Marine Pollution Bulletin 128 (2018) 287–294

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Historical trends of perfluoroalkyl substances (PFASs) in dated sediments from semi-enclosed bays of Korea

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ARTICLE INFO

Keywords:
Pollution history
PFOS
Inventory
Flux
Sediment core

ABSTRACT

Information is scarce on historical trends of perfluoroalkyl substances (PFASs) in the coastal environment. In this study, four sediment cores were collected from semi-enclosed bays of Korea to investigate the pollution history, contamination profiles, and environmental burden of PFASs. The total PFAS concentrations in sediment cores ranged from 6.61 to 821 pg/g dry weight. The highest concentrations of PFASs were found in surface or subsurface sediments, indicating on-going contamination by PFASs. Historical trends in PFASs showed a clear increase since the 1980s, which was consistent with the global PFAS consumption pattern. Concentrations of PFASs were dependent on the organic carbon content in sediment cores. PFOS and longer-chain PFASs were predominant in all of the sediment cores. In particular, a large proportion of longer-chain PFASs was observed in the upper layers of the sediment cores from industrialized coastal regions. Inventories and fluxes estimated for PFASs were similar to those for PCDD/Fs.

1. Introduction

Perfluoroalkyl substances (PFASs) are synthetic hydrocarbon based chemicals, in which hydrogen atoms are replaced by fluorine atoms. Due to the simultaneous repellence of water and oil, PFASs have been widely used as various industrial and commercial products such as fire retardants, textiles, and surfactants, for 60 years (Paul et al., 2009). Since the global distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) has been reported in wildlife species (Giesy and Kannan, 2001), many studies have confirmed the widespread contamination of PFASs in multiple environmental compartments as well as humans (Kannan et al., 2001; Saito et al., 2004; Higgins et al., 2005; Yamashita et al., 2005; Moon et al., 2010; Lee et al., 2018). Several toxicological studies have reported that PFOS and PFOA cause adverse health effects such as immunotoxicity, hepatotoxicity, and developmental toxicity, in laboratory animals and humans (Lau et al., 2007; Abbott, 2009; Hu and Hu, 2009). Based on their persistence, bioaccumulation, and long-range transport potentials, PFOS and its salts and perfluorooctyl sulfonyl fluoride (PFOSF) have been nominated as persistent organic pollutants (POPs) under the Stockholm Convention by the United Nations Environmental Programme (UNEP) since 2009 (UNEP, 2010).

3 M, the primary manufacturing company of PFASs, voluntarily phased out perfluorooctanesulfonyl fluoride (POSF)-based products in 2000 (Giesy and Kannan, 2001). The United States Environmental Protection Agency (US EPA) and several companies launched the stewardship program to reduce 95% of emissions and residual levels of PFOA and longer-chain PFASs by 2010, which was then extended to reduce 99% of PFASs by 2015 (Land et al., 2015). Following the global regulation of PFASs, the Korean government has also designated perfluoroalkyl acids (PFAAs) as restricted chemicals in order to eliminate PFASs from natural environments since 2010 (NIER, 2015). However, PFOS and PFOA have been replaced by shorter- or longer-chain PFASs with a growing demand for PFASs (Ahrens et al., 2009; Land et al., 2015; Wang et al., 2017). In addition, the major production of POSF-based chemicals has shifted from North America and Europe to China and other Asian countries (Cai et al., 2012).

Long-term trend studies on legacy POPs (e.g., PCBs) have been extensively conducted using environmental and biological matrices from different regions of world (Loganathan and Lam, 2012). These studies were valuable in understanding the past, present and future trends of persistent contaminants and help to make informed decisions to reduce exposure and to protect the health of wildlife and human (Loganathan, 2016; Loganathan et al., 2016). Coastal sediment is acted as an environmental medium to represent the contamination status and potential sources of persistent contaminants including PFASs (Ahrens et al., 2009; Naile et al., 2013). Moreover, sediment cores have been utilized to reconstruct the pollution history on persistent contaminants

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https://doi.org/10.1016/j.marpolbul.2018.01.039
Received 24 October 2017; Received in revised form 16 January 2018; Accepted 18 January 2018
Available online 06 February 2018
0025-326X/

in aquatic environments such as rivers, lakes, and oceans throughout the world (Alexander et al., 1999; Ahrens et al., 2009; Moon et al., 2009; Sadi and Loganathan, 2012). The chemical pollution history is essential piece of information to understand the current status of contamination and effectiveness of the regulation, and to predict future trends of persistent contaminants. Despite this, few studies are available on PFASs in sediments from the coastal waters of Korea (Naile et al., 2010, 2013). Moreover, limited studies have been conducted on historical trends in PFASs in aquatic environments worldwide (Ahrens et al., 2009; Zushi et al., 2010; Szalinska et al., 2011; Falandysz et al., 2012; Myers et al., 2012; Yeung et al., 2013; Codling et al., 2014). Most of these studies were reported for the Great Lakes of North America. The objectives of this study were to assess historical trends, contamination profiles, inventories, and fluxes in PFASs in dated sediment cores collected from semi-enclosed bays of Korea. This is the first report on historical PFAS trends in the coastal environment surrounding Korea.

2. Materials and methods

2.1. Sampling site, sample collection and sediment dating

Jinhae Bay, located in the southern part of Korea, is a representative semi-enclosed bay. It contains several small bays including Masan, Haengam, Gohyeon, and Jindong Bays, which are surrounded by industrial complexes, small- and middle-sized harbors, shipyards, and aquaculture farms. Several studies have reported severe contamination by many POPs, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) in these bays (Moon et al., 2007, 2008; Hong et al., 2010; Jin et al., 2016).

Sediment cores were collected from Masan Bay (Core 1), Haengam Bay (Core 2), Gohyeon Bay (Core 3), and Jindong Bay (Core 4) during October 2011 (Fig. 1). The sediment cores were obtained by scuba divers using acryl tubes (length 150 cm, internal diameter 11.3 cm). The length of each sediment core was 67.5, 62.5, 52.5, and 77.5 cm for Masan, Haengam, Gohyeon, and Jindong Bays, respectively. The cores were immediately sliced at 2 cm intervals up to 30 cm and the remaining portions were sliced at 5 cm intervals using stainless steel plates. The individual sectioned sediments were wrapped in aluminum foil which was pre-washed with methanol. The samples were transported to the laboratory and refrigerated at –20 °C until further analysis.

In order to measure the sedimentation rate of each sediment core, the radioisotope activities of ^{210}Pb and ^{226}Ra were measured with a well-type HPGe gamma detector (GCW3523, Canberra Industries Inc., Meriden, CT, USA) at the Korea Basic Science Institute (KBSI) located in Daejeon, Korea. The calculated sedimentation rates were 1.83, 1.05, 0.58, and 1.21 cm/year for the Masan, Haengam, Gohyeon, and Jindong Bays, respectively. The sedimentation rates measured in our study were similar to those reported for these bays from previous studies (Moon et al., 2009; Hong et al., 2010). The higher sedimentation rate for Masan Bay than that of the other bays was due to intensive industrial activities and slow water exchange (Moon et al., 2008; Jin et al., 2016).

2.2. Experimental procedures

The detailed experimental procedure for analyzing PFASs in sediment was similar to those described previously with minor modifications (Falandysz et al., 2012; Jin et al., 2016). The sediment samples (~5 g) were extracted by mechanical shaking (250 rpm) and sonicated with methanol (MeOH; HPLC grade, J.T. Baker, Center Valley, PA, USA), after spiking with mass-labeled internal standards ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHS, and $^{13}C_4$-PFOS; MPFAC-MXA, Wellington Laboratories, Guelph, ON, Canada) into the samples. The extracted samples were centrifuged at 3000 rpm and the supernatant was transferred into a polypropylene tube. This procedure was repeated twice, and all of the extracts were

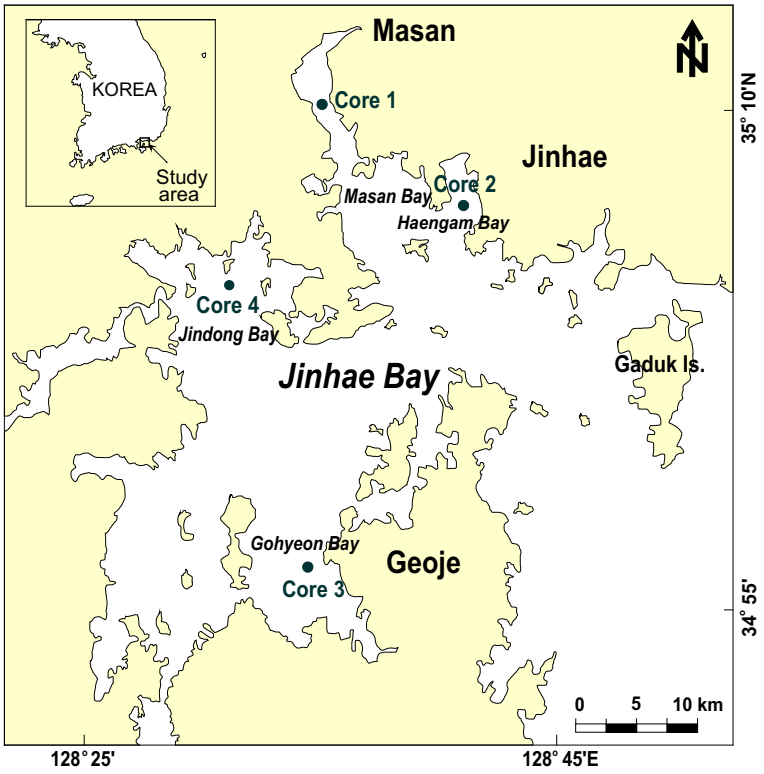

Fig. 1. Map showing the sampling locations of sediment cores from semi-enclosed bays in Korea. Core 1 (Masan Bay), Core 2 (Haengam Bay), Core 3 (Gohyeon Bay), and Core 4 (Jindong Bay).