TEMPORAL TRENDS OF PERFLUORINATED COMPOUNDS (PFCs) IN SURFACE SEDIMENT FROM LAKE SHIHWA, KOREA: BETWEEN 2001 AND 2011

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Introduction

Perfluorinated compounds (PFCs) have received worldwide attention because of their environmental persistence and widespread distribution[1]. PFCs are widely used in industry, particularly in the manufacture of electronic and textile products[2]. Due to the potential health risk of PFCs such as developmental, immunosuppressive and endocrine disruptive toxicity[5], many environmental samples have been analyzed for the presence of these compounds[3,6]. In previous studies, PFC concentration from the 1970s to the early 2000s showed increasing trends. One of the largest manufacture companies, 3M, voluntarily phased out of PFOS-related production in 2002. As a result of decreased production and increased restrictions, temporal trend studies are needed to examine changes in PFC environmental distribution. Lake Shihwa, an artificial lake, are located on the west coast of South Korea. As pollution-causing factories are located around Lake Shihwa, the Korean government designated Lake Shihwa as a special management coastal zone and constructed a water gate in 2000 to promote water exchange[7]. Many studies continue to report sediment contamination of Lake Shihwa by polychlorinated dibenzo-*p*-dioxin and furans (PCDD/Fs)[8], polybrominated diphenyl ethers (PBDEs)[7] and PFCs[9]. However, no information on temporal trend of PFCs in Lake Shihwa is available. In the present study, 18 PFCs and total fluorine (TF) were determined for mass-balance study, using combustion ion chromatography (CIC). In our knowledge, this is the first temporal trend study of PFCs using TF and known 18 PFCs data simultaneously. The objectives of our study were (1) to determine 18 PFCs concentration in surface sediment (2) to investigate temporal trends of PFCs, and (3) to evaluate mass balance for known 18 PFCs to total fluorine in surface sediment of Lake Shihwa.

Materials and methods

Surface sediments (0-4 cm depth) were collected from 15 sites of Lake Shihwa in 2001 and 2011 (Figure 1). Sediment samples were freeze-dried and analyzed for PFCs and TF. Detailed experimental procedures and instrumental analysis for individual PFCs and TF were described elsewhere[1,2]. Eighteen individual PFCs were analyzed using the ion-pairing method. Briefly, 15 g of the surface sediment samples were extracted using methanol. The extract was adjusted to 10 mL and 5 mL samples were diluted with 150 mL Milli-Q water. After spiking internal standard, all extracts were loaded to Oasis WAX cartridge for clean up procedure. The cleaned up extract was analyzed by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). The 50 mg of surface sediment was set on a ceramic sample board for combustion (900-1000 °C) in furnace. Combusted sample was absorbed into absorption solvent (11-13.5 mL). After adding 500 uL of 0.01M $Ca(OH)_2$, solvent was passed through the pre-conditioned OnGuard column. For instrumental analysis, 1 mL of passed sample was diluted with 1 mL of Milli-Q water. The concentration of F^- in the solution was analyzed using ion chromatography.

Results and discussion

Concentrations of PFCs in surface sediment of Lake Shihwa

Concentrations of 18 PFCs in surface sediment of Lake Shihwa are shown in Table 1. PFOS was the predominant compound, followed by PFUnDA and PFDoDA. The short-chain perfluorinated carboxylic acids (PFCAs, <C8) were exclusively detected in water, whereas the long-chain PFCAs (>C8) and perfluoroalkyls sulgonates (PFASs) are bound to sediment[10,11]. Compare to the results for Tokyo Bay (Japan)[12] and Dianchi Lake (China)[13], the concentrations of PFCs measured in our study (6569 pg/g dry weight) were higher.

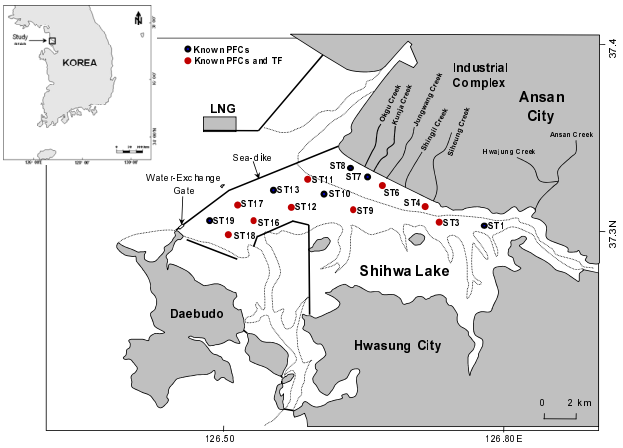

Figure 1. Sampling sites (n=15) of surface sediments from Lake Shihwa, Korea.

Table 1. Concentration of analyzed PFCs in sediments from Lake Shihwa between 2001 and 2011 (PFBS and PFOCDA were excluded for low detection frequency)

	2001			2011		
	Mean	SD	Range	Mean	SD	Range
Sulfonates						
PFHxS	18.1	14.2	<LOQ-53.6	4.91	5.78	<LOQ-17.4
PFOS	760	365	205-1469	396	285	133-1314
PFDS	63.4	63.8	<LOQ-194	25.5	37.8	<LOQ-140
FOSA	142	146	19.3-599	56.3	70.2	8.99-276
N-EtFOSA	11.6	15.0	<LOQ-52.2	4.93	6.74	<LOQ-20.9
Carboxylates						
PFBA	103	119	<LOQ-449	4.19	15.9	<LOQ-61.9
PFPeA	29.4	33.8	<LOQ-108	7.24	8.87	<LOQ-23.7
PFHxA	9.25	15.8	<LOQ-58.4	1.20	1.96	<LOQ-5.78
PFHpA	9.28	13.0	<LOQ-43.1	4.38	5.50	<LOQ-17.7
PFOA	69.9	49.2	7.90-145	30.8	23.8	5.22-76.9
PFNA	19.6	17.1	1.45-66.7	8.20	5.64	0.62-17.0
PFDA	69.9	79.6	6.09-314	56.2	38.2	7.60-131
PFUnDA	367	711	11.9-2821	225	317	21.8-1242
PFDoDA	133	185	3.20-622	119	102	15.9-322
PFTeDA	32.8	38.9	0.24-129	43.5	35.7	4.04-105
PFHxDA	6.12	4.92	<LOQ-14.0	7.70	6.54	<LOQ-21.3

Spatial and temporal trends of PFCs in sediment samples

The average concentrations of PFCs in sediment samples collected in 2001 and 2011 are shown in Figure 2. Compare to 2001, the total concentration of PFCs decreased in almost all sites. In 2001, St12 showed the highest concentration (6570 pg/g dry weight) with high contribution of PFUnDA and dramatically decreased after 10 years. The PFCs concentration in sediment from St13 increased but other site showed decreasing trend of PFCs. The concentration of individual PFC and their compositions in Lake Shihwa sediments are shown in Figure 3. Except for PFTeDA, all compounds decreased during 10 years. This is consistent with the worldwide production of PFOS-related compounds decreased from 2002. Although the concentrations of each compound of PFCs decreased, the composition patterns of two PFC group were different. Perfluoroalkyl sulfonates (PFASs), which are most common PFC group including PFOS, showed decreasing pattern between 2001 and 2011 while

perfluorocarboxylates (PFCAs) increased during 10 years. Our result indicates that carboxylates could be used as alternatives for sulfonates (e.g. PFOS), due to regulation.

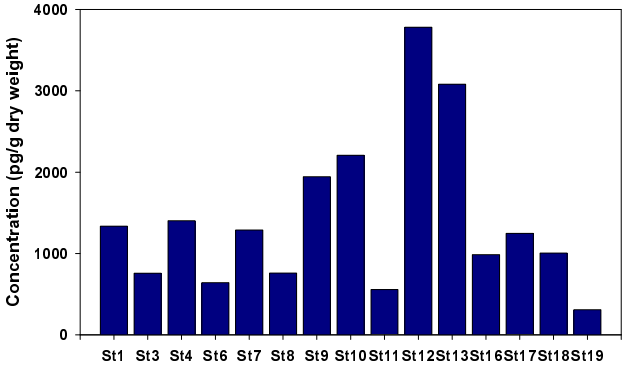

Figure 2. Spatial distribution of PFCs in sediments from in Lake Shihwa.

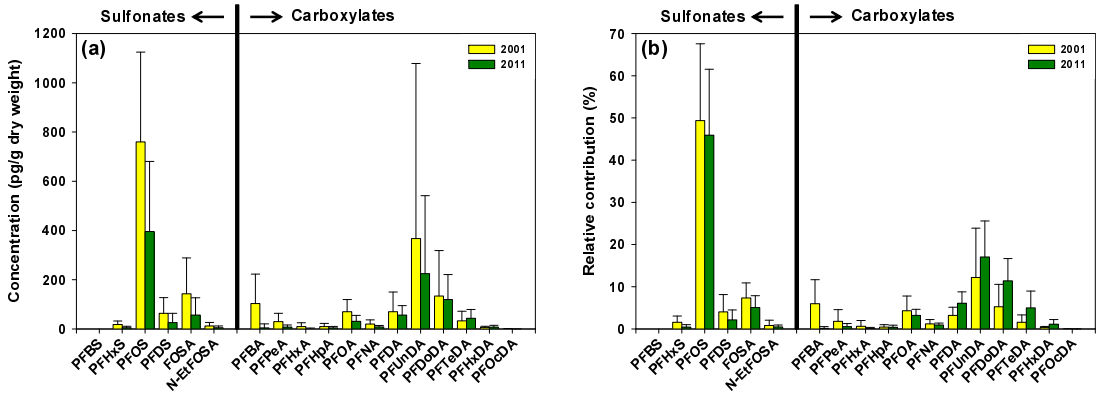

Figure 3. Temporal trends of (a) concentrations and (b) composition of PFCs in sediments from Lake Shihwa, Korea.

Table 2. Concentration of known PFCs and total fluorine (TF) in sediments from Lake Shihwa, Korea

	Known PFCs (pg-F/g dw)		Total Fluorine (μg-F/g dw)	
	2001	2011	2001	2011
St3	651	327	578	531
St4	985	800	376	395
St6	652	172	505	236
St9	1318	1181	326	406
St11	396	320	143	381
St12	4411	658	423	293
St16	837	423	268	392
St17	1100	527	245	317
St18	667	565	106	174

Concentrations of total fluorine and known PFCs

The concentration of TF was determined in sediments from 9 sites for mass balance study (Table 2). It was not enough to conduct mass balance study because of no extractable organic fluorine (EOF) data. Therefore, in our study, the contribution of known PFCs was evaluated to TF concentrations in sediments from Lake Shihwa. The concentrations of TF widely varied, dependent on the sampling site. Although significant decreasing trends of known PFCs in sediments between 2001 and 2011, no significant temporal trends were found in the concentrations of TF. Our finding indicates that unknown PFCs in EOR or inorganic fluorine would increase and be contributed to the total TF concentrations. Further study should be focused on the identification of these unidentified fluorines.

References

1. Miyake Y, Yamashita N, Rostkowski P, So MK, Taniyasu S, Lam PKS, Kannan K. (2007); *J. Chromatogr A*. 1143:98-104.
2. Yeong LWY, Miyake Y, Wang Y, Taniyasu S, Yamashita N, Lam PKS. (2009); *Environ Pollut.* 157:17-23.
3. Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DC. (2006); *Environ Sci Technol.* 40(11):3463-73.
4. Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. (2005); *Mar Pollut Bull.* 51(8-12):658-68.
5. Lau C, Anitole K, Hodes C, Lai D. (2007); *Toxicol Sci.* 99(2):366-94.
6. O'Connell SG, Arendt M, Segars AL, Kimmel T, Braun-Mcneill J, Avens L, Schroeder B, Ngai L, Kucklick JR, Keller JM. (2010); *Environ Sci Technol.*44:5202-9.
7. Moon HB, Choi M, Yu J, Jung RH, Choi HG. (2012); *Chemosphere.* 88:837-43.
8. Moon HB, Choi M, Choi HG, Kannan K. (2012); *Mar Pollut Bull.*64:2357-63.
9. Rostkowski P, Yamashita N, So IMK, Taniyasu S, Lam PKS, Falandysz J, Lee KT, Kim SK, Khim JS, Im SH, Newsted JL, Jones PD, Kannan K, Giesy JP. (2006). Environ Toxicol Chem. 25(9):2374-80.
10. Ahrens L, Yamashita N, Yeung LWY, Taniyasu S, Horii Y, Lam PKS. (2009); *Environ Sci Technol.* 43:6969-75.
11. Ahrens L, Taniyasu S, Yeong LWY, Yamashita N, Lam PKS, Ebinghaus R. (2010); *Chemosphere.* 79:266-72.
12. Ahrens L, Yamashita N, Yeong LWY, Taniyasu S, Horii Y, Lam PKS, Ebinghaus R. (2009); *Environ Sci Technol*. 43:6969-75.
13. Zhang Y, Meng W, Guo C, Xu J, Yu T, Fan W, Li L. (2012); *Chemosphere*. 88:1292-9.