Pollution Characteristics and Risk Assessment of Organophosphate Esters in Different Media

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Abstract. Organophosphate esters (OPEs) are widely used as alternatives to traditional brominated flame retardants, which are easily released into a variety of environmental media and have potential ecological and health risks. This article aims to review the pollution characteristics of OPEs in water bodies, sediment, dust, and organisms, and also evaluate the health risks of OPEs in water and indoor dust to the population. The health risk assessment model recommended by the US EPA was used to calculate the exposure of OPEs in water bodies and indoor dust, and to evaluate their non-carcinogenic risk (HQ/ HI) and carcinogenic risk (CR). Overall, in China, the high exposure level of OPEs in water has a carcinogenic risk to humans, and to the indoor dust, there is a non-carcinogenic risk to all regions and the people at the general exposure. This article provides a reference for understanding the multimedia pollution behaviour of OPEs and its health risk assessment, and also, it provides a basis for the differentiated risk management, risk prevention, and control of OPEs.

Keywords: Environmental protection, Environmental science, health risk assessment, Emerging pollutants

1. Introduction

As the modern industry develop rapidly, the types and concentration of pollutants are increasing. Traditional brominated flame retardants with persistent pollution characteristics are banned by many countries. OPEs are used as substitutes to increase the plasticity and flame-retardant properties of materials [1]. However, because OPEs are physically added flame retardants, they can be released into the environment through volatilization, leaching, and product wear [2]. A plenty of researches reflect that OPEs are detected in a variety of environmental media. In addition, OPEs and their metabolites were also detected in organisms and human body fluids. Some OPEs can affect the biological endocrine, nervous system and reproductive function, and have teratogenic and potential carcinogenic toxicity [3], posing a huge potential threat to human health.

Therefore, the environmental problems of OPEs have attracted wide attention at domestic and foreign. In the current research, most of them only focus on the analysis of OPEs in some media and regions. The pollution characteristics and risk assessment of OPEs in a single medium have formed a relatively mature system. However, for complex environments, such as urban environments, the pollution characteristics of OPEs are still not comprehensive enough. It poses a major challenge to

evaluate their hazards and interactions. In general, this paper summarizes the pollution status and risk assessment methods and conclusions of OPEs in multi-media. It is of great significance to provide support for understanding the environmental behaviour and the ecological and health risks of OPEs.

2. Pollution characteristics of OPEs in different media

2.1. Pollution characteristics in water

OPEs in the atmosphere usually enter the water body by precipitation or deposition. In addition, rainfall, surface runoff and water discharged after sewage treatment are also important sources of OPEs pollution in natural water bodies [4-6]. Upon the wide application in plastic, sewage discharge is the main source of OPEs in natural water bodies. At present, numerous studies have indicated that OPEs are detected in all kinds of water bodies in the world, but the concentration and type are different. The concentration is in the order of ng/L~μ/L, and the composition is mainly TCPP, TBOEP, TCEP and TBP. Table 1 demonstrates details of OPEs in different regions [7-12].

Table 1. The concentration and types of OPEs in surface water

Medium	Country or region	Minimum Concentration	Maximum Concentration	Main OPEs
Water environment Surface water	China	602 ng/L	9030ng/L	TEP, TCIPP
	United States	35 ng/L	290 ng/L	TDCIPP, TBOEP, TPhP
	Arctic Ocean	6 pg/L	440 pg/L	TCEP, TCIPP
	Vietnam	46 ng/L	3644 ng/L	TCIPP
	Canada	2.9 ng/L	67 ng/L	THP, TCIPP, TCEP
	Mediterranean	9 ng/L	1013 ng/L	TCIPP, TCEP

2.2. Pollution characteristics in sediment and dust

Soil and sediment are another important gathering place of OPEs, with concentrations ranging from ng/g to μg/g. In general, TCPP, TCEP, TBP, TBOEP and TPHP were the most frequently detected and accounted for the largest proportion in sediments, mainly due to the different local sources or local environment conditions of OPEs in different regions, as shown in Table 2 [13-18].

OPEs are easily migrated from furniture and released into the indoor environment, so the indoor environment is considered to be a material microenvironment exposure to OPEs for humanity. In recent years, the main OPEs in door dust are still dominated by traditional OPEs (T- OPEs), but the detection rate and concentration of new OPEs (NOPEs) are increasing year by year. The total mass fraction of OPEs in dust (∑OPEs) has reached alarming heights in some countries and regions, such as in the Midwest of the United States, where ∑OPEs is as high as 736330 ng/g; the mass fraction of the concentration of all kind of OPEs in indoor dust in the UK is as high as 1099519 ng/g. According to the existing research, the concentration of OPEs varies from regions to regions, and the specific values are demonstrated below.

Table 2. The concentration and types of OPEs in indoor dust and sediment

Medium	Country or region		Minimum value	Maximum value	Main OPEs
Sediment	China	Taihu lake	12.8 ng/g(dw)	9250 ng/g(dw)	TEHP, TDtBPP, TCIPP
		Liao river	19.7 ng/g(dw)	234 ng/g(dw)	TnBP, TBOEP
		Pearl River Estuary	23.5 ng/g(dw)	187 ng/g(dw)	TCEP, TCIPP, TPhP
	Nigeria		13.1 ng/g(dw)	2110 ng/g(dw)	TBOEP
Indoor dust	Globe	China	149 ng/g	4740 ng/g	TCEP, TPhP
		Colombia	54.6 ng/g	8130 ng/g	TBOEP, TCIPP, TPhP
		Greece	1690 ng/g	90200 ng/g	TnBP, TBOEP, TCEP, TCIPP
		India	7720 ng/g	9650 ng/g	TBOEP, TEHP, TDCIPP
		Japan	7720 ng/g	238000 ng/g	TBOEP, TCEP, TCIPP, TDCIPP
		South Korea	3090 ng/g	249000 ng/g	TBOEP, TCEP, TCIPP, TPhP, IDDP
		Kuwait	633 ng/g	44400 ng/g	TBOEP, TCEP, TCIPP, TDCIPP
		Pakistan	49.4 ng/g	473 ng/g	TBOEP, TPhP
		Romania	775 ng/g	54900 ng/g	TnBP, TBOEP, TCEP, TCIPP, TPhP
		Saudi Arabia	791 ng/g	35000 ng/g	TBOEP, TCEP, TCIPP, TDCIPP, TPhP
		United States	1930 ng/g	101000 ng/g	TBOEP, TCEP, TCIPP, TDCIPP, TPhP
		Vietnam	228 ng/g	79600 ng/g	TBOEP, TDCIPP, TCIPP, TPhP, BPDPP

2.3. Pollution characteristics in organism

OPEs can enter organisms in many ways, for example, through air or water exposure, bioaccumulation, and food chain transmission. The higher the concentration of OPEs in the water environment, the greater the risk of organisms exposed to OPEs. Fish accumulate OPEs through dietary intake, gill respiration and skin contact, and OPEs are also detected in other aquatic mammals. The concentration of OPEs in aquatic animals is closely intertwined with their trophic level, which generally increases with the increase of trophic level. At the same time, the distribution of OPEs in the variegated tissues of the same organism is also different. In addition, although there are few studies on OPEs in terrestrial high-trophic organisms, there are still some studies on the content of OPEs in eggs and serum of birds and the content of OPEs in feces of primates.

3. Risk assessment

3.1. Health risk assessment method of OPEs in water

In this article, the health risk assessment model which was used to rate the health risk of OPEs to the population is recommended by the US EPS. The exposure of OPEs in water through oral intake was calculated using formula (1).

$$ADD = (c \times IR \times EF \times ED)/(BW \times AT) = (c \times IR \times EF \times ED)/(BW \times 365 \times ED) = (c \times IR)/BW \tag{1}$$

According to the formula, ADD refers to average daily exposure, ng/(kg· d); c refers to the concentration of pollutants, ng ·/L; IR refers to average daily drinking water intake, L/d; EF refers to

the exposure frequency of drinking water, d/a, and the value was 365 d/a. ED is the drinking water exposure cycle, a; BW refers to body weight, kg; AT refers to lifetime drinking water exposure time, d. For the non-carcinogenic effect, ED is fixed at 25550, and for the carcinogenic effect is 70 a. When calculating, it is necessary to consider the difference in the parameters referenced by different populations. Table 3 shows the parameters of daily average water intake and human detail data of different ages and genders. The population parameter values adopted in the study refer to the Chinese population exposure parameter manual [19-21].

Table 3. Parameters of daily intake via drinking water

Groups		Average daily drinking water intake(IR)/L/d	Weight(BW)/kg
		P50(50th percentile of the compound concentration position)	
Child	Male	0.75	17.00
	Female	0.75	16.00
	The whole	0.75	16.00
Adolescent	Male	1.20	41.00
	Female	1.10	39.00
	The whole	1.20	40.00
Adult	Male	2.0	65.00
	Female	1.70	57.00
	The whole	1.90	61.00

The non-carcinogenic risk is represented by HQ (hazard quotient). The HQ of the oral intake pathway was calculated using formula (2).

$$HQ = ADD/RFD \tag{2}$$

From above, ADD refers to average daily exposure, ng/(kg·g); RfD refers to reference dose, ng/(kg·d), and the specific data are demonstrated in Table 4. When HQ≥ 1, there is a non-carcinogenic risk; when HQ< 1, there is no non-carcinogenic risk.

Cancer risk was represented by CR (carcinogenic risk). The CR of the oral intake pathway was calculated using Formula (3):

$$CR = ADD \times SF \tag{3}$$

From above, ADD refer to average daily exposure, ng/(kg·d); SF refer to a slope factor, (kg·d)/ng, and its specific value for different types of OPEs is shown in Table 4 [22-23]. When CR≥1×10-6 ,there is a risk of cancer; when CR<1×10-6 , there was no carcinogenic ri

Table 4. Values of RfD and SF

parameter	unit	TMP	TEP	TPrP	TiBP	TBEP	TEHP	TnBP	TCEP	TCPP	TDCP	TPhP	CDPP
RfD	Ng/(kg·d)	10000	125000	NA	NA	15000	10000	10000	7000	10000	20000	70000	NA
SF	(kg·d)/ng	2×10-8	NA	NA	9×10-8	NA	3×10-9	9×10-9	2×10-8	NA	3.1×10-8	NA	NA

1) NA indicates that no relevant data has been found.

3.2. Health risk assessment method of OPEs in indoor dust

For indoor dust, the influence of pollutants on individuals' health is mainly by oral intake and skin adsorption [24]. To evaluate the exposure level accepted by the mankind body, the chronic daily exposure (CDI) was calculated by these two ways. The calculation formulas are shown in equations (4) to (5).

$$EDI_D = \frac{C_i \times DIR \times IEF}{BW} \tag{4}$$

$$EDI_{DA} = \frac{C_i \times BSA \times SAS \times ABS \times IEF \times 10}{BW} \tag{5}$$

In the formula, EDID and EDIDA are the estimated daily exposure of oral intake and skin absorption, respectively, ng/ (kg d); ci refers to content of OPEs in dust, ng / g; DIR refers to daily intake rate of indoor dust, g / d; IEF refers to indoor exposure score, which refers to the proportion of people's 24-hour indoor time, %; BW refers to body weight, kg. BSA refers to the area of skin exposed to the environment, m2; SAS is the adsorption coefficient of dust on the skin, mg / cm^2; ABS refers to the absorption coefficient of OPFRs in dustfall by skin, which is dimensionless. Table 5 is the specific value of the above parameters for different age groups, which is mainly used to evaluate the estimated exposure of OPEs to different groups pf people.

Table 5. The values of parameters for exposure risk assessment

Types of population	age/year	IEF/%	DIR/g/d	BSA/m2	SAS/mg/cm2	ABS
Infant	<1	87.5	0.02	0.0801	0.096	0.1
Toddler	1~5	79.2	0.10	0.2564	0.096	0.1
Child	6~11	79.2	0.05	0.3067	0.096	0.1
Teenager	12~18	87.5	0.05	0.3692	0.096	0.1
Adult	19~59	87.5	0.05	0.4615	0.096	0.1
Elderly	≥60	87.5	0.05	0.4615	0.096	0.1

Non-carcinogenic risk assessment based on hazard index (HI) and HQ. Formula for HI calculated through two main ways of intake OPEs which is shown in formula (6) [25].

$$HI = \sum \left(HQ_{\text{ingestion}} + HQ_{\text{dermal contact}}\right) = \sum \left(\frac{EDI_D}{RfD} + \frac{EDI_{DA}}{RfD}\right) \tag{6}$$

In the formula, EDI refer to the daily exposure, ng / (kg · d), and RfD refer to the corresponding daily maximum allowable intake reference value mg / (kg · d). HI < 1 of OPEs risk is considered to be no health risk, and when HQ ≥ 1, there is a non-carcinogenic risk.

4. Conclusion

This paper mainly demonstrates and summarizes the health risks of OPEs' two media, water and indoor dust, and evaluates the risks of OPEs from multiple different approaches and global perspectives.

Studies show, on the whole, that exposure to water media is high, with average daily exposure to OPEs in China. For OPEs in water at general exposure levels, the non-carcinogenic risks of different

populations exposed to drinking water are within the acceptable range. At high exposure levels, some OPEs have carcinogenic risks to children, adolescents and adults.

Secondly, in the indoor environment, intake OPEs through mouth is the main exposure path of OPEs. The exposure concentrations in Europe, the United States, and East Asia were high, but at the general exposure level, the HI values of all regions and populations are far less than 1, indicating that OPEs in indoor dust have no significant non-carcinogenic health risk to all populations at the current concentration level.

However, at present, the use of OPEs is very large, and it is still continuously released into the environment, causing persistent environmental pollution, and the types of OPEs are also increasing, which brings great challenges to its risk assessment. In summary, we should preoccupy the long-term exposure risk of OPEs and health risk assessment of emerging OPEs.

References

[1] Y. W. Wang, Q. R. Zhang, N. Y. Yu et al. Emerging Pollutants. Progress in Chemistry, 2024, 36(11): 1607-1784.
[2] S. S. Wang, J. L. Zhao, Q. Wang et al. Study on Toxicity and Mechanisms of Organophosphates Based on Adverse Outcome Pathway (AOP) Analysis Integrated with Toxicological Databases. Asian Journal of Ecotoxicology, 2024, 19(05): 1-12.
[3] J. M. Zhou, J. Zhao, X. Wei et al. The pollution characteristics and health assessment of organophosphate esters in indoor dust from different microenvironments in Shanghai. Environmental Chemistry, 2023, 42(07): 2317-2327.
[4] J. Meyer, K. Bester. Organophosphate flame retardants and plasticisers in wastewater treatment plants. Journal of Environmental Monitoring, 2004, 6(7): 599-605.
[5] M. B. Woudneh, J. P. Benskin, G. Wang et al. Quantitative determination of 13 organophosphorous flame retardants and plasticizers in a wastewater treatment system by high performance liquid chromatography tandem mass spectrometry. Journal of Chromatography A, 2015, 1400: 149-155.
[6] J. Li, J. Wang, A. R. Taylor et al. Inference of Organophosphate Ester Emission History from Marine Sediment Cores Impacted by Wastewater Effluents. Environmental Science & Technology, 2019, 53(15): 8767-8775.
[7] S. Wang, J. Qian, B. Zhang et al. Unveiling the Occurrence and Potential Ecological Risks of Organophosphate Esters in Municipal Wastewater Treatment Plants across China. Environmental Science & Technology, 2023, 57(5): 1907-1918.
[8] I. Shimabuku, D. Chen, Y. Wu et al. Occurrence and risk assessment of organophosphate esters and bisphenols in San Francisco Bay, California, USA. Science of the Total Environment, 2022, 813: 152287.
[9] C. A. Mcdonough, A. O. De Silva, C. Sun et al. Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram Strait. Environmental Science & Technology, 2018, 52(11): 6208-6216.
[10] D. A. Truong, H. T. Trinh, G. T. Le et al. Occurrence and ecological risk assessment of organophosphate esters in surface water from rivers and lakes in urban Hanoi, Vietnam. Chemosphere, 2023, 331: 138805.
[11] R. Sühring, M. L. Diamond, S. Bernstein et al. Organophosphate Esters in the Canadian Arctic Ocean. Environmental Science & Technology, 2021, 55(1): 304-312.
[12] N. Schmidt, J. Castro-Jiménez, B. Oursel et al. Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring links with microplastic abundance and accumulation in the marine food web. Environmental Pollution, 2021, 272: 115970.
[13] A. Merchán-galvis, R. Anaya, M. Rodriguez et al. Quality of Life and Post-Surgical Complications in Patients on Chronic Antiplatelet Therapy with Proximal Femur Fracture: 12-Month Follow-Up after Implementing a Strategy to Shorten the Time to Surgery. Journal of Clinical Medicine, 2023, 12(3).
[14] L. Ye, G. Su. Elevated concentration and high Diversity of organophosphate esters (OPEs) were Discovered in Sediment from Industrial, and E-Waste Recycling Areas. Water Research, 2022, 217: 118362.
[15] Q. Luo, L. Gu, Z. Wu et al. Distribution, source apportionment and ecological risks of organophosphate esters in surface sediments from the Liao River, Northeast China. Chemosphere, 2020, 250: 126297.
[16] J. Xie, N. Pei, Y. Sun et al. Bioaccumulation and translocation of organophosphate esters in a Mangrove Nature Reserve from the Pearl River Estuary, South China. Journal of Hazardous Materials, 2022, 427: 127909.
[17] M. R. Gbadamosi, A. L. Ogunneye, D. O. Jegede et al. Occurrence, source apportionment, and ecological risk assessment of organophosphate esters in surface sediment from the Ogun and Osun Rivers, Southwest Nigeria.

Environmental Science and Pollution Research, 2023, 30(59): 124274-124285.

[18] W. Li, Y. Wang, A. G. Asimakopoulos et al. Organophosphate esters in indoor dust from 12 countries: Concentrations, composition profiles, and human exposure. Environment International, 2019, 133(Pt A): 105178.

[19] Ministry of Environmental Protection. Exposure Factors Handbook of Chinese Population (Adults). Beijing: China Environmental Science Press, 2013.

[20] Ministry of Environmental Protection. Exposure Factors Handbook of Chinese Population (Children 0-5 years). Beijing: China Environmental Science Press, 2016.

[21] Ministry of Environmental Protection. Exposure Factors Handbook of Chinese Population (Children 6–17 years). Beijing: China Environmental Science Press, 2016.

[22] J. Lv, C. Guo, Y. Luo et al. Spatial distribution, receptor modelling and risk assessment of organophosphate esters in surface water from the largest freshwater lake in China. Ecotoxicology and Environmental Safety, 2022, 238: 113618.

[23] M. Lian, C. Lin, Y. Li et al. Distribution, partitioning, and health risk assessment of organophosphate esters in a major tributary of middle Yangtze River using Monte Carlo simulation. Water Research, 2022, 219: 118559.

[24] W. Z. Qin, L. S. Mao, Y. H. Chen et al. Distribution characteristic and health risk assessment of five organophosphorus flame retardants in indoor dust in Shenzhen. Environmental Health, 2019, 36(12): 1074-1077.

[25] J. Li, Z. Zhang, L. Ma et al. Implementation of USEPA RfD and SFO for improved risk assessment of organophosphate esters (organophosphate flame retardants and plasticizers). Environment International, 2018, 114: 21-26.