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Bioaccumulation of emerging organic compounds (perfluoroalkyl substances and halogenated flame retardants) by earthworm in biosolid amended soils

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ABSTRACT

In the present work, the bioaccumulation behavior of 49 target emerging organic compounds (20 perfluoroalkyl substances, PFASs, and 29 halogenated flame retardants, HFRs) was studied in soil invertebrates (*Eisenia andrei*). Multi species soil systems (MS · 3) were used to assess the fate and the effects associated with the application of four biosolids in agricultural soil on terrestrial soil organisms. Biosolid amendment increased concentrations 1.5–14-fold for PFASs, 1.1–2.4-fold for polybrominated diphenyl ethers, PBDEs, and 1.1–3.6-fold for chlorinated flame retardants, CFRs. Perfluorooctanesulfonate, PFOS, (25%) and BDE-209 (60%) were the predominant PFAS and HFR compounds, respectively, in biosolids-amended soils. Total concentrations (ng/g dry weight) in earthworms from biosolid-amended soils ranged from 9.9 to 101 for PFASs, from 45 to 76 for PBDEs and 0.3–32 for CFRs. Bioaccumulation factors (BAFs) were calculated to evaluate the degree of exposure of pollutants in earthworms. The mean BAF ranged from 2.2 to 198 for PFASs, 0.6–17 for PBDEs and 0.5–20 for CFRs. The relationship of PFAS and PBDE BAFs in earthworms and their log K_{ow} were compared: PFAS BAFs increased while PBDE BAFs declined with increasing log K_{ow} values. The effect of the aging (21 days) on the bioavailability of the pollutants in amended soils was also assessed: the residence time affected differently to the compounds studied.

1. Introduction

Perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) as polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) have been detected in a variety of wildlife and environment (Giesy and Kannan., 2001; Hansen et al., 2001; De Wit, 2002; De Boer et al., 2003; Shoeib et al., 2004; Higgins et al., 2005; De la Torre et al., 2012a). These compounds have been intentionally incorporated in common consumer and industrial products and their production, use and disposal has led to their widespread distribution in the environment. One potential mechanism for introduction of these compounds to the environment is the application of biosolids to land. The recycling of biosolids to agriculture is the option favored internationally for biosolid management as it contributes to improve soil properties (EEC, 1986, 1991). However, the amendment in agricultural soils has been demonstrated to cause the contamination of the soil (Sellström et al., 2005; Washington et al., 2010). The migration of pollutants from soil to plants or soil organisms could facilitate a probable entry pathway into the food chain. Organisms can achieve high concentrations of certain organic contaminants relative to concentrations of these substances in the environment they inhabit. Food web analyses have shown that PFASs and HFRs can bioaccumulate and biomagnify in aquatic ecosystems (Law et al., 2003; Houde et al., 2006). In terrestrial ecosystems, earthworms are an important link in transporting environmental contaminants from soil to other organisms in terrestrial food webs (Sellström et al., 2005), being an appropriate model organism to assess bioavailability as it lives in close contact with soil, has thin and permeable cuticle, and also consumes large amounts of soil (Jager et al., 2005). Besides, these invertebrates can change the availability of inorganic and organic pollutants in soils. Zhao et al. (2014) detected that the co-presence of wheat and earthworms enhanced the bioavailability of PFASs in soil. Therefore, it is necessary studies focused on pollutants from soil to better

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understand their bioaccumulation potential in terrestrial environment. The accumulation of chemicals is a dynamic process consisting of uptake, partition, storage, and excretion, which is greatly influenced by biological (target organisms or organs) and geochemical (physicochemical properties of the pollutants and the medium) factors (Wen et al., 2011). Then, due to their different physicochemical properties of PFASs and HFRs, the comparison of the bioaccumulation behavior would be of great interest.

In the present study, multi species soil systems (MS · 3) are used to assess the fate and the effects associated with the application of biosolids in agricultural soil on terrestrial soil organisms. MS · 3 is a terrestrial microcosm, an artificial assemblage of soil macro-organisms (microorganisms, invertebrates and plants) lying on homogeneous columns of sieved natural soil that allows to simulate agricultural land conditions (Fernández et al., 2004; Carbonell et al., 2009). In this system, a light/dark period and daily irrigation produces a gradient of conditions from the top to the bottom of the column. For this reason, the soil-air interface, water transport and degradation/sorption kinetics are reproduced in a better way than in standard soil bioassays.

The main objective of this work was to determine the transfer and bioaccumulation of selected emerging organic compounds as PFASs, PBDEs, decabromodiphenylethane, DBDPE, Dechloranes (602, 603, 604, and DP), Chlordane Plus (CP) and Mirex from biosolid-amended soil to earthworm (*Eisenia andrei*) using MS · 3 systems. To the best of our knowledge, this is the first time to compare the bioaccumulation behavior of PFASs and HFRs in earthworms (*Eisenia andrei*) exposed to biosolids-amended soils.

2. Materials and methods

2.1. Standards and reagents

Analysis of PFASs (perfluorobutanesulfonate -PFBS-, perfluorohexanesulfonate -PFHxS-, perfluorooctanesulfonate -PFOS-, perfluorodecanesulfonate -PFDS-, perfluorobutanoic acid -PFBA-, perfluoropentanoic acid -PFPeA-, perfluorohexanoic acid -PFHxA-, perfluoroheptanoic acid -PFHpA-, perfluorooctanoic acid -PFOA-, perfluorononanoic acid -PFNA-, perfluorodecanoic acid -PFDA-, perfluoroundecanoic acid -PFUdA-, perfluorododecanoic acid -PFDoA-, perfluorotridecanoic acid -PFTrDA-, perfluorotetradecanoic acid -PFTeDA-, perfluorohexadecanoic acid -PFHxDA-, perfluorooctadecanoic acid -PFODA-, perfluorooctanesulfonamide -FOSA-, N-methyl perfluorooctanesulfonamide -N-MeFOSA- and N-ethyl perfluorooctanesulfonamide -N-EtFOSA-), PBDEs (IUPAC congener numbers: BDE-17, −28, −47, −66, −77, −85, −99, −100, −119, −138, −153, −154, −156, −183, −184, −191, −196, −197, −206, −207, −209), DBDPE and DP were performed by isotopic dilution using labelled ^{13}C, ^{18}O or deuterated standard solutions: MPFAC-MXA, N-d3-MeFOSA, N-d5-EtFOSA, $^{13}C_9$-PFNA, MBDE-MXE and BDE-CVS-EISS were purchased from Wellington Laboratories Inc. (Guelph, Canada) and MDP from Cambridge Isotope Laboratories. Inc. (Andover, MA, USA). Dec 602 (CAS# 31107-44-5), Dec 603 (CAS# 13560-91-4) and Dec 604 (CAS# 34571-16-9) were obtained from Toronto Research Chemical Inc. (Toronto, ON, Canada).

EnviCarb cartridges (500 mg, 6 mL) were provided from Sigma-Aldrich (St. Louis, MO, USA) and Oasis WAX cartridges (500 mg, 6 mL) from Waters (Milford, MA, USA), both used for solid phase extraction (SPE).

Other chemicals used as anhydrous sodium sulphate, copper fine powder, sulphuric acid (95–97%) and solvents (hexane, dichloromethane, ethyl acetate and toluene) for organic trace analysis were obtained from Merck (Darmstadt, Germany). Ammonium acetate, ammonium hydroxide, sodium acetate, siliceous earth extrapure, acetic acid, methanol, acetonitrile were purchased from Scharlau (Barcelona, Spain).

2.2. Study design

Multi species soil systems (MS · 3) were used as rapid tests for assessing in biosolid-amended soil and exposed earthworms the presence of 49 emerging organic compounds: 20 PFASs (4 sulphonates -PFSAs-, 13 carboxilic acids -PFCAs- and 3 sulphonamides), PBDEs (21 congeners from tri to decaBDE), DBDPE, DP, Dec 602, Dec 603, Dec 604, CP and Mirex.

Firstly, a pollutant characterization was conducted in 16 biosolids: 4 municipal solid waste (MSW) compost and 12 wastewater treatment plant (WWTP) biosolids. Samples were collected during 2011 and were kindly provided by Spanish waste management companies and wastewater treatment plants. Then, only four biosolids, with a higher burden of facing contaminants, were selected for MS · 3 experiment: an aerobically digested municipal solid waste (MSW) compost (W-1), an anaerobically digested thermal drying sludge (W-2), an aerobically digested composted sewage sludge (W-3) and an anaerobically digested MSW compost (W-4).

MS · 3 systems consisted in PVC cylinders (20 cm internal diameter and 30 cm high) covered by a fine nylon mesh at the bottom to avoid soil loss and connected to a leachate collection device. A mixture (8 kg) of each biosolid selected and a control soil was used to fill the microcosm columns. Then, the columns were saturated with spring water and 30 plant seeds (*Triticum aestivum*, *Brassica rapa* and *Vicia sativa*), and 20 earthworms (*Eisenia andrei*) were introduced. During the exposure period (21 days) the MS · 3 columns were daily irrigated (100 mL/day) to simulate 1000 mm rainfall/year. The experiments were conducted in a climate room with a light – dark cycle of 16–8 h, air condition of 21 ± 1 °C, and humidity of 55–60%.

The soil used in this study was a typical agricultural soil with known history; pesticides and fertilizers had not been applied at least for the last 10 years. The soil sample was taken within the top 20 cm soil layer, sieved (2 mm mesh), and homogenized before use. Biosolid application rates (0.12–0.56 kg biosolid/treatment) were calculated by considering the nitrogen agronomic requirement of plants sowed. The four treatments and the control were performed in triplicate, although due to small sample size (especially for earthworms) chemical analyses were conducted with pooled samples.

After MS · 3 experiment, earthworms were allowed to depurate for 24 h to avoid the presence of soil particulates that could interfere with the bioaccumulation study.

2.3. Sample preparation

PFASs from biosolids and soils were extracted and purified according to the analytical procedure previously described (Navarro et al., 2011). Earthworms spiked with MPFAC-MXA, N-d3-MeFOSA and N-d5-EtFOSA solutions were extracted with acetonitrile, vortex-mixed, shaken for 10 min, ultrasonicated at 40 °C for 30 min and centrifuged for 15 min at 3000 rpm. The extraction process was repeated twice with fresh acetonitrile. Extracts were then combined and evaporated to 2 mL under nitrogen. Then, 100 μL of acetic acid was added before centrifugation for 5 min at 2000 rpm and passed through EnviCarb SPE cartridges. The purified extract was reduced to 140 μL under a gentle stream of nitrogen using TurboVap II evaporator (Vertex, Technics, Madrid, Spain). 240 μL of methanol and 240 μL of 2 mM ammonium acetate in Milli-Q water were added to the final extract spiked with $^{13}C_9$-PFNA solution prior to HPLC-MS/MS injection.

For HFR determination, samples were processed according to