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# Organophosphate Ester Flame Retardants and Plasticizers in ocean sediments from the North Pacific to the Arctic Ocean

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# Abstract

The occurrence of organophosphate ester (OPE) flame retardants and plasticizers has been observed for the first time in surface sediment from the North Pacific to Arctic Ocean during the 4th National Arctic Research Expedition of China in the summer of 2010. The samples were analyzed for three halogenated OPEs (tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP) and tris(dichlorisopropyl) phosphate (TDCP)), three alkylated OPEs (tri-*iso*-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP) and tripentyl phosphate (TPeP)), as well as triphenyl phosphate (TPhP). $\Sigma_7$OPEs (total concentration of the observed OPEs) was in the range of 159 to 4658 pg $g^{-1}$ dry weight (dw). Halogenated OPEs were generally more abundant than the non-halogenated OPEs; TCEP and TiBP dominated overall concentrations. Except for Bering Sea, $\Sigma_7$OPEs concentrations increased with the increasing latitudes from Bering Strait to the Central Arctic Ocean. While the contributions of halogenated OPEs (typically TCEP and TCPP) to total OPE profile also increased from Bering Strait to the Central Arctic Ocean, indicating their higher potential of being transported to the remote Arctic. The median budget of 52 (range of 17-292) tons for $\Sigma_7$OPEs in sediment from the Central Arctic Ocean represents only a very small amount of their total production volume. Yet the amount of OPEs in Arctic Ocean sediment was significantly higher than the sum of polybrominated diphenylethers (PBDEs) in the sediment, indicating they are equally prone to long-range transport away from source regions. Given the increasing production and usage of OPEs as substitutes of PBDEs, OPEs will continue to

accumulate in the remote Arctic.

## Introduction

Organophosphate esters (OPEs) are kinds of man-made chemicals applied to many household and industrial products as flame retardants, plasticizers, as well as antifoaming agents and hydraulic fluids.[1] Specifically, halogenated OPEs are dominantly applied as flame retardants, while non-halogenated OPEs are mainly applied as plasticizers and in other applications.[2] During recent years the production and use of OPEs have increased since polybrominated diphenyl ethers (PBDEs), which is known as the most commonly used brominated flame retardants (BFRs), have been restricted in the early 2000s, especially the Penta- and Octa-BDE mixtures have been finally included in the Stockholm Convention list on Persistent Organic Pollutants (POPs) (http://www.pops.int). OPE production has increased by about 10% between 2001 and 2006 in Western Europe.[3] It is estimated that the global production of OPEs accounted for 30% of all flame retardants in 2013.[4]

OPEs can leach into the environment as they are additive flame retardants and do not covalently bind to the material to which they are added. The environmental occurrence of OPEs have recently been reported in a variety of environmental compartments such as indoor air,[2] fresh and marine water phase,[5, 6] as well as fresh water and marine coastal sediments;[7, 8] OPEs also enter and accumulate in marine and freshwater foodwebs.[9, 10] Even though the predicted half-lives of OPEs in atmosphere (<2 days) are not enough to meet the long-range atmospheric transport (LRAT) standard listed by Stockholm Convention[11], they were recently observed in atmospheric particles in remote European and Canadian Arctic sites,[12, 13] as well as open oceans, such as Mediterranean, Black and North Seas,[14, 15] northern Pacific and Indian Ocean toward the polar regions,[1] tropical and subtropical Atlantic, Pacific and Indian Oceans.[16] These existing studies suggest that these compounds are capable of LRAT.

However, little research focused on the fate of OPEs in remote oceans. Similar to traditional POPs, the net flux of OPEs in the remote marine environment might be typically following the route of air–surface waters–deeper waters and then burial in the benthic sediments, where the deep ocean is seemed as the long-term oceanic repository for these chemicals.[17, 18] OPEs have been detected in precipitation, indicating their atmospheric deposition processes.[19, 20] For remote pelagic environments, such as the North Pacific and Arctic Oceans, they could be further transferred from well-mixed surface waters to deep waters as well as sediment through particle settling. Part of the particle settling could be driven by the 'biological pump', which is the settling fluxes of particle organic carbon associated with primary production by phytoplankton.[17, 21] Previous research has observed positive relationship between concentrations of triphenyl phosphate (TPhP) and d$^{15}$N in demersal species, indicating the transfer process of TPhP through particle settling to the bottom sediment and their further accumulation through the benthic food web.[9]

To examine the presence of OPEs in remote ocean sediment, this study presents the observation results of OPEs in surficial ocean sediment through transect from the

North Pacific to the central Arctic Ocean (via the Bering Strait). Our aims were to investigate (i) the occurrence, latitudinal distribution and composition profile of OPEs in surficial sediment from remote ocean regions; (ii) contrast the presence of OPEs relative to PBDEs, established POPs, in these Arctic Ocean sediments, and (iii) derive a budget for OPEs in these remote sediment. Ultimately, our goal was to provide new insights into the fate and behavior of OPEs in the remote marine environment.

# Experimental Section

## Sampling

During the 4th Chinese National Arctic Research Expedition (CHINARE 4) held between July and September 2010, 0-2cm surficial marine sediment samples were collected onboard the ice-breaker R/V Xuelong (‘Snow Dragon’). The sampling cruise generally covered a northward transect from the Bering Sea, through the Bering Strait to the Chukchi Sea, and across the Canada Basin and central Arctic Ocean (53-88°N). Detailed information about the sampling work and the sediment samples are described in Supporting Information and listed in Table S1.

## Extraction, Analysis, QC/QA

The extraction, purification and analysis were conducted in the clean laboratory of the Helmholtz-Zentrum Geesthacht (HZG) in Germany based on our previously published method, and is described in more detail in the Supporting Information.[22] Briefly, approximately 10 g sediment sample was extracted with Soxhlet extractor, and then the extracts were rotary evaporated to 1–2 mL, and further purified on a silica column. OPEs were analyzed using a gas chromatograph coupled to a triple quadrupole mass spectrometer operated in electron impact mode. Native OPE standards $d_{27}$-TnBP and $d_{15}$-TPhP were spiked to 3 solvent-extracted sediment samples as deuterated surrogate standards to check matrix effects. And $^{13}C_6$–PCB 208 (Cambridge Isotope Laboratories) was added into the sample as injection standard. The recoveries of $d_{27}$-TnBP and $d_{15}$-TPhP in all sediment samples were 57 ± 11% and 93 ± 18%, respectively. The recoveries of OPEs ranged from 95 ± 2% for TiBP to 143 ± 7% for TCEP. Totally five procedural blanks were extracted, while the dominant OPE contaminations detected in the procedural blanks were 34 ± 6 pg/g for TCPPs, 23 ± 6 pg/g for TCEP and 18 ± 3 pg/g for TPhP, respectively (Table S2). The method detection limits (MDLs), with a range from 1 to 53 pg/g, were calculated by the average of procedural blanks plus three times the standard deviation ($3\sigma$) of procedural blanks. While the instrumental detection limits, ranging from 0.1 to 4 pg, were quantified as signal to noise ratio of 3.

## Results and Discussion

### OPE Concentrations and Composition

The total concentrations of 7 OPEs in the surface sediment ($\Sigma_7$OPEs, sum of the detected 4 non-halogenated OPEs and 3 halogenated OPEs) ranged from 159 to 4658 pg $g^{-1}$ dry weight (dw), with a mean of 878 ± 892 pg $g^{-1}$ dw. A summary of the chemical concentrations is presented in Table 1. Generally, the halogenated OPEs were more abundant than the non-halogenated OPEs and the composition profile of

OPEs along all the sampling stations is shown in Figure 1-a. For halogenated OPEs, TCEP was the dominant compound which was detected at all sampling stations with a median contribution of 54 ± 18% to $\Sigma_7$OPEs. TCEP concentrations were in a range of 81 to 3903 pg $g^{-1}$ dw. The second-most abundant chlorinated OPE, TCPPs (sum of three of isomers) ranged from 0.94 to 460 pg $g^{-1}$ dw, followed by TDCP, which was detected in 63% samples with concentrations from not detected (n.d.) to 165 pg $g^{-1}$ dw. Among the non-halogenated OPEs, TiBP was the dominant compound detected at all sampling stations, with a median contribution of 24 ± 15% to $\Sigma_7$OPEs during the entire cruise. Individual TiBP concentrations ranged from 47 to 552 pg $g^{-1}$ dw, followed by TnBP, which was also detected in all samples, for which concentrations ranged from 19 to 209 pg $g^{-1}$ dw. The detection frequency for TPhP and TPeP was 77% and 83%, with concentrations from n.d. to 105 pg $g^{-1}$ dw and n.d. to 81 pg $g^{-1}$ dw, respectively.

OPEs were also investigated in airborne particles from East Asia to the remote Arctic regions during the same polar expedition CHINARE 4.[1] Relatively higher levels of halogenated OPEs in comparison to non-halogenated OPEs, with the dominance of TCEP, in the surficial sediment was consistent with what was detected in the airborne particles of the same region.[1] Similar results of the predominance of halogenated OPEs and TCEP were shown in the atmospheric observing stations located in the Canadian Arctic.[13] Generally, halogenated OPEs display higher environmental persistence and historical production than non-halogenated OPEs.[23] Moreover, it is reported that TCEP has gradually been replaced by the structurally similar TCPP in

Europe due to the considerable carcinogenic and mutagenic effects.[24] Relatively higher detection frequency and levels of TCEP in our study might reflect its continuing usage in Asia and North America. With a relatively high water solubility of $7.0 \times 10^3$ mg $L^{-1}$,[25] much higher levels of TCEP could be assumed to be present dissolved in water bodies. However, for atmospheric particle phase samples collected at Longyearbyen on Svalbard in the European Arctic, the sum of all non-halogenated OPE concentrations comprised ~75% of the ΣOPE concentrations.[12] And high levels of non-halogenated OPEs, especially for TnBP and TiBP, were also observed in air samples of Japan urbanized area.[26] These indicated the existence of different concentrations and sources of OPEs in varied regions.

There is little literature data on OPEs in the remote ocean sediment. We summarized information on OPEs in estuary sediment and freshwater sediment in Table 2, together with the data of this research. OPE concentrations in urbanized locations such as Austria,[27] Norway,[28] Spain,[29] and China[7, 8] in the 1~4-digit μg $kg^{-1}$ dw range were significantly higher than our results.

The TOC composition in these surficial sediments (Table S1), displayed higher levels in the shelf regions such as the Bering Strait (average value of 0.64%) and Chukchi Sea (average value of 0.60%), and decreased towards the Bering Sea (average value of 0.43%), Canadian Basin margin region (average value of 0.27%), and the central Arctic Ocean (average value of 0.10%). Obviously, the distribution pattern of TOC is quite different from that of OPEs. And no significant relationships were discovered between any OPE compound and TOC ($p>0.05$, Table S3). For PBDEs, we also discovered a lack of correlation between the contaminants and TOC.[30] Thus TOC might not be a strong predictor for OPE concentrations in remote oceans.

## Geographic Distribution of OPEs

The sampling stations were separated into five geographical regions as Bering Sea, Bering Strait, Chukchi Sea, Canadian Basin margin and Central Arctic Ocean to assess the spatial distribution of OPEs. Significant differences in the mean concentrations of OPEs were demonstrated among the five geographical regions according to analysis of variance (ANOVA). Figure 2 showed the spatial distribution of $\Sigma_7$OPEs along transect of the cruise. The highest average $\Sigma_7$OPEs concentrations were observed in the Central Arctic Ocean (1463 ± 1574 pg $g^{-1}$ dw), followed by sampling sites in the Bering Sea (1207 ± 593 pg $g^{-1}$ dw) and Canadian Basin margin region (1035 ± 491 pg $g^{-1}$ dw), however, the Chukchi Sea (468 ± 219 pg $g^{-1}$ dw) and Bering Strait (350 ± 59 pg $g^{-1}$ dw) had relatively lower average concentrations. Except for the Bering Sea, $\Sigma_7$OPEs concentrations generally increased with the increasing latitudes from Bering Strait to the Central Arctic Ocean. Beyond these regional differences we also note that concentrations of $\Sigma_7$OPEs showed spatial variability in the Central Arctic Ocean. Elevated $\Sigma_7$OPEs levels were observed at sites BN06 (4658 pg $g^{-1}$ dw) and BN04 (2360 pg $g^{-1}$ dw), as well as the northern most site BN13 (1144 pg $g^{-1}$ dw). Notably high $\Sigma_7$OPEs concentrations were also shown at site B04 (2093 pg $g^{-1}$ dw) in the Bering Sea, as well as site MS02 (1855 pg $g^{-1}$ dw) in the Canadian Basin margin area, respectively. Moreover, for OPEs composition profile in the five different geographic areas, we observed that the contributions of halogenated OPEs (typically TCEP and TCPP) to total OPE profile increased from Bering Strait to the Central Arctic Ocean. In contrast, the contributions of non-halogenated OPEs (typically TiBP and TnBP) decreased from Bering Strait to the Central Arctic Ocean (Figure 1-b).

For the distribution of OPEs in airborne particles from East Asia to the remote Arctic, the highest concentrations were observed in the Sea of Japan, while the concentrations decreased dramatically to the open North Pacific Ocean.[1] The high OPE levels shown in East Asia were attributed to their release in Asian countries, such as production and usage of OPEs in factories as well as the treatment of e-waste. Although we do not have data about OPE concentrations in sediment of East Asia area, the relatively high level of OPEs in the sediment of Bering Sea might partly share these Asian sources followed by atmospheric deposition and further settling through water column.

Moreover, Möller et al. (2012) reported some high atmospheric OPE concentrations with-in the Arctic were due to air masses from continent of Russia and Alaska. For our surficial sediments observations, OPE concentrations generally increased with the increasing latitudes from Bering Strait to the Central Arctic Ocean, though highest overall OPE concentrations were not found at the northern most sampling site. This suggests that factors other than LRAT and ‘cold condensation effect’ affect OPEs, possibly indicating the existence of some with-in Arctic sources.[31]

In general, high concentrations of OPEs in high latitude regions were due to halogenated OPEs rather than non-halogenated OPEs. Some high concentrations of halogenated OPEs, typically TCEP and TCPP were displayed at Station BN06, BN04 and MS02 (Figure 2). Higher concentrations of halogenated OPEs were also observed around the river mouth of the Canadian Arctic close to Canadian Archipelago and Sühring et al. attributed it to river discharge.[13] Generally, halogenated OPEs possess higher water solubility compared to non-halogenated OPEs. And the characteristic travel distance of most halogenated OPEs was longer in water than in air.[32] In our study, the stations displayed relatively higher concentrations of halogenated OPEs at Canadian Basin margin and Central Arctic Ocean were quite close to the Beaufort Gyre. Seawater circulated in the Beaufort Sea was mainly through Canadian Archipelago and further transported to the remote Arctic. Therefore these stations with relatively high levels of halogenated OPEs might also share the source of river discharge of Canadian Arctic to a certain extent.

## Observations of Latitudinal Fractionation

To assess the influence of volatility on the LRAT potential of the individual OPE compound, the ratio of individual OPE concentrations at northern most 88°N (high Arctic station BN13) and their concentration at 61°N (Bering Strait station B14) as a function of log subcooled liquid vapor pressure ($p_L$) was obtained (Figure S1; TPeP was excluded for which $p_L$ was not known from the same literature source; TDCP was excluded as well because it was not detected at these two stations).[3] Distributions of various polychlorinated biphenyl congeners (PCBs) between northern and southern regions have been shown to strongly correlation with $p_L$.[33] It was thus a potentially valuable tool to gauge the compounds' propensity for LRAT to the Arctic.[34] No strong relationship was detected between increasing North/South ratio and $p_L$ for these five OPE compounds (Figure S1-a), but a strong correlation was shown if the more reactive TnBP and TiBP were excluded (Figure S1-b). The North/South ratios for both TnBP and TiBP were < 1 in our surficial sediment samples, implying they degrade during transport to the Arctic. Actually, TnBP and TiBP displayed high atmospheric concentrations in urbanized regions,[26] however their concentrations were quite low in remote Arctic atmospheric samples.[1] This indicated that non-halogenated OPEs, in particular TnBP and TiBP were heavily emitted to the atmosphere within urbanized regions, but they might be further degraded and/or trapped in soil/sediment during atmospheric transport. Moreover, decreasing contributions of both TnBP and TiBP to total investigated OPEs were observed in our surficial sediments from Bring Strait through Chukchi Sea to the Canadian Basin and central Arctic Ocean (Figure 1-b). This further demonstrated that they have relatively low potential of being transported to the remote Arctic regions. In contrast, the North/South ratios for TCEP and TCPP were > 1 (~8 and ~3) in our sediment samples. The strong relationship between North/South ratio and volatility together with their increasing contributions from low to high latitudes (Figure 1-b) demonstrated high potential of being transported to remote oceans for TCEP and TCPP.

Moreover, $K_{OW}$ is also used to investigate the relation with increasing North/South ratio. The results showed that there was a strong negative relationship between North/South ratio and $\log K_{OW}$ value (Figure S2). These again demonstrated that the compound with high value of $K_{OW}$, such as TiBP and TnBP, have relatively low potential of being transported to the Arctic Ocean (the North/South concentration ratio < 1). And they might be trapped in the ocean sediment of low latitude regions during their transport from low latitude to high latitude regions. In contrast, the contaminants with relative low value of $K_{OW}$, such as TCEP and TCPP, have relatively higher potential of being transported to remote oceans (the North/South concentration ratio > 1). And sediments in the remote Arctic could be seemed as their final sink.

## Budget of OPEs in the Central Arctic Ocean Basin

Since this work regularly observed OPE concentrations in remote Arctic Ocean surficial sediment, we were interested in deriving a mass budget of this reservoir. Considering the relatively low sedimentation rates, at about 1~2cm/kyr in the central Arctic Ocean,[35, 36] the sediment samples (top 2 cm) would have captured all of the industrial production since OPEs were produced. Therefore using the surficial sediment OPE concentrations obtained over Canada Basin and central Arctic Ocean, we estimated the inventories of OPEs in the sediment of the Central Arctic Ocean Basin. Any dilution through bioturbation will mean that our budget is an underestimation of total OPE masses stored in these remote sediments.

The method we used is as previously reported; a detailed calculation method is provided in supporting information.[37] The estimation results are shown in Table 3. Generally, for halogenated OPEs, the budget of the dominant TCEP to the Central

Arctic Ocean Basin was estimated in the range of 12-219 tons, with a median value of 39 tons. While for non-halogenated OPEs, the dominant TiBP budget was estimated in the ranges of 3.6-16 tons, with a median value of 6.2 tons. Compared with thousands tons of production/usage volumes of TCEP per year in Europe and United States,[23] the input to the Arctic Ocean sediment represented still a very small amount.

### Comparison of OPEs in Surficial Sediment with PBDEs

Since OPEs are used in many cases as substitutes of PBDEs, OPE concentrations are compared with PBDE concentrations observed in surficial sediment in the same research region during CHINARE 3, CHINARE 4 and 5 campaign. Concentrations of the most dominant PBDEs (BDE47, -99, -153, and -209) are given in Table S4 and comparison between dominant OPEs and PBDEs along northern latitude is shown in Figure 3. The data available showed that BDE-47, -99 and -153 were generally in the range of tens pg $g^{-1}$ dw, while BDE-209 were in hundreds pg $g^{-1}$ dw range. Moreover, the PBDEs (excluding BDE-209) concentrations generally decreased from 2008 to 2012, especially in the Bering Sea, Bering Strait, and Chukchi Sea area, although this temporal trend might not be so significant considering different analytical methods and sampling sites among these cruises.[30, 38]

In comparison, concentrations of the dominant OPEs (TiBP and TCEP) in the surficial sediment are in the hundreds to thousands pg $g^{-1}$ dw range (as data displayed in Table 1), already greater than key PBDEs. Concentrations of the other detected OPEs were generally comparable to or greater than BDE47, -99, -153, but lower than BDE-209.

Therefore the transport and fluxes of TCEP and TiBP to benthic sediment of the marine environment already exceed those of PBDEs. Similarly, higher concentrations of OPEs were observed in atmospheric particles at Polar Regions compared with concentrations of PBDEs.[1, 12, 13]

From our results, the remote marine sediments could be seemed as a great repository for OPEs, especially in the Arctic regions. Given the increasing production and usage of OPEs as substitutes of PBDEs, OPEs will continue to be emitted to the atmosphere, and transferred into the surface waters, and further transported to the deep water and sediment of the remote marine environment. And these sediments likely constitute OPEs' long term global sink. Given current sediment concentrations, OPEs are more efficiently transported to remote Arctic sediments than PBDEs.

**Supporting Information.** Details on the sampling and lab analysis information, PBDE concentrations, along with calculation method of OPE inventories. This material is available free of charge via the Internet at http://pubs.acs.org.

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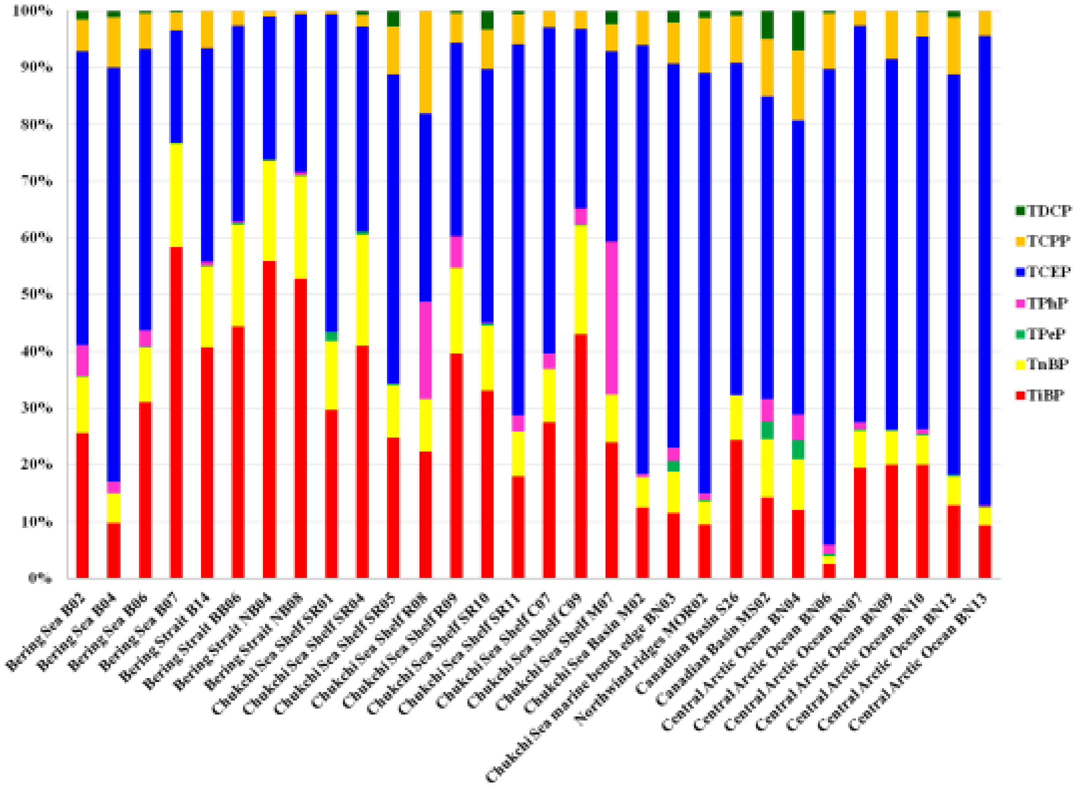
## Figure Captions

**Figure 1.** Composition profile of observed OPEs in surficial marine sediments along the sampling transect (a); Average contributions of investigated OPEs in the five geographical regions (b)

**Figure 2.** Spatial distributions of OPEs in the surface marine sediment along the sampling cruise

**Figure 3.** Comparison between dominant OPEs and PBDEs in surface marine sediment along northern latitude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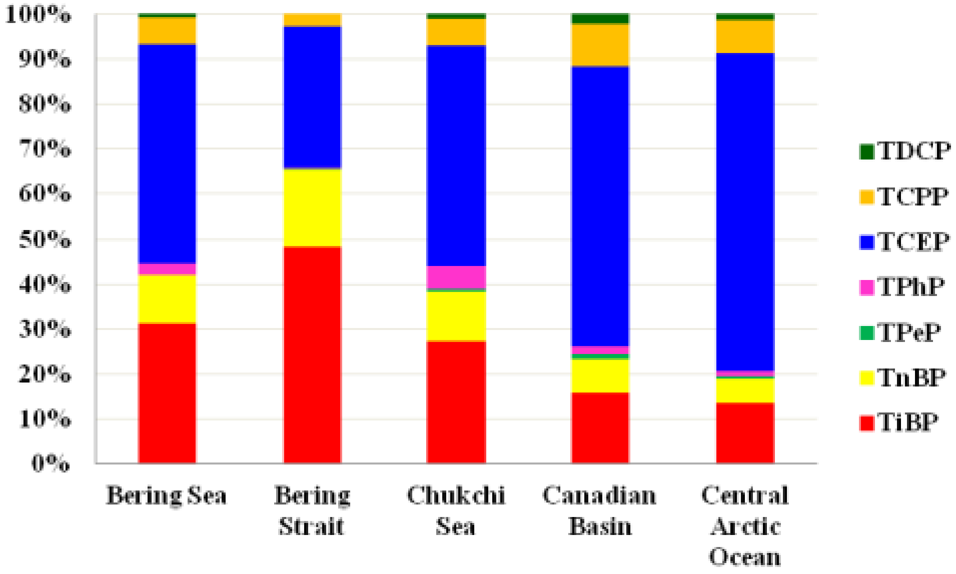
Bering Strait NB04
Bering Strait NB08
Chukchi Sea Shelf SR01
Chukchi Sea Shelf SR04
Chukchi Sea Shelf SR05
Chukchi Sea Shelf R08
Chukchi Sea Shelf R09
Chukchi Sea Shelf SR10
Chukchi Sea Shelf SR11
Chukchi Sea Shelf C07
Chukchi Sea Shelf C09
Chukchi Sea Shelf M07
Chukchi Sea Basin M02
Chukchi Sea marine bench edge BN03
Northwind ridges MOR02
Canadian Basin S26
Canadian Basin MS02
Central Arctic Ocean BN04
Central Arctic Ocean BN06
Central Arctic Ocean BN07
Central Arctic Ocean BN09
Central Arctic Ocean BN10
Central Arctic Ocean BN12
Central Arctic Ocean BN13
TDCP
TCPP
TCEP
TPhP
TPeP
TnBP
TiBP

(a)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Bering Strait
Chukchi Sea
Canadian Basin
Central Arctic Ocean
TDCP
TCPP
TCEP
TPhP
TPeP
TnBP
TiBP

(b)

**Figure 1**

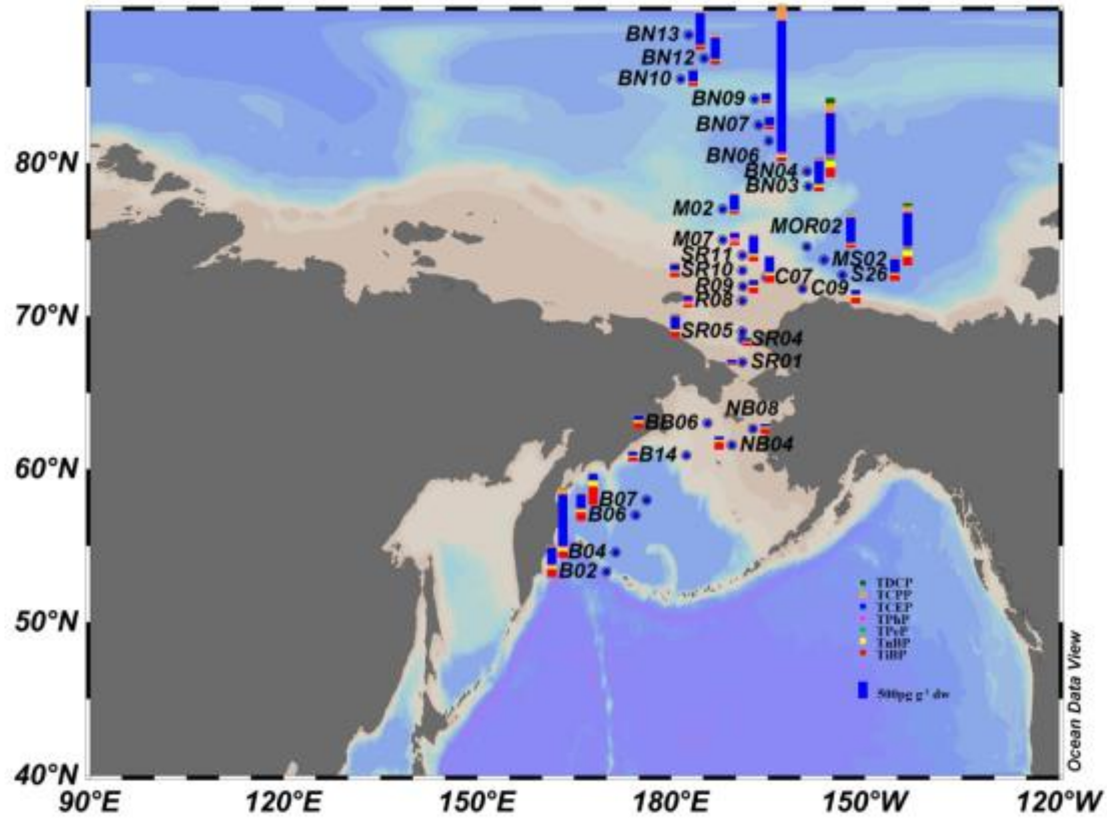

Figure 2

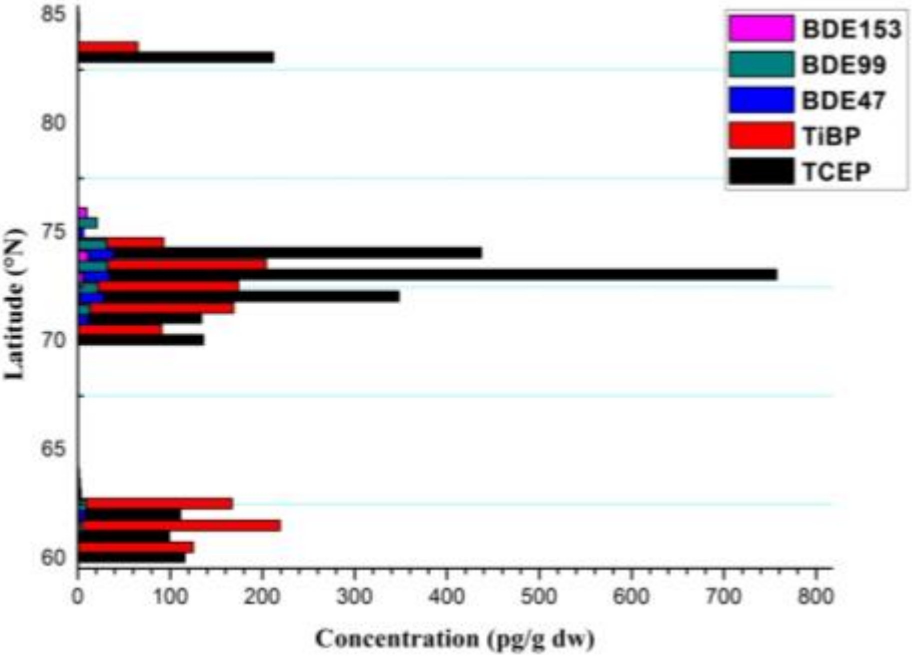

Figure 3

**Table 1.** Individual concentrations of OPEs in the surface sediment (pg $g^{-1}$ d.w.) at sampling sites from Bering Sea to the Central Arctic Ocean (n.d. = not detected)

| Location | Site | TiBP | TnBP | TPeP | TPhP | TCPP-1 | TCPP-2 | TCPP-3 | Sum of TCPPs | TCEP | TDCP | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Bering Sea** | **B02** | 244 | 95 | 2.0 | 51 | 40 | 13 | 0.67 | 54 | 493 | 14 | 954 |
| **Bering Sea** | **B04** | 204 | 108 | 0.65 | 44 | 146 | 37 | 3.5 | 186 | 1527 | 24 | 2093 |
| **Bering Sea** | **B06** | 260 | 80 | 2.1 | 23 | 42 | 8.6 | 1.3 | 52 | 415 | 3.7 | 836 |
| **Bering Sea** | **B07** | 552 | 173 | 2.0 | n.d. | 24 | 6.0 | 1.1 | 31 | 186 | 2.4 | 947 |
| **Average** | | 315 | 114 | 1.7 | 30 | 63 | 16 | 1.6 | 81 | 655 | 11 | 1207 |
| **Bering Strait** | **B14** | 125 | 43 | 0.58 | 2.1 | 17 | 3.8 | n.d. | 20 | 116 | n.d. | 308 |
| **Bering Strait** | **BB06** | 181 | 73 | 1.1 | 1.2 | 9.4 | 1.4 | n.d. | 11 | 141 | n.d. | 408 |
| **Bering Strait** | **NB04** | 219 | 70 | 0.27 | n.d. | 3.5 | 0.64 | n.d. | 4.2 | 99 | n.d. | 391 |
| **Bering Strait** | **NB08** | 154 | 53 | 0.42 | 1.9 | 1.8 | 0.12 | n.d. | 1.9 | 81 | n.d. | 292 |
| **Average** | | 170 | 60 | 0.60 | 1.3 | 7.8 | 1.5 | n.d. | 9.3 | 109 | n.d. | 350 |
| **Chukchi Sea Shelf** | **SR01** | 47 | 19 | 2.7 | n.d. | 0.94 | n.d. | n.d. | 0.94 | 89 | n.d. | 159 |
| **Chukchi Sea Shelf** | **SR04** | 94 | 45 | 1.1 | n.d. | 2.8 | 2.0 | n.d. | 4.9 | 83 | 1.6 | 228 |
| **Chukchi Sea Shelf** | **SR05** | 171 | 65 | 1.6 | n.d. | 46 | 11 | 1.5 | 59 | 376 | 19 | 690 |
| **Chukchi Sea Shelf** | **R08** | 91 | 38 | 0.075 | 71 | 61 | 12 | 0.80 | 74 | 136 | n.d. | 410 |
| **Chukchi Sea Shelf** | **R09** | 160 | 61 | n.d. | 23 | 17 | 3.8 | n.d. | 21 | 138 | 2.0 | 404 |
| **Chukchi Sea Shelf** | **SR10** | 136 | 47 | 1.6 | 0.86 | 22 | 6.1 | 0.52 | 29 | 183 | 14 | 411 |
| **Chukchi Sea Shelf** | **SR11** | 144 | 63 | n.d. | 23 | 35 | 7.4 | 0.22 | 42 | 523 | 4.6 | 800 |
| **Chukchi Sea Shelf** | **C07** | 215 | 73 | 0.59 | 21 | 18 | 4.2 | 0.94 | 23 | 449 | 0.53 | 782 |
| **Chukchi Sea Shelf** | **C09** | 178 | 79 | 0.14 | 12 | 10 | 3.3 | n.d. | 13 | 131 | n.d. | 413 |
| **Chukchi Sea Shelf** | **M07** | 91 | 32 | n.d. | 102 | 17 | 1.9 | n.d. | 19 | 127 | 8.8 | 381 |
| **Chukchi Sea Basin** | **M02** | 76 | 33 | n.d. | 3.1 | 29 | 7.7 | 0.29 | 37 | 461 | n.d. | 610 |
| **Chukchi Sea marine bench edge** | **BN03** | 116 | 71 | 19 | 23 | 56 | 15 | 1.1 | 72 | 676 | 21 | 998 |
| **Average** | | 126 | 52 | 2.3 | 23 | 26 | 6.2 | 0.45 | 33 | 281 | 5.9 | 524 |
| **Northwind ridges** | **MOR02** | 95 | 41 | 2.9 | 11 | 73 | 23 | 2.1 | 98 | 747 | 12 | 1007 |
| **Canadian Basin** | **MS02** | 265 | 189 | 58 | 74 | 143 | 40 | 3.5 | 186 | 990 | 92 | 1855 |
| **Canadian Basin** | **S26** | 172 | 56 | n.d. | n.d. | 48 | 10 | 1.1 | 59 | 413 | 6.0 | 706 |
| **Average** | | 177 | 95 | 20 | 28 | 88 | 24 | 2.3 | 114 | 717 | 37 | 1190 |
| **Central Arctic Ocean** | **BN04** | 286 | 209 | 81 | 105 | 218 | 67 | 6.4 | 291 | 1223 | 165 | 2360 |
| **Central Arctic Ocean** | **BN06** | 117 | 66 | 17 | 76 | 335 | 112 | 13 | 460 | 3903 | 18 | 4658 |
| **Central Arctic Ocean** | **BN07** | 74 | 25 | 1.0 | 4.9 | 7.3 | 2.8 | 0.13 | 10 | 268 | n.d. | 383 |
| **Central Arctic Ocean** | **BN09** | 65 | 20 | 0.31 | n.d. | 23 | 4.2 | 0.014 | 27 | 212 | n.d. | 323 |
| **Central Arctic Ocean** | **BN10** | 97 | 25 | 0.75 | 4.2 | 14 | 6.3 | n.d. | 21 | 335 | 1.2 | 483 |
| **Central Arctic Ocean** | **BN12** | 115 | 45 | 2.6 | 0.28 | 70 | 18 | 1.2 | 89 | 630 | 10 | 891 |
| **Central Arctic Ocean** | **BN13** | 107 | 36 | 0.61 | 4.5 | 40 | 10 | 0.32 | 51 | 945 | n.d. | 1144 |
| **Average** | | 123 | 61 | 15 | 28 | 101 | 32 | 3.0 | 136 | 1073 | 28 | 1463 |
| **Average of the cruise** | | 162 | 68 | 6.7 | 23 | 52 | 15 | 1.3 | 68 | 536 | 14 | 878 |

**Table 2.** Comparison of OPE concentration ranges (pg $g^{-1}$ d.w.) in surface sediment during CHINARE 4 with present literature data

| Location | TCPP | TCEP | TDCP | TPhP | Reference |
|---|---|---|---|---|---|
| **Bering Sea** | 31-186 (53) | 186-1527 (454) | 2.4-24 (9.1) | n.d.-51 (33) | this study |
| **Bering Strait** | 1.9-20 (7.5) | 81-141 (107) | n.d. | n.d.-2.1 (1.5) | this study |
| **Chukchi Sea** | 0.94-74 (26) | 83-676 (160) | n.d.-21 (1.8) | n.d.-102 (17) | this study |
| **Canadian Basin margin** | 59-186 (98) | 413-990 (747) | 6.0-92 (12) | n.d.-74 (11) | this study |
| **Central Arctic Ocean** | 10-460 (51) | 212-3903 (630) | n.d.-165 (1.2) | n.d.-105 (4.5) | this study |
| **Taihu lake (China)** | n.d.-2270 (1360) | 620-3170 (1750) | n.d.-5540 (1300) | n.d.-1190 (490) | ref[6] |
| **River Danube (Austria)** | <610-20000 | n.d.-<7700 | n.d. | n.d.-<790 | ref[22] |
| **River Schwechat (Austria)** | 1300000 | 160000 | <640 | 160000 | ref[22] |
| **River Liesig (Austria)** | 95000 | n.d. | <640 | 4300 | ref[22] |
| **Kåfjorden, Trondheim, Oslo, Mjøsa (Norway)** | <150-54000 | <160-8500 | <90-1000 | <100-6800 | ref[23] |
| **Rivers and marine estuaries of Galicia (Spain)** | 38000 | 45900 | n.d. | n.a. | ref[24] |
| **River at Chung-Li and coastal region at Tai-shi and Chi-ku (Taiwan)** | n.d.-9500 | n.d.-1500 | n.d.-1100 | n.d.-3100 | ref[5] |

Average concentrations are given in brackets

n.d. = not detected

n.a. = not analyzed

**Table 3.** Estimation results of the inventories of OPEs in the sediment for the Central Arctic Ocean Basin (tons)

| | **min** | **max** | **median** | **average** |
|---|---|---|---|---|
| **TiBP** | 3.6 | 16 | 6.2 | 7.8 |
| **TnBP** | 1.1 | 12 | 2.4 | 4.0 |
| **TPeP** | 0 | 4.6 | 0.10 | 0.93 |
| **TPhP** | 0 | 5.9 | 0.27 | 1.6 |
| **TCPP** | 0.57 | 26 | 4.2 | 7.3 |
| **TCEP** | 12 | 219 | 39 | 54 |
| **TDCP** | 0 | 9.2 | 0.45 | 1.7 |
| **Total** | 17 | 292 | 52 | 78 |