

2022

## Organophosphate ester pollution in the oceans

Zhiyong Xie

Pu Wang

Xin Wang

Javier Castro-Jiménez

Roland Kallenborn

*See next page for additional authors*

Follow this and additional works at: <https://digitalcommons.uri.edu/gsofacpubs>

The University of Rhode Island Faculty have made this article openly available.  
Please let us know how Open Access to this research benefits you.

This is a pre-publication author manuscript of the final, published article.

### Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

### Citation/Publisher Attribution

Xie, Z., Wang, P., Wang, X. *et al.* Organophosphate ester pollution in the oceans. *Nat Rev Earth Environ* (2022). <https://doi.org/10.1038/s43017-022-00277-w>

Available at: <https://doi.org/10.1038/s43017-022-00277-w>

This Article is brought to you for free and open access by the Graduate School of Oceanography at DigitalCommons@URI. It has been accepted for inclusion in Graduate School of Oceanography Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact [digitalcommons@etal.uri.edu](mailto:digitalcommons@etal.uri.edu).

---

---

**Authors**

Zhiyong Xie, Pu Wang, Xin Wang, Javier Castro-Jiménez, Roland Kallenborn, Chunyang Liao, Wenying Mi, Rainer Lohmann, Maria Villa-Costa, and Jordi Dachs

# Organophosphate esters in the ocean

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20

Zhiyong Xie<sup>1</sup>, Pu Wang<sup>2</sup>, Xin Wang<sup>3</sup>, Javier Castro-Jiménez<sup>4</sup>, Roland Kallenborn<sup>5</sup>, Chunyang Liao<sup>3</sup>, Wenyang Mi<sup>6</sup>, Rainer Lohmann<sup>7</sup>, Maria Vila-Costa<sup>8</sup>, Jordi Dachs<sup>8</sup>

<sup>1</sup>Institute of Coastal Environmental Chemistry, Helmholtz-Zentrum Hereon, Geesthacht 21502, Germany

<sup>2</sup>Hubei Key Laboratory of Environmental and Health Effects of Persistent Toxic Substances, Institute of Environment and Health, Jiangnan University, Wuhan 430056, China

<sup>3</sup>State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

<sup>4</sup>IFREMER, Laboratory of Biogeochemistry of Organic Contaminants (LBCO), Rue de l'Île d'Yeu, BP 21105, 44311, Nantes, Cedex 3, France

<sup>5</sup>Faculty of Chemistry, Biotechnology and Food Sciences (KBM), Norwegian University of Life Sciences (NMBU), 1432, Ås, Norway

<sup>6</sup>MINJIE Institute of Environmental Science and Health Research, Geesthacht 21502, Germany

<sup>7</sup>Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882, United States

<sup>8</sup>Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona, 18-26, 08034 Barcelona, Catalonia, Spain

21 **Abstract**

22 The large-scale application of organophosphate esters (OPEs) as flame-retardants and plasticizers  
23 has led to their ubiquitous occurrences in the environment with still unknown environmental  
24 impacts. This review summarizes current knowledge on the transport, biogeochemistry and effects  
25 of OPEs in the marine environment, including polar regions. Atmospheric long-range transport  
26 and Ocean currents are responsible for the regional and global distribution of OPEs from  
27 industrialized regions to open oceans. During transport, a number of biogeochemical processes  
28 such as degradation, settling to deep waters, modulate the OPEs concentrations and ultimately  
29 their impact and sinks. Trans-ocean studies provide evidence of the importance of air-water  
30 interactions, although the impact of this anthropogenic input of organic phosphorous has yet to be  
31 constrained. Moreover, the potential for bioaccumulation and biomagnification of OPEs have been  
32 investigated for different marine species, and OPEs can give rise to toxic effects. Future research  
33 needs to be focused on the biogeochemistry of OPEs in the water column, deep ocean sediments  
34 and organisms, on a better characterization of the total anthropogenic organic phosphorus, and to  
35 understand the impacts of a changing climate and human activities to the environmental fate,  
36 relevance and ocean health impacts of OPEs.

37           **Key points**

38   OPEs have been transported from continental sources to the ocean via both atmosphere and  
39   riverine discharge.

40   Air-water exchange and atmospheric deposition affect the cycling of OPEs from the coastal area  
41   to the remote ocean.

42   Re-emission of OPEs from melting snow and ice in the polar regions can impact their levels in the  
43   water columns in the high Arctic and the Southern Ocean.

44   Parent OPEs and their transformation products, especially their presence in marine mammals and  
45   fish, have become emerging concerns for the oceanic ecosystem, therefore international strategies  
46   are required to eliminate their environmental emissions.

47

48           **1. Introduction**

49   Organophosphate esters (OPEs) are synthesized organic chemicals used on large scale as flame-  
50   retardants, plasticizers and additives in industry production, electronics, household consumer  
51   products and personal care products.<sup>8</sup> The increased demand for alternative flame-retardants due  
52   to the regulation applied to polybrominated diphenyl ethers (PBDEs) in 2003, has driven the  
53   rapidly increasing consumption volume of OPEs.<sup>8</sup> Over the past 20 years, the annual worldwide  
54   use of OPEs increased from 300 kilotons in 2004 to 620 kilotons in 2013<sup>14,15</sup>. It is estimated that  
55   the OPEs market grew by 5.2% from 2016 to 2021<sup>16</sup>. Presently, OPEs account for approximately  
56   15% of the total volume for flame retardants employed globally<sup>14,24</sup>

57   Because of the risk that pose to human reproductive, genetic, and developmental functions,  
58   tris(2-chloroethyl) phosphate (TCEP) is now included in the European Commission (EC) second

59 priority list of chemicals developed within the EU-Strategy for Endocrine Disruptors<sup>25</sup>. Some  
60 OPEs such as TCEP, tributyl phosphate (TBP), and tris-(2-butoxyethyl) phosphate (TBEP) are  
61 also registered as high production volume (HPV, more than 1000 tons each year) chemicals under  
62 European REACH (Registration, Evaluation, Authorization and Restriction of Chemicals)<sup>26</sup>.  
63 However, there is no international regulation existing to tackle the increasing pressure from the  
64 OPEs emissions. Together with high level of usage and potential toxic risk to human being and  
65 ecosystems have made OPEs gain considerable prominence in recent international research.<sup>8,27,28</sup>

66 The broad application for OPEs and their use as additives in plastic products have contributed  
67 to their diffusive release and high environmental mobility, mainly by volatilization, leaching and  
68 abrasion<sup>29,30</sup>. For example, more than 44.7 million tons of electronic waste (e-waste) were  
69 generated worldwide in 2016, and most them were treated for re-cycling along the coastal cities,  
70 especially in developing countries<sup>31</sup>. The most commonly found flame retardants in older  
71 electronics are polybrominated diphenyl ethers (PBDEs), which were superseded in newer  
72 electronics by non-PBDE brominated flame retardants and OPEs<sup>32-34</sup>. Open air burning e-wastes  
73 may directly release organic additives including OPEs in ambient air<sup>35</sup>. For instance, OPE  
74 concentrations reached 740-1000 ng/m<sup>3</sup> in ambient air of Canadian e-waste recycling facilities,<sup>30</sup>  
75 and 3.8–57.7 ng/m<sup>3</sup> in the rural e-waste recycling area in south China<sup>36</sup>. The air mass back  
76 trajectories (BTs) from for the coastal sampling site<sup>37</sup>, demonstrated regional atmospheric  
77 transport of OPEs adsorbed to fine particulate matter (PM 2.5) from both industrial cities and the  
78 e-waste recycling region<sup>36</sup>. A number of studies have shown river to sea fluxes of OPEs, such as  
79 16-160 kg/d from the Elbe to the North Sea<sup>38</sup>, 16±3.2 t/year from 40 rivers to the Bohai Sea<sup>39</sup> and  
80 450–16,000 t OPEs to the Canadian Arctic Ocean<sup>40</sup>. Model predictions have shown that OPEs are

81 persistent and mobile in water<sup>41,42</sup>, which implying the riverine runoff plays an important role for  
82 the transportation of OPEs from terrestrial source to the ocean.

83 The concentrations of OPEs in seawater, sediment and air are generally 2 to 3 orders of  
84 magnitude higher than those of brominated flame retardants and other legacy persistent organic  
85 pollutants (POPs) in environmental matrices<sup>2,43</sup>, highlighting the need for further research on  
86 occurrence, environmental fates and biological accumulation in marine organisms and toxic  
87 impacts of OPEs in the global ocean<sup>8,44-48</sup>. In 2021, Suehring et al. reported an estimate of the  
88 OPE load in the Canadian Arctic Ocean<sup>40</sup>. While, the total amount of OPEs in the environment, as  
89 well the total amount of anthropogenic organophosphorus compounds remains unquantified.

90 In this Review, we summarize the studies for OPEs in the global ocean, including the Arctic  
91 and Antarctic. The major OPE sources are overviewed, and the environmental pathways are  
92 discussed for their effects on the transport processes in the ocean. Environmental concentrations  
93 and spatial trends of OPEs in air, sediment, seawater, biota and snow are separately presented. The  
94 most frequently targeted and detected OPEs in the ocean are covered in this review (**Table 1**).

## Box 1 | Analytical methodology for OPEs in environmental matrixes

Classical extraction methods including Soxhlet, solvent shaking, ultrasonication, microwave-assisted extraction (MAE), matrix solid-phase dispersion (MSPD), and accelerated solvent extraction (ASE) have been applied to the extraction of OPEs in solid samples<sup>1</sup>, such as airborne particles, sediment and organism. OPEs in air are generally sampled using active air sampler composed of glass/quartz fiber filters (GFFs/QFFs) and solid sorbent (such as polyurethane foam plugs, PUFs). Extraction of OPEs from fiber filters and PUFs can be performed with Soxhlet<sup>2-4</sup>, ultrasonication<sup>5,6</sup> or ASE<sup>7</sup>, followed by purification with different columns such as a preconditioned silica gel column (Table S1). Solid phase microextraction (SPME) is a passive sampling device used for the collection of OPEs in gas phase. The trapped compounds can be directly introduced into GC system for analysis after thermal desorption step, which has been developed as a fast and low-cost technique<sup>9</sup>.

For sediment and organism samples, a series of pretreatment procedures including freeze-drying and homogenization are generally needed before the extraction. Due to the complexity of these two matrices, ASE, solid phase extraction (SPE), Soxhlet<sup>1,8,10-13</sup> and ultrasonication<sup>17</sup> are typically used for the extraction and purification of OPEs in sediment and biota (Table S1). For the SPE cartridge, florisil and silica gel are commonly used packing materials. Moreover, the use of QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) could represent a fast and “green” alternative for the quantitative screening of OPEs in sediments and marine organisms<sup>18</sup>.

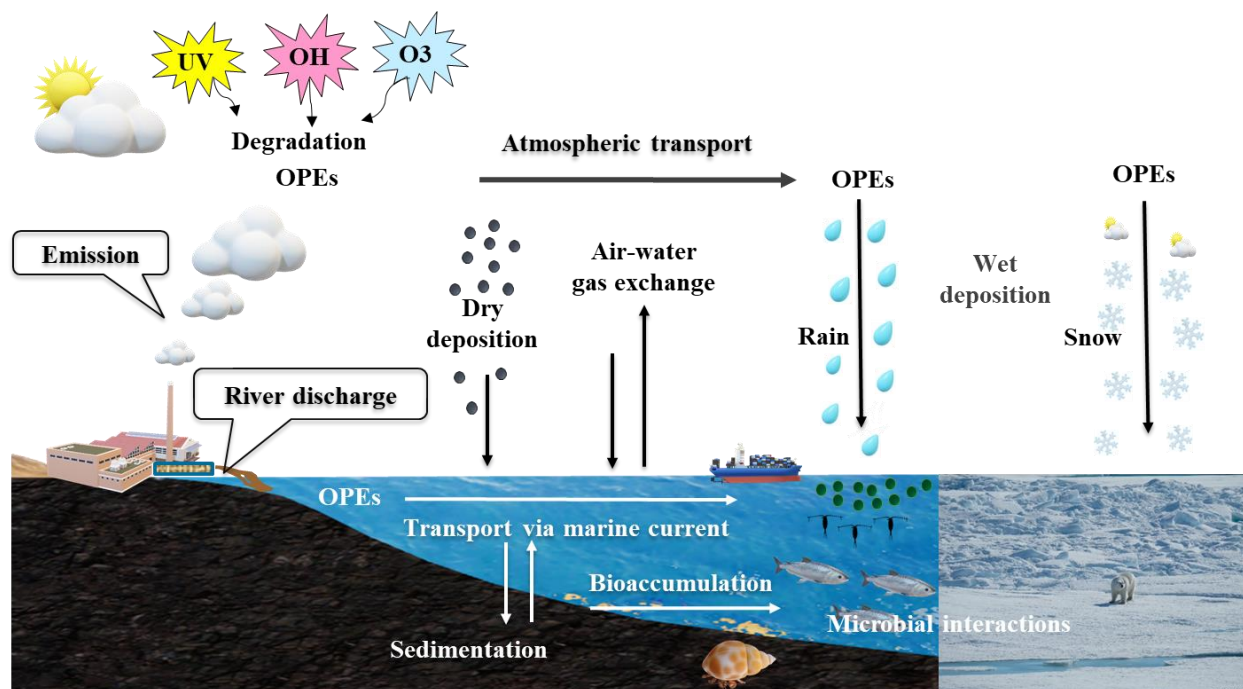
Liquid-liquid extraction (LLE), in which dichloromethane (DCM) is often selected as the extraction solvent<sup>7,19</sup>, or SPE<sup>15,17,19-24</sup> have been widely used for the extraction of OPEs from inland and seawater (typically 500-1000 mL sample volume). Several microextraction techniques have also been applied for the extraction of OPEs in water samples, with the advantages of easy operation, reduction of solvent consumption, and improvement in extraction selectivity<sup>1</sup>.

The determination of OPEs can be achieved by gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–tandem mass spectrometry (LC–MS-MS). It is widely acknowledged that background contamination is a common problem during the sampling and analytical processing of OPEs<sup>42,50,56</sup>. Therefore, work in a clean lab, solvent pre-cleaning, avoiding of use of plastics, as well as the monitoring of field and procedure blanks are needed.



## 96 2. Environmental sources and pathways

97 OPEs have multiple and concurrent sources in the oceanic environment. An important part of  
98 these sources is believed to be land-based<sup>48</sup>, such as direct volatilization from consumer products  
99 (for example, electronic waste) to the atmosphere<sup>36,49,50</sup> and direct inputs from rivers<sup>39,51,52</sup>. The  
100 riverine pathway integrates in turn a variety of sources at the river basin scale such as sewage  
101 treatment effluents<sup>53,54</sup>, direct leaks from industries, potential run-off from plastic and/or electronic  
102 waste sites, and atmospheric deposition<sup>13</sup>. These land-based sources result in environmental  
103 temporal stocks of OPEs reaching coastal and off-shore areas due to atmospheric transport and  
104 deposition<sup>55,56</sup> and /or waterborne transport associated with currents<sup>54</sup>. There is compelling  
105 evidence of the widespread occurrence of OPEs in wastewater<sup>25,57,58</sup>, inland surface water<sup>59</sup>,  
106 ground water<sup>60</sup> and seawater<sup>61</sup> from Europe, North America and Asia. Additionally, oceanic plastic  
107 debris may represent in-situ local sources of OPEs and other organic plastic additives due to  
108 leaching. For example, between 0.3 and 0.9 Mt/y of phthalic acid esters (PAEs) have been  
109 estimated to be leached to the global oceans from marine fragments of polyethylene (PE) based on  
110 laboratory release experiments conducted on PE plastic bags<sup>62</sup>. Effective release of OPEs and  
111 PAEs from PE and PVC was confirmed in another laboratory study performed on surface and  
112 deep-waters collected in the Mediterranean Sea<sup>63</sup>. Interestingly, a more efficient additive release  
113 at the ocean surface than in deep seawater was observed<sup>63</sup>, suggesting that the local sources of  
114 plastic additives could vary with depth pointing to differential exposure levels to deep and surface  
115 water marine organisms. Both laboratory experiments<sup>62,63</sup> highlighted as well the important role  
116 of marine prokaryotes promoting the release of OPEs. Once in the ocean, OPEs are known to  
117 accumulate in marine sediment and aquatic biota, such as fish and in the tissues of marine  
118 mammals<sup>8,19,64-66</sup>(Fig. 1).



119  
 120 **Figure 1.** Major environmental sources, processing and pathways of OPEs in the coastal and  
 121 open oceans. The major continental sources of OPEs include industries area, wastewater treatment  
 122 plant, e-waste cycling plants and ambient emissions. OPEs undertake environmental pathways e.g.  
 123 atmospheric and oceanic transport, air-water exchange, atmospheric dry and wet deposition,  
 124 sedimentation, bioaccumulation and microbial interactions.

125  
 126 **2.1. Transport from rivers**

127 The riverine transport of OPEs has been highlighted as an efficient pathway contributing to  
 128 their coastal inputs and subsequent water-borne oceanic stocks. Modeling estimations indicate that  
 129 chlorinated-OPEs are more efficiently transported by rivers than non-chlorinated OPEs due to their  
 130 higher water solubility and persistency<sup>40,41</sup>. Field studies investigating the riverine inputs of OPEs  
 131 are still discrete and not a large spatial distribution is covered allowing for effective integration  
 132 over regional and oceanic scales. However, available data support the important role of rivers  
 133 transporting OPEs<sup>67</sup>. For example, the presence of organic plastic additives (OPEs, PAEs and

134 bisphenols) in the dissolved water phase from the Rhone river (France), the main freshwater source  
135 of the NW Mediterranean Sea, accounted for more than 40% of the total dissolved anthropogenic  
136 organic contaminants in surface waters of the river, including PAHs, aliphatic hydrocarbons,  
137 pesticides and polyfluorinated alkyl substances.<sup>51</sup> The estimated OPEs inputs associated to the  
138 water dissolved phase from the Rhone river to coastal NW Mediterranean Sea varied from 2 to 11  
139 t/y ( $\Sigma_9$ OPEs). In addition, important inputs associated with the sedimentary material exported by  
140 the Rhone are expected in the Gulf of Lion, based on the OPE concentrations measured in the  
141 sediments at the river outlet<sup>68</sup>. OPEs have been measured at high concentrations in the dissolved  
142 water phase (up to  $\sim 1 \mu\text{g/L}$ ), at the Amazon river plume (in the Western Tropical Atlantic Ocean)  
143 suggesting the Amazon River as a major source of these contaminants to the tropical North Atlantic  
144 Ocean. This finding points to medium-/long-range contaminant transport, most certainly facilitated  
145 by the highly stratified conditions offered by the river plume<sup>52</sup>. Both rivers have been reported to  
146 export large amounts of plastic waste<sup>69,70</sup>. However, a direct link between the organic additive  
147 concentrations at the water surface and the abundance of floating plastics couldn't be established or  
148 was not investigated. The total riverine input of OPEs was estimated to be 18 t/y from 40 major  
149 rivers entering into the Bohai Sea, North China<sup>39</sup>. In Europe, the riverine input of OPs into the  
150 North Sea via Elbe, Ems, and Weser was estimated to be about 50 t/y.<sup>22,71</sup> Overall, the riverine  
151 discharges of OPEs to the coastal areas can be transported with ocean currents further to the open  
152 ocean.

153

154

155

156

## 157 **2.2. Long-range atmospheric transport**

158 Long-range transport especially via atmosphere has been considered an important pathway for  
159 global distribution of POPs<sup>72,73</sup>. Since early predictions of atmospheric half-live times of OPEs  
160 were generally below the threshold (2 days) to meet the long-range atmospheric transport (LRAT)  
161 criterion of the Stockholm Convention on POPs, these chemicals were thought to be degradable  
162 enough as to have low potential for LRAT<sup>74</sup>. However, improved modeling estimations  
163 considering episodic transport, sorption to the particle phase, impact of water-mass and the  
164 uncertainty of the environmental half-live times show that some of the most used OPEs could  
165 travel very long distance<sup>42</sup>. This is consistent with filed observations showing that OPEs are  
166 ubiquitous in the atmosphere globally. Indeed OPEs were measured in atmospheric particles from  
167 the North Sea, the North American Great Lakes, the Mediterranean Sea, across the Arctic, Pacific,  
168 Indian, Atlantic and Southern Oceans, and in ocean and Polar Regions indicating they undergo  
169 LRAT<sup>2-4,6,43,61,75</sup>.

170 Liu et al.<sup>76</sup> estimated heterogeneous reaction rate constants for OPEs in air, and demonstrated  
171 that particle-bound OPEs are highly persistent in the atmosphere. However, OPEs were initially  
172 thought to be degradable enough to have less persistency in the environment and therefore low  
173 potential for LRAT<sup>74</sup>. Reaction with the OH radicals in the atmosphere was expected to be the  
174 dominant atmospheric loss process for the OPEs<sup>77</sup>. The half-life time of TCIPP was estimated in  
175 the European Risk Assessment from 2008 to be 8.6 hours<sup>78</sup>. This led to the wrong conclusion, that  
176 LRAT of TCIPP can be excluded. The atmospheric lifetimes for OPEs are estimated to be less  
177 than 1.3 days based on their gaseous OH radical rate constants<sup>76</sup>. However, recent evidence that  
178 many OPEs present in the gas phase rather than the particle phase<sup>71,79</sup>. The persistence and LRAT  
179 potential of OPEs in gas phase might be lower estimated, as they are very water-soluble. Moreover,

180 heterogeneous OH initiated oxidation was studied for OPEs in air, and approximate atmospheric  
181 lifetimes were estimated to be 5.6 (5.2–6.0), 4.3 (3.5–5.6), and 13 (11–14) days for particle-bound  
182 TPhP, TEHP, and TDCIPP<sup>76</sup>. This calculated particle phase lifetime suggested medium-range or  
183 long-range transport potential of particle bound OPEs in atmosphere. Many studies have revealed  
184 the presence of OPEs in remote environments including oceanic and polar regions as discussed  
185 above, which also demonstrates their long-range transport potential<sup>5,6,43,80,81</sup>. In spite of this, OPEs  
186 include both halogenated and nonhalogenated compounds, and show a wide range of physical and  
187 chemical properties, suggesting that their atmospheric transport is going to be variable due to wide  
188 differences in persistence, particle sorption, and air-water partitioning. Most observations in the  
189 remote areas were associated with chlorinated OPEs (TCEP and TCIPP)<sup>61,81</sup>, which also implied  
190 stronger potential of LRAT for specific compounds.

191

### 192 **2.3. Air-water exchange and atmospheric dry and wet deposition**

193 During transport from source regions to remote oceans, OPEs will be subject to exchange at the  
194 interfaces between different environmental media.<sup>82,83</sup> Atmospheric depositional processes play  
195 important role in the environmental fate of OPEs, contribute to aquatic ecosystems burden and  
196 support OPEs accumulation in marine food webs<sup>61,84</sup>.

197 The magnitude of atmospheric deposition or volatilization is a function of the physicochemical  
198 properties (especially Henry's law constant) and the concentrations of OPEs in air and water, and  
199 will be further affected by a number of environmental variables such as wind speed, temperature,  
200 salinity, and precipitation frequency and intensity<sup>82,83</sup>. There are several major processes causing  
201 atmosphere-ocean interaction of OPEs, including diffusive air-water exchange between the  
202 gaseous and dissolved phases, atmospheric dry deposition of particle-bound OPEs, and wet

203 deposition by rain and snow<sup>5,61,81,85</sup>. Briefly, dry deposition ( $F_{DD}$ ), wet deposition ( $F_{WD}$ ), and air-  
204 water exchange ( $F_{AW}$ ) can be estimated by,

$$205 \quad F_{DD} = v_D C_A \quad [1]$$

$$206 \quad F_{WD} = C_{Rain} p \quad [2]$$

$$207 \quad F_{AW} = k_{AW} \left[ \frac{C_G}{H'} - C_W \right] \quad [3]$$

208 Where  $C_A$ ,  $C_G$ ,  $C_W$  and  $C_{Rain}$  are the chemical's concentrations in particles, gas phase, water  
209 (dissolved phase), and rain, respectively.  $H'$  is the dimensionless Henry's law constant,  $v_D$  is the  
210 deposition velocity of the particles,  $p$  is the rain precipitation, and  $k_{AW}$  is the air-water mass transfer  
211 coefficient.<sup>86</sup>

212 Air-water exchange fluxes of OPEs have been estimated in a few studies. Na et al. collected air  
213 and seawater samples simultaneously on an expedition from the North Pacific to the high Arctic<sup>5</sup>.  
214 The air-water exchange flux ranged from -0.79 to 0.59 ng/m<sup>2</sup>/d, and TiBP contributed the largest  
215 proportion with seawater to air volatilization ranging from 0.19 to 0.72 ng/m<sup>2</sup>/d. In contrast, TCIPP  
216 and TCEP exhibited net deposition fluxes. In the North Atlantic and European Arctic, Li et al.  
217 reported the net volatilization flux of 5 to 1080 ng/m<sup>2</sup>/d, 61 to 12300 ng/m<sup>2</sup>/d, 12 to 2050 ng/m<sup>2</sup>/d,  
218 and 3 to 943 ng/m<sup>2</sup>/d for TCEP, TCIPP, TiBP, and TnBP, respectively<sup>61</sup>. While in the coastal area  
219 of China, the gaseous exchange fluxes fluctuated in both directions<sup>7</sup>. TCIPP showed the highest  
220 air to seawater deposition flux of 395 ng/m<sup>2</sup>/d, however TCEP displayed the highest volatilization  
221 flux of 1410 ng/m<sup>2</sup>/d. McDonough et al. calculated fugacity ratios from average equilibrium-  
222 corrected OPE concentrations in passive air and water samples, and found OPEs at dynamic  
223 equilibrium across the Farm Strait in the Arctic, with the exception of some volatilization of TnBP

224 observed at Cape Bounty lake sites in 2016 and of TDCIPP in Barrow Strait in 2015, and  
225 deposition of TPHP<sup>85</sup>.

226 In the tropical and subtropical areas of the North and South Atlantic and Pacific Oceans, Castro-  
227 Jiménez et al. calculated gaseous concentrations of OPEs from their measured particle  
228 concentrations and Henry's law constants resulted from various models<sup>81</sup>. The resulting mean  
229 gross diffusive fluxes of 14 OPEs with the estimated gaseous phase OPEs varied from 200 to  
230 60000 ng/m<sup>2</sup>/d depending on the physicochemical properties used in the calculations. These  
231 studies showed that H values calculated from different models could cause the fluxes varying in  
232 1-2 orders of magnitude, which suggesting accurate H values of OPEs need to be determined with  
233 appropriate experiment design to decline the uncertainty of air-water exchange flux.

234 The magnitude of air-water exchange direction and flux depends non-linearly on wind speed,  
235 with enhanced fluxes at high wind speeds<sup>83,87</sup>. In addition, the processes affecting the dissolved  
236 and atmospheric concentrations of OPEs can affect the magnitude of air-water exchange. For the  
237 OPE components with relatively short half-live times in the atmosphere, volatilization from  
238 seawater to air may control the diffusion fluxes. In contrast, dissolved concentrations of  
239 hydrophobic OPEs such as TEHP and EHDPP can be depleted by partitioning to particular matters,  
240 which upon settling, may deplete OPEs in the surface ocean, a process known as the biological  
241 pump. Photo- and bio- degradation can also deplete dissolved phase OPEs, thus favoring the air-  
242 to-water diffusive fluxes. Therefore, both the biological and degradative pumps favor deposition  
243 of OPEs to the marine environment. These biogeochemical controls on atmospheric deposition  
244 have been extensively studied for other semivolatile compounds<sup>88</sup>, but remain unquantified for  
245 OPEs.

246 The particle-bound OPEs contributed to  $67 \pm 17\%$  of the total OPEs in the European Arctic<sup>61</sup>,  
247 accounted for  $52 \pm 23\%$  in the Bohai and Yellow seas<sup>89</sup>, 71-93% in the North Pacific to the Arctic,  
248  $35 \pm 17\%$  in the South China Sea<sup>79</sup>,  $86 \pm 25\%$  in the North Sea<sup>3</sup>, 45% at German coast (Büsum)<sup>71</sup>,  
249 59% at Dalian, China<sup>90</sup>. The other studies have only determined OPEs in particle  
250 phase<sup>2,4,14,43,56,81,91</sup>. In the Northeast Pacific and the Arctic, the dry particle-bound OPEs deposition  
251 fluxes were estimated ranging from 13.64 to 94.17 ng/m<sup>2</sup>/d<sup>5</sup>. The same pattern was present in the  
252 North Atlantic and European Arctic, while the deposition flux of OPEs was only 2-16 ng/m<sup>2</sup>/day<sup>61</sup>,  
253 which is similar to those estimated for the South China Sea<sup>79,91</sup>. More intensive particle-bound  
254 OPEs deposition processes were observed in the open Mediterranean (70 ~ 880 ng/m<sup>2</sup>/d) and Black  
255 Seas (300 ~ 1060 ng/m<sup>2</sup>/d)<sup>4</sup>, the North African coastal Mediterranean (18 ~ 180 ng/m<sup>2</sup>/d)<sup>56</sup>, and  
256 the Bohai and Yellow Seas (21 - 250 ng/m<sup>2</sup>/d)<sup>89</sup>. These results suggested atmospheric dry  
257 deposition can significant remove particle bound OPEs from atmosphere.

258 In the tropical and subtropical Atlantic, Pacific, and Indian Oceans, the dry deposition fluxes  
259 of particle-bound OPEs ranged from 4 to 140 ng/m<sup>2</sup>/d, with higher deposition fluxes in the North  
260 Pacific and Indian Oceans<sup>81</sup>. In most studies, TCIPP and TCEP dominated the total deposition  
261 flux in the oceans. It is estimated that the surface waters of the tropical and subtropical oceans  
262 receive a yearly-integrated amount of ~2 to 13 kt/year of OPEs (sum of 14 compounds) from the  
263 dry deposition of particle-bound OPEs<sup>81</sup>.

264 Wet deposition by rain and snow precipitation can be very important quantitatively in some  
265 climatic regions and for some seasons, as an input of OPEs and other organic pollutants to marine  
266 environments. Furthermore, both snow and rain amplify the concentrations of organic pollutants  
267 in the receiving waters<sup>92,93</sup>. This amplification of concentrations by snow is driven by the high  
268 specific surface area of snow-flakes and raindrops, which increase the rain-air washout ratios. The



269 high water solubility of some OPEs also favor wet deposition fluxes. Both the washout ratios for  
270 snow and rain are generally close to  $10^5$  for OPEs<sup>92</sup>. Although the measurements of OPEs in rain  
271 water are only available for samples collected on land by few studies<sup>92,94,95</sup>, these comprise  
272 temperate and polar environments. The high concentrations of OPEs measured in rain water imply  
273 that wet deposition cannot be ignored, especially for the coastal seas. OPEs in rain water have also  
274 been reported for the South Shetland islands (Antarctica)<sup>92</sup>. In the high latitude oceans, snow  
275 deposition plays as effective scavenger for atmospheric OPEs in the Arctic, the Southern Ocean  
276 and the Antarctic. The importance of snow deposition has been highlighted by the relatively high  
277 OPE concentrations found in the snow samples from the Arctic and Antarctic expeditions<sup>61,96,97</sup>.  
278 Snow scavenging followed by snow melting can represent an important flash of pollutants from  
279 coastal land to coastal waters, which has been assessed for other pollutant<sup>98-100</sup>, but its relevance  
280 need to be explored for OPEs.

281

#### 282 **2.4. Re-emission from melting ice and snow**

283 The areas of sea ice in the Polar Regions react very sensitively to climatic changes. Because of  
284 global warming, the areas of sea ice and snow cover are shrinking, and glaciers are transporting  
285 their ice toward the low latitudes more rapidly<sup>101</sup>. Along with the processes of ice retreat and snow  
286 melting, chemical contaminants trapped in snow including OPEs could be directly discharged into  
287 the water column. Consequently, the fresh input from melting ice and snow enhanced the OPE  
288 concentrations in seawater from the East Greenland coast, which are 2-5 times higher than those  
289 in the Farm Strait<sup>61</sup>. Besides, elevated OPE concentrations were measured in the high Arctic Lake  
290 Hazen (81°49.5'N, 70°42.8'W) with concentrations from 6.8-19.3 ng/L, which are 5-10 times  
291 higher than the North Atlantic Ocean and the Northeast Pacific Ocean<sup>5,61,102</sup>.

292 In the Southern Ocean and the Antarctic, raised atmospheric concentrations of OPEs have been  
293 measured along the Antarctic coast, which can be attributed to the re-emission from the melting  
294 snow and ice of the Antarctic<sup>43</sup>. The studies for organic contaminants in snow and air in the Arctic  
295 and Antarctic have shown that melted snow inputs could influence the relative abundance of the  
296 chemical components in coastal seawater and amplify their seawater-air fugacity gradient, such as  
297 polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), neutral polyfluoroalkyl  
298 substances (PFASs) and OPEs<sup>55,103</sup>.

299 Climate change may lead to an increase of the rain periods with a decrease of snow deposition  
300 periods, which would mean that for some regions, such as the western Antarctica peninsula, the  
301 deposition by rain could become more important during the coming decades<sup>92</sup>.

302

## 303 **2.5. Ocean current transport**

304 Previous studies indicated that chlorinated-OPEs can be efficiently transported via ocean  
305 currents due to their persistence, lower volatility and high solubility<sup>40-42</sup>. OPEs have a wide range  
306 of physical and chemical properties, and varied from very polar to highly hydrophobic, which may  
307 facilitate the transport of some OPEs by water. TCIPP was generally found to be the major  
308 chlorinated phosphates in urban rainwater and Elbe River in Germany.<sup>95,104</sup> Many studies also  
309 revealed higher levels of OPEs in the coastal water compared with those in the open seas.<sup>17,20</sup> The  
310 importance of water-borne transport for OPEs depends on the deposition and subsequent transfer  
311 of OPEs to the water compartment, followed by their persistence and mobility in the water  
312 compartment<sup>41</sup>. The model results showed larger portions of the OPE emissions could enter the  
313 water body, and with motilities from 85% for TPhP to 98% TCIPP<sup>41</sup>. The higher mobility of the  
314 Cl-OPEs versus non-Cl-OPEs was caused by the low degradation rate of Cl-OPE in water, which

315 have been also proved by the measurements of OPEs in lake water<sup>105,106</sup> and oceanic water<sup>40,52,61,107</sup>.  
316 Sühling et al determined 11 OPEs in surface water from Canadian Arctic. The median of  $\Sigma$ Cl-  
317 OPEs (10 ng/L) was 6 times higher than  $\Sigma$ non-Cl-OPEs 1.3 ng/L. High concentrations of OPEs in  
318 samples from the Mackenzie River plume suggested riverine discharges acting as an OPE source  
319 to the Canadian Arctic. The  $\Sigma_{11}$ OPE inventory was estimated with a median of 4100 tonnes of in  
320 the Canadian Arctic Ocean with >99% of the OPE inventory estimated to be in the water column<sup>40</sup>.  
321 This study highlighted water-borne OPEs can be subject to long-range transport via oceanic  
322 circulations. Moreover, OPEs are widely used plasticizers and flame retardants in plastic, and  
323 floating debris can transport between continents via ocean circulations<sup>108</sup>, it is speculated that  
324 ocean gyres can bring OPEs into the open waters such as in the Southern Ocean.<sup>6</sup>

325

## 326 **2.6. Degradation of OPEs**

327 The environmental degradation of OPEs is a key issue as it determines the persistence of these  
328 chemicals in the environment. The persistence is a key aspect when assessing the risk of  
329 anthropogenic chemicals. Furthermore, in the natural environment, photo- and bio- degradation  
330 are key sinks modulating the fate of many organic pollutants, including the marine  
331 environment<sup>109,110</sup>.

332 Generally, the atmosphere is a very efficient medium for the environmental degradation of  
333 organic compounds due to the occurrence of OH radicals, among others. There are few mechanistic  
334 studies for the atmospheric degradation of OPEs, though reaction rates for the OH heterogeneous  
335 oxidation of several OPEs such as TPhP, TBEP, TEHP, TDCIPP have been measured<sup>76</sup>. The very  
336 short half-life time proposed by the EU risk assessment in 2008 for TCIPP (8.6 h) leading to the  
337 wrong conclusion that TCIPP will be not subjected to LART<sup>78</sup>. From these reaction rates, the

338 atmospheric half-live times of these OPEs range from few days to weeks. These relatively long  
339 residence times in the atmosphere are enough to explain their potential for long-range atmospheric  
340 transport, and their occurrence in the global oceanic atmosphere.

341 In seawater, the degradation of several OPEs has been evidenced from a number of  
342 observations<sup>106</sup>. Organophosphate diesters are the degradation products of OPEs flame retardants  
343 and plasticizers, and their occurrence can be generally considered a field evidence of degradation  
344 of OPEs, although some OPE diesters may have also industrial sources (For example directly  
345 added to commercial products as flame retardants and plasticizers).<sup>111</sup> Organophosphate diesters  
346 have not only been found in rivers and lakes <sup>112,113</sup>, but also in fish from global marine  
347 environments <sup>114</sup>. However, the degree to which these chemicals came from riverine inputs or were  
348 in-situ transformation products is unclear<sup>115</sup>. Diesters have also been detected in polar bears <sup>116</sup>,  
349 top predators of the Arctic marine food web. Nevertheless, the in-situ production of diesters in  
350 seawater, such as by bacterial degradation, has not been proven so far.

351 Photodegradation of OPEs in water has been reported in a few laboratory studies. Although  
352 direct photolysis did not account as the main photodegradation mechanism, depletion of OPEs  
353 occurred in pure water with dissolved oxygen, and the removal rates could be enhanced in river  
354 water<sup>117</sup>. A study with lake water for photodegradation of 5 OPEs (TCEP, TCIPP, TBOEP, TiBP  
355 and TnBP) showed the sunlight could degrade TiBP, TnBP and TBOP in 15 days, but was less  
356 active for TCEP and TCIPP<sup>106</sup>. The photodegradation is more effective for nonchlorinated OPEs  
357 were also proved by the depletion of OPEs in snow and rainwater<sup>105</sup> and global presence of TCEP  
358 and TCIPP. While the photodegradation process of OPEs in both air and sewerage need to be further  
359 explored.

360 The capacity of microorganisms to degrade OPEs has been studied mostly in isolated bacteria  
361 that represent less than 1% of the wild bacteria inhabiting in the environment<sup>118</sup>. The isolation of  
362 OPE-degrading bacteria has been performed in an attempt to optimize environmental-friendly  
363 contamination removal strategies, especially for the chlorinated OPE compounds. However, only  
364 few OPE-degrading strains have been cultured to date, mainly from soil habitats. Isolated strains  
365 able to degrade and use TCEP and TDCIPP as the sole source of P belong to Alphaproteobacteria  
366 *Sphingobium* and *Sphingomonas* species<sup>119,120</sup>, Firmicutes *Brevibacillus brevis* sp. that is able to  
367 degrade TCP<sup>121,122</sup>, and the TPhP- and TCrP-degrading *Rhodococcus* and *Sphingopyxis*<sup>123</sup> and  
368 *Roseobacter*<sup>124</sup>.

369 Like other organophosphorus triesters, OPEs degradation involves the hydrolysis of the  
370 phosphorester bonds mediated by phosphotriesterases, then phosphodiesterases and then  
371 phosphomonoesterases. The only phosphotriesterase identified so far that mediates TCEP and  
372 TDCIPP biodegradation is a haloalkylphosphorus hydrolase (HAD) that differs from the common  
373 three families of phosphotriesterases used to degrade aryl dialkyl phosphates, such as parathion and  
374 paraoxon among others<sup>125-128</sup>.

375 OPEs can be biodegraded by activated sludge from domestic sewage treatment plants and are  
376 readily susceptible to biodegradation in rivers by naturally occurring microbial populations<sup>129</sup>.  
377 While, the biodegradation of OPEs and characterization of the associated microbial communities  
378 in the natural environment is poorly studied. Currently, only two studies have been performed: one  
379 in sediments of a river receiving wastewater discharges, that observed TCEP degradation rates in  
380 communities dominated by Burkholderiales, Rhizobiales, Rhodobacterales, and  
381 Methylophilaceae<sup>130</sup>; and one in phosphorus-limited natural seawater, in which consumption of  
382 several OPEs was observed along with an increase of activity of Flavobacteria<sup>131</sup>. Given the

383 widespread occurrence of Flavobacteria in the global oceans, OPEs biodegradation could be a  
384 common feature in the upper ocean<sup>132</sup>. Furthermore, if OPEs are especially degraded in P limiting  
385 waters, then OPEs would be more persistent when P is not a limiting nutrient. Recently, it has been  
386 shown that phosphodiesterase activities are much more abundant than expected in the water  
387 columns<sup>133</sup>, and they can account for relevant P acquisition by marine bacteria under inorganic P  
388 limitation, favoring the link between atmospheric inputs of anthropogenic organic P and its  
389 utilization as a nutrient by marine microbiomes. These processes could be important interactions  
390 between anthropogenic chemicals and the Earth system functioning<sup>131</sup>. In any case, with the  
391 current knowledge, the half-life of OPEs in marine waters remain unknown, but these may be  
392 dependent on the biogeochemical province.

393

### 394 **3. Occurrences of OPEs in the global ocean**

395 Previous review summarized occurrences of OPEs in various matrices, including atmosphere,  
396 water, sediment and biota<sup>134</sup>, which indicated their ubiquity in the world and possible adverse  
397 effect on ecosystem. Here we emphasized their occurrence of OPEs in the global ocean and Polar  
398 Regions as well as environmental fate of OPEs via long-range transport.

399

#### 400 **3.1. OPEs in atmosphere**

401 OPEs have been widely detected in the atmosphere of the marginal as well as the high seas (Fig.  
402 2a). Over the Pacific, Indian, Arctic, and Southern Oceans, the concentrations of  $\sum_8$ OPEs ranged  
403 from 120 to 2900 pg/m<sup>3</sup> in airborne particles in 2010-2011, with the predominant compounds of  
404 TCEP and TCIPP<sup>43</sup>. The level and profile were consistent with the observation from the  
405 Northwestern Pacific to the Arctic Ocean (232-1884 pg/m<sup>3</sup>) in 2018<sup>5</sup>. From the tropical and  
406 subtropical Atlantic, Pacific, and Indian Oceans, the concentrations of  $\sum_{14}$ OPEs ranged from 360

407 to 4400 pg/m<sup>3</sup> in particle samples collected mostly in 2011 during the MALASPINA  
408 circumnavigation campaign<sup>81</sup>, with TCIPP, TnBP and EHDPP being the predominant OPEs (Fig.  
409 2a). In the West Pacific, the Indian Ocean and the Southern Ocean, OPEs (sum of TBEP, TCEP,  
410 TCIPP and TDCIPP) were at the levels of a few to hundreds of pg/m<sup>3</sup> in the particle samples  
411 collected along a global cruise from China to Antarctic over 2009-2010<sup>6</sup>, suggesting their  
412 circumpolar and global distribution (Fig. 2a). These levels were generally two orders of magnitude  
413 higher than those of BFRs in the ocean atmosphere<sup>135</sup>.

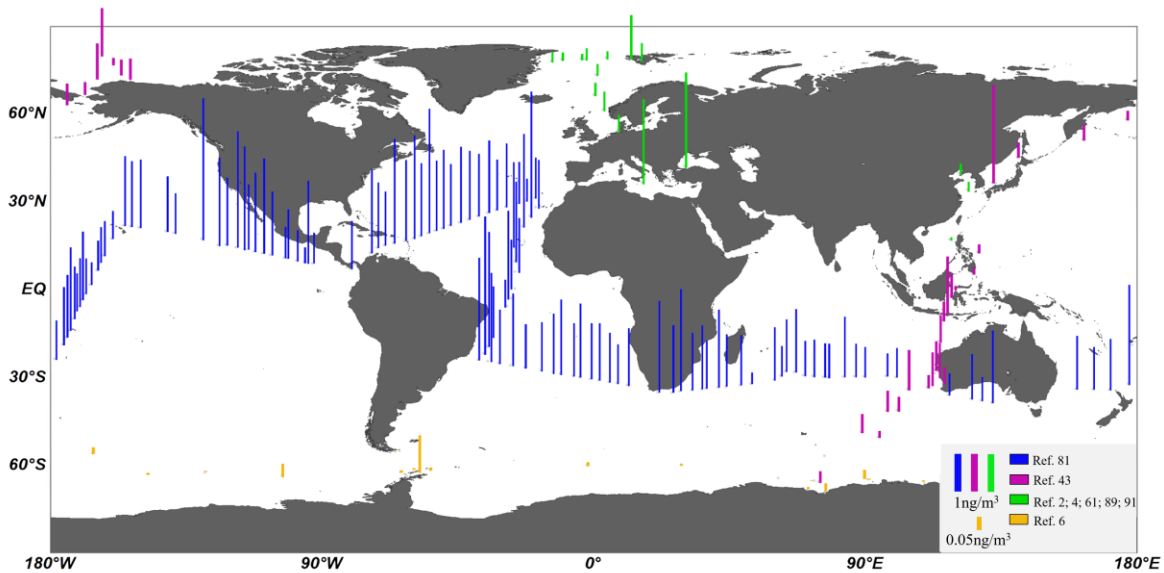
414 In the Polar Regions, OPEs have been frequently found in the Arctic for the past decade.<sup>136</sup> For  
415 instance,  $\sum_{13}$ OPEs in atmospheric particles was found at concentrations up to 1450 pg/m<sup>3</sup> in  
416 European Arctic from 2012 to 2013.<sup>2</sup> In Canadian Arctic, the level of  $\sum_{13}$ OPEs in atmospheric  
417 particles showed a generally increasing tendency from 2007 to 2013 with a median concentration  
418 of 50 pg/m<sup>3</sup><sup>14</sup>. Comparably, the concentrations of eight OPEs were found in the range of 29-180  
419 pg/m<sup>3</sup> for the particle phase and 7- 163 pg/m<sup>3</sup> for gas phase in Arctic 2014 (Fig. 2a)<sup>61</sup>. Whereas,  
420 at Longyearbyen in the European Arctic, a higher level of particle-bound OPEs were found with a  
421 median of 334 pg/m<sup>32</sup>, which might be caused by local emission. Furthermore, elevated  
422 concentrations of OPEs (357-852 pg/m<sup>3</sup>) were observed in the Arctic based on passive air sampling  
423 in 2015<sup>137</sup>, and higher level of OPEs (232 to 1884 pg/m<sup>3</sup>) was even obtained in the air samples  
424 from the Northwestern Pacific to the Arctic Ocean.<sup>5</sup> Recently, 4 OPEs in the particle phase were  
425 also found by non-target and suspect characterization of organic contaminants in Arctic air  
426 (Zeppelin Station), including TCEP and TCIPP.<sup>138</sup>

427

428

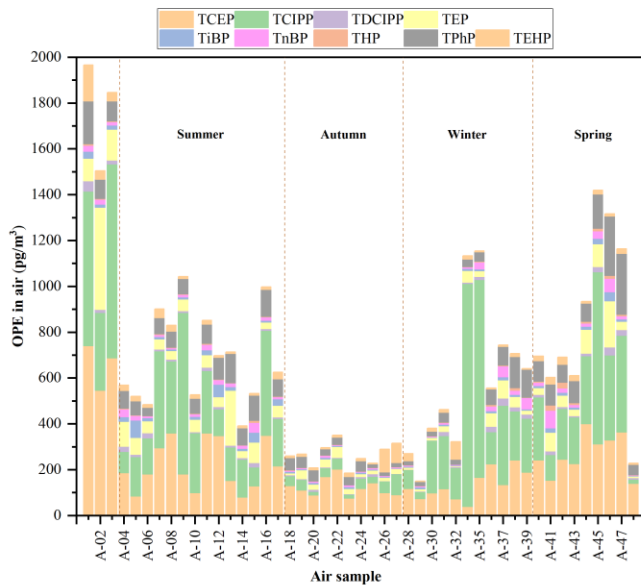
429

430 a



431

432 b



433

434 **Figure 2.** Global distribution of OPEs in the oceanic air <sup>2,4,6,43,61,81,89,91</sup>(a), which is synthesized  
435 with OPE data from research cruises, e.g. R/V Polarstern (Germany)<sup>61</sup>, Snow Dragon (China)<sup>6</sup> and  
436 Malaspina circumnavigation expedition (Spain)<sup>81</sup>. The lower figure shows seasonal variation of  
437 OPEs in air at Yongxing Island in the South China Sea in 2018 (b)<sup>79</sup>



438 There is limited data on these chemicals in the Antarctic. The concentrations of OPEs ranged  
439 from 6.0 to 141 pg/m<sup>3</sup> in four particle samples collected nearby the Antarctic Peninsula in 2010<sup>6</sup>.  
440 A long-term air monitoring campaign in the Western Antarctic Peninsula over 2014-2018 revealed  
441 that the concentrations (gas + particle phases) of  $\sum_8$ OPEs ranged from 33.9 to 404 pg/m<sup>3</sup> with a  
442 mean of 119±12.0 pg/m<sup>3</sup>.<sup>139</sup> The most abundant OPEs were TnBP and TCIPP in air, and  
443 chlorinated-OPEs (TCEP, TCIPP and TDCIPP) accounted for 51% of total OPEs on average. This  
444 level was even comparable to those found in Arctic air, suggesting input of OPEs into Antarctic  
445 via LRAT in recent years.

446 In general, elevated levels of OPEs in air are found in coast-near regions, especially near urban  
447 and industrial areas, followed by the Arctic and finally the Southern Ocean. This ubiquity of OPEs  
448 in the global atmosphere contrasts with previous model predictions of limited long-range  
449 atmospheric transport. Such discrepancy is probably related to a poor empirical knowledge of the  
450 physicochemical properties of OPEs.

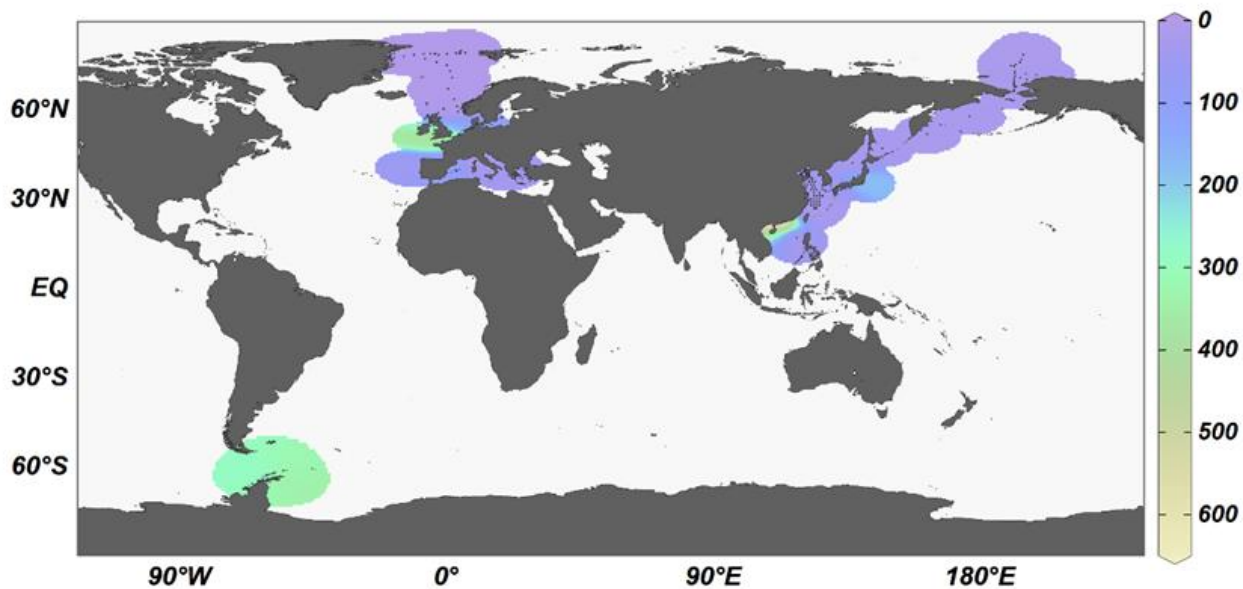
451

### 452 **3.2. OPEs in seawater**

453 Most available data on OPEs in water were from studies on effluents from the wastewater  
454 treatment plants (WWTPs), as well as inland surface waters<sup>28,41,51,57,134</sup>. WWTPs were considered  
455 an important sink of many POPs emitted from urban anthropogenic sources, where the OPEs reach  
456 concentrations up to µg/L<sup>134,140,141</sup>. Experiments for the removal rate of TCIPP from WWTPs in  
457 Germany have shown more than 50% of TCIPP found in effluent, which raising the concern for  
458 OPEs in surface water. Consequently, OPEs have been found in the surface waters from lakes and  
459 rivers with concentrations ranging from 10 to 1000 ng/L<sup>41,51,60,67,142</sup>.

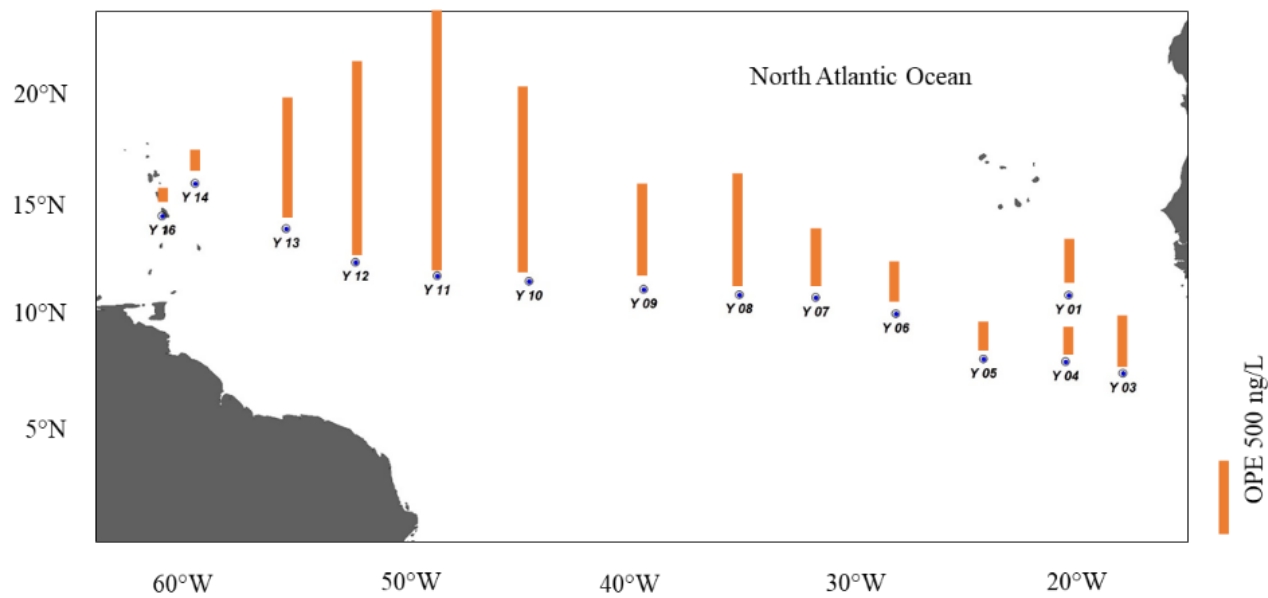
460

461 a



462

463 b



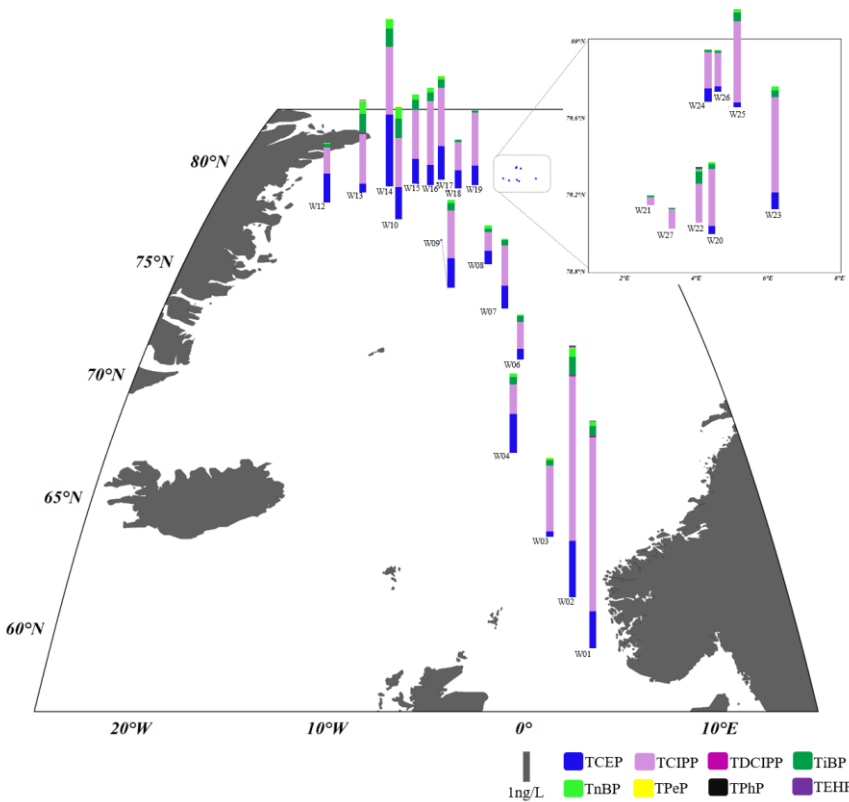
464

465

466

467

468



470

471 **Figure 3.** Concentrations of OPEs (ng/L) in seawater in the global oceans<sup>5,20,51,52,61,104,143-145</sup>,  
 472 which shows high levels of OPEs present at marginal seas of Asia and Europe (a); OPEs discharged  
 473 from the Amazon River were transported in the tropical Atlantic<sup>52</sup>(b), and oceanic transport of  
 474 OPEs from the North Atlantic to the Arctic Ocean<sup>61</sup> (c)

475

476 In a survey in coastal areas of seven European countries<sup>146</sup>, OPEs were detected in all samples  
 477 and the sum concentrations of OPEs (TBOEP, TCEP, TCIPP, EHDPP, TNBP, TPhP, and TDCIPP)  
 478 ranged from 0.43 to 867 ng/L in transitional/coastal water (Fig. 3a). High levels were found in the  
 479 seawaters from the UK ( $\sum_7$ OPEs,  $275 \pm 34.9$  ng/L) and Portugal ( $\sum_7$ OPEs,  $547 \pm 437$  ng/L),  
 480 correlating with the sampling sites that were the closest to urban areas. Comparable levels (mean  
 481  $243 \pm 327$  ng/L) were found for the  $\sum_9$ OPEs in the dissolved water phase samples collected in the

482 Bay of Marseille (NW Mediterranean Sea)<sup>65</sup>. Likewise, from the German Bight (North Sea), the  
483 concentrations of  $\sum_{18}$ OPEs were at a range of 5-50 ng/L in the seawater in 2010, correlating  
484 negatively ( $r=-0.94$ ) with salinity<sup>22</sup>. These results are generally consistent with those in coastal  
485 seas of China, where the concentrations of  $\sum_{7}$ OPEs were at a range of 8-98 ng/L in the Bohai  
486 Sea and Yellow Sea, and TCIPP and TCEP were the dominant pollutants<sup>147</sup>. However, relatively  
487 higher levels of OPEs were also observed in seawater near the coastal cities in China, e.g., 91.9–  
488 507 ng/L in the Yellow Sea and East China Sea<sup>21</sup>, 87.6 to 969.4 ng/L in the Laizhou Bay<sup>67</sup>, and  
489 810-3620 ng/L in the off-shore of Bohai Bay<sup>17</sup> (Fig. 3a). These values are consistent with  
490 observations in the Pearl River Delta, South China Sea, Yellow River Estuary and Tokyo Bay,  
491 where the sum concentrations of  $\sum_{14}$ OPEs in the range of 15-1790 ng/L, 1-147 ng/L, 253-1720  
492 ng/L, and 107-284 ng/L, respectively (Fig. 3a).<sup>145</sup> . In the Western Pacific, 10 OPEs were  
493 determined in seawater with the concentrations of  $\sum_{10}$ OPEs ranging from 3.0 to 48.4 ng/L (mean  
494  $25.0 \pm 10.5$  ng/L)<sup>107</sup>. TCEP was the predominant OPE. In the tropical North Atlantic, dissolved  
495 OPEs (1300 ng/L) from the Amazon River were transported more than 3000 km via the North  
496 Brazil Current and its retroflexion (Fig. 3b)<sup>52</sup>.

497 In the high seas, the sum concentrations of 3 Cl-OPEs ranged from 0.9 to 17.4 ng/L in the Arctic  
498 surface water sampled by passive polyethylene samplers (PEs)<sup>85</sup>. Similarly, the concentrations of  
499  $\sum_{8}$ OPEs in the North Atlantic and the Arctic were measured using liquid-liquid extraction for 0.8  
500 L seawater, which ranging from 0.35 to 8.4 ng/L. The four highest concentrations measured at  
501 sites near continents<sup>61</sup>, implying anthropogenic inputs into ocean. In the Canadian Arctic, the mean  
502 concentrations of  $\sum$ chlorinated-OPEs (Cl-OPEs) and  $\sum$ non-chlorinated-OPEs were 10 ng/L and  
503 1.3 ng/L, respectively, in surface water over 2013-2018<sup>40</sup>. Similarly, two chlorinated OPEs  
504 (TCIPP and TDCIPP) were observed at 2.7 to 8.4 ng/L in Arctic seawaters sampled by an on-board

505 passive sampling strategy<sup>148</sup>. Occurrence of OPEs was observed in seawater from the  
506 Northwestern Pacific to the Arctic in 2018, and the sum concentrations ranged from 8.5 to 143  
507 ng/L<sup>5</sup>, which are higher than those from the European Arctic<sup>61</sup> (Fig. 3c). In addition, there is no  
508 clear spatial trend for OPEs in seawater from China towards the Arctic, while a declining trend  
509 was noticed from the North Atlantic to the Arctic (Fig. 3c)<sup>61</sup>, which shows clearly oceanic  
510 transport from European seas to the Arctic. Interestingly, relatively high concentrations of  $\Sigma_6$ OPEs  
511 were found in the range of <5.0- 44.4 ng/L in seawater of Fildes Peninsula, Antarctica<sup>143</sup>, and 19.6-  
512 9209 ng/L in freshwater from the northern Antarctic Peninsula<sup>149</sup>, which are attributed to local  
513 emissions from scientific research stations and tourist vessels in the Antarctic Peninsula.

514

### 515 **3.3. OPEs in marine sediment**

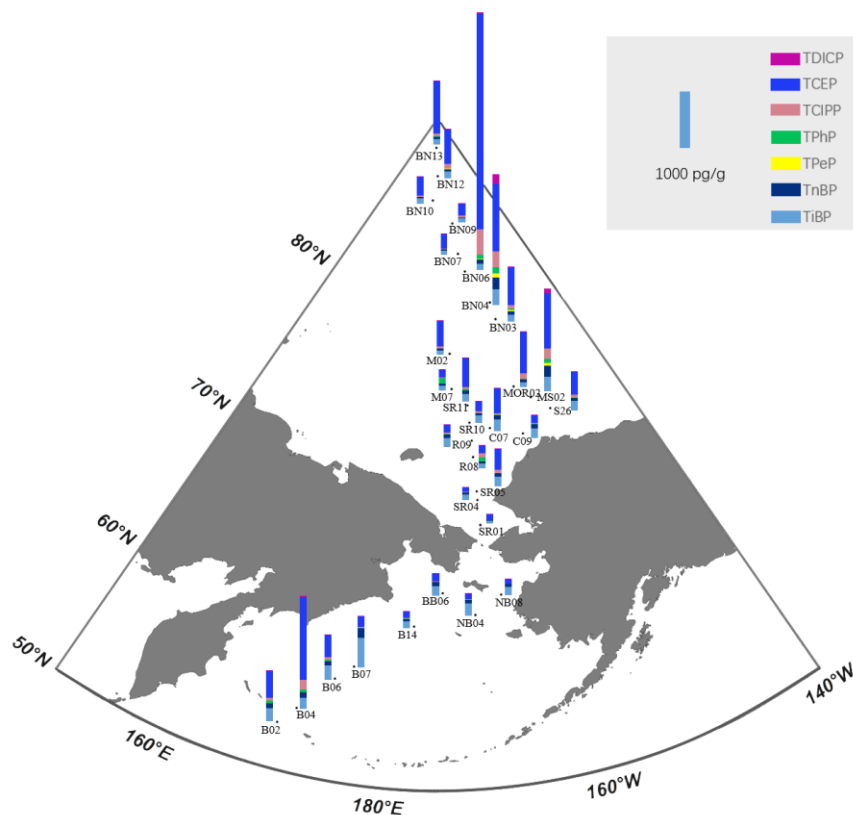
516 Influenced by the different degrees of human activities, average  $\Sigma$ OPEs concentrations  
517 ranging over two orders of magnitude (0.35-71 ng/g dw) have been reported in sediment from  
518 ocean regions, including straits, near-shore and off-shore areas (Figure 4c, Table S2). Elevated  
519 levels of  $\Sigma$ 18OPEs were found in sediments along the coast of Korea, with the maximum and  
520 average values of 347 and 71.0 ng/g dry weight (dw), respectively, among which the higher  
521 concentrations usually occurred in harbors<sup>150</sup>. In the Bohai region of China, decreasing levels of  
522  $\Sigma$ OPEs were reported in sediment with the extension of sampling areas: Laizhou Bay (6.65-102  
523 ng/g dw<sup>151</sup>; 0.100-96.9 ng/g dw<sup>152</sup>) > Bohai Bay (1.66-28.7 ng/g dw)<sup>17</sup> > Bohai Sea (0.205-4.55  
524 ng/g dw)<sup>153</sup> (Figure 4b). A few to tens of ng/g dw of  $\Sigma$ OPEs were found for sediments from Beibu  
525 Gulf (range: 4.35-22.1, ng/g dw)<sup>154</sup>, the Taiwan Strait (range: 5.26-34.2 ng/g dw)<sup>10</sup>, the Bohai and  
526 East China Sea (1.76-49.9 ng/g dw)<sup>155</sup>, the coast of Hainan Island (range: nd-60.0 ng/g dw)<sup>11</sup> and  
527 the Pearl River Estuary (range: 12.0–66.0 ng/g dw)<sup>156</sup> in China, the Maizuru Bay in Japan (range:

528 <0.500–56.0 ng/g dw)<sup>157</sup>, and the San Francisco Bay in USA (median: 23.0 ng/g dw)<sup>19</sup>. Recently,  
529 Alkan et al.<sup>68</sup> reported relatively high levels of  $\Sigma_9$ OPEs (range: 4-227 ng/g dw) in sediments across  
530 the Gulf of Lion in northwest Mediterranean Sea. Limited studies reveal that the levels of OPEs in  
531 ocean sediment are substantially lower than those found for the marginal seas. The detected  
532 concentrations of  $\Sigma_7$ OPEs from the North Pacific to the Arctic Ocean ranged from 0.2 to 4.7 ng/g  
533 dw, with the average value of 0.9 ng/g dw (Figure 4a)<sup>66</sup>. This study revealed that the concentrations  
534 of  $\Sigma_7$ OPEs, especially the chlorinated OPEs (TCEP, TCIPP and TDCIPP), increased from Bering  
535 Strait to the Central Arctic Ocean, implying the transference and accumulation of OPEs in oceanic  
536 sediments. Gao et al.<sup>144</sup> reported higher levels of  $\Sigma_7$ OPEs in the sediment of Ny-Ålesund, Svalbard,  
537 the Arctic (range: 0.01-14.9 ng/g dw) in comparison to those in Central Arctic Ocean (range: 0.32-  
538 4.7 ng/g dw) reported by Ma et al.<sup>66</sup>, suggesting low temperatures limit the degradation of OPEs  
539 in polar oceans<sup>144</sup>. Recently, Sühling et al. reported elevated concentrations of  $\Sigma_{11}$ OPEs (median:  
540 8.3 ng/g dw, range: 0.12-57 ng/g dw) in sediment in the Canadian Arctic Ocean, which has been  
541 attributed to the local riverine discharge<sup>40</sup>. In many studies, chlorinated OPEs (especially TCEP  
542 and TCIPP), have been the most abundant detected OPEs in ocean sediments, consistent with their  
543 extensive usage and their low degradation rates. Due to the relatively strong hydrophobicity, TEHP  
544 (log Kow: 9.49)<sup>19,153</sup> and TCrP (log Kow: 5.11)<sup>11</sup> have also been identified as the dominant OPEs  
545 in sediments by several studies. In contrast, TnBP and TBOEP were the most abundant OPEs in  
546 sediments from Taiwan Strait, China<sup>10</sup> and Western Scheldt estuary, Netherlands<sup>158</sup>, respectively.  
547 This regional pollution feature should be attributed to the large usage of these compounds locally.

548 Although the deep ocean is commonly considered as the final oceanic repository of OPEs,  
549 inventory analysis shows that only a small proportion of the produced OPEs in the world have  
550 been preserved in ocean sediment<sup>40,66,153</sup>, but the reservoir in the water column remains unknown.

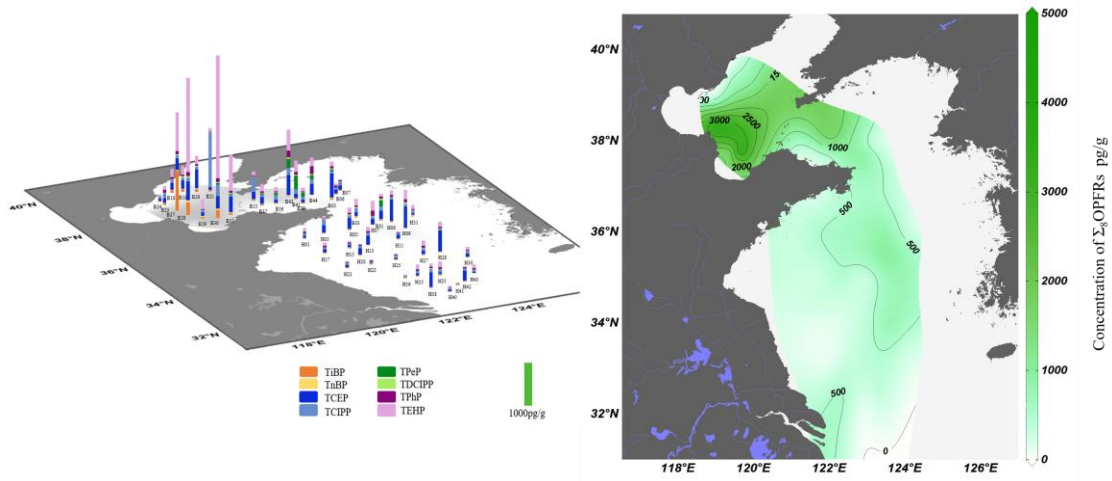
551 In a study on OPEs inventory in the Canadian Arctic Ocean, Sühling et al. estimated that water  
 552 column OPEs even accounted for ~99% of the total OPEs inventory<sup>40</sup>. The transfer of OPEs from  
 553 surface waters to sediments is mediated by the biological pump, thus the sorption of OPEs to  
 554 settling particles, a process especially relevant for the more hydrophobic OPEs. The study for  
 555 partitioning of OPEs between the water phase and sewage sludge in WWTPs has shown only 1 %  
 556 of the OPEs entering the WWTP retained by the sludge, and most of the chlorinated OPEs went  
 557 through the plant with water phase without degradation<sup>25</sup>. As marine sediment contents less  
 558 organic matter than sludge, during vertical transport, the microbial degradation of OPEs concurrent  
 559 with organic matter mineralization might be limited. Generally, the extent of sediments and water  
 560 column as a final sink of OPEs will depend on the water column biogeochemistry, that needs  
 561 further research.

562 a



564

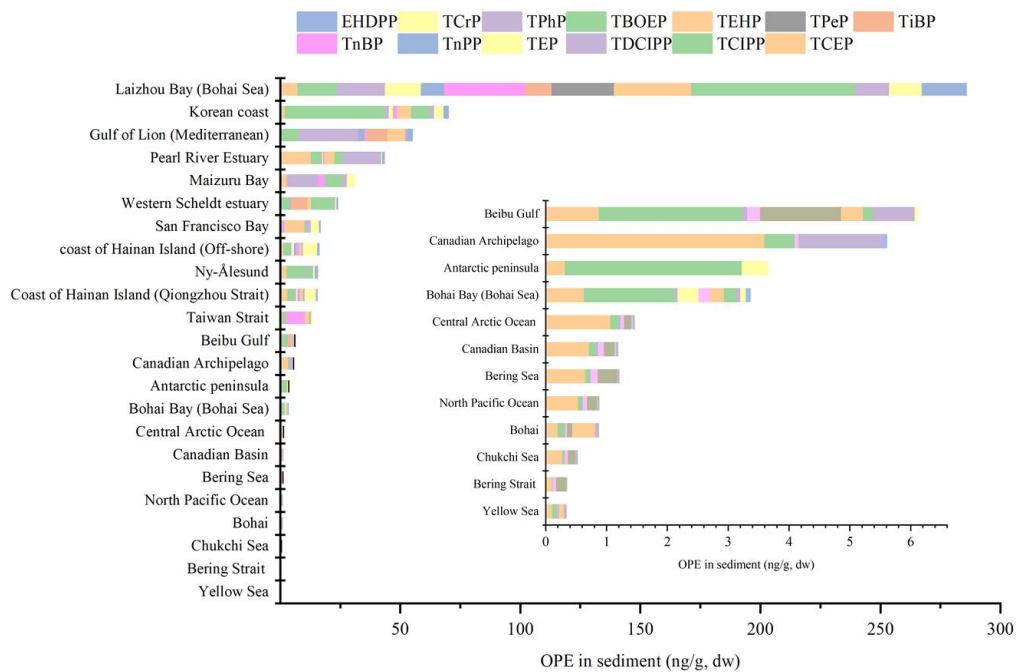
b



565

566

c



567

568

569

570

571

**Figure 4.** Spatial distribution of OPEs in the sediment from the North Pacific to the high Arctic<sup>66</sup> (a), and in the Bohai and Yellow Seas<sup>153</sup> (b). OPEs concentrations in sediments from different regions are summarized (c), shows the coastal areas play as important sink for OPEs.<sup>13,18,19,40,65,144,153,154,157,159</sup>



### 572 3.4. OPEs in snow from Polar Regions

573 Freshwater discharge from snow and ice to the ocean is increasing across the Arctic and  
574 Antarctic in response to anthropogenic climate change<sup>160</sup>. The strong seasonal changes in  
575 environmental conditions associated with emissions of organic chemicals from melting ice and  
576 snow in the polar regions may amplify their effects on the marine ecosystems<sup>93</sup>. In the Antarctic,  
577 OPEs were detected in surface snow on the ice sheet along a transect from Zhongshan Station  
578 (69.3733S, 76.3778E) to Kunlun Station (80.4169S, 77.1161E), near Dome Argus<sup>97</sup>. TCEP was  
579 the dominant component of 12 OPEs in all snow samples with concentrations ranging from 0.05  
580 to 2.0 ng/L, followed by TCIPP, TiBP and TBEP. The appearance of TCEP in fresh snow clearly  
581 indicates that TCEP is more persistent and could be transported to the Antarctic ice sheet. This  
582 finding is consistent with Xie et al., who reported the occurrence of OPEs in snow samples  
583 collected at Dome Concordia in 2016<sup>96</sup>. Nine OPEs were detected in all snow samples with the  
584 total concentrations ranging from 7.2 to 20.5 ng/L. TCIPP was the dominant compound and  
585 accounted for 64.6% of the sum, followed by TnBP (9.8%) and TCEP (8.9%). The mean  
586 concentration of TCIPP was 8.2 ng/L which was 7 times higher than those of TCEP (1.1 ng/L),  
587 TnBP (1.2 ng/L) and TEP (0.96 ng/L). Other detected OPEs were TDCIPP (0.32 ng/L), TPhP (0.44  
588 ng/L), TPeP (0.19 ng/L), TEHP (0.18 ng/L) and TPrP (0.026 ng/L). The ratio TnBP/TCIPP is  
589 similar to those in the snow from urban areas and indoor dusts<sup>95,161,162</sup>, implying that OPEs in snow  
590 at Dome C might be partially attribute to local sources, e.g. emissions from the research stations.  
591 However, LRAT of OPEs to the inland of the Antarctic need to be further explored.

592 In the Arctic, OPEs have been measured in surface snow collected along a transect between  
593 East Greenland and Svalbard<sup>61</sup>. The concentrations of  $\sum_8$ OPEs (TCEP, TCIPP, TDCIPP, TnBP,  
594 TiBP, TPhP, TEHP, TPeP) ranged from 4.36 to 10.6 ng/L with a mean of 7.83 ng/L. TCIPP was

595 the most abundant OPEs in Arctic snow with a mean of 3.89 ng/L, followed by TiBP (2.00 ng/L),  
596 TCEP (1.29 pg/L) and TnBP (0.63 pg/L). The concentrations of OPEs in snow samples collected  
597 from coastal sites were 2 times higher than those from the central Arctic, and the composition  
598 pattern of OPEs in snow was comparable with that of OPEs in seawater. These pioneering works  
599 showed the major role of long-range atmospheric transport and snow deposition in the global  
600 distribution of OPEs<sup>102</sup>.

601

### 602 **3.5. OPEs in organisms**

603 The investigations on OPEs in marine organisms including zooplankton, invertebrates,  
604 bivalves, fish, birds and mammals have revealed their widespread occurrence of OPEs across food  
605 webs in various oceanic environments (Fig. 5a). In general, markedly lower concentrations of  
606 OPEs were reported in biota samples collected from North America compared to those from  
607 European and Asia regions. For example, the levels of  $\Sigma_{13}$ OPEs of bivalve samples in San  
608 Francisco Bay, United States (US) ranged from 8.7-25 ng/g lw<sup>19</sup> as compared to those from the  
609 coast of Korea ( $\Sigma_{13}$ OPEs: 18.4-1516 ng/g lw)<sup>150</sup>, Sweden ( $\Sigma_{11}$ OPEs: 190-1600 ng/g lw)<sup>163</sup> and  
610 Spain (individual OPE: nd-623.6 ng/g lw)<sup>64</sup>. The concentrations of OPEs in harbor seal from US  
611 (nd-56 ng/g lw)<sup>19</sup> and in Polar bear from Canada (nd-0.902 ng/g lw)<sup>164</sup> were also much lower than  
612 those from Svalbard, Norway (nd-372.41 in harbor seal and nd- 52.5 ng/g lw in polar bear)<sup>84</sup> (Fig.  
613 5a). Comparable concentrations of  $\Sigma$ OPEs in fish were reported in several studies on samples from  
614 Svalbard, Norway (mean  $\Sigma_{14}$ OPEs: 713 ng/g lw)<sup>84</sup>, Manila Bay, Philippines (mean  $\Sigma_9$ OPEs: 683  
615 ng/g lw)<sup>165</sup>, NW Mediterranean Sea (mean  $\Sigma_{19}$ OPEs: 526 ng/g lw)<sup>166</sup> and coast of Sweden (mean  
616  $\Sigma_{11}$ OPEs: 342 ng/g lw)<sup>163</sup>, while relatively high levels (mean  $\Sigma_{20}$ OPEs: 1630 ng/g lw) were found  
617 for Laizhou Bay, Bohai Sea, China<sup>152</sup>. Sala et al. detected OPEs in edible fish from the  
618 Mediterranean Sea including European sardine (*Sardina pilchardus*), European anchovy (*Engraulis*

619 encrasicolus), and European hake (*Merluccius merluccius*), with concentrations between 0.38 and  
620 73.4 ng/g wet weight<sup>167</sup>. Pattern analysis of OPE congeners shows that TCIPP, TBOEP, TnBP,  
621 TPhP, TEHP and TDCIPP were commonly detected as the predominant OPEs in marine  
622 organisms.<sup>12,19,65,84,152,154,157,158,163-166</sup> The differences in the OPE patterns among studies may result  
623 from local pollutions from near-shore<sup>163</sup>.

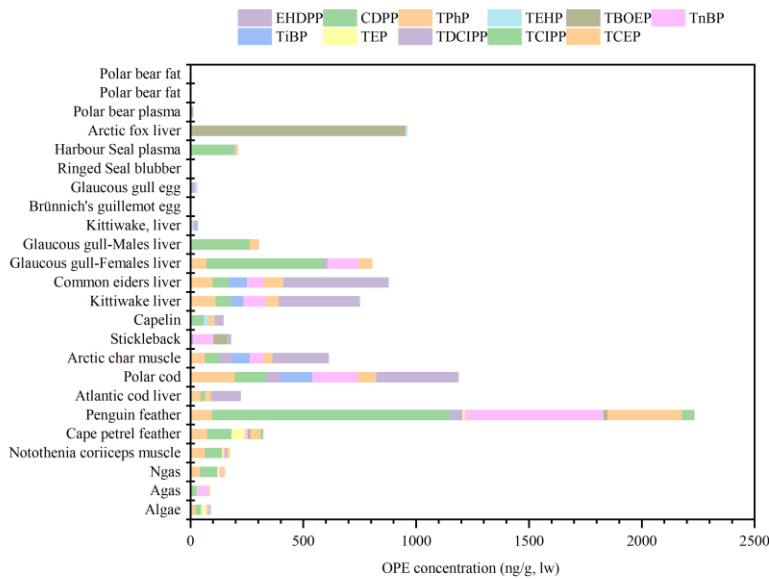
624 Species-dependent discrepancies in OPEs concentrations have been observed in marine  
625 organisms, which were significantly lower in birds and mammals than in fish. Hallanger et al.  
626 reported that 9 OPEs (TCEP, TCIPP, TDCIPP, TPHP, EHDPP, TBOEP, TCrP, TEHP and DPhBP;  
627 mean: 7.81-537.16 ng/g lw) were found in capelin collected from Svalbard, Norway, as compared  
628 to those of <5 OPEs found in most of the other species, including kittiwake, brünnich's guillemot,  
629 glaucous gull, ringed seal, harbour seal, arctic fox and polar bear (mean: 1.91-955.09 ng/g lw)<sup>84</sup>  
630 (Fig. 5a). Low concentrations of individual OPEs were reported for the peregrine nestlings in the  
631 Great Lakes Basin, ranging from 0 to 7.5 ng/g ww<sup>168</sup>. Another study measured OPEs in liver and  
632 blubber of harbour porpoises from the UK, and reported that only 5 OPEs (TEP, TPhP, TEHP,  
633 TBOEP and EHDPP) were detected with low detection frequencies (DFs) of 3-44%<sup>12</sup>. Four out of  
634 13 OPEs (TCEP, TCIPP, TDCIPP and TPhP) were found in harbor seal blubber in San Francisco  
635 Bay, United States with the median concentrations of <LOD to 13 ng/g lw<sup>19</sup>. Five out of 17 OPEs  
636 were quantifiable at sub-ppb levels in polar bear fat samples, but with variable and low detection  
637 frequencies<sup>164</sup>. This contrast with high levels of  $\Sigma$ OPEs detected in brain (1530 ng/g lw), muscle  
638 (645 ng/g lw) and blubber (267 ng/g lw) in dolphin collected from the Alboran Sea<sup>169</sup>.

639

640

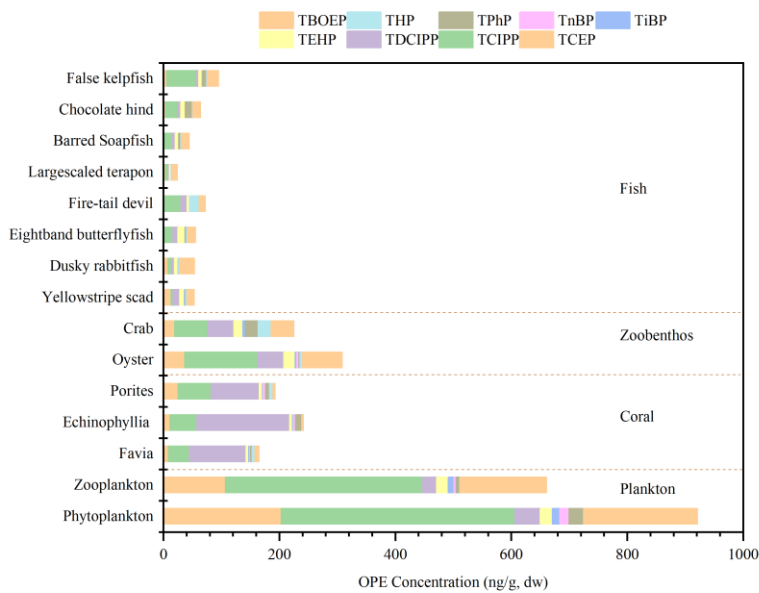
641

642 a



643

644 b



645

646 **Figure 5.** Concentrations of OPEs (ng/g lw) in organism samples from Antarctic Peninsula and  
 647 the Arctic ocean<sup>28,84,164,171-174</sup> (a); and nine OPEs (ng/g, dw) in different species in the South China  
 648 Sea<sup>170</sup>(b).

649 In tropical food webs, 11 OPEs were detected in fifteen types of organism from the South China  
650 Sea, and the concentrations of OPEs in the organisms decreased with the increase of their trophic  
651 levels in the order: phytoplankton (922 ng/g dw) > zooplankton (660 ng/g dw) > oysters (309 ng/g  
652 dw) > crabs (225 ng/g dw) > coral tissues (202) > fishes (58.2)<sup>170</sup> (Fig. 5b). TCIPP, TCEP and  
653 TCIDPP were dominant OPEs in phytoplankton, zooplankton and in coral tissues. While,  
654 Zoobenthos and the eight fish species had similar OPE composition profiles dominated by TCIPPs  
655 and TBOEP<sup>170</sup>.

656

#### 657 **4. Bioaccumulation and effects in marine organisms**

658 Several studies have shown that higher exposure to OPEs was observed in demersal marine  
659 organisms than in zooplankton and phytoplankton, indicating that greater accumulation of OPEs  
660 occurs in the benthic environment. For examples, in the organisms from coast of Sweden, the  
661 concentration of EHDPP was reported 14,000 ng/g lw in eelpout (bottom dwelling fish) compared  
662 with those found for other fish (< 78 ng/g lw)<sup>163</sup>. The concentrations of  $\Sigma_9$ OPEs in demersal fish  
663 (230-1900 ng/g lw) were significantly higher than those in pelagic fish (110-760 ng/g lw) from  
664 Manila Bay<sup>165</sup>. Bekele et al. also observed significant difference in  $\Sigma_{20}$ OPEs between benthic fish  
665 (mean: 2120 ng/g lw) and pelagic fish (1200 ng/g lw)<sup>152</sup>. However, high OPE concentrations have  
666 been found in zooplankton (i.e. at the base of many pelagic food webs) in coastal Mediterranean  
667 with vales reaching up to 4.6  $\mu$ g/g d.w for the  $\Sigma_9$ OPEs<sup>65</sup>. Overall, the profiles of OPEs in marine  
668 organisms are influenced by sampling sites, species and even developmental stages of such  
669 organisms, which could be attributed to different usage of OPEs in different regions, as well as the  
670 discrepancies in habitat, diet, and metabolic and accumulation behaviors of OPEs in the  
671 organisms<sup>84,163,165</sup>

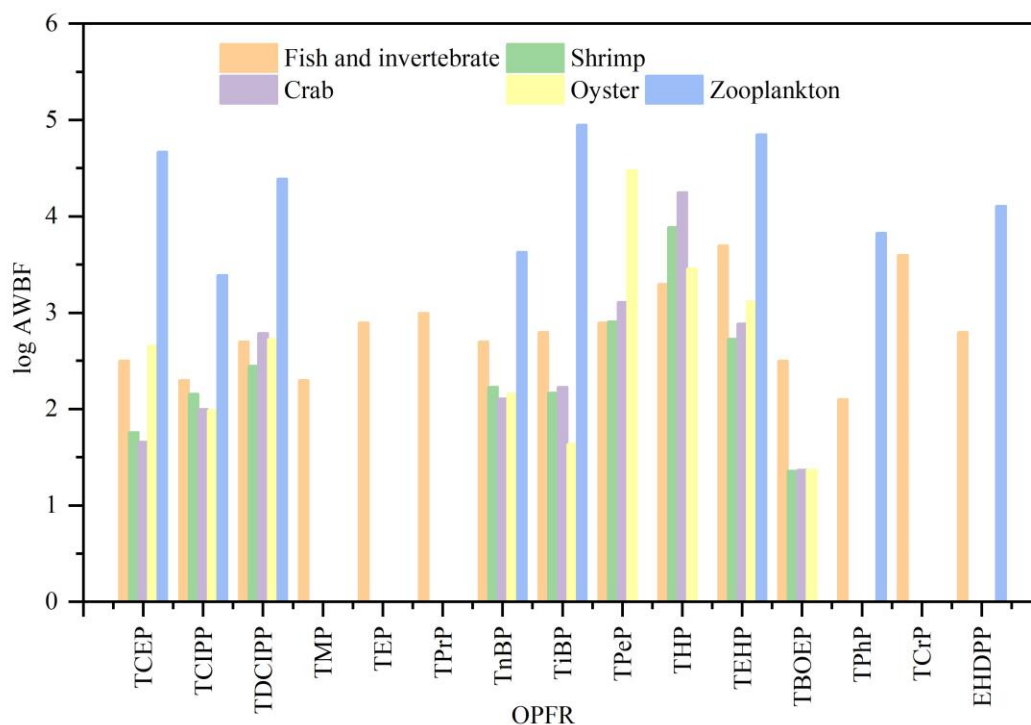
672 The bioaccumulation and biomagnification potential of OPEs in marine organisms depends on  
673 their physicochemical properties, bioavailability and extent of biotransformation<sup>165</sup>.  
674 Octanol–water partition coefficient ( $\log K_{ow}$ ) values of OPEs cover a large range from -0.65 (TMP)  
675 to 9.49 (TEHP)<sup>134</sup> (Tab. 1). Significant correlations of bioconcentration factors (BCFs) with  $\log$   
676  $K_{ow}$  values of OPEs are observed in marine biota, implying that hydrophobicity plays an important  
677 role in bioaccumulation of OPEs<sup>152,154</sup> (Fig. 6 and Tab. S4). While different result was obtained by  
678 Schmidt et al. that no relationship between BCFs and  $\log K_{ow}$  of OPEs was observed<sup>65</sup>. BCFs  
679 higher than the threshold value (5000 L/kg) used under the Stockholm Convention on POPs to  
680 identify bioaccumulative chemicals were generally found for TCEP, TDCIPP, TiBP, EHDPP and  
681 TEHP in this study<sup>65</sup>. Furthermore, several studies showed that most OPEs detected in marine  
682 organisms are not correlated with the lipid contents<sup>150,158,163,165</sup>, with the exception of TEP and  
683 TPpP reported by Kim et al. in fish<sup>165</sup>. Weak biomagnification of OPEs through food web also  
684 implies limited bioaccumulation of these compounds. As stated above, even lower detection  
685 frequencies (DFs) and concentrations of OPEs were observed in higher trophic levels (such as  
686 birds, seals, arctic foxes and polar bears) than in fish in Arctic biota<sup>84</sup>. This may be due to either  
687 poor assimilation from the diet or rapid metabolism of OPEs in these species such as birds and  
688 polar bears<sup>164</sup>.

689 Kim et al. investigated the biomagnification of OPEs in 20 species of fish in Manila Bay,  
690 Philippines by establishing the correlations of  $\delta^{15}N$  values with concentrations of OPEs in fish<sup>165</sup>.  
691 The result showed that OPEs did not bio-magnify through the food web except for TPhP in  
692 demersal fish<sup>165</sup>. However, Brandsma et al. reported that the levels of TPhP decreased with the  
693 increasing in trophic levels both in benthic and pelagic food web in Western Scheldt estuary,  
694 Netherlands, while the biomagnification of TBOEP, TCIPP and TCEP (trophic magnification

695 factors >1) through the benthic food web was observed<sup>158</sup>. In the food web in Laizhou Bay, China,  
696 8 OPEs (including TEP, TnBP, TCIPP, TDCIPP, TBOEP, TEHP, CDPP and TCrP) showed  
697 trophic magnification<sup>152</sup>. These results may be influenced by the distinct input of OPEs in local  
698 species and different metabolic processes among these species. Furthermore, research on  
699 bioaccumulation and biomagnification of OPEs through marine food webs is very limited, and just  
700 performed in select tissue, such as liver, and plasma in marine mammals<sup>84</sup>. More attention should  
701 be paid to the bioaccumulation behavior of OPEs in marine organisms to determine the  
702 biomagnification potential of these chemicals.

703 At present, little is known about the biological effects the OPEs elicited in marine species,  
704 populations, ecological systems, and humans, particularly from a one-health perspective. Wu et al.  
705 suggested that TCIPP could disturb the immune system of marine mussel by evaluating the  
706 endpoints including reactive oxygen species, apoptosis, antioxidant system and related gene  
707 expressions<sup>175</sup>. Several studies investigated toxic effects of OPEs to algae, which are important  
708 primary producers in the marine ecosystem and sensitive to pollutants<sup>176-178</sup>, and reported that  
709 TDCIPP inhibited the population growth of *Phaeodactylum tricorutum* in a concentration-  
710 dependent manner by disrupting photosynthesis<sup>177</sup>. Both TDCIPP and TnBP increased the levels  
711 of reactive oxygen species and led to oxidative damage in *Phaeodactylum tricorutum* cells at the  
712 experimental concentrations (2-10 mg/L for TDCIPP and 0.2-1.6 mg/L for TnBP)<sup>177,178</sup>. Although  
713 neurotoxicity, and developmental and reproductive toxicity of some OPE compounds (i.e.,  
714 TCEP<sup>179-182</sup>, TCIPP<sup>179,181</sup>, TDCIPP<sup>179,181-189</sup>, TPhP<sup>179,182,185,187,190</sup>, TCrP<sup>179,182,187</sup>, TBOEP<sup>179,180</sup> and  
715 TnBP<sup>180</sup>) have been reported for freshwater fish models, biological effects of OPEs in marine fish  
716 and more higher trophic levels of organisms are rarely investigated. A recent study found that  
717 TPhP could disrupt ecologically-relevant behaviours inof *Coturnix japonica* at environmentally

718 relevant or greater concentrations, implying the health risks of OPEs in wild birds<sup>191</sup>. In addition,  
 719 since OPEs tend to accumulate in the benthic marine environment as discussed above, much more  
 720 attention should be paid to the health risks of bottom dwelling species. The input of OPEs to the  
 721 marine environment is persistent and therefore, knowledge on potential ecological risks caused by  
 722 these compounds, especially adverse effects resulting from chronic exposure, antagonistic  
 723 interactions and biomagnification, is urgently required in the future<sup>19,152,165</sup>.



724  
 725 **Figure 6.** Biota-water accumulation factors (log BCF) of OPEs in marine organisms<sup>65,152,154</sup>  
 726

727 **5. Future perspectives**

728 Both ocean currents and the atmosphere are relevant pathways for OPEs transport on a global  
 729 scale, but they have different contributions to the global distribution of individual OPEs, which  
 730 needs more intensive studies in different oceanic regions. Chlorinated-OPEs can be efficiently  
 731 transported via ocean currents due to their persistence, lower volatility and high solubility<sup>14,41</sup>,



732 while non-chlorinated OPEs (excluding TnBP and EHDPP which may relate to local sources) are  
733 likely mainly transported via air advection due to potential adsorption onto particles<sup>14</sup>. Recently,  
734 it has been suggested that sea-spray aerosol can be an important vector for the regional and long-  
735 term transport of organic pollutants, and the relevance of this process needs to be assessed for  
736 OPEs. Furthermore, the role of oceanic plastics as significant in-situ and mobile sources of OPEs  
737 should be further investigated, also in relation to other potential OPE sources into the Ocean.  
738 Particularly, a qualitative and quantitative assessment of OPE leaching from microplastics  
739 accumulated in sediments, considered as final sinks of plastic debris, should be addressed. Existing  
740 data based on laboratory experiments point to a lower release of some OPEs from plastics under  
741 deep-sea conditions compared to surface waters<sup>63</sup>, but no data on direct release from plastics settled  
742 on the sediments exists, to the best of our knowledge. The occurrence of OPEs in the deep seafloor  
743 (and the water-sediment interface) and organisms should be further investigated, also in relation  
744 to the large plastic accumulation in this environment<sup>192</sup> and the potential longer-term or chronic  
745 exposure to OPEs and other plastic additives in profound oceanic environments<sup>63</sup>.

746 Local usage and environmental behaviors of OPEs, as well as discrepancies in habitat, diet,  
747 and metabolic behaviors of OPEs in different species, may play important roles in the occurrence  
748 and bioaccumulation of OPEs in marine organisms. Current studies on occurrence of OPEs in  
749 marine organisms mainly focus on near-shore regions. Further investigations in relation to off-  
750 shore regions could help to clarify the natural behaviors of these compounds and environmental  
751 impacts on the global ocean. Although OPEs seem not to bio-magnify like other POPs such as  
752 PBDEs, potential accumulation of hydrophobic OPEs with a high logK<sub>ow</sub> has been observed in  
753 marine organisms. The bioaccumulation and biomagnification behaviors of OPEs through food  
754 webs, particularly the entry mechanisms at the first steps (such as plankton), still need to be further

755 scrutinized in the future, also in relation to their potential biological effects. In addition, much  
756 attention should be paid to health risks induced by OPEs on benthic species, because benthos  
757 shows greater accumulation of these compounds than pelagic species.

758         Given the knowledge of OPEs in global ocean summarized in this review and other  
759 works<sup>28,42,193</sup>, it is shown that, OPEs are sufficiently persistent to be distributed globally and  
760 present health hazards potential to marine organisms due to their bioaccumulation and  
761 biomagnification behavior. Given the large volume of OPEs on the market and increasing  
762 consummation, national and international policies were called to regulate the production and  
763 application of OPEs, and to develop more safe alternative flame-retardants<sup>193,194</sup>. Especially, TCEP  
764 and TCIPP should gain more attention and be considered for global regulatory framework as soon  
765 as possible.

766         Phosphate esters could account for over 75% of the total dissolved organic phosphorus in the  
767 marine environment<sup>109</sup>. However, the contribution to this pool of OPEs and other anthropogenic  
768 organophosphate ester compounds (such as pesticides) remains unknown. The related organic  
769 phosphorus (OP) inputs coming from diffusive OPEs fluxes are estimated to potentially trigger up  
770 to 1.0% of the reported primary production in the most oligotrophic oceanic regions.<sup>81</sup>

771         At present, toxicological data of OPEs in marine organisms as well as environmental quality  
772 standards are lacking, which limits not only the accurate evaluation on ecotoxicological risk of  
773 OPEs to the oceanic ecosystem, especially under the long-term, chronic and interactive exposure  
774 to OPE pollutants, but also important elements to support an efficient chemical contamination  
775 management due to these compounds.

776         The environmental occurrence of OPEs (i.e. triester-OPEs) degradation products in marine  
777 environments has been little investigated. Experimental *in vivo* and *in vitro* studies have

778 demonstrated that a certain number of tri-OPEs can be transformed to di-ether metabolites (di-  
779 OPEs)<sup>195</sup>, Some di-OPEs could induce comparable or higher toxic effects than their respective  
780 triesters<sup>111,196</sup>. The few existing studies report di-OPEs in fish<sup>197,198</sup>, water<sup>112</sup> and sediments<sup>115</sup> from  
781 inland aquatic ecosystems. Only one study focused on marine sediment to the best of our  
782 knowledge.<sup>54</sup>

783 The use of airborne OPEs as source of nutrients suggest a direct link between the  
784 biogeochemical cycle of phosphorous and the environmental occurrence of OPE<sup>109</sup>. However, this  
785 is a not yet accounted process that could be of global relevance since phosphorous limits  
786 metabolism (primary production and respiration) in large oceanic regions. Future research should  
787 constraint the estimates of atmospheric deposition of anthropogenic OP and its use as a nutrient in  
788 the large oligotrophic oceanic regions.

789 Pioneering studies have highlighted the importance of atmosphere as a media for the long-  
790 range transport of OPEs and air-water exchange and dry deposition fluxes in the global ocean<sup>41,42,81</sup>.  
791 The accuracy of the physicochemical data of OPEs can affect the estimation of air/particle  
792 portioning process<sup>199</sup> and air-water exchange flux direction and intensity<sup>61</sup>, which requests  
793 experimental-derived physicochemical properties in order to constrain the relevance of  
794 atmospheric inputs of OPEs to the ocean. Further work should establish a budget for OPEs present  
795 in the Southern Ocean and focus on the oceanic transport from marginal seas to the open ocean,  
796 vertical deposition in the water column, microbial and photo degradation and sinking to deep ocean  
797 sediments.

798 In terms of global warming, new input of OPEs from the melting ice sheet and snow may  
799 alter the concentrations and vertical profile in the water columns at high latitude. This will  
800 subsequently change environmental pathways of OPEs in the ocean environment and related health

801 impacts. Consequently, future research will need to understand the various biogeochemical and  
802 geophysical processes under climate change and anthropogenic pressures to be able to predict the  
803 environmental fates and the global ocean health impacts of OPEs accurately.

804 **Acknowledgements**

805 We are very grateful to Derek Muir for his detailed and constructive internal review on the  
806 manuscript. We thank Wenhan Cheng for providing the data on OPEs in air and snow in the  
807 Antarctic. We thank Qicheng Meng, Lijie Mi, Jing Li and Lulu Zhang for technical support in  
808 creating Fig. 1, 2 and 3. Z.X. acknowledges the European Union's Horizon 2020 research and  
809 innovation programme under grant agreement No 689443 via project iCUPE (Integrative and  
810 Comprehensive Understanding on Polar Environments). We thank the researches who dedicated  
811 original data for OPEs in environmental and biological matrices and modeling predictions. We are  
812 very grateful to the reviewers for their insightful suggestions.

813 **Author contributions**

814 Z.X. initiated the project and assembled the authorship team. P.W., X.W., C.L., J.C., M.V.,  
815 J.D. and Z.X. researched the data and drafted the manuscript and figures. R.K., W.M. and R.L.  
816 contributed to writing and editing of the manuscript.

817 **Competing interests**

818 The authors declare no competing interests.

819 **ORCID iD**

820 Zhiyong Xie, 0000-0001-8997-3930

821 Pu Wang, 0000-0002-9003-2756

822 Xin Wang, 0000-0002-7858-5139

823 Javier Castro-Jiménez, 0000-0001-8456-3932

824 Roland Kallenborn, 0000-0003-1703-2538

825 Chunyang Liao, 0000-0003-2846-6614

826 Wenying Mi, 0000-0001-8856-9346

- 827 Rainer Lohmann, 0000-0001-8796-3229
- 828 Maria Vila-Costa, 0000-0003-1730-8418
- 829 Jordi Dachs, 0000-0002-4237-169X
- 830

831 **Literatures**

- 832
- 833 1 Quintana, J. B., Rodil, R., Reemtsma, T., Garcia-Lopez, M. & Rodriguez, I. Organophosphorus flame  
 834 retardants and plasticizers in water and air II. Analytical methodology. *Trac-Trends in Analytical*  
 835 *Chemistry* **27**, 904-915, doi:10.1016/j.trac.2008.08.004 (2008).
- 836 2 Salamova, A., Hermanson, M. H. & Hites, R. A. Organophosphate and Halogenated Flame Retardants  
 837 in Atmospheric Particles from a European Arctic Site. *Environ. Sci. Technol.* **48**, 6133-6140,  
 838 doi:10.1021/es500911d (2014).
- 839 3 Moeller, A., Xie, Z., Caba, A., Sturm, R. & Ebinghaus, R. Organophosphorus flame retardants and  
 840 plasticizers in the atmosphere of the North Sea. *Environmental Pollution* **159**, 3660-3665,  
 841 doi:10.1016/j.envpol.2011.07.022 (2011).
- 842 4 Castro-Jimenez, J., Berrojalbiz, N., Pizarro, M. & Dachs, J. Organophosphate Ester (OPE) Flame  
 843 Retardants and Plasticizers in the Open Mediterranean and Black Seas Atmosphere. *Environmental*  
 844 *Science & Technology* **48**, 3203-3209, doi:10.1021/es405337g (2014).
- 845 5 Na, G. S. *et al.* Occurrence, distribution, air-seawater exchange and atmospheric deposition of  
 846 organophosphate esters (OPEs) from the Northwestern Pacific to the Arctic Ocean. *Marine Pollution*  
 847 *Bulletin* **157**, doi:10.1016/j.marpolbul.2020.111243 (2020).
- 848 6 Cheng, W. *et al.* Organophosphorus esters in the oceans and possible relation with ocean gyres.  
 849 *Environmental Pollution* **180**, 159-164 (2013).
- 850 7 Wang, Y. *et al.* Occurrence, distribution, and air-water exchange of organophosphorus flame  
 851 retardants in a typical coastal area of China. *Chemosphere* **211**, 335-344,  
 852 doi:10.1016/j.chemosphere.2018.07.062 (2018).
- 853 8 van der Veen, I. & de Boer, J. Phosphorus flame retardants: Properties, production, environmental  
 854 occurrence, toxicity and analysis. *Chemosphere* **88**, 1119-1153,  
 855 doi:10.1016/j.chemosphere.2012.03.067 (2012).
- 856 9 Isetun, S., Nilsson, U. & Colmsjo, A. Evaluation of solid-phase microextraction with PDMS for air  
 857 sampling of gaseous organophosphate flame-retardants and plasticizers. *Analytical and Bioanalytical*  
 858 *Chemistry* **380**, 319-324, doi:10.1007/s00216-004-2760-5 (2004).
- 859 10 Zeng, X. *et al.* Occurrence and distribution of organophosphorus flame retardants/plasticizers in  
 860 coastal sediments from the Taiwan Strait in China. *Marine Pollution Bulletin* **151**,  
 861 doi:10.1016/j.marpolbul.2019.110843 (2020).
- 862 11 Mo, L. *et al.* Legacy and emerging contaminants in coastal surface sediments around Hainan Island in  
 863 South China. *Chemosphere* **215**, 133-141, doi:10.1016/j.chemosphere.2018.10.022 (2019).
- 864 12 Papachlimitzou, A. *et al.* Organophosphorus flame retardants (PFRs) and plasticisers in harbour  
 865 porpoises (*Phocoena phocoena*) stranded or bycaught in the UK during 2012. *Marine Pollution*  
 866 *Bulletin* **98**, 328-334, doi:10.1016/j.marpolbul.2015.06.034 (2015).
- 867 13 Li, H. R. *et al.* Brominated and organophosphate flame retardants along a sediment transect  
 868 encompassing the Guiyu, China e-waste recycling zone. *Science of the Total Environment* **646**, 58-67,  
 869 doi:10.1016/j.scitotenv.2018.07.276 (2019).
- 870 14 Suhring, R. *et al.* Organophosphate Esters in Canadian Arctic Air: Occurrence, Levels and Trends.  
 871 *Environmental Science & Technology* **50**, 7409-7415, doi:10.1021/acs.est.6b00365 (2016).
- 872 15 Makinen, M. S. E. *et al.* Respiratory and Dermal Exposure to Organophosphorus Flame Retardants  
 873 and Tetrabromobisphenol A at Five Work Environments. *Environmental Science & Technology* **43**,  
 874 941-947, doi:10.1021/es802593t (2009).
- 875 16 <https://www.lucintel.com/organophosphorus-flame-retardant-market-2016--2021.aspx>. *Growth*  
 876 *Opportunities in the Global Organophosphorus Flame Retardant Market*, 2016).
- 877 17 Chen, M. *et al.* Temporal and seasonal variation and ecological risk evaluation of flame retardants in  
 878 seawater and sediments from Bohai Bay near Tianjin, China during 2014 to 2017. *Marine Pollution*  
 879 *Bulletin* **146**, 874-883, doi:10.1016/j.marpolbul.2019.07.049 (2019).

- 880 18 Castro-Jimenez, J. & Ratola, N. An innovative approach for the simultaneous quantitative screening  
881 of organic plastic additives in complex matrices in marine coastal areas. *Environmental Science and*  
882 *Pollution Research* **27**, 11450-11457, doi:10.1007/s11356-020-08069-9 (2020).
- 883 19 Sutton, R., Chen, D., Sun, J., Greig, D. J. & Wu, Y. Characterization of brominated, chlorinated, and  
884 phosphate flame retardants in San Francisco Bay, an urban estuary. *Sci. Total Environ.* **652**, 212-223,  
885 doi:10.1016/j.scitotenv.2018.10.096 (2019).
- 886 20 Zhong, M. *et al.* Occurrence and spatial distribution of organophosphorus flame retardants and  
887 plasticizers in the Bohai, Yellow and East China seas. *Science of the Total Environment* **741**,  
888 doi:10.1016/j.scitotenv.2020.140434 (2020).
- 889 21 Hu, M. *et al.* Regional distribution of halogenated organophosphate flame retardants in seawater  
890 samples from three coastal cities in China. *Marine Pollution Bulletin* **86**, 569-574,  
891 doi:<https://doi.org/10.1016/j.marpolbul.2014.06.009> (2014).
- 892 22 Bollmann, U. E., Moeler, A., Xie, Z., Ebinghaus, R. & Einax, J. W. Occurrence and fate of  
893 organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water*  
894 *Research* **46**, 531-538, doi:10.1016/j.watres.2011.11.028 (2012).
- 895 23 <http://www.chinamarketresearchreports.com/114859.html>. *China Market Research Reports. Global*  
896 *and China Flame Retardant Industry Report, 2014–2016 by Research In China at China Market*  
897 *Research Reports*.
- 898 24 Reports, C. M. R. Global and China Flame Retardant Industry Report, 2014-2016.  
899 (<http://www.chinamarketresearchreports.com/114859.html>, 2016).
- 900 25 Marklund, A., Andersson, B. & Haglund, P. Organophosphorus flame retardants and plasticizers in  
901 Swedish sewage treatment plants. *Environmental Science & Technology* **39**, 7423-7429,  
902 doi:10.1021/es0510131 (2005).
- 903 26 Yang, J. W. *et al.* A Review of a Class of Emerging Contaminants: The Classification, Distribution,  
904 Intensity of Consumption, Synthesis Routes, Environmental Effects and Expectation of Pollution  
905 Abatement to Organophosphate Flame Retardants (OPFRs). *International Journal of Molecular*  
906 *Sciences* **20**, doi:10.3390/ijms20122874 (2019).
- 907 27 Bruchajzer, E., Frydrych, B. & Szymanska, J. A. [Organophosphorus Flame Retardants - Toxicity and  
908 Influence on Human Health]. *Med Pr* **66**, 235-264, doi:10.13075/mp.5893.00120 (2015).
- 909 28 Fu, J. *et al.* Long-Range Transport, Trophic Transfer, and Ecological Risks of Organophosphate Esters  
910 in Remote Areas. *Environmental Science & Technology* **55**, 10192-10209,  
911 doi:10.1021/acs.est.0c08822 (2021).
- 912 29 Brommer, S., Harrad, S., Van den Eede, N. & Covaci, A. Concentrations of organophosphate esters  
913 and brominated flame retardants in German indoor dust samples. *Journal of Environmental*  
914 *Monitoring* **14**, 2482-2487, doi:10.1039/c2em30303e (2012).
- 915 30 Gravel, S. *et al.* Halogenated flame retardants and organophosphate esters in the air of electronic waste  
916 recycling facilities: Evidence of high concentrations and multiple exposures. *Environment*  
917 *International* **128**, 244-253, doi:10.1016/j.envint.2019.04.027 (2019).
- 918 31 Baldé, C. P., V, F., Gray, V., Kuehr, R., Stegmann, P. The Global E-waste Monitor 2017 - Quantities,  
919 Flows, and Resources. . (United Nations University (UNU), International Telecommunication Union  
920 (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna, 2017).
- 921 32 Akram, R. *et al.* Trends of electronic waste pollution and its impact on the global environment and  
922 ecosystem. *Environmental Science and Pollution Research* **26**, 16923-16938, doi:10.1007/s11356-  
923 019-04998-2 (2019).
- 924 33 Lee, D., Offenhuber, D., Duarte, F., Biderman, A. & Ratti, C. Monitour: Tracking global routes of  
925 electronic waste. *Waste Management* **72**, 362-370, doi:10.1016/j.wasman.2017.11.014 (2018).
- 926 34 Zhang, Y. *et al.* Distribution of flame retardants in smartphones and identification of current-use  
927 organic chemicals including three novel aryl organophosphate esters. *Science of the Total Environment*  
928 **693**, doi:10.1016/j.scitotenv.2019.133654 (2019).



- 929 35 Ghimire, H. & Ariya, P. A. E-Wastes: Bridging the Knowledge Gaps in Global Production Budgets,  
930 Composition, Recycling and Sustainability Implications. *Sustainable Chemistry* **1**, 154-182,  
931 doi:doi:10.3390/suschem1020012 (2020).
- 932 36 Zeng, Y. *et al.* Organophosphate esters (OPEs) in fine particulate matter (PM<sub>2.5</sub>) in urban, e-waste,  
933 and background regions of South China. *Journal of Hazardous Materials* **385**,  
934 doi:10.1016/j.jhazmat.2019.121583 (2020).
- 935 37 Stein, A. F. *et al.* NOAA'S HYSPLIT ATMOSPHERIC TRANSPORT AND DISPERSION  
936 MODELING SYSTEM. *Bulletin of the American Meteorological Society* **96**, 2059-2077,  
937 doi:10.1175/bams-d-14-00110.1 (2015).
- 938 38 Wolschke, H., Suhling, R., Xie, Z. Y. & Ebinghaus, R. Organophosphorus flame retardants and  
939 plasticizers in the aquatic environment: A case study of the Elbe River, Germany. *Environmental*  
940 *Pollution* **206**, 488-493, doi:10.1016/j.envpol.2015.08.002 (2015).
- 941 39 Wang, R. M. *et al.* Occurrence and spatial distribution of organophosphate ester flame retardants and  
942 plasticizers in 40 rivers draining into the Bohai Sea, north China. *Environmental Pollution* **198**, 172-  
943 178, doi:10.1016/j.envpol.2014.12.037 (2015).
- 944 40 Suhling, R. *et al.* Organophosphate Esters in the Canadian Arctic Ocean. *Environmental Science &*  
945 *Technology* **55**, 304-312, doi:10.1021/acs.est.0c04422 (2021).
- 946 41 Rodgers, T. F. M., Truong, J. W., Jantunen, L. M., Helm, P. A. & Diamond, M. L. Organophosphate  
947 Ester Transport, Fate, and Emissions in Toronto, Canada, Estimated Using an Updated Multimedia  
948 Urban Model. *Environmental Science & Technology* **52**, 12465-12474, doi:10.1021/acs.est.8b02576  
949 (2018).
- 950 42 Suhling, R., Scheringer, M., Rodgers, T. F. M., Jantunen, L. M. & Diamond, M. L. Evaluation of the  
951 OECD P-OV and LRTP screening tool for estimating the long-range transport of organophosphate  
952 esters. *Environmental Science-Processes & Impacts* **22**, 207-216, doi:10.1039/c9em00410f (2020).
- 953 43 Moeller, A. *et al.* Organophosphorus Flame Retardants and Plasticizers in Airborne Particles over the  
954 Northern Pacific and Indian Ocean toward the Polar Regions: Evidence for Global Occurrence.  
955 *Environmental Science & Technology* **46**, 3127-3134, doi:10.1021/es204272v (2012).
- 956 44 Commission, E. EU Risk Assessment Report, Tris(2-chloroethyl) phosphate (TCEP) CAS-No.: 115-  
957 96-8. EINECS-No.: 204-118-5 (2009).
- 958 45 Ali, N. *et al.* Occurrence of alternative flame retardants in indoor dust from New Zealand: Indoor  
959 sources and human exposure assessment. *Chemosphere* **88**, 1276-1282,  
960 doi:10.1016/j.chemosphere.2012.03.100 (2012).
- 961 46 Waaijers, S. L. *et al.* Toxicity of new generation flame retardants to *Daphnia magna*. *The Science of*  
962 *the total environment* **463-464**, 1042-1048, doi:10.1016/j.scitotenv.2013.06.110 (2013).
- 963 47 Dishaw, L. V. *et al.* Is the PentaBDE replacement, tris (1,3-dichloropropyl) phosphate (TDCPP), a  
964 developmental neurotoxicant? Studies in PC12 cells. *Toxicol. Appl. Pharmacol.* **256**, 281-289,  
965 doi:10.1016/j.taap.2011.01.005 (2011).
- 966 48 Wei, G. L. *et al.* Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity  
967 and human exposure. *Environmental Pollution* **196**, 29-46, doi:10.1016/j.envpol.2014.09.012 (2015).
- 968 49 Nguyen, L. V. *et al.* Exposure of Canadian electronic waste dismantlers to flame retardants.  
969 *Environment International* **129**, 95-104, doi:10.1016/j.envint.2019.04.056 (2019).
- 970 50 Wang, Y. *et al.* Measuring exposure of e-waste dismantlers in Dhaka Bangladesh to organophosphate  
971 esters and halogenated flame retardants using silicone wristbands and T-shirts. *Science of the Total*  
972 *Environment* **720**, doi:10.1016/j.scitotenv.2020.137480 (2020).
- 973 51 Schmidt, N., Castro-Jimenez, J., Fauvelle, V., Ourgaud, M. & Sempere, R. Occurrence of organic  
974 plastic additives in surface waters of the Rhone River (France). *Environmental Pollution* **257**,  
975 doi:10.1016/j.envpol.2019.113637 (2020).
- 976 52 Schmidt, N. *et al.* The Amazon River: A Major Source of Organic Plastic Additives to the Tropical  
977 North Atlantic? *Environmental Science & Technology* **53**, 7513-7521, doi:10.1021/acs.est.9b01585  
978 (2019).

- 979 53 Fu, L. F. *et al.* Tracing the occurrence of organophosphate ester along the river flow path and textile  
980 wastewater treatment processes by using dissolved organic matters as an indicator. *Science of the Total*  
981 *Environment* **722**, doi:10.1016/j.scitotenv.2020.137895 (2020).
- 982 54 Li, J. *et al.* Inference of Organophosphate Ester Emission History from Marine Sediment Cores  
983 Impacted by Wastewater Effluents. *Environmental Science & Technology* **53**, 8767-8775,  
984 doi:10.1021/acs.est.9b01713 (2019).
- 985 55 Casal, P., Castro-Jimenez, J., Pizarro, M., Katsoyiannis, A. & Dachs, J. Seasonal soil/snow-air  
986 exchange of semivolatile organic pollutants at a coastal arctic site (Tromso, 69 degrees N). *Science of*  
987 *the Total Environment* **636**, 1109-1116, doi:10.1016/j.scitotenv.2018.04.330 (2018).
- 988 56 Castro-Jimenez, J. & Sempere, R. Atmospheric particle-bound organophosphate ester flame retardants  
989 and plasticizers in a North African Mediterranean coastal city (Bizerte, Tunisia). *Science of the Total*  
990 *Environment* **642**, 383-393, doi:10.1016/j.scitotenv.2018.06.010 (2018).
- 991 57 Meyer, J. & Bester, K. Organophosphate flame retardants and plasticisers in wastewater treatment  
992 plants. *Journal of Environmental Monitoring* **6**, 599-605, doi:10.1039/b403206c (2004).
- 993 58 Zeng, X. *et al.* Occurrence and distribution of organophosphate flame retardants/plasticizers in  
994 wastewater treatment plant sludges from the Pearl River Delta, China. *Environmental Toxicology and*  
995 *Chemistry* **33**, 1720-1725, doi:10.1002/etc.2604 (2014).
- 996 59 Kim, U. J. & Kannan, K. Occurrence and Distribution of Organophosphate Flame  
997 Retardants/Plasticizers in Surface Waters, Tap Water, and Rainwater: Implications for Human  
998 Exposure. *Environmental Science & Technology* **52**, 5625-5633, doi:10.1021/acs.est.8b00727 (2018).
- 999 60 Fries, E. & Puttmann, W. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in  
1000 river water and ground water (Oder, Germany). *Journal of Environmental Monitoring* **5**, 346-352,  
1001 doi:10.1039/b210342g (2003).
- 1002 61 Li, J. *et al.* Organophosphate Esters in Air, Snow, and Seawater in the North Atlantic and the Arctic.  
1003 *Environmental Science & Technology* **51**, 6887-6896, doi:10.1021/acs.est.7b01289 (2017).
- 1004 62 Paluselli, A., Fauvelle, V., Galgani, F. & Sempere, R. Phthalate Release from Plastic Fragments and  
1005 Degradation in Seawater. *Environmental Science & Technology* **53**, 166-175,  
1006 doi:10.1021/acs.est.8b05083 (2019).
- 1007 63 Fauvelle, V., Garel, M., Tamburini, C., Nerini, D., Castro-Jiménez, J., Schmidt, N., Paluselli, A., Fahs,  
1008 A., Papillon, L., Booth, A.M., Sempéré, R. Organic additive release from plastic to seawater is lower  
1009 under deep-sea conditions. *Nature Comm.* (2021).
- 1010 64 Castro, V., Montes, R., Quintana, J. B., Rodil, R. & Cela, R. Determination of 18 organophosphorus  
1011 flame retardants/plasticizers in mussel samples by matrix solid-phase dispersion combined to liquid  
1012 chromatography-tandem mass spectrometry. *Talanta* **208**, doi:10.1016/j.talanta.2019.120470 (2020).
- 1013 65 Schmidt, N., Castro-Jimenez, J., Oursel, B. & Sempere, R. Phthalates and organophosphate esters in  
1014 surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring links with  
1015 microplastic abundance and accumulation in the marine food web. *Environmental Pollution* **272**,  
1016 115970, doi:10.1016/j.envpol.2020.115970 (2021).
- 1017 66 Ma, Y. X., Xie, Z. Y., Lohmann, R., Mi, W. Y. & Gao, G. P. Organophosphate Ester Flame Retardants  
1018 and Plasticizers in Ocean Sediments from the North Pacific to the Arctic Ocean. *Environmental*  
1019 *Science & Technology* **51**, 3809-3815, doi:10.1021/acs.est.7b00755 (2017).
- 1020 67 Lian, M. S. *et al.* Occurrence, spatiotemporal distribution, and ecological risks of organophosphate  
1021 esters in the water of the Yellow River to the Laizhou Bay, Bohai Sea. *Science of the Total*  
1022 *Environment* **787**, doi:10.1016/j.scitotenv.2021.147528 (2021).
- 1023 68 Nigar, A., Ali, Alkan, Javier Castro-Jiménez, Florian, Royer, Laure, Papillon, Mélanie, Ourgaud,  
1024 Richard, Sempéré. Environmental occurrence of phthalate and organophosphate esters in sediments  
1025 across the Gulf of Lion (NW Mediterranean Sea). *Science of The Total Environment* **760**, 143412  
1026 (2021).
- 1027 69 Castro-Jimenez, J., Gonzalez-Fernandez, D., Fornier, M., Schmidt, N. & Sempere, R. Macro-litter in  
1028 surface waters from the Rhone River: Plastic pollution and loading to the NW Mediterranean Sea.  
1029 *Marine Pollution Bulletin* **146**, 60-66, doi:10.1016/j.marpolbul.2019.05.067 (2019).

- 1030 70 Lebreton, L. C. M. *et al.* River plastic emissions to the world's oceans. *Nature Communications* **8**,  
1031 doi:10.1038/ncomms15611 (2017).
- 1032 71 Wolschke, H. *et al.* Atmospheric occurrence and fate of organophosphorus flame retardants and  
1033 plasticizer at the German coast. *Atmospheric Environment* **137**, 1-5,  
1034 doi:10.1016/j.atmosenv.2016.04.028 (2016).
- 1035 72 Wania, F., Haugen, J.-E., Lei, Y. D. & Mackay, D. Temperature Dependence of Atmospheric  
1036 Concentrations of Semivolatile Organic Compounds. *Environmental Science & Technology* **32**, 1013-  
1037 1021, doi:10.1021/es970856c (1998).
- 1038 73 Octaviani, M., Stemmler, I., Lammel, G. & Graf, H. F. Atmospheric Transport of Persistent Organic  
1039 Pollutants to and from the Arctic under Present-Day and Future Climate. *Environmental Science &*  
1040 *Technology* **49**, 3593-3602, doi:10.1021/es505636g (2015).
- 1041 74 Zhang, X. *et al.* Novel flame retardants: Estimating the physical-chemical properties and  
1042 environmental fate of 94 halogenated and organophosphate PBDE replacements. *Chemosphere* **144**,  
1043 2401-2407, doi:10.1016/j.chemosphere.2015.11.017 (2016).
- 1044 75 Salamova, A., Ma, Y., Venier, M. & Hites, R. A. High Levels of Organophosphate Flame Retardants  
1045 in the Great Lakes Atmosphere. *Environmental Science & Technology Letters* **1**, 8-14,  
1046 doi:10.1021/ez400034n (2014).
- 1047 76 Liu, Y. C. *et al.* Heterogeneous OH Initiated Oxidation: A Possible Explanation for the Persistence of  
1048 Organophosphate Flame Retardants in Air. *Environmental Science & Technology* **48**, 1041-1048,  
1049 doi:10.1021/es404515k (2014).
- 1050 77 Aschmann, S. M., Long, W. D. & Atkinson, R. Temperature-dependent rate constants for the gas-  
1051 phase reactions of OH radicals with 1,3,5-trimethylbenzene, triethyl phosphate, and a series of  
1052 alkylphosphonates. *Journal of Physical Chemistry A* **110**, 7393-7400, doi:10.1021/jp061542r (2006).
- 1053 78 Commission, E. EU Risk Assessment Report, Tris(2-chloro-1-methylethyl) phosphate, TCPP. (2008).
- 1054 79 Zhang, L. *et al.* Atmospheric deposition, seasonal variation, and long-range transport of  
1055 organophosphate esters on Yongxing Island, South China Sea. *Science of the Total Environment* **806**,  
1056 150673 (2022).
- 1057 80 Chokwe, T. B., Abafe, O. A., Mbelu, S. P., Okonkwo, J. O. & Sibali, L. L. A review of sources, fate,  
1058 levels, toxicity, exposure and transformations of organophosphorus flame-retardants and plasticizers  
1059 in the environment. *Emerging Contaminants* **6**, 345-366,  
1060 doi:<https://doi.org/10.1016/j.emcon.2020.08.004> (2020).
- 1061 81 Castro-Jimenez, J. *et al.* Organophosphate Ester Flame Retardants and Plasticizers in the Global  
1062 Oceanic Atmosphere. *Environmental Science & Technology* **50**, 12831-12839,  
1063 doi:10.1021/acs.est.6b04344 (2016).
- 1064 82 Jurado, E. *et al.* Wet deposition of persistent organic pollutants to the global oceans. *Environmental*  
1065 *Science & Technology* **39**, 2426-2435, doi:10.1021/es048599g (2005).
- 1066 83 Jurado, E. *et al.* Atmospheric dry deposition of persistent organic pollutants to the Atlantic and  
1067 inferences for the global oceans. *Environmental Science & Technology* **38**, 5505-5513,  
1068 doi:10.1021/es049240v (2004).
- 1069 84 Hallanger, I. G. *et al.* Organophosphorous flame retardants in biota from Svalbard, Norway. *Marine*  
1070 *Pollution Bulletin* **101**, 442-447, doi:10.1016/j.marpolbul.2015.09.049 (2015).
- 1071 85 McDonough, C. A. *et al.* Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in  
1072 Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram  
1073 Strait. *Environmental Science & Technology* **52**, 6208-6216, doi:10.1021/acs.est.8b01127 (2018).
- 1074 86 Lohmann, R., Dachs, J. in *World Seas: an Environmental Evaluation* (ed C. Sheppard) Ch. 15, (2019).
- 1075 87 Gallban-Malagon, C. J., Del Vento, S., Cabrerizo, A. & Dachs, J. Factors affecting the atmospheric  
1076 occurrence and deposition of polychlorinated biphenyls in the Southern Ocean. *Atmospheric*  
1077 *Chemistry and Physics* **13**, 12029-12041, doi:10.5194/acp-13-12029-2013 (2013).
- 1078 88 Galban-Malagon, C., Berrojalbiz, N., Ojeda, M. J. & Dachs, J. The oceanic biological pump modulates  
1079 the atmospheric transport of persistent organic pollutants to the Arctic. *Nature Communications* **3**,  
1080 doi:10.1038/ncomms1858 (2012).

- 1081 89 Li, J. *et al.* Spatial Distribution and Seasonal Variation of Organophosphate Esters in Air above the  
1082 Bohai and Yellow Seas, China. *Environmental Science & Technology* **52**, 89-97,  
1083 doi:10.1021/acs.est.7b03807 (2018).
- 1084 90 Wang, Y. *et al.* Distribution of organophosphate esters between the gas phase and PM<sub>2.5</sub> in urban  
1085 Dalian, China. *Environmental Pollution* **259**, doi:10.1016/j.envpol.2019.113882 (2020).
- 1086 91 Lai, S. C. *et al.* Occurrence and dry deposition of organophosphate esters in atmospheric particles over  
1087 the northern South China Sea. *Chemosphere* **127**, 195-200, doi:10.1016/j.chemosphere.2015.02.015  
1088 (2015).
- 1089 92 Casas, G., Martinez-Varela, A., Vila-Costa, M., Jiménez, B. a. & Dachs, J. Rain Amplification of  
1090 Persistent Organic Pollutants. *Environmental Science & Technology* **55**, 12961-12972 (2021).
- 1091 93 Casal, P. *et al.* Snow Amplification of Persistent Organic Pollutants at Coastal Antarctica.  
1092 *Environmental Science & Technology* **53**, 8872-8882, doi:10.1021/acs.est.9b03006 (2019).
- 1093 94 Zhang, Z. G. *et al.* Occurrence, behavior, and fate of organophosphate esters (OPEs) in subtropical  
1094 paddy field environment: A case study in Nanning City of South China. *Environmental Pollution* **267**,  
1095 doi:10.1016/j.envpol.2020.115675 (2020).
- 1096 95 Regnery, J. & Puttmann, W. Organophosphorus Flame Retardants and Plasticizers in Rain and Snow  
1097 from Middle Germany. *Clean-Soil Air Water* **37**, 334-342, doi:10.1002/clen.200900050 (2009).
- 1098 96 Xie, Z. Y. *et al.* Occurrence of legacy and emerging organic contaminants in snow at Dome C in the  
1099 Antarctic. *Science of the Total Environment* **741**, doi:10.1016/j.scitotenv.2020.140200 (2020).
- 1100 97 Cheng, W. H. *et al.* Detection and distribution of Tris(2-chloroethyl) phosphate on the East Antarctic  
1101 ice sheet. *Chemosphere* **92**, 1017-1021, doi:10.1016/j.chemosphere.2013.03.038 (2013).
- 1102 98 Cabrerizo, A., Muir, D. C. G., Teixeira, C., Lamoureux, S. F. & Lafreniere, M. J. Snow Deposition  
1103 and Melting as Drivers of Polychlorinated Biphenyls and Organochlorine Pesticides in Arctic Rivers,  
1104 Lakes, and Ocean. *Environmental Science & Technology* **53**, 14377-14386,  
1105 doi:10.1021/acs.est.9b05150 (2019).
- 1106 99 Gustafsson, O. *et al.* Observations of the PCB distribution within and in-between ice, snow, ice-rafted  
1107 debris, ice-interstitial water, and seawater in the Barents Sea marginal ice zone and the North Pole  
1108 area. *Science of the Total Environment* **342**, 261-279, doi:10.1016/j.scitotenv.2004.12.044 (2005).
- 1109 100 Herbert, B. M. J., Halsall, C. J., Villa, S., Jones, K. C. & Kallenborn, R. Rapid changes in PCB and  
1110 OC pesticide concentrations in Arctic snow. *Environmental Science & Technology* **39**, 2998-3005,  
1111 doi:10.1021/es040076l (2005).
- 1112 101 Yadav, J., Kumar, A. & Mohan, R. Dramatic decline of Arctic sea ice linked to global warming.  
1113 *Natural Hazards* **103**, 2617-2621, doi:10.1007/s11069-020-04064-y (2020).
- 1114 102 Sun, Y. X. *et al.* Glacial Melt Inputs of Organophosphate Ester Flame Retardants to the Largest High  
1115 Arctic Lake. *Environmental Science & Technology* **54**, 2734-2743, doi:10.1021/acs.est.9b06333  
1116 (2020).
- 1117 103 Zhao, Z. *et al.* Distribution and long-range transport of polyfluoroalkyl substances in the Arctic,  
1118 Atlantic Ocean and Antarctic coast. *Environmental Pollution* **170**, 71-77,  
1119 doi:10.1016/j.envpol.2012.06.004 (2012).
- 1120 104 Wolschke, H., Suhring, R., Massei, R., Tang, J. H. & Ebinghaus, R. Regional variations of  
1121 organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe  
1122 compared with China. *Environmental Pollution* **236**, 391-395, doi:10.1016/j.envpol.2018.01.061  
1123 (2018).
- 1124 105 Regnery, J. & Puttmann, W. Seasonal fluctuations of organophosphate concentrations in precipitation  
1125 and storm water runoff. *Chemosphere* **78**, 958-964, doi:10.1016/j.chemosphere.2009.12.027 (2010).
- 1126 106 Regnery, J. & Puttmann, W. Occurrence and fate of organophosphorus flame retardants and  
1127 plasticizers in urban and remote surface waters in Germany. *Water Research* **44**, 4097-4104,  
1128 doi:10.1016/j.watres.2010.05.024 (2010).
- 1129 107 Xiao, K. Y. *et al.* Occurrence, distribution and risk assessment of organophosphate ester flame  
1130 retardants and plasticizers in surface seawater of the West Pacific. *Marine Pollution Bulletin* **170**,  
1131 doi:10.1016/j.marpolbul.2021.112691 (2021).

- 1132 108 Barnes, D. K. A., Galgani, F., Thompson, R. C. & Barlaz, M. Accumulation and fragmentation of  
1133 plastic debris in global environments. *Philosophical Transactions of the Royal Society B-Biological*  
1134 *Sciences* **364**, 1985-1998, doi:10.1098/rstb.2008.0205 (2009).
- 1135 109 Vila-Costa, M. *et al.* Microbial consumption of organophosphate esters in seawater under phosphorus  
1136 limited conditions. *Scientific Reports* **9**, doi:10.1038/s41598-018-36635-2 (2019).
- 1137 110 Gonzalez-Gaya, B. *et al.* Biodegradation as an important sink of aromatic hydrocarbons in the oceans.  
1138 *Nature Geoscience* **12**, 119-125, doi:10.1038/s41561-018-0285-3 (2019).
- 1139 111 Liu, Y. X. *et al.* Organophosphate (OP) diesters and a review of sources, chemical properties,  
1140 environmental occurrence, adverse effects, and future directions. *Environment International* **155**,  
1141 doi:10.1016/j.envint.2021.106691 (2021).
- 1142 112 Li, Y. *et al.* Occurrence and ecological implications of organophosphate triesters and diester  
1143 degradation products in wastewater, river water, and tap water. *Environmental Pollution* **259**,  
1144 doi:10.1016/j.envpol.2019.113810 (2020).
- 1145 113 Xu, L. *et al.* Occurrence and spatio-seasonal distribution of organophosphate tri- and di-esters in  
1146 surface water from Dongting Lake and their potential biological risk. *Environmental Pollution* **282**,  
1147 117031 (2021).
- 1148 114 Li, X. M. *et al.* Organophosphate Diesters (Di-OPEs) Play a Critical Role in Understanding Global  
1149 Organophosphate Esters (OPEs) in Fishmeal. *Environmental Science & Technology* **54**, 12130-12141,  
1150 doi:10.1021/acs.est.0c03274 (2020).
- 1151 115 Liang, C. *et al.* Organophosphate Diesters in Urban River Sediment from South China: Call for More  
1152 Research on Their Occurrence and Fate in Field Environment. *ACS EST Water* **1**, 871-880 (2021).
- 1153 116 Strobel, A., Wilimore, W. G., Sonne, C., Dietz, R. & Letcher, R. J. Organophosphate esters in East  
1154 Greenland polar bears and ringed seals: Adipose tissue concentrations and in vitro depletion and  
1155 metabolite formation. *Chemosphere* **196**, 240-250, doi:10.1016/j.chemosphere.2017.12.181 (2018).
- 1156 117 Cristale, J. *et al.* Role of oxygen and DOM in sunlight induced photodegradation of  
1157 organophosphorus flame retardants in river water. *Journal of Hazardous Materials* **323**, 242-249,  
1158 doi:10.1016/j.jhazmat.2016.05.019 (2017).
- 1159 118 Kellenberger, E. Exploring the unknown - The silent revolution of microbiology. *Embo Reports* **2**, 5-  
1160 7, doi:10.1093/embo-reports/kve014 (2001).
- 1161 119 Takahashi, S. *et al.* Isolation and Identification of Persistent Chlorinated Organophosphorus Flame  
1162 Retardant-Degrading Bacteria. *Applied and Environmental Microbiology* **76**, 5292-5296,  
1163 doi:10.1128/aem.00506-10 (2010).
- 1164 120 Kera, Y., Abe, K., Kasai, D., Fukuda, M. & Takahashi, S. Draft Genome Sequences of Sphingobium  
1165 sp. Strain TCM1 and Sphingomonas sp. Strain TDK1, Haloalkyl Phosphate Flame Retardant- and  
1166 Plasticizer-Degrading Bacteria. *Microbiology Resource Announcements* **4**,  
1167 doi:10.1128/genomeA.00668-16 (2016).
- 1168 121 Liu, Y. *et al.* Biodegradation of tricresyl phosphate isomers by *Brevibacillus brevis*: Degradation  
1169 pathway and metabolic mechanism. *Chemosphere* **232**, 195-203,  
1170 doi:10.1016/j.chemosphere.2019.05.188 (2019).
- 1171 122 Wei, K., Yin, H., Peng, H., Lu, G. N. & Dang, Z. Bioremediation of triphenyl phosphate by  
1172 *Brevibacillus brevis*: Degradation characteristics and role of cytochrome P450 monooxygenase.  
1173 *Science of the Total Environment* **627**, 1389-1395, doi:10.1016/j.scitotenv.2018.02.028 (2018).
- 1174 123 Wang, J. H. *et al.* Characterization and 16S metagenomic analysis of organophosphorus flame  
1175 retardants degrading consortia. *Journal of Hazardous Materials* **380**,  
1176 doi:10.1016/j.jhazmat.2019.120881 (2019).
- 1177 124 Kawagoshi, Y., Nakamura, S., Nishio, T. & Fukunaga, S. Isolation of aryl-phosphate ester-degrading  
1178 bacterium from leachate of a sea-based waste disposal site. *Journal of Bioscience and Bioengineering*  
1179 **98**, 464-469, doi:10.1263/jbb.98.464 (2004).
- 1180 125 Abe, K. *et al.* Haloalkylphosphorus Hydrolases Purified from *Sphingomonas* sp Strain TDK1 and  
1181 *Sphingobium* sp Strain TCM1. *Applied and Environmental Microbiology* **80**, 5866-5873,  
1182 doi:10.1128/aem.01845-14 (2014).

- 1183 126 Takahashi, S., Katanuma, H., Abe, K. & Kera, Y. Identification of alkaline phosphatase genes for  
 1184 utilizing a flame retardant, tris(2-chloroethyl) phosphate, in *Sphingobium* sp strain TCM1. *Applied*  
 1185 *Microbiology and Biotechnology* **101**, 2153-2162, doi:10.1007/s00253-016-7991-9 (2017).
- 1186 127 Takahashi, S., Abe, K. and Kera, Y. *Microbial degradation of persistent organophosphorus flame*  
 1187 *retardants*. (2013).
- 1188 128 Latip, W. *et al.* Microbial Phosphotriesterase: Structure, Function, and Biotechnological Applications.  
 1189 *Catalysts* **9**, doi:10.3390/catal9080671 (2019).
- 1190 129 Saeger, V. W. *et al.* ENVIRONMENTAL FATE OF SELECTED PHOSPHATE-ESTERS.  
 1191 *Environmental Science & Technology* **13**, 840-844, doi:10.1021/es60155a010 (1979).
- 1192 130 Zhou, X. Y. *et al.* Biotransformation of Tris(2-chloroethyl) Phosphate (TCEP) in Sediment  
 1193 Microcosms and the Adaptation of Microbial Communities to TCEP. *Environmental Science &*  
 1194 *Technology* **54**, 5489-5497, doi:10.1021/acs.est.9b07042 (2020).
- 1195 131 Vila-Costa, M., Cerro-Gálvez, E., Martínez-Varela, A., Casas, G., Dachs, J. Anthropogenic dissolved  
 1196 organic carbon and marine microbiomes. *ISME J* **14**, 2646–2648, doi:[https://doi.org/10.1038/s41396-](https://doi.org/10.1038/s41396-020-0712-5)  
 1197 [020-0712-5](https://doi.org/10.1038/s41396-020-0712-5) (2020).
- 1198 132 Nemergut, D. R. *et al.* Global patterns in the biogeography of bacterial taxa. *Environmental*  
 1199 *Microbiology* **13**, 135-144, doi:10.1111/j.1462-2920.2010.02315.x (2011).
- 1200 133 Thomson, B. *et al.* Relative Importance of Phosphodiesterase vs. Phosphomonoesterase (Alkaline  
 1201 Phosphatase) Activities for Dissolved Organic Phosphorus Hydrolysis in Epi- and Mesopelagic  
 1202 Waters. *Frontiers in Earth Science* **8**, doi:10.3389/feart.2020.560893 (2020).
- 1203 134 Wang, X. *et al.* A review of organophosphate flame retardants and plasticizers in the environment:  
 1204 Analysis, occurrence and risk assessment. *The Science of the total environment* **731**, 139071,  
 1205 doi:10.1016/j.scitotenv.2020.139071 (2020).
- 1206 135 Zhao, J. P. *et al.* Novel brominated flame retardants in West Antarctic atmosphere (2011-2018):  
 1207 Temporal trends, sources and chiral signature. *Science of the Total Environment* **720**,  
 1208 doi:10.1016/j.scitotenv.2020.137557 (2020).
- 1209 136 Cheng, W. *et al.* Response of polar regions to emerging organic pollutant organophosphorus  
 1210 esters(OPEs),a review. *Advances in Polar Science* **28**, 13-22 (2017).
- 1211 137 Han, X. *et al.* Occurrence and distribution of organophosphate esters in the air and soils of Ny-Ålesund  
 1212 and London Island, Svalbard, Arctic. *Environmental Pollution* **263**, 114495,  
 1213 doi:<https://doi.org/10.1016/j.envpol.2020.114495> (2020).
- 1214 138 Rohler, L. *et al.* Non-target and suspect characterisation of organic contaminants in Arctic air - Part 2:  
 1215 Application of a new tool for identification and prioritisation of chemicals of emerging Arctic concern  
 1216 in air. *Atmospheric Chemistry and Physics* **20**, 9031-9049, doi:10.5194/acp-20-9031-2020 (2020).
- 1217 139 Wang, C. *et al.* Atmospheric organophosphate esters in the Western Antarctic Peninsula over 2014-  
 1218 2018: Occurrence, temporal trend and source implication. *Environmental Pollution* **267**,  
 1219 doi:10.1016/j.envpol.2020.115428 (2020).
- 1220 140 Andresen, J. A., Grundmann, A. & Bester, K. Organophosphorus flame retardants and plasticisers in  
 1221 surface waters. *Science of the Total Environment* **332**, 155-166, doi:10.1016/j.scitotenv.2004.04.021  
 1222 (2004).
- 1223 141 Bester, K. Comparison of TCP concentrations in sludge and wastewater in a typical German sewage  
 1224 treatment plant - comparison of sewage sludge from 20 plants. *Journal of Environmental Monitoring*  
 1225 **7**, 509-513, doi:10.1039/b502318a (2005).
- 1226 142 Fries, E. & Puttmann, W. Occurrence of organophosphate esters in surface water and ground water in  
 1227 Germany. *Journal of Environmental Monitoring* **3**, 621-626, doi:10.1039/b105072a (2001).
- 1228 143 Gao, X. Z. *et al.* Occurrences, sources, and transport of hydrophobic organic contaminants in the  
 1229 waters of Fildes Peninsula, Antarctica. *Environmental Pollution* **241**, 950-958,  
 1230 doi:10.1016/j.envpol.2018.06.025 (2018).
- 1231 144 Gao, X. Z. *et al.* Distribution, sources and transport of organophosphorus flame retardants in the water  
 1232 and sediment of Ny-Alesund, Svalbard, the Arctic. *Environmental Pollution* **264**,  
 1233 doi:10.1016/j.envpol.2020.114792 (2020).



- 1234 145 Lai, N. L. S. *et al.* Assessment of organophosphorus flame retardants and plasticizers in aquatic  
1235 environments of China (Pearl River Delta, South China Sea, Yellow River Estuary) and Japan (Tokyo  
1236 Bay). *Journal of Hazardous Materials* **371**, 288-294,  
1237 doi:<https://doi.org/10.1016/j.jhazmat.2019.03.029> (2019).
- 1238 146 Aznar-Alemany, Ò. *et al.* Halogenated and organophosphorus flame retardants in European  
1239 aquaculture samples. *Science of The Total Environment* **612**, 492-500,  
1240 doi:<https://doi.org/10.1016/j.scitotenv.2017.08.199> (2018).
- 1241 147 Zhong, M. *et al.* Occurrence and spatial distribution of organophosphorus flame retardants and  
1242 plasticizers in the Bohai and Yellow Seas, China. *Marine Pollution Bulletin* **121**, 331-338,  
1243 doi:<https://doi.org/10.1016/j.marpolbul.2017.06.034> (2017).
- 1244 148 Gao, X. *et al.* Organophosphorus flame retardants and persistent, bioaccumulative, and toxic  
1245 contaminants in Arctic seawaters: On-board passive sampling coupled with target and non-target  
1246 analysis. *Environmental Pollution* **253**, 1-10, doi:<https://doi.org/10.1016/j.envpol.2019.06.094> (2019).
- 1247 149 Esteban, S. *et al.* Presence of endocrine disruptors in freshwater in the northern Antarctic Peninsula  
1248 region. *Environmental Research* **147**, 179-192, doi:<https://doi.org/10.1016/j.envres.2016.01.034>  
1249 (2016).
- 1250 150 Choi, W., Lee, S., Lee, H.-K. & Moon, H.-B. Organophosphate flame retardants and plasticizers in  
1251 sediment and bivalves along the Korean coast: Occurrence, geographical distribution, and a potential  
1252 for bioaccumulation. *Marine Pollution Bulletin* **156**, doi:10.1016/j.marpolbul.2020.111275 (2020).
- 1253 151 Wang, Y. *et al.* Organophosphate esters in sediment cores from coastal Laizhou Bay of the Bohai Sea,  
1254 China. *Science of the Total Environment* **607**, 103-108, doi:10.1016/j.scitotenv.2017.06.259 (2017).
- 1255 152 Bekele, T. G., Zhao, H., Wang, Q. & Chen, J. Bioaccumulation and Trophic Transfer of Emerging  
1256 Organophosphate Flame Retardants in the Marine Food Webs of Laizhou Bay, North China.  
1257 *Environmental Science & Technology* **53**, 13417-13426, doi:10.1021/acs.est.9b03687 (2019).
- 1258 153 Zhong, M. *et al.* Occurrences and distribution characteristics of organophosphate ester flame retardants  
1259 and plasticizers in the sediments of the Bohai and Yellow Seas, China. *Science of the Total*  
1260 *Environment* **615**, 1305-1311, doi:10.1016/j.scitotenv.2017.09.272 (2018).
- 1261 154 Zhang, R. *et al.* Occurrence, phase distribution, and bioaccumulation of organophosphate esters (OPEs)  
1262 in mariculture farms of the Beibu Gulf, China: A health risk assessment through seafood consumption.  
1263 *Environmental Pollution* **263**, 114426, doi:10.1016/j.envpol.2020.114426 (2020).
- 1264 155 Liao, C. Y., Kim, U. J. & Kannan, K. Occurrence and distribution of organophosphate esters in  
1265 sediment from northern Chinese coastal waters. *Science of the Total Environment* **704**,  
1266 doi:10.1016/j.scitotenv.2019.135328 (2020).
- 1267 156 Tan, X.-X. *et al.* Distribution of organophosphorus flame retardants in sediments from the Pearl River  
1268 Delta in South China. *Science of the Total Environment* **544**, 77-84,  
1269 doi:10.1016/j.scitotenv.2015.11.089 (2016).
- 1270 157 Harino, H., Yatsuzuka, E., Yamao, C., Ueno, M. & Ohji, M. Current status of organophosphorus  
1271 compounds contamination in Maizuru Bay, Japan. *Journal of the Marine Biological Association of the*  
1272 *United Kingdom* **94**, 43-49, doi:10.1017/s002531541300129x (2014).
- 1273 158 Brandsma, S. H., Leonards, P. E. G., Leslie, H. A. & de Boer, J. Tracing organophosphorus and  
1274 brominated flame retardants and plasticizers in an estuarine food web. *Science of the Total*  
1275 *Environment* **505**, 22-31, doi:10.1016/j.scitotenv.2014.08.072 (2015).
- 1276 159 Ma, Y., Xie, Z., Lohmann, R., Mi, W. & Gao, G. Organophosphate Ester Flame Retardants and  
1277 Plasticizers in Ocean Sediments from the North Pacific to the Arctic Ocean. *Environmental Science &*  
1278 *Technology* **51**, 3809-3815, doi:10.1021/acs.est.7b00755 (2017).
- 1279 160 Hopwood, M. J. *et al.* Review article: How does glacier discharge affect marine biogeochemistry and  
1280 primary production in the Arctic? *Cryosphere* **14**, 1347-1383, doi:10.5194/tc-14-1347-2020 (2020).
- 1281 161 Marklund, A., Andersson, B. & Haglund, P. Organophosphorus flame retardants and plasticizers in air  
1282 from various indoor environments. *Journal of Environmental Monitoring* **7**, 814-819,  
1283 doi:10.1039/b505587c (2005).

- 1284 162 Marklund, A., Andersson, B. & Haglund, P. Traffic as a source of organophosphorus flame retardants  
1285 and plasticizers in snow. *Environmental Science & Technology* **39**, 3555-3562,  
1286 doi:10.1021/es0482177 (2005).
- 1287 163 Sundkvist, A. M., Olofsson, U. & Haglund, P. Organophosphorus flame retardants and plasticizers in  
1288 marine and fresh water biota and in human milk. *Journal of Environmental Monitoring* **12**, 943-951,  
1289 doi:10.1039/b921910b (2010).
- 1290 164 Letcher, R. J. *et al.* Legacy and new halogenated persistent organic pollutants in polar bears from a  
1291 contamination hotspot in the Arctic, Hudson Bay Canada. *Science of the Total Environment* **610**, 121-  
1292 136, doi:10.1016/j.scitotenv.2017.08.035 (2018).
- 1293 165 Kim, J.-W. *et al.* Levels and distribution of organophosphorus flame retardants and plasticizers in  
1294 fishes from Manila Bay, the Philippines. *Environmental Pollution* **159**, 3653-3659,  
1295 doi:10.1016/j.envpol.2011.07.020 (2011).
- 1296 166 Garcia-Garin, O. *et al.* Assessment of organophosphate flame retardants in Mediterranean Boops  
1297 boops and their relationship to anthropization levels and microplastic ingestion. *Chemosphere* **252**,  
1298 doi:10.1016/j.chemosphere.2020.126569 (2020).
- 1299 167 Sala, B. *et al.* Organophosphate ester plasticizers in edible fish from the Mediterranean Sea: Marine  
1300 pollution and human exposure. *Environmental Pollution*,  
1301 doi:<https://doi.org/10.1016/j.envpol.2021.118377> (2021).
- 1302 168 Fernie, K. J. *et al.* Spatiotemporal patterns and relationships among the diet, biochemistry, and  
1303 exposure to flame retardants in an apex avian predator, the peregrine falcon. *Environmental Research*  
1304 **158**, 43-53, doi:10.1016/j.envres.2017.05.035 (2017).
- 1305 169 Sala, B., Gimenez, J., de Stephanis, R., Barcelo, D. & Eljarrat, E. First determination of high levels of  
1306 organophosphorus flame retardants and plasticizers in dolphins from Southern European waters.  
1307 *Environmental Research* **172**, 289-295, doi:10.1016/j.envres.2019.02.027 (2019).
- 1308 170 Ding, Y. *et al.* Bioaccumulation and trophic transfer of organophosphate esters in tropical marine food  
1309 web, South China Sea. *Environment International* **143**, doi:10.1016/j.envint.2020.105919 (2020).
- 1310 171 Fu, J. *et al.* Occurrence and Trophic Magnification of Organophosphate Esters in an Antarctic  
1311 Ecosystem: Insights into the Shift from Legacy to Emerging Pollutants. *Journal of Hazardous*  
1312 *Materials* **396**, doi:10.1016/j.jhazmat.2020.122742 (2020).
- 1313 172 Evenset, A. *et al.* SCREENING OF NEW CONTAMINANTS IN SAMPLES FROM THE  
1314 NORWEGIAN ARCTIC. (2009).
- 1315 173 Zheng, G. *et al.* Legacy and emerging semi-volatile organic compounds in sentinel fish from an arctic  
1316 formerly used defense site in Alaska. *Environmental Pollution* **259**, doi:10.1016/j.envpol.2019.113872  
1317 (2020).
- 1318 174 Verreault, J., Letcher, R. J., Gentes, M. L. & Braune, B. M. Unusually high Deca-BDE concentrations  
1319 and new flame retardants in a Canadian Arctic top predator, the glaucous gull. *Science of the Total*  
1320 *Environment* **639**, 977-987, doi:10.1016/j.scitotenv.2018.05.222 (2018).
- 1321 175 Wu, H. F. *et al.* Biological effects of tris (1-chloro-2-propyl) phosphate (TCPP) on immunity in mussel  
1322 *Mytilus galloprovincialis*. *Environmental Toxicology and Pharmacology* **61**, 102-106,  
1323 doi:10.1016/j.etap.2018.05.022 (2018).
- 1324 176 Song, H. *et al.* Inhibitory effects of tributyl phosphate on algal growth, photosynthesis, and fatty acid  
1325 synthesis in the marine diatom *Phaeodactylum tricornutum*. *Environmental Science and Pollution*  
1326 *Research* **23**, 24009-24018, doi:10.1007/s11356-016-7531-2 (2016).
- 1327 177 Liu, Q. *et al.* Toxic effect and mechanism of tris (1,3-dichloro-2-propyl)phosphate (TDCPP) on the  
1328 marine alga *Phaeodactylum tricornutum*. *Chemosphere* **252**, doi:10.1016/j.chemosphere.2020.126467  
1329 (2020).
- 1330 178 Liu, Q. *et al.* ROS changes are responsible for tributyl phosphate (TBP)-induced toxicity in the alga  
1331 *Phaeodactylum tricornutum*. *Aquatic Toxicology* **208**, 168-178, doi:10.1016/j.aquatox.2019.01.012  
1332 (2019).
- 1333 179 Noyes, P. D., Haggard, D. E., Gonnerman, G. D. & Tanguay, R. L. Advanced morphological -  
1334 behavioral test platform reveals neurodevelopmental defects in embryonic zebrafish exposed to



1335 comprehensive suite of halogenated and organophosphate flame retardants. *Toxicological Sciences An*  
1336 *Official Journal of the Society of Toxicology* **145**, 177-195 (2015).

1337 180 Sun, L. *et al.* Developmental exposure of zebrafish larvae to organophosphate flame retardants causes  
1338 neurotoxicity. *Neurotoxicology & Teratology* **55**, 16-22 (2016).

1339 181 Dishaw, L. V., Hunter, D. L., Beth, P., Stephanie, P. & Stapleton, H. M. Developmental exposure to  
1340 organophosphate flame retardants elicits overt toxicity and alters behavior in early life stage zebrafish  
1341 (*Danio rerio*). *Toxicological Sciences An Official Journal of the Society of Toxicology* **142**, 445-454  
1342 (2014).

1343 182 Jarema, K. A., Hunter, D. L., Shaffer, R. M., Behl, M. & Padilla, S. Acute and developmental  
1344 behavioral effects of flame retardants and related chemicals in zebrafish. *Neurotoxicology and*  
1345 *Teratology* **52**, 194-209, doi:10.1016/j.ntt.2015.08.010 (2015).

1346 183 Fu, J. *et al.* Toxicogenomic Responses of Zebrafish Embryos/Larvae to Tris(1,3-dichloro-2-propyl)  
1347 Phosphate (TDCPP) Reveal Possible Molecular Mechanisms of Developmental Toxicity.  
1348 *Environmental Science & Technology* **47**, 10574-10582, doi:10.1021/es401265q (2013).

1349 184 Mcgee, S. P., Cooper, E. M., Stapleton, H. M. & Volz, D. C. Early Zebrafish Embryogenesis Is  
1350 Susceptible to Developmental TDCPP Exposure. *Environmental Health Perspectives* **120**, 1585-1591  
1351 (2012).

1352 185 Liu, X., Ji, K., Jo, A., Moon, H. B. & Choi, K. Effects of TDCPP or TPP on gene transcriptions and  
1353 hormones of HPG axis, and their consequences on reproduction in adult zebrafish ( *Danio rerio* ).  
1354 *Aquatic Toxicology* **134**, 104-111, doi:<https://doi.org/10.1016/j.aquatox.2013.03.013> (2013).

1355 186 Wang, Q. *et al.* Bioconcentration, metabolism and neurotoxicity of the organophorous flame retardant  
1356 1,3-dichloro 2-propyl phosphate (TDCPP) to zebrafish. *Aquatic Toxicology* **158**, 108-115 (2015).

1357 187 Behl, M. *et al.* Use of alternative assays to identify and prioritize organophosphorus flame retardants  
1358 for potential developmental and neurotoxicity. *Neurotoxicology and Teratology* **52**, 181-193,  
1359 doi:10.1016/j.ntt.2015.09.003 (2015).

1360 188 Wang, Q. *et al.* Developmental exposure to the organophosphorus flame retardant tris(1,3-dichloro-2-  
1361 propyl) phosphate: Estrogenic activity, endocrine disruption and reproductive effects on zebrafish.  
1362 *Aquatic Toxicology* **160**, 163-171 (2015).

1363 189 Zhu, Y. *et al.* Environmentally Relevant Concentrations of the Flame Retardant Tris(1,3-dichloro-2-  
1364 propyl) Phosphate Inhibit Growth of Female Zebrafish and Decrease Fecundity. *Environmental*  
1365 *Science & Technology* **49**, 14579-14587, doi:10.1021/acs.est.5b03849 (2015).

1366 190 Shi, Q. *et al.* Developmental neurotoxicity of triphenyl phosphate in zebrafish larvae. *Aquatic*  
1367 *Toxicology* **203**, 80 (2018).

1368 191 Hanas, A. K. *et al.* Assessment of the effects of early life exposure to triphenyl phosphate on fear,  
1369 boldness, aggression, and activity in Japanese quail (*Coturnix japonica*) chicks. *Environmental*  
1370 *Pollution* **258**, doi:10.1016/j.envpol.2019.113695 (2020).

1371 192 Canals, M. *et al.* The quest for seafloor macrolitter: a critical review of background knowledge, current  
1372 methods and future prospects. *Environmental Research Letters* **16**, doi:10.1088/1748-9326/abc6d4  
1373 (2021).

1374 193 Blum, A. *et al.* Organophosphate Ester Flame Retardants: Are They a Regrettable Substitution for  
1375 Polybrominated Diphenyl Ethers? *Environmental Science & Technology Letters* **6**, 638-649,  
1376 doi:10.1021/acs.estlett.9b00582 (2019).

1377 194 Rao, W. H., Liao, W., Wang, H., Zhao, H. B. & Wang, Y. Z. Flame-retardant and smoke-suppressant  
1378 flexible polyurethane foams based on reactive phosphorus-containing polyol and expandable graphite.  
1379 *Journal of Hazardous Materials* **360**, 651-660, doi:10.1016/j.jhazmat.2018.08.053 (2018).

1380 195 Su, G. Y., Crump, D., Letcher, R. J. & Kennedy, S. W. Rapid in Vitro Metabolism of the Flame  
1381 Retardant Triphenyl Phosphate and Effects on Cytotoxicity and mRNA Expression in Chicken  
1382 Embryonic Hepatocytes. *Environmental Science & Technology* **48**, 13511-13519,  
1383 doi:10.1021/es5039547 (2014).

- 1384 196 Zhang, Q., Yu, C., Fu, L. L., Gu, S. J. & Wang, C. New Insights in the Endocrine Disrupting Effects  
1385 of Three Primary Metabolites of Organophosphate Flame Retardants. *Environmental Science &*  
1386 *Technology* **54**, 4465-4474, doi:10.1021/acs.est.9b07874 (2020).
- 1387 197 Hou, R. *et al.* Accumulation and distribution of organophosphate flame retardants (PFRs) and their di-  
1388 alkyl phosphates (DAPs) metabolites in different freshwater fish from locations around Beijing, China.  
1389 *Environmental Pollution* **229**, 548-556, doi:10.1016/j.envpol.2017.06.097 (2017).
- 1390 198 Li, Y. *et al.* 2-Ethylhexyl Diphenyl Phosphate and Its Hydroxylated Metabolites are Anti-androgenic  
1391 and Cause Adverse Reproductive Outcomes in Male Japanese Medaka (*Oryzias latipes*).  
1392 *Environmental Science & Technology* **54**, 8919-8925, doi:10.1021/acs.est.0c02775 (2020).
- 1393 199 Okeme, J. O., Rodgers, T. F. M., Jantunen, L. M. & Diamond, M. L. Examining the Gas-Particle  
1394 Partitioning of Organophosphate Esters: How Reliable Are Air Measurements? *Environmental*  
1395 *Science & Technology* **52**, 13834-13844, doi:10.1021/acs.est.8b04588 (2018).
- 1396 200 Liu, Y. *et al.* Heterogeneous OH Initiated Oxidation: A Possible Explanation for the Persistence of  
1397 Organophosphate Flame Retardants in Air. *Environmental Science & Technology* **48**, 1041-1048,  
1398 doi:10.1021/es404515k (2014).
- 1399 201 Liu, Q. F. *et al.* Experimental Study of OH-Initiated Heterogeneous Oxidation of Organophosphate  
1400 Flame Retardants: Kinetics, Mechanism, and Toxicity. *Environmental Science & Technology* **53**,  
1401 14398-14408, doi:10.1021/acs.est.9b05327 (2019).

1402

1403 **Table 1.** The names, abbreviations, chemical formulas and physicochemical properties of the most regularly detected organophosphate esters in the ocean

Compound	Abb.	CAS No.	Chemical formula	Solubility <sup>c</sup> (mg/L, 25°C)	VP <sup>b,c</sup> (Pa, 25 °C)	logKow <sup>c</sup>	logKoa <sup>c</sup>	t <sub>1/2</sub> (air) <sup>42</sup> (h)	t <sub>1/2</sub> (Water) <sup>42</sup> (h)	t(air) <sup>200</sup> (day)	t(particle) <sup>201</sup> (day)	t <sub>1/2</sub> (Microbial) <sup>109</sup> (h)
<b>Tris (2-chloroethyl) phosphate</b>	TCEP	115-96-8	C <sub>6</sub> H <sub>12</sub> Cl <sub>3</sub> O <sub>4</sub> P	877.9	8.17	1.44	5.311	12	2172	-	-	41.8
<b>Tris (1-chloro-2-propyl) phosphate</b>	TCIPP	13674-84-5	C <sub>9</sub> H <sub>18</sub> Cl <sub>3</sub> O <sub>4</sub> P	51.85	7.53×10 <sup>-3</sup>	2.59	8.203	7	3270	-	-	-
<b>Tris (1,3-dichloro-2-propyl) phosphate</b>	TDCIPP	13674-87-8	C <sub>9</sub> H <sub>15</sub> Cl <sub>6</sub> O <sub>4</sub> P	1.50	3.81×10 <sup>-5</sup>	3.65	10.62	12	4320	11-14	7.9-19.4	49.5
<b>Trimethyl phosphate</b>	TMP	512-56-1	C <sub>3</sub> H <sub>9</sub> O <sub>4</sub> P	3.004×10 <sup>5</sup>	55.3	-0.65	5.881	33	360	-	-	-
<b>Triethyl phosphate</b>	TEP	78-40-0	C <sub>6</sub> H <sub>15</sub> O <sub>4</sub> P	1.115×10 <sup>4</sup>	22	0.80	6.632	3	360	-	-	-
<b>Tripropyl phosphate</b>	TnPP	513-08-6	C <sub>9</sub> H <sub>21</sub> O <sub>4</sub> P	826.6	3.08	1.87	6.426	-	-	-	-	-
<b>Tri-isopropyl phosphate</b>	TiPrP	513-02-0	C <sub>9</sub> H <sub>21</sub> O <sub>4</sub> P	501.1	18.4	2.12	6.375	-	-	-	-	-
<b>Tributyl phosphate</b>	TnBP	126-73-8	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P	280	0.151	4.00	8.239	3	208.2	-	-	75.3
<b>Tri-isobutyl phosphate</b>	TiBP	126-71-6	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P	16.22	1.71	3.60	7.485	3	360	-	-	73.0
<b>Tripentyl phosphate</b>	TPeP	2528-38-3	C <sub>9</sub> H <sub>21</sub> O <sub>4</sub> P	0.3318	2.33×10 <sup>-3</sup>	5.29	8.805	-	-	-	-	-
<b>Trihexyl phosphate</b>	THP	2528-39-4	C <sub>18</sub> H <sub>39</sub> O <sub>4</sub> P	0.01023	3.29×10 <sup>-4</sup>	6.76	9.905	-	-	-	-	-
<b>Triphenyl phosphate</b>	TPhP	115-86-6	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	1.9	1.49×10 <sup>-3</sup>	4.59	8.459	24	795	5.2-6.0	3.4-8.5	97.6
<b>Tris(2-butoxyethyl) phosphate</b>	TBOEP	78-51-3	C <sub>18</sub> H <sub>39</sub> O <sub>7</sub> P	1.963	1.65×10 <sup>-4</sup>	3.75	13.06	2	456.4		2.4-5.8	-
<b>Tris(2-ethylhexyl) phosphate</b>	TEHP	78-42-2	C <sub>24</sub> H <sub>51</sub> O <sub>4</sub> P	1.461×10 <sup>-5</sup>	1.10×10 <sup>-5</sup>	9.49	14.98	3	240.4	3.5-5.6	2.7-6.6	52.5
<b>2-ethylhexyl diphenyl phosphate</b>	EHDPP	1241-94-7	C <sub>20</sub> H <sub>27</sub> O <sub>4</sub> P	0.06659	4.45×10 <sup>-3</sup>	5.73	8.384	8	780	-	6.5-15.9	30.5
<b>Tricresyl phosphate</b>	TCrP	1330-78-5	C <sub>21</sub> H <sub>21</sub> O <sub>4</sub> P	0.2073	1.62	5.11	9.591	19	909	-	2.6-6.5	29.1, 27.5, 25.2
<b>Di-n-octylphenyl phosphate</b>	DOPP	6161-81-5	C <sub>28</sub> H <sub>45</sub> O <sub>4</sub> P	4.246×10 <sup>-4</sup>	9.88×10 <sup>-6</sup>	8.04	11.74	-	-	-	-	-
<b>Methyl diphenyl phosphate</b>	MDPP	115-89-9	C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> P	61.59	1.55×10 <sup>-3</sup>	2.93	8.786	-	-	-	-	-

<sup>a</sup> The chemical structures are referred to ChemicalBook (<https://www.chemicalbook.com>)

<sup>b</sup> Vapor pressure; <sup>c</sup> Solubility, V<sub>p</sub>, logK<sub>ow</sub> and logK<sub>oa</sub> are adopted from EPIWEB 4.1.

t<sub>1/2</sub>: Half-life time; t: Life time

1404  
1405  
1406