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Perfluoroalkyl and polyfluoroalkyl substances in sediments from South Bohai coastal watersheds, China

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ABSTRACT

This study investigated the concentrations and distribution of Perfluoroalkyl and polyfluoroalkyl substances (PFAS) in sediments of 12 rivers from South Bohai coastal watersheds. The highest concentrations of ΣPFAS (31.920 ng g^{-1} dw) and PFOA (29.021 ng g^{-1} dw) were found in sediments from the Xiaoqing River, which was indicative of local point sources in this region. As for other rivers, concentrations of ΣPFAS ranged from 0.218 to 1.583 ng g^{-1} dw were found in the coastal sediments and from 0.167 to 1.953 ng g^{-1} dw in the riverine sediments. Predominant PFAS from coastal and riverine areas were PFOA and PFBS, with percentages of 30% and 35%, respectively. Partitioning analysis showed the concentrations of PFNA, PFDA and PFHxS were significantly correlated with organic carbon. The results of a preliminary environmental hazard assessment showed that PFOS posed the highest hazard in the Mi River, while PFOA posed a relative higher hazard in the Xiaoqing River.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) such as perfluorocarboxylates (PFCAs) and perfluoroalkanesulfonates (PFSAs), which have been produced for more than 50 years, have emerged as a new class of global environmental pollutants since they were first reported to be widespread in the environment (Giesy and Kannan, 2001, 2002; 3M Company, 1999). The unique physicochemical properties of PFAS, such as high surface activity, thermal stability, amphiphilicity, resistance to acidic and alkaline conditions and weak intermolecular interactions, make them popular in many industrial applications (e.g., fire-fighting foams, photolithography, and pesticides) and consumer applications (e.g., shampoos, surface coatings for carpets, stain repellents for furniture, and paper products) (Kissa, 2001; Giesy and Kannan, 2001; Higgins et al., 2005; Paul et al., 2008). PFAS can be released into the environment through their production and usage. The strong C–F bond of PFAS makes them extremely resistant to hydrolysis, thermal, microbiological and photolytical degradation (Wang et al., 2009). PFAS are ubiquitous in river water, oceans, sediment, soil, and tissues of wildlife and humans (Ahrens et al., 2010a; Higgins et al., 2005;Wang et al., 2013; Giesy and Kannan, 2001; Bao et al., 2010a; Kannan et al., 2001, 2002a,b). They are potentially harmful to fresh water and marine mammals (Ishibashi et al., 2008) and have potential adverse effects in wildlife species (Hoff et al., 2005; Fair et al., 2012; Beach et al., 2005; Newsted et al., 2005, 2008; Giesy et al., 2009).

Sediment is an important sink and reservoir of persistent organic pollutants and has a large impact on their distribution, transportation, and fate in the aquatic environment (Ahrens et al., 2009; Yang et al., 2011). Some researchers reported that the only environmental sink for perfluorooctanoate (PFO, refers to PFOA & PFOS) was sediment burial and transport to the deep oceans (Prevedouros et al., 2006). The distribution of PFAS between water and sediment is considered as an important process which controls their transport and fate (Prevedouros et al., 2006; You et al., 2010). Sediment–water distribution is a complex process, depending not only on the physicochemical characteristics of the compounds but also on the sediment nature such as the organic carbon fraction (f_{oc}) (Ahrens et al., 2010b; Zhao et al., 2012). Sorption of PFAS on sediment has been studied under laboratory conditions (Higgins and Luthy, 2006), but there are few field studies focused on partitioning behavior of PFAS in aquatic environments (Ahrens et al., 2009; Zhang et al., 2012; Zhao et al., 2013). Results of studies under laboratory conditions and those observed in the field can be different (Hong et al., 2013). To gain better understanding on the fate of PFAS in the whole environment, more information of field study is necessary on partitioning behavior of PFAS.

The Bohai Sea region in north China is an area where industry has been developing rapidly during the past few decades. The Bohai Sea, a semi-enclosed coastal water body with almost 40 rivers flowing directly into it, receives enormous amounts of

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contaminants through discharge of river water and sediment. The Bohai Sea region is currently one of the most polluted areas in China due to the industrial and agricultural activities (Hu et al., 2010; Luo et al., 2010; Naile et al., 2010; Zhao et al., 2013). Occurrence, spatial distribution, source and fate of PFAS in different matrices in estuarine and coastal areas of North Bohai Sea had been studied previously (Wang et al., 2011). Results of another study in the coastal area of Liao Dong Bay revealed that direct emission from industry parks was a major source of PFAS in soil (Wang et al., 2013). However, there are limited reports about PFAS in the southern part of the coast of the Bohai Sea compared with the northern part. Concentrations and distribution of PFAS in surface sediments from Laizhou Bay and its adjacent rivers have been measured and from that it was learned that concentrations of PFOA were extremely high in that area and might pose a potential threat for the benthic organisms (Zhao et al., 2013).

Currently, there is limited information about PFAS in sediments of coastal rivers along the South Bohai coast. The present study, launched in 2008, was conducted as a systematic investigation to trace sources and fates of toxic substances in various environmental media from adjacent riverine and estuarine areas including the Yellow and Bohai Seas of China. The specific objectives of this study were to: (1) determine concentrations and spatial distribution of PFAS in sediments from coastal rivers along the south coast of the Bohai Sea; (2) identify potential sources of PFAS; and (3) conduct a screening-level ecological hazard assessment for PFAS in local aquatic ecosystems. The results of the study provide information and support for future determinations of status and trends of PFAS emissions and their management at regional and national levels.

2. Materials and methods

2.1. Standards and reagents

17 kinds of PFAS standards, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), potassium perfluorooctanesulfonate (PFOS), sodium perfluorodecanesulfonate (PFDS), and 5 mass-labeled internal standards, including PFBA [1,2,3,4 ^{13}C], PFOA [1,2,3,4 ^{13}C], PFDoA [1,2 ^{13}C], PFHxS [1,2 ^{18}O] and PFOS [1,2,3,4 ^{13}C], were obtained from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). The mixed standards were prepared in 100% methanol and stored at 4 °C. HPLC grade methanol, acetonitrile and methyl *tert*-butyl ether (MTBE) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate, anhydrous sodium sulfate and tetrabutylammonium hydrogensulfate (TBAHS) were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Milli-Q water was obtained from a Milli-Q synthesis A10 (Millipore, Bedford, MA, USA) and used throughout the experiment.

2.2. Sediment sampling

A total of 36 surface (top 1–5 cm) samples of sediment were collected from 12 typical coastal rivers, which flow into the Bohai Sea through Shandong and Hebei Provinces (Fig. 1). For each river, at least 2 sites were chosen with the first one near the coast and the other a distance of 20–30 km from the former. All surface samples were collected in September 2011 by use of a clean, stainless steel trowel, and placed in clean 250 mL, largemouth, and polypropylene (PP) bottles. Wet sediments were immediately transported to the laboratory in ice-cooled boxes and then dried in a FreeZone 2.5 Liter Benchtop Freeze Dry System (LABCONCO, Kansas City, MO), ground and homogenized with a silica mortar and pestle, sieved through a 2-mm mesh, and stored in pre-cleaned glass jars in room temperature until further analysis.

2.3. Sample extraction and instrumental analysis

Detection of PFAS: Sediments were extracted according to a previously published method with minor modifications and optimizations (Naile et al., 2010; Wang et al., 2013). Briefly, a 50 ml polypropylene centrifuge tube was charged with 2.5 g homogenized sediments, which were soaked with 2 mL Milli-Q water and vortexed until the samples were visually homogenized. A 1 mL portion of 0.5 M tetrabutylammonium hydrogensulfate (TBAHS) and 2 mL of 25 mM sodium acetate were added, and spiked with 10 ng mass-labeled internal standards with vortexing. Subsequently, 5 mL of methyl *tert*-butyl ether (MTBE) was added and the mixture was extracted 20 min by vibration and then centrifuged at 3500 rpm for 30 min. This process of extraction with MTBE was repeated three times and the upper MTBE fraction was combined together into a 15 mL PP tube. The eluate was then evaporated to dryness under a gentle flow of high purity nitrogen, and reconstituted in 1 mL methanol, then filtered through a 0.2 mm nylon filter, transferred into a 1.5 mL PP snap top brown glass vial with polyethylene (PE) septa for HPLC analysis. The instrumental analysis was performed using a high performance liquid chromatography–negative electrospray ionization–tandem mass spectrometry system (HPLC–ESI–MS/MS) that consisted of an Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA). The instrument conditions are listed in Table S1.

Detection of organic carbon fraction (f_{oc}): The procedure used is based on a wet digestion method without heating followed by colorimetric determination (Chatterjee et al., 2009; Da Silva Dias et al., 2012). Briefly, a 0.5 g sediment sample was placed in a 100 mL Erlenmeyer flask, then 10 mL of potassium dichromate solution (0.667 mol L^{-1}) and 10 mL of sulfuric acid were added. Flasks were swirled for 5 min to homogenize the mixture. After reacting for 20 min and standing for 1 h to cool, 10 mL Milli-Q water was added to the flasks. After standing overnight (12 h), 15 mL supernatant solution was taken out and diluted to 50 mL by adding Milli-Q water. Then the solution was measured by a UV spectrophotometer under the light transmittance at 590-nm wavelength.

2.4. Quality assurance and quality control

All fluorinated materials that could come into contact with the samples during sampling and extraction were removed to avoid contaminations. Nine-point external standard curves ranging from 0.01 to 100 ng mL^{-1} were prepared for the quantification of individual PFAS with coefficients of determination (r^2) for all the target analytes higher than 0.99. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the peak of analyte required to yield a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. Recoveries of internal standards spiked into sediments ranged from 73% to 119%. Concentrations of PFAS were not corrected for recoveries. Procedure blanks using anhydrous sodium sulfate as alternative of sediment were conducted with every sample set and solvent blanks using 100% methanol were run every 4–5 samples to check for carryover and background contamination. No detectable PFAS were observed over LOQ in all the procedure and

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