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

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20 **Abstract**

21 The spatial distribution of polybrominated diphenyl ethers (PBDEs) and several
22 alternative non-PBDE, non-regulated brominated flame retardants (BFRs) in air and
23 seawater and the air-seawater exchange was investigated in East Greenland Sea using
24 high-volume air and water samples. Total PBDE concentrations (Σ_{10} PBDEs) ranged
25 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
26 alternative BFRs, Hexabromobenzene (HBB) and 2,3-dibromopropyl-2,4,6-
27 tribromophenyl ether (DPTE), showed similar concentrations and spatial trends as
28 PBDEs. The air-seawater gas exchange was dominated by deposition with fluxes up to -
29 492 and -1044 $\text{pg m}^{-2} \text{day}^{-1}$ for BDE-47 and DPTE, respectively. This study shows the
30 first occurrence of HBB, DPTE and other alternative flame retardants (e.g.,
31 pentabromotoluene (PBT)) in the Arctic atmosphere and seawater indicating that they
32 have a similar long-range atmospheric transport potential (LRAT) as the banned
33 PBDEs.

34

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

38

39 *Keywords:* flame retardants; PBDE; hexabromobenzene; 2,3-dibromopropyl-2,4,6-
40 tribromophenyl ether; air-seawater exchange; Arctic

41

42 **1. Introduction**

43 Brominated flame retardants (BFRs), in particular polybrominated diphenyl ethers
44 (PBDEs), have been used for several decades as additives in industrial and consumer
45 products to reduce their inflammability. PBDEs are persistent as well as
46 bioaccumulative and some are known to induce adverse health effects (Birnbaum and
47 Staskal, 2004). They are ubiquitous in various environmental matrices, presumably as a
48 result from PBDE-treated products, with increasing temporal trends, even in the remote
49 areas of the Arctic and Antarctica (Hites, 2004; Borghesi et al., 2008; de Wit et al.,
50 2010). The Arctic has been shown to be exposed to several legacy Persistent Organic
51 Pollutants (POPs) such as polychlorinated biphenyls, organochlorine pesticides and
52 polychlorinated dibenzodioxins- and furans (PCDD/DFs) (Hung et al., 2010; Verreault
53 et al., 2010). One important medium transporting POPs from source regions to remote
54 areas within a relatively short period of time is the atmosphere (Wania, 2003). Models
55 suggested that PBDEs have an adequate LRAT potential to reach the Arctic (Wania and
56 Dugani, 2003), including the completely brominated non-volatile BDE-209 which was
57 shown to undergo particle bound LRAT (Wang et al., 2005; Breivik et al., 2006).

58 In response to their known adverse properties, the production and usage of the
59 technical Penta- and OctaBDE mixtures in the European Union (EU) was banned by
60 2004 and the production in the United States (U.S.) was voluntarily phased out by the
61 end of 2004. The exemption of the technical DecaBDE from the EU restriction was
62 subsequently annulated in 2008 because of the possible environmental and healthy risks
63 (European Court of Justice, 2008). In the U.S., the usage of DecaBDE is already banned
64 by some states and a phase out is expected for 2013 (Hess, 2010). Recently, the Penta-
65 and OctaBDE mixtures were officially classified as POPs and included in Annex A

66 (elimination of production and use of all intentionally produced POPs) of the Stockholm
67 Convention on POPs at the 4th meeting of the parties (Stockholm Convention
68 Secretariat, 2009).

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

86 In this study, marine boundary layer air as well as seawater samples were
87 simultaneously taken from East Greenland Sea. The samples were analyzed for 10
88 PBDE congeners and several non-PBDE BFRs in order to (i) compare levels of banned

89 PBDEs with their alternatives, (ii) investigate their spatial distribution and (iii) estimate
90 direction and fluxes of air-seawater exchange and dry deposition fluxes.

91

92 **2. Material and Methods**

93 *2.1. Sampling cruise*

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

104

105 *2.2. Extraction and analysis*

106 Extraction and analysis of the samples are described more in detail in Möller et al.
107 (2010). Briefly, the samples were spiked with ¹³C-BDE-77 and ¹³C-BDE-138
108 (Wellington Laboratories) as surrogate standards, extracted in a Soxhlet apparatus and
109 further cleaned on a silica column (10 % water deactivated) topped on 3 g anhydrous
110 granulated sodium sulfate. Finally, one ng ¹³C-HCB (Cambridge Isotope Laboratories)
111 was added as a recovery standard prior to injection. Samples were analyzed for 10
112 PBDE congeners (-28, -47, -66, -85, -99, -100, -153, -154, -183, -209), and PBT, PBEB,

113 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB, BTBPE,
114 octabromotrimethylphenylindane (OBIND) and TBPH (all obtained from Wellington
115 Laboratories). ¹³C-BDE-77 was used as surrogate for BDE-28, -47, -66, -85, -99, -100,
116 PBT, PBEB, DPTE and HBB, and ¹³C-BDE-138 was used for BDE-153, -154, -183, -
117 209, BTBPE, OBIND and TBPH. Analysis was done by a GC/MS-system (6890
118 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI).

119

120 2.3. QA/QC

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

133

134 2.4. Air Mass Back Trajectories

135 Air mass origins were calculated for the air samples using NOAA's HYSPLIT model
136 (http://www.arl.noaa.gov/HYSPLIT_info.php). Back trajectories (BTs) were calculated

137 for each sample in 6 h steps along the sampling cruise. BTs were traced back for 120 h
138 with the sampling height as arrival height (see Figure S1 for individual BTs).

139

140 **3. Results and discussion**

141 *3.1. Atmospheric concentrations*

142 In East Greenland Sea atmosphere, all investigated PBDE congeners were detected with
143 a total PBDEs concentration (defined as Σ_{10} PBDEs hereafter) ranging from 0.06 to 1.6
144 pg m^{-3} and from 0.03 to 0.46 pg m^{-3} in the gaseous and particulate phase, respectively
145 (see Table S5 for individual BFR concentrations). The individual concentration of the
146 dominating congener BDE-47 ranged from 0.07 to 1.0 pg m^{-3} (gasous+particulate
147 phase). Following the increasing $\log K_{OA}$ of PBDEs with increasing degree of
148 bromination (9.5 for BDE-28, 11.96 for BDE-183 at 25 °C (Harner and Shoeib, 2002)),
149 the particulate associated fraction of PBDEs consequently increased from 7 ± 12 % for
150 BDE-28 (a tri-BDE) to 100 % for BDE-183 (a hepta-BDE) and BDE-209. The PBDE
151 congener profile was dominated by the main congeners which have been used in the
152 commercial PentaBDE mixture – BDE-47 > BDE-99 > BDE-100 – contributing 89 ± 8
153 % of Σ_{10} PBDEs (see Figure 1). BDE-209 was detected at three stations at
154 concentrations $<0.1 \text{ pg m}^{-3}$.

155 Bossi et al. (2008) observed similar concentrations in Nuuk, South-West Greenland,
156 between 0.14 and 3.26 pg m^{-3} for Σ_{11} PBDEs with a dominance of the PentaBDE
157 congeners, too, while Pozo et al. (2006) reported a Σ_{17} PBDEs concentration of 5.3 pg m^{-3}
158 on Svalbard. Wang et al. (2005) investigated particle-bound PBDEs during their
159 expedition cruise in the Arctic from the Bohai Sea towards the Canadian Arctic ranging

160 from <2.58 to 60.9 pg m^{-3} for Σ_{11} PBDEs, which is several times higher than the
161 concentrations from East Greenland Sea.

162 Among the non-PBDE BFRs, HBB and DPTE were detected in all samples, mainly
163 in the gaseous phase ($1 \pm 1 \%$ and $28 \pm 31 \%$ in the particulate phase, respectively). The
164 concentrations ranged between 0.001 and 0.66 pg m^{-3} for HBB and between 0.009 and
165 1.7 pg m^{-3} for DPTE (gaseous+particulate phase), respectively, which are similar to
166 those of the dominating PBDE congeners. DPTE was produced in the 1970/80s by the
167 Chemische Fabrik Kalk as the main compound in the commercial flame retardant
168 Bromkal 73-5 PE while no other manufacturer reported its production (de Kok et al.,
169 1979; von der Recke and Vetter, 2007). Environmental data on DPTE are rare. It was
170 firstly reported in 1997 in sewer slime from Germany (Sauer et al., 1997) and Arend et
171 al. (2002) detected DPTE in fish from the Northern Pacific from 0.3 to 5.6 ng g^{-1} lipid
172 weight (lw). Interestingly, von der Recke and Vetter (2007) observed concentrations
173 from 322 to 470 ng g^{-1} wet weight (ww) and from 130 to 340 ng g^{-1} ww in blubber and
174 brain from harp seals (*Phoca groenlandica*) from East Greenland Sea sampled in 1991,
175 respectively. PBDE concentrations in ringed seal blubber (*Phoca hispida*) from
176 Greenland Sea are reported to be one order of magnitude lower, e.g. from 21 to 74 ng g^{-1}
177 lw for Σ_{42} PBDEs in 2001 (Vorkamp et al., 2004). Furthermore, the enrichment of
178 DPTE in brain was found to be 5–30 fold higher compared to PBDEs (von der Recke
179 and Vetter, 2007). This, together with the findings of DPTE and PBDEs in the
180 atmosphere and seawater in this study, shows that DPTE might be emitted into the
181 environment and transported to remote areas in equal or higher extents as PBDEs in the
182 present and recent decades.

183 Hexabromobenzene (HBB) was widely used as an additive flame retardant in Japan
184 and is still produced in low volumes in Japan (Watanabe and Sakai, 2003) and
185 additionally in China, while no production is reported for the EU (Verreault et al.,
186 2007). Atmospheric concentrations of HBB reported in recent studies were in the range
187 of 0.02 – 0.09 pg m⁻³ in the Great Lakes atmosphere (Gouteux et al., 2008), 0.3 – 6.5 pg
188 m⁻³ in East China (Qiu et al., 2010) and up to 610 pg m⁻³ in Japanese air (Ministry of
189 Japan, 2006). In 2007, Verreault et al. (2007) reported HBB for the first time in Arctic
190 biota showing the third highest concentrations after PBDEs and
191 hexabromocyclododecane (HBCD).

192 PBT, BTBPE and TBPH were detected in comparably low concentrations in the
193 Arctic atmosphere which are summarized in Table 1. PBT and BTBPE have recently
194 been reported in Arctic biota (Verreault et al., 2007) and BTBPE in an ice core
195 (Hermanson et al., 2010) while this study shows the first occurrence of these BFRs in
196 the Arctic atmosphere. Venier and Hites (2008) reported BTBPE concentrations from
197 0.5 to 1.2 pg m⁻³ in the atmosphere of the Great Lakes and Qiu et al. (2010) reported an
198 annual mean concentration of 0.73 pg m⁻³ in East China. TBPH was detected in house
199 dust from 1.5 to 10630 ng g⁻¹ (Stapleton et al., 2008) and Lam et al. (2009) reported its
200 first occurrence in marine mammals from Hong Kong (<0.04 – 3859 ng g⁻¹ lw).

201

202 3.2. Seawater concentrations

203 The Σ_{10} PBDEs concentration in seawater ranged from 0.005 to 0.64 pg L⁻¹. The
204 congener pattern was generally dominated by BDE-47 (n.d. – 0.06 pg L⁻¹) and BDE-99
205 (n.d. – 0.04 pg L⁻¹) while the pattern was less clear than in the atmosphere (see Figure 1,
206 and Table S6 for individual BFR concentrations). Interestingly, BDE-66, BDE-85 and

207 BDE-183 were detected in comparably high concentrations while at station W12, BDE-
208 85 was even the only detected PBDE (see Figure 1). BDE-183 was the main congener
209 of the technical OctaBDE mixture while BDE-66 and -85 were used only in minor
210 percentages in the PentaBDE mixture (La Guardia et al., 2006). Several studies reported
211 a high relative abundance of BDE-66 in biota possibly resulted from metabolism of
212 higher brominated PBDEs (Meng et al., 2008; Wang et al., 2008) while both congeners
213 might also originate from photodegradation of BDE-209 (Bezares-Cruz et al., 2004;
214 Zeng et al., 2008) during LRAT to the Arctic. BDE-209 was detected only at one station
215 at a relatively high concentration of 0.48 pg L^{-1} . Similar to the Arctic atmosphere, the
216 fraction of particulate associated PBDEs increased with increasing degree of
217 bromination from 0 % and 6 ± 24 % for BDE-66 and -47, respectively, to 57 ± 51 % for
218 BDE-183.

219 There are very limited data on PBDEs in (sea-)water in the literature. Coastal
220 concentrations of 1, 0.5 and 0.1 pg L^{-1} were reported for BDE-47, -99 and -153 in the
221 North Sea (Booij et al., 2002), respectively, which are 1–2 orders of magnitude higher
222 than in the present study. In the San Francisco Estuary, $\Sigma_{22}\text{PBDEs}$ ranged from 3 to 513
223 pg L^{-1} (Oros et al., 2005) and concentrations in the Izmir Bay, Turkey, ranged from $87 \pm$
224 57 pg L^{-1} in the dissolved phase to $479 \pm 340 \text{ pg L}^{-1}$ in the particulate phase for
225 $\Sigma_7\text{PBDEs}$ (Cetin and Odabasi, 2007). Concentrations in Lake Michigan were 18 and 3.1
226 pg L^{-1} ($\Sigma_6\text{PBDEs}$) in the dissolved and particulate phase, respectively (Streets et al.,
227 2006). Carroll et al. (2008) reported concentrations between 1.8 and 10.8 pg L^{-1}
228 ($\Sigma_{43}\text{PBDEs}$) in the Rivers Ob and Yenisei and their estuaries discharging into the Arctic
229 Ocean and contributing to the PBDE contamination of the Arctic.

230 Regarding the non-PBDE BFRs, similar to the East Greenland Sea atmosphere
231 DPTE was found to be the dominating non-PBDE BFR in seawater in dissolved
232 concentrations from <MDL to 0.41 pg L⁻¹ (it was not detected in the particulate phase).
233 Concentrations of non-PBDE BFRs are included in Table 1. There are currently no data
234 on DPTE in the water environment available, but, as mentioned in section 3.1, relatively
235 high DPTE concentrations in seals (*Phoca groenlandica*) from this region (von der
236 Recke and Vetter, 2007) indicate LRAT of DPTE to East Greenland Sea, as proved in
237 this study, followed by deposition to seawater and bioaccumulation and possibly
238 biomagnification in marine organisms. Even though HBB was detected in the
239 atmosphere in concentrations similar to PBDEs, it was detected in only five seawater
240 samples slightly above the MDL (maximum 0.003 pg L⁻¹). HBB was recently observed
241 in a pond close to an e-waste recycling site in China at 0.52 ± 0.04 ng L⁻¹ (Wu et al.). In
242 the 1980s, Watanabe et al. (2003) reported HBB concentrations between 5.6 and 60 ng
243 g⁻¹ dry weight (dw) in Osaka sediment and Guerra et al. (2010) reported a maximum
244 concentration of 2.4 ng g⁻¹ dw in Llobregat River sediment. While PBT was not
245 detected in any seawater samples, TBPH and BTBPE were observed at four and one
246 stations, respectively (see Table 1).

247

248 3.3. Spatial trends and possible sources

249 The highest atmospheric concentrations for PBDEs as well as HBB, DPTE, BTBPE
250 and TBPH were observed at station A1 which originated from continental air masses
251 passing Ireland and the northern United Kingdom (U.K.) indicating that Western
252 Europe might be a source region of these compounds in the European Arctic (see Figure
253 2 for the spatial distribution of atmospheric BFRs). Since the congener pattern was

254 dominated by the PentaBDE congeners (see above) which were significantly correlated
255 in the atmosphere ($p < 0.01$), the PBDEs in the Arctic atmosphere can be related to the
256 formerly widespread usage of the technical PBDE mixtures. Gioia et al. (2006) reported
257 several times higher PBDE concentrations in the UK than in Norway resulting from
258 their production and usage in the UK. Sources of HBB in the Arctic atmosphere might
259 be (1) the emission from products containing HBB as additive flame retardant as known
260 for additive BFRs (Alaee et al., 2003), (2) formation by the pyrolysis of the widely used
261 BDE-209 (Thoma and Hutzinger, 1987) or (3) emission from polymeric BFRs (Gouteux
262 et al., 2008). The remaining atmospheric samples originated from rather diverse air
263 masses leading to a mixing of oceanic, continental (Greenland) and Arctic air masses
264 resulting in no clear spatial concentration trends in East Greenland Sea atmosphere.

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

277 are needed to verify the influence of possible source regions such as Western Europe on
278 BFR levels in the (European) Arctic.

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

295

296 3.4. Air-seawater exchange

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

$$299 \quad \frac{f_w}{f_A} = \frac{C_w H}{C_A R T_A} \quad (1)$$

300 where f_W and f_A are the fugacities in water and air, respectively, C_W and C_A are the
301 dissolved and gaseous concentrations in water and air ($\mu\text{g m}^{-3}$), respectively, H is the
302 Henry's Law constant at the given water temperature and corrected by the salinity
303 according to Schwarzenbach et al. (2003) ($\text{Pa m}^3 \text{mol}^{-1}$), R is the gas constant (8.31 Pa
304 $\text{m}^3 \text{K}^{-1} \text{mol}^{-1}$) and T_A is the air temperature. The Henry's Law constant of BDE-47 and -
305 99 and their temperature dependence was taken from Cetin and Odabasi (2005). Since
306 there is no measured or predicted Henry's Law constant for DPTE available, we
307 estimated it to be $0.0478 \text{ Pa m}^3 \text{mol}^{-1}$ using EPI Suite 4.0 developed by US EPA (US
308 EPA, 2010) and the temperature dependence was estimated to be similar to BDE-47. A
309 fugacity quotient <1 and >1 indicates net dry gaseous deposition and volatilization,
310 respectively, while $f_W/f_A = 1$ indicates thermodynamic equilibrium. The error associated
311 with the fugacity was propagated from the estimated relative standard deviations of the
312 water and air concentrations ($\pm 20 \%$) and the Henry's Law constant ($<13 \%$ for PBDEs
313 (Cetin and Odabasi, 2005)), and the air temperature during sampling ($\pm 5 \%$) resulting
314 in a total uncertainty of $\pm 32 \%$. Since no measured Henry's Law constant of DPTE is
315 available, we assumed an uncertainty of a factor of at least three for the fugacity ratio.
316 The calculations derived fugacity ratios for BDE-47 and -99 below 0.1 suggesting a net
317 deposition from the atmosphere to seawater, while the ratios of DPTE ranged from
318 <0.01 to 1.5 suggesting that DPTE might show dry gaseous deposition, equilibrium
319 conditions and possibly volatilization within East Greenland Sea.

320 The net air-seawater gas exchange flux was calculated based on the modified
321 version of the Whitman two-film resistance model (Liss and Slater, 1974; Bidleman and
322 McConnell, 1995) which has extensively been used to determine the air-water exchange

323 of POPs, also in the Arctic (e.g., Xie et al., 2007; Zhang and Lohmann, 2010). The net
324 flux (F_{AW} , $\text{pg m}^{-2} \text{ day}^{-1}$) is defined by equation (2):

$$325 \quad F_{AW} = K_{OL} \left(C_W - \frac{C_A}{H'_{salt,T}} \right) \quad (2)$$

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

$$329 \quad \frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'_{salt,T}} \quad (3)$$

330 Details on the calculation F_{AW} are given in the SI. The estimated air-seawater gas fluxes
331 are presented in Figure 4. The overall propagated uncertainty of BDE-47 and -99 was \pm
332 51 % based on an uncertainty of \pm 40 % for K_{OL} taken from Cetin et al. (2007). Since
333 the Henry's Law constant of DPTE was estimated, K_{OL} and consequently F_{AW} will have
334 higher uncertainties which were estimated to be at least \pm 500 % for F_{AW} . The gas
335 exchange process of BDE-47 and -99 was dominated by atmospheric dry gaseous
336 deposition with net fluxes ranging from -13 to -492 $\text{pg m}^{-2} \text{ day}^{-1}$ and from -7 to -272 pg
337 $\text{m}^{-2} \text{ day}^{-1}$, respectively. DPTE showed net dry gaseous deposition fluxes up to -
338 1044 $\text{pg m}^{-2} \text{ day}^{-1}$. The highest dry gaseous deposition fluxes were observed at station
339 W1 as a result of BFRs atmospherically transported from Western Europe to East
340 Greenland Sea (see above) suggesting that air-seawater gas exchange is a significant
341 process for the transport of BFRs to the Arctic. Several stations showed DPTE (and
342 BDE-47 and -99) nearly at air-seawater equilibrium while stations W3 even showed a
343 slight net volatilization of DPTE of 3 $\text{pg m}^{-2} \text{ day}^{-1}$, respectively. This might be a result
344 of BFRs emitted into East Greenland Sea, e.g., by glacier meltwater leading to a change

345 of the air-seawater gas exchange flux direction and to a further atmospheric transport of
346 BFRs within the Arctic.

347

348 3.5. *Dry particle-bound deposition*

349 Besides air-seawater gas exchange, dry particle-bound deposition is an important
350 deposition process of POPs into the global oceans and remote areas (Duce, 1990; Dachs
351 et al., 2002), especially for highly hydrophobic POPs such as BDE-209 (Wang et al.,
352 2005; Gouin et al., 2006). On the other hand, dry deposition of POPs leads to a removal
353 from the atmosphere and to a limitation of the LRAT potential of non-volatile POPs
354 (Wania, 2003). The dry particle-bound deposition flux (F_d , $\text{pg m}^{-2} \text{day}^{-1}$) was calculated
355 for PBDEs and DPTE using equation (4):

$$356 \quad F_d = V_d C_p \quad (4)$$

357 where V_d is the deposition velocity (m d^{-1}) and C_p is the concentration in the particulate
358 phase (pg m^{-3}). The deposition velocity strongly depends on meteorological parameters
359 (e.g., wind speed) and physicochemical parameters of the particle and the pollutant
360 (Franz et al., 1998). Therefore, we estimated an uncertainty of a factor of 3 for the
361 deposition velocity. There are no measured velocities for BFRs for open ocean
362 conditions available. Based on recent studies on the dry deposition of POPs (Castro-
363 Jiménez et al.; Jurado et al., 2004; Del Vento and Dachs, 2007), we used a constant
364 velocity of 0.1 cm s^{-1} (86.4 m d^{-1}) for the open sea conditions in this study. Since the dry
365 deposition was calculated based on a constant deposition velocity, the differences in the
366 fluxes resulted only from the differences in the particulate concentrations and higher
367 differences are expected if the velocities for the individual BFRs were known. The dry
368 deposition fluxes are shown in Figure 5. The dry particle-bound deposition flux for

369 Σ_{10} PBDEs ranged from -2.7 to -39.5 $\text{pg m}^{-2} \text{ day}^{-1}$ with individual fluxes from -1.1 to -
370 27.8 $\text{pg m}^{-2} \text{ day}^{-1}$ for BDE-47, -1.1 to -9.5 $\text{pg m}^{-2} \text{ day}^{-1}$ for BDE-99, -0.4 to -4.0 pg m^{-2}
371 day^{-1} for DPTE. Compared to the air-seawater gas fluxes, dry particle-bound deposition
372 fluxes are about one order of magnitude lower as a result of continuous dry deposition
373 along atmospheric transport from the source region to the Arctic. This shows that air-
374 seawater gas exchange is the dominating deposition pathway of BFRs into East
375 Greenland Sea. Nevertheless, there might be other input pathways such as riverine
376 discharge and wet deposition, which need to be investigated to estimate the flux of
377 PBDEs to East Greenland Sea and, in general, to the Arctic.

378

379 **4. Conclusions**

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

392

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398 the BTs.

399

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679 **TABLE 1**

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

	Atmosphere	
	gaseous	particulate
DPTE	n.d.–1.7 (89)	0.005–0.05 (100)
HBB	0.04–0.66 (100)	0.001–0.005 (100)
PBT	0.001–0.02 (100)	n.d.–0.001 (20)
TBPH	n.d.	n.d.–0.08 (40)
BTBPE	n.d.–0.06 (22)	n.d.–0.02 (70)

	Seawater	
	dissolved	particulate
DPTE	n.d.–0.3 (81)	n.d.
HBB	n.d.–0.003 (13)	n.d.–0.002 (19)
PBT	n.d.	n.d.
TBPH	n.d.–1.3 (25)	n.d.–0.12 (6)
BTBPE	n.d.	n.d.–0.002 (6)

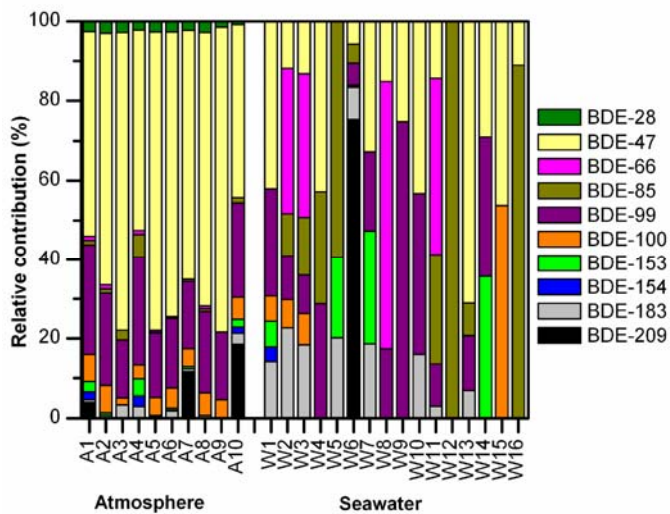
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686 **Fig. 1.** Relative contribution of individual PBDEs from Σ_{10} PBDEs in the atmosphere
 687 and seawater of East Greenland Sea

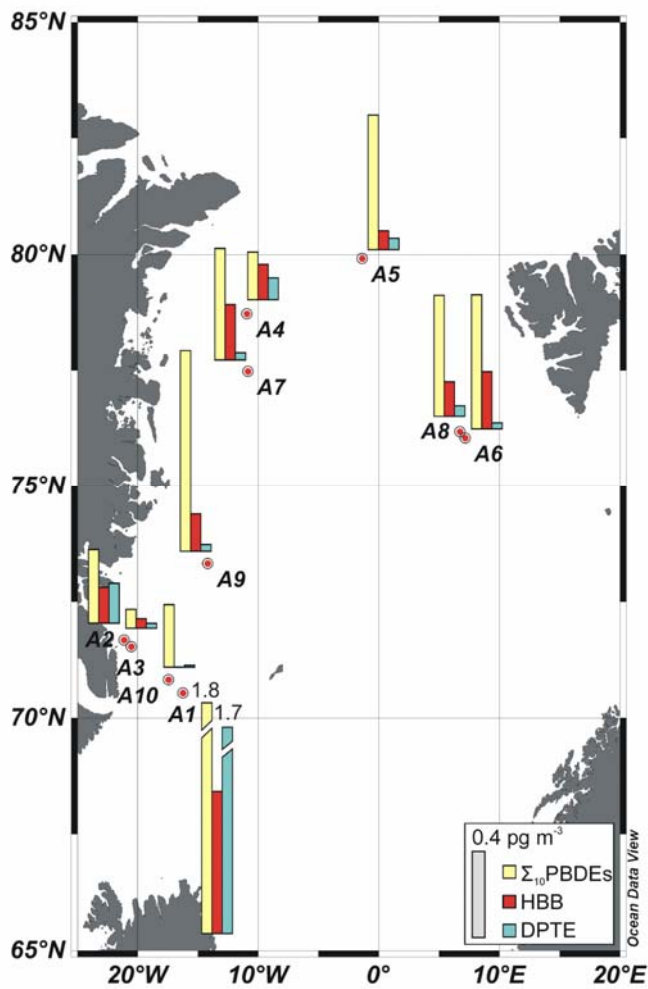


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691 **Fig. 2.** Map showing the concentrations of Σ_{10} PBDEs, HBB and DPTE in the East
692 Greenland Sea atmosphere. The stations represent mean stations since samples were
693 taken continuously along the cruise leg. NOTE: For station A10 only the particulate
694 phase was analyzed.



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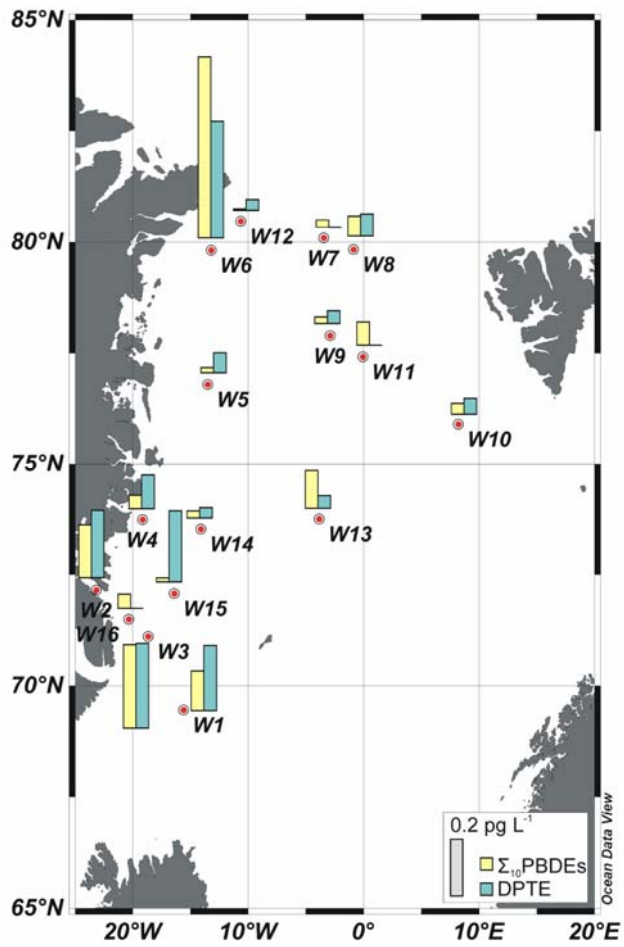
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702 **Fig. 3.** Map showing the concentrations of Σ_{10} PBDEs and DPTE in seawater from East
703 Greenland Sea.



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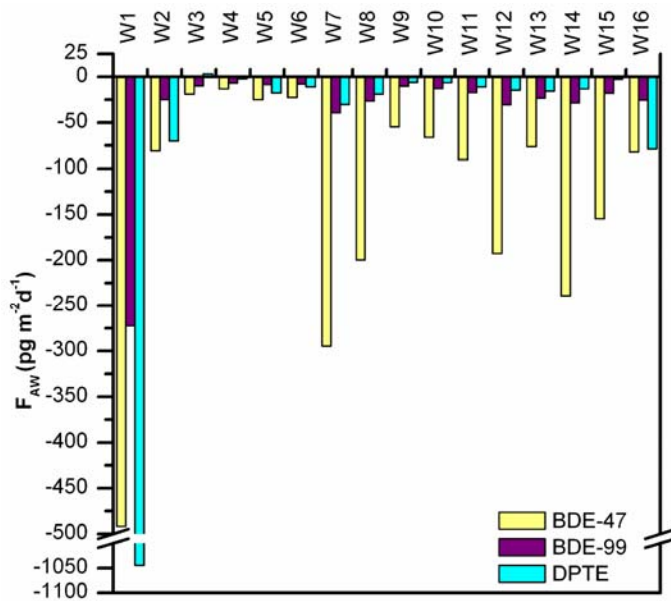
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711 **Fig. 4.** Air-sea gas exchange fluxes of BDE-47, -99 and DPTE in East Greenland Sea.
 712 Negative flux indicates net dry gaseous deposition into the water column.



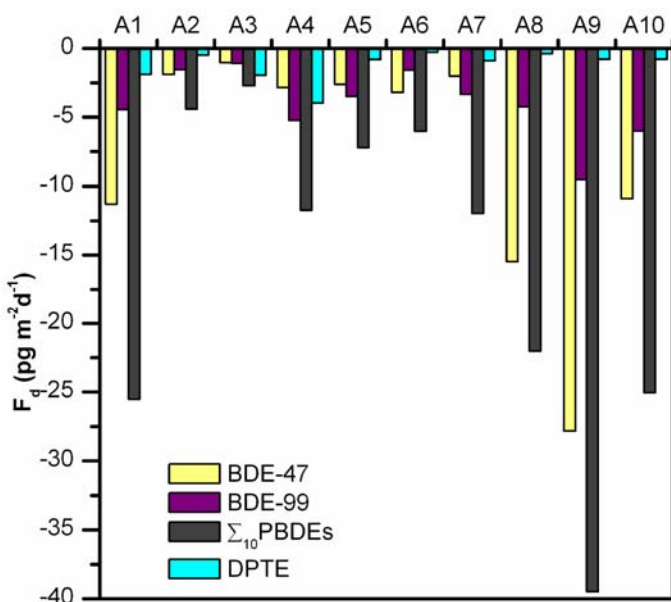
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716 **Fig. 5.** Dry particle-bound deposition fluxes of BDE-47, -99, Σ_{10} PBDEs and DPTE in
 717 East Greenland Sea. Negative (-) flux indicates net deposition into the water column.

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