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In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea

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HIGHLIGHTS

- ► In situ fate and partitioning of PFAAs were described along salinity gradients in estuaries.
- ► Salinity was found to be the key factor controlling adsorption of waterborne PFAAs.
- ► The K_d for longer-chain PFAAs ($C \geq 8$) increased as a function of salinity (salting-out effect).
- ► Salting constants of PFAAs were notably greater than those of other organic contaminants.
- ► Results of this study will provide better understanding of PFAAs fate in the field.

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ABSTRACT

Concentrations, distributions, fate, and partitioning of perfluoroalkyl acids (PFAAs) were investigated in surface water ($n = 34$) collected from the Youngsan and Nakdong River Estuaries of South Korea. Thirteen individual PFAAs in water and suspended solids (SS) were quantified by use of HPLC–MS/MS. PFAAs were detected in all samples, which indicated that they were widely distributed in the study area. Greater concentrations of PFAAs were found at some inland sites which seemed to be affected by direct input from point sources, such as wastewater treatment plants, and/or indirect diffusive sources, such as surface runoff. Spatial distributions of PFAAs in estuaries along transects toward the open sea demonstrated that these chemicals were transported to the outer region primarily by water discharged during the rainy season. Field-based partition coefficients (K_d) for long-chain PFAAs ($C \geq 8$) were significantly correlated with salinity ($r^2 = 0.48$ to 0.73, $p < 0.01$); K_d values increased exponentially as a function of salinity. Due to the 'salting-out' effect, PFAAs were largely scavenged by adsorption onto SS and/or sediments in estuarine environments. In addition, values for K_d of those PFAAs were directly proportional to the number of carbon atoms in the PFAAs. Salting constants of selected PFAAs were notably greater than those of other environmental organic contaminants, which indicated that adsorption of PFAAs is largely associated with salinity. Overall, the results of the present study will provide better understanding of the fate and transport of PFAAs in the zone of salinity boundary that can be used for developing fate models of PFAAs in the coastal marine environment.

1. Introduction

During the past half-century, perfluoroalkyl acids (PFAAs) have been used in various products and industrial applications including protectants for leather and textiles in clothing, furniture and carpets, personal care products, stain repellents, pesticides, and coatings such as paints, plastics, fire-fighting foams, and anti-static chemicals for production of electronics (Cai et al., 2012; Guo et al., 2008; Yu et al., 2009). Due to their widespread distribution in the environment and in tissues of wildlife and humans and especially since their first detection in wildlife in 2001 (Giesy and Kannan, 2001), PFAAs have been increasingly studied and come under regulatory scrutiny worldwide. PFAAs such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) have raised particular concern, because of their persistence, bioaccumulation, long-range transport potential, and possible effects on the environment (Labadie and Chevreuil, 2011a; Lau et al., 2007; Naile et al., 2010). The two most commonly

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studied PFAAs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). These two stable terminal products of transformation of a range of individual commercial chemicals, have been subject to restrictions in production and use in Europe, North America and Japan (EU, 2006; UNEP, 2009; US EPA, 2005) such that releases of both classes of chemicals have been lessened, but these chemicals are still manufactured and used in China and possibly some other Asian countries (Cai et al., 2012). Also, these compounds are still in the environment or have the potential to enter the environment.

In recent years, global fate and transport of PFAAs through water currents and/or the atmosphere have been recognized, however, the pathways and mechanisms of distribution and dissipation are still largely unknown (Ahrens et al., 2011a). PFAAs are frequently found in waters of rivers, lakes, estuaries, coastal areas, and even the open ocean (Ahrens et al., 2009a; Armitage et al., 2006; Cai et al., 2012; So et al., 2004; Yamashita et al., 2005, 2008). PFAAs have been reported to be transported mainly by ocean currents on a global scale (Zarfl et al., 2011). They can be introduced into aquatic ecosystems via direct sources such as historic contamination of sites by spills or use of fire-fighting foam, fluoro-chemical manufacturing plants, domestic and industrial wastewater treatment plants (WWTPs) or via diffuse sources such as surface runoff (Labadie and Chevreuil, 2011a; Loganathan et al., 2007; Möller et al., 2010; Sánchez-Avila et al., 2010). PFAAs can be further moved directly by rivers such that they can enter estuaries and coastal marine environments. This is an important pathway for transport of such pollutants in land-ocean connections (Cai et al., 2012; Pan and You, 2010). Thus, the behavior and fate of PFAAs occurring within estuarine environments including dilution, spreading, advection, adsorption, bioaccumulation, and sedimentation would be of importance for better understanding of global transport pathways.

Information on partitioning of PFAAs between water and suspended solids (SS) and/or sediments is crucial for understanding transport of PFAAs in estuarine environments (Pan and You, 2010). Due to effects on aqueous solubility of surfactants, salinity is a well-known factor controlling sorption of neutral organic compounds on SS (Turner and Rawling, 2001). However, mechanisms of adsorption of anionic PFAAs are probably not the same as those of neutral hydrophobic chemicals. Because of their pK_a values, PFAAs occur as anions at environmentally relevant pH values (Burns et al., 2008; US EPA, 2002). Partition coefficients (K_d) of PFAAs are known to be affected by electrostatic interactions, hydrophobicity, ion-exchange, and salinity (Higgins and Luthy, 2006; Jeon et al., 2011; Pan et al., 2009; Xiao et al., 2011). Anions of PFAAs can form strong ion pairs with some cations, which results in salting-out in natural saline waters that contain relatively great amounts of dissolved solids (Giesy et al., 2010). The solubility of PFOS in freshwater and saltwater was reported to be approximately 370 $mg\ L^{-1}$ and 12.4 $mg\ L^{-1}$, respectively (Giesy et al., 2010). As salt content increases, solubility of PFAAs decreases, a fact that could drastically change partitioning properties. Thus, the tendency for PFCAs and PFSAs to sorb to particles would be expected to vary among estuarine environments as a function of salinity. For example, it has been reported that PFAAs were largely scavenged to the sediment in the Yangtze River estuary due to the salinity gradient of the estuary (Pan and You, 2010). Also, K_d for PFAAs increased (2.1 to 2.7 fold) with the increase in water salinity (10 to 34) indicating salting-out effect from laboratory based experiments, and the salting constant was estimated to range from 0.80 to 1.1 (Jeon et al., 2010a, 2010b). However, there is limited information on the in situ effect of salinity on distribution of PFAA between water and particles in the estuarine environment.

The Youngsan and Nakdong rivers, two of the four major rivers in South Korea, flow toward the southwest and southeast and discharge into the Yellow Sea and South China Sea, respectively. Approximately 1.8 and 6.6 billion tons of freshwater are discharged annually into the Youngsan and Nakdong River Estuaries. The two estuaries have been completely separated between artificial lakes (freshwater) and estuarine areas (saltwater) since construction of estuary dams in 1981 and 1987, respectively (Cho et al., 2009; Du et al., 2010). Thus, they act as an estuary or a bay, depending on the discharge of freshwater through water gates. Inflow of freshwater can cause changes in salinity of the water column in these estuaries. Watersheds containing larger cities, such as the Youngsan watershed (Mokpo City) and the Nakdong watershed (Busan City) can be sources of contaminants to the sea. The industrial area of the Youngsan watershed contains cement, pulp, and paper factories while the Nakdong watershed has dyeing, fabric, textile, and leather as well as municipal complexes. Thus, inflow from inland creeks near cities, industrial, and municipal areas and discharged water from artificial lakes are likely the sources of pollution in these two estuaries. Despite several investigations on distribution and concentration of organic and inorganic toxic substances in the Youngsan and Nakdong River Estuaries (Jin et al., 2012; Kim et al., 2011), little is known about the fate and partitioning of PFAAs.

In this study, concentrations and distributions of waterborne PFAAs (dissolved and particulate phases) were determined in waters collected from the Youngsan and Nakdong watersheds including artificial lakes, inland creeks, and estuarine areas. Specifically, fate and partitioning of PFAAs in two estuaries were investigated. Field-based K_d values of PFAAs between water and SS were investigated along a natural salinity gradient. The relationship between magnitudes of K_d and structures of PFAAs, as described by the number of carbons, was also studied. The results from this study will provide better understanding on fate and transport of PFAAs from land to ocean and their boundary zones.

2. Materials and methods

2.1. Chemicals and reagents

Thirteen native PFAAs (perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, and perfluorodecane sulfonate (PFDS)) and 9 mass-labeled 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 surrogate standards, respectively. All standards were obtained from Wellington Laboratories (>98% purity, Guelph, Canada). HPLC-grade methanol was purchased from Burdick & Jackson (Muskegon, MI). All terminology and acronyms of PFAA compounds follow recommendations of a recent review article (Buck et al., 2011).

2.2. Sample collection

Samples of water were collected from artificial lakes ($n=5$), inland creeks ($n=14$), and estuarine areas ($n=15$) of the Youngsan and Nakdong watershed of South Korea during May of 2011 (Fig. 1). Four liters of surface water were collected for analysis of SS, particulate organic carbon (POC), dissolved organic carbon (DOC), and PFAAs by use of pre-cleaned polypropylene (PP) bottles that had been rinsed with methanol. All samples were filtered as soon as possible through GF/F filters (47 mm for SS and PFAAs; 25 mm for POC, Whatman, Maidstone, UK) for separation of the dissolved and particulate fractions and stored at 4 °C until further treatment.

2.3. Water quality analysis

Water quality parameters including temperature, salinity, dissolved oxygen (DO), and pH were measured in situ using an YSI 556 MPS

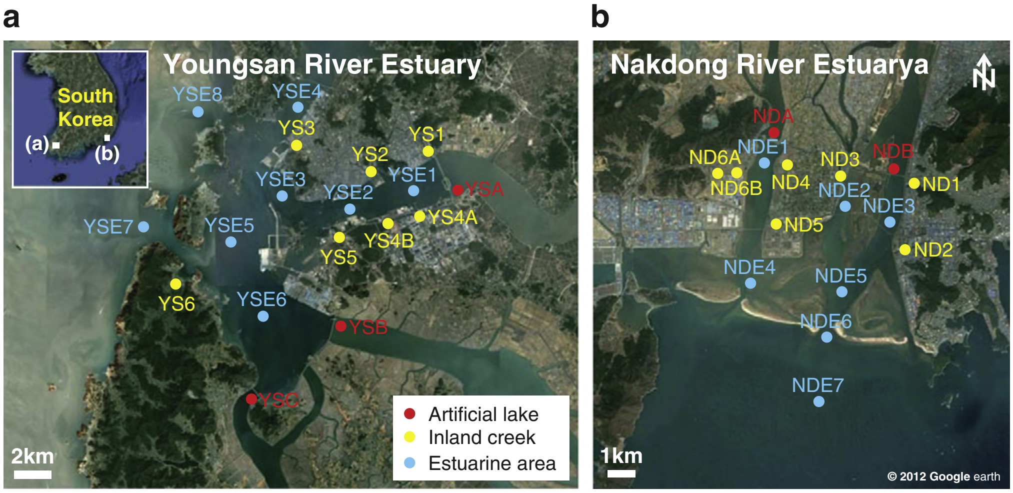

Fig. 1. Sampling sites of the (a) Youngsan River Estuary and (b) Nakdong River Estuary, South Korea.

(Multi-probe System, YSI, Yellow Springs, OH). SS were determined on pre-weighted GF/F filters (Whatman). Samples for POC analysis had been fumigated with HCl (Merck, Darmstadt, Germany) to remove all carbonate materials, dried, and weighed into tin capsules, then the POC was measured using an elemental analyzer (Flash 2000, Thermo Finnigan, Milan, Italy). DOC was analyzed following high-temperature combustion in a TOC analyzer (Shimadzu TOC-VCPH, Shimadzu Co., Japan).

2.4. PFAAs analysis

Water samples for PFAAs analysis were divided into two fractions (dissolved and particulate phases) by use of methanol-rinsed GF/F filters (Whatman). Dissolved PFAAs were extracted and cleaned-up using Oasis HLB extraction cartridges (0.2 g, 6 cm^3, Waters Co., Milford, MA) according to previously described methods (Naile et al., 2010; So et al., 2004). In brief, the cartridges were preconditioned by eluting with 5 mL of methanol and 5 mL of nano-pure water. One liter of water was then spiked with 5 ng of mass-labeled surrogate standards and then loaded onto the cartridge. The cartridge was then washed with 5 mL of 40% methanol in water and eluted with 10 mL of methanol. The eluate was concentrated to 1 mL under a gentle stream nitrogen gas, and filtered using a disposable PP filter (0.2 μm, Millipore, Bedford, MA, USA) for instrumental analysis.

PFAAs in the particulate fraction were analyzed by use of slight modifications of a previously described method (Higgins et al., 2005). The method employed an acetic acid wash followed by repeated extractions of the acidified SS by use of a solvent mixture of methanol and 1% acetic acid (90:10, v/v) in nano-pure water. Briefly, freeze-dried filter samples (1 L of water filtered) were transferred to 50 mL PP tubes and spiked with 5 ng of surrogate standards, to which 10 mL of 1% acetic acid solution was added. Each tube was vortexed for 5 min, and placed in a sonication bath (40 °C) for 20 min. After sonication the tube was centrifuged at 3000 rpm for 15 min and supernatant was decanted into a new 50 mL PP tube. Five milliliters of a methanol solution (methanol: 1% acetic acid, 90:10 (v/v)) was added to the original vial and the vial was again vortex mixed and sonicated, before being centrifuged and decanted into the second tube. This process was repeated once more, and a final 10 mL acetic acid wash was performed. All extracts (~40 mL) 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.

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). Mass spectra were collected using an Applied Bioscience SCIEX 3000 (Foster City, CA) tandem mass spectrometer, fitted with an electro-spray ionization source, operated in negative ionization mode. Gradient conditions were used at 0.3 mL min^{-1} 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 until 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 using MRM mode, and when possible at least two transitions per analyte were monitored (details in Table S1 of Supplemental materials (S)) (Benskin et al., 2007; Naile et al., 2010).

2.5. Quality control

Method detection limits (MDL) for dissolved and particulate PFAAs were calculated as the mean blank + 3 × SD (standard deviation, $n = 7$). MDL values of individual PFAAs ranged from 0.1 to 1.0 ng L^{-1} for the dissolved phase and from 0.5 to 5 ng kg^{-1} for the particle phase (assumed to be 100 mg L^{-1} as SS) as presented in Table S1. Recoveries of PFAAs in spiked matrices ranged from 75 to 120% for the dissolved phase and from 66 to 87% for the particle phase (Table S1). Prior to extraction, surrogate standards were spiked into all samples of water and particles. Recoveries of spiked surrogate standards ranged from 52 to 107% for waters and from 55 to 108% for particles in this study. A mid concentration of calibration standard was injected after every 10 samples as a check for drift in instrumental sensitivity. Also, procedural blanks and instrumental blanks were checked periodically for background contamination and/or carryover. Concentrations of all analytes in all blanks were less than the MDL.

2.6. Data analysis

The field-based partition coefficient (K_d) (L kg^{-1}) of PFAAs between water and particle were calculated (Eqs. (1) and (2)).

$$K_d = C_{ss}/C_w \tag{1}$$

Where: C_{ss} (ng kg^{-1} dry weight (dw)) is the PFAAs concentration in SS, and C_w is dissolved PFAAs in water (ng L^{-1}).

$$K_{oc} = K_d \times 100/f_{oc} \tag{2}$$

Where: K_{oc} ($cm^3\ g^{-1}$) is the organic carbon normalized partition coefficient and f_{oc} is the organic carbon fraction (%) in SS.

Correlation analysis was performed to identify relationship between water quality parameters and partition coefficient of PFAAs by SPSS (SPSS 12.0 for Windows, SPSS Inc., Chicago, IL, U.S.). Mathematical relationship between K_d and physico-chemical factors of PFAAs were estimated by SigmaPlot 10.0 for Windows (SPSS Inc.).

3. Results

3.1. PFAAs

PFAAs were detected in all samples of water and particles from artificial lakes, inland creeks, and estuarine areas of the Youngsan and Nakdong River Estuaries (Table 1, Fig. 1 and Fig. S1). This result is consistent with those of previous reports that PFAAs were widely distributed in waters of estuarine and coastal areas of South Korea (Naile et al., 2010, 2013; Yoo et al., 2009). Total concentrations of PFAAs (sum of the 13 PFAAs) as dissolved phase from the Youngsan watershed ranged from 32 to 140 ng L^{-1} in artificial lakes (mean: 94 ng L^{-1}), from 23 to 130 ng L^{-1} in inland creeks (mean: 58 ng L^{-1}), and from 12 to 34 ng L^{-1} in estuarine areas with a mean of 20 ng L^{-1}. In the Nakdong watershed, concentrations of PFAAs ranged from 44 to 52 ng L^{-1} in artificial lakes, from 45 to 190 in inland creeks (mean: 99 ng L^{-1}), and from 42 to 160 ng L^{-1} in estuarine areas (mean: 65 ng L^{-1}) (Table 1 and Fig. 2a). Concentrations of PFAAs as particulate phase ranged from 160 to 470 ng kg^{-1} dw in artificial lakes in Youngsan watershed with a mean of 350 ng kg^{-1} dw. The ranges of PFAAs were 82 to 580 ng kg^{-1} dw and 310 to 790 ng kg^{-1} dw in inland creeks (mean: 300 ng kg^{-1} dw), and estuarine area (mean: 530 ng kg^{-1} dw), respectively. In Nakdong watershed, particulate PFAAs was found at concentrations ranging from 130 to 400 ng kg^{-1} dw in artificial lakes, from 120 to 1100 ng kg^{-1} dw in inland creeks (mean: 540 ng kg^{-1} dw), and from 110 to 790 ng kg^{-1} dw in estuarine areas (mean: 380 ng kg^{-1} dw) (Table 1 and Fig. 2b).

3.2. Water quality parameters

Values of water quality parameters are shown in Table 1 and Fig. 3. Water quality parameters in the Youngsan River Estuary exhibited general characteristics of estuarine environments (Table 1). For example, salinity increased with distance seaward and SS, DOC, and POC also decreased (Fig. 3a). However, water of lesser-salinity spreads from inner to outer regions of the Nakdong River Estuary (Fig. 3b). In fact, during the sampling period (5 day) approximately 30 and 120 mm of rainfall was recorded in Mokpo City (Youngsan watershed) and Busan City (Nakdong watershed), respectively. Consequently, relatively large amounts of freshwater were discharged through the estuary dams. These events corresponded to approximately 20 and 380 million tons of freshwater discharge into the estuary through dams on the Youngsan and Nakdong rivers, respectively. Normal salinity conditions in both the Youngsan and Nakdong River Estuaries are ~0 in the inner region of the dam (e.g., YSA and NDB) and >20 in the outer region of the dam (e.g., YSE1 and NDE3) due to no and/or lesser amounts of freshwater discharge. However, salinity conditions were affected by heavy rainfall and large amounts of freshwater discharged during the sampling period (Table 1 and Fig. 3). Large

Table 1
Concentrations of dissolved and particulate PFAAs and water quality parameters from the Youngsan and Nakdong River Estuaries, South Korea.

Analysis		Youngsan River Estuary						Nakdong River Estuary					
		Artificial Lake ($n=3$)		Inland creek ($n=7$)		Estuarine area ($n=8$)		Artificial Lake ($n=2$)		Inland creek ($n=7$)		Estuarine area ($n=7$)	
		Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean
Water quality parameter	Temperature (°C)	15.9–18.8	17.7	15.6–19.9	18.1	15.4–17.0	16.4	18.4–18.7	18.6	14.8–18.7	16.2	16.8–20.2	18.3
	Salinity	0.33–3.3	2.2	0.24–8.0	1.7	5.5–28.89	19.4	0.12–0.34	0.23	0.12–1.9	0.79	0.17–8.6	2.9
	pH	7.8–8.0	7.9	7.4–8.2	7.7	6.3–7.7	7.4	7.0–7.1	7.1	7.2–7.9	7.6	8.4–8.5	8.5
	SS (mg L^{-1})	15–40	25	24–99	40	8.1–45	21	23–130	75	11–70	33	10–82	36
	DOC (mg L^{-1})	2.5–4.4	3.2	2.4–6.1	4.5	0.39–1.43	0.85	2.2–3.0	2.6	3.5–9.2	5.9	0.56–1.0	0.80
	POC (mg L^{-1})	0.53–0.91	0.78	0.84–3.2	1.8	0.24–0.60	0.35	1.5–1.9	1.7	0.47–8.5	3.0	0.27–0.79	0.51
Dissolved PFAAs (ng L^{-1})	PFBA	1.5–3.0	2.3	1.1–4.0	2.6	0.78–4.3	1.5	1.3–1.4	1.3	1.4–5.2	3.1	1.1–9.5	2.5
	PFPeA	0.78–3.0	1.8	0.85–5.7	3.4	0.41–3.2	1.1	0.98–2.3	1.6	2.0–8.4	4.4	0.73–5.1	2.6
	PFHxA	1.5–3.5	2.5	1.3–6.9	3.6	0.81–2.7	1.6	2.4–3.5	3.0	3.1–17	7.6	4.4–10	5.8
	PFHpA	7.0–110	65	1.6–8.3	4.5	2.4–9.3	4.4	3.3–5.7	4.5	4.7–21	11	4.5–34	9.8
	PFOA	4.1–7.1	5.2	2.6–10	6.2	1.3–3.6	2.4	11–12	11.4	8.9–28	16	11–23	15
	PFNA	1.4–1.9	1.7	0.62–3.2	1.7	0.45–2.1	1.2	4.6–5.2	4.9	2.5–12	6.7	3.6–7.7	4.9
	PFDA	0.53–1.6	0.94	0.59–2.4	1.2	0.17–0.63	0.38	1.8–2.3	2.1	1.1–9.6	3.4	2.7–4.9	3.5
	PFUnA	0.43–0.64	0.54	0.37–1.4	0.73	0.32–0.72	0.47	1.0–1.4	1.2	0.43–2.3	1.3	0.75–5.2	1.6
	PFDoA	0.56–0.76	0.63	0.31–0.80	0.59	0.10–0.92	0.32	0.39–0.45	0.42	0.65–1.7	1.1	0.24–2.8	0.80
	PFBS	3.4–5.1	4.3	2.1–8.6	4.5	1.0–4.6	2.0	1.3–2.1	1.7	3.7–12	7.4	2.1–15	5.1
	PFHxS	2.0–5.0	3.7	1.0–16	7.4	0.83–4.3	2.2	3.7–7.1	5.4	0.83–17	9.1	1.5–14	4.5
	PFOS	1.7–7.1	4.4	0.38–68	20	0.57–5.8	2.2	6.5–12	9.2	5.3–66	26	2.5–26	8.0
	PFDS	0.62–1.9	1.2	0.69–2.6	1.6	0.35–1.4	0.74	0.76–1.2	1.0	0.95–2.4	1.9	0.73–5.1	1.4
	Sum of PFAAs	32–140	94	23–130	58	12–34	20	44–52	48	45–190	99	42–160	65
Particulate PFAAs (ng kg^{-1} dw)	PFBA	16–37	28	7.0–36	21	32–110	54	6.4–26	16	8.5–67	32	12–57	31
	PFPeA	7.9–55	25	11–90	35	6.4–130	63	2.5–6.9	4.7	<DL–85	39	15–55	32
	PFHxA	18–45	34	11–42	26	16–80	43	4.9–32	18	7.7–63	28	7.0–75	30
	PFHpA	19–150	96	14–130	57	27–280	140	9.9–70	40	20–170	92	<DL–110	41
	PFOA	6.4–19	14	1.7–25	11	10–34	17	10–12	11	5.7–85	37	11–81	31
	PFNA	1.5–10	7.3	0.48–9.9	5.8	11–40	24	13–31	22	4.4–77	24	9.7–88	30
	PFDA	3.2–19	11	1.1–20	10	8.8–22	16	10–35	22	6.0–59	29	12–54	27
	PFUnA	4.9–16	12	2.1–12	7.3	5.5–28	16	3.1–12	7.8	4.0–36	16	4.6–29	14
	PFDoA	2.6–7.8	5.7	0.93–6.5	3.6	1.8–16	7.4	0.78–7.9	4.3	1.4–12	5.8	1.5–9.6	4.8
	PFBS	<DL–37	17	<DL–42	13	<DL–29	12	<DL	n	<DL–130	53	<DL–210	65
	PFHxS	<DL–127	57	<DL–63	24	<DL–77	34	37–55	46	2.3–160	53	5.9–74	29
	PFOS	13–43	24	13–360	77	20–140	72	23–98	61	17–350	110	<DL–90	27
	PFDS	8.6–25	19	5.5–24	14	8.4–46	28	4.4–18	11	7.9–35	20	4.6–56	20
	Sum of PFAAs	160–470	350	82–580	300	310–790	530	130–400	270	120–1100	540	110–790	380

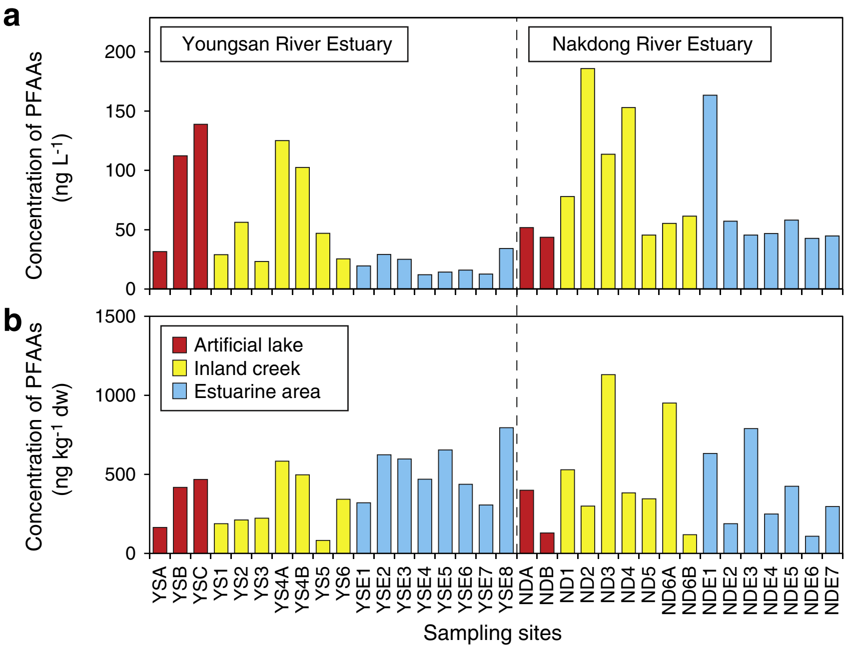

Fig. 2. Concentrations and distribution of (a) dissolved and (b) particulate PFAAs from the Youngsan and Nakdong watershed, South Korea.

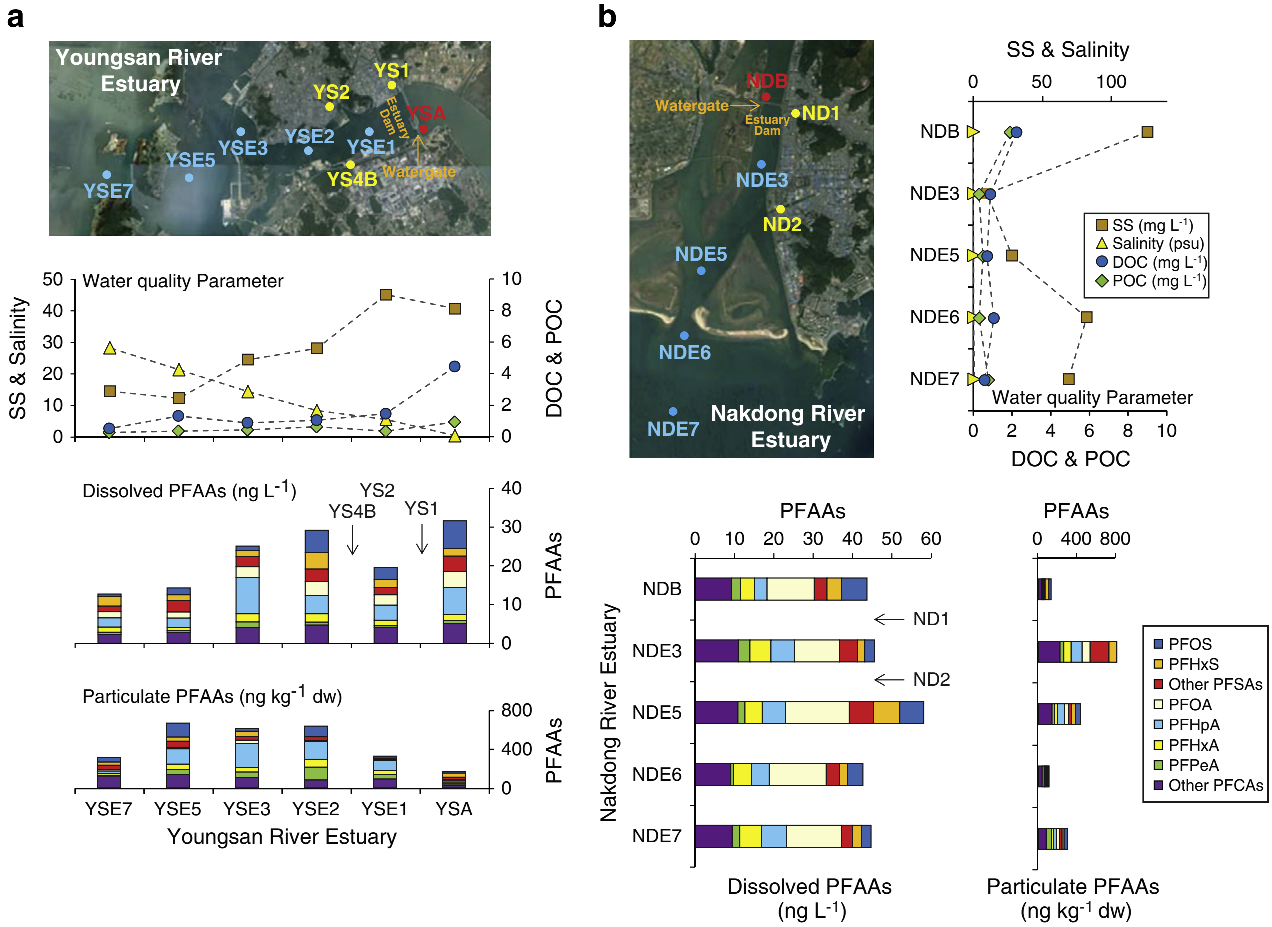

Fig. 3. Water quality parameters (SS, Salinity, DOC, and POC) and concentrations of dissolved and particulate PFAAs in water from selected sites based on predicted movements of water masses in the (a) Youngsan River Estuary and (b) Nakdong River Estuary. Pointing arrows indicate the locations of inflow from inland creeks to estuarine area. Concentration and composition of PFAAs in inland creeks are shown in Fig. 2 and Fig. S1.

amounts of contaminants such as PFAAs could be carried from the land to open coastal areas during rainy seasons.

4. Discussion

4.1. Distribution and potential sources of PFAAs

In the Youngsan watershed, greater concentrations of PFAAs were found in creeks (e.g., YS4A and YS4B), which have been developed as a National Industrial Complex (Daebul I.C.) manufacturing cement, pulp, and paper since 1996. Industrial activities at these sites seem to be the primary sources of PFAAs. However, greater concentrations of PFAAs occurred at two sites of artificial lakes such as YSB and YSC, for which there were no apparent sources and/or known activities. The occurrences of PFCs at these locations might be due to non-point sources such as surface runoff and/or carry-over effect from upstream to downstream regions (Kim et al., 2012). In the Nakdong watershed, greater concentrations of PFAAs were also detected in inland creeks such as sites ND2 and ND4. Site ND2 is located in the outfall of a WWTP that receives wastewater from dyeing, fabric, textile, and leather industrial complexes (Chop et al., 1999). Site ND4 is located near a small wood-processing company, which seems to be the potential source of PFAAs. Overall, concentrations of dissolved PFAAs were greater at inland sites and artificial lakes than in the estuarine areas of both the Youngsan and Nakdong watersheds. Some inland sites seemed to be affected by point and/or non-point sources from industrial activities and wastewater treatment plant outfall. It is indicated that PFAAs are mainly transported to estuarine areas via the inland waterways (creeks).

In South Korea, among various sources of PFAAs, WWTPs have been suggested to be major point sources to the aquatic environment, with about 1.6 ton of PFAAs discharged from this source annually (Kim et al., 2012). Relatively great concentrations of PFAAs were found in facilities treating mixtures of domestic and industrial wastewater which were originated from metal plating, textile/fabric, and paper-mill industries (Kim et al., 2012). Final effluents containing PFAAs seemed to be released into aquatic environments including lakes and rivers to estuarine and coastal environments. In 2010, the government of South Korea designated PFAAs as “restricted chemicals”, which restricts their use (Kim and Lee, 2010). However, because no suitable replacements have been developed, PFAAs are still used in some applications such as manufacturing of LCD, semi-conductor, pulp, paper, and fabric/clothing in South Korea. More monitoring study of the spatial and temporal distribution of PFAAs for protection of aquatic environments at industrial areas of South Korea is required.

4.2. Fate of PFAAs

In order to track the fate of waterborne PFAAs along the Youngsan and Nakdong River Estuaries, several locations including artificial lakes and estuarine areas were selected based on predicted movements of water masses in the lotic estuarine system (Fig. 3). In the Youngsan River Estuary, concentrations of dissolved PFAAs in water decreased from inner to outer regions, which is consistent with dilution due to dissipation during transportation of PFAAs in this region. Greater concentrations of PFAAs were found in water from locations YSE2 than YSE1, due to loadings of PFAAs from adjacent creeks such as YS2 and YS4B (Figs. 1a, 3a and Fig. S1). In the Nakdong River Estuary, a “hot spot” was observed at location ND2, which influenced concentrations at NDE5, which was a potential point source of PFAAs to the Nakdong River Estuary (Figs. 1b, 3b and Fig. S1). Meanwhile, in the Nakdong estuarine area, concentrations of dissolved PFAAs did not significantly decrease from inner to outer regions. This trend of spatial distribution of PFAAs between two estuaries was seemingly explained by the amount of precipitation during sampling periods and discharged freshwater through water gate.

Compositions of dissolved individual PFAAs in the Youngsan and Nakdong River Estuaries were investigated for tracking the fate of PFAAs (Fig. 3 and Fig. S1). In the Youngsan River Estuary, PFOS (~43%) was the most abundant PFAA at the “hot spot” creek, at location YS4B, followed by PFHxS (~15%) and PFOA (~9%). However, PFHpA (~22%) was the predominant PFAA in sites of the Youngsan River Estuary with the order of mean percent composition being: YSE1, YSE2, YSE3, YSE5, and YSE7, followed by PFHxS (~12%), PFOA (~12%), and PFOS (~11%). Also, in the Nakdong River Estuary, a relatively large proportion of PFOS (~36%) found in water from site ND2, followed by PFOA (~15%) and PFHxA (~8.9%). However, PFOA (~30%) and PFHpA (~12%) were the predominant PFAAs in estuaries with mean percent composition decreasing in the order of: NDE3, NDE5, NDE6, and NDE7 (Fig. S1). Patterns of relative contributions of PFAAs observed in this study were consistent with previous reports indicating that PFOS is rapidly removed from the water column to sediment (particles settle down) in estuarine area (Higgins and Luthy, 2006), whereas PFOA and PFHpA are more conservative in the water column (Cai et al., 2012).

Relative composition of PFAAs between the Youngsan and Nakdong River Estuaries were slightly different based on principal component analysis (Fig. S2). Such differences might be due to independent sources and/or different conditions along the salinity gradient. In general, the relative composition of PFAAs in waters from locations with known point sources, such as YS4B in Youngsan and ND2 in Nakdong watersheds did not vary significantly (Fig. S1). However, the salinity in the Youngsan River Estuary changed from 0.3 to 28, while that in the Nakdong River estuary ranged only between 0.1 and 0.7. This result suggested that salinity could be affecting the pattern of relative contribution and fate of waterborne PFAAs according to compound-specific partitioning behavior in certain estuarine environments (natural salinity gradient).

4.3. Field-based partition coefficient of PFAAs

There have been several factors reported to control adsorption of PFAAs onto suspended particles and/or sediments from both laboratory and field studies. Adsorption of PFAAs were generally greater with (i) greater salt concentration (e.g., NaCl, $CaCl_2$, and sea salt) of solution (Higgins and Luthy, 2006; Pan and You, 2010), (ii) decreasing pH of water (Higgins and Luthy, 2006), (iii) increasing organic carbon fractions of absorbents such as suspended particles and/or sediments (Ahrens et al., 2011b; You et al., 2010), and (iv) decreasing dissolved organic matter (DOM) concentrations of solution (Jeon et al., 2011).

In this study, correlations between values of water quality parameters such as temperature, pH, salinity, SS, DOC, POC, and f_{oc} and the field-based K_d values of PFAAs identified the major factor(s) controlling adsorption of PFAAs (Table S2). Salinity was significantly correlated with values of K_d for PFAAs in the Youngsan and Nakdong River Estuaries. Positive correlation of K_d values of long-chain ($C \geq 8$) PFCAs and PFSAs such as PFOA, PFNA, PFDA, PFUnA, PFDoA, PFOS, and PFDS with salinity was all relatively great ($r > 0.72$, $p < 0.01$). Salinity was more likely to affect adsorption of long-chain PFAAs than short-chain PFAAs. It is indicated that long-chain PFAAs can be removed more readily from the water column by adsorption onto suspended particles in estuarine environments due to the salting-out effect of increasing salinity (Jeon et al., 2010b; Pan and You, 2010). Adsorption of short-chain PFAAs ($C < 8$) could be less affected by salinity, but also controlled by other factors such as hydrophobicity and electrostatic interactions. Recently, C4-based perfluoroalkyl substances such as N-methyl perfluorobutane sulfonamidoethanol (MeFBSE) are increasingly used as replacement chemicals for the long-chain PFASs (Cai et al., 2012). Consequently, degradation products, such as PFBS have been frequently detected in coastal areas and they can potentially undergo long-range transportation via ocean currents (Cai et al., 2012; Yamashita et al., 2005). Thus, more

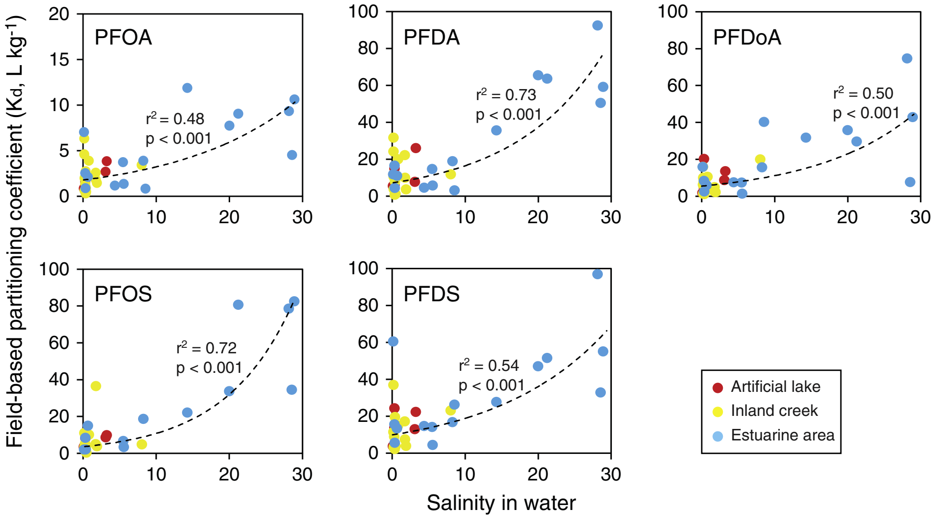

Fig. 4. Relationships (r^2) between salinity and water-particle partitioning coefficients (K_d) of selected PFAAs (PFOA, PFDA, PFDoA, PFOS, and PFDS) from artificial lakes, inland creeks, and estuarine areas of the Youngsan and Nakdong watershed, South Korea.

study of other factors controlling the fate and adsorption of short-chain PFAAs is needed. The pH and f_{oc} were not significantly correlated with values of K_d for PFAAs, which suggests that these parameters were not major factors controlling adsorption of PFAAs in the Youngsan and Nakdong River Estuarine system.

Partitioning of water and SS for PFAA was shown to be compound- and site-specific. The K_d values for long-chain PFAAs were exponentially increased with salinity in artificial lakes, inland creeks, and estuarine areas from the Youngsan and Nakdong watersheds (Fig. 4). An empirical relationship between K_d and number of carbon atoms was developed for PFAAs from samples collected from the Youngsan and Nakdong River Estuaries (Fig. 5). The observed range of field-based K_d values for PFAAs were generally greater with more carbon atoms from 8 to 12 and salinity from ~0 to 28.9. Affinity of adsorption of PFAAs to suspended particles is a function of both the physical–chemical properties of PFAAs as determined by the number of carbon atoms in the per-fluoro moiety as well as salinity. Values of K_d for PFCAs with ≥11 carbon atoms in the perfluorinated tail, such as PFUnA and PFDoA were less than those for PFDA at greater salinity. This might be due to the lesser affinity of adsorption of PFUnA and PFDoA, which exhibit greater hydrophobicity, due to their greater octanol-water partitioning coefficients (K_{ow}). Alternatively, incremental values of K_d for PFAAs as a function of increasing number of carbon atoms at lesser salinities was slightly weaker at greater salinities.

Field-based K_d values of long-chain PFAAs obtained from this study were compared to previous reports (Table 2 and Table S3). The operationally defined values of K_{oc} determined for PFAAs in this study were compound- and salinity-specific, which is consistent with the results of previous studies. Log K_{oc} values of PFOS were greater than those of PFOA, indicating that the K_{oc} value was strongly influenced by different sorption affinities according to the functional groups (sulfonates and carboxylate) (Ahrens et al., 2011b). Values of log K_d and log K_{oc} from estuarine and coastal areas (saltwater) were greater than those of lakes and rivers (freshwater). For example,

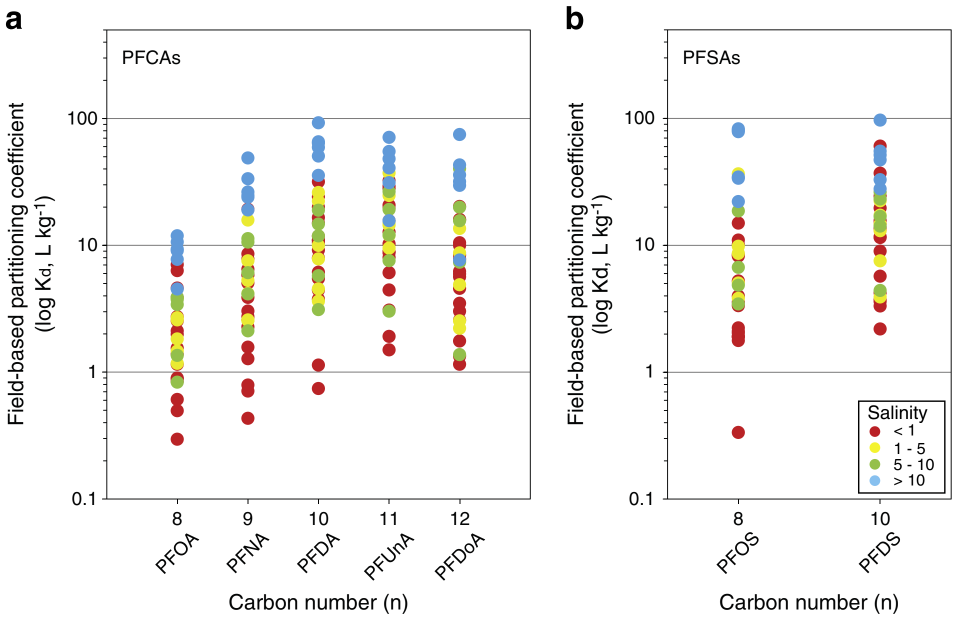

Fig. 5. Relationship between log K_d values and number of carbon chains for (a) PFCAs and (b) PFSAs along a salinity gradient.

Table 2
Log K_d and log K_{oc} for PFOA and PFOS obtained from the present study and compared with previous literatures.

Sampling regions (Country)	Field/Lab.[a]	Absorbent[b]	Salinity	n	PFOA		PFOS		References
					Log K_d (L kg^{-1})	Log K_{oc} (cm^3 g^{-1})	Log K_d (L kg^{-1})	Log K_{oc} (cm^3 g^{-1})	
Youngsan and Nakdong watershed (South Korea)	Field	Particles	0.12–0.82	17	0.21 ± 0.4	1.6 ± 0.6	0.53 ± 0.4	1.9 ± 0.7	This study
			1.8–4.4	6	0.32 ± 0.2	1.8 ± 0.3	0.95 ± 0.4	2.4 ± 0.6	
			5.5–8.6	5	0.35 ± 0.3	2.0 ± 0.5	0.83 ± 0.3	2.5 ± 0.5	
			14–29	6	0.93 ± 0.1	2.6 ± 0.3	1.7 ± 0.3	3.4 ± 0.3	
Seine River (France)	Field	Particles	ns[c]	16	–	–	3.1 ± 0.3[d] 2.9 ± 0.4[e]	4.0 ± 0.6[d] 3.8 ± 0.4[e]	Labadie and Chevreuil (2011b)
Tokyo Bay (Japan)	Field	Sediment	30–33	6	0.04 ± 0.03	1.9 ± 0.1	2.1 ± 0.1	3.8 ± 0.1	Ahrens et al. (2010)
Yangtze River Estuary (China)	Field	Sediment	0.18–3.31	4	–	–	3.2 ± 0.5	4.3 ± 0.5	Pan and You (2010)
Dianchi Lake (China)	Field	Sediment	ns	24	1.27 ± 0.40	2.63 ± 0.45			Zhang et al., 2012
				26			1.80 ± 0.29	3.35 ± 0.32	
Taihu Lake (China)	Field	Sediment	ns	22	–	2.28 ± 0.55	–	2.88 ± 0.62	Yang et al. (2011)
Rivers, lakes, and canals (The Netherland)	Field	Sediment	ns	19	1.83 ± 0.40	2.63 ± 0.34	2.35 ± 0.35	3.16 ± 0.28	Kwadijk et al. (2010)
Orge River (France)	Field	Sediment	ns	3	–	–	2.4 ± 0.2	3.7 ± 0.2	Labadie and Chevreuil (2011a)
Rivers and Tokyo Bay (Japan)	Lab.	Sediment	ns	6	–	2.4 ± 0.12	–	3.7 ± 0.56	Ahrens et al., 2011b
Dalian coast (China)	Lab.	Sediment	ns	5	–	–	1.4 ± 0.1	3.47 ± 0.07	Chen et al. (2012)
Riverine and lacustrine (USA)	Lab.	Sediment	ns	2	–	2.06	–		Higgins and Luthy (2006)
				4				2.57 ± 0.13	

[a] Field-derived or laboratory-derived partition coefficients.
[b] Suspended particles or sediment.
[c] ns = data not shown.
[d] Linear-PFOS.
[e] Branched-PFOS.

the value of log K_{oc} for PFOS was reported to be 2.88 cm^3 g^{-1} in the Taihu Rivers of China (Yang et al., 2011), while the value calculated from Tokyo Bay of Japan was 3.8 cm^3 g^{-1} from Yangtze River Estuary of China was 4.3 cm^3 g^{-1} (Ahrens et al., 2009b; Pan and You, 2010). Such differences in values of K_{oc} of PFOS between lakes and the open ocean might be due to differences in properties of sediments and water conditions (Yang et al., 2011). However, the discrepancy is most likely due to differences in salinity. In this study, the average log K_{oc} for PFOS observed for lesser salinities ($S = 1.8$ to 4.4) was 2.4 ± 0.6 cm^3 g^{-1}, while that observed at greater salinity ($S = 14$ to 29) was 3.4 ± 0.3 cm^3 g^{-1} (Table 2). Overall, different partition coefficients can be due to a variety of factors, including absorbent characteristics, field vs. laboratory-derived values, and salinity (Ahrens et al., 2011b).

4.4. Salting effect on adsorption of PFAAs

As discussed in the previous section, the existence of “salting-out” of PFAAs onto SS along a salinity gradient system was postulated. In order to represent the agents responsible for the observed K_d values in estuarine areas, the mathematical relationship between salinity and K_d values for long-chain PFAAs were further investigated by use of exponential models developed on previous reports (Jeon et al., 2010b; Turner and Rawling, 2001) (Eqs. (3) and (4)).

$$K_d{}^{sw} = K_d{}^{0} \times e^{k_{ads} S} \qquad (3)$$

$$k_{ads} = 0.0352\ \delta \qquad (4)$$

Where: K_d^{sw} and K_d^0 represent the partition coefficients (L kg^{-1}) in saline and freshwater, respectively. S is salinity and δ (L mol^{-1}) is an empirical salting constant and k_{ads} is a salting constant on a mass basis. Salting constants (δ, L mol^{-1}) for long-chain PFAAs from the Youngsan and Nakdong River Estuaries were calculated (Eqs. (3) and (4)). The effect of salinity on adsorption of PFAAs onto suspended particles was compared to those of other organic substances (Table 3). In previous reports, salting constants ranged from 0.091 to 0.480 L mol^{-1} for organochlorines, from 0.275 to 0.552 L mol^{-1} for polycyclic aromatic hydrocarbons (PAHs), and 1.08 L mol^{-1} for phthalates (Turner and Rawling, 2001). Salting constants for PFAAs have been estimated to range from 0.80 to 1.11 L mol^{-1} with the increase of salinity from 10 to 34 in laboratory experiment (between water and *Chlorella*) (Jeon et al., 2010b). However, salting constants of PFAAs from field-based K_d values obtained from present study were greater than those from laboratory-based K_d values, ranging from 1.34 to 2.57 L mol^{-1}. Differences in characteristics of solid phase between *Chlorella* and SS of field samples seemed to be the cause of the differences. Salting constants for longer-chain PFAAs were generally greater than those of other organic substances, which mean that adsorption affinities of long-chain PFAAs are significantly greater than other organic pollutants as a result of salinity changes in estuarine environment. These results show, to our knowledge for the first time, salt effect on sorption of PFAAs is greater than any other organic pollutants in estuarine environment. However, the empirical correlations are not very strong ($r^2 = 0.48$ to 0.73) which indicated that salinity cannot entirely explain the observed variation in K_d.

Mechanisms of adsorption of anionic PFAAs are probably different than those for neutral hydrophobic chemicals. Based on their pK_a values PFAAs are generally present as anions at environmentally relevant pH (Burns et al., 2008; US EPA, 2002). The effect of salinity adsorption of anionic PFCAs and PFSAs can be understood by the previous studies and/or explained by several theories. Some cations, such as Na^+ and K^+, present in sea salt act as ion-pairs for the PFSAs and PFCAs and thus change their partitioning properties. When ion-pairs are formed, hydrophobicity increases due to neutralization of charged moieties (Jeon et al., 2010b). Another possible explanation for salting effect on adsorption of PFAAs, is the presence of divalent cations, such

Table 3
Estimates of freshwater partitioning (K_d^0) and adsorption salting constants (δ) from this study and water-particle partition data reported in the previous. Study updated from previous literature (Turner and Rawling, 2001).

Compounds	Field/Lab.	Salinity range	SS range (mg L^{-1})	K_d^0 (L kg^{-1})	δ[a] (L mol^{-1})	r^2	References
PFAAs							
PFOA	Field	0.12–29	8.1–130	2.43	1.34	0.48	This study
PFNA				5.47	1.83	0.66	
PFDA				11.3	1.85	0.73	
PFUnA				12.2	1.53	0.65	
PFDoA				8.62	1.63	0.50	
PFOS				7.10	2.57	0.72	
PFDS				13.6	1.53	0.54	
PFOA	Lab.	10–34	500	751	0.86	0.93	Jeon et al., 2010b
PFDA				1006	0.94	0.99	
PFUnA				1640	1.11	0.99	
PFOS				1430	0.93	0.94	
Organochlorines							
2,2′,5,5′-tetrachloro biphenyl	Field	0.3–23.8	~200	60.2	0.480	0.52	Turner and Tyler, 1997
2,3,7,8-tetrachlorodibenzodioxin				243	0.366	0.60	
Endrin	Lab.	5–36	1000	0.860	0.341	0.94	González-Dávila et al., 1995
Heptachlor epoxide				0.790	0.091	0.98	
Polycyclic aromatic hydrocarbons							
Benzo(a)pyrene	Field	0–35	10,800	241	0.333	–	Hegeman et al., 1995
Phenanthrene				1.8	0.275	–	
Pyrene	Field	~0–32	~100,000	2.09–3.14	0.552	>0.88	Means, 1995
Phthalate							
Di(2-ethylhexyl)phthalate	Field	0.4–23.8	~250–300	49.9	1.08	0.75	Zhou and Rowland, 1997

[a] Salting constant was calculated using Eqs. (3) and (4) in the text.

as Ca^{2+}, Mg^{2+}, and Cu^{2+} that could form a bridge between the anionic organic matter functional groups, such as, carbonyl, phenolic, and hydroxyl and anionic PFAAs (Hyun and Lee, 2005; You et al., 2010). Therefore, complementary studies are needed to clarify influences of salt concentration and specific ion on adsorption characteristics of PFAAs.

5. Conclusion

The fate and partitioning of PFAAs in the Youngsan and Nakdong River Estuaries showed that salinity was the most important factor controlling the adsorption of PFAAs. Field-based partition coefficient (K_d) of longer-chain PFAAs ($C\geq8$) increased exponentially as a function of salinity, indicating that longer-chain PFAAs are largely scavenged by adsorption to suspended particles due to the salting-out effect. Alternatively, the K_d values of shorter-chain PFAAs ($C<8$) were less correlated with salinity, which suggested that they could be less affected by salinity, but rather controlled by other factors such as hydrophobicity and electrostatic interactions. Salting constants of PFAAs were notably greater than those of other neutral organic contaminants, which implied that adsorption affinities of long-chain PFAAs are significantly greater than those of other organic pollutants as a function of salinity. The results of the present study provide better understanding of in situ fate and transport of PFAAs in the boundary zone of salinity that can be used for developing the fate models of PFAAs.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.12.040.

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<Supplemental Materials>

In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea

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Table of Contents

Supplemental Materials: Tables

Supplemental Materials: Figures

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Supplemental Materials: Tables

Table S1. QA/QC data for dissolved and particulate PFAAs measured in the present study.

Analytes	Monitored Transitions	Retention time (min.)	Method detection limits (ng L^{-1}, ng kg^{-1}, $n = 7$)		Spike Recovery (%, $n = 5$)		Surrogate Recovery (%, $n = 33$)	
			Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate
PFBA	213 → 169	7.36	1.0	5	120 ± 10	68 ± 12		
PFPeA	263 → 219	13.63	0.2	1	78 ± 8.2	72 ± 15		
PFHxA	313 → 269	14.27	0.3	1	82 ± 5.7	72 ± 14		
PFHpA	363 → 319, 169	14.83	0.1	0.5	80 ± 8.4	75 ± 11		
PFOA	413 → 219, 169	15.00	0.2	1	92 ± 5.2	82 ± 12		
PFNA	463 → 419, 219	15.23	0.2	1	105 ± 4.2	87 ± 9.2		
PFDA	513 → 469, 269	15.42	0.3	2	92 ± 7.2	85 ± 7.3		
PFUnA	563 → 269, 219	15.69	0.2	1	81 ± 12	82 ± 8.2		
PFDoA	613 → 569, 169	15.75	0.1	0.5	75 ± 16	77 ± 9.8		
PFBS	299 → 99, 80	13.75	0.2	1	76 ± 14	66 ± 12		
PFHxS	399 → 99, 80	14.62	0.5	3	82 ± 9.9	77 ± 15		
PFOS	499 → 99, 80	15.22	0.1	0.5	95 ± 6.6	82 ± 17		
PFDS	599 → 99, 80	15.55	0.1	0.5	105 ± 14	75 ± 12		
PFBA-^{13}C	217 → 172	7.34					60 ± 21	74 ± 14
PFHxA-^{13}C	315 → 270	14.26					92 ± 21	99 ± 34
PFOA-^{13}C	417 → 372	14.97					75 ± 10	98 ± 23
PFNA-^{13}C	468 → 423	15.20					65 ± 10	108 ± 32
PFDA-^{13}C	515 → 470	15.40					79 ± 11	84 ± 25
PFUnA-^{13}C	565 → 520	15.66					69 ± 17	71 ± 27
PFDoA-^{13}C	615 → 570	15.73					52 ± 20	55 ± 15
PFHxS-^{18}O	403 → 103	14.60					107 ± 25	101 ± 24
PFOS-^{18}O	503 → 80	15.20					56 ± 22	87 ± 28

Table S2. Correlation coefficients (*r*) between water quality parameters and K_d values of individual PFAAs.

	Temperature	pH	Salinity	SS	DOC	POC	*f*oc
pH	0.23	1	-	-	-	-	-
Salinity	-0.42*	-0.13	1	-	-	-	-
SS	0.43*	-0.11	-0.39*	1	-	-	-
DOC	-0.03	-0.22	-0.51**	0.18	1	-	-
POC	0.10	-0.12	-0.38*	0.29	0.56**	1	-
f_{oc}	-0.05	-0.11	-0.30	-0.18	0.48**	0.78**	1
PFBA	-0.39*	-0.22	0.70**	-0.47**	-0.52**	-0.50**	-0.35*
PFPeA	-0.21	-0.35*	0.39*	-0.19	-0.38*	-0.33	-0.27
PFHxA	-0.13	-0.32	0.58**	-0.34*	-0.32	-0.38*	-0.28
PFHpA	-0.06	-0.31	0.37*	-0.25	-0.05	-0.25	-0.15
PFOA	-0.40*	-0.17	0.72**	-0.49**	-0.42*	-0.42*	-0.20
PFNA	-0.25	-0.15	0.83**	-0.38*	-0.47**	-0.41*	-0.29
PFDA	-0.48**	-0.19	0.86**	-0.46**	-0.38*	-0.38*	-0.18
PFUnA	-0.43**	-0.06	0.78**	-0.58**	-0.36*	-0.37*	-0.09
PFDoA	-0.37*	-0.06	0.74**	-0.44**	-0.48**	-0.37*	-0.25
PFBS	-0.10	0.32	0.03	-0.33	-0.15	-0.19	-0.02
PFHxS	-0.20	-0.03	0.44**	-0.29	-0.21	-0.31	-0.20
PFOS	-0.26	-0.15	0.84**	-0.29	-0.36*	-0.33	-0.27
PFDS	-0.39*	0.02	0.72**	-0.52**	-0.45**	-0.44**	-0.26

* $0.01 < p < 0.05$

** $p < 0.01$

Table S3. Log K_d and Log K_{oc} for selected PFCAs and PFSAs (longer-chain, C ≥ 8) obtained from the present study.

Chemicals	Log K_d (L kg^{-1}) Salinity				Log K_{oc} (cm^3 g^{-1}) Salinity			
	0 - 1 (*n* = 17)	1 - 5 (*n* = 6)	5 - 10 (*n* = 5)	10 - 30 (*n* = 6)	0 - 1 (*n* = 17)	1 - 5 (*n* = 6)	5 - 10 (*n* = 5)	10 - 30 (*n* = 6)
PFCAs								
PFOA	0.21 ± 0.39	0.32 ± 0.19	0.35 ± 0.30	0.93 ± 0.15	1.61 ± 0.57	1.79 ± 0.29	1.99 ± 0.52	2.60 ± 0.29
PFNA	0.48 ± 0.44	0.71 ± 0.30	0.76 ± 0.30	1.45 ± 0.14	1.88 ± 0.64	2.17 ± 0.46	2.40 ± 0.55	3.12 ± 0.26
PFDA	0.90 ± 0.43	0.98 ± 0.35	0.95 ± 0.32	1.77 ± 0.14	2.30 ± 0.60	2.44 ± 0.41	2.59 ± 0.54	3.44 ± 0.22
PFUnA	0.97 ± 0.40	1.23 ± 0.22	1.03 ± 0.37	1.59 ± 0.23	2.37 ± 0.53	2.69 ± 0.28	2.67 ± 0.47	3.26 ± 0.22
PFDoA	0.73 ± 0.38	0.73 ± 0.31	1.02 ± 0.56	1.49 ± 0.33	2.13 ± 0.53	2.20 ± 0.46	2.66 ± 0.62	3.16 ± 0.47
PFSAs								
PFOS	0.53 ± 0.41	0.95 ± 0.38	0.83 ± 0.32	1.69 ± 0.25	1.93 ± 0.66	2.36 ± 0.56	2.50 ± 0.53	3.36 ± 0.32
PFDS	1.01 ±0.40	1.06 ± 0.28	1.16 ± 0.31	1.68 ± 0.19	2.41 ± 0.60	2.52 ± 0.39	2.80 ± 0.44	3.35 ± 0.29

Supplemental Materials: Figures

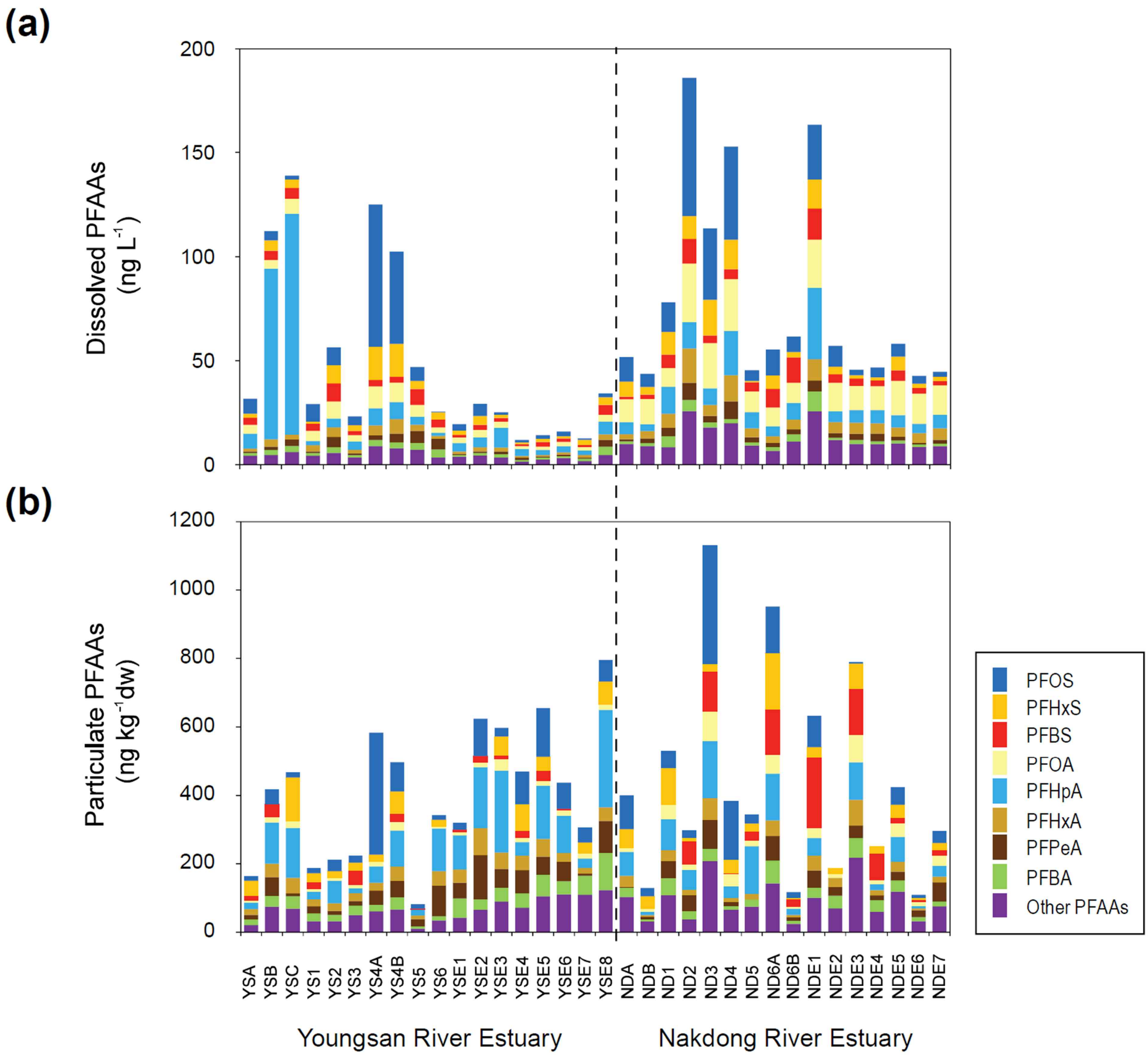
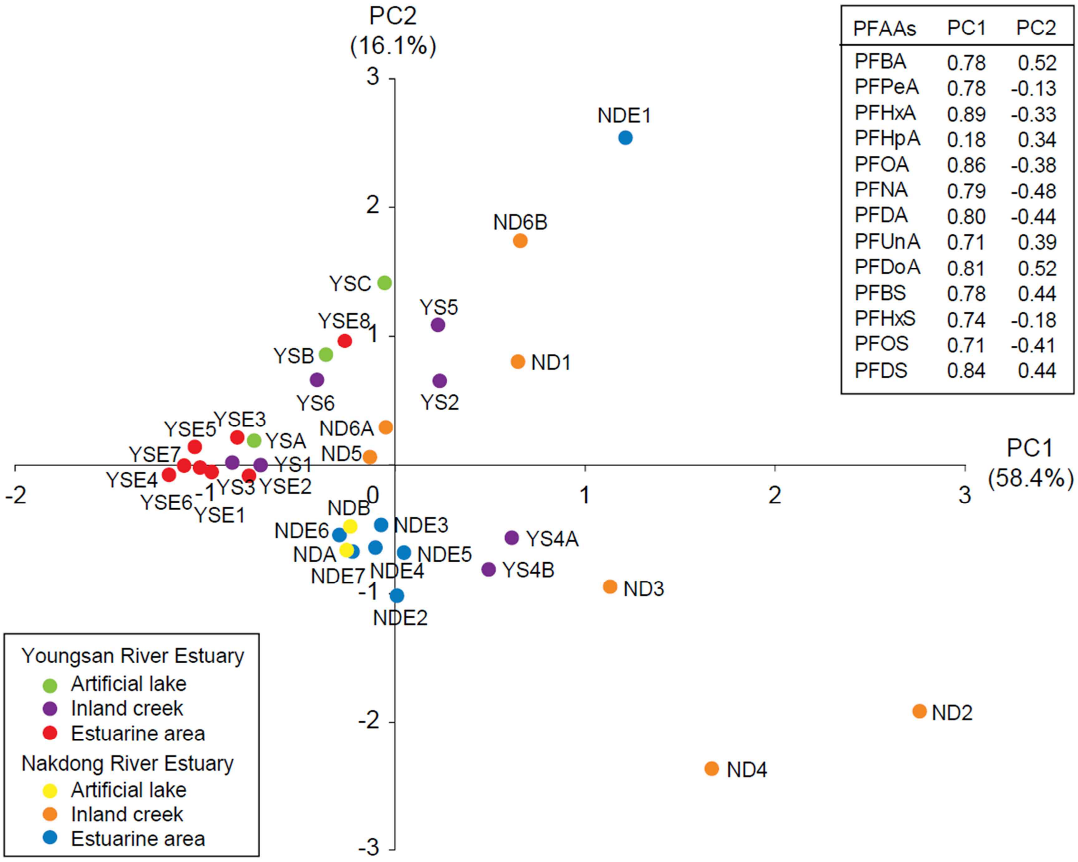


Fig. S1. Concentrations of individual PFAAs as (a) dissolved and (b) particulate phases in water samples from the Youngsan and Nakdong River Estuaries.



PFAAs	PC1	PC2
PFBA	0.78	0.52
PFPeA	0.78	-0.13
PFHxA	0.89	-0.33
PFHpA	0.18	0.34
PFOA	0.86	-0.38
PFNA	0.79	-0.48
PFDA	0.80	-0.44
PFUnA	0.71	0.39
PFDoA	0.81	0.52
PFBS	0.78	0.44
PFHxS	0.74	-0.18
PFOS	0.71	-0.41
PFDS	0.84	0.44

Fig. S2. Results of principal component analysis of individual PFAAs in waters (dissolved phase) collected from Youngsan and Nakdong River Estuaries.