



# Distribution and partitioning of perfluoroalkyl carboxylic acids in surface soil, plants, and earthworms at a contaminated site

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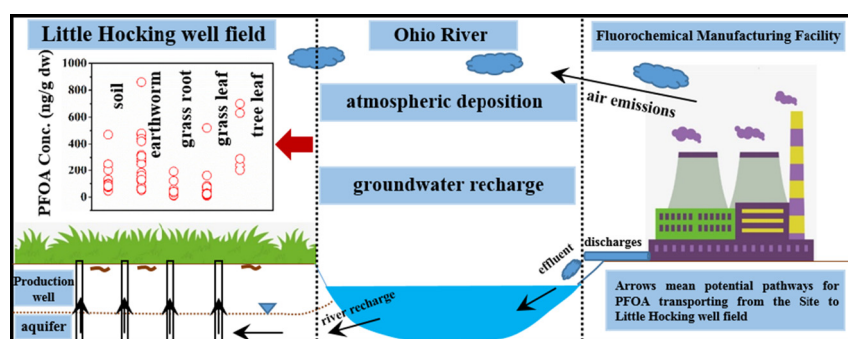
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## HIGHLIGHTS

- Partitioning of PFCAs among soil, plants and earthworms was studied at a contaminated site.
- Elevated PFOA concentrations were found in the environmental media analyzed.
- Biota-soil accumulation factors of PFCAs increased with perfluorocarbon chain length.
- Translocation of long-chain PFCAs in plants was weaker than that of short-chain PFCAs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A field study was conducted to elucidate distribution and partitioning of perfluoroalkyl carboxylic acids (PFCAs; C7–12) in a terrestrial ecosystem that was contaminated with industrial sources of release. Surface soil (0–6 cm), plants, and earthworms were collected from a field located within a 1-mile radius of a fluoropolymer industry that had been manufacturing fluorochemicals for over five decades. The mean concentrations of  $\Sigma$  PFCAs were 150, 420, 61, 68, and 430 ng/g dry weight (dw) in surface soil, earthworms, grass roots, grass leaves, and tree leaves, respectively. The measured concentrations were higher than those reported for corresponding matrices in other locations worldwide, suggesting that fluorochemical manufacturing operations have contributed to the contamination of this nearby land. Soil and plant tissues consisted mainly of perfluorooctanoic acid (PFOA; C8) (77.3–97.1% of the total PFCAs), whereas longer-chain PFCAs, such as perfluoroundecanoic acid (PFUnDA; C11: 17.6%) and perfluorododecanoic acid (PFDoDA; C12: 31.9%), accounted for relatively higher proportions in earthworms. Spatial distribution of PFCAs at this site suggested that both atmospheric deposition and groundwater recharge have contributed to the sources of contamination. Both earthworm- and grass-accumulated PFCAs from soil with biota-soil accumulation factors and root concentration factors increased with perfluorocarbon chain length. The translocation factors of PFCAs in grass decreased as the number of carbons in the fluorocarbon moiety increased. This field study is appropriate to improve our understanding of partitioning of PFCAs among soil, plants, and earthworms.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been extensively used as surfactants in textiles, paper packaging, and aqueous firefighting

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foams for over 60 years (Paul et al., 2009). Their widespread use, in combination with their high persistence (Buck et al., 2011), led to their ubiquitous occurrence in the global environment, including polar regions (Ahrens and Bundschuh, 2014; Kannan, 2011; Riget et al., 2013). Evidence suggests that PFAS exposure is linked to potential health risks in humans and wildlife (Dewitt et al., 2009; Rand and Mabury, 2017).

Studies have shown that historical use of firefighting foams in military bases, airports, and fire department training sites has resulted in contamination of local soils and groundwater. At least 47 PFAS-contaminated sites have been identified in the USA (SSEHRI, 2018). Similarly, several locations around military bases or airports in Australia and Canada have been contaminated by PFASs from the use of firefighting foams (AGDD, 2018; Milley et al., 2018). Regional contamination of groundwater at military bases and airports has attracted considerable attention in recent years among international and national regulatory agencies, which are interested in developing strategies to mitigate environmental release of PFASs. Within the PFAS class of chemicals, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most commonly used substances. PFOS has been identified as a persistent organic pollutant (POP) under the Stockholm Convention, whereas PFOA and its ammonium salts (APFO) have been characterized as substances of very high concern under the European REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) regulation.

Thus far, a considerable number of studies have focused on human exposure to PFASs, with an emphasis on sources such as drinking water (Hu et al., 2016), indoor dust (Yao et al., 2018), and diet (Tittlemier et al., 2007). Similarly, studies have described the toxicity and fate of PFASs in the aquatic environment (Ahrens and Bundschuh, 2014; Beach et al., 2006; Kannan, 2011; Lam et al., 2014, 2017; Liu et al., 2017; Wang et al., 2015). Information on the fate of PFASs in the terrestrial environment, however, is limited (Rankin et al., 2016). In addition to contamination that arises from the use of firefighting foams and industrial activities, land application of biosolids that contain PFOA and PFOS can release these compounds into the soil environment (Karnjanapiboonwong et al., 2018; Sepulvado et al., 2011; Yoo et al., 2011; Zareitalabad et al., 2013). A few studies have reported on the uptake of PFASs by plants and earthworms from soil. Yoo et al. (2011) studied PFASs uptake by plants from biosolid-amended fields; other studies involved soils fortified artificially with the target PFAS of interest under controlled environment. For instance, Zhao et al. (2014) reported bioavailability of PFASs in soil-wheat and soil-earthworm mesocosms by artificially fortifying soils with these chemicals. Xiang et al. (2018) studied accumulation of PFOA in various lettuce cultivars, using soils spiked with this chemical, and Bizkarguenaga et al. (2016) and Blaine et al. (2014) studied the uptake of PFOS and PFOA by carrot and lettuce or other plants in a compost/biosolid amended soil. Stahl et al. (2009) reported the uptake of PFOA and PFOS by plants in a pot culture study. Pot experiments do not entirely mimic the field conditions, such as fluctuations in temperature and moisture as well as interaction with other edaphic, biotic and climatic factors. This makes the translation of the results of pot culture studies challenging (Limpens et al., 2012). Therefore, studies on soil-plant and soil-invertebrate partitioning of PFASs under field conditions are needed.

The Little Hocking Water Association (LHWA) is a public water supply organization, with its well field located on the banks of the Ohio River, immediately across from a fluoropolymer manufacturing facility that has produced fluoropolymers for over five decades (Davis et al., 2007). Due to the long-term historical releases from the manufacturing facility, PFASs were detected at notable concentrations in LHWA well field water and has been a subject of investigation for over a decade (Shin et al., 2011; Steenland et al., 2009). The LHWA well field is a 45-acre floodplain meadow dominated by perennial grasses. Extensive PFOA contamination in the LHWA well field provided an opportunity to study the distribution and partitioning of perfluorocarboxylates (PFCAs) at this site. In this study, surface soil, earthworms, grass leaves,

and grass roots and tree leaves were collected and analyzed for PFOA, perfluoroheptanoic acid (PFHpA; C7), perfluorononanoic acid (PFNA; C9), perfluorodecanoic acid (PFDA; C10), perfluoroundecanoic acid (PFUnDA; C11), and perfluorododecanoic acid (PFDoDA; C12). The specific objectives of this study were to: (i) determine the concentrations, composition profile, and spatial distribution of PFCAs in soil, plants, and earthworms; (ii) evaluate potential migration pathways of PFCAs; and (iii) elucidate partitioning of PFCAs from soil to plants and earthworms. PFOS and related sulfonate-based compounds were found at only trace levels (much lower than those of PFCAs) and, therefore, were not included in this study.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Standards of PFHpA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA (C7–C12) as well as their corresponding <sup>13</sup>C-labeled internal standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada) (Table S1 in the Supporting Information). Reagent grade tetrabutylammonium hydrogen sulfate (TBA) was purchased from Tokyo Chemical Industry, Inc. (Tokyo, Japan). Other reagents, including methanol (MeOH), water, methyl-*tert*-butyl ether (MTBE), anhydrous sodium carbonate, and sodium bicarbonate, were purchased from J. T. Baker (Center Valley, PA, or Phillipsburg, NJ, USA).

### 2.2. Study site and sample collection

The sampling was conducted in the Little Hocking well field (Washington County, Ohio, USA) in October 2009 (Fig. 1). This well field is a floodplain meadowland dominated by perennial grasses, which is mowed periodically for hay. The well field has four production wells for the primary water supply. Within the site, two small drains, one that extends through the east-central portion of the site, and another shallower drain that extends through the northwestern area of the property exist (Fig. 1). The east-central drain flows intermittently, frequently at saturated conditions in late summer and fall. The 45-acre site was divided into eight regions for the analysis of spatial distribution of PFCAs, as northwest (NWR), southwest (SWR), midfield 1 (MIDR1), midfield 2 (MIDR2), northeast 1 (NER1), northeast 2 (NER2), southeast 1 (SER1), and southeast 2 (SER2), as shown in Fig. 1. Several species of grasses were found on this field, and two perennial grasses, Canada wildrye (*Elymus canadensis glaucifolius*) and Sedges (*Carex spp.*), were analyzed in this study. These two species are collectively referred to as “grass” in this study. Grass was uprooted with soil, using a solvent-rinsed shovel, so that soil, roots, and leaves from the same plant can be obtained. Whenever possible, earthworms (*Lumbricus terrestris*) were collected from the rhizosphere of the grasses. Otherwise, earthworms were collected close to the grass sampling location. In total, 19 paired samples, including two to three matching soil, grass, and earthworm samples from each quadrant, were obtained. Soil, grass, and earthworms were collected from multiple locations within a quadrant to obtain a representative sample.

In addition, we collected five sumac (*Rhus spp.*) tree leaf samples from SWR (2), MIDR2 (1), NER2 (1), and SER2 (1), based on their accessibility. The sumacs were found along the banks of the Ohio River, bordering the LHWA well field. Samples were placed in clean polyethylene bags (for tree leaves and grasses) or solvent-cleaned I-CHEM jars (for soil and earthworms), and kept at 4 °C until they were transported to the laboratory (within 12 h), where they were stored at –20 °C. The soil is silty clay in texture. The top 6 cm of soil layer was analyzed after sieving it through a 2 mm sieve. It rained heavily (>2 cm) on the day before sampling at the LHWA well field. Plant samples (leaves and roots) were washed with Milli-Q water to remove surface debris/soil, prior to analysis. Earthworms were placed in Milli-Q water overnight for depuration, and then prepared for analysis.

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