



# Perfluorinated Compounds (PFCs) in Soil of the Pearl River Delta, China: Spatial Distribution, Sources, and Ecological Risk Assessment

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## Abstract

This study investigated the levels, spatial distribution, sources, and ecological risks of 16 perfluorinated compounds (PFCs) in 68 surface soil samples (0–20 cm) from 7 cities in the Pearl River Delta (PRD), China. Sixteen target PFCs, including perfluoroalkyl carboxylic acids (PFCAs, C<sub>5</sub>–C<sub>14</sub>, C<sub>16</sub>, and C<sub>18</sub>) and perfluoroalkyl sulfonic acids (PFSAs, C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub>), were analyzed by high-performance liquid chromatography-negative electrospray ionization-tandem mass spectrometry (HPLC/ESI-MS/MS). Concentrations of total PFCs ( $\sum$ PFCs) ranged from 2.19 to 98.5  $\mu\text{g kg}^{-1}$  (dry weight, dw), with an average of 5.97  $\mu\text{g kg}^{-1}$  dw. Perfluorooctane sulfonate (PFOS) was the dominant PFC, accounting for 23.9% of  $\sum$ PFCs. The highest  $\sum$ PFCs was found in the soil sample collected from Dongguan with a large number of manufacturing industries. There were no significant differences of  $\sum$ PFCs among urban, industrial, and agricultural soils, indicating similar pollution sources in soil of the PRD. More than 70% of  $\sum$ PFCs in soil of the PRD could be attributed to the four principal components, represented by PFOS and perfluorooctanoic acid (PFOA), perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUDA). Ecological risk assessment indicated that PFOA had low risk to soil plants and animals. However, the risk of PFOS to soil plants was relatively high in some studied regions.

Perfluorinated compounds (PFCs), a family of synthetic compounds in which the functional groups bonded to carbon atoms are completely substituted by fluorine atoms, mainly consist of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). PFCs are widely used in industrial and consumer products, such as surfactants,

pesticides, nonstick coating, fire-retarding foams, and food packaging, due to their excellent thermal and chemical stabilities and high surface activities (Prevedouros et al. 2006). It has been reported that PFCs have environmental persistence, bioconcentration and long-range transport potential, and trophic magnification (Fang et al. 2014; Stock et al. 2007; Wang et al. 2015). As a result, perfluorooctane sulfonate (PFOS) and perfluorooctyl sulfonyl fluoride (PFOSF), were listed as new persistent organic pollutants (POPs) in May 2009.

Due to a few restriction agreements on the production of PFC-related chemicals in Europe and America, such as the perfluorooctanoic acid (PFOA) Stewardship Program and Stockholm Convention, an increasing industrial production demand for PFCs caused PFC-related manufacture industries entering developing countries, including China. Releasing of PFCs to the environment was found during fluoropolymers manufacturing and direct PFCs production (Wang et al. 2014). However, there are currently no laws or criterions restricting the PFC emissions in China. PFCs are ubiquitous in environment due to their high environmental stabilities. Fluorotelomer alcohols (FTOH), *N*-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) and EtFOSE-based phosphate diester, may act

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as the precursors for PFCAs and PFSA (Benskin et al. 2013; Ellis et al. 2004).

As a porous and heterogeneous system, soil plays an important role in environmental fate of PFCs. PFCs enter soil by point source pollution, atmospheric deposition, and surface runoff (Li et al. 2010; Milinovic et al. 2015); PFCs in soil can transfer to air and surface water by volatilization, leaching, and diffusion (Meng et al. 2013). A previous study has shown that the contents of PFCs increased with the increase of soil depth, indicating that PFCs leaching might pose a potential threat to ground water (Xiao et al. 2015). In addition, PFCs in soil can enter the food chain by soil-plant-animal/human system (Fang et al. 2014; Kelly et al. 2009; Loi et al. 2011). Therefore, the investigations on the occurrences of PFCs in soil would contribute to understand the transport, transformation, and ecological risk of PFCs in environment.

The Pearl River Delta (PRD), located in central and southern Guangdong Province, China, covers an area of 54,733 km<sup>2</sup> (Guangdong Statistics Bureau 2012). It is one of the most economically developed, highly industrialized, and densely populated regions in China (Yu et al. 2018). The PRD is famous for its worldwide manufacturing bases; those mainly produce consumer electronics, textiles and garments, household appliances, rubber products, and decorating materials.

The PRD includes many industrial cities, such as Guangzhou, Dongguan, Shenzhen, Huizhou, Foshan, Zhongshan, Zhuhai, Jiangmen, and Zhaoqing. Previous studies have shown that rapid industrialization of the PRD has led to severe contamination of persistent organic pollutants (POPs) in soil, such as polybrominated diphenyl ethers (PBDE) (Gao et al. 2011; Luo et al. 2009; Zou et al. 2007), polycyclic aromatic hydrocarbons (PAHs) (Liu et al. 2011), polychlorinated biphenyls (PCBs) (Zhang et al. 2013), and polychlorinated naphthalenes (PCNs) (Wang et al. 2012a). It was reported that the regional functions had significant effect on the total concentrations of PFCs ( $\sum$ PFCs) in surface soils of Shenzhen (Zhang et al. 2014). Lower levels of PFOS and PFOA were found in surface soils of Zhuhai (Hu et al. 2013). However, few studies have been performed to determine the levels of PFCs in soils of other cities of the PRD.

The objectives of the present study were to investigate the levels and distribution of PFCs in soils of the PRD, thereby to identify the sources of individual PFC and assess the potential ecological risks of typical PFCs. This study will provide information on PFC management and soil remediation.

## Materials and Methods

### Standards and Reagents

The external standard was a mixture of 16 PFCs (> 98%, Wellington Laboratories), including perfluoropentanoic acid

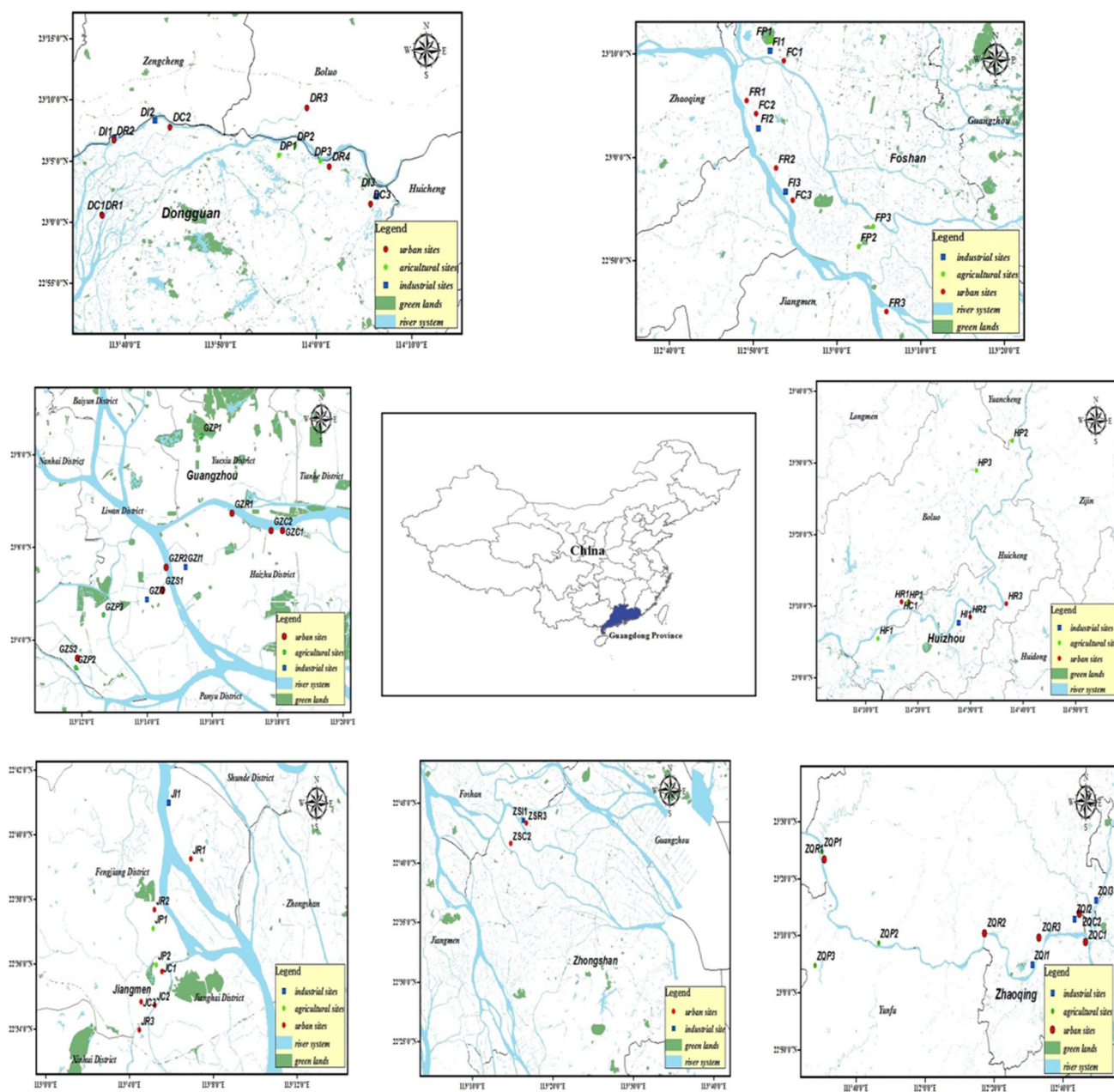
(PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUDA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), PFOS, and perfluorodecane sulfonic acid (PFDS). Eight mass-labeled PFCs purchased from Wellington Laboratories were used for the internal standards (IS), i.e., [<sup>13</sup>C<sub>2</sub>]-PFHxA, [<sup>13</sup>C<sub>4</sub>]-PFOA, [<sup>13</sup>C<sub>5</sub>]-PFNA, [<sup>13</sup>C<sub>2</sub>]-PFDA, [<sup>13</sup>C<sub>2</sub>]-PFUDA, [<sup>13</sup>C<sub>2</sub>]-PFDoDA, [<sup>18</sup>O<sub>2</sub>]-PFHxS, and [<sup>13</sup>C<sub>4</sub>]-PFOS. HPLC-grade methanol was purchased from J.T. Baker Technologies (Phillipsburg, NJ). HPLC-grade formic acid (96%) and ammonium acetate were obtained from Dikma Technologies (Foothill Ranch, CA). Ammonia hydroxide (25%) of guaranteed reagent (GR) grade was purchased from Acros Organics (Geel, Belgium). Milli-Q water had been pre-cleaned by Oasis WAX (6 mL, 150 mg, 30 μm) cartridge obtained from Waters Corporation (Milford, MA) to remove the residual PFCs before used throughout the study.

### Sampling Campaign

Surface soil samples (0–20 cm) ( $n=68$ ) were collected from seven cities of the PRD, including Guangzhou ( $n=11$ ), Dongguan ( $n=13$ ), Foshan ( $n=12$ ), Huizhou ( $n=9$ ), Jiangmen ( $n=9$ ), Zhongshan ( $n=3$ ), and Zhaoqing ( $n=11$ ), in August 2013 (Fig. 1; Table S1). Each soil sample was prepared by mixing five subsamples, which were mainly distributed at the center and four corners within an area of about 100 × 100 m<sup>2</sup>. All the soil samples were classified as urban soils (residential and commercial soils,  $n=36$ ), agricultural soils ( $n=18$ ), and industrial soils ( $n=14$ ; Table S1). Approximate 2.0 kg of soil samples were collected using a stainless-steel shovel pre-cleaned by methanol. The samples were then sealed in clean polypropylene (PP) bags. Field blanks were simultaneously collected in clean PP bags at each city and analyzed along with procedural blanks and each batch of samples. On arrival at the laboratory, the soil samples were air-dried at room temperature, homogenized with an agate mortar and pestle, passed through a 2-mm sieve, and then stored in pre-clean in 500 ml of PP bottles at 4 °C until extraction.

### Extraction and Cleanup

Soil samples were extracted using the method by Higgins et al (2005) with a minor change. Briefly, a 1.00 g of air-dried soil sample (dry weight equivalent) was accurately weighed and then transferred into a 50 mL of centrifuge tube to which 5 ng IS mixture and 10 mL of methanol were



**Fig. 1** Sampling sites of soils in the Pearl River Delta, China

subsequently added. Each vial was vortexed homogeneously, then ultrasonically extracted for 20 min at 40 °C, followed by centrifuging at 3000 r min<sup>-1</sup> for 10 min. This extraction was repeated in triplicate and the supernatants were combined. The extracts were reduced to 1–2 mL under a gentle stream of nitrogen gas, subsequently added with 8 mL of 2% formic acid solution and then diluted with ultrapure water to 50 mL. The mixture was load on the Oasis WAX cartridge, which was preconditioned by eluting with 2 mL of methanol followed by 2 mL of ultrapure water. The cartridge was washed with 2 mL of 2% formic acid, 2 mL of formic

acid-methanol (v:v = 1:1) and 2 mL of methanol, and the eluent was discarded. The target fraction was eluted with 5 mL of 9% ammonia-methanol solution. The eluent was evaporated to 1.0 mL using high-purity nitrogen gas and passed through a 0.22- $\mu$ m nylon membrane (Millipore, Billerica, MA) to ready the eluent for injecting into LC-MS/MS.

### Instrumental Analysis

A 20  $\mu$ L of extract was injected into a HP 1290 (Agilent Technologies) high-performance liquid chromatography system

(HPLC) fitted with an Agilent Eclipse XDB C<sub>18</sub> column (3.5 μm, 2.1 mm × 150 mm) where the target analytes were separated. The column temperature was set at 50 °C and the flow rate was 0.3 mL min<sup>-1</sup>. The mobile phase was the mixture of methanol (mobile phase A) and 2 mmol L<sup>-1</sup> of ammonium acetate (mobile phase B). The gradient elution began with 20% A and increased to 95% A at 8 min, continuously increased to 100% A at 13 min, then returned to the initial condition at 14 min and held for 6 min.

The target analytes were determined by an API 3000 tandem triple quadrupoles mass spectrometry (MS/MS) fitted with negative electrospray ionization (ESI) and recorded using a multiple reaction monitoring (MRM) mode. An internal standard method was selected to quantitatively analyze PFC concentrations under the conditions of 4,500 V of electrospray voltage, 450 °C of desolvation temperature, 9.0 L min<sup>-1</sup> of flow rate of air curtain gas, and 5.0 L min<sup>-1</sup> of auxiliary flow rate. The mass spectrum parameters involving parent and daughter ions, declustering potential, and collision energy of each target analyte and IS were detailed in Table S2.

### Quality Control and Quality Assurance (QC/QA)

To minimize exogenous contamination, all the experimental vessels made of PP were rinsed twice by methanol before use. A seven-point standard calibration curve was prepared at a concentration range of 5.0–60 μg L<sup>-1</sup> of all the target analytes with the correlation coefficients (*r*<sup>2</sup>) in the range of 0.9907–0.9997. All of the field and procedural blanks, which were extracted in duplicate for each batch of samples, were less than the limit of quantification (LOQ) defined as a signal-to-noise ratio of 10:1. The method detection limit (MDL) of the target analytes was determined with a signal-to-noise ratio of 3:1. The spiked recoveries ± standard deviation (SD) of the 16 PFCs ranged from 61.6 ± 13.2% (PFODA) to 127.3 ± 23.4% (PFDA). The MDL, LOQ, and spiked recoveries of 16 PFCs are summarized in Table S3.

### Ecological Risk Assessment

According to Liu et al. (2016), the ecological risk assessment of PFCs in soil was generalized as follows. First, the ecological toxicity data were collected to estimate the predicted no-effect concentration (PNEC). Second, the concentrations of PFCs (*C<sub>i</sub>*) were determined or collected in soil. Finally, the risk quotient (*Q*) was calculated by dividing *C<sub>i</sub>* by PNEC (Eq. 1). The PNEC was usually estimated based on the ratio of revised no observed effect concentration (NOEC) (Eq. 2) derived from laboratory plants or animals and evaluation coefficient (*K*) (Eq. 3).

$$Q = \frac{C_i}{\text{PNEC}} \quad (1)$$

$$\text{NOEC}_{\text{normalized}} = \text{NOEC}(\text{LC}_{50}) \times \frac{\text{Fom}_{\text{soil}(\text{standard})}}{\text{Fom}_{\text{soil}(\text{experiment})}} \quad (2)$$

LC<sub>50</sub>-median lethal concentration Fom<sub>soil(standard)</sub>-organic matter content in standard soil (kg kg<sup>-1</sup>) (3.4% derived from OCED); Fom<sub>soil(experiment)</sub>-organic matter content in experimental soil (kg·kg<sup>-1</sup>) (2.1% in this study)

$$\text{PNEC} = \frac{\text{NOEC}_{\text{normalized}}}{K} \quad (3)$$

*K* is taken as 100 in a long-term bioexperiment for soil plants and 50 for soil animals.

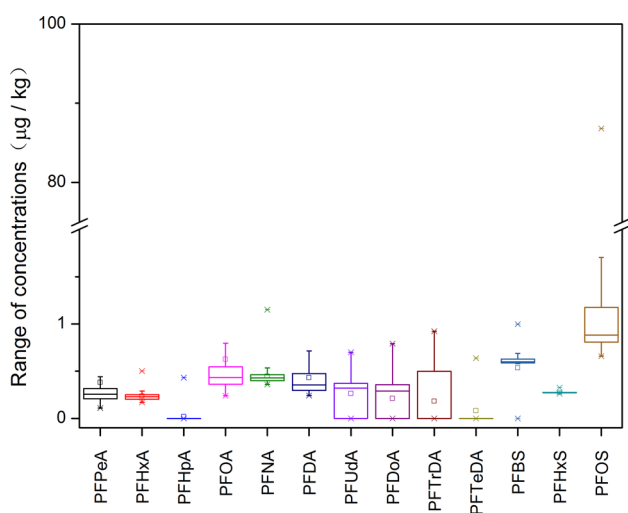
A summary of studies concerning the chronic and acute toxicities of PFOS and PFOA to soil organisms (Boudreau et al. 2003; Brignole et al. 2003; Joung et al. 2010; Li 2009; Sindermann et al. 2002; Stevens 2007; Zhang et al. 2012) is shown in Tables S4 and S5.

## Results and Discussion

### Concentrations of PFCs in Soil of the PRD and Comparison with Previous Studies

The concentrations of PFCs in 68 soil samples collected from the PRD are shown in Fig. 2. Among the 16 target compounds, concentrations of 13 PFCs were higher than their MDLs. PFPeA, PFHxA, PFOA, PFNA, PFDA, PFHxS, and PFOS were detected in all of the samples, whereas PFHxDA, PFODA, and PFDS were not detected in any sample. ∑PFCs ranged from 2.19 μg kg<sup>-1</sup> (dry weight, dw) to 98.5 μg kg<sup>-1</sup> dw, with a mean concentration of 5.97 μg kg<sup>-1</sup> dw. The highest mean concentration was observed for PFOS (2.23 μg kg<sup>-1</sup> dw), followed by PFOA (0.63 μg kg<sup>-1</sup> dw), PFBS (0.53 μg kg<sup>-1</sup> dw), and PFDA (0.43 μg kg<sup>-1</sup> dw). PFOS was the dominant PFC in soils of the PRD, accounting for 9.5% to 88.1% of the ∑PFCs with the highest mean proportion of 23.9%, followed by PFBS (11.8%), PFOA (11.4%), PFNA (10.1%), and PFDA (9.2%).

PFOS was the dominant pollutant in soil of the PRD, which is consistent with many other cities in China (Chen et al. 2016; Meng et al. 2013; Pan et al. 2011). The comparison of concentrations of PFOS and PFOA as well as ∑PFCs in this study with those from other regions in China is shown in Table 1. Higher concentrations of PFOS and PFOA as well as ∑PFCs were observed in this study when comparing with Guanting Reservoir (Wang et al. 2011a), North Bohai Sea (Wang et al. 2011b), coast and suburbs of Tianjin (Pan et al. 2011; Wang et al. 2012b), and the Huaihe River basin (Meng et al. 2013). The concentrations of PFOS and PFOA as well as ∑PFCs in this study were lower than those in agricultural soil of Shanghai (Li et al. 2010). In addition,



**Fig. 2** Concentrations of detected PFCs in soil samples of the Pearl River Delta

another area with heavily polluted PFOA was rural area in eastern China where the mean concentration of PFOA was approximate 1 order of magnitude higher than this study (Chen et al. 2016). On the whole, the concentrations of PFCs in soil of the industry-developed area, such as the Yangtze River Delta and the PRD were higher than those in soils of other regions in China.

### Spatial Distribution of PFCs in Soils from the PRD

The spatial distribution of  $\sum$ PFCs scarcely changed in 94% of soil samples of the PRD ( $< 6 \mu\text{g kg}^{-1}$  dw) except for several sampling sites. The predominant declining gradient of  $\sum$  PFCs was central, western, and eastern locations. The average concentration of  $\sum$ PFCs in Dongguan was significantly higher than those in other cities ( $p < 0.05$ ; Fig. S1). In recent years, the rapid development of manufacturing occurred in Dongguan where the industrial

structure consisted of electronic information, clothing textiles, paper making, and mechanical processing. As a result, Dongguan was known as “World Workshop.” The industrial wastes, including waste water, air, and residues, might be the main sources of PFCs in soil of Dongguan. In addition, standard deviation of  $\sum$ PFCs being greater than the average value of  $\sum$ PFCs was only observed in Dongguan, indicating the uneven distribution of PFCs in soil of Dongguan, which could be attributed to the spatial distribution of pollution sources.

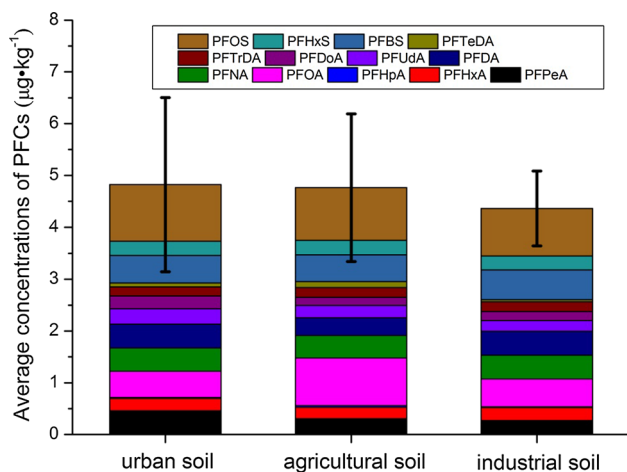
$\sum$ PFCs up to  $98.5 \mu\text{g kg}^{-1}$  dw were found in Site DP2 located in Shipai Town, Dongguan where the concentration of PFOS was  $86.8 \mu\text{g kg}^{-1}$  dw. Site DP2 was approximately 1 km from the Shichong Industrial Park where a large number of plants existed, such as clothing factories, plastic products factories, and hardware products factories, which could be main sources of PFCs in the soil. Other PFCs-polluted sites included DC2 ( $\sum$ PFCs  $10.1 \mu\text{g kg}^{-1}$  dw) located in Shilong Town of Dongguan, FR2 ( $\sum$ PFCs  $9.89 \mu\text{g kg}^{-1}$  dw) located in Nanhai District of Foshan, and ZQC1 ( $\sum$ PFCs  $8.36 \mu\text{g kg}^{-1}$  dw) located in Deqing Town of Zhaoqing. Some small-scale clothing factories, mold factories, and mechanical processing factories were distributed in the vicinities of the three sampling sites mentioned above.

The mean concentrations and composition of PFCs in soils from different functional areas are shown in Fig. 3.  $\sum$ PFCs in urban soils were slightly higher than those in industrial and agricultural soils. No significant differences of  $\sum$ PFCs were found among urban, industrial, and agricultural soils, which could be attributed to urbanization in the PRD. Meng et al. (2015) reported that the levels of PFCs were related to urbanization in China. It is not clear to distinguish land use in highly urbanized PRD. As a result, intensive anthropogenic activities and atmospheric precipitation could be considered as the main sources of PFCs in soil of the PRD when there were in the absence of local industrial pollution sources.

**Table 1** Comparison of concentrations of PFOS and PFOA as well as  $\sum$ PFCs in this study with those in other soil PFCs in China ( $\mu\text{g kg}^{-1}$  dw)

Survey region	Sampling period	PFOS	PFOA	$\sum$ PFCs	Reference
Guanting Reservoir	2008	0–0.86	0–2.8	0.13–8.5 (1.5)	Wang et al. (2011a)
North Bohai Sea	2008	0–0.70 (0.58)	0–0.47 (0.21)	0–1.7 (0.58)	Wang et al. (2011b)
Agricultural soil of Shanghai	2007	9.2–10.4 (9.5)	3.3–47.5 (35.2)	15–64 (49)	Li et al. (2010)
Tianjin City suburbs	2008	0.023–2.4 (0.32)	0–0.51 (0.19)	0.02–2.4 (1.0)	Pan et al. (2011)
Coastal Tianjin City	2008	0–9.4 (1.8)	0–0.93 (0.20)	1.3–11 (3.6)	Wang et al. (2012b)
Huaihe River basin	2008	0–0.21 (0.08)	0–0.20 (0.05)	0–1.2 (0.50)	Meng et al. (2013)
Rural areas in eastern China	2014–2015	0–1.56 (0.21)	0.16–62.5 (2.4)	0.34–65.8 (3.9)	Chen et al. (2016)
Pearl River Delta	2013	0.7–86.8 (2.23)	0.2–7.9 (0.63)	2.19–98.5 (5.97)	This study

Values in bracket represent mean concentrations of PFCs



**Fig. 3** Concentrations and composition of the 11 analytes detected at urban, agricultural and industrial soil from the Pearl River Delta

### Source Apportionment

The principal component analysis (PCA) model was employed to identify the sources of PFCs in soils from the PRD. A dataset with 9 PFCs with detection frequency > 70% at 68 sites was introduced to PCA. Four factors with eigenvalues greater than 1 were extracted after varimax rotation (Table 2). PFOS and PFOA got high loadings in factor 1, accounting for 31.8% of the total variance. Factor 2 (21.0% of the total variance) got high loadings for PFPeA and PFHxA. For factors 3 and 4, PFDA and PFUdA contributed high loadings with the total variance of 15.8% and 12.5%, respectively.

The varimax-rotated factors could be related to actual source categories based on the reported source markers. PFOS mainly emitted from electroplating (Kelly and Solem 2009; Xiao et al. 2012) and electronic products (Prevedouros et al. 2006), and PFOA largely released from food-packaging processes (Xiao et al. 2012; Xu et al. 2013), plastic and rubber products, and flame retardant (Prevedouros et al. 2006). There are a large number of electroplating and food-packing factories in the PRD (Liu et al. 2015). Thus, factor 1 might be identified as the emissions of PFC-containing industries. PFPeA and PFHxA might be the biodegradation products of 6:2 FTOH (Liu et al. 2010a, b). Factor 2 can be considered as biodegradation process of 6:2 FTOH in soil and mixed bacterial culture. Previous study reported that PFNA was the dominant PFCA yielded from 8:2 FTOH in atmosphere (Ellis et al. 2004), suggesting that factor 3 could be identified as atmospheric deposition. Considering that long-chain PFCs, such as PFUdA, might be from the degradations of FTOHs, fluoroctane sulfonamides (FOSAs), and fluoroctane sulfonamidoethanols (FOSEs) (D'Eon et al. 2006; Ellis et al. 2004; Martin et al. 2005), factor 4 could be the

**Table 2** Loading factors of PFCs in soils from the Pearl River Delta

PFCs	Factor 1	Factor 2	Factor 3	Factor 4
PFPeA	–	0.953	–	–
PFHxA	–	0.889	–	–
PFOA	0.927	–	–	–
PFNA	–	–	0.924	–
PFDA	–	–	–	–
PFUdA	–	–	–	0.811
PFBS	–	–	–	–
PFHxS	0.821	–	–	–
PFOS	0.981	–	–	–
Eigenvalue	2.863	1.887	1.424	1.129
Variance contribution ratio (%)	31.8	21.0	15.8	12.5

oxidation of precursors added in paint and ink additives, leather, and paper products, etc. (Loewen et al. 2005).

### Ecological Risk Assessment of PFOS and PFOA in Soils from the PRD

At present, most works are restricted to study the toxicities of typical PFCs, such as PFOS and PFOA in water or sediment (Liu et al. 2017; Zhu et al. 2015), which are rarely studied in soil. The chronic and acute toxicities of PFOS to soil organisms are listed in Table S4, including three toxic timepoints NOECs of seven plants and the LC<sub>50</sub> (28d) of two kinds of soil animals. The minimum NOEC of was found to be 3.91 mg kg<sup>-1</sup> (21d) for *Lolium perenne*, which was 6.33 mg kg<sup>-1</sup> of NOEC<sub>normalized</sub>. In consequence, PNEC was obtained to be 0.0633 mg kg<sup>-1</sup> for soil plants. The NOEC of *Folsomia candida* was found to be 0.05, which was 0.081 mg kg<sup>-1</sup> of NOEC<sub>normalized</sub>. Hence, PNEC was estimated to be 0.0016 mg kg<sup>-1</sup> for soil animals.

The filtrated toxicity data of PFOA to soil organisms are listed in Table S5. The minimum NOEC of was found to be 125 mg kg<sup>-1</sup> (5d) for *Brassica rapa chinensis* in the plants and 16 mg kg<sup>-1</sup> (28d) for *Eisenia fetida*, which were changed to be 202 mg kg<sup>-1</sup> and 25.9 mg kg<sup>-1</sup> of NOEC<sub>normalized</sub>, respectively. Therefore, PNEC was estimated to be 2.02 mg kg<sup>-1</sup> for soil plants and 0.52 mg kg<sup>-1</sup> for soil animals.

The comparisons of PFOS and PFOA concentrations with PNECs for soil plants and animals were shown in Fig. S2. PFOS concentrations in most soil samples were below PNECs in the present study, exhibiting a low risk to soil plants and animals. However, PFOS concentrations in some soil samples exceeded the PNECs for soil plants, indicating PFOS might lead to a potential risk to plants in partial soils of the PRD. PFOS concentration up to 86.8 µg kg<sup>-1</sup> dw at Sample DP2 exceeded both of the PNECs for plants and

animals, showing an extremely high risk to soil plants and animals. PFOA concentrations in all the sampling sites were much lower than both of the PNECs for plants and animals, indicating a low risk to plants and animals in soils of the PRD.

## Conclusions

Surface soil samples from the PRD were collected to determine PFCs. Among the 16 investigated PFCs, 13 PFCs were detected with PFOS being the predominant PFC.  $\Sigma$ PFCs were generally higher than other studied regions in China except for agricultural soil of Shanghai. The highest mean level of  $\Sigma$ PFCs was found in Dongguan, 2–4 times higher than concentrations of  $\Sigma$ PFCs in other studied cities of the PRD.  $\Sigma$ PFCs in urban soils were slightly higher than those in other soil types with no significant difference. PCA model suggested that the four main sources were PFOS and PFOA-factor, PFPeA and PFHxA-factor, PFDA-factor and PFUDA-factor, which accounted for the loadings with the total variance of 31.8%, 21.0%, 15.8%, and 12.5%, respectively. The ecological risk assessment suggested that PFOS in partial soils would pose a potential risk to soil plants and animals, whereas PFOA has no or low risk to soil plants and animals.

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