

# POLYBROMINATED DIPHENYL ETHERS VS. ALTERNATE BROMINATED FLAME RETARDANTS AND DECHLORANES FROM EAST ASIA TO THE ARCTIC

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## Introduction

A wide range of halogenated flame retardants (HFRs), mainly brominated (BFRs) have been applied to reduce the inflammability of various industrial and consumer products such as textiles and electronics for several decades. Among these, three technical mixtures of polybrominated diphenyl ethers (PBDEs) – PentaBDE, OctaBDE and DecaBDE – were the most used BFRs in the 1990s and early 2000s<sup>1, 2</sup>. They are known to be harmful for the environment caused by their toxicity, persistence (or degradation to lower brominated, highly persistent PBDEs), bioaccumulation potential and potential to undergo long-range atmospheric transport (LRAT)<sup>2, 3</sup>. They have been detected worldwide in various matrices<sup>4, 5</sup>. Since the early 2000s, the production and usage of Penta- and OctaBDE has been regulated worldwide, while the usage and production of DecaBDE is still not prohibited.

But, there are also several other HFRs which have been produced for several decades, too (e.g., hexabromobenzene (HBB), pentabromotoluene (PBT)), or which were only recently placed on the market as substitutes for the banned PBDEs (e.g., 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), bis-(2-ethylhexyl)-tetrabromophthalate (TBPH)). In addition, higher brominated FRs or polymeric BFRs might be degraded to lower brominated FRs leading to additional emissions into the environment despite their usage and emissions as such<sup>6</sup>. A highly chlorinated flame retardant, Dechlorane Plus (DP), has been introduced to replace the banned Mirex about 40 years ago but was reported in the environment for the first time in 2006<sup>7</sup>.

There is growing industrial, scientific, political as well as public interest on these non-regulated non-PBDE HFRs. Nevertheless, there are only a few data on their occurrence, especially in non-source regions such as the marine environment, and their transport behaviour. First studies proved their occurrence in marine remote biota samples and the marine atmosphere and seawater<sup>8, 9, 10, 11, 12</sup> showing a wide usage, emissions and LRAT of these compounds, while data on the marine environment of East Asia, the Pacific Ocean and the high Arctic are still lacking. Here we present the occurrence, transport behaviour and air-seawater exchange of PBDEs, several non-PBDE BFRs and Dechlorane compounds in the marine environment from the highly industrialized region of East Asia to the remote region of the high Arctic.

## Materials and methods

From June to September 2010, 17 high volume air samples (1–2 days, ~500 m<sup>3</sup>) and 18 high volume seawater samples (12–24 hours, ~900 L) were taken aboard the Chinese research ice-breaker *R/V Xuelong (Snow Dragon)* during the Arctic expedition CHINARE2010 from the Korean Strait (33.23 °N) to the high Arctic (84.5 °N). Air samples were taken at the ship's most upper deck using a glass fiber filter (GFF) for the particulate phase and a PUF/XAD-2 column for the gaseous phase. Seawater samples were taken via the ship's seawater intake system and passed through a GFF followed by a PAD-3 column for the particulate and dissolved phase, respectively.

Samples were extracted according to our previously described method<sup>8</sup>. Briefly, samples were spiked with 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 prior to extraction. Samples were Soxhlet extracted using dichloromethane and further purified on a 10% water deactivated silica column. Samples were analyzed by GC-MS in electron capture negative chemical ionization mode (ECNCI) equipped with a 30m HP-5ms column (J&W Scientific). Blank levels were in the low absolute pg range and method detection limits (MDLs) ranged from 0.002 to 0.27 pg m<sup>-3</sup> for air samples and from 0.001 to 0.17 pg L<sup>-1</sup> for seawater samples, respectively. Mean recoveries of the surrogates ranged from 78 ± 32% (<sup>13</sup>C-BDE-77) to 95 ± 57% (<sup>13</sup>C-BDE-209).

## Results and discussion

### Atmospheric and seawater concentrations

In the atmosphere,  $\sum_{10}$ PBDEs ranged from 0.07 to 8.1  $\text{pg m}^{-3}$  with BDE-209 being the predominating compound ranging from not detected (n.d.) to 4  $\text{pg m}^{-3}$  followed by the common PentaBDE congeners BDE-47 and BDE-99. According to their hydrophobicity, BDE-47 was mainly distributed in the gaseous phase while BDE-209 was predominantly attached to airborne particles. The observed PBDE concentrations were found to be several times lower than in 2005 reported by Wang et al.<sup>13</sup> along the same cruise leg.

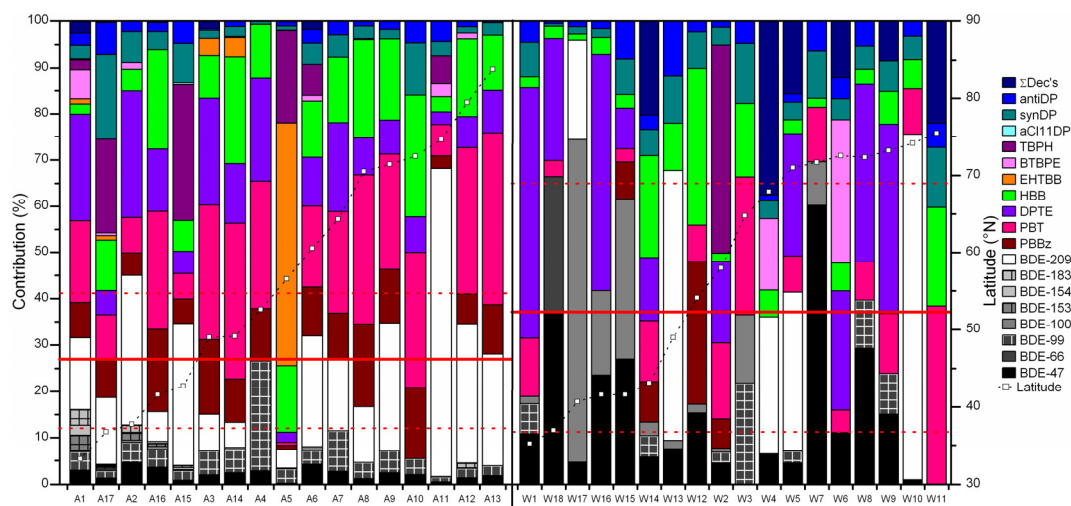
Among the non-PBDE BFRs, pentabromobenzene (PBBz), PBT, (2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB, EHTBB, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) and TBPH were detected. The most dominant compounds were PBBz, PBT, HBB and DPTE which ranged from 0.09 to 2  $\text{pg m}^{-3}$ , 0.1 to 4.5  $\text{pg m}^{-3}$ , 0.10 to 5.9  $\text{pg m}^{-3}$  and 0.1 to 2.5  $\text{pg m}^{-3}$ , respectively. EHTBB, BTBPE and TBPH were detected at a few stations only, but with maximum concentrations of 8.9, 1.6 and 3.4  $\text{pg m}^{-3}$ , respectively.

DP, which consists of the syn- and anti-stereoisomer, was detected in all air samples mainly in the particulate phase from 0.01 to 1.4  $\text{pg m}^{-3}$ . The mean atmospheric fractional abundance of the syn-isomer ( $f_{syn}$ ) was  $0.64 \pm 0.12$  without any spatial trends from East Asia towards higher latitudes. A similar atmospheric  $f_{syn}$  value was found in the Southern Atlantic atmosphere, likely caused by the alteration of  $f_{syn}$  due to a stereospecific depletion of antiDP during LRAT<sup>8</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, we observed the Dechloranes 602, 603 and 604 for the first time in the marine atmosphere at 0.01–0.2  $\text{pg m}^{-3}$ , 0.4  $\text{pg m}^{-3}$  and 0.03–0.05  $\text{pg m}^{-3}$ .

Seawater concentrations ranged from n.d. to 0.8  $\text{pg L}^{-1}$  for  $\sum_{10}$ PBDEs dominated by BDE-47 and -99 while BDE-209 was detected at five stations only. PBT, DPTE and HBB were detected in concentrations from n.d.–0.4, n.d.–1.6 and 0.006–0.1  $\text{pg L}^{-1}$  and PBBz, BTBPE and TBPH were detected in a few stations, too, in concentrations  $\leq 0.2 \text{ pg L}^{-1}$ .

DP was detected from 0.006 to 0.4  $\text{pg L}^{-1}$  with a mean  $f_{syn}$  value of  $0.61 \pm 0.11$  which is similar to the atmosphere. Dechlorane 602, 603 and 604 were detected at a few stations, too, with concentrations  $\leq 0.2 \text{ pg L}^{-1}$ .

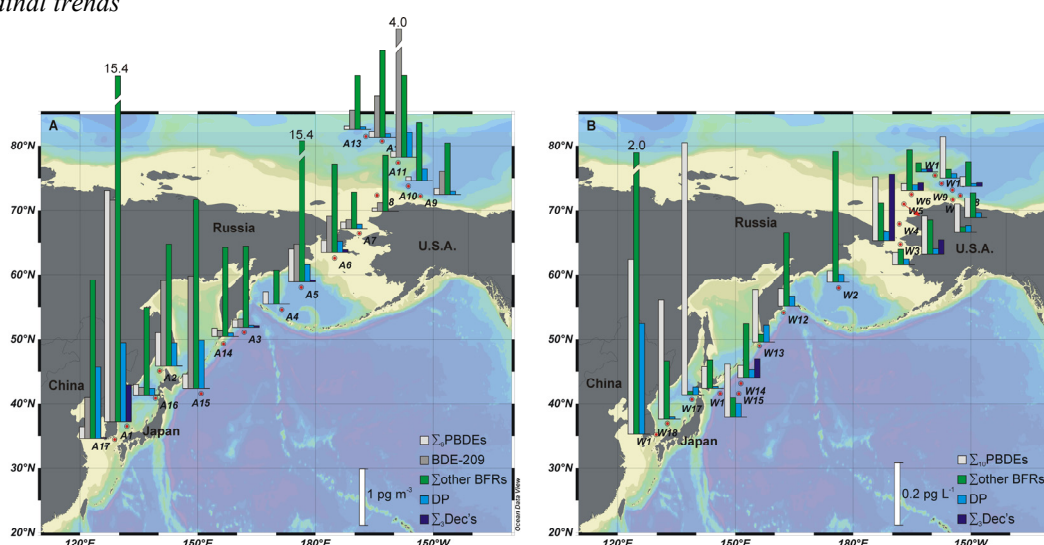
### PBDEs vs. alternate HFRs



**Figure 1.** Composition profile of HFRs in the atmosphere (left) and seawater (right) along the sampling transect. The red line indicates the median  $\sum_{10}$ 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.  $\sum_3$ Dec's = Dechlorane 602 + 603 + 604. The black dotted line indicates the latitude ( $^{\circ}$ N).

Both in air and seawater, the composition profile of investigated HFRs was dominated by non-PBDE FRs rather than the traditional PBDEs, even in air and seawater in the Arctic. Especially the East Asian samples showed a wide variety of different BFRs and Dechloranes. The composition profile is shown in Figure 1. PBDEs accounted only for  $27 \pm 15\%$  and  $38 \pm 27\%$  in air and seawater, respectively, while PBT ( $25 \pm 11\%$ ) and DPTE ( $11 \pm 19\%$ ) were the predominating compounds in air and seawater, respectively, showing the replacement of PBDEs by alternate HFRs both in the industrial usage as well as in the environmental occurrence. While Penta- and OctaBDE are not known to be produced in Asia, DecaBDE is presently still produced and used in Asian countries<sup>14</sup> resulting in BDE-209 being the predominant congener in the environment. PBT, HBB and DP are known to be produced in China<sup>11; 15</sup> showing primary sources of these compounds while PBT, HBB and PBBz could also be emitted from polymeric BFRs of formed in the environment<sup>6; 16</sup>. BTBPE, EHTBB and TBPH are known to be produced in the United States, but it can be assumed that they are produced in Asian countries, too. The sources of these non-PBDEs in Asia need to be investigated in future research.

### Latitudinal trends



**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.

The latitudinal distribution of the investigated HFRs is shown in Figure 2. In general, the highest air and seawater concentrations were found in the East Asian samples in the Korean Strait and the Sea of Japan where the highest variability of compounds was observed, too, as a result of East Asia as source region. Air mass back trajectories (BT) analysis showed only a slight influence of the East Asian air samples by continental (Asian) air masses, while the traveling times over the ocean mostly accounted for several days before being sampled. Elevated concentrations can be expected if samples would be dominated by continental, source-related air masses<sup>13</sup>. Peak concentrations were observed in the open North Pacific Ocean and the Arctic which could be a result of local sources such as open burning of waste in high northern latitudes.

### Atmospheric depositions

The air-seawater gas exchange of BFRs was calculated based on the Whitman two-film model<sup>17</sup> as described in detail in Möller et al. (2011)<sup>9</sup>. The gas exchange was generally dominated by net deposition while 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). The highest deposition fluxes were observed in the Korean Strait from  $178 \text{ pg m}^{-2} \text{ day}^{-1}$  for BDE-47 to  $3097 \text{ pg m}^{-2} \text{ day}^{-1}$  for DPTE driven by the relatively high atmospheric concentrations. 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  $1521 \text{ pg m}^{-2} \text{day}^{-1}$  was calculated for station W2 in the Pacific which might be influenced by Russian air masses.

The particle-bound dry deposition was estimated 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. Similar to the gaseous deposition, the particle-bound deposition was highest in the East Asian stations with a total flux of  $2930 \text{ pg m}^{-2} \text{day}^{-1}$  which was dominated by BDE-209, but also several other highly brominated FRs as well as Dechloranes are deposited into the ocean. 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.

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