Understanding the distribution, degradation and fate of organophosphate esters in an advanced municipal sewage treatment plant based on mass flow and mass balance analysis

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HIGHLIGHTS

- Mass flow and mass balance are used to study the behaviors and fate of OPEs in STP
- Activated sludge system plays an effective role in removing OPEs from raw sewage
- The behavior and fate of individual OPE showed a polarity-specific feature.
- Sorption of OPEs to suspended solids was resulted from hydrophobic interactions
- OPE degradation in activated sludge system is more relevant to molecular structure

GRAPHICAL ABSTRACT

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ABSTRACT

Although organophosphate esters (OPEs) in the ambient environment are from sewage treatment plants due to the discharge of effluent and application of sludge, the distribution, degradation and fate of OPEs in advanced municipal sewage treatment plants remain unclear. This work focused on the use of mass flow and mass balance analysis to understand the behaviors and fate of 14 OPEs in an advanced municipal sewage treatment plant. OPEs were detected in all sewage water and sludge samples with total OPEs (Σ OPEs) concentrations of 1399 ± 263 ng/L in raw sewage aqueous phase, 833 ± 175 ng/L in tertiary effluent aqueous phase, and 315 ± 89 ng/g dry weight in dewatered sludge. The dissolved concentrations of Σ OPEs significantly decreased during biological treatment, whereas negligible decrease was observed in mechanical and physical-chemical treatments. For individual OPE, the chlorinated tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloroisopropyl) phosphate (TCPP) did not decrease but increased during both biological treatment and physical-chemical treatment. Mass flow analysis indicated the total removal efficiency of Σ OPEs in aqueous phase was 40.5%, and the polarity-specific removal efficiencies for individual OPE were positively related to their solid-water partition coefficients (K_d). Furthermore, mass balance results showed that 53.1% and 6.3% of the initial OPE mass flow were eventually transferred to the effluents and dewatered sludge, respectively, while the remaining 39.9% and 0.7% were lost due to biodegradation and physical-chemical treatment, respectively. It was indicated that the

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activated sludge treatment system with anaerobic/anoxic/aerobic bioreactors was a major factor in the removal of OPEs from the raw sewage, while transfer to dewatered sludge governed by hydrophobic interactions was limited during the sewage treatment. Meanwhile, the degradation difference of OPEs in activated sludge treatment was more related with their molecular structure over their hydrophobicity.

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1. Introduction

Organophosphate esters (OPEs), one of the most commonly used organophosphorus flame retardants (OPFR) (van der Veen and de Boer, 2012), have been applied as flame retardant and plasticizer in plastics, electronic equipment, furniture, textiles, construction and transportation all over the world (Marklund et al., 2003; Reemtsma et al., 2008; Wang et al., 2010). Owing to the ban of some polybrominated diphenyl esters (Leung et al., 2007), the global consumption of alternative OPFR is under a rapid increase, up to 292,000 metric tons in 2011 from 198,000 metric tons in 2007 (Retardants-Online).

Along with their widespread production and application, OPEs can be slowly released into the environment by volatilization, leaching and abrasion (Sundkvist et al., 2010). As a result, they are now widely present in various environmental matrices worldwide, including water (Wang et al., 2011; Rodil et al., 2005; Marklund et al., 2005), soil (Fries and Mihajlovic, 2011; Mihajlovic et al., 2011), air (Moller et al., 2011; Moller et al., 2012), sediment (Cristale and Lacorte, 2013) and biota (Kim et al., 2011). Moreover, OPEs have already been detected in human milk (Sundkvist et al., 2010) and their metabolites were also found in human urine (van den Eede et al., 2013; Reemtsma et al., 2011; Schindler et al., 2009). However, due to the main toxic effects including eye and skin irritation, carcinogenicity, dermatitis, and neurotoxicity (Moller et al., 2012; van den Eede et al., 2012), OPEs were reported to show potential risk to human health. Given that, the frequent detection in environment and underlying threat for human health of OPEs call for insight studies on their transfer, transformation and fate in the environment.

At the same time, sewage water and sludge are the important media for OPEs to enter various environmental matrices. OPEs can directly get into the aquatic environment along with the sewage effluent (Fries and Puttmann, 2003), and enter the soil when the dewatered sludge are used as fertilizer in agriculture (Bester, 2005), resulting in water and

soil contamination gradually. Therefore, the elimination of OPEs in sewage treatment plants (STPs) plays an important role in their pollution control.

Current studies mainly focused on the detection of OPEs in sewage water (Rodil et al., 2005; Garcia-Lopez et al., 2008; Martinez-Carballo et al., 2007; Ellis et al., 2007; Rodriguez et al., 2006; Quintana and Reemtsma, 2006) and sludge (Bester, 2005; Chen and Bester, 2009; Zeng et al., 2014), as well as the elimination of OPEs from sewage water (Marklund et al., 2005; Meyer and Bester, 2004). Research conducted at STPs in Germany (Meyer and Bester, 2004) and Sweden (Marklund et al., 2005) showed great removal difference for various OPEs (Table 1) in aqueous phase during sewage treatment: chlorinated alkyl OPEs showed no obvious elimination, while alkyl OPEs (TMP, TnBP, TPhP and TBEP in Table 1) showed an elimination in the range of 20–100%. However, the elimination of individual OPE is dependent on the properties of specific OPE species and STPs. While the mean elimination of TBEP in Sweden STPs (23%) was much lower than that in German STPs (~90%), the mean elimination of TnBP in Sweden STPs (~85%) was higher than that in German STPs (~60%). Furthermore, it should be highlighted that the concentration of chlorinated OPEs (TCEP and TCPP) in sewage effluent water was higher than that in raw sewage water in both studies. Accordingly, understanding the elimination and behavior of individual OPE during the sewage treatment is of great importance for reducing their underlying environmental and ecological risk.

Few studies focusing on the elimination of OPEs during sewage treatment have been reported. Meyer and Bester examined the effect of filter tank and the combined effect of aeration tank and sedimentation tank in sewage treatment (Meyer and Bester, 2004). Marklund et al. studied the fate of OPEs during sewage treatment based on an estimated mass balance calculation (Marklund et al., 2005). For an advanced sewage treatment plant with typical sewage treatment procedures including primary treatment (screen, grit chamber and primary sedimentation), secondary treatment (activated sludge or biofilm

Table 1

Total mass flow loss percentage of OPEs (sum of dissolved and adsorbed) at different treatment units based on the mass flow in the inflow and outflow of individual treatment unit.

OPEs	Abbreviation	Traditional treatment (%)					Advanced treatment (%)			
		Anaerobic ^a	Anoxic	Oxic	Sec. Sdm. ^b	ΣTT ^c	Ultrafiltration	Ozonation	Chlorination	ΣAT ^d
Trimethyl phosphate	TMP	–11	–8.2	13	12	23	1.3	27	–23	11
Triethyl phosphate	TEP	2.5	5.1	0.2	6.8	22	14	–8.5	3.7	11
Tris(2-chloroethyl) phosphate	TCEP	14	16	–16	–41	–19	–6.6	–5.6	2.8	–9.4
Tri-n-propyl phosphate	TPrP	–	–	–	–	–	–	–	–	–
Tris(2-chloroisopropyl) phosphate	TCPP	19	35	–64	–5.7	–39	7.4	–12	–1.1	–4.6
Tris(2-chloro-1-(chloromethyl)ethyl) phosphate	TDCEP	–30	17	–14	21	39	12	–5.7	–21	–12
Triphenyl phosphate	TiBP	31	2.5	–12	–23	–7.4	30	–37	52	54
Triisobutyl phosphate	TiBP	12	12	–7.9	–16	29	44	–56	79	82
Tri-n-butyl phosphate	TnBP	–23	–10	16	28	71	–67	–30	52	–3.3
Cresyl diphenyl phosphate	CDPP	–	–	–	–	–	–	–	–	–
Tri(2-butoxyethyl) phosphate	TBEP	–57	26	27	1.5	90	–112	18	48	9.5
Tri-3-cresyl phosphate	TCrP	–8.3	27	–33	3.9	61	50	69	80	97
2-Ethylhexyl diphenyl phosphate	EHDPP	–24	18	–0.5	–24	64	100	–	–	–3.7
Tri(2-ethylhexyl) phosphate	TEHP	–39	5.4	15	–23	–3.1	–	–	–	–
Total OPEs	Σ OPEs	–11	21	–13	–6.0	40	–2.2	–5.8	11	3.4

– = data not available.

^a Mass flow loss percentage of anaerobic unit was calculated ignoring the mass flow in the supernatant of excess sludge which was negligible comparing to the mass flow of primary effluent and return sludge, considering the supernatant of excess sludge was not accessible for sampling.

^b Secondary sedimentation.

^c Total mass flow loss percentage of OPEs in traditional treatment.

^d Total mass flow loss percentage of OPEs in advanced treatment.

process), and tertiary treatment (ultrafiltration, ozonation, chlorination and ultraviolet disinfection), it is still unknown which process plays a key role in the elimination of OPEs during sewage treatment.

In this study, we try to gain insights into the behavior and fate of OPEs in the typical municipal STP. We analyzed the OPE concentration in sewage water and sludge samples, collected along the whole sewage treatment process in an advanced municipal STP with anaerobic/anoxic/aerobic (A/A/O) bioreactors as the core treatment units. More importantly, mass flow and mass balance analysis were performed to understand the transport and the potential removal mechanisms of these compounds inside the treatment units.

2. Materials and methods

2.1. Flow scheme of sewage treatment plant

The STP investigated in this work serves approximately 814,000 people in Beijing, China, with a total sewage treatment capability of 400,000 m³/day, which is mainly from domestic sources. The flow scheme of the STP is shown in Fig. 1. The raw sewage first passes through a screen and an aerated grit chamber successively. The primary sludge was pumped into the dehydrating house, while the primary effluent was directed to the activated sludge system, which is comprised of the anaerobic/anoxic/aerobic (A/A/O) bioreactors. After a secondary clarification step, 60% of the secondary effluent is directly discharged to a receiving river, while the other 40% of the secondary effluent was then pumped to an advanced tertiary treatment system including ultrafiltration, ozonation, and chlorination processes. After the advanced treatment, the tertiary effluent is used as irrigation water and landscape water. The hydraulic retention times in anaerobic tank, anoxic tank, aerobic tank and secondary sedimentation tank were 1.5, 3, 10.8, and 8 h, respectively, and the total solid retention time was about 20–25 days. After settling in the secondary clarifier, most of the activated sludge was returned to the anaerobic bioreactor, and the rest as excess sludge was conveyed to be dehydrated. After that, the dewatered sludge was carried away for final disposal.

2.2. Sample collection and pretreatment

To investigate the behavior and fate of OPEs in this STP, sampling was carried out along sewage treatment process under normal dry weather conditions on March 24, 25, 26, 2014, respectively. The

sampling locations in the STP are also shown in Fig. 1. All samples were taken at the outlet of every treatment step including aerated grit chamber, anaerobic tank, anoxic tank, aerobic tank, secondary sedimentation tank, ultrafiltration tank, ozonation tank and chlorination tank. Meanwhile, internal recirculation sludge from aerobic tank to anoxic tank, returned sludge from secondary sedimentation tank to anaerobic tank, excess sludge and dewatered sludge were also sampled, but raw sludge from aerated grit chamber and supernatant of excess sludge were not collected as they were inaccessible for sampling. All the samples were consisted of aqueous phase (water) and solid phase (suspended solid particles), except dewatered sludge, ultrafiltration effluent, ozonation effluent and the tertiary effluent. Single 24 h composite water samples of raw sewage and primary, secondary and tertiary effluents were collected by using automatic samplers at a sampling interval of 2 h. Other solid–liquid and dewatered sludge samples were obtained as time-proportional 24 h composite samples by combining four grab samples collected four times a day with sampling interval of 6 h. During the sampling period, the sewage influent to the STP kept around 200,000 m³/day. The water flow at each treatment unit and several regularly measured parameters (e.g., pH, DOC and TOC) are shown in Supporting information (Table S1).

All samples, except for dewatered sludge, ultrafiltration effluent, ozonation effluent and the tertiary effluent, were immediately separated to the aqueous phase (water) and solid phase (suspended solids) by centrifugation at 10,397 g for 7 min (3–18K centrifuge, Sigma, Germany) after sampling. Before analysis, aqueous samples were filtered through a 1.2 mm glass microfiber membrane GF/C (Whatman, Maidstone, UK) and stored at 4 °C; while suspended solids were frozen within hours and further freeze-dried, then ground before sifting through a sieve with 100 meshes, and finally stored at –20 °C in refrigerator. The OPEs in aqueous samples were analyzed according to the method reported in our previous paper (Liang et al., 2014), while those in suspended solids were determined by a method developed in this work. Briefly, for aqueous phase, the analytes were extracted from 100 mL filtered aqueous samples onto HLB cartridges (6 mL, 200 mg, Waters, Milford, USA), and eluted by 6 mL acetonitrile, then the extracts were concentrated to near dryness and redissolved in 1 mL of acetonitrile/water (40:60, v/v) before determination. For solid phase, the analytes were extracted from 0.5 g freeze-dried suspended solids onto Florisil cartridges (3 mL, 500 mg, Supelco, Bellefonte, USA), and eluted by 8 mL dichloromethane, then the extracts were concentrated to dryness and redissolved in 1 mL of acetonitrile/water (40:60, v/v) before

Fig. 1. Flow scheme and the total massflows (g/day) of detected organophosphate esters (OPEs) in the investigated municipal sewage treatment plant (STP), and mass fraction emitted by the plant in effluents and dewatered sludge relative to the total initial mass flow (100%) of raw sewage.

determination. Details about sample extraction and cleanup procedures of OPEs are given in Supporting information.

2.3. Chemical analysis

Using a UPLC apparatus (Acquity Ultra Performance LC, Waters, Milford, MA), 14 targeted OPEs were separated using a Waters Acquity UPLC BEH C18 column (100 × 2.1 mm, 1.7 μm particle size). The mobile phase was a mixture of 0.1% (v/v) formic acid in ultrapure water (A) and acetonitrile (B) with a flow rate of 0.2 mL/min under gradient conditions: 0 min, 40% B; 0.5 min, 40% B; 3 min, 50% B; 4.5 min, 55% B; 8.5 min, 70% B; 9 min, 100% B; 13.8 min, 100% B; 13.9 min, 40% B; and 15.5 min, 40% B. The injection volume was 10 μL and the column was maintained at 40 °C. Mass spectrometry determination was performed using a TSQ Quantum Access triple quadrupole mass spectrometer (Thermo Scientific, Waltham, MA) equipped with an electrospray ionization (ESI) source. The ESI was operated in the positive ion mode, and best conditions were set as follows: spray voltage of 4000 V, and capillary temperature of 300 °C. Nitrogen was used as the sheath gas (35 units) and aux gas (15 units). Argon was used as the collision gas at a pressure of 0.2 Pa. Detailed information on instrumental analysis can be found in our previous work (Liang et al., 2014).

2.4. Quantification and quality control

Method accuracy was evaluated by the recoveries of target analytes in aqueous samples and suspended solids, and the method precision was assessed by relative standard deviation (RSD). To correct the losses of analytes during extraction or sample preparation, and compensate for variations in instrument response from injection to injection, deuterated standards TMP-d9, TEP-d15, TPrP-d21 and TPhP-d15 were used as surrogate standards for TMP, TEP, TPrP and TPhP, respectively, while TnBP-d27 was for the other 10 OPEs. Spiked recoveries were determined by spiking at least three times the original concentration of standard OPEs into aqueous samples and solid samples. Quality control samples, consisting of spiked raw sewage aqueous sample, tertiary effluent water, and suspended solids collected from excess sludge, produced recoveries of 52.0–119%, 43.6–114% and 33.0–114%, respectively. The limits of method detection (mLODs) for the target OPEs, defined as the minimum concentrations of compounds that could be measured (Table S2), ranged from 0.57 to 6.6 ng/g in the suspended solid samples, and from 0.30 to 5.7 ng/L in aqueous samples. Details of method performance are present in Supporting information (Table S2). For each set of samples at least one procedure blank and one independent check standard were run in sequence to check the background contamination and system performance.

2.5. Mass balance calculation

Mass balance was calculated by multiplying concentration of OPEs by average daily flow rates as shown in Eq. (1):

$$W = C_{\text{dissolved}} \times Q + C_{\text{adsorbed}} \times Q \times C_{\text{TSS}} \quad (1)$$

where W (g/d) is the total mass flow of OPEs dissolved in aqueous phase and adsorbed to solid phase; $C_{\text{dissolved}}$ and C_{adsorbed} represent the dissolved (ng/L) and adsorbed (μg/g) concentrations, respectively; Q is water flow (m³/day); and C_{TSS} represents the content of total suspended solids (mg/L).

The mass flow loss of OPEs in individual treatment unit and mass flow loss percentage (removal efficiency) was calculated using Eq. (2) and Eq. (3), respectively:

$$W_{\text{loss}} = W_{\text{inflow}} - W_{\text{outflow}} \quad (2)$$

$$(W_{\text{inflow}} - W_{\text{outflow}}) / W_{\text{inflow}} \times 100\% \quad (3)$$

where W_{inflow} and W_{outflow} represent the mass flow of OPEs in the inflow and outflow of individual treatment unit, respectively.

In order to assess the contribution of sorption and degradation of OPEs in the STP, the mass flow loss of OPEs owing to sum of all transformation processes during traditional treatment ($W_{\text{loss-TT}}$, including primary and secondary treatment) and advanced treatment process ($W_{\text{loss-AT}}$, tertiary treatment) was calculated using Eq. (4) and Eq. (5), respectively:

$$W_{\text{loss-TT}} = W_{\text{raw}} - W_{\text{sec. eff.}} - W_{\text{sludge}} \quad (4)$$

$$W_{\text{loss-AT}} = 0.4 \times W_{\text{sec. eff.}} - W_{\text{ter. eff.}} \quad (5)$$

where W_{raw} , $W_{\text{sec. eff.}}$ and $W_{\text{ter. eff.}}$ represent the mass flow of OPEs in raw sewage, secondary effluent and tertiary effluent (g/day), respectively; W_{sludge} is the mass output of OPEs in dehydrated sludge (g/day).

3. Results and discussion

3.1. Concentrations of OPEs in sewage water and sludge along treatment process

OPEs were detected in either aqueous phase (dissolved, ng/L) or solid phase (adsorbed, ng/g d.w., d.w. refers to dry weight) of all samples collected through the STP. All the 14 target OPEs, except for TPrP, CDPP and TEHP, were detected in aqueous phase samples from the STP (Table S3). In raw sewage aqueous phase, TBEP (600 ± 173 ng/L), TCP (225 ± 23 ng/L) and TCEP (179 ± 27 ng/L) were the dominant OPEs, accounting for 42.9 ± 12.4%, 16.1 ± 1.7%, 12.8 ± 1.9% of total concentrations, respectively (Fig. 2). Relatively low concentrations were detected in raw sewage aqueous phase for TEP (114 ± 54 ng/L), TMP (99 ± 20 ng/L), TnBP (74 ± 12 ng/L), TiBP (45 ± 18 ng/L), TDCP (23 ± 2 ng/L), TPhP (21 ± 5 ng/L), TCrP (9 ± 5 ng/L) and EHDPP (14 ± 1 ng/L). Of all the target compounds in this study, the predominance of TBEP, TCP and TCEP were also observed in STP wastewater in most developed countries including Spain (Rodriguez et al., 2006; Quintana and Reemtsma, 2006; Garcia-Lopez et al., 2010), Germany (Rodil et al., 2005; Meyer and Bester, 2004), Austria (Martinez-Carballo et al., 2007) and Sweden (Marklund et al., 2005) (Table 2). In the present study, raw sewage aqueous phase concentrations of TBEP, TCP and TCEP were lower than those in surface water in Beijing: 10–740 ng/L TBEP, 145–1359 ng/L TCP, and 88.4–2918 ng/L TCEP (Gao et al., 2015), which may result from the separation of rain and sewage considering that rainwash can directly bring a plenty of OPEs from soil, dust and airborne particles into the river. Meanwhile, the raw sewage aqueous phase concentrations of these three OPEs were lower than those in most developed countries (Table 2), e.g. 680–3100 ng/L TBEP and 290–540 ng/L TCP in Spain (Garcia-Lopez et al., 2010); 5200–35,000 ng/L TBEP, 1100–18,000 ng/L TCP and 90–1000 ng/L TCEP in Sweden (Marklund et al., 2005); and 3700–8000 ng/L TBEP, 650–5800 ng/L TCP and 180–640 ng/L TCEP in Germany (Meyer and Bester, 2004). Such a profile of OPEs in this STP is in accordance with the low consumption of these compounds in China compared with other countries. It was documented that the consumption of OPFRs in China was only 7% that of global consumption in 2008, while the percentages of Europe and the United States were almost 40% and 35%, respectively (Posner, 2011). The total removal efficiencies of individual OPE in sewage water ranged from –50.6% (TCP) to 95.2% (TCrP) (Table 2). In tertiary effluent water, TCP and TCEP, which showed no significant removal during the secondary treatment and tertiary treatment, were the dominant OPEs.

In the suspended solids and dewatered sludge samples, of all the 14 OPEs only TMP, TEP, TPrP and CDPP were not detected, i.e., the concentration of TEP was lower than that of procedural blank, while the concentrations of TMP, TPrP and CDPP were below the lower detection limit of method. The suspended particles in raw sewage showed the

Fig. 2. Concentrations of OPEs in aqueous phase of raw sewage water, secondary effluent and tertiary effluent, and that in solid phase of raw sewage sludge and dewatered sludge.

highest levels of OPEs, with total adsorbed concentration up to 553 ± 80 ng/g, which was almost 2-fold higher than those of activated sludge in bioreactors. The adsorbed concentrations of OPEs in activated sludge along anaerobic/anoxic/aerobic (A/A/O) treatment units showed a slight decrease trend, which was from 337 ± 147 to 257 ± 33 ng/g d.w. Both the return sludge and excess sludge showed a comparable concentration to that of activated sludge in aerobic tank. The measured adsorbed concentrations of OPEs in various types of sludge were similar, mainly because a large amount of activated sludge was constantly cycled as internal recirculation and return sludge in the STP. The concentration of OPEs in dewatered sludge was 315 ± 89 ng/g d.w., which was equivalent to or slightly higher than those in activated sludge. The adsorbed concentrations of $\sum$ OPEs (214 – 553 ng/g d.w.) in the present study were higher than those of domestic wastewater in the Pearl River Delta, China (101 – 290 ng/g d.w.) (Zeng et al., 2014), but were lower than those of developed countries (620 – 6900 ng/g d.w. in Sweden, and 1000 – $20,000$ ng/g d.w. in Germany) (Marklund et al., 2005; Bester, 2005; Chen and Bester, 2009).

3.2. Mass flow analysis of OPEs during wastewater treatment

To better understand the behavior like partitioning, mass flow and transfer of OPEs in STP, the calculated mass flows of $\sum$ OPEs in aqueous and solid phases through the whole sewage treatment process were presented in Fig. 1. Based on Fig. 1 and the mass flows of individual OPE (Table S4 and Table S5), we further analyzed mass flow loss percentages in the four basic treatment units and three advanced treatment units to assess their contributions and potential mechanism in removal of OPEs in the STP (Table 1).

In raw sewage, the mass flow of $\sum$ OPEs combined aqueous and solid phase was about 320 g/day in this STP, i.e. 280 and 40 g/day in the dissolved and adsorbed phase, respectively. The mass losses rate of OPEs across the aerated grit chamber was not available because of the absence of sample in raw sludge. After the aerated grit chamber, 304 g/day $\sum$ OPEs remaining in primary effluent entered secondary activated sludge system. The mass flow of aqueous phase in primary effluent and raw sewage were very similar, while the mass flow of suspended solids in primary effluent was 47.0% less than that in raw

sewage (Table S6). This might be caused by the transfer of OPEs to raw sludge along with the suspended solids from raw sewage, in view of a 23.6% mass reduction (Table S6). As a result, the total mass flow of hydrophobic OPEs, mainly distributed in sludge, were largely decreased after primary treatment, e.g. TiBP 68% , TnBP 93% , TPhP 26% , TBEP 39% , TCrP 43% , EHDPP 60% and TEHP 27% (Table S6).

In the activated sludge treatment system, the mass flows in both aqueous and solid phase through the anaerobic and anoxic tanks significantly increased, which was mainly resulted from the large quantity recycling of activated sludge with high mass flow of OPEs from the return sludge and internal recirculation sludge. It was worth noting that the solid phase mass flow percent of anaerobic tank increased to 52% from 7% in primary effluent, which was owing to the incoming of return sludge with a high solid phase mass flow percentage of 69% (Table S4). Within the A/A/O treatment, the total mass flow loss percentages combined aqueous phase with solid phase were -11% , 21% , and -13% in anaerobic, anoxic, and aerobic treatment units, respectively (Table 1). The efficiency of anoxic treatment was better than that of anaerobic and aerobic treatment. The mass flow loss percentages in aqueous and solid phases were individually 39% and 7% through the secondary treatment units (Table S7).

For the secondary effluent, the aqueous-phase mass flow of OPEs were 172 ± 40 g/day, accounting for 53.8% of initial raw sewage mass flow, while the adsorbed part was negligible owing to the few content of suspended solids in secondary effluent. The traditional treatment removed about 38.4% of the initial OPEs mass flow from the aqueous phase (Table 2), indicating that, to a certain degree, the activated sludge system was effective to remove OPEs from sewage water by biosorption and biodegradation. Without further digestion, the excess sludge was then dehydrated to dewatered sludge with a total mass flow of OPEs 20 ± 3.7 g/day during the three sampling days.

For advanced treatment, the OPEs mass flow over ultrafiltration showed no remarkable decrease for the amount of suspended solids in secondary effluent was little. After the ozonation treatment, the mass flow of OPEs was slightly increased, which could be attributed to their potential variations during the three sampling days. On the contrast, the OPEs mass flow after chlorination process was slightly decreased, but the removal efficiency of OPEs by chlorination was not so noticeable.

Table 2

Comparison of measured OPEs by the current study with literature values reported in some developed countries and other regions of China.

OPEs	Log K_{OW} ^a	Log K_{OC} ^b	Current study						Spain	Germany		Austria	Sweden		China
			Influent (ng/L)	Secondary effluent (ng/L)	Tertiary effluent (ng/L)	E_{total} ^c (%)	E_{TT} ^d (%)	Raw sludge (ng/g, d.w.)	Influent ^e (ng/L)	Influent ^f (ng/L)	Sludge ^g (ng/g, d.w.)	Effluent ^h (ng/L)	Influent ⁱ (ng/L)	Sludge ⁱ (ng/g)	Sludge ⁱ (ng/g, d.w.)
TMP	−0.65	1.10	99.2	75.9	67.2	32.2	23.5	ND	NM	NM	NM	NM	0–584	NM	NM
TEP	0.80	1.68	113.8	88.3	79.0	30.6	22.4	ND	NM	NM	NM	22–210	NM	NM	NM
TCEP	1.44	2.48	179.1	213.0	232.9	−30.1	−18.9	ND	0–70	290–640	70	0–1600	90–1000	6.6–110	NM
TPrP	1.87	2.83	ND	ND	ND	–	–	ND	NM	NM	NM	NM	ND	NM	NM
TCPP	2.59	2.71	225.0	324.1	338.9	−50.6	−44.0	69.5	290–540	2000–5800	18,400	270–1400	1100–18,000	61–1900	7.9–35
TDCP	3.65	2.35	22.8	14.2	15.9	29.9	37.7	9.7	0–100	100–250	90	19–1400	210–450	3.0–260	12.6–64
TIBP	3.60	3.05	45.2	56.6	25.9	42.7	−25.3	26.4	39–188	840–2200	100	NM	NM	27–2700	NM
TPhP	4.59	3.72	21.3	15.9	4.4	79.4	25.5	75.0	ND	81–290	400	0–170	76–290	52–320	16–63
TnBP	4.00	3.28	74.4	28.8	29.8	59.9	61.2	100.8	0–82	260–5500	90	0–810	6600–52,000	39–780	7.1–44
CDPP	3.70	–	ND	ND	ND	–	–	ND	NM	NM	NM	NM	NM	NM	NM
TBEP	3.75	4.38	600.3	44.1	39.9	93.3	92.6	105.9	680–3100	3700–6100	NM	13–5400	5200–35,000	0–1900	26–169
TCrP	5.11	4.35	8.7	2.0	0.4	95.2	77.3	87.8	NM	NM	NM	0–55	NM	NM	3.8–14
EHDPP	6.64	–	14.0	0.8	0.9	93.9	94.1	56.7	NM	NM	NM	NM	NM	320–4600	NM
TEHP	9.49	6.87	ND	ND	ND	–	–	21.0	NM	NM	NM	ND	0–130	NM	NM
Σ OPEs			1399.0	862.4	832.9	40.5	38.4	552.7	1125.6–3994	8720–20,420	19,150	342–7777	17,000–69,000	620–6900	101–290

– = data not available; ND = not detected (below method detection limit); NM = not measured.

^a Reference: Reemtsma et al. (2008).^b Reference: van der Veen and de Boer (2012).^c Removal efficiency of total treatment.^d Removal efficiency of traditional treatment (combined of primary and secondary treatment).^e Reference: Garcia-Lopez et al. (2010).^f Reference: Meyer and Bester (2004).^g Reference: Chen and Bester (2009).^h Reference: Martinez-Carballo et al. (2007).ⁱ Reference: Marklund et al. (2005).^j Reference: Zeng et al. (2014) (domestic wastewater in the Pearl River Delta, China).

Fig. 3. Mass balance results: mass fraction (%) of detected individual OPE and total OPEs (Σ OPEs) in (i) tertiary effluents ($W_{\text{ter. eff.}}$), (ii) secondary effluent discharged into the river ($W_{\text{sec. eff. dis.}}$), (iii) dewatered sludge (W_{sludge}), (iv) loss in advanced treatment ($W_{\text{loss-AT}}$), and (v) loss in traditional treatment ($W_{\text{loss-TT}}$) relative to total initial loading (100%) in the STP.

It was suggested that, the capability of these three advanced treatment units for removing the remaining OPEs in secondary effluent, which were mainly composed of TCEP and TCPP, was limited.

3.3. Mass balance analysis of OPEs during wastewater treatment

To analyze the fate of OPEs during wastewater treatment, mass balance calculation was performed based on the mass flow through the STP (Fig. 3). Total mass flow in raw sewage, including dissolved and adsorbed phases, was taken as the system input (100%), while the system output consisted of (i) tertiary effluents, (ii) secondary effluent discharged to the river, (iii) dewatered sludge, (iv) loss in advanced treatment, and (v) loss in traditional treatment including the primary

and the secondary treatment, due to the total effect of degradation, transformation, and adsorption in each treatment unit in the STP.

The mass fraction of Σ OPEs in secondary effluent discharged to the river and tertiary effluent accounted for $32.2 \pm 2.5\%$ and $20.9 \pm 1.6\%$ of the initial loading, respectively, and only $6.3 \pm 0.3\%$ of the total amount of OPEs was transferred to dewatered sludge, while $39.9 \pm 4.4\%$ of them was lost due to biodegradation. The mass loss fraction in advanced treatment was only $0.7 \pm 0.7\%$, indicating the removal capacity of advanced treatment was negligible for OPEs with relatively high polarity (TEP, TCPP, TCEP), as most of the low polar OPEs (TBEP, TCrP, EHDPP, TEHP) were transformed or transferred during traditional treatment (Fig. 3).

For individual OPE, the behavior and fate showed a polarity-specific feature. OPEs with relatively high polarity (n -octanol–water partition coefficients, $K_{\text{OW}} < 3$), including TMP, TEP, TCEP, and TCPP, showed no significant removal during both conventional treatment and advanced treatment, given that their mass flow loss percentages in each treatment units were lower than 20%, except for that of TMP in ozonation unit (27%) and TCPP in anoxic unit (35%) (Table 1). As a result, these OPEs were mainly discharged along with the effluent. In contrast, for OPEs with medium polarity ($3 < K_{\text{OW}} \leq 4$), alkyl TnBP and TBEP were much easier to be degraded by activated sludge with a mass loss rate of 71% and 90% in secondary treatment, respectively; while most of TiBP (81%) and TDCP (56%) transferred to the effluent, except a small part of TiBP (22%) and TDCP (39%) were individually lost in advanced treatment and traditional treatment. Meanwhile, aryl OPEs with relatively lower polarity ($4.5 < K_{\text{OW}} < 7$), including TPhP, TCrP and EHDPP, were mainly degraded by microorganism (29%–64%) and adsorbed by activated sludge (35%–38%). In addition, alkyl TEHP with the lowest polarity ($K_{\text{OW}} = 9.5$) was mainly adsorbed by the activated sludge and showed no obvious biodegradation (Fig. 3).

It was noteworthy that there were negative mass fractions for several OPEs, especially for TCPP and TCEP (Fig. 3). The possible reason reported in literatures was that TCPP and TCEP included in polymeric particles of raw sewage may be released into the water phase during the sewage treatment, resulting the increased concentrations in effluent water compared to influent water (Bester, 2007). However, in present study, TCEP was not detected in solids phase of raw sewage (Fig. S2), and the mass flow of TCPP (Fig. S3) in solid phase of raw sewage (5.1

Fig. 4. Relationships of the removal efficiencies in water phase during traditional treatment ($R_{\text{water-TT}}$, %) and the dewatered sludge adsorption mass fraction ($W_{\text{dew. sludge}}$, %) with log value of apparent solid–water partition coefficients ($\log K_d$) of detected OPEs in the STP.

g/day) was almost equivalent to that of dewatered sludge (4.7 g/day), indicating the exist of other major sources rather than polymeric particles. The possible sources for the increased concentration in effluent water were plastic tubes and ultrafiltration membranes used in the treatment procedure.

3.4. Understanding the behavior and fate of OPEs during wastewater treatment

To further understand the polarity-specific behavior and fate of the individual OPE, the apparent solid–water partition coefficients (K_d) of different OPEs between solid phase and aqueous phase were calculated (Supporting information, Table S8). As shown in Fig. S1, the K_d values of detected OPEs are comparable to their K_{OW} and organic carbon partition coefficients (K_{OC}) (Reemtsma et al., 2008; van der Veen and de Boer, 2012). They significantly increased with carbon atom numbers, which was consistent with variations of polarity-specific behavior and fate in the STP. On the other hand, the K_d values of most hydrophobic OPEs also significantly increased along the anaerobic–anoxic–aerobic treatment process (Table S8), suggesting that sorption to sludge particles was an important removal mechanism for most hydrophobic OPEs.

The average log K_d values of detected OPEs (Table S8) showed a significant positive correlation with their dewatered sludge adsorption mass fraction (W_{sludge}) ($r^2 = 0.77$, $p < 0.01$, Fig. 4), suggesting that hydrophobic interactions resulted in their adsorption to suspended solids. OPEs with higher K_d values showed higher removal from the aqueous phase by activated sludge adsorption. This can explain why the average log K_d values of detected OPEs also showed a significant positive correlation with their removal efficiencies of water phase during traditional treatment ($R_{\text{water-TT}}$) ($r^2 = 0.42$, $p = 0.04$, Fig. 4).

In addition to suspended solid particles adsorption, biodegradation in activated sludge system also played an important role for the removal of OPEs in sewage (Fig. 3), but the degradation for individual OPE was very different from each other. Although hydrophobic OPEs are inclined to present in sludge where they have more opportunity to contact with zoogloea, the average log K_d values of detected OPEs presented a relatively weak correlation with the mass loss fraction in traditional treatment ($W_{\text{loss-TT}}$) ($r^2 = 0.29$, $p = 0.08$, Fig. S4), suggesting hydrophobicity was not the primary factor leading to the different degradation degree for OPEs. Nevertheless, the degradation differences of OPEs in activated sludge treatment was in accordance with some general ‘rules of thumb’ based on their structural factors (Lyman et al., 1982): (i) OPEs with short chains (TMP, TEP) were not as quickly degraded as those with long chains (TnBP, TBEP), whereas they were less resistance to biodegradation than similar OPEs with chlorinated hydrocarbon chains (TCEP and TCP); (ii) TiBP with branched hydrocarbon chains was less amenable to biodegradation compared to its unbranched isomer TnBP, while TEHP with longer branched hydrocarbon chains showed no obvious degradation; (iii) TBEP with 6C hydrocarbon chains was easier to be biodegraded than OPEs with phenyl or tolyl group (TPhP, TCrP and EHDPP); (iv) Among the three aryl OPEs, EHDPP with 2 rings was more biodegradable than the two other compounds with 3 rings (TPhP and TCrP); and (v) owing to the electron donor property of aromatic substituent methyl, the biodegradation of TCrP was largely promoted compared to TPhP.

4. Conclusion

In summary, our work provides an insight into the behavior and the fate of OPEs in an advanced municipal STP based on mass flow and mass balance analysis. Sorption to activated sludge, which was proved to be dominated by hydrophobic interactions, played an important role in sewage treatment for OPEs. Meanwhile, biodegradation behaviors of individual OPE show a structure-specific feature. Hydrophobic OPEs in raw sewage with long hydrocarbon chains and aromatic groups were largely biodegraded by activated sludge treatment and partly adsorbed

by suspended solid particles, with the remaining limited part transferring to the sewage effluent. Meanwhile, preferred to stay in water phase, hydrophilic OPEs with short non-chlorinated/chlorinated hydrocarbon chains were mostly discharged along with sewage effluent, with only a limited fraction biodegraded or transferred to the dewatered sludge during the activated sludge treatment. In this way, the different behaviors and distinct fate of individual OPE were presented in this municipal STP.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.11.112>.

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