Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2020, 54, 2163−2171

pubs.acs.org/est

Evidence for Major Contributions of Unintentionally Produced PCBs in the Air of China: Implications for the National Source Inventory

Shizhen Zhao,[†] Kevin C. Jones,[‡] Jun Li,[†] Andrew J. Sweetman,[‡] Xin Liu,[†] Yue Xu,[§] Yan Wang,[∥] Tian Lin,[⊥] Shuduan Mao,[#] Kechang Li,[†] Jiao Tang,[†] and Gan Zhang*[,†]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[‡]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.

[§]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

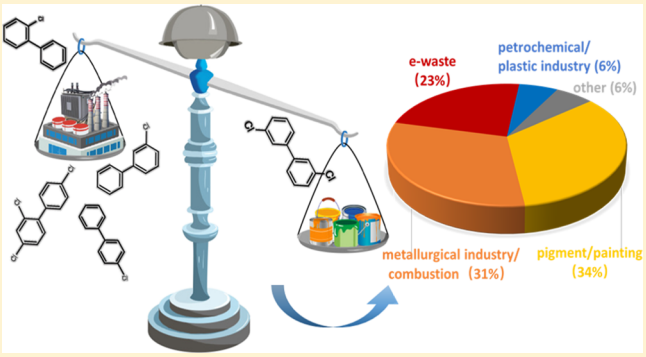
[∥]Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

[⊥]College of Marine Ecology and Environment, Shanghai Ocean University, Shanghai 201306, China

[#]College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

Supporting Information

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 that 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 hypothesized 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 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 sources were 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.



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 1930 and 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 tons 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 PCB (IP-PCB) and unintentionally produced PCB (UP-PCB) 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

Received: October 8, 2019
Revised: December 14, 2019
Accepted: December 18, 2019
Published: December 18, 2019

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

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 because 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, iron ore, and so forth.[15,16] However, this was just a pilot study, based on seven indicator Aroclor-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 dominated by IP-PCBs.[12,17,18] However, several monitoring studies have recently pointed out 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; and (3) discuss the implications for source controls and policy development. 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 nonsource sites. Source sites were close to areas with various industrial activities, namely steel production, coking, petrochemical, dyeing, pigment production, e-waste dismantling, and so forth. Samples from nonsource sites presented general PCB 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 samples 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 are 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 captures 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).[24−26] 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 sets 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 a calibrated model detailed elsewhere.[23] Prior to deployment, PUF-PAS was precleaned 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 °C 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 a rotary evaporator and solvent-exchanged into hexane with a 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. $^{13}C_{12}$-labeled PCBs (PCB 77, 101, 141, 178) were added as internal standards before instrumental analysis. Samples were analyzed on 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 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. Quality assurance and quality control (QA/QC) was conducted using field blanks, procedural blanks, and surrogate-spiked recoveries. Most congeners were not detected in the field blanks and procedural blanks. The average recovery rates of $^{13}C_{12}$ labeled 11, 155, and 206 were 62 ± 13, 71 ± 11, and 76 ± 12%, respectively. The reported concentration data was corrected for blanks and surrogate recovery. The method detection limits (MDLs) were assigned as the total of average values of field blanks and three times their standard deviations. MDLs were calculated as three times the instrumental detection limits (IDLs) and reported if a congener was not detected in field and procedural blanks. IDLs were defined as the amounts of analytes generating a signal-to-noise of 3:1 using the lowest standard concentration, assuming a linear increase of response. The IDLs and MDLs of 209 PCB congeners were in ranges of 0.2−470 pg and 0.002−16 pg/m^3 and are presented in Table S4.

Positive Matrix Factorization. The positive matrix factorization (PMF) method is a model for solving a receptor-only, bilinear unmixed model, which assumes that a measured dataset conforms to a mass-balance of a number of constant source profiles, contributing varied concentrations. Its advantages over principal component analysis are the uncertainty-weighting of each data point and matching the observation of the real-source signature without requiring the dataset orthogonal to each other.[27] Thus, it has been widely used to identify possible sources of PCBs and many other POPs.[27−29]

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

The input data file consisted of receptor concentration (C) and uncertainty (U) matrices. Measured PCB concentrations were entered separately for each deployment at every site. PCB congeners below the limit of detection in >50% of samples were excluded from the PMF model. U for each variable was calculated using C and the MDL as suggested.[27] In order to determine the optimal number of sources, the model was tested for 2−8 factors by running 20 times with a random seed to determine the stability of Q values, a parameter measuring the impact of data points with high-scaled residuals. To evaluate the degree of fitting of PCB congeners for estimating emission profiles, the coefficient of determination (R^2) measuring the goodness of fit between the measured and modeled concentrations was used. Calculated R^2 values were all greater than 0.5 for all congeners. The initial matrix was composed of 121 samples × 93 species, and the results are 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 congener patterns.[30] Selected PCB profiles included unaltered Aroclor mixtures (1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262, and 1268),[31,32] #1 PCB[33] (a commercial product of China), Kanechlor products (KC300, KC400, KC500, KC600) and emissions from incineration of municipal solid waste[5,24] and cement kilns coprocessing solid waste,[25] wood and coal combustion,[34,35] electronic arc furnaces,[16,24] water treatment plants,[36] and various types of pigments.[37,38] 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.[39]

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 concentration. 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 nonsource sites. On average, di-CBs accounted for ∼40% to the $\sum_{209}$ PCBs, mainly because of 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 are the dominant homologue group in China.[11,18]

No statistical difference was observed for the seasonal variation of $\sum_{209}$ PCB concentration shown in Figure S3a−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.[40,41] It has been demonstrated that combustion source profiles were largely dominated by the lower chlorinated congeners, including PCB 1, PCB 2, and PCB 3.[42,43] 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.[40]

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 PCB usage in China.[44] They are also the regions where e-waste recycling sites have been intensively located.[8,45] 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.[46]

Comparison with Other Studies. A significant reduction was observed when comparing the concentrations of 18 commonly measured PCB congeners with other passive air sampling studies conducted in China in 2004,[18] 2005,[47] and 2008[11] (see Table S7), with similar composition dominated by tri-CBs. 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 PCB emission from industrial thermal processes and e-waste sources.[17] The 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. However, there is no relevant regulation and rule on controlling PCB emission from unintentional sources so far.

A comparison of PCB levels with other regions is summarized in Table S8. PCB concentrations in Chinese air are often found to be comparable to regions with intensive historical manufacture and usage of PCBs, such as Japan, Korea, and the USA.[11,18,48] Levels are much higher than observations in King George Island[49] and the Group of Latin American and Caribbean (GRULAC) countries.[22] Several urban sites had high levels of PCBs, for example, Zhengzhou City in winter (1056 pg/m^3), which is comparable to the PCB level in Chicago,[48,50] 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.[46] Another factor possibly leading to the higher level is the inappropriate management and disposal of decommissioned capacitors.[18,51] Finally, UP-PCBs from multiple industrial processes may also contribute to the current levels of PCBs in Chinese ambient air.[9,15]

Spatial Transect. PCB levels measured at various sampling sites were ranked as follows: e-waste sites (3010 ± 2076 pg/m^3) ≫ industrial sites (152 ± 103) > urban sites (124 ± 126

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

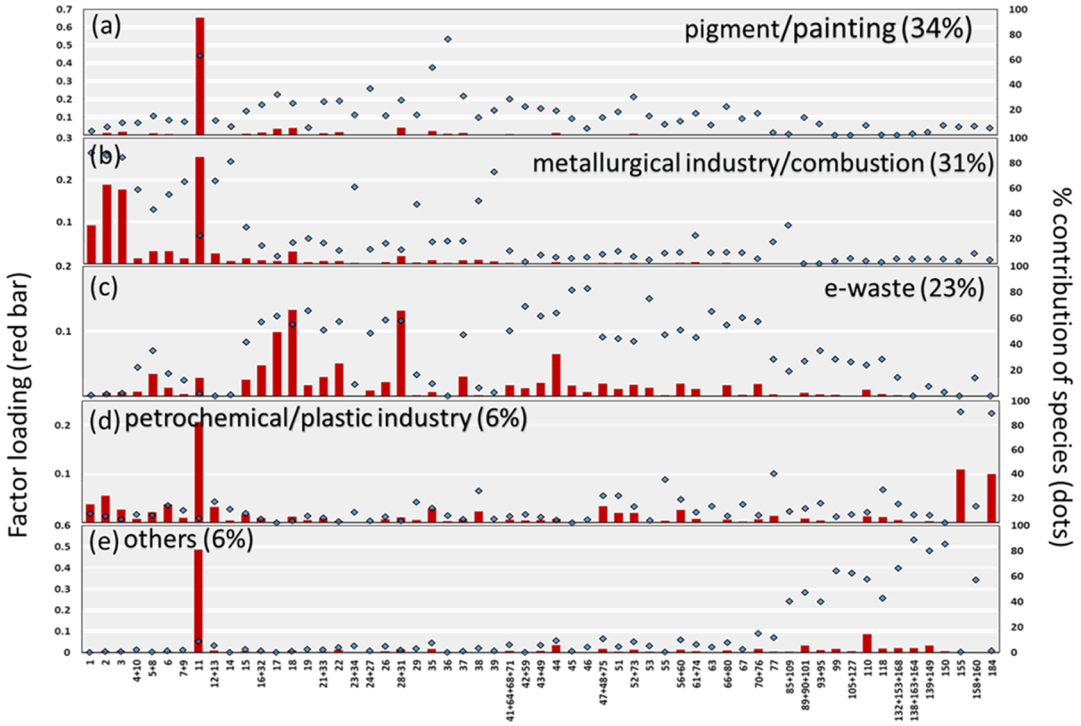


Figure 1. Source profiles gained from PMF analysis of airborne PCBs (a−e). Bars represent factor loading and dots represent contribution (%) of selected species of each source factor.

pg/m^3) > rural sites (87 ± 30 pg/m^3) > remote sites (70 ± 140 pg/m^3). In terms of $\sum_{209}$ PCB concentrations, all types of sites had statistically significant differences (Kruskal−Wallis H test, $p < 0.05$), except for the datasets between rural and urban sites ($p = 0.08$). The decreasing gradient indicated the important contribution of PCBs from e-waste and potential sources relate to multiple industrial activities.[15] However, the decreasing gradient was less pronounced than previously observed differences, which have ranged over 1−2 orders of magnitude.[52,53] This may be because of the relocation of various industrial activities from urban areas to semirural/rural areas, driven by the Chinese government[54] and an implementation gap of environmental policies in rural areas.[55] Another possible reason may be reduced usage of PCBs in urban areas of China, compared to some other countries, such as in building materials used in the US, Norway, and elsewhere.[56]

It is interesting to note that penta and hexa-CBs contributed most (~14 and ~9%) in remote sites as shown in Figure S3d. Normally, low-chlorinated PCBs with relatively high volatility are expected to move to remote regions more efficiently, whereas higher chlorinated PCBs with lower volatility tend to remain in the surface compartments within, or in the vicinity of, source regions.[53] The spatial distribution of PCB homologues in industrial, urban, and rural area satisfied this expectation. The sum contribution of penta- and hexa-CBs was ranked as remote sites > e-waste sites > industrial sites > urban sites > rural sites. The main penta-CBs in remote sites were PCB 125 and PCB 111/117, which were detected in commercial products of KC 500 and KC 400, and flue gas from incinerators in similar composition.[5] PCB 130 and PCB 162 were the main contributors of hexa-CBs, making no or very limited contributions to commercial products. These congeners are not routinely measured in previous studies. However, their levels and contributions were comparable to those in source sites, such as petrochemical and steel industry. The reason for contrasting from typical congener profiles dominated by tri-CBs is that the full set of 209 congeners measured here, highlighting the roles of penta- and hexa-CBs, which were potentially ignored before. Although most remote sites were selected from the network of national background air-monitoring sites, these sites were located and designed to monitor standard air quality compositions, such as $PM_{2.5}$ and NO_x, not for POPs. These "remote" sites dominated by penta and hexa-CBs were 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. In reality, these sites might be affected by local hidden stockpiles, potential illegal e-waste dismantling, and industrial sources, which have been relocated following the much-strengthened air pollution control policy in Chinese cities. They should not really be considered as "remote" sites for POPs.

Analysis of Source Factors. 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 1a) 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.[57] PCB 11 is the dominant congener in azo-pigments, as discussed previously.[43] This estimated profile (Figure 1a) had the highest similarity with samples from dyeing and pigment sources (cos θ = 0.96−0.99). Therefore, the first factor should represent volatilization from paints/pigments and/or wastewater receiving paint/pigment industries. However, all factors (Figure 1a,b,d,e) except for e-waste sources (Figure 1c) 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.

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

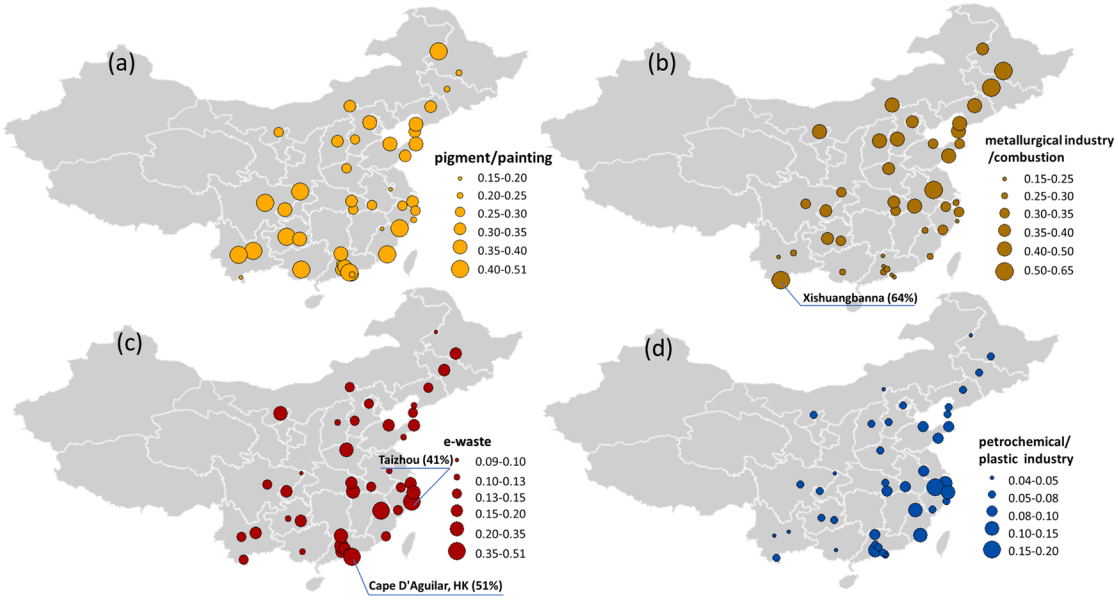


Figure 2. Normalized contributions of the PMF source factors for the autumn deployment (Oct to Dec, 2016). This figure was modified from outputs of ArcGIS 10.3 software, and the base map of China was from http://www.arcgisonline.cn.

The second factor (Figure 1b) 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.[42] As a result, the second factor was considered as the combined source of metallurgic industry and combustion.

The third factor (Figure 1c) 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%), and 18 (55%). Other typical Aroclor congeners, such as PCB 37, 44, 49, and 66 all greatly contributed to the species sum, ranging from 42 to 82%. This congener pattern is consistent with the commercial products, dominated by tri-CBs, similar to the composition of Aroclor 1248 (the US), KC400 (Japan), and #1 PCB (China). However, its similarity with these original and volatilized 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 1d), which only explained 6% of the total PCB masses, was also characterized by relatively high factor loadings of PCB 11, 155, and 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 industries in Shanghai and Dongying of Shandong Province (cos θ = 0.86−0.93) and source samples from plastic manufacture in Yuyao of Zhejiang Province (cos θ = 0.81−0.92). Yuyao owns the largest center of manufacturing and plastic production in China.[58] This factor was therefore regarded as the combined source from petrochemical and plastic industries. PCB 155 and 184 could be considered as potential markers of these two sources, requiring further confirmation.

Lastly, the fifth factor (Figure 1e) also contributed 6% to the total PCB masses. However, its congener pattern did not match well with source profiles from this study and the literature. This factor also had a high loading of PCB 11, and several Aroclor PCBs, like PCB 101, 110, 118, 138, and 139/149, contributing 47−88% to the species sum. These congeners are often dominant in Aroclor 1260 and equivalent commercial products. Shang et al. also observed PCB 101, 138, and 153 in yellow pigment samples in China.[59] Thus, we speculate that this factor could be from combined sources of pigment and Aroclor 1260 or its equivalents. However, labeled as "other" in Figure 1e, this needs to be investigated further and will not be discussed in detail here.

Source Apportionment of PCBs Across China. 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 2a) were relatively well-mixed across China, with a contribution ranging from 15 to 51%. Southern China is more strongly affected than the northern parts, which might be following a similar trend as PCB 11.[60] Warmer temperatures increase volatilization from 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 2b. 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 S6b), these sites mainly received air masses originating from Laos (61%) and Myanmar (39%),

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

regions with intensive opening burning of forests, crop residues, grassland, and savanna.[61] 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.[62]

E-waste sources (Figure 2c) 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

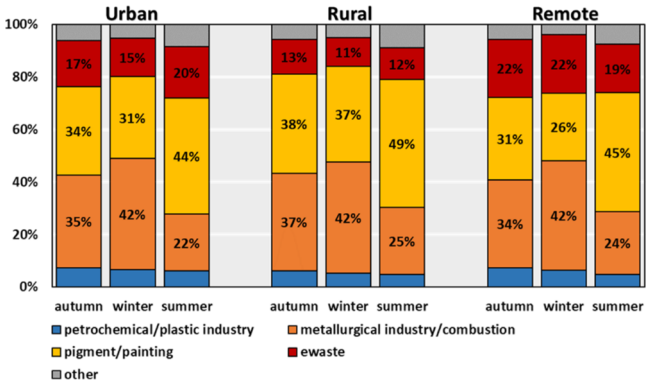


Figure 3. Relative contribution of identified source to the urban, rural, and remote sites in three deployments.

Kong was estimated to have the highest loading of e-waste sources (51%), even higher than the urban site (41%) of Taizhou, 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 LRAT. According to the backward trajectory analysis (Figure S6a), this sampling site mainly received air from eastern China (49%) and Taiwan (52%) during sampling in autumn of 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 was in the eastern regions of the country.[44]

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%), and 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 Dongying of Shandong Province and Shanghai. All these sites shared relatively high contributions (12−14%) from the emission of petrochemical industry. This spatial trend also matched well with the geographical distribution of petrochemical industry in China, which is most intensive in 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 because of 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 modeling result, indicating that e-waste still plays an important role in the current PCBs loading in the air of China.[9] Meanwhile, a substance-specific emission pattern was observed, as shown in Figure S7. For instance, PCB 28 originated mainly from 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%). Because 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 PCB emissions.

Comments on Pigment-Relevant Congeners. PCB 11 is the most important pigment-relevant congener.[19] Its spatial distribution and seasonal variation are shown in Figures S4 and 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.[49] The concentration of PCB-11 averaged 35 ± 33 pg/m^3 (<MDL-249 pg/m^3) and was higher in summer because of the relatively high volatility of di-CBs and suggested volatilization from surfaces to which it had been applied.[63] The ranking of PCB 11 levels in the various categories of sampling sites is in the 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[21,60] 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.[64] Other PCBs associated with pigments include PCB 35 and PCB 77 together with PCB 11 in azo-type pigments and PCB 209, 206, 207, and 208 in phthalocyanine-type pigments.[43] 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.[43] China has become the largest manufacturer of organic pigments in the world.[59] According to the report of the China Dyestuffs Industry Association (CDIA),[65] azo-type pigments and phthalocyanine pigments 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,[59] UK, Japan, the Netherlands, and so forth.[37,38] Chinese products contain a wider range of PCB 11 and other congeners, potentially leading to even higher PCB emissions.[59] 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 gaps for PCB emission sources are inevitable, such as the source profile of sewage treatment plants and indoor air. Our preliminary strategy is to

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

take advantage of the existing literature to close these gaps. However, reports of comparative patterns for sources are limited, which make pattern matching for fingerprint 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.

Passive air sampler monitoring studies often meet several common challenges.[66] First, because most PUF-PAS sets were installed by volunteers, uncertainty could exist in the placement of samples. Several abnormally high concentrations may be potentially caused by improper placement near ventilation systems with potential indoor sources. Second, PUF-PAS captured both particle and gas phases simultaneously.[23] Whilst, most studies used active samplers to obtain emission profiles, mostly focused on the particulate phase and/or merely considered the gas phase with selected congeners.[5,24,26] This could cause big challenges for congener profile matching between the source and nonsource PCB profiles. Hence, we considered that the emission profile consistently gained by PUF-PAS would have better comparability than that from the literature data.

More than four decades have passed since the international ban on PCB manufacture and use, but China still receives ongoing emissions of PCBs from multiple sources, particularly from unintentional sources (UP-PCBs). Our findings suggest that the UP-PCBs have become the dominant source across China, accounting for ∼65% to the total emissions. Volatilization from pigment/painting sources and metallurgical industry/combustion are shown here to be the most important sources nationally. This raises new issues for regulators and policy makers to develop relevant UP-PCB emission inventories and establish additional effective strategies to control unintentionally-produced sources. Meanwhile, the contribution of e-waste as a PCB source cannot be neglected, particularly for Aroclor-PCBs, like indicator PCBs (>50%). It is challenging to differentiate this source as either intentional or unintentional because of unknown mechanisms of PCB origin. If it comes from the de novo synthesis of e-waste dismantling activity, it is an unintentional source. Previous studies evaluating the mass fluxes of organic contaminants released during incomplete incineration concluded that incinerators could be sinks or sources, depending on the waste feed and combustion temperature.[26,67] 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 remote sites has shifted under the impact of human activities, as demonstrated in our study. We used 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 were assumed to be far from human activities, unexpectedly high concentrations of PCBs were observed, (e.g., in Cape D'Aguilar in Hongkong and Hengxi in Zhejiang province). These sites were originally designed to monitor regulated air pollutants instead of POPs. As a result, using their PCB levels may cause potential bias, and it is worthwhile to review the applicability of these national monitoring sites to monitor the background level of POPs-like chemicals, which has been banned for long time and may be well-mixed on a national scale. On the other hand, the relocation of intensive thermal industrial sources from urban to suburban, rural, and even "remote" regions, as a result of strengthened government policy,[54] leads to some potential hot spots of UP-PCBs in the rural and "remote" areas. More attention should be paid to investigate the impact of industrial relocation on the health risk of local population.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b06051.

Description of used samplers 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; and source contribution for varied sites and for selected Aroclor-PCBs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhanggan@gig.ac.cn. Phone: +86 (0) 8529 0805.

ORCID

Kevin C. Jones: 0000-0001-7108-9776
Jun Li: 0000-0002-3637-1642
Andrew J. Sweetman: 0000-0001-9230-8536
Yan Wang: 0000-0003-0899-7899
Gan Zhang: 0000-0002-9010-8140

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2017YFC0212004), Local Innovative Scientific Research Team Project of Guangdong "Pearl River Talents Plan" (2017BT01Z134), and China Postdoctoral Science Foundation (2017M622814, 2018T110898). Thanks to Li Jiangtao on helping sample pretreatment. We also greatly thank all the local volunteers for helping setting up and retrieving passive air samplers.

■ REFERENCES

(1) UNEP. *The Stockholm Convention on Persistent Organic Pollutants*; United Nations Environmental Programme, 2001.

(2) Jones, K. C.; de Voogt, P. Persistent organic pollutants (POPs): state of the science. *Environ. Pollut.* **1999**, *100*, 209−221.

(3) Desforges, J.-P.; Hall, A.; McConnell, B.; Rosing-Asvid, A.; Barber, J. L.; Brownlow, A.; De Guise, S.; Eulaers, I.; Jepson, P. D.; Letcher, R. J.; Levin, M.; Ross, P. S.; Samarra, F.; Víkingson, G.; Sonne, C.; Dietz, R. Predicting global killer whale population collapse from PCB pollution. *Science* **2018**, *361*, 1373.

(4) Breivik, K.; Sweetman, A.; Pacyna, J.; Jones, K. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach2. Emissions. *Sci. Total Environ.* **2002**, *290*, 199−224.

(5) Kim, K. S.; Hirai, Y.; Kato, M.; Urano, K.; Masunaga, S. Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). *Chemosphere* **2004**, *55*, 539−553.

(6) Xu, Y.; Tian, C.; Wang, X.; Ma, J.; Tang, J.; Chen, Y.; Li, J.; Zhang, G. An improved inventory of polychlorinated biphenyls in China: A case study on PCB-153. *Atmos. Environ.* **2018**, *183*, 40−48.

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

(7) Mao, S.; Zhang, G.; Zhao, S.; Li, J.; Liu, X.; Cheng, Z.; Zhong, G.; Malik, R. N.; Liu, X. High Abundance of Unintentionally Produced Tetrachlorobiphenyls (PCB47/48/75, 51, and 68) in the Atmosphere at a Regional Background Site in East China. *Environ. Sci. Technol.* **2019**, *53*, 3464−3470.
(8) Qiao, L.; Zheng, X.-B.; Zheng, J.; Chen, S.-J.; Zhong, C.-Q.; Chen, J.-H.; Yang, Z.-Y.; Mai, B.-X. Legacy and Currently Used Organic Contaminants in Human Hair and Hand Wipes of Female E-Waste Dismantling Workers and Workplace Dust in South China. *Environ. Sci. Technol.* **2019**, *53*, 2820−2829.
(9) Zhao, S.; Breivik, K.; Liu, G.; Zheng, M.; Jones, K. C.; Sweetman, A. J. Long-Term Temporal Trends of Polychlorinated Biphenyls and Their Controlling Sources in China. *Environ. Sci. Technol.* **2017**, *51*, 2838−2845.
(10) Breivik, K.; Armitage, J. M.; Wania, F.; Jones, K. C. Tracking the Global Generation and Exports of e-Waste. Do Existing Estimates Add up? *Environ. Sci. Technol.* **2014**, *48*, 8735−8743.
(11) Hogarh, J. N.; Seike, N.; Kobara, Y.; Habib, A.; Nam, J.-J.; Lee, J.-S.; Li, Q.; Liu, X.; Li, J.; Zhang, G.; Masunaga, S. Passive air monitoring of PCBs and PCNs across East Asia: A comprehensive congener evaluation for source characterization. *Chemosphere* **2012**, *86*, 718−726.
(12) Hung, H.; Katsoyiannis, A. A.; Brorström-Lundén, E.; Olafsdottir, K.; Aas, W.; Breivik, K.; Bohlin-Nizzetto, P.; Sigurdsson, A.; Hakola, H.; Bossi, R.; Skov, H.; Sverko, E.; Barresi, E.; Fellin, P.; Wilson, S. Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.* **2016**, *217*, 52−61.
(13) Sun, P.; Basu, I.; Blanchard, P.; Brice, K. A.; Hites, R. A. Temporal and Spatial Trends of Atmospheric Polychlorinated Biphenyl Concentrations near the Great Lakes. *Environ. Sci. Technol.* **2007**, *41*, 1131−1136.
(14) Graf, C.; Katsoyiannis, A.; Jones, K. C.; Sweetman, A. J. The TOMPs ambient air monitoring network - Continuous data on UK air quality for over 20 years. *Environ. Pollut.* **2016**, *217*, 42−51.
(15) Liu, G.; Zheng, M.; Jiang, X.; Jin, R.; Zhao, Y.; Zhan, J. Insights into the emission reductions of multiple unintentional persistent organic pollutants from industrial activities. *Chemosphere* **2016**, *144*, 420−424.
(16) Odabasi, M.; Bayram, A.; Elbir, T.; Seyfioglu, R.; Dumanoglu, Y.; Bozlaker, A.; Demircioglu, H.; Altiok, H.; Yatkin, S.; Cetin, B. Electric Arc Furnaces for Steel-Making: Hot Spots for Persistent Organic Pollutants. *Environ. Sci. Technol.* **2009**, *43*, 5205−5211.
(17) Wu, Z.; Lin, T.; Li, A.; Zhou, S.; He, H.; Guo, J.; Hu, L.; Li, Y.; Guo, Z. Sedimentary records of polychlorinated biphenyls in the East China Marginal Seas and Great Lakes: Significance of recent rise of emissions in China and environmental implications. *Environ. Pollut.* **2019**, *254*, 112972.
(18) Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive Air Sampling of Polychlorinated Biphenyls, Organochlorine Compounds, and Polybrominated Diphenyl Ethers Across Asia. *Environ. Sci. Technol.* **2005**, *39*, 8638−8645.
(19) Vorkamp, K. An overlooked environmental issue? A review of the inadvertent formation of PCB-11 and other PCB congeners and their occurrence in consumer products and in the environment. *Sci. Total Environ.* **2016**, *541*, 1463−1476.
(20) Bartlett, P. W.; Isaksson, E.; Hermanson, M. H. 'New' unintentionally produced PCBs in the Arctic. *Emerging Contam.* **2019**, *5*, 9−14.
(21) Hu, D.; Martinez, A.; Hornbuckle, K. C. Discovery of Non-Aroclor PCB (3,3′-Dichlorobiphenyl) in Chicago Air. *Environ. Sci. Technol.* **2008**, *42*, 7873−7877.
(22) Rauert, C.; Harner, T.; Schuster, J. K.; Eng, A.; Fillmann, G.; Castillo, L. E.; Fentanes, O.; Ibarra, M. V.; Miglioranza, K. S. B.; Rivadeneira, I. M.; Pozo, K.; Aristizábal Zuluaga, B. H. Air monitoring of new and legacy POPs in the Group of Latin America and Caribbean (GRULAC) region. *Environ. Pollut.* **2018**, *243*, 1252−1262.
(23) Herkert, N. J.; Spak, S. N.; Smith, A.; Schuster, J. K.; Harner, T.; Martinez, A.; Hornbuckle, K. C. Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network. *Environ. Sci.: Processes Impacts* **2018**, *20*, 210−219.
(24) Liu, G.; Zheng, M.; Cai, M.; Nie, Z.; Zhang, B.; Liu, W.; Du, B.; Dong, S.; Hu, J.; Xiao, K. Atmospheric emission of polychlorinated biphenyls from multiple industrial thermal processes. *Chemosphere* **2013**, *90*, 2453−2460.
(25) Jin, R.; Zhan, J.; Liu, G.; Zhao, Y.; Zheng, M.; Yang, L.; Wang, M. Profiles of polychlorinated biphenyls (PCBs) in cement kilns co-processing solid waste. *Chemosphere* **2017**, *174*, 165−172.
(26) Grosso, M.; Biganzoli, L.; Rigamonti, L.; Cernuschi, S.; Giugliano, M.; Poluzzi, V.; Biancolini, V. Experimental evaluation of PCDD/Fs and PCBs release and mass balance of a WTE plant. *Chemosphere* **2012**, *86*, 293−299.
(27) Aydin, Y. M.; Kara, M.; Dumanoglu, Y.; Odabasi, M.; Elbir, T. Source apportionment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in ambient air of an industrial region in Turkey. *Atmos. Environ.* **2014**, *97*, 271−285.
(28) Praipipat, P.; Meng, Q.; Miskewitz, R. J.; Rodenburg, L. A. Source Apportionment of Atmospheric Polychlorinated Biphenyls in New Jersey 1997-2011. *Environ. Sci. Technol.* **2017**, *51*, 1195−1202.
(29) Du, S.; Belton, T. J.; Rodenburg, L. A. Source apportionment of polychlorinated biphenyls in the tidal Delaware River. *Environ. Sci. Technol.* **2008**, *42*, 4044−4051.
(30) Rodenburg, L. A.; Du, S.; Xiao, B.; Fennell, D. E. Source apportionment of polychlorinated biphenyls in the New York/New Jersey Harbor. *Chemosphere* **2011**, *83*, 792−798.
(31) Frame, G. M.; Cochran, J. W.; Bøwadt, S. S. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chromatogr.* **1996**, *19*, 657−668.
(32) Wyrzykowska, B.; Bochentin, I.; Hanari, N.; Orlikowska, A.; Falandysz, J.; Yuichi, H.; Yamashita, N. Source determination of highly chlorinated biphenyl isomers in pine needles - Comparison to several PCB preparations. *Environ. Pollut.* **2006**, *143*, 46−59.
(33) Huang, J.; Matsumura, T.; Yu, G.; Deng, S.; Yamauchi, M.; Yamazaki, N.; Weber, R. Determination of PCBs, PCDDs and PCDFs in insulating oil samples from stored Chinese electrical capacitors by HRGC/HRMS. *Chemosphere* **2011**, *85*, 239−246.
(34) Lee, R. G. M.; Coleman, P.; Jones, J. L.; Jones, K. C.; Lohmann, R. Emission Factors and Importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10from the Domestic Burning of Coal and Wood in the U.K. *Environ. Sci. Technol.* **2005**, *39*, 1436−1447.
(35) Gullett, B. K.; Touati, A.; Hays, M. D. PCDD/F, PCB, HxCBz, PAH, and PM Emission Factors for Fireplace and Woodstove Combustion in the San Francisco Bay Region. *Environ. Sci. Technol.* **2003**, *37*, 1758−1765.
(36) Yao, M.; Li, Z.; Zhang, X.; Lei, L. Polychlorinated Biphenyls in the Centralized Wastewater Treatment Plant in a Chemical Industry Zone: Source, Distribution, and Removal. *J. Chem.* **2014**, *2014*, 1.
(37) Anezaki, K.; Nakano, T. Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments. *Environ. Sci. Pollut. Res.* **2014**, *21*, 998−1009.
(38) Anezaki, K.; Kannan, N.; Nakano, T. Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments. *Environ. Sci. Pollut. Res.* **2015**, *22*, 14478−14488.
(39) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. Improving Data Quality for Environmental Fate Models: A Least-Squares Adjustment Procedure for Harmonizing Physicochemical Properties of Organic Compounds. *Environ. Sci. Technol.* **2005**, *39*, 8434−8441.
(40) Dumanoglu, Y.; Gaga, E. O.; Gungormus, E.; Sofuoglu, S. C.; Odabasi, M. Spatial and seasonal variations, sources, air-soil exchange, and carcinogenic risk assessment for PAHs and PCBs in air and soil of Kutahya, Turkey, the province of thermal power plants. *Sci. Total Environ.* **2017**, *580*, 920−935.

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171

(41) Lohmann, R.; Northcott, G. L.; Jones, K. C. Assessing the Contribution of Diffuse Domestic Burning as a Source of PCDD/Fs, PCBs, and PAHs to the U.K. Atmosphere. *Environ. Sci. Technol.* **2000**, *34*, 2892−2899.
(42) Jansson, S.; Lundin, L.; Grabic, R. Characterisation and fingerprinting of PCBs in flue gas and ash from waste incineration and in technical mixtures. *Chemosphere* **2011**, *85*, 509−515.
(43) Anezaki, K.; Nakano, T.; Kashiwagi, N. Estimation of Polychlorinated Biphenyl Sources in Industrial Port Sediments Using a Bayesian Semifactor Model Considering Unidentified Sources. *Environ. Sci. Technol.* **2016**, *50*, 765−771.
(44) Cui, S.; Fu, Q.; Li, Y.-F.; Li, T.-x.; Liu, D.; Dong, W.-c.; Wang, M.; Li, K.-y. Spatial-temporal variations, possible sources and soil-air exchange of polychlorinated biphenyls in urban environments in China. *RSC Adv.* **2017**, *7*, 14797−14804.
(45) Zhang, K.; Schnoor, J. L.; Zeng, E. Y. E-Waste Recycling: Where Does It Go from Here? *Environ. Sci. Technol.* **2012**, *46*, 10861−10867.
(46) Liu, R.; Ma, S.; Li, G.; Yu, Y.; An, T. Comparing pollution patterns and human exposure to atmospheric PBDEs and PCBs emitted from different e-waste dismantling processes. *J. Hazard. Mater.* **2019**, *369*, 142−149.
(47) Zhang, Z.; Liu, L.; Li, Y.-F.; Wang, D.; Jia, H.; Harner, T.; Sverko, E.; Wan, X.; Xu, D.; Ren, N.; Ma, J.; Pozo, K. Analysis of Polychlorinated Biphenyls in Concurrently Sampled Chinese Air and Surface Soil. *Environ. Sci. Technol.* **2008**, *42*, 6514−6518.
(48) Hu, D.; Lehmler, H.-J.; Martinez, A.; Wang, K.; Hornbuckle, K. C. Atmospheric PCB congeners across Chicago. *Atmos. Environ.* **2010**, *44*, 1550−1557.
(49) Wang, P.; Li, Y.; Zhang, Q.; Yang, Q.; Zhang, L.; Liu, F.; Fu, J.; Meng, W.; Wang, D.; Sun, H.; Zheng, S.; Hao, Y.; Liang, Y.; Jiang, G. Three-year monitoring of atmospheric PCBs and PBDEs at the Chinese Great Wall Station, West Antarctica: Levels, chiral signature, environmental behaviors and source implication. *Atmos. Environ.* **2017**, *150*, 407−416.
(50) Persoon, C.; Peters, T. M.; Kumar, N.; Hornbuckle, K. C. Spatial Distribution of Airborne Polychlorinated Biphenyls in Cleveland, Ohio and Chicago, Illinois. *Environ. Sci. Technol.* **2010**, *44*, 2797−2802.
(51) Weber, R.; Schlumpf, M.; Nakano, T.; Vijgen, J. The need for better management and control of POPs stockpiles. *Environ. Sci. Pollut. Res.* **2015**, *22*, 14385−14390.
(52) Melymuk, L.; Robson, M.; Helm, P. A.; Diamond, M. L. PCBs, PBDEs, and PAHs in Toronto air: Spatial and seasonal trends and implications for contaminant transport. *Sci. Total Environ.* **2012**, *429*, 272−280.
(53) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using Passive Air Samplers To Assess Urban−Rural Trends for Persistent Organic Pollutants. 1. Polychlorinated Biphenyls and Organochlorine Pesticides. *Environ. Sci. Technol.* **2004**, *38*, 4474−4483.
(54) Wang, Y.; Liu, Y.; Li, Y.; Li, T. The spatio-temporal patterns of urban-rural development transformation in China since 1990. *Habitat Int.* **2016**, *53*, 178−187.
(55) Wang, M.; Webber, M.; Finlayson, B.; Barnett, J. Rural industries and water pollution in China. *J. Environ. Manage.* **2008**, *86*, 648−659.
(56) Marek, R. F.; Thorne, P. S.; Herkert, N. J.; Awad, A. M.; Hornbuckle, K. C. Airborne PCBs and OH-PCBs Inside and Outside Urban and Rural U.S. Schools. *Environ. Sci. Technol.* **2017**, *51*, 7853−7860.
(57) Khairy, M.; Muir, D.; Teixeira, C.; Lohmann, R. Spatial Distribution, Air-Water Fugacity Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes Basin. *Environ. Sci. Technol.* **2015**, *49*, 13787−13797.
(58) Sun, Z.; Perry, M. The role of trading cities in the development of chinese business cluster. *Int. Bus. Res.* **2009**, *1*, 69−81.
(59) Shang, H.; Li, Y.; Wang, T.; Wang, P.; Zhang, H.; Zhang, Q.; Jiang, G. The presence of polychlorinated biphenyls in yellow pigment products in China with emphasis on 3,3′-dichlorobiphenyl (PCB 11). *Chemosphere* **2014**, *98*, 44−50.
(60) Basu, I.; Arnold, K. A.; Venier, M.; Hites, R. A. Partial pressures of PCB-11 in air from several Great Lakes sites. *Environ. Sci. Technol.* **2009**, *43*, 6488−6492.
(61) Streets, D. G.; Yarber, K. F.; Woo, J.-H.; Carmichael, G. R. Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions. *Global Biogeochem. Cycles* **2003**, *17*, 1099.
(62) Liu, D.; Lin, T.; Syed, J. H.; Cheng, Z.; Xu, Y.; Li, K.; Zhang, G.; Li, J. Concentration, source identification, and exposure risk assessment of PM2.5-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese cities. *Sci. Rep.* **2017**, *7*, 10398.
(63) Hu, D.; Hornbuckle, K. C. Inadvertent Polychlorinated Biphenyls in Commercial Paint Pigments. *Environ. Sci. Technol.* **2010**, *44*, 2822−2827.
(64) Weizhe, H.; Yingming, L.; Linnan, Z.; Jia, B.; Pu, W.; Chaofei, Z.; Qinghua, Z. Levels and distribution of polychlorinated biphenyls in the atmosphere of Beijing. *Environ. Chem.* **2015**, *34*, 410−416.
(65) *Chinese Dyestuff Industry-Present Situation and Development* (in Chinese); CDIA, 2018.
(66) Rauert, C.; Harner, T.; Schuster, J. K.; Eng, A.; Fillmann, G.; Castillo, L. E.; Fentanes, O.; Villa Ibarra, M.; Miglioranza, K. S. B.; Moreno Rivadeneira, I.; Pozo, K.; Aristizábal Zuluaga, B. H. Atmospheric Concentrations of New Persistent Organic Pollutants and Emerging Chemicals of Concern in the Group of Latin America and Caribbean (GRULAC) Region. *Environ. Sci. Technol.* **2018**, *52*, 7240−7249.
(67) Van Caneghem, J.; Block, C.; Van Brecht, A.; Wauters, G.; Vandecasteele, C. Mass balance for POPs in hazardous and municipal solid waste incinerators. *Chemosphere* **2010**, *78*, 701−708.

DOI: 10.1021/acs.est.9b06051
Environ. Sci. Technol. 2020, 54, 2163−2171