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# Atmospheric PCB congeners across Chicago

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## Abstract

We have measured PCBs in 184 air samples collected at 37 sites in the city of Chicago using an innovative system of high-volume air samplers mounted on two health clinic vans. Here we describe results of sampling conducted from November 2006 to November 2007. The samples were analyzed for all 209 PCB congeners using a gas chromatograph with tandem mass spectrometry (GC-MS/MS). The ΣPCBs (sum of 169 peaks) in Chicago ranged from 75 pg $m^{-3}$ to 5500 pg $m^{-3}$ and primarily varied as a function of temperature. The congener patterns are surprisingly similar throughout the city even though the temperature-corrected concentrations vary by more than an order of magnitude. The average profile resembles a mixture of Aroclor 1242 and Aroclor 1254, and includes many congeners that have been identified as being aryl hydrocarbon receptor (AhR) agonists (dioxin-like) and/or neurotoxins. The toxic equivalence (TEQ) and neurotoxic equivalence (NEQ) in air were calculated and investigated for their spatial distribution throughout the urban-industrial complex of Chicago. The NEQ concentrations are linearly correlated with ΣPCBs while the TEQ concentrations are not predictable. The findings of this study suggest that airborne PCBs in Chicago are widely present and elevated in residential communities; there are multiple sources rather than one or a few locations of very high emissions; the emission includes congeners associated with dioxin-like and neurotoxic effects and congeners associated with unidentified sources.

## INTRODUCTION

PCBs are a group of 209 semi-volatile anthropogenic compounds (congeners) that are commonly measured in air throughout the globe and dispersed to regions far from human activity (Ockenden et al. 1998; MacDonald et al. 2000). PCBs are emitted to the air by volatilization and are elevated in industrialized and highly populated cities (Simcik et al. 1997; Breivik et al. 2002b; Hsu et al. 2003b; Wethington et al. 2005). Unfortunately, atmospheric sources of PCB congeners within urban areas are not well defined (Breivik et al. 2002a; Pacyna et al. 2003). Some studies have suggested that there may be localized sources within cities (Hsu et al. 2003b, a; Yi et al. 2008), and the relative importance of

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localized sources is not clear. In Chicago, it is unknown if PCB congeners in air are emitted from a small number of large sources or a large number of smaller sources.

Accurate determination of PCB emissions and subsequent deposition depends on accurate determination of the spatial distribution and local variability of PCB congener concentrations. However, it is quite difficult to accurately measure the spatial distribution of PCB concentrations and hence there are very few datasets available to support current modeling and estimation methods (Breivik et al. 2002a; Breivik et al. 2002c). The difficulty is due to the limitation in current sampling and analytical methods. The most accurate sampling methods use high volume air samplers (Hi-Vols) which require an electricity source and regular service (Harner et al. 2004). The electricity requirement limits the choice of sites. The necessity of regular service makes deployment of multiple Hi-Vols expensive and logistically challenging, especially in an urban area. For these reasons, the studies that have used Hi-Vols for this purpose either examine a very large area (the Great Lakes region), and/or deploy a small number of samplers (Brunciak et al. 2001; Basu et al. 2004). To overcome these challenges, some investigators (including ourselves) have deployed passive samplers across urban areas (Motelay-Massei et al. 2005; Du et al. 2009; Persoon et al. 2009). While these studies provide valuable information, there are large uncertainties for each measurement. The most important problem is each value represents the emissions and meteorological variability of many days. Another problem is that an estimation model is required to convert PCB mass per sample to PCB concentration in the air. The conversion method introduces a sampling and analytical uncertainty in sample concentration that is difficult to quantify. As a result, passive samplers should be deployed simultaneously for an internally-consistent dataset.

Accurate determination of congener-specific PCBs in urban air is important because of the different toxicities, bioaccumulation potential, and persistence of different congeners. Only a few studies have examined this variation across an urban area (Harner et al. 2004; Totten et al. 2004; Motelay-Massei et al. 2005; Jamshidi et al. 2007; Du et al. 2009). Recently, we reported the congener distributions using passive-samplers deployed over one month in Cleveland and Chicago (Persoon et al. 2009). These studies were done using passive air samplers and did not particularly investigate the annual variability of spatial distribution of dioxin-like and potentially neurotoxic congeners in ambient urban air, although these compounds have been measured in some studies (Harner et al. 2004; Ogura et al. 2004; Cleverly et al. 2007). Compounds with laboratory-determined neurotoxic effects have been observed in urban air but have only recently been ranked as to their potency (Simon et al. 2007). Both types of potentially toxic congeners, when present in Chicago air, would be expected to deposit in Lake Michigan and accumulate in fish and other living organisms.

This study focuses on accurate determination of the spatial variability of individual PCB congeners in an urban-industrial area. We focused on Chicago because the region is a known atmospheric source of PCBs and the spatial extent of the Chicago source is unknown. We were particularly interested in whether PCBs were elevated in the non-industrial residential regions of the city. We hypothesized that PCB congeners are present in residential communities throughout the city of Chicago; PCB concentrations vary with to local meteorology; and PCB congener distributions vary across the city. We have addressed these hypotheses through a study of airborne PCB congeners in air sampled throughout Chicago using an innovative sampling system based on high volume air samples (Hi-Vols) mounted on health clinic vans. With this approach, we collected 184 short-term (4–8 hour) air samples over one year at 37 locations. The samples were analyzed for all 209 possible PCB congeners, including those displaying dioxin-like toxicity (Toxic Equivalence or TEQ) and those congeners that have been identified as exerting neurotoxicity (Neurotoxic Equivalence or NEQ). The distribution of PCB concentrations and PCB congener signatures were used to

evaluate the spatial extent of PCB contamination of Chicago air and the distribution of PCB emission sources.

## MATERIALS AND METHODS

### Air sampling

In cooperation with the Mobile C.A.R.E. Foundation of Chicago, Hi-Vols were modified from the original factory model (Tisch Environmental, Cleves, OH) and mounted on the rear of two mobile medical clinic vans. The innovative design of the Hi-Vol air sampler has been previously described in a paper that reported only our discovery of PCB11 and did not describe the spatial variability of total PCBs or the remaining congeners (Hu et al. 2008). Our PCB monitoring campaign began in November 2006 and the samples collected during the first year were analyzed for this manuscript. The Hi-Vols collected gas-phase PCBs on Amberlite XAD-2 resin and collected particle-bound PCBs on quartz fiber filters. Previous studies have shown that the particle phase accounts for less than 10% of the total atmospheric PCBs (Sun et al. 2006) and so we did not analyze the filters for this report. The samplers were operated by trained personnel from the Mobile C.A.R.E. Foundation of Chicago. The sampling locations (Table S1) are in residential neighborhoods chosen for their proximity to families and schools. This study describes the 37 sites sampled in 2007. The Hi-Vols collect air samples for the 6 to 8 hour period when the van remained at the school with the engine off for serving clients. Usually both vans provided clinical services on the same day, so we collected two samples at two different sites on the same day, five days a week. The vans operated year-round except when the vans needed repair and for 2–3 week long breaks in December/January and in August. Each site was sampled five times, on average, although the frequency ranged from 1 sample to 11 samples at the individual sites. The Hi-Vols operated at a flow rate of 0.4 $m^3$ $min^{-1}$. The flow rate was monitored daily using a Magnehelic pressure gauge on each sampler. When the gauge reported a pressure outside of our normal variability (~ 0.25 inches), the operator would check for leaks and/or reinstall the resin cartridge or filter manifold until the pressure met acceptable criteria. The samplers were calibrated twice in 2007. Temperature and relative humidity data were recorded every 5 min on one of the two vans by the CR800 measurement and control system (Campbell scientific, inc., Logan, Utah).

### Sample analysis

The samples were extracted and analyzed as described elsewhere (Hu et al. 2008). Briefly, the samples were spiked with 100μL of 500ng/mL the surrogate standard containing 3,5-dichlorobiphenyl (PCB14), 2,3,5,6-tetrachlorbiphenyl (PCB 65) and 2,3,4,4′,5,6-hexachlorobiphenyl (PCB 166), then the spiked samples were extracted using accelerated solvent extraction (Dionex ASE-300). The concentrated extracts were spiked with 50μL of the internal standard containing 1,000 ng $mL^{-1}$ of 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (PCB 204). The samples were analyzed for all 209 PCB congeners, in 169 chromatographic peaks, using a gas chromatograph with mass selective detection (GC-MS/MS) modified from the EPA method 1668A (U.S.EPA 1999). The quantification of PCB homologs was performed by an Agilent 6890N gas chromatograph with an Agilent 7683 series autosampler coupled to a Waters Micromass Quattro micro GC mass spectrometer (Milford, MA, USA) operating under electron impact (EI) positive mode at 70 eV and multiple reaction monitoring (MRM), and the trap current was 200 μA. The retention windows were defined by PCB parent/daughter ion pairs from mono- to deca- homologs which were 188/152, 222/152.10, 255.96/186, 291.92/222, 325.88/255.90, 359.84/289.90, 393.80/323.90, 427.76/357.80, 461.72/391.83, 497.68/427.70, respectively.

### Quality Assurance/Quality Control

The quality of the method was determined through the collection of field blanks, solvent blanks, side-by-side samples, surrogate standard recovery and regular analysis of standard reference materials. Field blanks consisted of prepared XAD-2 resins that were shipped from Iowa to Chicago and back but not installed in a sampler. A solvent blank was used for each batch of 10 samples to check for system contamination in the lab, and no contamination and carryover after analysis of high concentration samples were observed. The method detection limit (MDL) was determined for each congener and calculated as three times the standard deviation of the congener mass in the field blank ($n$=14) plus the minimum peak response. The congener MDL ranged from 0.1 ng per sample to 2.2 ng per sample. When the typical air volume of 200 $m^3$ was applied, the congener MDL ranged from 0.5 to 11 pg $m^{-3}$. The recoveries of PCB 14, PCB 65 and PCB 166 surrogate standards injected in every sample were 95±11%, 100±18% and 105±14%, respectively. Samples were not corrected for surrogate recoveries or blanks. Data from 4 pairs of the air samples collected at the same time at the same location show that the coefficient of variance (COV) was 37% for PCB gas-phase samples collected on the XAD-2 resins. The analysis of SRM 1944 resulted in identification of all congeners, with an acceptable quantification results (15% difference for individual congeners on average) with respect to the certified values(Martinez et al. 2009).

## RESULTS AND DISCUSSION

### Magnitude and Profile

The average concentration of ΣPCBs was 840 pg $m^{-3}$, which ranged from 75 to 5500 pg $m^{-3}$ (Figure 1, Table 1). These values are in agreement with the ranges previously reported for the Chicago and other cities in North America (Hornbuckle et al. 1993;Panshin et al. 1994;Offenberg et al. 1999;Brunciak et al. 2001;Van Ry et al. 2002;Gouin et al. 2005;Wethington et al. 2005;Sun et al. 2006), (Figure 2). We observed large day-to-day variability in the measured concentrations, as we previously predicted (Green et al. 2000). The average concentrations we measured in Chicago are quite similar to those measured by one long-term monitoring site chosen by the Integrated Atmospheric Deposition Network (IADN) in Chicago in spite of the significant differences in the analytical methods, list of congeners, and sampling locations. Sun et al. reports concentrations from 100 to 9,500 pg $m^{-3}$ for samples collected by IADN from 1996 to 2003 (Sun et al. 2006). This similarity suggests that the average PCB magnitude is leveling off in the environment in recent years.

The average congener profile is shown in Figure 3 (top) and Table S2. The detected PCB congener numbers in air samples ranged from 45–105 with an average of 65. PCBs 8, 18/30, 20/28, 52, 31, 4, 11, 5, 17, 21/33, 16, 95, 90/101/113, and 82 in order from high to low concentrations accounted for more than 50% of total PCBs in the air, and the highest average concentration of an individual PCB congener reached as high as 56 pg $m^{-3}$. Among the highest concentration congeners, PCB 11 is unique; as it is not present in Aroclor mixtures. To date it has been detected in water or sediment (King et al. 2002;Litten et al. 2002) and more recently discovered in air (Choi et al. 2008;Hu et al. 2008;Basu et al. 2009;Du et al. 2009).

### Volatilization Sources

Potential sources of airborne PCBs include volatilization from surfaces that were contaminated through use and disposal of an Aroclor mixture, volatilization from previously deposited airborne PCBs, and emissions unrelated to volatilization. The congener pattern observed in Chicago air is enriched in lower chlorinated congeners (Figure 3 and Figure 4) as expected for volatilization sources and most strongly resembles Aroclor 1242 and Aroclor 1254 (Frame 1997). As a result, we have produced a mixture of 65% Aroclor 1242 and 35%

Aroclor 1254 to reasonably simulate the average Chicago air profile for animal exposure studies (Zhao et al. 2009). This type of congener signal has been reported for emissions from landfills (Lewis et al. 1985), although a preliminary assessment of land use did not identify any correlation between landfills and PCB concentrations. It is likely that Aroclor 1242 was commonly used in the Chicago area. This mixture was produced for use in electric transformers, heat transfer applications, hydraulic fluids, turbine, rubbers, carbonless copy paper, adhesives, and waxes (ATSDR 2000). However, there are several congeners that are present in Chicago air at much higher concentrations relative to their mass fraction in the most common Aroclor mixtures (PCB 11, for example (Hu et al. 2008), also PCB 5 and PCB 112), which might be resulted from an unidentified source or a weathering process. In the case of PCB 11, it appears to be unrelated to the production and use of Aroclors and may be related to inadvertent current uses of pigments or dyes. The detailed discussion of its presence, source and significance has been discussed elsewhere (Hu et al. 2008).

As expected for volatilization sources, airborne PCBs concentrations in Chicago are strongly correlated with temperature (Figure 1). Spring and fall were both ~ 2.5 times higher, and summer was ~5.5 times higher on average as compared to the average Σ PCB concentration in winter. The seasonal variability is also reported in other studies (Halsall et al. 1995;Robson et al. 2004;Motelay-Massei et al. 2005;Du et al. 2009). For example, a study in Toronto also showed PCB concentrations were ~ 2–3 times higher in the spring-summer period than in the winter period(Motelay-Massei et al. 2005). This phenomenon is believed to be caused by release of accumulated PCBs in the wintertime as the ground temperature increases. As reported by many other studies, the Clausius-Clapeyron equation is a good model describing the relationship between airborne PCBs and temperature in Chicago and thoroughly reviewed by Carlson and Hites (Carlson et al. 2005). The slope of the natural logarithm of partial pressure against inverse absolute temperature for PCBs measured in Chicago is – 4700 which agrees with the values reported (− 5030 ± 1070) for U.S. IADN sites (Carlson et al. 2005). The correlation with temperature does not, however, explain the majority of the variability in airborne PCB concentration. The coefficient of determination ($R^2$=0.36) is much less than 1. So while there is evidence that use of Aroclors and subsequent volatilization are important contributors to PCBs found in Chicago air, other factors like spatial variability and unidentified sources are needed to explain the variability in PCB concentrations in Chicago air.

## Spatial Variability

To examine the spatial variability of PCB congener concentrations across the city, we normalized atmospheric PCB concentrations to a reference temperature of 288K (Buehler et al. 2004). There has been much discussion in recent years about the interpretation of Clausius-Clapeyron temperature slopes. Some investigators claim that the relatively shallow slopes, often observed in more remote regions, are an indication of long-range transport of PCBs to the sampling site (Hoff et al. 1998; Wania et al. 1998). Carlson and Hites found that the slopes are associated with the size of data set, temperature range, concentrations near the detection limit, and the PCB congener profiles (Carlson et al. 2005). When we applied their model by setting temperatures to 273K when measured daily average temperatures were less than 273 K, the slope magnitude increased to −5600 ($R^2$=0.39). Nevertheless, because the correlation between temperature and PCB concentrations did not change much, we chose to use the simpler method for correcting PCB concentrations to a standard temperature.

Concentrations of temperature-corrected PCB concentrations across Chicago vary by about a factor of ten (Figure 5) – similar to the range observed at a single site over the course of a year. PCBs do not exhibit a few small areas of very high concentration close to a single source or small number of sources. Our previous study using passive air samplers also suggest airborne PCBs are distributed across the city and local emissions play a significant

contribution(Persoon et al. 2009). Nor do the highest concentrations cluster around facilities that may have used PCBs. Figure 5 shows location of facilities engaged in manufacturing electronic capacitors (SIC 3675), power, distribution, instrument, and specialty transformers (SIC 3612) and establishments primarily engaged in the collection and disposal of refuse by processing or destruction or in the operation of incinerators, waste treatment plants, landfills, or other sites for disposal of such materials (SIC 4953). We were unable to find intense and localized emission sources and any statistical correlation of spatial distribution of PCB magnitude with these facilities registered with EPA as the toxics release inventory although airborne PCBs are clearly present in residential communities throughout the city of Chicago.

Besides temperature, other meteorological conditions, and socio-economic and environmental conditions were investigated for their contributions to spatial variability of PCB concentrations. The investigated factors include dew point, wind direction, population density, road length, median household income and proximity to superfund sites (Table S3). Among these factors, the temperature, population density, wind direction, and proximity to high intensity developed area showed a significant association with PCB concentrations. However, the temperature is the dominant contributor ($R^2$=0.31), and all these factors explains a little more than one third of the total variability. There must be some other unidentified factors that contribute the variability of PCB concentrations in air.

## Toxic Equivalency

Toxic effects on humans through direct inhalation are not yet clear. However, lower chlorinated congeners, predominating in air, may expose humans to reactive, possibly genotoxic/carcinogenic intermediates because they are relatively easier metabolized (Ludewig et al. 2008). Chicago air is predominated by low chlorinated congeners and does contain PCB congeners that have been shown to exert toxic effects in laboratory studies. Of PCBs with four or more chlorines, the 12 PCB congeners with zero or one ortho- substituted chlorine atoms are often referred to as “dioxin-like” because of their similar mode of action as 2,3,7,8- tetrachlorodibenzo-p-dioxin (Patterson et al. 2008). These dioxin-like PCBs (DL-PCBs) are agonists of Aryl hydrocarbon receptor (Bandiera et al. 1982; Schrenk 2008). Toxic equivalency factors (TEF) were developed for chemicals with the same mode action through the AhR-mediated pathway by the World Health Organization (WHO). For PCBs, 12 dioxin-like PCBs have the TEFs that are scaled to the response of 2,3,7,8-TCDD. The toxic equivalency (TCDD-TEQ) concentrations can be expressed as the sum of the product of the individual PCB concentration and the respective TEF value (Van den Berg et al. 1998).

We calculated TCDD-TEQ concentrations for every sample using the most recently revised TEF values (Van den Berg et al. 2006). All twelve dioxin-like PCBs were found in concentrations above the MDL although the frequency of detection ranged from 3% to 60% of the samples (Figure 4). PCB118 was the most abundant congener with a TEF value, followed by PCBs 77, 123, 126, 105, 81, 114,189,156/157,169,167 in order in Chicago air. The concentrations of these compounds (when detected) are higher than reported by Cleverly for remote and rural U.S. air (Cleverly et al. 2007). However, PCB126 (3,3′,4,4′,5 pentachlorobiphenyl) is by far the major contributor to the mean TCDD-TEQ value in Chicago air (Figure 6, left), and it was only found in 12 samples above its MDL (~10 pg $m^{-3}$). The total concentration of TCDD-TEQ ranged from non-detectable to 5.6 pg $m^{-3}$ and were dominated by PCB 126, when present (Table 1). Although the spatial trends are not conclusive, this congener was most frequently detected in the central regions of the city (Figure S1). The range of TCDD-TEQ concentrations is larger than that reported for Yokahama (Ogura et al. 2004) and larger than reported for rural and remote United States (Cleverly et al. 2007). However, the high TEQ concentration in Chicago must be cautiously interpreted. Excluding PCB 126 and PCB 169 that were only detected in 7% and 10% of the

collected samples, the average and median TEQ concentration is 1.4 fg $m^{-3}$ and 0.4 fg $m^{-3}$, respectively, without temperature normalization.

Corresponding to 12 dioxin-like PCB congeners, the remaining congeners are referred to as the non-dioxin-like congeners (NDL-PCB). These congeners exert weak or no effect on Ah-receptors; however, they interfere with intracellular signaling pathways that are regulated and modulated by $Ca^{2+}$, such as those involving ryanodine receptors, protein kinase C, inositol triphosphate or arachidonic acid, and, thus, cause neurotoxicity (Kodavanti 2004; Simon et al. 2007). Neurotoxic Equivalency Factors (NEF) have been developed by Simon et al. in the same fashion that the dioxin TEQ scheme represents the Ah-receptor related toxicity (Simon et al. 2007). The higher NEFs were adopted for coeluting congeners although these values are similar. Chicago air is enriched with many congeners that have high relative NEF values. In Chicago air, PCB18/30 was the most abundant congener with a NEF value, followed by PCBs 20/28, 4, 31, 52, and 16, 17, 5 and more in that order (Figure 3 and 4). These congeners contributed more than 50% of the total NEQ (Figure 6, right). The total NEQ levels varied from 3.7 pg $m^{-3}$ to 2000 pg $m^{-3}$ within the Chicago area with the average of 280 ± 350 pg $m^{-3}$ and the median of 130 pg $m^{-3}$. Compared to the ΣPCB distribution, the TEQ distribution within Chicago is more variable than the NEQ distribution (Figure S1 and Figure 5).That indicates neurotoxic toxicity is predictable ($r^2$=0.98) based on ΣPCBs while the dioxin-like effect is not associated with the measured total PCB concentrations($r^2$=0.0069); see Figure S2. This study reports the widespread presence of PCBs in Chicago air, including many PCB congeners that have been identified as causing toxic effects in cells and laboratory animals although we do not know if the presence of these compounds in urban air is a concern.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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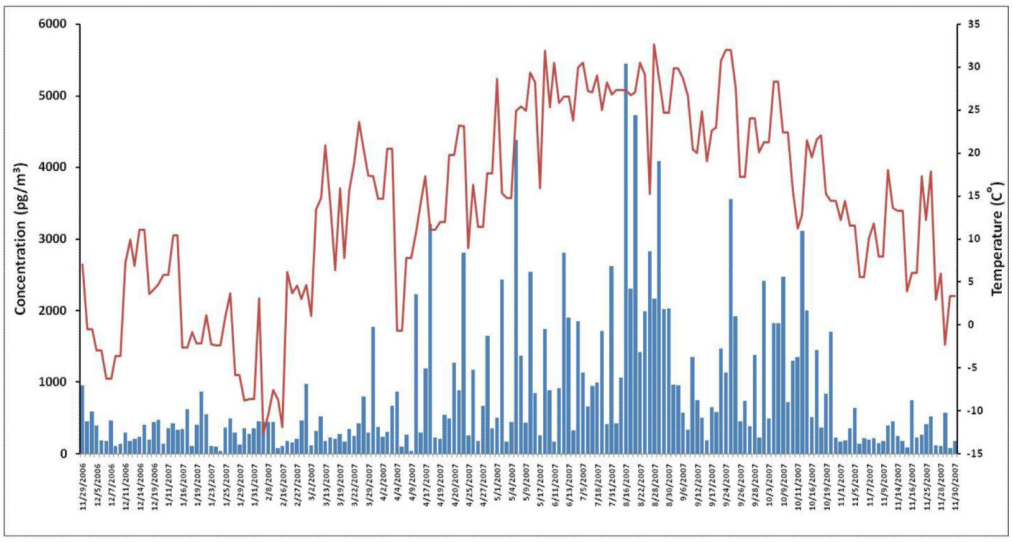


**Figure 1.**
Daytime total PCB concentrations from November 2006 to November 2007 in Chicago air (bars) and mean air temperature during sampling (red line).

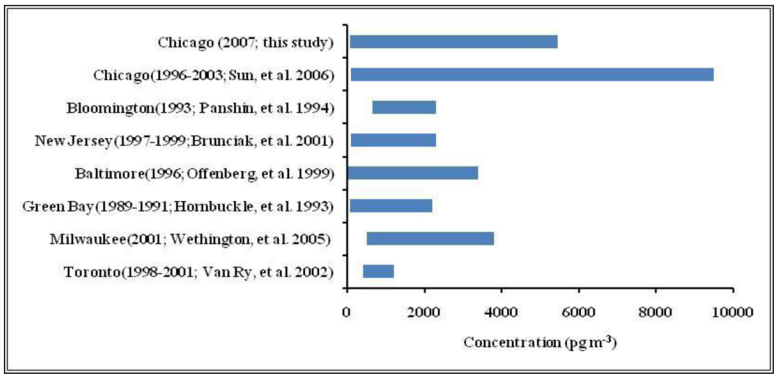


**Figure 2.**
PCB concentration ranges reported in the air of urban areas in North America.

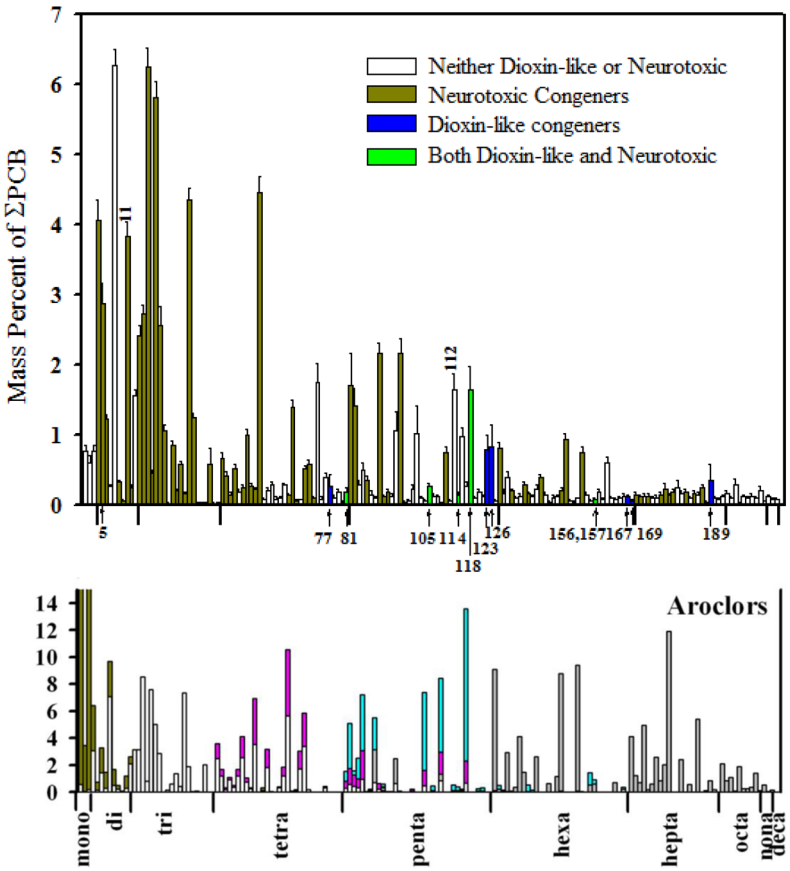


**Figure 3.**

Annual average PCB profile in Chicago with standard errors (top plot) and Aroclors 1221, 1242, 1248, 1254, and 1260 (in different colored bars, bottom plot). The legend applies to the top plot only.

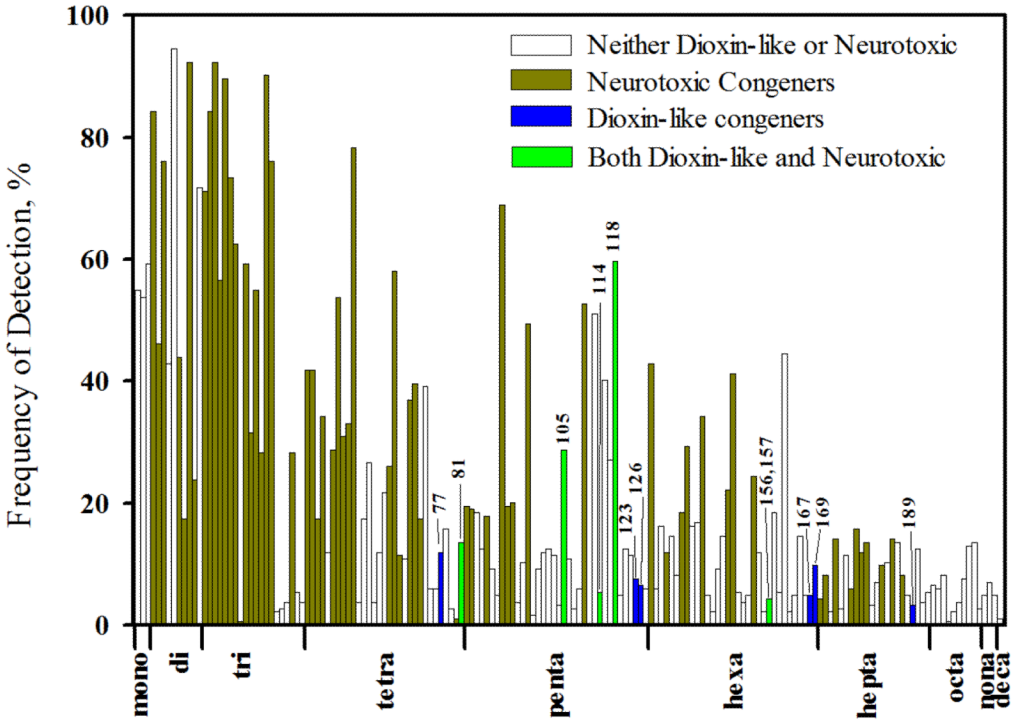


**Figure 4.**
Frequency of congeners measured in samples above the congener-specific detection limit.

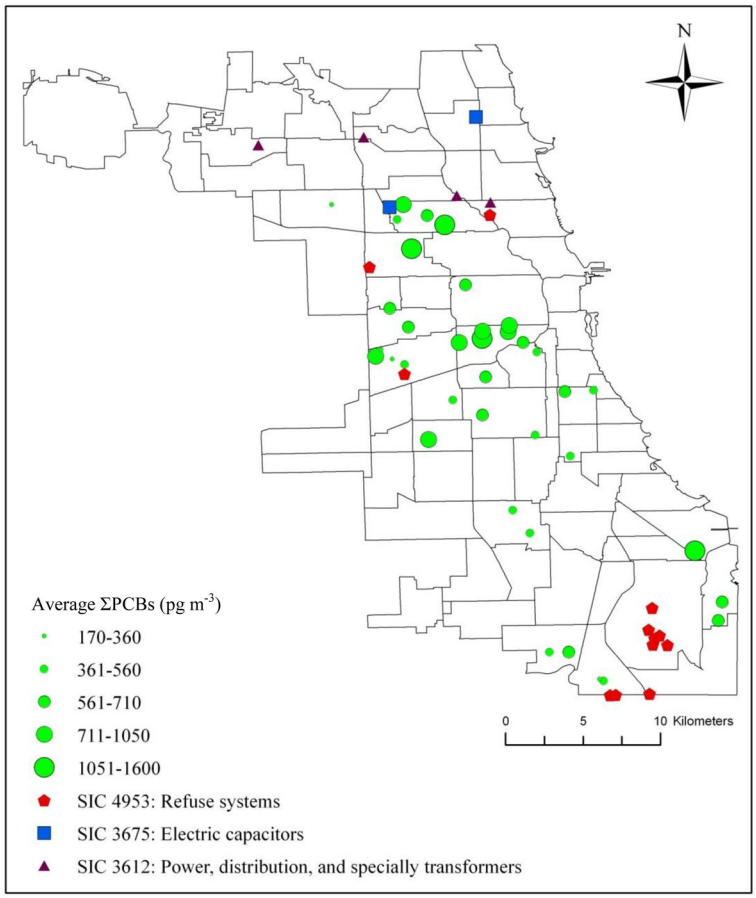


**Figure 5.**
The annual average PCBs (normalized to 15°C) in Chicago. Also shown are facilities with standard industrial classification (SIC) codes that are consistent with historical uses of PCB Aroclor mixtures.

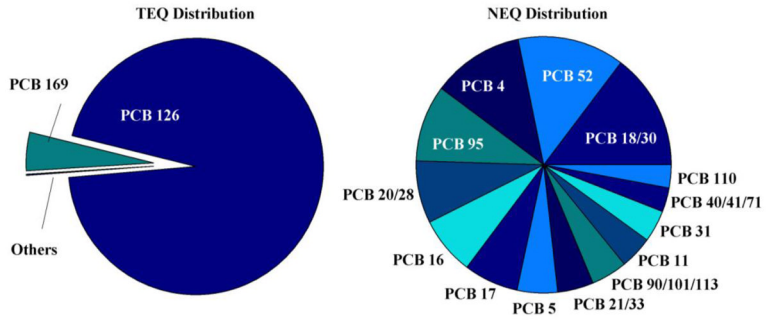


**Figure 6.**

Toxic Equivalency (left) in Chicago air is primarily due to PCB 126 (95%) and PCB 169 (4.8%) though they are not frequently detected. Neurotoxic Equivalence (right) in Chicago air is distributed between seventy congeners although only those contributing more than 2% of the total NEQ are labeled. The congener distribution shown here is the average for NEQ concentrations measured in the Chicago air samples, without temperature correction.

**TABLE 1**

Σ PCB, TEQ and NEQ concentrations in Chicago air

| | | Concentration (pg $m^{-3}$) | | | |
|---|---|---|---|---|---|
| | | **Min** | **Max** | **Median** | **Average ± SD** |
| Individual samples | Σ PCB | 75 | 5500 | 860 | 840 ± 940 |
| | TEQ | / | 5.6 | $8.0\times10^{-4}$ | 0.27 ± 0.86 |
| | NEQ | 3.7 | 2000 | 125 | 280 ± 350 |
| | $\Sigma PCB_{288}$ | 50 | 3970 | 460 | 710 ± 670 |
| | $TEQ_{288}$ | / | 7.2 | $7.0\times10^{-4}$ | 0.26 ± 0.92 |
| | $NEQ_{288}$ | 2.0 | 1220 | 130 | 210 ± 205 |
| Location average* | Σ PCB | 170 | 2900 | 770 | 885 ± 550 |
| | TEQ | / | 1.4 | 0.08 | 0.23 ± 0.34 |
| | NEQ | 67 | 440 | 200 | 208 ± 98 |
| | $\Sigma PCB_{288}$ | 170 | 1600 | 610 | 710 ± 340 |
| | $TEQ_{288}$ | / | 1.8 | 0.064 | 0.23 ± 0.38 |
| | $NEQ_{288}$ | 57 | 500 | 180 | 210 ± 100 |

/: non-detectable

*average values of individual sampling locations

$\Sigma PCB_{288}$, $TEQ_{288}$ and $NEQ_{288}$: calculated based on PCB concentrations normalized to 288K.