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Shifts in production of perfluoroalkyl acids affect emissions and concentrations in the environment of the Xiaoqing River Basin, China

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HIGHLIGHTS

- Mass loads demonstrated a greater pattern of increasing PFAAs emissions.
- High levels of PFOA were identified near a fluoropolymer facility.
- Production activities that could generate PFOA emissions were analyzed.
- Partitioning coefficients decreased with high levels of short-chain PFCAs in water.

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ABSTRACT

Perfluoroalkyl acids (PFAAs) have been widely used in surfactant applications, especially as processing acids for fluoropolymer production. This study provides an analysis of sources of certain PFAAs emitted from the intensive fluoropolymer facilities in the Xiaoqing River Basin of China. Concentrations of perfluorooctanoic acid (PFOA) as great as 0.97 mg/L in surface water and 10.5 μg/g dry weight in surface sediment have been detected near the effluent of one facility (F1) that produces polytetrafluoroethylene (PTFE) and other fluoropolymers with massive capacity. With the great emission of PFAAs to water in natural conditions, the log K_{OC} values decreased for short-chain PFCAs. Mass loads of PFAAs indicated that emissions of PFAAs from other facilities or sources were much less than those from F1, which emitted 174 kg/d of PFAAs including 159 kg/d of PFOA to the rivers. Even though production and emissions of PFOA have been strictly controlled in other countries since 2006, production of PFOA as well as several other fluoropolymers that use PFOA as processing aids has been increasing at F1 in recent years. We recommended that production shift should be taken into consideration in PFOA elimination actions.

1. Introduction

Perfluoroalkyl acids (PFAAs) are characterized by a hydrophobic perfluoalkyl moiety with chemical and thermal stability and a hydrophilic acid functional group. The unique properties of PFAAs have made them widely used as surfactants or processing aids during production of polymers [13]. In 2001, PFAAs, especially perfluorooctane sulfonic acid (PFOS), have been widely detected in wildlife [8] and human blood [10]. Concerns over persistence and potential for toxicological effects led to the phase-out of PFOS, and related compounds beginning in 2000 by the major global manufacturer in United States [24]. Since then, studies on environmental, toxicological and health effects of PFAAs have grown rapidly, and production, usage and emission of PFAAs with 8 or more carbons have been strictly controlled in more developed countries [2].

As a signatory of the Stockholm Convention on Persistent Organic Pollutants [23], China has restricted production and use of PFOS except specific exemptions by law [19]. However, other PFAAs have not yet been restricted. Although the eight major fluoropolymer and telomer manufacturers have been working on elimination of PFOA and related chemicals from production and emission by 2015 under the 2010/2015 PFOA Stewardship Program [25], the demand for PFOA as processing aids has not yet declined, especially in production of polytetrafluoroethylene (PTFE) [6]. It can be seen

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from their annual progress reports from 2007 to 2014 that both the amount released to all media from fluoro-polymer/-telomer manufacturing and percentage reduction in emission/product content of PFOA were less from non-U.S. operations than from U.S. operations of most manufacturers [26]. Although the program has brought the gradual elimination of PFOA emission from the major manufacturers, there is concern that without adequate substitutes or sufficient removal from wastewater in recent years, where will major manufacturers shift their production and what effects will that production have on local environments?

Known as fine chemicals which need intensive investment and other support, fluoropolymer facilities are often located in relatively developed areas of China, like the Bohai Coastal Economic Circle. In a previous study of 12 coastal rivers that flow into the Bohai Sea, concentration of PFOA as great as 4.5 μg/L was observed in the estuary of the Xiaoqing River. Several fluoropolymer facilities producing large amounts of PTFE and other fluoropolymers were disclosed along the river [29]. Studies by other researchers also indicated that PFOA was the predominant PFAA along the Xiaoqing River found in human blood in Zouping County [9], precipitation in Weifang City [36], mollusks in Laizhou Bay [18] and sediment in the Xiaoqing River [37,38]. However, the exact sources and fate of PFAAs, the contribution of different kinds of sources and the pollution history are still unqualified and unquantified in the Xiaoqing River Basin.

Unlike PFOS, the majority (upto 80%) of perfluoroalkyl carboxylic acids (PFCAs) was estimated to be released to the environment from fluoropolymer manufacture and use, especially for PFOA. In a study of global emission inventories for C4–C14 PFCAs from 1951 to 2030, it was also concluded that historically 98–100% of PFOA was emitted from direct sources during the life-cycle of related products [33]. So this study focused on direct sources of PFAAs emitted to the river. Considering the study area is relatively greatly urbanized and industrialized with a lot of farmland that need consistent irrigation, the water channels in the whole river basin were all studied with sampling sites selected to cover sources from production to transportation (Fig. 1). The overall aim of this study was to identify current emission sources of PFOA in the Xiaoqing River Basin, assess the potential effects of shifts in production by manufacturers to China. The results present useful information for control over emissions of certain PFAAs to ecosystems and a general protection of human health.

2. Materials and methods

2.1. Sample collection

The total length of the Xiaoqing River is 220 km. To assess the potential sources and transportation of PFAAs in the whole river basin, 12 sites (X1–X12) on the main stem of the river at intervals of approximately 20 km, 14 sites (X13–X26) on tributaries of the Xiaoqing River were selected, and 4 sites (R1–R4) in two adjacent rivers were set as references (Fig. 1). The field sampling campaign was carried out during June 19–23, 2013. Samples of surface water ($n = 30$) were collected using pre-rinsed 1 L polypropylene (PP) bottles. Surface sediments (top 0–2 cm) in all sites ($n = 25$) of the Xiaoqing River Basin except X24 were collected using a stainless steel trowel and kept in 250 mL PP boxes. Sediment cores of 20 cm depth were collected at sites X3,X6,X9 and X12, by use of a Beeker sediment core sampler (Eijkelkamp Agrisearch Equipment, Netherland), and sectioned in the field into 10 intervals of 2 cm, which were placed into 250 mL PP boxes. Samples were kept in ice box during transportation. After arrival in the lab, samples of water were left to stand for 24 h to settle most of the particles and only supernatants were taken for analysis. Samples of sediments were freeze-dried and passed through 2 mm mesh.

2.2. Target analytes, extraction, and analysis

A total of 12 linear PFAAs including 9 PFCAs with carbon lengths from C4 to C12, and 3 perfluoroalkane sulfonic acids (PFSAs) were measured in this study (Table S2). Aliquot of 400 mL of unfiltered water was extracted using OASIS WAX cartridges and clean-up. For sediments, 2 g of dry samples were extracted by use of ultra-sonic extraction followed by clean-up with ENVI-Carb and OASIS-WAX cartridges, respectively. Detailed information on extraction is given in the Supplementary material. Target PFAAs were quantified by use of an Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, USA) that was operated in the negative electrospray ionization (ESI) mode. Instrument conditions were listed in Table S4.

2.3. QA/QC

In order to avoid cross contamination during sampling in the field, the outside of bottles and boxes was washed with Milli-Q water after the samples were taken, wiped with clean towel paper and then kept in three-layers of sealed polyethylene (PE) bags. To monitor potential interferences during sampling, extraction and instrumental analysis, blanks including field, transport, procedure and solvent ones were prepared with every sample batch. Quantification of 12 PFAAs in all samples were carried out using 10-point internal quantification curves with concentrations of native standards ranging from 0.01 to 1000 ng/mL and 10 ng/mL of mass-labelled internal standards. Regression coefficients (R^2) for calibration curves for all target analytes were greater than 0.99. The injection volume was 5 μL. For concentrations of PFAAs in extracts that were initially greater than 1000 ng/mL, the volume or amount of the samples would be reduced and the samples would be extracted again to make sure the concentrations of PFAAs in the final extracts fall in the range of the calibration series. Limits of detection (LOD) and limits of quantification (LOQ) were defined as the peak of analyte that yielded a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. LOD and LOQ ranged from 0.002 to 0.01 ng/g and from 0.01 to 0.04 ng/g, dry weight (dw) for sediments. For water samples, LODs ranged from 0.01 to 0.08 ng/L, while LOQs ranged from 0.06 to 0.22 ng/L. Matrix spike recoveries ranged from 89 to 114% for water samples and 75–117% for sediment samples. Procedure recovery ranged from 81 to 122% for water samples and 71–108% for sediment samples. Detailed information on QA/QC was given in Supplementary material.

2.4. Statistical and spatial analysis

Data analysis was performed by use of SPSS Statistics V20.0 (SPSS Inc. Quarry Bay, HK), Microsoft Excel 2010 (Microsoft China, Beijing) and Origin Pro 9.1 (Northampton, MA, USA). 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/$\sqrt{2}$ [29]. Prior to the correlation analysis, tests of normality were carried out to ensure that data met the assumptions used for further analysis. Spatial distributions of PFAAs were analyzed using the Arcmap module in ArcGIS V10.2 (ESRI, Redland, CA). The precise river information for sampling design and spatial analysis was obtained from remote sensing data provided by the National Geomatics Center of China (Haidian, Beijing, China), and optimized by *in-situ* observation.