



# Perfluorinated compounds in soil, surface water, and groundwater from rural areas in eastern China<sup>☆</sup>



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## ABSTRACT

Little research on perfluorinated compounds (PFCs) has been conducted in rural areas, although rural PFC sources are less complicated than in urban and industrial areas. To determine the levels and geographical distribution of 17 PFC compounds, samples of soil, surface water, and groundwater were collected from eight rural areas in eastern China. The total PFC concentrations ( $\sum$ PFCs) in soils ranged from 0.34 to 65.8 ng/g  $\sum$ PFCs in surface waters ranged from 7.0 to 489 ng/L and  $\sum$ PFCs in groundwater ranged from 5.3 to 615 ng/L. Ratios of perfluorononanoic acid/perfluorooctanoic acid (PFNA/PFOA), perfluoro-n-butyric acid/perfluorooctanoic acid (PFBA/PFOA), and perfluoroheptanoic acid/perfluorooctanoic acid (PFHpA/PFOA) in rainwater increased due to the fluorine chemical plants in the surrounding rural and urban areas, suggesting that atmospheric precipitation may carry PFCs and their precursors from the fluorochemical industrial area to the adjacent rural areas.

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## 1. Introduction

Perfluorinated compounds (PFCs) contain a carbon chain with fluorine atoms attached in place of hydrogen atoms and one or more functional groups attached to the end. Due to the strength of the carbon/fluorine bond, the molecules are chemically very stable and are highly resistant to biological degradation. PFCs have been widely used in industrial products and processes and in a wide variety of consumer products, such as stain-resistant textiles and fabrics, fire-fighting foam, agrochemicals, surface cleaners, and cosmetics (Prevedouros et al., 2006; Wang et al., 2010). Among these compounds, perfluorooctane sulfonate (PFOS,  $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{H}$ ) and perfluorooctanoic acid (PFOA,  $\text{CF}_3(\text{CF}_2)_6\text{COOH}$ ) have received more attention than other PFCs because of their ubiquity in the environment. PFCs are globally distributed, environmentally persistent, and bioaccumulative. Numerous publications outline the negative effects of PFCs on human health; these chemicals may be ingested with food and drinking water, thereby posing a human health threat (Domingo, 2012).

Large-scale production of PFCs in China began in 2003 following 3M's 2002 global PFOS phase-out (Wang et al., 2010). The manufacturers of PFCs in China are mainly located in central and eastern China where concentrations of PFOA and PFOS in surface water have been reported, showing high levels in eastern China especially in the Yangtze River Delta region (Zhao et al., 2015; Wang et al., 2012, 2013; Lu et al., 2015). Pollution levels and spatial distributions of PFCs in soil and surface water are generally related to the extent of industrialization and urbanization (Wang et al., 2012). Therefore most previous researches on PFCs in China has focused on major rivers and lakes in industrial and urban areas as well as PFC sources such as municipal wastewater treatment plants (WWTPs) and fluorochemical plants (Sun et al., 2011; L. Wang et al., 2011; Wei et al., 2013). Although PFCs in remote areas of China have been reported (Wang et al., 2014), research on distribution of PFCs in rural and agricultural areas is scarce. Relatively speaking, the rural areas may serve as the "background areas" for PFC pollution of urban areas. PFC sources in rural areas may simply originate from domestic and farming wastewater and from atmospheric precipitation. However, rural areas in close proximity to cities may be affected by urban industrial pollution. Along with general urbanization, small enterprises have been developing rapidly over the past two decades in rural parts of the country, especially in eastern China which is one of China's most active economic regions. A

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Careful study of PFC distributions in rural areas in this region may reveal how urbanization and industrialization affect the PFC contamination levels in these areas and may help identify the sources that are transferring PFCs to the aquatic environment and soil. Thus, the aim of this study is to obtain information on the geographical distribution and characteristic PFC compositions in selected rural areas in eastern China which might help identifying PFC sources.

## 2. Material and methods

### 2.1. Reagents

Potassium salts of perfluorooctane sulphonate (PFOS), perfluorohexanesulphonate (PFHxS), perfluorobutanoic acid (PFBA), perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluoropentanoic acid (PFPeA), and perfluorohexanoic acid (PFHxA) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Perfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnDA), perfluorodecanoic acid (PFDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFOcDA), perfluorotetradecanoic acid (PFTrDA), perfluorodecane sulfonate (PFDS), and perfluorobutanesulphonate (PFBS) were purchased from Fluorochem Ltd. (Derbyshire, UK). 13C4-PFOS, 13C2-PFDA, 13C5-PFNA, 13C4-PFOA, 13C4-PFBA, 13C2PFHxA, 13C2PFUnDA, <sup>13</sup>C<sub>2</sub>PFDoDA, and <sup>18</sup>O<sub>2</sub>PFHxS were purchased from Wellington Laboratories Inc. (ON, Canada). The purity of all analytical standards was 95%. Oasis weak anion exchange (WAX; 6 cm<sup>2</sup>, 150 mg, 30 mm) solid phase extraction (SPE) cartridges were purchased from Waters Corp. (Milford, MA, USA). Milli-Q water was used during the course of the experiment. Methanol (residual pesticide and PCB analytical grade), ammonium acetate (97%), ammonium solution (25%), acetic acid (99.9%), were obtained from Wako Pure Chemical Industries Ltd.

### 2.2. Sampling

Soil (n = 76), surface water (n = 34), and shallow groundwater (n = 52) were collected from villages in rural areas of Changshu, Taicang, Yangzhou, Yancheng, Huai'an, Tai'an, Liaocheng, and Tianjin during May 2014 and April 2015 (Fig. 1). The villages in Changshu are located 1–10 km from a fluorine chemical industry park where samples were also collected. The other villages are 20–30 km from urban areas. For comparison, samples from a Suzhou urban area were collected.

Top soil samples (top 0–10 cm) were collected with a stainless steel trowel. Samples were then transferred and stored in clean polypropylene (PP) bags. Duplicates and field blanks were collected at each sampling area and were analyzed along with lab and procedural blanks with each group of samples. Upon arrival at the laboratory, samples were transferred to PP boxes, air dried, homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, and stored in 250 mL PP bottles at room temperature until extraction.

Surface water samples were collected in 500-mL PP bottles from the rivers in or near the villages. The shallow groundwater (water table: 8–40 m) samples were directly collected from the courtyards of farms. Every sampling site was recorded using GPS (Garmin Ltd., Olathe, KS, USA). The water samples were stored at 4 °C until analysis. The field blanks and travel blanks contained the Millipore water.

Rainwater samples were collected at the fluorine chemical industry park at Changshu and from the neighboring rural areas of Changshu and Taicang, and Suzhou urban area and in May 2015, in

order to better understand the influence of the fluorine chemical industry park on the surrounding areas. Rainwater samples were collected in Beijing urban area in September 2015 for the sake of comparison. Rainwater samples were collected using a stainless steel bucket and stored in the same manner as the other water samples.

The sampling information is listed in [Supplementary Table S1](#).

### 2.3. Pretreatment and purification

Soil and water samples were analyzed for 17 PFCs, including PFOS, PFHxS, PFBS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, and PFOcDA. Extraction of PFCs from soil samples was accomplished using a method similar to the authors' previously published method (Lu et al., 2011). The water samples were extracted using the solid phase extraction method. An Oasis WAX column (6 cc, 150 mg/6 mL, Waters Corp., Milford, MA, USA) was activated with 4 mL of 0.1% ammonia–methanol solution, methanol, and Milli-Q water before loading samples. A water sample of 500 mL was loaded into the column at a rate of 2–3 drops/s. Milli-Q water was used during the course of the entire experiment. The column was then leached with 4 mL of 25 mmol/L acetate buffer solution (pH = 4) to remove impurities, and then centrifuged to remove water. The analytes were eluted with 4 mL of methanol and 4 mL of 0.1% ammonia–methanol solution. The volume of eluent was reduced to 1 mL using high purity nitrogen gas to ready the eluent for the LC-MS/MS measurement.

The soil samples were air-dried and milled through a 60 mesh sieve. A 1 g soil sample was weighed and transferred to a 50 mL PP centrifuge tube, and 5 mL of methanol was added. The solution was mixed homogeneously by ultrasonic mixing for 8 min at 35 °C and centrifuged for 30 min at 2000 r/min. The supernatant was transferred to the new centrifuge tube and this process was repeated in triplicate. The total volume of the combined supernatant was 15 mL, which was then reduced to 1–2 mL under a gentle stream of high purity nitrogen. The subsequent cleanup steps were the same as in the water sample processing. Finally, the eluent was evaporated to 0.5 mL by high-purity nitrogen and passed through a 0.22 μm organic phase nylon syringe filter (ANPEL Laboratory Technologies (Shanghai) Inc., China), to ready the eluent for the LC-MS/MS measurement.

### 2.4. Instrumental quantification

PFCs were determined by a tandem mass spectrometer (API 4000, Applied Biosystems Inc., Framingham, MA, USA) coupled with HPLC (Agilent Technologies 1200) operated in the electrospray negative ion mode. The LC column used was an RSpak JJ-50 2D ion exchange column (2.0 mm × 150 mm, 5 μm; Shodex, China). The injection volume was 10 μL. The analytes were eluted with 50 mmol/L ammonium acetate–methanol mixed solution (volume ratio 2:8) in isocratic elution mode at a flow rate of 300 μL/min for 20 min. The column temperature was 40 °C. The electrospray ionization voltage was 4000 kV, using negative mode ion source, and the ion source temperature was 350 °C; the air curtain air pressure was 1.0 MPa, the atomizing air pressure 5.0 MPa, the desolvation gas pressure 5.0 MPa, the cone gas flow rate 20 L/h, and the collision gas pressure 1.0 MPa. The multiple reaction monitoring (MRM) mode was used. Calibration curves for the instrument were prepared with a series of seven concentrations at 0, 2, 10, 50, 200, 1000, 5000, and 25,000 pg mL<sup>-1</sup>. The standard deviation of every point was less than 20%. The instrumental response of target analytes was confirmed for quantification using individual chromatograms.

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