

Perfluorinated Compounds in Water, Sediment and Soil from Guanting Reservoir, China

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Abstract Concentrations of 12 perfluorinated compounds (PFCs) were measured in 21 representative water, sediment and soil samples from Guanting Reservoir and vicinity. Perfluorooctanoic acid (PFOA) was the predominant PFCs with concentrations of 0.55–2.3 ng/L, <LOQ to 0.68 ng/g dw and <LOQ to 2.8 ng/g dw in water, sediment and soil, respectively. Perfluorododecanoic acid (PFDoA) was frequently detected in solid matrices, with concentrations of <LOQ to 0.18 ng/g dw in sediment and 0.13–0.26 ng/g dw in soil. PFCs were detected in all environmental matrices sampled, but concentrations found throughout the watershed were less than those reported from other locations.

Keywords PFOS · PFOA · Exposure · Composition · Risk · Hazard

Due to their unique amphiphilic properties, perfluorinated compounds (PFCs) have been used in a variety of applications such as surfactants and surface protectors (Kissa 2001; Giesy and Kannan 2002). Widespread application as well as environmental persistence and bioaccumulation of terminal degradation products of PFCs has resulted in global occurrence in air (Dreyer 2009; Chaemfa et al. 2010); water and sediment (Rayne and Forest 2009); as well as wildlife (Houde et al. 2006).

Guanting Reservoir (GTR) is Beijing's second largest source of water for agricultural and industrial purposes, and was also used for drinking water until 1997. Since then, industrial pollution and contamination from farming have substantially degraded the quality of water in this reservoir. Contaminations of HCH, DDT, PAHs and metals and metalloids in water, sediment and soil from this watershed were reported in previous studies (Wang et al. 2005; Luo et al. 2007; Jiao et al. 2009). Previous reports have focused on traditional persistent toxic substances (PTS) with little information available for emerging PTS such as PFCs. Concentrations of PFCs in environmental matrices surrounding GTR are scarce. Hence there was a need for a thorough investigation and assessment of PFCs in water, sediment and soil around GTR, to determine the critical contaminants and their sources, so that GTR can be rehabilitated. The objectives of this study were to determine concentrations and distribution of PFCs in environmental matrices to identify potential sources, and thus provide information for future management and remediation efforts in the GTR.

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Materials and Methods

Each of seven of waters, soils and sediments, totaling 21 samples, were collected from the GTR and surrounding area during May of 2008 (Fig. 1). One liter of surface water was collected by dipping a clean, methanol-rinsed 1 L polypropylene (PP) bottle just under the surface of the water. Residual chlorine in each water sample was reduced by adding 200 μL of 200 mg/mL of a sodium thiosulfate solution using a disposable PP syringe. Surface (top 1–10 cm) soil and sediment samples were collected using a clean methanol rinsed stainless steel trowel. Representative composites were prepared by mixing five sub-samples from the area of about 5 m². Samples were transferred and stored in clean PP bags. Sample duplicates and field blanks were collected daily, and were analyzed along with laboratory and procedural blanks. All samples were stored on ice for transport to the laboratory and frozen at -20°C until analyses.

Water samples were extracted using Oasis HLB solid phase extraction cartridges (0.2 g, 6 cm³) (Waters Corp., Milford, MA) as previously reported (So et al. 2004). Cartridges were preconditioned by eluting with 10 mL of 100% methanol followed by 10 mL of nano-pure water at a rate of 2 drops a second. A 500 mL aliquant of water was spiked with 500 μL of 5 ng/mL of the internal standard (PFOS [¹⁸O₂] and PFOA [1,2,3,4-¹³C], >98%, (Wellington Laboratories, Guelph, ON, Canada) and then loaded onto the cartridge, at a rate of 1 drop a second. Cartridges were then washed with 5 mL of 40% methanol in water and allowed to run dry. Target compounds were eluted with 10 mL of methanol at a rate of 1 drop per second and collected in a 15 mL PP centrifuge tube. The eluate was then reduced to 1 mL under a gentle stream of nitrogen

gas, and filtered using a disposable PP syringe, fitted with nylon membrane Millex filter unit (pore diameter 0.2 μm , Whatman, Maidstone, United Kingdom). Soils and sediments were extracted using a method similar to that described by Higgins et al. (2005). Samples were freeze-dried, homogenized and passed through a 2.0 mm sieve. Approximately 1.0 g samples were transferred to a clean 50-mL PP centrifuge tube, and spiked with 500 μL of a 5 ng/mL internal standard, to which 10 mL of a 1% acetic acid solution was added. Each tube was then vortexed, and placed in a heated sonication bath for 15 min at 60°C. After sonication the tubes were centrifuged at 3,000 rpm for 3 min and the acetic acid solution was decanted into a new clean 50-mL PP tube. An aliquant of 2.5 mL of a 90:10 (v/v) methanol and 1% acetic acid mixture was then added to the original vial and the vial was again vortex mixed and sonicated for 15 min, before being centrifuged and decanted into the second tube. This process was repeated once more, and a final 10 mL acetic acid wash was preformed. All extracts were combined in the second tube before being passed through the SPE cartridge in a similar fashion as described above in the water extraction procedure. Sample extracts were stored and analyzed in PP auto-sampler vials.

A HP 1200 (Agilent Technologies) high performance liquid chromatography system (HPLC) was used for separation of all target analytes. The HPLC was fitted with a Thermo Scientific Betasil C₁₈ (100 $\times$ 2.1 mm, 5 μm particle size) analytical column, and a suitable guard column was used to prevent instrument and elute background contamination. Ammonium acetate (2 mM) was added as an ionization aid to methanol which was used as the mobile phases. Gradient conditions were as follows: Flow rate of 300 mL/min; 10 μL injection volume; Gradient began with 60% A (2 mM ammonium acetate) and 40% B (100% methanol) and was held for 2 min and then ramped to 20% A at 18 min, held until 20 min, decreased to 0% A at 21 min, increased to 100% A at 22 min, held until 22.5 min, returned to initial conditions at 23 min, and finally held constant until 26 min. The temperature of the column oven was kept constant at 35°C. Mass spectra were collected using an Applied Biosystems SCIEX 3000 (Foster City, CA) tandem mass spectrometer, fitted with an electrospray ionization source, operated in negative ionization mode. Chromatograms were recorded using a multiple reaction monitoring mode (MRM) with a dwell time of 40 ms. The following instrument parameters were used: desolvation temperature (450°C), desolvation (curtain) gas 6.0 arbitrary units (AU); nebulizer gas flow 5 AU; ion spray voltage $-3,500$ V; and collision gas 12 AU. The optimal settings for collision energies and declustering potential were determined for each analyte's transitions.

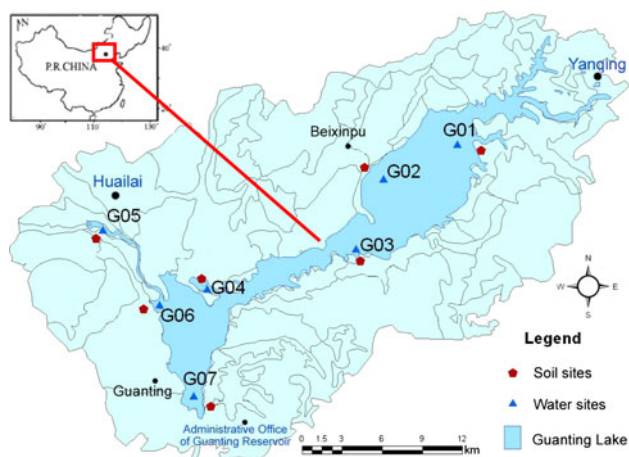


Fig. 1 Sampling locations for soil samples (filled circle), water and related sediment (filled triangle) around the Guanting Reservoir, China

In order to ensure accuracy of sampling, extraction, and analytical procedures, field blanks were obtained and analyzed with each set of water samples analyzed. Procedural blanks and recoveries were determined for each set of extractions. Quantification was performed using the internal standard method based on $^{18}\text{O}_2$ -PFOS and $^{13}\text{C}_4$ -PFOA as the surrogate. All field and laboratory blanks were less than the limit of quantification (LOQ), where the LOQ was defined as 5 times the background noise. The use of Teflon[®]-coated lab-ware was avoided during all steps of sample preparation and analysis to minimize contamination of the samples. HPLC grade methanol and ammonium acetate were purchased from J.T. Baker (Phillipsburg, NJ, USA). Analytical grade sodium thiosulfate was purchased from EMD Chemicals (Gibbstown, NJ, USA). The ions monitored, method detection limit (MDL), and matrix spike recoveries for all of the chemicals of interest are summarized (Table 1).

Results and Discussion

Although 12 PFCs were investigated, only six, PFOS, PFOA, perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA) and perfluorohexanoic acid (PFHxA) were detected in water from GTR, PFOS and PFOA were the predominate PFCs in water (Table 2). Concentrations of PFOS and PFOA ranged from <LOQ to 0.52 ng/L and from <LOQ to 2.3 ng/L, respectively. The greatest and second greatest concentrations of Σ PFCs (3.1 and 3.0 ng/L) occurred at locations G2 and G4, with correspondingly greater concentrations of PFOS and PFOA. The greatest concentration of PFOA

(2.3 ng/L) and relatively greater concentrations of PFOS (0.34 ng/L) were observed at G2. This sample was collected from a river in the Beixinpu region, which has intensive agricultural activities (Orchard and facility agriculture) with significant pesticide applications every year. Greater concentrations of HCH, DDT and heavy metals were also observed in soils near this location (Wang et al. 2005; Luo et al. 2007), which suggests local sources of pollution from agricultural run-off. Location G4, is in a wetland catchment used to treat industrial and agricultural runoff from the Yanghe River. The greatest concentration of PFOS (0.52 ng/L) and greater concentrations of PFOA (1.8 ng/L) observed at location G4 most likely resulted from local releases of treated sewage effluents.

Compared to the results of previous studies, concentrations of PFOS and PFOA in water from GTR were slightly greater than those from the offshore of Japan (0.04–0.07 and 0.14–1.1 ng/L) and oceanic samples including the Western Pacific Ocean (0.054–0.078 and 0.136–0.142 ng/L), Central to Eastern Pacific Ocean (0.001–0.02 and 0.015–0.062 ng/L) and North Atlantic Ocean (0.009–0.036 and 0.160–0.338 ng/L) (Yamashita et al. 2005), while either comparable to or less than those detected in Yichang (0.29–0.61 and 4.1–4.9 ng/L), Nanjing (0.33–0.38 and 2.1–2.4 ng/L) and Hong Kong (0.09–3.1 and 0.73–5.5 ng/L) in China (So et al. 2004, 2007) and South Korea coast (0.04–2.53 and 0.24–11.4 ng/L) (Yamashita et al. 2005). In the present study, maximum concentrations of PFOS (0.52 ng/L) and PFOA (2.3 ng/L) were several orders of magnitude less than those measured in Tokyo Bay, Japan (0.78–17 and 2.7–63 ng/L) and the Korea coast (4.11–450 and 2.95–68.6 ng/L) (Naile et al. 2010; Sakurai et al. 2010). Although PFOS and PFOA were the predominant

Table 1 Quality assurance of 12 target PFCs including limit of quantification (LOQ), method detection limit (MDL) and matrix spike recovery (MSR) for water, sediment and soil

Analyte	Acronym	LOQ		MDL		MSR	
		W (ng/L)	S (ng/g)	W (ng/L)	S (ng/g)	W (%)	S (%)
Perfluorobutanesulfonate	PFBS	0.5	1	1	1	94	32
Perfluorohexanesulfonate	PFHxS	0.1	0.5	0.2	0.5	136	134
Perfluorooctanesulfonate	PFOS	0.1	0.5	0.2	0.5	101	95
Perfluorodecanesulfonate	PFDS	0.1	0.5	0.2	0.5	101	43
Perfluorobutanoic acid	PFBA	1	1	2	1	120	IS
Perfluorohexanoic acid	PFHxA	0.5	0.1	1	0.1	85	79
Perfluoroheptanoic acid	PFHpA	0.5	0.1	1	0.1	103	123
Perfluorooctanoic acid	PFOA	0.5	0.5	1	0.5	88	89
Perfluorononanoic acid	PFNA	1	1	2	1	132	135
Perfluorodecanoic acid	PFDA	0.1	0.1	0.2	0.1	93	106
Perfluoroundecanoic acid	PFUnA	1	0.5	2	0.5	112	53
Perfluorododecanoic acid	PFDoA	1	0.1	2	0.1	77	70

W water; S soil and sediment; IS Insufficient recovery

Table 2 Concentrations of PFCs in water, sediment and soil samples collected in the Guanting Reservoir area

Sample	PFOS	PFOA	PFHpA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFCs
Water (ng/L)									
G1	nd	1.1	nd	nd	nd	nd	nd	nd	1.1
G2	0.34	2.3	0.22	nd	nd	nd	0.19	nd	3.1
G3	nd	1.1	nd	nd	nd	nd	nd	nd	1.1
G4	0.52	1.8	0.19	nd	0.23	nd	0.19	nd	3.0
G5	0.14	0.88	nd	nd	nd	nd	0.14	0.19	1.4
G6	nd	0.68	nd	nd	0.18	nd	0.29	nd	1.2
G7	0.15	0.55	nd	nd	nd	nd	nd	nd	0.70
Sediment (ng/g dw)									
GS1	nd	0.47	nd	nd	0.21	nd	nd	nd	0.68
GS2	nd	nd	nd	nd	nd	0.18	0.14	nd	0.32
GS3	nd	0.57	nd	nd	0.22	nd	0.09	nd	0.88
GS4	nd	nd	nd	nd	nd	0.12	0.15	nd	0.27
GS5	nd	0.21	nd	nd	nd	nd	0.18	nd	0.39
GS6	nd	0.68	0.35	nd	0.49	nd	0.09	nd	1.6
GS7	nd	nd	nd	nd	0.16	nd	nd	0.53	0.69
Soil (ng/g dw)									
GL1	nd	nd	nd	nd	nd	nd	0.19	nd	0.19
GL2	0.86	2.8	1.2	1.4	1.9	0.24	0.13	nd	8.5
GL3	nd	nd	nd	nd	nd	nd	0.13	nd	0.13
GL4	nd	nd	nd	nd	nd	0.10	0.17	nd	0.27
GL5	nd	nd	nd	nd	0.17	0.24	0.26	nd	0.67
GL6	nd	nd	nd	nd	nd	0.32	0.19	nd	0.51
GL7	nd	nd	0.11	nd	nd	0.23	0.13	nd	0.47

nd not detectable, means concentration less than LOQ

PFCs detected in water samples, PFDoA was detected in approximately 60% of the samples analyzed at concentrations greater than the LOQ, but concentrations of PFDoA were generally less than those of PFOS and PFOA, with a threshold of nd 0.29 ng/L. This indicates that in addition to PFOS and PFOA, PFDoA should be considered in future monitoring and risk assessments.

Concentrations of PFCs in sediments from GTR were generally less than the corresponding MDLs (Table 2). Total concentrations of PFCs ranged from <LOQ to 1.6 ng/g dw. Only PFOA, PFDA, PFUnA, PFDoA and in a few samples, PFHpA and PFHxS were detected in sediments. PFOA was the dominant PFC observed in sediments with concentrations ranging from <LOQ to 0.68 ng/g dw. The greatest concentration of PFOA was observed at location G6, which is at the mouth of the Yanghe River where it enters GTR. However, concentrations of PFOA and PFOS in sediments at locations G2 and G4 were all less than the LOQ, which suggests that further studies characterizing transportation and fate between water and sediment are needed. Compared to the results of previous studies, concentrations of PFOA in sediments from GTR were comparable to those from the Huangpu River

(0.20–0.64 ng/g dw) and the Zhujiang River (0.09–0.29 ng/g dw), China (Bao et al. 2010), and San Francisco Bay, USA (0.16–0.23 ng/g dw) (Higgins et al. 2005), whereas they were less than those of the Kyoto River, Japan (nd 3.9 ng/g dw) (Senthilkumar et al. 2007).

Releases from various PFCs sources not only contaminate surface waters but it also has the ability to contaminate soils and sediments. PFOS and PFOA have been shown to absorb onto sediment and sludge (Higgins et al. 2005). Therefore, soils could be another sink for PFCs. Previous studies have reported concentrations of PFCs in water, sediment and biota. However, there are few reports of the occurrence, distribution, sources and risks of PFCs in soils, especially in watersheds that are used as a source of drinking water. Concentrations of PFCs in soils were generally less than the LOQ, and only one location (G2) contained detectable PFOS, PFOA, PFHpA, PFNA, PFDA, PFUnA and PFDoA, with values of 0.86, 2.8, 1.2, 1.4, 1.9, 0.24, 0.13 ng/g dw, respectively. Again, the pervasive PFCs observed in water and soil at location G2 suggests possible input either from soil to surface water by runoff or from surface water to soil by irrigation. PFDoA was detected in 100% of soils (Table 2), with concentrations

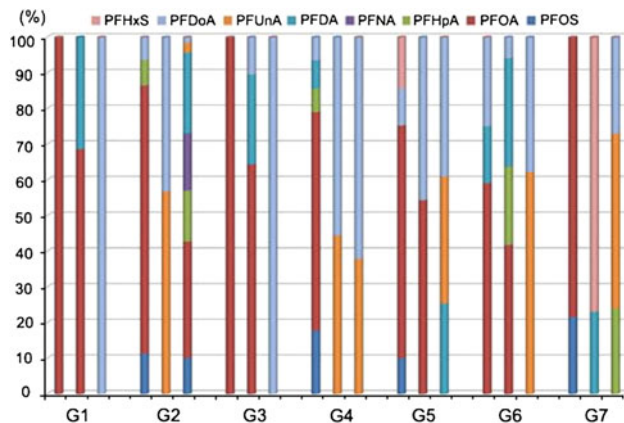


Fig. 2 Composition profile of various PFCs in samples from the Guanting Reservoir (water, sediment and soil from left to right in each cluster)

ranging from 0.13 to 0.26 ng/g dw. The results are consistent with the fact that PFDoA being found in waters and sediments, all of which suggest a regional source of PFDoA. There was no significant difference in trends in concentrations of PFCs between soils and sediments. In general, soils and sediments in the GTR contained small amounts of PFCs. In terms of matrix-dependent accumulation of PFCs, the results of the present study were similar to those observed previously in South Korea (Naile et al. 2010).

Profiles of relative concentrations of 8 detectable PFCs are shown (Fig. 2). Samples from the GTR region exhibited completely different profiles among water, sediment and soils. The ratio of the concentrations of PFOS to PFOA in water has been applied to identify potential sources of PFCs. The observation that PFOS/PFOA ratios in water from GTR were less than 1.0 is consistent with the results of values observed in South Korea, coastal China, and Hong Kong (So et al. 2004, 2007). However, the ratios were different from those reported by Naile et al. (2010) and Rostkowski et al. (2006), which were typically greater than 1.0. This indicates local sources of PFOA exist in the study area. PFOA was the dominant PFC in water, contributing 58%–100% of $\sum$ PFCs, while the relative contributions of PFOS and other PFCs were less. PFOA was the predominant PFC in sediments as well, contributed up to 68% of $\sum$ PFCs at location G1. Greater contributions of PFUnA and PFDoA were observed at locations G2 (54% and 46%) and G4 (42% and 58%), because neither PFOA nor PFOS were measured at these locations. Relatively large portions of $\sum$ PFCs were contributed by PFDoA and PFUnA in soils except for location G2, while concentrations of PFDoA and PFUnA were relatively small compared to other detectable PFCs. This result indicates the existence of potential sources of PFDoA and PFUnA in the study area.

Recently, Giesy et al. (2010) calculated suggested criteria maximum concentrations (CMC) for sensitive aquatic species, such as *Daphnia magna* for PFOS (21 μ g/L) and PFOA (25 mg/L), and criteria continuous concentration (CCC) for PFOS (5.1 μ g/L) and PFOA (2.9 mg/L), as well as avian wildlife values (AWV) for PFOS (47 ng/L). Concentrations of PFOA and PFOS in surface water of the GTR region (all ng/L level) were less than the suggested allowable concentrations to protect aquatic life. While the results indicate negligible risk to aquatic wildlife, several uncertainties on the toxicities of PFCs at less concentration exist.

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