Evidence for major contributions of unintentionally-produced PCBs in the air of China: implications for the national source inventory

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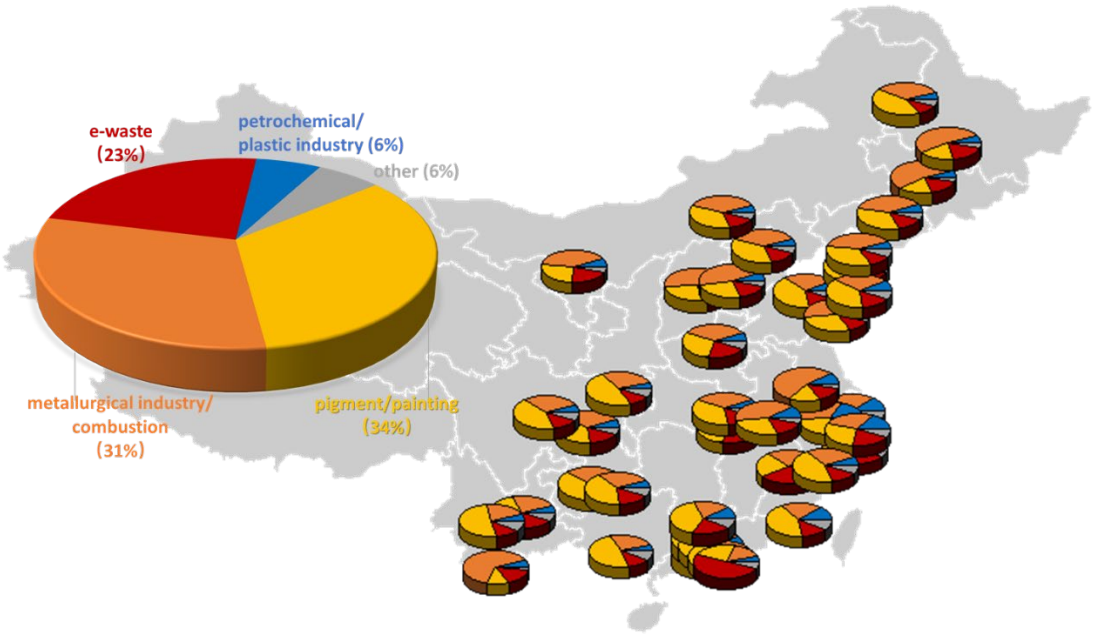
Abstract

Polychlorinated biphenyls (PCBs) were not widely manufactured or used in China before they became the subject of international bans on production. Recent work has shown they have reached China associated with imported wastes, and that there are considerable unintentional sources of PCBs that have only recently been identified. As such, it was hypothesised that the source inventory and profile of PCBs may be different or unique in China, compared to countries where they were widely used and which have been widely studied. For the first time in this study we therefore undertook a complete analysis of 209 PCB congeners and assessed the contribution of unintentionally-produced PCBs (UP-PCBs) in the atmosphere of China, using polyurethane foam passive air samplers (PUF-PAS) deployed across a wide range of Chinese locations. $\sum_{209}$ PCBs ranged from 9 to 6856 pg/m^3 (median: 95 pg/m^3) during three deployments in 2016-2017. PCB 11 was one of the most detected congeners, contributing 33±19% to $\sum_{209}$ PCBs. The main sources to airborne PCBs in China were estimated and ranked as pigment/painting (34%), metallurgical industry/combustion (31%), e-waste (23%) and petrochemical/plastic industry (6%). For typical Aroclor-PCBs, e-waste source dominated (>50%). Results from our study indicate that UP-PCBs have become the controlling source in the atmosphere of China and an effective control strategy is urgently needed to mitigate emissions from multiple industrial sources.

TOC



Keywords

Source apportionment; Passive air samplers; Polychlorinated biphenyls; unintentionally-produced PCBs (UP-PCBs)

Introduction

Polychlorinated biphenyls (PCBs) are one of twelve legacy persistent organic pollutants (POPs) initially regulated by the Stockholm Convention,[1] because they are toxic and stable in the environment, may undergo long-range atmospheric transport (LRAT), and bioaccumulate via the food chain, representing a potential threat to environmental and human health.[2, 3] PCBs were originally deliberately produced between 1930s - 1970s as complex mixtures with a theoretical possible 209 different congeners.[4, 5] They were given the trade name Aroclor in the US, thus we used "Aroclor-PCBs" here to denote PCB congeners with historical production. During this time, an estimated ~1.4 million tonnes of PCBs were deliberately manufactured. China was not a main PCB producer, only accounting for ~1% of the total global production, with Chinese production finishing in 1974.[6] Nonetheless, these compounds are still of great concern in China and are frequently detected in the Chinese environment.[7, 8] Much of this attention has arisen because of the presence of PCBs in imported e-wastes.[9, 10] Indeed, it was reported that airborne PCBs in China increased from 2004 to 2008[11] at a time when the trend in other parts of the world was the opposite.[12-14]

PCBs emitted into the atmosphere can originate from both intentionally produced (IP-PCBs) and unintentionally-produced (UP-PCBs) sources. The latter are by-products of industrial processes.[15] Attention on UP-PCBs is relatively recent. Given: (i) the very small production and use of Aroclor-PCBs in China; (ii) the huge industrial and chemical manufacturing base of China, (iii) China's commitment to the Stockholm Convention, which requires it to publish a national source inventory and assess the effectiveness of source abatement measures, a significant question is therefore 'what is the contribution of UP-PCBs in the Chinese atmosphere?' This question is of key interest for policy makers, since it will affect their perception of the need to reduce or

eliminate primary emissions and the effectiveness of emission reduction strategies. We have demonstrated that the UP-PCBs will probably become a main contributor from 2035 by modeling current and future emission sources for China.[9] These projections are mainly linked to widespread industrial thermal processes for producing steel, cement and iron ore, etc.[15, 16] However, this was just a pilot study, based on seven indicator Arolcor- PCBs, and needs to be tested by field observations.

Understanding atmospheric emission sources largely relies on accurate determination of the occurrence and spatial distribution of PCB ambient air concentrations. Previous studies have mainly focused on a selection of congeners which was dominated by IP-PCBs.[12, 17, 18] However, several monitoring studies have recently pointed out that that UP-PCBs, such as PCB 47/48/75[7] and PCB 11[19-21] contribute significantly to the present level of PCBs. Hence, monitoring merely based on a limited number of PCB congeners could bias the estimated contribution from various PCB sources.

In this study, we therefore conducted a national atmospheric PCB campaign from 2016 to 2017, using polyurethane foam passive air samplers (PUF-PAS) to: 1). investigate occurrence, spatial distribution and congener pattern of airborne PCBs in China; 2) estimate the relative contributions of PCB sources to China's atmospheric burden of PCBs, by source apportionment; 3) discuss the implications for source controls and policy. To the best of our knowledge, this is the first study to draw comprehensive source profiles of PCBs on a national scale in China.

Methods

Sampling design

We selected two types of sampling sites, source sites and non-sources sites. Sources sites were close to areas with various industrial activities, namely steel production, coking, petrochemical, dying, pigment, e-waste dismantling, etc. Samples from non-source sites presented the general PCBs profile in urban, rural and remote sites. The strategy behind site selection was to utilize measured emission profiles of source-sites as the fingerprint to decode the relative contribution of multiple sources to current airborne PCBs in China. PUF-PAS samplers integrate air over many weeks of deployment, and is a cost-effective method which can be used in multiple sites with no requirement for electricity. It has therefore been widely used in regional and global scale monitoring studies for PCBs and other POPs.[11, 18, 22] The specification and photos of used PUF-PAS were described in Figure S1 and Table S10. The advantages of utilizing PUF-PAS to investigate various emission profiles are: 1) well-mixed and long-term deployed passive air samples are more representative than grab samples. The traditional grab samples of flue gas/ash just represent instant short-term emission patterns. It may only capture PCBs in the gas or particle phase and significantly differentiate among various thermal industrial processes, whilst PUF-PAS capture both air and particle phases.[23] All PUF-PAS were deployed for 7-8 weeks near emission sites, representing a well-mixed and stable emission profile of a specific source; 2) most currently available emission profiling only has a limited number of congeners analyzed, mainly focused on the Aroclor-PCBs and dioxin like-PCBs (dl-PCBs). Emission profiles based on analysis of all 209 congeners can provide insight into the PCB emission pattern from a full range of industrial activities.

All the site information and sampling periods are detailed in Table S1. In summary, PUF-PAS were deployed at 62 sampling sites across China for three cycles in autumn and winter of 2016 and summer of 2017. The effective sampling rate was determined via calibrated model detailed elsewhere.[23] Prior to deployment, PUF-PAS were pre-cleaned and shipped to the sampling sites with installation instructions for local operators to deploy. All samples were delivered back to the lab and stored at -20 ℃ before analysis.

Sample pretreatment and analysis

The detailed methods for sample treatment and instrumental analysis are given in a previous study.[7] In short, each sampled PUF disk was spiked with $^{13}C_{12}$-labeled PCBs (PCB 11, 155 and 206) as recovery standards and extracted in a Soxhlet apparatus for 24 h with hexane and acetone (1:1, v/v). The extracts were concentrated via rotary evaporator and solvent-exchanged into hexane with reduced volume of 0.5-1 mL. They were then purified by a multilayer acidified silica gel column and concentrated into a vial under a gentle stream of nitrogen. $^{13}C_{12}$-labelled PCBs (PCB 77, 101, 141, 178) were added as internal standards before instrumental analysis. Samples were analyzed on an Agilent 7890A/7000A GC-MS/MS with a CP-Sil 8 CB column (50 m × 0.25 mm × 0.12 μm) in a multiple reaction monitoring (MRM) mode for measuring all 209 PCB congeners. The precursor and product ions are detailed in Table S2, and retention times are listed in Table S3.

Quality assurance and quality control (QA/QC)

QA/QC was conducted using field blanks, procedural blanks and surrogates spiked recoveries. Most congeners were not detected in the field blanks and procedural blanks. The average recovery rates of $^{13}C_{12}$ labelled 11, 155 and 206 were 62±13%, 71±11% and 76±12%, respectively. The reported concentration data were corrected for blanks and surrogate recovery. The method detection limits (MDLs) were assigned as the average values of field blanks plus 3 times their

133 standard deviations. MDLs were calculated as three times of instrumental detection limits (IDLs)
134 if a congener was not detected in field and procedural blanks. IDLs were defined as the amounts
135 of analytes generating a signal-to-noise of 3:1 using the lowest standard concentration, assuming
136 a linear increase of response. The IDLs and MDLs of 209 PCB congeners were in ranges of 0.2 - 470
137 pg and 0.002 - 16 pg/m^3 presented in Table S4.

138 Positive Matrix Factorization (PMF)

139 The Positive Matrix Factorization (PMF) method is a model for solving a receptor-only, bilinear
140 unmixed model which assumes that a measured dataset conforms to a mass-balance of a number
141 of constant source profiles, contributing varied concentrations. Its advantages over PCA is the
142 uncertainty-weighting of each data point and matches the observation of the real-source
143 signature without requiring the dataset orthogonal to each other.[24] Thus, it has been widely used
144 to identify possible sources of PCBs and many other POPs.[24-26]

145 The input data file consisted of receptor concentration (C) and uncertainty (U) matrixes. Measured
146 PCB concentrations were entered separately for each deployment at each site. PCB congeners
147 below the limit of detection in >50% of samples were excluded from the PMF model. U for each
148 variable was calculated using C and the MDL as suggested.[24] In order to determine the optimal
149 number of sources, the model was tested for 2-8 factors by running 20 times with a random seed
150 to determine the stability of Q values, a parameter measuring the impact of data points with high
151 scaled residuals. To evaluate the degree of fitting of PCB congeners for estimating emission
152 profiles, the coefficient of determination (R^2) measuring the goodness of fit between the
153 measured and modelled concentrations was used. Calculated R^2 were all greater than 0.5 for all
154 the congeners. The initial matrix was composed of 121 samples × 93 species and the results are
155 summarized in Table S5.

Identification of resolved factors

Spatial variation of the factor scores, comparison of congener patterns with known sources (both from a literature review and from observations in this study at source sites), and presence of the non-Aroclor congeners were considered to identify the resolved factors. The cosine theta similarity metric, a measure of similarities between two vectors, was used to match congeners patterns.[27] Selected PCB profiles included unaltered Aroclor mixtures (1221,1232,1016,1242,1248,1254,1260,1262 and 1268),[28, 29] #1 PCB[30] (a commercial product of China), Kanechlor products (KC300, KC400, KC500, KC600) and emissions from incineration of municipal solid waste[5, 31] and cement kilns co-processing solid waste,[32] wood and coal combustion,[33, 34] electronic arc furnaces,[16, 31] water treatment plants[35] and various types of pigments.[36, 37] To consider the potential contributions of emissions of PCBs from production banned in the past, profiles of volatilized Aroclor mixtures were also included and obtained by multiplying the individual congener concentration by corresponding subcooled liquid vapor pressure (Pa) from measurements or estimated from regressions, if measurements were not available.[38]

Results and Discussion

PCB profiles in the air of China

Measured PCB concentrations for all samples (n=167) are summarized in Table S6. In summary, $\sum_{209}$ PCBs broadly ranged from 9 to 6856 pg/m^3 (median: 95 pg/m^3) in varied sites as listed in Table S1. $\sum_7$ indicator PCBs (i-PCBs) and $\sum_{12}$ dl-PCBs contributed on average ~5% and ~1% to the total $\sum_{209}$ PCBs concentrations. Concentrations of $\sum_7$ i-PCBs were significantly positively related to the $\sum_{209}$ PCBs concentration as shown in Figure S2 (R^2>0.99, p<0.001). Lower chlorinated (mono to tri-) PCBs dominated the composition, contributing >70% at all non-source sites. On average, di-CBs

accounted for ~40% to the $\sum_{209}$ PCBs, mainly due to the contribution of PCB 11. Previous studies have quantified fewer congeners and usually excluded mono-CBs and di-CBs, therefore drawing a different conclusion that tri-CBs is the dominant homologue group in China.[11, 18]

No statistical difference was observed for the seasonal variation for concentrations of $\sum_{209}$ PCBs shown in Figure S3-a, b, c (Kruskal-Wallis H test, p=0.273), although significant differences were observed for mono-CBs (P<0.05), which were much higher in winter (47±63 pg/m^3), than autumn (22±26 pg/m^3) and summer (17±22 pg/m^3). This exhibits the same seasonal trend as combustion-related airborne pollutants, like PAHs, so it may indicate the contribution of combustion emissions and domestic heating.[39, 40] It has been demonstrated that combustion sources profiles were largely dominated by the lower chlorinated congeners, including PCB 1, PCB 2 and PCB 3.[41, 42] Meanwhile, mono-CBs are dominant in Aroclor 1221 and Aroclor 1232, accounting for up of 60%, which may also be a potential source via relevant recycling activities/combustion. In addition, lower mixing atmospheric height may increase pollutant concentration in winter.[39]

Higher concentrations of PCBs were observed in developed and populated zones along the Chinese east coast to the south coast, from the region of the Yangtze River Delta to the Pearl River Delta (see Figure S3). These two regions share the main proportion (>50%) of the historical PCBs usage in China. [43] They are also the regions where e-waste recycling sites have been intensively located.[8, 44] As expected, the highest concentration was observed at an e-waste dismantling site located in an industrial park of Taizhou, where concentrations averaged at 6460 ±460 pg/m^3. Another e-waste site in Qingyuan also had high PCB concentrations, but nearly an order of magnitude lower than in Taizhou (835±224 pg/m^3). This difference may have been caused by varied dismantling techniques of e-waste recycling activities.[45]

Comparison with other studies

A significant reduction was observed when comparing the concentrations of the 18 commonly measured PCB congeners with other passive air sampling studies conducted in China in 2004[18], 2005[46] and 2008[11] (see Table S7), with similar composition dominant by tri-PCBs. Our measurements were on a similar level (~60 pg/m^3) compared to those measured in 2004 and 2005, but an order of magnitude lower than the observation in 2008. An increasing trend was also observed in sedimentary records from Eastern China since 1990s, which closely follow the growth of PCBs emission from industrial thermal process and e-waste sources.[17] Chinese government released the standard for pollution control on PCBs in contaminated wastes (GB 13015-91) in 1991 and updated a new version (GB 13015-2017) in 2017. But there is no relevant regulation and rule on controlling PCBs emission from unintentional sources so far.

The comparison of PCB levels with other regions is summarized in Table S8. PCB concentrations in Chinese air are often found to be comparable with regions with intensive historical manufacture and usage of PCBs, such as Japan, Korea and the USA.[11, 18, 47] Levels are much higher than observations in King George Island[48] and the Group of Latin American and Caribbean (GRULAC) countries.[22] Several urban sites had high levels of PCBs, e.g. Zhengzhou City in winter (1056 pg/m^3), which is comparable to PCBs level in Chicago,[47, 49] London and Manchester.[14]

These observations are contradictory to the historically minor production and usage of PCBs in China, which only accounts for around 1% to the global production. One possible reason is the large importation of e-waste, which is illegal and difficult to track.[10] Improper dismantling and recycling activities give rise to elevated levels around these sites.[45] Another factor possibly contribution to the higher level is the inappropriate management and disposal of

223 decommissioned capacitors.[18, 50] Finally, unintentionally-produced PCBs from multiple industrial
224 processes may also contribute to the current levels of PCBs in Chinese ambient air.[9, 15]

225 ## Spatial transect

226 PCB levels measured at various sampling sites were ranked as follows: e-waste sites (3010±2076
227 pg/m^3) >> industrial sites (152±103) > urban sites (124±126 pg/m^3) > rural sites (87±30 pg/m^3) >
228 remote sites (70±140 pg/m^3). In terms of $\sum_{209}$ PCB concentrations, all types of sites had statistically
229 significant differences (Kruskal-Wallis H test, $p<0.05$), except for the datasets between rural and
230 urban sites ($p=0.08$). The decreasing gradient indicated the important contribution of PCBs from
231 e-waste and potential sources relate to multiple industrial activities.[15] However, the decreasing
232 gradient was less pronounced than previously observed differences, which have ranged over 1-2
233 orders of magnitude.[51, 52] This may be due to the re-location of various industrial activities from
234 urban areas to semirural/rural areas, driven by the Chinese government[53] and an implementation
235 gap of environmental policies in rural areas.[54] Another possible reason may be less usage of PCBs
236 in urban areas of China, compared to some other countries, such as in building materials used in
237 the US, Norway and elsewhere.[55]

238 It is interesting to note that, penta and hexa-CBs contributed most (~14% and ~9%) in remote sites
239 as shown in Figure S3-d. Normally, low chlorinated PCBs with relatively high volatility are expected
240 to move to remote regions more efficiently, whereas higher chlorinated PCBs with lower volatility
241 tend to remain in the surface compartments within, or in the vicinity of, source regions.[52] The
242 spatial distribution of PCB homologues in industrial, urban and rural area satisfied this expectation.
243 The sum contribution of penta- and hexa-CBs was ranked as remote sites > e-waste sites >
244 industrial sites > urban sites > rural sites. The penta-CBs in remote sites were mainly contributed
245 by PCB 125 and PCB 111+117, which were detected in commercial products of KC 500 and KC 400,

and the flue gas of incineration from incinerators in similar composition.[5] Whilst, PCB 130 and PCB 162 were the main contributors in hexa-CBs, occupying no or very limited portion in commercial products. These congeners are not routinely measured in previous studies. However, their levels and contributions were comparable to these in source sites, such as petrochemical and steel industry. The reason of contrasting with typical congeners profiles dominated by tri-CBs is that the measurement of the full set of 209 congeners here, highlighting the roles of penta- and hexa-CBs, which were potentially ignored before. Though most remote sites were selected from the network of national monitoring sites of background air, these sites were located and designed to monitor standard air quality compositions, such as $PM_{2.5}$ and NO_x, not for POPs. The remote sites greatly dominated by penta and hexa-CBs was mainly located in the developed and populated regions in eastern and southern China, such as Cape D'Aguilar in Hongkong and Hengxi in Zhejiang province, which were potentially affected by the local hidden stockpiles, potential illegal e-waste dismantling and industrial sources relocated therein owing to the much strengthened air pollution control policy in Chinese cities

Analysis of source factors

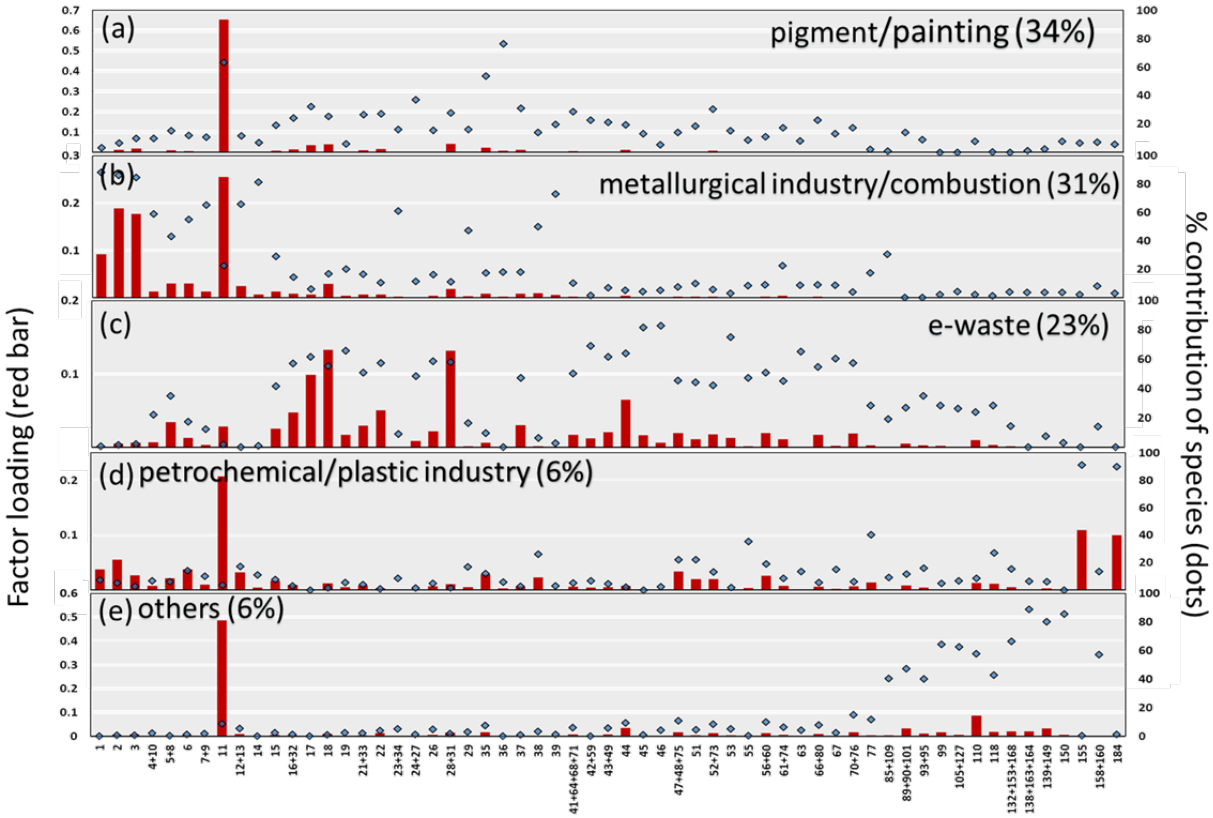


Figure 1. Source profiles gained from positive matrix factorization analysis of airborne PCBs (a-e). Bars represent factor loading and dots represent contribution (%) of selected species of each source factor.

Five source types were identified by PMF for airborne PCBs in China captured by PAS-PUF in this study and are presented in Figure 1. The first factor (Figure 1-a) was responsible for 34% of the PCB masses. with a high loading of PCB 11 (a non-Aroclor congener), contributing 63% of the sum, which is similar to previous studies conducted around the Great Lakes.[56] PCB 11 is the dominant congener present in azo-pigments, as discussed previously.[42] This estimated concentration profile (Figure 1-a) had the highest similarity with samples from dying and pigment sources (cos Θ= 0.96-0.99). Therefore, the first factor should represent volatilization from paints/pigments and/or wastewater receiving paints/pigments industries. However, all factors (Figure 1-a, b, d, e) except for e-waste sources (Figure 1-c) gained a high factor loading from PCB 11, with relatively low

contribution to total congeners (2-22%), indicating universal and potentially overlooked sources of PCB 11 requiring further investigation.

The second factor (Figure 1-b) could explain 31% of the total PCB masses with a high loading and contribution of lower-chlorinated PCBs (PCB 1,2,3, 85-88% of species sum). This estimated emission profile has a strong similarity (cos Θ= 0.93-0.99) to the measured profile in source regions of the steel, coking and motor industries. Previous direct measurements from waste incineration flue gas showed a similar congener pattern, which was dominated by low chlorinated congeners.[41] As a result, the second factor was considered as the combined source of metallurgic industry and combustion.

The third factor (Figure 1-c) was responsible for 23% of the total PCB masses, with a high factor loading of Aroclor-PCBs, mainly including PCB 28/31 (58%), 17 (62%), 18 (55%). Other typical Aroclor congeners, such as PCB 37, 44, 49 and 66 all greatly contributed to the total species sum, ranging from 42-82%. This congener pattern is consistent with the commercial products, dominated by tetra-CBs, similar to the composition of Aroclor 1248 (the US), KC400 (Japan) and #1 PCB (China). However, its similarity with these original and volatized Aroclor-type commercial products was relatively low (cos Θ= 0.05-0.38), possibly because the pattern could be altered during the transport and recycling of commercial products. Close similarity was observed with measurements of e-waste sources sampled in Qingyuan and Taizhou (cos Θ= 0.78-0.89). As a result, it is concluded that this factor is the characteristic emission from e-waste sources.

The fourth factor (Figure 1-d), only explained 6% of the total PCB masses, was also characterized relatively high factor loadings of PCB 11, 155, 184. All these congeners are non-Aroclor PCBs, with no link to intentional production and historical usage of PCBs. PCB 155 and 184 together contributed 90% of the sum of PCB species. This factor is similar to samples from petrochemical

297 industries in Shanghai and Dongying City in Shandong Province (cos Θ= 0.86-0.93) and source
298 samples from plastic manufacture in Yuyao city, Zhejiang Province (cos Θ= 0.81-0.92). Yuyao is the
299 largest center of manufacturing and producing plastic products in China.[57] This factor was
300 therefore regarded as the combined source from petrochemical and plastic industries. PCB 155
301 and 184 could be considered as potential markers of these two sources.

302 Lastly, the fifth factor (Figure 1-e), also contributed 6% to the total PCB masses. However, its
303 congener pattern did not match well with source profiles from this study or the literature. This
304 factor also had a high loading of PCB 11, and of several Aroclor PCBs, like PCB 101, 110, 118, 138
305 and 139/149, contributing 47-88% to the species sum. These congeners are often dominant in
306 Aroclor 1260 and equivalent commercial products. Shang *et al*. also observed PCB 101, 138 and
307 153 in yellow pigment samples in China.[58] Thus, we speculate that this factor could be from
308 combined sources of pigment and Aroclor 1260 or its equivalents. However, labeled as "other" in
309 Figure 1-e, this needs to be investigated further and will not be discussed in detail here.

Source apportionment of PCBs across China

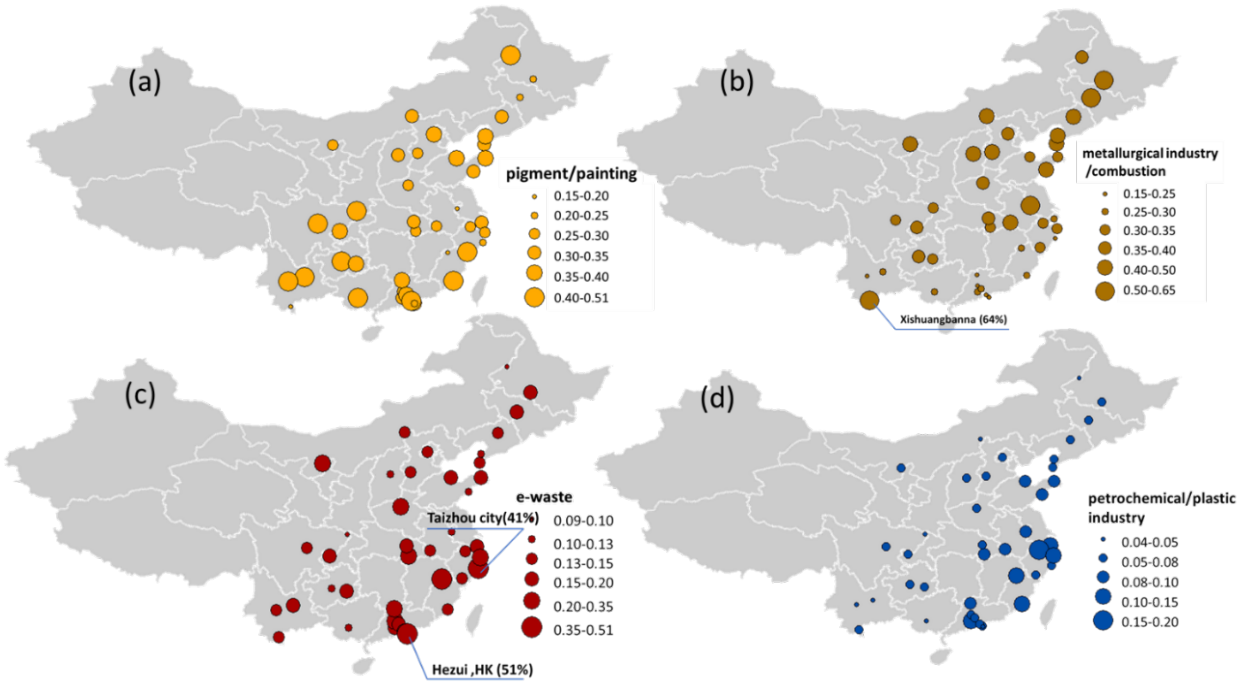


Figure 2. Normalized contributions of the PMF source factors for the autumn deployment (Oct-Dec, 2016).

Normalized contributions of the PMF source factors for the samples collected in autumn of 2016 are presented in Figure 2. The sources from volatilized pigment/paintings (Figure 2-a) were relatively well-mixed across China, with a contribution ranging from 15-51%. Southern China is more strongly affected than the northern parts, which might be following a similar trend as PCB 11.[59] Warmer temperatures increase the painted/pigmented surfaces. In addition, the pigment-related source also showed a seasonal variation with a significantly increased contribution in summer (45±6%) than that in autumn (31±8%) and winter (30±8%).

In contrast, the metallurgical industry and combustion sources were calculated to contribute larger proportions in northern China than in the south, as presented in Figure 2-b. This spatial pattern is consistent with the distribution of the metallurgical industries and heating supply in China. Higher contributions of this source type were observed in typical industrial cities like

Changchun, Shijiazhuang and Shenyang. However, the highest contribution from this source (64%) occurred in Xishuangbanna of Yunnan Province, which is probably related to biomass burning. Based on the backward trajectory analysis (Figure S6-b), these sites mainly received air masses originating from Laos (61%) and Myanmar (39%), regions with intensive opening burning of forests, crop residues, grassland and savanna.[60] With higher contributions in winter than in summer (36±11% vs. 22±3%), this source also showed opposite seasonal variation compared with the pigment/paint sources. Its temporal trend is very similar to that for PAHs which are known to be widely emitted from combustion sources.[61]

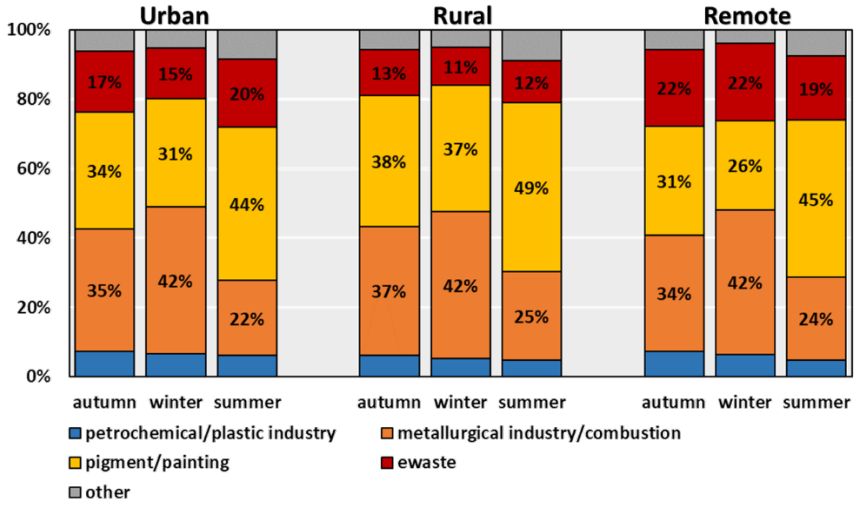


Figure 3. Relative contribution of identified source to the urban, rural and remote sites in three deployments.

E-waste sources (Figure 2-c) responsible for 10-51% of total PCB concentrations at multiple sampling sites (annual average 22±8%), showed no seasonal difference. It is noteworthy that several remote sites received much higher contributions from the e-waste related sources than urban and rural sites as shown in Figure 3. For example, the Cape D'Aguilar site in Hong Kong was estimated to have the highest loading of e-waste sources (51%), even higher than the urban site (41%) of Taizhou City, around 20 km away from an e-waste site. One potential explanation for this

could be the relocation of e-waste dismantling activities from suburban and/or rural areas to more remote sites, to try to avoid legal sanctions. Another possible reason may be that this site received pollutants from long-range atmospheric transport. According to the backward trajectory analysis (Figure S5-a), this sampling site mainly received air from eastern China (49%) and Taiwan (52%) during sampling in autumn 2016. This signal may be polluted by e-waste activities and/or release from storage of historical products. Half of the total amount of PCBs used in China were in the eastern regions of the country.[43]

The petrochemical industry/ plastic source was estimated to contribute 4-17% of the total PCBs. The highest contribution occurred in sites near the source regions of the plastic and petrochemical industries, such as the urban site in Hangzhou (17%), remote sites in Ningbo city, eastern China (14%), close to Yuyao city, the 'home' of China's plastics industry. On another hand, eastern and northern sites with major petrochemical industrial activities were in Donying city of Shandong Province and Shanghai. All these sites shared relatively high contributions (12-14%) from the sources of petrochemical industry. This spatial trend also matched well with the geographical distribution of petrochemical industry in China, which is most intensive in the eastern China.

UP-PCBs contribution to Aroclor-PCBs

The contribution of various sources to the typical Aroclor-PCB signal was estimated by taking six indicator PCB congeners as the key signature, namely PCB 28, 52, 101,118,138 and 153. PCB 180 was not included, due to low R^2 calculated by PMF. The main contributor to this profile was e-waste (51%), followed by the pigment/painting sources (10%). This is consistent with our previous modelling result, indicating that e-waste still plays an important role to the current PCBs loadings in the air of China.[9] Meanwhile, a substance-specific emission pattern was observed, as shown in Figure S7. For instance, PCB 28 was originated mainly from the e-waste (58%) and

pigment/painting sources (28%), whilst PCB 153 was dominated by other mixed sources (66%), the petrochemical/plastic industry signal (15%) and e-waste (15%). Since PCB 28 is the dominant congener amongst the six indicator PCBs, targeted control of the e-waste source will greatly mitigate the PCB emissions. Therefore, effective control measures should be developed for individual substance. Further studies to confirm the "other mixed sources" are also needed, though they contributed only a minor amount for total PCBs emission.

Comments on pigment-relevant congeners

PCB 11 is the most important pigment-relevant congener.[19] Its spatial distribution and seasonal variation are shown in Figure S4-S5. It is one of the most frequently detected congeners, with 99% detection frequency. It contributed most (33±19%) among all the congeners to the $\sum_{209}$ PCBs. This is much higher than the ~15% in Chicago in 2007,[21] but lower than the ~79% reported in Antarctica.[48] The concentration of PCB-11 averaged 35±33 pg/m^3 (<MDL-249 pg/m^3) and was higher in summer, due to the relatively high volatility of di-CBs and suggested volatilization from surfaces to which it had been applied.[62] The ranking of PCB 11 levels in the various categories of sampling sites is in order of industry > rural > urban > remote, indicating it is positively related to human activities. Our PCB 11 concentrations were comparable to those in the urban air of the US[21, 59] and higher than most studies in other regions as shown in Table S9. An increasing trend was observed from the first observation in 2012 of Beijing.[63] Other PCB associated with pigments include PCB 35 and PCB 77 together with PCB 11 in azo-type pigment, and PCB 209, 206, 207 and 208 in phthalocyanine-type pigment.[42] 100% and 57% detection rates were observed for PCB 35 and 77, whilst PCB 209, PCB 208, PCB 207 and PCB 206 were detected less frequently (46%, 4%, 24%, 17%) and at lower concentrations.

This study is the first to comprehensively assess the occurrence and fate of PCB 11 in the air of China. It has been demonstrated to be mainly emitted from azo-type pigments.[42] China has become the largest manufacturer of organic pigments in the world.[58] According to the report of the China Dyestuffs Industry Association (CDIA),[64] the azo-type pigment and phthalocyanine pigment contributed 59% and 24% to the total organic pigment/paints production in China, which would release approximately 130 and 0.1 tonnes of PCB 11 and PCB 209, respectively. This was just a crude emission estimate based on the formulation measurement of pigment produced by companies from China,[58] UK, Japan, the Netherlands and so on.[36, 37] Chinese products contain a wider range of PCB 11 and other congeners, potentially leading to even higher PCBs emission.[58] Therefore, further studies to confirm sources and develop their emission inventories are urgently needed.

Limitations and implications

There is still insufficient characterization of sources, particularly unknown sources, which limits the present study. Data gap of PCB emission sources is inevitable, such as the source profile of sewage treatment plants and indoor air. Our preliminary strategy is to take advantage of the existing literature to close these gaps. However, reports of comparative patterns for sources are limited, which makes pattern matching for fingerprints challenging. This may be the reason why the fifth source factor could not be fully-confirmed by existing emission profiles. With PCB 11 and other congeners volatilizing from the surface of pigments and paints, indoor air will be an important source contributing to PCB emissions and could raise health issues from indoor exposures. The occurrence of PCBs and their metabolites in indoor air and exposure risk to the general population are not well-studied so far in China.

409 Passive air sampler monitoring studies often meets several common challenges.[65] Firstly, since
410 most of PUF-PAS were installed by volunteers, uncertainty could exist in the placement of samples.
411 Several abnormally high concentrations may be potentially caused by improper placement near
412 ventilation systems with potential indoor sources. Secondly, PUF-PAS captured both particle and
413 atmospheric phase simultaneously. [23] Whilst, most studies used active sampler to obtain emission
414 profiles, mostly focused on the particulate phase and/or merely considered the gas phase with
415 selected congeners. [5, 31, 66] This could cause big challenge for congener profile matching between
416 source and non-source PCBs profile. Hence, we considered that the emission profile consistently
417 gained by PUF-PAS would have higher similarity than that from the literature data.

418 More than four decades have passed since the international ban on PCB manufacture and use,
419 but China still receives on-going emissions of PCBs from multiple sources, particularly from
420 unintentional sources (UP-PCBs). Our findings suggest that the UP-PCBs have become the
421 dominant source across China, accounting for ~65% to the total emissions. Volatilization from
422 pigment/painting sources and metallurgical industry/combustion are shown here to be the most
423 important sources nationally. This raises new issues for regulators and policy makers to develop
424 relevant UP-PCBs emission inventories and establish additional effective strategies to control
425 unintentionally-produced sources. Meanwhile, the contribution of e-waste as a PCB source
426 cannot be neglected, particularly for Aroclor-PCBs, like indicator PCBs (>50%). It is challenging to
427 differentiate this source as either intentional or unintentional, due to unknown mechanisms of
428 PCB origin. If it comes from the *de novo* synthesis of e-waste dismantling activity, this source is an
429 unintentional source. Previous studies evaluating the mass fluxes of organic contaminants
430 released during incomplete incineration concluded that incinerators could be sinks or sources,
431 depending on the waste feed and combustion temperature.[66, 67] It is important to understand the

mechanism of PCB emission during e-waste dismantling activities. Such studies are scarce, but would greatly enhance the effectiveness of source control.

The transect profile of PCBs among urban, rural and remotes sites has been shifted under the impact of human activities, as demonstrated in our study. We used to utilize the remote sites as the background sites to investigate the baseline environmental level of target compounds. However, in several selected remote sites in this study, which was assumed to be far-away from human activities, unexpected high concentrations of PCBs were observed, like in Cape D'Aguilar in Hongkong and Hengxi in Zhejiang province, both working as the regional background sties to offer the baseline information of air quality in China. But they are originally designed to monitor regulated air pollutants instead of POPs. As a result, using their PCBs level may cause potential bias and it's worthwhile to review the applicability of these national monitoring sites to monitor background level of POPs-like chemicals, which has been banned for long time and may be well-mixed on a national scale. On another hand, the relocation of intensive thermal industrial sources from urban region to suburban, rural regions and even "remote" regions, as a result of more strengthened government policy,[53] leads to some potential hot spots of UP-PCBs in the rural and remote area. More attention should be paid to investigate the impact of industrial relocation on the health risk of local population.

Supporting Information

Description of sampler and sampling campaign; methods on instrumental analysis; PMF outputs; summary of PCBs concentration; comparison with other studies; spatial-temporal plots of PCB 11; backward trajectory analysis; source contribution for varied sites and for selected Aroclor-PCBs.

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