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Distributions and bioconcentration characteristics of perfluorinated compounds in environmental samples collected from the west coast of Korea

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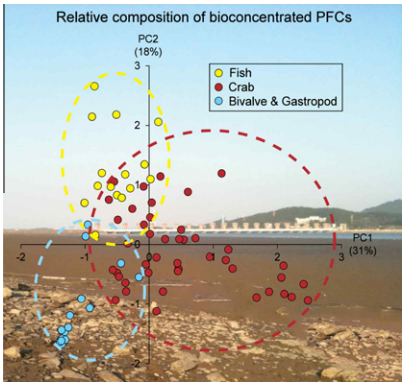
HIGHLIGHTS

- Waterborne concentrations of PFCs reflected land use and local activities.
- Concentrations of PFCs in soils and sediments were less than those in biota.
- Composition of PFCs cross target aquatic organisms reflected species-specific accumulation.
- Field-based BCFs for PFCs significantly varied among species and compounds.
- Compound- and organ-specific bioconcentration of PFCs in fishes was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

As part of an ongoing study of the status and trends of contaminants in the Yellow Sea, during May of 2009, the concentrations of perfluorinated compounds (PFCs) were determined in water ($n = 15$), sediment ($n = 12$), soil ($n = 13$), and biota ($n = 74$) from estuarine and coastal areas along the west coast of Korea. Of the 12 PFCs monitored, PFOS and PFOA were the most frequently detected compounds in water. Greater concentrations of PFCs were found in waters from the inner regions of sea dikes in three artificial lakes, Shihwa, Asan, and Sapgyo, than outer regions. Concentrations were also comparable in two estuarine areas, which indicated that most PFCs in coastal areas originated from industrial and local regions and river water flowing through estuaries. Concentrations of PFCs in soils and sediments were generally less than limits of quantification and were generally less than those measured in biota. Compound-specific bioaccumulation of PFBS and PFOS had the greatest BCF values in crab, while in fish it was PFOS and PFDA, and in gastropods and bivalves it was PFHxS. Distributions of BCFs for PFOS in body-parts of crab showed the greatest values in soft tissues followed by shells and then legs. Distribution among tissues and organs of fishes was more variable than those observed for crab. When compared to a similar study conducted by our group in 2008, concentrations of PFCs in water samples were significantly less in 2009. However, there was little change in bioconcentration from sediments into benthic organisms. Finally, we

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conducted the assessment of potential adverse effects for PFCs on aquatic life by use of current and previous reported data.

1. Introduction

Due to their widespread presence in both the environment and tissues of humans, perfluorinated compounds (PFCs) have garnered increasing worldwide attention since their detection in environmental samples in 2001 (Giesy and Kannan, 2001). Due to their amphiphilic nature, PFCs make excellent surfactants, and 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 (Paul et al., 2009). Some of these compounds are persistent in the environment, whereas others degrade to more environmentally stable compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which can make determining exposures and concentrations in organisms difficult (Dinglasan et al., 2004; Martin et al., 2010). While production of PFOS-based products was voluntarily halted in 2000 by North America's largest producer, the 3M company (3M, 2000), PFOS is still being produced in relatively large quantities in China (So et al., 2007; Ruisheng, 2008; Pan et al., 2010).

Moreover, PFCs have the potential to bioaccumulate, particularly in aquatic organisms (Taniyasu et al., 2003; Conder et al., 2008), with reported compound- and species-specific characteristics (Kannan et al., 2002; Naile et al., 2010). Unlike other persistent organic chemicals, which accumulate into lipids, PFCs bind to proteins and accumulate in blood and liver. Due to their surfactant properties, they also accumulate in gall bladders of organisms that have such an organ (OECD, 2002; Bossi et al., 2005; Yeung et al., 2009). There are published reports concerning bioconcentration of PFCs in blood, liver, and tissues from aquatic organisms such as marine mammals, birds, seals, fishes, and marine invertebrates (Kannan et al., 2001; Taniyasu et al., 2003; Kannan et al., 2005; Van De Vijver et al., 2005; Verreault et al., 2005). However, there is still limited information on bioconcentration of PFCs in intertidal organisms (Nakata et al., 2006). Thus, more research was necessary to fully understand the bioaccumulation characteristics of PFCs in aquatic wildlife worldwide including coastal regions.

The western coast of Korea is an industrialized and urbanized region of Asia that is home to millions of people and is vital for both industry and tourism. The western coast of Korea forms the eastern boundary of the Yellow Sea, which is significant from both a transportation and industrial standpoint. In fact, the economic contribution of the Yellow Sea is about one tenth of the gross national production for all of China (Hu et al., 2010). Recently our group showed that concentrations of PFCs in the Korean coastal environment were sufficient to potentially cause adverse effects to wildlife (Naile et al., 2010). While information on magnitudes and distributions of concentrations of PFCs in Korea is accumulating, uncertainties about annual variation in concentrations of PFCs and their distributions in tissues of organisms remain.

As part of an ongoing study to determine the current status and extent of PFCs concentrations, as well as the potential for detrimental environmental effects in the Yellow Sea, samples of water, sediments, soils and biota were collected in 2009 from along the western coast of Korea. To allow for inter-annual comparisons of PFCs concentrations and to detect possible changes in the localized point-sources, samples were collected from locations near to those studied in 2008 (Naile et al., 2010). Bioconcentration and biomagnification in various coastal organisms was determined based on whole body and organ-specific concentrations of PFCs. Finally, interim Korean water quality criteria (IKWQC) for PFOS and PFOA were developed by use of current and previous reported data and adopting the method of the National Status & Trends (NS&T) monitoring program conducted by the National Oceanographic and Atmospheric Administration (NOAA) in the United States. Concentrations of PFCs were compared to the IKWQC to determine the potential for adverse effects on marine organisms that prey upon them, including humans.

2. Materials and methods

2.1. Sampling and sample preparation

Water ($n = 15$), soil ($n = 13$), sediment ($n = 12$), and biota ($n = 74$) were collected from estuarine and coastal areas along the western side of Korea during May of 2009 (Fig. 1). One liter of surface water was collected by dipping a clean, 1 L polypropylene (PP) bottle, which had been rinsed with methanol, just under the surface of the water. Surface (top 1–5 cm) soils and sediments were collected by use of a clean methanol-rinsed stainless steel trowel. Samples were transferred to and stored in clean PP bags. Samples of biota were collected by hand in coastal tidal pools and along the shore of inland bodies of water, and were transferred to and stored in clean PP bags. Duplicate samples and field blanks were collected daily, and were analyzed along with laboratory and procedural blanks. All samples were transported on ice at 4 °C to the laboratory and frozen at −20 °C until analyses. Some samples of biota, including fish and crab, were necropsied to allow for specific tissue analysis. All samples of biota were pooled, homogenized, and freeze-dried.

2.2. Target chemicals and pretreatment

Twelve PFCs (>98%, Wellington Laboratories) including perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, perfluorodecane sulfonate (PFDS), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA) were quantified. Water, sediment, soil, and samples of biota were extracted and cleaned-up by use of Oasis HLB extraction cartridges (0.2 g, 6 cm^3, Waters Corp., Milford, MA) (Naile et al., 2010). Detailed procedures for identification and quantification of PFCs are provided in Supplementary material.

2.3. Instrumental analysis

Separation of analytes was accomplished by use of an Agilent 1200 HPLC system fitted with a Thermo Scientific Betasil C18 (100 × 2.1 mm, 5 μm particle size) analytical column which was operated at 35 °C. Mass spectral data were collected by use of an Applied Bioscience SCIEX 3000 API (Foster City, CA) tandem mass spectrometer, which was fitted with an electro-spray ionization source, operated in the negative ionization mode. Chromatograms were recorded in MRM mode, and when possible at least two transitions per-analyte were monitored. More detailed instrumental conditions are presented in Supplementary material.

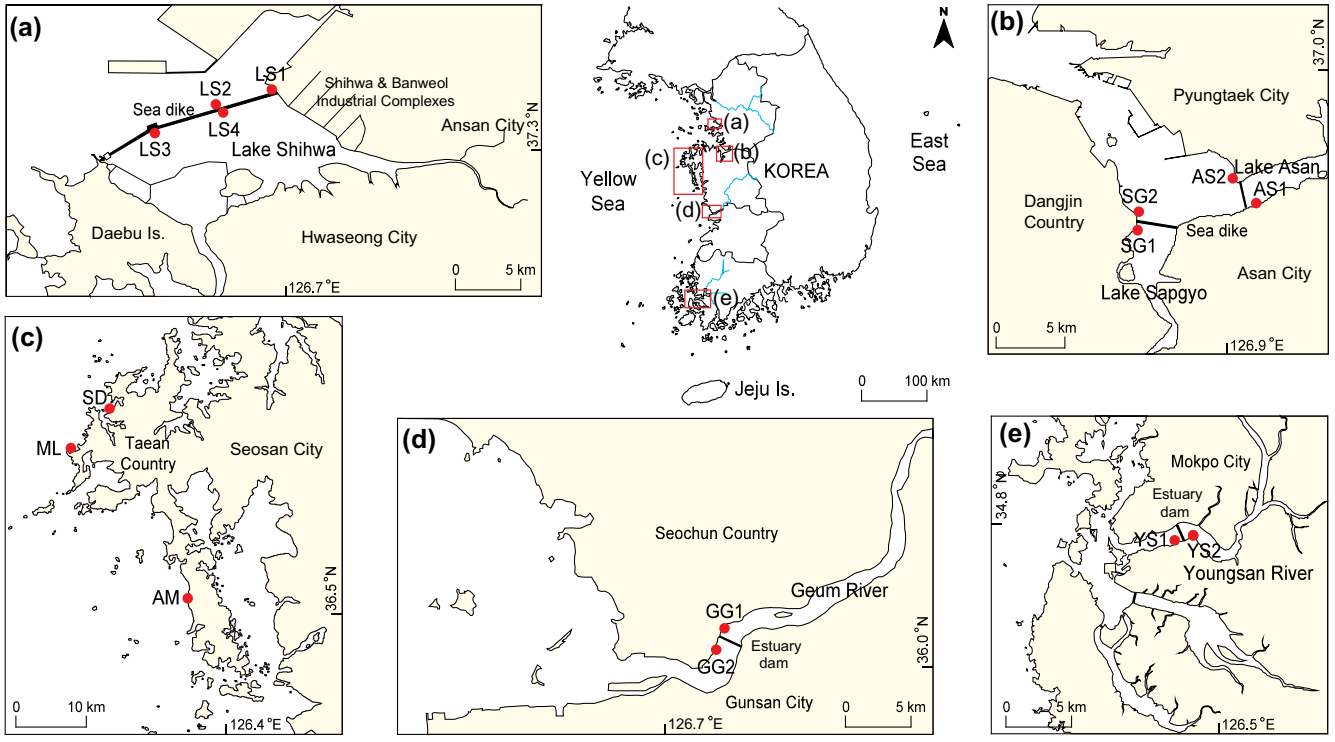

Fig. 1. Sampling sites in estuarine and coastal areas along the west coast of Korea during May of 2009. (a) Lake Shihwa, (b) Lake Asan and Sapgyo, (c) Taean area, (d) Geum River Estuary, and (e) Youngsan River Estuary.

2.4. Quality control

To reduce background contamination coming from the HPLC or solvents, a ZORBAX (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). Solvent blanks were run every 4–5 samples to check for carryover and background contamination. Concentrations of all field and solvent blanks were found to be less than the limit of quantification (LOQ), which was defined as 5× the signal measured in solvent blanks. Teflon coated labware was avoided during all steps of sample and standard solution preparation to minimize contamination. The ions monitored, method detection limit (MDL), and matrix spike recoveries for all of the chemicals of interest are given in Table S1 of Supplementary material.

3. Results and discussions

3.1. PFCs in water, sediment, and soil samples

In water samples from western Korea, PFOS, PFOA, and PFHpA were the most frequently detected analytes among the 12 PFCs examined (Table 1). The spatial distribution of concentrations of PFCs along the west coast of Korea is shown in Fig. 2a. The greatest concentrations of 12 PFCs were found at AS1 (inner region of Lake Asan) followed by GG1, AS2, and YS2. Lesser and/or comparable concentrations of PFCs were detected at other locations (SD, ML, and AM) along the beach areas.

Greater concentrations of PFCs were found in the inner regions of Lakes Shihwa, Asan, and Sapgyo, which are areas of brackish water that are separated from the sea by dikes, than the outer regions, which are open to the sea (Fig. 2a). A similar trend was observed for samples from the estuaries of the Geum and Youngsan Rivers (Fig. 2b), which are both dammed at their outlets to the sea. This observation indicates that most sources of PFCs in this coastal area are directly from inland activities such as industrial and domestic use or production rather than via indirect or long-range transport. In addition, there appears to be a decreasing trend of concentration of PFCs in water between inner and outer regions of the sea dikes and dams, which is likely due to the effects of salinity. Due to changes in salinity when freshwaters enter the marine environment, PFCs are largely scavenged to sediment in estuaries (Pan and You, 2010). Results of this study were in agreement with observations that salinity affects the ability of PFCs to partition into water and results in greater sorption of PFOA (Jeon et al., 2010). Concentrations of PFBS, PFHpA, and PFOA were also significantly less in outer regions compared to the inner areas studied here. Since the sea dikes and estuary dams in the surveyed areas, except for Lake Shihwa, block natural flow of water, which results in a separation of the coastal marine environment into more freshwater inner locations and more saltwater at the outer locations, such spatial distribution characteristics of PFCs are likely.

Concentrations of PFCs in soils and sediments were generally less than the MDL, and when detected, concentrations were generally less than those measured in biota. PFOS and PFOA were detected in 7 and 5 out of 12 sediment samples respectively, and in only 4 and 2 out of 13 soil samples, respectively (Table 1). There was a slightly greater prevalence of detection of PFOS and PFOA in sediments compared to soils, but the difference was not significant. It appears that soils and sediments collected along the western coast of Korea contain only small amounts of PFCs and do not appear to be significant contributors to the exposure of marine benthic or pelagic organisms (Naile et al., 2010).

Concentrations of PFCs in soils and sediments were similar to those reported previously for other areas of Asia (Nakata et al., 2006; Bao et al., 2009; Naile et al., 2010; Pan and You, 2010), but slightly less than those reported for European countries (De Voogt et al., 2005) and the United States (Higgins et al., 2005). Recently, greater concentrations of PFOS were found in sediments from the

Table 1
Concentrations of PFCs in water, sediment, soil, and various biological samples collected along the west coast of Korea.

Samples	*n*		PFBS	PFHxS	PFOS	PFDS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	ΣPFCs
Water (ng L^{-1})	15	Detected number	**10**	**12**	**15**	**0**	**0**	**0**	**13**	**15**	**14**	**11**	**15**	**0**	**15**
		Min.–Max.	<0.2–16	<0.2–8.7	0.35–47	–	–	–	<1.0–110	0.54–31	<0.20–5.9	<0.20–9.3	0.22–1.3	–	5.9–170
		Mean (median)	4.1 (1.1)	1.7 (0.5)	8.7 (4)	–	–	–	15 (5.9)	6.8 (3.7)	2.3 (2.1)	2.3 (1.6)	0.58 (0.53)	–	37 (30)
Sediment (ng g^{-1} dw)	12	Detected number	**0**	**0**	**7**	**0**	**0**	**0**	**0**	**5**	**0**	**0**	**0**	**0**	**8**
		Min.–Max.	–	–	<0.2–5.8	–	–	–	–	<0.2–2.4	–	–	–	–	0.59–8.2
		Mean (median)	–	–	1.5 (1)	–	–	–	–	1 (0.69)	–	–	–	–	2.1 (1.1)
Soil (ng g^{-1} dw)	13	Detected number	**0**	**0**	**4**	**0**	**0**	**0**	**0**	**2**	**0**	**0**	**0**	**0**	**4**
		Min.–Max.	–	–	<0.2–1.7	–	–	–	–	<0.2–3.4	–	–	–	–	0.28–3.9
		Mean (median)	–	–	0.82 (0.65)	–	–	–	–	2.2	–	–	–	–	2.1 (2.1)
Biota (ng g^{-1} ww)															
Fish	15[a]	Detected number	**10**	**15**	**15**	**3**	**12**	**15**	**13**	**5**	**13**	**14**	**15**	**11**	**15**
		Min.–Max.	<0.044–0.24	0.020–1.2	0.73–51	<0.11–0.096	<0.44–2.5	0.019–1.8	<0.11–0.84	<0.044–0.23	<0.044–0.035	<0.044–0.13	0.014–0.10	<0.044–0.060	1.4–52
		Mean (median)	0.065 (0.040)	0.28 (0.17)	13 (9.3)	0.048 (0.040)	0.39 (0.11)	0.26 (0.12)	0.23 (0.12)	0.062 (0.021)	0.021 (0.022)	0.051 (0.038)	0.043 (0.033)	0.032 (0.029)	15 (10)
Crab	44[b]	Detected number	**40**	**44**	**44**	**15**	**36**	**37**	**28**	**40**	**41**	**42**	**43**	**37**	**44**
		Min.–Max.	<0.068–1.6	0.039–3.3	0.089–3.7	<0.17–0.69	<0.68–2.7	<0.17–0.68	<0.17–1.3	<0.068–1.8	0.068–0.34	<0.068–0.80	<0.068–0.96	<0.068–0.40	0.52–9.9
		Mean (median)	0.25 (0.17)	0.30 (0.15)	1.1 (0.83)	0.21 (0.17)	0.40 (0.11)	0.14 (0.12)	0.17 (0.12)	0.33 (0.26)	0.10 (0.076)	0.16 (0.080)	0.20 (0.11)	0.089 (0.053)	3.0 (2.5)
Gatropod	11[c]	Detected number	**10**	**11**	**7**	**2**	**10**	**11**	**8**	**7**	**10**	**7**	**10**	**5**	**11**
		Min.–Max.	<0.046–0.21	0.16–1.1	<0.046–0.95	<0.12–0.36	<0.46–1.5	0.028–2.8	<0.12–0.62	<0.046–0.088	<0.046–0.12	<0.046–0.10	<0.046–0.13	<0.046–0.029	0.77–5.3
		Mean (median)	0.096 (0.077)	0.45 (0.42)	0.36 (0.27)	0.22	0.71 (0.70)	0.38 (0.14)	0.23 (0.14)	0.045 (0.038)	0.042 (0.033)	0.031 (0.023)	0.045 (0.027)	0.016 (0.014)	2.1 (1.8)
Bivalve	5[c]	Detected number	**4**	**5**	**5**	**2**	**5**	**5**	**4**	**3**	**2**	**4**	**4**	**2**	**5**
		Min.–Max.	<0.036–0.12	0.073–1.4	0.11–0.17	<0.09–0.39	0.012–−4.8	0.028–0.83	<0.09–0.66	<0.036–0.29	<0.036–0.060	<0.036–0.061	<0.036–0.15	<0.036–0.028	1.3–5.3
		Mean (median)	0.044 (0.023)	0.47 (0.19)	0.13 (0.12)	0.20	1.4 (0.77)	0.25 (0.12)	0.22 (0.084)	0.12 (0.042)	0.033	0.031 (0.028)	0.062 (0.040)	0.022	2.7 (1.4)

[a] Intestine + fillet + liver + legs.
[b] Whole body + soft tissue + shell + legs.
[c] Soft tissue.

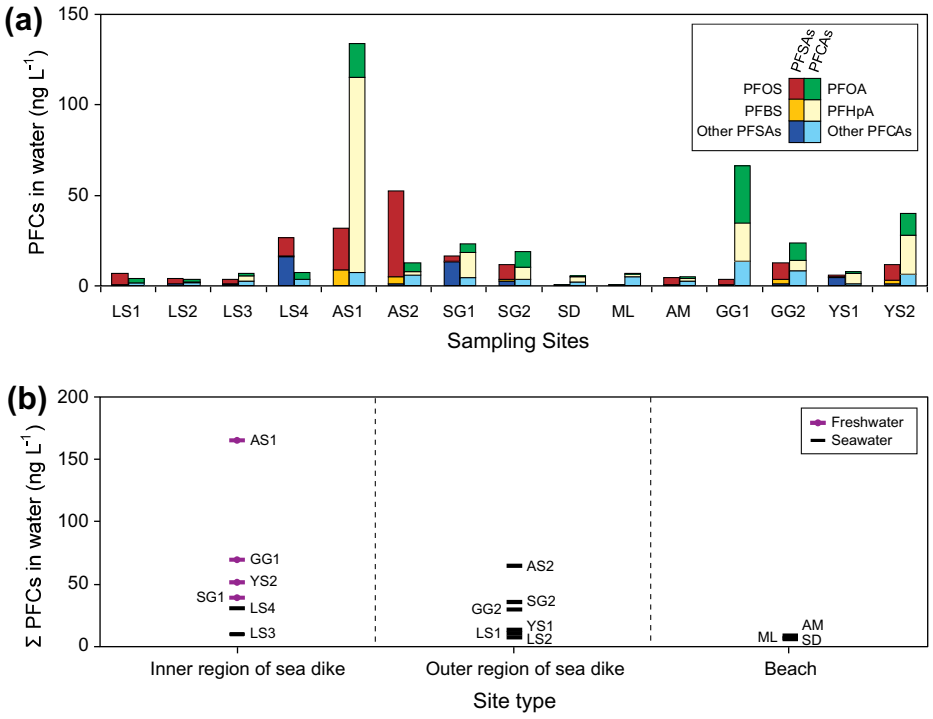

Fig. 2. (a) Concentration, distribution, and composition of PFCs in waters and (b) comparison of concentration of ΣPFCs in water according to their site types.

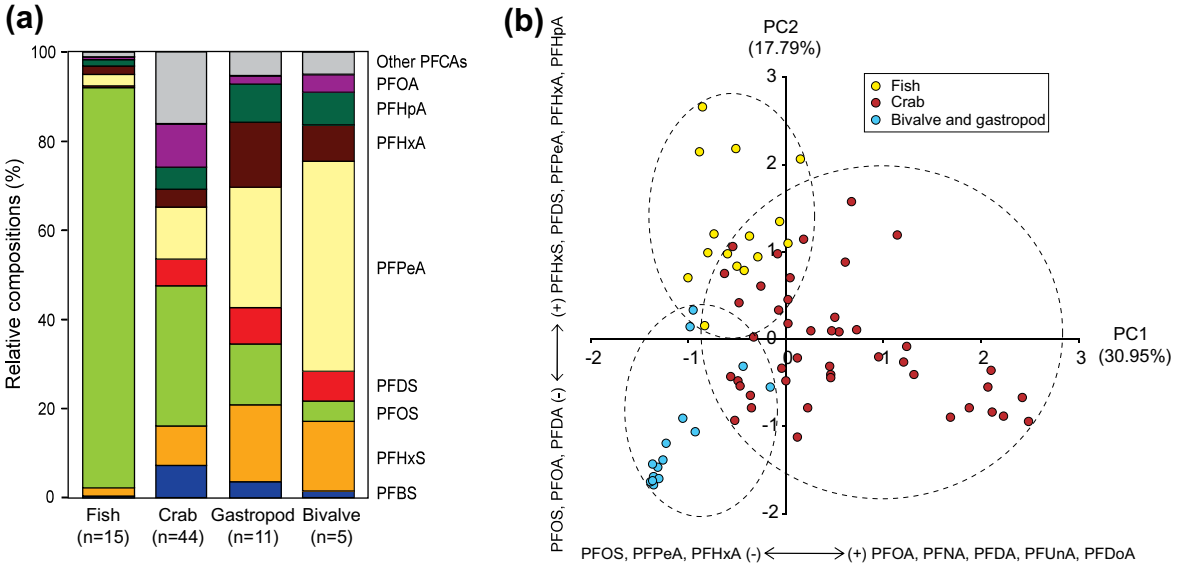

Fig. 3. (a) Relative compositions of PFCs in fish, crab, gastropod, and bivalve and (b) result for PCA using relative compositions of 12 PFCs in each sample of biota.

mouth of the Yangtze River (73–540 ng g^{-1} dw) (Pan and You, 2010), while Bao et al. (2009) found lesser concentrations of PFOS (<LOQ to 0.37 ng g^{-1} dw) and PFOA (<LOQ to 0.17 ng g^{-1} dw) in sediments from the upstream region of a tributary of the Daliao River, China. Overall, transfer of PFCs appear to occur through flow of dissolved chemicals rather than in association with sediments and soils in the study area of the western coast of Korea.

3.2. PFCs in biota

Detectable concentrations of some PFCs were observed in all biota, including fish ($n = 15$), crab ($n = 44$), gastropod ($n = 11$), and bivalve ($n = 5$). Fishes contained the greatest concentrations of PFCs, ranging from 1.4 to 52 ng g^{-1} wet weight (ww), followed by crab (0.52–9.9 ng g^{-1} ww), bivalves (1.3–5.3 ng g^{-1} ww), and gastropods (0.77–5.3 ng g^{-1} ww), respectively (Table 1). The range of concentrations of PFCs in fishes was probably due to differences in habitat and feeding guilds of the fishes. For example, the sum of concentrations of 12 PFCs in whole fish ($n = 7$) ranged from 1.8 to 37 ng g^{-1} ww with concentrations of 1.4–11 ng g^{-1} ww in fillets ($n = 3$), and 14–52 ng g^{-1} ww in intestine ($n = 2$). Patterns of concentrations of PFCs in fish varied among organs.

When concentrations of PFCs were compared among species, PFOS was the most abundant PFC (Fig. 3a). Fishes accumulated

Table 2
Bioconcentration factors (BCFs) of detected PFCs in various biota samples (mean ± SD).[a]

Samples		PFBS	PFHxS	PFOS	PFHpA	PFOA	PFNA	PFDA	PFUnA
Fish[b]	Whole body	1.84 ± 0.64	2.58 ± 0.55	3.43 ± 0.69	1.70 ± 0.81	1.05	1.07 ± 0.22	2.40	1.92 ± 0.36
	Intestine	1.51	3.53	4.16	1.89	–	–	1.90	1.93
	Liver	–	3.08	4.49	1.22	–	–	–	2.00
	Fillet	1.38	2.34	3.22 ± 0.84	2.26	1.21	1.47	1.50	1.62 ± 0.19
	Gill	1.52	1.77	2.92	0.753	2.24	1.51	2.13	2.03
Crab[c]	Whole body	2.04 ± 0.70	2.76 ± 0.76	2.41 ± 0.26	1.40 ± 0.48	1.47 ± 0.64	1.71 ± 0.27	1.98 ± 0.44	2.43 ± 0.39
	Soft tissue	1.95 ± 0.72	2.05 ± 0.64	2.15 ± 0.31	1.45 ± 1.0	1.89 ± 0.54	1.75 ± 0.49	2.21 ± 0.45	2.32 ± 0.57
	Shell	1.83 ± 0.56	2.19 ± 0.67	2.01 ± 0.49	1.14 ± 0.49	1.62 ± 0.44	1.51 ± 0.46	1.91 ± 0.45	2.19 ± 0.44
	Legs	1.69 ± 0.62	2.03 ± 0.65	1.72 ± 0.50	1.61 ± 0.48	1.69 ± 0.59	1.50 ± 0.47	1.84 ± 0.47	2.18 ± 0.37
Gastropod[d]	Whole body	2.03 ± 0.23	3.28 ± 0.22	2.33 ± 0.56	1.81 ± 0.51	1.70 ± 0.28	1.62 ± 0.36	1.51 ± 0.81	1.88 ± 0.46
Bivalve[e]	Whole body	1.09	2.61 ± 0.41	1.89 ± 0.69	1.69 ± 0.64	1.65 ± 0.20	0.850	1.21 ± 0.87	1.84 ± 0.16

[a] Log BCF = log (concentration in biota (ng kg^{-1} ww)/concentration in water (ng L^{-1})).
[b] Mean concentrations including *Hemigrapsus sanguineus*, *Sesarma pictum*, *Hemigrapsus penicillatus*, *Helice tridens tridens*, and *Philyra pisum*.
[c] Mean concentrations including *Acanthogobius flavimanus*, *Sebastes schlegeli*, *Tridentiger obscurus*, *Hexagrammos otakii*, and *Mugil cephalus*.
[d] Mean concentrations including *Littorina brevicula*, *Monodonta labio*, *Umbonium thomasi*, *Glossaulax didyma*, and *Monodonta labio*.
[e] Mean concentrations including *Mytilus edulis*, *Mactra veneriformis*, *Nuttallia olivacea*, and *Sinonovacula constricta*.

PFCs to a greater extent than other biota. PFOS was also the dominant PFC in crab, and composed approximately 32% of the total concentration of PFCs. However, PFOS was not the major component in gastropods or bivalves, in which PFPeA was dominant among the 12 PFCs with average percentages of approximately 27% and 47% of the total concentration, respectively. There were some discordant tendencies for PFC concentrations in fishes, crab, gastropods, and bivalves, which suggest that bioconcentration of PFCs in marine organisms is dependent on their taxonomic features and/or natural histories.

3.3. Species, compound and organ-specific bioconcentration of PFCs

To characterize compound- and species-specific bioconcentration of PFCs in various organisms, principal components analysis (PCA) was conducted by use of the relative compositions of each chemical (12 PFCs) in each species or organ (Fig. 3b). Results of the PCA indicated that there are three main groups, which can be classified based on their taxonomic features. This seems to be collectively due to differences in sources of food, feeding type, rates of uptake and excretion, and metabolism among crab, fishes, bivalves, and gastropods. Based on the results of the PCA, crab tended to accumulate relatively greater amounts of long-chain perfluorinated acids (PFCAs) including PFOA, PFNA, PFDA, PFUnA, and PFDoA than other PFCs. In contrast, PFOS, PFPeA, and PFHxA were abundant in fishes, gastropods and bivalves, which primarily accumulated PFOS. A significant positive correlation between concentrations of PFUnA and PFDA was observed in all biota (Fig. S1 of Supplementary material). This result indicates a common source for PFCAs on the west coast of Korea (Yoo et al., 2009). Differences in accumulation of PFCs by biota, considering their residual compositions, seemed to be due to the species-specific accumulation from numerous sources of PFCs on the west coast of Korea.

Compound-specific, field-based bioconcentration factors (BCFs) were calculated for aquatic organisms based on site-specific, concentrations of PFCs in waters of estuarine and coastal areas of western Korea (Table 2). In various organisms (whole body) BCFs varied significantly among both species and compound. Compounds with the greatest BCF values were PFBS, PFOS, and PFUnA in crab, PFOS, PFDA, and PFHpA in fishes and PFHxS in gastropods and bivalves, respectively. The measured apparent BCFs for PFCs were greater for fishes and comparable for crab to those previously observed in Korea. The mean BCF for mullet was calculated to be between 3700 and 12,400 and a BCF for blue crab has been estimated to be 575 (Yoo et al., 2009). In this study, calculated BCFs were also comparable to those observed in a recent study of the Yellow Sea of China, where BCFs in fishes ranged from 3100 to 85,000 (Wang et al., 2011). As is often the case for values of BCF, the field-BCFs in this study were greater than those determined during studies done under laboratory conditions (Giesy et al., 2010). This discrepancy between BCFs derived from exposures under field and laboratory conditions has not been well explained, but could be a function of the bioaccessible fraction.

Scatter plots of concentrations of PFCs in biota as a function of those in water, demonstrated linear relationships for crab and fishes, but presented exponential relationships between gastropods and bivalves (Fig. S2 of Supplementary material). To further understand how biota accumulate PFCs, organisms were necropsied to allow for quantification of PFCs in individual tissues and organs. Distributions of PFCs among tissues of both fishes and crab are shown (Table 2). There were some differences in the BCF values for PFCs among soft tissues, shells, and legs of crab. Distributions of BCFs for PFOS in body-parts of crab were greatest in soft tissues followed by those in shells and legs. Compound- and tissue-specific bioaccumulation of PFCs in fishes was evident and the distribution of PFCs among organs and tissues of fishes was more variable than that observed for crab. BCFs for PFOS were greatest for intestine, liver, fillet, and gills with values of 4.16, 4.49, 3.22 and 2.92, respectively. However, long-chain PFCAs including PFOA and PFNA were not concentrated in intestine and liver. These results are consistent with those observed in the previous year's study where greater concentrations of PFOS were observed in intestine (Naile et al., 2010). The liver had the greatest concentration of PFOS, which is not surprising since PFOS is routinely detected at greatest concentrations in the livers of aquatic organisms (Kannan et al., 2001, 2002; Martin et al., 2004).

3.4. Comparisons between 2008 and 2009

When compared to data collected from the same locations in 2008 (Naile et al., 2010) and 2009, concentrations of PFCs were found, on average, to be lesser in 2009. Concentrations of PFOS were only greater at two locations in 2009 than 2008 (AS2 and AM1), and concentrations of PFOA was greater only at ML1. Concentrations of PFCs in water were less in 2009 than in 2008, but concentrations of PFCs in sediment, soil, and biota were not significantly different between 2008 and 2009 (Fig. S3 of Supplementary material). Also, when comparing the response of benthic organisms, using metrics such as bioconcentration relatively little variation was observed. Due to these conflicting findings, and the

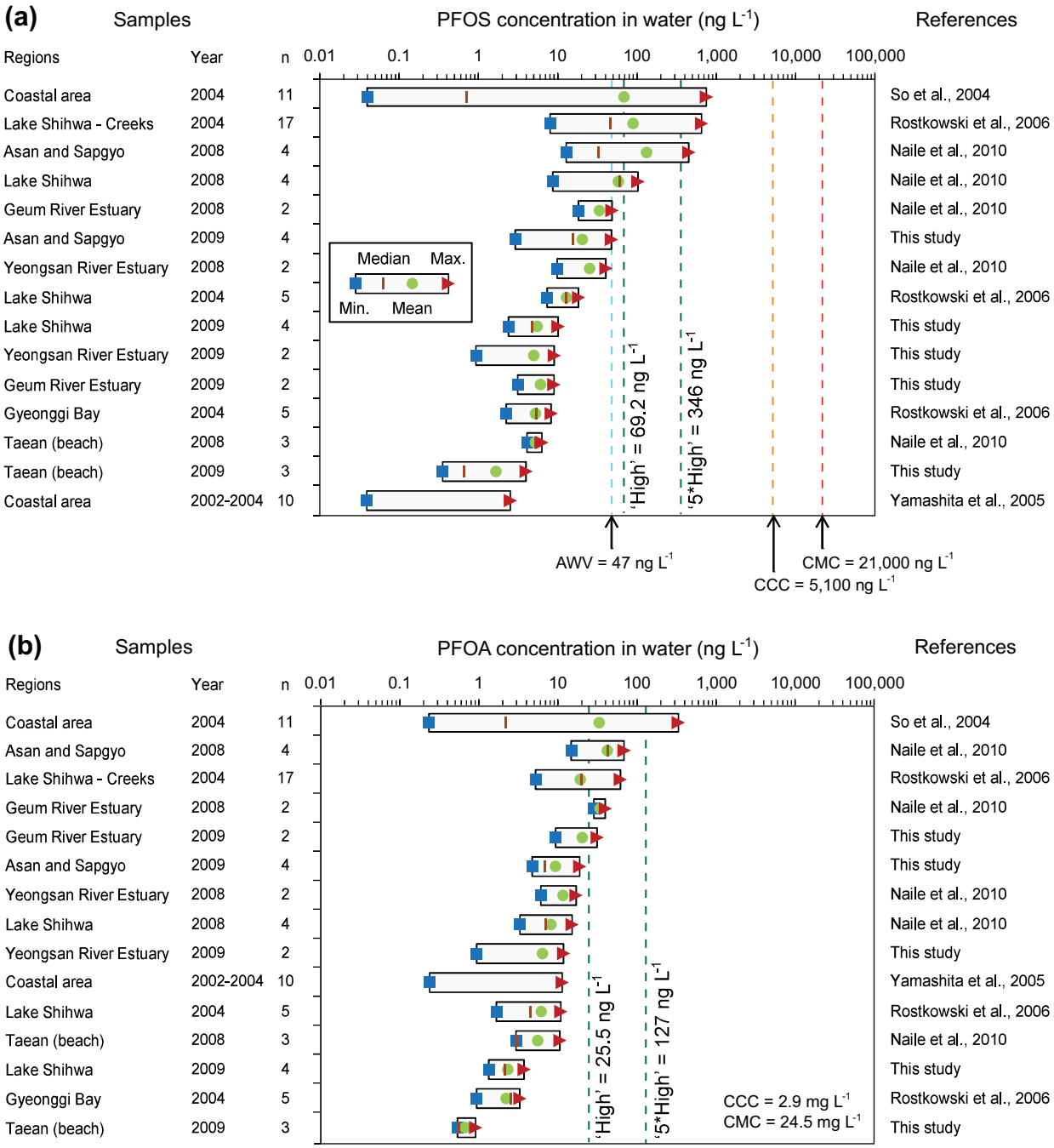

Fig. 4. Concentrations of (a) PFOS and (b) PFOA in waters collected from estuarine and coastal environments of South Korea from this study as well as previous studies ('High': mean + one-SD of the log-normal distribution (85th centile value); AWV: Avian Wildlife Value; CCC: Criteria Continuous Concentration; CMC: Criteria Maximum Concentration).

difficultly of making yearly temporal observations from only 2 years of data, it is difficult to determine if sources and transports of PFCs in west coast of Korea in 2009 have decreased substantially over a year.

Concentrations and BCF values of PFOS for the same species collected from 2008 and 2009 surveys were compared (Fig. S4 of Supplementary material). Alternatively, site-specific BCFs for PFOS in biota, including fishes, crab, and gastropods were greater in 2009 than 2008, which indicates that biota are responding more slowly than water to changes in releases to the environment. There could be several reasons for this, including the sediments serving as a source of PFCs or slower rates of turnover in the tissues of animals.

3.5. Assessment of potential effects on aquatic life

All of the published data of PFCs in water samples from estuarine and coastal areas of Korea (So et al., 2004; Yamashita et al., 2005; Rostkowski et al., 2006; Naile et al., 2010) were compiled (Fig. 4). The 'High' and '5 × High' concentration limits for PFOS and PFOA as IKWQC were calculated based on all previous reported data and that collected during this study (Fig. 4). A total of 78 samples of water were available for PFCs, 3 PFOS values and 1 PFOA value out of 78 samples exceeded the '5 × High' concentrations, respectively. Our suggested IKWQC for PFOS and PFOA were less than previous reported criteria such as CCC (Criteria Continuous

Concentration) and CMC (Criteria Maximum Concentration) for the protection of aquatic life (Giesy et al., 2010). The AWV (Avian Wildlife Value) for PFOS was similar to our 'High' concentration (Giesy et al., 2010). Current concentrations of PFOS and PFOA in estuarine and coastal areas of Korea were relatively small when compared to those reported in other countries. The current findings will assist in monitoring the status and trends of PFCs and will allow determination of the risk to both humans and wildlife, in the estuarine and coastal areas of the western coast of Korea.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.07.033.

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