Bioavailability of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in biosolids-amended soils to earthworms (*Eisenia fetida*)

Bei Wen^{a,*}, Hongna Zhang^a, Longfei Li^a, Xiaoyu Hu^b, Yu Liu^a, 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 Beijing Center for Disease Prevention and Control, Beijing 100031, China

HIGHLIGHTS

- Bioavailability of PFOS and PFOA by earthworm in biosolids-amended soils was studied.
- The uptake and elimination kinetics fit a one-compartment first-order kinetic model.
- PFOS displayed higher k_u , lower k_e , and longer t_{ss} than those of PFOA.
- The bioaccumulation factors and t_{ss} decreased with soil concentrations increasing.
- Soil concentration and OM contents accounted for earthworm bioavailability.

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ABSTRACT

The bioavailability of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in seven biosolids-amended soils without any additionally spiking to earthworms (*Eisenia fetida*) was studied. The uptake and elimination kinetics of PFOS and PFOA fit a one-compartment first-order kinetic model. PFOS displayed higher uptake and lower elimination rate coefficients, and longer time to reach steady-state (t_{ss}) than those of PFOA. The bioaccumulation factors (BAFs) of PFOS and PFOA ranged 1.54–4.12 and 0.52–1.34 $g_{soil} g_{worm}^{-1}$, respectively. The BAFs and t_{ss} decreased with increasing concentrations of PFOS and PFOA. The results showed that the total concentrations of PFOS and PFOA, and organic matter (OM) contents in soils explained 87.2% and 91.3% of the variation in bioavailable PFOS and PFOA, respectively. PFOS and PFOA concentrations exhibited positive influence and OM contents showed the negative influence on the accumulation of PFOS and PFOA in earthworms. Soil pH and clay contents played relatively unimportant role in PFOS and PFOA bioavailability.

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1. Introduction

Perfluoroalkyl substances (PFASs) have been used for over the past 60 years in an increasing variety of consumer and industrial products, such as fire-retardant foams, inks, paper, lubricants, cosmetics, upholstery and so on. As a result of the large production and wide application, PFASs are broadly present in the environment. Within the PFAS group, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most commonly used and found compounds (Hu et al., 2011). They have garnered intense scientific and regulatory interests due to their

extraordinary persistence, bioaccumulation tendencies and potential toxicological effects. So far, PFOS and PFOA have been found in atmosphere (Li et al., 2011), soil (Yoo et al., 2010), surface water (Hu et al., 2011), sediment (Higgins et al., 2005), and biota (Müller et al., 2011). They were also present in the serum of wildlife and humans and could be biomagnified in terrestrial and aquatic food webs (Müller et al., 2011; Houde et al., 2011).

Sewage sludge is an important sink of PFOS and PFOA (Higgins et al., 2005; Sun et al., 2011). The land application of treated sewage sludge (biosolids) is the option favored internationally for sludge management as it contributes to improve soil fertility and properties (Clarke and Smith, 2011). However, the use of biosolids as fertilizer in agriculture can cause contamination of

* Corresponding author. Tel.: +86 10 62849329; fax: +86 10 62923563.

E-mail address: bw@rcees.ac.cn (B. Wen).

PFASs in soils (Yoo et al., 2010; Washington et al., 2010; Sepulvado et al., 2011; Wen et al., 2014).

Organisms are liable to take up organic contaminants and may accumulate high level of PFASs when they live in contaminated soil environment. A few studies have been conducted and revealed plant uptake of PFASs from soils (Yoo et al., 2011; Wen et al., 2014; Zhao et al., 2014). Organic matter (OM) in soil was reported to play an important role in limiting plant uptake of PFASs. Earthworms comprise the largest part of the soil fauna biomass and are able to accumulate various organic contaminants, including polybrominated diphenyl ethers (PBDEs, Liang et al., 2010), polycyclic aromatic hydrocarbons (PAHs, Gomez-Eyles et al., 2011), and antimicrobials (Wen et al., 2011), etc. Accumulation of organic contaminants implies a risk to not only earthworm populations but also many vertebrate species feeding on earthworms. So far information about the accumulation of PFASs by earthworms from soil is quite limited. The work of Zhao et al. (2013) is perhaps the only available research on earthworm uptake of PFASs from artificially-contaminated soil, which suggested that the biota-to-soil accumulation factors (BSAFs) increased with perfluorinated carbon chain length. However, artificially polluted soils do not reflect the actual behavior of weathered PFASs in field soils. Moreover, it is still unknown how soil properties affect the accumulation of PFASs in earthworms.

In this study, seven soil samples collected from biosolids-amended fields without any additionally spiking were used to investigate the bioavailability of PFASs by earthworm (*Eisenia fetida*) in the laboratory. The objectives of the study were (i) to evaluate the uptake and elimination kinetics of PFOS and PFOA in earthworms and (ii) to investigate the key factors controlling the bioavailability of PFOS and PFOA in soils.

2. Materials and methods

2.1. Materials

Purities of all of the analytical standards were $\geq 95\%$. Potassium PFOS and PFOA were obtained from Sigma (St. Louis, MO). $^{13}\text{C}_4$ -PFOS and $^{13}\text{C}_4$ -PFOA purchased from Wellington Laboratories (Guelph, Canada) were used as-received. HPLC-grade methyl tert-butyl ether (MTBE), methanol (MeOH), and acetonitrile were purchased from Fisher Chemical (Firlawn, NJ, USA). Tetrabutylammonium hydrogen sulfate (TBAHS), sodium carbonate, sodium hydroxide and ammonium acetate were purchased from Aldrich Chemical (Milwaukee, WI, USA). Oasis[®] WAX (6 cc, 150 mg, 30 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA). Distilled water was used throughout the experimental work.

2.2. Soil sample collection and preparation

Seven soil samples (Nos. 1–7) were collected from surface layer (0–20 cm) of biosolids-amended agricultural fields in Changping, Beijing (40°13'N, 116°15'E) and Dezhou, Shandong province (37°20'N, 116°38'E). Soils were classified according to the American Classification System. The orders of soils in Changping and Dezhou were Mollisols. Uncontaminated soil was collected from an experimental field at Beijing Academy of Agriculture and Forestry Sciences. The soils were air-dried, ground and screened through a methanol-washed, 2-mm stainless-steel sieve to remove stones, plant roots, and other large particles. PFOS and PFOA in soils were determined.

Soil pH was measured in CaCl_2 (0.01 M) at a soil to solution ratio of 1:5 (w:v). Cation-exchange capacity (CEC) was determined by the method of Rhoades (1982). Organic matter was determined

by the Walkley–Black procedure (Nelson and Sommers, 1982). The selected soil properties and concentrations of PFOS and PFOA in the soils are given in Table S1.

2.3. Earthworms

Mature (clitellate) earthworms were purchased from the Agricultural University of China (Beijing, China) and maintained in moistened uncontaminated soil (40% water holding capacity) at $22 \pm 2^\circ\text{C}$ for at least two weeks before use. The wet weight of an individual earthworm was on average 350 ± 20 mg ($n = 30$). Before the experiment was commenced, earthworms were allowed to depurate for 24 h on moist filter paper. Earthworms were kept in the dark during all tests. The PFOS and PFOA in earthworm were determined.

2.4. Uptake kinetics of PFOS and PFOA from biosolids-amended soils

Earthworms were exposed to a 1000 mL polypropylene beaker containing 1 kg of biosolids-amended soils (Nos. 1–7). Autoclaved distilled water was added to give a moisture content of 40% water holding capacity (WHC). There were 33 beakers for each soil and each beaker held ten earthworms. Earthworms were randomly sampled after 0, 2, 5, 7, 13, 20 and 30 d to study the uptake kinetics. Remaining earthworms were then transferred into beakers containing uncontaminated soils, and were randomly sampled after 32, 35, 43, 50 and 60 d to study the excretion kinetics. Three replicates were carried out for each time point. The collected earthworms were placed in wet filter paper for 12 h to allow the gut to empty. Initial experiments indicated no difference in earthworm PFOA and PFOS body burdens after 12 or 24 h of depuration. After 12 h, the earthworms were transferred and rinsed with distilled water, wiped with clean towel paper, weighed and frozen at $-20 \pm 1^\circ\text{C}$ for 24 h. Earthworms cultured in uncontaminated soil was used as control. Then the earthworms were freeze-dried, weighed again, ground and stored at $-20 \pm 1^\circ\text{C}$ before chemical analysis. Results obtained by our preliminary study showed that PFOA and PFOS losses caused by freeze drying are neglectable.

The concentrations of PFOS and PFOA in the earthworms were expressed as ng g^{-1} dry weight and corrected for the earthworm weight changes during the exposure time. Triplicate tests were used for statistical analysis of PFOS and PFOA uptake and elimination kinetics.

2.5. Determination of PFOS and PFOA in soils and earthworms

PFOS and PFOA in soils were extracted by MTBE–NaOH according to the method of Wen et al. (2014). PFOS and PFOA in earthworms were extracted by MeOH–NaOH according to the method of Zhao et al. (2013). The two extraction methods and purification were detailed in the Supplementary materials.

An ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) was used to determine the concentrations of PFOS and PFOA. 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^{-1} ammonium acetate (50/50, v/v) was used as mobile phase at a flow rate of 0.2 mL min^{-1} . 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 S2).

2.6. Quality assurance and quality control

Quality control was done by regular analyses of procedural blanks, blind duplicate samples, and random injection of solvent blanks and standards. Blank matrix was obtained from uncontaminated soils and earthworms cultured in uncontaminated soils. Matrix calibration curves using spiked uncontaminated 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 concentration corresponding to the mean peak area plus three standard deviations ($\bar{x} + 3\sigma$) of extract from uncontaminated soil and earthworms incubated in the uncontaminated soil. The limits of quantitation (LOQs) were defined as the concentration corresponding to the mean peak area plus ten standard deviations ($\bar{x} + 10\sigma$) of extract from uncontaminated soil and earthworms incubated in the uncontaminated soil (Yoo et al., 2011). MDLs and LOQs were measured for each matrix on replicate analyses ($n = 6$) (Table S2). All samples were injected in triplicate. The accuracy of PFOS and PFOA determination was assessed by testing the recoveries of $^{13}\text{C}_4$ -PFOS and $^{13}\text{C}_4$ -PFOA. The recoveries of $^{13}\text{C}_4$ -PFOS and $^{13}\text{C}_4$ -PFOA were 92–105% and 89–103%, respectively for soils, and 81–101% and 78–95%, respectively for earthworms.

2.7. Modeling

In this experiment, the masses of the earthworms were measured. The concentrations of PFOS and PFOA in the earthworms were expressed as ng g^{-1} dry weight and corrected for the earthworm mass changes during the exposure experiment. Triplicate tests were used for statistical analysis of PFOS and PFOA accumulation kinetics. It was shown that accumulation of organic pollutants by earthworms can be described by a one-compartment model (Wen et al., 2011). To model PFOS and PFOA accumulation and calculate their uptake and elimination rates over both the uptake and elimination phases of the experiment, the experimental data were fitted with Eqs. (1) and (2) below:

$$Q_t = Q_0 + \alpha/k_e(1 - e^{-k_e t}) \quad (1)$$

where Q_t is the total concentrations of PFOS and/or PFOA ($\text{ng g}_{\text{worm}}^{-1}$) in earthworms at time t (d), k_e is the elimination rate constant (d^{-1}), and α is the uptake flux constant ($\text{ng g}_{\text{worm}}^{-1} \text{d}^{-1}$), which equals to $k_u C_{\text{soil}}$, where k_u is the uptake rate constant ($\text{g}_{\text{soil}} \text{g}_{\text{worm}}^{-1} \text{d}^{-1}$) and C_{soil} is the PFOS or PFOA concentrations in soils ($\text{ng g}_{\text{soil}}^{-1}$). The concentration of PFOS or PFOA in earthworms at the beginning of the experiment, Q_0 , was assumed to be a pool of constant magnitude.

Once transferred to uncontaminated soil, PFOS or PFOA concentrations in earthworms varied with time according to the following equation:

$$Q_t = Q_e + (Q_{tc} - Q_e)e^{-k_e(t-t_c)} \quad (2)$$

where Q_e is the residue concentrations of PFOS or PFOA in earthworms ($\text{ng g}_{\text{worm}}^{-1}$) at the end of the elimination period (day 60) and Q_{tc} is the PFOS or PFOA concentrations in earthworms ($\text{ng g}_{\text{worm}}^{-1}$) at the end of the accumulation period (day 30). t_c is the time (d) at which earthworms were transferred to the clean pot, and t is the time (d) since the beginning of the experiment. Subsequently, Eq. (1) was used to calculate steady-state tissue PFOS and PFOA concentrations (C_{ss}) for earthworms, and time to reach 90% of the steady state concentration (t_{ss}):

$$C_{ss} = \alpha/k_e \quad (3)$$

$$t_{ss} = -1/k_e \ln(1 - 90\%) \quad (4)$$

The steady-state concentrations were used to calculate bioaccumulation factors (the ratio of the PFOS or PFOA concentrations in earthworms to those in soils, BAF).

2.8. Data analysis

All statistical analyses were conducted with the software SPSS 11.5 for Windows (SPSS Inc., Chicago, IL). Linear and nonlinear regression analyses were conducted by the least and least-squares methods, respectively. A stepwise multiple linear regression technique was used to derive the relationship among variables. Statements of significant differences are based on $P < 0.05$.

3. Results and discussion

3.1. Concentrations of PFOA and PFOS in soils

The concentrations of PFOS and PFOA in uncontaminated soil are below their MDL levels. The properties and concentrations of PFOA and PFOS in biosolids-amended soils are given in Table S1. All soils are alkaline, with soil pH ranging from 7.36 to 8.43. The organic matter contents varied from 1.38% to 3.90%. The PFOS and PFOA contents ranged 1.44–43.2 ng g^{-1} , and 1.21–28.5 ng g^{-1} , respectively. The PFOS and PFOA concentrations in the soils sampled from the same site increased with increasing OM contents. For example, significant correlation was found between PFOA concentrations in soils sampled from Changping and their OM contents ($P < 0.05$, Fig. S1), suggesting that land application of biosolids not only increases the OM contents, but also results in the accumulation of PFASs in soils.

3.2. Uptake and elimination kinetics

During the 60 d experiment period, all earthworms had a healthy appearance, and no mortality occurred. The average wet weight loss was from 15% to 40%, with varying time. No significant difference of weight losses was found between earthworms exposed in biosolid-amended soils and in uncontaminated control soil. The initial concentrations of PFOA and PFOS in earthworms were under their MDLs.

During the exposure phase, the uptake of PFOA and PFOS by earthworms was nonlinear (Fig. 1). Tissue PFOS and PFOA concentrations showed an initial rapid increase in the first 7 days followed by a leveling off. Uptake saturation was reached within the 30 days. On the day 30, the PFOS concentrations in the earthworms were 5.90 ± 0.60 , 36.1 ± 2.3 , 51.2 ± 2.9 , 79.9 ± 3.3 , 129 ± 8 , 96.6 ± 8.2 and $66.6 \pm 6.6 \text{ ng g}^{-1}$, respectively, while PFOA concentrations in the earthworms were 1.60 ± 0.14 , 4.9 ± 0.1 , 13.3 ± 2.2 , 18.2 ± 1.1 , 22.8 ± 1.1 , 22.2 ± 1.0 and $14.8 \pm 1.2 \text{ ng g}^{-1}$, respectively, for the seven soils (Nos. 1–7). During the 30 d depuration period, the concentrations of PFOA and PFOS in earthworms decreased gradually. About 90% PFOS and PFOA were lost at the end of the elimination experiment.

The individual uptake and elimination data of PFOS and PFOA fitted well with Eqs. (1) and (2), respectively, with high R^2 values (>0.98) and low mean weighted square errors (MWSE; Fig. 1, Table 1). The k_e values calculated from Eq. (1) were consistent with those calculated from Eq. (2), confirming the validity of the estimation. The calculated steady-state tissue concentrations (C_{ss}) of PFOS and PFOA were in the range of those determined at the end of uptake period (day 30). Liu et al. (2011) found the discrepancy between the kinetic and the steady-state approaches for the accumulation of PFASs in green mussel (*Perna viridis*), and suggested that the first order uptake reaction was inappropriate in the case of PFASs bioaccumulation. However, Zhao et al. (2013) found that

Fig. 1. Accumulation and elimination kinetics of PFOS (a) and PFOA (b) in soils (Nos. 1–7). Dots: experimental data. Lines: fits to Eqs. (1) and (2) for the uptake and elimination, respectively.

the first order kinetics could be used to describe the earthworm accumulation of PFASs from contaminated soil well, which was

consistent with our results. The estimated k_u values ranged from 0.379 to 0.823 $\text{g}_{\text{soil}} \text{g}_{\text{worm}}^{-1} \text{d}^{-1}$ for PFOS, and from 0.293 to 0.416 $\text{g}_{\text{soil}} \text{g}_{\text{worm}}^{-1} \text{d}^{-1}$ for PFOA, while the k_e values ranged from 0.158 to 0.265 d^{-1} for PFOS, and from 0.216 to 0.363 d^{-1} for PFOA. For PFOS and PFOA in soil No. 1, whose PFOS and PFOA concentrations were similar (Table S1), PFOS displayed higher k_u and lower k_e values than those of PFOA. This revealed that PFOS was taken up at a higher rate whereas depurated at a lower rate than PFOA. The higher k_u and the lower k_e values resulted in a relative higher steady-state tissue PFOS concentration (C_{ss}) and bioaccumulation factor (BAF). The BAF values of PFOS were in the range of 1.54–4.12, which were higher than those of PFOA (0.516–1.36). These results of high BAF values of PFOS are in accordance with what reported by Zhao et al. (2013), in which bioaccumulation kinetics of PFASs in earthworms exposed in lab-contaminated water or soils were investigated. Bioaccumulation of PFASs was believed to be related with their fluorinated carbon chain length and ionic functional groups for both aquatic and terrestrial organisms. The BAF values of PFASs increased with the increase of fluorinated carbon chain length. The fluorinated carbon length of PFOS was longer than that of PFOA. In addition, the binding affinity by sulfonate was higher than carboxylate with the same fluorinated perfluorinated chain (Martin et al., 2003; Woodcroft et al., 2010; Liu et al., 2011; Zhao et al., 2013).

Among the soils studied, the concentrations of PFOS and PFOA in soil No. 1 were the lowest, while the t_{ss} and BAF values of soil No. 1 were the highest (Table 1). This indicates that uptake kinetics of PFOS and PFOA may be affected by their soil concentrations. In order to further assess the concentration effect, relationship between the soil PFOS and/or PFOA concentrations and their uptake kinetic parameters were investigated. No significant relationship between PFOS and/or PFOA concentrations in the soils and the k_u values was found (data not shown), while soil concentrations of PFOS and/or PFOA correlated positively with the k_e values, and thus correlated negatively with the t_{ss} ($P < 0.05$, Fig. S2a–d). A similar significantly negative relationship was found between soil PFOS and/or PFOA concentrations and BAF values ($P < 0.05$, Fig. S2e and f). This suggests that the time to reach steady state and the bioaccumulation factor decrease with the increase of soil PFAS concentrations. Such phenomena of the concentration-dependent BAF values of PFASs were observed by Giesy et al. (2010) and Zhao et al. (2013). Also Liu et al. (2011) reported that not only the BAF but also the t_{ss} values of PFASs in green mussels decreased with the increasing exposure concentration. It is recognized that lipid is not the bioaccumulation compartment for PFASs

Table 1
Estimates of kinetic parameters for PFOS and PFOA uptake and elimination.

Soils	Calculated from Eq. (1)								Calculated from Eq. (2)		
	α ($\text{ng g}_{\text{worm}}^{-1} \text{d}^{-1}$)	k_u ($\text{g}_{\text{soil}} \text{g}_{\text{worm}}^{-1} \text{d}^{-1}$)	k_e (d^{-1})	C_{ss} ($\text{ng g}_{\text{worm}}^{-1}$)	t_{ss} (d)	BAF	R^2	MWSE ^a	k_e (d^{-1})	R^2	MWSE
PFOS											
No. 1	0.938 (0.050)	0.379	0.158 (0.009)	5.94	14.6	4.12	0.996	0.012	0.160 (0.006)	0.992	0.103
No. 2	5.96 (0.23)	0.573	0.165 (0.008)	36.1	14.0	3.47	0.991	0.004	0.162 (0.007)	0.991	0.178
No. 3	11.8 (0.4)	0.769	0.231 (0.009)	51.3	9.97	3.33	0.994	0.005	0.231 (0.009)	0.993	0.147
No. 4	18.9 (0.8)	0.666	0.236 (0.009)	79.5	9.76	2.82	0.994	0.002	0.239 (0.009)	0.990	0.175
No. 5	33.6 (0.9)	0.823	0.264 (0.011)	127	8.72	3.12	0.995	0.002	0.266 (0.014)	0.997	0.097
No. 6	25.2 (0.7)	0.600	0.265 (0.009)	95.1	8.69	2.26	0.995	0.002	0.263 (0.007)	0.997	0.092
No. 7	16.9 (0.4)	0.390	0.254 (0.007)	66.3	9.07	1.54	0.997	0.001	0.262 (0.007)	0.997	0.098
PFOA											
No. 1	0.355 (0.016)	0.293	0.216 (0.012)	1.64	10.7	1.36	0.995	0.045	0.208 (0.008)	0.988	0.088
No. 2	1.10 (0.04)	0.254	0.224 (0.009)	4.91	10.3	1.14	0.995	0.011	0.227 (0.007)	0.995	0.096
No. 3	3.04 (0.08)	0.241	0.229 (0.007)	13.3	10.1	1.05	0.996	0.001	0.229 (0.008)	0.996	0.041
No. 4	4.69 (0.10)	0.233	0.260 (0.006)	18.1	9.84	0.913	0.997	0.003	0.258 (0.008)	0.995	0.085
No. 5	10.9 (1.0)	0.416	0.485 (0.049)	22.4	4.75	0.857	0.986	0.008	0.414 (0.027)	0.986	0.105
No. 6	8.69 (0.43)	0.317	0.397 (0.022)	21.9	5.80	0.799	0.989	0.003	0.394 (0.019)	0.988	0.096
No. 7	5.34 (0.24)	0.187	0.363 (0.018)	14.7	6.34	0.516	0.991	0.001	0.364 (0.018)	0.990	0.085

^a Mean weighted square error, equal to $1/\gamma \sum [(q_{\text{measured}} - q_{\text{model}})^2 / q_{\text{measured}}^2]$, where γ is the amount of freedom; $\gamma = N - 2$ for Eq. (1), while $\gamma = N - 1$ for Eq. (2).

Table 2

The stepwise multiple linear regression equations for PFOS and PFOA in earthworms as function of their concentrations in soils and soil characteristics.

	Multiple linear equation	R ²	P	S.E.
<i>The stepwise regression for PFOS</i>				
1	[PFOS] _{worm} = 2.045 [PFOS] _{soil} + 13.323	0.696	0.012	22.2
2	[PFOS] _{worm} = 4.439 [PFOS] _{soil} − 47.483[OM] + 70.629	0.872	0.007	14.4
<i>The stepwise regression for PFOA</i>				
1	[PFOA] _{worm} = 0.658 [PFOA] _{soil} + 2.678	0.792	0.005	3.72
2	[PFOA] _{worm} = 1.382 [PFOA] _{soil} − 9.300[OM] + 13.655	0.913	0.003	2.41

even though a portion of PFAS molecules is hydrophobic and may interact with lipid (Zhao et al., 2013). Bioaccumulation of PFASs is an adsorption-like process. The adsorption sites are likely some proteins in bioorganism, which could strongly bind with PFASs (Washington et al., 2010; Bischel et al., 2010; Han et al., 2012). Desorption rates of PFASs from these proteins may be slower than those from lipid. These adsorption sites are occupied and gradually saturated with PFAS concentration increasing. Alternatively, the concentration-dependent BAF values of PFOS and PFOA may be due to their resistant desorption at high concentrations. When Sormunen et al. (2008) studied the desorption and bioavailability of 3,3',4,4'-tetrachlorobiphenyl (PCB 77), they found that the rapid-desorbing fractions and the biota-sediment accumulation factor of PCB 77 decreased with increasing concentration in sediment. Although the desorption resistance for PFOS and PFOA from sediments and humic acid was reported (Pan et al., 2009; Jia et al., 2010), further studies are necessary to assess the concentration-dependent effects on the desorption and bioavailability of PFASs.

3.3. Quantification of the relationship between PFAS accumulation and soil properties

Earthworms may take up contaminants from soil and porewater, both through their skin (dermal) and by ingestion (oral). It is assumed that only contaminants that can be released from soil/sediment are available to biological receptors. Qi and Chen (2010) suggested that for readily desorbable contaminants, the primary biouptake route is the porewater uptake. But for the desorption-resistant contaminants, the uptake from ingested soil particles can be also important. It remains unclear what the relative important pathways for PFASs accumulation by earthworm is, however, the importance of porewater uptake is estimated based on their high water solubility when compared with those of PAHs and PBDEs. The PFAS concentrations in porewater depend on their soil concentrations and soil properties. It has been reported that organic carbon is the most important parameter dominating PFOS sorption (Higgins and Luthy, 2006; Johnson et al., 2007; Jia et al., 2010). In addition, pH, sand and clay contents play roles in PFOS retention (Higgins and Luthy, 2006; Johnson et al., 2007). Considering the multi-contributions of various soil properties, including soil pH, organic matter and clay content, it is expected that multi linear regression model would quantify the bioaccumulation of PFOS and PFOA by earthworms. Based on the stepwise regressions, the best regression models describing the relationship between PFOS and PFOA concentrations in earthworm tissues and their concentrations in the soils and soil properties were obtained (Table 2). The results verified that the soil PFOS and PFOA concentrations and soil OM content ([OM]) are two key factors controlling the bioavailability of PFOS and PFOA in soils. Specifically, PFOS concentration in soil ([PFOS]_{soil}) was the first independent variable fitted to the PFOS concentrations in earthworm ([PFOS]_{worm}) and could explain 69.6% ($P < 0.05$) of the variability in [PFOS]_{worm}. Including OM content as a predictor

(explanatory variables) improved the model fitting to 87.2% ($P < 0.01$). Other soil properties, such as pH, CEC, sand, silt and clay contents, did not improve the model fitting. This suggests that PFOS concentration in soil and soil organic carbon content dominant the accumulation of PFOS in earthworm. Similarly, PFOA concentration in soil ([PFOA]_{soil}) could explain 79.2% of the variability in PFOA concentration in earthworm ([PFOA]_{worm}), and including OM content as a predictor improved the model to 91.3%. Soil properties other than OM content as factors could not improve the model fitting. These suggested that soil concentration and OM content dominated the bioavailability of PFASs in soils. Soil pH and clay content appeared relatively unimportant for PFOS and PFOA bioavailability.

4. Conclusion

The results of this study demonstrated that contamination of PFOS and PFOA in soils as a result of biosolids land application led to accumulation of PFOS and PFOA in earthworms with higher concentration of PFOS than that of PFOA. The finding that the BAFs decreased with increase of PFOS and PFOA concentrations in soils indicated that the uptake of PFOS and PFOA by earthworms from biosolids-amended soil may not be a process of partitioning equilibrium. Soil PFOS and PFOA concentration and soil organic carbon content can act as better predictors of bioavailable PFOS and PFOA in biosolids-amended soils than soil pH and clay content. Current findings would help understand the bioavailability of PFASs in soils and assess the risks of PFASs in soils as a result of biosolids application.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.08.009>.

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