RESEARCH ARTICLE

Perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs) in surface and tap water around Lake Taihu in China

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Abstract Perfluorinated compounds (PFCs) are ubiquitously distributed in the environment mainly as perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs). In this paper, six PFCAs and two PFASs were quantified in surface and tap water samples from 12 sites around Lake Taihu near Shanghai City in East China. Predominant PFCs were perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), of which the concentration ranges were 6.8–206 and 1.2–45 ng·L^{-1}, the geometric means were 35.3 and 9.4 ng·L^{-1}, and the median (quartile range) values were 31.4 (34.4) and 10.4 (10.7) ng·L^{-1}, respectively. Other PFCs were also detected but in much lower concentrations than PFOA. The sources of the PFCs were expected to be direct industrial discharges in the Lake Taihu area, and this area was also a possible source of PFCs contaminations in Shanghai district in the downstream. PFCs distributions were found different in the upstream, downstream and north part of Lake Taihu. Occurrences of PFCs in the tap water in Lake Taihu area indicated their exposure to the local people. A brief estimation of the environmental risks by PFCs implied no acute or immediate risks from PFCs to local human health, but chronic risks from PFOA in the tap water should be considered in the downstream regions.

Keywords surface and tap water, perfluorocarboxylic acids (PFCAs), perfluoroalkyl sulfonates (PFASs), Lake Taihu area, ultra performance liquid chromatography with tandem mass spectrometry (UPLC-MS)

1 Introduction

Perfluorinated compounds (PFCs) are a family of new persistent organic pollutants which have been ubiquitously distributed in the environment after 50 years of popular utilization as industrial materials. Because the perfluorinated tails of PFCs molecules are very stable in chemical and thermal conditions, these chemicals are popularly used in surfactants, coating, foaming and polymerization processes. Typical PFCs used in practice are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), belonging to the group of perfluorocarboxylic acids (PFCAs, F$(CF_2)_{n-1}COO^-$) and perlfuoroalkyl sulfonates (PFASs, F$(CF_2)_nSO_3^-$) respectively.

Occurrences of PFCs in the water environment have been frequently reported in North America [1–4], Europe [5–8], and Asia [9–12]. The environmental monitoring attempts are helpful to understand the distribution, source, transportation and behavior of PFCs in the water environment. The major sources of PFCs were considered as the discharges from fluorochemical industries, although PFCs in the environment may also come from domestic consumption. PFCs with long carbon chains are too stable to be biodegraded and subject able to accumulate in biological food chains, which result in risks to the ecosystem. Lab-scale studies proposed the possible neural and carcinogenic toxicities of PFOS [13].

Distributions and behaviors of PFCs in the environment and organisms in China have been intensively studied recently [13,14]. PFOA and PFOS have been reported in the run-off water of the Pearl and Yangtze Rivers [15], in sea water along the China coast [9,16,17] and in tap water from municipal cities [14]. PFCs were also found in wild animals such as giant pandas [18], lions and tigers [19], in fishes in the Tibetan plateau lakes [20], in seafood in eastern China [21], in the eggs of chickens [22] and coastal

water birds [23], and in human serum [24,25] and breast milk [26].

However, PFCs contaminations in the big lakes of China and their influences on tap water have not been reported yet. The inadequate data accumulation of PFCs in the environment also blocked the necessary assessment and measures for their environmental risks. In this paper, eight kinds of PFCs were investigated in the surface and tap water around Lake Taihu in order to understand their behaviors and environmental risks.

2　Materials and methods

2.1　Chemicals and reagents

Six kinds of PFCAs and two kinds of PFASs are investigated in this study, as shown in Table 1. PFC reagents were selected from the available products from different suppliers to get higher purities. Perfluoroheptanoic acid (PFHpA, CAS: 375-85-9, 98%), perfluorononanoic acid (PFNA, CAS: 375-95-1, 97%), perfluorodecanoic acid (PFDA, CAS: 335-76-2, 97%) were ordered from the Alfa Aesar Company in USA. Perfluorooctanoic acid (PFOA, CAS: 335-67-1, 96%) was obtained from the Acrös Organic Company in USA. Perfluorohexanesulfonic acid potassium salt (PFHxS, CAS: 3871-99-6, 98%) was obtained from the Sigma-Aldrich Company in Italy. Perfluoroundecanoic acid (PFUnA, CAS: 2058-94-8, 96%), perfluorododecanoic acid (PFDoA, CAS: 307-55-1, 96%) and perfluorootane sulfonic acid potassium salt (PFOS, CAS: 2795-39-3, 96%) were ordered from the Matrix Scientific Company in USA. Liquid chromatography (LC) grade pure methanol was obtained from Fisher Company in Germany. Milli-Q ultra pure water was used throughout the experiments.

Stock solutions were prepared in $2\,mmol\cdot L^{-1}$ for each PFC by dissolving the chemical into pure methanol. Mixed standard solutions of PFCs in 4, 8, 20, 40, 160 and $400\,nmol\cdot L^{-1}$ (equal to 1.6–$165\,\mu g\cdot L^{-1}$ PFOA) were prepared by spiking diluted stock solutions into 50% (v/v) methanol in pure water. PFC concentrations were calculated by external calibration curves ($R^2 > 0.99$) with modifications by the reagent purities.

2.2　Sampling campaigns

Field surveys were duplicated at twelve sampling sites around Lake Taihu on Feb. 26 and Apr. 27, 2009 respectively. As shown in Fig. 1, the sampling sites represent lake shore water (Site 6, 10–12), river water (Site 1–5, 9), wastewater treatment effluent (Site 8) and city runoff (Site 7). The flow directions of the lake water and the important rivers are also shown in the map, as well as the positions of tap water sources. The surface water sampling was conducted in both surveys, and four tap water samples were collected in the restaurants near Sites 3, 4, 8 and 11 at the second survey.

Pure drinking water was ordered from supermarkets to get 600 mL polyethylene terephthalate (PET) bottles as sample containers due to their lower less adsorption and release of PFCs. Before sampling, the bottle was pre-cleaned by methanol and further rinsed by pure water several times. At each sampling site, two bottles were first rinsed by the sample water three times, then filled with the sample and finally stored in a thermostat box with ice. Finally, the samples were transported back to the laboratory and stored overnight in a refrigerator at 4°C. All the pretreatment procedures were accomplished on the second day.

2.3　Solid phase extraction (SPE)

The water samples were first passed through membrane filtration papers (Millipore, 0.45 μm, 47 mm) and then the filtrates were concentrated for one thousand times by the solid phase extraction (SPE) process. At first, Oasis® HLB cartridges (Waters, 60 mg, 3 mL) were pre-conditioned by 3 mL of methanol and 3 mL of pure water in gravitational

Table 1　Quality control of instrumental analysis for PFCs in environmental samples

PFCs	structure	MRM/($-m/z$)		limit[a]/($\mu g\cdot L^{-1}$)		pre-SPE recovery rates[b]/%		
		parent	daughter	LOD	LOQ	PW($n = 3$)	TW($n = 4$)	SW($n = 19$)
PFHpA	$CF_3(CF_2)_5COO^-$	363	319	0.7	3.5	111±29	82±5	59±26
PFOA	$CF_3(CF_2)_6COO^-$	413	369	0.5	1.2	114±30	78±26	72±38
PFNA	$CF_3(CF_2)_7COO^-$	463	419	0.6	1.9	108±8	68±7	55±15
PFDA	$CF_3(CF_2)_8COO^-$	513	469	0.6	2.5	113±18	65±6	54±9
PFUnA	$CF_3(CF_2)_9COO^-$	563	519	0.7	1.4	101±22	59±10	52±9
PFDoA	$CF_3(CF_2)_{10}COO^-$	613	569	0.8	3.3	75±40	50±12	38±10
PFHxS	$CF_3(CF_2)_5SO_3^-$	399	79	0.8	2.6	109±10	109±12	90±18
PFOS	$CF_3(CF_2)_7SO_3^-$	499	79	1.0	2.4	104±8	97±6	82±25

Notes: a) LOD: limit of detection; LOQ: limit of quantification; b) spiking 40 pmol·L^{-1} of mixed standards into different matrices before SPE; PW is pure water; TW is tap water; and SW is surface water.
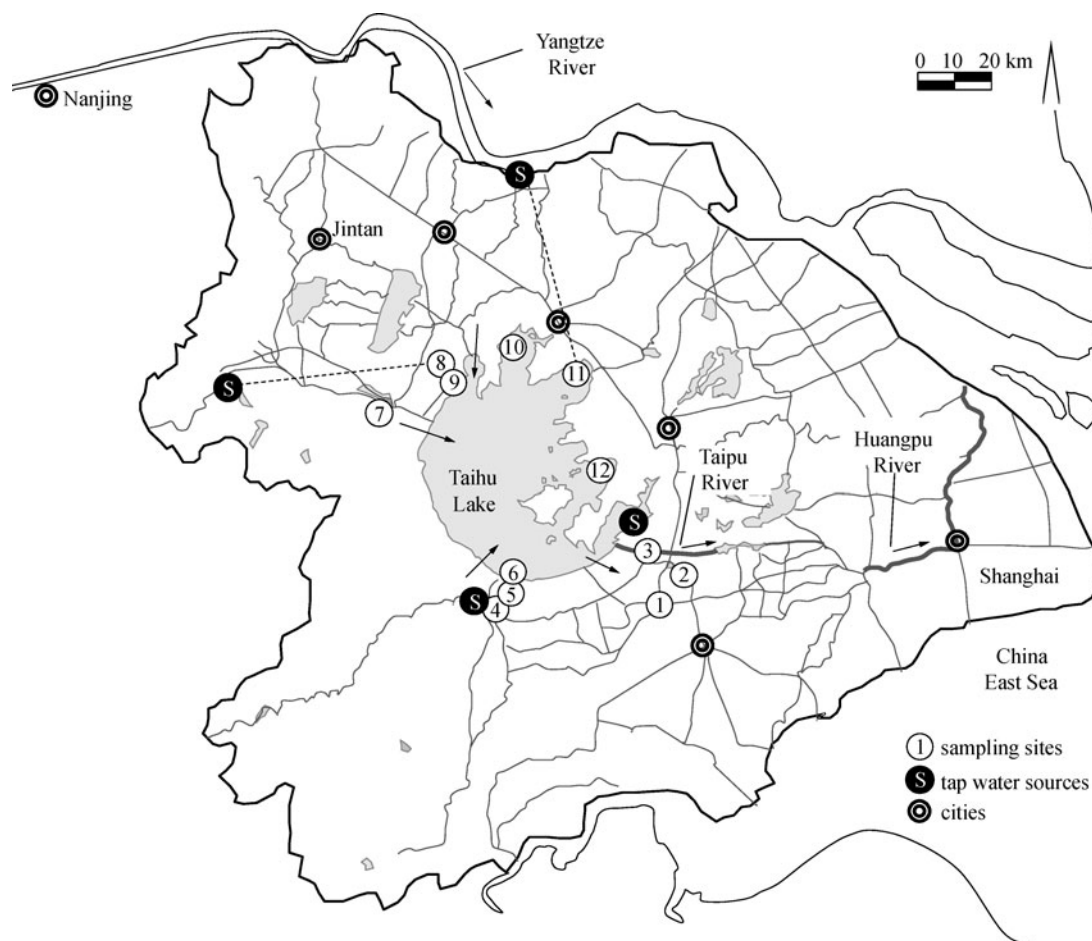
Fig. 1 Map of Lake Taihu area of China

drops. Following that, the 0.5 L samples were loaded onto the wet cartridges by a peristaltic pump at the flow rate of 10 mL·min⁻¹ approximately. After the loading of samples, the cartridges were additionally rinsed with 5 mL of pure water. The next step was to dehydrate the cartridges by a vacuum pump for two hours and sequentially elute the cartridge by gravity with 3 mL of methanol. The extracts were dried in gentle nitrogen gas flows and then reconstituted by 0.5 mL of 50% (by volume) methanol in pure water. Finally, the solutions were stored in 1.5 mL polypropylene (PP) centrifuge tubes for analysis.

2.4 Instrumental analysis

Instrumental analysis was performed by the reversed-phase ultra performance liquid chromatography (Acquity UPLC, Waters Company, USA) with negative electrospray ionization interface and tandem mass spectrometry (ESI-MS-MS), using a triple-quadrupole MS-MS integrated platform (Quattro Premier, Waters Company, USA). A UPLC column (BEH C18, 2.1 × 100 mm, 1.7 μm, Waters Company, USA) protected by a guard column (BEH C18, 2.1 × 15 mm, 1.7 μm, Waters Company, USA) was used as

the stationary phase for LC separation, while the methanol in pure water was used as the mobile phase. The UPLC column was maintained at 40°C and the flow rate of the mobile phase was constant at 0.1 mL·min⁻¹. In the analytical process, 10 μL of samples in 0.2 mL LC vials were periodically injected into the system with gradient flows to accelerate the LC separation in 8 min. The methanol in pure water was increased from 50% to 95% in the first 4 min, and then the composition was held for 1.5 min and returned to the start condition in another 1.5 min, followed by 1 min of equilibration.

Instrumental control software (Masslynx®, Waters Company, USA) was applied to assist the optimization of the parameters for mass spectrometry. The capillary voltage was −2.0 kV, and those of the cone, extractor and RF lenses were 30 eV, 4 eV and 0.1 eV respectively. Nitrogen was used as the nebulizer and collision gas, and the temperatures of source and desolvation were 120°C and 250°C respectively. Analyzer conditions of MS-MS system were 12.0, 12.0 and 1.0 for LM1, HM1 and ion energy 1, as well as LM2, HM2 and ion energy 2. The conditions of entrance, collision, exit and multiplier were −1.0 V, 2.0 V, 1.0 V and 650 V, respectively. Flow rates of

the desolvation gas and cone gas were $650 \text{ L} \cdot \text{h}^{-1}$ and $50 \text{ L} \cdot \text{h}^{-1}$, respectively.

Quantitative analysis was conducted in multi-reaction-mode (MRM) in MS-MS system. The daughter ions of the destroyed PFCs molecules were anion carboxylic groups $(F(CF_2)^-_{n-1})$ for PFCAs and sulfonate group (FSO_3^-) for PFASs respectively. Retention times of PFCs in chromatograms varied from 2.4 to 5.8 min, indicating quick and efficient separation by the system. Quantification software (QuanLynx®, Waters Company, USA) was used to calibrate PFC concentrations by external standard curves automatically.

2.5 Quality control

The limits of detection (LODs) for PFCs analysis were summarized according to the signal-to-noise value ($S/N = 3$), and the limits of quantification (LOQs) were equal to three times of the standard deviations during seven sequential injections of mixed standards in $4 \text{ nmol} \cdot \text{L}^{-1}$ ($\sim 1.65 \text{ μg} \cdot \text{L}^{-1}$ PFOA). Pre-SPE experiments were conducted by spiking mixed standards in $40 \text{ pmol} \cdot \text{L}^{-1}$ ($\sim 16.5 \text{ ng} \cdot \text{L}^{-1}$ PFOA) into the samples before cartridge loading, and post-SPE ones by adding mixed standards in $40 \text{ nmol} \cdot \text{L}^{-1}$ ($\sim 16.5 \text{ μg} \cdot \text{L}^{-1}$ PFOA) into the SPE extractions before UPLC injection. The recovery rates were calculated with the concentrations of spiked samples and original samples.

Table 1 shows LODs, LOQs and process recoveries of PFCs analysis in this study. Matrix effects on analysis were demonstrated by the pre-SPE recoveries of PFCs, which also implied that analytical qualities of PFCs in pure water and in tap water were better than those in surface water. The pre-SPE recovery combines the effects of both SPE loss and ionization suppression, while the post-SPE recovery represents only the effect on ionization. Post-SPE recoveries are also called ionization suppression rates (ISRs). In this study, ISRs of PFASs were 98%–100% and those of PFCAs were 76%–99%, but ISR of PFOA was $130 \pm 37\%$ ($n = 14$). The result meant that the ionization of PFOA was obviously enhanced by the extractable background organics in the samples and the ionizations of other PFCs were more or less suppressed. Furthermore, the loss of PFCs during SPE process could be estimated by dividing the pre-SPE recoveries by the ISRs, which implied that PFASs (loss of 17%–19%) had been more effectively extracted than PFCAs (loss of 21%–46%).

3 Results and discussion

3.1 PFCs concentrations in surface and tap water

As shown in Table 2, PFCs were detected in most of the surface and tap water samples, indicating their ubiquitous distributions around Lake Taihu. The dominant PFCs were PFOA and PFOS, with M(QR) values (median and interquartile range) of 31.4 (34.4) and 10.4 (10.7) $\text{ng} \cdot \text{L}^{-1}$ respectively. PFHpA, PFNA and PFHxS were in much lower concentrations than PFOA, with M(QR) values of 5.4 (5.5), 2.8 (1.7) and 1.1 (3.9) $\text{ng} \cdot \text{L}^{-1}$, respectively. Although PFDA, PFUnA, and PFDoA were also detected, their concentrations in the samples were almost lower than LOQ, and their geometric means were roughly estimated to be 1.5, 1.0 and 0.5 $\text{ng} \cdot \text{L}^{-1}$, respectively.

It was reported that PFOS and PFOA concentrations in the run-off water of Yangtze River in Nanjing City (0.33–0.38 and 2.1–2.4 $\text{ng} \cdot \text{L}^{-1}$) were much lower than those in Shanghai City (0.62–14 and 22–260 $\text{ng} \cdot \text{L}^{-1}$) [15]. PFOS and PFOA in the tap water of Nanjing City (0.94 and 5.9 $\text{ng} \cdot \text{L}^{-1}$) were about 10-fold less than those in Shanghai City (7.6 and 78 $\text{ng} \cdot \text{L}^{-1}$) [27]. In this study, concentration ranges of PFOS and PFOA in surface and tap water around Lake Taihu were close to those in Shanghai City and much higher than those in Nanjing City. By considering the water flow directions from Yangtze River near Nanjing City to Lake Taihu and finally to Shanghai City, the pollution of PFOA and PFOS in Lake Taihu area could greatly contribute to the PFCs pollution in Shanghai district. Furthermore, PFOS was usually dominant in the solid phase due to its stronger hydrophobicity than PFOA, but it was reported that PFOA concentrations were higher than PFOS in the sediments and soils along Huangpu River (see Fig. 1) [28]. In this study, very high concentrations of PFOA were detected in the run-off water in Taipu River (Site 3), implying that a large amount of PFOA has been transported to Shanghai district via the river system, which should be related with the PFOA accumulation in the solids in Huangpu River.

The effluent of wastewater treatment plants (WWTPs) was often considered an important source of PFCs in urban areas due to the possible biological degradations of PFCs-related precursors from industrial wastewater [29]. In this study, although 70% of the raw influent was from industries, the effluent of Yixing Zhoutie Municipal WWTP (Site 8) contained PFCs in very low concentrations, which might be caused by the very few fluorochemical plants in the nearby industrial zones. Further investigations are necessary to identify the industrial sources in the service area of the sewer system.

Table 3 lists some recent surveys of PFCs in surface and tap water all over the world. First, dominant PFCs in those surveys were PFOS and/or PFOA. They often occurred in run-off water in hundreds of ppb ($\text{ng} \cdot \text{L}^{-1}$) in European countries and the USA, where direct industrial sources could be identified. Second, PFOA concentrations in river water in China were higher than in most other countries, indicating serious pollution by PFOA in the surface water environment in China. Finally, the PFOS and PFOA concentrations obtained in this study were similar to the results from other surveys in China.

Table 2 PFCs concentrations in surface and tap water around Lake Taihu

site	group[a]	PFC concentrations [b]/(ng·L^{-1}, by anion)							
		PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
1	R	5.8–7.5	83–86	2.7–3.7	LQ [c]	ND [d]-2.0	LQ	LQ-4.6	9.0–13
2	R	10–12	55–98	7.4–19	2.5–9.2	1.9–5.8	ND	ND-2.9	10–13
3	R	4.8–9.2	72–206	4.7–5.4	LQ	1.6–2.2	ND	LQ-4.2	10–11
4	R,D	LQ	20–29	2.8–3.3	LQ	LQ	ND	ND-1.3	5.0–13
5	R	LQ-4.9	24–27	LQ-2.9	LQ	LQ	ND	LQ	6.9–7.6
6	L	4.8–7.7	25–34	2.3–3.6	LQ	LQ	ND	LQ	3.5–9.4
7	C	4.0–12	19–26	LQ-3.3	LQ	LQ	LQ	ND-2.8	LQ-3.0
8	W	3.7–5.7	14–26	2.0–2.0	LQ	LQ	ND	ND-6.9	8.0–12
9	R	5.4–9.3	22–22	LQ-2.6	LQ	ND-1.7	ND	ND-16	22–32
10	L	10–13	52–55	2.8–7.1	LQ-3.6	LQ	ND	ND-14	29–45
11	L	5.4–12	49–60	2.4–3.8	LQ-2.8	1.8–2.9	LQ	ND-36	17–23
12	L	4.7–14	45–108	4.5–5.0	LQ-2.9	1.4–1.8	LQ	ND-5.8	21–25
3 [e]	T	4.4	40	3.2	LQ	LQ	LQ	4.0	14
4 [e]	T	LQ	20	2.5	LQ	ND	ND	LQ	6.7
8 [e]	T	LQ	6.8	ND	LQ	ND	ND	ND	3.2
11 [e]	T	LQ	6.8	LQ	ND	LQ	ND	ND	LQ
range		LQ-14	6.8–206	ND-19	ND-9.2	ND-5.8	ND-LQ	ND-36	LQ-45
G. mean [f]		5.5	35.3	2.9	1.5	1.0	0.5	1.4	9.4
median [g]		5.4	31.4	2.8	–	–	–	1.1	10.4
(quartile range)		(5.5)	(34.4)	(1.7)	–	–	–	(3.9)	(10.7)

Notes: a) Symbol R as river water, L as lake water, D as source for tap water, C as municipal city runoff, W as effluent of wastewater treatment plant, T as tap water. b) Concentrations are based on PFC anions, without modification by spiking recovery rates. c) LQ means higher than LOD but lower than LOQ. d) ND means not detected or lower than LOD. e) Tap water samples are collected at the restaurants near the numbered sites. f) Geometric means of all observations ($n = 28$), with ND and LQ in the table assigned by the half values of LOD and LOQ in Table 1 respectively. g) Medians and interquartile ranges (M(QR)) are used to show the distribution properties of PFC concentrations. M(QR) values for PFDA, PFUnA and PFDoA were not calculated because most of their concentrations were lower than LOQ.

3.2 Possible sources of PFCs around Lake Taihu

PFCs in surface water are usually discharged from industrial point sources like fluorochemical plants [3,11] or originate from non-point sources like fluorinated pharmaceutics and pesticides [24]. Although current available data around Lake Taihu were inadequate to identify the sources of the PFCs, their properties could be described from the scope of other studies in the literature. For example, PFCs with longer carbon chains were often found in lower concentrations in surface water [5,7,30] and sea water [9,15], which were partially governed by their increased hydrophobic properties. In this study, concentrations of PFCAs except PFOA were also found negatively correlated ($R = -0.985$, $p < 0.005$) to their carbon chain lengths. The coincidence of the concentrations and molecular properties of PFCAs implied that those PFCAs except PFOA may all have similar sources.

The sources of PFOA around Lake Taihu could be traced to direct discharges from PFOA related fluorochemical manufacturers, such as semiconductor, electronics and optoelectronic industries [11,31], because very high concentrations of PFOA in surface water were usually caused by intensive discharges from industries [6,30]. Also, the possible sources of PFOA might be traced back to the direct discharges from industries around Lake Taihu over the past decades, which resulted in the accumulation of PFCs-related organics in the sediments and soils.

The diverse sources of PFCs around Lake Taihu would result in complicated exposure of PFCs to local human health. Usually the distribution of PFCs in human serum was correlated with those in the water environment. It was reported that PFCs in human blood in Jintan City (see Fig. 1) occupied only 30% of the extractable organic fluorine in the serum, which was much lower than other places in the world [25] and implied the different exposures by the diverse sources.

3.3 Profiles of PFCs distribution in surface water

One method of applying the ANOVA test was to estimate the site dependence of PFCs concentrations in surface water. Results showed that correlation between sampling sites and PFOS concentrations was significant ($p = 0.0004 < 0.05$), but those of PFCAs were not significant, e.g., PFOA ($p = 0.055$) and PFNA ($p = 0.051$). This result implied that PFOS concentrations were dependent on the

sampling sites while distributions of PFCAs were less affected by the locations.

Distribution patterns of PFCs in surface water were often estimated by the profiles of PFCs compositions [15,24,27,32]. Figure 2 shows the profiles of PFC concentrations in surface water of Lake Taihu area. PFOA was dominant among the investigated PFCs at most sampling sites, with occupational percentiles of 52–82% in the south area and 36–62% in the north area. PFOS occupational rates were increased from 6–21% in the south area to 19–39% in the north area, indicating that it was more easily accumulated in the sediments of the north part of Lake Taihu. As shown in the figure, three patterns could be identified for the distributions of total PFCs or PFOA: (I) very serious pollution in the downstream of the lake (see Fig. 1, Site 1-3); (II) less pollution in the upstream of the lake (Site 4–9); and (III) serious pollution in the north part of the lake (Site 10–12).

PFC distributions in profiles I and II could be explained by the urbanization intensities in the upstream and downstream. In other words, intensities of point sources in the upstream were much less than those in the downstream because of the less intensive urbanization, resulting in the aqueous PFC concentrations in upstream samples that were only a third of those taken from the downstream sites. For profile III, however, the point sources were already prevented from reaching the lake water by the sluice gates along the north lake shore to cut all connections between the rivers and the lake water. The high PFC concentrations in the north part of the lake might be explained by the historic accumulation of PFCs in the sediments. The water flow in the small bays around the north lake shore was very slow because of the special hydraulic dynamics in the lake, so that the discharged PFCs in the past decades could be accumulated in the sediments and released back into the aqueous phase again.

3.4 Correlations of PFCs in surface and tap water

The cross correlation between the concentrations of investigated PFCs might hint at common sources for the correlated compounds [15,24,27,32]. As shown in Table 4, the bi-variant correlations among PFNA, PFDA and PFUnA were strongly significant ($p < 0.01$) and the correlations of PFHpA to PFOA, PFNA and PFDA were also significant ($p < 0.05$). The results inferred that those PFCAs may have common sources, which was coincident with the earlier discussion on the sources of the PFCAs. The correlation between PFOA and PFOS in river water is often reported [11,12], but PFOA in Taihu Lake area was not correlated with PFOS, which might be related to the very low consumption of PFOS-related chemicals in the area.

The correlations between the concentrations of PFCs in tap water and in surface water were proposed as the evidence for the failure of current water purification processes to remove PFCs effectively [10,30]. Figure 3 shows the PFCs in surface and tap water at the same sampling sites, represented by x and y respectively. The points are scattered in the band of $y = x$ and $y = 0.1x$, but half of them locate between $y = x$ and $y = 0.5x$, inferring that the concentrations of the PFCs in tap water were naturally lower, but not much lower than those in surface water.

By considering the position of tap water sources and sampling sites (see Fig. 1), Site 4 was selected for the discussion of PFCs removal efficiency, because it is located directly adjacent to the intake well of a water supply plant. At Site 4, PFC concentrations in tap water showed good linearity with those in surface water as $y =$

Table 3 Recent studies on PFOA and PFOS in surface and tap water (unit: ng·L^{-1})

site	samples[a]	time	PFCs[b]	PFOS[c]	PFOA[c]	reference
Canada	lake water	2004	8 kinds	21–70	27–50	[1]
Japan	river water	2004	S, A	ND-12	0.7–40	[12]
USA	river water	2005	4 kinds	2.6–4	4.4–15	[2]
USA	surface water	2006	4 kinds	1.6–756	15–49	[3]
German	river water	2006	12 kinds	ND-193	2–3640	[30]
Italy	river water	2007	7 kinds	ND-38	0.6–16	[8]
Europe	surface water	2009	7 kinds	ND-1371	ND-174	[6]
Japan	tap water	2008	S, A	0.16–22	2.3–84	[10]
Spain	tap water	2009	13 kinds	ND-58	ND-57	[7]
China	river water	2007	14 kinds	ND-99	0.85–260	[15]
China	tap water	2009	20 kinds	0.04–11	0.44–78	[27]
this study	surface water	2009	8 kinds	1.2–45	14–206	
	tap water			1.2–14	6.8–40	

Notes: a) Surface water samples include river, canal and city runoff. b) *S, A* means PFOS and PFOA, *n* kinds means *n* kinds of investigated PFCs including PFOS and PFOA. c) Range of aqueous concentrations (min. – max.) with the digits of maximum numbers rounded.
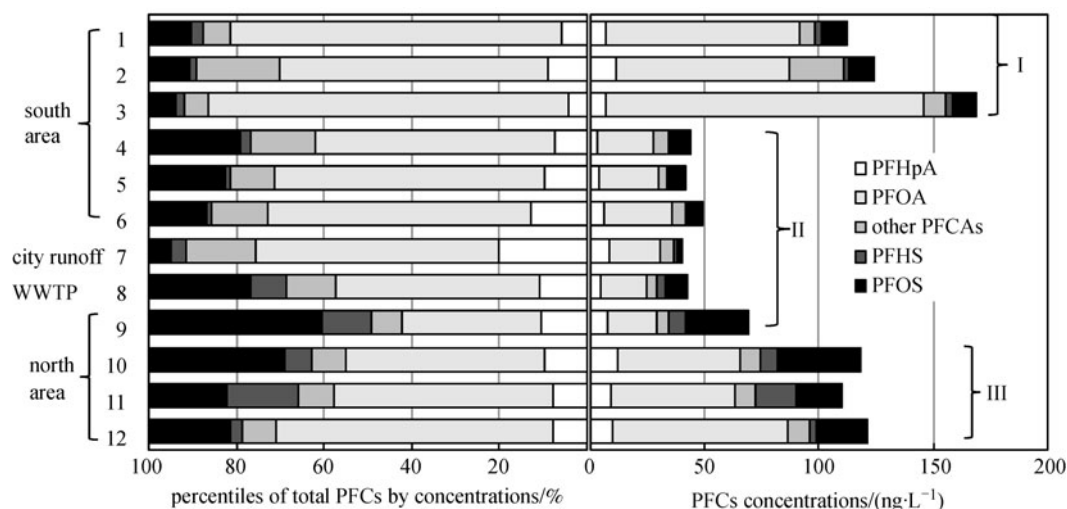
Fig. 2 Distribution profiles of investigated PFCs in surface water

Table 4 Correlations between PFCs concentrations in surface water in Lake Taihu area

	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS
PFOA	0.410 [a]						
PFNA	0.412 [a]	0.248					
PFDA	0.411 [a]	0.195	0.962 [b]				
PFUna	0.399	0.296	0.867 [b]	0.887 [b]			
PFDoA	−0.259	−0.171	0.043	0.118	0.289		
PFHxS	−0.177	−0.017	0.028	0.117	0.200	0.620 [a]	
PFOS	0.390	0.091	0.115	0.122	0.033	0.004	0.369

Notes: a) significant correlation at 0.05 level (2-tailed). b) significant correlation at 0.01 level (2-tailed).

$0.80x$ ($R = 0.997$), indicating the total removal efficiency at around 20%. The results meant that the coagulation process and sand filtration in the water supply plant were ineffective at removing PFCs, being especially unsatisfactory for PFOA and PFOS with removal rates of 18% and 27% respectively.

3.5 Exposures and environmental risks

Global concerns about tap water contamination by PFOS and PFOA stimulated the attempts to estimate their exposure and risks to human health. Assuming the consumption of tap water was 2 L·day^{-1} from Site 3, the exposures of PFOA, PFOS and total PFCs to a person of 70 kg weight were estimated to be 0.2–1.2, 0.05–0.4 and 0.4–2.2 ng·kg^{-1}·d^{-1}, respectively, which were much lower than reported dosages in toxicology studies [33,34]. The US EPA issued provisional health advisories on PFOS and PFOA in tap water [33], which were 200 ng·L^{-1} and 400 ng·L^{-1} respectively. Therefore, concentrations of PFOS and PFOA in the tap water samples around Lake Taihu were 10-fold less than the advised values, indicating that there were no acute or immediate risks from PFCs in

tap water to local human health.

However, by considering the persistence and biomagnification of PFCs in the ecosystem and food chains [4], chronic threats of PFCs in surface water to aquatic lives should be considered during the estimation of environmental risks. Indicative warning levels (IWL) for both PFOS and PFOA in river water in Europe were proposed as 30 ng·L^{-1}, which were derived from 90 percentile of observations during an EU-wide river water survey at 122 sites [6]. According to this limit, surface water at half of the sample sites (Site 1–3, 10–12) around Lake Taihu were definitely contaminated by PFOA. Advanced and industrialized fisheries in Lake Taihu might introduce PFCs into the human body through the food chains, which has not been carefully studied yet. Studies revealed that PFOS was significantly accumulated in fishes but PFOA was not [35]. Therefore, by considering the high concentrations of PFOA and low concentrations of PFOS in the surface water around Lake Taihu, biomagnification of PFCs in the food chains would not result in acute risks in the Lake Taihu area.

Recent risk assessment studies concerning life-time exposures proposed a health-based PFOA limit in tap
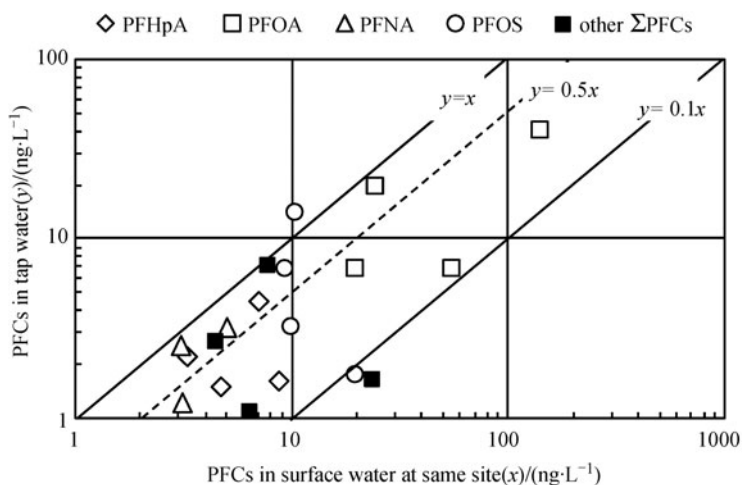
Fig. 3   PFCs in surface and tap water at same sampling sites

water as 40 ng·L^{-1}, one tenth of the limit in provisional health advisories by the US EPA [7]. Therefore, PFOA in tap water at Site 3 is not safe for human health by the chronic exposures. By considering the ineffective removal of PFOA by traditional treatment processes in the water supply plant at Site 4, additional purification processes such as adsorption and membrane filtration should be integrated into current processes or utilized in household tap water purifiers to reduce the chronic risks of PFOA in tap water. Furthermore, the exposure of PFOA in tap water includes various pathways such as cooking and washing. Therefore, more systematic surveys are required to estimate the likely exposures to PFCs and to reduce their environmental risks.

4   Conclusions

Six kinds of PFCAs and two kinds of PFASs were investigated in surface and tap water in Lake Taihu area to understand their behavior and risks to the local water environment. The conclusions are as follows:

1) PFOA and PFOS were the first and second predominant PFCs in surface and tap water samples around Lake Taihu. Concentration ranges of PFOA and PFOS were 6.8–206 and 1.2–45 ng·L^{-1}, with geometric means of 35.3 and 9.4 ng·L^{-1} respectively. Median (interquartile range) values of PFOA and PFOS were 31.4 (34.4) and 10.4 (10.7) ng·L^{-1} respectively. Other PFCs were detected in much lower concentrations.

2) PFOA in surface water was expected from direct industrial discharges, and cross correlation indicated that other PFCAs had common sources. PFOA contamination around Lake Taihu was considered as one source of the PFOA pollution in Shanghai district in the downstream.

3) The correlation analysis implied the dependence of PFOS on the locations. The PFC distributions in surface

water were different in the upstream, downstream and north part of Lake Taihu.

4) Occurrences of PFCs in tap water indicated their exposures to local people. Removal rates of aqueous PFOA and PFOS in the investigated water supply plant were only 18% and 27% respectively.

5) Brief estimation of environmental risks implied that PFCs in the water environment have no acute or immediate risks to local human health. However, chronic risks of PFOA in the tap water should be considered at the downstream locations in Lake Taihu area.

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