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Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China

Wei Zhang [a], Yating Zhang [a], Sachi Taniyasu [b], Leo W.Y. Yeung [b,c], Paul K.S. Lam [c], Jianshe Wang [a], Xinhai Li [a], Nobuyoshi Yamashita [b,*], Jiayin Dai [a,*]

[a] Key Laboratory of Animal Ecology and Conservation Biology, Institute of Zoology, Chinese Academy of Sciences, Beijing 100101, PR China
[b] Environmental Measurement Group, National Institute of Advanced Industrial Science and Technology, Onogawa 16-1, Tsukuba, Ibaraki 305-8569, Japan
[c] State Key Laboratory in Marine Pollution, Department of Biology and Chemistry, City University of Hong Kong, HK SAR, PR China

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ABSTRACT

Wastewater treatment plants (WWTPs) are a significant source for poly-/perfluoroalkyl substances (PFASs) entering the environment. The presence of PFASs in twenty-eight municipal WWTPs from eleven cites in economically developed areas of China were screened. Overall, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were dominant in wastewater and sludge, and were not effectively removed during wastewater treatment. Elevated influent concentration ratios of perfluorobutanoic acid (PFBA) to PFOA and perfluorobutane sulfonate (PFBS) to PFOS in some WWTPs suggested that short chains substitution were adopted in these cities. Cluster analysis showed treatment processes had important impacts on PFASs profiles in effluent and sludge. Average concentration of total PFCAs in influent from each city and its gross domestic product (GDP) had significant positive correlation. This study provides a snapshot of both domestic and industrial discharges of PFAS to WWTPs as well as PFAS discharge from WWTPs to the aquatic environment in China.

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1. Introduction

Poly-/perfluoroalkyl substances (PFASs) are a class of man-made chemicals, which have been used in products such as surfactants, fire retardants, coating materials, and other applications for more than 50 years (Kissa, 2001). These compounds were released into the environment during production, application, and waste disposal (Boulanger et al., 2005a; Huset et al., 2008). Recognized for their thermally and chemically stable properties, PFASs are an important emerging pollutant with broad environmental distribution in the atmosphere (Jahnke et al., 2007; Loewen et al., 2008), water (Ju et al., 2008; Kim and Kannan, 2007), soil (Higgins et al., 2005; Nakata et al., 2006), and wildlife (Kannan et al., 2002; Li et al., 2008). Perfluoroalkyl acids (PFAAs) mainly exist in the aqueous phase due to their relatively high water solubility and low volatility, with PFAA water pollution increasing in recent years (Bao et al., 2009; Boulanger et al., 2005b). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), two important and well-known PFAAs, have been detected in rain water, surface water, groundwater, seawater, and tap water throughout the world (Prevedouros et al., 2006; Guo et al., 2010; Fujii et al., 2007). Different drinking, river, and groundwater contamination incidents related to PFASs have been reviewed (Rumsby et al., 2009). Apart from the PFAA burden resulting from fluorochemical manufacturing plant waste discharge, effluents of wastewater treatment plants (WWTPs) are a major source of PFAAs to the aquatic environment (Prevedouros et al., 2006; Loganathan et al., 2007). In Japan, the PFOS concentrations found in rivers were positively correlated to the PFOS discharge of effluent from WWTPs (Murakami et al., 2008). Wastewater treatment in some WWTPs in Switzerland has been shown inefficient to remove PFASs in sewage, and the PFAS effluent then discharged into the Glatt River (Huset et al., 2008). A recent study has suggested WWTP effluents to be a major source of PFAS discharged into Lake Ontario (Boulanger et al., 2005b). Although perfluorooctanesulfonyl fluoride-based products phased out in 2002, the occurrence of PFOS from WWTPs has still been observed in several countries in recent years (Guo et al., 2010; Schultz et al., 2006a,b; Sinclair and Kannan, 2006).

At present, only limited research has focused on PFAS in wastewater from urban areas; such studies confined to either small

* Corresponding authors.
E-mail addresses: nob.yamashita@aist.go.jp (N. Yamashita), daijy@ioz.ac.cn (J. Dai).

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numbers of WWTPs or limited number of PFASs (only PFOS or PFOA) (Boulanger et al., 2005a; Becker et al., 2008). According to the Ministry of Environmental Protection of China, in 2009 there were 1993 WWTPs in China; more than 5897 billion tons of wastewater was discharged. To our knowledge, however, only two studies have investigated PFAS levels in WWTPs: four in Shenyang and seven in Beijing (Sun et al., 2011; Pan et al., 2011). To date, no comprehensive research has been conducted on PFAS pollution status in economically developed areas of China, which are recognized as having large human populations and intensive anthropogenic activities.

Dealing with increasing sewage due to the increasing number of WWTPs is a major environmental issue in China. The production of sewage sludge is estimated to be approximately 0.3%–0.5% of the volume or 1%–2% of the mass flow of wastewater, and the amount will increase 0.5–1 times after the implementation of advanced water treatment technology (Yang, 2001). Although the city sewage treatment rate in China is relatively low at present, the amount of sludge is increasing at an annual rate of 10%. Currently, the major outlet of sewage sludge is agricultural land and landfill (Bhogal et al., 2003; Walker et al., 2003). In 2008, annual sludge production was about 1.3 million tons dry sludge, and 45% of the dry sludge was applied to agricultural land (Wang et al., 2006). Studies have demonstrated that PFAS contaminated sludge-amended soil had adverse effects on local environments. Of particular concern is the ability of transport of PFASs into crop plants from such soil, thereby increasing human and livestock exposure to PFASs consumed with contaminated food crops (Lindstrom et al., 2011; Sepulvado et al., 2011). It is important to determine PFAS levels in sludge before the application to agricultural land. However, limited published information on PFASs in sewage sludge exists in China.

To investigate the distribution and fate of PFASs from municipal WWTPs in China, 16 PFASs in wastewater and 15 PFASs in sludge were measured in 28 WWTPs from 11 cities; most WWTPs were from economically developed areas of China. In addition, changes in PFAS concentrations in Beijing city were explored in wet and dry seasons. The relationship between PFAS concentrations in influent and city gross domestic product (GDP) was also investigated. Finally, annual mass flows of PFASs in effluent and production of sewage sludge from WWTPs were estimated. The results of this study provided a snapshot of the PFAS pollution status from WWTPs in economically developed areas of China.

2. Materials and methods

2.1. Standards and reagents

The details of standards and reagents are given in Supporting information.

2.2. Sample collection

Influent, effluent, and sludge samples ($n = 78$) were collected from 28 WWTPs in 11 cities in China. Beijing, Shanghai, and Guangzhou represented economically developed areas in China. Sampling locations are shown in Fig. S1 (Supporting information). The population density and GDP for each city and descriptions of the WWTP treatment processes are given in Table S1 (Supporting information). These WWTPs serving an area with no known manufacturing or industrial application of PFASs were reported. Two WWTPs (DQ WWTP in Shanghai and JXZ WWTP in Nanjing) received wastewater from both residential and industrial areas. All samples were collected between September 21 and November 27, 2009 and stored in polypropylene (PP) bottles and kept frozen (−20 °C) until analysis.

2.3. PFAS extraction

Unfiltered sewage samples were extracted using Oasis® WAX cartridges based on published methods (Taniyasu et al., 2003; Yamashita et al., 2005; Taniyasu et al., 2008). Briefly, the cartridge was pre-conditioned by the passage of a sequence of 4 mL of 0.1% NH_4OH/methanol, 4 mL of methanol, and 4 mL of Milli-Q water. One nanogram of mass-labeled standards including $^{13}C_4$–PFBA, $^{13}C_4$–PFOA, $^{13}C_5$–PFNA, $^{13}C_2$–PFDA, and $^{13}C_4$–PFOS were spiked into the samples before extraction. These mass-labeled standards were used to check for overall recoveries of the analytical procedures. The sewage sample (100 mL) was diluted to 250 mL with Milli-Q water and then loaded onto the pre-conditioned cartridges at a rate of 1 drop per second.

One gram of dry sludge sample was first diluted into 1 mL of Milli-Q water in a glass tube, 1 ng of mass-labeled standards including $^{13}C_4$–PFBA, $^{13}C_4$–PFOA, $^{13}C_5$–PFNA, $^{13}C_2$–PFDA, and $^{13}C_4$–PFOS were spiked into the samples. Details of the extraction procedures are given in the Supporting information.

2.4. Instrumental analysis

Separation of the target analytes was performed using an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) coupled to a tandem mass spectrometer in negative ionization mode. Details are given in the Supporting information. The MS/MS parameters for the instrument were optimized for individual analytes and are shown in Tables S2 and S3 in the Supporting information.

2.5. Quality control and quality assurance

An external calibration curve was prepared from a series of concentrations (0, 2, 10, 50, 200, 1000, 5000, and 20,000 pg/mL) and standard deviations from the theoretical values were less than 20%. Procedural blanks and recoveries were evaluated in every batch of extraction following the procedure described above. The blanks were all below the limit of quantifications (LOQs) and mean recoveries ranged from 75% to 109% (Table S2 and S3). Matrix recoveries ranged from 72% to 122% (Table S3). The concentrations of PFASs in the samples were not corrected for their corresponding recoveries. Detailed information is given in the Supporting information.

2.6. Statistical analysis

Raw data were analyzed using SPSS for Windows 16.0 Software (SPSS, Inc., Chicago, IL). The plot was created by Origin 8.5 (OriginLab, MA, USA). Principal component analysis (PCA) and cluster analysis were conducted using R statistical Software. Canonical correlation analysis (CCA) was performed with SAS 9.2 software (SAS Institute Inc., Cary, North Carolina). Complete linkage was used in the cluster analysis. Non-parametric Spearman rank correlation analysis was used to evaluate relationships among PFASs in influent, effluent, and sludge samples. For PCA, the raw data (measured concentrations of PFASs) was suitably transformed. Values below limits of detection were assigned a value of one-half of the limits of detection. The concentrations of PFASs were log-transformed and standardized by subtracting the mean and dividing by the standard deviation to remove the different magnitude of PFAS concentrations (Yannarell and Triplett, 2005).

3. Results and discussion

3.1. Concentrations and composition profiles of PFASs in wastewater

Concentrations of PFASs detected in wastewater samples are summarized in Table S4. The 16 PFASs concentrations ranged from 0.04 to 91 ng/L in influent and 0.01 to 107 ng/L in effluent. PFOA was in greatest concentrations in both influents and effluents, and ranged from 2 to 91 ng/L in influents and 3 to 107 ng/L in effluents, respectively. The highest PFOA levels in influent and effluent were both found at DQ WWTP in Shanghai (Fig. S2A). This high PFOA level might originate from the surrounding textile mills, paper factories, printing plants, and metallurgical plants; industrial wastewater accounted for 25% of influent of DQ WWTP. Studies have shown industrial activity to be an important source of PFASs to the aquatic environment (Prevedouros et al., 2006; Kunacheva et al., 2011) because the PFOA level in industrial wastewater is consistently higher than those in municipal wastewater (Guo et al., 2010). The second dominant compound was PFOS, which ranged from 1 to 32 ng/L in influent and 1 to 67 ng/L in effluent. The highest PFOS concentrations in influent and effluent were both found at JXZ WWTP, the biggest WWTP in Nanjing City (Fig. S2A and S2B). There are several chemical factories (e.g., pesticide plants, detergent plants, and petrochemical plants) in the service range of JXZ WWTP. Therefore, the high PFOS levels in the present study were believed to originate from the pesticide and chemical factories around that region. Further work will evaluate the discharge of PFASs in different chemical-related factories. The high PFOA and

PFOS levels in influents in the present study suggest that PFOA, PFOS, and/or related precursors be still in use (Pan et al., 2011).

Compared the PFOA and PFOS influent concentrations to those in other countries, such as the Kanto region, Japan (PFOA: 14–41 ng/L; PFOS: 14–336 ng/L), Denmark (PFOA: <LOQ – 24 ng/L; PFOS: <LOQ – 10 ng/L), Korea (PFOA: 2–615 ng/L; PFOS: <LOQ – 68 ng/L), and Northern Bavaria of Germany (PFOA: 20–73 ng/L; PFOS: 1–85 ng/L), the mean concentrations of PFOA (18 ng/L) and PFOS (9 ng/L) in the present study were lower, except for Denmark (Bossi et al., 2008; Guo et al., 2010; Murakami et al., 2009; Becker et al., 2008).

For the composition profiles of PFASs in wastewater (Fig. S2C and S2D), short-chain PFCAs (PFPrA, PFBA, and PFHxA) were at a higher proportion than long-chain PFCAs (PFNA, PFDA, PFUnDA, PFDoDA, and PFTeDA). This may relate to short-chain PFCA-based compounds being produced and consumed more frequently than long-chain ones, or the degradation of fluorotelomer based products giving rise of short-chain PFCAs (Boulanger et al., 2005a; Rayne et al., 2009). In addition, there was a higher proportion of even-chain PFCAs (PFDA, PFOA, PFHxA, and PFBA) than odd-chain PFCAs (PFUnDA, PFNA, PFHpA, and PFPeA). The relationship between the even- and odd-chain PFCAs was significantly correlated ($R^2 = 0.73$ for influent, $R^2 = 0.60$ for effluent, $p = 0.01$, Fig. S2E). This pattern was consistent with the biodegradation products of FTOHs, which yield predominantly even-chain length PFCAs under aerobic conditions (Dinglasan et al., 2004).

3.2. Concentrations and composition profiles of PFASs in sludge

With the exception of FOSA, 15 PFASs were detected in sludge (Table S5). Ranging from 1 to 23 ng/g d.w, PFOS was the dominant compound in all sludge samples, with the highest concentration found in KFQ WWTP in Dalian (Fig. S3A). In the present study, PFOS concentrations in sludge were much lower compared to those from other countries (Higgins et al., 2005; Guo et al., 2010; Loganathan et al., 2007; Sinclair and Kannan, 2006; Bossi et al., 2008). In contrast to the dominance of short-chain PFCAs in wastewater, long-chain PFCAs in sludge accounted for the major portion of total PFAS (Fig. S3B). PFBA was also detected in the WWTP sludge in China, with concentrations ranging from 0.6 to 4.6 ng/g d.w. (65% frequency of detection). The highest concentration of total PFASs was found in KFQ WWTP from Dalian followed in QY WWTP from Shanghai. Even-chain length PFCAs (PFDA, PFOA, PFHxA, and PFBA) had a higher relative proportion than the odd-chain length PFCAs (PFUnDA, PFNA, PFHpA and PFPeA) in sludge. The relationship between the even-chain and odd-chain PFCAs was significantly correlated ($R^2 = 0.77$, $p = 0.01$, Fig. S3C).

3.3. Cluster analysis and principal component analysis for PFASs in wastewater and sludge

Cluster analysis was performed to identify the homogeneous groups of sampling sites. We conducted cluster analysis to aggregate the PFAS patterns (six dominant PFASs) of 28 WWTPs in influents (Fig. 1A), effluents, and sludge (Fig. S4A and 4B), respectively.

Seven well-differentiated clusters were observed in the influent (Fig. 1A): cluster 1 was characterized by low concentrations of PFOS and PFOA, which included XHM, GBD, QH, WJC, JXQ, FZ and BXH in Beijing, WT and WXY in Hefei, NQ and ZH in Ningbo, TS in Bangbu, CB in Wuxi, XL in Guangzhou, CL in Dalian, and ZA in Foshan; cluster 2 with TH and LC in Wuxi was characterized by high composition of PFHxA, cluster 3 with TP in Shanghai was characterized by high composition of PFPrA; cluster 4 with LWZ and SHH in Wuhan was characterized by high composition of PFBA; cluster 5 with JXZ in Nanjing, DTS and LD in Guangzhou, and KFQ in Dalian was characterized by high composition of PFOS; cluster 6 included CTP in Hefei characterized by high composition of PFOA; and cluster 7 included QY and DQ in Shanghai with high total PFAS concentration inputs compared to other WWTPs as well as substantially high levels of PFOA and PFHxA. High specific per capita discharges can be an indicator of potential industrial inputs (Huset et al., 2008; Clara et al., 2009). Our results indicated that industrial

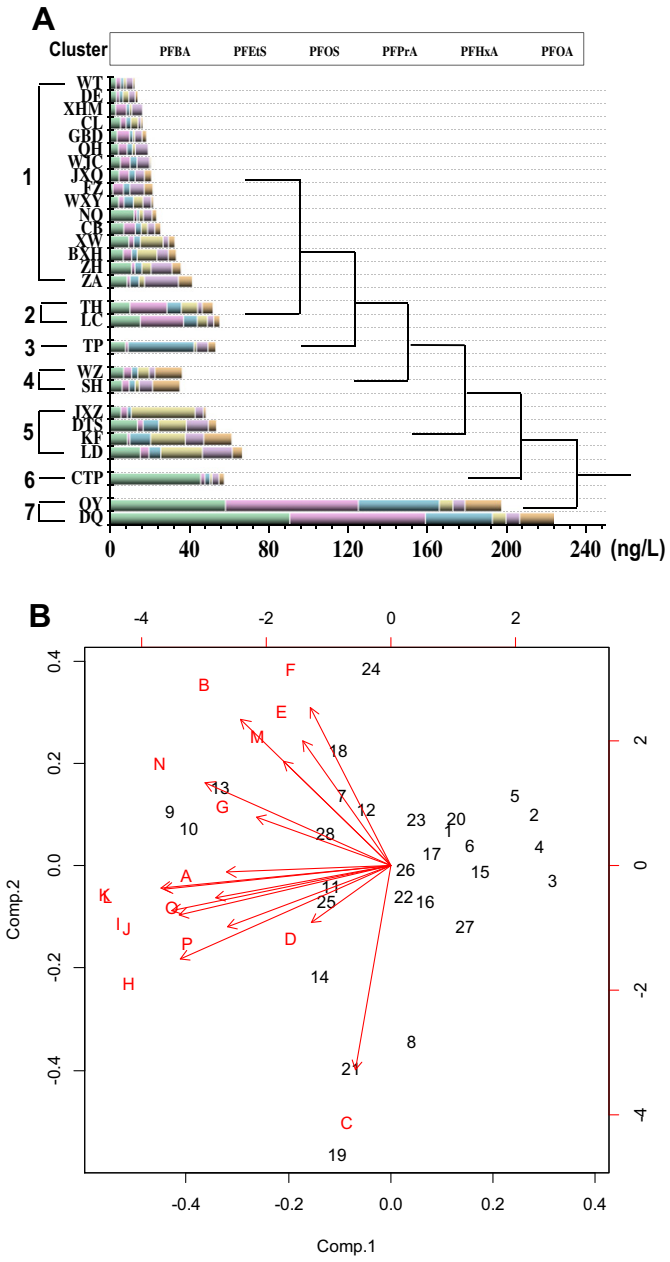

Fig. 1. Correlation and cluster analysis on PFASs based on influent concentrations. (A) Cluster analysis on six dominated PFASs based on influent concentrations. (B) PCA analysis on 16 PFASs. 1: GBD, Gaobeidian; 2: QH, Qinghe; 3: FZ, Fangzhuang; 4: WJC, Wujiacun; 5: XHM, Xiaohongmen; 6: JXQ, Jiuxianqiao; 7: BXH, Beixiaohe; 8: TP, Taopu; 9: DQ, Dongqu; 10: QY, Quyang; 11: DTS, Datansha; 12: XL, Xilang; 13: LD, Liede; 14: CTP, Caitianpu; 15: WT, Wangtang; 16: WXY, Wangxiaoying; 17: JXZ, Jiangxinzhou; 18: CB, Chengbei; 19: KFQ, Kaifaqu; 20: CL, Chunliu-Dongda; 21: ZH, Zhenhai; 22: NQ, Nanqu; 23: SHH, Shahe; 24: LWZ, Longwangzui; 25: LC, Lucun; 26: TH, Taihuxincheng; 27: TS, The second; and 28: ZA, Zhen'an. A: PFOS; B: PFBS; C: PFPrS; D: PFEtS; E: FOSA; F: EtFOSAA; G: PFDoDA; H: PFUnDA; I: PFDA; J: PFNA; K: PFOA; L: PFHpA; M: PFHxA; N: PFPeA; O: PFBA; and P: PFPrA.

sources of PFOA and PFHxA were probably present in Cluster 7 of the WWTPs' catchment areas, contributing PFOA and PFHxA in QY and DQ WWTPs from Shanghai. The data provided by WWTP operators showed that industrial wastewater accounted for 25% and 7% of influent in DQ and QY WWTPs, respectively.

Six well-differentiated clusters were observed in the effluent (Fig. S4A): cluster 1 characterized by high composition of PFOA; cluster 2, 3 and 4 characterized by low concentrations of PFOA and PFOS; cluster 5 characterized by high concentration of PFOS; and cluster 6 with high total PFASs concentration outputs compared to other WWTPs and characterized by substantially high levels of PFOA and PFHxA.

Six well-differentiated clusters were observed in the sludge (Fig. S4B): cluster 1 was characterized by high concentrations of PFOS and PFDA; cluster 2, 3 and 4 with high concentration outputs compared to other WWTPs and characterized by low concentration of PFOS; cluster 5 characterized by high concentration of PFOS and EtFOSAA; and cluster 6 with high total PFASs of concentration outputs compared to other WWTPs and characterized by substantially high levels of PFOS and PFUnDA.

Principal component analysis (PCA) was conducted to illustrate the association of different PFAS variables and the integrative level of PFASs in each WWTP (Fig. 1B). We performed PCA on the correlation matrix of the log-transformed PFASs concentrations, which revealed that the two principal components accounted for 52.1% of the total variances (Table S6). Results showed PC1 had 39.0% of total variances, and was characterized by high loadings of PFHpA, PFOA, PFDA, PFNA, and PFUnDA. Consequently, PC1 indicated that long-chain PFCAs (C7–C11) were a major source in the influent of these WWTPs. Additionally, PC2 accounted for 13.1% of total variances, and was predominated by EtFOSA, FOSA, PFPrS, and PFBS. Thus, PC2 represented the source contribution of influent PFSAs (C8 precursor and short-chain PFSAs). Although the proportion of explained variance in PC1 and PC2 was below 80%, it was helpful to reduce the multidimensionality of datasets to a smaller number of new composite dimensions (Yan, 2010). As evident in the Biplot, the variables of H (PFUnDA) and L (PFHpA) and of I (PFDA) and J (PFNA) displayed a significant correlation with each other, suggesting a relationship between the sources of each of these compounds. Similarly, the cluster of P (PFPrA), O (PFBA), K (PFOA), D (PFEtS), A (PFOS) and G (PFDoDA), N (PFPeA), B (PFBS), E (FOSA), and F (EtFOSAA) showed the same correlations (correlation coefficients were calculated by SPSS and are shown in Table S7). Highly relevant PFASs might come from similar sources or the existence of their potential precursors in wastewater.

Based on the six principal component scores (cumulative proportion = 84.5%) and comprehensive score of each WWTP, we evaluated the integrative pollution level of PFASs in each WWTP and corresponding city. For example, 9 (DQ) and 10 (QY) WWTPs in Shanghai had the highest scores on PC1, indicating high levels of long-chain PFCAs (C7–C11); 19 (KFQ) WWTP in Dalian had the highest scores on PC2, indicating high levels of PFSAs (C8 precursor, PFPrS and PFBS). Three (FZ), 9 (DQ), 4 (WJC), 10 (QY), and 13 (LD) WWTPs had higher comprehensive scores than others WWTPs, indicating higher integrative levels of PFASs. The five WWTPs located in the relatively economically developed Beijing, Shanghai, and Guangzhou suggested a positive correlation between PFAS levels and economic development.

3.4. Relation of PFAS concentrations between influent and effluent from WWTPs

More than half of the studied WWTPs showed higher concentrations of PFHpA, PFOA, PFNA, PFDA, PFBS, and PFOS in effluent than those in influent, with a 32–290 times cumulative increase (Fig. S5 and Table S8). These results indicate that the WWTPs received wastewater containing a large amount of PFAS precursors, and the increase from influent to effluent might be ascribed to precursor biodegradation producing different forms of PFASs (Loganathan et al., 2007; Sinclair and Kannan, 2006; Bossi et al., 2008). For example, PFOA might come from the biodegradation of fluorotelomer-based compounds such as 8:2 fluorotelomer alcohols (8:2 FTOH) or polyfluoroalkyl phosphate esters (PAPs), while PFOS might result from EtFOSAA biodegradation (Martin et al., 2004). Further, EtFOSAA can transform at a slow rate to *N*-ethyl perfluorooctane sulfonamide (EtFOSA), which then transforms to perfluorooctane sulfonamide (FOSA) and then to PFOS (Boulanger et al., 2005a). Recent research demonstrated the microbially mediated biodegradation of PAPs to PFCAs. Together with the di-substituted PAP (diPAP) concentrations observed in WWTP sludge, it is suggested that PAP-containing commercial products might be a significant contributor to the increased PFCA mass flows observed in WWTP effluents (Lee et al., 2010). Further work on diPAP concentrations in sewage and sewage sludge is needed to evaluate whether diPAPs are indirect sources to PFCAs in WWTPs. In addition, desorption of PFASs from solid materials might be another reason causing the increased PFAS concentrations in the effluent (Kunacheva et al., 2011).

Canonical correlation analysis (CCA) was brought to light the internal relations of PFASs between the first set of variables (influent) and the second set of variables (effluent). Concentrations of individual PFASs in influent (PFASs_in) and effluent (PFASs_out) in 26 WWTPS were analyzed separately on PFSAs and PFCAs. We defined (*Ui*, *Vi*) as the *i*th canonical variate pair. For PFSAs, the result showed that the first four canonical correlations were important ($p < 0.001$); while for PFCAs, the first six canonical correlations were observed with high canonical correlation ($p \leq 0.0003$). These results suggested that the PFASs concentrations of effluent be significantly associated with influent. The scatter plot for the first canonical variate pair is given in Fig. S6A and S6B.

These results indicated that there was no effective scavenging across most WWTPs, and the PFAS levels in effluent depended on the levels of those in influent. This accorded with some reports on water treatment technologies (Takagi et al., 2008; Quinones and Snyder, 2009). In China, wastewater treatment processes include MBR, MBBR, PASF, A2/O, modified A2/O, oxidation ditch, and A2/O oxidation ditch, which may be inadequate for the removal of PFASs. Some studies have also demonstrated the failure of physicochemical and biological treatment processes to capture PFASs (Schultz et al., 2006b; Sinclair and Kannan, 2006; Schroder and Meesters, 2005; Yu et al., 2009; Loganathan et al., 2007). The effluents of WWTPs are shown to be an important source of PFASs into the environment, which calls for significant and expensive modification of the current plant treatment processes to remove PFASs.

3.5. Concentration ratios of PFBS/PFOS and PFBA/PFOA in influent

The concentration ratios of PFBS/PFOS and PFBA/PFOA in influent from all WWTPs were calculated (Table S10). The highest ratios of PFBS/PFOS (13.6, 4.5, and 3.0) were observed in SHH and LWZ WWTPs from Wuhan and ZA WWTP from Foshan City, respectively (Fig. 2A). In addition, the highest ratios of PFBA/PFOA (3.0, 2.2, 2.0, and 1.6) were observed in FZ from Beijing, SHH and LWZ WWTPs from Wuhan, and KFQ from Dalian, respectively (Fig. 2B and Table S10). Recently, major global manufacturers have made commitments to work toward eliminating the manufacture of "long-chain" PFASs, such as PFOA/PFOS, replacing these C8 compounds with C4 compounds (PFBS and PFBA). Thus, commercial production has shifted to short-chain alternatives, such as PFBA or PFBS (Ritter,

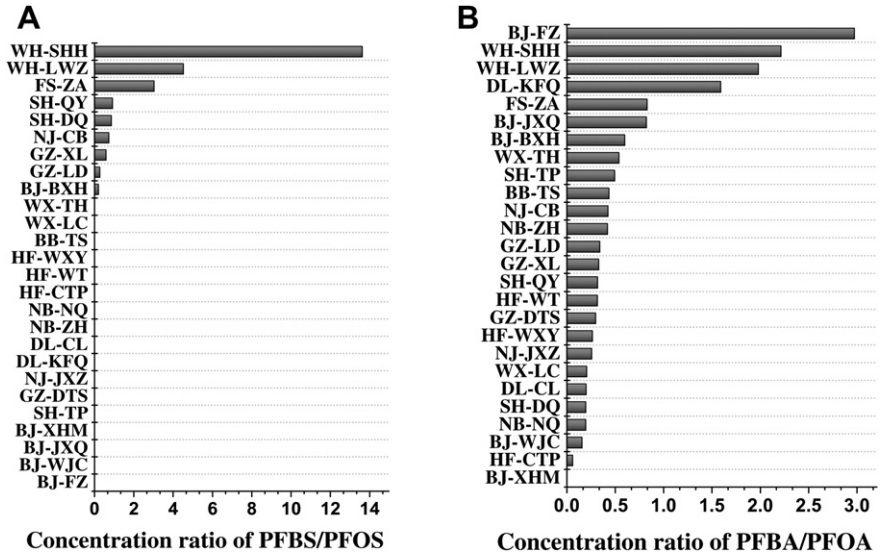

Fig. 2. Concentration ratios of PFBS/PFOS (A) and PFBA/PFOA (B) in sampling city (BB: Bengbu; HF: Heifei; GZ: Guangzhou; FS: Foshan; WH: Wuhan; DL: Dalian; SH: Shanghai; NB: Ningbo; BJ: Beijing; NJ: Nanjing; WX: Wuxi).

2010). Short-chain PFASs have substantial benefit over long-chain PFASs, particularly in relation to their low toxicity and non-accumulation in aquatic organisms (Xiao et al., 2012). In addition, there are no current restrictions on the production and use of short-chain PFASs such PFBA and PFBS, making them a more attractive alternative to long-chain PFASs. The results of the present study indicated that Wuhan and Foshan city have made substitutive measures in relation to long- and short-chain PFASs.

3.6. Correlation between influent PFAS concentrations and GDP

The relationship between PFAS concentrations in influents and GDP in each city were analyzed (Fig. 3). A positive correlation between total PFCAs (sum of short-chain and long-chain) or PFOA concentration and the GDP for each city was found ($p < 0.01$) (Fig. 3A and B). The squares of correlation coefficients were 0.80 and 0.64 between PFCAs or PFOA and GDP, respectively. These results suggest that local anthropogenic activities be greatly influenced total PFCAs or PFOA concentrations in influent. However, PFSAs or PFOS did not show these trends ($R^2 = 0.19$, $p > 0.05$) in those cities. In addition, natural logarithmic concentrations of PFOA in influents of WWTP from each city were also strongly correlated with population density ($R^2 = 0.55$, $p = 0.009$) (Fig. 3C and D), suggesting that these chemicals be derived from urban activities. The previous research showed that concentrations of PFOS, PFHpA, and PFNA in rivers were strongly correlated with population density while PFOA showed a significant but weak correlation (Murakami et al., 2008). Our results for PFOS differ from previous research. This might relate to PFCAs being more widely used than PFASs in common products (Boulanger et al., 2005a; Rayne et al., 2009). Increased GDP, especially in the production and consumption of products in these developed cities, might increase the occurrence of contamination if replacements for these chemicals are not considered. Continuous monitoring and management is required in these cities due to the environmental health risks of PFASs. Our results clearly showed the impact of regional economic development on the aquatic environment.

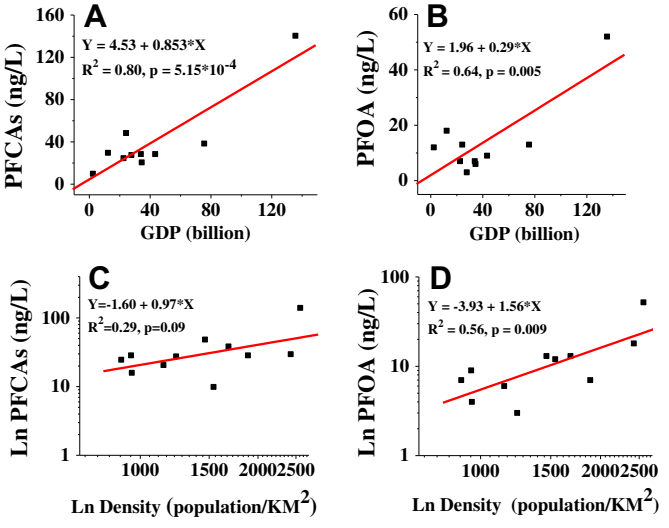

Fig. 3. Correlation analysis between influent concentrations of PFASs and GDP and density of population. (A) Total PFCAs and GDP; (B) PFOA and GDP; (C) Total PFCAs and density; and (D) PFOA and density.

3.7. Seasonal variation in Beijing WWTPs

Beijing is the biggest city in northern China with an area of 16,400 km^2 and a population of over 22 million. Beijing has an uneven annual rainfall distribution, experiencing distinct wet (April–September) and dry (October–March) seasons. The concentrations of PFAS from seven major Beijing WWTPs were investigated for seasonal variation (Fig. 4). Concentrations of total PFCAs in influent in the wet season were lower than those in the dry season, while concentrations of PFSAs presented the opposite trend. The variation of PFOS in this study was different from previous findings in influent in Singapore WWTPs, which reported PFOS were lower during the wet season than during the dry season (Yu et al., 2009). This might relate to the dilution effect of summer rainfall for PFCAs, which mainly dissolve in water. In addition, increased rainfall might lead to greater wastewater mass flow running from the surface or sludge of WWTPs; PFSAs existing in the soil might get washed away. Research has also found that street

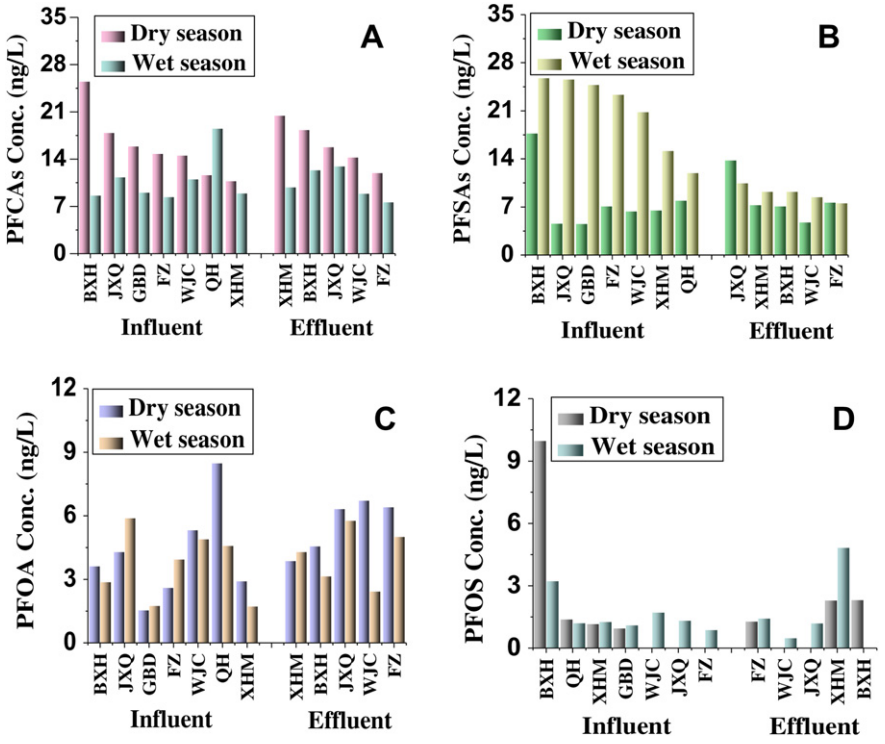

Fig. 4. Variation of concentrations in Beijing WWTPs between wet season and dry season. (A) ΣPFCAs; (B) PFOA; (C) ΣPFASs; and (D) PFOS.

dust contained PFSAs, making it possible for PFSA content to rise due to rainfall instigating street-runoff pollution (Murakami et al., 2009). Thus, the concentration of PFSAs might rise with increased rainfall during the wet season. Additionally, seasonal variation in domestic and industrial use of PFAS-containing products can be another reason for PFASs fluctuation in wastewater. For example, the use of PFOS related substances (e.g., industrial and household cleaning products, pesticides and insecticides, food packaging) might increase in summer compared to winter. In addition, increased dry-cleaning of cold weather clothing in the wet season might contribute to the increase in PFOS in the Beijing wet season. However, the specific sources of PFASs associated with human consumption and disposal of PFASs are not well understood and require further investigation.

3.8. Estimation of PFASs amount in effluent and sludge

Annual wastewater mass flows and sludge discharge of PFASs were calculated. The PFAS estimation of national annual mass flow was as follows (t/yr):

(1) Percentage of annual mass flow of the 28 WWTPs out of 1993 WWTPs = total annual mass flow of 28 WWTPs (1985.6 million t/yr)/total annual mass flow in China (58,970 million t/yr) = 3%
(2) Annual mass flow of PFASs in each WWTP = concentration of PFASs in each WWTP × annual mass flow of each WWTP
(3) Annual mass flow of PFASs in China (t/yr) = total annual mass flow of PFASs of 28 WWTPs/3%

Since annual discharge sludge data for each WWTP were lacking, the estimation of PFASs in sludge produced nationwide annually was as follows (t/yr):

Annual discharge of PFASs in sludge (kg/yr) = total annual discharge of sludge in the country (8.45 million t/yr) × average concentration of PFASs in sludge (ng/g).

Total annual mass flows of ΣPFASs, ΣPFCAs (C_8–C_{12}), ΣPFSAs (PFOS, FOSA, EtFOSAA), PFOS, and PFOA in 28 WWTPs were 114 kg, 31 kg, 29 kg, 27 kg, and 25 kg, respectively. Overall, the annual discharge of ΣPFASs, ΣPFCAs (C_8–C_{12}), ΣPFSAs (PFOS, FOSA, EtFOSAA), PFOS, and PFOA in WWTP effluents nationwide were estimated at more than 3.3 tons, 0.9 tons, 0.9 tons, 0.8 tons and 0.7 tons, respectively (Fig. S7A). These results were much lower than the total fluxes of sewage-derived PFOA and PFOS found in Japan (5.6 and 3.6 t/year) (Murakami et al., 2008). With an increase in PFAS-containing (especially long-chain PFCAs) wastewater discharge into lakes and rivers, fresh-water pollution has become of increasing concern.

For mass flow in sewage sludge, according to the rate of 1.5 tons of dry sludge produced by 10,000 tons of wastewater, there were approximately 8.45 million tons (d. w.) of municipal sewage sludge produced in China in 2009. The average concentrations of ΣPFASs, ΣPFCAs (C_8–C_{14}), ΣPFSAs (PFOS and EtFOSAA), PFOS, and PFOA in sludge were 22 ng/g, 11 ng/g, 7 ng/g, 5 ng/g, and 2 ng/g, respectively. The annual discharge amounts of ΣPFASs, ΣPFCAs, ΣPFSAs, PFOA, and PFOS in WWTPs nationwide were estimated at over 186 kg, 90 kg, 56 kg, 43 kg, and 18 kg, respectively (Fig. S7B).

3.9. Implications

Due to its ecotoxicological effects, the release of PFASs via recycling water into sensitive ecosystems requires further evaluation, with particular attention paid to those PFASs having more than eight fluorinated carbons because they are considered bioaccumulative in aquatic and terrestrial organisms. For example, bioconcentration factors of PFOS have been found to range from 1100 to 5400 in bluegill sunfish (*Lepomis macrochirus*) and rainbow trout (*Oncorhynchus mykiss*) (Giesy et al., 2010). Land application techniques are deemed one of the most effective and efficient disposition methods, and sludge can be applied to agricultural land, forest, disturbed land, and dedicated disposal sites (Crites, 1984).

However, any form of sludge disposal into the environment requires evaluation to protect human and environmental health, especially when sewage sludge potentially contains PFASs. In China, to date, no specific legislation exists regarding the maximum equivalent levels of PFASs in sewage sludge for land application. Due to the lipophilic nature and lower water solubility of long-chain PFASs in water, these compounds are expected to remain in sewage sludge during wastewater treatment process.

PFASs were detected in all influent samples from the 28 WWTPs in 11 cities, indicating that these chemicals were still in use and ubiquitous in the environment of economically developed areas of China. Conventional biological/mechanical wastewater treatment had limited effectiveness in removing PFASs in the effluents and sewage. Effluent and sewage sludge from WWTPs were point sources for PFASs to the environment. Secondary contamination and pollution will result during water recycling.

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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.envpol.2012.12.019.

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