Environmental Pollution 287 (2021) 117642

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Characterization of the distribution, source, and potential ecological risk of perfluorinated alkyl substances (PFASs) in the inland river basin of Longgang District, South China ☆

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ARTICLE INFO

Keywords:
Perfluorinated alkyl substances
Pollution characteristics
Source apportionment
Risk assessment

ABSTRACT

Previous studies of perfluorinated alkyl substances (PFASs) in receiving water bodies of typical industrial parks under the low-carbon development mode are scarce. In the present study, 18 PFASs were analyzed in surface water and sediment samples of the inland river basin in Longgang District in 2017. The ΣPFAS concentrations in surface water (drought and rainy periods) and sediment ranged from 15.17 to 948.50 ng/L, 11.56–561.14 ng/L, and 1.07–28.94 ng/g dw, respectively. Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonate (PFBS) were the dominant pollutants in surface water, with maximum concentrations of 867.68 ng/L, 288.28 ng/L, and 245.09 ng/L, respectively. Meanwhile, PFOS, perfluoroundecanoic acid (PFUdA), PFBS, and perfluorodecanoic acid (PFDA) were the major PFASs in the sediment samples, with maximum concentrations of 9.83 ng/g dw, 11.86 ng/g dw, 5.30 ng/g dw, and 5.23 ng/g dw, respectively. In addition, PFOA and PFOS resulted from similar sources in sediment and surface water samples ($P < 0.05$). The risk quotient value (RQ) results showed that the control of PFOS in the treatment of pollutants in the inland river basin of Longgang District deserves more attention.

1. Introduction

Perfluorinated alkyl substances (PFASs) are a class of man-made persistent organic pollutants (POPs) which possess unique properties, including excellent thermal and chemical stability, high surface activity, hydrophobicity, and oleophobicity (Buck et al., 2011; Lindstrom et al., 2011; Liu et al., 2014). Therefore, PFASs have exhibited broad usage in commercial and industrial applications, including surface treatments, firefighting foams, paper plates, pesticides, repellents, lubricants, personal care products, and food packaging products (Herzke et al., 2012; Zushi et al., 2012). PFASs in environmental media and human biological tissues have been studied in developed countries since the early 2000s worldwide (Olsen et al., 2005), including in water (Pan et al., 2014b; Wang et al., 2016), sediment (Qi et al., 2015; Zhao et al., 2016), soil (Jin et al., 2015; Rankin et al., 2016), dust (Yao et al., 2016), air (Wong et al., 2018), wildlife (Houde et al., 2011; Pan et al., 2018) and human (Lau et al., 2007; Loi et al., 2013) samples. Due to their persistence, bioaccumulation potential, and toxicity (Domingo, 2012; Mudumbi et al., 2014; Oldham et al., 2012), they pose a threat to the human and ecological environment to some extent. PFOS, its salts and its precursor perfluorooctane sulfonyl fluoride (PFOSF) have been restricted in production and use (UNEP, 2009), and PFOA, perfluorohexane sulfonate (PFHxS), and its salts were also listed as highly concerning substances (UNEP, 2015; UNEP, 2017). With legacy PFASs gradually reduced through regulation, shorter-chain PFASs, such as perfluorobutanoic acid (PFBA) and PFBS, have been used as alternatives and additives (Wang et al., 2013). However, there is evidence that exposure to these alternatives can interfere with heart development and impair the visual

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☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

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https://doi.org/10.1016/j.envpol.2021.117642
Received 22 February 2021; Received in revised form 17 June 2021; Accepted 21 June 2021

function of fish (Chen et al., 2018; Shi et al., 2017).

The water-soluble functional groups of PFASs increase their solubility in aquatic environments relative to other POPs, such as polycyclic aromatic hydrocarbons (PAHs). Studies suggest that accumulation in the aquatic environment is the main trend of ionic PFASs (Buck et al., 2011; Wang et al., 2018; Yao et al., 2016). Effluent from sewage treatment plants is one of the main sources of PFASs entering natural water (Seo et al., 2019; Sinclair and Kannan, 2006). Although studies of PFASs in aquatic environments have been conducted extensively, including in polar regions, seawater, lakes, and rivers, little is known about PFAS pollution and potential ecological risk in the aquatic environment of urban rivers in areas under the low-carbon development mode.

Longgang District is one of the most important economic growth poles and a site of intensive industrial activity in Shenzhen City in China. An inland river in Longgang District, the Longgang River is the upper reach of the Danshui River, a secondary tributary of the Dongjiang River, which is an important source of drinking water in South China. Therefore, the water quality of the Longgang River directly affects the drinking water safety of downstream habitants. In the context of the global response to climate change and the transformation and upgrading of traditional industries in China, a planning area of 55 square kilometers of international low-carbon city development is settled in Longgang District, which will build a green and low-carbon innovation industrial base based on new materials. The core area of the international low-carbon city design was constructed beginning in 2012. As typical representative pollutants of the new material industry, PFASs need to be paid further attention as potential risks to water quality in Longgang District.

This study investigated the occurrence and distribution of PFASs in surface water and sediment in the inland river basin of Longgang District. Additionally, the potential sources of PFASs were further elucidated. Finally, the potential ecological risk from the studied PFASs was evaluated to indicate the impact on aquatic organisms in this region. Using Longgang District as a case study, this study aimed to determine the occurrence of and provide a theoretical basis for the potential water quality risk from emerging complex pollutants under the low-carbon development mode.

2. Materials and methods

2.1. Sampling design and collection

Considering the distribution and flow direction of inland rivers in Longgang District, a total of 54 surface water samples and 20 sediment samples were collected in the Longgang River, the Pingshan River, and the confluence of the two rivers during the rainy period of September 2017 and the drought period of March 2017 (Fig. 1). The surface water (0–20 cm) samples were collected with 1 L polypropylene bottles, which were rinsed three times with methanol and Milli-Q® water before use. The sediment (top 10 cm) samples were collected in polypropylene (PP) tubes. All samples were chilled during transportation and then stored at −20 °C in the laboratory until analysis was performed within 2 weeks. General water characteristics were measured, as listed in Table S1.

Effluent from sewage treatment plants is the main supplement to surface water, and the degree of effluent contamination directly affects the pollution level of surface water. To elucidate the potential sources of PFASs in the inland river basin of Longgang District, the removal effect of PFASs by the dominant sewage treatment technology was analyzed. The anaerobic/anoxic/oxic (A^2/O) process is the leading sewage treatment process of sewage treatment plants, accounting for 76.39% of the total sewage treatment capacity in Longgang District. In October 2017, a total of 7 samples were collected at different steps of the treatment process (Fig. 2), including influent (raw water) and effluent, at a plant in the survey region located next to sampling site W25. The method of collecting, transporting, and preserving samples was the same for the sewage water as described for the surface water.

2.2. Chemicals and reagents

The standard solutions of 18 target analytes and 10 internal standards, listed in Table S2, were purchased from Wellington Laboratories Inc. (Ontario, Canada). Purities of the mixed PFAS standards were higher than 95%, and the single PFAS standard was higher than 98%. Methanol (purity 99.8%) was purchased from Honeywell Burdick & Jackson Co. (Texas, USA). Acetic acid (99.9%), ammonium solution

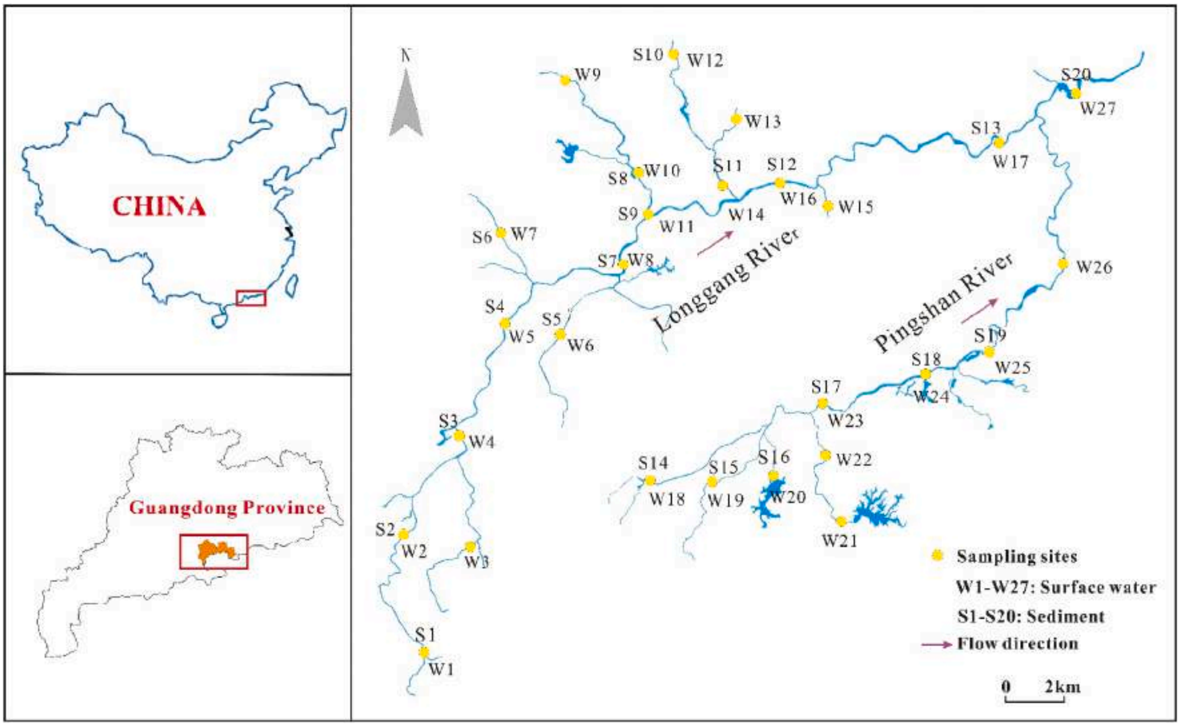

Fig. 1. Geography of the study area and location of sampling sites in Shenzhen City of Guangdong Province, China.

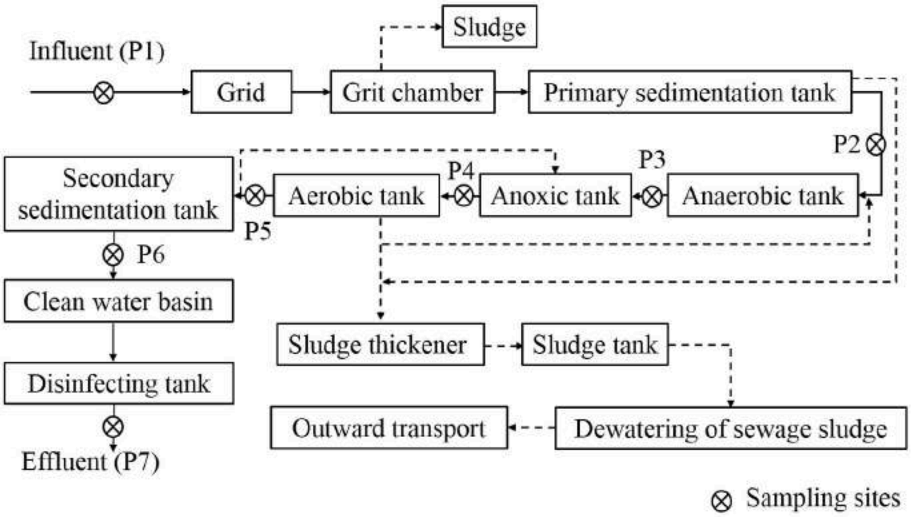

Fig. 2. Location of sampling sites in the sewage treatment works of Shenzhen City of Guangdong Province, China. (P1) The influent (raw water) of the sewage treatment plant. (P2) The effluent of the primary sedimentation tank. (P3) The effluent of the anaerobic tank. (P4) The effluent of the anoxic tank. (P5) The effluent of the aerobic tank. (P6) The effluent of the secondary sedimentation tank. (P7) The effluent of the sewage treatment plant.

(25%), and ammonium acetate (97%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.3. *Sample extraction*

The environmental water, influent and effluent samples (1 L) were filtered through a glass filter with a nylon membrane (0.45 μm) and spiked with 2 ng MPFAS mix. PFAS extraction in water was conducted using the solid-phase extraction (SPE) technique (Taniyasu et al., 2005). The filtered water samples were spiked with an internal standard, and a preconditioned Oasis Wax (6 cc, 150 mg) cartridge was cleaned with 4 mL 25 mM ammonium acetate (pH = 4) in Milli-Q water and then eluted with 4 mL methanol and 4 ml of 0.5% NH_4OH in methanol successively.

Wet sediment was freeze-dried and homogenized using an agate mortar and pestle. Afterward, 1 g of sediment was spiked with 2 ng MPFAS mix containing each of the mass-labeled internal standards. After 30 min, 10 mL methanol was mixed thoroughly and extracted at 60 °C in an ultrasonic water bath. Samples were centrifuged (4 °C, 5 min, 3500 rpm) and then extracted by the SPE technique. The eluents were condensed to 1 mL by nitrogen and filtered by nylon filter into 1.5 mL amber glass LC/MS vials. All extracts were kept at −20 °C in the laboratory until instrumental analysis was performed within 1 week.

Instrumental analysis was performed by LC-MS/MS using an Agilent LC 1260 coupled to an AB SCIEX API-4000 triple quadrupole mass spectrometer in negative electrospray ionization (ESI) mode. An ACQUITY BEH C18 column (2.1 × 150 mm; 3 μm, Waters, USA) was used for the separation of PFASs. Mobile phases A and B were methanol and 0.01 mol/L ammonium acetate in Milli-Q water, respectively. The gradient was ramped from 0 to 20% A in 2 min, held for 2 min, linearly increased to 90% A from 2 min to 2.5 min, held at this percentage for 8.5 min, and then reduced to 20% at 11 min until 14 min. Instrumental parameters for PFASs are listed in Table S2.

2.4. *Quality assurance and quality control*

To avoid contamination, all steps from sample collection to instrumental analysis avoided using Teflon-coated materials. Additionally, 5 field blanks were taken by filling sampling bottles with ultrapure water at different sampling sites and treating them as if they were samples from that step forward. Methanol and Milli-Q water were used for cleaning three times before all steps. Procedural blanks and parallel samples (one per ten samples) were inserted during all testing as a regular part of the analysis. Results in the field and procedural blanks for all analytes were below the method detection limit (MDL). The relative standard deviation values of parallel samples ranged from 2.76% to 5.16%. The internal standard method was used for quantification with standard curves of 11 points ranging from 0.1 ng/mL to 150.0 ng/mL. The coefficients (R^2) for all target analytes were over 0.99 (Table S3).

2.5. *Ecological risk assessment*

In several previous studies, RQs were used to determine the potential ecological risks of PFASs (Li et al., 2016; Liu et al., 2015). It is accepted that RQ values higher than 1 represent a significant risk while RQ values lower than 1 are considered negligible risks (Yan et al., 2013).

$$RQ = MEC/PNEC$$

where MEC = measured environmental concentration; and PNEC = predicted no effect concentration.

2.6. *Statistical analysis*

Statistical analyses were conducted using SPSS (Version 22.0, SPSS Incorporate). One-way ANOVA was used to detect differences in the measured concentrations between locations and seasons. To examine characterize the similarity among various PFASs in water and sediment samples, principal component analysis was performed. The diagram showing the concentrations was drawn by applying OriginPro 2016 64Bit (OriginLab Company, USA).

3. Results

3.1. *Occurrence and composition profiles of PFASs in surface water*

Among the surface water samples in the study, 18 and 15 targeted PFASs were found in drought and rainy periods, respectively. The detection frequencies and concentrations of individual PFASs in both periods are presented in Fig. 3. In the drought period, the detection rates were 100% for eleven PFASs, including PFOS, PFOA, PFBS, perfluorohexanoic acid (PFHxA), PFHxS, perfluoropentanoic acid (PFPeA), PFDA, perfluorononanoic acid (PFNA), perfluorohexadecanoic acid (PFHxDA), perfluorododecanoic acid (PFDoA), and perfluorotetradecanoic acid (PFTeDA). The detection rates for perfluoroheptanoic acid (PFHpA), perfluorooctadecanoic acid (PFODA),

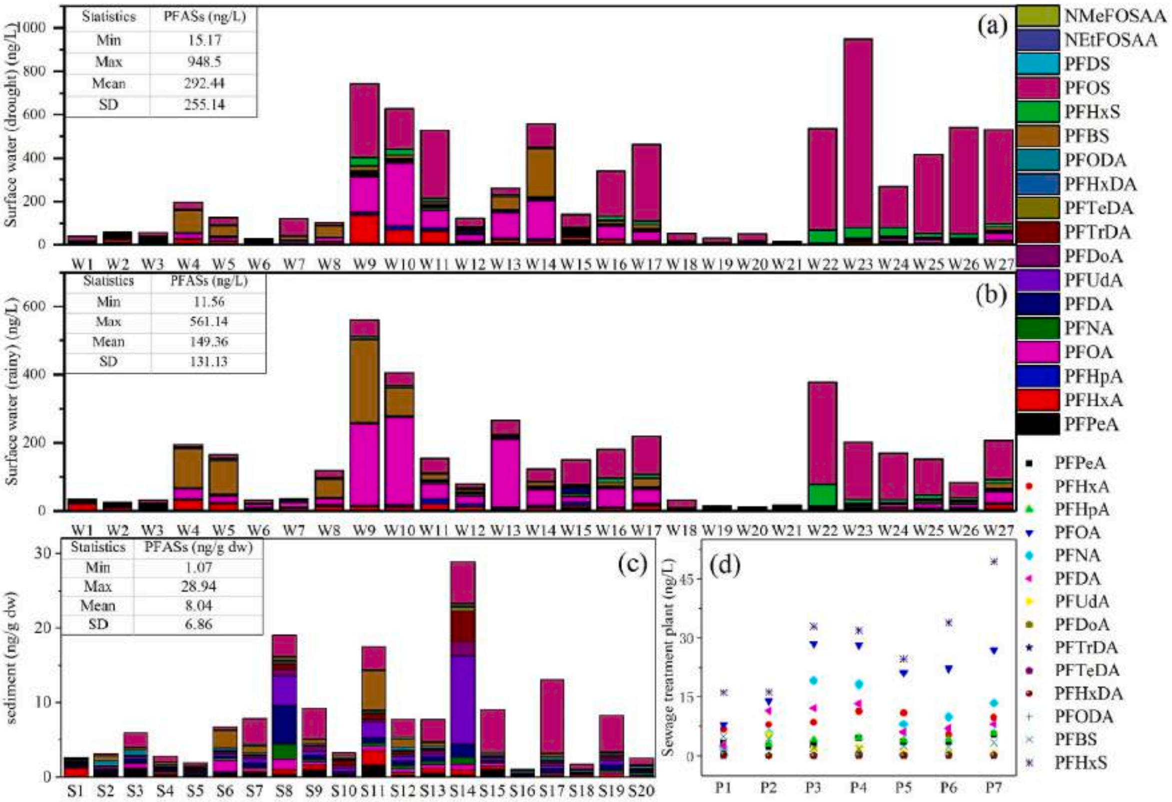

Fig. 3. Total concentrations of PFASs and their relative compositions in surface water and sediment and the concentrations of individual PFASs in sewage in Longgang District, Shenzhen, China (a) Total contents of PFASs and their relative compositions in surface water samples in the drought period. (b) Total contents of PFASs and their relative compositions in surface water samples in the rainy period. (c) Total contents of PFASs and their relative compositions in sediment samples. (d) The concentrations of individual PFASs in sewage samples.

PFUdA, perfluorotridecanoic acid (PFTrDA), N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA), N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA) and perfluorodecane sulfonate (PFDS) were 96.30%, 96.30%, 85.19%, 81.48%, 33.33%, 18.52% and 11.11%, respectively. In contrast, during the rainy period, PFHpA was detected in all surface water samples, followed by PFODA, PFTrDA, PFHxDA and PFUdA, while PFDS, NEtFOSAA, and NMeFOSAA were almost not detected. The ΣPFAS levels ranged from 15.17 to 948.50 ng/L with a mean value of 292.44 ng/L in the drought period. ΣPFASs had concentrations in the range of 11.56–561.14 ng/L with a mean value of 149.36 ng/L in the rainy period. Among the evaluated PFASs, the concentrations of PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS and PFOS in surface water during the drought period were significantly higher than those during the rainy period (all $P < 0.01$).

In the Longgang River, a relatively high total PFAS concentration was detected at sampling site W9, where the dominant constituents were PFOS (46%) during the drought period and PFBS (44%) and PFOA (42%) during the rainy period. The results of previous studies have shown that the presence of PFOA can mainly be attributed to the emulsification of plastic and rubber products, textile flame retardants, paper coatings and fire extinguishing agents (Moller et al., 2010), and PFBS and PFOS are mainly discharged from electroplating and electrochemical fluorination processing (Lu et al., 2015). In this study, site W9 was located next to Langming Industrial Park and Dexinsheng Industrial Park, which are heavy chemical industry zones specializing in plastic and rubber products, hardware products, furniture customization, and oil paint products. Thus, the high contamination at site W9 was contributed by the emulsification of plastic and rubber products, electroplating and electrochemical fluorination processing discharge. In addition, the core area of the international low-carbon city design was located next to sites W9 and W10. The higher PFAS pollution at these sites might result from the superposition of traditional hardware and rubber factories and the new material industry. In the Pingshan River, there was a relatively high total PFAS concentration at sampling site W23 in the drought period and sampling site W22 in the rainy period, and PFOS was the dominant constituent of ΣPFASs at these high concentration sites, reaching 92% at site W23 and 79% at site W22. Site W23 is at a bend in the river, and the low flow rate of surface water in the drought period allowed the PFASs to aggregate. Site W22 is located next to the BYD automobile plant. Thus, the heavy contamination at site W22 was contributed by electroplating and electrochemical fluorination processing discharge.

The PFAS composition of water samples in the drought period was similar to that in the rainy period. PFOS, PFOA, and PFBS were the predominant compounds in the Longgang River. PFOS had concentrations in the ranges of 6.41–432.62 ng/L and 0.49–113.61 ng/L in drought and rainy periods, respectively. The concentrations of PFOA ranged from 3.33 to 288.28 ng/L in the drought period and from 3.22 to 257.86 ng/L in the rainy period. PFBS was the constituent accounting for 2.68%–52.86% of the ΣPFASs in the drought period and from 1.26% to 60.21% in the rainy period. PFOS was the dominant constituent in the Pingshan River. It had concentrations in the ranges of 33.53–867.68 ng/L and 3.75–300.41 ng/L in the drought and rainy periods, respectively.

Compared with data reported in other studies on PFASs in rivers (Table 1), the concentrations of PFOA and PFOS in the inland river basin of Longgang District were slightly higher than those previously measured in the Danube River of Austria (Clara et al., 2009), the Elbe River of Germany (Ahrens et al., 2009) and most parts of China (Pan et al., 2014a; Wang et al., 2012; Yang et al., 2011; Zhang et al., 2013). The higher concentrations of PFOS in Longgang District can mainly be

Table 1
Concentrations in surface waters and sediments reported in the referenced literature.

Location	PFOA	PFOS	Reference
	Mean value (range)		
Surface water [ng/L]			
This study (in drought period)	41.49 (2.30–288.28)	175.45 (6.17–867.68)	
This study (in rainy period)	40.76 (1.49–257.86)	53.50 (0.49–300.41)	
Yangtze River	9.55 (0.52–18.00)	0.70 (n.d.-3.06)	Pan et al. (2014a)
Yellow River	2.70 (0.43–15.00)	0.93 (n.d.-5.70)	Wang et al. (2012)
Liao River	10.90 (n. d.–27.90)	0.33 (n.d.-6.60)	Yang et al. (2011)
Pearl River	3.70 (0.71–8.70)	3.36 (0.52–11.00)	Zhang et al. (2013)
Tennessee River	108.42 (n.d.-598.00)	69.19 (16.80–144.00)	Hansen et al. (2002)
Po River	89.00 (2.00–337.00)	6.09 (2.00–12.00)	Loos et al. (2008)
Danube River	10.64 (n. d.–19.00)	12.34 (n.d.-35.00)	Clara et al. (2009)
Elbe River	6.36 (2.80–9.60)	1.62 (0.50–2.90)	Ahrens et al. (2009)
Sediment [ng/g dw]			
This study	0.40 (n.d.-1.47)	2.52 (0.01–9.83)	
Liao River	0.08 (0.02–0.18)	0.15 (0.04–0.48)	Yang et al. (2011)
Yangtze River	0.24 (0.07–0.55)	0.06 (n.d.–0.59)	Pan et al. (2014a)
Danube River	1.37 (0.65–2.80)	0.54(n.d.-0.91)	Clara et al. (2009)
Ganges River	8.57 (n.d.-14.09)	n.d.	Corsolini et al. (2012)
Roter Main River	27.00 (n.d.-52.00)	105.00 (n.d.-290.00)	Becker et al. (2008)

n.d. = Not detected.

attributed to the metal machining and plating factories within the survey region in the dense mode. Nevertheless, the levels of PFOA detected were lower than those in the Tennessee River in America (Hansen et al., 2002) and the Po River in Italy (Loos et al., 2008).

3.2. Occurrence and composition profiles of PFASs in the sewage treatment plant

There were 15 PFASs found in the influent (raw water) and effluent samples of each treatment process (sites P1 to P7) in the sewage treatment plants (Fig. 2). PFDS, NEtFOSAA, and NMeFOSAA were almost not detected in these samples. The removal effect on PFASs of the existing technological process of the sewage treatment plant was analyzed. The total PFAS concentrations were 410.75 ng/L in P1, 358.54 ng/L in P2, 390.09 ng/L in P3, 501.90 ng/L in P4, 207.17 ng/L in P5, 350.01 ng/L in P6, and 516.62 ng/L in P7. This indicates that the wastewater treatment process does not effectively remove PFASs in wastewater, which is one of the main pollution sources of PFASs in the surface water of Longgang District. In the present study, the common wastewater treatment processes of 16 wastewater treatment plants, including the CAS process, A^2/O process, 4-stage BNR process, NPR process, Bio-SAC process, CNR process, CSBR process, DNR process, and MLE process, were also discovered to have no obvious effect on the removal of PFASs commonly seen in sewage treatment plants (Guo et al., 2010). The concentrations of individual PFASs in the influent and effluent are listed in Table S4.

To examine characterize the similarity among various PFASs in surface water and effluents discharged from industries, the composition profiles of PFASs were analyzed. PFOS was the dominant constituent accounting for 88% and 76% of the ΣPFASs in the sewage treatment plant influent and effluent, respectively. It can be concluded from the above results of surface water samples that PFOS is the dominant constituent in the inland river basin of Longgang District, it contributed an average of 60% and 36% of the ΣPFASs in the samples taken in the drought and rainy periods, respectively. This further validates the conclusion that the effluent from sewage treatment plants is the main supplement to surface water. The wastewater discharge from industries results in a significant increase in PFAS concentrations in the river.

3.3. Occurrence and composition profiles of PFASs in sediment

The concentrations and detection frequencies of PFASs in sediment samples are summarized in Fig. 3. Fourteen of the PFASs tested for in the sediment were detected, and PFHpA, PFDS, NMeFOSAA and NEtFOSAA were not detected in any of the sediment samples. The detection rates of 9 PFASs including PFOS, PFBS, PFDA, PFHxA, PFDoA, PFNA, PFODA, PFHxS, and PFTeDA, were 100%, followed by PFOA (95.00%), PFUdA (95.00%), PFTrDA (80.00%), PFHxDA (80.00%) and PFPeA (75.00%). In the Longgang River, the total PFAS concentrations in sediment varied from 1.97 to 19.10 ng/g dw, with the greatest value observed at sampling site S8, where the dominant constituent of ΣPFASs was PFDA (27%). PFDA mainly originates from perfluorocarboxylic acid production process emissions (Moller et al., 2010). In this study, site S8 was located near industrial areas. For the Pingshan River, the ΣPFAS levels ranged from 1.07 to 28.94 ng/g dw, with the greatest value observed at sampling site S14, where the dominant constituent of ΣPFASs was PFUdA (41%). PFUdA is widely used in industrial and household products (Tang et al., 2021). In this study, site S14 was located near an area densely packed with homes. Thus, the heavy contamination at site S14 was contributed by the discharge of domestic sewage. In addition, PFOS and PFBS were predominant PFASs in the survey region, with mean percentages of 31% and 9%, respectively.

Sediment has been regarded as a repository of organic contaminants including PFASs in previous studies (Nakata et al., 2006; Pignotti et al., 2017). Because high concentrations of PFOA, PFOS, and PFBS were detected in the surface water and sediment and the sediment samples were collected in the drought period, we computed the correlations between sediment samples and water samples in the corresponding locations in the drought period (Fig. 4). The results showed that the total PFAS and PFBS correlations were not significant at the 0.05 level ($R^2 = 0.0559$, $P = 0.162$ and $R^2 = -0.0483$, $P = 0.684$), while for PFOA and PFOS, the correlations were significant at the 0.05 level ($R^2 = 0.2553$, $P = 0.013$, $R^2 = 0.3656$, $P = 0.003$).

Compared with other reported data about PFASs in sediment (Table 1), the concentrations of PFOA and PFOS in the inland river basin of Longgang District were slightly higher than those previously measured in the Liao River and the Yangtze River of China (Pan et al., 2014a; Yang et al., 2011), which could be explained by the fact that the fluorochemical industrial discharge within the survey region is extensive. Nevertheless, the levels of PFOA were lower than those from the Danube River of Austria (Clara et al., 2009), the Ganges River of India (Corsolini et al., 2012) and the Roter Main River of Germany (Becker et al., 2008).The PFOS levels were higher than those in the Ganges River of India.

3.4. Source apportionment of PFASs based on environmental metrics

The relationships of 9 PFASs with relatively high concentrations detected in surface water (drought period) and 10 PFASs detected in the sediment of the Longgang region were studied through principal component analysis (PCA) (Fig. 5). The 9 PFASs in surface water in Longgang District can be summarized into 2 principal components, with the cumulative variance contribution rate reaching 63.5%. In principal component 1 (PC1), PFHpA, PFOA and PFDA have higher loading values. The results of previous studies have shown that PFHpA mainly comes from the decomposition of food packaging and fabric coating

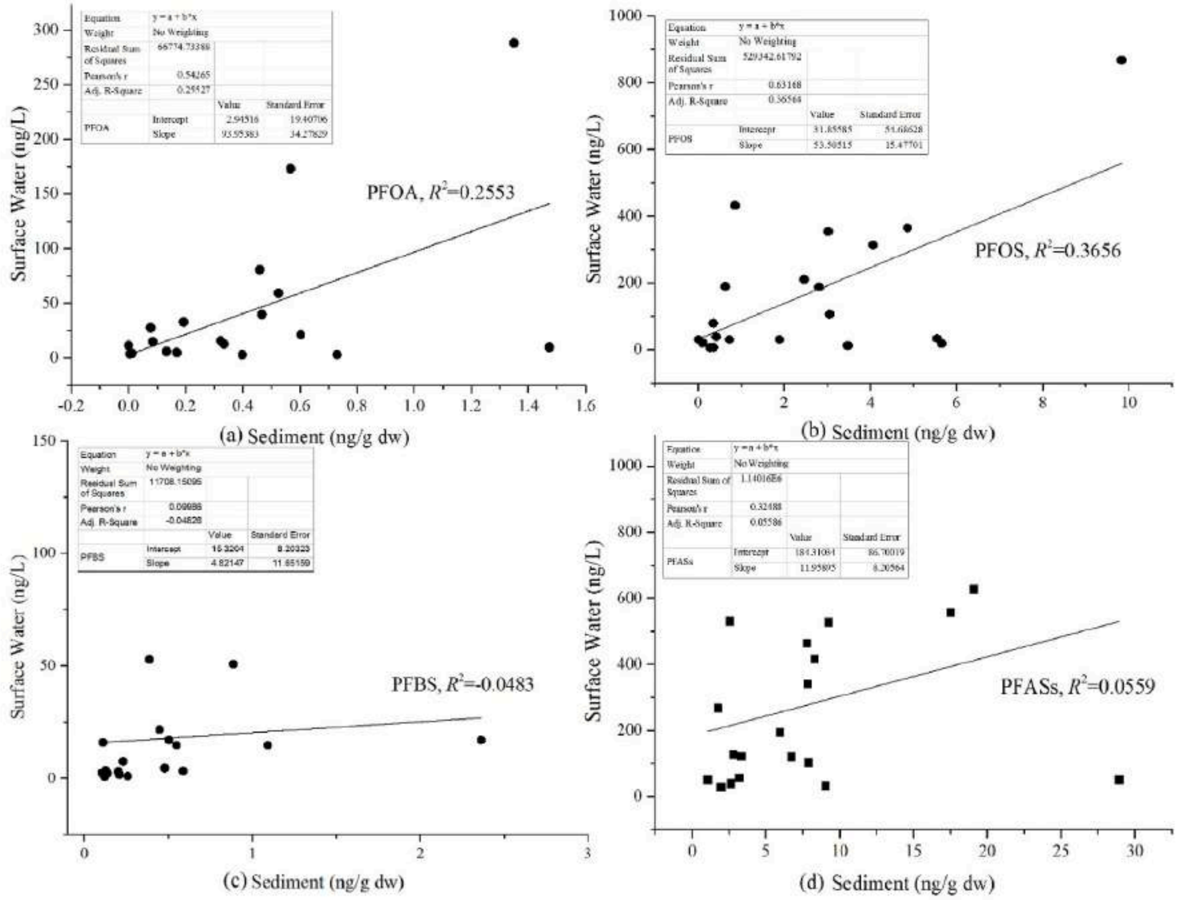

Fig. 4. Correlations of PFASs, PFBS, PFOS and PFOA concentrations between surface water samples and sediment samples in the drought period (R^2 denotes the correlation coefficient). (a) Correlations of PFOA concentrations between surface water samples and sediment samples. (b) Correlations of PFOS concentrations between surface water samples and sediment samples. (c) Correlations of PFBS concentrations between surface water samples and sediment samples. (d) Correlations of PFAS concentrations between surface water samples and sediment samples.

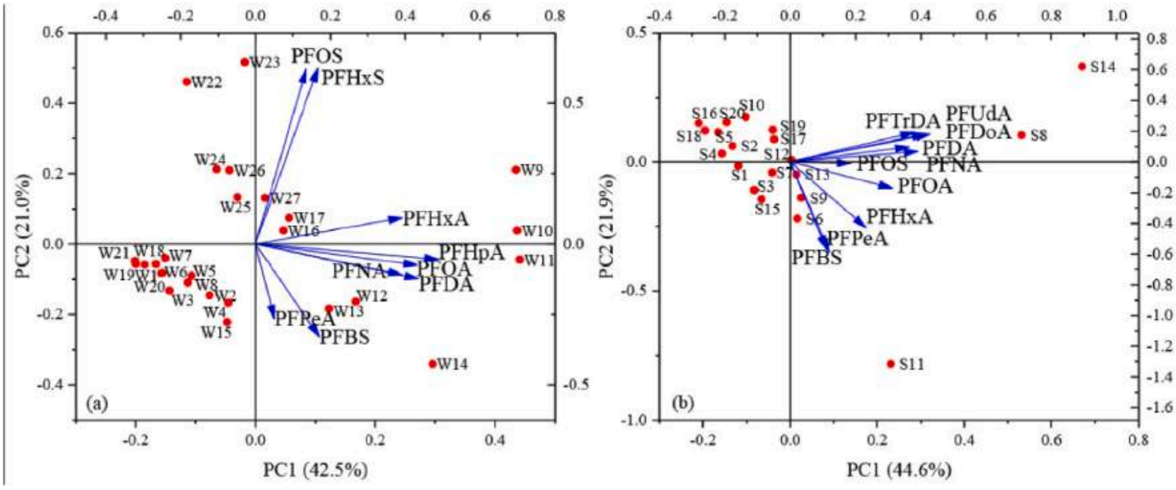

Fig. 5. Plot of PC1 and PC2 from principal component analysis (PCA) of PFASs as variables for surface water during drought period (a) and sediment (b). (Blue arrow means vector resultant of PC1 and PC2.). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

materials (Tang et al., 2021). In this study, higher concentrations of PFHpA and PFOA were found at sampling site W10, at 18.37 and 288.28 ng/L, respectively. Site W10 was located next to Jinshuiqiao Industrial Park, which specializes in fabricated metal products, leather and textile processing, and food processing. The concentration of PFDA (11.11 ng/L) at sampling site W12 was highest in all sampling events. Site W12 was located near industrial areas specializing in plastic products, fabricated metal products, and furniture manufacturing. Thus, it can be inferred that PC1 is contributed by fluorochemical industrial discharge. In PC2, PFHxS and PFOS have higher loading values. PFHxS mainly originates from the emulsification of plastic and rubber products, textile flame retardants, paper coating and fire extinguishing agents (Moller et al., 2010). In this study, the highest concentrations of PFOS and PFHxS were 867.68 ng/L (site W23) and 56.82 ng/L (site W22), respectively. The source apportionment of PFASs at sites W22 and W23 was analyzed in section 3.1. Thus, it can be concluded that PC2 is contributed by electroplating and electrochemical processes.

The 10 PFASs in the sediments of Longgang District could be summarized into 2 principal components, and the cumulative variance contribution rate reached 66.5%. PFDoA, PFUdA and PFNA had higher load values in PC1. The results of previous studies have shown that PFDoA is oxidized by FTOH, a precursor of PFASs added by paint ink additives, leather and paper finishing adhesives (Prevedouros et al., 2006), and PFNA mainly originates from perfluorocarboxylic acid production process emissions (Moller et al., 2010). The highest concentrations of PFDoA and PFUdA occurred at site S14, which was located near an area densely packed with homes. The highest concentration of PFNA occurred at site S8, which was located near industrial areas. Thus, PC1 is contributed by discharge resulting from daily activities. In PC2, PFBS and PFPeA had higher loading values. PFPeA is mainly generated from the decomposition of packaging and coating materials (Tang et al., 2021). The highest concentrations of PFBS and PFPeA occurred at site S11, which was located next to Yintaihemei Industrial Park, a chemical industry zone specializing in waterproof materials, electronic products, and packaging. Thus, PC2 is contributed by electroplating and the decomposition of packaging and coating materials.

3.5. *Ecological risk assessment and environmental implications*

The potential environmental effects of PFASs remain unclear. PFASs levels that correspond to certain effects have been put forward in several studies. The AQUATOX model, assessment factor (AF) and species sensitivity distribution (SSD) analysis methods have been proposed to predict the PNECs of organic chemicals and toxicants in aquatic ecosystems on aquatic organisms. For river ecosystems, studies predicted PNECs for the most sensitive aquatic species (caddisfly, *Trichoptera*) of 0.000023 μg/L for PFOS and 2546 μg/L for PFOA (AQUATOX), 4.9 μg/L for PFOS and 400 μg/L for PFOA (AF), or 15.95 μg/L for PFOS and 1065.70 μg/L for PFOA (SSD) (Gredelj et al., 2018).

The risk assessment showed that all RQ values of PFOA in surface water, estimated by the three methods, were less than 1. All RQ values of PFOS in surface water estimated by the AF and SSD methods were less than 1. However, the RQ values of PFOS estimated by the AQUATOX model at most sampling sites were higher than 1 in drought and rainy periods, with proportions of 74% and 52% respectively. This suggests that current PFOS levels in Longgang District present a significant risk to aquatic organisms.

Unlike in the AF and SSD methods, the AQUATOX model highlights that sublethal toxicity and ecological relationships are potentially important in river ecosystems. Therefore, a very precautionary protective threshold concentration on PFOS was proposed. However, the model did not faithfully reproduce all seasonal dynamics in the river ecosystem (Grechi et al., 2016) and needs to be validated in the future.

4. Conclusion

The present study described the occurrence, composition profiles, source apportionment, and ecological risks of PFASs in surface waters and sediments in Longgang District. The concentrations of individual PFASs ranged from tens of pg/L to hundreds of ng/L in surface water and tens of pg/g dw to tens of ng/g dw in sediments in the present survey. Among the aforementioned PFASs, some short- or mid-chained PFASs such as PFOS, PFOA, PFBS and PFHxS were the predominant compounds in the surface water. The sediments exhibited significant accumulation of mid- or long-chained PFASs, such as PFOS, PFUdA, PFBS and PFDA. In addition, the PFASs mainly resulted from the wastewater of upstream industries, as the wastewater treatment processes do not remove PFASs effectively. These findings suggest that Longgang District is relatively more polluted by PFASs than other drainage areas worldwide. The RQ values showed that the control of PFOS in the treatment of pollutants in the inland river basin of Longgang District deserves more attention.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support was received from the National Science and Technology of Water Pollution Control and Treatment Major Special Project of China (2015ZX07206-006-04, 2018ZX07601-002) and the National Key Research and Development Program of China (2018YFC1801505). The authors are grateful to anonymous reviewers for their helpful comments on the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117642.

Author statement

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