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

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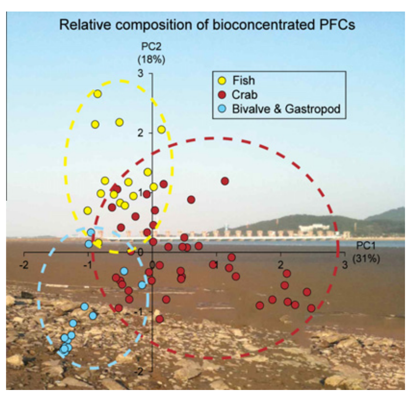
HIGHLIGHTS

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

GRAPHICAL ABSTRACT



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ABSTRACT

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

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

1. Introduction

Due to their widespread presence in both the environment and tissues of humans, perfluorinated compounds (PFCs) have garnered increasing worldwide attention since their detection in environmental samples in 2001 (Giesy and Kannan, 2001). Due to their amphiphilic nature, PFCs make excellent surfactants, and have been produced in relatively large quantities since the 1950s for a wide range of applications such as carpet coatings, food packaging, shampoos, paper, and fire-fighting foams (Paul et al., 2009). Some of these compounds are persistent in the environment, whereas others degrade to more environmentally stable compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which can make determining exposures and concentrations in organisms difficult (Dinglasan et al., 2004; Martin et al., 2010). While production of PFOS-based products was voluntarily halted in 2000 by North America's largest producer, the 3M company (3M, 2000), PFOS is still being produced in relatively large quantities in China (So et al., 2007; Ruisheng, 2008; Pan et al., 2010).

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

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

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

2. Materials and methods

2.1. Sampling and sample preparation

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

2.2. Target chemicals and pretreatment

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

2.3. Instrumental analysis

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