Field study on the uptake and translocation of perfluoroalkyl acids (PFAAs) by wheat (*Triticum aestivum* L.) grown in biosolids-amended soils

Bei Wen^{a,*}, Longfei Li^a, Hongna Zhang^a, Yibing Ma^b, Xiao-Quan Shan^a, Shuzhen Zhang^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b Ministry of Agriculture Key Laboratory of Plant Nutrition and Nutrient Cycling, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, 12 Southern Street of Zhongguancun, Beijing 100081, China

ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form

18 September 2013

Accepted 20 September 2013

Keywords:

Biosolid

Wheat

Perfluoroalkyl acids

Field study

Uptake

Translocation

ABSTRACT

Field experiments were performed to evaluate the uptake and translocation of perfluoroalkyl acids (PFAAs) in wheat (*Triticum aestivum* L.) grown in soils amended with biosolids at different rates. Nine perfluorocarboxylic acids (PFCAs) and three perfluorosulfonic acids (PFSAs) were detected in the soils and wheat tissues. Total concentrations of PFAAs in the soils and wheat root, straw, husk and grain increased with increasing application of biosolids. PFCA concentrations in grain increased logarithmically with increasing PFCA concentrations in soils ($P < 0.01$) while PFSAs in grain were correlated linearly with PFSA concentrations in soils ($P < 0.01$), indicating that PFCAs and PFSAs may have different transport pathways from soil to grain. While no significant correlation was found between the root concentration factors ($C_{\text{root}}/C_{\text{soil}}$) and PFAA carbon chain length, the transfer factors from roots to straws ($C_{\text{straw}}/C_{\text{root}}$) and from straws to grains ($C_{\text{grain}}/C_{\text{straw}}$) correlated negatively with PFAA carbon chain length ($P < 0.01$).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Land application of biosolids (treated sewage sludges) from municipal, agricultural and industrial waste water treatment plants is becoming an increasingly important global practice. It is considered a useful approach for the final disposition and an important recycling and resource recovery option (Clarke and Smith, 2011; Farrell and Jones, 2009). Biosolids constitute a valuable source of essential nutrients for agricultural cultivation. Organic matter from biosolids improves physical and chemical properties of soil. However this practice possesses potential risks associated with contaminant accumulation in surface soils. Previous studies focus on the phytoavailability and toxicity of metals in soils extensively in order to conduct risk assessment of biosolids application (Li et al., 2012; McLaughlin et al., 2006). Besides metals, biosolids are known to contain significant levels of organic contaminants. Particular attention has been given to the selected priority groups of persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated

biphenyls (PCBs) and chlorinated dioxins/furans (PCDD/Fs) (Clarke and Smith, 2011; Farrell and Jones, 2009; Harrison et al., 2006). These POPs are highly persistent in the environment, leading to an accumulation in the terrestrial environment.

Perfluoroalkyl acids (PFAAs) have been employed in materials such as wetting agents, lubricants, corrosion inhibitors, stain-resistant treatments, and foam fire extinguishers. They have received great scientific concerns due to their wide occurrence in atmosphere (Li et al., 2011; Ahrens et al., 2011), soil (Yoo et al., 2010), surface water (Eschauzier et al., 2010), sediment (Kwadijk et al., 2010) and biota (Houde et al., 2011), and due to their toxicity as well (Olsen et al., 2009). One of the prevalent PFAAs, perfluorooctane sulfonate (PFOS), is recognized as an emerging persistent organic pollutant (Stockholm Convention, 2009).

Sewage sludge is widely recognized as a major sink of some PFAAs (Sun et al., 2011; Guo et al., 2010; Higgins et al., 2005). Higgins et al. (2005) reported that the concentrations of PFAAs in domestic sludge ranged from 5 to 152 ng/g for total perfluorocarboxylates and 55–3370 ng/g for total perfluoroalkyl sulfonyl-based chemicals. The use of biosolids as fertilizers in agriculture may present an exposure route of PFAAs into the soils. Sepulvado et al. (2011) found that concentrations of PFOS ranged 2–483 ng/g in biosolids-amended soils. In Decatur, Alabama, PFAAs

* Corresponding author.

E-mail addresses: bwenn@rcees.ac.cn, cucumbermooncake@163.com (B. Wen).

and their precursors were notably accumulated in soils as a result of land use of industrially-contaminated biosolids (Yoo et al., 2010; Washington et al., 2010). Clarke and Smith (2011) pointed out that PFAAs are one of the main priority groups of compounds in biosolids requiring additional research.

Perfluoroalkyl acids in contaminated soils may be transferred to the food chain by plant uptake and exert a potential health risk. It is therefore necessary to understand the behavior of PFAAs in the soil-plant system as a result of biosolids application. So far very few studies have dealt with this issue in the soil-plant system. Pot studies by Zhao et al. (2013), Felizeter et al. (2012), Lechner and Knapp (2011) and Stahl et al. (2009) showed that PFAAs could be taken up, for example, by maize, oats, wheat, potatoes, lettuce, cucumbers and carrots. Plant accumulation of PFAAs was dose-dependent and varied with plant species. However, most of these studies only focused on two PFAAs, perfluorooctanoic acid (PFOA) and PFOS in pot experiments. The physical properties and molecular structures of different PFAA congeners may have different effects on their accumulation in plants. Moreover, greenhouse pot experiments and artificially polluted soils do not present the actual behavior of weathered PFAAs in field soils. Stahl et al. (2013) described a long-term lysimeter experiment that demonstrated the carry-over of PFAAs from spiked soil to plant under field conditions. Evidence for accumulation of PFAA congeners and fluorotelomer alcohols in the above-ground part of grasses grown in sludge contaminated soils was provided by Yoo et al. (2011). However, the unknown distribution pattern of PFAAs in grasses limits the understanding of PFAA congener uptake and translocation mechanisms in plant.

The aim of this study was to investigate the uptake of PFAAs from biosolids-applied field soils by wheat (*Triticum aestivum* L.) roots and their translocation to wheat above-ground tissues. Wheat was chosen as a model plant because it is widely cultivated and is an important dietary staple. PFAAs-contaminated wheat grains may present a threat to human health. Also, wheat straw is widely used as cattle feed and may pose another pathway for PFAAs to enter into the food chain. To our knowledge, this is the first report on the enrichment and distribution patterns of PFAAs in wheat grown in biosolids-amended agricultural fields.

2. Materials and methods

2.1. Materials

A standard solution of PFAAs containing eleven perfluorocarboxylic acids (PFCAs) and five perfluorosulfonic acids (PFSAs), and solutions of $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_4$ -PFOS were purchased from Wellington Laboratories (Guelph, Canada) and were used as-received. HPLC-grade methyl tert-butyl ether (MTBE, >99.98%), methanol (MeOH, >99.9%), dichloromethane (DCM, >99.9%) and acetonitrile (>99.9%) were purchased from Fisher Chemical (Firlawn, NJ, USA). Tetrabutylammonium hydrogen sulfate (TBAHS, >99%), sodium carbonate (>99%), sodium hydroxide (>95%), and

ammonium acetate (>99%) were purchased from Sigma Aldrich Chemical (Milwaukee, WI, USA). Milli-Q water was used throughout the experimental work.

2.2. Sample collection

Soils and plants were collected from Research Stations of Fertility and Fertilizer Effects in Fluvo-Aquic Soil in Changping, Beijing (40° 13' N, 116° 15' E). Air-dried biosolids from Beijing Sludge Disposal Plant have been applied as the basic fertilizer before wheat sowing (November) at the station once a year since 2006 (Li et al., 2012). There were five biosolids application rates in soils with the wheat-maize cropping system (Control and Plots 1–4, Table 1). Each application rate had three replications. The 15 plots (5 m × 8 m each plot) were arranged in a randomized complete block design. Soil and wheat plants were collected after wheat harvest in June, 2012. Soil samples of the plots were taken at 0–20 cm depth for chemical analysis. Five soil samples were taken from each plot and mixed into one composite sample. Visible stones and roots were taken away from soil samples. Ten wheat plants from each replication were randomly sampled. Each plant sample was divided into roots, straws, husks and grains. The subsamples of wheat were washed carefully with tap water and distilled water sequentially. The plant and soil samples were freeze-dried at the temperature of –50 °C for 48 h in a lyophilizer (FD-1, Beijing Boyikang Instrument Ltd, Beijing, China), ground, and weighed. The dried samples were then stored separately at –20 °C before analysis.

The soil samples were passed through a 2-mm sieve. Total nitrogen (TN), phosphorus (TP), and potassium (TK) in the soils were determined (Li et al., 2012). Soil pH, soil organic matter (SOM), and heavy metal concentrations, including Zn, Cu, Cr, Ni, Cd and Pb, were measured according to the methods of Fang et al. (2007). The chemical properties of soils are presented in Table 1. Root lipid content was determined following the same procedure that we previously employed (Huang et al., 2010), which was detailed in the Supplementary materials.

2.3. Selection of extractants for PFAAs in soil and plant samples

Studies have shown MTBE-NaOH (Felizeter et al., 2012) and MeOH-DCM (Yoo et al., 2010) to be efficient for the extraction of PFAAs from plant tissues. To evaluate the capability of different solvents, PFCAs and PFSAs in soils and wheat roots and straws collected from Plot 4 were extracted with MTBE-NaOH and MeOH-DCM according to the methods reported with some modifications, and cleaned up according to the method of Shi et al. (2012). Before extraction, recovery internal standards, 2 ng of $^{13}\text{C}_4$ -PFOA and 2 ng of $^{13}\text{C}_4$ -PFOS were spiked into 1 g soil or wheat tissues and aged for 24 h. The two extraction methods were detailed in the Supplementary materials. There were four replicates per treatment.

2.4. LC/MS/MS analysis and quantitation

An ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) was used to determine the concentrations of PFAAs. The UPLC system (ACQUITY, Waters Corp., USA) was equipped with a UPLC BEH C18 column (2.1 × 150 mm, 1.7 μm, Waters Corp., USA) that was maintained at 40 °C in column oven. The Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) was equipped with an electrospray ionization source. The mixture of acetonitrile/10 mmol/L ammonium acetate (50/50, v/v) was used as mobile phase at a flow rate of 0.2 mL/min. The MS/MS was operated in electrospray negative ionization mode. The collision energies, cone voltages, and MS/MS parameters for the instrument were optimized for individual analytes (Table S1).

2.5. Quality assurance and quality control measures

Quality control was done by regular analyses of procedural blanks, blind duplicate samples, and random injection of solvent blanks and standards. Uncontaminated soil and plant samples without biosolids applied were collected 5 miles away from the station. Matrix calibration curves using spiked uncontaminated

Table 1
Biosolids amendment rates and the chemical properties of the soils.

	Control	Plot 1	Plot 2	Plot 3	Plot 4
Biosolids applied (dry weight, t ha ⁻¹ y ⁻¹)	0	4.5	9.0	18.0	36.0
pH (Soil:CaCl ₂ = 1:5)	8.11 (0.05) ^a	8.21 (0.06)	8.43 (0.10)	8.15 (0.08)	8.20 (0.10)
Soil Organic matter (%)	0.78 (0.04)	1.42 (0.03)	2.29 (0.06)	2.53 (0.08)	2.76 (0.07)
Total N (g kg ⁻¹)	0.83 (0.04)	0.98 (0.08)	1.92 (0.15)	2.30 (0.17)	2.64 (0.21)
Total P (g kg ⁻¹)	0.68 (0.08)	0.79 (0.06)	0.98 (0.10)	1.36 (0.12)	2.61 (0.44)
Total K (g kg ⁻¹)	23.7 (1.5)	25.4 (2.1)	24.6 (2.4)	25.6 (2.0)	28.5 (0.16)
Zn (mg kg ⁻¹)	43.9 (3.3)	48.6 (3.1)	58.7 (3.4)	64.6 (4.8)	78.6 (4.4)
Cu (mg kg ⁻¹)	18.4 (0.9)	19.6 (1.9)	20.5 (1.6)	21.5 (1.3)	21.9 (0.8)
Cr (mg kg ⁻¹)	55.6 (1.8)	58.8 (4.2)	54.6 (4.8)	59.4 (2.3)	59.7 (2.1)
Ni (mg kg ⁻¹)	33.6 (2.8)	34.6 (1.9)	33.8 (2.9)	34.8 (1.9)	36.7 (2.9)
Cd (mg kg ⁻¹)	0.114 (0.010)	0.111 (0.009)	0.113 (0.005)	0.112 (0.004)	0.117 (0.004)
Pb (mg kg ⁻¹)	16.7 (1.8)	17.2 (1.9)	17.8 (0.9)	18.8 (0.8)	19.8 (0.7)

^a Standard deviation (σ).

samples that were extracted in analogy to the samples were applied for quantification. An eighteen-point calibration line was used for quantification. The fitted lines had r^2 values of at least 0.99 for all analytes. The method-detection limits (MDLs) were defined as the lowest concentration that could be distinguished from a sample containing no analyte and calculated with the mean peak area plus three standard deviations, $MDLs = y_0 + 3\sigma(y_0)$, average of measured values for the blank matrix; σ , standard deviation of the measured values for the blank matrix). The limit of quantitation (LOQ) was calculated with the formula $LOQ = y_0 + 10\sigma$ (Lechner and Knapp, 2011). MDLs and LOQs were measured for each matrix on replicate analyses ($n = 6$) of blank samples (Table S1). Mean sample concentrations less than the calculated MDLs or LOQs were reported as <MDL and <LOQ, respectively. For the calculation of total concentrations, PFAA values <MDL were treated as zero and <LOQ values were assigned 1/2 LOQ. PFAA values <LOQ were not involved in the modeling. All samples were extracted and injected in triplicate. The accuracy of the determination was assessed by testing the recoveries of $^{13}C_4$ -PFOA and $^{13}C_4$ -PFOS from the spiked blank matrix in comparison to matrix-matched standards. The recoveries of $^{13}C_4$ -PFOA and $^{13}C_4$ -PFOS were found to be 91–108% with standard deviations ranging from 2 to 7% for all soil and plant samples. Because these two internal standards may not represent all PFAAs studied, the recoveries of PFAAs with different carbon chain length were determined by spiking a certain amount of nonlabeled PFAA standards in uncontaminated samples using the chosen extractant, i.e., MTBE-NaOH. The recoveries of PFAAs were 76–105, 73–110 and 76–105% for soil, root and straw, respectively (Table S2). The only exception is PFBA, in which recoveries were much lower (38–47%) than other PFAAs. Similar relatively low recoveries of PFBA were reported by Felizeter et al. (2012). Thus, it is assumed that the concentrations of PFBA may be underestimated when only two isotope-labeled internal standards were used. The results of PFBA were included due to its consistent recoveries.

2.6. Data analysis

All statistical analyses were conducted with the software SPSS 11.5 for Windows (SPSS Inc., Chicago, IL). One-way ANOVA was used to assess the significance of the difference between groups, and linear and nonlinear regression analyses were conducted by the least and least-squares methods, respectively. Statements of significant differences are based on $P < 0.05$.

3. Results and discussion

3.1. Section of extractant for PFAAs

The results of soil and plant tissue powder extraction by two solvents, MTBE-NaOH and MeOH-DCM are shown in Fig. S1. The extraction recoveries of $^{13}C_4$ -PFOA and $^{13}C_4$ -PFOS were 93–102% and 94–103% for MTBE-NaOH and MeOH-DCM, respectively (data not shown). No significant difference of recoveries between soils and plant tissues was found. The extractabilities of MTBE-NaOH were 1.4–2.0 times those of MeOH-DCM for short carbon chain PFCAs (C4–C6). No significant difference between the two extractants for most PFCAs (C7–C11) and PFSAs (C4–C8) was found. The extractabilities of MeOH-DCM were about 1.4 times those of MTBE-NaOH for PFTeA. Total concentrations of PFAAs extracted by MTBE-

NaOH were higher than those of MeOH-DCM. Thus MTBE-NaOH was used in the following study.

3.2. Concentrations of PFAAs in soils

Concentrations of all PFAAs in the biosolids-amended soils are presented in Table 2. Nine PFCAs and three PFSAs have been detected in the soils, which ranged from 18.0 to 113 ng/g for PFCAs and from 23.4 to 107 ng/g for PFSAs, respectively. PFDoA, PFTTrA, PFHpS and PFDS have not been found in soil samples. The total concentrations of PFAAs in biosolids-amended soils (Plots 1–4) are in the range of 41.4–220 ng/g. Only low contents of PFOA (0.6 ng/g) and PFOS (0.6 ng/g) were detected in the control soil, accounting for <5% of the corresponding PFAA concentrations in Plot 1 with the lowest biosolids application rate. Total PFAA concentrations in the soils positively correlated with the amount of biosolids applied ($P < 0.01$, Fig. S2), suggesting that biosolids application is the main source of PFAAs in the soils. Based on the Chinese sewage sludge regulation (GB4284-84) (Department of Rural and Urban Construction and Environmental Protection, China, 1984), a maximum level of 30 tons (dry matter) per hectare per year was tolerated, accumulation of PFAAs in soils would be more than 200 ng/g after seven-year application at this maximum level according to the regression line.

3.3. Distribution patterns of PFAAs in wheat

PFAAs have been detected in different parts of wheat: roots, straws, husks and grains, indicating that wheat has the ability not only to take up PFAAs from soils by roots, but also to translocate PFAAs to the above-ground parts (Table 3). Nine PFCAs and three PFSAs have been quantified in the roots and straws, but only seven PFCAs and two PFSAs have been detected quantitatively in the husks and grains. PFBS has not been detected in husks and grains, while the concentrations of PFUnA and PFTeA in husks and grains are below the LOQs. The total concentrations of PFAAs in roots, straws, husks and grains are in the range of 140–472, 36.2–178, 6.15–37.8 and 7.32–35.6 ng/g, respectively. The distribution of PFAAs followed the order of roots > straws > grains ≥ husks. This order was also verified by another study (Stahl et al., 2009).

Organic contaminants reach aerial plant organs in two ways: from the air and with the transpiration stream (Huang et al., 2010; Tao et al., 2009). It is possible that PFAAs in the soils evaporate into the ambient air and enter plants via gaseous uptake, contributing to their accumulation in the above-ground part of wheat, because PFAAs can be detected in the atmosphere (Li et al., 2011; Ahrens

Table 2
Total PFAA concentrations in soils (ng/g dry weight).

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFTeA	PFBS	PFHxS	PFOS	ΣPFAAs ^a
Control													
Mean	<MDL	<MDL	<MDL	<MDL	0.61	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.61	1.22
SD					0.04							0.02	0.06
Plot 1													
Mean	1.19	<LOQ	5.43	1.21	4.33	2.01	<MDL	0.17	0.28	<MDL	13.0	10.4	41.4
SD	0.09		0.56	0.07	0.45	0.18		0.01	0.03		1.1	1.0	3.5
Plot 2													
Mean	1.52	6.68	10.2	1.81	12.6	3.36	0.70	0.76	0.37	<MDL	25.8	15.4	79.1
SD	0.15	0.63	1.3	0.15	2.3	0.12	0.05	0.04	0.03		2.1	1.2	8.1
Plot 3													
Mean	5.91	10.1	22.8	7.33	19.8	12.5	4.50	0.62	0.39	19.4	31.1	28.3	163
SD	0.32	0.5	1.5	0.74	2.1	1.3	0.47	0.05	0.04	2.0	2.5	2.5	14.0
Plot 4													
Mean	13.5	12.4	15.2	12.9	26.1	22.0	7.82	0.89	1.89	31.2	34.9	40.8	220
SD	1.3	0.9	1.3	1.2	0.4	2.1	0.80	0.09	0.22	1.7	2.9	2.9	15.8

^a PFAA value <MDL was treated as zero and <LOQ was assigned as 1/2 LOQ.

Table 3

Distribution of PFAA concentrations in the different part of wheat (ng/g dry weight).

		PFBA	PFPeA	PFHxA	PFHpA	PFDA	PFNA	PFDA	PFUnA	PFTeA	PFBS	PFHxS	PFOS	ΣPFAAs ^a
Control														
Roots	Mean	<MDL	<MDL	<MDL	<MDL	1.09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.93	2.02
	SD					0.11							0.07	0.18
Straws	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Husks	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Grains	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Plot 1														
Roots	Mean	5.28	10.3	24.8	5.79	21.4	8.34	<MDL	0.88	1.05	<LOQ	35.8	16.8	140
	SD	0.47	1.0	1.8	0.41	2.3	0.77		0.02	0.12		2.1	0.3	
Straws	Mean	3.05	<LOQ	6.59	1.95	6.67	2.45	<MDL	<LOQ	<LOQ	<MDL	8.66	3.45	36.2
	SD	0.14		0.44	0.08	0.68	0.17					0.93	0.41	
Husks	Mean	0.96	<MDL	1.45	<MDL	1.33	<LOQ	<MDL	<MDL	<LOQ	<MDL	1.96	<LOQ	6.15
	SD	0.08		0.09		0.09						0.21		
Grains	Mean	1.09	<MDL	1.58	<MDL	1.01	0.51	<MDL	<MDL	<LOQ	<MDL	2.45	0.80	7.32
	SD	0.11		0.12		0.10	0.05					0.11	0.02	
Plot 2														
Roots	Mean	6.21	28.2	31.6	6.42	31.6	9.10	1.85	2.08	1.06	21.9	54.1	18.3	212
	SD	0.66	2.5	1.2	0.65	1.7	0.72	0.18	0.20	0.08	1.7	3.6	1.5	
Straws	Mean	3.78	12.6	12.8	2.95	9.63	3.91	0.45	0.42	0.30	<MDL	12.0	3.66	62.5
	SD	0.27	0.9	1.01	0.17	0.66	0.22	0.01	0.01	0.03		1.3	0.34	
Husks	Mean	1.30	<MDL	4.02	<MDL	1.18	0.55	<MDL	<MDL	<MDL	<MDL	3.78	<LOQ	11.3
	SD	0.07		0.24		0.14	0.04					0.19		
Grains	Mean	1.52	<MDL	3.59	<MDL	2.01	1.09	<MDL	<LOQ	<MDL	<MDL	3.42	0.95	12.6
	SD	0.11		0.05		0.21	0.09					0.23	0.09	
Plot 3														
Roots	Mean	14.6	34.7	60.2	17.7	38.4	35.6	9.62	2.51	1.10	32.0	65.6	37.5	350
	SD	1.2	4.0	3.4	1.3	3.1	3.2	0.66	0.26	0.12	1.2	5.4	3.6	
Straws	Mean	12.2	18.0	25.3	7.25	14.8	8.11	3.02	0.71	0.34	<LOQ	13.7	7.25	121
	SD	0.9	1.3	1.7	0.58	0.98	0.79	0.33	0.03	0.02		1.4	0.79	
Husks	Mean	3.10	<LOQ	6.88	0.99	2.56	3.08	<MDL	<LOQ	<MDL	<MDL	3.98	1.89	25.9
	SD	0.22		0.41	0.10	0.21	0.19					0.43	0.08	
Grains	Mean	4.39	4.74	6.21	1.61	2.64	2.22	0.51	<MDL	<LOQ	<MDL	3.92	1.72	26.7
	SD	0.33	0.25	0.41	0.16	0.21	0.19	0.05				0.23	0.08	
Plot 4														
Roots	Mean	36.5	44.6	43.0	34.6	45.1	62.9	15.6	2.86	3.91	59.6	67.6	55.3	472
	SD	3.1	3.8	4.6	2.7	4.1	5.3	1.7	0.31	0.30	4.1	5.6	5.1	
Straws	Mean	22.2	20.2	20.5	15.9	22.1	21.4	6.28	0.80	0.95	21.8	14.9	11.0	178
	SD	1.1	1.5	1.8	0.4	1.7	1.8	0.43	0.05	0.10	2.0	1.2	1.2	
Husks	Mean	5.77	6.26	6.51	2.59	4.19	4.72	1.41	<LOQ	<LOQ	<MDL	3.86	2.20	37.8
	SD	0.54	0.32	0.41	0.23	0.38	0.50	0.11				0.31	0.12	
Grains	Mean	6.49	6.58	5.02	3.33	2.90	3.05	0.95	<LOQ	<LOQ	<MDL	4.37	2.53	35.6
	SD	0.24	0.23	0.49	0.17	0.20	0.23	0.08				0.22	0.21	

et al., 2011), though they do not readily volatilize (Giesy et al., 2010). An alternative pathway for PFAAs transport is via aerial transport of volatile PFAA precursors with subsequent oxidation of the plant-bound PFAA precursors, such as fluorotelomer alcohols (FTOHs) or 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFO-SAA), to form PFAAs (Yoo et al., 2011). In order to identify the contribution of acropetal transport of PFAAs to their accumulation in aerial plant organs, PFAA concentrations in the control plants were determined and considered to be due to their gaseous uptake, on the assumption that PFAAs evenly diffuse in the ambient air and equally absorb onto aerial plant organs of biosolids-treated plants and their nearby blank control plants (Tao et al., 2009). The results showed that PFAA concentrations in wheat straws, husks and grains of control are lower than MLD (Table 3), suggesting that the effect of aerial transport of PFAAs and the oxidation of absorbed PFAA precursors on PFAA accumulation is negligible.

3.4. Uptake of PFAAs by wheat roots

The concentrations of PFAAs in the wheat roots were significantly influenced by biosolids application rate. Total concentrations of PFAAs in roots grown in different plots followed the order: Plot

1 < Plot 2 < Plot 3 < Plot 4, which was consistent with the same order of PFAAs in the soils. Single correlation analysis was performed to assess the relationships between concentrations of PFAAs in soils and uptake by roots. The correlation coefficients obtained are listed in Table S3. Consistently positive correlations existed between the contents of PFAAs in the soils and in wheat roots ($R^2 = 0.981–0.999$) for all PFAAs detected in the soils and wheat with the sole exception of PFPeA. Root concentration factors (RCFs) were calculated based on the ratio of PFAA levels in wheat roots to those in the soils ($C_{\text{root}}/C_{\text{soil}}$, (ng/g_{root})/(ng/g_{soil})). The RCFs of PFCAs and PFSAAs were 1.73–5.18 and 1.19–2.75, respectively (Table S4). Among four plots studied, the RCFs of Plot 1 were the largest (1.62–5.18), which may be due to the lowest soil organic matter (SOM) content of Plot 1 (Table 1). Hydrophobic organic compounds (HOCs) in soil tend to be sorbed by SOM, and their uptake by plant roots is essentially controlled by SOM rather than by HOC concentration in the whole soil (Huang et al., 2010; Li et al., 2005; Chiou et al., 2001). Though PFAAs are expected to behave differently from traditional HOCs because of their both hydrophobic and hydrophilic functionalities, the importance of SOM on the sorption of PFAAs was reported (Higgins and Luthy, 2006). Thus, wheat root/organic matter concentration factors (ROMCFs, (ng/

$C_{\text{root}}/C_{\text{soil}}/C_{\text{SOM}}))$ based on the ratio of PFAA concentrations in roots to those in SOM ($C_{\text{root}}/C_{\text{soil}}/C_{\text{SOM}}))$ were further calculated (Table S4). The average ROMCFs were 0.023–0.099, with the relative standard derivations (RSD) of 6.13–21.3%. The RSD of ROMCFs were lower than those of RCFs (9.04–46.1%), which indicated that SOM is one of the important factors limiting the uptake of PFAAs by wheat roots. It is suggested that the uptake of HOCs by plant roots is mainly characterized by lipid dominating partition processes and might be expected to be similar to their accumulation by lipid containing passive samplers (Huang et al., 2010; Tao et al., 2009). The root lipid/organic matter accumulation factors (LROMCFs, $(\text{ng/g}_{\text{root lipid}})/(\text{ng/g}_{\text{SOM}}))$ on the basis of root lipid and SOM ($(C_{\text{root}}/C_{\text{lipid}})/C_{\text{soil}}/C_{\text{SOM}}))$ were calculated (Table S4) in order to make a comparison, though it is reported that lipid is not the main compartment of PFAAs in animals and fish (Peng et al., 2010; Hoff et al., 2003). The lipid concentration of wheat roots was found to be 2.18%. The LLOMAFs ranged from 1.05 to 4.55, which were higher than those of polybrominated diphenyl ethers (PBDEs, 0.02–0.71, Huang et al., 2011), but was similar to 4-ring polycyclic aromatic hydrocarbons (PAHs, 1.59–2.66, Tao et al., 2009). Yoo et al. (2011) suggested that the transfer potential of long-chain PFCAs from soils to plants was lower than that of short-chain PFCAs. However no significant correlations were found between the RCFs of PFCAs or PFSA and their chain length in this study (Fig. S3).

3.5. Accumulation of PFAAs in straws

Concentrations of PFAAs in straws are shown in Table 3. A positive correlation existed between all PFAAs in straws and in soils ($P < 0.05$), with correlation coefficients (R^2) of 0.939–0.999, except for PFPeA, PFUnA, and PFDA (Table S3). The straw/soil concentration factors based on the ratio of PFAA concentrations in straws to those in soils (SCFs, $(\text{ng/g}_{\text{straw}})/(\text{ng/g}_{\text{soil}}))$ and the wheat straw/organic matter concentration factors (SOMCFs, $(\text{ng/g}_{\text{straw}})/(\text{ng/g}_{\text{SOM}}))$ based on the ratio of PFAA concentrations in straws to those in SOM ($C_{\text{straw}}/C_{\text{soil}}/C_{\text{SOM}}))$ were calculated (Table S5). The SOMCFs ranged from 0.00471 to 0.0569. Yoo et al. (2010) also calculated the grass/organic-matter accumulation factors (GOMAFs), which is the ratio of PFAA concentrations in above-ground portion of grasses to those in SOM, and reported that the values were 0.001–0.61. Our values were in the range of theirs. Concentrations of PFAAs in wheat straws were also found to correlate well with the corresponding concentrations in roots for PFBA, PFHxA, PFHpA, PFOA, PFNA, PFTeA, PFHxS, and PFOS ($P < 0.05$, Table S6), indicating that root uptake of PFAAs and subsequent translocation from roots to straws may make significant contribution to their accumulation in straws. The transfer factors from roots to straws were defined as the ratio of the PFAA concentrations in straws to those in roots on a dry weight basis ($TF_{r-s} = C_{\text{straw}}/C_{\text{root}}, (\text{ng/g}_{\text{straw}})/(\text{ng/g}_{\text{root}})$, Table S7). The TF_{r-s} values calculated were 0.202–0.836 for PFCAs, which was higher than TF_{r-s} values for PFSA (0.193–0.366). The TF_{r-s} values of short carbon chain PFAAs were higher than those of long carbon chain PFAAs. For example, the average TF_{r-s} of PFBA was 2.4 times that of PFTeA. An inverse relationship exists between TF_{r-s} and carbon chain length of PFCAs ($n = 32$, $R^2 = 0.504$, $P < 0.01$, Fig. 1a). Similar inverse correlation was found between TF_{r-s} and carbon chain length of PFSA ($n = 9$, $R^2 = 0.700$, $P < 0.01$, Fig. 1b). Similar results of foliage/root concentration factors decrease with increasing carbon chain length for both PFCAs and PFSA were reported by Felizeter et al. (2012). The inverse relationship indicated that the acropetal transfer potential from roots to straws for short-chain PFAAs was higher than that for long-chain PFAAs, which may be due to the relatively large molecule and/or high lipophilicity of long-chain PFAAs when compared with short-chain PFAAs. It is suggested that the transport of POPs from roots to stems was

Fig. 1. Linear regression between transfer factors from roots to straws (TF_{r-s}) of PFCAs (a), PFSA (b) and their carbon chain length.

mainly through transpiration (Murano et al., 2010; Collins et al., 2006; Burken and Schnoor, 1998). POPs with smaller size and lower lipophilicity are more easily translocated from root to shoot (Zhao et al., 2012; Satchivi et al., 2006).

3.6. Accumulation of PFAAs in grains

The PFAA concentrations in wheat grain are presented in Table 3. The grain concentrations increased with an increase of PFAA concentrations in soils, which suggests that soil PFAA accumulation could cause contamination to grain. The grain/soil concentration factors based on the ratio of PFAA concentrations in grains to those in soils (GCFs, $(\text{ng/g}_{\text{grain}})/(\text{ng/g}_{\text{soil}}))$ and the grain/organic matter concentration factors (GOMCFs, $(\text{ng/g}_{\text{grain}})/(\text{ng/g}_{\text{SOM}}))$ based on the ratio of PFAA concentrations in grains to PFAA concentrations in SOM ($C_{\text{grain}}/C_{\text{soil}}/C_{\text{SOM}}))$ were calculated (Table S8). The GCFs ranged from 0.0608 to 1.00. Grain PFAAs must be derived from either direct xylem transport from roots or remobilization of straw PFAA pools through phloem during grain filling. Different relationships between PFAAs in grains and in soils between PFCAs and PFSA were found (Fig. 2). The concentrations of PFSA in grains increased linearly with those in soils for PFHxS and PFOS ($R^2 = 0.997$ – 0.998 , $P < 0.01$); whereas for PFCAs, there appears to

Fig. 2. Relationship between PFAA concentrations in grains and soils.

be a plateau effect. PFCA concentrations in grains increased logarithmically with increasing PFCA in soils for PFBA, PFHxA, PFOA and PFNA ($R^2 = 0.982–0.997$). This difference indicated that the transport mechanisms from soils to grains between PFCA and PFSA may be different. The transport of PFAs from soils to grains includes the uptake by roots, the translocation from roots to straws and the translocation from straws to grains. In order to understand the translocation of PFAs from straws to grains, a straw-to-grain

translocation factor defined as the ratio of PFA concentrations in grains to those in straws on a dry weight basis was calculated ($TF_{s-g} = C_{\text{grain}}/C_{\text{straw}}$, (ng/g_{grain})/(ng/g_{straw})). The TF_{s-g} for PFCA and PFSA were in the range of 0.131–0.402 and 0.230–0.293, respectively (Table S7). For PFCA and PFSA with the same carbon chain length, the TF_{s-g} values of PFSA were higher than those of PFCA, which was opposite to TF_{r-s} . For example, the TF_{r-s} of PFOA (0.373 ± 0.086) was higher than that of PFOS (0.199 ± 0.005) while

Fig. 3. Linear regression between transfer factors from straws to grains (TF_{s-g}) of PFCAs and their carbon chain length.

TF_{s-g} of PFOS (0.240 ± 0.013) was higher than that of PFOA (0.167 ± 0.034). Stahl et al. (2009) detailed the concentrations of PFOA and PFOS in wheat straws and ears. Based on their results, the C_{ear}/C_{straw} value calculated for PFOS (0.040 ± 0.018) was higher than that of PFOA (0.025 ± 0.007). This result revealed that PFCAs are easier than PFSA to be translocated from roots to straws, while PFSA are easier than PFCAs to be translocated from straws to grains. The TF_{s-g} values of short carbon-chain length were higher than that of long-chain length. For example, the average TF_{s-g} of PFBA was 2.2 times that of PFDA, and the TF_{r-s} of PFHxS was higher than PFOS. Inverse relationship existed between the translocation factors and carbon chain length of PFCAs ($n = 22$, $R^2 = 0.626$, $P < 0.01$, Fig. 3). These results indicated that the transfer potential for PFAAs from straws to grains of short-chain PFAAs was higher than that of long-chain PFAAs.

4. Conclusion

The results from this study demonstrated that the land application of biosolids could lead to the contamination of PFAAs in soils and crops in field circumstances. Contact of plants with PFAA contaminated soils could be a primary route of PFAAs transport via the roots into different plant tissues. Thus the application of biosolids provides an avenue for input of PFAAs into the food chain by following exposure pathways: contaminated soils $\rightarrow$ plants $\rightarrow$ human and/or contaminated soils $\rightarrow$ plants $\rightarrow$ livestock $\rightarrow$ human. The finding that the transfer potential for PFAAs from roots to straws and further to the grains for short-chain PFAAs was higher than that of long-chain PFAAs and that PFCAs and PFSA may have different transport behaviors from soils to grains may help to understand the accumulation mechanisms of PFAAs in wheat, although an exact explanation for the observation remains to be provided from plant physiology.

Acknowledgments

We thank Dr. Autumn Starcher of University of Delaware, United States, and Dr. Amanda Tan Pei Shan of Nanyang Technological University, Singapore for their English polishing. This work was supported by the National Natural Science Foundation of China (Project 41371460) and the National Key Basic Research Program of China (973 Program) (Grant No. 2014CB441102).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2013.09.040>.

References

- Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E.J., 2011. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environ. Sci. Technol.* 45, 8098–8105.
- Burken, J.G., Schnoor, J.L., 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ. Sci. Technol.* 32, 3379–3385.
- Chiou, C.T., Sheng, G.Y., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. *Environ. Sci. Technol.* 35, 1437–1444.
- Clarke, B.O., Smith, S.R., 2011. Review of ‘emerging’ organic contaminants in biosolid and assessment of international research priorities for the agricultural use of biosolids. *Environ. Int.* 37, 226–247.
- Collins, C., Fryer, M., Grosso, A., 2006. Plant uptake of non-ionic organic chemicals. *Environ. Sci. Technol.* 40, 45–52.
- Department of Rural and Urban Construction and Environmental Protection, China, 1984. Control Standards for Pollutants in Sludges from Agricultural Use, GB4284–84 (in Chinese). Web site <http://www.mep.gov.cn/gkml/hbb/bgth/201104/W020110402553781240073.pdf>.
- Eschauer, C., Haftka, J., Stuyfzand, P.J., de Voogt, P., 2010. Perfluorinated compounds in infiltrated river rhine water and infiltrated rainwater in coastal dunes. *Environ. Sci. Technol.* 44, 7450–7455.
- Fang, J., Wen, B., Shan, X.Q., Lin, J.M., Owens, G., 2007. Is an adjusted rhizosphere-based method valid for field assessment of metal phytoavailability? Application to non-contaminated soils. *Environ. Pollut.* 150, 209–217.
- Farrell, M., Jones, D.L., 2009. Critical evaluation of municipal solid waste composting and potential compost markets. *Bioresour. Technol.* 100, 4301–4310.
- Felizeter, S., McLachlan, M.S., de Voogt, P., 2012. Uptake of perfluorinated alkyl acids by hydroponically grown lettuce (*Lactuca sativa*). *Environ. Sci. Technol.* 46, 11735–11743.
- Giesy, J.P., Naile, J.E., Khim, J.S., Jones, K.C., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. *Rev. Environ. Contam. Toxicol.* 202, 1–52.
- Guo, R., Sim, W.J., Lee, E.S., Lee, J.H., Oha, J.E., 2010. Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants. *Water Res.* 44, 3476–3486.
- Harrison, E.Z., Oakes, S.R., Hysell, M., Hay, A., 2006. Organic chemicals in sewage sludges. *Sci. Total Environ.* 367, 481–497.
- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39, 3946–3956.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 40, 7251–7256.
- Hoff, P.T., Van de Vijver, K., Dongen, W.V., Esmans, E.L., Blust, R., De Coen, W.M., 2003. Perfluorooctane sulfonic acid in Bib (*Trisopterus luscus*) and plaice (*Pleuronectes platessa*) from the western Scheldt and the Belgian north sea: distribution and biochemical effects. *Environ. Toxicol. Chem.* 22, 608–614.
- Houde, M., De Silva, M.O., Derek, C.G., Muir, D.C.G., Letcher, R.J., 2011. Monitoring of perfluorinated compounds in aquatic biota: an updated reviews. *Environ. Sci. Technol.* 45, 7962–7973.
- Huang, H.L., Zhang, S.Z., Christie, P., 2011. Plant uptake and dissipation of PBDEs in the soils of electronic waste recycling sites. *Environ. Pollut.* 159, 238–243.
- Huang, H.L., Zhang, S.Z., Christie, P., Wang, S., Xie, M., 2010. Behavior of decabromodiphenyl ether (BDE-209) in the soil-plant system: uptake, translocation, and metabolism in plants and dissipation in soil. *Environ. Sci. Technol.* 44, 663–667.
- Kwadijk, C.J.A.F., Korytar, P., Koelmans, A.A., 2010. Distribution of perfluorinated compounds in aquatic systems in The Netherlands. *Environ. Sci. Technol.* 44, 3746–3751.
- Lechner, M., Knapp, H., 2011. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and distribution to the different plant compartments studied in cultures of carrots (*Daucus carota* ssp. *sativus*), potatoes (*Solanum tuberosum*), and cucumbers (*Cucumis Sativus*). *J. Agric. Food Chem.* 59, 11011–11018.
- Li, H., Sheng, G., Chiou, C., Xu, O., 2005. Relation of organic contaminant equilibrium sorption and kinetic uptake in plant. *Environ. Sci. Technol.* 39, 4864–4870.
- Li, J., Vento, S.D., Schuster, J., Zhang, G., Chakraborty, P., Kobara, Y., Jones, D.C., 2011. Perfluorinated compounds in the Asian atmosphere. *Environ. Sci. Technol.* 45, 7241–7248.
- Li, Q., Guo, X.Y., Xu, X.H., Zuo, Y.B., Wei, D.P., Ma, Y.B., 2012. Phytoavailability of copper, zinc and cadmium in sewage sludge-amended calcareous soils. *Pedosphere* 22, 254–262.
- McLaughlin, M.J., Whatmuff, M., Warne, M., Heemsbergen, D., Barry, G., Bell, M., Nash, D., Pritchard, D., 2006. A field investigation of solubility and food chain accumulation of biosolid-cadmium across diverse soil types. *Environ. Chem.* 3, 428–432.
- Murano, H., Otani, T., Seike, N., Sakai, M., 2010. Dieldrin uptake and translocation in plants growing in hydroponic medium. *Environ. Toxicol. Chem.* 29, 142–148.

- Olsen, G.W., Butenhoff, J.L., Zobel, L.R., 2009. Perfluoroalkyl chemicals and human fetal development: an epidemiologic review with clinical and toxicological perspectives. *Reprod. Toxicol.* 27, 212–230.
- Peng, H., Wei, Q., Wan, Y., Giesy, J.P., Li, L.X., Hu, J., 2010. Tissue distribution and maternal transfer of poly- and perfluorinated compounds in Chinese sturgeon (*Acipenser sinensis*): implications for reproductive risk. *Environ. Sci. Technol.* 44, 1868–1874.
- Satchivi, N.M., Stoller, E.W., Wax, L.M., Briskin, D.P., 2006. A nonlinear, dynamic, simulation model for transport, and whole plant allocation of systemic xenobiotics following foliar application. IV: physicochemical properties requirements for optimum absorption and translocation. *Pestic. Biochem. Physiol.* 84, 83–97.
- Sepulvado, J.G., Blaine, A.C., Hundal, L.S., Higgins, C.P., 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environ. Sci. Technol.* 45, 8106–8112.
- Shi, Y.L., Pan, Y.Y., Wang, J.M., Cai, Y.Q., 2012. Distribution of perfluorinated compounds in water, sediment, biota and floating plants in Baiyangdian Lake, China. *J. Environ. Monit.* 14, 636–642.
- Stahl, T., Heyn, J., Thiele, H., Hüther, J., Failing, K., Georgii, S., Brunn, H., 2009. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant. *Arch. Environ. Contam. Toxicol.* 57, 289–298.
- Stahl, T., Riebe, R.A., Falk, S., Brunn, H., 2013. Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: results of a pilot study. *J. Agric. Food Chem.* 61, 1784–1793.
- Stockholm Convention, 2009. Available from: <http://chm.pops.int/Convention/Pressrelease/COP4Geneva8May2009/tabid/542/language/en-US/Default.aspx> (accessed 11.08.11.).
- Sun, H.W., Gerecke, A.C., Giger, W., Alder, A.C., 2011. Long-chain perfluorinated chemicals in digested sewage sludges in Switzerland. *Environ. Pollut.* 159, 654–662.
- Tao, Y.Q., Zhang, S.Z., Zhu, Y.H., Christie, P., 2009. Uptake and acropetal translocation of polycyclic aromatic hydrocarbons by wheat (*Triticum aestivum* L.) grown in field-contaminated soils. *Environ. Sci. Technol.* 43, 3556–3560.
- Washington, J.W., Yoo, H., Ellington, J.J., Jenkins, T.M., Libelo, E.L., 2010. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. *Environ. Sci. Technol.* 44, 8390–8396.
- Yoo, H., Washington, J.W., Ellington, J.J., Jenkin, T.M., Neill, M.P., 2010. Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA. *Environ. Sci. Technol.* 44, 8397–8402.
- Yoo, H., Washington, J.W., Jenkins, T.M., Ellington, J.J., 2011. Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS. *Environ. Sci. Technol.* 45, 7985–7990.
- Zhao, H.X., Guan, Y., Zhang, G.L., Zhang, Z., Tan, F., Quan, X., Chen, J.W., 2013. Uptake of perfluorooctane sulfonate (PFOS) by wheat (*Triticum aestivum* L.) plant. *Chemosphere* 91, 139–144.
- Zhao, M.M., Zhang, S.Z., Wang, S., Huang, H.L., 2012. Uptake, translocation, and debromination of polybrominated diphenyl ethers in maize. *J. Environ. Sci.* 24, 402–409.