Fate of phthalate esters in municipal wastewater treatment plant and their environmental impact

Minghao Kong, Yonghui Song, Yizhang Zhang, Ruixia Liu, Jian Wei and Lei Zheng

ABSTRACT

The fate and distribution of six phthalate esters (PAEs) in a municipal wastewater treatment plant (WWTP) employing an anaerobic/anoxic/oxic (A²/O) process were investigated. The process achieved relatively high removal efficiencies of PAEs in the range 55–97%. It illustrated that biotransformation and sludge-adsorption were major elimination pathways by analyzing the mass balance and flux of PAEs. About 83% of $\sum$PAEs was entirely removed by A²/O bioreactors indicating biotransformation is the dominant removal mechanism. PAEs with shorter alkyl chain length and higher water solubility were more biodegradable. Less than 6% of $\sum$PAEs were removed by excess sludge adsorption. The sludge-adsorption capacity of PAE depends on its hydrophobicity. The levels and fluxes of PAEs were analyzed by monitoring different sites of the receiving river of the WWTP effluent to clarify the potential impact of discharge. Daily flux of PAEs upstream and downstream of the discharging point were 113 kg·d⁻¹ and 205 kg·d⁻¹, respectively, which were higher than the effluent devotion value of 6.67 kg·d⁻¹. It suggested that the emissions from the WWTP appeared to be less than those from the other possible sources, such as potential untreated discharge and surface runoff. Improvement of wastewater collection efficiencies is necessary to eliminate the PAE load in the urban river.

Key words | A²/O, fate, phthalates, wastewater treatment plant

INTRODUCTION

Phthalate esters (PAEs) are a group of industrial chemicals with annual production of several million tons worldwide. PAEs with relatively low molecular weight including dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-n-butyl phthalate (DBP) are widely used in the production of cosmetics, pharmaceuticals, and personal care products. Most of the high molecular weight PAEs, like butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP), are utilized as plasticizers to improve the performance of plastics, especially in polyvinyl chloride manufacturing.

Since PAEs are not bonded with the polymer matrices chemically, they could be easily dispersed into the environment during manufacture, use or disposal (Dargnat et al. 2009). PAEs are ubiquitous in various environmental media, such as water, biota, sediment, air and soil (Staples et al. 1997; Fromme et al. 2002). PAEs have been reported to cause carcinogenic and teratogenic effects. Moreover, some studies reported that PAEs show endocrine effects. Therefore, the US Environmental Protection Agency (US-EPA) put six PAEs (DMP, DEP, DBP, BBP, DEHP, and DOP) into the list of priority pollutants. The environmental fate of PAEs has recently received increasing attention.

Effluent from wastewater treatment plants (WWTPs), urban runoff, and atmospheric deposition are several major environmental sources of PAEs (Dargnat et al. 2009). WWTPs are the key connections between wastewater and the water environment in analyzing the environmental fate of hazardous chemicals from household and industrial products. Thus, the PAE removal efficiency in WWTPs is vital to the quality of the surrounding water. However, most WWTPs are not designed to treat these persistent micro-organic pollutants but rather nitrogen and phosphate. Studies on the elimination of PAEs in WWTPs are found with a large range of removal efficiencies. For example, Tan et al. (2007) found the removal efficiency of DEP, DBP, BBP and DEHP in an Australian WWTP to be 97.7%, 94.0%, 53.1% and 96.1%, respectively; while Gao et al. (2014) found that WWTPs in Harbin of
North China only achieved 30–70% removal efficiencies. Up to now, only a few studies have focused on the fate of PAEs in different units of the WWTP (Gao et al. 2014), especially studies about the anaerobic/anoxic/oxic (A2/O) process involved both dissolved and adsorbed PAEs.

The aim of our study is to clarify the removal and the fate of PAEs in both water and the sludge phase in different units along the full-scale A2/O process of WWTPs. For that purpose, a WWTP applying the A2/O process in Wuxi City was investigated. Sampling points including influent, primary settling tank (PST), A2/O bioreactors and final settling tank (FST) were collected. Concentrations and mass flux of PAEs in both water and sludge along the treatment process were determined. Finally, we attempted to evaluate the WWTP effluent discharge’s impact on the levels of PAE in the receiving river (Beijing-Hangzhou Grand Canal). This may provide useful information for future management and remediation efforts for PAEs.

**MATERIALS AND METHODS**

**Reagents**

Six PAEs (DMP, DEP, DBP, BBP, DEHP and DOP) were purchased from Supelco (USA). The internal standard Phenthanthrene-d10 was purchased from AccuStandard (USA). All solvents used for PAE extraction and dilution were of high performance liquid chromatography (HPLC) quality from J. T. Baker (USA).

**Study area and sampling**

Wuxi City is a modern industrial city with a dense river net. A prosperous economy is mainly supported by manufacturing, including textile, petrochemical, and metallurgy industries. The manufacturing consumes a large amount of water and then discharges the wastewater, containing some hazardous chemicals, back into the river. A municipal WWTP with the A2/O process which was fed with both household and industrial wastewater was investigated. Its mean daily inflow during the sampling period was 280,000 m³, and the daily excess sludge discharged was 40,000 kg d.w.

Samples were collected from the units of WWTP including: (1) the influent after grid screen; (2) effluent of PST; (3) effluent of A2/O bioreactors; and (4) effluent of FST. In addition, the sites located upstream (river cross-section A 11 km) and downstream (river cross-section B 3.34 km, and C 12.55 km) of the WWTP discharge point were also sampled in order to clarify the impact of the WWTP effluent on the receiving river. The urban area, which is highly industrialized, is located between sites A and B. There is also a suburban area between B and C (profiled in Supplementary Material, Figure S1, available with the online version of this paper). In Wuxi City the pollution emission density in A-B area is higher than that of B-C because of the population and manufacturing density (Gao et al. 2011). A total of 21 samples were taken during the rainy season on 5 August 2012, including 12 samples consisting of three collections from each of four points in the WWTP (1–4), taken at 3 h intervals from 10:00–16:00, and nine samples of the receiving river (A, B and C, three horizontal samples from each section). The excess sludge sample was collected from a sludge dewatering basin.

**Chemical analysis and quality assurance**

Each sample (2 L) was immediately filtered with 0.45 μm glass microfiber filters (Whatman, UK) to separate the water phase (filtrate) and sludge phase (suspended solids). Water samples were then kept at 4°C and extracted within 24 h, while the sludge samples were covered by aluminum foil and stored at −20°C until freeze-dried (using Alpha 1–2 LD plus, Christ, Germany). PAE extraction from water and sludge phases was carried out following the methods described by Roslev et al. (2007). PAEs were extracted from the filtrate (2 L) using C18 solid phase extraction (SPE) cartridges (Supelco, USA) and were eluted with 10 ml of hexane:acetone (1:1). Freeze-dried samples (weighed suspended solid samples and 10.0 g excess sludge) were ultrasonically extracted with dichloromethane. PAE extracts in both the water and sludge phases were concentrated under N2 and were analyzed with gas chromatography–mass spectrometry (Agilent GC 6890 coupled with Agilent MS 5975, and a 50 m × 0.25 mm × 0.25 μm HP-5 ms capillary column). The method used is presented in the Supplementary Material. The quantification was conducted using an internal calibration method with calibration standards at seven concentration levels, and a good linearity was obtained ($r^2 > 0.99$).

**RESULTS AND DISCUSSION**

**Levels of PAEs along the WWTP units and the receiving river**

The average concentrations of the selected six PAEs in influent and effluent of the WWTP are presented in Table 1(a) (the corresponding Mean, Min–Max and SE values are listed in Table S1, available with the online version of this paper). The concentrations of the six PAEs in the influent ranged from 0.11–14.70 μg·L⁻¹ in the water phase, and 0.15–168.49 μg·L⁻¹ in the sludge phase. The most abundant compound in the
The changes in PAE concentration in water along the whole process are provided to describe the removal of PAEs in detail (Figure 1(a)). All the PAEs showed a continuous decline except DOP. The removal efficiencies of low or intermediate molecular weight (LMW, IMW, respectively) PAEs (DMP, DEP and DBP) were notably higher than that of PAEs with high molecular weight (HMW) (BBP, DEHP and DOP) (Gao et al. 2014).

To clarify the contribution of the A2/O bioreactors, the water phase PAE treatment efficiency in the whole WWTP and the A2/O bioreactors was compared, and profiled as seen in Figure 1(b). With respect to the decrease of PAE concentration in the water phase, the A2/O bioreactors are more efficient than both PST and FST. The removal efficiencies in water in the A2/O bioreactors can be defined into three categories. Category 1 is DMP and DEP with relative high efficiency (average 65%). Category 2 is DBP and BBP with medium efficiency (average 53%). Category 3 is DEHP and DOP with low (<45%) or negative efficiency.

By comparing results with the properties in Table 1(b), the removal efficiency of PAEs seems to be largely dependent on their physico-chemical properties, like the water solubility and alkyl chain length (Yuan et al. 2002). For instance, Category 1 with short alkyl chain length and high water solubility tends to be efficiently removed by the A2/O bioreactors, while Category 3 with long alkyl chain length and low water solubility tends to be poorly removed. The possible reason for this is that the solubility of hydrophobic PAEs limited the biodegradation, and the removal of PAEs throughout A2/O bioreactors largely depends on biodegradation activity. Comparable conclusions have been drawn by many researchers. Gao et al. (2014) observed that HMW PAEs are more resistant to biodegradation than LMW PAEs. Ejlertsson et al. (1997) also found...
that the water solubility of PAEs appeared to be a primary factor in limiting their biodegradation; Zeng et al. (2004) indicated the biodegradability of PAEs seems to correlate to the length of alkyl side chains and the alkyl branch chains. Generally, longer alkyl branch chains, lower solubility, and higher octanol-water partition coefficient are all rate-limiting factors in the biotransformation of PAEs.

Behavior of PAEs in sludge along the treatment process

In this study, the PAEs in the sludge phase accounted for 61% of the total amounts of PAEs in the effluent. So it is important to study the behavior of PAEs in the sludge phase throughout the WWTP process. In the influent, more than 96% of the PAEs in the sludge phase were made up of DEHP, DBP was 2%, and DEP, DMP, BBP, and DOP were less than 1%. This pattern is in accordance with the octanol-water partition coefficient (log $k_{ow}$) of different PAEs, which suggests the contribution of PAEs in suspended solids is strongly based on the adsorption behavior. In the $A^2/O$ process about 95% of adsorbed DEHP was eliminated by discharge of excess sludge, release or degradation in bioreactors.

To obtain further information about the role of adsorption in the PAE removal, the solid partition coefficients ($k_s$) for all six PAEs along the whole process were calculated as:

$$k_{sij} = \frac{C_{sij}}{(C_{wij} + C_{wij})} \times 100\%$$

The relationships between octanol-water partition coefficient and $k_s$ value are given in Figure 2. It is shown that the $k_s$ values for PAEs with higher hydrophobicity were generally larger than those for PAEs with lower hydrophobicity, indicating that $k_s$, or adsorption propensity was largely determined by the characteristics of PAEs. Furthermore, the $k_s$ values showed different tendencies through the treatment process: for the PAEs with lower log $k_{ow}$ value ($<5$) the $k_s$ values rose throughout the process, while for the PAEs with higher log $k_{ow}$ value ($>5$) they decreased, indicating that the $k_s$ values were also attributed to the sludge conditions. This can be ascribed from two aspects. (a) The PAEs with lower log $k_{ow}$ value ($<5$) were mainly quantified in the dissolved fraction. Their rates of biotransformation were relatively high. And the adsorption of suspended organic matter could make the adsorbed fraction not degrade further. However the degradation or hydrolysis of suspended organic matter during the biological process could release some adsorbed PAEs into the water. The rate of release was relatively small compared with that of biotransformation. So the $k_s$ of PAEs with lower log $k_{ow}$ value ($<5$) rose throughout the process. (b) The biodegradation rates of PAEs with higher log $k_{ow}$ value ($>5$) are relatively low, while the release rate increases throughout the treatment processes. In the influent, most of the hydrophobic PAEs were adsorbed on the sludge because hydrophobic PAEs have low solubility and large molecular weight which limited the transport, while they became more soluble in $A^2/O$ bioreactors and FST. On the one hand, the structure of suspended organic
matter that the PAEs adsorbed on would change in the A2/O bioreactors because of the degradation or hydrolysis, and this process would release some hydrophobic PAEs into the water phase. On the other hand, the biosurfactants produced in aerobic sludge could increase the solubility of hydrophobic PAEs. As a consequence, the rate of PAEs releasing from adsorbed suspended organic matter was higher compared with that of biotransformation. So the $k_s$ of PAEs with higher log $k_{ow}$ value (> 5) decreased throughout the process.

**PAE removal efficiencies and mass flux in WWTP**

To understand the removal mechanisms of PAEs in the A2/O process, the mass fluxes in different units are calculated and shown in Figure 3(a). It can be seen that, after assuming that the different bioreactors act as one single reactor (Fauser et al. 2005), the internal recirculation from the oxic tank to the anoxic tank might be regarded as internal exchanges of A2/O bioreactors. The PAEs in the returned sludge would be a burden to the anaerobic tank. It means the PAE inputs to the A2/O bioreactors were larger than the outputs of PST. Also the outputs of the A2/O bioreactors include a part of the returned sludge that would return to the system, so it should be deducted as shown in Figure 3(a). It is noteworthy that the system was in dynamic equilibrium, indicating that the A2/O bioreactors could treat a part of the PAEs in the returned sludge.

PAEs were removed by both biotransformation and adsorption. In order to obtain further insight into the contributions of different pathways, mass balances (Figure 3(b)) were calculated based on mass flux, assuming that the sum of mass proportions of transformation, the discharge from effluent and the excess sludge was 100%. As suggested by others, volatilization and abiotic hydrolysis of PAEs was considered negligible compared with biotransformation, which means the biodegradation dominated the transformation (Staples et al. 1997). The overall removal efficiency of PAEs was 89.3%, of which 6.0% was removed by adsorption on the excess sludge and 83.3% was eliminated via biotransformation. It can be seen that all six PAEs behaved in a biodegradation-dominating pattern. The PAEs with lower water solubility were removed more by adsorption on excess sludge. However, the removal efficiency of PAEs with lower water solubility achieved by adsorption on excess sludge is still lower than that achieved by biotransformation (Figure 3(b)). The possible reasons for this are listed as follows. (a) The PAEs with low solubility adsorbed on suspended organic matter might have released into water when the sludge condition changed in the bioreactors. (b) In the A2/O process, the adsorbed PAEs recirculated with both internal recirculation and returned sludge. A large part of the PAEs adsorbed on the sludge were accumulated in the system or transformed. (c) Ejlertsson et al. (1997) suggested that aerobic sludge was able to produce solubilized material (detergents) that could increase the solubility of DEHP to 4.7 mg·L$^{-1}$ in the water phase.

**Impact upon water quality of the receiving river**

The occurrence of PAEs in the final effluent of the WWTP and three different sites of the Beijing-Hangzhou Grand
Canal located upstream (A) and downstream (B and C) of the WWTP discharge are presented in Table 1(c). The $\Sigma$PAE concentrations in the WWTP effluent were higher than those sampling sites of the receiving river.

To determine the importance of the contribution played by the WWTP discharge in its receiving river, the mass fluxes of the river cross-sections A, B, and C and the effluent were calculated. Compared with A (upstream), the $\Sigma$PAE mass fluxes of B and C (downstream) were notably higher. The PAE flux increased between the river cross-sections A and B, where the urban section of the Grand Canal was. However, the mass flux increase contributed by the WWTP effluent is minor. The possible reasons for this can be listed as follows. (a) The canal in the investigated area has many branches, so the tributaries contributed a part of the mass flux to the main river. (b) In August the investigated area is under rainy conditions, and the urban storm overflows, surface runoff, and atmospheric deposition might be potential sources. (c) In some urban catchments the coverage of the sewer system is limited, in consequence some untreated discharge of industrial wastewater might be a potential source of PAEs in surface water. (d) The sediments could act as a long term PAE source to the river.

CONCLUSIONS

The fate of six PAEs (dissolved and adsorbed) in a full-scale WWTP with the A²/O process was investigated. A relatively high removal efficiency of PAEs (>89%) was found, which was attributed to both biotransformation and sludge adsorption. While biotransformation was the major pathway of the PAE removal in this case. Removal of PAEs seems to be dependent on their physical-chemical properties. Different PAEs showed different removal efficiencies in the water phase of the bioreactors, and this suggested that biodegradability of hydrophobic PAEs was limited by solubility. Relationships between adsorption proportion and log $k_{oa}$ indicated that adsorption was significant for the removal of hydrophobic PAEs. The mass flux in the receiving river was calculated in order to clarify the impact of the effluent discharge, and the results indicated that the increase of mass flux contributed by effluent of the WWTP is minor; besides the effluent from the WWTP, other potential sources may have a stronger impact on the river.

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