



Final Draft **of the original manuscript**

Ma, Y.; Xie, Z.; Lohmann, R.; Mi, W.; Gao, G.:

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Ocean Sediments from the North Pacific to the Arctic Ocean.**

In: Environmental Science and Technology. Vol. 51 (2017) 7, 3809 –
3815.

First published online by ACS: 28.02.2017

<http://dx.doi.org/10.1021/acs.est.7b00755>

1 Organophosphate Ester Flame Retardants and
2 Plasticizers in ocean sediments from the North
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4

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17

18 **Abstract**

19 The occurrence of organophosphate ester (OPE) flame retardants and plasticizers has
20 been observed for the first time in surface sediment from the North Pacific to Arctic
21 Ocean during the 4th National Arctic Research Expedition of China in the summer of
22 2010. The samples were analyzed for three halogenated OPEs (tris(2-chloroethyl)
23 phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP) and
24 tris(dichlorisopropyl) phosphate (TDCP)), three alkylated OPEs (tri-*iso*-butyl
25 phosphate (TiBP), tri-*n*-butyl phosphate (TnBP) and tripentyl phosphate (TPeP)), as
26 well as triphenyl phosphate (TPhP). Σ_7 OPEs (total concentration of the observed
27 OPEs) was in the range of 159 to 4658 pg g⁻¹ dry weight (dw). Halogenated OPEs
28 were generally more abundant than the non-halogenated OPEs; TCEP and TiBP
29 dominated overall concentrations. Except for Bering Sea, Σ_7 OPEs concentrations
30 increased with the increasing latitudes from Bering Strait to the Central Arctic Ocean.
31 While the contributions of halogenated OPEs (typically TCEP and TCPP) to total
32 OPE profile also increased from Bering Strait to the Central Arctic Ocean, indicating
33 their higher potential of being transported to the remote Arctic. The median budget of
34 52 (range of 17-292) tons for Σ_7 OPEs in sediment from the Central Arctic Ocean
35 represents only a very small amount of their total production volume. Yet the amount
36 of OPEs in Arctic Ocean sediment was significantly higher than the sum of
37 polybrominated diphenylethers (PBDEs) in the sediment, indicating they are equally
38 prone to long-range transport away from source regions. Given the increasing
39 production and usage of OPEs as substitutes of PBDEs, OPEs will continue to

40 accumulate in the remote Arctic.

41

42 **Introduction**

43 Organophosphate esters (OPEs) are kinds of man-made chemicals applied to many
44 household and industrial products as flame retardants, plasticizers, as well as
45 antifoaming agents and hydraulic fluids.¹ Specifically, halogenated OPEs are
46 dominantly applied as flame retardants, while non-halogenated OPEs are mainly
47 applied as plasticizers and in other applications.² During recent years the production
48 and use of OPEs have increased since polybrominated diphenyl ethers (PBDEs),
49 which is known as the most commonly used brominated flame retardants (BFRs),
50 have been restricted in the early 2000s, especially the Penta- and Octa-BDE mixtures
51 have been finally included in the Stockholm Convention list on Persistent Organic
52 Pollutants (POPs) (<http://www.pops.int>). OPE production has increased by about 10%
53 between 2001 and 2006 in Western Europe.³ It is estimated that the global production
54 of OPEs accounted for 30% of all flame retardants in 2013.⁴

55 OPEs can leach into the environment as they are additive flame retardants and do not
56 covalently bind to the material to which they are added. The environmental
57 occurrence of OPEs have recently been reported in a variety of environmental
58 compartments such as indoor air,² fresh and marine water phase,^{5, 6} as well as fresh
59 water and marine coastal sediments;^{7, 8} OPEs also enter and accumulate in marine and
60 freshwater foodwebs.^{9, 10} Even though the predicted half-lives of OPEs in atmosphere
61 (<2 days) are not enough to meet the long-range atmospheric transport (LRAT)

62 standard listed by Stockholm Convention¹¹, they were recently observed in
63 atmospheric particles in remote European and Canadian Arctic sites,^{12, 13} as well as
64 open oceans, such as Mediterranean, Black and North Seas,^{14, 15} northern Pacific and
65 Indian Ocean toward the polar regions,¹ tropical and subtropical Atlantic, Pacific and
66 Indian Oceans.¹⁶ These existing studies suggest that these compounds are capable of
67 LRAT.

68 However, little research focused on the fate of OPEs in remote oceans. Similar to
69 traditional POPs, the net flux of OPEs in the remote marine environment might be
70 typically following the route of air–surface waters–deeper waters and then burial in
71 the benthic sediments, where the deep ocean is seemed as the long-term oceanic
72 repository for these chemicals.^{17, 18} OPEs have been detected in precipitation,
73 indicating their atmospheric deposition processes.^{19, 20} For remote pelagic
74 environments, such as the North Pacific and Arctic Oceans, they could be further
75 transferred from well-mixed surface waters to deep waters as well as sediment
76 through particle settling. Part of the particle settling could be driven by the ‘biological
77 pump’, which is the settling fluxes of particle organic carbon associated with primary
78 production by phytoplankton.^{17, 21} Previous research has observed positive
79 relationship between concentrations of triphenyl phosphate (TPhP) and d¹⁵N in
80 demersal species, indicating the transfer process of TPhP through particle settling to
81 the bottom sediment and their further accumulation through the benthic food web.⁹

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

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

90

91 **Experimental Section**

92 **Sampling**

93 During the 4th Chinese National Arctic Research Expedition (CHINARE 4) held
94 between July and September 2010, 0-2cm surficial marine sediment samples were
95 collected onboard the ice-breaker R/V Xuelong ('Snow Dragon'). The sampling
96 cruise generally covered a northward transect from the Bering Sea, through the Bering
97 Strait to the Chukchi Sea, and across the Canada Basin and central Arctic Ocean
98 (53-88°N). Detailed information about the sampling work and the sediment samples
99 are described in Supporting Information and listed in Table S1.

100

101 **Extraction, Analysis, QC/QA**

102 The extraction, purification and analysis were conducted in the clean laboratory of the
103 Helmholtz-Zentrum Geesthacht (HZG) in Germany based on our previously
104 published method, and is described in more detail in the Supporting Information.²²
105 Briefly, approximately 10 g sediment sample was extracted with Soxhlet extractor,
106 and then the extracts were rotary evaporated to 1–2 mL, and further purified on a

107 silica column. OPEs were analyzed using a gas chromatograph coupled to a triple
108 quadrupole mass spectrometer operated in electron impact mode. Native OPE
109 standards d_{27} -TnBP and d_{15} -TPhP were spiked to 3 solvent-extracted sediment
110 samples as deuterated surrogate standards to check matrix effects. And $^{13}\text{C}_6$ -PCB 208
111 (Cambridge Isotope Laboratories) was added into the sample as injection standard.
112 The recoveries of d_{27} -TnBP and d_{15} -TPhP in all sediment samples were $57 \pm 11\%$ and
113 $93 \pm 18\%$, respectively. The recoveries of OPEs ranged from $95 \pm 2\%$ for TiBP to 143
114 $\pm 7\%$ for TCEP. Totally five procedural blanks were extracted, while the dominant
115 OPE contaminations detected in the procedural blanks were 34 ± 6 pg/g for TCPPs,
116 23 ± 6 pg/g for TCEP and 18 ± 3 pg/g for TPhP, respectively (Table S2). The method
117 detection limits (MDLs), with a range from 1 to 53 pg/g, were calculated by the
118 average of procedural blanks plus three times the standard deviation (3σ) of
119 procedural blanks. While the instrumental detection limits, ranging from 0.1 to 4 pg,
120 were quantified as signal to noise ratio of 3.

121

122 **Results and Discussion**

123 **OPE Concentrations and Composition**

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

129 OPEs along all the sampling stations is shown in Figure 1-a. For halogenated OPEs,
130 TCEP was the dominant compound which was detected at all sampling stations with a
131 median contribution of $54 \pm 18\%$ to Σ_7 OPEs. TCEP concentrations were in a range of
132 81 to 3903 pg g^{-1} dw. The second-most abundant chlorinated OPE, TCPPs (sum of
133 three of isomers) ranged from 0.94 to 460 pg g^{-1} dw, followed by TDCP, which was
134 detected in 63% samples with concentrations from not detected (n.d.) to 165 pg g^{-1} dw.
135 Among the non-halogenated OPEs, TiBP was the dominant compound detected at all
136 sampling stations, with a median contribution of $24 \pm 15\%$ to Σ_7 OPEs during the
137 entire cruise. Individual TiBP concentrations ranged from 47 to 552 pg g^{-1} dw,
138 followed by TnBP, which was also detected in all samples, for which concentrations
139 ranged from 19 to 209 pg g^{-1} dw. The detection frequency for TPhP and TPeP was 77%
140 and 83%, with concentrations from n.d. to 105 pg g^{-1} dw and n.d. to 81 pg g^{-1} dw,
141 respectively.

142 OPEs were also investigated in airborne particles from East Asia to the remote Arctic
143 regions during the same polar expedition CHINARE 4.¹ Relatively higher levels of
144 halogenated OPEs in comparison to non-halogenated OPEs, with the dominance of
145 TCEP, in the surficial sediment was consistent with what was detected in the airborne
146 particles of the same region.¹ Similar results of the predominance of halogenated
147 OPEs and TCEP were shown in the atmospheric observing stations located in the
148 Canadian Arctic.¹³ Generally, halogenated OPEs display higher environmental
149 persistence and historical production than non-halogenated OPEs.²³ Moreover, it is
150 reported that TCEP has gradually been replaced by the structurally similar TCPP in

151 Europe due to the considerable carcinogenic and mutagenic effects.²⁴ Relatively
152 higher detection frequency and levels of TCEP in our study might reflect its
153 continuing usage in Asia and North America. With a relatively high water solubility of
154 $7.0 \times 10^3 \text{ mg L}^{-1}$,²⁵ much higher levels of TCEP could be assumed to be present
155 dissolved in water bodies. However, for atmospheric particle phase samples collected
156 at Longyearbyen on Svalbard in the European Arctic, the sum of all non-halogenated
157 OPE concentrations comprised ~75% of the Σ OPE concentrations.¹² And high levels
158 of non-halogenated OPEs, especially for TnBP and TiBP, were also observed in air
159 samples of Japan urbanized area.²⁶ These indicated the existence of different
160 concentrations and sources of OPEs in varied regions.

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

166 The TOC composition in these surficial sediments (Table S1), displayed higher levels
167 in the shelf regions such as the Bering Strait (average value of 0.64%) and Chukchi
168 Sea (average value of 0.60%), and decreased towards the Bering Sea (average value
169 of 0.43%), Canadian Basin margin region (average value of 0.27%), and the central
170 Arctic Ocean (average value of 0.10%). Obviously, the distribution pattern of TOC is
171 quite different from that of OPEs. And no significant relationships were discovered
172 between any OPE compound and TOC ($p > 0.05$, Table S3). For PBDEs, we also

173 discovered a lack of correlation between the contaminants and TOC.³⁰ Thus TOC
174 might not be a strong predictor for OPE concentrations in remote oceans.

175

176 **Geographic Distribution of OPEs**

177 The sampling stations were separated into five geographical regions as Bering Sea,
178 Bering Strait, Chukchi Sea, Canadian Basin margin and Central Arctic Ocean to
179 assess the spatial distribution of OPEs. Significant differences in the mean
180 concentrations of OPEs were demonstrated among the five geographical regions
181 according to analysis of variance (ANOVA). Figure 2 showed the spatial distribution
182 of Σ_7 OPEs along transect of the cruise. The highest average Σ_7 OPEs concentrations
183 were observed in the Central Arctic Ocean (1463 ± 1574 pg g⁻¹ dw), followed by
184 sampling sites in the Bering Sea (1207 ± 593 pg g⁻¹ dw) and Canadian Basin margin
185 region (1035 ± 491 pg g⁻¹ dw), however, the Chukchi Sea (468 ± 219 pg g⁻¹ dw) and
186 Bering Strait (350 ± 59 pg g⁻¹ dw) had relatively lower average concentrations. Except
187 for the Bering Sea, Σ_7 OPEs concentrations generally increased with the increasing
188 latitudes from Bering Strait to the Central Arctic Ocean. Beyond these regional
189 differences we also note that concentrations of Σ_7 OPEs showed spatial variability in
190 the Central Arctic Ocean. Elevated Σ_7 OPEs levels were observed at sites BN06 (4658
191 pg g⁻¹ dw) and BN04 (2360 pg g⁻¹ dw), as well as the northern most site BN13 (1144
192 pg g⁻¹ dw). Notably high Σ_7 OPEs concentrations were also shown at site B04 (2093 pg
193 g⁻¹ dw) in the Bering Sea, as well as site MS02 (1855 pg g⁻¹ dw) in the Canadian
194 Basin margin area, respectively. Moreover, for OPEs composition profile in the five

195 different geographic areas, we observed that the contributions of halogenated OPEs
196 (typically TCEP and TCPP) to total OPE profile increased from Bering Strait to the
197 Central Arctic Ocean. In contrast, the contributions of non-halogenated OPEs
198 (typically TiBP and TnBP) decreased from Bering Strait to the Central Arctic Ocean
199 (Figure 1-b).

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

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

215 In general, high concentrations of OPEs in high latitude regions were due to
216 halogenated OPEs rather than non-halogenated OPEs. Some high concentrations of

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

229

230 **Observations of Latitudinal Fractionation**

231 To assess the influence of volatility on the LRAT potential of the individual OPE
232 compound, the ratio of individual OPE concentrations at northern most 88°N (high
233 Arctic station BN13) and their concentration at 61°N (Bering Strait station B14) as a
234 function of log subcooled liquid vapor pressure (p_L) was obtained (Figure S1; TPeP
235 was excluded for which p_L was not known from the same literature source; TDCP was
236 excluded as well because it was not detected at these two stations).³ Distributions of
237 various polychlorinated biphenyl congeners (PCBs) between northern and southern
238 regions have been shown to strongly correlation with p_L .³³ It was thus a potentially

239 valuable tool to gauge the compounds' propensity for LRAT to the Arctic.³⁴ No strong
240 relationship was detected between increasing North/South ratio and p_L for these five
241 OPE compounds (Figure S1-a), but a strong correlation was shown if the more
242 reactive TnBP and TiBP were excluded (Figure S1-b). The North/South ratios for both
243 TnBP and TiBP were < 1 in our surficial sediment samples, implying they degrade
244 during transport to the Arctic. Actually, TnBP and TiBP displayed high atmospheric
245 concentrations in urbanized regions,²⁶ however their concentrations were quite low in
246 remote Arctic atmospheric samples.¹ This indicated that non-halogenated OPEs, in
247 particular TnBP and TiBP were heavily emitted to the atmosphere within urbanized
248 regions, but they might be further degraded and/or trapped in soil/sediment during
249 atmospheric transport. Moreover, decreasing contributions of both TnBP and TiBP to
250 total investigated OPEs were observed in our surficial sediments from Bring Strait
251 through Chukchi Sea to the Canadian Basin and central Arctic Ocean (Figure 1-b).
252 This further demonstrated that they have relatively low potential of being transported
253 to the remote Arctic regions. In contrast, the North/South ratios for TCEP and TCPP
254 were > 1 (~ 8 and ~ 3) in our sediment samples. The strong relationship between
255 North/South ratio and volatility together with their increasing contributions from low
256 to high latitudes (Figure 1-b) demonstrated high potential of being transported to
257 remote oceans for TCEP and TCPP.

258 Moreover, K_{ow} is also used to investigate the relation with increasing North/South
259 ratio. The results showed that there was a strong negative relationship between
260 North/South ratio and $\log K_{ow}$ value (Figure S2). These again demonstrated that the

261 compound with high value of K_{ow} , such as TiBP and TnBP, have relatively low
262 potential of being transported to the Arctic Ocean (the North/South concentration
263 ratio < 1). And they might be trapped in the ocean sediment of low latitude regions
264 during their transport from low latitude to high latitude regions. In contrast, the
265 contaminants with relative low value of K_{ow} , such as TCEP and TCPP, have
266 relatively higher potential of being transported to remote oceans (the North/South
267 concentration ratio > 1). And sediments in the remote Arctic could be seemed as their
268 final sink.

269

270 **Budget of OPEs in the Central Arctic Ocean Basin**

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

280 The method we used is as previously reported; a detailed calculation method is
281 provided in supporting information.³⁷ The estimation results are shown in Table 3.

282 Generally, for halogenated OPEs, the budget of the dominant TCEP to the Central

283 Arctic Ocean Basin was estimated in the range of 12-219 tons, with a median value of
284 39 tons. While for non-halogenated OPEs, the dominant TiBP budget was estimated in
285 the ranges of 3.6-16 tons, with a median value of 6.2 tons. Compared with thousands
286 tons of production/usage volumes of TCEP per year in Europe and United States,²³ the
287 input to the Arctic Ocean sediment represented still a very small amount.

288

289 **Comparison of OPEs in Surficial Sediment with PBDEs**

290 Since OPEs are used in many cases as substitutes of PBDEs, OPE concentrations are
291 compared with PBDE concentrations observed in surficial sediment in the same
292 research region during CHINARE 3, CHINARE 4 and 5 campaign. Concentrations of
293 the most dominant PBDEs (BDE47, -99, -153, and -209) are given in Table S4 and
294 comparison between dominant OPEs and PBDEs along northern latitude is shown in
295 Figure 3. The data available showed that BDE-47, -99 and -153 were generally in the
296 range of tens pg g^{-1} dw, while BDE-209 were in hundreds pg g^{-1} dw range. Moreover,
297 the PBDEs (excluding BDE-209) concentrations generally decreased from 2008 to
298 2012, especially in the Bering Sea, Bering Strait, and Chukchi Sea area, although this
299 temporal trend might not be so significant considering different analytical methods
300 and sampling sites among these cruises.^{30, 38}

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

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

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

316

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

320

321 **Acknowledgements.** We would like to appreciate staff of the 4th Chinese National
322 Arctic Research Expedition. The research is supported by Youth Fund of National
323 Natural Science Foundation of China (41506215), Shanghai Sailing Program
324 (15YF1405100) and Science and Technology Development Fund of Shanghai Ocean
325 University (A2-0209-15-200001). The samples were obtained from Polar Sediment
326 Sample Chamber of China. The sample analysis was supported by the General

327 Program of National Natural Science Foundation of China (41276197) and the Global
328 Change Research Program of China (2015CB953900).

329

330 **References**

- 331 1. Moller, A.; Sturm, R.; Xie, Z. Y.; Cai, M. H.; He, J. F.; Ebinghaus, R., Organophosphorus Flame
332 Retardants and Plasticizers in Airborne Particles over the Northern Pacific and Indian Ocean toward
333 the Polar Regions: Evidence for Global Occurrence. *Environ Sci Technol* **2012**, *46*, (6), 3127-3134.
- 334 2. Marklund, A.; Andersson, B.; Haglund, P., Screening of organophosphorus compounds and their
335 distribution in various indoor environments. *Chemosphere* **2003**, *53*, (9), 1137-1146.
- 336 3. Reemtsma, T.; Quintana, J. B.; Rodil, R.; Garcia-Lopez, M.; Rodriguez, I., Organophosphorus flame
337 retardants and plasticizers in water and air I. Occurrence and fate. *Trac-Trends in Analytical Chemistry*
338 **2008**, *27*, (9), 727-737.
- 339 4. *Global and China Flame Retardant Industry Report, 2014-2016*; Research In China at China
340 Market Research Report: 2016.
- 341 5. Bollmann, U. E.; Moler, A.; Xie, Z. Y.; Ebinghaus, R.; Einax, J. W., Occurrence and fate of
342 organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water*
343 *Research* **2012**, *46*, (2), 531-538.
- 344 6. Wang, R. M.; Tang, J. H.; Xie, Z. Y.; Mi, W. Y.; Chen, Y. J.; Wolschke, H.; Tian, C. G.; Pan, X. H.; Luo, Y.
345 M.; Ebinghaus, R., Occurrence and spatial distribution of organophosphate ester flame retardants and
346 plasticizers in 40 rivers draining into the Bohai Sea, north China. *Environ Pollut* **2015**, *198*, 172-178.
- 347 7. Chung, H. W.; Ding, W. H., Determination of organophosphate flame retardants in sediments by
348 microwave-assisted extraction and gas chromatography-mass spectrometry with electron impact and
349 chemical ionization. *Anal Bioanal Chem* **2009**, *395*, (7), 2325-2334.
- 350 8. Cao, S. X.; Zeng, X. Y.; Song, H.; Li, H. R.; Yu, Z. Q.; Sheng, G. Y.; Fu, J. M., Levels and distributions
351 of organophosphate flame retardants and plasticizers in sediment from Taihu Lake, China. *Environ*
352 *Toxicol Chem* **2012**, *31*, (7), 1478-1484.
- 353 9. Kim, J. W.; Isobe, T.; Chang, K. H.; Amano, A.; Maneja, R. H.; Zamora, P. B.; Siringan, F. P.; Tanabe,
354 S., Levels and distribution of organophosphorus flame retardants and plasticizers in fishes from Manila
355 Bay, the Philippines. *Environ Pollut* **2011**, *159*, (12), 3653-3659.
- 356 10. Sundkvist, A. M.; Olofsson, U.; Haglund, P., Organophosphorus flame retardants and plasticizers
357 in marine and fresh water biota and in human milk. *Journal of Environmental Monitoring* **2010**, *12*, (4),
358 943-951.
- 359 11. Zhang, X.; Suehring, R.; Serodio, D.; Bonnell, M.; Sundin, N.; Diamond, M. L., Novel flame
360 retardants: Estimating the physical-chemical properties and environmental fate of 94 halogenated and
361 organophosphate PBDE replacements. *Chemosphere* **2016**, *144*, 2401-2407.
- 362 12. Salamova, A.; Hermanson, M. H.; Hites, R. A., Organophosphate and Halogenated Flame
363 Retardants in Atmospheric Particles from a European Arctic Site. *Environ Sci Technol* **2014**, *48*, (11),
364 6133-6140.
- 365 13. Suhring, R.; Diamond, M. L.; Scheringer, M.; Wong, F.; Pucko, M.; Stern, G.; Burt, A.; Hung, H.;
366 Fellin, P.; Li, H.; Jantunen, L. M., Organophosphate Esters in Canadian Arctic Air: Occurrence, Levels

367 and Trends. *Environ Sci Technol* **2016**, *50*, (14), 7409-7415.

368 14. Castro-Jimenez, J.; Berrojalbiz, N.; Pizarro, M.; Dachs, J., Organophosphate Ester (OPE) Flame
369 Retardants and Plasticizers in the Open Mediterranean and Black Seas Atmosphere. *Environ Sci*
370 *Technol* **2014**, *48*, (6), 3203-3209.

371 15. Moller, A.; Xie, Z. Y.; Caba, A.; Sturm, R.; Ebinghaus, R., Organophosphorus flame retardants and
372 plasticizers in the atmosphere of the North Sea. *Environ Pollut* **2011**, *159*, (12), 3660-3665.

373 16. Castro Jimenez, J.; Gonzalez-Gaya, B.; Pizarro, M.; Casal, P.; Pizarro-Alvarez, C.; Dachs, J.,
374 ORGANOPHOSPHATE ESTER FLAME RETARDANTS AND PLASTICIZERS IN THE GLOBAL OCEANIC
375 ATMOSPHERE. *Environ Sci Technol* **2016**.

376 17. Dachs, J.; Lohmann, R.; Ockenden, W. A.; Mejanelle, L.; Eisenreich, S. J.; Jones, K. C., Oceanic
377 biogeochemical controls on global dynamics of persistent organic pollutants. *Environ Sci Technol* **2002**,
378 *36*, (20), 4229-4237.

379 18. Jaward, F. M.; Barber, J. L.; Booiij, K.; Dachs, J.; Lohmann, R.; Jones, K. C., Evidence for dynamic
380 air-water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environ*
381 *Sci Technol* **2004**, *38*, (9), 2617-2625.

382 19. Regnery, J.; Puttmann, W., Organophosphorus Flame Retardants and Plasticizers in Rain and
383 Snow from Middle Germany. *Clean-Soil Air Water* **2009**, *37*, (4-5), 334-342.

384 20. Regnery, J.; Puttmann, W., Seasonal fluctuations of organophosphate concentrations in
385 precipitation and storm water runoff. *Chemosphere* **2010**, *78*, (8), 958-964.

386 21. Dachs, J.; Eisenreich, S. J.; Baker, J. E.; Ko, F. C.; Jeremiason, J. D., Coupling of phytoplankton
387 uptake and air-water exchange of persistent organic pollutants. *Environ Sci Technol* **1999**, *33*, (20),
388 3653-3660.

389 22. Chen, W.-L.; Xie, Z.; Wolschke, H.; Gandrass, J.; Koetke, D.; Winkelmann, M.; Ebinghaus, R.,
390 Quantitative determination of ultra-trace carbazoles in sediments in the coastal environment.
391 *Chemosphere* **2016**, *150*, 586-595.

392 23. van der Veen, I.; de Boer, J., Phosphorus flame retardants: Properties, production, environmental
393 occurrence, toxicity and analysis. *Chemosphere* **2012**, *88*, (10), 1119-1153.

394 24. Stachel, B.; Jantzen, E.; Knoth, W.; Kruger, F.; Lepom, P.; Oetken, M.; Reincke, H.; Sawal, G.;
395 Schwartz, R.; Uhlig, S., The Elbe flood in August 2002 - Organic contaminants in sediment samples
396 taken after the flood event. *J Environ Sci Heal A* **2005**, *40*, (2), 265-287.

397 25. Fisk, P. R.; Girling, A. E.; Wildey, R. J., Prioritisation of Flame Retardants for Environmental Risk
398 Assessment. In Agency, E., Ed. United Kingdom, 2003.

399 26. Ohura, T.; Amagai, T.; Senga, Y.; Fusaya, M., Organic air pollutants inside and outside residences in
400 Shimizu, Japan: Levels, sources and risks. *Sci Total Environ* **2006**, *366*, (2-3), 485-499.

401 27. Martinez-Carballo, E.; Gonzalez-Barreiro, C.; Sitka, A.; Scharf, S.; Gans, O., Determination of
402 selected organophosphate esters in the aquatic environment of Austria. *Sci Total Environ* **2007**, *388*,
403 (1-3), 290-299.

404 28. Leonards, P.; Steindal, E. H.; van der Veen, I.; Berg, V.; Bustnes, J. O.; van Leeuwen, S. *Screening of*
405 *Organophosphor Flame Retardants 2010*; 2011.

406 29. Garcia-Lopez, M.; Rodriguez, I.; Cela, R., Pressurized liquid extraction of organophosphate
407 triesters from sediment samples using aqueous solutions. *Journal of Chromatography A* **2009**, *1216*,
408 (42), 6986-6993.

409 30. Ma, Y. X.; Halsall, C. J.; Crosse, J. D.; Graf, C.; Cai, M. H.; He, J. F.; Gao, G. P.; Jones, K., Persistent
410 organic pollutants in ocean sediments from the North Pacific to the Arctic Ocean. *Journal of*

411 *Geophysical Research-Oceans* **2015**, *120*, (4), 2723-2735.

412 31. Wania, F.; Mackay, D., Global Fractionation and Cold Condensation of Low Volatility
413 Organochlorine Compounds in Polar-Regions. *Ambio* **1993**, *22*, (1), 10-18.

414 32. Cristale, J.; Katsoyiannis, A.; Chen, C. E.; Jones, K. C.; Lacorte, S., Assessment of flame retardants
415 in river water using a ceramic dosimeter passive sampler. *Environ Pollut* **2013**, *172*, 163-169.

416 33. Sun, C. X.; Soltwedel, T.; Bauerfeind, E.; Adelman, D. A.; Lohmann, R., Depth Profiles of Persistent
417 Organic Pollutants in the North and Tropical Atlantic Ocean. *Environ Sci Technol* **2016**, *50*, (12),
418 6172-6179.

419 34. Sobek, A.; Gustafsson, O., Latitudinal fractionation of polychlorinated biphenyls in surface
420 seawater along a 62 degrees N-89 degrees N transect from the southern Norwegian Sea to the North
421 Pole area. *Environ Sci Technol* **2004**, *38*, (10), 2746-2751.

422 35. Backman, J.; Jakobsson, M.; Lovlie, R.; Polyak, L.; Febo, L. A., Is the central Arctic Ocean a
423 sediment starved basin? *Quaternary Sci Rev* **2004**, *23*, (11-13), 1435-1454.

424 36. Darby, D. A.; Ortiz, J.; Polyak, L.; Lund, S.; Jakobsson, M.; Woodgate, R. A., The role of currents
425 and sea ice in both slowly deposited central Arctic and rapidly deposited Chukchi-Alaskan margin
426 sediments. *Global Planet Change* **2009**, *68*, (1-2), 56-70.

427 37. Jonsson, A.; Gustafsson, O.; Axelman, J.; Sundberg, H., Global accounting of PCBs in the
428 continental shelf sediments. *Environ Sci Technol* **2003**, *37*, (2), 245-255.

429 38. Cai, M. G.; Hong, Q. Q.; Wang, Y.; Luo, X. J.; Chen, S. J.; Cai, M. H.; Qiu, C. R.; Huang, S. Y.; Mai, B.
430 X., Distribution of polybrominated diphenyl ethers and decabromodiphenylethane in surface
431 sediments from the Bering Sea, Chukchi Sea, and Canada Basin. *Deep-Sea Res Pt II* **2012**, *81-84*,
432 95-101.

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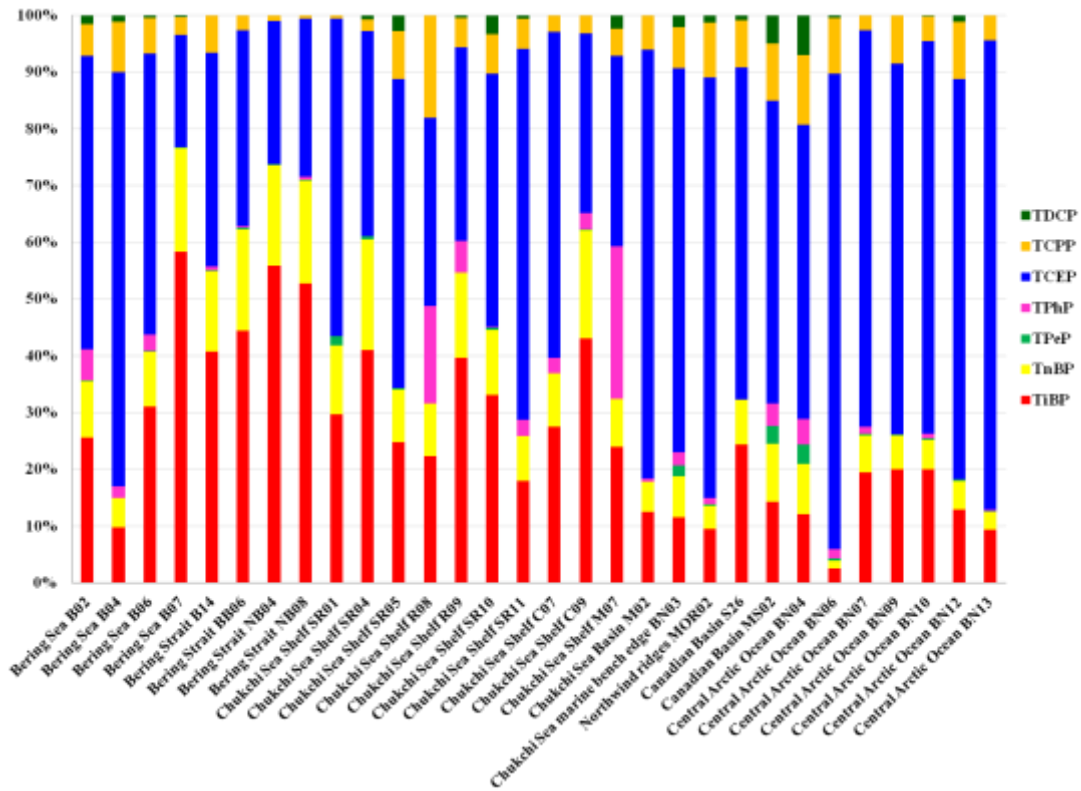
436 **Figure Captions**

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

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

442 **Figure 3.** Comparison between dominant OPEs and PBDEs in surface marine
443 sediment along northern latitude

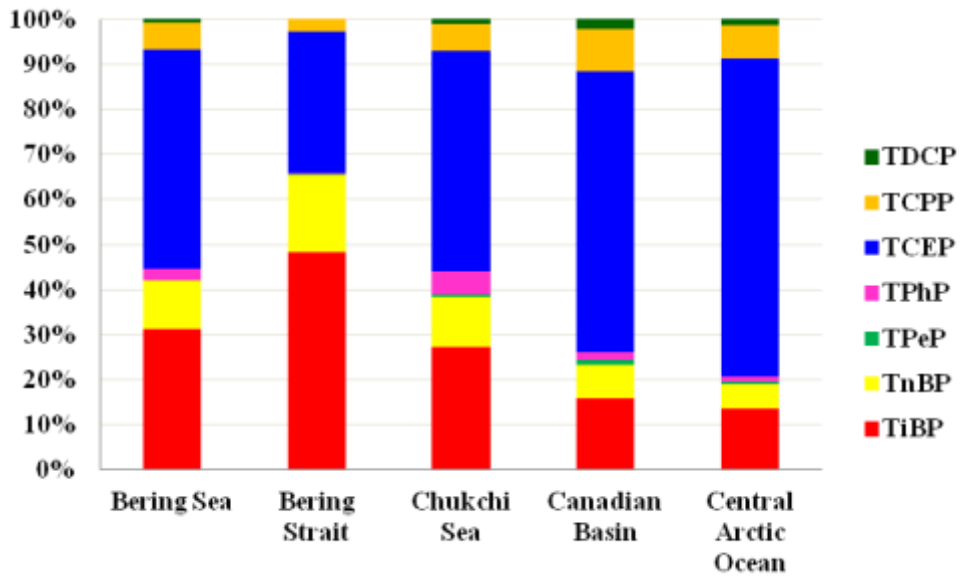
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(a)

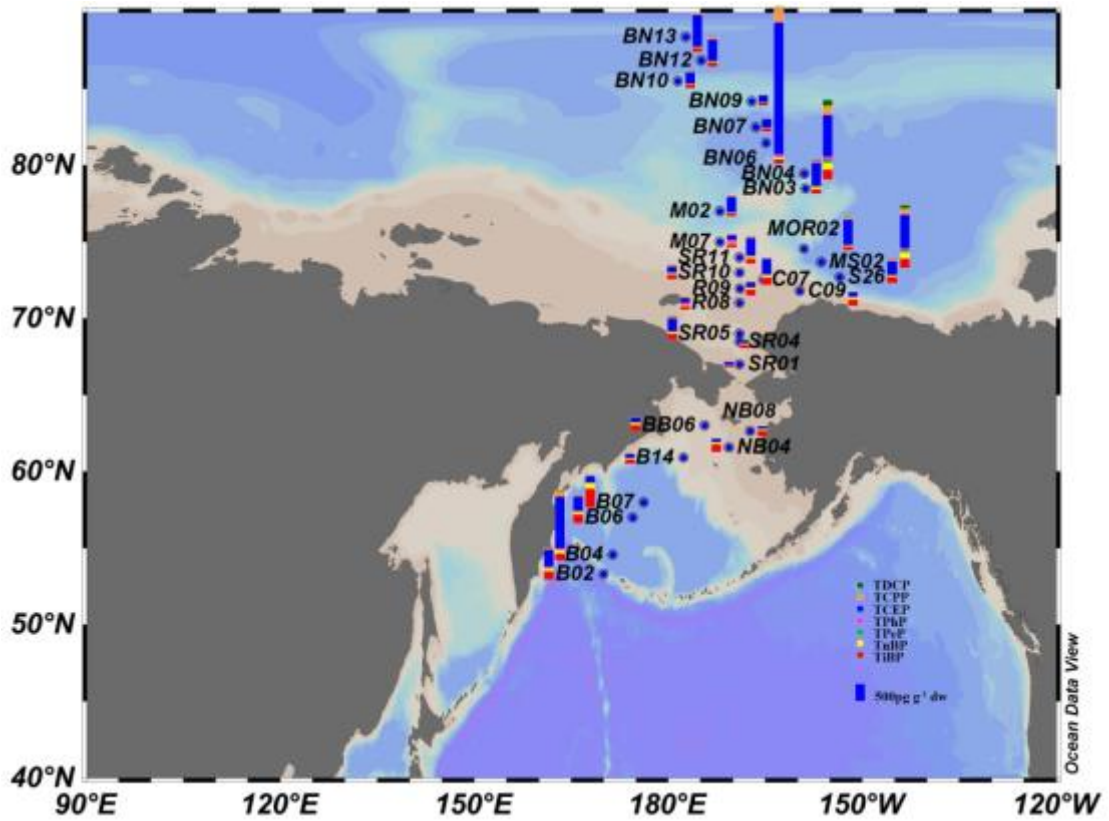


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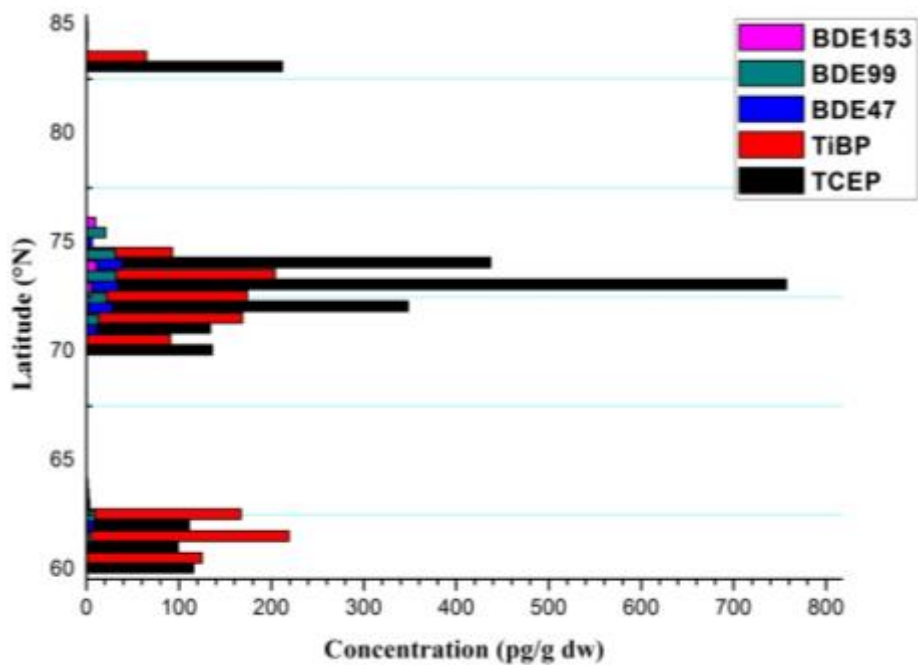
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449 **Figure 1**



450

451 **Figure 2**



452

453 **Figure 3**

454

455 **Table 1.** Individual concentrations of OPEs in the surface sediment (pg g⁻¹ d.w.) at
 456 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

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458

459 **Table 2.** Comparison of OPE concentration ranges (pg g⁻¹ d.w.) in surface sediment
 460 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
Kålfjorden, 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

461

462 Average concentrations are given in brackets

463 n.d. = not detected

464 n.a. = not analyzed

465

466

467 **Table 3.** Estimation results of the inventories of OPEs in the sediment for the Central
 468 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

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