$ PCBs in passive samples (ng per sample) as a function of spherical Euclidian distance (in km) from the PCB source assuming the source is at a best-fit location ( $\text{lat}_{\text{sor}} = 39.95466$  N,  $\text{lon}_{\text{sor}} = 75.12594$  W), 1.3 km from the Camden site. The uncertainties of the slope and intercept are 95% confidence levels.

**Population density** Population density was calculated by census tract using data from the 2000 census ([www.census.gov](http://www.census.gov)). As noted above, PCB sources that are associated with human activities such as energy distribution and buildings are assumedly correlated with population density, and we choose to label these as “urban” sources. Breivik et al. (Breivik et al. 2002a; Breivik et al. 2002b) used global population density as a surrogate parameter to distribute the national usage and emission inventory data. Meijer et al. (Meijer et al. 2003b) also found significant correlation between PCB concentrations in soil samples and estimated national PCB usage that is calculated by population density. However, the correlation between PCB levels and population density in the present study is weak. The correlation is only significant ( $P < 10^{-4}$ ,  $r^2 = 0.51$ ; Fig.3.6) when five sites are excluded: Camden (site 3), Swarthmore (both sites 26 and 27), Welty house (site 30), and Fairmount Park (site 6). We speculate that the Swarthmore sites are outliers because they are impacted by industrial PCB sources. It is less clear why the other sites are outliers in this plot. We hypothesize that the weak relationship between atmospheric PCB levels and population density may be due to the smaller spatial scale investigated, in contrast to the continental scale covered in other studies (Breivik et al. 2002a; Breivik et al. 2002b; Meijer et al. 2003b). Thus it is not clear that PCB emissions are a direct function of population on this smaller (10’s of km) scale, possibly due to the importance of industrial PCB sources. The correlation between PCB 11 mass and population density was similarly weak (Fig.3. 7).

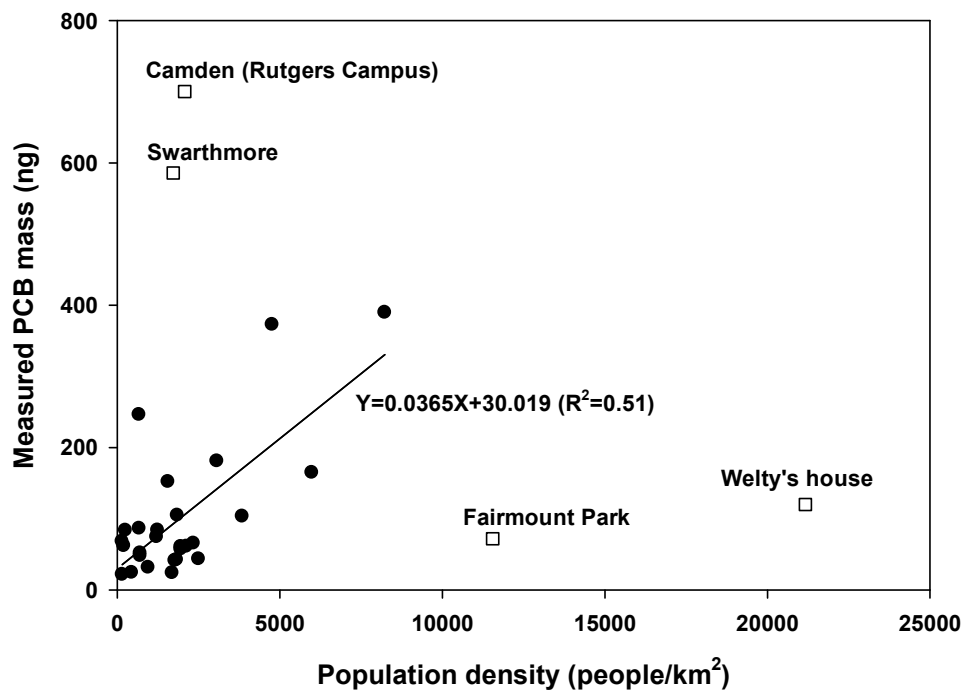


Figure 3.6. Correlation between  $\Sigma$ PCB mass detected in passive samples and population density from the 2000 census. Open symbols are not included in the regression.

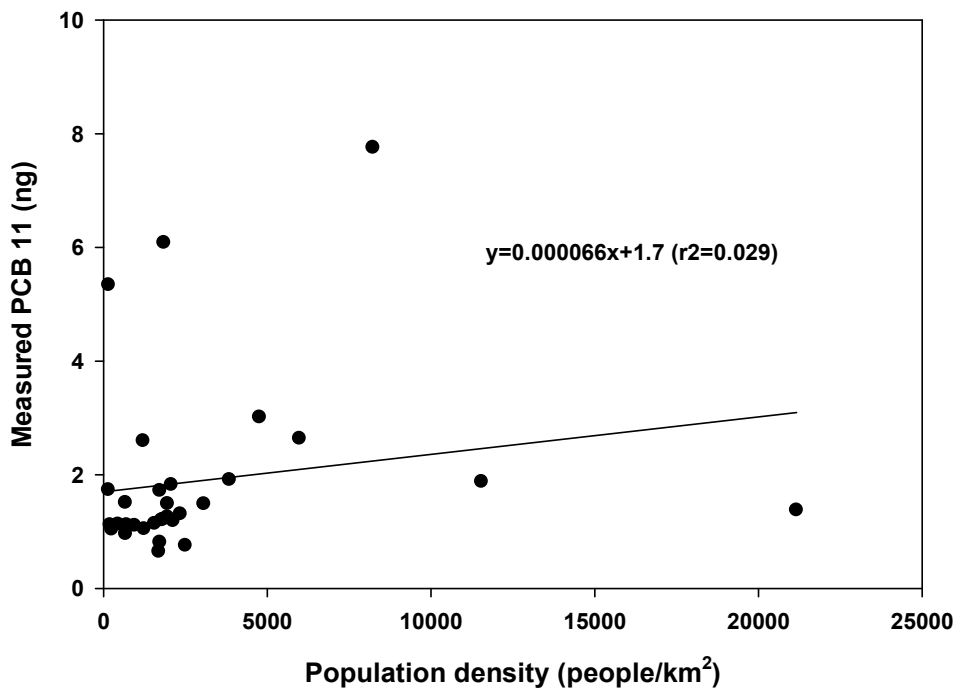


Figure 3.7. Correlation between population density and measured mass of PCB 11 in the passive samples.

**Positive Matrix Factorization** (Paatero and Tapper 1994) was used to identify discrete PCB congener fingerprints in the data set. This was done to identify PCB source types and to allow comparison of this study with earlier work using the Camden NJADN data (Du and Rodenburg 2007). In order to facilitate this comparison, the measured PCB congeners in the present work were composited to mimic the coeluting congener pattern in NJADN data which measured PCBs by ECD. Because 32 samples were available in the present study, the congener list was likewise limited to 32 peaks (50 congeners) for the PMF model input. Two factors were determined for this dataset. The correct number of factors was judged by evaluating goodness-of-fit on a congener-by-congener basis using Miesch coefficient of determination (CD)(Miesch 1976). Given a perfect fit, all data points will plot on a 1:1 slope and the Miesch coefficient of determination will be 1.0. An excellent fit ( $CD > 0.90$ ) was observed for 27 out of 32 PCB congeners when two factors were requested, which indicates that the two-factor model adequately describes most congeners. Not surprisingly, PCB 11 was one of the congeners that was not well described. The interpretation and identification of these factors is based on the congener pattern and the spatial distribution of each factor (Figure 1d-e). Factor A comprised 39% of the  $\Sigma$ PCB mass in the data set, and is similar to the congener profiles of volatilized low molecular Aroclors with  $\cos\theta$  values ranging from 0.83 (for Aroclor 1242) to 0.95 (for Aroclor 1248). Factor B comprised 61% of the  $\Sigma$ PCB mass in the data set and resembles the congener profiles of both the original (unvolatilized) Aroclor 1254 ( $\cos\theta=0.91$ ) and volatilized Aroclor 1254 ( $\cos\theta=0.66$ ). This factor constitutes more than 95% of the PCB signal at Swarthmore (Figure 1e).



Our earlier study of PCB sources in the Philadelphia/Camden area used active air monitoring data from the NJADN collected at the Camden site (52 peaks in 84 samples). The PCB data were collected during 1999-2002 at 12<sup>th</sup> day frequencies using a modified high-volume air sampler. This data was analyzed via PMF to identify PCB source types and then used to construct source probability maps using PSCF. Four PCB factors were identified. Factor 1 was interpreted as a volatilized lower MW Aroclor, such as 1242 or 1248, and comprised 27% of total PCB mass. Factor 2 (41% of  $\Sigma$ PCBs) was thought to represent a volatilized higher MW Aroclor, such as 1254 or 1254+1248. Factor 3 (25% of  $\Sigma$ PCBs) was identified as a high MW signal from the Swarthmore area, and factor 4 appeared to be the particle phase (6.5% of  $\Sigma$ PCBs). The Camden study no doubt identified more factors because it utilized a larger data set; if more passive air samples had been collected, the present study would probably have identified more factors. However, no passive air study would be expected to identify a particle phase factor (factor 4), since particles are not well sampled by the passive approach.

Factor A (from the present study) and factor 1 (from the Camden study) are similar ( $\cos\theta=0.90$ ). Factor A appears to be slightly higher in MW than factor 1, but this can be attributed to the higher sampling volumes for heavier PCB congeners in passive air sampling. The two studies are therefore in good agreement in that they both suggest that low MW Aroclors (1242, 1248) comprise a substantial fraction (27 to 39%) of the gas-phase PCBs in this area, and that this source is diffuse and located throughout the region. Factor B is similar to both factor 2 ( $\cos\theta=0.88$ ) and factor 3 ( $\cos\theta=0.90$ ) with the removal of the outlier PCB 66+95. Both studies therefore also suggest that a significant source of high MW PCBs exists near Swarthmore, although the PSCF model used in the

Camden NJADN study was not able to pinpoint its location and instead projected it outward south and west of the city. Additional passive air sampling is underway to try to pinpoint this source.

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## Chapter 4

### Source Apportionment of Polychlorinated Biphenyls in the Tidal Delaware River

Du, S., Belton, T.J. and Rodenburg, L.A., 2008. Source apportionment of polychlorinated biphenyls in the tidal Delaware River. *Environ. Sci. Technol.* 42: 4044-4051.

#### Abstract

The Delaware River, similar to many surface water bodies throughout the United States, is impaired due to polychlorinated biphenyl (PCB) concentrations that exceed the federal water quality standard. A total maximum daily load (TMDL) for PCBs in the Delaware was promulgated in 2003 after construction of a detailed water quality model that relied upon estimated PCB loadings from sources such as wastewater treatment plant effluents, contaminated sites, and tributaries. The purpose of this project was to corroborate this loading estimate by analyzing ambient water column data on PCB concentrations in the Delaware River via Positive Matrix Factorization (PMF) in order to identify covarying congener patterns that are, in theory, associated with sources. The PMF program identified 6 factors (covarying congener patterns) that appear to be associated with sources such as sediment resuspension, contaminated sites, and wastewater effluents and combined sewer overflows (CSOs). PCB 11 was found to be a useful tracer for CSO/wastewater inputs despite the fact that no known dye manufacturers exist in the watershed. This analysis generally corroborates the PCB loading estimate used in the water quality model.

## Introduction

The Delaware River was one of the first water bodies in the US to receive a total maximum daily load (TMDL) for total polychlorinated biphenyls (PCBs). Currently, PCB concentrations in the Delaware river are about 2-3 ng L<sup>-1</sup> in zones 2 and 3 near Camden and Philadelphia (Fig. 4.1), exceeding the water quality criterion established by the Delaware River Basin Commission (DRBC) of 7.9 pg L<sup>-1</sup> by nearly 3 orders of magnitude (Fikslin and Suk 2003). The absence of a single major source of PCBs sets the Delaware apart from most rivers where PCB contamination has been extensively studied and modeled, for example, the Lower Fox (Wisconsin Department of Natural Resources and Usepa 2002; Wisconsin Department of Natural Resources and Usepa 2003) and Hudson Rivers (Usepa 2001). The types of PCB sources important in the Delaware River are probably typical of most urbanized rivers/estuaries in the United States.

In 2003, the DRBC promulgated a Stage 1 TMDL for PCBs in the tidal Delaware River of 380 mg d<sup>-1</sup> (Fikslin and Suk 2003). Refinement of this TMDL is planned. The TMDL was developed based on a detailed water quality model (Fikslin and Suk 2003) that used penta-PCB loading estimates from all potential sources, including atmospheric deposition, point discharges, nonpoint sources, and tributaries. This loading estimate suggests that the current  $\Sigma$ PCB loads are about 60,000 mg d<sup>-1</sup>. Thus substantial reductions in PCB discharges to the river must be made. To determine a reliable stage 2 TMDL, it is essential that the uncertainty in the loading estimates for all PCB homologues be reduced. Also, to implement the current TMDL, PCB emissions must be controlled; therefore, PCB source regions and processes must be identified. This project

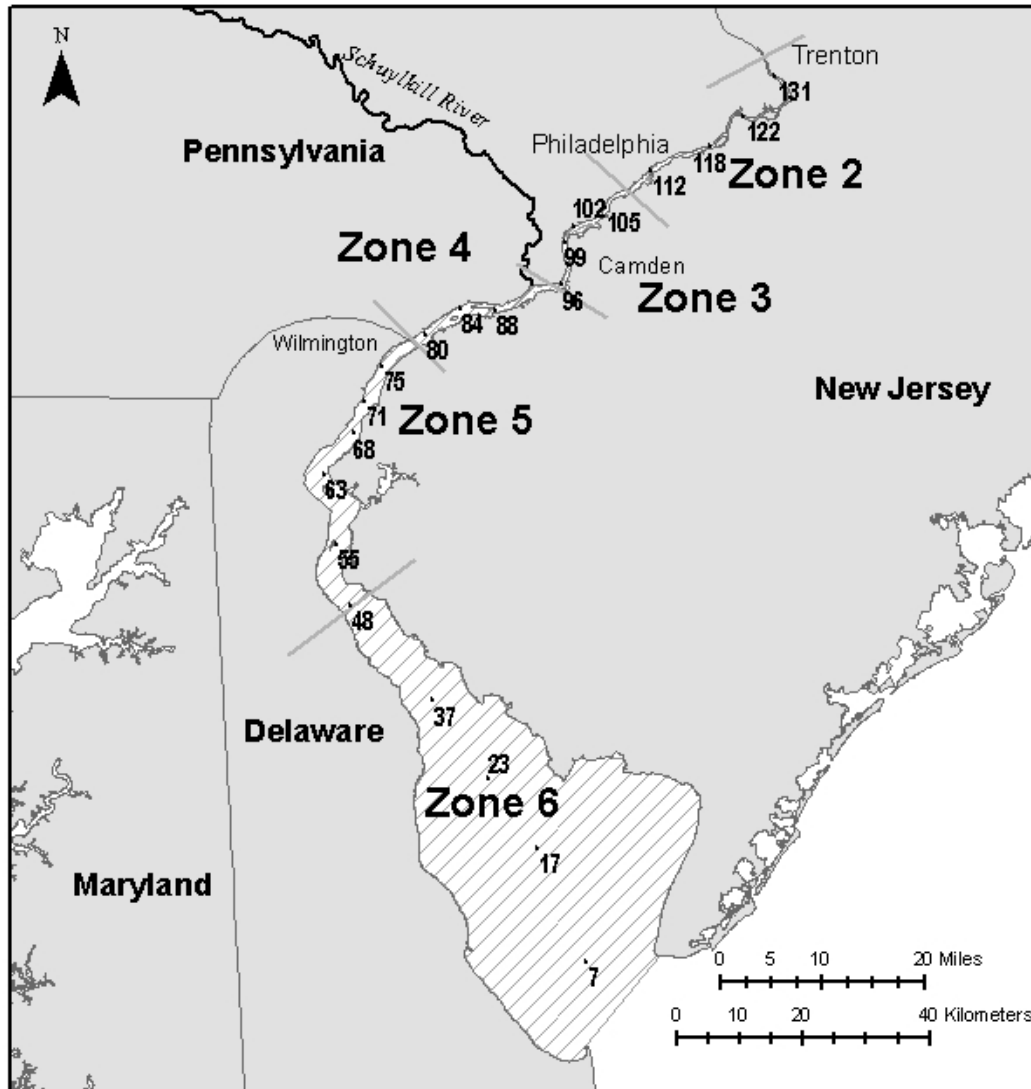


Figure 4.1. Map of the tidal portion of the Delaware River showing water quality zones and sampling locations (dots) designated by river mile. Labels for states are in bold, rivers are in italics, and cities are in plain font.



was designed to address these needs by analyzing the ambient water data via the statistical technique of positive matrix factorization (PMF).

PMF has received wide application as a tool for pollution source apportionment in air resource management (Larsen and Baker 2003; Paterson et al. 1999; Polissar and Hopke 2001), but applications of this technique in the aquatic environment are relatively limited. Recently, PMF has been applied to source identification of PCBs in lake or river sediments (Bzdusek et al. 2006b; Bzdusek et al. 2006c). In these studies, between 32 and 58 PCB congeners were measured in between 32 and 106 samples (Bzdusek et al. 2006b; Bzdusek et al. 2006c). Gigliotti (Gigliotti 2003) applied PMF to PCB patterns in the water column of the NY/NJ Harbor, but because of the small dataset (35 samples and 27 peaks), only three factors were resolved. Another factor analysis method, polytopic vector analysis (PVA), has been used for source apportionment of contaminants such as PCBs and polychlorinated dibenzo-p-dioxins in sediments (Barabas et al. 2004a; Barabas et al. 2004b; Imamoglu et al. 2004; Johnson et al. 2000; Magar et al. 2005). Johnson et al. (Johnson et al. 2000) conducted a source apportionment study on PCBs in San Francisco Bay, applying PVA to a data set of 27 PCB congeners measured in 56 samples. They resolved five end members.

In contrast to PVA or principle components analysis (PCA), PMF takes variable experimental errors into account. Inclusion of experimental errors allows congeners present at both high and low concentrations to be reflected accurately (Bzdusek et al. 2006c). In this study, a larger data set (90 PCB congeners in 140 samples) allowed identification of six factors. The goal of this project was to use PMF analysis of the ambient water data to apportion the sources of PCBs in the Delaware River in order to

corroborate the PCB loads estimated by DRBC for the PCB and to attempt to identify specific PCB sources. The strength of each of these sources was determined in each water sample, and their geographic distribution was examined to reveal the geographical location of PCB sources.

## **Experiment Section**

### ***Sampling and Chemical Analysis***

The initial data set consisted of ~150 samples from the Delaware River, each consisting of a dissolved and a particle phase sample, taken during 13 cruises in 23 ambient water locations and 17 tributary sites (Fig. 4.1). The Delaware River is tidal to Trenton, NJ. For this reason, the Delaware River at Trenton is considered to be a tributary in the TMDL model, and will be referred to as such herein. The ambient water sampling locations will be referred to by river mile (RM). Samples were analyzed for 148 PCB congeners via EPA method 1668A (Usepa 1999). Samples were collected in 20 L stainless steel “pepsi cans” and shipped to Axys Analytical Services in British Columbia, Canada for PCB analysis. 20-L samples were passed through a 0.7  $\mu\text{m}$  quartz fiber filter (QFF) to capture the particle phase and then through a column containing XAD-2 resin to capture the dissolved phase. Samples were analyzed for 148 PCB congeners using a Micromass Ultima high-resolution mass spectrometer coupled to an Agilent 6890 gas chromatography in accordance with EPA method 1668A.

### ***PMF Data Matrix***

The values used in the data matrix were whole-water concentrations, which were calculated by summing the dissolved-phase and particle-phase PCB concentrations. All samples in which both dissolved- and particle- phase PCBs were measured were included in the data set. Both the ambient and major tributary (Delaware at Trenton, Schuylkill) data were included in the model. The reported PCB concentrations were not corrected for laboratory blanks because masses in the blanks were less than 5% of the masses in the samples. If either the dissolved- or particle-phase PCB congener concentration was below the detection limit (DL), then one half the congener-specific DL was used as a proxy. Among the 148 PCB congeners measured, 48 of them were below detection limit in more than 90% of samples. Therefore these congeners were removed from the data matrix. A few congeners (PCBs 5, 7, 10, 89, 181, 204) that were below detection limit in more than 50% of samples were also excluded. The data were further reduced by removal of four PCB congeners (PCBs 14, 63, 81, and 207), which were not reported in the trip or equipment blanks. Most of the excluded congeners were not present in significant amounts in the Aroclors (Rushneck et al. 2004). Three samples were excluded from the data matrix due to high concentrations (above the 95<sup>th</sup> percentile) of most congeners. Another two samples were also identified as outliers since only these samples reported the concentration of those 48 PCB congeners that were not detectable in all the other samples. The final data matrix consisted of 140 samples and 90 congeners (12600 data points).

### **PMF**

The PMF2 software (YP-Tekniika KY Co., Helsinki, Finland) was used in this study. PMF is an advanced factor analysis method, described in detail by Paatero and Tapper (Paatero and Tapper 1994) and briefly summarized here. PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix (eq1).

$$X = GF + E \quad (1)$$

The sample matrix ( $X$ ) is composed of  $m$  observed samples and  $n$  chemical species.  $F$  is a matrix of chemical profiles of  $p$  factors or sources. The  $G$  matrix describes the contribution of each factor to any given sample, and  $E$  is the matrix of residuals. The PMF solution, that is,  $G$  and  $F$  matrices, are obtained by minimizing the objective function  $Q$  through the iterative algorithm shown in eq 2.

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (2)$$

$Q$  is the sum of the squares of the difference (i.e.  $e_{ij}$ ) between the observations ( $X$ ) and the model ( $GF$ ), weighted by the measurement uncertainties ( $s_{ij}$ ).

### *Uncertainty Estimate*

PMF computes the error estimate ( $S_{ij}$ ) for each data point ( $X_{ij}$ ) based on the data point and its original error estimate. The present study utilizes the EM = -14 error model (Paatero 2003a):

$$S_{ij} = t_{ij} + u_{ij} \sqrt{\max(|x_{ij}|, |y_{ij}|)} + v_{ij} \max(|x_{ij}|, |y_{ij}|) \quad (3)$$

Where  $t$  is the congener- and sample-specific detection limit,  $u$  is the Poisson distribution (here designated as 0),  $v$  is the measurement precision,  $x$  is the observed data value, and  $y$

is the modeled value. The option EM = -14 is recommended for general-purpose environmental work (Paatero 2003b). The reason for recommending this alternative instead of the standard EM = -12 model is as follows: EM = -12 computes the relative standard deviation (RSD) as a percentage of the observed value. For a large value (a possible contamination-type outlier), a large RSD is obtained, thus a contaminated value never gets an unduly large weight. But for a small observed value, EM = -12 computes a small RSD, giving the low value an unduly high weight. In such cases, the fitted  $y_{ij}$  is significantly larger than  $x_{ij}$ . The alternative EM = -14 model avoids generating unreasonably small RSD values by taking the larger of  $y_{ij}$  and  $x_{ij}$  as the basis for the uncertainty. For non-outlier data, the choice of error model is unimportant. Thus the alternative EM = -14 is never a bad choice. EM = -12 runs faster than other error models, but this effect is insignificant for the relatively small data set used in the present study.

The uncertainties associated with the measured PCB concentrations include instrumental precision, extraction efficiency, and sampling precision. In previous work (Gigliotti 2003), extraction efficiency was shown to be the most important factor contributing to the uncertainty. Sampling precision and instrument precision were negligible. The uncertainty associated with the extraction efficiency is calculated as the variability in the recovery of the surrogate associated with that congener. In method 1668A, some congeners are associated with more than one surrogate. In these cases, the average recovery for all surrogates used in the quantification of that congener was calculated for each sample, and the standard deviation of these averages over all 140 samples was used for measurement uncertainty. Uncertainties in the dissolved and particle phases were calculated separately and propagated to yield the total error ( $V$ ):

## Results and Discussions

### *Determination of the Number of Factors*

PMF suffers from the same difficulties in determining the correct number of factors as all other forms of factor analysis. It is important to choose the number of factors that provide clear, physically meaningful results while reducing matrix dimensionality as much as possible. If the errors are properly estimated, the calculated  $Q$  value should be approximately equal the number of degrees of freedom or the theoretical  $Q$  value =  $m \times n - p \times (m + n)$ , where  $m$  is the number of samples,  $n$  is the number of PCB congeners, and  $p$  is the number of the factors requested (Bzdusek et al. 2006a; Polissar and Hopke 2001).

The PMF model was run requesting 3 to 9 factors, and each run was initialized with different starting points, that is, changing the seed value from 1 to 10. The appropriate number of factors was determined to be six. The six-factor model produces a  $Q$  value (9317) similar to the theoretical  $Q$ . Fig. 4.2 demonstrates the relationship between the calculated  $Q$  as a function of the number of factors and the theoretical  $Q$ . There is some mismatch between the calculated  $Q$  for the 6-factor model (9317) and the theoretical  $Q$  (11220). A perfect correlation between the two is only expected when the errors are accurately estimated, which is never certain. The actual  $Q$  value is somewhat lower than the theoretical  $Q$ , probably due to overestimated uncertainty in the modeling input. The fit between the modeled total PCB concentrations using 6 factors and the measured concentration yielded  $r^2 = 0.999$ , a slope that is not statistically different from

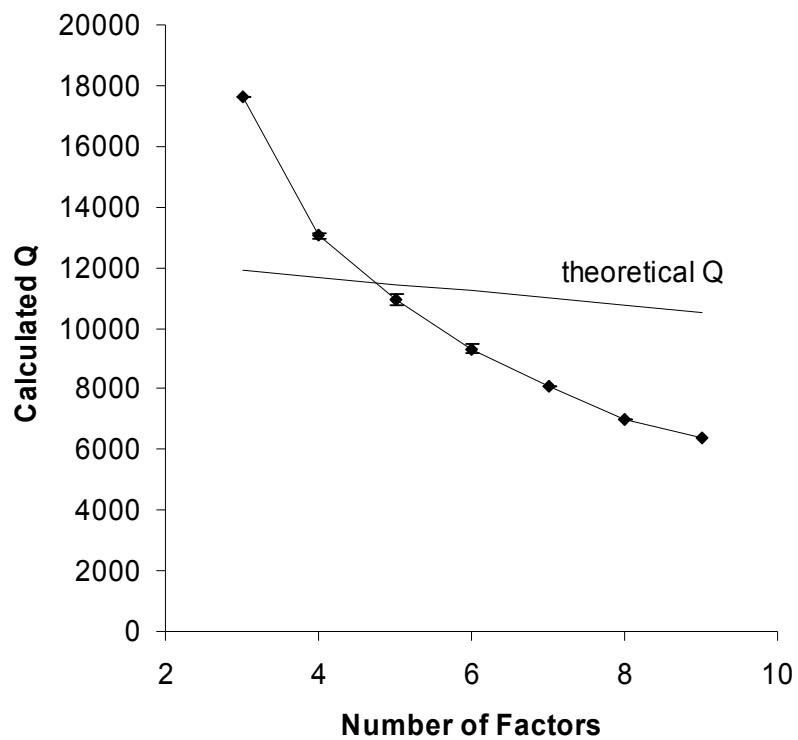


Figure. 4.2. Correlation between the calculated Q as a function of the number of factors and the theoretical Q for six-factor model. Error bars represent one standard deviation.

one, and no significant intercept. This further validates the choice of six factors for the PMF model.

### ***Congener Profiles of Resolved Factors***

The six resolved source profiles (factors) generated by the PMF model are shown in Fig. 4.3. The compositions of the resolved factors are normalized to indicate the percent contribution of each congener to the sum of PCBs. Factors 1 and 2, which comprise about 14 and 5% of the total amount of PCBs measured in the water column, respectively, are dominated by low molecular weight congeners. Factor 3 represents 23% of the total PCB mass in the data set and is dominated by tetra- and penta-PCBs. Factor 5, which accounts for 19% of the PCBs, is dominated by the nona- and deca-chlorinated congeners, PCBs 206, 208, and 209. These congeners are characteristic of the PCB signal inadvertently produced via the carbochlorination process used to produce  $\text{TiCl}_2$  at a plant near Wilmington, DE (Rowe et al. 2007). When these three congeners are removed, Factor 5 and Factor 4 (which constitutes 24% of the total PCBs) are similar ( $r^2 > 0.8$ ) to each other. Factor 6 is dominated by high molecular PCBs, and constitutes 14% of the measured PCBs.

### ***Spatial Variation of the Resolved Factor Scores***

Spatial variations in the resolved factor scores were examined to aid in factor identification. Fig. 4.4 displays the spatial variation in factors scores for three cruises at high (4/2/2003,  $925 \text{ kL s}^{-1}$ ), medium (5/6/2002,  $456 \text{ kL s}^{-1}$ ), and low (3/15/2002,  $164 \text{ kL s}^{-1}$ ) river flow. The contributions of Factors 1, 3, and 4 display little spatial variation under all three flow regimes, characteristic of universal sources affecting the



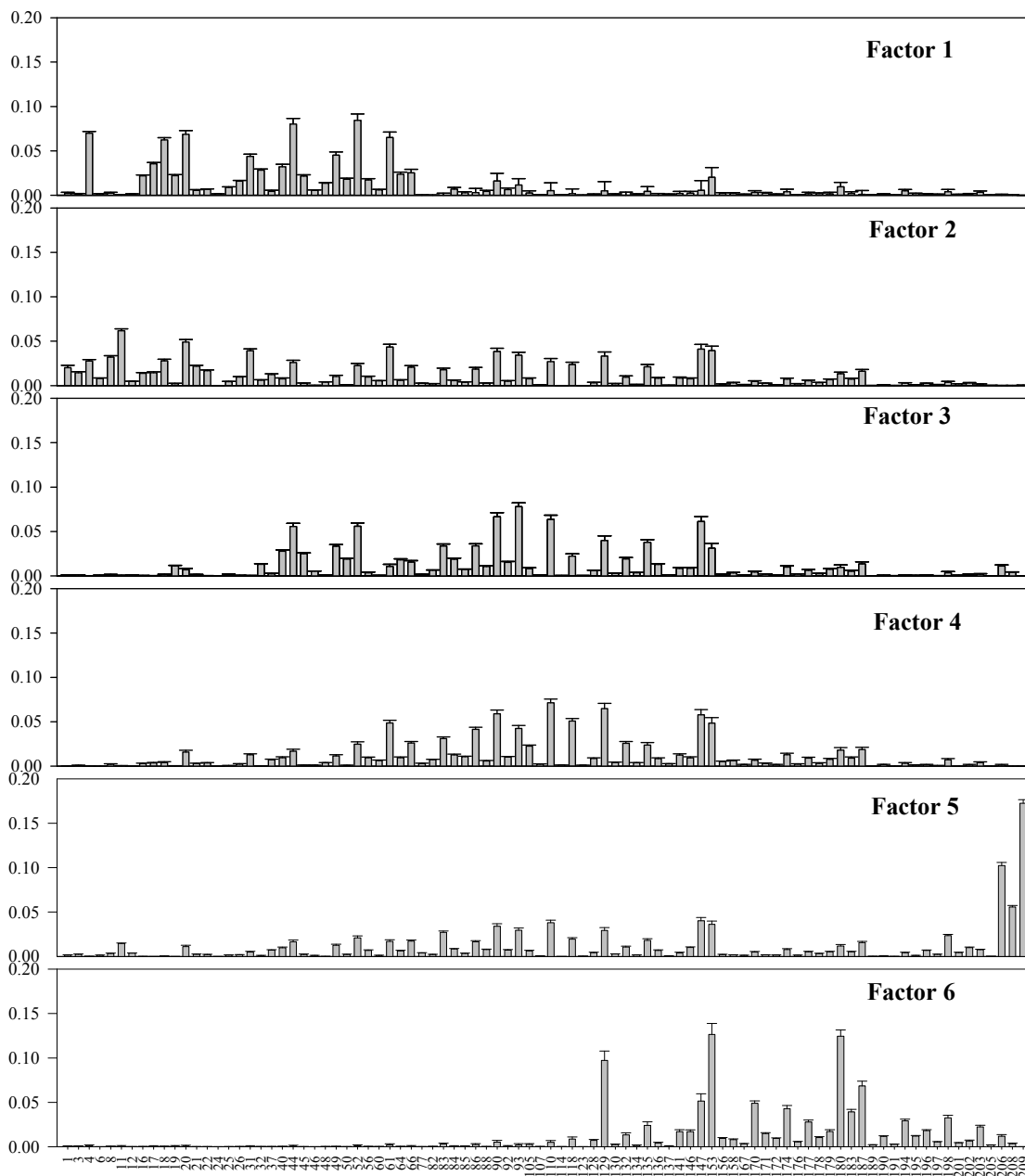


Figure 4.3. Normalized congener patterns of the six resolved source profiles (factors). PCB congener numbers on the x-axis are plotted vs. their fractional contribution to the sum of PCBs on the y-axis.

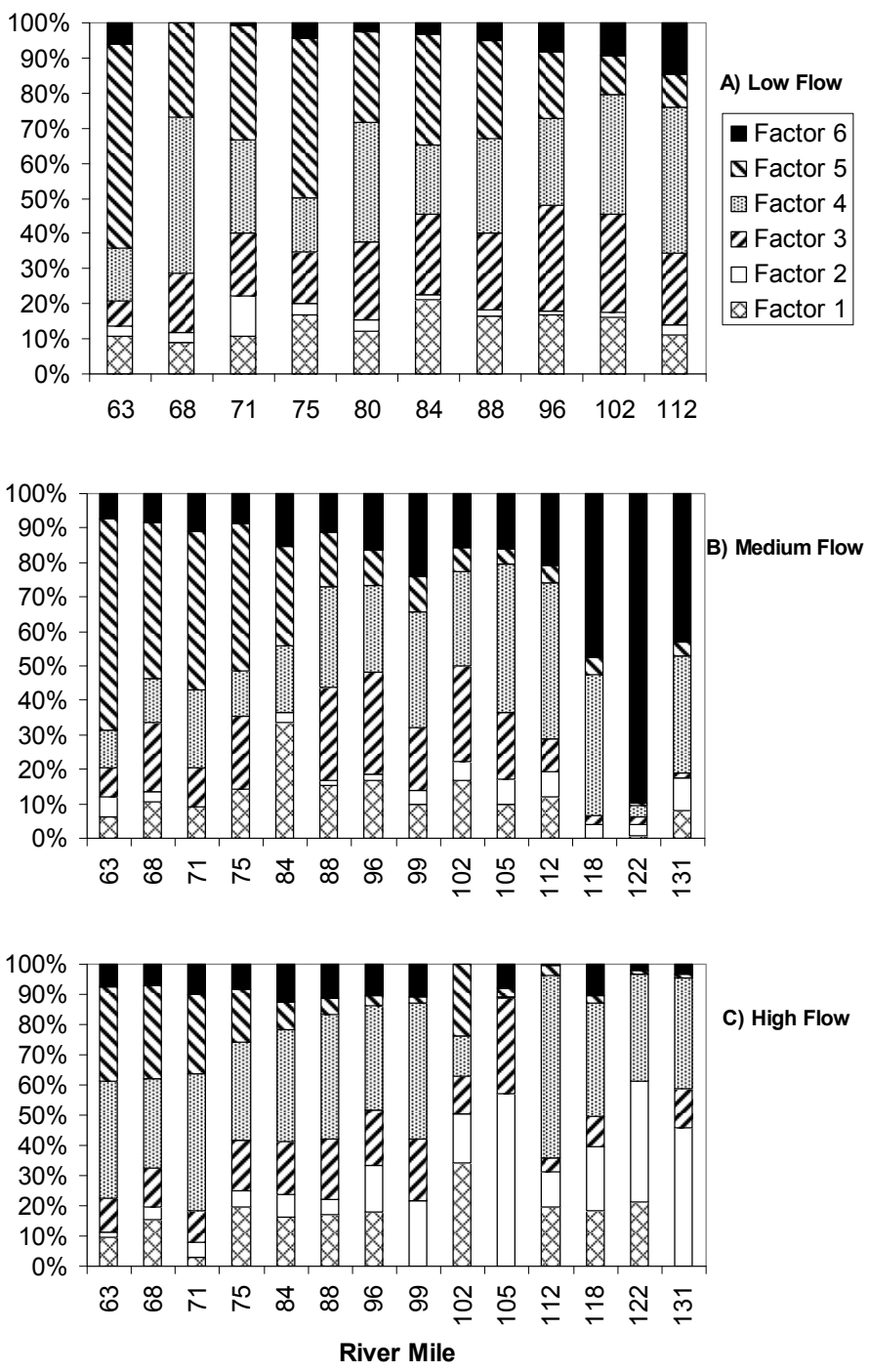


Figure. 4.4. Spatial variation of the relative contribution of the resolved factors in different flow conditions: (A) low flow; (B) medium flow; (C) high flow. River flow is from right to left.

whole river. Factor 2 contributes a relatively small fraction of the sum of PCBs at most of the sampling sites under both low and medium flow conditions. In contrast, its contribution is higher at upstream sites under high flow, reaching ~50% at RM 105 and RM 131. The contribution of Factor 5 increases downstream and is lessened at high flow (Fig. 4.4). This pattern is consistent with Factor 5 originating in the southern portion of the River. Conversely, the contribution of Factor 6 is highest upstream. This increasing trend in the upstream direction is most conspicuous at medium flow conditions. During medium flow, Factor 6 is the dominant source of PCBs in zone 2, constituting about 90% of the PCBs at RM 122 and ~50% at RM 112 and RM 118. The location is surprising since these sites are all well north of the largest urban center on the river, Philadelphia (about RM 100). This may indicate a large point source of PCBs near Trenton.

### ***Temporal Variations of the Resolved Factor Scores***

Another source of information that could aid in factor identification is their variation over time. For example, it would be extremely useful to know if individual factors were increasing or decreasing in strength over the course of the data collection period, which lasted more than one year. In practice it is difficult to determine whether variations in source strength result from the passage of time or from the changes in flow observed in the River, because high flow events were sampled during the last few sampling cruises. Fig. 4.5 shows the variations in the contributions of the various factors over several cruises, with the flow regime (low, medium, or high) designated by the letter above each bar (L, M, or H, respectively) for one sampling site (RM 96 in Zone 3) where the most complete data set is available. Fig. 4.5 demonstrates that the contribution of

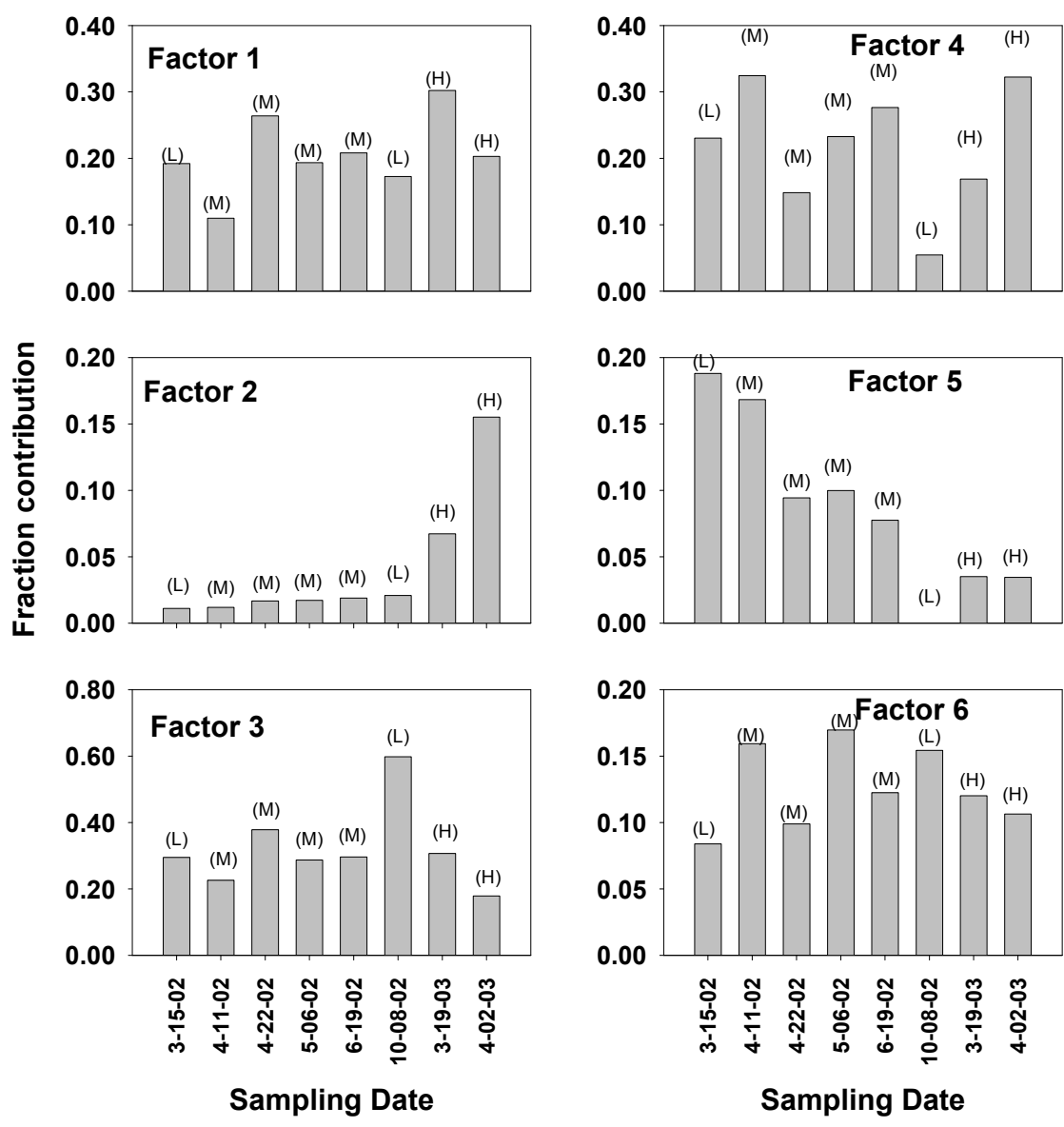


Figure. 4.5. Temporal variations of factor scores at River Mile 96 at high (H), medium (M), and low (L) river flow.

Factor 2 increases substantially over time, but this may be due to the higher flow conditions sampled in March and April of 2003. The opposite trend is observed for Factor 5, with the relative contribution diminishing over time and/or under high flow conditions. The same trends were observed at many of the other stations. In contrast, no obvious effect of flow condition or time on the proportional contribution was observed for the other factors.

### ***Identification of the Resolved Source Profiles***

We have attempted to identify the factors by a “weight of evidence” approach, using the information on their spatial variations presented above as well as comparison of the congener patterns of the factors with congener patterns from suspected sources, including Aroclors, sediment, and tributaries. Many methods have been developed to attempt to identify the original source Aroclor contamination in environmental field samples. These include the least square mean approach (Sather et al. 2001), characteristic ratio approach (Karcher et al. 2004; Newman et al. 1998), and the cosine similarity measurement (Magar et al. 2005). However, pattern matching remains a subjective process since no established consistent congener list exists, and the various criteria used by the analyst cause many uncertainties. The cosine theta similarity metric ( $\cos\theta$ ) is used here (Table 3.1). This metric calculates the cosine of the angle between two multivariate vectors (Davis 1986) and 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 ( $\cos\theta = 0$ ).

### *Comparisons with Aroclors*

Implicit in the comparison of the factor congener patterns with Aroclor congener patterns is the assumption that weathering processes have not substantially altered the PCB congener profile in the environmental samples. Weathering processes can include chemical, physical, and biological degradation, including anaerobic dechlorination. Aroclor compositions were taken from high resolution GC/MS analysis of the Aroclors of Rushneck et al. (Rushneck et al. 2004), in which multiple lots of nine different commercial Aroclors (A1221, A1232, A1016, A1242, A1248, A1254, A1260, A1262, and A1268) were analyzed by the same method as the samples. Despite the similarity in analytical methods, it was still necessary to composite some of the congeners and eliminate others to enable a comparison between the Aroclor data and the Delaware River data because of slight differences in the way the data was reported. During initial comparisons of factor and Aroclor congener fingerprints, three congeners were consistently found to be outliers: PCBs 61, 86, and 129. These congeners co-elute via method 1668A with other congeners: PCB 61 co-elutes with 70, 74, and 76; PCB 86 co-elutes with 119, 108, 97, 125, and 87; and PCB 129 co-elutes with 138, 163, and 160. Due to uncertainties in their identification and their high residuals in the Aroclor regressions, these three congeners were not used in the comparison. As a result, 71 PCB congeners were included in the comparison with Aroclors.

Each factor bore some similarity ( $\cos\theta > 0.79$ ) to at least one Aroclor (Table 4.1). The best Aroclor/factor match occurred for Factor 6, which closely resembles Aroclor 1260 ( $\cos\theta = 0.97$ ). This may indicate a source of Aroclor 1260 near Trenton (about RM 135). We also constructed a chemical mass balance of the factor profiles assuming they

Table 4.1. Cosine theta ( $\cos\theta$ ) values for comparisons of resolved source profile congener patterns with Aroclor (A), sediment and tributary congener patterns. If PCBs 206, 208 and 209 are excluded,  $\cos\theta$  between the average sediment profile and factor 4 is 0.95.

	A1242	A1248	A1254	A1260	Sediment profile	Delaware tributary (dissolved phase)	Delaware tributary (particle phase)
Factor 1	0.79	0.84	0.55	0.14	0.44	0.62	0.38
Factor 2	0.69	0.56	0.47	0.40	0.59	0.72	0.70
Factor 3	0.40	0.72	0.82	0.38	0.66	0.98	0.80
Factor 4	0.37	0.56	0.84	0.71	0.72	0.85	0.88
Factor 5	0.10	0.16	0.22	0.22	0.92	0.51	0.74
Factor 6	0.01	0.02	0.38	0.97	0.53	0.42	0.70

consist of linear combinations of Aroclors 1242, 1248, 1254, and 1260 (Totten et al. 2006c). The results (Table 4.2) demonstrate that all but factors 2 and 5 can be reasonably well (74 - 89%) described as a linear combination of Aroclors. The Aroclor correlation is especially strong for Factors 1 and 6. We speculate that this strong correlation may indicate that these sources have undergone minimal weathering. In contrast, even after removing congeners 206, 208, and 209 from the correlation, Factor 5 has only a marginal similarity to the Aroclors (40%). We speculate that this marginal similarity means that the process that produces PCBs 206, 208, and 209 also produces a variety of other PCB congeners in a non-Aroclor pattern or that the other congeners associated with Factor 5 have undergone substantial weathering. Despite the similarity between Factors 4 and 5, Factor 4 is better described as a linear combination of Aroclors (74%). Even when two outliers (PCBs 11 and 153+168) are removed from the data set, Factor 2 is not well-described as a linear combination of Aroclors, which may indicate that this source has undergone substantial weathering.

PCB 11 (3,3'-dichlorobiphenyl) is an unusual, and therefore informative, congener. PCB 11 accounts for 9.3% of Factor 2 and 2.0% of Factor 5 despite being virtually absent in the Aroclors. PCB 11 is an inadvertent product of the manufacture of diarylide yellow pigment (Litten et al. 2002). This dye is used in paints, plastics, printing inks, textile printing, and paper and is the dominant yellow pigment used in printing ink applications (Barrow et al. 2002). PCB 11 is a particular problem in the NY/NJ Harbor, where a load of nearly  $100 \text{ kg y}^{-1}$  of this congener alone is thought to enter the Harbor



Table 4.2. Chemical mass balance model best-fit descriptions of each factor as a combination of Aroclors.

Aroclor	Factor 1	Factor 2	Factor 2*	Factor 3	Factor 4	Factor 5**	Factor 6
1242	36%	39%	48%	0%	0%	0%	0%
1248	33%	0%	0%	28%	17%	10%	0%
1254	20%	0%	0%	46%	28%	12%	0%
1260	0%	0%	0%	0%	28%	17%	87%
sum	89%	39%	48%	74%	74%	40%	87%

\* When PCBs 11 and 153 are excluded.

\*\* When PCBs 206, 208, and 209 are excluded

from a single wastewater treatment plant in northern New Jersey (Litten et al. 2002; Totten 2005a). The Toxics Release Inventory (USEPA 2007) lists no dye manufacturers in the Delaware River watershed that release 3,3'-dichlorobenzidine, 3,3'-dichlorobenzidine dihydrochloride, or 3,3'-dichlorobenzidine sulfate, all intermediates in the production of diarylide yellow. Thus we speculate that PCB 11 enters wastewater treatment plants in the Delaware River basin via the use of diarylide yellow in consumer goods such as printed paper. The high contribution of this congener in Factor 2 may then indicate that this factor is associated with wastewater treatment plant (WWTP) effluents. Although congener-specific PCB data is not available, data on PCB homologue levels in effluents from WWTPs in the Delaware River basin show high levels (as high as 22% of total PCBs) of dichloro PCBs. Factor 2 accounts for only a small fraction of the overall PCB loading to the River during low and medium flow, in keeping with the DRBC's estimate that wastewater treatment is a relatively minor source of penta-PCB to the River (Fikslin and Suk 2003). However, at high flow (Fig. 4.4), this factor dominates the total PCB loading in the northern part of the River around Philadelphia. Thus we hypothesize that Factor 2 represents wastewater and (under heavy flow) combined sewer overflow (CSO) inputs of PCBs to the River from the Philadelphia/Camden area. A linear combination of Aroclor congener profiles provides only a 39% match to the congener pattern of Factor 2. We speculate that this mismatch may be the result of weathering occurring during travel through the wastewater collection and treatment system.

Ferric chloride was produced via the same carbochlorination process that results in the inadvertent production of PCBs 206, 208, and 209, and was reportedly sold to

water treatment plants in Philadelphia as a flocculant. This may explain the association of PCB 11 with Factor 5.

#### *Comparison with the Sediment Profile*

PCB-laden sediments are likely to serve as a long-term source of PCBs to the Delaware River via resuspension. The TMDL model suggests that at least 40% of the mass load of PCBs to the water column comes from sediment resuspension under current loadings (Suk, #205). DRBC conducted extensive sampling of the surface sediment throughout zones 2-5. Congener specific analysis was conducted on these samples via EPA Method 1668A. Significant similarity was found between the resulting average sediment PCB profile and the congener patterns of resolved Factors 5 ( $\cos\theta = 0.92$ ) and 4 ( $\cos\theta = 0.95$ ) when PCBs 206, 208, and 209 are removed, demonstrating that sediment resuspension is an important source of PCBs to the water column.

Normally a high molecular weight factor such as Factor 6 would be strongly associated with the sediments, but there is little similarity between Factor 6 and the average sediment congener profile. Thus, we speculate that there is a source of Aroclor 1260 near RM 122 that is relatively unweathered and is not associated with the sediments. The source may be an input of fresh Aroclor 1260, such as a contaminated site.

#### *Comparison with tributary samples*

Factor 3 strongly resembles the PCB profile measured in the dissolved phase in the Delaware River north of Trenton ( $\cos\theta = 0.98$ ). The loading estimate of DRBC

suggests that the Delaware above Trenton contributes about 7% of the penta-PCB loads to the tidal River, which is less than the ~23% of the total PCBs that Factor 3 represents. In addition, it must be remembered that Factor 3 appears to be dissolved-phase only, and the Delaware at Trenton also contributes a suspended sediment load to the tidal Delaware.

Factor 4 is most similar to the particle-phase PCB profile measured in the Schuylkill River ( $\cos\theta = 0.93$ ). It is also similar to the particle-phase PCB profile of the Delaware above Trenton ( $\cos\theta = 0.88$ ). Factor 4 does not demonstrate the kind of strong spatial variation that would be expected if it were associated solely with either the Delaware or Schuylkill tributaries. As noted above, Factor 4 is also very similar to the sediment PCB profile in the northern half of the River (and throughout the entire river if PCBs 206, 208, and 209 are excluded). Therefore, we hypothesize that Factor 4 represents the ambient particle-bound PCB burden in the northern part of the River that is *not* impacted by PCBs 206, 208, and 209. Thus, although Factor 4 constitutes about 24% of the total PCBs measured in the River, it is not clear what fraction of this comes from the Delaware at Trenton, the Schuylkill, and other sources in the system.

### ***Summary***

Factor 1 can be explained by a linear combination of Aroclors 1242, 1248, and 1254. We interpret this to mean that although it is an integrated source (comprised of many Aroclors), it is relatively unweathered. This factor displays little variation in intensity with location or river flow. We hypothesize that this factor represents the ambient dissolved phase PCB background. Factor 2 is probably associated with

wastewater treatment plant effluents and CSOs and accounts for 5% of the total PCBs in the River. Factor 3 is very similar to the congener pattern observed in the dissolved phase in the tributary samples collected in the Delaware north of Trenton. It is also similar to a combination of Aroclors 1248 and 1254. It is relatively unweathered and is evenly distributed in space and time. It may represent the dissolved- phase load of PCBs from the Delaware above Trenton; however, this assignment is difficult to reconcile with the fact that this factor only accounts for about 10-20% of the total PCB signal at RM 131. We can only speculate that the sediment associated load of PCBs from the Delaware at Trenton, which may be partially represented in Factor 4, is more significant than the dissolved load. Also, in the ~ 3 miles separating the Delaware at Trenton tributary sampling point and RM 131, PCB inputs from wastewater effluents, sediment resuspension, and the factor 6 Aroclor 1260 source may be sufficient to dilute the contribution of the Delaware at Trenton to ~20% of the total PCB burden.

Factors 4 and 5 are related to sediments, and together make up about 44% of the total PCB signal in the River, in good agreement with DRBC's estimate of sediment resuspension. In agreement with our results, the DRBC's analysis of congener profiles in the surficial sediment indicated that there are two sediment-associated congener profiles in the river that are similar but for the presence of the PCB 209 signal (Yagecic et al. 2004).

Factor 6 strongly resembles unweathered Aroclor 1260 and is predominant in the northern part of the River just south of Trenton. We speculate that factor 6 represents fresh inputs of Aroclor 1260 from a contaminated site near Trenton.

### *Comparison to TMDL loading estimates*

Currently only the loading estimates for penta-PCB are available. The TMDL data collection process demonstrated that penta-PCB represents ~25% of  $\Sigma$ PCBs in most samples, therefore, in the TMDL process, it was assumed that all penta-PCB loads represented 25% of the  $\Sigma$ PCB loads (Fikslin and Suk 2003). The DRBC's penta-PCB loading estimate of about  $31 \text{ kg y}^{-1}$  did not include the internal load due to sediment resuspension (Fikslin and Suk 2003). If we assume that sediment resuspension is 50% of all the loadings, then the loading estimate is: sediment resuspension 50% of total, non-point sources 13%, point sources (including wastewater effluents) 9%, Delaware at Trenton 7%, Schuylkill 5%, contaminated sites 5%, all other tributaries 5%, atmospheric deposition 3%, and CSOs 3% (Fikslin and Suk 2003).

This analysis has produced factors associated with four of the top five categories in the loading estimate (contaminated sites, the Delaware and Schuylkill tributaries, and wastewater effluents plus CSOs). Thus, this analysis generally corroborates the TMDL loading estimate. If we have interpreted the factors correctly, sediment resuspension constitutes at least 40% of the PCB loads in the system, and wastewater effluents plus CSOs about 5%.

Our analysis is sometimes at odds with DRBC's loading estimates. The PMF results suggest that the Delaware at Trenton may be responsible for more than the 7% of total PCB loads estimated by DRBC. More importantly, our analysis suggests that there may be a single contaminated site that is responsible for about 13% of the total PCB loads to the River, more than the 5% attributed to *all* contaminated sites in the loading estimate. Our analysis also failed to identify a factor associated with non-point source

loadings. This is not surprising, however, because this load enters at a number of locations and presumably is not associated with a single identifiable congener pattern. The non-point source load may be associated with Factors 1 and 4.

#### *Comparison with San Francisco Bay study*

Johnson et al. (Johnson et al. 2000) applied polytopic vector analysis to a data set of 27 PCB congeners in 56 particle-phase samples from San Francisco Bay and resolved 5 end members. The whole water approach used here is likely to separate the dissolved and particle data into different factors. For example, Factors 3 and 4 appear to be associated with dissolved and particle phase PCBs, respectively. The data set used in the present study includes data on non-Aroclor PCB congeners, especially PCBs 11, 206, 208, and 209. These congeners provided important clues about the identities of the resolved factors.

Both studies identified the importance of sediment resuspension as a source of PCB contamination in estuaries. Johnson et al. (Johnson et al. 2000) hypothesized that their end member #5, which represented about 20% of PCB mass in their data set, was related to sewage outfalls. In our results, sewage outfalls plus CSOs are thought to be related to Factor 2 and represent only about 5% of PCB mass in the data set. They also speculated that end member #5 could be related to atmospheric deposition. This is plausible in San Francisco Bay, where the median whole-water  $\Sigma$ PCB concentration was about 450 pg L<sup>-1</sup> in 2002-2003 (2005). In the Delaware, where the median whole water  $\Sigma$ PCB concentration in this data set was 2,500 pg L<sup>-1</sup>, atmospheric deposition is probably proportionately less important. Indeed, the TMDL loading estimate (Fikslin and Suk

2003; Totten et al. 2006a) predicts that atmospheric deposition (wet plus dry particle deposition) represents only about 6% of the total load of PCBs to the River, and other evidence suggests that the atmosphere acts as a net sink for PCBs via volatilization (Rowe et al. 2007). Taken together, these two studies suggest, not surprisingly, that sediment resuspension and wastewater effluents are important sources of PCBs to urbanized estuaries. Other PCB sources are more difficult to identify via traditional source apportionment techniques, but the addition of non-Aroclor congeners to the data set vastly improves its utility for source apportionment.



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## Chapter 5

### Source Apportionment of PCBs in NY/NJ Harbor

#### Abstract

The Polychlorinated Biphenyl (PCB) contamination in Upper Hudson River has been well documented, but sources of PCBs to NY/NJ Harbor Estuary are less well understood. Previous attempts to construct mass balances on PCB contamination in the Harbor have suggested that the Upper Hudson is responsible for about half of the PCBs entering the Harbor. The mass balance study based on the data from Contaminant Assessment and Reduction Project (CARP) indicated that stormwater and combined sewer overflows (CSOs) are important contributor to PCBs in the estuary. Because of the uncertainty involved in the calculation of stormwater load, a better understanding about the magnitude and makeup of the stormwater load is needed for the dramatic improvement of water quality model of the estuary being developed by Hydroqual for the calculation of Total maximum daily load (TMDL) for PCBs in the Harbor. Therefore the purpose of this project was to apply Positive Matrix Factorization (PMF) to the database of PCB concentrations in the water column of the Harbor collected by the CARP to apportion the source of PCBs in the Hudson River with an emphasis on NY/NJ Harbor Estuary. Seven factors were resolved. These factors are associated with four top loading categories identified in the previous mass balance study: the Upper Hudson River; stormwater; CSOs and wastewater effluents. In addition, a factor that is very similar to

Aroclor 1260 was identified that contribute about half of the high molecular weight PCBs to the Harbor. We speculate that this factor could be associated with contaminated sites. Thus the mass balance study appears to have missed the importance of contaminated sites.

## **Introduction**

Polychlorinated biphenyls (PCBs) are well-documented contaminants in the Hudson River, and consequently in the NY/NJ Harbor Estuary, which contains some of the highest PCB concentrations in water, sediment, and biota in the world. PCBs were introduced into the River by General Electric plants in the Upper Hudson (Usepa 2001). Currently,  $\Sigma$ PCB concentrations throughout the Estuary exceed the NY State water quality standard of  $1 \text{ pg L}^{-1}$  by several orders of magnitude. Thus substantial reductions in PCB discharges to the river must be made and will be required by the imminent PCB total maximum daily load (TMDL). These reductions will no doubt prove difficult, especially in the light of the fact that, at present levels, atmospheric deposition alone supports water column concentrations of PCBs in excess of the WQS (Totten et al. 2004).

The PCB contamination in the upper and lower Hudson River has been well documented, but sources of PCBs to the Estuary are less well understood. The Upper Hudson load is relatively well characterized and is thought to contribute about 50% of the PCB load to the NY/NJ Harbor Estuary (Farley et al. 1999; Totten 2005b). Contaminant Assessment and Reduction Project (CARP) was designed to find sources of POPs to the Harbor. Samples were collected during 1998-2001 in areas extending from the Upper Hudson near Fort Edward and out to the Bight Apex. Point discharges, stormwater,

sediments, etc were all sampled. List all the classes of chemicals sampled. The classes of compounds investigated are PCBs, polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs). CARP data suggests that the other sources of PCB contributing to the estuary include the minor tributaries (e.g. Passaic, Hackensack, Rahway, and Raritan Rivers) and other point- and non-point sources including treated water pollution control plant (WPCP) discharges and combined sewer overflows (CSOs). Totten (Totten 2005b) has estimated based on CARP data that CSOs and stormwater are the second most important sources of PCBs to the estuary, each contributing about 17% of the total  $\Sigma$ PCB load. These calculated stormwater loads are currently the most uncertain of all loads, because both the flow of stormwater into the Estuary and the concentrations of contaminants in the stormwater are highly variable and minimally understood. Therefore, reduction in the uncertainty about the magnitude and makeup of the stormwater load would dramatically improve the water model of the Estuary being developed by Hydroqual for the calculation of TMDLs.

Previous studies have investigated the source apportionment of PCBs in the NY/NJ Harbor Estuary. Principle components analysis (PCA) was applied to 40 surface sediment samples from the Passaic River to assess differences in the distributional patterns of 11 coplanar PCBs and 17 PCDD/F congeners at four CSO sampling sites (Huntley et al. 1997). The resolved congener patterns matched that observed in CSOs, which suggested that CSOs are important sources of PCBs and PCDD/F congeners to the Passaic River. Application of PCA to PCBs fingerprints in mummichog caught in a variety of locations within the NY/NJ Harbor demonstrated that mummichog from Newark Bay were depleted in the less chlorinated congeners relative to fish from

Piermont Marsh and Iona Marsh Estuary (Monosson et al. 2003). Another source apportionment study conducted in this area is by Gigliotti (Gigliotti 2003), a former member of our research group, who used PMF to examine PCB congener patterns in a relatively small data set (35 samples) of ambient water samples collected in Raritan Bay and analyzed via Electron Capture Detection. The modeling results identified three sources contributing to the measured PCBs in Raritan Bay, including the sediment from upper Hudson, the advection of water from upper Hudson and an unknown factor.

This study is an extension of our previous efforts. In this study, we applied PMF to the existing data on ambient water concentrations of PCBs in the NY/NJ Harbor Estuary collected by the CARP. As opposed to previous efforts, this study uses data for 90 PCB congeners measured via EPA Method 1668A and employs a much larger data set (93 samples). The results of the proposed study will provide corroborating evidence to determine the accuracy of existing mass balance estimates and models and will aid in the identification of additional and heretofore unrecognized sources of PCBs to the Estuary. In addition, our research group used the same PMF approach to examine PCBs in the ambient waters of the Delaware River. Throughout this paper, we attempted to relate the findings in the NY/NJ Harbor to those in the Delaware River.

## **Methodology**

### ***PMF Data Matrix***

Thirty-eight sampling sites were repeatedly sampled between September 1998 and October 2001 at sampling locations ranging from Upper Hudson to NY/NJ Harbor

Estuary (Fig. 5.1). The identifier for each sample includes a site ID followed by a sampling date (Table 5.1). PCB data were obtained from AAS [I think there were several



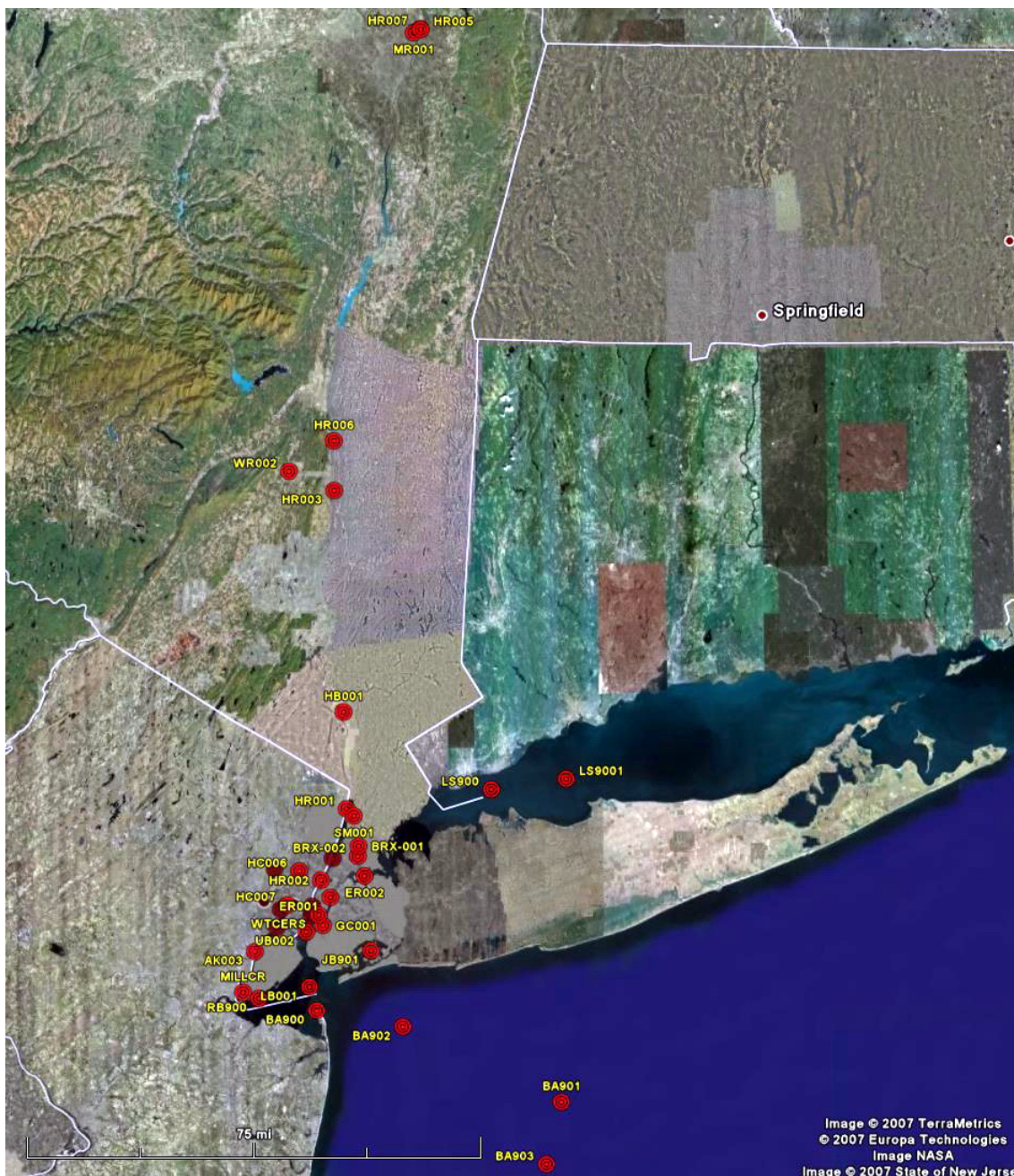


Table 5.1. Sampling site information

#	Site ID	Full Name of Site	Lat.	Long.	Sample Type
1	AK003	Northern Arthur Kill	40.6162	-74.2020	AMB_Kills
2	BA900	New York Bight, Anderson	40.4775	-74.0101	Ambient-clean
3	BA901	New York Bight Apex	40.2612	-73.2531	Ambient-clean
4	BA902	New York Bight	40.4400	-73.7417	Ambient-clean
5	BA903	New York Bight, March	40.1141	-73.3025	Ambient-clean
6	BRX-001	Bronx River at Botanical Garden	40.8659	-73.8749	Minor tributary
7	BRX-002	Bronx River, below zoo	40.8422	-73.8770	Minor tributary
8	ER001	Lower East R., Brooklyn Br. To Hell Gate	40.745	-73.9643	AMB_Non_Kills
9	ER002	Upper East R., Hell Gate to Throgs Neck	40.7955	-73.8573	AMB_Non_Kills
10	GC001	Gowanus Canal	40.6782	-73.9892	Minor tributary
11	HB001	Haverstraw Bay	41.1811	-73.9191	Ambient-Hudson
12	HC006	Hackensack R., Mid-Tidal	40.8069	-74.0612	AMB_Kills
13	HC007	Hackensack R., Mouth	40.7268	-74.0988	AMB_Kills
14	HR001	Hudson R. btw Tappen Zee & Harlem R.	40.9536	-73.9112	Ambient-Hudson
15	HR002	Hudson R. South of Harlem R.	40.7857	-73.9932	Ambient-Hudson
16	HR003	Hudson R. at Poughkeepsie	41.7013	-73.9467	Ambient-Hudson
17	HR005	Hudson R. (Pleasantdale)	42.7870	-73.6714	Major tributary
18	HR006	Hudson R. btw Kingston & Poughkeepsie	41.8178	-73.9482	Ambient-Hudson
19	HR007	Hudson R. (Waterford)	42.7888	-73.6746	Major Tributary
20	JB901	Jamaica Bay	40.6193	-73.8387	AMB_Non_Kills
21	LB001	Lower Bay	40.5333	-74.0317	AMB_Non_Kills
22	LS900	Long Island Sound off Eaton's Neck	40.9983	-73.4582	Ambient-clean
23	LS9001	Long Island Sound, Port Jefferson	41.0215	-73.2243	Ambient-clean
24	MILLCR	Mill Creek at Arthur Kill Rd	40.5195	-74.2401	Minor tributary
25	MR001	Mohawk R. (Cohoes)	42.7796	-73.6944	Major tributary
26	NB901	Newark Bay	40.6732	-74.1323	AMB_Kills
27	PR005	Passaic River, Mid-Tidal	40.8111	-74.1386	AMB_Kills
28	PR006	Passaic R., Mouth, Surface	40.7159	-74.1202	AMB_Kills
29	PR007	Passaic R., Mouth, Bottom	40.7159	-74.1202	AMB_Kills
30	RB900	Raritan Bay	40.5053	-74.1905	AMB_Non_Kills
31	SM001	Saw Mill River (Yonkers)	40.9369	-73.8891	Minor tributary
32	UB002	Upper Bay	40.6635	-74.0406	AMB_Non_Kills
33	WR002	Wallkill R., New Paltz, Rt. 299	41.7469	-74.0905	Major tributary
34	WTCERS	WTC East River, South St.	40.7035	-74.0012	Ambient-Hudson
35	WTCGW	WTC George Washington Bridge	40.8368	-73.9564	Ambient-Hudson
36	WTCHRN	WTC Hudson River, North	40.7238	-74.0212	Ambient-Hudson
37	WTCHRS	WTC Hudson River South	40.7022	-74.0236	Ambient-Hudson
38	WTCHRW	WTC Hudson River West	40.7151	-74.0222	Ambient-Hudson

contract labs]. Although 209 congeners were measured, only 90 were included in the PMF model. This was done primarily to provide the highest degree of comparability with the Delaware River study (Du et al. 2008a). In that study, 148 congeners were measured. The 61 congeners measured in CARP but not in the Delaware River data set were predominantly non-Aroclor congeners that were below detection limit in a majority of samples. Therefore it was concluded that little or no useful information would be lost in excluding them from the CARP data analysis. In the Delaware study, among the 148 PCB congeners measured, 48 of them were below detection limit in more than 90% of samples. Therefore these congeners were removed from the data matrix. A few congeners (PCBs 5, 7, 10, 89, 181, 204) that were below detection limit in more than 50% of samples were also excluded. The data were further reduced by removal of four PCB congeners (PCBs 14, 63, 81, and 207), which were not reported in the trip or equipment blanks. Most of the excluded congeners were not present in significant amounts in the Aroclors (Rushneck et al. 2004). Ninety congeners were therefore present in the data set used for PMF analysis.

We included both the ambient water data in the model whenever both the dissolved and particulate measurements were available. Greater than 50% of these 90 congeners were below detection limit in 26 of the samples, which were therefore excluded from the dataset. As a result, 93 samples were selected for the final modeling input. The values used in the data matrix were whole-water concentrations, which were calculated by adding the dissolved-phase PCB concentration to the particle-phase PCB concentration. All samples in which both dissolved and particle phase PCBs were measured were included in the data set. If either the dissolved or particle PCB congener

concentration was below the detection limit, then one half the congener-specific detection limit was used as a proxy. The final matrix submitted for PMF modeling analysis therefore consisted of 93 samples and 90 congeners (8370 data points).

### ***PMF***

PMF is an advanced factor analysis method, described in detail by Paatero and Tapper and briefly summarized here. PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix ( $X$ ) is composed of  $n$  observed samples and  $m$  chemical species.  $F$  is a matrix of chemical profiles of  $p$  factors or sources. The  $G$  matrix describes the contribution of each factor to any given sample, while  $E$  is the matrix of residuals. The PMF solution, i.e.  $G$  and  $F$  matrices, are obtained by minimizing the objective function  $Q$  through the iterative algorithm:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (2)$$

$Q$  is the sum of the squares of the difference (i.e.  $e_{ij}$ ) between the observations ( $X$ ) and the model ( $GF$ ), weighted by the measurement uncertainties ( $s_{ij}$ ).

Theoretical  $Q$  should approximately equal the number of degree of freedom, i.e.

$$Q = m \times n - p \times (n + m) \quad (\text{The Astm Standard Practice for Determining Volatile Organic Compounds (Voc) Contents of Paints and Related Coating (D3960)})$$

### *Uncertainty Estimate*

PMF computes the error estimate ( $S_{ij}$ ) for each data point ( $X_{ij}$ ) based on the data point and its original error estimate. In the present study, we choose to use the EM = -14 error model (Paatero 2003b):

$$S_{ij} = t_{ij} + u_{ij} \sqrt{\max(|x_{ij}|, |y_{ij}|)} + v_{ij} \max(|x_{ij}|, |y_{ij}|) \quad (\text{Code of}$$

Federal Regulations. Title 40: Protection of Environment. Chapter I: Environmental Protection Agency. Subchapter C: Air Programs. Part 51)

Where  $t$  is the congener- and sample-specific detection limit,  $u$  is the Poisson distribution (here designated as 0),  $v$  is the measurement precision,  $x$  is the observed data value, and  $y$  is the modeled value.

Uncertainties for PCBs were adapted from our previous work in the Delaware River (Du et al. 2008b), because this study used virtually identical sampling and analysis protocols. Previous work has shown that the extraction efficiency, quantified by the recoveries of surrogates, dominated the overall measurement uncertainty; sampling precision and instrument precision were shown to be negligible (Du and Rodenburg 2007). For two-phase samples, uncertainties for the dissolved ( $SD_{\text{surrogate-D}}$ ) and particle ( $SD_{\text{surrogate-P}}$ ) phases were calculated individually, and uncertainty of the bulk water sample ( $v$ ) was propagated via the following equation:

$$v = \sqrt{(SD_{\text{surrogate-D}})^2 + (SD_{\text{surrogate-P}})^2} \quad (\text{Code of}$$

Federal Regulations. Title 40: Protection of Environment. Chapter I: Environmental Protection Agency. Subchapter C: Air Programs. Part 51)

In some cases, higher uncertainties were applied. Three times the normal uncertainty was assigned for below detection limit data and five times the normal uncertainty was assigned for missing data.

## **Results and Discussion**

### ***Determination of the Number of Factors***

The plot of calculated  $Q$  vs. the number of requested factors clearly indicated that 7 was the “right” number of factors (Fig. 5.2), since the calculated  $Q$  (7116) is very close to the theoretical  $Q$  (7089). Determination of the number of factors can also be accomplished by evaluating goodness-of-fit on a congener-by-congener basis using Miesch coefficient of determination (CD) (Johnson et al. 2000; Miesch 1976). The CD was determined for each PCB congener by the calculation of correlation coefficient (with respect to the 1:1 fit line) of the measured amount of each PCB congener with the back-calculated value from the chosen seven factor model. Given a perfect fit, all data points will plot on a 1:1 slope and the Miesch coefficient of determination will be 1.0 (Miesch 1976). An excellent fit ( $CD > 0.90$ ) was observed for 64 out of 90 PCB congeners, while a good fit ( $CD > 0.5$ ) was observed for 83 out of 90 samples. The fitness of 13 PCB congeners can be improved dramatically only by the removal of two samples (HR002 12/17/98, NB901 12/15/99), for which the predicted concentration was much lower than the measured concentration.

### ***Congener Profiles of Resolved Factors***

The 7 resolved PCB factors are shown in Fig. 5.3. The distribution of PCB mass in the data set by factor is examined not only in total but also in homologue bases and is tabulated in Table 5.2. As an attempt to compare with the mass balance study of Totten (Totten 2005b), the distribution of the “high MW” and “low MW” homologs is also presented (Table 5.2). Factor 1 is a relatively low MW PCB signal, and represents about 32% of the mass of PCBs in the data set. Factor 2 constitutes ~19 % of the PCB mass in the data set, containing about 0.32% of PCB 11 and is higher in average molecular weight than Factor 1. Factor 3, containing 0.36% of PCB 11, contribute about 23% of the PCB mass in the data set , and accounts for more than half of the nona- and deca-PCB in the whole data set. Factor 4 has the relatively evenly distributed PCB congeners from different homologue group with the exclusion of nona- and deca-PCB, and constitutes 8% of the PCB mass in the data set. Factor 5 constitutes just 2.4% of the PCB mass in the data set and the dominant congener in this factor is PCB 11 (28%). Factors 6 and 7 are dominated by high molecular PCBs and constitute about 8% of total PCB respectively.

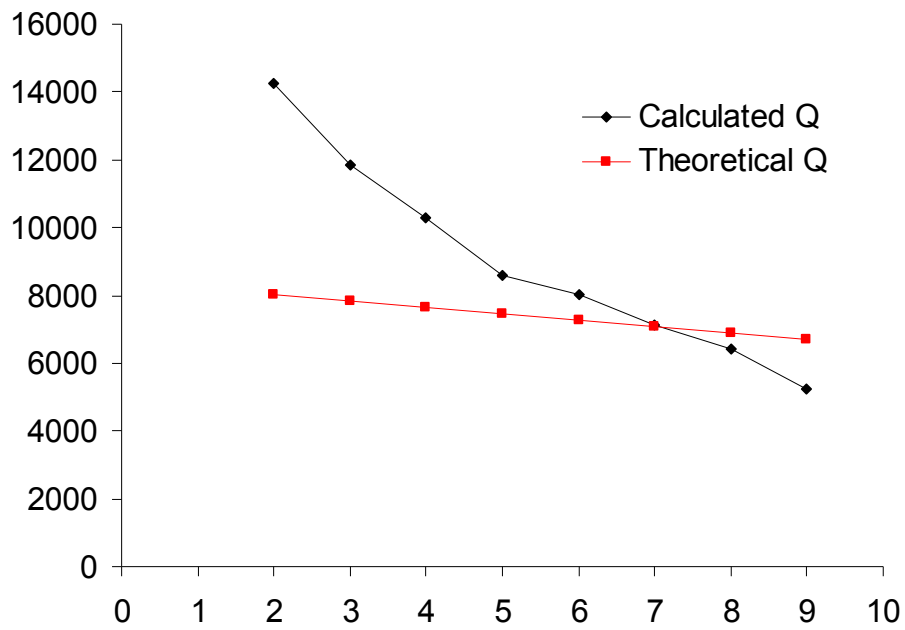


Figure. 5.2. Correlation between the calculated Q as a function of the number of factors and the theoretical Q for six-factor model.



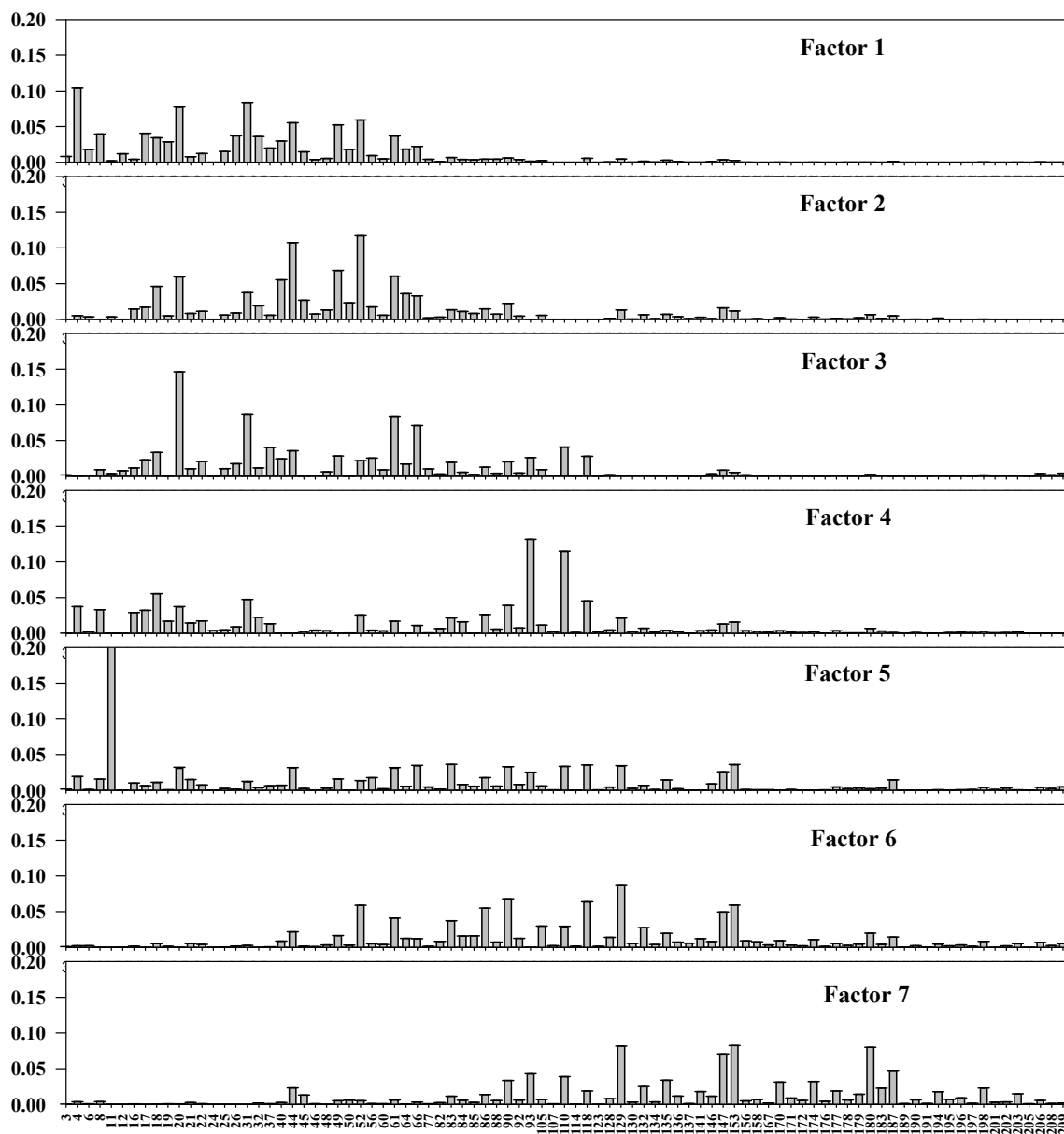


Figure 5.3. Normalized congener patterns of the seven resolved source profiles (factors). PCB congener numbers on the x-axis are plotted vs. their fractional contribution to the sum of PCBs on the y-axis. Error bars stand for the calculated standard deviation of the fractional contribution of each PCB congener.

Table 5.2. Distribution of mass of PCB homologues in each resolved factor.

Homologues	F1	F2	F3	F4	F5	F6	F7
1	87%	0%	6%	4%	0%	1%	1%
2	72%	3%	7%	7%	10%	0%	1%
3	43%	15%	33%	8%	1%	1%	0%
4	33%	34%	24%	2%	1%	5%	2%
5	9%	11%	27%	22%	3%	19%	9%
6	7%	14%	7%	7%	4%	30%	31%
7	2%	12%	5%	5%	2%	18%	57%
8	3%	4%	13%	6%	2%	19%	53%
9	11%	0%	43%	0%	5%	24%	17%
10	4%	0%	55%	0%	7%	25%	9%
Total PCBs	32%	19%	23%	8%	2%	8%	8%
Low MW PCBs (3-6cl)	29%	21%	26%	8%	2%	8%	6%
High MW PCBs (7-9cl)	3%	9%	9%	5%	2%	18%	54%

### ***Identification of Resolved Source Profiles***

As an attempt to identify the resolved factors, we integrated the various information including spatial variation of the factor scores, comparison of the resolved congener patterns with congener patterns from known sources such as Aroclors, and clues from the presence of non-Aroclor congeners such as PCB 11 and PCB 209. The cosine theta similarity metric ( $\cos\theta$ ) is used for the pattern matching. This metric calculated the cosine of the angle between two multivariate vectors and assign 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 ( $\cos\theta=0$ ) (Davis 1986). This similarity measurement has been used in the previous studies for the identification of resolved factors (Du et al. 2008b; Du and Rodenburg 2007; Magar et al. 2005).

### *Comparison with Aroclors*

The tacit assumption in the comparison of the factor congener patterns with Aroclor congener patterns is that weathering processes have not substantially altered the PCB congener profile in the environmental samples. Weathering processes can include chemical, physical, and biological degradation including anaerobic dechlorination. Aroclor compositions were taken from high resolution GC/MS analysis of the Aroclors of Rushneck et al. (Rushneck et al. 2004)

The determined  $\cos\theta$  similarity for these resolved factors are summarized in Table 5.3. The highest similarity occurred to Factors 5 and 6, which closely resemble Aroclor 1254 ( $\cos\theta=0.96$ , with the exclusion of two outliers, i.e. PCB 93, 110) and Aroclor 1260 ( $\cos\theta=0.96$ ), respectively. Aroclor 1254 constituted about 16% of US PCB production and was used in the widest variety of application from transformers and capacitors to plasticizers, hydraulic fluids, and a variety of open applications such as adhesives, pesticide extenders, sealants and caulks, cutting oils, inks, and dedusting agents (Erickson 1997; Nisbet and Sarofim 1972). Aroclor 1260 constituted about 11% of US production of PCBs and was limited to only four uses; transformers, hydraulic fluids, as a plasticizers in synthetic resins, and dedusting agents (Erickson 1997; Nisbet and Sarofim 1972). We constructed a chemical mass balance (CMB) model for the resolved factors assuming they consist of linear combinations of Aroclors 1242, 1248, 1254, and 1260. The slope coefficients represent the fraction of the factor congener profile that can be described by that Aroclor, and the sum of the slopes would ideally equal one. The residue implies either extensive weathering or non-Aroclor source. The

Table 5.3. Cosine theta ( $\cos\theta$ ) values for comparisons of resolved source profile congener patterns with Aroclor, average congener profile of dissolved and particle phase PCB in Hudson River.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
A1242	0.83	0.72	0.82	0.52	0.24	0.28	0.11
A1248	0.66	0.87	0.79	0.47	0.29	0.52	0.21
A1254	0.21	0.39	0.79	0.70	0.33	0.87	0.64
A1260	0.04	0.14	0.09	0.26	0.20	0.64	0.96
Dissolved phase	0.90	0.84	0.69	0.58	0.43	0.46	0.28
Particle phase	0.70	0.75	0.86	0.60	0.41	0.73	0.58

results (Table 5.4) demonstrate that except Factor 5, all other resolved factors can be well described as a combination of Aroclors.

*Tracer for wastewater treatment plant*

PCB 11 is present in very high concentrations in effluent from the PVSC wastewater treatment plant. It is produced inadvertently during diarylide yellow pigment manufacture (Litten et al. 2002). This dye is used in paints, plastics, printing inks, textile printing, and paper and is the dominant yellow pigment used in printing ink applications (Barrow et al. 2002). About 100 kg of PCB 11 are released to the Estuary each year from the Passaic Valley Sewerage Commission (PVSC) WWTP (Totten 2005b). NYSDEC has analyzed batches of the diarylide pigment associated with PCB 11 and found other dioxin-like PCB congeners, such as PCB 77, in the finished product (Simon Litten, NYSDEC, personal communication, 2004). Our investigation of the PCB patterns in Delaware River indicated that PCB 11 may be a tracer for wastewater effluents and CSO inputs even in watersheds where there are no known dye manufactures. PCB 11 has been observed in significant quantities in the air in this region, at a level of about 1% of  $\sum$ PCBs (Du and Rodenburg, unpubl. data), and therefore can be expected to present in stormwater as well as CSOs and wastewater effluents.

A final clue to identifying the factors was the presence of PCBS 206, 208, and 209. In the Delaware River, it is known that these congeners were produced inadvertently during titanium chloride manufacture at a plant in Delaware, and that a by-product of this process, ferric chloride, was sold to wastewater treatment plants in the Philadelphia area as a flocculant. Titanium chloride from Dupont was also reported having been sold to water and wastewater treatment plants that discharge into the Harbor

Table 5.4. Chemical mass balance model best-fit descriptions of each factor as a combination of Aroclors.

Aroclor	Factor1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
1242	79%	7%	58%	45%	21%	0%	0%
1248	5%	84%	36%	0%	6%	7%	4%
1254	1%	0%	0%	25%	27%	69%	10%
1260	1%	9%	3%	3%	10%	20%	74%
Sum	87%	100%	97%	72%	65%	95%	89%

(Personal Communication. with Greg Cavallo). This could serve as evidence that the presence of PCB 209 can be used as a tracer for treated wastewater effluents, as opposed to CSOs or stormwater that are untreated. In the Delaware River, the ratio of 206/208/209 was 1.8/1/3.1.

## Summary

Factor 1 represents about 32% of the mass of PCBs in the data set. It is most prevalent in samples from the northernmost Hudson River station (HR005), where it constitutes on average 75% of total PCBs. This factor resembles the average dissolved-phase PCB profile in the data set ( $\cos\theta=0.90$ ). Factor 1 probably represents the dissolved phase PCB load from the Upper Hudson. PCB 4 (2,2'-dichlorobiphenyl) accounts for 10% of factor 1. Factor 1 is somewhat similar to Aroclor 1242 (Table 5.1). We speculate that Factor 1 is associated with the Upper Hudson source from several lines of evidences. First, the aforementioned spatial distribution of this factor corroborates its association with Upper Hudson; Second, this factor is most similar to Aroclor 1242 ( $\cos\theta=0.83$ ), which is the primary Aroclor used by GE (Usepa 2001); Third, this factor is enriched in some of the PCB congeners that are characteristic dechlorination end products in Hudson River sediment. Significant anaerobic dechlorination of PCBs has occurred within the buried sediment, resulting in the shift of the congener profile from more chlorinated congeners to less-chlorinated congeners in Hudson River sediment samples (Abramowicz et al. 1993; Butcher and Garvey 2004; Fish and Principe 1994). These patterns resulted from substitution of hydrogens for chlorine atoms at meta- and para- positions. Thus, many Hudson River sediments demonstrate elevated levels of the end products of



dechlorination process( 2-chlorobiphenyl (PCB 1), 2,2'-dichlorobiphenyl (PCB 4), 2,6-dichlorobiphenyl (PCB 10), 2,2',6-trichlorobiphenyl (PCB 19), and 2,2',6,6'-tetrachlorobiphenyl (PCB 54), 2,5,3'-trichlorobiphenyl (PCB 26), 2,4,3'-trichlorobiphenyl (PCB 25), 2,5,4'-trichlorobiphenyl (PCB 31), 2,4,2',5'-tetrachlorobiphenyl (PCB 49)) with the observed loss of more highly chlorinated congeners (2,3,3',4'-tetrachlorobiphenyl (PCB56), 2,3,6,3'4'-pentachlorobiphenyl (PCB 110), 2,3,4,2'3'-tetrachlorobiphenyl (PCB 82)) (Abramowicz et al. 1993; Fish and Principe 1994). The observed discrepancy between the composition of Factor 1 and Aroclor 1242 is consistent with that caused by this dechlorination process.

Factor 2 dominates at the New Jersey sites (Hackensack and Passaic Rivers, Newark Bay, Arthur Kill), where it constitutes on average of 39% of total PCBs. This factor is most similar to Aroclor 1248 ( $\cos\theta=0.87$ ). This factor contains some PCB 11 (0.3%), but virtually no PCB 206, 208, or 209. We therefore speculate that this factor maybe associated with CSO or stormwater inputs to the area, as opposed to treated wastewater effluents.

Factor 3 constitutes 23% of the PCB mass in the data set. It contains some PCB 11 (0.4%) and accounts for more than half of all the nona- and deca-PCB in the data set, i.e. PCB 206, 208, 209. It can be well described as a linear combination of all four Aroclors. The factor score distribute most evenly among all the resolved seven factors (RSD=70%) and most similar to the average particle-phase PCB profile in the data set ( $\cos\theta=0.86$ ). Therefore, we speculate that this factor represents the particle-bound PCB burden in the Hudson River. This factor is relatively evenly distributed spatially within the Harbor, which supports the hypothesis that it represents sediment-bound PCBs, since

these sediments travel throughout the Harbor area and then are deposited and remain available for resuspension for decades.

Factor 4 constitutes 8% of the PCB mass in the data set. It contains virtually no PCB 11, 206, 208 or 209, suggesting that it is not related to stormwater, CSO, or treated wastewater inputs. It is somewhat similar to Aroclor 1242, and is best described as a linear combination of Aroclors 1242 (41%) and 1254 (63%). It is most prevalent in the Saw Mill, where it constitutes 15% to 35% of  $\Sigma$ PCBs. It is the most evenly distributed of all the PCB factors, with a RSD for its concentrations of 114%. We speculate that it represents the PCB background in the Harbor, with vestiges of the Upper Hudson 1242 signal and the Aroclor (1254) most widely used in open applications.

Factor 5 accounts for a relatively small fraction of PCBs (2.4%) and is dominated by PCB 11 (28%). PCB 11 is present in very high concentrations in effluent from the PVSC wastewater treatment plant. In addition, our investigation of the PCB patterns in the Delaware River indicated that PCB 11 may be a tracer for wastewater and CSO inputs even in watersheds where there are no known dye manufacturers. The spatial distribution of this factor is in keeping with a wastewater sources. It is prevalent in the East, Hackensack, Passaic, and Walkill Rivers, Upper Bay, Arthur Kill, HR002, and Jamaica Bay. All of these areas are located near wastewater treatment plant effluents. The CMB results for this factor revealed its bearing no similarity to any of the prevalent Aroclors (Table 5.1), which corroborated the interpretation that it is associated with wastewater effluents considering the intensive weathering occurred during the treatment process. It should be noted, however, that this factor could be related to blank contamination. We have been aware of the contamination of the Long Island Sound samples with PCB 11

(Personal communication with Simon Litten), though the total mass of PCB 11 in the Long Island Sound samples represents just 1.4% of the total mass of PCB 11 in the data set. Because PCB 11 is a non-Aroclor congener, it might be expected to vary in patterns that are very different from most of the other congeners. Most likely, the PMF program constructed a factor consisting primarily of PCB 11 in order to account for its variability independently from the other congeners. The PMF output did not include a factor that was dominated by PCB 11 when 5 or 6 factors were requested, and as a result, those models did a poor job of reproducing the measured PCB 11 concentrations (Fig. 5.4).

Factor 5 therefore probably represents a combination of WWTP effluents and blank contamination of PCB 11, although the blank contamination probably represents a small portion of the mass of this factor. The small percentage of contribution deduced from PMF modeling is consistent with the conclusion drawn from previous study. Durell and Lizotte estimated that the annual PCB contribution from the 26 New York City and New Jersey Water Pollution Control Plant (WPCPs) to the New York/New Jersey Harbor Estuary is estimated to be 88 kg, with only a small portion (~3%) of this being diverted and bypassed by the WPCPs and discharged through CSOs due to precipitation events (Durell and Lizotte 1998). This estimated 88 kg of PCB discharge from the NY/NJ waste water effluents only accounts for a very small fraction of the input of PCBs to the NY/NJ Harbor Estuary, which contains tens of thousands of kilograms of PCB stored in the sediment (Bopp et al. 1981), and receives several hundred kilograms of PCBs annually from river sources (Jones et al. 1989), and unknown amounts from other sources.

Factor 6 constitutes about 8% of total PCBs in the data set. It is most similar to Aroclor 1254, and contains virtually no PCB 11 (just 0.06%). It represents about half of

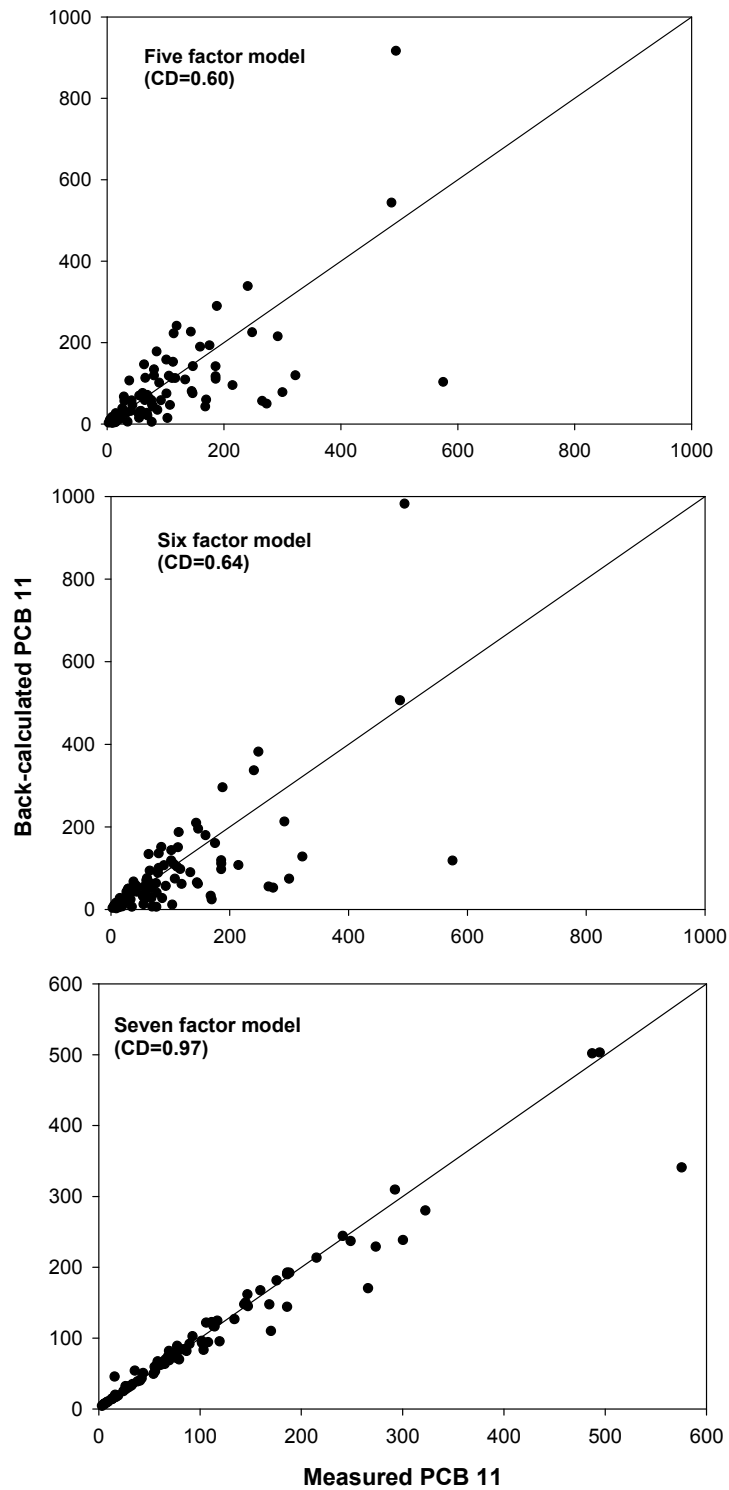


Figure. 5.4. Goodness-of-fit scatter plots and Miesch coefficient of determination (CD) for PCB 11 in five, six, seven factor models.

all the PCBs in the Walkill River, and is also prevalent just downstream at HR003. It is also present in significant quantities in the Saw Mill and Mohawk Rivers, and Jamaica Bay. Aroclor 1254 represents about 16% of US PCB production and was used in the widest variety of applications from transformers and capacitors to plasticizers, hydraulic fluids, and a variety of open applications such as adhesives, pesticide extenders, sealants and caulks, cutting oils, inks, and dedusting agents (Erickson 1997; Nisbet and Sarofim 1972). Aroclor 1254 was used in caulks and sealants, which are thought to be significant sources of atmospheric PCBs in buildings (Kohler et al. 2005b) (Herrick et al. 2004a; Kohler et al. 2005b). Recent study also suggested that PCBs in caulking can be mobilized as complexes with dissolved organic matter that also leach off the caulking material, which caused the contamination of PCBs in soil generated in the process of removing the caulking as well as natural weathering and deterioration of the caulking (Herrick et al. 2007). For this reason, its presence in these tributaries may simply represent its widespread use in open applications, and is not necessarily indicative of contaminated sites.

Factor 7 closely resembles Aroclor 1260 and makes up about 80% of the PCBs measured in the Bronx River. It is also present in the Arthur Kill (30% of total PCBs), Walkill River (18%), and Long Island Sound (17%). Because of the large distance between the Bronx and Walkill Rivers and the Arthur Kill, it is unlikely that factor 7 represents a single source of PCBs, but rather that it may represent a few localized contaminated sites where Aroclor 1260 was used. The strong correlation ( $\cos\theta=0.96$ ) with Aroclor 1260 suggest that this factor has undergone minimal weathering, which is also consistent with a contaminated site or spill source. This factor constitutes about 8%

of total PCBs in data set. Only 11% of US production of PCBs consisted of Aroclor 1260 (Brown 1994) and it was limited to only four uses: transformers, hydraulic fluids, as a plasticizer in synthetic resins, and dedusting agents (Erickson 1997; Nisbet and Sarofim 1972). It is therefore not surprising that the water waste water/ CSO signals are not similar to this Aroclor. Because the congener pattern of Aroclor 1260 is so distinct from the more widely used Aroclors (1242, 1248, and 1254), the PMF program easily recognizes Aroclor 1260 as a separate factor, which is useful since it allows us to pinpoint the locations of sites with Aroclor 1260 contamination. The same phenomenon was observed in the Delaware River, where a single Aroclor 1260 source just source of Trenton was identified (Du et al. 2008b).

### ***Comparison to mass balance study***

The previous mass balance study on PCBs in the Harbor based on CARP data suggests that the Upper Hudson contributes about half of  $\Sigma$ PCBs to the harbor; stormwater and CSOs contribute about 30% of  $\Sigma$ PCBs and 75% of high molecular weight PCBs (those with 7 to 9 chlorines), and the combination of loadings from tributaries other than the Hudson River, wastewater treatment plants, and atmospheric deposition account for about 10% of the total PCB loads to the estuary.

As an attempt to compare the mass balance results with the PMF results, we only include samples collected in Harbor area, i.e. Upper Bay (UB002), Lower Bay (LB001), Raritan Bay (RB900). In these areas, Factor 1 through Factor 7 constitute 15%, 23%, 33%, 8%, 9%, 6%, and 6% of  $\Sigma$ PCBs, respectively. Factor 1 and 3, which are thought to be related to the dissolved and particle phase of PCBs respectively, represent about 48%

of the PCB burden in the Harbor area, which is in good agreement with the mass balance study that about half of PCB input to Harbor is from the Upper Hudson. The mass balance study also concluded that treated wastewater effluents contribute about 5% of  $\Sigma$ PCBs, 5% of low MW PCBs, and 6% of high MW PCBs to the Harbor. As a contrast, the corresponding contributions of Factor 5 determined from PMF modeling, which are 9%, 6%, 9% for  $\Sigma$ PCBs, low MW PCBs, high MW PCBs respectively, agree quite well with the mass balance study.

However, there are some mismatches between these two studies. The mass balance study indicated that stormwater and CSOs contribute about 30% of  $\Sigma$ PCBs and 75% of high molecular weight PCBs in the Harbor. The PMF model suggested that the stormwater and CSOs associated factor (Factor 2) accounts for 23% of  $\Sigma$ PCBs and 12% of high MW PCBs to the Harbor Core. Therefore, good agreement has reached for the estimated contribution of  $\Sigma$ PCBs from stormwater and CSOs, but not for the high MW PCBs. This discrepancy could be attributed to the fact that the resolved factor of Aroclor 1260 contamination in PMF model dominates the high MW PCB inputs, while this was absent in mass balance study. This discrepancy still exists, though having been diminished by excluding factor 7, which resulted in an estimated fraction of about 23% of high MW PCBs contributed from the stormwater and CSOs sources. Thus the contribution of high MW PCB from stormwater/CSOs is much lower than estimated in mass balance study.

### ***Compared with San Francisco Bay study***

We compare this study results with those conducted in other complex estuary system including Delaware River ((Du et al. 2008b) and San Francisco Bay (Johnson et al. 2000). In contrast, Hudson River has a distinctive major source of PCBs, i.e. the Upper Hudson Aroclor 1242 source, which is absent in other water bodies. All these studies pointed out the important roles that sediment suspension and sewage effluents played in contributing sources to these urbanized estuaries. If we have interpreted the factors correctly, Factor 2 (believed to be associated with CSOs or stormwater) contributes 19% of PCBs to the Harbor, which is much higher than that in Delaware River, where only 5% of the PCB mass was thought to be associated with wastewater effluents and CSOs. It is more similar to the results from San Francisco Bay, where their end member # 5, which represents about 20% of PCB mass, was thought to be related to sewage outfalls.

### **Conclusion**

PMF has been proven to be an effective tool for source apportionment of PCBs in the NY/NJ Harbor Estuary. The application of PMF generates both quantitative and qualitative results for the contributing sources of PCBs input to the NY/NJ Harbor area. The PMF model produced factors associated with the four top loading categories identified in the mass balance study: Upper Hudson River, stormwater, CSOs, and wastewater. A factor associated with Aroclor 1260 was identified which may be associated with contaminated sites. This type of source was not included in the previous mass balance study. The mass balance study therefore appears to have missed the



importance of contaminated sites. This Aroclor 1260 factor contributes about half of all the high MW PCBs to the Harbor area.

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## **Chapter 6**

### **Conclusions**

This dissertation is targeted on addressing some of the questions raised in the development and implementation of TMDL process for PCBs. Atmospheric deposition is always being considered as an important source in water quality modeling. One question that this thesis is designed to address is how to identify and locate the source contributing to the PCBs in urban air. The coupling of PMF with PSCF provides a good example of the use of statistical methods to analyze urban ambient air persistent organic pollutant data. The successful resolving of four distinct congener patterns and their respective locations demonstrate the usefulness of these source apportionment tools, however it also indicates the limitation of applying PSCF in identifying urban PCB sources due to the mismatch between the proximity of the sources and the resolution of the PSCF model. Another question proposed to study about atmospheric deposition loading category is how to refine the atmospheric deposition input in models used to develop TMDL. The intensively deployed passive samplers across the Philadelphia-Camden area in this study provide refined geographical mapping information that will be used to refinement of modeling input.

The validation of the loading estimate used in developing TMDL reminds to be another question to be answered. We extend the application of PMF from air to two representative urban aquatic systems, i.e., Delaware River and NY/NJ Harbor, though the application in the aquatic system is just beginning. Our application of PMF to the PCB

data collected from these two complex urbanized river systems successfully untangle the source contributing to the measured PCBs in these systems and provide a way to corroborate the loading estimates used in the development of TMDLs.

Taken together, this thesis suggests that the linkage between the air and water sources of PCB is not very strong. There is not much similarity between the atmospheric sources and aquatic ones. For instance, the PMF modeling results for Camden air revealed that the low molecular weight Aroclors (1016, 1042, 1048) represent an ubiquitous PCB background of urban air, comprising about 27% of the total PCB burden at Camden. However, this low Aroclor signal is not necessarily observed in each aquatic system investigated. The presence of Aroclor 1242 signal is not representative of the aquatic system because of the recorded distinctive uses of this Aroclor in this region.

One similarity that does exist between the air and water sources is the Aroclor 1254 signal. This signal is observed both in NY/NJ Harbor and Camden air. Aroclor 1254 was used in caulks and sealants, which are thought to be significant sources of atmospheric PCBs in building. It was found that PCBs in caulking can be mobilized as complexes with dissolved organic matter that also leach off the caulking material, which caused the contamination of PCBs in soil generated in the process of removing the caulking as well as natural weathering and deterioration of the caulking. Therefore, we speculate that this A1254 signal arises from its use in open applications, especially in building material (caulks).

One of the strength of this study is the size of the data sets having been applied into modeling compared with the previous studies in the source apportionment of PCBs. However, even the CARP data set is really too small. Another advantage associated with

this study is the quality of modeling input data set of PCBs obtained from method 1668A. Method 1668A is currently the reference method for determination of PCBs. The high sensitivity and powerful identification capability are provided by this method through the application of the coupled high resolution gas chromatography and mass spectrometry. Additionally, the identification of some informative non-Aroclor congeners is very helpful for the interpretation of resolved factors. Furthermore, the fact that the PCB data collected from the two aquatic systems are obtained from the same methodology could eliminate the discrepancy caused by different methodology and provide maximum comparability.

Overall, this dissertation represents an innovative approach to the investigation of POP sources in urban systems. However, this thesis work also gives rise to some new questions remained to be answered. We propose the following directions in the following part, which might be helpful in the continual exploration of source of urban POPs:

1. Tracking down the Swarthmore PCB source using densely deployed passive air samplers and modeling the air data; using PMF or other statistical tools to resolve the observed congener patterns in this passive sampling study and other possible data set.
2. In addition to the application of PMF modeling to single chemical class, analysis of data from combined chemical classes will reveal the integrated source profiles, i.e., secondary sources, such as stormwater runoff. The combination of these modellings will provide more complete information about the potential sources.
3. Sampling of soil might help to identify the atmospheric sources. For instance, we can analyze the enantiomer signature of chiral PCBs in the air and soil samples to distinguish the sources of PCBs to the ambient air. In order to testify the association

of A1254 signal in air with the open application such as caulks, we can collect soil sample surrounding buildings where PCB-containing caulks are still in place to see if caulks are a possible source for the atmospheric PCBs.

4. Source apportionment of POPs in other environment media, such as sediment core will give some implications of the change of these POP sources overtime.

Additionally, the availability of long term data is also going to be helpful in tracking the historical source patterns of these POPs.

**Appendix I. Complete tables and figures from chapter 2-4**



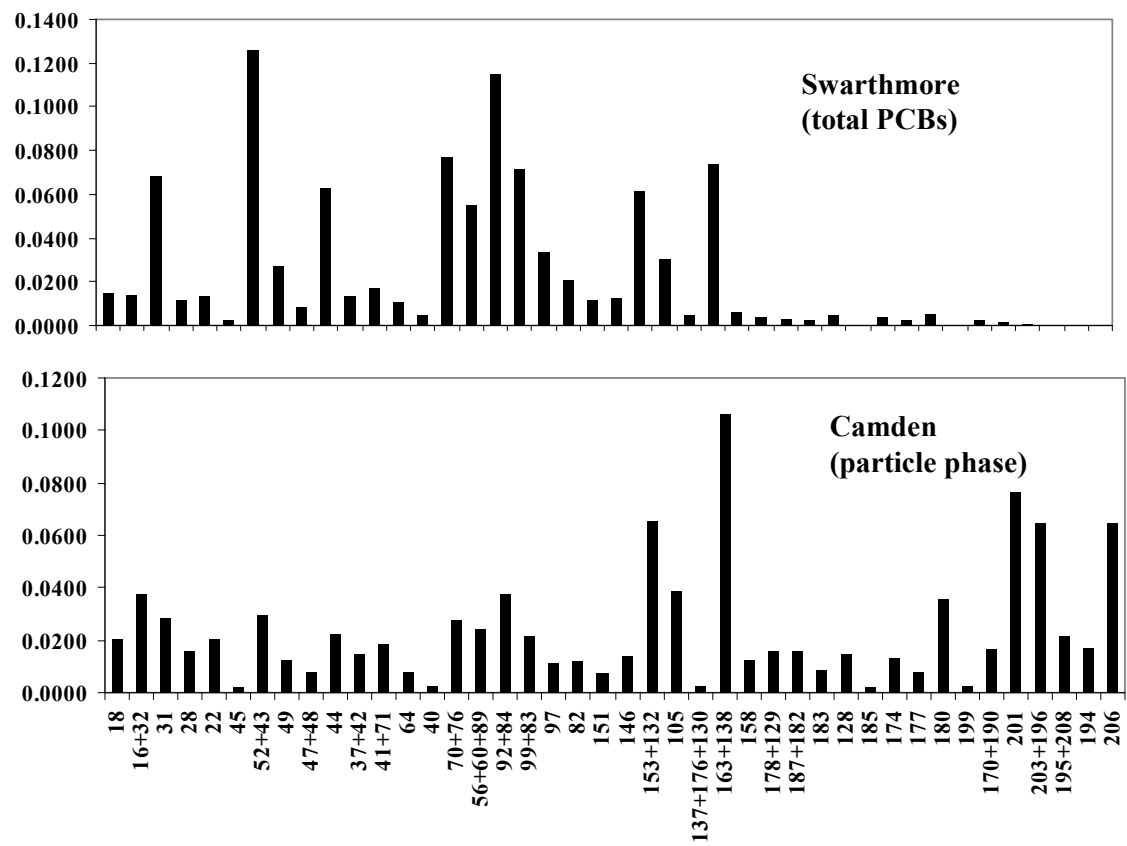


Figure I-1. Total PCB congener patterns in Swarthmore and particle phase PCB congener pattern in Camden. PCB congener numbers on the x-axis are plotted vs their fractional contribution to the sum of PCBs on the y-axis.

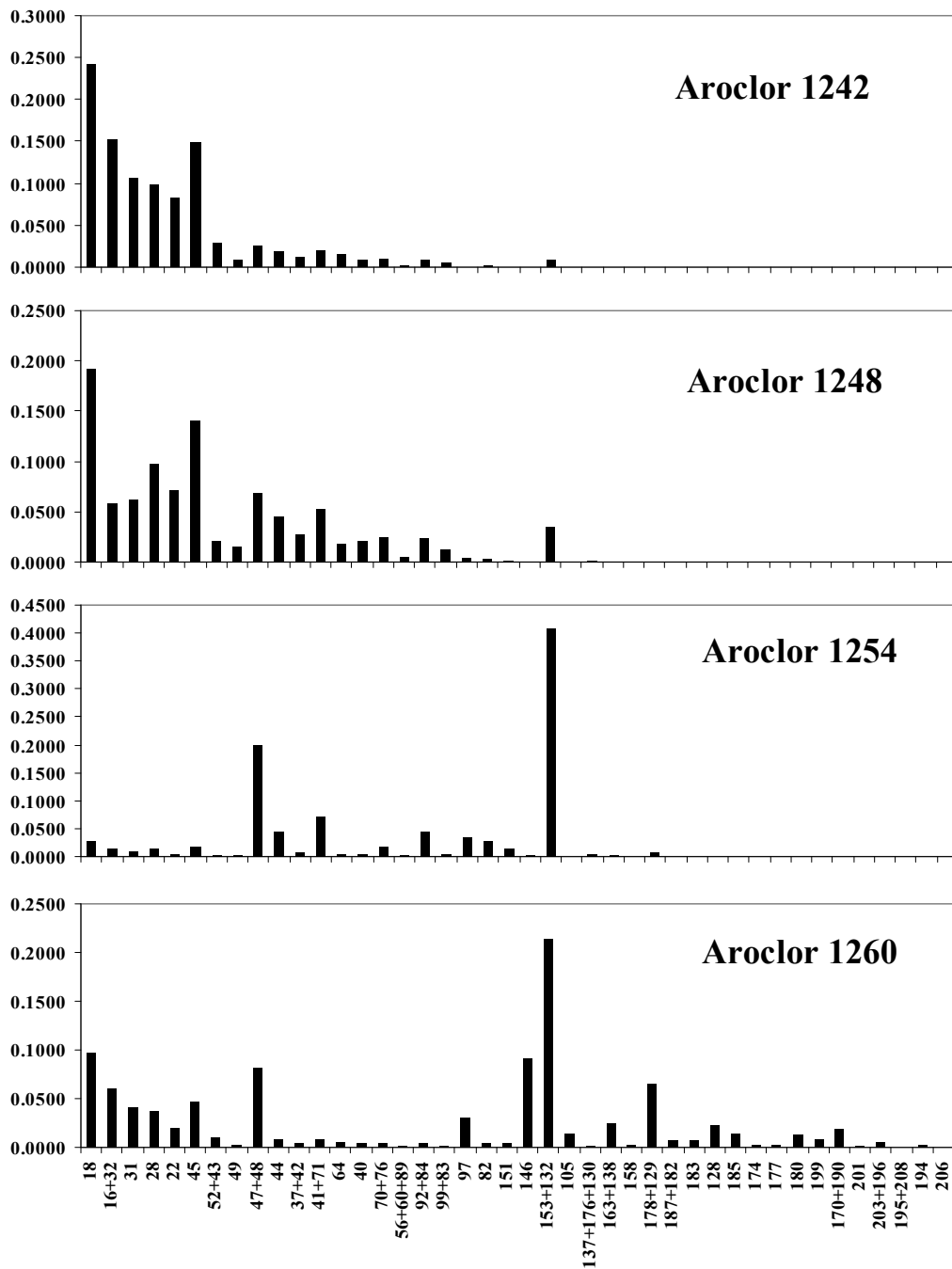


Figure I-2. Normalized PCB congener patterns by vapor pressure in Aroclors. PCB congener numbers on the x-axis are plotted vs their fractional contribution to the sum of PCBs on the y-axis.

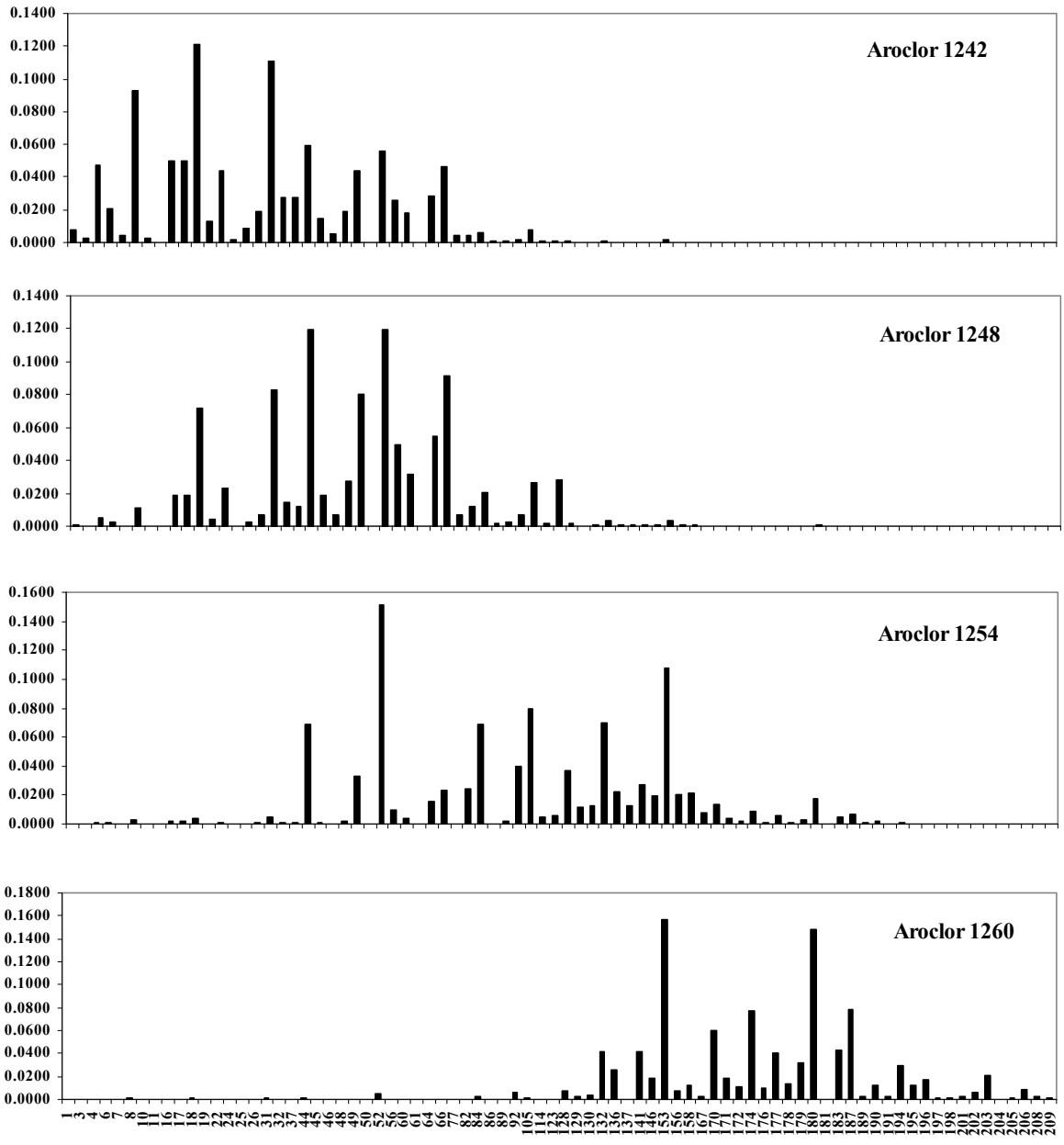


Figure I-3. PCB congener patterns in Aroclors compiled for ambient PCB data in Delaware River analyzed by EPA 1668A. PCB congener numbers on the x-axis are plotted vs their fractional contribution to the sum of PCBs on the y-axis.

Table I-1. Determined mass of PCB in each passive sampler (ng).

	2	4	7	8+5	14	11	15	30	18	17	32+16	23	31
<b>Bellevue State Park</b>	0.00	1.20	0.00	1.32	15.48	1.12	0.00	41.84	2.81	0.83	1.41	17.64	1.99
<b>Billing sport elementary school</b>	0.00	1.85	0.00	2.00	14.74	2.60	0.00	41.24	3.81	1.11	2.04	17.12	2.79
<b>Camden</b>	0.35	10.23	0.14	14.76	13.96	1.83	0.78	40.57	24.56	6.52	11.84	15.24	20.78
<b>Cinnaminson</b>	0.00	1.58	0.00	1.44	14.15	1.11	0.00	38.83	2.77	0.79	1.37	16.70	1.78
<b>Cooper River</b>	0.00	2.09	0.00	2.19	14.71	1.31	0.12	38.91	4.24	1.16	1.99	17.03	3.35
<b>Fairmont Park</b>	0.00	1.68	0.00	1.93	14.53	1.88	0.12	40.24	3.83	1.01	1.75	16.87	2.96
<b>FDR Park</b>	0.15	8.55	0.00	9.11	13.97	1.48	0.33	40.98	14.29	4.16	6.44	16.16	10.08
<b>Fort Mifflin</b>	0.00	2.15	0.00	1.93	12.50	1.04	0.00	35.52	3.72	1.03	1.89	14.46	2.69
<b>Fort Washington</b>	0.00	1.91	0.00	2.45	41.19	1.73	0.00	107.53	4.72	1.90	1.98	47.10	2.94
<b>Greenwich Park</b>	0.00	1.01	0.00	1.45	14.29	1.12	0.00	39.22	2.80	0.80	1.39	16.86	1.80
<b>Hadden Lake Park</b>	0.00	2.06	0.00	2.33	14.97	1.26	0.00	39.45	4.13	1.24	1.90	16.90	3.04
<b>Hopkins Pond Park</b>	0.00	0.98	0.00	0.86	13.55	0.65	0.05	40.98	1.42	0.48	0.69	16.15	1.02
<b>Hunting Park</b>	0.14	3.95	0.00	4.91	14.63	2.64	0.25	38.02	9.46	2.70	4.65	16.73	7.91
<b>JHZ(NWR)</b>	0.00	1.96	0.00	2.13	15.27	1.07	0.10	39.92	3.73	0.00	1.77	18.34	2.57
<b>Knollwood Park</b>	0.00	6.49	0.00	7.82	13.58	1.14	0.55	39.92	14.46	3.98	6.65	15.68	10.29
<b>La Salle University</b>	0.00	0.96	0.00	1.01	7.53	0.75	0.06	40.90	1.76	0.44	0.88	8.80	1.47
<b>Lum's Pond</b>	0.00	0.62	0.00	0.61	14.91	1.13	0.00	39.53	1.39	0.00	0.63	16.87	1.09
<b>Mill Creek Park</b>	0.00	1.29	0.00	1.34	14.61	1.21	0.00	41.75	2.61	0.68	1.33	16.66	1.93
<b>Morris Park</b>	0.00	1.41	0.00	1.58	15.60	5.87	0.09	105.26	2.94	0.85	1.24	18.41	2.04
<b>Neshaminy Park</b>	0.00	1.17	0.00	1.39	13.46	0.96	0.00	41.15	2.91	0.68	1.31	15.80	2.38
<b>New Brunswick(Rutgers Garden)</b>	0.00	0.00	0.00	1.96	14.23	1.20	0.15	39.45	3.96	1.13	1.94	17.06	3.10
<b>Northeast Philadelphia Airport</b>	0.00	1.54	0.00	2.03	12.05	1.49	0.00	41.15	3.91	1.11	2.16	13.84	3.18
<b>Philidelphia University</b>	0.00	2.01	0.00	2.00	28.31	1.19	0.12	39.06	3.59	1.00	1.77	33.18	2.84
<b>Red Bank Battlefield</b>	0.00	2.94	0.00	1.94	15.33	1.05	0.09	40.08	4.65	1.51	2.81	17.58	3.08
<b>Ridley Creek State Park</b>	0.00	0.79	0.04	0.77	13.98	5.34	0.04	102.88	1.23	0.39	0.52	15.26	0.91
<b>Swarthmore (Hicks roof)</b>	0.00	1.54	0.00	1.96	14.05	0.81	0.16	39.84	3.83	1.04	1.86	16.60	3.94
<b>Swathmore(Science Center)</b>	0.00	1.67	0.00	2.23	14.16	1.72	0.13	40.82	5.51	1.54	2.80	16.93	6.18
<b>Von Neida Park</b>	0.00	4.54	0.00	5.16	15.38	1.91	0.24	39.14	8.61	2.57	4.12	17.44	6.07
<b>Washington Square Park</b>	0.15	6.36	0.00	8.17	16.72	7.76	0.29	94.88	14.39	4.05	6.63	18.77	12.43
<b>Claire Welty's house</b>	0.00	2.92	0.00	3.28	10.96	1.37	0.12	39.53	5.15	1.45	2.17	13.16	3.68
<b>Widener University</b>	0.00	2.72	0.00	3.32	14.35	3.01	0.17	40.24	7.85	2.10	4.11	16.72	8.93
<b>Wiggins Park Marina</b>	0.00	0.00	0.00	6.59	13.51	1.51	0.22	98.43	15.04	4.12	7.52	16.66	11.81

	28	21+33	22	46	52+43	49	47+48	65	44	37	42	41+71	64
<b>Bellevue State Park</b>	1.99	1.44	0.85	0.32	3.19	1.39	0.84	15.65	1.69	0.31	0.22	0.33	1.14
<b>Billing sport elementary school</b>	2.72	1.85	1.15	0.29	3.97	1.94	1.25	15.92	2.38	0.54	0.58	0.62	1.39
<b>Camden</b>	18.47	15.11	8.25	2.53	41.07	14.59	7.59	14.59	24.89	1.26	3.57	3.98	12.19
<b>Cinnaminson</b>	2.03	1.20	0.66	0.21	1.96	1.07	0.63	15.18	1.28	0.28	0.48	0.31	0.89
<b>Cooper River</b>	2.97	2.06	1.09	0.31	3.51	1.65	1.10	15.84	2.43	0.50	0.53	0.50	1.36
<b>Fairmont Park</b>	2.58	1.71	1.05	0.37	3.92	1.71	0.97	15.64	2.57	0.35	0.49	0.54	1.47
<b>FDR Park</b>	9.44	7.23	3.97	1.31	8.16	4.71	3.31	15.04	6.26	1.52	1.51	1.75	4.00
<b>Fort Mifflin</b>	2.38	1.49	0.96	0.42	3.55	1.81	1.16	13.44	2.34	0.42	0.60	0.64	1.49
<b>Fort Washington</b>	2.81	1.84	1.08	0.49	4.33	1.67	1.10	41.53	3.09	0.48	0.60	0.67	1.60
<b>Greenwich Park</b>	2.05	1.21	0.66	0.21	1.98	1.09	0.63	15.33	1.29	0.29	0.48	0.31	0.90
<b>Hadden Lake Park</b>	2.81	2.09	1.12	0.36	3.25	1.39	0.96	15.21	2.22	0.00	0.50	0.47	1.26
<b>Hopkins Pond Park</b>	1.00	0.74	0.38	0.11	1.38	0.61	0.45	14.31	0.79	0.00	0.07	0.21	0.42
<b>Hunting Park</b>	6.98	5.31	2.91	0.92	8.84	4.16	2.59	15.29	6.01	0.95	1.30	1.24	3.66
<b>JHZ(NWR)</b>	2.52	1.59	0.86	0.36	2.65	1.41	0.97	17.10	2.01	0.16	0.57	0.51	1.02
<b>Knollwood Park</b>	8.95	6.83	3.66	1.10	7.68	4.42	3.05	14.00	6.05	1.42	1.37	1.53	3.70
<b>La Salle University</b>	1.41	0.86	0.72	0.13	2.34	1.13	0.64	8.58	1.34	0.24	0.21	0.27	0.73
<b>Lum's Pond</b>	0.97	0.60	0.44	0.22	1.42	0.83	0.63	14.92	0.93	0.07	0.17	0.00	0.84
<b>Mill Creek Park</b>	1.89	1.21	0.72	0.30	2.47	1.11	0.64	15.72	1.59	0.29	0.43	0.00	0.84
<b>Morris Park</b>	1.86	1.33	0.71	0.18	2.91	1.21	0.83	16.84	1.95	0.00	0.55	0.37	0.94
<b>Neshaminy Park</b>	2.02	1.28	0.60	0.37	2.45	1.43	0.93	14.37	1.61	0.16	0.46	0.30	1.13
<b>New Brunswick(Rutgers Garden)</b>	2.86	1.90	1.32	0.43	3.52	1.95	1.20	14.69	2.45	0.47	0.40	0.51	1.53
<b>Northeast Philadelphia Airport</b>	3.08	2.08	1.24	0.41	4.75	2.07	1.38	12.74	3.18	0.48	0.69	0.64	1.56
<b>Philidelphia University</b>	2.50	1.59	0.98	0.34	3.59	1.77	0.85	29.67	2.16	0.38	0.55	0.47	1.29
<b>Red Bank Battlefield</b>	3.39	1.72	1.14	0.50	5.46	2.98	2.22	16.19	3.29	0.37	0.86	1.05	2.16
<b>Ridley Creek State Park</b>	0.85	0.58	0.31	0.15	1.08	0.70	0.44	14.48	0.68	0.00	0.13	0.00	0.52
<b>Swarthmore (Hicks roof)</b>	3.42	2.53	1.44	0.54	28.10	7.20	2.22	14.68	15.29	0.77	1.17	1.45	5.63
<b>Swathmore(Science Center)</b>	5.03	3.81	2.32	0.99	54.96	12.54	3.67	15.57	26.28	0.42	1.97	2.21	9.63
<b>Von Neida Park</b>	5.55	4.17	2.11	0.69	5.40	2.67	1.71	15.98	3.93	0.79	0.94	0.90	2.33
<b>Washington Square Park</b>	10.77	8.30	4.12	1.37	22.66	8.58	4.73	17.30	13.87	0.27	2.20	2.53	6.76
<b>Claire Welty's house</b>	3.32	2.45	1.31	0.48	7.04	2.74	1.40	12.52	3.99	0.63	0.69	0.67	2.04
<b>Widener University</b>	7.34	5.21	3.14	1.54	26.72	9.79	5.52	15.41	16.80	0.21	2.82	3.49	8.99
<b>Wiggins Park Marina</b>	11.57	7.64	3.93	1.59	14.01	7.52	5.45	14.79	9.83	0.08	2.14	2.19	5.27

	40	74	70+76	66	56+60	81	77	95	91+88	89	101+90	99	97	87+86
<b>Bellevue State Park</b>	0.00	0.47	1.59	0.81	0.67	0.00	0.00	2.51	0.44	0.47	2.47	1.14	0.68	1.52
<b>Billing sport elementary school</b>	0.24	0.67	2.33	1.25	0.90	0.00	0.00	4.16	0.61	0.73	4.47	1.67	0.82	2.51
<b>Camden</b>	2.14	8.59	31.57	12.26	9.00	0.35	0.81	44.75	6.24	8.01	51.12	17.57	12.22	25.53
<b>Cinnaminson</b>	0.14	0.39	1.09	0.55	0.42	0.00	0.00	1.40	0.31	0.19	1.57	0.62	0.34	0.85
<b>Cooper River</b>	0.24	0.73	2.10	1.22	1.02	0.07	0.16	3.08	0.41	0.45	3.13	1.10	0.74	1.98
<b>Fairmont Park</b>	0.30	0.77	2.17	1.18	0.79	0.05	0.07	3.43	0.45	0.57	3.66	1.29	0.70	1.88
<b>FDR Park</b>	0.87	2.05	5.37	3.07	2.62	0.11	0.35	5.69	0.94	0.96	5.80	2.22	1.41	3.16
<b>Fort Mifflin</b>	0.31	0.63	1.79	0.93	0.71	0.00	0.00	3.07	0.66	0.46	3.02	1.00	0.79	1.39
<b>Fort Washington</b>	0.00	0.71	1.88	0.93	1.02	0.14	0.00	3.20	0.37	0.00	3.26	0.92	0.61	1.89
<b>Greenwich Park</b>	0.15	0.39	1.10	0.55	0.05	0.00	0.00	1.41	0.31	0.19	1.59	0.62	0.35	0.86
<b>Hadden Lake Park</b>	0.29	0.58	1.74	0.85	0.70	0.00	0.00	2.48	0.53	0.00	2.33	0.86	0.50	1.31
<b>Hopkins Pond Park</b>	0.20	0.25	0.60	0.28	0.16	0.00	0.00	1.06	0.11	0.00	1.12	0.31	0.25	0.71
<b>Hunting Park</b>	0.55	1.86	5.91	3.05	2.35	0.06	0.00	7.86	1.14	1.39	8.25	2.79	1.94	4.15
<b>JHZ(NWR)</b>	0.00	0.55	1.43	0.85	0.62	0.00	0.00	2.39	0.25	0.41	2.29	0.76	0.61	1.28
<b>Knollwood Park</b>	0.83	1.53	4.17	2.57	1.95	0.00	0.00	4.30	0.65	0.70	4.27	1.60	1.22	2.70
<b>La Salle University</b>	0.23	0.52	1.50	0.56	0.34	0.00	0.20	2.14	0.31	0.43	2.76	0.99	0.48	1.21
<b>Lum's Pond</b>	0.00	0.26	0.67	0.41	0.31	0.00	0.00	1.12	0.19	0.24	1.33	0.45	0.32	0.37
<b>Mill Creek Park</b>	0.16	0.37	1.37	0.62	0.52	0.00	0.00	1.92	0.34	0.25	2.13	0.80	0.48	0.81
<b>Morris Park</b>	0.09	0.47	1.72	0.70	0.60	0.00	0.00	2.37	0.41	0.38	2.50	1.08	0.00	0.88
<b>Neshaminy Park</b>	0.19	0.44	1.45	0.82	0.59	0.00	0.07	1.95	0.42	0.36	1.76	0.60	0.22	0.90
<b>New Brunswick(Rutgers Garden)</b>	0.41	0.85	2.01	1.08	0.77	0.00	0.00	2.81	0.52	0.44	2.83	1.06	0.64	1.36
<b>Northeast Philadelphia Airport</b>	0.39	1.02	3.11	1.36	1.17	0.00	0.00	4.61	0.77	0.70	5.05	1.76	1.15	2.87
<b>Philidelphia University</b>	0.17	0.53	2.35	1.00	0.72	0.00	0.00	3.19	0.40	0.45	3.14	1.15	0.64	1.87
<b>Red Bank Battlefield</b>	0.51	0.90	2.44	1.65	1.23	0.00	0.00	4.24	0.86	0.73	4.10	1.46	0.80	1.82
<b>Ridley Creek State Park</b>	0.00	0.21	0.61	0.33	0.18	0.00	0.00	0.80	0.00	0.19	0.70	0.27	0.17	0.46
<b>Swarthmore (Hicks roof)</b>	0.73	5.56	26.62	7.73	5.24	0.47	1.75	46.61	6.63	9.24	58.53	19.89	15.04	31.36
<b>Swathmore(Science Center)</b>	1.36	7.28	35.72	10.21	6.09	0.43	0.07	61.82	8.28	10.39	63.65	22.49	15.70	31.50
<b>Von Neida Park</b>	0.53	1.13	2.85	1.62	1.38	0.00	0.00	3.68	0.59	0.66	3.69	1.29	0.83	1.67
<b>Washington Square Park</b>	1.02	4.68	16.93	6.69	4.62	0.12	0.46	24.67	3.44	4.32	26.83	9.41	6.61	13.43
<b>Claire Welty's house</b>	0.62	1.24	4.46	2.00	1.17	0.00	0.15	7.58	1.01	1.33	7.55	2.64	1.92	3.39
<b>Widener University</b>	1.50	6.26	22.20	10.18	8.03	0.27	0.00	25.66	3.98	4.31	26.86	10.67	7.10	13.81
<b>Wiggins Park Marina</b>	1.13	2.82	8.82	4.54	3.02	0.06	0.00	11.38	1.59	2.12	11.98	4.48	2.68	5.68

	85	110	82	124	118	114	105	151	135+144+147	149	146	153	132
<b>Bellevue State Park</b>	0.00	2.11	0.00	0.00	1.38	0.00	0.48	0.56	0.42	1.92	0.00	1.26	0.86
<b>Billing sport elementary school</b>	0.39	3.60	0.00	0.00	2.50	0.00	0.85	0.00	0.49	2.47	0.18	2.07	1.17
<b>Camden</b>	6.28	43.53	4.02	0.00	31.58	0.87	10.07	6.45	5.32	24.83	3.59	17.81	9.92
<b>Cinnaminson</b>	0.00	1.15	0.00	0.00	0.65	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cooper River</b>	0.00	2.64	0.00	0.00	1.53	0.12	0.67	0.49	0.51	1.70	0.00	1.38	0.73
<b>Fairmont Park</b>	0.51	2.76	0.30	0.08	1.90	0.09	0.47	0.59	0.54	2.41	0.27	1.74	0.67
<b>FDR Park</b>	0.98	4.86	0.55	0.00	3.53	0.00	1.35	1.29	0.82	3.80	0.79	3.79	1.45
<b>Fort Mifflin</b>	0.48	2.34	0.18	0.24	1.35	0.00	0.42	0.55	0.40	1.97	0.14	1.34	0.64
<b>Fort Washington</b>	0.00	2.40	0.00	0.00	1.21	0.87	0.53	0.00	0.00	0.00	0.00	0.00	0.00
<b>Greenwich Park</b>	0.00	1.16	0.00	0.00	0.82	0.00	0.16	0.29	0.00	0.91	0.00	0.66	0.00
<b>Hadden Lake Park</b>	0.34	2.09	0.00	0.00	1.35	0.00	0.40	0.30	0.42	1.47	0.09	1.08	0.34
<b>Hopkins Pond Park</b>	0.00	0.67	0.00	0.00	0.63	0.00	0.00	0.00	0.00	0.63	0.19	0.64	0.00
<b>Hunting Park</b>	1.10	6.90	0.60	0.44	4.34	0.00	1.62	1.41	1.02	4.95	0.68	3.98	1.91
<b>JHZ(NWR)</b>	0.27	1.93	0.00	0.00	0.87	0.00	0.09	0.00	0.00	1.06	0.00	0.91	0.00
<b>Knollwood Park</b>	0.64	3.67	0.46	0.00	3.16	0.00	1.04	0.77	0.59	2.34	0.55	1.90	1.01
<b>La Salle University</b>	0.00	1.97	0.00	0.00	1.59	0.00	0.00	0.58	0.00	1.76	0.00	1.31	0.58
<b>Lum's Pond</b>	0.00	1.13	0.00	0.00	0.58	0.00	0.00	0.00	0.00	0.94	0.00	0.80	0.00
<b>Mill Creek Park</b>	0.00	1.42	0.00	0.00	1.05	0.00	0.28	0.45	0.49	1.38	0.15	0.89	0.54
<b>Morris Park</b>	0.33	1.94	0.00	0.00	1.23	0.00	0.35	0.60	0.00	1.34	0.20	1.01	0.44
<b>Neshaminy Park</b>	0.00	1.37	0.00	0.00	1.01	0.00	0.27	0.00	0.10	0.78	0.00	0.80	0.22
<b>New Brunswick(Rutgers Garden)</b>	0.00	1.98	0.00	0.00	1.50	0.00	0.48	0.56	0.00	1.76	0.00	1.35	0.59
<b>Northeast Philadelphia Airport</b>	0.62	4.47	0.43	0.00	2.69	0.00	0.88	0.79	0.45	2.81	0.41	2.23	0.85
<b>Philidelphia University</b>	0.44	2.32	0.00	0.00	1.50	0.00	0.69	0.55	0.00	1.61	0.39	1.36	0.66
<b>Red Bank Battlefield</b>	0.62	3.24	0.28	0.00	1.78	0.00	0.67	0.96	0.62	2.22	0.45	1.87	0.75
<b>Ridley Creek State Park</b>	0.00	0.51	0.00	0.00	0.00	0.00	0.11	0.18	0.00	0.52	0.00	0.45	0.00
<b>Swarthmore (Hicks roof)</b>	7.61	56.66	5.18	2.42	42.18	1.27	13.98	7.04	6.02	29.01	4.11	23.50	12.64
<b>Swathmore</b>	7.76	54.49	4.73	1.84	35.66	0.81	11.30	5.45	5.01	24.05	2.94	17.53	10.06
<b>Von Neida Park</b>	0.48	2.87	0.00	0.00	1.82	0.00	0.71	0.75	0.48	2.12	0.32	1.90	0.98
<b>Washington Square Park</b>	3.38	21.93	1.72	0.84	15.25	0.50	4.76	4.00	2.93	13.76	1.99	10.79	4.83
<b>Claire Welty's house</b>	0.80	5.71	0.58	0.00	4.51	0.00	1.18	1.56	1.03	4.64	0.70	3.42	1.64
<b>Widener University</b>	3.93	22.75	2.33	1.13	15.82	0.56	5.39	2.87	2.42	11.36	1.57	8.33	4.28
<b>Wiggins Park Marina</b>	1.33	9.92	0.75	0.00	7.27	0.00	2.45	2.39	1.41	7.41	0.97	5.88	2.29

	141	138+163	158	121	126	166	167	156+157	169	179	178	187	183
<b>Bellevue State Park</b>	0.39	1.38	0.00	1.03	0.17	20.62	0.00	0.00	0.00	0.00	0.30	0.72	0.28
<b>Billing sport elementary school</b>	0.00	2.18	0.29	0.96	0.00	19.17	0.14	0.00	0.00	0.17	0.00	0.66	0.14
<b>Camden</b>	4.39	21.59	2.13	0.66	1.60	16.97	1.61	0.33	0.00	2.79	0.62	6.25	1.53
<b>Cinnaminson</b>	0.00	0.00	0.00	0.00	0.00	18.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cooper River</b>	0.32	1.38	0.13	0.87	0.00	18.84	0.00	0.00	0.00	0.00	0.00	0.67	0.00
<b>Fairmont Park</b>	2.89	1.62	0.17	1.10	0.25	18.31	0.00	0.00	0.00	0.00	0.00	0.82	0.32
<b>FDR Park</b>	0.74	3.61	0.40	0.84	0.45	17.58	0.70	0.00	0.00	0.87	0.28	1.83	1.37
<b>Fort Mifflin</b>	0.26	1.38	0.16	22.84	0.00	12.53	0.00	0.00	0.00	0.37	0.00	0.51	0.13
<b>Fort Washington</b>	0.00	1.53	0.00	2.73	0.39	56.11	0.00	0.00	1.88	0.00	0.00	0.00	0.00
<b>Greenwich Park</b>	0.00	0.67	0.00	26.45	0.00	18.50	0.00	0.00	0.00	0.17	0.00	0.24	0.12
<b>Hadden Lake Park</b>	0.18	1.33	0.00	0.76	0.12	19.13	0.00	0.00	0.00	0.00	0.00	0.32	0.33
<b>Hopkins Pond Park</b>	0.00	0.42	0.00	0.99	0.00	16.64	0.00	0.00	0.00	0.66	0.16	0.00	0.00
<b>Hunting Park</b>	1.01	3.94	0.35	0.83	0.32	18.12	0.11	0.00	0.18	1.08	0.00	1.07	0.55
<b>JHZ(NWR)</b>	0.00	0.86	0.00	0.86	0.00	18.76	0.00	0.00	0.00	0.00	0.23	0.24	0.15
<b>Knollwood Park</b>	0.48	2.94	0.26	1.03	0.20	17.07	0.17	0.00	0.00	0.65	0.00	0.57	0.28
<b>La Salle University</b>	0.27	1.57	0.20	0.52	0.00	12.12	0.00	0.00	0.00	0.00	0.00	0.68	0.51
<b>Lum's Pond</b>	0.00	0.56	0.00	0.71	0.00	19.62	0.00	0.00	0.00	0.00	0.00	0.46	0.00
<b>Mill Creek Park</b>	0.25	0.86	0.00	1.01	0.00	23.54	0.00	0.00	0.00	0.45	0.00	0.61	0.00
<b>Morris Park</b>	0.18	1.02	0.00	0.85	0.00	18.86	0.00	0.00	0.00	0.00	0.00	0.37	0.00
<b>Neshaminy Park</b>	0.41	0.96	0.00	0.69	0.00	17.47	0.00	0.00	0.00	0.00	0.00	0.31	0.00
<b>New Brunswick(Rutgers Garden)</b>	0.00	1.52	0.00	0.81	0.00	17.47	0.00	0.00	0.00	0.00	0.00	0.98	0.35
<b>Northeast Philadelphia Airport</b>	0.44	2.63	0.44	0.78	0.14	15.69	0.09	0.00	0.00	0.52	0.00	0.91	0.31
<b>Philidelphia University</b>	0.00	1.53	0.00	1.42	0.00	34.71	0.00	0.00	0.00	0.00	0.00	0.37	0.30
<b>Red Bank Battlefield</b>	0.00	1.59	0.00	0.77	0.24	18.11	0.00	0.00	0.00	0.69	0.00	0.93	0.23
<b>Ridley Creek State Park</b>	0.00	0.24	0.00	0.00	0.00	17.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Swarthmore (Hicks roof)</b>	5.26	27.18	3.31	1.03	0.58	18.86	1.29	0.31	0.00	1.93	0.43	2.40	1.19
<b>Swathmore(Science Center)</b>	3.56	20.96	2.47	0.84	0.39	18.75	0.97	0.00	0.00	1.66	0.51	1.90	0.82
<b>Von Neida Park</b>	0.32	1.73	0.16	1.13	0.25	18.41	0.00	0.00	0.00	0.54	0.00	0.66	0.27
<b>Washington Square Park</b>	2.59	11.56	1.17	1.06	0.66	20.82	0.78	0.00	0.00	1.59	0.37	2.87	1.14
<b>Claire Welty's house</b>	0.92	3.82	0.39	0.80	0.30	16.67	0.17	0.00	0.00	0.68	0.00	1.31	0.58
<b>Widener University</b>	1.62	9.71	1.07	0.86	0.45	18.00	0.54	0.00	0.00	1.40	0.00	1.96	0.84
<b>Wiggins Park Marina</b>	1.14	6.19	0.79	0.88	0.65	17.64	0.27	0.00	0.00	1.75	1.09	2.50	0.81



	185	174	177	173	171	172	180	170+190	189	202	199	203+196
<b>Bellevue State Park</b>	0.00	0.00	0.00	0.00	0.90	0.00	0.28	0.22	0.00	0.00	0.00	0.00
<b>Billing sport elementary school</b>	0.23	0.17	0.00	0.00	0.66	0.00	0.39	0.00	0.00	0.00	0.00	0.00
<b>Camden</b>	0.15	1.44	0.87	0.00	0.62	0.27	2.64	1.19	0.00	0.98	5.00	2.11
<b>Cinnaminson</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cooper River</b>	0.00	0.47	0.00	0.00	0.81	0.00	0.38	0.00	0.00	0.00	0.00	0.00
<b>Fairmont Park</b>	0.00	0.43	0.29	0.00	0.86	0.00	0.54	0.26	0.00	0.00	0.00	0.00
<b>FDR Park</b>	0.15	0.73	0.98	0.00	1.08	0.00	1.29	0.28	0.00	0.00	0.56	0.48
<b>Fort Mifflin</b>	0.00	0.40	0.14	0.00	0.64	0.00	0.30	0.17	0.00	0.00	0.00	0.00
<b>Fort Washington</b>	0.00	0.00	0.00	0.00	2.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Greenwich Park</b>	0.00	0.00	0.00	0.00	1.03	0.00	0.19	0.00	0.00	0.00	0.00	0.00
<b>Hadden Lake Park</b>	0.00	0.37	0.00	0.00	0.66	0.00	0.17	0.18	0.00	0.00	0.00	0.00
<b>Hopkins Pond Park</b>	0.00	0.00	0.00	0.00	0.71	0.00	0.22	0.00	0.00	0.00	0.00	0.00
<b>Hunting Park</b>	0.09	0.62	0.42	0.00	0.70	0.00	0.98	0.45	0.00	0.00	0.72	0.21
<b>JHZ(NWR)</b>	0.00	0.13	0.00	0.00	0.78	0.00	0.28	0.00	0.00	0.00	0.00	0.00
<b>Knollwood Park</b>	0.00	0.44	0.35	0.00	0.77	0.00	0.53	0.34	0.00	0.00	0.40	0.00
<b>La Salle University</b>	0.37	0.38	0.19	0.00	0.81	0.00	0.38	0.25	0.00	0.00	0.67	0.00
<b>Lum's Pond</b>	0.00	0.00	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Mill Creek Park</b>	0.00	0.18	0.00	0.00	0.63	0.00	0.17	0.00	0.00	0.00	0.00	0.00
<b>Morris Park</b>	0.00	0.00	0.00	0.00	2.08	0.00	0.26	0.00	0.00	0.29	0.00	0.00
<b>Neshaminy Park</b>	0.00	0.00	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>New Brunswick(Rutgers Garden)</b>	0.00	0.17	0.00	0.00	0.83	0.00	0.37	0.30	0.00	0.28	0.35	0.00
<b>Northeast Philadelphia Airport</b>	0.00	0.43	0.28	0.00	0.89	0.00	0.55	0.41	0.00	0.00	0.00	0.00
<b>Philidelphia University</b>	0.00	0.25	0.00	0.00	0.80	0.00	0.43	0.00	0.00	0.00	0.00	0.00
<b>Red Bank Battlefield</b>	0.00	0.41	0.28	0.00	0.67	0.00	0.52	0.30	0.00	0.00	0.00	0.00
<b>Ridley Creek State Park</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Swarthmore (Hicks roof)</b>	0.11	1.95	1.33	0.00	0.94	0.21	1.88	1.04	0.00	0.00	0.00	0.00
<b>Swathmore(Science Center)</b>	0.09	1.28	0.85	0.00	0.84	0.35	1.71	1.22	0.00	0.00	0.22	0.00
<b>Von Neida Park</b>	0.00	0.48	0.15	0.00	0.54	0.18	0.52	0.25	0.00	0.00	0.00	0.00
<b>Washington Square Park</b>	0.39	1.29	0.77	0.00	1.78	0.32	2.05	1.01	0.00	0.00	0.77	0.37
<b>Claire Welty's house</b>	0.00	0.61	0.48	0.00	0.69	0.17	1.29	0.38	0.00	0.00	0.00	0.00
<b>Widener University</b>	0.15	1.07	0.67	0.00	0.74	0.00	1.86	0.84	0.00	0.00	0.53	0.27
<b>Wiggins Park Marina</b>	0.00	1.88	0.77	0.00	2.16	0.00	1.81	0.78	0.00	0.43	1.01	0.39

	195	194	208	206	Sum	Surr 14 (%)	Surr 23(%)	Surr (65)	Surr166 (%)
<b>Bellevue State Park</b>	0.00	0.00	0.00	0.00	93.63	77.40	88.22	78.26	103.08
<b>Billing sport elementary school</b>	0.00	0.00	0.00	0.00	116.14	73.71	85.62	79.61	95.83
<b>Camden</b>	0.96	0.96	0.00	0.00	740.01	69.78	76.20	72.97	84.87
<b>Cinnaminson</b>	0.00	0.00	0.00	0.00	70.48	70.74	83.50	75.90	91.26
<b>Cooper River</b>	0.00	0.00	0.00	0.00	104.58	73.56	85.16	79.19	94.18
<b>Fairmont Park</b>	0.00	0.00	0.00	0.00	112.34	72.63	84.34	78.21	91.53
<b>FDR Park</b>	0.00	0.00	0.00	0.00	223.18	69.87	80.80	75.21	87.92
<b>Fort Mifflin</b>	0.00	0.00	0.00	0.00	119.37	62.51	72.32	67.20	62.67
<b>Fort Washington</b>	0.00	2.43	0.00	0.00	176.02	102.97	117.74	103.84	140.27
<b>Greenwich Park</b>	0.00	0.00	0.00	0.00	101.13	71.44	84.32	76.65	92.51
<b>Hadden Lake Park</b>	0.00	0.00	0.00	0.00	96.29	74.86	84.49	76.03	95.67
<b>Hopkins Pond Park</b>	0.44	0.00	0.00	0.00	64.69	67.75	80.73	71.55	83.19
<b>Hunting Park</b>	0.00	0.00	0.00	0.00	203.35	73.16	83.66	76.44	90.59
<b>JHZ(NWR)</b>	0.00	0.00	0.00	0.00	88.03	76.36	91.68	85.51	93.81
<b>Knollwood Park</b>	0.00	0.00	0.00	0.00	193.08	67.88	78.42	69.99	85.34
<b>La Salle University</b>	0.00	0.00	0.00	0.00	84.50				
<b>Lum's Pond</b>	0.00	0.00	0.00	0.00	63.66	74.55	84.35	74.59	98.12
<b>Mill Creek Park</b>	0.00	0.00	0.00	0.00	84.20	73.06	83.30	78.62	117.72
<b>Morris Park</b>	0.00	0.00	0.00	0.00	157.81	78.01	92.03	84.19	94.31
<b>Neshaminy Park</b>	0.00	0.00	0.00	0.00	82.24	67.32	78.99	71.86	87.34
<b>New Brunswick(Rutgers Garden)</b>	0.00	0.00	0.00	0.00	100.35	71.14	85.29	73.46	87.35
<b>Northeast Philadelphia Airport</b>	0.00	0.00	0.00	0.00	127.56	60.25	69.18	63.72	78.46
<b>Philidelphia University</b>	0.00	0.00	0.00	0.00	100.31	70.77	82.95	74.18	86.77
<b>Red Bank Battlefield</b>	0.00	0.00	0.00	0.00	124.15	76.65	87.88	80.95	90.54
<b>Ridley Creek State Park</b>	0.00	0.00	0.00	0.00	124.28	69.88	76.32	72.40	89.67
<b>Swarthmore (Hicks roof)</b>	0.00	0.00	0.00	0.00	624.13	70.27	83.01	73.42	94.32
<b>Swathmore(Science Center)</b>	0.00	0.00	0.00	0.00	683.64	70.78	84.63	77.84	93.73
<b>Von Neida Park</b>	0.00	0.00	0.00	0.00	143.08	76.88	87.19	79.92	92.06
<b>Washington Square Park</b>	0.00	0.00	0.00	0.00	483.71	83.58	93.85	86.51	104.11
<b>Claire Welty's house</b>	0.00	0.00	0.00	0.00	159.86	54.82	65.78	62.58	83.33
<b>Widener University</b>	0.00	0.00	0.00	0.00	412.15	71.74	83.59	77.03	90.01
<b>Wiggins Park Marina</b>	0.00	0.00	0.00	67.54	83.29	67.54	83.29	73.96	88.20

Table I- 2. Determined mass of OCPs in each passive sampler (ng).

	alpha-HCH	gamma-HCH	Heptachlor epoxide	trans chlordane	Cis-Chlordane	Endosulfan I	Cis-nonachlor	4,4' DDT
Bellevue State Park	1.15	2.16	1.21	7.87	3.88	0.99	0.37	1.21
Billing sport elementary school	0.83	2.24	1.33	10.75	6.38	6.89	0.73	0.00
Camden	1.55	2.06	1.65	9.41	10.49	2.21	0.53	1.68
Cinnaminson	1.28	1.49	0.07	6.00	5.38	2.83	0.36	0.21
Cooper River	1.48	2.02	1.74	10.25	8.40	2.39	0.54	1.53
Fairmont Park	2.19	2.30	1.21	7.67	6.37	2.98	0.40	1.55
FDR Park	1.45	2.21	1.29	8.66	9.71	7.16	0.56	2.27
Fort Mifflin	1.30	2.06	1.38	6.27	4.69	3.68	0.50	0.89
Fort Washington	0.67	1.09	0.00	2.57	3.38	0.97	0.16	0.00
Greenwich Park	1.24	3.88	0.80	3.99	4.73	9.16	0.22	1.04
Hadden Lake Park	1.33	2.08	1.94	14.28	12.43	2.88	0.75	0.85
Hopkins Pond Park	0.81	1.02	0.93	3.87	3.02	0.85	0.17	0.92
Hunting Park	1.85	2.97	1.94	16.38	13.21	4.35	0.82	5.20
JHZ(NWR)	1.26	1.61	1.03	5.31	4.43	2.57	0.32	0.60
Knollwood Park	1.58	2.01	0.90	4.82	3.53	1.07	0.29	0.97
La Salle University	0.80	1.13	0.49	4.58	3.50	1.36	0.20	0.94
Lum's Pond	1.32	3.14	0.34	4.08	4.78	1.29	0.39	0.24
Morris Park	0.50	0.74	7.52	5.15	3.99	0.53	0.20	0.69
Neshaminy Park	0.88	1.24	0.88	3.48	3.07	0.66	0.20	0.96
New Brunswick(Rutgers Garden)	1.37	1.84	3.01	7.54	9.66	1.36	0.58	2.04
Northeast Philadelphia Airport	1.56	1.99	1.19	7.75	3.82	4.53	0.36	0.00
Philidelphia University	1.23	1.78	1.55	8.55	6.32	1.68	0.37	0.51
Red Bank Battlefield	1.32	2.39	1.47	7.40	7.25	5.48	0.50	1.23
Ridley Creek State Park	0.64	0.81	0.00	1.86	2.01	0.37	0.07	0.00
Swarthmore (Hicks roof)	1.04	1.81	1.27	10.45	6.15	2.01	0.47	0.85
Swathmore(Science Center)	1.75	4.32	2.40	19.28	15.82	4.52	1.07	3.40
Von Neida Park	1.21	1.89	1.08	9.99	5.38	2.14	0.52	1.63
Washington Square Park	2.29	3.23	1.86	17.84	18.40	7.97	0.97	20.83
Claire Welty's house	0.45	0.67	0.00	1.92	1.14	1.01	0.14	1.04
Widener University	1.75	3.20	2.31	18.68	14.54	8.94	1.16	3.12
Wiggins Park Marina	1.51	2.75	1.76	12.15	14.83	6.35	0.74	3.37

	Heptachlor	4,4' DDE	Sum HCH	alpha/gamma	Sum CHL	TC/CC	Sum DDT	DDT/DDE
Bellevue State Park	3.49	0.00	3.31	0.53	12.11	2.03	1.21	
Billing sport elementary school	8.62	4.53	3.06	0.37	17.86	1.68	4.53	0.00
Camden	8.92	4.95	3.61	0.75	20.43	0.90	6.64	0.34
Cinnaminson	1.44	1.25	2.77	0.86	11.74	1.12	1.45	0.16
Cooper River	5.14	3.32	3.50	0.73	19.20	1.22	4.85	0.46
Fairmont Park	4.19	3.18	4.49	0.96	14.44	1.20	4.74	0.49
FDR Park	3.64	5.65	3.66	0.65	18.93	0.89	7.92	0.40
Fort Mifflin	3.84	4.55	3.36	0.63	11.46	1.34	5.43	0.20
Fort Washington	0.29	0.26	1.76	0.62	6.11	0.76	0.26	0.00
Greenwich Park	1.35	ND	5.12	0.32	8.93	0.84	1.04	
Hadden Lake Park	6.22	3.35	3.41	0.64	27.46	1.15	4.21	0.25
Hopkins Pond Park	2.25	1.02	1.83	0.80	7.06	1.28	1.94	0.89
Hunting Park	9.62	7.62	4.82	0.62	30.40	1.24	12.82	0.68
JHZ(NWR)	2.71	2.57	2.86	0.78	10.06	1.20	3.17	0.24
Knollwood Park	3.68	2.34	3.60	0.79	8.65	1.37	3.31	0.42
La Salle University	4.30	1.24	1.93	0.71	8.28	1.31	2.19	0.76
Lum's Pond	0.60	1.38	4.45	0.42	9.25	0.85	1.62	0.17
Morris Park	5.26	3.01	1.25	0.68	9.34	1.29	3.69	0.23
Neshaminy Park	1.60	1.87	2.12	0.70	6.75	1.13	2.82	0.51
New Brunswick(Rutgers Garden)	2.80	13.88	3.21	0.75	17.79	0.78	15.92	0.15
Northeast Philadelphia Airport	4.30	6.15	3.56	0.78	11.93	2.03	6.15	0.00
Philidelphia University	7.94	2.37	3.01	0.69	15.24	1.35	2.88	0.22
Red Bank Battlefield	2.13	3.83	3.72	0.55	15.15	1.02	5.06	0.32
Ridley Creek State Park	1.80	1.47	1.44	0.79	3.94	0.92	1.47	0.00
Swarthmore (Hicks roof)	3.74	2.73	2.84	0.57	17.07	1.70	3.59	0.31
Swathmore(Science Center)	9.98	6.43	6.07	0.40	36.17	1.22	9.82	0.53
Von Neida Park	6.40	4.02	3.10	0.64	15.89	1.86	5.65	0.40
Washington Square Park	11.72	10.46	5.52	0.71	37.22	0.97	31.29	1.99
Claire Welty's house	5.44	2.30	1.12	0.67	3.20	1.69	3.34	0.45
Widener University	7.33	8.13	4.95	0.55	34.38	1.29	11.25	0.38
Wiggins Park Marina	94.63	9.74	4.26	0.55	27.71	0.82	13.10	0.35

Table I-3. Determined mass of PAHs in each passive sampler (ng).

	F	Ph	An	MeF	DBT	4,5 MePh	MePh/MeAn	Fl	Pyr
<b>Bellevue State Park</b>	154.08	768.76	8.68	28.79	22.87	33.15	36.98	247.10	113.93
<b>Billing sport elementary school</b>	192.64	1057.26	11.08	29.40	36.58	46.06	63.84	369.87	148.74
<b>Camden</b>	221.86	1150.23	14.16	45.51	71.66	53.80	100.49	446.80	218.14
<b>Cinnaminson</b>	147.83	534.72	3.64	19.64	26.82	18.46	23.25	139.36	56.63
<b>Cooper River</b>	173.89	684.90	7.98	27.70	38.05	31.75	38.09	281.78	147.49
<b>Fairmont Park</b>	270.37	921.62	10.49	26.47	53.15	40.31	67.61	302.23	136.23
<b>FDR Park</b>	359.57	1099.92	13.62	46.94	67.50	51.22	66.25	379.04	192.98
<b>Fort Mifflin</b>	193.07	671.61	7.19	43.14	38.56	33.99	87.71	228.94	102.42
<b>Fort Washington</b>	129.62	393.52	2.68	13.07	23.91	13.96	15.10	98.66	36.71
<b>Greenwich Park</b>	240.50	851.80	10.89	35.05	51.39	34.03	61.76	300.80	140.37
<b>Hadden Lake Park</b>	174.86	666.09	5.32	27.34	37.78	27.01	36.90	224.21	95.88
<b>Hopkins Pond Park</b>	99.49	262.80	1.77	12.03	15.90	8.82	11.16	59.90	28.48
<b>Hunting Park</b>	408.49	1801.63	25.29	63.48	102.70	84.44	147.04	695.85	331.04
<b>JHZ(NWR)</b>	152.82	582.84	3.80	32.34	36.89	24.06	36.88	170.67	69.69
<b>Knollwood Park</b>	160.05	656.68	8.60	35.07	31.89	31.94	91.13	208.85	105.41
<b>La Salle University</b>	97.71	458.98	5.47	13.13	25.47	18.31	20.61	171.91	82.06
<b>Lum's Pond</b>	59.74	246.65	2.12	10.47	12.73	10.26	14.64	96.64	37.81
<b>Morris Park</b>	175.66	684.31	6.71	21.20	39.43	25.29	25.33	195.31	85.17
<b>Neshaminy Park</b>	153.12	574.04	3.97	21.89	34.68	22.87	29.47	190.26	83.44
<b>New Brunswick(Rutgers Garden)</b>	153.03	610.06	4.23	23.04	35.03	23.85	34.29	193.57	78.29
<b>Northeast Philadelphia Airport</b>	172.80	1455.22	19.72	35.55	63.80	63.55	72.44	1026.84	367.82
<b>Philidelphia University</b>	212.98	758.04	6.84	18.82	42.30	28.32	29.47	230.81	93.77
<b>Red Bank Battlefield</b>	149.95	510.91	3.67	23.54	36.39	25.20	40.98	172.48	89.32
<b>Ridley Creek State Park</b>	70.87	237.65	1.08	6.01	12.45	6.72	5.54	42.66	15.30
<b>Swarthmore (Hicks roof)</b>	126.59	562.92	3.24	16.20	21.31	21.85	22.53	176.21	70.18
<b>Swathmore(Science Center)</b>	197.17	1016.41	6.47	31.33	55.53	45.69	54.20	391.76	141.62
<b>Von Neida Park</b>	577.34	2202.40	29.59	66.24	83.98	89.19	109.31	669.06	252.63
<b>Washington Square Park</b>	319.32	1585.68	23.56	84.79	90.36	80.27	126.16	679.68	370.95
<b>Claire Welty's house</b>	104.11	355.79	10.99	10.07	15.89	18.79	35.74	175.68	93.37
<b>Widener University</b>	206.35	1204.36	8.65	50.38	68.66	63.52	123.95	664.14	406.34
<b>Wiggins Park Marina</b>	255.81	1158.17	7.82	60.19	66.77	171.95	12.62	482.24	243.89

	<b>3,6 DMP</b>	<b>BaF</b>	<b>BbF</b>	<b>Ret</b>	<b>BNT</b>	<b>cyclo</b>	<b>BaA</b>	<b>chr/tri</b>	<b>Naph</b>
<b>Bellevue State Park</b>	11.93	24.56	7.14	3.78	4.54	5.44	13.71	49.52	1.05
<b>Billing sport elementary school</b>	22.34	34.81	11.79	4.21	8.07	8.17	20.82	75.77	1.74
<b>Camden</b>	43.22	55.21	8.96	6.53	13.74	9.42	25.09	79.81	1.46
<b>Cinnaminson</b>	6.97	11.26	3.07	1.74	1.84	2.47	6.14	23.55	0.53
<b>Cooper River</b>	13.11	42.27	11.14	2.84	9.31	22.80	58.17	145.64	4.87
<b>Fairmont Park</b>	15.20	28.82	9.34	3.22	4.55	7.13	17.58	47.11	1.24
<b>FDR Park</b>	24.37	53.49	16.03	4.54	11.24	22.15	56.97	121.47	3.61
<b>Fort Mifflin</b>	19.88	24.46	6.74	3.51	4.15	3.36	8.45	31.99	0.79
<b>Fort Washington</b>	3.74	7.67	1.92	1.66	2.04	1.22	3.03	12.57	0.38
<b>Greenwich Park</b>	12.38	55.77	11.32	3.32	10.41	21.57	52.10	150.56	4.57
<b>Hadden Lake Park</b>	10.40	21.23	6.20	4.00	4.50	5.32	13.64	44.03	1.16
<b>Hopkins Pond Park</b>	3.26	7.41	2.59	1.54	2.06	2.47	6.36	17.53	0.76
<b>Hunting Park</b>	34.04	75.49	21.50	8.31	13.48	20.71	53.59	122.69	3.21
<b>JHZ(NWR)</b>	10.16	15.39	4.95	2.22	3.25	2.98	7.70	23.97	0.72
<b>Knollwood Park</b>	14.78	24.73	7.41	4.89	4.54	4.70	12.30	37.65	1.17
<b>La Salle University</b>	6.45	15.58	4.42	1.52	3.40	4.92	12.30	41.53	1.12
<b>Lum's Pond</b>	5.33	10.59	3.03	3.32	3.18	2.52	6.49	30.65	0.31
<b>Morris Park</b>	7.89	16.02	6.33	2.54	3.19	4.11	10.81	32.95	1.17
<b>Neshaminy Park</b>	9.88	18.17	5.39	4.26	4.08	4.06	10.66	37.99	0.95
<b>New Brunswick(Rutgers Garden)</b>	10.69	19.05	5.63	2.36	4.58	5.64	14.68	41.44	1.22
<b>Northeast Philadelphia Airport</b>	20.33	99.17	19.12	2.58	30.18	65.38	173.98	432.84	10.00
<b>Philidelphia University</b>	8.42	19.12	4.94	2.87	3.93	8.73	22.61	57.07	1.22
<b>Red Bank Battlefield</b>	15.36	25.58	7.32	4.57	4.71	5.31	13.09	41.80	1.28
<b>Ridley Creek State Park</b>	1.37	2.77	0.88	1.02	1.09	0.42	1.13	4.97	0.38
<b>Swarthmore (Hicks roof)</b>	6.90	11.79	2.95	2.69	1.99	2.06	5.69	22.16	0.49
<b>Swathmore(Science Center)</b>	19.03	29.51	6.79	8.71	4.86	5.79	15.30	56.78	0.99
<b>Von Neida Park</b>	39.18	52.62	11.17	3.57	6.87	8.21	21.21	66.48	1.40
<b>Washington Square Park</b>	46.63	115.29	47.42	8.94	20.30	52.42	134.98	233.15	9.19
<b>Claire Welty's house</b>	5.00	22.35	6.64	1.08	4.97	13.87	35.07	73.88	2.46
<b>Widener University</b>	44.94	76.38	18.72	15.58	15.38	19.17	49.81	156.94	3.10
<b>Wiggins Park Marina</b>	37.51	70.31	20.73	8.98	12.31	16.63	43.73	127.74	2.66

	<b>B(b+k)F</b>	<b>BeP</b>	<b>BaP</b>	<b>pery</b>	<b>indeno</b>	<b>Bghip</b>	<b>DBA</b>	<b>Cor</b>	<b>Sum</b>
<b>Bellevue State Park</b>	12.62	10.00	9.23	1.35	7.37	4.62	0.31	0.90	1582.39
<b>Billing sport elementary school</b>	20.35	16.88	17.87	3.00	14.33	11.45	0.86	1.86	2229.81
<b>Camden</b>	16.24	13.91	10.90	2.13	6.37	5.49	0.39	0.87	2622.36
<b>Cinnaminson</b>	5.75	6.56	6.20	1.07	2.96	2.20	0.28	0.32	1053.28
<b>Cooper River</b>	67.70	52.10	39.19	9.58	47.76	32.76	2.54	3.38	1996.79
<b>Fairmont Park</b>	13.68	12.55	9.13	2.37	8.15	7.34	0.50	1.56	2017.93
<b>FDR Park</b>	42.39	29.74	26.51	5.68	27.42	17.30	1.32	2.41	2743.69
<b>Fort Mifflin</b>	7.89	5.98	4.57	0.85	3.56	2.81	0.21	0.61	1536.44
<b>Fort Washington</b>	3.41	2.34	1.75	0.38	2.26	1.20	0.09	0.20	773.10
<b>Greenwich Park</b>	75.13	60.25	36.00	8.98	69.98	42.24	3.09	4.65	2348.91
<b>Hadden Lake Park</b>	14.01	11.04	9.48	1.78	9.31	5.42	0.39	0.92	1458.20
<b>Hopkins Pond Park</b>	5.57	4.54	8.10	1.00	4.05	3.39	0.32	0.97	572.31
<b>Hunting Park</b>	36.23	25.85	22.81	4.93	15.82	16.87	1.12	3.34	4139.95
<b>JHZ(NWR)</b>	7.18	6.44	4.29	1.31	4.94	4.11	0.40	1.11	1211.11
<b>Knollwood Park</b>	9.68	7.55	5.51	1.11	3.63	2.83	0.20	0.53	1472.85
<b>La Salle University</b>	8.99	9.66	6.74	1.69	3.45	2.70	0.36	0.36	1018.84
<b>Lum's Pond</b>	6.94	5.09	4.57	0.68	3.23	2.59	0.18	0.58	580.31
<b>Morris Park</b>	8.61	8.74	6.97	2.19	4.95	3.72	0.75	0.77	1380.13
<b>Neshaminy Park</b>	10.43	7.26	9.67	1.17	4.90	3.90	0.28	0.70	1247.48
<b>New Brunswick(Rutgers Garden)</b>	13.31	10.78	6.64	1.49	8.68	5.30	0.42	0.81	1308.12
<b>Northeast Philadelphia Airport</b>	146.98	95.31	99.28	18.15	79.45	51.25	4.27	3.87	4629.88
<b>Philidelphia University</b>	19.19	16.47	14.02	2.75	9.69	7.38	0.74	1.01	1621.54
<b>Red Bank Battlefield</b>	12.08	8.56	7.83	1.55	8.01	5.39	0.37	1.00	1216.23
<b>Ridley Creek State Park</b>	1.26	0.89	1.74	0.20	0.86	0.71	0.12	0.22	418.31
<b>Swarthmore (Hicks roof)</b>	5.25	4.33	4.35	0.76	4.31	2.59	0.23	0.64	1100.18
<b>Swathmore(Science Center)</b>	14.62	11.60	6.50	1.29	10.18	5.77	0.44	0.89	2139.22
<b>Von Neida Park</b>	13.63	9.92	10.19	1.79	6.94	3.96	0.35	0.61	4337.84
<b>Washington Square Park</b>	77.19	54.28	59.80	14.76	55.80	37.67	3.07	5.34	4336.99
<b>Claire Welty's house</b>	20.55	15.86	17.35	3.86	11.35	10.55	0.76	2.92	1068.95
<b>Widener University</b>	41.99	50.70	29.18	5.66	37.37	34.14	2.16	4.07	3401.63
<b>Wiggins Park Marina</b>	36.07	27.55	23.21	4.62	25.85	19.75	1.46	3.21	2941.80

Table I- 4. Determined mass of BDEs in each passive sampler (ng) .

	BDE-17	BDE-28	BDE-71	BDE-47	BDE-66	BDE-100	BDE-99	BDE-85	BDE-154
Bellevue State Park	0.00	0.00	0.00	0.00	0.00	0.16	0.60	0.00	0.08
Billing sport elementary school	0.00	0.00	0.00	0.17	0.00	0.27	1.04	0.00	0.06
Camden	0.05	0.16	0.00	1.62	0.04	0.24	0.82	0.00	0.04
Cinnaminson	0.00	0.00	0.00	0.30	0.00	0.23	0.77	0.00	0.15
Cooper River	0.01	0.06	0.00	0.52	0.00	0.24	0.84	0.00	0.08
Fairmont Park	0.05	0.05	0.00	0.33	0.00	0.15	0.40	0.00	0.00
FDR Park	0.02	0.04	0.00	0.50	0.03	0.53	1.77	0.01	0.18
Fort Mifflin	0.00	0.01	0.00	0.14	0.00	0.18	0.70	0.00	0.06
Greenwich Park	0.05	0.04	0.00	0.57	0.00	0.27	0.97	0.00	0.15
Hadden Lake Park	0.00	0.11	0.58	0.66	0.75	0.15	0.42	0.00	0.00
Hopkins Pond Park	0.00	0.04	0.00	0.31	0.00	0.12	0.23	0.00	0.05
Hunting Park	0.14	0.16	0.00	1.46	0.07	0.34	1.23	0.04	0.10
JHZ(NWR)	0.04	0.08	0.00	0.51	0.00	0.14	0.42	0.00	0.00
Knollwood Park	0.00	0.02	0.00	0.12	0.00	0.21	0.91	0.03	0.04
La Salle University	0.00	0.07	0.00	0.82	0.00	0.13	0.42	0.00	0.05
Lum's Pond	0.00	0.00	0.00	0.20	0.00	0.17	0.67	0.03	0.05
Morris Park	0.05	0.08	0.00	0.69	0.03	0.08	0.37	0.01	0.04
Neshaminy Park	0.02	0.03	0.00	0.32	0.00	0.14	0.27	0.01	0.00
New Brunswick(Rutgers Garden)	0.00	0.06	0.00	0.49	0.04	0.18	0.72	0.04	0.00
Northeast Philadelphia Airport	0.04	0.07	0.00	0.82	0.05	0.33	0.94	0.03	0.03
Philidelphia University	0.03	0.09	0.00	2.37	0.10	0.65	1.71	0.04	0.09
Red Bank Battlefield	0.08	0.08	0.00	0.95	0.00	0.28	0.76	0.03	0.12
Ridley Creek State Park	0.04	0.07	0.00	0.67	0.00	0.08	0.29	0.00	0.02
Swarthmore (Hicks roof)	0.00	0.00	0.00	0.10	0.00	0.14	0.51	0.00	0.04
Swathmore(Science Center)	0.13	0.31	0.00	4.01	0.11	0.40	1.02	0.04	0.10
Von Neida Park	0.01	0.01	0.00	0.04	0.01	0.36	1.29	0.03	0.10
Washington Square Park	0.13	0.43	0.00	4.68	0.13	0.57	1.95	0.12	0.12
Welty's house	0.00	0.00	0.00	0.06	0.00	0.24	0.90	0.01	0.08
Widener University	0.07	0.18	0.00	2.10	0.06	0.32	0.83	0.02	0.08
Wiggins Park Marina	0.16	0.31	0.00	4.04	0.11	0.47	1.92	0.09	0.21



	<b>BDE-153</b>	<b>BDE-138</b>	<b>BDE-183</b>	<b>BDE-190</b>	<b>Sum</b>
<b>Bellevue State Park</b>	0.08	0.00	0.00	0.00	0.92
<b>Billing sport elementary school</b>	0.06	0.00	0.00	0.00	1.60
<b>Camden</b>	0.13	0.00	0.00	0.00	3.10
<b>Cinnaminson</b>	0.16	0.00	0.00	0.00	1.60
<b>Cooper River</b>	0.12	0.00	0.00	0.00	1.86
<b>Fairmont Park</b>	0.00	0.00	0.00	0.00	0.98
<b>FDR Park</b>	0.23	0.00	0.00	0.00	3.31
<b>Fort Mifflin</b>	0.09	0.00	0.00	0.00	1.18
<b>Greenwich Park</b>	0.16	0.00	0.10	0.00	2.32
<b>Hadden Lake Park</b>	0.03	0.00	0.11	0.00	2.81
<b>Hopkins Pond Park</b>	0.10	0.00	0.03	0.00	0.88
<b>Hunting Park</b>	0.13	0.00	0.03	0.00	3.71
<b>JHZ(NWR)</b>	0.02	0.00	0.02	0.00	1.25
<b>Knollwood Park</b>	0.08	0.00	0.00	0.00	1.41
<b>La Salle University</b>	0.00	0.00	0.04	0.00	1.53
<b>Lum's Pond</b>	0.10	0.00	0.00	0.00	1.22
<b>Morris Park</b>	0.02	0.00	0.06	0.00	1.43
<b>Neshaminy Park</b>	0.01	0.00	0.01	0.00	0.82
<b>New Brunswick(Rutgers Garden)</b>	0.02	0.00	0.00	0.00	1.55
<b>Northeast Philadelphia Airport</b>	0.13	0.00	0.03	0.00	2.48
<b>Philidelphia University</b>	0.02	0.00	0.00	0.00	5.11
<b>Red Bank Battlefield</b>	0.14	0.00	0.08	0.00	2.52
<b>Ridley Creek State Park</b>	0.00	0.00	0.00	0.00	1.18
<b>Swarthmore (Hicks roof)</b>	0.00	0.00	0.00	0.00	0.79
<b>Swathmore(Science Center)</b>	0.04	0.00	0.05	0.00	6.21
<b>Von Neida Park</b>	0.15	0.00	0.00	0.00	2.00
<b>Washington Square Park</b>	0.17	0.00	0.04	0.00	8.33
<b>Welty's house</b>	0.06	0.00	0.00	0.00	1.35
<b>Widener University</b>	0.10	0.00	0.08	0.00	3.84
<b>Wiggins Park Marina</b>	0.16	0.00	0.10	0.00	7.57

Table I-5. Quantification information for the detected PCB congeners.

PCB congener	RT	RRF	Ref. compounds for quantification
1	19	0.59	2
2	20.81	0.59	2
4	22.24	0.73	4
7	23.42	1.34	7
8+5	24.82	1.48	5/8
14	25.74	1.65	14
11	27.17	1.46	11
15	27.66	1.4825	7/8+5/14/11
18	27.91	0.59	18
17	28.08	0.83	18/23/28
32+16	29.48	0.83	18/23/28
23	30.27	1	23
31	31.72	0.83	18/23/28
28	31.86	0.9	28
21+33	32.78	0.83	18/23/28
22	33.51	0.83	18/23/28
46	34.04	0.76125	52/49/65/44/74/66/81/77
52+43	35.2	0.73	52
49	35.65	0.73	49
47+48	35.95-36.06	0.76125	52/49/65/44/74/66/81/77
65	36.39	0.8	65
44	37.38	0.6	44
37	37.76	0.83	18/23/28
42	37.77	0.76125	52/49/65/44/74/66/81/77
41+71	38.6	0.76125	52/49/65/44/74/66/81/77
64	38.74	0.76125	52/49/65/44/74/66/81/77
40	39.68	0.76125	52/49/65/44/74/66/81/77
74	41.36	0.82	74

70+76	41.81	0.76125	52/49/65/44/74/66/81/77
66	42.24	0.79	66
56+60	44.31	0.76125	52/49/65/44/74/66/81/77
81	48.57	0.81	81
77	49.87	0.81	77
95	42.35	0.55	95
91	43.12	0.582	95/101/99/87/110
89	44.43	0.582	95/101/99/87/110
101or 101+90	45.13	0.59	101
99 (C79?)	45.81	0.61	99
83	47.23	0.582	95/101/99/87/110
97	47.9	0.582	95/101/99/87/110
87	48.59	0.5	87
85	49.14	0.582	95/101/99/87/110
110	49.89	0.66	110
30	26.82	1	
110	49.89	0.66	110
82	51.42	1.88	123/118/114/105/126
124?	52.22	1.88	123/118/114/105/126
107+123+118	53.39	1.78	123/118
114	54.93	1.75	114
105	57.12	1.75	105
151	51.54	1.27	151
135+144+147	52.14	1.551	151/149/146/153/138/158/166/167/156/157/169
149	53.18	1.35	149
146	55.74	1.39	146
153	56.6	1.63	153
132	56.98	1.551	151/149/146/153/138/158/166/167/156/157/169
141	58.4	1.551	151/149/146/153/138/158/166/167/156/157/169
138+163	60.36	1.46	138
158	60.63	1.63	158

121	61.92	1.88	123/118/114/105/126
126	62.21	2.24	126
166	61.92	1.9	166
167	65.19	1.62	167
156+157	65.63	1.71	156/157
169	67.85	1.55	169
179	58.68	1.12	
178	61.34	1	178
187	62.2	1.18	187
183	62.69	1.26	183
185?	63.66	1.12	178/187/183/177/172/180/170/189
174	64.32	1.12	
177	64.78	0.94	177
173		1.12	178/187/183/177/172/180/170/189
171	65.79	1.12	178/187/183/177/172/180/170/189
172	66	0.96	172
180	66.46	1.26	180
170+190	68.43	1.01	170
189	70.05	1.35	189
202?	65.06	0.785	199/203/196/195/194
199	68.97	0.59	199
203+196	69.27	1.33	203/196
195	70.85	0.61	195
194	71.85	0.61	194
208	70.77	0.61	208
206	73.78	0.61	206
204	65.79	1	

## Appendix II

### Passive Air Sampling for PAHs, OCPs, BDEs in the Philadelphia Metropolitan Area

#### Abstract

Passive air samplers, using polyurethane foam disks as sampling media, were deployed at 32 sites across the Philadelphia –Camden area to investigate the spatial extent of the urban-impacted elevated atmospheric persistent organic pollutants (POPs) including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated diphenyl ethers (BDEs). The spatial variation of derived air concentration of PAHs, OCPs, and BDEs reflected the different source characteristics for these chemicals. PAHs and BDEs all showed urban-rural gradients with maximum concentrations found in the urban center. For OCPs, the highest concentrations of *trans*- and *cis*- chlordanes, *p,p'*-dichloro-diphenyl-trichloroethane (DDT) and related compounds as well as heptachlor were found in the urban area. Other OCPs exhibited either a relatively uniform concentration level across the sampling area (for example, the hexachlorocyclohexanes) or a relatively random spatial distribution (for example, endosulfans and *cis*-nanochlor).

#### Introduction

The atmosphere plays a major role in the cycling of the semi-volatile compounds (SOCs) including persistent organic pollutants (POPs) such as polychlorinated

biphenyls (PCBs), organochlorine pesticides (OCPs) and brominated diphenyl ethers (BDEs) as well as polycyclic aromatic hydrocarbons (PAHs). PAHs are differentiated from other classic POPs by their shorter atmospheric half-lives (range of hours to days), their affinity to soot carbon and the influence of ongoing primary sources on their distribution (Nizzetto et al 2008). Although the usage of banned OCPs has decreased over the last few decades as a direct result of effective regulatory activity, these chemicals have been continually detected in the atmosphere. BDEs are a class of new emerging environment pollutant, in contrast to the decreasing levels of “legacy POPs” over the last a few of decades, PBDE levels in the environment are increasing.

Because of their persistence and mobility in the environment, they can be transported over long distance and distributed universally. Furthermore, many of these chemicals also tend to bioaccumulate and pose risks to biota and human being. Therefore, knowledge of their atmospheric concentration is needed in order to assess their potential impact on public health.

The urban area causes special concern where the majority people reside and also the emission of industrial chemicals can be significant. The emissions of the chemicals in this urban area may lead to substantial load to the adjacent water bodies via direct or indirect atmospheric deposition. Strong spatial gradients of contaminant concentration always exist in this area. An open question here is how the measured concentration can be accurately converted to the atmospheric deposition load. To answer this question, the address of their spatial variations over a better refined geographical scale becomes necessary. Active monitoring networks such as NJADN

and IADN have a limited ability to characterize spatial gradients due to the small number of monitoring sites, which is dictated by the high cost and difficulties associate with active monitoring (Harner et al. 2004). In contrast, passive air sampling (PAS) is a more cost-effective tool, which can provide integrated atmospheric POP concentrations over a period of months and assess concentrations in air simultaneously at multiple sites at far lower cost. The use of passive sampling methods to monitor atmospheric concentrations has greatly increased over the past few years. Passive samplers have been used to investigate the vertical (Moreau-Guigon et al. 2007), temporal (Meijer et al. 2003a; Moreau-Guigon et al. 2007; Motelay-Massei et al. 2005), and spatial (Harner et al. 2006b; Meijer et al. 2003a) distribution of atmospheric POP concentrations. The utility of PASs has been demonstrated not only at the local scale but also at global scale (Jaward et al. 2004; Jaward et al. 2005).

In this study, PAS, using polyurethane foam disks as sampling media, were deployed at 32 sites across the Philadelphia –Camden area (including 5 sites operated under the NJADN) over a three month period between April and July of 2005. This urban area is adjacent to the Delaware River, where the total maximum daily load (TMDL) process has been established for PCBs. Therefore, the goal of the current mapping study is to determine the spatial extent of urban-impacted elevated atmospheric POP concentrations (PCBs, OCPs, PAHs and BDEs) to enhance understanding of the significance of urban areas as source of POPs and to identify

potential source regions or “hot spots” as well. The analysis of PCBs has been presented in Chapter 3, and the rest of the chemical classes are presented here.

## **Methodology**

### ***Sample analysis***

Detailed sampling information has been presented in chapter 3. Passive samples were extracted in the same way as gas-phase (PUF) samples collected by the NJADN (Gigliotti 2003). Prior to the extraction, they were spiked with the following surrogate standards: 100  $\mu\text{L}$  PCB surrogates including PCB 14, PCB 23, PCB 65, and PCB 166 at 200  $\text{ng mL}^{-1}$ ; 100  $\mu\text{L}$  BDE surrogate standards (BDE-206) at 200  $\text{ng mL}^{-1}$ , and 50  $\mu\text{L}$  PAH surrogate including d10-anthracene, d10-fluoranthene, and d12-benzopyrene at 1000  $\text{ng mL}^{-1}$ . The subsequent clean up and collection of different chemical classes are detailed in previous papers (Gigliotti 2003; Gioia et al. 2005; Zarnadze and Rodenburg 2008). Briefly, these extracts were reduced in volume by rotary evaporation and were then separated into two fractions on a column of 3% water-deactivated alumina. Each fraction was concentrated under a gentle stream of nitrogen gas to about 0.5 mL, and injected with internal standard containing PCB 30 and 204 and BDE-75 (Fraction 1) or phenanthrene- $d_{10}$ , pyrene- $d_{10}$ , benzo[a]pyrene- $d_{12}$  and BDE-75 (Fraction 2) prior to analysis.

The OCPs were analyzed using gas chromatography/mass spectrometry in negative chemical ionization mode (GC/MS-NCI) operating in selective ion monitoring mode (SIM) with a Agilent 6890 gas chromatograph coupled to an Agilent



5973 mass spectrometer. The details for this method has been reported elsewhere (Gioia et al. 2005). The BDEs were analyzed by GC/MS using NCI in SIM mode with methane as a reagent gas. Concentrations were determined using the same Agilent GC/MS instrument as the OCPs. The details for the GC/MS methods have been reported (Zarnadze and Rodenburg 2008). In order to avoid the degradation of BDE 209 in the heated injection port, a cold on-column injection port was used. The PAHs were analyzed on the same Agilent GC/MS system operating in Selective Ion Monitoring (SIM) mode using a 30m × 0.25mm i.d., J&W Scientific 122-5062 DB-5 (5% diphenyl-dimethylpolysiloxane) capillary column with a film thickness of 0.25 μm (Gigliotti 2003).

#### *Quality Assurance*

Surrogate recoveries for PCBs and PAHs were calculated. Recoveries for PCBs 14, 23, 65, 166 ranged from 72(± xx%) to 92%(± xx%). The recovery of D<sub>10</sub>-anthracene, D<sub>10</sub>-fluoranthene and D<sub>10</sub>-benzo[e]pyrene range from 115(± 15%) to 118 (± 15%) PAHs ranges from 115 to 118%. We spiked BDE 206 as a surrogate before extraction. However, we noticed that the relative response factor (RRF) and the calculated recovery of BDE-206 varied significantly. For methods without compound or class specific stable isotope labeled standards, large differences in relative MS responses or analytical method recoveries could skew BDE congener profiles and lead to misinterpretation (Ackerman et al. 2005). Therefore, the calculated surrogate recoveries of BDE-206 are not reported here. All the reported concentration for these chemical classes are not surrogate corrected.

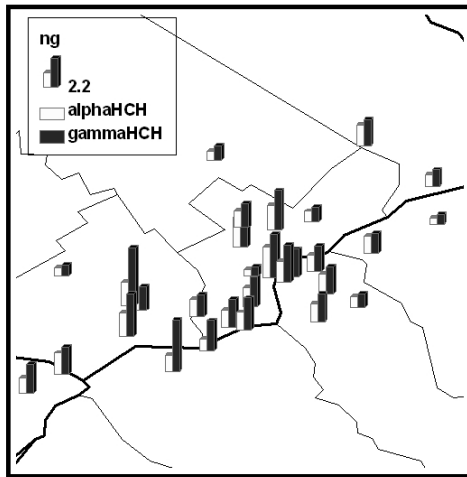
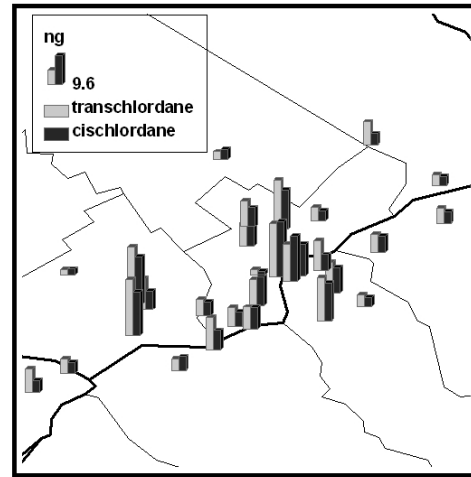
Two travel blanks were shipped overnight to Philadelphia and back and analyzed to evaluate the various sources of contamination during the trip. Lab blanks were run to check for the contamination from the laboratory or equipment. All PAHs, OCPs and BDEs were below the detection limit in all blanks.

## **Results and Discussion**

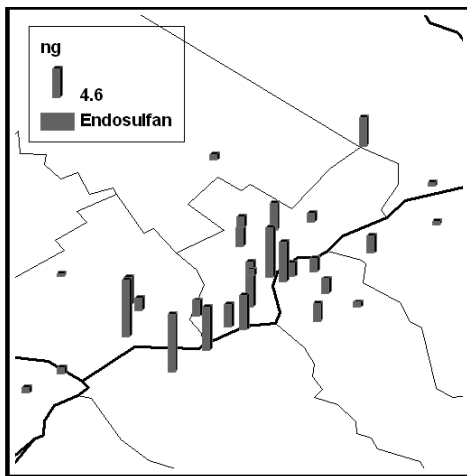
The determination of the atmospheric concentration of these measured chemicals requires the knowledge of sampling volume. Because of the availability of measured PCB data at the 5 NJADN sites around the same sampling time in 2000, the sampled air volume for each PCB homologue group can be derived by plotting the mass of PCB in the passive samples versus concentrations measured at the 5 NJADN sites (Totten et al. 2004; Totten et al. 2006b). The estimated sampling volume for OCPs, PAH and PBDEs can be interpolated in light of the similarity of their  $K_{oa}$  value with different PCB homologue. The sampled air volume ranged from 160 m<sup>3</sup> for tri-PCB to 175, 262, 341, and 349 m<sup>3</sup> for tetra, penta, hexa, hepta-PCB respectively and 224 m<sup>3</sup> for total PCBs (Fig.3.x). When normalized to surface area of the PUF media, the sampling rates in the present study agree to within 15% of others reported in literature (Harner et al. 2004; Shoeib and Harner 2002).

**OCPs** Since some of the OCPs have been banned years ago, it is appropriate to map their spatial distribution and gain some insights on the impact of the use restrictions and the extent to which their continuing use in this area on present-day contamination. The NJADN study showed that OCPs are found predominantly in the gas phase in all

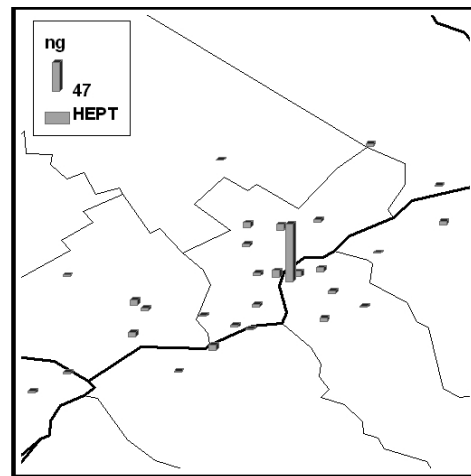
seasons, with the gas phase representing over 95% of the total air concentrations (Gioia et al. 2005). Furthermore, the NJADN study also revealed no significant correlation between urbanization and pesticide concentrations though highest concentrations have been found in Camden and New Brunswick (Gioia et al. 2005). The discussion of the spatial distribution of the measured OCPs from this passive sampling study will be divided into two groups: “legacy POPs” and “current use POPs”. The determined air volume of tri-PCB ( $160 \text{ m}^3$ ) was applied to HCHs, while that of penta-PCB ( $262 \text{ m}^3$ ) was used for chlordanes and hexa-PCB ( $341 \text{ m}^3$ ) was used for DDX compounds.

a)  $\alpha$ -HCH and  $\gamma$ -HCHb) *trans*- and *Cis*-Chlordane

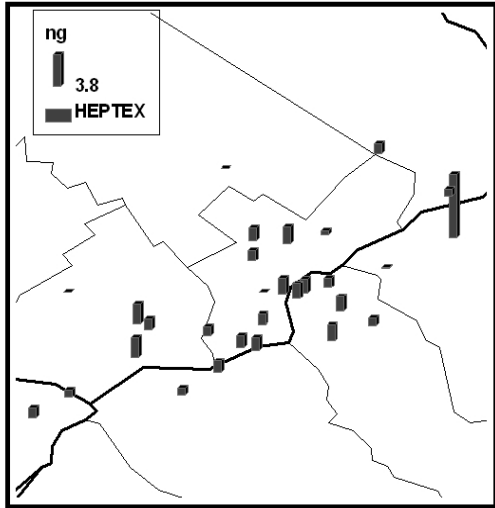
c) Endosulphan



d) HEPT



e) HPTX



f) DDE &amp; DDT

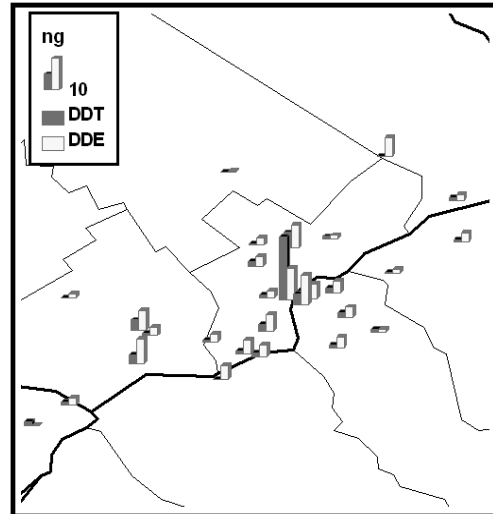


Figure. 1. Passive air sampler derived organochloride pesticide mass(ng): a)  $\alpha$ -HCH ( and  $\gamma$ -HCH; b) *trans*- and *Cis*-Chlordane; c) Endosulphan; d) HPT; e)HPTX; f) DDE & DDT.

*Endosulfans* Endosulfan is a current-use pesticide that it is widely used throughout the world. The technical product of endosulfan is a racemic mixture of two isomers, endosulfan I and endosulfan II, in a proportion of 7:3. Endosulfan II and endosulfan sulfate were below detection limit in all samples. The spatial distribution of measured endosulfan I is shown in Fig. 1c. High masses were found in both urban and rural areas and therefore no clear urban-rural gradient was found. This is likely a reflection of applications at some specific sites. Endosulfan I masses ranged from 0.37 to 9.16 ng with a geometric mean value of 2.39 ng. Applying an sampled air volume of 160 m<sup>3</sup>, this corresponds to concentrations ranging from 2.3 to 57.2 pg m<sup>-3</sup>. These are much lower than those reported by the NJADN (Gioia et al. 2005) and the urban-rural transect study in Toronto (Harner et al. 2004) (Table 1).

Table 1. Mean (geometric mean) atmospheric concentrations of organochlorine pesticide in the Mid-Atlantic, great lake and Canada.

	$\Sigma$ -HCH	$\Sigma$ -Chlordanes	Endosulfan I	$\Sigma$ -DDTs
<b>NJADN 2000<sup>a</sup></b>				
Camden	254	518	102	133
New Brunswick	149	474	168	237
Pinelands	103	127	59	31
<b>IADN 1996-1998<sup>b</sup></b>				
Chicago	130	130		71
Sturgeon Point	82	38		31
Sleeping Bear Dunes	99	14		11
Eagle Harbor	96	8.6		4.4
<b>Toronto<sup>c</sup></b>				
	107	90	254-817	109
<b>This Study</b>				
Camden	20	76	14	19
New Brunswick	22	64	8	47

a-(Gioia et al. 2005)

b-(Buehler et al. 2001)

c-(Harner et al. 2004)

*HEPT and HEPTX* HEPT is an organochlorine cyclodine insecticide. HEPTX is a product of the photolysis of HEPT. HEPT was phased out in the US starting in 1988. The only commercial use still permitted is for fire ant control in power transformers (Gioia et al. 2005). The spatial variations of measured HEPT and HEPTX are presented in Fig.1d and Fig.1e respectively. HEPT masses ranged from 0.3 to 11.7 ng with a geometric mean value of 3.6 ng. HEPTX masses ranged from below detection to 7.5 ng with a geometric mean value of 1.2 ng. HEPT and HEPTX are generally higher at urban sites such as Washington Square Park and Camden. Surprisingly, the measured mass of HEPTX in Morris Park is as high as 7.5 ng, which is well above the geometric mean. The higher concentration of HEPT and HEPTX at urban sites probably results from their current use in these areas.

*Hexachlorocyclohexanes ( $\alpha$ - and  $\gamma$ -HCH)* Technical HCH is a mixture of several isomers of which  $\alpha$ -HCH comprises 60-70% and  $\gamma$ -HCH comprises 10-12%. The technical HCH mixture typically has a ratio of  $\alpha$ -HCH /  $\gamma$ -HCH ranging from 4 to 7 (Karlsson et al. 2000). Because it is fairly volatile ( $\log K_{oa} = 7.93$ ) and degrades slowly in the atmosphere,  $\alpha$ -HCH is easily transported in the atmosphere and attains fairly uniform air concentrations globally.  $\gamma$ -HCH is the main component of lindane, which replaced technical HCH and is still used in some countries.

The spatial distribution of  $\alpha$ - and  $\gamma$ -HCH masses is displayed in Fig.1a. Masses of  $\alpha$ -HCH ranged from 0.5 to 2.3 ng, while slightly higher masses were measured for  $\gamma$ -HCH (0.7 to 4.3 ng).  $\Sigma$ HCH masses ranged from 1.1 to 6.7 ng and display less



spatial variation than other analytes, including PCBs. The ratio of highest to lowest masses for  $\alpha$ -HCH and  $\gamma$ -HCH are 4 and 6 respectively, which are much lower than that of 35 for PCBs. When an air volume of 160 m<sup>3</sup> is used to convert mass to concentration, the concentrations for the Camden and New Brunswick sites are lower than those reported by NJADN and the Toronto study (Table 1).

The range of  $\alpha$ -HCH/ $\gamma$ -HCH ratios throughout the whole sampling area (0.32-0.96) is also fairly uniform and typical of background air. The average  $\alpha$ -HCH/ $\gamma$ -HCH ratio in active sampling in this region ranged from 1.37 in Camden to 2.77 at the coastal Sandy Hook (Gioia et al. 2005). These values are in the same range of those reported for the northeast Atlantic (0.3–4.6) and also for the Arctic (0.9–4.7) (Kelly et al. 1994; Schreitmuller and Ballschmiter 1995).

*Chlordanes* ( $\Sigma$ -*trans- and cis-chlordane, trans-nonachlor*) Technical chlordane is a mixture of components consisting mainly of *trans*-chlordane (TC), *cis*-chlordane (CC), and *trans*-nanochlor (TN) in the proportion 1.00/0.77/0.62, respectively (i.e., TC/CC=1.3) (Sovocool et al. 1977). In the environment, TC degrades more quickly than CC, resulting in a TC/CC ratio of <1 for aged chlordanes. The TC/CC ratio in the passive samples ranges from 0.76 to 2.02. The highest TC/CC ratios were found at Northeast Philadelphia airport and Bellevue SP. Comparing with the technical mixture value of 1.3, these high ratios are indicative of relatively fresh chlordane. The spatial distribution of chlordanes is shown in Fig.1b. Gas-phase  $\Sigma$ chlordanes at these sampling sites ranged from 3 to 37 ng. When a sampled air volume of 262 m<sup>3</sup> is used to convert mass to concentration, the resulting

concentrations at Camden and New Brunswick are lower than that reported in NJADN study, but comparable to those reported by the IADN and the Toronto passive sampling study (Table 1). Similar to PCBs, chlordanes exhibit two maxima at Washington Square Park and Swarthmore. An urban-rural gradient for chlordanes was found in Toronto area, which was presumed as the result of past usage of chlordane on residential lawns and emissions from treated house foundations (Harner et al. 2004). Significant correlation was observed between chlordane masses and population density ( $P < 0.05$ ,  $r^2 = 0.39$ ). Previous studies have demonstrated that cities could either act as receptors of pesticides that are used either nearby or in distant agricultural regions (Blanchoud et al. 2002) or as sources of pesticides under certain circumstances. For instance, Motelay-Massei et al. (Motelay-Massei et al. 2005) showed that Toronto was a regional source of chlordane, related to its historic use on house foundations and lawns.

*DDT isomers* Technical DDT consists of p,p'-DDT and o,p'-DDT in proportions 1:0.15 (i.e. p,p'-DDT/o,p'-DDT = 6.7). In the environment, p,p'-DDT is transformed to p,p'-DDE and p,p'-DDD. In this study, only p,p'-DDT and p,p'-DDE were detected in most samples. The measured mass of the sum of DDTs and DDEs ( $\Sigma$ DDX) ranged from 0.26 to 31 ng. The estimated concentration in Camden and New Brunswick, converted from the measured mass by estimating a sampling volume of  $341\text{m}^3$ , are lower than that reported in NJADN study, but comparable to those reported by the IADN and the Toronto passive sampling study (Table 1).

Interestingly, the highest  $\Sigma$ DDX mass was observed in the center of Philadelphia (Washington Square Park). DDT and DDE masses were significantly correlated with population density ( $r^2 = 0.62$ ,  $r^2 = 0.47$  respectively).

In general, a DDT/DDE ratio less than one is indicative of aged DDT, whereas a ratio greater than one suggests fresh inputs. The spatial distribution of DDT isomers (Fig.1f) indicates that at all but a few sites, DDE is more abundant than DDT, i.e. the ratio of DDT/DDE is less than 1, indicating the relative lack of new sources of DDT. At Washington Square, the masses of both DDT and DDE are quite high, and the ratio of DDT/DDE is about 2, which suggest a new source of DDT. At another two sites, only DDT was detected, while DDE is below detection limit (Bellevue SP, Greenwich Park). Therefore the DDT/DDE ratio ranged from 0 (DDT is not detectable) to 1.9. In comparison, the average DDT/DDE ratio in active air sampling in this region ranged from  $0.477 \pm 0.23$  at Pinelands to  $0.187 \pm 0.08$  at New Brunswick (Gioia et al. 2005). In urban and rural sites in Toronto, the DDT/DDE ratios ranged from 0.17 to 1.45 (Harner et al. 2004).

**PAHs** PAHs are toxic and carcinogenic pollutants resulting from the incomplete combustion of fossil fuels or organic matter and considered as ubiquitous environmental contaminants. PAH emission sources are well known to be proportional to population density (Garban et al. 2002; Motelay-Massei et al. 2005), which is also demonstrated in this study ( $P < 0.05$ ). The gas phase distribution is dominated by low to medium MW PAHs.  $\Sigma_{27}$ PAH masses ranged from 418 to 4630

ng, and were dominated by phenanthrene, followed by fluoranthene and flourene, which exist primarily in the gas phases in ambient air. In general, PAH masses were higher in urban areas such as Camden and Washington Square Park, and lower in rural areas such as Ridley Creek and Lum's Pond. Interestingly, the highest PAH masses were observed at Northeast (Fig.2), possibly due to the airplane traffic at that site.

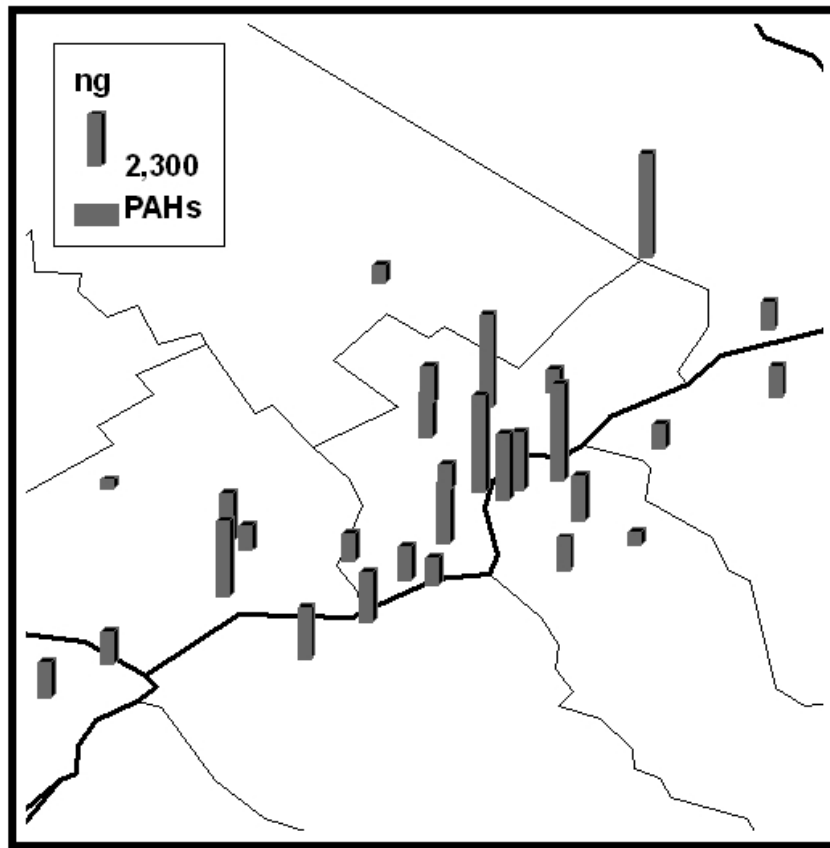


Figure.2. Passive sampler derived air concentration for  $\Sigma 26$ PAH for the integration period of April-July 2005.

Although the masses vary spatially in New Jersey-Philadelphia area, the PAH profiles at all sites (except Philadelphia University) are similar ( $r^2 = 0.90-0.99$ ), indicating that while the source strength is different at each site, the mix of sources is similar. This is in agreement with the findings of NJADN (Gigliotti et al. 2005). In agreement with the present study, the NJADN study demonstrated that the highest PAH concentrations are measured at the most highly urban and industrial sites, Camden and Jersey City. Midrange concentrations are measured in the suburban areas, e.g. New Brunswick. The lowest concentration were found in coastal and rural areas (Gigliotti et al. 2005).

**BDEs** BDEs are a class of brominated flame retardants that are added to commercial and household products such as furniture foams, textiles, and electronic components such as TVs and computers. Because of its potential toxicity, BDEs has been banned in Europe and some states in US, but its manufacture is still ongoing in other countries. Human exposure to PBDEs is of concern owing to their presence in the diet and human tissues, coupled with the evidence relating to their potential adverse effects on human health. There remain strong concerns that the existing reservoir of BDEs represents a substantial source of current and future exposure to these chemicals (Harrad and Hunter 2006).

BDEs are produced in three commercial formulations (penta-BDE, octa-BDE and deca-BDE), the prefixes indicate the average degree of bromination with 209 different congeners possible for mono-through deca-BDE. The Penta product, containing mainly 4-6 Br congeners, has been most widely investigated because of its occurrence

and rapid accumulation in biological samples from remote regions. Worldwide, PBDE production is dominated by the deca commercial formulation (McDonald 2002).

BDEs were detected in all of the passive samples, which is indicative of their widespread use. BDEs 17, 28, 47, 66, 100, 99, 85, 154, 153, 183 and 209 were above detection limit in at least some samples. Other congeners (BDEs 71, 138, 190) were below detection limit in all samples. With a log  $K_{ow}$  of about 9.97 and a low vapor pressure (Strandberg et al. 2001), BDE-209 is strongly bound to particles and should not, therefore, be captured by the passive air samplers. However, we observed quite high levels of BDE 209 in our passive samples, despite its absence in the blanks.

Therefore, we exclude BDE 209 for the current discussion, and  $\Sigma$ BDEs in this discussion represents BDEs 17, 28, 47, 66, 100, 99, 85, 154, 153, and 183. Fig.3 presents the spatial distribution for the  $\Sigma$ BDEs, which range from 0.53 to 8.33 ng, with a geometric mean of 1.54 ng. The highest  $\Sigma$ BDEs levels were found in Washington Square Park and Wiggins Park Marina (both urban sites) with masses of 8.33 and 7.57 ng per sampler, respectively. Lower  $\Sigma$ BDEs masses were found in background areas such as Lum's Pond and Hopkins Pond. Gas-phase  $\Sigma$ BDEs levels are dominated by lower molecular weight congeners such as tetra and penta- BDEs due to their higher vapor pressures. BDEs 47, 100 and 99 are the dominant congeners in the gas phase. Geometric means (and ranges) of these three dominant congeners, calculated as a percent of the total mass, were as follows: BDE-47, 31% (3-65%); BDE-99, 35% (14-68%); BDE-100, 10% (4-17%). This composition resembles the Penta (pentabromodiphenylether) commercial product. The BDE study conducted in

Great Lakes indicated that BDE-47 and BDE-99 accounted for 50-65% and 35-40% of the total mass of BDEs respectively (Strandberg et al. 2001).



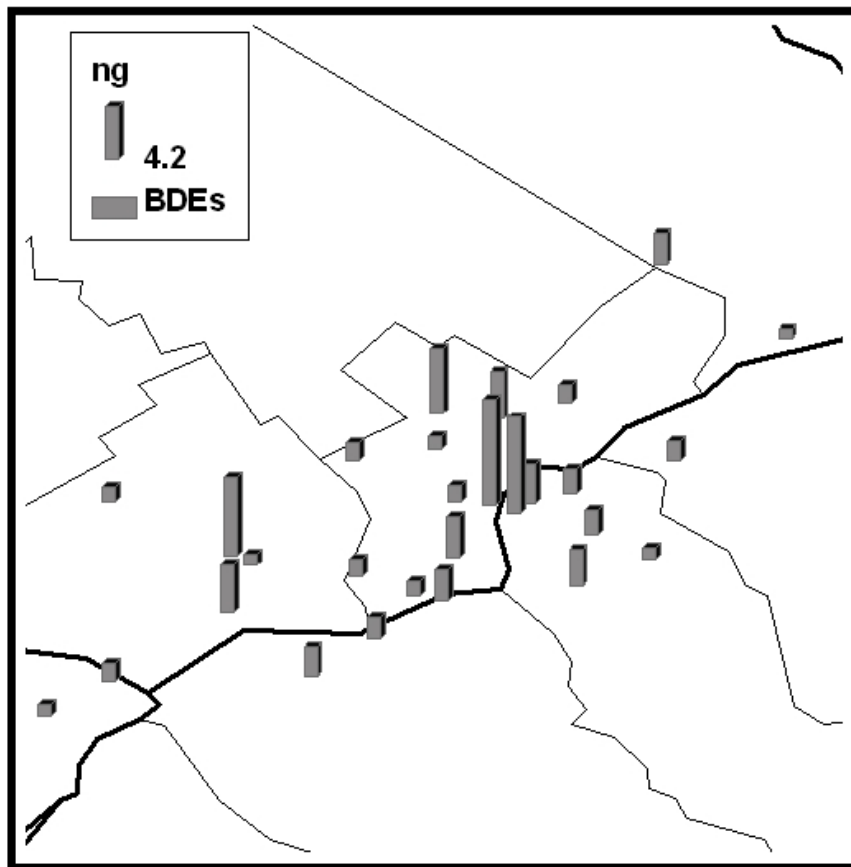


Figure. 3. Passive sampler derived air concentration for  $\Sigma$ BDE for the integration period of April-July 2005.

Analogous to other chemicals presented above, the BDE data also demonstrated a connection between atmospheric BDE concentrations and population density implying that urban sites are potential source of BDEs. Previous studies have revealed a clear “urban pulse”, whereby BDE concentrations are highest at the city center and decrease with distance (Harner et al. 2006a; Harrad and Hunter 2004). Urban sites are potential sources of BDEs (Butt et al. 2004; Strandberg et al. 2001). Additionally, there is a significant correlation between the  $\Sigma$ PCB and  $\Sigma$ BDE masses in most of the samples in this study ( $P < 0.005$ ) when Swarthmore (Hicks Hall) and Camden are excluded.

The measured mass of BDEs are converted to concentrations by applying the calibrated sample volume of hepta-PCB ( $347 \text{ m}^3$ ), which has most close  $K_{oa}$  value to the BDEs. The concentrations of  $\Sigma$ BDEs range from 3.0 to  $25.2 \text{ pg m}^{-3}$ . We compared this study results with other two urban-rural transect passive sampling study in Toronto (Harner et al. 2006a) and Birmingham, UK (Harrad and Hunter 2006) as well as the study conducted in Ottawa, Canada. Table 3.7 demonstrates that BDE concentrations (gas phase only) from this study are well within the ranges reported in Toronto and Birmingham. We also compared these results with the  $\Sigma$ BDE concentration acquired in some of the NJADN sampling sites (Sandy Hook, Jersey City and New Brunswick). Particularly relevant are those measured via active air monitoring at New Brunswick (Zarnadze and Totten 2006) (Table 2). On average, the

gas phase  $\Sigma$ BDE concentrations at New Brunswick were  $3.7 \pm 1.5 \text{ pg}\cdot\text{m}^{-3}$  in 2000, which is in good agreement with the passive sampling result ( $6.1 \text{ pg m}^{-3}$ )

Table 2. Gas phase concentrations ( $\mu\text{g m}^{-3}$ ) of BDEs in this and other studies. The numbers in parentheses standard for the standard deviation of measurements.

Site	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	$\Sigma$ BDE
<b>Birmingham, UK<sup>a</sup></b>							
<i>Urban</i>	2.04 (0.77)	13.73 (2.72)	4.26 (1.13)	2.08 (0.60)	0.63 (0.22)	0.53 (0.08)	23.3 (4.23)
<i>Suburban</i>	0.87 (0.50)	5.89 (1.86)	1.98 (0.69)	0.89 (0.40)	0.40 (0.36)	0.26 (0.14)	10.3 (3.39)
<i>Rural</i>	0.87 (0.41)	4.95 (1.73)	1.55 (0.62)	0.73 (0.31)	0.20 (0.07)	0.17 (0.10)	8.47 (3.04)
<b>Canada</b>							
<i>Toronto<sup>b</sup></i>	0.29-1.93	2.89-15.7	1.75-7.34	0.52-2.36	0.19-0.61	0.12-0.46	6.2-30.0
<i>Ottawa<sup>c</sup></i>	0.095 (0.16)	0.87 (0.87)	1.10 (0.78)	0.11 (0.15)			2.20 (1.70)
<b>US</b>							
<i>New Brunswick<sup>d</sup></i>	ND	2.8 (1.2)	0.7 (0.2)	0.2 (0.2)	ND	ND	3.7 (1.5)
<i>Jersey City<sup>d</sup></i>	ND	11.8 (9.3)	2.5 (2.6)	0.7 (0.6)	ND	ND	14.6 (12.0)
<i>Sandy Hook<sup>d</sup></i>	ND	4.0 (5.0)	3.0(4.7)	0.6 (0.7)	ND	ND	7.0 (9.8)
<i>New Brunswick (this study)</i>	0.18	1.4	3.2	1.0	0.06	ND	6.1
<i>All sites (this study)</i>	0.02-1.24	0.12-13.49	0.66-7.87	0.23-3.57	0-1.07	0-0.95	3.0-25.2

<sup>a</sup> Sum of BDEs 28,47,99,100,153,154. <sup>b</sup>Sum of BDEs17,28,47,49,66,71,77,85,99,100,119,138,153,154,183. <sup>c</sup> Sum of BDEs 17,28,47,100,99. <sup>d</sup> Sum of BDEs 17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 209. ND = not detectable. The present study has the same congener list as reference *d* except the absence of BDE209

a-(Harrad and Hunter 2006)

b-(Harner et al. 2006a)

c- (Wilford et al. 2004)

d-(Zarnadze and Totten 2006)

### ***Gaussian diffusion model for other compound classes***

The Gaussian diffusion model was applied to the following chemical classes: OCPs, PAHs, and BDEs. Fig.4 to 6 showed the plots of log-transformed concentration of these chemicals versus log-transformed distance from the source, where the location of the source is one of the fitting parameters (eqn 5). As we hypothesized earlier, higher slopes seem to indicate more localized sources, while lower slopes indicate more diffuse sources. For the selected OCPs, the sum of DDT and DDE displayed the highest slope ( $a_1+a_2 = 0.99$ ), with good agreement between the observed and predicted values ( $r^2 = 0.89$ ) (Fig. 4c). The results indicate that there is a single relatively strong local source of DDT about 1.1 km from Washington Square Park. The relatively high slope ( $a_1+a_2 = 0.84$ ) observed for HEPT is caused by the one point which is associated with the highest concentration detected and the abnormally high  $r^2$  between the observed and predicted values is an artifact caused by this one point (Fig. 4b). A lower slope was observed for  $\Sigma$ chlordanes corresponding to a lower  $r^2$  between the observed and predicted concentrations, which is indicative the presence of diffuse sources of chlordane in this area (Fig. 4a).

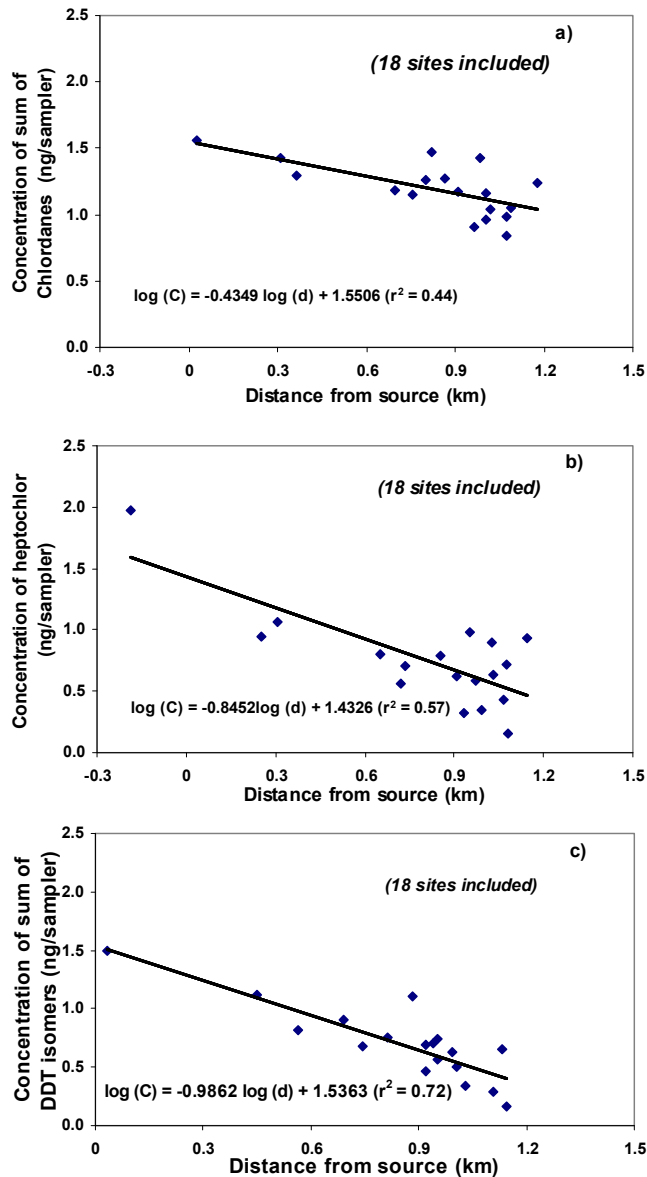


Figure. 4. Masses of selected OCPs in passive samples (ng per sampler) as a function of spherical Euclidian distance (in km) assuming the source is at a best-fit source and the correlation coefficients ( $r^2$ ) between the observed and predicted values are: a) *trans*- and *cis*-chlordane ( $\text{lat}_{\text{sor}} = 39.94786$  N,  $\text{lon}_{\text{sor}} = 75.16415$  W,  $r^2 = 0.52$ ); b) Heptochlor ( $\text{lat}_{\text{sor}} = 39.93555$  N,  $\text{lon}_{\text{sor}} = 75.13344$  W,  $r^2 = 0.97$ ); c) DDT & DDE ( $\text{lat}_{\text{sor}}$

= 39.94786 N,  $\ln_{\text{sor}} = 75.16415$  W,  $r^2 = 0.89$ ). Note: the high  $r^2$  for HEPT is skewed by the highest concentration point.

The determined slopes for PAHs (Fig.5) and BDEs (Fig.6) are similar to each other ( $a_1+a_2 = 0.67$  and  $0.65$  respectively). Nonetheless, a higher  $r^2$  between the measured and predicted concentrations was observed for BDEs ( $0.79$  vs  $0.49$  for PAHs). These observed slopes are lower than that observed for PCBs ( $a_1+a_2 = 0.74$ ) and DDT isomers ( $a_1+a_2 = 0.99$ ), which may suggest more diffuse sources of PAH and BDEs across the Philadelphia area. This may be due to the fact that PAH and BDEs are currently in use/production, compared with DDTs and PCBs which have been banned for decades.

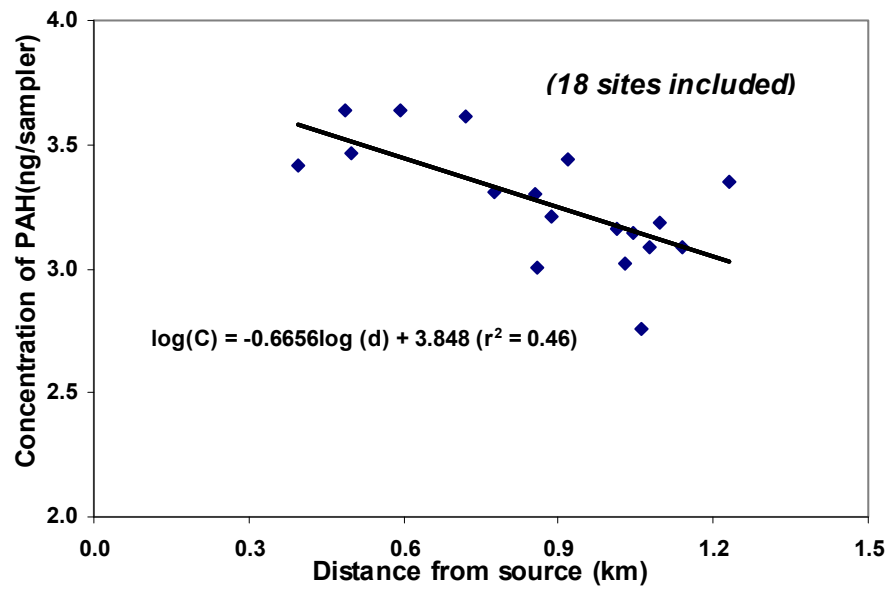


Figure.5. Concentrations of PAHs in passive samples ( $\text{ng. sampler}^{-1}$ ) as a function of spherical Euclidian distance (in km) assuming the source is at a best-fit location ( $\text{lat}_{\text{sor}} = 39.96976 \text{ N}$ ,  $\text{lon}_{\text{sor}} = 75.13084 \text{ W}$ ). The correlation coefficient ( $r^2$ ) between the observed and predicted PAH concentration is 0.49.



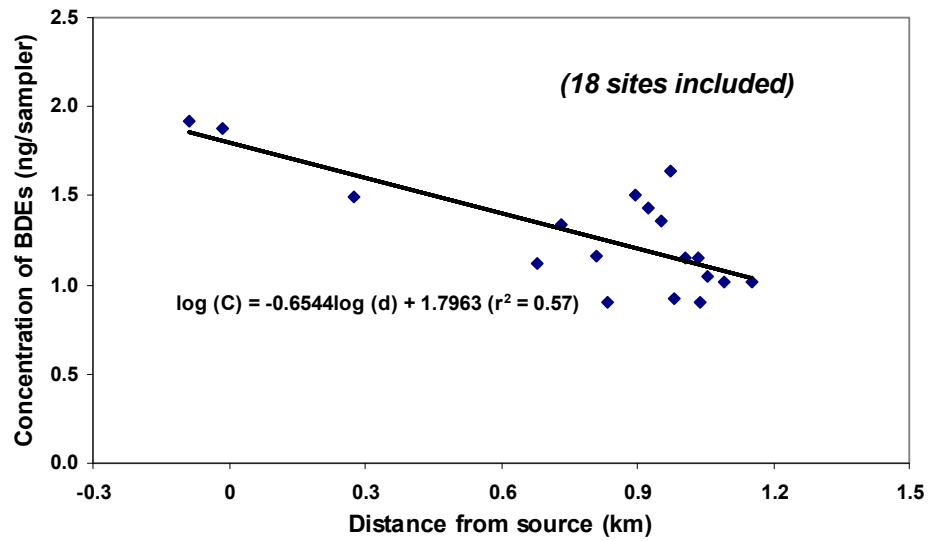


Figure.6. Concentrations of BDEs in passive samples ( $\text{ng sampler}^{-1}$ ) as a function of spherical Euclidian distance (in km) assuming the source is at a best-fit location ( $\text{lat}_{\text{sor}} = 39.94461$  N,  $\text{lon}_{\text{sor}} = 75.14270$  W). The correlation coefficient ( $r^2$ ) between the observed and predicted PAH concentrations is 0.79.

## **Conclusion**

The results from this study demonstrate the practical application of PAS to investigate spatial trends of POPs in urban area. Additionally, the Gaussian diffusion model suggests (not surprisingly) a large number of diffuse sources for these measured POPs.

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**Curriculum Vitae**  
**Songyan Du**

**Education**

- **Ph.D., Environmental Science** (2009), Rutgers University, New Brunswick, NJ
- **M.S., Marine Environmental Science** (2004), Stony Brook University, NY
- **M.S., Chemical Oceanography** (2001), Institute of Oceanography, Chinese Academy of Sciences
- **B.E., Chemical Engineering** (1998), Henan University, P.R.China

**Professional Experience**

Research Assistant (Sept. 2003 – present)  
Rutgers University, New Brunswick, NJ

Research Assistant (Sept.2001 – June. 2003)  
Stony Brook University, Stony Brook, NY

**Teaching Experience**

- Spring, 2006 - 01:160:200 Introduction to Research in Chemistry - Supervised undergraduates for research

**Publications**

- **Du, S.;** Wall, S.J.; Cacia, D.; Rodenburg, L.A. Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia, USA Metropolitan Area. *Environmental Science & Technology*. Accepted.
- **Du, S.;** Belton, T. J.; Rodenburg, L.A. Source Apportionment of PCBs in the Tidal Delaware River. *Environmental Science & Technology*. 2008, 42: 4044-4051.
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