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Partitioning behavior, source identification, and risk assessment of perfluorinated compounds in an industry-influenced river

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Abstract

Background: The widespread application of perfluorinated compounds (PFCs) makes them ubiquitously distributed in the environment. Investigation of contamination profiles, distribution, possible sources and risks of PFCs in Liaohe River, an industry-influenced river in northeast China was conducted in the present study.

Results: The total PFCs concentrations (Σ PFCs) were in the range 0.38–127.88 ng/L (average value of 36.41 ng/L) in water and 1.72–10.44 ng/g dry weight (average of 4.99 ng/g) in sediment. Perfluorooctanoic acid (PFOA) was the dominant individual in water and sediment phases, in the range 0.38–73.94 ng/L in water and below detection limit (BDL) to 7.88 ng/g dw in the sediments. The organic carbon normalized partition coefficients (K_{oc}) ranged from 2.46 L/kg (PFHxA) to 4.29 L/kg (PFUnDA). The average K_{oc} values for perfluorocarboxylic acids (PFCAs) increased by 0.13–0.62 log unit with each increasing CF_2 moiety, and the K_{oc} values were lower than perfluoroalkyl sulfonates (PFASs). The sources of PFCs identified from diagnostic ratios suggested that the contaminants were mainly from the emission of manufacturing processes and precursors degradation. Result from risk assessment indicated that the immediate health impact through intaking water was negligible, but the levels of PFOA in surface water might cause effects on aquatic ecosystem. The mass inventories of Σ PFCs and PFOA were estimated to be 328.74 t and 103.43 t in the study area, respectively, suggesting that the sediment in Liaohe River may act as a potential PFCs source to the surrounding areas.

Conclusion: This study demonstrated that PFCs were widely presented in the water and sediments of Liaohe River. In general, PFCAs had higher concentrations and detection frequency than PFASs, and PFCAs with short carbon chains had much higher detection frequencies than long-carbon chain compounds in water. Among all PFC homologues, the average K_{oc} increased with the increased carbon chain. K_{oc} values were higher for PFASs than PFCAs. The risk assessment suggested that PFOA in water may exert adverse effect on the aquatic ecosystem. Liaohe River was likely acting as a PFCs source to the surrounding area.

Keywords: Perfluorinated compounds, Distribution, Source, Risks, Inventory, Liaohe River

Background

Perfluorinated compounds (PFCs) have been widely used as surfactants, surface protectors and performance chemicals in fire-fighting foams, leather, food packing and shampoos [1], due to their high surface activities, thermal

and chemical resistances, and hydrophilic and hydrophobic properties [2]. The widespread application of PFCs makes them ubiquitously distributed in the environment [3], such as in the air [4], rivers [5], lakes [6], and even in remote areas (Antarctic and Arctic areas) [7]. Previous studies revealed PFCs could accumulate in biota, including fish [8], invertebrates [9], birds [10], marine mammal [11], and human bodies [12], and magnify along the food webs [13]. They could exert adverse effect to aquatic and terrestrial organisms. Toxicological studies indicated

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that adverse effect in organisms and their offspring was observed when exposed to PFCs during embryonic stage. Perfluorooctane sulfonate (PFOS) together with its salts and perfluorooctane sulfonyl fluoride (POSF) has been listed under the Stockholm Convention as the persistent organic pollutants in 2009.

In 2003, POSF began to be produced in China and used in commercial products, with the annual production less than 100 tons. From 2004 to 2009, the annual production grew steadily, with the annual production of 91, 165, 247, 195, 250, 300 tons, respectively, among which half was consumed domestically [14, 15]. The cumulative historical production volume of PFOS and related chemicals was estimated to be 1800 tons by 2011.

Due to the intrinsic properties of most PFCs such as moderate water solubility and low vapor pressure, PFCs tend to finally accumulate to water and sediments in the aquatic ecosystem [10, 16]. Ubiquitous detection of PFCs has been reported in different regions of Chinese water environments. Primary sources of PFCs in the aquatic environment included atmospheric precipitation, emission from manufacturing process [17], the precursor transformation, effluents of treated wastewater [18] and street runoff [19].

Liaohe River is located in northeast China, and it runs across areas with petrochemical industry, steel factories, pharmacy, machinery, and building materials [20], and finally enters Bohai Sea [21]. In recent years, the water quality of Liaohe River continuously decreased because of the rapid population growth and the increasing industrial and agricultural activities [22]. Many contaminants have been detected in Liaohe River including polycyclic aromatic hydrocarbons [23], organochlorine pesticides [24], polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls [25], and short chain chlorinated paraffins [26]. Previous study also showed that PFCs were detected in Liaohe River, with concentrations in the range of <LOQ to 31 ng/L. PFOA and PFOS were the dominant PFCs, with mean concentrations of 27 and 4.7 ng/L, respectively [15]. The occurrence of PFCs in sediments of Daliao River system was also reported in the range of 0.29 to 1.03 ng/g, dominated by PFOA and PFOS [3]. To the best of our knowledge, information is scarce on the PFCs source characterization, health risks, and their inventory in this area.

This paper was focused on the occurrence of PFCs in surface water and sediments in Liaohe River. The measured data allowed us to evaluate the partitioning behavior, the preliminary estimation of PFCs inventories and the screening-level ecological risk assessment for PFCs in the aquatic environment. Possible pollution sources of PFCs were also discussed.

Materials and methods

Sampling area and sample collection

Liaohe River includes Liao River, Daliao River, Hun River and Taizi River (Fig. 1). Fifty sites were selected from ten rivers (Liao River, Hun River, Taizi River, Daliao River and their tributaries including Qing River, Chai River, Xiushui River, Yangximu River, Liu River, and Shahe River) for collecting surface water and sediments in October 2012.

A clean stainless steel bucket was used to collect surface water, which was stored in polypropylene (PP) bottles. The stainless steel grab sampler was used to collect surface sediments which were placed in PP bags. All equipments were rinsed by methanol and Milli-Q water before use.

Chemicals and reagents

Perfluorobutanoate (PFBA), perfluoropentanoate (PFPA), perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTrDA), perfluorooctane sulfonamide (PFOSA), perfluorodecane sulfonate (PFDS), perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Perfluoroundecanoate (PFUnDA), perfluoroheptanoate (PFHpA) and perfluorohexanoate (PFHxA) were obtained from Matrix Scientific (Columbia, SC, USA). Perfluorononanoate (PFNA), perfluorooctanoate (PFOA), perfluorodecanoate (PFDA), potassium salts of perfluorohexane sulfonate (PFHxS), perfluoro-*n*-[¹³C₈] octanoic acid (¹³C₈-PFOA) and sodium perfluoro-1-[1,2,3,4-¹³C₄]octane-sulfonate (¹³C₄-PFOS) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Solvents including methanol and NH₄OH were HPLC grade from Beijing Chemical Factory (Beijing, China). All stock solutions were prepared in methanol and stored in polypropylene (PP) tubes or vials at 4 °C.

Extraction, cleanup and analysis

The pretreatment of water and sediment samples were described elsewhere [27]. In brief, 1 L water sample spiked with 5 ng surrogate standard was extracted with Oasis WAX-SPE cartridge (6 cc, 150 mg; Waters Corp. Milford, USA). Prior to water loading, the cartridges were pre-conditioned with 4 mL 0.5% NH₄OH/CH₃OH (v/v), 4 mL methanol and 4 mL Milli-Q water. The cartridge was then vacuum-dried for 2 h. Elution was carried out with 4 mL methanol and 4 mL 0.5% NH₄OH/CH₃OH (v/v) with gravity. The eluate was then concentrated to 1 mL for instrumental analysis.

Sediments were sonic extracted by methanol. Generally, two grams of homogenized freeze-dried samples were weighted and transferred into 50 mL PP centrifuge tubes and spiked with 5 ng surrogate standard. The tubes

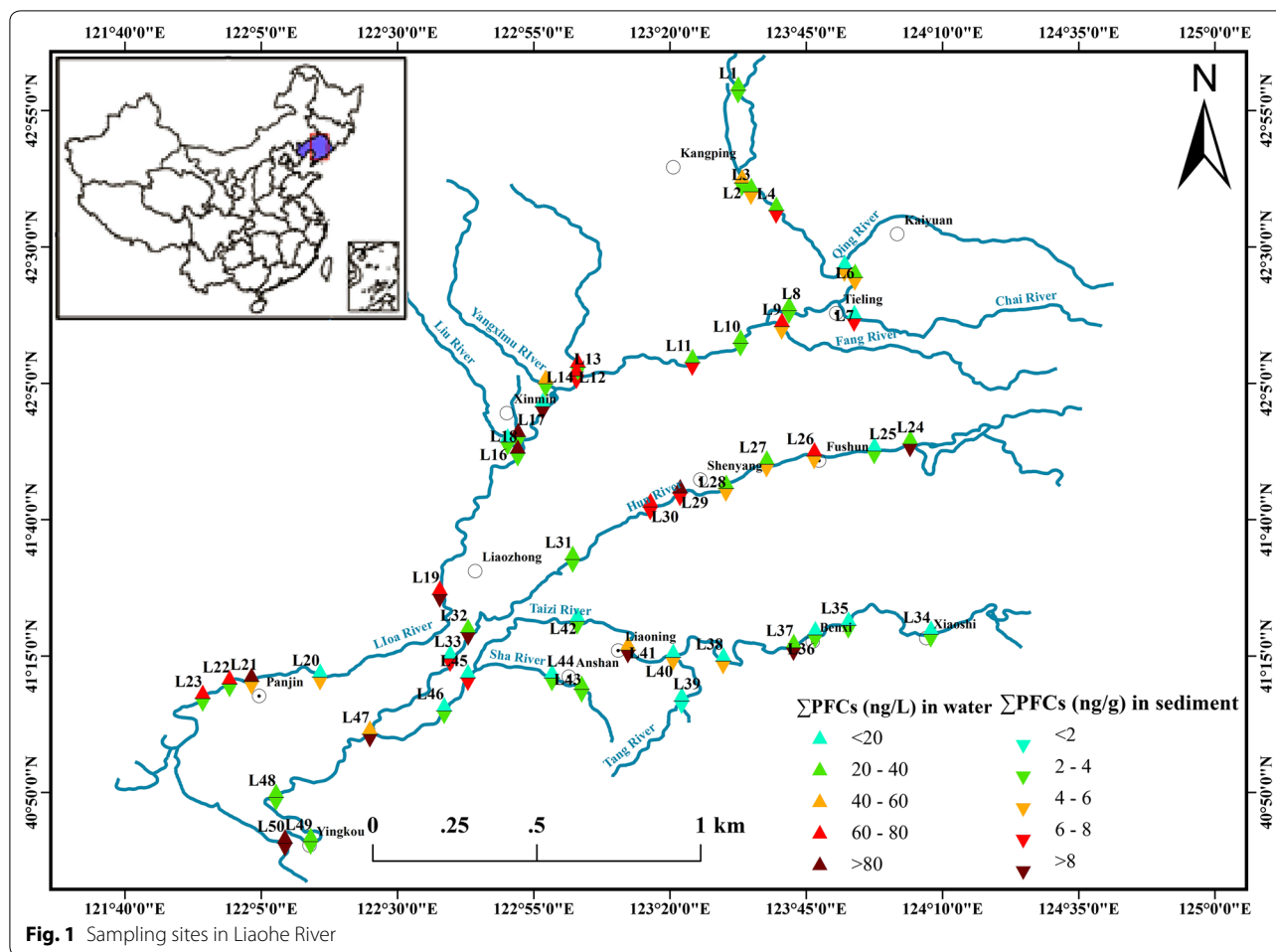


Fig. 1 Sampling sites in Liaohe River

were added with 8 mL of methanol and shaken for 20 min at the speed of 250 rpm at 25 °C, sonicated for 10 min, and then centrifuged at 8000 rpm for 10 min. After centrifugation, the supernatant was collected and decanted to a clean beaker. The extraction was repeated 2 more times, and the extracts were combined. The extracts were diluted to 200 mL with ultrapure water, and passed through Oasis WAX-SPE cartridges at a rate of 3 mL/min. The analytes were then eluted with 4 mL methanol and 4 mL 0.5% NH₄OH/CH₃OH (v/v). The extract was blown down to 1 mL under a nitrogen stream and transferred into GC vials for analysis.

Instrumental analysis

The target compounds were quantified with an Agilent 1200 LC equipped with a ZORBAX Eclipse XDB-C18 column (2.1 × 100 mm, 5 μm) and a 6410A mass spectrometer (Agilent, Palo Alto, CA). The column was maintained at 40 °C during the sample analysis. The mobile phase consisted of eluent A (methanol) and eluent B (2.5 mM ammonium acetate solution). Flow rate

was kept at 0.25 mL/min, and the injection volume was 20 μL. The separation of PFCs was achieved with a gradient program, with an initial gradient of 30% A, increased to 40% A at 4 min, and continuously increased to 90% A at 9 min. The gradient was reverted to 30% A at 13 min and maintained for 2 min. The operating parameters for LC instrumental analysis could refer to the previous publication, and the MS/MS parameters for optimizing the instrument were the same as our previous study [27].

Analytes were identified with multiple responses monitoring analysis. Internal calibration was used to quantify analytes. ¹³C₈-PFOA was the internal standard for PFCA and ¹³C₄-PFOS for PFOS, respectively. The analytical process was conducted in triplicate to evaluate the precision.

Quality assurance and quality control (QA/QC)

During the experimental processes, the polytetrafluoroethylene (PTFE) and fluoropolymer materials were avoided to reduce the background contamination. The recoveries of the target compounds were determined by subtraction

of the background concentrations from the detected spiking concentration of the compounds in the test samples. Quantification of each PFCs compound was obtained using the internal standard method. Calibration curves were constructed in the range of 0.2 µg/L to 50 µg/L for the PFCs, with linearity $r^2 > 0.995$. The mean recoveries of PFCs spiked into water and sediment samples were from 61 to 118% for water, and from 69 to 128% for sediment, respectively. Matrix recovery test was carried out in triplicate, and the relative standard deviations were below 18%. The LOQs were determined by the injection of spiked water extracts ($n=3$) and estimated as the minimum detectable amount of analyte with a signal-to-noise ratio of 10:1 and the deviations were within $\pm 20\%$ from theoretical values of the triplicate injection. The LOQs for each compound ranged from 0.10 to 0.60 ng/L in water, and 0.02 to 0.10 ng/g in sediment.

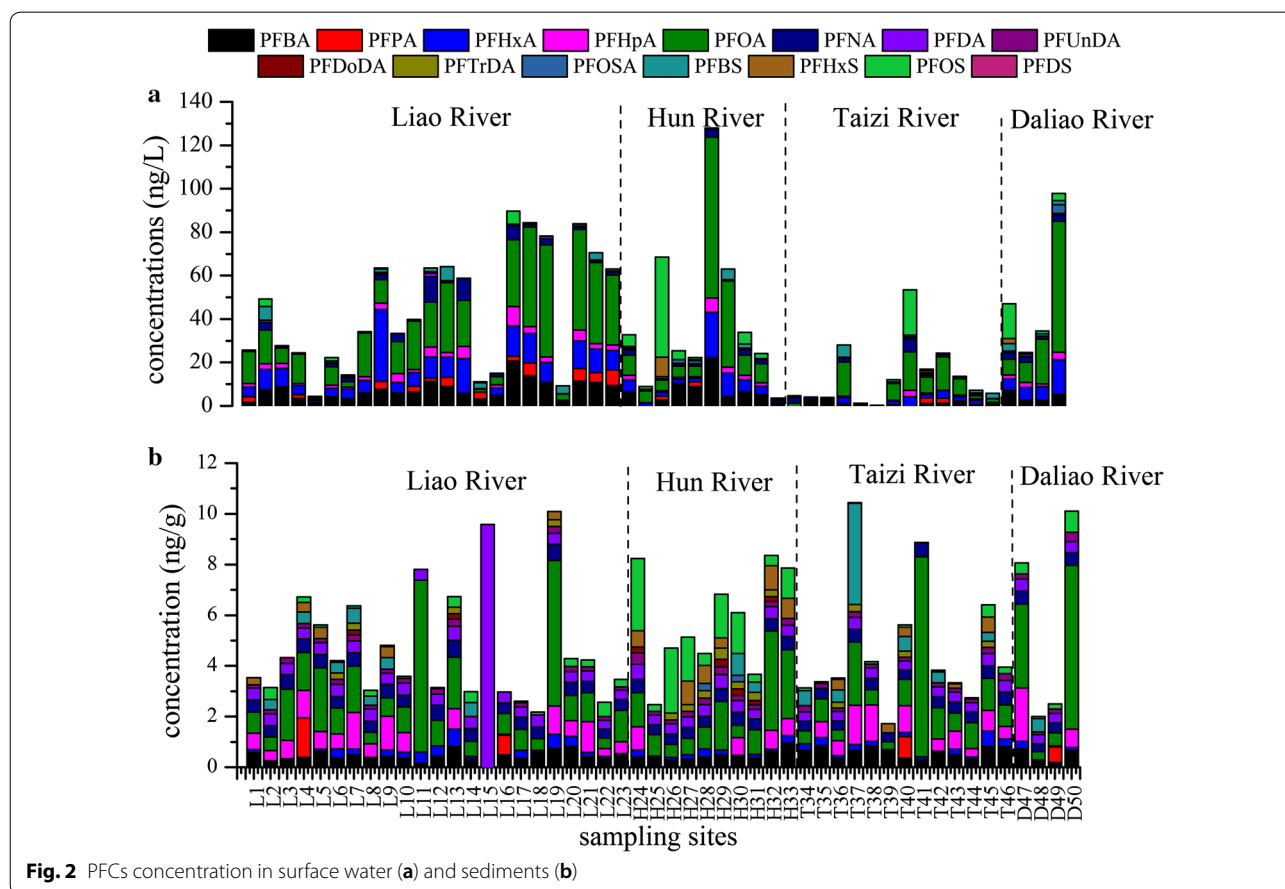
Results and discussion

Distribution of PFCs in surface water and sediments

The aqueous concentrations of PFCs in Liaohe River were shown in Fig. 2. A total of 15 PFCs including C4–C13 perfluorocarboxylic acids (PFCA) (e.g. PFBA,

PFPA, PFHxA, PFOA, PFHpA, PFNA, PFUnDA, PFDA, PFDoDA and PFTrDA), C4, C6, C8 and C10 perfluoroalkyl sulfonates (PFASs) (e.g. PFHxS, PFBS, PFOS and PFDS) and one non-ionic PFC (PFOSA) were quantified. The Σ PFCs concentration in the water phase ranged between 0.38 and 127.88 ng/L, with the mean concentration value of 36.41 ng/L. The concentrations of PFCAs and PFASs were in the range of 0.38 to 127.88 ng/L and below detection limit (BDL) to 55.96 ng/L, respectively.

Geographically, the spatial distribution of PFCs was associated with urbanization and industrialization. The average value of Σ PFCs (the mean concentrations of 15 PFCs in this study) of Daliao River (51.01 ng/L) was higher than the other three rivers (44.79 ng/L for Liao River, 41.05 ng/L for Hun River and 13.52 ng/L for Taizi River). Of all the sampling sites, site H29 in Hun River presented the highest Σ PFCs up to 127.88 ng/L, followed by D50 in Daliao River (97.75 ng/L) and L17 in Liao River (89.70 ng/L). It is obvious that human activities affected the PFCs distribution in the water samples. For instance, Σ PFCs in sites L1, L3–L7 in the upstream of Liao River were lower than in the midstream and downstream of the river, where wastewater from the



surrounding cities, such as Xinmin City (L12–L14, L17–L18), Liaozhong City (L19), and Panjin City (L21–L23) was discharged into the river water. Similarly, in Hun River, the low \sum PFCs at H24 and H25 were resulted from their locations close to Dahuofang Reservoir which was the drinking water source for Fushun City and surrounding districts, whereas high PFCs concentrations were detected at sites adjacent to Shenyang City (H29 and H30) and Fushun City (H26). This was similar to the results reported by Sun et al. [28], who found that high PFCs concentrations were detected in highly industrialized districts in Hun River. For instance, Shenyang City and Fushun City contributed significant loads of PFCs to the Hun River. The PFCs contribution from Shenyang City was obviously greater than those from Fushun City, which could be explained by the population and economic level. The PFCs concentration in the upstream of the Hun River was quite low. Generally, the PFCs concentrations showed geographical variations. Industrial and municipal cities were characterized by higher contamination concentrations. Similarly, a research estimating the emission of PFOS in China found that most intensively industrialized regions on eastern coastal areas showed higher emission rates and density of PFOS than those in western and northern China [15].

Relatively low PFCs concentrations were determined in Taizi River, except for site T41 which was close to Liaoyang City. Domestic sewage and industrial wastewater from these cities influenced the \sum PFCs level in the river water. Low PFC levels in Taizi River were mainly due to the low anthropogenic activities in the river basin.

In general, the PFCAs had higher concentrations and detection frequency than PFASs. The detection frequencies of short-carbon chain PFCAs (PFBA, PFHxA, PFHpA, PFOA and PFNA) were much higher than long-carbon chain compounds (PFDA, PFUnDA, PFDoDA and PFTrDA). Figure 3 showed that PFOA was the predominant pollutant in the river water. PFOA was reported to be the intermediate compound during the other PFCs synthesis and the final metabolite or degradation product of some related compounds [29]. This result was consistent with previous studies such as in Pearl River Delta region [30], Liaodong Bay [31], Haihe River Basin [32], and Yangtze River Delta [33].

The \sum PFCs in sediments in Liaohe River ranged from 1.72 to 10.44 ng/g, with an average concentration of 4.99 ng/g. The highest \sum PFCs was found in T37 (10.44 ng/g), followed by D50 (10.11 ng/g) and L19 (10.09 ng/g). Generally, Hun River (mean value of 5.78 ng/g) and Daliao River (mean 5.67 ng/g) were more polluted than Liao River (mean 4.70 ng/g) and Taizi River (mean 4.70 ng/g). The predominant compound PFOA ranged from BDL to 7.88 ng/g, with the

average contribution of 28.03% to \sum PFCs. In contrast to the water samples, the PFCs showed a different compositional profile. Long carbon chain PFCs such as PFDA, PFUnDA, PFDoDA and PFTrDA were observed in sediment samples with high concentration and detection frequencies, indicating that long chain PFCs were tending to partition into sediment.

Partitioning of PFCs between water and sediments

Partitioning is an important process in the fate and transport of pollutants in the aquatic environment. The sediment–water partitioning coefficients (K_d) were determined using $K_d = C_s/C_w$, where C_s and C_w are the PFCs concentrations in sediments (ng/kg) and water (ng/L), respectively. The organic carbon normalized adsorption coefficient (K_{oc}) was calculated by $K_{oc} = K_d/f_{oc}$, where f_{oc} is the sediment organic carbon fraction.

Different K_{oc} and K_d values reflected different sorption potentials and partition of PFCs in riverine environment. The average $\log K_d$ of PFCs in Liaohe River were in the range of 1.58 (PFHxA) to 3.14 (PFUnDA), and average $\log K_{oc}$ ranging from 2.46 (PFHxA) to 4.29 (PFUnDA) (Table 1). The $\log K_{oc}$ value of PFOS (3.33 ± 0.74) in this study was consistent with the laboratory experiment result (3.7 ± 0.56), but $\log K_{oc}$ of PFOA showed a discrepancy (3.07 ± 0.63 vs. 2.4 ± 0.12). The $\log K_d$ and $\log K_{oc}$ values obtained in the present study were similar to those in Haihe River [32], but significantly different from those in aquatic systems in the Netherlands [34] and Tangxun Lake [35]. The field-based partitioning values may be influenced by many factors, such as the composition and property of sediment and water. Earlier researches proposed that sediment and water conditions (such as pH, aqueous Ca^{2+} and salinity) were significantly correlated with their sorption [36]. Similar correlations were found in this study as shown in Table 2.

Among the PFCs homologues, the average K_{oc} generally increased with the increasing carbon chain. As shown in Table 1, the values followed the order of PFHxA < PFHpA < PFOA < PFNA < PFDA < PFUnDA, increasing by 0.13–0.62 log units with each CF_2 moiety. Similarly, in Haihe River, the average $\log K_{oc}$ ranged from 3.3 for PFHpA to 4.4 for PFUnDA, increasing by 0.1–0.6 log units with each CF_2 moiety [32]. Previous research showed that the hydrophobic interaction was the main factor affecting the sediment–water partition of C8–C12 PFCAs and C6, C8 PFASs, and with the increasing perfluoroalkyl chain length the sediment sorption potential increased [35]. It confirmed that the perfluorocarbon chain length was the dominant structure feature affecting the PFCs sorption. Interestingly, the slope of the regression of PFCAs $\log K_{oc}$ versus perfluoroalkyl chain length (Fig. 4) was 0.39 ($R^2 = 0.97$), which was slightly lower than that from

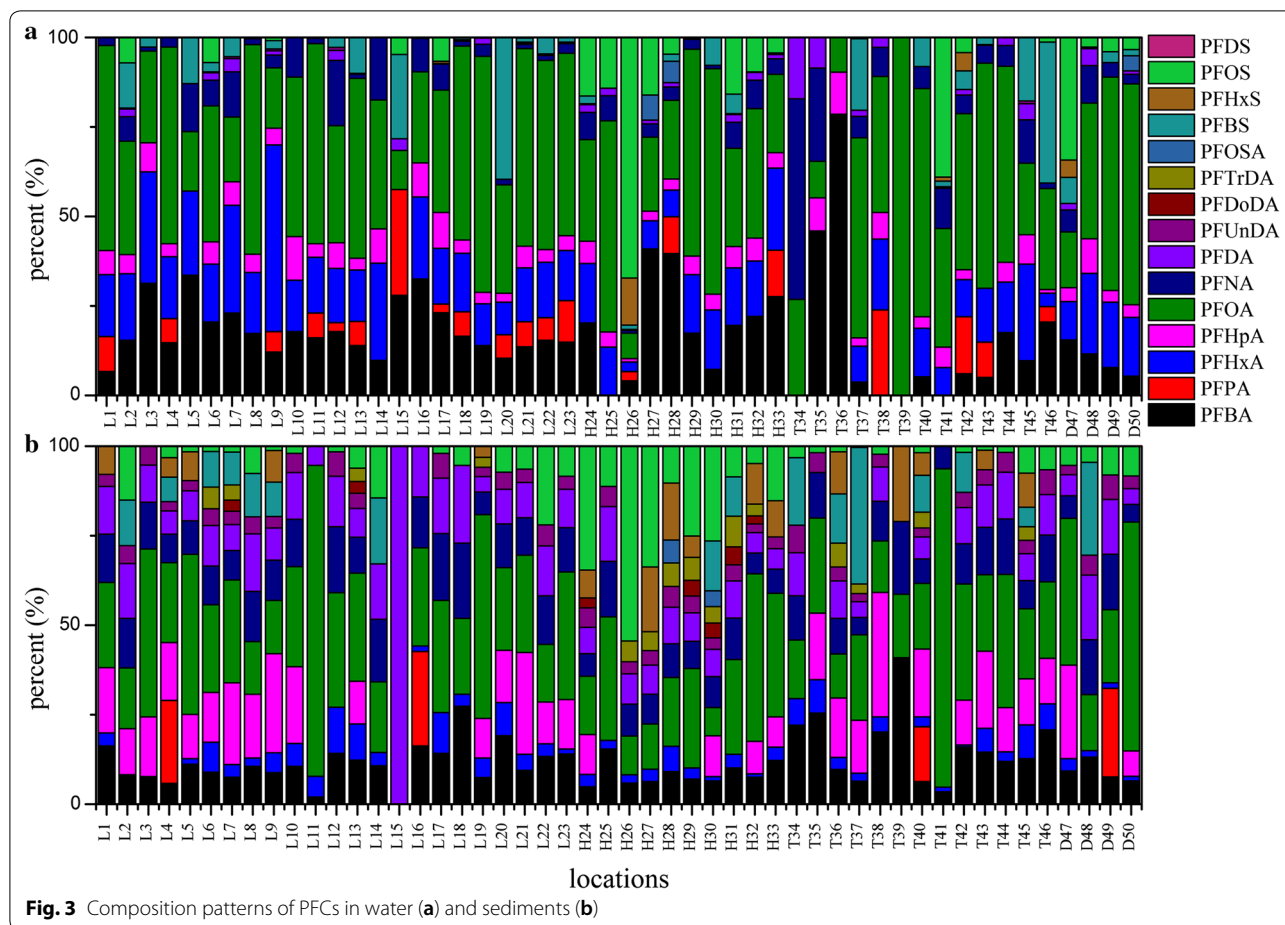


Table 1 log_{K_d} and log_{K_{oc}} values of PFCs from Liaohe River

Compound	This study		Haihe River, China [32]		Aquatic system, Netherlands [34]	Tangxun Lake, China [35]
	log K _d	log K _{oc}	log K _d	log K _{oc}	log K _d	log K _{oc}
PFBA	2.03 ± 0.49	3.01 ± 0.51	– ^a	–	–	2.5 ^b
PFHxA	1.58 ± 0.60	2.46 ± 0.63	2.2 ± 0.4	3.4 ± 0.4	–	–
PFHpA	2.06 ± 0.53	2.75 ± 0.53	2.0 ± 0.5	3.3 ± 0.5	–	1.9
PFOA	2.14 ± 0.64	3.07 ± 0.63	2.1 ± 0.4	3.4 ± 0.4	1.83 ± 0.40	2.3 ± 0.23
PFNA	2.57 ± 0.47	3.54 ± 0.51	2.3 ± 0.4	3.6 ± 0.4	2.89 ± 0.53	–
PFDA	3.12 ± 0.46	4.16 ± 0.56	2.9 ± 0.4	4.2 ± 0.3	2.87 ± 0.23	–
PFUnDA	3.14 ± 0.45	4.29 ± 0.55	3.1	4.4 ± 0.3	–	–
PFBS	2.54 ± 0.35	3.54 ± 0.19	3.2 ± 0.2	4.4 ± 0.3	1.42 ± 0.50	–
PFOS	2.31 ± 0.71	3.33 ± 0.74	–	–	2.35 ± 0.35	3.7 ± 0.38

^a Not obtained

^b Average value

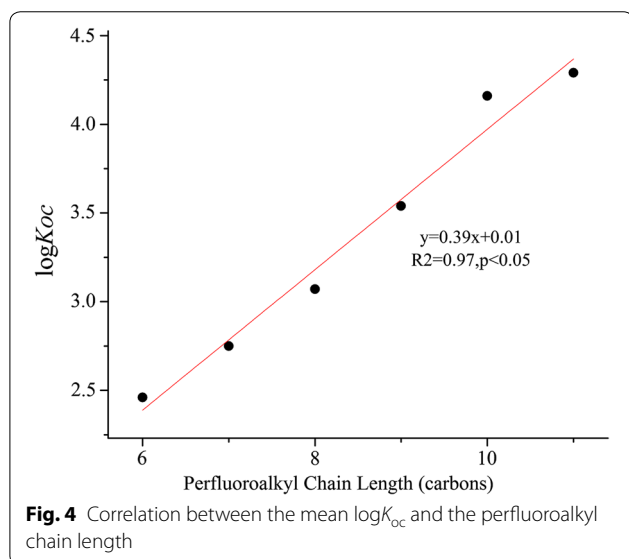
Kwadijk et al.'s [34] and Higgins and Luthy's reports [37]. The difference was mainly affected by the different PFC homologues in different studies.

Potential source identification

The diagnostic ratios, such as PFOS/PFOA, PFOA/PFNA and PFHpA/PFOA, have been applied to identify the

Table 2 Pearson correlation analysis for the water quality parameters and K_{oc} values in the water samples collected from the Liaohe River

$\log K_{oc}$	T	DO	Electrical conductivity	TDS	Salinity	ORP	pH
PFBA	-0.089	-0.159	0.028	0.107	0.168	-0.168	-0.138
PFHxA	-0.195	0.002	-0.317*	-0.22	-0.146	0.067	0.031
PFHpA	-0.124	-0.154	-0.345	-0.223	-0.323	0.1	-0.123
PFOA	-0.19	-0.033	-0.454**	-0.387**	-0.337*	0.234	-0.092
PFNA	0.028	-0.175	-0.01	0	0.045	-0.03	0.041
PFDA	0.146	-0.18	0.015	-0.088	-0.039	-0.078	-0.06
PFUnDA	-0.317	-0.242	0.047	0.255	0.274	0.449	-0.613**
PFBS	-0.442	0.152	-0.576	-0.571	-0.355	0.463	0.127
PFOS	-0.214	-0.456*	0.069	0.246	0.136	0.075	-0.153

* $p < 0.05$, ** $p < 0.01$ 

potential sources of PFCs in the environment. In most of the water samples in this study, PFOA showed higher concentration than PFOS, and the ratios of PFOS/PFOA were generally less than 1.0. In several sampling sites, such as H26 (9.57) from Fushun, T41 (1.18) from Liaoyang and D47 (2.20) which was the confluence of Taizi River and Hun River, higher PFOS concentrations were observed than PFOA, indicating of potential PFOS point sources. It should be stated that above mentioned sites were close to petrochemical industrial areas. Ratios of PFOS/PFOA calculated in this study were consistent with findings in surface waters from northern China [38], the Tennessee River and Lake Michigan in USA [16] and 20 wastewater treatment plants effluents in 11 cities in economically developed areas of China [39].

PFHpA was found in most water samples with a detection frequency of 90%, and it was also the dominant individual in some sampling sites. Several researches have reported the dominance of this compound in surface water. Simcik and Dorweiler [40] proposed that relatively high concentrations of PFHpA were due to the atmospheric deposition. The ratio of PFHpA/PFOA was, therefore, used as a tracer of atmospheric deposition. The ratios of PFHpA/PFOA in this study was less than 1, but at T36 from Benxi City the ratio was 1.22, suggesting that atmosphere deposition may not be the major source of PFCs in the study area, and T36 might be affected by point-source pollution as a result of industrialization.

The ratio of PFOA/PFNA in the range of 7 to 15 indicated the direct emission of manufacturing process [41]. The ratios of PFOA/PFNA in this study were in the range of 0.39 to 67.43. The sites with ratios for PFOA/PFNA in the range of 7–15 were mostly adjacent to industrial cities, such as Fushun [e.g. H25 (8.44), H26 (8.62)], Benxi [e.g. T37 (9.34)], Liaoyang [e.g. T42 (8.45)], Anshan [e.g. T43 (12.53), T44 (9.43)], Yingkou [e.g. D49 (14.79)], verifying that manufacturing processes did influence the PFCs levels in the study area. High ratios of PFOA/PFNA also indicated the degradation of precursors. Thus, the PFCs in Liaohe River were from the emission of manufacturing processes and precursors degradation.

Risk assessment

In this study, the assessment of risks to aquatic biota exposed to PFCs was conducted based on the risk quotient (RQ) method, which was determined by comparing the detected concentrations of the target individuals with the advisory guideline values. The RQ values greater than 1 indicate that the water could pose a risk to aquatic ecosystem. In this study, the risk of three indicator

individuals, PFBS, PFOS and PFOA was assessed, with their environmental quality standards (EQS) shown in Table 3. As there were different environmental quality standards in different areas, the strictest standards were used in this study. All RQ values of PFBA, PFPA, PFHxA, PFNA, PFDA, PFBS, and PFOS were below 1, indicating that no risk existed to the aquatic organisms in Liaohe River. However, the RQs of PFOA in several sites were higher than 1, suggesting that PFOA in surface water may exert adverse effect to the aquatic ecosystem. Even so, the risk of PFCs contamination in surface water to ecosystem should get more attention because of their bioaccumulation.

Liaohe River is the drinking water source of the region's population. For instance, Dahuofang Reservoir located in the upstream of Hun River serves as the drinking water source for Shenyang City, Fushun City, and Anshan City. Guanying Reservoir and Caowo Reservoir in the upstream and midstream of Taizi River are the drinking water source of downstream region. So the hazard ratio (HR) was used to estimate the potential health risk of PFOA and PFOS through water intake for biota through reference dose (RD) [27]:

$$HR_{\text{water}} = ADC_{\text{water}}/RD_{\text{water}}$$

$$ADC_{\text{water}} = C_{\text{water}} \times V_{\text{water}} \times 10^{-3}/W,$$

where ADC_{water} is the estimated average daily consumptions ($\mu\text{g}/(\text{kg d})$), C_{water} represents the PFOA or PFOS concentration in water (ng/L), V_{water} is the volume of drinking water for an adult each day (L), W is the average weight of an adult (kg). RD_{water} is $0.333 \mu\text{g}/(\text{kg d})$ for PFOA and $0.025 \mu\text{g}/(\text{kg d})$ for PFOS. With the HR_{water} value below 1, the PFCs could not exert emerging health effects to biota. In this study, the adult average weight was assumed as 60 kg and the volume of water intake was 2 L each day. According to the concentration of PFOA

and PFOS in Liaohe River, the highest HR_{water} value was 0.0074 for PFOA and 0.061 for PFOS through the water intake, respectively, suggesting that the levels of PFOA and PFOS in Liaohe River would not result in the immediate health impact via water intake alone.

Mass inventory of PFCs

Riverine sink is one major process for the transportation and mobilization of pollutants to the sea. In this study, the potential of sediments as a PFCs source to the surrounding environment was assessed by the estimation of $\sum\text{PFCs}$ and PFOA mass inventories. The mass inventory was calculated by the equation $I = \sum k C_i A_i d \rho$, where C_i (ng/g) is the average sediment concentration of $\sum\text{PFCs}$ and PFOA, A_i is the area (km^2), d is the sediment thickness (cm), ρ is the bulk density of the dry sediment (g/cm^3), and k is the unit conversion factor. Assuming a depth of 20 cm, a bulk density of $1.5 \text{ g}/\text{cm}^3$ and an area of $219,600 \text{ km}^2$ [45], the mass inventories of $\sum\text{PFCs}$ and PFOA were 328.74 t and 103.43 t in Liaohe River, respectively. A study conducted in Taihu Lake showed that the mass inventory of perfluoroalkyl acids in the lake was 989 kg [46], which was much higher than in the present study. However, the mass inventory of PFCs in Liaohe River was still able to contribute to the PFCs contamination in the coastal area.

Conclusions

This study demonstrated that PFCs were widely presented in the water and sediments of Liaohe River. In general, PFCAs had higher concentrations and detection frequency than PFASs, and PFCAs with short carbon chains (PFBA, PFHxA, PFOA, PFHpA and PFNA) had much higher detection frequencies than long-carbon chain compounds (PFDA, PFUnDA, PFDoDA and PFTrDA) in water. Among all PFC homologues, the average K_{oc} increased with the increased carbon chain, by 0.13–0.62 log units with each CF_2 moiety. K_{oc} values were higher for PFASs than PFCAs. The risk assessment suggested that PFOA in water may exert adverse effect on the aquatic ecosystem. The mass inventories of $\sum\text{PFCs}$ and PFOA at 328.74 t and 103.43 t in the study area indicated that Liaohe River was likely acting as a PFCs source to the surrounding area.

Abbreviations

PFC: perfluorinated compounds; PFCAs: perfluorocarboxylic acids; PFASs: perfluoroalkyl sulfonates; PFBA: perfluorobutanoate; PFPA: perfluoropentanoate; PFHxA: perfluorohexanoate; PFHpA: perfluoroheptanoate; PFOA: perfluorooctanoic acid; PFNA: perfluorononanoate; PFDA: perfluorodecanoate; PFUnDA: perfluoroundecanoate; PFDoDA: perfluorododecanoate; PFTrDA: perfluorotridecanoate; PFBS: perfluorobutane sulfonate; PFOS: perfluorooctane sulfonate; PFDS: perfluorodecane sulfonate; PFHxA: potassium salts of perfluorohexane sulfonate; PFOSA: perfluorooctane sulfonamide; POSF: perfluorooctane

Table 3 Estimated risk quotients of 6 PFCs in surface water in Liaohe River

Compound	Range of concentrations in surface water (ng/L)	EQS ^a (ng/L)	RQ
PFBA	n.d–22.26	1400	0–0.0159
PFPA	n.d–7.26	600	0–0.0121
PFHxA	n.d–33.14	200	0–0.1657
PFOA	0.37–73.94	20	0.01889–3.3971
PFNA	n.d–11.56	100,000	0–0.0001
PFDA	n.d–1.76	11,000	0–0.0001
PFBS	n.d–6.44	600	0–0.0107
PFOS	n.d–46.12	50	0–0.9223

^a EQS of PFBA, PFPA, PFHxA, PFOA, PFBS were obtained from Valsecchi et al. [42]; EQS of PFOS was obtained from Brooke et al. [43]; EQS of PFNA and PFDA were obtained from Hoke et al. [44]

sulfonyl fluoride; PP: polypropylene; PTFE: polytetrafluoroethylene; BDL: below detection limit; LOD: limit of detection; LOQ: limit of quantification; S/N: signal/noise ratios; RQ: risk quotient; EQS: environmental quality standards; HR: hazard ratio; RD: reference dose.

Acknowledgements

Not applicable.

Authors' contributions

JL, CG and JX involved in the experiments and manuscript writing, SL and YZ were responsible for the data analysis and study designing. JL and JX contributed to the manuscript correction. All authors read and approved the final manuscript.

Funding

This work was financially supported by Major Science and Technology Program for Water Pollution Control and Treatment (2017ZX07302001) and Free Exploration Foundation of State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences.

Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Received: 4 July 2019 Accepted: 26 August 2019

Published online: 10 September 2019

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