



# Estimating industrial and domestic environmental releases of perfluorooctanoic acid and its salts in China from 2004 to 2012



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## HIGHLIGHTS

- China's first source-specific inventory of PFOA/PFO environmental releases.
- More PFOA/PFO came from industrial activities than domestic sources.
- East China was the emission hotspot because of the agglomeration of fluorochemical industry.
- China is now the world's largest PFOA/PFO emitter.

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## ABSTRACT

China has been documented as one of the few remaining producers of perfluorooctanoic acid and its salts (PFOA/PFO) and the world's major contamination hotspot. However, limited information has been available for evaluating their environmental releases in China and the contribution to global PFOA/PFO burden. Here we present the first source-specific inventory for environmental releases of PFOA/PFO in China from 2004 to 2012, using a bottom-up approach for industrial sources and an inverse approach for domestic sources. Our results show that China became the current world's largest PFOA/PFO emitter, with cumulative environmental releases reaching 250 tonnes (t) over the period of nine years. The eastern region was identified as the hotspot of environmental releases. Most of the national environmental releases were due to the activities of the fluorochemical industry (94.0%) rather than domestic use of PFOA/PFO-related consumer products (6.0%). Fluoropolymer manufacturing and processing, a dominating industrial source, contributed 83.7% of the national environmental releases. In contrast to the general decline trends in annual industrial environmental releases of PFOA/PFO in most industrialized countries, the trend increased in China because of the expansion of production as a result of the global geographical transition in fluorochemical industry. Based on these results, we recommend that the future reduction options are required in industrial sector in China.

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## 1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been used as water, oil, grease, and stain repellent surfactants in a vast array of industrial and commercial end products over decades (Kissa, 2001; Posner, 2012; OECD, 2013). Most of long-chain PFASs gained increasing global attentions (Renner, 2001; Scheringer et al., 2014) because of their persistence (e.g., Parsons et al., 2008), tendency to bioaccumulate (Conder et al., 2008), global distribution (Giesy and Kannan, 2001) and potential carcinogenicity (Steenland

et al., 2010). Among the PFAS family are the two most abundant old-generation members, perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their corresponding derivatives. Because of their adverse environmental impacts, PFOA and its salts (collectively referred as PFOA/PFO), as well as PFOS and its related chemicals, have been covered by a series of national and multilateral regulation agreements (OECD, 2013); for example, the U.S. Environmental Protection Agency (USEPA) and the world's eight major fluoropolymer and fluorotelomer manufacturers initiated the voluntary 2010/2015 PFOA Stewardship Program, to achieve a 95% reduction in industrial PFOA emissions and residual PFOA content in commercial products by 2010 and a complete elimination by 2015 (USEPA, 2013). Furthermore, PFOS and its related chemicals have been subjected to international restriction and elimination

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as a persistent organic pollutant under the *Stockholm Convention on Persistent Organic Pollutants* (POPRC, 2006).

China is a hotspot of PFOA/PFO contamination (e.g., Yamashita et al., 2005; Mak et al., 2009). First, China is one of the few remaining major producers (Wang et al., 2014) and the largest consumer of PFOA/PFO thus far (Mei, 2007). China's national production capacity of PFOA/PFO plateaued at approximately 150 t year<sup>-1</sup> by 2013 after a decade of continuous expansion (CAFSI, personal communication). The capacity expansion was the epitome of the global geographical transition in fluorochemical industry after voluntary withdrawal of the world's major fluorochemical manufacturers (Huang et al., 2010). Meanwhile, materials associated with PFOA/PFO and their precursors are not banned for use in various industrial and domestic applications (Mei, 2008). PFOA/PFO are detectable, as impurities, residuals or degradation products, in a wide range of commercialized technical goods and consumer products, even in food-contact materials such as packaging bags ( $12.9 \pm 1.3 \text{ ng cm}^{-3}$ ) and disposable cups ( $8.8 \pm 2.4 \text{ ng cm}^{-3}$ ) (Feng, 2011). Moreover, PFOA/PFO are frequently detected at appreciable levels in the ambient environment, dairy foods and human serum near fluorochemical manufacturing sites (Bao et al., 2010; Wang et al., 2010) and in populated urban areas (Zhang et al., 2006; Jin et al., 2007; So et al., 2007). The documented extreme values of PFOA/PFO concentrations suggest enormous potential risks of PFOA/PFO to the environment and inhabitants; for example, a concentration of up to 1595 ng l<sup>-1</sup> in surface water of urban Shanghai (Zhang et al., 2006) is triple the calculated predicted non-effect concentration (PNEC) of 570 ng l<sup>-1</sup> (Cao et al., 2013). The risk implied by China's PFOA/PFO contamination status has become a pressing issue for both the scientific community and government regulators.

The spatial and temporal PFOA/PFO risk profile must be elucidated for better risk-based decision making in regulatory efforts; this necessitates a quantitative inventory of the production and environmental releases of PFOA/PFO (Renner, 2001; Armitage et al., 2009). An inventory also facilitates the identification and prioritization of environmental risks to enable the formulation of appropriate time- and site-specific action plans (Secretariat of the Stockholm Convention, 2012). Heretofore, source-specific inventories are only available on the global scale (Prevedouros et al., 2006; Wang et al., 2014); inverse estimates based on monitoring data in riverine runoff (McLachlan et al., 2007; Pistocchi and Loos, 2009) and wastewater treatment plant effluents (Kim et al., 2012) are available for a few industrialized regions. The national environmental releases of PFOA/PFO in China remains poorly investigated, apart from some brief reports from industrial surveys (Mei, 2007, 2008). To bridge the data gap, this study presents the first national source-specific inventory of the environmental releases of PFOA/PFO from industrial and domestic sources at the regional resolution across China (the terminology and division of regions are detailed in Text S1 and Fig. S1 of the Supplementary Information).

In this study, we first identified possible PFOA/PFO sources throughout the life-cycle of manufacturing, processing and use activities. Next, we separately estimated environmental releases from industrial and domestic sources (for terminology, see Text S1) using distinct methods to accommodate their dissimilar emission behaviors. A “bottom-up” approach was adopted for industrial sources because of their isolated and discrete distribution and their relatively fixed, measurable and quantifiable emission factors. An “inverse” approach was applied for domestic sources because of their diffuse and widespread distribution and their variable, untraceable and elusive emission factors. Environmental releases of PFOA/PFO in China were compared with those in industrialized countries, and potential future reduction options were discussed.

## 2. Source identification and estimation of environmental releases

### 2.1. Industrial sources

Fig. 1 presents the entire life-cycle of the fluorochemical industry from which PFOA/PFO are released. In this study, we estimated environmental releases from industrial sources using the “bottom-up” approach in line with Prevedouros et al. (2006) and Wang et al. (2014). Specifically, environmental releases are products of surveyed production and consumption data on PFOA/PFO and their downstream products (activity data) and the relative emission intensity per unit of industrial activities (emission factor). The national environmental releases were spatially allocated to a regional level using surrogate data (Table S2). Here, we outline the major features of our calculation; we detail the sources, assumptions and estimates of the data and the associated uncertainties in Text S3.

#### (1) Source #1: PFOA/PFO production

A total of 480 t of PFOA/PFO was produced in China during the period of 2004–2012 (CPCIF, 2005–2013; Mei, 2007; CAFSI, personal communication). During the manufacturing process, PFOA/PFO are released on-site as tail gas, wastewater and solid waste, and off-site in landfills (3M Company, 2000). Worldwide, there are two principal synthesis routes in PFOA/PFO production (Buck et al., 2011): electrochemical fluorination (ECF) and telomerization (TM) (for details, see Text S2 and Fig. S2). Whereas in China, only the ECF process is used in PFOA/PFO production, largely because of its advantages in yield and cost over the ECF process (CAFSI, personal communication) (CAFSI, personal communication). The dominance of the ECF process is consistent with the results of environmental monitoring of linear and branched PFOA isomer profiles in the waters of Shanghai and Hangzhou (Benskin et al., 2010). The TM process has recently been implemented by two manufacturers (Ni, 2006; Ruan et al., 2010; Tao, 2011) to manufacture and process fluorotelomers and certain derived fluorocarbon surfactants, rather than PFOA/PFO. At present, no on-site mass balance analyses are available for China-specific emission factors in PFOA/PFO production process. Given that there were few technical differences between China's ECF process and that used in other countries (CAFSI, personal communication), here we performed our own estimation (Eq. (1)) using the emission factors available from the manufacturing facilities of 3M Company (3M Company, 2000), which is the historical world's largest ECF PFOA/PFO manufacturer. The emission factors were assigned an uncertainty in normal distribution with a 95% confidence interval of  $\pm 20\%$  of the mean value, to characterize the difference and variability in the performance of pollution abatement technologies between and within 3M Company and Chinese manufacturers.

$$\text{Environmental releases} = \text{Production volume of PFOA/PFO} \times \text{Emission factors} \quad (1)$$

#### (2) Source #2: Fluoropolymer (FP) manufacturing and processing

The produced PFOA/PFO are predominantly used as emulsifiers, i.e., processing aid agents used to homogeneously solubilize suspensions of backbone fluoropolymers and fluoroelastomers in suspension and emulsion polymerizations (Fig. 1) (USEPA, 2002; IPCS, 2009). During FP manufacturing and processing, aerial PFOA/PFO are released from the heating and drying process, and liquid and solid PFOA/PFO wastes are discharged from aqueous dispersion processes (Paustenbach et al., 2006). In China, PFOA-based emulsifiers are employed in manufacturing and processing

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