



Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

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

Jonathan E. Naile^a, Jong Seong Khim^{b,*}, Seongjin Hong^b, Jinsoon Park^b, Bong-Oh Kwon^b, Jong Seong Ryu^c, Jin Hwan Hwang^d, Paul D. Jones^e, John P. Giesy^{a,f,g,h}

^aToxicology Centre, University of Saskatchewan, Saskatoon, SK, Canada

^bDivision of Environmental Science and Ecological Engineering, Korea University, Seoul, Republic of Korea

^cDepartment of Marine Biotechnology, Anyang University, Ganghwa-gun, Incheon, Republic of Korea

^dDepartment of Civil & Environmental Engineering, Dongguk University, Seoul, Republic of Korea

^eSchool of Environment and Sustainability, University of Saskatchewan, Saskatoon, SK, Canada

^fDepartment of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, SK, Canada

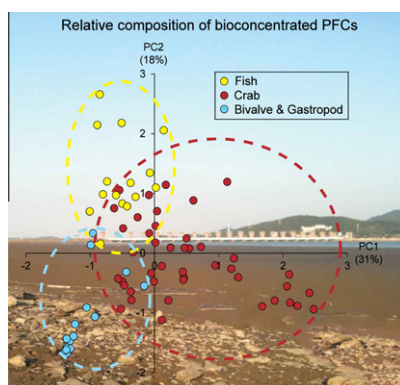
^gDepartment of Biology and Chemistry and State Key Laboratory for Marine Pollution, City University of Hong Kong, Kowloon, Hong Kong, China

^hDepartment of Zoology and Center for Integrative Toxicology, Michigan State University, E. Lansing, MI, USA

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



ARTICLE INFO

Article history:

Received 10 March 2012

Received in revised form 5 July 2012

Accepted 10 July 2012

Available online 3 September 2012

Keywords:

PFOS

PFOA

HPLC–MS/MS

Yellow Sea

Bioconcentration factor (BCF)

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

* Corresponding author. Tel.: +82 2 3290 3041; fax: +82 2 953 0737.

E-mail address: jongseongkhim@korea.ac.kr (J.S. Khim).

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

© 2012 Elsevier Ltd. All rights reserved.

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 cm³, 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.

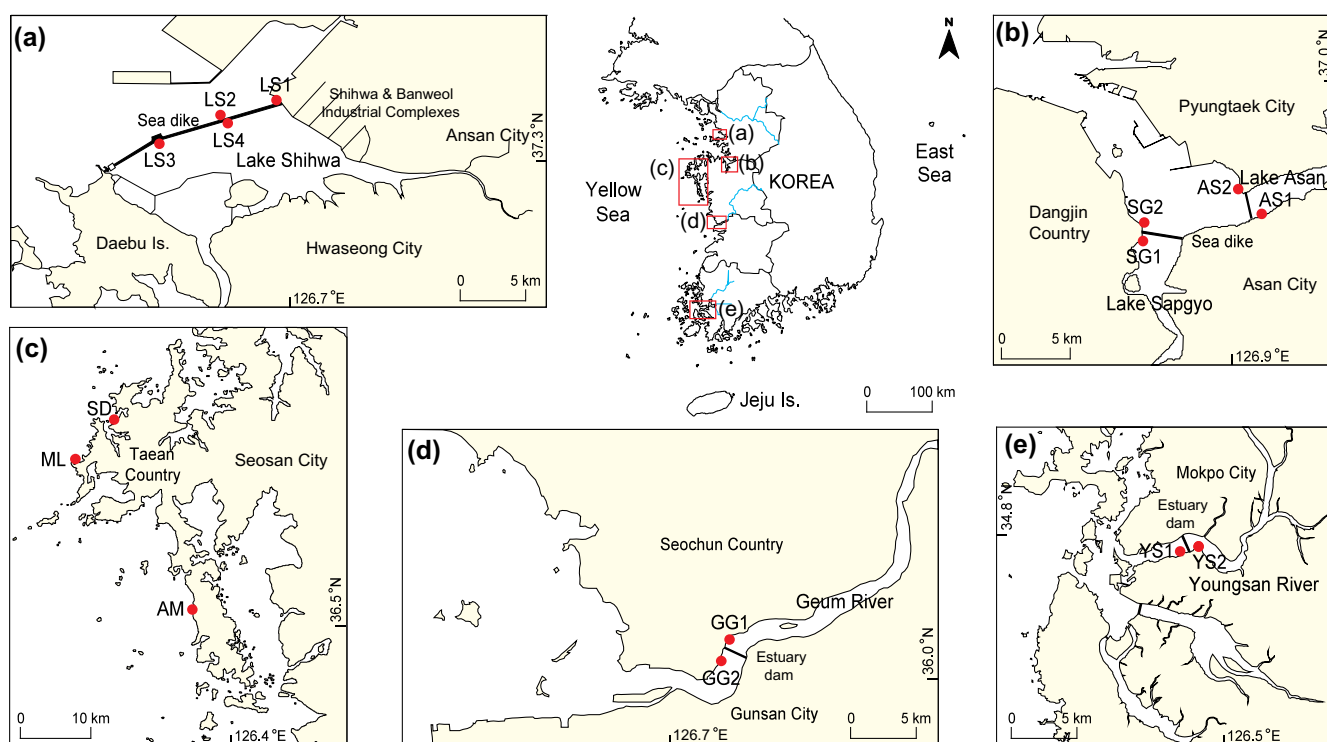


Fig. 1. Sampling sites in estuarine and coastal areas along the west coast of Korea during May of 2009. (a) Lake Shihwa, (b) Lake Asan and Sapggyo, (c) Taean area, (d) Geum River Estuary, and (e) Youngsan River Estuary.

2.4. Quality control

To reduce background contamination coming from the HPLC or solvents, a ZORBAX (Thermo Scientific, 50×2.1 mm, $5 \mu\text{m}$ 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 $5 \times$ 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 Sapggyo, 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	15	0	0	0	13	15	14	11	15	0	15
		Min.-Max.	<0.2–16	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)	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	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	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)	15 ^a	Detected number	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	0.014–0.10	<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)
Crab	44 ^b	Detected number	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
		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)
Gastropod	11 ^c	Detected number	10	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	<0.046–0.13	<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)
Bivalve	5 ^c	Detected number	4	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	<0.036–0.15	<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

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

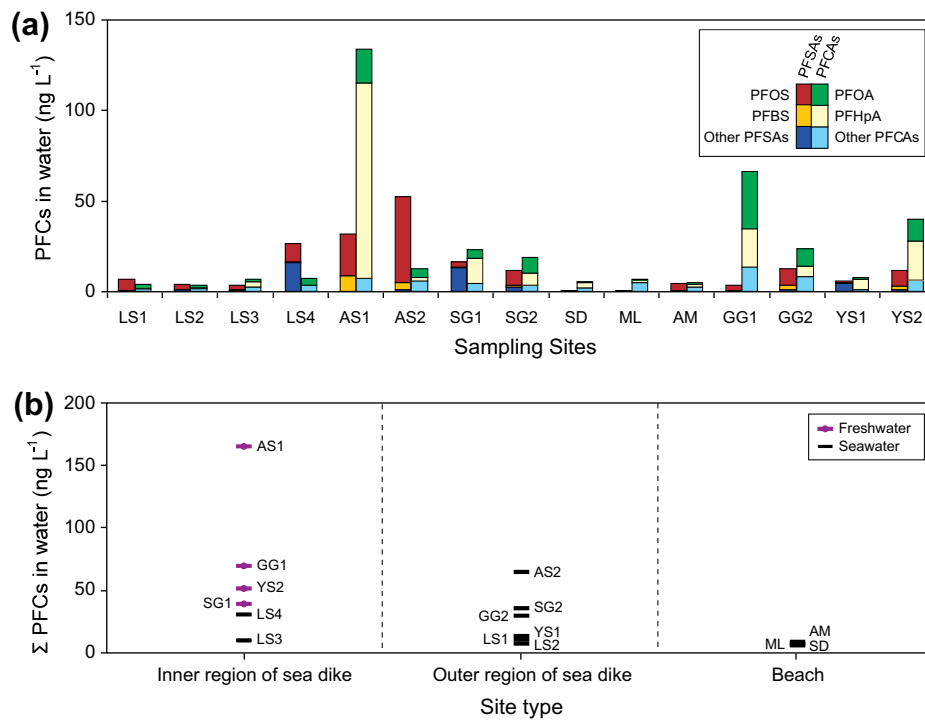


Fig. 2. (a) Concentration, distribution, and composition of PFCs in waters and (b) comparison of concentration of ΣPFCs in water according to their site types.

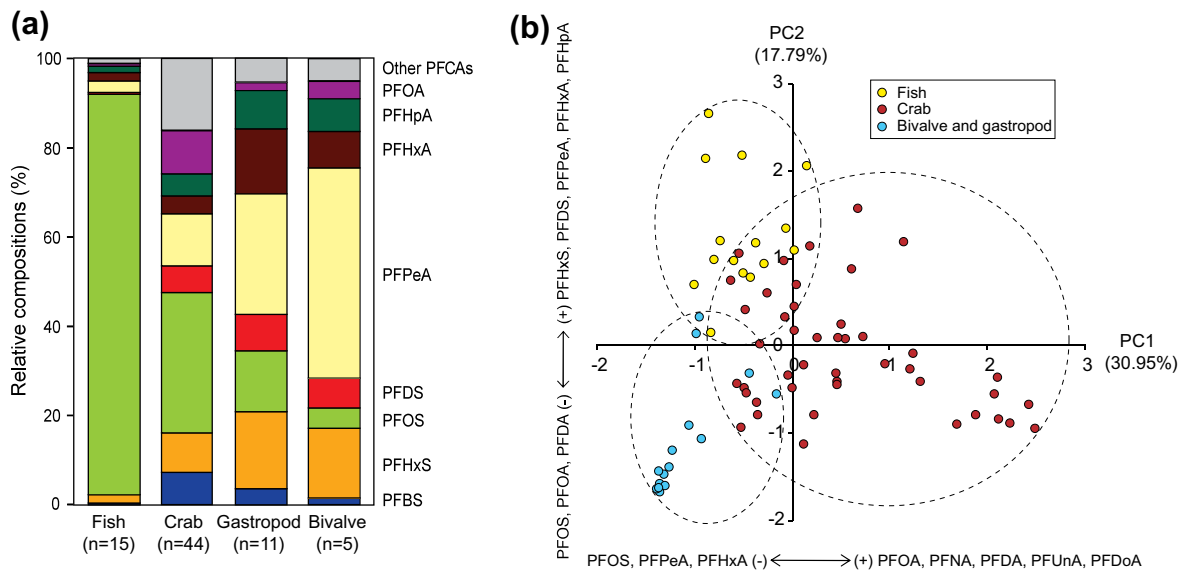


Fig. 3. (a) Relative compositions of PFCs in fish, crab, gastropod, and bivalve and (b) result for PCA using relative compositions of 12 PFCs in each sample of biota.

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 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 \pm SD).^a

Samples		PFBS	PFHxS	PFOS	PFHpA	PFOA	PFNA	PFDA	PFUnA
Fish ^b	Whole body	1.84 \pm 0.64	2.58 \pm 0.55	3.43 \pm 0.69	1.70 \pm 0.81	1.05	1.07 \pm 0.22	2.40	1.92 \pm 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 \pm 0.84	2.26	1.21	1.47	1.50	1.62 \pm 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 \pm 0.70	2.76 \pm 0.76	2.41 \pm 0.26	1.40 \pm 0.48	1.47 \pm 0.64	1.71 \pm 0.27	1.98 \pm 0.44	2.43 \pm 0.39
	Soft tissue	1.95 \pm 0.72	2.05 \pm 0.64	2.15 \pm 0.31	1.45 \pm 1.0	1.89 \pm 0.54	1.75 \pm 0.49	2.21 \pm 0.45	2.32 \pm 0.57
	Shell	1.83 \pm 0.56	2.19 \pm 0.67	2.01 \pm 0.49	1.14 \pm 0.49	1.62 \pm 0.44	1.51 \pm 0.46	1.91 \pm 0.45	2.19 \pm 0.44
	Legs	1.69 \pm 0.62	2.03 \pm 0.65	1.72 \pm 0.50	1.61 \pm 0.48	1.69 \pm 0.59	1.50 \pm 0.47	1.84 \pm 0.47	2.18 \pm 0.37
Gastropod ^d	Whole body	2.03 \pm 0.23	3.28 \pm 0.22	2.33 \pm 0.56	1.81 \pm 0.51	1.70 \pm 0.28	1.62 \pm 0.36	1.51 \pm 0.81	1.88 \pm 0.46
Bivalve ^e	Whole body	1.09	2.61 \pm 0.41	1.89 \pm 0.69	1.69 \pm 0.64	1.65 \pm 0.20	0.850	1.21 \pm 0.87	1.84 \pm 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*, *Macrta 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

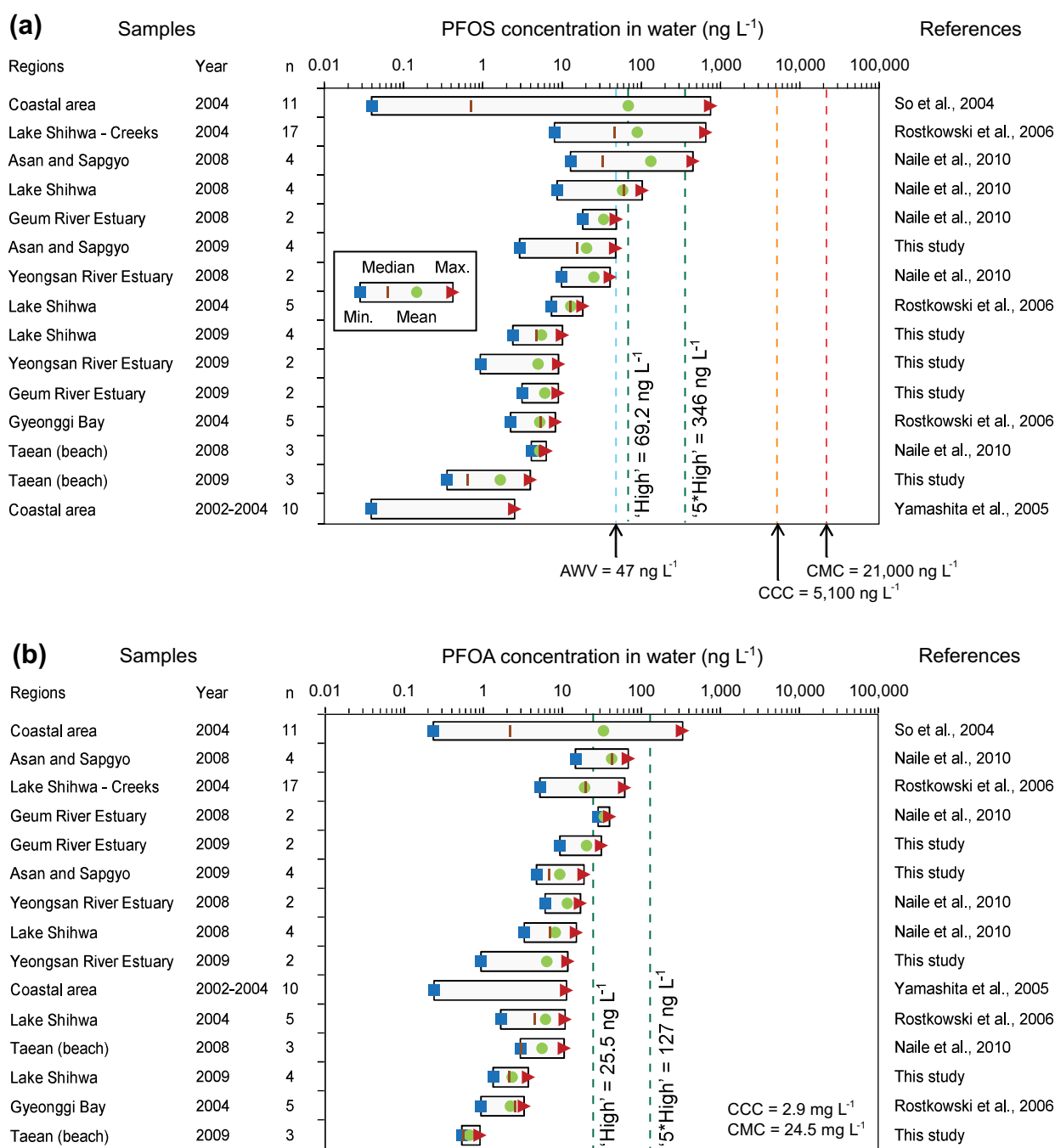


Fig. 4. Concentrations of (a) PFOS and (b) PFOA in waters collected from estuarine and coastal environments of South Korea from this study as well as previous studies ('High': mean + one-SD of the log-normal distribution (85th centile value); AWW: Avian Wildlife Value; CCC: Criteria Continuous Concentration;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

Acknowledgements

This work was supported by the projects entitled "Development of Technology for CO₂ Marine Geological Storage" and "Development of Integrated Estuarine Management System" funded by the Korean Ministry of Land, Transport, and Maritime Affairs given to Prof. J.S. Khim. The research was also supported, in part by a Discovery Grant from the Natural Science and Engineering Research Council of Canada (Project # 326415-07). The authors wish to acknowledge the support of an instrumentation grant from the Canada Foundation for Infrastructure. Prof. J.P. Giesy was supported by the Canada Research Chair program and an at large Chair Professorship at the Department of Biology and Chemistry and Research Centre for Coastal Pollution and Conservation, City University of Hong Kong, and the Einstein Professor Program of the Chinese Academy of Sciences.

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>.

References

- 3M, 2000. Phase-out Plan for PFOS-based Products. US Environmental Protection Agency. Public Docket. AR226-0588.
- Bao, J., Jin, Y., Liu, W., Ran, X., Zhang, Z., 2009. Perfluorinated compounds in sediments from the Daliao River system of northeast China. *Chemosphere* 77, 652–657.
- Benskin, J.P., Bataineh, M., Martin, J.W., 2007. Simultaneous characterization of perfluoroalkyl carboxylate, sulfonate, and sulfonamide isomers by liquid chromatography–tandem mass spectrometry. *Anal. Chem.* 79, 6455–6464.
- Bossi, R., Riget, F.F., Dietz, R., Sonne, C., Fauser, P., Dam, M., Vorkamp, K., 2005. Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands. *Environ. Pollut.* 136, 323–329.
- Conder, J.M., Hoke, R.A., De Wolf, W., Russell, M.H., Buck, R.C., 2008. Are PFCAs bioaccumulative? a critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* 42, 995–1003.
- De Voogt, P., Sáez, M., Van Roon, A., 2005. Perfluorinated chemicals in sediments, particulate matter, soil and water samples from The Netherlands. *Organohalogen Compd.* 67, 790–793.
- Dinglasan, M.J., Ye, J., Edwards, E.A., Mabury, S.A., 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environ. Sci. Technol.* 38, 2857–2864.
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* 35, 1339–1342.
- Giesy, J.P., Naile, J.E., Khim, J.S., Jones, P.D., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. *Rev. Environ. Contam. T.* 202, 1–52.
- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39, 3946–3956.
- Hu, W., Wang, T., Khim, J.S., Luo, W., Jiao, W., Lu, Y., Naile, J.E., Giesy, J.P., 2010. Organochlorine pesticides (HCHs and DDTs) in soils along the north coastal areas of the Bohai Sea. *China Chem. Ecol.* 26, 339–352.
- Jeon, J., Kannan, K., Lim, H.K., Moon, H.B., Ra, J.S., Kim, S.D., 2010. Bioaccumulation of perfluorochemicals in pacific oyster under different salinity gradients. *Environ. Sci. Technol.* 44, 2695–2701.
- Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J.F., Hansen, K.J., Jones, P.D., Helle, E., Nyman, M., Giesy, J.P., 2001. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ. Sci. Technol.* 35, 1593–1598.
- Kannan, K., Corsolini, S., Falandysz, J., Oehme, G., Focardi, S., Giesy, J.P., 2002. Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and the Mediterranean Seas. *Environ. Sci. Technol.* 36, 3210–3216.
- Kannan, K., Tao, L., Sinclair, E., Pastva, S.D., Jude, D.J., Giesy, J.P., 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Arch. Environ. Con. Tox.* 48, 559–566.
- Martin, J.W., Smithwick, M.M., Braune, B.M., Hoekstra, P.F., Muir, D.C., Mabury, S.A., 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* 38, 373–380.
- Martin, J.W., Asher, B.J., Beesoon, S., Benskin, J.P., Ross, M.S., 2010. PFOS or PreFOS? are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* 12, 1979–2004.
- Naile, J.E., Khim, J.S., Wang, T., Chen, C., Luo, W., Kwon, B.-O., Park, J., Koh, C.-H., Jones, P.D., Lu, Y., Giesy, J.P., 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. *Environ. Pollut.* 158, 1237–1244.
- Nakata, H., Kannan, K., Nasu, T., Cho, H.-S., Sinclair, E., Takemura, A., 2006. Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat regions of the Ariake Sea: fate of PFOS in aquatic ecosystem. *Environ. Sci. Technol.* 40, 4916–4921.
- OECD (Organization for Economic Cooperation and Development), 2002. Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and its Salts. ENV/JM/RD 17/ Final, Paris, 21 November, 2002, p. 362.
- Pan, G., You, C., 2010. Sediment–water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River Estuary. *Environ. Pollut.* 158, 1363–1367.
- Pan, Y., Shi, Y., Wang, J., Cai, Y., Wu, Y., 2010. Concentrations of perfluorinated compounds in human blood from 12 cities in China. *Environ. Toxicol. Chem.* 29, 2695–2701.
- Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environ. Sci. Technol.* 43, 386–392.
- Rostkowski, P., Yamashita, N., So, I.M.K., Taniyasu, S., Lam, P.K.S., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K., Giesy, J.P., 2006. Perfluorinated compounds in streams of the Shihwa industrial zone and Lake Shihwa, South Korea. *Environ. Toxicol. Chem.* 25, 2374–2380.
- Ruisheng, Y., 2008. Additional Information of Production and Use of PFOS. Ministry of Environmental Protection of China. Stockholm Convention Secretariat, Geneva, Switzerland. <http://chm.pops.int/portals/0/repository/addinfo_2008/UNEP-POPS-POPRC-SUB-F08-PFOS-ADIN-CHI.english.pdf>.
- So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K.S., 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* 38, 4056–4063.
- So, M.K., Miyake, Y., Yeung, W.Y., Ho, Y.M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam, P.K.S., 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere* 68, 2085–2095.
- 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.
- Van De Vijver, K.L., Hoff, P., Das, K., Brasseur, S., Van Dongen, W., Esmans, E., Reijnders, P., Blust, R., De Coen, W., 2005. Tissue distribution of perfluorinated chemicals in harbor seals (*Phoca vitulina*) from the Dutch Wadden Sea. *Environ. Sci. Technol.* 39, 6978–6984.
- Verreault, J., Houde, M., Gabrielsen, G.W., Berger, U., Haukås, M., Letcher, R.J., Muir, D.C.G., 2005. Perfluorinated alkyl substances in plasma, liver, brain, and eggs of glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic. *Environ. Sci. Technol.* 39, 7439–7445.
- Wang, T., Lu, Y., Chen, C., Naile, J.E., Khim, J.S., Park, J., Luo, W., Jiao, W., Hu, W., Giesy, J.P., 2011. Perfluorinated compounds in estuarine and coastal areas of north Bohai Sea, China. *Mar. Pollut. Bull.* 62, 1905–1914.
- 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.
- Yeung, L.W.Y., Loi, E.I.H., Wong, V.Y.Y., Guruge, K.S., Yamanaka, N., Yanimura, N., Hasegawa, J., Yamashita, N., Miyazaki, S., Lam, P.K.S., 2009. Biochemical responses and accumulation properties of long-chain perfluorinated compounds (PFOS/PFOA/PFOA) in juvenile chickens (*Gallus gallus*). *Arch. Environ. Con. Tox.* 57, 377–386.
- Yoo, H., Yamashita, N., Taniyasu, S., Lee, K.T., Jones, P.D., Newsted, J.L., Khim, J.S., Giesy, J.P., 2009. Perfluoroalkyl acids in marine organisms from lake Shihwa, Korea. *Arch. Environ. Con. Tox.* 57, 552–560.

<Supplementary Materials>

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

Jonathan E. Naile, Jong Seong Khim^{*}, Seongjin Hong, Jinsoon Park, Bong-Oh Kwon,
Jongseong Ryu, Jin Hwan Hwang, Paul D. Jones, John P. Giesy

* Corresponding author. Tel.: +82 2 3290 3041; fax: +82 2 953 0737. *E-mail address:*
jongseongkhim@korea.ac.kr (J.S. Khim).

Analytical methods

Chemicals

Extraction and clean-up

Instrumental analysis

References

Supplementary table

Table S1. Target analytes of 12 perfluorinated compounds measured in the present study with QA/QC information including monitoring transitions, method detection limit, and matrix-spike recovery for water, soil and sediment, and biological samples.

Supplementary figures

Fig. S1. Relationship between (a) PFDA and PFUnA and (b) PFOA and PFNA in biological samples (red: crabs; yellow: fishes; and blue: gastropods and bivalves).

Fig. S2. Relationship between water and biota concentrations of PFOS including (a) fish, (b) crab, (c) gastropod and bivalve samples. Organ- and body part-specific distribution of PFOS in (d) fishes and (e) crabs.

Fig. S3. Box plot for the quantification levels of 12 PFCs in water, sediment, soil and biota samples from 2008 and 2009 surveys. (PFCs data in 2008 refer from Naile et al. (2010)).

Fig. S4. Concentrations and BCFs for PFOS in biota collected in 2008 and 2009.

Analytical methods

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 perfluorooctanoic acid (PFOA) [1,2,3,4 ¹³C] (>98%, Wellington Laboratories), and PFOS [¹⁸O₂] (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), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA).

Extraction and clean-up

Waters were extracted by use of Oasis HLB cartridges (0.2 g, 6 cm³) (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 mL of water was then spiked with 500 µL of 5 ng/mL of the internal standard (Isotopically labelled 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). Since it has been shown that glass vials and PTFE septa can cause loss of analyte and increased contamination, respectively, samples were stored and analyzed in PP auto-sampler vials fitted with PP septa (Canadian Life Science, Peterborough, ON, CAN (Yamashita et al., 2004).

Soil and sediments were extracted by use of a previously published method (Higgins et al.,

2005), which was modified slightly for application in this study. Briefly, homogenized freeze-dried 1 g samples were transferred to 50 mL PP centrifuge tubes and spiked with 500 μ L 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 the a 1% acetic acid mixture was 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.

Biota was extracted by use of an alkaline digestion 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 μ l 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 hours. 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.

Instrumental analysis

Gradient conditions were used at 300 μ L/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 untill 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. Chromatograms were recorded in MRM mode, and when possible at least two transitions per-analyte were monitored (Table 2.0). The following instrument parameters were used: desolvation temperature (450 $^{\circ}$ 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 msec. 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).

References

- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. *Environ. Sci. Technol.* 39, 3946-3956.
- So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K.S., 2004. Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* 38, 4056-4063.
- So, M.K., Taniyasu, S., Lam, P.K.S., Zheng, G.J., Giesy, J.P., Yamashita, N., 2006. Alkaline Digestion and Solid Phase Extraction Method for Perfluorinated Compounds in Mussels and Oysters from South China and Japan. *Arch. Environ. Contam. Toxicol.* 50, 240-248.
- 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.

Supplementary table

Table S1. QA/QC information including monitoring transitions, method detection limit, and matrix spike recovery for water, soil and sediment, and biological samples for perfluorinated compounds measured in the present study.

Analyte	Abb.	Monitored Transitions	Method Detection Limits ^a			Matrix Spike Recovery		
			Water (ng/L)	Soil/Sed (ng/g dw)	Biota (ng/g dw)	Water (%)	Soil/Sed (%)	Biota (%)
Perfluorobutanesulfonate	PFBS	299 → 99, 80	0.2	0.2	0.2	94	32	97
Perfluorohexanesulfonate	PFHxS	399 → 99, 80	0.2	0.2	0.2	93	134	113
Perfluorooctanesulfonate	PFOS	499 → 99, 80	0.2	0.2	0.2	97	95	89
Perfluorodecane sulfonate	PFDS	599 → 99, 80	1	0.5	0.5	101	43	70
Perfluorobutanoic acid	PFBA	213 → 169	0.2	2	2	120	IS	IS
Perfluoropentanoic acid	PFPnA	263 → 219	2	2	2	82	72	79
Perfluorohexanoic acid	PFHxA	313 → 269	1	0.5	0.5	85	78	73
Perfluoroheptanoic acid	PFHpA	363 → 319, 169	1	0.5	0.5	80	123	112
Perfluorooctanoic acid	PFOA	413 → 219, 169	0.2	0.2	0.2	88	89	88
Perfluorononanoic acid	PFNA	463 → 419, 219	0.2	0.2	0.2	99	135	133
Perfluorodecanoic acid	PFDA	513 → 469, 269	0.2	0.2	0.2	89	106	75
Perfluoroundecanoic acid	PFUnA	563 → 269, 219	0.2	0.2	0.2	99	53	93

^aMDL was defined as the amount of chemical which could be detected in a given amount of sample after the entire method was performed.

Supplementary figures

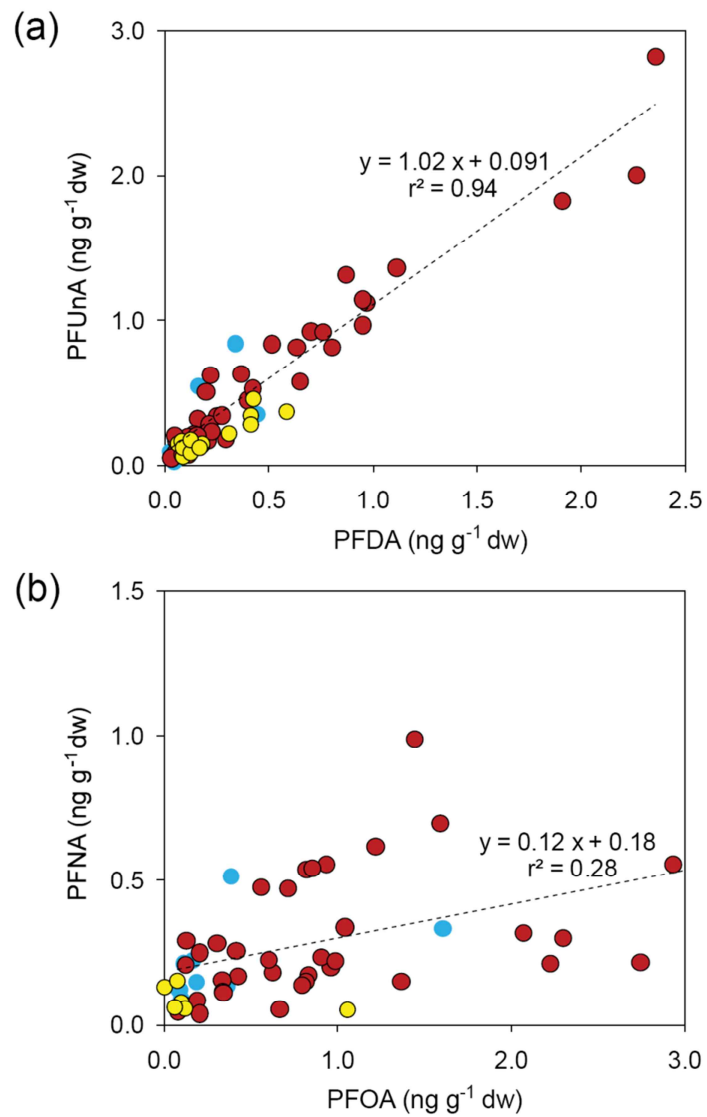


Fig. S1. Relationship between (a) PFDA and PFUnA and (b) PFOA and PFNA in biological samples (red = crabs; yellow = fishes; and blue = gastropods and bivalves).

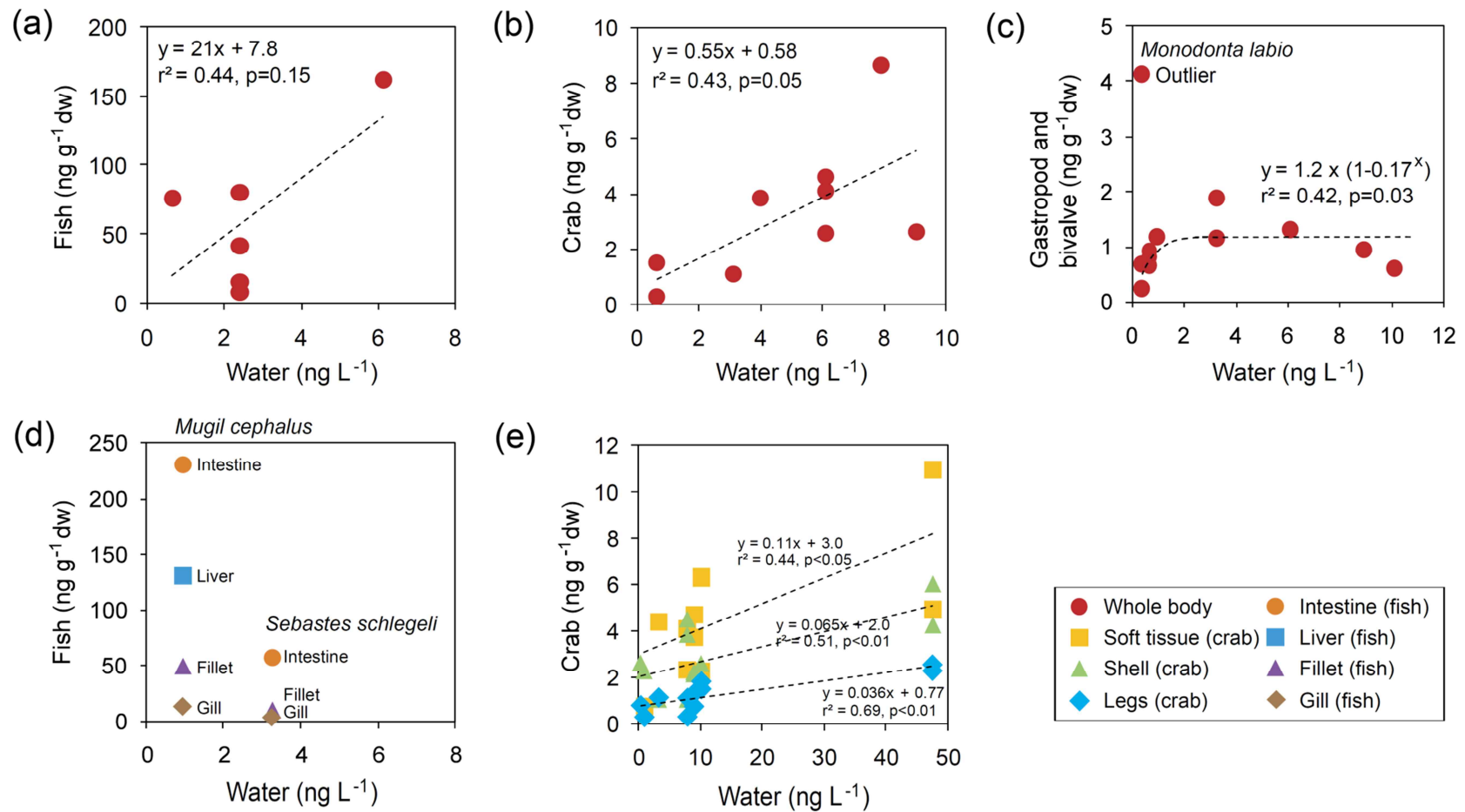


Fig. S2. Relationship between water and biota concentrations of PFOS including (a) fish, (b) crab, (c) gastropod and bivalve samples. Organ and body part-specific distribution of PFOS in (d) fishes and (e) crabs..

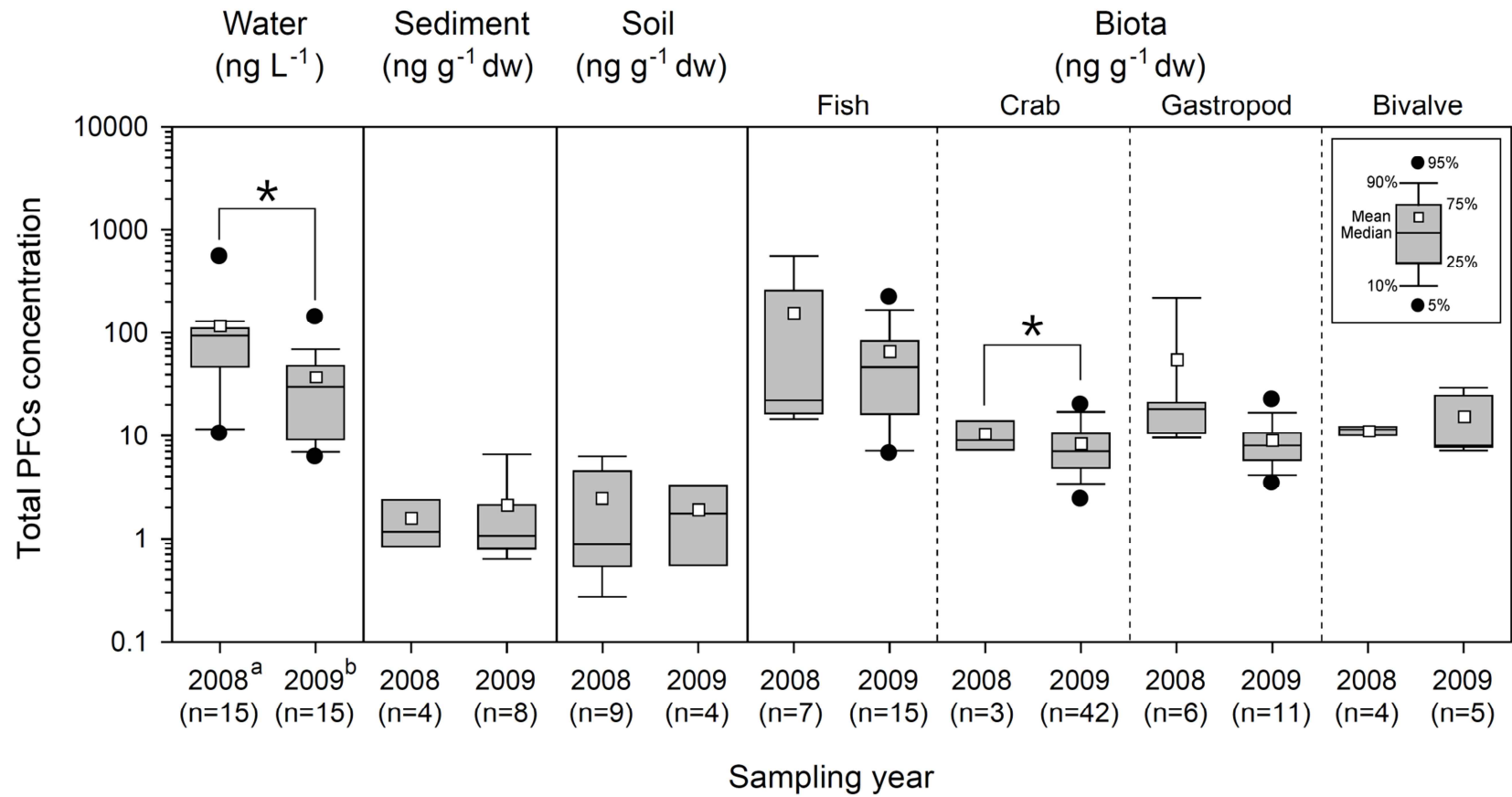


Fig. S3. Box plot for the quantification levels of 12 PFCs in water, sediment, soil and biota samples from 2008 and 2009 surveys. (PFCs data in 2008 refers to Naile et al. (2010)).

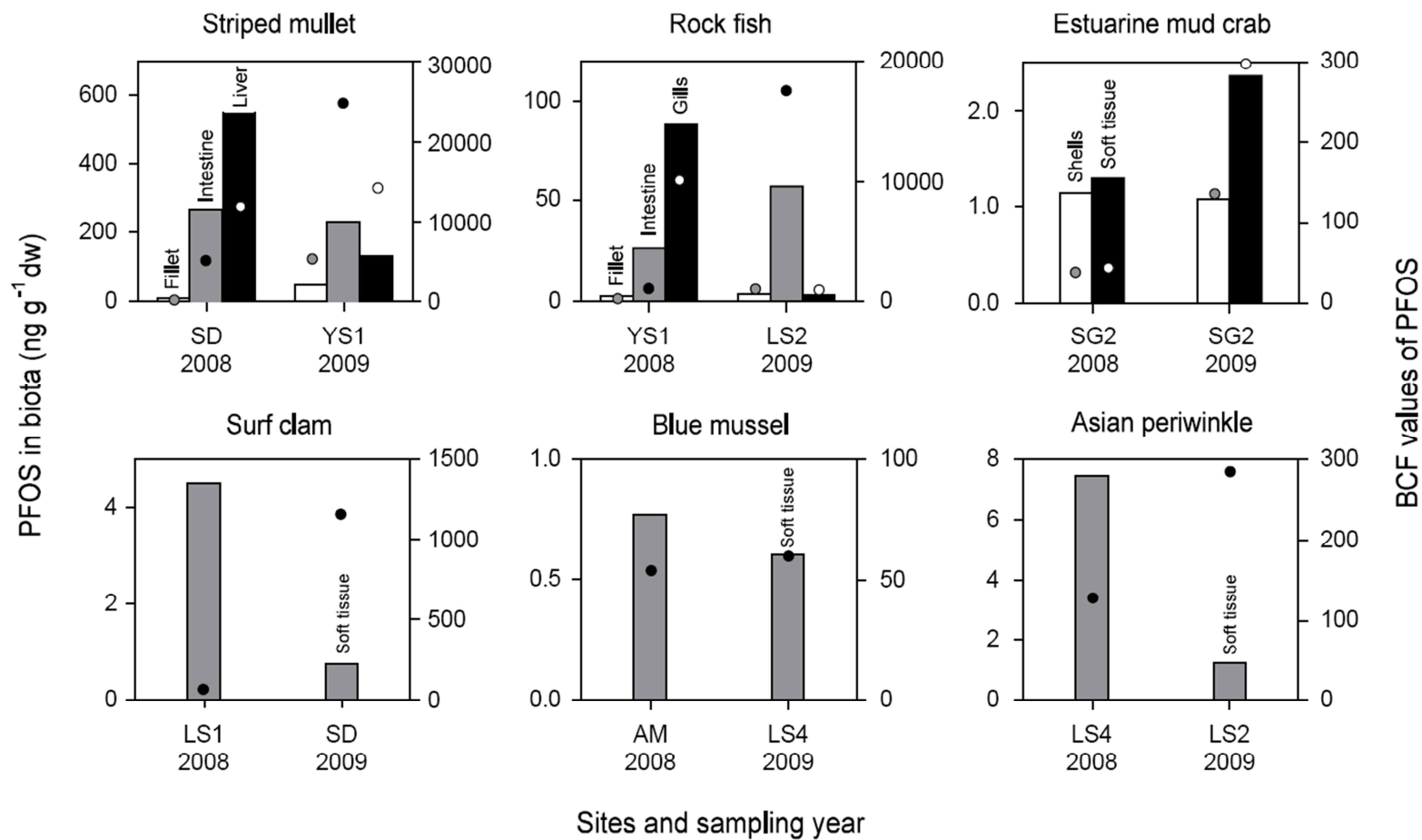


Fig. S4. Concentrations and BCFs for PFOS in biota collected in 2008 and 2009.