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# Occurrence, Fate, and Mass Balance Analysis of Organophosphate Flame Retardants in a Municipal Wastewater Treatment Plant in Hunan Province, China

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**Abstract:** The occurrence, distribution, removal, and mass loadings of common organophosphate flame retardants (OPFRs) in an advanced municipal wastewater treatment plant (WWTP) were comprehensively investigated. The OPFRs were mainly partitioning in the dissolved phase, and the total concentrations ranged from 1364 to 1701 ng/L in influent, 678~1064 in effluent, and 177~470 ng/g dw in residual sludge. Tributoxyethyl phosphate and tris(2-chloroethyl) phosphate were the abundant compounds in both the dissolved phase and adsorbed phase. The removal frequencies and mechanisms of the OPFRs were highly associated with the properties of compounds. According to the mass balance analysis, 14.9%, 13.0%, and 11.2% of the total OPFR loads were removed in the traditional treatment, tertiary treatment, and to the sludge, respectively. The mass loadings and environmental emissions of the OPFRs were 0.67~291 μg/d/person and 0.57~107 μg/d/person, respectively. The effluent discharged from the WWTP posed ecological risks to the receiving river, which requires being paid more attention.

**Keywords:** organophosphate flame retardants; municipal wastewater treatment plant; mass balance analysis; mass loadings; environmental emissions

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**Citation:** Liu, Y.; Song, Y.; Li, H.; Yang, Z. Occurrence, Fate, and Mass Balance Analysis of Organophosphate Flame Retardants in a Municipal Wastewater Treatment Plant in Hunan Province, China. *Water* **2024**, *16*, 1462. https://doi.org/10.3390/w16111462

Academic Editors: Xiaohu Lin, Binbin Shao and Jingcheng Xu

Received: 22 April 2024
Revised: 18 May 2024
Accepted: 18 May 2024
Published: 21 May 2024

## 1. Introduction

In recent years, the production and consumption of organophosphate flame retardants (OPFRs) have grown significantly due to the restricted application of brominated flame retardants. OPFRs have been widely used in plastics, building materials, textiles, electronic products, lubricate oil, and other industrial products [1]. The global consumption of OPFRs increased to 1 million tons in 2018 [2], and the growth rate in China could achieve 15% annually [3]. OPFRs are used by physically adding them to the product without chemical bonding, which allows for their easy release into the environment [4]. As a result, they are widely present in a range of environmental media and even in living organisms. Numerous studies have been reported on the occurrence of OPFRs in water [4–7], air [8–10], dust [10–12], sediment [2,4,13], soil [14,15], and biota samples [16,17]. Given the high detection frequency and potential toxicity to organisms, OPFRs might pose a potential threat to ecology and humans, which need to be paid attention to.

A wastewater treatment plant (WWTP) is the final treatment site for pollutants in wastewater. Traditional pollutants like COD, BOD, and total suspended solid (TSS) collect here and are eventually removed through a sequence of treatments [18]. Nevertheless, several studies have indicated that the removal efficiencies of OPFRs by a WWTP are limited [19–21]. As a result, the residual OPFRs may be released into the environment along with effluent or residual sludge, making a WWTP the main source of OPFRs into the environment rather than the elimination site.

Currently, several studies have been carried out to study the concentration level and removal efficiency of OPFRs in a WWTP [18,22–24]. Yin et al. [22] investigated the concentration and distribution of seven OPFRs in water samples from a WWTP, the total removal rate was found to be 57.2%, and the average concentrations of influent and effluent were 978.2 ± 166.5 ng/L and 418.3 ± 12.0 ng/L, respectively. Kim et al. [20] researched the removal efficiencies of OPFRs in a WWTP from New York State, the removal efficiencies ranged from negative values to about 60%, showing incomplete removal and a significant difference in OPFRs. However, the behavior and emissions of OPFRs in the various treatment stages in a WWTP have not been thoroughly investigated and reported [25–27]. Liang and Liu [25] performed the mass flow and mass balance analysis in an advanced municipal WWTP to unveil the potential removal mechanisms. Additionally, the behavior of pollutants in the WWTP would have been affected by a variety of factors, including the population, climate, and WWTP treatment conditions. Wang et al. [28] investigated the occurrence of OPFRs in 25 municipal WWTPs across China and found that the removal frequencies of OPFRs using the same treatment process might vary significantly in different districts. Therefore, more efforts should be made to study the fate of OPFRs in a WWTP.

In this study, we investigate the occurrence, behavior, and removal of 12 common OPFRs in a municipal WWTP in Changsha, Hunan Province, which has a typical Anaerobic/Anoxic/Oxic bioreactor and an advanced treatment stage. Both the dissolved phase and adsorbed phase (suspended particulate matter and sludge) were involved in the analysis to comprehensively assess the fate of OPFRs in the WWTP. The mass balance analysis was introduced to study the removal mechanisms. The mass loadings and environmental emissions were also calculated to evaluate the consumption and pollution emissions of OPFRs in this area for the first time.

## 2. Materials and Methods

### 2.1. Chemicals and Standards

Twelve common OPFRs were set as the target compounds in this study, including tri-isobutyl phosphate (TIBP), tri-nbutyl phosphate (TNBP), tributoxyethyl phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), tricresyl phosphate (TMPP), cresyl diphenyl phosphate (CDP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroethyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and triphenylphosphine oxide (TPPO). Among them, TNBP and EHDPP were purchased from Aladdin (Shanghai, China), the other ten target OPFRs were purchased from Macklin (Shanghai, China). Deuterated TNBP-d27 and TPHP-d15 were used as the surrogate standards and bought from Toronto Research Chemicals Inc. (Toronto, ON, Canada). Detailed information on the compounds is listed in Table S1.

### 2.2. Study Plant and Sample Collection

The municipal WWTP was located in Changsha, Hunan Province, China. The service area of the plant was 62.98 km$^2$ with about 9,815,000 residents. The treatment process scheme of the WWTP included four main stages: (1) primary treatment (screen and grit chamber); (2) secondary treatment (Anaerobic/Anoxic/Oxic treatment and secondary clarifier); (3) tertiary treatment (high-efficient sedimentation tank, deep-bed filter, and UV disinfection); (4) sludge dewatering system (Figure 1). Among the stages, stage 1 and stage 2 were the traditional treatment process. During the sampling period, the average daily capacity of the plant was about 430,000 m$^3$/d, and the sludge production was about 250 t/d (wet weight, contained 80% moisture).

The sampling campaigns were conducted in September 2020. The wastewater samples, including influent, primary treatment effluent, secondary treatment effluent, and tertiary treatment effluent (also the final effluent), were collected in a 2.5 L amber glass bottle. The sludge samples were collected after the sludge dewatering system. The sampling points are shown in Figure 1. All of the samples were kept in a cooler and immediately transported to the lab for further analysis.

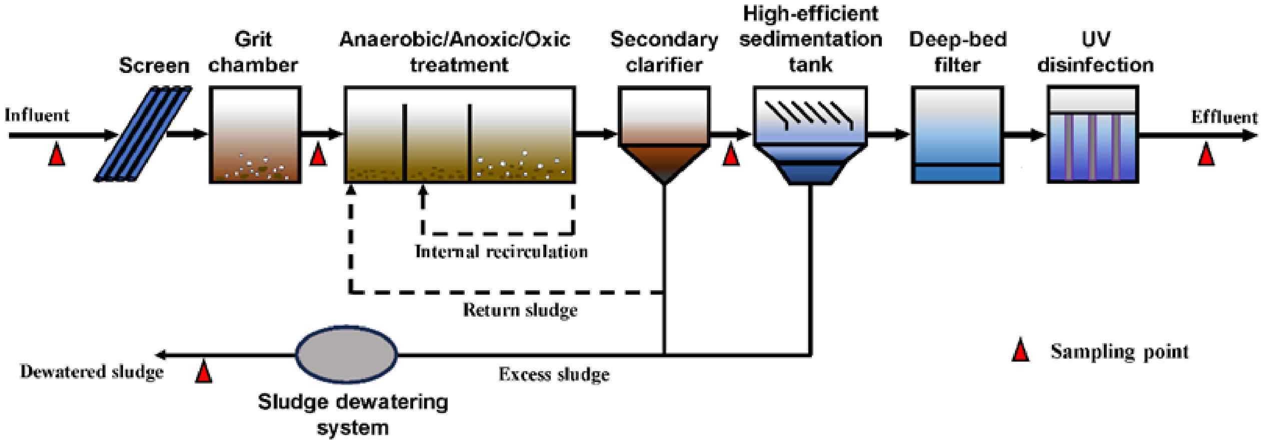

**Figure 1.** Schematic diagram of the studied wastewater treatment plant.

### 2.3. Sample Preparation

The wastewater samples were filtered using glass fiber filters (GF/F, Whatman, Kent, UK), which were pre-treated in a muffle furnace at 450 °C for 4 h. The solid interceptions were collected as suspended particulate matter (SPM) samples and also used to further calculate the TSS. The preparation of filtered water samples was conducted according to our previous study [5] with some modifications. Briefly, the water samples with surrogate standards (TNBP-d27 and TPHP-d15) were passed through the HLB cartridges (6 mL, 200 mg, ANPEL, Shanghai, China) and the target compounds were extracted using acetonitrile from the loaded HLB cartridges. The acetonitrile eluent was collected and concentrated to 1 mL for instrument analysis. The freeze-dried solid samples (SPM and sludge) were spiked with surrogate standards (TNBP-d27 and TPHP-d15), and then ultrasonic-assisted extracted for 15 min using acetonitrile (10 mL) as the ex-traction solution. The extractant was obtained by centrifugation, and the extraction process was repeated three times. A total of 30 mL of the collected extractant was concentrated and redissolved in 100 mL of ultra-pure water. The subsequent operation is the same as the extraction process of water samples.

The determination of 12 target OPFRs was performed on a liquid chromatography system (HPLC, Agilent 1260, Santa Clara, CA, USA) coupled with a triple quadrupole mass spectrometer (MS/MS, Agilent 6460, Santa Clara, CA, USA). The separation of target OPFRs was performed on the Poroshell 120EC-C18 column (50 mm × 4.6 mm i.d., 2.7 µm, Santa Clara, CA, USA). The column temperature was 30 °C, and the injection volume of samples was 5 µL. Gradient elution was performed using a binary mobile phase consisting of 0.1% (*v*/*v*) formic acid (A) and acetonitrile (B). The elution gradients are listed in Table S2. Using the multiple reaction monitoring (MRM) in positive ionization mode to quantify the target OPFRs in the samples, the optimized MS parameters were set as follows: the source temperature was 330 °C; the source gas flow was 8 mL/min; the nebulizer gas pressure was 40 psi. The optimized mass spectrum parameters of target OPFRs are listed in Table S3.

### 2.4. QA/QC

The equipment that might be in direct contact with the samples was thoroughly washed with methanol and ultra-pure water before use to avoid introducing contamination. The internal standard method was used to quantify the target OPFRs, and the recoveries of TNBP-d27 and TPHP-d15 were 91.7 ± 10.1% and 94.6 ± 4.7% for the water samples, and 98.1 ± 5.9% and 95.5 ± 9.7% for the solid samples, respectively. The limits of method quantification (LOQ) for the target OPFRs were defined as 10 times the signal-to-noise ratio, and the LOQ values of the water samples and solid samples were 0.005~0.05 µg/L and 0.06~3.89 µg/kg dw, respectively (Table S4). The recoveries and matrix effects of the water samples and solid samples are listed in Table S5. For instrument analysis, a solvent blank and a standard sample of specific concentration were detected every 10 samples to monitor the operating status of the instrument.

### 2.5. Data Analysis

The mass balance analysis for the OPFRs could be calculated as follows:

$$M_{\text{influent/effluent}} = C_{\text{dissolved}} \times Q \times 10^{-6} + C_{\text{adsorbed}} \times Q \times C_{\text{TSS}} \times 10^{-9} \tag{1}$$

$$M_{\text{sludge}} = C_{\text{sludge}} \times P_s \times 10^{-6} \tag{2}$$

$$M_{\text{influent}} = M_{\text{effluent}} + M_{\text{sludge}} + M_{\text{loss}} \tag{3}$$

$$M_{\text{loss-TT}} = M_{\text{influent}} - M_{\text{se,effluent}} - M_{\text{sludge}} \tag{4}$$

$$M_{\text{loss-AT}} = M_{\text{se,effluent}} - M_{\text{effluent}} \tag{5}$$

where $C_{\text{dissolved}}$ (ng/L), $C_{\text{adsorbed}}$ (ng/g, dw), and $C_{\text{sludge}}$ (ng/g, dw) are the concentrations of OPFRs in the aqueous phase, SPM, and residual sludge, respectively; Q ($m^3$/d) is the daily water follow of the plant; $P_s$ (kg/d, dw) is the average daily sludge output of the plant; $M_{\text{influent}}$, $M_{\text{se,effluent}}$, $M_{\text{effluent,}}$ and $M_{\text{sludge}}$ (g/d) represented the mass loads of OPFRs in influent, secondary treatment effluent, tertiary treatment effluent, and residual sludge, respectively; among them, the influent, secondary treatment effluent, and tertiary treatment effluent load contain both OPFRs dissolved in water and adsorbed on suspended particles; $M_{\text{loss}}$ (g/d) is the mass load loss of OPFRs during the wastewater treatment process, which can be considered as the loss caused by biodegradation and/or adsorption, including the $M_{\text{loss-TT}}$ (the loss occurred in the traditional treatment process) and the loss $M_{\text{loss-AT}}$ (the loss occurred in the advanced treatment process stage).

The total removal efficiency of OPFRs ($R_M$) could be calculated as follows:

$$R_M = \frac{M_{\text{influent}} - \left(M_{\text{effluent}} + M_{\text{sludge}}\right)}{M_{\text{influent}}} \times 100\% \tag{6}$$

Furthermore, the per capita consumption of OPFRs can be estimated by the pollution mass loadings of the WWTP influent, and the environmental emissions of OPFRs discharged from the WWTP can infer the total amount of pollution discharged in the region.

$$M_{\text{load}} = \frac{M_{\text{inffluent}} \times 10^9}{N_s} \tag{7}$$

$$E = \frac{\left(M_{\text{effluent}} + M_{\text{sludge}}\right) \times 10^9}{N_s} \tag{8}$$

where $M_{\text{load}}$ (µg/d/person) is the per capita pollution mass loadings of influent water, E (µg/d/person) is the per capita environmental emissions, and $N_s$ (person) is the total population served by the plant, which is 981,500 people in this study.

### 2.6. Ecological Risk Assessment

The risk quotient (RQ) method was used to assess the risk of residual OPFR discharge in wastewater to the aquatic environment.

$$RQ = \frac{MEC}{PNEC} \tag{9}$$

where MEC is the concentration of OPFRs (ng/L) in the effluent water of the WWTP, and PNEC is the predicted concentration of no effect (ng/g). To estimate the possible ecological threat caused by the total OPFRs, the risk quotient $RQ_{\text{mix}}$ is calculated, which is the sum of the RQ for each OPFRs [29].

## 3. Results and Discussion

### *3.1. Occurrence of OPFRs in Wastewater Treatment*

OPFRs in water and adsorbed on SPM were detected in water samples collected from the WWTP. The results showed that all the 12 target pollutants were detected at least once (Figure 2, Tables S8 and S9).

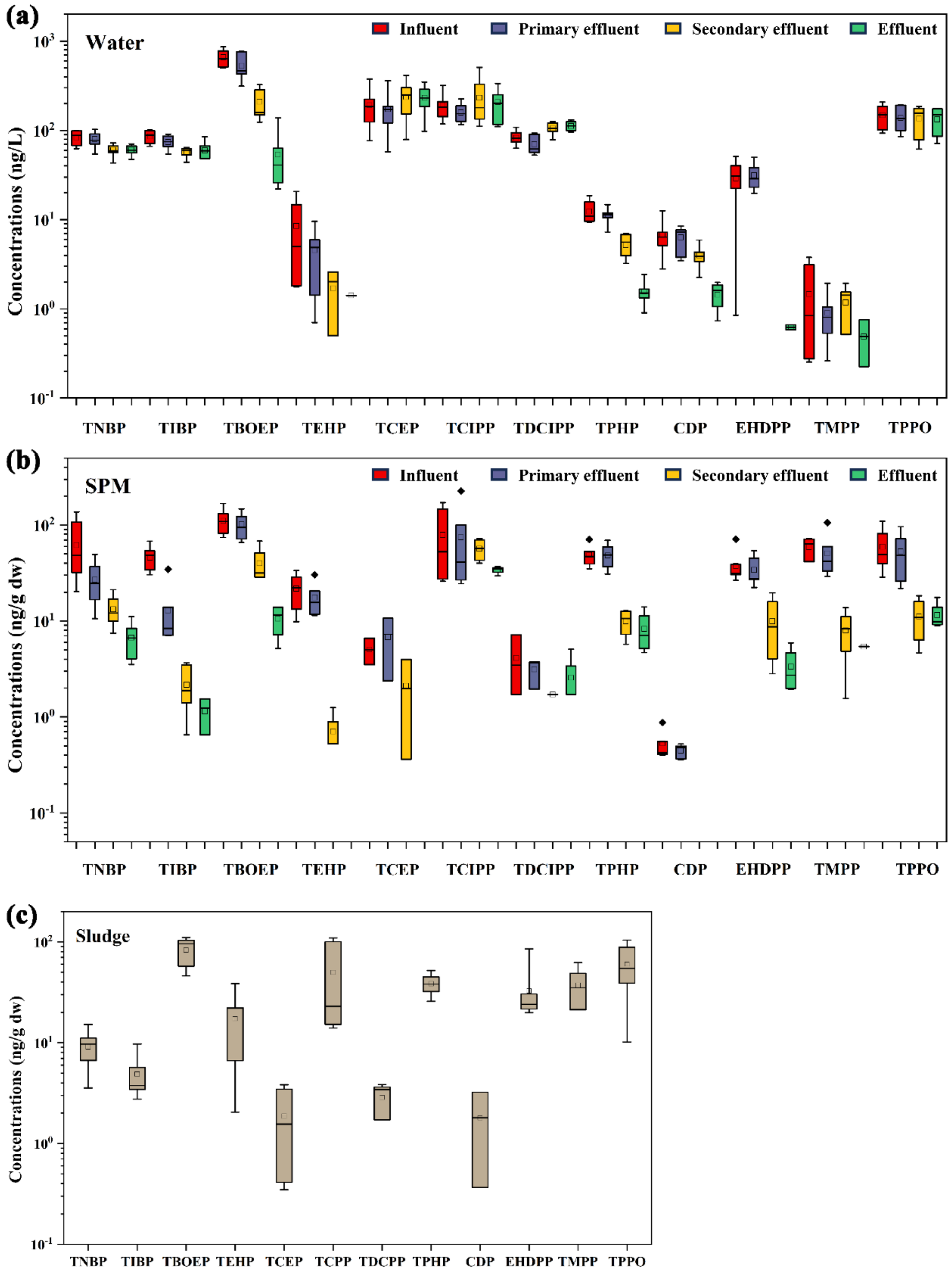

**Figure 2.** Concentrations of OPFRs in (**a**) water, (**b**) SPM, and (**c**) sludge from the studied WWTP. The horizontal line in the box marks the median. The box represents a range of 25% to 75%. The whiskers represent the range of minimum to maximum. Squares (□) and rhomboids (◆) represent mean values and outliers.

In the water of the influent sample, TBOEP (499~866 ng/L, mean 661 ± 126 ng/L) was the most abundant compound, accounting for about 44% of OPFRs in the dissolved phase, followed by TCEP (76.8~376 ng/L. mean 190 ± 90 ng/L) and TCIPP (118~320 ng/L, mean

191 ± 60 ng/L). Most of the compounds had high detection frequencies (DF > 50%), indicating the incomplete removal of OPFRs in the WWTP. TCEP (97.8~348 ng/L, 232 ± 76.8 ng/L) and TCIPP (110~336 ng/L, mean 207 ± 72.6 ng/L) were the most abundant compounds in the water of the effluent sample, accounting for 27% and 23% of the total OPFR concentration, respectively. Several studies from Spain [30], Germany [31], the United States [20], Greece [26], and a WWTP in Beijing [25] all indicated that TBOEP, TCEP, and TCIPP were the most abundant individual OPFRs, which was consistent with the results of this study. TBOEP has a variety of applications in home improvement materials, such as floor polish, added to paint or glue [7]; TCIPP and TCEP are widely used as flame retardants for polyurethane foams and other materials [1]. They had been widely detected in indoor dust, which was confirmed to be an important source of pollutants in domestic sewage [7]. Therefore, certain TBOEP, TCEP, and TCIPP were easily able to enter the urban sewage network through indoor dust or residents' flushing water. The total concentration of OPFRs (∑OPFRs) in the influent and effluent ranged from 1364 to 1701 ng/L and from 678 to 1064 ng/L, respectively. Compared with other countries and regions, both the individual OPFRs and ∑OPFRs in sewage in this study are at a relatively low level (Table S10).

The OPFRs of the SPM in the influent and effluent are listed in Table S9. TBOEP (71.8~168 ng/g, mean 108 ± 32.4 ng/g) and TCIPP (25.9~171 ng/g, mean 79.1 ± 56.2 ng/g) were the most important compounds in the SPM of the influent. However, TCEP with a high content in the aquatic phase has a lower content, which might be related to the physicochemical properties of the OPFRs with a lower n-octanol/water partition coefficient ($\log K_{\mathrm{ow}} = 1.44$) and higher solubility ($W_S = 7000$ mg/L), making the substance more likely to appear in the aquatic phase. In addition, TNBP, TPPO, and TMPP also had relatively high detected concentrations in the SPM of the influent, and the mean concentrations were 61.9 ± 40.3, 59.3 ± 25.7, and 58.6 ± 11.8 ng/g dw, respectively. ∑OPFRs in the SPM of the influent was 405~717 ng/g dw, while that in the effluent was 5.07~76.9 ng/g dw. The concentrations of all compounds in the SPM of the effluent decreased significantly, and the detection frequency of TMPP was only 14%, while TEHP, TCEP, and CDP were not detected. Because the effluent from the WWTP has been processed by deep treatment processes, the suspended particles were almost removed (removal frequency > 99.5%), so the OPFR concentrations on the SPM in the effluent also decreased. At present, the relevant studies on the OPFR concentration of SPM are limited, the result in this study was lower than that in WWTPs in Thessaloniki, Greece [7], and the residue level was the same as that in a WWTP in Beijing [25].

Most of the target OPFRs had high detection frequencies in the residual sludge, except CDP, which had a detection frequency of 29%. TBOEP (46.0~111 ng/g dw, mean 83.0 ± 23.4 ng/g) was again the most important compound, followed by TPPO (10.2~104 ng/g dw, mean 60.0 ± 30.9 ng/g dw) and TCIPP (14.0~110 ng/g dw, mean 49.7 ± 39.4 ng/g dw). ∑OPFRs in the residual sludge ranged from 177 to 470 ng/g dw, which was the same as that of a WWTP in Beijing [25] and other sewage treatment plants in Henan Province [32], but much lower than that reported in Spain [23], the United States [20], and Greece [26].

### *3.2. Distributions and Removal Efficiencies of OPFRs*

Understanding the distribution patterns of OPFRs between the dissolved phase (water) and adsorbed phase (solid) in wastewater treatment systems helps investigate the path and mechanism of pollutant removal. The distribution of pollutants in the two phases may be related to various factors, such as the load of pollutants in the influents, the partitioning of pollutants in each phase, and the properties of organic matter itself, such as persistence [33]. The OPFRs of the adsorbed phase were converted into ng/L, to facilitate direct comparison with the OPFRs of the dissolved phase. It was found that in this study, individual OPFRs except TPHP were mainly located in the dissolved phase, and the adsorbed phase only accounted for 9.77~29.6%. The fraction of OPFRs in the adsorbed phase was further decreased along with the treatment process. According to the results, the OPFRs were mainly dissolved in the aquatic phase, and only a small extent of OPFRs were removed by adsorbing onto the SPM in the secondary treatment stage. For TEHP, TPHP, and TMPP, which were more hydrophobic, the fractions of the adsorbed phase in the influent were high, while they were eliminated as the solid phases in the secondary effluent were removed. Therefore, the adsorption of SPM and sludge might be an important way for the removal of these OPFRs. However, the fractions of OPFRs in the adsorbed phases in the effluent for two WWTPs in Greece were still above 20% [26], and the difference might be caused by the specificity of the source and composition of the sewage and the sludge.

The removal efficiencies of OPFRs in each stage of the WWTP are shown in Figure 3. The total removal efficiency of OPFRs was 39.1% ± 9.58%, and the removal efficiencies of each OPFR were significantly different. Among them, the removal efficiencies of Aryl-OPFRs (TPHP, CDP, EHDPP, and TMPP) were all above 85%, while those of Halo-OPFRs (TCEP, TCIPP, and TDCIPP) were all negative. Alkyl-OPFRs (TIBP, TNBP, TBOEP, and TEHP) differed from each other greatly. The removal efficiency of TEHP, which had long branched chains in its molecular structure, was high, while the removal efficiencies of TNBP and TIBP were about 30%. The negative removal efficiencies of Halo-OPFRs in WWTPs have also been reported in other areas [20,26,34,35]. In this study, the fractions of Halo-OPFRs in the adsorbed phase were low, implying limited removal efficiencies by adsorption to solid. As reported, Halo-OPFRs were recalcitrant to biodegradation [25], photodegradation [6], and hydrolyzation [36]; therefore, the negative removal efficiencies of Halo-OPFRs might be associated with their resistance to transformation and formation from precursor compounds [20,25]. Additionally, Halo-OPFRs are widely used as the flame retardant and plasticizer in the plastic materials of WWTP; the Halo-OPFRs might be released during the treatment process, resulting in a higher effluent concentration [25,37,38]. However, as the pollutant concentrations of influent may vary greatly within a day, the negative removal efficiency might also be attributed to the imperfect sampling schemes [26].

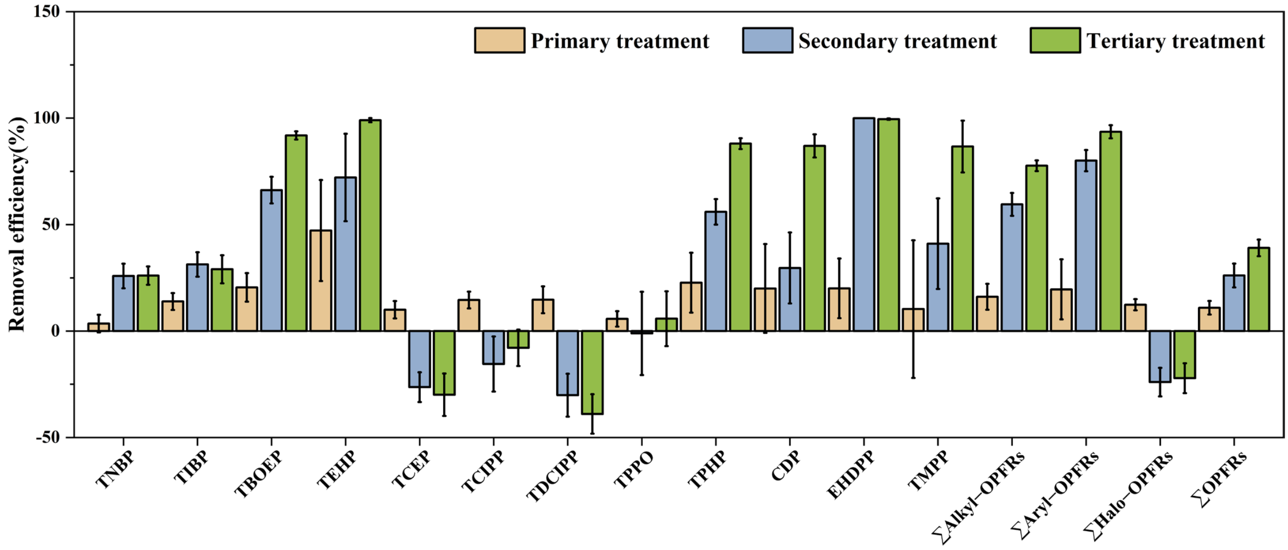

**Figure 3.** Removal efficiencies of OPFRs in different stages of WWTP.

Comparing the removal efficiencies of different stages of the wastewater treatment process, the removal of most OPFRs (especially Aryl-OPFRs) mainly occurred in the secondary biological treatment stage through adsorption or biodegradation. In the tertiary treatment stage, the removal frequencies of most OPFRs were further increased. As Alkyl-OPFRs are considered to be photostable without absorption bands at 200 to 400 nm [39], the increase in the removal frequency of TEHP at this process stage might be caused by adsorption and interception at the high-efficient sedimentation tank and deep-bed filter.

### 3.3. Mass Balance Analysis

Mass balance analysis is an effective way to investigate the removal mechanism of OPFRs in WWTPs and can reflect the true trend of OPFRs in WWTPs. The influent and effluent mass loads of OPFRs in the WWTP were calculated (Figure 4). The influent load ($M_{influent}$) was used as the system input, while the system output included effluent ($M_{effluent}$), dehydrated sludge ($M_{sludge}$), traditional treatment process (primary and secondary treatment) losses ($M_{loss\text{-}TT}$), and tertiary treatment losses ($M_{loss\text{-}AT}$).

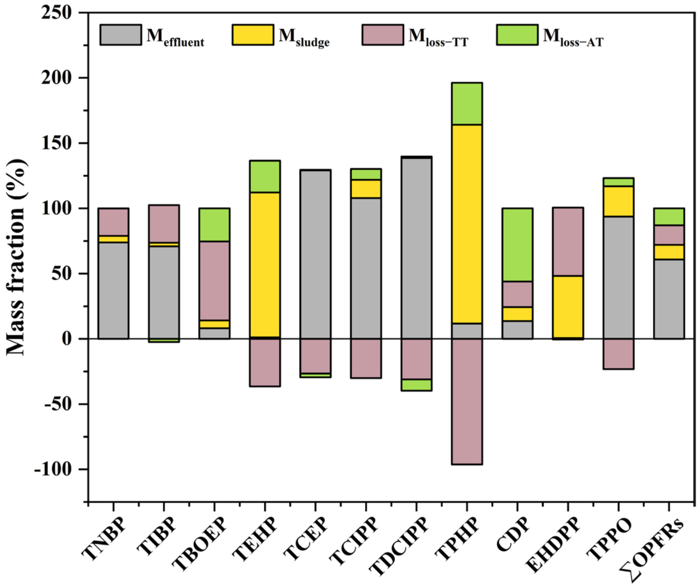

**Figure 4.** Mass balance analysis of OPFRs between effluent, sludge, and loss during the studied WWTP.

The mass fraction of ∑OPFRs in the final effluent of the WWTP accounted for 60.9 ± 8.96% of the $M_{influent}$, and only 11.2 ± 3.68% of the total load was transferred into the sludge. Mass loads lost in the traditional treatment process and tertiary treatment process were 14.9 ± 13.4% and 13.0 ± 11.2%, respectively. Most OPFRs, especially Halo-OPFRs, were not effectively removed in the wastewater treatment process and were discharged into the environmental water body. The removal processes of TNBP, TIBP, TBOEP, and EHDPP mainly occurred in traditional processes, indicating that biodegradation/biotransformation played an important role in this process. Most TEHP and TPHP and a portion of EHDPP were transferred to the sludge, indicating that they are mainly removed by adsorption. Except for CDP, other OPFRs had limited removal effectiveness in the tertiary treatment stage. In addition, TMPP was detected in large quantities in sludge and limited in influent water, which may be due to the instantaneous sampling method, which could not detect real-time changes in concentration and hydraulic retention time during treatment [26].

### 3.4. Mass Loadings and Environmental Emissions

The per capita daily OPFR pollution mass loadings and environmental emissions were calculated based on the total concentrations of OPFRs in the dissolved phase of sewage, the adsorbed phase on suspended particulate matter, and the sludge.

As shown in Figure 5, the daily pollution mass loadings of each OPFR in the WWTP involved in this study ranged from 0.67 to 291 µg/d/person. TBOEP (290 ± 67.7 µg/d/person), TCEP (85.9 ± 41.1 µg/d/person), TCIPP (83.9 ± 27.5 µg/d/person), and TPPO (64.7 ± 19.7 µg/d/person) were the main pollutants. The higher mass loadings of these pollutants might be related to their higher yields [20]. The per capita environmental emissions ranged from 0.57 to 107 µg/d/person, with the highest emission of TCEP (107 ± 45.1 µg/d/person). It was followed by TCIPP (101 ± 32.7 µg/d/person), TPPO

(70.7 ± 19.0 μg/d/person), and TDCIPP (50.6 ± 11.4 μg/d/person). Although TBOEP was in a high concentration level in the influent, its environmental emissions were reduced to 40.3 ± 15.5 μg/d/person due to the effective removal in the WWTP.

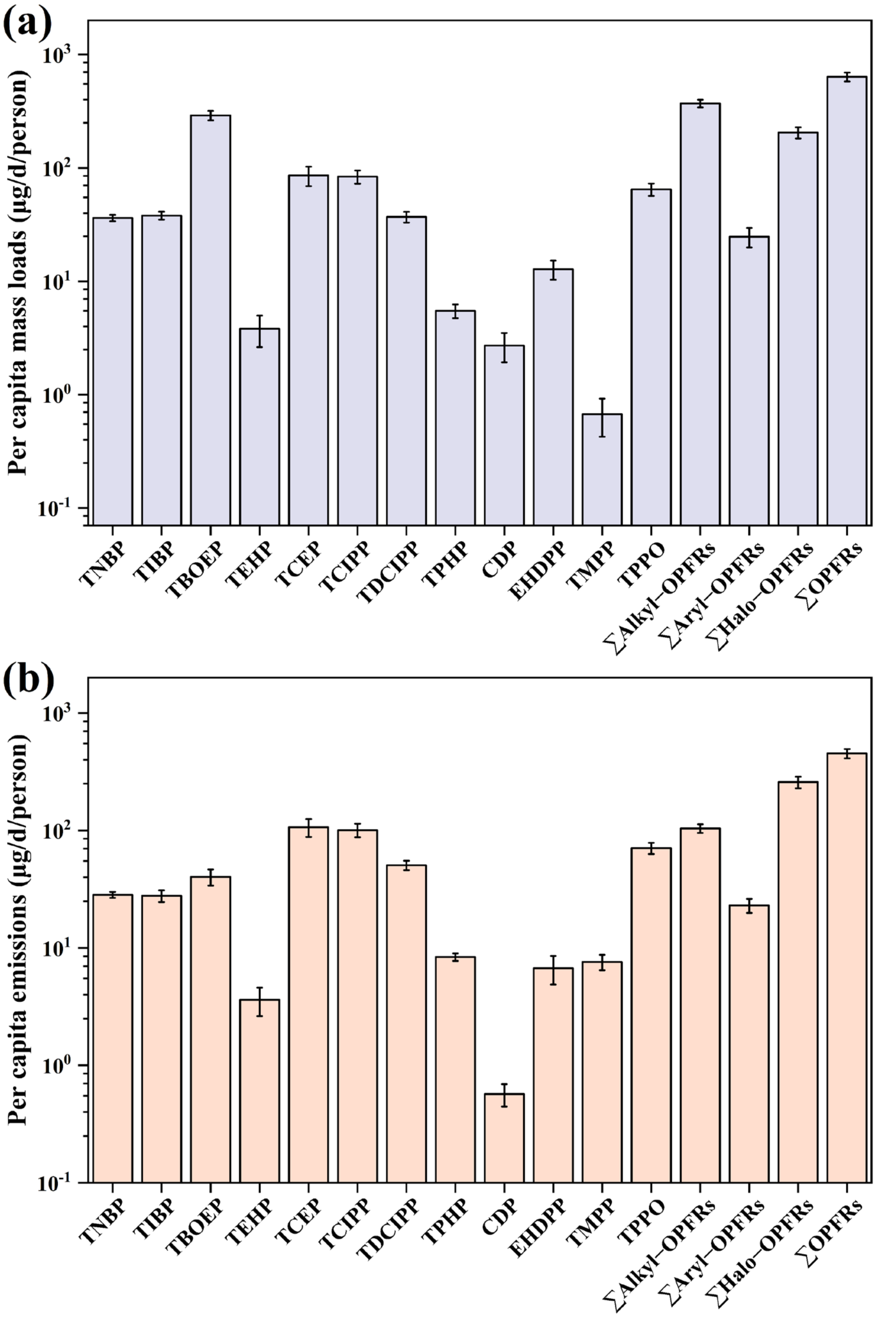

**Figure 5.** (**a**,**b**) Mass loadings and environmental emissions of the OPFRs in the studied WWTP.

Few literatures have paid attention to the pollution mass loadings and environmental emissions of OPFRs in WWTPs. According to reports, the pollution mass loadings of OPFRs in this study were lower than those in other areas. A study on two sewage treatment plants in Greece showed that the pollution mass loadings of individual OPFRs in this area ranged from 20 μg/d/person (tripropyl phosphate, TPP) to 540 μg/d/person (TBOEP) [26]. The mass loadings of sewage plants in Australia and the United States could reach 850~2860 μg/d/person and 20~28,700 μg/d/person, respectively [20,40].

Compared with other regions, the average daily environmental emissions of OPFRs per capita in this study were also at a low level. The emissions of total OPFRs were

2100 μg/d/person, which takes into account only the content in the dissolved phase [40]. Kim estimated the environmental emissions of a sewage plant in the United States [20]. The average daily emissions of TCIPP in the WWTP were the highest at 5120 μg/d/person, followed by TBOEP (3720 μg/d/person) and TDCIPP (2890 μg/d/person), which were much higher than the results of this study.

### *3.5. Ecological Risk Assessment*

Figure 6 shows the potential ecological risks of effluent from the studied WWTP. Four levels of ecological risk could be identified based on the RQ values: $RQ \leq 0.1$, no risk; $0.1 < RQ \leq 1$, medium risk; $RQ > 1$, high risk [41].

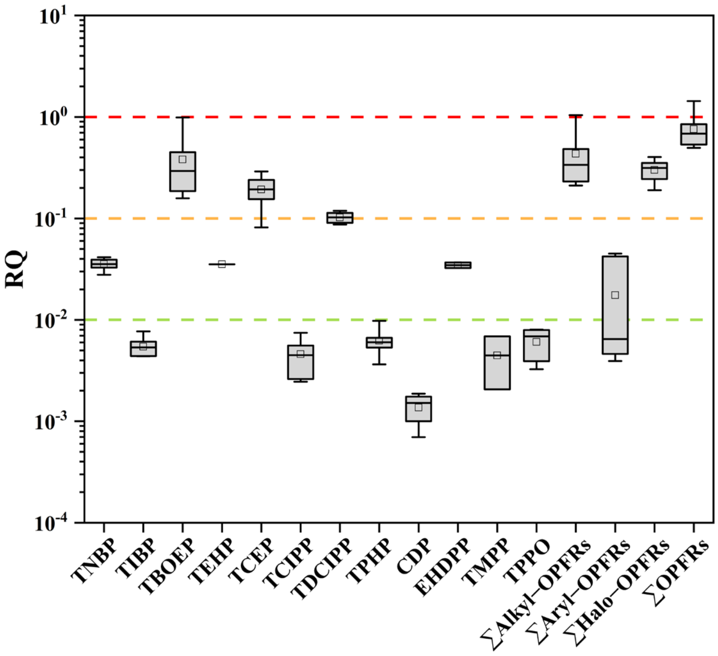

**Figure 6.** Estimated RQ values of individual and total OPFRs from the effluent. Squares (□) represent mean values. The dash lines in red, yellow, and green are located at values of 1.0, 0.1, and 0.01 for RQ, respectively.

The majority of individual OPFRs posed no to low ecological risk. TBOEP, TCEP, and TDCIPP required special attention due to their medium ecological risks. The mixed ecological risk ($RQ_{mix}$) of 12 OPFRs was close to the boundary of $RQ = 1$, indicating that there might be ecological threats. As a result, it is necessary to pay attention to the ecological security of the receiving river's water environment, especially during the dry season when the dilution effect of the river is further diminished.

## 4. Conclusions

Twelve common OPFRs were universally detected in both the dissolved phase and adsorbed phase in the studied WWTP. The mean concentration ranges were 1.47~661 ng/L (dissolved phase) in the influent, 0.14~232 ng/L (dissolved phase) in the effluent, and nd~83.0 ng/g dw adsorbed onto the sludge, which were all at relatively low levels compared to other reports. TBOEP and TCIPP were the most abundant individual OPFRs. The distribution and partitioning of individual OPFRs were significantly different, and was associated with their physicochemical properties. The removal efficiency of the total OPFRs was 39.1%, and Halo-OPFRs present a negative removal efficiency. The removal of OPFRs in the wastewater treatment could be attributed to biodegradation/biotransformation, adsorption onto the sludge, and physical adsorption in the tertiary treatment stage. Mass loadings and environmental emissions were 0.67~291 μg/d/person and 0.57~107 μg/d/person, respectively. The effluent of the studied WWTP might cause an ecological risk to the receiving river.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16111462/s1, Table S1: physicochemical information of the target OPFRs; Table S2: LC conditions for the target OPFRs; Table S3: the retention times and optimized MS/MS transitions of target OPFRs; Table S4: linearity, limits of quantitation (LOQs), and validated analytical method of target OPFRs; Table S5: matrix effects and recoveries (%, n = 5) of target OPFRs.; Table S6: the water quality parameters in the influent and effluent water; Table S7: predicted no-effective concentration (PNEC) based on effective concentration 50 or lethal concentration 50 (EC50 or LC50); Table S8: occurrence of target OPFRs in the dissolved phase of influent and effluent; Table S9: occurrence of target OPFRs in the adsorbed phase of influent, effluent, and sludge; Table S10: the occurrence of OPFRs in influent (ng/L), effluent (ng/L), and sludge (ng/g dw) from WWTP around the world. References [42–48] are cited in the Supplementary Materials.

**Author Contributions:** Conceptualization, Y.L. and H.L.; methodology, Y.L. and Y.S.; investigation, Y.L. and Y.S.; writing—original draft preparation, Y.L.; writing—review and editing, Y.L. and H.L.; visualization, Y.L.; project administration, Z.Y.; funding acquisition, Z.Y. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Special Fund for Agro-scientific Research in the Public Interest of China, No. 201503108 and the Hydraulic Science & Technology Project of Hunan Province (2017-230-13).

**Data Availability Statement:** Data are contained within the article and Supplementary Materials.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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