Research Paper

Plant uptake of perfluoroalkyl substances in freshwater environments (Dongzhulong and Xiaoqing Rivers, China)

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ABSTRACT

This study provides new knowledge on the mobility, behavior, and partitioning of 17 perfluoroalkyl substances (PFASs) in the water-sediment-plant system along the Dongzhulong and Xiaoqing Rivers. The fate of PFASs in these rivers is also discussed. The study area is affected by the industrial production of perfluorooctanoic acid (PFOA). The sum of PFASs in water and sediments close to the industrial discharge were 84,000 ± 2000 ng/L and 2300 ± 200 ng/g dw, respectively, with the concentrations decreasing along the river due to dilution. PFOA was the dominant compound (74–97%) of the sum of PFASs, although other PFASs were identified close to urban areas. Principal component analysis and solid-liquid distribution coefficients revealed that long-chain PFASs accumulated in the sediment whereas short-chain PFASs remained in the water all along the river. PFASs were taken up by plants and remobilized to different plant compartments according to shoot concentration factors (SCFs), root concentration factors (RCF), and transfer factors (TFs). Among the four plant species studied, floating plants absorbed high levels of PFASs, while rooted species translocated short-chain PFASs from the roots to the shoots. Therefore, floating species, due to their high uptake capacity and large proliferation rate, could eventually be used for phytoremediation.

1. Introduction

Perfluoroalkyl substances (PFASs) are industrial compounds whose production started in the 1950s for commercial purposes (Remner, 2001). PFASs have excellent thermal and chemical stability and are used as polymers, surfactants, stain repellents, and flame retardants in several products such as carpets, leather, paper, textiles, and fire-fighting foams (Remner, 2006), as well as in essential products such as medical devices and occupational protective clothing (Cousins et al., 2019). PFASs are ubiquitous in the environment through their presence in discharges from various point sources such as manufacturing and processing industries, as well as in aqueous film-forming foams (Barton et al., 2020), wastewater discharges, sewage sludge (Stahli et al., 2018), landfills, and air emissions (Wang et al., 2014a). They remain in the aquatic system due to their persistent and bioaccumulative properties (Wang et al., 2014b). Once in the environment, PFASs can remain solubilized in water, sorb into sediments, or be taken up by plants. It depends on the physicochemical properties of the compounds (e.g., perfluorocarbon chain length, head of the functional group, water solubility, and volatility), plant physiology (e.g., transpiration rate, and lipid and protein contents), and abiotic factors (e.g., soil organic matter, pH, salinity, and temperature) (Wang et al., 2020). To evaluate the accumulation and mobility of PFASs in the water-sediment-plant system, partitioning factors (Kj) (Milinovic et al., 2015) and plant uptake rates (Bizzakgurer et al., 2016; Wang et al., 2020) are important as they provide information on the distribution and final fate of PFASs. However, these processes have not been widely studied in a river basin affected by local discharges of PFASs from a manufacturing plant and in the transport of
PFASs along a river.

As a consequence of fast economic growth over the last decades, industrial development has expanded to satisfy the global needs of PFASs and related chemicals. The People’s Republic of China is one of the main producers of PFASs. The fluoropolymer-producing facility located in the highly urbanized and industrialized Bohai Sea Economic Rim in northeastern China in 2012 produced 37,000 tons of polytetrafluoroethylene, 50,000 tons of tetrafluoroethylene, 10,000 tons of hexafluoropropylene, 500 tons of perfluorinated ethylene-propylene copolymers, 300 tons of polyvinylidene fluoride, 40 tons of perfluorooctanoic acid (PFOA) ammonium salt, and more than 200,000 tons of different types of fluorinated refrigerants (Wang et al., 2014b). As a result of this production, the Xiaoqing River and its Dongzhulong tributary are affected by the emissions of PFASs, with the Bohai Sea receiving around 87.3 tons per year (Chen et al., 2017) that accounts for approximately 10–30% of the global PFOA emissions (Shi et al., 2015). Due to the PFOA-manufacturing plant, this compound has been recurrently detected in water samples and sediments from the Xiaoqing River (Song et al., 2018) and the Laizhou Bay and Bohai Sea (Zhou et al., 2018; Zhu et al., 2014). However, the water-sediment partitioning factors and the role of plants in the uptake and remobilization of PFASs have not been elucidated. This information is relevant to determine the fate of PFASs in such an impacted river.

The main objective of the present study was to investigate the distribution and fate of 17 PFASs along the Dongzhulong and Xiaoqing River basin, an area receiving direct PFOA discharges from a manufacturing plant in China. Specific objectives were to: (i) evaluate the occurrence and partitioning of these 17 PFASs in surface waters and surface sediments along the river, (ii) assess the uptake of PFASs by four plant species, two floating and two rooted, and (iii) elucidate the mobilization of PFASs by plants. Principal component analysis (PCA) was used to assess the sources of pollution and distribution trends. Overall, this study provides new information on the occurrence, transport, partitioning, and plant uptake of PFASs in an impacted river to better understand the processes that explain the behavior of PFASs in real environmental conditions.

2. Materials and methods

2.1. Study area and sample collection

The study area comprised the Xiaoping River basin. The Dongzhulong River is a tributary of the Xiaoqing River and receives industrial discharges from the biggest fluoropolymer-producing facility in China that is part of the Dongyue Group (Wang et al., 2014a–c). It also receives wastewater from major cities (Jinan, Zibo, Binzhou, and Dongying) where petrochemical, chemical, electronic, iron, and steel industries are located (Chen et al., 2017).

Eleven sampling points along the Dongzhulong and Xiaoqing Rivers were sampled in August 2017. The first sampling point was just after the water discharge area of the fluoropolymer-producing facility (0.16 km) and the last sampling point was just before a dam (38.16 km) (Fig. 1). Sampling points 1–5 were in the Dongzhulong River, while sampling points 6–11 were in the Xiaoqing River. The samples collected at each point included: (i) 1-L grab sample of surface water; (ii) freshwater surface sediment (top 0–20 cm) collected with a drag, and (iii) two plant species floating on the surface water (Lemna minor and Ceratophyllum demersum) and two plant species with roots (Alternanthera sessilis and Eriochloa villosa) collected manually alongside sediment from around the roots. For each plant species, six individuals were collected at each site and pooled, except for L. minor, for which a composite sample of dozens of individuals was taken due to the small individual size. Details

Fig. 1. Sampling area. (A) Map of China with the Shandong Province shown in red. (B) Red dot indicates the Xiaoqing River basin. (C) Map showing the river from the fluoropolymer-producing facility (red) to the dam. Urban settlements are shown in yellow, the river flow is indicated by the arrows (blue), and the sampling points are shown as white dot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
of the sampling information are listed in Table S1 and a further description of the plant species are provided in Supplement S1 of the Supplementary Information (SI). Not all the plants were growing at all the sampling points. Therefore, the plants reported at some of the sampling points indicate their specific presence in that given area.

Water samples were stored in cold conditions (4 °C) until extraction. Surface sediments were freeze-dried for 48 h, homogenized with a blender, and frozen (−20 °C) in bags before analysis. Rooted plants were divided into shoots and roots. Each part was washed sequentially with tap water and Milli-Q water and dried with tissue paper. All plant materials were freeze-dried for 48 h, homogenized with a blender, and frozen (−20 °C) in bags before analysis. Sediments taken from around the roots were separated manually and processed as river sediments.

2.2. Chemicals and reagents

Standards of PFAS mixtures were purchased from Wellington Laboratories and contained perfluoro-n-butanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA), perfluoro-n-hexanoic acid (PFHxA), perfluoro-n-heptanoic acid (PFHpA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-nonanoic acid (PFNA), perfluoro-1-decanoic acid (PFDA), perfluoro-1-dodecanoic acid (PFDoA), perfluoro-1-tridecanoic acid (PFTrDA), perfluoro-1-tetradecanoic acid (PFTeDA), perfluoro-1-hexadecanoic acid (PFHxDA), and perfluoro-1-octadecanoic acid (PFODA), potassium perfluoro-1-butanesulfonate (PFBS), sodium perfluoro-1-hexanesulfonate (PFHxS), sodium perfluoro-1-octanesulfonate (PFOS), and sodium perfluoro-1-decanesulfonate (PFDS).

A working solution was prepared in methanol at a concentration of 0.2 µg/mL and stored at −18 °C. Mass-labeled perfluoro-1-[13C9]-octane sulfonamide (MBFOSA-I, 1.2 mL × 50 µg/mL in isopropanol) from Wellington Laboratories was used as an internal standard (IS). MBFOSA-I was prepared in methanol at a concentration of 1 µg/mL and was stored at −18 °C. Methanol and acetonitrile were supplied by Merck & Co (New Jersey, USA), tetrabutylammonium hydrogen sulfate (TBAHS) by Sigma-Aldrich (St. Louis, USA), and methyl tert-butyl ether (MTBE) by Macklin (Shanghai, China). Supelclean ENVIL-Carb SPE Tube cartridges were obtained from Supelco (Bellefonte, USA).

2.3. Extraction and instrumental method

Regarding surface water samples, the extraction method used was adapted from Heydebreck et al. (2015) and applied to non-filtered water in order to quantify the total concentration of PFASs in water including the small amount sorbed to particulate matter. Briefly, 100 µL of the MBFOSA-I IS at a concentration of 1 µg/mL were added to 1 L of water and solid-phase extraction (SPE) was performed at approximately 2 mL/min using the Supelclean ENVIL-Carb SPE cartridges (250 mg, volume of 3 mL, obtained from Supelco). The cartridges were conditioned with 10 mL of acetone, methanol, and methanol containing 0.25% ammonium hydroxide, respectively. After sample preconcentration, the cartridges were washed with 5 mL of Millipore water, dried using a vacuum pump, and finally eluted with 10 mL of 0.25% ammonium hydroxide in methanol. The extract was reduced under a gentle stream of nitrogen and reconstituted in 1 mL of methanol.

In the case of the sediments, 1 g of sample was spiked with 100 ng of the IS (100 µL of a solution at 1 µg/mL) and left at 4 °C overnight. Solid-liquid extraction was performed (3 times) with 5 mL of methanol and 5 mL of dichloromethane in an ultrasonic bath for 20 min, before the mixture was centrifuged (10,000 rpm, 30 min). The resulting supernatant was collected and evaporated under a gentle stream of nitrogen and filtered through a 0.22-µm nylon mesh filter and reconstituted in 1 mL of methanol.

Plant extraction was performed according to the method of Wen et al. (2013), with some modifications. Briefly, 1 g of shoot or root was spiked with 100 ng of the IS (100 µL of a solution at 1 µg/mL) and 4 mL of methanol containing 0.4 mol/L of NaOH were added and left overnight at 4 °C. Solid-liquid extraction was conducted (3 times) with 4 mL of 0.25 mol/L of the sodium carbonate buffer, 2 mL of 0.5 mol/L of TBAHS, and 5 mL of MTBE. The mixture was manually shaken for 20 min and centrifuged (4200 rpm, 10 min). The supernatant was reduced under a gentle stream of nitrogen, filtered through a 0.22-µm nylon mesh filter into a chromatography vial, and reconstituted in 1 mL of methanol.

PFASs were analyzed using a Liquid Chromatography system from the Agilent 1220 Series coupled to an Agilent 6410 Triple Quadrupole Mass Spectrometer (Agilent Technologies, California, USA) (LC-MS/MS). A Synergi Hydro-RP 80A column (150 mm × 2 mm, 4 µm particle size) was used (Phenomenex, California, USA). 5 µL of the extract were injected. The mobile phase consisted of water (A) and methanol (B), both containing 10 mmol of ammonium acetate. The chromatographic gradient started at 30% B (condition held for 10 min), increased to 70% B over 3 min, and to 90% B over 25 min, and then increased to 100% B over 5 min, which was maintained for 15 min. The flow was set at 0.2 mL/min and the column temperature was 30°C.

A calibration curve with six points was built over a concentration of 2, 5, 10, 25, 50, and 100 ng/mL. The PFAS calibration curve, regression coefficients, and instrumental detection limits (IDL) are shown in Table S2 of the SI. Detailed recoveries of each compound can be found in Heydebreck et al. (2015) for water and in Wen et al. (2013) for plants. Method efficiency was calculated using the recoveries of the MBFOSA-I IS (10 ng/g level), which ranged from 43% to 121% in water, 52–109% in sediment, and 70–115% in plants.

2.4. Data treatment and analysis

The pollutants partitioning between water and sediments were studied through the solid-liquid distribution coefficient (Kd, L/kg).

\[
K_d = \frac{[\text{PFAS ng/g dw in sediment}]}{[\text{PFAS ng/L in surface water}]} \quad (1)
\]

The transfer of pollutants between plant compartments and the surroundings were analyzed using the shoot concentration factor from water (SCFw) in floating species, the shoot concentration factor from sediment around the root (SCFs) in root species, the root concentration factor (RCF), and the translocation factor (TF) between the shoot and root.

\[
\text{SCFw (L/g)} = \frac{[\text{PFAS ng/g dw in shoots}]}{[\text{PFAS ng/L in surface water}]} \quad (2)
\]

\[
\text{SCFs (g/g)} = \frac{[\text{PFAS ng/g dw in shoots}]}{[\text{PFAS ng/g dw in sediment around the roots}]} \quad (3)
\]

\[
\text{RCF (g/g)} = \frac{[\text{PFAS ng/g dw in roots}]}{[\text{PFAS ng/g dw in shoots}]} \quad (4)
\]

\[
\text{TF (g/g)} = \frac{[\text{PFAS ng/g dw in shoots}]}{[\text{PFAS ng/g dw in roots}]} \quad (5)
\]

Each quotient was calculated for the compounds detected simultaneously in the different matrices. The sediments used in the calculation of the RCF and the TF were those surrounding the roots.

PCA was performed using the R-3.4.4 software (https://www.r-project.org/). We performed PCA on PFAS concentrations detected at all the locations using the covariance matrix to explore the sources of pollution, distribution trends and patterns of association among the PFASs and the sampling points for surface water and sediments, as well
as the bioaccumulation factors (SCF and RCF) of the rooted species. We used the Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy for each variable in the model and for the complete model to assess the usefulness of the PCA. The KMO value ranges from 0 to 1 and should be well above 0.5, with a value above 0.6–0.7 considered adequate for the variables to be sufficiently interdependent for PCA to be useful (Tabachnick and Fidell, 2000). In this study, the PFASs were classified by their functional group and chain length. They included perfluoroalkyl carboxylic acids with seven or fewer carbons (short-chain PFCAs), perfluoroalkyl carboxylic acids with eight or more carbons (long-chain PFCAs), perfluorokane sulfonates with five or fewer carbons (short-chain PFSAs), and perfluorokane sulfonates with six or more carbons (long-chain PFSAs) (Buck et al., 2011).

3. Results and discussion

3.1. Occurrence and partitioning of PFASs along the Xiaoqing River basin

The impact of the PFOA-manufacturing plant located at the Xiaoqing River and urban discharges of PFASs was evaluated by determining the accumulation and distribution trends of PFASs in water and sediment samples along the basin, specifically assessing the uptake ability of PFASs by different plant species. Fig. 2 shows the concentration of PFOA and $\sum$PFASs in water, sediment, and floating and rooted plants along the river basin. A clear dilution trend was observed from the 1st sampling point next to the fluoropolymer-producing facility to the 11th sampling point just before a dam. Consistent with the production of PFOA at the facility belonging to the Dongyue Group, PFOA was the dominant compound in all the matrices studied, comprising 74–82% of the $\sum$PFASs in surface water, 91–93% in sediments, and 82–97% in the floating and rooted plant species (Tables S3–S5 of the SI, respectively).

Fig. 2. Mean concentration of PFOA and $\sum$PFASs in (a) surface water (ng/L) and (b) sediments (ng/g dw), as well as in the shoots and roots of (c) Lemna minor and (d) Ceratophyllum demersum (ng/g dw) and in the shoots of (e) Alternanthera sessilis and (f) Eriochloa villosa (ng/g dw) at the sampling points in the Dongzhulong and Xiaoqing Rivers. Error bars indicate the standard deviation (n = 3).
3.1.1. PFASs in surface water

In surface water (Fig. 2a), PFOA had the highest concentration ranging from 18,250 ± 480 to 69,500 ± 1660 ng/L, followed by PFHxA > PFBA > PFPeA, which comprised 2.8–8.4% of the ∑PFASs at concentrations from 860 to 4300 ng/L (Table S6 of the SI). Long-chain PFCAs and PFSAs were found at a concentration that was one order of magnitude lower, in a range from 0.44 ± 0.04 to 374 ± 4.4 ng/L, or were not detected, as was the case for PFHxDA, PFODA, and PFDS. Our results are in agreement with those of previous studies from the Xiaoqing River that report PFOA as the dominant compound in surface water, with a concentration ranging from 4.06 to 61,900 ng/L, followed by PFHxA and PFHpA (Chen et al., 2017). Next to the same fluoropolymer-producing facility, 106,000 ng/L (Heydebreck et al., 2015) and 496,000 ng/L of ∑PFASs (Shi et al., 2015) have been recorded previously, with dilution occurring when the river waters are discharged at the Laizhou Bay in the Bohai Sea, resulting in ∑PFAS concentrations of 99.4 ng/L (Chen et al., 2016), 3.9–118 ng/L (Zhao et al., 2017), and 4.55–556 ng/L (Zhou et al., 2018). All the earlier studies report the predominance of PFOA, suggesting that the Xiaoqing River is a significant source of PFOA contamination in this area.

PCA of PFASs in surface water samples shows the distribution pattern according to scores (sample points) and loadings (compounds) (Fig. 3a). The KMO value of 0.76 indicated that the PFAS concentrations were interdependent and significantly intercorrelated with the co-predominance of all the PFASs. PCA enabled the identification of possible sources of pollution. The first and second principal components explained 69.2% and 12.5% of the total variance, respectively. PFBA, PFPeA, PFHxA, PFHpA, and PFOA had a similar contribution in the water samples, while PFNA, PFDA, PFUnA, and PFDoA were segregated, with a higher contribution at the first two sampling points. PFOS showed a high contribution at sampling point 3, located downstream of the cities of Qifengzhen, Boxing City, and Hubinzhen, with a mean concentration of 58.4 ± 13.8 ng/L. At sampling point 4, which received waters from Mata Lake (wetland and a fishing hotspot) and had irrigation channels, the mean concentration of PFOS was 93.3 ± 10 ng/L. PFOS was not manufactured nor widely applied in the industrial processes in this

Fig. 3. PCA of the PFASs detected in (a) surface water (ng/L) and (b) sediments (ng/g dw) along the Dongzhulong and Xiaoqing Rivers. The numbers represent the sampling points analyzed in triplicate.
region (Xie et al., 2013). Previous studies have suggested that its presence is mainly from urban activities, street runoff, and wastewater treatment discharges from the very densely populated area (Shi et al., 2015). At sampling point 5, where the Dongzhulong River joins the Xiaoqing River (Fig. 1), a slight decrease in concentration was observed due to a dilution effect of both rivers, with a lower contribution in both the PCI and PC2. Thereafter (sampling points 6–11), a specific source of PFBS and PFHxS pollution was observed in the PCA (Fig. S1 of the SI).

The high levels of PFASs found in the surface waters sampled has serious implications regarding the potential effects in wildlife as PFASs can be incorporated to organisms through diet, can be accumulated and biomagnified along the food chain and produce effects in wildlife, as observed for birds, mammals (Sonne et al., 2020), fish and other aquatic organisms (Mhadihi et al., 2012). In addition, humans might be exposed to PFASs through the consumption of contaminated fish or edible plants and this can have effects as PFASs are cytotoxic and endocrine disruptors (Gorrochategui et al., 2016).

### 3.1.3. PFASs in plant species

In the sediments, PFOA was the dominant compound with a concentration of 2120 ± 182 ng/g dw at sampling point 1 and a concentration of 290 ± 17 ng/g dw at sampling point 11, thus showing a clear dilution along the basin (Fig. 2b). Previous studies in the area have reported a PFOA concentration of 3640 ng/g dw in the Dongzhulong tributary and 382 ng/g dw downstream (Shi et al., 2015). The prevalence of PFOA in sediments and the dilution effect along the Xiaoqing River basin is in agreement with previous studies reporting decreasing concentrations at downstream waters of the Xiaoqing River close to the river mouth, with Zhao et al. (2013) reporting a decreasing trend with 76.9, 2.6, and 2.1 ng/g dw and Zhu et al. (2014) reporting similar trends with 29.0, 13.0, and 2.45 ng/g dw. In terms of concentration, other PFASs were detected at levels up to 37.8 ± 8.1 ng/g dw, representing <2.4% of the ΣPFASs. PFODA, PFDS, and PFBS were not detected (Table S7 of the SI). Long-chain PFASs contributed more to the total ΣPFASs in sediment than in water due to their affinity for sediments (Chen et al., 2017; Shi et al., 2015). The PCA shown in Fig. 3b indicates that most of the PFAS concentrations were interdependent and significantly intercorrelated (KMO = 0.79). The first and second principal components explained 76.7% and 13.5% of the total variance, respectively. The first principal component was predominantly explained by PFCAs that had high concentrations at sampling points 1 and 2, while the second principal component was mainly explained by the presence of PFHxS and PFOS at sampling points 3 and 4, similar to that observed in water. PCA also showed that at sampling points 5–11, the contribution of all the PFASs was very low. For all the compounds, a decreasing trend was observed along the river, except for PFOS, whose concentration increased from sampling point 5–11, presumably due to urban effluent discharges, as observed for the water samples (Fig. S2 of the SI).

### 3.1.4. PFASs in plant species

There is little information regarding the accumulation of PFASs in aquatic plants, especially in real environmental conditions. The two free-floating species were the macrophyte Lemna minor, with a single 2-cm root, and Ceratophyllum demersum, a submerged, aquatic plant. The rooted species were Alternanthera sessilis, which has a taproot, and Eriochloa villosa, which has an adventitious root that branches as a taproot. Roots are known to play a major role in nutrient uptake as well as in the uptake of contaminants, thus having ecological relevance in freshwater ecosystems (Ghisi et al., 2019). The uptake of PFASs should first occur in the root of all four plant species, being absorbed either from the water or sediment (Pi et al., 2017). Fig. 2 (c–f) shows that the levels and distribution trends of PFASs in plants along the river followed that of the water and sediment samples, indicating that plants are also affected by river pollution. Throughout the river, PFOA was the main PFAS detected in all the plant species followed by short-chain PFASs. This reflects once more that the PFOA discharge area has an impact all along the river ecosystem.

In floating species, PFOA had the highest concentration, ranging from 3240 ± 430 to 19,600 ± 330 ng/g dw in L. minor and from 2390 ± 230 to 6190 ± 500 ng/g dw in C. demersum, followed by short-chain PFCAs, which had levels up to 280 ± 10 ng/g dw with a very low contribution to the ΣPFASs (Table S8 of the SI). Other PFASs were detected at lower concentrations or not detected, as was the case for PFHxDA, PFODA, PFBS, PFHxS, and PFDS. There are only a few studies on PFASs in floating plant species in the literature. ΣPFAS levels of 405 ng/g dw have been reported in L. minor from the Mississippi River (USA) (Oliasei et al., 2013), while levels ranging from 4.78 to 7.63 ng/g dw have been observed in C. demersum pooled with other aquatic plants (Myriophyllum spicatum and Vallisneria spiralis) from the Rhone River (France) (Sabet et al., 2017). These levels are much lower compared to those in our study (ΣPFAS ranges from 2500 ± 240 to 8700 ± 1750 ng/g dw).

In rooted species, the PFOA concentration in A. sessilis ranged from 570 ± 21 to 3960 ± 160 ng/g dw in the shoots and from 800 ± 28 to 6320 ± 310 ng/g dw in the roots. In E. villosa, these values ranged from 740 ± 53 to 4260 ± 42 ng/g dw in the shoots and from 1980 ± 290 to 8140 ± 1470 ng/g dw in the roots. The relatively higher levels in E. villosa compared to A. sessilis may reflect a higher root uptake due to the adventitious root of the former. However, PFHxS and PFOS had higher levels in the roots of A. sessilis. Tables S9 and S10 of the SI show the concentration of PFASs in the plants. Short-chain PFCAs were detected at much lower concentrations in both species, with levels up to 333 ± 35 and 126 ± 21 ng/g dw in the shoots and roots, respectively, comprising <11% of the ΣPFASs (Tables S5, S9 and S10 of the SI). PFODA, PFBS, and PFDS were not detected. In both rooted species, most PFASs showed a general decreasing trend along the river (Figs. S3 and S4 of the SI), except for PFDA, PFUnA, PFDoA, and PFtDA in A. sessilis and the shoots of E. villosa and PFHxS and PFOS in E. villosa due to their low concentrations.

### 3.2. Distribution of PFASs in the water-sediment system

PFASs in surface water and freshwater sediments had a similar profile along the Dongzhulong and Xiaoqing Rivers. Solid-liquid distribution coefficients (Kd) were calculated for each PFAS to assess the relationship between the chain length of the PFASs and their distribution in the water-sediment system. As illustrated in Fig. 4, the Kd values increased with the increasing chain length of the PFASs. Thus, short-chain PFCAs had low Kd values (less than 10 L/kg), indicating that these compounds are preferentially partitioned into the water as they have higher water solubility and mobility. By contrast, long-chain PFCAs, due to their higher hydrophobicity, are expected to be sorbed more readily into the organic matter in the sediment. Thus, PFOA and PFNA showed intermediate values (from 5.6 ± 0.2 to 30.5 ± 3 L/kg), while the PFASs with C-F chain >10 (PFDA, PFUnA, and PFDoA)
presented the highest \( K_p \) values (from 51.8 ± 5.1 to 7800 ± 1260 L/kg), thereby preferentially accumulating in sediments. Table S11 in the SI shows the individual mean \( K_p \) values of the PFASs at each sampling point. Our results are supported by those of previous studies demonstrating that the \( K_p \) values for PFASs increase with the chain length (Liu et al., 2019a; Zhang et al., 2012). On the other hand, PFHxS and PFOS had higher \( K_p \) values than the PFCAs with the same number of fluorinated carbons (i.e., PFHpA and PFNA, respectively), suggesting that the functional group also plays a role in the distribution of PFASs in the water-sediment system. The partitioning of PFASs into sediments is favored compared to their PFCA analogs due to their greater hydrophobicity and the larger size of the sulfonate moiety that has more specific electrostatic interactions with sediments compared to the carboxylate moiety (Higgins and Luthy, 2006).

### 3.3. Uptake of PFASs in floating and rooted plants

In this study, the PFAS uptake ability of floating vs. rooted plant species was compared and the uptake trends along the basin were evaluated. To do so, the SCFw, SCFs, RCF, and TF were calculated to assess the mobility of PFASs in the water-plant system for both floating and rooted species. Compounds not detected were omitted and were PFTrDA, PFTcDA, PFHxDA, PFODA, and PFDS in water, PFHxDA, PFODA, PFBS, and PFDS in sediment, and PFHxDA, PFODA, PFBS, PFHxs, and PFDS in rooted plant species. Table 1 shows the mean values considering all sampling points. Individual values for each sampling point are indicated in Tables S12–S14 of the SI. The uptake of PFASs from water/sediment varies among plants according to the species and the environmental concentration (Krippner et al., 2014). Indeed, differences in uptake factors were observed among all four plant species in this study. PFAS concentrations in water and sediment samples decreased along the Xiaoping River, while the PFAS profile remained constant along the sampling points. We found that floating species had a higher concentration of PFASs than rooted species at the same sampling points. Thus, uptake from water might be enhanced compared to sorption from sediments in the rooted species, with PFAS bioavailability from sediment being lower and active internal transport from the roots to shoots being required (Pi et al., 2017; Wang et al., 2020).

Regarding the floating plant species, \( L. \) minor and \( C. \) demersum had an SCFw < 1 for PFASs with 10 or fewer carbons, while SCFw > 1 for PFUnA and PFDoA, demonstrating an increase in the SCFw with an increasing chain length of the PFASs. PFOS and PFHxS also showed higher SCFw values than the PFCAs with the same chain length (PFNA and PFHpA, respectively). In concordance with our findings in floating species, a mesocosm study demonstrated that PFCAs with 10 or more carbons exhibited the highest plant-water bioaccumulation potential in \( Echinochloa \) horemanni, while PFASs with 4–9 carbons had the lowest bioaccumulation potential (Pi et al., 2017).

Both rooted species had a similar behavior regarding the uptake and translocation of PFASs (Fig. 5). PCA indicated that the SCFs and RCFs were interdependent and significantly intercorrelated (KMO = 0.72). The first two axes explained 51.0% and 17.5% of the total variance, respectively. Short-chain PFASs (i.e., PFBA, PFPeA, and PFHxA) positively contributed to the SCF, while long-chain PFASs (i.e., PFDA, PFUnA, PFDoA, PFTcDA, PFOS, PFPOA, and PFNA) were related to the RCF. Furthermore, PFHpA had an intermediate position between these groups. We observed that short-chain PFCAs (PFBA, PFPeA, and PFHxA)

**Table 1**

| Species                  | Mean (Min - Max) | Mean (Min - Max) | Mean (Min - Max) | Mean (Min - Max) | Mean (Min - Max) | Mean (Min - Max) |
|--------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| **SCFw**                 |                  |                  |                  |                  |                  |                  |
| Alternanthera sessilis    | 0.07 (0.003-0.2)  | 0.03 (0.01-0.06) | 23 (3-39)        | 6 (0.5-21)       | 12 (1-39)        | 16 (7-32)        |
| Eriochloa villosa         | 0.03 (0.008-0.08)| 0.01 (0.006-0.02)| 7 (3-11)         | 2 (0.9-4)        | 5 (1-10)         | 7 (3-19)         |
| PFHxDA                   | 0.04 (0.002-0.08)| 0.02 (0.01-0.03) | 4 (2-6)          | 2 (4-8)          | 1 (0.5-2)        | 4 (2-7)          |
| PFHxS                    | 0.3 (0.1-0.6)    | 0.2 (0.1-0.3)    | 2.3 (1.7-2.7)    | 3 (2-5)          | 0.7 (0.5-1)      | 3 (2-5)          |
| PFNA                     | 0.1 (0.02-0.2)   | 0.1 (0.06-0.2)   | 0.7 (0.3-1)      | 2 (1-3)          | 0.4 (0.2-0.6)    | 2 (0.6-7)        |
| PFDA                     | 0.7 (0.4-1)      | 0.6 (0.3-1)      | 0.6 (0.3-0.8)    | 2 (1-3)          | 0.3 (0.2-0.4)    | 0.9 (0.3-2)      |
| PFUnA                    | 4 (2-6)          | 3 (1-5)          | 0.5 (0.2-0.8)    | 2 (1-3)          | 0.2 (0.1-0.3)    | 0.9 (0.3-2)      |
| PFDa                     | 11 (8-16)        | 7 (12-3)         | 0.3 (0.1-0.4)    | 2 (1-2)          | 0.2 (0.1-0.4)    | 0.8 (0.1-2)      |
| PFTrDA                   | 1.0 *a*          | 0.7 (0.4-1)      | 3 (1-5)          | 0.3 (0.1-0.8)    | 1 (0.2-3)        | 1 (0.2-3)        |
| PFHpA                    | *a*              | *a*              | *a*              | 0.3               | *a*              | 2 (0.2-5)        |
| PFDoA                    | *a*              | *a*              | *a*              | 0.3               | *a*              | 2 (0.2-5)        |
| PFHxA                    | 0.16 (0.09-0.3)  | 3 (1-4)          | 14 (4-31)        | 0.3 (0.1-0.4)    | 6 (4-11)         | 0.2 (0.2-3)      |
| PFOS                     | 0.5 (0.1-1)      | 0.2 (0.1-0.4)    | 0.9 (0.4-2)      | 6 (2-16)         | 0.2 (0.1-0.3)    | 4 (2-7)          |
| *a* The corresponding compound was not detected in the water sample.
| *b* The corresponding compound was not detected in the plants.
| *c* The corresponding compound was only detected once in the plants.

**Fig. 5.** PCA of the shoot concentration factor in blue (SCFs, \( \text{Alternanthera sessilis} \)) and the root concentration factor in red (RCF, \( \text{Eriochloa villosa} \)) of PFASs in the rooted species \( \text{Alternanthera sessilis} \) and \( \text{Eriochloa villosa} \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
accumulated more in the shoots than in the roots due to the translocation produced by the water potential gradient created by plant transpiration that promotes the upward transport through the xylem. By contrast, long-chain PFASs preferentially accumulated in the roots due to the proteinophilic-linked sorption. This was also demonstrated by the TF values (Table 1), which decreased with increasing chain length, as reported in previous studies (Blaine et al., 2014; Liu et al., 2017). Bizkarguenaga et al. (2016) observed that PFOA was taken up in the translocation stream and accumulated more than PFOS in the edible part of lettuce. Krippner et al. (2014) also showed that in maize, PFBA, PFPeA, and PFHxSA were more readily translocated from the roots to the shoots compared to long-chain PFASs, which bounded strongly to the surface of the roots, presumably because long-chain PFASs positively correlate with the protein content (Wen et al., 2016). However, environmental concentration and the protein and lipid contents of the plant alongside different translocation processes may explain the differences among the species. Moreover, chemical properties such as polarity, molecular size, and functional group are key in the penetration through the plasma membrane of root cells (Krippner et al., 2014). No differences in the translocation of PFASs in the roots and shoots between the two rooted species were observed.

In the Dongzhulong and Xiaoqing River area, previous studies have reported crop bioaccumulation and human exposure to PFASs (Liu et al., 2019b), suggesting that the area is contaminated at levels that can affect food safety and the environment. Because PFASs are taken up by plants, its use can be proposed as a phytoremediation procedure to eliminate the loads of these contaminants (Huff et al., 2020), as demonstrated for juncus (Zhang et al., 2019) and macrophytes (Pi et al., 2017). L. minor has a large proliferation rate, a high uptake capacity (Boudreau et al., 2003; Pietrini et al., 2019), and is considered a good phytoremediator of PFASs in surface water (Zhang and Liang, 2020). Similarly, Cyperus demersus was previously used in PFAS bioaccumulation studies in natural environments (Babut et al., 2017; Shi et al., 2012). Regarding rooted species, A. sessilis was previously used in the phytoremediation of nitrates (Thurairajah and Gnanavelrajah, 2017), PCBs (Salimizadeh et al., 2020), and heavy metals (Liu et al., 2007; Wang and Qin, 2006). E. villosa is a widely spread pest and its uptake capacity was evaluated at a super-large antimony depot in China (Qi et al., 2011). The target species used in the present study can be used as pollutant remediators in freshwater environments due to their uptake mechanisms (Dixit et al., 2011).

4. Conclusions

This study investigated the environmental impact of the fluoropolymer-producing facility located next to the Dongzhulong and Xiaoqing River aquatic environment, focusing on the behavior of PFASs in the water-sediment-plant system. A dilution of PFASs was observed along the river in all the matrices. According to the PCA, PFOA was the main contaminant in the water and sediments due to the point source contamination from the Gongyang Group facility, while PFASs were punctually detected and attributed to urban discharges. KN values indicated that long-chain PFASs preferentially remained sorbed in the sediment, while short-chain PFASs were mobile in the water column and taken up by different plant species. Differences between the floating and rooted plants were observed, with floating species easily taking up long-chain PFASs directly from the water and rooted species competing with the sediment for the uptake of PFASs. Moreover, in the rooted species, long-chain PFASs remained accumulated in the roots because of protein affinity, while short-chain PFASs were more mobile and translocated to the shoots. Overall, this study provides new information on the occurrence and distribution of PFASs in a river basin, sediment accumulation, and plant uptake in real environmental conditions, which is useful in assessing the final fate of PFASs in areas highly affected by direct discharges and environmental pollution.

CRediT authorship contribution statement

Pere Colomer-Vidal: Conceptualization, Investigation, Formal analysis, Writing – original draft, Review & editing. Longfei Jiang: Conceptualization, Investigation, Writing – review & editing. Weiping Mei: Conceptualization, Investigation, Writing – review & editing. Chunling Luo: Conceptualization, Investigation, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition. Silvia Lacorte: Conceptualization, Investigation, Validation, Writing – review & editing, Supervision, Funding acquisition. Anna Rigol: Conceptualization, Investigation, Validation, Writing – review & editing, Supervision. Gan Zhang: Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126768.

References

Babut, M., Labadie, P., Simonet-Laprade, C., Munoz, G., Roger, M.C., Ferrari, B.J.D., Budzinski, H., Sivade, E., 2017. Per- and poly-fluoroalkyl compounds in freshwater fish from the Rhone River: influence of fish size, diet, prey contamination and biotransformation. Sci. Total Environ. 605–606, 38–47. https://doi.org/10.1016/j. scitotenv.2017.06.111.

Barton, K.E., Starling, A.P., Higgins, C.P., McDonough, C.A., Calafat, A.M., Adgate, J.L., 2020. Sociodemographic and behavioral determinants of serum concentrations of per- and polyfluoroalkyl substances in a community highly exposed to aqueous film-forming foam contaminants in drinking water. Int. J. Hyg. Environ. Health 223, 256–266. https://doi.org/10.1016/j.ijheh.2019.07.012.

Bizkarguenaga, E., Zabaleta, L., Mijangos, L., Iparraquiguirre, A., Fernandez, L.A., Prieto, A., Zuloaga, O., 2016. Uptake of perfluorooctanoic acid, perfluorooctane sulfonate and perfluorooctane sulfonamide by carrot and lettuce from compost amended soil. Sci. Total Environ. 571, 444–451. https://doi.org/10.1016/j.scitotenv.2016.07.010.

Blaine, A.C., Rich, C.D., Sedlacko, E.M., Hyland, K.C., Stuhnflock, C., Dickerson, E.R.V., Higgins, C.P., 2014. Perfluorooctanoic acid uptake in lettuce (Lactuca sativa) and Strawberry (Fragaria ananassa) irrigated with reclaimed water. Sci. Total Environ. 48, 14361–14368. https://doi.org/10.1016/j.scitotenv.2014.09.009.

Boudreau, T.M., Sibley, P.K., Mabury, S.A., Muir, D.G.C., Solomon, K.R., 2003. Long-chain perfluoroalkyl substances in the environment: terminology, classification, and biotransformation. Sci. Total Environ. 256, 1–39. https://doi.org/10.1016/S0048-9697(01)00918-2.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P., De, Jensen, A., Boudreau, T.M., Sibley, P.K., Mabury, S.A., Muir, D.G.C., Solomon, K.R., 2003. Laboratory evaluation of the toxicity of perfluorooctane sulfonate (PFOS) on Selenastrum capricornutum, Chlorella vulgaris, Lemna gibba, Daphnia magna, and Daphnia pulex. Arch. Environ. Contam. Toxicol. 44, 307–313. https://doi.org/10.1007/s00244-002-2102-6.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P., De, Jensen, A.A., Knapan, K., Mabury, S.A., van Leeuwen, S.P.P., 2011. Perfluorooctyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manag. 7, 513–541. https://doi.org/10.1002/ieam.256.

Chen, H., Sun, R., Zhang, C., Han, J., Wang, X., Han, G., He, X., 2016. Occurrence, spatial and temporal distributions of perfluoroalkyl substances in wastewater, seawater and sediment from Bohai Sea. China Environ. Pollut. 219, 389–398. https://doi.org/10.1016/j.envpol.2016.05.017.

Chen, H., Wang, X., Zhang, C., Sun, R., Han, J., Han, G., Yang, W., He, X., 2017. Occurrence and inputs of perfluoralkyl substances (PFASs) from rivers and drain
outlets to the Bohai Sea, China. Environ. Pollut. 221, 234–243. https://doi.org/10.1016/j.envpol.2016.11.070.

Costis, I.T., Goldenmess, N.Z., Grabe, D., Lohmann, R., Miller, M., Ng, C.A., Patton, S., Scheringer, M., Trier, X., Vierke, L., Wang, Z., DeWitt, J.C., 2019. The concept of essential use for determining when uses of PFASs can be phased out. Environ. Sci. Process. Impacts 21, 1803–1815. https://doi.org/10.1039/c9em00233j.

Díaz, A., Díaz, S., Godfray, H., 2011. Process for plants to remediate wastewater: a review. Sci. Rev. Chem. Commun. 1, 71–77.

Ghorbache, E., Lacorte, S., Tauler, R., Martin, F.L., 2016. Perfluoroalkylated substances in soils. Sci. Total Environ. 511, 63–72. https://doi.org/10.1016/j.scitotenv.2015.04.085.

Oliaei, F., Kriens, D., Weber, R., Watson, A., 2013. PFOS and PFC releases and associated substances in soils. Sci. Total Environ. 511, 63–72. https://doi.org/10.1016/j.scitotenv.2015.04.085.

Qi, C., Wu, F., Deng, Q., Liu, G., Mo, C., Liu, B., Zhu, J., 2011. Distribution and transport from a mega fluorochemical industrial park, China. Environ. Int. 36, 115–122. https://doi.org/10.1016/j.envint.2011.03.030.

Hoffman, D., Pollution and Release Estimation Software (PORE) – version 1.0. Tech. Rep. EPA 600/R-07/030, National Health and Environmental Effects Laboratory, Cincinnati, OH.

Zhang, W.S., Xie, G., 2009. Direct emissions of perfluoroalkyl substances from ongoing fluoropolymer manufacturing facilities in China. Environ. Sci. Technol. 43, 7256–7263. https://doi.org/10.1021/es901482s.

Wang, W., Rhodes, G., J., Yu, X., Li, H., 2020. Uptake and accumulation of per- and polyfluoralkyl substances in plants. Chemosphere 261, 127584. https://doi.org/10.1016/j.chemosphere.2020.127584.

Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014a. Global emission inventories for C4–C14 perfluoralkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. Environ. Sci. Technol. 48, 7763–7773. https://doi.org/10.1021/es5017276.

Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014b. Global emission inventories for C4–C14 perfluoralkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part II: The remaining pieces of the puzzle. Environ. Sci. Technol. 48, 7774–7780. https://doi.org/10.1021/es501728j.

Wang, B., Li, L., Liu, Y., Zhang, H., Hu, X., Shan, X., quan, Zhang, S., 2013. Mechanistic studies of perfluorooctane sulfonate, perfluorooctanoic acid uptake by maize (Zea mays L. cv. TY2). Plant Soil 370, 345–354. https://doi.org/10.1007/s11104-013-1571-y.

Xie, S., Wang, T., Liu, S., Jones, K.C., Sweetman, A.J., Lu, Y., 2014. Accumulation of Cd, Pb and Zn by 19 green algal species. J. Environ. Monit. 16, 1375–1381. https://doi.org/10.1039/c4em00248c.

Xie, S., Wang, T., Liu, S., Jones, K.C., Sweetman, A.J., Lu, Y., 2014. Accumulation of Cd, Pb and Zn by 19 green algal species. J. Environ. Monit. 16, 1375–1381. https://doi.org/10.1039/c4em00248c.

Zhang, W., Liang, Y., 2020. Removal of eight perfluoroalkyl acids from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, Z., Liang, Y., 2020. Uptake and accumulation of perfluorooctanoic acid from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.