Polybrominated Diphenyl Ethers in Soils, Sediments, and Human Hair in a Plastic Waste Recycling Area: A Neglected Heavily Polluted Area

Zhenwu Tang,‡ Qifei Huang,* Jiali Cheng,§ Yufei Yang,‡ Jun Yang,∥ Wei Guo,† Zhiqiang Nie,‡ Ning Zeng,† and Lu Jin†

†MOE Key Laboratory of Regional Energy and Environmental Systems Optimization, Resources and Environmental Research Academy, North China Electric Power University, Beijing 102206, China
‡State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
§National Institute for Nutrition and Food Safety, Chinese CDC, Beijing 100021, China
∥Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

Supporting Information

ABSTRACT: The release of pollutants during the recycling of contaminated plastics is a problem which has drawn worldwide attention; however, little information on the transfer of polybrominated diphenyl ethers (PBDEs) in these processes is available. We conducted a survey of PBDEs in soils, sediments, and human hair in a typical plastic waste recycling area in northern China. The total concentrations (ng/g) of 21 PBDEs were 1.25–5504 (average 600), 18.2–9889 (average 1619), and 1.50–861 (average 112) in soils, sediments, and hair, respectively. The PBDE concentrations were comparable to concentrations observed in e-waste recycling areas; however, the concentrations in soils and sediments were 1–3 orders of magnitude higher than in other areas, and the concentrations in hair were much higher than in other areas. This indicates that this area is highly polluted with PBDEs. BDE-209 was the dominant congener (representing 91.23%, 92.3%, and 91.5% of the total PBDEs observed in soils, sediments, and hair, respectively), indicating that the commercial deca-BDE product was dominant. The commercial penta- and octa-BDE products made small contributions to the total PBDE concentrations, unlike what has been found in some e-waste recycling areas. Our results show that crude plastic waste processing is a major contributor of PBDEs to the environment and humans, which should be of great concern.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of persistent and bioaccumulative brominated flame retardants, and they have typically been produced as commercial penta-, octa-, and deca-BDE formulations. The penta- and octa-BDE commercial formulations were classified as persistent organic pollutants (POPs) by the Stockholm Convention in May 2009. BDE-209 is the dominant component of the deca-BDE formulation, and a growing number of studies have shown that it can be metabolized in the environment to form toxic less-brominated PBDEs. The production and use of penta- and octa-BDE commercial products are currently banned only in the European Union and the United States. Currently, the United States has extended this ban to include the deca-BDE product. PBDEs, especially the deca-BDE, are still being produced and used in many other countries, including China. PBDEs have been widely used in polymeric materials to improve the fire safety performance of electrical products. Morf et al. analyzed electrical waste plastics and found average concentrations of 510 and 530 mg/kg for deca- and octa-BDE, respectively. PBDEs can be emitted into the environment during the recycling of e-waste. High PBDE concentrations have been found in soils, sediments, and organisms (including humans) in electronic waste recycling areas in many countries, especially in developing countries in Asia. Among these areas, Guiyu, Taizhou, and Qingyuan in China have become the

Received: November 4, 2013
Revised: December 26, 2013
Accepted: January 8, 2014
Published: January 8, 2014
most PBDE-contaminated e-waste recycling sites because of the 
crude recycling methods being used in those areas.11

PBDEs have also been used extensively as flame retardants in 
many nonelectrical plastics.3,4,12 Deca-BDE is used commonly 
in many types of polymers, including polyolefins, acrylonitrile 
butadiene styrene (ABS), polyamides, and polyvinyl chloride. 
Some previous studies have shown that other PBDE products 
have also been extensively added to these plastics.3,11,12 Chen et 
al.12 found median and maximum PBDE concentrations in hard 
plastics in children’s toys of 53 and 5,344 μg/g, respectively. 
Deca-BDE was found at a concentration of 1500 mg/kg in 
high-impact polystyrene by Kajiwara et al.3 Most of the PBDE 
formulations are used as additives that are physically mixed into 
the product, rather than being chemically bound. As a result, 
PBDEs can easily be released into the ambient environment 
from the products containing them. It can be inferred that high 
levels of PBDE release might also occur through the disposal of 
non-electrical plastics.

The amount of plastic waste generated by households and 
industries globally has grown rapidly in recent years.13 Recycling is the primary method of treating plastic wastes in 
many countries. Although chemical recycling (by cracking, 
gasification, hydrogenation, and pyrolysis) and energy recovery 
are encouraged in some developed countries, material recycling 
becoming the key disposal method of plastic waste in 
developing countries due to relatively low level of investments 
and simple technology requirements.14,15 Unfortunately, 
limited pollution control measures have traditionally been 
applied to plastic material recycling processes,14,16 resulting in 
many crude plastic waste recycling sites being formed in many 
low-income countries, especially in Asia and Africa.16−18 In 
China, chemical recycling and energy recovery are not 
encouraged by the government because of fears about the 
exhaust pollution produced in the recycling processes, and 
primitive material recycling of plastic waste is common. As a 
consequence, there are a number of plastic recycling sites 
contaminated by these uncontrolled activities in Guangdong, 
Zhejiang, Jiangsu, Hebei, and other districts.18

There have been many studies on the recycling methods of 
plastic waste.15−17 To date, however, little is known about the 
release of emerging contaminants during the recycling of plastic 
wastes, some of which contain PBDEs.13,16 To our knowledge, 
no studies have been performed on the release of PBDEs into 
the environment in plastic waste recycling areas where primitive 
methods are used, and the potential adverse human health 
impacts of PBDEs released from such sites remain unknown. In 
this study, we used Wen’an, in northern China, as a plastic 
recycling area case study. Our main aim is to characterize 
the concentrations and distributions of PBDEs in soil, 
sediment, and human hair in Wen’an. We then compared the 
congener profiles and risks from PBDE exposure in Wen’an 
with the profiles and risks that have been found in other areas, 
particularly heavily polluted e-waste recycling areas. The results 
will improve our understanding of the extent of PBDE 
pollution caused by plastic waste recycling and provide 
information that will be useful in planning risk management 
measures.

■ MATERIALS AND METHODS

Study Area. Wen’an County, in northeast Hebei, China, has 
a population of 460,000 and an area of 1028 km². It is 
approximately 80 km west of Tianjin and about 120 km south 
of Beijing. The crude material recycling of plastic waste has 
been practiced intensively in 101 villages in eight towns in 
Wen’an, employing nearly 100,000 people.18,19 A complete 
industrial chain of plastic recycling exists in the area, with an 
estimated value of more than 1.3 billion Yuan in 2007.18 
Wen’an is known as the main center for plastic waste recycling 
in northern China. Valuable materials have been reclaimed 
from different types of plastic wastes for more than 20 years in 
the village of Yincun, located in the central part of 
ZhaogeZhuang, Wen’an. In the town of Dalu, next to the 
ZhaogeZhuang, the intensive plastic waste recycling processes 
were also active and have lasted for more than a decade. In 
Wen’an, recycling operations consist of sorting, rinsing, and 
grinding the plastic, then heating the plastic to remold it, 
followed by granulating it, forming a film from it, or drawing 
wire from it. These processes were previously performed using 
crude techniques on a small scale in family workshops. Crude
Table 1. Means and Ranges of Individual Polybrominated Diphenyl Ether (PBDE) Congener Concentrations (ng/g dry wt) in Surface Soils, Sediments, and Human Hair from a Waste Plastic Recycling Area in Wen’an, Northern China

<table>
<thead>
<tr>
<th>Congener</th>
<th>REP$^a$</th>
<th>Soils</th>
<th>Sediments</th>
<th>Human Hair</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zhaoge Zhang</td>
<td>Xianbaiche River</td>
<td>Renwen Canal</td>
</tr>
<tr>
<td>BDE-28</td>
<td></td>
<td>n = 40</td>
<td>n = 10</td>
<td>n = 6</td>
</tr>
<tr>
<td>BDE-47</td>
<td>&lt;1.1 $\times 10^{-6}$</td>
<td>0.06 (ND-0.32)</td>
<td>0.23 (0.00-1.84)</td>
<td>0.24 (0.10-8.90)</td>
</tr>
<tr>
<td>BDE-66</td>
<td>&lt;2.0 $\times 10^{-6}$</td>
<td>0.07 (ND-0.29)</td>
<td>0.06 (ND-0.31)</td>
<td>0.14 (ND-0.31)</td>
</tr>
<tr>
<td>BDE-85</td>
<td>&lt;2.1 $\times 10^{-6}$</td>
<td>0.06 (ND-0.89)</td>
<td>0.37 (ND-0.42)</td>
<td>0.08 (ND-0.17)</td>
</tr>
<tr>
<td>BDE-99</td>
<td>&lt;5.6 $\times 10^{-7}$</td>
<td>0.37 (ND-2.02)</td>
<td>0.01 (ND-0.05)</td>
<td>0.01 (ND-0.05)</td>
</tr>
<tr>
<td>BDE-100</td>
<td>&lt;1.2 $\times 10^{-6}$</td>
<td>0.08 (ND-0.40)</td>
<td>0.13 (ND-0.40)</td>
<td>0.13 (ND-0.40)</td>
</tr>
<tr>
<td>BDE-138</td>
<td></td>
<td>0.16 (ND-4.29)</td>
<td>0.13 (ND-2.05)</td>
<td>0.15 (ND-1.21)</td>
</tr>
<tr>
<td>BDE-153</td>
<td>&lt;2.3 $\times 10^{-6}$</td>
<td>0.42 (ND-3.25)</td>
<td>0.13 (ND-2.05)</td>
<td>0.15 (ND-1.21)</td>
</tr>
<tr>
<td>BDE-183</td>
<td>&lt;1.5 $\times 10^{-6}$</td>
<td>1.82 (ND-17.1)</td>
<td>0.07 (ND-0.45)</td>
<td>0.07 (ND-0.45)</td>
</tr>
<tr>
<td>BDE-190</td>
<td>&lt;4.6 $\times 10^{-7}$</td>
<td>1.30 (ND-42.4)</td>
<td>0.40 (ND-2.24)</td>
<td>0.40 (ND-2.24)</td>
</tr>
<tr>
<td>BDE-196</td>
<td></td>
<td>1.23 (ND-8.84)</td>
<td>0.40 (ND-2.24)</td>
<td>0.40 (ND-2.24)</td>
</tr>
<tr>
<td>BDE-197</td>
<td></td>
<td>1.87 (ND-21.4)</td>
<td>0.40 (ND-2.24)</td>
<td>0.40 (ND-2.24)</td>
</tr>
<tr>
<td>BDE-201</td>
<td></td>
<td>0.55 (ND-3.80)</td>
<td>0.40 (ND-2.24)</td>
<td>0.40 (ND-2.24)</td>
</tr>
<tr>
<td>BDE-202</td>
<td>&lt;2.4 $\times 10^{-7}$</td>
<td>0.24 (ND-1.71)</td>
<td>0.18 (ND-1.41)</td>
<td>0.18 (ND-1.41)</td>
</tr>
<tr>
<td>BDE-205</td>
<td></td>
<td>0.82 (ND-13.0)</td>
<td>0.02 (ND-0.50)</td>
<td>0.02 (ND-0.50)</td>
</tr>
<tr>
<td>BDE-206</td>
<td></td>
<td>5.72 (ND-35.7)</td>
<td>5.53 (ND-75.1)</td>
<td>5.53 (ND-75.1)</td>
</tr>
<tr>
<td>BDE-207</td>
<td></td>
<td>3.94 (0.44-18.7)</td>
<td>1.91 (ND-18.2)</td>
<td>1.91 (ND-18.2)</td>
</tr>
<tr>
<td>BDE-208</td>
<td></td>
<td>2.10 (0.35-8.87)</td>
<td>1.30 (ND-11.3)</td>
<td>1.30 (ND-11.3)</td>
</tr>
<tr>
<td>BDE-209</td>
<td>1.6 $\times 10^{-3}$</td>
<td>665 (0.39-3060)</td>
<td>412 (2.73-5206)</td>
<td>181 (14.5-1389)</td>
</tr>
<tr>
<td>ΣPBDE-17</td>
<td></td>
<td>690 (1.25-3673)</td>
<td>437 (3.11-15504)</td>
<td>190 (18.2-1435)</td>
</tr>
<tr>
<td>ΣTEQ (pg TEQ/g)</td>
<td>10.0 (0.01-54.1)</td>
<td>6.20 (0.04-78.5)</td>
<td>2.71 (0.22-20.9)</td>
<td>41.23 (2.94-144)</td>
</tr>
</tbody>
</table>

$^a$Average concentrations were calculated using ND = 0. $^b$REPs (relative potencies), derived from a chemically activated luciferase gene expression (CALUX) cell bioassay (EC$_{50coli}$), were used to calculate the toxic equivalents (TEQs). $^c$ΣTEQ concentrations were calculated as the mean of the sum of BDE-47, -66, -85, -99, -100, -153, -183, -190, and -209.
recycling processes have now ceased and are prohibited by the local government. However, the legacy of these recycling techniques, including environmental contamination, are still of concern.

Sampling. Samples of soil, sediment, and human hair were collected from villages in Zhaogezhuang and the adjacent Dalu in November 2011. Soil samples (0–10 cm deep) were collected from a total of 62 sites (four replicate samples from each site) using a stainless steel shovel. The soil sampling site density was increased in Yincun, where has been the site of the longest-running continuous recycling activities in Wen’an. Sediment samples (the top 10 cm) were collected using a grab sampler from the Xiaoibaihe River, the Renwen Canal, and the Yincun Ditch, which have each received wastewater from plastic recycling activities. A total of 25 sediment samples were collected. The soil and sediment sampling locations are shown in Figure 1. Each soil and sediment sample was placed in a precleaned aluminum box and freeze-dried before being ground, homogenized, and stored at −20 °C until analysis.

Hair samples were collected from villages in Zhaogezhuang. The method of hair sampling applied was that used in a previous hair pollution study in e-waste recycling area. Information of individual’s age, gender, health status, occupational history, hair treatment, and place of residence were provided under informed consent. A total of 45 healthy participants (8 females and 37 males) agreed to provide hair samples. The volunteers were 9–71 years old; 19 volunteers were occupationally exposed plastic waste recycling workers, and 26 were nonoccupationally exposed residents of the plastic waste recycling area. The occupational workers had been employed in plastic waste recycling for 3–16 years. Dyed or bleached hair samples were excluded. Hair samples were cut about 2 cm from the scalp and the nape of the neck using stainless steel scissors and then incubated in Milli-Q water in a shaking incubator (for 1 h at 25 °C) twice to remove external contamination. The samples were then air-dried, cut into lengths of less than 1 cm, mixed well, and wrapped in aluminum foil before being transported to the laboratory, where they were kept at −4 °C until analysis.

Sample Preparation and Analysis. The extraction and cleanup procedures were based on methods described elsewhere, with some modifications, and are described in the Supporting Information. Briefly, the samples were spiked with 13C-labeled PCB-141, which was used as a surrogate recovery standard, and then extracted using a 1:1 (v/v) mixture of hexane and dichloromethane. The extracts were treated with Cu to remove sulfur, and the sediment extracts were sulfonated using concentrated sulfuric acid before being cleaned further. The concentrated extracts were then cleaned and fractionated using neutral, acid, and alkaline multilayer silica gel columns eluted with 70 mL of a 1:1 (v/v) mixture of hexane and dichloromethane. The extracts were again concentrated, and a known amount of 13C-labeled PCB-208, which was used as an internal standard, was added. The extracts were then analyzed by gas chromatography–mass spectrometry (GC/MS). The instrumental conditions and procedures used and the quality assurance/quality control (QA/QC) steps taken are described in the Supporting Information. Twenty-one PBDE congeners (BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -190, -196, -197, -201, -202, -203, -205, -206, -207, -208, and -209) were measured. The recoveries of the 21 target PBDEs were 81.5–127% for soil and sediment samples and 88.8–138% for hair samples.

RESULTS AND DISCUSSION

PBDE Concentrations in Soils and Sediments. The means and ranges of the 21 PBDE congener concentrations and the total PBDE (ΣPBDE) concentrations in the soil samples from the waste plastic recycling area are summarized in Table 1. The BDE-209 and ΣPBDE concentrations ranged from 0.39 to 5260 ng/g and from 1.25 to 5504 ng/g, respectively, in the soil samples. The ΣPBDE concentrations in the soil samples varied by a factor of about 4000. There was no statistically significant difference between the ΣPBDE concentrations in the soils from Dalu and those from Zhaogezhuang. As expected, however, relatively high ΣPBDE concentrations were found at sampling sites Y15 (3673 ng/g), Y27 (3462 ng/g), and Y22 (2824 ng/g), which were collected in and near Yincun. The PBDE emissions from the low-tech plastic waste recycling methods used in Yincun could have caused the high PBDE concentrations found in the soil samples from there. Interestingly, the highest ΣPBDE concentration was found at sampling site D209, which is in an agricultural area in Dalu where waste plastic combustion residues were found. The high PBDE concentrations in this soil sample could have been caused by PBDE emissions from the burning of PBDE-treated plastics, a similar conclusion having been drawn from a previous study in an e-waste recycling area.

Table 1 shows the PBDE concentrations found in sediments from waterways in Wen’an. The BDE-209 and ΣPBDE concentrations in sediments from the three waterways were significantly (p < 0.05) different. The mean ΣPBDE concentrations in the sediments occurred in the following order: Renwen Canal > Yincun Ditch > Xiaoibaihe River, with the PBDE concentration in the Xiaoibaihe River sediment being an order of magnitude lower than the concentrations in the Renwen Canal and Yincun Ditch sediments. There were no significant positive correlations between the total organic carbon (TOC) and BDE-209 or ΣPBDE concentrations in the sediment samples. The high PBDE concentrations found in the Renwen Canal and Yincun Ditch, which flow through the plastic recycling area, suggest that the PBDE contamination was mainly derived from waste discharges from the waste plastic recycling facilities. Xiaoibaihe River is the largest river in the study area and flows through the edge of the recycling areas, unlike the other two waterways, which flow across the center of the recycling areas. Relatively lower levels of PBDEs in sediment from Xiaoibaihe River might be attributed mainly to the dilution of water from upstream. Unexpectedly, the highest BDE-209 concentration (9816 ng/g) and ΣPBDE concentration (9889 ng/g) were found at site R2 in the Renwen Canal and not at any of the Yincun Ditch sites. This may have been caused by the dumping and combustion of waste plastic debris in the area around the Renwen Canal.

Homologue Profiles in Soil and Sediment Samples. As is shown in Table 1 and Figure 2, BDE-209 was the predominant congener in the surface soils, contributing an average of 92.9% and 88.1% of the ΣPBDE concentrations in the samples from Zhaogezhuang and Dalu, respectively. The octa- and nona-BDE homologue groups were also found in relatively high abundances compared to the other homologue groups in most of the soils. The tri-, tetra-, penta-, hexa-, and hepta-BDE homologue groups each represented less than 1% of the ΣPBDE concentration, which indicates how strongly the congener patterns in soils in the waste plastic recycling area...
were dominated by the highly brominated PBDEs. Relatively high concentrations of the higher molecular weight PBDE congeners (BDE-183, -203, -206, -207, and -208) were found in the soils. Soil samples from Daliu also contained relatively high concentrations of BDE-99 and -153, reflecting some differences in the PBDE congener profiles in the soil samples from the two towns.

Figure 2 also shows the relative abundances of different PBDE congeners in the sediment samples. Overall, BDE-209 was the predominant congener, contributing 79.9−97.2% of the ΣPBDE concentration in all of the sediment samples, followed by BDE-206, -207, -208, -183, -203, -197, and -196. BDE-85, -138, -190, and -205 were only found in a few sediment samples. The PBDE congener profiles of sediments from the three waterways were different. As is shown in Figure 2, the proportions that BDE-209 and the less brominated PBDEs (tri- to hexa-BDEs) contributed to the ΣPBDE concentrations in the Xiaobaihe River sediment samples were significantly different from the contributions in the Renwen Canal and Yincun Ditch sediment samples (p < 0.05). Specifically, the average contribution of BDE-209 to the ΣPBDE concentration in the Xiaobaihe River sediment samples was 89.7%, whereas it was 94.1% in the sediment samples from the other two waterways. In the present study, the contribution of lower brominated PBDEs (tri- to hepta-BDEs) to the total PBDEs in sediments was higher in Yincun Ditch than Renwen Canal, though the differences were not significant. Yincun Ditch received sewage and runoff from the recycling activities in Yincun. Many workshops or small factories with thermal recycling, such as heating to remold, and granulating, were concentrated in Yincun. The phenomena in Yincun Ditch might be attributed to more degradation of highly brominated PBDEs in plastics caused by thermal processes during waste recycling.

As shown in Figure 2, the PBDE congener profiles in most of the soils were generally similar to those in sediment samples from Renwen Canal and Yincun Ditch, suggesting that common source of PBDEs in this area. On the other hand, the collected sediments in the present study were directly contaminated by the discharges from the crude plastic recycling.

**Principal Component Analysis of PBDE Congener Patterns.** Principal component analysis (PCA) was conducted on the PBDE concentrations in the soil and sediment samples to further examine the PBDE congener patterns and to identify the possible sources of the PBDEs. Using data published elsewhere, we included PBDE congener patterns for commercial formulations (penta-, octa-, and deca-BDE mixtures) so that we could explore the possibilities of these commercial products being major PBDE sources in the study area and the potential effects of the transport of PBDEs on the congener patterns. Principal component 1 (PC1) and principal component 2 (PC2) accounted for 37.1% and 19.5%, respectively, of the total variance in the PBDE concentrations in the soil samples (Figure 3A). BDE-209 had a high negative loading in PC1, indicating strong contributions from commercial deca-BDE formulations. There were also strongly positive PC1 values that probably indicated contributions from technical penta-BDE products (DE-71 and Bromkal 70-5DE). PC2 was characterized by high loadings for BDE-206, -196, -197, -203, -206, and -207, which are major components of technical octa-BDE products, so this indicates contributions from sources of technical octa-BDE products. The first two components explained 60.6% of the total variance in the PBDE concentrations in the sediment samples (Figure 3B), and the PC1 and PC2 loading plots were similar to those for the soils.
Most of the soil samples were clustered with two deca-BDE mixtures (Saytex 102E and Bromkal 82-0DE), indicating that the major PBDE sources to the soils in the study area could have been technical deca-BDE products. This can be explained by the fact that commercial deca-BDE mixtures account for most of the PBDE use as flame retardants in plastics in China.\textsuperscript{11,12} Deca-BDE has been found to dominate the brominated flame retardant signature in samples of hard plastic toys, which contained a median BDE-209 concentration of 34,300 ng/g.\textsuperscript{2} As shown in Figure 3A, some soil samples (such as D\textsubscript{12}, Y\textsubscript{14}, and D\textsubscript{17}) had relatively high positive PC1 scores, indicating that penta-BDE formulations had influenced these samples. Loading plots for individual congeners are shown in Figure S1 (A) (in the Supporting Information). Some of the octa- and nona-BDE congeners, such as BDE-206, -207, and -208, are separated from BDE-209 and -183 in Figure S1 (A). There were significant negative correlations ($p < 0.05$) between BDE-209 and BDE-206, -207, and -208. The degradation of highly brominated PBDEs in the environment remains controversial. Our results suggest that highly brominated PBDEs may have been subject to degradation caused by complex physical and chemical processes during the plastic manufacturing and/or waste plastic recycling processes, in addition to degradation in the environment, in the studied area.

The sediment samples and deca-BDE products (Saytex 102E and Bromkal 82-0DE) were grouped together, showing similar loadings for both principal components (Figure 3B), indicating that the dominant PBDE sources to the sediment samples were deca-BDE products. Some sediment samples from the Xiaobao River (e.g., X\textsubscript{9} and X\textsubscript{10}) had slightly higher PC2 loadings, indicating a certain amount of influence on the occurrence of PBDEs in the sediments from octa-BDE formulations. These findings were not completely consistent with the results of previous studies of sediments collected in e-waste recycling areas, in which PBDEs have usually clearly been mixtures of penta-, octa-, and deca-BDE commercial formulations.\textsuperscript{9,23,23} BDE-28 and -66, which are commonly derived from penta-BDE products,\textsuperscript{7} were not grouped with BDE-47, -99, and -100 (major congeners in penta-BDE products) but with BDE-205 and -190 (shown in Figure S1 (B)) in our study. This was likely to indicate that these less brominated congeners in the sediment samples originated from both commercial products and from the decomposition of more brominated PBDEs.

**PBDEs in Human Hair.** The means and ranges of the PBDE concentrations in the hair samples are shown in Table 1. The \(\Sigma PBDE\) concentrations in the hair samples ranged from 1.50 to 861 ng/g (mean 112 ng/g). Zheng et al. reported that PBDE concentrations in hair were higher in the senior (>60 years) and preschooler (<7 years) than in adult group (19–60 years).\textsuperscript{10} The \(\Sigma PBDE\) concentrations in the hair samples occurred in the following order: young group (15–45 years old) > middle-aged group (>45 years old) > children (<15 years old), although the differences between the three age groups were not significant. The higher PBDE concentrations in the young group could be attributed to the members of this group being more occupationally exposed to PBDEs during plastic waste recycling activities. The highest \(\Sigma PBDE\) concentration (861 ng/g) was found in a 40-year-old recycling worker who had been employed in a waste plastic recycling factory for 10 years. The \(\Sigma PBDE\) concentrations were significantly higher ($p < 0.01$) in hair samples from waste plastic recycling workers (6.57 to 861 ng/g) than from nonoccupationally exposed residents of the study area (1.50 to 418 ng/g). There were no statistically significant gender-related differences in the PBDE concentrations in the hair samples. The number of the samples taken from females was much lower than the number of samples taken from males, which may affect the results of statistical analysis.

The abundances of individual PBDE congeners in the hair samples were investigated. As shown in Table 1 and Figure 2, BDE-209 was the most abundant congener in all of the samples, accounting for 87.7%, 95.2%, and 90.5% of the \(\Sigma PBDE\) concentrations in the hair samples from the children, young group, and middle-aged group, respectively. Significant differences ($p < 0.05$) were found between the BDE-209 abundances in the young and middle-aged groups. Significantly different abundances of the tri-, tetra-, penta-, and hexa-BDEs were also found between the three age groups, indicating that age was a key factor that influenced the PBDE congener profile. Several highly brominated BDEs (BDE-206, -207, and -208) were found at the next highest concentrations after BDE-209, but they only contributed <3% of the \(\Sigma PBDE\) concentrations. The notable congeners BDE-47, -99, and -100 were found at relatively low abundances in the hair samples analyzed, whereas they have been found at much higher relative abundances in other studies.\textsuperscript{21,24} Our results are, however, consistent with results found in e-waste recycling, urban, and rural areas in southern China.\textsuperscript{10,25,26}

**Comparison with PBDE Pollution in Other Regions.** To better understand the PBDE contamination status and the possible PBDE sources in the waste plastic recycling area, we compared the PBDE concentrations and congener patterns found in the study area with those observed in previous studies in other regions. Inconsistencies in the methods used to analyze the congeners made it difficult to draw comparisons, so simple comparisons were made using the same congener or homologue, where this was possible. Based on PBDE relative potencies (REPs) reported in the literature,\textsuperscript{27} toxic equivalent (TEQ) concentrations for selected indicative PBDE congeners were also calculated according to the soil PBDE concentrations reported in this and other studies. The mean TEQ concentrations of PBDEs in soils from different regions were compared to understand the risks associated with PBDEs emitted from the waste plastic recycling facilities.

The PBDE and TEQ concentrations found in soils from different regions are shown in Figure S2. The BDE-209, \(\Sigma PBDE\), and TEQ concentrations in soils from e-waste recycling sites were 2−3, 3−5, and 2−4 times higher,\textsuperscript{28,29} respectively, than the concentrations found in soils from the plastic recycling area in this study. However, the BDE-209 and TEQ concentrations in the soils in the study area were comparable to concentrations observed in soils at a printer roller dump site in Guiyu Town. The level of PBDE contamination in Wen’an was similar to that around a deca-BDE production area.\textsuperscript{30} The BDE-209, \(\Sigma PBDE\), and TEQ concentrations in the plastic recycling area were an order of magnitude higher than those found in regional soils from Qianguan and Guangzhou,\textsuperscript{6} China and Kuwait City.\textsuperscript{31} PBDE and TEQ concentrations were 2−3 orders of magnitude lower in some other areas than in Wen’an. Compared with these areas, the surface soils in the plastic recycling areas in Wen’an have suffered from relatively high levels of PBDE pollution.

\(\text{dx.doi.org/10.1021/es404905u} \mid \text{Environ. Sci. Technol.} \text{2014, 48, 1508−1516}\)
PBDE concentrations in sediments from different areas are summarized in Table S1. Lower ΣPBDE but higher BDE-209 concentrations were found in sediments from the plastic recycling area than in sediments from the Nanyang River in an e-waste recycling area. The PBDE concentrations in the Xiaobaihe River sediments in our study were lower than the concentrations found in sediments from the Maohzhou River, \(^{20}\) in Shenzhen, and the Pearl River. \(^{55}\) The BDE-209 and ΣPBDE concentrations in the sediments were much higher in the Renwen Canal and Yincun Ditch than those from the Maohzhou River\(^ {20}\) and Pearl River\(^ {55}\) but were also 1–3 orders of magnitude higher than those in many other rivers and lakes in China\(^ {36,37}\) and much higher than those from other Asian canals and rivers. \(^{38}\)

The plastic waste that has been recycled in the study area has mainly comprised abandoned household and industrial plastics, such as plastic toys, furniture, and automobile parts, in which PBDE concentrations are usually lower than in e-waste. \(^{4,7,8,12}\) It has been reported that ΣPBDE concentrations in printed circuit boards often reach thousands to tens of thousands of milligrams per kilogram. \(^{5,7}\) Furthermore, some extremely destructive methods, such as acid washing and burning, are often used to recover valuable metals and nonmetals from e-waste, resulting in massive PBDE releases. \(^{5}\) In contrast, relatively moderate methods, such as rinsing, grinding, and heating, are generally used to recycle plastic waste. These differences may lead to differences in PBDE pollution characteristics between plastic waste recycling areas and e-waste dismantling areas.

The homologue profiles in the soils and sediments analyzed were different from those found in other studies. In some e-waste recycling areas, \(^{3,9,22,39}\) besides the commercial deca-BDE formulation, BDE-47, -99, and -183 have been found to be dominated by or clearly enriched in the soil and sediment, reflecting a previously use combination of the three commercial PBDEs in electronic products. In contrast, BDE-209 contributed the highest proportion (nearly 90%) of the ΣPBDE concentrations in the soil and sediment samples from Wen’an, while weak or indistinguishable sources from penta- and octa-BDE products were exhibited. In China, approximately 80% of the total deca-BDE product produced is used in ABS and high-impact polystyrene. \(^{51}\) Other minor uses, including polybutylene terephthalate and polyamide polymers, account for the remaining 20% of the deca-BDE product. \(^{11}\) Octa-BDE has never been commercially produced in China, and only relatively small quantities of penta-BDE have been produced and used (in the past) in polyurethane foam used in electronic equipment. \(^{11}\) The PBDE pollution patterns described above therefore reflect the different usage patterns of the three different major PBDE products.

Hair PBDEs in this study were compared with some previous reports in other areas. As shown in Figure S3, the BDE-209 and ΣPBDE concentrations in the hair were even comparable to those observed in most other areas, \(^{10,21,41}\) indicating that hair PBDEs were mainly from the use of deca-BDE. However, BDE-209 accounted for a higher percentage of total PBDEs in hair from the study area, indicating more distinguishable sources of deca-BDE products than those in e-waste recycling areas and other areas. An elevated percentage of low brominated BDEs (e.g., BDE-47, 99) and the decreased contribution of BDE-209 in the e-waste areas may be due to the use of penta-PBDE and octa-PBDE mixtures in the e-wastes before their restriction. \(^{10,29}\)

There are some studies showing that there are significant relationships between concentrations of halogenated compounds in hair and internal tissues. \(^{42,43}\) and hair is considered to be a good indicator of internal exposure. However, some previous studies identified that dust is a major pathway for halogenated chemical exposure in hair. \(^{10,44}\) Although high levels of PBDE in soils might result in heavily polluted atmospheric particles under suitable conditions, it is still hard to speculate on the contribution of soil PBDEs to hair PBDEs, because the soil samples were not paired with human hair samples in this study. For this study, it is also difficult to differentiate PBDEs transported to human hair via endogenous or exogenous exposure pathways, since the levels of PBDEs in blood and other human tissues were not analyzed. Further investigations are needed to determine the sources of high PBDE concentrations in hair and the concomitant human health risks in this plastic recycling area.

The data reported here confirm that poorly controlled plastic waste recycling operations are significant sources of PBDEs to the environment, resulting in locally severe and regionally significant environmental contamination. More research is required to determine PBDE concentrations in different environmental media, a range of organisms, and the body burden in a number of humans in this area to better understand the risks associated with chemicals emitted during waste plastic recycling activities.

### ASSOCIATED CONTENT

#### Supporting Information

Additional information regarding sample cleanup procedures, instrumental analysis, quality assurance, and quality control; Table S1; and Figures S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

#### Corresponding Author

Phone: +86-10-8491-5162. Fax: +86-10-8491-3903. E-mail: huangqf@craes.org.cn.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (41001329), the National Environmental Protection Public Welfare Science and Technology Research Program of China (201209020 and 201309023), and the Natural Science Foundation of Hebei Province (No. B2011502017).

### REFERENCES


2. La Guardia, M. J.; Hale, R. C.; Harvey, E. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from...


