Evaluation of perfluorinated compounds in seven wastewater treatment plants in Beijing urban areas

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The presence of perfluorinated compounds (PFCs) in seven major wastewater treatment plants (WWTPs) in Beijing was investigated in the current study. We detected nine PFCs in all the wastewater and sludge samples. Perfluorooctane acid (PFOA) is the dominant PFCs in influents and effluents, while perfluorooctane sulfonate (PFOS) is the major contaminant in sludge. The highest PFC concentration was found in plants at Qinghe and Jiuxianqiao WWTP, while the lowest was found at Fangzhuang WWTP. The total values of PFC range from 2.88 to 176 ng/L in influents, from 5.48 to 498 ng/L in effluents, and from 1.21 to 32.0 ng/g (dry wt) in sludge. The fact that effluents usually contain higher levels of PFCs than influents suggests that additional PFCs are produced during the wastewater treatment processes. However, PFOS decreases in effluents than in influents in 62% of the water samples. This may be due to the adsorption and removal of the sludge during the active process. Perfluoroalkyl carboxylates (PFCAs) were found significantly correlated with each other in the effluents, which may indicate their similar sources or the existence of their potential precursors in the wastewater or treatment processes. The mass flows of PFC discharges into WWTPs are 0.4–51.4 mg/day, and the mass flows of Σ PFCs in effluents exceed those in influents by 127%. Domestic and commercial wastewaters are suggested to be the major sources of PFC pollution in WWTPs in Beijing.

perfluorinated compounds, wastewater, sludge, mass flow

1 Introduction

Perfluorinated compounds (PFCs) are a kind of environmental contaminants and have been detected in the atmosphere [1, 2], water [3, 4], soil [5, 6] and wildlife [7, 8] all over the world, even in Antarctic and Arctic areas [9, 10]. Due to their long-term persistence and potential hazards in the environment, PFCs are of increasing interest in recent years. Although the specific environmental degradation mechanisms remain undefined yet, recent advances in the knowledge of PFCs have led to the increasing analysis and studies on the environmental distribution, fate and degradation mechanisms. Perfluorooctane sulfonate (PFOS) is the most prominent PFCs in environmental samples. Previous

reports have implied that PFOS is highly bioaccumulative in biota [11], and can be magnified along the aquatic food webs [12]. In May 2009, perfluorooctane sulfonic acid, as well as its salts and perfluorooctane sulfonyl fluoride (POSF), was acknowledged as one of the persistent organic pollutants (POPs) under the Stockholm Convention [13]. However, a large variety of PFCs related chemicals, such as perfluorocarboxylic acids with shorter or longer alkyl chains and telomers, which may be degraded to PFCs, are still in use without any official ban.

It has been assumed that the contaminated wastewaters from domestic, commercial, or industrial areas may be one of the principal and significant potential sources of PFCs [14, 15]. WWTPs are believed as a major source of PFCs to natural waters. Boulanger et al. reported that WWTP effluent was the largest source of PFCs discharged into the Lake Ontario [15]. Murakami et al. also proposed that most PFCs

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in surface waters during dry weather are derived from wastewater and manufacturing effluents [16]. The occurrence of PFC contamination in wastewater treatment plants (WWTPs) has been observed in several countries [17–19], although the distribution and fate of PFCs during the wastewater treatment process remain vague. The occurrence of PFCs in sludge from several WWTPs suggests a portion of PFCs in wastewater may transfer to the solid during the treatment process. For strongly sorbing compounds, the sludge in WWTPs may be a significant sink and transforming pathway in WWTPs. Higgins et al. has reported that substances such as 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) and 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA) are present in sludge [5], which may be degraded to PFOS. Some other research also showed that fluorotelomer alcohol will rapidly and irreversibly adsorb onto the solid phase such as soil or sludge and may be transferred to the related PFCs through the biodegradation of microorganisms [20, 21]. Under this condition, these solids will become another source of PFCs when discharged into the environment through the disposal of the biosolid or landfill, and cause potential risks to humans and the environment.

To our knowledge, this is the first paper on systematical investigation of the PFCs levels in wastewater and sludge from municipal wastewater plants in China. In current study, the raw influents, secondary effluents and activated sludge were collected from seven major WWTPs in Beijing, China. From these samples we analyzed the distribution and contamination situation of PFCs. And the mass loadings of PFCs in wastewater were calculated to estimate its potential risk for environment and humans. The results of this study would help us to understand the PFCs' transport and fate in WWTPs and identify an important potential source of PFCs into the Chinese aquatic environment.

2 Materials and methods

2.1 Sample collection and preparation

On Jan 16, May 29 and Sep 24 of 2008, influents (water entering the plants), effluents (water before discharging) and the activated sludge samples were collected from seven main municipal WWTPs in operation in Beijing, China. They are Gaobeidian (GBD), Jiuxianqiao (JXQ), Qinghe (QH), Xiaohongmen (XHM), Fangzhuang (FZ), Wujiaocun (WJC) and Beixiaohe (BXH). The detailed information about the WWTPs is listed in Table S1 (Supporting Information). Generally, these seven WWTPs were all operated with primary and secondary treatment processes despite some minor differences among them.

For the influents and effluents, the 24 h composite samples were collected using flow proportional samplers on a weekly basis. These wastewater samples were collected using polypropylene bottles (500 mL) that have been pre-

viously rinsed in the order of *n*-hexane, acetone, methanol and water. Water samples were stored below 4 °C on arriving at the laboratory and extracted within one week. These samples were first filtered with nylon film (0.45 μm). After filtration, 200 mL of the sample was spiked with 5 ng of sodium perfluoro-1-[1,2,3,4-¹³C₄]octanesulfonate (¹³C₄-PFOS, Wellington Laboratories) as the internal standard and extracted with Oasis® HLB cartridge (6 cc, 200 mg; Waters Corp. Milford, USA) [22]. The final elution was concentrated to 1 mL for injection.

Sludge samples were collected in polyethylene (PE) bags and transported to the laboratory on ice and immediately frozen-dried. The sludge was ground with a quartzes pestle and mortar, and then stored at –20 °C until analysis. The sludge samples were pretreated with methanol sonication. Generally, 0.1 g of the dry sludge was spiked with 5 ng of ¹³C₄-PFOS, sonicated in 5 mL of methanol at 60 °C for 20 min, and then the supernatant was collected after centrifugation (3000 r/min). The procedure was repeated for four times. Each supernatant was mixed together and the total volume of the extract was approximately 20 mL. To remove the impurity, the extract was further extracted with a HLB cartridge following the SPE procedure the same as the wastewater.

2.2 Quality control

The experimental information has been described in our previous study [23]. Only disposable PP tubes or containers were employed during the sample preparation and analysis procedure. The calibration curve was prepared with a series of concentrations (0.05–50 μg/L) and showed strong linearity with correlation coefficients > 0.99. The instrumental limit of detection (LOD) for PFOS was determined as three times the signal-to-noise ratio (S/N = 3), equal to 0.014 μg/L for PFHxS, 0.015 μg/L for PFOS, 0.1 μg/L for PFHpA and PFOA, 0.03 μg/L for PFNA, PFDA, PFUnDA, 0.04 μg/L for PFDoDA, and 0.02 μg/L for PFTA. The spiked recoveries of nine PFCs were all > 70% in the sludge and water matrix, except PFTA (26% in sludge and 42% in water). Standard solutions (1 μg/L) were run every 10 injections during the analysis to monitor the stability of the system. The procedure blank was also checked in each batch analysis to serve as quality controls.

3 Results and discussion

3.1 PFCs in wastewaters

PFC concentrations detected in wastewater samples are summarized in Table 1. From all the quantitatively determined PFCs in this study, PFOA was the predominant PFCs. It has been detected in all samples, and accounted for 19.7%–94.4% (median 52.5%) of the total PFCs (Figure 1). This suggests that there must be a source of PFOA

Table 1 Mass loadings of seven WWTPs in Beijing (mean (range)) (mg/d)

		PFHxS	PFHpA	PFOA	PFOS	PFNA	PFDA	PFUnDA	Σ PFCs
GBD	influent	1.3 (0.8–1.3)	1.3 (0.6–2.4)	9.2 (4.4–13.1)	1.0 (<0.07–1.9)	0.6 (0.4–0.9)	<0.15 (<0.15–0.3)	<0.15 (<0.15–0.3)	13.6 (8.5–18.2)
	effluent	2.7 (1.9–3.4)	5.1 (2.1–7.2)	13.6 (12.6–15.2)	2.8 (0.8–3.9)	2.6 (1.1–3.6)	1.3 (0.7–2.0)	0.6 (0.2–0.9)	30.9 (25.9–35.6)
JXQ	influent	0.1 (<0.01–0.25)	0.9 (0.1–2.4)	2.7 (1.2–4.3)	0.6 (0.2–0.9)	1.7 (0.2–4.7)	0.1 (<0.03–0.3)	0.05 (<0.03–0.07)	6.3 (1.9–11.2)
	effluent	0.2 (0.05–0.3)	18.8 (0.3–55.2)	10.7 (2.3–20.8)	0.7 (0.1–1.4)	5.7 (0.3–16.2)	0.8 (0.07–2.1)	1.0 (<0.03–3.0)	38.3 (4.2–99.6)
QH	influent	0.2 (0.1–0.4)	2.2 (0.4–4.6)	36.0 (14.2–54.0)	5.0 (1.4–12.0)	8.1 (0.2–23.8)	0.1 (<0.08–0.26)	<0.08 (<0.08–0.26)	51.5 (26.9–70.4)
	effluent	0.3 (0.3–0.3)	1.8 (0.9–3.2)	19.0 (16.8–20.8)	0.9 (0.8–1.2)	0.7 (0.3–1.3)	0.4 (<0.08–0.9)	<0.08 (<0.08–0.9)	23.5 (19.7–27.5)
BXH	influent	0.04 (<0.007–0.09)	0.5 (<0.05–1.2)	1.1 (0.6–1.7)	0.2 (0.08–0.2)	0.1 (<0.02–0.4)	0.04 (<0.02–0.06)	0.03 (<0.02–0.07)	1.9 (0.8–3.7)
	effluent	0.1 (<0.007–0.2)	0.4 (0.2–1.0)	1.4 (0.8–2.1)	0.2 (0.06–0.3)	0.1 (0.04–0.3)	0.07 (0.05–0.1)	0.03 (<0.03–0.07)	2.4 (1.3–3.7)
XHM	influent	0.5 (<0.04–1.1)	11.3 (0.4–32.7)	12.0 (3.2–21.8)	1.1 (0.6–1.5)	3.7 (0.3–10.2)	0.7 (<0.09–1.6)	0.6 (<0.09–1.5)	30.0 (5.4–70.2)
	effluent	1.1 (0.3–2.1)	14.1 (0.6–40.8)	12.5 (3.4–26.2)	3.2 (0.3–7.3)	4.4 (0.4–12.1)	0.9 (0.2–1.8)	0.8 (<0.09–2.3)	37.4 (7.1–87.6)
FZ	influent	0.03 (<0.003–0.08)	0.1 (0.02–0.3)	0.09 (0.05–0.1)	0.06 (0.03–0.08)	0.03 (<0.006–0.08)	0.01 (0.006–0.03)	<0.006 (<0.006–0.07)	0.4 (0.1–0.7)
	effluent	0.05 (<0.003–0.1)	0.4 (0.03–1.1)	0.3 (0.09–0.5)	0.1 (0.03–0.4)	0.1 (0.02–0.3)	0.02 (<0.006–0.06)	0.02 (<0.006–0.07)	1.0 (0.2–2.0)
WJC	influent	0.08 (<0.006–0.2)	1.3 (<0.04–4.0)	0.9 (0.2–1.8)	0.3 (0.1–0.4)	0.4 (<0.01–1.2)	0.06 (<0.01–0.2)	0.06 (<0.01–0.2)	3.1 (0.4–7.7)
	effluent	0.1 (0.08–0.2)	1.0 (0.06–2.9)	0.9 (0.4–1.9)	0.09 (0.04–0.2)	0.3 (<0.01–0.9)	0.06 (<0.01–0.1)	0.06 (<0.01–0.2)	2.6 (0.8–6.3)

Figure 1 Composition profiles of PFCs in wastewaters of the seven WWTPs.

constantly discharged into the aqueous system and then the WWTPs. The concentrations of PFOA ranged from 1.33 to 135 ng/L (median 10.2 ng/L) in influents and from 3.8 to 104 ng/L (median 13.1 ng/L) in effluents (Table S2). PFOA concentration was generally higher in effluents than in influents (Figure 2 and Table S2), except those samples collected on May 29 and Sep 24 from plant QH, and from plant WJC (Sep 24). The increase of PFOA in effluents may be due to the wastewater treatment processes that might cause

biodegradation of some precursors or the potential additional sources. This phenomenon has also been reported in studies in New York [19], Kentucky and Georgia [24], and also in Denmark [25]. Earlier studies in New York (NY), Cleveland (OH) and North Carolina have reported that the PFOA concentrations were about several hundreds of ng/L in the effluents in WWTPs [14, 19, 26, 27]. In our study from the seven WWTPs, the PFOA concentrations were much higher in wastewaters from plants QH and JXQ than

Figure 2 PFOA concentrations in influents and effluents (ng/L).

those from the other plants, while the lowest PFOA was found in plant FZ. Generally, for influents, the PFOA concentrations were in the order of $QH > XHM > JXQ > BXH \approx WJC > GBD > FZ$, while for effluents, the order was $JXQ > QH > XHM > BXH \approx GBD > WJC > FZ$. Because of the similarities in the operating process of the seven WWTPs, the differences of the PFOA concentration are most likely due to the diversity of their receiving wastewater. Concentrations of PFOA were found the highest in samples collected on May 29 (Figure 2). PFOA concentrations in influents collected in May were about 1.6- to 8.6-fold higher than those collected in January and September. Similarly, PFOA concentrations in effluent waters collected in May were about 1.9- to 5.2-fold higher than those collected in January and September in plants XHM, WJC, BXH and FZ (Table S2), though the seasonal variation was not significant ($p > 0.05$).

Contrary to the previous report [28], in which PFHpA was not found in wastewater, PFHpA was the second dominant PFCs and detected in 91% of the wastewater samples in the current study. PFHpA concentrations ranged from 0.5 to 54.5 ng/L (median 1.18 ng/L) in influents and from 0.8 to 276 ng/L (median 2.38 ng/L) in effluents. The extreme value 276 ng/L was found in effluents collected on May 29 from plant JXQ. It was also found that PFHpA concentrations in influents collected in May were higher than those from other sampling dates, ranging from 3.1 to 100 folds. Higher PFHpA concentration in samples was also found in effluents collected in May from most of the seven plants (XHM, WJC, BXH and FZ), and the ratio of May/Jan or May/Sep (PFHpA concentrations) ranged from 4.0 to 63. PFOS and PFHxS were found in over 90% of the water samples, though PFHxS was in lower levels than PFOS. There were little variations of the concentrations among the seven WWTPs for both compounds. The PFOS concentration was at similar levels as reported in studies from Schultz *et al.* [17, 18], Sinclair and Kannan [19] but lower than those from Murakami *et al.* and Becker *et al.* [22, 28].

The C9-11 acids were also found in more than 50% of the water samples, and their concentrations and frequency

were found to correlate with the carbon length. As shown in Table S2, the longer-chain PFCs were found in higher concentration levels and more often detected in the effluents than influents. Typically, PFDoDA concentrations were measured only in effluents at over 0.2 ng/L. In addition, we can also consider this as an increase of PFDoDA concentration in effluents. Similar results were also reported in the USA and Japan [17–19, 24, 28]. Overall, the prevalent increase of the PFC concentrations in the effluent versus the influent suggested that additional PFCs may be produced during the wastewater processes.

3.2 Potential sources of PFCs in wastewaters

In previous studies, industrial and commercial wastewaters have been implicated as a likely source of PFCs [5, 29]. The existence of PFOA and PFOS in WWTPs suggests that PFOA, PFOS or related precursors are still in use and constantly released to the aqueous system, though the exact source of PFOA, PFOS and other PFCs in the wastewater has not been well defined yet. It has been assumed that the direct release of PFCs to municipal wastewater may occur through the production, use or disposal of consumer products that contain the related compounds [18]. Scientists have proposed that the everyday cleaning of fluorochemical-treated products in hospitals or shopping malls would be a significant source of PFCs to wastewaters. According to a study of WWTPs conducted in Iowa City, IA [29], care and cleaning of treated surfaces may be a source of PFCs to the WWTPs from down-to-drain disposal. It has also been hypothesized that the highly substituted perfluorooctane surfactants commercially used as fabric protectors can be transformed to PFOS and PFOA, and become a possible source of PFCs in the wastewater.

The seven WWTPs involved in the current study mainly processed the wastewater from the domestic sources. Especially, the plant QH, where the highest PFOA concentrations were found, received only domestic and commercial wastewaters. This result implied that PFOA can reach high concentrations without industrial influence. The domestic wastewaters may take major responsibility for the PFC contamination in the wastewater, at least in the WWTP plants we studied. It is interesting to note that in plants GBD and XHM, the two largest plants in Beijing, PFC concentration levels were comparable with those of the other WWTPs. Plant GBD is the largest WWTP in Beijing, located at the eastside of the city. It accounts for the treatment of 40% of municipal wastewater of Beijing. Both GBD and XHM plants treat domestic and industrial wastewaters, but the ratio (domestic/industrial) is unknown. The low PFC levels in these two plants indicated that the industrial influence on PFC profiles in wastewater in Beijing was not significant. The much lower concentrations of PFCs in plant FZ were probably due to the relatively small population it serves.

Boulanger *et al.* have testified that perfluorooctane sul-

fonate potassium salt (PFOSulfinate) and perfluorooctane-sulfonylethylamide (N-EtFOSA), as well as several other precursors, may be transformed to PFOS during the wastewater treatment [29]. This could result in higher concentrations of PFOS in effluents. The studies on WWTPs in Kentucky and Georgia also indicated that PFOS concentrations increased significantly in effluents [24]. However, in the current study a decrease of PFOS in effluents versus influents was observed in 62% of the water samples. This indicates that the transformation of PFOS observed in the studies above may not occur in the WWTPs in Beijing. As PFOS can be easily adsorbed to the solid due to its hydrophobic characteristic, the decrease may be due to the adsorption and removal by the sludge. The reduction of PFOS in effluents has also been observed in WWTPs by Schultz *et al.* [17].

The existence of potential sources of PFCs in the form of precursor compounds or other telomers within the wastewater treatment, such as POSF (perfluorooctane sulfonyl-fluoride)-based perfluorochemicals and fluorotelomer alcohols (FTOHs), has been reported in several earlier studies [20, 30, 31]. These compounds have been widely used as surfactants and in the process of a variety of products from the 1950s and some of them are still in use today. During the activated sludge treatment process, these compounds were biodegraded, becoming a likely source of PFCs in the effluent [17–19]. Particularly, perfluorocarboxylates have been demonstrated to be the end biodegradation products from FTOHs in activated sludge [21, 32]. In the current study, most perfluorocarboxylic acids (C7, C9, C10 and C11) were found significantly correlated with each other in effluents. This suggests that the sources of these compounds in wastewater are highly correlated, and there should be some additional sources of PFCs in the wastewater treatment processes which produce PFC products. (The extreme values of plant JXQ on May 29 were omitted when the correlation was calculated.) PFOA and PFOS concentrations

were found associated with each other in wastewaters in plants from the USA [24], while in the current study, no significant correlation was found for PFOA and PFOS. PFHxS concentration between the influent and the effluent was found significantly and positively correlated in this study.

3.3 PFCs in sludge

In water samples, PFOA accounts for the majority of the detected PFCs. However, this dominance was changed in the sludge. PFOS was the dominant compounds in all sludge samples (Figure 3 and Table S3). This finding provides a favorable indication of the fate of PFOS. This result was similar to a study from Higgins *et al.* (2005), but different from a report from Sinclair and Kannan, who found that PFOA was the dominant PFCs in the sludge [19]. In the current study, PFOS was the prominent PFCs in 79% of sludge samples (Figure 3), with concentrations ranging from 0.69 to 16.7 ng/g (median 3.14 ng/g, dry wt). The highest concentration was found in plant JXQ, and the lowest in plant FZ. PFOS levels were much lower as compared to those analyzed in WWTPs from the USA and Denmark [5, 24, 25]. PFHxS was not found in sludge samples.

PFOA was found in 59% of the sludge samples, with the highest concentration (12.6 ng/g, dry wt) from plant JXQ (Sep 24) (median 2.58 ng/g, dry wt). PFHpA, PFNA, PFDA, PFUnDA and PFDoDA were also detected. Detectable PFHpA (1.50 ng/g – 7.15 ng/g, dry wt) was only found in six samples, all of which were collected on Jan 16. PFDA and PFUnDA were detected in 90.9% of sludge samples, with concentrations ranging from <0.3 to 4.10 ng/g (median 1.8 ng/g, dry wt) and from <0.3 to 2.65 ng/g (median 0.75 ng/g, dry wt), respectively. The detected frequency for PFNA was 54.5% and 59.1% for PFDoDA in sludge samples. Concentrations of PFDA were found higher than those of PFNA, PFUnDA and PFDoDA in most sludge samples. A

Figure 3 Composition profiles of PFCs in sludge.

previous study has also reported high concentrations of PFDA or PFUnDA than PFNA in the sludge [5]. It was reported by Dinglasan *et al.* [20] that FTOHs are possibly degraded under aerobic conditions to form even-chain-length perfluorocarboxylates, which may explain the greater concentrations of PFOA, PFDA and PFDoDA than those of odd-chain length compounds. PFDA concentrations were also found correlated with PFOS, PFOA and PFDoDA in sludge, which may further confirm the FTOHs as potential sources of PFCs in the sludge during wastewater treatment. Generally, PFC concentrations in the sludge were at the similar level among the seven WWTPs except plant FZ, where only low levels of PFOS, PFNA and PFUnDA were found (Table S3).

3.4 Mass flows in wastewaters

Daily mass flows were calculated for PFCs in influents and effluents of the seven WWTPs and shown in Table 1. The mass flows of Σ PFCs were in the range of 0.4–51.5 mg/d in influents and 1.0–38.3 mg/d in effluents. Each day, there was 106.8 mg of PFCs discharged into WWTPs in Beijing urban areas, and mass flows of Σ PFCs in effluents exceeded those in influents by 127%. The mass flow analysis has been conducted in several studies. Due to the diversity of PFCs analyzed in the reported studies, the most prominent PFCs, the mass flow of PFOA was analyzed to compare with the results of other studies. In the current study, mass flows of PFOA ranged from 0.3 to 19.0 mg/d in effluents (Table 1). Loganathan *et al.* reported mass flows of PFOA were 2715–14320 mg/d from a Kentucky WWTP, and 394–5600 mg/d in a Georgia WWTP [24]. Yu *et al.* reported mass flows of PFOA were 739–47191 mg/d in a Singapore WWTP [33]. A little lower mass flows of PFOA were reported by Sinclair and Kannan (16.5–30.6 mg/d) in New York WWTPs [19]. These values were much higher than the results from the current study. Therefore, we proposed that Beijing is not facing severe PFC contamination in the wastewater treatment system as other cities.

4 Conclusions

PFCs were found in all water and sludge samples from the seven major WWTPs in Beijing urban areas, indicating PFC contaminants are discharged into the WWTPs in Beijing. PFOA was the predominant PFC in water samples, while PFOS was the dominant compound in sludge. PFHpA rather than PFOS was the second dominant PFC detected in 91% of the wastewater samples. Generally, PFC concentrations in effluents were greater than those in influents except PFOS, which was possibly attributed to the additional sources or the biodegradation of potential precursors in the process. Considering the decrease of PFOS in effluents and the dominance of PFOS in sludge, we assumed that the ad-

sorption of sludge may play a significant role in the PFOS distribution in wastewater treatment processes. Among the seven WWTPs, the highest PFC concentrations were found in QH and JXQ, while the lowest was found in PZ. The mass loadings of PFCs in wastewater were calculated to be several tens of mg/d from the WWTPs in Beijing.

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