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Perfluorinated alkyl substances in water, sediment, plankton and fish from Korean rivers and lakes: A nationwide survey

Nguyen-Hoang Lam [a], Chon-Rae Cho [b], Jung-Sick Lee [a], Ho-Young Soh [a], Byoung-Cheun Lee [c], Jae-An Lee [c], Norihisa Tatarozako [d], Kazuaki Sasaki [e], Norimitsu Saito [e], Katsumi Iwabuchi [e], Kurunthachalam Kannan [f], Hyeon-Seo Cho [a,*]

[a] College of Fisheries and Ocean Sciences, Chonnam National University, Yeosu 550-749, Republic of Korea
[b] Korea Research Institute of Chemical Technology, Daejeon 305-600, Republic of Korea
[c] National Institute of Environmental Research, Incheon 404-408, Republic of Korea
[d] National Institute for Environmental Studies, Tsukuba, Ibaraki 305-8506, Japan
[e] Research Institute for Environmental Sciences and Public Health of Iwate Prefecture, Iwate 020-0852, Japan
[f] Wadsworth Center, New York State Department of Health, and School of Public Health, State University of New York at Albany, Empire State Plaza, PO Box 509, Albany, NY 12201-0509, USA

HIGHLIGHTS

- PFOS was found at greatest concentrations in water, sediment, plankton and fish.
- High concentrations of long chain PFCAs were found in sediment samples.
- Mean ratios of PFASs concentration in fish blood to liver were mostly >2.
- PFOS, PFUnA, PFDoA and PFDA accounted for 94–99% of ∑PFASs concentration in fish.
- Only PFOS and PFNA were concentrated in plankton samples.

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ABSTRACT

Water, sediment, plankton, and blood and liver tissues of crucian carp (*Carassius auratus*) and mandarin fish (*Siniperca scherzeri*) were collected from six major rivers and lakes in South Korea (including Namhan River, Bukhan River, Nakdong River, Nam River, Yeongsan River and Sangsa Lake) and analyzed for perfluorinated alkyl substances (PFASs). Perfluorooctane sulfonate (PFOS) was consistently detected at the greatest concentrations in all media surveyed with the maximum concentration in water of 15 ng L^{-1} and in biota of 234 ng mL^{-1} (fish blood). A general ascending order of PFAS concentration of water < sediment < plankton < crucian carp tissues < mandarin fish tissues was found. Except for the Nakdong River and Yeongsan River, the sum PFAS concentrations in water samples were below 10 ng L^{-1}. The PFOS and perfluorooctanoic acid (PFOA) concentrations in water did not exceed levels for acute and/or chronic effects in aquatic organisms. High concentrations of long chain perfluorocarboxylates (LCPFCAs) were found in sediment samples. PFOS, perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA) and perfluorodecanoic acid (PFDA) accounted for 94–99% of the total PFASs concentration in fish tissues. The mean ratios of PFAS concentration between fish blood and fish liver were above 2 suggesting higher levels in blood than in liver. Significant positive correlations ($r > 0.80$, $p < 0.001$) were observed between PFOS concentration in blood and liver tissues of both crucian carp and mandarin fish. This result suggests that blood can be used for non-lethal monitoring of PFOS in fish. Overall, the rank order of mean bioconcentration factors (BCFs) of PFOS in biota was; phytoplankton (196 L/kg) < zooplankton (3233 L/kg) < crucian carp liver (4567 L/kg) < crucian carp blood (11,167 L/kg) < mandarin liver (24,718 L/kg) < mandarin blood (73,612 L/kg).

1. Introduction

The unique properties such as resistance to hydrolysis, photolysis, bio-degradation and thermal stability, in combination with widespread application of perfluoroalkyl substances (PFASs), made them global pollutants in abiotic and biotic matrices including food stuffs (Picó et al., 2011), human blood (Kannan et al., 2004; Harada et al., 2010), breast milk (Llorca et al., 2010), wildlife such as fish, birds and marine mammals (Giesy and Kannan, 2001), sediment (Nakata et al., 2006), water (Yamashita et al., 2005) and atmosphere (Li et al., 2011). The worldwide distribution of PFASs was reported in urban and remote areas including

* Corresponding author. Tel.: +82 616597146; fax: +82 61 654 2975.
E-mail address: hscho@jnu.ac.kr (H.-S. Cho).

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deep oceanic water of up to 5000 m (Yamashita et al., 2005) and in polar bears from the Arctic Ocean (Giesy and Kannan, 2001).

Due to their persistence and bioaccumulation, some PFASs can elicit harmful effects in terrestrial and aquatic organisms (Lau et al., 2004). Perfluorooctane sulfonate (PFOS) also biomagnifies in wildlife at higher trophic levels in the food chain (Giesy and Kannan, 2001; Kannan et al., 2005). To humans, the major routes of PFAS exposures include diet (Tittlemier et al., 2007; Zhang et al., 2010), drinking water (Takagi et al., 2008; Nolan et al., 2010; Llorca et al., 2012) and indoor dust (Strynar and Lindstrom, 2008; Björklund et al., 2009).

Following the discovery of widespread global contamination by PFOS, the 3 M Company, a major producer of this compound, phased out its production in the USA from 2001 (Giesy and Kannan, 2001). Several other countries have put forward some regulations to ban or limit the use of PFASs; for example, in industrial and domestic products in Canada and European Union in 2006. PFOS and, its salts and perfluorooctane sulfonyl fluoride were listed on Annex B of The Stockholm Convention on persistent organic pollutants by the Fourth Conference of Parties in May 2009 (Kannan, 2011).

South Korea is a developed and industrialized country. PFASs have been used extensively in various industries including electronic and textile industries in South Korea. The concentrations of PFASs in surface water from certain industrial areas in South Korea are the highest among several Asian countries as well as globally (Rostkowski et al., 2006; Cho et al., 2010). Previous studies have also reported high accumulation of PFASs in human blood (Kannan et al., 2004; Harada et al., 2010; Ji et al., 2012), birds (Kannan et al., 2002a; Yoo et al., 2008), minke whales and common dolphins (Moon et al., 2010), Asian periwinkles and rockfish (Naile et al., 2010) and coastal and ocean waters from Korea (So et al., 2004; Yamashita et al., 2005; Rostkowski et al., 2006; Naile et al., 2010). Despite this, available studies on PFASs in Korean freshwater ecosystems such as lakes or rivers are limited. Here, we carried out a systematic study during 2010 to 2012 to determine the current status and extent of PFAS concentrations in both abiotic and biotic matrices in six major rivers and lakes in Korea. Rivers and lakes were surveyed along a spatial gradient representing upstream and downstream locations to identify sources of pollution. Accumulation in tissues (blood and liver) of various freshwater aquatic organisms was investigated.

2. Materials and methods

2.1. Chemicals and reagents

MPFAC-MXA, a mixture of 9 surrogate standards containing $^{13}C_4$-PFOS (sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octane sulfonate), and $^{13}C_4$-PFOA (Perfluoro-n-[1,2,3,4-$^{13}C_4$]) octanoic acid were purchased with PFAC-MXB, a mixture of 17 native perfluorocarboxylate acids (PFCAs) and perfluoroalkyl sulfonates from Wellington Laboratories (Guelph, ON, Canada). $^{13}C_4$-PFOS was used as a surrogate for the perfluoroalkyl sulfonates and $^{13}C_4$-PFOA was used as a surrogate for the PFCAs. PFAC-MXB mixture was used for standard calibration at concentrations ranging from 0.1 to 50 ng/mL. High performance liquid chromatography (HPLC) grade reagents including methanol (Kanto Chemical, Tokyo, Japan), water (J.T Baker, USA) and ammonium acetate (Junsei, Japan) were used. Milli-Q water was prepared by a Barnstead Nanopure Infinity ™ water purification system (Thermo Scientific, USA).

2.2. Sample collection

Samples of water, sediment, plankton, and blood and liver tissues of an omnivorous fish species (crucian carp) and a carnivorous fish species (mandarin fish) were collected from 17 sampling sites in six major rivers and lakes in South Korea including Bukhan, Namhan, Nakdong, Nam, Yeongsan Rivers and Sangsa Lake (Fig. 1). The Nakdong River, Yeongsan

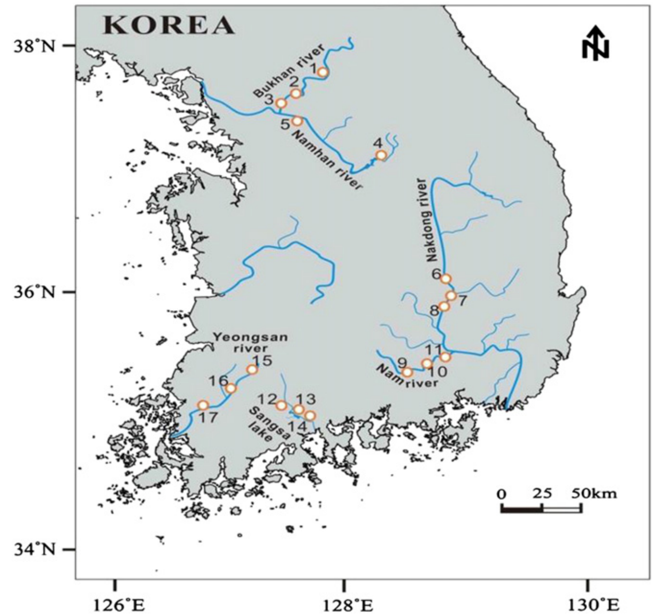

Fig. 1. Map showing 17 sampling sites located in six major rivers and lakes from South Korea.

River and Han River are three of four largest river basins in South Korea and play an important role as a water resource for agriculture, industry, recreational and drinking water for millions of people living in metropolitan cities of Seoul, Daegu, Busan and Gwangju. The Bukhan and Namhan Rivers are two major tributaries of the Han River. The Nakdong River, and its main tributary, Nam River are located in the southeastern region; the Yeongsan River and Sangsa Lake are located in the southwestern region and the Namhan and Bukhan Rivers are located in the northeastern region of the Korean peninsula. The sampling areas were divided generally into 3 groups as highly industrialized areas (Yeongsan River and Nakdong River), moderately industrialized areas (Namhan River and Nam River) and less industrialized areas (Sangsa Lake and Bukhan River). In order to survey the effects of discharge of waste water treatment plant (WWTP) effluents on PFASs concentration in surface water samples, the sampling sites 7 and 13 were from downstream of industrial waste water treatment plants (I-WWTP) in Daegu metropolitan city (treatment capacity of 520,000 ton/day) and in Haman town (treatment capacity of 3400 ton/day), respectively; the sampling sites 16 and 13 were located downstream of domestic waste water treatment plants (D-WWTP) in Gwangju metropolitan city (treatment capacity of 600,000 ton/day) and in Seungju town (capacity of 2500 ton/day), respectively. Because the sampling sites were selected to represent Korea, and involved various levels of industrialization, the results of this study represent PFAS concentrations in freshwater ecosystems in Korea.

One liter clean polypropylene (PP) bottles pre-rinsed with Milli-Q water, methanol and water from a specific sampling site were sunk to collect surface waters. Surface layer (1–5 cm) of sediment samples was collected using a clean, methanol rinsed PP spatula and stored in pre-cleaned 50 mL PP tubes. Phytoplankton, micro-zooplankton and meso-zooplankton samples were collected vertically by using NORPAC® plankton net with 3 mesh sizes of 20, 60, 200 μm, respectively. Depending on the depth of water column and topography of fishing sites, fish samples were collected by drift gill net, cast net or fish and hook. Fresh blood and liver tissues were obtained from fish. Sexes, body weight, body length, hepatosomatic index (HSI) and gonadosomatic index (GSI) of fishes were also determined. Water and sediment samples were transported on ice, to the laboratory, and keep at 4 °C until extraction. Biota samples were stored in dry ice immediately after collection in the field and kept at −20 °C in the laboratory until extraction.