

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51488169>

# Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic

ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · AUGUST 2011

Impact Factor: 5.33 · DOI: 10.1021/es201850n · Source: PubMed

CITATIONS

43

READS

53

9 AUTHORS, INCLUDING:



**Axel Möller**

Gesellschaft für Bioanalytik mbH

37 PUBLICATIONS 680 CITATIONS

SEE PROFILE



**Zhiyong Xie**

Helmholtz-Zentrum Geesthacht

74 PUBLICATIONS 1,766 CITATIONS

SEE PROFILE



**Jianfeng He**

Polar Research Institute of China

39 PUBLICATIONS 315 CITATIONS

SEE PROFILE



**Ralf Ebinghaus**

Helmholtz-Zentrum Geesthacht

225 PUBLICATIONS 6,514 CITATIONS

SEE PROFILE

# Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic

Axel Möller,<sup>\*,†</sup> Zhiyong Xie,<sup>†</sup> Minghong Cai,<sup>\*,‡</sup> Guangcai Zhong,<sup>†,§,||</sup> Peng Huang,<sup>⊥</sup> Minggang Cai,<sup>⊥</sup> Renate Sturm,<sup>†</sup> Jianfeng He,<sup>‡</sup> and Ralf Ebinghaus<sup>†</sup>

<sup>†</sup>Department for Environmental Chemistry, Institute of Coastal Research, Helmholtz–Zentrum Geesthacht, Centre for Materials and Coastal Research, Max–Planck–Strasse 1, 21502 Geesthacht, Germany

<sup>‡</sup>SOA Key Laboratory for Polar Science, Polar Research Institute of China, Shanghai 200136, China

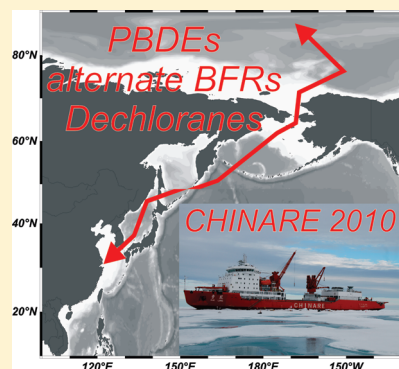
<sup>§</sup>Yantai Institute of Coastal Zone Research, CAS, Yantai 264003, China

<sup>||</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

<sup>⊥</sup>College of Oceanography and Environmental Science, Xiamen University, Xiamen 361005, China

**S** Supporting Information

**ABSTRACT:** Marine boundary layer air and seawater samples taken during a polar expedition cruise from East China Sea to the Arctic were analyzed in order to compare the occurrence, distribution, and fate of the banned polybrominated diphenyl ethers (PBDEs) with their brominated alternatives as well as the chlorinated Dechloranes. The sum of PBDEs ( $\Sigma_{10}$ PBDEs) in the atmosphere ranged from 0.07 to 8.1 pg m<sup>-3</sup> with BDE-209 being the dominating congener and from not detected (n.d.) to 0.6 pg L<sup>-1</sup> in seawater. Alternate brominated flame retardants (BFRs), especially hexabromobenzene (HBB), (2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), pentabromotoluene (PBT), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), bis-(2-ethylhexyl)-tetrabromophthalate (TBPH), were detected in higher concentrations than PBDEs, even in the high Arctic (0.6 to 15.4 pg m<sup>-3</sup> for sum of alternate BFRs), indicating the change of PBDEs toward alternate BFRs in the environmental predominance. In addition, Dechlorane Plus (DP) as well as Dechlorane 602, 603, and 604 were detected both in the atmosphere and in seawater. The highest concentrations as well as the highest compound variability were observed in East Asian samples suggesting the Asian continent as source of these compounds in the marine environment. The air–seawater exchange indicates strong deposition, especially of alternate BFRs, as well as dry particle-bound deposition of BDE-209 into the ocean.



## INTRODUCTION

Halogenated, mainly brominated flame retardants (BFRs) have been applied in electronics, (building) foams, and furnishing since the 1960s.<sup>1</sup> Thereby, the polybrominated diphenyl ethers (PBDEs) have been the most scientifically, politically, and publicly focused group in the 2000s and are still the dominating species in terms of environmental research on halogenated flame retardants (HFRs). PBDEs are known to be harmful for the environment caused by their bioaccumulation potential, toxicity, persistence, and potential for atmospheric transport over (very) long distances<sup>2,3</sup> leading to “flame-proofing” of remote regions such as the Arctic environment.<sup>4</sup> Since the early 2000s, the production and usage of PBDEs has been strictly regulated and partly banned, i.e., voluntary production phase-out of Penta- and OctaBDE in 2004<sup>5</sup> and expected production phase-out of DecaBDE by 2012<sup>6</sup> in the United States (U.S.), and ban of Penta-, Octa- (2004), and DecaBDE (2008, only in electrical and electronic equipment) in the European Union (EU).<sup>7</sup> Finally, components of the Penta- and OctaBDE mixtures were included in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009 (www.pops.int).

Nevertheless, a global annual HFR production increase of ~5% was reported<sup>8</sup> which can be traced back to increasing usage in Asia, in particular China,<sup>9</sup> with an annual increase of the BFR demand of 8% in 2005.<sup>10</sup> Non-PBDE BFRs include both BFRs which have been (only recently) developed as substitutes for the banned PBDEs (e.g., 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), bis-(2-ethylhexyl)-tetrabromophthalate (TBPH)) as well as traditional non-PBDE BFRs such as hexabromobenzene (HBB) and pentabromotoluene (PBT) which have been produced and used similar to PBDEs for several decades. There is very little knowledge on their behavior in terms of persistence and long-range atmospheric transport (LRAT) in the environment which are important criteria for POPs, but models assessed a sufficient POP potential of some new BFRs to reach remote regions<sup>11,12</sup> or they were prioritized for further research in the (remote) environment.<sup>13</sup>

**Received:** May 31, 2011

**Accepted:** July 13, 2011

**Revised:** July 11, 2011

**Published:** July 13, 2011

Several non-PBDE BFRs have been investigated and detected in the environment, primarily in source regions such as urban areas or the indoor environment (e.g., 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE),<sup>14</sup> TBPB,<sup>15</sup> HBB<sup>16</sup>), but also in non-source outdoor regions and even remote areas such as the Arctic and Antarctica,<sup>2,17</sup> again, indicating their LRAT potential. Another HFR, the highly chlorinated flame retardant Dechlorane Plus (DP), has been produced and likely unnoticed emitted into the environment for more than forty years. Since its first detection in the environment in 2006,<sup>18</sup> reports on DP in the environment increased rapidly, and it has been recently observed in the remote regions of the Arctic and Antarctica.<sup>19</sup> Nevertheless, data on the occurrence and environmental fate on non-PBDE BFRs and Dechloranes, in particular in remote regions, are still lacking.

In the present study, marine boundary layer air samples and seawater samples were taken during a polar expedition of the Chinese research vessel *Xuelong* from East China Sea to the high Arctic in 2010. The samples were analyzed for PBDEs, non-PBDEs BFRs, Dechlorane Plus and its transformation products, and the Dechloranes 602, 603, and 604 in order to investigate their occurrence and latitudinal distribution, and air-sea exchange including air-seawater gas exchange and dry particle-bound deposition, both with special consideration of the non-PBDEs HFRs compared to the banned PBDEs.

## MATERIALS AND METHODS

**Sampling Cruise.** Onboard the Arctic expedition CHINARE2010 of the research ice-breaker *R/V Xuelong* (*Snow Dragon*) of the Polar Research Institute of China from June to September 2010, air and seawater samples were taken from the East China Sea to the high Arctic (33.23–84.5°N). Air samples (1–2 days, 17 samples) were taken via a high-volume air sampler placed in the front of the ship's upper deck. About 500 m<sup>3</sup> air was passed through a glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) to trap airborne particles followed by a self-packed PUF/Amberlite XAD-2 glass column. Both air column and filters were stored at –20 °C until analysis. Seawater samples (12–24 h, 18 samples) were taken by passing 176–1120 L seawater obtained by the ship's intake system through a GFF (GF/C, pore size: 1.2 μm) following self-packed Serdolit PAD-3 glass column. Seawater filter and columns were stored at –20 and 4 °C, respectively. Sampling parameters including date, position, temperature, and wind speed are included in Tables S1 and S2 in the Supporting Information (SI).

**Extraction, Analysis, QC/QA.** Extraction, clean-up, and analysis of the samples was done based on our previously published method<sup>19,20</sup> and is described in more detail in the SI. Three field blanks were run for each sample type, while blanks showed very low HFR values which were generally in the one- to two-digit absolute pg range (see Table S4 in the SI). Method detection limits (MDLs) ranged from 0.002 to 0.27 pg m<sup>-3</sup> for atmospheric samples and from 0.001 to 0.17 pg L<sup>-1</sup> for seawater samples, respectively (see Table S5 for details). Recoveries of the surrogate standards <sup>13</sup>C-HBB, <sup>13</sup>C-BDE-77, <sup>13</sup>C-BDE-138, <sup>13</sup>C-BDE-209, and <sup>13</sup>C-synDP ranged from 78 ± 32% (<sup>13</sup>C-BDE-77) to 95 ± 57% (<sup>13</sup>C-BDE-209), and spiked recoveries of the analyzed HFRs were in the same range.<sup>17,19,20</sup> Samples were analyzed for 10 PBDE congeners, 8 alternate BFRs, DP, the one- and 2-fold dechlorinated DP species (aCl<sub>11</sub>DP [-1Cl+1H], aCl<sub>10</sub>DP [-2Cl+2H]), and Dechlorane

602, 603, and 604 by GC-MS in electron capture negative chemical ionization mode (ECNCI) (see Table S6 for the chemical structures). The total estimated method uncertainty according to Eurachem guidelines<sup>21</sup> ranged from 9.8% (PBT) to 45.3% (EHTBB) with a median uncertainty of the detected analytes of 16 ± 19%.

**Air Mass Back Trajectories.** Air mass origins along the cruise segments of the individual air samples were calculated using NOAA's HYSPLIT model.<sup>22</sup> Air mass back trajectories (BTs) were calculated in 6 h steps tracing back the air masses for 5 days using the sampling height as arrival height (see Figure S1 for individual BTs).

## RESULTS AND DISCUSSION

**Polybrominated Diphenyl Ethers (PBDEs).** Among the investigated PBDEs, the common Penta-, Octa-, and DecaBDE congeners – BDE-47, –99, and –209 – were detected in almost all atmospheric samples within a concentration range for Σ<sub>10</sub>PBDEs from 0.07 pg m<sup>-3</sup> to 8.1 pg m<sup>-3</sup> (gaseous+particulate, see Table S7 for individual concentrations of all analytes). BDE-209 was found to be the dominating congener with a median contribution of 72 ± 25% of Σ<sub>10</sub>PBDEs and individual concentrations from not detected (n.d.) to 4 pg m<sup>-3</sup>, while it was found mainly in the particulate phase with a mean particle-bound fraction of 74 ± 35% (median 100%). BDE-47 and –99 were detected from 0.02 to 0.8 pg m<sup>-3</sup> and from 0.04 to 1.0 pg m<sup>-3</sup> contributing 8 ± 9% and 13 ± 17% to Σ<sub>10</sub>PBDEs, respectively. Among the other congeners, BDE-100, –153, –154, and –183 were detected in 41%, 18%, 17% and 18% of the air samples. In 2005, Wang et al. reported particle-bound PBDEs along the same sampling transect in concentrations which are several times higher with median concentrations for Σ<sub>11</sub>PBDEs of 47.5 pg m<sup>-3</sup> in Far East Asia and 15.2 pg m<sup>-3</sup> in the Arctic.<sup>23</sup> The elevated concentrations in East Asia were traced back to continental air masses which were not observed within this study (see chapter *Latitudinal trends*). High concentrations in the Arctic were supposed to be caused by impact from North America where PBDEs were still produced at this time.<sup>23</sup> The production phase-out in the U.S may have led to decreasing concentrations in the Arctic as reflected by the lower Arctic concentrations in this study, while, in addition, no continental air masses from Northern America were sampled in the Arctic during this study. Concentrations in the Canadian Arctic were 0.78–48 pg m<sup>-3</sup> for Σ<sub>15</sub>PBDEs in 2002–2003<sup>24</sup> which are, again, significantly higher than in the present study. Jaward et al.<sup>25</sup> reported concentrations in the East Asian terrestrial atmosphere mainly in the low pg m<sup>-3</sup> range which are similar to the concentrations observed in the East Asian samples in this study. The observed concentrations in the Arctic are similar to those recently observed in Greenland and East Greenland Sea<sup>20,26</sup> and the Southern Ocean<sup>17</sup> representing remote concentrations derived from LRAT.

Total seawater concentrations ranged from n.d. to 0.8 pg L<sup>-1</sup> for Σ<sub>10</sub>PBDEs (dissolved+particulate) with BDE-47 and –99 being the dominating congeners with individual concentrations from n.d. to 0.3 pg L<sup>-1</sup> and n.d. to 0.2 pg L<sup>-1</sup>, respectively, which were mainly distributed in the dissolved phase (see Table S8 for individual concentrations). In contrast to the atmosphere, BDE-209 was detected at five stations only, with concentrations from 0.1 to 0.2 pg L<sup>-1</sup>. The observed concentrations are similar to those observed in East Greenland Sea<sup>20</sup> and in the Atlantic and

Southern Ocean.<sup>17</sup> Guan et al.<sup>27</sup> reported concentrations for  $\Sigma_{17}$ PBDEs from 2.69 to 19.1 pg L<sup>-1</sup> in the Pearl River Delta, China, which are at least 2 orders of magnitude higher indicating that riverine discharge might contribute significantly to the PBDE pollution of the (coastal) marine Asian environment.

**Alternate Brominated Flame Retardants.** Among the non-PBDE BFRs, 7 different compounds were observed in the atmosphere: PBBz, PBT, DPTE, HBB, EHTBB, BTBPE, and TBPH. The most dominant compounds were PBBz, PBT, HBB, and DPTE which were detected at all stations mainly in the gaseous phase and ranged from 0.09 to 2 pg m<sup>-3</sup>, 0.1 to 4.5 pg m<sup>-3</sup>, 0.10 to 5.9 pg m<sup>-3</sup>, and 0.1 to 2.5 pg m<sup>-3</sup>, respectively, which are mostly higher than the dominating PBDE congeners. EHTBB, BTBPE, and TBPH were detected at a few stations only but with maximum concentrations of 8.9, 1.6, and 3.4 pg m<sup>-3</sup>, respectively.

Data on new BFRs, especially in the atmosphere, are extremely limited. Lee et al. reported PBBz within their Global Atmospheric Passive Sampling (GAPS) network, but concentrations are not given.<sup>28</sup> It was found in human tissue from Japan<sup>29</sup> and in Danish and Finnish breast milk and placentas,<sup>30</sup> while it was shown to be produced by in-situ debromination of HBB in rats.<sup>31</sup> PBT was detected in Canada from <0.01–0.02 pg m<sup>-3</sup><sup>32</sup> and only recently in the Atlantic Ocean and in East Greenland Sea in concentrations <0.05 pg m<sup>-3</sup>,<sup>17,20</sup> which are several times lower to the concentrations observed in this study, both for the East Asian samples (0.36–4.53 pg m<sup>-3</sup>) as well as for the North Pacific and Arctic stations (0.12–0.79 pg m<sup>-3</sup>). HBB has been reported in concentrations from 0.3–6.5 pg m<sup>-3</sup> and up to 610 pg m<sup>-3</sup> in East China<sup>33</sup> and Japan,<sup>34</sup> respectively. Concentrations of HBB and DPTE similar to the present study were observed in the marine environment of the Atlantic and Southern Ocean and East Greenland Sea,<sup>17,20</sup> too. We recently reported BTBPE and TBPH for the first time in the Arctic atmosphere,<sup>20</sup> while the concentrations were clearly lower than in the present study. High atmospheric concentrations of BTBPE were observed in the U.S. (4–70 pg m<sup>-3</sup><sup>14</sup>) and in Guangzhou, China (3.8–67 pg m<sup>-3</sup><sup>35</sup>). EHTBB was first reported in house dust from the U.S.,<sup>15</sup> and Lee et al. reported qualitatively their worldwide occurrence within the GAPS Network.<sup>28</sup>

In seawater, PBT, DPTE, and HBB were the most frequently detected compounds (78%, 56%, and 100% detection frequency, respectively) with concentrations from n.d.–0.4, n.d.–1.6, and 0.006–0.1 pg L<sup>-1</sup>. Besides, PPBz, BTBPE, and TBPH were detected at four, two, and one station, respectively, with a maximum concentration of 0.2 pg L<sup>-1</sup> for TBPH, while PBBz and BTBPE remained below 0.1 pg L<sup>-1</sup> at all stations. Only a few data on new BFRs in (sea)–water have been published so far. PBT was detected in the Western Scheldt from <0.1–2.4 ng L<sup>-1</sup> and HBB in a Chinese source–near pond at 0.52 ± 0.04 ng L<sup>-1</sup>.<sup>36</sup> DPTE, HBB, TBPH, and BTBPE were recently reported for the first times in (remote) seawater in comparable concentrations to the present study.<sup>17,20</sup>

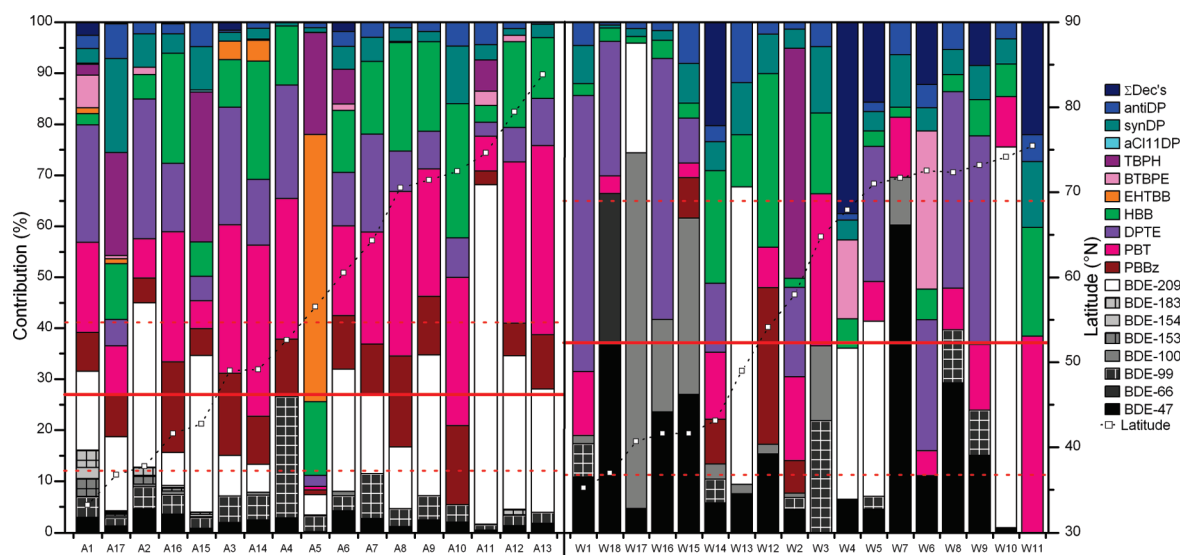
**Dechloranes.** DP, consisting of the syn- and anti-stereoisomer, was detected in all air samples mainly in the particulate phase from 0.01 to 1.4 pg m<sup>-3</sup>. Seawater concentrations ranged from 0.006 to 0.4 pg L<sup>-1</sup>. In addition, the onefold dechlorinated species aCl<sub>11</sub>DP was observed in five air samples at concentrations <0.1 pg m<sup>-3</sup>. In addition, we observed the Dechloranes 602, 603, and 604 in the atmosphere in concentrations of 0.01–0.2 pg m<sup>-3</sup>, 0.4 pg m<sup>-3</sup>, and 0.03–0.05 pg m<sup>-3</sup>, respectively, while they were also present in a few seawater samples in

concentrations of 0.2 pg L<sup>-1</sup>, 0.007–0.2 pg L<sup>-1</sup>, and 0.02–0.05 pg L<sup>-1</sup>, respectively. The atmospheric DP concentrations are similar to those observed in the marine Arctic and Atlantic environment,<sup>19</sup> U.S. non-source sites<sup>18,37</sup> and Chinese rural sites.<sup>38</sup> The mean atmospheric fractional abundance of the syn-isomer ( $f_{syn}$ ) was 0.64 ± 0.12 without any spatial trends from East Asia toward higher latitudes. The mean seawater  $f_{syn}$  value was comparable with 0.61 ± 0.11. Recent studies showed an increase of  $f_{syn}$  value during atmospheric transport caused by stereoselective depletion of the anti-isomer.<sup>14,19</sup> Since the air masses, even in the Korean Strait close to coastline, in the present study were rather oceanic than directly source-related, the present study emphasizes this conclusion. In addition, sampling took place in summer at high temperatures in East Asia above 25 °C with a high sun-irradiation which might lead to a quite fast alteration of  $f_{syn}$ . Dechlorane 602, 603, and 604 were first reported in sediment and fish of the Great Lakes and their tributaries.<sup>39,40</sup> Wang et al. reported Dechlorane 602 in soil and air in eastern China close to a production facility with atmospheric concentrations of ~5 pg m<sup>-3</sup>,<sup>41</sup> and Jia et al. observed Dechlorane 602 and 603 in marine coastal sediment and oysters from China Sea indicating emissions of these compounds into the marine environment.<sup>42</sup> This is the first finding of these Dechloranes in the marine atmosphere.

**Composition Profile of HFRs.** The composition profiles of all HFRs in air and seawater are shown in Figure 1. The atmospheric composition profile was dominated by PBT, BDE-209, HBB, PBBz, and DPTE with median contributions of 25 ± 11%, 15 ± 16%, 12 ± 7%, 10 ± 5%, and 9 ± 8%, respectively. In seawater, DPTE, BDE-47, PBT, and HBB generally dominated with median percentages of 11 ± 19%, 9 ± 16%, 8 ± 10%, and 5 ± 9%, respectively, while the profile differed since a number of HFRs were detected at a few stations only but then with a relatively high contribution. No significant latitudinal trends were observed between East Asia and the Arctic. Comparing PBDEs to their brominated and chlorinated alternates, PBDEs accounted only for 27 ± 15% and 38 ± 27% (median values), while the non-PBDE BFRs dominated with 65 ± 16% and 48 ± 25% in air and seawater, respectively. This shows that non-PBDE BFRs are (meanwhile) the dominating HFRs in the marine atmosphere and seawater in East Asia and, at least in the studied part, also in the Arctic. Especially the samples in the Korean Strait and the Sea of Japan (stations A1, A2, A16, and A17) showed a wide range of HFRs, including both highly-brominated BFRs (i.e., BTBPE, EHTBB, TBPH) which are substitutes for the banned BDE-mixtures as well as the more volatile BFRs (i.e., HBB, PBT) which have been used as BFRs for several decades and Dechloranes.

The predomination of BDE-209 among the PBDEs is a result of DecaBDE being the mostly used (and produced) BDE-mixture in the Asian countries.<sup>43</sup> HBB was widely used in Japan with about 350 tons/year (2001)<sup>44</sup> and is additionally produced in China with 600 tons/year.<sup>9</sup> PBT is produced by the same factory with 600 tons/year, too, while the total global production volume ranges between 1000–5000 tons/year.<sup>9</sup> BTBPE, EHTBB, and TBPH are known to be produced in the U.S.,<sup>14,15</sup> while it can be assumed that they are produced in Asian countries, too, caused by the increasing demand of flame retardants. Dechlorane Plus is produced in Huai'an, China, with an annual production of 300–1000 tons.<sup>41</sup> Besides these production sites located in Eastern China which might be primary sources, the general usage of HFRs in consumer and industrial





**Figure 1.** Composition profile of HFRs in the atmosphere (left) and seawater (right) along the sampling transect. The red line indicates the median  $\Sigma_{10}$ PBDEs contribution (the red dashed line shows the median plus/minus one SD). Note that for station A4 only the gaseous phase and for stations W1, W2, W16, and W18 only the dissolved phase was analyzed.  $\Sigma_3$ Dec's = Decchlorane 602 + 603 + 604. The black dotted line indicates the latitude ( $^{\circ}$ N).

products and subsequently the emission of HFRs from products into the environment, especially in urbanized and industrialized regions, and e-waste disposals, which are known to be important sources of PBDEs in the (Asian) environment,<sup>45</sup> contribute to the HFR pollution of the (marine) environment. Another possible source, especially of HBB, PBBz, and PBT, could be the release from polymeric BFRs or highly brominated FRs such as BDE-209.<sup>32,46,47</sup> Arp et al. proposed the possible breakdown of decabromodiphenyl ethane (DBDPE), a substitute of DecaBDE, to PBT<sup>48</sup> which needs to be experimentally confirmed in future research. DPTE is currently not known to be produced, but its occurrence in air, seawater,<sup>17,20</sup> and marine mammals,<sup>49,50</sup> both in the Pacific, Atlantic, and Southern Ocean and the Arctic in concentrations similar or higher to PBDEs, indicates that it still might be somehow emitted into or formed in the environment.

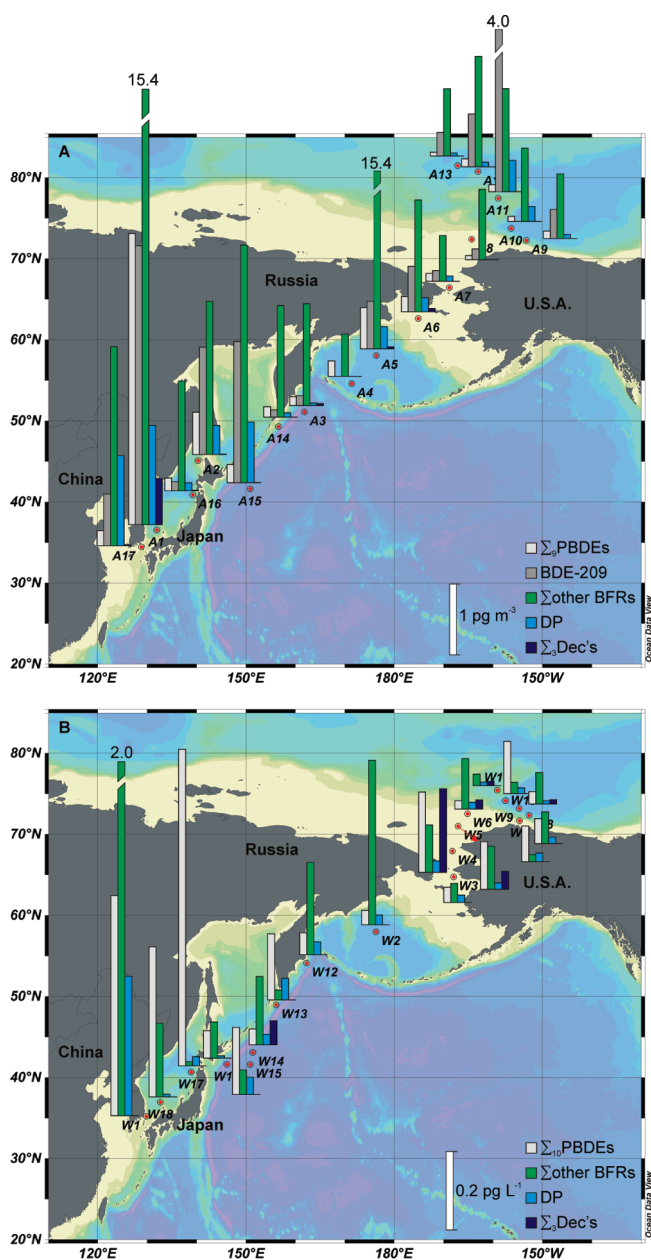
**Latitudinal Trends.** The latitudinal distribution of PBDEs, other BFRs, DP, and other Dechloranes in air and seawater along the sampling transect is shown in Figure 2. The latitudinal trend of the individual compounds in the atmosphere is additionally shown in Figure S2. The highest concentrations, both in air and in seawater, were generally observed in the Korean Strait and the Sea of Japan where the most different compounds were observed (see chapter *Composition profile of HFRs*) as a result of East Asia as source region of HFRs in the environment. But, the air mass back trajectories (BT) analysis showed only a slight influence of the air samples in Korea Strait and the Sea of Japan by continental (Asian) air masses, while the traveling times over the ocean mostly accounted for several days before being sampled. Highly elevated concentrations can be expected if samples would have been dominated by continental, source-related air masses as observed by Wang et al.<sup>23</sup>

Peak concentrations were observed for HBB, EHTBB, and TBPH at station A5 in the North Pacific, while also BDE-99 showed slightly higher concentrations and BDE-153 and -183 were detected above the MDLs, too. Interestingly, TBPH was found in the corresponding seawater station (W2), too. Another elevated concentration was observed for BDE-209 at station A11 in the Arctic, where BTBPE and TBPH were detected, too.

The BT analysis showed no clear explanations for the observed peaks. In contrast to stations A4 and A6, station A5 was influenced by air masses passing part of Eastern Russia where local sources such as waste burning could be located. The origin of the elevated concentrations in the Arctic as well as the general sources of alternate BFRs and Dechloranes in the Arctic, which can be assumed to be the LRAT both from the Eurasian and the American continent, need further global long-term study.

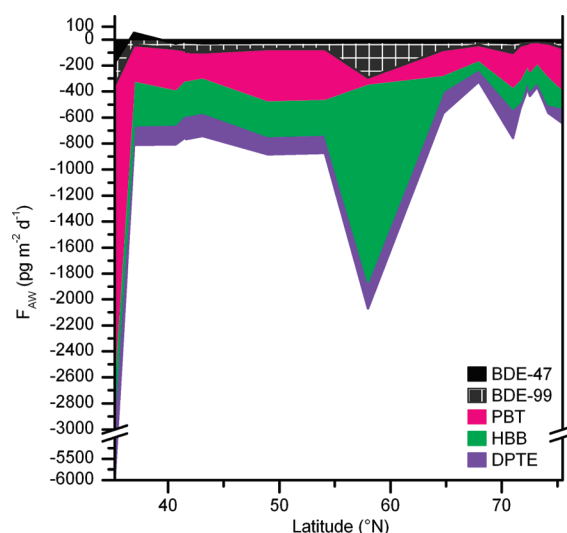
The atmospheric concentrations of most BFRs decreased rapidly from the source region toward the North Pacific and the Arctic where they remained relatively stable. The Pacific and Arctic air masses representing remote concentrations of HFRs being influenced by deposition and/or degradation during LRAT. Significant correlations ( $p < 0.05$  and  $0.01$ , respectively; see Table S9) were observed for several PBDEs as well as for PBBz, PBT, DPTE, and DP indicating similar source regions and comparable LRAT behavior. Even BDE-209 was significantly correlated with other PBDE congeners (except BDE-100) and other HFRs, although it has been shown to undergo photochemical degradation.<sup>51</sup> But, the degradation behavior of BDE-209 attached to airborne particles is not yet studied, while this paper emphasizes the particle-bound LRAT of BDE-209 into remote areas.<sup>20,23,52</sup>

The seawater concentrations were found to be the highest in the samples in the Korea Strait, too, with a strong latitudinal decrease toward the Pacific Ocean (see Figure S3 for the latitudinal trends of the individual compounds). Again, significant correlations were observed between several PBDEs and their alternates ( $p < 0.05$  and  $0.01$ , respectively; see Table S10). The high seawater concentrations could be resulted either by aquatic discharges from coastal sources of HFRs in Asia, as shown for e.g., the Korean coast<sup>53</sup> and the Pearl River,<sup>27</sup> or by atmospheric deposition processes as observed in coastal areas of Korea<sup>54</sup> and shown in chapter *Atmospheric depositions*. However, the riverine discharge into the investigated region is not known and needs to be studied to evaluate the influence of the different sources.



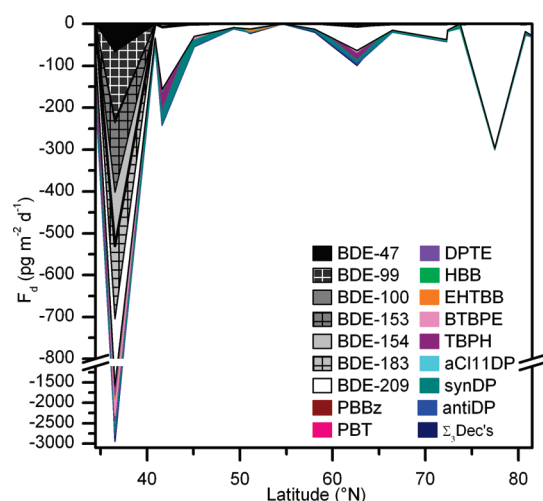
**Figure 2.** Concentrations of PBDEs, other BFRs, DP (synDP + antiDP), and sum of Dechlorane 602, 603, and 604 in the atmosphere (A) and seawater (B) along the sampling cruise. Note that for station A4 only the gaseous phase and for stations W1, W2, W16, and W18 only the dissolved phase was analyzed.

**Atmospheric Depositions.** In order to estimate the influence of air–seawater coupling and the atmospheric input of HFRs into the ocean, we calculated the air–seawater gas exchange and estimated the particle–bound dry deposition flux of HFRs into the ocean. To estimate the direction (or equilibrium status) of the gas exchange, we calculated the fugacity ratio  $f_W/f_A$  of the dominating BFRs (see the SI for details of the calculation; see Figure S4 for plots of the ratios for the individual BFRs). In general, the ratios were  $<1$  within the uncertainty suggesting net deposition at almost all sites for all compounds along the entire transect indicating the atmosphere as a source of BFRs in the ocean. The net air–seawater gas exchange was calculated for



**Figure 3.** Air–sea gas exchange fluxes ( $F_{AW}$ ) of BDE–47, –99, PBT, HBB, and DPTE based on the modified version of the Whitman two–film resistance model.<sup>55,56</sup> The calculation for BFRs has been described elsewhere<sup>20</sup> and is described in detail in the SI. The estimated air–seawater gas exchange fluxes are shown in Figure 3. The net flux was generally dominated by net deposition, while the highest deposition flux was observed in the Korea Strait with individual deposition fluxes from  $180 \text{ pg m}^{-2} \text{ day}^{-1}$  for BDE–47 to  $3100 \text{ pg m}^{-2} \text{ day}^{-1}$  for DPTE driven by the relatively high atmospheric concentrations apparently resulting from emissions by the East Asian countries. The non–PBDEs showed generally higher fluxes than the PBDEs which were lower than  $50 \text{ pg m}^{-2} \text{ day}^{-1}$  at most stations or showed even slight volatilization (BDE–47 at station W18). This shows that atmospheric transport and deposition is an important source of non–PBDEs BFRs in the (coastal) marine environment, while the gaseous atmospheric input of PBDEs is comparably low. In the Pacific Ocean and the Arctic, the flux was relatively constant in the 2 to 3–digit  $\text{pg m}^{-2} \text{ day}^{-1}$  range, while a higher deposition flux of  $1500 \text{ pg m}^{-2} \text{ day}^{-1}$  was calculated for station W2 in the Pacific which might be influenced by Russian air masses.

To investigate the particle–bound deposition flux of highly hydrophobic HFRs, we estimated the dry particle–bound using deposition velocities of  $0.3 \text{ cm s}^{-1}$  and  $0.1 \text{ cm s}^{-1}$  for the East Asian and the Pacific Ocean and the Arctic, respectively (see the SI for details). The dry deposition flux is shown in Figure 4. Similar to the gaseous deposition, the particle–bound deposition was highest in the East Asian stations with a total flux of  $2900 \text{ pg m}^{-2} \text{ day}^{-1}$  which was dominated by BDE–209 but also several other highly brominated FRs as well as Dechloranes are deposited into the ocean. Excluding station A11, the dry deposition in the Arctic was relatively constant ranging from 12 to  $99 \text{ pg m}^{-2} \text{ day}^{-1}$ , while, again, BDE–209 dominated. The dry particle–bound flux of BDE–209 is comparable to the gaseous deposition of the lower brominated FRs, while the particle–bound flux of BDE–47 and BDE–99 is negligible. In any case, BDE–209, DP, and alternate BFRs are emitted into the atmosphere by East Asian countries and further deposited into the ocean, especially into coastal areas. The sources of those alternate BFRs and



**Figure 4.** Dry particle-bound deposition fluxes ( $F_d$ ) of HFRs vs latitude along the sampling transect.

Dechloranes in the environment of the East Asian countries as well as their atmospheric and aqueous emissions into the ocean, especially into the coastal areas such as the Bohai Bay, require future research.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Tables on the sampling sites,  $m/z$  values, blanks, MDLs, chemical structures, BTs, individual concentrations, latitudinal trends, correlations, method description, and a description of the air–seawater exchange calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: +49–4152–87–2353. Fax: +49–4152–87–2332. E-mail: [axel.moeller@hzg.de](mailto:axel.moeller@hzg.de) (A.M.), Phone: +86–21–58717635. Fax: +86–21–58711663. E-mail: [caiminghong@pric.gov.cn](mailto:caiminghong@pric.gov.cn) (M.C.).

## ■ ACKNOWLEDGMENT

We acknowledge the crew of the *R/V Xuelong* and the support from the Chinese Arctic and Antarctic Administration, State Oceanic Administration of China. Volker Matthias (HZG) is acknowledged for help plotting the BTs.

## ■ REFERENCES

- (1) Alaee, M.; Arias, P.; Sjödin, A.; Bergman, A. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* **2003**, *29*, 683–689.
- (2) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated flame retardants in the Arctic environment – trends and new candidates. *Sci. Total Environ.* **2010**, *408*, 2885–2918.
- (3) Birnbaum, L. S.; Staskal, D. F. Brominated flame retardants: Cause for concern? *Environ. Health Perspect.* **2004**, *112*, 9–17.
- (4) Betts, K. S. Flame-Proofing the Arctic? *Environ. Sci. Technol.* **2002**, *36*, 188A–192A.
- (5) Renner, R. Government Watch: In U.S., flame retardants will be voluntarily phased out. *Environ. Sci. Technol.* **2004**, *38*, 14A–14A.

- (6) Hess, G. Industry Drops Flame Retardant. *Chem. Eng. News* **2010**, *88*, 10.
- (7) European Court of Justice, Joined Cases C–14/06 and C–295/06, Judgement of the Court, 1 April 2008, Directive 2002/95/EC and Commission Decision 2005/717/EC.
- (8) Fink, U.; Hajduk, F.; Mori, H.; Wei, Y. *Flame retardants*, SCUP report; SRI Consulting: 2008.
- (9) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de, W. C. A. Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. *Environ. Int.* **2011**, *37*, 532–556.
- (10) Mai, B.; Chen, S.; Luo, X.; Chen, L.; Yang, Q.; Sheng, G.; Peng, P.; Fu, J.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005**, *39*, 3521–3527.
- (11) Brown, T. N.; Wania, F. Screening chemicals for the potential to be persistent organic pollutants: A case study of Arctic contaminants. *Environ. Sci. Technol.* **2008**, *42*, S202–S209.
- (12) Howard, P. H.; Muir, D. C. G. Identifying new persistent and bioaccumulative organics among chemicals in commerce. *Environ. Sci. Technol.* **2010**, *44*, 2277–2285.
- (13) Harju, M.; Heimstad, E. S.; Herzke, D.; Sandanger, T.; Posner, S.; Wania, F. *Emerging “new” Brominated flame retardants in flame retarded products and the environment*; Norwegian Pollution Control Authority: Oslo, 2009.
- (14) Hoh, E.; Zhu, L. Y.; Hites, R. A. Novel flame retardants, 1,2-bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States’ environmental samples. *Environ. Sci. Technol.* **2005**, *39*, 2472–2477.
- (15) Stapleton, H. M.; Allen, J. G.; Kelly, S. M.; Konstantinov, A.; Klosterhaus, S.; Watkins, D.; McClean, M. D.; Webster, T. F. Alternate and new brominated flame retardants detected in US house dust. *Environ. Sci. Technol.* **2008**, *42*, 6910–6916.
- (16) Zhang, Y.; Luo, X.-J.; Wu, J.-P.; Liu, J.; Wang, J.; Chen, S.-J.; Mai, B.-X. Contaminant pattern and bioaccumulation of legacy and emerging organohalogen pollutants in the aquatic biota from an e-waste recycling region in South China. *Environ. Toxicol. Chem.* **2010**, *29*, 852–859.
- (17) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated flame retardants in seawater and atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45*, 1820–1826.
- (18) Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1184–1189.
- (19) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica. *Environ. Sci. Technol.* **2010**, *44*, 8977–8982.
- (20) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. *Environ. Pollut.* **2011**, *159*, 1577–1583.
- (21) EURACHEM/CITAC guide CG 04, Quantifying Uncertainty in Analytical Measurement. Eurachem/CITAC, 2000. <http://www.eurachem.org/guides/pdf/QUAM2000-1.pdf> (accessed March 11, 2011).
- (22) Draxler, R. R.; Hess, G. D. Description of the HYSPLIT\_4 modeling system. NOAA Tech. Memo. ERL ARL–224, NOAA Air Resources Laboratory, Silver Spring, MD, 1997; 24pp.
- (23) Wang, X. M.; Ding, X.; Mai, B. X.; Xie, Z. Q.; Xiang, C. H.; Sun, L. G.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Polybrominated diphenyl ethers in airborne particulates collected during a research expedition from the Bohai Sea to the Arctic. *Environ. Sci. Technol.* **2005**, *39*, 7803–7809.
- (24) Su, Y.; Hung, H.; Sverko, E.; Fellin, P.; Li, H. Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. *Atmos. Environ.* **2007**, *41*, 8725–8735.
- (25) Jaward, T. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39*, 8638–8645.



- (26) Bossi, R.; Skov, H.; Vorkamp, K.; Christensen, J.; Rastogi, S. C.; Egelov, A.; Petersen, D. Atmospheric concentrations of organochlorine pesticides, polybrominated diphenyl ethers and polychloronaphthalenes in Nuuk, South-West Greenland. *Atmos. Environ.* **2008**, *42*, 7293–7303.
- (27) Guan, Y. F.; Wang, J. Z.; Ni, H. G.; Luo, X. J.; Mai, B. X.; Zeng, E. Y. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environ. Sci. Technol.* **2007**, *41*, 6007–6013.
- (28) Lee, S. C.; Sverko, E.; Harner, T.; Schachtschneider, J.; Zaruk, D.; DeJong, M.; Barresi, E. "New" Flame Retardants in the Global Atmosphere under the GAPS Network, Proceedings BFR 2010, Kyoto, 2010.
- (29) Yamaguchi, Y.; Kawano, M.; Tatsukawa, R.; Moriwaki, S. Hexabromobenzene and its debrominated compounds in human adipose tissues of Japan. *Chemosphere* **1988**, *17*, 703–707.
- (30) Shen, H.; Main, K. M.; Andersson, A.-M.; Damgaard, I. N.; Virtanen, H. E.; Skakkebaek, N. E.; Toppari, J.; Schramm, K.-W. Concentrations of persistent organochlorine compounds in human milk and placenta are higher in Denmark than in Finland. *Hum. Reprod.* **2008**, *23*, 201–210.
- (31) Yamaguchi, Y.; Kawano, M.; Tatsukawa, R. Tissue distribution and excretion of hexabromobenzene and its debrominated metabolites in the rat. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 807–12.
- (32) Gouteux, B.; Alae, M.; Mabury, S. A.; Pacepavicius, G.; Muir, D. C. G. Polymeric brominated flame retardants: Are they a relevant source of emerging brominated aromatic compounds in the environment? *Environ. Sci. Technol.* **2008**, *42*, 9039–9044.
- (33) Qiu, X.; Zhu, T.; Hu, J. Polybrominated diphenyl ethers (PBDEs) and other flame retardants in the atmosphere and water from Taihu Lake, East China. *Chemosphere* **2010**, *80*, 1207–1212.
- (34) Ministry of Japan. *Chemicals in the environment. Report on Environmental Survey and Monitoring of Chemicals in FY2005*; Environmental Health Department, Ministry of the Environment. Ministry of Japan: Tokyo, 2006. <http://www.env.gov.jp/chemi/kurohon/en/http2005e/03-cie2005.pdf> (accessed September 17, 2010).
- (35) Shi, T.; Chen, S.-J.; Luo, X.-J.; Zhang, X.-L.; Tang, C.-M.; Luo, Y.; Ma, Y.-J.; Wu, J.-P.; Peng, X.-Z.; Mai, B.-X. Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. *Chemosphere* **2009**, *74*, 910–916.
- (36) Wu, J.-P.; Guan, Y.-T.; Zhang, Y.; Luo, X.-J.; Zhi, H.; Chen, S.-J.; Mai, B.-X. Trophodynamics of hexabromocyclododecanes and several other non-PBDE brominated flame retardants in a freshwater food web. *Environ. Sci. Technol.* **2010**, *44*, 5490–5495.
- (37) Venier, M.; Hites, R. A. Flame retardants in the atmosphere near the Great Lakes. *Environ. Sci. Technol.* **2008**, *42*, 4745–4751.
- (38) Ren, N.; Sverko, E.; Li, Y.-F.; Zhang, Z.; Harner, T.; Wang, D.; Wan, X.; McCarry, B. E. Levels and isomer profiles of Dechlorane Plus in Chinese air. *Environ. Sci. Technol.* **2008**, *42*, 6476–6480.
- (39) Shen, L.; Reiner, E. J.; MacPherson, K. A.; Kolic, T. M.; Helm, P. A.; Richman, L. A.; Marvin, C. H.; Burniston, D. A.; Hill, B.; Brindle, I. D.; McCrindle, R.; Chittim, B. G. Dechloranes 602, 603, 604, Dechlorane Plus, and Chlordene Plus, a Newly Detected Analogue, in Tributary Sediments of the Laurentian Great Lakes. *Environ. Sci. Technol.* **2011**, *45*, 693–699.
- (40) Shen, L.; Reiner, E. J.; Macpherson, K. A.; Kolic, T. M.; Sverko, E.; Helm, P. A.; Bhavsar, S. P.; Brindle, I. D.; Marvin, C. H. Identification and screening analysis of halogenated Norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. *Environ. Sci. Technol.* **2010**, *44*, 760–766.
- (41) Wang, D.-G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W.-L.; Li, Y.-F.; Alae, M.; Reiner, E. J.; Shen, L. An Asia-specific source of Dechlorane Plus: Concentration, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010**, *44*, 6608–6613.
- (42) Jia, H.; Sun, Y.; Liu, X.; Yang, M.; Wang, D.; Qi, H.; Shen, L.; Sverko, E.; Reiner, E. J.; Li, Y.-F. Concentration and bioaccumulation of dechlorane compounds in coastal environment of Northern China. *Environ. Sci. Technol.* **2011**, *45*, 2613–2618.
- (43) Tanabe, S.; Ramu, K.; Isobe, T.; Takahashi, S. Brominated flame retardants in the environment of Asia-Pacific: an overview of spatial and temporal trends. *J. Environ. Monit.* **2008**, *10*, 188–197.
- (44) Watanabe, I.; Sakai, S. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29*, 665–682.
- (45) Chen, D.; Bi, X.; Liu, M.; Huang, B.; Sheng, G.; Fu, J. Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site. *Chemosphere* **2011**, *82*, 1246–1252.
- (46) Thoma, H.; Hutzinger, O. Pyrolysis and GC/MS—analysis of brominated flame retardants in on-line operation. *Chemosphere* **1987**, *16*, 1353–1360.
- (47) Klusmeier, W.; Voegler, P.; Ohrbach, K. H.; Weber, H.; Kettrup, A. Thermal decomposition of decabromodiphenyl ether. *J. Anal. Appl. Pyrolysis* **1988**, *13*, 277–85.
- (48) Arp, H. P. H.; Moskeland, T.; Andersson, P. L.; Nyholm, J. R. Presence and partitioning properties of the flame retardants pentabromotoluene, pentabromoethylbenzene and hexabromobenzene near suspected source zones in Norway. *J. Environ. Monit.* **2011**, *13*, 505–13.
- (49) Arend, M. W.; Jarman, W. M.; Ballschmiter, K. Organohalogen POPs in fish of the Northern Pacific. *Organohalogen Compd.* **2002**, *58*, 437–440.
- (50) von der Recke, R.; Vetter, W. Synthesis and characterization of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and structurally related compounds evidenced in seal blubber and brain. *Environ. Sci. Technol.* **2007**, *41*, 1590–5.
- (51) Söderström, G.; Sellström, U.; de Wit, C. A.; Tysklind, M. Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environ. Sci. Technol.* **2003**, *38*, 127–132.
- (52) Gouin, T.; Thomas, G. O.; Chaemfa, C.; Harner, T.; Mackay, D.; Jones, K. C. Concentrations of decabromodiphenyl ether in air from Southern Ontario: Implications for particle-bound transport. *Chemosphere* **2006**, *64*, 256–261.
- (53) Hong, S. H.; Kannan, N.; Jin, Y.; Won, J. H.; Han, G. M.; Shim, W. J. Temporal trend, spatial distribution, and terrestrial sources of PBDEs and PCBs in Masan Bay, Korea. *Mar. Pollut. Bull.* **2010**, *60*, 1836–1841.
- (54) Moon, H. B.; Kannan, K.; Lee, S. J.; Choi, M. Atmospheric deposition of polybrominated diphenyl ethers (PBDEs) in coastal areas in Korea. *Chemosphere* **2007**, *66*, 585–593.
- (55) Bidleman, T. F.; McConnell, L. L. A review of field experiments to determine air–water gas exchange of persistent organic pollutants. *Sci. Total Environ.* **1995**, *159*, 101–117.
- (56) Liss, P. S.; Slater, P. G. Flux of gases across air–sea interface. *Nature* **1974**, *247*, 181–184.