Occurrence and transport of 17 perfluoroalkyl acids in 12 coastal rivers in south Bohai coastal region of China with concentrated fluoropolymer facilities

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ABSTRACT

Perfluoroalkyl acids (PFAAs) are emerging contaminants that have raised great concern in recent years. While PFAAs manufacturing becomes regulated in developed countries, production has been partly shifted to China. Eight fluoropolymer manufacturing facilities located in the South Bohai coastal region, one of the most populated areas of China, have been used to manufacture PFAA-related substances since 2001. The environmental consequence of the intensive production of PFAAs in this region remains largely unknown. We analyzed 17 PFAAs in twelve coastal rivers of this region, and found staggeringly high concentrations of perfluorooctanoic acid (PFOA) ranging from 0.96 to 4534.41 ng/L. The highest concentration was observed in the Xiaoqing River which received effluents from certain fluoropolymer facilities. Principal component analysis indicated similar sources of several perfluoroalkyl carboxylic acids (PFCAs) in all rivers, which indicated that atmospheric transport, wastewater treatment and surface runoff also acted as important supplements to direct discharge to surface water.

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1. Introduction

Perfluoroalkyl acids (PFAAs) have unique properties including surface activity, repellency of water and oil, and resistance of acid and heat (Giesy and Kannan, 2002). In industry, they are widely used in manufacturing processes and products (Giesy et al., 2006), but when dispersed into the environment, they can transport over long distances and accumulate to toxic concentrations, due to their persistence (Giesy et al., 2010). Ionic PFAAs, mostly known as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), are relatively soluble compared to many of the organochlorine compounds with similar molecular size such as DDT and Hexachlorocyclohexane. Thus, water is the primary reservoir of PFAAs and the major medium for their transportation (Prevedouros et al., 2005).

Concerns over sources, transport and fate of PFAAs in the aquatic environment have grown rapidly in recent years.

Perfluorooctane sulfonic acid (PFOS) is the most frequently detected PFAA that is released from a variety of diffuse sources, and is usually the predominant PFAAs detected in aquatic biota (Giesy et al., 2010). Perfluorooctanoic acid (PFOA) is discharged primarily from point-sources in industrial regions, especially from manufacturing facilities (Pistocchi and Loos, 2009). Wastewater treatment plants (WWTPs) are also important point sources of releasing PFAAs, along with more diffuse inputs including rain, dry deposition and release during the use of products (Muller et al., 2011). The majority of PFAAs reach the coastal marine environment dissolved in water, while for long chain PFCAs (C12–C15), about a half of the load was absorbed to particles during transportation (Zushi et al., 2012). Higher affinity for organic carbon leads to enhanced sorption of longer chain PFCAs to particles and solids in sediment and sludge (Armitage et al., 2009). The transportation of PFAAs in water indicated that rivers would be the main source of PFAAs for coastal water. Due to the restriction on the production and use of C8 PFOS and PFOA, the C4 and C6 chemicals have been developed well to adequately replace most current C8 and higher homologues. However, this has also led to the emergence of short chain PFAAs in the environment

(Moller et al., 2010; Oliaei et al., 2013). This suggested the importance of the measurement of PFAAs with different carbon chain lengths with different properties, in order to trace the trend of PFAAs contamination in the environment.

The Bohai-Rim Economic Circle is a highly urbanized and industrialized region in Northern China (Fig. S1). There are more than 40 rivers flowing into the Bohai Sea, a semi-enclosed sea. Based on estimation of mass fluxes of several chemical pollutants (i.e. petroleum hydrocarbons, heavy metals) to the Bohai Sea, the rivers contributed 50%–70% of the total inventory among the five sources: rivers, drains, atmospheric deposition, cultivation and non-point sources (Wang and Li, 2006). The authors have conducted systematic studies on PFAAs in the northern part of the Bohai coastal region since 2008, and found that PFAAs were widely distributed in the environmental matrices with PFOA dominant in the Northern Bohai coastal region (Wang et al., 2011b), PFOS was dominant in the aquatic products in Tianjin (Chen et al., 2011), PFAAs concentrations in surface water were correlated with the level of industrialization in Northern China (Wang et al., 2011a), Fluoropolymer production in the northern Bohai coastal region had posed potential impacts to local soils (Wang et al., 2013b), and the PFOS emissions from industrial and domestic sources in the eastern coastal region of China were identified and estimated (Chen et al., 2009; Xie et al., 2013a, 2013b). Results of the studies conducted by other researchers in the northern part also indicated the presence of great concentrations of PFAAs in river water, sediment, soil, precipitation, organisms and human blood from various sources including fluorine industry parks (Jin et al., 2007; Bao et al., 2009, 2010; Liu et al., 2009; Li et al., 2011; Pan et al., 2011). In recent years, urbanization has also sped up in the southern part of the Bohai coastal region, while information on the concentrations of PFAAs in the rapidly urbanized southern portion of Bohai-Rim is still limited.

This study is an extension of our research on tracing the source and fate of PFAAs from adjacent riverine and estuarine areas of the Bohai Sea. The major aim was to investigate the key species of PFAAs in southern Bohai coastal region, and to identify their potential sources and fate. With less usage and strict control over emissions of PFOS in the world, it is still necessary to measure the whole series of known PFCAs and PFSAs in surface water for understanding the status and trends of their production and presence in the environment. Spatial analysis of integrated geographic information will help to discover potential effluents and understand fate and transport from sources to surface water and from rivers to the sea. The hydrological cycle between land and ocean brings PFAAs from the land to the sea through river flow. Thus, the quantification of PFAAs loading in each river to the southern Bohai Sea will contribute information not only to understanding the behavior of PFAAs, but also to more accurate modeling of trace contaminants in these systems for estimating potential risks.

2. Materials and methods

2.1. Collection of water samples

Twelve coastal rivers within latitude 38°22′ north and longitude 120°44′ east, which flow into the Bohai Sea from the south were selected. For each river, at least 2 sites were chosen considering different volumes of discharge at distances of 20–30 km from the estuary (Fig. S1). In September 2011, 35 samples of surface water were collected using 1 L polypropylene bottles, stored in icebox during transportation and left in room temperature as all samples were extracted within one week after arrival in the lab, the left was stored at −20 °C for long-term storage. Parameters including turbidity, pH, dissolved oxygen, conductance, water temperature, concentrations of chloride ion and fluorine ion, and salinity were measured in situ using a HQd Portable and Benchtop Meter Configurator (HACH Company, USA) (Table S2). Before analysis, all the samples were left to stand for 24 h to settle non-suspended substances, and 400 mL supernatant for each sample was taken for the following analysis.

2.2. Extraction, identification and quantification of target analytes

17 PFAAs, including 13 PFCAs with carbon lengths from C4 to C18, and 4 PFSAs were identified and quantified (Table S3). A 400 mL aliquot of unfiltered water was extracted using OASIS WAX-SPE following published methods (Taniyasu et al., 2005) with some modifications. Briefly, prior to loading samples, the Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water. After loading the samples, cartridges were washed with 4 mL 25 mM ammonium acetate (pH 4) and air-dried overnight. Target analytes were then eluted with 4 mL of methanol and 4 mL of 0.1% NH_4OH in methanol, respectively. The latter fraction was reduced to 0.5 mL under high purity nitrogen (99.999%, Haidian District, BJ) and passed through a nylon filter (13 mm, 0.2 μm, Chromspec, Ontario, Canada), then transferred into a 1.5 mL PP snap top brown glass vial with polyethylene (PE) septa. Individual PFAA was separated and quantified via Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA) that was operated in the negative electrospray ionization (ESI) mode. Conditions under which the instrument was operated were listed in Table S4.

2.3. QA/QC

Field blanks, transport blanks, procedure blanks and solvent blanks were conducted with every sample set. External standard curves of 9-point ranging from 0.01 ng/mL to 100 ng/mL were prepared for quantification of individual PFAA with coefficients (r^2) for all target analytes exceeding 0.99. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. Matrix spike recoveries ranged from 75% to 126%, while procedure recoveries ranged from 77% to 122%. Concentrations of PFAAs were not corrected for recoveries. Detailed QA/QC measurements of PFAAs in water were given in the Supplementary data.

2.4. Statistical and spatial analysis

Statistical analysis was performed by use of SPSS Statistics V20.0 (SPSS Inc. Quarry Bay, HK). During the analysis, values of concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned values of LOD/$\sqrt{2}$ (Bao et al., 2010). Prior to the principal component analysis (PCA), tests of normality were carried out to ensure that data met the assumptions used for further analysis. More details on PCA were given in the Supplementary data. Spatial distributions of PFAAs were analyzed using the Arcmap module in ArcGIS V10.0 software (ESRI, Redland, CA). Layers including Digital Elevation Model (DEM) of land and sea, land use and vegetation were obtained from the National Geomatics Center of China (Haidian District, BJ).

3. Results and discussion

3.1. PFAAs in South Bohai coastal rivers

Among the 17 PFAAs quantified, the concentrations of perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), Perfluorooctadecanoic acid (PFODA) and perfluorodecanesulfonate (PFDS) were less than the LOQ in all samples, therefore they were not discussed further in this or the following sections. Concentrations of the remaining PFAAs were listed in Fig. 1 and Table S5.

PFAAs were detected in all the rivers with concentrations of sum PFAAs ($\sum$PFAAs) ranging from 2.21 to 5068.97 ng/L. In the Xiaoqing River, PFOA was the dominant PFAA with a mean concentration of 3112.28 ng/L, which contributed 90.1% of the $\sum$PFAAs, and was followed by short chain PFCAs, including PFBA (mean concentration of 49.80 ng/L, 1.4%), PFPeA (mean concentration of 70.97 ng/L, 2.0%), PFHxA (mean concentration of 123.34 ng/L, 3.5%) and PFHpA (mean concentration of 91.72 ng/L, 2.6%). For concentrations of the other long chain PFCAs and all PFSAs, the total contribution was less than 1%. In the remaining 11 rivers, the mean concentration of $\sum$PFAAs was 25.78 ng/L with the average contribution of individual PFAA in decreasing order of percentage: PFOA (38.2%) > PFBA (19.5%) > PFOS (14.3%) > PFHxA (6.7%) > PFPeA (6%) > PFBS (3.9%) > PFNA (4.6%) > PFHpA (4.3%) > PFDA.

(1.1%) > PFHxS (1%) > PFUdA (0.2%) (Fig. 2a). PCA analysis on the 11 PFAAs and 9 water parameters showed that PFBA, PFPeA, PFHxA, and PFOA were associated when the Xiaoqing River was excluded