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INTRACITY OCCURRENCE AND DISTRIBUTION OF AIRBORNE PCB CONGENERS IN CHICAGO

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Abstract

To evaluate the magnitude and extent of airborne PCBs in an urban area, we measured and investigated the temporal and spatial behavior of atmospheric concentrations of individual polychlorinated biphenyl (PCB) congeners as well as the sum of all congeners (ΣPCB) in both gas and particle phases at 27 locations across the City of Chicago in a single year (2009). In total, 141 gas-phase air samples were collected, including 22 pairs (44 samples) deployed at the same time but at two different locations, and 46 particle-phase samples. ΣPCB in the gas-phase ranged from 80 to 3000 pg/m^3, with a geometric mean (GM) of 530 pg/m^3, whereas particle-phase ranged from 8 to 160 pg/m^3, with a GM of 28 pg/m^3. We found the temporal variability to be about three times larger than the variability over space for all gas-phase congeners and ΣPCB. Around 50% of the sample PCB profiles resembled a mixture of a 1:1 vapor Aroclor mixture of 1016+1254, with most of the rest (30%) showing enrichment of PCB 3 (> 0.1), which did not match any Aroclor profiles. PCB 11 contributed to ~ 5% in all samples. The fractions of PCB congeners bound to particles ranged from 0.001 to 0.97. Our analysis shows that airborne PCBs are widely distributed across Chicago and confirms that most locations have a similar PCB distribution, but differ in the concentration levels. Volatilization continues to be the main release process of PCBs into the atmosphere, including both Aroclor and non-Aroclor congeners.

Graphical Abstract

Credit author statement

Andres Martinez: Conceptualization, writing-original draft preparation, data curation, visualization, methodology, investigation, project administration.

Andrew M. Awad: Formal analysis.

Michael P. Jones: Methodology, software.

Keri C. Hornbuckle: Writing-Review & Editing, Funding acquisition.

Declaration of competing interest

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

INTRODUCTION

Little is known about intracity spatial variability of airborne polychlorinated biphenyls (PCBs) in major metropolitan areas, and especially at the individual PCB congener level. More is known about the temporal variability at individual sites where long-term studies of airborne PCBs are conducted, clearly showing that concentrations of airborne PCBs in cities are correlated with temperature (Venier and Hites 2010; Salamova et al. 2015). However, the relative importance of spatial distribution of sources within a city compared to the temporal variability caused by local meteorological changes is not clear, and this hinders progress in identifying remediation strategies for airborne PCBs and for utilizing measurements for modeling regional and global fate and transport of these bioaccumulating, persistent and toxic compounds.

Industrialized activities in major cities left a legacy of pollution, including airborne sources of PCBs. In Chicago for example, a few airborne PCB sources including transformer storage yards, municipal sludge drying beds (Calumet, IN) and the CID Landfill have been identified, although their contribution to the total burden of airborne PCB to the Chicago airshed is not clear (Hsu et al. 2003; Yi et al. 2008). Further, the building boom during the second half of the 20th century, when PCBs were commonly used as additives to construction materials, left another potential source of airborne PCBs (Melymuk et al. 2013; Shanahan et al. 2015; Diefenbacher et al. 2016). Additionally, paint and pigment manufacturing results in PCB byproducts that are then released upon use (Hu and Hornbuckle 2010; Jahnke and Hornbuckle 2019). A small number of additional sources have been identified, including silicon products and sealant manufacturing and use (Anezaki and Nakano 2013; Anezaki et al. 2015; Anezaki and Nakano 2015; Herkert et al. 2018; Mao et al. 2019; Hombrecher et al. 2021; Mao et al. 2021). As a result, cities exhibit elevated levels of airborne PCBs (Hu et al. 2010; Melymuk et al. 2012; Salamova et al. 2015; Diefenbacher et al. 2016).

Due to all these likely sources and perhaps different emission behaviors, most of the time driven by meteorological conditions, airborne PCB concentrations can vary over 2 to 3 orders of magnitude during a few days for the same location, but also nearby sites can show this same level of variability when sampled at the same time. Thus, identification and understanding on how airborne PCB sources behave in a major city are challenging and therefore, not well understood. A few studies have attempted to determine spatial

and temporal variabilities of airborne PCBs in a major city, including Chicago, USA and Toronto, Canada (Hu et al. 2010; Melymuk et al. 2012), with the main goal of identifying PCB sources and their behavior.

High levels of airborne PCBs in cities have two major implications. (i) People are being constantly exposed to airborne PCBs via inhalation. Recent studies have shown that this exposure route could be as important as diet, especially for the more volatile congeners (Ampleman et al. 2015; Marek et al. 2017; Saktrakulkla et al. 2020). (ii) Major cities became important source emissions of PCBs that are transported and deposited elsewhere. Chicago, for example, is a constant atmospheric source of PCBs to Lake Michigan, and contributes the concentrations that provoke a consumption advisories for sport fish (Hornbuckle and Green 2003; Hornbuckle et al. 2006; Boesen et al. 2020). Further, PCBs can be transported via the atmosphere far from their sources, impacting cooler areas of the earth, such as the Arctic (Wania and Mackay 1996; Kallenborn et al. 2007; Hung et al. 2016).

Although it is well understood that ambient airborne PCBs are mostly present in the gas-phase, gas/particle partitioning is a relevant process affecting the fate and transport of PCBs, which could also affect human exposure to PCB (Harner and Bidleman 1998; Simcik et al. 1998; Dachs and Eisenreich 2000). Interestingly, few studies in the USA and around the world have measured PCBs bound to particles in ambient air, so there is a lack of data to enable better understanding of this partitioning process (Harner and Bidleman 1998; Simcik et al. 1998; Cindoruk and Tasdemir 2007; Kim et al. 2011; Li et al. 2015; Wu et al. 2017).

Here, we present results from a year-long field study designed to examine both spatial and temporal distributions of gas and particle airborne phases of individual PCB congeners in Chicago. We measured and report here the sum of all PCB congeners (ΣPCB) measured in 141 samples collected within the City of Chicago, Il, in 2009. We repeated measured airborne PCBs in 27 locations across the city, and on 22 days we collected a pair of samples at different locations. Our unique sampling approach was designed to evaluate the spatial and temporal variability of airborne PCBs in Chicago air. This study was part of a long-term sampling effort and although the concentrations of hydroxylated polychlorinated biphenyls measured in a subset of these samples have been previously discussed, the PCB congener concentrations described here have not been previously reported (Awad et al. 2016). We previously reported findings from 2007 and assessment of reported PCB inventories across the city but neither reports evaluated the particulate phase concentrations nor the spatial and temporal variability of the full suite of airborne PCB congeners (Hu et al. 2008; Hu et al. 2010; Shanahan et al. 2015).

We hypothesize that airborne sources of PCBs across the City of Chicago are heterogenous, where the differences are driven by meteorological conditions. The corollary hypothesis is that temporal variability of airborne PCB concentrations is larger than spatial variability. Further, we expect that that non-Aroclor congeners are emitted through volatilization and exhibit a similar temporal trend as Aroclor congeners. To address these hypotheses, the following aims were completed. (i) Analysis of the occurrence and distribution of airborne PCBs in both gas and particle phases; (ii) Investigation of the temporal and spatial variability

of airborne PCBs; (iii) Determination of the particle/gas partitioning behavior of individual PCB congeners.

MATERIAL AND METHODS

Airborne PCB Concentration Measurements:

High-volume air samplers (Hi-Vols) were mounted on the rear of two mobile medical clinic vans (Chicago Mobile C.A.R.E. Foundation of Chicago) to collect air samples throughout Chicago from January to December 2009. Details of the design and operation of the Hi-Vols are presented elsewhere (Hu et al. 2008; Hu et al. 2010). The sampling locations were primarily elementary schools where the mobile clinics provide service to the students and their families for diagnosis and treatment of asthma and related respiratory illness. When the vans visited the schools for clinical service, the Hi-Vols collected air samples for the 6 to 8 hour period that the van remained at the school. The samplers were operated with the assistance of the trained staff at Mobile C.A.R.E. The air was pumped at a flow rate of ~ 0.4 m^3/min through a quartz fiber filter (QFF) to retain particles and then through a XAD-2 resin cartridge to collect PCBs from the gas-phase. In total, 141 XAD-2 samples were collected from 27 locations, with an average of 5 samples per location, ranging from one to eight samples per location. From these 141 samples, 22 pairs (44 samples) were deployed at the same time but at two different locations. These 22 pairs allowed us to specifically investigate the spatial distribution of PCBs. We notice that this paired sampling approach is unique for a city like Chicago or even any city and, to our knowledge, is the first time it has been used at this scale. A subset of 46 QFF samples were collected and analyzed from 17 locations, with an average of three samples per locations, ranging from one to six samples per location, where six locations have only one sample. This subset of 17 locations represents the spatial extent of our sampling campaign. A map and a table with location information and number of samples collected are presented in the Supplementary Material (Table S1 and Fig. S1).

Preparation of Sampling Media:

The Amberlite XAD-2 resin (20–60 mesh, Supelco, Bellefonte, PA) was prepared by first suspending the material in nanopure water and removing fine particles. The resins were then refluxed in Soxhlet apparatuses with a series of solvents including methanol, acetone, hexane, acetone/hexane (1:1, v/v) in order. Cleaned XAD-2 resins were packed in 40 g aliquots in glass jars and then sealed in plastic ziplock bags. The QFF (20.3 cm × 25.4 cm, Whatman, Maidstone, England) were combusted in their aluminum sleeves at 450 °C overnight. When cool, the QFFs were weighed individually and labeled on the aluminum sleeves. The tared weights were recorded and the filters were resealed individually in the aluminum foil and stored in sealed plastic bags (Hu et al. 2010; Martinez et al. 2010; Awad et al. 2016).

Sample Extraction and Analysis.

The sample extraction method is described in detail elsewhere (Persoon et al. 2010; Ampleman et al. 2015; Herkert et al. 2016; Martinez et al. 2017). Briefly, XAD-2 and QFF were spiked with 25 ng of surrogate standards (PCB 14 (3,5-

dichlorobiphenyl), PCB 65-d5 (2,3,5,6-tetrachlorobiphenyl-d5, deuterated) and PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl)), and extracted by pressurized liquid extraction (ASE, Dionex ASE-300). ASE parameters were as follows; 1:1 (v/v) acetone and hexane mixture, pressure 1500 psi, temperature 100 °C, static time 5 minutes, static cycles 1, flush volume 60% and purge time 200 seconds. The extracts were cleaned through a Pasteur pipette filled with 0.1 g of combusted silica gel and 1 g of acidified silica gel (2:1 silica gel:sulfuric acid w/w) and eluted with hexane. The eluates were concentrated to ~ 0.5 mL and 25 ng of internal standard [PCB 30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)] was added. PCBs were detected and quantified as previously reported (USEPA 2010; Martinez et al. 2017). Tandem Mass Spectrometry GC-MS/MS (Agilent 7000) in multiple reaction monitoring (MRM) mode was used to quantify all 209 congeners in 171 individual or coeluting congener peaks. The GC was equipped with a Supelco SBP-Octyl capillary column (30 m × 0.25 mm ID, 0.25 mm film thicknesses) with helium as carrier gas.

QA/QC.

The performance of our methods was determined using field blanks, solvent blanks and surrogate standard recoveries. Field blanks consisted of cleaned XAD-2 resin and QFF were shipped from Iowa to Chicago and back but not installed in a sampler. A solvent blank was used for each batch of samples to check for system contamination especially for carryover after analysis of high concentration samples. Surrogate standards were added to every sample to correct for losses and improve precision. Performance standards were spiked on clean media and used to evaluate extraction methods. Both XAD-2 and QFF field blank data were consistent with a log-normal distribution. Thus, the limits of quantifications (LOQ) were calculated as the upper limit of the 95% confidence interval of the log10 transformed field blanks. The raw (i.e., untransformed) congener-specific LOQ for the XAD-2 samples ranged from 0.9 pg to 200 pg per sample with an average of 20 pg per sample. Regarding QFF, the congener-specific LOQ ranged from 1 pg to 300 pg per sample with an average of 30 pg per sample. Any congener value below the LOQ was replaced by $\mathrm{LOQ}/\sqrt{2}$. The statistical method used in this study, such as the Linear Mixed-Effects Model and the absolute deviation from the mean (see Data and Statistical Analysis section), require one to use a specific value for each variable in order to carry out the analysis. $\mathrm{LOQ}/\sqrt{2}$ was selected due to the number of values below the LOQ. Hornung and Reed (1990) argued that if less than 50% of the observations are below the LOQ, then the $\mathrm{LOQ}/\sqrt{2}$ is a better approach than the LOQ/2 approach. Surrogate standard recoveries were as follow; for XAD-2 the average surrogate percent recoveries of PCB 14, PCB 65-d5 and PCB 166 were 95 ± 11%, 100 ± 18% and 105 ± 14%, respectively. For QFF the average surrogate percent recoveries for PCB 14, PCB 65-d5, and PCB 166 were 62% ± 27%, 73% ± 23%, and 81% ± 20%, respectively. Recovery correction was performed on all samples to account for any losses during laboratory processes; PCB 1 to 39, PCB 40 to 127, and PCB 128 to 209 corrected with recoveries from PCB 14, PCB 65-d5, and PCB 166, respectively. Although we quantified 171 individual or coeluting congener peaks, further evaluation focused on 103 individual congeners in the gas phase with ≥ 90% frequency detection and 101 congeners in the particle phase with ≥ 60% frequency detection (see Tables S2 and Table S3 for geometric mean of the individual congeners). Individual

congener masses captured by the XAD and QFF samples, including blanks, concentrations, TSP and meteorological data (atmospheric temperature and wind speed) are published open access at https:doi.org/10.1594/PANGAEA.935238 (Martinez et al. 2021).

Data and Statistical Analysis.

Gas and particle phase measurements were consistent with a log-normal distribution, and thus they were log10-transformed for future analysis. Atmospheric hourly temperature, wind speed and direction, atmospheric pressure and cloud cover were obtained from Integrated Surface Database (ISD) released by the National Oceanic and Atmospheric Administration's (NOAA) National Environmental Information (NCEI), Chicago Midway Airport. (National Centers For Environmental Information) These hourly values were averaged for each deployment time and used to analyze correlations with the gas and particle phases.

Temporal variability of the gas-phase was further evaluated using a Linear Mixed-Effects Model (LME), where seasonality, time expressed in Julian days starting from January 1 2009 to December 31 2009, the inverse of the atmospheric temperature, and wind speed were included as fixed covariates. Preliminary results from the LME model showed that only atmospheric temperature and wind speed coefficients were statistically significant most of the time, thus the other meteorological parameters were no longer considered in the model. We combined all samples across all sites into the analysis. To account for correlation among concentrations measured at the same site, the model includes site as a random effect. In addition, temporal changes were modeled in terms of a linear time trend, as well as sine and cosine time fluctuations. We did not find any evidence of autocorrelation nor partial autocorrelation in our samples.

$$log_{10}C_{jt,i} = \beta_0 + \beta_{1i} \times \sin(z \times t) + \beta_{2i} \times \cos(z \times t) + \beta_{3i}t + \beta_{4i}(1000/T_{jt}) + \beta_{5i}WS_{jt} + S_{ji} + \epsilon_{jt,i} \quad \text{Eq. 1}$$

where jt indexes the sample taken at site j at time t and i indexes the specific PCB congener or ΣPCB. $C_{jt,i}$ is the airborne concentration of the ith PCB or ΣPCB in pg/m^3, the $\beta_i s$ are the regression coefficients for modeling the ith PCB or ΣPCB, z equals (2 π)/365.25, t is the time in days when the sampler was turned on, T_{jt} is the atmospheric temperature in Kelvin, WS_{jt} is the wind speed in m/s, S_{ji} is the random effect for site i, and $\epsilon_{jt,i}$ is the error term for the ith PCB or ΣPCB. We examined the possibility of autocorrelation and partial autocorrelation in our time series (Eq. 1) for each individual congener and ΣPCB using both acf and pacf functions in R. We did not find any evidence of autocorrelation in our samples.

Regarding the possibility of including spatial information into the temporal model, such as building construction age and surface buildings next to our sampler locations, it was unfortunately not possible to find reliable data for Chicago. Others have shown that the construction age of buildings might be related to the concentration of PCBs in the surroundings air, due to the use of Aroclors in sealants and caulking (Diefenbacher et al. 2016). The t-test, Anova and Tukey test for multiple pairwise comparisons were utilized to determine statistical significance between sampling sites and collection time.

To compare the spatial and temporal distributions of individual PCB congeners and ΣPCB, we express the variability for both distributions in terms of the absolute deviation from the mean (ADM)

$$ADM(PCB_i) = \frac{1}{n}\sum_{j=1}^{n}\left|X_{j,i} - \overline{X_i}\right| \quad \text{Eq. 2}$$

where $X_{j,i}$ is the log10 of the *i-th* PCB congener measured on the sample *j* and $\overline{X_i}$ is the average of the log-transformed congener *i* values over the n samples. For the spatial analysis, $\overline{X_i}$ is the average concentration of the two samples collected at the same time. Using this pairwise sampling approach to estimate spatial variability, we did not need to correct for season (mainly temperature) (Buehler et al. 2004; Hu et al. 2010). For the temporal analysis, $\overline{X_i}$ is the average concentration of all the samples collected at the same location but on different days. This method was carried out for each of the 103 congeners and for ΣPCB.

To evaluate similarity between PCB conger profiles, cosine theta ($cos\ \theta$) was used. $Cos\ \theta$ is the cosine of the angle between two multivariable vectors (PCB congener profiles); a value of 0.0 indicates that the two vectors are completely different (perpendicular) and 1.0 describes two identical vectors (DeCaprio et al. 2005; Martinez et al. 2015; Martinez et al. 2017). All statistical analyses were performed using R (Version 3.6.0).

RESULTS AND DISCUSSION

Gas PCB Phase.

Gas-phase ΣPCB concentrations range from 80 to 3000 pg/m^3, with a geometric mean (GM (Geometric standard deviation, GSD)) of 530 (2.2) pg/m^3 and an interquartile range (IQR) of 480 pg/m^3 (n = 141) (Fig. 1, top right panel). These values are somewhat larger than our 2006–07 measurements of the City of Chicago (n = 184, t-test of log10 values, p = 0.051). They ranged from 75 to 5400 pg/m^3, with a GM of 450 (2.9) pg/m^3 and an IQR of 760 pg/m^3 (Hu et al. 2010). The range is also similar to concentrations reported by Hites and coworkers from samples collected in 2009 at the long-term monitoring site in Chicago (n = 28) (t-test of log10 values, p = 0.5), with a range of 140 to 1800 pg/m^3, GM of 530 (2.1) pg/m^3, and IQR of 620 pg/m^3 (Indiana University 2021). Individual congeners range from non-detected to 440 pg/m^3, with GMs varying from 0.09 to 35 pg/m^3 (Fig. 1, top left panel). A 100 times reduction in the untransformed concentration levels is observed with increasing chlorination. For example, geometric means of PCBs 3 and 203 were 35 and 0.23 pg/m^3, respectively.

We find no clear evidence of spatial trends in concentrations of any congener or ΣPCB across the City of Chicago. We find no clusters of sites with statistically higher or lower concentrations. We do find evidence that some sites exhibit statistically different concentrations than other sites. To evaluate these differences between sites, we examine locations where we collected three or more samples. We have 136 samples and 24 locations that meet this criterion (Fig. 2). Only 24 of the individual congeners yield a significant difference in the log10 concentration among locations (Anova, $p < 0.05$), e.g., PCBs 1, 4, 5, 8, 9, 10, 16, 18+30, 19, 24, 90+101+113 and 99. ΣPCB did not show significant variability

across locations. Of these 24 congeners, a multiple comparison corrected test for differences among sites indicated significance only for PCBs 1, 4, 5, 9, 10, 19 and 50+53 (Tukey test, $p < 0.05$), where no clear site was lower or higher in levels between these congeners and locations. All the sites are located in residential zoning. These results indicate that there is little spatial difference between our sampled sites across the City of Chicago.

The LME model reveals that inverse atmospheric temperature and wind speed are significant predictors of airborne concentrations of PCBs and ΣPCB (Table S4). Their estimated coefficients in Eq. 1 are negative, indicating that as temperature increases and wind speed decreases, the predicted value increases. As expected, the predicted values show that PCB concentrations are higher during warmer months, with factor of 5 to 10 between colder and warmer months (Fig. 3). Even though we have only 2009 data, time (with coefficient β_3) is a significant predictor of the log10 concentration for 24 individual congeners (e.g., PCBs 2, 3, 15, 54, 77, 83, 90+101+113, 105, and 203), where all of them, with the exception of PCBs 3 and 90+101+113, are significantly decreasing with time, consistent with previous reports of half-times of PCBs for the City of Chicago (Salamova et al. 2015). Although PCBs 90+101+113 coelute in our analytical method and PCB 101 is relatively high in Aroclor 1254 (~ 7%) (Frame et al. 1996), it is interesting that PCB 90 and 113 are not Aroclor congeners and we observe an increase of them in the air. The PCBs 90+101+113 has been detected in paint colorants (Jahnke and Hornbuckle 2019).

Our model resolves 50% or more of the variability in concentrations for most congeners. In general, we see an average increase of 25% in the resolved variability in the concentrations when the random effect (site) is included in the model (Table S4). For example, PCBs 11 and 52 yielded a R^2 of 0.62 and 0.41, respectively. However, the model did not perform well for congener PCB 3 with R^2 of 0.09. Overall, the LME model yielded a mean square error (MSE) of 0.07 and predicted an error, defined as the ratio between the predicted and measured values, within a factor of 2, 20% of the time.

Most of the total variability is resolved by the meteorological parameters. We investigated how the individual parameters such as seasonality together with time, and both meteorological parameters (inverse temperature and wind speed), and the random effect, alter the fitness of the model. On average, the seasonality with time, meteorological parameters and random effect resolved 37%, 48% and 6% of the variability in concentration for all congeners and ΣPCB, respectively (Table S5).

Our spatial and temporal comparisons indicate that temporal variability is larger than spatial variability for all 103 individual PCB congeners and ΣPCB, but the magnitude of the difference is congener dependent. We compared temporal and spatial variability using the ADM metric in Eq. 2. To investigate temporal variability, we did not want to adjust for any factors that change with time, namely seasonal meteorological variables. To remove temporality from spatial variability, we used data from sites measured at the same time. As seen in Fig. 4, temporal variability is larger than the spatial variability at each of the 3 percentiles (25^{th}, 50^{th} and 75^{th}). For ΣPCB the median temporal variability is 3 times higher than the median spatial variability, and for most individual congeners, this factor is typically above 2. For example, PCBs 3, 11, 52, 118 and 187 yield factors of 2.0, 2.0, 2.4, 3.9 and

7.4 (median), respectively (Fig. 4). We observe a slight increase in the difference between the spatial and temporal variabilities with increasing chlorination in the congeners (Fig. S2). We previously reported that both spatial and temporal variabilities were in the same range in the City of Chicago (Hu et al. 2010). The results indicate that temporal variability is more important than spatial variability in Chicago and the city could be considered as a homogenized source of airborne PCBs.

The gas-phase congener profiles are mostly dominated by congeners with one to four chlorines, including PCBs 3, 8, 11, 18+30, 20+28, 31 and 52, with an average fraction of at least 0.045 from untransformed data. Most congeners only contribute a relatively small amount to the variability of total PCB, with the exception of PCBs 8 and 11 (standard deviation (std dev) = 0.02), and PCB 3 (std dev = 0.1). This is shown in Fig. 5 by the relatively large error bars for PCBs 3, 8 and 11. The average of the congener profile resembles a vapor mixture (Du and Rodenburg 2007; Rodenburg and Meng 2013) 1:1 of Aroclors 1016 (or 1242) and 1254, with a $cos\,\theta$ of 0.72, and if PCBs 3 and 11 are removed from the samples, the $cos\,\theta$ increases to 0.89. The similarity of Chicago airborne PCB distribution to these Aroclors has been reported before by our group and others (Hu et al. 2010; Rodenburg and Meng 2013). In general, the samples are similar among them, with an average of $cos\,\theta$ of 0.82 ± 0.15, but ranging from 0.13 to 0.99 (Fig. S3 shows a heat chart of pairwise $cos\,\theta$ comparison). If only PCB 3 is removed from the samples, we observe an increase in the similarity among samples (average of $cos\,\theta$ of 0.91 ± 0.08). These findings suggest that temporal and spatial variabilities marginally affect the distribution of PCBs, indicating that the locations are constantly being impacted by the same PCB source or sources, independent of the time of the year. One probable source can be volatilization of PCB from Lake Michigan. The average $cos\,\theta$ between the individual samples and a PCB volatilization profile estimated by our group (Boesen et al. 2020) was 0.92 ± 0.06 (PCB 3 was not included).

Many samples were enriched in PCB 3 (41 samples with fraction > 0.1). Our analytical method provides us a high level of confidence in our identification of PCB 3 in our air samples: Our sampling methods, extraction methods, chromatographic method, and detection using tandem mass spectrometry is optimized for the whole suite of PCBs and reduces the probability of misidentification and quantification. These enriched PCB 3 samples show an unusual temporal trend, with highest concentrations in early and late winter. We previously noted enriched PCB 3 in air samples from East Chicago, IN, southeast of the City of Chicago (Martinez et al. 2015). Interestingly, those samples were also collected at the end of February, but in 2008. Our findings suggest a non-Aroclor source from later winter-time anthropogenic activities.

Particle PCB Phase.

ΣPCB captured on QFF filters range from 8 to 160 pg/m^3, with a GM of 28 (2) pg/m^3 and an IQR of 23 pg/m^3 (n = 46). Individual congeners range from non-detected to 30 pg/m^3, with GMs varying from 0.02 (2.1) to 2.1 (1.4) pg/m^3 (Fig. 1, bottom panels). Unlike what we found in the gas-phase, there is no relationship between congener chlorination and concentration. Similar to the gas-phase, there is little evidence of spatial trends or site-based

differences in the particle-bound PCBs (Fig. 6). Of the sites with three or more samples (n = 37), only 18 of the 101 congeners exhibit difference in log10 concentration among sites. Of these 18 congeners, a multiple comparison corrected test for differences among sites indicated significance only for 10 congeners: PCBs 90+101+113, 92, 95, 131, 145, 152, 161, 171+173, 175 and 176 (Tukey test, $p < 0.05$), where no clear pattern was observed between these congeners and locations. These results indicate that there is little spatial difference between sites across the City of Chicago. Further, no temporal trend was observed for most congeners in the particle phase, although a few high value samples were observed during the warmer months, as is shown in Fig. S4.

Total suspended particle (TSP) range from 20 to 1000 μg/m^3, with an average of 550 ± 320 μg/m^3. These values are relatively high in comparison to other studies (Harner and Bidleman 1998; Simcik et al. 1998), although no effect was observed in the particle fraction or the particle/gas partition coefficient (K_p) calculations. ΣPCB particle fraction (Φ) averages 0.1 ± 0.08, but there are three samples with considerably higher values (> 0.2). The particle fraction from individual PCB congeners range from 0.001 to 0.97, with the greatest contribution found in the higher chlorinated congeners (Fig. 7). We sometimes observe a high variability on the Φ, especially in the low molecular congeners, which could be a due to an artifact in our particle measurements. However and due to the number of samples (n = 46), the medians yield reasonable results. This indicate that the number of samples can be important to avoid misinterpretations. Our findings are consistent with other studies that have reported congener-specific particle concentrations in a major urban area (Harner and Bidleman 1998; Simcik et al. 1998; Yeo et al. 2003; Kuzu et al. 2014).

The log10 K_p of individual congeners range from −5.7 to −0.54 m^3/μg with an increase in the K_p values with increasing chlorination. We also observe a large variability of the K_p values for the same congeners, averaging between the minimum and maximum values for the same congener of 2.6 ± 0.4 log units (Fig. S5). The log10 of K_p correlated with the octanol – air partition coefficient (K_{oa}) corrected by temperature (Li et al. 2003; Herkert et al. 2016) (Fig. S5). These results suggest absorption into the organic layer of the particles as the dominant gas-particle process for PCBs (Harner and Bidleman 1998; Simcik et al. 1998; Kim et al. 2011). Site-specific analyses also yield a positive correlation between log K_p and log K_{oa} ($p < 0.05$), with the exception of the 5/28/09 sample collected at site OW, which had a relative high fraction of PCBs in the particles in relation to the gas-phase, and inconsistent with chemical equilibrium (Fig. S6 shows as examples sites OW and SO). The slopes were between 0.14 and 0.64, consistent with previous reports (Harner and Bidleman 1998; Lohmann et al. 2000; Kim et al. 2011; Wu et al. 2017), with the exception of the OW sample already mentioned and a sample collected at site AD (9/9/09).

We investigated the performance of two Kp sorption models based on organic matter and a dual sorption model based on organic matter and soot, respectively (details are described in the Supplementary Material). In general, the organic matter prediction model does a better prediction for the high chlorinated congeners (from ~ PCB 158), but underestimates the rest of the congeners by at least 1 log unit (Fig. S7, blue line). The dual model (organic matter and soot) yields a better fit for the low to middle chlorinated congeners, but slightly overpredicts the highly chlorinated congeners (Fig. S7, red line). Although the dual model

fits the data better than the single model, each deployment time seems unique, thus, making it difficult to generalize (Fig. S8). For example, the dual model fits very well with the measured values for deployment 3/5/09, whereas the single model fits very well the high chlorinated congeners from deployment 7/31/09. Further, the dual model fits very well most of the low to middle PCB congeners from deployment 8/10/09, but the single mode fit better the high chlorinated PCBs (Fig. S8). This finding suggests that the organic matter and soot composition of the particles are not constant, which it does not support a general sorption model for our TSP measurements all size of particles, with unknown variability in chemical composition.

Conclusions.

Through an airborne sampling campaign designed to examine spatial and seasonal variability of airborne PCBs in the City of Chicago, we found no evidence of large individual sources of airborne PCBs. This study showed that Chicago is burdened with a large number of active sources of airborne PCBs characteristic of volatilization of gas-phase PCBs from Aroclor-contamination. We found no spatial pattern or location with low or high values. Most airborne PCBs are found in the gas-phase and concentrations are highest in warm weather and during calm winds. Atmospheric temperature and wind speed are the most relevant environmental parameters that drive airborne PCB concentration in the atmosphere. Our study indicates that legacy sources are the most important contributors to Chicago air, with Aroclor 1016 (and/or the highly similar Aroclor 1242) and Aroclor 1254 dominating. There is evidence of non-Aroclor sources of PCBs 11, 19, 24, 35, 67, 68, 152, 175, 207 and 209. Even though PCB 3 is found in Aroclor mixtures (~ 0.002 fraction in Aroclors 1016 and 1242), the levels and temporal trend found from 41 samples are inconsistent with an Aroclor legacy airborne source. Currently, there is insufficient data to support any hypotheses of PCB 3 origin. Individual fractions of PCB bound to particles ranged from 0.001 to 0.97, with only the most chlorinated PCBs having significant burden in the particulate phase. We found that PCB particle-gas partitioning to be more consistent with a model predicting absorption into organic matter and adsorption onto soot. However, the model results were also time dependent, suggesting that organic matter and soot composition in the particles vary, and that PCB airborne and particle matter sources may be independent of each other.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Novel sampling strategy to evaluate PCB spatial variability in Chicago via Hi-Vols.
- Temporal variability ~ 3 times larger than spatial variability for gas-phase PCBs.
- Most locations show a similar PCB congener distribution across Chicago.
- Third of samples show enrichment of PCB 3 (> 10%) in gas-phase.
- Volatilization continues to be the major release process of PCBs into air.

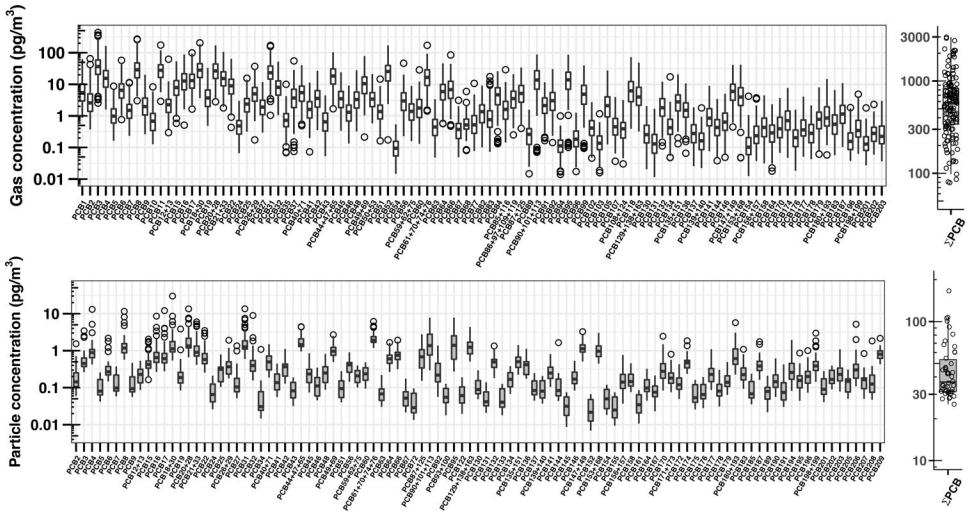

Figure 1.

Summary of individual congener and ΣPCB concentrations in gas and particle phases. Top panels represent gas-phase (n = 141, 103 congeners) and bottom panels represent particle-phase (n = 46, 101 congeners) from 2009 samples in Chicago. The box plots include the maximum, 75th percentile, median, 25th percentile and the minimum value. Please note the difference in the x-axes scale for the individual PCB congeners plots and y-axis scale.

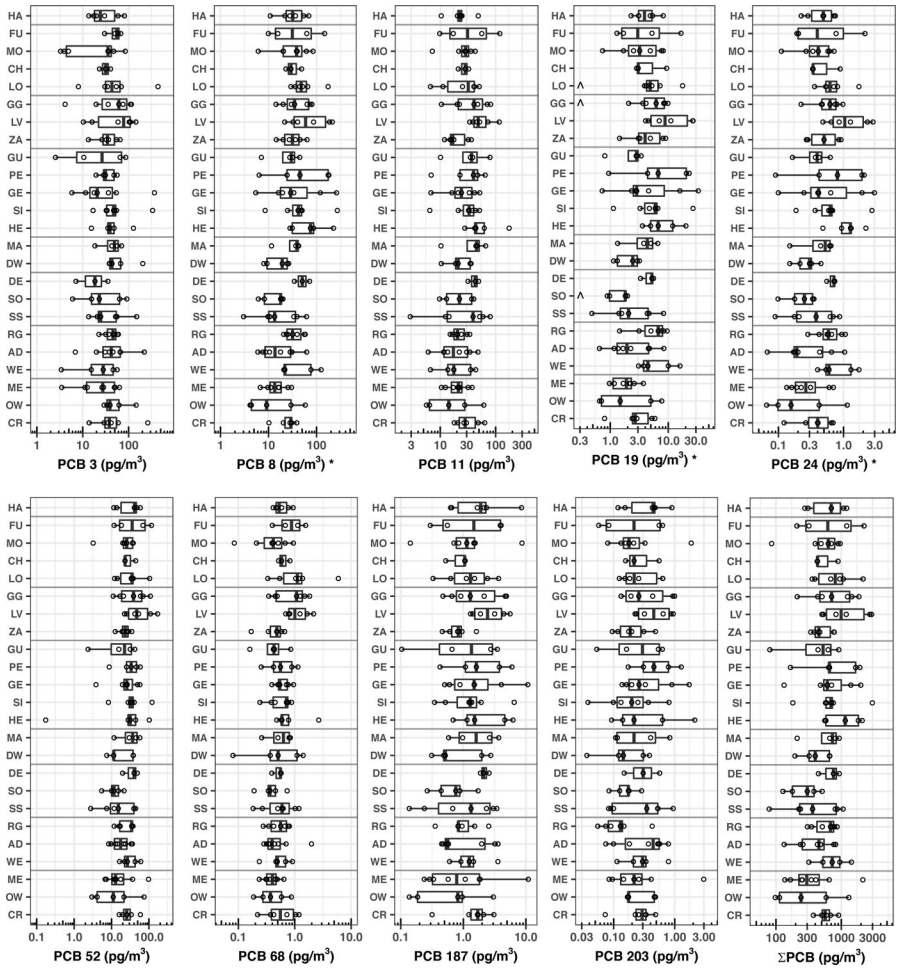

Figure 2.

Site-specific concentrations of selected PCB and ΣPCB (n = 136). Grey horizontal lines separate clusters of sites of less than 2.5 km of distance, circa from north to south. Sites with three or more samples were included. Asterisks (*) indicate significant differences in log10 concentration among locations (Anova, $p < 0.05$). Carets (^) in PCB 19 plot indicate a significant difference between locations SO - GG and SO - LO (Tukey test, $p < 0.05$, See text). The box plots include the maximum, 75th percentile, median, 25th percentile and the minimum value. Please note the difference in the x-axis scale.

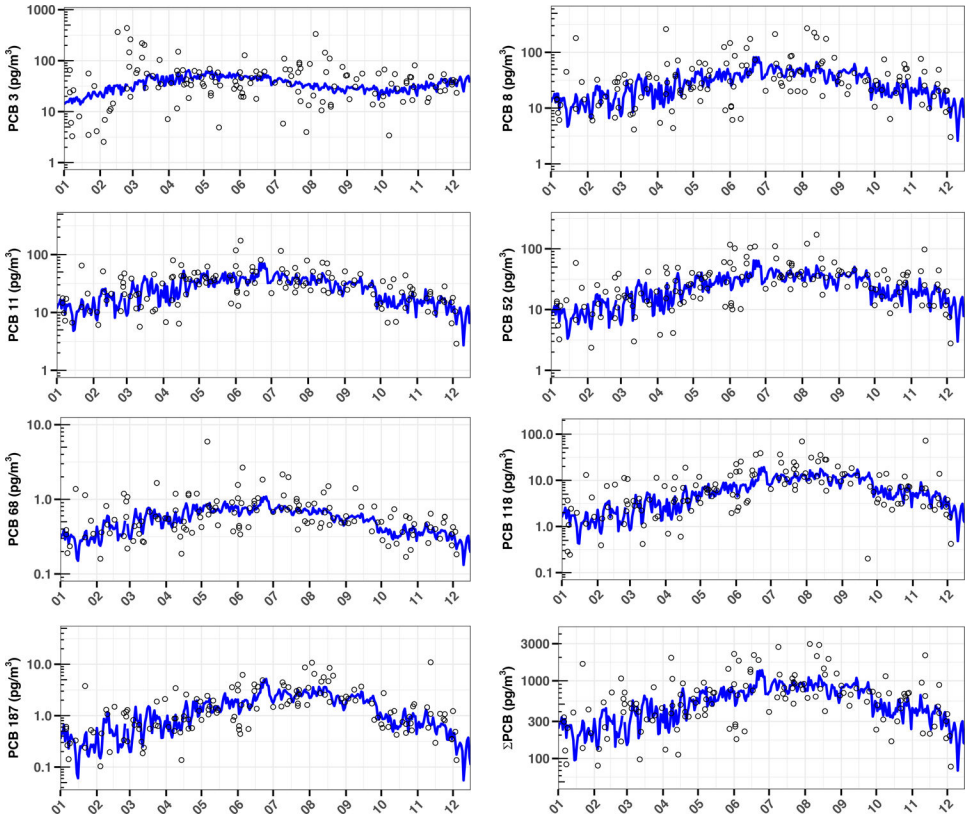

Figure 3.

Time series of selected congeners and ΣPCB for Chicago. Void circles are observations (n = 141) and blue line represents LME model (Eq. 1). LMER predictions were calculated using daily meteorological data. The x-axis represents the months of the year. Please note the difference in the y-axis scale.

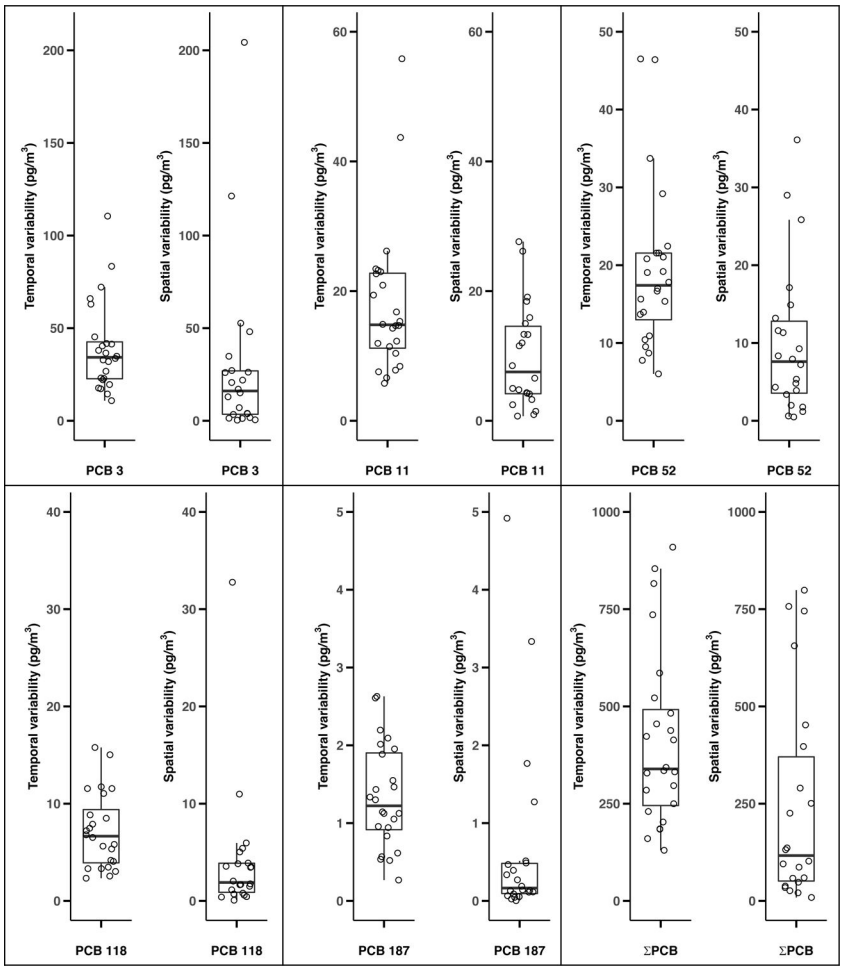

Figure 4.

Spatial and temporal variability as defined as ADM in Eq. (2) for selected PCB and ΣPCB. Spatial variability was calculated from 22 paired samples that were collected at the same time but at different locations. Temporal variability was calculated for locations with 3 or more samples taken at different deployment times. The box plots include the maximum, 75th percentile, median, 25th percentile and the minimum value. Please note the difference in the y-axis scale.

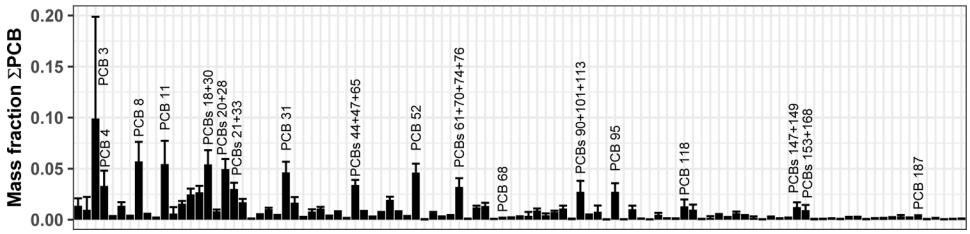

Figure 5.

Average PCB congener profile in mass fraction of ΣPCB (n = 141) using untransformed data in the gas phase. Error bars represent one standard deviation above the average.

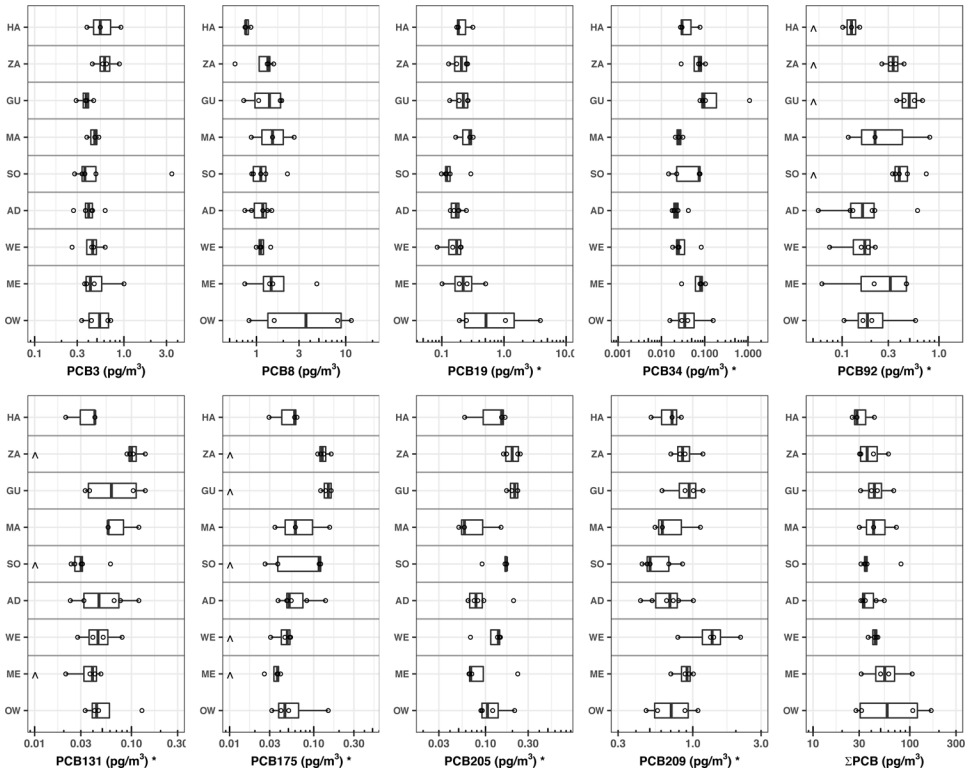

Figure 6.

Site-specific concentrations of selected PCB congeners and ΣPCB (n = 37) in particle-phase. Grey horizontal lines separate clusters of sites of less than 2.5 km of distance, roughly from north to south. Sites with three or more samples were included. Asterisks (*) indicate significant differences in log10 concentration among locations (Anova, $p < 0.05$). Further, carets (^) in PCB plots indicate a significant difference between locations (Tukey test, $p < 0.05$, See text). The box plots include the maximum, 75th percentile, median, 25th percentile and the minimum value. Please note the difference in the x-axis scale.

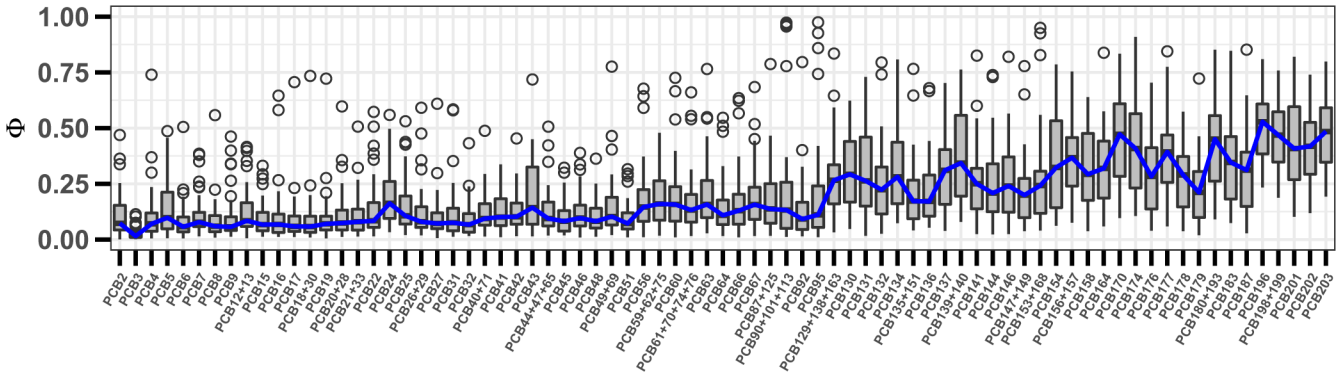

Figure 7.

Particle fraction (Φ) of individual PCB congeners in Chicago air (77 congeners, n = 46). The blue line connects the median of each congener. The box plots include the maximum, 75th percentile, median, 25th percentile and the minimum value.