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Bioaccumulation characteristics of perfluoroalkyl acids (PFAAs) in coastal organisms from the west coast of South Korea

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ABSTRACT

Year-round monitoring for perfluoroalkyl acids (PFAAs) along the west coast of South Korea targeting long-term changes in water and coastal organisms has been conducted since 2008. In this study, we present the most recent 5-years of accumulated data and scrutinize the relationship between concentrations in water and biota highlighting bioaccumulation characteristics. Twelve individual PFAAs in samples of water ($n = 43$) and biota ($n = 59$) were quantified by use of HPLC–MS/MS after solid phase extraction. In recent years, concentrations of PFAAs in water have been generally decreasing, but profiles of relative concentrations of individual PFAAs vary among location and year. Bioaccumulation of PFAAs in various organisms including fishes, bivalves, crabs, gastropods, shrimps, starfish, and polychaetes varied among species. However, overall bioaccumulation of PFAAs was dependent on corresponding concentrations of PFAAs in water within an area. In organ-specific distributions of PFAAs, greater concentrations of PFAAs were found in intestine of fish (green eel goby). This result suggests that PFAAs are mainly accumulated via dietary exposure, while greater concentrations were found in gill and intestine of bivalve (oyster) which suggests both waterborne and dietary exposures to these organisms. Concentrations of PFAAs in biota did not decrease over time (2008–2010), indicating that continuing bioaccumulation followed by slow degradation or excretion of PFAAs accumulated in biota. Overall, spatio-temporal distributions of PFAAs in water and bioaccumulation characteristics seemed to be associated with recent restrictions of PFOS-based products and uses of PFBS-based substitutes.

1. Introduction

Perfluoroalkyl acids (PFAAs) have been used, for the past six decades, as refrigerants, surfactants, and polymers in various products and industrial applications including leather protectants, textiles, furniture, carpets, and coating materials (Giesy and Kannan, 2001; Lindstrom et al., 2011). Due to their persistence, potential to bioaccumulate, long-range transport, and potential toxic effects on wildlife and humans, PFAAs including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are of concern, recognized as persistent toxic chemicals (Lau et al., 2007; Conder et al., 2008; Houde et al., 2011).

The two most studied PFAAs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have been subject to restrictions in production and use in North America, Europe, and Japan (US EPA, 2005; EU, 2006; UNEP, 2009), but these chemicals are still manufactured and somehow widely used in some Asian countries, particularly in China (Cai et al., 2012; Wang et al., 2014) and South Korea (Kim, 2012). PFOS and its salts have been listed as new persistent organic pollutants (POPs) under the Stockholm Convention in 2009. In 2010, the Korean government designated PFAAs as "restricted chemicals" (Kim and Lee, 2010). However, because no suitable replacements have been developed

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PFAAs are still used in Korea in some applications such as manufacturing of LCD, semi-conductor, pulp, paper, and fabric/clothing.

Due to its lesser bioaccumulation potential and toxic potency, perfluorobutane sulfonate (PFBS)-based products have been used as substitutes for PFOS-based products (Cai et al., 2012). Consequently, relative contributions of PFBS to total PFSAs has been increasing in samples of waters of lakes and coastal waters (Cai et al., 2012; Zhou et al., 2013) and sediments (Codling et al., 2014). Such studies are examples of improvement in quality of the environment following implementation of regulations, such as restriction of uses and ultimate phase-outs of PFOS-based products. However, of temporal, seasonal to inter-annual variations of PFAAs in environments based on the long-term monitoring surveys are sparse. In addition, biological stress such as bioaccumulation of PFAAs on coastal organisms has not been fully understood, especially the causal association with temporal trends of waterborne concentrations of PFAAs.

Some field studies have reported bioaccumulation and biomagnification in aquatic food chains of PFAAs with eight to twelve carbons such as PFOS and PFCAs (Conder et al., 2008; Houde et al., 2011). However, PFAAs accumulated into organisms inhabiting the intertidal mudflat and coastal organisms in freshwater and seawater have been less studied (Van De Vijver et al., 2003; Nakata et al., 2006; Zhao et al., 2011). Previous studies on PFAAs in various organisms collected from the west coast of Korea indicated that bioaccumulation of PFAAs was species-dependent. The cause of this seemed to be collectively due to differences among species in sources of food, feeding guild, rates of uptake and excretion, and metabolism (Naile et al., 2010, 2013). However, empirical bioaccumulation factors (BAF) calculated for individual PFAAs in various organisms varied, possibly due to the nature of field data. Thus, more field-based biological data should provide a better understanding of species-specific bioaccumulation characteristics.

An ongoing study is being conducted to determine the current status and trends and spatial extent of concentrations of PFAAs as well as their potential for detrimental effects in the Yellow Sea. Samples of water and biota were collected from 15 monitoring stations along the west coast of the Korea from 2010 to 2012. To determine spatio-temporal distributions of PFAAs and to detect possible changes in localized point-sources, samples were collected from locations near areas previously sampled in 2008 and 2009 (Naile et al., 2010, 2013). The specific purposes of the present study are to: (i) find recurring trends in spatio-temporal distributions of PFAAs in waters during the last five years, (ii) determine general and specific features of bioaccumulation of PFAAs in various aquatic organisms (by species and/or by organs), (iii) determine *in situ*, empirical, compound-specific BAF values of PFAAs, and (iv) assess temporal trends of PFAAs in aquatic organisms and address their association to waterborne PFAAs, in selected environments along the west coast of Korea.

2. Materials and methods

2.1. Study area, sampling, and sample preparation

Samples of water and biota were collected from the same locations in 2008 and 2009 (Naile et al., 2010, 2013). Samples of water were collected from 15 locations of estuarine and coastal areas along the west coast of Korea during May of 2010, 2011, and 2012 (Table 1 and Fig. 1). To minimize seasonal variations in concentrations of target analytes, collections were made during the same period over the three years of surveys. 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. Biological samples were collected (in 2010) by hand from coastal tidal pools and along the shore of inland bodies of water, and were transferred to and stored in clean PP bags. All samples were transported to the laboratory at 4 °C and frozen at −20 °C until analyses. Some samples of biota, including fish, bivalve, and crab, were necropsied to allow for tissue specific analyses. Samples of biota were composited, homogenized, and freeze-dried and concentrations of twelve PFAAs were reported based on wet mass (wm) of target organisms.

2.2. Target PFAAs

Twelve native PFAAs including: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFBS, PFHxS, PFOS, and PFDS and 9 labeled with stable isotopes: PFAAs (MPFAC-MXA, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnA, $^{13}C_2$-PFDoA, $^{18}O_2$-PFHxS, and $^{13}C_4$-PFOS) were used as target compounds and internal standards (IS), respectively. All standards were obtained from Wellington Laboratories (>98% purity, Guelph, Canada). All acronyms of PFAAs are presented in the footnote of Table 1.

2.3. PFAAs in water and biota

Samples of water were extracted by use of Oasis HLB cartridges (0.2 g, 6 cm^3, Waters Corp., Milford, MA) as described previously (So et al., 2004; Naile et al., 2010). In brief, the cartridges were preconditioned by eluting with 5 mL of methanol followed by 5 mL of nano-pure water. Five hundred milliliters of samples of water was loaded onto the cartridge at a rate of ~1 drop a second after spiking with 500 μL of 5 ng mL^{-1} of the IS. The cartridge was then washed with 5 mL of 40% methanol (in nano-pure water), and once complete was allowed to run dry. The target fraction was eluted with 10 mL of methanol and collected in a 15 mL PP tube and reduced to 1 mL under a gentle stream of nitrogen gas.

Biota was extracted by use of an alkaline digestion SPE method (Naile et al., 2010, 2013). A 1 g aliquant of homogenized freeze-dried tissue was transferred to a 50 mL PP tube and spiked with 500 μl of 5 ng mL^{-1} IS, and 30 mL of 0.01 N KOH/methanol was added. The mixture was then shaken at 250 rpm for 16 h. After this digestion 2 mL of the tissue solution was added to a 250 mL PP bottle containing 200 mL of nano-pure water and then shaken thoroughly. This tissue-water mixture was next extracted using SPE cartridges as described above.

2.4. Instrumental analysis

An Agilent 1200 HPLC (Agilent Technologies, Vintage Park, CA) was used with a Thermo Scientific Betasil C18 column (100 × 2.1 mm, 5 μm particle size, Thermo Electron Corp., Bellefonte, PA). 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 using MRM mode, and when possible at least two transitions per analyte were monitored (Table S1 of Supplemental Materials (S)). 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 (Benskin et al., 2007; Naile et al., 2010).

2.5. Quality control

Method detection limits (MDLs) for PFAAs in water and biota were calculated as the mean blank + 3 × SD (standard deviation, $n = 7$). MDLs for individual PFAAs ranged from 0.2 to 2.0 ng L^{-1} for samples of waters and from 0.2 to 2.0 ng g^{-1} dm for samples

Table 1
Sampling locations and sum of PFAAs concentrations in water collected from west coast of Korea.

Region	Locations	Geographical description	Sample types	Σ PFAAs in water (ng L^{-1})[a]		
				2010	2011	2012
Lake Shihwa	LS1	Outside of sea dike	Seawater	75	nc[b]	nc
	LS2	Outside of sea dike	Seawater	30	24	9.5
	LS3	Inside of sea dike	Seawater	19	17	7.5
	LS4	Inside of sea dike	Seawater	61	21	7.6
Lake Asan	AS1	Inside of sea dike	Freshwater	180	82	130
	AS2	Outside of sea dike	Seawater	98	89	22
	SG1	Inside of lake	Freshwater	45	37	18
	SG2	Outside of sea dike	Seawater	69	38	7.5
Taean Coast	SD	Coastal area, beach	Seawater	44	25	2.5
	ML	Coastal area, beach	Seawater	37	38	1.4
	AM	Coastal area, beach	Seawater	23	14	1.2
Geum River	GG1	Inside of estuary dam	Freshwater	75	49	20
	GG2	Outside of estuary dam	Seawater	64	46	17
Yeongsan River	YS1	Outside of estuary dam	Seawater	17	17	3.6
	YS2	Inside of estuary dam	Freshwater	21	33	19
			Mean ± SD	57 ± 43	38 ± 23	19 ± 33

[a] Σ PFAAs: Sum of the 12 PFAAs concentrations including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonic acid (PFOS), and perfluorodecane sulfonate (PFDS).
[b] nc: not collected.

of as presented in Table S1. Recoveries of PFAAs in spiked matrices ranged from 82% to 120% for water and from 65% to 133% for biota (Table S1). Solvent blanks and a mid-concentration of calibration standard were injected after every ten samples to check for carry-over and background contamination and instrumental sensitivity. Concentrations of all solvent blanks than the limit of quantifications (LOQs), which were defined as 5× the signal measured in solvent blanks.

3. Results and discussion

3.1. Spatio-temporal distributions of PFAAs in water

Nearly all of the PFAAs were detected in samples of waters collected from the estuarine and coastal areas of the west coast of Korea (Tables 1 and S2). Total concentrations of PFAAs (sum of the 12 target compounds; ∑ PFAAs) in waters varied among areas and locations ranging from 17 to 180 ng L^{-1} (mean: 57 ng L^{-1}), from 14 to 89 ng L^{-1} (mean: 38 ng L^{-1}), and from 1.2 to 130 ng L^{-1} (mean: 19 ng L^{-1}) in 2010, 2011, and 2012, respectively (Fig. 2). Concentrations of waterborne PFAAs along the west coast of Korea generally decreased over the years for five years with an average decrease of 6-fold (Naile et al., 2010, 2013). Concentrations of PFAAs at locations in freshwater were greater than those in seawater, which indicated that PFAAs originated from point sources on surrounding inland areas rather than non-point sources (Naile et al., 2013). Greatest concentrations of PFAAs in water were found in the Lake Asan area (AS1 and AS2) from 2008 to 2012, which indicated continuing releases of PFAAs from that area. PFOS was the major PFAA found in samples of waters along the west coast of Korea, followed by PFOA and PFHpA. This result is consistent with results of previous studies (Naile et al., 2010, 2013).

The results of monitoring over the past 5 years indicated that concentrations of PFAAs in water have decreased since 2008 (Naile et al., 2010, 2013) (Table 1 and Fig. 1). However, profiles of relative concentrations of PFAAs in waters varied from year to year, except for PFOA (Fig. 1b). In particular, relative contributions of PFOS in water to the ∑ PFAAs decreased each year except for 2012, and overall by 3-fold from 2008 to 2011, but doubled in 2012 (29%). Relative proportions of the ∑ PFAAs contributed by shorter-chain PFAAs such as PFBS and PFPeA have increased over recent consecutive years. Alternatively, the relative contribution of PFOA was fairly consistent with an average of approximately 20%, which indicates continuing of input or possible *in situ* equilibrium in areas. Decreasing concentrations of waterborne PFAAs seemed to be associated with recent global restrictions on the use of some PFAAs together with additional regulations promulgated by the Korean government (Kim and Lee, 2010). In 2010, the government of the Korea designated PFAAs as "restricted chemicals", which limits their commercial use followed by possible decrease of lotic sources in the coastal ecosystem. Increasing concentrations of shorter-chain PFAAs could be explained by the recent increasing uses of PFBS-based chemicals as substituents (Cai et al., 2012; Zhou et al., 2013). Overall, temporal trends of waterborne PFAAs in coastal waters of Korea demonstrated effective control of point sources but also indicated possible continuing exposure of such alternative materials, thus remains as concern.

3.2. Species- and compound-specific bioaccumulations of PFAAs

PFAAs were detected in all samples of biota from the west coast of Korea in 2010 (Fig. 3 and Table S3). Among the various species, fish contained the greatest mean concentrations of PFAAs (∑ PFAAs), ranging from 3.2 to 180 ng g^{-1} wm (mean: 56 ng g^{-1} wm), followed by marine worm (32–71 ng g^{-1} wm), gastropod

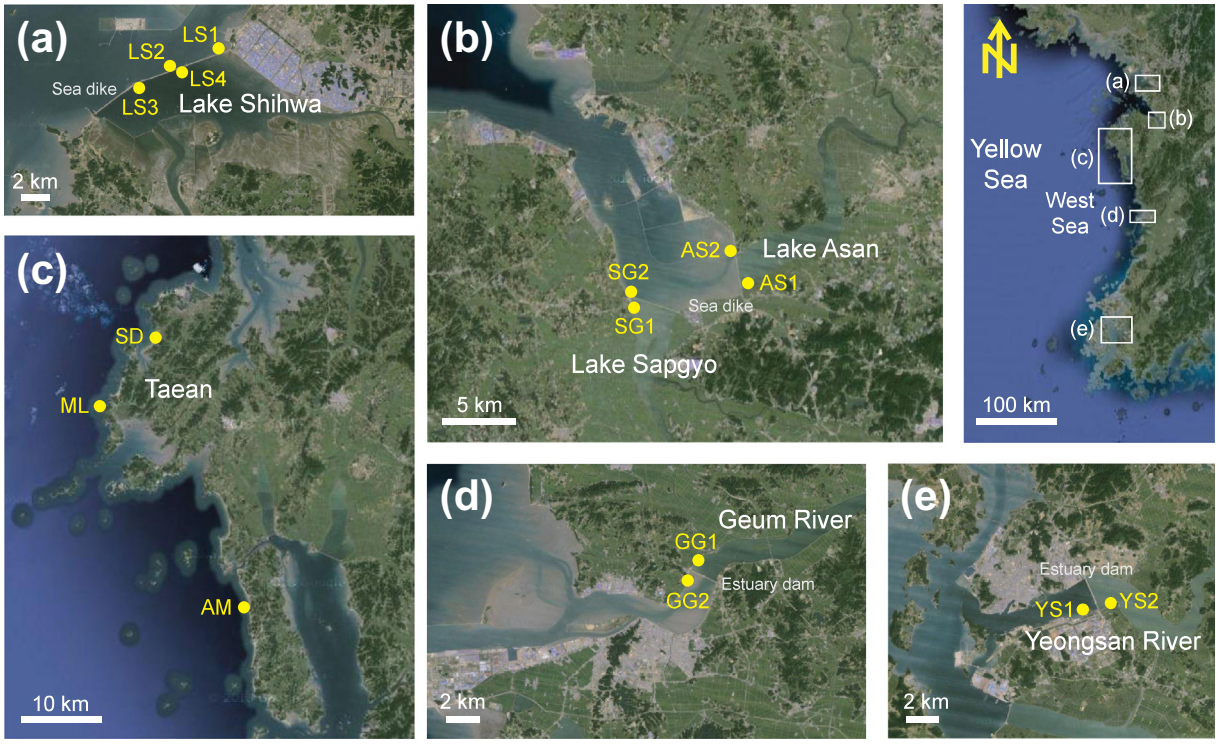

Fig. 1. Map showing sampling locations on the west coast of Korea, Wes Sea, during 2010–2012. (a) Lake Shihwa, (b) Lake Asan and Lake Sapgyo, (c) Taean Coast, (d) Geum River Estuary, and (e) Yeongsan River Estuary.

(2.1–200 ng g^{-1} wm), shrimp (3.4–135 ng g^{-1} wm), crab (2.6–53 ng g^{-1} wm), bivalve (5.1–47 ng g^{-1} wm), and starfish (2.4–15 ng g^{-1} wm), respectively. Compositions of PFAAs accumulated in samples were slightly different among species. For example, PFOS was the predominant PFAA in fish and shrimp, while other PFAAs such as PFBS, PFPeA, and PFOA were dominant in bivalve, crab, and gastropod. Great concentrations of PFAAs were found in samples of fishes (crucian carp and paradise goby) collected from AS1 and in samples of shrimp (lake prawn) collected from SG2, of which waterborne concentrations of PFAAs in AS1 (most contaminated location) and SG2 were found to be relatively great.

Absolute and relative concentrations of PFAAs in various aquatic organisms indicated that bioaccumulation of PFAAs was both species- and compound-specific. For example, PFOS was the dominant PFAA compound in fish and shrimp, while PFPeA was predominant in gastropod and crab, thus fate through water and biological systems vary depending on species and compounds. Concentrations of PFAAs in more motile aquatic organisms, such as fish and shrimp, contained greater concentrations PFAAs than those of benthic species with limited motility, such as bivalves and crab (Fig. 3). A similar trend was observed in a previous study, thus additional studies conducted in both the field and laboratory would be useful to describe behavior associated bioaccumulation (Naile et al., 2013). Species- and compound-specific bioaccumulations of PFAAs seemed to be collectively due to differences in occupied habitats including surrounding media, sources of food, feeding type, uptake and excretion kinetics, and metabolism rates and pathways among species (Yang et al., 2012; Naile et al., 2013). However, absolute and relative concentrations of PFAAs in biological samples could not be obviously grouped according to the taxonomic features in a statistical manner, such as a principal component analysis (data not shown). There could be unknown factor(s) controlling bioaccumulation of PFAAs, of which study of which is urgent and would be valuable additions to PFAAs biochemistry.

Concentrations of PFAAs in biota were significantly correlated with concentrations of PFAAs in water ($n = 59$, $r^2 = 0.57$, $p < 0.01$). Bioaccumulation of PFAAs in aquatic organisms is strongly dependent on the concentrations of PFAAs in water regardless of species. A significant correlation between concentrations of PFDA and PFUnA was found in samples of biota, with the most significant correlations for samples collected from the most contaminated area of Lake Asan (Fig. S1). This result indicates a common source for PFAAs on the west coast of Korea except for the Lake Asan area (Yoo et al., 2009). More complementary studies would be necessary in the future to address this phenomenon by emphasizing source- or compound-, or concentration-specific bioaccumulations of PFAAs against various habitats and environments.

3.3. Organ-specific distributions of PFAAs

Concentrations of PFAAs also varied among organs of fish (green eel goby), bivalve (oyster), and crab (shore crab) in organ-specific manner (Fig. 4). The intestine of fish contained the greater concentrations of PFAAs compared to other organs and tissues such as liver, gill, and fillet (Fig. 4a). However, in bivalves, concentrations of PFAAs were comparable in gill and intestine, and relatively small concentrations were detected in mantle (Fig. 4b). In crab, greatest concentrations of PFAAs were found in soft tissues, but shell and legs also contained about half of the soft tissues, indicating possible direct absorption from surrounding waters (Fig. 4c).

A previous study reported that great concentrations of benzo[*a*]pyrene were found in gills of fish exposed via the water (rainbow trout), while, in the dietary exposed fish, great concentrations were found in intestines and bile (Sandvik et al., 1998). Thus, organ-specific distributions of such organic chemicals in biological samples could be a good indicator determining the major routes of possible exposure. Relatively great concentrations of PFAAs found in intestine of green eel goby suggest that infaunal fish could accumulate PFAAs through dietary exposure route taking food sources

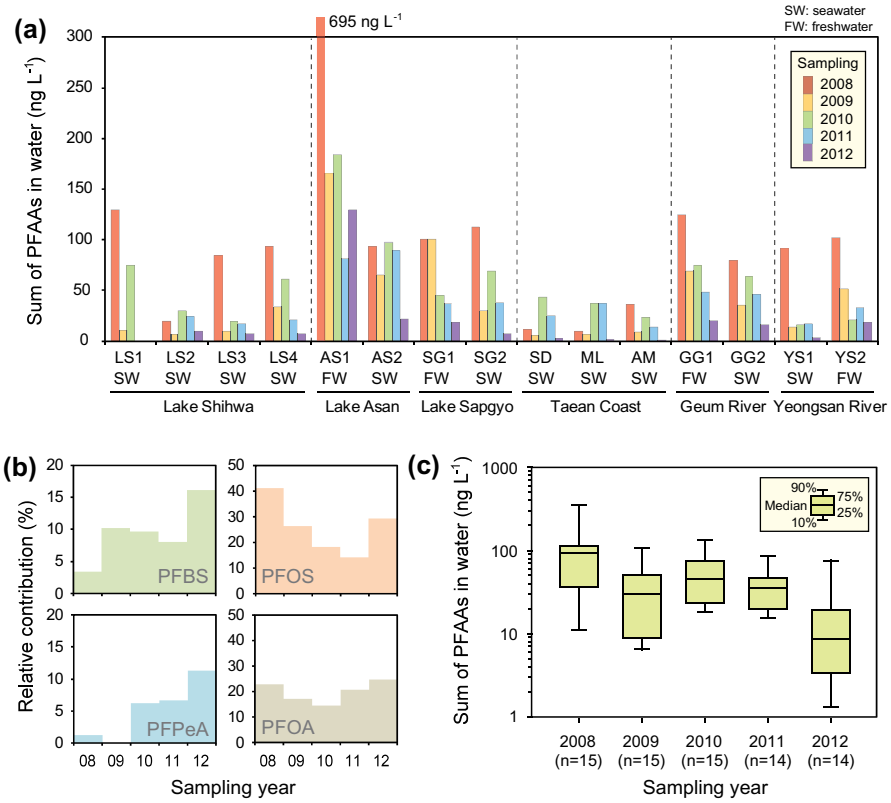

Fig. 2. PFAAs in water from 2008 to 2012. (a) Spatio-temporal distribution, (b) relative contribution of selected PFAAs, and (c) temporal trends of PFAAs (sum of 12 PFAAs). Data of 2008 and 2009 refer to Naile et al. (2010) and Naile et al. (2013), respectively.

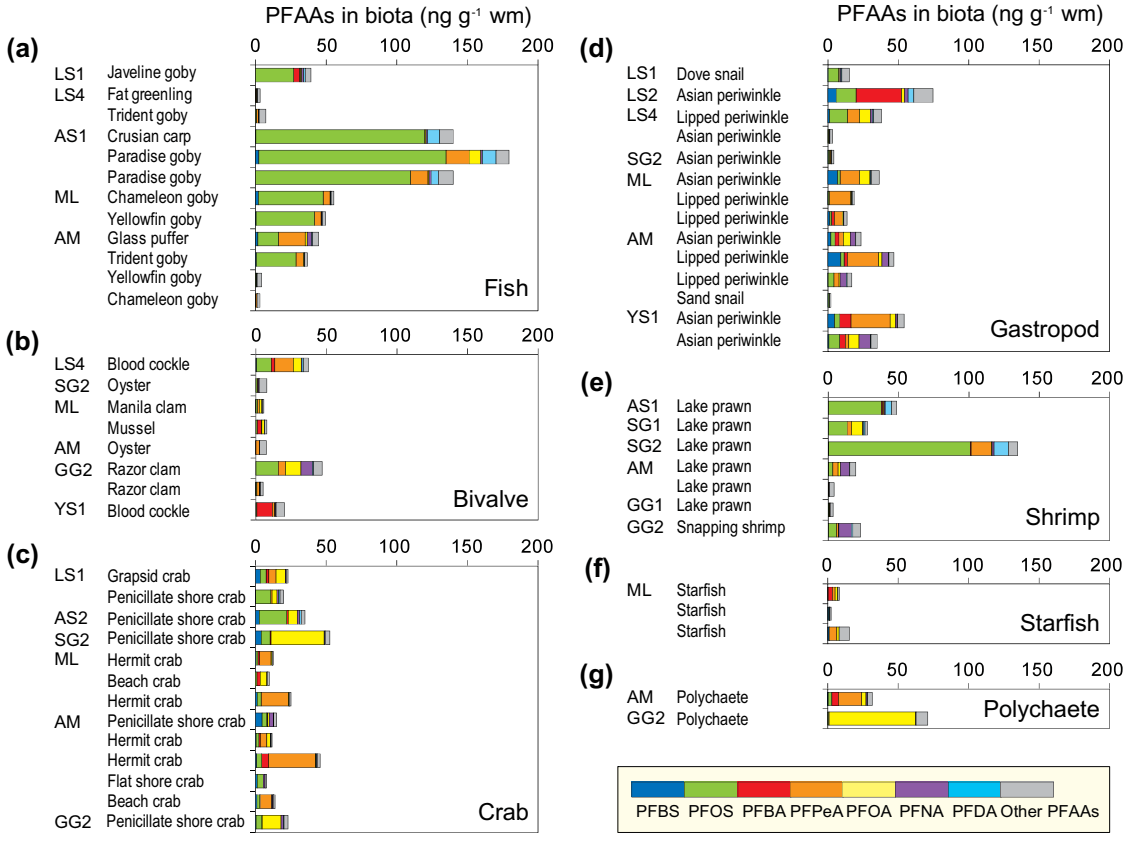

Fig. 3. Concentration of PFAAs in (a) fish, (b) bivalve, (c) crab, (d) gastropod, (e) shrimp, (f) starfish, and (g) polychaetes collected from the west coast of Korea in 2010.

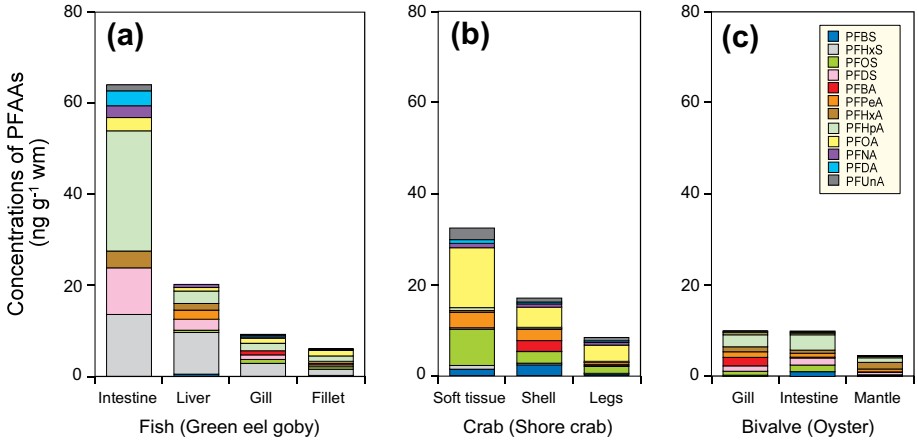

Fig. 4. Organ-specific distributions of PFAAs in (a) fish (green eel goby, collected from GG2) and (b) crab and (c) oyster (collected from LS4, SG2, ML, AM, and YS1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

from surrounding sediment and water (Fig. 4a). Relatively greater portions of PFAAs were accumulated in shell and legs of crab, of which amounts were collectively comparable to that in soft tissue, reflecting possible absorption through skin by epifauna species (Fig. 4b). In contrast, in the oyster, concentrations of PFAAs were relatively great in gill and intestine and only half was found in the mantle, which suggests both waterborne and dietary exposures of PFFAs to suspension-feeding organisms such as oyster as well as dietary exposure (Fig. 4c) (Tomy et al., 2004; Xu et al., 2014).

3.4. Field-based bioaccumulation factors of PFAAs

Field-based bioaccumulation factors (BAFs) of PFAAs in various aquatic organisms were calculated based on concentrations in water and biota (wet mass basis) (Fig. 5 and Table S4). The log BAFs of PFAAs were compound-specific and proportional to chain length given as carbon number or molecular weight. In general, log BAFs of PFOA, PFNA, PFUnA, and PFOS were greater than those of shorter-chain PFAAs (C6- to C7-PFCAs and C4- to C6-PFSAs) and longer-chain PFAAs including PFDA and PFDS. This result indicated that PFSAs are more bioaccumulative than PFCAs, for analogous compounds of the same fluorinated carbon chain length (e.g., PFOS > PFOA) (Conder et al., 2008). However log BAFs of PFAAs differed slightly among organisms (Table S4). Differences in log BAFs might be due to differential capacities to accumulate and/or metabolize PFAAs. For example, gastropods seem to accumulate shorter-chain of PFAAs (C6- to C9-PFCAs and C4- to C6-PFSAs), but fish or shrimp tend to accumulate longer-chain of PFAAs (C10- to C11-PFCAs and C8- to C10-PFSAs). The results of present study were generally in agreement with previous findings that the shorter-chain PFCAs ($C \leqslant 7$) are not considered bioaccumulative, and longer-chain PFCAs with >10 fluorinated carbons are limited bioaccumulation potentially due to large molecular size (Conder et al., 2008; Xu et al., 2014). Results of a recent study suggested that the BAFs of PFAAs varied among species according to the trophic levels, say PFCAs with C9 to C12 compounds and PFOS possess biomagnification potential (Xu et al., 2014).

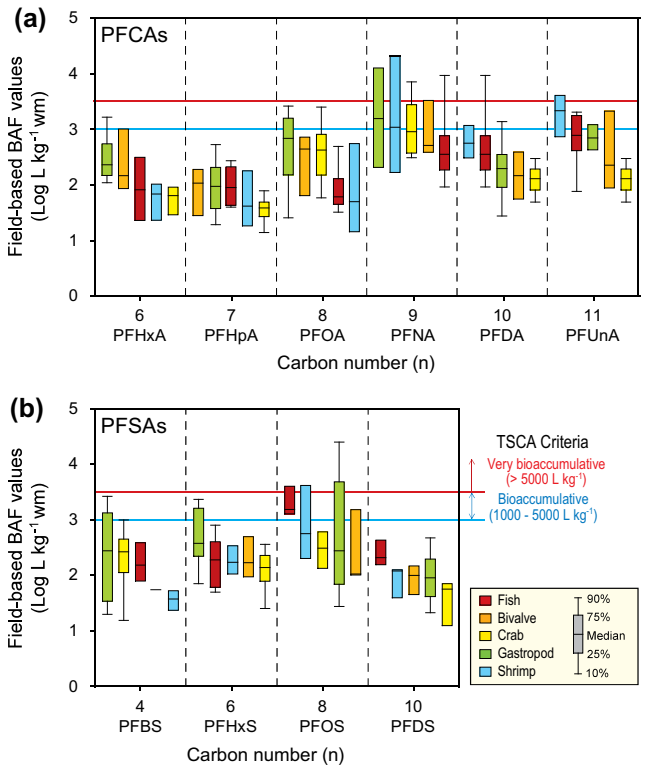

Fig. 5. Field-based bioaccumulation factors (BAFs) of (a) PFCAs and (b) PFSAs according to the carbon number of compounds in various aquatic organisms collected from the west coast of Korea.

Log BAFs were proportional to numbers of carbons in PFAAs, similar to the those of logK_d values (water-particle partitioning coefficient) observed from estuarine and coastal areas (Hong et al., 2013). The logK_d values of PFAAs generally increased with more carbon numbers from 8 to 12, which showed exponentially increase as a function of salinity (Hong et al., 2013). It means that the elevated K_d values might result in greater bioaccumulation of PFAAs in the aquatic organisms through food sources (i.e., mediated by particulate organic matter) (Jeon et al., 2010). Thus, incremental values of K_d for PFAAs as functions of increasing number of carbon numbers and salinity suggest that seems to be one of the key mechanisms of PFFAs bioaccumulation in coastal seawater organisms.

4. Conclusion

Temporal trends of PFAAs in aquatic organisms did not indicate decreasing concentrations despite rapid decreases in concentrations of many PFAAs in water. It is indicated that continuing bioaccumulation was evident but slow degradation or lesser excretion of hydrophobic PFAAs in biota. PFBS and PFHxS were not detected in samples collected in 2008, but those compounds were commonly

detected in 2010, also suggesting a possible continuing input of PFAAs into the coastal environments of Korea. Overall, the long-term monitoring of PFAAs in biota together with corresponding waters in estuarine and coastal areas across the west coast of Korea was valuable addition to understand the bioaccumulation characteristics of coastal pelagic and benthic organisms. The current findings provide useful information on status and trends of PFAAs and future management of PFAAs in Korea and neighboring China sharing the Yellow Sea, including the West Sea 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.2014.06.023.

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