Distinguishing Aroclor and non-Aroclor sources to Chicago Air

Jacob C. Jahnke, **Andres Martinez**, **Keri C. Hornbuckle**[*]

Department of Civil and Environmental Engineering, IIHR-Hydroscience & Engineering University of Iowa, Iowa City, Iowa USA 52242

Abstract

Many polychlorinated biphenyl (PCB) congeners are found in both legacy Aroclor mixtures and modern materials, and both contribute to PCBs levels in ambient air. The various sources of PCBs make it difficult to quantify the relative importance of emissions from remaining legacy materials and emissions of PCBs released from production and use of modern products. To address this challenge, we utilized active and passive sampling, analytical methods optimized for PCBs, and Positive Matrix Factorization (PMF) and cos theta to examine the chemical signature of PCBs in Chicago air. Here we report our findings for over 640 samples collected over seven years and analyzed for all 209 congeners. We conclude that Aroclor sources (1254, 1016/1242, and 1260) are consistent and dominant contributors to Chicago air. However, non-Aroclors sources accounted for 13% – 16% of the total PCBs measured. Our analysis indicates non-Aroclor sources explain 99% of PCB11, 90% of PCB 68, and 58 – 69% of congeners with 8 to 10 chlorines in Chicago air. All of these are known to be emitted from paints or silicone polymers. Additionally, we identified over 20 congeners that have non-Aroclor contributions of more than 50% including PCB 3 (4-monochlorobiphenyl, 83% non-Aroclor) as well as 7 congeners of unknown sources: PCBs 43, 46, 55, 89, 96, 137, and 139+140. Non-Aroclor emission sources contribute to the entire range of congeners from mono- to decachlorobiphenyls. We found evidence of highly localized non-Aroclor sources including a signature similar to that of green paint. We also found source signals similar to the PCB congeners volatilizing from and absorbing to neighboring Lake Michigan. The measured profiles vary from season to season: lower chlorinated congeners dominate in winter months while higher chlorinated congeners contribute more in summer.

Graphical Abstract

[*]Corresponding author keri-hornbuckle@uiowa.edu Ph (319 384-0789).
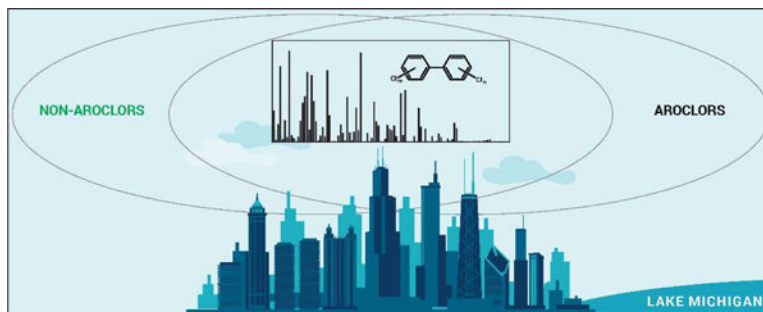
Introduction

Airborne polychlorinated biphenyls (PCBs) are found throughout the world, in both urban and remote locations. Purposeful manufacturing is the original source of PCBs and there is no report of natural sources of these persistent, bioaccumulating and toxic compounds. In North America, Aroclors were sold until their ban in 1979. Their presence in the environment is widely documented and results from the magnitude of use, the wide variety of applications, and poor handling of waste [1]. While legacy use of Aroclors is often assumed to be the sole source of PCBs to air, many studies have shown that new sources of PCBs also contribute [2–8]. It is unclear, however, what effect these previously unrecognized non-Aroclor sources have on the total measured PCBs in air and how they can be distinguished from the legacy sources. The importance of non-Aroclor sources was first identified by multiple groups when PCB 11 was found in air (Chicago, Antarctica, and around the Great Lakes) and in consumer goods [2–4, 9]. Its presence in air was linked to modern production of colored pigments used in paints applied on both indoor and outdoor surfaces [2, 10–12]. However, PCB 11 is not the only congener found in paint pigments and colorants [13–16] and Rodenburg et al provide explanations for the presence of PCBs in paint pigments [17]. Other congeners are found at similar or higher concentrations and may also contribute to the total PCBs found in air.

Non-Aroclor sources may be important contributors to PCBs measured in air, but it is difficult to quantify their importance for a few reasons. First, many of the same PCBs volatilize from non-Aroclor sources and Aroclor sources (Figure 1). There have been at least 146 individual and co-eluting congeners reported as non-Aroclors [13–16, 18, 19]. Most of these congeners are also found in Aroclor mixtures. Second, there are many different non-Aroclor sources. Modern production of colored pigments and cabinet sealants, and other industrial activities create PCBs as byproducts that are released into the environment around the world [15, 18–20]. These non-Aroclor sources may be significant. Many studies have found PCB 11 and other congeners in pigments, colorants, and common consumer goods and found that these congeners can be emitted into air and leached into water [13–16, 21]. Pigments and paint were found to be the largest source of PCBs to air in China from 2016 to 2017 [22]. In Chicago alone, modern paint sources emit about 3 kg of PCBs each year [23]. It is likely that there are many other non-Aroclor sources of airborne PCBs that have not yet been discovered. Finally, besides the many congeners that are present in both Aroclors and non-Aroclors, PCBs vary in chemical mass, vapor pressure, tendency to partition between

environmental matrices, and vulnerability to reaction and decay [1, 24, 25]. Gradually, the profile of PCB congeners in air will change due to these variable characteristics and environmental conditions. Also, both Aroclor and non-Aroclor emission sources to a region vary over space and time [3, 26, 27]. The varying properties of PCBs, the different sources of PCBs, and the different PCBs in those sources make linking PCBs measured in air to their emitters difficult.

PCB emissions can lead to inhalation exposure comparable to that of diet, the commonly assumed largest source of PCBs to humans [28, 29]. PCBs are group 1 carcinogens and potential neurotoxins and endocrine disruptors [30]. They are implicated in the development of metabolic syndrome and associated with many neurodevelopmental disorders such as attention deficit/hyperactivity disorder (ADHD), autism, and abnormal scores for conduct and can lead to deficits in executive function [31–39].

With a goal of linking airborne PCBs to sources, we established in 2006 a network of air sampling platforms across the City of Chicago and surrounding area [41, 42]. The network was maintained and evolved over six years and included two distinct methods for sampling air for PCBs: high volume air samplers (Hi-Vols) and polyurethane foam passive air samplers (PUF-PAS). Our initial findings from the network included the discovery of PCB 11 in every Chicago air sample. Airborne PCBs were widely distributed across Chicago and most locations had a similar PCB distribution. Volatilization was the main release process of both Aroclor congeners and non-Aroclor PCB 11 into the atmosphere and explains why airborne PCB concentrations in Chicago vary over time more than space [42, 43]. Shanahan et al. examine PCB reservoirs in Chicago and their emissions and found they are not correlated with population density [23]. Previously, Chicago air was shown to be contaminated by commonly produced Aroclors 1242 and 1254 from 1996 to 2007 [44].

We designed an analytical method optimized for its selectivity and sensitivity for airborne PCB congeners. There are other ways to analyze PCBs in an environmental sample, but they can lead to different results as many methods have shortcomings. For example, EPA methods 608 and 8082 measure select congeners commonly found in Aroclors. The measured congeners are compared to Aroclor profiles and reported in Aroclor concentrations. Both primarily use gas chromatography with electron capture detection (GC/ECD) and are relatively inexpensive methods to measure PCB concentrations in many samples [45]. These methods assume Aroclors are completely unaltered from the time they were used to the time they were measured in air. This is often not the case, however, as many mechanisms can alter Aroclor profiles causing them to change over time [46, 47]. The United Nations recommends a group of seven commonly measured congeners (iPCB7 – PCBs 28, 52, 101, 118, 138, 153, and 180) that are used to predict total concentrations [48]. The iPCB7 congeners are relatively easy and inexpensive to measure and can be compared to many other studies that also use just those congeners [49–51]. This method has been reported to severely underestimate concentrations, however [45]. The EPA methods 608 and 8082 and the iPCB7 methods also ignore the many congeners emitted from non-Aroclor sources but not in Aroclor mixtures, such as PCB 11 and many lower chlorinated congeners, which can cause non-Aroclor sources to remain undetected. To measure all 209 congeners, a mass selective detector is required. EPA method 1668 requires a high-resolution mass

spectrometer [52]. In this study, we use triple quadrupole technology to identify and quantify PCB congeners with a high level of sensitivity and selectivity adequate for our required detection limits [2, 12, 53, 54].

Several studies have used techniques such as Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA) to identify sources of PCBs and their locations. These techniques have successfully identified Aroclor sources in air and sediment and have even noted non-Aroclor sources [44, 53, 55]. However, distinguishing non-Aroclor sources from Aroclor sources has received limited attention [22]. Together with our sampling and analytical chemistry methods, we hypothesized that with PMF, coupled with cos theta and other statistical methods for examining similarities in PCB signatures, we could quantitatively identify the contributions of both Aroclor and non-Aroclor sources.

In Chicago, we expected Aroclors to be the dominant source of PCBs, regardless of sampling method. We also expected to detect non-Aroclor signals, including those that are localized and only appear intermittently. Most importantly, we hypothesized that a PCB signature from non-Aroclor sources could be distinguished from a PCB signature from multiple Aroclor sources, even though both categories of sources emit common congeners. To address these hypotheses, we utilized PMF to analyze a dataset of airborne PCBs measured in Chicago over six years using two different sampling approaches. We explored how various conditions (season, year, location) affect the PCB signals measured and the sources identified.

Materials/Methods

The dataset examined in this study contained airborne PCB concentration data previously generated by several studies conducted by Iowa Superfund Research Program researchers (Table 1). Between 2006 and 2013, the University of Iowa team collected airborne PCBs in Chicago air using two distinct sampling methods. First, high volume air samplers (Hi-Vols) mounted on two health clinic vans collected gas-phase PCBs on Amberlite XAD-2 resin and particle-bound PCBs on quartz fiber filters (this study only considers the former) for 6–8 hours at 37 locations from 2006 to 2008 [2, 42]. Second, polyurethane foam passive air samplers (PUF-PAS) were hung on the walls of buildings or trees at various sites including many of the same schools sampled by the mobile Hi-Vols. The PUF-PAS collected combined gas- and particle-phase PCBs at approximately 6 week intervals from January 2011 to January 2013 [41]. Hi-Vols collect air over a relatively short period of time while PUF-PAS sample air over a long period of time. PUF-PAS integrate much larger changes in temperature and wind direction over the sampling period. Also, PUF-PAS capture an unknown fraction of fine particles.

Samples were extracted and analyzed as described elsewhere [2, 41, 42]. The samples were analyzed for all 209 PCB congeners in 169 (Hi-Vol) or 156 (PUF-PAS) individual or coeluting chromatographic peaks using gas chromatography with tandem mass spectrometry (GC-MS/MS, Agilent 6890N) in multiple reaction monitoring mode (MRM). Quality assurance and control was ensured by use of field blanks, solvent blanks, side-by-side sampling, surrogate standard recovery, and analysis of reference materials. A congener

specific limit of quantification (LOQ) for Hi-Vol and PUF-PAS samples was used as discussed in their publications. PCBs were quantified using a calibration standard (AccuStandard, New Haven, CT) containing all 209 PCBs, the surrogate standard (d-PCB 65), and internal standard (d-PCB 30) and was not constructed from Aroclor mixtures. Hi-Vol concentrations are calculated by dividing the mass measured on the XAD-2 resin by the measured volume of air sampled (m^3) and PUF-PAS concentrations are calculated by dividing the mass measured on the PUF with congener-specific effective sampling volumes as described in the original report [41]. The dataset consists of 640 samples, each with concentrations of 154 sets of single and coeluting PCB congeners. In this study, we focused on the congener signal as a distinct indicator of unique sources of PCBs and normalized all congener concentrations to the concentration of the sum of PCBs in each sample [56]. The congener concentration data used in this research are available at doi.org/10.1594/PANGAEA.935238 [57].

Statistical Methods:

To evaluate the sources of PCBs to Chicago air from 2006 to 2013, positive matrix factorization (PMF) and a cosine theta similarity metric (cos θ) were used [58]. PMF is an analysis tool that decomposes a matrix of data (consisting of samples and PCB congeners) into factor profiles and contributions [59]. PMF finds a best fit between the factors and contributions and the data as the factor profiles can be combined with each other at different contributions to recreate every sample profile in the dataset. This technique is helpful at breaking down a large number of samples into a small number of signals that can be explored further. The signals can be linked to various sources and traced back to the samples to see how those sources affect the entire dataset. PMF has previously been used to identify PCB profiles in sediment, biota, and indoor and outdoor air by comparing the factor profiles to known source profiles [44, 59, 60]. One of the limitations of PMF is that it does not provide values for uncertainty or variability in the factor values. Each value in a factor profile comes from real data, however. There are no values found in the factor profiles that are not found in a data profile. We applied displacement and bootstrap error estimation techniques to ensure the factors do not contain rotational or random ambiguity in the solution.

Our dataset is robust for PMF analysis: we achieved a consistent group of 205 PCBs (not including standards) measured in 154 individual or coeluting congeners in the 640 samples collected over seven years. However, the detection limits changed over the course of the study and were different between the PUF-PAS and Hi-Vol samples and varied by congener. Although all samples were handled by our laboratory group using comparable method and quality control protocols, inconsistencies in the data reporting are evident. The most important parameter responsible for excessive uncertainty in the dataset is the congener-specific limits of quantification (LOQ), which varied over the study period. Many more measurements were reported as <LOQ in the beginning of our study period and were removed from the dataset. PMF requires no values of 0 in the dataset, and because of the inconsistency in the LOQ values over the course of this study, we replaced all reports of concentrations <LOQ with a new non-zero value equal to 50% of the smallest measured value for each congener [53, 61–65]. To address their fundamental differences, we analyzed

the PUF-PAS and Hi-Vol data separately. Lastly, to allow for a more stable solution and improvement of resolved factors, we removed from the datasets all congeners measured below the LOQ in 50% of the samples or more: 48 congeners were removed from both the Hi-Vol and PUF-PAS datasets [22, 55, 61–64].

As important as the data matrix is the uncertainty matrix. Uncertainties for the concentrations are 20% for Hi-Vol samples and 15% for PUF-PAS samples estimated as the average standard deviation of the respective recoveries [44, 62, 66]. Values that were replaced with 50% of the smallest value were assigned an uncertainty of 166% [44, 53, 63]. The final data and uncertainty matrices were entered into the EPA's PMF 5.0 Software with relaxed criteria [58].

To find the optimal number of factors, the model was tested for 2 to 8 factors for 20 runs with a random start. For converging runs, the number of factors with the lowest Q values (the function minimized to derive factor profiles and contributions) were initially selected to investigate further. We then ran displacement and bootstrap methods and found that high numbers of factors resulted in rotational ambiguity. So, the selected number of factors had the lowest Q values and resulted in no rotational ambiguity.

Congener and factor profiles are compared using cos θ, a measure of similarity between two vectors. This method is more appropriate than a Pearson correlation because it assigns equal weight to all congeners regardless of the concentration [45]. Cos θ varies from 0 (no correlation) to 1 (complete correlation). The factors were compared to individual Aroclors and mixtures of Aroclors using cos θ [22, 62, 63, 67, 68]. We used Aroclor data reported by Frame et al and measured in our laboratory [40, 69]. Gas-phase PCB profiles of Aroclors differ from the pure liquid mixture due to congener difference in volatility and are a function of the vapor pressure of each congener. Therefore, for the purpose of calculating the cosine similarity, each congener in the Aroclor profiles is normalized by its volatility by multiplying by its subcooled liquid vapor pressure at standard temperature and pressure [44, 70]. Cos θ measurements were conducted using MATLAB R2019a.

Results

Our initial PMF screening of the passive sample dataset identified three sampling locations with significantly different congener signals: samples collected at Joliet Township (JT), and at the Jardine Water Plan (JS and JN) (Figure S3). PMF identified them as outliers. Unlike the rest of the dataset, these samples showed a very clear Aroclor source and were similar to mixtures of Aroclors 1254 and 1260 (Cos θ > 0.86). One of these samples was deployed for a much longer period (344 days) as well [41]. We believe a highly localized source of Aroclors unrepresentative of our study region is present at these sites. All 36 samples from these three locations were excluded from further analysis. The final 2009 Hi-Vol dataset contained 141 samples with 106 congeners each and the final 2011–2013 PUF-PAS dataset contained 143 samples also with 106 congeners.

We identified five factors that described the 2009 Hi-Vol data and five factors that described the 2011–2013 PUF-PAS data. Five factors were selected because they resulted in a stable

solution with the lowest Q values for each dataset [58]. Increasing the number of factors resulted in rotational ambiguity from the displacement and bootstrap methods run within the software (see the Supplementary Material for error estimation analysis). These factors contributed to the PCB profiles of every location and were able to reflect the variance found in the air.

Aroclor Sources:

We evaluated the similarity between the PMF factors and Aroclors. An iterative method was used to calculate combinations of two Aroclors that are most similar to each factor and yielded the highest cos θ [56]. All but one of the Hi-Vol and PUF-PAS factors matched a mixture of Aroclors that included 1254 (either 1254 KC, lot KC12–638 measured in our lab and reported by Koh et al., or 1254 G4, a different lot reported by Frame et al.) (Figure 2 and Figure 3). The factors that contributed the most to the total PCBs (Hi-Vol factor 3 at 32% and PUF-PAS factor 2 at 33%) both showed a match to a mixture containing mainly Aroclor 1254 G4. The high contribution of Aroclor 1254 and its prevalence in the factors show it is a dominant source to Chicago air. The other Aroclors identified were 1016 or 1242, 1221 A1, and 1260. Aroclor 1016 is a distillation of Aroclor 1242 where some of the higher chlorinated congeners are removed and was developed and used after 1971, later than the other Aroclors [1]. Hi-Vol factor 2 was the only factor that had the closest match with Aroclor 1016. These results are consistent with other studies of Chicago air that also identified Aroclors 1254 and 1242 as sources [3, 44]. Previous studies noted Aroclor 1248 as a likely source to the air [44]. Our analysis also showed Aroclor 1248 resulted in good cos θ (Figures S4 and S5). However, Aroclor 1248 had low usage amounts compared to Aroclors 1254 and 1242 and its profile is similar to a mixture of 1254 and 1016/1242 [1, 71]. Therefore, we are not considering 1248 further. Previous studies have not mentioned Aroclors 1221 and 1260 as potential sources [3, 44]. The similarity between the factor profiles and Aroclors shows Aroclors are the dominant sources to Chicago air.

Our study is not the first to show that the PUF-PAS and Hi-Vol method are comparable methods for determining the concentration of airborne PCBs. However, this study is the first to illustrate how the two methods capture the complexity of airborne PCB congener signals. Used together, these two methods deployed in different years and locations, with different sorption materials, and with different deployment periods provide strong evidence of consistent sources. Four of the Hi-Vol factors resembled four of the PUF-PAS factors (Figure S6). Hi-Vol factors 1 and 4 are similar to PUF-PAS factor 1 (cos θ = 0.83 and cos θ = 0.84, respectively). These factors resemble Aroclor 1254 (1254 KC or 1254 G4). Hi-Vol factor 2 is similar to PUF-PAS factor 2 (cos θ = 0.92), and both are dominated by lower chlorinated congeners and resemble Aroclor 1016 (Figure 4). Hi-Vol factor 5 is similar to PUF-PAS factor 5 (cos θ = 0.86) and they are the only factors to resemble Aroclor 1260. Although Hi-Vol factor 4 and PUF-PAS factor 4 are not similar (cos θ = 0.66) they have an enrichment of higher chlorinated congeners that are not seen in the other factors. The similarity between the Hi-Vol and PUF-PAS factors shows there are consistent sources to Chicago air over time and space.

Influence of Lake Michigan:

Neighboring Lake Michigan can act both as a sink of PCBs from, and as source of PCBs to, Chicago air. Deposition and volatilization have different PCB congener signals. The deposition signal is a function of the congeners in air: the volatilization signal is a function of the PCB congeners in lake water and the congener-specific Henry's law constant. We hypothesized that these two signals should be apparent in our dataset. To test this hypothesis, we examined the PCB congener signal measured and calculated by Boesen et al. from measurements conducted in 2010 [72]. In the Boesen study, air and water samples were collected aboard the U.S. EPA R/V Lake Guardian and analyzed for PCB congeners at the University of Iowa with comparable methods to this study. The fluxes between the air and water were then calculated using the gradient-flux law, i.e., mass transfer velocity multiplied by the concentration gradient calculated relative to Henry's law to create deposition and volatilization profiles of PCBs [72].

We found PMF factors representing both the deposition and volatilization signals. The PMF factors reflect airborne PCB sources in the city contribute to the deposition signal measured over Lake Michigan. Hi-Vol Factor 5 strongly resembled the absorption profile (cos θ = 0.95) (Figure S7). The PMF factors also reflect the reverse: PCBs volatilizing from Lake Michigan are a source to PCB congeners in Chicago air. We found that PUF-PAS factor 1 strongly resembled the volatilization profile (cos θ = 0.95) (Figure 5). PUF-PAS factor 1 was the factor with the second most important contribution to all the PUF-PAS samples. Hi-Vol factor 5 and PUF-PAS factor 1 are not associated with any specific location, and instead have consistent contributions for all measured sites (Figures S8 and S9). Our finding is consistent with 1) Lake Michigan as regional source of airborne PCBs to Chicago air; 2) Chicago air as a source of PCBs to Lake Michigan; and/or 3) evidence of the addition of contemporary PCB sources to both Chicago air and Lake Michigan water.

Evidence of Non-Aroclor Sources:

We addressed our hypothesis that modern, non-Aroclor sources contribute to PCBs in Chicago air in three steps. First, we inspected the ten PMF factors for the presence of congeners with established non-Aroclor sources such as pigments, colorants, and sealants. Next, the ten Aroclor mixtures that best matched the factors were removed by subtraction from their factor profiles to examine the contribution of non-Aroclors. Finally, we used factors with the highest contributions of congeners with known non-Aroclor sources to identify congener patterns and samples that are not consistent with Aroclors sources.

Non-Aroclor congeners were observed in every Hi-Vol and PUF-PAS factor. Each of the top ten congeners found in eight paint colorants (green, blue, yellow, orange, red, and maroon) were also found in at least eight of the ten factors [16]. PCBs 47 and 51, notable non-Aroclor congeners from silicone polymer manufacturing, were also found in at least 8 of the 10 factors [19]. This is evidence that non-Aroclors sources are contributing to Chicago air. Many of the congeners found in non-Aroclor sources are also found in Aroclors, however. To distinguish congeners due to non-Aroclors from congeners due to Aroclors, we explored the difference between factor profiles and Aroclor profiles by subtracting the dominant Aroclor mixture from the factor. For example, Hi-Vol factor 1 best resembles a

mixture of 58% of 1254 G4 and 42% 1254 KC. The contribution of each congener to 1254 G4 is multiplied by 0.58 and each congener contributing to 1254 KC is multiplied by 0.42. These two new profiles are then added together and subtracted from Hi-Vol factor 1 profile.

By subtracting the identified Aroclor mixtures we can see how much of the factor profile is due to Aroclors versus non-Aroclors. After this removal, some factors still resembled Aroclor 1242, so this profile was subtracted as well for a consistent and conservative estimate of which congeners are not from Aroclor sources. The removal of the Aroclor signals leaves behind congeners that are potentially coming from non-Aroclors. The contributions of the remaining congeners are summed. This total represents the amount of the factor profile that is not explained by the Aroclor mixtures. Some factor profiles have a larger non-Aroclor contributions than other factors (Figure 6 and Figure S10). Congeners found in the factor profiles can be due to Aroclors, non-Aroclors or both. For example, PCB 11 is known to originate from non-Aroclors sources; it is non-detectable (<0.05%) in most Aroclors. PCB 3, on the other hand, is found in Aroclors and non-Aroclors and has contributions from both. On average, Aroclors are the largest source to the factor profiles, but non-Aroclor sources contribute more than 30% of the PCBs in some factors (Figure 6).

We calculated the amount Aroclor and non-Aroclor sources contributed to the total PCBs in Chicago air on a per congener basis by combining the amount Aroclors and non-Aroclors contribute to each factor and how much each factor contributes to the total dataset (Figure 7). These plots represent the profiles of all Aroclor and all non-Aroclor sources that we measured in Chicago air. Our analysis indicates that Aroclors contribute more than 80% of the PCBs in Chicago air (84% for the Hi-Vol dataset and 87% for the PUF-PAS dataset) and the remaining are due to non-Aroclor sources. Through this analysis we are also able to identify the amount Aroclors or non-Aroclors are contributing to individual congeners. For example, for the Hi-Vol samples, non-Aroclor sources explain 83% of PCB 3, a congener with known Aroclor and non-Aroclor sources, and 90% of PCB 68, a non-Aroclor congener from silicone manufacturing. Non-Aroclor sources explain on average 58 – 69% of PCBs 194 – 209, found in green paint, measured in Chicago air. In total 36 congeners were found that have non-Aroclor contributions of more than 50% (Table S7).

The congeners found in the non-Aroclor profiles are due to modern sources. A majority (85%) of those congeners have been reported in either commercial pigments or sealants [13–16, 18]. Seven additional congeners (PCBs 43, 46, 55, 89, 96, 137, and 139+140) are found at less than 1% of any Aroclor and have not been reported in any non-Aroclor source; their source to air is unknown. We have previously reported PCB 46 in indoor air [73]. The congener with the largest contribution to the non-Aroclor profiles was PCB 3 from Hi-Vol factor 3. PCB 3 is measured in some Aroclor mixtures, but they do not explain the levels seen in this factor. The Aroclor with the highest contribution of PCB 3 is 1221 A1, but it would need to be at least 70% of the best mixture to explain the levels we observed. Having Aroclor 1221 A1 as 70% of the best mixture results in poor cos θ values (<0.45) between the mixture and Hi-Vol factor 3. Every single factor in both Hi-Vol and PUF-PAS datasets has some contribution of the non-Aroclor congener PCB 11 to its residuals.

Hi-Vol factor 4 and PUF-PAS factor 4 have an enrichment of higher chlorinated congeners not seen in any of the other factors. These higher chlorinated congeners have been found in green colorants [16]. The sample with the highest contribution of PUF-PAS factor 4 was a measurement of Portage Park (PP) (67% of the profile). In the sample's profile the higher chlorinated congeners found in factor 4 can clearly be seen. Interestingly, a near-by site (Jefferson Park) exhibits no evidence of this non-Aroclor source. Even though the two sites are very near to each other (~2.5 km), and they were sampled at overlapping times, they exhibit different congener signals (Figure S11). This suggests a localized source of the higher chlorinated congeners at that site, such as a recent use of green paint.

Temporal and Spatial Analysis:

We have previously shown through analysis of the Hi-Vol data that there is much less variation in PCB concentrations over space than over time [43]. Here we show that the source signatures of PCB congeners also change over time. Hi-Vol factor 3 showed higher contributions during the colder months (average contribution November through April = 0.32; May through October = 0.13) while Hi-Vol factor 5 showed higher contributions during the summer (average contribution November through April = 0.08; May through October = 0.29) (Figure S12). We are not sure why some PCB sources identified from PMF analysis of the Hi-Vol data change over season. Although volatilization sources are a function of temperature, this effect should be evident for both sampling methods. It may be additional evidence of emission sources from manufacturing or other anthropogenic activity. Notably, Hi-Vol factor 3 is dominated by PCB 3; and Hi-Vol factor 5 has a strong contribution from highly chlorinated congeners found in paint. The other factors show no temporal trends.

We did not observe any dominant PUF-PAS factor at any specific location through the city, supporting previous findings that PCB sources are widely distributed through Chicago [23, 43, 44]. For example, PUF-PAS factor 1 has consistent contributions (~ 20%) for all measured sites (Figure S7). Further, in four locations sampled over the same time period, only two locations showed similar contributions of factors, but those two locations were a far distance from each other.

Implications

Approximately 1.3 million tons of PCBs were produced in the form of Aroclors and used in caulking, transformers, capacitors, adhesives, sealants, and paints and other applications [1, 74]. In 1976, the Toxic Substances Control Act (TSCA) gave the EPA the authority to regulate to toxic chemicals. The toxic effects of PCBs and their persistence in the environment led the EPA to ban the manufacturing of PCBs in 1979 [1]. Some manufacturing processes are excluded from regulation however, allowing some PCBs to be produced in the form of non-Aroclors [75]. Currently, non-Aroclor sources are emitting PCBs into air worldwide [2, 22, 76], but they can only be measured and identified by using analytical methods that measure the total suite of congeners, as done in this work.

Identifying non-Aroclor sources has led to regulatory action and changes in a manufacturing process. For example, Hombrecher et at. found PCBs 47, 51, and 68 emissions from

a manufacturing plant due to a cross-linking agent, bis(2,4)-dichlorobenzoylperoxide (2,4-DCBP), used to produce silicone rubber. When the cross-linking agent was replaced with a chlorine-free option and emission reduction measures implemented, contamination of these PCBs was reduced [76]. The study was conducted in Germany, but 2,4-DCBP was also hypothesized to be reason the same PCBs 47, 51, and 68 were seen in residential homes in the United States [19]. There is also evidence that manufacturing processes may be changing to limit the amount of PCB 11 found in pigments. PCB 11 was found to be a dominant congener in paint colorants measured in 2009 [15]. However, PCB 11 levels were much lower when colorants were measured in 2018 [16]. One of the newer colorants was the same color and contained similar PCBs to older colorants except that it was missing PCB 11. This study identifies additional non-Aroclor PCBs that should be considered for further regulatory action.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Highlights

- Non-Aroclor emission sources contribute to the entire range of congeners from mono- to decachlorobiphenyls, including 7 congeners of unknown sources.

- Chicago air has a signal of PCB congeners volatilizing from and absorbing to neighboring Lake Michigan

- Active and passive sampling indicate Aroclor sources are dominant in Chicago air but non-Aroclor sources account for 13% – 16% of the total PCBs measured.

- Sampling, analytical and statistical methods identify the chemical signatures of PCB sources in air.
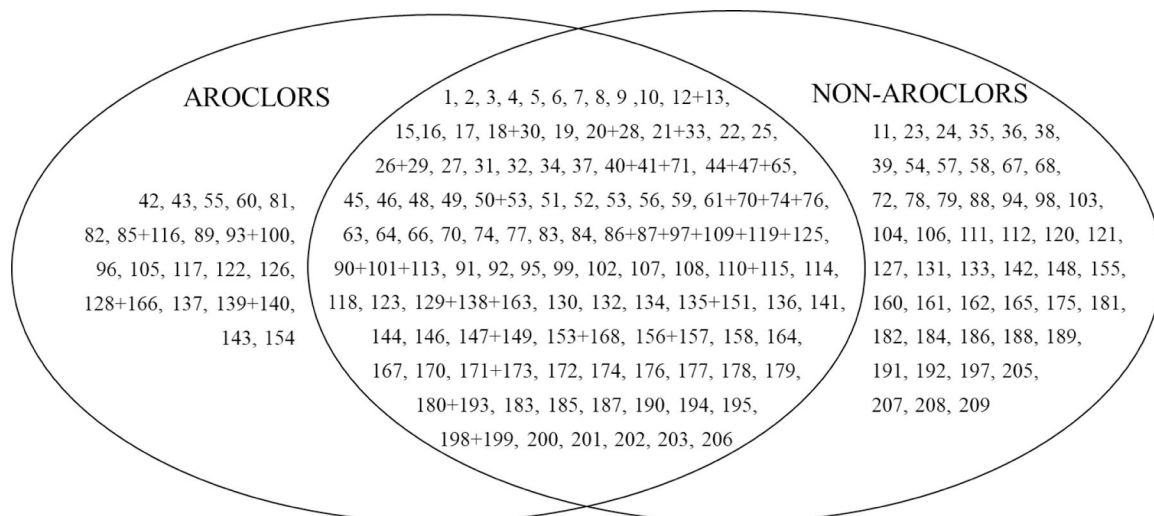
Figure 1.
PCB congeners known to be present in Aroclors, known to be present in non-Aroclor mixtures, or present in both. Aroclor congeners are found (>0.20 wt %) in Aroclors 1016, 1221, 1242, 1248, 1254, 1260, or 1262 [40]. Non-Aroclor congeners are found in paint pigments/colorants, adhesives, and sealants [13–16, 18, 19]. For this illustration, we used the coelution scheme produced by the SPB-Octyl capillary column.
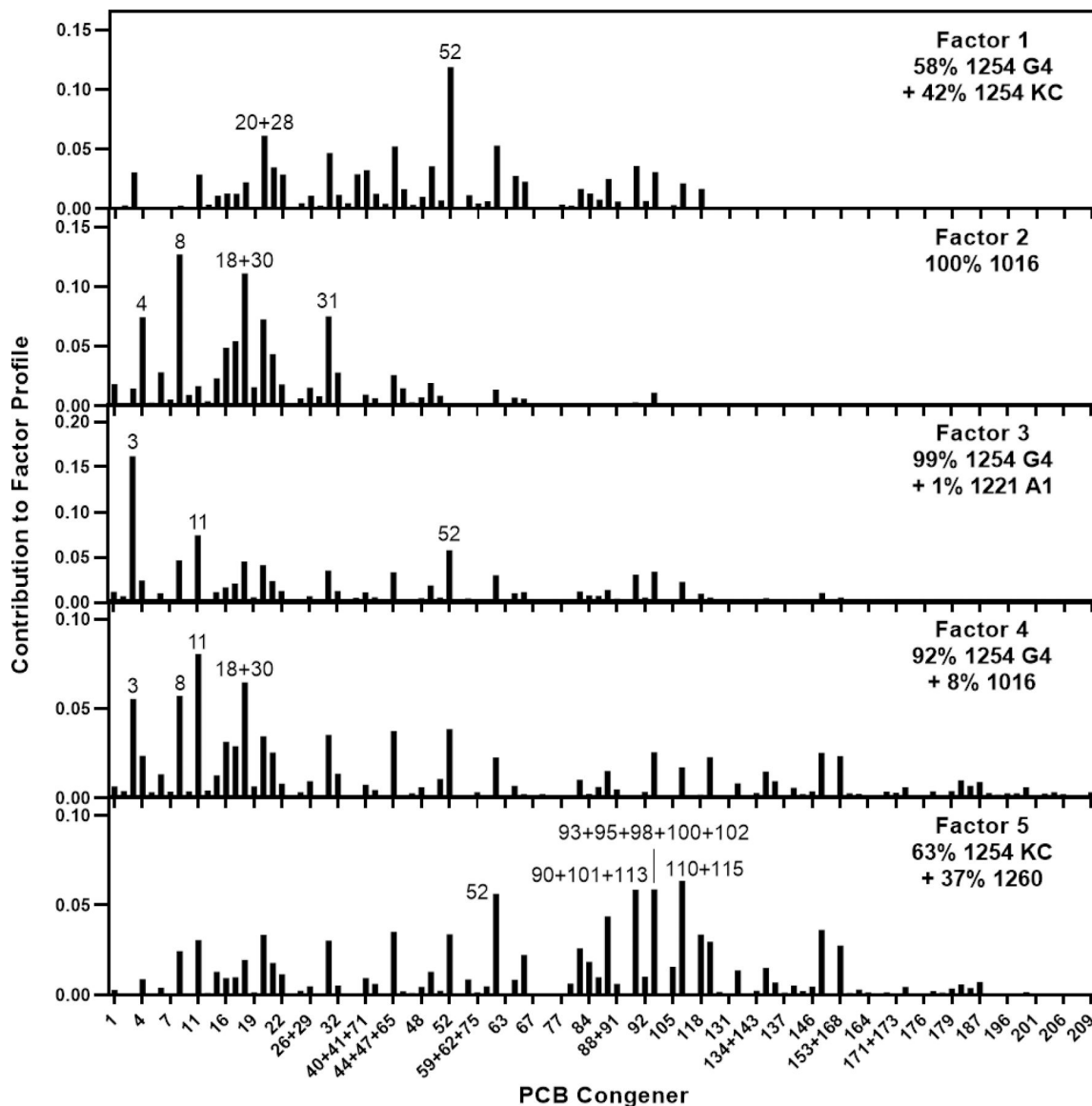
Figure 2.
PCB profiles of the 5 Hi-Vol factors that describe Chicago air in 2009. Included are the
Aroclor mixtures that best match the factor profiles. The congeners are ordered on the x-axis
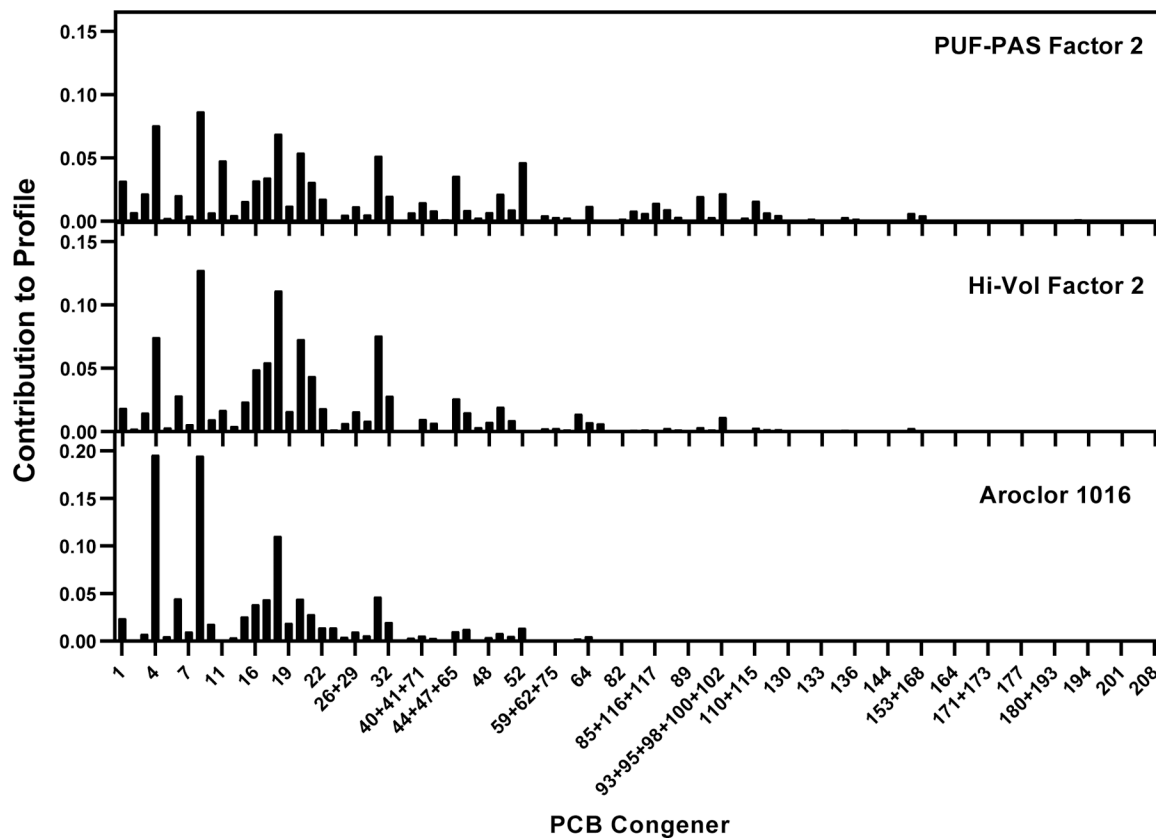as listed in Table S4.
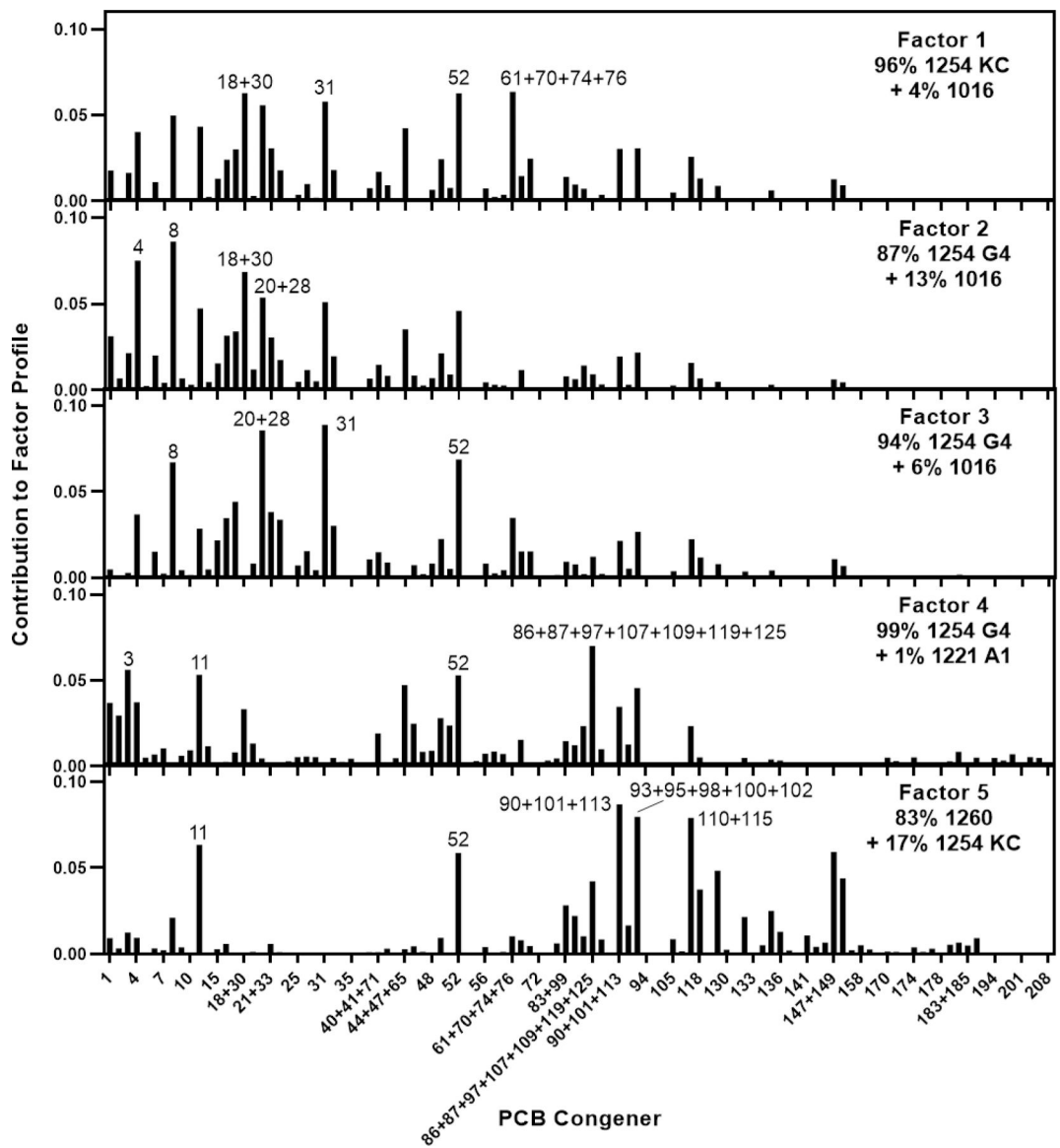
Figure 3.
PCB profiles of the 5 PUF-PAS factors that describe Chicago air from 2011 to 2013.
Included are the Aroclor mixtures that best match the factor profiles. The congeners are
ordered on the x-axis as listed in Table S5.

Figure 4.
PUF-PAS factor 2 and Hi-Vol factor 2 both capture the signal from Aroclor 1016 in Chicago air (cos θ = 0.92). The factor bars (black) and the Aroclor 1016 bars (orange) are overlayed with whichever bar is smaller in front. The congeners are ordered on the x-axis as listed in Table S6.
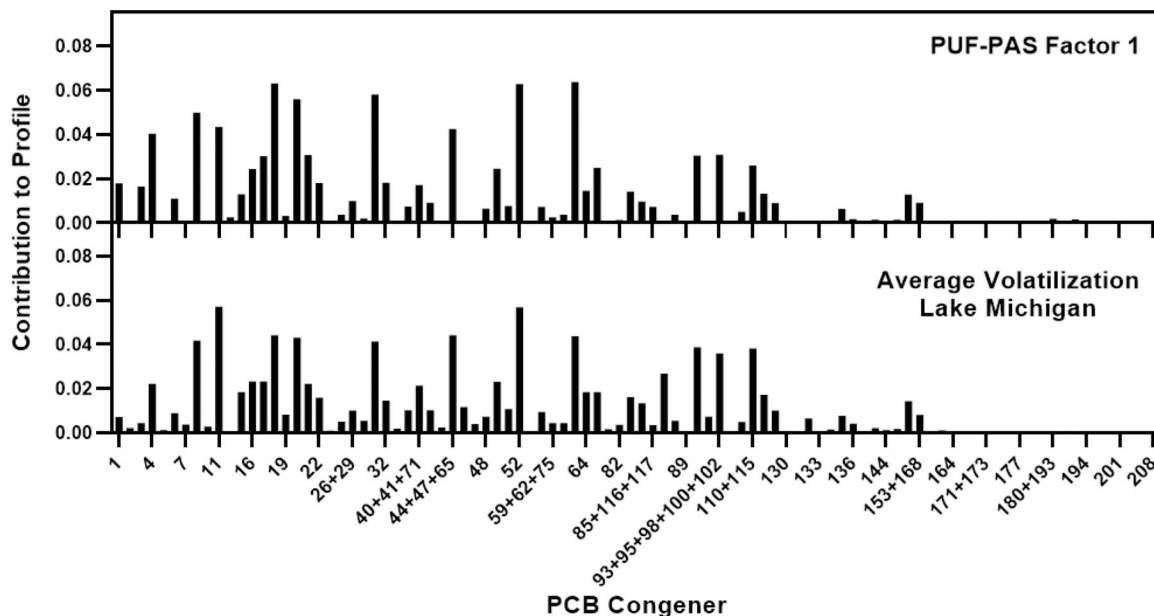
Figure 5.
PUF-PAS factor 1 (top) captures the signal from PCBs emitted from Lake Michigan (cos θ = 0.95). PCB emissions from Lake Michigan (bottom) were calculated from measurements of PCBs in water collected ~ 2 km from Chicago in 2010 [72]. The congeners are ordered on the x-axis as listed in Table S6.
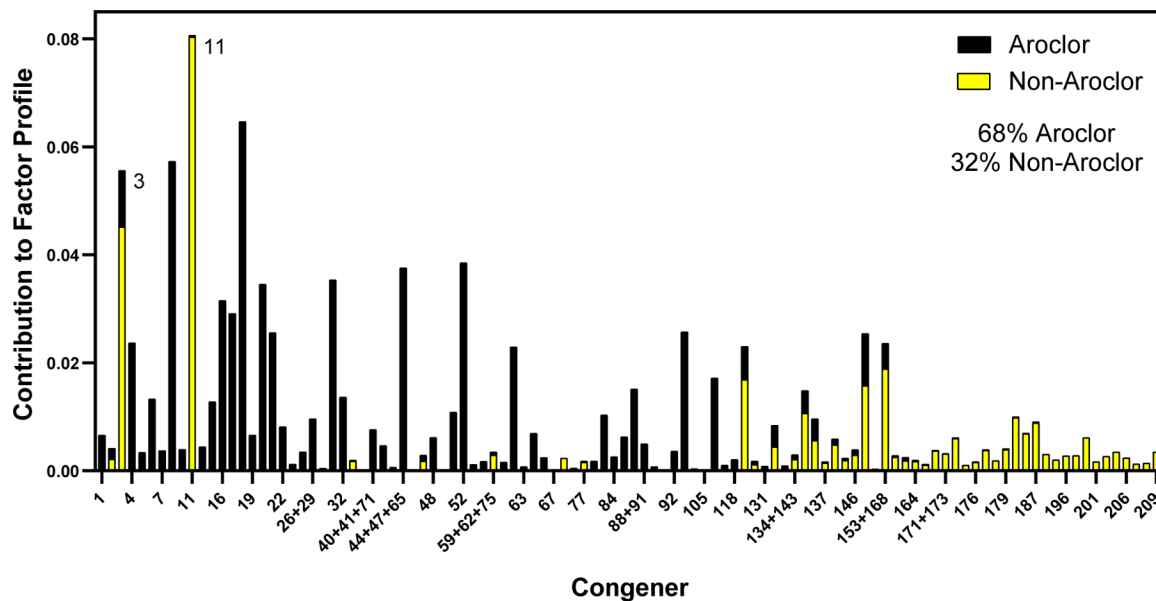
Figure 6.
Contribution of the non-Aroclors (yellow) to Hi-Vol factor 4 (black). Aroclors are 68% of the factor profile and non-Aroclors contribute 32% of the factor profile.
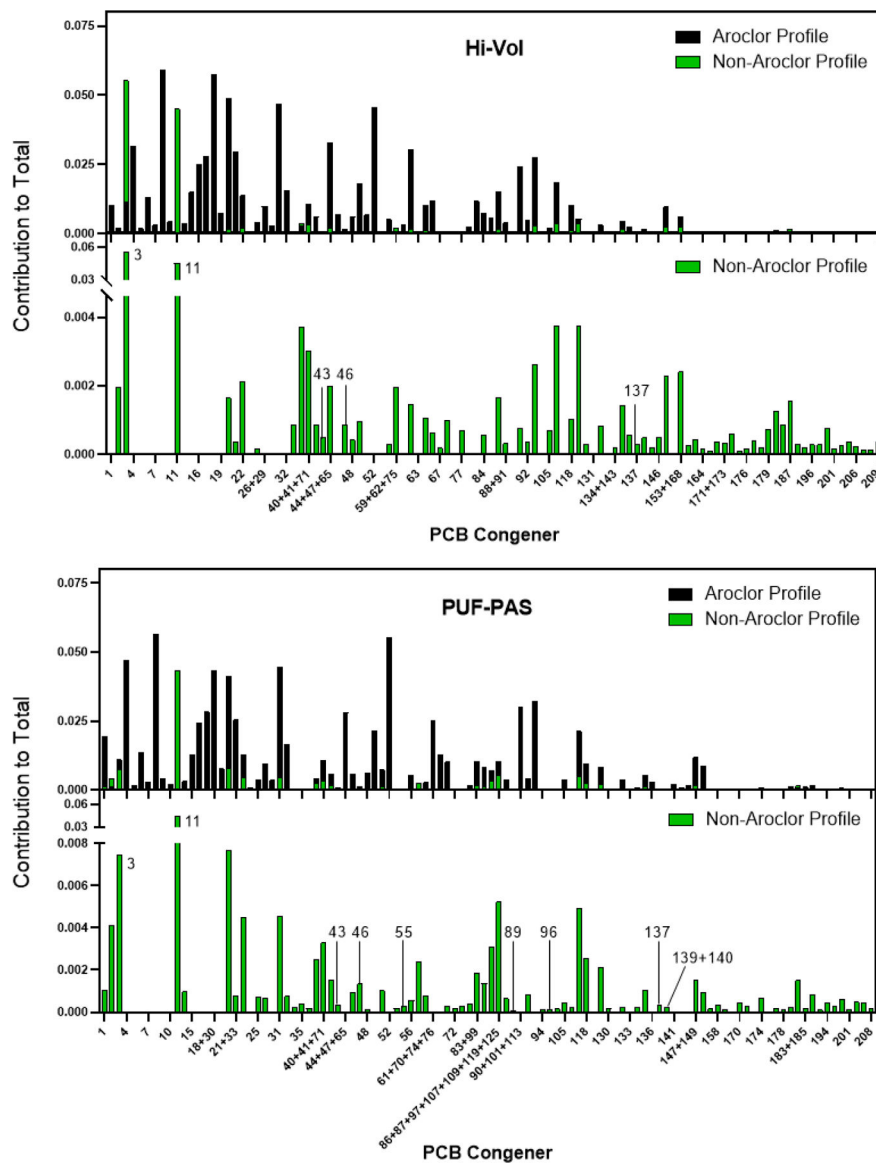
Figure 7.
Profiles of Aroclor (black) and non-Aroclor sources (green) that are measured in Chicago air using Hi-Vols (top pair) or PUF-PAS (bottom pair). The bottom plot of each pair includes only the non-Aroclor mixture. The congeners are ordered on the x-axis as listed in Table S4 for the top pair and Table S5 for the bottom pair. Labeled congeners are discussed in the text.

Table 1:

Number of samples and locations for each publication used.

Year	Sample Media	Number Samples	Locations	Publication
2006 – 2008	Hi-Vol with XAD	320	**Figure SI1**	[2, 42]
2009	Hi-Vol with XAD	141	**Figure SI2**	[43]
2011 – 2013	PUF-PAS	179	**Figure SI3**	[41]