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Organophosphate esters in the ocean

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Abstract

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

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

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

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

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

1. Introduction

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

Because of the risk that pose to human reproductive, genetic, and developmental functions, tris(2-chloroethyl) phosphate (TCEP) is now included in the European Commission (EC) second
priority list of chemicals developed within the EU-Strategy for Endocrine Disruptors. Some OPEs such as TCEP, tributyl phosphate (TBP), and tris-(2-butoxyethyl) phosphate (TBEP) are also registered as high production volume (HPV, more than 1000 tons each year) chemicals under European REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). However, there is no international regulation existing to tackle the increasing pressure from the OPEs emissions. Together with high level of usage and potential toxic risk to human being and ecosystems have made OPEs gain considerable prominence in recent international research.

The broad application for OPEs and their use as additives in plastic products have contributed to their diffusive release and high environmental mobility, mainly by volatilization, leaching and abrasion. For example, more than 44.7 million tons of electronic waste (e-waste) were generated worldwide in 2016, and most them were treated for re-cycling along the coastal cities, especially in developing countries. The most commonly found flame retardants in older electronics are polybrominated diphenyl ethers (PBDEs), which were superseded in newer electronics by non-PBDE brominated flame retardants and OPEs. Open air burning e-wastes may directly release organic additives including OPEs in ambient air. For instance, OPE concentrations reached 740-1000 ng/m³ in in ambient air of Canadian e-waste recycling facilities, and 3.8–57.7 ng/m³ in the rural e-waste recycling area in south China. The air mass back trajectories (BTs) from for the coastal sampling site, demonstrated regional atmospheric transport of OPEs adsorbed to fine particulate matter (PM 2.5) from both industrial cities and the e-waste recycling region. A number of studies have shown river to sea fluxes of OPEs, such as 16-160 kg/d from the Elbe to the North Sea, 16±3.2 t/year from 40 rivers to the Bohai Sea and 450–16,000 t OPEs to the Canadian Arctic Ocean. Model predictions have shown that OPEs are
persistent and mobile in water\textsuperscript{41,42}, which implying the riverine runoff plays an important role for the transportation of OPEs from terrestrial source to the ocean.

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

In this Review, we summarize the studies for OPEs in the global ocean, including the Arctic and Antarctic. The major OPE sources are overviewed, and the environmental pathways are discussed for their effects on the transport processes in the ocean. Environmental concentrations and spatial trends of OPEs in air, sediment, seawater, biota and snow are separately presented. The 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\(^1\), 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\(^2\)-\(^4\), ultrasonication\(^5\),\(^6\) or ASE\(^7\), 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\(^9\).

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\(^1\),\(^8\),\(^10\)-\(^13\) and ultrasonication\(^17\) 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\(^18\).

Liquid-liquid extraction (LLE), in which dichloromethane (DCM) is often selected as the extraction solvent\(^7\),\(^19\), or SPE\(^15\),\(^17\),\(^19\)-\(^24\) 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\(^1\).

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\(^42\),\(^50\),\(^56\). 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.
2. Environmental sources and pathways

OPEs have multiple and concurrent sources in the oceanic environment. An important part of these sources is believed to be land-based \(^{48}\), such as direct volatilization from consumer products (for example, electronic waste) to the atmosphere \(^{36,49,50}\) and direct inputs from rivers \(^{39,51,52}\). The riverine pathway integrates in turn a variety of sources at the river basin scale such as sewage treatment effluents \(^{53,54}\), direct leaks from industries, potential run-off from plastic and/or electronic waste sites, and atmospheric deposition \(^{13}\). These land-based sources result in environmental temporal stocks of OPEs reaching coastal and off-shore areas due to atmospheric transport and deposition \(^{55,56}\) and/or waterborne transport associated with currents \(^{54}\). There is compelling evidence of the widespread occurrence of OPEs in wastewater \(^{25,57,58}\), inland surface water \(^{59}\), ground water \(^{60}\) and seawater \(^{61}\) from Europe, North America and Asia. Additionally, oceanic plastic debris may represent in-situ local sources of OPEs and other organic plastic additives due to leaching. For example, between 0.3 and 0.9 Mt/y of phthalic acid esters (PAEs) have been estimated to be leached to the global oceans from marine fragments of polyethylene (PE) based on laboratory release experiments conducted on PE plastic bags \(^{62}\). Effective release of OPEs and PAEs from PE and PVC was confirmed in another laboratory study performed on surface and deep-waters collected in the Mediterranean Sea \(^{63}\). Interestingly, a more efficient additive release at the ocean surface than in deep seawater was observed \(^{63}\), suggesting that the local sources of plastic additives could vary with depth pointing to differential exposure levels to deep and surface water marine organisms. Both laboratory experiments \(^{62,63}\) highlighted as well the important role of marine prokaryotes promoting the release of OPEs. Once in the ocean, OPEs are known to accumulate in marine sediment and aquatic biota, such as fish and in the tissues of marine mammals \(^{8,19,64-66}\) (Fig. 1).
**Figure 1.** Major environmental sources, processing and pathways of OPEs in the coastal and open oceans. The major continental sources of OPEs include industries area, wastewater treatment plant, e-waste cycling plants and ambient emissions. OPEs undertake environmental pathways e.g. atmospheric and oceanic transport, air-water exchange, atmospheric dry and wet deposition, sedimentation, bioaccumulation and microbial interactions.

### 2.1. Transport from rivers

The riverine transport of OPEs has been highlighted as an efficient pathway contributing to their coastal inputs and subsequent water-borne oceanic stocks. Modeling estimations indicate that chlorinated-OPEs are more efficiently transported by rivers than non-chlorinated OPEs due to their higher water solubility and persistency. Field studies investigating the riverine inputs of OPEs are still discrete and not a large spatial distribution is covered allowing for effective integration over regional and oceanic scales. However, available data support the important role of rivers transporting OPEs. For example, the presence of organic plastic additives (OPEs, PAEs and
bisphenols) in the dissolved water phase from the Rhone river (France), the main freshwater source of the NW Mediterranean Sea, accounted for more than 40% of the total dissolved anthropogenic organic contaminants in surface waters of the river, including PAHs, aliphatic hydrocarbons, pesticides and polyfluorinated alkyl substances. The estimated OPEs inputs associated to the water dissolved phase from the Rhone river to coastal NW Mediterranean Sea varied from 2 to 11 t/y ($\Sigma_9$ OPEs). In addition, important inputs associated with the sedimentary material exported by the Rhone are expected in the Gulf of Lion, based on the OPE concentrations measured in the sediments at the river outlet. OPEs have been measured at high concentrations in the dissolved water phase (up to ~1 µg/L), at the Amazon river plume (in the Western Tropical Atlantic Ocean) suggesting the Amazon River as a major source of these contaminants to the tropical North Atlantic Ocean. This finding points to medium-/long-range contaminant transport, most certainly facilitated by the highly stratified conditions offered by the river plume. Both rivers have been reported to export large amounts of plastic waste. However, a direct link between the organic additive concentrations at the water surface and the abundance of floating plastics couldn’t be established or was not investigated. The total riverine input of OPEs was estimated to be 18 t/y from 40 major rivers entering into the Bohai Sea, North China. In Europe, the riverine input of OPs into the North Sea via Elbe, Ems, and Weser was estimated to be about 50 t/y. Overall, the riverine discharges of OPEs to the coastal areas can be transported with ocean currents further to the open ocean.
2.2. Long-range atmospheric transport

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

Liu et al. estimated heterogeneous reaction rate constants for OPEs in air, and demonstrated that particle-bound OPEs are highly persistent in the atmosphere. However, OPEs were initially thought to be degradable enough to have less persistency in the environment and therefore low potential for LRAT. Reaction with the OH radicals in the atmosphere was expected to be the dominant atmospheric loss process for the OPEs. The half-life time of TCIPP was estimated in the European Risk Assessment from 2008 to be 8.6 hours. This led to the wrong conclusion, that LRAT of TCIPP can be excluded. The atmospheric lifetimes for OPEs are estimated to be less than 1.3 days based on their gaseous OH radical rate constants. However, recent evidence that many OPEs present in the gas phase rather than the particle phase. The persistence and LRAT potential of OPEs in gas phase might be lower estimated, as they are very water-soluble. Moreover,
heterogeneous OH initiated oxidation was studied for OPEs in air, and approximate atmospheric 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 TPhP, TEHP, and TDCIPP. This calculated particle phase lifetime suggested medium-range or long-range transport potential of particle bound OPEs in atmosphere. Many studies have revealed the presence of OPEs in remote environments including oceanic and polar regions as discussed above, which also demonstrates their long-range transport potential. In spite of this, OPEs include both halogenated and nonhalogenated compounds, and show a wide range of physical and chemical properties, suggesting that their atmospheric transport is going to be variable due to wide differences in persistence, particle sorption, and air-water partitioning. Most observations in the remote areas were associated with chlorinated OPEs (TCEP and TCIPP), which also implied stronger potential of LRAT for specific compounds.

2.3. Air-water exchange and atmospheric dry and wet deposition

During transport from source regions to remote oceans, OPEs will be subject to exchange at the interfaces between different environmental media. Atmospheric depositional processes play important role in the environmental fate of OPEs, contribute to aquatic ecosystems burden and support OPEs accumulation in marine food webs.

The magnitude of atmospheric deposition or volatilization is a function of the physicochemical properties (especially Henry’s law constant) and the concentrations of OPEs in air and water, and will be further affected by a number of environmental variables such as wind speed, temperature, salinity, and precipitation frequency and intensity. There are several major processes causing atmosphere-ocean interaction of OPEs, including diffusive air-water exchange between the gaseous and dissolved phases, atmospheric dry deposition of particle-bound OPEs, and wet
deposition by rain and snow$^{5,61,81,85}$. Briefly, dry deposition ($F_{DD}$), wet deposition ($F_{WD}$), and air-water exchange ($F_{AW}$) can be estimated by,

\begin{align*}
F_{DD} &= v_D C_A \quad [1] \\
F_{WD} &= C_{\text{Rain}} p \quad [2] \\
F_{AW} &= k_{AW} \left( \frac{C_G}{H'} - C_W \right) \quad [3]
\end{align*}

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

Air-water exchange fluxes of OPEs have been estimated in a few studies. Na et al. collected air and seawater samples simultaneously on an expedition from the North Pacific to the high Arctic$^5$. The air-water exchange flux ranged from -0.79 to 0.59 ng/m²/d, and TiBP contributed the largest proportion with seawater to air volatilization ranging from 0.19 to 0.72 ng/m²/d. In contrast, TCIPP and TCEP exhibited net deposition fluxes. In the North Atlantic and European Arctic, Li et al. reported the net volatilization flux of 5 to 1080 ng/m²/d, 61 to 12300 ng/m²/d, 12 to 2050 ng/m²/d, and 3 to 954 ng/m²/d for TCEP, TCIPP, TiBP, and TnBP, respectively$^{61}$. While in the coastal area of China, the gaseous exchange fluxes fluctuated in both directions$^7$. TCIPP showed the highest air to seawater deposition flux of 395 ng/m²/d, however TCEP displayed the highest volatilization flux of 1410 ng/m²/d. McDonough et al. calculated fugacity ratios from average equilibrium-corrected OPE concentrations in passive air and water samples, and found OPEs at dynamic equilibrium across the Farm Strait in the Arctic, with the exception of some volatilization of TnBP.
observed at Cape Bounty lake sites in 2016 and of TDCIPP in Barrow Strait in 2015, and deposition of TPHP\textsuperscript{85}.

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

The magnitude of air-water exchange direction and flux depends non-linearly on wind speed, with enhanced fluxes at high wind speeds \textsuperscript{83,87}. In addition, the processes affecting the dissolved and atmospheric concentrations of OPEs can affect the magnitude of air-water exchange. For the OPE components with relatively short half-live times in the atmosphere, volatilization from seawater to air may control the diffusion fluxes. In contrast, dissolved concentrations of hydrophobic OPEs such as TEHP and EHDPP can be depleted by partitioning to particular matters, which upon settling, may deplete OPEs in the surface ocean, a process known as the biological pump. Photo- and bio-degradation can also deplete dissolved phase OPEs, thus favoring the air-to-water diffusive fluxes. Therefore, both the biological and degradative pumps favor deposition of OPEs to the marine environment. These biogeochemical controls on atmospheric deposition have been extensively studied for other semivolatile compounds\textsuperscript{88}, but remain unquantified for OPEs.
The particle-bound OPEs contributed to 67 ± 17% of the total OPEs in the European Arctic\textsuperscript{61}, accounted for 52 ± 23% in the Bohai and Yellow seas\textsuperscript{89}, 71-93% in the North Pacific to the Arctic, 35 ± 17% in the South China Sea\textsuperscript{79}, 86 ± 25% in the North Sea\textsuperscript{3}, 45% at German coast (Büsum)\textsuperscript{71}, 59% at Dalian, China\textsuperscript{90}. The other studies have only determined OPEs in particle phase\textsuperscript{2,4,14,43,56,81,91}. In the Northeast Pacific and the Arctic, the dry particle-bound OPEs deposition fluxes were estimated ranging from 13.64 to 94.17 ng/m\textsuperscript{2}/d\textsuperscript{5}. The same pattern was present in the North Atlantic and European Arctic, while the deposition flux of OPEs was only 2-16 ng/m\textsuperscript{2}/day\textsuperscript{61}, which is similar to those estimated for the South China Sea\textsuperscript{79,91}. More intensive particle-bound OPEs deposition processes were observed in the open Mediterranean (70 ~ 880 ng/m\textsuperscript{2}/d) and Black Seas (300 ~ 1060 ng/m\textsuperscript{2}/d)\textsuperscript{4}, the North African coastal Mediterranean (18 ~ 180 ng/m\textsuperscript{2}/d)\textsuperscript{56}, and the Bohai and Yellow Seas (21 - 250 ng/m\textsuperscript{2}/d)\textsuperscript{89}. These results suggested atmospheric dry deposition can significantly remove particle-bound OPEs from the atmosphere.

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

Wet deposition by rain and snow precipitation can be very important quantitatively in some climatic regions and for some seasons, as an input of OPEs and other organic pollutants to marine environments. Furthermore, both snow and rain amplify the concentrations of organic pollutants in the receiving waters\textsuperscript{92,93}. This amplification of concentrations by snow is driven by the high specific surface area of snowflakes and raindrops, which increase the rain-air washout ratios. The
high water solubility of some OPEs also favor wet deposition fluxes. Both the washout ratios for snow and rain are generally close to $10^5$ for OPEs\textsuperscript{92}. Although the measurements of OPEs in rain water are only available for samples collected on land by few studies\textsuperscript{92,94,95}, these comprise temperate and polar environments. The high concentrations of OPEs measured in rain water imply that wet deposition cannot be ignored, especially for the coastal seas. OPEs in rain water have also been reported for the South Shetland islands (Antarctica)\textsuperscript{92}. In the high latitude oceans, snow deposition plays as effective scavenger for atmospheric OPEs in the Arctic, the Southern Ocean and the Antarctic. The importance of snow deposition has been highlighted by the relatively high OPE concentrations found in the snow samples from the Arctic and Antarctic expeditions \textsuperscript{61,96,97}. Snow scavenging followed by snow melting can represent an important flash of pollutants from coastal land to coastal waters, which has been assessed for other pollutant\textsuperscript{98-100}, but its relevance need to be explored for OPEs.

2.4. Re-emission from melting ice and snow

The areas of sea ice in the Polar Regions react very sensitively to climatic changes. Because of global warming, the areas of sea ice and snow cover are shrinking, and glaciers are transporting their ice toward the low latitudes more rapidly\textsuperscript{101}. Along with the processes of ice retreat and snow melting, chemical contaminants trapped in snow including OPEs could be directly discharged into the water column. Consequently, the fresh input from melting ice and snow enhanced the OPE concentrations in seawater from the East Greenland coast, which are 2-5 times higher than those in the Farm Strait\textsuperscript{61}. Besides, elevated OPE concentrations were measured in the high Arctic Lake Hazen (81°49.5′N, 70°42.8′W) with concentrations from 6.8-19.3 ng/L, which are 5-10 times higher than the North Atlantic Ocean and the Northeast Pacific Ocean\textsuperscript{5,61,102}.
In the Southern Ocean and the Antarctic, raised atmospheric concentrations of OPEs have been measured along the Antarctic coast, which can be attributed to the re-emission from the melting snow and ice of the Antarctic. The studies for organic contaminants in snow and air in the Arctic and Antarctic have shown that melted snow inputs could influence the relative abundance of the chemical components in coastal seawater and amplify their seawater-air fugacity gradient, such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), neutral polyfluoroalkyl substances (PFASs) and OPEs.

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

2.5. Ocean current transport

Previous studies indicated that chlorinated-OPEs can be efficiently transported via ocean currents due to their persistence, lower volatility and high solubility. OPEs have a wide range of physical and chemical properties, and varied from very polar to highly hydrophobic, which may facilitate the transport of some OPEs by water. TCIPP was generally found to be the major chlorinated phosphates in urban rainwater and Elbe River in Germany. Many studies also revealed higher levels of OPEs in the coastal water compared with those in the open seas. The importance of water-borne transport for OPEs depends on the deposition and subsequent transfer of OPEs to the water compartment, followed by their persistence and mobility in the water compartment. The model results showed larger portions of the OPE emissions could enter the water body, and with motilities from 85% for TPhP to 98% TCIPP. The higher mobility of the Cl-OPEs versus non-Cl-OPEs was caused by the low degradation rate of Cl-OPE in water, which
have been also proved by the measurements of OPEs in lake water\textsuperscript{105,106} and oceanic water\textsuperscript{40,52,61,107}. Sühring et al determined 11 OPEs in surface water from Canadian Arctic. The median of ΣCl-OPEs (10 ng/L) was 6 times higher than Σnon-Cl-OPEs 1.3 ng/L. High concentrations of OPEs in samples from the Mackenzie River plume suggested riverine discharges acting as an OPE source to the Canadian Arctic. The Σ\textsubscript{11}OPE inventory was estimated with a median of 4100 tonnes of in the Canadian Arctic Ocean with >99% of the OPE inventory estimated to be in the water column\textsuperscript{40}. This study highlighted water-borne OPEs can be subject to long-range transport via oceanic circulations. Moreover, OPEs are widely used plasticizers and flame retardants in plastic, and floating debris can transport between continents via ocean circulations\textsuperscript{108}, it is speculated that ocean gyres can bring OPEs into the open waters such as in the Southern Ocean.\textsuperscript{6}

\textbf{2.6. Degradation of OPEs}

The environmental degradation of OPEs is a key issue as it determines the persistence of these chemicals in the environment. The persistence is a key aspect when assessing the risk of anthropogenic chemicals. Furthermore, in the natural environment, photo- and bio-degradation are key sinks modulating the fate of many organic pollutants, including the marine environment\textsuperscript{109,110}. Generally, the atmosphere is a very efficient medium for the environmental degradation of organic compounds due to the occurrence of OH radicals, among others. There are few mechanistic studies for the atmospheric degradation of OPEs, though reaction rates for the OH heterogeneous oxidation of several OPEs such as TPhP, TBEP, TEHP, TDCIPP have been measured\textsuperscript{76}. The very short half-life time proposed by the EU risk assessment in 2008 for TCIPP (8.6 h) leading to the wrong conclusion that TCIPP will be not subjected to LART\textsuperscript{78}. From these reaction rates, the
atmospheric half-live times of these OPEs range from few days to weeks. These relatively long residence times in the atmosphere are enough to explain their potential for long-range atmospheric transport, and their occurrence in the global oceanic atmosphere.

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

Photodegradation of OPEs in water has been reported in a few laboratory studies. Although direct photolysis did not account as the main photodegradation mechanism, depletion of OPEs occurred in pure water with dissolved oxygen, and the removal rates could be enhanced in river water. A study with lake water for photodegradation of 5 OPEs (TCEP, TCIPP, TBOEP, TiBP and TnBP) showed the sunlight could degrade TiBP, TnBP and TBOP in 15 days, but was less active for TCEP and TCIPP. The photodegradation is more effective for nonchlorinated OPEs were also proved by the depletion of OPEs in snow and rainwater and global presence of TCEP and TCIPP. While the photodegradation process of OPEs in both air and seawater need to be further explored.
The capacity of microorganisms to degrade OPEs has been studied mostly in isolated bacteria that represent less than 1% of the wild bacteria inhabiting in the environment\textsuperscript{118}. The isolation of OPE-degrading bacteria has been performed in an attempt to optimize environmental-friendly contamination removal strategies, especially for the chlorinated OPE compounds. However, only few OPE-degrading strains have been cultured to date, mainly from soil habitats. Isolated strains able to degrade and use TCEP and TDCIPP as the sole source of P belong to Alphaproteobacteria Sphingobium and Sphingomonas species\textsuperscript{119,120}, Firmicultes \textit{Brevibacillus brevis} sp. that is able to degrade TCP\textsuperscript{121,122}, and the TPhP- and TCrP-degrading \textit{Rhodococcus} and \textit{Sphingopyxis}\textsuperscript{123} and \textit{Roseobacter}\textsuperscript{124}.

Like other organophosphorus triesters, OPEs degradation involves the hydrolysis of the phosphorester bonds mediated by phosphotriesterases, then phosphodiesterases and then phosphomonoesterases. The only phosphotriesterase identified so far that mediates TCEP and TDCIPP biodegradation is a haloalkylphosphorus hydrolase (HAD) that differs from the common families of phosphotriesterases used to degrade aryl dialkyl phosphates, such as parathion and paraoxon among others\textsuperscript{125-128}.

OPEs can be biodegraded by activated sludge from domestic sewage treatment plants and are readily susceptible to biodegradation in rivers by naturally occurring microbial populations\textsuperscript{129}. While, the biodegradation of OPEs and characterization of the associated microbial communities in the natural environment is poorly studied. Currently, only two studies have been performed: one in sediments of a river receiving wastewater discharges, that observed TCEP degradation rates in communities dominated by Burkholderiales, Rhizobiales, Rhodobacterales, and Methylphilaceae\textsuperscript{130}, and one in phosphorus-limited natural seawater, in which consumption of several OPEs was observed along with an increase of activity of Flavobacteria\textsuperscript{131}. Given the
widespread occurrence of Flavobacteria in the global oceans, OPEs biodegradation could be a common feature in the upper ocean\textsuperscript{132}. Furthermore, if OPEs are especially degraded in P limiting waters, then OPEs would be more persistent when P is not a limiting nutrient. Recently, it has been shown that phosphodiesterase activities are much more abundant than expected in the water columns\textsuperscript{133}, and they can account for relevant P acquisition by marine bacteria under inorganic P limitation, favoring the link between atmospheric inputs of anthropogenic organic P and its utilization as a nutrient by marine microbiomes. These processes could be important interactions between anthropogenic chemicals and the Earth system functioning\textsuperscript{131}. In any case, with the current knowledge, the half-live of OPEs in marine waters remain unknown, but these may be dependent on the biogeochemical province.

3. Occurrences of OPEs in the global ocean
Previous review summarized occurrences of OPEs in various matrices, including atmosphere, water, sediment and biota\textsuperscript{134}, which indicated their ubiquity in the world and possible adverse effect on ecosystem. Here we emphasized their occurrence of OPEs in the global ocean and Polar Regions as well as environmental fate of OPEs via long-range transport.

3.1. OPEs in atmosphere
OPEs have been widely detected in the atmosphere of the marginal as well as the high seas (Fig. 2a). Over the Pacific, Indian, Arctic, and Southern Oceans, the concentrations of $\sum_8$OPEs ranged from 120 to 2900 pg/m$^3$ in airborne particles in 2010-2011, with the predominant compounds of TCEP and TCIPP\textsuperscript{43}. The level and profile were consistent with the observation from the Northwestern Pacific to the Arctic Ocean (232-1884 pg/m$^3$) in 2018\textsuperscript{5}. From the tropical and subtropical Atlantic, Pacific, and Indian Oceans, the concentrations of $\sum_{14}$OPEs ranged from 360
to 4400 pg/m³ in particle samples collected mostly in 2011 during the MALASPINA circumnavigation campaign, with TCIPP, TnBP and EHDPP being the predominant OPEs (Fig. 2a). In the West Pacific, the Indian Ocean and the Southern Ocean, OPEs (sum of TBP, TCEP, TCIPP and TDCIPP) were at the levels of a few to hundreds of pg/m³ in the particle samples collected along a global cruise from China to Antarctic over 2009-2010, suggesting their circumpolar and global distribution (Fig. 2a). These levels were generally two orders of magnitude higher than those of BFRs in the ocean atmosphere.

In the Polar Regions, OPEs have been frequently found in the Arctic for the past decade. For instance, $\sum_{13}$OPEs in atmospheric particles was found at concentrations up to 1450 pg/m³ in European Arctic from 2012 to 2013. In Canadian Arctic, the level of $\sum_{13}$OPEs in atmospheric particles showed a generally increasing tendency from 2007 to 2013 with a median concentration of 50 pg/m³. Comparably, the concentrations of eight OPEs were found in the range of 29-180 pg/m³ for the particle phase and 7-163 pg/m³ for gas phase in Arctic 2014 (Fig. 2a). Whereas, at Longyearbyen in the European Arctic, a higher level of particle-bound OPEs were found with a median of 334 pg/m³, which might be caused by local emission. Furthermore, elevated concentrations of OPEs (357-852 pg/m³) were observed in the Arctic based on passive air sampling in 2015, and higher level of OPEs (232 to 1884 pg/m³) was even obtained in the air samples from the Northwestern Pacific to the Arctic Ocean. Recently, 4 OPEs in the particle phase were also found by non-target and suspect characterization of organic contaminants in Arctic air (Zeppelin Station), including TCEP and TCIPP.
Figure 2. Global distribution of OPEs in the oceanic air \(2,4,6,43,61,81,89,91\) (a), which is synthesized with OPE data from research cruises, e.g. R/V Polarstern (Germany)\(^{61}\), Snow Dragon (China)\(^6\) and Malaspina circumnavigation expedition (Spain)\(^{81}\). The lower figure shows seasonal variation of OPEs in air at Yongxing Island in the South China Sea in 2018 (b)\(^{79}\)
There is limited data on these chemicals in the Antarctic. The concentrations of OPEs ranged from 6.0 to 141 pg/m$^3$ in four particle samples collected nearby the Antarctic Peninsula in 2010\textsuperscript{6}. A long-term air monitoring campaign in the Western Antarctic Peninsula over 2014-2018 revealed that the concentrations (gas + particle phases) of $\Sigma_8$OPEs ranged from 33.9 to 404 pg/m$^3$ with a mean of 119±12.0 pg/m$^3$.\textsuperscript{139} The most abundant OPEs were TnBP and TCIPP in air, and chlorinated-OPEs (TCEP, TCIPP and TDCIPP) accounted for 51% of total OPEs on average. This level was even comparable to those found in Arctic air, suggesting input of OPEs into Antarctic via LRAT in recent years.

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

3.2. OPEs in seawater

Most available data on OPEs in water were from studies on effluents from the wastewater treatment plants (WWTPs), as well as inland surface waters\textsuperscript{28,41,51,57,134}. WWTPs were considered an important sink of many POPs emitted from urban anthropogenic sources, where the OPEs reach concentrations up to μg/L\textsuperscript{134,140,141}. Experiments for the removal rate of TCIPP from WWTPs in Germany have shown more than 50% of TCIPP found in effluent, which rinsing the concern for OPEs in surface water. Consequently, OPEs have been found in the surface waters from lakes and rivers with concentrations ranging from 10 to 1000 ng/L\textsuperscript{41,51,60,67,142}.
Figure 3. Concentrations of OPEs (ng/L) in seawater in the global oceans\cite{5,20,51,52,61,65,104,143-145}, which shows high levels of OPEs present at marginal seas of Asia and Europe (a); OPEs discharged from the Amazon River were transported in the tropical Atlantic\cite{52}(b), and oceanic transport of OPEs from the North Atlantic to the Arctic Ocean\cite{61} (c).

In a survey in coastal areas of seven European countries\cite{146}, OPEs were detected in all samples and the sum concentrations of OPEs (TBOEP, TCEP, TCIPP, EHDPP, TNBP, TPHP, and TDCIPP) ranged from 0.43 to 867 ng/L in transitional/coastal water (Fig. 3a). High levels were found in the seawaters from the UK ($\Sigma_7$OPEs, 275±34.9 ng/L) and Portugal ($\Sigma_7$OPEs, 547±437 ng/L), correlating with the sampling sites that were the closest to urban areas. Comparable levels (mean 243 ± 327 ng/L) were found for the $\Sigma_9$OPEs in the dissolved water phase samples collected in the
Bay of Marseille (NW Mediterranean Sea). Likewise, from the German Bight (North Sea), the concentrations of ∑18OPEs were at a range of 5-50 ng/L in the seawater in 2010, correlating negatively (r=−0.94) with salinity. These results are generally consistent with those in coastal seas of China, where the concentrations of ∑7OPEs were at a range of 8-98 ng/L in the Bohai Sea and Yellow Sea, and TCIPP and TCEP were the dominant pollutants. However, relatively higher levels of OPEs were also observed in seawater near the coastal cities in China, e.g., 91.9-507 ng/L in the Yellow Sea and East China Sea, 87.6 to 969.4 ng/L in the Laizhou Bay, and 810-3620 ng/L in the off-shore of Bohai Bay (Fig. 3a). These values are consistent with observations in the Pearl River Delta, South China Sea, Yellow River Estuary and Tokyo Bay, where the sum concentrations of ∑14OPEs in the range of 15-1790 ng/L, 1-147 ng/L, 253-1720 ng/L, and 107-284 ng/L, respectively (Fig. 3a). In the Western Pacific, 10 OPEs were determined in seawater with the contraptions of ∑10OPEs ranging from 3.0 to 48.4 ng/L (mean 25.0 ± 10.5 ng/L). TCEP was the predominant OPE. In the tropical North Atlantic, dissolved OPEs (1300 ng/L) from the Amazon River were transported more than 3000 km via the North Brazil Current and its retroflection (Fig. 3b).

In the high seas, the sum concentrations of 3 Cl-OPEs ranged from 0.9 to 17.4 ng/L in the Arctic surface water sampled by passive polyethylene samplers (PEs). Similarly, the concentrations of ∑8OPEs in the North Atlantic and the Arctic were measured using liquid-liquid extraction for 0.8 L seawater, which ranging from 0.35 to 8.4 ng/L. The four highest concentrations measured at sites near continents, implying anthropogenic inputs into ocean. In the Canadian Arctic, the mean concentrations of ∑chlorinated-OPEs (Cl-OPEs) and ∑non-chlorinated-OPEs were 10 ng/L and 1.3 ng/L, respectively, in surface water over 2013-2018. Similarly, two chlorinated OPEs (TCIPP and TDCIPP) were observed at 2.7 to 8.4 ng/L in Arctic seawaters sampled by an on-board
passive sampling strategy\textsuperscript{148}. Occurrence of OPEs was observed in seawater from the Northwestern Pacific to the Arctic in 2018, and the sum concentrations ranged from 8.5 to 143 ng/L\textsuperscript{5}, which are higher than those from the European Arctic\textsuperscript{61} (Fig. 3c). In addition, there is no clear spatial trend for OPEs in seawater from China towards the Arctic, while a declining trend was noticed from the North Atlantic to the Arctic (Fig. 3c)\textsuperscript{61}, which shows clearly oceanic transport from European seas to the Arctic. Interestingly, relatively high concentrations of $\Sigma_6$OPEs were found in the range of <5.0-44.4 ng/L in seawater of Fildes Peninsula, Antarctica\textsuperscript{143}, and 19.6-9209 ng/L in freshwater from the northern Antarctic Peninsula\textsuperscript{149}, which are attributed to local emissions from scientific research stations and tourist vessels in the Antarctic Peninsula.

### 3.3. OPEs in marine sediment

Influenced by the different degrees of human activities, average $\Sigma$OPEs concentrations ranging over two orders of magnitude (0.35-71 ng/g dw) have been reported in sediment from ocean regions, including straits, near-shore and off-shore areas (Figure 4c, Table S2). Elevated levels of $\Sigma_{18}$OPEs were found in sediments along the coast of Korea, with the maximum and average values of 347 and 71.0 ng/g dry weight (dw), respectively, among which the higher concentrations usually occurred in harbors\textsuperscript{150}. In the Bohai region of China, decreasing levels of $\Sigma$OPEs were reported in sediment with the extension of sampling areas: Laizhou Bay (6.65-102 ng/g dw\textsuperscript{151}, 0.100-96.9 ng/g dw\textsuperscript{152}) > Bohai Bay (1.66-28.7 ng/g dw)\textsuperscript{17} > Bohai Sea (0.205-4.55 ng/g dw)\textsuperscript{153} (Figure 4b). A few to tens of ng/g dw of $\Sigma$OPEs were found for sediments from Beibu Gulf (range: 4.35-22.1,ng/g dw)\textsuperscript{154}, the Taiwan Strait (range: 5.26-34.2,ng/g dw)\textsuperscript{10}, the Bohai and East China Sea (1.76-49.9,ng/g dw)\textsuperscript{155}, the coast of Hainan Island (range: nd-60.0,ng/g dw)\textsuperscript{11} and the Pearl River Estuary (range: 12.0–66.0,ng/g dw)\textsuperscript{156} in China, the Maizuru Bay in Japan (range:
<0.500–56.0 ng/g dw)\textsuperscript{157}, and the San Francisco Bay in USA (median: 23.0 ng/g dw)\textsuperscript{19}. Recently, Alkan et al.\textsuperscript{68} reported relatively high levels of Σ₉OPEs (range: 4-227 ng/g dw) in sediments across the Gulf of Lion in northwest Mediterranean Sea. Limited studies reveal that the levels of OPEs in ocean sediment are substantially lower than those found for the marginal seas. The detected concentrations of Σ₇OPEs from the North Pacific to the Arctic Ocean ranged from 0.2 to 4.7 ng/g dw, with the average value of 0.9 ng/g dw (Figure 4a)\textsuperscript{66}. This study revealed that the concentrations of Σ₇OPEs, especially the chlorinated OPEs (TCEP, TCIPP and TDCIPP), increased from Bering Strait to the Central Arctic Ocean, implying the transference and accumulation of OPEs in oceanic sediments. Gao et al.\textsuperscript{144} reported higher levels of Σ₇OPEs in the sediment of Ny-Ålesund, Svalbard, the Arctic (range: 0.01-14.9 ng/g dw) in comparison to those in Central Arctic Ocean (range: 0.32-4.7 ng/g dw) reported by Ma et al.\textsuperscript{66}, suggesting low temperatures limit the degradation of OPEs in polar oceans\textsuperscript{144}. Recently, Sühring et al. reported elevated concentrations of Σ₁₁OPEs (median: 8.3 ng/g dw, range: 0.12-57 ng/g dw) in sediment in the Canadian Arctic Ocean, which has been attributed to the local riverine discharge\textsuperscript{40}. In many studies, chlorinated OPEs (especially TCEP and TCIPP), have been the most abundant detected OPEs in ocean sediments, consistent with their extensive usage and their low degradation rates. Due to the relatively strong hydrophobicity, TEHP (log Kow: 9.49)\textsuperscript{19,153} and TCrP (log Kow: 5.11)\textsuperscript{11} have also been identified as the dominant OPEs in sediments by several studies. In contrast, TnBP and TBOEP were the most abundant OPEs in sediments from Taiwan Strait, China\textsuperscript{10} and Western Scheldt estuary, Netherlands\textsuperscript{158}, respectively. This regional pollution feature should be attributed to the large usage of these compounds locally.

Although the deep ocean is commonly considered as the final oceanic repository of OPEs, inventory analysis shows that only a small proportion of the produced OPEs in the world have been preserved in ocean sediment\textsuperscript{40,66,153}, but the reservoir in the water column remains unknown.
In a study on OPEs inventory in the Canadian Arctic Ocean, Sühring et al. estimated that water column OPEs even accounted for ~99% of the total OPEs inventory\(^{40}\). The transfer of OPEs from surface waters to sediments is mediated by the biological pump, thus the sorption of OPEs to settling particles, a process especially relevant for the more hydrophobic OPEs. The study for partitioning of OPEs between the water phase and sewage sludge in WWTPs has shown only 1% of the OPEs entering the WWTP retained by the sludge, and most of the chlorinated OPEs went through the plant with water phase without degradation\(^{25}\). As marine sediment contents less organic matter than sludge, during vertical transport, the microbial degradation of OPEs concurrent with organic matter mineralization might be limited. Generally, the extent of sediments and water column as a final sink of OPEs will depend on the water column biogeochemistry, that needs further research.
Figure 4. Spatial distribution of OPEs in the sediment from the North Pacific to the high Arctic (a), and in the Bohai and Yellow Seas (b). OPEs concentrations in sediments from different regions are summarized (c), shows the coastal areas play as important sink for OPEs.\textsuperscript{13,18,19,40,65,144,153,154,157,159}
3.4. OPEs in snow from Polar Regions

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

In the Arctic, OPEs have been measured in surface snow collected along a transect between East Greenland and Svalbard\textsuperscript{61}. The concentrations of $\sum_8$OPEs (TCEP, TCIPP, TDCIPP, TnBP, TiBP, TPhP, TEHP, TPeP) ranged from 4.36 to 10.6 ng/L with a mean of 7.83 ng/L. TCIPP was
the most abundant OPEs in Arctic snow with a mean of 3.89 ng/L, followed by TiBP (2.00 ng/L), TCEP (1.29 pg/L) and TnBP (0.63 pg/L). The concentrations of OPEs in snow samples collected from coastal sites were 2 times higher than those from the central Arctic, and the composition pattern of OPEs in snow was comparable with that of OPEs in seawater. These pioneering works showed the major role of long-range atmospheric transport and snow deposition in the global distribution of OPEs.

3.5. OPEs in organisms

The investigations on OPEs in marine organisms including zooplankton, invertebrates, bivalves, fish, birds and mammals have revealed their widespread occurrence of OPEs across food webs in various oceanic environments (Fig. 5a). In general, markedly lower concentrations of OPEs were reported in biota samples collected from North America compared to those from European and Asia regions. For example, the levels of Σ13OPEs of bivalve samples in San Francisco Bay, United States (US) ranged from 8.7-25 ng/g lw\(^1\) as compared to those from the coast of Korea (Σ13OPEs: 18.4-1516 ng/g lw\(^2\))\(^1\)50, Sweden (Σ11OPEs: 190-1600 ng/g lw\(^2\))\(^63\) and Spain (individual OPE: nd-623.6 ng/g lw\(^2\))\(^64\). The concentrations of OPEs in harbor seal from US (nd-56 ng/g lw\(^2\))\(^19\) and in Polar bear from Canada (nd-0.902 ng/g lw\(^2\))\(^164\) were also much lower than those from Svalbard, Norway (nd-372.41 in harbor seal and nd- 52.5 ng/g lw in polar bear\(^84\) (Fig. 5a). Comparable concentrations of ΣOPEs in fish were reported in several studies on samples from Svalbard, Norway (mean Σ14OPEs: 713 ng/g lw\(^84\), Manila Bay, Philippines (mean Σ9OPEs: 683 ng/g lw\(^165\), NW Mediterranean Sea (meanΣ19OPEs: 526 ng/g lw\(^166\) and coast of Sweden (mean Σ11OPEs: 342 ng/g lw\(^163\), while relatively high levels (mean Σ20OPEs: 1630 ng/g lw) were found for Laizhou Bay, Bohai Sea, China\(^152\). Sala et al. detected OPEs in edible fish from the Mediterranean Sea including European sardine (Sardina pilchardus), European anchovy (Engraulis
encrasicolus), and European hake (Merluccius merluccius), with concentrations between 0.38 and 73.4 ng/g wet weight. Pattern analysis of OPE congeners shows that TCIPP, TBOEP, TnBP, TPhP, TEHP and TDCIPP were commonly detected as the predominant OPEs in marine organisms. The differences in the OPE patterns among studies may result from local pollutions from near-shore.

Species-dependent discrepancies in OPEs concentrations have been observed in marine organisms, which were significantly lower in birds and mammals than in fish. Hallanger et al. reported that 9 OPEs (TCEP, TCIPP, TDCIPP, TPHP, EHDPP, TBOEP, TCrP, TEHP and DPhBP; mean: 7.81-537.16 ng/g lw) were found in capelin collected from Svalbard, Norway, as compared to those of <5 OPEs found in most of the other species, including kittiwake, brünnich's guillemot, glaucous gull, ringed seal, harbour seal, arctic fox and polar bear (mean: 1.91-955.09 ng/g lw). Low concentrations of individual OPEs were reported for the peregrine nestlings in the Great Lakes Basin, ranging from 0 to 7.5 ng/g ww. Another study measured OPEs in liver and blubber of harbour porpoises from the UK, and reported that only 5 OPEs (TEP, TPhP, TEHP, TBOEP and EHDPP) were detected with low detection frequencies (DFs) of 3-44%. Four out of 13 OPEs (TCEP, TCIPP, TDCIPP and TPhP) were found in harbor seal blubber in San Francisco Bay, United States with the median concentrations of <LOD to 13 ng/g lw. Five out of 17 OPEs were quantifiable at sub-ppb levels in polar bear fat samples, but with variable and low detection frequencies. This contrast with high levels of ΣOPEs detected in brain (1530 ng/g lw), muscle (645 ng/g lw) and blubber (267 ng/g lw) in dolphin collected from the Alboran Sea.
Figure 5. Concentrations of OPEs (ng/g lw) in organism samples from Antarctic Peninsula and the Arctic ocean ($^{28,84,164,171-174}$) (a); and nine OPEs (ng/g, dw) in different species in the South China Sea ($^{170}$) (b).
In tropical food webs, 11 OPEs were detected in fifteen types of organism from the South China Sea, and the concentrations of OPEs in the organisms decreased with the increase of their trophic levels in the order: phytoplankton (922 ng/g dw) > zooplankton (660 ng/g dw) > oysters (309 ng/g dw) > crabs (225 ng/g dw) > coral tissues (202) > fishes (58.2)\textsuperscript{170} (Fig. 5b). TCIPP, TCEP and TCIDPP were dominant OPEs in phytoplankton, zooplankton and in coral tissues. While, Zoobenthos and the eight fish species had similar OPE composition profiles dominated by TCIPPs and TBOEP\textsuperscript{170}.

4. Bioaccumulation and effects in marine organisms

Several studies have shown that higher exposure to OPEs was observed in demersal marine organisms than in zooplankton and phytoplankton, indicating that greater accumulation of OPEs occurs in the benthic environment. For examples, in the organisms from coast of Sweden, the concentration of EHDPP was reported 14,000 ng/g lw in eelpout (bottom dwelling fish) compared with those found for other fish (< 78 ng/g lw)\textsuperscript{163}. The concentrations of $\Sigma_9$OPEs in demersal fish (230-1900 ng/g lw) were significantly higher than those in pelagic fish (110-760 ng/g lw) from Manila Bay\textsuperscript{165}. Bekele et al. also observed significant difference in $\Sigma_{20}$OPEs between benthic fish (mean: 2120 ng/g lw) and pelagic fish (1200 ng/g lw)\textsuperscript{152}. However, high OPE concentrations have been found in zooplankton (i.e. at the base of many pelagic food webs) in coastal Mediterranean with vales reaching up to 4.6 $\mu$g/g d.w for the $\Sigma_9$OPEs\textsuperscript{65}. Overall, the profiles of OPEs in marine organisms are influenced by sampling sites, species and even developmental stages of such organisms, which could be attributed to different usage of OPEs in different regions, as well as the discrepancies in habitat, diet, and metabolic and accumulation behaviors of OPEs in the organisms\textsuperscript{84,163,165}.
The bioaccumulation and biomagnification potential of OPEs in marine organisms depends on their physicochemical properties, bioavailability and extent of biotransformation\textsuperscript{165}. Octanol–water partition coefficient (log $K_{ow}$) values of OPEs cover a large range from -0.65 (TMP) to 9.49 (TEHP)\textsuperscript{134} (Tab. 1). Significant correlations of bioconcentration factors (BCFs) with log $K_{ow}$ values of OPEs are observed in marine biota, implying that hydrophobicity plays an important role in bioaccumulation of OPEs\textsuperscript{152,154} (Fig. 6 and Tab. S4). While different result was obtained by Schmidt et al. that no relationship between BCFs and log $K_{ow}$ of OPEs was observed\textsuperscript{65}. BCFs higher than the threshold value (5000 L/kg) used under the Stockholm Convention on POPs to identify bioaccumulative chemicals were generally found for TCEP, TDCIPP, TiBP, EHDPP and TEHP in this study\textsuperscript{65}. Furthermore, several studies showed that most OPEs detected in marine organisms are not correlated with the lipid contents\textsuperscript{150,158,163,165}, with the exception of TEP and TPeP reported by Kim et al. in fish\textsuperscript{165}. Weak biomagnification of OPEs through food web also implies limited bioaccumulation of these compounds. As stated above, even lower detection frequencies (DFs) and concentrations of OPEs were observed in higher trophic levels (such as birds, seals, arctic foxes and polar bears) than in fish in Arctic biota\textsuperscript{84}. This may be due to either poor assimilation from the diet or rapid metabolism of OPEs in these species such as birds and polar bears\textsuperscript{164}.

Kim et al. investigated the biomagnification of OPEs in 20 species of fish in Manila Bay, Philippines by establishing the correlations of $\delta^{15}$N values with concentrations of OPEs in fish\textsuperscript{165}. The result showed that OPEs did not bio-magnify through the food web except for TPhP in demersal fish\textsuperscript{165}. However, Brandsma et al. reported that the levels of TPhP decreased with the increasing in trophic levels both in benthic and pelagic food web in Western Scheldt estuary, Netherlands, while the biomagnification of TBOEP, TCIPP and TCEP (trophic magnification
factors >1) through the benthic food web was observed\textsuperscript{158}. In the food web in Laizhou Bay, China, 8 OPEs (including TEP, TnBP, TCIPP, TDCIPP, TBOEP, TEHP, CDPP and TCrP) showed trophic magnification\textsuperscript{152}. These results may be influenced by the distinct input of OPEs in local species and different metabolic processes among these species. Furthermore, research on bioaccumulation and biomagnification of OPEs through marine food webs is very limited, and just performed in select tissue, such as liver, and plasma in marine mammals\textsuperscript{84}. More attention should be paid to the bioaccumulation behavior of OPEs in marine organisms to determine the biomagnification potential of these chemicals.

At present, little is known about the biological effects the OPEs elicited in marine species, populations, ecological systems, and humans, particularly from a one-health perspective. Wu et al. suggested that TCIPP could disturb the immune system of marine mussel by evaluating the endpoints including reactive oxygen species, apoptosis, antioxidant system and related gene expressions\textsuperscript{175}. Several studies investigated toxic effects of OPEs to algae, which are important primary producers in the marine ecosystem and sensitive to pollutants\textsuperscript{176-178}, and reported that TDCIPP inhibited the population growth of \textit{Phaeodactylum tricornutum} in a concentration-dependent manner by disrupting photosynthesis\textsuperscript{177}. Both TDCIPP and TnBP increased the levels of reactive oxygen species and led to oxidative damage in \textit{Phaeodactylum tricornutum} cells at the experimental concentrations (2-10 mg/L for TDCIPP and 0.2-1.6 mg/L for TnBP)\textsuperscript{177,178}. Although neurotoxicity, and developmental and reproductive toxicity of some OPE compounds (i.e., TCEP\textsuperscript{179-182}, TCIPP\textsuperscript{179,181}, TDCIPP\textsuperscript{179,181-189}, TPhP\textsuperscript{179,182,185,187,190}, TCrP\textsuperscript{179,182,187}, TBOEP\textsuperscript{179,180} and TnBP\textsuperscript{180}) have been reported for freshwater fish models, biological effects of OPEs in marine fish and more higher trophic levels of organisms are rarely investigated. A recent study found that TPhP could disrupt ecologically-relevant behaviours inof Coturnix japonica at environmentally
relevant or greater concentrations, implying the health risks of OPEs in wild birds\textsuperscript{191}. In addition, since OPEs tend to accumulate in the benthic marine environment as discussed above, much more attention should be paid to the health risks of bottom dwelling species. The input of OPEs to the marine environment is persistent and therefore, knowledge on potential ecological risks caused by these compounds, especially adverse effects resulting from chronic exposure, antagonistic interactions and biomagnification, is urgently required in the future\textsuperscript{19,152,165}.

Figure 6. Biota-water accumulation factors (log BCF) of OPEs in marine organisms\textsuperscript{65,152,154}

5. Future perspectives

Both ocean currents and the atmosphere are relevant pathways for OPEs transport on a global scale, but they have different contributions to the global distribution of individual OPEs, which needs more intensive studies in different oceanic regions. Chlorinated-OPEs can be efficiently transported via ocean currents due to their persistence, lower volatility and high solubility\textsuperscript{14,41,
while non-chlorinated OPEs (excluding TnBP and EHDPP which may relate to local sources) are likely mainly transported via air advection due to potential adsorption onto particles. Recently, it has been suggested that sea-spray aerosol can be an important vector for the regional and long-term transport of organic pollutants, and the relevance of this process needs to be assessed for OPEs. Furthermore, the role of oceanic plastics as significant in-situ and mobile sources of OPEs should be further investigated, also in relation to other potential OPE sources into the Ocean. Particularly, a qualitative and quantitative assessment of OPE leaching from microplastics accumulated in sediments, considered as final sinks of plastic debris, should be addressed. Existing data based on laboratory experiments point to a lower release of some OPEs from plastics under deep-sea conditions compared to surface waters, but no data on direct release from plastics settled on the sediments exists, to the best of our knowledge. The occurrence of OPEs in the deep seafloor (and the water-sediment interface) and organisms should be further investigated, also in relation to the large plastic accumulation in this environment and the potential longer-term or chronic exposure to OPEs and other plastic additives in profound oceanic environments.

Local usage and environmental behaviors of OPEs, as well as discrepancies in habitat, diet, and metabolic behaviors of OPEs in different species, may play important roles in the occurrence and bioaccumulation of OPEs in marine organisms. Current studies on occurrence of OPEs in marine organisms mainly focus on near-shore regions. Further investigations in relation to off-shore regions could help to clarify the natural behaviors of these compounds and environmental impacts on the global ocean. Although OPEs seem not to bio-magnify like other POPs such as PBDEs, potential accumulation of hydrophobic OPEs with a high logK_{ow} has been observed in marine organisms. The bioaccumulation and biomagnification behaviors of OPEs through food webs, particularly the entry mechanisms at the first steps (such as plankton), still need to be further
scrutinized in the future, also in relation to their potential biological effects. In addition, much attention should be paid to health risks induced by OPEs on benthic species, because benthos shows greater accumulation of these compounds than pelagic species.

Given the knowledge of OPEs in global ocean summarized in this review and other works, it is shown that, OPEs are sufficiently persistent to be distributed globally and present health hazards potential to marine organisms due to their bioaccumulation and biomagnification behavior. Given the large volume of OPEs on the market and increasing consumption, national and international policies were called to regulate the production and application of OPEs, and to develop more safe alternative flame-retardants. Especially, TCEP and TCIPP should gain more attention and be considered for global regulatory framework as soon as possible.

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

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

The environmental occurrence of OPEs (i.e. triester-OPEs) degradation products in marine environments has been little investigated. Experimental in vivo and in vitro studies have
demonstrated that a certain number of tri-OPEs can be transformed to di-ether metabolites (di-OPEs)\textsuperscript{105}, Some di-OPEs could induce comparable or higher toxic effects than their respective triesters\textsuperscript{111,196}. The few existing studies report di-OPEs in fish\textsuperscript{197,198}, water\textsuperscript{112} and sediments\textsuperscript{115} from inland aquatic ecosystems. Only one study focused on marine sediment to the best of our knowledge.\textsuperscript{54}

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

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

In terms of global warming, new input of OPEs from the melting ice sheet and snow may alter the concentrations and vertical profile in the water columns at high latitude. This will subsequently change environmental pathways of OPEs in the ocean environment and related health
impacts. Consequently, future research will need to understand the various biogeochemical and
geophysical processes under climate change and anthropogenic pressures to be able to predict the
environmental fates and the global ocean health impacts of OPEs accurately.
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Author contributions

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

Competing interests

The authors declare no competing interests.

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179 Noyes, P. D., Haggard, D. E., Gonnerman, G. D. & Tanguay, R. L. Advanced morphological - behavioral test platform reveals neurodevelopmental defects in embryonic zebrafish exposed to


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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abb.</th>
<th>CAS No.</th>
<th>Chemical formula</th>
<th>Solubility * (mg/L, 25°C)</th>
<th>VP^ab (Pa, 25°C)</th>
<th>logKow</th>
<th>logKoa</th>
<th>t1/2 (air) ^c</th>
<th>t1/2 (Water)</th>
<th>t(air)^2h</th>
<th>t(particle)^2h</th>
<th>t1/2 (Microbial)^100</th>
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<tr>
<td>Tris (2-chloroethyl) phosphate</td>
<td>TCEP</td>
<td>115-96-8</td>
<td>C₆H₅Cl₃O₆P</td>
<td>877.9</td>
<td>8.17</td>
<td>1.44</td>
<td>5.311</td>
<td>12</td>
<td>2172</td>
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<td>-</td>
<td>41.8</td>
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<td>Tris (1-chloro-2-propyl) phosphate</td>
<td>TCIPP</td>
<td>13674-84-5</td>
<td>C₆H₅Cl₃O₆P</td>
<td>51.85</td>
<td>7.53×10⁻³</td>
<td>2.59</td>
<td>8.203</td>
<td>7</td>
<td>3274</td>
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<td>-</td>
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<td>Tris (1,3-dichloro-2-propyl) phosphate</td>
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<td>13674-87-8</td>
<td>C₆H₅Cl₃O₆P</td>
<td>1.50</td>
<td>3.81×10⁻⁴</td>
<td>3.65</td>
<td>10.62</td>
<td>12</td>
<td>4320</td>
<td>11-14</td>
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<td>Trimethyl phosphate</td>
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<td>3.08</td>
<td>1.87</td>
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<td>Tri-isopropyl phosphate</td>
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<td>501.1</td>
<td>18.4</td>
<td>2.12</td>
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<td>Tributyl phosphate</td>
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<td>Tri-isobutyl phosphate</td>
<td>TiBP</td>
<td>126-71-6</td>
<td>C₆H₅O₆P</td>
<td>16.22</td>
<td>1.71</td>
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<td>Tri-pentyl phosphate</td>
<td>TPeP</td>
<td>2528-38-3</td>
<td>C₆H₅O₆P</td>
<td>0.3318</td>
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<td>Trihexyl phosphate</td>
<td>THP</td>
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<td>C₆H₅O₆P</td>
<td>0.01023</td>
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<td>Triphenyl phosphate</td>
<td>TPhP</td>
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<td>1.49×10⁻³</td>
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<td>8.459</td>
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<td>795</td>
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<td>3.4-8.5</td>
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<td>Tris (2-butoxyethyl) phosphate</td>
<td>TBOEP</td>
<td>78-51-3</td>
<td>C₆H₅O₆P</td>
<td>1.963</td>
<td>1.65×10⁻¹</td>
<td>3.75</td>
<td>13.06</td>
<td>2</td>
<td>456.4</td>
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<td>-</td>
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<td>TEHP</td>
<td>78-42-2</td>
<td>C₆H₅O₆P</td>
<td>1.461×10⁻³</td>
<td>1.10×10⁻¹</td>
<td>9.49</td>
<td>14.98</td>
<td>3</td>
<td>240.4</td>
<td>3.5-5.6</td>
<td>2.7-6.6</td>
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<td>2-ethylhexyl diphenyl phosphate</td>
<td>EHDPP</td>
<td>1241-94-7</td>
<td>C₁₀H₁₂O₄P</td>
<td>0.06659</td>
<td>4.45×10⁻¹</td>
<td>5.73</td>
<td>8.384</td>
<td>8</td>
<td>780</td>
<td>-</td>
<td>-</td>
<td>6.5-15.9</td>
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<td>Tricresyl phosphate</td>
<td>TCP</td>
<td>1330-78-5</td>
<td>C₁₀H₃O₆P</td>
<td>0.2073</td>
<td>1.62</td>
<td>5.11</td>
<td>9.591</td>
<td>19</td>
<td>909</td>
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<td>2.6-6.5</td>
<td>29.1, 27.5</td>
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<td>Di-n-octylphenyl phosphate</td>
<td>DOPP</td>
<td>6161-81-5</td>
<td>C₈H₁₀O₆P</td>
<td>4.246×10⁻⁴</td>
<td>9.88×10⁻⁴</td>
<td>8.04</td>
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<td>Methyl diphenyl phosphate</td>
<td>MDPP</td>
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<td>C₁₀H₃O₆P</td>
<td>61.59</td>
<td>1.55×10⁻¹</td>
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<td>8.786</td>
<td>-</td>
<td>-</td>
<td>-</td>
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* The chemical structures are refered to ChemicalBook (https://www.chemicalbook.com)
^bVapor pressure; c Solubility, VP, logKow and logKoa are adopted from EPIWEB 4.1.
^c Half-life time; t: Life time