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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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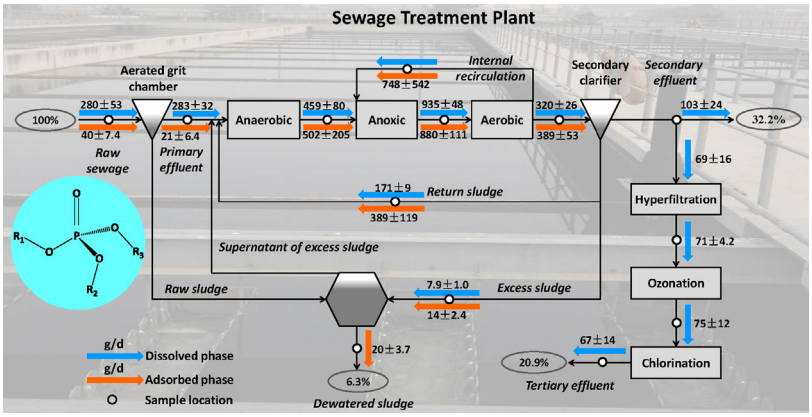
HIGHLIGHTS

- 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 (ΣOPEs) 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 ΣOPEs 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 ΣOPEs 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.

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]	∑TT[c]	Ultrafiltration	Ozonation	Chlorination	∑AT[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	TDCP	−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	TPhP	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	∑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.