Occurrence and partitioning behavior of per- and polyfluoroalkyl substances (PFASs) in water and sediment from the Jiulong Estuary-Xiamen Bay, China

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HIGHLIGHTS

- Concentrations and compositions of PFASs in the JEXB had significant seasonal variations.
- Short chain PFASs were dominated in water. Long chain PFASs were high in sediment.
- PFBA as an alternative increased in water compared with our previous data.
- The river discharge, airport, harbor and wastewater treatment plant were the most important sources.
- Log K_d of PFASs increased with the increasing carbon chain length and salinity.

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ABSTRACT:

Twenty-four per- and polyfluoroalkyl substances (PFASs) were analyzed in water and sediment from the Jiulong Estuary-Xiamen Bay to study their seasonal variations, transport, partitioning behavior and ecological risks. The total concentration of PFASs in water ranged from 11 to 98 ng L^{-1} (average 45 ng L^{-1}) during the dry season, 0.19–5.7 ng L^{-1} (average 1.5 ng L^{-1}) during the wet season, and 3.0–5.4 ng g^{-1} dw (average 3.9 ng g^{-1} dw) in sediment. In water samples, short-chain PFASs were dominated by per-fluorooctanoic acid (PFBA) in the dry season and perfluorobutane sulfonate (PFBS) in the wet season, while long chain PFASs, such as perfluorooctane sulfonate (PFOS), dominated in the sediment. The highest concentration of PFASs in water were found in the estuary; in contrast, the highest level of PFASs in sediment were found in Xiamen Bay. These spatial distributions of PFASs indicate that river discharge is the main source of PFASs in estuarine water, while the harbor, airport and wastewater treatment plant near Xiamen Bay may be responsible for the high PFBS and PFOS concentrations in water and sediment. The partition coefficients (log K_d) of PFASs between sediment and water (range from 1.64 to 4.14) increased with carbon chain length ($R^2 = 0.99$) and also showed a positive relationship with salinity. A preliminary environmental risk assessment indicated that PFOS and perfluorooctanoic acid (PFOA) in water and sediment pose no significant ecological risk to organisms.

1. Introduction

The use of per- and polyfluoroalkyl substances (PFASs) in industrial and commercial products has resulted in their widespread distribution in the environment (Yamashita et al., 2008; Pignotti et al., 2017; Wang et al., 2017; Rauert et al., 2018). Due to their toxicity to wildlife and humans (Seacat et al., 2002; Olsen et al., 2007), PFASs are of increasing concern. PFASs are widely detected in the aquatic environment (Ahrens, 2011). The concentration and composition of PFASs in rivers varies widely during different seasons due to the impacts of runoff influx and human activities. For example, dilution by rainfall could lead to low levels of PFASs in

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rivers. There were significant negative correlations between the concentrations of PFOS and river flow rate (0.66−0.85 of R^2) in the Seine River, France, indicating point-source PFAS inputs (Munoz et al., 2018). However, higher concentrations of PFASs were found in the Huangpu River during the wet season than during the dry season (Sun et al., 2017). Surface runoff (nonpoint source pollution) may act as a carrier of PFAS-containing pollutants from urban environments, resulting in an increase of PFASs in the Huangpu River. Human activity is another factor; for example, high concentrations of PFASs were found in influent from a wastewater treatment plant (WWTP) in winter (Chen et al., 2018). There is a ski resort near the WWTP, and the skiwear, which is made of waterproof materials rich in PFASs, could be responsible. In addition, seasonal variations of PFASs in rivers can also be affected by industrial activities. PFASs had their highest average concentration (2500 ng L^{-1}) during the wet season near fluorine industries, and their lowest average concentration during the dry season (740 ng L^{-1}) (Zhu et al., 2015). The seasonal distribution of PFASs in water samples from the Daling River was consistent with the observed seasonal trend in production capacity of fluorinated chemical manufacturers, which had the highest yield in summer (5200 t) and the lowest yield in winter (2700 t) (Zhu et al., 2015). Overall, the seasonal trends of PFAS concentrations and PFAS sources are affected by many factors, which are worthy of study.

Sediment is considered to be a sink for PFASs, especially for perfluorosulfonic acids (PFSAs) and long chain perfluorocarboxylic acids (PFCAs) (Munoz et al., 2015; Wang et al., 2017). The partition coefficient (K_d) of PFASs between water and sediment is helpful to understand their environmental behaviors. K_d is mainly controlled by suspended particulate matter, organic matter, salinity and pH (Higgins and Luthy, 2006; Ahrens et al., 2011; Hong et al., 2013; Munoz et al., 2017a; Wang et al., 2017). Our previous study focused on the occurrence and seasonal variations of PFASs in water from the Jiulong River Estuary (Cai et al., 2018). However, data about the K_d and occurrence of PFASs in sediments of the Jiulong River and Xiamen Bay are limited.

The Jiulong River serves as a drinking water source for Xiamen Island. In 2018, there were more than 2 million residents on the island (Xiamen Bureau of Statistics, http://tjj.xm.gov.cn/zfxxgk/zfxxgkml/tjsjzl/tjfx/201902/t20190225_2227407.htm). However, there is an organic fluoride manufacturing plant midstream in the Jiulong River. Therefore, a better understanding of the concentration and spatial distribution of PFASs in the Jiulong River and Xiamen Bay will be helpful to protect ecosystems and human health. Thus, the objectives of this study were to (1) investigate the levels, spatial distribution and temporal trends of PFASs in water and sediment from the Jiulong Estuary-Xiamen Bay (JEXB), and (2) study partition coefficients and their influencing factors to explore the environmental fate of PFASs.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards of 24 native PFASs and 9 mass-labeled PFASs were purchased from Wellington Laboratories Inc. (Canada). These mass labeled PFASs were used as surrogate standards. Detailed information of native and mass labeled standards is provided in Table S3. All stock solutions were prepared in methanol and stored in polypropylene (PP) tubes at 4 °C. Other reagents included methanol for HPLC analysis, ≥99.9% (Sigma-Aldrich, USA), ammonium hydroxide (25%, ACOS Organics, USA), and ammonium acetate (CNW, Germany). Solid phase extraction cartridges were purchased from Waters (6 mL, 150 mg, Oasis® WAX) and Supelco (3 mL, 250 mg, ENVI Carb).

2.2. Sample collection

During the dry season, surface water samples (sampled approximately 0.5 m below the surface) were collected onboard the research vessel Haiyang II at 21 sites from the JEXB in April 2017 (Fig. 1). During the wet season, 16 surface water (sampled approximately 0.5 m below the surface), 14 bottom water (sampled about 0.5 m above the bottom) and 12 surface sediment samples were collected from the JEXB in September 2017. Detailed sampling information is given in Table S1. Surface water samples (1 L) were collected with a stainless steel bucket. Bottom water was collected with a 4 L PP water sampler. Water samples were stored in wide-mouthed PP bottles with screw caps. Sediment samples were collected with a stainless steel grab bucket, wrapped with baked aluminum foil, and sealed in PP bags. Water and sediment samples were preserved at temperatures below −20 °C.

2.3. Sample extraction

The extraction protocol of PFASs from water samples was modified from a previous study (Cai et al., 2018). Briefly, water samples were filtered with a 0.45 μm PP membrane (CNW, Germany). The WAX cartridges were preconditioned with 4 mL of a 0.1% (v/v) NH$_4$OH solution in methanol followed by 4 mL methanol and finally 4 mL MilliQ water. Water samples were then spiked with 100 μL of a surrogate standard solution (10 ng mL^{-1}) and loaded onto the cartridge at a rate of 2−3 drops per second. After all the samples had passed through the cartridges, the cartridges were cleaned with 4 mL of an ammonium acetate buffer (25 mmol L^{-1}) and 4 mL MilliQ water. The cartridges were dried by centrifuging at 3000 r/min for 4 min. The target fraction was eluted with 4 mL methanol followed by 4 mL 0.1% (v/v) NH$_4$OH in methanol and collected in 15 mL PP tubes. The eluate was then concentrated to 1 mL under a gentle stream of nitrogen.

The extraction and cleanup for sediment samples were based on a method developed by Higgins et al. and were performed with modifications (Higgins et al., 2005). Sediment samples were freeze-dried, ground with an agate mortar, and passed through an 80 mesh screen. Then, each sediment sample (5 g) was wetted with 2 mL sodium hydroxide methanol solution (0.2 mol L^{-1}) and spiked with 1 ng surrogate standards in a 50 mL PP tube. 10 mL methanol was added to each tube, then the tube was vortexed for 1 min and sonicated for 15 min. After sonication, the solution was stayed for 12 h, then centrifuged at 3000 r min^{-1} for 4 min, and the supernatant was transferred into a new 50 mL PP tube. 0.2 mL hydrochloric acid (2 mol L^{-1}) was add into supernatant. Sediment samples were sonicated three times. A total of 30 mL extraction was concentrated to 3 mL under a gentle stream of nitrogen. Concentrated extraction was diluted with 40 mL MilliQ water. Diluted supernatant was loaded onto the WAX cartridge in the same way as the seawater sample. Then, the concentrated extracts were cleaned with the ENVI Carb cartridges, which were preconditioned with 3 mL methanol three times. Next, the extract was loaded into the cartridge at a rate of 2−3 drops per second, and the eluate was collected in a 15 mL PP tube. The residual target compounds in the cartridge were washed with 3 mL methanol three times. A total of 12 mL eluate was concentrated to 1 mL under a gentle stream of nitrogen.

2.4. Instrumental analysis

PFASs were analyzed with an Agilent 1290 LC coupled to an Agilent 6490 Triple Quadrupole MS in negative ionization mode. 10 μL of extract was injected into a Waters Symmetry C18 column (2.1 mm i. d. × 150 mm length, 5 μm), with 9:1 (v/v) water to
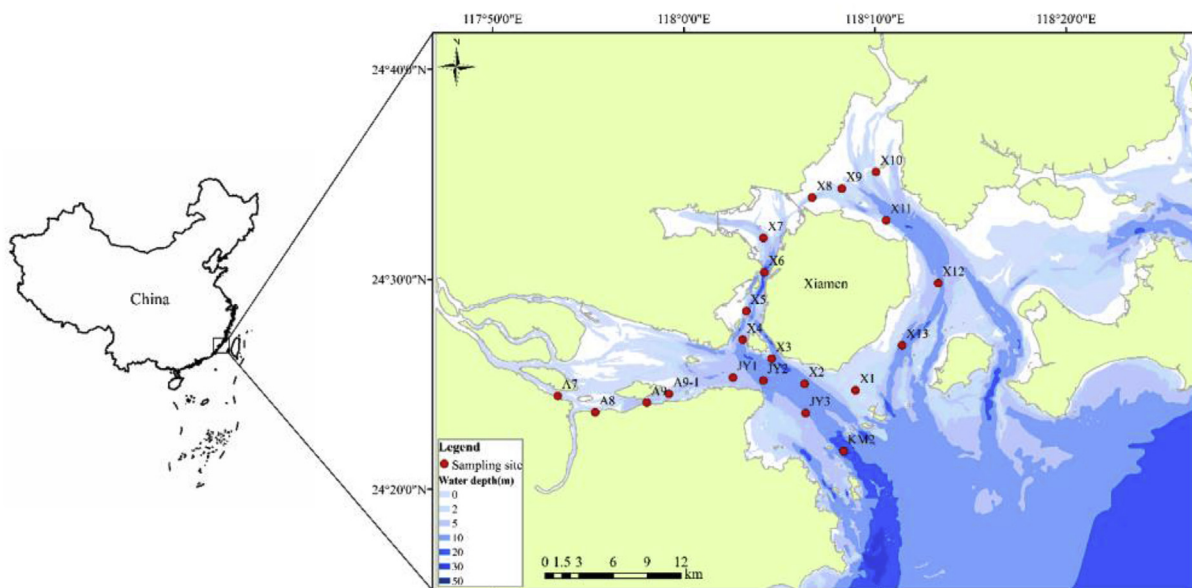
Fig. 1. Sampling sites of water and sediment samples from the JEXB, China.
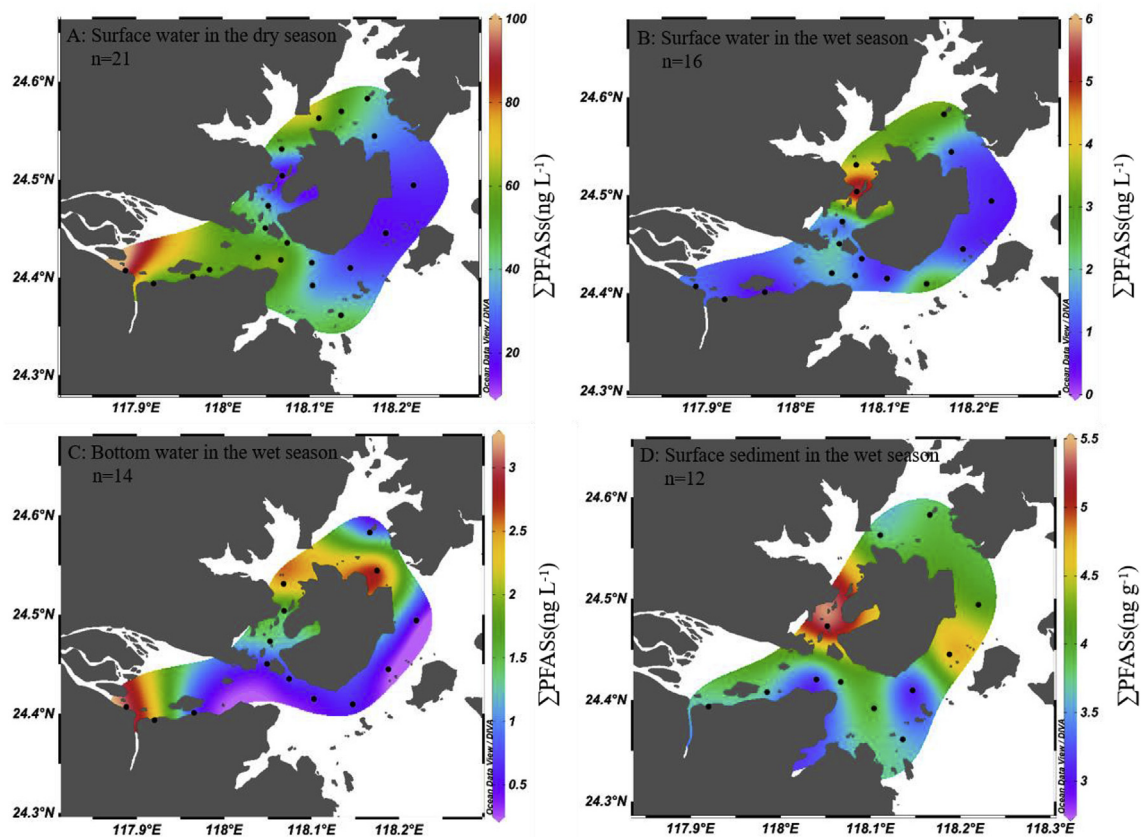

Fig. 2. Concentrations and spatial distributions of total PFASs in the JEXB, China. (A) Surface water during the dry season, (B) surface water during the wet season, (C) bottom water during the wet season, and (D) surface sediment during the wet season.

methanol containing 10 mM ammonium acetate (solvent A) and methanol (solvent B) as the mobile phases at a flow rate of 0.25 mL min^{-1}. A solvent gradient was programmed as follows: 10% B at 0 min, increasing to 100% B at 10 min, 100% B held until 14 min, and decreasing back to 10% B by 20 min. The capillary voltage was

4000 V. The flow rate and temperature of the sheath gas (nitrogen) were 8 L min^{-1} and 350 °C, respectively. Multiple reaction monitoring (MRM) analysis was employed to identify analytes. The MS/MS mass transition ions, fragmentation voltage and collision energy are listed in Table S3. The salinity and temperature (Table S2)

of water samples was recorded by a shipboard instrument (YSI 6600, Xylem Inc. USA). The total organic carbon (TOC) of sediment was measured using an elemental analyser (Vario EL Cube, Germany).

2.5. Quality assurance and quality control (QA/QC)

Before sampling, PP bottles and tubes, methanol and nitrogen were tested, and no contamination was found in these blank samples. Field blanks and procedure blanks were performed for each set of extractions. The limit of detection (LOD) was defined as the amount of compound that was needed to yield a signal-to-noise (S/N) ratio of 3:1, and the limit of quantification (LOQ) was defined as the lowest point of the calibration curve calculated to be within 30% of its actual value, or the amount of compound that was needed to yield a S/N ratio of 10:1. PFOA was detected in the field blank, but below the LOQ. Concentrations of compounds that were lower than the LOD were reported as nd (not detected). The concentration between LOD and LOQ were reported as "<LOQ". LOQs ranged from 0.01 to 0.1 $ng\,L^{-1}$ for water samples and 0.002–0.02 $ng\,g^{-1}$ for sediment samples (Table S4). The matrix spike recoveries varied from $55 \pm 2\%$ to $110 \pm 8\%$ for seawater samples, and ranged from $45 \pm 2\%$ to $92 \pm 2\%$ for sediment samples (Table S4). Surrogate recoveries for seawater samples ranged from 41% to 119%. Surrogate recoveries for sediment samples ranged from 53% to 107%. Internal calibration was used for quantification.

3. Results and discussion

3.1. Concentrations and spatial distributions of PFASs in water and sediment

In water and sediment samples, 18 of the 24 PFASs were detected in the JEXB, ranging from 11 to 98 $ng\,L^{-1}$ in surface water during the dry season. During the wet season, concentrations ranged from 0.33 to 5.7 $ng\,L^{-1}$ in surface water, 0.19–3.0 $ng\,L^{-1}$ in bottom water, and 3.0–5.4 $ng\,g^{-1}$ in sediment (Fig. 2). Detailed information of PFASs concentrations is provided in Table S5 to Table S8. PFASs were one to two orders of magnitude lower during the wet season than the dry season because of the higher runoff from the Jiulong River in summer. The highest concentration of PFASs in water was found at site A7 during the dry season. In sediment, site X5 exhibited the highest concentration of PFASs.

The annual average concentration of PFASs in water from the JEXB was 20 $ng\,L^{-1}$, which is comparable values from Chaohu Lake (14 $ng\,L^{-1}$) (Liu et al., 2015b) and the Pearl River Delta (7.6 $ng\,L^{-1}$) (Liu et al., 2015a), but lower than values from Jiangsu Province (43 $ng\,L^{-1}$) (Wei et al., 2018) and the Yangtze River (190 $ng\,L^{-1}$) (Zheng et al., 2017). The average concentration of PFASs in sediments from the JEXB was 3.9 $ng\,g^{-1}$, comparable to those from the Shandong peninsula (5.9 $ng\,g^{-1}$) (Wan et al., 2017) and the Pearl River Delta (3.5 $ng\,g^{-1}$) (Liu et al., 2017), but lower than those from the Yangtze River Estuary (34 $ng\,g^{-1}$) (Yan et al., 2015). Overall, the average concentrations of PFASs in water and sediment were in the middle of the range of studied regions in China.

During the wet season, PFASs in surface water from Xiamen Bay (X1-X7 and X10-X13) were significantly higher than in bottom water ($P < 0.05$, t-test), indicating surface discharge from Xiamen Island. In 2018, there are more than 2 million residents on this island (Xiamen Bureau of Statistics, http://tjj.xm.gov.cn/zfxxgk/zfxxgkml/tjsjzl/tjfx/201902/t201902252227407.htm). It is reasonable that PFASs in station X1 to X13 (water samples at X8 and X9 were not collected in the wet season) were from the Xiamen Island. Sewage effluent is more influential at the surface because its density is less than that of seawater. In Tokyo Bay of Japan, the levels of

PFOS and PFOA are also higher in surface water (5.5 $ng\,L^{-1}$ and 16 $ng\,L^{-1}$) than in bottom water (2.5 $ng\,L^{-1}$ and 6.2 $ng\,L^{-1}$) (Sakurai et al., 2010). However, the higher concentrations of PFASs in bottom water than that in surface water at sites X5 and X11 may be caused by unexpected factors (e.g. ship activities or meandering riverbed) that disturbed the water column. A decreasing trend in PFASs was observed from site X3 to X1 and from site X8 to X13 due dilution by seawater.

In the Jiulong Estuary, PFASs at sites A7 to A9 were higher in bottom water compared to surface water. One possible reason was that PFASs in sediments were released to bottom waters by tidal flushing (Pohlman et al., 2002). In the Pearl River Estuary, a heavily contaminated zone of dissolved polycyclic aromatic hydrocarbons (PAHs) is observed in bottom waters, which are affected by tidal currents (Niu et al., 2018).

3.2. Composition profiles and sources of PFASs in water and sediment

PFBA, PFOS and PFBS were dominant in water during the dry season, accounting for 37%, 16% and 11% of total PFASs. While, PFBS, PFOS and PFHxA were the main compounds in water during the wet season, accounting for 43%, 19% and 14% of total PFASs, respectively.

PFBA was the dominant compound in water from the JEXB during the dry season (Fig. 3). PFASs in 19 Chinese rivers were investigated, including the Jiulong River. Their results showed that PFBA was the dominant compound in the Jiulong River (Wang et al., 2016). However, one previous study suggested that in the dry season of 2014. PFOS was the most abundant compound in the Juilong Estuary (Cai et al., 2018). The different composition profiles of PFASs in the Jiulong Estuary may be attributed to the banned production of PFOS. The increased percentage and concentration of PFBA we observed suggests an increase in the production of PFBA as an alternative. This finding is also consistent with the trend toward an increasing proportion of short chain PFASs in the environment (Munoz et al., 2017b). During the dry season, PFBA concentrations were highest in water from site A7. There is an organic fluoride manufacturing plant midstream in the Jiulong River. Wastewater from this organic fluoride manufacturing plant could be responsible for the high levels of PFBA from site A7 to site JY3 downstream.

The high level of PFOS in water from sites X7 and X8 during the dry season could be caused by the Gaoqi Airport. Previous studies showed that the airport is a source of PFOS due to the use of fire-fighting foams during fire training (de Solla et al., 2012; Ahrens et al., 2015). For example, the mean concentrations of PFOS in water and biota downstream of the John C. Munro International Airport were 78 $ng\,L^{-1}$ and 578 $ng\,g^{-1}$ (wet weight), accounting for 58% and 94% of total PFASs (Filipovic et al., 2015), respectively.

PFBS was the main compound in surface and bottom waters during the wet season at sites X6 and X7 in Xiamen Bay. A nearby WWTP may be responsible for this. According to previous studies, PFBS was the most abundant PFAS in wastewater from Wuhan, China (19–1000 $ng\,L^{-1}$) (Zhou et al., 2017) and Saale, Germany (170 $ng\,L^{-1}$) (Shafique et al., 2017).

In sediment, PFOS was the dominant compound, and contributed 25% to the total PFAS abundance. This is consistent with other studies, as PFOS also dominated in sediment from the Shandong peninsula (Wan et al., 2017), Yangtze River Estuary (Yan et al., 2015), and Pearl River Delta (Liu et al., 2017). Long chain PFASs (C7−C14) accounted for 75% of total PFASs in sediment, and were present in higher concentrations than in water (40%). Additionally, PFHxS, PFHpS, PFOS, PFDS and PFOSA made up a larger proportion (63%) in sediment than in water (35%). The results from the present study indicate that sedimentary absorption of short chain PFASs is
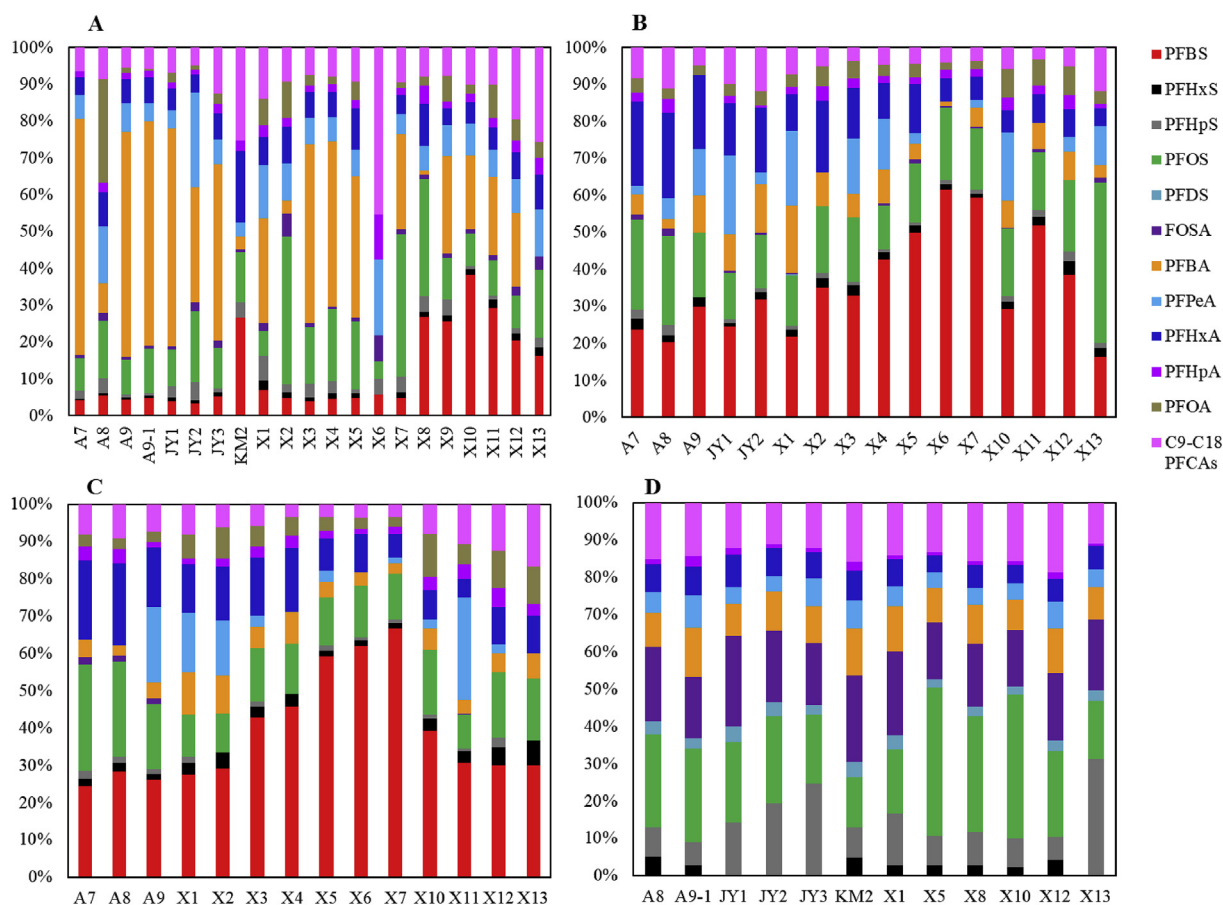
Fig. 3. Composition profiles of PFASs in the JEXB, China. (A) Surface water during the dry season, (B) surface water during the wet season, (C) bottom water during the wet season, and (D) surface sediment during the wet season.

difficult because of their high water solubility, while long chain PFASs were more likely to be present in sediment (Yan et al., 2015). Moreover, PFSAs can be more easily adsorbed by sediment than PFCAs due to differences in functional groups. (Cai et al., 2012; Ding et al., 2018). The highest concentration of PFOS found in sediment from site X5 could be caused by proximity to the Xiamen Port. The cargo throughput of the Xiamen Port is 13−15 million tons per month (Ministry of Transport of the People's Republic of China, http://www.mot.gov.cn/). It was previously reported that the use of paints and grease repellents for ship and dock protection and maintenance could contribute to the high levels of PFOS in sediment (White et al., 2015; Habibullah-Al-Mamun et al., 2016).

3.3. Partition of PFASs between sediment and seawater

The sediment-water K_d values of individual PFASs were determined using the following equation: $K_d = C_s/C_w \times 1000$, where C_s is the PFAS concentration in sediment (ng g^{-1}), and C_w is the dissolved PFAS concentration in water (ng L^{-1}). Table S9 shows the log K_d values of 13 PFASs obtained for the JEXB. The average log K_d values during the wet season ranged from 2.69 to 3.54 for C4−C13 PFCAs and 3.69 to 4.14 for C6−C8 PFSAs, and during the dry season ranged from 1.64 to 2.63 for C4−C13 PFCAs and 2.31 to 2.71 for C6−C8 PFSAs. The log K_d values of PFASs were comparable to those in the Bay of Bengal coast, Bangladesh (Habibullah-Al-Mamun et al., 2016), Tokyo Bay, Japan (Ahrens et al., 2010), and Dianchi Lake, China (Zhang et al., 2012). The log K_d of PFASs varied greatly from season to season, by more than 2 log units, which may be

caused by changes in hydrological conditions (Zhao et al., 2016). For individual PFASs and PFCAs with the same carbon chain length, the K_d of PFSAs was higher than for PFCAs. For example, during the wet season, the average log K_d of PFHxS was 3.69 ± 0.30, while the log K_d of PFHxA was 3.28 ± 0.34. In addition, the log K_d of long-chain PFCAs increased linearly with an increase of carbon chain length, with an R^2 for the dry season of 0.99 (Fig. 4). The observed linear
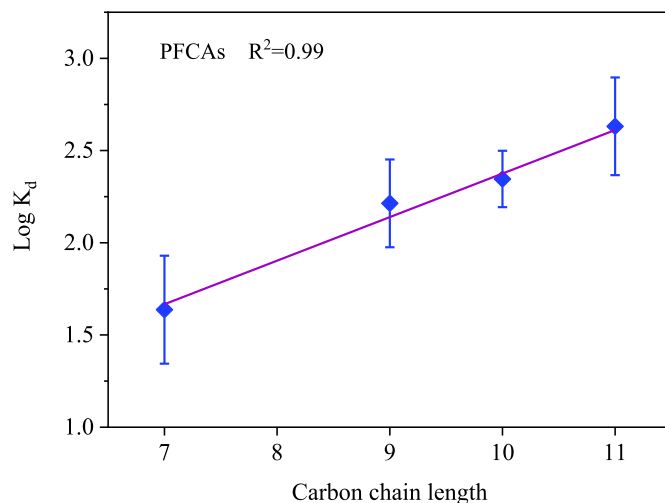

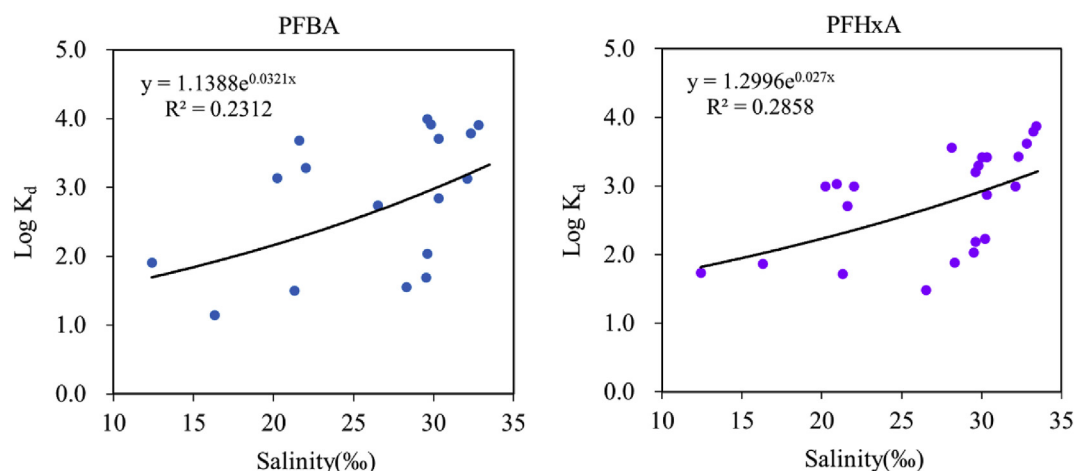**Fig. 4.** Correlation between log K_d and the carbon chain length of PFCAs.

Fig. 5. The relationship between the log K_d of PFBA, PFHxA and salinity (‰).

relationship was in accordance with previous studies (Wan et al., 2017; Wang et al., 2017). The higher K_d values of PFSAs and long-chain PFCAs indicates their preferential presence in sediment. Previous studies reported that PFSAs and long-chain PFCAs have a strong potential for transport along with resuspended sediments and suspended particulate matter (Zushi et al., 2012; Liu et al., 2015a). Therefore, the environmental behavior and fate of PFSAs and long-chain PFCAs are more affected by sediment dynamics. Concentrations of PFASs were thought to be positively correlated with TOC (Wang et al., 2017). However, in some literatures, there was no positive correlation between TOC and the concentrations or Log K_d of PFASs (Wan et al., 2017; Wang et al., 2018). In this study, no significant ($p > 0.05$) positive relationship between concentrations of PFASs and TOC was found. One possible reason was the low f_{OC} (average 0.47%) of sediment samples in this study. Hence, TOC was not the main factor in controlling the partitioning of PFASs between sediment and water in this study.

A salinity gradient at the river-sea interface is present because of mixing between seawater and freshwater. Previous studies show an exponential relationship between values of K_d and salinity (Hong et al., 2013; Munoz et al., 2017a). In this study, an exponential relationship between salinity and the K_d values of PFBA, PFHxA and PFOS was found (Fig. 5 and Fig. S1), indicating a "salting out" effect that promotes the transport of these compounds from water to sediment. Some cations, such as Na^+ and K^+ in seawater act as ion-pairs with anionic PFASs. When ion-pairs are formed, the partitioning properties of PFASs change, and hydrophobicity increases due to neutralization of charged moieties (Jeon et al., 2010). Another possible explanation is the bridging effect caused by divalent cations, such as Ca^{2+} and Mg^{2+}, that may form a bridge between the anionic organic matter functional groups, such as carbonyl, phenolic, and hydroxyl and anionic PFASs (You et al., 2010; Wang and Shih, 2011). The R^2 of PFBA and PFHxA was 0.23 and 0.28 in this study, respectively. Water and sediment samples in low salinity (0−10‰) were absent, which limited the accuracy of fitting curve.

3.4. Environmental risk assessment of PFOS and PFOA

The risk quotient (RQ) was used to perform an environmental risk assessment (ERA) of PFASs in water and sediments from the JEXB. RQ is defined as the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC). An RQ value below 1 means no potential risk. This method only provides a rough estimation of the environmental risk of PFOS and PFOA in water and sediments because of uncertainties. The PNEC of PFOS and PFOA in water are $25\,\mu g\,L^{-1}$ and $1250\,\mu g\,L^{-1}$, respectively, based on work from Brooke et al. (2004) and Colombo et al. (2008). These PNEC values were accepted by previous researchers and used to assess the environmental risk of PFOS and PFOA (Zhao et al., 2013; Gao et al., 2015; Liu et al., 2017). The non-TOC-normalized PNEC for PFOS is $4.9\,ng\,g^{-1}$ in estuarine sediments (Zhao et al., 2013). All water and sediment samples from the JEXB returned RQ values below 1 (Table S10), which suggests no significant risk for the benthic organisms in the study region.

4. Conclusions

The concentrations and composition profiles of PFASs in the JEXB varied across different seasons. The average concentration of total PFASs was higher during the dry season than the wet season, which might be related to changes in discharge from the Jiulong River. PFBA and PFBS were the predominant compounds in water, while PFOS had the highest concentrations in sediment. The concentration of PFBA as an alternative to PFOS showed an increasing trend in this study. High concentrations of PFASs in water and sediment from Xiamen Bay are attributed to inputs from the harbor, airport and WWTP. The log K_d values of PFASs were higher during the dry season than the wet season. In addition, K_d increased with increasing carbon chain length and salinity, indicating that sediment was a sink for PFSAs and long-chain PFCAs. The environmental risk assessment indicates that the concentrations of PFOS and PFOA in the water and sediments of the JEXB pose no risks to organisms.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124578.

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