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Spatial and seasonal trends of atmospheric PCBs in urban areas captured by passive sampling

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SPATIAL AND SEASONAL TRENDS OF ATMOSPHERIC PCBS IN URBAN AREAS CAPTURED BY PASSIVE SAMPLING

by

Carolyn Lee Persoon

An Abstract

Of a thesis submitted in partial fulfillment
of the requirements for the Doctor of
Philosophy degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

December 2010

Thesis Supervisor: Professor Keri C. Hornbuckle

ABSTRACT

The overall hypothesis of this research is that the use of passive samplers is an effective method to measure spatial and seasonal trends of atmospheric PCBs in an urban environment. In support of this, I extracted, analyzed and quantified congener specific concentrations from over 200 passive samples and over 200 active sampler, or Hi-Vols. I studied best practices for the use of methods to derive R-values and the application of R-values on mass accumulated on passive samplers for both indoor and outdoor air and found that indoor air uptake of PCBs was consistent over time and at different locations. I suggest that depuration compounds be used for outdoor sampling when using passive samplers for the most accurate measurement of effective sampling volume. I then applied these practices to passive samplers deployed in two major cities along the Great Lakes, Cleveland and Chicago. I found that these cities had different concentrations as well as different congener profiles. I compared toxicological equivalencies (TEQ) of the WHO dioxin-like PCBs between the two cities and discovered that although Cleveland had higher total PCB concentrations, it had a lower TEQ. I then compared spatial distributions and temporal trends between Hi-Vols and passive samplers and found that passive samplers were accurate at collecting spatial and seasonal trends when compared to Hi-vols, and were consistent at identifying hot-spots of atmospheric PCBs in Chicago. Finally, I developed an instrumental method to identify and quantify OH-PCBs from environmental samples to be used in future research involving the fate of atmospheric PCBs.

Abstract Approved: ______________________________
Thesis Supervisor

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Title and Department

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Date

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CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

Carolyn Lee Persoon

has been approved by the Examining Committee
for the thesis requirement for the Doctor of Philosophy
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graduation.

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CHAPTER I. INTRODUCTION

Polychlorinated Biphenyls

Polychlorinated Biphenyls (PCBs) are persistent organic contaminants that are considered probable carcinogens by the US EPA, and production in the US was banned in the early 1970's. Current studies on the toxicity of PCBs and PCB metabolites (OH-PCBs) suggest that they are not only probable carcinogens but have significant neurological and developmental impacts on health, especially on children (Bowman *et al*. 1978,Bergman *et al*. 1992, Bernhoft *et al*. 1994, Schantz *et al*. 1995, Harper *et al*. 1995, Vena *et al.* 1996,Schuur *et al*. 1998).

PCBs are of particular concern in the Great Lakes, because of the elevated concentrations of PCBs in sport fish. All the lakes now issue consumption advisories for at least one species of fish. Since their ban in the early 1970's, PCB concentrations in the Great Lakes have declined at a 9% loss rate until the 1990's when the loss rate of PCBs from the Great Lakes decreased to only 2% loss per year (Hornbuckle *et al.* 2006). This decrease in the loss rate has been attributed to atmospheric sources of PCBs contributing to the concentrations of PCBs into the Great Lakes. Studies have in fact identified atmospheric sources from major urban areas as an input of PCBs into the Great Lakes system (Halsall *et al*. 1995, Hillery *et al*. 1995, Zhang *et al.* 1999, Gingich and Diamond 2001, Miller *et al*. 2001 , Hafner *et al.* 2003, Harner *et al*. 2004,Wethington *et al.* 2005, Du *et al.* 2009).

Atmospheric sources are of interest not only because they play a role as a source of PCB deposition into the Lakes, but perhaps as a source of inhalation exposure. The fact that PCB concentrations in the atmosphere are ubiquitous makes identification of sources difficult. Current studies have identified urban areas as 'hot spots', with high concentrations of PCBs, compared to lower concentrations in rural areas. Multiple studies have shown urban-rural gradients as well as showing an 'urban pulse' or high concentrations of PCBs centralized in urban areas (Halsall *et al.* 1995,Gingrich and Diamond 2001, Harner *et al.* 2004, Du *et al.* 2009).

However, little is known about what happens within urban areas, or the intra-city distribution of PCBs. Are atmospheric PCB concentrations and congener profiles homogeneous within urban areas or are distinct sources of PCBs identifiable within urban areas? Are urban areas different in their concentrations and congener profiles? Do different urban areas have different spatial distributions of PCBs between them? Can sources of atmospheric PCBs in intra-city environments be identified? Are spatial distributions of intra-city 'hot spots' consistent over time? These questions are pertinent in understanding the dynamics of intra-city PCB atmospheric concentrations and important in order to identifying possible sources for remediation efforts. If direct sources of PCBs could be identified and remediated it could effectively decrease atmospheric concentrations in urban areas, thus reducing deposition into the Great Lakes, and ultimately decreasing human exposure through consumption of Great Lakes fish.

Previous research of atmospheric PCBs was greatly limited by sample collection methods of active, high-volume sampling (Hi-Vols) which require energy sources, maintenance, and intense personal labor in collecting samples. Recent advances in passive air sampling (PAS-PUF) have circumvented the problems with Hi-Vols and have made it possible to sample cheaply over large spatial areas *(*Gingrich and Diamond 2001, Harner *et al*. 2004, Jaward *et al*. 2004, Pozo *et al*. 2004, Gouin *et al.* 2005, Pozo *et al.* 2006 , Gouin *et al*. 2007, Chaemfa *et al.* 2009, Du *et al*. 2009, Persoon and Hornbuckle 2009*).*

Study Area

The studies described in this dissertation were conducted in two urban areas along the Great Lakes: Chicago, Illinois and Cleveland, Ohio (Figure 1). The studies were designed to explain both inter and intra-city variations in PCB concentrations and congener profiles in the atmosphere, and the spatial and temporal trends of atmospheric PCBs in urban areas to lead to better understanding and future identification of sources.

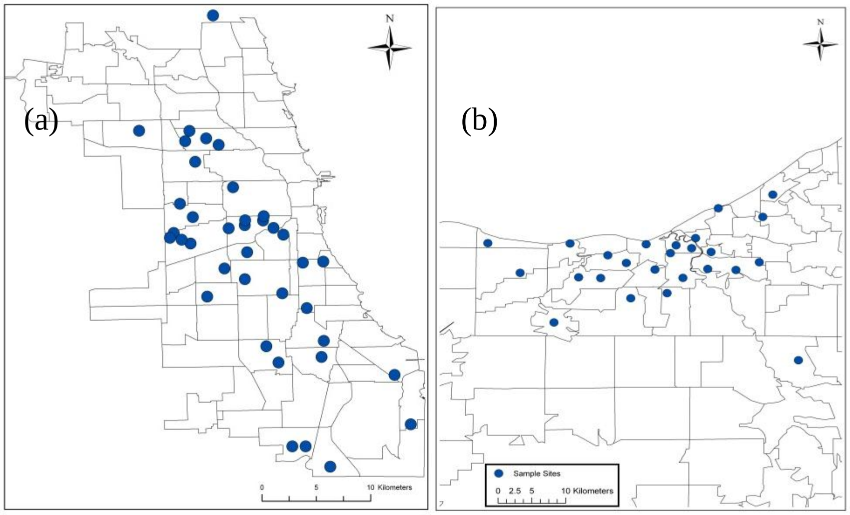

Figure 1. Maps of sample sites for passive sampling in both Chicago(a) and Cleveland(b). Hi-vol sampler sites are the same for Chicago(a).

Chicago is a large urban area along the western shore of the Great Lakes and has been identified as a source of atmospheric PCBs into Lake Michigan. Recent studies from the IADN monitoring network site at the Illinois Institute of Technology suggest that concentrations of atmospheric PCBs in Chicago are declining due to the city's efforts to cover sludge beds and brown fields, considered sources of PCBs into the atmosphere **(**Sun *et al*. 2006, Sun *et al.* 2007). However, no published data exists on spatial distributions of atmospheric PCBs across the cities, and current conclusions on the decline of concentrations in Chicago are based from one site, which may not be a representative sample of the concentrations across the entire city.

Cleveland is a large urban area along the Southeastern shore of Lake Erie and is a source of deposition of atmospheric PCBs into the lake. Cleveland is the site of GE Ballast and Lighting and a known source of PCBs; however, little is known about the PCB concentrations in

Cleveland atmosphere, beyond publication of congener profiles and potential wet deposition from Cleveland into Lake Erie (Hillery *et al*. 1998). Prior to the publication in Chapter 3, spatial distributions had never been reported for the city's PCB concentrations.

Objectives and Hypothesis

Overall hypothesis:

Passive samplers provide accurate information about the spatial and temporal variations of atmospheric PCBs in urban areas.

Objective 1: Development of best practices for passive air-sampling.

- Hypothesis 1: Indoor passive air sampling provides reliable isokinetic uptake rate of PCBs using our design.
- Hypothesis 2: Use of depuration compounds to determine sampling rates for outdoor passive air sampling is the best practice for determining PCB concentrations.

Objective 2: Identification of inter and intra city spatial variations in airborne PCB concentrations and congener profiles by deploying passive samplers across Chicago and Cleveland.

- Hypothesis 3: Spatial distribution of PCB concentrations and congener profiles are significantly different between Cleveland and Chicago.
- Hypothesis 4: Intra-city distributions of PCB concentrations and congener profiles vary spatially.
- Hypothesis 5: Passive sampling can identify localized intra-city potential sources.

Objective 3: Comparison of passive sampling and Hi-Vol airborne PCB data over space and time.

- Hypothesis 6: Measurements of PCB concentrations from passive samplers are comparable to Hi-vol samples over space and time.
- Hypothesis 7: Congener profiles between passive samplers and Hi-Vols differ due to difference in sampling methods.

Objective 4: Identification of consistent spatial distribution of hot-spots over time, and identification of their potential sources

- Hypothesis 8: Hot-spots of atmospheric PCBs are consistently identified over time.
- Hypothesis 9: Spatial distribution of atmospheric PCBs is localized over time in Chicago.

Objective 5: Development of a method for analysis of hydroxylated-PCBs on GC/MS/MS for air samples.

- Hypothesis 10: GC/MS/MS is a highly selective analysis instrument for hydroxylated PCBs in environmental samples.

Thesis Overview

This thesis is outlined with respect to the above objectives and hypotheses. Chapter II addresses objective 1 and the associated hypotheses with respect to best practices for passive air sampling in indoor and outdoor environments. Chapter III undertakes objective 2 and hypotheses 3 through 5 addressing spatial distribution of atmospheric PCBs in two urban areas. Chapter IV addresses both objective 3 and objective 4 and their respective hypotheses by looking at spatial and seasonal trends captured by Hi-Vols and passive samplers throughout Chicago for multiple years. Chapter V expands on our current knowledge of atmospheric PCBs to develop a method for analyzing methoxylated-PCBs from air filters in order to better quantify fate of atmospheric PCBs and addresses objective 5.

Chapter II compares the use of depuration compounds as well as uptake of PCBs in determining the kinetic rates of PCB mass transfer onto PUF disks for two environments, indoor and outdoor. The study found that rates of uptake for indoor air were consistent using both the depuration method and the uptake method, and that indoor uptake and elimination rates followed the first order mathematical model used in passive sampling theory. In outdoor environments, elimination rates for depuration compounds were consistent and followed the theoretical model, however; uptake rates were highly variable over time, most likely due to the fact that the concentration of PCBs in the air was not a constant over time as assumed in the mathematical model. Due to this inconsistency in uptake, we suggest that depuration compounds be used to determine the mass transfer coefficients for PCBs used to determine the effective air volume sampled as they reflect only the air volume sample and are not skewed by changes in the ambient air concentrations as seen with the uptake rates.   This publication (*Chemosphere* 2009) was the first to compare both methods side by side in the indoor and outdoor environments for PCBs.

Chapter III addresses spatial distribution of atmospheric PCBs across two cities: Cleveland and Chicago using passive samplers. Results from this study show that a spatial resolution over an urban area is important to capture representative ΣPCB concentrations of that urban area. ΣPCB concentration and site specific congener profiles also vary spatially within urban areas. Both Cleveland and Chicago have no significant autocorrelation between sites, suggesting local emissions are important. Sites with high ΣPCB concentrations (‘hot spots’) have a good correlation to known Aroclor mixes, and sites with low ΣPCB concentrations have enrichment in lower chlorinated PCBs and poor correlation to Aroclors within urban areas. This study resulted in a publication (*Environmental Science and Technology* 2010) that was the first publication of spatial distributions of atmospheric PCBs across both Cleveland and Chicago.

Chapter IV examines the question of how Hi-Vols and passive samplers compare when looking at consistent spatial distributions across the city of Chicago, as a foundation of using both sampling methods for future identification of sources of atmospheric PCBs in Chicago. Passive samplers and Hi-Vols represent very different collection methods, highly spatial or temporally resolved data. On large scales, both methods measure similar concentrations; however, at specific sites there can be significant differences in annual average concentrations due to non-continuous Hi-Vol sampling. Congener profiles between the two methods are similar for the summer; however can differ in the winter due to the passive samplers poor collection of higher chlorinated PCBs and the enrichment in lower chlorinated PCBs. The use of passive samplers coupled with spatial statistical methods of identification described in this section give a novel approach to identifying hot-spots of atmospheric PCBs, which could lead to more rapid source identification. This chapter has been submitted for publication to *Environmental Science and Technology*, and is the first study to our knowledge to compare Hi-Vols and passive samplers spatial distributions across a city, and the first to look at consistent spatial distribution within a city over time.

Chapter V is dedicated to analytical method development for identification and quantification of hydroxylated -PCBs using a GC/MS/MS. The results of this chapter show a robust method for identification and quantification using the GC/MS/MS. However air sample filters from Chicago that were extracted and analyzed using this method show low frequency of detection. Possible causes of the low detection frequency for real world samples could be due to a selective, but not sensitive method on the GC/MS/MS, or could be attributed to losses of the parent compound, hydroxylated-PCBs. This method is the first to our knowledge, of a hydroxylated -PCB method on a GC/MS/MS and has been developed to use for environmental samples, in order to truly understand both the fate of PCBs in the environment and the potential for exposure to hydroxylated -PCBs for humans from the environment.

Appendix A contains supplementary information referenced in Chapter II, such as Standard Reference Material used in QA/QC. Appendix B contains supplementary information for Chapter III, multiple tables and figures used to support our arguments for localized sources to atmospheric PCBs. Appendix C is referenced in regards to Chapter IV and contains multiple tables and figures used in analysis for Hi-Vols and passive samplers in Chicago. Appendix D contains calibration curves for the method described in Chapter V.

CHAPTER II. CALCULATION OF PASSIVE SAMPLING RATES FROM BOTH NATIVE PCBS AND DEPURATION COMPOUNDS IN INDOOR AND OUTDOOR ENVIRONMENTS

Abstract

Passive sampling has become a practical way of sampling persistent organic pollutants over large spatial and remote areas; however, its ease in use is also coupled with some uncertainty in calculating air concentrations from accumulated mass. Here we report a comparison study of polyurethane-foam-based passive samplers (PUF-PAS) for quantitatively determining the sampling rates of polychlorinated biphenyls (PCBs) from air. We measured both uptake of native PCBs and loss of depuration compounds and determined the sampling rates (R-values) for multiple samplers harvested at three different time periods. The uptake of native PCBs in the linear phase was similar to the loss of depuration compounds for indoor air and behaved as predicted. A single R- value of 2.6 m^3d^{-1} was calculated from the mean of 12 samplers deployed indoors from three harvest dates with a range of 2.0 to 3.4 m^3d^{-1} for both uptake of native PCBs and loss of depuration compounds. Loss of depuration compounds in outdoor air also followed the predicted linear behavior with a range of calculated R-value of 4.4 – 8.4 m^3d^{-1}. Uptake of native PCBs behavior was extremely variable, probably due to changes in ambient air concentrations and resulted in R-values of 1.6-11.5 m^3d^{-1} with greater variation seen in higher chlorinated homologue groups.

Introduction

The global and regional distribution of persistent organic pollutants (POPs) is now well understood, thanks in part to the development of passive samplers that are lightweight, uniform, inexpensive and unobtrusive (Farrar *et al.* 2005, Gouin *et al.* 2007, Kot-Wasik, *et al.* 2007, Partyka *et al.* 2007).

Passive samplers that use polyurethane foam, soils, and semi-permeable membranes (Law *et.al.* 1998, Migazweski *et. al.* 1999,Shoeib and Harner 2002, Harner *et.al.* 2004) have been used world-wide and have been particularly effective in remote areas, across large spatial areas, and indoors where high -volume samplers (Hi-Vols) are impractical (Shoeib and Harner 2002).

Currently, the comparison between Hi-Vol data and passive sampling data collected for specific compounds, such as PCBs, is difficult due to the difference in temporal resolution, low detection limits for Hi-Vol samples, and differences in calculating concentrations. Researchers, however, have already compared the differences in reported calculated concentrations between Hi-Vols and passive samplers (Gouin *et.al.* 2005a, Gouin *et. al.* 2005b, Harner *et. al.* 2006). Similar to Hi-Vol data and PAS-PUF data, PCB concentrations for PAS-PUFs are calculated in different ways as well. Researchers derive a sampling rate, or R-value (m^3d^{-1}), from either loss of depuration compounds or uptake of native compounds coupled with known air concentrations, yet these methods have never been compared side-by-side, to our knowledge, until this study.

Several studies have determined effective sampling rates of passive samplers by injecting depuration compounds onto the sampling media (Jaward *et al.* 2004, Pozo *et al.* 2004, Gouin *et al.* 2005b). The sampling rate, R-value, is determined by measuring the loss rate (k_e) of these compounds. Alternatively, researchers have estimated R-values by correlating the mass of POPs on the passive sampler with the concentrations measured using Hi-Vols (Harner *et al.* 2004, Motelay-Massei *et al.* 2005, Klanova *et al.* 2008, Hazrati and Harrad 2007). The uncertainty of the relationship between Hi-Vol concentrations and PUF concentrations, which have distinctly different time resolutions, makes this method imprecise. Hi-Vol data collected in the field that is not continuous may also not be accurate in representing ambient air concentrations, especially when these concentrations are not constant.

One issue affecting the interpretation of passive sampling concentrations is that two different methods are used to derive R-values in order to calculate concentrations. The problem is the ability to relate concentrations from different studies using PAS-PUFs. The Hi-Vol method of calculating concentrations is straightforward and no groups deviate from each other when using this method to report ambient air concentrations of PCBs; however, with PAS-PUFs the different methods to calculate reported concentrations leave some uncertainty on how these two methods compare.

Hazrati and Harrad (2007) and Klanova *et al*. (2008) have described the calculation of R-values and mass transfer coefficients by uptake in both indoor and outdoor environments respectively. However, to our knowledge, no study to date has examined both uptake of native congeners and loss of depuration compounds simultaneously for both indoor and outdoor environments in order to compare methods of deriving R values. In this paper we have calculated the sampling rates from both elimination ($k_{e)}$ and uptake (k_u) for our PAS-PUF design to better understand how these different methods of deriving concentrations may differ and to understand the best practices of deriving R-values in the field. We will use the term "*R-value*" to distinguish the sampling rate from the correlation coefficient, r.

We have evaluated the reproducibility of sampling rates between indoor sites and calibrated the PAS-PUF for indoor sites in order to apply one constant R-value to all samples harvested from a specific design. We have also compared differences of calculated R-values for outdoor samplers. Finally, we compared the behavior of labeled PCBs used as depuration compounds to that of native PCBs in both indoor and outdoor environments.

The Sampling Rate

The mass of gas-phase PCBs (M_{PUF}, ng) accumulated on the PUF media is a function of a mass transfer coefficient as well as the concentration gradient between the air and the PUF disk (Bartkow *et al*. 2005)

$$\frac{dM_{PUF}}{dt} = k_v \cdot A_s \cdot (C_{Air} - \frac{C_{PUF}}{K_{PUF}}) \qquad \text{Equation 1}$$

where A_s is the PUF surface area (m^2), k_v is the mass transfer coefficient ($m\ s^{-1}$), C_{Air} is the analyte concentration in the air ($ng\ m^{-3}$), C_{PUF} is the PCB concentration on the PUF($ng\ m^{-3}$) and K_{PUF} is the dimensionless PUF/air equilibrium partition coefficient. For PCBs, K_{PUF} is large and therefore the mass of PCBs on the PUF is a linear function of time. The concentration of PCBs in air, as measured by the passive sampler, can then be determined as in Equation 2, assuming that C_{Air} is a constant.

$$C_{Air} = M_{PUF} (k_v A_s t)^{-1} \qquad \text{Equation 2}$$

The product $k_v \cdot A_s$ must be determined by experiment and is called the sampling rate, R-value.

R-values can be calculated from either the loss of depuration compounds from the PUF, or the uptake of native compounds onto the PUF.

The R-value calculated from the loss of depuration compounds is determined by calculating the mass transfer coefficient as a function of the first order elimination rate constant (k_e, sec^{-1}), and the stagnant air layer over the PUF surface (δ_{film}, m) as defined by Shoeib and Harner (2002):

$$k_v = k_e \cdot K_{PUF} \cdot \delta_{film} \qquad \text{Equation 3}$$

where

$$k_e = \frac{\ln(\frac{m}{m_0})}{t} \qquad \text{Equation 4}$$

Alternatively, R-values may be derived from linear uptake curve of native congeners from ambient air of known concentration:

$$R = \frac{b}{C_{Air}} \qquad \text{Equation 5}$$

where b is the slope of mass accumulated versus time.

In this study we calculated the R-value from both uptake and loss of PCB congeners for each sampler deployed.

Materials and Methods

Air Sampling

Passive samplers were deployed both indoors and outdoors at the Institute of Rural and Environmental Health (IREH) at the Oakdale Campus of The University of Iowa beginning the last week of August 2006 and ending in the first week of October 2006. Two indoor sites were chosen; the first was an older laboratory that was built in 1960s and the second was a laboratory addition built in the 1990s. A third site was located outdoors approximately 150 meters from the IREH building. Twelve passive samplers (specifications: 18 cm lower bowl diameter, 23 cm upper bowl diameter, 3 cm gap between bowls, six ventilation holes in bottom) were deployed approximately 2.7 meters from the ground at each site, with three spiked and one unspiked PUF disks (specifications: 14 cm diameter, 1.35 cm thick, 365 cm^2 surface area, 4.40 g mass, 207 cm^3 volume, 0.0213 g cm^{-3} density) harvested for each time frame (21, 28, and 46 days). A Hi-Vol sampler (Tisch Environmental, Cleves, OH) was deployed at each site and was equipped with quartz fiber filters and XAD Amber-lite 2 (Supelco, Inc) media. The Hi-Vols were operated for 8-hour periods at night on the three days that the passive samplers were harvested. A total of three Hi-Vol samples were collected at each site over the total deployment time for the PUF disks. PCB congeners were extracted and quantified using the same method as for the PAS-

PUF. Because PCBs exist primarily in the gas-phase, PCBs were only measured in the XAD-2 and not in the quartz filters.

Analysis

PUF disks were cleaned (Soxhlet extraction 24 h in hexane followed by 24 h in acetone), dried in a desiccator, and spiked with 40 ng per congener of a mixture of EPA Method 1668A Labeled Toxics/LOC/Window defining solution (Cambridge Isotope Laboratories). PUFs were spiked by placing them in amber jars and then adding depuration compounds. PUFs were dried in the jars, then capped with Teflon lids, sealed in zip lock bags, and stored in a -20ºC freezer until deployment. PAS-PUF sampling chambers were solvent-rinsed with hexane and acetone just prior to deployment. Exposed PUF disks were placed in amber jars with Teflon lids, sealed in zip lock bags and immediately transferred to a freezer. XAD Amberlite 2 resin was cleaned by using a comparable method (Peck and Hornbuckle 2006).

All sample media were extracted with pressurized fluid extraction (Dionex ASE-200), using a 1:1 hexane: acetone mixture with parameters as follows: pressure 10.3 MPa (1,500 psi), 100 ºC, 5 minutes static time, 1 static cycle, 60% of flush volume, and purge at 90 seconds. Extracts were concentrated to 1 mL (Caliper TurboVap II). Surrogate standards (50 ng each of PCB 14, 65, 166 from Accustandard) were added just prior to extraction. Internal standards (60 ng each of PCB 30 and 204 from Accustandard) were added just prior to analysis. All samples were analyzed using a modified EPA Method 1668A on Tandem Mass Spectrometry GC/MS/MS (Quattro Micro^{TM} GC, Micromass MS Technologies) using a Supelco SPB-Octyl (30m x 0.25mm x .25µm) with GC inlet parameters of inlet temperature 270 °C ,oven temperature ramp as initial temperature 75 °C , initial time 1 minute, ramp 15 °C/min to 150 °C, ramp 2.5 °C/min to 290 °C, with an interface temperate of 290 °C. Using this method we were able to identify 172 unique congeners, with an additional 37 congeners coeluting. Identification of 35 Carbon-13 labeled congeners (1, 3, 4, 9, 15, 19, 28, 37, 52, 54, 77, 81, 101, 104, 105, 111, 114, 118, 123, 126, 138, 155, 156, 157, 167, 169, 178, 188, 189, 194, 202, 205, 206, 208, 209) used as depuration compounds, was also achieved using this method.

Results and Discussion

Quality Control/Quality Assurance

Unspiked passive samplers (n=3) were deployed alongside passive samplers spiked with labeled PCBs to determine if labeled standards were re-depositing but none were detected. The average (± std dev.) recovery of the three surrogate standards were PCB 14, 82.4% ± 10.4; PCB 65, 98.0% ± 9.1 %; and PCB 166, 95. % ± 12.8%. A field blank was installed and removed at each site at the beginning of the study, and all were determined to be less than 10% of lowest calculated mass. Method blanks run with each extraction batch were also determined to be less than the detection limit (1 ng/mL mono-tri, 2 ng/mL tetra-hepta, and 3 ng/mL octa-deca). Three spiked PUF disks were also extracted the day of deployment to measure any significant loss of spiked congener mass while stored in the freezer, but no significant loss was detected. Standard Reference Material, NIST 2274 PCBs in iso-octane, was run in triplicates on two separate dates (Figure A1). Our method is acceptable for congener-specific analyses.

Indoor Air Sampling Rates

In order to be able to deploy PAS-PUF in indoor environments without depuration compounds, the samplers must be calibrated with depuration compounds. Ideally, one R- value can be applied to all target compounds. A recent study by Hazrati and Harrad (2007) show that passive samplers used for indoor environments can be reliably calibrated and an R-value calculated for specific sampler designs. For our study, both the uptake of native compounds and loss of depuration compounds were measured. R-values were calculated from both methods. Samplers were calibrated, resulting in one R- value that could be confidently applied to all indoor samples acquired with this design, thus eliminating the need for depuration compounds at indoor sites.

Uptake of native PCB congeners over time was determined by deploying fifteen PAS-PUF samplers in one laboratory (Indoor 1) and fifteen in another laboratory (Indoor 2). At each location, a subset of one or four samplers was collected at four time intervals. The first sample was collected immediately (time = 0). A set of four samples was collected on day 21. Another set of four samples was collected on day 28 and also on day 46. PCB congeners were extracted and measured on each PUF. The mass accumulated is compared to the linear uptake described by Equation 1, and the results are shown in Figure 2.

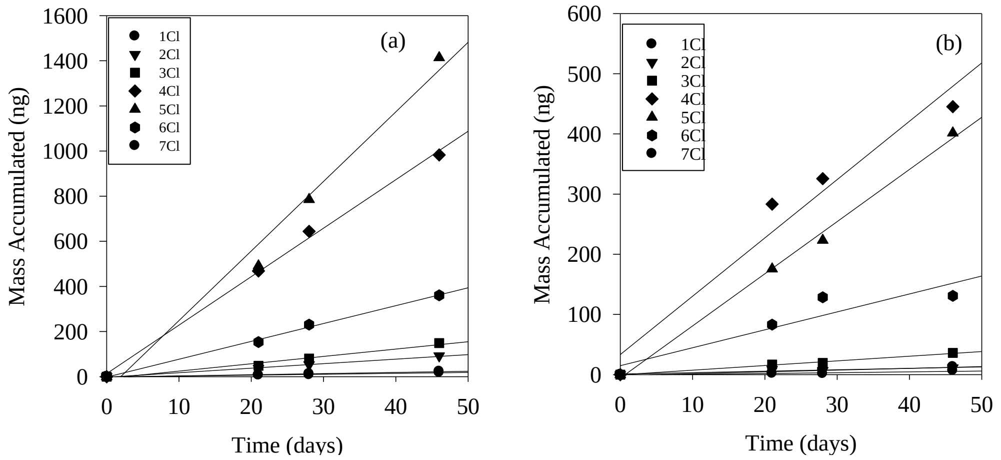

Figure 2. Mass uptake of native PCB homologue groups for indoor site 1 (a) and site 2 (b) onto PUF disks for 0, 21, 28, and 46 days.

The linear regression resulted in r^2 values ranging from 0.97 to 0.99. The high coefficients of determination suggest that PCBs in indoor environments behave as predicted by the mathematical model for compounds where air side resistance dominates (Shoeib and Harner 2002, Bartkow *et al.* 2005). By using uptake plots in Figure 1 and applying Hi-Vol data we derived R-values for indoor air (Table A1).

The assumption that C_{Air} stays constant in indoor air seems to be valid as the uptake curve is linear and the resulting R- values show good agreement with R-values calculated from depuration compounds.

The congeners measured for the uptake experiment were also collected and measured from the Hi-Vol samplers operated at the same two laboratories. The concentration of total PCBs ranged from 0.05 to 10.5 ng/m^3. The concentrations in the older laboratory were greater than the newer laboratory by one order of magnitude, possibly due to differences in building materials used (Table A1).

Loss of labeled PCB congeners was determined from the same samples as described for the uptake experiments. Each PUF media was spiked with four Carbon-13 labeled PCB congeners. The resulting loss of the four labeled PCBs from the thirteen deployed samples is shown in Figure 3.

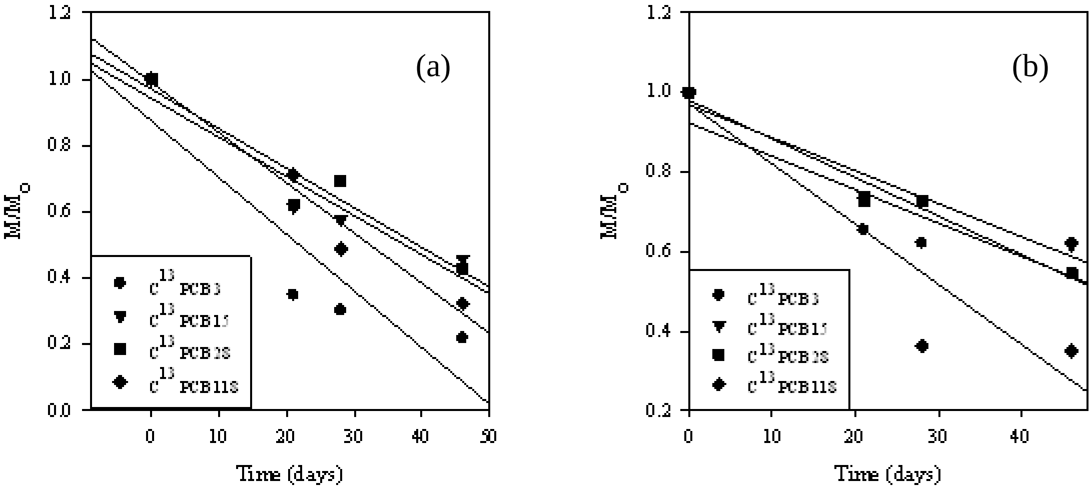

Figure 3. Loss of depuration compounds for indoor site 1 (a) and site 2 (b) onto PUF disks for 0, 21, 28, and 46 days.

The linear regression resulted in coefficients of determination ranging from 0.73 to 0.99. As found for the uptake of native PCBs from indoor air, the loss is consistent with the first order uptake model (Equation 1).

Reproducibility of Indoor R-values

Using measurements from both uptake of native congeners and loss of depuration compounds, we calculated R-values for native homologue groups (Equation 5*)* as well as individual depuration compounds (Equation 4*)*. R-values ranged from 2.0 m^3d^{-1} to 3.5 m^3d^{-1} for both native compounds and depuration compounds (Table A1), similar to R-values of 2.5 m^3d^{-1} for PBDEs calculated by Wilford *et.al.* (2004). The calculated R-values are within the range of reported values from other indoor studies. For example Shoeib and Harner (2002) report R-values of 1.8 m^3d^{-1} to 8.3 m^3d^{-1} for many semivolatile compounds. Hazrati and Harrad (2007), report a slightly lower range of values: 0.57 m^3d^{-1} to1.55 m^3d^{-1} for PCBs.

Outdoor Air Sampling Rates

Labeled PCBs in outdoor air, like indoor air, behave in a predictable manner with a good linear fit for each congener with the coefficients of determination ranging from 0.82 to 0.97 (Table A2 and Figure 4d).

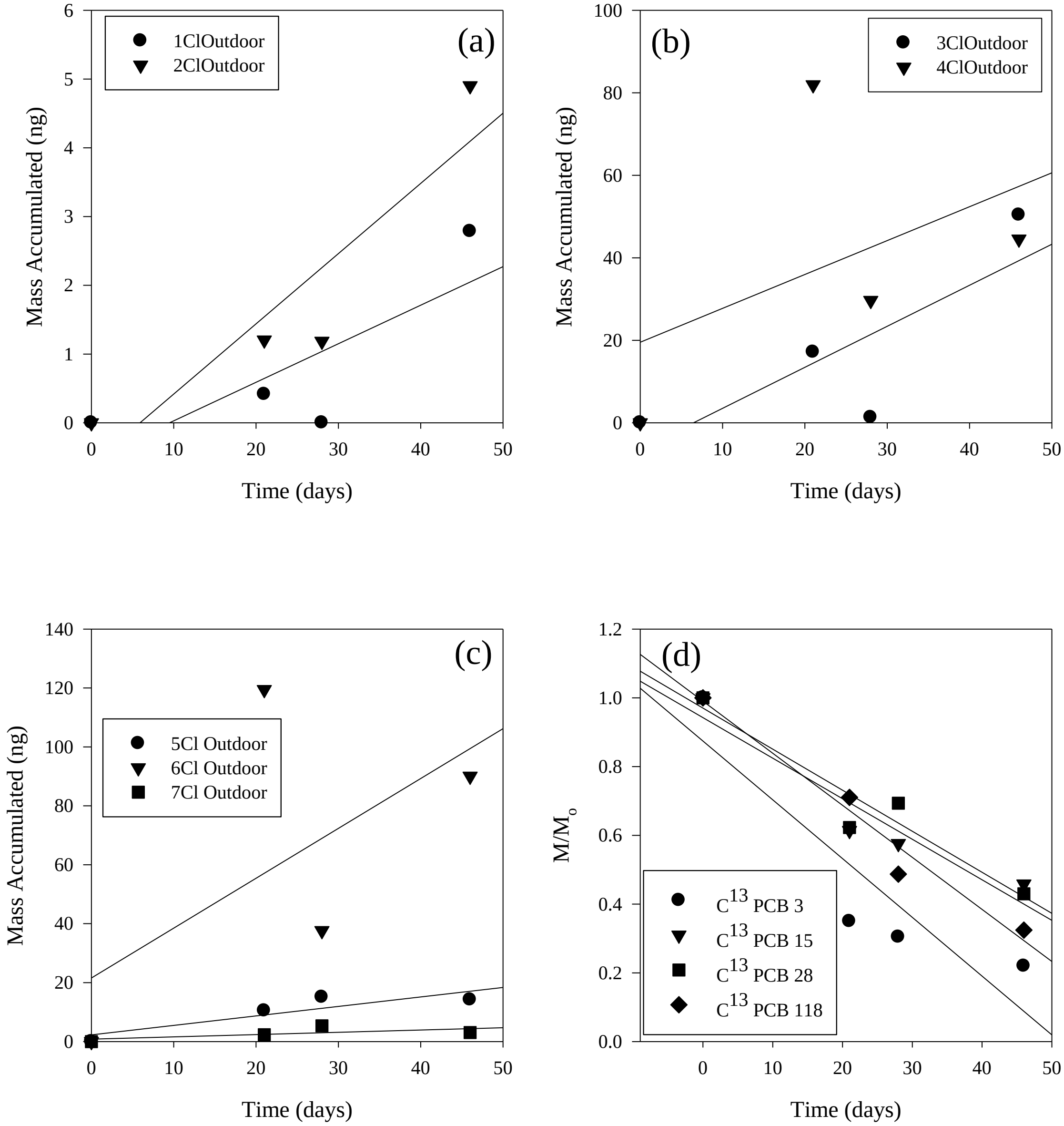

Figure 4. Mass uptake of native congeners mono and dichlorinated (a), tri and tetrachlorinated (b), and penta, hexa, and heptachlorinated compounds (c) and loss of depuration compounds (d) from PUF disks for 0, 21, 28, and 46 days at outdoor site.

Mass accumulated onto the PUF for seven homologue groups as a linear function of time. For mono-trichlorinated homologue groups, the coefficient of determination ranges from 0.64 to 0.93 (Table A2 and Figure 4a). However, a very poor correlation was observed for the higher chlorinated homologue groups tetra through hepta chlorinated, with the coefficients of determination ranging from 0.0001 to 0.33 (Table A2 and Figure 4bc). The data suggests that lower chlorinated PCBs will accumulate onto PUF disks in a predictable manner, but the accumulation of higher chlorinated PCBs onto PUF disks can vary significantly as a function of time harvested.

The high variability in the uptake of most native congeners over time is most likely caused by changes in the ambient air concentration (C_{Air}) during the study. Equation 1 assumes a constant C_{Air}; however, the concentrations of PCBs in the ambient air during this study may vary, particularly as a function of the large temperature changes (Cortes *et.al.* 1998, Simcik *et. al.* 1999, Sun *et.al.* 2007, Sun *et. al.* 2006) that occurred during our study of outdoor air. High variability in ambient air concentrations over a time frame of a single month at one site have been reported (Offenberg *et.al.* 1999, Wethington and Hornbuckle 2005, Macleod *et.al.* 2007), and show that C_{Air} can vary two orders of magnitude (Offenberg *et.al.* 1999). Although the uptake of native congeners would be affected by temperature changes, the loss of depuration compounds would remain relatively constant since the loss mechanism is dominated by the large concentration gradient between spiked PUF and the ambient air. For this reason, uptake of higher chlorinated PCBs is extremely variable but loss of depuration compounds follows the linear trend.

Reproducibility of outdoor R-values

Sampling rates vary much more in outdoor air than in indoor air. Our outdoor R-values for individual congeners ranged from 3.4 m3d-1 to 9.3 m3d-1 with an average of 6.5 m3d-1 ± 2.4 m3d-1 (Table A2). This is within the range of reported values. Jaward et al. (2004) found outdoor R-values ranging from 3.0 m3d-1 to 4.0m3d-1. Others found average R-values between 3.0 m3d-1 and 5.0 m3d-1 (Harner et al. 2006, 2004, Pozo et al. 2004, Gouin et al. 2005b, Motelay-Massei et al.2005). This large variation in R-values calculated from uptake rates could be attributed to the fact that R-values are dependent on short-term Hi-Vol measurements that may not reflect the integrated average concentration captured by the PUF.

For outdoor deployment, R-values determined from depuration compounds vary less than R-values calculated from the native PCB congeners. The calculations derived from depuration compounds reflect the current literature that states outdoor air concentrations of POPs between Hi-Vol and PAS-PUF could be off by a factor of 2 (Shoeib and Harner 2002, Gouin *et.al.* 2005b, Tuduri *et al.* 2006, Yao *et al*. 2007), which would be a more conservative calculation than concentrations derived from using R-values derived from uptake curves.

Due to the variations in C_{Air} in outdoor air, as well as the variation between homologue groups studied, we chose to look at qualitative aspects of PCB masses collected on the PUF as well. Although PCB mass accumulated onto PUF varied depending on the date harvested, congener distribution had little variation with exception to the mono chlorinated PCBs which were seen at 21 and 46 days, but were not detected at 28 days (Figure 5).

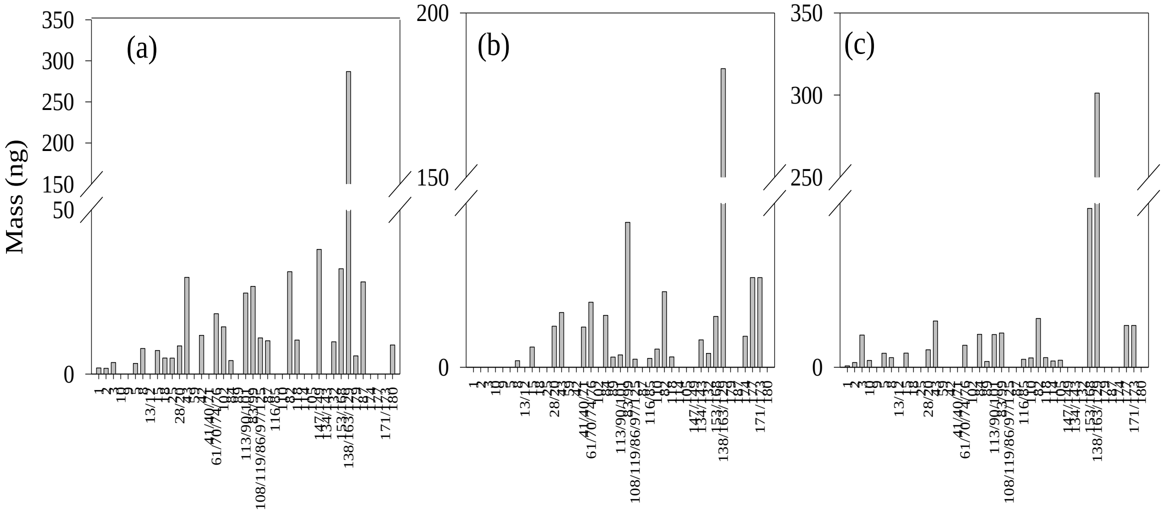

Figure 5.Congener distributions from outdoor air for 21 (a), 28(b), and 46(c) days. High concentrations of PCB 153/168 were detected in all samples, the possible source is the indoor air ventilation system from labs where PCB 153 may be used for toxicological studies.

The similarity in the congener distribution histograms suggest that the PUF is sampling from the same ambient air source, but physical factors such as temperature and wind effects are changing the rate of uptake from this ambient air source and therefore the magnitude of the mass quantified.

Conclusions

For indoor air, the average R-value of 2.6 m^3d^{-1} calculated from both uptake and loss of PCBs is recommended for application to samples using this passive sampler design for indoor sites. For outdoor applications using this passive sampler design, we suggest using depuration compounds to reduce the uncertainty by nearly a factor of 2. Since PCB concentrations are not constant in outdoor air, uptake of native congeners was not linear. The Hi-Vol data collected was not continuous and therefore was not representative of the changes in C_{Air}. The inconsistency in C_{Air} leads to large variation in derived uptake R-values derived concentrations when compared to depuration derived concentrations Comparing PCB concentrations derived from uptake of native congener to those derived from loss of depuration compounds is difficult, as uptake derived R-values are dependent on C_{Air} which may vary greatly, where depuration compound loss is independent of this variability.

CHAPTER III. SPATIAL DISTRIBUTION OF AIRBORNE POLYCHLORINATED BIPHENYLS IN CLEVELAND, OHIO AND CHICAGO, ILLINOIS

Abstract

Passive samplers were deployed across Cleveland, OH and Chicago, IL to evaluate the spatial variability of airborne PCBs in urban areas. We measured Σ_{151}PCB concentrations, the sum of 151 congeners or congener groups, quantified using tandem mass spectrometry, spatial distributions, and congener profiles in two urban areas in the Great Lakes region. Mean ΣPCB concentrations were significantly different between Cleveland (1.73±1.16 ng m^{-3}) and Chicago (1.13 ± 0.58 ng m^{-3}). Mean congener profiles were compared with commercial Aroclor mixtures and found to be similar to Aroclor 1242 in Cleveland and similar to a mixture of 1242 and 1254 in Chicago. We observed large spatial variation in concentrations and weak or no significant autocorrelation between sites in both cities. 'Hot spots' of high ΣPCB concentrations were identified in both urban areas and the congener profile at these locations were most strongly correlated to that of PCB Aroclor mixtures. Congener profiles showed important differences including the enrichment of dioxin-like congeners in Chicago.

Introduction

Urban areas are known sources of PCB concentrations to the atmosphere (Halsall *et al.* 1995, Hoff *et al.* 1996, Hillery *et al.* 1997, Simcik *et al.* 1997, Offenburg *et al.* 1999, Brunciak *et al.* 2001, Gingrich and Diamond 2001,Miller *et al*. 2001, Totten *et al*. 2001, Hafner *et al*. 2003, Helm and Bidleman 2003, Totten *et al*. 2003, Harner *et al*. 2004, Pozo *et al.* 2004, Totten *et al.* 2004, Gouin *et al*. 2005, Offenburg *et al*. 2005, Wethington *et al*. 2005, Hornbuckle *et al.* 2006). Although a number of studies have examined city specific PCBs concentration, little is known about inter- and intra-city variability of PCBs concentration. Only a few studies have examined the spatial distribution of airborne PCBs within large urban areas. Basu *et.al* 2004 measured airborne PCBs at two locations in Chicago, Du *et.al* 2009 measured airborne PCBs at 32 sites across Philadelphia, and Hu *et.al* 2008 measured airborne PCBs at 37 sites across Chicago although they reported only the concentration of one congener (3,3'dichlorobiphenyl). Historically, PCB measurements of urban air have been made using single-site high-volume (Hi-Vols) samplers (Halsall *et al.* 1995, Hoff *et al.* 1996, Hillery *et al.* 1997, Simcik *et al.* 1997, Offenburg *et al.* 1999, Brunciak *et al.* 2001, Gingrich and Diamond 2001,Miller *et al*. 2001, Totten *et al*. 2001, Hafner *et al*. 2003, Helm and Bidleman 2003, Totten *et al*. 2003, Harner *et al*. 2004, Pozo *et al.* 2004, Totten *et al.* 2004, Gouin *et al*. 2005, Offenburg *et al*. 2005, Wethington *et al*. 2005, Hornbuckle *et al.* 2006). Although these long term monitoring studies have provided important information about temporal trends in PCB concentrations (Hillery *et al.* 1998, Simcik *et al*. 1999, Sun *et al*. 2006, Sun *et al*. 2007) they do not represent spatial trends of PCBs across an urban area.

Recently, researchers have turned to passive sampling to measure the spatial distribution of PCBs, such as Yeo *et.al* 2004 and Baek *et al.* 2008 in South Korea, Jaward *et.al* 2004 in Europe, and Pozo *et.al.* 2006 globally with the GAPS study. Passive sampling can acquire important information on the spatial distribution of PCBs across an urban area. First, 'hot spots', areas of high concentrations of PCBs can be identified (Broughton *et al*. 2003,Gouin *et al.* 2005, Heidtke *et al*. 2006). These 'hot spots' can form the basis for further studies that pin-point the sources of PCBs and remediation efforts. Second, a more accurate representation of mean PCB concentration for urban areas may be estimated from many passive sampling results rather than single-point measurements. Better understanding of airborne PCBs in cities near the Great Lakes is particularly important because urban areas have been identified as a major source of PCBs now entering the lakes and accumulating in the fish. All the Great Lakes have fish consumption advisories, established primarily because of continued elevated concentrations of PCBs.

This is the first study, to our knowledge, to compare PCB concentrations spatially distributed across two major urban areas with data collected during the same time period. We hypothesized that the two urban areas, Cleveland and Chicago, would exhibit different PCB concentrations and congener profiles. Our specific objectives in this study were to compare the spatial variation of PCBs in Cleveland and Chicago in terms of ΣPCB concentrations, congener profiles, and toxicologically-relevant congener concentrations.

Methods and Materials

Selection of Sampling Sites

Different methods were used to select sampling sites in the two cities. Both methods required a prior knowledge about the pollutant in question to optimize site selection (Ott *et al*. 2008, Kumar 2009). Since spatially detailed intra-city PCB data does not exist in either of the selected cities we relied on two different criteria for identifying sample sites. In Cleveland, we used a novel hybrid-regression approach to capture the spatial variability in air pollution while minimizing the number of sites required (Ott *et al*. 2008, Kumar 2009). Specifically, we estimated the spatial distribution of mass concentrations of airborne particles smaller than 10 μm (PM_{10}) as a proxy for PCB concentrations. Following Kumar 2009, we used land-use and land-cover data, proximity of the site to potential emission sources for PM_{10}, primarily industrial facilities, and aerosol optical depth data taken from satellites and corrected for meteorological conditions. Next, we defined the maximum variance of concentrations within the 21 sample sites (n) that our budget allowed. We calculated the maximum variance using Equation 6 as the locations where spatial autocorrelation is near 0 ($\rho_z \sim 0$) between a sampling site (Z_i) and its neighboring sites (Z_j). In the case of PM_{10}, Z has units of μg m^{-3}. K is defined as Z_i / Z_j *(36).*

$$\max|Z| = \sum_{i=1}^{n}\sum_{j=1}^{K} \rho z (Z_i - Z_j)^2 \qquad \text{Equation 6}$$

In Chicago, site selection was based on opportunity rather than optimization (Hu et al. 2008). The 17 sites sampled in August were chosen based on existing arrangements with local schools and businesses, all in residential areas, and although the sites provide an extensive spatial distribution in the urban area of Chicago, there was no design to capture maximum variability. The Chicago sample site distribution was designed to identify mean concentrations and 'hot spots' within residential areas and to characterize congener profiles in Chicago.

PCB Passive Air Sampling

We used passive air samplers coupled with polyurethane foam (PAS-PUF) to quantitatively measure airborne PCBs at locations where it is difficult or impractical to install and maintain Hi-Vol vacuum pump samplers. Passive samplers also have the advantage of accumulating high masses of PCBs, resulting in fewer non-detects than Hi-Vols. The collection of higher PCB mass, as well as uptake of particle bound congeners, only at a slower uptake rate (Klanova *et al.* 2008*)*, with passive samplers can result in a more accurate comparison of congener profiles between sites (Klanova *et al*. 2008,Persoon and Hornbuckle 2009*)*. We have applied the passive sampler design of Shoeib and Harner 2002, and have tested it to determine the sampling flow rates for PCB congeners (Persoon and Hornbuckle 2009*)*.

PAS-PUF samplers were deployed at both urban locations in the beginning of August 2008, with total deployment periods for Cleveland samples from 20-22 days (Table B1), and Chicago from 13-47 days (Table B2). Concentrations for both Cleveland and Chicago were calculated using sampling rates (m^3d^{-1}), called R-values (Shoeib and Harner 2002, Bartkow *et al.* 2005, Persoon and Hornbuckle 2009), derived from the loss of the depuration compounds spiked onto the PUF disks prior to deployment. R-values derived for each individual site in Cleveland ranged from 4.1-6.6 m^3d^{-1} (Table B1), and site specific R-values were applied in order to calculated PCB concentrations. R-values for Chicago were derived from three sites and ranged from 4.8-6.7 m^3d^{-1} (Table B2), with a mean R-value of 5.8 m^3d^{-1} applied to all samples collected from Chicago. Applied R-values are similar to previously reported mean values for PCBs in outdoor air using this passive sampling design (Persoon and Hornbuckle 2009).

Sampling Media Preparation

PUF disks were cleaned (Soxhlet extraction 24 h in hexane followed by 24 h in acetone), dried in a desiccator, and a subset of the samples was spiked with depuration compounds: 50 ng per congener of PCBs ^{13}C-labeled 28, ^{13}C-labeled 111, ^{13}C-labeled 178 (Cambridge Isotope Laboratories). The method used to spike depuration compounds onto PUF is described previously (Persoon and Hornbuckle 2009), where depuration compounds are added to hexane and poured onto PUF disks and dried under nitrogen blow-down. PAS-PUF sampling chambers were solvent-rinsed with hexane and acetone just prior to deployment. Exposed PUF disks were placed in sealed zip lock bags and immediately transferred to a freezer.

Sample Extraction and Analysis

All sample media were extracted with pressurized fluid extraction (Dionex ASE-200), using pesticide grade hexane as described previously (Persoon and Hornbuckle 2009). Extracts were concentrated to 0.5 mL (Caliper TurboVap II). Surrogate standards (50 ng each of PCB 14, 65, 166 from Accustandard) were added just prior to extraction. Internal standards (50 ng of PCB 204 from Accustandard) were added just prior to analysis. All samples were analyzed using a modified EPA Method 1668A on Tandem Mass Spectrometry GC/MS/MS (Quattro Micro$^{\text{TM}}$ GC, Micromass MS Technologies) using a Supelco SPB-Octyl (30m x 0.25mm x .25µm) with GC inlet parameters previously reported (Persoon and Hornbuckle 2009). Using this method we were able to identify 156 unique congeners, with an additional 53 congeners coeluting. Identification of three ^{13}C-labeled congeners (28, 111, and 178 from Accustandard) used as depuration compounds was also achieved using this method. After removal of compounds used as standards, this study quantified 151 PCB peaks.

Quality Assurance and Quality Control

Masses were corrected using surrogate recoveries of PCB 14 and 166. PCB 65 was not used for correction as it occasionally coeluted with PCB congeners 44 and 47, which were subsequently eliminated from our analysis. Surrogate recoveries for Cleveland ranged from 60-80% and for Chicago from 70-99%. Instrument detection limits (IDL) were 0.01ng for mono-trichlorinated congeners, 0.02 ng for tetra-heptachlorinated congeners, and 0.03 ng for octa-decachlorinated. Limit of quantification (LOQ) was calculated as three times the standard deviation of peaks from the method blank plus the background level from instrumental blanks, and was calculated as 0.07 ng per congener. Field, trip, and method blanks were all less than LOQ. The mean field duplicate for Cleveland was 13% relative difference for three sites, Chicago field duplicates were a mean of 9% relative difference for three sites. Instrument duplicates show a 7% relative difference for all samples run.

Results and Discussion

Differences in ΣPCB Concentrations for Cleveland and Chicago

Air

Measured ΣPCB concentrations are summarized in Table 1. The mean concentrations were higher in Cleveland (1.73±1.16 ng m^{-3}) than in Chicago (1.13±0.58 ng m^{-3}) at the 95% confidence level. A Wilcoxon signed rank test was applied to determine significant difference; a t-test could not be applied since ΣPCB concentrations from Chicago do not follow a log normal distribution (Figure 6).

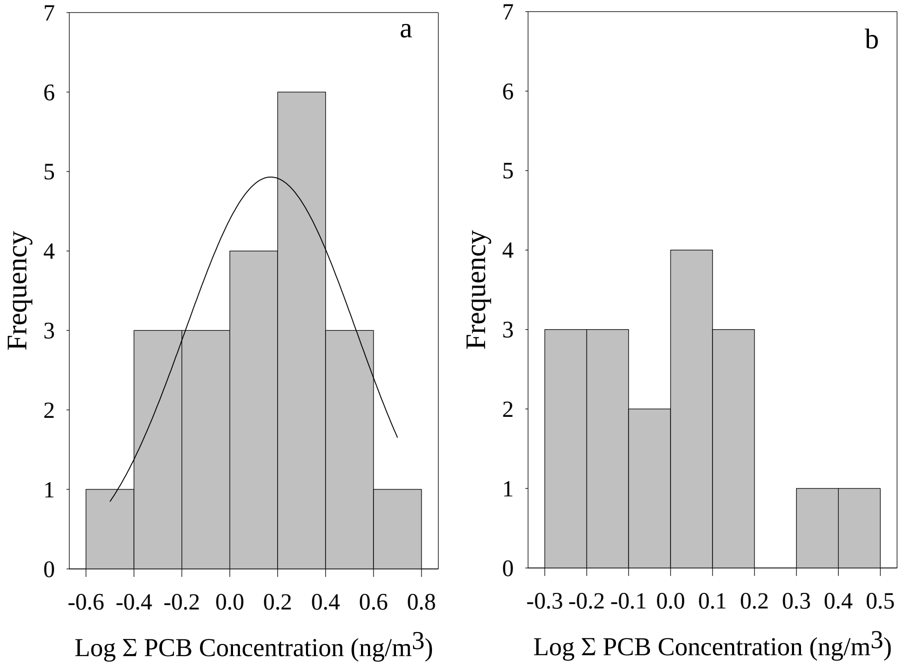

Figure 6. Log transformed concentration distribution for ΣPCBs for Cleveland air(a) and Chicago air(b). Concentration distribution for Cleveland has a Gaussian 3-parameter fit applied. Differences in distribution are probably due to differences in sample site land use; Chicago samples represent primarily residential areas where Cleveland represents industrial, residential and rural land uses.

Results of the Wilcoxon test conclude that the samples from Cleveland and Chicago are significantly different ($p = 0.005781$ for $\alpha = 0.01$). Cleveland exhibited a wider range of concentrations than Chicago, from 0.52-3.92 ng m^{-3} and 0.60-2.25 ng m^{-3} for 5th and 95th percentiles, respectively (Table 3). As shown in Figure 6, the concentration distribution for Chicago is skewed to the left of the distribution plot, toward lower concentrations. To test if the difference between Cleveland and Chicago was due to different applications of R-values to calculate concentrations, average for Chicago and site specific for Cleveland, we used a the average R-value for Cleveland applied to all samples. Results still showed greater variation in Cleveland and significantly different concentrations ($p<0.01$). Since the samples were collected during the same time, R-value application did not affect the difference in variation, and have similar mean temperatures during the deployment (Table B1 and Table B2), the higher variation in concentrations may be due to the sampling sites and land use around the sampler.

Table 1. Statistical analysis of ΣPCB concentrations (ng m^{-3}) for Cleveland air and Chicago air.

	Cleveland		Chicago
Mean (ng m^{-3})	1.73	1.37 (geometric)	1.13
Standard Deviation (ng m^{-3})	1.16	2.06 (geometric)	0.58
Median (ng m^{-3})	1.54		1.07
95th percentile (ng m^{-3})	3.92		2.25
5th percentile (ng m^{-3})	0.52		0.60
Range (ng m^{-3})	0.34-4.24		0.57-2.69

The difference in ΣPCB concentrations is probably due to the different distribution of samplers within each city: the Cleveland samplers covered more area and a larger variety of land uses (Figure B1). The area sampled in Cleveland is four times the area of sampler placement in Chicago. Furthermore, the land uses in the area sampled in Cleveland include industrial sites, residential sites, and rural sites. In Chicago, most of the sampling sites were urban residential (Figure B1).

The spatial distribution of ΣPCB concentrations were plotted for both Cleveland and Chicago (Figure 7). The maps show multiple locations of high ΣPCB concentration (‘hot spots’) in both Chicago and Cleveland, similar to results from other studies using passive sampling in urban areas (Harner *et al*. 2004, Gouin *et al.* 2005, Du *et al*. 2009). Interestingly, spatial autocorrelation between sites was not significant in either city as determined using Moran's I in the R program (R Development Core Team 2006) (Figure B2 and Table B3). For example, consider three sites in western Chicago (Figure 7). Although the sites lie within 1.68 km of each other, PCB concentrations at once site were recorded as 1.4 ng m^{-3} while its two closest neighbors record 0.4 ng m^{-3} and 0.6 ng m^{-3}, respectively. Similarly, in Cleveland, site proximity does not predict their similarity (Figure B2). The lack of PCB concentration autocorrelation in the two cities suggests that results from each sampler is representative of only the immediate area near where it is deployed. This suggests that sources of airborne PCBs are distributed across the city and atmospheric dispersion is less important than local emissions.

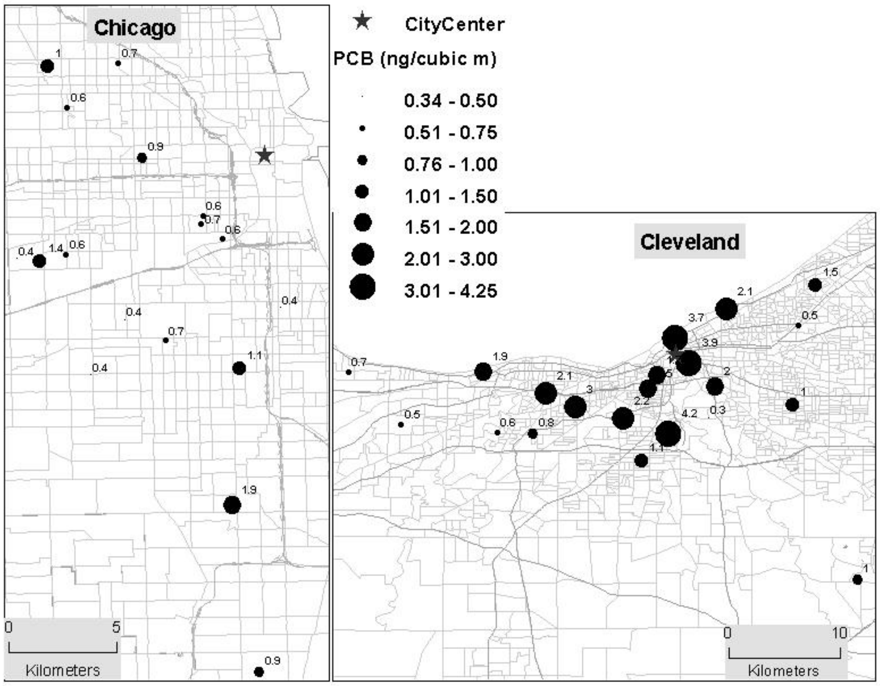

Figure 7. Multiple 'hot spots' are seen in spatial distributions for Σ PCB concentrations in Chicago air and Cleveland air for August-September 2008. No significant autocorrelation for either urban area suggesting that atmospheric concentrations sample are from local emissions in both cities.

Inter-city Variation in Congener Profiles

Mean PCB congener profiles measured in Cleveland and Chicago have significantly different individual congeners between the two profiles (Figure 8). These results may be attributed to different potential sources of PCBs, as the mean profiles from each city are well correlated to different Aroclor mixtures. A Wilcoxon signed rank test ($p < 0.01$) was applied to determine significantly different individual congeners between the two urban areas and fifteen congener/congener pairs were shown to be significantly different (PCBs 1,2, 19, 20/28, 33, 45/51, 50/53, 52, 110/115, 112,121, 134/143, 184, 201).

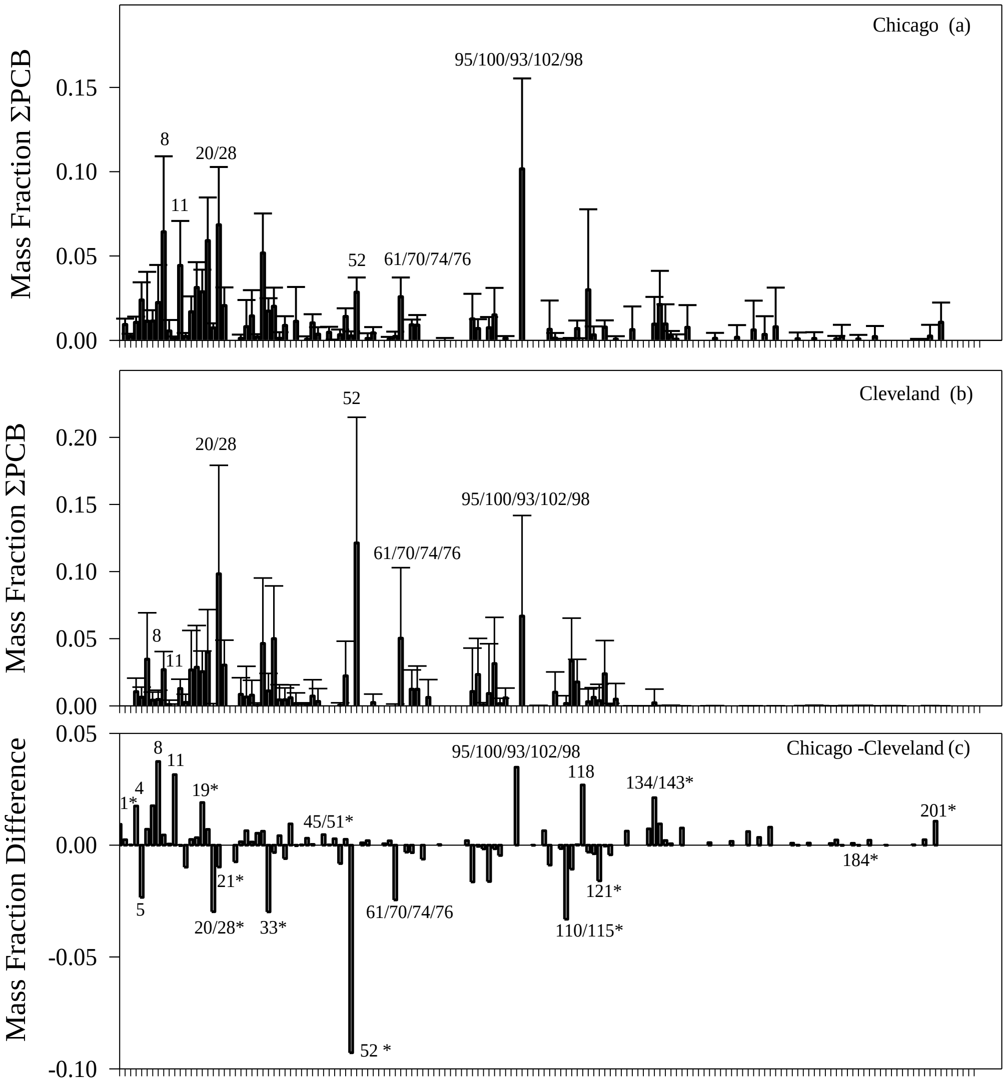

Figure 8. Congener profiles of average normalized mass with relative standard deviation error bars plotted for Chicago air(a), Cleveland air(b), and the mean difference, Chicago-Cleveland(c) with congeners enriched in Chicago above the bar and those in Cleveland below the bar, where * indicates a congener that is significantly different. Chicago's mean profile was correlated to Aroclor mixture of 1242:1254 (65:35) and Cleveland to Aroclor 1242.

Mean congener profiles of both Cleveland and Chicago correlate well to different Aroclor mixtures. A linear regression was applied to a plot comparing the mean congener profile for

Cleveland sites against the normalized mass fraction of each congener in Aroclor 1242 *(38).* The relationship is considered strong with an $R^2 = 0.789$. We compared the Chicago congener profile to a synthetic mixture of congeners (Aroclor 1242:1254 at 65:35 ratio) used in animal studies to mimic the distribution of PCBs in Chicago (Zhao *et al.* 2009*).* The 65:35 mixture of Aroclors 1242:1254 plotted against Chicago, also shows a good linear relationship with $R^2 = 0.672$. Other Aroclor mixtures were compared to both Cleveland and Chicago, but resulted in R^2 values <0.320.

Intra-city Variation in Congener Profiles

Within both Cleveland and Chicago sites with the highest concentrations, 'hot spots' show a congener pattern that is more similar to commercial Aroclor mixtures than the congener patterns observed at locations with low airborne PCB concentrations. Congener profiles for two sites from each urban area are shown in Figure 9, representing sites with lowest and highest ΣPCB concentration. Sites with high ΣPCB concentrations, such as site 15 in Cleveland and site 18 in Chicago (Tables B1 and B2), have congener profiles that have strong linear relationships to Aroclor mixes. Results for Cleveland site 15 against Aroclor 1242 was an R^2 of 0.802.

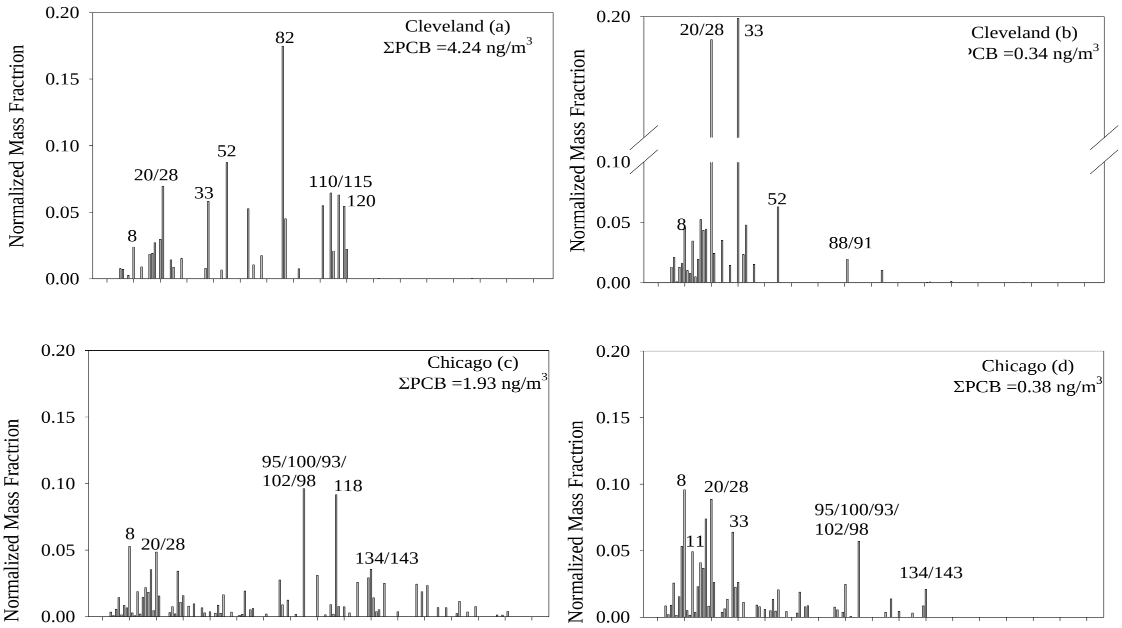

Figure 9. Site specific congener profiles for Cleveland sites 15(a) and 20(b) and Chicago sites 18(c) and 45(d). Site 15 for Cleveland and site 18 for Chicago represent high Σ PCB concentrations and are well correlated to Aroclor mixture profiles. Site 20 for Cleveland and site 45 for Chicago represent low Σ PCB concentrations and are poorly correlated to Aroclors, exemplifying the differences in congener profiles in intra-city environments.

Linear regression for Chicago site 18 congener profiles against 65:35 Aroclor 1242:1254 resulted in an R^2 value of 0.720. Sites from both Chicago and Cleveland that have low ΣPCB concentrations, sites 45 and site 20 respectively, show enrichment in lower chlorinated PCBs, similar to remote areas (Gingrich and Diamond 2001, Harner *et al.* 2004, Gouin *et al*. 2005, Jamshidi *et al*. 2007). Sites with low ΣPCB concentrations also have a very weak correlation to Aroclors (R^2=0.321 Cleveland/1242 and R^2 = 0.213Chicago/1242:1254).

A plot of site specific ΣPCB concentrations against R^2 values from linear regressions between the site and 65:35 Aroclor 1242:1254 in Chicago and Aroclor 1242 for Cleveland show a good relationship between ΣPCB concentration and similarity to Aroclors (Figure 10). Results show that site specific congener profiles within urban areas vary spatially and correlations indicate that sites with high ΣPCB concentrations are good indicators of potential sources of PCBs from Aroclors.

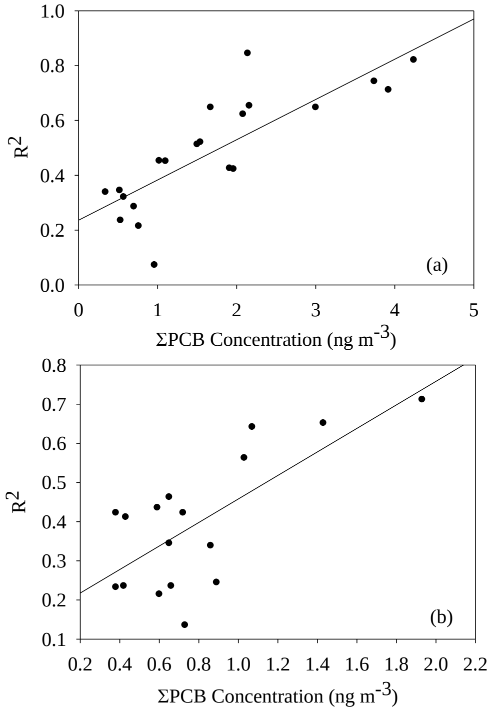

Figure 10. Plot of site specific R^2 values calculated from linear regression between site specific congener distributions and Aroclor mixes (Aroclor 1242 for Cleveland samples and 65:35 Aroclor 1242:1254 for Chicago) and site specific Σ PCB concentrations for Cleveland (a) and Chicago (b), demonstrating the high amount of variability in intra-city congener profiles.

Toxicological Equivalence

Toxicological equivalency factors (TEQ) (Van den Berg *et al.* 2006*)* for PCBs in the air of Cleveland and Chicago were calculated using toxicological equivalence factors (TEF) from the World Health Organization for twelve dioxin-like PCB congeners (Van den Berg *et al*. 2006*)*. The presence of toxicologically relevant congeners in air suggests a potential for human exposure to these compounds. Airborne PCBs are deposited into the Great Lakes and accumulate in sport fish which may be consumed by humans. Airborne PCBs in these cities may also indicate the presence of contaminated soils or building materials that may pose direct hazards to humans. The TEQ concentration for airborne PCBs in Chicago was is 9.22 x 10^{-7} ng m^{-3}, while Cleveland TEQ is lower at 4.81 x 10^{-7} ng m^{-3}; although both are significantly lower than pure Aroclor TEQs which range from 0.14- 46.4 ug g^{-1} (Rushneck *et al.* 2004*).* Contributions of individual congeners (Figure 11) show that Chicago TEQ is dominated by PCB 118 at 78% of the total TEQ, followed by PCB 105 at 17%. Cleveland TEQ is dominated primarily by PCB 118 and PCB 123. The differences in TEQs for the two urban areas stress the importance of reporting congener profiles and individual PCB concentrations, because although Cleveland mean ΣPCB concentration is higher than Chicago, the TEQ is lower.

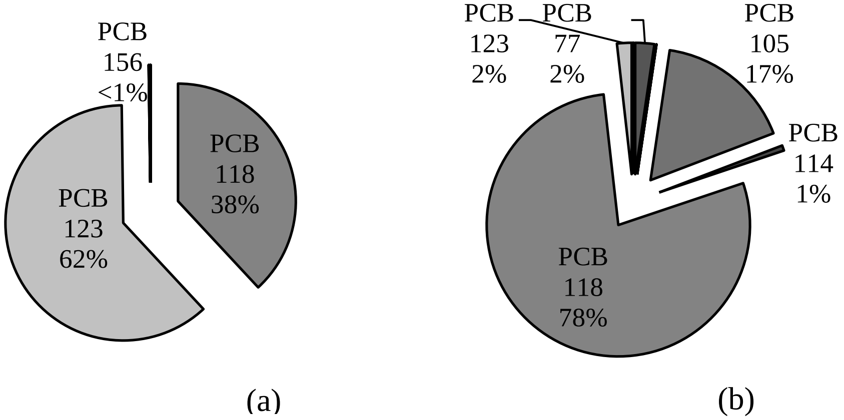

Figure 11. Percentage of contribution from individual congeners for Cleveland(a) and Chicago(b) to total TEQs for each city.

Conclusions

Results from this study show that optimization of sampling, and spatial resolutions over an urban area is important to capture representative ΣPCB concentrations of that urban area. ΣPCB concentration and site specific congener profiles also vary spatially within urban areas. Both Cleveland and Chicago have no significant autocorrelation between sites, suggesting local emissions are important. Sites with high ΣPCB concentrations ('hot spots') have a good correlation to known Aroclor mixes, and sites with low ΣPCB concentrations have enrichment in lower chlorinated PCBs and poor correlation to Aroclors within urban areas. Results from this study also suggest that individual congener concentrations, as well as ΣPCB concentrations are important to understanding the potential for deposition of toxicologically relevant PCBs into the Great Lakes from urban areas.

CHAPTER IV. SPATIAL DISTRIBUTION OF AIRBORNE PCBS IN CHICAGO USING ACTIVE AND PASSIVE SAMPLING

Abstract

Airborne PCBs were collected using passive air samplers (n=202) and Hi-Vol samplers (n=412) across Chicago in 2007-2009, and 2007-2008, respectively. Concentrations of 168 PCB congeners (Σ_{168}PCBs) were determined at 29 sites throughout Chicago. Passive and Hi-Vol sampling methods found statistically similar annual city-wide concentrations (1.26±0.45 ng m^{-3} and 0.99±0.49 ng m^{-3}, respectively) although the passive samplers consistently identified spatial hot-spots and low concentrations of atmospheric PCBs, while Hi-Vol samples showed high variability in identification of hot-spots. The difference between the two methods is most likely due to variable meteorological conditions and concentrations during the different periods of sampling. Congener profiles collected using passive samplers and Hi-Vols were similar for summer deployments (cosine $\theta = 0.83$), but showed differences in winter and annual average congener profiles (cosine θ=0.23), where lower chlorinated PCBs were enriched in passive samplers. Neither method showed significant spatial autocorrelation in the airborne PCBs, indicating spatial localization of airborne PCBs in the city. The localized hot-spots are used for preliminary identification of possible sources of atmospheric PCBs.

Introduction

Urban and industrialized areas are important regional sources of atmospheric PCBs (Offenberg *et al.* 1994, Simcik *et al.* 1997, Zhang *et al.* 1999, Gingrich and Diamond 2001, Hafner and Hites 2003,Gouin *et al.* 2005, Hornbuckle *et al.* 2006,Pozo *et al.* 2006), and although elevated concentrations of atmospheric PCBs are well documented in urban areas, specific sources of atmospheric PCBs remain ambiguous. A few single site sources have been identified using high volume air samplers (Hi-Vols) (Simcik *et al.* 1997, Helm and Bidleman 2003, Hsu *et al.* 2003, Herrick *et al.* 2004, Tasdemir *et al.* 2004,Martinez *et al.* 2010) but the Hi-Vol method is expensive to deploy and impractical for the identification of unknown sources. The development of passive sampling as a technique for sampling atmospheric PCBs has led to a greater ability to characterize spatial distributions in urban areas (Baek *et al.* 2009, Du *et al.* 2009, Persoon *et al.* 2010), but until now no approach has been suggested in how to use spatial distributions to identify unknown sources (hot spots).

Passive samplers have been used in urban areas to identify spatial distributions of ΣPCBs and hot-spots of atmospheric PCBs (Baek *et al.* 2009, Du *et al.* 2009, Persoon *et al.* 2010). However, most studies only report spatial distributions of PCBs for a single deployment period, so there is uncertainty if the spatial distributions for one deployment period are representative of spatial distributions captured during a subsequent deployment period. Passive samplers are shown to be accurate at measuring PCB spatial distributions at large scales, such as urban rural gradients and global distributions (Gingrich and Diamond 2001, Harner *et al.*2004 , Pozo *et al.* 2004, Gouin *et al.* 2005), over multiple deployment periods. This study aims to show that passive samplers are accurate at identifying consistent hot-spots of atmospheric PCBs over multiple deployment periods in a dynamic environment such as an intra-city environment where there are multiple sources (Baek *et al.* 2009, Du *et al.* 2009, Hu *et al.* 2009, Persoon *et al.* 2010).

This study’s objective is to show that passive samplers identify the same spatial distributions of atmospheric PCBs over multiple deployment periods, and will address three major questions. First, how do Hi-Vol and passive samplers compare when capturing spatial distribution of atmospheric PCBs over time? Second, can passive samplers and Hi-Vols identify hot-spots of atmospheric PCBs consistently over time? Finally, are atmospheric PCBs captured at a site always localized regardless of the deployment period? The questions addressed in this study will support the use of passive samplers for a single deployment period for identification of hot-spots in an urban area and has interesting implications for a novel method of identifying potential areas to begin looking for sources of atmospheric PCBs within urban areas which could lead to a more rapid remediation of PCBs contributing to atmospheric concentrations.

Methods and Materials

Sampling Methods

The city of Chicago has been identified as a source of atmospheric PCBs into Lake Michigan (Offenberg *et al.* 1994, Simcik *et al.* 1997, Zhang *et al.* 1999, Hafner and Hites 2003, Hornbuckle *et al.* 2006). However, to date only a few studies have reported multiple sites of atmospheric PCBs throughout Chicago (Basu *et al.* 2004,Hu *et al.* 2009, Persoon *et al.* 2010) and no other studies have evaluated trends over time at multiple sites. This study's sample set is unique in that we have deployed both passive samplers (n=202) and Hi-Vols (n=412) at the same sites starting in 2007 through 2008, and continued passive sampling through 2009.

Passive sampling efforts in Chicago were coordinated by Mobile C.A.R.E. Foundation of Chicago (Comprehensive Care for Chicagoland's Children with Asthma) and deployment was done by local volunteers. In total 29 sites volunteered to deploy passive samplers with polyurethane foam disks year-round, with deployment times for each sample being 4-6 weeks (Table C1). Each site is continuously sampled by the passive samplers For each deployment period, three PUF disks were spiked with depuration compounds, described later, and *R*-values or sampling rates (m^3 d^{-1}) were derived from the loss of the depuration compounds as described previously (Persoon and Hornbuckle 2009) and by Bartkow in 2005 as well as Shoeib and Harner in 2002. The average *R*-value for each deployment (Table C1) was then applied to the mass accumulated on the PUF disk in order to calculate ambient air concentrations as previously reported (Persoon *et al.* 2010).

Hi-Vols were mounted on platforms attached to the rear of two medical clinic vans (Figure C1) and collected gas-phase and particle-phase PCBs as previously reported (Hu *et al.* 2009, Hu *et al.* 2010). The samplers were operated with the assistance of the trained staff at Mobile C.A.R.E. Air samples were collected for a 6−8 h period by each van at different sites each day. Hi-Vol samples had 25 sites in common with passive samplers. Because PCBs are primarily found in the gas phase in Chicago, only the gas phase is reported here (Hu *et al.* 2009). Temperature and relative humidity were recorded every 5 min on one van by the CR800 measurement and control system (Campbell scientific, inc., Logan, UT). The flow pressure drop was recorded daily using a magnehelic pressure gauge mounted on each sampler. Hi-Vol samples were collected starting September 2007 until September 2008.

Sampling Media Preparation

PUF disks were cleaned (Soxhlet extraction 24 h in hexane followed by 24 h in acetone), dried in a desiccator, and a subset of the samples, one to three per deployment period, were spiked with depuration compounds: 40 ng per congener of PCBs ^{13}C-labeled 28, ^{13}C-labeled 111, ^{13}C-labeled 178 (Cambridge Isotope Laboratories). The method used to spike depuration compounds onto PUF is described previously (Persoon and Hornbuckle 2009). Exposed PUF disks were placed in sealed zip lock bags and immediately transferred to a freezer. XAD-2 Amberlite resin was cleaned (Soxhlet extraction for 24hrs each of methanol, DCM, hexane, and acetone). After collection, all samples were placed in sealed ziplock bags and stored in a refrigerator until shipped to the laboratory. Once the samples were transported to the laboratory, they were logged and stored at 4 °C until extracted (Hu *et al.* 2009).

Sample Extraction and Analysis

All sample media were extracted with pressurized fluid extraction (Dionex ASE-200), using pesticide grade acetone: hexane (1:1) and concentrated to 0.5 mL (Caliper TurboVap II) as described previously (Persoon and Hornbuckle 2009). Surrogate standards (50 ng each of PCB 14 and 166 from Accustandard) were added just prior to extraction and used to correct sample masses. Internal standard (50 ng of PCB 204 from Accustandard) were added just prior to analysis. All samples were analyzed using a modified EPA Method 1668A on Tandem Mass Spectrometry GC/MS/MS (Quattro Micro^{TM} GC, Micromass MS Technologies) using a Supelco SPB-Octyl (30m x 0.25mm x .25µm) with GC inlet parameters previously reported (Persoon and Hornbuckle 2009). After removal of compounds used as standards, this study quantified 168 PCB peaks.

Quality Assurance and Quality Control

Surrogate recoveries for PUF from 75-98% and Hi-Vol samples ranged from 82-110%. Instrument detection limits (IDL) were 0.01ng for mono-trichlorinated congeners, 0.02 ng for tetra-heptachlorinated congeners, and 0.03 ng for octa-decachlorinated. Limit of quantification (LOQ) was calculated as three times the standard deviation of peaks from the method blank plus the background level from instrumental blanks, and was calculated as 0.03 ng per congener per sample. Field, trip, and method blanks were all less than LOQ. The mean field duplicate for

PUF was 15% relative difference for three sites, while no field duplicates were available for Hi-Vol samples. Instrument duplicates show a 5% relative difference for Hi-Vol samples and 6% relative difference for PUF. NIST SRM 2274 was previously reported for this analytical method with 8% relative difference between the certified masses and calculated masses (Persoon and Hornbuckle 2009).

Statistical Methods

Cosine theta (θ) was used to determine similarities between congener profiles. This analysis uses the cosine angle between two multivariable vectors (congener profiles) where 0.0 describes two completely different vectors, and 1.0 describes identical vectors. It is important to note that this comparison only uses averages in this case and does not take into account standard deviations (DeCaprio *et al.* 2005, Magar *et al.* 2005).

An underlying assumption in spatial statistics is that samples collected at each site are independent of each other. In order to test for spatial independence, we have used spatial autocorrelation, the correlation of a variable on itself over space. Moran's I (Moran 1950*)* was used to calculated statistically significant spatial autocorrelation(Cliff and Ord 1973), described by:

$$I = \frac{N\sum_i \sum_j W_{i,j}(X_i - \bar{X})(X_j - \bar{X})}{(\sum_i \sum_j W_{i,j})\sum_i (X_i - \bar{X})^2} \qquad \text{Equation 7}$$

Where N is the number of sites, $W_{i,j}$ is a spatial weight between sites calculated from the inverse distance matrix, X_i is the site mean concentration , and X bar is the total mean concentration. A z-score can also be calculated from the Moran's I, where a value above 1.96 (clustering) or below -1.96 (dispersion) indicates statistically significant spatial autocorrelation.

Results and Discussion

Differences in Passive samplers and Hi-Vols: ΣPCB

We hypothesized that Hi-Vols and passive samplers would not be significantly different over large scales, but that significant differences would be seen when data collected by the different methods was resolved on spatial and temporal scales. Indeed, the two methods produce similar concentrations over large temporal and spatial scales. The annual average concentration from September 2007 to September 2008 for the entire city of Chicago collected by Hi-Vols is 0.99±0.49 ng m^{-3} (n=412) and passive samplers is 1.26±0.45 ng m^{-3} (n=127). These mean values are not significantly different at the 95th percent confidence level. This was usually also the case for individual sites: the Hi-Vol and passive samplers exhibited similar annual mean PCB concentrations. However, at 3 sites the annual concentrations were significantly different ($p<0.08$) for the two methods (sites 4, 15, and 31, Figure 12). All other sites showed no statistical difference (Table C2) in the annual mean concentrations between passive samplers and Hi-Vols. This difference may be due to incomplete Hi-Vol sampling during the spring season. This discrepancy in continuous sampling between the two methods probably explains most of the statistically significant differences in site specific annual average concentrations.

Hi-Vol and passive sampler concentrations of atmospheric PCBs show similar seasonal trends, (Figure 13). The record of seasonal trends is evident using both methods at when sites are represented by Hi-Vol samples collected for each month during a year. The mean annual ΣPCB concentrations between passive samplers and Hi-Vols at all sites differs by less than a factor of 2.5, similar to other reported (Klanova *et al.* 2008, Hayward *et al*, 2010).

Similar to other reports (Gouin *et al.* 2005, Pozo *et al.* 2006, Klanova *et al.* 2008, Hayward *et al.* 2010), Hi-Vols and passive samplers are not significantly different in determining the mean concentration over a large area for a long period of time. Passive sampling also shows good agreement with Hi-Vols when seasonally resolved. However, when concentrations from both methods are compared spatially, we see some significant differences which could be due to non-continuous Hi-Vol sampling.

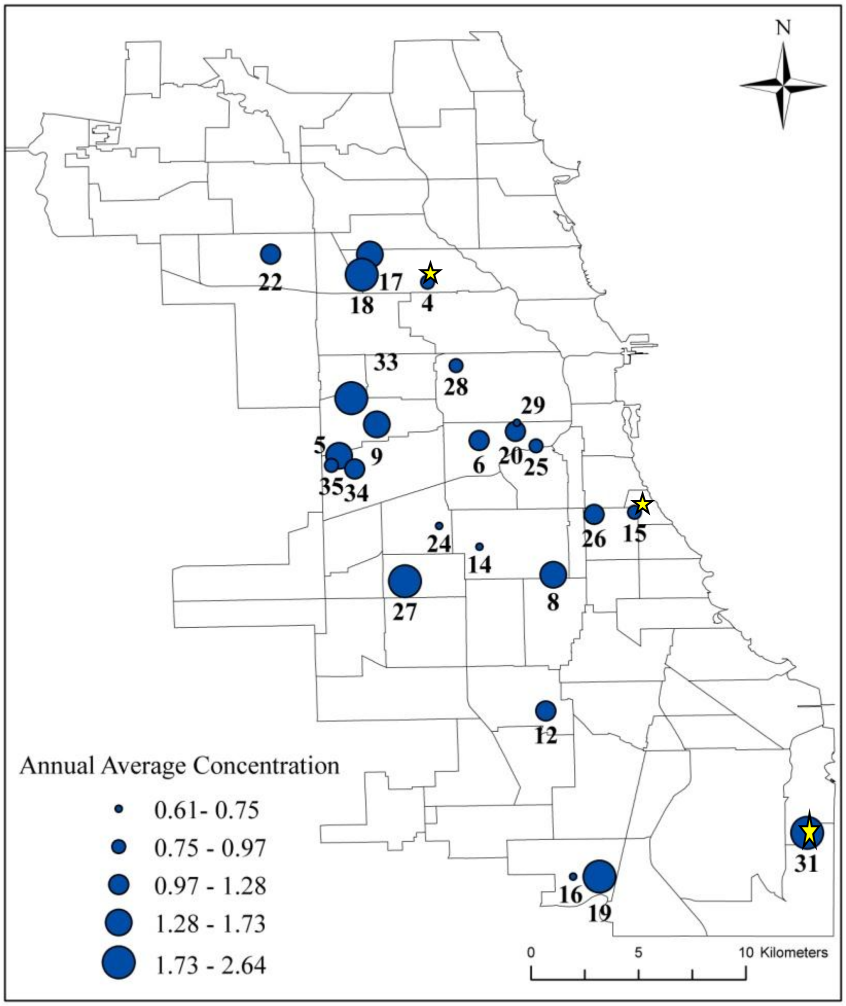

Figure 12. Map of the spatial distribution annual average atmospheric ΣPCB concentrations collected across Chicago for September 2007 through September 2008 from both passive samplers and Hi-Vols (n=539). Sites identified with a yellow star were calculated to have significant difference using a t-test ($p<0.08$) between Hi-Vol and passive samplers.

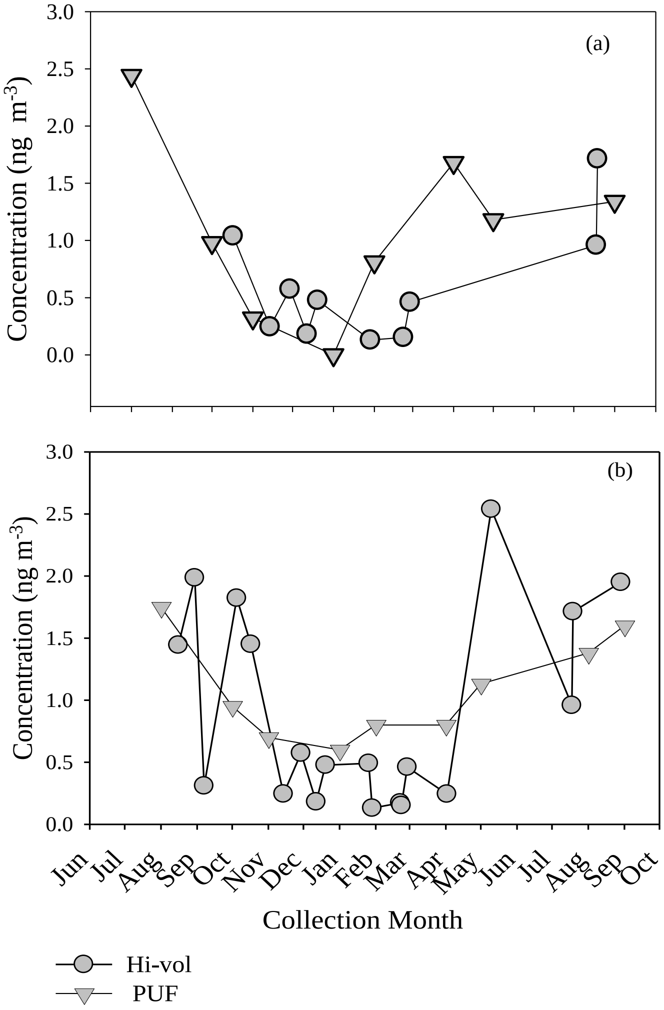

Figure 13. Atmospheric ΣPCB concentrations collected from site 4(a), a site that is significantly different between Hi-Vols and passive samplers annual average. However, sites with more representative Hi-Vol samples show the seasonal variation of atmospheric ΣPCB concentrations in both passive sampling and Hi-Vols from Site 3(b).

Differences in Passive samplers and Hi-Vols: Congener Distributions

Passive samplers congener distributions are significantly different than Hi-Vol congener distributions. Average congener distributions for Chicago collected by passive samplers was compared to congener distributions collected by Hi-Vols, using both cosine theta to compare similarities in overall congener distribution, and a t-test to identify specific congeners that are significantly different between the two profiles. Comparison of the overall similarity of the two congener profiles resulted in a cosine $\theta = 0.26$, a weak similarity. A t-test between the annual average congener profile for Chicago from passive samplers and Hi-Vol resulted in a significant difference ($p<0.05$) for 4 congeners or congener pairs (55,83/99,117/116/85,110/115). Figure 14 shows a plot of annual average congener profiles for passive samplers and Hi-Vols. Passive samplers are skewed to the left compared to Hi-Vols, not due to equilibrium of lower congeners as calculated by Shoeib and Harner in 2002 as our deployment period is approximately 40 days. The difference between the two congener profiles could be explained by two factors: first, passive samplers collect higher-chlorinated congeners that are particulate bound at a slower rate than gaseous congeners (Klanova *et al.* 2008). Second, that passive samplers collect a higher relative mass than Hi-Vols in the winter therefore over-representing the lower more volitale congeners, as shown in seasonal congener profiles for both in Figure 15. Passive samplers have been shown in Figure 13 and in previous reports (Gouin *et al.* 2005, Klanova *et al.* 2008, Hayward *et al.* 2010 *)* to collect higher concentrations that Hi-Vols in the winter and slightly lower in the summer, also consistent with the idea that passive samplers over represent winter congener profiles for an annual average.

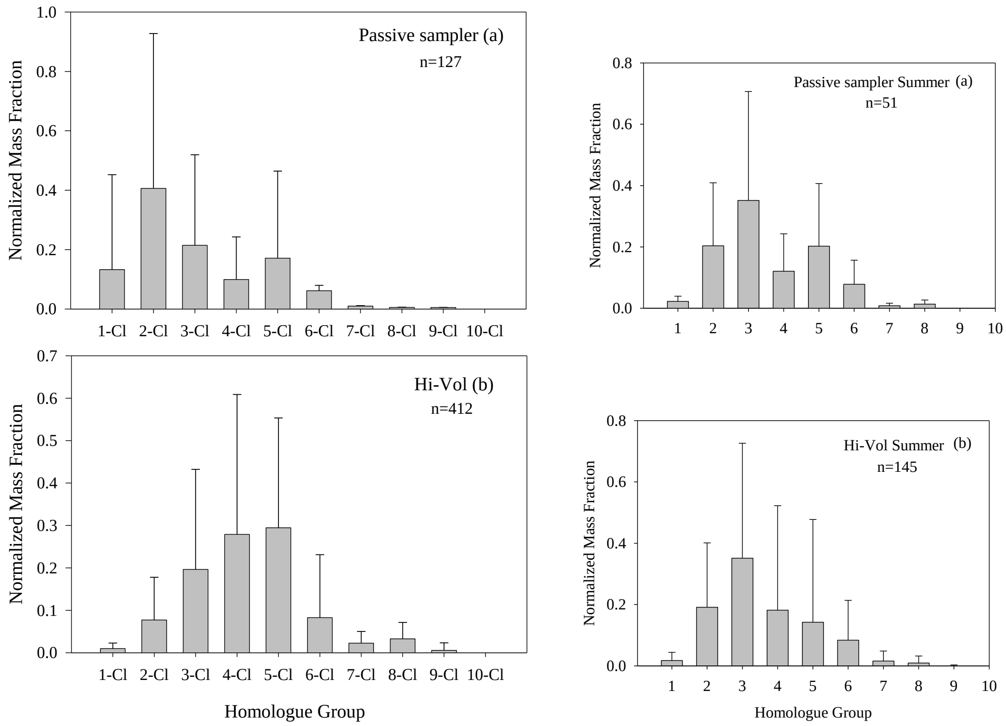

Figure 14. Annual average and summer (June- September) average congener profiles for Chicago using passive samplers (a) and (c) and for Hi-Vol (b) and (d).

Comparing Hi-Vols and passive samplers seasonally, summer (June-September) average congener profiles for 2008 were very similar between the two methods with a cosine θ = 0.83 (Figure 14). Comparison at hot-spots seasonally results in congener profiles with more similarities, except for winter congener profiles (Figure 15), with cosine θ ranging from 0.84 (summer) to 0.42 (winter). However at low concentrated sites congener profiles differ greatly throughout the seasons with cosine θ ranging from 0.32(summer) to 0.12 (winter). Differences in congener profiles between passive samplers and Hi-Vols are most likely due to differences in collecting high chlorinated PCBs and differences in masses collected in the winter.

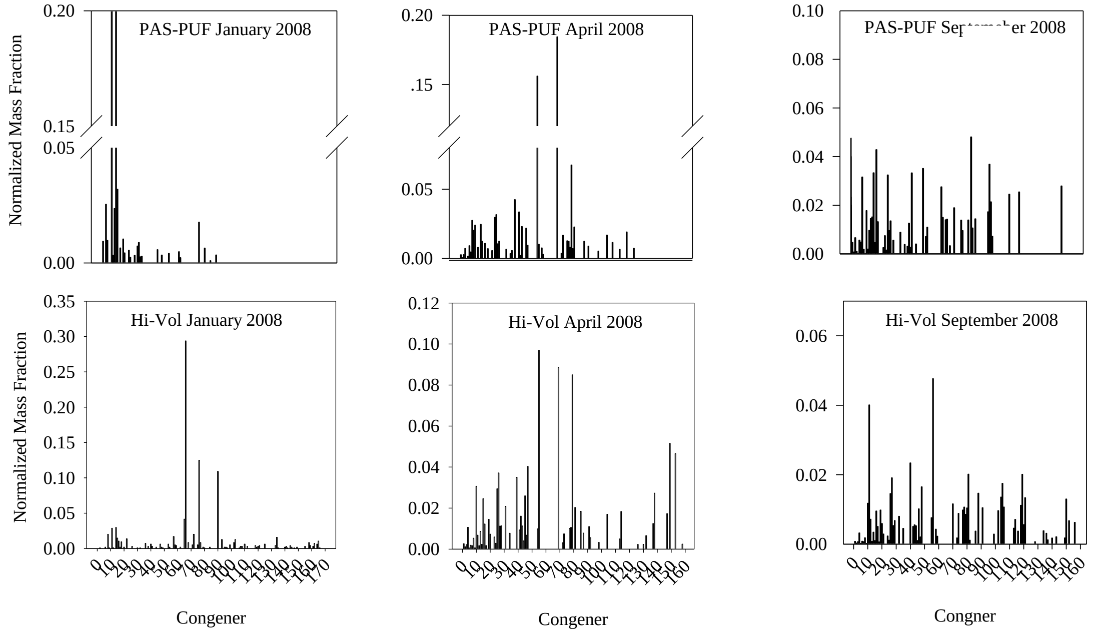

Figure 15. Seasonal variations in congener profiles for passive sampling (top) and Hi-Vols (bottom). Passive samplers collect similar profile to Hi-Vols in spring and summer, but in the winter profiles passive samplers are skewed towards the lower chlorinated congeners for site 27.

Consistent Hot-spots

We hypothesized that passive samplers and Hi-Vols collected over multiple deployment periods would consistently identify hot-spots spatially distributed in Chicago. Indeed, passive samplers consistently identified hot-spots across Chicago over time. Hot-spots were defined as sites that in any deployment period were ≥95th percentile of concentration (Table C3 and C4). The frequency of these identified hot-spots falling in the >50th percentile group was then calculated. Six sites in Chicago were identified at 100% frequency >50th percentile in concentration relative to other sites collected during that time period (Table 2). Interestingly, four sites with low relative concentrations of atmospheric PCBs were also consistently identified using the same method. (Table 2).

Table 2. Hot-spots and sites with low concentrations consistently identified by passive samplers across Chicago.

Hot Spots	n=	% Frequency	Low Concentrations	n=	% Frequency
Site		>50th Percentile	Site		<50th Percentile
27	9	100%	14	9	100%
17	7	100%	24	5	100%
12	10	100%	29	8	100%
8	8	100%	16	11	100%
37	9	100%			
31*	5	100%			

Using the same methodology as described for passive samplers, Hi-Vol data was used to attempt to identify hot-spots of atmospheric PCBs over time. Site specific ΣPCB concentrations were grouped into mock deployment periods that mirrored passive samplers deployment periods and concentrations were corrected using the Clausius-Clapeyron equation (Simcik *et al.*1998, Wania *et al.* 1998, Carlson and **)** and evaluated as ΣPCB partial pressures (atm). This correction removed the variability caused by daily temperature fluctuations. Sites were ranked in the same fashion as passive sampler concentrations (Table C4).

Hi-Vol data showed much higher variability than passive samplers when identifying hot-spots. For example, in November 2007, Hi-Vol samples were collected three times at site 16 and ranked near the 95th percentile, near the 5th percentile, and near the 50th percentile (Table C4). Variation in temperature corrected concentrations is most likely due to changes in wind direction or speed (Simcik *et al.* 1997, Tasdemir *et al.* 2004, Figure C3) which is why Hi-Vols are ideal for use in back trajectories, but are difficult to identify relative spatial distributions of atmospheric PCBs. Although three of the hot-spots identified by passive samplers were also identified by Hi-Vols, it was with much less consistency, with frequency of detection in the >50th percentile being 60-80%.

Hot-spots identified with passive samplers show greater concentration variation over seasons compared to sites with low concentrations (Figure 16). This greater variation over seasons has been suggested by Sweetman and Jones in 2000, to be an indication of a site that is near a source of atmospheric PCBs. Concentration plotted against temperature also show steeper slopes for hot-spots compared to low concentrated sites (Figure C4).

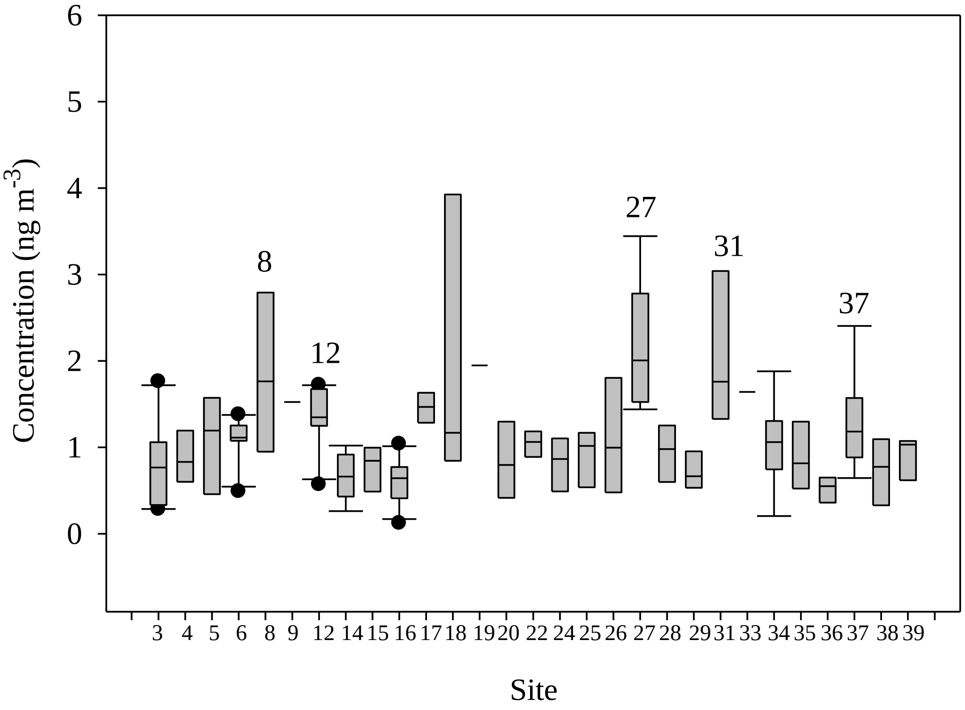

Figure 16. Box plot showing variation within (temporal variation) and between (spatial variation) atmospheric ΣPCB concentrations collected by passive samplers deployed between September 2007 and September 2009. Sites with dashes represent sites where only one or two samples were collected. Spatial variation shows multiple hot-spots (labeled above the bar) identified throughout Chicago, with these hot-spots showing much greater variation temporally compared to low concentrated sites.

Passive samplers identified both hot-spots and sites with very low concentrations of atmospheric ΣPCBs consistently. Hi-Vols show much more variation in relative ranking, probably due to changes in meteorological conditions such as wind direction and speed which are constants in passive sampling, but are ideal for use in back trajectories. Plots of spatial-temporal variations show that hot-spots vary greatly over time, where sites with low concentrations have less variation over time, indicating that hot-spots are likely near primary sources where volatilization from direct sources is more temperature dependent.

Spatial Localization of Sites

We hypothesized that there are concentrated surface PCB emission near the hot spots identified with the passive samplers. To address this hypothesis, we examined the correlation between PCBs measured at adjoining sites, drew boundaries around the regions of Chicago represented by each sampling site, and examined the land use near the identified hotspots. Moran's I and a z-score (R Development Core Team, 2005) were calculated for each deployment period (Table C5), and no significant spatial autocorrelation was calculated for any of the deployment periods. The spatial localization of sites, coupling with consistent identification of atmospheric PCB hot-spots allows us to identify localized sources of PCBs to these hot-spots.

An example of how to utilize passive sampler spatial distribution to begin identifying potential sources is the construction of Voronio diagrams (Voronio 1907) to delineate areas around sites. Annual averages of ΣPCB concentrations were used in ArcGIS© (*50*) to create the Voronoi diagram. Maps from Google Earth (Version 5.1.3533.1731 Google Inc. 2009*)* were imposed onto the delineated map of annual average passive samplers concentrations (Figure 17).

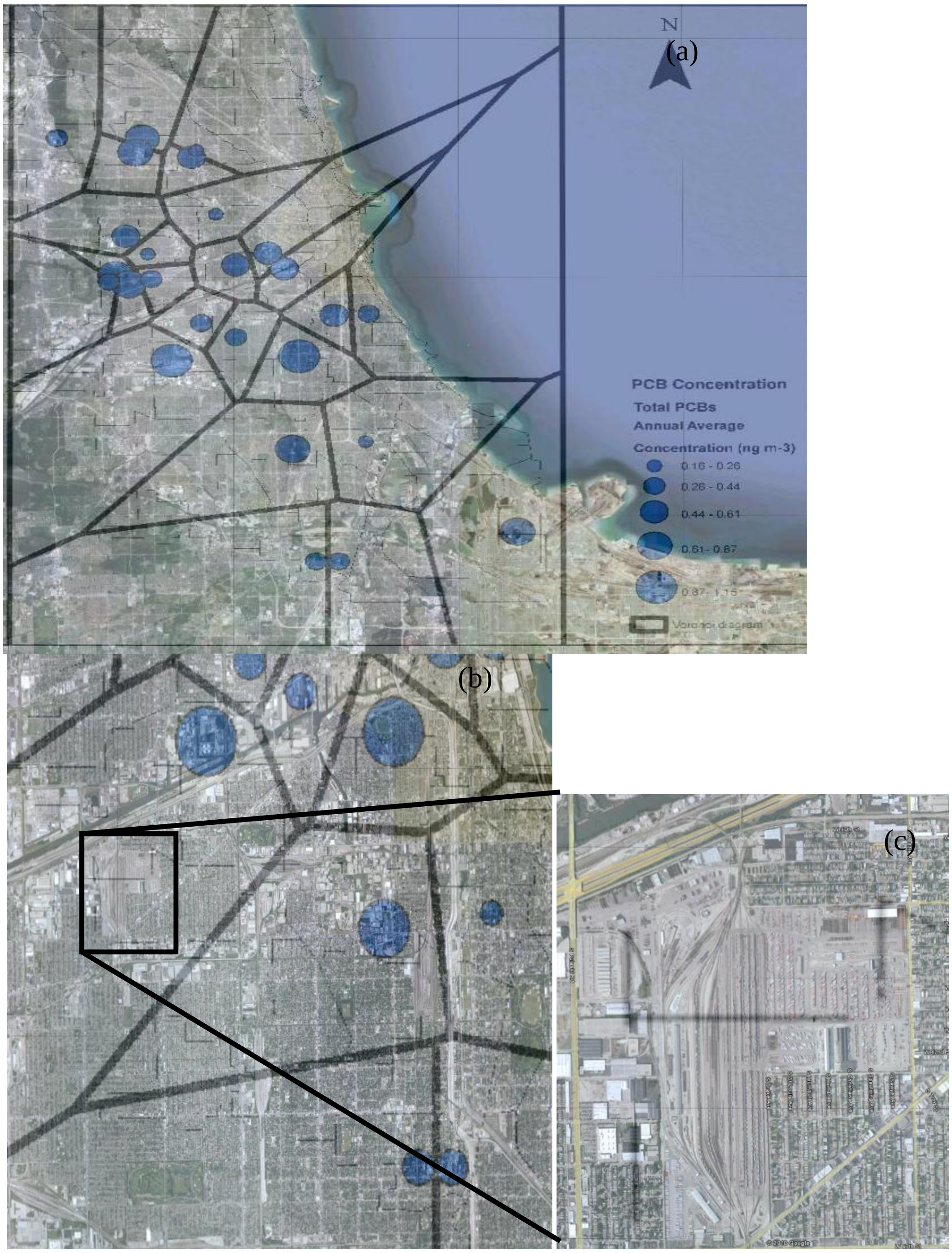

Figure 17. An aerial view from Google Earth© map of site 27(indicated by the red star) site 8 (yellow star) and site 12 (green star), with the Voronoi diagram overlaid for all of Chicago PUF averaged sites for 2007-2009 (a) and zoomed on the site (b). The map shows large container and box cars from transport by truck and train (c) setting in large facilities found in all three hot-spot Voronoi diagrams circled on map (b). The South and South-West direction are also the main direction vectors for the Chicago wind rose (Figure S4).

Site 27 was of interest because it was identified as a hot-spot by both passive samplers and Hi-Vols and had the highest relative concentrations. An aerial map of this site, with its delineated boundaries, shows that to the South and South-West there are container and box car sites used by trucking and rail transport, and to the west Midway Airport. When the wind rose for Chicago is applied (Figure C5), we see that sources to the passive sampler at site 27 are most likely South to South-West , towards the container and box-car facilities. Three hot-spots, sites 27, 8 and 12, had rail and shipping container open storage sites (Figure 17).

Back trajectories calculated using Hi-Vol data also suggested sources of atmospheric PCBs at this site are coming from the South. Back trajectories were calculated for days with the highest reported concentration of atmospheric PCBs collected by Hi-Vols at site 27 for the sampling period, August 22, 2007. We then used HYSPLIT Trajectory Model from NOAA (http://ready.arl.noaa.gov/HYSPLIT.php) to model back trajectories for this day (Figure C6), which show the source direction to be South of site 27 , the same direction shown by Tasmedir *et al.* in 2004. Results from the back trajectory suggest that the sources to site 27 are indeed from the South, where the container sites are.

Conclusions

Passive samplers and Hi-Vols represent very different collection methods, highly spatial or temporally resolved data. On large scales, both methods measure similar concentrations; however, at specific sites there can be significant differences in annual average concentrations due to non-continuous Hi-Vol sampling. Congener profiles between the two methods are similar for the summer; however can differ in the winter due to the passive samplers poor collection of higher chlorinated PCBs and the enrichment in lower chlorinated PCBs.

The use of passive samplers coupled with spatial statistical methods of identification described in this section give a novel approach to identifying hot-spots of atmospheric PCBs, which could lead to more rapid source identification. The approach can be easily be integrated with back trajectories as shown, where passive sampling can be used to spatially identify hot-spots and delineate the area surrounding these hot-spots and traditional Hi-Vols can be used at identified hot-spots to calculate back trajectories towards potential sites. This approach results in exciting potential for remediation of PCBs in urban areas, where passive samplers and Hi-Vols can be used to identify areas of interest coupled with soil sampling at potential sites and further identification of types of sources to atmospheric PCBs in urban areas.

CHAPTER V.METHOD DEVELOPMENT FOR THE DETECTION OF HYDROXLATED PCBS IN AIR

Abstract

A method for the analysis of hydroxylated-PCBs (OH-PCBs) was developed and tested. The method uses gas chromatography with tandem mass spectrometry (GC/MS/MS) to provide high selectivity for the target compounds. Precision, accuracy, and sensitivity of the instrumental and extraction methods were evaluated for the method applied to aerosol particles captured on quartz fiber filters in Chicago. This study reports an instrument detection limit and method detection limit and limit of quantification of 0.10, 0.30 and 0.20 pg per sample, respectively. Instrument response was linear between 3 and 0.01 ng/mL for solution concentration and on column masses ranging from 30-0.1 pg. Although method recoveries were good at 72± 12%, n=10, detection frequency of OH-PCBs from air filters (n=30) was low at 10%.

Introduction

Occasional observations of and low daytime concentrations in ambient gas-phase polychlorinated biphenyls (PCBs) concentrations have been attributed to the destruction of PCBs by hydroxyl radicals (Kwok *et al.*1995, Anderson and Hites 1996, Burcat *et al.* 2003, Totten *et al*. 2002, Gasic *et al*. 2009, Macleod *et al*. 2007, Mandalakis *et al*. 2003, Sweetman and Jones 2000). The depletion of gas-phase PCBs during daytime cannot be explained by surface exchange processes because volatilization and sorption induces the opposite diurnal effect with elevated concentrations in the day (Hornbuckle and Eisenreich, 1997; Zhang and Lohmann, 2010).

The appearance of hydroxylated PCB (OH-PCB) decay products has not been directly observed in ambient air, although the reaction has been studied in the laboratory and the decay mechanism has been theoretically defined. The kinetics of hydroxyl radical reaction with PCBs to form OH-PCBs has been mathematically modeled by Atkinson and reaction rates have been determined in laboratory settings by Kwok *et al.* 1995 as well as Anderson and Hites in 1996. Other studies have suggested that the removal of PCBs by hydroxyl radicals may lead to decreasing atmospheric concentrations. However there is disagreement on the magnitude of removal effects on urban areas (Sweetman and Jones 2000Mandalakis *et al*. 2003). There are theoretically over 800 OH-PCB congeners, compared to the 209 native PCB congeners. This is due to the fact that each native PCB congener has multiple possible OH-PCB congeners (Figure 18).

Although atmospheric concentrations of OH-PCBs are of great interest for modeling fate of PCBs and OH-PCBs as well as determining exposure of potentially toxic OH-PCBs to public health, few data are available on environmental concentrations. Measurements of hydroxyl radical concentrations together with measurements of diurnal variations of PCB concentrations have been used to calculate kinetic rates of loss and to infer that hydroxyl destruction of PCBs and the formation of OH-PCBs is happening in the atmosphere (Sweetman and Jones 2000,Totten et al. 2002, Mandalakis et al. 2003, Macleod et al. 2007, Gasic et al. 2009). However, only one publication to date directly reports OH-PCBs in the environment (Ueno et al. 2008) measuring OH-PCBs in waters, snow and precipitation as well as empirically measuring K_{ow}, partitioning coefficients. Currently no reports exist on direct measurements of OH-PCBs from atmospheric gas or particulate phase, and no data exists for atmospheric particulate OH-PCBs.

In humans, OH-PCBs with OH-bound groups in the *para*- and *meta*- positions may lead to thyroid disruption (Van den Berg *et al.* 1990, Lans *et al.* 1993, Schuur *et al.* 1998, 1999) and are retained in the plasma of humans (Bergman *et al.* 1994). The toxicity of OH-PCBs and their retention in plasma are of concern, but little is known about the origin of OH-PCBs in human plasma. Do these arise solely from human metabolism of the parent compounds or from potential exposure of OH-PCBs from the environment?

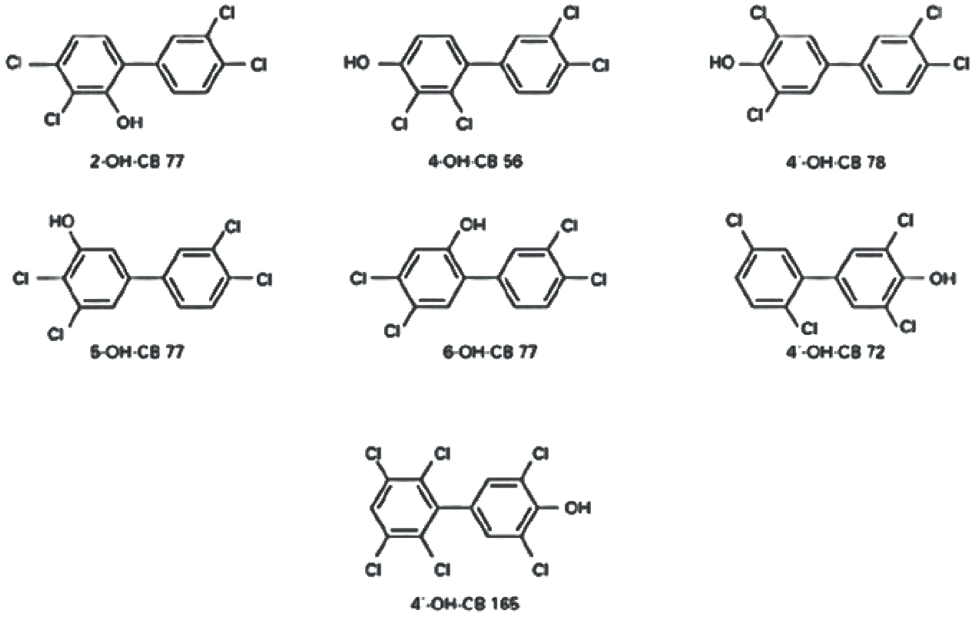
2-OH-CB 77
4-OH-CB 56
4'-OH-CB 78
5-OH-CB 77
6-OH-CB 77
4'-OH-CB 72
4'-OH-CB 165

Figure 18. Example of OH-PCB structures for multiple congeners, reproduced from Van der Hurk et al. 2002.

In order to identify and quantify OH-PCBs on a gas chromatograph (GC), the OH-PCBs must be derivatized into a more volatile form (Figure 19), a methoxylated-PCB (MeO-PCB). This processes substitutes a methoxy group where the hydroxyl group was placed on the native PCB. This process is necessary for this instrument as OH-PCBs are much more hydrophilic and less volatile than their parent compounds, native PCBs.

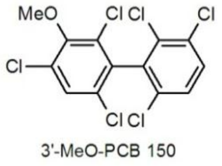

Figure 19. MeO-PCB structure, the derivatized form of OH-PCBs used to quantify OH-PCBs on GCs.

The objective of this study was to create a robust method of identification and quantification of OH-PCB derivatives (MeO-PCBs) from environmental air samples on a GC/MS/MS. The complete method includes the determination of appropriate standards, sample extraction and concentration techniques, sample derivatization, GC/MS/MS operating parameters, and identification of measures of quality control and assurance.

We use the method to test our hypothesis that OH-PCBs are present in air filters collected in Chicago, IL.

Standards

We created four distinct standards to use in quality assurance and quality control as well as quantification of OH-PCB derivatives from environmental samples. The first standard is the **performance reference compound** solution (PRCs) which was used to calculate recoveries for the entire method. This standard contains six OH-PCBs (Accustandard), which are injected onto filters prior to extraction. The second standard solution includes the **surrogate** compounds. A known aliquot of surrogate standard was injected into every sample prior to extraction used to calculate recoveries for each sample. The surrogate standard contains six carbon-13 labeled hydroxylated PCBs (Wellington Laboratories). The third standard solution is the **internal standard** solution (IS). The internal standard is used to quantify mass from analyzed samples. This standard contains PCB congener 204 (2,2',3,4,4',5,6,6'-Octachlorobiphenyl, Cambridge Isotopes) at 10 ng mL^{-1}. The fourth standard solution is the **calibration** standard solution used for every batch analyzed on the GC/MS/MS to calculate relative response factors (RRF) used to calculate masses using the internal standard method. This calibration standard contains the 31 MeO-PCBs commercially produced currently (Accustandard) (Table 3) at a concentration of 10 ng mL^{-1} per congener. The Calibration standard solution also includes the surrogate standard (Table 4) and the internal standard at 5 ng mL^{-1} per congener and 10 ng mL^{-1}, respectively.

Table 3. Identification of retention time, parent and daughter ions for 31 methoxylated PCB congeners by single congener solutions run in daughter scan mode on a GC/MS/MS

Lab ID	Chemical ID	time (min)	Parent Ion	Daughter Ion
MOPCB-1001S	2-Methoxy-5-chlorobiphenyl	18.19	219	176
MOPCB-1002S	4-Methoxy-2-chlorobiphenyl	18.55	219	176
MOPCB-1003S	4-Methoxy-3-chlorobiphenyl	23.79	219	176
MOPCB-1004S	4-Methoxy-4'-chlorobiphenyl	25.96	219	176
MOPCB-2002S	3-Methoxy-2',5'-dichlorobiphenyl	23.80	253	208
MOPCB-2003S	4-Methoxy-2',5'-dichlorobiphenyl	28.02	253	208
MOPCB-2004S	4-Methoxy-3,5-dichlorobiphenyl	28.59	253	208
MOPCB-2005S	2-Methoxy-2’,3’-dichlorobiphenyl	30.69	253	208
MOPCB-2006S	2-Methoxy-3',4'-dichlorobiphenyl	34.05	253	208
MOPCB-3001S	2-Methoxy-2’,4’,6’-trichlorobiphenyl	28.21	287	244
MOPCB-3002S	2-Methoxy-2’,5,5’-trichlorobiphenyl	34.14	287	244
MOPCB-3003S	3-Methoxy-2’,4’,6’-trichlorobiphenyl	33.68	287	244
MOPCB-3004S	4-Methoxy-2,2’,5’-trichlorobiphenyl	35.47	287	244
MOPCB-3005S	4-Methoxy-2’,3,5’-trichlorobiphenyl	41.47	287	244
MOPCB-3006S	4-Methoxy-2’,4’,6’-trichlorobiphenyl	35.93	287	244
MOPCB-4001S	2-Methoxy-2’,3’,4’,5’- tetrachlorobiphenyl	38.75	325	282
MOPCB-4002S	2-Methoxy-2’,3’,5’,6’-tetrachlorobiphenyl	38.81	325	282
MOPCB-4003S	2-Methoxy-2’,4’,5,6’-tetrachlorobiphenyl	38.82	325	282
MOPCB-4004S	3-Methoxy-2’,3’,4’,5’-tetrachlorobiphenyl	49.89	325	282
MOPCB-4005S	3-Methoxy-2’,3’,5’,6’-tetrachlorobiphenyl	44.30	325	282
MOPCB-4007S	4-Methoxy-2’,3’,4’,5’-tetrachlorobiphenyl	51.97	325	282
MOPCB-4008S	4-Methoxy-2’,3,4’,6’-tetrachlorobiphenyl	45.53	325	282
MOPCB-4009S	4-Methoxy-2’,3,5,5’-tetrachlorobiphenyl	45.13	325	282
MOPCB-5001S	2-Methoxy-2’,3’,4’,5,5’-pentachlorobiphenyl	54.03	357	314
MOPCB-5002S	2-Methoxy-2’,3’,5,5’,6’-pentachlorobiphenyl	48.11	357	314
MOPCB-5003S	4-Methoxy-2,2’,3’,4’,5’-pentachlorobiphenyl	48.11	357	314
MOPCB-5004S	4-Methoxy-2,2’,3’,5’,6’-pentachlorobiphenyl	49.88	357	314
MOPCB-5009S	4-Methoxy-2,2’,4’,5,5’-pentachlorobiphenyl	54.59	357	314
MOPCB-5010S	2-Methoxy-2’,3,4’,5’,6-pentachlorobiphenyl	55.07	357	314
MOPCB-6001S	4-Methoxy-2’,3,3’,4’,5,5’-hexachlorobiphenyl	63.38	389	346
MOPCB-7001S	4’-Methoxy-2,2’,3,3’,4,5,5’-heptachlorobiphenyl	66.16	423	380

Table 4. List of performance reference compound standards and surrogate standards composition and concentration.

Lab ID	Chemical ID	Concentrations (ng mL^{-1})
Performance Refernce Compound Standard		
HPCB-1002S	4-Hydroxy-2-chlorobiphenyl	50
HPCB-2002S	2-Hydroxy-2',5'-dichlorobiphenyl	50
HPCB-3003S	3-Hydroxy-2',4',6'-trichlorobiphenyl	50
HPCB-4004S	3-Hydroxy-2',3',4',5'-tetrachlorobiphenyl	50
HPCB-5001S	2-Hydroxy-2',3',4',5,5'-pentachlorobiphenyl	50
HPCB-6002S	4-Hydroxy-2',3,3',5,5',6'-hexachlorobiphenyl	50
Surrogate Standard		
S1	4-Hydroxy-2-chlorobiphenyl	10
S2	2-Hydroxy-2',5'-dichlorobiphenyl	10
S3	3-Hydroxy-2',4',6'-trichlorobiphenyl	10
S4	3-Hydroxy-2',3',4',5'-tetrachlorobiphenyl	10
S5	2-Hydroxy-2',3',4',5,5'-pentachlorobiphenyl	10
S6	4-Hydroxy-2',3,3',5,5',6'-hexachlorobiphenyl	10

Extraction Method

Quartz fiber filters were extracted with pressurized fluid extraction (Dionex ASE-300), using dichloromethane with parameters as follows: pressure 10.3 MPa (1,500 psi), 100 ºC, 5 minutes static time, 1 static cycle, 60% of flush volume, and purge at 90 seconds. Extracts were concentrated to 1 mL (Caliper TurboVap II). Surrogate standards

(100 µL) were added to the sampling in the extraction cell just prior to beginning extractions.

The extract from the previous step was evaporated with N_2 in a water bath heated to 30^{o} C. A small amount of 1:1 hexane and methyl *tert*-butyl ether (HX:MTBE) was added when sample volume was evaporated to ~0.5 mL. The sample was then added 2 mL KOH-solution (0.5 M in 50% ethanol), inverted for 3 min and centrifuged for 3 min. The organic solvent phase (neutral fraction) was then transferred to a new test tube and the PCBs were re-extracted from the alkaline solution with 3 mL hexane (Hovander *et al*. 2000).

The alkaline solution was then acidified with 0.5 mL HCl (2 M), and the pH checked to ensure the acidity (<6), and added an additional alloquot if not acidic. The OH-PCBs were extracted with 4 mL hexane/MTBE (9:1), and the tube was inverted for 3 min and centrifuged for 3 min. The organic solvent phase (phenolic fraction) was then transferred to a new test tube, and the acidic phase was re-extracted with 7 mL Hx/MTBE (9:1). The OH-PCB fraction was dissolved in 7 mL Hx:MTBE (9:1) and was then derivatized to form methoxylate (MeO) PCBs for the OH-PCBs to be detected on a GC. (Hovander *et al*. 2000).

The derivatization of OH-PCBs was carried out by adding 0.5 mL of diazomethane was added to samples and kept the samples in a refrigerator at 4-8 °C for at least 3 hours or overnight. The next day we evaporated the excess of ether and diazomethane under a gentle flow of N_2 and concentrated to100 µL. Samples were stored at -20 ^{0}C until analysis and internal standard (100 µL) was added just prior to analysis.

Analytical Method

Instrumental Method development

An instrumental method was developed to detect OH-PCBs on a GC/MS/MS in order to having a highly selective method of quantification of PCBs. Although there are over 800 possible OH-PCBs, the lack of analytical standards make it impossible to accurately identify all possible congeners. The current strategy described by Ueno *et al.* 2008, is to report known MeO-PCBs as known OH-PCBs, and all other congeners MeO-PCBs identified as unknown total OH-PCBs. Reporting unknown MeO-PCBs requires highly selective instrumentation, such as a tandem mass spectrometer, in order to be confident that the unknown congeners are in fact MeO-PCBs.

Method development included inlet method development and parent and daughter ion identification. The inlet method is a modification of GC parameters reported by Ueno *et al.* 2007 with modification in the GC column and oven ramps (Table 5).

Once the retention times and parent ions were identified through full scan, a daughter scan on one parent ion per homologue group was run using the calibration solution. The resulting chromatogram and spectra are shown in Figure 20 and Figure 21.

Finally, an MRM method used to select both parent/daughter ion pairs was set up using masses calculated from chemical structure and validated by full scan and daughter scans (Table 3). Figure 22 shows the chromatogram from MRM method for the calibration solution.

Table 5. GC parameters used for GC/MS/MS (Quattro Micro^{TM} GC, Micromass MS Technologies, Waters Corp. Milford, MA)with a 30 m x 0.25 mm x 0.25µm SPB-Octyl column.

Parameter		Setting
Injector	Splitless	
	Carrier gas	1 kPa (He)
	Temp	280 °C
Oven	Initial temp	80 °C
	Hold (min)	1 min
	Ramp 1	20 °C/min to 170 °C
	Hold at 170 °C (min)	15 min
	Ramp 2	2 °C/min to 285 °C
	Hold at 285 °C (min)	24 min
Transfer line	Temp	250 °C

The multiple reaction monitoring (MRM) method selects a parent/daughter ion pair. MRM method is the most selective and sensitive mass detection method available on a mass spectra because it allows for multiple user defined fragment ions. That is, the molecules coming into the mass detectors are ionized twice in sequence, making the method extremely selective on the specific fragments of a compound. We determined the appropriate retention time and parent/daughter pair by analyzing single congener solutions of each of the 31 methoxylated congeners available commercially. The single congener solutions were run on full scan mode, which results in two identifications:

1. **Identification of each congener's retention time (Table 3)**
2. **Validation of theoretically calculated parent ion, and in this case molecular ion.**

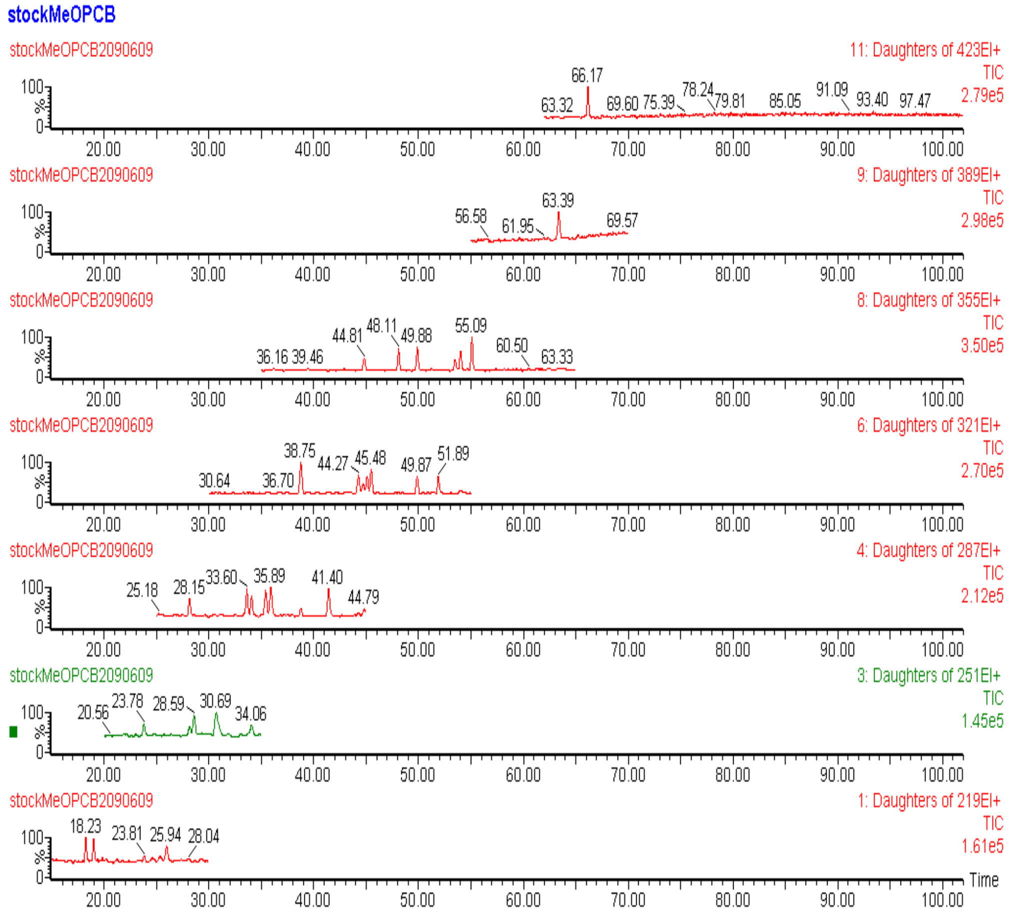

Figure 20. Chromatogram of calibration solution containing 31 methoxylated PCB congeners run on GC/MS/MS. Where x-axis is retention time (mins) and y-axis is individual homologue group windows (mono-heptachlorobiphenyls).

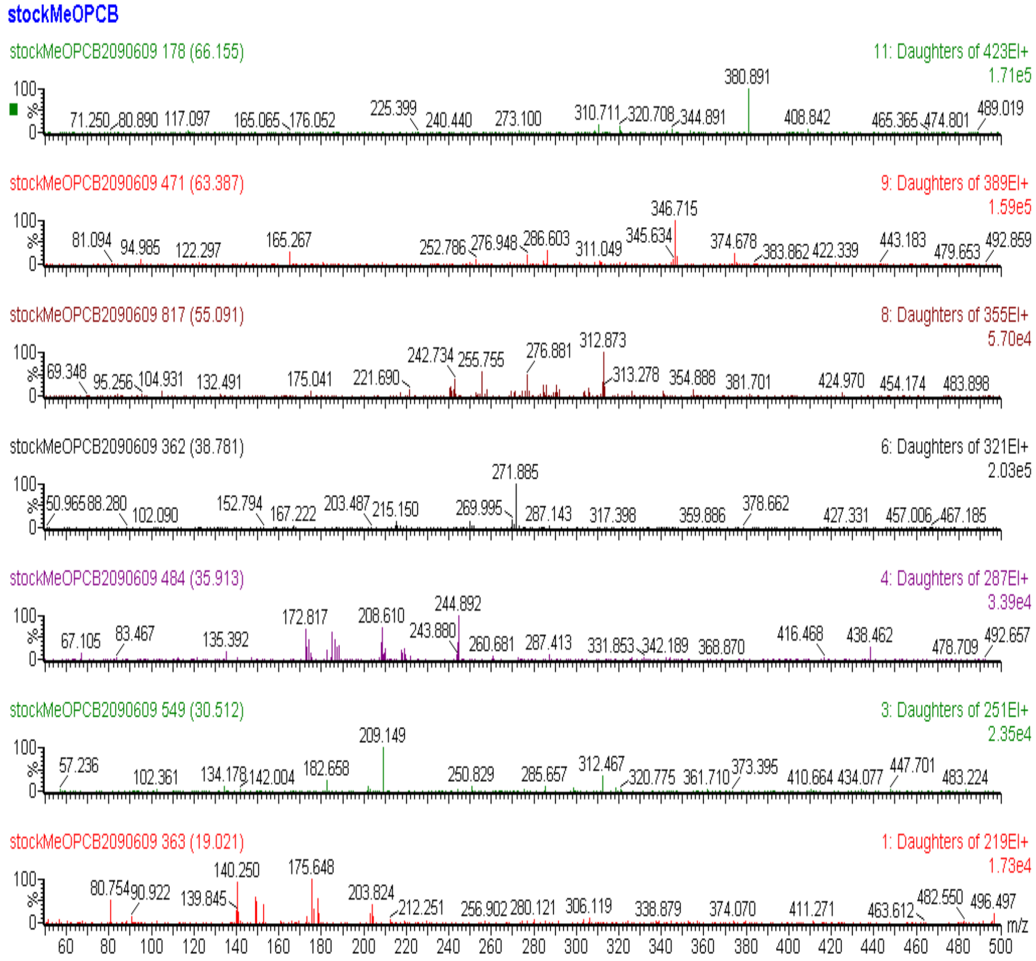

Figure 21. Spectra of daughter fragments from a daughter scan of homologue groups mono-heptachlorobiphenyl on a GC/MS/MS. Where x-axis is m/z and y-axis is the abundance. Theoretically calculated daughters from fragmenting MeO-PCB proved to match base peaks seen in daughter scan.

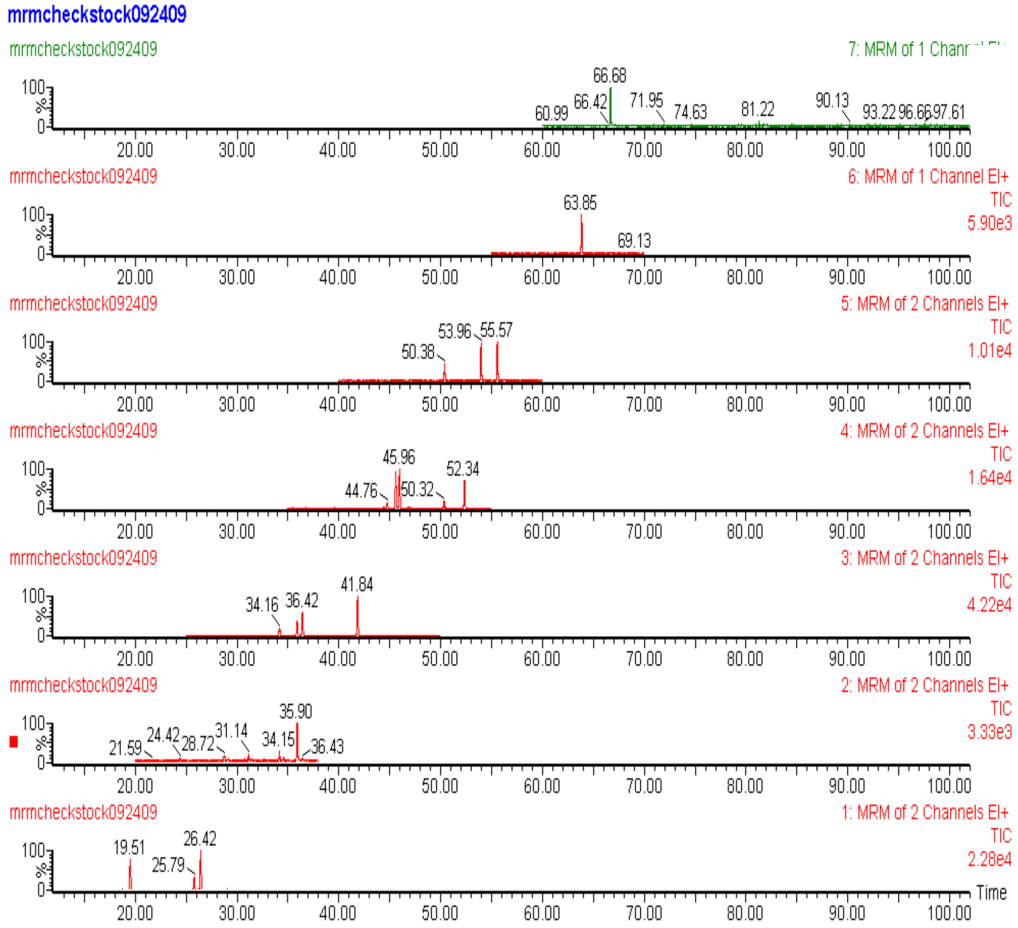

Figure 22. Chromatogram of stock standard containing 31 methoxylated PCB congeners run with MRM method on GC/MS/MS. Where x-axis is retention time (mins) and y-axis is individual homologue group windows (mono-heptachlorinated)

Calibration curves

To use the internal standard method, each congener must have a linear relationship between response (area) and concentration in the range of concentrations expected to be quantified. In order to prove linearity for each congener quantified, external calibration curves were plotted for each of the 31 MeO-PCB congeners with masses ranges from 30-0.1 pg and solution concentrations 3-0.01ng/mL and R^2 values from 0.92-0.99. (Figure D1).

Quality Assurance/Quality Control

Method quality assurance and quality control were implemented to determine the accuracy and precision of the extraction and instrumental methods in recovering and measuring MeO-PCBs. Instrumental detection limits (IDL) were determined from the external calibration curves run determined from the lowest detectable mass on column that had a signal to noise ratio above a 95% confidence limit.

The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte :

$$\text{MDL} = (s)\ (t\text{-value}) \qquad \text{Equation 8}$$

Where s is the sample standard deviation for replicates and t-value is the 99% confidence value from a student t-test. From the sample replicates run (n=10) t-value was 5.68 and s was 0.02 pg per sample.

The limit of quantification (LOQ) is the lowest quantity of a substance that can be distinguished from the absence of that substance with a specified degree of confidence and was determined by.:

$$\text{LOQ} = 10\,(s) \qquad \text{Equation 9}$$

Where s is the sample standard deviation (0.02 pg) for replicates (n=10) as reported above.

The critical signal/noise (S/N) ratio was calculated from samples. The signal to noise ratio describes the effect of random error on a particular measurement, and estimates the expected precision of a series of measurements. Samples spiked in the appropriate range for an MDL determination typically have a S/N in the range of 2.5 to 10. A signal to noise ratio less than 2.5 indicates that the random error in a series of measurements is too high, and the determined MDL is probably invalid. The critical S/N ratio for a series of measurements can be estimated by:

$$S/N_{critical} = X_{avg}/S \qquad \text{Equation 10}$$

Where X_{avg} is the average signals (area) for the replicates and s is the sample standard deviation for the replicates (n=10) with an s of 30 (area count) and an X_{avg} of 76 (area count).

In addition, there is a need for a test to evaluate the overall performance of the method from extraction to analysis. Performance reference compounds (PRCs) containing 6 OH-PCBs described in section were spiked at the beginning of extraction to determine recoveries, and instrument duplicates were determined for PCRs. All QA/QC parameters are shown in Table 6.

Table 6. Quality assurance and quality control metrics for the OH-PCB method developed for GC/MS/MS using 10 replicate samples.

Quality Assurance/Quality Control	
IDL (pg)	0.10
MDL(pg)	0.30
LOQ(pg)	0.20
Critical S:N	2.56
PRC Recoveries	72 ± 12%
Method replicates (relative standard deviation)	15%
Instrument duplicates (relative difference)	11%

Sample Collection

High-volume air samplers (Hi-Vols) equipped with quartz fiber filters and XAD-2 resin were used to collect air samples across Chicago. Aerosol particles are captured on the filters and gas-phase compounds are captured by the resin. The concentrations of PCBs on the resins have been reported elsewhere and gas-phase compounds are not the subject of this study (Hu *et al*. 2008,Hu and Hornbuckle, 2010,Persoon et al., submitted). We expect OH-PCBs to accumulate on the filters.

The 30 samples examined in this study were collected from June to August in 2008 at various locations in Chicago.

Results and Discussion

Frequency of detection was low with only 10% of the thirty samples (n=3) having OH-PCBs above the critical S/N ratio (Figure 21). The three samples from which OH-PCBs were detected were all taken in July from sites that have high total PCB concentration, identified in the previous Chapter.

Each of these three samples contain <7 total peaks, with masses from the samples ranging from 0.70-1.02 pg (Table 7). These total masses result in concentrations of 0.60

to 1.36 pg g^{-1}, the same magnitude as concentrations reported by Ueno *et al.* in 2008 for precipitation. The identity of each detected OH-PCB compound is not known. However, the method does identify the compound molecular weight and chlorination (homologue group).

Table 7. Calculated mass for homologue groups of unknown OH-PCBs detected in three air samples.

Sample ID	ΣOH-PCBs peaks per homologue group	n =	Total mass (pg sample^{-1})	Concentration on airborne particles (pg g^{-1} d.w.)	Concentration (pg m^{-3})
FV0414					
	dichloro, monohydroxybiphenyl	4	0.7	0.6	0.004
	trichloro, monohydroxybiphenyl	1			
FV0422					
	dichloro, monohydroxybiphenyl	1			
	trichloro, monohydroxybiphenyl	2	0.9	1	0.005
	tetrachloro, monohydroxybiphenyl	2			
FV0430					
	trichloro, monohydroxybiphenyl	2	1.02	1.36	0.005
	tetrachloro, monohydroxybiphenyl	4			

Although our recovery studies for the method, from extraction through analysis, resulted in good percentage of recovery (68-85%), we saw low frequency of detection for our samples. The low detection frequency could be due to the low concentration of these compounds in air and our relatively high detection limits. Analysis with a more sensitive instrument or collection of more air could address this problem. GC/MS/MS is not as sensitive as other instruments that have been used for this analysis, such as the GC/ECD for blood samples (Dirtu *et al.* 2010) or the GC/HRMS (Ueno *et al.* 2008). It is also possible that the OH-PCBs are not easily collected on the filters or decay before or after collection (Mandalakis et al. 2003, Macleod et al. 2007, Gasic et al. 2009).

It is interesting to note that the OH-PCBs detected were all unknown congeners: that is, we do not have a specific standard analyte at that retention time, and they were all found in the homologue groups with two, three, or four chlorines. This detection of peaks in the lower homologue groups is similar to the detected peaks reported by Ueno *et al.* in 2008, the only publication to date of environmental hydroxylated-PCBs.

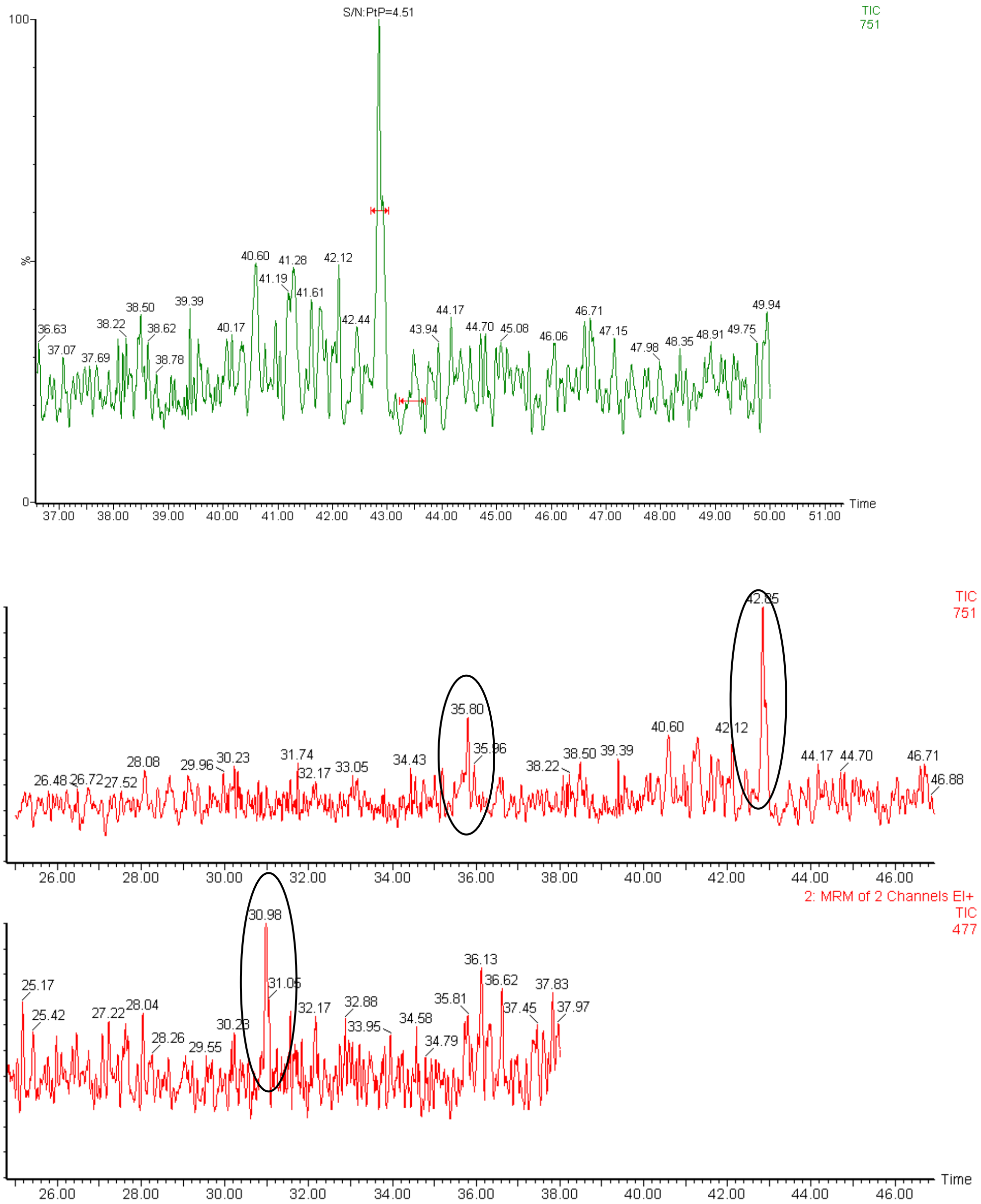

Figure 23. Chromatogram of a quartz fiber filter (atmospheric particulate phase) sample analyzed using the OH-PCB method developed for GC/MS/MS (bottom), where the peaks circled represent peaks with S/N ratio above the critical S:N, as demonstrated on the top chromatogram.

Conclusions

The method developed for identification and quantification of hydroxylated-PCBs (OH-PCBs) on the GC/MS/MS is precise and accurate as determined by quality assurance and quality control standards. Detection of OH-PCBs in airborne particles was low (10%), with all the peaks detected being unknown congeners, and all within the lower chlorinated homologue groups. This may be due to either extremely low concentrations of OH –PCBs in the air, or due to the high reactivity of hydroxylated-PCBs making them unstable and difficult to measure in the air.

CHAPTER VI. SUMMARY AND CONCLUSIONS

The research in this thesis reported the use of passive sampling as a tool for collecting spatial data for atmospheric PCBs in an urban area, with the intention of using passive samplers to identify and characterize sources of atmospheric PCBs in future studies. The thesis addresses best practices in calculating air concentrations from sorbed mass of PCBs on passive samplers coupled with polyurethane foam in both indoor and outdoor environments. This thesis also reports the use of passive samplers across two major cities, and the captured differences in both inter and intra-city concentrations and congener distributions. This study also addressed the consistency of spatial distributions, particularly hot-spots, in Chicago over time, are described in order to understand and interpret single deployment period data as well as to understand spatial distribution dynamics across the city over time. Finally, this thesis presents a method for identifying and quantifying hydroxylated-PCBs, with the intention of it being used for future research in understanding fate of atmospheric PCBs in both the environment as well as to quantify potential for human exposure. Eleven major conclusions have resulted from this thesis, and are summarized here:

1. For indoor air, the average R-value of 2.6 m^3d^{-1} calculated from both uptake and loss of PCBs is recommended for application to samples using this passive sampler design for indoor sites. For indoor air, both uptake and elimination of PCBs followed the mathematical model of first-order kinetics, and for our deployment period were in the linear stages of uptake and elimination.
2. For outdoor applications using this passive sampler design, we suggest using depuration compounds to reduce the uncertainty by nearly a factor of 2. Since PCB concentrations are not constant in outdoor air, uptake of native congeners was not linear, which leads to large variation in R-values derived from uptake.

We suggest depuration compounds as best practice as they reflect effective sample volume, where uptake derived R-values are dependent on C_{Air} which may vary greatly, where depuration compound loss is independent of this variability.

3. A spatial resolution over an urban area is important to capture representative ΣPCB concentrations of that urban area. From spatially distributed air sampling, we found that the average atmospheric ΣPCB concentrations are significantly different between Cleveland and Chicago; although both had multiple hot-spots of atmospheric PCBs spatially distributed throughout the sampling area. Both cities average congener profiles were similar to Aroclors; however, Cleveland was most similar to 1242, where Chicago air was similar to a 1242:1254 mixture 35:65.
4. Samples from both Cleveland and Chicago had no significant spatial autocorrelation, suggesting localized sources to our sample sites.
5. ΣPCB concentration and site specific congener profiles also vary spatially within urban areas. Sites with high ΣPCB concentrations (‘hot spots’) have a good correlation to known Aroclor mixes, and sites with low ΣPCB concentrations have enrichment in lower chlorinated PCBs and poor correlation to Aroclors.
6. Although the average atmospheric PCB concentration was higher in Cleveland than Chicago, Chicago had a higher average concentration of dioxin-like PCBs, or toxic equivalent (TEQ), suggesting that total atmospheric PCB concentration is not a predictor to TEQ, but rather congener specific analysis is important as well.
7. Our work in Chicago showed that passive samplers and Hi-Vols represent very different collection methods and produce chemical data that can be either spatially resolved or temporally resolved. On large scales, both methods measure similar concentrations; however, at specific sites there can be significant differences in annual average concentrations due to non-continuous Hi-Vol sampling.

8. Our work in Chicago showed that congener profiles between passive samplers and Hi-Vols are similar in the summer. However they can differ in the winter, probably due to the passive samplers poor collection of higher chlorinated PCBs and the enrichment in lower chlorinated PCBs.
9. Our work in Chicago showed that passive samplers consistently identified the spatial distribution of hot-spots at six sites, and consistent low spots as four sites over sixteen separate deployments.
10. The use of passive samplers coupled with spatial statistical methods of delineation, such as Voronoi diagrams, give a novel approach to identifying hot-spots of atmospheric PCBs, which could lead to more rapid source identification.
11. Hydroxylated-PCBs from air filter samples can be detected and quantified using a GC/MS/MS method; however, detection frequency was low at 10%.

CHAPTER VII. FUTURE RESEARCH

The studies presented in this thesis are the foundation to identifying and characterizing sources of atmospheric PCBs within cities, known sources of PCBs for deposition and global transport. The results presented in Chapter IV are an exciting step forward as a novel method of identifying new sources of atmospheric PCBs within urban areas. The use of passive samplers to identify spatial hot-spots in a single deployment period can lead to more rapid source identification and then remediation. Future researchers can utilize passive samplers to find a spatial area, and then place Hi-Vols at the hot-spot site to determine direction of the source relative to the site with back trajectories. Finally, understanding the differences in congener pattern collected by Hi-Vols and passive samplers allows better statistical analysis between air congener profiles and possible source or soil congener profiles from suspected sources. Rapid identification of new sources of atmospheric PCBs will lead to rapid remediation or containment of PCB sources, and essentially could lead to a more rapid decline of PCB deposition into the Great Lakes and decrease potential for global dispersion of PCBs through the atmosphere.

Chapter V also opens the door for new research on hydroxylated-PCBs (OH-PCBs). The method will allow for quantification of environmental sources of OH-PCBs, such as atmospheric reactions, bacterial hydrolysis, or chemical hydrolysis in sediment or water systems. The method will allow future researchers to look at relative magnitudes of these different environmental sources as well, which could answer the question of whether OH-PCBs found in human serum are from environmental source exposure to OH-PCBs or solely from human metabolism of PCBs. Chamber studies on the uptake of OH-PCBs could also utilize this method if investigating if inhalation of OH-PCBs exposure increases body burden.

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APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER II

Table A1. Calculated R-values, coefficients of determination (r^2), linear equations used, and Hi-Vol concentration averages over the PUF deployment period for native uptake and depuration loss for indoor sites.

Site	Congener	R-value (m^3d^{-1})	r^2	Equation for linear range	C_{Air} Hi-vols Average (ng/m^3)
Indoor 1					
Native	1Cl	2.5	0.97	y = 0.4696x - 3.91	0.19
	2Cl	3.1	1.00	y = 2.2256x - 10.181	0.72
	3Cl	2.9	1.00	y = 3.9789x - 33.462	1.36
	4Cl	2.4	1.00	y = 20.215x + 58.052	8.55
	5Cl	3.5	1.00	y = 36.508x - 259.47	10.5
	6Cl	2.7	0.99	y = 8.0818x - 7.6742	3.00
	7Cl	2.0	0.99	y = 0.6529x - 6.5037	0.32
Depuration	^{13}C PCB 3	2.2	0.81	y = -0.142x + 1.140	ND
	^{13}C PCB 15	2.1	0.99	y = -0.114x + 1.086	ND
	^{13}C PCB 28	2.7	0.96	y = -0.132x + 1.079	ND
	^{13}C PCB 118	2.4	0.73	y = -0.226x + 1.226	ND
Indoor 2					
Native	1Cl	2.3	0.89	y = 0.2072x - 3.3027	0.09
	2Cl	2.8	0.62	y = 0.1413x + 4.2812	0.05
	3Cl	2.7	0.98	y = 0.8011x - 1.302	0.29
	4Cl	2.2	0.99	y = 6.5104x + 145.21	3.01
	5Cl	2.9	0.99	y = 9.2099x - 24.787	3.21
	6Cl	2.0	0.56	y = 1.5591x + 64.776	0.77
	7Cl	2.4	0.97	y = 0.4001x - 5.0823	0.17
Depuration	^{13}C PCB 3	2.1	0.75	y = -0.117x + 1.017	ND
	^{13}C PCB 15	2.3	0.94	y = -0.116x + 1.063	ND
	^{13}C PCB 28	2.2	0.97	y = -0.136x + 1.090	ND
	^{13}C PCB 118	2.6	0.84	y = -0.231x + 1.191	ND

Table A2. Calculated R-values, coefficients of determination, linear equations used, and Hi-Vol average concentrations from native uptake and depuration loss for outdoor sites.

Site	Congener	R-value (m^{3}d^{-1})	r^2	Equation for linear range	C_{Air} Hi-vols Average (ng/m^3)
Outdoor					
Native	1Cl	5.3	0.84	$y = 0.1067x - 2.3134$	0.02
	2Cl	3.9	0.93	$y = 2.3138x - 54.175$	0.60
	3Cl	4.2	0.64	$y = -3.8003x + 164.59$	0.91
	4Cl	11.5	0.25	$y = -1.0346x + 84.787$	0.09
	5Cl	1.6	0.33	$y = 0.1096x + 9.7431$	0.07
	6Cl	7.9	0.01	$y = -0.3646x + 93.924$	0.05
	7Cl	-	0.0001	$y = -0.0013x + 3.6028$	0.00
	PCB 73	7.8	0.32	$y = 0.0508x + 2.5467$	0.007
	PCB 101/113/90	8.0	0.16	$y = 0.0642x + 2.2393$	0.008
	PCB 153	3.4	0.77	$y = 0.0136x + 0.0622$	0.004
	PCB 163	9.3	0.02	$y = -0.2518x + 82.41$	0.027
Depuration	^{13}C PCB 3	8.4	0.82	$y = -0.238x + 1.065$	ND
	^{13}C PCB 15	4.4	0.91	$y = -0.166x + 1.077$	ND
	^{13}C PCB 28	4.8	0.92	$y = -0.164x + 1.096$	ND
	^{13}C PCB 118	6.2	0.97	$y = -0.225x + 1.193$	ND

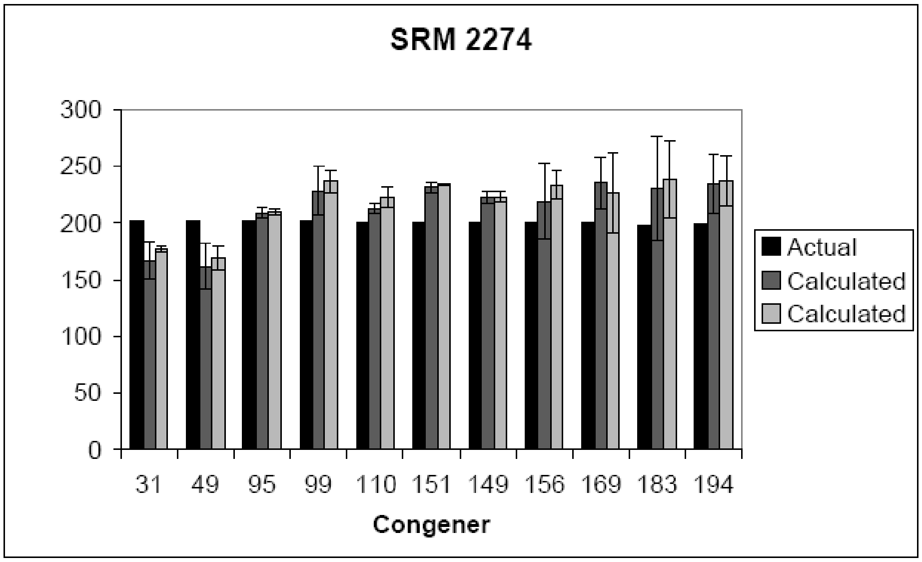

Figure A1. Concentration (ng mL^{-1}) of PCB congeners in Standard Reference Material 2274. The first black bar is the certified value of each congener. The second (dark gray) bar is the mean calculated concentrations of three SRM samples extracted in April, 2008. The third (gray) bar is the mean calculated concentration of three SRM samples extracted in May, 2008.

APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER III

Table B1. Metadata for Cleveland samples.

Site ID	ΣPCB Concentration (ng m^{-3})	Y	X	Deployment Date	Collection Date
1	3.74	41.51194	-81.68889	8/12/2008	9/3/2008
2	2.08	41.53472	-81.64722	8/12/2008	9/2/2008
4	1.54	41.47000	-81.71111	8/12/2008	9/2/2008
4A	1.67	41.48139	-81.70361	8/12/2008	9/3/2008
5	2.14	41.46694	-81.79444	8/12/2008	9/2/2008
6	3.92	41.49167	-81.67750	8/12/2008	9/2/2008
9	3.00	41.45583	-81.76972	8/12/2008	9/2/2008
10	1.96	41.47167	-81.65694	8/13/2008	9/2/2008
11	2.16	41.44639	-81.73167	8/12/2008	9/2/2008
12	1.91	41.48389	-81.84472	8/12/2008	9/3/2008
15	4.24	41.43444	-81.69444	8/12/2008	9/2/2008
16	1.50	41.55417	-81.57472	8/13/2008	9/2/2008
17	0.76	41.43417	-81.80389	8/12/2008	9/2/2008
18	0.52	41.52222	-81.58806	8/13/2008	9/2/2008
20	0.34	41.44722	-81.66139	8/12/2008	9/2/2008
21	1.10	41.41250	-81.71556	8/12/2008	9/2/2008
22	0.57	41.43528	-81.83333	8/12/2008	9/2/2008
23	0.70	41.48444	-81.95417	8/12/2008	9/3/2008
26	1.02	41.45694	-81.59278	8/12/2008	9/2/2008
27	0.53	41.44167	-81.91111	8/12/2008	9/3/2008
30	0.96	41.31583	-81.54056	8/13/2008	9/2/2008

Table B2. Metadata for Chicago samples.

Sample ID	ΣPCB Concentration (ng m^{-3})	X	Y	Deployment date	Collection date
3	0.60	-87.71411	41.90427	8/8/2008	9/19/2008
10	1.07	-87.64219	41.79583	8/8/2008	9/16/2008
18	1.93	-87.64531	41.73879	8/8/2008	9/19/2008
20	0.73	-87.67309	41.80752	8/12/2008	9/24/2008
24	0.89	-87.63391	41.66953	8/8/2008	9/24/2008
26	1.03	-87.72238	41.92135	8/8/2008	9/19/2008
28	0.72	-87.65804	41.85582	8/8/2008	9/19/2008
32	0.38	-87.68998	41.81626	8/17/2008	9/30/2008
34	0.59	-87.64942	41.84971	8/8/2008	9/23/2008
35	0.43	-87.62509	41.82107	8/8/2008	9/19/2008
37	0.42	-87.70427	41.79309	8/8/2008	9/24/2008
38	0.86	-87.68289	41.88329	8/8/2008	8/21/2008
39	0.65	-87.65746	41.85941	8/17/2008	9/19/2008
44	1.43	-87.72533	41.84007	8/8/2008	9/19/2008
45	0.38	-87.73509	41.84154	8/8/2008	9/18/2008
46	0.66	-87.69277	41.92276	8/8/2008	9/19/2008
47	0.65	-87.71468	41.84327	8/8/2008	9/19/2008
Field Blank	<LOQ			8/8/2008	8/8/2008

Table B3. Test of spatial autocorrelation in the distribution of total PCB using Moran's I in Cleveland and Chicago.

City	Moran's I (p > 0)	Expected Moran's I
Cleveland	0.080 (0.066)	-0.050
Chicago	-0.112 (0.685)	-0.063

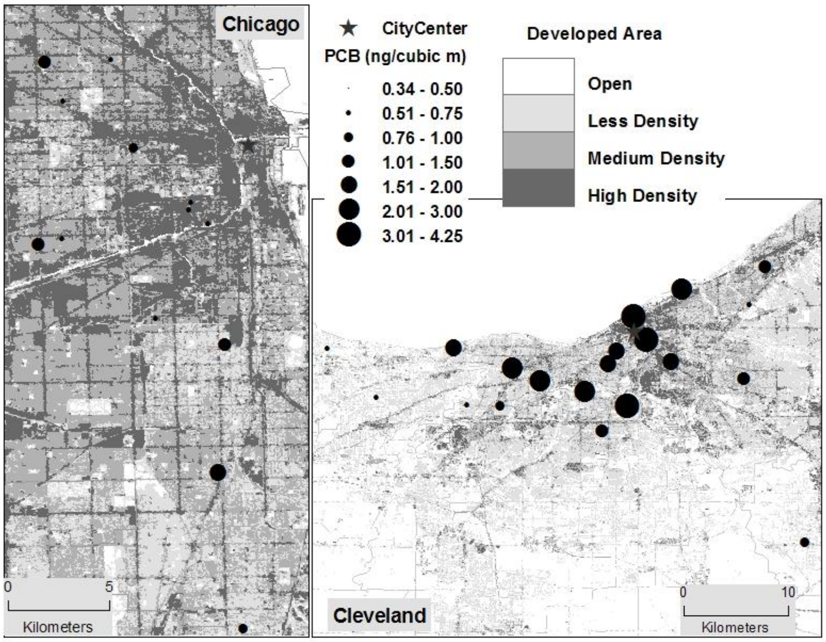

Figure B1. Maps of Chicago(a) and Cleveland(b) for August-September,2008, showing land cover and ΣPCB concentration at each sampled site. Land-use and land-cover data were acquired from the National Land-Cover database (MRLC 2008). The developed area was grouped into four categories, namely open, low-density, medium density and high-density. Land cover categories are defined as follows: **Developed, Open Space** - Includes areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses. Impervious surfaces account for less than 20 percent of total cover. These areas most commonly include large-lot single-family housing units, parks, golf courses, and vegetation planted in developed settings for recreation, erosion control, or aesthetic purposes **Developed, Low Intensity** - Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 20-49 percent of total cover. These areas most commonly include single-family housing units. **Developed, Medium Intensity** - Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 50-79 percent of the total cover. These areas most commonly include single-family housing units. **Developed, High Intensity** - Includes highly developed areas where people reside or work in high numbers. Examples include apartment complexes, row houses and commercial/industrial. Impervious surfaces account for 80 to100 percent of the total cover.

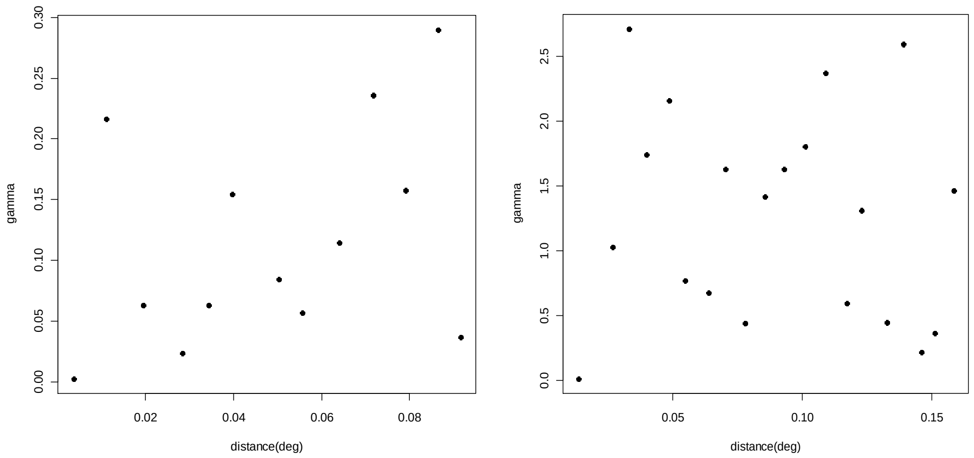

Figure B2. Variogram of ΣPCB distribution in Chicago(a) and Cleveland(b) for August-September, 2008 showing no autocorrelation between sites both cities, where gamma is a unit less calculated variance and distance is the distance in degrees between sites.

APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER IV

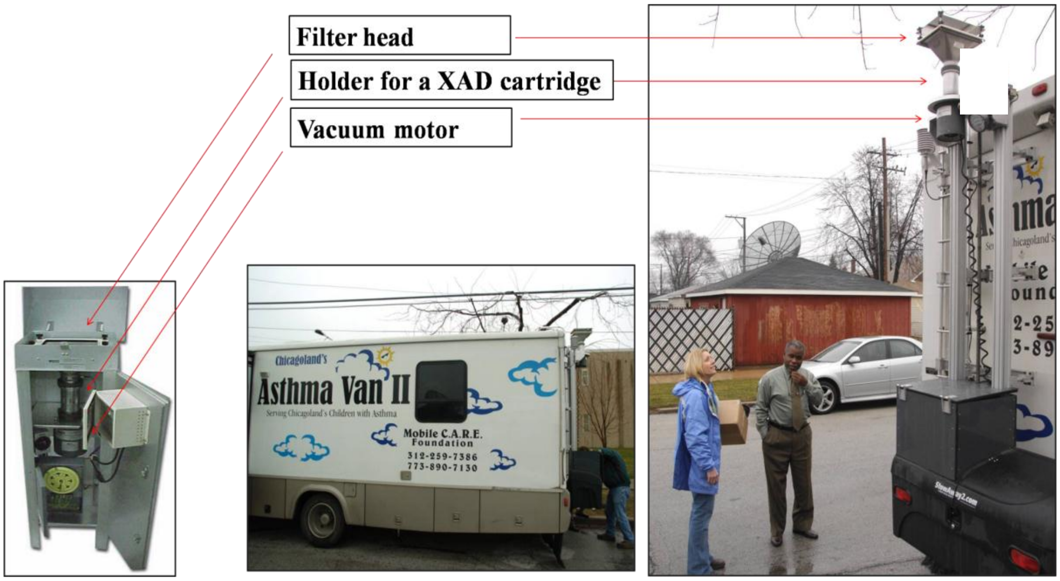

Figure C1. Photos of typical a Hi-Vol, Mobile C.A.R.E. Foundation Asthma Van II, and a mounted Hi- Vol (left to right) used for sampling air in metro Chicago.

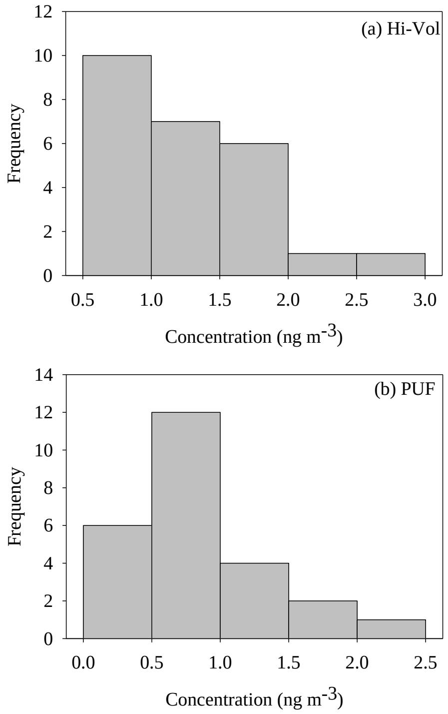

Figure C2. Concentration distributions of annual average concentrations across Chicago for Hi-Vol (a) and passive sampler (b). Both are parametrically distributed, and therefore t-test are applicable for statistical test.

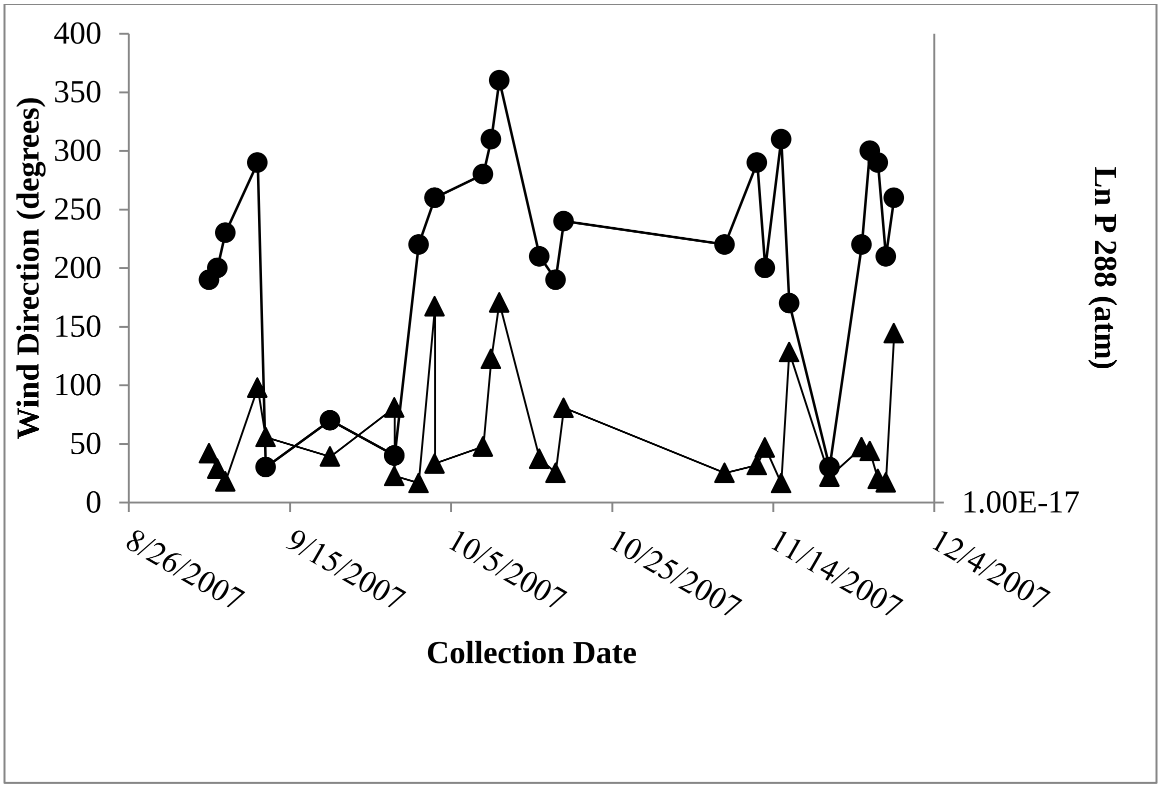

Figure C3. Plot of both temperature normalized partial pressure of ΣPCBs (P_{288} atm) and wind direction on days Hi-Vols are collected for site 16. Variations in temperature normalized partial pressures coincide with changes in wind direction. This aspect of Hi-Vols high temporal resolution and ability to capture specific meteorological events make it a good tool for back trajectories, but difficult to compare relative spatial distributions of atmospheric PCB hot-spots.

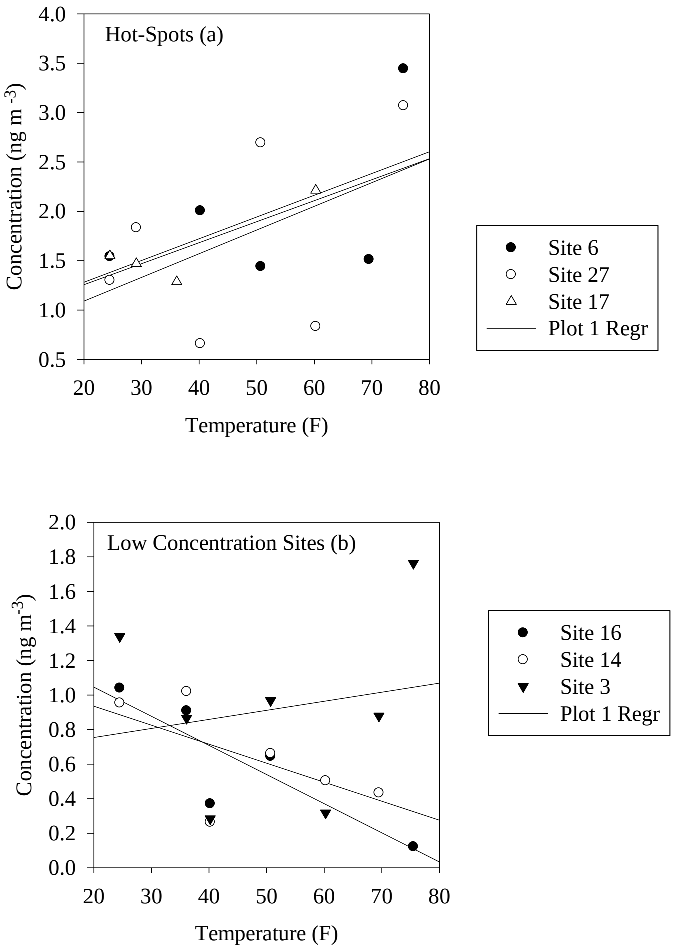

Figure C4. Plots of atmospheric ΣPCB concentrations for hot-spots (a) and low concentrated sites (b) versus temperature. Plots show greater temperature dependency, steeper slope, for hot-spots than low concentrated sites, suggesting volatilization from a primary source at hot-spots. Low concentrated sites also have negative correlation between concentration and temperature for two of the sites plotted, suggesting secondary sources or transport from multiple sources to the low concentrated sites.

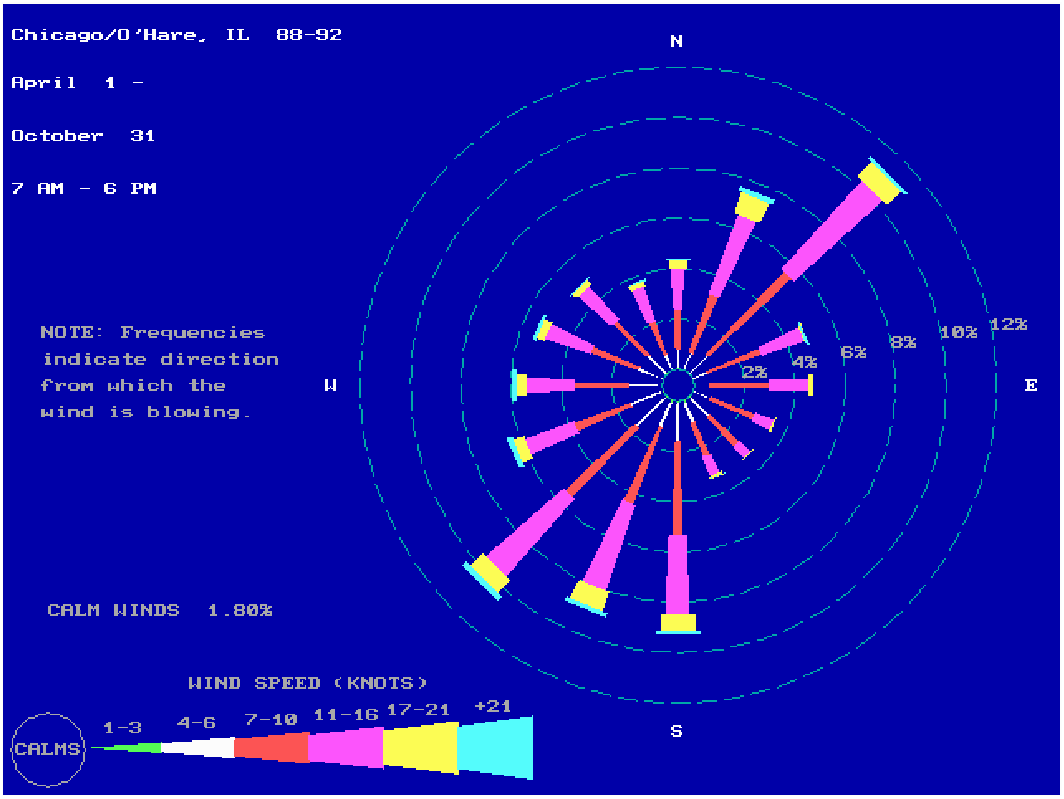

Figure C5. Annual wind rose for Chicago taken from Pacific Environmental Services (PES) created for the EPA.

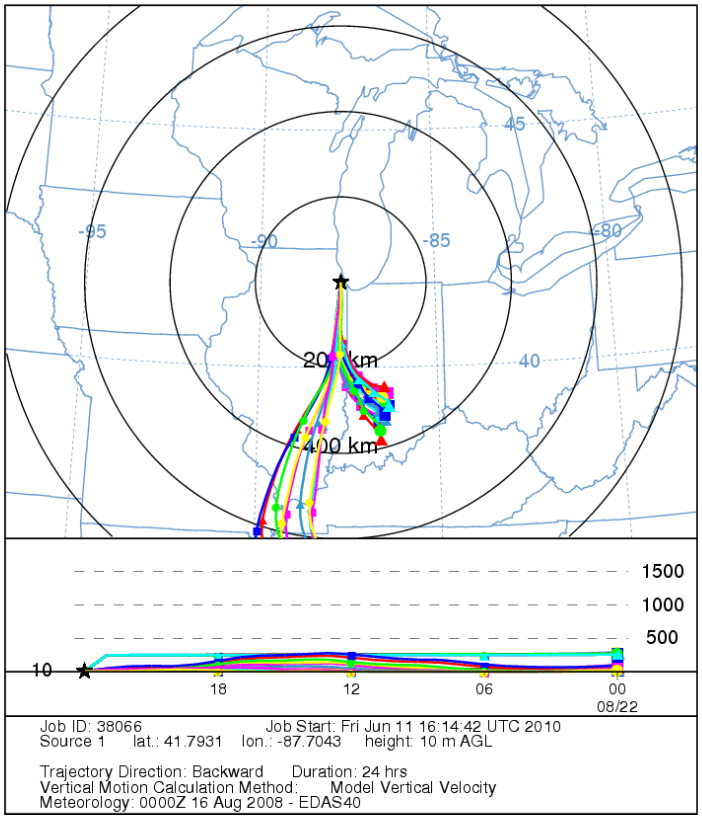

Figure C6. Back trajectory model showing source direction for site 27 on August 22, 2007, the highest reported PCB concentration for this site sampled by Hi-Vols. The back trajectory shows a source from the South, similar to the source direction suggested

Table C1. Concentrations of ΣPCBs collected by passive samplers at 29 sites throughout 2007, 2008, and 2009.

			Concentration (ng/m^3) for Collection Dates														
ID	X	Y	Sep-07	Oct-07	Nov-07	Jan-08	Feb-08	Apr-08	May-08	Jul-08	Aug-08	Sep-08	Oct-08	Dec-08	Feb-09	Mar-09	Apr-09
3	-87.7141	41.9043	1.76	0.88	0.32	0.28	0.40	0.90	1.72		1.20	1.44		0.34		0.67	1.46
4	-87.6948	41.9183	2.55	1.02	0.49	0.20		0.93	1.78	1.20	1.40						1.29
5	-87.7319	41.8456		0.69		2.25	0.35	1.58	1.02	1.37	1.54			0.38			
6	-87.6732	41.8520		1.10			0.49	1.22	1.13	1.03	1.35		1.10	1.09	1.38	1.20	1.43
8	-87.6422	41.7958	3.07		0.83	0.66	1.83	1.30	3.75			1.69				1.96	2.92
9	-87.7161	41.8587	1.53														
12	-87.6453	41.7388			1.27	0.57	1.72	1.19	1.39		1.70	1.55	1.67	1.30		1.31	2.47
14	-87.6731	41.8075		0.43	0.50	0.26		0.95	0.72		1.02	0.66	0.43		0.88		1.08
15	-87.6082	41.8219		1.07	0.80	0.55		0.97						0.32		0.89	
16	-87.6339	41.6695	0.12			0.37	0.56	1.04	0.77	0.77	0.91	0.64		0.54	0.41	0.67	1.01
17	-87.7190	41.9298			2.21		1.47	1.55			1.29		1.63	1.06	1.35		
18	-87.7224	41.9214	4.79				0.79	1.01				1.33					1.68
19	-87.6229	41.6695	2.44	1.46													
20	-87.6580	41.8558									1.41	0.98	0.62			0.35	1.02
22	-87.7606	41.9300	1.28	0.69				1.18	0.95					0.89	1.10	1.06	1.23
24	-87.6900	41.8163	1.17			0.38	0.87			1.04		0.60					
25	-87.6494	41.8497			0.94	0.44	1.14		1.25			1.09				0.57	
26	-87.6251	41.8211	0.57			0.39		1.47			1.00	2.14					1.26
27	-87.7043	41.7931	3.44	1.51		2.01		1.54			1.97	1.44	3.06		2.30	2.50	1.47
28	-87.6829	41.8833				0.60	1.25				0.98						0.9
29	-87.6575	41.8594	0.35		0.76	0.60		1.02	1.07			0.69	0.64			0.51	1.67
31	-87.5359	41.6878	3.44				1.21				1.84					1.68	
33	-87.7268	41.8697				2.73	0.56										
34	-87.7253	41.8401			0.21	1.32	0.96	1.29		1.17	1.88	0.63	1.06			0.86	
35	-87.7351	41.8415		0.89			0.54	0.74		1.96		1.08				0.47	
36	-87.6097	41.7433		0.56	0.21	0.55	0.51	0.75									
37	-87.7167	47.7447	1.65	1.18	0.71	0.65		1.06	1.09	2.41				1.49	1.34		1.57
38	-87.7144	41.8433			1.14	0.27		0.98	1.08			0.57				0.35	1.06
39	-87.6925	41.9225							1.03			1.07	0.62				
R-Value			5.80	6.40	5.20	4.80	4.60	5.70	6.20	5.90	6.60	6.10	5.80	4.90	5.10	5.70	6.2

Table C2. Mean concentrations and standard deviations for each site averaged from September 2007 to September 2008 for both Hi-Vols (n=412) and passive samplers (n=175).

			Hi-Vol			PUF		
Site ID	X	Y	Mean (ng m^{-3})	Standard Deviation (ng m^{-3})	n	Mean (ng m^{-3})	Standard Deviation (ng m^{-3})	n
3	-87.7141	41.9043	1.53	1.27	18	0.93	0.59	9
4*	-87.6948	41.9183	2.30	1.21	10	1.20	0.73	8
5	-87.7319	41.8456	1.36	1.68	20	1.26	0.60	7
6	-87.6732	41.8520	1.24	1.14	22	1.05	0.33	6
8	-87.6422	41.7958	0.54	0.02	19	1.88	0.99	7
9	-87.7161	41.8587	1.04	1.21	15	1.53		1
12	-87.6453	41.7388	0.36	1.26	20	1.34	0.39	7
14	-87.6731	41.8075	0.72	0.74	12	0.65	0.30	7
15*	-87.6082	41.8219	0.47	0.30	8	0.85	0.23	4
16	-87.6339	41.6695	0.69	0.46	22	0.65	0.38	8
17	-87.7190	41.9298	1.50	0.55	18	1.63	0.40	4
18	-87.7224	41.9214	0.66	0.33	17	1.98	1.89	4
19	-87.6229	41.6695	1.68	1.20	15	1.95	0.69	2
20	-87.6580	41.8558	0.96	0.96	20	1.19	0.30	2
22	-87.7606	41.9300	1.09	0.26	17	1.03	0.32	4
24	-87.6900	41.8163	0.49	0.55	15	0.81	0.34	5
25	-87.6494	41.8497	0.72	1.18	17	0.97	0.32	5
26	-87.6251	41.8211	0.87	0.93	16	1.11	0.71	5
27	-87.7043	41.7931	1.83	1.72	20	1.99	0.81	6
28	-87.6829	41.8833	1.30	0.90	18	0.94	0.46	3
29	-87.6575	41.8594	0.67	0.40	17	0.75	0.27	6
31*	-87.5359	41.6878	0.60	0.54	4	2.16	1.15	3
33	-87.7268	41.8697	0.78	0.68	15	1.64	0.12	2
34	-87.7253	41.8401	0.50	0.46	19	1.07	1.05	7
35	-87.7351	41.8415	0.74	0.51	18	1.04	0.17	5

Table C3. Example of ranking hot-spots by using percentile groups for passive samplers

Collection date 10/2007		
Site	Concentration ΣPCBs (ng m^{-3})	
27	1.51	95th percentile
19	1.46	
37	1.18	>50th percentile
6	1.10	
15	1.07	
35	0.89	
3	0.88	<50th percentile
22	0.69	
5	0.69	
36	0.56	
14	0.43	5th percentile

Table C4. Example of ranking hot-spots by using percentile groups for Hi-Vol, where site 16 is highly variable for the month of November, 2007 and is circled in red.

Collection Date	Site	Ln P_{288} (atm)	
11/29/2007	31	1.45E-15	
11/16/2007	20	1.29E-15	95th percentile
11/5/2007	3	8.42E-16	
11/25/2007	16	4.79E-16	
11/13/2007	33	4.77E-16	
11/26/2007	8	4.46E-16	
11/5/2007	1	4.29E-16	
11/16/2007	24	3.78E-16	>50th percentile
11/6/2007	24	3.71E-16	
11/30/2007	11	3.38E-16	
11/12/2007	16	3.27E-16	
11/14/2007	31	2.69E-16	
11/8/2007	21	2.60E-16	
11/7/2007	13	2.51E-16	
11/9/2007	19	2.46E-16	
11/6/2007	10	2.40E-16	
11/21/2007	2	2.30E-16	
11/27/2007	24	2.10E-16	<50th percentile
11/9/2007	40	2.03E-16	
11/1/2007	23	1.95E-16	
11/2/2007	25	1.91E-16	
11/14/2007	34	1.90E-16	
11/28/2007	16	1.80E-16	
11/15/2007	21	1.74E-16	5th percentile
11/30/2007	2	1.33E-16	

Table C5. Moran's I and the resulting z-score calculated for each deployment period that passive samplers collected across Chicago.

	Aug-07	Oct-07	Nov-07	Jan-08	Feb-08	Apr-08	May-08	Jul-08	Aug-08
z-score	-0.25	-0.19	-1.88	-1.32	-0.40	-1.22	-1.05	-0.91	-1.88
p-value	0.6	0.57	0.97	0.08	0.66	0.89	0.31	0.28	0.03
Moran I statis	-0.11	-0.13	-0.35	0.12	-0.18	-0.2	-0.14	-0.16	0.18
Expected	-0.08	-0.1	-0.08	-0.06	-0.11	-0.05	-0.04	-0.08	-0.06
Variance	0.02	0.03	0.02	0.02	0.03	0.01	0.03	0.02	0.02

APPENDIX D. SUPPORTING INFORMATION FOR CHAPTER V

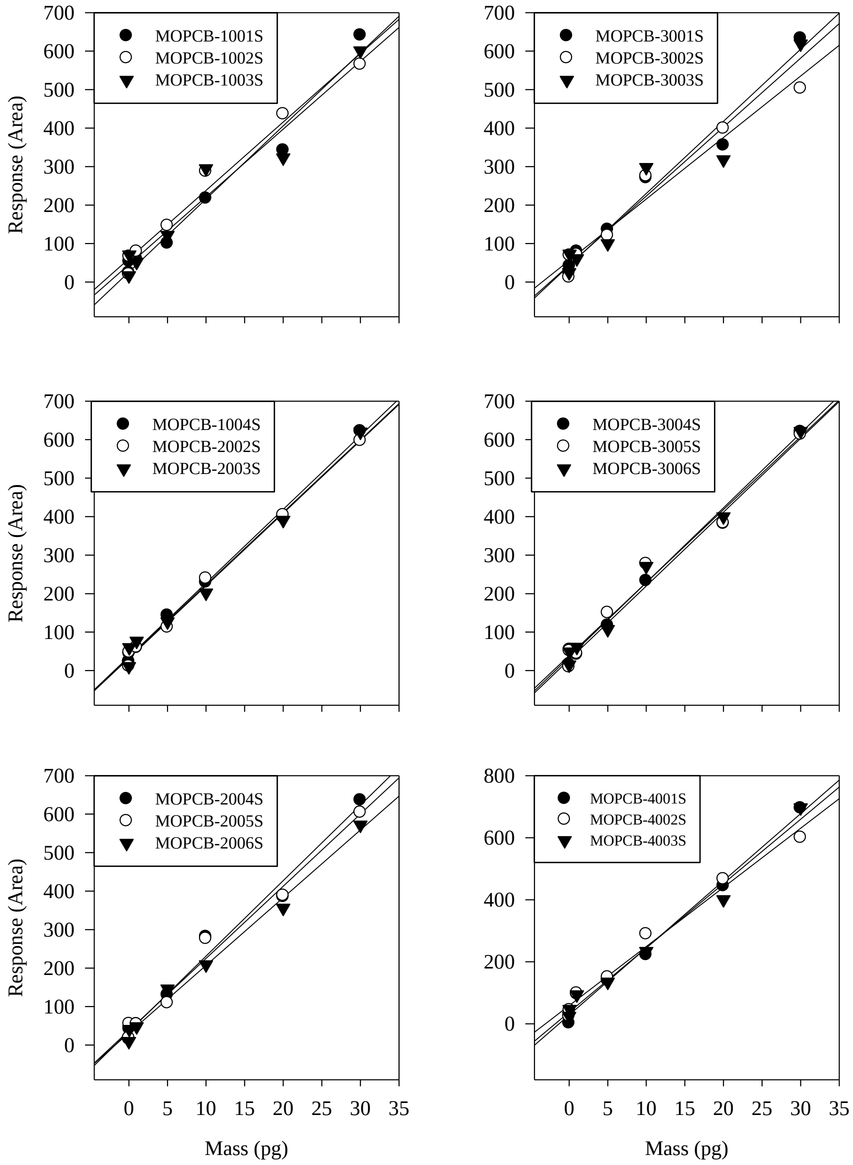

Figure D1. Calibration curves for the 31 MeO-PCBs with masses injected on column ranging from 0.1-30 pg.

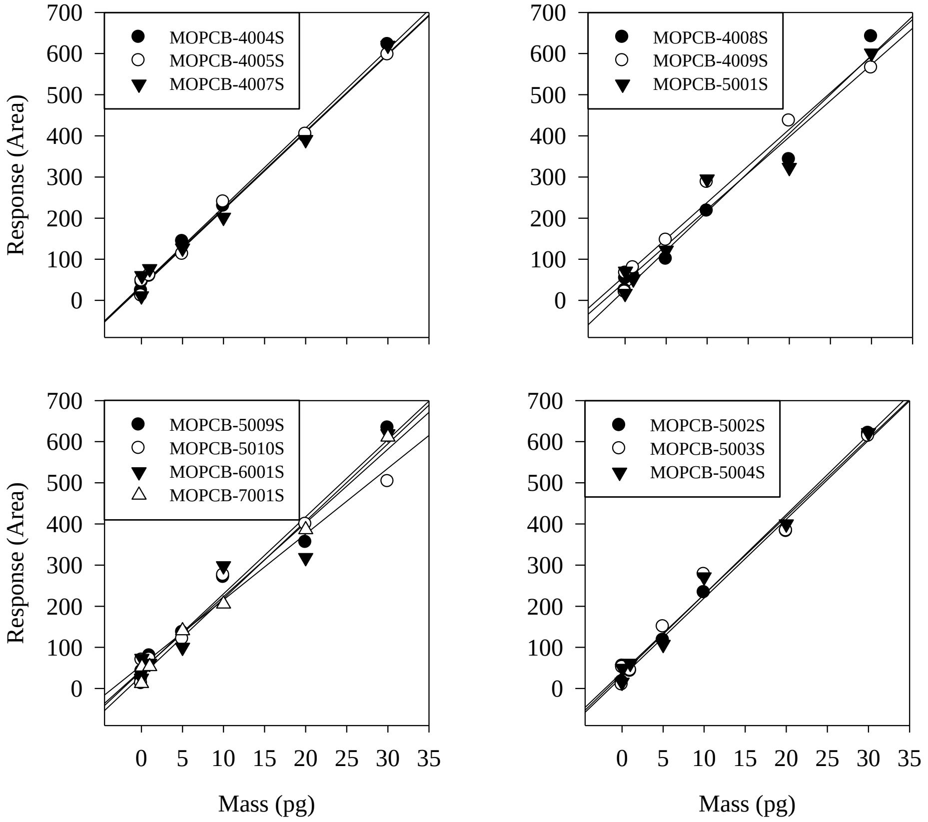

Figure D1 Continued.