



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.

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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 (PFSAAs) 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, $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_2$ -PFUnA, $^{13}\text{C}_2$ -PFDoA, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -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

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