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Perfluorinated compounds in soil, surface water, and groundwater from rural areas in eastern China[☆]



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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, ¹³C₂PFDoDA, and ¹⁸O₂PFHxS were purchased from Wellington Laboratories Inc. (ON, Canada). The purity of all analytical standards was 95%. Oasis weak anion exchange (WAX; 6 cm², 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⁻¹. The standard deviation of every point was less than 20%. The instrumental response of target analytes was confirmed for quantification using individual chromatograms.



Fig. 1. Maps of the sampling areas.

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

To achieve lower detection limits, all of the accessible PTFE and fluoropolymer materials in the instruments and apparatus were replaced with materials made of polyetheretherketones (PEEK) to minimize a background signal caused by contamination. Procedure and travel blanks for water were collected. The recovery test was carried out using both surrogates and native standard chemicals. If the recovery exceeded the acceptable range (65–125%), samples were reanalyzed. Matrix recoveries were also conducted by adding surrogates and native standard chemicals to real samples (Table 1). Quantitative responses according to the amount of standards added were evaluated. The concentrations of analytes were calculated using an external calibration curve.

Blanks and recoveries were extracted in duplicate for every twelfth sample to ensure stable repeatability. When repeatability was realized, the peak area was greater than the procedure blank, and signal/noise ratio (S/N) was ≥ 3 , then the lowest concentration of the target analyte was defined as the LOD of the method.

3. Results and discussion

3.1. Soils

The mean total PFC concentrations in soil from eight rural areas (Changshu, Taicang, Yangzhou, Yancheng, Huai'an, Tai'an, Liao-cheng, and Tianjin) and one urban area (Suzhou) in eastern China are summarized in Fig. 2. Detailed concentrations of individual PFC compounds are provided in Table S2. Seventeen PFCs (C4–C10) were detected in all samples with detection rates of most compounds > 80%. In general, PFOA and PFUnDA were the most prominent PFCs detected in soil, at a rate of 100%, followed by PFBA and PFDA. The most frequently detected perfluoroalkane sulfonate

(PFSA) was PFOS, while PFHxS and PFBS were almost undetectable.

The total PFC concentrations (\sum PFCs) in soils ranged from 0.34 to 65.8 ng/g dw (dry weight). Changshu was the most contaminated region in the study area, with PFOA as the predominant compound accounting for 73% of total PFCs, which may be attributable to the fluorine-related industries in the Changshu Fluorochemical Industrial Park (Wei et al., 2013). The composition of PFCs in soil shifted gradually with a greater distance from the industrial park, with more PFBA, PFNA, and PFOS detected (Fig. 3(a)). The influence of the fluorine-related industries on the rural soils extended to a distance of 11 km judging from the changes in PFC composition.

Except for samples from Changshu, PFCs were detected at low levels in the rural areas where PFOA, PFDA, and PFBA were the most abundant perfluorocarboxylic acids (PFCAs) in the soils and PFOS was the most abundant PFSA (Fig. 3(a)). The lowest \sum PFCs was found in Huai'an. These levels are well below the health-based guidelines for PFCs in soil proposed by the U.S. Environmental Protection Agency (6 mg/kg for PFOS and 16 mg/kg for PFOA) (MDH, 2014).

Except for Tianjin, the PFC concentration levels in soil were generally high in the Yangtze River Delta region, and generally low in the Huai River watershed area (Yancheng and Huai'an) and Yellow River watershed area (Tai'an and Liao-cheng), with a decreasing trend from south to north between the Yangtze River and the Yellow River. Compared to the Yangtze River Delta and Tianjin areas, the Huai River and Yellow River watershed areas are less populated and industrialized. Therefore they may be regarded as typical rural areas.

PFoCDA, PFHxDA, PFHxS, PFDS, and PFBS were not detected in most areas except for Changshu and Tianjin. Compared with reported data of PFCs in soil from other parts of China, the PFOA concentrations in soil from Changshu was the highest, exceeding

Table 1
Parameters of mass spectrometry, recoveries, and the limits of detection (LODs) for individual PFCs in water (ng/L) and soil (ng/g) samples.

Compounds	Precursor ion (m/z)	Product ions (m/z)	Declustering potential (DP/V)	Entrance potential (EP/V)	Collision energy (eV)	Collision cell exit potential (CXP/V)	LOD		Average recovery (%)		Matrix recovery (%)	
							Water (ng L ⁻¹)	Soil (ng g ⁻¹)	Water	Soil	Water	Soil
PFBA	212.8	168.9	-26	-10	-14	-10	0.1	0.01	92.0	57.8	94.7	93.2
PFPeA	262.8	218.9	-30	-10	-13	-15	0.2	0.005	91.5	60.1	90.5	76.8
PFHxA	313	268.9	-35	-10	-13	-18	0.2	0.005	89.2	59.5	103.8	104.3
PFHpA	363	319	-40	-10	-14	-6	0.5	0.01	90.6	62.6	108.3	102.9
PFOA	412.8	369	-43	-10	-16	-8	0.1	0.005	85.9	73.8	98.4	92.6
PFNA	462.8	419	-40	-10	-15	-20	0.1	0.01	96.1	71.2	86.0	77.4
PFDA	512.8	469	-45	-10	-15	-6	0.5	0.005	85.3	66.5	89.4	84.9
PFUnDA	562.8	519	-45	-10	-18	-22	0.2	0.01	82.1	69.7	73.4	67.6
PFDoDA	612.8	569	-50	-10	-18	-30	0.5	0.01	67.3	62.2	53.8	71.6
PFTTrDA	662.8	619	-34	-10	-18	-25	0.5	0.01	41.5	51.5	58.5	67.5
PFTeDA	712.8	669	-50	-10	-20	-35	0.2	0.01	28.3	59.6	54.8	54.3
PFHxDA	813	769	-45	-10	-20	-35	0.2	0.01	86.6	84.7	56.0	71.7
PFOcDA	912.8	869	-48	-10	-22	-36	0.2	0.01	58.0	88.8	81.6	72.6
PFBS	298.8	80	-70	-10	-55	-10	0.5	0.005	93.5	65.8	71.0	79.3
PFHxS	398.8	80	-90	-10	-75	-6	0.5	0.005	95.8	69.5	65.1	61.2
PFOS	499	80	-90	-10	-90	-8	0.5	0.005	96.1	72.0	82.3	70.5
PFDS	598.8	80	-150	-10	-110	-13	0.5	0.01	75.7	61.7	64.1	52.9
¹³ C ₄ PFBA	217	172	-40	-10	-14	-6					70.6	88.0
¹³ C ₄ PFHxA	315	270	-40	-10	-14	-6					92.4	95.0
¹³ C ₄ PFOA	417	372	-40	-10	-14	-6					87.2	96.5
¹³ C ₅ PFNA	468	423	-50	-10	-15	-6					82.1	96.1
¹³ C ₂ PFDA	515	470	-50	-10	-15	-6					62.7	98.0
¹³ C ₂ PFUnDA	565	520	-50	-10	-16	-6					59.0	82.3
¹³ C ₂ PFDoDA	615	570	-50	-10	-17	-6					39.8	76.7
¹⁸ O ₂ PFHxS	403	103	-100	-10	-55	-6					74.4	76.9
¹³ C ₄ PFOS	503	99	-100	-10	-70	-6					87.0	73.6

those of Shanghai, Beijing, and Tianjin (Pan et al., 2011; Wang et al., 2012a,b, 2011; Li et al., 2010; T.Y. Wang et al., 2011). Although higher levels were found in Tianjin, the nature of the contamination differs from Changshu. Tianjin is a metropolitan industrial city and one of the most severely contaminated areas in China. PFDA, PFDS, PFBS, and PFHxS were detected in the Tianjin rural area, and a strong WWTP influence on the surface waters in Tianjin was suggested (Pan et al., 2011; Wang et al., 2012a,b).

In several soil samples, higher levels of PFOA than PFOS were observed, which is contrary to reports of soils with higher PFOS than PFOA concentrations, such as soils in the Pearl River Delta (Hu et al., 2013). It has been reported that the global level of PFOS in soil averages 0.47 ng/g dw and PFOA averages 0.12 ng/g dw (Rebecca, 2001). With a higher K_d (solid–liquid partition coefficient), PFOS is more easily adsorbed onto particles than PFOA (Milinovic et al., 2015). However, soils in rural areas are subject to atmospheric precipitation and agricultural irrigation, in which the PFOA concentration is generally higher than PFOS. The most abundant PFC in rainwater in eastern China has been reported as PFOA (Zhao et al., 2013); therefore, higher PFOA than PFOS may occur in soil shortly after precipitation occurs. As our sampling period took place in the rainy season (April) of eastern China, higher concentrations of PFOA than PFOS could be expected. Fig. 2(a) also shows the annual precipitations in the studied areas.

3.2. Surface waters

The mean total concentrations of PFCs in surface waters from rural areas of the eight regions in eastern China are illustrated in Fig. 2(b). Detailed concentrations of individual PFC compounds are provided in Table S3. C₄–C₁₀ PFCs were detected in all samples, whereas the detection rate of long-chain (C₁₁–C₁₈) compounds was low. PFOA, PFHxA, and PFBA were the most abundant PFCAs.

PFOS was the most abundant PFAS, followed by PFHxS and PFBS. PFBS was detected in Changshu, Tai'an, and Liaocheng. The lowest detected compound was PFDS which was detected only in Tai'an.

The \sum PFCs in surface waters ranged from 7.0 to 489 ng/L. The most contaminated surface water observed was from Changshu. Except for Changshu and Tianjin, the PFC concentration levels generally showed a decreasing trend from south to north. Compared with PFC levels in surface waters reported in other parts of eastern China, PFC levels in the rural areas except for Changshu area were lower than those of the Shanghai section of the Yangtze River (170 ng/L) (Lu et al., 2011) and Taihu Lake (66.6 ng/L) (Zhang et al., 2012). The difference in \sum PFCs in surface waters between the rural and urban areas can also be seen from Fig. 2(b), in which \sum PFCs in Suzhou urban area were significantly higher than those in certain rural areas at Changshu even the later is located nearer to the Fluorochemical Plants than Suzhou.

3.3. Groundwater

The mean total PFC concentrations in groundwater samples from six rural areas in eastern China are shown in Fig. 2(c). Detailed concentrations of individual PFC compounds are provided in Table S4. In general, the detection rates of compounds were low in groundwater compared to surface waters. C₄–C₁₀ PFCs were detected in all samples. The most detected PFCAs in groundwater were PFBA and PFOA, followed by PFNA, PFHpA, and PFHxA. The most detected PFAS was PFBS, followed by PFOS and PFHxS. PFDS was almost undetectable. The number of detected PFC compounds in groundwater samples was much smaller compared to soil and surface water samples, and the long-chain PFCAs were almost undetectable.

The total PFC concentrations in the groundwater samples ranged from 5.3 to 615 ng/L, with the highest concentration

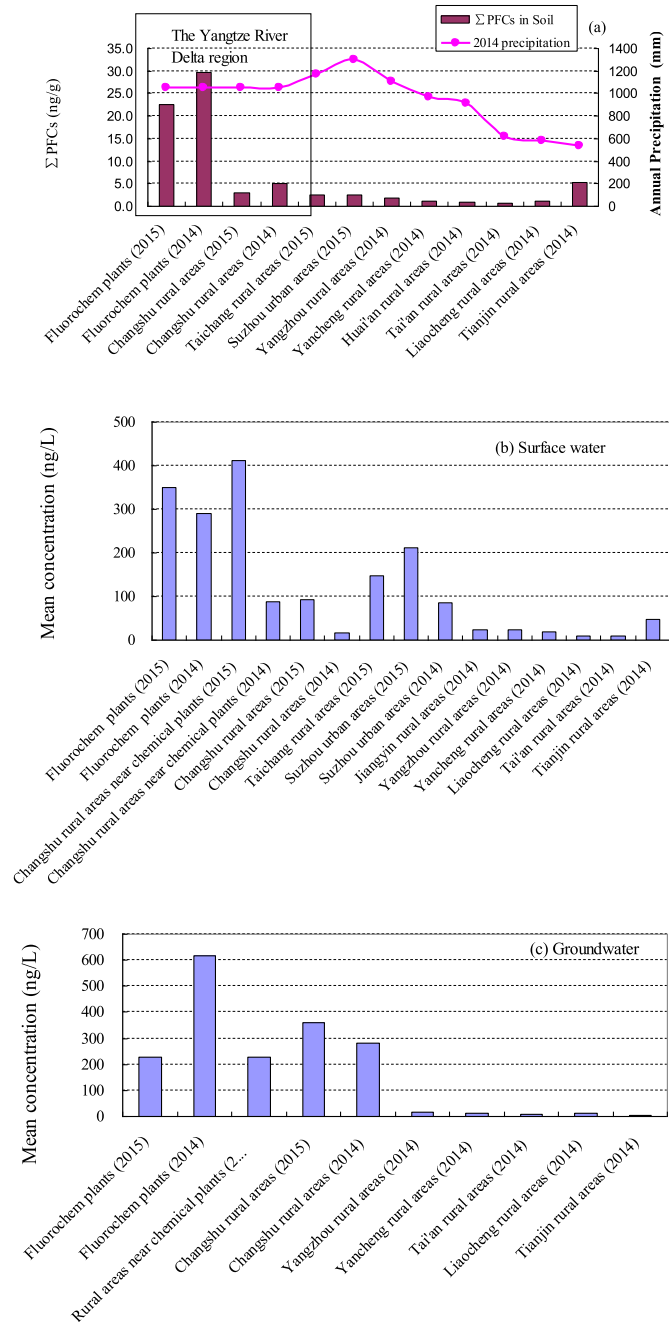


Fig. 2. Geographical distributions of the mean total concentrations of PFCs in (a) surface soil, (b) surface water, and (c) groundwater in rural areas of eastern China.

occurring in the fluorochemical industrial area. Except for Changshu and Tianjin, PFC concentration levels in groundwater were generally higher in the Yangtze River Delta region and showed a decreasing trend from south to north as follows: Changshu (269.1 ng/L) > Yangzhou (8.5 ng/L) > Yancheng (3.57 ng/L) > Tai'an (1.68 ng/L) > Liaocheng (0.45 ng/L) > Tianjin (0.20 ng/L) in 2014 (Fig. 2(c)).

PFC concentrations in groundwater were significantly lower than those in surface waters except for Changshu; PFCAs in groundwater were twofold higher than in surface water in Changshu rural areas, whereas PFSAs in groundwater were at levels similar to the surface water. Changshu is located in the

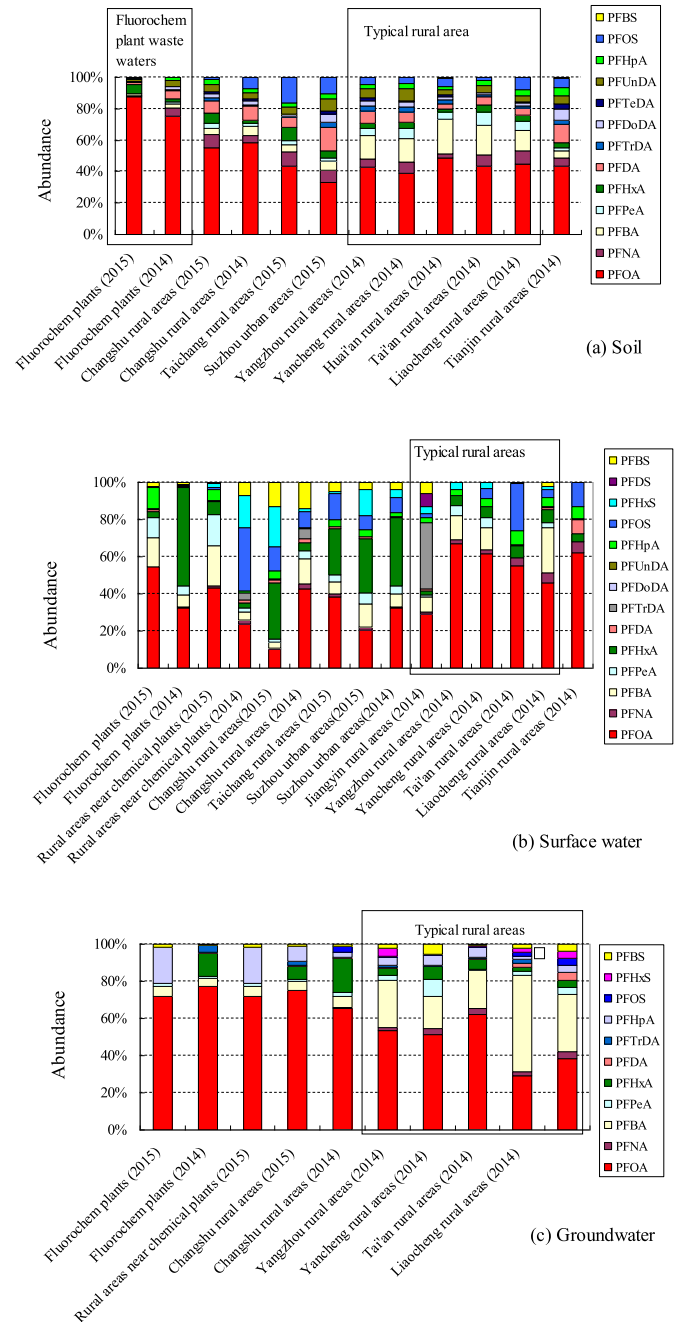


Fig. 3. Geographical distributions of concentrations of individual PFCs in (a) surface soil, (b) surface water, and (c) groundwater in rural areas of eastern China.

Yangtze River Delta with a densely distributed river network and higher water tables in the groundwater aquifers. Therefore, river water may penetrate into the aquifers. The proportion of PFOA increases and PFOS and PFHxA decrease from the surface water to the groundwater. In addition, the short-chain C4 compound PFBS was detected in surface water although it was significantly less present in soil and groundwater samples. Due to low toxicity, PFBS has been used by the fluorochemical industry as a replacement for PFOS in production; it is also a degradation product of PFCs. It has been reported that PFBS exists in effluent from many WWTPs in Europe (Möller et al., 2009).

3.4. The influence of fluorochemical industries on the surrounding rural areas

The major components in wastewater effluent discharged from Changshu Fluorochemical Industrial Park were found to be PFOA (99%), and small amount of PFHxA and PFPeA (Wei et al., 2013) (Fig. 3(b)). However, in rural areas of Changshu, the proportions of compounds other than PFOA detected in surface water increased with distance from the industrial park (Fig. 3(b)), indicating an increasing contribution of PFC contamination from other sources (for example, domestic sewers and atmospheric precipitation).

Although the C8 compound PFOA was dominant in soils in the Changshu fluorochemical industrial area, proportions of C9 compound PFNA increased in the surrounding rural areas at a distance from the industrial park. It has been suggested that the increase in C9 compounds may reflect atmospheric transport and degradation of relatively volatile precursors of PFCs such as 8:2, 10:2, and 12:2 fluorinated telomer alcohols (FTOHs) (Armitage et al., 2009). Therefore, the PFCs in the environmental media at a distance from the fluorochemical industrial park may partly result from atmospheric sources associated with direct air emissions from the manufacturing plants.

Compositions of PFCs in rainwater samples collected at the fluorine chemical industry park at Changshu and the neighboring Suzhou and Taicang are shown in Fig. 4(a). For comparison, compositions of PFC compounds in rainwater samples collected in

Beijing are also shown in Fig. 4(a). The compositions of PFC compounds in rainwater samples from the adjacent areas were similar to the composition of rainwater at the fluorine chemical industry park but differed significantly from those in Beijing, suggesting the strong influence of the fluorine chemical industry park on the surrounding areas through atmospheric transport of either PFC compounds or their precursors. It also can be seen from Fig. 4(b) that PFNA/PFOA, PFBA/PFOA, and PFHpA/PFOA ratios in rain increased from the fluorine chemical plant area to the surrounding Taicang rural area and Suzhou urban area, and were higher in Beijing.

3.5. Source analysis

The composition of PFCs in samples may provide information on pollution sources to some extent. Some indicators, such as ratios of PFOS to PFOA and PFHpA to PFOA, have been employed to identify potential sources of PFCs (Simcik et al., 2005; So et al., 2004). Atmospheric precipitation has relatively higher PFHpA concentrations than surface water and, thus, the PFHpA/PFOA ratio has been used as a tracer for atmospheric precipitation sources (Simcik et al., 2005).

PFCs in sewage from rural areas may originate from kitchen and toilet sewers, as well as the waste from domestic animal production. The former includes food wrappers, non-stick pans, and food of animal origin, and the latter may include cosmetics, pharmaceuticals, and human/animal urine/feces. The short-chain compound PFBA, which is not easily degradable and has migration capability, may be a degradation product of other PFC compounds, as evidenced by the increasing detection rate in recent years in both wastewater and atmospheric precipitation (Yao et al., 2014; Taniyasu et al., 2013). Unlike PFOS and PFOA, PFBA does not easily bioaccumulate and may be quickly eliminated (Minnesota Department of Health (2015)). Human and animal feces are often directly discharged into surface waters in rural areas of China without any treatment. Perez et al. have reported that the PFBA content in urine samples from 30 people in Barcelona, Spain, measured up to 483.5 ng/L (Perez et al., 2012).

Atmospheric precipitation also contains more volatile degradation products such as fluorotelomer alcohols. PFNA can be a degradation product of fluorotelomer alcohols, as well as a raw material used to manufacture 8:2 fluorotelomer alcohol (OECD, 2007). PFBA and PFHpA may reflect human and livestock excretion (therefore serving as an indirect index of domestic and farm sewage) and atmospheric precipitation sources, respectively, and PFNA reflects the sources of degradation of fluorotelomer alcohols and other industrial sources; thus, this relates a ratio–ratio mixing inverse problem in a binary mixing model for (Sohn, 2005). Based on this concept, the ratios of PFBA/PFOA and PFNA/PFOA versus PFHpA/PFOA were plotted in Fig. 5 for the rural and urban areas surrounding the fluorochemical industrial park. Since PFOA is ubiquitous in the aquatic environment, the concentration of each compound was normalized by PFOA concentration to highlight the changes of these indicative compounds relative to PFOA. The two plots are shown in Fig. 5

Except for two Changshu rural area sampling sites near fluorine chemical plants and two Suzhou urban sampling sites, the two plots generally show good linear correlations for the surface water samples eastern China rural areas with the correlation coefficients of $R = 0.76$ and $R = 0.84$ ($p < 0.05$), respectively. These linear correlations may be understood as a mutual dilution of two-end members, i.e., rural sewage and atmospheric precipitation carrying PFCs and precursors. In addition, the linear correlation between PFNA/PFOA and PFHpA/PFOA ratios can be regarded as indirect proof of PFNA in the atmosphere being a fluorotelomer

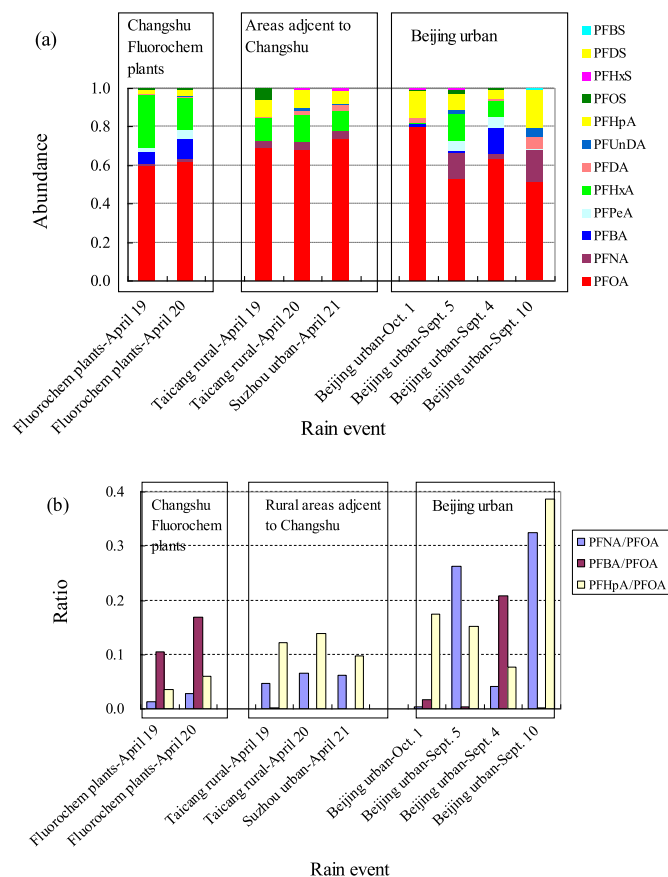


Fig. 4. (a) Comparisons of compositions of PFCs in rainwater at the fluorochemical plant, the surrounding Taicang rural area and Suzhou urban area, and Beijing; (b) PFNA/PFOA, PFBA/PFOA, and PFHpA/PFOA ratios in rainwater from the fluorine chemical plant, the surrounding Taicang rural area, Suzhou urban area, and Beijing urban area.

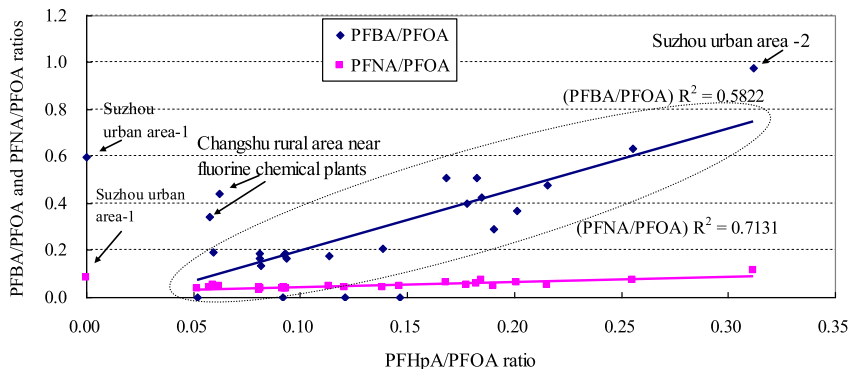


Fig. 5. PFBA/PFOA and PFNA/PFOA ratios versus the PFHpA/PFOA ratio in the surface water samples in eastern China rural areas and the Suzhou urban area.

alcohol degradation product. The abnormal data points in the plots in the plot may indicate sources other than rural sewage and atmospheric precipitation.

4. Conclusions

- (1) PFCs were widely detected, although at low levels, in soil from rural areas in eastern China. Except for samples from Changshu areas, PFCs were detected at low levels in rural areas. PFOA, PFDA, and PFBA were the most abundant PFCAs in the soils and PFOS was the most abundant PFSAs. PFC levels in the Changshu area can be attributed to effects of the nearby fluorochemical industry along with contributions from household and farming sewers and atmospheric precipitation. Except for the Changshu and Tianjin areas, PFC levels in soils decreased from south to north.
- (2) PFOA, PFHxA, and PFBA were the predominant compounds in the surface waters and groundwater in the study area. The PFC level was highest in Changshu, measuring four to eight times higher than levels in other areas studied. Except for the Changshu and Tianjin areas, the PFC concentration levels were generally higher in the sections south of the Yangtze River than sections in the north.
- (3) The detection rates of long-chain PFC compounds were generally lower in groundwater samples than in surface water samples. The levels in groundwater followed an increasing trend from south to north, suggesting a decreasing contribution of atmospheric precipitation. The PFC level in groundwater in the Changshu rural area was higher than levels in the surface water of the same area, the cause of which needs further investigation.
- (4) The PFBA/PFOA and PFNA/PFOA ratios versus the PFHpA/PFOA ratio in surface water were employed to analyze the sources of PFCs in surface water in the eastern China rural areas. The good linear correlation may be understood as a mutual dilution of rural sewage with atmospheric precipitation carrying PFCs and precursors. The abnormal data points in the plots in the plot may indicate sources other than rural sewage and atmospheric precipitation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.12.024>.

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