Comparison of wastewater treatment processes on the removal efficiency of organophosphate esters

Long Pang, Peijie Yang, Jihong Zhao and Hongzhong Zhang

ABSTRACT

Organophosphate esters (OPs), widely used as flame retardants and plasticizers, are regarded as a class of emerging pollutants. The effluent of municipal wastewater treatment plants is generally considered to be the main contributor of OP pollution to the surface water. In this study, anoxic–oxic (AO) and University of Capetown (UCT) processes were selected to investigate the removal efficiency of OPs. The results indicated that the UCT process showed better removal efficiency than that of the AO process. For the chlorinated OPs, approximately 12.3% of tri(2-chloroethyl)phosphate and 11.8% of tri(chloropropyl)phosphate can be removed in the UCT process, which was 12% and 7.8% higher than that of the AO process. In contrast, non-chlorinated OPs, including tris(2-butoxyethyl) phosphate, triphenyl phosphate, and tributyl phosphate, were able to be removed in both processes, with the removal rate of 85.1%, 74.9%, and 29.1% in the AO process, and 88.4%, 63.6%, and 25.2% in the UCT process. Furthermore, linear correlation between the removal rate and log $K_{ow}$ of OPs ($r^2 = 0.539$) was observed in the AO process, indicating that OPs with high $K_{ow}$ value (e.g. tri(dichloropropyl)phosphate and triphenyl phosphate) are prone to be removed by adsorption on the residual activated sludge.

Key words | adsorption, organophosphate esters, removal efficiency, wastewater treatment processes

INTRODUCTION

Organophosphate esters (OPs) are extensively used as flame retardants and plasticizers. Chlorinated OPs, such as tri(2-chloroethyl)phosphate (TCEP), tri(chloropropyl)phosphate (TCP), and tri(dichloropropyl)phosphate (TDCP), are employed as flame retardants. Nonhalogenated OPs, mainly including tris(2-butoxyethyl)phosphate (TBEP), tributyl phosphate (TrBP), and triphenyl phosphate (TPhP), are widely used as plasticizers, lubricants, antifoaming agents, and additives (Andresen et al. 2004). Owing to the ban on the usage of some polybrominated diphenyl ethers, mainly including penta-BDE, octa-BDE, and deca-BDE in the European Union since 2008 (Betts 2008), the production and consumption of OPs as alternative flame retardants has been increasing worldwide. Hitherto, the production volume of some OPs already exceeds 1,000 t per year in Western Europe, and have been regarded as high-production volume chemicals (Marklund et al. 2005; Stapleton et al. 2011).

Generally, OPs are not chemically bound to the products, which would induce the release of OPs into the environment by volatilization, abrasion, and dissolution. Since OPs can remain long term in the environment (Lai et al. 2015), these compounds have been detected in the aquatic (Zeng et al. 2014; Peverly et al. 2015), terrestrial (Matsukami et al. 2015), and atmospheric environments (Mizouchi et al. 2015), and even in drinking water (Li et al. 2014), greatly increasing the exposure risk for human beings. It has been confirmed that OPs and their metabolites have already been detected in human hair, nails, and urine (Cequier et al. 2014, 2015; Liu et al. 2015). The effluent of municipal wastewater treatment plants (WWTPs) is generally believed to be the main contributor of OPs to aquatic environments (Quintana et al. 2006). The concentration of OPs detected in the sewage of WWTPs ranged from nanogram per liter to a few micrograms per liter, such as in South Korea (92–2,620 μg L$^{-1}$) (Kim et al. 2007), Australia (20–900 ng L$^{-1}$) (Martinez-Carballo et al. 2007), Spain (20–3,700 ng L$^{-1}$) (Garcia-Lopez et al. 2008; Rodil et al. 2009), Germany (25–62,000 ng L$^{-1}$) (Bester 2005; Rodil et al. 2009; Rodríguez et al. 2009).
2005; Quintana et al. 2006), and Sweden (40–3,000 ng L\(^{-1}\)) (Marklund et al. 2005). Meanwhile, because of the sorption of residual activated sludge, high concentrations of OPs were also detected in dewatered sludge with the dominant OPs of TBEP and TPhP (Zeng et al. 2014). In the wastewater treatment process, non-chlorinated OPs can be efficiently removed after treatment by WWTPs, but chlorinated OPs were persistent and barely eliminated in WWTPs (Bester 2005).

Although some studies have already reported on the occurrence, distribution, and degradation of OPs in WWTPs (Marklund et al. 2005; Zeng et al. 2014; Liang et al. 2016), there are scarcely any studies reporting on the wastewater treatment processes on the removal efficiency of OPs. In this study, anoxic–oxic (AO) and University of Capetown (UCT) processes were selected for investigating the removal of six commonly used OPs. Based on this, a comparison was made between these two processes on the removal efficiency of OPs, and then the changes of concentration and composition of OPs in the wastewater treatment processes were analyzed. This study is expected to help to understand the influence of the wastewater treatment process on the removal of OPs.

MATERIALS AND METHODS

Chemicals and materials

OP standards (TCEP, TCPP, TDCP, TnBP, TPhP, and TBEP) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Surrogate tri-n-butyl-d\(_{27}\) phosphate (TnBP-d\(_{27}\), 98%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Acetonitrile (ACN), ethyl acetate, and methanol were obtained from Fisher Scientific (Shanghai, China), and all solvents used in this work were of chromatographic grade. Ultra-pure water (18.2 MΩ) was provided by Milli-Q Gradient system (Millipore, Bedford, USA) in our laboratory. Individual OP stock solution (1,000 mg L\(^{-1}\)) was prepared in ACN. A mixed stock solution containing 10 mg L\(^{-1}\) of each of the six OPs was prepared by dilution of the stock solutions with water/ACN (50/50, v/v). All the stock solutions were stored in the dark under 4 °C.

Filtration of water was conducted with a solvent filtration/degassing system (1,000 mL) obtained from Jinteng (Tianjin, China), and GF/C membrane (glass fiber, 1.2 μm, 45 mm, Whatman, UK). Oasis HLB cartridge (200 mg, 6 mL), purchased from Waters (Milford, MA, USA), was used for solid phase extraction (SPE). The eluent from SPE cartridges was collected in glass bottles (8 mL), and then concentrated with a nitrogen evaporator (Anpel, Shanghai, China).

Ultra-performance liquid chromatography–tandem mass spectrometry analysis

Identification and quantification of OPs were performed using an ultra-performance liquid chromatography system (ACQUITY UPLC, Waters, USA) equipped with a triple quadrupole mass spectrometer (TSQ Quantum Access, Thermo Scientific, USA) using a Waters BEH C18 column (2.1 mm × 100 mm, 1.7 μm). The injection volume was 10 μL and the column temperature was 45 °C. Eluent A was 0.1% (V/V) formic acid, and B was ACN. The gradient was as follows: 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 ultra-performance liquid chromatography–tandem mass spectrometry (UPLC-MS/MS) detection parameters for the studied OPs are shown in Table 1.

Sample collection

Sewage samples were collected from two WWTPs located in Zhengzhou city in central China. The AO process was applied in Wangxinzhuan WWTP, mainly including sand screen, anaerobic tank, aerobic tank, secondary clarifier, and ultraviolet filter (Figure 1(a)). The UCT process, an improved technology of anaerobic–oxic–oxic, with the advantages of improving the capacity of removing the phosphorus and nitrogen in urban sewage by sending the returned activated sludge to the anoxic tank instead of anaerobic tank, was applied in Matougang WWTP, mainly including sand screen, anaerobic tank, anoxic tank, aerobic tank, secondary clarifier, and ultraviolet filter (Figure 1(b)). Detailed descriptions of the WWTPs are listed in Table 2. Sewage samples of each WWTP were collected every 4 h within 24 h, and mixed in equal volume. After being delivered to the laboratory, sewage samples were filtered immediately through GF/C membrane, and then stored in an amber glass bottle under 4 °C. Dewatered sludge samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 80 mm mesh sieve, and then stored in an amber glass bottle under 4 °C. The sewage and dewatered sludge samples were collected during April and May 2015. The flow schemes of the WWTPs and sampling sites are shown in Figure 1.
Sample pretreatment procedure

Sewage samples

Detailed descriptions of the pretreatment procedure have been published previously (Wang et al., 2011). Briefly, an approximately 200 mL sewage sample was loaded into a 250 mL flask, spiked with 10 μL TnBP-d27 at 5 mg L⁻¹ as surrogate, and then subjected to an Oasis HLB cartridge (200 mg, 6 mL), which was preconditioned with 4 mL ACN and ultrapure water. After the extract was loaded, the cartridge was washed with 5 mL ultrapure water, and then dried under ambient conditions for 10 min. The analytes were finally eluted with 8 mL ACN. The eluate was then concentrated to almost dryness under gentle N₂, after which it was redissolved in 500 μL ACN/water (50/50, v/v). 10 mL of the solution were injected into the UPLC-MS/MS for analysis.
The analytes were extracted using ultrasonic assistance, as described previously, with slight modification (Zeng et al. 2014). Briefly, approximately 0.5 g dry sludge was loaded into the bottom of a 50 mL Teflon centrifuge tube (Nalgene™ Oak Ridge centrifuge tube, Thermo, USA), spiked with 10 μL of TnBP-d27 at 5 mg L⁻¹ as a surrogate, and extracted by ultrasonic assistance with a 20 mL mixture of ACN/water (25/75, v/v) for 30 min at ambient temperature. The extract was then centrifuged at 9,000 rpm for 15 min into the bottom of a 50 mL Teﬂon centrifuge tube, Thermo, USA), spiked samples (standards ¼ 3), spiked blanks (standards ¼ 3), spiked matrix (standards ¼ 3), and replicate samples (n = 3) were analyzed with real samples in every batch. In each spiked sample, a 50 ng mixture of six OPs was added. All samples were spiked with TnBP-d27 as a surrogate. TDCP was not found in blanks; TBEP and TnBP were found in every method blank at the LOD; TCEP, TPhP, and TCPP were detected at 7.5 ± 0.5 μg L⁻¹, 1.5 ± 0.4 μg L⁻¹, and 2.5 ± 0.3 μg L⁻¹ in blanks. Acceptable recoveries were obtained with the ranges of 53 ± 6.0% to 102 ± 4.7% and 89 ± 4.0% to 114 ± 6.4% being observed for spiked blanks and spiked matrix, respectively (Table 3). The concentrations of OPs measured in the influent, effluent, and dewatered sludge samples were background-subtracted but not recovery corrected.

### RESULTS AND DISCUSSION

#### Concentration of OPs in sewage and sludge samples

The concentrations of the six OPs in the influent, effluent, and sludge samples are shown in Table 4. The results show that all target OPs were detected in both WWTPs, indicating the universal pollution of OPs in urban sewage. The dominant OPs were TBEP, TCPP, and TCEP in the influent of both WWTPs, indicating that the composition of OP pollutants in urban sewage was similar. The concentration of TBEP, TCPP, and TCEP was lower than the two WWTPs, in Germany in 2004 (3,700–4,000 μg L⁻¹ for TBEP and 650–2,000 μg L⁻¹ for TCPP) (Meyer & Bester 2004), but higher than 11 WWTPs in Sweden in 2005 (5,200–35,000 ng L⁻¹ for TBEP, 6,600–52,000 ng L⁻¹ for TnBP, and 1,100–18,000 ng L⁻¹ for TCPP) (Marklund et al. 2005). However, until recently, limited data were available regarding the occurrence and distribution of OPs in the WWTPs of China. Zeng et al. (2015) reported that the dominant OPs
Table 4  Concentration of OPs in sewage and dewatered sludge samples in the WWTPs

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Influent</th>
<th>Anaerobic</th>
<th>Aerobic</th>
<th>Secondary clarifier</th>
<th>Effluent</th>
<th>Sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wangxinzhuang</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBP</td>
<td>648.7 ± 35.4</td>
<td>226.4 ± 84</td>
<td>56.6 ± 30.5</td>
<td>194.8 ± 4.3</td>
<td>96.6 ± 22.4</td>
<td>48.0 ± 2.3</td>
</tr>
<tr>
<td>TCEP</td>
<td>172.3 ± 2.8</td>
<td>150.7 ± 3.1</td>
<td>94.4 ± 32.0</td>
<td>100.8 ± 24.2</td>
<td>171.8 ± 37.3</td>
<td>21.5 ± 4.8</td>
</tr>
<tr>
<td>TDCP</td>
<td>15.6 ± 1.3</td>
<td>8.3 ± 1.1</td>
<td>8.8 ± 1.4</td>
<td>7.8 ± 0.9</td>
<td>7.5 ± 1.2</td>
<td>28.0 ± 3.7</td>
</tr>
<tr>
<td>TnBP</td>
<td>50.6 ± 5.4</td>
<td>19.5 ± 9.5</td>
<td>31.5 ± 7.1</td>
<td>28.5 ± 3.8</td>
<td>35.9 ± 1.1</td>
<td>53.2 ± 3.9</td>
</tr>
<tr>
<td>TPhP</td>
<td>15.2 ± 0.7</td>
<td>2.8 ± 0.6</td>
<td>2.8 ± 0.7</td>
<td>4.4 ± 1.7</td>
<td>3.8 ± 0.8</td>
<td>16.9 ± 8.1</td>
</tr>
<tr>
<td>TCPP</td>
<td>204.2 ± 3.8</td>
<td>182.3 ± 9.9</td>
<td>155.6 ± 51.1</td>
<td>198.9 ± 40</td>
<td>196.0 ± 19.1</td>
<td>60.7 ± 12.7</td>
</tr>
<tr>
<td>ΣOPs</td>
<td>1,106.5 ± 590</td>
<td>590 ± 349.7</td>
<td>535.2 ± 117</td>
<td>228.3 ± 0.3</td>
<td>528.6 ± 253.1</td>
<td>249.6 ± 22.6</td>
</tr>
<tr>
<td>Matougang</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBP</td>
<td>294.4 ± 14.7</td>
<td>338.4 ± 23.3</td>
<td>82.2 ± 15.3</td>
<td>59.1 ± 4.2</td>
<td>34.1 ± 1.8</td>
<td>67.0 ± 7.1</td>
</tr>
<tr>
<td>TCEP</td>
<td>70.0 ± 7.5</td>
<td>49.1 ± 24.7</td>
<td>59.3 ± 21.4</td>
<td>44.2 ± 15.7</td>
<td>61.4 ± 6.9</td>
<td>45.7 ± 2.5</td>
</tr>
<tr>
<td>TDCP</td>
<td>11.1 ± 0.7</td>
<td>7.8 ± 1.7</td>
<td>7.2 ± 0.1</td>
<td>7.7 ± 1.3</td>
<td>8.4 ± 0.8</td>
<td>30.9 ± 1.9</td>
</tr>
<tr>
<td>TnBP</td>
<td>53.6 ± 8.5</td>
<td>51.6 ± 18.8</td>
<td>23.1 ± 1.2</td>
<td>34.7 ± 8.7</td>
<td>40.1 ± 7.6</td>
<td>31.0 ± 4.7</td>
</tr>
<tr>
<td>TPhP</td>
<td>8.8 ± 1.4</td>
<td>6.1 ± 0.5</td>
<td>2.5 ± 0.4</td>
<td>5.1 ± 0.3</td>
<td>3.2 ± 0.8</td>
<td>38.7 ± 3.3</td>
</tr>
<tr>
<td>TCPP</td>
<td>90.8 ± 3.7</td>
<td>70.1 ± 15.2</td>
<td>75.3 ± 6.7</td>
<td>73.8 ± 15.4</td>
<td>80.1 ± 4.9</td>
<td>52.9 ± 7.5</td>
</tr>
<tr>
<td>ΣOPs</td>
<td>528.6</td>
<td>523.1</td>
<td>249.6</td>
<td>222.6</td>
<td>227.4</td>
<td>266.2</td>
</tr>
</tbody>
</table>

*Data reported are μg L<sup>-1</sup> for sewage samples, and μg kg<sup>-1</sup> for sludge samples.

TBP, tris(2-butoxyethyl)phosphate; TCEP, tris(2-chloroethyl)phosphate; TDCP, tris(1,3-dichloro-2-propyl)phosphate; TnBP, tributyl phosphate; TPhP, trisphenyl phosphate; TCPP, tris(2-chloroisopropyl)phosphate; ΣOPs, total concentration of OPs.
removed in the aerobic process with a removal rate of 75.7%, and only 12.3% of TBEP was further removed in the following step. Similarly, approximately 55.2% of TnBP was able to be removed during the aerobic process. It was noted that the concentration of TnBP increased to 40.1 μg L⁻¹ in the effluent, and thus 25.2% of TBEP was removed in the UCT process. Chlorinated OPs, including TCPP, TCEP, and TDPC, exhibited a slight decrease during the anaerobic step, but no further decrease was found in the following steps. Finally, only 11.8%, 12.3%, and 23.9% of TCPP, TCEP, and TDPC were able to be removed by the UCT process. The removal of TPhP also mainly occurred in the aerobic process with a removal rate of 58.8%. Finally, more than 63% of TPhP can be removed after treatment by the UCT process.

In general, for OP removal, the UCT process has the advantage over the AO process. The UCT process exhibited better performance on the removal of TCEP, TCPP, and TBEP, and comparable efficiency with TnBP and TPhP, although worse for TDPC. Especially for TCEP and TCPP, the removal rate of the UCT process was higher than the AO process – about 12% and 8%. The reasons may possibly include: (1) in the UCT process, the anaerobic-aerobic environment is suitable for the structure of denitrification phosphorus-removing bacteria, which may contribute to the degradation of OPs (Kawagoshi et al. 2002; Takahashi et al. 2008); (2) because of the additional anoxia step in the UCT process, the adsorption of residual activated sludge and biodegradation also can increase the removal efficiency.

As a high concentration of OPs was found in the dewated sludge, it can be concluded that the adsorption of OPs on the residual activated sludge was an important factor on the removal of OPs in the wastewater treatment process. However, the hydraulic retention time was different with the solid retention time, and thus it was unable to build a mass balance between sewage and residual activated sludge. In this study, removal rate of six OPs in different processes versus their log \( K_{ow} \) was made, and the result was shown in Figure 2. The removal of six OPs has relatively high linear correlation coefficient with log \( K_{ow} \) (\( r^2 = 0.539 \) for AO process), indicating the OPs with high octanol-water partition coefficient \( (K_{ow}) \) are prone to be removed by adsorbing on the residual activated sludge. However, the linear correlation coefficient of the UCT process \( (r^2 = 0.212) \) was poorer than that of the AO process, probably due to the difference of the degradation mechanisms and technical flow between the two processes; further study is needed in future work.

![Figure 2: Percent removal of the six OPs versus log \( K_{ow} \)](https://iwaponline.com/wst/article-pdf/74/7/1602/458116/wst074071602.pdf)

**Variation in composition of OPs in different processes**

The total concentration of OPs (ΣOPs) in the influent and effluent of Wangxinhuang WWTP (AO process) was 1,106.5 and 511.7 μg L⁻¹, respectively. TBEP (58.6%), TCPP (18.5%), and TCEP (15.6%) accounted for about 92.7% of the ΣOPs in the influent; while, TCPP (38.3%), TCEP (33.6%), and TBEP (18.9%) were found to be dominant in the effluent, which comprised 86.1% of the ΣOPs (Figure 3(a)). As for the UCT process, the ΣOPs in the influent and effluent of Matougang WWTP was 528.6 and 227.4 μg L⁻¹, respectively. A similar composition was found with the percentage of TBEP (55.7%), TCPP (17.2%), and TCEP (13.2%) in the influent, and TCPP (38.3%), TCEP (33.6%), and TBEP (18.9%) in the effluent (Figure 3(b)).

After treatment by the wastewater treatment process, approximately 53.8% of the ΣOPs can be removed by the AO process, and the removal rate of each OP was in the order of TBEP (85.1%) > TPhP (75%) > TDCP (51.9%) > TnBP (29.1%) > TCPC (4%) > TCEP (0.5%). For comparison, approximately 57% of the ΣOPs can be removed by the UCT process with the removal rate of TBEP (88.4%), TPhP (63.6%), TnBP (25.2%), TDCP (24.3%), TCEP (12.3%), and TCPP (11.8%).

In the anaerobic process, ΣOPs significantly decreased by 40.2% in the AO process, which was mainly contributed to by the decrease of TBEP with a removal rate of 65.1%. In contrast, the concentration of TBEP barely decreased in the anoxia and anaerobic steps in the UCT process, probably because of the interference of the matrix factor in the wastewater treatment system. However, the removal rate of TCPP...
and TCEP in the UCT process was 22.8% and 29.9%, which was 17.3% and 12.1% higher than that of the AO process.

In the aerobic process, the total concentration of OPs decreased by about 20% (AO process) and 53.6% (UCT process) compared with the anaerobic process. TBEP, TCPP, and TCEP were still the dominant OPs, but the concentration of TBEP accounted for \( \Sigma \) OPs decreasing to 16.2% (AO process) and 32.9% (UCT process).

In the following steps, a slight increase of \( \Sigma \) OPs was found in the secondary filter in the AO process, and remained constant after treatment by UV filter. TCPP and TCEP were dominant in the effluent, which accounted for 38.3% and 38.6% of \( \Sigma \) OPs, respectively. Similarly, in the UCT process, no significant decrease was found in the secondary filter and UV filter. TCEP and TCPP became the dominant OPs, which accounted for 27% and 35.2% of OPs, respectively.

**CONCLUSION**

All six selected OPs could be detected in all sewage samples collected from two WWTPs in a central city in China. The composition profiles were similar, with TBEP, TCPP, and TCEP being dominant OPs, although the concentration of OPs in the influent varied. TBEP, TPhP, and TDCP were readily removed in both AO and UCT processes. However, chlorinated OPs, TCEP and TCPP, were persistent and recalcitrant to removal in both the AO and UCT processes. In general, the UCT process exhibited better removal efficiency than the AO process. Significant linear correlations between \( \log K_{ow} \) of OPs and removal rate were observed, indicating that OPs with high \( K_{ow} \) value were more prone to be removed by adsorption on the activated sludge.

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