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Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea

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Among various environmental media measured, water and biological samples showed relatively high degrees of PFC contamination with the existence of point sources mainly upstream of coastal areas in Korea.

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ABSTRACT

Soil, sediment, water, and biota collected from the western coast of Korea were analyzed to determine occurrence and sources of perfluorinated compounds (PFCs). PFCs were significantly concentrations of PFCs were measured in some water and biological samples, while concentrations of PFCs in soils and sediments were relatively low. The most widely detected compound was found to be perfluorooctanesulfonate (PFOS), with a maximum concentration in water of 450 ng/L and in fish of 612 ng/g, dw. PFOS concentrations in water and biota were both less than those thought to cause toxicity. However, in both cases concentrations were within a factor of 10 of the toxicity threshold concentration. Concentrations of PFCs were significantly greater downstream than those upstream on the same river, suggesting point sources. Overall, the detection of PFCs at relatively great concentrations in various environmental matrixes from this region of Korea suggests that further studies characterizing PFCs and their potential risk to both humans and wildlife are needed.

1. Introduction

Perfluorinated compounds (PFCs) have been produced in relatively large quantities since the 1950s for a wide range of applications such as carpet coatings, food packaging, shampoos, paper, and fire-fighting foams (Giesy and Kannan, 2001; Paul et al., 2009). PFCs make excellent surfactants and surface protectors due to their unique properties of repelling both water and oil. Some of these compounds are persistent in the environment, whereas others degrade to more environmentally stable compounds (Dinglasan et al., 2004). These properties arise from the characteristics imparted by the elemental fluorine atom, which is the most electronegative of the halogens (Giesy and Kannan, 2002). These properties cause the C–F covalent bond, which makes up the back bone of any PFCs to be very strong and resistant to hydrolysis, photolysis, metabolism, and biodegradation (Kissa, 2001). It is these properties that cause PFCs to be environmentally persistent and hence have the potential to be bioaccumulative (Giesy et al., 2010).

PFCs are globally ubiquitous in both remote and urban environments (Ellis et al., 2004; Yamashita et al., 2005). PFCs are present in various matrices including; human blood (whole, plasma and serum), sediments, water, and wildlife (Giesy and Kannan, 2001; Kannan et al., 2004; Yamashita et al., 2005). Due to their widespread uses in many common products, PFCs are routinely found in the blood and serum of both occupationally and non-occupationally exposed people (Olsen et al., 2003; Kannan et al., 2004). The most widely distributed, and also the most studied PFC is perfluorooctanesulfonate (PFOS). While production of PFOS-based products was voluntarily halted by North America's largest producer; the 3M company in 2000 (3M, 2000), PFOS is still in environmental and human blood samples throughout Asia (Rostkowski et al., 2006; Yeung et al., 2006; So et al., 2007).

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Although PFCs have been produced on a large scale for more than 40 yr, it was not until the late 1990's that researchers started detecting PFCs in the environment (Giesy and Kannan, 2001). This was due to a number of factors including: lack of accurate and sensitive methods for extraction, lack of standards, especially isotopically labeled ones, and lack of instrumentation with sufficient sensitivity (Martin et al., 2004). With the advent of high performance liquid chromatography (HPLC) coupled with electrospray-ionization tandem mass spectrometry, PFCs could be accurately and routinely measured in the environment (Hansen et al., 2001).

Previous studies have reported concentrations of PFCs in Korea to be relatively great, particularly among the Asian countries, and when compared to other regions around the globe (Kannan et al., 2004; So et al., 2004; Yamashita et al., 2005; Rostkowski et al., 2006; Yoo et al., 2009). However, relatively little was known about sources, distribution and fate among matrices including sediment, soil, water, and biota. As part of an ongoing study to determine the current status and extent of PFC concentrations, as well as the potential for detrimental environmental effects in the Yellow Sea region of China and Korea, environmental samples were collected along the western coast of Korea during May of 2008. Locations were chosen based on previous work showing elevated concentrations of PFCs in the region (So et al., 2004; Rostkowski et al., 2006; Yoo et al., 2009) and to further detect possible point sources. Concentrations of PFOS and 12 other PFCs in environmental samples collected from estuarine and coastal areas of Korea, were determined to assess the potential risk of PFCs to both humans and wildlife.

2. Materials and methods

2.1. Chemicals

Omni-Solv grade methanol was purchased from EMD Chemicals (Gibbstown, NJ, USA). HPLC grade ammonium acetate was purchased from J.T. Baker (Phillipsburg, NJ, USA). Sodium thiosulfate was purchased from EMD Chemicals (Gibbstown, NJ, USA). The internal standard consisted of perfluorononanoic acid (PFOA) [1,2,3,4 ^{13}C] (>98%, Wellington Laboratories), and PFOS [$^{18}O_2$] (RTI International). The external standard used for all matrix spikes was a mixture of 12 different PFCs (>98%, Wellington Laboratories) including perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, and perfluorodecane sulfonate (PFDS), perfluorobutyric acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA).

2.2. Sample collection

Water, soil, sediment, and biota were collected from 8 estuarine and coastal areas along the western coast of Korea during May of 2008 (Table 1 and 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 1–5 cm) soil and sediment samples were collected using a clean methanol rinsed stainless steel trowel. Samples were transferred and stored in clean PP bags. Biological samples were collected by hand in coastal tidal pools and along the shore of inland water bodies, and were transferred and stored in clean PP bags. Sample duplicates and field blanks were collected daily, and were analyzed along with lab and procedural blanks. All samples were transported on ice at 4 °C to the laboratory and frozen at −20 °C until analyses.

2.3. Extraction and cleanup

Water samples were extracted using Oasis HLB extraction cartridges (0.2 g, 6 cm^3) (Waters Corp., Milford, MA) as previously reported (So et al., 2004). In brief, the cartridges were preconditioned by eluting with 5 mL of methanol followed by 5 mL of nano-pure water at a rate of 2 drops a second. Five hundred milliliter of water was then spiked with 500 μl of 5 ng/mL of the internal standard (Isotopically labeled PFOS and PFOA) and then loaded onto the cartridge, at a rate of 1 drop a second. The eluent was discarded. The cartridge was then washed with 5 mL of 40% methanol in water, and the eluent was again discarded, and once complete was allowed to run dry. Lastly, the target fraction was eluted with 10 mL of methanol at a rate of 1 drop a second and collected in a 15 mL PP centrifuge tube. The resulting eluate was then reduced to 1 mL under a gentle stream of nitrogen gas, and filtered using a disposable PP syringe, fitted with a disposable PP 0.2 μm filter (Millipore, Bedford, MA, USA). Samples were stored and analyzed in PP auto-sampler vials fitted with PP septa (Canadian Life Science, Peterborough, ON, CAN), as it has been shown that glass vials and PTFE septa may cause loss of analyte and increased contamination, respectively (Yamashita et al., 2004).

Soil and sediment samples were extracted using a previously published method (Higgins et al., 2005) with minor changes. Briefly, homogenized freeze-dried 1 g samples were transferred to 50 mL PP centrifuge tubes 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 vial was then vortexed, and placed in a heated sonication bath for 15 min. After sonication the tubes were centrifuged at 3000 rpm for 2 min and the acetic acid solution was decanted into a new clean 50-mL PP tube. 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 was described above in the water extraction procedure.

Table 1
Sampling details including location description and type of samples collected during the survey along the west coast of Korea.

Sampling				Sample details (# of samples)			
Area	Date	Location	Geological description	Water	Soil	Sediment	Biological (# of indv.)
Lake Shihwa	29-Apr	LS1	Outside of lake, Gyeonggi Bay	1	1	1	Surf Clam (7)
		LS2	Outside of lake, Gyeonggi Bay	1	NA[a]	NA	Oyster (20)
		LS3	Inside of lake	1	NA	NA	Asian Periwinkle (50)
		LS4	Inside of lake	1	NA	NA	Asian Periwinkle (50)
Asan	30-Apr	AS1	Inside of lake	1	NA	1	NA
		AS2	Outside of lake, Asan Bay	1	1	1	NA
SapGyo	30-Apr	SG1	Inside of lake	1	1	1	NA
		SG2	Outside of lake, Asan Bay	1	1	1	Crab (10)
SinDuri	30-Apr	SD	Beach	1	1	1	Striped Mullet (1)
ManLipo	30-Apr	ML	Beach (Oil spill site)	1	1	1	Asian Periwinkle (200)
AnMyundo	30-Apr	AM	Beach	1	1	1	Mussel (4) Blue Mussel (15) Neritid Gastropod (40) Asian Periwinkle (100)
GeumGang	1-May	GG1	Upstream, inside of dam	1	1	1	NA
		GG2	Downstream, outside of dam	1	1	1	NA
YeongSangang	1-May	YS1	Downstream, outside of dam	1	1	1	Asian Periwinkle (75) Rockfish (1)
		YS2	Upstream, inside of dam	1	1	1	NA
No. of location				15	11	12	9
No. of samples				15	11	12	13 (573 individuals)

[a] NA: Not available.

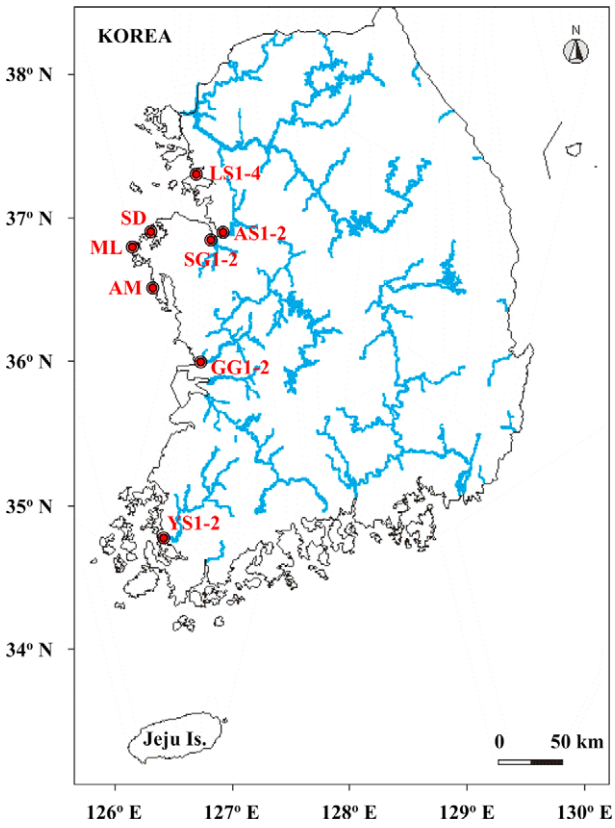

Fig. 1. Map of study area. Water, soil, sediment, and biota collected from 15 locations in 8 estuarine and coastal areas of Korea. Sampling design and sample information is given in Table 1.

Biological samples were extracted using an alkaline digestion solid phase extraction (SPE) method (So et al., 2006). A 1 g aliquant of homogenized freeze-dried tissue was transferred to a 50-mL PP centrifuge tube and spiked with 500 μl of 5 ng/mL internal standard, and 30 mL of 0.01 N KOH/methanol was added to the tube. The mixture was then shaken at 250 rpm for 16 h. After this digestion 1 mL of the resulting tissue solution was added to a 1-L PP bottle containing 100 mL of nano-pure water and shaken thoroughly. This tissue–water mixture was then extracted using SPE cartridges as previously stated above.

2.4. Analysis

Analytical methods were optimized to allow for simultaneous detection of all target analytes. Analyte separation was accomplished by use of an Agilent 1200 HPLC fitted with a Thermo Scientific Betasil C18 (100 × 2.1 mm, 5 μm particle size) analytical column operated at 35 °C. Gradient conditions were used at 300 μL/min flow rate, starting with 60% A (2 mM ammonium acetate) and 40% B (100% methanol). Initial conditions were held for 2 min and then ramped to 20% A at 18 min, held till 20 min, decreased to 0% A at 21 min, increased to 100% A at 22 min, held until 22.5 min, returned to initial condition at 23 min, and finally held constant until 26 min.

Mass spectra were collected using an Applied Bioscience SCIEX 3000 (Foster City, CA) tandem mass spectrometer, fitted with an electrospray ionization source, operated in negative ionization mode. Chromatograms were recorded using MRM mode, and when possible at least two transitions per-analyte were monitored (Table 2). 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 −3500 V; collision gas 12 AU; and a dwell time of 40 ms. The optimal settings for collision energies and declustering potential were determined for each analyte's transitions. Quantification using these transitions was performed using Analyst 1.4.1 software provided by SCIEX (Applied Bioscience, Foster City, CA).

2.5. Quality control

To reduce instrument background contamination coming from the HPLC or solvents, a ZORBEX (Thermo Scientific, 50 × 2.1 mm, 5 μm particle size) column was inserted directly before the injection-valve, as adapted from Benskin et al. (2007). Blanks were run every 4–5 samples to check for carryover and background contamination. All blanks were found to be below the limit of quantification (LOQ), where the LOQ was defined as 5× the background. Teflon coated lab-ware was avoided during all steps of standard solution preparation to minimize contamination of the samples. The ions monitored, method detection limit (MDL), and matrix spike recoveries for all of the chemicals of interest are given (Table 2).

3. Results and discussion

3.1. PFCs in water

Although 12 different compounds were investigated the following discussion will focus primarily on PFOS and PFOA since these compounds were consistently found at the greatest concentrations. The occurrence and concentrations of PFCs in samples collected from western Korea during the summer of 2008 are summarized (Tables 3–5). All PFCs except for PFDoA were detected in water samples and particularly some PFCs including PFHxS, PFOS, PFOA, PFNA, and PFDA were detected in all water samples (Table 3). PFOS (mean = 59.5 ng/L) and PFOA (20.6 ng/L) were found to be the predominant waterborne PFCs and concentrations of PFOS and PFOA in water ranged from 4.11 to 450 and from 2.95 to 68.6 ng/L, respectively. The next greatest mean PFC concentration was 10.0 ng PFHpA/L with a range of 1.11–47.2 ng/L.

The greatest concentration of PFOS (450 ng/L) was found at location AS1 which is located in the Asan reservoir adjacent to the city of Asan. This sample showed relatively great concentrations of all of the PFCs monitored, and had a total PFC (sum of all 13 compounds; ∑PFC) concentration of approximately 700 ng/L. When the top two predominant PFCs (viz. PFOS and PFOA) were compared to other regions in Asia, the sum of PFOS and PFOA (500 ng/L) found at AS1 was among one of the greatest concentrations ever reported in water from this region (Table 6). Due to poor water circulation and a large amount of industrial development in the vicinity, Asan reservoir has had poor water quality since the completion of dike construction in the early 1970s. Due to dilution, corresponding concentrations of PFCs at the outer location AS2 were less than those at the inner location. The least PFC concentrations were found at SinDuri, which represents coastal ocean water where concentrations of PFOS and PFOA were 5.21 and 2.95 ng/L, respectively, with the concentration of ∑PFC less than 10 ng/L.

Concentrations of PFCs in Korean waters were relatively greater than those in other areas such as the North American Great Lakes, South China Sea, Arctic, Antarctic, and Pacific oceans (Boulanger et al., 2004; So et al., 2004; Yamashita et al., 2005). For example, the greatest concentration of PFOS ever reported in water from Tokyo Bay, Japan was 59 ng/L, while the mean PFOS concentration from all of the Korean locations was approximately 59.5 ng/L (Taniyasu et al., 2003). Concentrations measured in this study were similar to those reported previously for Korea (Rostkowski et al., 2006; Yoo et al., 2009), except for greater concentrations of PFOS in water from Lake Shihwa. All the locations for Lake Shihwa are situated along the dike (2 from outside of the dike and 2 from inside of the dike) in our study the mean PFOS concentrations (mean = 57.9 ng/L, $n = 4$) were relatively greater than those reported in a similar previous study (mean = 9.03 ng/L, $n = 10$) (Rostkowski et al., 2006). Considering the sampling years of 2004 and 2008 in the previous and present study, respectively, the increase of PFOS concentrations in this region indicated continuing and recent input of PFOS. Lake Shihwa is a man-made lake on the outskirts of Seoul, which is heavily used and influenced by a wide variety of local industries encompassing >7000 companies mainly with steel/mechanical (ca. 50%), electric/electronic (ca. 15%), and petrochemical companies (ca. 10%). Thus all of these local activities are thought to be potential sources for PFCs contamination in this region at this

Table 2
Target analytes of 12 perfluorinated compounds measured in the present study with QA/QC information including monitoring transitions, method detection limit (MDL), and matrix spike recovery (MSR) for water, soil and sediment, and biological samples (Mean ± SD).

Analyte	Acronym	Monitoring transitions	MDL			MSR		
			Water (ng/L)	Soil/Sed (ng/ml)	Biological (ng/g)	Water (%)	Soil/Sed (%)	Biological (%)
Perfluorobutane sulfonate	PFBS	299 → 99, 80	1	1	1	94 ± 40	32 ± 9	97 ± 7
Perfluorohexane sulfonate	PFHxS	399 → 99, 80	0.2	0.5	1	137 ± 15	134 ± 38	68 ± 26
Perfluorooctanesulfonate	PFOS	499 → 99, 80	0.2	0.5	0.1	101 ± 22	95 ± 30	89 ± 8
Perfluorodecane sulfonate	PFDS	599 → 99, 80	0.2	0.5	0.1	101 ± 21	43 ± 16	70 ± 18
Perfluorobutanoic acid	PFBA	213 → 169	2	1	1	120 ± 19	IS[a]	10 ± 4
Perfluorohexanoic acid	PFHxA	313 → 269	1	0.1	1	84.6 ± 58	78 ± 8	73 ± 6
Perfluoroheptanoic acid	PFHpA	363 → 319, 169	1	0.1	0.1	103 ± 16	123 ± 16	112 ± 17
Perfluorooctanoic acid	PFOA	413 → 219, 169	1	0.5	0.5	88 ± 25	89 ± 7	88 ± 7
Perfluorononanoic acid	PFNA	463 → 419, 219	2	1	1	133 ± 23	135 ± 18	133 ± 19
Perfluorodecanoic acid	PFDA	513 → 469, 269	0.2	0.1	0.1	93 ± 13	46 ± 11	75 ± 7
Perfluoroundecanoic acid	PFUnA	563 → 269, 219	2	0.5	1	112 ± 22	53 ± 12	90 ± 21
Perfluorododecanoic acid	PFDoA	613 → 569, 319	2	0.1	0.5	77 ± 17	22 ± 12	47 ± 13

[a] IS: Insufficient recovery.

time (Rostkowski et al., 2006; Yoo et al., 2009). In general, the concentration ratio of PFOS to PFOA (mean of >4) agrees well with previously published values (Fig. 2) in Lake Shihwa indicating unique local sources of both PFOS and PFOA in this region, but concentrations of PFOS measured in waters of Lake Shihwa were 6-fold greater in 2008 than they had been in 2004 (Rostkowski et al., 2006), indicating again the increase of PFOS contamination in this region.

3.2. PFCs in soils and sediments

Concentrations of PFCs in soils and sediments were generally less than the MDL, but when detected were generally less than those in biota. Concentrations were comparable to those previously reported in other areas of Asia but slightly less than those reported in Europe and the United States (Higgins et al., 2005; Nakata et al., 2006). Only 5 soil and 3 sediment samples contained detectable concentrations of PFCs, but when PFCs were detected, the longer-chain PFCs such as PFOS and PFDA were predominant, There did not seem to be a difference between soils and sediments, neither had a PFOS concentration greater than 2.0 ng/g. In general, it appears that soil and sediment samples in Korea contain only small amounts of PFCs and do not appear to contribute significantly to the exposure of benthic or terrestrial organisms.

Table 3
Overview of PFCs analysis results (number of samples detected and %-occurrence in parenthesis given) for water, soil, sediment, and biological samples collected along the west coast of Korea.

Area	Water	Soil	Sediment	Biological
Sampling location (*n*)	15	11	12	9
Samples analyzed (*n*)	15	11	12	13
Samples detected	*n* (%)	*n* (%)	*n* (%)	*n* (%)
PFBS	11 (73)	0 (0)	0 (0)	0 (0)
PFHxS	15 (100)	0 (0)	0 (0)	0 (0)
PFOS	15 (100)	4 (36)	3 (25)	13 (100)
PFDS	5 (33)	0 (0)	0 (0)	6 (46)
PFBA	6 (40)	0 (0)	0 (0)	1 (8)
PFHxA	14 (93)	1 (9)	0 (0)	13 (100)
PFHpA	13 (87)	3 (27)	2 (17)	3 (23)
PFOA	15 (100)	2 (18)	1 (8)	7 (54)
PFNA	15 (100)	1 (9)	0 (0)	1 (8)
PFDA	15 (100)	5 (45)	3 (25)	11 (85)
PFUnA	3 (20)	2 (18)	3 (25)	12 (92)
PFDoA	0 (0)	1 (9)	1 (8)	5 (38)
Average detected	11 (67)	2 (13)	1 (8)	6 (46)

3.3. PFCs in biota

Similar to sediments, concentrations of PFCs in biota were relatively small (Table 5). PFOS was the predominant PFC in biota with a mean concentration of 64.2 ng/g dw and values ranging from 0.26 to 612 ng/g. Concentrations of PFOA in biota were less than those of PFOS with concentrations ranging from less than the MDL to 1.46 ng/g. Other PFCs consistently detected were PFHxA, PFDA and PFUnA which had maximum concentrations of 34.6, 2.08 and 4.40 ng/g, and average concentrations of 5.91, 0.76, and 2.01 ng/g, respectively. The greatest concentration of PFOS (612 ng/g) was found in liver of fish collected from SinDuri Beach and the second greatest concentration (266 ng/g) was found in intestines of fish collected from the same location, indicating point sources near SinDuri Beach.

Also soft tissues of Asian Periwinkles (*Littorina brevicula*) and gills of Rockfish (*Sebastes schlegeli*) from downstream of Yeong-Sangang (YS1) contained relatively great concentrations of PFOS (233 and 99.2 ng/g, respectively), which suggested accumulation of PFOS in filter-feeding biota in the water column. The relatively great concentration of PFCs found in biota at these locations, relative to measured water concentrations, highlights significant bioconcentration. However this trend was not seen at all sites, as the levels measured in biota collected from LS3, were significantly less than concentrations measured in the surrounding water. This variation may indicate different uptake pathways, where depending on the site, waterborne or dietary exposure may be more important. Concentrations of PFOS from all other locations were relatively less. In Lake Shihwa and YeongSangang, higher trophic level organisms contained greater concentrations of PFCs. For example, at YeongSangang the mean concentration of most PFCs was found to be greater in Rockfish than those in Asian Periwinkles, although the number of fish collected was rather small (Table 5).

Concentrations of PFOS in fish collected from Korean waters during this study were similar to those observed previously in Korea and Japan (Taniyasu et al., 2003; Nakata et al., 2006; Yoo et al., 2009). However, the concentration of 612 ng/g PFOS measured in this study is among the greatest ever reported in fish liver from this region.

3.4. Pattern of relative concentrations

PFOS and PFOA were the most dominant PFCs observed. PFOS was the dominant PFC in both water and biota (Figs. 2 and 3). PFOS was the dominat PFC in 10 of the 15 water samples, whereas

Table 4
Concentrations (ng/L) of PFCs detected in water samples collected from the west coast of Korea.

Location	PFBS	PFHxS	PFOS	PFDS	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA
LS1	4.68	2.27	103	ND	ND	3.63	2.40	9.58	2.79	1.27	ND
LS2	1.35	1.18	8.69	ND	ND	1.66	1.11	3.30	1.83	0.31	ND
LS3	1.43	1.34	66.3	ND	ND	1.70	1.36	4.54	3.43	4.23	ND
LS4	ND[a]	3.66	53.7	ND	ND	3.79	3.58	15.1	5.58	5.22	2.88
AS1	39.8	41.8	450	ND	3.98	47.0	29.7	50.1	14.3	15.4	2.84
AS2	8.00	8.58	36.2	ND	ND	8.89	6.02	14.7	3.82	0.83	ND
SG1	ND	2.53	12.8	0.20	4.48	5.15	3.87	68.6	2.61	0.53	ND
SG2	7.84	8.18	28.5	ND	3.10	13.0	10.6	35.1	5.49	1.04	ND
SD	ND	0.58	5.21	ND	ND	1.28	ND	2.95	1.38	0.23	ND
ML	ND	0.38	4.11	0.23	ND	ND	ND	3.04	2.03	0.26	ND
AM	2.05	1.76	6.32	0.22	3.90	4.98	3.89	10.6	2.65	0.34	ND
GG1	3.30	4.51	48.4	0.22	ND	5.43	4.94	39.7	7.48	4.38	3.52
GG2	4.68	4.83	18.3	5.28	ND	5.91	4.01	28.4	4.66	1.08	ND
YS1	1.51	1.52	9.83	ND	9.55	4.86	47.2	6.09	4.37	0.67	ND
YS2	2.57	10.2	40.5	ND	4.66	8.12	11.5	17.0	6.13	1.16	ND
Min	ND	0.38	4.11	ND	ND	ND	ND	2.95	1.38	0.23	ND
Max	39.8	41.8	450	5.28	9.55	47.0	47.2	68.6	14.3	15.4	3.52
Mean	7.02	6.22	59.5	1.23	4.95	8.25	10.0	20.6	4.57	2.46	3.08
SD	11.1	10.3	112	2.26	2.32	11.6	13.5	19.8	3.21	3.93	0.38

[a] ND: below the method detection limit.

PFOA was predominant in water from only 5 locations. This observation is different than what is often observed at other locations in Asia (Table 6), where PFOA is often the dominat PFC in water, but it should be noted that similar results were also found for the Pearl River, China (So et al., 2007) and the Ganges River, India (Yeung et al., 2009). The relatively large percentage of PFOS in water samples suggests localized sources that are unique to the study region at this time.

Site-specific, apparent bioconcentration factors (BCF) were calculated for PFOS in fish by dividing the concentration of PFOS in fish by that in water at the same location. Due to a lack of fish samples BCFs could only be calculated for PFOS at two locations. The BCF was calculated by dividing the concentration measured in the liver, by the concentration measured in water from the same location. The mean BCF for both locations was 60 000 with a maximum value of 117 000 at SinDuri and the minimum value of 1600 at YeongSangang. These values are comparable to other values measured in the area (Yoo et al., 2009), and are slightly less than values reported for fish living in Etobicoke Creek, Ontario (Moody et al., 2002), which was heavily contaminated by PFCs due to a fire-fighting foam spill.

3.5. Potential adverse effects

An evaluation of the ecological risk to aquatic animals associated with exposure to selected PFCs including PFBS, PFOS, and PFOA were performed by comparing concentrations in water with recently reported water quality values (Giesy et al., 2010).

Table 5
Concentrations (ng/g, dw) of PFCs detected in biological samples collected from the west coast of Korea.

Location	Species	Samples	PFOS	PFDS	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
LS1	Surf Clam	Soft tissue	4.50	0.14	ND	1.52	ND	ND	ND	0.80	2.24	ND
LS2	Oyster	Soft tissue	1.53	ND[a]	ND	5.04	ND	ND	ND	ND	ND	ND
LS3	Asian Periwinkle	Soft tissue	6.50	0.79	ND	1.15	ND	1.45	ND	1.41	2.33	0.75
LS4	Asian Periwinkle	Soft tissue	8.40	ND	ND	1.58	ND	1.10	1.27	2.08	3.88	1.58
SG2	Crab	Eggs	8.89	ND	ND	1.07	ND	0.51	ND	0.49	1.97	ND
		Shells	1.14	ND	ND	ND	ND	ND	ND	0.32	ND	ND
		Soft tissue	1.30	ND	ND	ND	ND	0.76	ND	1.46	1.81	ND
SD	Striped Mullet	Fillet	8.83	ND	ND	ND	ND	ND	ND	0.13	1.28	ND
		Intestines	266	ND	ND	34.6	ND	ND	ND	ND	1.46	ND
		Liver	612	ND	ND	10.0	ND	ND	ND	0.13	2.38	ND
ML	Asian Periwinkle	Soft tissue	0.26	ND	ND	4.08	ND	ND	ND	ND	1.32	0.99
AM	Mussel	Soft tissue	0.77	0.21	ND	4.97	0.96	0.94	ND	0.28	1.61	0.54
	Blue Mussel	Soft tissue	0.34	0.22	ND	3.81	ND	ND	ND	0.67	1.09	ND
	Neritid Gastropod	Soft tissue	0.75	0.15	ND	3.75	ND	0.62	ND	1.31	1.31	ND
	Asian Periwinkle	Soft tissue	0.59	ND	5.81	5.01	0.98	0.69	ND	1.02	4.40	ND
YS1	Rockfish	Fillet	2.97	0.44	ND	3.74	0.52	1.46	ND	0.53	1.86	1.78
		Intestines	11.2	0.18	ND	2.45	ND	ND	ND	1.27	2.27	ND
		Liver	15.3	ND	ND	ND	0.18	ND	ND	0.19	2.36	ND
		Gills	99.2	0.24	ND	9.43	ND	ND	ND	0.21	1.40	ND
YS1	Asian Periwinkle	Soft tissue	233	ND	ND	2.42	ND	ND	ND	0.56	1.26	ND
Min			0.26	ND	ND	ND	ND	ND	ND	ND	ND	ND
Max			612	0.79	5.81	34.6	0.98	1.46	1.27	2.08	4.40	1.78
Mean			64.2	0.30	5.81	5.91	0.66	0.94	1.27	0.76	2.01	1.13
SD			150	0.22	–	8.07	0.38	0.37	–	0.58	0.89	0.53

[a] ND: below the method detection limit.

Table 6
Concentrations (ng/L) of PFOS and PFOA in water samples reported in Asian countries including Korea, China, and Japan.

Sampling				PFOS			PFOA			References
Location	Area type	Year	*n*	Mean	Min	Max	Mean	Min	Max	
Korea										
Lake Shihwa Area	Streams	2004	21	89.1	8.03	651	19.2	5.21	61.7	Rostkowski et al., 2006
	Lake	2004	5	12.9	7.33	18.3	6.14	1.67	10.9	Rostkowski et al., 2006
	Gyeonggi Bay	2004	5	5.21	8.26	2.24	0.47	0.44	0.50	Rostkowski et al., 2006
West Coast	Open ocean	2003	5	147	0.62	730	65.7	1.30	320	So et al., 2004
Southern Coast	Open ocean	2003	6	0.75	0.04	2.30	4.84	0.24	11.0	So et al., 2004
Korean Coast	Open ocean	2002–2004	10		0.04	2.53		0.24	11.4	Yamashita et al., 2005
Korean Coast	Lake, rivers, coastal	2008	15	59.5	4.11	450	20.6	2.95	68.6	This study
China										
Shanghai	Tap water	2006–2008	5	7.60			78.0			Mak et al., 2009
Nanjing	Tap water	2006–2008	5	0.94			5.90			Mak et al., 2009
Hong Kong	Tap water	2006–2008	5	7.00			1.10			Mak et al., 2009
Shenyang	Tap water	2006–2008	3	0.39			0.79			Mak et al., 2009
Beijing	Tap water	2006–2008	4	0.04			0.44			Mak et al., 2009
Hong Kong Coast	Open ocean	2002–2004	12		0.07	2.60		0.67	5.45	Yamashita et al., 2005
China Coast	Open ocean	2002–2004	14		0.02	9.68		0.24	15.3	Yamashita et al., 2005
South China Sea	Open ocean	2002–2004	2		0.01	0.11		0.16	0.42	Yamashita et al., 2005
Western Pacific	Open ocean	2002–2004	2		0.05	0.08		0.14	0.14	Yamashita et al., 2005
Dalian	Rain water	2006	2	61.5	9.92	113	36.9	32.9	40.8	Liu et al., 2009
Dalian	Snow	2006	3	120	42.2	138	12.6	9.16	16.7	Liu et al., 2009
Dalian	Snow	2007	2	72.8	108	37.5	32.2	7.74	56.7	Liu et al., 2009
Dalian	Coastal surface water	2006	14	0.23	0.10	0.96	0.56	0.27	2.12	Ju et al., 2008
Guangzhou	Pearl River	2005	12	23.1	0.90	99.0	4.28	0.85	13.0	So et al., 2007
Nanjing	Yangtze River	2005	6	0.36	0.33	0.39	2.25	2.00	2.60	So et al., 2007
Shanghai	Yangtze River	2005	6	5.14	0.62	14.0	101	22	260.0	So et al., 2007
Japan										
Osaka	Tap water	2006–2008	3	1.60			18.0			Mak et al., 2009
Tokyo	Tap water	2006–2008	1	1.60			40.0			Mak et al., 2009
Tokyo Bay	Open ocean	2002–2004	8		0.38	57.7		1.80	192	Yamashita et al., 2005
Offshore of Japan	Open ocean	2002–2004	4		0.04	0.07		0.14	1.10	Yamashita et al., 2005
Survey of Japan	River samples	2002	126	2.37	0.30	157				Saito et al., 2003
Survey of Japan	Costal sea water	2002	16	1.52	0.20	25.2				Saito et al., 2003
Tokyo Bay	Surface water	2002	4	26.0	8.00	59.0				Taniyasu et al., 2003
Osaska Bay	Surface water	2002	3	8.70	4.00	21.0				Taniyasu et al., 2003
Lake Biwa	Surface water	2002	3	3.80	4.00	7.40				Taniyasu et al., 2003
Ariake Bay	Surface water	2002	4	4.80	9.00	11.0				Taniyasu et al., 2003
Kyoto Area	River water	2005	5	6.50	7.90	110	58.6	5.12	10.0	Senthilkumar et al., 2007
Yodo River Basin	Surface water	2004–2005	81	3.90	0.40	123	4.20	2600	29.9	Lein et al., 2008
Survey of Japan	Sewage effluent	2005	5	179	42	635	46.4	10.0	68.0	Murakami et al., 2008

Concentrations of PFCs measured in Korean waters from the present study (all ng/L level) did not approach the numerical water quality criteria (all > several μg/L), viz. either the criteria maximum concentration (CMC) or criteria continuous concentration (CCC) values (Fig. 4). However, compared to the reported avian wildlife values (AWV) of PFBS (17 ng/L) and PFOS (47 ng/L) the waterborne concentrations at some locations were sufficient to potentially cause adverse effects to some wildlife at the top of the food chain,

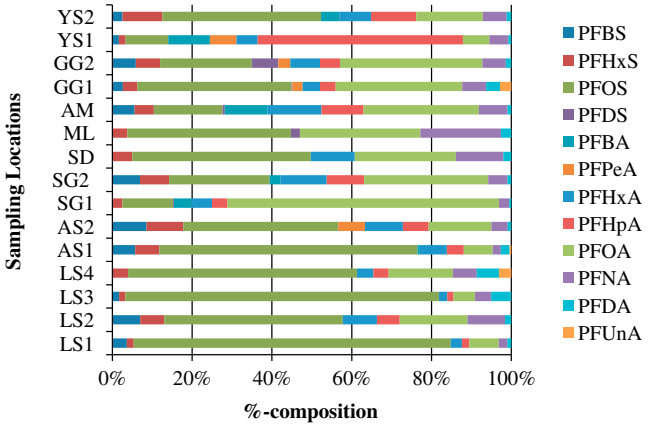

Fig. 2. Patterns of relative concentrations of individual PFCs (%-composition) in water collected from the west coast of Korea.

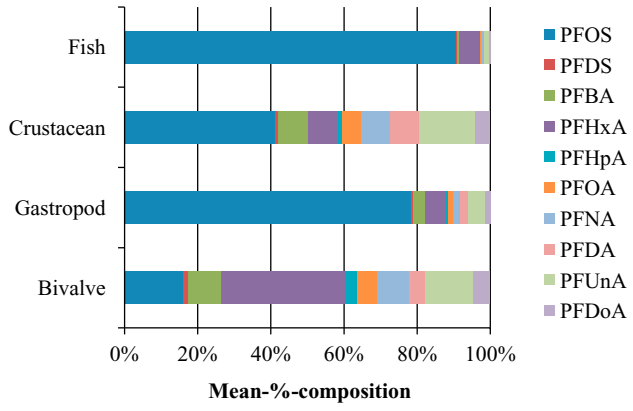

Fig. 3. Patterns of relative concentrations of individual PFCs (mean-%-composition) in fish, crustacean, gastropod, and bivalve collected from the west coast of Korea.

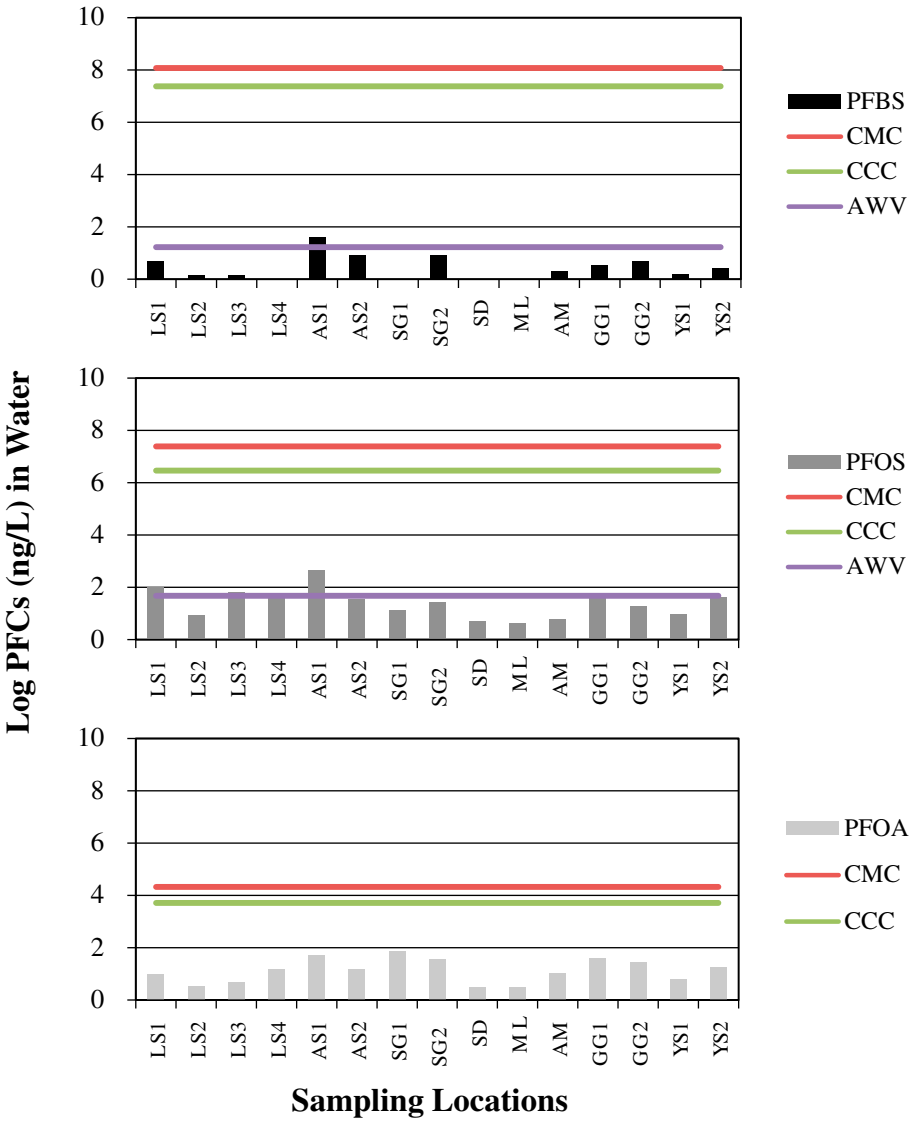

Fig. 4. Comparison of selected PFCs (viz. PFBS, PFOS, and PFOA) in waters from the west coast of Korea with suggested water quality criteria values for the protection of aquatic organisms (CMC: criteria maximum concentration; CCC: criteria continuous concentration) and wildlife (AWV: avian wildlife value).

such as birds (Giesy et al., 2010). Toxicity threshold values are meant to be protective and not predictive so many safety factors were included in their derivation. Thus, the actual potential for adverse effects in the most exposed species is small, but this analysis illustrates the potential for adverse effects to sensitive species at some locations.

4. Conclusions

The western coast of Korea is a highly developed region of Asia that is home to millions of people and is vital for both industry and tourism alike. Previous studies found relatively great PFC concentrations in Korean water but little was known about their sources, distribution and transport in a region that is known to have used PFCs extensively. As part of an ongoing study to determine the current status and extent of PFC concentrations, as well as potential for detrimental environmental effects in the Yellow Sea eco-region of China and Korea, the present study determined overall concentrations of PFCs in various environmental samples along the estuarine and coastal areas of Korea. Overall, the results of this study indicated that:

- Concentrations of PFCs in estuarine and coastal areas of Korea were relatively greater than those reported in other Asian countries,
- Among 12 target PFCs measured, PFOS was consistently found at the greatest concentrations throughout the environmental media,
- Some longer-chain PFCs such as PFHxA, PFDA and PFUnA as well as PFOS were concentrated in biota samples, particularly in higher trophic level organisms, supporting bioaccumulation of PFCs,
- Occurrence and spatial distribution of detected PFCs in various environmental media between upstream and downstream indicated the continuing input from existing PFCs sources in Korea,
- Concentrations of PFOS or PFOA found at some locations were sufficient to potentially cause adverse effects to some wildlife, thus monitoring effort of such PFCs should be of great attention in Korea.

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