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ORGANOPHOSPHATE FLAME RETARDANTS AND PLASTICIZERS IN THE ATMOSPHERE AND SNOW OF THE NORTH ATLANTIC AND THE ARCTIC

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Introduction

Organophosphate esters (OPEs) are a group of man-made industrial chemicals which have been widely applied in many industrial processes and household products. Chlorinated OPEs are predominantly utilized as flame retardants, while non-chlorinated OPEs are mainly used as plasticizers and other applications. Recently, the production and usage of OPEs have increased continually as OPEs can be used in many cases as substitutes of PBDEs.

The broad application of OPEs and the fact that they are applied as additives may allow them to easily spread diffusively into the environment by volatilization, leaching, and abrasion. Several chlorinated OPEs have known various toxic effects such as skin irritation, carcinogenicity, dermatitis and neurotoxicity. The potential of OPEs to bio-accumulate and -magnify is limited due to their relatively low $\log k_{ow}$ value (<5 for most OPEs), while the OPEs have been observed in marine coastal biota samples. The concentrations of OPEs were generally 2 to 3 orders of magnitude higher than those of brominated flame retardants in the air, highlighted the importance for further research on the global occurrence and environmental fate of OPEs in both source and remote regions.

In this work, we present the concentrations of 8 OPEs (including TCPPs, TCEP, TDCP, TiBP, TnBP, TEHP, TPeP, TPhP) in air and snow samples collected during an expedition cruise ARK-XXVIII/2 from 8th to 28th June 2014 across the North Atlantic and the Arctic. This work will improve the knowledge for understanding of the long-range transport and the fate of the OPEs in the arctic ecosystem.

Materials and Methods

Air samples were collected with a high volume air sampler onboard the FS Polarstern in the northeast Atlantic and the Arctic Ocean (50°N–80°N) in June 2014. Atmospheric particle samples were collected with a glass fiber filter (GFF: diameter, 150 mm, pore size, 0.7 μm) and following with a PUF/XAD-2 resin column for gaseous phase. Each air sample was collected with the high-volume air pump operating at ~15 m^3/h for 24 to 48 h. Field blanks were prepared by shortly espousing the columns to the sampling site. Air samples were stored at 0 °C in cooling room. Six snow samples were collected on the Arctic sea ice using 10-L stainless steel barrels with helicopter and boat, and then stored at -20 °C in cooling room. The samples were further handled in a clean-lab at Helmholtz-Zentrum Geesthacht. PUF/XAD-2, and GF filters were spiked with 20 ng of d27-TnBP and d15-TPhP as surrogates, and extracted with MX-Soxhlet for 16 h using DCM. 0.8 liter of melting snow water from each sample was performed with liquid-liquid extraction using 50 ml DCM for 3 times. All samples were concentrated down to 150 μl and then spiked with 500 pg $^{13}C_6$-PCB 208 as injection standard. Analyses were performed by Agilent 7010 gas chromatograph - tandem mass spectrometer (GC-MS/MS) equipped with a programmed temperature vaporizer (PTV) injector. The MS transfer line and the high sensitivity electron impact ionization source (HSEI) were held at 280 °C and 230 °C, respectively. The MS was operated in multiple reactions monitoring (MRM) mode.

Results and Discussion

Atmospheric Concentrations of OPEs. The concentrations of 8 OPEs have been investigated in particle and gaseous phases across the North Atlantic and the Arctic. The spatial distribution of the sum of OPEs in the air is shown in Figure 1. As air sample A1 was collected when the wind direction was from the backside of the vessel, contamination from ship emission and combustion may cause the high OPE concentrations. Therefore we use samples A2-A10 for statistical analysis. Among the chlorinated OPEs,

TCPP (Sum of three isomers) and TCEP were detected in all air samples, while TDCP was detected in 44% of the air samples. Among the non-chlorinated OPEs, TiBP, TnBP, TPhP and TEHP were presented in all air samples, and TPeP was detected in 89% of the air samples. The sum of the 8 OPEs (ΣOPEs) concentrations ranged from 64 to 600 pg/m^3, with a mean concentration of 160 ± 170 pg/m^3. The 3 chlorinated OPEs accounted for 94 ± 3%, and the 5 non-chlorinated OPEs accounted for 6 ± 3% of the ΣOPEs in the atmosphere. The most abundant OPE congener was TCEP, with concentrations ranging from 60 to 490 pg/m^3 (mean, 140 pg/m^3), which is followed by 3 major OPE congeners, e.g. TCPP ranging from 0.6 to 81 pg/m^3 (mean, 16 pg/m^3), TnBP ranging from 2 to 18 pg/m^3 (mean, 5.3 pg/m^3) and TiBP ranging from 0.3 to 14 pg/m^3 (mean, 4 pg/m^3), respectively.

OPEs in snow. The concentrations of OPEs have been determined in snow samples collected during cruise ARK-XXVIII/2 from 15th to 25th June 2014 across the North Atlantic and the Arctic, which are shown in Figure 2. TCPP, TiBP, TnBP, TPhP and TEHP were detected in all snow samples. TCEP, TPeP, TDCP were detected in 83%, 50%, 33% of all samples, respectively. The concentrations of ΣOPEs ranged from 3390-9720 pg/L with a mean of 6800 pg/L. Chlorinated OPEs, TCPP (53%), TCEP (8%) and TDCPP (0.004%) accounted for 61% of the ΣOPEs , and non-chlorinated OPEs accounted for 39%. TCPP was the most abundant OPE in Arctic snow with concentrations ranging from 1300 to 5990 pg/L, and followed by TiBP (range 1110-5110 pg/L), TnBP (range 370-1020 pg/L), TCEP (range 0-1300 pg/L) and TPhP (range 1-36 pg/L). In general, snow is almost an ideal matrix for accumulation of deposited contaminants, particularly in polar region. While the varying profiles of OPE in snow may be interfered with the atmospheric deposition, snow melting and air-snow exchange processes.

Acknowledgements

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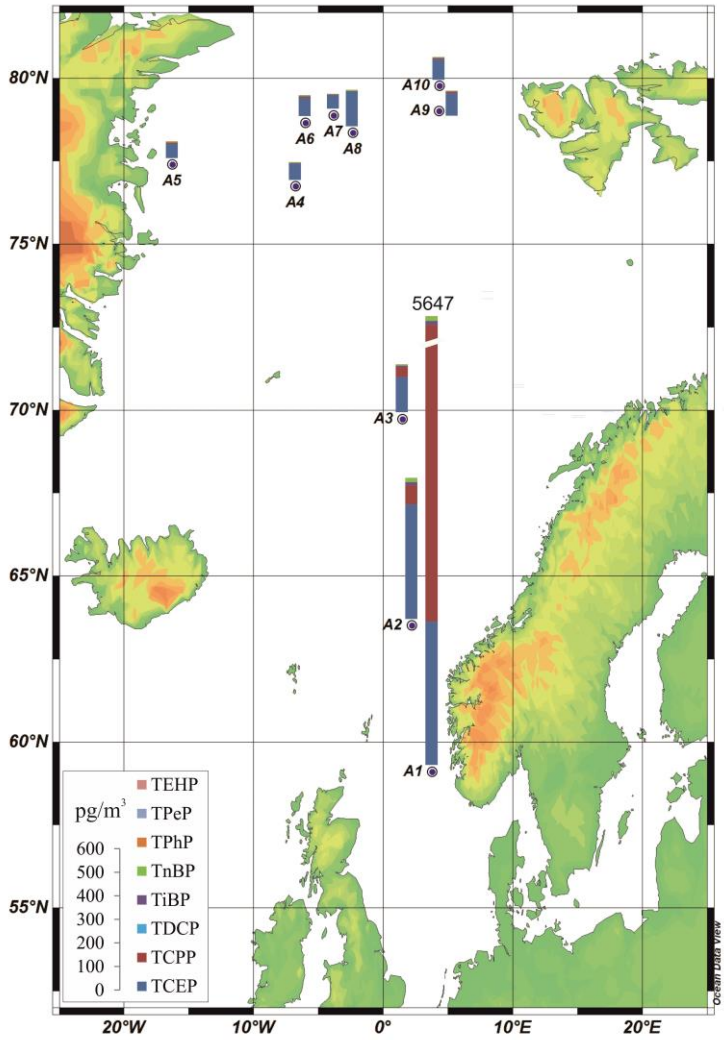

Figure1. Spatial distribution of OPEs in the atmosphere of the North Atlantic and the Arctic

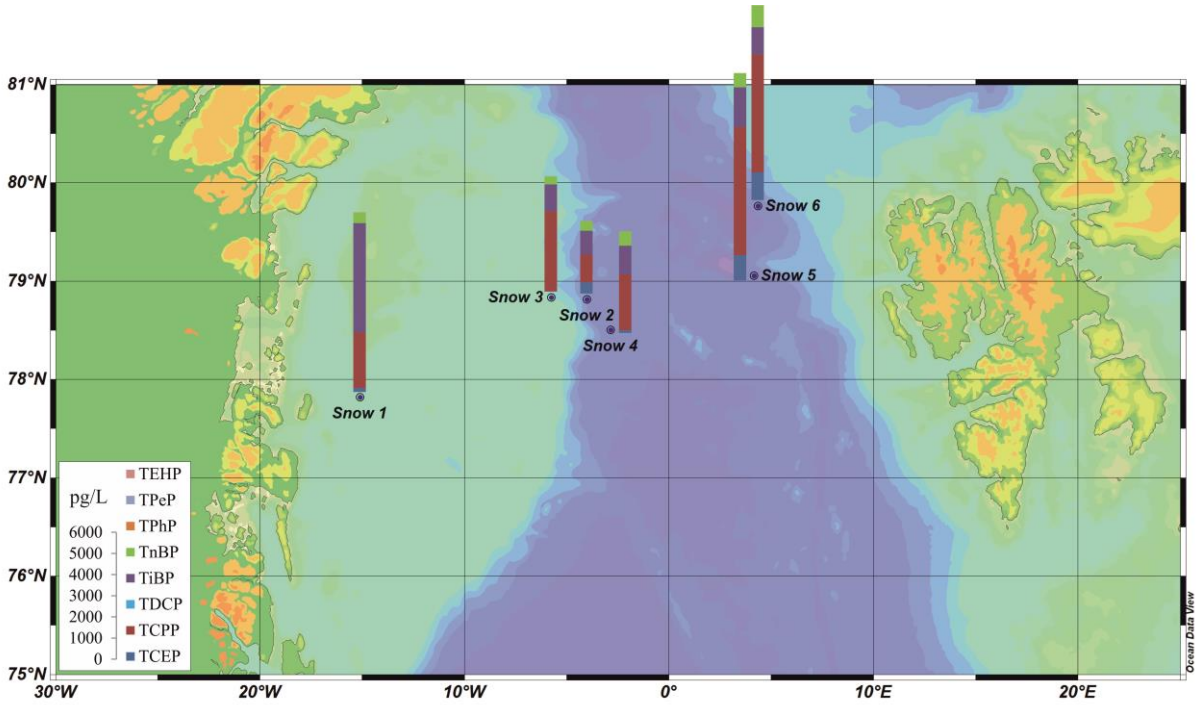

Figure2. Spatial distribution of OPEs in snow of the North Atlantic and the Arctic