Brominated flame-retardants and dechlorane plus in air and sea water of the Atlantic Ocean and the Antarctic

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Introduction

Brominated flame-retardants (BFRs) have been used in a variety of commercial application to prevent fire. They are more likely to leach out of the products during the lifetime. The impacts of BFRs on the environment and their potential risk from animals and humans have been increasing concern to the scientific community. Results from a number of studies indicate that these chemicals are ubiquitous in various environmental compartments (Law et al., 2006, de Wit et al. 2006). In response to increasing international regulations by governments and agencies on certain PBDEs, alternatively, non-BDE additive flame-retardants for achieving commercial product fire safety standards are being developed and used in BFR industry, such as 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), Hexabromobenzene (HBB), pentabromotoluene (PBT). Recently, non-BDE BFRs, such as DPTE, HBB and PBT, have been determined in environmental or biological samples of North America and Europe (Gauthier, et al., 2009, Venier and Hites, 2008, Verreault, et al., 2007).

In this study, we analyzed marine boundary layer air and surface water samples of the Atlantic and the southern oceans for the determination of PBDEs, non-BDE BFRs and dechlorane plus isomers (DPs). The cruise track enabled us to determine the concentration patterns of BFRs and DPs in both northern and southern hemisphere and degree to which the different regions affected atmospheric concentrations of BFRs and DPs, and the degree to which fractionation, reactions and cold condensation affected patterns of BFRs and DPs in the southern oceans.

Materials and Methods

Analytical standards. All analytical standards e.g., PBDEs (BDE-MXF including BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE153, BDE-154, BDE-183), ATE, DPTE, PBT, PTBX, HBB, EHTBB, DP isomers and internal standard mix (^{13}C labeled BDE-77 and BDE-138) were obtained from Wellington Laboratories.

Sampling, extraction, clean-up and GC-MS analysis High volume air and sea water samples were collected aboard German Research vessel FS Polarstern in November 2008 as described in (Xie et al. 2007). After spiked with internal standards, filters, PAD-2, PUF-PAD-2 columns were extracted using dichloromethane and acetone/hexane (1:1v:v), respectively. Concentrated extracts were cleaned up on a 2.5 g silica gel column and then eluted with 15 mL of hexane. The elution was concentrated down to 30 µL under gentle nitrogen blower for analysis. Sample analyses for PBDEs, non-BDE BFRs and DPs were performed using GC-MS with negative chemical ionization mode (NCI).

Results and Discussion

Total concentrations of PBDEs, non-BDE BFRs, and DPs in air and water are shown in Figure 1.

PBDEs in air PBDEs are present in the atmosphere in both the gas and particle phases. Among the PBDEs measured in this study, BDE-47 and BDE-99 were the major congeners, which can be detected in all air samples; whereas BDE-153, -154, -183, -100, -85, -66 and -28 were only present in a few gaseous or particle samples. The gaseous and particle concentrations of total PBDEs in air ranged from 0.31-2.85 pg m^{-3} and from 0.04 (MDL)-2.16 pg m^{-3}, with average concentrations of 1.12 and 0.33 pg m^{-3}, respectively. High PBDE concentrations were observed in the north hemisphere where the air mass originated from European and North Africa continents. In the south hemisphere, from the equator towards the Antarctic, the concentrations of PBDEs were fairly constant ranging from 0.40 – 1.33 pg m-^{3}.

PBDEs in sea water Among the measured 8 PBDE congeners, BDE-47 and BDE-99 were present in both dissolved and TSM phases. BDE-153, -154, -183, -100, -85 were just detectable in a few sea water samples, while BDE-28 and BDE-66 were below the method detection limit in both dissolved and TSM phases (<0.004 pg L^{-1}). The highest concentrations of ∑PBDEs were present in the English Channel (0.81 pg L^{-1}) and in the surface water collected close to the South Africa Coast (2.19 pg L^{-1}), respectively. Apart from

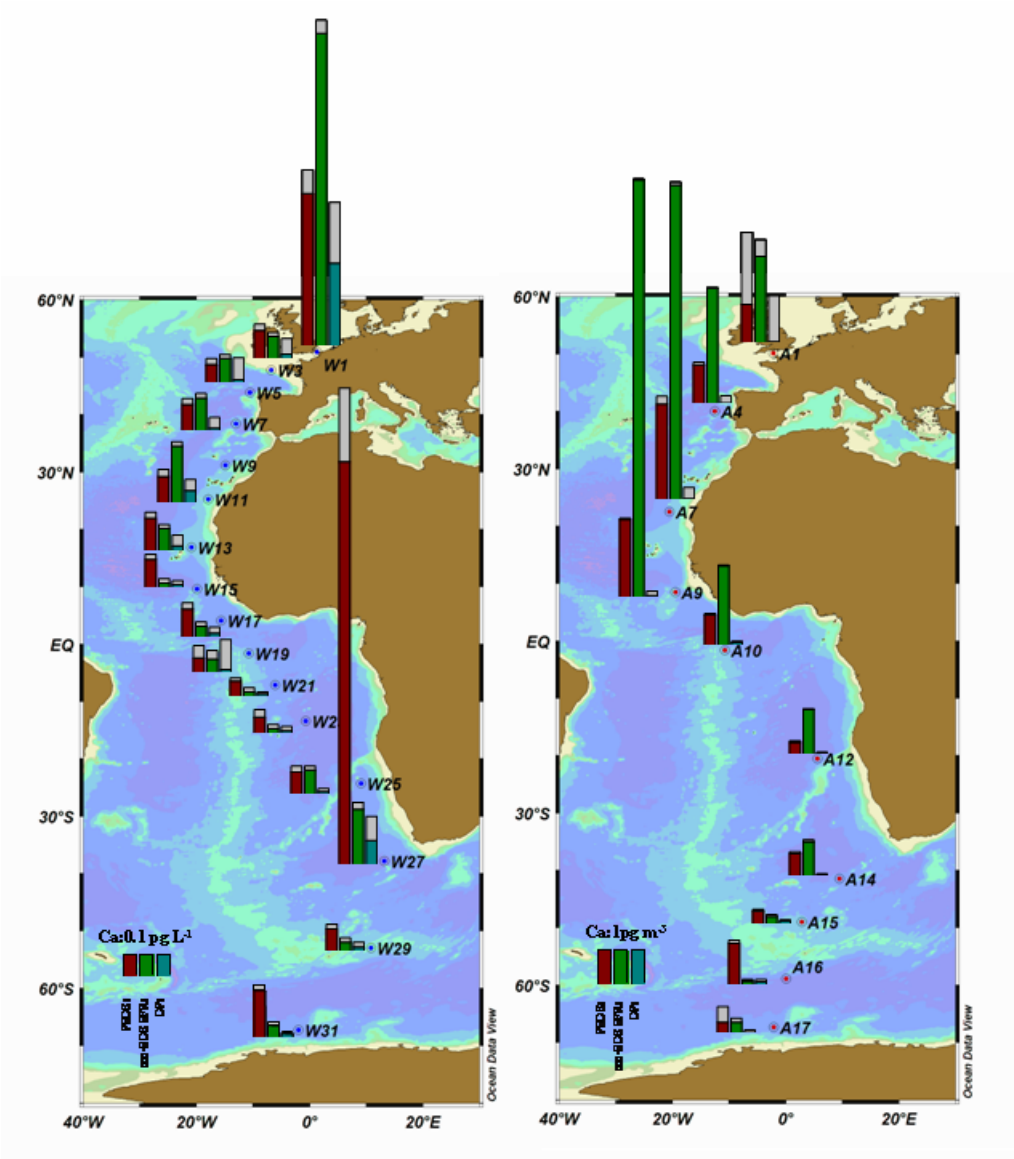

Figure 1. Total concentrations of PBDEs, non-BDE BFRs and DPs in sea water (left) and air (right)

these two peak concentrations, the levels of PBDEs through the north to south Atlantic transit were relatively constant with ∑PBDEs ranging from 0.09-0.23 pg L^{-1}.

Non-BDE BFRs in air Of the 8 non-BDE BFR compounds that are presently measured, DPTE and HBB were determined in all gaseous samples, and PTBX and PBT were detectable in ~30% gaseous samples. In all air samples ATE, HCDBCO and EHTBB were below their method detection limits (0.003, 0.014 and

0.016 pg m^{-3}). Between 50°N and 35°S the total concentrations of DPTE, HBB, PTBX and PBT are higher than those of ∑PBDEs, whereas, a reversed trend was showed in the southern ocean.

Non-BDE BFRs in sea water Dissolved DPTE was detected in most sea water samples with concentrations ranging from 0.008-0.77 pg L^{-1}. Dissolved PTBX was found in the North Atlantic and in two samples from the South Africa coast. Although HBB has shown high concentrations in air, it was just detectable in three water samples with concentration slightly higher than the method detection limit (0.006 pg L^{-1}). In the TSM phase, only DPTE was found in two water samples, other non-BDE BFRs were below their method detection limits.

Dechlorane plus in air and sea water DP was first reported in the atmosphere of the Great Lakes in 2006 (Hoh et al., 2006). The long-range atmospheric transport of DP isomers has been evidenced by the measurement of DP in tree barks (Qiu and Hites, 2007). In this study, both DP isomers have been determined in the air and water samples through the north to south Atlantic transect. The ∑DPs ranged from 0.073-1.40 pg m^{-3} in air, and from 0.020-0.66 pg L^{-1} in sea water, respectively.

References

de Wit, C.A., Alaee, M., Muir, D. Chemosphere 2006, 64: 209-233.

Gauthier, L. T., Potter, D., Hebert, C. E. and Letcher, R. J. 2009. Environ. Sci. Technol. 43: 312-317.

Hoh, E., Zhu, L.Y., Hites, R.A., 2006. Environ. Sci. Technol. 40 : 1184-1189.

Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S. Chemosphere 2006, 64: 187-208.

Qiu, X.H. and Hites, R.A., 2007. Environ. Sci. Technol. 42: 31-36.

Venier, M. and Hites. R.A. 2008. Environ. Sci. Technol. 42: 4745-4751.

Verreault, J., Gebbink, W.A., Gauthier, L.T., Gabrilsen, G.W., Letcher, R.J., 2007. Environ. Sci. Technol. 41: 4925-4931.

Xie, Z., Ebinghaus, R., Temme, C., Heemken, O., Ruck, W. 2007 Environ. Sci. Technol. 41: 5654-5659.