Crop bioaccumulation and human exposure of perfluoroalkyl acids through multi-media transport from a mega fluorochemical industrial park, China

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ABSTRCT: Significant quantities of perfluoroalkyl acids (PFAAs) are released to the environment from fluorochemical manufacturing processes in China which may lead to human exposure and health risks through crop bioaccumulation. This paper systematically studied the multi-media contamination and transport of PFAAs, followed by crop bioaccumulation and finally human exposure of PFAAs within a 10 km radius around a mega-fluorochemical industrial park (FIP). Hotspots of contamination by PFAAs were found near the FIP and downstream of the effluent discharge point with the maximum concentrations of 641ng/g in agricultural soil, 640 ng/g in wheat grain, 509 ng/g in maize grain and 4,862 ng/L in precipitation. As the distance increased from the FIP, PFAAs concentrations in all media showed a sharp initial decrease followed by a more gentle decline. Elevated PFAA concentrations in soil and grain were still present within a radius of 10 km of the FIP. The soil contamination was associated with the presence of PFAAs in irrigation water and precipitation. In abiotic media, perfluorooctanoic acid (PFOA) was the dominant PFAA component. However due to bioaccumulation preference, short-chain perfluoroalkyl carboxylic acids (PFCAs), especially perfluorobutanoic acid (PFBA), became the major PFAA contaminants in grains of wheat and maize. The bioaccumulation factors (BAFs) for both grains showed a decrease with increasing chain length of PFAAs (approximately 0.5 log decrease per CF_2 group). Compared to maize grain, wheat grain showed higher BAFs, possibly related to its higher protein content. The PFCA (C4-C8) concentrations in agricultural soil (on a $\log_{10}$ basis) and grain were found to show a significant linear positive correlation. Local human exposure of PFAAs via the consumption of contaminated grains represent a health risk for local residents, especially for toddlers and children.

KEYWORDS: PFAAs; farmland soil; precipitation; crop bioaccumulation; human exposure

1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in industrial processes and household products, including performance chemicals, lubricants, pesticides, surfactants and surface protectors, owing to their excellent chemical stability, high surface activity, with water and oil repellence (Giesy and Kannan, 2001; 2002). However, their persistence, bioaccumulation, potential toxicity and long-range transport make them contaminants of emerging concern (Lescord et al., 2015; Liu et al., 2015; Wang et al., 2015b). As a result of their widespread use and resulting emissions, PFAAs have been detected in numerous environmental compartments, such as air (Taniyasu et al., 2013), water (Wang et al., 2012), soil (Meng et al., 2015), sediment (Yeung et al., 2013), wildlife (Persson et al., 2013), plants (Vestergren et al., 2012) and even human tissues (Kannan et al., 2004). Furthermore, due to their mobility in both surface waters and the atmosphere, they have become primary modes of PFAA transportation with soil considered as one of the major sinks (Liu et al., 2015).

Manufacturing and use facilities often lead to pollution hotspots of PFAAs in surrounding environments (Xie et al., 2013; Liu et al., 2016a). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two of the most frequently detected PFAAs in the environment (Wang et al., 2015a). The discharge of wastes from a manufacturing facility in Alabama, in the USA, have led to high levels of

PFOS (144 ng/L) and PFOA (598 ng/L) in the nearby Tennessee River (Hansen et al., 2002). Affected by a former manufacturing facility in Minneapolis-St. Paul, in the USA, PFAA levels in soil are still as high as 126 ng/g for PFOA and 28.2 ng/g for PFOS (Xiao et al., 2015). PFAAs have been detected in precipitation in regions associated with PFAA-related industries with reports of 152 ng/L in Weifang and 229 ng/L in Tianjin, China (Zhao et al., 2013a; Shan et al., 2015). However, to date, a comprehensive assessment of multi-media distribution and transport of PFAAs around a manufacturing facility has yet to be carried out.

A human health concern may arise from the accumulation of PFAAs in food crops. Previous studies have demonstrated that PFAAs can be taken up from contaminated soils, translocated and stored in different plant organs (Stahl et al., 2009; Lechner and Knapp, 2011). Several experimental plots planted with maize, wheat and vegetables in PFAA-spiked or biosolids-amended soil have indicated a bioaccumulation potential of PFAAs. The bioaccumulation potential has been reported to vary with PFAA concentrations in soil, functional group and chain length, soil properties and plant species (Yoo et al., 2011; Blaine et al., 2013; Blaine et al., 2014; Wen et al., 2014; Krippner et al., 2015). However, to date, almost all studies on the bioaccumulation of PFAAs in plants have been carried out in controlled plots or nutrient solution experiments, which cannot accurately reflect the natural conditions in the 'natural' field. Risk assessments have confirmed that ingestion via diet is the most likely mechanism for significant exposure to PFAAs to humans (D'Hollander et al., 2010; Vestergren et al., 2012). This could occur from the consumption of crops grown on

PFAA contaminated soils or indirectly via carryover of PFAA contaminated fodder fed to animals raised as food for humans (Domingo, 2012; Kowalczyk et al., 2013).

Restriction agreements on the production of PFAAs in Europe and America, such as the 2010/2015 PFOA Stewardship Program and Stockholm Convention, have led to a large number of PFAA-related industries transferred to developing countries including China to meet the continuing demands (USEPA, 2006; UNEP, 2009). One such site is the mega-fluorochemical industrial park (FIP) studied here, which is a production centre for PFAAs and fluoropolymers with an annual capacity of several hundred thousand tons (Wang et al., 2016). The FIP is located in an area with large tracts of farmland and scattered villages. Within a radius of 10km from the FIP, a previous study has investigated the distribution and transport of PFAAs in surface and ground water with the highest reported concentrations of 1.86 mg/L and 273 μg/L respectively (Liu et al., 2016b). However, to systematically investigate multi-media contamination and transport of PFAAs from the FIP, PFAAs in other major media including soil, precipitation and crops needs to be studied. These results can then be integrated with PFAAs present in local water bodies. Furthermore, the assessment of bioaccumulation of PFAAs in crops under weathered field conditions is of vital importance to produce a more accurate risk assessment. This study would provide an assessment of the multi-media transport of PFAAs from the FIP to soil followed by crop accumulation and consumption by local residents.

The objectives of this study were, therefore, to examine the contamination and risk from PFAAs around the FIP with particular emphasis on (i) contamination patterns, composition changes and removal processes for PFAAs in different environmental compartments, (ii) analyzing the sources and transport of PFAAs, (iii) assessment of bioaccumulation in locally produced wheat and maize, and (iv) conducting a risk analysis for the environment regarding the soil and risk to human health from local grain.

2. Materials and methods

2.1. Sampling design and collection

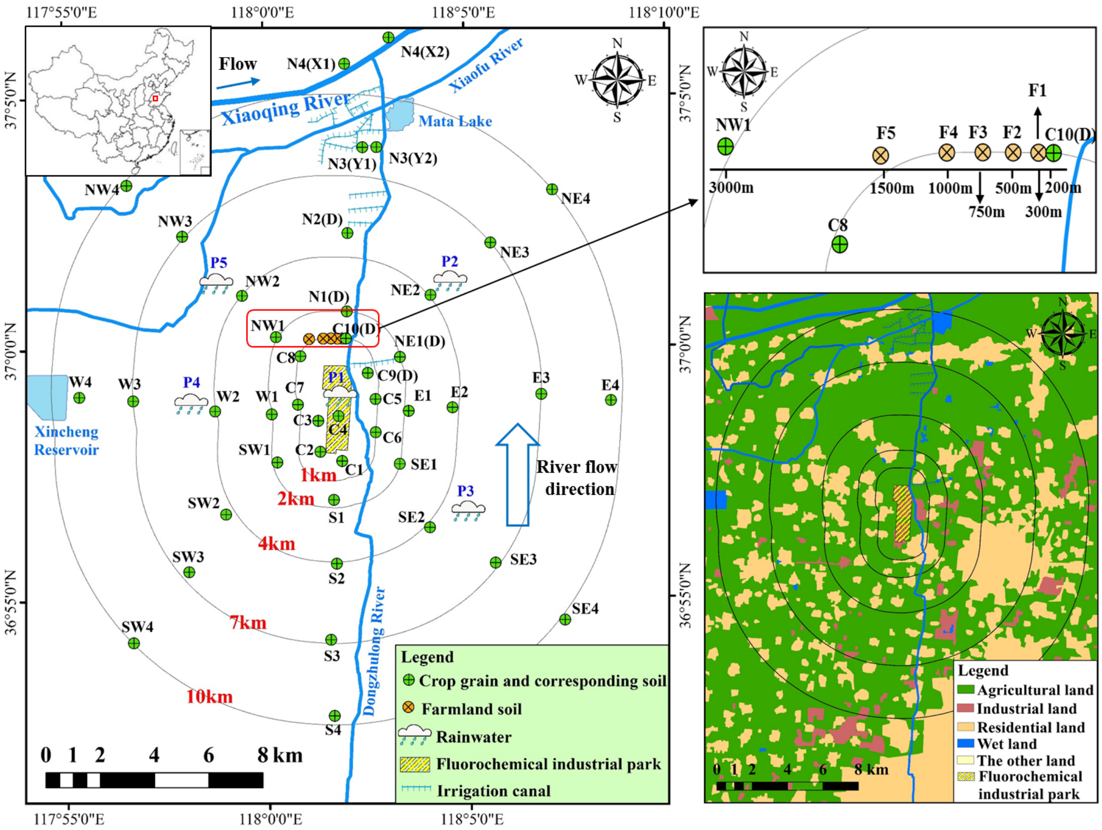


Fig.1 The map of the sampling locations for crop grain (wheat and maize), farmland soil and rainfall collection around the FIP in Huantai County.

The study area surrounding the FIP is a major grain-producing region with large tracts of farmland and scattered villages, where wheat and maize provide the local staple food source. With the FIP in Huantai at the center, samples were collected in central areas (C) within a radius of 1km and in eight directions (East, E; Southeast, SE; South, S; Southwest, SW; West, W; Northwest, NW; North, N; Northeast, NE) and this was repeated with at increasing distances from the site of 2, 4, 7 and 10 km. The 44 sample locations required the collection of mature wheat and maize grain and corresponding soil samples (Fig. 1). In addition, some agricultural soil samples in the transverse direction of the Dongzhulong River were also collected to study the influence of the contaminated river on PFAAs present in the soil. At each sampling site, wheat grains from 20 plants were randomly sampled from the center and four corners of an area of 10m × 10m, and mixed into one composite sample in June 2014. The corresponding rhizosphere soils (top 0-20cm) of these wheat plants were collected at the same time with a stainless steel trowel that had been rinsed with methanol and mixed into one composite sample. Maize grain and their corresponding soils were also sampled in the same way in October 2014. The collected grain samples were wrapped in aluminum foil and stored in clean paper bags. Large stones and roots were removed from the soil samples with methanol rinsed tweezers before being sealed in polypropylene (PP) bags. Furthermore, taking into account average wind direction and rainfall frequency, 20 rainwater samples from 6 precipitation events were collected in pre-cleaned PP bottles close to the FIP and with a radius of 5km in the northeast, southeast, west and northwest during October to November in 2014. Rainwater parameters, including pH, dissolved oxygen, conductance and salinity, were determined in situ using a HQd Portable and Benchtop Meter

Configurator (HACH Company, USA) (Table S1). All collected samples including grain, soil and rainwater were stored in an icebox during transport. The site information and ambient description were also noted in Table S2.

After arriving at the laboratory, grain samples were washed carefully with Milli-Q water followed by distilled water before freeze-drying at a temperature of -50 ℃ for 48 h in a lyophilizer. A sample of 100 g was then ground and homogenized in a knife mill Grindomix GM 200 and then stored separately at -20℃ before analysis. To avoid cross-contamination during grinding, the mill was rinsed with 20 mL of methanol after each use. The soil samples were transferred to PP boxes, dried in air, 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. The total carbon (TC) and total nitrogen (TN) contents of the soil samples were determined using an Elemental analyzer (Table S3). The soil organic matter was measured using the Walkley–Black procedure (Nelson and Sommers, 1982) while pH was determined at a soil to 0.01 M $CaCl_2$ solution ratio of 1:5 (w/v) (Table S3). Rainwater samples were allowed to stand for 24 h to settle any sediment and then 400 mL of supernatant was taken from each sample for analysis. All these rainwater samples were extracted within 1 week after arrival in the lab, and the remainder were stored at −20 °C for long-term reference.

2.2 Standards and Reagents

12 PFAAs in all samples were analyzed, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane

sulfonate (PFBS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctane sulfonate (PFOS), perfluoroundecanoate acid (PFUdA), and perfluorododecanoic acid (PFDoA) and 9 mass-labeled PFAAs, containing $^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA,$^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). More detailed descriptions on standards and reagents are available in the Supporting Information.

2.3 Extraction and cleanup

The rainwater, soil and plant samples were extracted mainly by solid phase extraction (SPE) using methods with minor modifications described previously by Taniyasu et al. (2005), Loi et al. (2011) and Felizeter et al. (2012) (Supplementary Information). Individual PFAA were separated and quantified using Agilent 1290 Infinity HPLC System equipped with an Agilent 6460 Triple Quadrupole MS/MS System (Agilent Technologies, Palo Alto, CA, USA) in the negative electrospray ionization (ESI) mode. The detailed descriptions of extraction and instrumental analysis are available in the Supplementary Information and Table S4.

2.4 Quality Assurance and Quality Control (QA/QC)

In order to avoid cross contamination during field sampling in the outside of the bottles was washed with Milli-Q water after the samples were taken, wiped with clean paper towel and then kept in three-layers of sealed polyethylene bags. The soil samples were kept in three-layers of sealed PP bags while grain samples were kept in three-layers of sealed paper bags. Field blanks, transport blanks, procedure blanks and solvent blanks were carried out with every sample set to examine if any external contamination occurred during the sampling/extraction and analytical stages. The internal standard calibration curve consisting of a concentration gradient (0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, and 100 ng/mL) of native standards, spiked with a 5 ng internal standard. This was prepared for quantification of the individual PFAA with coefficients (r^2) for all target analytes exceeding 0.99. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. When the concentrations of PFAAs in any extract that was greater than 100 ng/mL, the volume or amount of the samples would be reduced and the samples would be extracted again to fit the range of the calibration series. The different matrices were spiked with a standard solution and then analyzed to determine the recovery of each target PFAA. The matrix spike recoveries (MSRs) ranged from 79.0% to 109% for rainwater, 72 to 93% for soil and 66 to 102% for plant material. Supplementary Information and Table S5 described detailed QA/QC information.

2.5 Statistical and spatial analyses

Statistical analysis was performed using SPSS Statistics V22.0 (SPSS Inc. Quarry Bay, HK). During the analysis, concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned to values of $\mathrm{LOD}/\sqrt{2}$ (Bao et al., 2011). Spatial distributions of PFAAs were analyzed using the ArcMap module in ArcGIS V10.2 software (ESRI, Redland, CA, USA).

2.6 Bioaccumulation Metrics and Daily Intake Estimation

The bioaccumulation factors (BAFs), defined as ratios between the chemical concentration determined on a dry weight basis in the grain and corresponding soil, were calculated by Eq. (1) (Blaine et al., 2013). Due to the lower volatility of PFAAs at environmental, PFAAs entry into the stomata from the air was negligible and all these substances in grain were assumed to be derived from uptake through the roots.

$$BAF = \frac{PFAA\ concentration\ in\ grain\ (ng/g\ dw)}{PFAA\ concentration\ in\ soil\ (ng/g\ dw)} \qquad \text{Eq. (1)}$$

$$EDI = \frac{Daily\ consumption\ (g/d\ dw)\ \times PFAA\ concentration\ in\ grain\ (ng/g\ dw)}{Body\ weight\ (kg)} \qquad \text{Eq. (2)}$$

The estimated daily intake (EDI, ng/kg·bw/day) of PFAAs through the consumption of wheat and maize can be calculated based on averaging the intake dose by body weight by Eq. (2). Further details are contained in Table S6. Considering that body weights and consumption rates vary by age, the EDIs were estimated for four age groups: toddlers (2-5 years), children (6-10 years), teenagers (11-17 years), and adults (⩾18 years). As for the EDI calculation for residents with different radius from the FIP, the average concentrations of PFAAs in wheat and maize grain collected in that radius were used.

3. Results and discussion

3.1 Multi-media distribution and transport of PFAAs around the FIP

3.1.1 Occurrence and distribution of PFAAs in farmland soil

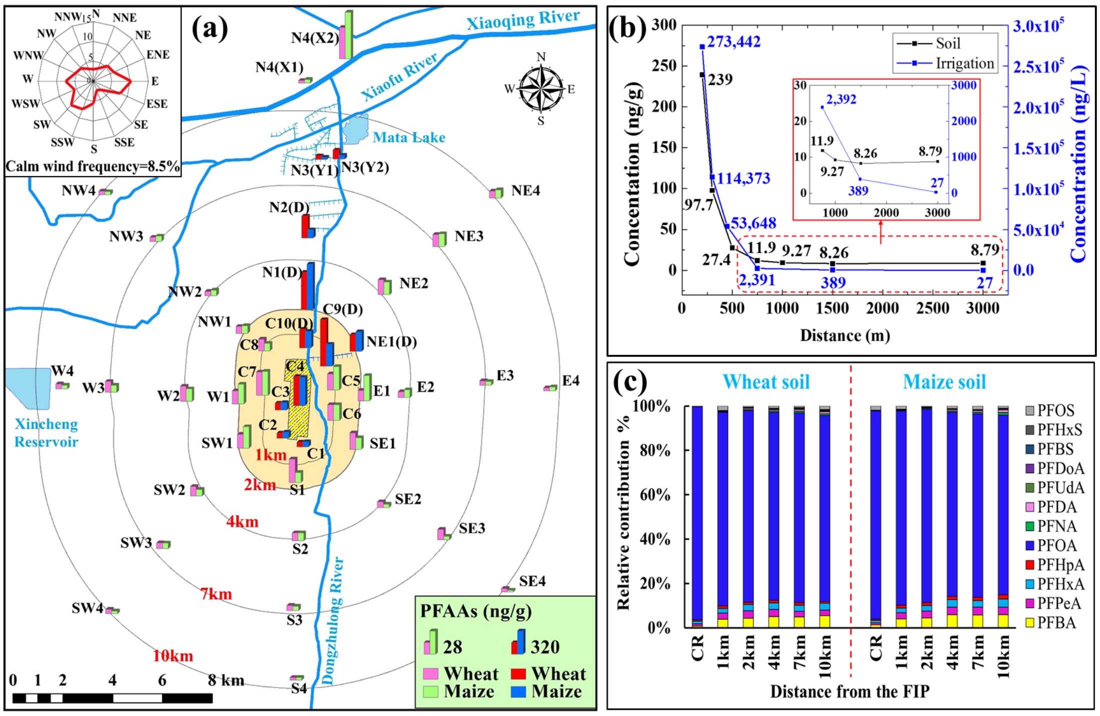


Fig. 2. The spatial distribution of ∑PFAAs and relative abundance of individual PFAA in farmland soil with the increase in distance from the FIP [(a) and (c)]; the decline curve of ∑PFAAs in farmland soil with distance from the polluted river (b).

Note: CR represented contaminated riverfront along the wastewater river, the same as below.

The concentration of the sum of PFAAs (∑PFAAs) ranged from 2.92 ng/g to 640 ng/g in agricultural soils (Table S7-S8). Of the PFAAs, PFOA was the dominant component with an average contribution of 86% of the ∑PFAAs, followed by C4-C7 short-chain perfluoroalkyl carboxylic acids (PFCAs) including PFBA (4%), PFPeA

(2.7%), PFHxA (2.50%) and PFHpA (1.2%). Long-chain PFCAs (C9-C12) and perfluoroalkane sulfonic acids (PFSAs) including PFBS, PFHxS and PFOS were only observed at low concentrations or below the MDL, which is most likely to be related to their limited production and application of these components in this region (Wang et al., 2014a; Wang et al., 2016). In most sampling locations, the concentration and composition of PFAAs in wheat soil showed no significant differences from those in maize soil. To the best of our knowledge, the maximum PFOA concentration in farmland soil (623 ng/g) reported in this study is the highest ever reported, which even exceeded soil receiving WWTP biosoilds as a soil amendment at 4.33-68 ng/g (Sepulvado et al., 2011). The spearman rank correlation analyses on the 12 PFAAs in agricultural soils showed that the concentrations of PFCAs, including PFBA, PFPeA, PFHxA, PFHpA, PFOA and PFNA, were strongly associated ($p<0.01$), indicating that these compounds came from similar sources (Tables S9–S10). Previous studies of the area have confirmed the FIP as the only point source in the area, which included not only PFCA production but also FP manufacturing and processing (Liu et al., 2016b). Global source inventories demonstrated that release of PFCAs are largely attributed to these industrial processes (Wang et al., 2014b). Furthermore, the increasing concentrations of PFAAs in soil with proximity to the FIP also supported site as the principal source.

The contamination hotspots of PFAAs in soil were found near the FIP and the Dongzhulong River, which received wastewater from the FIP. As the distance increased from these sources, the levels of PFAAs in soil decreased with an exponential trend, showing a sharp initial decrease followed by a gentle decline. The average concentrations of ∑PFAAs in wheat soil within 1km from the FIP was up to 88.7 ng/g, then sharply decreased by about 81% to 16.8 ng/g at 2km and further fell by 13.4% to 4.94 ng/g within the distance of 2-10km; while those in maize soil within 1km was up to 91 ng/g, then reduced by 79% to 19 ng/g at 2km and then slowly decreased by 16% to 4.41 ng/g within the distance of 2-10km (Fig. 2a). For soil along the lateral direction from the Dongzhulong River, the concentration of ∑PFAAs also rapidly dropped by 95% (from 239 ng/g to 11.9 ng/g) within a distance of 200-750m, then declined by 1.3% to 8.79 ng/g within a distance of 750-3000m (Fig. 2b). Influenced by the presence of the FIP, even the lowest concentrations of ∑PFAAs detected at a distance of 10km were still above most reported soil concentrations in China (reviewed in Table S11). With the increasing distance from the FIP, the shorter-chained PFAAs (C4-C6) increased in proportion to PFOA (C8) due to their greater persistence and mobility in the environment (Ferrey et al., 2009; Ahrens et al., 2010). PFAAs in agricultural soil may be associated with residues in local surface and ground waters, which also showed a similar decline in concentration and compositional change (Liu et al., 2016b). The confluence of the effluent from the FIP with the Xiaoqing River resulted in PFAAs concentrations that increased by orders of magnitude, while the concentrations in agricultural soil irrigated by the river also increased by about 12 times. It was noted that higher concentrations of PFAAs in the agricultural soil were found primarily on the downwind (i.e. west and northeast) side of the FIP, implying another likely contamination pathway through atmospheric emission, transport and local deposition (Davis et al., 2007) (Fig. S1).

3.1.2 Pollution association of PFAAs in irrigation water and farmland soil

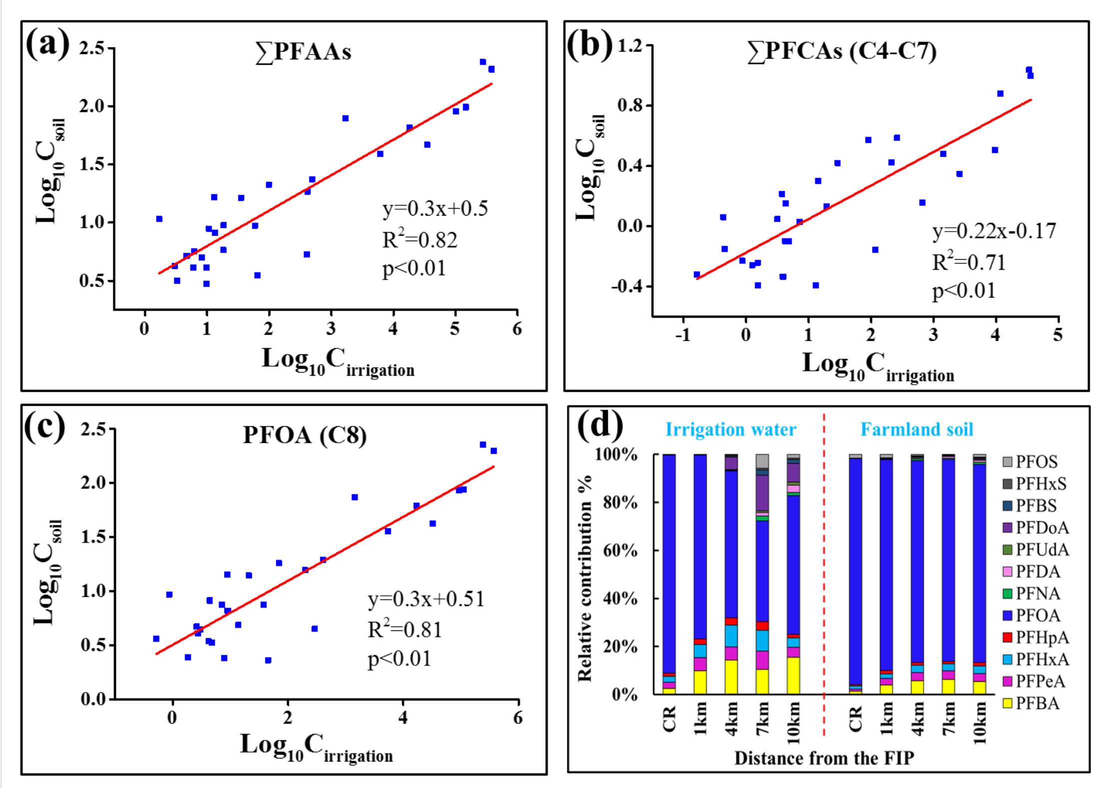


Fig3. The relationship (a, b, c) between PFAAs, PFCAs and PFOA found in farmland soil and corresponding irrigation water and the differing profiles (d) of PFAAs in farmland soil and irrigation water.

Note: $C_{irrigation}$ represented concentrations of PFAAs in irrigation water; C_{soil} represented concentrations of PFAAs in farmland soil.

The contamination of PFAAs in local surface and ground water, which are mainly used as irrigation water for farmlands, have been investigated in a previous study. Combining these results, the contamination associated PFAAs in agricultural soils and irrigation water will be discussed further. For ∑PFAAs and several main PFAA components, there was a significant linear positive correlation between the logarithm of concentrations in agricultural soils and corresponding irrigation water (Fig. 3a, 3b and 3c). Thus, contaminated irrigation water was considered as an important input of PFAAs in agricultural soils. However, it is worth mentioning that the increases for longer-chain PFAAs yielded steeper slopes compared to those for shorter-chain homologues (Fig. 3b, 3c; Table S12). This phenomenon can be explained by stronger adsorption to soil by longer-chain PFAAs (Higgins and Luthy, 2006). With higher aqueous solubilities and lower adsorption affinity (Ferrey et al., 2009; Ahrens et al., 2010), shorter-chained PFAAs present in irrigation water are more likely to leach through the soil profile compared to the more hydrophobic components. Therefore, short-chain PFAAs were present at lower proportions in agricultural soils than those in corresponding irrigation water (Fig. 3d).

3.1.3 PFAAs levels and composition in precipitation

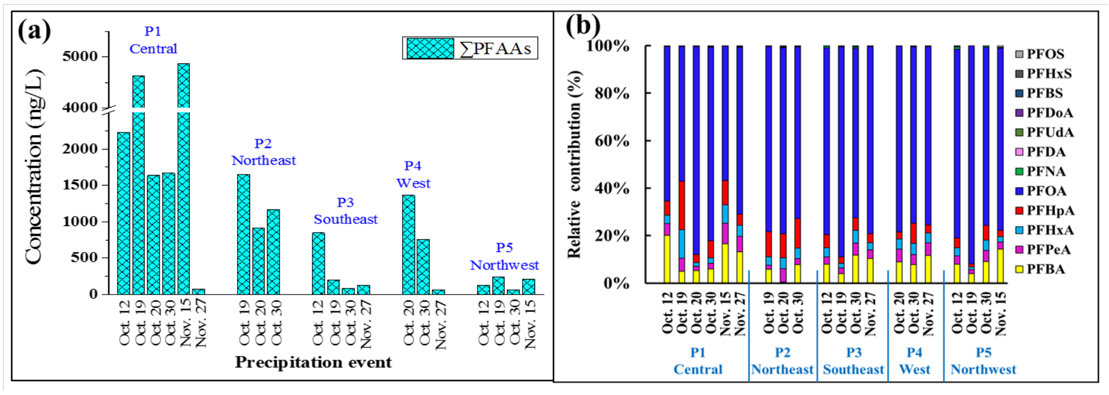


Fig. 4 The concentrations (a) and composition (b) of PFAAs in rainwater collected near the FIP.

As the most effective atmospheric removal mechanism for PFAAs (Taniyasu et al., 2013), rainwater was collected to examine the importance of local precipitation as a source of soil contamination near the FIP. High levels of PFAAs were found in rainwater within 5km from the FIP with the concentrations of 60 to 4,862 ng/L (Fig. 4a; Table S13). PFOA was predominant with the average relative abundance of 76%, followed by PFBA (8.9%), PFHpA (6.6%), PFHxA (4.1%) and PFPeA (4.1%) (Fig. 4b). The maximum concentration of PFOA (2,752 ng/L) found here was the highest ever reported in precipitation, which far exceeded high values previously reported such as in Tianjin (107 ng/L) and Dalian (65.8 ng/L) of China, in Yokohama (95.3 ng/L) of Japan, in Albany (23.9 ng/L) of the USA and in the northern regions (45.5 ng/L) of Germany (reviewed in Table S14). These contamination levels of PFAAs were comparable to those in house dust (73-13,500 ng/g) and street dust (5-9,495 ng/g) around this FIP, which were likely from dry deposition (Su et al., 2016). The phenomenon confirmed that manufacturing and use facilities were important sources of resulting in PFAA hotspots (Barton et al., 2006; Zhao et al., 2013b). High levels of airborne PFAAs were inferred to mainly originate from the direct release from the FIP associated with particles (Harada et al., 2006; Shan et al., 2015), which have limited long-ranged transport potential and are easily removed by precipitation (McMurdo et al., 2008; Mader, 2009). The spearman rank correlation analysis on 12 PFAA components in precipitation samples further confirmed the FIP as the dominant source of airborne PFAAs (Table S15).

The levels of PFAAs in rainwater sharply reduced with distance from the FIP, especially for short-chained PFCAs and PFOA. The highest levels of PFAAs associated with precipitation occurred immediately around the FIP with an average concentration of 2,265 ng/L, but rapidly decreased by 45.2%-92.9% within only 5km. Other high concentrations of PFAAs in rainwater were found in the northeast (average 1,241ng/L) and west (average 513ng/L) of the FIP, followed by those in southeast (average 315ng/L) and northwest (average 161ng/L). This would be expected on the basis of the prevailing wind in the area (Barton et al., 2006). PFAAs levels in house and street dust around the FIP mainly from dry deposition followed a similar trend (Su et al., 2016).

3.2 Crop grain contamination and bioaccumulation of PFAAs around the FIP

3.2.1 Occurrence of PFAAs in wheat and maize grain around the FIP

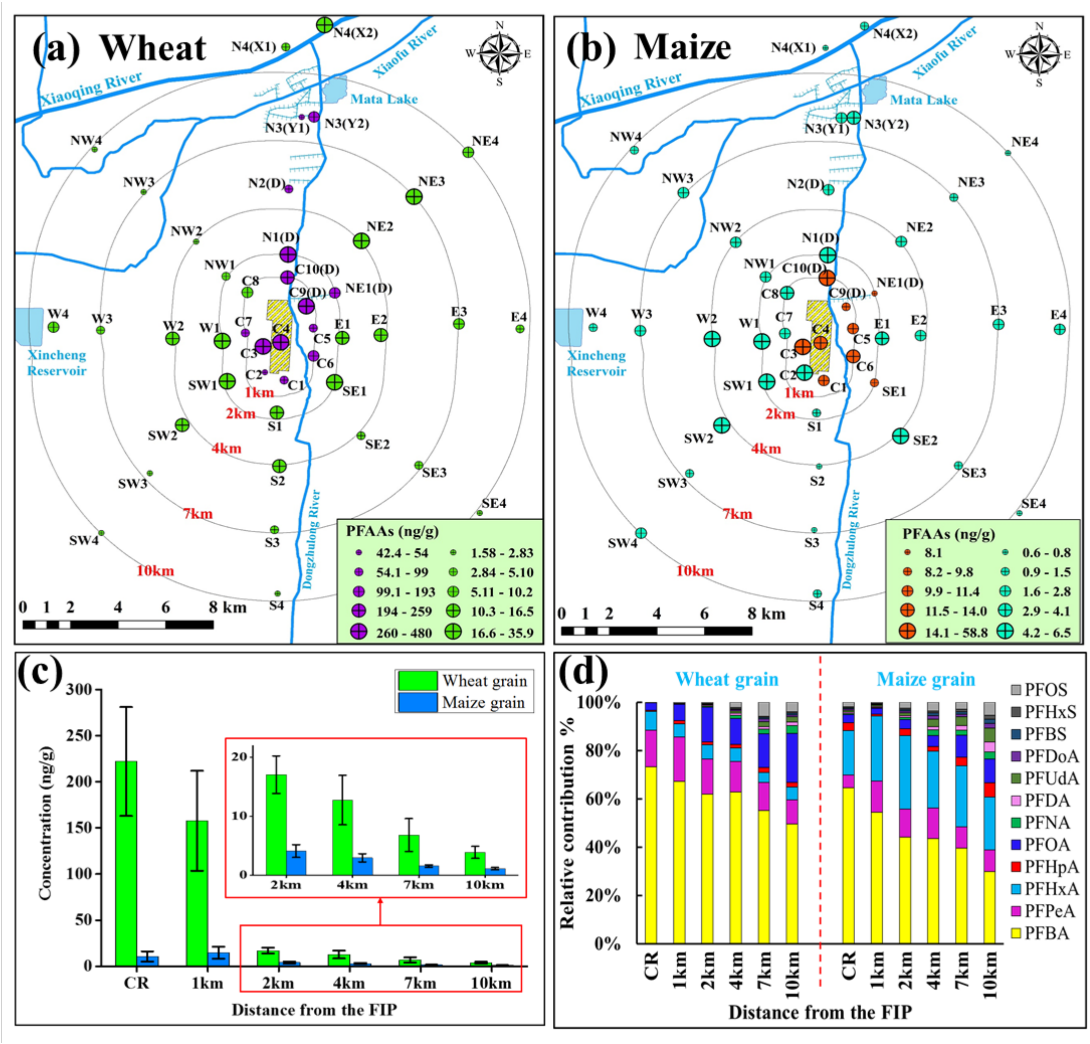


Fig. 5 Occurrence, distribution and composition of PFAAs in wheat and maize grain

The concentrations of ∑PFAAs ranged from 2.92 ng/g to 640 ng/g in wheat grain and from 0.63 ng/g to 509 ng/g in maize grain within 10km of the FIP (Table S16-S17). Similar to the agricultural soil, the FIP was also identified as the predominant source of PFAA in grains based on the spearman rank correlation analyses (Table S18-S19). Unlike irrigation water, agricultural soil and precipitation, short-chained PFCAs (C4-C7) were the major PFAA components in wheat and maize grains, indicating there must be a bioaccumulation preference for these homologues (Krippner et al., 2014; Wen et al., 2014). In the case of the grain, PFBA was the dominant form, representing 61.4% in wheat grain and 45.5% in maize grain of the total PFAAs (Fig. 5d). Long-chained PFCAs (C9-C12) and PFSAs were only found in trace amounts or below the MDL. Compared to wheat grain, maize grain showed stronger bioaccumulation tendency for PFHxA and PFHpA.

PFAAs concentrations in grains also showed a sharp decrease in a short distance from the FIP, followed by a gentle decline. The average concentrations of ∑PFAAs in wheat grain within 1km from the FIP were as high as 161 ng/g, rapidly reducing by 89.4% to 17ng/g at 2km followed by slower decrease by 6.87% to 5.94 ng/g within the distance of 2-10km; while residues in maize grain within 1km were up to 76 ng/g, although falling sharply by 94.3% to 4.34ng/g at 2km with a further slower decline by 2.96% to 2.09 ng/g within the distance of 2-10km (Fig. 5c). Contamination hotspots of ∑PFAAs present in grains were also associated with plants grown along the banks of the heavily polluted Dongzhulong River with average concentrations of 223 ng/g for wheat grain and 10.5 ng/g for maize grain. Within the study area, ∑PFAAs levels in wheat grain were typically 11.3 fold higher than those in maize grain (Fig. 5a, 5b), which may be attributed to stronger PFAA bioaccumulation potential for wheat grain.

3.2.2 Cop bioaccumulation rules of PFAAs around the FIP

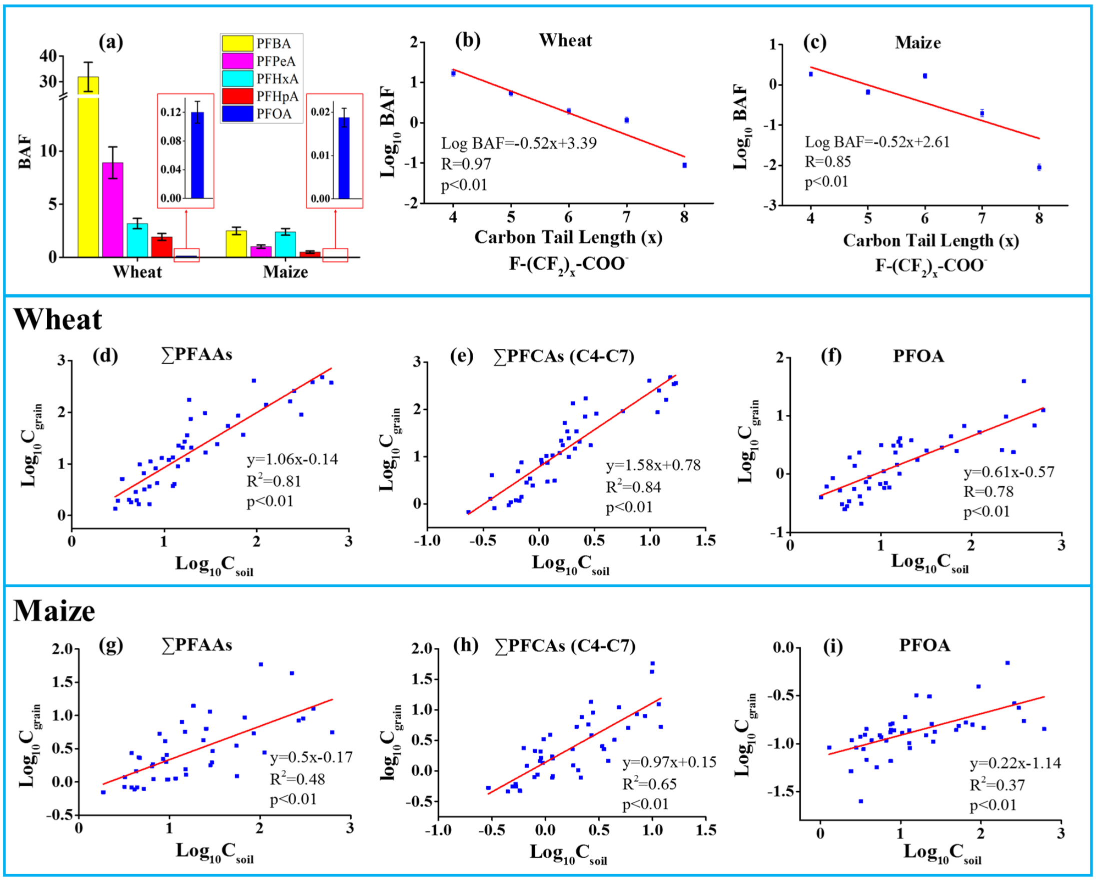


Figure 6. BAFs for several major PFCAs (a), correlations between log BAF and carbon chain length (b, c), and bioaccumulation equations of PFAAs (d-i). Means and standard errors are shown (n = 44).

Soil properties such as organic matter content and pH across the study area were relatively similar (including both wheat and maize growing areas) (Table S1). The bioaccumulation factors (BAF) for ∑PFAAs in wheat grain were typically 11.6 times higher than those in maize grain (Fig. 6a). The phenomenon may be related to the higher protein contents in wheat gain (11.2%) than those in maize grain (3.8%). Previous studies have found the high affinity of PFAAs to proteins and further confirmed the effect of protein content on the accumulation of PFAAs in plants

(Zhang et al., 2013; Bischel et al., 2011, 2010) (Wen et al., 2016).

In the wheat and maize grain, total concentrations of shorter-chained PFCAs (C4-C7) were about 20-fold and 33-fold respectively larger than those of PFOA, despite the soil concentrations of PFOA being more than average 19 times that of the shorter-chained PFCA concentrations. The significant contrast of PFAA profiles in grain and soil were mainly caused by crop bioaccumulation preference for short-chain PFAAs. In fact, the BAF for wheat and maize grain showed a decreasing tendency with increasing chain length. PFBA (C4) showed the highest BAFs averaging 33.1 for wheat grain and 2.5 for maize grain while PFOA showed the lowest values averaging 0.12 for wheat grain and 0.02 for maize grain. The $\log_{10}$ BAFs for wheat and maize grain were correlated with carbon chain length for several major PFCAs. The BAFs in both grains decreased by approximately 0.5 log units per CF2 group for these PFCAs (Fig. 6b, 6c). The higher BAFs for shorter-chain PFAAs may be related to their lower sorption by soil particles and smaller molecular size (Higgins and Luthy, 2006). This would have the effect of greater availability to the plants as well as to a higher mobility and translocation rate within the plants (Felizeter et al., 2012; Felizeter et al., 2014; Krippner et al., 2014).

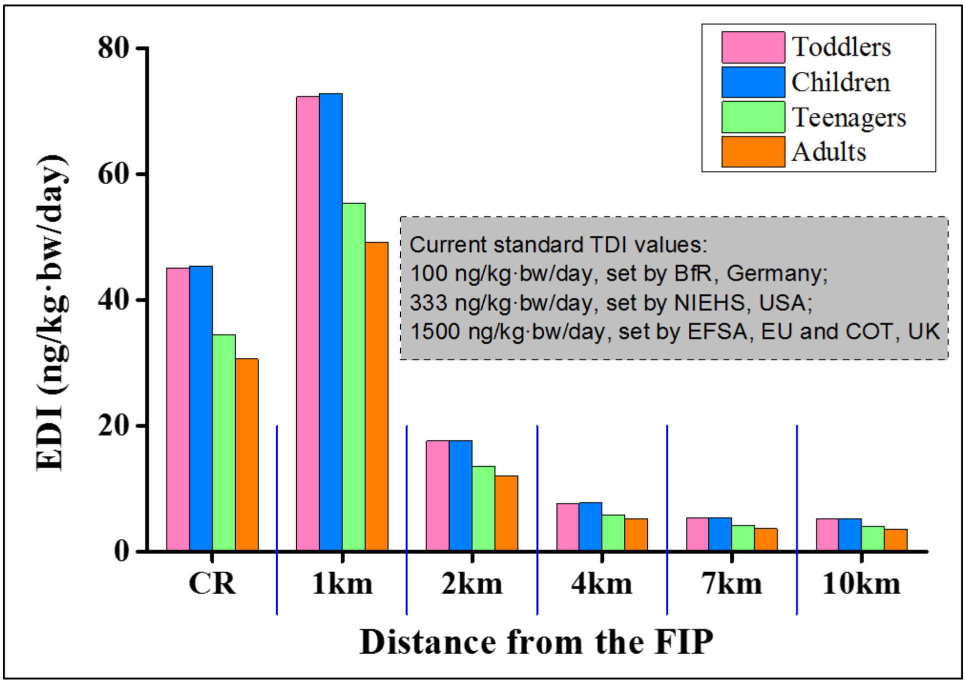
The uptake and storage of PFAAs in wheat and maize grain unsurprisingly had a link with agricultural soil concentrations. For Σ PFAAs and several main PFAA components, the logarithms of concentrations in agricultural soil and grain showed significant linear positive correlations ($p<0.01$) (Stahl et al., 2009). However, the slopes of soil-grain equations, which were closely associated with BAF, also showed a declining trend with the increase of carbon chain length. When soil concentration increased, a steeper slope for short-chain PFCAs would result in a greater concentration increase in grain. This can explain the proportional increase of short-chain homologues in grains with proximity to the FIP (Fig. 4d). Moreover, higher slopes in soil-wheat equations than soil-maize equations further confirmed stronger bioaccumulation potential for wheat grain.

3.3 Risk assessment of PFAAs in soil and crop to human health and ecology

Some high concentrations of PFOA in agricultural soil near the FIP and along the heavily polluted Dongzhulong River exceeded the predicted non-effect concentration (PNEC) of 160 ng/g (Amundsen et al., 2008), indicating a potential ecological risk to soil organisms. However, such soil levels were still much lower than the commonly used health risk thresholds (e.g. 16,000 ng/g for PFOA by the USEPA), indicating health risk via direct exposure of contaminated soil would be very low. However, an exposure pathway for PFAAs of greater concern for human health would be through the diet (Vestergren et al., 2012). In the study area, wheat and maize account for 73% and 7% respectively of staple food, and most local residents consume their grains from their own cereal crops (Bureau of Statistics of Shandong Province, China, 2015). The estimated daily intakes (EDIs) of PFAAs for different age groups via consumption of contaminated wheat and maize grain was calculated to assess health risks to local residents.

For local residents, the EDIs of PFAAs through wheat consumption was about 83 times higher than that through maize consumption (Table S21). The EDIs of major PFAA components via consumption of wheat and maize varied, depending on the distance and the age group of the residents living around the FIP (Table S22). Consistent with PFAAs distribution in grains, the highest EDIs of PFAAs for the different age groups occurred within 1km from the FIP and along the river receiving the wastewater discharge. For residents within 1 km from the FIP, the total exposure of ΣPFAAs via consumption of these grains were 1,219 ng/kg·bw/day for toddlers and 1,228 ng/kg·bw/day for children, followed by teenagers (934 ng/kg·bw/day) and adults (828 ng/kg·bw/day) (Table S22). As expected, for major components and ∑PFAAs in all sampling locations, the EDI for toddlers and children were also comparable, but both higher than those for teenagers and adults. The higher food consumption per body weight for toddlers and children compared to teenagers and adults can explain this difference (Klenow et al., 2013). Similar results were also found in China from consumption of meat and eggs with PFOA EDIs of 15.9 to 19.7 ng/kg·bw/day for toddlers and 7.75 to 10.5 ng/kg·bw/day for adults (Zhang et al., 2010), and in Belgium through multiple foodstuffs with PFOA EDIs ranging from 0.28 to 0.39 ng/kg·bw/day for children and 0.19 to 0.23 ng/kg·bw/day for adults (Klenow et al., 2013).

As far as we are aware, the tolerable daily intake (TDI) values are only available for PFOA. Compared to current recommended TDI values of 100 to 1,500 ng/kg·bw/day for PFOA proposed by several countries (Fig.4, Table S14), the EDI of PFOA via consumption of wheat and maize for residents in the study area are less than these thresholds. However, it is noteworthy that the EDI values via wheat and maize consumption for toddlers (72.3 ng/kg·bw/day), children (72.8 ng/kg·bw/day), teenagers (55.4 ng/kg·bw/day), adults (49.2 ng/kg·bw/day) within 1km from the FIP were close to the Health-based guide value (HBGV) (100 ng/kg·bw/day) for Germany (BfR, 2006) (Fig. 7). Besides consumption of wheat and maize grain, other exposure pathways exist. Groundwater is often used as a source of drinking water, and at this location PFOA levels in groundwater within a radius of 1km from the FIP were up to a orders of magnitude higher than Provisional Health Advisory (PHA) recommended by the USEPA (400ng/L) (Liu et al., 2016b). Within 2km from the FIP, the EDIs of PFOA via dust ingestion and dermal absorption has also been estimated to be 26 ng/kg·bw/day for toddlers, 10.5 ng/kg·bw/day for children, 5.52 ng/kg·bw/day for teenagers and 4.42 ng/kg·bw/day for adults (Su et al., 2016). Moreover, consumption of contaminated vegetables and fruits, also grown in the area, although not studied here, may also contribute to the dietary load. When combined with these exposure pathways, the EDIs of PFOA for residents, especially toddlers and children, within 1km from the FIP are likely to exceed the HBGV (100 ng/kg·bw/day) from Germany, indicating a high level of human health risk. Residents along the Dongzhulong River downstream of the FIP were exposed to the next highest health risk owing to the contaminated water and soil.



Current standard TDI values:
100 ng/kg·bw/day, set by BfR, Germany;
333 ng/kg·bw/day, set by NIEHS, USA;
1500 ng/kg·bw/day, set by EFSA, EU and COT, UK

Fig 7. Estimated daily intake (EDI) of PFOA via consumption of wheat and maize (ng/kg·bw/day) for various age groups.

Note: current standard tolerable daily intake (TDI, ng/kg·bw/day) values are derived from ThayerandHoulihan (2002), BfR (2006), Benford et al. (2008) and COT (2009).

The EDIs of PFOA via dietary intake from multiple food sources have been reported in China (7.75-10.5 ng/kg·bw/day) (Zhang et al., 2010), Japan (0.72-1.3 ng/kg·bw/day) (Kärrman et al., 2009), Germany (2.9 ng/kg·bw/day) (Fromme et al., 2007), the US (0.82 ng/kg·bw/day) (Schecter et al., 2010), Norway (0.42 ng/kg·bw/day) (Haug et al., 2010) and Sweden (0.35-0.69 ng/kg·bw/day) (Vestergren et al., 2012). Unquestionably, the EDIs of PFOA (adults: 49.2 ng/kg·bw/day) reported in this study were higher than those values previously reported. Even at 10km away from the FIP, the EDIs of PFOA (adults: 3.51 ng/kg·bw/day) via the consumption of wheat and maize only were still comparable or higher than the upper limits of most reported EDI values, indicating the effective distance of the FIP on crops was at least 10km. These considerations are only for PFOA, which is only one component of the PFAA family. Crop bioaccumulation preference results in the EDIs of shorter chained PFCAs for residents being much higher than those for PFOA. However, the health risk of these short-chain homologues cannot be assessed due to shortage their TDI values. So health risks of PFAAs for local residents may go further than just PFOA. Moreover, PTFE production has been expanded in the FIP with an average annual growth rate of 25% since 2001 (Wang et al., 2016). If without suitable substitutes for PFAAs in the production of most fluoropolymers or improvement in the 'quality' of local food sources, local residents may face continuous or even higher exposure.

4. Conclusions and perspectives

Overall, the results of this study indicated that:

- The highest concentrations of $\sum$PFAAs in agricultural soil were observed near the FIP (max 402 ng/g) and along the banks of the FIP effluent dominated river (max 641 ng/g). As the distance increased from these sources, PFAAs levels in soil showed a sharp initial decrease followed by a slower decline. Higher PFAAs concentrations in agricultural soil showed some correlation with the prevailing wind direction.

- The use of contaminated irrigation water and the influence of contaminated precipitation are two of the dominant pollution pathways of PFAAs to agricultural soil. Longer-chained PFAAs in irrigation water were more susceptible to adsorption to soil particles. For precipitation, unprecedented levels of ΣPFAAs were found immediately near the FIP with an average concentration of 2265 ng/L, although they decreased significantly beyond 5km. In these abiotic media, PFOA (C8) was the predominant PFAA, followed by shorter-chained PFCAs (C4-C7).

- A pollution signal from the FIP could be found as far away as 10 km within cereals with concentrations ranging from 2.92-640 ng/L in wheat grain to 0.63-509 ng/L in maize grain. The hotspot distribution and decline process of ΣPFAAs in grain were similar to those in soil. The shorter chain varieties such as PFBA (C4) were accumulated by these crops preferentially, accounting for an average of 61.4% in wheat grain and 45.5% in maize grain, followed by other short-chained PFCAs (C5-C7) and PFOA (C8).
- The uptake and storage of PFAAs in wheat and maize grain showed a decreasing tendency with the increase of carbon chain length and the BAFs in both grains decreased by approximately 0.5 log units per CF2 group. The BAF of ΣPFAAs in wheat grain were on average 11.6 times higher than those in maize grain, which may be linked to higher protein contents in wheat gain. Significant linear positive correlations were found between the logarithms of PFCA (C4-C8) concentration in agricultural soil and grain.
- High concentrations of PFOA in agricultural soil may lead to potential soil

ecological risks. Consumption of contaminated grain grown within a radius of 1km from the FIP and downstream of effluent dominated river could have impacts on human health. The group most at risk would be toddlers and children due to their weight relative to exposure.

- Based on crop bioaccumulation preference for short-chained PFCAs, it may be worthwhile to consider whether it is desirable to substitute longer-chain PFAAs with shorter-chain compounds in industrial processes. Therefore, more toxicological studies on short-chained PFAAs are urgently needed for a more comprehensive assessment of health and ecological risks. Moreover, further consideration is also required for the potential hazards of aquatic products, livestock and poultry, and vegetables from these chemicals.
- This study has linked the high local contamination with polluted wastewater leaving the FIP and airborne emissions. These sources could potentially be reduced with granular activated carbon wastewater treatment systems and an exhaust gas purification. In addition, non-fluorinated alternatives that are neither persistent nor toxic should be also developed to eliminate the PFAA risk from the source.

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