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Gridded Field Observations of Polybrominated Diphenyl Ethers and Decabromodiphenyl Ethane in the Atmosphere of North China

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S *Supporting Information*

ABSTRACT: Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) are important pollutants, yet few data on ambient BFRs levels have been available for North China, one of the most developed regions of the country. In this study, we investigated levels and spatial distributions of BFRs based on gridded field observations coupled with passive air sampling in the aforementioned region. A model incorporating both point and nonpoint sources was developed to simulate the spatial distribution and to achieve source apportionment. Although high concentration was observed at an electronic-waste (e-waste) recycling site, the median level of the sum of tri-, tetra-, hepta-, hexa-, and hepta-PBDEs ($\sum_{10}$PBDEs) was 0.56 ng/sample, which was lower than those observed previously in mainland China. Source apportionment revealed that nonpoint emissions contributed nearly 78% of $\sum_{10}$PBDEs observed in this study. In contrast, high levels of BDE-209 and DBDPE were observed, with median concentrations of 4.0 and 10.2 ng/sample, respectively. Point sources located in the region around Laizhou Bay, Shandong Province were the major sources, which contributed 31% of BDE-209 and 70% of DBDPE observed in this study, indicating that this manufacturing base was the most important source region for atmospheric deca-BFRs in North China. To our knowledge, this is the first study to report source apportionment of atmospheric BFRs based on gridded field observations.
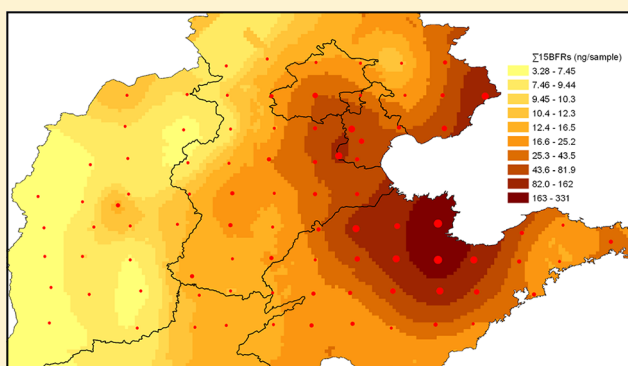
INTRODUCTION

Over the past decades, the demand for brominated flame retardants (BFRs) has grown rapidly because of regulations aimed at reducing death and injury from fires. This class of human-made chemicals has been widely used in household materials, and especially in electrical and electronic equipment.[1] The most important and widely used BFRs, polybrominated diphenyl ethers (PBDEs), have been mass-produced and consumed worldwide.[2] PBDEs have drawn much attention for their ubiquity in the environment and potential adverse effects on human health,[1] since they have similar structures to polychlorinated biphenyls (PCBs).[3] A series of studies demonstrated that PBDEs are endocrine-disrupting chemicals. Exposure to these pollutants was associated with alteration of neuropsychological, immune, and thyroid function, and maternal exposure to PBDEs might result in developmental disturbances, such as low birth weights.[4−7] As a result, four groups of PBDE homologues, namely tetra-, penta-, hexa-, and hepta-BDEs, have been added to the Stockholm Convention on Persistent Organic Pollutants for global regulation since 2009.[8]

The official production of PBDEs in China started late in the 1980s; however, with the rapid development of the economy, market demand for BFRs, including PBDEs, has increased at a rate of 8% per annum.[9] The production of commercial Deca-BDE in China was reported as 15 000 tons in 2006.[10] In addition, decabromodiphenyl ethane (DBDPE), the substitute for commercial Deca-BDE, reached a production capacity of approximately 11 000 tons in the first year of its launch in China in 2006.[10] As a result, high atmospheric concentrations of PBDEs were observed, particularly in the two BFRs production bases of Shandong and Jiangsu Provinces.[11−13]

In addition to the production and consumption of PBDEs, there could be other current sources of PBDEs in China, for example, from electronic waste (e-waste). It was estimated that nearly 80% of the world's e-waste was exported to Asian countries, and 90% of this amount flowed into China.[14] In 2010, 28 million tons of e-waste was imported into China, most of which was recycled at several sites located in coastal regions.[15] At these sites, crude dismantling activities such as open incineration could release unbounded PBDEs into the environment. At such a site in Taizhou, Zhejiang Province, the
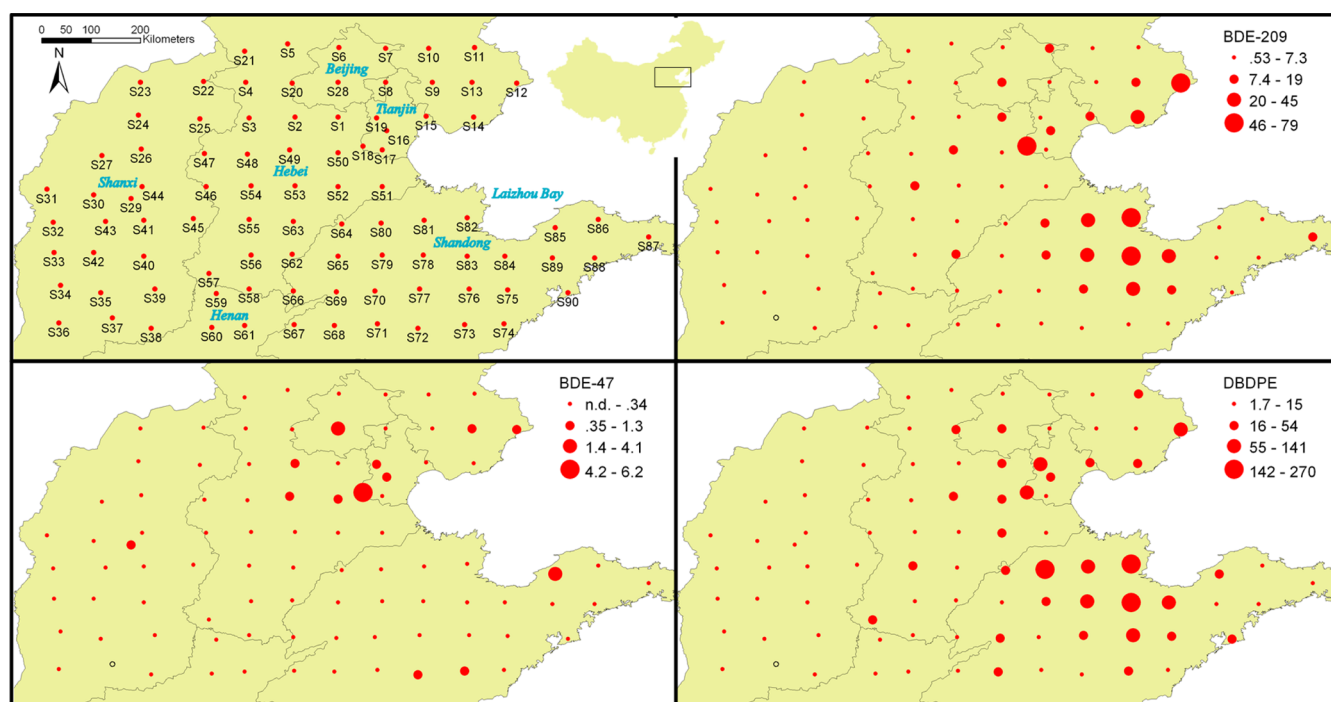
Figure 1. Locations of sampling sites and graduated concentrations (in ng/sample) of BDE-47, BDE-209, and DBDPE in North China. (The sample from site S37 was lost).

concentration of BFRs in ambient air was as high as 9900 pg m^{-3} in summer.[16]

North China is one of the most developed regions of the country with more than 300 million people,[17] and heavy pollution of BFRs (including PBDEs) could be expected for the manufacturing base and e-waste recycling sites in this region. However, little information on the levels or regional distributions of BFRs has been available for this important region. Hence, it is difficult to evaluate the potential health risks of exposure to these chemicals for the large population.

Passive air sampling, which was developed and widely used in the past decade, is a powerful and easy-to-use technique for monitoring atmospheric persistent organic pollutants (POPs)[18,19] even given its disadvantages such as low sampling efficiency for particle-bound pollutants and sampling variation caused by environmental conditions.[20−23] Using this technique, we undertook a gridded field observation campaign to monitor BFRs, including PBDEs, in North China in order to explore their air concentrations, spatial distribution, and sources, and to provide data for use in further evaluations of human exposure and the potential health risks. To the best of our knowledge, this is the first report describing regional atmospheric BFRs through strictly designed gridded field observations.

■ EXPERIMENTAL SECTION

Sample Collection. Field observations were undertaken in North China from early June to early October 2011. Briefly, passive air sampling was based on a gridded design, with grid spacing of approximately 70 km (Figure 1). Some sites in mountainous regions were modified for the convenience of access. Three additional sites were placed in the downtown regions of Tianjin (S16) and Taiyuan (S29) and at an e-waste recycling site located in the rural area of Tianjin (S18). In total, 90 sites were set, representing various functional divisions of megacity, town, and countryside. At each site one sampler was

placed, while parallel samples were taken at four sites. Each sampler operated continually for 90 days. Finally, 93 samples from 89 sites were reclaimed; unfortunately, the sample from S37 was lost.

The passive air sampler designed by Harner et al.[24] was used in this study, with polyurethane foam (PUF; 14 cm in diameter, 1 cm in thickness, and 0.021 g cm^{-3} density) as the adsorbent. Before sampling, PUF disks were Soxhlet extracted with acetone and hexane sequentially, each for 22 h. PUF disks were dried and stored in brown glass jars with Teflon lined caps until assembly at the sampling sites. After sampling, PUF disks were sealed in the same jars, posted to our laboratory, and stored at −20 °C until analysis.

Chemicals. A standard mixture of BFRs, including 37 PBDE congeners, 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153), 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE), and decabromodiphenyl ethane (DBDPE), was obtained from Wellington Laboratories (Guelph, ON, Canada) and used as calibration standard. BDE-77 and -118 were purchased from AccuStandard (New Haven, CT), $^{13}C_{12}$−BDE-209 was from Wellington Laboratories, and $^{13}C_{12}$−BDE-208 was from Cambridge Isotope Laboratories (Andover, MA). All of the solvents used for the extraction and cleanup were residue grade from Fisher Scientific (Fair Lawn, NJ).

Sample Preparation. Each PUF disk was spiked with BDE-77 and $^{13}C_{12}$−BDE-209 as recovery surrogate standards, and was Soxhlet extracted with 200 mL hexane/acetone (1:1, v/v) for 22 h. The extract was concentrated and washed with 1.5 mL KOH solution (0.5 M) to remove acidic interferences. Then, samples were cleaned by alumina column chromatography (3% water deactivated; 0.6 cm i.d., 6 cm length, with 0.5 cm anhydrous Na_2SO_4 on the top), with 8 mL of hexane/dichloromethane (3:2, v/v) as the eluent. The eluent was blown down and further cleaned with 2 mL of concentrated H_2SO_4. Finally, samples were concentrated and spiked with
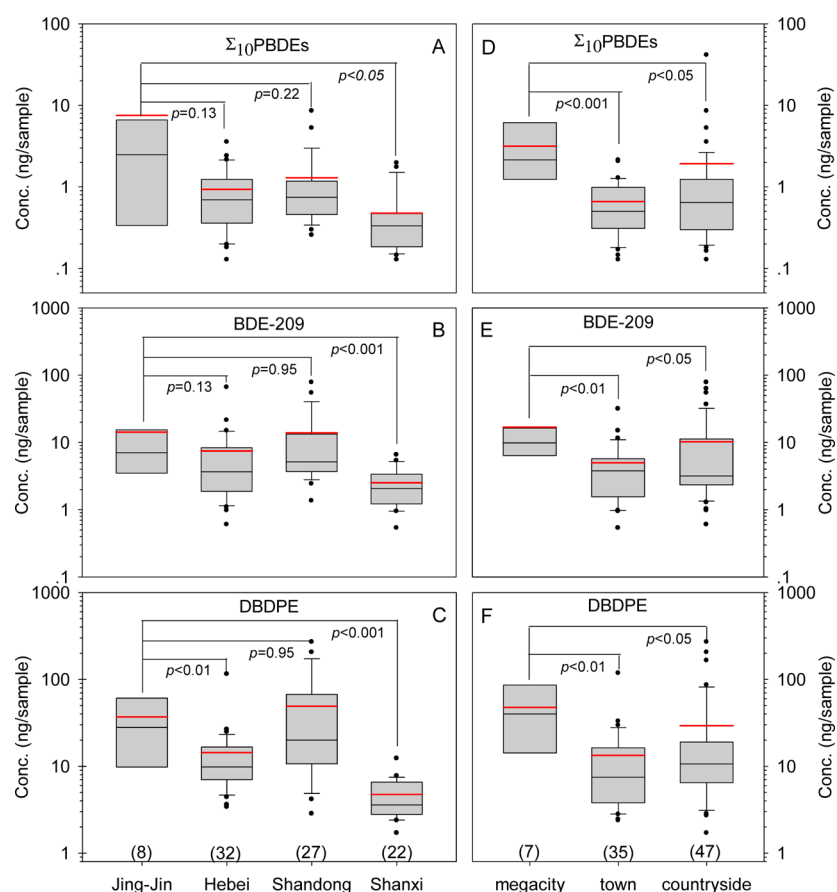
Figure 2. Comparison of $\sum_{10}$PBDEs, BDE-209, and DBDPE among provinces (panels A, B, and C) and among function divisions (panels D, E, and F). The black horizontal line represents the median and the red line represents the mean. The box represents the 25th−75th percentiles, and the whiskers represent the 10th-90th percentiles. The numbers in parentheses are the number of sampling sites. The two-tailed p-values were from t-test after logarithmic transformation of the concentration data.

BDE-118 (for tri- through hepta-BDEs and TBE) and $^{13}C_{12}-$BDE-208 (for octa- through deca-BDEs and DBDPE) as internal standards for the gas chromatography−mass spectrometry (GC-MS) analysis. Throughout the extraction and analysis procedure, samples were protected from potential photolysis through the use of amber containers or by wrapping containers with aluminum foil.

Instrumental Analysis. All BFRs were measured with an Agilent 7890A-5975C GC-MS with an electron-capture-negative ionization (ECNI) ion source. The GC injection port was held at 280 °C, with an injection volume of 1 μL. A 15 m Rtx-5MS column (250 μm i.d., 0.10 μm film thickness; Restek Corp., Bellefonte, PA) was used to separate analytes at a constant flow rate of 1.5 mL min^{-1}. The GC oven temperature program was as follows: held at 90 °C for 1 min; 20 °C min^{-1} to 200 °C; 5 °C min^{-1} to 300 °C, and held for 3.5 min. A 30 m DB-5MS column (250 μm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA) was used to achieve baseline separation of BDE-28 and pentabromotoluene with the following temperature program: held at 90 °C for 1 min; 8 °C min^{-1} to 280 °C; 20 °C min^{-1} to 300 °C, and held for 10 min. The following ion couples were monitored: 487 and 489 for BDE-204, -206, -207, -208, and -209; m/z 495 and 497 for $^{13}C_{12}-$BDE-208 and $^{13}C_{12}-$BDE-209; m/z 409 and 411 for BDE-197 and -201; and m/z 81 and 79 for the other brominated compounds.

Quality Control. To ensure the correct identification and quantitation of target compounds, the following quality control criteria were applied: (a) The GC retention times matched those of the standard material within ±0.1 min, (b) the signal-to-noise ratio was greater than 5:1, and (c) the isotope ratios of selected ion couples were within 15% of the theoretical values. For each batch of eight samples, one procedural blank sample was prepared. Concentrations of analytes in the blank samples ($n = 12$) were less than 9% of those in the field samples, except for BDE-153, BDE-183, and TBE, for which the blank to field sample ratios were 49%, 30%, and 17%, respectively. For these analytes, blank correction was performed. The recoveries (mean ± standard deviation) of the surrogate standards were 97.4 ± 4.2% and 91.6 ± 7.0% for BDE-77 and $^{13}C_{12}-$BDE-209, respectively. All concentrations were not corrected for recovery. For the field samples deployed in replicate at four sites, the relative deviation was 9.2% (range, 2.3−14.5%) for all detected BFRs. The estimated method detection limits ranged from 4.7 to 143 pg/sample (Table S4 in the Supporting Information (SI)).

■ RESULTS AND DISCUSSION

Levels of BFRs in the Atmosphere of North China. Among all analytes, 15 species (i.e., BDE-17, -28, -47, -49, -66, -99, -100, -153, -154, -183, -207, -208, -209, TBE, and DBDPE) were detected in most field samples, and the results are shown in Table S4 and Figure S1 of the SI. In brief, DBDPE was the

most abundant pollutant with the median concentration of 10.2 ng/sample (range, 1.7−270 ng/sample; average 24.6 ng/sample), followed by BDE-209 with the median of 4.0 ng/sample (range, 0.54−78.2 ng/sample; average 8.8 ng/sample) in spite of low sampling rate for these two particle-bound pollutants.[21] The median concentration of the sum of 10 PBDE congeners ($\sum_{10}$PBDEs, including BDE-17, -28, -47, -49, -66, -99, -100, -153, -154, and -183; which were mainly from commercial penta- and octa-BDEs [25]) was 0.56 ng/sample (range, 0.13−41.4 ng/sample; average 1.52 ng/sample). It should be pointed out that weather conditions might have an influence on the sampling rate (particularly for particle-bound pollutants);[20,22] however, these factors were not considered in the following sections because of the lack of meteorological data.

Because there were few data on BDE-209 or DBDPE available, here we mainly compared concentrations of PBDEs with lower molecular weight observed in this and in other studies. As shown in Table S5 of the SI, the sampling interval normalized average concentration of $\sum_{10}$PBDEs observed in North China was 17 pg sample^{-1} day^{-1}. This level was similar to that observed at the residential area in Brisbane, Australia (average 13 pg sample^{-1} day^{-1}),[23] and lower than those observed previously in Japan (68 pg sample^{-1} day^{-1}), South Korea (31 pg sample^{-1} day^{-1}), Singapore (67 pg sample^{-1} day^{-1}), and Europe (130 pg sample^{-1} day^{-1}).[18,19] It is noteworthy that concentration of $\sum_{10}$PBDEs observed in the present study was much lower than that observed in mainland China in the autumn of 2004 (average 119 pg sample^{-1} day^{-1}),[19] which could probably be contributed to the ban of commercial penta- and octa-BDEs in China in 2007.[26]

Spatial Distribution of BFRs in North China. The spatial distributions of three typical pollutants (i.e., BDE-47, BDE-209, and DBDPE) are shown in Figure 1, and significant variations in the spatial distributions were observed in the study region of North China. The highest values of BDE-47 (and $\sum_{10}$PBDEs) mainly occurred in the region of Beijing-Tianjin, while those of BDE-209 and DBDPE mainly occurred in the region around Laizhou Bay, Shandong Province. To better describe the spatial distribution of BFRs and to explore their sources, we categorized field data by administrative regions and functional divisions. Given the similarity of neighboring regions, sampling sites located in Beijing and Tianjin were combined, and the three sites located in Henan Province were combined into Hebei Province.

As shown in Figure 2, the highest concentrations of $\sum_{10}$PBDEs were observed in the region of Beijing-Tianjin, with a median of 2.48 ng/sample (average 7.55 ng/sample), followed by 0.75 ng/sample (average 1.29 ng/sample) in Shandong Province, and 0.69 ng/sample (average 0.93 ng/sample) in Hebei Province. Concentrations in Shanxi Province (median 0.33 ng/sample; average 0.48 ng/sample) were significantly lower than those in Beijing-Tianjin region ($p < 0.05$, t-test). For BDE-209, however, there was no significant difference ($p > 0.05$, t-test) among Beijing-Tianjin (median 7.04 ng/sample; average 14.3 ng/sample), Shandong Province (median 5.14 ng/sample; average 13.9 ng/sample) and Hebei Province (median 3.67 ng/sample; average 7.45 ng/sample). Similar to $\sum_{10}$PBDEs, levels of BDE-209 in Shanxi Province (median 2.06 ng/sample; average 2.53 ng/sample) were the lowest among all provinces in this study. As for DBDPE, Shandong Province (median 20.0 ng/sample; average 49.1 ng/sample) and Beijing-Tianjin (median 28.0 ng/sample; average

37.1 ng/sample) present the highest levels, both significantly higher than those in Shanxi Province ($p < 0.05$, t-test). Using levels of BFRs in Shanxi Province as a baseline for quantitative description, $\sum_{10}$PBDEs in Beijing-Tianjin, Shandong, and Hebei were 5.8, 2.4, and 1.9 times higher than those in Shanxi Province; for BDE-209, the values were 3.8, 3.7, and 2.0 times higher; and for DBDPE, the values were 5.9, 5.8, and 2.5 times higher, respectively.

We hypothesized that the elevated levels of BFRs observed in the region of Beijing-Tianjin might have been the result of high population density of these two megacities. To test this, sampling sites were divided into three classes of megacity, town, or countryside, based on the administrative location of each site. As shown in Figure 2, the median concentrations of $\sum_{10}$PBDEs, BDE-209, and DBDPE in megacities were 2.15, 9.87, and 40.0 ng/sample (average 3.16, 17.9, and 48.7 ng/sample), respectively, which were significantly higher than those in the other two classes of areas (all $p < 0.05$, t-test), indicating more severe pollution of BFRs in megacities. Consistent with previous research by Venier and Hites,[27] this could be a result of the consumption of BFR-containing products by high-density populations, leading to considerable BFR pollution in large cities.[28]

It is notable that although higher levels of atmospheric PBDEs were generally observed in megacities, the highest concentrations were observed mostly at sites located in the countryside or in towns. For $\sum_{10}$PBDEs, the highest concentration was observed at S18 (41.4 ng/sample; countryside), followed by S85 (8.54 ng/sample; countryside), the highest concentration (H) at the e-waste recycling site (S18) was 324 times higher than the lowest concentration (L) of 0.13 ng/sample at site S27; for BDE-209, the highest level was observed at S83 (78.2 ng/sample; countryside), followed by S12 (66.3 ng/sample; megacity), S18 (63.0 ng/sample; countryside), S82 (54.5 ng/sample; countryside), and S78 (36.8 ng/sample; countryside), the highest concentration was 145 times higher than the lowest concentration (L) of 0.54 ng/sample at site S27; for DBDPE, the highest level was observed at S82 (270 ng/sample; countryside), followed by S83 (205 ng/sample; countryside), S80 (165 ng/sample; countryside), S76 (118 ng/sample; town), and S12 (115 ng/sample; megacity), the highest concentration was 159 times higher than the lowest concentration (L) of 1.70 ng/sample recorded at site S39. Since sites S18, S83, and S82 were all located in countryside, the H/L value of >100 suggested significant point sources, that is, manufacturing or other strong releases of BFRs at or near these high concentration sites.[18]

Modeling of Atmospheric BFRs in North China. To further investigate the potential point sources, a Grubbs test was applied to screen for abnormal values as potential point sources. The transport of BFRs from point source j to sampling site i was simulated by a simplified Gaussian diffusion model as described previously:[29]

$$C_{i,\text{point}} = K_1 \sum_j Q_j d_{ij}^{-\alpha} \tag{1}$$

where $C_{i,\text{point}}$ is the atmospheric concentration at site i contributed by all point sources, Q_j is the intensity of source j, d_{ij} is the Euclidean distance between the two locations, and K_1 and α are constants. Linear superposition was assumed for multipoint sources, and the diffusion coefficient of α was adopted from previous literature.[30]

Following the identification of point sources, correlation analysis was performed between field data and the modeled values, and almost all analytes exhibited significant (i.e., $p <$ 0.05) or marginal significant (i.e., p-values ∼0.05) correlations. TBE was the only exception ($p = 0.17$), and it was rejected for further analysis in the following section. This simulation provided evidence supporting the atmospheric transportation of BFRs from point sources in the study region.

However, these identified point sources could not explain all the measured values. To explore potential nonpoint sources, population density and GDP per capita were selected as surrogate parameters, and partial coefficient analyses were performed. The population and GDP data at county level were from the Statistical Yearbook of each province.[17] As shown in Table 1, for most of the target pollutants, measured

Table 1. Partial Coefficients between Measured BFR Concentrations against Simulated BFR Concentrations from the Gaussian Diffusion Model, and against Population Density and GDP Per Capita[a]

measured conc. of BFRs	vs simulated conc. of BFRs	vs population density	vs GDP per capita
BDE-17	0.41^b	0.55^b	0.13
BDE-28	0.43^b	0.37^b	0.24^c
BDE-47	0.42^b	0.47^b	0.23^c
BDE-49	0.40^b	0.36^b	0.16
BDE-66	0.46^b	0.52^b	0.096
BDE-99	0.23 ($p = 0.058$)	0.36^b	0.12
BDE-100	0.53^b	0.39^b	0.13
BDE-153	0.21 ($p = 0.051$)	0.29^c	0.25^c
BDE-154	0.51^b	0.41^b	0.21
BDE-183	0.22 ($p = 0.052$)	0.26^c	0.30^b
TBE	0.17 ($p = 0.17$)	0.045	0.34^b
BDE-207	0.27^c	0.10	0.41^b
BDE-208	0.34^b	0.17	0.36^b
BDE-209	0.51^b	0.19	0.20
DBDPE	0.65^b	0.30^b	0.26^c

[a]All variables were log-transformed to obtain a normal or quasi-normal distribution. [b]$p < 0.01$. [c]$p < 0.05$.

concentrations were significantly correlated with population density, whereas correlations between measured concentrations and GDP per capita were not significant for most pollutants. This result indicates that population density could be used as a surrogate for nonpoint sources.

From the discussion above, we could conclude that the observed atmospheric BFRs in North China originated from both significant point sources and nonpoint local sources. Obviously, a qualitative source apportionment is valuable in indicating the contribution of various sources. To achieve this objective, we developed a model to describe the atmospheric concentrations of BFRs:

$$C_i = C_{i,\text{point}} + C_{i,\text{local}} \tag{2}$$

where C_i is the air concentration of any BFR congener at sampling site i; $C_{i,\text{point}}$ is the contribution from point sources, which is indicated by eq 1; and $C_{i,\text{local}}$ is that from nonpoint local sources, which could be surrogated by local population density P_i as discussed above:
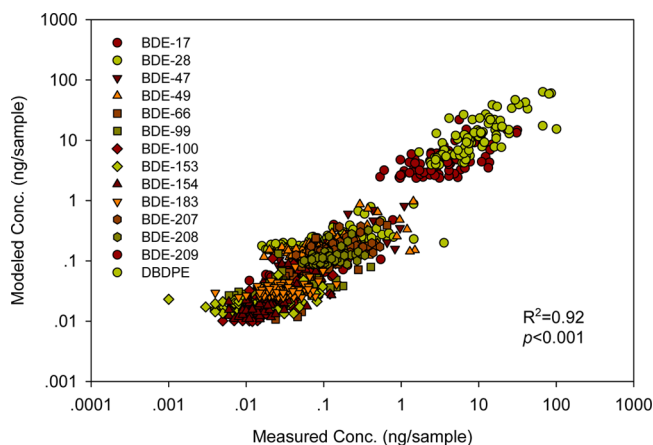
$$C_{i,\text{local}} = K_2 P_i + b \tag{3}$$

where both K_2 and b are constants. Synthesizing eqs 1, 2, and 3:

$$C_i = K_1 \sum_j Q_j d_{ij}^{-\alpha} + K_2 P_i + b \tag{4}$$

and we could access the constants of K_1, K_2, and b by minimizing ξ by the least-squares method:[29,31]

$$\xi = \sum_i \left(K_1 \sum_j Q_j d_{ij}^{-\alpha} + K_2 P_i + b - C_i\right)^2 \tag{5}$$

Comparisons between modeled concentrations and field data are shown in Figure 3. The R^2 value of 0.92 indicated

Figure 3. Correlation analysis between measured and modeled concentrations of BFRs.

satisfactory modeling of the field observations. Nonetheless, it should be pointed out that this model was applied at regional scale in this study; while in other cases (e.g., at city scale), other approach could be applied to investigate the sources and spatial variation of air-borne pollutants.[32]

On the basis of this quantitative model, we could apportion the contribution from various sources to the observed atmospheric BFRs. For instance, two rural sites (i.e., S18 and S85) were identified as point sources of BDE-47. Actually, S18 was the largest e-waste dismantling site in North China, which has a history of more than 20 years in e-waste dismantling.[33,34] Primitive dismantling processes such as the open incineration of e-waste could release large quantities of BFRs into the atmosphere. Correspondingly, the air concentration of BDE-47 (6.14 ng/sample) at this site was 57 times higher than those at all other sites. As a result, up to 20% of the atmospheric BDE-47 observed in this study was contributed by this significant point source, demonstrating that e-waste dismantling activities have caused considerable pollution to local environments, and even to a large region through atmospheric transport. Similarly, S85 is a village site located in Shandong Province, with a small BFR plant nearby. At this site, BDE-47 concentration of 2.17 ng/sample was higher than those observed in megacities such as Beijing and Tianjin. However, as it is located on the edge of Shandong Peninsula, S85 contributed only about 3% of the BDE-47 observed in this study. Besides these two identified point sources, nonpoint local emissions accounted for 77% of the observed BDE-47, indicating that release from PBDE-containing products was the major source of atmospheric BDE-47 in North China. Similar results were acquired for $\sum_{10}$PBDEs, with 78% originating from nonpoint local sources and 20% from site S18. Nonetheless, low levels of BDE-47 (median 0.11 ng/sample; average 0.28 ng/sample) and

$\sum_{10}$PBDEs (median 0.56 ng/sample; average 1.52 ng/sample) suggested that PBDEs with lower molecular weights were not dominant pollutants in North China, except at some hot spots such as the e-waste recycling site.

For BFRs with higher molecular weights, mainly BDE-209 from commercial deca-BDE and its substitute, DBDPE, the results were different. For these pollutants, five sites were identified as point sources, and they were responsible for 59% of the BDE-209 and 76% of the DBDPE observed in this study. Most of these point sources (S78, S82, and S83 for BDE-209; and S76, S80, S82, and S83 for DBDPE) were located in the region around Laizhou Bay, Shandong Province (Figure 1), which is the largest production base for BFRs in China. As a result, the concentrations of deca-brominated chemicals detected at these sites were extremely high (Figure 1) and contributed 31% (S83, 14.4%; S82, 8.2%; and S78, 7.9%) of BDE-209 and 70% (S82, 20.5%; S83, 17.8%; S80, 21.1%; and S76, 10.7%) of DBDPE observed in this study. In addition, the e-waste recycling site (S18) contributed 22% of observed BDE-209, but it was not a significant point source of DBDPE. This difference could be explained by the fact that the production of commercial deca-BDE began in the late 1970s,[35] while DBDPE was applied as a substitute for commercial deca-BDE in the early 1990s,[36] that is, most e-waste currently recycled contained BDE-209 instead of DBDPE.

In conclusion, based on gridded field observations, a quantitative model incorporating both nonpoint and point sources was developed to achieve source apportionment in this study. It suggested that 78% of $\sum_{10}$PBDEs observed in North China was from nonpoint emissions. In contrast, BDE-209 and DBDPE were mainly from point sources, particularly from those located in the manufacturing base of BFRs in the region around Laizhou Bay, Shandong Province. These findings could be helpful in understanding the pollution status of BFRs in this important region, and thus in formulating control policy and regulations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information noted in the text is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Yifan Zhao and Jin Ma contributed equally to the work.

Notes
The authors declare no competing financial interest.

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