Bull Environ Contam Toxicol (2012) 89:519–524
DOI 10.1007/s00128-012-0745-1

Perfluorinated Compounds in Surface Water and Organisms from Baiyangdian Lake in North China: Source Profiles, Bioaccumulation and Potential Risk

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Received: 11 January 2012 / Accepted: 10 July 2012 / Published online: 21 July 2012

Abstract The concentrations of 16 perfluorinated compounds (PFCs) were measured in surface water and organisms from Baiyangdian Lake. Perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid, and perfluorobutanoic acid (PFBA) were the major PFC species in the water at 6.8–56.8, 0.1–17.5 and 3.0–14.6 ng/L, respectively. The PFC contamination in Baiyangdian Lake was significantly impacted by the inflow from Pinghe River and Fuhe River. There was no significant correlation between the concentrations of PFCs and the trophic levels in aquatic organisms. There were no significant PFC risks in Baiyangdian Lake according to the risk assessment of PFCs in water.

Keywords Perfluorinated compounds · Baiyangdian Lake · Surface water · Bioaccumulation · Risk assessment

Perfluorinated compounds (PFCs), such as perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), have been widely used in industrial and household products for over 50 years due to their high surface activities, thermal and chemical resistances, and hydro- and lipophobic properties (Kissa 2001). In May 2009, the Stockholm Convention has included perfluorooctane sulfonic acid (PFOS), along with its salts and perfluorooctane sulfonyl fluoride (POSF) in the list of persistent organic pollutants (POPs) (http://chm.pops.int/Programmes/NewPOPs/Publications/tabid/695/language/en-US/Default.aspx). PFCs have been found in biotic and abiotic matrices around the world including water, sediment, wildlife, human milk and serum (Kärrman et al. 2006; Senthilkumar et al. 2007). As one of the world's largest economies, environment issues in China are increasing with a rapid industrial development. Thus monitoring the extent of PFC pollution has become necessary. After the 3 M product phase-out in 2002, China has still been reported to continue producing perfluorooctanesulfonyl fluoride (POSF), and the annual production of POSF increases dramatically. In China, the annual production of POSF in 2007, 2008 and 2009 was 195, 250, and 300 tons, respectively, and about half of the POSF was used domestically (Lim et al. 2011). Wang et al. (2010) have found high levels of PFCs from a manufacturing plant and the ambient environment in China, which indicates that the production site is the primary source of PFCs in that region. The identifications of PFCs in several aquatic environments in China have been reported, including coastal seawaters of Hong Kong, Pearl River Delta (So et al. 2004), Dalian Coastal waters (Ju et al. 2008), Hun River and Liao River (Yang et al. 2011). However, most studies have focused on the point source (the ambient environment around facilities manufacturing and/or consuming PFCs), marine, and estuary environment.

Lakes are special nature waters that are different from rivers and seas because of the unusually slow exchange of water. Contaminants in the atmosphere and land can be received by lakes, and persist for a long time. Therefore, it is important to investigate the levels of PFCs in lakes and their risks to wildlife in the lakes. Yang et al. (2011) have determined the distributions of PFCs in water and sediment in Taihu Lake, which is the second largest freshwater lake

Electronic supplementary material The online version of this article (doi:10.1007/s00128-012-0745-1) contains supplementary material, which is available to authorized users.

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in China. But reports on the identification of PFCs from lakes in China are few. Baiyangdian Lake is the largest natural freshwater body in the North China Plain. It covers a surface area of 366 km^2 and a catchment of 31,200 m^2. It is not only a crucial reservoir but also an important production base of freshwater aquacultures. It is well known as the "pearl of North China" due to its beautiful scenery and rich water resources. In the present study, the PFC contamination and bio-accumulation were investigated in Baiyangdian Lake as a representative of lakes in China. Meanwhile, point/nonpoint source phenomena of PFCs, such as upstream pollution, point source discharge, and population density (human activities), were also evaluated.

Materials and Methods

Twenty-six surface water samples were collected in October 2010, of which 21 (S1–S21) were from Baiyangdian Lake and five (R1–R5) were from four upstream rivers of Baiyangdian Lake, including Baigouyin River, Pinghe River, Fuhe River, and Tanghe River. The sampling sites are shown in Fig. 1. Nine kinds of biological samples were collected from Baiyangdian Lake, including plankton (n = 1, site S4), ceratophyllum demersum (*Ceratophyllum demersum L.*, n = 4, sites S4, S9, S11, and S23), salvinia natans (*Salvinia natans* (*L.*) *All.*, n = 3, sites S9, S11, and S23), shrimp (*Macrobrachium nipponense*, n = 1, site S10), crab (*Eriocheir sinensis*, n = 1, site S10), river snail (*Viviparus*, n = 1, site S10), loach (*Misgurnus anguillicaudatus*, n = 1, site S10), common carp (*Cyprinus carpio*, n = 4, sites S9, S10, S11, and S18), and Chinese pond heron (*Ardeola bacchus*, n = 4, sites S9, S10, S11, and

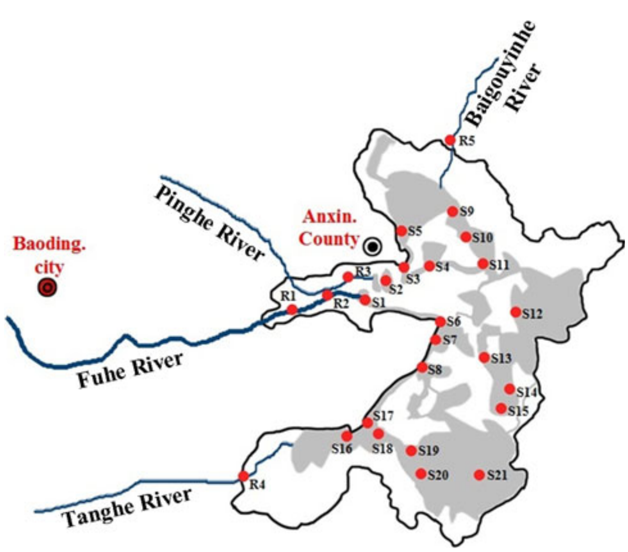

Fig. 1 Sampling locations of Baiyangdian Lake for the study

S18). The common floating aquatic plants were washed and homogenized as one pooled sample for each species, which was collected from each sampling site. Due to their small sizes, shrimp, crab, river snail, and loach were pooled with more than five animals and homogenized in whole body. Common carp and Chinese pond heron were dissected to obtain muscle tissues. All samples were stored in an icebox after collection and transported to the laboratory. Water was kept at 4°C, and the other samples were frozen and kept at −20°C until further analysis.

A total of 500 mL of water sample was spiked with 2 ng of $^{13}C_4$-PFOS and 2 ng of $^{13}C_4$-PFOA as internal standards. Then the samples were passed through Oasis WAX cartridges preconditioned with 0.5 % ammonium hydroxide (in methanol), methanol and Milli-Q water. The target compounds were eluted with 4 mL of methanol and 4 mL of 0.5 % ammonium hydroxide (in methanol) at a flow rate of one drop per second. Finally, the eluate was concentrated to 1 mL under nitrogen before injection.

Biological samples were homogenized and freeze-dried. Approximately 0.2 g of solid was spiked with 2 ng of $^{13}C_4$-PFOS and 2 ng of $^{13}C_4$-PFOA as internal standards. The sample was sonicated at 60°C for 30 min in 10 mL of 10 mM KOH (in methanol), shaken at 250 rpm for 16 h, and then centrifuged. The supernatant was concentrated to 1–2 mL under nitrogen and then diluted with 50 mL water. The dilution was loaded onto a preconditioned Oasis WAX cartridge. Samples were then treated with the same procedures as those for treating water samples.

Sample analyses for the sixteen PFCs were accomplished with a high performance liquid chromatograph equipped with an electrospray ionization tandem mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, US) (HPLC-ESI/MS/MS) operated in negative mode. The separation was achieved on an Acclaim 120 C18 column (5 µm, 4.6 mm i.d. × 150 mm length; Dionex, Sunnyvale, CA, USA) with an aliquot of 10 µL injection. A 10 min dualistic gradient of 0.1 % ammonium hydroxide (in methanol) and 50 mM NH_4OAc at a flow rate of 1.0 mL/min was optimized as follows: initiated at 28 % 50 mM NH_4OAc, and reduced NH_4OAc to 5 % at 4 min before returning to the original condition at 7 min. Then the quantitative analyses were conducted using ESI/MS/MS.

Procedural blanks were conducted for every ten samples to check for possible laboratory contamination and interferences, and the values of blank were all lower than MLQs. The samples were spiked with 2 ng of target standards and aged for 2 h before treated with procedures described above. The mean recoveries of PFCs spiked into water and biological samples were 78 %–117 % and 75 %–131 %, respectively. Sample concentrations were quantified based on a nine-point standard calibration curve

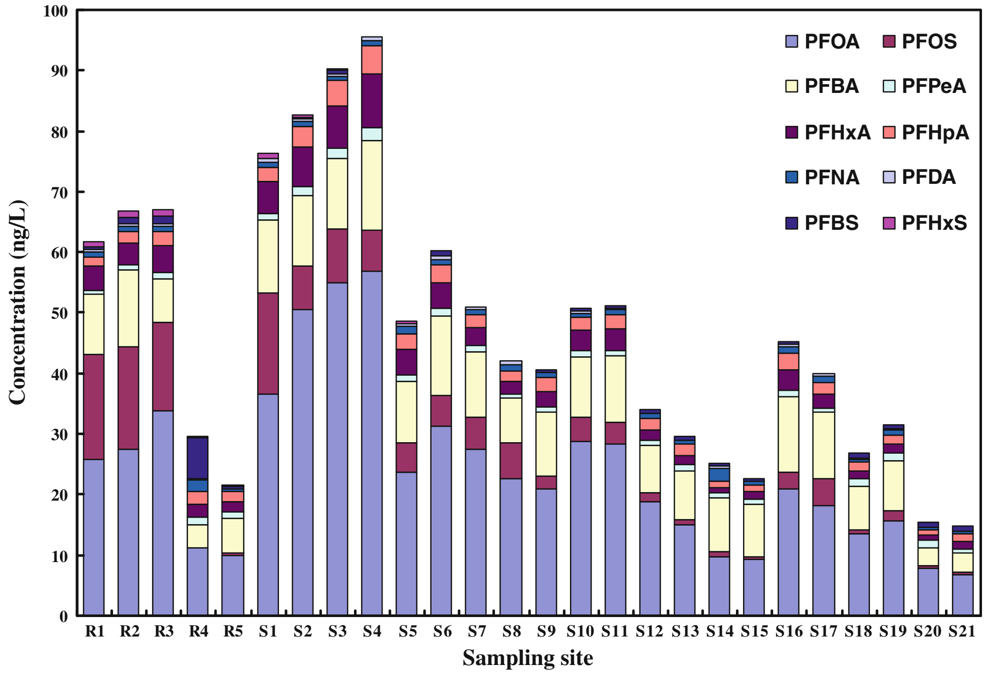

Fig. 2 Distribution of PFCs in surface water samples from Baiyangdian Lake and four upstream rivers

(50, 100, 200, 500, 1,000, 2,000, 5,000, 20,000, 50,000 ng/L). Method limit of quantifications (MLQs) were determined at the lowest concentration resulting in a signal-to noise ratio (S/N) $\geq$10, which were 0.1 ng/L for water samples, 0.5 ng/g dry weight for aquatic floating plants, and 0.25 ng/g dry weight for plankton and animal samples. A PFC standard at 1,000 ng/L was checked after every 10 injections during the analysis for calibration verification.

Results and Discussion

A total of 16 PFCs were measured in Baiyangdian Lake and four upstream rivers (ESM: Table S1). However, the concentrations of six PFCAs (PFUnDA, PFDoDA, PFTrA, PFTeDA, PFHxDA, and PFOcDA) were all lower than MLQs. Therefore, results for these chemicals were not discussed in the present study. In water samples, C4–C9 PFCAs and PFOS were detected in all the samples analyzed, except PFDA (76.9 % detected), PFBS (76.9 % detected), and PFHxS (50 % detected). The concentration of total PFCs ranged from 14.8 to 95.6 ng/L in water, with a predominance of perfluorooctanoic acid (PFOA) (6.8–56.8 ng/L), which generally accounted for 37.8 %–61.1 % of total PFCs. Concentrations of PFOS and perfluorobutanoic acid (PFBA) in water were 0.1–17.5 and 3.0–14.6 ng/L, respectively. Lower concentrations were found for PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFBS and PFHxS, with the maximum concentrations of 2.1, 9.0, 4.6, 2.2, 0.6, 6.7 and 1.0 ng/L, respectively.

The distribution of PFCs in surface water samples from Baiyangdian Lake and four upstream rivers is shown in Fig. 2. The concentrations of PFBA at all sites were similar, except that relative lower levels were found at sites R4, R5, S20, and S21. The levels of PFPeA, PFNA, PFDA, PFBS, and PFHxS were similar at all sites. However, in Baiyangdian Lake, the highest concentrations of the two predominant PFCs, PFOA and PFOS, were found in samples from S4 (56.8 ng/L PFOA) and S1 (16.6 ng/L PFOS), respectively. These two sites were near the Anxin County and the entrances of Pinghe River and Fuhe River. Similarly, the concentrations of PFHxA and PFHpA at sites S1–S4 were slightly higher than those at other sampling sites. In the four upstream rivers, the concentrations of PFOA and PFOS at R1–R3 (25.7–33.8 ng/L PFOA, 14.7–17.5 ng/L PFOS) were significantly higher than those at R4–R5 (9.9–11.2 ng/L PFOA, 0.1–0.5 ng/L PFOS). Sites R1–R3 were located in the estuary of Pinghe River and Fuhe River, and sites R4–R5 were located in the estuary of Tanghe River and Baigouyin River. The concentrations of PFOA at S1–S4 from Baiyangdian Lake were comparable to those at R1–R3 from Pinghe River and Fuhe River, while the concentrations of PFOS in Baiyangdian Lake were lower than those in the two rivers. The concentrations of PFOA and PFOS decreased significantly in lake water with an increasing distance from sampling sites to Anxin County and the entrance of the two rivers. The results indicated that the discharges of Pinghe River and Fuhe River were potential sources of PFCs contamination in Baiyangdian Lake. Pinghe River and Fuhe River flow through a medium-sized city in which many paper, printing and dyeing, leather manufacture, and chemical and pesticide industries reside. Hu et al. (2010) have investigated the occurrence and spatial distribution of other environment pollutants such as polybrominated diphenyl ethers (PBDEs) and decabromodiphenylethane (DBDPE) in Baiyangdian Lake and Fuhe River, and shown that the level of contamination in Fuhe River is significantly higher than those in Baiyangdian Lake. The total area of Baiyangdian Lake is 366 km^2, and 85 % of water body is covered by Anxin County with large amount of anthropogenic activities and several industries. According to our data, it was evident that PFCs in Baiyangdian Lake partly resulted from the human and industrial activities in Anxin County. Furthermore, we concluded that the discharges of Pinghe River and Fuhe River were responsible for the PFC contamination in Baiyangdian Lake.

A Spearman rank correlation analysis of various PFCs from all the sampling locations was conducted. Significant positive correlations were observed among PFOS and other even-chain PFCAs and PFSAs, including PFBA, PFOA, PFHxA, PFDA and PFHxS. This result indicated the possibility of a common pollution source for these chemicals in Baiyangdian Lake. Significant correlations were also found among most of the PFCAs. Our data supported the hypothesis that there might be indirect sources of contamination, such as chemical impurities released to the environment after the manufacture of POSF, or after the breakdown of precursors such as telomere alcohols (FTOHs) (Paul et al. 2009).

Of the 16 PFCs (13 PFCAs and 3 PFSAs) analyzed, all but PFHxDA and PFOcDA were detected in biological samples (ESM: Table S2). Four even-chain PFCs, including PFHxA, PFOA, PFDA, and PFOS, were detected in all biological species. Total PFCs in the biological samples ranged from 14.53 to 109.87 ng/g dry weight, with the lowest concentration found in plankton and the highest concentration found in shrimp. Concentrations of PFOS and PFOA were 6.70–69.86 and 2.07–16.84 ng/g dry weight, respectively. Consistent with the results from previous reports, PFOS was the predominant compound in biological samples except for loach (ESM: Fig S1). PFOS contributed to more than 40 % of the total PFCs in almost all biological samples, except that PFOS accounted for less than 20 % and PFOA accounted for more than 40 % of the total PFCs in loach. The highest levels of PFOS were observed in common carp (69.86 ng/g dw), and the highest levels of PFOA were observed in loach (16.84 ng/g dw). The highest concentration of PFHxA (31.39 ng/g dw) was detected in river snail, which was much higher than the mean levels of PFHxA (7.82 ng/g, dw) in all nine species. PFDA was found in all samples, ranging from 0.76 to 14.11 ng/g dry weight. Unlike in water samples, PFUnDA (C11), PFDoDA (C12), PFTrA (C13), and PFTeDA (C14), PFCAs with longer chains, were detected in biological samples, and the highest levels were 7.83 (in crab), 2.59 (in common carp), 2.04 (in common carp), and 1.48 (in loach) ng/g dry weight, respectively. It was suggested that the K_{OW} of PFC increases with an increasing perfluorinated chain length or molecular size (Wang et al. 2011). Long chain PFCAs have lower free energy costs for cavity formation, and are easier to partition into the organic phase (sediment, sludge, and organism). Therefore, PFCAs with longer chains were detected in biological samples rather than in water samples. In generally, the lowest levels of PFCs were found in plankton in all biological species.

Bioaccumulation factors (BAFs) were used to investigate the accumulation of pollutants in organisms. BAF is defined as the ratio of the concentrations of PFCs in tissues (ng/kg, ww) and the concentrations in the dissolved phase of water (ng/L). BAFs were calculated independently site-to-site by concentrations in aquatic organisms and the water (Table 1). PFDA had the highest mean logBAFs (4.25), followed by PFOS (3.75), PFNA (3.55), PFUnDA (3.52) and PFHxA (3.12). The lowest logBAFs were found for PFOA (1.77–2.78), which is comparable to those from previous report (2 for fish from Charleston) (Houde et al. 2006). In our study, the LogBAFs for PFOS ranged from

Table 1 Bioaccumulation factors (BAFs, presented as LogBAFs) for aquatic organisms in Baiyangdian Lake

	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFOS
Common carp	3.07	2.26	3.53	4.24	3.44	4.07
Loach	2.60	2.77	3.80	3.88	3.45	3.23
Crab	3.61	2.32	3.23	4.47	3.89	3.99
Shrimp	3.31	2.56	3.96	4.49	3.63	4.20
River snail	3.96	2.50	3.98	4.27	2.34	3.92
Ceratophyllum demersum	3.51	2.61	3.65	4.75	4.46	3.91
Salvinia natans	2.34	2.78	3.78	4.84	4.22	3.98
Plankton	2.59	1.77	2.48	3.09	2.77	2.68
Average (SE)	3.12 ± 0.20	2.45 ± 0.12	3.55 ± 0.18	4.25 ± 0.20	3.52 ± 0.25	3.75 ± 0.18

2.68 to 4.20, consistent with the values in Lake Trout from the Great Lakes (Furdui et al. 2007). It was determined that there was higher accumulation potential for long-chain PFCAs and PFOS in aquatic organisms (Martin et al. 2003). The differences in logBAFs reflect different capacities to bio-accumulate and metabolize PFCs in various species. In addition, trophic levels (TLs) of each aquatic organism were calculated using the previously defined relationship, derived from the stable isotope ratio of nitrogen δ^{15}N for the consumer and first trophic level plankton: $TL_{consumer} = 2 + (\delta^{15}N_{consumer} - \delta^{15}N_{plankton})/3.4$. There was no significant correlation between concentrations of PFCs and TLs in aquatic organisms from Baiyangdian Lake, although the lowest logBAFs was found in plankton. However, statistically significant relationships between trophic level and logarithmic concentrations were found for PFCs in terrestrial food webs (Muller et al. 2011). In the present study, BAFs were tested using concentrations from whole body and specific tissue (muscle), which possibly impacted the inter-comparison among species. Moreover, the aquatic organism species were collected randomly with no standard food source, which may introduce additional variations, hamper food web, and influence the TL values.

The concentrations of PFOS in water samples from Baiyangdian Lake were comparable to those measured in the Pearl River Delta region (So et al. 2004), but were much higher than those measured in Hun River, Liao River, coastal seawaters in Dalian (Ju et al. 2008) and Hong Kong (So et al. 2004). The concentrations of PFOA obtained in the present study were generally higher than those measured in Hong Kong (So et al. 2004), Dalian (Ju et al. 2008), Hun River, Liao River and the Pearl River Delta region (So et al. 2004). Tai Hu is the second largest freshwater lake in China with high PFOS (3.6–394 ng/L) and low PFOA (10.6–36.7 ng/L) levels (Yang et al. 2011). Comparing with results from researches in other countries, the mean concentrations of PFOS and PFOA in water samples in our study were both higher than those observed in Lake Ontario, Lake Erie, Finger Lakes, Lake Champlain and Lake Shihwa, but lower than those observed in Lake Onondaga (Rostkowski et al. 2006; Sinclair et al. 2006).

According to the 2011 Edition of the Drinking Water Standards and Health Advisories in USEPA, the Health Advisory values of PFOS and PFOA concentration in drinking water are provisionally set at 200 and 400 ng/L, respectively. The Health Protection Agency (HPA) advises that the maximum acceptable concentration of PFOS and PFOA in drinking water is 300 and 10,000 ng/L, respectively. In the present study, all of the concentrations of PFOS and PFOA in water samples from Baiyangdian Lakes were lower than the values advised by USEPA and HPA. However, the results of three out of the 26 samples (S2, S3 and S4) exceeded the New Jersey guidance for PFOA in drinking water, which recommended that 40 ng/L should be used as preliminary health-based guidance. S2, S3 and S4 are tourist attractions very close to Anxin County with large amount of anthropogenic activities. Although the water from Baiyangdian Lake is not used as drinking water, the levels of contaminant are noteworthy concerning the risk of PFCs in aquatic ecosystem in the region.

Acknowledgments This work was jointly supported by the National Natural Science Foundation of China (No. 41023005, 20907063, 20890111), State Environmental Protection Welfare Scientific Research Project (201009026) and the National Basic Research Program of China (2009CB421605).

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