

High Abundance of Unintentionally Produced Tetrachlorobiphenyls (PCB47/48/75, 51, and 68) in the Atmosphere at a Regional Background Site in East China

Shuduan Mao,^{†,‡} Gan Zhang,^{*,†} Shizhen Zhao,[†] Jun Li,[†] Xin Liu,[†] Zhineng Cheng,[†] Guangcai Zhong,[†] Riffat Naseem Malik,[§] and Xiang Liu[†]

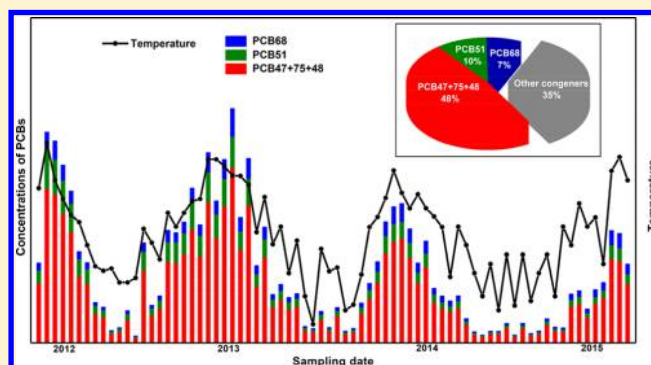
[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

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

[§]Environmental Biology and Ecotoxicology Laboratory, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan

Supporting Information

ABSTRACT: Although polychlorinated biphenyls (PCBs) have been banned for several decades, they are still detected with elevated levels due to their unintentional production from combustion and industrial thermal processes (UP-PCBs). To investigate the composition and current levels of UP-PCBs and understand which sources are controlling PCB burdens in ambient atmosphere, air samples were collected from August 2012 to August 2015 at a background site in east China. An unexpected high abundance of PCB47+48+75 was observed to be the predominant congener with an average concentration of 786 ± 637 pg/m³. It accounted for $48 \pm 16\%$ of Σ PCBs, followed by PCB51 ($10 \pm 4\%$), PCB11 ($8 \pm 6\%$), and PCB68 ($7 \pm 3\%$). Seasonal variations with high levels in summer and lowest levels in winter were observed for PCB47+48+75, 51, and 68. These tetrachlorobiphenyl congeners were strongly correlated with temperature ($r^2 > 0.7$), suggesting the control of temperature-dependent volatilization processes from contaminated surfaces. The decreased occurrence of PCB47+48+75, 51, and 68 in commercial products and their negative correlations ($|r| < 0.35$) with polycyclic aromatic hydrocarbon (PAHs) and weak correlation with other PCB congeners suggested unique unintentional sources that differ from combustion and industrial thermal processes or pigment, such as the use of polymer sealant, for PCB47+48+75, 51, and 68 in the ambient air.



INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous contaminants of great concern due to their toxicity, persistence, bioaccumulation, and long-range transport potential.¹ They are among the dirty dozen persistent organic pollutants (POPs) initially regulated by the Stockholm Convention (SC). There are three major sources for PCBs in the environment: (1) historical emissions from commercial PCB-containing products which were intentionally produced and used in industry (referred to as IP-PCBs), (2) unintentionally produced emissions from combustion and thermal processes (referred to as UP-PCBs), and (3) emissions from e-waste dismantling and recycling activities (referred to as EW-PCBs).^{2,3} IP-PCBs have shown a constantly decreasing trend since the ban on production and use of commercial products.^{4–6} Additionally, many old open burning sites for e-waste recycling activities have been abandoned due to increasingly stringent environmental laws and regulations in recent years.⁷ However, PCBs can still be detected with elevated or stable levels in the

environment due to emissions of UP-PCBs,^{8–12} which likely become more important. On the basis of emission factors of PCBs from several industrial thermal processes in China, Cui et al. estimated that historical emissions of UP-indicator PCBs in China were 8.56 t from 1965 to 2010, which were just 14 times smaller than IP-indicator PCBs emissions.² Zhao et al. predicted that unintentional sources will become a main contributor of PCB contamination in China by 2035.³

To investigate the current compositions and levels of UP-PCBs and understand which sources are controlling PCB burdens in ambient atmosphere, air samples were collected from August 2012 to August 2015 at a background site in east China. Surprisingly, PCB47+48+75, 51, and 68 were observed to be predominant in PCBs with incredibly high levels in

Received: January 9, 2019

Revised: February 27, 2019

Accepted: March 7, 2019

Published: March 7, 2019

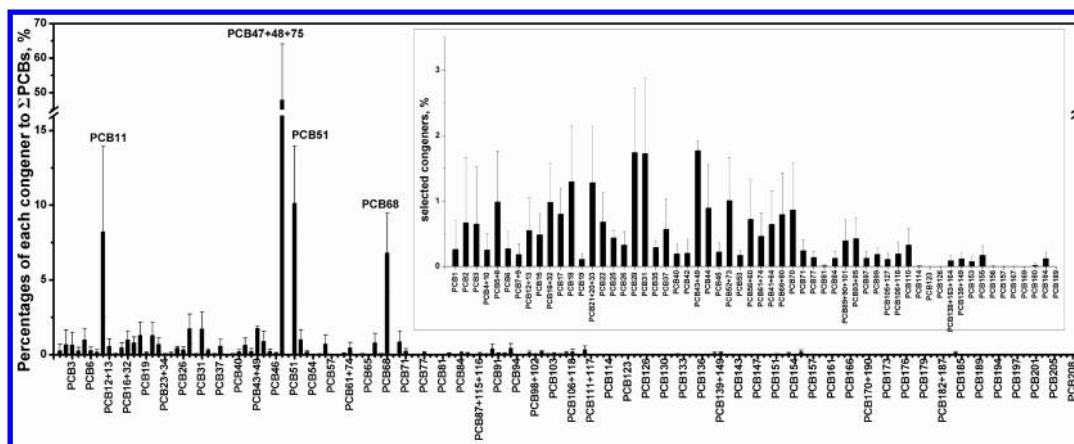


Figure 1. PCB congener profile of air samples at NAEO.

ambient air. However, the total mass fraction of these congeners were presented at low levels in commercial PCB products, suggesting the contribution of unintentional sources. Here, we report the concentrations of PCB47+48+75, 51, and 68 in the atmosphere, analyze their seasonal trends, and discuss their potential sources.

MATERIALS AND METHODS

Sampling Site. The sampling site, Ningbo Atmospheric Environment Observatory (NAEO, 29°40′48.73″N, 121°37′4.41″E, 550 m ASL), is a regional background site located on a rural mountaintop in Ningbo, Zhejiang Province, in east China, surrounded by forest and hills with an elevation less than 600 m. The sampling site has a subtropical monsoon climate that can be influenced by air masses transported from the Southeast Asia in summer and by those from north China in winter. It is a key site on the outlet transport route for aerosols from the Chinese continent to the Pacific Ocean. The sampling site has been described in a previous report.¹³

Sample Collection. Successive 24 h air samples were collected once a week at NAEO by a high-volume air sampler operating at 300 L/min. The sampler was fitted with polyurethane foam plugs (PUFs) (6.5 cm diameter, 7.5 cm length) for gas samples and with quartz microfiber filters (QFFs) (grade GF/A, 20.3 × 12.7 cm; Ahlstrom Munktell, Falun, Sweden) for aerosol particle samples. The PUFs were extracted with dichloromethane/acetone (40:3 v/v) for 48 h, and the QFFs were baked at 450 °C for 6 h before sampling and then sealed and stored at −20 °C after collection. Only 74 PUF samples, i.e., 1 from each fortnight from August 2012 to August 2015, were used in this study.

Sample Pretreatment and Analysis. Details of sample treatments and analytical methods can be found in the Supporting Information. Briefly, each PUF sample was spiked with PCB30, PCB198, and PCB209 as surrogates and extracted in a Soxhlet apparatus for 24 h with dichloromethane (DCM). The extracts were further purified on a multilayer acidic silica gel column. An Agilent 7890/7000 GC-MS/MS with a CP-Sil 8 CB column (50 m × 0.25 mm × 0.12 μm; Agilent, Santa Clara, CA, U.S.A.) was used and operated under an electron ion (EI) source (−70 eV) in a multiple reaction monitoring (MRM) mode for the measurement of all 209 PCB congeners. The GC oven temperature was set at 100 °C for 0.5 min, 100–160 °C at 10 °C/min, 160–250 °C at 3 °C/min, 250–295 °C at 10 °C/min, and a final hold for 10 min. A

splitless injection mode with an injection volume of 1 μL was used. The 209 congener analyses yielded 168 peaks (coelvents were counted as multiple congeners). An Agilent 7890/5975 gas GC-MS with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent, Santa Clara, CA, U.S.A.) was used and operated under an EI source (−70 eV) in a selective ion monitoring (SIM) mode for the measurement 15 polycyclic aromatic hydrocarbons (PAHs).

Quality Control and Quality Assurance (QC/QA). Details are given in the Supporting Information. Briefly, field and laboratory blank PUFs were analyzed. Among the 168 single or coeluting congeners, more than 45% of them were not detected in the blanks. The average blank values for the detectable congeners were less than 1.55 ng/sample. The average value of ΣPCBs for blanks was 6.98 ng/sample. The method detection limits (MDL) of PCBs are listed in Table S6. The average recoveries were 71 ± 8%, 103 ± 15%, and 108 ± 10% for PCB30, PCB198, and PCB209, respectively. All reported values were corrected using the recoveries and the mean of blanks.

Identifications of tetrachlorobiphenyls, to be exact, PCB47+48+75, 51, and 68, were conducted by comparing chromatograms of samples with those of individual PCB standard mixtures. Then comprehensive two-dimensional GC and a gas chromatography high resolution mass spectrometry were applied to further confirm these congeners. Details are presented in the Supporting Information.

Air Mass Back Trajectories. Five day back trajectories were calculated as described in our previous study.¹⁴ The air masses mostly originated from the west Pacific and the South China Sea in the summer and passed over the continental regions in Mongolia and north China during other seasons.¹⁴

RESULTS AND DISCUSSION

Concentrations and Compositions. A descriptive statistic of atmospheric concentrations for individual PCB congeners is given in Table S6. The sum concentrations of 206 PCBs (PCB30, 198, and 209 were excluded because they have been added to samples as surrogates) ranged from 140 to 3908 pg/m³, with an average value of 1474 ± 878 pg/m³. To compare with other studies, the summations of seven indicator PCB congeners (Σ_i-i-PCBs, i.e., PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180), which have frequently been reported in previous studies, were conducted as shown in

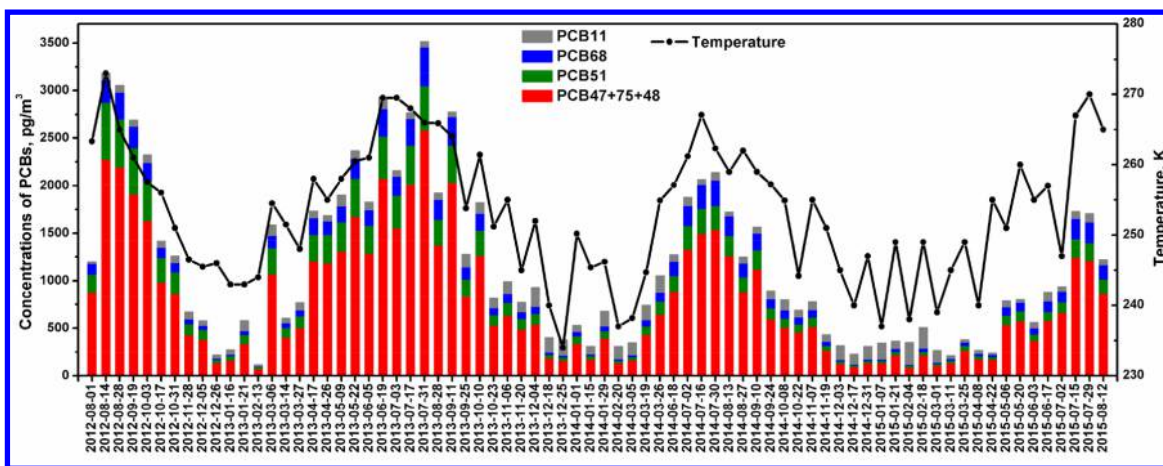


Figure 2. Time-series of PCB47+48+75, 51, 68, and 11 in air from August 2012 to August 2015.

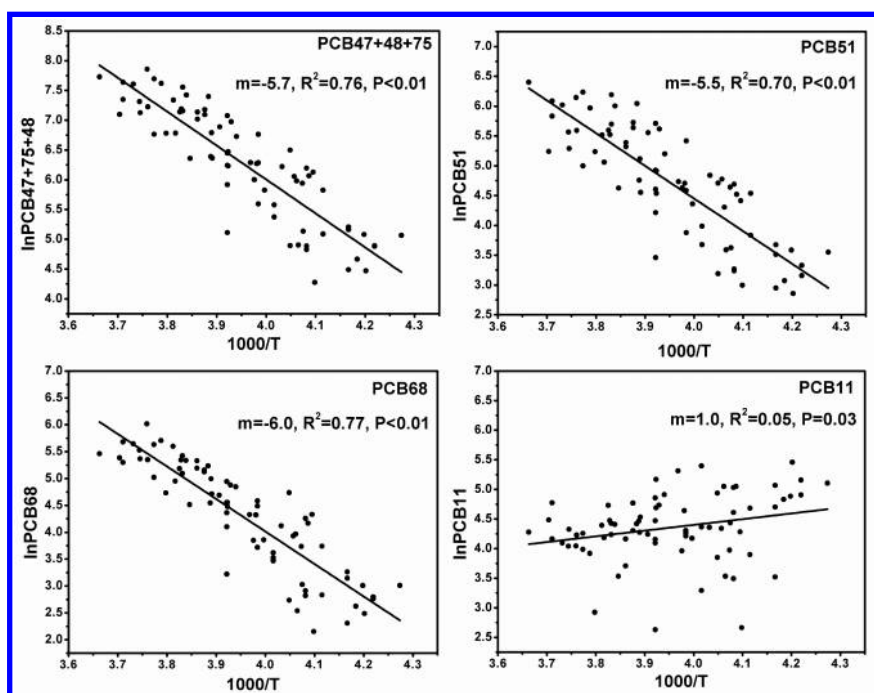


Figure 3. Regression of logarithm concentrations versus $1/T$ for PCB47+48+75, 51, 68, and 11.

Table S6. The concentrations of Σ_7 -PCBs were in the range of 3–89 pg/m^3 , with an average value of $42 \pm 22 \text{ g}/\text{m}^3$. The comparison of concentrations of PCBs in the current study with those in previous measurements is shown in Table S7. The atmospheric levels of indicator PCBs reported in this study were higher than those observed at other background sites in central China and southwest China^{15,16} but lower than that measured over the northern South China Sea.¹⁷

The average congener profile is presented in Figure 1. It is noteworthy that PCB47+48+75 was dominant with an average concentration of $786 \pm 637 \text{ pg}/\text{m}^3$ ($72\text{--}2582 \text{ pg}/\text{m}^3$), which was 15 times higher than the average concentration of Σ_7 -PCBs. It accounted for $48 \pm 16\%$ of Σ PCBs, followed by congeners: PCB51 ($10 \pm 4\%$) > PCB11 ($8 \pm 6\%$) > PCB68 ($7 \pm 3\%$), with mean concentrations of $166 \pm 141 \text{ pg}/\text{m}^3$ ($17\text{--}603 \text{ pg}/\text{m}^3$), $90 \pm 47 \text{ pg}/\text{m}^3$ ($14\text{--}235 \text{ pg}/\text{m}^3$), $112 \pm 91 \text{ pg}/\text{m}^3$ ($7\text{--}411 \text{ pg}/\text{m}^3$), respectively. These results differed significantly from the global historical production list of individual PCB congeners estimated by Breivik et al.⁶ In China,

the major PCB commercial products were known as #1 PCB and #2 PCB, which mainly contained trichlorobiphenyl and pentachlorobiphenyl, respectively.¹⁸ The compositions of commercial PCB products in China were similar to Aroclor 1242 and 1254,¹⁸ which were two groups of representative technical PCB mixtures produced in the United States under the trade name Aroclor. As reported, the total mass fractions of PCB47, 48, and 75 in Aroclor products were at levels less than 4%.¹⁹ PCB51 was present at low levels in Aroclors with mass fractions less than 0.4%.¹⁹ PCB68 was not present in Aroclors.¹⁹ Similarly, very low fractions of these tetra-CB congeners were reported in Kaneclors, another set of commercial PCB mixtures produced in Japan, where the mass percentages of PCB47+75+48, PCB51, and PCB64+41+68 were less than 3.1%, 0.3%, and 5%, respectively.²⁰ Therefore, the high abundances of PCB47+48+75, 51, and 68 were unrelated to the production and use of commercial mixtures. PCB11 has frequently been reported as a non-Aroclor congener with relatively high levels

in the environment.^{21–23} However, the high abundances of PCB47, 48, or 75, PCB68, and PCB51 in the outdoor environment were rarely reported in previous studies, except for studies in Antarctica, Venice, and Guangzhou (Table S7).^{24–26} All of these studies reported the high mass fraction of PCB47 but without additional details. Recently, high concentrations of PCB47, 51, 68, which account for up to 50% of measured Σ PCBs, were observed in the kitchen of a residence in the United States.²⁷

Seasonal Variations and Influence Factors. The time-series of PCB47+48+75, 51, 68, and 11 were plotted in Figure 2. Average concentrations of PCB47+48+75, 51, 68, and 11 in different seasons were listed in Table S8. On the basis of average concentrations, seasonal variations with the following descending order were observed for PCB47+48+75, 51, and 68: summer (June to August) > fall (September to November) and spring (March to May) > winter (December to February). Conversely, PCB11 was observed with the highest concentrations in winter and with comparable levels in other seasons. Seasonal trends may be affected by the transport of air masses under the control of a monsoon. Namely, elevated concentrations of contaminants in the receptor site may be observed if emission sources are located in an upwind domain. The pollutant-containing air mass outflows driven by monsoon may cause a “fake” seasonal characteristic. However, according to the calculated five day backward trajectories, air masses originated from the west Pacific or the South China Sea in the summer, which has frequently been reported to have a low abundance of pollutants.^{28,29} During the other seasons, air masses originated from or passed over north China, the most industrialized and urbanized area that contains many megacities and highly polluted regions, such as Beijing, Tianjin, and Shanxi. Moreover, the elevated use of biofuel and fossil fuel for household heating in north China during the winter will increase the pollution both in north China and the downwind domain. Considering the results of the air mass backward trajectories analysis, the seasonal characteristic of PCB11 was most likely attributed to the influence of anthropogenic air pollution outflows from north China. However, the high abundances of PCB47+48+75, 51, and 68 in the summer were not likely due to long-range transport.

Given that the concentrations of PCB47+48+75, 51, and 68 showed similar trends with the ambient temperature, the logarithms of the concentrations of PCBs ($\ln C$) were regressed with reciprocal temperature ($1/T$) to investigate the temperature dependence of PCBs. As presented in Figure 3, the concentration of PCB11 showed little significant temperature dependence. However, significantly high correlations with steep negative slopes (m) and high R^2 ($R^2 > 0.70$) values of these regressions were observed between PCB47+48+75, 51, and 68 versus temperature. These findings differed from previous studies, which indicated that the influence of temperature on lower chlorinated PCBs was more pronounced than that on higher chlorinated PCBs.^{15,30} The inconsistent relationship between PCB11 and temperature may be explained by the influence of primary sources and long-range transport as mentioned. For the air concentrations of PCB47+48+75, 51, and 68, increased volatilization from contaminated surfaces at higher temperatures was likely to be the major driver of the seasonal variability because of the regressed steep negative slopes (m) and high R^2 values.

Possible Sources. Combustion and industrial thermal processes have been recognized as a major source of

unintentionally produced PCBs.^{3,10,11,31} Numerous PCB congeners (including 7 indicator congeners, 12 dioxin-like congeners, and others) were detected with high amounts in emissions from industrial activities and combustion processes. Ikonomou et al. reported that PCB47/75/48, 51, and 68 have a large proportion in municipal waste incinerator stack emissions.³² To identify whether the combustion and thermal processes were sources of PCB47+48+75, 51, and 68 in the ambient atmosphere in this area, correlations were analyzed between these dominant PCB congeners and polycyclic aromatic hydrocarbons (PAHs) (correlation coefficients were listed in Table S9), because PAHs are generated by incomplete combustion processes and can be used as indicators of combustion sources. According to Table S9, PCB47+48+75, 51, and 68 showed negative correlations with PAHs but with low correlation coefficients ($|r| < 0.35$), suggesting different sources of these tetra-CB congeners with PAHs. Conversely, PCB11 positively correlated significantly with PAHs ($r = 0.708$), which may be attributed to the influence of the same source regions and long-range transport. Generally, emissions from combustion and industrial thermal processes can be independent of the seasons, similar to constant emissions. Even if emissions from combustion and industrial thermal processes presented seasonal characteristics, the relative emission concentration could be higher in winter. This can be attributed to the increased use of biofuel and fossil fuel for household heating in winter, especially in north China. Moreover, the incomplete combustion process has been reported to be more severe in the winter which may elevate the emissions of contaminants, such as polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F).³³ These emission characteristics of combustion-related primary sources were inconsistent with our seasonal trends of PCB47+48+75, 51, and 68. In this study, relatively high concentrations of PCB47+48+75, 51, and 68 were recorded in the summer. The long-range transport of air masses polluted by primary emissions showed little influence on the seasonal characteristics of these tetra-CBs as indicated above. Therefore, primary emissions from combustion and industrial thermal processes mostly cannot be considered as the major source of these tetra-CB congeners in the atmosphere.

Correlations between PCB47+48+75, 51, 68 and other PCB congeners were also investigated. As shown in Table S9, PCB47+48+75, 51, and 68 showed little correlation with other congeners including PCB11, an indicator of emissions from pigment. The results suggested different sources and environmental fates between these tetra-CBs and other PCB congeners. In other words, these three abundant tetra-CB congeners might come from unique unintentional sources that differ from combustion and industrial thermal processes or pigment emissions.

Rodenburg et al. identified PCB47 and PCB51 as intermediate dechlorination products from highly chlorinated congeners in groundwater, landfills, and wastewater collection systems.³⁴ The dechlorination process in wastewater treatment plants may have an effect on atmospheric concentrations of PCB47+48+75, 51, and 68 and the temperature-dependent seasonal trends of these congeners. However, pentachlorobiphenyl and other high chlorinated congeners were not the dominant homologues in the environment or in commercial products in China.¹⁸ Therefore, it is difficult to explain the reason for the high abundances of these tetra-CB congeners in the environment using the dechlorination theory.

Recently, Herkert et al. reported high concentrations of PCB47 (2,2',4,4'), 51 (2,2',4,6'), and 68 (2,3',4,5') in surface emissions from finished cabinets in the kitchen of a residence and hypothesized that they were inadvertently produced from the decomposition of 2,4-dichlorobenzoyl peroxide, an initiator in the free-radical polymerization of polymer production (such as polymer sealant manufacturing).²⁷ These inadvertently produced PCBs can volatilize from the surfaces of household cabinets. In our study, the average atmospheric concentrations of PCB47+48+75, 51, and 68 were at the relative proportions of 74%, 16%, and 10% to each other, consistent with the compositions of PCB47, 51, and 68 from the polymer sealant reported by Herkert et al. (70%, 20%, and 10%).²⁷ Polymer sealant is a common caulking sealant and adhesive that is widely used in houses, civil buildings, and public infrastructure, as well as in industrial manufacturing. It is also widely used as a wood finish during furniture manufacture. As reported, China was the largest consumer of silicone sealant globally, with an estimated consumption of 0.74 million tons and a production of 0.76 million tons in 2015, four times higher than that estimated in North America and Western Europe.³⁵ The high-consumption materials in China may have resulted in the large emissions of tetra-CBs (PCB47, 51, and 68), which can be employed to explain the high levels of PCB47+48+75, 51, and 68 in the environment. Furthermore, the polymer sealant is able to emit these tetra-CBs through the temperature-driven volatilization process, which is consistent with the temperature-dependent trends of PCB47+48+75 and 51 in our study. Therefore, the high abundances of PCB47+48+75, 51, and 68 in the environment are most likely due to unintentional emissions during the use of polymer products such as polymer sealant. Besides, the polymer-containing waste effluents could become "secondary-like" sources that can influence concentrations of PCB47+48+75, 51, and 68 in the atmosphere via the volatilization process.

In addition, the soil has widely been accepted as a significant secondary source which can trap and accumulate contaminants and then contribute to the levels of atmospheric PCBs during the summer.³⁰ Therefore, we presumed that soils around the sampling site may act as sinks that accumulate large numbers of these tetra-CBs (PCB47, 51, and 68) emitted from polymer manufacturing and become significant secondary sources of tetra-CBs when they reach equilibrium. However, we cannot verify this hypothesis due to the lack of soil samples from this site. The soil–air partitioning and exchanges of PCB47+48+75, 51, and 68 should be further studied.

Toxicological Effects. PCBs in the environment are of great interest because of their toxicity. However, most toxicity and risk assessments were focused on dioxin-like PCBs (*dl*-PCBs, i.e., PCB77, PCB81, PCB105, PCB114, PCB118, PCB123, PCB126, PCB156, PCB157, PCB167, PCB169, and PCB189) on the basis of the toxic equivalency (TEQ) concept. An effective risk assessment model similar to the TEQ was not available for nondioxin-like congeners such as PCB47, 48, 75, 51, and 68. Nevertheless, there were various toxicological studies about the adverse health effects of those congeners. PCB47, 51, 68, and 75 have been reported to be more potent neurotoxic congeners compared with PCB77 and 126 based on the neurotoxic relative potency values estimated by Simon et al.³⁶ Additionally, PCB47 and 51 could act as partial or full agonists on human GABA_A receptors, which provide the main inhibitory feedback for learning and memory as well as motor activity.³⁷ Moreover, based on the relative potency (REP)

factors calculated by Hamers et al., PCB47 and 51 were reported to show comparable high androgen receptor (AR)-antagonistic potencies with PCB126.³⁸ According to Hamers et al., the gap junctional intercellular communication (GJIC)-inhibiting and estradiol-sulfotransferase (E2SULT)-inhibiting potencies were higher, but the plasma transport protein TTR binding potencies and uridine-glucuronyl transferase isozymes (UGT1A6)-inducing potencies were weaker for PCB47 and 51, compared with those for PCB126.³⁸ Given that PCB126 is the most toxic (relative aryl hydrocarbon receptor AhR-mediated toxicity) congener among the 12 *dl*-PCBs based on toxicity equivalency factor (TEF) values derived by the World Health Organization, although the TTR binding and UGT1A6-inducing potencies for PCB47 and 51 were lower, the comparable AR-antagonistic potencies and higher GJIC-inhibiting and E2SULT-inhibiting potencies may suggest the non-negligible toxicological effects of PCB47 and 51. Therefore, we conclude with the suggestion that this group of UP-PCBs should be given great attention, given their higher concentration levels and dominance over other PCB congeners in the atmosphere. Further investigation concerning their sources, emission factors, and health risks are of critical need.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b07286.

Description of sample pretreatments; instrumental analysis; PCBs standards; identification of tetrachlorobiphenyls; QC/AC; atmospheric concentrations, method detection limit, and detection frequency for individual PCB congeners in gas phase; comparison of the concentrations of the sum of seven indicator PCBs and the PCB47, 51, or 68 in different locations obtained in the present study with those reported previously; average concentrations of PCB47+48+75, 51, 68, and 11 in different seasons; Pearson correlation coefficients between PCB congeners and PAHs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhanggan@gig.ac.cn.

ORCID

Gan Zhang: 0000-0002-9010-8140

Jun Li: 0000-0002-3637-1642

Zhineng Cheng: 0000-0002-6598-849X

Guangcai Zhong: 0000-0002-5647-5940

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Key R&D Program of China (2017YFC0212000), the National Scientific Foundation of China (No. 41430645 and 41390240), and the Chinese Academy of Sciences President's International Fellowship for visiting Scientist Grant (No. 2018VCA0035). We are grateful to the crew of the Ningbo Atmospheric Environment Observatory for collecting the air samples. This is contribution No. IS-2670 from GIGCAS.

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