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Shifts in production of perfluoroalkyl acids affect emissions and concentrations in the environment of the Xiaoqing River Basin, China

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HIGHLIGHTS

- Mass loads demonstrated a greater pattern of increasing PFAAs emissions.
- High levels of PFOA were identified near a fluoropolymer facility.
- Production activities that could generate PFOA emissions were analyzed.
- Partitioning coefficients decreased with high levels of short-chain PFCAs in water.

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ABSTRACT

Perfluoroalkyl acids (PFAAs) have been widely used in surfactant applications, especially as processing acids for fluoropolymer production. This study provides an analysis of sources of certain PFAAs emitted from the intensive fluoropolymer facilities in the Xiaoqing River Basin of China. Concentrations of perfluorooctanoic acid (PFOA) as great as 0.97 mg/L in surface water and 10.5 μg/g dry weight in surface sediment have been detected near the effluent of one facility (F1) that produces polytetrafluoroethylene (PTFE) and other fluoropolymers with massive capacity. With the great emission of PFAAs to water in natural conditions, the log K_{OC} values decreased for short-chain PFCAs. Mass loads of PFAAs indicated that emissions of PFAAs from other facilities or sources were much less than those from F1, which emitted 174 kg/d of PFAAs including 159 kg/d of PFOA to the rivers. Even though production and emissions of PFOA have been strictly controlled in other countries since 2006, production of PFOA as well as several other fluoropolymers that use PFOA as processing aids has been increasing at F1 in recent years. We recommended that production shift should be taken into consideration in PFOA elimination actions.

1. Introduction

Perfluoroalkyl acids (PFAAs) are characterized by a hydrophobic perfluoalkyl moiety with chemical and thermal stability and a hydrophilic acid functional group. The unique properties of PFAAs have made them widely used as surfactants or processing aids during production of polymers [13]. In 2001, PFAAs, especially perfluorooctane sulfonic acid (PFOS), have been widely detected in wildlife [8] and human blood [10]. Concerns over persistence and potential for toxicological effects led to the phase-out of PFOS, and related compounds beginning in 2000 by the major global manufacturer in United States [24]. Since then, studies on environmental, toxicological and health effects of PFAAs have grown rapidly, and production, usage and emission of PFAAs with 8 or more carbons have been strictly controlled in more developed countries [2].

As a signatory of the Stockholm Convention on Persistent Organic Pollutants [23], China has restricted production and use of PFOS except specific exemptions by law [19]. However, other PFAAs have not yet been restricted. Although the eight major fluoropolymer and telomer manufacturers have been working on elimination of PFOA and related chemicals from production and emission by 2015 under the 2010/2015 PFOA Stewardship Program [25], the demand for PFOA as processing aids has not yet declined, especially in production of polytetrafluoroethylene (PTFE) [6]. It can be seen

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from their annual progress reports from 2007 to 2014 that both the amount released to all media from fluoro-polymer/-telomer manufacturing and percentage reduction in emission/product content of PFOA were less from non-U.S. operations than from U.S. operations of most manufacturers [26]. Although the program has brought the gradual elimination of PFOA emission from the major manufacturers, there is concern that without adequate substitutes or sufficient removal from wastewater in recent years, where will major manufacturers shift their production and what effects will that production have on local environments?

Known as fine chemicals which need intensive investment and other support, fluoropolymer facilities are often located in relatively developed areas of China, like the Bohai Coastal Economic Circle. In a previous study of 12 coastal rivers that flow into the Bohai Sea, concentration of PFOA as great as 4.5 μg/L was observed in the estuary of the Xiaoqing River. Several fluoropolymer facilities producing large amounts of PTFE and other fluoropolymers were disclosed along the river [29]. Studies by other researchers also indicated that PFOA was the predominant PFAA along the Xiaoqing River found in human blood in Zouping County [9], precipitation in Weifang City [36], mollusks in Laizhou Bay [18] and sediment in the Xiaoqing River [37,38]. However, the exact sources and fate of PFAAs, the contribution of different kinds of sources and the pollution history are still unqualified and unquantified in the Xiaoqing River Basin.

Unlike PFOS, the majority (upto 80%) of perfluoroalkyl carboxylic acids (PFCAs) was estimated to be released to the environment from fluoropolymer manufacture and use, especially for PFOA. In a study of global emission inventories for C4–C14 PFCAs from 1951 to 2030, it was also concluded that historically 98–100% of PFOA was emitted from direct sources during the life-cycle of related products [33]. So this study focused on direct sources of PFAAs emitted to the river. Considering the study area is relatively greatly urbanized and industrialized with a lot of farmland that need consistent irrigation, the water channels in the whole river basin were all studied with sampling sites selected to cover sources from production to transportation (Fig. 1). The overall aim of this study was to identify current emission sources of PFOA in the Xiaoqing River Basin, assess the potential effects of shifts in production by manufacturers to China. The results present useful information for control over emissions of certain PFAAs to ecosystems and a general protection of human health.

2. Materials and methods

2.1. Sample collection

The total length of the Xiaoqing River is 220 km. To assess the potential sources and transportation of PFAAs in the whole river basin, 12 sites (X1–X12) on the main stem of the river at intervals of approximately 20 km, 14 sites (X13–X26) on tributaries of the Xiaoqing River were selected, and 4 sites (R1–R4) in two adjacent rivers were set as references (Fig. 1). The field sampling campaign was carried out during June 19–23, 2013. Samples of surface water ($n = 30$) were collected using pre-rinsed 1 L polypropylene (PP) bottles. Surface sediments (top 0–2 cm) in all sites ($n = 25$) of the Xiaoqing River Basin except X24 were collected using a stainless steel trowel and kept in 250 mL PP boxes. Sediment cores of 20 cm depth were collected at sites X3,X6,X9 and X12, by use of a Beeker sediment core sampler (Eijkelkamp Agrisearch Equipment, Netherland), and sectioned in the field into 10 intervals of 2 cm, which were placed into 250 mL PP boxes. Samples were kept in ice box during transportation. After arrival in the lab, samples of water were left to stand for 24 h to settle most of the particles and only supernatants were taken for analysis. Samples of sediments were freeze-dried and passed through 2 mm mesh.

2.2. Target analytes, extraction, and analysis

A total of 12 linear PFAAs including 9 PFCAs with carbon lengths from C4 to C12, and 3 perfluoroalkane sulfonic acids (PFSAs) were measured in this study (Table S2). Aliquot of 400 mL of unfiltered water was extracted using OASIS WAX cartridges and clean-up. For sediments, 2 g of dry samples were extracted by use of ultra-sonic extraction followed by clean-up with ENVI-Carb and OASIS-WAX cartridges, respectively. Detailed information on extraction is given in the Supplementary material. Target PFAAs were quantified by use of an Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, USA) that was operated in the negative electrospray ionization (ESI) mode. Instrument conditions were listed in Table S4.

2.3. QA/QC

In order to avoid cross contamination during sampling in the field, the outside of bottles and boxes was washed with Milli-Q water after the samples were taken, wiped with clean towel paper and then kept in three-layers of sealed polyethylene (PE) bags. To monitor potential interferences during sampling, extraction and instrumental analysis, blanks including field, transport, procedure and solvent ones were prepared with every sample batch. Quantification of 12 PFAAs in all samples were carried out using 10-point internal quantification curves with concentrations of native standards ranging from 0.01 to 1000 ng/mL and 10 ng/mL of mass-labelled internal standards. Regression coefficients (R^2) for calibration curves for all target analytes were greater than 0.99. The injection volume was 5 μL. For concentrations of PFAAs in extracts that were initially greater than 1000 ng/mL, the volume or amount of the samples would be reduced and the samples would be extracted again to make sure the concentrations of PFAAs in the final extracts fall in the range of the calibration series. Limits of detection (LOD) and limits of quantification (LOQ) were defined as the peak of analyte that yielded a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. LOD and LOQ ranged from 0.002 to 0.01 ng/g and from 0.01 to 0.04 ng/g, dry weight (dw) for sediments. For water samples, LODs ranged from 0.01 to 0.08 ng/L, while LOQs ranged from 0.06 to 0.22 ng/L. Matrix spike recoveries ranged from 89 to 114% for water samples and 75–117% for sediment samples. Procedure recovery ranged from 81 to 122% for water samples and 71–108% for sediment samples. Detailed information on QA/QC was given in Supplementary material.

2.4. Statistical and spatial analysis

Data analysis was performed by use of SPSS Statistics V20.0 (SPSS Inc. Quarry Bay, HK), Microsoft Excel 2010 (Microsoft China, Beijing) and Origin Pro 9.1 (Northampton, MA, USA). During the analysis, values of concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned values of $\mathrm{LOD}/\sqrt{2}$ [29]. Prior to the correlation analysis, tests of normality were carried out to ensure that data met the assumptions used for further analysis. Spatial distributions of PFAAs were analyzed using the Arcmap module in ArcGIS V10.2 (ESRI, Redland, CA). The precise river information for sampling design and spatial analysis was obtained from remote sensing data provided by the National Geomatics Center of China (Haidian, Beijing, China), and optimized by *in-situ* observation.

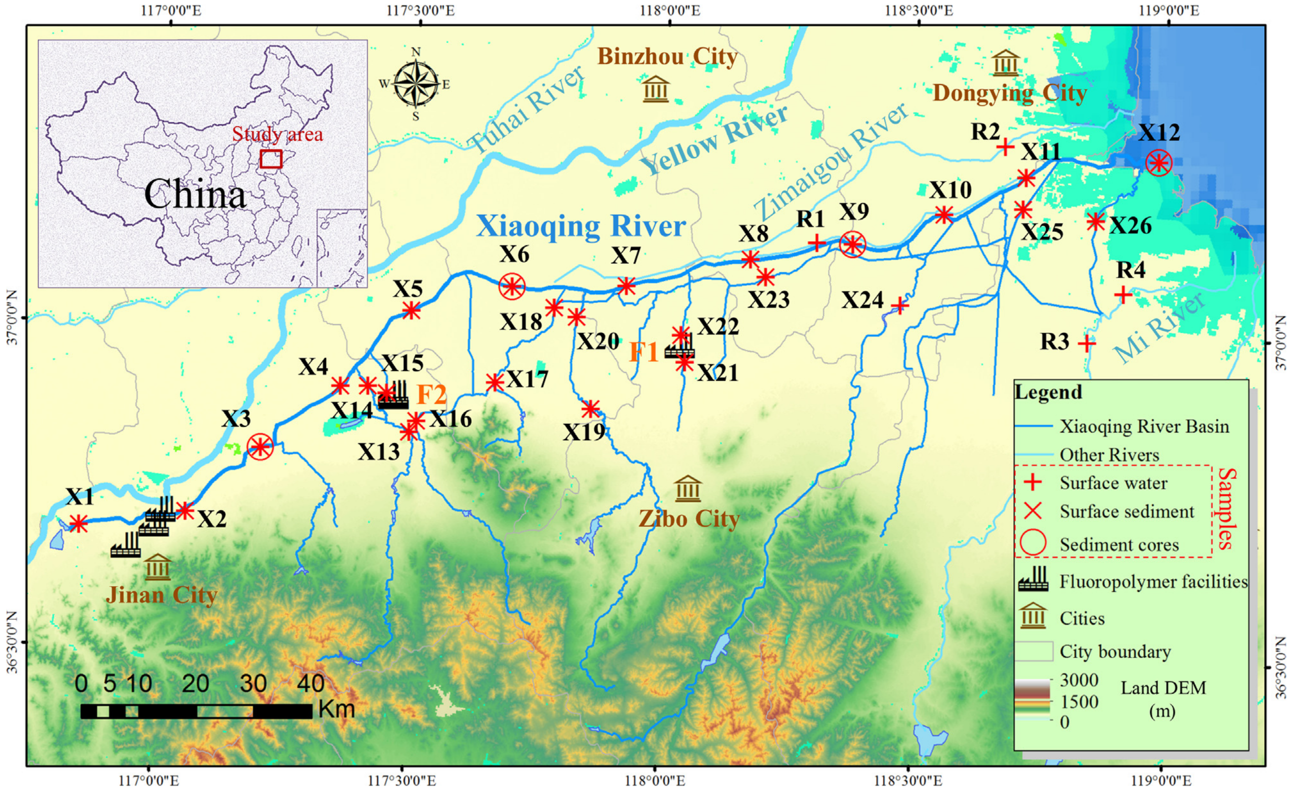

Fig. 1. Sampling sites in the Xiaoqing River Basin.

2.5. Data representation

Due to the large variation on the orders of magnitude, and the fact that the accuracy of all data were presented with three significant figures, values had units for concentrations in water were ng/L, μg/L or mg/L while concentrations in sediments were ng/g and μg/g dw.

3. Results and discussion

3.1. PFAAs in water of the Xiaoqing River

C4–C12 PFCAs and PFOS were detected in most samples from the Xiaoqing River. Perfluorobutane sulfonate (PFBS) and perfluorohexane sulfonate (PFHxS) were scarcely detected, which indicated there are limited sulfonation production in this region. $\sum$PFAAs (sum of PFAAs) ranged from 32.2 ng/L to 1.06 mg/L. PFOA was dominant with proportions ranging from 43.1% to 95.2%, and a mean contribution of 66.1% (Fig. 2b). Based on concentrations of PFAAs, the Xiaoqing River was stratified into three sections: Section 1 (S1) from X1-X4; Section 2 (S2) from X5–X7, and section 3 (S3) from X8–X12. Concentrations of PFAAs increased from S1 to S3, but were consistent within each section (Fig. 2). There are various sources of PFAAs along the Xiaoing River. In particular, several manufacturers of fluoropolymers were investigated in a previous study [29]. Contributions of PFAAs from fluoropolymer facilities were greater than those from cities and other sources, especially for facilities located in F1. Increasing concentrations of PFAAs from S1 to S2 came primarily from F2. X15 was located at the downstream of F2. PFOA was dominant with concentration of 479 ng/L and a contribution of 64.6% of $\sum$PFAAs. Concentrations of C10–C12 PFCAs in water from X15 were the greatest among all sites investigated during this study. PFAAs levels from X19–X20 were also notable, which implied greater domestic emission from the Zibo City than from the Jinan City. From S1 to S2, concentrations of PFAAs increased, but the relative contributions of individual PFAA varied little. However, from S2 to S3, concentrations of PFAAs increased greatly and relative contributions of individual PFAA also changed. This was unquestionably due to F1. Location X22 was immediately downstream of the effluent from F1 into the river. The concentration of $\sum$PFAAs was 1.06 mg/L in water. PFOA was dominant with concentration of 0.97 mg/L, which was 91.3% of $\sum$PFAAs, followed by PFBA (34.3 μg/L, 3.2%), PFHxA (25.6 μg/L, 2.4%), PFPeA (20.1 μg/L, 1.9%) and PFHpA (12.1 μg/L, 1.1%). Concentrations and relative contributions of longer-chain PFCAs and PFOS were negligible. After the confluence with the Xiaoqing River, concentrations of $\sum$PFAAs were still up to 32.8 μg/L in water at X8. The concentrations of $\sum$PFAAs gradually decreased to 13.7 μg/L in water at X12, which was in the estuary. From X8 to X12, contributions of PFOA to $\sum$PFAAs were greater than 90%. For other sites located on tributary (X13, X14, X16–X21, X24–X26) of the Xiaoqing River, as well as reference rivers (R1–R4), no obvious sources of PFAAs were found. Concentrations of PFAAs in water from X23 and R1 are all influenced by F1 and the Xiaoqing River.

Compared with results of previous studies conducted in 2011 [29], concentrations of $\sum$PFAAs and PFOA observed in water at the same sites during this study increased more than four-fold. Results including PFAAs levels and contribution of individual PFAAs are comparable between this study and other studies in the Xiaoqing River. For example, the concentration of PFOA in the water downstream of F1 was 0.97 mg/L in this study, comparable with 0.58 mg/L [11] and 0.37 mg/L [21] in other studies. In recent years, studies on the production and emissions of PFAAs from fluoropolymer facilities in China have been increasing. But the patterns of PFAAs vary among locations. At a sulfonation facility in Wuhan, Hubei Province of central China, PFOS was dominant with concentration of 1.02 mg/L found in the effluents from the wastewater treatment plant at one facility, followed by PFOA and PFHxS [32]. At

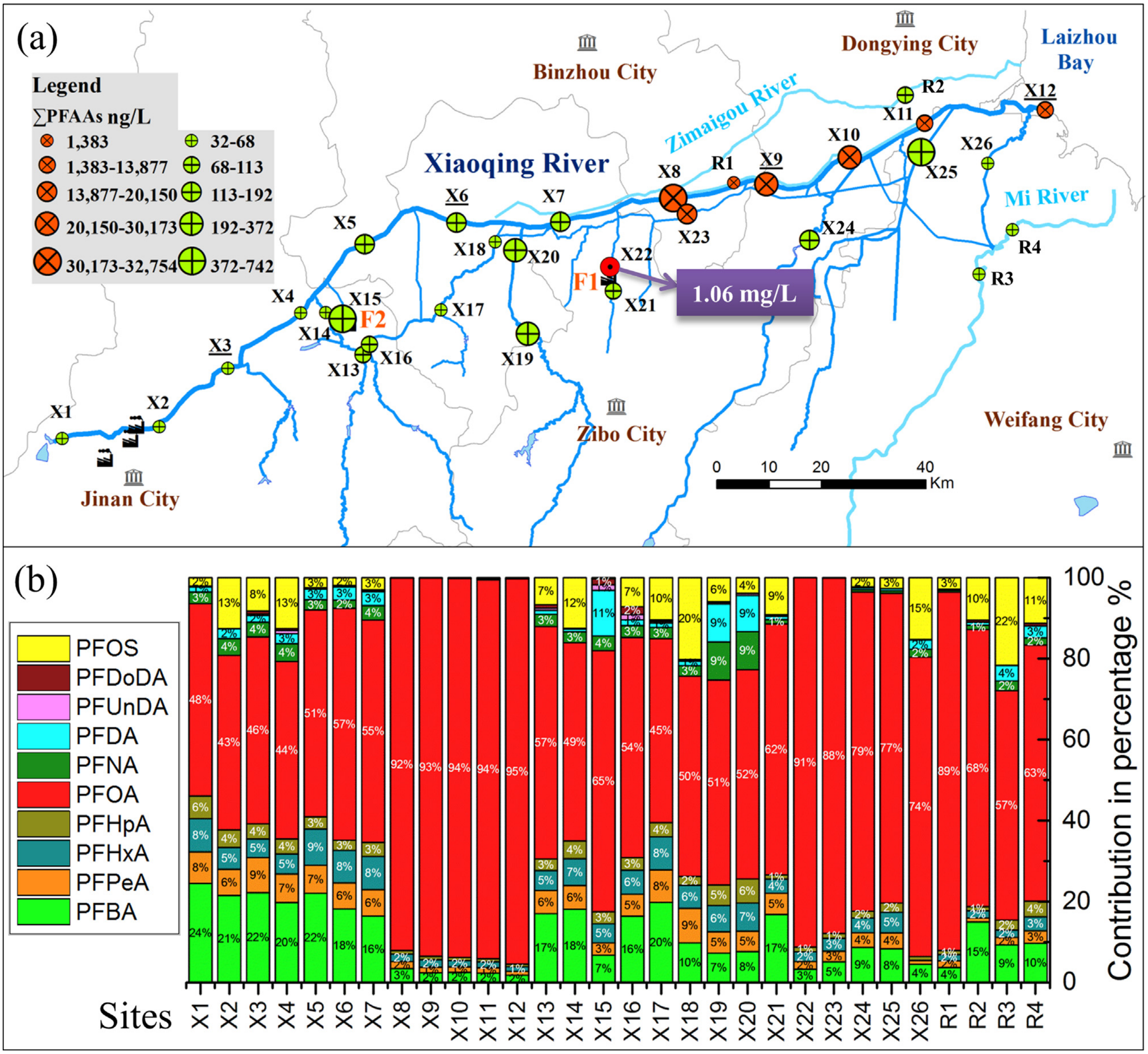

Fig. 2. (a) Concentrations of ∑PFAAs and (b) relative contributions of individual PFAA in water of the Xiaoqing River Basin.

facilities located in Daling River Basin of North China, short-chain PFBS and PFBA were dominant in surface water with maximum measured concentrations of 2.9 µg/L and 1.3 µg/L, respectively [30]; PFHxA were dominant in water around facilities located in Jiangsu Province of East China with maximum measured concentrations of 10.3 µg/L [20]. At a 3 M facility in Minnesota (USA), concentrations of PFOA as great as 42 µg/L in groundwater, 82 µg/L in landfill leachates and 84 µg/L in landfill gas condensate in 2004 have been reported [16]. However, since 2000 when 3 M voluntarily phased out production of PFOS and related substances, emissions of long chain PFAAs have been decreasing, but concentrations short-chain PFAAs have been increasing in USA. This increase in PFBS has been observed in sediment cores from Lake Michigan [4], which is to the west of the 3 M facility. At another fluoropolymer facility owned by DuPont located in West Virginia, concentrations of PFOA as great as 78 µg/L have been observed in groundwater [5]. This has brought high concerns for health of local residents and they have been supplied with alternative sources of water [22]. Although recent studies implied that PFOA is becoming the dominant PFAA in surface waters, such as Taihu Lake, China (max. 136 ng/L) [17], Hanjiang River, China (max. 256 ng/L) [28]; Yodo River Basin, Japan (max. 2.6 µg/L) [14]; River Po, Italy (max. 6.5 µg/L) [27]. But no apparent point source was reported in those studies.

3.2. PFAAs profiles in surface sediment and sediment cores

Concentrations of ∑PFAAs ranged from 2.0 ng/g, dw to 10.7 µg/g, dw in surface sediment from X1 to X26 (Table S6). The greatest concentration was found in sediment from X22, which was located immediately downstream of F1. Spatial distributions of PFAAs in surface sediment were consistent with those observed in water (Fig. 3a), but profiles of relative concentrations varied among locations (Fig. 3b). PFOA was still the predominant PFAA at most of the sites, especially those downstream of F1, including site X8–X12 and X22–X23, with average contributions of PFOA greater than 90%. However, in other sites, especially the upstream ones, contributions of PFOS and long-chain PFCAs were greater in surface sediment than in water. The greatest concentration of PFOS was 10.6 ng/g, dw in sediment from X22, while the greatest contribution of PFOS was 54% in sediment from X6. Among the long-chain

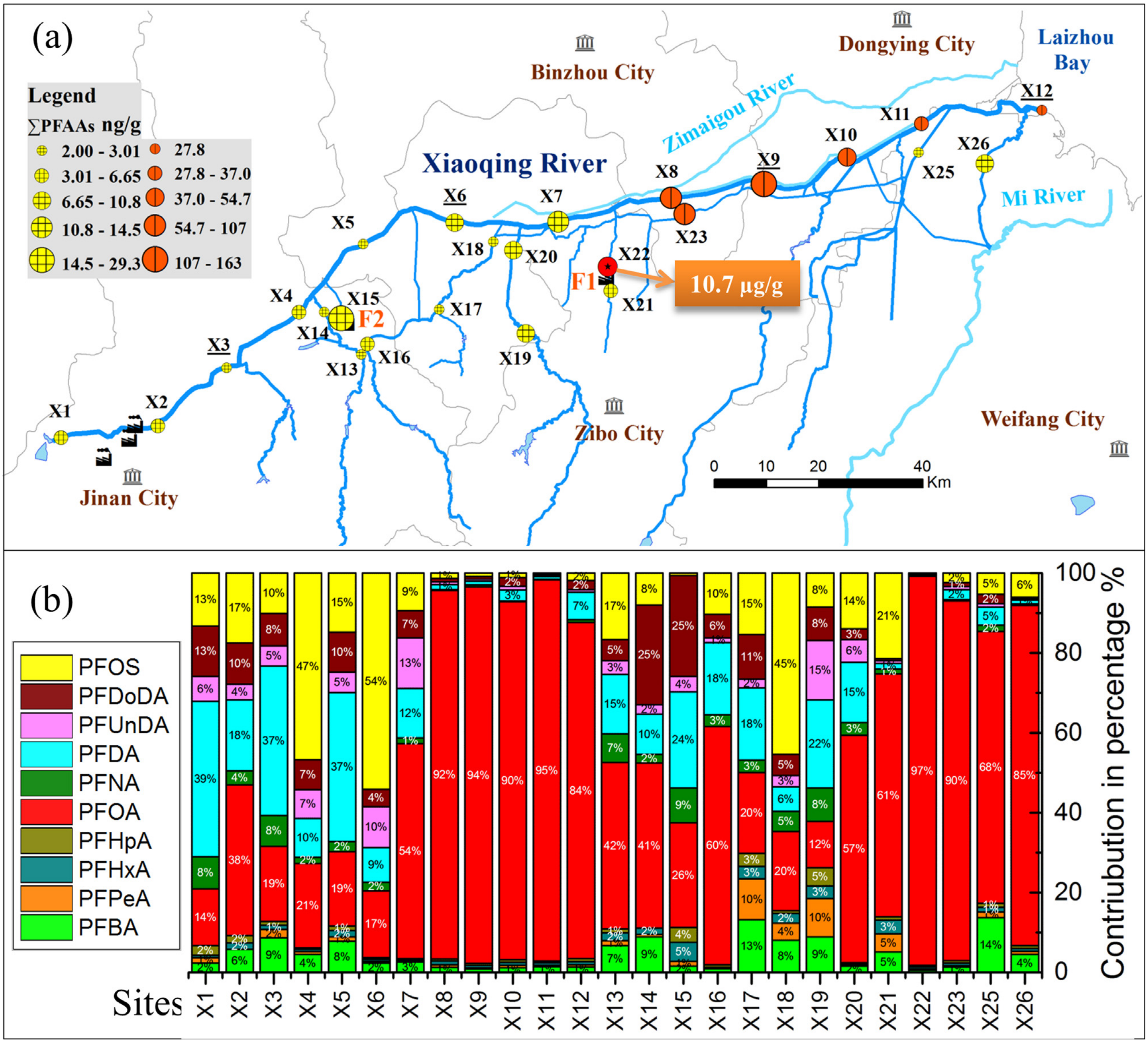

Fig. 3. (a) Concentrations of $\sum$PFAAs and (b) relative contributions of individual PFAA in surface sediment from the Xiaoqing River Basin.

PFCAs, C10 perfluorodecanoic acid (PFDA) was dominant with a mean contribution of 12.5%, ranging from 0.14% to 38.9%, followed by C12 perfluorododecanoic acid (PFDoDA) (6.37%, 0.14–25.3%), C11 perfluoroundecanoic acid (PFUnDA) (3.71%, 0.17–14.9%) and C9 perfluorononanoic acid (PFNA) (2.91%, 0.14–8.74%). The different profiles of PFAAs observed in water and surface sediment indicated their different partitioning behaviors.

Since PFAAs have limited vapor pressure [34], partitioning of PFAAs between water and sediment is necessary to evaluate the fate of PFAAs during the transport along the river. Methods used to calculate partitioning coefficients including log K_d and log K_{OC} were the same as other studies [1]. Both log K_d and log K_{OC} were directly proportional to length of the carbon chain from C5 PFPeA to C12 PFDoDA. Both values of PFOS were between those of C9 PFNA and C10 PFDA. Introduction of additional one carbon to the carbon chain made log K_{OC} 1.78 log unit higher than log K_d for all PFAAs (Table S9, Fig. 4a). In this study with high concentrations of PFOA and short-chain PFCAs in water from X8–X12, values of log K_{OC} were less than those from X1-X7 with less concentrations of C4–C8 PFCAs. These trends were not observed for longer-chain PFCAs or PFOS (Fig. 4b). This finding is also applicable for all the log K_{OC} values in other sites of this study. Although the partitioning behavior of PFAAs can be affected by many factors including hydrology properties, water flow and so on, the trend was obviously discovered under the different PFAAs levels rather than other factors. This finding indicated that with increasing emission of C4–C8 PFCAs to water, the log K_{OC} values would decrease.

Profiles of relative concentrations of PFAAs in sediment cores were similar to those in surface sediments, but vertical trends of absolute concentrations of PFAAs were different among sediment cores (Fig. 5). In Core X3, PFOS was at lower levels within the depth from 0–2 cm to 4–6 cm, but higher and consistent in deeper sections. Concentrations of PFOA fluctuated while concentrations of PFDA were more consistent. PFCAs with chain length of C4–C7, C9, C11–C12 were less dominant. Concentrations of PFAAs in core X6 generally decreased with depth from 14–16 cm to 8–10 cm and then increased from 8–10 cm to 0–2 cm. In core X9, due to the large point source of F1, concentrations of PFOA ranged from 43.4 in 18–20 cm to 333 ng/g dw in 12–14 cm. Concentrations of PFAAs were greater below a depth of 10 cm, while at depths above 10 cm, concentrations of PFAAs were constant. Besides PFOA, other PFAAs in core X9 exhibited the same trend as PFOA with concentrations

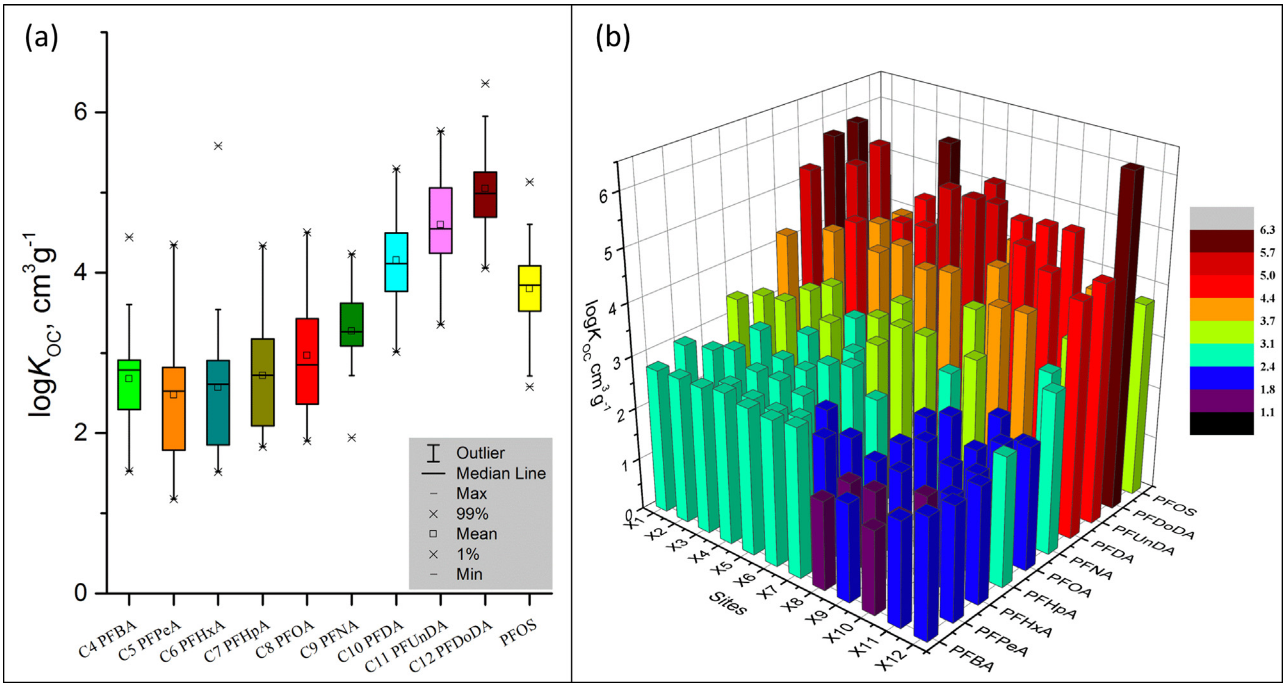

Fig. 4. (a) log K_{OC} values for PFAAs for sediments from X1-X26 and (b) variation of log K_{OC} for individual PFAA in sediments from X1- X12 in the Xiaoqing River.

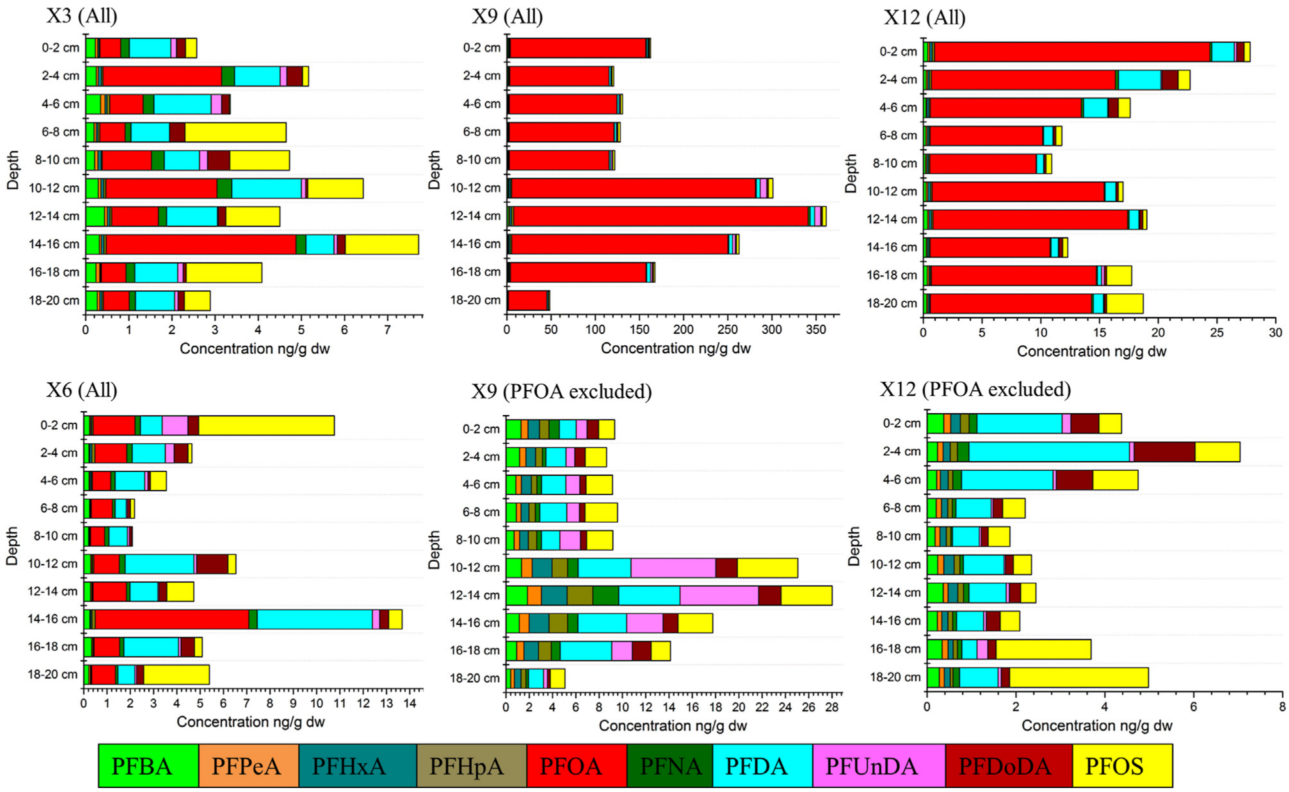

Fig. 5. Concentrations of $\sum$PFAAs in sediment cores of the Xiaoqing River Basin.

greater than those in core X3 or X6. Correlations among all the 12 PFAAs in core X9 were significant at the 0.01 level, except that correlations between PFOS and PFBA, PFOS and PFDoDA were significant at the 0.05 level (Table S12). This indicated that all PFAAs in core X9 were associated with emissions from F1. Core X12 showed a trend of decreasing concentrations of PFAAs with depth from surface to 10 cm and then the concentrations increased slightly. Correlations among all PFAAs were not significant as much as those observed in X9, indicating the influence of sea water exchange. Sorption of PFAAs from water to sediment is mainly influenced by the fraction of organic carbon (f_{OC}) in sediment [12,1]. In this study, core X9 had the greatest f_{OC} with an average value of 3.05%, followed by core X3 (2.10%), X6 (1.18%) and X12 (0.56%) (Table S7, Fig. S1a). The trend of f_{OC} was similar to that of concentrations of PFAAs in core

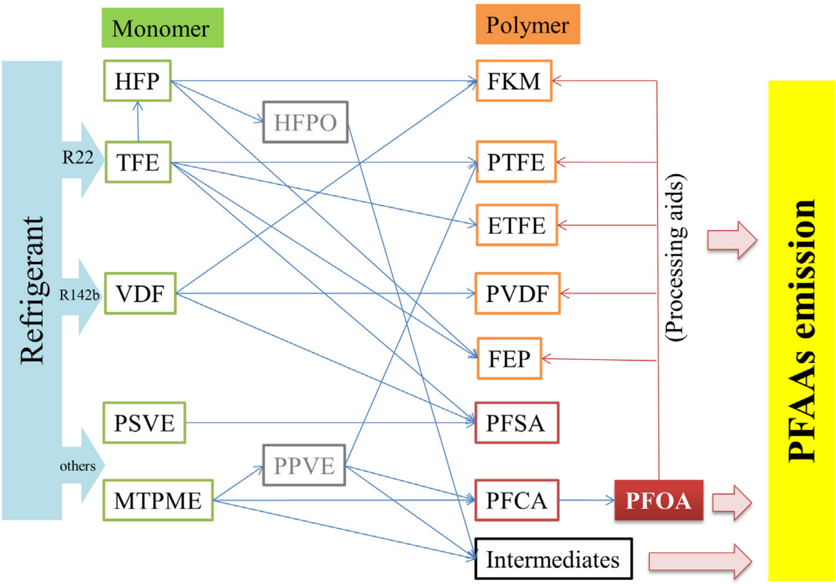

Fig. 6. Main products and processes that can generate emissions of PFAAs at F1.

X9, with significant correlations among f_{OC} and all PFAAs (Table S12). This indicated that differences in PFAAs concentrations were mainly affected by various sources at different locations, but by f_{OC} at the same location. And when evaluating the time trend of concentrations of PFAAs using sediment cores, changes in concentrations should not be used directly as equivalent with changes in emission. Meanwhile, other factors like particle size and density could also influence sorption of PFAAs to sediment [35]. Unlike lakes and seas, sedimentation in rivers can be influenced by such factors as flow rate, flood events, people fishing on foot in the river and dredging. Thus, it is difficult to date cores of sediment from rivers, but they can be used as an indicator for pollution on a larger time scale.

3.3. *Mass loads of PFAAs from various sources*

When assessing the input and output of PFAAs from various sources and tributaries along the Xiaoqing River, concentrations are not sufficient. Concentrations might be diluted by multiple water inputs, so mass loads (g/d) of PFAAs were calculated using water discharge (m^3/second) multiplied by concentrations of individual PFAA (ng/L) in water from each site (Table S8). Even if concentrations of PFAAs only increased 1.5-fold from X1 to X2, mass loads of PFAAs in X1 and X2 indicated that the industrial and domestic emissions in Jinan City contributed 40.5 g/d of PFAAs to the Xiaoqing River. Due to the relatively small discharge, F2 was estimated to have emitted only 83.9 g/d to the gutter. However, Emissions of PFAAs from F1 to the Xiaoqing River was calculated to be 174 kg/d. PFOA accounted for 159 kg/d, followed by PFBA (5.6 kg/d), PFHxA (4.2 kg/d), PFPeA (3.3 kg/d) and PFHpA (2.0 kg/d). After the confluence with the Xiaoqing River, mass loads of PFAAs decreased to 127 kg/d at X8. Although X23 took away 6.3 kg/d, there was still 41 kg/d missing. In our field survey, we found that there were many small irrigation canals with large areas of farmland in the downstream of the Xiaoqing River Basin. It was also found that PFAAs, especially PFOA can migrate downward with river discharge into the underlying aquifer [5]. So the missing masses of PFAAs could be lost via horizontal flow into irrigation canals and vertical migration to the underlying aquifer. Fluctuation of mass loads from X8 to X12 could also be explained by the involvement of irrigation canals. Based on the mass loads of PFAAs in the downstream reaches of the Xiaoqing River, mass loads of PFAAs from the Xiaoqing River to Laizhou Bay could also be established. As X12 located in the estuary, the salinity indicated that river water in this site was frequently mixed with the sea water (Table S1), so values in X12 was not suitable for estimation of mass loads from river to sea. Salinity in water at X11 was consistent with salinities in more upstream sites, so X11 was favorable. Mass loads of $\sum$PFAAs from the Xiaoqing River to Laizhou Bay were estimated to be 118 kg/d, including 111 kg/d of PFOA. The mass loads of PFAAs in the Xiaoqing River in 2014 increased almost 10-fold compared with our calculation in 2011 [29], and were also much higher than those in North Bohai coastal rivers [31]. Mass loads demonstrated a greater pattern of increasing emissions than did concentrations.

3.4. *What happened in F1 under global PFOA emission reduction operations?*

PFOA is the PFAAs of next greatest global concern after PFOS. Since 2006, several organizations have been conducting hazard assessments of PFOA [15,6,7], which resulted in restraint on production and import of PFOA and related chemicals in the market. However, in China, with no regulation on PFOA by the government, production and use of PFOA could be immoderate. Meanwhile, developed countries in the EU and North America will still import fluoro-polymer/-telomer based products in which PFOA was used as a processing aid during production processes. Thus, residual levels of PFOA, released as an unintended by-product would be expected to increase, especially in China where it is currently produced. If residuals of PFOA in consumer products allowed for import were also restrained, it is not known if this would also result in changes in emissions. Of the facilities studied, F1 started production in 1987, and mass production of PTFE begun in 2001, with annual capacity of 3000 tons. At the end of 2013, the capacity of PTFE was expanded to over 49,000 tons, with an average annual growth of approximately 25% from 2001 to 2013. Besides PTFE, four other fluoropolymers are produced at F1 use PFOA as a process aid during production with certain monomers as raw materials (Fig. 6). Meanwhile, F1 is a self-sufficient manufacturer, which means PFOA and other PFAAs are important products for direct application in production of fluoropolymers or sale to other manufacturers. PFAAs can be used in production of numerous intermediates or surfactants as well. So at F1 PFAAs can be generated or released through three ways: (1) direct production of PFAAs; (2) used as processing aids during production of five fluoropolymers; (3) used in production of numerous intermediates. PFOA is the predominant PFAA used in these processes, leading to the greatest emission to the environment. This is consistent with the results in this study. In the beginning of 2013, F1 acquired another important fluoropolymer facility with large production capacity. This could be an important reason for the rapidly increasing mass loads of PFAAs observed in this study compared with those in 2011. According to managers at F1, a large portion of their products are exported to other countries, including several manufacturers that joined the USEPA 2010/2015 PFOA Stewardship Program. Found in their annual progress reports of the Program, Emissions of PFOA, precursors and greater homologues to all media from fluoro-polymer/-telomer manufacturing including all operations of the eight manufacturers were more than 50 tons in 2006. The amount was reduced by 90% to approximately 4 tons in 2013. However, mass loads at X22 indicated that the emission of PFOA from F1 to the Xiaoqing River was 159 kg/d, equivalent to approximately 58 tons for 2013. This situation can be attributed to the following three facts: (1) Global demand for fluoropolymers are currently very strong; (2) There are no suitable substitutes that can replace PFOA in production of most fluoropolymers in F1. Heydebreck et al. investigated a new fluorinated alternative called 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy) propanoic acid (HFPO-DA), but the concentration of HFPO-DA is only 0.4% of that of PFOA in the downstream of F1 [11]; (3) Existing treatment technologies used in F1 cannot efficiently remove PFOA from wastewater. Degradation of PFOA precursors like fluorotelomer alcohols (FTOHs), results in loads of PFOA in effluents that might be even greater than in the influents [3]. So, it is strongly recommended that the shifts in emissions should be taken into consideration when evaluating the actual reductions in emission from the major manufacturers.

4. Conclusion and perspectives

This paper presented a systematic research on the source identification of PFAAs emitted from various sources. High concentrations of $\sum$PFAAs were observed in the Xiaoqing River, downstream of F1's effluent, including 1.06 mg/L in surface water and 10.7 μg/g, dw in surface sediment, respectively. PFOA was the predominant PFAA in both water and sediment downstream of F1 to the estuary with average contributions over 90%. Mass loads indicated that emissions of PFAAs from other fluoropolymer facilities or cities were far less than those from F1, and F1 contributed 174 kg/d of PFAAs including 159 kg/d of PFOA to the rivers. Log K_{OC} indicated that partitioning of shorter-chain PFAAs between water and sediment might decrease with the great concentrations observed in this study. Concentrations of PFAAs in the sediment cores indicated that the great emissions of PFAAs from F1 might have been occurring for many years. Information on development of F1 indicated that production capacities of PFOA and several fluoropolymers that use PFOA as processing aids have been scaling up in recent years. This brought critical evidences on the pollution shift of PFOA from other countries or manufacturers to China. Based on the above analysis, it is recommended that more attention should be given to sewage discharge into aquatic ecosystems including freshwater and marine ecosystems, and more studies are needed on the adverse effects of great emissions of PFOA to ecosystem and human health.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.12.059.

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Shifts in production of perfluoroalkyl acids affect emissions and concentrations in the environment of the Xiaoqing River Basin, China

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Content

Table S8. Mass loads of PFAAs from X1 to X26 (g/d).

Table S9. Partition coefficient (logK_d, cm^{3}g^{-1}) and organic carbon normalized partition coefficient (log$K_{OC,}$ cm^{3}g^{-1}) between water and sediment from X1 to X26.

Table S10. Comparison of log K_{OC} (mean±SD, cm^{3}g^{-1}) of the 10 PFAAs in this study with other published researches.

Table S11. The main products of F1.

Table S12. Pearson correlation of PFAAs concentrations and fOC in sediment core X9.

Figures

Figure S1. f_{OC} in (a) sediment cores and (b) surface sediment from X1 to X12 in the Xiaoqing River.

References

Standards and Reagents

A mixture of 17 native linear PFAAs (PFAC-MXB) and a mixture of 9 mass-labeled linear PFAAs (MPFAC-MXA) were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada) (Table S2). HPLC grade methanol and acetonitrile (ACN) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate (~98%), anhydrous sodium sulfate, hydrochloric acid (HCl, ⩾ 37%, for trace analysis), sodium hydroxide (NaOH), and ammonium hydroxide solution (28%~30% NH_3 basis) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Milli-Q water was obtained from a Milli-Q synthesis A10 (Millipore, Bedford, MA, USA) and used throughout the experiment.

Water parameters analysis

Parameters including pH, turbidity and salinity were measured *in situ* using a HQd Portable and Benchtop Meter Configurator (HACH Company, USA). Total organic carbon (TOC) was measured using a Vario TOC analyzer (Elementar, Germany) right after the water samples arrived the lab.

Extraction and cleanup

An aliquot of 400 mL of water spiked with 10 ng mass-labelled internal standards was extracted by OASIS WAX-SPE extraction with few modifications (Taniyasu et al., 2005). Firstly, the Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were successively preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water. Then water samples were loaded, and the cartridges were washed with 4 mL 25 mM ammonium acetate (pH 4) and air-dried for several days, and finally target analytes were eluted with 4 mL of methanol followed by 4 mL of 0.1% NH_4OH in methanol, respectively. The flow velocity was kept at 1 drop per second in the whole process. The final elution was reduced to 1 mL under a gentle stream of high purity nitrogen (>99.999%) and passed through a nylon filter (13 mm, 0.2 μm, Chromspec, Ontario, Canada), then transferred into a 1.5 mL polyethylene (PE) snap top brown glass vial with silica septa.

Sediments were extracted based on published methods (Loi et al., 2011) with some modifications. 2 g dry sediment were placed into a 50 mL PP centrifuge tube, and spiked with 10 ng mass-labelled internal standards. Sediment was digested with 2 mL of 100 mM NaOH in MeOH (8:2/MeOH:Milli-Q water), and ultra-sonicated for 30 min. 20 mL MeOH was added to the mixture and shaken for 30 min at 250 rpm. 0.1 mL of 2M HCl was added to the mixture and the sediment was separated by centrifugation at 3000 rpm for 15 min. The supernatant was transferred into a new 50 mL tube. The extraction procedure was repeated once except that 10 mL of MeOH was used instead of 20 mL. Both supernatants were combined into the same tube and reduced to 1 mL under a gentle stream of high purity nitrogen. The 1 mL extracts were further purified by use of ENVI-Carb and OASIS-WAX SPE cartridges. The Supelco ENVI-Carb cartridges (250mg, 3mL, Sigma-Aldrich, St. Louis, USA) were preconditioned by passing through 1 mL MeOH three times, and then the extracts were loaded and collected. Analytes were washed with another three aliquots of 1 mL MeOH and collected together with the extracts. After ENVI-Carb cleanup, all the extracts were diluted to 100 mL with Milli-Q water and subjected to OASIS WAX-SPE cleanup with the same procedure as water samples. The final 1 mL extracts were filtered by a 13 mm/0.2 um nylon filter, and transferred into a 1.5 mL PE snap top brown glass vial with silica septa.

Calculation of log K_d and log K_{OC}

Partition coefficients were calculated based on published methods (Ahrens et al., 2010). The sediment-water partition coefficient (log K_d) was calculated using Equation 1.

$$\log K_d = \log C_S/C_W \qquad (1)$$

Where: C_S and C_W are the concentrations of PFAAs in sediment (ng/g) and water (ng/mL), respectively. The organic carbon fraction (f_{OC}, %) normalized partition coefficient (log K_{OC}) was calculated using Equation 2.

$$\log K_{OC} = \log (K_d \times 100/f_{OC}) \qquad (2)$$

Organic Carbon fraction (f_{OC}) analysis in sediment

Organic Carbon (OC) in sediment was determined using external heating potassium dichromate method according to the Agricultural Standard of China (NY/T 1121.6-2006) with some modifications. Briefly, 0.3g soil ground through 0.15mm sieve was weighed into a 150mL triangular flask, with 5mL 0.8mol/L potassium dichromate solution and 5mL concentrated sulfuric acid added. After shaking the mixture well and put a crookneck funnel over the flask, heat the flask to 170-180℃ and kept boiling 5 min and then cooled off. Washing the funnel with Milli-Q water to keep the volume of solution 60-70mL, here the color of the solution should be orange yellow or jasmine. Then Phenanthroline indicator 3-4 drops were added and titrated with 0.198mol/L green copperas solution to turn the color of the solution to green, pea green and finally redbrown. Two blanks were necessary for each set of samples and 0.5g mealiness silicon-dioxide was used for surrogate. The OC content was calculated using the following formula:

$$f_{\mathrm{OC}}(\%) = \frac{C \times (V_0 - V) \times 3 \times 1.1 \times 10^{-2}}{m}$$

Where C is 0.198 mol/L green copperas solution, V_0 is the volume (mean value) of blanks used to titrate green copperas solution (mL), V is the volume of samples used to titrate green copperas solution (mL), 3 stands for a quarter mole mass of a carbon atom (g/mol), 1.1 is oxidation correction factor and m is the weight of a sample (kg).

Quality Assurance and Quality Control (QA/QC)

To minimize background contamination, use of polytetrafluoroethylene (PTFE) or other fluoropolymer materials was avoided during collection and extraction of samples. And in order to avoid cross contamination in the field sampling, after the samples were taken, outside of the containers including PP bottles for water and PP boxes for sediment were washed thoroughly with Milli-Q water, wiped with clean absorbent paper and then kept in three-layers sealed PE bags for further storage and transportation.

Water samples were not filtered or centrifuged further after the settlement treatment because most of the particles in water can be removed in the settlement process. The supernatant of the water samples can go through the cartridges smoothly. This treatment can ensure the extraction efficiency both fast and precisely.

Field blank and transportation blank prepared in Milli-Q water were introduced to monitor if there was still cross contamination after this treatment. To monitor cross and background contamination during extraction and clean-up, procedure blanks were executed along with every sample batch by use of Milli-Q water. Solvent blank was prepared using 100% methanol and ran after 10 samples to monitor background contamination of the instrument and minimize cross contamination. A guard column immediately in front of the injector loop was used to displace any contaminants introduced in the instrument from analytes in samples. No detectable PFAAs were observed at concentrations greater than the Limit of Quantification (LOQ) in any of the field, transport, procedure or solvent blanks.

Concentrations of 12 PFAAs in water and sediment were quantified using 10-point internal calibration curves containing a concentration series of 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 500 and 1000 ng/mL for native standards and 10 ng/mL for mass-labelled standards (Table S2). Curves for all PFAAs showed strong linearity with $R^2 > 0.99$ and the deviation of every calibration point was less than ±20% from its theoretical value. The concentration of 10 ng/mL in the calibration curve was also used as calibration check standard (CCS) and ran after every 10 samples. When the deviation of a CCS was more than ±20% from its theoretical value, a new calibration curve was prepared. For concentrations of PFAAs in any extracts measured over 1000 ng/mL for the first time, the volume or amount of the samples would be reduced and the samples would be extracted again to make sure the concentrations of PFAAs in the final extracts fit the range of the calibration series.

In order to assess overall efficiency of extraction, two kinds of recovery experiments were performed (Loi et al., 2011). For procedure recovery test and matrix spike recovery test in water, 20 ng mixtures of 12 native PFAAs standards were spiked into 400 mL Milli-Q water via 4 duplicates and 400 mL water samples at site X3, X6, X9 and X12, respectively. For the same tests in sediment, 20 ng mixtures of 12 native PFAAs standards were spiked into 2 g anhydrous sodium sulfate via 4 duplicates and 2 g sediment samples at site X3, X6, X9 and X12, respectively. Results are listed in Table S3.

The limit of detection (LOD) was defined as the lowest concentrations that provided a signal/noise (S/N) > 3 (peak height), and the limit of quantification (LOQ) was defined as the lowest concentration providing S/N >10. Both values were determined in three successive injections with a standard deviation less than 20%. The values are listed in Table S3.

Table S1. Parameters measured along with water samples in situ (TOC: Total Organic Carbon).

Site	pH	Turbidity	Salinity ‰	TOC mg/L	Discharge* m^3/s
X1	7.34	106	0.42	1.58	6.0
X2	6.82	23	0.51	3.91	13.8
X3	7.25	33.7	0.53	1.38	9.9
X4	7.22	30.8	0.39	2.41	13.2
X5	7.31	25.6	0.64	1.46	12.6
X6	7.28	17.1	0.57	1.45	18.5
X7	7.32	21.8	1.70	2.25	25.2
X8	7.13	72.2	1.40	2.05	44.8
X9	7.25	206	2.15	0.95	52.3
X10	6.94	88.7	1.57	2.94	65.8
X11	7.28	79.3	1.68	1.90	98.6
X12	7.03	12.5	8.70	4.57	110.8
X13	7.47	7.7	0.56	1.11	0.68
X14	7.34	13.4	0.44	1.84	1.2
X15	7.55	6.1	2.16	8.08	1.3
X16	7.15	8.4	0.49	1.20	0.65
X17	7.36	37.7	0.47	1.48	0.66
X18	7.35	16.4	1.17	2.22	4.7
X19	7.39	12	1.50	1.61	5.6
X20	7.42	18.5	1.73	1.72	1.8
X21	7.56	6.2	2.44	1.89	1.3
X22	7.18	7.5	2.92	4.16	1.9
X23	7.01	54.1	1.89	14.24	3.6
X24	4.60	5.7	0.62	1.70	10.1
X25	6.95	65.2	9.37	5.57	1.7
X26	7.41	11.8	8.83	5.14	7.8
R1	8.17	2.6	0.62	0.87	-
R2	8.07	3.9	2.65	1.45	-
R3	8.15	5.1	0.58	1.99	-
R4	7.66	6.3	0.17	1.83	-

*: Discharge data was obtained from the Ministry of Water Resources of the People’s Republic of China databases closest to the sampling sites (http://www.mwr.gov.cn/) and corrected by in-situ measurements.

Table S2. Target analytes and optimized MS/MS parameters used for identifying and quantifying individual PFAAs (Frag=fragment voltage, CE= collision energy).

Analyte	Acronym	Carbon number	MS/MS transition	Frag (V)	CE (V)	Type of Quantification
Perfluoroalkyl carboxylic acids	**PFCAs**					
Perfluorobutanoic acid	PFBA	C4	213.0 → 169.1	57	1	$^{13}C_4$ PFBA internal
Perfluoropentanoic acid	PFPeA	C5	263.0 → 218.9	68	2	$^{13}C_4$ PFBA internal
Perfluorohexanoic acid	PFHxA	C6	313.0 → 269.0	68	3	$^{13}C_4$ PFHxA internal
			313.0 → 119.0	62	15	
Perfluoroheptanoic acid	PFHpA	C7	363.0 → 318.9	68	4	$^{13}C_4$ PFHxA internal
			363.0 → 169.0	70	9	
Perfluorooctanoic acid	PFOA	C8	413.0 → 368.9	82	4	$^{13}C_4$ PFOA internal
			413.0 → 169.0	82	12	
			413.0 → 219.0	82	10	
Perfluorononanoic acid	PFNA	C9	463.0 → 419.0	82	3	$^{13}C_4$ PFNA internal
			463.0 → 169.0	66	15	
Perfluorodecanoic acid	PFDA	C10	513.0 → 468.9	86	3	$^{13}C_4$ PFDA internal
			513.0 → 219.0	78	13	
Perfluoroundecanoic acid	PFUnDA	C11	563.0 → 519.0	90	5	$^{13}C_4$ PFUnDA internal
			563.0 → 319.0	84	15	
Perfluorododecanoic acid	PFDoDA	C12	613.0 → 569.0	90	5	$^{13}C_2$ PFDoDA internal
			613.0 → 169.0	80	23	
Perfluoroalkane sulfonic acids	**PFSAs**					
Perfluorobutane sulfonate	PFBS	C4	299.0 → 80.0	135	32	$^{18}O_2$ PFHxS internal
			299.0 → 99.0	132	24	
Perfluorohexane sulfonate	PFHxS	C6	399.0 → 80.0	150	40	$^{18}O_2$ PFHxS internal
			399.0 → 99.0	146	34	
Perfluorooctane sulfonate	PFOS	C8	498.9 → 80.0	154	47	$^{13}C_4$ PFOS internal
			498.9 → 99.0	150	42	

Internal standards						
$^{13}C_4$ Perfluorobutanoic acid	$^{13}C_4$ PFBA	-	217.0 → 172.0	57	1	-
$^{13}C_4$ Perfluorohexanoic acid	$^{13}C_4$ PFHxA	-	315.0 → 270.0	68	3	-
$^{13}C_4$ Perfluorooctanoic acid	$^{13}C_4$ PFOA	-	417.0 → 372.0	82	4	-
$^{13}C_4$ Perfluorononanoic acid	$^{13}C_4$ PFNA	-	468.0 → 423.0	82	3	-
$^{13}C_4$ Perfluorodecanoic acid	$^{13}C_4$ PFDA	-	515.0 → 470.0	86	3	-
$^{13}C_4$ Perfluoroundecanoic acid	$^{13}C_4$ PFUnDA	-	565.0 → 520.0	90	5	-
$^{13}C_2$ Perfluorododecanoic acid	$^{13}C_2$ PFDoDA	-	615.0 → 570.0	90	5	-
$^{18}O_2$ Perfluorohexane sulfonate	$^{18}O_2$ PFHxS	-	403.0 → 103.0	150	40	-
$^{13}C_4$ Perfluorooctane sulfonate	$^{13}C_4$ PFOS	-	503.0 → 99.0	154	47	-

NOTE: a) The terminology used in this study was according to Buck et al. (2011).
b) PFBS and PFHxS were analyzed but scarcely detected in this study, so they were not listed or discussed in the results.

Table S3. QA/QC information including matrix spike recovery (MSR) and procedure recovery (PR), which were presented as Mean±SD (Mean: Arithmetic mean; SD: Standard deviation; n indicates the number of samples analyzed.), limit of detection (LOD), and limit of quantification (LOQ).

Acronym	Sediment				Water			
	%MSR (n=4)	%PR (n=4)	LOD (ng/g dw)	LOQ (ng/g dw)	%MSR (n=4)	%PR (n=4)	LOD (ng/L)	LOQ (ng/L)
PFCAs								
PFBA	92±7	85±5	0.010	0.04	91±12	107±5	0.08	0.22
PFPeA	98±8	102±6	0.010	0.03	104±5	99±11	0.05	0.15
PFHxA	82±4	71±3	0.004	0.01	114±7	109±5	0.04	0.15
PFHpA	96±8	94±9	0.006	0.02	107±3	101±10	0.06	0.15
PFOA	105±12	102±9	0.002	0.01	103±7	94±8	0.05	0.19
PFNA	117±5	108±10	0.002	0.01	113±6	111±8	0.06	0.13
PFDA	109±4	101±8	0.004	0.01	107±14	122±11	0.05	0.15
PFUnDA	92±7	86±12	0.008	0.02	102±8	91±13	0.03	0.08
PFDoDA	85±7	92±7	0.005	0.02	91±5	96±7	0.05	0.13
PFSAs								
PFBS	92±7	81±9	0.004	0.01	96±11	90±6	0.03	0.09
PFHxS	75±8	74±5	0.004	0.01	93±7	81±12	0.01	0.06
PFOS	86±4	91±8	0.004	0.01	89±9	93±11	0.03	0.10

Table S4. HPLC and ESI- MS Instrument Conditions.

HPLC conditions

Analytical column	Agilent ZORBAX Eclipse Plus C18, 2.1×100 mm, 1.8 μm	
Guard column	Agilent 1290 Infinity In-line filter with 3 μm SS frit	
Column temperature	40 ℃	
Injection volume	5 μL	
Mobile phase	A= 2 mM ammonium acetate B= 100% Acetonitrile	
Run time	10 min + 5 min post time	
Flow rate	0.3 mL/min	
Gradient	Time (min)	Mobile phase
	0	20% B
	0.5	20% B
	8	90% B
	10	90% B

MS conditions

Acquisition parameters	ESI mode, negative ionization; MRM
Source gas temperature	350 ℃
Source gas flow rate	9 L/min
Nebulizer pressure	40 psi
Capillary	3500 V negative
Delta EMV(-)	400 V

Table S5. Concentrations of PFAAs in water (ng/L).

Sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS	∑PFAAs
X1	7.86	2.50	2.65	1.79	15.3	0.94	0.39	nd	nd	0.68	32.2
X2	10.3	3.11	2.59	2.12	20.7	2.00	1.15	nd	nd	6.04	48.1
X3	13.9	5.45	2.87	2.37	29.0	2.27	1.07	0.24	0.43	5.18	62.8
X4	13.3	4.77	3.37	2.49	29.7	2.98	1.69	0.54	0.32	8.49	67.7
X5	37.6	11.7	15.4	5.20	87.3	4.31	4.56	0.46	nd	4.29	171
X6	34.8	12.3	15.4	4.80	110	3.93	6.17	0.37	0.37	3.69	192
X7	22.0	8.69	11.0	4.67	73.6	4.77	4.56	0.33	0.35	3.99	134
X8	1 111	566	613	278	30 142	20.6	11.8	1.70	0.46	10.7	32 755
X9	714	409	568	248	28 192	25.9	7.88	0.62	0.46	8.17	30 173
X10	685	375	432	205	26 007	24.1	7.27	0.71	0.52	21.5	27 758
X11	314	180	21	104	12 995	37.7	15.4	1.62	0.67	17.0	13 877
X12	242	129	162	84.4	13 083	18.7	7.97	0.65	nd	11.8	13 740
X13	12.9	4.34	3.75	2.18	43.6	2.30	0.74	0.40	0.66	5.06	75.9
X14	9.92	3.22	3.63	2.42	26.9	1.51	0.34	0.10	nd	6.85	54.9
X15	49.8	22.6	34.7	22.2	479	26.6	83.8	10.1	11.0	2.04	742
X16	18.5	6.11	6.71	3.59	61.6	3.31	1.69	1.49	2.11	8.16	113
X17	9.98	4.05	4.13	1.79	22.9	1.40	0.56	0.22	0.19	5.24	50.5
X18	6.36	5.57	3.72	1.43	32.3	1.69	0.74	nd	0.19	13.2	65.2
X19	26.9	19.6	24.1	18.9	188	35.0	34.8	1.24	0.92	22.0	372
X20	22.2	14.7	20.3	17.4	151	27.5	25.9	1.25	0.38	11.3	292
X21	15.4	4.79	3.21	0.97	56.8	1.00	0.79	0.27	nd	8.37	91.6
X22	34 306	20 144	25 552	12 071	967 611	552	48.1	5.05	0.51	5.33	1 060 295
X23	1 026	524	641	241	17 703	6.96	2.15	0.14	0.20	6.12	20 150
X24	11.4	4.88	4.76	2.25	105	0.74	0.68	<0.08	0.27	2.93	133
X25	58.6	27.9	35.8	16.1	541	4.51	3.36	0.68	nd	18.7	707
X26	1.77	0.38	nd	0.39	29.4	0.78	0.90	nd	nd	6.06	39.7
R1	50.8	22.2	21.7	13.9	1 225	6.12	3.90	nd	nd	39.2	1 383
R2	11.2	0.71	1.37	0.76	51.4	0.83	0.52	nd	0.39	7.85	75.0
R3	5.77	1.16	1.14	1.54	35.4	1.54	2.34	nd	nd	13.5	62.5
R4	5.62	1.80	2.00	2.25	36.9	1.03	1.72	nd	0.38	6.55	58.2

nd: below LOD (the same below).

Table S6. Concentrations of PFAAs in surface sediment (ng/g dry mass). f_{OC} represents the organic carbon fraction in the samples.

Sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS	f_{OC} %
X1	0.09	0.05	0.03	0.10	0.57	0.32	1.55	0.25	0.51	0.53	2.00
X2	0.25	0.00	0.07	0.08	1.62	0.15	0.76	0.17	0.45	0.75	3.72
X3	0.22	0.05	0.03	0.02	0.49	0.20	0.96	0.13	0.21	0.26	2.43
X4	0.27	0.04	0.03	0.02	1.26	0.09	0.58	0.43	0.44	2.77	2.46
X5	0.16	0.02	0.03	0.02	0.37	0.05	0.75	0.10	0.20	0.30	0.63
X6	0.25	0.05	0.05	0.05	1.80	0.23	0.93	1.10	0.47	5.82	1.16
X7	0.37	0.05	0.03	0.04	7.80	0.20	1.79	1.83	0.99	1.35	2.39
X8	1.19	0.67	0.93	0.48	89.9	0.23	1.24	0.64	0.78	1.32	2.15
X9	1.28	0.60	0.98	0.83	153	0.89	1.44	0.93	1.00	1.38	2.41
X10	0.65	0.29	0.42	0.36	49.1	0.10	1.50	0.49	1.20	0.59	2.37
X11	0.53	0.13	0.24	0.15	35.4	0.06	0.27	0.06	0.13	0.11	1.68
X12	0.37	0.15	0.22	0.20	23.4	0.18	1.91	0.19	0.64	0.51	0.78
X13	0.15	0.03	0.04	0.02	0.96	0.17	0.34	0.08	0.12	0.38	1.48
X14	0.24	0.02	0.04	nd	1.10	0.06	0.27	0.06	0.66	0.21	0.91
X15	0.46	0.35	1.40	1.07	7.70	2.56	7.03	1.13	7.40	0.17	2.77
X16	0.06	nd	0.02	0.04	3.59	0.18	1.08	0.07	0.35	0.62	0.49
X17	0.30	0.24	0.07	0.08	0.46	0.07	0.42	0.05	0.26	0.35	0.75
X18	0.24	0.13	0.07	0.02	0.60	0.15	0.18	0.09	0.16	1.37	2.60
X19	0.83	0.90	0.29	0.42	1.08	0.79	2.04	1.39	0.78	0.79	1.50
X20	0.14	0.04	0.02	0.02	5.16	0.29	1.36	0.51	0.24	1.26	1.19
X21	0.34	0.30	0.23	0.06	4.05	0.08	0.09	0.04	nd	1.42	2.03
X22	56.9	37.5	57.2	40.0	10 467	14.8	15.2	23.2	15.5	10.6	4.94
X23	1.39	0.40	0.69	0.64	96.1	0.36	2.61	0.84	1.10	2.46	3.28
X24	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
X25	0.40	0.04	0.03	0.03	1.98	0.04	0.13	0.03	0.07	0.15	1.60
X26	0.38	0.07	0.06	0.06	7.30	0.03	0.09	0.02	0.04	0.51	0.78

NA: no sediment sample was taken in this site due to the cement riverbed.

Table S7. *C*oncentrations *of* PFAAs in sediment cores (ng/g dry mass).

Sites	Depth	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS	f_{OC} %
X3	0-2 cm	0.22	0.05	0.03	0.02	0.49	0.20	0.96	0.13	0.21	0.26	2.43
	2-4 cm	0.24	0.05	0.08	0.03	2.75	0.30	1.05	0.16	0.36	0.14	2.54
	4-6 cm	0.34	0.10	0.05	0.06	0.77	0.25	1.32	0.24	0.18	nd	2.51
	6-8 cm	0.19	0.05	0.04	0.04	0.59	0.14	0.89	nd	0.36	2.34	2.14
	8-10 cm	0.21	0.08	0.08	0.02	1.14	0.30	0.82	0.19	0.51	1.39	2.52
	10-12 cm	0.29	0.06	0.06	0.05	2.57	0.34	1.61	0.10	0.05	1.29	2.65
	12-14 cm	0.43	0.06	0.06	0.04	1.08	0.19	1.18	nd	0.18	1.25	2.09
	14-16 cm	0.32	0.04	0.06	0.06	4.40	0.23	0.65	0.07	0.19	1.70	1.40
	16-18 cm	0.24	0.09	0.02	0.02	0.57	0.20	0.99	0.13	0.07	1.75	1.36
	18-20 cm	0.27	0.06	0.05	0.04	0.60	0.15	0.91	0.08	0.15	0.60	1.42
X6	0-2 cm	0.25	0.05	0.05	0.05	1.80	0.23	0.93	1.10	0.47	5.82	1.16
	2-4 cm	0.22	0.03	0.09	0.13	1.37	0.23	1.42	0.38	0.59	0.17	1.57
	4-6 cm	0.22	0.04	0.05	0.04	0.79	0.19	1.27	0.14	0.10	0.69	1.10
	6-8 cm	0.25	0.03	0.02	0.03	0.90	0.12	0.48	0.05	0.13	0.18	1.04
	8-10 cm	0.21	0.03	0.03	0.01	0.60	0.19	0.79	0.09	0.11	nd	1.11
	10-12 cm	0.30	0.05	0.03	0.05	1.09	0.25	2.95	0.12	1.35	0.33	1.42
	12-14 cm	0.29	0.05	0.03	0.03	1.43	0.15	1.20	0.05	0.34	1.16	1.06
	14-16 cm	0.26	0.03	0.05	0.14	6.60	0.36	4.95	0.31	0.39	0.58	0.86
	16-18 cm	0.34	0.05	0.03	0.02	1.10	0.18	2.34	0.11	0.59	0.33	0.96
	18-20 cm	0.22	0.06	0.04	0.03	1.02	0.10	0.73	0.07	0.31	2.82	1.53
X9	0-2 cm	1.28	0.60	0.98	0.83	153	0.89	1.44	0.93	1.00	1.38	2.41
	2-4 cm	1.17	0.53	0.84	0.59	112	0.30	1.73	0.74	0.90	1.83	2.70
	4-6 cm	0.84	0.47	0.85	0.48	122	0.39	2.08	1.20	0.54	2.28	2.21
	6-8 cm	0.88	0.41	0.67	0.55	119	0.38	2.32	1.08	0.49	2.78	2.09
	8-10 cm	0.70	0.47	0.75	0.72	113	0.40	1.58	1.77	0.54	2.24	1.93
	10-12 cm	1.33	0.92	1.70	1.34	276	0.91	4.54	7.28	1.85	5.20	4.13
	12-14 cm	1.84	1.20	2.20	2.21	333	2.22	5.26	6.75	1.93	4.39	5.38
	14-16 cm	1.13	0.85	1.71	1.59	245	0.89	4.18	3.13	1.28	2.99	4.81
	16-18 cm	0.91	0.63	1.24	1.10	153	0.77	4.43	1.76	1.62	1.65	3.37
	18-20 cm	0.40	0.32	0.56	0.42	43.4	0.22	1.29	0.35	0.24	1.27	1.44
X12	0-2 cm	0.37	0.15	0.22	0.20	23.4	0.18	1.91	0.19	0.64	0.51	0.78
	2-4 cm	0.23	0.13	0.16	0.16	15.7	0.26	3.61	0.10	1.37	1.01	0.54
	4-6 cm	0.22	0.08	0.18	0.10	12.9	0.20	2.06	0.07	0.83	1.02	0.50
	6-8 cm	0.20	0.12	0.14	0.10	9.58	0.08	0.79	0.04	0.22	0.51	0.32
	8-10 cm	0.18	0.11	0.14	0.10	9.06	0.04	0.60	0.04	0.16	0.49	0.28
	10-12 cm	0.24	0.14	0.23	0.13	14.7	0.08	0.92	0.03	0.18	0.41	0.57
	12-14 cm	0.36	0.11	0.22	0.13	16.6	0.12	0.84	0.07	0.26	0.35	0.78
	14-16 cm	0.23	0.10	0.14	0.11	10.2	0.09	0.61	0.06	0.32	0.44	0.38
	16-18 cm	0.33	0.13	0.12	0.09	14.0	0.10	0.34	0.24	0.19	2.14	0.55
	18-20 cm	0.27	0.11	0.14	0.06	13.7	0.15	0.87	0.07	0.19	3.12	0.89

Table S8. Mass loads of PFAAs from X1 to X26 (g/d).

Sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS	∑PFAAs
X1	4.08	1.30	1.37	0.93	7.93	0.49	0.20	0.01	0.02	0.35	16.7
X2	12.3	3.70	3.08	2.52	24.6	2.37	1.37	0.03	0.04	7.17	57.2
X3	11.9	4.66	2.45	2.03	24.8	1.94	0.91	0.21	0.36	4.43	53.7
X4	15.2	5.44	3.84	2.84	33.8	3.40	1.93	0.62	0.36	9.68	77.2
X5	41.0	12.8	16.7	5.66	95.0	4.69	4.96	0.50	0.04	4.67	186
X6	55.5	19.6	24.6	7.65	175	6.27	9.84	0.59	0.58	5.88	306
X7	47.8	18.9	23.9	10.2	160	10.4	9.94	0.71	0.75	8.70	292
X8	4 300	2 190	2 371	1 077	116 671	79.5	45.8	6.58	1.77	41.2	126 784
X9	3 223	1 846	2 563	1 120	127 268	117	35.6	2.79	2.09	36.9	136 215
X10	3 894	2 130	2 453	1 165	147 738	137	41.3	4.03	2.94	122	157 687
X11	2 677	1 534	1 806	884	110 703	321	131	13.8	5.69	145	118 221
X12	2 321	1 238	1 551	808	125 242	179	76.3	6.20	0.34	113	131 535
X13	0.75	0.25	0.22	0.13	2.54	0.13	0.04	0.02	0.04	0.29	4.43
X14	1.05	0.34	0.38	0.25	2.84	0.16	0.04	0.01	<0.01	0.72	5.79
X15	5.63	2.56	3.93	2.52	54.2	3.01	9.48	1.14	1.25	0.23	83.9
X16	1.04	0.34	0.38	0.20	3.46	0.19	0.09	0.08	0.12	0.46	6.36
X17	0.57	0.23	0.24	0.10	1.31	0.08	0.03	0.01	0.01	0.30	2.88
X18	2.55	2.24	1.49	0.57	13.0	0.68	0.30	0.01	0.08	5.31	26.2
X19	13.0	9.47	11.7	9.13	91.1	16.9	16.9	0.60	0.44	10.7	180
X20	3.44	2.29	3.16	2.70	23.5	4.28	4.03	0.19	0.06	1.75	45.4
X21	1.73	0.54	0.36	0.11	6.38	0.11	0.09	0.03	<0.01	0.94	10.3
X22	5 632	3 307	4 195	1 982	158 843	90.7	7.89	0.83	0.08	0.87	174 058
X23	319	163	199	74.9	5 506	2.16	0.67	0.04	0.06	1.90	6 267
X24	9.92	4.24	4.14	1.95	91.0	0.65	0.59	0.03	0.23	2.54	115
X25	8.48	4.04	5.18	2.33	78.3	0.65	0.49	0.10	0.01	2.70	102
X26	1.19	0.26	<0.01	0.26	19.8	0.52	0.61	0.01	0.02	4.08	26.8

Table S9. Partition coefficient ($\log K_d$, cm^3g^{-1}) and organic carbon normalized partition coefficient ($\log K_{OC}$, cm^3g^{-1}) between water and sediment from X1 to X26.

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS
$\log K_d$	Mean	0.90	0.70	0.79	0.94	1.19	1.50	2.38	2.82	3.27	2.02
	SD	0.60	0.70	0.79	0.59	0.59	0.50	0.53	0.73	0.63	0.60
$\log K_{OC}$	Mean	2.68	2.48	2.57	2.72	2.97	3.27	4.16	4.60	5.05	3.80
	SD	0.69	0.79	0.86	0.67	0.66	0.52	0.57	0.64	0.63	0.56
Difference 1		1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78	1.78
Difference 2			-0.20	0.09	0.15	0.25	0.31	0.88	0.44	0.45	

Difference 1*: The value was calculated by subtracting the mean value of $\log K_d$ from the mean value of $\log K_{OC}$.

Difference 2*: The value was calculated by subtracting the mean value of $\log K_{OC}$ from the next mean value of $\log K_{OC}$ with one CF_2 moiety more. For example

The value -0.20 = $\log K_{OC}$ (PFPeA) - $\log K_{OC}$ (PFBA)

Table S10. Comparison of log K_{OC} (mean ± SD, cm^3g^{-1}) of the 10 PFAAs in this study with other published researches.

Compounds	n	log K_{OC}	Area	Reference
PFBA	26	2.68±0.69	Xiaoqing River, China	This study
	14	3.41±0.68	Daling river, China	(Wang et al., 2015)
PFPeA	26	2.48±0.79	Xiaoqing River, China	This study
	14	3.32±0.68	Daling river, China	(Wang et al., 2015)
	8	1.70±0.02	Haihe River, China	(Zhao et al., 2012)
	8	2.11±0.05	Qilihai wetland, China	(Zhao et al., 2012)
PFHxA	26	2.57±0.86	Xiaoqing River, China	This study
	14	3.39±0.56	Daling river, China	(Wang et al., 2015)
PFHpA	26	2.72±0.67	Xiaoqing River, China	This study
	14	3.37±0.82	Daling river, China	(Wang et al., 2015)
	8	1.72±0.01	Haihe River, China	(Zhao et al., 2012)
	8	2.05±0.02	Qilihai wetland, China	(Zhao et al., 2012)
PFOA	26	2.97±0.66	Xiaoqing River, China	This study
	14	3.57±0.66	Daling river, China	(Wang et al., 2015)
	8	2.09±0.01	Haihe River, China	(Zhao et al., 2012)
	8	2.17±0.01	Qilihai wetland, China	(Zhao et al., 2012)
	6	1.9±0.1	Tokyo Bay, Japan	(Ahrens et al., 2010)
	3	2.37	Laboratory	(Ahrens et al., 2011)
	2	2.06	various riverine and lacustrine sites throughout the U.S.	(Higgins and Luthy, 2006)
	19	1.85±0.41	21 major rivers, lakes, and canals in The Netherland	(Kwadijk et al., 2010)
PFNA	26	3.27±0.52	Xiaoqing River, China	This study
	14	4.13±1.00	Daling river, China	(Wang et al., 2015)
	8	2.50±0.01	Haihe River, China	(Zhao et al., 2012)
	8	2.35±0.01	Qilihai wetland, China	(Zhao et al., 2012)

	6	2.4±0.1	Tokyo Bay, Japan	(Ahrens et al., 2010)
	3	2.39±0.09	various riverine and lacustrine sites throughout the U.S.	(Higgins and Luthy, 2006)
	14	2.89±0.53	21 major rivers, lakes, and canals in The Netherland	(Kwadijk et al., 2010)
PFDA	26	4.16±0.57	Xiaoqing River, China	This study
	14	4.74±1.04	Daling river, China	(Wang et al., 2015)
	8	3.23±0.07	Haihe River, China	(Zhao et al., 2012)
	8	2.78±0.06	Qilihai wetland, China	(Zhao et al., 2012)
	6	3.6±0.1	Tokyo Bay, Japan	(Ahrens et al., 2010)
	5	2.76±0.11	various riverine and lacustrine sites throughout the U.S.	(Higgins and Luthy, 2006)
	9	2.87±0.23	21 major rivers, lakes, and canals in The Netherland	(Kwadijk et al., 2010)
PFUnDA	26	4.60±0.64	Xiaoqing River, China	This study
	14	5.69±1.08	Daling River, China	(Wang et al., 2015)
	6	4.8±0.2	Tokyo Bay, Japan	(Ahrens et al., 2010)
	5	3.30±0.11	various riverine and lacustrine sites throughout the U.S.	(Higgins and Luthy, 2006)
PFDoDA	26	5.05±0.63	Xiaoqing River, China	This study
PFOS	26	3.80±0.56	Xiaoqing River, China	This study
	14	5.11±0.88	Daling river, China	(Wang et al., 2015)
	8	2.97±0.03	Haihe River, China	(Zhao et al., 2012)
	8	2.68±0.01	Qilihai wetland, China	(Zhao et al., 2012)
	6	3.8±0.1	Tokyo Bay, Japan	(Ahrens et al., 2010)
	3	3.53	Laboratory	(Ahrens et al., 2011)
	4	2.57±0.13	various riverine and lacustrine sites throughout the U.S.	(Higgins and Luthy, 2006)
	19	2.46±0.33	21 major rivers, lakes, and canals in The Netherland	(Kwadijk et al., 2010)

Table S11. The main products in F1.

Name	Abbreviation	CAS No.	Molecular formula	Annual capacity, ton (2013)
Hexafluoropropylene	HFP	116-15-4	C_3F_6	>10,000
Tetrafluoroethylene	TFE	116-14-3	C_2F_4	60,000
Vinylidene fluoride	VDF	75-38-7	$C_2H_2F_2$	NA
Perfluoro(4-methyl-3,6-dioxaoct-7-ene)sulfonyl fluoride	PSVE	16090-14-5	$C_7F_{14}O_4S$	NA
Propanoic acid,2,2,3,3-tetrafluoro-3-methoxy-, methyl ester	MTPME	755-73-7	$C_5H_6F_4O_3$	NA
Hexafluoropropylene oxide	HFPO	428-59-1	C_3F_6O	NA
Perfluoro n-propyl vinyl ether	PPVE	1623-05-8	$C_5F_{10}O$	NA
Fluorine rubber	FKM	-	$(C_2H_2F_2)x(C_3F_6)y$	NA
Poly-tetra-fluoro-ethylene	PTFE	9002-84-0	$(C_2F_4)n$	49,000
Ethylene-tetra-fluoro-ethylene	ETFE	25038-71-5	$(C_2H_4)x(C_2F_4)y$	NA
Polyvinylidene Fluoride	PVDF	24937-79-9	$(C_2H_2F_2)n$	NA
Fluorinated Ethylene Propylene	FEP	-	$(C_2F_4)x(C_3F_6)y$	NA
Perfluoroalkane sulfonic acid	PFSA	-	$C_nF_{2n+1}SO_3H$	NA
Perfluoroalkyl carboxylic acid	PFCA	-	$C_nF_{2n+1}COOH$	NA
Intermediates	-	-	-	>10,000
Refrigerant	-	-	-	>300,000
Difluorochloromethane	R22	75-45-6	$CHClF_2$	>200,000
1-Chloro-1,1-difluoroethane	R142b	75-68-3	$C_2H_3ClF_2$	NA

NA: not available.

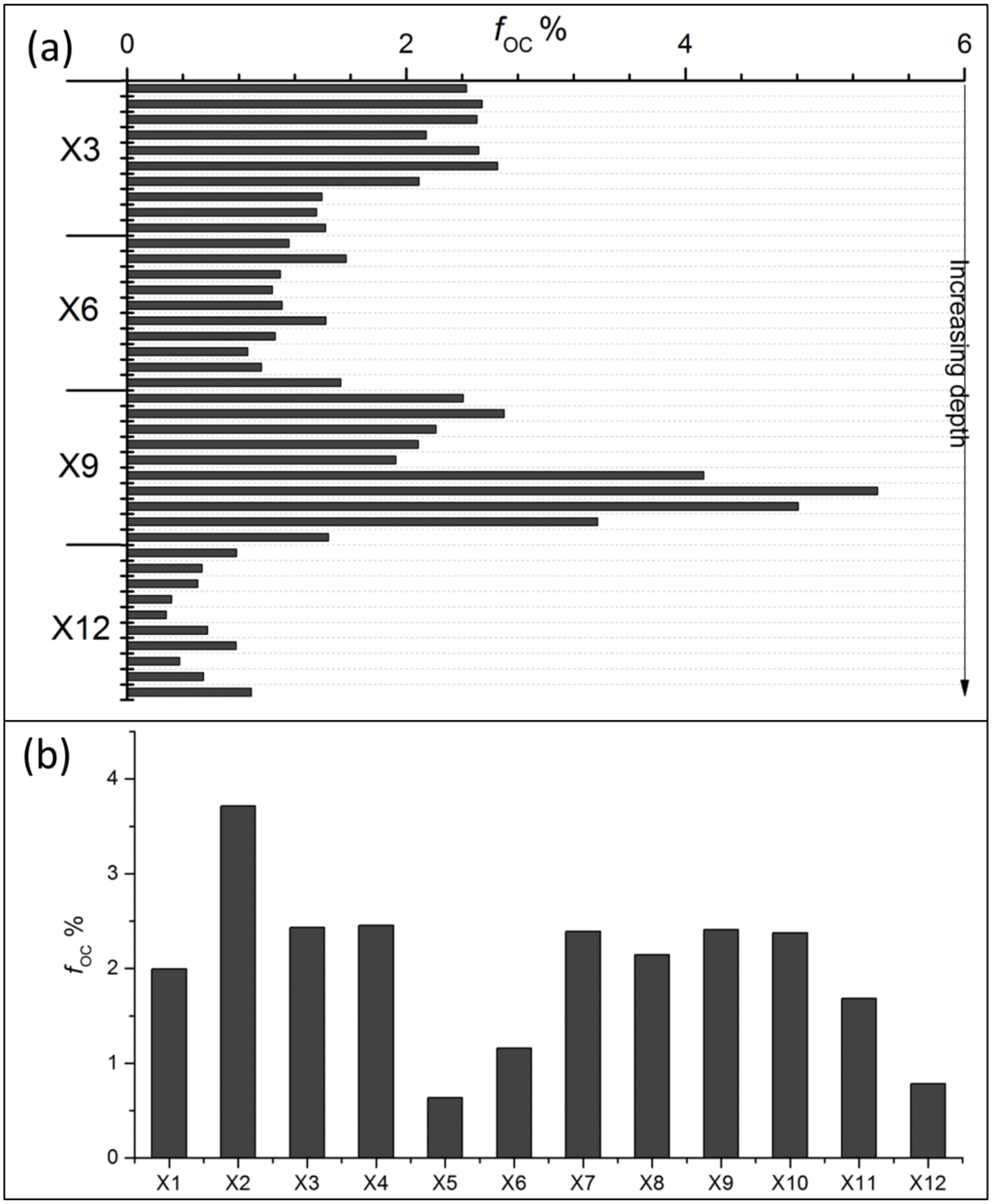
Table S12. Pearson correlation of PFAAs concentrations and f_{OC} in sediment of core X9.

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOS	∑PFAAs	f_{OC}
PFBA	1											
PFPeA	.887**	1										
PFHxA	.826**	.989**	1									
PFHpA	.802**	.970**	.977**	1								
PFOA	.872**	.984**	.976**	.946**	1							
PFNA	.859**	.919**	.891**	.927**	.879**	1						
PFDA	.644*	.865**	.911**	.882**	.871**	.753**	1					
PFUnDA	.723**	.896**	.881**	.830**	.916**	.761**	.819**	1				
PFDoDA	.803**	.905**	.908**	.863**	.885**	.788**	.901**	.821**	1			
PFOS	.640*	.775**	.758**	.690*	.839**	.604*	.727**	.944**	.665*	1		
PFAAs	.868**	.984**	.977**	.946**	1.000**	.879**	.876**	.921**	.888**	.844**	1	
f_{OC}	.810**	.960**	.981**	.959**	.950**	.832**	.914**	.815**	.889**	.715*	.949**	1

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

Figure S1. f_{OC} in (a) sediment cores and (b) surface sediment from X1 to X12 in the Xiaoqing River.



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