

DISTRIBUTION CHARACTERISTICS OF PERFLUORINATED COMPOUNDS IN NAMHAN RIVER WATER AND SEDIMENTS IN KOREA

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Introduction

Perfluorinated compounds (PFCs) are used throughout the world and have been recently recognized as a global environmental pollutants.¹ PFCs are used in industrial applications and are characterized by a fluorinated carbon tail with a hydrophilic head. Because PFCs are water resistant and oil repellent and can also be used in making materials stain resistant,² they have been used in textiles, paper, cosmetics, insecticides, and firefighting foams. The most ubiquitous PFC in human samples is perfluorooctane sulfonate (PFOS), however, other perfluoro carboxylic acids (PFACs) and sulfonates are also frequently detected.³⁻⁵ PFCs are highly persistent, bioaccumulative, and toxic,¹ and therefore, they could potentially have significant adverse effects on human health and the environment.⁶⁻⁷ Although humans are exposed to PFCs from a variety of sources, drinking water is probably the major intake pathway.⁸ In a previous survey, a site along the Namhan River was identified as being a likely hot spot for PFCs, and the objective of this study is to evaluate the levels of PFCs in the vicinity of this hot spot as a part of a monitoring program.

Materials and Methods

Sample collection and preparation: Water and sediments were collected from ten estuarine sites along the Namhan River in Korea during December of 2012. Two liters of surface water were collected in carefully rinsed 2-L polypropylene (PP) containers. Sediment samples were collected using a stainless steel trowel, which was pre-rinsed with methanol. Samples were stored in clean PP bags, and transported immediately to our laboratory. Water samples were filtered using glass-fiber filters. Sediment samples were air-dried, ground and homogenized with a kitchen mixer, and then passed through a 100-mesh sieve.

Sample extraction and analysis: Water samples were extracted based on US EPA Method 537 with minor modifications and using the Oasis HLB extraction cartridges (200 mg, 6 cc Waters Corp., Milford, Massachusetts, USA). First, the cartridges were preconditioned by diluting with 10 mL of methanol followed by 20 mL of HPLC grade water at a rate of one drop per second, and then the cartridges were fully dried. Five hundred milliliters of water spiked with 5 ng of an internal standard (MPFAC-MXA, Wellington Lab., Guelph, Canada) were loaded onto the cartridge and eluted at a rate of one drop per second, and then dried completely. Finally, the target fraction was eluted with 13 mL of methanol at a rate half a drop per second and this was collected in a 15-mL PP centrifuge tube. The extract was then reduced to 1 mL under a gentle stream of nitrogen gas, and spiked with 5 ng of the labeled syringe standard (M8PFOA), and filtered using a disposable PP syringe fitted with a disposable 0.2- μ m nylon filter. Sediment samples were extracted based on a previously reported method⁹ with minor modifications. In brief, 1 g of the sample was transferred to a 15-mL PP tube, spiked with 5 ng of the internal standard, 7.5 mL of methanol were added, and the sample was mixed for 1 min using a vortex mixer. Ultrasonic extraction was performed for 30 min, centrifuged at 3,000 rpm for 10 min, and the supernatant was transferred to a 50-mL conical tube. This extraction process was repeated three times. The extract was centrifuged at 8,000 rpm for 1 hour, and then reduced to 1 mL under a gentle stream of nitrogen gas, before being spiked with 5 ng of the labeled syringe standard (M8PFOA) and filtered using a disposable PP syringe fitted with a disposable 0.2- μ m nylon filter. The instrumental analysis was performed on an Agilent 1200 series liquid chromatograph with a 6460 tandem mass spectrometer system.

Results and Discussion

The total concentration of PFCs in the water samples ranged from 1.5 ng L⁻¹ to 7.5 ng L⁻¹. PFHxA, PFHpA, PFOA, PFNA, PFHxS, and PFOS were frequently detected among the twelve PFCs investigated. PFHxS was the predominant compound, followed by PFHpA. PFC concentrations in the water and sediments are listed in detail in Tables 1 and 2, respectively. The highest concentration of total PFCs was found at the site near Mokhaeng-bridge, followed by the sites near Yeoju-bo and Hageomdan-bridge. These sites were likely influenced by

nearby effluence of municipal or industrial wastewaters. The total concentration of PFCs in the sediment samples ranged from 0.050 ng g⁻¹ dry wt. to 3.5 ng g⁻¹ dry wt. Concentrations of PFCs in sediments were generally below the detection limits of the method used. PFOA was the only congener that was detected in all sediment samples. PFOS was detected in six out of ten sediment samples. In summary, the site near Mokhaeng-bridge showed the highest PFC level, indicating the most contaminated site. The average levels of PFOA and PFOS were 1.0 and 0.16 ng L⁻¹ in water, and 0.71 and 0.56 ng g⁻¹ dry wt. in sediments, respectively. Concentrations of PFCs were gradually diluted by the flow of water from the Tangeumdae-bridge. Compared to concentrations of PFCs in water obtained from the Youngsan and Nakdong River reported in other studies¹⁰ (ranged from 12 to 34 ng L⁻¹ in estuarine areas) the values here were lower; in the case of sediment, the average concentration of PFCs obtained from the Youngsan and Nakdong River was 0.53 ng g⁻¹ dry wt., which is very close to that found in this study.



Figure 1. Description of sampling site from the Namhan river, Korea in 2012

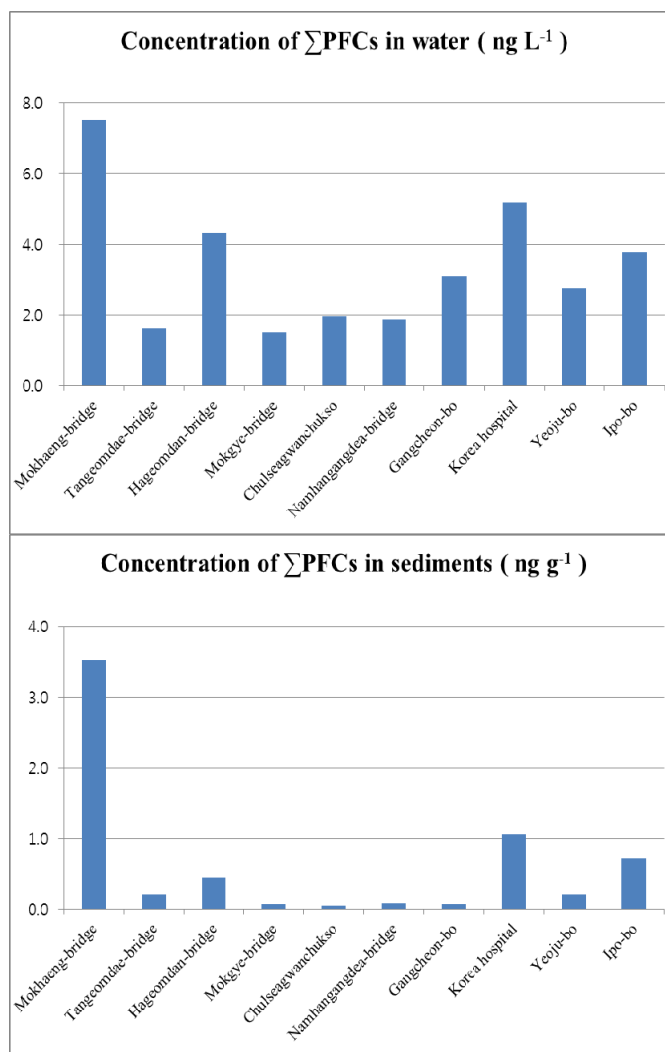


Figure 2. Concentration change through upstream to downstream in water and sediment

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Table. 1. PFCAs, PFSA concentrations in water in Namhan river, Korea (ng L⁻¹ wet wt.)

Location	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	∑PFCAs	PFHxS	PFOS	PFDS	∑PFSA	∑PFCs
MDL	0.33	0.11	0.12	0.10	0.11	0.15	0.10	0.16	0.10		0.19	0.13	0.19		
Mokhaeng-bridge	1.2	1.3	0.83	0.36	0.16	-	-	-	-	2.7	3.7	1.2	-	4.9	7.5
Tangeomdae-bridge	-	0.37	0.44	0.13	-	-	-	-	-	0.94	0.37	0.33	-	0.70	1.6
Hageomdan-bridge	1.1	0.90	2.1	0.49	-	0.18	-	-	-	3.7	0.38	0.29	-	0.67	4.3
Mokgye-bridge	0.37	0.26	0.51	0.11	-	-	-	-	-	0.88	0.31	0.34	-	0.65	1.5
Chulseagwanchukso	0.44	0.28	0.51	0.17	-	-	-	-	-	0.96	0.40	0.60	-	1.0	2.0
Namhangangdae-bridge	0.33	0.57	0.47	0.17	-	-	-	-	-	1.2	0.31	0.37	-	0.7	1.9
Gangcheon-bo	0.55	0.66	0.85	0.21	-	-	-	-	-	1.7	0.57	0.80	-	1.4	3.1
Korea hospital	0.45	0.63	2.2	0.20	-	-	-	-	-	3.1	0.62	1.5	-	2.1	5.2
Yeoju-bo	0.61	0.61	0.72	0.16	-	-	-	-	-	1.5	0.56	0.71	-	1.3	2.8
Ipo-bo	1.0	0.49	1.3	0.24	0.13	-	-	-	-	2.2	0.63	0.96	-	1.6	3.8
Sum	6.0	6.1	10	2.2	0.29	0.18				19	7.8	7.1		15	34

Table. 2. PFCAs, PFSA concentrations in sediment in Namhan river in Korea (ng g⁻¹ dry wt.)

Location	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	∑PFCAs	PFHxS	PFOS	PFDS	∑PFSA	∑PFCs
MDL	0.07	0.08	0.05	0.07	0.05	0.08	0.06	0.09	0.09		0.10	0.12	0.12		
Mokhaeng-bridge	0.15	-	0.13	0.08	0.16	0.19	0.08	0.21	-	0.85	0.24	2.43	-	2.7	3.5
Tangeomdae-bridge	0.07	-	0.09	-	-	-	-	-	-	0.09	-	0.12	-	0.12	0.21
Hageomdan-bridge	-	-	0.14	-	0.09	0.10	-	-	-	0.32	-	0.13	-	0.13	0.45
Mokgye-bridge	-	-	0.07	-	-	-	-	-	-	0.07	-	-	-	0.00	0.07
Chulseagwanchukso	-	-	0.05	-	-	-	-	-	-	0.05	-	-	-	0.00	0.05
Namhangangdae-bridge	-	-	0.08	-	-	-	-	-	-	0.08	-	-	-	0.00	0.08
Gangcheon-bo	-	-	0.07	-	-	-	-	-	-	0.07	-	-	-	0.00	0.07
Korea hospital	-	-	0.77	-	0.05	-	-	-	-	0.83	-	0.23	-	0.23	1.1
Yeoju-bo	-	-	0.09	-	-	-	-	-	-	0.09	-	0.13	-	0.13	0.21
Ipo-bo	-	-	0.11	0.07	0.12	0.13	-	-	-	0.42	-	0.29	-	0.29	0.71
Sum	0.22	0.00	1.6	0.14	0.41	0.42	0.08	0.21	0.00	2.9	0.24	3.3	0.00	3.6	6.4

* - : below detection limits.

**MDL values are indicated at the top of table