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

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A B S T R A C T

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.

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 per-fluorooctanesulfonyl 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 per-fluorohexanoic 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$_X$A,

PFHpA, PFOA, PFNA, PFDA, PFDoDA, PFTeDA, PFUnDA, PFTrDA, PFBS, PFH$_X$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 polyprolene (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-) 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.