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Short communication

The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils☆

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ABSTRACT

The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in seven species of plants from biosolids-amended soils were investigated. The PFOS and PFOA root concentration factors (C_{root}/C_{soil}) ranged from 1.37 to 4.68 and 1.69 to 10.3 $(ng/g_{root})/(ng/g_{soil})$, respectively, while the translocation factors (C_{shoot}/C_{root}) ranged from 0.055 to 0.16 and 0.093 to 1.8 $(ng/g_{shoot})/(ng/g_{root})$, respectively. The PFOS and PFOA accumulations in roots correlated positively with root protein contents ($P < 0.05$), while negatively with root lipid contents ($P < 0.05$). These suggested the promotion effects of protein and inhibition effects of lipid on root uptake. The translocation factors correlated positively with the ratios between protein contents in shoots to those in roots ($P < 0.05$), showing the importance of protein on PFOS and PFOA translocation. This study is the first to reveal the different roles of protein and lipid in the accumulation and distribution of PFOS and PFOA in plants.

1. Introduction

Perfluoroalkyl substances (PFASs) are a class of emerging persistent organic pollutants (POPs). They have been manufactured and used in many industrial and household applications for more than half century. Within the PFAS group, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly used and found compounds (Arvaniti and Stasinakis, 2015). Up until now, PFOS and PFOA have been detected in all environmental and biological matrices, including the atmosphere (Wang et al., 2015; Ahrens et al., 2011; Dreyer et al., 2009), soil (Kim et al., 2015; Wen et al., 2014; Washington et al., 2010), water (Eschauzier et al., 2010; Bossi et al., 2008), sediment (Kwadijk et al., 2010), biota (Houde et al., 2011), and human serum (Gao et al., 2015). Adverse effects of PFOS and PFOA on plants, animals and humans have been reported (Wen et al., 2013; Stevenson et al., 2006). Due to their global distribution, environmental persistence, long distance transportation, and potential accumulation and toxicity, PFASs have been at the center of an increasing number of environmental monitoring studies.

Industrial and municipal wastewater treatment plants (WWTPs) are significant sources for dispersing PFASs into the environment (Kim et al., 2015; Wen et al., 2014; Washington et al., 2010; Bossi et al., 2008). High concentrations of PFASs have been found in the sludge from WWTPs (Vierke et al., 2013; Sun et al., 2011; Higgins et al., 2005). Land-application of biosolids (treated sludge) may lead to the accumulation of PFASs in soils, and consequently facilitate the entry of PFASs into the terrestrial food web by plant uptake (Wen et al., 2014; Sepulvado et al., 2011; Yoo et al., 2011; Washington et al., 2010). Both field and controlled laboratory studies have demonstrated that PFASs can be taken up from biosolids-amended soils, translocated and stored in different plant organs (Wen et al., 2014; Felizeter et al., 2014; Yoo et al., 2011; Blaine et al., 2014, 2013; Stahl et al., 2013; Lechner and Knapp, 2011). Soil organic carbon plays an important role in decreasing the accumulation of PFASs in plants (Wen et al., 2014; Yoo et al.,

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2011). Accumulation and distribution of PFASs depend on plant species and varied with PFAS properties. Radish and celery showed preference for uptake of short perfluorinated carbon-chain of PFASs. However, wheat, sugar snap pea and tomato showed no preference for uptake of PFASs with different perfluorinated carbon-chain (Wen et al., 2014; Blaine et al., 2014). Translocation from roots to the above ground part of plants showed a decrease with increasing PFAS carbon chain length (Wen et al., 2014; Blaine et al., 2014; Felizeter et al., 2014). As a result, long-chain PFASs are mainly distributed in plant roots, while short-chain PFASs are mainly found in leaves and fruits (Felizeter et al., 2014). Blaine et al. (2014) reported that PFOS root to shoot translocation factors (TFs) from roots to shoots were less than 1 for celery and tomato, and were more than 1 for radish and pea.

Bioaccumulation of hydrophobic organic compounds (HOCs) in plants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) is mainly characterized by lipid dominating partition processes. Lipid is the major reservoir for accumulation of HOCs in plant (Chiou et al., 2001; Li et al., 2010). Huang et al. (2010) reported that root concentration factors (RCFs) of HOCs correlated positively with root lipid contents, while TFs correlated negatively with root lipid contents. PFASs are ionizable organic pollutants and mainly exist as anions in environmental relevant pH conditions. They tend to accumulate in protein-rich tissues in fish and animals, such as liver and blood, rather than in fat tissues (Hoff et al., 2003). Wen et al. (2013) found that the kinetics of PFOS and PFOA uptake by plant fitted Mechaelis-Menten equation well, suggesting their transport protein-mediated influx processes. In contrast, Felizeter et al. (2012) suggested that uptake of PFASs by lettuce root was mainly governed by sorption to lipid-rich root solids. Though species-dependent uptake and tissue distribution of PFASs in plants have been reported, there is still limited mechanistic understanding of the biotic parameters on PFASs accumulation in plants.

In this study, we conducted a greenhouse pot experiment to explore the uptake and translocation of PFOS and PFOA in seven species of plants from biosolids-amended soil. Protein and lipid contents in plant roots and shoots were determined in order to test their influences. To the best of our knowledge, this is the first attempt to elucidate the roles of protein and lipid on the accumulation and distribution of PFOS and PFOA in plant.

2. Experimental section

2.1. Materials

Perfluorooctanesulfonic acid (potassium salt, > 98%), perfluorooctanoic acid (PFOA, > 96%), tetrabutylammonium hydrogen sulfate (TBAHS, > 99%), sodium carbonate (>99%), sodium hydroxide (>98%) and ammonium acetate (>99%) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA). HPLC-grade methyl tert-butyl ether (MTBE, >99.9%), chloroform, hexane, acetonitrile and methanol were from Fisher Scientific Co. (Fair Lawn, NJ, USA). Surrogate standards ($^{13}C_4$-PFOA and $^{13}C_4$-PFOS) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) and were used as-received. Milli-Q water was applied throughout the experimental work.

2.2. Biosolids-amended soil

Biosolids-amended soil was collected from surface layer (0–20 cm) of biosolids-amended agricultural fields in Dezhou Experiment Station, Chinese Academy of Agricultural Sciences (Dezhou, Shandong province, China). The soil has received municipal biosolids at the rate of 20 tons (dry matter) per hectare per year for more than nine years. Uncontaminated soil without detectable PFOS and PFOA was collected from an experimental field at Beijing Academy of Agriculture and Forestry Sciences. The soil samples were air-dried and sieved through a 2-mm fiber sieve to remove stones, plant roots, and other large particles prior to the determination of PFOS and PFOA and pot experiments. The selected properties and PFOS and PFOA concentrations in the soils are given in Table 1.

2.3. Pot experiment

Maize (*Zea mays* L. cv. Nongda 108), soybean (*Glycine max* L. Merrill), radish (*Raphnus sativus* L. cv. Dahongpao), mung bean (*Vigna radiata* L. Wilczek), lettuce (*Lactuca sativa* L.), alfalfa (*Medicago sativa* L. cv. Chaoren) and Italian ryegrass (*Lolium multiflorum* Lam.) were used as test plants. Seeds were purchased from the Chinese Academy of Agricultural Sciences, Beijing, China. They were sterilized in 10% (w/w) H_2O_2 solution for 15 min, thoroughly washed with Milli-Q water, soaked in a 3 mM solution of $Ca(NO_3)_2$ for 6 h in the dark, and subsequently germinated on moist filter paper in the dark.

Each polypropylene pot (upper diameter 18 cm, lower diameter 12.8 cm, height 16 cm) received 1.5 kg of soil. Polypropylene bags were placed inside the pots to prevent contamination and water drainage. Twenty pregerminated seeds were sown in each pot. After emergence for 3 days the seedlings were thinned to 18 (ryegrass), 15 (alfalfa), and 5 (maize, soy bean, lettuce, green bean and radish). Pots were kept in a controlled environment growth chamber for 45 d at a light intensity of 250 μmol m^{-2} s^{-1} provided by supplementary illumination with a photoperiod of 14 h each day, at a 25/20 °C day/night temperature regime, and a relative humidity of 70%. Plants in uncontaminated soil grown in the same chamber as those in biosolids-amended were set up as control. Plants in uncontaminated soil grown in another chamber were set up as blank. Four replicate pots of each treatment were prepared. The pots were positioned randomly and randomized every two days. Milli-Q water was added as required to maintain moisture content at 60–70% of water holding capacity by regular weighing.

2.4. Sample preparation

Plant shoots above ground and roots below ground were harvested separately after growth for 45 d. Root samples were carefully washed with tap water to remove any adhering soil particles. Then root and shoot samples were thoroughly rinsed with Milli-Q water, blotted with tissue paper and weighed. The protein contents in fresh roots and shoots were determined. Plant tissues were then frozen at −80 °C overnight, freeze-dried for 48 h in a lyophilizer (FD-1, Beijing Boyikang Instrument Ltd., Beijing, China) and weighed again. The water contents of roots and shoots are calculated by mass balance. The lipid contents in dry roots and shoots were determined. The dried root and shoot samples were ground and stored in polypropylene pot containers at −20 °C before chemical analysis.

2.5. Determination of protein and lipid contents in plant roots and shoots

Protein contents in fresh plant roots and shoots were determined according to the method of Jones et al. (1989) with some modifications. Lipid contents in dried roots and shoots were determined following the same principles as employed previously in our laboratory (Zhu et al., 2007). Information of protein and lipid determination was given in Supplementary materials.

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