



Oxidative conversion of potential perfluoroalkyl acid precursors in Jiaozhou Bay and nearby rivers and sewage treatment plant effluent in China

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ARTICLE INFO

Keywords:

Perfluorinated
Perfluoroalkyl acid precursor
Oxidation
Effluent
Qingdao city

ABSTRACT

Precursors that can be transformed into perfluoroalkyl acids (PFAAs) have not been investigated in detail. In this study, the levels of potential PFAA precursors in the Jiaozhou Bay, inflowing rivers, and STP (sewage treatment plant) effluents were investigated by converting all PFAA precursors into perfluorinated carboxylic acids (PFCAs) by chemical oxidation. The significance of controlling PFAA precursors was indicated by the ratios of PFCAs converted by the oxidative treatment of precursors to PFAAs before oxidation ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]/\Sigma[\text{PFAA}]_{\text{before oxidation}}$). The higher levels of $\Delta[\text{PFCA}_{\text{C4-C12}}]$ (average = 18.89 ng/L) and lower ratios ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]/\Sigma[\text{PFAA}]_{\text{before oxidation}}$, average = 0.21) were revealed in the STP effluents rather than in the water of the Jiaozhou Bay and rivers, which implied the precursors conversion during the sewage treatment process. The concentrations of $\Delta[\text{PFCAs}]$ and the aforementioned ratios showed apparent spatial and temporal differences. These results indicated that STPs were the important sources of precursors to other water bodies.

1. Introduction

In recent years, perfluoroalkyl acids (PFAAs), most known as perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), have been a hot spot in the scientific community due to their widespread use and impact on the environment. Because of the high energy of carbon-fluorine bonds, PFAAs are difficult to decompose and show unique physical and chemical properties such as thermal stability, amphiphilicity, high surface activity, and resistance to specific acidic and alkaline conditions (Paul et al., 2008; Buck et al., 2011; OECD, 2013; Pahigian and Zuo, 2018). In the past 60 years or so, PFAAs have been used intensively in some industrial products such as metal plating, pesticides, fire-fighting foams, semiconductors, aviation and surface protectors on leather, textile, carpet, furniture, paper products, and food containers, owing to their high physical and chemical stability (Giesy and Kannan, 2002). During production and usage processes, PFAAs have been directly or indirectly discharged into the environment. Numerous previous studies have found that PFAAs, especially PFCAs and PFSAs, are ubiquitously detected in various environmental matrices including water (Furdui et al., 2007; Takazawa et al., 2009), sediment (Becker et al., 2008; Gómez et al., 2011), and air (Shoeb et al., 2006). In addition, PFAAs indicate high bioaccumulation and bioconcentration capacities for the tissues of the organisms (Martin

et al., 2003; Thompson et al., 2012) and have potential toxicity for organisms (Giesy and Kannan, 2002; Giesy et al., 2010; Thompson et al., 2012). Moreover, some researchers have found that PFAAs are distributed globally in biota (Bossi et al., 2005; Smithwick et al., 2006; Quinete et al., 2009; Houde et al., 2011; Sun et al., 2015) and humans (Olsen et al., 2005, 2007; Gebbink et al., 2015). Thus, considerable attention has been paid by scientists, politicians, and administrators in the past few years to the PFAA contamination.

Manufacture and application processes might be one of the most important pollution resources for PFAAs. Some PFAAs, especially PFCAs and PFSAs, enter the environment through the transformation of precursors (Prevedouros et al., 2006). For example, perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamides (FOSAs) can be biotransformed to perfluorooctane sulfonate (PFOS) in activated sludge under aerobic conditions (Rhoads et al., 2008). The 8:2 fluorotelomer unsaturated acid (8:2 FTUCA) and 8:2 fluorotelomer acid (8:2 FTCA) can be photodegraded to perfluorononanoate (PFNA) and perfluorooctanoic acid (PFOA) (Gauthier and Mabury, 2005). Fluorotelomer alcohols (FTOHs) can be converted into a homologous series of PFCAs in the atmosphere (Ellis et al., 2004; Wallington et al., 2006). In addition, the increased concentrations of PFCAs have been found in the STP effluents, which might be induced by the conversion of PFAA precursors during the processes of sewage treatment (Sinclair and

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Kannan, 2006; Murakami et al., 2009). Most prior efforts to quantify the concentration and distribution of PFAAs in various environmental matrices have focused mainly on PFCAs and PFSAs. In recent years, some researchers have started to investigate the occurrence and fate of PFAA precursors in the environment. For example, measured results showed that the concentrations of some PFAA precursors were apparently lower than the concentrations of PFAAs in water (Schultz et al., 2006). FOSAs and FOSEs were the most frequently detected precursors in some environmental matrices (Martin et al., 2010). However, systematic investigations of the occurrence and behavior of PFAA precursors in the environment are still very rare to date. Many types of precursors such as fluorotelomer sulfonamides (FtS), FTOHs, FTUCA, polyfluoroalkyl phosphate mono, and diesters (mono- and di-PAPs) have rarely been investigated.

Although the concentrations of some precursors were very low or lower than the detection limit, PFAA precursors can convert into PFCAs and PFSAs in an aquatic environment at appreciable concentrations (Kim and Kannan, 2007; Murakami et al., 2009; Pisarenko et al., 2015; Anumol et al., 2016). A method of oxidation treatment was built to estimate the concentrations of total PFAA precursors in water (Houtz and Sedlak, 2012). The increased concentrations of total PFCAs after oxidation treatment were induced by transformation of the PFAA precursors and were used to infer the PFAA precursor concentrations in water. This method of oxidation treatment has been used to determine the concentrations of total PFAA precursors and show the spatial distribution tendencies of total PFAA precursors in the Tama River in Japan (Ye et al., 2014).

Qingdao City is an important economic center in China with a relatively high industrialization and urbanization level. Industries such as shipbuilding, metallurgy, print circuit board manufacture, automobile, electroplating and battery manufacture, mechanical manufacturing, and textile factories have been well developed in this city. Jiaozhou Bay is a semi-enclosed bay and embraced by Qingdao City. Similar to some other bays in the world, Jiaozhou Bay is also strongly impacted by anthropogenic activities. During the process of rapid development of industry and agriculture in Qingdao City, large quantities of industrial wastewater and domestic sewage were discharged into this bay through some inflowing rivers. Data on the concentrations and distributions of PFAAs and their precursors in the water bodies in and around Qingdao city are also rare to date. Information about the transformation of PFAA precursors is especially very limited at present. Therefore, the total concentrations of PFAAs and their precursors in the river and STP effluents in and around Qingdao City and Jiaozhou Bay were systematically studied. Rivers mentioned in this study are the main water bodies receiving industrial wastewater, domestic sewage, and STP effluents discharged from Qingdao City, and these rivers flow into Jiaozhou Bay in the end. Thus, investigations on the spatial-temporal distribution of PFAAs and the impact of oxidative conversion of their precursors to PFAA pollution in the water bodies of Jiaozhou Bay will be helpful for understanding the environmental occurrences and fates of PFAAs and their precursors.

Therefore, the total concentrations of PFAAs and their precursors in the Jiaozhou Bay were studied. The increased concentrations of PFCAs induced by the proposed method of hydroxyl radical oxidative conversion of PFAA precursors (Δ [PFCAs]) were determined. This method converts PFAA precursors into PFCAs, which shows a potential source of PFAAs in water. Therefore, the spatial-temporal distribution of PFAAs, including the Δ [PFCAs], was induced from the PFAA precursor conversion from the Jiaozhou Bay and the river water and STP effluents. The ratio of the PFCAs formed from precursor conversion to PFAAs originally present ($\Sigma\Delta$ [PFCAs_{C4-C12}]/ Σ [PFAA]_{before oxidation}) was calculated to indicate the importance of the PFAA precursors as a potential source of PFAA in the water bodies. To our knowledge, this study is the first to quantify the level and the conversion capacity of PFAA precursors in the water bodies of bay and river and the STP effluents. The results of this study will show the importance of controlling

the PFAA precursors in the water.

2. Materials and methods

2.1. Water sample collection

In this study, water samples were collected using a high-density polyethylene (HDPE) bucket in April, August, and November in 2016 (Fig. 1). April, August, and November represent the average, high, and low water season, respectively. The water samples from bay and river were collected from the surface (0–20 cm in depth), and the samples from STP effluents were collected from the outflow of plants. These collected water samples were poured into HDPE bottles rinsed with methanol, kept in an ice bath before arriving at the laboratory, and always stored at 4 °C until extraction in the laboratory. Meanwhile, water sampling blanks from each sampling location were obtained by filling the HDPE bottles with Milli-Q water and storing under the same conditions as the water samples. Any vessels containing Teflon were not used during all the sampling and experimental processes to prevent possible PFAA contamination.

2.2. PFAA precursor oxidation

The method of hydroxyl radical (\cdot OH) oxidation was referenced and utilized in this study to quantify the conversion capacities of the PFAA precursors (Houtz and Sedlak, 2012; Ye et al., 2014). Thermolysis of persulfate ($S_2O_8^{2-}$) can produce \cdot OH under basic pH conditions. The reactions between \cdot OH and PFAA precursors can lead to the formation of PFCAs. Briefly, the unfiltered samples (125 mL) were decanted into HDPE bottles. For the water samples collected from each sampling stations, the water sample was sub-collected in triplicate, and then, potassium persulfate (2 g, 60 mM) and NaOH (1.9 mL, 150 mM) were added. These samples in HDPE bottles were first cultured in a water bath (80 °C, 6 h) and then were cooled to room temperature by an ice bath before analysis.

2.3. Extraction and analysis

The extraction procedure reported by Taniyasu et al. (2005) and Zuo (2014) was referenced and adopted in this study. To correct the recovery rates of experimental analysis, 4 ng of isotope-labeled surrogate standards were added to the blanks and samples before extraction. Solid-phase extraction (SPE) (Oasis WAX SPE cartridges, 6 cm³, 150 mg, 30 μ m; Waters, Milford, MA) was used to treat the original (before oxidation) and the treated samples (after oxidation). NH₄OH (in methanol) (4 mL, 0.1%), methanol, and ultrapure water were successively applied to pretreat the cartridges. Then, using an SPE manifold (GL Sciences, Tokyo, Japan) jointed to a gum tube, the samples (125 mL) before and after oxidation treatment were passed through the SPE cartridges under the conditions of vacuum. Methanol in ultrapure water (4 mL, 50%) was used to rinse the HDPE bottles after sample loading, and the rinsed solution was also passed through the SPE cartridge for thorough extraction. When the extraction procedures were finished, ultrapure water (4 mL) was used to rinse the cartridge. After the SPE cartridge dried, methanol (2 mL) and NH₄OH (in methanol) (0.1%, 2 mL) were successively passed through the SPE cartridge for eluting it. During the drying process, the elution solution was evaporated to 400 μ L to avoid the loss of the target compounds. In the end, high-performance liquid chromatography (HPLC, Agilent 1100LC, Agilent Technologies, Palo Alto, CA, USA) interfaced with a tandem mass spectrometer (MS/MS; Micromass Quattro, Waters, Milford, MA, USA) was applied to determine the concentrations of the target compounds, including 15 PFAAs and 3 precursors (Table 1).

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