Atmospheric Deposition of Halogenated Flame Retardants at Urban, E-Waste, and Rural Locations in Southern China

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Ⓢ *Supporting Information*

ABSTRACT: Measurements of atmospheric deposition fluxes and temporal variation of halogenated flame retardants (HFRs) from 2007 to 2008 at urban, electronic waste (e-waste), and rural sites in southern China are presented. The deposition fluxes of total HFRs at the urban (99.3−1327 ng m^{-2} day^{-1}) and e-waste (79.1−1200 ng m^{-2} day^{-1}) sites were much higher than at the rural site (9.27−79.5 ng m^{-2} day^{-1}), demonstrating that e-waste recycling and industrial activities in southern China are two important sources of HFRs in the environment. The urban deposition profile was dominated by current-use HFRs (decabrominated diphenyl ether and decabromodiphenyl ethane), whereas the profile at the e-waste site reflects the past when significant amounts of PBDEs and Dechlorane Plus were used. Source apportionment estimated by principal component analyses with multiple linear regression analysis showed that deposition HFRs at the rural site were primarily contributed by the urban and e-waste sources (45% and 38%, respectively) compared to the contribution from local emission (17%). Our results suggest that the HFRs that are readily present in gas or sorbed onto fine particle phases have enhanced potential for long-range atmospheric transport.
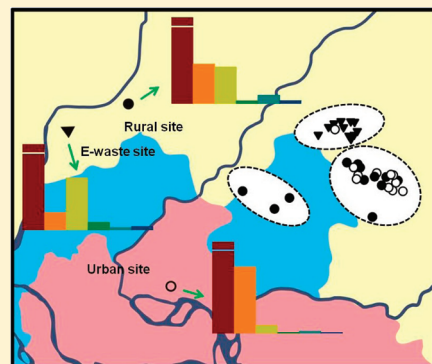
■ INTRODUCTION

Due to the increasing production and use of various consumer products brominated and chlorinated flame retardants have become important classes of flame retardants, which are widely used in textiles, furniture, electronics, and automotive interiors. Most of these halogenated flame retardants (HFRs) are physically mixed into products and are readily released into the environment. However, many HFRs exhibit persistence, bioaccumulation, and long-range transport properties similar to many semivolatile organic compounds (SOCs) and have been frequently detected in the environment, even though adequate toxicity information for these chemicals is lacking.[1,2] As a major class of HFRs, some polybrominated diphenyl ethers (PBDEs) have been included in the newly listed persistent organic pollutants of the 2009 Stockholm Convention. Hexabromocyclododecane (HBCD) is under evaluation because of its ubiquitous presence and concerns about its potential deleterious effects on humans and wildlife.[3] Due to bans or restriction on PBDEs in some regions of the world, there is increasing evidence of the environmental occurrence of some nonregulated flame retardants.[4,5]

Atmospheric deposition constitutes an important input pathway for delivering SOCs to aquatic and terrestrial ecosystems. SOCs can be removed from the atmosphere via dry particle deposition, wet deposition, gaseous adsorption, and atmospheric transformation.[6] While numerous studies in different regions have monitored the atmospheric deposition of SOCs, most of them were conducted at background locations away from the local sources.[7] Atmospheric deposition and behaviors of SOCs (especially HFRs) near emission sources have not been adequately investigated.

Recent investigations from southern China have raised serious concerns about the extensive contamination of HFRs in urban and electronic waste (e-waste) recycling areas.[8,9] Although HFR levels (particularly of PBDEs) in the air from urban and e-waste areas have been reported previously,[10,11] data are scarce with respect to their sources and environmental behaviors in the atmosphere. In the present study, deposition samples were collected at three different types of locations (urban, e-waste, and rural) in southern China and were analyzed for a group of additive HFRs. We aimed to examine the atmospheric deposition fluxes and temporal variations of HFRs in these areas and to evaluate the influence of HFRs from the urban and e-waste areas on the rural area. We also aimed to understand the current emission sources and profiles as well as the environmental behaviors of HFRs in the atmosphere, particularly after the 2006 restrictions on two technical PBDE mixtures in China.

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■ EXPERIMENTAL SECTION

Sample Collection. The urban site is located in Guangzhou City within the Pearl River Delta (PRD) region, a highly urbanized and industrialized region of China (Figure S1, Supporting Information (SI)). The e-waste site is located in the rural area of Qingyuan, ~70 km north of the urban site. A large amount of e-waste (~700 000 t) is processed each year within an area of 330 km^2 around this site using primitive methods (e.g., mechanical shredding, acid processing, and open burning).[12] The rural site is located in a rural agricultural area 25 km northeast of the e-waste site and with no e-waste recycling or industrial activities. The studied area has a subtropical climate, with an annual average temperature of ~22 °C. Rainfall between April and September (wet season) accounts for over 80% of the year compared to that (<20%) between October and March (dry season) with an annual average of ~200 cm.

Bulk atmospheric deposition samples were obtained from October 2007 to September 2008 using round stainless steel buckets with an inner diameter of 85 cm and height of 27 cm. The samplers were placed on buildings at the urban and e-waste sites and on the ground at the rural site (1.2 m above the rooftop or ground). Different amounts (5−20 L) of purified water (depending on the season) and copper sulfate were added to each sampler to reduce the resuspension loss of deposited particles and to prevent algal growth.[13] The samples were collected monthly (each sample for a whole month).

Sample Preparation and Instrumental Analysis. The detailed analytical method is provided in the SI. Briefly, HFRs including PBDEs, decabromodiphenyl ethane (DBDPE), 1,2-*bis*-(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), hexabromobenzene (HBB), 2,3,5,6-tetrabromo-*p*-xylene (pTBX), polybrominated biphenyls (PBBs), and Dechlorane Plus (DP) were analyzed using a gas chromatograph coupled to mass spectrometer in electron capture negative ionization mode (GC-ECNI-MS). HBCD diastereomers (α-, β-, and γ-) were separated and quantified with a liquid chromatography (LC) and MS/MS in electrospray negative ionization (ESI) mode.

Quality Control. A procedural blank and a spiked blank (clean baked filter) were processed for each batch of 11 field samples. Only trace amounts of BDE47, 99, and 209 and DBDPE were found in the blanks (<1.2% of their amounts in the sample extracts) and the concentrations in the sample extracts were blank corrected using the corresponding blank values. The recoveries of the surrogate standards were 95.9 ± 11.5% for BDE77, 86.5 ± 13.6% for BDE181, and 93.8 ± 15.2% for ^{13}C-PCB141. The recoveries of target compounds were 62.5%−142% (standard deviations <16.1%) in the spiked blanks and 78.6%−122% (<14.6%) in the six matrix spiked samples (extracted air filters). The repeatability of analysis was assessed by analyzing five air filter replicates. The relative standard deviations were within 1.12%−21.7%. Reported concentrations were not surrogate-recovery corrected. The method detection limits, defined as the mean blank mass plus three standard deviations, were between 0.01 and 0.90 ng/g based on an average deposition particle mass of 1.4 g.

■ RESULTS AND DISCUSSION

Temporal Patterns. Figure 1 shows the temporal patterns of deposition fluxes of HFRs and particles during the sampling year for the three sites. At the urban site, the deposition fluxes of total HFRs varied from 79.1 to 1200 ng m^{-2} day^{-1}, with higher
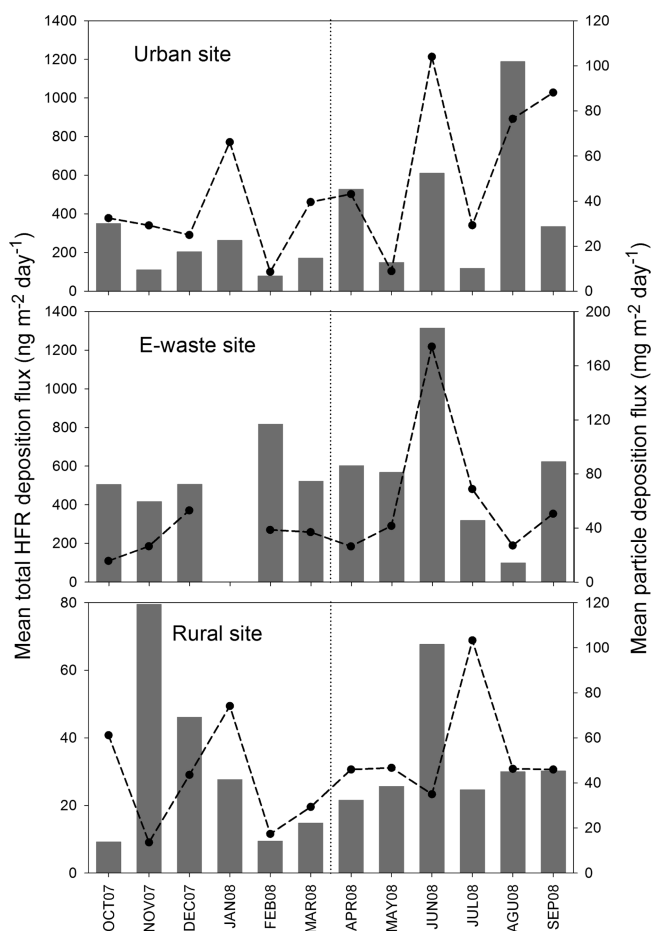
Figure 1. Temporal distributions of the mean HFR (bars) and particle (dots) deposition fluxes (October 2007−September 2008) at the urban, e-waste, and rural sites. The vertical dotted lines make a distinction between the dry (left) and wet (right) seasons.

deposition fluxes occurring in the wet season (with a mean value of 491 ng m^{-2} day^{-1}) than in the dry season (with a mean value of 197 ng m^{-2} day^{-1}). The monthly HFR deposition fluxes exhibited a significant relationship with particle deposition fluxes at this site ($p = 0.03$), suggesting that the scavenging of these HFRs from the atmosphere is largely associated with particles. Relative to the urban site, HFR deposition fluxes at the e-waste site varied less, with most data ranging from 400 to 600 ng m^{-2} day^{-1}. Although the highest value (1327 ng m^{-2} day^{-1}) occurred during the wet season, the deposition fluxes during the wet and dry seasons were similar (with mean values of 592 versus 557 ng m^{-2} day^{-1}). Data from January 2008 are missing because one sample was ruined.

There was also large variation in the HFR deposition fluxes at the rural site (9.27−79.5 ng m^{-2} day^{-1}) but no clear seasonal pattern. The high deposition fluxes in November and December 2007 were attributed to unexpectedly high amounts of PBDE congeners derived from technical penta-BDE mixture. If these congeners were excluded, a pronounced seasonal pattern with higher deposition fluxes during the wet season was observed (SI Figure S2). In addition, the prevailing southerly wind during the wet season facilitated transport of pollutants from the urban and e-waste areas to this site. There were no significant relationships between the HFR and particle fluxes for the e-waste and rural
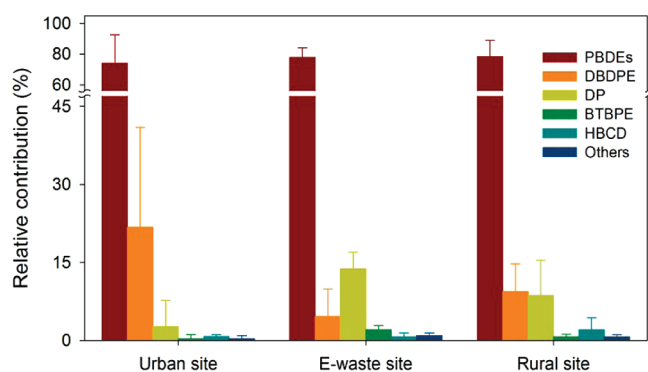
Figure 2. Atmospheric deposition profiles of HFRs in the urban, e-waste, and rural sites.

sites. This result may be attributed to the heterogeneity of deposition particles in the rural area, which consist of coarser particles derived from agricultural fields. In contrast, urban deposition particles consist of abundant fine carbonaceous particles emitted from automobiles and industry and are strongly associated with SOCs including HFRs.[14]

Although rainfall is a crucial mechanism for removing pollutants from the atmosphere, significant relationships between the deposition flux and rainfall were observed for only a few HFRs at the sites (SI Table S1). One reason is that the temporal variations and deposition fluxes are related to the strength of emission sources in addition to the ambient meteorological and climatic conditions. Another reason is probably that pollutants are largely washed off in the initial stage of a rainfall event. Thus, the temporal pattern at the e-waste site probably indicated a steady emission of HFRs into the ambient environment that resulted from e-waste recycling.

Spatial Differences and Deposition Profiles. The annual deposition fluxes of particulate matter were similar among the three sites, with mean values of 16.8, 18.5, and 17.1 g m^{-2} yr^{-1} at the urban, e-waste, and rural sites, respectively. PBDEs constituted the most important group of HFRs at all the sites, with average contributions of 74.1−78.5% to the fluxes (Figure 2). As expected, the annual deposition fluxes of PBDEs were the highest at the e-waste site (165 000 ng m^{-2} yr^{-1}) (SI Table S2). The deposition flux of PBDEs at the urban site (79 900 ng m^{-2} yr^{-1}) was lower than that at the e-waste site by a factor of 2, while it was approximately 1 order of magnitude higher than the deposition flux at the rural site (9860 ng m^{-2} yr^{-1}). The dominance of PBDEs is attributed to the wide use of PBDEs (especially deca-BDE mixture) in various products over many years.[15] It is noteworthy that PBDE congeners that are derived from technical penta- and octa-BDE mixtures were present in significant amounts in all of the deposition samples despite their phased-out in China since 2006.[21] Together they accounted for 1.4%, 4.3%, and 4.7% (on average) of the HFRs in the urban, e-waste, and rural samples, respectively (except for three rural samples with contributions >40%). This finding suggests that the emission sources of these congeners are still significant. They could originate from products treated with these mixtures before and/ or from historically contaminated environmental media. Their higher proportion at the rural site may also contributed by atmospheric transport, as further discussed below.

DBDPE exhibited the second most dominant HFR deposition fluxes (21.8%) at the urban site, with a value of 41 600 ng m^{-2} yr^{-1};

however, its deposition flux at the e-waste site was only 9780 ng m^{-2} yr^{-1} and has a low proportion (4.6%) of the total deposition. This is not surprising, as DBDPE is marketed as an alternative to the deca-BDE mixture introduced in the 1990s[16] and has become one of the major flame retardant products currently used in China;[17] however, it was not used in substantial quantities in obsolete electronic products. The deposition flux and contribution of DBDPE at the rural site was only 850 ng m^{-2} yr^{-1} and 9.4% of the total deposition.

Studies motivated by recent concerns about DP have shown its wide occurrence in the environment.[18,19] DP showed significant amounts in the deposition samples from the e-waste site (27 900 ng m^{-2} yr^{-1}) and accounted for 13.7% of the total flux of HFRs. The deposition fluxes at the urban and rural sites were relatively lower, with contributions of only 2.6% and 8.7%, respectively. The high deposition flux and contribution of DP at the e-waste site suggest that it has been used in large amounts overseas, as the e-waste recycled in southern China is mostly imported from overseas. This finding is consistent with previous results from the Great Lakes (U.S.A.) that DP in core sediments reached its peak level in the mid-1990s.[19] The deposition fluxes of BTBPE (a replacement of octa-BDE mixture), with values between 73.0 and 4380 ng m^{-2} yr^{-1} in the studied area, followed the same spatial pattern as that of DP. Few data were available on HBCD in the atmospheric environment in China.[20] The deposition fluxes of HBCD were 1520, 920, and 193 ng m^{-2} yr^{-1} at the e-waste, urban, and rural sites, respectively. HBCD had a higher proportion (2.0%) at the rural site than at the e-waste (0.69%) and urban (0.76%) sites, possibly implying the great potential for atmospheric transport of HBCD compared to other HFRs because of its higher vapor pressure (SI Table S3). The deposition fluxes of other HFRs (pTBX, PBT, HBB, PBBs, and PBEB) were considerably lower and were all found in amounts that followed an order of e-waste site > urban site > rural site. In total, they accounted for less than 1.0% of the HFR fluxes.

The spatial differences in the HFR deposition fluxes from these sites demonstrate that both e-waste recycling and industrial activities serve as two important emission sources of these chemicals to the environment of southern China. The deposition profiles of HFRs reveal that e-waste recycling is a major source of those HFRs that were used historically, while industrial activities in southern China release predominantly PBDEs and DBDPE that are in current use. Although many of these flame retardants (such as DP, BTBPE, and HBCD) are manufactured and used in China, our results indicate that these HFRs are used in small quantities in southern China compared to deca-BDE mixture and DBDPE. The rural deposition profile with medium contributions of DPBDE and DP implies an influence from both the urban and e-waste areas.

Very limited data are available for comparison with the HFR deposition fluxes measured in this study. The deposition fluxes of PBDEs reported from urban/industrial areas in Turkey and Korea were 54 000 and 42 500 ng m^{-2} yr^{-1}, respectively.[21,22] The PBDE deposition fluxes to the Great Lakes ranged from 1180 to 5360 ng m^{-2} yr^{-1}.[23] These values are lower than the deposition fluxes observed in the present study. Hermanson et al.[24] recently found that deposition fluxes to the ice sheet in Svalbard (Norway) were the highest for HBCD and BDE209 (9100 and 3200 ng m^{-2} yr^{-1}, respectively) and were much lower (<60 ng m^{-2} yr^{-1}) for other HFRs (DBDPE, BTBPE, and PBEB), following the usage trends of these chemicals in Europe. It should be noted that the measurements could be affected by the methodologies used in these studies. The sampling technique in the present study may have its limitations in measuring atmospheric deposition to nonaqueous surfaces.
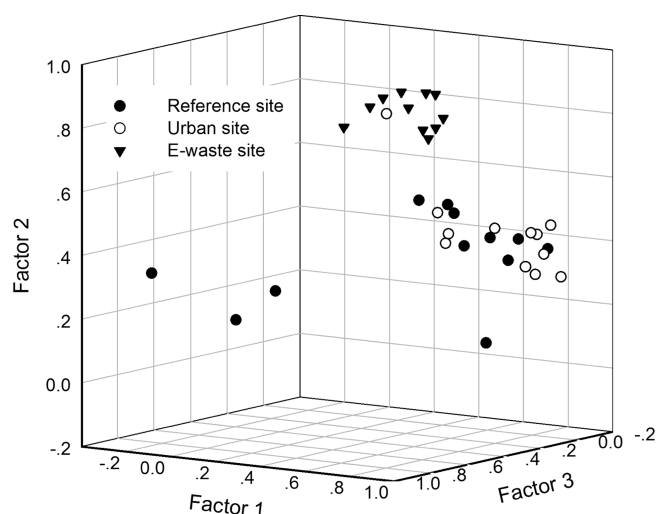
Figure 3. Loading plot of the principal component analysis (PCA) for the deposition samples from the urban, e-waste, and rural sites.

Figure 4. Ratios of average percentage contributions of the individual HFRs in the rural versus urban samples and the rural versus e-waste samples (excluding three rural samples with high "penta-BDE" concentrations). HFRs are arranged in order of decreasing low vapor pressures or increasing K_{OA} (SI Table S3).

Deposition Rates. Since the bulk deposition samples from each sampling session remained in the buckets for one month, the observed deposition fluxes reflect the net deposition rates. Thus, we determined the net total HFR deposition rates (= deposition flux × area) of HFRs to the urban (Guangzhou) and e-waste areas. Because the rural region covers a very large area (SI Figure S1) and the deposition fluxes may vary significantly with distance from the source (urban and e-waste) regions, the rural deposition rate was not calculated. The overall deposition rate of HFRs to the urban area (500 kg yr^{-1}) is 1 order of magnitude higher than that to the e-waste area (70 kg yr^{-1}). This is because of the much larger area of urban development (4000 km^2) compared to the e-waste area (330 km^2). The depletion of low-brominated PBDEs in the deposition samples compared to the air[10] suggests net volatilization of these compounds from warm to cold regions of the earth (global distillation). Zhang et al.[25] recently estimated a deposition rate of 10 000 kg yr^{-1} for PBDEs in the PRD region (54 000 km^2) in 2006−2007. Assuming that HFR deposition at the urban site represents that of the PRD, the deposition rate of PBDEs to the PRD would be 4300 kg yr^{-1} based on our data. The likely reasons for this difference are that the deposition rate in their study was estimated based on air concentrations and washout ratios, without considering the volatilization from ground/water to the air and that the samples in the two studies were collected at different locations and time.

Source Identification and Apportionment. SI Table S4 summarizes the factor loadings of the 26 variables in principal component analysis (PCA) (Data Analysis in the SI). For the urban site, the first factor (factor 1) is dominated by particle and deca-BDE-derived congeners. It also shows positive correlations with DBDPE and BTBPE (which have low vapor pressures) suggesting the association of these HFRs with particles. Factor 2 represents a mixed source of non-PBDE HFRs (HBB, BTBPE, DP, and HBCD) and a penta-BDE mixture. Factor 3 is also a source of penta-BDE mixture but mostly for low-brominated congeners. The separation of the penta-BDE-mixture source is possibly a result of the different environmental behaviors of the congeners. Factor 4 contains BDE202, BDE209, DBDPE, and HBCD. BDE202 is thought to be a marker of environmental debromination of BDE209;[26] this process may occur in the air
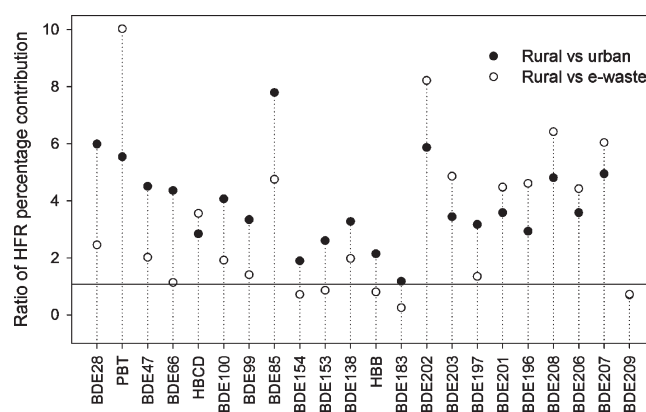
and/or after deposition. Thus, this factor may suggest the influence of environmental breakdown on these HFRs (although the breakdown of DBDPE and HBCD has rarely been investigated).[27] Positive factor loadings of PBT and BDE28 were observed for factor 5. These two compounds have the highest vapor pressures and are removed from the air mainly via gaseous adsorption.

For the e-waste site, most of the HFRs show high factor loadings in factor 1, suggesting their common source from e-waste recycling. Factor 2 involves BDE28, PBT, BDE202, and DBDPE. Likewise, this factor may reflect the different scavenging pathways and environmental breakdown. Factor 3 clearly represents the particle source, which differs from the HFR sources (as indicated above). For the rural site, factors 1 and 2 are characteristic of PBDEs from penta- and deca-BDE mixtures, respectively, and are identified as sources of these mixtures. Factor 3 is highly loaded in some non-PBDE HFRs and BDE183 derived from octa-BDE mixture. Factor 4 shows good correlations with PBT, HBCD and particles. We speculated that a significant amount of PBT and HBCD in the rural area might originate from resuspension from local soils because SOCs with high vapor pressures (SI Table S3) tend to travel long distances and deposit to soils. This source may become prominent when other sources (from urban or e-waste sites) are weak. High loading of BDE202 in factor 5 identifies this factor as a breakdown source.

In the factor-loading plot, PCA performed on all of the deposition samples from the sites divided them into three discrete clusters (Figure 3). Most samples from the urban and rural sites fall into one group that is related to factor 1, whereas samples from the e-waste site collectively show high factor loadings in factor 2. This demonstrates the different sources of HFRs in the urban and e-waste areas and also implies that HFRs in the air of the rural site are largely affected by the urban area instead of the e-waste area. There is one urban sample present in the e-waste sample group, suggesting an influence from the e-waste area on the urban area during this sampling month. This urban sample was collected in January 2008 when the northerly wind is dominant. It showed noticeably high deposition fluxes of DP and BTBPE, which are two of the major HFRs at the e-waste site. Unfortunately, the HFR deposition fluxes in this month at the e-waste site are not available. Factor 3 shows correlation with three samples from the rural site, implying different sources for these samples from others at this site. These samples had

extremely high values for penta-BDE-derived PBDEs (SI Table S2). A possible explanation is that this was caused by occasional contamination with penta-BDE-containing material particles (for example, particles migrating from worn furniture to the ground and subsequently to the collection buckets).

Source apportionment estimated by PCA with multiple linear regression analysis showed that the urban source is responsible for 45% of the HFRs at the rural site. In contrast and despite its proximity, the e-waste source contributes 38% to the rural HFRs. This provides evidence that industrial activities are a more important source of HFRs to rural areas in southern China relative to e-waste recycling because of their much larger magnitude. Other sources (likely local emission) account for 17% of the HFRs at the rural site.

Implications for Environmental Processes. SOCs will be subject to different environment processes after being released into the environment. There are different observations on the potential for long-range atmospheric transport (LRAT) of particle- and gas-phase SOCs. Wania et al.[28] found that particle-bound highly brominated PBDEs have a very low potential for reaching remote areas compared to gas-phase low-brominated congeners. However, there is also evidence for the importance of particle-bound transport of brominated FRs to remote areas.[14,29] Ratios of average percentage contributions of the individual HFRs in the rural versus urban samples and rural versus e-waste samples were calculated and compared in Figure 4. These ratios can partially reflect their potential for atmospheric transport from the source regions to the rural region. It is interesting to found that HFRs with high and low vapor pressures and octanol-air partition coefficients (K_{OA}) have high transport tendencies and those (e.g., hexa- and hepta-BDEs) with intermediate vapor pressures and K_{OA} values (SI Table S3) exhibit low transport tendencies. Vapor pressure and K_{OA} are good descriptors of air-particle partitioning of SOCs.[30] This finding suggests that SOCs present in gas phase or sorbed onto particles are readily subject to transport in the atmosphere. BDE209 with a high log K_{OA} (15.3) shows ratios of <1. A possible reason is that BDE209 may undergo degradation during transport. This is also supported by the exceptionally high ratios for BDE202. Presumably, BDE85 (with similarly high ratios) is also a debromination product of highly brominated PBDEs. Our observation is in good agreement with previous results that suggest that photodegradation during LRAT of BDE209 on mineral aerosols is an important fate process for BDE209 in the environment.[31] In contrast, the findings of Raff and Hites suggest that atmospheric particle-bound SOCs are not susceptible to photodegradation due to the shielding effects of carbonaceous aerosols.[14] DP, BTBPE, and DBDPE were not included in the ratio calculation because of the large differences in their deposition fluxes between the urban and e-waste sites; for each of these chemicals the differences will result in a ratio of <1 and another of >1.

The mean f_{anti} value (defined as the ratio of anti-DP to the total DP) in the deposition samples at the rural site was 0.66 ± 0.09, which was significantly lower than values from the urban (0.71 ± 0.05) and e-waste (0.73 ± 0.02) sites. This result suggests isomer-specific atmospheric transport or degradation during atmospheric transport. Decreased f_{anti} values were also observed in the air from the Great Lakes and Arctic regions.[18,32] Two dechlorinated anti-DP compounds (Cl_{11} and Cl_{10} DP) were also detected in the deposition samples. Small amounts of anti-Cl_{11} DP (SI Table S2) were present in 10, 4, and 1 of the samples from the e-waste, urban, and rural sites, respectively. No anti-Cl_{10} DP was found in the samples. However, the chromatograms of DP clearly show the presence of other dechlorinated DP products (SI Figure S3) that could not be quantified due to the lack of standards.

HBCD diastereoisomer profiles in the deposition samples from the rural site (40.5% α-HBCD, 7.2% β-HBCD, and 52.4% γ-HBCD) were close to the profiles from the urban site (37.1% α-HBCD, 10.0% β-HBCD, and 52.3% γ-HBCD). HBCD at the e-waste site consists of 62.3% α-HBCD, 12.8% β-HBCD, and 22.9% γ-HBCD, a composition that is clearly different from those of the other two sites (SI Figure S4). Compared with technical products dominated by γ-HBCD (75%−89%), the deposition samples showed enrichment of α-HBCD and depletion of γ-HBCD. The different diastereoisomer profiles at the e-waste site could be explained by the thermal rearrangement of HBCD diastereoisomers during the process of e-waste burning. Conversion of γ-HBCD to α-HBCD at temperatures above 160 °C has been observed.[33]

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Information of materials, detailed descriptions of sample preparation and instrument analysis, data analysis, and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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