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Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic

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Abstract

The spatial distribution of polybrominated diphenyl ethers (PBDEs) and several alternative non-PBDE, non-regulated brominated flame retardants (BFRs) in air and seawater and the air-seawater exchange was investigated in East Greenland Sea using high-volume air and water samples. Total PBDE concentrations (Σ_{i=0}^{10}PBDEs) ranged from 0.09 to 1.8 pg m\(^{-3}\) in the atmosphere and from 0.03 to 0.64 pg L\(^{-1}\) in seawater. Two alternative BFRs, Hexabromobenzene (HBB) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), showed similar concentrations and spatial trends as PBDEs. The air-seawater gas exchange was dominated by deposition with fluxes up to -492 and -1044 pg m\(^{-2}\) day\(^{-1}\) for BDE-47 and DPTE, respectively. This study shows the first occurrence of HBB, DPTE and other alternative flame retardants (e.g., pentabromotoluene (PBT)) in the Arctic atmosphere and seawater indicating that they have a similar long-range atmospheric transport potential (LRAT) as the banned PBDEs.

Capsule: Alternative flame retardants hexabromobenzene (HBB) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) undergo long-range atmospheric transport to the Arctic.

Keywords: flame retardants; PBDE; hexabromobenzene; 2,3-dibromopropyl-2,4,6-tribromophenyl ether; air-seawater exchange; Arctic
1. Introduction

Brominated flame retardants (BFRs), in particular polybrominated diphenyl ethers (PBDEs), have been used for several decades as additives in industrial and consumer products to reduce their inflammability. PBDEs are persistent as well as bioaccumulative and some are known to induce adverse health effects (Birnbaum and Staskal, 2004). They are ubiquitous in various environmental matrices, presumably as a result from PBDE-treated products, with increasing temporal trends, even in the remote areas of the Arctic and Antarctica (Hites, 2004; Borghesi et al., 2008; de Wit et al., 2010). The Arctic has been shown to be exposed to several legacy Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls, organochlorine pesticides and polychlorinated dibenzodioxins- and furans (PCDD/DFs) (Hung et al., 2010; Verreault et al., 2010). One important medium transporting POPs from source regions to remote areas within a relatively short period of time is the atmosphere (Wania, 2003). Models suggested that PBDEs have an adequate LRAT potential to reach the Arctic (Wania and Dugani, 2003), including the completely brominated non-volatile BDE-209 which was shown to undergo particle bound LRAT (Wang et al., 2005; Breivik et al., 2006).

In response to their known adverse properties, the production and usage of the technical Penta- and OctaBDE mixtures in the European Union (EU) was banned by 2004 and the production in the United States (U.S.) was voluntarily phased out by the end of 2004. The exemption of the technical DecaBDE from the EU restriction was subsequently annulated in 2008 because of the possible environmental and healthy risks (European Court of Justice, 2008). In the U.S., the usage of DecaBDE is already banned by some states and a phase out is expected for 2013 (Hess, 2010). Recently, the Penta- and OctaBDE mixtures were officially classified as POPs and included in Annex A.
(elimination of production and use of all intentionally produced POPs) of the Stockholm Convention on POPs at the 4th meeting of the parties (Stockholm Convention Secretariat, 2009).

This resulted in an industrial shift towards alternative non-regulated, non-PBDE flame retardants. 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) was developed to replace the OctaBDE mixture (Hoh et al., 2005) while 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) were applied in Firemaster 550 replacing the PentaBDE-mixture (Stapleton et al., 2008). Even though some non-PBDE BFRs have been used for several decades and have been firstly observed in the environment in the 1970/80s (Mattsson et al., 1975; Watanabe et al., 1986; Qiu et al., 2007), they have received only little public and scientific attention until the banishment of PBDEs and the increasing demand of replacement compounds in the past decade. An increasing number of publications on non-PBDE BFRs has been published within the last years, including first findings in the Arctic region, e.g., hexabromobenzene (HBB), pentabromotoluene (PBT), BTBPE and pentabromoethylbenzene (PBEB) in seabird eggs from the Norwegian Arctic (Verreault et al., 2007) and BTBPE in seabird eggs from the Faroe Islands (Karlsson et al., 2006) indicating that they can undergo LRAT to remote areas. Nevertheless, only BTBPE was reported in the abiotic Arctic environment in an ice core from Svalbard (Norway) (Hermanson et al., 2010) while data on the atmosphere are lacking.

In this study, marine boundary layer air as well as seawater samples were simultaneously taken from East Greenland Sea. The samples were analyzed for 10 PBDE congeners and several non-PBDE BFRs in order to (i) compare levels of banned
PBDEs with their alternatives, (ii) investigate their spatial distribution and (iii) estimate direction and fluxes of air-seawater exchange and dry deposition fluxes.

2. Material and Methods

2.1. Sampling cruise

Air and seawater samples were simultaneously taken aboard the German research vessel R/V Polarstern during the expedition cruise ARK-XXIV/3 in East Greenland Sea in August and September 2009 (69–80.5 °N). Details on sampling are given in Möller et al. (2010). Ten high volume air samples (700–2700m³) using glass fibre filters (GFF) combined with a glass column packed with PUF/Amercite® XAD-2 were taken at the upper deck. 16 seawater samples (~1000 L) were collected via the ship intake system using a GFF and a glass column packed with Serdolit® PAD-2 (SERVA Electrophoresis). Sampling parameters such as latitude, longitude, air and water temperature and salinity are included in Tables S1 and S2 in the Supporting Information (SI).

2.2. Extraction and analysis

Extraction and analysis of the samples are described more in detail in Möller et al. (2010). Briefly, the samples were spiked with 13C-BDE-77 and 13C-BDE-138 (Wellington Laboratories) as surrogate standards, extracted in a Soxhlet apparatus and further cleaned on a silica column (10 % water deactivated) topped on 3 g anhydrous granulated sodium sulfate. Finally, one ng 13C-HCB (Cambridge Isotope Laboratories) was added as a recovery standard prior to injection. Samples were analyzed for 10 PBDE congeners (-28, -47, -66, -85, -99, -100, -153, -154, -183, -209), and PBT, PBEB,
2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB, BTBPE, octabromotrimethylphenylindane (OBIND) and TBPH (all obtained from Wellington Laboratories). $^{13}$C-BDE-77 was used as surrogate for BDE-28, -47, -66, -85, -99, -100, PBT, PBEB, DPTE and HBB, and $^{13}$C-BDE-138 was used for BDE-153, -154, -183, -209, BTBPE, OBIND and TBPH. Analysis was done by a GC/MS-system (6890 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI).

2.3. QA/QC

Breakthrough of the target compounds was checked for both seawater and air samples using tandem columns during the present cruise and the cruise ANT-XXV/1+2 reported in our recent study (Möller et al., 2010). No target compounds were observed above the method detection limits (MDLs) in the lower columns. Three field blanks were taken for each sample type resulting in blank values maximum in the one to two digit absolute pg range (see Table S3 for individual blank values). MDLs were derived from mean blank values plus three times the standard deviation or, for those BFRs showing no blank values, from the instrumental detection limits at signal-to-noise ($S/N$) ratios of three. MDLs ranged from 0.0001 pg m$^{-3}$ for PBT (air filter) to 0.24 pg L$^{-1}$ for BDE-209 (water column) (see Table S4 for individual MDLs). The method recovery was examined by spike tests resulting in recoveries of 69 ± 10 % for PBDEs and 73 ± 12 % for non-PBDE BFRs.

2.4. Air Mass Back Trajectories

Air mass origins were calculated for the air samples using NOAA’s HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php). Back trajectories (BTs) were calculated...
for each sample in 6 h steps along the sampling cruise. BTs were traced back for 120 h with the sampling height as arrival height (see Figure S1 for individual BTs).

3. Results and discussion

3.1. Atmospheric concentrations

In East Greenland Sea atmosphere, all investigated PBDE congeners were detected with a total PBDEs concentration (defined as $\Sigma_{10}$PBDEs hereafter) ranging from 0.06 to 1.6 pg m$^{-3}$ and from 0.03 to 0.46 pg m$^{-3}$ in the gaseous and particulate phase, respectively (see Table S5 for individual BFR concentrations). The individual concentration of the dominating congener BDE-47 ranged from 0.07 to 1.0 pg m$^{-3}$ (gasous+particulate phase). Following the increasing log$K_{OA}$ of PBDEs with increasing degree of bromination (9.5 for BDE-28, 11.96 for BDE-183 at 25 °C (Harner and Shoeib, 2002)), the particulate associated fraction of PBDEs consequently increased from 7 ± 12 % for BDE-28 (a tri-BDE) to 100 % for BDE-183 (a hepta-BDE) and BDE-209. The PBDE congener profile was dominated by the main congeners which have been used in the commercial PentaBDE mixture – BDE-47 > BDE-99 > BDE-100 – contributing 89 ± 8 % of $\Sigma_{10}$PBDEs (see Figure 1). BDE-209 was detected at three stations at concentrations <0.1 pg m$^{-3}$.

Bossi et al. (2008) observed similar concentrations in Nuuk, South-West Greenland, between 0.14 and 3.26 pg m$^{-3}$ for $\Sigma_{11}$PBDEs with a dominance of the PentaBDE congeners, too, while Pozo et al. (2006) reported a $\Sigma_{17}$PBDEs concentration of 5.3 pg m$^{-3}$ on Svalbard. Wang et al. (2005) investigated particle-bound PBDEs during their expedition cruise in the Arctic from the Bohai Sea towards the Canadian Arctic ranging
from <2.58 to 60.9 pg m$^{-3}$ for $\Sigma_{11}$PBDEs, which is several times higher than the concentrations from East Greenland Sea.

Among the non-PBDE BFRs, HBB and DPTE were detected in all samples, mainly in the gaseous phase (1 ± 1 % and 28 ± 31 % in the particulate phase, respectively). The concentrations ranged between 0.001 and 0.66 pg m$^{-3}$ for HBB and between 0.009 and 1.7 pg m$^{-3}$ for DPTE (gaseous+particulate phase), respectively, which are similar to those of the dominating PBDE congeners. DPTE was produced in the 1970/80s by the Chemische Fabrik Kalk as the main compound in the commercial flame retardant Bromkal 73-5 PE while no other manufacturer reported its production (de Kok et al., 1979; von der Recke and Vetter, 2007). Environmental data on DPTE are rare. It was firstly reported in 1997 in sewer slime from Germany (Sauer et al., 1997) and Arend et al. (2002) detected DPTE in fish from the Northern Pacific from 0.3 to 5.6 ng g$^{-1}$ lipid weight (lw). Interestingly, von der Recke and Vetter (2007) observed concentrations from 322 to 470 ng g$^{-1}$ wet weight (ww) and from 130 to 340 ng g$^{-1}$ ww in blubber and brain from harp seals (Phoca groenlandica) from East Greenland Sea sampled in 1991, respectively. PBDE concentrations in ringed seal blubber (Phoca hispida) from Greenland Sea are reported to be one order of magnitude lower, e.g. from 21 to 74 ng g$^{-1}$ lw for $\Sigma_{42}$PBDEs in 2001 (Vorkamp et al., 2004). Furthermore, the enrichment of DPTE in brain was found to be 5–30 fold higher compared to PBDEs (von der Recke and Vetter, 2007). This, together with the findings of DPTE and PBDEs in the atmosphere and seawater in this study, shows that DPTE might be emitted into the environment and transported to remote areas in equal or higher extents as PBDEs in the present and recent decades.
Hexabromobenzene (HBB) was widely used as an additive flame retardant in Japan
and is still produced in low volumes in Japan (Watanabe and Sakai, 2003) and
additionally in China, while no production is reported for the EU (Verreault et al.,
2007). Atmospheric concentrations of HBB reported in recent studies were in the range
of 0.02 – 0.09 pg m⁻³ in the Great Lakes atmosphere (Gouteux et al., 2008), 0.3 – 6.5 pg
m⁻³ in East China (Qiu et al., 2010) and up to 610 pg m⁻³ in Japanese air (Ministry of
Japan, 2006). In 2007, Verreault et al. (2007) reported HBB for the first time in Arctic
biota showing the third highest concentrations after PBDEs and
hexabromocyclododecane (HBCD).

PBT, BTBPE and TBPH were detected in comparably low concentrations in the
Arctic atmosphere which are summarized in Table 1. PBT and BTBPE have recently
been reported in Arctic biota (Verreault et al., 2007) and BTBPE in an ice core
(Hermanson et al., 2010) while this study shows the first occurrence of these BFRs in
the Arctic atmosphere. Venier and Hites (2008) reported BTBPE concentrations from
0.5 to 1.2 pg m⁻³ in the atmosphere of the Great Lakes and Qiu et al. (2010) reported an
annual mean concentration of 0.73 pg m⁻³ in East China. TBPH was detected in house
dust from 1.5 to 10630 ng g⁻¹ (Stapleton et al., 2008) and Lam et al. (2009) reported its
first occurrence in marine mammals from Hong Kong (<0.04 – 3859 ng g⁻¹ lw).

3.2. Seawater concentrations

The Σ₁₀PBDEs concentration in seawater ranged from 0.005 to 0.64 pg L⁻¹. The
congener pattern was generally dominated by BDE-47 (n.d. – 0.06 pg L⁻¹) and BDE-99
(n.d. – 0.04 pg L⁻¹) while the pattern was less clear than in the atmosphere (see Figure 1,
and Table S6 for individual BFR concentrations). Interestingly, BDE-66, BDE-85 and
BDE-183 were detected in comparably high concentrations while at station W12, BDE-85 was even the only detected PBDE (see Figure 1). BDE-183 was the main congener of the technical OctaBDE mixture while BDE-66 and -85 were used only in minor percentages in the PentaBDE mixture (La Guardia et al., 2006). Several studies reported a high relative abundance of BDE-66 in biota possibly resulted from metabolism of higher brominated PBDEs (Meng et al., 2008; Wang et al., 2008) while both congeners might also originate from photodegradation of BDE-209 (Bezares-Cruz et al., 2004; Zeng et al., 2008) during LRAT to the Arctic. BDE-209 was detected only at one station at a relatively high concentration of 0.48 pg L⁻¹. Similar to the Arctic atmosphere, the fraction of particulate associated PBDEs increased with increasing degree of bromination from 0 % and 6 ± 24 % for BDE-66 and -47, respectively, to 57 ± 51 % for BDE-183.

There are very limited data on PBDEs in (sea-)water in the literature. Coastal concentrations of 1, 0.5 and 0.1 pg L⁻¹ were reported for BDE-47, -99 and -153 in the North Sea (Booij et al., 2002), respectively, which are 1–2 orders of magnitude higher than in the present study. In the San Francisco Estuary, Σ₂₂PBDEs ranged from 3 to 513 pg L⁻¹ (Oros et al., 2005) and concentrations in the Izmir Bay, Turkey, ranged from 87 ± 57 pg L⁻¹ in the dissolved phase to 479 ± 340 pg L⁻¹ in the particulate phase for Σ₇PBDEs (Cetin and Odabasi, 2007). Concentrations in Lake Michigan were 18 and 3.1 pg L⁻¹ (Σ₆PBDEs) in the dissolved and particulate phase, respectively (Streets et al., 2006). Carroll et al. (2008) reported concentrations between 1.8 and 10.8 pg L⁻¹ (Σ₄₃PBDEs) in the Rivers Ob and Yenisei and their estuaries discharging into the Arctic Ocean and contributing to the PBDE contamination of the Arctic.
Regarding the non-PBDE BFRs, similar to the East Greenland Sea atmosphere, DPTE was found to be the dominating non-PBDE BFR in seawater in dissolved concentrations from <MDL to 0.41 pg L\(^{-1}\) (it was not detected in the particulate phase). Concentrations of non-PBDE BFRs are included in Table 1. There are currently no data on DPTE in the water environment available, but, as mentioned in section 3.1, relatively high DPTE concentrations in seals (Phoca groenlandica) from this region (von der Recke and Vetter, 2007) indicate LRAT of DPTE to East Greenland Sea, as proved in this study, followed by deposition to seawater and bioaccumulation and possibly biomagnification in marine organisms. Even though HBB was detected in the atmosphere in concentrations similar to PBDEs, it was detected in only five seawater samples slightly above the MDL (maximum 0.003 pg L\(^{-1}\)). HBB was recently observed in a pond close to an e-waste recycling site in China at 0.52 ± 0.04 ng L\(^{-1}\) (Wu et al.). In the 1980s, Watanabe et al. (2003) reported HBB concentrations between 5.6 and 60 ng g\(^{-1}\) dry weight (dw) in Osaka sediment and Guerra et al. (2010) reported a maximum concentration of 2.4 ng g\(^{-1}\) dw in Llobregat River sediment. While PBT was not detected in any seawater samples, TBPH and BTBPE were observed at four and one stations, respectively (see Table 1).

3.3. Spatial trends and possible sources

The highest atmospheric concentrations for PBDEs as well as HBB, DPTE, BTBPE and TBPH were observed at station A1 which originated from continental air masses passing Ireland and the northern United Kingdom (U.K.) indicating that Western Europe might be a source region of these compounds in the European Arctic (see Figure 2 for the spatial distribution of atmospheric BFRs). Since the congener pattern was
dominated by the PentaBDE congeners (see above) which were significantly correlated in the atmosphere (p<0.01), the PBDEs in the Arctic atmosphere can be related to the formerly widespread usage of the technical PBDE mixtures. Gioia et al. (2006) reported several times higher PBDE concentrations in the UK than in Norway resulting from their production and usage in the UK. Sources of HBB in the Arctic atmosphere might be (1) the emission from products containing HBB as additive flame retardant as known for additive BFRs (Alaee et al., 2003), (2) formation by the pyrolysis of the widely used BDE-209 (Thoma and Hutzinger, 1987) or (3) emission from polymeric BFRs (Gouteux et al., 2008). The remaining atmospheric samples originated from rather diverse air masses leading to a mixing of oceanic, continental (Greenland) and Arctic air masses resulting in no clear spatial concentration trends in East Greenland Sea atmosphere.

The PentaBDE congeners (BDE-47, -99, -100), HBB and DPTE were significantly correlated in the atmosphere East Greenland Sea (p<0.01/0.05) indicating that they have similar sources and a similar LRAT potential. A similar spatial trend has been additionally observed for Dechlorane Plus (DP), a highly chlorinated flame retardant, as published in our recent study on DP (Möller et al., 2010) showing that PBDEs as well as several alternative halogenated flame retardants were transported from Western Europe to the European Arctic. Harju et al. (2009) placed HBB in the transition area between single and multiple hopper within the global transport model of POPs developed by Wania (2003, 2006). Thus, HBB has a high LRAT potential to the Arctic compared to those of established POPs. So far, DPTE and HBB have not been reported in continental air from Europe which is needed in order to estimate the emission of HBB and DPTE in source regions to the (marine) environment while long-term studies
are needed to verify the influence of possible source regions such as Western Europe on BFR levels in the (European) Arctic.

In seawater, the highest PBDE and DPTE concentrations were generally observed at stations close to the Eastern coast of Greenland while values at stations in the open ocean were lower (see Figure 3). This can be explained by the East Greenland current transporting Arctic Ocean water masses, and >90% of the seaice from the Arctic Ocean southwards along the Eastern coastline of Greenland (Woodgate et al., 1999). POPs are known to accumulate in ice-/snowpacks (Gustafsson et al., 2005) while they might be released to seawater during ice melt periods. In ice cores from the Arctic Ocean, concentrations between 0.5 and 2.3 pg L\(^{-1}\) for BDE-47 and-99 were reported (Lacorte et al., 2009) which are approximately one order of magnitude higher than the observed seawater concentrations. In addition, glacier melt water from Greenland might transport relatively high fluxes of BFRs into East Greenland Sea, too. However, the samples were taken continuously along the cruise leg what might lead to a mixing of different water masses such as Atlantic water, Arctic water, seaice meltwater and glacier meltwater. Interestingly, TBPH was observed at station W6 at a concentration of 1.3 g L\(^{-1}\), where the highest BDE-209 and DPTE concentrations were observed, too. This shows that they might have similar sources in East Greenland Sea.

### 3.4. Air-seawater exchange

The air-seawater exchange direction was predicted for BDE-47, BDE-99 and DPTE by calculating the fugacity ratio between both phases using equation (1)

\[
\frac{f_W}{f_A} = \frac{C_H}{C_A R T_A}
\]  

(1)
where $f_W$ and $f_A$ are the fugacities in water and air, respectively, $C_W$ and $C_A$ are the dissolved and gaseous concentrations in water and air (pg m$^{-3}$), respectively, $H$ is the Henry’s Law constant at the given water temperature and corrected by the salinity according to Schwarzenbach et al. (2003) (Pa m$^{3}$ mol$^{-1}$), $R$ is the gas constant (8.31 Pa m$^{3}$ K$^{-1}$ mol$^{-1}$) and $T_A$ is the air temperature. The Henry’s Law constant of BDE-47 and -99 and their temperature dependence was taken from Cetin and Odabasi (2005). Since there is no measured or predicted Henry’s Law constant for DPTE available, we estimated it to be 0.0478 Pa m$^{3}$ mol$^{-1}$ using EPI Suite 4.0 developed by US EPA (US EPA, 2010) and the temperature dependence was estimated to be similar to BDE-47. A fugacity quotient $<1$ and $>1$ indicates net dry gaseous deposition and volatilization, respectively, while $f_W/f_A = 1$ indicates thermodynamic equilibrium. The error associated with the fugacity was propagated from the estimated relative standard deviations of the water and air concentrations ($\pm$ 20 %) and the Henry’s Law constant ($<13$ % for PBDEs (Cetin and Odabasi, 2005)), and the air temperature during sampling ($\pm$ 5 %) resulting in a total uncertainty of $\pm$ 32 %. Since no measured Henry’s Law constant of DPTE is available, we assumed an uncertainty of a factor of at least three for the fugacity ratio. The calculations derived fugacity ratios for BDE-47 and -99 below 0.1 suggesting a net deposition from the atmosphere to seawater, while the ratios of DPTE ranged from $<0.01$ to 1.5 suggesting that DPTE might show dry gaseous deposition, equilibrium conditions and possibly volatilization within East Greenland Sea.

The net air-seawater gas exchange flux was calculated based on the modified version of the Whitman two-film resistance model (Liss and Slater, 1974; Bidleman and McConnell, 1995) which has extensively been used to determine the air-water exchange
of POPs, also in the Arctic (e.g., Xie et al., 2007; Zhang and Lohmann, 2010). The net flux \( F_{AW} \) (pg m\(^{-2}\) day\(^{-1}\)) is defined by equation (2):

\[
F_{AW} = K_{OL} \left( C_W - \frac{C_A}{H'_{salt,T}} \right)
\]  

(2)

where \( H' \) is the dimensionless temperature and salinity corrected Henry’s Law constant and \( K_{OL} \) (m day\(^{-1}\)) is the gas phase overall mass transfer coefficient compromising the resistances to mass transfer in both water \( (K_W) \) and air \( (K_A) \):

\[
\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'_{salt,T}}
\]  

(3)

Details on the calculation \( F_{AW} \) are given in the SI. The estimated air-seawater gas fluxes are presented in Figure 4. The overall propagated uncertainty of BDE-47 and -99 was ± 51% based on an uncertainty of ± 40% for \( K_{OL} \) taken from Cetin et al. (2007). Since the Henry’s Law constant of DPTE was estimated, \( K_{OL} \) and consequently \( F_{AW} \) will have higher uncertainties which were estimated to be at least ± 500% for \( F_{AW} \). The gas exchange process of BDE-47 and -99 was dominated by atmospheric dry gaseous deposition with net fluxes ranging from -13 to -492 pg m\(^{-2}\) day\(^{-1}\) and from -7 to -272 pg m\(^{-2}\) day\(^{-1}\), respectively. DPTE showed net dry gaseous deposition fluxes up to -1044 pg m\(^{-2}\) day\(^{-1}\). The highest dry gaseous deposition fluxes were observed at station W1 as a result of BFRs atmospherically transported from Western Europe to East Greenland Sea (see above) suggesting that air-seawater gas exchange is a significant process for the transport of BFRs to the Arctic. Several stations showed DPTE (and BDE-47 and -99) nearly at air-seawater equilibrium while stations W3 even showed a slight net volatilization of DPTE of 3 pg m\(^{-2}\) day\(^{-1}\), respectively. This might be a result of BFRs emitted into East Greenland Sea, e.g., by glacier meltwater leading to a change
of the air-seawater gas exchange flux direction and to a further atmospheric transport of BFRs within the Arctic.

3.5. Dry particle-bound deposition

Besides air-seawater gas exchange, dry particle-bound deposition is an important deposition process of POPs into the global oceans and remote areas (Duce, 1990; Dachs et al., 2002), especially for highly hydrophobic POPs such as BDE-209 (Wang et al., 2005; Gouin et al., 2006). On the other hand, dry deposition of POPs leads to a removal from the atmosphere and to a limitation of the LRAT potential of non-volatile POPs (Wania, 2003). The dry particle-bound deposition flux \( F_d \), pg m\(^{-2}\) day\(^{-1}\) was calculated for PBDEs and DPTE using equation (4):

\[
F_d = V_d C_p
\]  

(4)

where \( V_d \) is the deposition velocity (m d\(^{-1}\)) and \( C_p \) is the concentration in the particulate phase (pg m\(^{-3}\)). The deposition velocity strongly depends on meteorological parameters (e.g., wind speed) and physicochemical parameters of the particle and the pollutant (Franz et al., 1998). Therefore, we estimated an uncertainty of a factor of 3 for the deposition velocity. There are no measured velocities for BFRs for open ocean conditions available. Based on recent studies on the dry deposition of POPs (Castro-Jiménez et al.; Jurado et al., 2004; Del Vento and Dachs, 2007), we used a constant velocity of 0.1 cm s\(^{-1}\) (86.4 m d\(^{-1}\)) for the open sea conditions in this study. Since the dry deposition was calculated based on a constant deposition velocity, the differences in the fluxes resulted only from the differences in the particulate concentrations and higher differences are expected if the velocities for the individual BFRs were known. The dry deposition fluxes are shown in Figure 5. The dry particle-bound deposition flux for
\[ \sum_{i=10}^{16} \text{PBDEs} \text{ ranged from -2.7 to -39.5 pg m}^{-2} \text{ day}^{-1} \text{ with individual fluxes from -1.1 to -27.8 pg m}^{-2} \text{ day}^{-1} \text{ for BDE-47, -1.1 to -9.5 pg m}^{-2} \text{ day}^{-1} \text{ for BDE-99, -0.4 to -4.0 pg m}^{-2} \text{ day}^{-1} \text{ for DPTE. Compared to the air-seawater gas fluxes, dry particle-bound deposition fluxes are about one order of magnitude lower as a result of continuous dry deposition along atmospheric transport from the source region to the Arctic. This shows that air-seawater gas exchange is the dominating deposition pathway of BFRs into East Greenland Sea. Nevertheless, there might be other input pathways such as riverine discharge and wet deposition, which need to be investigated to estimate the flux of PBDEs to East Greenland Sea and, in general, to the Arctic.}

4. Conclusions

The investigation of PBDEs and alternative brominated flame retardants showed the dominance of the common PentaBDE congeners BDE-47 -99, and, interestingly, two non-PBDE BFRs: HBB and DPTE. Even though both have been produced for several decades, they were detected for the first time in the Arctic atmosphere and seawater. The concentrations and spatial trends were similar to PBDEs as a result of similar sources and of an apparently similar LRAT potential as the known POPs BDE-47 and -99. Thereby, the origin of HBB needs to be investigated in future research since it might be a degradation product of BDE-209 which is still being produced and used, e.g., in the U.S. and in China. Both air-seawater gas transfer and dry particle-bound deposition contribute do the input of BFRs into East Greenland Sea. Besides, PBT, BTBPT and TBPH were detected in the Arctic atmosphere for the first times which need to be included in further studies on non-PBDE BFRs in the Arctic environment.
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9044.


**TABLE 1**

Non-PBDE BFRs in the atmosphere (pg m\(^{-3}\)) and seawater (pg L\(^{-1}\)). The value in brackets represents the detection frequency in %. n.d. = not detected

<table>
<thead>
<tr>
<th></th>
<th>Atmosphere gaseous</th>
<th>particulate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPTE</td>
<td>n.d.–1.7 (89)</td>
<td>0.005–0.05 (100)</td>
</tr>
<tr>
<td>HBB</td>
<td>0.04–0.66 (100)</td>
<td>0.001–0.005 (100)</td>
</tr>
<tr>
<td>PBT</td>
<td>0.001–0.02 (100)</td>
<td>n.d.–0.001 (20)</td>
</tr>
<tr>
<td>TBPB</td>
<td>n.d.</td>
<td>n.d.–0.08 (40)</td>
</tr>
<tr>
<td>BTBPE</td>
<td>n.d.–0.06 (22)</td>
<td>n.d.–0.02 (70)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Seawater dissolved</th>
<th>particulate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPTE</td>
<td>n.d.–0.3 (81)</td>
<td>n.d.</td>
</tr>
<tr>
<td>HBB</td>
<td>n.d.–0.003 (13)</td>
<td>n.d.–0.002 (19)</td>
</tr>
<tr>
<td>PBT</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>TBPB</td>
<td>n.d.–1.3 (25)</td>
<td>n.d.–0.12 (6)</td>
</tr>
<tr>
<td>BTBPE</td>
<td>n.d.</td>
<td>n.d.–0.002 (6)</td>
</tr>
</tbody>
</table>

**Fig. 1.** Relative contribution of individual PBDEs from Σ\(_{10}\)PBDEs in the atmosphere and seawater of East Greenland Sea
Fig. 2. Map showing the concentrations of $\Sigma_{10}$PBDEs, HBB and DPTE in the East Greenland Sea atmosphere. The stations represent mean stations since samples were taken continuously along the cruise leg. NOTE: For station A10 only the particulate phase was analyzed.
Fig. 3. Map showing the concentrations of $\Sigma_{10}$PBDEs and DPTE in seawater from East Greenland Sea.
Fig. 4. Air–sea gas exchange fluxes of BDE-47, -99 and DPTE in East Greenland Sea. Negative flux indicates net dry gaseous deposition into the water column.

Fig. 5. Dry particle-bound deposition fluxes of BDE-47, -99, Σ_{10}PBDEs and DPTE in East Greenland Sea. Negative (-) flux indicates net deposition into the water column.