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Review

A Review of Organophosphate Esters in Aquatic Environments: Levels, Distribution, and Human Exposure

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Abstract: Organophosphate esters (OPEs) are increasingly used as flame retardants and plasticizers in various products. Most of them are physically mixed rather than chemical bonded to the polymeric products, leading to OPEs being readily released into the surrounding environment. Due to their relatively high solubility and mobility, OPEs are ubiquitous in the aquatic environment and may pose potential hazards to human health and aquatic organisms. This review systematically summarized the fate and distribution of OPEs in the aquatic environment and the potential effects of OPEs on humans. Data analysis shows that the concentrations of OPEs vary widely in various types of aquatic environments, including surface water (range: 25–3671 ng/L), drinking water (4–719 ng/L), and wastewater (104–29,800 ng/L). The results of human exposure assessments via aquatic products and drinking water ingestion indicate that all OPEs pose low, but not negligible, risks to human health. In addition, the limitations of previous studies are summarized, and the outlook is provided. This review provides valuable information on the occurrence and distribution of OPEs in the aquatic environment.

Keywords: organophosphate esters; aquatic environment; distribution characteristics; aquatic organisms

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1. Introduction

Organophosphate esters (OPEs), a new type of flame retardant, are considered the ideal replacement for brominated flame retardants (BFRs) due to fewer production steps, simpler processes, low prices, good flame retardant performance, and long-lasting effects [1]. Generally, OPEs, though they have wide variety, are primarily classified into two categories: monomeric OPEs and oligomeric OPEs. Table 1 lists the primary information for the most common OPEs in this review. OPEs are commonly used in electronic products, textile coatings, lubricants, hydraulic fluids, building materials, and children's toys [2,3]. In recent years, with the gradual prohibition of BFRs [4], the global consumption of OPEs continues to rise [5,6], from 0.68 million tons in 2015 to more than 100 million tons in 2018. China is one of the nations with the highest consumption and production of OPEs worldwide [7], and the annual production volume of OPEs was about 0.36 million tons in 2020. These data suggest that OPEs have become a major flame retardant [8,9].

As OPEs are usually present in the final products through physical additions rather than chemical bonds, and as most OPEs are semi-volatile, they may easily enter and contaminate the environment via volatilization, dissolution, and abrasion. Over the past few decades, the rapid increase in the global consumption and production of OPEs had led to the widespread occurrence of OPEs in all water bodies including wastewater, rivers, oceans, drinking water [10], and even in biota [11].

In terms of toxicity, previous studies reported that OPEs may show genetic toxicity, reproductive system disorders, deterioration of immune system function, and carcinogenic dermatitis to animals due to short-term and long-term exposure [12,13]. Currently, most studies have focused on chlorinated OPEs (Cl-OPEs), such as TCEP, TCPP, and TDCPP, which may be more cytotoxic than alkyl-OPEs and aryl-OPEs. Some countries have begun

to legislate in order to restrict its production and use [14]. In addition, some studies have reported the biological toxicity of alkyl-OPEs and aryl-OPEs. TBOEP may cause a delay in gonadal development and an inhibition in the growth of zebrafish [13]. TPhP have been demonstrated to cause hepatotoxicity and metabolic disorders in male Chinese rare minnows [15].

Table 1. Properties and applications of common organophosphate esters.

Compound	Abbr.	CAS No.	Molecular Formula	Molecular Mass	LogK_{ow}	Solubility (mg/L, 25 °C)
Trimethyl phosphate	TMP	512-56-1	$C_3H_9O_4P$	140.07	−0.65	3.00×10^5
Triethyl phosphate	TEP	78-40-0	$C_6H_{15}O_4P$	182.16	0.8	5×10^5
Tri-n-butyl phosphate	TnBP	126-73-8	$C_{12}H_{27}O_4P$	266.32	4	280
Tri-iso-butyl phosphate	TiBP	126-71-6	$C_{12}H_{27}O_4P$	266.31	3.60	3.72
Tripropyl phosphate	TPP	513-08-6	$C_9H_{21}O_4P$	224.23	2.35	6450
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	$C_{24}H_{51}O_4P$	434.64	9.43	2
Tris(2-butoxyethyl) phosphate	TBOEP	78-51-3	$C_{18}H_{39}O_7P$	398.48	3.75	1100
2-Ethylhexyl diphenyl phosphate	EHDPP	1241-94-7	$C_{20}H_{27}O_4P$	362.40	6.30	1.9
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$	285.48	1.44	7000
Tris(1-chloro-2-propyl) phosphate	TCPP	13674-84-5	$C_9H_{18}Cl_3O_4P$	327.56	2.59	1200
Tris(2-chloro-1-(chloromethyl)ethyl) phosphate	TDCPP	13674-87-8	$C_9H_{15}Cl_6O_4P$	430.90	3.80	1.50
Triphenyl phosphate	TPhP	115-86-6	$C_{18}H_{15}O_4P$	326.29	4.59	1.9
Tri-3-cresyl phosphate	TCrP	563-04-2	$C_{21}H_{21}O_4P$	368.36	5.11	1.20×10^{-2}
Cresyl diphenyl phosphate	CDPP	26444-49-5	$C_{19}H_{17}O_4P$	340.31	4.51	0.24
2,2-bis(chloromethyl)trimethylenebis(bis(2-chloroethyl)phosphate)	V6	38051-10-4	$C_{13}H_{24}Cl_6O_8P_2$	582.99	1.92	2.1
Bisphenol-A bis(diphenyl phosphate)	BDP	5945-33-5	$C_{39}H_{34}O_8P_2$	692.63	7.41	0.42
Tetraphenyl resorcinol bis(diphenylphosphate)	RDP	57583-54-7	$C_{30}H_{24}O_8P_2$	574.45	4.50	1.1×10^4

Note—abbr.: abbreviation; CAS no.: chemical abstract service number; and log Kow: octanol-water partition coefficient.

OPEs can enter the aquatic environment via several paths, such as atmospheric deposition, rainfall, and surface runoff [16,17]. OPEs have a complex migration and transformation process under different hydrodynamic forces in the water environment, which makes the distribution of OPEs change constantly. The differences in the partitioning behavior of OPEs in an aquatic environment were observed due to their different physicochemical properties. Generally, chlorinated OPEs are more hydrophilic than others. For example, TCEP, TCPP, and TDCPP are hard to transform or degrade in aquatic environments and therefore have a higher proportion in water than in sediment. Nevertheless, some water-soluble OPEs (i.e., TEP and TCEP) can also enter sediment by combining with suspended matter, such as plankton, in the water via gravity. OPEs with poor water solubility are more likely to be adsorbed in sediments [18]. OPEs in the water may be diluted [19,20] or enriched during transport, or may be carbonized by microbial decomposition. However, OPEs that are difficult to degrade will be continuously enriched in sediment and will become long-term and potential secondary pollution sources. Large quantities of OPEs have been observed in various water bodies and corresponding sediments worldwide; this is especially the case in Arctic marine sediments and seawater, indicating that OPEs can be transported over great distances through the atmosphere to remote areas, making the aquatic environment the long-term global sink for OPEs [21].

As one kind of emerging contaminant, OPEs have been monitored in relation with stricter national regulations [22]. A variety of instrumental methods have been reported in the correlative literature for the determination of OPEs in surface water, wastewater, etc. [2,8,23]. Chromatography-mass spectrometry is playing an increasingly important role in OPEs analysis due to the high development of mass spectrometry (MS) and chromatographic techniques. These compounds are separated and detected by using gas or liquid chromatography (GC or LC) combined with mass spectrometry after previous extraction/purification steps. Of these, UPLC-MS/MS is an advanced tool for structural identification due to its higher selectivity and sensitivity. It improves the selectivity for identifying OPEs with high polarity, large molecular weight, and low volatility.

Recently, the majority of studies have only focused on the occurrences and fate of a few typical OPEs, while the environmental behavior of OPEs has not been as thoroughly studied. Therefore, the fate of OPEs in an aquatic environment and in organisms has raised widespread concern. At present, the characteristics of pollution and the health risks associated with OPEs in the aquatic environment have not yet been systematically summarized. A comprehensive study of OPEs in different aquatic environments is essential to understand the risk that these emerging contaminants pose to human health. Therefore, we performed a comprehensive review of the current literature on the pollution situation of OPEs in wastewater, surface water, drinking water, and aquatic organisms, and summarized the human health risk assessment of OPEs via seafood and drinking water (Figure 1). We collected the relevant publications from the Web of Science, Google Scholar, and ScienceDirect databases from 2014 to 2023. The search terms used for the articles were "OPEs in water", "aquatic environment", "MS", and "human exposure".

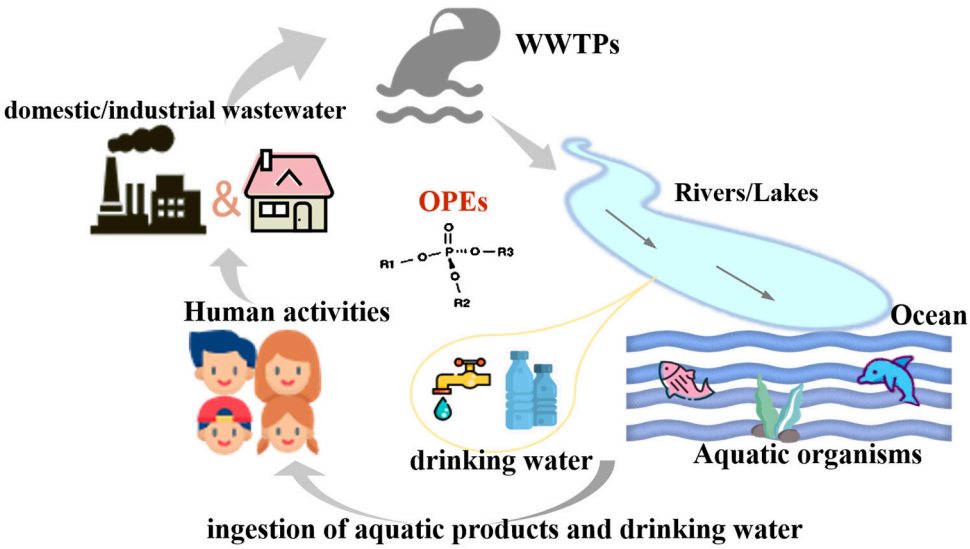

Figure 1. The pathway of OPEs in an aquatic environment.

2. OPEs in Aquatic Environment

2.1. Wastewater

Wastewater treatment plants (WWTPs) receive and treat domestic and industrial wastewater, which play a certain role in the process of OPEs entering the environment [24]. The concentration of OPEs in wastewater and sludge from various WWTPs of recent studies are summarized in Table 2.

Table 2. Concentration of OPEs in wastewater and sludge from various WWTPS.

Location of Sampling			TCPP	TDCPP	TCEP	TBOEP	TNBP	TPhP	TEHP	EHDPP	ΣOPE	Analysis Instrument	Year	Ref.
New York (The United States)	Wastewater (ng/L)	Influent	5120	1722	1427	30,143	291	491	392	ND	2230–117,000	HPLC-MS/MS	2017	[25]
		Effluent	5949	3106	1106	12,641	301	293	50.5	ND	-			
Beijing (China)	Wastewater (ng/L)	Influent	465	-	150	398	120	15.4	7.10	-	-	HPLC-MS/MS	2016	[26]
		Effluent	605	-	254	103	93.1	6.20	<LOD	-	-			
The Pearl River Delta (China)	Wastewater (ng/L)	Influent	299.0	60.3	438.2	4349.4	21,271.8	149.2	-	-	-	GC-MS	2015	[27]
		Effluent	472.9	94.5	372.2	494.5	3105.1	24.8	-	-	-			
Beijing (China)	Wastewater (ng/L)	Influent	225.0	22.8	179.1	600.3	74.4	21.3	ND	14.0	1399	UPLC-MS	2016	[28]
		Effluent	338.9	15.9	232.9	39.9	29.8	4.4	ND	0.9	833			
Beijing (China)	Wastewater (ng/L)	Influent	440	28	245	31	3.8	0.6	ND	ND	-	GC-MS	2016	[29]
		Effluent	413	47	250	47	48	ND	ND	ND	-			
Catalonia (Spain) Wastewater (ng/L)	WWTP1 (ng/L)	Influent	1700	129	180	1560	<MDL	101	<MDL	<MDL	3670	GC-MS	2016	[30]
		Effluent	2400	136	250	207	220	40	<MDL	<MDL	3060			
	WWTP2 (ng/L)	Influent	6750	290	320	1200	210	250	131	270	2170			
		Effluent	3000	354	373	620	90	64	<MDL	<MDL	5240			
	WWTP3 (ng/L)	Influent	3600	111	295	7000	900	177	120	440	151,000			
		Effluent	3700	319	570	1970	174	37	<MDL	<MDL	29,800			
	WWTP4 (ng/L)	Influent	3200	220	220	4600	305	95	12	84	50,500			
		Effluent	2800	210	240	1500	136	55	<MDL	<MDL	5170			
	WWTP5 (ng/L)	Influent	3710	67	320	8600	135	124	35	240	13,500			
		Effluent	3100	174	330	3600	65	70	<MDL	<MDL	7530			
25 WWTPs (China)	Wastewater (ng/L)	Influent	265	31	56	288	183	8.1	8.1	5.5	-	UHPLC-MS/MS	2023	[31]
		Effluent	238	26	45	71	11	2.9	1.9	0.5	-			
WWTP Wastewater (ng/L)	Spring (ng/L)	Influent	435.9	70.2	216.1	91.9	-	15	2.3	3.2	838.3	UPLC-MS	2020	[32]
	Autumn (ng/L)	Influent	323.3	54.7	236.9	0.7	-	10.2	7.4	8.7	595.2			
	Winter (ng/L)	Influent	223.5	35.1	79.9	45.7	-	7.9	3.9	6.5	-			
	Spring (ng/L)	Influent	368.8	44.6	184.1	115.9	-	9	2.2	1.4	-			

Table 2. *Cont.*

Location of Sampling			TCPP	TDCPP	TCEP	TBOEP	TNBP	TPhP	TEHP	EHDPP	ΣOPE	Analysis Instrument	Year	Ref.
Guangzhou (China)	Wastewater (ng/L)	Influent	756.9	92	254.2	-	353.2	20.3	192.3	-	-	GC-MS	2019	[33]
		Effluent	651.6	88.4	218.7	-	28.36	1.63	15.44	-	-			
Guangzhou (China)	Wastewater (ng/L)	Influent	3872	<LOD	928	<LOD	-	-	-	-	4807	GC-MS	2018	[34]
		Effluent	54.1	<LOD	31.5	<LOD	-	-	-	-	103.9			
WWTP (Greece)	Wastewater (ng/L)	Influent	864–3277	29.8–310	50.3–186	476–4037	28.9–129.8	69.5–1299	33.3–376	-	2144–9743	GC-MS	2022	[35]
		Effluent	460–1444	9.9–214	46.3–161.4	98.9–783	4.58–83.3	34.1–377	28.3–130	-	1237–2909			
Shandong Peninsula (China)	Wastewater (ng/L)	Effluent	518.6	55.3	545.8	12.3	30.9	7.2	-	-	1568	UPLC-MS/MS	2022	[36]
Ontario (Canada)	Wastewater (ng/L)	Effluent	1250–2390	210–400	140–340	290–10,200	-	5760	-	-	-	LC-MS/MS	2018	[37]
The Pearl River Delta (China)	Wastewater (ng/L)	Influent	14–638	<LOQ-95.7	<LOQ-113	ND-311	ND-2248	10.1–290	ND-84.9	-	65.8–2842	GC-MS	2019	[38]
		Effluent	5.4–104	<LOQ-21.5	<LOQ-31.9	ND-23.1	ND-2541	1–108	<LOQ	-	6.37–2710			
Zhengzhou (China)	Wastewater (ng/L) Sludge (ng/L)	Influent	204.2	15.6	172.3	648.7	50.6	15.2	-	-	1106.5	UPLC-MS/MS	2016	[39]
		Effluent	196	7.5	171.8	96.6	35.9	3.8	-	-	511.7			
		Sludge	60.7	28	21.5	48	53.2	16.9	-	-	228.3			
		Influent	90.8	11.1	70	294.4	53.6	8.8	-	-	528.6			
		Effluent	80.1	8.4	61.4	34.1	401	3.2	-	-	227.4			
		Sludge	52.9	30.9	45.7	67	31	38.7	-	-	266.2			
67 WWTPs (The United States)	Sludge (ng/g)	sludge	61.7	101	10.6	1760	127	30.4	199	189	3070	HPLC-MS/MS	2019	[40]

Note—MDL: the method detection limit; "-": not measured; ND: not detected; LOD: limit of detection; and LOQ: the limit of quantitation.

The mean values or range (min–max) are shown. The most abundant and frequent OPEs in wastewater were TCPP, TCEP, TBOEP, and TnBP. The existence of OPEs in WWTPs could be due to their widespread application in consumer and industrial material products [24]. A recent study investigated 20 OPEs in influents from 25 WWTPs in China. TEP, TBOEP, TCPP, TMP, TnBP, TCEP, TDCPP, and TPhP were found in all samples, with the first three compounds at a high concentration (mean: 392, 288, and 265 ng/L, respectively). The low detection frequency (16%) and concentration (≤16 ng/L) for TPrP could be explained by its seldom use [31]. Liu et al. (2019) used GC-MS to study OPEs in wastewater from a WWTP for one year in China, and revealed that seven of the nine targeted OPEs were detected in all influent samples. TCPP (mean: 741 ng/L) and TEP (mean: 687 ng/L) were the dominant OPEs in the influent [33]. Deng et al. (2018) revealed that a high level of OPEs (2144–4807 ng/L) were observed in a municipal landfill leachate treatment system in Guangzhou, China. The wastewater samples obtained in each treatment stage contained five common OPEs. TCPP was dominant throughout the treatment process and accounted for more than 80% and 50% of OPEs in influents and effluents, respectively [34]. Pantelaki et al. (2022) studied the fate of OPEs in two WWTPs in Greece [35]. The total OPE concentration varied from 2144 ng/L to 4807 ng/L in influents and from 1237 ng/L to 2909 ng/L in effluents. TBOEP and TCPP were the most abundant compounds in both WWTPs. In a survey of wastewater effluents in the Toronto area, it was shown that the highest concentration of TBOEP was up to 10,000 ng/L [37]. Recently, most studies about the fate of OPEs in WWTPs only focused on monomeric OPEs, whereas there are fewer studies on oligomeric OPEs. Liang et al. (2018) used UPLC-MS/MS to determine the concentration of three oligomeric OPEs (V6/BDP/RDP) in sewage and sludge [41]. The results showed that V6 was detected throughout the whole treatment stages of WWTP, and the concentration in the water phase was 10.2–27.1 ng/L. Compared with fourteen widely used OPEs, the concentration levels of oligomeric OPEs in WWTPs were relatively low, indicating that its market share was limited. Similarly, Wang et al. (2019) revealed RDP (nd-9.2 ng/L), BDP (nd-6.8 ng/L) and V6 (nd-6.4 ng/L) in the sludge of the United States [40]. Sufficient research data suggested that OPEs were ubiquitous in wastewater [41–43].

Previous studies reported that WWTP has a certain removal efficiency for OPEs in wastewater. The concentration of OPEs was mostly reduced in WWTPs through activated sludge adsorption and microbial degradation [32]. Crisdale et al. (2016) studied the sludge of five wastewater treatment plants in Spain and found that the concentration of TEHP in the influent was not high (<139 ng/L); however, the TEHP concentration was the highest in the sludge (367–1570 ng/kg) [30]. In addition, EHDPP can be detected in sludge but not in effluent. These results indicated that sludge adsorption is a primary method by which to remove these hydrophobic OPEs. Zeng et al. (2015) revealed that with the decrease in water solubility, the distribution of TCPP and TDCPP in the solid phase increased, and they were transferred to the sludge and discharged during the purification process [27]. In addition, biodegradation also plays a vital part in the removal of OPEs from influents [28]. Nevertheless, the different degradation efficiencies of OPEs in WWTPs were observed due to their various physical and chemical properties. Previous studies from Kim et al. (2017) and Zeng et al. (2015) proposed that linear alkyl substances (e.g., TnBP) are degraded by microorganisms more rapidly than branched substances (e.g., TiBP), and chlorinated OPEs are more resistant to degradation than non-chlorinated OPEs [25,27]. In view of the different treatment and degradation methods of WWTPs, the concentration and distribution of OPEs vary significantly [38].

Wastewater was regarded as a primary source of OPEs due to the relatively low removal of OPEs in WWTPs [25,29,31,35,40]. The composition and concentration of OPEs in wastewater are closely related to their usage, physicochemical properties, and sources. Kim U.J. et al. (2017) detected 16 types of OPEs in the wastewater from a New York WWTP using HPLC-MS/MS, with total concentrations ranging from 2230 ng/L to 117,000 ng/L. Six types of OPEs were detected in all samples (n = 48). The removal efficiency was calculated by comparing the total concentration in influent wastewater and final effluents.

The removal rates of TBOEP and TEHP were slightly higher than 60%, while the other OPEs were lower than 40%. The three chlorinated OPEs analyzed in this study showed negative removal efficiencies, indicating that the removal process in WWTPs is incomplete [25]. Wang et al. (2019) found that OPE triesters and diesters were ubiquitous in the sludge collected by WWTP around the United States, and that TBOEP and BBOEP were dominant in the sludge [40]. Most diesters were detected with a high detection frequency (85–100%), while only two chlorinated diesters, BCEP and BCIPP, showed a low detection frequency of 62% and 32%. This indicated that chlorinated OPEs were more resistant to degradation and less efficient in purification than aryl-OPEs and alkyl-OPEs. Zang et al. (2020) revealed that negative removal may be caused by pollution from sewage treatment facilities and purification pipelines [14,32] or through the sludge release from sedimentation tanks. Despite their relatively high removal efficiencies, a fair amount of the OPEs in the effluent was still released into the aquatic environment, which again indicated that effluent from WWTPs is a vital source of OPEs in the aquatic environment [36].

Compared with the abovementioned studies, the concentration of OPEs in wastewater is comparatively high. As an emerging contaminant with bioaccumulation and toxicity [44,45], if it cannot be effectively controlled by the WWTPs, then there will be potential environmental and ecological risks. Sludge and wastewater are significant media for OPEs to enter various environments [33]. Moreover, dehydrated sludge can be used as fertilizer in agriculture [46,47] and then absorbed and transferred to crops, which gradually leads to water and soil pollution, affecting the quality of agricultural products. Therefore, it is necessary to treat sludge reasonably in order to safely and sustainably use it as a fertilizer.

2.2. Surface Water (Rivers, Lakes, and Coastal Seawater)

In general, surface water receives OPEs via several paths, such as from industrial wastewater, atmospheric deposition, and surface runoff [48,49]. The specific concentrations of OPEs in various lakes and oceans of recent studies are summarized in Table 3.

Table 3. Concentration of OPEs in surface water from various regions (ng/L).

Location of Sampling	ΣOPE	Alkyl-OPEs				Chlorinated-OPEs			Aryl-OPEs		Analysis Instrument	Year	Ref.
		TMP	TEP	TnBP	TBOEP	TCEP	TCPP	TDCPP	TPhP	TCrP			
Luoma Lake, China	0.8–708	<MDL-127	<MDL-32.1	0.01–5.9	0.002–0.2	0.01–552	0.02–10.8	0.03–2.0	0.15–8.2	0.7–54.6	HPLC-MS/MS	2018	[50]
Jiaozhou Bay, China	474.9–6776.3	ND-8.1	172.0–904.4	1.3–328.3	3.1–152.8	ΣChlorinated-OPEs: 206.7–5614.8			ΣAryl-OPEs: 3.1–20.0		HPLC-MS/MS	2022	[36]
Laizhou Bay, China	262.8–2907.3	<MDL-90	55.6–2390.1	1.3–86.3	2.4–247.2	ΣChlorinated-OPEs: 143.4–1096.1			ΣAryl-OPEs: 2.3–25.9				
Zijiang River, China	18.8–439	ND-2.89	0.3–9.9	1.2–58	0.97–33.1	1.29–26.6	ND-366	ND-10.1	ND-14.8	-	UPLC-MS	2022	[51]
Taihu Lake, China	100–1700	2.7–84	53–1400	0	ND-2.7	14–76	12–2900	ND-6.0	ND-14	ND-1.5	HPLC-MS	2018	[52]
Bohai Sea, China	10.9–516.4	-	0.7–168.1	-	-	4.8–474.0	ND	-	ND	-	GC-MS/MS	2021	[53]
Poyang Lake, China	38.4–428.9	ND-1.22	2.3–60.7	-	ND-3.52	6.4–52.1	13.4–143.4	ND-70.7	ND-18.9	ND-10.5	UPLC-MS/MS	2022	[54]
The western South China Sea	2.3–24.4	-	-	0.1–2.2	-	0.8–22.6	0.4–6.2	ND-0.3	0.01–0.1	-	GC-MS	2022	[48]
Shanghai, China (Urban/Rural)	340–1688.7	-	-	11.6–63.3	15.9–100.6	67.5–865.2	123.9–523	<LOQ-45.3	1.67–47.7	-	GC-MS	2019	[55]
	185.4–321	-	-	6.91–44.8	<LOQ-47.9	30–63.3	60–154.2	<LOQ	5.03–34.3	-			
Source water, Shanghai	415.7–822.6	-	100.8–182.0	19.8–138.6	1.2–27.5	70.8–129.5	184.3–363.3	4.9–18.1	<MDL-3.6	<MDL	UPLC-MS/MS	2022	[56]
Nanjing, China	4.4–195,269	ND-18.5	ND-932.6	ND-385.3	1.1–547.3	ND-15,483	ND-244.3	ND-16273	ND-290	ND-126.6	HPLC-MS/MS	2022	[57]
Beibu Gulf, China (Summer/winter)	34.2–1227	0.05–14.8	-	0.4–1033	0.8–10.3	1.2–44.9	13.4–164	ND-6.7	0–26	-	GC-MS/MS	2022	[58]
	20.6–840	ND		ND-782	10–22.8	0.7–13.2	3.4–112	0.7–2.7	ND	-			
Xiangjiang River, China	6.1–25.3	-	-	0.1–8.9	-	ND-0.5	2–13.5		0.1–8.4	-	GC-MS/MS	2021	[20]
Qinzhou Bay, China	150–885	<LOD-2.4	ND-14	ND-139.8	-	30.9–370.3	23.7–568.4	ND-61.4	<LOD-11.5	-	GC-MS	2021	[59]
The West Pacific Ocean	3.02–48.4	-	-	0.5–16.7	-	0.7–26.4	0.8–3.3	0.5–8.3	<LOD-0.2	-	GC-MS	2021	[60]
The Canadian Arctic	0.02–306	-	-	<LOD-8.1	<LOD	<LOD-246	0.2–53	<LOD-11	<LOD-63	-	GC-MS	2021	[61]

Table 3. *Cont.*

Location of Sampling	ΣOPE	Alkyl-OPEs				Chlorinated-OPEs			Aryl-OPEs		Analysis Instrument	Year	Ref.
		TMP	TEP	TnBP	TBOEP	TCEP	TCPP	TDCPP	TPhP	TCrP			
Greece (River water/Coastal water/Streams)	400–2158	-	<MDL-134	15–374	<LOD-997	18–163	59–208	<LOD-14	40–258	77–95	GC-MS/MS	2021	[19]
	408–1270	-	<MDL-126	17–92	<LOD-625	17–162	67–113	<LOD-21	41–260	59–126			
	377–30,560	-	<MDL-352	16–5961	<LOD-11418	19–1018	55–10,742	<LOD-1988	45–1142	77–718			
The Rhone River, France	84.8–264.6	-	-	4.4–138.1	-	ND-25	36.6–173.1	3.1–8.7	ND-10.7	-	GC-MS	2020	[49]
Lake Shihwa, Korea	597–16,000	-	42.2–3677	-	145–839	86.5–5963	68.3–5102	<LOQ-325	5.1–96.2	-	GC-MS/MS	2018	[18]
Amazon River	74–1341.1	-	-		<LOQ-6.5	<LOQ-1.6	74–1300	-	<LOQ-6.9	-	GC/MS	2019	[62]
San Francisco Bay, US	170–5100	-	-	7.8–43	24–1000	7.4–300	46–2900	14–450	41–360	-	GC-MS	2019	[63]
New York State (River/Lake/Seawater)	37.2–510	<LOQ-4	<LOQ-24.8	-	2.53–366	<LOQ-79.5	3.3–214	<LOQ-86.7	<LOQ-36.5	-	HPLC-MS/MS	2018	[64]
	8.2–1280	<LOQ-5.2	<LOQ-92.1	-	0.6–689	<LOQ-123	4.7–329	<LOQ-159	<LOQ-28.7	-			
	40–60.8	<LOQ-0.1	0.8–1.8	-	<LOQ-7.7	-	25.8–36.3	8.9–25.4	<LOQ-1.6	-			

Note—MDL: the method detection limit; "-": not measured; ND: not detected; LOD: limit of detection; and LOQ: the limit of quantitation.

The most abundant and frequent OPEs reported in surface water were TCPP, TCEP, TBOEP, and TPhP. However, the dominant OPEs in different regions and different types of water environment were evidently different [50,55,65]. According to previous research on wastewater in WWTPs, Cl-OPEs were recalcitrant to traditional wastewater treatment technology. Therefore, chlorinated OPEs will enter the surface water with effluents and will occupy the main part [61]. Lian et al. (2022) revealed the total OPE concentration in the near WWTP effluents were higher than those in the Jiaozhou Bay [36]. Due to the low removal rate, Cl-OPEs were the dominant fraction in the Jiaozhou Bay, accounting for 63% of the total concentration. The concentration of TCEP was the highest (a mean of 546 ng/L). This behavior was in agreement with most of the investigations into surface water, such as the West Pacific [60] and the Canadian Arctic Ocean [61]. Zhu et al. (2022) revealed that chlorinated OPEs were the main pollutants at 23 water sites, and Cl-OPEs accounted for 65% of the total concentration. TCEP (mean 193.2 ng/L) and TCPP (mean 51.8 ng/L) accounted for 79% and 21% of all Cl-OPEs, respectively [66]. The concentration of chlorinated OPEs was comparable to those in Taihu Lake [52] and Poyang Lake [54].

The concentrations of OPEs in dissolved phase water showed similar spatial distribution, i.e., the pollution in tributaries was higher than those in the main stream. Xing et al. (2018) investigated 12 OPEs in the surface water of Luoma Lake and several tributaries [50]. The results showed that the concentrations of ΣOPEs in Louma Lake (127–708 ng/L) was lower than those in its tributary, the Fangting River (1066 ng/L), which is where a large number of villages and factories surround the area. Liu et al. (2018) detected 12 OPEs in the surface water and sediments from Taihu Lake using HPLC-MS, and the results showed that elevated levels of OPEs were found in the sampling sites of the northern region [52]. As industrial wastewater and livestock wastewater are mainly discharged to the north of Taihu Lake, the complicated inflow/outflow system and high pollutant discharge lead to poor water quality in the north. Moreover, there are plenty of chemical plants around the tributaries of Taihu Lake, resulting in higher levels of OPEs in the tributaries than in the main stream. The conclusion is similar to Chen et al. [67] and Xing et al. [50].

The concentrations of OPEs in rivers and lakes range widely, depending on local industrial distribution and human activities, especially in the manufacturing and construction industry [42,68]. OPEs are usually observed near urban and industrial areas [59,65]. For example, Lian et al. (2022) studied the Zijiang River, which has large mining operations occurring in its downstream [51]. The results showed that TCEP, TCPP, TEP, TNBP, and TBOEP were detected in almost all samples, with TNBP and TBOEP accounting for 14.2% and 9.3% of the OPEs, respectively. TNBP and TBOEP are widely used in hydraulic fluids and lubricants, which may be released into the surrounding environment during mining. Human activity is a main factor in causing the different spatial distribution of OPEs [54]. Zhang et al. (2018) used GC-MS to study eight OPEs of urban and rural surface water samples [55]. The concentrations of the OPEs detected in urban rivers (340–1688.7 ng/L) were higher than those in rural rivers (185.4–321 ng/L). The concentrations of three Cl-OPEs in urban surface water were significantly higher than those in rural surface water, indicating that there may be more potential pollution sources in urban areas. The amount and type of OPEs in surface water also reflects the industrial development level between urban and rural areas [55,65].

Significant differences in the level of OPEs were found in different seasons [56,57,62]. Chen et al. (2019) sampled seawater and sediments in northwestern Bohai Bay from 2014 to 2017, and detected the concentrations of 12 OPEs using GC-MS/MS [69]. The concentration of TEP in summer was the highest among the three seasons investigated, which may be caused by the high temperature and frequent rainfall in Tianjin in the summer. High temperature may lead to the release of OPEs from the materials, and the wet deposition utilizes the atmosphere to migrate OPEs from the air to the aquatic system. Among the OPEs studied, TEP has the highest water solubility among all the investigated OPEs, so it is more readily soluble in water. However, for TCEP and TBOEP, the trend is the complete

opposite. The concentrations of TCEP and TBOEP were the lowest in summer, and this difference may be related to the physical and chemical characteristics of OPEs. Besides the impact of high temperature [69,70], floods can also affect the level of OPEs in rivers. Increased discharge during floods reduces the levels of OPEs in water and results in a relatively uniform distribution throughout the river [19].

The coastal environment is an important sink of OPEs [68]. The release of OPEs from the inland is accompanied by the flow of rivers into the sea. At the same time, the pollution from intensive fishery activities, aquaculture wastewater discharge, and even some ports and tourism activities, all lead to great environmental stress [58]. The Bohai Sea, Yellow Sea, and East China Sea are important marginal sea areas for China. According to Zhong et al. (2020), Qi at al. (2021), and Lin et al. (2022), high concentrations of OPEs were detected in the Bohai Sea and the Yellow Sea. The total concentration of OPEs in the Bohai Sea (10.9–516.4 ng/L) was the highest, followed by the Yellow Sea (12.7–202.6 ng/L) and then the East China Sea [53,71,72], which was attributed to there being more pollution sources and poor seawater exchange around the Bohai Sea. Due to a low boiling point and semi-volatility, the OPEs in coastal seawater can be deposited into sediments and be volatilized into the atmosphere [73]. The long-distance migration of the atmosphere and ocean currents transport OPEs from industrialized regions to the sea [74,75]. Na et al. (2020) demonstrated the long-distance migration ability of OPEs [76]. Ten OPEs were found in seawater samples from the northwestern Pacific and the Arctic, with the concentration varying from 8.5 to 143 ng/L. Xiao et al. (2021) collected surface seawater from the West Pacific Ocean [60]. The total concentration of OPEs was 3.02–48.4 ng/L, which were comparable with those in the surface water of the largest High Arctic lake (mean: 12.9 ng/L) [77]. In addition, Li et al. (2017) revealed there were OPEs (0.3–8.4 ng/L, mean: 2.9 ng/L) in the seawater of the northeast Atlantic and the Arctic Ocean [74]. Compared with the open sea, the concentrations of OPEs in coastal waters were higher [64].

Previous studies have shown that some OPEs can accumulate in sediments and persist in aquatic environments [18,50,52,53,59,63,67,69]. OPEs may even produce more toxic transformation products through biotransformation, photodegradation, or hydrolysis. Rivers are the main vehicle for transporting and mobilizing OPEs from the mainland to the coastal marine environment. Monitoring and controlling the concentration of pollutants in rivers and lakes can effectively prevent marine pollution.

2.3. Drinking Water (Tap Water, Bottled Water, and Barreled Water)

Drinking water is regarded as one of the main ways for OPEs to come into contact with humans. In general, bottled water, tap water, and barreled water are the three common types of drinking water [78]. At present, plenty of studies on the fate of OPEs in drinking water have been carried out in China [20,56,79–82], Pakistan [83], South Korea [84,85], Canada [86], USA [64,87], and in other countries and regions [88]. The concentrations of OPEs in different types of drinking water are summarized in Table 4.

Table 4. Concentration of OPEs in several types of drinking water (ng/L).

Location of Sampling		TCPP	TDCPP	TCEP	TBOEP	TNBP	TPhP	ΣOPE	Analysis Instrument	Year	Ref
Nanjing, China	Bottled water	1.3–16.2	ND	ND-48.8	19.5–81.7	-	-	165	UPLC-MS/MS	2014	[79]
Eastern China	Well water	1.3–3.8	ND-1.1	0.1–3.5	0.01–0.6	0.1–0.4	ND-0.5	4.5	UPLC-MS/MS	2015	[80]
	Barreled Water	ND-48.5	ND-7.0	0.2–44.2	ND-0.3	ND-1.6	0.05–0.9	27.6			
	Filtered drinking water	1.6–26.5	ND-6.6	1.9–48.5	ND-5.3	0.2–6.6	ND-1.8	59.2			
	Tap water	21.5–109	5.4–6.8	28.5–139	1.4–6.6	3.9–76.3	0.3–4.0	192			

Table 4. *Cont.*

Location of Sampling		TCPP	TDCPP	TCEP	TBOEP	TNBP	TPhP	ΣOPE	Analysis Instrument	Year	Ref
Pakistan	Industrial zones	0.03–85.7	<MDL-21.4	0.09–31.2	-	-	-	<MDL-71.1	GC-MS	2016	[83]
	Rural zones	<MDL-13.1	<MDL-9.2	<MDL-12.1	-	-	-	<MDL-12.1			
	Background zones	<MDL	<MDL	<MDL-0.06	-	-	-	<MDL-0.08			
Korea	Tap water	67.0	-	38.8	26.1	3.40	-	137.4	GC-MS	2016	[84]
	Purified water	155	-	70.1	10.7	1.27	-	264.7			
	Bottled water	79.6	-	25.3	35.6	4.29	-	53			
The Pearl River Delta, China	Bottled water	<MDL-170	<MDL-1.9	<MDL-3.1	<MDL-2.2	<MDL-4.5	0	34	UPLC-MS/MS	2022	[81]
	Barreled water	9.8–100	65	<MDL-1.6	94	<MDL-0.6	<MDL-14	24			
	Tap water	<MDL-350	100	<MDL-180	100	<MDL-120	<MDL-36	72			
Shanghai, China	DWTP	100.5–220.4	1.9–16.4	33.8–47.6	<MDL-7.0	3.5–39.5	<MDL-1.6	312.1	UPLC-MS/MS	2022	[56]
Nakdong River, South Korea	DWTP	15–35.9	2.2–3.2	13.5–21.8	5.7–20.6	0.8–2.7	2.8–7.5	49.4–86.5	GC-MS	2020	[85]
Nanjing, China	Tap water	78	41.4	207.6	6.7	27.7	179.7	719.8	HPLC-MS/MS	2022	[57]
Xiangjiang River, China	Tap water	9	-	0.3	-	6.2	7.5	23.6	GC-MS/MS	2021	[20]
New York State, US	Tap water	<LOQ-67.1	<LOQ-124	<LOQ-17.4	<LOQ-109	-	<LOQ-39.9	41.6	HPLC-MS/MS	2018	[64]
Hefei China	Tap water	15.8	2.2	15.5	0.5	1.1	1.3	-	UPLC-MS	2020	[89]
Beijing, China	Barreled Water	ND-6.3	ND-2.2	ND-8,2	ND	ND-1.6	ND-0.25	0.5–23.9	UPLC-MS/MS	2021	[78]
Major metropolitan cities, Korea	Tap water	49.4	2	39.5	43.9	11.8	23	169	GC-MS	2018	[90]

Note—MDL: the method detection limit; "-": not measured; ND: not detected; LOD: limit of detection; and LOQ: the limit of quantitation.

The mean values or range (min–max) are shown. Tap water is the cheapest and most common drinking water in cities and contains abundant OPEs [91]. Tap water is frequently obtained from rivers and lakes near urban areas [92], and the levels of OPEs in treated tap water are usually significantly lower than those in rivers or lakes (Figure 2). This is due to the purification of OPEs in water sources by drinking water treatment plants (DWTP) [56]. Park et al. [90] used GC-MS to detect the level of OPEs (total concentrations 74–342 ng/L) in the tap water of Korean cities. TnBP, TCEP, TCPP, and TBOEP were detected in all samples. Li et al. [87] proposed that OPEs are widely distributed in tap water, and that the level of OPEs varies greatly in different cities. The total concentration of halogenated OPEs is 3.1–207 ng/L (mean: 50.3), accounting for 65% (mean) of the total OPEs. The potential risks posed by tap water to human beings vary depending on the raw water source and treatment process used. Compared with conventional drinking water treatment technology (DWTT), advanced DWTT can reduce the concentration of OPEs by about 47.8%, indicating that DWTT plays a significant role in the purification of OPEs and is a key factor affecting the OPEs level of drinking water. Choo et al. (2020) further compared the removal efficiency of OPEs between traditional and advanced DWTP [85]. The results show that advanced treatment processes such as ozonation and granular-activated carbon filtration are more efficient in removing most OPEs. For example, the average removal rates

of the two Cl-OPEs were negative for conventional DWTP (TCEP: −87%, TCPP: −41%) and positive for advanced DWTP filtration that uses granular-activated carbon (TCEP: 46%, TCPP: 49%). This shows that upgrading the DWTT capabilities of water plants is a successful strategy through which to lessen the threat that OPEs pose to tap-water safety.

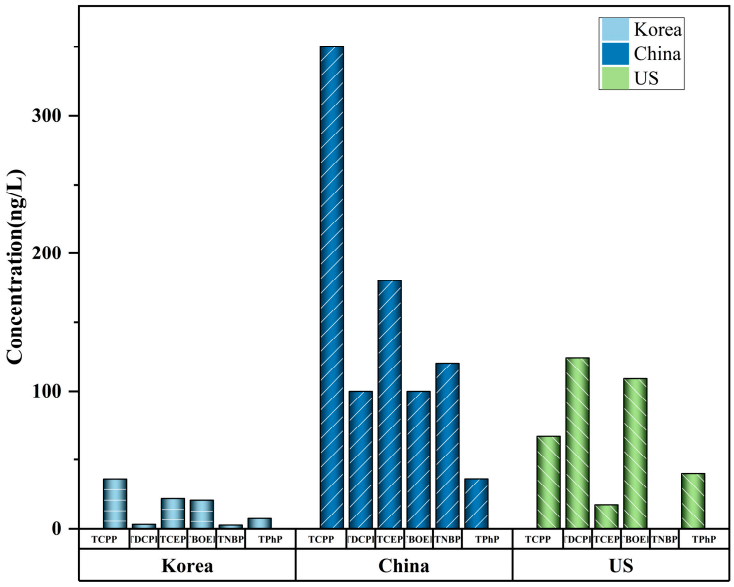

Figure 2. Max values of OPEs in tap water. Data are compiled from Table 4.

Some studies have shown that OPEs were observed in barreled water and bottled water. Liang et al. (2022) found that the OPE contaminations of bottled water (<MDL-180 ng/L) and barreled water (11–100 ng/L) were much lower than those of tap water (3.1–940 ng/L) and river water (25–840 ng/L) [81]. The level of OPEs in bottled water was comparable to those in Korea (median: 104 ng/L) (Lee et al., 2016) [84]. The level of OPEs in tap water were higher than those in bottled water, which may be caused by the widespread use of PVC pipes carrying residual OPEs. The pollution of OPEs in bottled and barreled water may be caused by many reasons: the water source, packaging materials, purification process, etc. Lao et al. (2022) pointed out that OPEs could potentially leak out of plastic containers. [93]. OPEs will leak out more from plastic containers into barreled and bottled water during long-term and high-temperature storage. For this reason, short-time storage and maintaining room temperature are essential to avoid the leaching of OPEs. At the same time, the use of clean water from natural reserves and advanced purification technology in the manufacturing process is a feasible approach through which to reduce the pollution of bottled water.

The concentration of OPEs in drinking water is significantly affected by the economic development and population density of different regions [87]. Zhang et al. (2021) determined that OPEs in drinking water showed a downward trend from coastal cities (mean: 154 ng/L) to inland cities (mean: 119 ng/L) [94]. The highest ΣOPE concentrations of the tap water in Korea were found from large-scale industrialized cities, such as Ulsan (mean 144 ng/L) and Ansan (mean 74.0 ng/L) [84]. However, the relatively lowest concentrations of OPEs were observed in several coastal cities with developed industries, such as Shanghai and Dalian. The use of advanced process treatment technologies may be the cause of these variations in the levels of OPEs

These data indicate that drinking water, which is generally considered to be relatively safe, was being polluted on a large scale. Overall, the mean concentration of OPEs in drinking water decreased in the following sequence: tap water > bottled water > barreled water. Nevertheless, studies on the pollution level of OPEs in drinking water are relatively limited. It is very important for human safety to upgrade the DWTT capabilities of water

plants, and to also regularly monitor raw water sources in order to reduce the OPE pollution of drinking water.

2.4. Aquatic Organisms

Aquatic environments are of great importance for protecting biodiversity and maintaining fishery resources. OPEs are mainly transported into remote areas through long-distance atmospheric deposition or ocean currents. Therefore, the potential effects of OPEs on freshwater and marine ecosystems must be given special consideration. The concentration of OPEs in different kinds of aquatic organisms are summarized in Table 5.

Table 5. Concentration of OPEs in several aquatic organisms (ng/L).

Location	Species	Number of OPEs Analyzed	TCPP	TDCPP	TCEP	TBOEP	TNBP	TPhP	ΣOPE	Analysis Instrument	Year	Ref.
Antarctic	algae	16	23.4	ND	25.5	1.33	9.7	2.6	88.3 (ng/g lw)	LC-MS/MS	2020	[95]
Laizhou Bay, China	fish and inverte-brate	20	-	-	-	-	-	-	21.1–3510 (ng/g lw)	GC-MS	2019	[96]
Alaska	sentinel fish	24	-	-	-	-	5.5	0.1	5.95 (ng/g ww)	UPLC-QQQ MS	2020	[97]
Spain	mussels	18	3.8–29.6	ND	<LOQ	5.6–12.4	0.9–9.4	23.6–623.6	-(ng/g dw)	LC-MS/MS	2020	[98]
7 European countries	mussel	-	-	-	-	-	-	-	0.50–102 (ng/g dw)	LC-MS	2018	[99]
Great Lakes	lake trout	22	-	-	-	-	-	-	9–122 (ng/g ww)	LC-MS/MS	2022	[100]
Great Lakes	fish	18	6.7	9.6	13.3	-	1.6	17.1	36.6 (ng/g lw)	GC-MS	2017	[101]
Laizhou Bay, China	fish muscle	20	ND-6.1	ND-2.5	ND-5.8	-	ND-13.1	ND-8.4	6.6–107 (ng/g dw)	GC-MS	2021	[102]
Indian Ocean	dolphin	14	ND	ND	ND	952–31,841	ND-1333	ND	10,452 ± 11,301 (ng/g lw)	LC-MS/MS	2019	[103]
Alboran Sea, Spain	dolphin muscle	16	ND	-	32.1	66.9	1309	ND	69.5–2939 (ng/g lw)	LC-MS	2019	[104]
US	harbor seal	13	ND-30	ND-56	ND-8.3	<2.5	<1.5	ND-27	17–67 (ng/g lw)	LC-MS/MS	2019	[63]
Canada (in SHB/WHB)	polar bear	17	-	-	-	-	-	-	0.163/0.308 (ng/g lw)	UPLC-MS/MS	2018	[105]

Note—"-": not mentioned; ND: not measured; and LOQ: the limit of quantitation.

The mean values or range (min–max) are shown. Generally, chlorinated OPEs were the main fraction of the total OPEs in biota samples [106]. The average relative abundance of chlorinated OPEs (34.7%−58.2%) was higher than those of aryl OPEs (4.06–32.2%) and alkyl OPEs (18.1–40.6%), which may be due to their higher bioaccumulation and lower biotransformation. These features make chlorinated OPEs more resistant to metabolism and more persistent in aquatic organisms than other OPE individuals [95].

Several studies have investigated OPEs in algae, invertebrate species, and fish from different regions. Fu et al. (2020) detected sixteen OPEs in six algae samples collected from Antarctica using LC-MS/MS [95]. TEP, TCEP, TCPP, TPhP, and TNBP were detected in more than 75% of the samples, with the total concentration of 1.60 ng/g dw. Bekele et al. [96] collected marine species from Laizhou Bay, North China. The results showed that the concentrations of 20 analyzed OPEs in organisms varied from 21 to 3510 ng/g lipid weight (lw). A total of 17 of 20 OPEs were detected in biota samples with the highest detection frequency of TCPP (85%), TiBP (80%), and TBEP (77%). The high detection frequencies were evidence of the extensive use and widespread contamination of OPEs in Laizhou Bay. Zheng et al. (2020) revealed the median concentration of ΣOPE was 4.97 ng/g wet

weight (ww) in sentinel fish [97]. Castro et al. (2020) collected seven mussel samples from Galicia [98]. Then, 8 out of 18 OPEs were detected in these samples (total concentration LOQ-291 ng/g dry weight (dw)). Aznar-Alemany et al. [99] monitored the OPEs in the mussel from different European fish and shellfish farming sites. OPEs were found in all 17 samples with the concentrations ranging from 7 to 2005 ng/g lw. Choi et al. (2022) collected lake trout from five locations in the Great Lakes between 2001 and 2017 [100]. A total of 12 of 22 OPEs were detected above the MDLs, while only 3 of them (TEP, TCPP, and TBOEP) showed high detection frequencies (>50%). The total OPE concentration was 9–122 ng/g ww. Guo et al. (2017) studied lake trout and walleye samples from the Great Lakes basin (n = 3 for each lake) [101]. Of these, 6 out of 18 OPEs were detected in the fish samples (mean: 36.6 ng/g lw), and TNBP was detected in 47% (mean: 1.63 ng/g lw). TPhP, TCPP, TNBP, and TCEP were detected in more than 7 samples. Bekele et al. [102] analyzed ten fish species from Laizhou Bay, North China. Of these, 17 out of 20 OPEs were detected in the fish samples, with a total concentration ranging from 7 to 107 ng/g dw.

As for mammals, OPEs were detected in dolphins, seals, and polar bears. Aznar-Alemany et al. [103] investigated the concentrations of OPEs in the muscles of Indian Ocean dolphins. The mean concentration of OPEs was 10,452 ± 11,301 ng/g lw, with TBOEP accounting for 82 ± 28% of the total OPE contamination. Sala et al. (2019) reported OPEs in the dolphin samples from the Alboran Sea [104]. The concentrations of OPEs in the muscle tissue varied from 70 to 2939 ng/g lw, and were one order of magnitude lower than those detected in the Indian Ocean [103]. According to Sutton et al. (2019), four types of OPEs were detected in harbor seal blubber: TDCPP (nd-56 ng/g lw), TCPP (nd-30 ng/g lw), TCEP (nd-8.3 ng/g lw), and TPhP (nd-27 ng/g lw) [63]. Letche et al. [105] collected tissue samples from the polar bears of various Hudson Bay subpopulations. Only TEHP could be quantified in the samples despite the presence of several types of OPEs, indicating limited intake and absorption due to the rapid metabolism in polar bears.

These studies demonstrated the presence of the OPEs observed in aquatic organisms. As some OPEs have a relatively large $\log K_{ow}$ through bioaccumulation, they can be transferred from low trophic organisms to high trophic organisms through the food web [63,107,108]. The survival and reproduction of organisms may be threatened by the toxicity of OPEs, which mainly manifests as growth inhibition [89,104,109], developmental delay [110,111], reproduction toxicity [13], neurotoxicity toxicity [12], and apoptosis [15].

3. Human Exposure

OPEs could potentially accumulate in primary producers through food chain accumulation and will eventually reach our dinner table. The ingestion of aquatic products and drinking water may pose potential harmful effects on human health, which is a topic worthy of further exploration [112–114]. Studies have demonstrated that consuming aquatic products is a significant way in which humans can be exposed to OPEs. [115–117]. The industrial processing and packaging of food products are the main contributors to OPE contamination in foodstuffs. Thus far, certain research have estimated the exposure dose of OPEs through the ingestion of aquatic products. For example, Choi et al. (2022) studied the lake trout from the Great Lakes and assessed the estimated daily intake (EDI) of OPEs to be in the range of 9.6–27 ng/kg body weight (bw)/day [100]. Bekele et al. (2019) estimated the EDI of OPEs via wild marine fish ingestion [102]. The values were 3.1–22.1 ng/kg bw/day and 1.7–12.0 ng/kg bw/day for urban and rural residents, respectively. Urban residents had a higher exposure to OPEs due to the fact that they consume more fish than rural residents. According to Ding et al. (2018), the daily intake of 10 types of OPEs for local children and adults were calculated at 97.7 and 55.0 ng/kg bw/day, respectively [118]. Zhang et al. (2020) collected shrimps, crabs, and oysters from the marine aquaculture farms to assess the dietary risk of OPEs [119]. The EDI values of the total OPEs ranged from 9.31 to 23.75 ng/kg bw/day. Based on the above studies, the exposure through aquatic products is at least three orders of magnitude lower than the corresponding reference dose

values. The assessment on the dietary risk in these works does not pose a health risk to humans at present.

Kim et al. [64] assessed human exposure via the drinking water in North America. The EDI values of 14 types of OPEs in New York State ranged between 0.2 and 1.3 ng/kg bw/day (normal exposure) and 1.2–9.7 ng/kg bw/day (high exposure). The results were comparable to the values of adults in Korea (1.8–11.8 ng/kg bw/day) [84]. Hou et al. (2021) assessed the exposure of adults to OPEs from barreled water and drinking water from water dispensers [78]. Under normal-exposure scenarios, the EDIs of 11 types of OPEs via the ingestion of drinking water from water dispensers (0.7–3.7 ng/kg bw/day) were 39 times of those via the ingestion of barreled water (0.02–0.1 ng/kg bw/day). Under high-exposure scenarios, there was a difference of 343 times between the two values. These findings demonstrated the marked increase in the human exposure risk of OPEs via drinking water due to the use of water dispensers. Liu et al. (2019) estimated the average daily dose of a total of 5 types of OPEs, which was in the range of 3.6–7.1 ng/kg bw/day (average-exposure scenarios) and 38.9–64.8 ng/kg bw/day (high-exposure scenarios) in Nanjing, China [120].

Overall, these results showed that there is a low, but not negligible, risk to human health from OPEs, specifically in relation to the ingestion of seafood and drinking water. However, the long-term and sustained consumption of OPE-contaminated diets can increase the risk of exposure. Therefore, it is worth conducting more detailed assessments of aquatic organisms in coastal areas, such as ports and urban river discharge areas, and it isalso necessary to upgrade drinking water treatment technology.

4. Conclusions and Future Perspectives

In summary, a large number of studies showed that OPEs are ubiquitous in various aquatic environments. Since human beings are easily exposed to such substances, the process and mechanism of its environmental behavior and the potential ecological risks caused by OPEs deserve continuous attention. At present, the research on the pollution traceability and environmental risk of OPEs has not been fully carried out, and the following gaps still exist:

(1) Thus far, most studies have mainly focused on the commonly used monomeric OPEs, while scant research is available on oligomeric OPEs and their metabolites. Therefore, further studies should be encouraged to study their fate and the process of metabolic/degradation in aquatic environments. More specific studies on OPEs in water are needed;

(2) In addition to the various water bodies, sediments are the final sink of OPEs in water sources. More monitoring studies on the multimedia analysis associated with OPEs are needed, which is extremely important for us to understand the origin and migration of OPEs. More specifically, the previous studies involved in the detection of OPEs in aquatic environments were only conducted in one or two environmental media simultaneously. Only a minority of studies have confirmed the accumulation of OPEs in aquatic organisms and scant research is available on the partitioning of OPEs between water and aquatic organisms. In view of the current research status and existing limitations of OPEs, future relevant research should focus on tracing the pollution sources and environmental behaviors of various OPEs in different environmental media;

(3) For the human exposure risk assessments of OPEs, most studies ignored OPE bioaccessibility, which possibly overestimated or underestimated the risk posed by OPEs by not taking into account their specific chemical fractions. Systematic studies on the toxicity of OPEs and their metabolites should be carried out to lay a scientific foundation for the accurate assessment of their potential ecological and health risks.

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