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Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China

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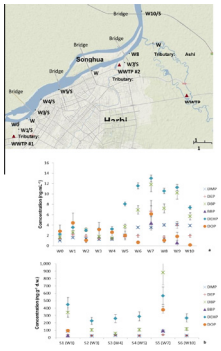
HIGHLIGHTS

- Biotransformation dominates the fate of PAE in CAST process.
- Adsorption dominates the fate of PAE in A/O and A/A/O process.
- The six PAEs were detected in all surface water samples from Songhua River China.
- PAEs with high molecular weight of discharge more impact surface water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and fate of six phthalates: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis (2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP) were investigated as phthalates passed through three full-scale wastewater treatment plants (WWTPs) with different treatment processes, and ultimately into the recipient Songhua River water in Harbin (China). The six phthalates were detected in the majority of aqueous and solid samples, with DEHP being the most abundant compound. The overall removal efficiency of ΣPAEs in the Cyclic Activated Sludge Technology (CAST) process was over 72%, while both the A/O and A/A/O processes achieved approximately 30% removal. The better performance of the CAST process relative to the Anoxic/Oxic (A/O) and Anaerobic/Anoxic/Oxic (A/A/O) processes was attributed to the indoor-conditions of the CAST plants, which effectively maintained the temperature of the treatment system. The fate of PAEs within two different types of WWTPs (CAST and A/A/O) were assessed qualitatively using mass balances. The results suggested that PAEs removal resulted from both biotransformation and adsorption, of which the former was particularly significant in the CAST process, while the latter was more significant in the A/A/O process. Substantial levels of several PAEs were detected in the Songhua River, especially downstream of the WWTPs, which means that the discharge from WWTPs has a strong impact on the water quality of the Songhua River during cold winter conditions.

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1. Introduction

Phthalate esters (PAEs) are a family of synthetic compounds mainly used as additives to improve the flexibility, transparency, durability, and longevity of plastics. As well as being added to polyvinyl chloride (PVC), PAEs are also used in a wide variety of products ranging from pharmaceuticals and personal care products (PPCPs) such as pharmaceutical pills, medical devices, and detergents, to children's toys, packaging, cosmetics, paints, and pesticides (Staples et al., 1997). The most widely used representative PAEs is bis(2-ethylhexyl) phthalate (DEHP) (Clara et al., 2010), which is the dominant plasticizer used in PVC production. Another common PAE is Benzylbutylphthalate (BBP), which is also used in the manufacture of foamed PVC. The PAEs with relatively short alkyl chains such as dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-n-butyl phthalate (DBP) are used as solvents in perfumes and pesticides (Oliver et al., 2005).

A variety of PAEs are known to bioaccumulate in aquatic organisms and produce endocrine disrupting effects (Nallii et al., 2002; Horn et al., 2004). Exposure to some PAEs may result in carcinogenic and teratogenic effects (Becker et al., 2004). Due to the potential hazard of these compounds, the environmental fate of PAEs has received increasing global attention. The use of some PAEs has been restricted or phased out in the European Union (Becker et al., 2004). In 1999, the European Commission has prohibited the use of DEHP in the production of childcare articles and toys for children under three (Brussels, 1999). In 2007, the Consumer Product Safety Improvement Act (CPSIA) became public law in the United States, which declared a ban on children's toys or child care articles containing more than 0.1% of 6 PAEs (Hileman, 2007). The European community even has defined an environmental quality standard (EQS) for the concentration DEHP in surface waters of less than 1.3 ng mL^{-1} (Fromme et al., 2002; EU, 2008).

Since PAEs are not covalently bonded to the polymeric matrix in soft PVC, they are easily leached into the environment during the process of plastic aging and decomposition (Dargnat et al., 2009). Previous researches have demonstrated the ubiquitous presence of PAE compounds in the environment, including rainwater/stormwater, surface water, sediments, and soils (Loraine and Pettigrove, 2006; Gasperi et al., 2009). The presence of PAE compounds in full scale WWTPs has been widely reported, with PAEs being found in treated/untreated wastewater and sewage sludge (Fromme et al., 2002; Dargnat et al., 2009; Clara et al., 2010). Tan et al. (2007) found that 0.716 ng mL^{-1} DEHP, 1.08 ng mL^{-1} DEP, 0.201 ng mL^{-1} DBP, 0.134 ng mL^{-1} BBP were in WWTP influent, even higher concentrations have been detected in some effluents. Fromme et al. (2002) found the concentrations of DEHP ranging from 1.74 to 182 ng mL^{-1} and DBP from 0.2 to 10.4 ng mL^{-1} in treated sewage, while Marttinen et al. (2003) observed 6 ± 1 ng mL^{-1} DEHP in the secondary effluent of a full-scale STP in Finland.

The effluent from wastewater treatment plants (WWTP) has been considered the primary source of plasticizers in the aquatic environment (Kolpin et al., 2002; Loraine and Pettigrove, 2006). Since most conventional wastewater treatment processes are not designed to remove these persistent micro-organic pollutants, the performance of full scale WWTPs are usually unsatisfactory with regard to PAE removal (Nakada et al., 2006; Xue et al., 2010). Previous studies have found that the removal of PAE by WWTPs can vary from 60% to 100% (Marttinen et al., 2003; Oliver et al., 2005). Roslev et al. (2007) found that the overall microbial degradation of DEHP, BBP, DMP and DBP in the WWTP was estimated to be 81%, 90%, 93% and 91%, respectively. Fauser et al. (2003) found that approximately 70%, 48%, 71%, 63% and 61% of DEHP, BBP, DPP, DOP and DNP in the WWTP was subjected to microbial degradation, respectively. However, most of the studies have tended to focus on the concentration of PAE in the influents, effluents and sludge. Few studies have investigated the fate of PAE throughout the entire process of different treatment systems in detail.

The treatment processes: Cyclic activated sludge technology (CAST), Anoxic/Oxic (A/O), and Anaerobic/Anoxic/Oxic (A/A/O) are commonly used in domestic wastewater treatment and each of which has excellent performance with regard to biological nutrient removal (BNR). However, to date there has been little research focusing on PAE removal during full-scale BNR, and there are few reports regarding the performance of these processes in winter.

The purpose of the study was to investigate the fate of six PAE compounds as they passed through three WWTPs employing different treatment processes during the cold winter. The PAE compounds were monitored in the aqueous phase as they passed through the various stages of the WWTPs, and mass balances were evaluated. The occurrence of PAE pollutants downstream from the WWTPs in the recipient river water was also investigated to provide a preliminary assessment of the impact of discharge from WWTPs on water quality.

2. Materials and methods

2.1. Chemicals and materials

The target PAEs including DMP, DEP, DBP, BBP, DEHP and di-n-octyl phthalate (DOP) were selected because they were representative of PAEs with different molecular weights, water solubilities, and octanol–water partition coefficients. The physical–chemical properties for the target PAEs are summarized in Table 1. The phthalate ester standards and the internal standard di-n-phenyl phthalate-D4 (DPP-D4) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Residue grade N-hexane solvents were purchased from Tedia Company Inc. (Carson, CA, USA) and high purity pesticide analytical grade solvents (acetone, etc.) were purchased from J.T. Baker Co., USA.

2.2. Wastewater treatment plants

Harbin is the capital and largest city with a population of approximately 4.52 million locating in the northeast of China. Three WWTPs applying different treatment technologies (CAST, A/O and A/A/O process) in Harbin were selected for the investigation. WWTP #1 operates an indoor CAST process, where the influent sewage is treated by primary sedimentation before being passed through a sequence of biological selectors and finally entering the CAST bioreactors. The CAST tanks employ intermittent aeration with a cycle of 6 h (1.5 h feeding, 3 h aeration, and 1.5 h settlement). WWTP #2 employs an A/O process which utilizes 8 h of hydraulic retention time (HRT) and 19 d of sludge retention time (SRT). WWTP #3 uses A/A/O process, utilizing 9.5 h of HRT and 17 d of SRT. The mean daily inflow during the sampling collec-

Table 1
Characterization of the six investigated PAEs.

Compound	Formula	Alkyl chain length	MW	S_W (mg L^{-1})	logK_{OW}
DMP	$C_{10}H_{10}O_4$	1	194.19	4000	1.61
DEP	$C_{12}H_{14}O_4$	2	222.24	1080	2.38
DBP	$C_{16}H_{22}O_4$	4	278.34	10	4.45
BBP	$C_{19}H_{20}O_4$	4	312.37	2.8	4.84
DEHP	$C_{24}H_{38}O_4$	8	390.57	0.003	7.5
DOP	$C_{24}H_{38}O_4$	8	390.57	0.022	8.1

Data taken from reference Becker et al. (2004) and Cai et al. (2007); MW: molecular weight; S_W: solubility in water; K_{OW}: octanol–water partition coefficient.