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Organophosphate Esters in Air, Snow, and Seawater in the North Atlantic and the Arctic

Jing Li,[†,‡] Zhiyong Xie,* Wenying Mi,[§] Senchao Lai,[‖] Chongguo Tian,[⊥] Kay-Christian Emeis,[†,‡] and Ralf Ebinghaus[†]

[†]Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research, Geesthacht, 21502, Germany

[‡]University of Hamburg, School of Integrated Climate System Sciences, Hamburg, 20144, Germany

[§]MINJIE Analytical Laboratory, Geesthacht, 21502, Germany

[‖]Guangdong Provincial Engineering and Technology Research Center for Environmental Risk Prevention and Emergency Disposal, School of Environment and Energy, South China University of Technology, Guangzhou, 510006, China

[⊥]Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, CAS, Yantai, 264003, China

ABSTRACT:

The concentrations of eight organophosphate esters (OPEs) have been investigated in air, snow and seawater samples collected during the cruise of ARK-XXVIII/2 from sixth June to third July 2014 across the North Atlantic and the Arctic. The sum of gaseous and particle concentrations (ΣOPE) ranged from 35 to 343 pg/m^3. The three chlorinated OPEs accounted for $88 \pm 5\%$ of the ΣOPE. The most abundant OPE was tris(2-chloroethyl) phosphate (TCEP), with concentrations ranging from 30 to 227 pg/m^3, followed by three major OPEs, such as tris(1-chloro-2-propyl) phosphate (TCPP, 0.8 to 82 pg/m^3), tri-n-butyl phosphate (TnBP, 2 to 19 pg/m^3), and tri-iso-butyl phosphate (TiBP, 0.3 to 14 pg/m^3). The ΣOPE con- centrations in snow and seawater ranged from 4356 to 10561 pg/L and from 348 to 8396 pg/L, respectively. The atmospheric particle-bound dry depositions of TCEP ranged from 2 to 12 ng/m^2/day. The air−seawater gas exchange fluxes were dominated by net volatilization from seawater to air for TCEP (mean, 146 ± 239 ng/m^2/day), TCPP (mean, 1670 ± 3031 ng/m^2/day), TiBP (mean, 537 ± 581 ng/m^2/day) and TnBP (mean, 230 ± 254 ng/m^2/day). This study highlighted that OPEs are subject to long-range transport via both air and seawater from the European continent and seas to the North Atlantic and the Arctic.

INTRODUCTION

Organophosphate esters (OPEs) are a group of man-made industrial chemicals, which have been widely applied in many industrial processes and household products, such as flame-retardants, plasticizers, antifoaming agents, and additives in hydraulic fluids, lacquers, and floor polishes.[1,2] Chlorinated OPEs are predominantly utilized as flame retardants, while nonchlorinated OPEs are mainly used as plasticizers and in other applications. Recently, the production and usage of OPEs has increased continually as OPEs can be used in many cases as substitutes for polybrominated diphenyl ether (PBDEs).[2,3] The global consumption of OPEs was 186 000 tons in 2001, which rose to 370 000 tons in 2004.[4,5] In western Europe, the con-sumption of OPEs increased from 58 000 tons in 1998 to 91 000 tons in 2006 and to 110 000 tons in 2013.[2,4,6] In Germany, the annual production volumes of tris(2-chloroethyl) phosphate (TCEP) and the sum of tri-iso-butylphosphate (TiBP) and tri-n-butylphosphate (TnBP) in 1991 were estimated at approximately 4000−5000 and 500 tons/year, respectively.[7] In Sweden, the annual import quantities of several OPEs ranged from 30 to 200 tons in 2000.[4]

The broad application of OPEs and the fact that they are applied as additives may allow them to easily spread into the environment by volatilization, leaching, and abrasion.[1] Several chlorinated OPEs have various toxic effects.[8,9] For example, tris(1-chloro-2-propyl) phosphate (TCPP) is considered poten-tially carcinogenic and could accumulate in human livers and kidneys.[10] TCEP is toxic to aquatic organisms, carcinogenic for animals, and has adverse effects on human health, such as hemolytic and reproductive effects.[10] Tris(1,3-dichloro-2-propyl) phosphate (TDCP) is harmful when inhaled and can easily enter the bloodstream.[10] The potential of OPEs to bioaccumulate and magnify might be limited, owing to their relatively low log k_{ow} value (<5 for most OPEs).[2] However, Sundkvist et al. detected OPEs in human breast milk as well as in fish and mussels from Swedish lakes and coastal areas.[11] Kim et al. also found OPEs in fish collected from Manila Bay, the Philippines.[12]

The occurrence of OPEs in remote areas was reported in a few studies. Liu et al. found that particle-bound OPEs are highly persistent in the air (TPhP, 5.6 days; TEHP, 13 days), indicating that OPEs can undergo medium or long-range transport in the atmosphere.[13−15] The concentrations of OPEs that detected in the air were generally 1−2 orders of magnitude higher than those of brominated flame retardants, highlighting the importance of research on the global occurrence and environmental fate of OPEs.[13,16]

Polar regions have been used as monitoring sites to represent global background levels of persistent organic pollutants (POPs), and research on POPs in polar regions such as the Arctic provides important knowledge about the fate of these compounds.[16] Several studies that analyzed OPEs in the Arctic, such as nine OPEs were found in Ny-Ålesund, Svalbard air by Green et al. in 2008;[17] Möller et al. reported eight OPEs in air from the northern Pacific Ocean to the Arctic Ocean in 2012;[13] Salamova et al. analyzed eight OPEs in Longyearbyen, Svalbard in 2014;[16] Sühring et al. detected 14 OPEs in Canadian Arctic air in 2016.[18] There is, however, no report on OPEs in the North Atlantic, and there is a lack of data on OPEs in seawater and snow in the Arctic. More research is necessary to understand the occurrence, transport, and interaction between different environmental phases for OPEs in the remote Arctic.

In this work, the occurrence and spatial distribution of eight OPEs was investigated in air, snow, and seawater samples collected during an expedition cruise in the North Atlantic and the Arctic, and atmospheric particle-bound dry deposition and the air−seawater gas exchange fluxes of OPEs were estimated. This work will improve understanding of long-range transport and the fate of OPEs in the Arctic ecosystem.

MATERIALS AND METHODS

Sampling Campaign. The samples were collected in the northeast Atlantic and the Arctic Ocean (50°N−80°N) during the expedition cruise ARK-XXVIII/2 on board R/V *Polarstern*. Nine air samples were collected with a high volume air sampler from eighth to 24th June 2014. Six snow samples were collected from 15th to 25th June 2014. Twenty-five seawater samples were collected from eighth to 26th June 2014. Atmospheric particle samples were collected with a glass fiber filter (GFF diameter, 150 mm; pore size, 0.7 μm) and a PUF/XAD-2 resin column was used to collect the gaseous phase, respectively. Each set of air samples was collected using a high-volume air pump operating at ∼15 m³/h for 24−48 h. Field blanks were prepared by shortly exposing the columns and filters to the sampling site. PUF/XAD-2 and GFF samples were stored at 4 and −20 °C in a cooling room, respectively. Snow samples were collected on the Arctic sea ice via helicopter and boat using 10-L stainless steel barrels and then stored at −20 °C in a cooling room. 1 L seawater samples were collected in glass bottles from the ship's intake system located in the keel (depth: 11 m), and stored at 4 °C in a cooling room. Details on the air, snow, and seawater sampling information are summarized in Tables S1−S3.

Analysis. Air sample pretreatment and analysis followed the approach given by Möller et al.[14] Briefly, PUF/XAD-2 and GFFs were spiked with 20 ng of d_{27}-TnBP, d_{12}-TCEP, and d_{15}-TPhP as surrogates, and extracted with MX-Soxhlet using dichloromethane (DCM) for 16 h. Eight hundred milliliters (800 mL) of melting snow water and seawater from each sample were performed with liquid−liquid extraction using 50 mL DCM three times. All samples were concentrated down

to 150 μL and then spiked with 500 pg $^{13}C_6$-PCB 208 as the injection standard. The samples were then analyzed using a gas chromatograph couple to a triple quadrupole mass spectrometer (GC-MS/MS) equipped with a programmed temperature vaporizer (PTV) injector (Agilent, USA). The parameter details for GC-MS/MS are given in Text S1.

Eight OPEs have been analyzed in this work, which include tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro- 2-propyl) phosphate (TCPP, including three isomers), tris(1,3- dichloro-2-propyl) phosphate (TDCP), tri-iso-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), triphenyl phosphate (TPhP), tripentyl phosphate (TPeP), and tris(2-ethylhexyl) phosphate (TEHP). More details about these OPEs are shown in Table S4.

Quality Assurance/Quality Control (QA/QC). The method detection limits (MDLs) were derived from the mean field blank concentrations plus three times the standard deviation (3σ) of the field blanks,[19] which were within 0.0003−1.5 pg/m³ for the gaseous phase, 0.0002−6.5 pg/m³ for the particle phase, 7−210 pg/L for snow and seawater. The OPE concentrations are corrected with the recoveries of internal standards.[19] The mean recovery rates of spiked experiments were from 88 ± 13% (TiBP) to 145 ± 9% (TCEP) for PUF/XAD-2 columns (n = 5), from 107 ± 4% (TCCP) to 139 ± 12% (TEHP) for the filters (n = 3), and from 78 ± 3% (TiBP) to 95 ± 8% (TCEP) for LLE extraction (n = 5), respectively. Detailed information for recovery rates, field blanks and MDLs is summarized in Table S6.

To monitor the background levels of OPEs in the air of the working places during the cruise, XAD-2-based passive air samplers were deployed on the upper deck next to the high-volume air sampler and in the chemical lab. The result shows that total OPE masses in the chemical lab (235 ng) were about eight times higher than those of the upper deck (28.4 ng, see Table S7). During this cruise, the air columns and filters were placed on the upper deck directly, which could eliminate certain contamination from the indoor lab air.

Breakthrough of target compounds for the vapor phase was evaluated using tandem columns for samples A2 and A9 aboard R/V *Polarstern*. In the lower columns, no TnBP, TPhP, or TEHP was detected above MDLs; TDCP was only observed at sample A2, which accounted for 28% to total TDCP (sum concentration of upper and lower columns); TiBP contributed to 15% of total TiBP and TCEP contributed to 28%; TCPP accounted for 46%, which was a little higher than other OPEs. Since the breakthrough of compounds is a complicated process, it is difficult to find an appropriate method to correct the concentrations. Therefore, only the concentrations on the first column were reported in this study, which was inevitable to underestimate the OPE concentrations.

OPEs are subject to air sampling artifacts, as sorption to the filter could occur when the vapor phase OPEs pass through, and fine aerosol particles may pass the filter and end up trapped on the column during sampling. The diameter of the filters used in this work is <0.7 mm, which might allow the fine particles to pass through. Pankow et al. described the possible impact that could increase the uncertainties, such as temperature change, adsorption and desorption during sampling.[20] Those factors discussed above will lead to over or underestimation of OPEs in the gaseous and particle phases, and as a consequence lead to uncertainties when estimating the air-particle partitioning, the dry deposition fluxes and the air−seawater gas exchange fluxes.

Air Mass Back Trajectories. Air mass back trajectories (BTs) were calculated for the air stations using NOAA's HYSPLIT model.[21] BTs were calculated for every sample in 6 h steps during the sampling cruises, and were tracked for 120 h at 10 m above sea level (see Figure S1).

RESULTS AND DISCUSSION

Atmospheric Concentrations of OPEs. The concentrations of eight OPEs have been investigated in both particle and gaseous phases. The minimum, maximum, mean, and median concentrations of individual OPEs in the air are presented in Table 1. Among the chlorinated OPEs, TCPP (sum of three isomers) and TCEP were detected in all air samples, while TDCP was detected in 33%. Among the nonchlorinated OPEs, TiBP, TnBP, TPhP, and TEHP were present in all air samples, while TPeP was detected in 56%. The sum concentrations of the eight OPEs (ΣOPE) ranged from 35 to 343 pg/m³, with a mean of 98 ± 98 pg/m³. The three chlorinated OPEs accounted for 88 ± 5% of the total ΣOPE, and the five nonchlorinated OPEs accounted for 12 ± 5%. The most abundant OPE was TCEP, with concentrations ranging from 30 to 227 pg/m³ (mean = 71 ± 62 pg/m³), which was followed by three major OPEs, such as TCPP ranging from 0.8 to 82 pg/m³ (mean = 17 ± 28 pg/m³), TnBP ranging from 2 to 19 pg/m³ (mean = 5.7 ± 5 pg/m³), and TiBP ranging from 0.3 to 14.5 pg/m³ (mean = 4.5 ± 4.5 pg/m³).

To compare with previous reports, OPE concentrations measured in the air of different remote areas are summarized in Table 2. Chlorinated OPEs (TCPP, TCEP, and TDCP) have been reported as the dominant OPE congeners in different geographic regions, except from an Arctic site.[16] The mean total OPE concentrations varied from 100 pg/m³ in this study to 2800 pg/m³ over the Black Sea.[3] The OPE levels in this work are similar to those detected over the South China Sea,[19] 2−6 times lower than those of the Canadian Arctic,[18] Longyearbyen,[16] the North Sea,[14] the Great Lakes,[22] the Latin America,[23] and the Pacific and Indian Oceans.[13] High concentrations (≥1000 pg/m³) were detected in three areas, that is, in East Asia, such as in the East China Sea and Japan Sea;[13,15] in Europe, such as in the Mediterranean Sea and Black Sea;[3] in North America, such as in the Great Lakes.[24] Western Europe, North America and East Asia are the highest consumption regions for flame retardants.[25] In 2013, the usage of OPEs in Western Europe (110 000 tons) and North America (70 000 tons) accounted for approximately 30% and 20% of worldwide usage, respectively.[6] The production of OPEs in China was 179 000 tons in 2012.[26] Relatively low concentrations, however, were also detected in those areas, such as 100 pg/m³ over the South China Sea and 400 pg/m³ over the North Sea.[14,19] In this study, the most abundant OPE was TCEP (mean, 71 pg/m³), which was lower than in other remote areas, with the exception of Longyearbyen (mean, 19 pg/m³) and near the Antarctic Peninsula (mean, 41 pg/m³).[15,16] In addition to TCEP, the other seven OPEs (i.e., TCPP, TDCP, TiBP, TnBP, TPeP, TPhP, and TEHP) were all lower than those measured in the atmosphere of other oceans.

The ratio of mean concentration of TCEP to TCPP was ~4 in this study, which was ten times as high as that of a German coast site (0.4).[27] This might result from the slower photochemical degradation of TCEP than TCPP in the atmosphere.[27] The half-life of TCEP (17.5 h) is two times as long as TCPP (8.6 h) in the gaseous phase.[28,29] The TiBP/TnBP ratios were ~1 in this work and the German coast site, with the two

Table 1. Minimum, Maximum, Mean, and Median of Individual OPE Concentrations in Air (pg/m³), Snow (pg/L), and Seawater (pg/L)

OPE	gaseous phase (pg/m³)				particle phase (pg/m³)				snow (pg/L)				seawater (pg/L)			
	min	max	mean	median	min	max	mean	median	min	max	mean	median	min	max	mean	median
TCEP	4	92	23	10	26	136	48	35	554	2440	1293	1147	n.d.	2401	695	605
TCPP	0.8	55	12	1.9	n.d.	27	5	2.3	1522	6256	3890	3451	279	5773	1843	1626
TDCP	n.d.	0.06	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.8	0.8	n.d.	n.d.	43	7	4
TiBP	0.3	7.5	2.7	1.7	n.d.	7	1.8	2	1121	5129	2004	1319	39	638	258	230
TnBP	n.d.	8.8	2.2	1.4	1.6	10	3.5	3	390	1044	630	596	n.d.	412	122	105
TPeP	n.d.	0.02	0.01	0.001	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	0.3	0.14	n.d.	35	5	n.d.
TPhP	0.01	1.5	0.2	0.017	n.d.	0.09	0.01	0.03	2.5	38	11	4	n.d.	n.d.	n.d.	n.d.
TEHP	n.d.	0.6	0.1	n.d.	n.d.	0.06	0.02	0.02	1.3	13	5.5	4	n.d.	69	6	n.d.
ΣOPE	7	163	40	17	29	180	58	48	4356	10561	7834	7922	348	8396	2935	2635

Table 2. Comparison of Atmospheric Concentrations (pg/m³) of OPEs (Range and Mean Value) in This Study and Those Measured in Open Seas and Remote Areas[a]

location	TCEP	TCPP	TDCP	TiBP	TnBP	TPhP	TPeP	TEHP	other OPEs	ΣOPE (mean value)[g]	refs
North Sea[b]	6−160 (43)	38−1200 (331)	n.d.−78 (6)	n.d.−150 (45)	n.d.−150 (29)	4−290 (35)	n.a.	n.d.−31 (6)		500	14
Sea of Japan[c]	237/1960	130/620	16/52	11/63	10/33	25/97	n.a.	5/38	15/81	1700	13
Northern Pacific Ocean[c]	160−280 (204)	98−270 (160)	5−8 (5)	14−21 (17)	6−14 (11)	9−24 (19)	n.a.	1−12 (2)	n.d.−16	400	13
Philippine Sea[c]	20−156 (77)	22−411 (74)	50−780 (80)	10−23 (16)	10−100 (14)	n.d.−155 (17)	n.a.	6−92 (12)	n.d.−77	500	13
Indian Ocean[c]	46−570 (223)	37−550 (251)	n.d.−220 (52)	7−96 (31)	7−75 (27)	n.d.−74 (26)	n.a.	4−51 (20)	n.d.−44	650	13
East China Sea	134	9	828	n.a.	n.a.	n.a.	n.a.	n.a.	95	1000	15
Coral Sea	88	7	370	n.a.	n.a.	n.a.	n.a.	n.a.	66	500	15
Southern Ocean	74	55	80	16	14	19	n.a.	7		300	13
Near Antarctic Peninsula	41	4	76	n.a.	n.a.	n.a.	n.a.	n.a.	20	140	15
Arctic Ocean[c]	126−585 (289)	85−529 (281)	n.d.−5 (−)	16−35 (25)	n.d.−36 (11)	10−60 (19)	n.a.	n.d.−6 (1)	n.d.−11	600	13
Mediterranean Sea[d]	70−854 (300)	126−2340 (963)	n.d.−460 (135)	4−650 (237)	56−600 (295)	n.d.−80 (28)	n.a.	56−307 (149)	∼500	2500	3
Black Sea	300−2417 (869)	540−2722 (1159)	n.d.−97 (80)	66−190 (139)	202−370 (298)	3−40 (28)	n.a.	36−190 (144)	∼380	2800	3
Great Lakes(2014)[e]	5.5 ± 0.9−180 ± 25 (93)	25 ± 7−850 ± 300 (345)	n.d.−520 ± 220 (154)	n.a.	34 ± 7−250 ± 53 (148)	42 ± 9−200 ± 27 (103)	n.a.	4.7 ± 0.7−66 ± 9 (28)	∼200	1000	24
Great Lakes(2016)[f]	193	173	36	n.a.	110	82	n.a.	n.a.	38	600	22
Longyearbyen	4.0−63 (19)	10−186 (62)	2.3−294 (59)	n.a.	5.6−1000 (174)	1.1−52 (20)	n.a.	1.0−42 (12)	∼200	550	16
Ny-Ålesund	<200−270	<200−330	87−250	<10−140	n.a.	<50	n.a.	n.a.	<500	<1300	17
South China Sea	14−107 (46)	15−38 (25)	1.3−4.5 (2.6)	1.1−3.8 (2.3)	1.4−4.8 (2.7)	3.4−15 (8.1)	n.a.	2.3−16 (5.1)	2	100	19
Canadian Arctic (ship-based)	187 ± 181	85 ± 105	2.7 ± 2.9	n.a.	2.3 ± 15	84 ± 264	n.a.	0.56 ± 1.4	1.6	400	18
Canadian Arctic (land-based)	118 ± 120	92 ± 88	10 ± 12	n.a.	747 ± 876	22 ± 26	n.a.	n.a.	12	300	18
North Atlantic and Arctic (g.)	4−92 (23)	0.8−55 (12)	n.d.−0.06 (0.01)	0.3−7.5 (2.7)	n.d.−8.8 (2.2)	0.01−1.5 (0.2)	n.d.−0.02 (0.01)	n.d.−0.6 (0.1)		40	this study
North Atlantic and Arctic (p.)	26−136 (48)	n.d.−27 (5)	n.d.	n.d.−7 (1.8)	2−10 (3.5)	n.d.−0.09 (0.01)	n.d.	n.d.−0.06 (0.02)		60	this study
North Atlantic and Arctic (sum)	30−227 (71)	0.8−82 (17)	n.d.−0.06 (0.01)	0.3−14.5 (4.5)	2−19 (5.7)	0.02−1.5 (0.2)	n.d.−0.02 (0.01)	n.d.−0.7 (0.1)		100	this study

[a]n.d. = not detected; n.a. = not analyzed; g. = gaseous phase; p. = particle phase; sum = sum of gaseous and particle phase. [b]Mean values and the range of TDCP were from the source document (Table S5 of ref 14). [c]Median concentrations are given in brackets. [d]Calculated mean values from the source document (Table S4 of ref 3). [e]Calculated mean values from the source document (Table 1 of ref 24). [f]Calculated mean values from the source document with the median values of 50% percentiles (Table 1 of ref 22). [g]The mean values of total OPEs were estimated according to the source document of the references.
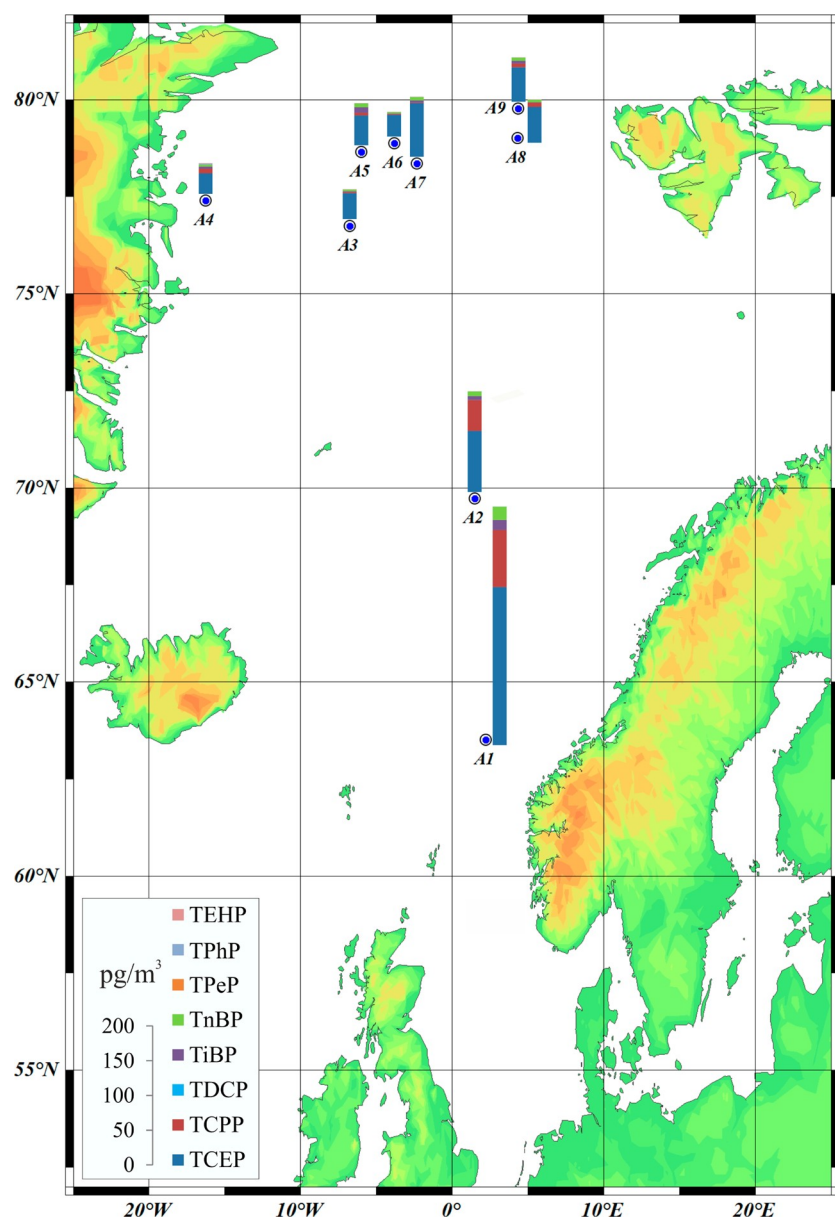
Figure 1. Spatial distribution of OPEs in air of the North Atlantic and the Arctic.

OPEs both present relatively low half-life (<5 h) in the gaseous phase.[27,28]

Brominated flame retardants, that is, decabromdiphenylether (BDE-209, <0.1 pg/m³), hexabromobenzene (HBB, <1 pg/m³) and dechlorane plus isomers (DPs, 0.01−4.1 pg/m³) have been determined in the European Arctic. In comparison to the results of this study, OPE concentrations were 1−2 orders of magnitude higher than those of BFRs.[30,31]

Spatial Distribution in the Atmosphere. The spatial distribution of OPEs in the atmosphere is shown in Figure 1. The air mass back trajectories are shown in Figure S1. The highest two ΣOPE concentrations in the air were observed at samples A1 and A2, with their mean concentration was ~3 times higher than that of others (samples A3−A9), which mainly resulted from the varying air masses. Sample A1 was influenced by air masses passing the Ireland, the United Kingdom and the eastern coastline of the North Sea. At sample A2, the air masses were influenced by North Sea air. However, the other Samples were dominated by high Arctic oceanic air masses.

At samples A1 and A2, TCEP was still detected as the dominant OPE, although TCEP has already been replaced by TCPP in Europe, demonstrating that the emission of TCEP still exists on the European continent.[17]

Gas/Particle Partitioning. The concentrations of ΣOPE ranged from 7 to 163 pg/m³ (mean, 40 ± 53 pg/m³) in the gaseous phase and from 29 to 180 pg/m³ (mean, 58 ± 48 pg/m³) in the particle phase. TCEP was the dominant OPE in both the gaseous and particle phases. The composition profile of OPEs in the air is shown in Figure S2. Particle phase OPEs contributed to 67 ± 17% of the total OPEs on average, which was lower than in the North Sea reported by Möller et al. (mean, 86 ± 25%)[14] and an indoor environment analyzed by Carlsson et al. (>99%).[32] The particle-bound fractions of four major OPEs were found in the sequence of TCEP (74%) > TnBP (72%) > TiBP (30%) > TCPP (27%). As the breakthrough of the OPEs occurred during sampling, the particle fraction might be overestimated.

The ambient temperature, relative humidity (RH), the type and concentration of particles could impact the gas/particle
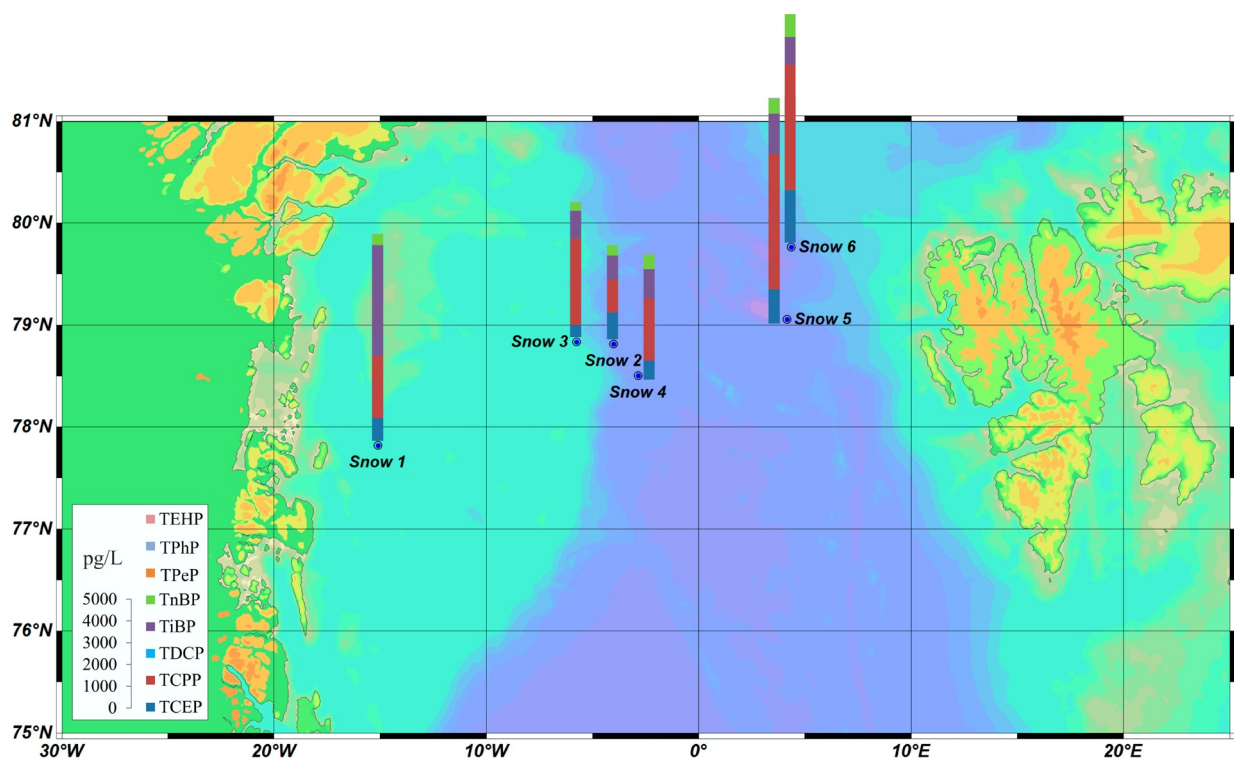
Figure 2. Spatial distribution of OPEs in snow of the North Atlantic and the Arctic.

partitioning. Strong reverse correlations between partitioning coefficients and temperatures were confirmed for volatile organic compounds by Goss et al.[33] Storey et al. reported that the partitioning coefficients will decrease by more than a log unit, with the increase of RH by 10% to over 70%.[34] Pankow et al. stated that the coefficients were unlikely to be exactly the same from one type of particle to another, even under the same atmospheric conditions.[20] In this study, the particle fractions at samples A1 (52%) and A2 (38%) were lower than others. At those two samples, the temperatures (7−12 °C) were higher than others (−4−4 °C), while the RHs were similar (75−98%), and the C_{TSP} lay in between.

OPEs in Snow. The concentrations and spatial distribution of OPEs in snow are shown in Figure 2. The details of individual OPE concentrations are shown in Table 1. TCEP, TCPP, TiBP, TnBP, TPhP, and TEHP were detected in all snow samples, while TPeP and TDCP were detected in 60% and 40% of samples, respectively. The concentrations of ΣOPE ranged from 4356 to 10560 pg/L with a mean of 7834 ± 2684 pg/L. Chlorinated OPEs accounted for 66 ± 14% and nonchlorinated OPEs accounted for 34 ± 14% of total OPEs, respectively. TCPP was the most abundant OPE in snow with concentrations ranging from 1522 to 6256 pg/L, with a mean of 3890 ± 1838 pg/L, followed by TiBP (1121−5129 pg/L, mean 2004 ± 1552 pg/L), TCEP (554−2440 pg/L, mean 1293 ± 661 pg/L) and TnBP (390−1044 pg/L, mean 630 ± 234 pg/L). There was a decreasing trend for ΣOPE concentrations from coast to open ocean, with the mean concentration of costal snow samples (snows 1, 5, and 6) was ∼2 times as high as the open ocean samples (snows 2−4).

The dominant OPE (TCPP) is compared to concentrations from urban precipitation, as reports on OPEs in polar region snow are rare. The mean concentration of TCPP (∼3.9 ng/L) in this study was 1−3 orders of magnitude lower than in the

urban areas, such as in central Germany (range 46−2659 ng/L, rainwater),[35] Italy (range 633−739 ng/L, rainwater),[36] and northern Sweden (range 100−220 ng/kg, snow).[1]

OPEs in Seawater. The concentrations and spatial distribution of OPEs in seawater are shown in Figure 3. Among the measured eight OPEs, TCPP, and TiBP were detected in all seawater samples, while TPhP was not detected in any seawater sample. Other OPEs, TnBP, TCEP, TDCP, TPeP, and TEHP were detected in 92%, 88%, 56%, 32%, and 16% of the seawater samples, respectively. The total OPE concentrations ranged from 348 to 8396 pg/L, with a mean of 2935 ± 1890 pg/L. The three chlorinated OPEs accounted for 87 ± 8% of the total ΣOPE in seawater, and the five nonchlorinated OPEs accounted for 13 ± 8%. The concentrations of OPEs were found in sequence of TCPP (279−5773 pg/L, mean 1843 ± 1323pg/L) > TCEP (MDL−2401 pg/L, mean 695 ± 589 pg/L) > TiBP(39−638 pg/L, mean, 258 ± 191 pg/L) > TnBP (MDL−412 pg/L, mean 122 ± 116 pg/L). The details of individual OPE concentrations are summarized in Table 1.

Literature data on OPEs in seawater from the oceans is rare. Bollmann et al. have reported OPEs in coastal surface waters of the River Elbe and marine surface waters of the German Bight (North Sea), with total OPE concentrations ranging from 85 to 500 ng/L and from 5 to 50 ng/L, respectively.[37] Harino et al. measured OPEs in water samples from Maizuru Bay, with total concentrations ranging from 3.0 to 62 ng/L.[38] Regnery et al. detected OPEs in urban and remote lentic surface waters in Germany, with a mean of 200 and 25 ng/L, respectively.[39] The concentrations of ΣOPE (0.2−8 ng/L) determined in this study are 1−2 orders of magnitude lower than those detected in rural regions and 2−3 orders of magnitude lower than in urban areas.

Latitudinal Trends in Seawater. The four highest concentrations of ΣOPE were measured at sites near continents,
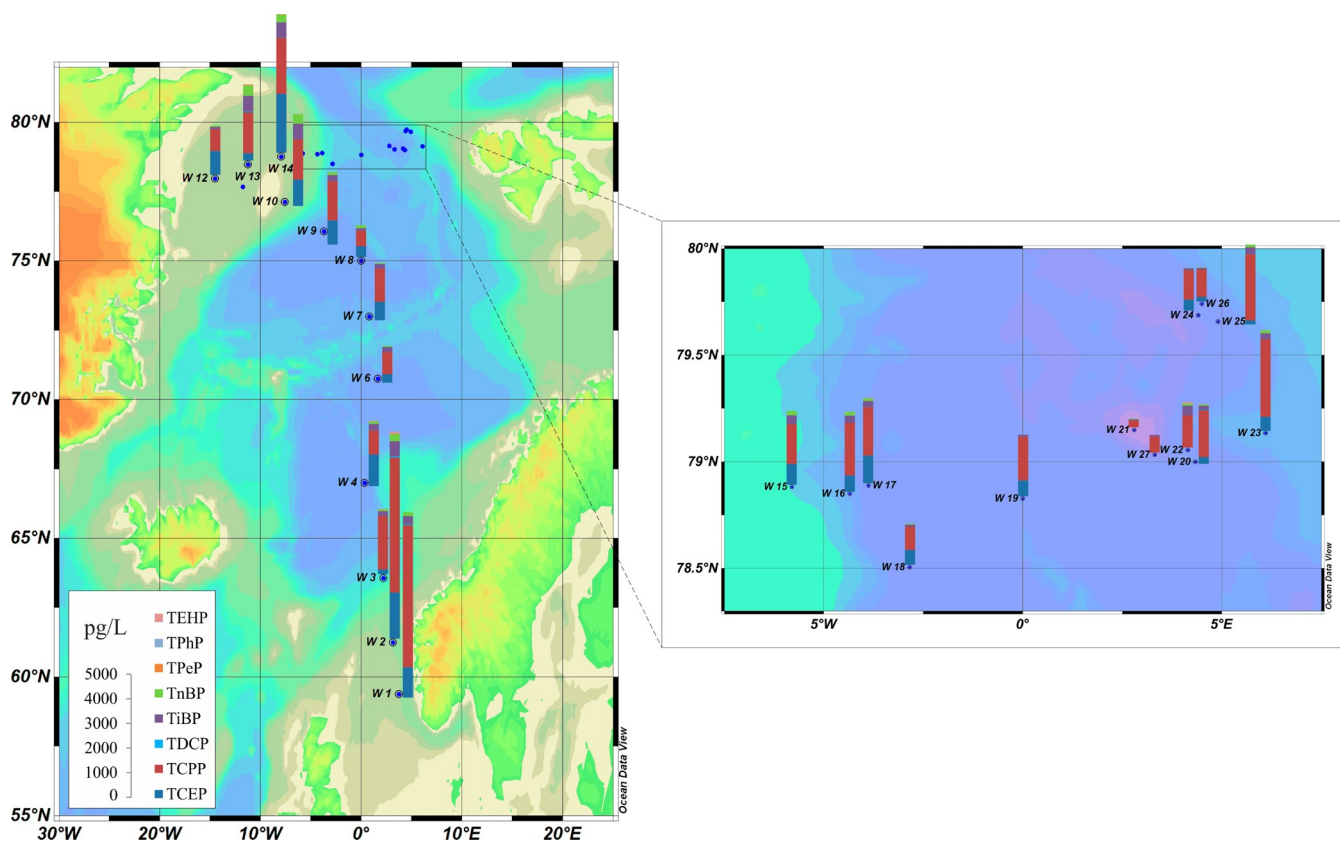
Figure 3. Spatial distribution of OPEs in seawater of the North Atlantic and the Arctic.

including samples W2 (8396 pg/L), W1 (7541 pg/L) (close to the European continent), W14 (5636 pg/L, near Greenland), and W23 (4086 pg/L, near Svalbard). When the ship was heading to the open ocean, much lower ΣOPE concentrations were measured. Near the European continent, fresh discharge of OPEs might have originated from the North Sea. Bollmann et al.[37] reported OPE concentrations in the German Bight (North Sea), ranging from 5 to 50 ng/L, which are 5−10 times higher than at samples W1−W6 in this study (range 1.5−8 ng/L), suggesting that there was a decreasing trend of ΣOPE concentrations from the North Sea to the Arctic. At the Greenland and Svalbard coasts, the glacier and snow melting contributed to OPEs in seawater to some degree, considering the high OPE concentrations in snow detected in this study (mean 7834 pg/L). Furthermore, closer to Greenland and Svalbard, higher ΣOPE concentrations were detected in snow. The discharge of melting snow and ice in the Arctic summer can be a secondary source of the organic contaminates and may cause elevated concentrations in the Arctic.

Particle Dry Deposition Fluxes. The dry particle deposition flux was determined by multiplying the concentration of particle OPEs by a dry deposition velocity (details see Text S2).[3,40] As no measured velocities for OPEs are available in the target area, a value of 0.1 cm/s (86.4 m/day) has been chosen, which was proposed by Möller et al. for calculating the dry deposition of PBDEs in the European Arctic.[30]

The dry deposition fluxes of four major OPEs in the individual air samples are shown in Figure 4a. The particle phase dry depositions of ΣOPE ranged from 2 to 16 ng/m²/day, with a mean of 5 ± 4 ng/m²/day. The atmospheric dry deposition was dominated by TCEP, ranging from 2 to 12 ng/m²/day, and followed by TCPP from 0 to 2 ng/m²/day, TnBP from 0.1 to

0.9 ng/m²/day and TiBP from 0 to 0.6 ng/m²/day, respectively. Possible uncertainties in the OPE dry deposition calculation are related to the estimated deposition velocity and to gas-particle interactions during sampling and have been explained in more detail in the QA/QC section.

The dry deposition fluxes of ΣOPE in this study were comparable to the levels estimated in the South China Sea (mean 16.3 ± 6.7 ng/m²/day),[19] and were 1−2 orders of magnitude lower than those estimated in the North Sea (46− 237 ng/m²/day),[14] the Mediterranean Sea (70−880 ng/m²/day),[3] and the Black Sea (~300−1060 ng/m²/day).[3]

Air−Seawater Gas Exchange Fluxes. The equilibrium status (f_A/f_W) and fluxes (F_{AW}) of air−seawater gas exchange for four major OPEs (TCEP, TCPP, TiBP, TnBP) were estimated in this study. The results of f_A/f_W and F_{AW} are shown in Figures S3 and Figure 4b, respectively. The details of the calculation method are presented in Text S3. Generally, f_A/f_W = 1 indicates equilibrium status of a system, whereas f_A/f_W < 1 and f_A/f_W > 1 indicate volatilization and deposition, respectively.[41] The Henry's law constants (HLCs) of OPEs were estimated by SPARC as suggested by Zhang et al., and corrected by the given temperature and salinity.[42] Considering the uncertainties existing with H values, a range of 0.3 to 3 is adopted for f_A/f_W, which shows a system at dynamic equilibrium.[41,43,44]

The f_A/f_W values of TCEP ranged from 0.01 to 0.7, indicating that volatilization from seawater to air dominated in all samples. The fluxes of TCEP ranged from 5 to 1075 ng/m²/day. Equilibrium was reached at sample W3 and five samples near Svalbard (samples W20−W22, W25, and W27), which were caused by relatively low TCEP concentrations in seawater. There was a net volatilization for TCPP, with all f_A/f_W values lower
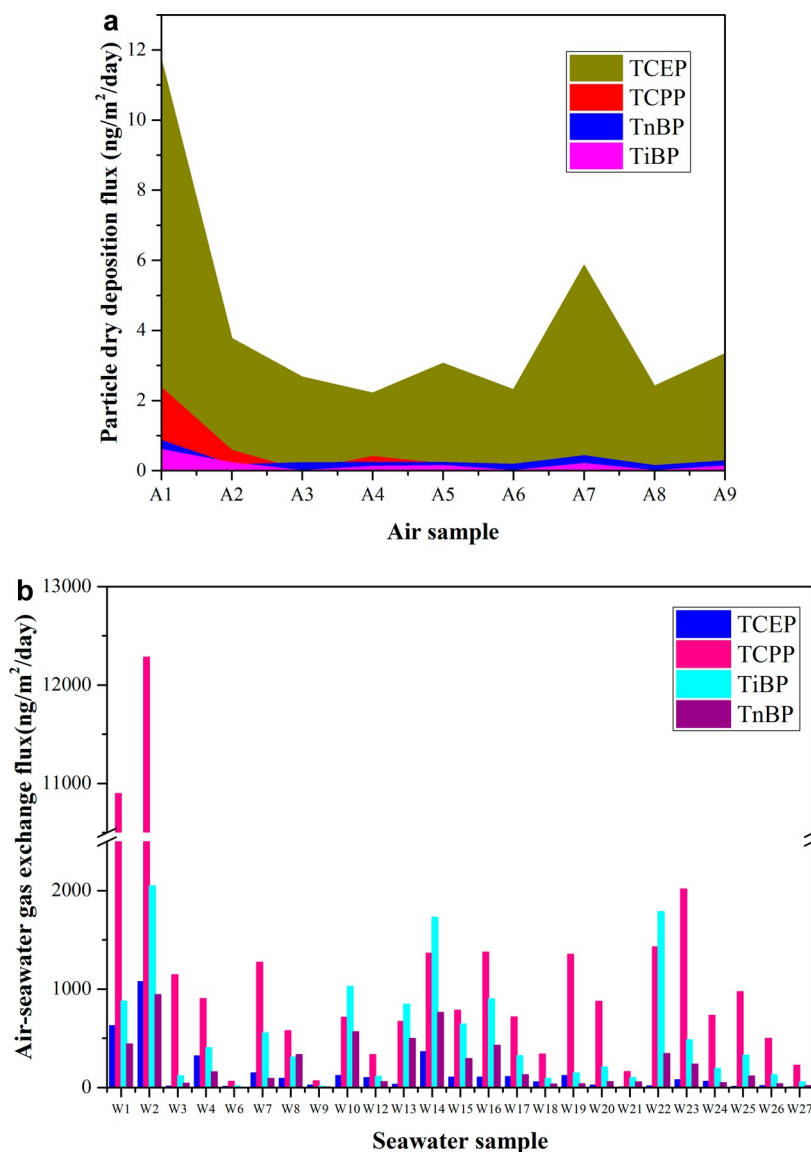
Figure 4. (a) Particle dry deposition fluxes of four major OPEs over the sea in the North Atlantic and the Arctic. (b) Air−seawater exchange fluxes of four major OPEs over the sea in the North Atlantic and the Arctic.

than 0.3, and the fluxes ranged from 61 to 12283 ng/m²/day, with a mean of 1670 ± 3031 ng/m²/day. The highest volatilization flux was observed at sample W2 as a result of relatively high TCPP concentration in seawater and high surface water temperature, as well as the strong wind speed (9 m/s). As for TiBP and TnBP, the f_A/f_W values were all lower than 0.3, with the fluxes ranging from 12 to 2049 ng/m²/day for TiBP and from 3 to 943 ng/m²/day for TnBP. These results indicated that air−seawater gas exchange processes may interfere with long-range transport potential for OPEs and drive their remobilization in the Arctic summer (or ice free period).

Because of the low concentrations of the other four OPEs (i.e., TDCP, TPhP, TPeP, and TEHP), their fluxes were not estimated considering the high uncertainty. Nevertheless, to our knowledge, this is the first report for air-seawater gas exchange fluxes of OPEs. The deviation of the measured OPE concentrations and HLCs can increase the uncertainty of the estimated fluxes. Further investigations on more accurate HLCs for OPEs are required to improve the understanding of their air-seawater gas exchange processes.

Implications. This work presents a decreasing trend for ΣOPE concentrations in the atmosphere and seawater from the North Atlantic to the Arctic, indicating the current ongoing atmospheric and water releases of these compounds from Europe. Although TCEP was replaced by TCPP in Europe, TCEP was still detected as the dominant OPE in the atmosphere and was about nine times higher than the mean TCPP concentration. On the other hand, in snow and seawater, the dominant OPE was TCPP. This suggests that TCEP is more stable than TCPP in the atmosphere. More research is necessary for understanding OPE properties and their fate in the environment. The mean ΣOPE concentration in snow was 7834 pg/L, which was about two times as high as that in seawater (2935 pg/L), suggesting that snow is an important intermediate for OPE accumulation in the Arctic. From the Greenland and Svalbard coasts to the open ocean, there was a slightly decreasing trend for ΣOPE concentrations in seawater, which was due to the glacier and snow melting to some degree. In terms of the effect of global warming on the Arctic, OPEs deposited in sinks such as snow and ice in the polar region are

expected to remobilize into the atmosphere and water. Consequently, it is suggested that more studies are required to elucidate the influences of climate change on the occurrence, transport and fate of persistent or semipersistent compounds such as OPEs in the Arctic.

ASSOCIATED CONTENT

Supporting Information

AUTHOR INFORMATION

Corresponding Author

*Phone: +49-4152-872330. E-mail: zhiyong.xie@hzg.de.

ORCID

Zhiyong Xie: 0000-0001-8997-3930

Senchao Lai: 0000-0002-4990-3679

Chongguo Tian: 0000-0001-6058-9353

Author Contributions

J.L. and Z.X. conducted data management and wrote the manuscript; Z.X. designed the research and carried out the field work; W.M. and Z.X. performed sample preparation and instrumental analysis; C.T. guided the calculation method; S.L., K.E., and R.E. provided important comments and polished the manuscript.

Notes

The authors declare no competing financial interest.

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