Environmental Science & Technology

Article

pubs.acs.org/est

Occurrence and Concentrations of Halogenated Flame Retardants in the Atmospheric Fine Particles in Chinese Cities

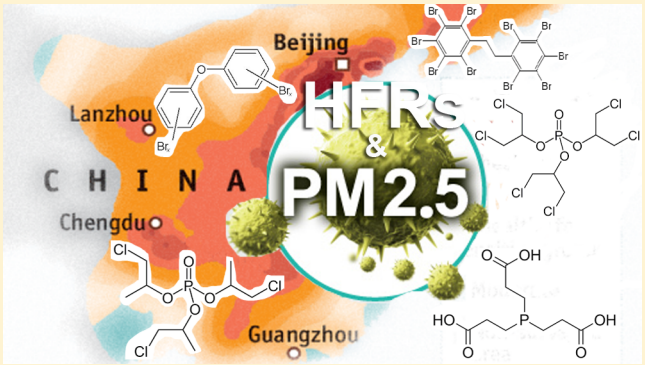
Di Liu,[†] Tian Lin,[*,‡] Kaijun Shen,[†] Jun Li,[†] Zhiqiang Yu,[†] and Gan Zhang[†]

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

[‡]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

Supporting Information

ABSTRACT: The concentrations of halogenated flame retardants (HFRs) in $PM_{2.5}$ were monitored for one year at 10 urban sites in China during 2013−2014. This study investigated four classes of HFRs: nine polybrominated diphenyl ethers (PBDEs), six nonbromodiphenyl ether (BDE) brominated flame retardants, two dechlorane plus (DP) flame retardants, and three chlorinated organophosphate flame retardants (OPFRs). Extremely high concentrations of BDE-209 and DBDPE were observed in only one city (Guangzhou), which was a consequence of the intensive e-waste recycling and disposal operations in the Pearl River Delta. This result differed from the tris(monochloropropyl) phosphate (TCPP) and tris(2-chloroethyl) phosphate (TCEP) distributions, which showed high concentrations in most cities, suggesting wide usage and large emissions in China in recent years. The highest TCPP and TCEP concentrations were observed in the summer, indicating that emission from local sources was an important factor controlling the levels in the air. This was not the case for BDE-209 and DBDPE, for which higher concentrations were found in winter. When bound to particulate matter due to low vapor pressure, these compounds may be more persistent in air, and temperature-dependent gas-particle partitioning was a key factor. Moreover, regional pollution and long-range transport had a significant influence on the seasonal distributions of BDE-209 and DBDPE, especially in cities (Guangzhou and Shanghai) close to electrical/electronic waste recycling sites. Residents in urban areas were exposed to higher levels of chlorinated OPFRs. This raises considerable concern, and an appropriate risk assessment is required.



1. INTRODUCTION

Flame retardants are compounds that are added to manufactured materials, such as plastics, textiles, polyurethane foam, wire, and cable, to prevent combustion and delay the spread of fire after ignition.[1] Flame retardants can be broadly classified into halogenated and nonhalogenated flame retardants. Halogenated flame retardants (HFRs), which contain chlorine or bromine bonded to carbon, have been a focus of concern due to their persistence, bioaccumulation, and potential human health effects.[2] All 22 chemicals globally banned as persistent organic pollutants (POPs) under the Stockholm Convention are halogenated compounds, and three of them are brominated flame retardants (hexabromobiphenyl and penta- and octa-bromodiphenyl ether (BDE)). New products are constantly being introduced into the global HFR market. Unfortunately, these HFRs are usually substitutions of one harmful flame retardant for another, from penta- and octa-BDEs, deca-BDE, decabromodiphenyl ethane (DPDPE), dechlorane plus (DP), to organophosphate flame retardants (OPFRs), in a phenomenon termed "regrettable substitution."[3,4]

HFRs, which have low vapor pressure and a high octanol−water partition coefficient (K_{ow}) in the atmosphere, tend to bind to particulate matter and may be more resistant to photodegradation and metabolic breakdown.[5,6] Among the various classes of particle matter, fine particles ($PM_{2.5}$) are a pollutant of primary concern in China.[7] Very high concentrations of urban $PM_{2.5}$ are frequently recorded in Chinese cities, which could lead to adverse effects on human health because, once inhaled, they can be deposited much more deeply in the lungs than coarse particles.[8] Various toxic materials are associated with $PM_{2.5}$, including HFRs; therefore, people are at a high risk from $PM_{2.5}$ exposure in China.[9,10]

In this study, a broad array of HFR chemicals were measured in $PM_{2.5}$ samples, to provide a tool to better understand the status of HFR pollution in China. The chemicals included nine

Received: April 5, 2016
Revised: August 18, 2016
Accepted: August 18, 2016
Published: August 19, 2016

ACS Publications © 2016 American Chemical Society

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

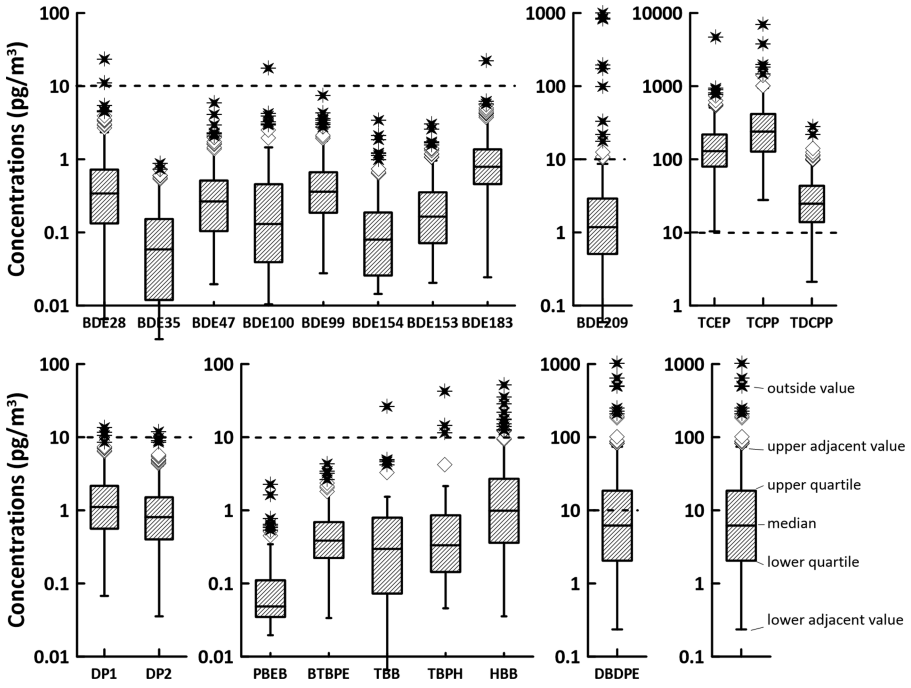


Figure 1. Box-whisker-symbol plots representing the lower and upper values of the HFRs in $PM_{2.5}$ during 2013−2014. The lower and upper ends of the box are the 25th and 75th percentiles of the data, and the median is shown as the middle line. The stars and diagonal symbols represent the extreme values and outliers that are >1.5-fold and >3-fold beyond the interquartile range, respectively.

PBDEs, six non-BDE brominated flame retardants, two DPs, and three chlorinated OPFRs from 10 urban cities (Beijing, Shanghai, Guangzhou, Nanjing, Wuhan, Taiyuan, Chengdu, Lanzhou, Guiyang, and Xinxiang). A sampling campaign was conducted for one year (October 2013 to August 2014). The objectives of the study were to (i) report the concentrations and profiles of legacy and emerging HFRs in the urban $PM_{2.5}$ in China; (ii) investigate their spatiotemporal trends and possible factors contributing to the measured HFR concentrations; and (iii) assess the current risk of population exposure to HFRs in the $PM_{2.5}$ in the region.

2. MATERIALS AND METHODS

2.1. Sampling Information. $PM_{2.5}$ samples were collected in 10 urban cities (Beijing, Shanghai, Guangzhou, Nanjing, Wuhan, Taiyuan, Chengdu, Lanzhou, Guiyang, and Xinxiang) across China during four seasons (Supporting Information (SI) Figure S1). The sampling locations were densely inhabited districts of these cities, with the sampling sites located on rooftops approximately 15−20 m above ground level. The details of the sampling sites are summarized in the SI (Table S1). Each sample was collected for 24 h on 20.3 × 25.4 cm preheated (5 h at 450 °C) Whatman quartz microfiber filters (QFFs) using high-volume samplers (Andersen Instruments/GMW) operated at 300 L/min. Four sampling campaigns were conducted, 22 October 2013 to 13 November 2013, 30 December 2013 to 20 January 2014, 30 March to 20 April 2014, and 26 June to 24 August 2014, to represent the four seasons. A total of 16 $PM_{2.5}$ samples were analyzed for HFRs for each season at each site.

2.2. Analysis of HFRs. The treatment and analytical procedure for eluting HFRs from the $PM_{2.5}$ samples and the instrument analysis are described in the SI (section S2.2).

2.3. Quality Assurance/Quality Control (QA/QC) of the HFR Analysis. QA/QC was conducted by analyzing field and laboratory blanks, standard spiked recoveries, and gas chromatography mass spectrometry (GC-MS) detection limits. Prior to extraction, each sample was spiked with a known amount of tris(2-chloroethyl) phosphate (TCEP)−d12 and polychlorinated biphenyl (PCB)-209 to monitor the analytical recovery efficiency. The recoveries of PCB-209 and d12-TCEP ranged from 60 to 108% and 86 to 139%, respectively. The final reported concentrations were not surrogate recovery corrected. The method detection limits (MDLs) were assigned as the average values of the field blanks plus 3 times the standard deviation of the field blank values. When compounds were not found in the field blanks, the MDLs were calculated as 3 times the instrumental detection limits (IDLs). The IDL values were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. The target compounds were below the IDLs in the field and laboratory blanks. The IDL and MDL for nine PBDEs ranged from 0.002 to 0.016 ng and from <0.01 to 0.05 pg/m^3, respectively. The IDL and MDL for the six non-BDE brominated flame retardants ranged from 0.018 to 0.08 ng (mean 0.043 ng) and from 0.06 to 0.27 pg/m^3, respectively. The IDL and MDL for the three chlorinated OPFRs ranged from 0.24 to 0.73 ng and from 1.14 to 3.25 pg/m^3, respectively. See the SI for details of the MDL (Table S2). The standard spiked recoveries were 77−112%, and the relative standard deviations were less than 15%.

The details of the thermal-optical carbon analysis and QA/QC (section S2.4), back trajectories (SI section S2.5), and data analysis (section S2.6) are presented in the SI.

3. RESULTS AND DISCUSSION

3.1. Concentrations and Profile. *3.1.1. PBDEs.* The nine targeted PBDEs (BDE-28, BDE-35, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) were detected in all $PM_{2.5}$ samples. SI Table S3 and Figure 1

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

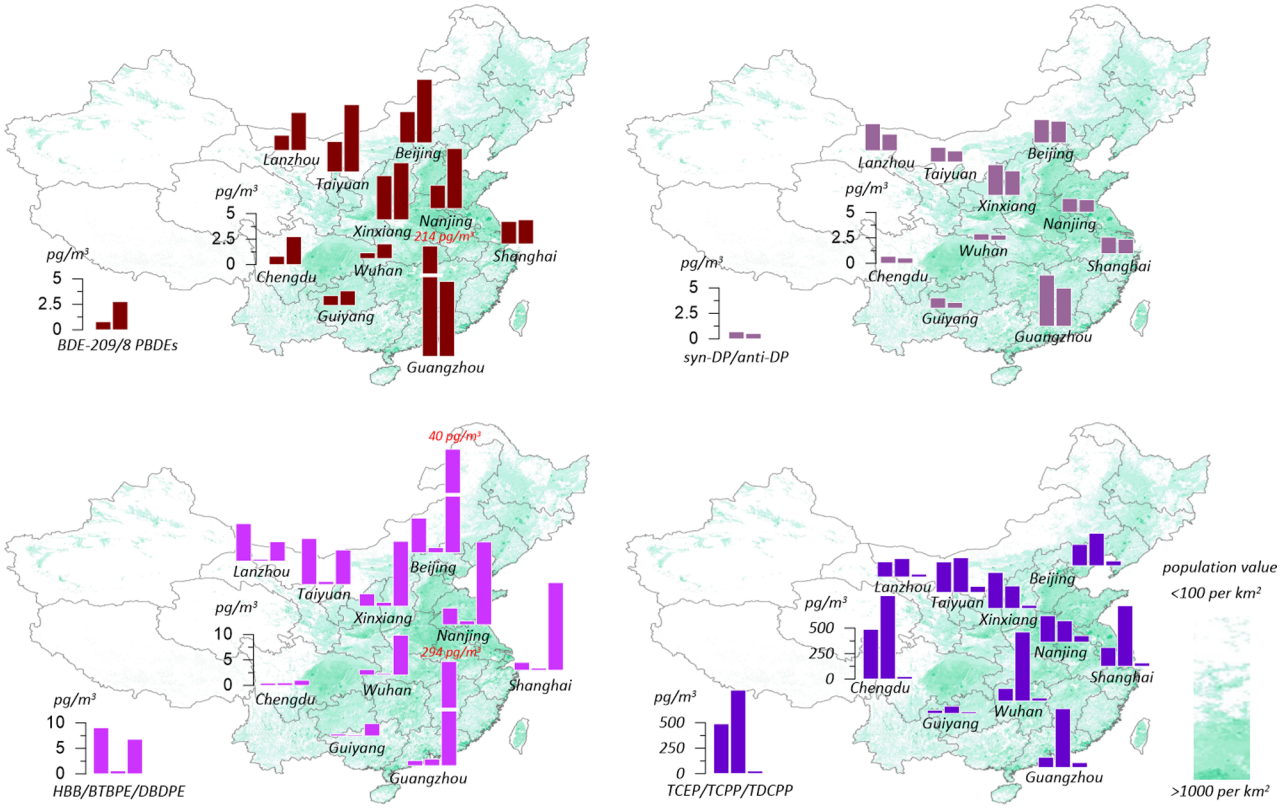


Figure 2. Spatial distributions of the concentration of individual HFRs in the $PM_{2.5}$ from 10 urban cities.

summarize the concentrations of the targeted HFRs at the 10 sampling sites. The mean, median, minimum, and maximum concentrations of the PBDE congeners are listed in SI Table S3. The detection frequencies of the PBDEs were in the range of 67−99% in all samples, suggesting that these compounds were ubiquitous in the atmosphere of the 10 cities. PBDEs, one of the earliest commercially produced HFRs, have been widely used in developed countries since the 1970s, but were banned 10 years ago. In China, recent results showed that there was a persistent increase from the 1970s and no clear sign of the decline of PBDEs until now.[11] In this study, the concentrations of the total PBDEs ($\sum_9$PBDE) measured in the $PM_{2.5}$ at all sites varied from <0.01 to 1,000 pg/m^3 (mean of 35 ± 150 pg/m^3, n = 149). The overall concentrations of $\sum_9$PBDE measured at most sites were generally lower than the levels reported several years ago in cities in developed countries, such as Chicago, Athens, Izmir, Chilton, Osaka, and Tokyo.[12−16] However, they were still higher than the levels recently reported in European air.[17,18] The lowest concentrations were recorded in Wuhan and Guiyang, with mean concentrations of $\sum_9$PBDE 2.0 ± 1.4 pg/m^3 (0.62−5.1 pg/m^3, n = 16) and 2.2 ± 2.2 pg/m^3 (0.28−7.0 pg/m^3, n = 16), respectively. The lower concentrations of PBDEs measured in this study were comparable to the previously reported levels in the $PM_{2.5}$ on a remote island in the East China Sea, which was regarded as a background site, where contaminants were supplied by long-range atmospheric transport from the East China Sea rather than local sources.[19] The highest concentrations of $\sum_9$PBDE, ranging from 2.5 to 1000 pg/m^3 (mean of 210 ± 350 pg/m^3, n = 16), were observed in Guangzhou, where the values were nearly 10- to 100-fold higher than those measured at the other sites in this study (Figure 2). A similar high level in the $PM_{2.5}$ from local households was also found in Guangzhou (52−2000 pg/m^3, mean 240 pg/m^3).[20] Compared with the city of Guiyu (which is a major e-waste dismantling area near Guangzhou, with concentrations of 21 000 ± 7200 pg/m^3 and 6200 ± 800 pg/m^3 at an e-waste site and an outside area, respectively), the highest $PM_{2.5}$-bound PBDE concentration observed in Guangzhou in this study was exceedingly low,[21] which suggests that the observed high PBDE concentration in Guangzhou is the regional background level caused by emissions from intensive e-waste recycling and disposal operations in the Pearl River Delta.[21,22]

Among the individual BDE congeners, BDE-209 was the most abundant in all but a few samples (n < 10). The concentration of BDE-209 in this study was in the range of <0.01−1000, with a mean of 31 ± 150 pg/m^3. In Guangzhou, extremely high concentrations of BDE-209 accounted for 74 ± 13% of the total PBDEs in $PM_{2.5}$, consistent with the results of previous studies (Figure 2).[16,17,23] This suggests that the emissions originated from the current application of deca-BDE in industrial and manufacturing processes or electrical/electronic waste recycling sites in adjacent areas. According to the World Trade Organization (WTO) statistics, the annual global consumption of PBDEs is approximately 40 000 tons, of which approximately 10% is commercial penta-BDE, 15% is octa-BDE, and 75% is deca-BDE. The global consumption of deca-BDE mixtures, as the major technical PBDE product, increased approximately 2-fold from 1999 to 2003.[24] This increase coincided with the fact that deca-BDE is the most widely used commercial additive in the polymer industry, and the use of deca-BDE is currently not restricted in China. Since the major PBDE products octa-BDE and penta-BDE were banned in China in 2004 and 2007, respectively, the huge production and consumption of deca-BDE has resulted in high atmospheric levels of BDE-209. In contrast, lower total PBDE

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

concentrations and lower proportions of BDE-209 were observed in the midwestern undeveloped region, for example, Lanzhou, Wuhan, Chengdu, and Guiyang. In Chengdu, BDE-183 had a relatively high (24%) abundance, and in Lanzhou, BDE-99 was more abundant (35%) than BDE-209 and BDE-183. This suggests a major contribution from octa-BDE or penta-BDE, with a minor contribution of deca-BDE in the two cities. The release of products containing octa-BDE or penta-BDE was identified as a potential source due to the vaporization from these aged products during day-to-day use and disposal. In addition, BDE-209 exists exclusively in the particulate phase rather than the gas phase due to the less volatile nature of BDE-209, whereas the other PBDE congeners are distributed in both the gaseous and particulate phases. The portion in the particulate phase decreases from the highly brominated congeners to the less brominated congeners. Lower temperatures and higher $PM_{2.5}$ concentrations are the important factors in the formation of BDE-209 bound to particulates in the case of Beijing, Taiyuan, and Xinxiang.

3.1.2. Non-BDE Brominated Flame Retardants. The $PM_{2.5}$ samples were analyzed for the six non-BDE brominated flame retardants, namely, 2,3,4,5-tetrabromobenzoate (TBB), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), tetrabromophthalate (TBPH), 1,2-bis(2,4,6 tribromophenoxy) ethane (BTBPE), and decabromodiphenyl ethane (DBDPE). Three compounds (HBB, BTBPE, and DBDPE) had high detection frequencies and were detected in 97, 95, and 80% of the samples, respectively, whereas PBEB, TBB, and TBPH were only detected in 67, 41, and 22% of the samples.

The non-BDE brominated flame retardant with the highest concentration in $PM_{2.5}$ was DBDPE, a novel brominated flame retardant that is used as a replacement for the structurally similar BDE-209.[25] The concentration of DBDPE in the $PM_{2.5}$ at all sites varied from 0.24 to 1000 pg/m^3 (mean of 50 ± 160 pg/m^3, n = 120), and it was the only compound among the brominated flame retardants measured in this study that could be compared to the BDE-209 concentration (Figure 1). Similar to BDE-209, extremely high concentrations of DBDPE were only observed in Guangzhou, where they were 1−2 orders of magnitude greater than those in other cities (Figure 2). E-waste recycling and disposal operations in the region were identified as the major source of DBDPE.[6]

HBB has been widely used as an additive flame retardant in Japan, where it is still produced in low volumes.[26] The mean and median concentrations were 3.5 and 1.3 pg/m^3, with higher values, 8.3−52 pg/m^3 (n = 15), observed in the $PM_{2.5}$ samples. HBB has been detected in remote air over the East China Sea and the Arctic (0.10−5.9 pg/m^3) and over the Atlantic and Southern oceans (0.92 pg/m^3).[27,28] The high concentrations in several samples from different sites suggest that sporadic emission sources of the compound still exist in China.

BTBPE was introduced to the market in the mid-1970s as a replacement for penta-BDE and octa-BDE.[29] BTBPE, under the trade name FF-680, was only produced by the Great Lakes Chemical Company in North America at a maximum annual production of 225 000 t in 1994 but just 500−5000 t produced in 2006.[30] No information is available regarding its consumption in China. In this study, the $PM_{2.5}$-bound concentrations of BTBPEs in all samples varied from 0.03 to 4.4 pg/m^3, with a mean of 0.64 pg/m^3, similar to the reported levels at Taihu Lake in China (less than 1 pg/m^3 in the total suspended particulate (TSP)).[31] The concentration of atmospheric BTBPE observed in China was low, comparable to that detected in pristine areas, such as the Canadian High Arctic and the Tibetan Plateau.[32] This result suggests that there is no significant source of BTBPE in China.

3.1.3. Dechlorane Plus. DP, a highly chlorinated flame retardant, exists as two stereoisomers (syn-DP and anti-DP) in commercial products.[33] In this study, low $PM_{2.5}$-bound concentrations of syn-DP and anti-DP were observed in all cities, with concentration ranges of 0.07−14 pg/m^3 (2.0 ± 2.3 pg/m^3, n = 141) and 0.04−12 pg/m^3 (1.5 ± 1.9 pg/m^3, n = 146), respectively. The mean DP concentrations in this study were similar to those recently observed in the atmosphere near Taihu Lake (3.5 pg/m^3 for all DPs),[31] in the atmosphere of northeast China (mean air concentrations of 1.9 and 5.8 pg/m^3 for syn-DP and anti-DP, respectively),[34] and in TSP samples from Beijing (2.0 ± 3.9 pg/m^3 for all DPs), Dalian (3 ± 6 pg/m^3 for all DPs), and Shanghai (Jiading District had the highest levels of 5.5 ± 1.3 pg/m^3 for all DPs).[35] However, they were significantly lower than those measured 10 years ago in air samples from 97 Chinese sites (mean air concentration of 15 ± 15 and 3.5 ± 5.6 pg/m^3 at urban and rural sites, respectively, for all DPs).[36] Vorkamp et al. reported mean air concentrations of syn- and anti-DP of 2.3 and 5.2 pg/m^3, respectively, in Greenland.[37] Salamova et al. reported DP concentrations (syn- + anti-DP) ranging from 0.05 to 5.0 pg/m^3 in atmospheric particles from a European Arctic site.[38] Möller et al. reported that the total DP concentrations ranged from not detected (<0.05 pg/m^3) to 2.1 pg/m^3 in the atmosphere of the Canadian High Arctic.[39] Yu et al. reported that the total concentrations of syn- and anti-DP ranged from 0.01 to 1.8 pg/m^3 in Canada's Western Sub-Arctic.[40] Hoh et al. (2006) reported atmospheric levels of DP in the Great Lakes area of the U.S., with the highest mean value of 34 ± 24 pg/m^3 at the station nearest the DP manufacturing plant.[41] Very high atmospheric DP concentrations (7700−27 000 pg/m^3) have been reported near a DP manufacturing factory (Anpon) in Jiangsu Province, China, and the values reported at an e-waste site (Qingyuan, Guangdong Province, China) were in the range of 13−1800 pg/m^3.[42,43] Overall, the DP concentrations measured in this study fell within the lower-middle ranges of the levels reported in previous studies around the world.

The isomeric composition of DP is a useful tool to track the movement and processing of this chemical. The fractional abundance (fanti) is defined as the concentration of the anti-isomer divided by the sum of the concentrations of the anti- and syn-isomers: fanti = anti-DP/(anti-DP + syn-DP). The fanti values observed in the $PM_{2.5}$ in this study ranged from 0.24 to 0.72, with a mean of 0.54 ± 0.07, lower than those in the commercial DP products Anpon and OxyChem (0.80−0.64 and 0.60, respectively).[43] Considering the preferential atmospheric photodegradation of the anti-isomer and the isomerization of the anti-isomer over the syn-isomer, long-range transport may make an important contribution to the atmospheric DP levels measured in this study. Because DP is only detected in the particulate phase, these results for the $PM_{2.5}$ samples indicated that low levels of DP contamination were prevalent in the atmosphere of China, and there was no significant pollution source in the vicinity of the sampling sites.

3.1.4. Chlorinated OPFRs: TCPP, TCEP, and Tris (ßß-Dichloroisopropyl) Phosphate (TDCPP). OPFRs are gradually replacing other restricted flame retardants, such as PBDEs. In 2004, the worldwide consumption of flame retardants was 1.5 million tons, of which OPFRs accounted for 14%, making them the third-most-used group of flame retardants.[44] Although

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

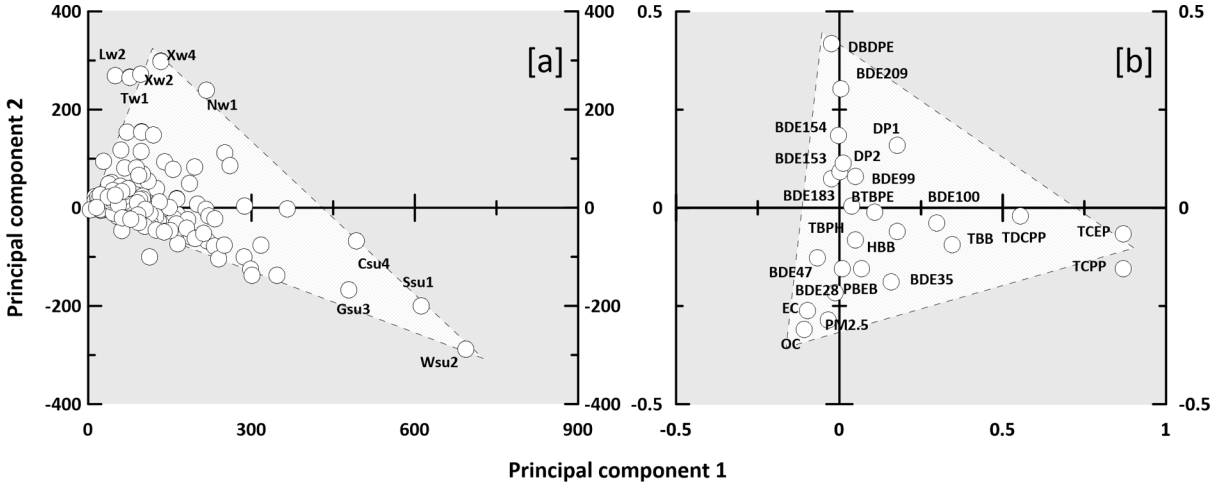


Figure 3. PCA scores (a) and loadings (b) plots for the first two components of all HFRs in $PM_{2.5}$ from 10 urban sites (please see the SI Table S1 for the sample numbers).

OPFRs may be less toxic to organisms and are used as PBDE replacements, some chlorinated OPFRs, such as TDCPP, TCPP, and TCEP, are persistent in the environment and potentially carcinogenic.[45] They also exhibit the characteristics of POPs, and their presence in the environment has caused great concern in the past decade.[45] In this study, the chlorinated OPFRs TCPP, TCEP, and TDCPP were detected in all $PM_{2.5}$ samples, suggesting that they are ubiquitous contaminants in ambient air. The sum of the concentrations of the three compounds ranged from 45 to 12 000 pg/m^3 (680 ± 1000 pg/m^3). The mean concentration of chlorinated OPFRs was significantly higher than that of PBDEs and non-BDE brominated flame retardants and two and 3 orders of magnitude higher than that of DPs. High concentrations of chlorinated OPFRs were observed at most sites, not only in Guangzhou, as was the case for BDE-209 and DBDPE, suggesting that they are widely produced and used in China (Figure 2). China is a large OPFR consumer because of the rapid development of its manufacturing industry, and the demands for OPFRs are expected to increase by approximately 15% annually. The annual mean concentrations of the total chlorinated OPFRs were the highest in Chengdu (1300 ± 2800 pg/m^3), followed by Wuhan (830 ± 1000 pg/m^3), Shanghai (810 ± 560 pg/m^3), Guangzhou (720 ± 380pg/m^3), Taiyuan (700 ± 400 pg/m^3), Xinxiang (600 ± 240 pg/m^3), Beijing (570 ± 380 pg/m^3), and Nanjing (530 ± 380 pg/m^3). Higher annual mean concentrations of total chlorinated OPFRs but lower concentrations of PBDEs were found in Chengdu and Wuhan, which are located in the middle section of the Yangtze River. This indicates that OPFRs were widely used as alternative HFRs in industrial and manufacturing processes during the shift of labor-intensive manufacturing from the coastal developed areas to inland regions. Lower annual mean concentrations were observed in Lanzhou (350 ± 240 pg/m^3) and Guiyang (110 ± 40 pg/m^3), similar to the PBDEs, reconfirm the fact that the industrial and manufacturing levels are still relatively low in those cities.

TCPP, the most abundant compound in the $PM_{2.5}$ samples, was detected in the range of 28−7000 pg/m^3 (410 ± 690 pg/m^3, n = 149). The concentrations of TCPP found in this study were comparable to those in TSP samples from urban sites around the North American Great Lakes Basin, such as Chicago (530 ± 80 pg/m^3) and Cleveland (850 ± 300 pg/m^3), but were higher than those in samples from rural sites in the same region of North America, such as Sleeping Bear Dunes (25 ± 7 pg/m^3) and Eagle Harbor (32 ± 9 pg/m^3).[46] In Europe, Marklund et al. (2005) reported a concentration of 810 pg/m^3 TCPP in air from northern Finland, Green et al. (2008) reported a concentration of 330 pg/m^3 in air from New Ålesund, Svalbard, and Möller et al. (2011) reported a concentration of 1200 pg/m^3 in the atmosphere over the North Sea, which were comparable to the concentrations observed in this study.[47,48]

The concentrations of TCEP measured in the $PM_{2.5}$ samples in this study were in the range of 10−4700 pg/m^3 (230 ± 410 pg/m^3, n = 149). These concentrations were similar to the range of values measured in the sites mentioned in the TCPP results above, in which both TECP and TCPP were frequently detected in high abundance. The observed abundance of TCEP was lower than that of TCPP in this study, similar to reports from the Mediterranean,[49] North Sea (Germany),[47] and the Great Lakes;[46] this could be attributed to the use of TCPP as a worldwide replacement for the more toxic TCEP in recent years. However, the observed profiles of TCEP and TCPP in the $PM_{2.5}$ samples were different from those obtained from a long-range cruise campaign conducted from Shanghai, China to the Arctic region[27] and around the northern South China Sea.[50] This can be explained by the shorter atmospheric half-life of TCPP (the calculated half-lives for the atmospheric reaction with hydroxyl radicals are 8.6 h for TCPP and 17.5 h for TCEP) or by the higher potential of TCPP to adsorb to airborne particles, which may then be removed through dry and wet deposition during long-range transport.[51]

Among the chlorinated OPFRs, the range of TDCPP concentrations across all the cities was 2.1−280 pg/m^3 (39 ± 38 pg/m^3, n = 149) in the $PM_{2.5}$ samples, which was much lower than the corresponding values for TCPP and TCEP. Most studies in the indoor environment have shown the dominance of different compounds (TCPP, TCEP, or TDCPP) due to different types, amounts, and ages of flame retardant-treated products within these environments.[52] However, the similar concentration profiles of the three compounds (TCPP > TECP > TDCPP) observed in this study were consistent with the results from other nonurbanized outdoor environments and urban areas, which reflects the recent volumes of the flame retardants used in China (Figure 2).

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

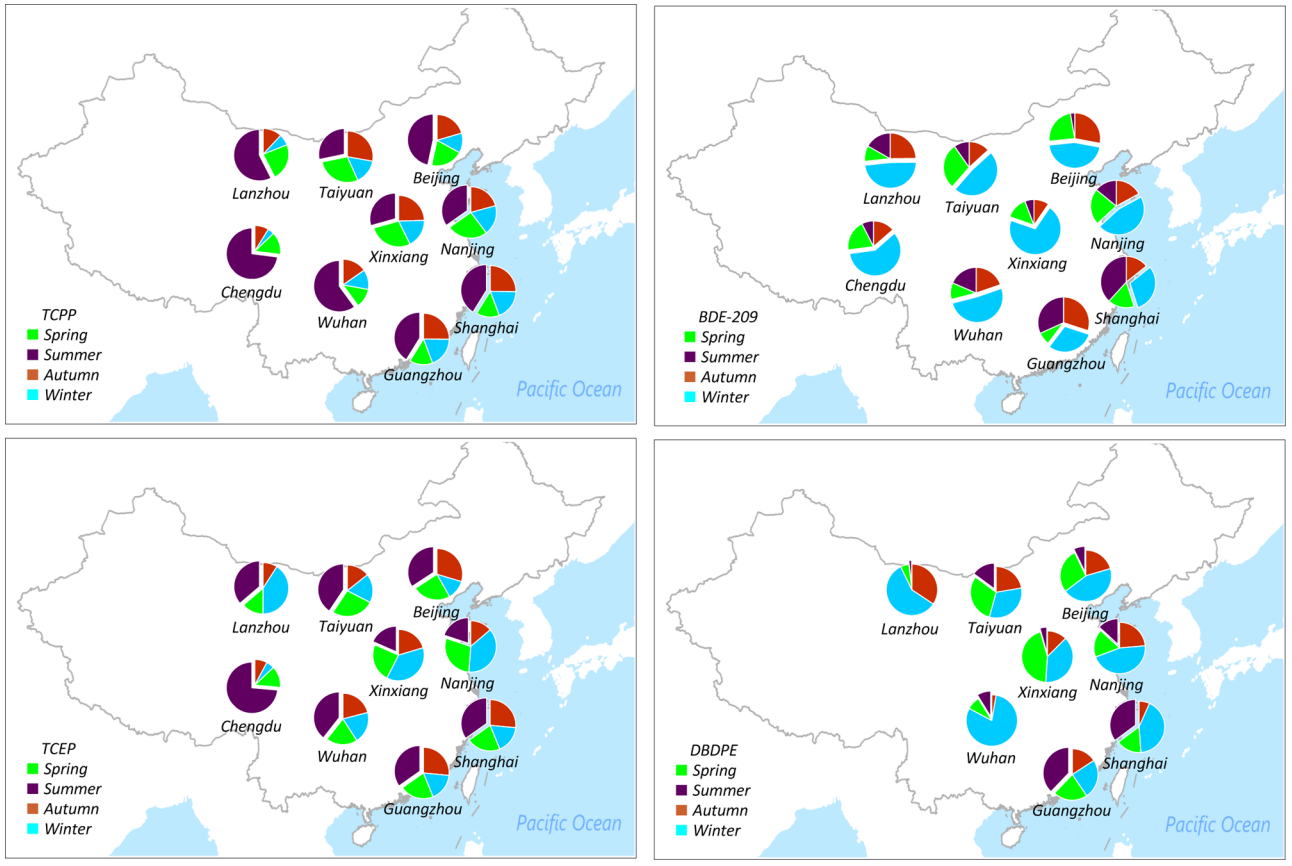


Figure 4. Pie charts represent the relative abundance of compounds in the $PM_{2.5}$ of nine urban cities during four seasons.

3.2. Spatial and Seasonal Variations and Associated Factors. The principal component analysis (PCA) method is an unsupervised, statistical, data-driven technique that is mostly suitable for databases that contain images with wide spatial and seasonal variation. Prior to analysis, the nondetectable values were reassigned with concentration values of one-half the detection limits. Then, the raw data matrix was Z-score standardized to eliminate the influence of different units and to give each determined variable an equal weighting in the PCA. PCA with varimax rotation was conducted using factor extraction with an eigenvalue >1 based on the covariance matrix. In this study, PCA was conducted to check the covariance of individual compounds that may originate from similar sources and/or experience a similar environmental fate based on variations in their concentrations. The PCA loading and score plots of all HFRs in $PM_{2.5}$ are shown in Figure 3. Most samples were concentrated in the area with low PC1 and PC2 scores, and no obvious seasonal or spatial separation was observed from the PCA score plot (in addition to sites that are not shown in the plot due to their extremely high values; see Figure 3a). The low scores for each site do not indicate a lack of contamination but rather proximity to the average level of regional contamination. They suggest that most HFRs had similar spatial or seasonal variation under the influence of meteorological parameters due to the homologous chemical and physical properties. It is also likely that the most targeted compounds had a wide range of sources across China, and most were still present at relatively uniform levels. However, the loading plot revealed a separation of compounds between BDE-209 and DBDPE and the chlorinated OPFRs, indicating that they might originate from different sources or have different fates in the air. PC1 explained 46% of the total variance, with a high loading of TCPP and TCEP. High scores were observed in the summer samples Wsu2, Gsu3, Ssu1, and Csu4 (in addition to Wsu4 and Csu2, which are not shown in the plot due to their extremely high values; see Figure 3a and SI Figure S2), reflecting the high levels of TCPP and TCEP pollution during the sampling periods. The second component (PC2, 23% of the total variance) had positive loadings for BDE-209 and DBDPE. Samples Lw2, Xw1, Xw4, Tw2, and Nw1 (in addition to Gw2 and Gw4, which are not shown in the plot due to their extremely high values; see Figure 3a and SI Figure S2) were collected in winter and were considered typical because of their very high BDE-209 and DBDPE concentrations. Moreover, the loading plot suggested a strong correlation between the $PM_{2.5}$ indices ($PM_{2.5}$ concentration, OC, and EC) and the low-brominated PBDEs (Figure 3b). The results indicated that gas absorption could be an important factor in controlling the variation of the concentration of the low-brominated species in the $PM_{2.5}$.

The major pollutants (BDE-209, DBDPE, TCPP, and TCEP) displayed significant seasonal variation (Figure 4 and SI Figure S3). For BDE-209, higher concentrations were found in winter, and lower concentrations were observed in summer. BDE-209 was mainly associated with particles in air due to its low vapor pressure (1.3×10^{-12} Pa) and high octanol−water partition coefficient (log K_{ow} = 9.97). Due to the strong dependence of air-particle partitioning on temperature, higher BDE-209 levels are associated with aerosol in the cold season. Particularly in North China, high BDE-209 in the wintertime is frequently characterized by high concentrations of fine particulate matter due to the domestic heating and favorable

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

conditions, for example, a more stable atmospheric boundary-layer. This may explain the high concentrations of BDE-209 observed in Xinxiang, Taiyuan, and Beijing during winter in this study. The situation was different in Guangzhou and Shanghai, where very high BDE-209 and DBDPE concentrations were observed in summer. The Pearl River Delta is one of China's leading economic regions and is a major global manufacturing center, and Guangzhou is located in the immediate region. The high concentration of BDE-209 in Guangzhou may be associated with emissions from the huge amounts of technical deca-BDE used in manufacturing plants and e-waste recycling activities in the surrounding area. Similarly, Shanghai is the center of the Yangtze River Delta Economic Circle. The higher abundance of BDE-209 in summer suggests that regional pollution and long-range transport have a significant influence on the seasonal distribution, consistent with previous studies.[19] Using air-mass back trajectories, we determined that the major potential source regions of BDE-209 were the areas near the coastal e-waste dismantling/recycling industry in Zhejiang Province, for example, Taizhou (SI Figure S4). High concentrations of TCPP were found in all seasons but were particularly significant in summer. In recent years, OPFRs have been widely used in a broad range of applications as a substitute for traditional HFRs. They are used as additives, but significant emissions to the environment can occur during the industrial and manufacturing processes or through volatilization, leaching, and abrasion throughout the entire lifetime of the products to which they are added. Unlike BDE-209, TCPP has relatively high vapor pressure (2.02×10^{-5} Pa) and a low octanol–water partition coefficient (log K_{ow} = 2.59). Higher temperatures promote the release of TCPP from various products into the atmosphere in the warm season. Temperature-dependent air-particle partitioning has less of an effect on the concentration of TCPP in the particle phase than it has for BDE-209. Thus, the concentrations and seasonal variation of TCPP observed in $PM_{2.5}$ indicated significant local sources of TCPP in the urban areas of China.

3.3. Human Exposure Assessment. Human exposure to HFRs can occur from air inhalation, dust ingestion, food consumption, and dermal contact. In this study, exposure was assessed only via air inhalation in the outdoor environment. The daily exposure dose (DED) of HFRs by $PM_{2.5}$ inhalation in the outdoor environment was calculated using equation<1>:

$$\mathrm{DEDPM}_{2.5} = C \times \mathrm{IR} \times T/\mathrm{BW} \quad (1)$$

where C is the sum of the HFR concentration in each sample (pg/m^3), IR is the inhalation rate (m^3/d), T is the exposure time in the outdoor environment (h), and BW is body weight (kg). The exposed persons were assumed to be adults. A mean daily inhalation rate of 16.0 m^3/day was used, and it was assumed that a person spends 6 h/day (i.e., $^1/_4$ of the day) in an outdoor environment. The body weight of an average adult is 60 kg. Because scant data are available for HFRs in outdoor air, except BDE-209, data for BDE-209 was used as a reference for comparison with other studies. In the outdoor environment, Fromme et al. reported an estimated DED of BDE-209 of 0.6, 0.6, and 0.3 pg/kg-BW/day for an average adult in Germany, the UK, and the U.S., respectively.[53] Li et al. reported that 1.2 pg/kg-BW/day $PM_{2.5}$-bound BDE-209 may be inhaled deep into the lungs and reach the pulmonary alveoli based on research in Shanghai.[9] He et al. estimated that the DEDs of the particulate BDE-209 for an adult group ranged from 0.13 to 7.1 pg/kg-BW/day (mean of 1.2 pg/kg-BW/day) at an urban site and from 0.08 to 6.1 pg/kg-BW/day (mean of 0.69 pg/kg-BW/day) at a rural site near Lake Chaohu, China.[54] In this study, the mean exposure levels of 12 pg/kg-BW/day and 83 pg/kg-BW/day were observed in Guangzhou for BDE-209 and HFRs, indicating high exposure risk. Overall, the estimated $\mathrm{DEDPM}_{2.5}$ values for all HFRs were 3.2–160 pg/kg-BW/day, with a mean value of 49 ± 33 pg/kg-BW/day (SI Figure S5). Most importantly, the estimated results indicated that the DEDs of all HFRs were much higher than the DEDs of BDE-209, although the systemic toxicity of individual compounds was not considered. Thus, the exposure pathway and toxicological data of emerging HFRs, especially chlorinated OPFRs, are urgently needed to enable an appropriate risk assessment.

Geographically, higher exposure risks were observed in large cities, such as Guangzhou, Shanghai, Wuhan, and Chengdu. In contrast, lower exposure risks were found in undeveloped areas, such as Lanzhou and Guiyang (SI Figure S5). This suggests that the increase in exposure risk in urban areas is accompanied by an even faster increase in economic development and consumption of household products. A strong correlation was observed between the mean value of DED and the size of the local population, indicating that residents in larger cities had a higher risk of exposure to various levels of HFR contamination (SI Figure S5). Therefore, further studies are needed to identify exposure sources in addition to e-waste recycling sites to reduce the exposure risk of residents in larger cities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01685.

Brief statements in nonsentence format on the detailed sampling information, method detection limit of the targeted compounds, statistical summary of the data set, results of the backward trajectories, and seasonal variation (pie and bar charts) are provided (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone/fax: (86)-851-85895239; e-mail: lintian@vip.gyig.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Key Technology Research and Development Program of the Ministry of Science and Technology of China (2014BAC22B04), the National Scientific Foundation of China (41390242, 41573134) and the Joint Funds of the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province, China (No. U1501234).

■ REFERENCES

(1) Wikipedia. 2016. https://en.wikipedia.org/wiki/Flame_retardant.

(2) Zhang, X.; Sühring, R.; Serodio, D.; Bonnell, M.; Sundin, N.; Diamond, M. L. Novel flame retardants: Estimating the physical–chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. *Chemosphere* **2016**, *144*, 2401–2407.

(3) Stapleton, H. M.; Allen, J. G.; Kelly, S. M.; Konstantinov, A.; Klosterhaus, S.; Watkins, D.; McClean, M. D.; Webster, T. F. Alternate

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846–9854

and New Brominated Flame Retardants Detected in U.S. House Dust. *Environ. Sci. Technol.* **2008**, *42* (18), 6910−6916.
(4) Dodson, R. E.; Perovich, L. J.; Covaci, A.; Van den Eede, N.; Ionas, A. C.; Dirtu, A. C.; Brody, J. G.; Rudel, R. A. After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California. *Environ. Sci. Technol.* **2012**, *46* (24), 13056−13066.
(5) Qi, H.; Li, W. L.; Liu, L. Y.; Song, W. W.; Ma, W. L.; Li, Y. F. Brominated flame retardants in the urban atmosphere of Northeast China: Concentrations, temperature dependence and gas−particle partitioning. *Sci. Total Environ.* **2014***491*−*492*, 60−66.10.1016/j.scitotenv.2014.03.002
(6) Tian, M.; Chen, S. J.; Wang, J.; Zheng, X. B.; Luo, X. J.; Mai, B. X. Brominated Flame Retardants in the Atmosphere of E-Waste and Rural Sites in Southern China: Seasonal Variation, Temperature Dependence, and Gas-Particle Partitioning. *Environ. Sci. Technol.* **2011**, *45* (20), 8819−8825.
(7) Cheng, Z.; Luo, L.; Wang, S.; Wang, Y.; Sharma, S.; Shimadera, H.; Wang, X.; Bressi, M.; de Miranda, R. M.; Jiang, J.; Zhou, W.; Fajardo, O.; Yan, N.; Hao, J. Status and characteristics of ambient PM2.5 pollution in global megacities. *Environ. Int.* **2016**, *89*−*90*, 212−221.
(8) Pui, D. Y. H.; Chen, S. C.; Zuo, Z. PM2.5 in China: Measurements, sources, visibility and health effects, and mitigation. *Particuology* **2014**, *13*, 1−26.
(9) Li, Y.; Chen, L.; Ngoc, D. M.; Duan, Y. P.; Lu, Z. B.; Wen, Z. H.; Meng, X. Z. Polybrominated Diphenyl Ethers (PBDEs) in PM2.5, PM10, TSP and Gas Phase in Office Environment in Shanghai, China: Occurrence and Human Exposure. *PLoS One* **2015**, *10* (3), e0119144.
(10) Zhang, A.; Qi, Q.; Jiang, L.; Zhou, F.; Wang, J. Population Exposure to PM2.5in the Urban Area of Beijing. *PLoS One* **2013**, *8* (5), e63486.
(11) Li, Y.; Lin, T.; Hu, L.; Feng, J.; Guo, Z. Time trends of polybrominated diphenyl ethers in East China Seas: Response to the booming of PBDE pollution industry in China. *Environ. Int.* **2016**, *92*−*93*, 507−514.
(12) Hayakawa, K.; Takatsuki, H.; Watanabe, I.; Sakai, S. I. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. *Chemosphere* **2004**, *57* (5), 343−356.
(13) Mandalakis, M.; Besis, A.; Stephanou, E. G. Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. *Environ. Pollut.* **2009**, *157* (4), 1227−1233.
(14) Lee, R. G. M.; Thomas, G. O.; Jones, K. C. PBDEs in the Atmosphere of Three Locations in Western Europe. *Environ. Sci. Technol.* **2004**, *38* (3), 699−706.
(15) Hoh, E.; Hites, R. A. Brominated Flame Retardants in the Atmosphere of the East-Central United States. *Environ. Sci. Technol.* **2005**, *39* (20), 7794−7802.
(16) Cetin, B.; Odabasi, M. Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Chemosphere* **2008**, *71* (6), 1067−1078.
(17) Birgul, A.; Katsoyiannis, A.; Gioia, R.; Crosse, J.; Earnshaw, M.; Ratola, N.; Jones, K. C.; Sweetman, A. J. Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom. *Environ. Pollut.* **2012**, *169*, 105−111.
(18) 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**, DOI: 10.1016/j.envpol.2016.01.079.
(19) Li, Y.; Lin, T.; Wang, F.; Ji, T.; Guo, Z. Seasonal variation of polybrominated diphenyl ethers in PM2.5 aerosols over the East China Sea. *Chemosphere* **2015**, *119*, 675−681.
(20) Wang, W.; Zheng, J.; Chan, C.-Y.; Huang, M.-j.; Cheung, K. C.; Wong, M. H. Health risk assessment of exposure to polybrominated diphenyl ethers (PBDEs) contained in residential air particulate and dust in Guangzhou and Hong Kong. *Atmos. Environ.* **2014**, *89*, 786−796.
(21) Deng, W. J.; Zheng, J. S.; Bi, X. H.; Fu, J. M.; Wong, M. H. Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environ. Int.* **2007**, *33* (8), 1063−1069.
(22) Chen, D.; Bi, X.; Liu, M.; Huang, B.; Sheng, G.; Fu, J. Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site. *Chemosphere* **2011**, *82* (9), 1246−1252.
(23) Gouin, T.; Thomas, G. O.; Chaemfa, C.; Harner, T.; Mackay, D.; Jones, K. C. Concentrations of decabromodiphenyl ether in air from Southern Ontario: Implications for particle-bound transport. *Chemosphere* **2006**, *64* (2), 256−261.
(24) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* **2001**, *275* (1−3), 1−17.
(25) Kierkegaard, A.; Björklund, J.; Fridén, U. Identification of the Flame Retardant Decabromodiphenyl Ethane in the Environment. *Environ. Sci. Technol.* **2004**, *38* (12), 3247−3253.
(26) Watanabe, I.; Sakai, S. I. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29* (6), 665−682.
(27) Möller, A.; Xie, Z.; Cai, M.; Zhong, G.; Huang, P.; Cai, M.; Sturm, R.; He, J.; Ebinghaus, R. Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic. *Environ. Sci. Technol.* **2011**, *45* (16), 6793−6799.
(28) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820−1826.
(29) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. *Environ. Int.* **2011**, *37* (2), 532−556.
(30) Hoh, E.; Zhu; Hites, R. A. Novel Flame Retardants, 1,2-Bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-Pentabromoethylbenzene, in United States' Environmental Samples. *Environ. Sci. Technol.* **2005**, *39* (8), 2472−2477.
(31) Qiu, X.; Zhu, T.; Hu, J. Polybrominated diphenyl ethers (PBDEs) and other flame retardants in the atmosphere and water from Taihu Lake, East China. *Chemosphere* **2010**, *80* (10), 1207−1212.
(32) Xiao, H.; Shen, L.; Su, Y.; Barresi, E.; DeJong, M.; Hung, H.; Lei, Y. D.; Wania, F.; Reiner, E. J.; Sverko, E.; Kang, S. C. Atmospheric concentrations of halogenated flame retardants at two remote locations: The Canadian High Arctic and the Tibetan Plateau. *Environ. Pollut.* **2012**, *161*, 154−161.
(33) OxyChem, OxyChem's official website about Dechlorane Plus. http://www.oxy.com/Our_Businesses/chemicals/Documents/dechlorane_plus/dechlorane_plus.pdf. 2004.
(34) Li, W. L.; Liu, L. Y.; Song, W. W.; Zhang, Z. F.; Qiao, L. N.; Ma, W. L.; Li, Y. F. Five-year trends of selected halogenated flame retardants in the atmosphere of Northeast China. *Sci. Total Environ.* **2016**, *539*, 286−293.
(35) Yu, Z.; Liao, R. e.; Li, H.; Mo, L.; Zeng, X.; Sheng, G.; Fu, J. Particle-bound Dechlorane Plus and polybrominated diphenyl ethers in ambient air around Shanghai, China. *Environ. Pollut.* **2011**, *159* (10), 2982−2988.
(36) Ren, N.; Sverko, E.; Li, Y. F.; Zhang, Z.; Harner, T.; Wang, D.; Wan, X.; McCarry, B. E. Levels and Isomer Profiles of Dechlorane Plus in Chinese Air. *Environ. Sci. Technol.* **2008**, *42* (17), 6476−6480.
(37) Vorkamp, K.; Bossi, R.; Rigét, F. F.; Skov, H.; Sonne, C.; Dietz, R. Novel brominated flame retardants and dechlorane plus in Greenland air and biota. *Environ. Pollut.* **2015**, *196*, 284−291.
(38) Salamova, A.; Hermanson, M. H.; Hites, R. A. Organophosphate and Halogenated Flame Retardants in Atmospheric Particles from a European Arctic Site. *Environ. Sci. Technol.* **2014**, *48* (11), 6133−6140.

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854

(39) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-Scale Distribution of Dechlorane Plus in Air and Seawater from the Arctic to Antarctica. *Environ. Sci. Technol.* **2010**, *44* (23), 8977−8982.
(40) Yu, Y.; Hung, H.; Alexandrou, N.; Roach, P.; Nordin, K. Multiyear Measurements of Flame Retardants and Organochlorine Pesticides in Air in Canada's Western Sub-Arctic. *Environ. Sci. Technol.* **2015**, *49* (14), 8623−8630.
(41) Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a Chlorinated Flame Retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40* (4), 1184−1189.
(42) Chen, S.-J.; Tian, M.; Wang, J.; Shi, T.; Luo, Y.; Luo, X.-J.; Mai, B.-X. Dechlorane Plus (DP) in air and plants at an electronic waste (e-waste) site in South China. *Environ. Pollut.* **2011**, *159* (5), 1290−1296.
(43) Wang, D. G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W. L.; Li, Y. F.; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-Specific Source of Dechlorane Plus: Concentration, Isomer Profiles, and Other Related Compounds. *Environ. Sci. Technol.* **2010**, *44* (17), 6608−6613.
(44) Reemtsma, T.; Quintana, J. B.; Rodil, R.; García-López, M.; Rodríguez, I. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *TrAC, Trends Anal. Chem.* **2008**, *27* (9), 727−737.
(45) van der Veen, I.; de Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012**, *88* (10), 1119−1153.
(46) Salamova, A.; Ma, Y.; Venier, M.; Hites, R. A. High Levels of Organophosphate Flame Retardants in the Great Lakes Atmosphere. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 8−14.
(47) Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. *Environ. Pollut.* **2011**, *159* (12), 3660−3665.
(48) Marklund, A.; Andersson, B.; Haglund, P. Traffic as a Source of Organophosphorus Flame Retardants and Plasticizers in Snow. *Environ. Sci. Technol.* **2005**, *39* (10), 3555−3562.
(49) Castro-Jiménez, J.; Berrojalbiz, N.; Pizarro, M.; Dachs, J. Organophosphate Ester (OPE) Flame Retardants and Plasticizers in the Open Mediterranean and Black Seas Atmosphere. *Environ. Sci. Technol.* **2014**, *48* (6), 3203−3209.
(50) Lai, S.; Xie, Z.; Song, T.; Tang, J.; Zhang, Y.; Mi, W.; Peng, J.; Zhao, Y.; Zou, S.; Ebinghaus, R. Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. *Chemosphere* **2015**, *127*, 195−200.
(51) Regnery, J.; Püttmann, W. Organophosphorus Flame Retardants and Plasticizers in Rain and Snow from Middle Germany. *Clean: Soil, Air, Water* **2009**, *37* (4−5), 334−342.
(52) Hartmann, P. C.; Bürgi, D.; Giger, W. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere* **2004**, *57* (8), 781−787.
(53) Fromme, H.; Becher, G.; Hilger, B.; Völkel, W. Brominated flame retardants − Exposure and risk assessment for the general population. *Int. J. Hyg. Environ. Health* **2016**, *219* (1), 1−23.
(54) He, W.; Qin, N.; He, Q. S.; Kong, X. Z.; Liu, W. X.; Wang, Q. M.; Yang, C.; Jiang, Y. J.; Yang, B.; Bai, Z. L.; Wu, W. J.; Xu, F. L. Atmospheric PBDEs at rural and urban sites in central China from 2010 to 2013: Residual levels, potential sources and human exposure. *Environ. Pollut.* **2014**, *192*, 232−243.

DOI: 10.1021/acs.est.6b01685
Environ. Sci. Technol. 2016, 50, 9846−9854