# Passive air sampling networks combined with multivariate statistics reveal widespread non-Aroclor polychlorinated biphenyl sources to the Canadian atmosphere

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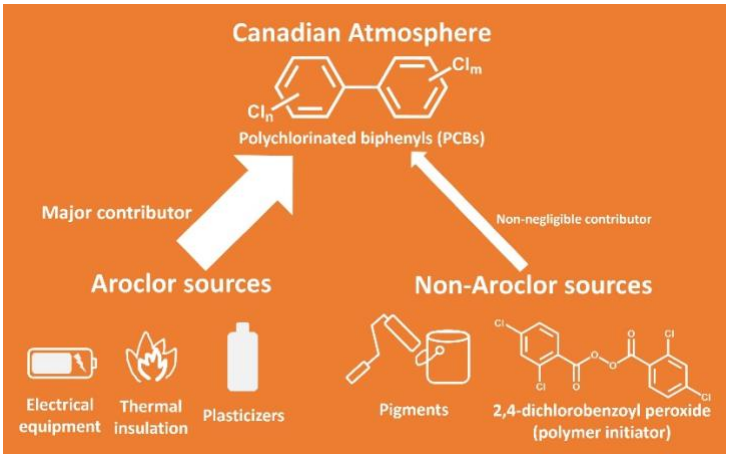



**Synopsis:** Clusters of PCB congeners 7, 25, 47, 51, and 68 identified in two different coastal regions of Canada strongly indicate that use of 2,4-dichlorobenzoyl peroxide is an ongoing source of PCBs to the atmosphere.

# Abstract

Polychlorinated biphenyls (PCBs) in the North American atmosphere were originally thought to arise through volatilization of commercial Aroclor mixtures, but there is growing evidence of atmospheric emissions of non-Aroclor, i.e., unintentionally produced, PCBs. Here, we report on measurements of all 209 PCB congeners in 169 passive air samples collected between 2019 and 2022 using networks established around the Salish Sea, British Columbia (BC) and along the St. Lawrence River and Estuary, Quebec (QC) in Canada. Hierarchical cluster analysis and positive matrix factorization were employed to identify, distinguish and quantify different PCB sources to the atmosphere. PCBs were detected at every single site, with elevated levels found in the urban centers of the region (Vancouver, BC; Montreal and Quebec City, QC), including in the vicinity of a municipal waste incinerator. We found evidence that suggests legacy Aroclor emissions, e.g., associated with electrical equipment storage in Pointe-Claire, QC, and building emissions in Burnaby, BC. We also identified several locations (e.g., in Sept-Îles and Alma, QC) where non-Aroclor sources are estimated to contribute over 40% of PCBs. In particular, PCB congeners 47, 51, and 68, known by-products of 2,4-dichlorobenzoyl peroxide (2,4-DCBP) decomposition during silicone rubber and polyester production, were strongly associated with PCB-7 and 25. Although Aroclors were estimated to remain the main contributors of PCBs to the Canadian atmosphere, unintentional production is making non-negligible contribution (estimated to be at least 10%). Of the known non-Aroclor sources, 2,4-DCBP is likely still used in North America with little to no regulation.



# Keywords

Polychlorinated biphenyls, Aroclor, non-Aroclor, positive matrix factorization, hierarchical cluster analysis, passive air samplers, Quebec, British Columbia


# Introduction

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants (POPs) that were produced and used extensively worldwide starting from the 1930s. In North America, PCB mixtures under the trademark name Aroclor were used for a wide variety of applications, such as dielectric fluids and plasticizers.[1] However, with their toxicity, bioaccumulation potential, and persistence in the environment becoming evident, North American Aroclor production officially ceased in 1979,[2] which later became an international ban under the Stockholm Convention.[3] Under similar regulations, other POPs, such as certain organochlorine pesticides, have shown steadily declining levels.[4] PCBs, however, remain globally detected

in the atmosphere to this day, decades after international regulations were put in place.[5-7] Through atmospheric transport, volatilized PCBs are delivered to land[8] and water bodies.[9] These hydrophobic contaminants can subsequently magnify through aquatic and terrestrial food chains to reach appreciable levels in humans and high trophic level animals.[10] Long term exposure to PCBs has been linked to numerous adverse effects such as immune[11] or reproductive system[12] dysfunction and neurodevelopmental disorders.[13, 14] Therefore, ambient PCBs pose a potential risk to human and wildlife health. In particular, the detrimental impacts of PCBs have been implicated in the critical endangerment of two Canadian whale populations, the Southern resident killer whales (*Orcinus orca*)[15, 16] and the St. Lawrence Estuary beluga whales (*Delphinapterus leucas*).[17, 18] These whale populations struggle to sustain their numbers, despite many conservation efforts. Therefore, even years after the PCB production ban, it is crucial to identify sources of atmospheric PCBs, focusing on the endangered whale habitats and the areas in the vicinity where source identification has been non-existent.

Initially, the legacy use of Aroclors, i.e., intentionally produced PCBs during the mid-20$^{th}$ century, was assumed to be the sole source of atmospheric PCBs in North America. However, the detection of PCB-11, a congener not present in commercial mixtures, in the global atmosphere[19-24] revealed new sources of PCBs. Dubbed as non-Aroclors, these congeners originate as side products from unrelated processes, such as pigment,[22, 25, 26] cabinet sealing,[27] and silicone rubber production,[28] as well as incineration of waste[29, 30] and e-waste dismantling.[31] Over the years, non-Aroclor sources have been shown to make non-negligible contributions to atmospheric PCB levels.[21, 23, 32] However, there are several challenges in distinguishing and quantifying contributions from non-Aroclor and Aroclor sources. Many congeners originating from known non-Aroclor sources can also be found in Aroclor mixtures.[33, 34] There are also possibly more non-Aroclor sources yet to be discovered. Moreover, the differing vapour pressures and partition ratios of PCB congeners[35] will result in the gradual deviation from the original Aroclor and non-Aroclor source profiles in the atmosphere. Their varying properties can also cause methodological challenges in measuring all PCBs in the air. For example, using active air samplers may underestimate the contribution of volatile congeners, as they are prone to breakthrough losses, especially when using low-capacity sorbents such as polyurethane foam (PUF).[36-38] All these factors combined make it challenging to attribute atmospheric PCBs to specific sources and quantify their contributions.

Due to their low-cost and easy deployment, many passive air samplers (PASs) can be deployed concurrently to build large regional sampling networks, mapping the spatial variability of atmospheric contaminants.[39] By identifying regions with specific congeners or elevated air concentrations, PAS

networks can be effective in atmospheric source tracking, which has been used previously in identifying local sources of PCBs.[33, 40-43] Employing multivariate statistics and receptor models has also been proven to be useful for source appointment or contribution quantification of PCBs and other POPs, such as hierarchical clustering analysis (HCA)[44-46] and positive matrix factorization (PMF).[33, 45, 47] Multivariate receptor models (e.g., PMF) have also been used in distinguishing Aroclor and non-Aroclor sources,[21, 33] but the number of published studies has been limited. In particular, multivariate statistics has not been applied to PCB data obtained from a passive air sampling network.

With the objective to identify the occurrences of PCBs and quantify both Aroclor and non-Aroclor sources affecting the habitat of the two endangered Canadian whale populations, we investigated PCB congener profiles in PASs deployed in two networks comprising coastal regions of Quebec (QC) and British Columbia (BC). The measured profiles were then quantitatively investigated with (i) HCA, to identify distinct PCB sources in the region, and (ii) a PMF model, to quantify Aroclor and non-Aroclor PCBs contributions to the Canadian atmosphere. With all 209 PCB congeners analyzed, this is the first comprehensive study on Aroclor and non-Aroclor source appointment in Canada.

# Materials and Methods

**Air Sampling.** Two networks of XAD-2 resin based PASs were deployed in the Southern coastal regions of QC and BC to study gas-phase contaminants in the atmosphere as described elsewhere.[48] In brief, two XAD-2 resin-filled mesh cylinders were deployed in metal housings at 118 unique sites between 2019 and 2022, with one cylinder used for analysis and the other being archived. PASs were deployed at some sites more than once, resulting in a total of 169 PASs during the sampling period. Maps of the networks are shown in Figure S1, while coordinates of the sampling sites, dates of deployment and retrieval, and deployment duration are provided in Table S1 in the Supporting Information.

**Sample Extraction.** All air samples were extracted with a Dionex ASE 350 using hexane/acetone (V/V = 1:1) at 75°C and 1500 psi with a heat- and static-time of 6 min using three extraction cycles. Prior to extraction, ten $^{13}$C-labelled surrogates ($^{13}C_{12}$-PCB-11, 28, 52, 77, 101, 155, 178, 202, 206, and 209) were spiked into all samples. All extracts were reduced in volume to 1 mL using a rotary evaporator and dried with baked anhydrous sodium sulfate ($Na_2SO_4$) to remove any residual water. The extracts were then concentrated and solvent-exchanged into iso-octane, with a final volume of ~0.5 mL. An injection standard ($^{13}C_{12}$-PCB-105) was added to the final extracts.

**Instrumental Analysis.** Instrumental analysis for the quantification of 209 PCB congeners (124 individual congeners and 85 co-eluting congeners; Table S2) in all air sample extracts was conducted by gas chromatography (GC, Agilent 8890) coupled to a triple quadrupole mass spectrometer (Agilent 7010B), operated in multiple reaction mode under EI conditions. A volume of 1.0 µL of each extract was injected using an autosampler. Chromatographic separation was carried out using CP-Sil column (50 m length, 0.25 mm I.D., 0.15 µm film thickness), with helium as the carrier gas at a flow rate of 1.1 mL $min^{-1}$. The transfer line, ion source, and interface temperature were set to 280 °C, 230 °C, and 290 °C, respectively. The GC oven temperature was set at 100 °C for 0.5 minutes, increased to 160 °C at 10 °C $min^{-1}$, then increased to 250 °C at 3 °C $min^{-1}$, and finally increased to 300 °C at 10 °C $min^{-1}$ before being held for 10 min. The precursor and product ions, as well as the collision energies (CEs) of the target compounds are tabulated in Table S3. An internal quantification method was employed to quantify PCB congeners in all air samples. The reported PCB data are recovery corrected.

**QA/QC.** All glassware was machine-washed with detergent, rinsed with DI water, and baked at 450°C for 24 hours before use. All laboratory equipment in contact with samples and extracts were cleaned and rinsed with acetone and hexane three times. Procedural (solvent blanks) and field blanks were used to quantify any contamination that may have occurred during the handling and processing of air samples. Field blanks are sorbents that underwent the same handling and processing as exposed samplers. PAS field blanks (BC: n=47; QC: n=19; ON: n=6) consisted of XAD-2-filled mesh cylinders that were briefly exposed to the air during the deployment of a PAS. Afterwards, they were stored in a sealed shipping container at the sampling site for the duration of deployment. All blanks went through the entire extraction and quantification procedure with the samples. The reported PCB concentrations (Supplementary Excel File) were not blank corrected as the amount in blanks was always less than 5% of the amount in exposed samples. The Method Detection Limit (MDL) for each sampling technique was defined as the standard deviation of the field blanks multiplied by three for compounds that were detected. Otherwise, the MDL was defined as the concentration at which the signal-to-noise ratio was ten. The MDLs are tabulated for each target analyte in Table S4. The average recoveries of the $^{13}C$-labelled surrogates were within acceptable range and are summarized in Table S5.

**Data analysis and statistical methods.** Volumetric air concentrations (pg $m^{-3}$), averaged over the deployment period of the PASs, were calculated by dividing the quantified amount of the analyte (pg) by the product of the deployment period (days) and a sampling rate ($m^3$ $day^{-1}$). Congener-specific sampling rates at the average air temperature during the deployment period (Table S1) and an average wind speed

of 1.7 m $s^{-1}$ were estimated as described in Li et al.[49] The concentrations below the MDL were represented by half the value of the compound specific MDL when calculating summary statistics, but were assigned a very low value ($10^{-6}$) for the HCA and PMF, because the latter does not allow zeroes in the sample matrix.[50, 51] HCA was performed on the detected congener concentrations from the PASs using Euclidean Distance. Heatmaps, generated using the pheatmap package in R,[52] were used to visualize results. The U.S. Environmental Protection Agency's PMF model (version 5.0) was used on the air sample matrices of all analyzed congeners. To observe regional differences, the BC and QC networks were analyzed separately in both HCA and PMF. The PMF model resolved six and four factors from the BC and QC sample matrices, respectively. More details on the PMF analysis are provided in Text S1.

## Results and Discussion

**Absolute PCB concentrations and comparisons with previous measurements in Canada.** Gas-phase PCBs were present above the MDL in every air sampler. The number of congeners detected in a PAS extract varied from 2 to 84 congeners (co-eluted congeners were counted as two or three individual congeners accordingly) and averaged 41 congeners. Total PCB concentrations were slightly higher in PASs deployed across BC (mean 220 pg $m^{-3}$; median 130 pg $m^{-3}$) than in Quebec (mean 148 pg $m^{-3}$; median 89 pg $m^{-3}$), possibly because of the more urban character of the sampling network in BC, which included many sampling sites in the greater Vancouver metropolitan region. A contributing factor could also be the generally higher temperatures on the West coast (Table S1).

Due to their volatility, light PCB congeners were typically most frequently detected. Table 1 summarizes the results of the five congeners most consistently detected in BC and QC, appearing in at least 86% of the samples, while the concentrations of all detected congeners for each individual sample are tabulated in the supplementary Excel file. While PCBs have been extensively monitored in the atmosphere,[53-56] this has not been the case in Canadian coastal regions. Only a few measurements of PCBs in the BC and QC coastal areas exist in the literature, with most of them either several decades old,[57, 58] and therefore may not reflect current conditions, exclude many congeners,[58, 59] or did not resolve individual congeners.[60] Moreover, only one study had sampled in Quebec near the St. Lawrence River (Villeroy), with air concentrations recorded for two congeners over three decades ago.[58] On Saturna Island, previous air concentrations for PCB congeners were reported as the sum of gas and particle phase,[57] making it difficult to compare to the measurements in this study, which are in the gas phase only. Nevertheless, the mean and range of the air concentrations reported here aligns with those measured in urban and rural locations

elsewhere in North America, such as in Chicago,[61] Toronto,[49] and sites within the Laurentian Great Lakes basin.[62]

Table 1. The detection frequency, median, mean, and maximum of the concentrations of the fifteen most frequently detected PCB congeners and the total PCB concentration in the passive air samples in Canada. All concentrations are expressed as pg $m^{-3}$. For statistical purposes, the measurements below the MDL were represented by half the value of the congener specific MDL.

| BC (n=83) | | | | |
|---|---|---|---|---|
| Congener | n>LOD | Mean | Median | Max |
| 4+10 | 81 | 1.32 | 0.95 | 6.08 |
| 8+5 | 77 | 4.32 | 3.58 | 13.5 |
| 21+33+20 | 74 | 3.05 | 2.21 | 10.2 |
| 43+49 | 74 | 8.80 | 5.38 | 31.1 |
| 28 | 72 | 3.58 | 2.33 | 13.9 |
| 31 | 71 | 4.58 | 2.89 | 17.4 |
| 11 | 69 | 14.2 | 12.5 | 68.2 |
| 18 | 67 | 6.01 | 3.95 | 22.1 |
| 15 | 66 | 0.85 | 0.65 | 2.97 |
| 6 | 65 | 0.95 | 0.84 | 3.28 |
| 1 | 64 | 1.25 | 1.13 | 3.87 |
| 3 | 62 | 0.97 | 0.92 | 3.68 |
| 47+48+75 | 61 | 10.7 | 6.00 | 74.0 |
| 26 | 59 | 1.74 | 1.62 | 5.33 |
| 17 | 56 | 2.20 | 1.64 | 8.78 |
| ΣPCBs | | 220 | 130 | 749 |

| QC (n=86) | | | | |
|---|---|---|---|---|
| Congener | n>LOD | Mean | Median | Max |
| 1 | 86 | 1.95 | 1.46 | 12.8 |
| 2 | 86 | 1.43 | 1.39 | 3.82 |
| 4+10 | 86 | 2.05 | 1.11 | 14.3 |
| 8+5 | 86 | 5.84 | 3.78 | 34.3 |
| 21+33+20 | 86 | 2.93 | 1.93 | 17.5 |
| 3 | 85 | 1.33 | 1.19 | 3.63 |
| 6 | 85 | 1.07 | 0.68 | 6.60 |
| 43+49 | 84 | 5.76 | 4.73 | 23.0 |
| 53 | 82 | 1.60 | 1.38 | 5.76 |
| 28 | 78 | 3.20 | 2.14 | 19.4 |
| 18 | 77 | 5.85 | 3.83 | 36.9 |
| 31 | 76 | 4.19 | 2.75 | 27.0 |
| 11 | 75 | 8.44 | 7.60 | 33.6 |
| 17 | 65 | 2.50 | 1.51 | 16.6 |
| 16+32 | 64 | 3.13 | 1.88 | 23.8 |
| ΣPCBs | | 146 | 89 | 776 |

**Spatial variability of total PCB concentrations in Canadian coastal regions.** The PAS networks provide information on the spatial variability of the total PCB concentration in the atmosphere (Figure 1). Concentrations are elevated in populated urban areas, a trend that has already been observed in previous studies elsewhere in the world.[63-66] In QC, high levels of PCBs were found on the Island of Montreal and in Quebec City. Two QC sites, in particular, had some of the highest concentrations of PCBs measured in this study; one located near a municipal waste incinerator in Quebec City (S37 and the surrounding sites, S36-S40) and one close to a former storage facility for PCB-containing equipment near Montreal (S1).[67] In BC, the Vancouver metropolitan area contained several urbanized or industrialized locations with elevated levels of PCBs, such as sites close to or on the Burnaby Campus of Simon Fraser University (L3-L5), near Boundary Bay Airport (L16), and near an industrial park in Maple Ridge (L25).

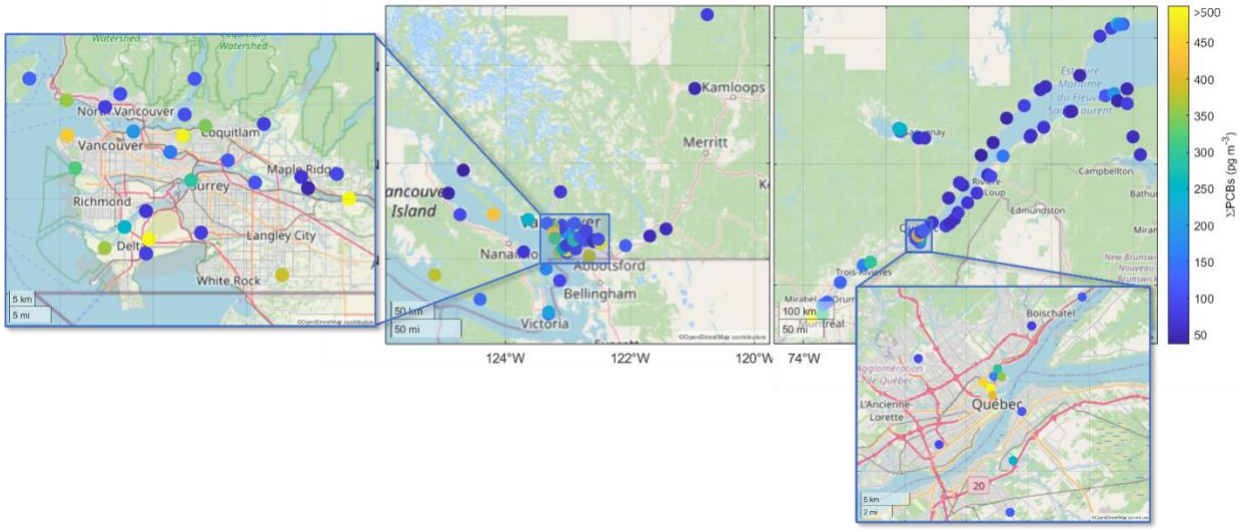



Figure 1. The spatial distribution of the total PCB air concentrations in British Columbia and Quebec. Close up maps provide a detailed view of the sites in the Vancouver metropolitan area (left) and Quebec City (right). Average total PCB concentrations are displayed for sites with replicate deployments. Maps were generated using OpenStreetMap data, available under the Open Database License (https://www.openstreetmap.org/copyright).

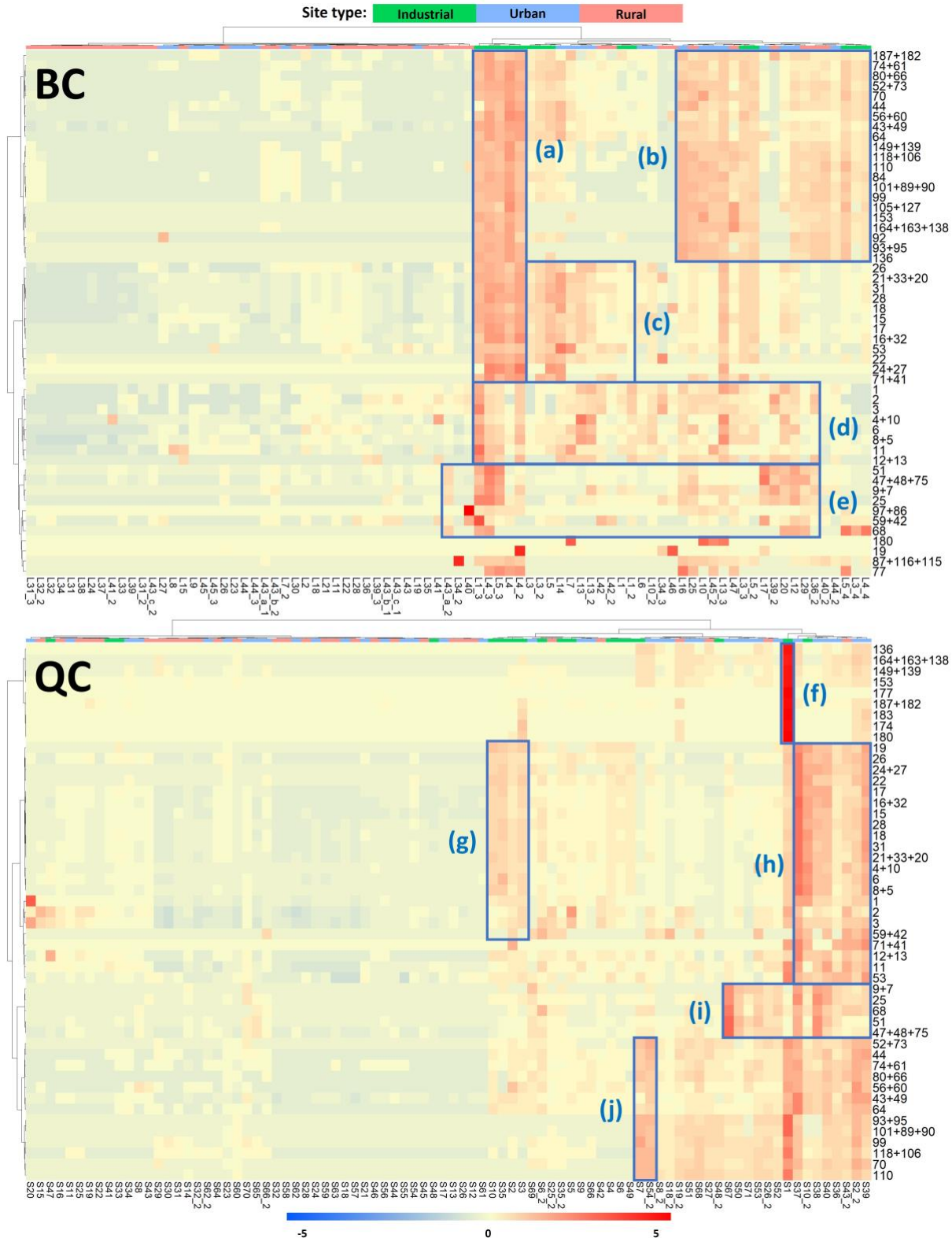
**Hierarchical cluster analysis on British Columbia PAS network.** HCA was applied to the results of the PAS networks to investigate the origin of PCBs in the atmosphere. The clustered heatmap for the BC PAS network (Figure 2) featured five spatial clusters, mostly consisting of sites located in the Vancouver metropolitan area. High levels of a wide range of congeners observed at sites from cluster (a) suggest origins from Aroclor use. We suspect that buildings are a source of airborne PCBs to PASs deployed near Simon Fraser University, as much of the Burnaby Campus was built in the 1960s and 1970s, when PCBs were used extensively in construction applications, e.g., in sealants. Clusters (b) and (c), despite comprising a few sites outside of Vancouver, also capture the Aroclor signature seen in (a), with heavier and lighter congeners separated into clusters (b) and (c), respectively. This separation can be explained by different deployment temperatures, as the PASs in cluster (b) were primarily deployed during summer (> 13°C), whereas those in (c) were sampled during the colder season (< 10°C).

Congeners from clusters (d) and (e) likely arise from non-Aroclor sources, due to the presence of several congeners believed to be exclusively non-Aroclor. PCB-11 has been previously detected in various commercial pigments[22, 25, 26] and is clustered within (d) with several other light congeners (e.g., PCB-1, 2, 3, and 6). This combination of congeners was reported to be a by-product of several yellow azo-type pigments,[25] suggesting volatilization from painted surfaces and products, including newspapers and magazines,[32] predominantly in the Vancouver area. Cluster (e) includes PCB-47(+48+75), 51, and 68, which

were documented by-products of the decomposition of diacyl peroxides, initiators often used in the free-radical polymerization of products such as silicone rubber and polyester.[27, 28, 68, 69] As these substances have a wide range of commercial applications, it is plausible that these congeners have volatilized from populated urban areas with generally greater usage of silicone or polyester-containing products. These congeners are also clustered with PCB-7(+9) and 25, which are mostly detected in lesser but nontrivial amounts. However, the two congeners are not often mentioned in the literature as by-products of diacyl peroxide decomposition. This congeneric clustering is also seen in the heatmap of the QC PAS network and is further discussed below.

**Hierarchical cluster analysis on Quebec PAS network.** The HCA also grouped the congeners detected in the QC PAS network (Figure 2) into five distinct clusters. Cluster (f) included some of the heaviest, least volatile PCB congeners detected in the PAS network (PCB-136 to 187), which may have originated from a nearby former storage facility for PCB-containing equipment.[67] Clusters (g) and (h) have similar congener patterns and represent an urban signature, i.e., volatilization of Aroclors from Montreal (S2 and S3) and Quebec City (S10, S35-39, S43), consistent with the region's high population density and industrial history. Other locations in QC known for their industrial activities, and therefore potentially connected to Aroclor use, include Le Bas-de-Cournoyer (S7) and Saguenay (S54), which comprise cluster (j). Some sites in Quebec City are located near the municipal waste incinerator (S35-40), which could potentially explain why more congeners are detected at the Quebec City sites in (h) (S36-39). This incinerator has previously been suspected to be a source of POPs to the local atmosphere.[70] Moreover, PCB-11 and the other volatile congeners found in commercial paints are present in (h) and (i), consistent with the volatilized pigment clustering observed, typically at the urbanized sites of BC.

Similar to BC, cluster (i) in the QC heatmap shows the characteristic pattern related to silicone and polyester production, i.e., PCB-47, 51, and 68. Several sites in this cluster only show strong levels of the congeners in (i), such as Sept-Îles (S67) and near (S50) and within Alma (S52 and 53). PCB-7(+9) and 25 are again grouped closely with these congeners in the heatmap, often observed in concentrations at the same order of magnitude as PCB-68, but one magnitude less than PCB-47 and 51. While the link between PCB-47, 51, and 68 with silicone rubber and polyester production has been documented recently,[27, 28, 71, 72] only one group had previously reported the formation of other PCBs from this process, including PCB-7 and 25, as well as several other congeners.[68, 69]

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242 Figure 2. The clustered heatmap of the detected PCB congeners (listed on the y-axis) in the BC and QC PAS
243 networks. Sites in the networks (listed on the x-axis) are labelled as industrial, rural, or urban on the top
244 of each heatmap. Boxed spatial clusters (a-j) are discussed in the text.

We hypothesize that PCB-47 is the primary congener unintentionally produced during silicone rubber and polyester production from the decomposition of the initiator, e.g., 2,4-dichlorobenzoyl peroxide (2,4-DCBP), with PCB-51 and 68 as secondary by-products (Figure 3). In addition, PCB-7 and 25 are likely minor but non-negligible products formed through other pathways. The decomposition of 2,4-DCBP produces the 2,4-dichlorophenyl radical, which can then form 1,3-dichlorobenzene (1,3-DCBz). Propagation of the radical species with 1,3-DCBz could lead to PCB-47 as the major product due to the *ortho*- and *para*-directing nature of the chlorine substituents, followed by PCB-51 and 68 (II). The former could also be produced from the dimerization of the radical species (I), contributing to the overall dominance of PCB-47. This is also in agreement with the higher concentrations of PCB-47 observed at the sites in (e) and (i) compared to PCB-51 and 68 (although it is possible that PCB-48 and 75 which are co-eluting with PCB-47 may be skewing its relative abundance). Other possible pathways include: the elimination of a chlorine radical from 1,3-DCBz with the radical species, resulting in the formation of PCB-25 (III), and the elimination of a hydrogen radical from benzene with the radical species, producing PCB-7 (IV). Other reaction pathways were conjectured to produce other congeners, such as PCB-49 and 66 through the formation of 1,2,4-chlorobenzene.[68] However, their connection to (i) was tenuous in QC, and they were not clustered at all to (e) in BC.

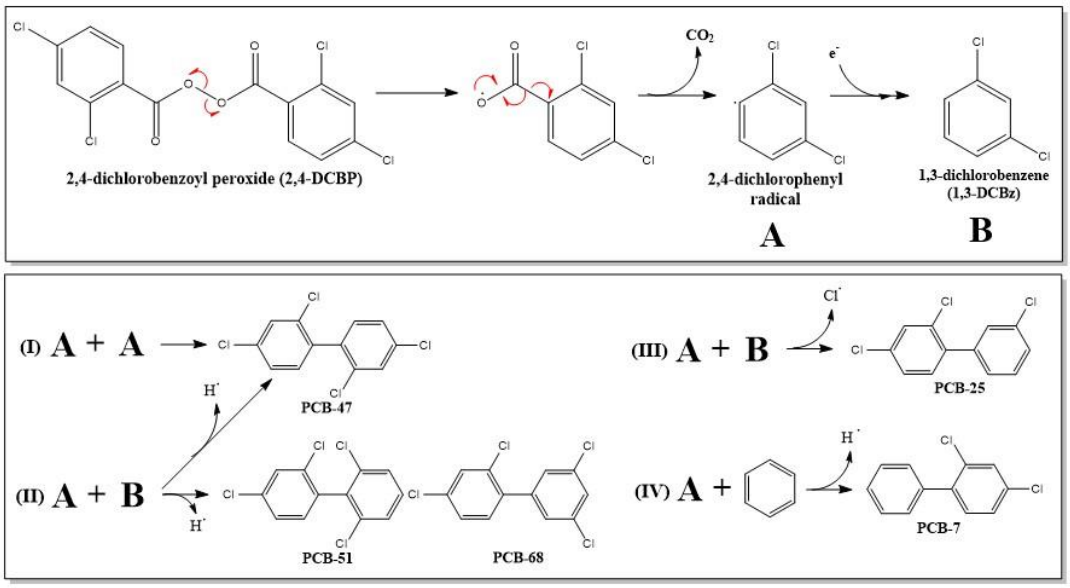


Figure 3. The proposed PCB formation pathways from the decomposition of 2,4-DCBP. Possible reaction pathways include: (I) the dimerization of the 2,4-dichlorophenyl radical, (II) the chain propagation of the 2,4-dichlorophenyl radical with 1,3-DCBz, (III) the elimination of a chlorine radical from 1,3-DCBz, and (IV) the elimination of a hydrogen radical from benzene.

**Aroclor sources in Canadian coastal regions identified by PMF.** The PMF model identified six and four factors in the BC and QC PAS network data, respectively (Figure S2 and S3), which included all 209 congeners analyzed. We compared these factors to those calculated using only detected congeners in the sample matrix and found negligible change in the results. This is further explained in Text S2. We then used the cosine theta similarity metric (cos θ) to compare factors with Aroclor mixtures and assess their similarity. However, more volatile PCB congeners preferentially volatilize from an Aroclor mixture emissions, resulting in a shift in the composition of the volatilized emissions. Therefore, we multiplied each congener in the Aroclor profiles reported by Frame *et al.*[73] by its vapour pressure at the average deployment temperature in each regional network, normalized by the total volatilized PCB concentration, to obtain BC and QC-specific volatilized Aroclor profiles, as described elsewhere.[51] We also applied an iterative method to identify the mixture of two volatilized Aroclor profiles that most closely resembled each factor (highest cos θ).

At least one factor from each region resembled a mixture of Aroclors, with Factor 1 in BC and QC bearing the most similarity to Aroclors (cos θ = 0.82 and 0.91 for BC and QC, respectively; Figure S2 and S3). Moreover, Factor 1 in both regions matched the same combination of Aroclors, G3 1242 and G3.5 1248, which were some of the most sold Aroclors in the U.S. in the mid-20$^{th}$ century.[74] While Canada did not manufacture PCBs, it was estimated that 40 kilotons of Aroclors were cumulatively imported into Canada, consisting of 7% of the total U.S. sales.[74, 75] Therefore, it is reasonable that the Aroclor mixtures most produced and used in the U.S. would also appear in Canada. Aroclors 1242 and 1248 have been previously identified as likely sources of PCBs to the atmosphere in North America,[33, 40, 76, 77] with weathered Aroclor 1242 sometimes resembling unaltered Aroclor 1248.[78]

Several factors matched poorly with mixtures of Aroclors, e.g., Factors 2 and 4 from both regions (cos θ ≤ 0.58) but had relatively high percentages of non-Aroclor exclusive congeners (PCB-11 in Factor 2) or combinations of congeners linked to non-Aroclors (PCB-47, 51, and 68 in Factor 4). It is likely that at least some of the congeners in these profiles originate from non-Aroclor sources. The remaining factors were only marginally similar to Aroclor mixtures (e.g., Factor 5 from BC; cos θ = 0.39), suggesting that these sources have: a) undergone substantial weathering, b) are combined with secondary sources (e.g., re-volatilization from terrestrial and aquatic surfaces), or c) do not have Aroclor origins. These factors can still be used to deduce the major Aroclor mixtures historically used in Canada. Factor 6 of BC, for example, which was calculated to be most similar to G4 1254 and A4 1254, resembles the congeneric profiles of Figure 2 cluster (a) of BC, i.e., of Simon Fraser University, particularly with site L4 (cos θ = 0.92). Aroclor

297 1254 was used in construction applications,[1, 74] and therefore can be found in building emissions, agreeing
298 with the results of the HCA.

299 **Potential non-Aroclor sources in Canadian coastal regions identified by PMF.** To quantify the contribution
300 of possible non-Aroclor sources to the Canadian coastal atmosphere, we selected for further analysis those
301 factors that were deemed most likely to represent Aroclor and non-Aroclor sources. These were
302 dominated by congeners from known non-Aroclor sources, such as pigments and sealants (Factors 2 and
303 4) or were most similar to Aroclor sources (Factor 1). The PCB profiles of the Aroclor mixtures that best
304 matched the factors were then subtracted from the factor profiles, as described by Jahnke *et al*.[33] The PCB
305 profile remaining after the subtraction cannot be explained by PCBs volatilized from Aroclor sources and
306 therefore may have instead emerged from non-Aroclors. By summing the remaining profile, the
307 contribution from Aroclors vs. non-Aroclors can be quantified for each factor (Figure S4 and S5). Some
308 factors had more non-Aroclors potentially contributing to their total profile than Aroclors, such as Factor
309 4 of BC and QC (66% and 54%, respectively). Nevertheless, all factors had varying estimated contributions
310 of non-Aroclors in their profile (≥25%). Moreover, we calculated for each site the weighted average of the
311 potential non-Aroclor contribution from Factors 1, 2, and 4 using the contribution of each factor to each
312 site in the network. The spatial distribution of the potential non-Aroclor contribution in the Canadian
313 coastal regions (Figure 4) shows various sites in the Vancouver metropolitan area in BC, as well as Alma
314 and Sept-Îles in QC with substantial non-Aroclor contribution (≥40%) to their PCB profile, in agreement
315 with the results from the HCA. Other locations with strong presence of non-Aroclors include Comox, BC,
316 (L38) and the shores of the upper St. Lawrence estuary between Quebec City and Riviere-du-Loup (e.g.,
317 S15, 16, 45-47). The latter is part of the primary habitat of the St. Lawrence belugas. Despite relatively low
318 total PCB levels, the profiles in those areas contain sizeable amounts of non-Aroclor congeners (e.g., PCB-
319 11). Finally we calculated the overall potential non-Aroclor contribution to the total PCBs in the BC and QC
320 atmosphere by combining the estimated non-Aroclor contribution to each factor and the contribution per
321 congener by each factor to the total dataset. To express the contribution from each region as a range,
322 maximum and minimum values were determined by using all identified factors and by using only the
323 contributions of known exclusively non-Aroclor congeners (i.e., PCB-11, 47, 51, and 68) from selected
324 factors (Factors 1, 2, and 4), respectively in the analysis, as these represent the most lenient and stringent
325 estimations. This resulted in comparable upper and lower bounds between the regions (BC: 10%-46%; QC:
326 13%-43%). Modifying the minimum estimate by using non-Aroclor contributions of all possible congeners
327 from the selected factors resulted in values between the ranges (BC: 16%; QC: 27%), which we suspect are

the likely non-Aroclor contributions from each region. In summary, all estimations indicate that a non-negligible portion of the total air PCBs in Canada originates from non-Aroclor sources.

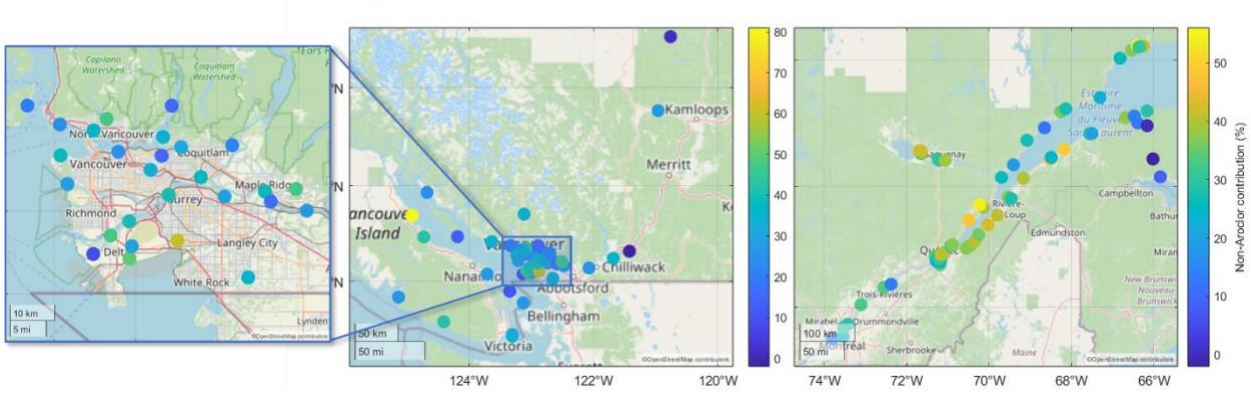


Figure 4. The potential non-Aroclor contribution at the BC and QC sites, using contributions from factors 1, 2, and 4 of each region. Maps were generated using OpenStreetMap data, available under the Open Database License (https://www.openstreetmap.org/copyright).

## Implications

Although we attribute the majority of PCBs in the Canadian atmosphere to the volatilization of Aroclors, we also find a non-negligible contribution of PCBs (estimated to be at least 10%) originating from non-Aroclor sources. Non-Aroclors were not only detected in urban areas (e.g., Vancouver, Montreal), but also near the habitats of the St. Lawrence belugas, indicating a possible source of exposure. Non-Aroclors have been reported in other whale species,[79] suggesting the potential for uptake of non-Aroclors by the belugas.

Most congeners found in the non-Aroclor profiles have been detected in commercial products such as pigments and colourants,[22, 25, 26] with the notorious example being PCB-11. Several of these congeners can also be found in Aroclors, such as PCB-3 and 6, and we calculated both Aroclor and non-Aroclor contributions to these volatilized PCB profiles. The remaining congeners are rarely present in the major Aroclor mixtures historically used in North America, accounting for less than 1% of their pure and volatilized profiles, such as PCB-73 and 80. Despite being detected in the PAS network with estimated non-Aroclor contributions, no other sources of these congeners have been reported in the literature. It is probable that there are non-Aroclor sources to the atmosphere currently residing in Canada that remain undiscovered.

PCBs are listed in Annex C of the Stockholm Convention, which includes the unintentionally produced POPs. According to Article 5, Parties are required to identify, characterize, quantify and prioritize sources of releases of these compounds, and develop strategies with concrete measures, timelines and goals to

minimize or eliminate these releases. This study produced compelling evidence that use of 2,4-DCBP is currently a non-negligible source of non-Aroclor PCBs to the atmosphere in Canada. Estimates on its manufacture and imports in Canada are unknown, as it was not included in the 2017 Chemical Inventory Update of Environment and Climate Change Canada.[80] The United States Environmental Protection Agency's Toxic Substances Control Act (TSCA) Chemical Substance Inventory, however, lists 2,4-DCBP as commercially active in the US.[81]

The use of 2,4-DCBP is known as a potential source of PCBs for three decades.[68, 69] It was confirmed as a PCB source to the indoor environment in 2018.[27] A point source to the ambient atmosphere was reported in 2021.[28] Here we show that outdoor PCB emissions originating from the use of 2,4-DCBP are widespread. While a 2015 expert meeting on unintentionally produced POPs of the Stockholm Convention discussed implementing regulations on unintentionally released POPs from pigments, this has not been the case for 2,4-DCBP.[82] Therefore, it is likely that 2,4-DCBP is still prevalent in the manufacturing of commercial products not just in North America but also elsewhere in the world. This is the case, even though alternative non-chlorinated cross-linkers are available, such as bis(4-methylbenzoyl)peroxide. Regulatory action on non-Aroclor PCBs can be initiated by identifying their sources, as seen on a local scale in North Rhine-Westphalia, Germany.[28] Therefore, the results of this study highlight that PCBs and their related processes require further assessment and regulations.

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# ASSOCIATED CONTENT

## Supporting Information

Maps of passive air sampling networks. Table with detailed information on PAS deployments. Tables with detail on the analytical method (e.g. precursor and product ions and collision energies, method detection limits, recoveries). Text, tables and figures with details on the PMF. Excel sheet with all concentration data. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.XXX.

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Supporting Information for

# Passive air sampling networks combined with multivariate statistics reveal widespread non-Aroclor polychlorinated biphenyl sources to the Canadian atmosphere

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Supporting Information Summary: 19 pages including 7 figures, 9 tables, 2 texts, and references. 3 datasets are in the separate Supplementary Excel file.

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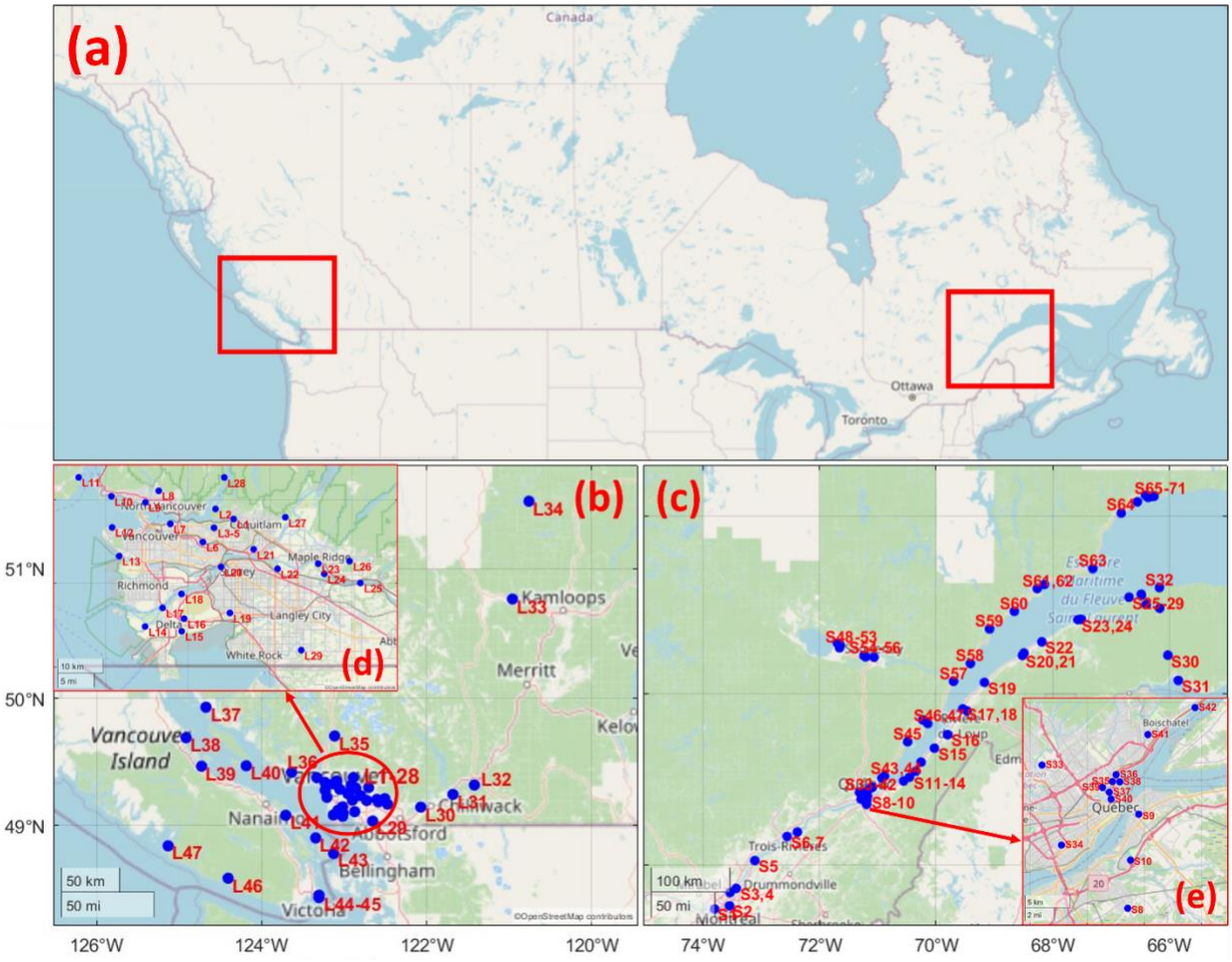


Figure S1 The maps of the passive air sampling sites and their codes in British Columbia (b) and Quebec (c). The inset map in the upper left (d) and lower right (e) shows the Vancouver metropolitan region and Quebec City, respectively. The map of Canada (a) is included to show the location of the sampling regions on the east coast and west coast. Maps were generated using OpenStreetMap data, available under the Open Database License (https://www.openstreetmap.org/copyright).

Table S1 Information on the passive air samples taken in Quebec and British Columbia: Geographical coordinates, deployment and retrieval date, deployment period, and average temperature during the deployment period obtained from the nearest weather station to each site.[1]

| Site name | Latitude | Longitude | Deployment date | Retrieval date | Deployment period (d) | Temperature (°C) |
|---|---|---|---|---|---|---|
| **Quebec** | | | | | | |
| S1 | 45.4692 | -73.8004 | 2021-10-14 | 2022-05-21 | 219 | 0.2 |
| S2 | 45.5058 | -73.5437 | 2019-11-25 | 2020-08-17 | 266 | 6.8 |
| S2_2 | 45.5058 | -73.5437 | 2020-08-17 | 2021-07-27 | 344 | 8.0 |
| S3 | 45.6657 | -73.5340 | 2019-11-25 | 2020-08-17 | 266 | 6.4 |
| S4 | 45.7154 | -73.4286 | 2019-11-25 | 2020-08-16 | 265 | 6.3 |
| S5 | 46.0479 | -73.1099 | 2019-11-25 | 2020-08-16 | 265 | 6.7 |
| S6 | 46.3333 | -72.5548 | 2019-11-24 | 2020-08-16 | 266 | 5.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| S6_2 | 46.3333 | -72.5548 | 2020-08-16 | 2021-07-27 | 345 | 6.0 |
| S7 | 46.3869 | -72.3790 | 2020-09-22 | 2021-07-27 | 308 | 5.0 |
| S8 | 46.7120 | -71.1909 | 2019-11-24 | 2020-08-15 | 265 | 4.7 |
| S8_2 | 46.7120 | -71.1909 | 2020-08-15 | 2021-07-28 | 347 | 5.6 |
| S9 | 46.8057 | -71.1749 | 2019-11-24 | 2020-08-15 | 265 | 3.7 |
| S10 | 46.7600 | -71.1869 | 2019-11-24 | 2020-08-15 | 265 | 4.7 |
| S10_2 | 46.7600 | -71.1869 | 2020-08-15 | 2021-07-28 | 347 | 5.6 |
| S11 | 46.9866 | -70.5566 | 2019-11-26 | 2020-08-14 | 262 | 4.4 |
| S12 | 47.0323 | -70.4550 | 2019-11-26 | 2020-08-14 | 262 | 4.4 |
| S13 | 47.1017 | -70.3445 | 2019-11-26 | 2020-08-14 | 262 | -0.3 |
| S14 | 47.2076 | -70.2573 | 2019-11-26 | 2020-08-14 | 262 | 3.8 |
| S15 | 47.3697 | -70.0288 | 2019-11-26 | 2020-08-13 | 261 | 3.7 |
| S16 | 47.5275 | -69.8029 | 2019-11-26 | 2020-08-13 | 261 | 3.7 |
| S17 | 47.8237 | -69.5414 | 2019-11-26 | 2020-08-13 | 261 | 2.7 |
| S18 | 47.8005 | -69.4689 | 2019-11-26 | 2020-08-13 | 261 | 2.7 |
| S18_2 | 47.8005 | -69.4689 | 2020-08-13 | 2021-07-26 | 347 | 4.4 |
| S19 | 48.1287 | -69.1699 | 2019-11-27 | 2020-08-13 | 260 | 2.4 |
| S19_2 | 48.1287 | -69.1699 | 2020-08-13 | 2021-07-26 | 347 | 3.7 |
| S20 | 48.4367 | -68.5170 | 2019-11-27 | 2020-08-10 | 257 | 2.4 |
| S21 | 48.4641 | -68.4925 | 2019-11-27 | 2020-08-10 | 257 | 2.4 |
| S22 | 48.5913 | -68.1850 | 2019-11-27 | 2020-08-11 | 258 | 2.8 |
| S23 | 48.8420 | -67.5647 | 2019-11-27 | 2020-08-11 | 258 | 0.9 |
| S24 | 48.8460 | -67.5077 | 2019-11-27 | 2020-08-11 | 258 | 0.9 |
| S25 | 49.0951 | -66.6902 | 2019-11-27 | 2020-08-11 | 258 | 2.3 |
| S25_2 | 49.0951 | -66.6902 | 2020-08-11 | 2021-08-01 | 355 | 4.2 |
| S26 | 49.1279 | -66.4807 | 2019-11-28 | 2020-08-12 | 258 | 2.4 |
| S26_2 | 49.1279 | -66.4807 | 2021-08-02 | 2022-05-06 | 277 | 1.1 |
| S27 | 49.1189 | -66.4779 | 2021-08-02 | 2022-05-06 | 277 | 1.1 |
| S28 | 49.0139 | -66.3949 | 2021-08-02 | 2022-05-06 | 277 | 1.1 |
| S29 | 48.9701 | -66.1630 | 2021-08-02 | 2022-05-06 | 277 | 1.1 |
| S30 | 48.4392 | -66.0229 | 2021-08-02 | 2022-05-06 | 277 | 1.3 |
| S31 | 48.1509 | -65.8442 | 2021-08-02 | 2022-05-06 | 277 | 1.3 |
| S32 | 49.2032 | -66.1672 | 2019-11-28 | 2020-08-12 | 258 | 2.4 |
| S32_2 | 49.2032 | -66.1672 | 2020-08-12 | 2021-08-01 | 354 | 4.2 |
| S33 | 46.8547 | -71.3156 | 2019-11-24 | 2020-08-18 | 268 | 3.7 |
| S34 | 46.7750 | -71.2873 | 2019-11-25 | 2020-09-24 | 304 | 6.0 |
| S35 | 46.8383 | -71.2133 | 2019-11-25 | 2020-08-19 | 268 | 4.9 |
| S35_2 | 46.8383 | -71.2133 | 2020-08-19 | 2021-07-28 | 343 | 5.5 |
| S36 | 46.8452 | -71.2079 | 2021-07-28 | 2022-05-02 | 278 | 2.8 |
| S37 | 46.8276 | -71.2178 | 2021-07-28 | 2022-05-02 | 278 | 2.8 |
| S38 | 46.8379 | -71.2024 | 2021-07-28 | 2022-05-02 | 278 | 2.8 |
| S39 | 46.8324 | -71.2277 | 2021-07-28 | 2022-05-02 | 278 | 2.8 |
| S40 | 46.8207 | -71.2150 | 2021-07-28 | 2022-05-02 | 278 | 2.8 |
| S41 | 46.8850 | -71.1617 | 2019-11-25 | 2020-08-19 | 268 | 4.0 |
| S42 | 46.9118 | -71.0931 | 2019-11-25 | 2020-08-20 | 269 | 4.6 |
| S43 | 47.0208 | -70.9278 | 2019-11-25 | 2020-08-20 | 269 | 4.6 |
| S43_2 | 47.0227 | -70.9270 | 2020-08-20 | 2022-05-02 | 620 | 2.3 |
| S44 | 47.0453 | -70.8831 | 2019-11-25 | 2020-08-20 | 269 | 4.7 |
| S45 | 47.4452 | -70.4880 | 2019-11-26 | 2020-08-21 | 269 | 0.1 |
| S46 | 47.6559 | -70.1430 | 2019-11-26 | 2020-08-21 | 269 | 4.1 |
| S47 | 47.6975 | -70.2263 | 2019-11-26 | 2020-08-21 | 269 | 4.1 |
| S48 | 48.5513 | -71.6443 | 2019-11-27 | 2020-08-22 | 269 | 2.9 |
| S48_2 | 48.5513 | -71.6443 | 2020-08-22 | 2021-07-30 | 342 | 3.5 |
| S49 | 48.5233 | -71.6555 | 2019-11-27 | 2020-08-22 | 269 | 2.9 |
| S50 | 48.5758 | -71.6941 | 2021-07-30 | 2022-05-03 | 277 | -0.8 |
| S51 | 48.5581 | -71.6549 | 2021-07-30 | 2022-05-03 | 277 | -0.8 |
| S52 | 48.5663 | -71.6533 | 2021-07-30 | 2022-05-03 | 277 | -0.8 |
| S53 | 48.5616 | -71.6478 | 2021-07-30 | 2022-05-03 | 277 | -0.8 |
| S54 | 48.4335 | -71.2378 | 2019-11-27 | 2020-08-22 | 269 | 2.5 |
| S54_2 | 48.4335 | -71.2378 | 2020-08-22 | 2021-07-29 | 341 | 3.6 |
| S55 | 48.4199 | -71.2083 | 2019-11-27 | 2020-08-23 | 270 | 2.6 |
| S56 | 48.4171 | -71.0649 | 2019-11-27 | 2020-08-23 | 270 | 2.6 |
| S57 | 48.1415 | -69.6991 | 2019-11-29 | 2020-08-24 | 269 | 3.8 |
| S58 | 48.3446 | -69.4105 | 2019-11-29 | 2020-08-24 | 269 | 1.7 |
| S59 | 48.7375 | -69.0827 | 2019-11-29 | 2020-08-24 | 269 | 3.1 |
| S60 | 48.9360 | -68.6566 | 2019-11-30 | 2021-07-30 | 608 | 2.5 |
| S61 | 49.1914 | -68.2645 | 2019-11-30 | 2020-08-25 | 269 | 1.9 |
| S62 | 49.2380 | -68.1424 | 2019-11-30 | 2020-08-25 | 269 | 1.9 |
| S62_2 | 49.2380 | -68.1424 | 2020-08-25 | 2021-07-31 | 340 | 2.8 |
| S63 | 49.4150 | -67.3112 | 2019-12-01 | 2020-08-25 | 268 | 2.3 |
| S64 | 50.0310 | -66.8235 | 2019-12-01 | 2020-08-25 | 268 | 0.6 |
| S65 | 50.1550 | -66.5472 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |
| S66 | 50.2208 | -66.3638 | 2019-12-01 | 2020-08-26 | 269 | 0.7 |
| S66_2 | 50.2208 | -66.3638 | 2020-08-26 | 2021-07-31 | 339 | 1.7 |
| S67 | 50.2249 | -66.4064 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| S68 | 50.2042 | -66.3639 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |
| S69 | 50.2127 | -66.3125 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |
| S70 | 50.2161 | -66.2625 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |
| S71 | 50.2067 | -66.3531 | 2021-07-31 | 2022-05-04 | 277 | -1.1 |
| **British Columbia** | | | | | | |
| L1 | 49.2947 | -122.8607 | 2020-03-04 | 2020-08-18 | 167 | 13.3 |
| L1_2 | 49.2946 | -122.8607 | 2020-08-18 | 2021-03-26 | 220 | 8.5 |
| L1_3 | 49.2946 | -122.8607 | 2021-03-26 | 2021-08-16 | 143 | 15.7 |
| L2 | 49.3148 | -122.9161 | 2021-05-17 | 2021-12-03 | 200 | 14.7 |
| L3 | 49.2772 | -122.9203 | 2020-01-23 | 2020-06-17 | 146 | 8.9 |
| L3_2 | 49.2772 | -122.9203 | 2020-06-17 | 2020-11-20 | 156 | 15.0 |
| L3_3 | 49.2772 | -122.9203 | 2020-11-20 | 2021-04-29 | 160 | 6.0 |
| L3_4 | 49.2772 | -122.9203 | 2021-10-01 | 2022-04-04 | 185 | 5.2 |
| L4 | 49.2774 | -122.9209 | 2020-06-17 | 2020-11-20 | 156 | 15.0 |
| L4_2 | 49.2774 | -122.9209 | 2020-11-20 | 2021-04-29 | 160 | 6.0 |
| L4_3 | 49.2774 | -122.9209 | 2021-04-29 | 2021-10-01 | 155 | 17.1 |
| L4_4 | 49.2774 | -122.9209 | 2021-10-01 | 2022-04-04 | 185 | 5.2 |
| L5 | 49.2774 | -122.9209 | 2020-06-17 | 2020-11-20 | 156 | 15.0 |
| L5_2 | 49.2774 | -122.9209 | 2020-11-20 | 2021-04-29 | 160 | 6.0 |
| L5_3 | 49.2771 | -122.9210 | 2021-04-29 | 2021-10-01 | 155 | 17.1 |
| L5_4 | 49.2774 | -122.9209 | 2021-10-01 | 2022-04-04 | 185 | 5.2 |
| L6 | 49.2491 | -122.9546 | 2021-05-12 | 2021-12-04 | 206 | 14.6 |
| L7 | 49.2851 | -123.0538 | 2021-05-03 | 2021-10-03 | 153 | 17.7 |
| L7_2 | 49.2851 | -123.0538 | 2021-10-03 | 2022-04-06 | 185 | 6.8 |
| L8 | 49.3507 | -123.0891 | 2020-02-16 | 2020-10-16 | 243 | 9.1 |
| L9 | 49.3279 | -123.1295 | 2021-05-25 | 2021-12-03 | 192 | 15.4 |
| L10 | 49.3398 | -123.2333 | 2020-10-05 | 2021-05-14 | 221 | 7.7 |
| L10_2 | 49.3398 | -123.2333 | 2021-05-14 | 2021-12-03 | 203 | 14.9 |
| L11 | 49.3775 | -123.3329 | 2021-05-15 | 2021-12-05 | 204 | 14.8 |
| L12 | 49.2781 | -123.2311 | 2021-05-26 | 2021-12-04 | 192 | 15.0 |
| L13 | 49.2210 | -123.2096 | 2020-06-23 | 2020-11-16 | 146 | 14.7 |
| L13_2 | 49.2210 | -123.2096 | 2020-11-16 | 2021-05-04 | 169 | 6.1 |
| L13_3 | 49.2210 | -123.2096 | 2021-05-04 | 2021-12-04 | 214 | 14.3 |
| L14 | 49.0807 | -123.1307 | 2021-06-03 | 2021-12-05 | 185 | 14.6 |
| L15 | 49.0712 | -123.0192 | 2020-05-08 | 2020-09-29 | 144 | 16.2 |
| L16 | 49.0965 | -123.0120 | 2021-08-24 | 2022-02-24 | 184 | 6.6 |
| L17 | 49.1179 | -123.0775 | 2021-05-04 | 2021-12-04 | 214 | 13.8 |
| L18 | 49.1458 | -123.0198 | 2021-08-24 | 2022-02-24 | 184 | 6.6 |
| L19 | 49.1078 | -122.8722 | 2021-06-30 | 2022-01-21 | 205 | 10.5 |
| L20 | 49.1995 | -122.8992 | 2021-08-24 | 2022-02-24 | 184 | 6.6 |
| L21 | 49.2347 | -122.8001 | 2021-05-12 | 2021-12-16 | 218 | 14.0 |
| L22 | 49.1958 | -122.7272 | 2021-05-06 | 2021-12-16 | 224 | 14.6 |
| L23 | 49.2058 | -122.6035 | 2021-05-06 | 2021-12-16 | 224 | 14.6 |
| L24 | 49.1859 | -122.5850 | 2021-05-06 | 2021-12-16 | 224 | 14.6 |
| L25 | 49.1675 | -122.4749 | 2021-06-03 | 2021-12-16 | 196 | 14.6 |
| L26 | 49.2109 | -122.5078 | 2021-05-12 | 2021-12-03 | 205 | 15.4 |
| L27 | 49.2982 | -122.7036 | 2021-06-04 | 2021-12-03 | 182 | 15.4 |
| L28 | 49.3773 | -122.8893 | 2021-05-17 | 2021-12-03 | 200 | 14.7 |
| L29 | 49.0337 | -122.6548 | 2021-05-04 | 2021-12-04 | 214 | 14.6 |
| L30 | 49.1439 | -122.0710 | 2021-08-27 | 2022-02-28 | 185 | 6.5 |
| L31 | 49.2447 | -121.6812 | 2020-02-27 | 2020-10-10 | 226 | 14.5 |
| L31_2 | 49.2447 | -121.6812 | 2020-10-10 | 2021-06-18 | 251 | 8.1 |
| L31_3 | 49.2447 | -121.6812 | 2021-06-18 | 2022-03-13 | 268 | 10.6 |
| L32 | 49.3188 | -121.4209 | 2020-02-15 | 2020-10-10 | 238 | 13.9 |
| L32_2 | 49.3188 | -121.4209 | 2021-05-23 | 2022-04-30 | 342 | 10.0 |
| L33 | 50.7674 | -120.9586 | 2020-02-27 | 2020-10-09 | 225 | 15.8 |
| L34 | 51.5114 | -120.7590 | 2020-05-23 | 2020-10-13 | 143 | 13.2 |
| L34_2 | 51.5114 | -120.7590 | 2020-10-13 | 2021-05-20 | 219 | -0.8 |
| L34_3 | 51.5114 | -120.7590 | 2021-05-20 | 2021-10-10 | 143 | 14.3 |
| L35 | 49.7054 | -123.1161 | 2020-02-28 | 2020-09-22 | 207 | 13.7 |
| L36 | 49.4194 | -123.6375 | 2020-02-18 | 2020-10-17 | 242 | 12.4 |
| L36_2 | 49.4194 | -123.6375 | 2020-10-07 | 2021-05-21 | 226 | 6.6 |
| L37 | 49.9300 | -124.6765 | 2020-02-21 | 2020-08-04 | 165 | 11.1 |
| L38 | 49.6914 | -124.9178 | 2020-06-07 | 2020-11-15 | 161 | 15.6 |
| L39 | 49.4673 | -124.7299 | 2020-05-24 | 2020-10-25 | 154 | 15.5 |
| L39_2 | 49.4673 | -124.7299 | 2020-10-25 | 2021-06-02 | 220 | 6.6 |
| L39_3 | 49.4673 | -124.7299 | 2021-06-02 | 2022-01-21 | 233 | 10.8 |
| L40 | 49.4711 | -124.1881 | 2020-06-20 | 2021-01-29 | 223 | 12.6 |
| L40_2 | 49.4711 | -124.1881 | 2021-01-29 | 2021-10-01 | 245 | 13.6 |
| L41 | 49.0787 | -123.7091 | 2020-04-14 | 2021-02-18 | 310 | 11.1 |
| L41_2 | 49.0787 | -123.7091 | 2021-02-18 | 2021-09-07 | 201 | 13.9 |
| L42 | 48.8983 | -123.3459 | 2020-07-12 | 2021-04-18 | 280 | 10.1 |
| L42_2 | 48.8983 | -123.3459 | 2021-04-18 | 2021-12-01 | 227 | 15.0 |
| L43 | 48.7753 | -123.1283 | 2020-05-28 | 2020-10-11 | 136 | 15.2 |
| L43_a_1 | 48.7753 | -123.1283 | 2020-07-02 | 2021-04-03 | 275 | 8.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| L43_a_2 | 48.7753 | -123.1283 | 2021-04-03 | 2021-11-26 | 237 | 13.6 |
| L43_b_1 | 48.7753 | -123.1283 | 2020-07-02 | 2021-04-03 | 275 | 8.1 |
| L43_b_2 | 48.7753 | -123.1283 | 2021-04-03 | 2021-11-26 | 237 | 13.6 |
| L43_c_1 | 48.7753 | -123.1283 | 2020-07-02 | 2021-04-03 | 275 | 8.1 |
| L43_c_2 | 48.7753 | -123.1283 | 2021-04-03 | 2021-11-26 | 237 | 13.6 |
| L44 | 48.4210 | -123.3049 | 2020-05-06 | 2020-10-04 | 151 | 15.8 |
| L44_2 | 48.4210 | -123.3049 | 2020-10-04 | 2021-05-29 | 237 | 7.6 |
| L44_3 | 48.4210 | -123.3000 | 2021-05-29 | 2021-10-08 | 132 | 16.5 |
| L45 | 48.4406 | -123.3054 | 2020-04-13 | 2020-10-03 | 173 | 15.1 |
| L45_2 | 48.4406 | -123.3054 | 2020-10-03 | 2021-05-29 | 238 | 7.7 |
| L45_3 | 48.4406 | -123.3054 | 2021-05-29 | 2021-10-10 | 134 | 16.4 |
| L46 | 48.5762 | -124.4079 | 2020-10-23 | 2021-08-04 | 285 | 8.7 |
| L47 | 48.8357 | -125.1354 | 2020-10-27 | 2021-06-23 | 239 | 8.3 |

Table S2 The list of PCB congeners (including co-eluted congeners) of this study, ordered in decreasing volatility.

| | | | |
|---|---|---|---|
| 1 | 104 | 125 | 129 |
| 2 | 44 | 111+117 | 126 |
| 3 | 59+42 | 81 | 178 |
| 4+10 | 37 | 145 | 166 |
| 9+7 | 72 | 87+116+115 | 175 |
| 6 | 71+41 | 148 | 159 |
| 8+5 | 64 | 109+85 | 187+182 |
| 14 | 68 | 136 | 183 |
| 19 | 96 | 77 | 162 |
| 30 | 103 | 110 | 128 |
| 11 | 40+57 | 154 | 167 |
| 12+13 | 67 | 82 | 185 |
| 18 | 100 | 151 | 174 |
| 15 | 58 | 135+144 | 181 |
| 17 | 63 | 124 | 177 |
| 24+27 | 94 | 147 | 202 |
| 16+32 | 74+61 | 108+107 | 171 |
| 34+23 | 70 | 123 | 156 |
| 29 | 76 | 149+139 | 173 |
| 54 | 98+102 | 118+106 | 157 |
| 26 | 80+66 | 143 | 201 |
| 25 | 93+95 | 140+134 | 204 |
| 31 | 88+121 | 114 | 172+192 |
| 50 | 91 | 133 | 197 |
| 28 | 55 | 122 | 180 |
| 21+33+20 | 155 | 131+142 | 193 |
| 53 | 56+60 | 188 | 191 |
| 51 | 92 | 165 | 200 |
| 22 | 84 | 146+161 | 169 |
| 45 | 101+89+90 | 184 | 170+190 |
| 36 | 113 | 153 | 198 |
| 46 | 99 | 132+168 | 199 |
| 39 | 79 | 105+127 | 203+196 |
| 69 | 119 | 141 | 189 |
| 52+73 | 150 | 179 | 208 |
| 43+49 | 112 | 137 | 195 |
| 38 | 83 | 176 | 207 |
| 47+48+75 | 120 | 130 | 194 |
| 65 | 78 | 164+163+138 | 205 |
| 62 | 152 | 160+158 | 206 |
| 35 | 97+86 | 186 | 209 |

Table S3 The precursor and product ions and the collision energies (CEs in eV) of the PCB congeners, internal standards, and injection standards.

| Compound | Precursor | Product | CE |
|---|---|---|---|
| PCB-1 | 188 | 153 | 55 |
| PCB-2 | 188 | 153 | 55 |
| PCB-3 | 188 | 153 | 55 |
| PCB-4+10 | 222 | 152 | 55 |
| PCB-9+7 | 222 | 152 | 55 |
| PCB-6 | 222 | 152 | 55 |
| PCB-8+5 | 222 | 152 | 55 |
| PCB-14 | 222 | 152 | 55 |
| PCB-19 | 256 | 186 | 55 |
| PCB-30 | 256 | 186 | 55 |
| $^{13}C_{12}$-PCB-11 | 234 | 164 | 55 |
| PCB-11 | 222 | 152 | 55 |
| PCB-12+13 | 222 | 152 | 55 |
| PCB-18 | 256 | 186 | 55 |
| PCB-15 | 222 | 152 | 55 |
| PCB-17 | 256 | 186 | 55 |
| PCB-24+27 | 256 | 186 | 55 |
| PCB-16+32 | 256 | 186 | 55 |
| PCB-34+23 | 256 | 186 | 55 |
| PCB-29 | 256 | 186 | 55 |
| PCB-54 | 290 | 220 | 55 |
| PCB-26 | 256 | 186 | 55 |
| PCB-25 | 256 | 186 | 55 |
| PCB-31 | 256 | 186 | 55 |
| PCB-50 | 290 | 220 | 55 |
| $^{13}C_{12}$-PCB-28 | 270 | 198 | 55 |
| PCB-28 | 256 | 186 | 55 |
| PCB-21+33+20 | 256 | 186 | 55 |
| PCB-53 | 290 | 220 | 55 |
| PCB-51 | 290 | 220 | 55 |
| PCB-22 | 256 | 186 | 55 |
| PCB-45 | 290 | 220 | 55 |
| PCB-36 | 256 | 186 | 55 |
| PCB-46 | 290 | 220 | 55 |
| PCB-39 | 256 | 186 | 55 |
| PCB-69 | 290 | 220 | 55 |
| $^{13}C_{12}$-PCB-52 | 302 | 232 | 55 |
| PCB-52+73 | 290 | 220 | 55 |
| PCB-43+49 | 290 | 220 | 55 |
| PCB-38 | 256 | 186 | 55 |
| PCB-47+48+75 | 290 | 220 | 55 |
| PCB-65 | 290 | 220 | 55 |
| PCB-62 | 290 | 220 | 55 |
| PCB-35 | 256 | 186 | 55 |
| PCB-104 | 326 | 256 | 55 |
| PCB-44 | 290 | 220 | 55 |
| PCB-59+42 | 290 | 220 | 55 |
| PCB-37 | 256 | 186 | 55 |
| PCB-72 | 290 | 220 | 55 |
| PCB-71+41 | 290 | 220 | 55 |
| PCB-64 | 290 | 220 | 55 |
| PCB-68 | 290 | 220 | 55 |
| PCB-96 | 326 | 256 | 55 |
| PCB-103 | 326 | 256 | 55 |
| PCB-40+57 | 290 | 220 | 55 |
| PCB-67 | 290 | 220 | 55 |
| PCB-100 | 326 | 256 | 55 |
| PCB-58 | 290 | 220 | 55 |

| Compound | Precursor | Product | CE |
|---|---|---|---|
| PCB-111+117 | 326 | 256 | 55 |
| PCB-81 | 290 | 220 | 55 |
| PCB-145 | 360 | 290 | 55 |
| PCB-87+116+115 | 326 | 256 | 55 |
| PCB-148 | 360 | 290 | 55 |
| PCB-109+85 | 326 | 256 | 55 |
| PCB-136 | 360 | 290 | 55 |
| $^{13}C_{12}$-PCB-77 | 302 | 232 | 55 |
| PCB-77 | 290 | 220 | 55 |
| PCB-110 | 326 | 256 | 55 |
| PCB-154 | 360 | 290 | 55 |
| PCB-82 | 326 | 256 | 55 |
| PCB-151 | 360 | 290 | 55 |
| PCB-135+144 | 360 | 290 | 55 |
| PCB-124 | 326 | 256 | 55 |
| PCB-147 | 360 | 290 | 55 |
| PCB-108+107 | 326 | 256 | 55 |
| PCB-123 | 326 | 256 | 55 |
| PCB-149+139 | 360 | 290 | 55 |
| PCB-118+106 | 326 | 256 | 55 |
| PCB-143 | 360 | 290 | 55 |
| PCB-140+134 | 360 | 290 | 55 |
| PCB-114 | 326 | 256 | 55 |
| PCB-133 | 360 | 290 | 55 |
| PCB-122 | 326 | 256 | 55 |
| PCB-131+142 | 360 | 290 | 55 |
| PCB-188 | 394 | 359 | 55 |
| PCB-165 | 360 | 290 | 55 |
| PCB-146+161 | 360 | 290 | 55 |
| PCB-184 | 394 | 359 | 55 |
| PCB-153 | 360 | 290 | 55 |
| PCB-132+168 | 360 | 290 | 55 |
| $^{13}C_{12}$-PCB-105 | 336 | 266 | 55 |
| PCB-105+127 | 326 | 256 | 55 |
| PCB-141 | 360 | 290 | 55 |
| PCB-179 | 394 | 359 | 55 |
| PCB-137 | 360 | 290 | 55 |
| PCB-176 | 394 | 359 | 55 |
| PCB-130 | 360 | 290 | 55 |
| PCB-164+163+138 | 360 | 290 | 55 |
| PCB-160+158 | 360 | 290 | 55 |
| PCB-186 | 394 | 359 | 55 |
| PCB-129 | 360 | 290 | 55 |
| PCB-126 | 326 | 256 | 55 |
| $^{13}C_{12}$-PCB-178 | 408 | 373 | 55 |
| PCB-178 | 394 | 359 | 55 |
| PCB-166 | 360 | 290 | 55 |
| PCB-175 | 394 | 359 | 55 |
| PCB-159 | 360 | 290 | 55 |
| PCB-187+182 | 394 | 359 | 55 |
| PCB-183 | 394 | 359 | 55 |
| PCB-162 | 360 | 290 | 55 |
| PCB-128 | 360 | 290 | 55 |
| PCB-167 | 360 | 290 | 55 |
| PCB-185 | 394 | 359 | 55 |
| PCB-174 | 394 | 359 | 55 |
| PCB-181 | 394 | 359 | 55 |
| PCB-177 | 394 | 359 | 55 |

| | | | |
|---|---|---|---|
| PCB-63 | 290 | 220 | 55 |
| PCB-94 | 326 | 256 | 55 |
| PCB-74+61 | 290 | 220 | 55 |
| PCB-70 | 290 | 220 | 55 |
| PCB-76 | 290 | 220 | 55 |
| PCB-98+102 | 326 | 256 | 55 |
| PCB-80+66 | 290 | 220 | 55 |
| PCB-93+95 | 326 | 256 | 55 |
| PCB-88+121 | 326 | 256 | 55 |
| PCB-91 | 326 | 256 | 55 |
| PCB-55 | 290 | 220 | 55 |
| $^{13}C_{12}$-PCB-155 | 372 | 302 | 55 |
| PCB-155 | 360 | 290 | 55 |
| PCB-56+60 | 290 | 220 | 55 |
| PCB-92 | 326 | 256 | 55 |
| PCB-84 | 326 | 256 | 55 |
| $^{13}C_{12}$-PCB-101 | 336 | 266 | 55 |
| PCB-101+89+90 | 326 | 256 | 55 |
| PCB-113 | 326 | 256 | 55 |
| PCB-99 | 326 | 256 | 55 |
| PCB-79 | 290 | 220 | 55 |
| PCB-119 | 326 | 256 | 55 |
| PCB-150 | 360 | 290 | 55 |
| PCB-112 | 326 | 256 | 55 |
| PCB-83 | 326 | 256 | 55 |
| PCB-120 | 326 | 256 | 55 |
| PCB-78 | 290 | 220 | 55 |
| PCB-152 | 360 | 290 | 55 |
| PCB-97+86 | 326 | 256 | 55 |
| PCB-125 | 326 | 256 | 55 |

| | | | |
|---|---|---|---|
| $^{13}C_{12}$-PCB-202 | 440 | 370 | 55 |
| PCB-202 | 430 | 395 | 55 |
| PCB-171 | 394 | 359 | 55 |
| PCB-156 | 360 | 290 | 55 |
| PCB-173 | 394 | 359 | 55 |
| PCB-157 | 360 | 290 | 55 |
| PCB-201 | 430 | 395 | 55 |
| PCB-204 | 430 | 395 | 55 |
| PCB-172+192 | 394 | 359 | 55 |
| PCB-197 | 430 | 395 | 55 |
| PCB-180 | 394 | 359 | 55 |
| PCB-193 | 394 | 359 | 55 |
| PCB-191 | 394 | 359 | 55 |
| PCB-200 | 430 | 395 | 55 |
| PCB-169 | 360 | 290 | 55 |
| PCB-170+190 | 394 | 359 | 55 |
| PCB-198 | 430 | 395 | 55 |
| PCB-199 | 430 | 395 | 55 |
| PCB-203+196 | 430 | 395 | 55 |
| PCB-189 | 394 | 359 | 55 |
| PCB-208 | 462 | 392 | 55 |
| PCB-195 | 430 | 395 | 55 |
| PCB-207 | 462 | 392 | 55 |
| PCB-194 | 430 | 395 | 55 |
| PCB-205 | 428 | 358 | 55 |
| $^{13}C_{12}$-PCB-206 | 476 | 406 | 55 |
| PCB-206 | 462 | 392 | 55 |
| $^{13}C_{12}$-PCB-209 | 510 | 440 | 55 |
| PCB-209 | 498 | 426 | 55 |

Table S4 The Method Detection Limits (MDLs) in pg $m^{-3}$ of the PCB congeners from the passive air sampler network.

| PCB congener | MDL | PCB congener | MDL | PCB congener | MDL | PCB congener | MDL |
|---|---|---|---|---|---|---|---|
| 1 | 0.20 | 104 | 0.20 | 125 | 4.55 | 129 | 20.19 |
| 2 | 0.22 | 44 | 1.78 | 111+117 | 5.16 | 126 | 5.39 |
| 3 | 0.17 | 59+42 | 1.01 | 81 | 1.39 | 178 | 0.22 |
| 4+10 | 0.08 | 37 | 0.54 | 145 | 0.99 | 166 | 2.21 |
| 9+7 | 1.28 | 72 | 1.79 | 87+116+115 | 1.46 | 175 | 0.79 |
| 6 | 0.12 | 71+41 | 0.91 | 148 | 3.29 | 159 | 2.40 |
| 8+5 | 0.66 | 64 | 0.54 | 109+85 | 13.39 | 187+182 | 0.16 |
| 14 | 0.16 | 68 | 0.61 | 136 | 1.09 | 183 | 0.57 |
| 19 | 0.49 | 96 | 0.27 | 77 | 1.05 | 162 | 2.63 |
| 30 | 0.12 | 103 | 1.05 | 110 | 5.29 | 128 | 9.67 |
| 11 | 1.53 | 40+57 | 3.37 | 154 | 1.86 | 167 | 7.81 |
| 12+13 | 0.16 | 67 | 2.50 | 82 | 15.49 | 185 | 2.61 |
| 18 | 0.84 | 100 | 1.33 | 151 | 6.14 | 174 | 0.55 |
| 15 | 0.16 | 58 | 1.19 | 135+144 | 3.87 | 181 | 2.25 |
| 17 | 0.45 | 63 | 0.78 | 124 | 4.74 | 177 | 0.72 |
| 24+27 | 0.39 | 94 | 1.89 | 147 | 4.25 | 202 | 4.13 |
| 16+32 | 0.49 | 74+61 | 0.55 | 108+107 | 4.63 | 171 | 2.15 |
| 34+23 | 1.04 | 70 | 2.94 | 123 | 4.13 | 156 | 7.98 |
| 29 | 0.79 | 76 | 1.72 | 149+139 | 1.93 | 173 | 2.06 |
| 54 | 0.10 | 98+102 | 2.39 | 118+106 | 2.03 | 157 | 5.19 |
| 26 | 0.37 | 80+66 | 0.99 | 143 | 4.25 | 201 | 3.93 |
| 25 | 0.32 | 93+95 | 7.15 | 140+134 | 11.10 | 204 | 5.29 |
| 31 | 0.51 | 88+121 | 0.99 | 114 | 4.06 | 172+192 | 5.29 |
| 50 | 0.34 | 91 | 2.10 | 133 | 15.78 | 197 | 6.98 |
| 28 | 0.36 | 55 | 2.34 | 122 | 3.48 | 180 | 0.92 |
| 21+33+20 | 0.20 | 155 | 0.51 | 131+142 | 13.50 | 193 | 10.98 |
| 53 | 0.37 | 56+60 | 0.60 | 188 | 1.24 | 191 | 13.98 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 51 | 0.54 | 92 | 0.55 | 165 | 6.54 | 200 | 4.39 |
| 22 | 0.50 | 84 | 0.98 | 146+161 | 5.20 | 169 | 5.82 |
| 45 | 0.93 | 101+89+90 | 3.95 | 184 | 1.58 | 170+190 | 3.06 |
| 36 | 2.52 | 113 | 2.10 | 153 | 2.00 | 198 | 1.36 |
| 46 | 2.71 | 99 | 0.94 | 132+168 | 7.51 | 199 | 1.53 |
| 39 | 1.60 | 79 | 1.39 | 105+127 | 1.68 | 203+196 | 2.54 |
| 69 | 0.75 | 119 | 3.91 | 141 | 18.96 | 189 | 44.84 |
| 52+73 | 1.62 | 150 | 0.47 | 179 | 2.85 | 208 | 6.65 |
| 43+49 | 0.89 | 112 | 2.44 | 137 | 6.18 | 195 | 0.97 |
| 38 | 3.28 | 83 | 2.80 | 176 | 1.20 | 207 | 6.58 |
| 47+48+75 | 1.07 | 120 | 2.99 | 130 | 7.64 | 194 | 2.67 |
| 65 | 1.10 | 78 | 1.33 | 164+163+138 | 1.90 | 205 | 18.67 |
| 62 | 0.76 | 152 | 0.54 | 160+158 | 10.72 | 206 | 62.68 |
| 35 | 0.49 | 97+86 | 10.52 | 186 | 0.99 | 209 | 20.87 |

Table S5 Summary of the recoveries of the $^{13}C$-labeled surrogates from the samples of this study.

| **Compound** | **Recoveries (%)** |
|---|---|
| $^{13}C_{12}$-PCB-11 | 82.3±20.4 |
| $^{13}C_{12}$-PCB-28 | 76.7±17.0 |
| $^{13}C_{12}$-PCB-52 | 54.8±11.1 |
| $^{13}C_{12}$-PCB-77 | 97.5±19.9 |
| $^{13}C_{12}$-PCB-101 | 70.8±10.6 |
| $^{13}C_{12}$-PCB-155 | 70.5±10.7 |
| $^{13}C_{12}$-PCB-178 | 76.7±11.9 |
| $^{13}C_{12}$-PCB-202 | 83.3±14.3 |
| $^{13}C_{12}$-PCB-206 | 104.2±27.8 |
| $^{13}C_{12}$-PCB-209 | 98.9±30.5 |

## Text S1 Details on positive matrix factorization (PMF)

To investigate the atmospheric sources of PCBs to Canadian coastal regions and quantify their Aroclor and non-Aroclor contributions, positive matrix factorization (PMF) was used on the passive air sample concentrations from British Columbia and Quebec. PMF is a receptor model used for quantifying the contribution of sources to samples by decomposing the input sample matrix into factor profiles and their contributions. Details of the model are described elsewhere.[2, 3] To summarize, the sample matrix *X* with *i* by *j* dimensions, where *i* is the number of samples and *j* is the number of analytes measured, is viewed as a chemical mass balance between the species profile matrix *F* of each source, the mass matrix *G* contributed by each factor to each individual sample, and a residue matrix *E* for *p* number of factors:

$$x_{ij} = \sum_{k=1}^{p} f_{kj} g_{ik} + e_{ij} \quad \text{(eq 1)}$$

Matrices *F* and *G* are the solutions to the PMF model and are obtained by minimizing the objective function *Q*:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} f_{kj} g_{ik}}{u_{ij}} \right]^2 \quad \text{(eq 2)}$$

where *U* is the uncertainty matrix of the measured concentrations.

Along with the sample matrix *X*, the uncertainty matrix *U* is also required as input to the PMF model. An uncertainty of 15% was assigned to the air concentrations above the MDL, based on the average standard deviation of the recoveries. For values below the MDL, an uncertainty of 166% was used. One advantage of the PMF model is that it can account for the confidence in each measurement provided by the user, i.e., matrix *U*. Since function *Q* is weighted on the uncertainty $u_{ji}$ of sample $x_{ij}$, data points with higher uncertainty will have lesser influence on the solutions of the model. Therefore, measurements below the MDL can be used as input, with their uncertainties fitted such that they have less influence on the model than the measurements above the MDL.

To determine the optimal number of factors *p* for each PAS network (BC and QC), the model was tested sequentially for three to seven factors for 20 runs with a random seed. From the trials, the factors resulting in the lowest Q values were chosen for further investigation. The displacement (DISP) and bootstrap (BS) error estimates calculated by the EPA PMF 5.0 software were then used to select the optimal number of factors from the pool. For the BC and QC datasets, the DISP analysis resulted in no swap counts. The swap counts indicate the stability of the PMF solution, meaning that there is no rotational ambiguity in the factors for both datasets and that the resulting solutions are robust. The BS analysis showed that after 100 BS runs, the BS factors mapped to their base factors at least 84% and 99% of the time when using six and four factors in the BC and QC datasets, respectively (Table S6 and S7). To ensure that the appropriate number of factors is chosen, the BS factors should map with only one distinct base factor at least 80% of the time.[3] Using too few factors will cause the correct mapping percentage to drop below 80%. To assess if the number of factors chosen was optimal, the BS analysis was also performed using five and three factors for the BC and QC datasets, respectively. Selecting these factors resulted in higher Q values and lower correct mapping percentages (BC: >77%; QC: >71%; Table S8 and S9). The higher number of correct

mappings, coupled with the low swap counts, confirm that six and four factors for the BC and QC datasets, respectively, are optimal.

Table S6 The number BS runs with BS factors correctly matched to their base factors out of 100 runs for the BC data.

| Bootstrap | Base | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 4** | **Factor 5** | **Factor 6** | **Unmapped** |
| **Factor 1** | 84 | 4 | 6 | 1 | 0 | 1 | 4 |
| **Factor 2** | 1 | 86 | 3 | 2 | 6 | 0 | 2 |
| **Factor 3** | 0 | 0 | 100 | 0 | 0 | 0 | 0 |
| **Factor 4** | 0 | 0 | 0 | 100 | 0 | 0 | 0 |
| **Factor 5** | 1 | 12 | 0 | 1 | 84 | 0 | 2 |
| **Factor 6** | 0 | 0 | 0 | 0 | 0 | 100 | 0 |

Table S7 The number BS runs with BS factors correctly matched to their base factors out of 100 runs for the QC data.

| Bootstrap | Base | | | | |
|---|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 4** | **Unmapped** |
| **Factor 1** | 100 | 0 | 0 | 0 | 0 |
| **Factor 2** | 0 | 100 | 0 | 0 | 0 |
| **Factor 3** | 0 | 0 | 100 | 0 | 0 |
| **Factor 4** | 0 | 0 | 1 | 99 | 0 |

Table S8 The number BS runs with BS factors correctly matched to their base factors out of 100 runs for the BC data with five factors.

| Bootstrap | Base | | | | | |
|---|---|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 4** | **Factor 5** | **Unmapped** |
| **Factor 1** | 77 | 5 | 13 | 0 | 0 | 5 |
| **Factor 2** | 0 | 100 | 0 | 0 | 0 | 0 |
| **Factor 3** | 0 | 1 | 99 | 0 | 0 | 0 |
| **Factor 4** | 0 | 0 | 0 | 99 | 0 | 1 |
| **Factor 5** | 0 | 0 | 0 | 0 | 100 | 0 |

Table S9 The number BS runs with BS factors correctly matched to their base factors out of 100 runs for the QC data with three factors.

| Bootstrap | Base | | | |
|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Unmapped** |
| **Factor 1** | 71 | 9 | 20 | 0 |
| **Factor 2** | 0 | 99 | 1 | 0 |
| **Factor 3** | 0 | 0 | 100 | 0 |

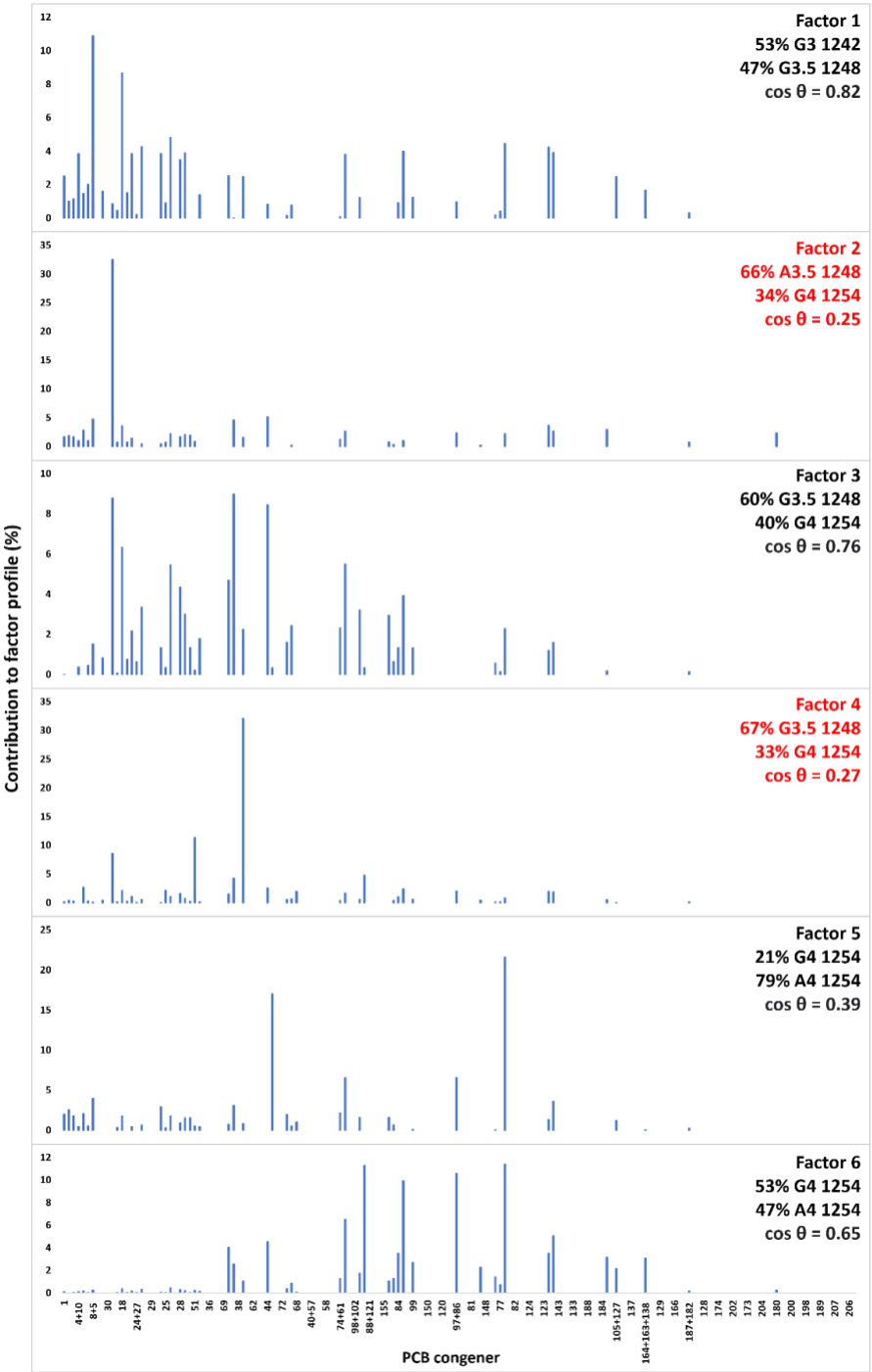


Figure S2 The PCB profiles of the six factors that describe the BC PAS dataset. The Aroclor mixture that best matches the factor profile and the cos θ similarity are included in each panel. Factors with relatively high amounts of non-Aroclor exclusive congeners (i.e., PCB-11) or set of congeners (i.e., PCB-47, 51, and 68) are in red. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1. Contributions of each congener to the factors are tabulated in the Supplementary Excel file.

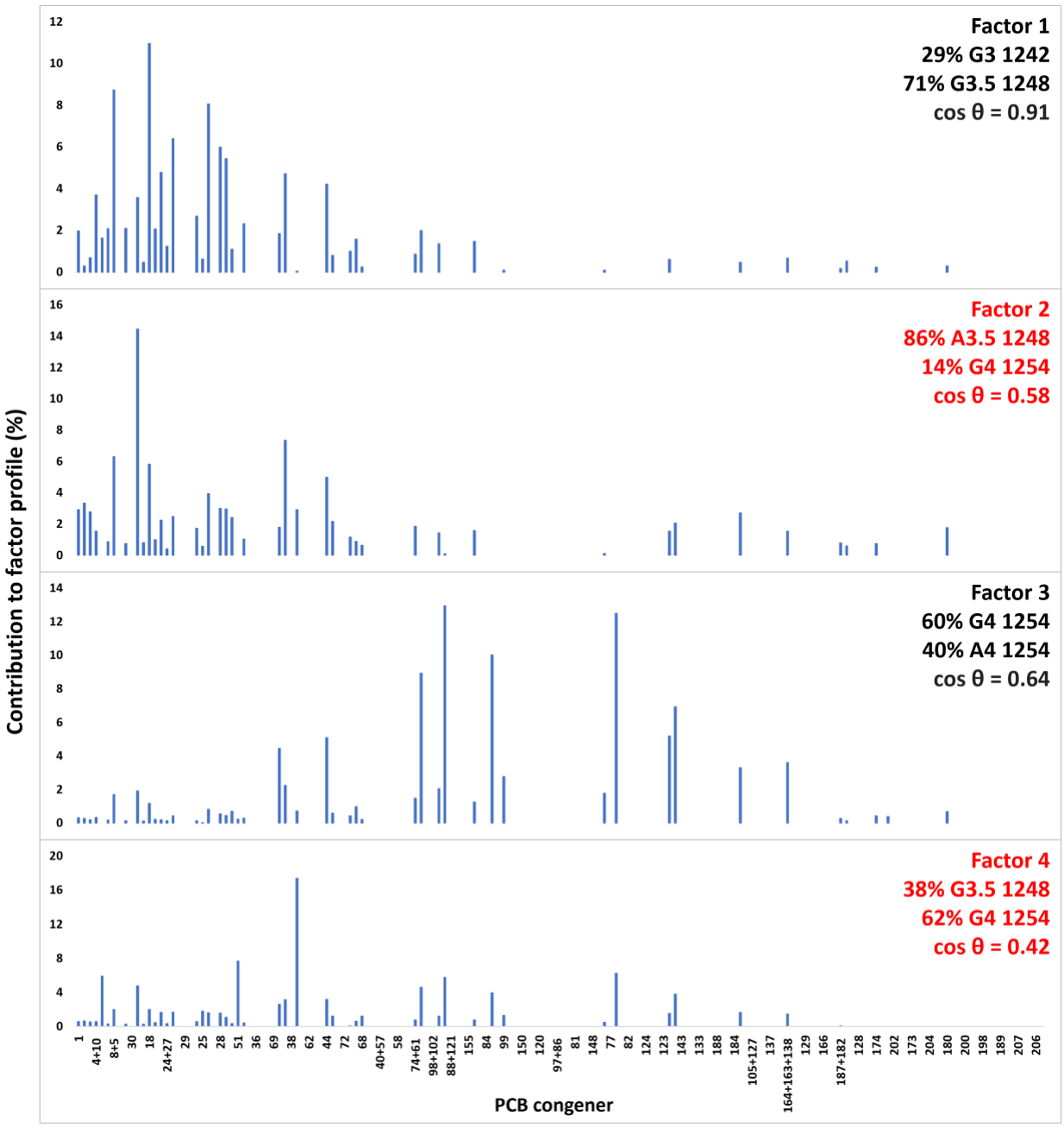


Figure S3 The PCB profiles of the four factors that describe the QC PAS dataset. The Aroclor mixture that best matches the factor profile and the cos θ similarity are included in each panel. Factors with relatively high amounts of non-Aroclor exclusive congeners (i.e., PCB-11) or set of congeners (i.e., PCB-47, 51, and 68) are in red. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1. Contributions of each congener to the factors are tabulated in the Supplementary Excel file.

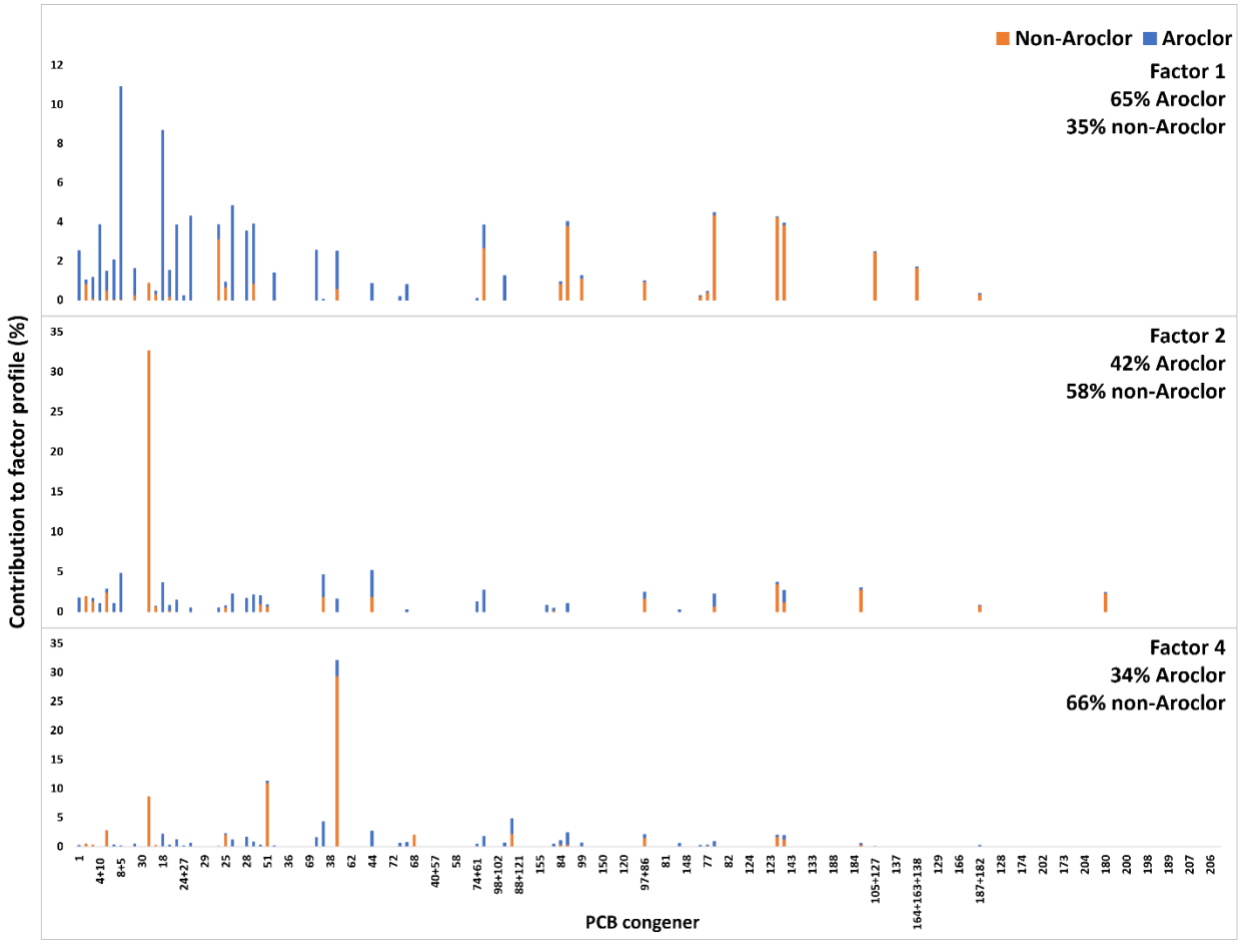


Figure S4 The potential contribution of non-Aroclors to the profile of Factor 1, 2, and 4 of the BC PAS network. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1.

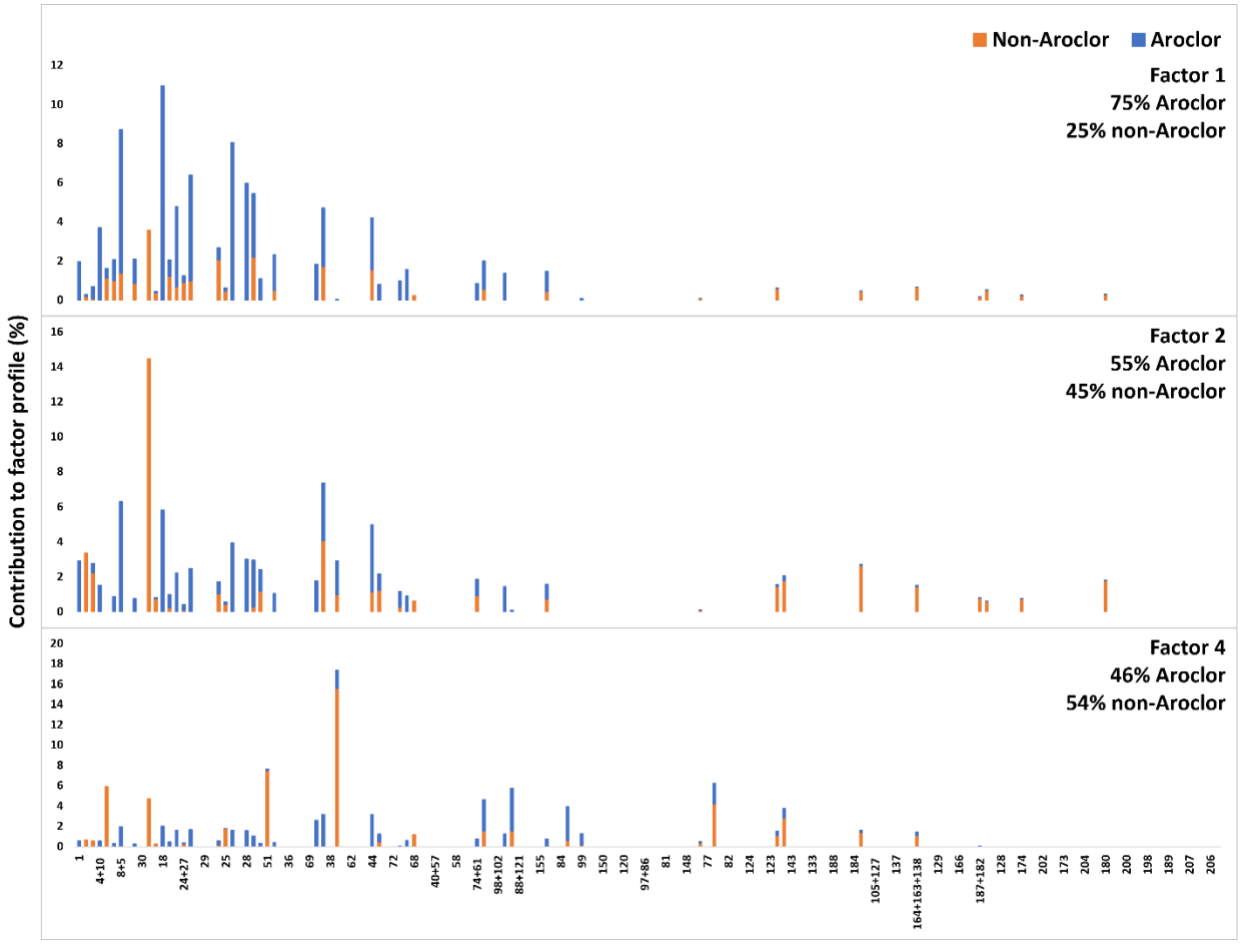


Figure S5 The potential contribution of non-Aroclors to the profile of Factor 1, 2, and 4 of the QC PAS network. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1.

## Text S2 Investigating the exclusion of undetected congeners in PMF analysis

To investigate the effects of excluding undetected congeners in the sample matrix on the resulting factors of the PMF analysis, the model was tested with sample matrix *X* that contained measurements of the detected congeners only. This still resulted in the same optimal number of factors for each regional dataset, six and four factors for BC and QC, respectively. These factors have similar profiles as the ones generated using the dataset with all congeners included (Figure S6 and S7). The similarity between the factors calculated using all congeners and the factors calculated using only detected congeners in the dataset was high ($\cos \theta > 0.82$) for all factors. An exception was Factor 1 of BC, which was only moderately similar to its counterpart ($\cos \theta = 0.56$). One main difference between their profiles was the contribution of PCB-11 to the factor profile, which was 12% in the test run but <1% in the original analysis.

Moreover, two distinct factors were identified from each region with relatively high percentages of PCB-11 (Factor 2) and PCB-47, 51, and 68 (Factor 4) in their profiles. The potential non-Aroclor contributions to the profiles of Factors 1, 2, and 4 were calculated using a similar approach to the one used for Figure S4 and S5. While some of the estimated non-Aroclor contributions of BC (50%, 41%, and 69% for Factor 1, 2, and 4, respectively) slightly deviated from their original counterparts, the estimated non-Aroclor contributions of QC (25%, 49%, and 53% for Factor 1, 2, and 4, respectively) were almost identical. Nevertheless, calculating the overall potential non-Aroclor contribution to the BC and QC atmosphere, as done similarly in the main text, still resulted in comparable ranges (11%-46% and 13%-43%, respectively) to the original ranges. Therefore, we determined that including all the non-detected congeners in the dataset changed neither the overall results of the PMF analysis nor the conclusion drawn from these results.

We also compared these factor profiles to the ones that were generated when assigning half the value of the MDL to non-detected measurements in the dataset. The resulting factor profiles were similar to their original counterparts ($\cos \theta > 0.70$), except for Factor 3 of QC ($\cos \theta = 0.49$) which had less congeners overall contributing to the factor profile. Nevertheless, the overall conclusions did not change when estimating the potential non-Aroclor contribution from each region regardless of which value for non-detects was used.

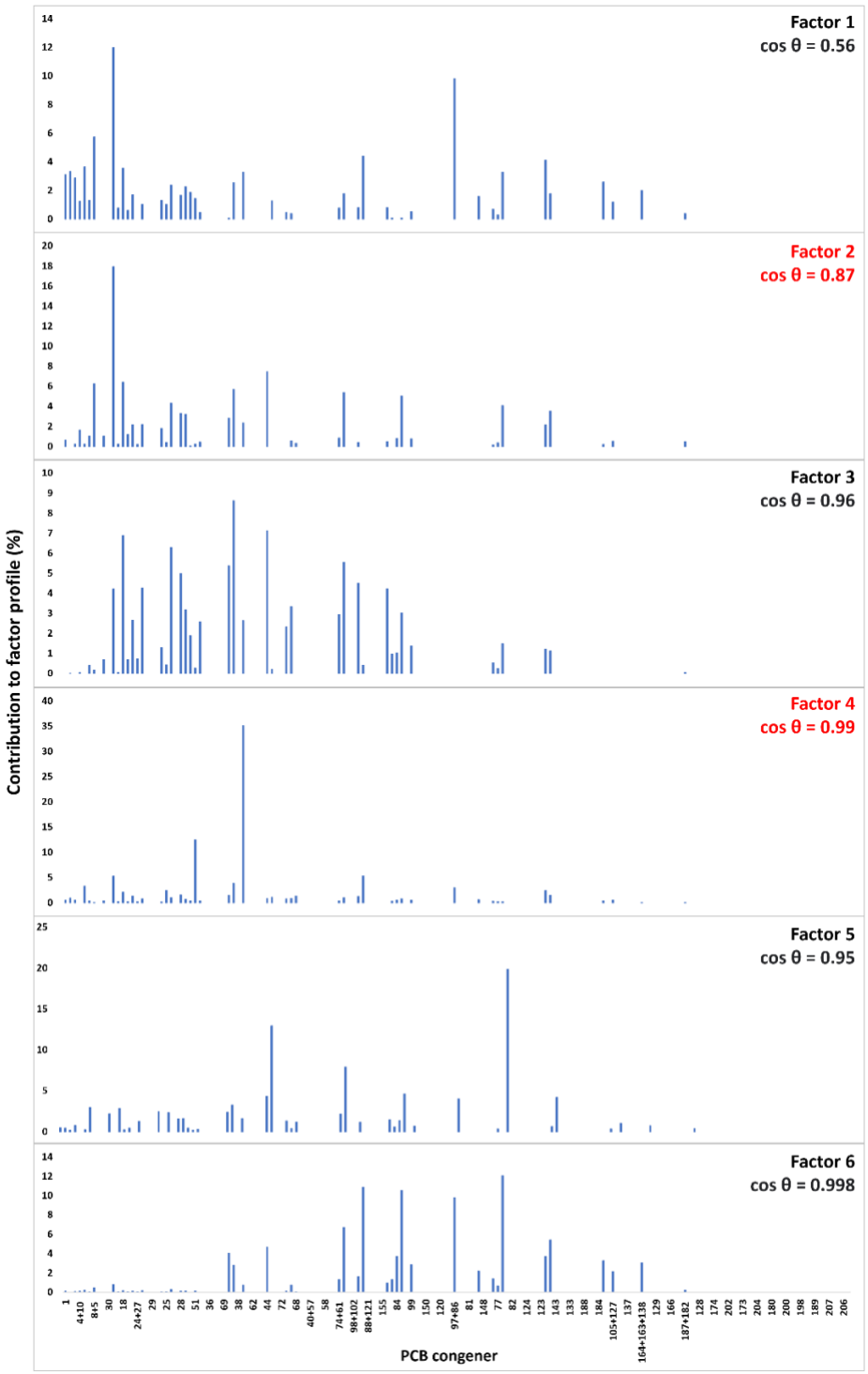


Figure S6 The PCB profiles of the six factors that describe the BC PAS dataset, excluding all undetected congeners in the regional network. The cos θ similarity to their corresponding factors in Figure S2 is included in each panel. Factors with relatively high amounts of non-Aroclor exclusive congeners (i.e., PCB-11) or set of congeners (i.e., PCB-47, 51, and 68) are in red. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1.

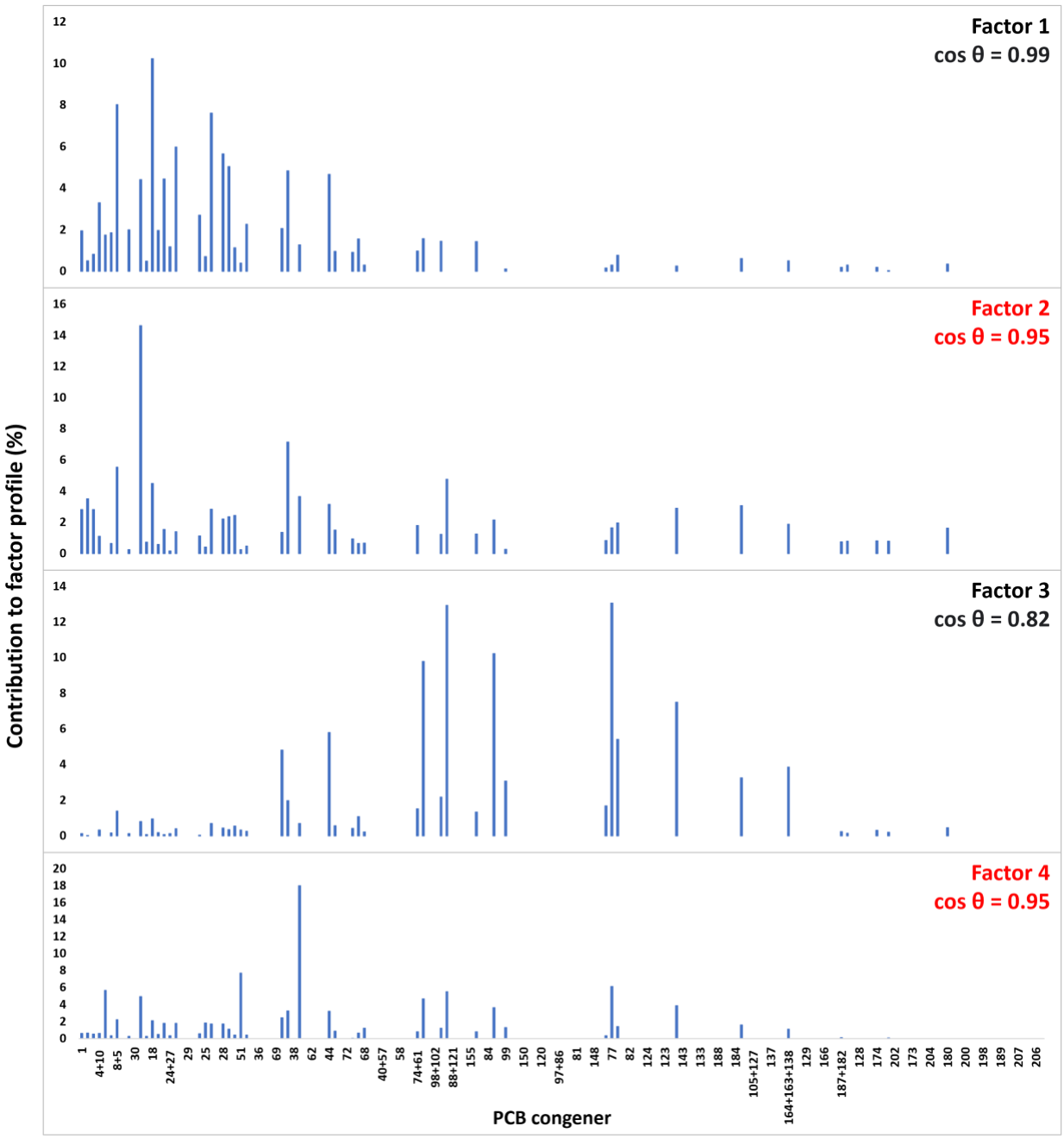


Figure S7 The PCB profiles of the six factors that describe the QC PAS dataset, excluding all undetected congeners in the regional network. The cos θ similarity to their corresponding factors in Figure S3 is included in each panel. Factors with relatively high amounts of non-Aroclor exclusive congeners (i.e., PCB-11) or set of congeners (i.e., PCB-47, 51, and 68) are in red. PCB congeners on the x-axis are listed in the same order as Table S2, with every third congener labelled starting from PCB-1.

# References


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3. Norris, G. R. D., Brown, S.; Bai, S. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. United States Environmental Protection Agency, 2014.