

# Perfluoroalkyl substances (PFASs) in wastewater treatment plants and drinking water treatment plants: Removal efficiency and exposure risk



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## ABSTRACT

Perfluoroalkyl substances (PFASs) are a group of chemicals with wide industrial and commercial applications, and have been received great attentions due to their persistence in the environment. The information about their presence in urban water cycle is still limited. This study aimed to investigate the occurrence and removal efficiency of eighteen PFASs in wastewater treatment plants (WWTPs) and drinking water plants (DWTPs) with different treatment processes. The results showed that both perfluorobutane sulfonic acid (PFBS) and perfluorooctane sulfonic acid (PFOS) were the predominant compounds in the water phase of WWTPs and DWTPs, while PFOS was dominant in dewatered sludge of WWTPs. The average total PFASs concentrations in the three selected WWTPs were 19.6–232 ng/L in influents, 15.5–234 ng/L in effluents, and 31.5–49.1 ng/g dry weight in sludge. The distribution pattern of PFASs differed between the wastewater and sludge samples, indicating strong partition of PFASs with long carbon chains to sludge. In the WWTPs, most PFASs were not eliminated efficiently in conventional activated sludge treatment, while the membrane bio-reactor (MBR) and Unitank removed approximately 50% of long chain ( $C \geq 8$ ) perfluorocarboxylic acids (PFCAs). The daily mass loads of total PFASs in WWTPs were in the range of 1956–24773 mg in influent and 1548–25085 mg in effluent. PFASs were found at higher concentrations in the wastewater from plant A with some industrial wastewater input than from the other two plants (plant B and plant C) with mainly domestic wastewater sources. Meanwhile, the average total PFASs concentrations in the two selected DWTPs were detected at 4.74–14.3 ng/L in the influent and 3.34–13.9 ng/L in the effluent. In DWTPs, only granular activated carbon (GAC) and powder activated carbon (PAC) showed significant removal of PFASs. The PFASs detected in the tap water would not pose immediate health risks in the short term exposure. The findings from this study showed that effective treatment technology should be applied to eliminate this group of chemicals in the urban water cycle based on the precautionary principle.

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## 1. Introduction

Perfluoroalkyl substances (PFASs) are a class of synthetic organic compounds used in a wide range of industrial and commercial applications, including insecticide formulations, paper, textiles, fire retardants, pesticides, food packaging and other applications (Key et al., 1997; Kissa, 2001). PFASs have an anionic functional group and nonpolar perfluoroalkyl chain and can repel both water and oil. Because of the high energy of the C–F covalent bond (approximately 466 kJ/mol), PFASs are extremely resistant to biological and

chemical degradation and show various toxicological effects (Mattsson et al., 2015; Khalil et al., 2016). PFASs have been detected in water (Post et al., 2013; Pan et al., 2014a; Lorenzo et al., 2016), sediment (Naile et al., 2010; Zhao et al., 2013; Qi et al., 2016), sludge (Llorca et al., 2011; Armstrong et al., 2016), wildlife (Pan et al., 2014b; Letcher et al., 2015), and non-occupationally exposed humans throughout the world (Hansen et al., 2001; Buser and Scinicariello, 2016). Long chain PFASs are highly bioaccumulative in biota, with bioaccumulation factors (BAF) up to 23,000 for perfluorotridecanoic acid (PFTrDA) in rainbow trout (Banks et al., 1994; Martin et al., 2003), and they can be biomagnified along the food web (Xu et al., 2014). Among the various PFASs, the most intensively studied PFASs are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Loganathan et al., 2007; Yu et al.,

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2009a). 3M Company, the former largest global producer of perfluorooctanesulfonyl fluoride (PFOSF)-derived products, phased out production of PFOSF-derived products in 2002. Subsequently, PFOS and perfluorooctane sulfonyl fluoride (POSF) were listed as POPs under the Stockholm Convention in 2009 (UNEP, 2009), chemical contaminants on the Drinking Water Contaminant Candidate List CCL3 (USEPA, 2009). Additionally in 2016 EPA has established the health advisory levels at 70 parts per trillion (ppt) as the sum of PFOA and PFOS in drinking waters (USEPA, 2016) and PFOS was also added to the Directive 2013/39/EU as a priority substance to be monitored and regulated in all surface waters in Europe (<http://eur-lex.europa.eu/legal-content/IT/TXT/?uri=celexZ%3A32013L0039>).

Wastewater treatment plants (WWTPs) are considered to be a major source of PFASs to the aquatic environment (Schultz et al., 2006; Sinclair and Kannan, 2006; Zhang et al., 2013). The fate and removal of PFASs in WWTPs are important for understanding the mass flux to the receiving rivers and later occurrence in drinking water treatment plants (DWTPs). A previous work showed that PFOA could not be efficiently removed by activated sludge treatment, but perfluorohexane sulfonic acid (PFHxS) and perfluorohexanoic acid (PFHxA) were significantly decreased during the treatment (Schultz et al., 2006). The mass loads of PFOA, PFOS, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA) were found increased in the secondary biochemical treatment of a WWTP due to the biodegradation of precursors (Sinclair and Kannan, 2006). Concentrations of PFASs varied greatly among different WWTPs, and most studies focused on the activated sludge process (Bossi et al., 2008; Murakami et al., 2008; Guo et al., 2010; Pan et al., 2011; Zhang et al., 2013).

In DWTPs, previous studies showed that coagulation, sand filtration, ozonation, chlorination, and ultraviolet (UV) irradiation are unlikely to be effective for PFASs removal (Quiñones and Snyder, 2009; Eschauzier et al., 2010; Thompson et al., 2011). But granular activated carbon (GAC) and reverse osmosis (RO) can remove PFASs completely when GAC is new (Takagi et al., 2011; Flores et al., 2013). To the best of our knowledge, only a few previous studies investigated multiple PFASs levels in different stages of drinking water treatment plants and most of the previous works were mainly focused on PFOA and PFOS (Shivakoti et al., 2010; Takagi et al., 2011; Thompson et al., 2011; Eschauzier et al., 2012; Flores et al., 2013). Therefore, there is still a need to understand the occurrence, fate and removal mechanism of various PFASs in various WWTPs such as membrane bio-reactor (MBR) and Unitank process as well as in DWTPs.

The objective of this study was to determine the fate of 18 PFASs in urban water cycle. Three WWTPs and two DWTPs with different treatment technologies were selected for this study. Mass flows and remove efficiencies of PFASs in different treatment stages of WWTPs and DWTPs were investigated and compared. Then exposure risks of PFASs via drinking tap water were assessed for Guangzhou city, south China. The results from this study can help us better understand the contamination levels and removal mechanisms of PFASs during urban wastewater and drinking water treatment processes and provide scientific basis for the optimization of treatment techniques.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Eighteen perfluoroalkyl substances (PFASs) were selected for investigation in this study, and they are PFBA, PFPeA, PFH<sub>x</sub>A,

PFHpA, PFOA, PFNA, PFDA, PFDoDA, PFTeDA, PFUnDA, PFTrDA, PFBS, PFH<sub>x</sub>S, PFHpS, PFOS, PFDS, FOSA and EtFOSAA. Their full names, corresponding internal standards, formula and suppliers are given in Table S1. Purities of all the authentic standards were at least 95%. The details of chemicals and reagents used in this study are presented in Supporting Information (SI).

### 2.2. Sample collection

Three WWTPs (plant A, plant B and plant C) and two DWTPs (plant D and plant E) in Guangzhou city, south China were chosen for detailed investigation into removal mechanism in this study (Fig. S1). Plant A is located in an industrial zone in the east part of Guangzhou, where both industrial and domestic wastewaters are the input sources, while plant B and plant C are located at the central part of Guangzhou city, where domestic wastewater is the main source. Plant D and plant E are also located in the city center of Guangzhou. The plant E is a pilot plant with GAC and PAC used in parallel to optimize the process parameters. In addition, tap water samples from plant D and another two DWTPs (plant F and plant G) in Guangzhou city were also collected for the exposure risk assessment, whereas four source waters for the four DWTPs (Plants D, E, F, and G) were also sampled from the four corresponding rivers (Beijiang, Zhujiang, Dongjiang and Xijiang Rivers). Detailed information of these treatment plants are listed in Table 1, Figs. S1 and S2.

Sampling campaigns were carried out in 2014–2015. Water samples in individual treatment stage and dewatered sludge samples were collected as 24 h composite samples. Detailed sampling location is given in Fig. S2. Water and solid samples were collected in clean high density polyethylene (HDPE) bottles and polypropylene (PP) centrifuge tubes, respectively. Prior to the use, the containers were rinsed with Milli-Q water, methanol, and water from the corresponding sampling sites. The collected sludge samples were stored in a cold room (4 °C) in darkness once arriving at the laboratory, then lyophilized, homogenized and passed through a 0.83 mm mesh, and finally stored in –18 °C until extraction. Three replications were performed for each sample type.

### 2.3. Sample preparation and extraction

The collected water samples were filtered using glass fiber filters (GFF, Whatman, O.D. 47 mm, 0.7 μm), placed in a dark room at 4 °C and extracted within two days. The water samples were extracted by following a previous reported method (Taniyasu et al., 2005), while the lyophilized sludge samples were extracted according to another reported method (Higgins et al., 2005). Briefly the water samples (500 mL each) were extracted by solid phase extraction (SPE) using Waters Oasis WAX Cartridges. The sludge samples were extracted by ultrasonic-assisted extraction with solvents (acetic acid, methanol), followed by clean-up with WAX cartridges. Detailed procedure is given in the Supporting Information.

### 2.4. Instrumental analysis

The target chemicals were analyzed using Agilent 1200 liquid chromatograph (Agilent, Palo Alto, CA) coupled to a 6460 Triple Quadrupole mass spectrometer under electrospray negative ionization mode (HPLC-MS/MS, ESI<sup>-</sup>) with a Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA, USA). The MS/MS parameters for the instrument were optimized for individual analytes (Table S1). For detailed instrumental parameters, please refer to the Supporting Information.

**Table 1**  
Characteristics of the studied wastewater treatment plants (WWTPs) and drinking water treatment plants (DWTPs).

Plant code	Main process <sup>a</sup>	Disinfection treatment	HRT (h) <sup>b</sup>	Average flow (m <sup>3</sup> /day)	Population equivalent (× 10 <sup>4</sup> )	Sludge production (t/d)	Sludge loading rate (kgCOD/kgVSS.d)	Temperature (°C)	Main source
WWTPs A	Modified A <sup>2</sup> /O	UV	12.5	107000	41	30	0.18	24.0	Domestic and industrial wastewater
B	A <sup>2</sup> /O + MBR	UV	9.5	100000	13	36	0.12	28.6	Domestic wastewater
C	Unitank	Chlorine	13	220000	39	47	0.21	28.8	Domestic wastewater
DWTPs D	Ozonation + GAC	Ozonation	—	1000000	150	—	—	—	Beijiang River
E <sup>c</sup>	GAC&PAC	Chlorine	—	3000	—	—	—	—	Zhujiang River
F <sup>d</sup>	GAC + Chlorine	Chlorine	—	700000	100	—	—	—	Dongjiang River

<sup>a</sup> A<sup>2</sup>/O: Anaerobic + Anoxic + Aerobic; MBR: Membrane Bio-Reactor; GAC: Granular activated carbon; PAC: Powder activated carbon.

<sup>b</sup> HRT: hydraulic retention time.

<sup>c</sup> Plant E is a pilot plant built for research purpose.

<sup>d</sup> Only source water and tap water samples were collected from plant F and plant G, with no collection of water samples within the plants due to accessibility problem.

## 2.5. Quality control and method performance

Quality assurance and quality control (QA&QC) procedures were strictly observed during the whole experiment procedure, including sampling, extraction and analysis. Teflon coated lab ware and glassware were avoided during the experiment. In order to decrease the signal of the background, a ZORBAX SB-AQ trap column (Agilent technologies, 50 × 4.6 mm, 3.5 μm particle size) was installed in the water-eluent line, immediately above the solvent-mixing cell. An internal standard calibration method was used for the quantitative analysis. Procedural blanks and recoveries were evaluated for every batch of samples. The limit of detection (LOD) and limit of quantification (LOQ) were defined as three and ten times of signal to noise ratios calculated using the Agilent Masshunter qualitative software. The blanks were all below the LOQs and the recoveries mostly ranged between 70% and 110% in all three matrices. Detailed information about LOD, LOQ and recovery are given in Table S2.

## 2.6. Mass flow analysis

Mass flow approach was used to analyze a target chemical entering and leaving a treatment system. The average mass loads of each PFAS in aqueous and sludge samples were determined by multiplying the average PFAS concentration by flow rate and sludge volume. Aqueous phase removal percentage was calculated according to the equation below:

$$\text{Removal (\%)} = [(C_{\text{Influent}} - C_{\text{Effluent}}) / C_{\text{Influent}}] \times 100\%$$

where  $C_{\text{Influent}}$  and  $C_{\text{Effluent}}$  represent the concentrations of a target chemical in influent and effluent (ng/L) of a treatment unit, respectively.

The removal efficiency for individual PFAS in a treatment system was calculated by the equations below:

$$W_{\text{Loss}} = W_{\text{Influent}} - W_{\text{Effluent}} - W_{\text{Sludge}}$$

$$W_{\text{Loss}\%} = (W_{\text{Influent}} - W_{\text{Effluent}} - W_{\text{Sludge}}) / W_{\text{Influent}} \times 100\%$$

where  $W_{\text{Loss}}$  is the loss mass of a target chemical during the whole treatment process.  $W_{\text{Influent}}$  and  $W_{\text{Effluent}}$  represent the mass loads of the target chemical in influent and effluent (mg/d), respectively. And  $W_{\text{Sludge}}$  is the mass load of the chemical in sludge (mg/d). Mass loads of PFASs in aqueous phase and sludge can be calculated as follows:

$$W_{\text{Aqueous}} = C_{\text{Aqueous}} \times Q_{\text{Aqueous}} / 10^3$$

$$W_{\text{Sludge}} = C_{\text{Sludge}} \times Q_{\text{Sludge}} \times 0.25 / 10^3$$

where  $W_{\text{Aqueous}}$  (mg/d) is the daily mass load of a target chemical passing through individual treatment stage;  $Q_{\text{aqueous}}$  (m<sup>3</sup>/d) represents the daily water flow;  $W_{\text{Sludge}}$  (mg) is the daily mass load of the chemical in dewatered sludge.  $Q_{\text{Sludge}}$  (kg/d) denotes the average dry weight of dewatered sludge produced in the WWTP each day;  $C_{\text{Sludge}}$  (ng/g) is the concentration of the chemical in dry dewatered sludge, the water content in dewatered sludge was approximately 75%. The parameters used in the equations can be found in Table 1.

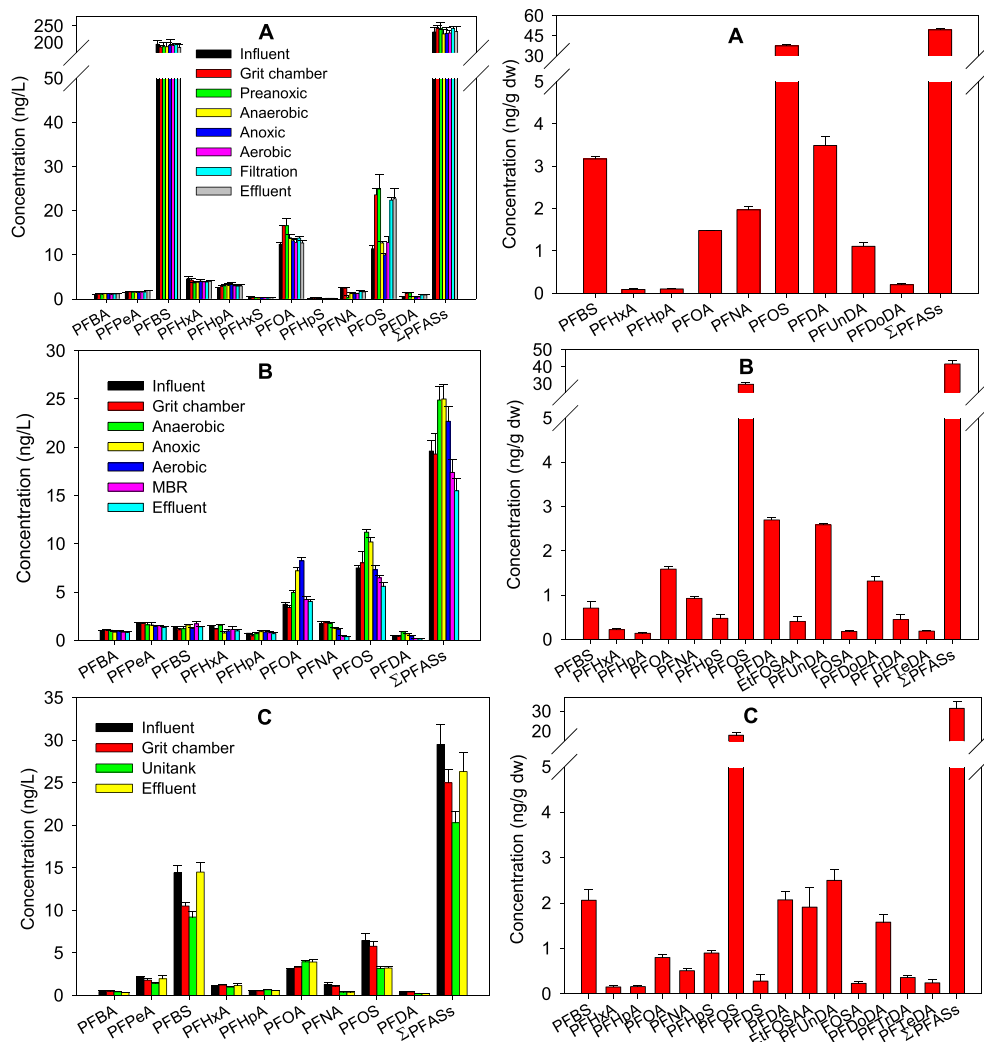
## 3. Results and discussion

### 3.1. Concentrations and composition profiles of PFASs in WWTPs

Aqueous and dewatered sludge samples from three wastewater treatment plants were analyzed for the PFASs. Concentrations of eighteen individual PFASs in water and sludge samples are illustrated in Fig. 1, Tables S3 and S4. Out of the 18 target compounds, 11 PFASs were detected in the aqueous samples of the three WWTPs. The average total PFASs concentrations in the aqueous phase of plant A, plant B and plant C were 232 ng/L, 19.6 ng/L, 29.5 ng/L in the influent, and 234 ng/L, 15.5 ng/L, 26.3 ng/L in the effluent, respectively. Specifically, for plant A, 11 PFASs were detected with concentrations ranging from 0.19 to 195 ng/L in the influent, and from 0.17 to 186 ng/L in the effluent. For the other two WWTPs, only 9 PFASs were detected in the influent with concentrations of 0.38–7.50 ng/L for plant B and 0.30–14.4 ng/L for plant C, and in the effluent with concentrations of 0.16–5.61 ng/L for plant B and 0.24–14.5 ng/L for plant C.

PFBS, PFOS and PFOA were the predominant target compounds in the three WWTPs with their detection frequency of 100%, which is consistent with some previous studies (Loganathan et al., 2007; Lin et al., 2010; Arvaniti et al., 2012; Zhang et al., 2013). This could be related to the fact that PFBS, PFOS and PFOA are the most frequently used PFASs in industrial applications. PFBS was dominant in the influent and effluent with its concentrations of 1.29–195 ng/L and 1.41–186 ng/L, respectively. PFOS was the second predominant compound, with its concentrations of 6.45–11.4 ng/L in the influent and 3.21–22.7 ng/L in the effluent, respectively. PFOA was the third predominant compound in the three plants with its concentrations at 3.04–12.4 ng/L in the influent and 3.93–12.7 ng/L in the effluent, respectively (Table S3).

Among all PFASs, the largest contributor was PFBS, which contributed 79.5% and 55.1% to the total PFASs in the effluent of plant A and plant C, respectively. However, in plant B, PFOS was the largest contributor, which contributed approximated to 38% in the



**Fig. 1.** Concentrations of PFASs in aqueous phase and dewatered sludge of the three wastewater treatment plants. Error bars represent standard deviations of the measured concentrations ( $n = 3$ ).

influent and 36% in the effluent. The concentrations of PFBS in plant A were much higher than plant B, which can be explained by the difference in source wastewater. The plant B mainly treats domestic wastewater from the central part of Guangzhou, while plant A has industrial wastewater input from an industrial park with textile industry. PFBS concentration in the influent of plant C was also quite high (up to 14.4 ng/L), resulting from some industrial wastewater discharge. Since PFOS based products were phased out by 3M Company in 2002 (UNEP, 2009), PFBS as a substitute for PFOS has been widely used in various applications. However, the PFOS and PFOA concentrations were still higher than 10 ng/L in plant A, which indicates that PFOS, PFOA or related precursors are still in use.

The increased concentrations for some PFASs from influent to effluent could be due to the biodegradation of precursors (Sinclair and Kannan, 2006; Schultz et al., 2006). Previous studies reported that *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), 8:2 FTOH and 10:2 FTOH can be degraded to form PFOS, PFOA, PFDA and PFUnDA (Lange, 2002; Kannan et al., 2005), and polyfluoroalkyl phosphate esters can be biologically transformed to PFCAs, resulting in the increased concentrations of these chemicals in WWTPs (Lee et al., 2010).

In the aqueous samples, the PFASs with short carbon chains

(C4–C8: PFOS, PFOA, PFBA, PFPeA, PFBS, PFHxA and PFHpA) exhibited much higher detection frequencies (42–100%) and higher concentrations than those PFASs with long carbon chains (C9–C14: PFDA, PFUnDA, PFDODA, PFTrDA, PFTeDA and PFDS) (Fig. 1 and Table S3). This could be due to more usage of the short chain PFASs than the long chain PFASs, or biodegradation of PFASs-related precursors generating the short chain PFASs (Lange, 2002; Kannan et al., 2005; Lee et al., 2010).

For the dewatered sludge samples, 14 out of 18 PFASs were detected in the three WWTPs (Fig. 1 and Table S4). The highest total concentrations of PFASs in sludge was found in plant A, followed by plant B and plant C. For plant A, 9 PFASs were detected with concentrations of 0.09–37.5 ng/g. For plant B and plant C, 14 PFASs were detected with concentrations of 0.14–29.8 ng/g and 0.15–18.0 ng/g, respectively.

PFOS was dominant in sludge samples of all three plants with concentrations of 37.5 ng/g, 29.8 ng/g and 18.0 ng/g in the plant A, plant B and plant C, respectively. PFDA was the second predominant compound in the sludge samples with concentrations of 3.49 ng/g, 2.70 ng/g and 2.07 ng/g in the plant A, plant B and plant C, respectively.

In contrast, the composition pattern of PFASs in sludge was totally different from that in the aqueous phase. The long chain

PFASs had relatively high detection frequencies and concentrations in sludge in comparison with those in aqueous phase (Fig. 1 and Table S3). These can be explained by higher adsorption ability of the long chain PFASs to sludge as a previous study found that  $\text{CF}_2$  moiety contributed 0.50–0.60 log units to  $K_{oc}$ , suggesting that the carbon chain length of PFASs is the dominant structural feature influencing the sorption process (Higgins and Luthy, 2006).

The concentrations of PFOS and PFOA in the aqueous phase of the three WWTPs were almost at the same level, but the concentration of PFOS in sludge is approximately 20 folds higher than PFOA concentrations (Fig. 1). This could be due to the fact that sulfonate moiety contributed an extra 0.23 log units to the measured  $K_{oc}$  when compared to PFCAs (Higgins and Luthy, 2006). Thus PFOS partitions onto sludge in preference to PFOA, which generates the big concentration difference in sludge and wastewater.

### 3.2. Concentrations and composition profiles of PFASs in DWTPs

The aqueous samples from two DWTPs (plant D and plant E) were analyzed for the target PFASs, and the results are shown in Fig. 2 and Table S5. The water sources for plant D and plant E were from Beijiang River and Zhujiang River, respectively (Table 1 and Fig. S1).

Out of the 18 target compounds, 10 PFASs were detected in the aqueous samples of the two DWTPs in Guangzhou, south China. The ten PFASs were also detected in the source waters for the DWTPs at the total concentrations of 1.67–19.43 ng/L (Table S5).

For plant D, the total concentrations of PFASs were 4.74 ng/L in the influent and 4.81 ng/L in the effluent. For individual PFAS compound, 8 out of 18 PFASs were detected in the plant with its concentrations ranging from 0.12 to 1.90 ng/L in the influent and from 0.10 to 1.80 ng/L in the effluent. For plant E, 10 out of 18 PFASs were quantified with its concentrations ranging from 0.14 to 5.00 ng/L in the influent. After treated with GAC and PAC, the concentrations of PFASs were detected at 0.18–5.20 ng/L and <LOD–1.60 ng/L, respectively.

PFOS was dominant in plant D with its concentrations of 1.90 ng/L in the influent and 1.80 ng/L in the effluent. For plant E, both PFOA and PFOS were the predominant compounds, with their concentrations of 5.00 ng/L and 4.99 ng/L in the influents, respectively. However, the concentrations of PFOA and PFOS in PAC effluents (0.28 ng/L and 0.44 ng/L) were much lower when compared with those in GAC effluents (4.20 ng/L and 5.20 ng/L, respectively) (Table S5). In the DWTPs, PFOS contributed approximated to 40% and 35% to the total PFASs in the influent of plant D and plant E,

respectively. This is consistent with other studies (Jin et al., 2009; Mak et al., 2009), which indicates PFOS is the major PFAS in tap water of Guangzhou.

The distribution pattern of PFASs in the DWTPs was similar to that for the WWTPs, the PFASs with short carbon chains (C4–C8: PFOS, PFOA, PFBA, PFPeA, PFBS, PFHxA and PFHpA) were detected at all treatment units, while those PFASs with long carbon chains (C9–C14: PFUnDA, PFDoDA, PFTTrDA, PFTeDA and PFDS) were seldom detected.

So far, several previous studies have reported the occurrence of PFASs, especially PFOA and PFOS in WWTPs and tap water globally (Ericson et al., 2008; Huset et al., 2008; Jin et al., 2009; Quiñones and Snyder, 2009; Quinete et al., 2009; Arvaniti et al., 2012; Zhang et al., 2013; Schwanz et al., 2016). However, very limited information is available for the various PFASs in DWTPs (Shivakoti et al., 2010; Takagi et al., 2011; Thompson et al., 2011; Eschauzier et al., 2012; Flores et al., 2013). The concentrations of PFOS and PFOA in influent and effluent of WWTPs and tap water around the world are listed in Tables S6 and S7. In general, PFOS concentrations in aqueous and sludge samples of WWTPs in this study were higher than those in most other WWTPs in China, but much lower than some WWTPs in other countries. Similarly with WWTPs, the PFOS concentrations in tap water in this study were higher than in most previous studies in China. However the PFOA concentrations in WWTPs and tap water of this study were lower than those reported in the literature (Tables S6 and S7). This can be explained by the presence of PFOS-related industries in this region, which results in high PFOS concentrations and low PFOA concentrations in this region. This is consistent with previous studies (So et al., 2007; Mak et al., 2009). It should also be remembered that the selected WWTPs in the present study were used to treat mainly domestic wastewaters, with exception of plant A having a small proportion of industrial wastewaters. Thus the differences in PFASs concentrations in WWTPs or DWTPs are related to regional industrial structures and input water sources.

Generally, PFASs concentrations in WWTPs are positively linked to those in tap water as these chemicals are basically not removed by conventional WWTPs, then released into rivers and eventually to some water sources for DWTPs. According to the data reported by other studies in China, the highest concentration of PFOS in tap water was 14.8 ng/L in Shenzhen (Jin et al., 2009), which is almost at the same level as the present study. This can be explained by the fact that some DWTPs in Guangzhou and Shenzhen share the same raw drinking water source from Dongjiang River. The greatest concentration of PFOS in Shanghai was 7.6 ng/L (Mak et al., 2009), which is approximately half of that found in the present study.

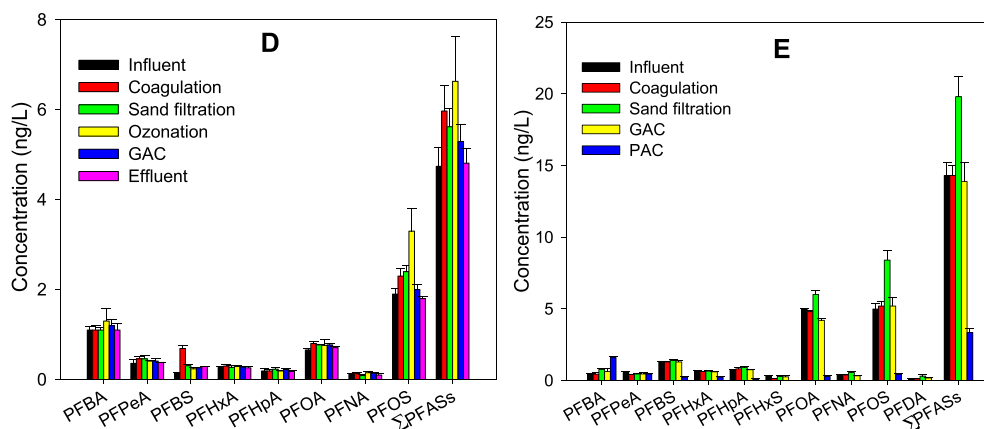


Fig. 2. Concentrations of PFASs in aqueous phase of selected two drinking water treatment plants. Error bars represent standard deviations of the measured concentrations ( $n = 3$ ).

Meanwhile, the highest concentration of PFOA was 78.4 ng/L in Shanghai (Mak et al., 2009), which is much higher than the concentration in Guangzhou of this work. This may be caused by the different industrial structures of these two cities (Mak et al., 2009; Zhang et al., 2012).

### 3.3. Removal efficiencies and mechanisms of PFASs in WWTPs and DWTPs

The concentrations and fate of PFASs in treatment systems varied depending on the treatment process used. The aqueous phase removal percentages in whole treatment process and individual treatment units of the five treatment systems are presented in Table 2. To be specific, the removal percentages ranged from –119% to 100% and –104% to 100% for the eleven detected PFASs in whole treatment process and individual treatment units of the five treatment systems, respectively.

The removal percentages ranged from about –99% for PFOS to 33% for PFNA using the A<sup>2</sup>O (Anaerobic + Anoxic + Aerobic) treatment in plant A, indicating that conventional activated sludge treatment could not remove PFASs efficiently in WWTPs, which is consistent with the previous results (Schultz et al., 2006; Yu et al., 2009a). The removal of PFNA in plant A could be attributed to its adsorption to sludge. Most compounds in the influent and effluent of plant A were found almost at the same levels, suggesting that biodegradation in activated sludge process and UV degradation played negligible role in their removal. This can be explained by the structures of PFCAs and PFSAs containing strong C–F bond and the electron withdrawing functional groups –COOH and –SO<sub>3</sub>H, also indicating that these compounds will be likely resistant to oxidation, biodegradation, and reaction by hydroxyl radicals (Rahman et al., 2014). Plant B consists of conventional A<sup>2</sup>O combined with advanced MBR process, of which the MBR removed approximately 49% for PFOA, 55% for PFNA and 56% for PFDA, respectively; in contrast the removal of the short chain PFASs was very limited. The reason might be that PFCAs with large molecules adsorbed on

sludge could not pass through the membrane. Plant C employs Unitank process, which also showed relatively good removal efficiencies compared with plant A, and removed 64%, 46% and 47% of PFNA, PFOS and PFDA, respectively. The results could be explained by relatively longer hydraulic retention time in Unitank process and adsorption of the long chain PFASs onto sludge. Besides, chlorine disinfection employed in plant C resulted in the removal rates of –57% and –39% for PFBS and PFPeA, respectively. This indicates chemical transformation of the longer chain PFASs under chlorination process.

Ozonation is the only chemical process used in the plant D, PFNA and PFOS concentrations increased during this process (ozone dosage: 1.0–2.5 mg/L; primary ozonation zone), while other compounds were almost at the same levels, indicating ozonation could not efficiently remove PFASs, which is consistent with the result from a previous study (Schröder and Meesters, 2005). This also suggests that the influent contained PFAS related precursors, which generated PFNA and PFOS under ozonation process. PFOS and PFNA can be produced from the degradation of precursor compounds (Nabb et al., 2007; Rhoads et al., 2008). These precursors are mostly polyfluorinated compounds containing C–H bonds which can be oxidized. In plant D, GAC removed 39% of PFOS, suggesting its physical adsorption to GAC. However, the capacity of adsorption for other PFASs was very low, which might be caused by the long-term use of the GAC resulting in adsorption saturation. A previous study found that GAC was unable to effectively remove PFOA and PFOS when not reactivated for more than one year (Takagi et al., 2011). Higher adsorption ability were found for longer chain PFASs compared to short chain PFASs by GAC in plant E (Table 2 and Table S5), this can be explained by the increased K<sub>oc</sub> values with increasing carbon chain length (Higgins and Luthy, 2006). Other processes such as sand filtration had no effect in removing PFASs in the present study, which is in agreement with other studies (Takagi et al., 2008; Rumsby et al., 2009; Eschauzier et al., 2012).

Plant E was chosen to investigate different removals of PFASs by PAC and GAC. After sand filtration, the water flow divided into two

**Table 2**  
Aqueous removal percentages of PFASs in different stages of three WWTPs and two DWTPs.

		PFBA	PFPeA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFHpS	PFNA	PFOS	PFDA	ΣPFASs
A	Grit chamber	–7.2%	–7.4%	3.7%	7.2%	–19%	24%	–34%	–5.9%	–1.1%	–106%	–170%	–4.4%
	Preanoxic	1.3%	4.0%	–0.5%	15%	–4.7%	3.5%	–0.2%	–58%	5.1%	–5.4%	–5.1%	–0.7%
	Anaerobic	–10%	1.1%	0.3%	–4.3%	–3.1%	34%	16%	56%	41%	49%	60%	7.0%
	Anoxic	–2.5%	2.4%	–2.4%	–7.1%	–9.2%	–35%	5.1%	7.7%	15%	22%	22%	–0.6%
	Aerobic	10%	–5.2%	0.3%	4.9%	12%	–22%	3.0%	–12%	–9.1%	–29%	–6.5%	–0.6%
	Filtration	–4.9%	–1.1%	–1.3%	0.1%	1.5%	41%	–7.7%	–6.3%	–51%	–75%	–96%	–6.1%
	UV	–2.1%	–25%	4.3%	–3.9%	–0.9%	–70%	8.1%	–9.6%	16%	–1.4%	–2.3%	3.6%
	Total	–15%	–32%	4.5%	13%	–23%	21%	–2.4%	12%	33%	–99%	–87%	–1.3%
B	Grit chamber	–13%	0.9%	16%	20%	36%	NA	8.4%	NA	–5.0%	–7.3%	–14%	1.4%
	Anaerobic	3.0%	7.9%	–12%	–32%	–49%	NA	–46%	NA	4.1%	–39%	–108%	–29%
	Anoxic	18%	2.1%	–31%	52%	–32%	NA	–45%	NA	2%	9.0%	25%	–0.4%
	Aerobic	–13%	7.7%	22%	–27%	4.9%	NA	–14%	NA	12%	28%	33%	9.6%
	MBR	11%	–5.4%	–37%	–16%	9.6%	NA	49%	NA	55%	11%	56%	23%
	UV	2.4%	12%	18%	13%	11%	NA	4.3%	NA	23%	13%	18%	11%
	Total	13%	24%	–9.3%	33%	3.7%	NA	–8.4%	NA	78%	25%	57%	21%
C	Grit chamber	2.2%	15%	27%	–17%	–0.8%	NA	–8.8%	NA	18%	10%	–33%	15%
	Unitank	5.7%	22%	12%	20%	–28%	NA	–19%	NA	64%	46%	47%	19%
	Cl <sub>2</sub>	21%	–39%	–57%	–20%	13%	NA	0.3%	NA	2.2%	–1.8%	–15%	–29%
	Total	27%	7.3%	–0.8%	–13%	–12%	NA	–29%	NA	71%	50%	20%	11%
	D	Sand filtration	0.1%	0.4%	56%	8.4%	–20%	NA	3.6%	NA	33%	–4.3%	ND
Ozonation	–18%	9.0%	21%	–6.1%	18%	NA	2.3%	NA	–67%	–37%	ND	–18%	
GAC	7.5%	1.5%	–7.8%	3.4%	–18%	NA	–1.9%	NA	3.1%	39%	ND	20%	
Total	0.9%	–4.9%	–119%	3.7%	6.0%	NA	–6.8%	NA	15%	5.5%	ND	–1.4%	
E	Coagulation	–4.3%	25%	–2.1%	2.0%	–9.4%	47%	4.7%	NA	–3.8%	–7.1%	15%	0.5%
	Sand filtration	–76%	–17%	–8.2%	–4.2%	–12%	–86%	–25%	NA	–45%	–61%	–157%	–39%
	GAC	–20%	1.1%	6.9%	7.3%	19%	9.5%	30%	NA	40%	38%	42%	30%
	PAC	–104%	1.3%	84%	64%	90%	100%	95%	NA	100%	95%	100%	83%

NA: not available; ND: not detected.

directions with half to GAC and half to PAC. After GAC process, PFASs concentrations except PFPeA were all declined, and the removal rates ranged from 7.0% to 42%. Particularly, the removal rates for PFOA, PFNA and PFOS were very similar with values around 40%. These removal efficiencies were attributed to the adsorption of PFASs to the GAC, which suggests that the GAC can partially remove some PFASs in DWTPs. Meanwhile, the concentrations of PFASs were decreased sharply after PAC treatment, with removal rates for most target chemicals ranging from 80% to 100%, of which PFHxS, PFNA and PFDA were removed by 100% while PFOA and PFOS removed by 95% and 95%, respectively. The different removal rates with the GAC and PAC could be attributed to different particle sizes of the activated carbon materials. PAC has a smaller size compared with GAC, and it has more micropores, surface functional groups and active adsorption sites, leading to the higher adsorption capacity (Yu et al., 2009b). Thus, PAC would adsorb PFASs faster than GAC due to its smaller particle size resulting in larger specific surface area for the same amount of carbon, extra surface functional groups, and shorter internal diffusion distances (Yu et al., 2009b; Hansen et al., 2010). Yu et al. (2009b) found GAC and PAC were reached equilibrium at 168 h and 4 h for PFOA and PFOS, respectively. An additional explanation of the poorer performance of GAC compared with PAC may be due to the rigidity of the CF<sub>2</sub> backbone which may render its sorption to the inner pore surface area of GAC energetically unfavorable (Hansen et al., 2010).

#### 3.4. Mass flow in treatment plants

Daily average mass loads and mass loss of PFASs were calculated by multiplying average PFASs concentrations and recorded average daily hydraulic flows in the three WWTPs and two DWTPs, and the results are shown in Tables S8–S10.

The daily mass loads of total PFASs were in the range of 1956–24773 mg in influent and 1548–25085 mg in effluents of three WWTPs. For the DWTPs, the daily mass loads of total PFASs in the influent and effluent of plant D were 4729 mg and 4819 mg, respectively. Daily mass loads of the three predominant compounds PFBS, PFOS and PFOA in the influent of three WWTPs were 20,822 mg, 1222 mg and 1326 mg in the plant A, 128 mg, 751 mg and 373 mg in the plant B, 3156 mg, 1419 mg and 668 mg in the plant C, respectively. And the mass loads for the three chemicals in the effluent of three WWTPs were 19,885 mg, 2430 mg, 1359 mg in the plant A, 141 mg, 562 mg, 403 mg in the plant B, and 3184 mg, 704 mg, 863 mg in the plant C, respectively (Tables S8 and S9).

Mass flow of most PFASs in individual treatment of each WWTP were almost at the same level. This can be explained that PFOS and PFOA are known to be non-biodegradable by an activated sludge process (Lange, 2002). As fully fluorinated homologues, other PFASs, like PFBA, PFPeA, PFHxS, PFBS, PFNA, PFDA and PFUnDA are also considered to be non-biodegradable. PFOA and PFOS loading in the dissolved phase increased in activated sludge process, which is consistent with previous researches in municipal WWTPs (Schultz et al., 2006; Yu et al., 2009a) since biodegradation of precursors such as fluorotelomer alcohols (FTOHs), perfluoroalkyl phosphates (PAPS), or fluorotelomer sulfonates (FTSs) can generate PFOS and PFOA (Lange, 2002; Kannan et al., 2005; Rhoads et al., 2008; Lee et al., 2010).

Daily mass loadings for PFASs in the sludge were also calculated in the three WWTPs using average daily dewatered sludge volume (Table 1). For mass loads in the sewage sludge, the daily discharge amounts of total PFASs in the three WWTPs (plant A, plant B and plant C) were 367 mg, 370 mg and 359 mg, respectively. PFOS and PFOA mass loads in sludge were in the range of 211–281 mg/d and 9.40–14.3 mg/d in the three WWTPs, respectively. The short chain PFASs (C ≤ 8) mainly existed in the aqueous phase, while long chain

PFASs (C > 8) were mainly in the sludge phase (Table S8). The longer chain PFASs which is more hydrophobic, exhibits the higher accumulation in solid phase. The PFOS is more bioaccumulative than PFOA, as reported in previous studies (Higgins and Luthy, 2006; Sinclair and Kannan, 2006).

Averaged mass proportions of the detected PFASs in effluent, dewatered sludge and total loss relative to the calculated initial mass loading are illustrated in Fig. 3. As can be seen, the mass loads of PFASs were mainly in aqueous phase. The average loss of PFNA was more than 50% and PFDA around 40% in the three WWTPs. As for each WWTP, the losses of total PFASs in the plant A, plant B and plant C were –2.8%, 1.7% and 5.6%, respectively (Table S8).

For the two DWTPs, the daily mass load of total PFASs in plant D changed from 4729 mg/d in the influent to 4819 mg/d in the effluent; while in plant E, it changed from 43 mg/d in the influent to 42 mg/d in the effluent by GAC, but was reduced to 10 mg/d by PAC (Table S10). The reduction of mass flow of PFASs in DWTPs was attributed to the physical adsorption of GAC and PAC.

#### 3.5. Exposure risks via tap water consumption

As most of tap water were drunk after boiling (100 °C) in China, tap water samples (F) in our laboratory were collected to figure out how individual PFAS concentration changed. It should be noted that the tap water in our lab was supplied by another DWTP of Guangzhou, and the results are presented in Fig. S3. As illustrated, the concentrations of all detected PFASs excluding PFBA in the boiled tap water increased 16–46% compared with those in the original tap water. This resulted from the transformation of the PFAS precursors. In contrast, the concentration of PFBA decreased, which could be explained by its thermal instability. In order to assess the exposure risks via tap water consumption in whole Guangzhou city, tap water samples supplied by three different DWTPs (plant D, F and G) in Guangzhou metropolitan area were collected and analyzed for the PFASs concentrations (Table S11). Human health risks were assessed for the exposure to PFOS, PFBS, PFOA and PFBA via tap water consumption in Guangzhou using risk quotient (RQ) approach based on the measured concentrations in tap water and Health Advisories or Health Risk Limits (HRLs) (Minnesota Department of Health, 2011; USEPA, 2016). The Health Advisories or HRLs used in the risk assessment and the assessment results are listed in Table 3.

As can be seen, the calculated RQs for PFOS, PFOA, PFBA, PFHxS,

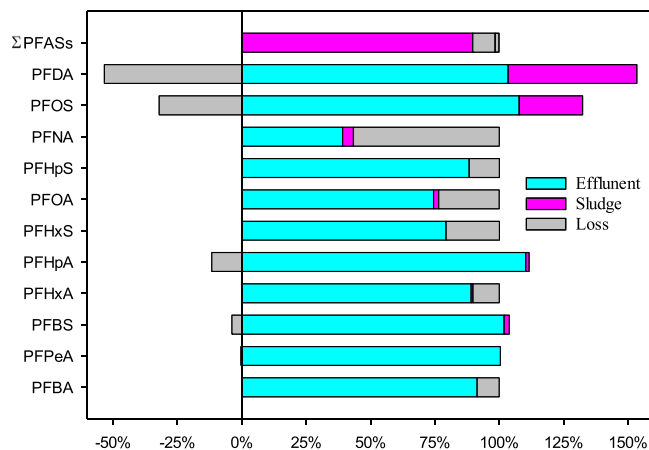


Fig. 3. Mass proportions of the detected PFASs in effluent, dewatered sludge and total loss relative to the calculated initial mass loading in three wastewater treatment plants.

**Table 3**  
HRLs (ng/L), and measured concentrations (ng/L) and risk quotients (RQs) for PFASs in tap water from three drinking water plants in Guangzhou city.

Compounds	Health Advisories or HRLs	Plant D		Plant F		Plant G	
		Concentration <sup>a</sup>	RQ	Concentration <sup>a</sup>	RQ	Concentration <sup>a</sup>	RQ
PFBA	7000	1.10 ± 0.14	1.57 × 10 <sup>-4</sup>	0.88 ± 0.03	1.26 × 10 <sup>-4</sup>	0.38 ± 0.10	5.43 × 10 <sup>-5</sup>
PFBS	7000	0.29 ± 0.01	4.14 × 10 <sup>-5</sup>	3.20 ± 0.16	4.57 × 10 <sup>-4</sup>	0.09 ± 0.01	1.29 × 10 <sup>-5</sup>
PFOA	70	0.71 ± 0.02	1.0 × 10 <sup>-2</sup>	2.1 ± 0.07	3.0 × 10 <sup>-2</sup>	0.16 ± 0.04	2.3 × 10 <sup>-3</sup>
PFOS	70	1.80 ± 0.04	2.6 × 10 <sup>-2</sup>	10.0 ± 0.45	1.4 × 10 <sup>-1</sup>	0.60 ± 0.14	8.6 × 10 <sup>-3</sup>

<sup>a</sup> Mean ± standard deviation (n = 3).

PFBS, PFHxA and PFPeA from drinking tap water were much lower than 1, indicating that individual PFASs in the tap water of Guangzhou should not pose health risks to local residents in the short term exposure. However, long-chain PFASs are highly bio-accumulative and persistent in the environment and biota, even in human (Martin et al., 2003; Post et al., 2013). Caution is still needed in terms of the risks from this group of chemicals, especially for the long term exposure.

#### 4. Conclusions

The results from this study demonstrated that PFASs were widespread in urban water cycle in Guangzhou, south China. PFASs were released from WWTPs at several hundreds to thousands milligrams per day. PFBS, PFOS and PFOA were the predominant PFASs in aqueous phase of the treatment systems, while PFOS is the only predominant compound in the dewatered sludge. The observed distribution pattern of PFASs differed between wastewater and sludge, indicating that PFASs with long carbon chains showed strong adsorption onto the sludge. Conventional activated sludge process used in WWTPs could not efficiently remove PFASs, while MBR and Unitank could effectively remove the long chain PFASs with satisfactory removal rates. In DWTPs, activated carbon could partially remove PFASs, with PAC being more effective than GAC. Moreover, other treatment processes including UV, chlorine disinfection, ozonation and sand filtration showed ineffectiveness in the removal of PFASs. Fortunately, risk assessment showed no immediate risks to local residents from PFASs in tap water in Guangzhou for the short term exposure. However, effective treatment technologies should be applied to remove this group of persistent chemicals based on the precautionary principle.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.10.045>.

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