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Perfluoroalkyl acids in surface seawater from the North Pacific to the Arctic Ocean: Contamination, distribution and transportation

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ABSTRACT

The bioaccumulative, persistent and toxic properties of long-chain perfluoroalkyl acids (PFAAs) resulted in strict regulations on PFAAs, especially in developed countries. Consequently, the industry manufacturing of PFAAs shifts from long-chain to short-chain. In order to better understand the pollution situation of PFAAs in marine environment under this new circumstance, the occurrence of 17 linear PFAAs was investigated in 30 surface seawater samples from the North Pacific to Arctic Ocean (123°E to 24°W, 32 to 82°N) during the sixth Chinese Arctic Expedition in 2014. Total concentrations of PFAAs ($\sum$PFAAs) were between 346.9 pg per liter (pg/L) to 3045.3 pg/L. The average concentrations of $\sum$PFAAs decreased in the order of East China Sea (2791.4 pg/L, $n = 2$), Sea of Japan (East Sea) (832.8 pg/L, $n = 6$), Arctic Ocean (516.9 pg/L, $n = 7$), Chukchi Sea (505.2 pg/L, $n = 4$), Bering Sea (501.2 pg/L, $n = 8$) and Sea of Okhotsk (417.7 pg/L, $n = 3$). C4 to C9 perfluoroalkyl carboxylic acids (PFCAs) were detected in more than 80% of the surface water samples. Perfluorobutanoic acid (PFBA) was the most prevalent compound and perfluorooctanoic acid (PFOA) was the second abundant homolog. The concentration of individual PFAAs in the surface seawater of East China Sea was much higher than other sampling seas. As the spatial distribution of PFAAs in the marine environment was mainly influenced by the river inflow from the basin countries, which proved the large input from China. Furthermore, the marginal seas of China were found with the greatest burden of PFOA comparing the pollution level in surface seawater worldwide. PFBA concentration in the surrounding seas of China was also high, but distributed more evenly with an obvious increase in recent years. This large-scale monitoring survey will help the improvement and development of PFAAs regulations and management, where production shift should be taken into consideration.

1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluoroalkyl carboxylate acids (PFCAs) and perfluoroalkyl sulfonate acids (PFSAs) are a group of anthropogenic chemicals, which are most widely used in in industry and daily necessities such as surfactants, aqueous fire-forming foam, fabrics, coatings and food packaging (Wang et al., 2015a). During their production and usage, PFAAs have been inevitably released into the environment since the 1950s (Xiao, 2017). The widespread of PFAAs has elevated the potential risk of human and wildlife exposure and become an ecological and toxicological concern owing to their bioaccumulative, persistent and toxic properties (Wang et al., 2015b). Moreover, PFAAs have been detected in virous environmental matrices, human bodies, and even remote regions, such as the Arctic and Antarctica (Wang et al., 2015c; Hanssen et al., 2013; Wong et al., 2018).

Among the PFAAs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have raised particular concern because of their adverse impacts and have been subjected to restrictions in production and use in America, Europe and Japan (3M, 2000; USEPA, 2006; EC, 2006; UNEP, 2009; ECHA, 2013). However, a great demand for PFAAs-related commercial products drive a

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geographical shit of fluorinated industry from developed regions to East Asian economies (Cai et al., 2012a; Wang et al., 2016a). Consequently, China has become both the main global producer and the main consumer of these chemicals due to the less stringent regulations, especially for PFOA and its salts (Li et al., 2015; Meng et al., 2017).

Previous studies show that long-range atmospheric transport (LRAT) and ocean currents were suggested to be the main transport pathways for the global fraction of PFAAs (Wang et al., 2015c; Xie et al., 2015). The residence of PFAAs in the snow, ice caps, and the lake water in the Antarctica demonstrate that the degradation of PFAAs precursors, such as fluorotelomer acrylates (FTAs) and fluorotelomer alcohols (FTOHs), is an important pathway to conduct the LRAT (Ellis et al., 2004; Martin et al., 2006; Young et al., 2007; Wang et al., 2014a,b). PFASs could have an exchange between the atmosphere and surface seawater and the aqueous phase PFAAs could be a net source for the neutral PFASs in the atmosphere (Reth et al., 2011; Ahrens et al., 2011). However, ocean current is the dominant pathway for PFAAs migrate from the source regions to the high-latitude Arctic in the aqueous (Cai et al., 2012a,b; Yeung et al., 2017). In recent years, the investigations of the occurrence and fate of PFAAs in the low-latitude source regions have been developed, especially in the water column of lakes (Möller et al., 2010; Wang et al., 2015a), rivers (Li et al., 2017), estuaries (Hong et al., 2013; Shao et al., 2016) and coastal regions (Beškoski et al., 2017; Zheng et al., 2017). But the occurrence and fate of PFAAs in the open sea or remote regions, especially in the high-latitude Arctic and Antarctica, was limited and by the challenging sampling conditions (Benskin et al., 2012; Cai et al., 2012b; Stemmler and Lammel, 2010). And further investigation of the PFAAs on large scale is desperate to have a better understanding of the transport pathway from the new hotspot, East Asia, to the high Arctic. Latest monitoring surveys are also imperative to be answerable for the geographic shift of PFAAs. In this study, we presented a first-hand data of PFAAs distribution and inventory in surface seawater from the North Pacific to the Arctic Ocean.

In the new situation of the manufacture and use of fluorine chemicals in the world, the study about the marine environment pollution from PFAAs on a large scale is urgently needed, where China as the new hotspot should be included. In this study, we presented a large-scale monitoring survey on PFAAs in surface seawater from the North Pacific to the Arctic Ocean. The objective of this study was to (1) investigate the occurrence, spatial distribution and profiles of PFAAs in this region including the long-chain PFAAs and their substitutes; (2) identify the main factors that influencing the PFAAs distribution in seawater; (3) observe the global variations of PFAAs concentrations in surface seawater to get comprehensive information about the impact of the geographical transition and production shifts of fluorochemical-related activities. This study provides the large-scale empirical data of PFAAs concentration and spatial distribution in surface seawaters, especially for some key fluorinated alternatives. These investigations will be useful for emission control over certain PFAAs in the aquatic environment and contribute to the general protection of marine ecosystems.

2. Materials and methods

2.1. Sampling campaign

Surface water samples (0–20 cm) were taken onboard the research vessel *Snow Dragon* at 30 stations (123° E to 24° W, 32–82° N) from North Pacific Ocean (NPO) to the Arctic Ocean (AO) during the sixth Chinese Arctic Expedition from July to September in 2014 (Fig. 1). In order to better elucidate the locations of PFAAs in the surface water samples, station sites were geographically separated into 6 groups: East China Sea (ECS, E1-E2), Sea of Japan (East Sea) (JS, J1-J6), Sea of Okhotsk (OS, O1-O3), Bering Sea (BS, B1-B7), Chukchi Sea (CS, C1-C5) and Arctic Ocean (AO, A1-A7).

Four liters (L) of the surface seawater was collected from each sampling site by a stainless steel bucket. 2 L polypropylene (PP) bottles were used to store water samples. All the sampling equipment such as the stainless steel bucket and PP bottles were precleaned and rinsed with methanol, distilled water and seawater from the specific locations before sampling. All samples were stored at 4 °C in darkness before pretreatment. The detailed information of the sampling date, location, and sampling parameter can be found in Supporting Information (Table S1).

2.2. Extraction and analysis of target analytes

Concentrations of 17 linear PFAAs including 13 PFCAs (C4 to C14, C16 and C18) and 4 PFSAs (C4, C6, C8 and C10) were measured in this study (Table S2), including perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), PFOA, Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUndA), Perfluorododecanoic acid (PFDoA), Perfluorotridecanoic acid (PFTrDA), Perfluorotetradecanoic acid (PFTeDA), Perfluorohexadecanoic acid (PFHxDA), Perfluorooctadecanoic acid (PFODA), Potassium Perfluorobutanesulfonate (PFBS), Sodium Perfluorohexanesulfonate (PFHxS), Potassium Perfluorooctanesulfonate (PFOS) and Sodium Perfluorodecanesulfonate (PFDS). After filtered with glass fiber filters (GFF, Whatman, O.D. 47 mm, 0.7 μm), water samples were spiked with 5 ng mass-labeled standards and then extracted using OASIS WAX-SPE following a previously published method with some modifications (Wang et al., 2012). Briefly, prior to extraction, the Oasis WAX cartridges (250 mg, 3 mL, Sigma-Aldrich, St. Louis, USA) were preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol and 4 mL of Milli-Q water in sequence. After loading the sample at approximately 1–2 drops per second, cartridges were washed with 4 mL 25 mM ammonium acetate (pH = 4) and then air-dried. Then 4 mL of methanol and 4 mL of 0.1% NH_4OH in methanol were added to cartridges to elute the target analytes. The sample volume was reduced to 1 mL under a gentle stream of high purity nitrogen (99.999%, Haidian District, BJ) and followed by filtered through a nylon filter (13 mm, 0.2 mm, Chromspec, Ontario, Canada). Then the samples were transferred into a 1.5 mL auto-sampler vial fitted with a polypropylene cap. PFAAs analysis was performed via Agilent 1290 high-performance liquid chromatography (HPLC) system equipped with an Agilent 6460 triple-quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA), which was operated in a negative electrospray ionization (ESI) mode. The details of the standards and reagents, as well as the instrument conditions of HPLC and ESI-MS, were given in the Supplementary and Table S2.

2.3. Quality assurance and quality control (QA/QC)

To minimize cross contamination, the usage of any polytetrafluoroethylene (PTFE) or fluoropolymer materials was avoided during sampling, extraction and instrumental analysis. In order to check for potential contamination, field blanks, transport blanks, procedure blanks and solvent blanks were conducted with every sample set. The 8-point (0.01, 0.05, 0.1, 0.5, 1, 5, 10 and 50 ng/mL) standard calibration curves of native standards were prepared for quantification of individual PFAA, which was spiked with 5 ng mass-labeled internal standards. The PFAAs concentrations of the final extracts all fall in the range of the calibration series. Regression