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Emissions of Tetrachlorobiphenyls (PCBs 47, 51 and 68) from Polymer Resin on Kitchen Cabinets as a Non-Aroclor Source to Residential Air

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Abstract

We found both Aroclor and non-Aroclor sources of airborne polychlorinated biphenyls (PCBs) in residential homes. We deployed passive air samplers at sixteen residences and found PCB-47, PCB-51, and PCB-68 to account for up to 50% of measured indoor Σ PCBs (2700 pg m^{-3}). Although PCB-47 and PCB-51 are neurotoxins present in Aroclor mixtures (<2.5 and <0.3 wt%, respectively), we found them at much higher levels than expected for any Aroclor source. PCB-68 is not present in Aroclor mixtures. Another non-Aroclor congener, PCB-11, a byproduct of pigment manufacturing, was found inside and outside of every household and was frequently the predominate congener. We conducted direct measurements of surface emissions and identify finished cabinetry to be a major source of PCB-47, PCB-51 and PCB-68. We hypothesize that these congeners are inadvertent byproducts of polymer sealant manufacturing and produced from the decomposition of 2,4-dichlorobenzoyl peroxide used as an initiator in free-radical polymerization of polyester resins. The presence of these three compounds in polymer products, such as silicone, has been widely noted, but to our knowledge it has never been shown to be a significant environment source of PCBs.

Graphical Abstract

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Supporting Information

The Supporting information contains method information, quality assurance data, tabulated statistics, select congener profiles, and full sample data tables.

The authors declare no competing financial interest.

Introduction

The presence of polychlorinated biphenyls (PCBs) in the air of schools, offices, and residential homes is as important an issue today as it was four decades ago when PCBs were banned. The risk posed to adults and children from airborne PCBs is a function of the specific congeners present, as PCBs exert toxicity through a variety of biological pathways. As a group, PCBs are classified as known human carcinogens by the International Agency for Research on Cancer (IARC).^{1, 2} Animal and laboratory studies show that many individual congeners are neurotoxins and endocrine disruptors.^{1–4} Some congeners are benign, yet their metabolic breakdown products are toxic.⁵

PCBs were originally produced and sold in the United States under the tradename Aroclor by Monsanto, until production ceased in the 1970s.⁶ Most commonly Aroclor mixtures were used as dielectric fluids in capacitors (Aroclors 1242 and 1016) and transformers (1254 and 1260). However, Aroclor mixtures were also added to many other products such as paints, lubricants (1232–1260), carbonless copy paper (1242), inks (1254), sealants (primarily 1254), adhesives (1221–1254), and various other plastics.⁶

PCBs have also been detected in modern building material as inadvertent manufacturing byproducts.^{7–11} Modern pigments, including those used in household paint, are contaminated with many different PCB congeners, such as PCBs 4, 8, 11, 28, 52, 77, and 209, as byproducts of pigment manufacturing.^{7, 9} PCB 11 is an important congener when analyzing PCB signals because it is one of the most prominent congeners from pigment, has been detected ubiquitously in the environment, and is not present in the original Aroclor mixtures.¹⁰ These non-Aroclor sources of PCBs are changing our understanding of PCB sources in the environment.

Due to the widespread historical and modern sources of PCBs, many schools, workplaces and residential homes today have significant airborne concentrations.^{12–14} In some instances airborne PCBs levels in schools have led to litigation and school closure.^{13, 15–17} Recently it has been shown that the inhalation exposure of PCBs for some children is equal to or greater than their dietary exposure.^{14, 18} More work is needed to fully understand the significance of inhalation exposures, the quantity of Aroclor PCB sources in modern buildings, and the role of modern non-Aroclor PCB sources. Here we report indoor and outdoor airborne concentrations and surface emissions in residences. We characterize the Aroclor and non-Aroclor sources of PCBs in these residences and identify a common building material as a previously unknown non-Aroclor source of PCBs.

Materials and Methods

Air Sampling

Passive air samples were collected inside and outside 16 residences in the greater Iowa City area using polyurethane equipped passive air samplers (PUF-PAS) for a 6-week interval from August 22nd to October 2nd, 2017. The double-dome PUF-PAS sampler design (with a 24 cm top bowl and 19.5 cm bottom bowl) used for this study is based on a commonly used

PUF-PAS design.^{19–22} The PUF disk used in the passive air samplers were purchased from Tisch Environmental (Clevs, OH).

Surface Emission Sampling

We designed a polyurethane foam passive emission sampler (PUF-PES) to measure volatilization of PCBs from walls, floors, and other interior surfaces. The PUF-PES consisted of a solvent-cleaned polyurethane foam disk placed inside a glass Petri dish and sealed over the surface (Figure 1). The glass Petri dish (14 cm diameter, 2 cm rim height) and the air gap assured that the PUF disk captured gas phase PCBs emitted from the surface and not from room air or from direct contact. Duplicate surface emission samplers were placed on five different surfaces at one residence. All surfaces were wiped prior to attaching the samplers to minimize the influence of dust. After fixing the PUF-PES to the respective surfaces the samplers were covered with aluminum foil and sealed. Field blanks consisted of a PUF-PES applied to foil at the same time as the other surfaces to isolate any infiltration effects. These control samples did not exhibit PCB levels above other blanks in the study, indicating no measurable air infiltration occurred. In the analysis of surface emissions, congeners were only reported if there were detected at levels above the limit of quantification (LOQ) in both duplicate samples deployed on each respective surface (Figure S6, Table S6).

Analytical Methods and Quality Control

The PUF disks were analyzed for all 209 PCB congeners with methods described previously.^{14, 23–26} Briefly, PUF disks were extracted using a pressured and heated mixture of 1:1 hexane:acetone (Dionex ASE 350). Sample extracts were cleaned with acidified silica gel and analyzed using a GC-MS/MS (Agilent 7890A GC system, Agilent 7000 Triple Quad, Agilent 7693 autosampler) in multiple-reaction monitoring (MRM) mode. The quality of the chemical measurements was assessed using surrogate recoveries, blanks, and duplicate sampling for emissions samplers. All 209 PCB congeners were initially analyzed as 173 single or co-eluting chromatographic peaks on a Supelco SPB-Octyl capillary column. In this paper, we report the Σ PCBs as the sum of 205 PCB congeners because PCBs 14, 166, and 204 are used as analytical standards and PCB 128 coelutes with PCB 166.

In specific instances of unexpectedly high congener results, specifically PCBs 44/47/65, 51, and 68, peak identification was confirmed by running the individual PCB standards and the sample on both a DB-5 and DB-1701 capillary column (Agilent Technologies). Figure 2 shows the MRM results for five tetrachlorobiphenyls (PCBs 44, 47, 65, 51, and 68) on all three capillary columns. PCB 44 and PCB 65 are included because they co-elute with PCB 47 in the SPB-Octyl column. The confirmation columns show that these two congeners were not present in our samples. In addition to the use of confirmation columns, mass spectra were examined to confirm the identity as a tetrachlorinated PCB congener. An example mass spectra for PCB 47 in a sample is provided in the SI (Figure S1).

Determining Air Concentrations

For PUF-PAS samples collected in the outdoor environment the sampling rate (R_s), and subsequent effective sampling volume (V_{eff}), were calculated using a model previously

described.^{24, 27, 28} The model calculates a deployment-, compound-, and site-specific V_{eff} based on the hourly meteorological data with wind speed as the primary component. For this study, the average outdoor R_s was $2.45 \text{ m}^3 \text{ d}^{-1}$ and the V_{eff} ranged from 30 to 200 m^3 . For the PUF-PAS samples collected indoors, we assumed a sampling rate of $1.0 \text{ m}^3 \text{ d}^{-1}$. A few studies have estimated the indoor R_s of PCB congeners for the sampler style used in this study. Bohlin and colleagues found an R_s in a lecture room of $1.2 \text{ m}^3 \text{ d}^{-1}$, Hazrati and Harrad measured an R_s in a vacant office of $0.8 \text{ m}^3 \text{ d}^{-1}$, and we have estimated an R_s for an occupied office of $1.0 \text{ m}^3 \text{ d}^{-1}$.^{29–31} We suspect the different R_s values reported for these studies are primarily a result of different air ventilation rates for the different room styles and placement within a room.

Statistics

The limit of quantification (LOQ) was calculated as the upper limit of a 95% confidence interval of blank level for each congener and concentrations below the LOQ were treated as zero. Pearson correlations were used to compare sample and source PCB profiles. Aroclor profiles were obtained from Frame et. al. (2001).³² Leverage values and Cook's distances were used to identify outliers. Large values for leverage and Cook's distance indicate an observation is not well explained in the correlation and may be an outlier.³³ These values were calculated with Minitab 17.

Results and Discussion

Outside Residences

The average outdoor airborne concentration of the sum of detected congeners (ΣPCB) was 142 pg m^{-3} (ranging from 70 to 250 pg m^{-3}), similar to previous reports for rural Iowa.¹⁸ The outdoor concentration of PCBs varied little across our study area, with a RSD of 38% for the ΣPCBs . As expected, the outdoor concentrations were lower than reported for larger metropolitan areas.^{34–39} The outdoor air profiles are similar among the samples and their sources appear to be a mixture of Aroclors and modern pigment (PCB 11). The air profile most closely resembles Aroclor 1254 but also shows contributions from 1016, 1242, and 1248 (Table S1). PCB 11 was the predominant congener in the average outdoor air profile and was measured at a level ($11 \pm 9 \text{ pg m}^{-3}$) comparable to what we have previously measured for a much larger metropolitan area, Chicago ($15 \pm 13 \text{ pg m}^{-3}$).¹⁰ This suggests that the non-Aroclor sources of PCBs, including pigments, are significant and may be less influenced by the metropolitan size than Aroclor sources, a finding also noticed by Hites.⁴⁰

Indoor Residences

The average indoor airborne ΣPCB concentration was 2830 pg m^{-3} (ranging from 450 to 6970 pg m^{-3}). This is comparable to previous reports from private residences, and lower than many schools.^{13, 14, 18} In a recent study reporting PCB levels in schools, ΣPCB levels were measured up to 194 ng m^{-3} , which is over 25 times greater than the maximum measured in this study.¹⁴ The indoor air profiles varied significantly between locations and appeared to be a mixture of Aroclor and non-Aroclor sources. The indoor air had more contributions from lighter Aroclor mixtures such as 1016 and 1242, than the outdoor air (Table S1). As with the outdoor air samples, PCB 11 was frequently the predominant

congener measured in indoor air. The average indoor air concentration for PCB 11 in this study was 370 pg m^{-3} (ranging from 100 to 2170 pg m^{-3}). At some locations PCB 11 contributed up to 30% of the PCB levels. It is unsurprising that PCB 11 is a significant congener in residential home air given the known primary source of PCB 11 in the environment is pigments.

In the most recently constructed buildings, PCBs 47, 51, and 68 appeared at levels that could not be attributed to any known Aroclor or non-Aroclor sources. On average, PCBs 47, 51, and 68 contributed 15%, 4% and 2% mass fraction to the Σ PCBs, respectively, in the five residences built in the last five years (Figure S5). The construction of the newest building in this study was completed in July of 2017, just one month prior to the start of air sampling campaign. In this residence (R1), PCBs 47, 51, and 68 contributed 37%, 11% and 5% mass fraction to the Σ PCBs, and 1900 pg m^{-3} , 530 pg m^{-3} , and 270 pg m^{-3} , respectively. PCB 68 has not been reported in any Aroclor, PCB 51 was present in one or more Aroclor at levels less than 0.25% mass fraction, and PCB 47 was present at levels less than 2.5% mass fraction.³² Residences with elevated levels of these three PCBs were identified using leverages and Cook's distances for tetra-PCBs in linear correlations between samples and Aroclors (Figure 3, Table S2). Large values for leverage and Cook's distance found for the newest buildings demonstrate that these congener concentrations are outliers and inconsistent with the congener distributions found in Aroclors.³³ All the sampled buildings that were constructed in the last five years exhibited the PCB 47/51/68 signal as did one building recently remodeled in 2017. Residence 16 had the kitchen replaced in 2017.

We investigated potential sources of PCBs by directly measuring the surface emissions in duplicate on five different surface types in the kitchen of the residence with the highest PCB 47/51/68 signal (R1). An additional air sample was collected while the PUF-PES samples were deployed. There was no statistical difference between the profiles of the two different air sampling periods ($p > 0.08$), however the measured Σ PCB concentration was different (2000 pg m^{-3} versus 5000 pg m^{-3} previously). The airborne concentration change was not surprising as the two sampling periods were months apart and occurred in different seasons (summer and winter). The Σ PCB emissions were highest from the finished cabinet ($33 \text{ ng m}^{-2} \text{ d}^{-1}$) and less from the kitchen floor ($20 \text{ ng m}^{-2} \text{ d}^{-1}$), the painted wall ($8.3 \text{ ng m}^{-2} \text{ d}^{-1}$), the stovetop ($1.6 \text{ ng m}^{-2} \text{ d}^{-1}$), and unfinished cabinet (below LOQ). Interestingly, the finished cabinet surface displayed the largest emission while the unfinished cabinet surface had no measured emissions. Under sampling conditions, the emissions value is likely at the lowest magnitude that would be observed within the residence (i.e. diffusive emissions). With increased air movement across each respective surface, the surface/air mass transfer coefficient and total emissions increase.

The finished cabinet surface is a distinct source of the PCB 47/51/68 signal to the air. These three congeners account for almost a third of the total PCB emission from the cabinet surface (Figure 4). The surfaces arranged in order from largest to smallest PCB 47+51+68 emission are finished cabinet ($16 \text{ ng m}^{-2} \text{ d}^{-1}$), painted wall ($5.0 \text{ ng m}^{-2} \text{ d}^{-1}$), kitchen floor ($4.1 \text{ ng m}^{-2} \text{ d}^{-1}$), stovetop ($1.2 \text{ ng m}^{-2} \text{ d}^{-1}$), and unfinished cabinet (below LOQ). Given the close proximity of the painted wall surface tested to the kitchen cabinets, it is possible that the elevated level of these three congeners emitting from the painted wall originate from the

finished cabinet. Emissions from newly finished cabinets may explain why these three PCBs were found in more recently constructed (R1, R6, R9, R10, R11) or remodeled (R16) buildings. Omitting the emissions of PCBs 47, 51, and 68, the finished cabinet and floor have very similar Σ PCB emissions, $17 \text{ ng m}^{-2} \text{ d}^{-1}$ and $16 \text{ ng m}^{-2} \text{ d}^{-1}$, respectively.

We hypothesize that PCBs 47, 51, and 68 are inadvertent byproducts in the cabinet manufacturing process. Given that the cabinets were supplied by different companies, the PCB source of these PCB congeners to the air may be due to a general production process rather than a single commercial product, similar to a pigment source. Perdih and Jan (1994) reported PCBs 47, 51, and 68 at trace levels in silicone rubber as a byproduct of the decomposition of 2,4-dichlorobenzoyl peroxide.^{41, 42} Diacyl peroxides (such as 2,4-dichlorobenzoyl peroxides) are often used as initiators in the free-radical polymerization of certain commercial products such as silicone and polyester.^{43–47} Polyester is a very common and widely used polymer with many important commercial applications, including wood finishing products.

The decomposition of diacyl peroxides, including 2,4-dichlorobenzoyl peroxide, has been extensively studied for decades because they are crucial to many different polymer production processes.^{41–43, 48–50} During the decomposition of 2,4-dichlorobenzoyl peroxide, 2,4-dichlorophenyl radicals are produced which can then form any number of inadvertent byproducts. The predominate products of this decomposition process are 1,3 Dichlorobenzene and PCB 47 (2,2',4,4'-Tetrachlorobiphenyl). However, the 2,4-dichlorophenyl radical and 1,3 Dichlorobenzene could react to also produce PCB 51 (2,2',4,6'-Tetrachlorobiphenyl), and PCB 68 (2,3',4,5'-Tetrachlorobiphenyl) (Figure 5). This decomposition has also been shown to produce other chlorinated benzene and polychlorinated biphenyl products in the presence of other chlorinated compounds and aromatics, such as 1,2,4-trichlorobenzene, PCB 91, and PCB 99.^{41, 42} We did not detect PCB 91 or 99 as significant levels in our PUF-PES samples, suggesting this particular production process does not include other chlorinated compounds or aromatics. The decomposition of 2,4-dichlorobenzoyl peroxide has even been intentionally used to synthesize PCBs.⁵¹

While PCBs as a chemical class have been shown to have adverse health effects, each individual congener has unique toxicological properties.¹ In toxicological studies PCB 47 has been shown to cause a massive release of arachidonic acid in rat liver tissue.⁵² Both PCBs 47 and 51 have been shown to have weak androgen receptor (AR) antagonistic potential and weak estrogenic activity.⁵³ PCBs 47, 51, and 68 can all be considered to have neurotoxic potential.^{54, 55} Based on their relative potency as reported by Simon et al., PCB 51 is a more potent neurotoxic congener (REP = 0.692) than both PCB 47 (REP = 0.497) and PCB 68 (REP = 0.209).⁵⁵ PCB 47 has been shown to be a potent inducer of Ca²⁺-dependent apoptosis in rat neurons.^{56, 57} Both PCBs 47 and 51 have been shown to be potent partial and full antagonist to human GABA_A receptors. Fernandes et al. reported PCB 47 as the most potent non-dioxin like PCB congener for activation and potentiation of the GABA_A receptor.⁵⁸ It is difficult to address the direct potential effects of these potent neurotoxic congeners in the context of our study as we do not yet fully understand the fate and toxicities of inhaled PCBs.^{59–62}

Implications

Discovery of non-Aroclor PCB sources is changing our understanding of PCBs sources in indoor and outdoor environments. Non-Aroclor PCB sources such as pigments and polymer resins may contribute significant levels of PCBs to air both inside and outside residences. Inside the residences we examined, non-Aroclor sources of PCBs often dominated the indoor air signal (Figure 6). Here we identify non-Aroclor sources as sources of PCBs other than Aroclor mixtures (i.e. pigment and polymer resin). In 76% of the indoor air samples collected in this study, PCB 11 or PCB 47 were the predominant congener, which are both present from non-Aroclor sources. On average 23% of the Σ PCB profile can be attributed to non-Aroclor sources of PCBs, with 5 residences having greater than one-third of the Σ PCB attributed to non-Aroclor sources (Figure 6). While some of these residences (R6, R9, R10, R11) had low overall Σ PCB levels compared to other residences with largely Aroclor PCB sources, residence 1 had the fourth highest Σ PCB level. The airborne PCB levels at this residences is from almost entirely non-Aroclor sources (>60% of total).

It is likely that other PCB congeners have non-Aroclor source contributions and therefore we are underestimating the total non-Aroclor contributions. For example, we only considered the PCB 47+51+68 signal as a non-Aroclor signal at the 6 residences we identified with the new source, but this source may be contributing low levels of PCBs at other residences. At residence 14, PCB 8 is the predominate congener and has a high Cook's distance (>4), indicating there may be a non-Aroclor source, such as pigment, in addition to Aroclor sources. Similarly, at residence 8, PCB 1 has a high Cook's distance (>2), indicating it could also be present from both pigment and Aroclor sources.

As PCB sources are further characterized more non-Aroclor sources may be discovered. Diacyl peroxides, such as 2,4-dichlorobenzoyl peroxides, are used as initiators in a wide array of commercial and industrial process involving polymers.⁴⁶ Muir and Howard have suggested that heavy industrial use of peroxides may be important persistent organic pollutants, in part due to decomposition.⁶³ It is possible that PCBs 47, 51, 68 and other congeners are present in yet unidentified products given the near ubiquitous presence of polymers, such as silicone and polyester, in commercial use. We found >6,000 patents in the PubChem database that mention the potential use 2,4-dichlorobenzoyl peroxide.

It is widely accepted that PCBs 47, 51, 68 and other congeners exist in polymer products at trace levels, such as silicone, but to our knowledge it has never been identified as a significant environment source of PCBs. This signal has likely not been seen in the environment previously for two primary reasons. Firstly, the signal is dominated by PCB 47 which can be present due to Aroclor mixtures therefore making it difficult to identify in complex mixtures unless the signal is large. Secondly, many studies conducted on PCBs in the environment only measure a few indicator congeners, which often do not include the analysis PCBs 47, 51 and 68. A significant benefit of analyzing all 209 PCB congeners individual is the ability to characterize the contributions of both Aroclor and non-Aroclor sources.

Rodenburg et al. identified PCBs 44+47+65, and PCBs 45+51 as a unique factor in an analysis of groundwater, landfills and wastewater collections systems.⁶⁴ They identified this factor primarily in waste water treatment plant effluents and attributed it to a partial dechlorination process, given that PCBs 47 and 51 have both been documented as partial dechlorination products previously.^{64–66} PCBs 47 and 51 contributed up to 60% of ΣPCBs in this factor. Although Rodenburg et al identified these compounds as products of Aroclor dechlorination, it is possible that they found PCBs 47 and 51 in wastewater due to polymer manufacturing discharges in the New Jersey area.⁶⁴ This non-Aroclor source of PCB congeners may be in industrial waste effluent and an important source to the aquatic environment as it appears to be in indoor air.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1:
Schematic of polyurethane equipped passive emission sampler (PUF-PES).

Figure 2: GC/MS/MS chromatograms of PCBs 47, 51, and 68 on (i) Supelco SPB-Octyl capillary column (ii) Agilent Technologies DB-5 capillary column and (iii) Agilent Technologies DB-1701 capillary column.

Figure 3:

Summary of average Cook's Distance and Leverage for the tetrachlorobiphenyls profile between Aroclors and each residence for PCB 47 (Tables S2). The larger the value the more important the signal is to the total and the less likely it can be explained by Aroclor sources. Residence R16 had the kitchen remodeled in 2017.

Figure 4:
PCB surface emissions measurements of 5 different surfaces for ΣPCBs, PCB11, PCB52, and PCBs 47+51+68. The bars represent the mean of the duplicate samples and error bars represent the largest of the two measurements.

Figure 5:

PCB formation pathways in polymer production using 2,4 dichlorobenzoyl peroxide as an initiator in free-radical polymerization. The most probable inadvertent byproducts are 1,3 Dichlorobenzene and PCB 47 (2,2',4,4' Tetrachlorobiphenyl) with PCB 51 (2,2',4,6' Tetrachlorobiphenyl), and PCB 68 (2,3',4,5' Tetrachlorobiphenyl) likely being secondary byproduct reactions.

Figure 6:

Percent of the indoor air PCB levels attributed to non-Aroclor sources for each residence arranged in order of building construction age. On average 23% (range 4% to 60%) of the Σ PCB profile can be attributed to non-Aroclor sources.