# Occurrence, seasonal variation, and environmental impact of phthalic acid esters in a large wastewater treatment plant located in Guangzhou, China

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### ABSTRACT

The occurrence and fate of 14 widely used phthalic acid esters (PAEs) in a wastewater treatment plant (WWTP) located in Guangzhou, China were investigated for 1 y. Results showed that PAEs were widely detected but the levels of PAEs in effluent were below the international standard. Seasonal variation of PAEs levels in the influent was observed, with higher levels in winter and spring and lower levels in summer and autumn. The mean overall removal efficiency of PAEs was 70.9% in WWTP. Results also indicated that the PAE pollution in sewage sludge was more severe than a previous report in Guangzhou. The annual emission of PAEs from effluent and sludge was 1,110 and 238 kg/y, respectively. The ecological risk of PAEs was considered to be medium, which suggested the need for advanced treatment in current full-scale WWTPs to improve the removal of PAEs and consequently, to prevent the receiving water body from the impact of PAEs.

*Keywords:* Municipal sewage; Phthalic acid esters; Seasonal variation; Emission; Ecological risk

## 1. Introduction

Phthalic acid esters (PAEs) are widely used in plastic products to improve the flexibility of the plastic [1]. PAEs could be readily discharged from plastic to the environment as they are not chemically but only physically bonded to the plastic polymers [2]. The toxicity and bioaccumulation potential of PAEs make their impact on the environment a global concern [3]. PAEs are endocrine disruptors that could decrease microbial diversity and crop quality [4]. Di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) were reported to have reproductive and developmental toxicities [5]. For example, a recent study on long-term low-dose integrated exposure to rats showed that six priority

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controlled PAEs have posed reproductive toxicity to male rats [6]. Human exposure to PAEs could result in an adverse effect on reproductive, hepatic and renal functions, hepatocellular carcinoma, anovulation, and decreased fetal growth [7]. As PAEs are widely used in our daily life discharged from municipal wastewater every day, PAEs might cause more serious hazards to the human and natural environment than those that have been reported. Discharge from municipal wastewater treatment plants (WWTPs) is considered as a major source of organic chemicals to the environment, since WWTPs are not designed to remove emerging contaminants, such as PAEs. Therefore, there is an urgent need to systematically study the distribution and removal mechanism of PAEs during wastewater treatment.

WWTPs play a critical role in helping to preserve the quality of surface water. Growing concern about the pollution of water bodies has led to increasingly stringent sewage discharge standards in China [8]. Given that WWTPs with conventional treatment technology was unable to meet this challenge effectively and economically, it is important to investigate the fate of PAEs so as to further improve their removal in existing conventional WWTPs.

PAEs have been widely detected in WWTPs worldwide at low concentrations (μg/L levels) [3]. Previous studies have mostly focused on the detection of PAEs in influent, effluent, and sludge from WWTPs with secondary treatment [9–11]. Tracking the levels of PAEs based on treatment processes can reveal their fate and removal efficiencies within the wastewater treatment system. Studies on PAEs in the wastewater treatment process were increasing [12–14]. It is reported that the concentration of PAEs in WWTPs varied by seasons [11]. However, few studies have reported the removal efficiency of PAEs during different treatment stages for a whole year [15].

This study aimed to understand the removal efficiency, emission to surface water, and ecological risk associated with PAEs in a large municipal WWTP in Guangzhou, a metropolitan and industrial hub located in the Pearl River Delta, China. Specifically, this study (1) measured the concentrations of the selected PAEs in wastewater and sludge samples obtained from a WWTP in Guangzhou, (2) characterized the removal efficiency of PAEs during the different treatment processes, (3) investigated the seasonal variation of PAEs in the WWTP, (4) estimated the annual emission of PAEs via effluent and sludge, and (5) assessed the ecological risks of PAEs associated with the effluent.

## 2. Materials and methods

### 2.1. Standards and reagents

Fourteen standards of PAEs were purchased. Standards for dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), DBP, bis(4-methyl-2-pentyl) phthalate (BMPP), bis(2-methoxyethyl) phthalate (DMEP), bis(2-ethoxyethyl)phthalate (DEEP), diamyl phthalate (DPP), di-n-hexyl phthalate (DHXP), butyl benzyl phthalate (BBP), dicyclohexyl phthalate (DCHP), bis(2-butoxyethyl) phthalate (DBEP), DEHP, and di-n-octyl phthalate (DNOP) were purchased from o2si smart solutions (Charleston, SC, USA).

Reagents for acetone (Pesticide residues grade) and neutral alumina ($Al_2O_3$, reagent grade) were obtained from CNW (Germany), while hexane was purchased from J&K Scientific Ltd. (Beijing, China). Anhydrous sodium sulfate ($Na_2SO_4$, reagent grade) was obtained from Sinopharm Group Co. Ltd. (Shanghai, China). Dichloromethane, ethyl acetate, and methanol were HPLC grade and purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA).

### 2.2. Sample collection

The targeted WWTP (Population served ~$5.7 \times 10^6$), located in Guangzhou, China, has a design treatment capacity of $2.2 \times 10^5$ m³/d and daily discharge of 124.3 tons dewatering sludge. The core biological treatment is the anoxic-anaerobic-aerobic process. All tanks and units except the secondary clarifier in the WWTP are closed from the atmosphere and have been installed with deodorization devices and ventilation systems. Hydraulic residence time in the WWTP is approximately 12 h. The moisture content of dewatering sludge is roughly 80%.

Wastewater samples were collected from each of the six sampling points (Fig. 1), including the influent (IN), the water-sludge mixture of the front end of anoxic stage (AN), the water-sludge mixture in the aerobic stage (AE), the distribution well (DW), the secondary clarifier effluent (SE), and the final effluent (FE). At each sampling point, 8 grab samples were collected every 3 h to produce an 8 L 24 h composite sample. Dewatered sludge samples (DS) were collected from the dewatering facility. The samples were collected monthly from December 2015 to November 2016. All the wastewater samples were stored in 10 L amber wide-mouth bottles under normal temperature and sent back to the laboratory for immediately filtering. The wastewater samples were filtered with pre-combusted (muffle furnace at 450°C for 5 h) glass-fiber filters (0.7 μm diameter, Whatman, UK, GF/F) to remove suspended solids. Filtered wastewater samples were stored at 4°C, while sludge samples were stored at –20°C.

### 2.3. Chemical analyses and data quality control

The filtered wastewater samples (500 mL) were extracted for PAEs with solid-phase extraction using an automated extractor (AQUA Trace ASPE799, GL Sciences, Inc. Japan). The Oasis HLB cartridge (200 mg, 6 mL, Waters™, Milford, MA, USA) were conditioned with sequential elution of dichloromethane (5 mL), ethyl acetate (5 mL), methanol (10 mL), and ultrapure water (10 mL). The samples were passed through the cartridges at a flow rate of 10 mL/min. After loading, the cartridges were dried under high purity nitrogen and the target analytes were subsequently eluted by ethyl acetate (3 mL) and dichloromethane (3 mL). The extracts were further concentrated under a gentle stream of nitrogen almost to dryness and reconstituted in 0.5 mL of ethyl acetate. The resulting extracts were stored in amber glass vials and stored at 4°C before chemical analysis using gas chromatography–mass spectrometry (GC/MS) measurement.

Sludge sample extraction was performed according to previously reported methods [14] with modification.
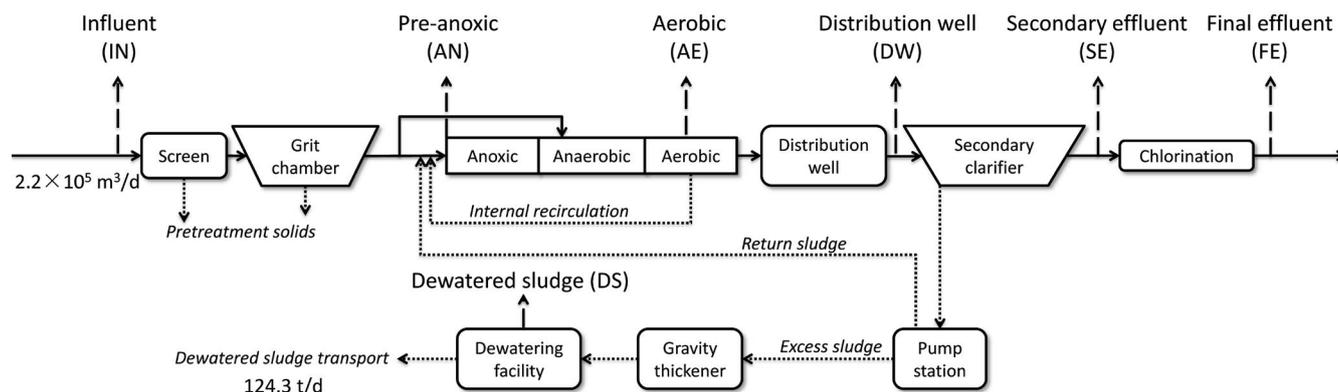
Fig. 1. Treatment stages in the investigated WWTP and the sampling points for PAEs. Dashed arrow indicates sampling locations.

Briefly, the dewatered sludge sample was freeze-dried, ground into a powder, and passed through an 80-mesh stainless steel sieve. Two grams of homogenized sample, 2 g anhydrous sodium sulfate, and 1 g neutral alumina were mixed in a centrifuge tube. Then, the sample was extracted by 10 mL of acetone/*n*-hexane (1:1, v:v) under mechanical shaking for 1 h. The extraction was repeated twice. The supernatants were combined and concentrated to 1 mL with a rotary evaporator and a gentle stream of nitrogen. The resulting extract was filtered through a 0.22 μm membrane and then stored in an amber glass vial at 4°C before chemical analysis using GC/MS measurement.

PAEs were analyzed by GC/MS (7890/5975C, Agilent Technologies, USA). A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm; J&W Scientific, Folsom, CA) with helium as carrier gas (1.0 mL/min) was used for separation. The mass spectrometer had an electron impact (EI) ion source (70 eV) and was operated in the selective ion monitoring mode. The GC temperature program was set as follows: 60°C for 1 min, ramped with 20°C/min to 220°C, and held for 0.5 min, then ramped with 50°C/min to 300°C and held for 5 min. One microliter sample was injected in the splitless mode at 260°C. The temperatures of the interface, the ion source, and the quadrupole were 280°C, 230°C, and 150°C, respectively. Calibration curves for PAEs were linear ($R^2 > 0.99$). Procedural blanks (i.e., solvents without analytes), standards (i.e., solvents with 200 ng/L of analytes), and spiked matrices (samples with 200 ng/L of analytes) were also analyzed for quality control. The recovery rates ranged between 67.8% and 126.3%.

Total organic carbon (TOC) analysis was performed on the freeze-dried sample using an elemental analyzer (Vario EL III, Elementar, Germany) after removing inorganic carbonates with 1 M hydrochloric acid.

*2.4. Environmental risk assessment*

Environmental risk of effluent PAEs was evaluated using risk quotient. Risk quotient (RQ) has been widely employed in WWTP effluent risk assessment [13,16]. Risk quotient was a ratio of the measured environmental concentrations (MEC, i.e., the maximum concentration in final effluent in the present study) and the predicted no effect concentrations (PNEC). If the RQ is less than 0.1, the risk to the environment is considered low. If the RQ is higher than 0.1 but lower than 1, the risk is considered medium. If the RQ is higher than or equal to 1, the risk is considered high. RQ was calculated using Eq. (1).

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

## 3. Results and discussion

### 3.1. PAEs in wastewater

#### 3.1.1. Occurrence of PAEs

Only five of the 14 targeted PAEs were detected in all influent and effluent samples. DEP and DBP were the dominant PAEs with average concentrations of 1.96 and 1.62 μg/L, and accounted for 35% and 30% of $\Sigma_{14}$PAEs in the influent, respectively (Fig. 2). The detection frequency of DMP, DEP, DIBP, DBP, and DEHP were 8%, 25%, 100%, 100%, and 100% in the effluent, respectively. In the effluent, DBP was also the dominant PAEs with an average concentration of 0.63 μg/L (45% of $\Sigma_{14}$PAEs), followed by DIBP with an average concentration of 0.49 μg/L (35% of $\Sigma_{14}$PAEs). The concentrations of DEHP and DBP in final effluent were below the discharge standard of 100 μg/L in China (GB 18918-2002) and the tapwater screening level (DBP: 900 μg/L; DEHP: 5.6 μg/L) proposed by the United State Environmental Protection Agency [17]. The concentrations of DEHP were also lower than the environmental quality standard of 1.3 μg/L set by the European Union in surface water (Directive 2008/105/EC).

The presence of PAEs in raw sewage has been reported in previous studies. In China, the DEP and DBP were detected as the dominant PAEs in WWTPs, with a varied concentration between 1 and 30 μg/L [12–14]. In South Africa, DBP was also the most abundant PAE in influent, with a concentration ranging from 2.7 to 2,488 μg/L [9]. In France, the major PAE was DEHP with a mean concentration of 33.3 μg/L [11]. In the present study, the average concentrations of DEP and DBP were at 1.95 and 1.61 μg/L, respectively, which were much lower than in other regions. The average concentration of total PAEs was 5.34 μg/L in influent in the
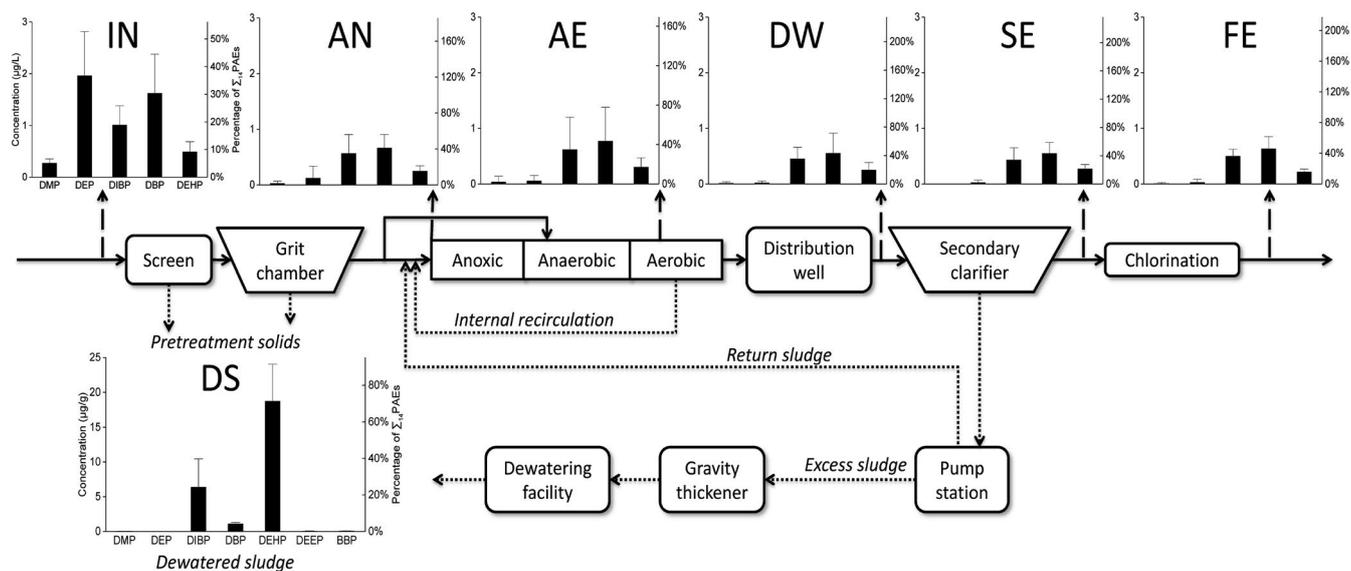
Fig. 2. Concentrations of PAEs in the investigated WWTP. Error bars represent one standard deviation of the mean. IN, the influent; AN, the water-sludge mixture of the front end of anoxic stage; AE, the water-sludge mixture in the aerobic stage; DW, the distribution well; SE, the secondary clarifier effluent; FE, the final effluent; DS, the dewatered sludge. Dashed arrow indicates sampling locations.

present study, which was higher than the value reported in a WWTP in China (approximately 3 µg/L; [13]), but significantly lower than those reported in other WWTPs in China (7–55 µg/L; [12–14]), South Africa (122 µg/L; [9]), and France (120 µg/L; [11]).

### 3.1.2. Overall removal efficiencies of PAEs

The removal efficiencies of PAEs were ranged widely from 34% to 82% with an average efficiency of 70.9%. DEP and DMP were efficiently removed with average efficiencies of 97.8% and 99.0%, respectively. DIBP, DBP and DEHP had similar removal efficiencies (DIBP: 45.2%; DBP: 55.3%; DEHP: 49.5%).

To further investigate the relationship between removal efficiency and molecular weight, the five detected PAEs were grouped into low molecular weight (LMW) PAEs (i.e., DMP and DEP), intermediate molecular weight (IMW) PAEs (i.e., DIBP and DBP), and high molecular weight (HMW) PAEs (i.e., DEHP) [14]. The removal efficiencies followed the order of LMW PAEs > IMW PAEs > HMW, which was consistent with findings from previous studies in domestic WWTPs equipped with biological treatment processes [12,14]. The possible reason was that the biodegradability of PAE is related to the length of the alkyl chain [18], as compounds with longer alkyl chain were observed with slower biodegradation. However, it is reported that all PAEs had over 90% removal efficiencies in a WWTP using a combined tank (decantation and activated sludge) [11]. Moreover, different results were found in WWTPs using chemical and biological treatment processes, which showed a different order of removal efficiencies [13]. The relationship between molecular weight and removal efficiency of PAEs in full-scale WWTPs with conventional treatment processes was still not clear.

### 3.1.3. Fate of PAEs during treatment processes

From influent (IN) to pre-anoxic (AN), the wastewater went through primary treatment and then mixed with internal recirculation and returned sludge in the present study. The annual average $\sum_{14}$PAEs declined sharply from 5.34 to 1.61 µg/L (Table 1) with the influence of internal and returned sludge recycling. The annual average removal efficiency of DMP, DEP, DIBP, DBP, and DEHP were 92.3%, 87.8%, 37.2%, 50.9%, and 47.0%, respectively (Fig. S1). Previous studies reported that less than 50% of PAEs were removed in primary treatment [12–14]. In the present study, the high removal efficiencies from influent (IN) to pre-anoxic (AN) were partly due to the dilution of internal recirculation.

From the pre-anoxic (AN) to the secondary effluent (SE) was the core biological treatment process. Here, the annual average $\sum_{14}$PAEs declined from 1.61 to 1.27 µg/L, indicating that further transformation or biodegradation of PAEs occurred during biological treatment. The annual average removal efficiencies of DEP, DIBP, DBP, DEHP, and $\sum_{14}$PAEs in the biological process were 69%, 10%, 11%, –9%, and 14%, respectively. DMP was only detected in four of twelve pre-anoxic samples and not detected in secondary effluent samples. During pre-anoxic (AN) and aerobic (AE), the increases of PAEs except DEP were found. Similar increases of DIBP, DBP, and $\sum$PAEs were found in an aeration basin, which was attributed to the transformation of other macromolecules [16]. In the distribution well, for phosphate removing and faster sludge sedimentation, coagulant was added, which may facilitate the removal of PAEs by sludge sorption. In the last treatment stage, the annual average $\sum_{14}$PAEs increased from 1.27 to 1.38 µg/L. A similar increase was also reported in Harbin WWTPs including a WWTP with the anaerobic-anoxic-aerobic process [14].

Table 1
Concentration of PAEs in dissolved phase samples (µg/L) and sludge samples (µg/g)

| | Stage[1] | DMP | DEP | DIBP | DBP | DEHP | DEEP | BBP | $\sum_{14}$PAEs |
|---|---|---|---|---|---|---|---|---|---|
| Winter | IN | 0.32 ± 0.06 | 2.88 ± 0.71 | 1.38 ± 0.44 | 2.38 ± 0.98 | 0.51 ± 0.25 | n.d.[2] | n.d.[2] | 7.48 ± 2.39 |
| | AN | 0.04 ± 0.04 | 0.33 ± 0.37 | 0.39 ± 0.07 | 0.78 ± 0.24 | 0.26 ± 0.05 | n.d.[2] | n.d.[2] | 1.81 ± 0.71 |
| | AE | 0.02 ± 0.04 | 0.08 ± 0.10 | 0.38 ± 0.11 | 0.80 ± 0.32 | 0.25 ± 0.08 | n.d.[2] | n.d.[2] | 1.55 ± 0.61 |
| | DW | n.d.[2] | 0.01 ± 0.02 | 0.26 ± 0.24 | 0.62 ± 0.67 | 0.17 ± 0.17 | n.d.[2] | n.d.[2] | 1.08 ± 1.10 |
| | SE | n.d.[2] | 0.04 ± 0.07 | 0.32 ± 0.01 | 0.71 ± 0.25 | 0.22 ± 0.02 | n.d.[2] | n.d.[2] | 1.31 ± 0.31 |
| | FE | n.d.[2] | 0.07 ± 0.08 | 0.46 ± 0.02 | 0.83 ± 0.18 | 0.24 ± 0.03 | n.d.[2] | n.d.[2] | 1.62 ± 0.22 |
| | DS | 0.039 ± 0.004 | 0.019 ± 0.003 | 7.36 ± 5.19 | 1.00 ± 0.11 | 20.0 ± 2.93 | 0.055 ± 0.073 | 0.040 ± 0.07 | 28.5 ± 5.26 |
| Spring | IN | 0.27 ± 0.04 | 2.03 ± 0.02 | 1.08 ± 0.17 | 1.48 ± 0.30 | 0.37 ± 0.03 | n.d.[2] | n.d.[2] | 5.24 ± 0.45 |
| | AN | 0.04 ± 0.08 | 0.04 ± 0.06 | 0.72 ± 0.71 | 0.62 ± 0.43 | 0.17 ± 0.09 | n.d.[2] | n.d.[2] | 1.60 ± 1.37 |
| | AE | 0.12 ± 0.20 | 0.10 ± 0.18 | 1.01 ± 1.20 | 1.08 ± 1.26 | 0.34 ± 0.35 | n.d.[2] | n.d.[2] | 2.67 ± 3.21 |
| | DW | 0.03 ± 0.06 | 0.03 ± 0.06 | 0.58 ± 0.24 | 0.62 ± 0.21 | 0.16 ± 0.06 | n.d.[2] | n.d.[2] | 1.44 ± 0.63 |
| | SE | n.d.[2] | 0.04 ± 0.06 | 0.49 ± 0.33 | 0.53 ± 0.24 | 0.22 ± 0.08 | n.d.[2] | n.d.[2] | 1.29 ± 0.59 |
| | FE | 0.02 ± 0.04 | 0.03 ± 0.06 | 0.57 ± 0.09 | 0.69 ± 0.24 | 0.14 ± 0.03 | n.d.[2] | n.d.[2] | 1.47 ± 0.46 |
| | DS | 0.035 ± 0.004 | 0.015 ± 0.004 | 5.76 ± 4.52 | 1.23 ± 0.36 | 17.8 ± 10.89 | 0.035 ± 0.06 | 0.033 ± 0.057 | 24.9 ± 10.4 |
| Summer | IN | 0.26 ± 0.15 | 1.44 ± 1.14 | 0.84 ± 0.37 | 1.34 ± 0.83 | 0.41 ± 0.02 | n.d.[2] | n.d.[2] | 4.31 ± 2.40 |
| | AN | n.d.[2] | 0.09 ± 0.12 | 0.57 ± 0.21 | 0.65 ± 0.17 | 0.20 ± 0.01 | n.d.[2] | n.d.[2] | 1.52 ± 0.36 |
| | AE | n.d.[2] | 0.01 ± 0.01 | 0.45 ± 0.08 | 0.54 ± 0.14 | 0.33 ± 0.11 | n.d.[2] | n.d.[2] | 1.34 ± 0.21 |
| | DW | n.d.[2] | 0.006 ± 0.01 | 0.43 ± 0.16 | 0.46 ± 0.28 | 0.33 ± 0.12 | n.d.[2] | n.d.[2] | 1.24 ± 0.09 |
| | SE | n.d.[2] | 0.006 ± 0.01 | 0.33 ± 0.18 | 0.48 ± 0.04 | 0.31 ± 0.02 | n.d.[2] | n.d.[2] | 1.14 ± 0.24 |
| | FE | n.d.[2] | n.d.[2] | 0.42 ± 0.15 | 0.53 ± 0.10 | 0.25 ± 0.04 | n.d.[2] | n.d.[2] | 1.20 ± 0.14 |
| | DS | 0.031 ± 0.001 | 0.015 ± 0.001 | 7.84 ± 4.74 | 0.92 ± 0.05 | 19.8 ± 3.07 | n.d.[2] | 0.062 ± 0.054 | 28.7 ± 5.63 |
| Autumn | IN | 0.21 ± 0.03 | 1.46 ± 0.41 | 0.72 ± 0.07 | 1.26 ± 0.43 | 0.65 ± 0.29 | n.d.[2] | n.d.[2] | 4.31 ± 1.07 |
| | AN | n.d.[2] | 0.01 ± 0.02 | 0.56 ± 0.04 | 0.58 ± 0.15 | 0.35 ± 0.10 | n.d.[2] | n.d.[2] | 1.51 ± 0.08 |
| | AE | n.d.[2] | 0.01 ± 0.02 | 0.60 ± 0.26 | 0.63 ± 0.25 | 0.26 ± 0.03 | n.d.[2] | n.d.[2] | 1.52 ± 0.56 |
| | DW | n.d.[2] | 0.01 ± 0.02 | 0.52 ± 0.06 | 0.48 ± 0.34 | 0.33 ± 0.09 | n.d.[2] | n.d.[2] | 1.35 ± 0.39 |
| | SE | n.d.[2] | n.d.[2] | 0.56 ± 0.24 | 0.45 ± 0.15 | 0.32 ± 0.11 | n.d.[2] | n.d.[2] | 1.33 ± 0.35 |
| | FE | n.d.[2] | n.d.[2] | 0.53 ± 0.18 | 0.46 ± 0.18 | 0.22 ± 0.04 | n.d.[2] | n.d.[2] | 1.21 ± 0.36 |
| | DS | 0.032 ± 0.004 | 0.016 ± 0.005 | 4.49 ± 3.30 | 1.12 ± 0.01 | 17.2 ± 3.39 | 0.033 ± 0.058 | 0.031 ± 0.054 | 22.9 ± 1.09 |
| All year | IN | 0.26 ± 0.08 | 1.95 ± 0.85 | 1.00 ± 0.37 | 1.61 ± 0.75 | 0.48 ± 0.19 | n.d.[2] | n.d.[2] | 5.34 ± 2.04 |
| | AN | 0.02 ± 0.04 | 0.12 ± 0.21 | 0.56 ± 0.34 | 0.66 ± 0.24 | 0.24 ± 0.09 | n.d.[2] | n.d.[2] | 1.61 ± 0.68 |
| | AE | 0.03 ± 0.10 | 0.05 ± 0.10 | 0.61 ± 0.58 | 0.76 ± 0.61 | 0.30 ± 0.16 | n.d.[2] | n.d.[2] | 1.77 ± 1.52 |
| | DW | 0.009 ± 0.03 | 0.01 ± 0.03 | 0.45 ± 0.20 | 0.54 ± 0.36 | 0.24 ± 0.13 | n.d.[2] | n.d.[2] | 1.27 ± 0.58 |
| | SE | n.d.[2] | 0.02 ± 0.04 | 0.43 ± 0.22 | 0.54 ± 0.19 | 0.27 ± 0.07 | n.d.[2] | n.d.[2] | 1.27 ± 0.34 |
| | FE | 0.006 ± 0.02 | 0.02 ± 0.05 | 0.49 ± 0.12 | 0.63 ± 0.21 | 0.21 ± 0.05 | n.d.[2] | n.d.[2] | 1.38 ± 0.33 |
| | DS | 0.034 ± 0.004 | 0.016 ± 0.003 | 6.36 ± 4.07 | 1.07 ± 0.20 | 18.7 ± 5.34 | 0.030 ± 0.051 | 0.042 ± 0.052 | 26.3 ± 6.09 |

[1]IN, the influent; AN, the water-sludge mixture of the front end of anoxic stage; AE, the water-sludge mixture in the aerobic stage; DW, the distribution well; SE, the secondary clarifier effluent; FE, the final effluent; DS, the dewatered sludge.
[2]n.d., not detected.

### 3.1.4. Seasonal variations of PAEs

The variation of the concentration of PAEs in different seasons was shown in Fig. 3. The concentration of $\sum_{14}$PAEs in winter was 1.74 times that in summer and autumn. The concentrations of DMP, DEP, DIBP, and DBP were higher in winter and spring than in summer and autumn (Table 1). The greatest fluctuation of concentration was found in DEP. The concentration of DEP in winter was two times that in summer. A previous study showed an opposite result in small WWTPs (Design capacity: 1.8 × 10³– 3.8 × 10³ m³/d), where higher DEP concentration was detected in summer than in winter [15]. This contradiction may be due to the complex source (e.g., domestic and industrial sewage discharge and rain) of raw wastewater resulting from a wide service range of the big WWTP in the present study. With regard to DEHP, the high concentration was detected in winter and autumn, while the low concentration was observed in spring and summer. The distribution of PAEs in the influent and the final effluent was stable in four seasons (Fig. 3). The dominant PAEs in the whole year were DEP and DBP in influent while DIBP and DBP were dominant in effluent. The variation of the removal efficiency of PAEs was shown in Fig. 4. The removal efficiencies of DMP
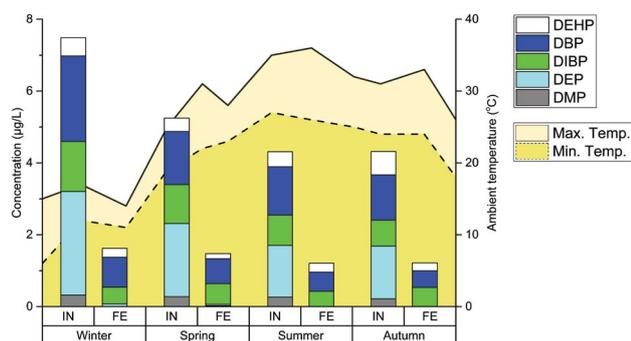
Fig. 3. Seasonal variations of PAEs in the influent and final effluent of the investigated WWTP. Samples were collected between December 2015 and November 2016. IN, the influent; FE, the final effluent.

and DEP were over 97% in four seasons except for DMP in spring (91.4%). A previous study showed that in WWTPs with different biological treatment processes, the removal efficiency of DEP was lower in winter than in summer due to the influence of temperature on removing processes [15]. In the present study, the removal efficiency of DEP was also lower in winter (~14°C) than other seasons (~25°C).

### 3.2. PAEs in sludge

In sewage sludge, five of the 14 targeted PAEs were, similar to influent samples, found in all samples, while DEEP and BBP were detected in some samples. The concentrations of $\Sigma_{14}$PAEs ranged from 14.4 to 35.3 µg/g (dry weight, dw), with a TOC content of 21.4% ± 3.6%. DEHP was the most dominant PAE, accounting for 71% of $\Sigma_{14}$PAEs, followed by DIBP. One possible reason is that DEHP was one of the most commonly used PAEs in the world [19] and accounted for 80% of PAE production/consumption in China [20]. PAEs with a high value of octanol-water coefficient (log$K_{ow}$) are considered prone to be adsorbed by sludge [11]. DEHP was found with high level in sludge but low level in dissolved phase indicating that DEHP was prone to be adsorbed in sludge due to its log$K_{ow}$ (7.5). DIBP (log-$K_{ow}$ = 4.46) was reported as the second dominant PAE in the sewage sludge in Hong Kong [13], Guangzhou (the present study), and Guangdong province [21], while not in other regions of China [20,21], suggesting that DIBP may be a specific PAE pollutant in the Pearl River Delta. In addition, the seasonal influence on sludge PAEs appeared to be limited.

PAEs were detected in sewage sludge in different regions. A wide range survey indicated that the concentrations of PAEs ranged from 0.632 to 68.7 µg/g (dw) in WWTPs in China [21], where the most abundant PAEs were of DEHP, DIBP, and DBP. The average concentration of PAEs was 26.1 µg/g in India, where the dominant PAEs were DEHP (25.7 µg/g) and DBP (1.75 µg/g) [22]. DEHP (27–29 µg/g) and DBP (0.64–1.2 µg/g) were also the major sludge PAEs in Austria [23]. It is reported that the most abundant PAE was DEP followed by DEHP in sewage sludge sampled in Guangzhou during 1998 and 1999 [24], while in the present study, DEHP was the most abundant PAE and DEP only accounted for 0.1% of $\Sigma_{14}$PAEs, indicating that there was a
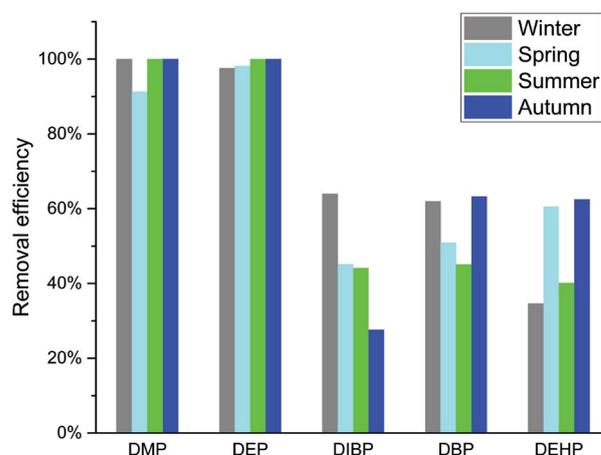


Fig. 4. Seasonal removal efficiencies of PAEs in the investigated WWTP.

temporal variation of PAE pollution in sludge. Besides, the average concentration of total PAEs was higher in the present study (in 2016: 26.3 µg/g) than a previous study (in 1998–1999: 18 µg/g; [24]) in Guangzhou where the permanent population increased from ~6.8 to ~8.7 million [25].

### 3.3. Inflow and emission of PAEs

Annual inflow and emission of PAEs were calculated based on the concentration of PAEs, the capacity of WWTP and the sludge yield. The estimated inflow of $\Sigma_{14}$PAEs was 4,290 kg/y (Table 2). The estimated emission of $\Sigma_{14}$PAEs was 1,110 and 238 kg/y through the discharge of effluent and sludge, respectively. Compared to short-chain PAEs, DEHP was prone to ending up in sludge (43.35%), suggesting that adsorption to solid-phase contributed significantly to DEHP removal, which accorded with the research of Wu et al. [13].

The inflow of DEP was over ten times of that in Harbin WWTPs (90–117 kg/y), where $6.4 \times 10^3$–$1.1 \times 10^5$ m³ of wastewater was treated daily [14]. Zhu et al. [21] found that the high mass loading of DIBP and DBP in sludge were due to the large sludge production in Guangdong, where Guangzhou is the provincial capital. In the present study, the high inflow of DIBP and DBP may also lead to those high mass loading. The emission of DBP was higher than those in Harbin WWTPs (80–165 kg/y) through the discharge of effluent [14]. In addition, the total emission of PAEs was higher than Harbin WWTPs (<400 kg/y; [14]), but lower than a Wuxi WWTP (2,434 kg/y; [12]). Overall, the inflow of DEP in the present study was much higher than in a previous report. The emission of DBP and total PAEs were at a medium level in China.

The amount of emission of PAEs in the effluent was higher than that of polycyclic aromatic hydrocarbons (PAHs) in a Guangzhou WWTP (<200 kg/y; [26]) and pharmaceuticals and personal care products (PPCPs) in the Pearl River Delta WWTPs (26–180 kg/y; [27]). The estimate of PAEs emitted in the WWTP effluent was also higher than the total emission of BDE 209 (one of the most abundant halogenated flame retardants) in Guangzhou downtown WWTPs

Table 2
Mass balance of PAEs in the investigated WWTP

| Num[1] | Item | DMP | DEP | DIBP | DBP | DEHP | DEEP | BBP | $\Sigma_{14}$PAEs |
|---|---|---|---|---|---|---|---|---|---|
| a | Influent, kg/y | 215 | 1,571 | 810 | 1,300 | 391 | n.a.[2] | n.a.[2] | 4,290 |
| b | Effluent, kg/y | 4.68 | 22.8 | 400 | 508 | 173 | n.a.[2] | n.a.[2] | 1,110 |
| c | Effluent, %t | 2.2 | 1.4 | 49.4 | 39.1 | 44.1 | n.a.[2] | n.a.[2] | 25.8 |
| d | Sludge, kg/y | 0.32 | 0.15 | 57.8 | 9.73 | 170 | 0.28 | 0.38 | 238 |
| e | Sludge, % | 0.15 | 0.010 | 7.14 | 0.75 | 43.4 | n.a.[2] | n.a.[2] | 5.6 |
| f | Net loss[3], % | 97.7 | 98.5 | 43.4 | 60.2 | 12.5 | n.a.[2] | n.a.[2] | 68.6 |

[1]a, Average concentration in influent × design treatment capacity; b, average concentration in effluent × design treatment capacity; c = b ÷ a; d, average concentration in sludge × sludge yield × (1 – moisture content); e = d ÷ a; f = 1 – c – e.
[2]n.a., not available.
[3]Net loss including biodegradation or transformation, and volatilization.

(228 kg/y; [28]). Overall, the amount of emission of PAEs was an order of magnitude higher than PAHs, PPCPs, and BDE 209 in WWTPs. More attention should be paid to the fate of PAEs in WWTPs for emission reduction and environmental protection.

Mass balance was done based on the capacity of WWTP, the sludge production and the average concentration of PAEs. Twenty-five percent of PAEs in influent entered the receiving water body and only 5.6% of that was adsorbed in sludge (Table 2). This was comparable to values reported in a WWTP with the anaerobic-anoxic-aerobic process where 10% of influent PAEs were discharged with the effluent while sludge PAEs accounted for 6% of influent PAEs [12]. Also, a similar result was found in a WWTP with the CAST process, where approximately 25% of PAEs in the influent entered the receiving water body and 10% of that was adsorbed in the sludge [14]. PAEs in full-scale WWTPs with biological treatment have similar mass flux according to the existing reports. PAEs in wastewater can be removed by the way of biodegradation, adsorption, and volatilization. In addition, in the present study, a considerable proportion of influent DEHP (43.4%) was discharged with the sludge. As for other influent PAEs, the discharged amount was minor (<10%).

### 3.4. Ecological risk of PAEs in WWTP

A considerable amount of PAEs was discharged by WWTP to surface water systems. It is necessary to evaluate their ecological impacts on the aquatic organism in the receiving water body. The value of RQ ranged from $1.00 \times 10^{-5}$ to $1.76 \times 10^{-1}$, which indicated that effluent PAEs present medium ecological risk (Table 3). The RQ values in the final effluent followed the order: DEHP > DBP and DIBP > DMP and DEP, which were similar to the surrounding area including Guangdong [16] and Jiulong River [29].

DEHP had the highest RQ (0.027–0.176) while other PAEs had RQs over one magnitude lower than those of DEHP. The RQs of DEHP, DIBP, and DBP reported in the present study were all lower than those of treated textile-dyeing wastewater in Guangdong (DEHP: 1.4; DIBP: 0.011; DBP: 0.004; [16]), surface water in Jiulong River (DEHP: >10; DIBP: 1–10; DBP: 0.01–0.1; [29]), and seawater in Bohai and Yellow sea (DEHP: >10; DIBP: 0.1–1; DBP: 0.01–0.1; [30]). Noteworthy, the methods of risk assessment in PAEs were

Table 3
Measured environmental concentration (MEC) (µg/L) and risk quotient (RQ) of PAEs in the final effluent of the investigated WWTP

| Analytes | Taxonomic group | PNEC[1] | MEC[2] | RQ |
|---|---|---|---|---|
| DMP | Fish | 35,000 | 0.07 | 2.00E–06 |
| | Daphnid | 70,000 | | 1.00E–06 |
| | Green algae | 35,000 | | 2.00E–06 |
| DEP | Fish | 10,000 | 0.17 | 1.70E–05 |
| | Daphnid | 20,000 | | 8.50E–06 |
| | Green algae | 10,000 | | 1.70E–05 |
| DIBP | Fish | 1,343 | 0.70 | 5.21E–04 |
| | Daphnid | 2,193 | | 3.19E–04 |
| | Green algae | 598 | | 1.17E–03 |
| DBP | Fish | 1,100 | 0.97 | 8.82E–04 |
| | Daphnid | 1,800 | | 5.39E–04 |
| | Green algae | 495 | | 1.96E–03 |
| DEHP | Fish | 10.1 | 0.28 | 2.76E–02 |
| | Daphnid | 10.1 | | 2.76E–02 |
| | Green algae | 1.6 | | 1.76E–01 |

[1]PNEC was obtained from (Liang et al. [16]).
[2]MEC adopted the maximum concentration in the final effluent.

not completely consistent [16,29,30]. For example, the $LC_{50}$ of DEHP to fish was 1,113 µg/L in a study [16] but 900 µg/L in another study [29]. However, it is clear that the concentration of PAEs in the targeted WWTP effluent was below the $E(L)C_{50}$ summarized by Liang et al. [16], and thus the effluent PAEs pose no acute toxicity to aquatic biota.

## 4. Conclusions and implication

The occurrence and fate of 14 PAEs in a wastewater treatment facility in Guangzhou were monitored for a year. Only five of the 14 targeted PAEs were detected in the raw wastewater, with DEP and DBP as the dominant individuals. PAEs with LMW were effectively removed by the anoxic-anaerobic-aerobic process throughout the year. The concentrations of PAEs in raw wastewater were higher in winter and spring compared to the concentrations

in summer and autumn. Although the removal efficiencies of PAEs were influenced by seasonal variation, similar PAEs distributions in the influent and final effluent were observed in the four seasons. In sludge, DIBP was found to be the second dominant PAE following DEHP, which might be a specific PAE pollutant in the Pearl River Delta, which suggested an extra concern for the DIBP should be paid to PAE pollution assessment in the surrounding area. The concentrations of PAEs in sludge in Guangzhou increased from 1998 to 2016. The discharge of PAEs from the targeted WWTP was higher than some persistent pollutants, pharmaceuticals, and personal care products. The risk assessment showed the risk of effluent PAEs could not be neglected, and the potential risk of PAEs in the aquatic environment may increase due to the bioaccumulation and persistence.

## Acknowledgments

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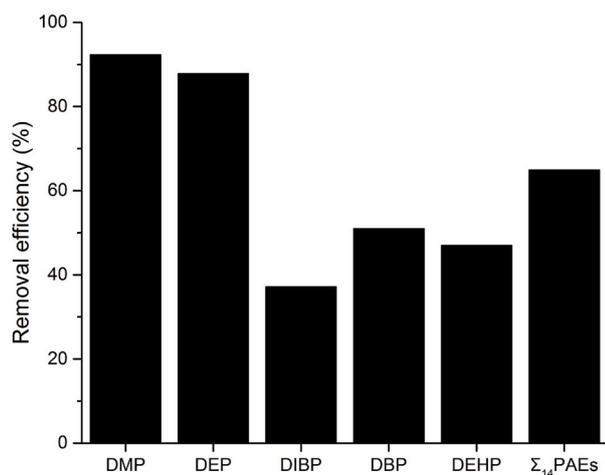**Supplementary information**



Fig. S1. Annual average removal efficiencies of PAEs from the influent to the pre-anoxic.