Occurrence and Risk of Organophosphate Flame Retardants in Multiple Urban Water of Beijing, China

Yanmeng Zhang · Weihua Cui · Na Zhang · Pan Qin · Ying Zhang · Xiaochun Guo · Zhi Wang · Shaoyong Lu

Received: 15 February 2023 / Accepted: 28 March 2023 / Published online: 26 May 2023
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2023

Abstract Investigating the organophosphate flame retardants (OPFRs) concentration and attenuation in multiple water of Beijing would provide valuable insight into OPFR management and reduction; thus, 6 OPFRs were determined by solid phase extraction-high performance liquid chromatography-tandem mass spectrometry to explore the pollution characteristics, and ecological risk of OPFRs. The results showed that 5 OPFRs were detected with a concentration ranging from ND to 394.77 ng/L except for tris(2,3-dibromopropyl) phosphate (TDBP). The chloroalkyl phosphate was the main compound and tris(chloropropyl) phosphate (TCPP) was the most abundant OPFRs with the highest concentration. The concentration of aryl-OPFRs in surface water and groundwater was much lower than that of chlorinated ones, and the concentration of chlorinated OPFRs in...
surface water was higher than that in groundwater. The treatment effect of chlorinated OPFRs including TCPP, TCEP, and TDCPP in STPs was negative. Ecological risk assessment showed that low risk of OPFRs for the organisms (algae, crustacean, and fish).

**Keywords** Organophosphate flame retardants (OPFRs) · Multiple urban water · Occurrence · Risk assessment · Beijing

1 Introduction

Organophosphate flame retardants (OPFRs) were widely used in building materials, electronic equipment (Yu et al., 2022). In 2020, it was estimated that the annual production volume of OPFRs was 598,422 metric tons in Mainland China (Huang et al., 2022). Especially in industrial process, OPFRs are usually applied as antifoaming agents, and as flame retardants or plasticizers in consumer goods (Van der Veen & de Boer, 2012; Wei et al., 2015). OPFRs are generally classified into alkyl-OPFRs, aryl-OPFRs, chlorinated OPFRs, bromine OPFRs, and other organophosphate esters. Because of the ban and restriction of partial bromine flame retardants in Stockholm Convention and RoHS of the European Union, chlorinated OPFRs such as tris(chloropropyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), and tris(dichloropropyl) phosphate (TDCPP) are widely used all over the world. Triphenyl phosphate (TPP) is widely used for the production of foams (Batrool et al., 2020). Tri(2-butoxyethyl) phosphate (TBEP) is use as a leveling agent (Saquib et al., 2022).

Organophosphorus flame retardants are added to polymer materials under the action of physical mixing rather than chemical bonds (Pang et al., 2017), and most of the OPFRs are semi-volatile (Wen et al., 2018); therefore, the OPFRs may easily diffused into the environment through volatilization, abrasion, and dissolution (Yang et al., 2017). OPFRs may release from furniture, plastics, vehicle, or industrial process into air, then afflux into surface water through wet deposition. OPFRs may directly discharged into municipal drainage network, and let it into surface water followed by STPs treatment. Several researches had shown that the ratio for mass loadings of TPP, TCPP, TDCPP, and tri-n-butyl phosphate (TNBP) in STPs influent to the production was about 1.3–2.8% (Kim et al., 2017; Marklund et al., 2005; Schreder & La Guardia, 2014a, b). As we surveyed and reported in other studies (Kim et al., 2017), OPFRs cannot be treated in STPs and would finally transport into the potable water. Researches had reported the occurrence and distribution of OPFRs in air, water, and STPs. In 2018, China’s annual organophosphorus flame retardant emissions were 1000 tones (He et al., 2021). Möller et al. (2012) detected OPFRs in the atmosphere of the Arctic and Antarctic, demonstrating for the first time the long-range migration capability of OPFRs worldwide. A survey of the water quality of sewage treatment plants (STPs) in European countries showed that TCPP and TCEP could be detected in the effluent of most STPs at a concentration of several hundred ng/L (Loos et al., 2013).

The phase out of brominated flame retardants (BFRs) has led to increasing usage of OPFRs (Zhang et al., 2022), making them widely disseminated in aquatic environments, such as drinking water, surface water, groundwater, and municipal STPs (Shi et al., 2016). Studies have found that OPFRs exposed to the surrounding environments can enter the human body through ingestion, inhalation, gill absorption, and dermal absorption, resulting in their detection in fingernails (Chen et al., 2019; Hou et al., 2016). Therefore, OPFRs pose a potential threat to human health and water environmental safety, there are articles showing that OPFRs have the potential carcogenicity and can result the elevation of the blood total cholesterol level (Zhang et al., 2021). As the capital of China, Beijing is the center of national political, economic, and cultural development, with a total area of 16,410 square kilometers. In 2020, the population of Beijing was 21.89 million (National Bureau of Statistics of China, 2021); thus, it is conceivable that OPFRs would be used and consumed in significant quantities in this city (Shi et al., 2016). However, the current research on the occurrence and risk of OPFRs is still limited, especially lacking of comprehensive data on OPFRs exposure in different water bodies of high population density cities, such as Beijing.

Based above, we studied the distribution of six kinds of flame retardants such as TPP, tricresyl phosphate (TCP), TCPP, TCEP, TDCPP, and tris(2,3-dibromopropyl) phosphate (TDBP) in typical urban water (surface river, underground water, sewage treatment plants (STPs)) of Beijing, China. Finally,
environmental risk of OPFRs in water was evaluated to explore the impact of these chemicals on aquatic organisms. These results will help to understand the pollution levels and environmental risks of OPFRs in typical urban water bodies of modern metropolis, and provide data support for the establishment of OPFRs regulatory standards.

2 Materials and Methods

2.1 Sampling Sites

Seven sampling sites (W1~W7, according to the direction of water flow: Shahe floodgate/Mafang bridge/Xisishang village/Wenyu bridge/Yigezhuang bridge/Wenyu river Bridge/Beiguan floodgate) of surface water in the Wenyu River, five sampling sites (G1~G5; especially G3 is a multi-stage monitoring well with depths of 6.79 m, 11.64 m, and 22.53 m, and the corresponding sampling points are G3H, G3M, and G3L respectively) of groundwater in Shunyi District, three STPs (M, H, and C) from Miyun District, Haidian District, and Chaoyang District including influents (M1, H1, and C1), effluents of secondary sedimentation (M2 and H2), and effluents (M3, H3, and C2) in Haidian District were collected to investigate the OPFRs pollution in triplicate on winter, 2018. The detailed information of Wenyu River, groundwater and STPS were provided in Fig. 1 and Table S1, S2. The water samples were saved in the brown glass bottle at 4 °C before laboratory analysis, which were treated within 24 h after being transported to the laboratory.

2.2 Instruments and Quantification

For the LC separation, UHPLC Dionex Ultimate 3000 (Thermo Scientific, San Jose, USA) equipped with cooling auto-sampler, column oven and UV detector were utilized. An ACQUITY UPLC BEH C18 Column (2.1 mm×50 mm, 1.7 μm) was employed, and the column temperature was set at 35 °C.

![Fig. 1 Sampling locations of surface water, groundwater, and sewage treatment plants (STPs) samples in urban Beijing, China](image)
For the MS separation, the Q-Orbitrap mass spectrometer (Thermo Scientific, San Jose, USA) was equipped with a heat electrospray ionization (HESI) and operated in the full scan mode. The sheath gas, auxiliary gas, and sweep gas was at a flow rate of 45, 15, and 0 (arbitrary units), respectively. The spray voltage was set at +3.00 kV. The capillary temperature and auxiliary gas heater temperature were maintained at 375 °C and 300 °C, respectively. The S-lens RF level was set at 50 V. Nitrogen was used for spray stabilization and as the damping gas in the C-trap. Control (AGC) target (the number of ions to fill C-Trap) was set at 1.0e6 with a maximum injection time (IT) of 100 ms. The full MS scan ranges were set from 100 to 760 m/z with a resolution of 70,000. In MS2 mode, samples were analyzed at 30 NCE (normalized collisional energy). All data collected in profile mode were acquired and processed by Thermo Xcalibur 3.0 software (Thermo Scientific, San Jose, USA).

Quantification using external standard was the approach to determine the concentration of OPFRs. The calibration curves for the OPs detection exhibited good linear relationship ($R^2 > 0.99$). The limit of quantification (LOQ) calculated with a signal/noise ratio of 10 was 0.08 ~ 0.14 ng/L.

2.3 Sample Preparation

Method used to extract of OPFRs were followed the procedure by Zhong et al., (2017) with small modification. After sample collection, urban water (1 L for each sample) was filtered through 0.45 μm pore size glass microfiber filters, and extracted using solid phase extraction by gravity with HLB (hydrophilic-lipophilic balance) columns (6 cm³, 200 mg). Before use, all the columns were conditioned by adding 6 mL of ethyl acetate and 6 mL of methanol. Then, the columns were drained and eluted with 10 mL of ethyl acetate. The extracts adjusted to 1 mL with methanol (nitrogen blow down).

2.4 Statistical Analysis

The statistical significance of differences was evaluated by AVOVA, which was considered significant at $p < 0.05$. The correlation analysis of OPFRs and environmental factors were carried out using SPSS 20.0 and Canoco 4.5 software.

2.5 Ecological Risk Characterization

The risk of OPEs for aquatic organisms was evaluated by the determination of risk quotient (RQ) values, as described by the previous reports (Yadav et al., 2018). RQ value of each compound in water was calculated using the following formula:

$$RQ = \frac{MEC}{PNEC}$$

where the MEC is the actual measured environmental concentration, PNEC is the no effect concentration, usually obtained by dividing the acute and chronic toxicity data (half lethal concentration LC50, half effect concentration EC50, etc.) by the assessment factor (AF). When $RQ < 0.1$, the risk is low or negligible; when $0.1 < RQ < 1.0$, there is a medium risk; and when $RQ > 1.0$, it is considered to have a high risk.

3 Results and Discussion

3.1 Occurrence of OPFRs in Urban Surface Water and Groundwater

Six kinds of OPFRs were detected at seven sites in Wenyu River, as well as five sites for underground

Fig. 2 Concentration of OPFRs in surface water and groundwater
The detection frequencies of three OPFRs (i.e., TPP, TCPP, TCEP) were 100%, while those of TDBP, TDCPP, and TCP were 0%, 28.57%, and 35.71%, respectively. Notably, TDBP was not detected in all of samples, which may be related with its high $\log_{k_{ow}}$ (4.29) and the substitutes of the new flame retardants (Table S2). The total concentration of five OPFRs in surface water of Wenyu river varied between 261.13 ~ 581.69 (mean: 374.05) ng/L, which was comparable to those of 14 OPFRs (37.20 ~ 510 ng/L) in river water located in New York state with high population (Kim & Kannan, 2018), but apparently higher than those in lake water from less populated cities of Germany (Regnery and Püttmann, 2010). This phenomenon reflects that frequent human activities in densely populated cities have important contribution to OPERs pollution of surface water. In contrast, the total concentrations of five OPFRs in underground water varied between 16.68 ~ 58.29 (mean: 39.27) ng/L, which was significantly lower than that in surface water ($P < 0.05$).

Similar to other researches (Kim & Kannan, 2018), TCPP was the predominate OPFRs with a concentration of 203.70 ~ 394.77 (mean value: 262) ng/L in river and 12.02 ~ 52.43 (mean-value: 28) ng/L in underground water, followed by TCEP. Studies have confirmed that TCPP and TCEP appear to be the most ubiquitous in environment (Yan et al., 2012). The concentration-percent composition of these two OPFRs ($[\text{TCPP}] + [\text{TCEP}]$) accounted for 86.62 ~ 99.48% in river and 76.13 ~ 98.54% in underground water of the total, with an average of 91.65% and 86.50%, respectively, partly because their high solubility (TCPP: 1600 mg/L; TCEP: 7000 mg/L) in water and the widely applications (Table S2) in Beijing. This result was consistent with the investigation by Shi et al. (2016) in which TCPP and TCEP were the most abundant compounds in Beijing surface water in 2013–2014, with average concentration of 291 ng/L and 219 ng/L, respectively.

The concentration of all chlorinated OPFRs (i.e., TCPP, TCEP, and TDCPP) were significantly higher than aryl-OPFRs (i.e., TPP and TCP) ($P < 0.05$), mostly because that the chlorinated OPFRs are considered as very persistent and were not degraded during wastewater treatment (Marklund et al., 2005). There shows different characteristics of the fate of aryl and chlorinated OPFRs in surface water and underground water (Fig. 2). For the former, the concentration was equal or a little higher in the underground water. However, the concentration of chlorinated OPFRs was much higher in surface water than those in underground water. That may because the aryl-OPFRs have a higher $\log_{k_{ow}}$ (Table S2) thus was trapped in the soil. In addition, the OPFRs concentration at different sampling points, especially TCPP, has obvious spatial difference, but has no obvious regularity along the water flow direction (Fig. 2).

What we would like to emphasize is that the trace amounts of OPFRs in groundwater also had a potential threat to aquatic life and result a long-term health risk through diet (He et al., 2020), which should be further addressed. Notably, the sampling time of this study was in winter, and the average temperature is usually 20 ~ 25 °C lower than summer, Regnery and Püttmann (2009) found that the proportions of OPFRs in condensate and internal vehicle air reveal an increase as the temperature goes up. Therefore, it is foreseeable that the emissions of ORFPs, especially the more volatile ORFPs (TCPP and TCEP etc.), from vehicles and buildings will be higher in summer than in winter, which means that there is still a more serious risk of OPFRs exposure in Beijing’s surface water and groundwater.

### 3.2 Occurrence and Removal Efficiency of OPFRs in STPs

#### 3.2.1 Occurrence OPFRs in STPs

We detected the distribution of OPFRs in the influent and effluent water in STPs (Fig. 3a). The total concentration of OPFRs in STPs ranges from 57.09 to approximately 535.09 (mean: 296.91) ng/L, which are lower than that in surface water and higher than that in groundwater. Undoubtedly, in densely populated cities, domestic sewage is the main source of OPFRs, which is directly related to human health (Kim et al., 2017), and the concentration of OPFRs in the downstream of STPs has increased significantly (Andresen et al., 2004).

In our study, the content of STPs influent may reflect the relative degree of the application of different OPFRs. For the influent of the STP in Miyun District, the concentration of TCPP was highest with a concentration between 40.94 and approximately 216.01 ng/L, which was persistence with the concentration in surface water. TCPP was the
most abundant OPFRs in surface water (Hou et al., 2019). The secondary predominant compound was TCEP (15.50–39.10 ng/L), followed by TDCPP (ND–24.80 ng/L). The distribution of OPFRs in the distribution was persistence with the surface water. In the research of Kim et al., (2017), TBOEP was the predominant compound in the influent of a STP in Albany area of New York State followed by TCIPP with a concentration of 5120 ng/L, TDCIPP (1720 ng/L) and TCEP (1430 ng/L) that much higher than this study. Interestingly, there shows a higher content of TCPP in Miyun STP which may be related with the contribution of industry. According to the “13th Five-Year Plan” (2015–2020), general manufacturing should be evacuated from the six core districts including Chaoyang and Haidian. Besides, the leaching from the plastic films used for agriculture (Cho et al., 1996) may be one of the reasons causing the increase of TCPP in Miyun. Li et al. (2017) revealed that the degradation of TCPP in may be worse because of the occurrence of the ·OH, which results the accumulation of it and increase the ecological risk.

3.2.2 Removal Efficiency of OPFRs in STPs

STPs can remove most organic contaminants, but not all pollutants were always satisfactorily removed because of the differences in physicochemical properties of contaminants (Ibáñez et al., 2013; Pang et al., 2016a, b). There showed different treatment rate in STPs as sees in Fig. 3b. As the concentration of some OPFRs in the influents was none detected, the removal rate was not reflected in the figure. What shocked us was that the removal efficiency of OPFRs in STPs was even more unsatisfactory, or even negative, with a total removal rate of –856.67–55.15% (Table S3). For TCPP, the major pollution factors in STPs, its total removal efficiency was from –398.23 to –35.83% in municipal STPs. The treatment rate of STPs for OPFRs may related with the physical chemistry properties and influent concentration of different OPFRs, or technique of STPs, such as retention times. It showed that linear alkyl OPFRs are easier to be degraded than branched compounds, and chlorinated OPFRs are more persistent than non-chlorinated ones (Liang & Liu, 2016; Reemtsma et al., 2008). The removal rate of TBEP was reported to be 85.10–88.40% (Pang et al., 2016a, b). In this study, the treatment rates of all the chlorinated OPFRs were negative, showing strong resistance to biotransformation, and biotransformation has a significant impact on bioaccumulation which is relation with the health risk (Yao et al., 2021). In the USA, Schreder and La Guardia (2014a, b) and Kim et al., (2017) observed that the removal for TCPP, TCEP, and TDCPP was negative. Merely 0.30% of TCEP and 4.00% of TCPP was removed in Pang’s studies (Pang et al., 2016a, b); however, TPP could be removed with a rate of about 80% in the same STP.

The worst removal capabilities were found at the STP in Chaoyang District, which applied the cyclic
activated sludge technology (CAST) (STP in Chaoyang District). The reason may be that the large quantity recycling of activated sludge with high mass flow of OPFRs from the return sludge and internal recirculation sludge, the chlorinated OPFRs are easily absorbed by the biological particles and the coarse particles (Liang & Liu, 2016), and the sludge is refluxed in the primary sedimentation tank or the secondary sedimentation tank, thereby causing an analytical effect to increase the concentration of OPFRs in the effluent. Therefore, the STPs are unsuitable to handle the chlorinated OPFRs. However, compared with CAST and A2/O (STP in Miyun District), A/O MBR technology may be more effective for the removal of OPFRs, which showed the high removal efficiencies for TCP.

However, researches showed that the sorption of OPFRs to sludge happened to some extends. The concentration of TCPP in sludge ranged from 6.70 to 161 µg/kg from 24 STPs in Henan, China (Pang et al., 2016a, b); the average concentration of TCPP in sludge from 20 German STPs was 5000 ng/g. In one wastewater treatment plant sludge from the Pearl River Delta, the concentration of OPFRs in sewage sludge was 96.70–1312.90 ng/g (Zeng et al., 2014). Pang et al. and’s (2016a, b) research further showed activated sludge adsorption was the major process for TCPP removed in the anoxic–oxic press.

The STPs had a certain treatment effect on the alkyl OPFRs, and the effluent concentration of TPP was lower than the influent (Table S3). Some articles had showed that the occurrence and distribution were persistence with the density of population (Shi et al., 2016), and higher concentrations of OPFRs were often found in metropolitan areas (Kim & Kannan, 2018).

3.3 Ecological Risk Assessment

The continuous inputs and potential toxicity of OPFRs have drawn an increasing concern on their effects towards the ecosystem. In this study, the risk assessment to aquatic organisms was estimated for the most frequently detected OPFRs, including TPP, TCP, TCPP, TCEP, and TDCPP in the multiple urban water bodies of Beijing. Acute median effective concentrations (LC$_{50}$ or EC$_{50}$) of 5 OPFRs for different aquatic organisms (algae, fish, and crustacean) were obtained according to the environmental risk limits report for organophosphorus flame retardants (Verbruggen et al., 2006). As shown in Table 1, low (RQ < 0.1) risk of 5 OPFRs was observed for three organisms in urban water from Beijing. In addition, the risks of the five OPFRs in multiple urban water bodies were different. The RQ values of TCPP and TDCPP in Wenyu River and the three STPs are relatively higher than in groundwater (Table S1), indicating that the TCPP and TDCPP in surface water and domestic wastewater in Beijing may be the main contributors to potential aquatic ecological risks.

OPFRs are bioaccumulative to animals and humans (Du et al., 2019), even TCPP (LogK$_{ow}$ = 2.59; Table S2) with a low octanol–water partition coefficient (Reemtsma et al., 2008). TPP has potential adverse impact on aquatic ecosystems (Liu et al., 2013). For the chronic toxicity, an estimated NOEC of TPP for daphnia and fish were 0.1 mg/L and 0.0014 mg/L, respectively, which levels were highly regarded by the US-EPA (2007). Since the highest concentration detected for TPP in multiple urban water was 2.42 ng/L, and its MEC/PNEC ratio were 2.40×10$^{-5}$ (daphnia) and 0.60×10$^{-2}$ (fish), which means no chronic adverse effects are expected. However, it cannot be ignored that the degradation of these OPFRs is not effective, chronic toxicity will still occur under long-term accumulation, which ultimately endanger ecological health (Yang et al., 2019). Therefore, it is necessary to further investigate the occurrence characteristics of OPFRs in aquatic environment and its bioaccumulation and bio-amplification in biota for a more comprehensive risk assessment.

4 Conclusion

In the present study, the occurrence and distribution of 6 OPFRs in urban multiple water of Beijing, China were explored. Five OPFRs were detected in the urban water samples, and TCPP were the most abundant compounds followed by TCEP and TDCPP. The order of concentration of OPFRs from high to low is surface water, the effluent and influent of STP and underground water. The levels of chlorinated OPFRs in urban surface water in Beijing were higher than or similar to those detected in most of other sites in literature. Risk assessment based on acute toxicity data
suggested the low risk of OPFRs to three aquatic organisms (algae, crustacean, and fish). However, taking into account the high levels of OPFRs in surface water and STPs in Beijing, long-term exposure of the human body and bioaccumulation of these contaminants in aquatic environment should be further explored.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (41877409) and Ministry of Science and Technology of China (Grant No. 2015FY110900).

Author Contribution Shaoyong Lu, Weihua Cui, and Ying Zhang contributed to the conception of the study; Pan Qin and Xiaochun Guo contributed significantly to analysis and manuscript preparation; Yanmeng Zhang, Weihua Cui, and Na Zhang performed the data analyses and wrote the manuscript; Zhi Wang helped perform the analysis with constructive discussions.

Data Availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Table 1 RQs for the aquatic organisms as calculated from MECs and PNECs

| Analytes | Organisms                  | L(E)C50 a (mg/L) | AF | PNEC (ng/L) | MEC (ng/L) | RQs |
|----------|-----------------------------|------------------|----|-------------|------------|-----|
|          |                             |                  |    |             |            |     |
| TCEP     | Algae (*Scenedesmus subspicatus*) | 51.0             | 1000 | 51,000      | 3.30       | 169.37 |
|          | Crustacean (*Daphnia magna*)  | 330.0            | 1000 | 330,000     | 9.98E-06   | 5.13E-04 |
|          | Fish (*Carassius auratus*)   | 90.0             | 1000 | 90,000      | 3.66E-05   | 1.88E-03 |
| TCPP     | Algae (*Scenedesmus subspicatus*) | 45.0             | 1000 | 45,000      | 12.02      | 394.77 |
|          | Crustacean (*Daphnia magna*)  | 91.0             | 1000 | 91,000      | 1.32E-04   | 4.34E-03 |
|          | Fish (*Carassius auratus*)   | 30.0             | 1000 | 30,000      | 4.01E-04   | 1.32E-02 |
| TDCPP    | Algae (*Scenedesmus subspicatus*) | 39.0             | 1000 | 39,000      | ND         | 76.85 |
|          | Crustacean (*Daphnia magna*)  | 4.20             | 1000 | 4200        | /          | 1.83E-02 |
|          | Fish (*Carassius auratus*)   | 5.10             | 1000 | 5100        | /          | 1.51E-02 |
| TCP      | Algae (*Scenedesmus subspicatus*) | 0.29             | 1000 | 290         | ND         | 0.46  |
|          | Crustacean (*Daphnia magna*)  | 0.27             | 1000 | 270         | /          | 1.69E-03 |
|          | Fish (*Carassius auratus*)   | 0.11             | 1000 | 110         | /          | 4.15E-03 |
| TPP      | Algae (*Scenedesmus subspicatus*) | 0.50             | 1000 | 500         | 0.52       | 2.42  |
|          | Crustacean (*Daphnia magna*)  | 1.00             | 1000 | 1000        | 5.17E-04   | 2.42E-03 |
|          | Fish (*Carassius auratus*)   | 0.70             | 1000 | 700         | 7.39E-04   | 3.45E-03 |

a Acute toxicity (LC50 or EC50) data were obtained according to Verbruggen et al. (2006). L(E)C50 Lowest median effective concentration value obtained from existing studies. AF the evaluation factor, PNEC the predicted no-effect concentration of organophosphate flame retardants (OPFRs), MEC the measured environmental concentration of OPFRs, RQ the environmental risk quotient of OPFRs

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interest The authors declare no competing interests.

References

Andresen, J., Grundmann, A., & Bester, K. (2004). Organophosphorus flame retardants and plasticisers in surface waters. *Science of the Total Environment, 332*, 155–166. [https://doi.org/10.1016/j.scitotenv.2004.04.021](https://doi.org/10.1016/j.scitotenv.2004.04.021)

Batool, S., Gill, R., Ma, C., Reddy, G.C.S., Guo, W.W., & Hu, Y. (2020). Epoxy-based multilayers for flame resistant flexible polyurethane foam (FPUF). *Journal of Applied Polymer Science, 137*(29). [https://doi.org/10.1002/app.48890](https://doi.org/10.1002/app.48890)

Chen, Y., Cao, Z., Covaci, A., Li, C., & Cui, X. (2019). Novel and legacy flame retardants in paired human fingernails and indoor dust samples. *Environment International, 133*, 105227. [https://doi.org/10.1016/j.envint.2019.105227](https://doi.org/10.1016/j.envint.2019.105227)

Cho, K. J., Hirakawa, T., Mukai, T., Takimoto, K., & Okada, M. (1996). Origin and stormwater runoff of TCP
(tricresyl phosphate) isomers. *Water Research*, 30, 1431–1438. https://doi.org/10.1016/0043-1354(96)00029-2

Du, J., Li, H., Xu, S., Zhou, Q., Jin, M., & Tang, J. (2019). A review of organophosphorus flame retardants (OPFRs): Occurrence, bioaccumulation, toxicity, and organism exposure. *Environmental Science and Pollution Research*, 26(22), 22126–22136. https://doi.org/10.1007/s11356-019-05669-y

He, C., Lin, C. Y., & Mueller, J. F. (2020). Organophosphate flame retardants in the environment: Source, occurrence, and human exposure - ScienceDirect. *Comprehensive Analytical Chemistry*, 88, 341–365. https://doi.org/10.1016/bs.coac.2019.10.008

He, J., Wang, Z., Zhao, L., Ma, H., Huang, J., Li, H., Mao, X., Huang, T., Gao, H., & Ma, J. (2021). Gridded emission inventory of organophosphate flame retardants in China and inventory validation. *Environmental Pollution*, 290, 118071. https://doi.org/10.1016/j.envpol.2021.118071

Hou, R., Xu, Y., & Wang, Z. (2016). Review of OPFRs in animals and humans: Absorption, bioaccumulation, metabolism, and internal exposure research. *Chemosphere*, 153, 78–90. https://doi.org/10.1016/j.chemosphere.2016.03.003

Hou, L., Jiang, J., Gan, Z., Dai, Y., Yang, P., Yan, Y., Ding, S., Su, S., & Bao, X. (2019). Spatial distribution of organophosphorous and brominated flame retardants in surface water, sediment, groundwater, and wild fish in Chengdu, China. *Archives of Environmental Contamination and Toxicology*, 77(2), 279–290. https://doi.org/10.1007/s00244-019-00624-x

Huang, J., Ye, L., Fang, M., & Su, G. (2022). Industrial production of organophosphate flame retardants (OPFRs): Big knowledge gaps need to be filled? *Bulletin of Environmental Contamination and Toxicology*, 108(5), 809–818. https://doi.org/10.1007/s00128-021-03454-7

Ibáñez, M., Gracia-Lor, E., Bijlsma, L., Morales, E., Pastor, L., & Hernández, F. (2013). Removal of emerging contaminants in sewage water subjected to advanced oxidation with ozone. *Journal of Hazardous Materials*, 260, 389–398. https://doi.org/10.1016/j.jhazmat.2013.05.023

Kim, U.-J., & Kannan, K. (2018). Occurrence and distribution of organophosphate flame retardants/plasticizers in surface waters, tap water, and rainwater: Implications for human exposure. *Environmental Science and Technology*, 52, 5625–5633. https://doi.org/10.1021/acs.est.b800727

Kim, U.-J., Oh, J. K., & Kannan, K. (2017). Occurrence, removal, and environmental emission of organophosphate flame retardants/plasticizers in a wastewater treatment plant in New York State. *Environmental Science and Technology*, 51, 7872–7880. https://doi.org/10.1021/acs.est.b7b02035

Li, C., Chen, J. W., Xie, H. B., Zhao, Y. H., Xia, D. M., Xu, T., et al. (2017). Effects of atmospheric water on center dot OH-initiated oxidation of organophosphate flame retardants: A DFT investigation on TCPP. *Environmental Science and Technology*, 51(9), 5043–5051. https://doi.org/10.1021/acs.est.7b00347

Liang, K., & Liu, J. (2016). Understanding the distribution, degradation and fate of organophosphate esters in an advanced municipal sewage treatment plant based on mass flow and mass balance analysis. *Science of the Total Environment*, 544, 262–270. https://doi.org/10.1016/j.scitotenv.2015.11.112

Liu, X., Ji, K., Jo, A., Moon, H.-B., & Choi, K. (2013). Effects of TDCPP or TPP on gene transcriptions and hormones of HPG axis, and their consequences on reproduction in adult zebrafish (Danio rerio). *Aquatic Toxicology*, 134–135, 104–111. https://doi.org/10.1016/j.aquatox.2013.03.013

Loos, R., Carvalho, R., António, D. C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., & Blaha, L. (2013). EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. *Water Research*, 47, 6475–6487. https://doi.org/10.1016/j.watres.2013.08.024

Marklund, A., Andersson, B., & Haglund, P. (2005). Organophosphate flame retardants and plasticizers in Swedish sewage treatment plants. *Environmental Science and Technology*, 39, 7423–7429. https://doi.org/10.1039/B505587C

Möller, A., Sturm, R., Xie, Z., Cai, M., He, J., & Ebinghaus, R. (2012). Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the polar regions: Evidence for global occurrence. *Environmental Science and Technology*, 46, 3127–3134. https://doi.org/10.1021/es204272v

National Bureau of Statistics of China. (2021). Main data of the seventh national population census. Retrieved from http://www.stats.gov.cn/sj/tjgb/kjgb/q月底/pkgb/202032/20203206_1902003.html. Accessed 25 May 2023

Pang, L., Yang, P., Zhao, J., & Zhang, H. (2016). Comparison of wastewater treatment processes on the removal efficiency of organophosphate esters. *Water Science and Technology*, 74, 1602–1609. https://doi.org/10.2166/wst.2016.356

Pang, L., Yuan, Y., He, H., Liang, K., Zhang, H., & Zhao, J. (2016). Occurrence, distribution, and potential affecting factors of organophosphate flame retardants in sewage sludge of wastewater treatment plants in Henan Province, Central China. *Chemosphere*, 152, 245–251. https://doi.org/10.1016/j.chemosphere.2016.02.104

Pang, L., Yang, H. Q., Yang, P. J., Zhang, H. Z., & Zhao, J. H. (2017). Trace determination of organophosphate esters in white wine, red wine, and beer samples using dispersive liquid-liquid microextraction combined with ultra-high-performance liquid chromatography-tandem mass spectrometry. *Food Chemistry*, 229, 445–451. https://doi.org/10.1016/j.foodchem.2017.02.103

Reemtsma, T., Quintana, J. B., Rodil, R., Garcì, M., & Rodri, I. (2008). Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *TrAC Trends in Analytical Chemistry*, 27, 727–737. https://doi.org/10.1016/j.trac.2008.07.002

Regnery, J., & Puttmann, W. (2009). Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. *Clean-soil Air Water*, 37(4–5), 334–342. https://doi.org/10.1002/clen.200900050

Regnery, J., & Püttmann, W. (2010). Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. *Water
Vol.: (1234567890)

Schreder, E. D., & La Guardia, M. J. (2014). Flame retardant transfers from US households (dust and laundry wastewater) to the aquatic environment. *Environmental Science and Technology, 48*, 11575–11583. https://doi.org/10.1021/es502227h

Schreder, E. D., & La Guardia, M. J. (2014). Flame retardant transfers from U.S. households (dust and laundry wastewater) to the aquatic environment. *Environmental Science and Technology, 48*(19), 11575–11583. https://doi.org/10.1021/es502227h

Shi, Y.-L., Gao, L.-H., Li, W.-H., Wang, Y., Liu, J.-M., Cai, Y.-Q. (2016). Occurrence, distribution and seasonal variation of organophosphate flame retardants and plasticizers in urban surface water in Beijing, China. *Environmental Pollution*, 209, 1–10. https://doi.org/10.1016/j.envpol.2015.11.008

Van der Veen, I., & de Boer, J. (2012). Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere, 88*, 1119–1153. https://doi.org/10.1016/j.chemosphere.2012.03.067

Verbruggen, E., Rila, J., Traas, T., Posthuma-Doodeman, C., & Posthumus, R. (2006). Environmental risk limits for several phosphate esters, with possible application as flame retardant. RIVM rapport 601501024.

Wei, G.-L., Li, D.-Q., Zhuo, M.-N., Liao, Y.-S., Xie, Z.-Y., Guo, T.-L., Li, J.-J., Zhang, S.-Y., & Liang, Z.-Q. (2015). Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human exposure. *Environmental Pollution, 196*, 29–46. https://doi.org/10.1016/j.envpol.2014.09.012

Wen, X., Shen, M., Han, H., Wang, A., & Zhai, J. (2018). Exposure level, toxicity effects and health risk assessment of organophosphorus flame retardants in water environment. *Agricultural Science and Technology, 19*(6), 31–42. https://doi.org/10.16175/j.cnki.1009-4229.2018.06.006

Yadav, I. C., Devi, N. L., Li, J., Zhang, G., & Covaci, A. (2018). Concentration and spatial distribution of organophosphate esters in the soil-sediment profile of Kathmandu Valley, Nepal: Implication for risk assessment. *Science of the Total Environment, 613*, 502–512. https://doi.org/10.1016/j.scitotenv.2017.09.039

Yan, X.-J., He, H., Peng, Y., Wang, X.-M., Gao, Z.-Q., Yang, S.-G., & Sun, C. (2012). Determination of organophosphorus flame retardants in surface water by solid phase extraction coupled with gas chromatography-mass spectrometry. *Chinese Journal of Analytical Chemistry, 40*(11), 1693–1697. https://doi.org/10.1016/S1872-2040(11)60586-0

Yang, C. M., Li, Y., Zha, D. P., Lu, G. H., Sun, Q., & Wu, D. H. (2017). A passive sampling method for assessing the occurrence and risk of organophosphate flame retardants in aquatic environments. *Chemosphere, 167*, 1–9. https://doi.org/10.1016/j.chemosphere.2016.09.141

Yang, J., Zhao, Y., Li, M., Du, M., Li, X., & Li, Y. (2019). A review of a class of emerging contaminants: The classification, distribution, intensity of consumption, synthesis routes, environmental effects and expectation of pollution abatement to organophosphate flame retardants (OPFRs). *International Journal of Molecular Sciences, 20*(12). https://doi.org/10.3390/ijms2012287450

Yao, C., Yang, H., Li, Y. (2021). A review on organophosphate flame retardants in the environment: Occurrence, accumulation, metabolism and toxicity. *Science of The Total Environment, 795*. https://doi.org/10.1016/j.scitotenv.2014.08.147

Yu, K., Du, Z., Xuan, H., et al. (2022). Comprehensive analysis based in silico study of organophosphate flame retardants - Environmental explanation of bladder cancer progression[J]. *Environmental Toxicology and Pharmacology, 92*, 103851. https://doi.org/10.1016/j.etap.2022.103851

Zeng, X., He, L., Cao, S., Ma, S., Yu, Z., Gui, H., Sheng, G., & Fu, J. (2014). Occurrence and distribution of organophosphate flame retardants/plasticizers in wastewater treatment plant sludges from the Pearl River Delta, China. *Environmental Toxicology and Chemistry, 33*, 1720–1725. https://doi.org/10.1002/etc.2604

Zhang, L., Lu, L., Zhu, W., Yang, B., Lu, D., Dan, S. F., et al. (2021). Organophosphorus flame retardants (OPFRs) in the seawater and sediments of the Qinzhou Bay, Northern Beibu Gulf: Occurrence, distribution, and ecological risks. *Marine Pollution Bulletin, 168*, 112368. https://doi.org/10.1016/j.marpolbul.2021.112368

Zhang, Q., Li, J., Lin, S., Ying, Z., Hu, S., Wang, Y., & Mo, X. (2022). Organophosphate flame retardants in Hangzhou tap water system: Occurrence, distribution, and exposure risk assessment. *Science of The Total Environment, 849*, 157644. https://doi.org/10.1016/j.scitotenv.2022.157644

Zhong, M., Tang, J., Mi, L., Li, F., Wang, R., Huang, G., & Wu, H. (2017). Occurrence and spatial distribution of organophosphorus flame retardants and plasticizers in the Bohai and Yellow Seas, China. *Marine Pollution Bulletin, 121*, 331–338. https://doi.org/10.1016/j.marpolbul.2017.06.034

**Publisher’s Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.