



Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China



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ABSTRACT

The spatial trend of perfluoroalkyl substances (PFASs) along Xiaoqing River and its tributaries was studied to characterize isomer profiles and quantify emissions from fluoropolymer (FP) manufacturers in China. Substantially elevated Σ PFAS concentrations downstream of tributary 4 demonstrated that the emissions from this FP manufacturer dominated total riverine discharges. Isomer profiles of perfluorooctanoic acid (PFOA) in water displayed a stepwise increase in percentage branched PFOA downstream of tributary 3 (14.0%) and 4 (22.7%) reflecting the importance of FP sources. Strong positive correlations between PFOA isomers in water downstream of tributary 4 indicated that isomer profiles were conserved from emission sources to the final reservoir. Riverine discharges of PFOA (23–67 t/yr) were in agreement with theoretical emission calculations from FP production (68 t/yr) whereas large discrepancies between the two methodologies were observed for perfluorobutanoic acid and perfluoropentanoic acid. Collectively, this study fills critical knowledge gaps for understanding ongoing global sources of PFASs.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of man-made chemicals which have been widely used in commercial products and industrial processes due to their unique amphiphilic properties and chemical stability (Posner, 2012). However, the same properties that make PFASs useful in commercial applications also make them problematic contaminants when released to the environment (Buck et al., 2011) and the global contamination of PFASs has attracted significant attention from scientists and regulators (Lindstrom et al., 2011). Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been recognized as two of the most problematic PFASs due to their persistence, ubiquitous presence in environmental samples, wildlife, and humans (Buck et al., 2011) and toxicity in animal models (Seacat et al., 2003;

Lau et al., 2007).

The adverse environmental profile of PFASs has led to a series of regulatory actions and voluntary phase-out initiatives by the chemical industry. Between 2000 and 2002, the major global manufacturer of PFOS and PFOA phased out production of perfluorooctyl compounds (3M, 2000, 2003; Buck et al., 2011). In 2006, eight other leading global companies agreed to a stewardship program to reduce emissions and product content of PFOA and related chemicals by 95% by 2010 and to work towards their elimination by 2015 (US EPA, 2006). PFOS, its salts and perfluorooctylsulfonyl fluoride (POSF) were listed as Persistent Organic Pollutants (POPs) in Annex B of the Stockholm Convention in 2009 (UNEP, 2009), and PFOA and its ammonium salt (ammonium perfluorooctanoate, APFO) were added to the European chemicals regulation REACH candidate list as Substance of Very High Concern (SVHC) in 2013 (European Chemicals Agency, 2013). The initiatives to phase out perfluorooctyl compounds including PFOS and PFOA have been generally achieved by substituting to short-chain PFAS homologues. A parallel trend is the geographical shift in the

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production and use of PFASs from Europe and North America to emerging economies including China (Wang et al., 2014a). This change of place of production has also led to a continued or increasing production and use of perfluorooctyl compounds which have largely been phased out in Europe and North America (Xie et al., 2013; Wang et al., 2014a). Although, numerous studies have reported highly elevated concentrations of both legacy and replacement PFASs in environmental samples and human blood serum from China (Bao et al., 2011; Zhou et al., 2013, 2014; Shan et al., 2014), a comprehensive understanding of the major emission sources is lacking.

Global source inventories have demonstrated that the historical emissions of PFOA can be largely attributed to the use of APFO in fluoropolymer (FP) production (Prevedouros et al., 2006; Cousins et al., 2011). The relative importance of emission sources may, however, vary considerably for different PFCA homologues and over time as a consequence of phase out actions (Wang et al., 2014a). For example, direct emission from manufacture and use of APFO can account for 98–100% of the historical emissions of PFOA, whereas impurities of PFCAs in fluorotelomer products (Washburn et al., 2005) or degradation of fluorotelomer precursors (Ellis et al., 2004) are relatively more important for C4–C7 PFCAs (Wang et al., 2014a). Although theoretical cumulative emissions of PFOA and perfluorononaic acid (PFNA) are broadly consistent with ocean water inventories based on measurement data (Armitage et al., 2006, 2009a, b; Prevedouros et al., 2006), large discrepancies between modeled and observed values are observed for short-chain PFCAs ($C_nF_{2n+1}COOH$, $n < 7$) (Wang et al., 2014a). Further studies are therefore needed to evaluate the assumptions of global emission inventories which are sometimes derived from limited empirical data (Wang et al., 2014a).

A different approach to investigate the emission sources of PFOA is the use of isomer profiles (Benskin et al., 2010a, b; 2012a). The principal idea behind this source apportionment tool is that the two major synthesis routes to produce PFOA result in distinct profiles of branched and linear isomers. Provided that ocean water is the final reservoir of PFOA, isomer profiles in water samples from industrialized or remote regions can be used for tracking production sources (Benskin et al., 2010b, 2012a; Yu et al., 2013; Fang et al., 2014a, 2014b). Electrochemical fluorination (ECF), which results in a mixture of branched and linear isomers, was used to produce the majority of APFO in Europe and North America between 1951 and 2000 (Prevedouros et al., 2006). Since 2003, the production of ECF-products has rapidly increased in China to meet the demand of APFO as a polymerization aid in FP production (Wang et al., 2014a). Telomerization, which was developed in the 1970s, is distinct from ECF in that the composition of products is isomerically pure and typically >99% linear (Buck et al., 2011). However, production of isopropyl PFOA using the telomerization process has also been reported (Kissa, 2005; Benskin et al., 2010a). Although telomerization has been widely used to produce APFO in Europe and North America in the period 2003–2015, its use in China has been fairly limited (Ruan et al., 2010; Fuxin, 2013; Wang et al., 2014a). Fluorotelomer products, some of which can degrade to PFCAs in the environment (Wallington et al., 2006; Wang et al., 2009; Butt et al., 2010), are however used in numerous consumer product applications including textile and paper treatment (Wang et al., 2014a). A complicating factor of using isomer profiles for source elucidation is, however, that the differences in physico-chemical properties of structural isomers may lead to a fractionation in the environment (Benskin et al., 2010a; Kärrman et al., 2011). Furthermore, it is not well established if the isomer profiles in Chinese APFO products are similar to historically used products in North America and Europe (Benskin et al., 2010a).

The aim of this study was to advance our understanding of PFAS

emissions related to ongoing FP production with particular emphasis on (i) evaluating and improving methods for emission estimation and (ii) evaluating the applicability of isomer profiles as a source apportionment tool for ongoing sources. To this end, we assessed the spatial trends, isomer profiles and riverine discharges of PFASs in Xiaoqing River which receives emissions from one of the major FP producers in China (Wang et al., 2014a, b). Although the focus of this paper is on identifying and quantifying sources of PFCAs, other PFASs are discussed with respect to their contrasting sources, transport and fate.

2. Materials and methods

2.1. Study area

Xiaoqing River is located in Shandong province on the eastern edge of the North China plain stretching from the approximate coordinates $36^{\circ} 38' - 37^{\circ} 16'$ north and $116^{\circ} 48' - 118^{\circ} 52'$ east. The 216 km long Xiaoqing River has an SW–NE orientation and flows parallel to the Huang He River before emptying into Laizhou Bay of the Bohai Sea. Xiaoqing River has a catchment area of 13 000 km² and five major tributaries feeding into the main river stream (Gao et al., 2014). The river basin is densely populated, flowing through the major cities of Jinan, Zibo, Binzhou, Dongying, and highly industrialized. The average annual precipitation is about 620 mm, with more than 60% of the rainfall during June, July and August. The average river water flux to the Bohai Sea has been estimated to 1.9×10^9 m³ per annum (m³/yr) (Wang et al., 2014b).

Previous monitoring studies performed by our research group (Table S3) and others (Wang et al., 2014b) have observed highly elevated concentrations of PFCAs in water samples from Xiaoqing River. Based on a recent emission inventory (Wang et al., 2014a) and detailed studies of Chinese industry patent literature (Tang et al., 2009; Cao et al., 2010; Wang et al., 2010; Xie et al., 2011; Xia and Wei, 2013), we identified two FP production facilities with suspected discharge to Xiaoqing River (Fig. 1) (Wang et al., 2014a, b). One FP production facility located in tributary 4 (T4) belongs to the Dongyue group and is currently one of the major facilities for polytetrafluoroethylene (PTFE) production in China with a reported production of 37 000 tonnes per annum (t/yr). The same facility also produces approximately 500 t/yr of perfluorinated ethylene-propylene copolymers (FEP), 300 t/yr of polyvinylidene fluoride (PVDF) and 40 t/yr of APFO. The other FP production facility at tributary 3 belongs to the company 3F Jinan and has a substantially lower production capacity (100–1000 t PTFE/yr) (Wang et al., 2014b).

2.2. Sampling of water and sediment

Based on suspected point sources, the sampling area was divided into four sections: urban and waste water effluents (Section 1), minor FP point source (Section 2), major FP source (Section 3) and marine estuary (Section 4). In total, 36 surface water (W1–W36) and 33 sediment samples (S1–S28, S32, S34–S36) were collected every 5–10 km from the main river stream and the Bohai Sea. One or two water (TW1, TW2, TW3-1, TW3-2, TW4-1, TW4-2, TW5) and sediment samples (TS1, TS2, TS3-1, TS3-2, TS4-1, TS4-2 and TS5) were also collected from each of the five main tributaries. All samples included in the spatial trend were collected on April 24–26th, 2014. Prior to the spatially resolved sampling campaign, two pilot studies on water samples from Xiaoqing River had been conducted. In the first pilot study, six water samples were collected on May 29th 2013 between site 22–24. In the second pilot study, five water samples were collected on August 28th 2013 from sampling sites 22–26.

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