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Multiple crop bioaccumulation and human exposure of perfluoroalkyl substances around a mega fluorochemical industrial park, China: Implication for planting optimization and food safety

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ABSTRACT

Perfluoroalkyl substances (PFASs) have become a recognized concern due to their mobility, persistence, ubiquity and health hazards in the environment. In this study, ten types of vegetables and three types of grain crops were collected in two open-air fields with different distances (0.3 km, 10 km) from a mega fluorochemical industrial park (FIP), China. Bioaccumulation characteristics of PFASs in light of crop types and organs were explored, followed by analyzing human exposure and risks to local residents with different age groups and dietary habits. Elevated levels of ΣPFASs were found nearby the FIP ranging from 79.9 ng/g to 200 ng/g in soils and from 58.8 ng/g to 8085 ng/g in crops. Perfluorooctanoic acid (PFOA) was the predominant PFAS component in soil; while shorter-chain perfluoroalkyl carboxylic acids (PFCAs), especially perfluorobutanoic acid (PFBA), were the major PFAS contaminants in multiple crops, resulting from their bioaccumulation preference. Depending on the crop types, the bioaccumulation factors (BAFs) of ΣPFASs for edible parts varied from 0.36 to 48.0, and the highest values were found in shoot vegetables compared with those in fruit vegetables, flower vegetables, root vegetables and grain crops. For typical grains, the BAFs of ΣPFASs decreased in the order of soybean (*Glycine* max (Linn.) Merr.), wheat (*Triticum aestivum* L.) and corn (*Zea mays* L.), possibly related to their protein and lipid content. Among specific organs in the whole plants, leaves exhibited the highest BAFs of ΣPFASs compared with corresponding roots, stems, husks or grains. With increasing carbon chain lengths of individual PFCAs (C4-C8), the logarithm of their BAFs for edible parts of various crops showed a linear decrease (0.1–1.16 log decrease per CF_2 unit), and the largest decrease was observed in grains. Human exposure to PFOA via the consumption of contaminated crops represents a health risk for local residents, especially for low-age consumers or urban consumers with higher vegetable diet. Implications for planting optimization and food safety were provided aiming to reduce health hazards of PFASs.

1. Introduction

Perfluoroalkyl substances (PFASs) have been widely used in a variety of consumer products and industrial processes (e.g. nonstick food packaging, pesticides, stain repellents, surfactants and surface protectors), thanks to their excellent chemical stability, water and oil repellence, and high surface activity (Giesy and Kannan, 2002; Post et al., 2012). However, recent studies on animal toxicology and disease investigation have suggested that PFASs exposure could lead to adverse health effects such as infertility, endocrine disorder, abnormal maturation and even cancers (Hardell et al., 2014; Harris et al., 2018; Salihovic et al., 2018; Seo et al., 2018). With their potential toxicity,

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bioaccumulation, persistence and long-range transport, these substances have become priority contaminants of great concern (Lescord et al., 2015; Wang et al., 2015b; Li et al., 2016). Their widespread use and the resulting emissions have led to PFAS being detected in various environmental media including water (Wang et al., 2015a), sediment (Yeung et al., 2013), soil (Meng et al., 2018), air (Taniyasu et al., 2013a), plant (Vestergren et al., 2012), wildlife (Persson et al., 2013) and even human issues (Tian et al., 2018b).

Crops may be contaminated by PFASs from local soil and air, which may lead to human exposure and health risk to PFASs via crop consumption (Liu et al., 2015; Chen et al., 2018; Tian et al., 2018a). Industrial emissions were identified as major contributors to hot spots of PFASs contamination in soil and air, particularly perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Xie et al., 2013; Liu et al., 2017b). Affected by two fluorochemical manufacturing parks in Fuxin, China, the mean concentrations of total ionizable PFASs and total neutral PFASs in the surrounding air were found to be as high as 4900 pg/m^3 and 1400 pg/m^3, respectively (Chen et al., 2018). Even if a former manufacturing facility in Minneapolis-St. Paul of the USA had been in discontinuation for ten years, the soil concentrations of PFASs were still up to 28.2 ng/g for PFOS and 126 ng/g for PFOA (Xiao et al., 2015).

Crop uptake of PFASs from polluted soil has been identified as a key pathway for PFAS entry into the terrestrial food webs (Lechner and Knapp, 2011; Blaine et al., 2013; Wen et al., 2014; Krippner et al., 2015). Moreover, plant uptake potential for airborne PFASs has been revealed (Chen et al., 2018; Tian et al., 2018a). Contaminated crops contributed significantly to human exposure to PFASs, through either direct ingestion or indirect consumption of animals fed with these crops, which might cause human health risks (Domingo, 2012; Kowalczyk et al., 2013; Blaine et al., 2014b). The uptake capacities of PFASs by wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), soybean (*Glycine* max (Linn.) Merr.) and some vegetables have been demonstrated in PFAS-spiked soil plots or nutrient solutions (Felizeter et al., 2012; Zhao et al., 2013; Wen et al., 2016; Lan et al., 2018; Zhang et al., 2019), but those artificial control experiments cannot accurately reflect fully open-air field conditions. Considering most crops grown in the open-air fields, it is critical and valuable to explore the PFASs bioaccumulation characteristics of multiple field crops for risk control (Domingo, 2012).

Limited by agreements on restrictive production and emission of PFASs in Europe and America, large amounts of PFAS manufacturing and application industries were transferred to developing countries including China to meet the expanding huge market demands (UNEP, 2009; USEPA, 2013). The mega-fluorochemical industrial park (FIP) studied here is of such a case, with massive production and use of PFASs during fluoropolymers manufacturing. Available official information showed that (i) the FIP started production in 1987; (ii) after years of growth, the annual production capacities of fluoropolymers were up to 60,000 tons for tetrafluoroethylene (TFE) and 49,000 tons for polytetrafluoroethylene (PTFE) in 2013, and 10,000 tons for hexafluoropropylene (HFP) and > 200,000 tons for different types of fluorinated refrigerants in 2012; (iii) the production capacities of the FIP has been further expanding in recent years (Dongyue Group Limited, 2012, 2014, 2017). As critical processing aids during fluoropolymer manufacturing, PFASs, especially PFOA, were also produced in large quantities (Wang et al., 2016).

In our previous studies, the occurrence and multiple media transport of PFASs around the FIP have been systematically studied with the highest reported PFASs concentrations of 1,860,000 ng/L in surface water, 273,000 ng/L in groundwater, 641 ng/g in soil, 4862 ng/L in precipitation, 480 ng/g in wheat grain and 58.8 ng/g in corn grain (Liu et al., 2016; Liu et al., 2017a). The study on PFASs contamination for the grains of wheat and corn preliminarily revealed the effects of PFASs industrial sources on local agricultural product safety. However, except for these two grains, the occurrence and bioaccumulation characteristics of PFASs for multiple vegetables, which were extremely important parts of local plant food, were still unknown. This study would be indispensable for a more comprehensive assessment of crop contamination and health risk of PFASs caused by the FIP.

In this paper, the edible parts of ten species of local representative vegetables (including root vegetable, shoot vegetable, fruit vegetable and flower vegetable), as well as three local dominant grains (wheat, corn and soybean) were integrated to conduct a comprehensive study on the PFASs bioaccumulation patterns for multiple crops and subsequent human exposure for different consumers. Furthermore, PFASs bioaccumulation characteristics of the specific organs of some whole plants including vegetables and grain crops were systematically explored, which was intended to reveal the intercompartmental translocation and distribution of PFASs in the plants. Based on contamination levels of PFASs in agricultural soils as well as bioaccumulation characteristics of PFASs in various types and organs of crops, some valuable measures for planting optimization and food safety were suggested to reduce human exposure and health risk of PFASs from the FIP.

The objectives of this study were, therefore, to examine the crop bioaccumulation and human exposure from PFASs around the FIP with emphasis on (i) the concentrations and profiles of PFASs in soils and multiple crops, (ii) the bioaccumulation and translocation of PFASs in crops associated with soil concentrations and chemical structures of PFASs and physiological characteristics of crops, (iii) human exposure and risk assessment of PFASs based on their crop concentrations, and dietary habits as well as the age groups of consumers, (iv) implications for planting optimization and food safety around a manufacturing facility for risk control.

2. Materials and methods

2.1. Sampling design and collection

The study area around the FIP is a major crop-producing region with large tracts of agricultural land and scattered villages, where staple grains and various vegetables are important local food. Two fields planted with vegetables and grains were chosen for the study: one is named as “FIP-0.3 km field” only 0.3 km away from the FIP; while the other one is called as “FIP-10 km field” about 10 km away from the FIP (Fig. 1). In these two fields, crops were planted under open-air field conditions and irrigated with local groundwater, and the irrigation frequencies were based on normal agricultural practices during growth periods of different crops. The edible parts of representative ten vegetables and three grain crops in the two fields were collected at maturity in June (wheat) and October (corn, soybean and various vegetables), 2014. Root vegetables (vegetables with edible roots) included radish (*Raphanus sativus* L.) root and carrot (*Daucus carota* L.) root, and shoot vegetables (vegetables with edible shoots) included radish shoot, carrot shoot, Chinese cabbage (*Brassica campestris* L. ssp. *Pekinensis*), Chinese chives (*Allium tuberosum* Rottler ex Sprengel), lettuce (*Lactuca sativa* L.) and Welsh onion (*Allium fistulosum* L.). Pepper (*Capsicum annuum* L.) represented a fruit vegetable (the vegetable with edible fruits) while cauliflower (*Brassica oleracea* L. var. *botrytis*) was collected as the representation of a flower vegetable (the vegetable with edible flowers). Wheat (*Triticum aestivum* L.) and corn (*Zea mays* L.) were sampled as grain crops (crops with edible grains). All the crops listed above were collected in each of the two fields. Pumpkin (*Cucurbita moschata* (Duch. ex Lam.) Duch. ex Poiret) (fruit vegetable), celery (*Apium graveolens* L.) (shoot vegetable) and soybean (*Glycine* max (Linn.) Merr.) (grain crop) were only found in the FIP-0.3 km field. To further explore the bioaccumulation and translocation of PFASs in different organs of the whole plant, some vegetables (including Welsh onion, celery and carrot) and grain crops (including wheat, corn and soybean) were divided into detailed parts.

For each species of crop, five replicates were sampled from the center and four corners of an area of 5 m × 5 m, and then mixed into

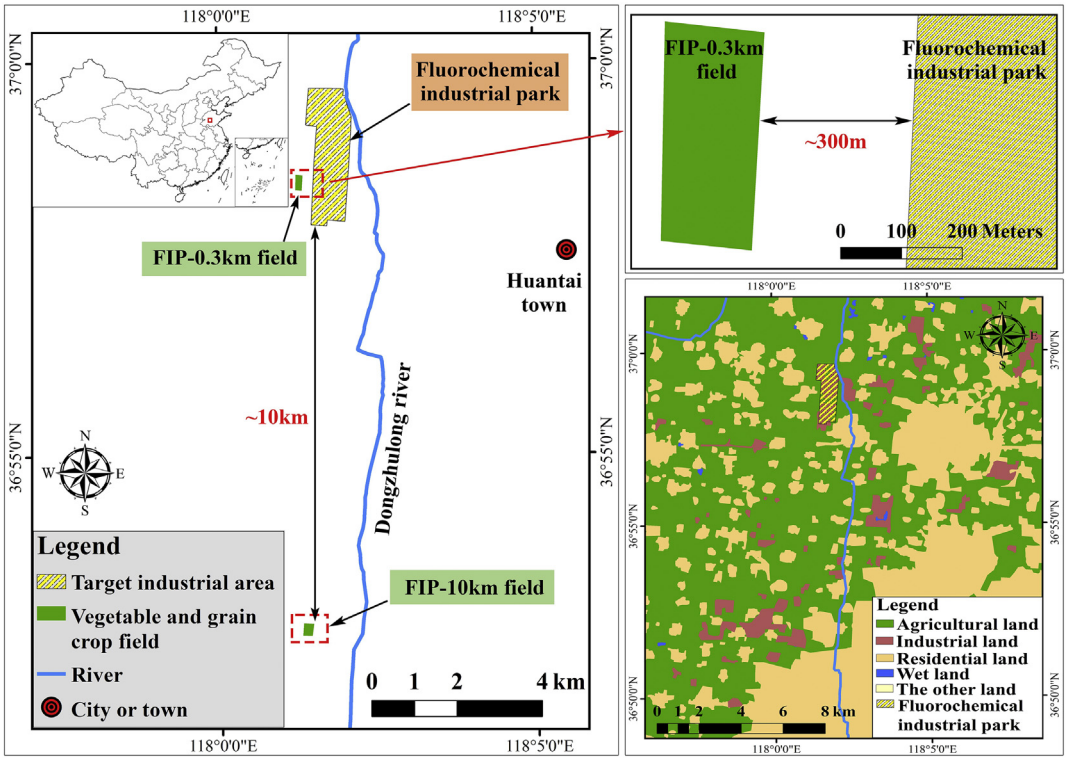

Fig. 1. The two selected fields for crop sampling around the FIP in Huantai County, Shandong Province, China.

one composite sample. The collected crop samples were wrapped in aluminum foil and stored in clean paper bags. The corresponding soils (top 0–20 cm) around each plant of the five replicates for the same crop species were collected with a stainless steel trowel that had been rinsed with ultra-pure water and methanol successively, and then mixed into one composite sample. Before soil samples were sealed in polypropylene (PP) bags, large stones and roots were removed with methanol rinsed tweezers. All collected samples were stored in an icebox during transport to the laboratory. Site information and ambient description are shown in Table S1. Once returned to the laboratory, the crop samples were washed carefully with distilled water followed by Milli-Q water before freeze-drying at a temperature of −50 °C for 72 h in a lyophilizer. A 100 g subsample was then ground and homogenized in a knife mill (Grindomix GM 200) and then stored separately at −20 °C before analysis. To avoid cross-contamination during grinding, after each use, we cleared out the plant residue carefully, and then rinsed the mill with 5 mL Milli-Q water four times followed by 5 mL methanol four times. Some previously detected crop samples with extremely low concentrations of PFASs were used as procedure blanks to examine if cross-contamination occurred during grinding. The soil samples were transferred to polypropylene (PP) boxes, dried in air, homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, before storage in 250 mL PP bottles at room temperature until extraction. An elemental analyzer was used to determine the total carbon (TC) and total nitrogen (TN) contents of the soil samples. The pH was determined at a soil to 0.01 M CaCl2 solution ratio of 1:5 (*w/v*) (Table S2) while the soil organic matter (SOM) was measured using the Walkley–Black procedure (Nelson and Sommers, 1982).

2.2. Standards and reagents

A total of 12 linear PFASs including 9 perfluoroalkyl carboxylic acids (PFCAs) with carbon lengths from C4 to C12, and 3 perfluoroalkane sulfonic acids (PFSAs) were identified and quantified in all samples. These substances were 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). Together with 12 above PFAS native standards, 9 mass-labeled PFASs, 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) for precise quantification. More detailed descriptions on standards and reagents can be found in the Supporting information.

2.3. Extraction and cleanup

The soil and plant samples were extracted mainly by solid phase extraction (SPE) using methods with minor modifications described previously by Loi et al. (2011) and Felizeter et al. (2012) (Supporting information). Quantitative analysis of PFASs was achieved by high performance liquid chromatography (Agilent 1290 Infinity HPLC System, Agilent Technologies, USA) coupled with electrospray ionization tandem mass spectrometry (Agilent 6460 Triple Quadrupole MS/MS System, Agilent Technologies, USA) in the negative electrospray ionization (ESI) mode. An Acclaim 120 C_{18} column (5 µm, 4.6 mm × 150 mm, Thermo Fisher Scientific Co.) was used to separate the target PFASs. The detailed descriptions of extraction and instrumental analysis are available in the Supporting information and Table S3.

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

In order to avoid cross contamination during field sampling, the soil samples were kept in three layers of sealed polyethylene bags while crop samples were kept in three-layers of sealed paper bags. For the purpose of examining if any external contamination occurred during the sampling, extraction and instrumental analysis, field blanks, transport blanks, procedure blanks and solvent blanks were conducted

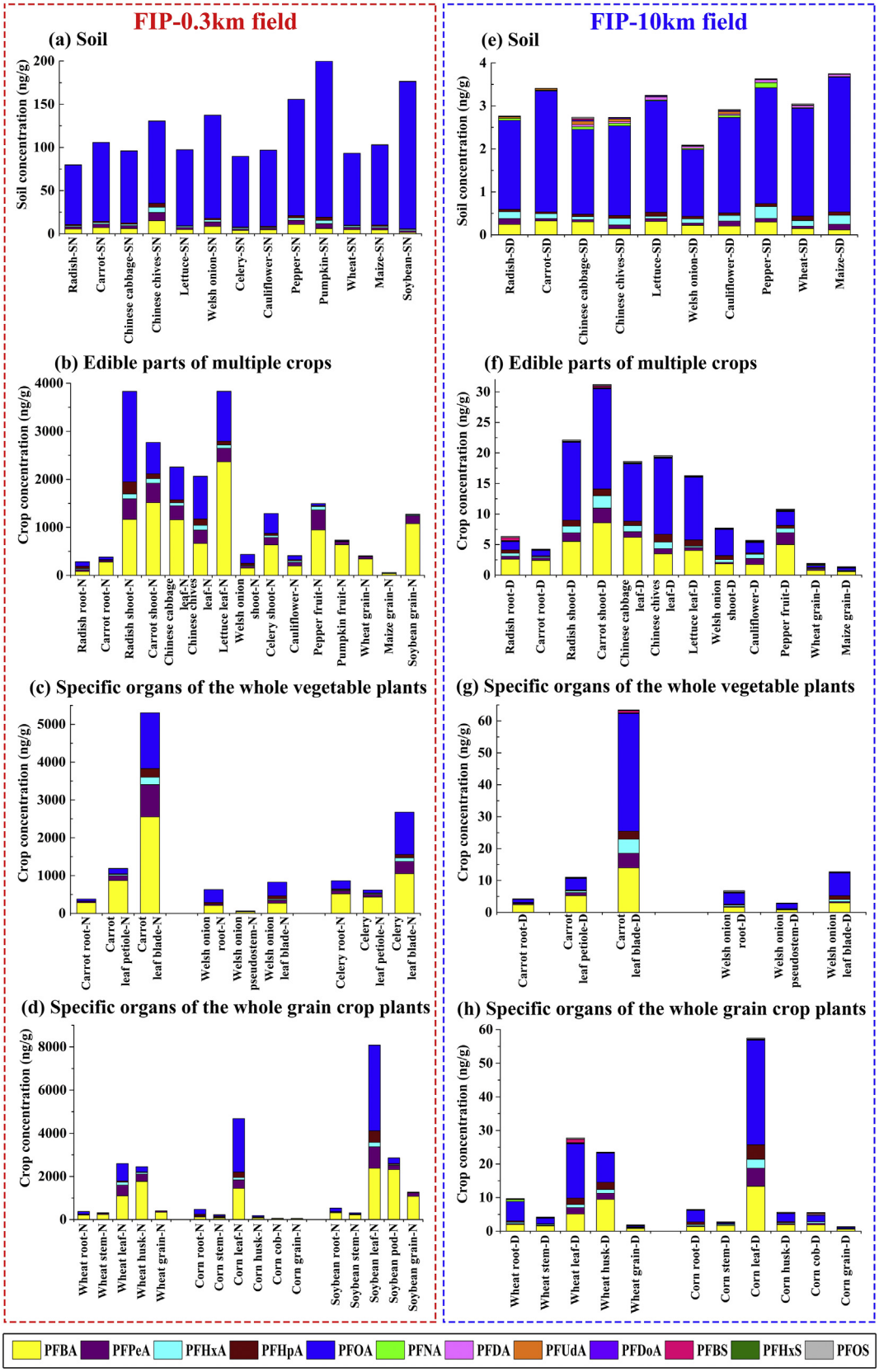

Fig. 2. Concentrations and compositions of PFASs in soil and edible parts of multiple crops.

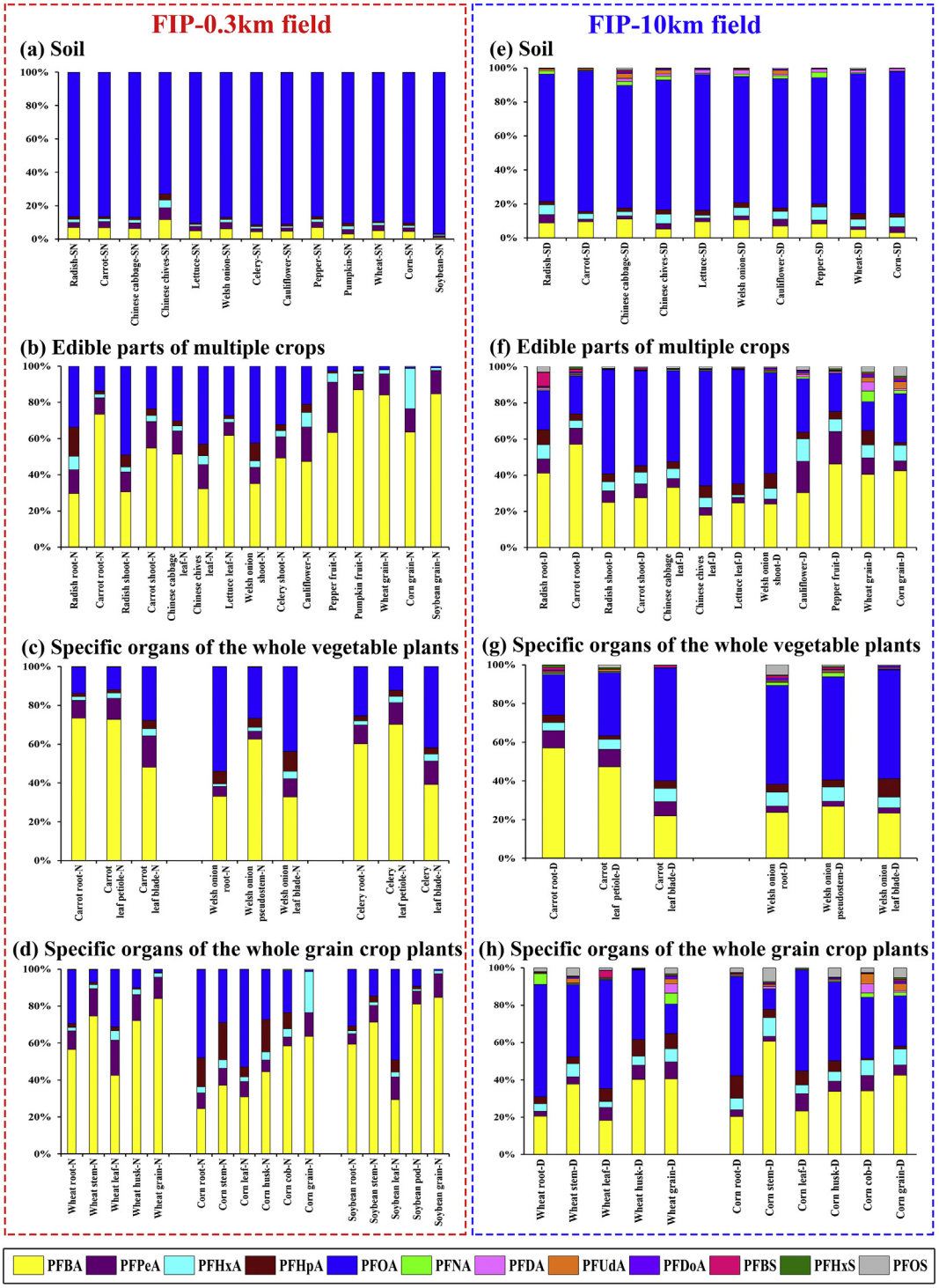

Fig. 3. The profiles of individual PFAS components in agricultural soils and corresponding crops.

for every sample batch. PFAS-related materials, such as polytetrafluoroethylene (PTFE) containers or coverings, were avoided to be used as much as possible throughout the study. Quantification of the 12 PFASs were carried out using a 10-point solvent based internal standard calibration curve with concentrations of native standards ranging from 0.01 to 100 ng/mL, spiked with a 5 ng internal standard. Regression coefficients (R^2) for calibration curves for all target analytes were > 0.99. The limit of quantification (LOQ) and limit of detection (LOD) were defined as the peak of the analyte that needed to yield a signal-to-noise (S/N) ratio of 10:1 and 3:1, respectively. If the concentrations of PFASs in any extract were > 100 ng/mL, then the samples would be reduced in volume or amount, and then extracted and quantified 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 PFAS. The matrix spike recoveries (MSRs) ranged from 72% to 93% for soil and 66% to 102% for plant. Replicate experiments were also conducted to ensure the precision of extraction and analysis. Detailed QA/QC information were given in Supporting information and Table S4.

2.5. Statistical analyses and graphic plotting

In this study, the concentration units of PFASs in both soil samples and crop samples were based on dry weight (dw). Statistical analysis and graphical representation were performed using SPSS Statistics V22.0 (SPSS Inc. Quarry Bay, HK), OriginPro 9.0 (OriginLab Corporation, USA) and Excel 2016 (Microsoft Corporation, USA). 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 LOD/ $\sqrt{2}$ (Hornung and Reed, 1990; Bao et al., 2011). Mapping of sampling sites and land use type were analyzed using ArcGIS V10.2 software (ESRI, Redland, CA, USA).

2.6. Bioaccumulation metrics and daily intake estimation

Bioaccumulation factors (BAFs), expressed as ratios between chemical concentration determined on a dry weight basis in the respective crop organs and corresponding soils, were calculated by Eq. (1) (Schwarzenbach et al., 2005). Transfer factors from root to shoot (TF) were calculated by Eq. (2), through dividing the chemical concentration in shoot by the chemical concentration in root on a dry weight basis (Lan et al., 2018).

$$\mathrm{BAF} = \frac{\text{PFAS concentration in crop (ng/g dw)}}{\text{PFAS concentration in soil (ng/g dw)}} \quad (1)$$

$$\mathrm{TF} = \frac{\text{PFAS concentration in shoot (ng/g dw)}}{\text{PFAS concentration in root (ng/g dw)}} \quad (2)$$

$$\mathrm{EDI} = \frac{\text{Daily consumption (g/d dw)} \times \text{PFAS concentration in crop (ng/g dw)}}{\text{Body weigh (kg)}} \quad (3)$$

Based on averaging the intake dose by body weight, the estimated daily intake (EDI, ng/kg·bw/day) of PFASs through the consumption of crop food can be calculated using Eq. (3). Parameters used for calculation were based on survey data from the Chinese Center for Disease Control and Bureau of Statistics of Shandong Province, China, illustrated in Table S5. Since body weights and consumption rates vary by age, the EDIs were estimated for three age groups: toddlers (2–5 years), children & teenagers (6–17 years), and adults (≥18 years) (Zhai, 2008; Zhang et al., 2010). Considering that the study area was located in the rural-urban fringe, the crops contaminated by PFASs may be consumed by both urban and rural residents. Based on statistical data concerning diet and body weight as well as crop concentrations, the EDIs of PFASs via consumption of grains and vegetables were estimated to assess health risk according to four possible scenarios: urban residents consuming crops with high concentrations grown in FIP-0.3 km field (Urban-high-exposure scenario) or low concentrations grown in FIP-10 km field (Urban-low-exposure scenario), and rural residents consuming crops with high concentrations grown in FIP-0.3 km field (Rural-high-exposure scenario) or low concentrations grown in FIP-10 km field (Rural-low-exposure scenario). For every scenario, the EDIs of PFASs for adults, teenagers & children, toddlers were further calculated to explore the relationship of age groups and health risks caused by PFASs exposure.

3. Results and discussion

3.1. Occurrence and source identification of PFASs in agricultural soil and crops

3.1.1. Concentrations and profiles of PFASs in agricultural soils

The presence of 12 PFASs were examined in this study. The soil concentrations of sum PFASs (ΣPFASs) ranged from 79.9 ng/g to 200 ng/g in FIP-0.3 km field and from 2.09 ng/g to 3.75 ng/g in FIP-10 km field (Fig. 2; Tables S6, S7). The profiles of PFASs in the soil samples for different crops were similar, and PFOA (C8) was the predominant component with an average contribution of 83.4% of the ΣPFASs, followed by shorter-chain PFCAs including PFBA (C4) (6.54%), PFPeA (C5) (2.96%), PFHxA (C6) (2.96%) and PFHpA (C7) (1.78%) (Fig. 3). Longer-chain PFCAs (C9–C12) and PFSAs including PFBS, PFHxS and PFOS were only observed in low concentrations or below the limit of detection (LOD), perhaps due to the limited production and application of these chemicals in this region (Wang et al., 2014a; Wang et al., 2016). The maximum PFOA concentration (181 ng/g) in agricultural soil of this study far exceeded most of PFOA concentrations (nd-47.5 ng/g) in soils reported in China (reviewed in Table S8), including soils collected in most developed industrial areas.

3.1.2. Concentrations and profiles of PFASs in crops

The crop concentrations of ΣPFASs ranged from 58.8 ng/g to 8085 ng/g in the FIP-0.3 km field and from 1.36 ng/g to 63.4 ng/g in the FIP-10 km field (Fig. 2; Table S9, S10, S11, S12). Unlike similar concentrations in the soil samples, the ΣPFASs concentrations varied largely in different types of crops. In the FIP-0.3 km field, edible parts showed significant higher concentrations of ΣPFASs in shoot vegetables (2355 ng/g, averagely), compared with those in fruit vegetables (1115 ng/g, averagely), flower vegetables (cauliflower, 410 ng/g), root vegetables (333 ng/g, averagely), and grain crops (580 ng/g, averagely) (Fig. 2). Similar tendency also occurred in FIP-10 km field (Fig. 2). It is noteworthy that the highest concentration of PFOA, the widely health-concerned component, in vegetables of this study reached up to the shocking level of 1880 ng/g, which was about 2–5 orders of magnitude higher than those collected in markets reviewed in previous studies (Jian et al., 2017; Sungur, 2018). The high concentrations of PFOA in crops indicated possible health risks for potential consumers.

Even for the same crop, the ΣPFASs concentrations in different organs also showed some discrepancies. The shoots of celery, radish and carrot showed much higher concentrations of ΣPFASs compared to their roots (Fig. 2). Furthermore, for specific parts of shoots, the ΣPFASs concentrations in leaf blades were higher than those in their long leaf petioles or pseudostems, which could be found in the FIP-0.3 km field with ΣPFASs concentrations of carrot leaf blade (5303 ng/g), carrot leaf petiole (1189 ng/g), celery leaf blade (2678 ng/g), celery leaf petiole (617 ng/g), Welsh onion leaf blade (825 ng/g), Welsh onion pseudostem (64.8 ng/g), and in FIP-10 km field with ΣPFASs concentrations of carrot leaf blade (63.4 ng/g), carrot leaf petiole (11.1 ng/g), Welsh onion leaf blade (12.7 ng/g), and Welsh onion pseudostem (2.90 ng/g) (Fig. 2). These findings can explain the relatively low ΣPFASs concentrations for whole shoots of Welsh onion, carrot and celery, which are with large weight proportion of the long leaf petiole or pseudostem.

As important sources of livestock feed, straws/stovers and grains of wheat, corn and soybean were also contaminated by PFASs. For wheat and soybean in FIP-0.3 km field, the highest ΣPFASs concentrations were found in leaves (wheat, 2597 ng/g; soybean, 8085 ng/g), followed by wheat husk (2452 ng/g) or soybean pod (2861 ng/g), grains (wheat, 407 ng/g; soybean, 1274 ng/g), roots (wheat, 371 ng/g; soybean, 532 ng/g) and stem (wheat, 319 ng/g; soybean, 312 ng/g) (Fig. 2). The corn plants in the same field also showed the highest ΣPFASs concentration of 4683 ng/g in the leaves. For corn, lower concentrations were found in the root (474 ng/g), followed by stem (223 ng/g), husk (187 ng/g), cob (63.8 ng/g) and grain (58.8 ng/g) (Fig. 2). PFASs levels in various types and organs of crops may be associated with their growth periods and physiological characteristics such as biological barriers (e.g., Casparian strip, cambium), root surface area, contents of protein and lipid, and transpiration capacity (Wen et al., 2016; Blaine et al., 2014a).

Unlike in soils, shorter-chain PFCAs (C4-C7) in crops accounted for a greater proportion of the total PFASs, indicating that there was a bioaccumulation preference for these homologues (Krippner et al., 2014; Wen et al., 2014). For edible parts in FIP-0.3 km field, PFBA (C4),

instead of PFOA (C8), became the dominant form, representing, on average, 56.5% of the total PFASs, followed by PFOA (C8) (21.6%), PFPeA (C5) (13.1%), PFHxA (C6) (4.84%) and PFHpA (C7) (3.93%). The longer-chain PFCAs (C9-C12) and PFSAs only contributed < 0.2% of ΣPFASs (Fig. 3). Compared to soil, the proportions of shorter-chain PFCAs (C4-C7) in multiple crops of the FIP-10 km field also exhibited the similar increase tendency.

The profiles of PFAS molecules varied across crops types. For edible parts of multiple crops in the FIP-0.3 km field, the average percentage of total shorter-chain PFCAs (C4-C7) was found to be the highest in grain crops (98.7%), followed by fruit vegetable (97.6%), flower vegetable (78.9%), root vegetables (76.2%), and shoot vegetables (64.6%) (Fig. 3). Compared to shorter-chain PFCAs (C4-C7), PFOA (C8) with larger molecular and greater $\log_{10}K_{OW}$ values may be more likely retained by biological barriers and plant issues during acropetal movement of PFASs in the crops (Blaine et al., 2014a; Lan et al., 2018). However, the proportions of PFOA in shoots of radish (49.1%), carrot (23.5%) and celery (32.3%) were higher than their roots (radish, 33.6%; carrot, 13.5%; celery, 25.3%) in the FIP-0.3 km field; while significant higher proportions of PFOA were also found in shoots of radish (57.7%) and carrot (52.5%) compared with their roots (radish, 21.5%; carrot, 21.1%) in the FIP-10 km field. Furthermore, for specific parts of the edible shoots, the leaf blades of carrot, celery and Welsh onion showed higher proportions of PFOA than their long leaf petioles or pseudostems (Fig. 2). Moreover, relatively high proportions of PFOA were also found in the leaves of wheat, corn and soybean compared to their other organs. This phenomenon implied that the composition of PFASs in leaves may be affected by other translocation or uptake pathways besides root uptake. For example, recent studies have gradually confirmed that plant leaves may absorb neutral PFASs in gas phase and ionizable PFASs occurred in fine particulate matters of the atmosphere (Zhu et al., 2016; Chen et al., 2018; Tian et al., 2018a). Except leaves, the proportions of sum shorter-chain PFASs compared to PFOA in specific organs of crops showed increase tendencies with the translocation distance through the plant.

3.1.3. Source identification of PFASs in agricultural soils and crops

Principal component analysis (PCA) and Spearman's correlation analysis on the 12 PFASs in the soils and crops showed that the concentrations of PFCAs, including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA, were strongly associated, indicating that these compounds may be derived from a similar parent source (Fig. 4; Table S13, S14, S15). Previous studies have confirmed the FIP as the predominant point source in the area (Liu et al., 2016; Liu et al., 2017a). The environmental PFASs may be derived from direct emissions during PFASs production and fluoropolymer manufacturing, as well as degradations of PFAS precursors and fluoropolymers (Dinglasan et al., 2004; Taniyasu et al., 2013b; Wang et al., 2014b; Rebecca, 2009). In addition, the PCA results showed that some PFAS components were discrete and not gathered together intensively with most PFCAs mentioned above (Fig. 4), which indicated other possible sources of PFASs, such as domestic emission or other industrial emissions, may exist in the area (Li et al., 2015).

PFASs in agricultural soils were inferred to come from irrigation water and atmospheric deposition contaminated by the FIP emissions (Liu et al., 2017a). In our previous studies, the concentrations of ΣPFASs in irrigation water were detected to be 147,165 ng/L in FIP-0.3 km field and 3.14 ng/L in FIP-10 km field, respectively (Liu et al., 2016). Although the occurrence of PFASs in the atmosphere has not been directly studied in this area, extremely high concentrations of ΣPFASs (4862 ng/L) reported in local precipitation may indirectly confirm the existence of substantial PFASs in the air (Liu et al., 2017a). Like composition profiles of PFASs in soil samples, the dominant component of the ΣPFASs in samples of irrigation water and precipitation was also PFOA, followed by shorter-chain PFCAs including PFBA, PFPeA, PFHxA and PFHpA. Root uptake from soil has been identified as a major source of PFASs in crops (Stahl et al., 2009; Lechner and Knapp, 2011). Based on recent studies, the significant relevance of PFAS concentrations between air/aerosol and plant leaves gradually revealed the potential of leaf uptake from airborne PFASs (Zhu et al., 2016; Chen et al., 2018; Tian et al., 2018a), which may be another possible source of PFASs in crops.

3.2. Crop bioaccumulation of PFASs in contaminated farmland

3.2.1. Bioaccumulation factors of ΣPFASs for multiple crops

The bioaccumulation factors (BAFs) provide an insight into the processes governing PFAS accumulation in crops. Soil properties such as SOM (17.9 ± 2.47 g/kg), pH (7.40 ± 0.24), TC (1.48 ± 0.28%) and TN (0.11 ± 0.01%) in both FIP-0.3 km field and FIP-10 km field were relatively similar (Table S2). In general, the edible parts and other organs of multiple crops in the FIP-0.3 km field showed higher BAFs of ΣPFASs compared to those in FIP-10 km field (Fig. 5). Similar phenomenon that higher BAFs of ΣPFASs in crops occurred in more seriously polluted soils was found in control experiments for vegetables previously reported (Blaine et al., 2014a; Krippner et al., 2015).

Depending on the crop types, the bioaccumulation factors (BAFs) of ΣPFASs for edible parts showed different values. The highest average BAF values of ΣPFASs were found in shoot vegetables (FIP-0.3 km field, 24.3; FIP-10 km field, 6.64), followed by fruit vegetables (FIP-0.3 km field, 6.63; FIP-10 km field, 2.98), flower vegetable (FIP-0.3 km field, 4.23; FIP-10 km field, 1.96), grain crops (FIP-0.3 km field, 4.05; FIP-10 km field, 0.50), and root vegetables (FIP-0.3 km field, 3.58; FIP-10 km field, 1.77) (Fig. 5). Previous studies have confirmed transpiration as the main driver for PFASs uptake by plants, and PFASs may transport from the root to shoot along with the transpiration stream (Blaine et al., 2013; Trapp and Eggen, 2013). However, it is noteworthy that longer-chain PFASs, with more hydrophobic perfluoroalkyl tails

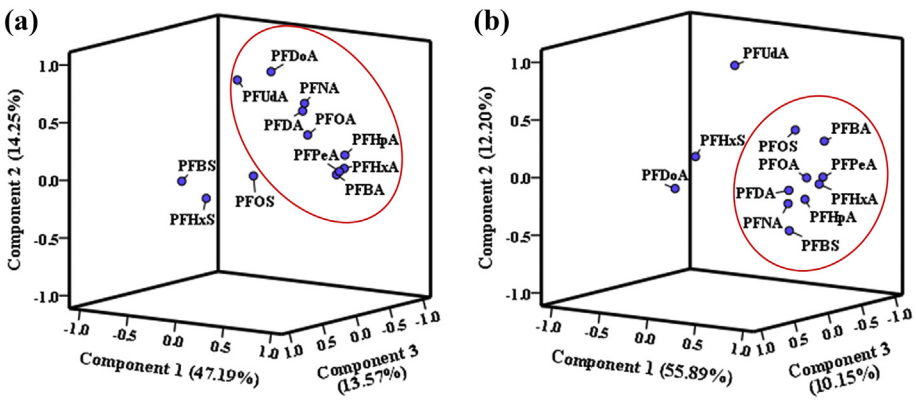

Fig. 4. PCA results using concentrations of 12 PFASs in agricultural soils (a) and crops (b).

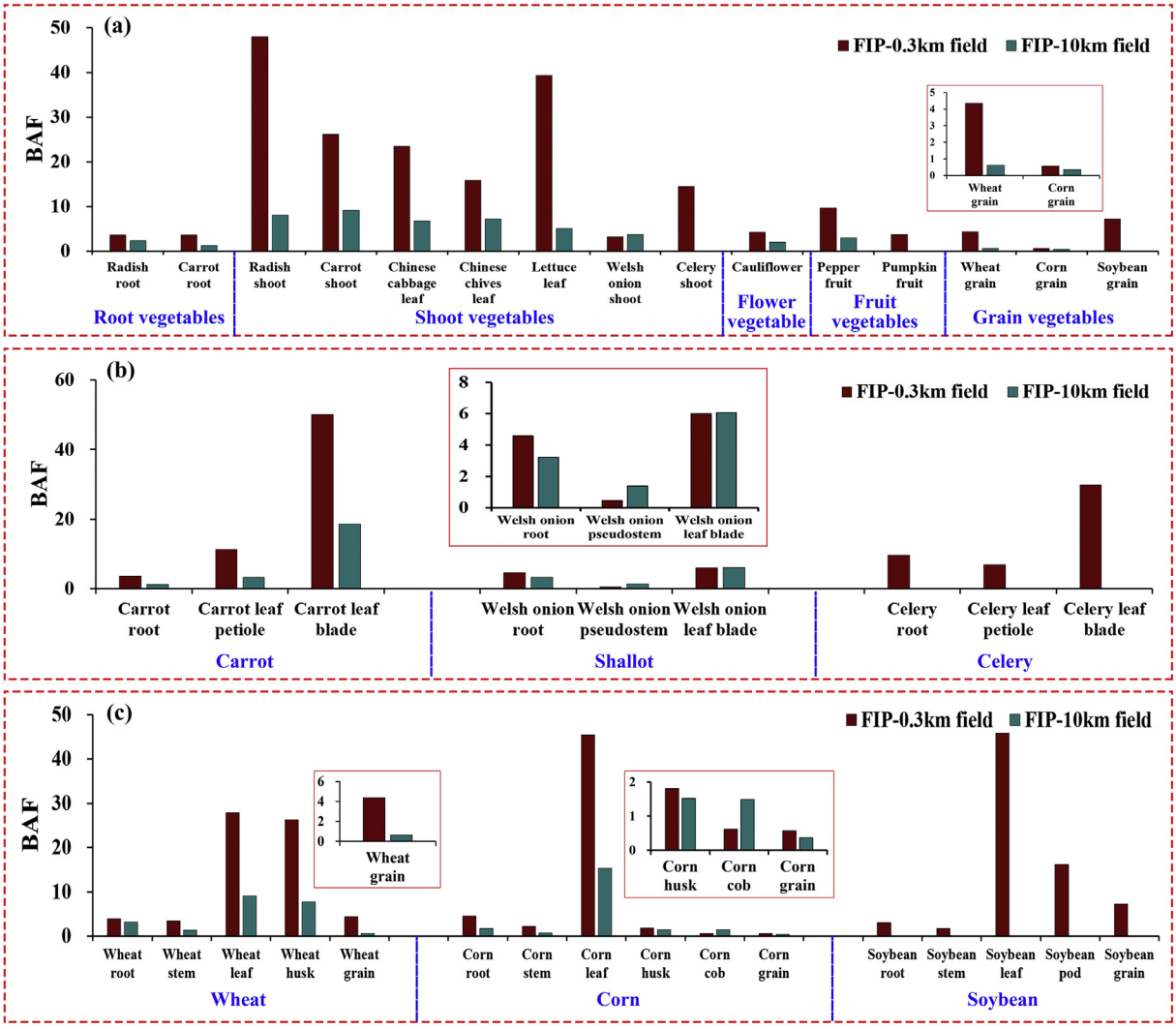

Fig. 5. Bioaccumulation factors (BAFs) of ΣPFASs for the edible parts of multiple crops (a) and for specific organs of vegetables (b) and grain crops (c).

and larger molecular volume, tend to be retained by biological macromolecules (such as protein and lipid) and barriers (e.g., Casparian strip) in roots, and less portions could be transferred to shoots (Taiz and Zeiger, 2010; Lan et al., 2018; Zhang et al., 2019). The transfer factors (TFs) of PFCAs (C4-C8) from roots to stems in grain crops exhibited a downward trend with the increasing carbon chain lengths, which also confirmed the existence of PFASs retention in roots. Besides root uptake, large amounts of airborne PFASs from the FIP might also have some contributions to the high concentrations of PFASs in shoots via leaf uptake (Zhu et al., 2016; Chen et al., 2018; Tian et al., 2018a). These facts may explain the higher BAFs of ΣPFASs for shoot vegetables. For other edible parts such as fruit, flower, grain, bulb root, PFASs would encounter additional membrane barriers (e.g., the cambium) in order to be loaded into the phloem and transported to these organs (Mench et al., 2009; Trapp and Eggen, 2013; Trapp, 2015).

The BAFs of ΣPFASs also varied in the specific organs of the whole plant. The pseudostems of the Welsh onion showed much lower BAFs of ΣPFASs (FIP-0.3 km field, 0.47; FIP-10 km field, 1.39) than the leaf blades (FIP-0.3 km field, 6.00; FIP-10 km field, 6.08); the BAFs of ΣPFASs for long leaf petioles of carrot (FIP-0.3 km field, 11.2; FIP-10 km field, 3.24) and celery (FIP-0.3 km field, 6.87) were far below those for leaf blades of carrot (FIP-0.3 km field, 50.1; FIP-10 km field, 18.6) and celery (FIP-0.3 km field, 29.8) (Fig. 5). Similar to the above vegetables, the leaves of wheat, corn and soybean also exhibited quite high BAFs of ΣPFASs compared with other organs. Considering the retention of PFASs by biological macromolecules and barriers from root to shoot, direct leaf uptake from the air was inferred as a potential contributor to the higher BAFs of ΣPFASs in crop leaves (Blaine et al., 2013; Chen et al., 2018). The shoot morphologies of carrot, radish and celery have similar characteristics with leaf blades grown on the long leaf petioles. However, the TFs of ΣPFASs from root to shoot in the carrot (FIP-0.3 km field, 7.26) and radish (FIP-0.3 km field, 13.5) showed much higher values compared with the celery (FIP-0.3 km field, 1.50). The phenomenon was attributed to the lack of Casparian strip between the edible root and the above ground shoot in radish and carrot, which would permit the unrestricted upward flow of PFASs (Suga et al., 2003). Previous studies have found that lipids and proteins in plants have a high affinity to PFASs, which may affect the plant bioaccumulation of PFASs (Bischel et al., 2011; Xia et al., 2013; Wen et al., 2016). In the FIP-0.3 km field, the BAF of ΣPFASs in the corn root (4.59) was higher than that in the soybean root (3.01), which may be related to the higher lipid content in the corn root (4.35%) compared with the soybean root (2.45%) (Wen et al., 2016). For three types of grains, the BAFs of ΣPFASs for the soybean (FIP-0.3 km field, 7.22) were highest, followed by the wheat (FIP-0.3 km field, 4.35; FIP-10 km field, 0.63) and the corn (FIP-0.3 km field, 0.57; FIP-10 km field, 0.36) (Fig. 5). These discrepancies may be inferred to associate with lipid and protein contents of these crops, which are the higher for soybean grain (lipid, 15.9%; protein, 33.1%), than wheat grain (lipid, 2.5%; protein, 15.7%) or corn grain (lipid, 0.8%; protein, 8%) (Yang, 2008).

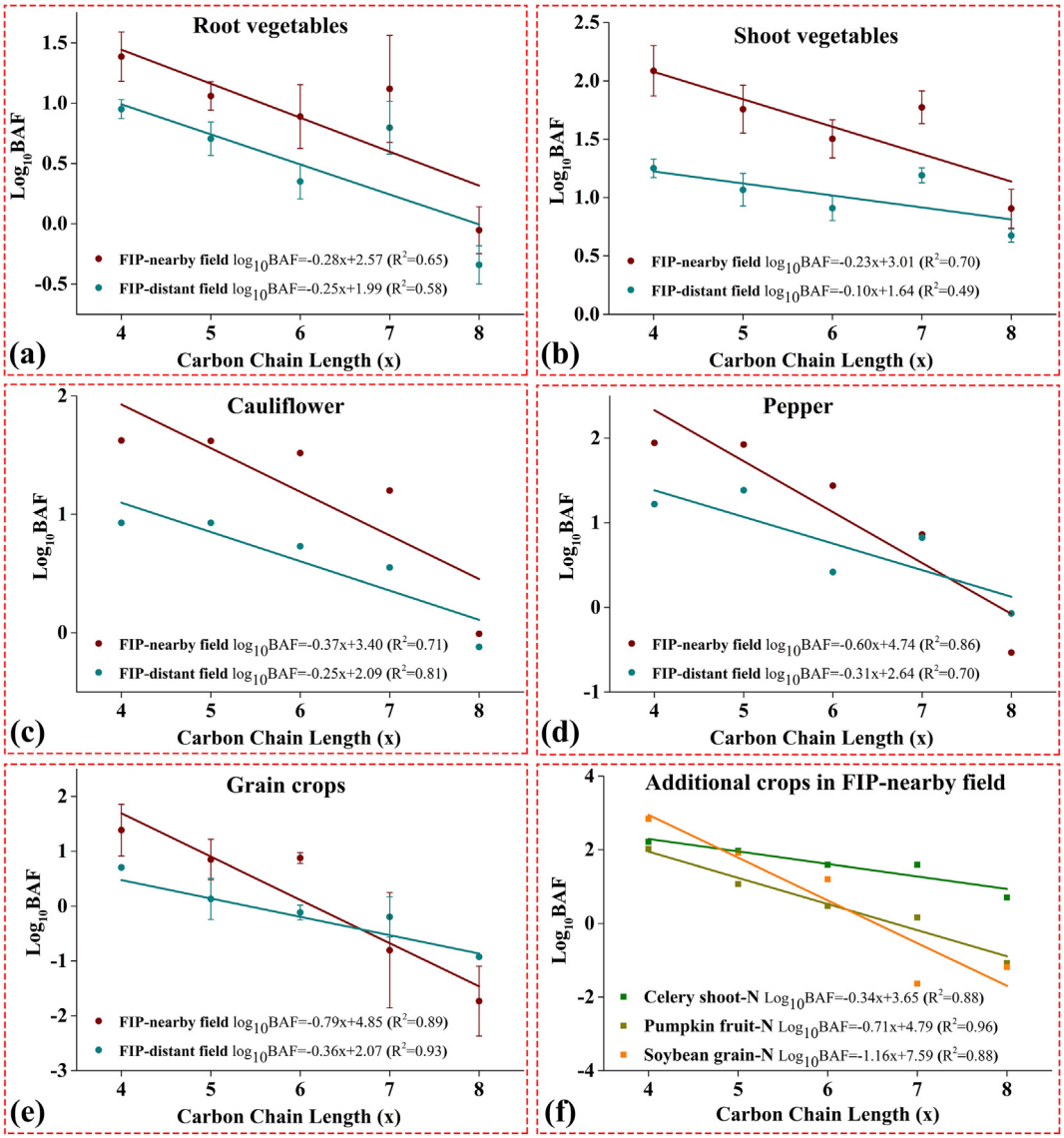

Fig. 6. The relationship between bioaccumulation factors of individual PFASs and their carbon chain lengths for edible parts of multiple crops.

3.2.2. Bioaccumulation equations of individual PFAS components for multiple crops

The crops showed different bioaccumulation capacities for various PFAS components. For crops in FIP-0.3 km field, the total concentrations of shorter-chain PFCAs (C4-C7) were about 14-fold larger than those of PFOA (C8), despite the soil concentrations of PFOA (C8) being an average of 9.41 times higher than the sum of shorter-chain PFCA (C4-C7) concentrations. Similar concentration trends were also found for crops in the FIP-10 km field. These findings indicated a preferential uptake of shorter-chain PFCAs for crops, as observed previously in controlled experiments (Krippner et al., 2015). Longer-chain PFASs, with higher $\log_{10}K_{OW}$ values, were more easily combined with organic matters in soils, and may exhibit lower rhizospheric mobility and bioavailability. To further explore effects of crop physiological characteristics on bioaccumulation of individual PFAS, same crop types in the two fields were selected and then classified as different categories, and subsequently carbon chain lengths of main PFCAs (C4-C8) versus the logarithm of corresponding BAFs ($\log_{10}$BAFs) were plotted with trend line, equations and correlation coefficients (Fig. 6).

In general, the $\log_{10}$BAFs for multiple crops presented a linear decrease trend with increasing carbon chain lengths of PFCAs (C4-C8). However, the decrease rate of $\log_{10}$BAFs per CF_2 unit, reflecting bioaccumulation discrepancies of individual PFCA components, varied depending on crop types. For edible parts of multiple crops, the largest decrease rates of $\log_{10}$BAFs per CF_2 unit were observed in grain crops with the average value of 0.79 in FIP-0.3 km field and 0.36 in FIP-10 km field, followed by those in fruit vegetables (pepper) (FIP-0.3 km field, 0.60; FIP-10 km field, 0.31), flower vegetables (cauliflower) (FIP-0.3 km field, 0.37; FIP-10 km field, 0.25), root vegetables (FIP-0.3 km field, 0.28; FIP-10 km field, 0.25) and shoot vegetables (FIP-0.3 km field, 0.23; FIP-10 km field, 0.10) (Fig. 6). When large amounts of PFASs stored in leaves through transpiration, shorter-chain homologues were easier to cross additional membrane barriers (e.g., the cambium) in order to be loaded into the phloem and transported to storage organs (e.g., fruit, flower, bulb root, grain) together with nutrients from photosynthesis (Trapp, 2004; Wen et al., 2013). Therefore, more shorter-chain PFCAs compared to PFOA would flow out from leaves to storage organs. The uptake potential of airborne PFASs by leaves was found to be positively associated with their $\log_{10}K_{OA}$ values (Chen et al., 2018). Considering that PFOA may be the primary component of local airborne PFASs (Liu et al., 2017a) and the $\log_{10}K_{OA}$ of PFOA is higher than those of shorter-chain PFCAs (Table S16), more PFOA is inferred to be absorbed by crop leaves from the air. Loss of shorter-chain PFCAs as well as potential uptake of PFOA reduced the gap of main PFCAs

concentrations in leaves, and further led to relatively small decrease of log_{10}BAFs per CF_2 unit. Due to the lack of the typical barrier (Casparian strip) in roots of carrot and radish, not only short-chained PFASs but also long-chained ones were transported to shoot unrestrictedly. Therefore, with the increase of PFCAs carbon chain length, these edible roots showed similar decline trend of log_{10}BAF compared to edible shoots. For storage organs, considerable PFASs bioaccumulation was by means of nutrient delivery from the leaf photosynthesis and water transport from the root. PFASs retention, especially for longer-chain ones, by gradually increasing biological barriers raised with the transport distance, which exhibited larger decrease rate of log_{10}BAFs per CF_2 unit for cauliflower, pepper and grain. Moreover, similar tendencies were also found in additional vegetables in FIP-0.3 km field with smallest decrease of log_{10}BAF per CF_2 unit for celery shoot (0.34), followed by pumpkin fruit (0.71) and soybean grain (1.16) (Fig. 6). It was worth emphasizing that with the increase of carbon chain length, the BAFs of individual PFASs for crops in FIP-0.3 km field with high soil concentrations were found to decrease faster than those in FIP-10 km field with low soil concentrations (Fig. 6).

For specific organs of the whole plants, the decrease in log_{10}BAFs per CF_2 unit was the smallest in leaves compared to other organs (Table S17), which may also be due to loss of shorter-chain PFCAs through outflow from the leaves as well as potential leaf uptake of PFOA from air or aerosol. Except for leaves, the decrease rate of Log10BAF per CF2 unit in stems were larger than those in roots, mainly due to the retention of longer-chain components by biological macromolecules and barriers during upward transport. Moreover, the log_{10}BAFs decrease rates with the carbon chain lengths of PFCAs for wheat husk, corn cob and soybean pod all showed smaller values than their grains, the organs with the longest distance from root and leaf. As mentioned above, the bioaccumulation discrepancies of individual PFCAs became gradually larger with the increase of transport distance and biological barriers in crops.

3.3. Human exposure estimation and health risks of PFASs for local urban and rural residents

3.3.1. Human exposure estimation of PFASs via crop consumption for local residents

Some high soil concentrations of PFOA in FIP-0.3 km field were similar to or even exceeded the predicted non-effect concentration (PNEC) of 160 ng/g (Amundsen et al., 2008), implying a potential ecological risk to local soil organisms. But such soil contamination levels were still far below the residential soil screening level (16,000 ng/g for PFOA) recommended by the USEPA, indicating that health risk caused by ingestion, inhalation and dermal exposure of contaminated soils would be very low (USEPA, 2016). However, consuming contaminated crops has been identified as an indispensable exposure pathway of concern for PFASs for human health (Vestergren et al., 2012; Jian et al., 2017). According to official statistics, vegetables and grains account for more than half of the total food for local residents (Bureau of Statistics of Shandong Province, 2015). Due to richness of nutrients, dietary fiber and phytochemicals, more vegetables were consumed as a healthy diet by urban residents in China, whose living conditions are better than rural residents (National Bureau of Statistics, 2014). When estimating human exposure of PFASs for local residents, the average PFASs concentrations of eight identical vegetables, representing dominant types of local vegetables, were used to estimate PFASs exposure via vegetable consumption. In addition, wheat and corn, accounting for 80% of local grain food (Bureau of Statistics of Shandong Province, 2015), were selected for exposure estimation of PFASs through grain consumption. Distinct PFASs exposure patterns may be caused by contamination levels of edible crops and dietary habits of local residents.

The estimated daily intake (EDIs) of major PFAS components via crop consumption varied depending on crop concentrations of PFASs, dietary habits and age groups of consumers. In general, the EDIs of ΣPFASs (1986–3544 ng/kg·bw/day) via consumption of crops from the FIP-0.3 km field were about 2 orders of magnitude higher than those (11.5–19.5 ng/kg·bw/day) from FIP-10 km field (Fig. 7; Table S18). Similarly, the average EDI of ΣPFASs via diet exposure were also up to 998 ng/kg·bw/day for adults near a PFASs manufacturing facility in Hubei Province, China (Zhang et al., 2017), which further confirmed that PFAS-related industries were important sources of local contaminated foods and high human exposure of PFASs for nearby residents. In terms of the consumption of crops from FIP-0.3 km field, the EDIs of ΣPFASs were highest for toddlers (urban: 3019 ng/kg·bw/day, rural: 3544 ng/kg·bw/day), followed by children & teenagers (urban: 2498 ng/kg·bw/day, rural: 2994 ng/kg·bw/day) and adults (urban: 1986 ng/kg·bw/day, rural: 2395 ng/kg·bw/day) (Fig. 7; Table S18). Toddlers and children & teenagers are exposed to higher amounts of PFASs than adults, which is a consequence of higher consumption per body weight (Klenow et al., 2013). Similar trends were also found in China via dietary intake with average PFOA EDIs of 1.99 ng/kg·bw/day for children and 0.96 ng/kg·bw/day for adults (Zhang et al., 2017), via 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 PFOA EDIs ranged from 0.28 to 0.39 ng/kg·bw/day for children and from 0.19 to 0.23 ng/kg·bw/day for adults (Klenow et al., 2013). These findings indicated that low-age groups of residents were particularly susceptible to long-term dietary exposure to PFASs. Additionally, the EDIs of ΣPFASs in two scenarios for rural residents showed higher values compared to those for urban residents, due to lower total consumption of wheat, corn and vegetables for urban residents. However, the EDIs of PFOA showed higher values for urban residents than those for rural residents (Fig. 7; Table S19). This may be explained by larger proportion of vegetables in urban diet as well as stronger bioaccumulation capacities of PFOA in vegetables compared with grains of wheat and corn. Previous study also reported higher EDI of PFOA for urban residents (6.8 ng/kg·bw/day) than those for rural residents (5.1 ng/kg·bw/day) (Zhang et al., 2016). Furthermore, larger proportions of animal-derived food with strong bioaccumulation potential of PFASs, may contribute to higher human exposure of PFASs, especially longer-chain PFASs, for urban residents.

3.3.2. Health risk assessment of PFASs exposure for local residents

The high EDIs of PFASs demonstrated the necessity of human health risk assessment associated with these exposures. Although there is no guideline for dietary intake of PFASs in China, the tolerable daily intake (TDI) values for PFOA have been established in other parts of the world. Compared to current recommended TDI values of 100 to 1500 ng/kg·bw/day for PFOA proposed by several countries (Fig. 7), the EDIs of PFOA in high-exposure scenarios for both urban or rural residents with different age groups were more than twice of the TDI value of 100 ng/kg·bw/day recommended by the Federal Environment Agency, Germany (BfR, 2006; TWK, 2006) (Fig. 7). While the EDIs of PFOA for toddlers were even approximately to the TDI value of 333 ng/kg·bw/day recommended by the USEPA (Thayer and Houlihan, 2008). Therefore, it can be concluded that the EDIs for PFOA are associated with risks for adverse human health effects, especially for local toddlers. Even if in low-exposure scenarios, cumulative body burdens of PFOA may increase the risk of health effects.

In addition, other exposure pathways of PFOA may exist for local residents. Local groundwater was once used as a source of drinking water, in that case the EDIs of PFOA for adults were estimated to be 3755 ng/kg·bw/day in FIP-0.3 km field and 0.07 ng/kg·bw/day in FIP-10 km field (Liu et al., 2016). Fortunately, local government has built improved tap water systems for rural and urban residents, aiming to reduce health hazards and risks from contaminated water. However, effective measures for reducing the human exposure to PFASs from crop consumption have not been taken, which is essential and urgent to

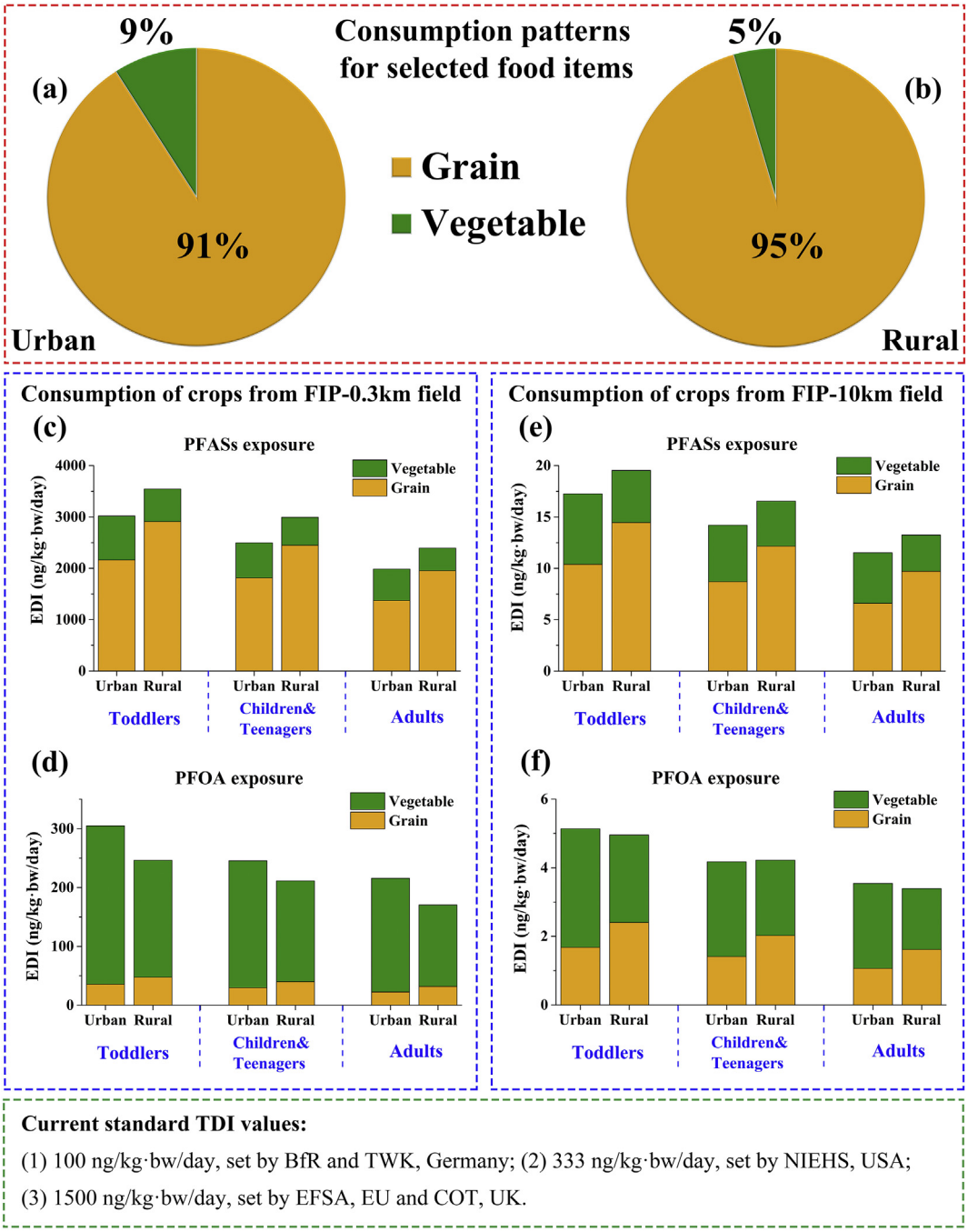

Fig. 7. Estimated daily intakes (EDI) of PFASs via consumption of contaminated crops (ng/kg·bw/day) for local urban and rural residents. Note: The detailed explanations about the calculation methods of above TDI values of PFOA are shown in the Supporting information.

safeguard the health of local residents. Besides consumption of grains and vegetables, local animal-derived foods, mostly not yet studied here, may also contribute to the dietary load of PFOA. Moreover, human exposures of PFOA for adults via dust ingestion and dermal absorption have been found to be 8.34 ng/kg·bw/day near the FIP-0.3 km field and 0.25 ng/kg·bw/day near the FIP-10 km fields (Su et al., 2016). Considering these potential intake pathways, the EDIs and health risks of PFOA in high-exposure scenarios would become more serious while those in low-exposure scenarios would be elevated to be a level of concern.

Based on dietary intake, the EDIs of PFOA for adults have been reported in China (0.59–10.5 ng/kg·bw/day) (Zhang et al., 2010; Zhang et al., 2017), Japan (0.72–1.3 ng/kg·bw/day) (Kärrman et al., 2009), Norway (0.086 ng/kg·bw/day, averagely) (Papadopoulou et al., 2017), Italy (0.39 ng kg·bw/day, averagely), Czech Republic (0.23 ng/kg·bw/day, averagely), Belgium (0.65 ng/kg·bw/day, averagely) (Klenow et al., 2013), Germany (2.9 ng/kg·bw/day, averagely) (Fromme et al., 2007), Sweden (0.35–0.69 ng/kg·bw/day) (Vestergren et al., 2012), and the US (0.82 ng/kg·bw/day, averagely) (Schecter et al., 2010). Obviously, the elevated EDIs of PFOA (adults: 216 ng/kg·bw/day) reported in urban-high-exposure scenario far exceeded those values previously reported. Even in low-exposure scenarios with consuming crop produced from the FIP-10 km field, the EDIs of PFOA (urban adults: 3.54 ng/kg·bw/day, rural adults: 3.39 ng/kg·bw/day) were still comparable or higher than the upper limits of most reported EDI values, implying that the contamination distance of the FIP for crops can be

farther than 10 km.

Those risk assessments were mostly conducted for PFOA, just one component of the PFAS family. Crop bioaccumulation preference led to the EDIs of shorter-chain PFCAs for local residents being much higher than those of PFOA (Jian et al., 2017). However, accurate risk assessment of short-chain PFASs cannot be conducted due to a paucity of their TDI values, as a result of shortage of human and eco-toxicological data for these chemicals (USEPA, 2018). Therefore, health risks from multiple PFASs via crop consumption for local residents may be more serious than just PFOA. In addition, it is worth emphasizing that the FIP has been expanding their fluoropolymers production (Wang et al., 2016). If without suitable substitutes for PFASs used in fluoropolymer productions or safety improvement for local food, continuous or even higher exposure of these substances would pose a risk to the local residents.

4. Conclusions and perspectives

Overall, it can be concluded in this study that:

- The highest concentrations of ΣPFASs were up to 200 ng/g in agricultural soils and 8085 ng/g in crops nearby the FIP. The profiles of PFASs in soils were dominated by PFOA (C8) with an average contribution of 83.4%, while in their crops shorter-chain PFASs (C4-C7), especially PFBA (C4), became major components, indicating crop bioaccumulation preference for these homologues.
- For edible parts of multiple crops, the highest BAFs of ΣPFASs were found in shoot vegetables compared with those in fruit vegetables, flower vegetable, root vegetables and grain crops. For specific organs of some crops, significantly higher BAFs of ΣPFASs were also found in leaves. Root uptake from the soil and leaf uptake from the air may be two potential sources of crop bioaccumulation of PFASs. Some PFASs, especially longer-chain homologues, may be retained by biological macromolecules and barriers during acropetal movement. For three grains, the BAFs of ΣPFASs for the soybean were highest, followed by wheat and corn, which may be related to decreasing content of lipid and protein.
- Shorter-chain PFASs showed higher bioaccumulation capacities, probably related to their greater mobility and less retention than longer-chain homologues during translocation in the plant. With increasing carbon chain lengths of PFCAs (C4-C8), their $\log_{10}$BAF values for edible parts of various crops showed a linear decrease, and the steepest decrease slopes were observed in grain crops, followed by fruit vegetables, flower vegetables, root vegetables and shoot vegetables. For specific organs of the whole crops, PFCAs (C4-C8) in leaves also showed relatively flat decrease slopes of $\log_{10}$BAF per CF_2 unit compared to other organs. Longer-chain PFCAs with higher $\log_{10}K_{OA}$ values in the air are inferred to be more easily absorbed by leaves, which may reduce bioaccumulation discrepancies of individual PFCAs.
- The EDIs of PFASs via crop consumption varied by crop concentrations, and age groups and dietary habits of consumers. Compared to those from FIP-10 km field, the predicted EDIs of ΣPFASs via consumption of crops from the FIP-0.3 km field showed about 2 orders of magnitude higher values. This could lead to potential human health risks for all age groups based on TDIs of PFOA. Toddlers and children & teenagers are exposed to more PFASs as well as higher health risk than adults, as a result of their higher consumption per body weight. The larger proportion of vegetables in plant origin foods for urban diet contributed higher human exposure of PFOA, mainly due to stronger PFOA bioaccumulation capacities for vegetables compared with grains. Furthermore, potential soil ecological risks may also be caused by high concentrations of PFOA.

Implications and perspectives

- **Land-use and planting optimization:** Agricultural soils heavily-polluted by PFASs should be remediated or changed into other land uses such as forest or grass land. Planting the inedible economic crops like cotton in PFAS-contaminated fields is also a good choice, which will not only reduce human exposure to PFASs but also increase the farmers' income. However, if edible crop planting is inevitable, grain crops, especially those with low content of protein and lipid, are suggested. While vegetables, especially shoot vegetables, should be reduced as much as possible due to their high bioaccumulation capacity of PFASs.
- **Food safety implication:** High-efficient systems for origin traceability and safety scrutiny of agricultural products are vital to reduce human exposure of PFASs as much as possible. When consuming suspected PFAS-contaminated shoots of Welsh onion, carrot and celery, the long pseudostems or leaf petioles are suggested to be eaten, rather than their leaf blades with higher bioaccumulation of PFASs. If PFAS-contaminated plants were used as animal fodders, it would be better not use leaves to reduce the PFASs exposure for livestock or poultries.
- **Limitations and prospects of this study:** In this paper, the degradation of PFASs precursors and fluoropolymers in the environment was not fully discussed, and the occurrence of PFASs in the air as well as the mechanisms of leaf uptake of airborne PFASs were not yet systematically studied. The above-mentioned aspects may provide more valuable information for detailly revealing pollution sources and crop bioaccumulation mechanisms of environmental PFASs, and need to be further explored in future studies. In addition, a more comprehensive risk assessment taking into account of the hazards of shorter-chain PFASs and other exposure pathways is also essential to safeguard the health of local residents.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.04.008.

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