

PERFLUORINATED COMPOUNDS IN STREAMS OF THE SHIHWA INDUSTRIAL ZONE
AND LAKE SHIHWA, SOUTH KOREA

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Abstract—Concentrations of perfluorinated alkyl compounds (PFAs), including perfluorooctane sulfonate (PFOS), perfluorohexanesulfonate, perfluorobutanesulfonate, perfluorooctanesulfonamide, perfluorodecanoate, perfluorononanoic acid, perfluorooctanoate (PFOA), perfluoroheptanoate, and perfluorohexanoate, were measured in the streams of the Shihwa and Banweol industrial areas on the west coast of South Korea as well as the adjacent Lake Shihwa (an artificial lake) and Gyeonggi Bay. Perfluorinated alkyl compounds were concentrated from water using solid-phase extraction and were identified and quantified by liquid chromatography/triple-quadrupole tandem mass spectrometry. Of the PFAs measured, PFOS and PFOA occurred at the greatest concentrations. Concentrations of PFOS ranged from 2.24 to 651 ng/L, and concentrations of PFOA ranged from 0.9 to 62 ng/L. The concentrations of PFOS observed in Lake Shihwa were among the greatest ever measured in the environment. These results suggest local industrial sources of PFOS and PFOA as well as other PFAs. Because of dilution, the greatest concentrations occur in a rather restricted area, near the points of discharge of the streams that empty into the lake. The greatest measured concentration of PFOS exceeded the threshold for effects predicted for predatory birds consuming aquatic organisms continuously exposed to this level.

Keywords—Wastewater Solid-phase extraction Perfluorinated alkyl compounds Perfluorooctane sulfonate Asia

INTRODUCTION

Perfluorinated alkyl compounds (PFAs) have been manufactured for more than 50 years and, because of their unique properties of repelling both water and oil, have been used as surfactants and surface protectors in many products [1]. A number of PFAs are used commercially that can occur in the environment, including those that belong to perfluorinated sulfonate group, such as perfluorooctane sulfonate (PFOS), perfluorooctanesulfonamide (PFOSA), perfluorohexanesulfonate (PFHxS), and perfluorobutanesulfonate (PFBS), and compounds belonging to the perfluorinated carboxylate group, including perfluorooctanoate (PFOA) and perfluorononanoic acid (PFNA) [2]. Many of these compounds are persistent in the environment, whereas others degrade to environmentally stable compounds [2,3]. Perfluorooctane sulfonate and PFOA are two PFAs that are widespread globally in many environmental media, even in remote regions far from sources, such

as the Arctic and Antarctic [2,4,5], and in human serum [6–9]. In 2000, the 3M Company, one of the largest producers of PFAs, ceased most production of PFOS and of the intermediates critical for the manufacturing of PFOS [10]. However, other manufacturers still produce some PFAs, including fluorotelomer alcohols and olefins. In an earlier study, PFOS was measured at 730 ng/L in water collected from Lake Shihwa (Republic of South Korea) in January 2003 [11]. At the time, this was the greatest concentration of PFOS that had ever been observed in either freshwaters or marine waters. To our knowledge, this was the only reported concentration in seawater that would exceed the threshold of PFOS (160 ng/L) deemed to be safe for predatory birds feeding on biota from the region [11]. The present study was conducted to determine if the relatively great concentrations of PFOS and PFOA could still be observed in Lake Shihwa during 2004. In addition, concentrations of PFHxS, PFBS, PFOSA, perfluorodecanoic acid (PFDA), PFNA, perfluoroheptanoic acid, and perfluorohexanoic acid were determined.

The Shihwa and Banweol industrial areas are located on the west coast of South Korea, 30 km southwest of Seoul, encompassing the cities of Ansan and Shiheung (Fig. 1). The

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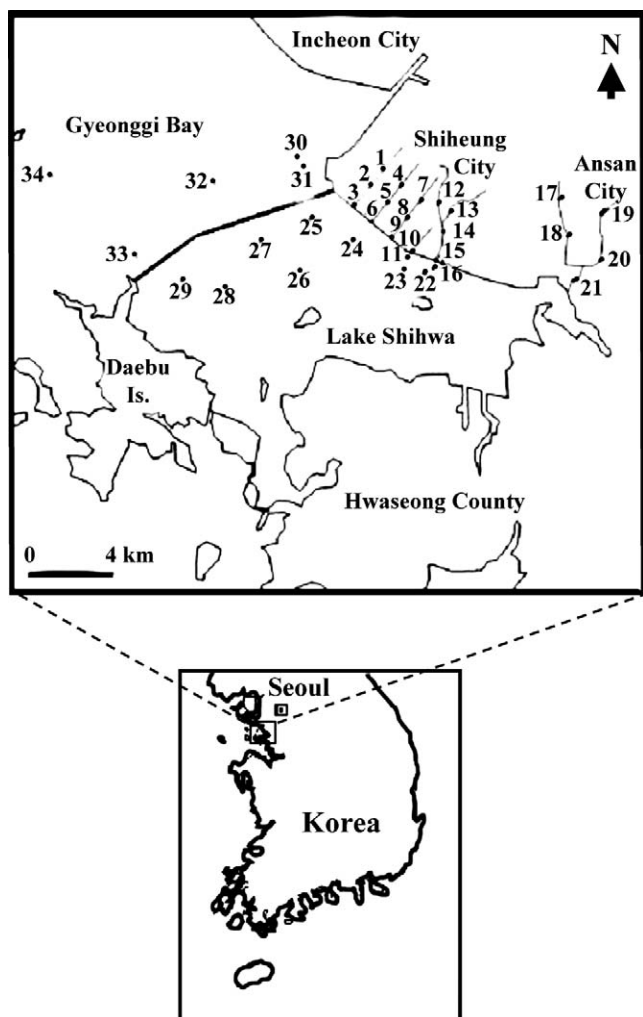


Fig. 1. Map showing the sampling locations in the streams of the Shihwa and Banweol industrial areas ($n = 21$), saltwater lake ($n = 8$), and outer Gyeonggi Bay ($n = 5$), Korea.

Banweol industrial complex is an area of approximately 15 km² that was constructed between 1978 and 1987. Small and medium-sized companies that had been located in Seoul moved to these areas during the 1970s. The Shihwa industrial district, with an area of approximately 16 km², was constructed between 1986 and 2002. A wide variety of manufacturing industries are clustered in this area. Approximately 7,000 companies, largely steel/mechanical (48.9%), electrical/electronic (14.6%), and petrochemical companies (10.1%), currently operate in the Shihwa and Banweol industrial areas. Lake Shihwa is an artificial saltwater lake created by the construction of 12.7-km sea dike in 1994 to provide water for industrial and agricultural uses.

Other than a few reports of organic contaminants in depositional areas and open bay sites, little information was available regarding the state of the environment of Lake Shihwa. Several reports have indicated severe contamination of both water and sediments of Lake Shihwa and upper inland areas with both metals and trace organic contaminants [12–14]. The quality of the environment, including both surface water and sediments of Lake Shihwa and nearby areas, became worse after dike construction in 1994. Because a number of wildlife species, particularly birds, including migratory species, use Lake Shihwa, it was deemed to be important to de-

termine the current status of PFAs in the lake and to determine possible sources and loading rates from the tributary rivers entering the lake. Thus, in the present study, we revisited Lake Shihwa in 2004 and extended the sampling locations to landward regions to find sources and origins of PFOS and PFOA and other related contaminants.

MATERIALS AND METHODS

Sample collection

Thirty-four samples of water were collected in December 2004 from streams flowing into Lake Shihwa ($n = 21$), from Lake Shihwa ($n = 8$), and from Gyeonggi Bay outside the sea dike ($n = 5$) (Fig. 1 and Table 1). Water samples were collected by dipping a clean polypropylene sampling bottle (500 ml) just under the surface of the water. Water samples were transported to the laboratory, where they were stored at 4°C until analysis.

Chemicals and standards

A mixture of perfluorinated compounds (PFA mix), containing PFOS, PFHxS, PFBS, PFOA, PFDA, PFNA, PFOA, perfluoroheptanoic acid, and perfluorohexanoic acid at concentrations of 100 ng/ml each, was used as an external standard (National Institute of Advanced Industrial Science and Technology), whereas [¹³C]PFOA (Wellington Laboratories, Toronto, ON, Canada) was used as an internal standard. Methanol, ammonium acetate, and acetic acid were purchased from Wako Pure Chemicals Industries (Tokyo, Japan). Milli-Q® water was obtained from a Milli-Q Gradient A-10 (Millipore, Bedford, MA, USA).

Sample extraction

The target perfluorinated analytes were concentrated from seawater using solid-phase extraction [11,15,16]. Water samples were extracted using Oasis WAX (6 ml, 150 mg, 30 μm) solid-phase extraction cartridges (Waters, Milford, MA, USA). Before the extraction of PFAs from water samples, the cartridge was preconditioned by elution with 4 ml of 0.1% NH₄OH/MeOH followed by 4 ml of MeOH and 4 ml of Milli-Q water. The flow rate was set to one drop per second. An aliquot of water (400 ml) was then loaded onto the cartridge, eluting at a rate of one drop per second, and the eluate was discarded. The cartridge was prevented from drying during the loading of the water sample. The cartridge was washed with 4 ml of buffer (acetic acid/sodium acetate, pH 4) and dried by vacuum. Perfluorinated alkyl compounds were eluted from the cartridge in two fractions. The first fraction was eluted with 4 ml of MeOH, and the second fraction was eluted with 4 ml of 0.1% NH₄OH/MeOH. Each fraction was placed into a separate polypropylene vial and concentrated to 100 μl for instrumental analysis.

Instrumental analysis

Perfluorinated alkyl compounds in water samples were identified, and concentrations of each PFA were determined by use of high-performance liquid chromatography with high-resolution electrospray tandem mass spectrometry as described elsewhere [11,15–17]. Separation of analytes was accomplished on an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA, USA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters) operated in electrospray negative-ion mode. A 10-μl aliquot of extract was injected onto a guard column (length, 12.5 mm; inner diameter, 2.1

Table 1. Sampling locations and environmental parameters in Lake Shihwa and Gyeonggi Bay, Korea (Fig. 1)

Map key location ^a	Sample ID	Location		Salinity (‰)	Temp (°C)	Depth (m)	Site description (remark)
		Longitude (E)	Latitude (N)				
Streams							
1	IL1	126°43'04"	37°20'35"	0.0	8.7	<1.0	Okgu Creek
2	IL2	126°42'34"	37°20'09"	0.0	7.9	<1.0	
4	IL4	126°43'35"	37°20'13"	0.0	9.1	<1.0	Gunja Creek
5	IL5	126°43'09"	37°19'46"	0.0	8.9	<1.0	
7	IL7	126°44'19"	37°19'46"	0.0	10.2	<1.0	Jeongwang Creek
8	IL8	126°43'52"	37°19'20"	0.0	9.1	<1.0	
9	IL9	126°43'26"	37°18'53"	4.0	8.6	<1.0	
10	IL10	126°44'05"	37°18'32"	0.0	6.7	<1.0	Anonymous Creek
12	IL12	126°44'55"	37°19'46"	0.0	16.5	<1.0	
12	IL12Dup ^b						
13	IL13	126°45'14"	37°19'31"	0.0	7.3	<1.0	Shingil Stream
14	IL14	126°44'60"	37°19'03"	0.0	8.2	<1.0	
15	IL15	126°44'54"	37°18'19"	0.0	8.2	<1.0	
16	IL16	126°44'48"	37°18'04"	0.0	8.4	<1.0	
18	IL18	126°49'17"	37°19'03"	0.0	9.1	<1.0	
20	IL20	126°50'31"	37°18'23"	0.0	8.0	<1.0	
21	IL21	126°49'02"	37°17'55"	0.0	8.6	<1.0	Near incinerator and WTP ^c
Lake Shihwa							
22	LS8	126°44'25"	37°17'56"	26.5	8.4	7.0	
23	LS1	126°43'45"	37°17'58"	28.5	8.6	2.3	
24	LS2	126°42'03"	37°18'44"	28.6	9.0	2.3	
25	LS3	126°40'38"	37°19'17"	28.4	8.8	7.4	
27	LS5	126°39'00"	37°18'40"	28.9	9.1	3.4	
Gyeonggi Bay							
31	LS9	126°40'23"	37°20'38"	30.5	9.6	6.4	
31	LS9Dup						
32	LS10	126°37'22"	37°20'11"	30.9	10.1	11.3	
33	LS11	126°34'44"	37°18'07"	31.5	10.5	15.5	Near water gate
34	LS12	126°31'44"	37°20'17"	31.8	11.3	11.0	

^a See Figure 1 for locations sampled.

mm; film thickness, 5 μm ; Zorbax XDB-C8; Agilent Technologies) connected to a Betasil C18 column (length, 50 mm; inner diameter, 2.1 mm; film thickness, 5 μm ; Thermo Electron, Waltham, MA, USA). The mobile phase was 2 mM ammonium acetate/methanol, in which the methanol proportion in the mobile phase was 10% methanol that was increased to 100% and held at this concentration for 10 min. The conditions then reverted to the original conditions after 12 min. The flow rate was 300 $\mu\text{l}/\text{min}$. The desolvation gas flow was 650 L/h, and temperature was 450°C. The collision energies, cone voltages, and tandem mass spectrometry parameters for the instrument were optimized individually for each analyte [13].

Quality assurance/quality control

To determine the precision and accuracy of the extraction and analytical procedures, recovery and blank laboratory tests were performed. To determine the recovery of PFOS and other PFAs, 40 μl of PFA mix was spiked into 400 ml of Milli-Q water samples and then extracted with the same procedures used for water samples. Travel blanks, travel recovery samples, and duplicate samples from location 12 also were analyzed for the target analytes. Results of the blank and recovery tests are summarized (Table 2). Concentrations of all target analytes were quantified by use of calibration curves constructed using external standards. The limit of quantification was determined for each analyte based on the extraction concentration factor and the least concentration standard injected. The limit of quantification for all target analytes was 0.5 ng/L.

RESULTS AND DISCUSSION

Distribution and sources

Perfluorinated alkyl compounds were identified and quantified in 27 samples (Fig. 2 and Table 3). The results of duplicate samples (samples 12 and 31) showed acceptable repeatability for most chemicals except for PFBS in sample 12. Concentrations of PFAs observed in Lake Shihwa and in several of the streams running into the lake were relatively high compared to those measured in other places, including the South China Sea and the Arctic, Antarctic, and Pacific oceans [15,16]. Of the PFAs measured, PFOS and PFOA occurred at the greatest concentrations. Concentrations of PFOS ranged from 2.24 to 651 ng/L, with the greatest concentrations observed at location 10 (651 ng/L) and location 5 (283 ng/L). Concentrations of PFOA ranged from 0.9 to 62 ng/L, with the greatest concentrations observed at location 10 (62 ng/L), location 13 (34 ng/L), and location 16 (29 ng/L). The greatest concentration of PFOA also was observed at location 10, but unlike PFOS, the next greatest concentration was not observed at location 5. The results of the present study were similar to those reported previously [11], and they suggest possible point sources of PFOS from industries that discharge to the small channels that drain into Lake Shihwa located within the study area. The least concentration of PFOS was detected in water from location 34 in Gyeonggi Bay, which is the sample location most remote from the industrial area.

To assess whether PFOS and PFOA had common sources

Table 2. Recoveries and a level of blank for individual perfluorinated alkyl compounds^a

Compound	Recovery				Laboratory blank (ng/L)	Travel blank A (ng/L)	Travel recovery (%)
	Range (%)	Median (%)	RSD (%)	Samples (n)			
PFSA							
PFOS	88–94	91	3	4	<0.5	<0.5	88
PFHxS	80–105	92	11	4	<0.5	0.58	86
PFBS	80–92	87	5	4	<0.5	<0.5	89
PFOSA	88–139	112	24	4	<0.5	<0.5	95
PFCAs							
PFDA	83–97	88	6	4	<0.5	<0.5	83
PFNA	92–106	99	6	4	<0.5	<0.5	102
PFOA	86–105	95	8	4	<0.5	<0.5	95
PFHpA	80–103	94	10	4	<0.5	<0.5	103
PFHxA	77–105	95	12	4	<0.5	<0.5	94

^a PFSA = perfluorosulfonic acids; PFOS = perfluorooctane sulfonic acid; PFHxS = perfluorohexane sulfonic acid; PFBS = perfluorobutane sulfonic acid; PFOSA = perfluorooctane sulfonamide; PFCAs = perfluorocarboxylic acids; PFDA = perfluorodecanoic acid; PFNA = perfluorononanoic acid; PFOA = perfluorooctanoic acid; PFHpA = perfluoroheptanoic acid; RSD = relative standard deviation.

in the region and to identify possible sources, the ratio of the concentrations of PFOS to PFOA was calculated. In all locations except location 18, the PFOS to PFOA ratio was greater than 1.0 (Fig. 3). This is similar to the PFOS to PFOA ratio observed in Etobicoke Creek, where fire-fighting foam was washed into the creek [17]. This suggests that aqueous fire-fighting foams may be one of the sources of PFAs in the area of Lake Shihwa, but other local industrial sources cannot be discounted without additional investigation. The PFOS to PFOA ratio for most locations in the Lake Shihwa area were different from those previously reported in waters from other areas in South Korea, coastal China, and Hong Kong, typically less than 1.0 [11]. This indicates that unique local sources of both PFOS and PFOA exist in the study area.

After PFOS and PFOA, the next most prevalent PFAs were PFOSA, PFDA, and PFBS (Table 3). Concentrations of PFOSA ranged from 0.59 to 2.36 ng/L. Perfluorooctanesulfonamide was detected at locations 2, 4, 5, 9, 10, 12, 15, and 21, with the greatest concentration observed at location 2. Perfluorodecanoate was detected in 90% of analyzed samples at concentrations ranging from 0.56 to 6.00 ng/L at location 2. Perfluorobutanesulfonate concentrations ranged from 0.6 to 24 ng/L, with the greatest concentrations at location 5 (18 ng/L) and location 10 (24 ng/L). These locations are suspected to

be possible point sources of this compound, used as a PFOS replacement, in the Lake Shihwa area.

Comparison to other areas

Concentrations of PFOS and PFOA in Lake Shihwa and associated streams generally were greater than those observed in freshwater and coastal environments in China, Hong Kong, and Japan [9,15,16,18–20]. For instance, the greatest PFOS concentration observed in Tokyo Bay was 59 ng/L, which was approximately 10-fold less than the concentration observed at location 10. The greatest concentration of PFOS was at location 10 at the outlet channel to Lake Shihwa, but this value was more than 10-fold greater than the concentration recorded in Gyeonggi Bay. It also was fivefold greater than the greatest concentration of PFOS observed in the Tennessee River (USA) downstream of a fluorochemical manufacturing facility and 10-fold greater than that at an upstream site from the same study [21]. Even in the Tama River, which flows through the suburban and metropolitan areas of Tokyo, the greatest concentration of PFOS (157 ng/L) is fivefold less than the concentration observed at sampling location 10.

The smallest concentration of PFOS was found at location 34 (2.2 ng/L), outside the sea dike in Gyeonggi Bay. Perfluorooctanoic acid could not be detected in coastal waters of Japan in Hiroshima Bay, Kin Bay, and Lake Shikatsu [9]. In coastal waters of Hong Kong, the greatest concentrations of PFOS were 3.0 and 3.1 ng/L, which are greater than those observed in Gyeonggi Bay but approximately 10-fold less than those observed in Lake Shihwa [11]. In the coastal waters of China, the greatest concentration of PFOS reported is 12 ng/L, which is comparable with some locations in Lake Shihwa that are more remote from the associated streams that are the possible sources of this compound to the lake.

Relatively great concentrations of PFBS were detected in water from locations 5 and 10 (18 and 24 ng/L, respectively), whereas this compound was not detected in Tokyo Bay, Japan [9]. Perfluorobutanesulfonate was detected in the coastal waters of China and Hong Kong, with values ranging from less than 0.005 to 0.62 ng/L [9].

Relatively high concentrations of PFNA have been reported to occur in some biological matrices [22,23]. It has been suggested that PFNA is a relevant compound to consider during risk assessments. In the present study, concentrations of PFNA

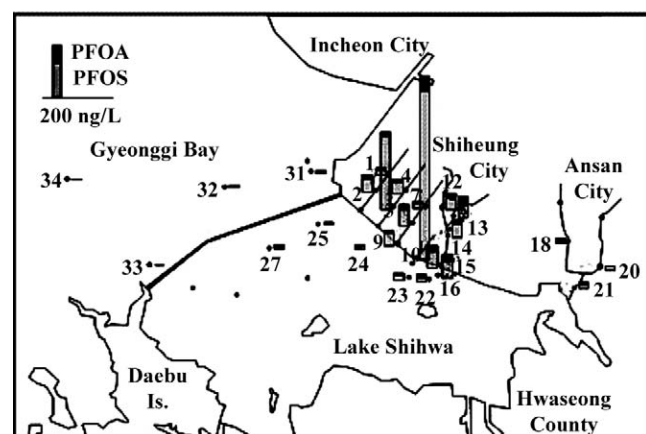


Fig. 2. Concentrations (ng/L) of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water samples from Lake Shihwa and Gyeonggi Bay, Korea.

Table 3. Concentrations of individual PFAs in samples from Lake Shihwa and Gyeonggi Bay, Korea^a

Map key ^b	Sample ID	Perfluorinated sulfonic acids (ng/L)				Perfluorinated carboxylic acids (ng/L)				
		PFOS	PFHxS	PFBS	PFOSA	PFDA	PFNA	PFOA	PFHpA	PFHxA
Streams										
1	IL1	20.15	2.02	0.89	<0.50	1.00	1.18	7.32	0.91	0.77
2	IL2	47.68	4.27	1.55	2.36	6.01	4.75	20.19	2.17	2.94
4	IL4	45.21	7.94	3.83	0.59	0.63	1.83	7.53	1.28	3.88
5	IL5	283.44	18.32	18.11	1.19	3.18	5.29	19.39	3.58	10.50
7	IL7	20.79	2.90	1.61	<0.50	0.56	1.30	6.20	1.03	1.13
8	IL8	64.59	5.10	1.50	<0.50	2.34	5.58	20.98	2.20	2.00
9	IL9	46.45	5.03	1.29	0.60	2.41	4.18	13.39	2.18	2.58
10	IL10	651.35	84.61	24.03	1.69	2.40	6.95	61.69	7.10	27.27
12	IL12	45.47	8.93	<0.50	0.58	<0.50	2.81	20.46	3.50	6.05
12	IL12Dup ^c	37.77	6.77	2.93	<0.5	1.06	2.00	19.59	2.93	4.05
13	IL13	47.45	5.25	1.18	<0.5	2.69	5.42	33.62	3.54	6.39
14	IL14	48.52	6.97	2.74	<0.5	0.86	2.75	19.69	2.58	3.48
15	IL15	60.58	8.91	2.45	0.79	1.53	3.71	21.11	3.21	5.06
16	IL16	59.45	7.51	<0.50	<0.50	2.25	3.87	29.36	2.44	2.52
18	IL18	8.03	2.25	0.58	<0.50	<0.50	1.36	11.63	1.27	1.16
20	IL20	10.38	3.18	0.79	<0.50	<0.50	0.83	5.21	1.14	1.26
21	IL21	17.51	1.94	0.64	0.58	0.76	1.69	9.44	1.40	1.60
Mean		89.11	10.70	4.27	1.05	1.98	3.26	19.22	2.50	4.86
Lake Shihwa										
22	LS8	18.32	2.04	1.03	<0.50	0.90	2.10	10.86	1.10	1.37
23	LS1	16.09	1.74	<0.50	<0.50	0.56	1.65	9.18	0.98	0.98
24	LS2	12.59	0.63	<0.50	<0.50	<0.50	1.29	4.52	<0.50	0.70
25	LS3	7.33	0.89	0.58	<0.50	<0.50	0.63	1.67	<0.50	<0.50
27	LS5	9.92	1.26	0.54	<0.50	<0.50	0.93	4.47	0.60	0.54
Mean		12.85	1.31	0.72	<0.50	0.73	1.32	6.14	0.89	0.90
Gyeonggi Bay										
31	LS9	8.26	0.55	<0.50	<0.50	<0.50	0.83	3.29	<0.50	0.60
31	LS9Dup	7.68	0.55	<0.50	<0.50	<0.50	0.69	3.21	0.50	0.52
32	LS10	5.31	0.99	<0.50	<0.50	<0.50	0.51	2.51	0.44	0.49
33	LS11	2.58	0.79	<0.50	<0.50	<0.50	<0.50	0.94	<0.50	<0.50
34	LS12	2.24	<0.50	2.53	<0.50	<0.50	<0.50	1.07	<0.50	<0.50
Mean		5.21	0.72	2.53	<0.50	<0.50	0.68	2.20	0.47	0.54

^a See Table 2 for definition of compounds.

^b See Figure 1 for locations sampled.

^c Dup = samples were collected in duplicate.

ranged from 0.6 to 5.8 ng/L, which were approximately 10-fold greater than those observed in coastal waters of China and Hong Kong, where values ranged from less than 0.02 to 0.69 ng/L.

Sources of PFOS and PFOA in Gyeonggi Bay

Concentrations of PFOS and PFOA decreased as a function of distance from the water gates in the dike forming Lake Shihwa. Concentrations of both PFOS and PFOA were greater

in Lake Shihwa than in Gyeonggi Bay. Concentrations of PFOS and PFOA observed in Gyeonggi Bay most likely result from releases of treated sewage effluent (near locations 30 and 31) and, to a lesser extent, from releases of water through the water gate because of tidal action (near location 33). Concentrations of PFOS and PFOA are greater in the eastern part of Gyeonggi Bay, nearer to the effluent pipe outlet, than those in the western part of Gyeonggi Bay. The gradient of decreasing concentrations among locations 31, 32, 33, and 34 most likely results from dilution through tidal action.

Input pathways into the lake from the watershed

Contaminants generated in the nearby watershed enter the lake primarily via wastewater discharge to waterways. Four drains and seven streams carry a large amount of municipal and industrial wastewater into the lake (Fig. 1). Wastewaters from the four drains in the Shihwa industrial complex and three streams (Shingil, Hwajeong, and Ansan) are collected and treated without separating wastewater at the Shihwa wastewater treatment plant (WTP; 455,000 ton/d) and the Ansan WTP (537,000 ton/d). Treated wastewater is discharged to the sea outside Lake Shihwa (near location 30) and also has been discharged at locations 24 and 25 within Lake Shihwa. During the rainy season, wastewaters frequently overflow the WTP and enter the lake. The eastern streams, including Banwoel,

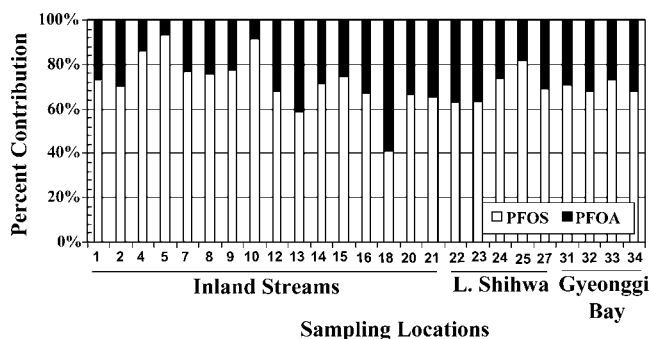


Fig. 3. Percentage composition (%) of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water samples from Lake Shihwa and Gyeonggi Bay, Korea.

Donghwa, and Namjeon, flow through a constructed wetland for self-cleanup. In the rainy season, which occurs during the summer, an annual average rainfall of 1,252 mm results in contaminants being washed out from the nearby watershed and into the west side of the lake.

Hazard assessment of PFOS exposure to aquatic species

An evaluation of the ecological risk to aquatic animals associated with exposure to PFOS was performed by comparing the measured concentrations of PFOS in water with water-quality (guideline) values that are protective of aquatic organisms [24]. Currently, no guidelines are specifically derived for saltwater, but guideline values have been developed following the procedures outlined in the U.S. Environmental Protection Agency Great Lakes Initiative [25] and based on the results of toxicity testing with freshwater organisms [24]. The screening value for PFOS for the protection of aquatic plants was determined to be 2.3 mg/L. Tier II water-quality values for aquatic animals are represented by the secondary maximum concentration (SMC) and secondary continuous concentration (SCC). The PFOS values for SMC and SCC were 8,500 and 1,200 ng/L, respectively. These values represent concentrations at which aquatic organisms would not be unacceptably affected if the 4-d average and 1-h average concentrations of PFOS did not exceed 1,200 or 8,500 ng/L more than once every three years respectively. To evaluate the protectiveness of this value to saltwater/brackish-water organisms, a tentative water value was estimated using chronic toxicity data with the mysid shrimp, *Mysidopsis bahia* [24]. In that study, a no-observed-effect concentration and a lowest-observed-effect concentration of PFOS were determined to be 240 and 530 $\mu\text{g/L}$, respectively. Using an application factor to take into account possible extrapolation uncertainties [25], a saltwater aquatic value for PFOS of 2,400 ng/L was calculated. However, because the tier II aquatic life SCC value based on freshwater species was less than either the screening plant value or the saltwater value, the SCC value for aquatic organism also would be protective for aquatic plants.

A preliminary estimate of risk was determined by comparing the concentrations of PFOS to these protective values (Fig. 4). None of the PFOS concentrations exceeded the SMC or SCC. In fact, even the greatest measured concentration of PFOS (651 ng/L) was approximately twofold less than the SCC and approximately 13-fold less than the SMC. However, the SCC value was based on toxicity data with an aquatic species that was approximately 40-fold more sensitive than any other aquatic species tested to date. Thus, it represents a conservative measure of risk to most aquatic organisms.

Because PFOS can be accumulated in the food chain [26], we also assessed the potential adverse effects of PFOS at the observed concentrations to adversely affect trophic level IV organisms, such as fish-eating birds [27]. The safe water concentration or avian wildlife value that is protective of trophic level IV avian species that might consume organisms at equilibrium with concentrations in the water was determined to be 50 ng/L of PFOS [27]. Concentrations of PFOS at only five locations (locations 5, 8, 10, 15, and 16) exceeded 50 ng/L, but concentrations at other sites were near 50 ng/L. In all cases, these exceedances only occurred in streams that discharged into Lake Shihwa and not in either the lake or the bay. Of the locations that exceeded the wildlife value, the PFOS concentrations in samples from Gunja Creek (location 5) and an unnamed Creek (location 10) exceeded the wildlife value by

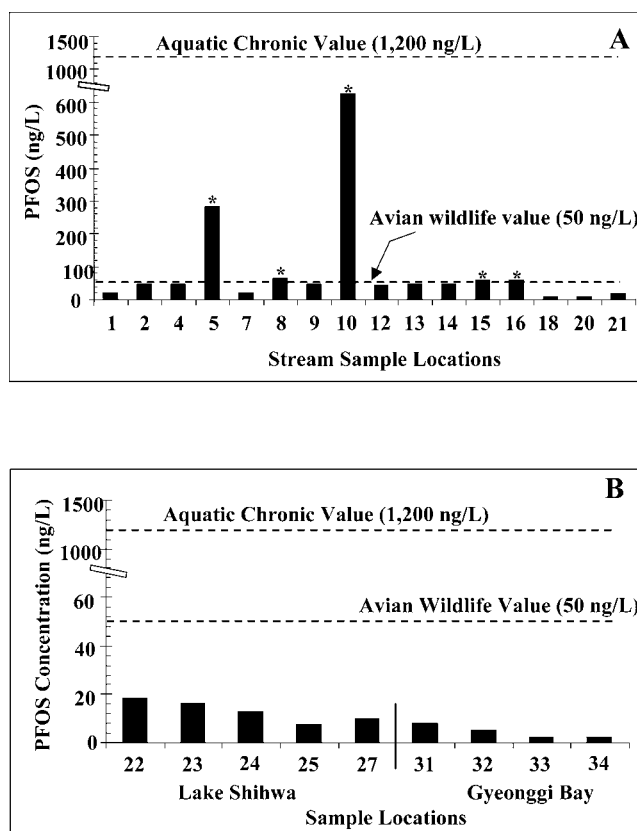


Fig. 4. Comparison of perfluorooctane sulfonate concentrations measured in Korean samples to values protective of aquatic and avian life. See text for details of derivation of quality criteria. (A). Streams flowing into Lake Shihwa. (B). Areas in Lake Chihwa and Gyeonggi Bay.

approximately 5- and 13-fold, respectively. However, because of the conservative nature of the risk analyses used to extrapolate from birds to safe water concentrations and the very localized nature of the PFOS concentrations in these two creeks, adverse effects at the population level would not be expected.

Because limited information was available, particularly for chronic effects, uncertainty factors and a conservative acute to chronic ratio were used to derive the threshold levels for the protection of aquatic life. For this reason, these values probably are overly conservative, possibly by as much as 50- to 100-fold, depending on the true distribution of sensitivities among organisms and differences in sensitivities between freshwater and saltwater organisms. Furthermore, the threshold value assumes that the target wildlife stayed in the area where the concentration of PFOS was determined and had eaten sufficient dietary items to have come to steady state with food in the diet. This may be true of some species, but it is unlikely that many of the larger piscivorous birds would remain in only one area. In addition, if the greatest concentrations measured in water are compared to the threshold water concentration, it is likely that the actual risk would be less. The only way to reduce the uncertainty of the assessment would be to measure concentrations of PFOS in the tissues of birds. If this were done, the measured concentrations in liver, blood plasma, or eggs could be compared to toxicity reference values calculated for birds. Furthermore, to determine if the actual exposures produced concentrations in predatory birds causing any ad-

verse effects, the measurement of appropriate biomarkers of the effects of PFOS would be necessary [28,29].

Perfluorooctanoate was present at the second greatest concentration of the PFAs measured. Because PFOA is accumulated less into biota compared with PFOS [26], a conservative estimate for the potential risk of the two compounds occurring at the greatest concentrations could be made by assuming that the toxic potencies of these two compounds are equal but that PFOA would accumulate approximately 10-fold less into biota. Thus, it can be concluded that the contribution of PFOA to the toxicity of the combination of PFOS and PFOA would be less than 1% in most cases. Thus, an assessment of the potential risk of the total mixture of PFAs was not conducted.

Because little information is available on the toxic potency of PFAs other than PFOS and PFOA, these compounds were not included in the risk assessment. However, because all these compounds not only occurred at lesser concentrations and would be expected to accumulate less and also be less toxic than PFOS [30,31], not assessing these compounds likely would not lead to significant underestimation of potential hazards.

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REFERENCES

- Organization for Economic Cooperation and Development. 2005. Draft assessment of perfluorooctanesulfonate (PFOS) and its salts: Complete assessment. ENV/JM/RD (2002). Paris, France.
- Giesy JP, Kannan K. 2002. Perfluorochemical surfactants in the environment. *Environ Sci Technol* 36:146A–152A.
- Kissa E. 2005. *Fluorinated Surfactants and Repellents*, 2nd ed. Marcel Dekker, New York, NY, USA.
- Giesy JP, Kannan K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol* 35:1339–1342.
- Kannan K, Koistinen J, Beckmen K, Evans T, Gorzelany JF, Hansen KJ, Jones PD, Helle E, Nyman M, Giesy JP. 2001. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ Sci Technol* 35:1593–1598.
- Olsen GW, Burris JM, Mandel JH, Zobel L. 1999. Serum perfluorooctane sulfonate and hepatic and lipid clinical chemistry tests in fluorochemical production employees. *Occup Environ Med* 41:799–806.
- Inoue K, Okada F, Ito R, Kato S, Sasaki S, Nakajima S, Uno A, Saijo Y, Sata F, Yoshimura Y, Kishi R, Nakazawa H. 2004. Perfluorooctane sulfonate (PFOS) and related perfluorinated compounds in human maternal and cord blood samples: Assessment of PFOS exposure in a susceptible population during pregnancy. *Environ Health Perspect* 112:1204–1207.
- Kannan K, Corsolini S, Falandysz J, Fillmann G, Kumar KS, Loganathan BG, Mohd MA, Olivero J, Van Wouwe N, Yang JH, Aldous KM. 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ Sci Technol* 38:4489–4495.
- Taniyasu S, Kannan K, Horii Y, Hanari N, Yamashita N. 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. *Environ Sci Technol* 37:2634–2639.
- Martin JW, Kannan K, Berger U, de Voigt P, Field J, Franklin J, Giesy JP, Harner T, Muir DCG, Scott B, Kaiser M, Jarnberg U, Jones KC, Mabury SA, Schroeder H, Simcik M, Sottani C, van Bavel B, Karrman A, Lindstrom G, Van Leeuwen S. 2004. Analytical challenges hamper perfluoroalkyl research. *Environ Sci Technol* 38:249A–255A.
- So MK, Taniyasu S, Yamashita N, Giesy JP, Zheng J, Fang Z, Im SH, Lam PKS. 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. *Environ Sci Technol* 38:4056–4063.
- Li Z, Li D, Oh JR, Je JG. 2004. Seasonal and spatial distribution of nonylphenol in Shihwa Lake, Korea. *Chemosphere* 56:611–618.
- Koh CH, Khim JS, Villeneuve DL, Kannan K, Johnson BG, Giesy JP. 2005. Instrumental and bioanalytical measures of dioxin-like and estrogenic compounds and activities associated with sediment from the Korean coast. *Ecotoxicol Environ Saf* 61:366–279.
- Khim JS, Villeneuve DL, Kannan K, Koh CH, Snyder SA, Giesy JP. 1999. Alkylphenols, polycyclic aromatic hydrocarbons (PAHs) and organochlorines in sediment from Lake Shihwa, Korea: Instrumental and bioanalytical characterization. *Environ Toxicol Chem* 18:2424–2432.
- Taniyasu S, Kannan K, So MK, Gulkowska A, Sinclair E, Okazawa T, Yamashita N. 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short and long-chain perfluorinated acids in water and biota. *J Chromatogr A* 1093:89–97.
- Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. 2005. A global survey of perfluorinated acids in oceans. *Mar Pollut Bull* 51:658–668.
- Moody CA, Martin JW, Kwan WC, Muir DC, Mabury SA. 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ Sci Technol* 36:545–551.
- Yamashita N, Taniyasu S, Horii Y, Okazawa T, Petrick G, Gamo T. 2004. Global monitoring survey of PFOS and related chemicals in marine environment. *Proceedings, 4th International Conference on Marine Pollution and Ecotoxicology*, Hong Kong, China, June 1–5, p K-8.
- Yamashita N, Kannan K, Taniyasu S, Horii Y. 2003. Bioaccumulation of perfluorooctane sulfonate (PFOS) and related compounds in Japanese environmental samples. *Abstracts, SETAC Europe, 13th Annual Meeting, April 27–May 1, Hamburg, Germany*.
- Taniyasu S, Kannan K, Horii Y, Yamashita N. 2002. The first environmental survey of perfluorooctane sulfonate (PFOS) and related compounds in Japan. *Organohalogen Compounds* 59:311–314.
- Hansen KJ, Johnson HO, Eldridge JS, Buitenhoff JL, Dick LA. 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ Sci Technol* 36:1681–1685.
- Martin JW, Smithwick MM, Braune BM, Hoekstra PF, Muir DC, Mabury SA. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ Sci Technol* 38:373–380.
- Gulkowska A, Falandysz J, Taniyasu S, Okazawa T, Shulte-Ochlmann U, Zalewski K, Yamashita N. 2005. PFOS and related chemicals in humans and several wild animals from Poland. *Proceedings, Symposium on Environmental Chemistry, Matsuyama, Japan, March 18–20, 2004*. Ehime University, Matsuyama, Japan, pp 576–577.
- Beach SA, Newsted JL, Coady K, Giesy JP. 2005. Ecological evaluation of perfluorooctanesulfonate (PFOS). *Rev Environ Contam Toxicol* 186:133–174.
- U.S. Environmental Protection Agency. 1995. Great Lakes water quality initiative technical support document for wildlife criteria. EPA 820B95009. Washington, DC, pp 1–53.
- Kannan K, Tao L, Sinclair E, Pastva SD, Jude JD, Giesy JP. 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Arch Environ Contam Toxicol* 48:559–566.
- Newsted JL, Jones PD, Coady K, Giesy JP. 2005. Avian toxicity reference values for perfluorooctane sulfonate. *Environ Sci Technol* 39:9357–9362.
- Hu W, Jones PD, DeCoen W, Newsted JL, Giesy JP. 2005. Comparison of gene expression methods to identify genes responsive to perfluorooctane sulfonic acid. *Environ Toxicol Pharmacol* 19:153–160.
- Hu W, Jones PD, Celius T, Giesy JP. 2005. Identification of genes responsive to PFOS using gene expression profiling. *Environ Toxicol Pharmacol* 19:57–70.
- Hu W, Jones PD, DeCoen W, King L, Fraker P, Newsted JL, Giesy JP. 2003. Alterations in cell membrane properties caused by perfluorinated compounds. *Comp Biochem Physiol Part C* 135:77–88.
- Hu W, Jones PD, Upham BL, Trosko JE, Lau C, Giesy JP. 2002. Inhibition of gap junctional intercellular communication by perfluorinated compounds in rat liver and dolphin kidney epithelial cell lines in vitro and Sprague-Dawley rats in vivo. *Toxicol Sci* 68:429–436.