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Seasonal Changes of PFOS and PFOA Concentrations in Lake Biwa Water

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Abstract A survey on seasonal concentration changes of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) was performed for surface water in Lake Biwa (14 sites) from February to November in 2009. The concentrations of PFOS and PFOA were 0.8–1.6 and 7.0–10 ng/L in northern basin of Lake Biwa (eight sites), 0.9–1.7 and 8.3–13 ng/L in southern basin of Lake Biwa except Akanoi Bay (four sites), 1.4–2.8 and 9.1–17 ng/L in Akanoi Bay (8C) and 2.4–5.3 and 12–26 ng/L in Akanoi Bay (168), respectively. Seasonal changes were recognized for both of PFOS and PFOA in the two sites of Akanoi Bay but not in the other sites of the southern and northern basins of Lake Biwa. Monthly detailed surveys in the surface water were performed on the changes of PFOS and PFOA concentrations from June in 2009 to May in 2010 and further on the changes of conductivity values. The changes of PFOS and PFOA concentrations were well consistent with those of conductivity values.

Keywords PFOS · PFOA · Lake Biwa · Water

Perfluorinated compounds (PFCs) have been used as important components of many common industrial and commercial applications, including stain repellents, corrosion inhibitors, surfactants, fire-fighting foams and photolithographic film for more than 50 years. The PFCs have been found to be stable in the environment and further it has become apparent that perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are especially stable (Giesy et al. 2006), bioaccmulative and toxic (Kudo and Kawashima 2003; Kennedy et al. 2004) of them. Many field data on the PFCs contamination of surface water in rivers and lakes have been reported in Japan (Matsumura et al. 2009; Murakami et al. 2008; Saito et al. 2003, 2004; Senthilkumar et al. 2007; Taniyasu et al. 2003; Takashima et al. 2009; Zushi et al. 2008; Zushi and Masunaga 2009a, b), in Asia (Jin et al. 2009; Kunacheva et al. 2009; Lin et al. 2009; Yeung et al. 2009), and in Europe and America (Boulanger et al. 2004; Ericson et al. 2008; Hansen et al. 2002; Loos et al. 2008, 2009; Maclaghlan et al. 2007; Rostkowski et al. 2009).

Since 2009, we have performed surveys on PFOS and PFOA concentrations in surface water from Lake Biwa and rivers around Lake Biwa. We have already reported the results of the survey on Lake Biwa and Seta River in February, 2009 (Tsuda and Inoue 2009). From this survey, it was clarified that the concentration levels of PFOS (1.0–2.4 ng/L) and PFOA (7.6–15.6 ng/L) in surface water from Lake Biwa (14 sites) and Seta River (a site) were not so high as those in the rivers and lakes in Japan (Matsumura et al. 2009; Murakami et al. 2008; Saito et al. 2003, 2004; Senthilkumar et al. 2007; Taniyasu et al. 2003; Takashima et al. 2009; Zushi et al. 2008; Zushi and Masunaga 2009a, b).

In this report, seasonal changes of PFOS and PFOA concentrations were surveyed in the same 14 sites of Lake Biwa from February to November in 2009. Further, monthly detailed surveys were performed on the PFOS and PFOA concentrations from June in 2009 to May in 2010 for two sites of Akanoi Bay (8C and 168) where the seasonal changes of both chemical concentrations were recognized.

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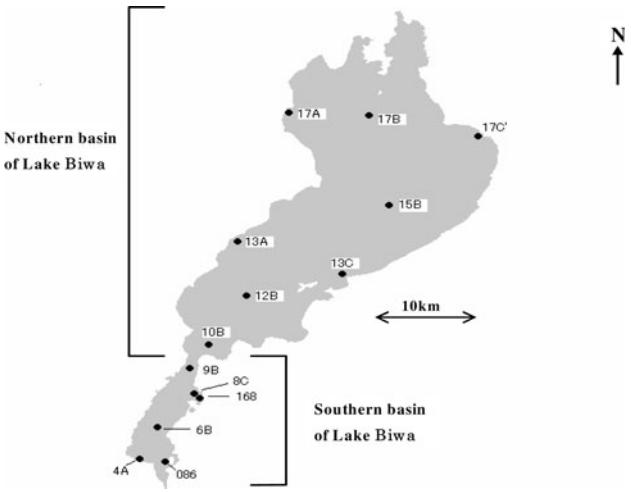

Fig. 1 Map of sampling locations

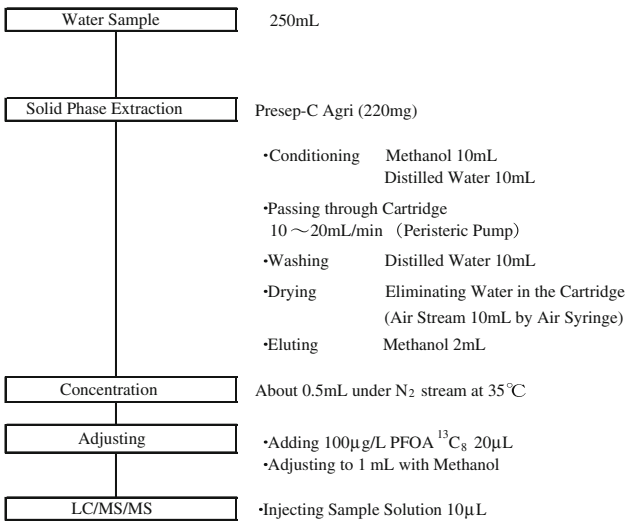

Fig. 2 Analytical procedure for PFOS and PFOA in water

Table 1 LC/MS/MS measurement conditions of PFOS and PFOA

LC operating conditions (Water ACQUITY UPLC)	
Column	ACQUITY UPLC BEH SHIELD RP18(2.1 × 100 mm, 1.7 μm)
Column temperature	50°C
Mobile phase	A:B = 50:50(A, 10 mM CH_3COONH_4/H_2O; B, Acetonitrile)
Flow rate	0.4 mL/min
Injection volume	10 μL

MS operating conditions (Waters Quattro Premier)	
Ionization mode	ESI^- (Negative)
Capillary voltage	0.5 kV
Ion source temperature	100°C
Desolvation gas temperature	450°C
Desolvation gas flow	1000 L/h

Chemicals	Precursor [m/z]	Product [m/z]	Cone voltage [V]	Collision energy [eV]	Dwell time [s]
Monitor ions					
PFOS (Determination)	499	499	60	10	0.05
PFOS (Confirmation)	499	99	60	40	0.05
PFOA (Determination)	413	369	15	10	0.10
PFOA (Confirmation)	413	169	15	10	0.10
PFOA$^{13}C_8$ (Determination)	421	376	15	10	0.10
PFOA$^{13}C_8$ (Confirmation)	421	172	15	20	0.10

Materials and Methods

Standard solutions of PFOS and PFOA were purchased from Accu Standard, Inc. (USA) and Wako Pure Chemical Industries Ltd. (Japan), respectively. An internal standard solution of PFOA$^{13}C_8$ (50 μg/mL) in methanal were purchased from Cambridge Isotope Laboratories Inc. (USA). A cartridge column (Presep-C Agri, 220 mg) from Wako Pure Chemical Industries Ltd. (Japan) was used for solid-phase extraction of PFOS and PFOA in water samples. Nanopure water and solvents (methanol and acetonitrile) for PFOS and PFOA analyses were used throughout.

Sampling locations are shown in Fig. 1. Surface water samples were collected from northern basin (eight sites) and southern basin (six sites) of Lake Biwa once in February, June, August and November, 2009. For Akanoy Bay (8C and 168) in southern basin of Lake Biwa, surface water samples were collected once every month from June in 2009 to May in 2010. The water samples were analyzed immediately after the sample collection was finished.

The PFOS and PFOA concentrations in the water samples were performed by the analytical procedure (Ministry of the Environment, Japan 2004) shown in Fig. 2. In brief, a measured volume (250 mL) of the water sample was passed through a cartridge column (Presep-C Agri, 220 mg) using peristeric pump after conditioning with 10 mL of methanol and 10 mL of nanopure water. The column was washed with 10 mL of nanopure water and eluted with 2 mL of methanol after eliminating water in the column with air stream by air syringe. The eluate was evaporated to about 0.5 mL under N_2 stream at 35°C and adjusted to 1 mL with methanol after addition of 20 μL of PFOA$^{13}C_8$ (100 μg/L). The sample solution was analyzed using LC/MS/MS (LC: Waters ACQUITY UPLC and MS:

Table 2 PFOS and PFOA concentrations in surface water from Lake Biwa throughout the survey from February to November in 2009

Sampling locations	n	PFOS (ng/L)		PFOA (ng/L)	
		Range	Average	Range	Average
Northern basin of Lake Biwa (eight sites)	32	0.8–1.6	1.1	7.0–10	8.7
Southern basin of Lake Biwa except Akanoi Bay (four sites)	16	0.9–1.7	1.3	8.3–13	9.8
Akanoi Bay (8C)	4	1.4–2.8	1.8	9.1–17	13
Akanoi Bay (168)	4	2.4–5.3	3.7	12–26	20

Waters Quattro Premier). The LC/ MS/ MS measurement conditions are shown in Table 1. Recoveries (n = 3) were 91–99% for PFOS and 89–96% for PFOA at a spiked level of 40 ng/L. Quantification limits were 0.6 ng/L for PFOS and 0.9 ng/L for PFOA.

Results and Discussion

Results of the survey in the surface water from northern and southern basins of Lake Biwa are summarized in Table 2. The concentrations of PFOS and PFOA were 0.8–1.6 and 7.0–10 ng/L in the northern basin (eight sites), 0.9–1.7 and 8.3–13 ng/L in the southern basin except Akanoi Bay (four sites), 1.4–2.8 and 9.1–17 ng/L in Akanoi Bay (8C) and 2.4–5.3 and 12–26 ng/L in Akanoi Bay (168), respectively.

There were little differences in the PFOS and PFOA concentrations between northern and southern basins of Lake Biwa but the concentrations of both chemicals in the two sites of Akanoi Bay (8C and 168) were higher than those in the other 12 sites of Lake Biwa. The changes of PFOS and PFOA concentrations are shown in Fig. 3 for this survey from February to November in 2009. Seasonal changes were recognized for both of PFOS and PFOA in the two sites of Akanoi Bay in the southern basin but not in the other sites of the southern and northern basins of Lake Biwa. For the sites (8C and 168), monthly detailed surveys

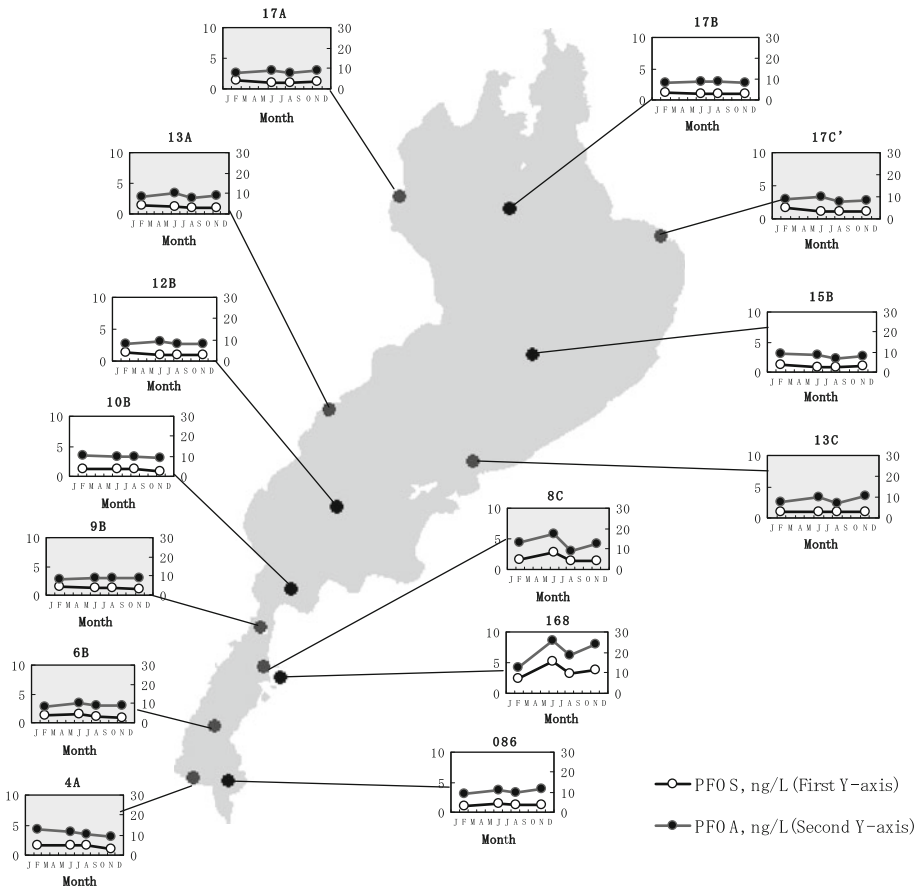

Fig. 3 Seasonal changes of PFOS and PFOA concentrations in surface water from Lake Biwa throughout the survey from February to November in 2009

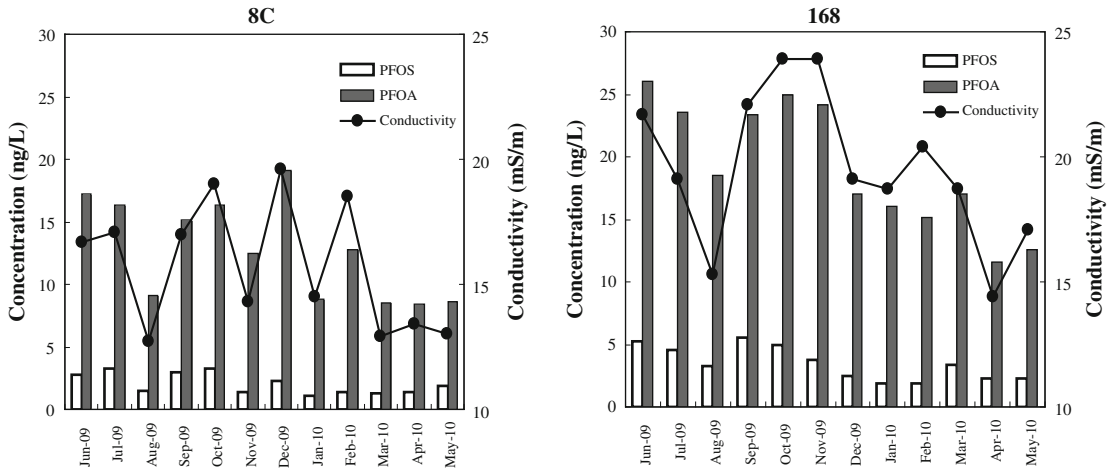

Fig. 4 Monthly changes of PFOS and PFOA concentrations in surface water from two sites of Akanoi Bay (8C and 168) in southern basin of Lake Biwa throughout the survey from June in 2009 to May in 2010

in the surface water were performed on the changes of PFOS and PFOA concentrations from June in 2009 to May in 2010 and further on the changes of conductivity values to evaluate the influence from rivers flowing into the two sites. The results of the surveys are shown in Fig. 4. The changes of PFOS and PFOA concentrations were well consistent with those of the conductivity values. The concentrations of PFOS and PFOA were presumed to be influenced by the inflows of both chemicals from rivers around the two sites in Akanoi Bay from the survey data. On the other hand, the stable PFOS and PFOA concentrations in littoral area of Lake Biwa (17A, 13A, 4A, 086, 13C and 17C′) except Akanoi Bay (two sites) were probably due to little changes of inflow amounts of both chemicals from rivers around the six sites. Little differences in the PFOS and PFOA concentrations among the 12 sites in the northern and southern basins of Lake Biwa were probably due to the diffusion of both chemicals by Lake Biwa water flows.

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