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RESEARCH ARTICLE

Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities to the Daling River estuary, China

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Abstract After global commercialization of short-chain perfluoroalkyl acids (PFAAs) as substitutes to conventional long-chain PFAAs by the major manufacturers, two fluorine industry parks for production of short-chain PFAAs located in the Daling River Basin of northern China have developed rapidly in the last few years. This study provides a systematic assessment of sources, emissions, transportation, and potential risks of the PFAAs in this area. The C4 perfluorobutane sulfonic acid (PFBS) and perfluorobutanoic acid (PFBA) were the predominant short-chain PFAAs in river water, with maximum concentrations of 2.90 and 1.35 μg/L, respectively. Park 1 equipped with a telomerization process was identified to be the source of linear and branched mixtures of PFBS, PFBA, and perfluorooctanoic acid (PFOA), while park 2 with an electrochemical fluorination process (ECF) was identified to be the source of linear and branched mixtures of PFBS and PFOA. Partition coefficients between water and sediment were consistent for C4-C8 perfluoroalkyl carboxylic acids (PFCAs) but directly proportional to C9-C11 PFCAs and perfluoroalkyl sulfonic acids (PFSAs). Analysis on the health risk of PFBS and PFBA suggested that they were not without risk since short chain PFAAs are known to be recalcitrant during water treatment.

Keywords Perfluoroalkyl acids · Fluoropolymer facilities · PFBS · PFBA · Partition coefficient · Daling River Basin

Introduction

Perfluoroalkyl acids (PFAAs) are synthetic, fully fluorinated chemicals that are characterized by a perfluoro-alkyl chain and a terminal group. Carboxylate acids (PFCAs) and sulfonate acids (PFSAs) groups are the most widely produced PFAAs and consequently found in predominant quantities in the environment (Buck et al. 2011). PFAAs are persistent due to the high-energy carbon-fluorine (C-F) bond (Giesy et al. 2010). Toxicity and bioaccumulative potential of PFAAs are directly proportional to length of the fluorinated carbon chain (Conder et al. 2008; Olsen et al. 2009), while solubility in water is inversely proportional to length of the perfluoroalkyl chain (Prevedouros et al. 2006; Armitage et al. 2009). Among the different PFAAs produced, the C8 perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were mostly produced and widely distributed and posed great risks of health concern (Lau et al. 2007; Houde et al. 2011; Lindstrom et al. 2011; Olsen et al. 2012). As a result, even though there was no evidence of adverse effect, in 2000, the 3M Company started to voluntarily phase out the production of PFOA, PFOS, and PFOS-related products (3M 2000). In 2006, the US EPA invited eight leading companies to participate in a stewardship program to reduce use and emission of PFOA and related substances by 2010 and work toward final elimination by 2015 (USEPA 2006). In 2006, the European

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Union restricted use of products containing PFOS (EC 2006). In 2009, PFOS, its salts, and perfluorooctane sulfonyl fluoride were listed in appendix B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP 2009). As a signatory of the Stockholm Convention, China began implementation of control over PFOS and related chemicals in 2009. Until now, the action has been focused on review of production, sale, and usage and how substitutes can be introduced. Since 2003, a lot of studies in China have been conducted on occurrence of PFASs in different matrices including soil, water, sediment, biota, food stuff, human blood, etc. (Wang et al. 2014b). General industrial and domestic emissions of PFOS have also been evaluated (Xie et al. 2013a, b). However, information related to fluorine industries, their direct emission, and environmental consequences is still very limited. In addition, there is still no governmental constraint on use or emission of PFAAs in China (POPs Action in China 2014).

The C4 and C6 chemicals have been frequently used to replace most applications previously met by use of C8 and greater chain-length homologues (Holt 2011). Consequently, production of short-chain PFAAs has increased rapidly in recent years (Oliaei et al. 2013). The presence of short-chain PFAAs in the environment and drinking water (Kwok et al. 2010; Moller et al. 2010; Wilhelm et al. 2010; Eschauzier et al. 2013) and sediments (Codling et al. 2014) has already been reported. While in China, high levels of perfluorobutane sulfonic acid (PFBS) and perfluorobutanoic acid (PFBA) have been reported in surface water of Tangxun Lake, with potential sources from untreated industrial wastewater and WWTP effluents (Zhou et al. 2013), which also brought high exposure to local fishery employees (Zhou et al. 2014).

In recent years, production of PFAAs-related chemicals has increased rapidly in China. For example, production of PFOS-related chemicals has grown from 30 t in 2001 to 250 t in 2006, and kept almost consistent until 2011 (Xie et al. 2013b). Two fluorine industry parks located in Fuxin City, Liaoning Province, were built in 2004 (park 1) and 2006 (park 2) for production of PFAAs (Fig. 1). Emissions of eight PFAAs from park 1 in the ambient environment and the local residents were investigated in 2009 (Bao et al. 2010). Results of that study indicated that PFOA was the predominant PFAA followed by PFBS. However, construction is still underway for expansion and will last for several years. This could have resulted in dynamic changes in patterns of production and possible emissions of PFAAs from the two parks. Considering the persistence and mobility of PFAAs in water, research on the areas affected by the two parks was deemed to be updated with expanded scale, especially for the discharge-received rivers, which are Xihe River and Daling River.

Found in a systemic assessment conducted in 2008 on water, sediments, and adjacent soils of coastal rivers draining into North Bohai sea, the concentrations of PFAAs were greatest in the Daling River (Wang et al. 2011), and the two parks posed a great potential as the sources to the PFAAs detected in soils (Wang et al. 2013b). This paper is an extension to the systematic research with the objective to trace influences of the two rapidly developing parks on most part of the Daling River Basin and study the transport and fate of PFAAs as well as the risk assessment from point source to estuary along the river.

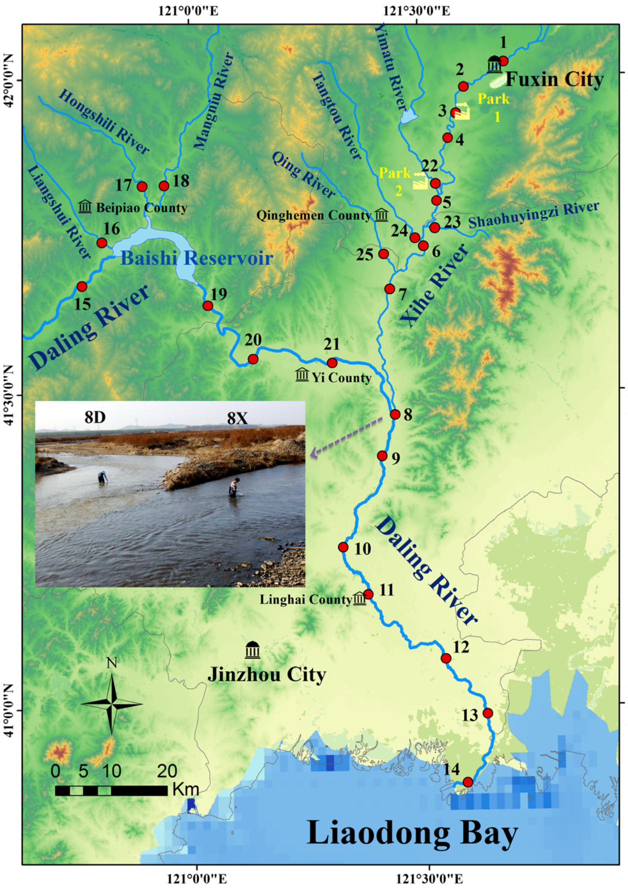

Fig. 1 Sampling sites (*red plots*) in the Daling River basin, China

Materials and methods

Sampling campaign

From October 11–19, 2011, samples of surface water and sediment were collected from 25 sites along the Daling River and its four tributaries as well as four tributaries of the Xihe River (Fig. 1). The distance from site 1 to site 8 is 82 km and from site 8 to site 14 is 90 km. Samples of surface water (top 1–20 cm) were collected using 1 L polypropylene (PP) bottles. Sediments (top 1-5 cm) were collected using a stainless steel trowel, and then stored in clean 250-mL PP boxes. All samples were kept on ice for transport. Before analysis, sediment samples were freeze-dried and ground through 2-mm mesh. Non-suspended substances in water samples were removed by defecating for 24 h. All samples were extracted within 2 weeks after arriving in the lab. Detailed information on sampling was given in Supplementary Material.

Extraction, identification, and quantification of target analytes

Seventeen PFAAs including 13 PFCAs and 4 PFSAs were investigated (Table S3). A volume of 400 mL of unfiltered water was extracted by use of OASIS WAX solid-phase extraction (SPE) cartridge (6 cc, 150 mg, 30 μm) (Taniyasu et al. 2005). For sediments, 2 g of dry mass (dm) samples were extracted by use of ultra-sonic extraction with methanol followed by clean-up with ENVI-Carb and OASIS-WAX cartridges (Loi et al. 2011). Detailed information on extraction is given in the Supplementary Material. Individual PFAA was separated and quantified by use of an Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA) that was operated in the negative electrospray ionization (ESI) mode. The instrument conditions were listed in Table S4.

QA/QC

In order to monitor potential contamination, a series of blanks, including field, transport, procedure, and solvent blanks were prepared with every sample batch. Quantification of 17 PFAAs in water and 11 PFAAs in sediment was carried out using 9-point external and internal quantification curves with concentrations of native standards ranging from 0.01 to 100 ng/mL, respectively. The regression coefficients (R^2) for all the target analytes were over 0.99. The injection volume of the extract was 5 μL. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield a signal-to-noise (S/N) ratio of 3:1 and 10:1. LOD and LOQ ranged from 0.002 to 0.02 ng/g and from 0.01 to 0.1 ng/g, dm for sediments. For water samples, LODs ranged from 0.01 to 0.13 ng/L, while LOQs ranged from 0.06 to 0.63 ng/L. Matrix spike recoveries ranged from 75 to 110 % for water samples and 73 to 119 % for sediment samples. Procedure recovery ranged from 77 to 122 % for water samples and 78 to 120 % for sediment samples. For concentrations of PFAAs in any extract measured over 100 ng/mL for the first time, fewer volume or weight of samples would be taken and extracted again to make sure that the concentrations in the final extracts would fit in with the range of the calibration series. Detailed QA/QC measurements of PFAAs are given in the Supplementary Material.

Statistical and spatial analysis

Statistical analysis was performed with SPSS Statistics V20.0 (SPSS Inc. Quarry Bay, HK). Normality was confirmed by the Kolmogorov-Smirnov test and homogeneity of variance was confirmed by use of Levine's test. During the analysis, concentrations less than the LOQ were set to a value equivalent to half of the LOQ, and those less than the LOD were assigned values equivalent to the LOD/ $\sqrt{2}$ (Calafat et al. 2007). Positions of sampling sites and spatial distributions of concentrations of PFAAs were performed with the Arcmap module in ArcGIS V10.0 software (ESRI, Redland, CA).

Partition coefficient analysis

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

$$\log K_\mathrm{d} = \log C_S / C_W \tag{1}$$

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 Eq. 2.

$$\log K_\mathrm{OC} = \log\left(K_\mathrm{d} \times 100/f_\mathrm{OC}\right) \tag{2}$$

Results and discussion

Distribution of PFAAs in surface water of Daling River Basin

PFAAs were detected in all surface waters with concentrations of sum PFAAs (∑PFAAs) ranging from 1.01 to 4.74 μg/L (Table S6). PFBS (0.2 to 70.6 %, 35.9 % on average) and PFBA (8.0 to 87.4 %, 32.8 % on average) were the predominant PFAAs, followed by PFOA (1.8 to 63.5 %, 17.5 % on average). In site 2, PFBA, PFOA, and PFBS accounted for 96 % of the ∑PFAAs. These are the largest concentrations of PFBS and PFBA reported in rivers of China so far (Wang et al. 2013a). In order to better understand source and transport of PFAAs within the Daling River Basin, the study area was divided into four sections: (1) the Xihe River where the two fluorotelomer industry parks are located, from site 1 to site 8X; (2) four tributaries of the Xihe River, to find potential emissions, from site 22 to site 25; (3) the Daling River before its confluence (at site 8) with the Xihe River, from site 15 to site 21 and site 8D; and (4) after its confluence with the Xihe River, from site 9 to site 14 (Fig. 2).

From site 1 to site 2 in the Xihe River, concentrations of PFBA, PFOA, and PFBS all increased, this indicated that there were small-scale sources in the upstream of the Xihe River or in the city of Fuxin. Between site 2 and site 3, which is located downstream of one of park 1's wastewater effluents (effluent 1), concentrations increased from 144 ng/L to 962 ng/L for PFBA and from 19.5 ng/L to 1.82 μg/L for PFBS, respectively. But for

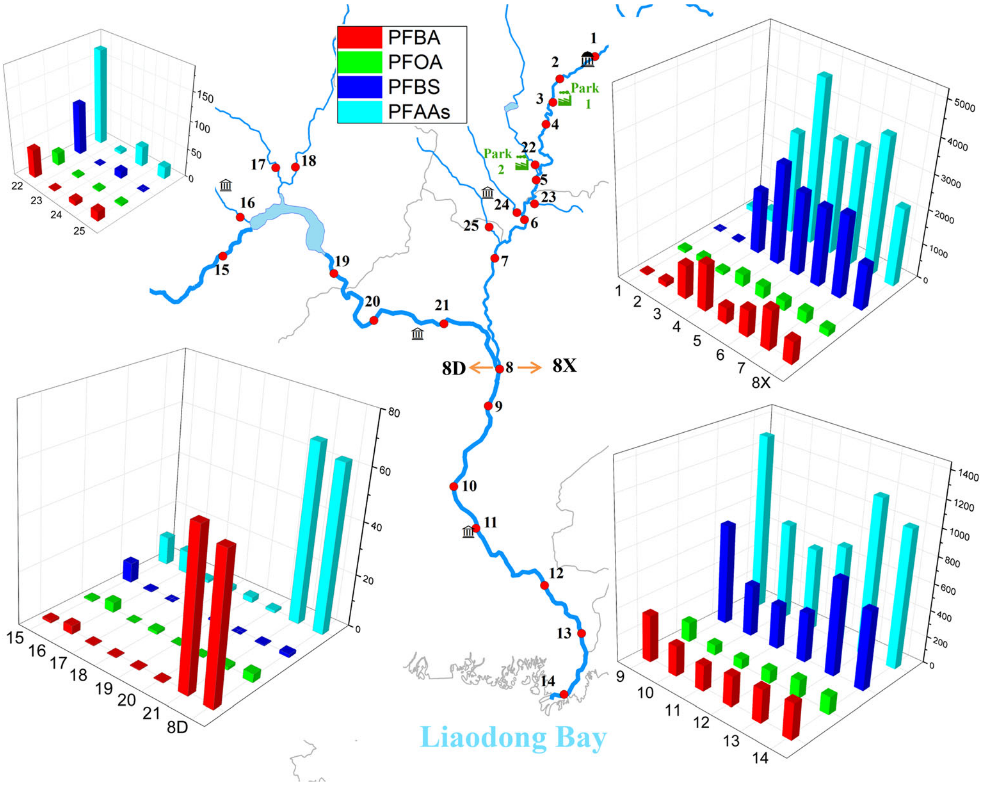

Fig. 2 Concentrations of PFAAs (ng/L) in surface waters of the Xihe and Daling Rivers and their tributaries

PFOA, the concentration decreased from 167 ng/L to 102 ng/L. This indicated effluent 1 was a major source of PFBA and PFBS. From site 3 to site 4, concentrations of several PFAAs increased. This result was consistent with that of a previous study conducted in 2009 in which another effluent (effluent 2) in park 1 located between site 3 and site 4 was found to be a major point source of PFOA (Bao et al. 2010). At this time, effluent 2 was also a major point source of PFBS and PFBA as well as PFOA. From site 4 to site 5, the Yimatu River joined the Xihe River; levels of PFBS, PFBA, and PFOA changed 1.2, 3.0, and 1.0 times, respectively. The almost unchanged levels of PFOA and PFBS indicated that park 2 was a major point source of both PFOA and PFBS. However, concentrations of PFAAs at site 22 on the Yimatu River were 19 times lower compared with those at site 5 in the Xihe River, which implied that park 2 was emitting sewage directly to the Xihe River. Between site 5 and site 7, concentrations of PFAAs were consistent from 3.26 μg/L to 3.97 μg/L, and concentrations in water from sites 23 (5.26 ng/L), 24 (35.8 ng/L), and 25 (21.3 ng/L) indicated no input from the three tributaries. Concentration of PFBA increased gradually from 455 ng/L in site 5 to 1.15 μg/L in site 7 along the Xihe River. There were two reasons for the stable levels of PFOA and PFBS from site 5 to site 7. First, the discharge from the tributaries was much less than that of the Xihe River, so the dilution effect was not obvious; secondly, fluorine industry was strongly supported by the local government; even if the facilities were mostly concentrated in the two parks, there might be small-scale facilities along the river, which would bring emissions of certain PFASs to the Xihe River. At site 8, concentrations of PFAAs were diluted almost by half by some unmeasured tributaries at the downstream of site 7. After the confluence of the Daling and Xihe Rivers, concentrations of PFAAs were diluted by a factor of two, and then remained constant until the river discharged into the estuary at site 14. In the Daling River, upstream of site 8D, PFAAs were detected infrequently except for a small amount of PFBA emitted from Yi County (site 21). Results from the four sections suggested that PFAAs in the Daling River came from the two parks located on the Xihe River where outfalls emitted sewage directly to the Xihe River and little PFAAs were contributed from the other tributaries. The concentrations of PFFAs were diluted after the Daling River converged with the Xihe River.

Recently, PFOA has been found to be the dominant PFAA in coastal rivers of Northern Bohai Bay (Wang et al. 2011) and South Bohai Bay(Wang et al. 2014a), rivers in Tianjin city (Pan et al. 2011), and the Hanjiang River (Wang et al. 2013a). But, there was little information on short-chain PFAAs such as PFBA and PFBS, largely due to their recent emergence. Only Tangxun Lake presented levels of PFBS and PFBA as high as those in this study (Zhou et al. 2013). Even for the study conducted on effluent 2 of park 1 in 2009, PFOA and PFBS were identified to be the predominant PFAAs (Bao et al. 2010). However, after 2 years, concentrations of PFBS in the Xihe River increased 6.9-fold and PFOA increased 3.7-fold (Fig. 3), and great concentrations of PFBA were also

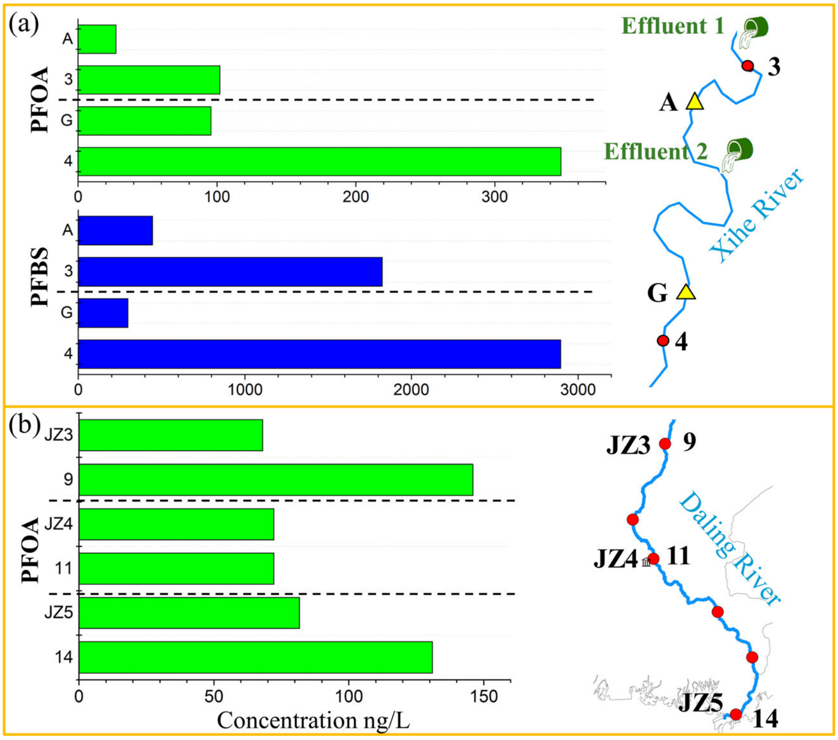

Fig. 3 Comparison of concentrations of PFAAs in this study with those from Bao et al. (site A and G) conducted in 2009 (**a**) and Wang et al. (Site JZ3, JZ4, and JZ5) conducted in 2008 (**b**)

observed. Considering the rapid and consistent expansion of fluoropolymer facilities in the two parks, the main products, and the increasing levels of PFASs from 2009 to 2011, these results indicated rapid growth of production and application of short-chain PFAAs in the two parks. In a study in Minnesota (USA) during the period 2002 to 2006, relatively great concentrations of PFAAs were found in wastewater effluents of the 3 M plant that were directly discharged into the Mississippi River (Oliaei et al. 2013). PFBS was the dominant PFAA with concentration as great as 120 μg/L, which was almost 40-fold greater than that observed in this study. These results are consistent with that of studies on dated sediment cores in which concentrations of PFBS have been found to be increasing in recent years while concentrations of PFOS are decreasing (Codling et al. 2014). With short-chain PFAAs continuing to be produced and used in the world, it is necessary to monitor the production and emission processes in the two parks continuously.

Identification of potential sources associated with the two parks

Production and use of organofluorine compounds at the two parks were investigated in 2011 (Wang et al. 2013b); since then, dozens of additional facilities have been added to the two industrial parks. The data presented here allows for an assessment of emissions of PFAAs from the new facilities as well as efficiency of emission mitigation. Many facilities have been used to produce intermediates like fluorobenzene for use in pharmaceutical drugs, pesticides, and dyes, but limited information is available on their relationship with PFAAs emissions. In park 1, there is one facility (F1) producing various fluoropolymers and fluorotelomers. For fluoropolymers, the main products include fluorinated surfactant used for fabric finishing agents and leather treatment and polytetrafluoroethylene (PTFE) with an annual capacity of 1200 tons for suspension PTFE resin and 600 tons for dispersion PTFE resin, respectively (Fuxin Fluorine Industry Development Zone 2012). Ammonium perfluorooctanoate (APFO) is known to be used in dispersion polymerization processes for making PTFE from TFE, which can bring emission of PFOA to the environment (European Commission 2010). This is consistent with the observation of PFOA emissions in outfall 2 of park 1 (Bao et al. 2010). Another kind of key products for F1 was fluorotelomers, including (n=2) fluorotelomer alcohol (FTOH) produced in telomerization (TM) process using perfluoroalkyl iodide (PFAI) and tetrafluoroethylene (TFE), with an annual capacity of 3000 tons. According to the manufacturer, fluorotelomers included various perfluoroalkyl telomers and monomers with even numbers of carbons and chain lengths from 2 to 12 or longer. Those with 6 or fewer carbons in the perfluoro-moiety are liquids at standard temperature and pressure so they are prone to spill and to be emitted to water, while longer-chain PFAAs would be emitted as solid waste. This is also consistent with the observation in effluent 1 of park 1, where concentrations of PFBA and PFBS have increased with production of these two chemicals. However, the emissions of a fluorotelomers manufacturer are very complex and not limited to water and solid waste. For example, some FTOHs are volatile. In addition, the emissions are not limited to PFAAs. There are several PFASs with chemical properties not directly related to the length of the perfluorinated chain. In park 2, the largest facility (F2), which was built in 2002, has been producing fluoropolymers by use of electrochemical fluorination (ECF) for several years, with the main products including PFBA, potassium-PFBS, perfluorobutanesulfonyl fluoride (PFBSF), PFOA, and APFO (Fuxin Fluorine Industry Development Zone 2012). Potential emissions of related PFAAs from F2 to the river were also consistent with observations at sites 5, 6, and 7 in this study. Other facilities, without direct production of perfluoalkyl substances, would use them as raw materials or additives. And, this might also be a heavy source of PFASs emission. Consistent with the results of this study, the main PFAAs produced or used in the two parks were PFBS, PFBA, and PFOA, and the others were mostly byproducts (Table 1).

The two processes used to produce fluorotelomer substances generate different profiles of isomers. Historically, ECF was used to synthesize PFOS and PFOA, with about 70–80 % linear and 20–30 % branched isomers, respectively. As a primitive technology, ECF would also generate complex mixtures of homologues with 4 to 9 carbons and other intermediates or by-products, some of which were regarded as precursors of PFAAs (Paul et al. 2009). ECF process is now used to make alternative products like PFBS and PFBA at F2 based on perfluorobutane (Buck et al. 2011). The standards used in this study were all for linear isomers. Although branched isomers account for the minor portion of the total, if they were included, it would result in greater concentrations of ∑PFAAs, even greater in the effluent of park 2 and in the river. F1 used TM process, according to Buck et al. 2011, when a linear telogen is used, linear PFASs are obtained with the TM process and vice versa (Buck et al. 2011). However, branched isomers could also be generated during this process, which could be illustrated by the chromatogram of the three predominant PFAAs in the water of site 3 (Fig. S2). According to the same study, the extent to which branched telogen may have been actually used in commercial practice is unclear. Nevertheless, when branched PFCA isomers (isopropyl mainly) were detected in environmental samples, their levels were low compared to their linear counterparts. So, effluent 1 was also the source of linear and branched PFAAs (Table 1). Furthermore, there were predictably more per- and poly-fluorinated substances in the effluent water, which should not be ignored in the future studies.

Partition of PFAAs between water and sediment along the transport route

For the ionic PFAAs detected in this study, the main reservoir and transport routes are the rivers. The primary route to

Table 1 Major production activities in the two fluorine industry parks

	Park 1		Park 2
Facility	F1		F2
Manufacturing process	Telomerization process (TM)		Electrochemical fluorination process (ECF)
Materials	Tetrafluoro-ethylene (TFE)	Perfluoroalkyl iodide (PFAI) and TFE	NA
Products	Polytetrafluoro-ethylene (PTFE) resin	($n=2$) fluorotelomer alcohol (FTOH)	PFBA, Potassium PFBS, Perfluorobutanesulfonyl fluoride (PFBSF), PFOA and APFO
Annual capacity, tons/year	1 800	3 000	NA
PFAAs emission	PFOA	PFBA and PFBS	PFBS, PFBA, and PFOA
Isomer profile	Mixture of linear and branched isomers		Mixture of linear and branched isomers
Effluent	2	1	NA

NA not available

the river is between sites 1 and 14. PFBA and PFBS were also predominant in sediment, followed by PFOA and PFOS. Concentrations ranged from 0.92 ng/g to 30.4 ng/g for PFBA and from 0.06 ng/g to 11.08 ng/g for PFBS, respectively (Table S7). Since the vapor pressure for ionic PFAAs is limited (Wania 2007), the main partition behavior would be between water and surface sediment. In this study, no samples were taken right in the effluents of the facilities to minimize influence of fresh sources on the calculation of the partition coefficients. For the eight PFCAs, the value of log K_d was similar among PFBA, PFPeA, PFHxA, and PFHpA, but increased from PFHpA (1.03±0.46) to PFUnDA (3.35±0.70) and was proportional to length of the carbon chain from C7 to C11. The same trend was observed for the three PFSAs, from PFBS (0.34±0.61) to PFOS (2.77±0.67) (Fig. 4a, Table S8). The fraction of organic carbon is the dominant parameter influencing sorption of PFAAs to sediment (Higgins and Luthy 2006; Ahrens et al. 2010). The log K_{OC} was consistently 2.34 log units greater than log K_d (Fig. 4b, Table S8), which demonstrated the effect of organic carbon in sediment on sorption of PFAAs quantitatively. There were indeed several minus values of log K_d for PFBS, which indicated that there would be limited sorption of PFBS to sediment from water without the inclusion of organic carbon. Along the primary route, log K_d didn't vary much for PFBA, PFOA, and PFBS, but log K_{OC} changed apparently, especially in site 3 (Fig. 4c), which was the closest site to the effluent from the facilities. Concentrations of PFBA and PFBS increased dramatically from site 2 to site 3; this indicated that water effluent could induce low log K_{OC}. Site-specific log K_{OC} values of individual PFAAs in this study were overall greater than those in the Haihe River and Qilihai wetland in China (Zhao et al. 2012), Tokyo Bay in Japan (Ahrens et al. 2010), various riverine and lacustrine locations in the USA (Higgins and Luthy 2006), and 21 major rivers, lakes, and canals in the Netherland (Kwadijk et al. 2010) (Table S9) as well as observed during laboratory experiments (Ahrens et al. 2011). The fraction of organic matter in sediments ranged from 0.06 to 6.23 % from site 1 to site 14 (Table S7). There are two main reasons for the relatively large proportion of organic contents in the sediments. Fuxin City is famous for coal industry, and there are still lots of coal mining along the Xihe River, which brought heavy pollution of ash to the river. In the Daling River from Yi County downriver, there is intensive mining of sand in the riverbed. Both activities not only destroy the natural sedimentation process but also make the sediment mix with the water more frequently. This will increase the chance for the sorption of PFAAs to the sediment. Another is that the relatively great concentrations of PFAAs detected in surface water in this study might also increase the absolute amount of PFAAs adsorbed to sediment. More research is needed on the influence of concentrations of PFAAs in water on log K_{OC}.

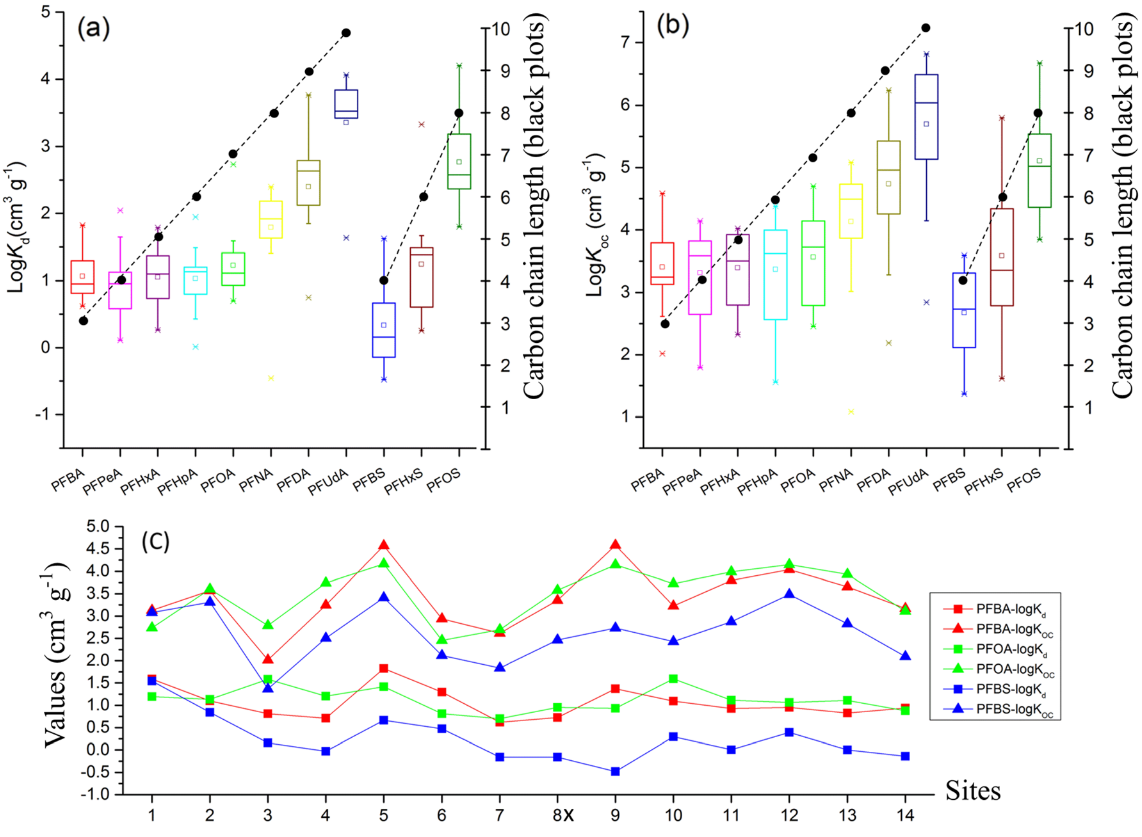

Fig. 4 Log K_d (**a**) and log K_{OC} (**b**) values for 11 PFAAs and the trend of the values for PFBA, PFOA, and PFBS (**c**) from site 1 to site 14

Previous studies have focused mostly on regions contaminated by non-point sources of PFAAs, and there is limited information on partitioning behavior of PFAAs near more concentrated, point sources. Therefore, the information reported here would contribute to the modeling of transport and fate of PFAAs at these types of sites.

Each additional CF_2 moiety increased the log K_{OC} by 0.20 to 0.96 log units for C7 to C11 PFCAs and 0.91 to 1.52 log units for the three PFSAs, respectively (Table S8). For the same carbon chain length between PFCAs and PFSAs, log K_{OC} of PFBS is 0.64 log units smaller than that of PFPeA, while log K_{OC} of PFHxS is 0.22 log units greater than that of PFHpA and log K_{OC} of PFOS is 0.98 log units greater than that of PFNA. This indicated that PFSAs are more absorbed to sediment organic carbon than PFCAs with the increasing carbon chain length, especially for PFOS. This trend was also found in previous studies, but the values observed in this study were greater. Besides the local conditions, hydrophobic interaction was found to play a key role in partitioning of longer-chain PFAAs, while electrostatic interaction could affect the sorption of short-chain PFAAs to sediments (Zhao et al. 2012). Other parameters, like Ca^{2+}, pH, heterogeneity of organic carbon, particulate structure, and the presence of organisms have also been reported to influence partitioning of PFAAs between water and sediment, but varies in different natural environment (Higgins and Luthy 2006; Ahrens et al. 2010).

Is there any risk for the short-chain substitutes?

Over last decade, along with the phase-out announcement of longer-chain PFAAs by 3 M, numerous studies on the toxicology of PFOS and PFOA have been conducted and PFOS is now listed under the Stockholm Convention, and several countries or regions have put strict control over production, usage, and releases of PFOS and PFOA. Meanwhile, some countries have also established drinking water criteria for PFOS and PFOA, and criteria maximum concentration (CMC) and criteria continuous concentration (CCC) of the two PFAAs have also been derived in China and North America for the protection of fresh water aquatic organisms (Giesy et al. 2010; Yang et al. 2014). The greatest concentration of PFOA (348 ng/L) in this study exceeded the New Jersey guidance value for PFOA in drinking water (40 ng/L), but was less than the US EPA provisional health index for PFOA (400 ng/L) and the Health Canada drinking water guidance value for PFOA (700 ng/L). For the C4 substitutes PFBS and PFBA, many studies have found that they are much less accumulated and have less toxic potencies than longer-chain PFAAs such as PFOS and PFOA, due to their fast elimination rate in blood of humans and wildlife (NICNAS 2005; Rickard 2009). For example, PFBA takes 5 days and PFBS takes 1 month, on average, to be eliminated in the human body, while for PFOA and PFOS, the time for elimination are 3.8 and 5.4 years, respectively (Betts 2007). However, this does not mean that there is no accumulation of PFBS. In a study on the blood of Swedish women conducted from 1996 to 2010, concentrations of PFBS increased by 11 % per year and doubled every 6.3 years (Glynn et al. 2012). Results of other studies suggested that PFBS is tightly bound to human albumin with indications of a saturated binding to serum albumin (NICNAS 2005). Based on the mean elimination half-life of PFBS in the human, in Minnesota of USA, where one of the 3 M's largest per/polyfluorinated chemicals production facilities is located, Minnesota Department of Health (MDH) has developed health risk limits for PFBS for groundwater in 2011, including the subchronic noncancer health-risk limit (nHRL) (9 μg/L) and chronic nHRL (7 μg/L) (MDH 2011). Provisional health-related indication values (HRIV) as safe in drinking water were also derived for PFBA (7 μg/L) and PFBS (3 μg/L) in Germany (Wilhelm et al. 2010). The greatest concentration of PFBS in this study (2.9 μg/L) was slightly less than values reported for HRIV in Germany and was about half or a third of the nHRLs provided by MDH (Fig. 5). Although the river water is no longer used for drinking, there is intensive farmland along the Xihe and Daling Rivers where the water would be used for irrigation. Field surveys also suggested that individuals still collected fish from the Daling River. Meanwhile, the groundwater could be polluted by the river water through infiltration process, and

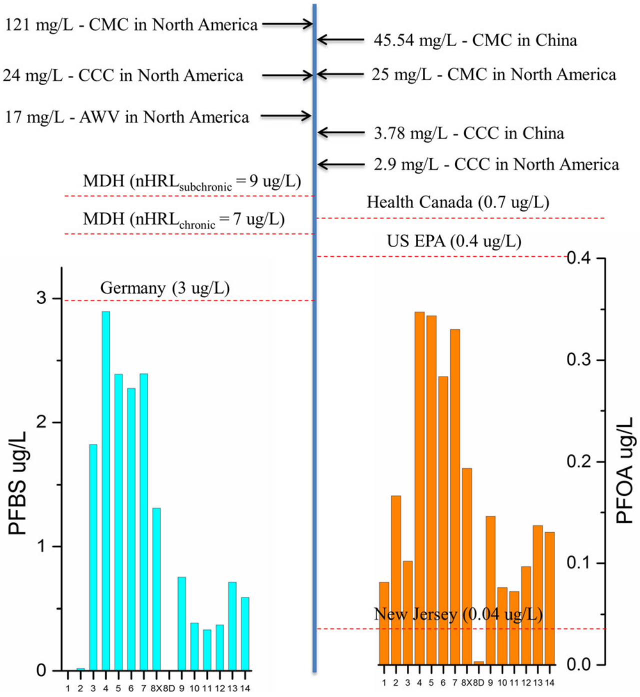

Fig. 5 Comparison of PFAAs concentrations in river water from site 1 to site 14 with criteria values for protection of drinking water (with *red dotted line*) and aquatic organism in China and other countries (with *black arrows*).

groundwater has always been used as drinking water. So, the potential pathway of PFAAs from river water to human through crops, vegetation, fish, and polluted groundwater still existed for local residents. Besides, there are two more health concerns over the PFAAs pollution. One is that FTOHs can form nonvolatile PFSAs and PFCAs through atmospheric transport and degradation (Simcik and Dorweiler 2005). However, the atmospheric pathway would not only influence surface water but also the underlying aquifer by migration downward with precipitation and river recharge (Davis et al. 2007). In 2009 relatively great concentrations of PFAAs had already been detected in groundwater of park 1 (Bao et al. 2010). Another is that PFOA and PFOS can be removed from drinking water by percolation over granular activated carbon, but that technology is ineffective for elimination of short-chain PFAAs (Wilhelm et al. 2010). All concentrations of PFAAs in this study were far below the CCC and CMC values in both China and North America, indicating their low risk to local aquatic ecosystem. However, with fast growing production capacity in the two parks, the potential risk of PFAAs should be listed as one of the health issues by the local government, and long-term monitoring is necessary to make sure that the concentrations are controlled below the criteria.

Conclusions

This study investigated two fluorine industry parks in northern China. The study area was divided into four sections geographically to give a distinctive expression on the distribution of PFAAs in Daling River Basin. The greatest concentrations of all PFAAs were found in the Xihe River, where the two fluorine industry parks are located. Source identification was made based on concentrations of PFAAs in the river near potential effluents, together with the information on types and volumes of production in the two parks. Results showed that park 1, where telomerization was used for production, was the major source of linear and branched PFBS, PFBA, and PFOA, while park 2 where ECF applied was the major source of linear and branched PFBS and PFOA. The predominant pathway for transportation of PFAAs was between sites 1 and 14. Partitioning coefficients including log K_d and log K_{OC} were consistent for short-chain PFCAs but increased with increasing chain length for longer-chain PFCAs and PFSAs. This indicated that PFBS and PFBA had a higher transport potential in the water phase than longer chained since they were less removed by sedimentation. Concentrations of individual PFAAs were compared with related criteria for drinking water or for protection of aquatic organisms. The greatest concentration of PFOA exceeded the New Jersey guidance value for drinking water (40 ng/L). Greatest concentrations of PFBS observed in this study were close to the related guidance values for PFBS, indicating the relatively large risk. However, if the surface water were treated properly and untreated water not consumed, the risks to humans could be minimized, but these measures would not mitigate potential risks to wildlife. With the growing global demand for fluoropolymer, the production capacity in the two parks will increase. Long-term and systematic monitoring is needed on emissions of PFAAs in the two parks, and their environmental behavior in the Daling River Basin or even a larger region. Potential risks posed by PFAAs intake to the health of the local residents and wildlife should become one of the major issues of great concern for the local government.

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Supplementary Material

Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities to the Daling River estuary, China

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Content

Table S7. Concentrations (ng/g dw) of 8 PFCAs and 3 PFSAs in surface sediment from site 1 to site 14 in the Daling River Basin. f_{OC} represents the organic carbon fraction in the samples.

Table S8. Partition coefficient (logK_d, cm^3g^{-1}) and organic carbon normalized partition coefficient (logK_{OC}, cm^3g^{-1}) between water and sediment for sites 1 to 14.

Table S9. Comparison of log K_{OC} (mean ± SD, cm^3g^{-1}) of the 11 PFAAs in this study with published results.

Figure S1. Chromatogram of 17 PFAAs by MRM with the concentration of 0.05 ng/mL.

Figure S2. Chromatogram of three predominant PFAAs in water samples of site 3.

References

Standards and Reagents

A mixture of seventeen native PFAAs and nine mass-labeled PFAAs was purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada) (Table S3). HPLC grade methanol (MeOH) 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.

Samples collection and pre-treatment

To assess sources of PFAAs in the city and the two fluoropolymer production industrial parks, sampling locations were distributed along the Xihe River from the city of Fuxin to the confluence with the Daling River. Locations on the 4 tributaries of the Xihe River were used to locate potential sources such as wastewater discharges or to be used as reference locations. Sampling sites on the Daling River were located from upstream of the Baishi Reservior to the estuary, while the sites at upstream of the junction and on the other 3 tributaries were used as regional references. Sites on the Daling River from the junction to the estuary were used to determine the transport of PFAAs in the Xihe River. Descriptions of all sampling sites were listed in Table S1.

Water samples were collected from mid-channel of the river into 1-L PP bottles, which were opened and closed beneath the water, and filled and emptied three times before an actual sample was taken. All samples were stored on ice during transport (McLachlan et al., 2007). No flood event or heavy rain occurred during the sampling period. Parameters including turbidity, pH, dissolved oxygen, conductance, water temperature, concentrations of chloride ion and fluorine ion, and oxidation reduction potential were measured *in situ* by use of a HQd Portable and Benchtop Meter Configurator (HACH Company, USA) (Table. S2). Water samples were stored at -20 ℃ before extraction.

Samples of sediments (Top 5 cm) were collected by use of a stainless grabber at the same location where samples of water were taken, and stored on ice during transport. After arriving at the lab, all sediments were dried in a FreeZone 2.5 Liter Benchtop Freeze Dry System (LABCONCO, Kansas City, MO) and then homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, then stored in new clean 250 mL PP bottles at room temperature until extraction.

All samples were extracted within two weeks after arrival in the lab.

Extraction and cleanup.

Samples of 400 mL of unfiltered water were extracted with few modifications of published methods by use of OASIS WAX-SPE (Taniyasu et al., 2005). Prior to loading samples onto the Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA), they were preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water. Cartridges were washed with 4 mL 25 mM ammonium acetate (pH 4) and air-dried. Target analytes were then eluted with 4 mL of methanol and 4 mL of 0.1% NH_4OH in methanol, respectively. The latter fraction was reduced to 1 mL under a gentle stream of high purity nitrogen and passed through a nylon filter (13 mm, 0.2 μm, Chromspec, Ontario, Canada), then transferred into a 1.5 mL PP snap top brown glass vial with polyethylene (PE) septa.

Sediments were extracted based on published methods (Loi et al., 2011) with some modifications. Aliquants of 2 g dry sediment were placed into a 50 mL PP centrifuge tube, and spiked with 5 ng mass-labelled internal standards. Sediment was digested with 2 mL of 100 mM NaOH in methanol (8:2/MeOH:Milli-Q water), and ultra-sonicated for 30 min. 20 mL methanol 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 methanol 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 were preconditioned by passing through 1 mL methanol three times, and then the extracts were loaded and collected. Analytes of interest were washed with another three aliquots containing 1 mL methanol and collected together with the extracts. After ENVI-Carb cleanup, all the extracts were diluted in 100 mL of 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 PP snap top brown glass vial with polyethylene (PE) cap.

Organic Carbon fraction (f_{OC}) analysis

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:

$$f_{\mathrm{OC}}(\%)=\frac{C\times(V_0-V)\times3\times1.1\times10^{-2}}{m}$$

Where C is 0.198mol/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. Field and transport blanks were prepared daily using 1 L Milli-Q water during the sampling campaign, with the amount of 9; procedure blanks were prepared using 400 mL Milli-Q water for water samples and 2 g anhydrous sodium sulfate for sediment samples with every sample batch for extraction, with the amount of 4 for water and 4 for sediment. Results of these blanks were used to check for contamination during sampling and extraction. Certain parts in the 6460 mass spectrum that are made of PTFE wern’t replaced. Solvent blank was prepared using 100%

methanol and ran after 10 samples during instrumental analysis to monitor background contamination of the instrument and minimize cross contamination, with the amount of 6. 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 17 PFAAs in water were quantified by use of external calibration curves containing a concentration series of 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, or 100 ng/mL. In order to improve sensitivity of the instrument, 6 time segments were applied in MS QQQ analysis according to different retention time for the 17 native PFAAs (Fig. S1). Optimized △EMV of 200-400V were then applied to each time segment to increase the ratio of signal-to-noise. After 17 PFAAs levels in water were analyzed, those PFAAs with detection ratios less than 10% and concentrations less than 1 ng/L were selected and excluded in the following sediment analysis. Then concentrations of 11 PFAAs in sediment samples were quantified using internal calibration curves with the same concentration series and 5 ng mass-labeled internal standards. 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 was also used as calibration check standard (CCS) and ran after every 10 samples during instrumental analysis. 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 extract measured over 100 ng/mL for the first time, fewer volume or weight of samples would be taken and extracted again to make sure that the concentrations in the final extracts would fit in with 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 17 native PFAAs standards were spiked into 400 mL Milli-Q water and 400 mL water samples taken at site 15 to 18 via 4 duplicates, respectively. For the same tests in sediment, 2 ng mixtures of 17 native PFAAs standards were spiked into 2 g anhydrous sodium sulfate and 2 g sediment samples taken at site 15 via 4 duplicates, respectively. Results are listed in Table S4.

The limit of detection (LOD) was defined as the lowest concentration 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 S4.

Table S1. Sampling sites and ambient conditions.

Site	Ambient conditions	Longtitude	Latitude	Flow rate* (m/s)
1	Downstream of the junction of 3 riverway	121.68784	42.02185	0.1
2	Downstream of Fuxin City, upstream of park 1, small water column	121.59971	41.98277	<0.1
3	Downstream of one effluent of park 1, black water, farmland on the bank	121.58190	41.94097	0.6
4	Farmland around, black water due to coal mining	121.56385	41.90167	0.5
5	Downstream of where Yimatu River joins Xihe River, black water, farmland on the bank	121.53707	41.80181	0.4
6	Downstream of where Shaohuyingzi River joins Xihe River, black water, farmland on the bank	121.50677	41.73090	0.4
7	Downstream of where Qing River joins Xihe River, black water, farmland on the bank	121.43224	41.66286	0.8
8X	In Xihe River, upstream of the confluence of Daling River and Xihe River, black water	121.44010	41.46353	0.8
8D	In Daling River, upstream of the confluence of Daling River and Xihe River, yellow water	121.44010	41.46353	0.5
9	Sand mining about 1km upstream, pebbles around	121.41116	41.39800	0.4
10	Sand mining has destroyed the river bed badly	121.32383	41.25406	0.1
11	Downstream of Linghai County, a large paper plant upstream	121.37675	41.17851	0.2
12	Wood along the bank, foam on the surface water	121.54254	41.07483	0.6
13	Farmland and wasteland, oil wells around	121.63081	40.98718	0.4
14	Estuary of Daling River, reed on the bank, large area of wetland	121.58580	40.87826	0.4
15	Upstream of Baishi Reservoir, wood on the bank	120.76215	41.67225	0.7
16	Farmland, good environment	120.80584	41.74133	0.3
17	Good environment, but coal mine upstream led to black water	120.89467	41.82984	<0.1
18	Large dried riverbed, good environment	120.94314	41.83037	0.2
19	Downstream of Baishi Reservoir,good environment	121.03569	41.63930	<0.1
20	Ecological construction and rehabilitation, wood along the bank	121.13280	41.55387	0.2
21	People were fishing. A steel plant,a coke plant and a power plant around,and a electroplate plant upstream in Yi County.Bad smell in the air and dead animals on the ground.	121.30464	41.54641	0.2
22	In Yimatu River, Riverbed had been destroyed badly, farmland and wood around	121.53550	41.82948	<0.1
23	In Shaohuyingzi River, clear water with water plant, farmland on the bank	121.53217	41.75900	0.1
24	In Tangtou River, black water, farmland on the bank	121.48856	41.74395	0.5
25	In Qing River, Black water due to coal mining, small riverway	121.41966	41.71861	0.2

*: Flow rates of water were measured 30cm beneath the water surface.

Table S2. Parameters measured along with water samples in situ. (DO: Dissolved oxygen; WT: water temperature; CD: Conductivity; C_{Cl^-}: concentration of chloride ion; C_{F^-}: concentration of fluoride ion; ORP: oxidation reduction potential.)

Site	**Turbidity**	**pH**	**DO** mg/L	**WT** ℃	**CD** μs/cm	**C_{Cl^-}** mg/L	**C_{F^-}** mg/L	**ORP** mV
1	114.00	8.85	10.57	17.4	1130	591	0.619	177.9
2	5.82	7.47	11.22	11.0	2640	1127	0.599	90.3
3	141.60	7.49	0.22	18.2	1618	476	1.640	144.4
4	464.60	7.70	0.60	18.4	1554	609	1.570	143.4
5	****	7.93	2.96	15.4	1615	793	1.800	126.9
6	****	8.16	4.37	14.4	1785	795	2.320	125.9
7	****	8.05	5.05	17.2	1702	620	1.600	166.8
8X	93.20	8.13	7.53	12.3	1564	585	1.690	185.1
8D	51.40	8.34	12.24	12.3	757	247	0.319	178.0
9	108.00	8.03	6.82	14.2	1217	523	1.010	240.8
10	48.33	7.88	8.41	15.3	1006	379	0.763	230.4
11	55.33	8.33	10.68	14.5	1046	430	0.822	179.6
12	12.70	8.26	10.24	16.4	1052	379	0.970	203.3
13	14.73	8.21	10.43	15.3	1038	358	0.996	196.6
14	68.60	8.34	10.03	14.7	1876	1411	0.735	171.8
15	16.46	8.10	13.22	10.8	712	299	0.273	185.8
16	28.50	8.12	8.42	15.0	1364	549	0.385	228.8
17	281.00	8.06	9.54	15.2	983	194	0.507	230.8
18	1.76	8.32	11.13	16.5	471	124	0.309	232.4
19	1.05	8.14	10.42	9.5	539	250	0.310	192.8
20	28.87	8.22	10.79	17.0	558	157	0.316	230.6
21	12.43	8.16	12.35	15.0	729	204	0.312	237.3
22	10.13	8.35	10.81	17.5	705	238	0.344	192.0
23	3.76	8.15	9.92	17.3	722	238	0.130	194.2
24	111.00	8.78	10.50	22.6	2840	660	4.580	177.9
25	****	8.58	8.94	17.6	2830	1373	1.270	180.0

****: Exceed the range of the equipment.

Table S3. Target analytes and the MS/MS parameters used in this study (Frag: fragment voltage, CE: collision energy).

Analyte	Acronym	Chain length	MS/MS transition	Frag (V)	CE (V)	Quantification in sediment
Perfluorocarboxylic acid	**PFCAs**					
Perfluoro-butanoic acid	PFBA	C4	213.0 → 169.1	57	1	$^{13}C_4$ PFBA internal
Perfluoro-pentanoic acid	PFPeA	C5	263.0 → 218.9	68	2	$^{13}C_4$ PFBA internal
Perfluoro-hexanoic acid	PFHxA	C6	313.0 → 269.0	68	3	$^{13}C_4$ PFHxA internal
			313.0 → 119.0	62	15	
Perfluoro-heptanoic acid	PFHpA	C7	363.0 → 318.9	68	4	$^{13}C_4$ PFHxA internal
			363.0 → 169.0	70	9	
Perfluoro-octanoic 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	
Perfluoro-nonanoic acid	PFNA	C9	463.0 → 419.0	82	3	$^{13}C_4$ PFNA internal
			463.0 → 169.0	66	15	
Perfluoro-decanoic acid	PFDA	C10	513.0 → 468.9	86	3	$^{13}C_4$ PFDA internal
			513.0 → 219.0	78	13	
Perfluoro-undecanoic acid	PFUnDA	C11	563.0 → 519.0	90	5	$^{13}C_4$ PFUnDA internal
			563.0 → 319.0	84	15	
Perfluoro-dodecanoic acid	PFDoA	C12	613.0 → 569.0	90	5	
			613.0 → 169.0	80	23	
Perfluoro-tridecanoic acid	PFTrDA	C13	662.9 → 619.0	80	5	
Perfluoro-tetradecanoic acid	PFTeDA	C14	713.1 → 669.0	100	7	
Perfluoro-hexadecanoic acid	PFHxDA	C16	813.0 → 769.0	100	9	
Perfluoro-octadecanoic acid	PFODA	C18	913.0 → 869.0	118	10	
Perfluorinated sulfonic acid	**PFSAs**					
Perfluoro-butanesulfonate	PFBS	C4	299.0 → 80.0	135	32	$^{18}O_2$ PFHxS internal
			299.0 → 99.0	132	24	

Perfluoro-hexanesulfonate	PFHxS	C6	399.0 → 80.0	150	40	$^{18}O_2$ PFHxS internal
			399.0 → 99.0	146	34	
Perfluoro-octanesulfonate	PFOS	C8	498.9 → 80.0	154	47	$^{13}C_4$ PFOS internal
			498.9 → 99.0	150	42	
Perfluoro-decanesulfonate	PFDS	C10	599.0 → 79.9	160	65	
Internal standards						
$^{13}C_4$ Perfluoro-butanoic acid	$^{13}C_4$ PFBA	-	217.0 → 172.0	57	1	-
$^{13}C_4$ Perfluoro-hexanoic acid	$^{13}C_4$ PFHxA	-	315.0 → 270.0	68	3	-
$^{13}C_4$ Perfluoro-octanoic acid	$^{13}C_4$ PFOA	-	417.0 → 372.0	82	4	-
$^{13}C_4$ Perfluoro-nonanoic acid	$^{13}C_4$ PFNA	-	468.0 → 423.0	82	3	-
$^{13}C_4$ Perfluoro-decanoic acid	$^{13}C_4$ PFDA	-	515.0 → 470.0	86	3	-
$^{13}C_4$ Perfluoro-undecanoic acid	$^{13}C_4$ PFUnDA	-	565.0 → 520.0	90	5	-
$^{13}C_2$ Perfluoro-dodecanoic acid	$^{13}C_2$ PFDoA	-	615.0 → 570.0	90	5	-
$^{18}O_2$ Perfluoro-hexanesulfonate	$^{18}O_2$ PFHxS	-	403.0 → 103.0	150	40	-
$^{13}C_4$ Perfluoro-octanesulfonate	$^{13}C_4$ PFOS	-	503.0 → 99.0	154	47	-

Table S4. 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	100±5	103±7	0.020	0.10	93±12	105±7	0.13	0.63
PFPeA	104±3	101±9	0.010	0.03	100±3	99±9	0.05	0.15
PFHxA	110±3	102±5	0.004	0.01	111±3	112±7	0.04	0.15
PFHpA	96±6	92±2	0.006	0.02	106±4	106±10	0.06	0.15
PFOA	100±11	107±3	0.002	0.01	105±4	112±9	0.05	0.19
PFNA	109±2	120±6	0.002	0.01	111±5	115±8	0.06	0.13
PFDA	103±7	101±9	0.004	0.01	115±4	121±12	0.05	0.15
PFUnDA	90±4	101±10	0.008	0.02	104±10	108±15	0.03	0.08
PFDoA	89±4	92±5	0.004	0.01	87±7	97±8	0.05	0.13
PFTrDA	93±2	96±1	0.006	0.02	75±7	77±4	0.05	0.15
PFTeDA	73±4	74±6	0.006	0.02	82±8	77±5	0.04	0.13
PFHxDA	73±1	79±4	0.006	0.02	91±6	89±12	0.05	0.11
PFODA	87±5	91±3	0.006	0.02	96±12	106±6	0.06	0.18
PFSAs								
PFBS	119±4	103±9	0.004	0.01	101±5	102±8	0.03	0.09
PFHxS	114±8	112±4	0.004	0.01	110±4	113±10	0.01	0.06
PFOS	117±2	92±6	0.004	0.01	93±8	122±10	0.03	0.10
PFDS	86±6	85±9	0.010	0.02	76±4	89±11	0.03	0.06

Table S5. HPLC and ESI- MS Instrument Conditions

HPLC conditions

Analytical column	Agilent ZORBAX Eclipse Plus C18, 2.1×100 mm, 3.5 μm	
Guard column	Agilent 1290 Infinity In-line filter with 0.3 μm SS frit	
Column temperature	40 ℃	
Injection volume	5 μL	
Mobile phase	A= 2 mM ammonium acetate B= 100% Acetonitrile	
Run time	16 min + 4 min post time	
Flow rate	0.3 mL/min	
Gradient	Time (min)	Mobile phase
	0	20% B
	14	90% B
	16	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(-)	200-400 V

Table S6. Concentrations of PFAAs in surface water of the Daling River basin (ng/L).

Sites	**PFCAs**							**PFSAs**			**∑PFAAs**
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	
1	34.6	1.4	3.19	4.11	81.4	4.07	0.60	3.18	0.22	5.92	139
2	144	2.49	4.23	7.07	167	0.25	<0.15	19.5	<0.06	0.11	344
3	962	47.2	15.2	3.52	102	0.81	0.29	1824	1.56	0.69	2957
4	1346	82.2	49.2	15.9	348	1.24	0.51	2896	2.23	0.77	4742
5	455	43.1	39.8	7.03	344	1.44	0.30	2389	3.47	12.6	3295
6	763	28.1	31.9	6.57	284	1.36	0.37	2276	4.06	9.35	3404
7	1147	39.2	37.3	11.0	330	1.17	0.47	2393	2.97	6.23	3969
8X	654	27.6	59.2	5.92	194	3.58	0.43	1311	1.57	5.59	2263
8D	55.2	1.03	0.73	0.24	3.25	0.59	<0.15	1.34	0.12	1.27	63.9
9	348	21.8	21.3	3.27	146	2.27	0.52	752	0.83	7.90	1305
10	224	15.9	14.3	2.44	76.1	1.45	0.27	386	0.28	2.42	723
11	189	12.4	11.3	2.50	72.2	1.63	0.31	331	0.28	1.29	622
12	223	14.1	13.9	2.74	96.6	1.82	0.31	371	0.33	2.50	725
13	243	29.2	26.7	4.59	137	1.62	0.20	714	0.65	9.47	1166
14	264	19.4	19.2	3.34	131	2.53	0.37	589	1.04	3.95	1033
15	0.87	0.64	0.27	0.18	0.60	0.22	0.17	7.63	<0.06	<0.10	10.8
16	3.21	<0.15	0.20	<0.15	3.82	0.22	<0.15	0.41	<0.06	0.63	8.71
17	<0.63	<0.15	<0.15	<0.15	<0.19	<0.13	<0.15	<0.09	<0.06	0.34	1.09
18	<0.63	<0.15	<0.15	<0.15	1.15	<0.13	<0.15	<0.09	<0.06	<0.10	1.81
19	<0.63	<0.15	<0.15	<0.15	<0.19	0.14	<0.15	0.64	<0.06	0.71	2.07
20	<0.63	<0.15	<0.15	<0.15	<0.19	0.25	<0.15	<0.09	<0.06	<0.10	1.01
21	59.2	1.18	0.65	<0.15	1.22	0.40	<0.15	0.39	<0.06	4.53	67.7
22	51.1	1.11	1.43	1.47	22.8	0.42	<0.15	92.8	<0.06	0.36	172
23	1.38	<0.15	0.17	0.18	2.84	<0.13	<0.15	0.10	<0.06	0.40	5.26
24	8.06	7.75	4.03	0.39	2.77	<0.13	<0.15	12.7	<0.06	<0.10	35.8
25	16.7	0.45	0.43	0.27	3.22	<0.13	<0.15	<0.09	<0.06	<0.10	21.3

Note: Among the 17 PFAAs analyzed in water, PFCAs with carbon chain lengths more than 10 and PFDS were all detected in less than 10% of samples and had concentrations less than 1.00 ng/L in water. Therefore, these compounds were not listed.

Table S7. Concentrations (ng/g dw) of 8 PFCAs and 3 PFSAs in surface sediment from site 1 to site 14 in Daling River Basin. f_{OC} represents the organic carbon fraction in the samples.

Site	PFCAs								PFSAs			f_{OC} %
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFOS	
1	1.34	0.16	0.14	nd	1.27	nd	0.31	0.35	0.11	nd	1.53	2.88
2	1.81	0.11	0.15	0.04	2.27	0.06	0.47	0.14	0.13	0.02	1.77	0.34
3	6.23	0.18	0.20	0.06	3.92	0.05	nd	nd	2.63	<0.01	0.35	6.23
4	6.95	0.11	0.09	0.04	5.59	0.09	nd	0.26	2.71	<0.01	6.68	0.29
5	30.4	0.51	0.60	0.10	8.97	0.31	0.37	0.28	11.08	0.10	2.36	0.18
6	15.1	0.23	0.32	0.05	1.84	0.13	0.16	0.12	6.76	0.07	1.48	2.27
7	4.80	0.11	0.19	0.04	1.65	0.11	0.25	nd	1.66	0.01	1.45	1.01
8X	3.49	0.28	0.74	0.11	1.74	0.40	0.28	0.28	0.91	<0.01	4.48	0.24
8D	0.92	0.05	0.05	0.02	1.76	0.09	nd	0.13	0.06	nd	3.73	1.07
9	8.21	0.07	0.12	0.05	1.25	0.08	0.07	0.08	0.25	0.03	0.50	0.06
10	2.76	0.21	0.34	0.08	2.96	0.34	0.16	0.07	0.76	nd	0.94	0.74
11	1.59	0.11	0.14	0.03	0.94	0.14	0.11	0.08	0.33	0.01	1.98	0.14
12	2.00	0.16	0.09	0.04	1.12	0.05	0.04	0.05	0.92	0.02	0.71	0.08
13	1.62	0.12	0.07	0.07	1.75	0.12	0.04	nd	0.72	0.02	2.48	0.15
14	2.27	0.17	0.21	0.04	0.98	0.11	0.19	0.23	0.43	0.03	1.49	0.58
15	1.04	0.22	0.21	0.02	1.96	nd	0.68	nd	0.05	0.03	1.31	0.79
16	1.35	0.24	0.09	0.10	2.38	0.19	0.19	0.14	0.10	0.02	2.18	0.24
17	1.03	0.20	0.17	0.10	1.53	0.47	0.32	0.55	0.13	0.01	0.62	4.41

18	0.88	0.03	0.04	0.02	1.28	0.05	nd	0.10	0.07	0.00	2.74	0.28
19	0.55	0.43	0.12	0.12	1.58	0.41	0.79	0.24	nd	0.01	1.21	0.10
20	1.54	0.18	0.10	0.10	1.84	0.28	0.16	0.12	0.03	0.05	0.66	0.07
21	8.49	0.29	0.09	0.11	2.00	0.25	0.18	0.20	0.03	0.02	0.95	0.10
22	1.38	0.05	0.06	0.04	0.89	0.35	nd	0.26	0.15	nd	9.85	1.22
23	1.35	0.14	0.02	0.04	0.66	0.05	0.19	nd	0.04	nd	1.27	0.34
24	1.17	0.14	0.09	0.00	1.62	0.05	nd	nd	0.17	0.00	2.02	5.62
25	1.05	0.10	0.06	0.08	2.12	0.05	0.29	0.18	0.07	0.01	2.92	4.90

nd: less than LOD

Table S8. 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 site 1 to site 14.

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFOS
Log K_d	Mean	1.07	0.98	1.05	1.03	1.23	1.79	2.40	3.35	0.34	1.25	2.77
	SD	0.34	0.51	0.43	0.46	0.49	0.69	0.77	0.70	0.61	0.74	0.67
Log K_{OC}	Mean	3.41	3.32	3.39	3.37	3.57	4.13	4.74	5.69	2.68	3.59	5.11
	SD	0.68	0.68	0.56	0.82	0.66	1.00	1.04	1.08	0.65	1.08	0.88
Difference 1*		2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34
Difference 2*					0.20	0.56	0.61	0.96		0.91	1.52	

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

Difference 2*: The value of difference 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} (PFOA) - Log K_{OC} (PFHpA)

Table S9. Comparison of log K_{OC} (mean ± SD, cm^3g^{-1}) of the 11 PFAAs in this study with published researches.

Compounds	n	log K_{OC}	Area	Reference
PFBA	14	3.41±0.68	Daling river, China	This study
PFPeA	14	3.32±0.68	Daling river, China	This study
	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	14	3.39±0.56	Daling river, China	This study
PFHpA	14	3.37±0.82	Daling river, China	This study
	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	14	3.57±0.66	Daling river, China	This study
	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	14	4.13±1.00	Daling river, China	This study
	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	14	4.74±1.04	Daling river, China	This study

	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	14	5.69±1.08	Daling River, China	This study
	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)
PFBS	14	2.68±0.65	River	This study
	8	1.75±0.01	Haihe River, China	(Zhao et al., 2012)
	8	2.09±0.02	Qilihai wetland, China	(Zhao et al., 2012)
	9	1.42±0.50	21 major rivers, lakes, and canals in The Netherlands	(Kwadijk et al., 2010)
PFHxS	14	3.59±1.08	Daling river, China	This study
	8	2.02±0.01	Haihe River, China	(Zhao et al., 2012)
	8	2.14±0.02	Qilihai wetland, China	(Zhao et al., 2012)
	6	3.6±0.1	Tokyo Bay, Japan	(Ahrens et al., 2010)
PFOS	14	5.11±0.88	Daling river, China	This study
	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)

Figure S1. Chromatogram of 17 PFAAs by MRM with the concentration of 0.05 ng/mL.

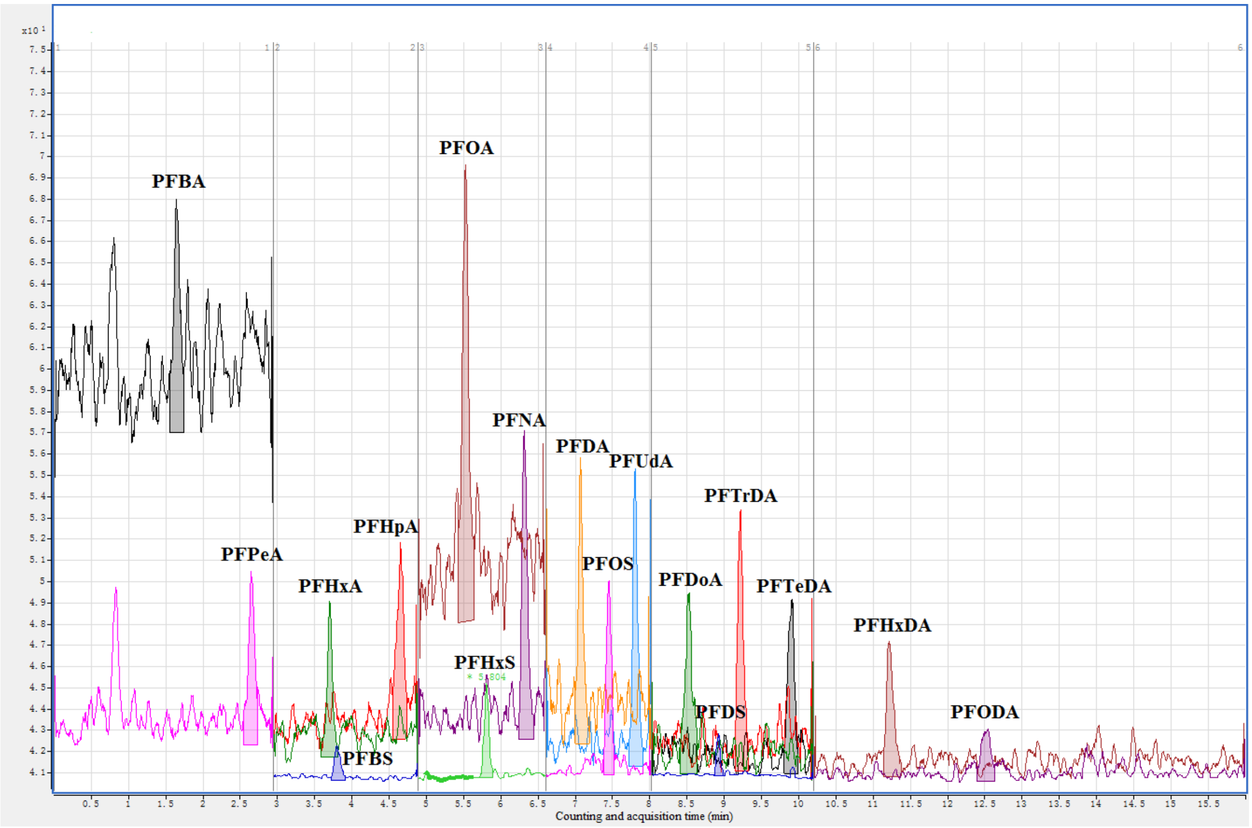
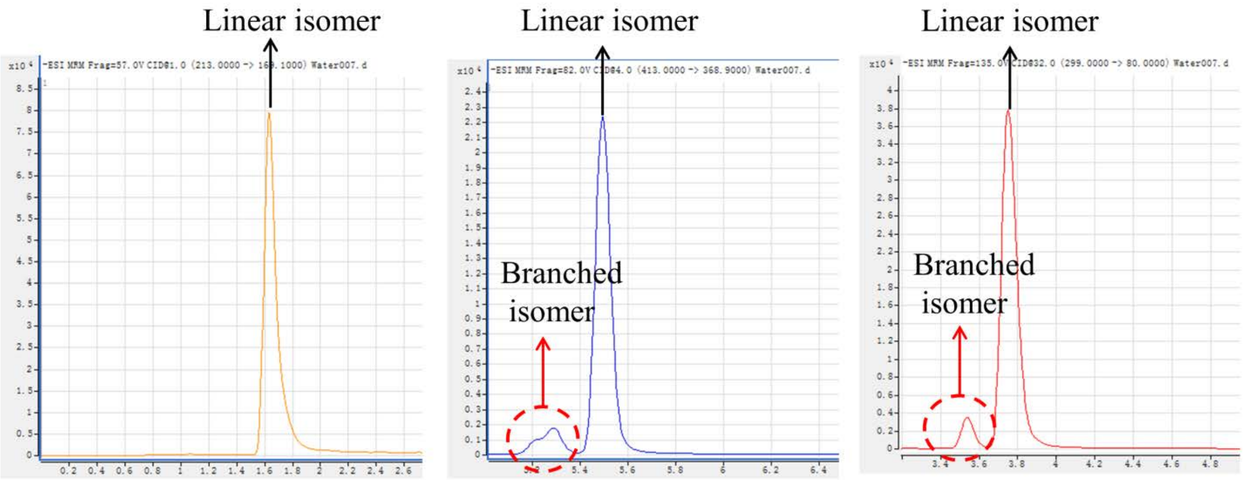


Figure S2. Chromatogram of three predominant PFAAs in water samples taken from site 3.



PFBA PFOA PFBS

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