Non-PBDE brominated flame retardants and Dechlorane Plus in air and seawater of the Arctic

Axel Möller[1], Zhiyong Xie[1], Jan Busch[1], Renate Sturm[1], Ralf Ebinghaus[1]

GKSS Research Centre, Institute for Coastal Research, 21502 Geesthacht, Germany

Introduction

Brominated flame retardants (BFRs) have been used for more than 50 years to reduce the flammability of various industrial and commercial products like plastics, textiles and furniture. Polybrominated diphenyl ethers (PBDEs), which are currently the most well studied BFRs, are known to be toxic, bioaccumulative, persistent and undergo atmospheric long-range transport (Birnbaum & Staskal 2004; Wania & Dugani 2003). As a result of their excessive use and long-range transport potential, they have been found worldwide in various environmental compartments with an increasing temporal trend, even in remote areas like the Arctic (de Wit et al. 2006; Hites 2004). Therefore, PBDEs have been regulated or banned by national and international regulations. Recently, tetra-heptaBDEs were included in the Stockholm Convention on Persistent Organic Pollutants (POPs) (Stockholm Convention Secretariat 2009). This leads to increasing demand and usage of "new" non-regulated BFRs such as hexabromobenzene (HBB) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) as replacement products which have already been found in organisms from the Arctic (Karlsson et al. 2006; Verreault et al. 2007).

However, there is only little knowledge on the environmental fate and effects of these compounds and abiotic levels in remote areas are unknown. Here we present the occurrence and distribution of several non-PBDE BFRs and the most common PBDEs in air and surface water in eastern Greenland Sea.

Materials and Methods

Water and air sampling

Sampling took place in eastern Greenland Sea during the polar expedition cruise ARK-XXIV-3 with the German research vessel 'FS Polarstern' in summer 2009 (Figure 1). Air samples (~1000m³) were collected at the upper deck using high-volume air sampler equipped with glass fiber filters (GF/F 8) for airborne particles and a column packed with PUF/XAD-2 resin for the gas phase. Water samples (~1000L) were taken via the ship intake system using glass fiber filters (GF/F 52) combined with PUF/PAD-2 packed glass columns. Air samples and filters were stored at -20°C and water samples at 0°C until analysis.

Extraction and analysis

The extraction of the samples was done in a clean-lab class 10000. All samples were spiked with 200 pg of ^{13}C-BDE-77 and ^{13}C-BDE-138 as internal standards. Seawater and filter samples were extracted for 16h in a Soxleth apparatus using dichloromethane while hexane/dichloromethane (1:1 v/v) was used for air samples. The extracts were evaporated to 1-2 mL using hexane as keeper and further cleaned on a 2.5 g silica column (10% deactivated). BFRs and DPs were eluted with 15 mL hexane and evaporated to the final volume of 30 µL and 1 ng ^{13}C-hexachlorobenzene was added as injection standard.

The samples were analyzed for 10 PBDEs (BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), 9 non-PBDE BFRs (2,4,6-tribromophenyl allylether (ATE), BTBPE, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB, pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), tetrabromo-p-xylene (PTBX), octabromotrimethylphenylindane (OBIND), 2-ethyl-1-hexyl-2,3,4,5-tetrabromobenzoate (EHTBB)), syn- and anti-Dechlorane Plus® (sDP and aDP) and 3 DP related compounds (Cl11DP, Cl10DP and DP mono adduct).

Analysis was performed by a gas chromatography-mass spectrometry system (GC-MS) operated in negative chemical ionization mode (NCI). The analytes were separated on a 30 m HP-5ms column with 0.25 mm internal diameter and 0.25 µm film thickness. Quantification was done by the response of the analytes and the corresponding internal standard.

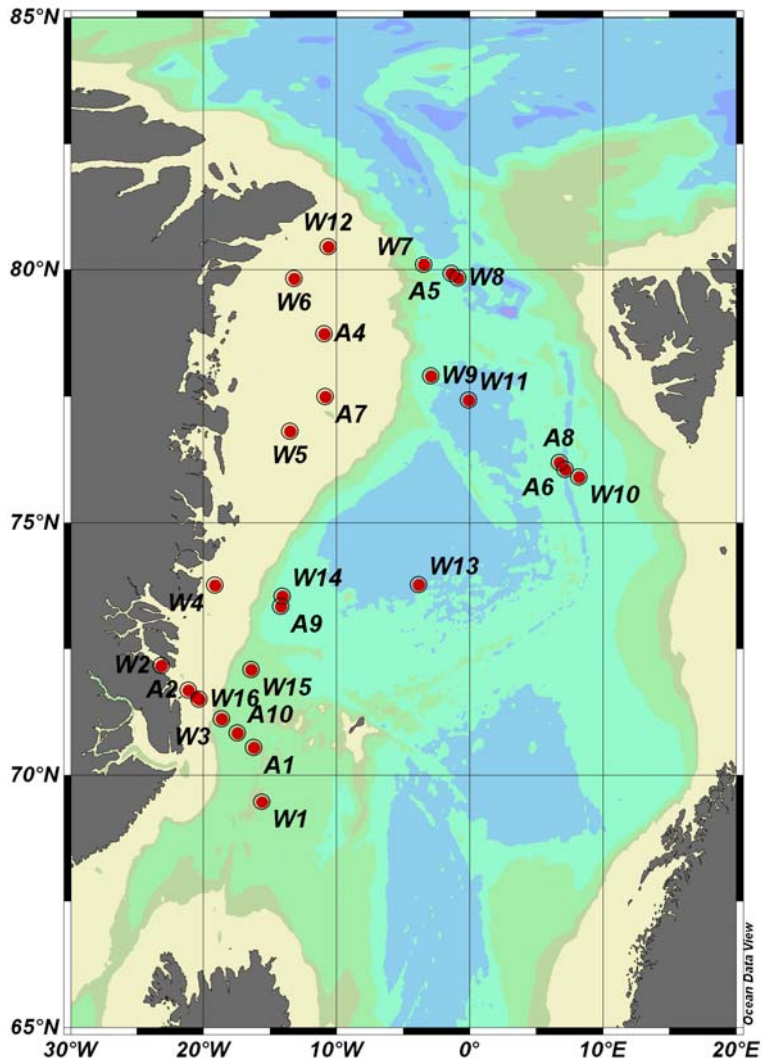

Figure 1. Water (W) and air (A) sampling stations aboard ‘FS Polarstern’.

Results and Discussion

The observed concentrations in the atmosphere were relatively constant with a few pg per cubic metre. Volatile BFRs like BDE-47 and HBB were found almost exclusively in the gaseous phase whereas higher brominated PBDEs and BFRs were attached to airborne particles. Seawater samples showed concentrations in the lower ng per litre range and the spatial distribution of dissolved BFRs decreased from Greenland coast to the open ocean.

The results of this study confirm comparable long-range transport behaviour of several current-use BFRs to PBDEs as previously derived from findings in biota from the Arctic (Verreault et al. 2007). The observed abiotic concentrations of the common PBDEs and their non-regulated alternatives in the Arctic are quite comparable. Furthermore, this study indicates that atmospheric depositions dominate the air-water exchange process of BFRs.

Acknowledgement

We kindly acknowledge the Alfred Wegener Institute for Polar and Marine Research (AWI), Bremerhaven, for the possibility of taking part in the polar expedition cruise ARK-XXIV-3.

References

Birnbaum LS, Staskal DF 2004. Environ Health Perspect 112:9

de Wit CA, Alaee M, Muir DCG 2006. Chemosphere 64:209

Hites RA 2004. Environ Sci Technol 38:945

Karlsson M, Ericson I, van Bavel B, Jensen JK, Dam M 2006. Sci Total Environ 367:840

Stockholm Convention Secretariat 2009. The 9 new POPs under the Stockholm Convention, Geneve, Suisse. http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx.

Verreault J, Gebbink WA, Gauthier LT, Gabrielsen GW, Letcher RJ 2007. Environ Sci Technol 41:4925

Wania F, Dugani CB 2003. Environ Toxicol and Chem 22:1252