Environmental Research 152 (2017) 199–206

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Uptake of perfluoroalkyl substances and halogenated flame retardants by crop plants grown in biosolids-amended soils

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ARTICLE INFO

Keywords:
Perfluoroalkyl substances
Polybrominated diphenyl ethers
Biosolid
Transfer factors
Earthworm

ABSTRACT

The bioaccumulation behavior of perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) was examined in three horticultural crops and earthworms. Two species, spinach (*Spinacia oleracea*) and tomato (*Solanum lycopersicum* L.), were grown in field soil amended with a single application of biosolids (at agronomic rate for nitrogen), to represent the scenario using commercial biosolids as fertilizer, and the third crop, corn (*Zea mays*) was grown in spiked soil (~50 mg PFOS/kg soil, ~5 mg Deca-BDE/kg soil and a mixture of both, ~50 mg PFOS and ~5 mg Deca-BDE/kg soil) to represent a worst-case scenario. To examine the bioaccumulation in soil invertebrates, earthworms (*Eisenia andrei*) were exposed to the spiked soil where corn had been grown. PFASs and HFRs were detected in the three crops and earthworms. To evaluate the distribution of the compounds in the different plant tissues, transfer factors (TFs) were calculated, with TF values higher for PFASs than PBDEs in all crop plants: from 2 to 9-fold in spinach, 2 to 34-fold in tomato and 11 to 309-fold in corn. Bioaccumulation factor (BAF) values in earthworms were also higher for PFASs (4.06 ± 2.23) than PBDEs (0.02 ± 0.02).

1. Introduction

Recycling biosolids on land is recognized internationally as the most sustainable option for managing the residual sludge from urban wastewater treatment (European Economic Community, 1986, 1991a). The substantial nitrogen, phosphorus and organic carbon contained in biosolids make the spreading of this waste material on land as a crop fertilizer or an organic soil amendment suitable. An estimated 40% of the sewage sludge produced in Europe is used as a fertilizer in agriculture (European Commission, 2010). However, the recycling rates of sludge to agriculture vary greatly among European Union (EU) Member States. For example, about 1,205,000 t (dry solid) of sludge were produced in Spain during 2010, and about 995,000 t (dry solid) were recycled to agriculture, equivalent to 82% of the sludge produced (Eurostat, 2015).

Degradation and attenuation during wastewater and sludge treatment remove significant amounts of organic pollutants (Clarke and Smith, 2011). However, many of those have lipophilic properties and may be present in sewage sludges in remaining concentrations. Particular attention concerning emerging organic contaminants such as perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) has been given due to their widespread distribution in the environment, toxicity, and potential for bioaccumulation (Braune et al., 2014; Wen et al., 2015). The presence of PFASs and HFRs as polybrominated diphenyl ethers (PBDEs) and their alternatives decabromodiphenyl ethane (DBDPE), declorane plus (DP) and related compounds, in waste material have been documented in some countries (De la Torre et al., 2011a; Navarro et al., 2011; Ricklund et al., 2009; Sun et al., 2011). However, there is still a lack of information regarding their behavior and occurrence in the environment, but in recent years the interest in these compounds has greatly increased. For example, PFASs and PBDEs, due to their presence in biosolids, were assessed as emerging organic contaminants of potential concern for land application (Clarke and Smith, 2011). In that study, PFASs were the first compounds identified for priority attention for presenting properties that make them theoretically possible to enter human food-chain from biosolids-amended soil. Organisms are liable to take up organic contaminants and may accumulate high levels of them when they live in contaminated soil environments. Once organic compounds are introduced to the environment, two of the primary concerns for human health are the capacity for contamination of water and food. The migration of chemicals from soil to plants could facilitate a

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http://dx.doi.org/10.1016/j.envres.2016.10.018
Received 7 June 2016; Received in revised form 4 October 2016; Accepted 19 October 2016

probable entry pathway into the food chain (Lechner and Knapp, 2011; Stahl et al., 2009, 2013; Felizeter et al., 2014). Plant uptake and distribution have been shown to be dependent on the physical-chemical properties of the chemicals, the soil and irrigation water characteristics, and the plant species and physiology, including properties such as lipid or water content and transpiration rates (Felizeter et al., 2012; Wen et al., 2013; Krippner et al., 2014; Wang et al., 2014). The study of the uptake of PFASs and HFRs by different crop plants grown in waste-amended soils provides a starting point for assessing the possible risks related to applications of biosolids to agricultural soils. Besides, organic contaminants can be taken up by organisms that live in direct contact with contaminated soil, such as soil invertebrates. The bioaccumulation of pollutants by these organisms implies a risk for earthworm population and many vertebrate species which feed on earthworms. Earthworms consume large amounts of soil and their thin cuticle is in almost constant contact with soil. If an organic contaminant is bioavailable and bioaccumulates in earthworms, it will enter the terrestrial food chain, as earthworms are eaten by many organisms from higher trophic levels. Therefore, earthworms have become common model organisms for testing toxicity and bioavailability of contaminants in soil, especially for organic compounds.

Few studies have been published detailing the behavior of organic pollutants in crops after application of contaminated sewage sludge to agricultural land. There are works describing the uptake of PFASs and PBDEs by plants in nutrient solution experiments (Felizeter et al., 2014; Krippner et al., 2014; Wang et al., 2011), from soil to plants (Stahl et al., 2009; Lechner and Knapp, 2011; Huang et al., 2011; Wang et al., 2014) from biosolids-amended soils (Yoo et al., 2011; Wen et al., 2014) and directly from undiluted biosolids (Vrkoslavová et al., 2010). These studies showed that plant accumulation of organic compounds could be dose-dependent and varied with plant species. Organofluorine compounds behave very differently to the organobromines and have unusual partitioning properties. The physical properties and molecular structures of the different compounds will likely have different effects on their accumulation in plants. Yet, although the land application of biosolids is regulated and a target value for the sum of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) of 100 μg/kg dry mass has been established in Germany for agriculturally used sewage sludge, no EU legislation is currently in place with respect to PFASs and HFRs in biosolids (Grümping et al., 2007). Consequently, continued vigilance is required to monitor and determine the significance and implications of emerging organic compounds in land-applied biosolids.

To address this need, the main objectives of this study were: (1) to determine the transfer, bioaccumulation and distribution of selected emerging organic compounds such as PFASs, PBDEs, Dechloranes (602, 603, 604, and DP), Chlordane Plus (CP) and Mirex from biosolids-amended soil to spinach (*Spinacia oleracea*) and tomato (*Solanum lycopersicum* L.) plant under agronomic conditions. (2) to study the uptake, bioaccumulation and distribution of PFOS and BDE-209 in corn (*Zea mays*) plants under a worst case scenario. (3) to determine pollutants bioaccumulation in earthworm *(Eisenia andrei)* from contaminated soil. To the best of our knowledge, this is the first study examining PFAS uptake in spinach, PBDEs in spinach and tomato and DP uptake in crops from biosolids-amended soils.

2. Materials and methods

2.1. Study design

Three sorts of plants were chosen: spinach (*Spinacia oleracea*), tomato (*Solanum lycopersicum* L.) and corn (*Zea mays*). In spinach and tomato transfer experiments, two different organic wastes were applied to soil: anaerobically digested thermal drying sludge (W1) and anaerobically digested municipal solid waste compost (W2). The physicochemical characteristics of the soil and the two biosolids used are detailed in Table S1. Waste application rates were calculated by considering the nitrogen requirement of plants and restrictions established in the Council Directive 91/676/EEC: spinach (120 kg N/ha) and tomato (150 kg N/ha) (European Economic Community, 1991b). To represent a worst-case scenario, soils fortified by the addition of PFOS (~50 mg/kg soil, T1), Deca-BDE (~5 mg/kg soil, T2), and a mixture of both commercial mixtures (~50 and ~5 mg/kg for PFOS and Deca-BDE, respectively, T3) were used to cultivate corn plants. The experiments were performed in a climate controlled room with a light:dark cycle (16:8 h), temperature (21 ± 1 °C), humidity (55–60%), and irrigation (100 mL/d≈1000 mm/year) controlled conditions. In the spinach and corn cases the growth period consisted of 28 days, while tomato plants were exposed to amended soils for six months (time needed to reach fruiting). A total of 72 pots were used, 24 pots for each crop test (spinach, tomato and corn). Eight replicates per treatment were used for spinach and tomato whereas six replicates were used for corn. Control pots (not amended/fortified soil) and fertilizer-free pots were also prepared. After the corn experiment, ten earthworms (*Eisenia andrei*) per treatment were added to soils and a 28 days exposure study was also performed. More details are given in Supplementary material.

2.2. Sample preparation

Waste and soil samples were air-dried and processed according to methods reported previously (De la Torre et al., 2011a, 2011b, 2012; Navarro et al., 2011). Earthworms were allowed to depurate for 24 h to avoid the presence of soil particulates that could interfere with the bioaccumulation study. Plant material and earthworms were frozen and freeze-dried at low temperature (~−50 °C) for 24 h in a lyophilizer (Cryodos-50, Telstar Instrument). PFASs from spinach, tomato, corn and earthworm samples were extracted with acetonitrile by agitation, ultrasonication and centrifugation techniques. EnviCarb SPE cartridges were used to purify the extracts. For HFR determination, plant material and earthworm samples were Soxhlet extracted with hexane/acetone (50:50, v/v) and hexane/dichloromethane (50:50, v/v), respectively. Purification was accomplished using a sulphuric acid digestion and a silica column. Fractionation step was then performed in an automated purification Power Prep™ System (FMS Inc., USA). Detailed information is given in Supplementary material.

2.3. Instrumental analysis

PFASs were determined by HPLC-MS/MS (Varian 212 Liquid Chromatograph coupled to a Varian 320 triple cuadrupole MS). The chromatographic separation was carried out in an ACE C18-PFP (50×2.1 mm, 3 μm) analytical column. PBDEs were analyzed by LRMS (Agilent 6890 Gas Chromatograph connected to an Agilent 5973 MSD) for wastes and soils but in the case of biotic samples (spinach, tomato, corn and earthworms) the sensitivity of the HRMS (Micromass Autospec Ultima) was needed. In both cases chromatographic separation was performed with short and narrow capillary column (15 m×0.25 mm i.d.×0.10 μm film thickness; DB5 MS from J & W Scientific, Folson CA). Dechlorane compounds were analyzed by ECNI-MS (Agilent 5973MSD) using methane as a reagent gas. Complete details of instrumental method are described elsewhere (De la Torre et al., 2011a, 2011b; Navarro et al., 2011), see Supplementary material.

2.4. Quality assurance

Procedural blanks were processed and analyzed with every batch of samples under the same conditions. In addition, instrumental blanks consisting of methanol or nonane were run before each sample injection to check for memory effects and contamination from the LC and GC system. In the case of PFASs determination, to avoid any

contamination, any contact with fluoropolymers was prevented at all times and polytetrafluoroethylene material was avoided during sample treatment and analysis. Mean recoveries (mean ± SD) were: 76 ± 28% (PFASs), 84 ± 21% (PBDEs) and 103 ± 6% (DP). Limits of detection (LODs), defined as the concentration giving a signal to noise ratio greater than 3 were in the range of 0.01–0.90 ng/g for PFASs, 2.1–7.9 pg/g for PBDEs, 0.1 pg/g for DBDPE and 0.1–1.2 pg/g for dechlorane related compounds (Table S2).

2.5. Calculations and statistical evaluation

Transfer factors (TFs) were used to evaluate the compound-specific uptake by plants. Accumulation or transfer factors are commonly used to assess the bioavailability and bioconcentration of chemicals from media such as water, soil or sediments (Yoo et al., 2011; Felizeter et al., 2014). The knowledge of these factors could help to deduce the potential toxicological risk related to vegetables grown in soils with pollutant content. TFs were calculated by division of the amount found in the plant tissue on a dry weight basis (ng/g d.w.) by the concentration determined in the soil on a dry weight basis (ng/g d.w.). Transfer factors between plant parts were also calculated for each compound to evaluate their translocation within the tomato plant: root to leaf concentration factors (LCF; ratio between the concentration found in leaf, ng/g d.w., and the concentration detected in root, ng/g d.w.) and leaf to fruit or edible part concentration factors (ECF; ratio between the amount found in fruit, ng/g d.w., and the concentration determined in leaf, ng/g d.w.). The translocation of the compounds to the fruit was evaluated by the ratio between leaf to fruit concentrations instead of stem to fruit concentrations, because the material for the fruit development is provided by the phloem sap, which is produced in the leaves (Felizeter et al., 2014). Therefore, it is to be expected that compounds reach the fruits primarily via phloem sap and their transfer to the fruit could be assess by their ECF value.

Bioaccumulation factors (BAF) in earthworms were calculated by division of the amount found in earthworms (ng/g d.w.) by concentrations determined in soil (ng/g d.w.; soil t=final).

Statistical analyses were conducted with the software SPSS 23.0 for Windows. Data were tested for normal distribution using the Kolmogorov-Smirnov and Shapiro-Wilk tests. Student's *t*-tests were also performed to evaluate differences between compound groups. Statements regarding differences in this study are based on a significance level of $p < 0.05$. Linear regressions were established to detect correlations and checked by Spearman test.

3. Results and discussion

3.1. Uptake of PFASs, PBDEs and DP by spinach plant

Concentrations in wastes, soils (at initial time and the end of the experiment) and spinach plants are detailed in Table 1. Total concentrations in the anaerobically digested thermal drying sludge (W1) – 105.43 ng/g d.w. (PFASs), 333.33 ng/g d.w. (PBDEs), 14.57 ng/g d.w. (DP) – were higher than those detected in the anaerobically digested municipal solid waste compost (W2) – 17.54 ng/g d.w. (PFASs), 167.98 ng/g d.w. (PBDEs), 5.45 ng/g d.w. (DP) –. Total concentrations in amended soils were also higher in the treatment-1 (T1) than treatment-2 (T2) for PFASs (6.24–0.94 ng/g d.w., T1-T2), but similar for PBDEs (10.57–9.78 ng/g d.w., T1-T2) and DP (0.11–0.14 ng/g d.w., T1-T2). PFASs, PBDEs and DP were detected in spinach plants growing in the waste-amended soils. Total concentrations for PFASs in spinach were 1.72 ng/g d.w., 5.33 ng/g d.w. and 0.99 ng/g d.w. for control, T1 and T2, respectively. Lower values were detected for PBDEs: 0.27 ng/g d.w., 0.48 ng/g d.w. and 0.43 ng/g d.w. for the different treatments, respectively. In the case of DP, total concentrations were 2.27 ng/g d.w., 2.40 ng/g d.w. and 2.21 ng/g d.w., respectively. The fraction of *syn*-DP (f_{syn}) was defined as the concentration of *syn*-DP divided by the total DP. f_{syn} value in soil (0.34 ± 0.04; mean ± SD) closely resembles the one reported for OxyChem's technical DP mixture (f_{syn}=0.35) (Tomy et al., 2007). Nevertheless, this value decreases to 0.14 ± 0.03 in the spinach plant. This result could be attributed to the isomer-specific uptake of DP from the soil by the plants or the difference in physicochemical properties of *anti*- and *syn*-DP (Sverko et al., 2008).

Percentage distributions of the PFASs, PBDE congeners and DP found in the spinach plants in the different treatments are shown in Fig. S1 and Table S3. PFOS (29.1 ± 10.5%; mean ± SD) and *anti*-DP (41.1 ± 13.4%; mean ± SD) were present in higher proportions than the rest of the compounds. To further demonstrate compound-specific uptake by plants, transfer factors (TFs) were calculated and compared between compounds (Table S4). The obtained PFOS TF was 4.76 ± 1.12, mean ± SD. This value correlates well with other PFOS TFs reported in the literature for potato vegetative compartments (3.85) and carrot foliage (2.94) (Lechner and Knapp, 2011). As mentioned before, important differences were found for DP isomers, where the calculated TF for *anti*-DP (21.3 ± 6.23) was higher than the one obtained for *syn*-DP (6.28 ± 1.06). Values for PBDEs ranged from 0.23 to 2.68. Only BDE-47 and BDE-17 showed TF values higher than 1 (1.59 ± 0.55 and 2.68 ± 0.56, respectively). These results provide evidence that PFOS and DP (mainly *anti*-DP) are more liable to be taken up by spinach plants.

For nonionic organic chemicals the degree of uptake via plant roots seems to be inversely related to their hydrophobicity, which is often described by the octanol-water partition coefficient (K_{ow}) (McKone and Maddalena, 2007). Significant linear correlation (n=16, R^2=−0.799, $p < 0.01$, Spearman test) between transfer factor of the different treatments and log K_{ow} for PBDEs was found (Fig. S2). The TF value gradually declined with increasing log K_{ow} value. The higher brominated PBDEs with higher partition coefficients showed a more difficult soil-to-plant translocation.

3.2. Uptake and distribution of compounds in tomato plants

Concentrations in soils (at initial time and the end of the experiment) and different compartments of tomato plants are shown in Table 2 and Table S7. Mean concentrations for total PFASs, PBDEs, DBDPE and DP in soils after biosolid application were: 7.82–0.88 ng/g d.w., 10.5–11 ng/g d.w., 6.35–26.5 ng/g d.w. and 0.24–0.18 ng/g d.w. (T1-T2), respectively. As mentioned before, waste application rates were calculated considering nitrogen plant requirements (European Economic Community, 1991b), which at the end resulted in a relatively low pollutant content in the amended soils. However, levels of PFASs, PBDEs, DBDPE and DP were detected in different parts of this crop: indicating that the plant has the ability not only to take up these compounds from soils by roots, but also to translocate these compounds to the above-ground parts. Total concentrations for PFASs in tomato fruit were 61.3 ± 8.04 ng/g d.w. and 3.47 ± 1.55 ng/g d.w. (mean ± SD) for T1 and T2, respectively. In the case of PBDEs, lower levels were detected: 10.77 ± 6.61 ng/g d.w. and 11.27 ± 0.89 ng/g d.w. for the two treatments, respectively. DP total concentrations were: 0.15 ± 0.16 ng/g d.w. and 0.09 ± 0.03 ng/g d.w. (T1 and T2). Similar to spinach soil, the mean f_{syn} value in tomato soil was 0.31 ± 0.03, (mean ± S.D.), close to the OxyChem's technical DP mixture. As described in the spinach experiments, an isomer-specific uptake of DP from the soil by the tomato plants could have happened (f_{syn} values in tomato plant were: 0.15 ± 0.05 (root), 0.15 ± 0.09 (stem), 0.15 ± 0.03 (leaf) and 0.11 ± 0.02 (fruit); mean ± SD).

For characterization of the uptake and distribution of compounds in tomato plants, transfer factors within the plant were calculated. The mass distribution of the compounds in different plant tissues (Fig. 1) shows that PFOS (75%) and the long-chain perfluorinated carboxylic acids, PFCAs, (C7–C10: PFHpA, PFOA, PFNA, PFDA) (54–96%) preferentially remained in roots and the short-chain PFCAs (C4–C6:

Table 1
Concentrations of PFASs and HFRs (ng/g d.w.) in wastes, soils and spinach plants.

	Control				Treatment-1				Treatment-2			
	$Soil_{t=0}$	$Soil_{t=final}$	Seedbed spinach	Spinach	Waste	$Soil_{t=0}$	$Soil_{t=final}$	Spinach	Waste	$Soil_{t=0}$	$Soil_{t=final}$	Spinach
PFBS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.20	N.D.	2.05	N.D.	N.D.	N.D.
PFOS	0.29	0.29	N.D.	1.72	28.20	0.35	0.50	1.62	0.65	0.22	0.23	0.99
PFBA	0.40	0.03	N.D.	N.D.	34.25	0.45	0.90	N.D.	5.74	0.43	0.12	N.D.
PFPeA	0.14	N.D.	N.D.	N.D.	2.11	0.12	2.40	1.34	2.29	N.D.	0.10	N.D.
PFHxA	N.D.	N.D.	N.D.	N.D.	4.77	0.15	2.12	N.D.	1.78	N.D.	0.13	N.D.
PFHpA	N.D.	N.D.	N.D.	N.D.	0.85	N.D.	0.34	N.D.	0.80	N.D.	N.D.	N.D.
PFOA	0.20	0.13	N.D.	N.D.	8.90	0.19	2.73	2.37	2.52	0.18	0.23	N.D.
PFNA	N.D.	N.D.	N.D.	N.D.	2.58	N.D.	0.18	N.D.	0.73	N.D.	N.D.	N.D.
PFDA	0.14	0.07	N.D.	N.D.	19.0	0.18	1.34	N.D.	0.64	0.13	0.11	N.D.
PFUdA	N.D.	N.D.	N.D.	N.D.	2.57	N.D.	0.10	N.D.	0.17	N.D.	N.D.	N.D.
PFDoA	N.D.	N.D.	N.D.	N.D.	2.20	N.D.	0.23	N.D.	0.17	N.D.	N.D.	N.D.
Σ PFASs	1.17	0.52	N.D.	1.72	105.43	1.44	11.04	5.33	17.54	0.96	0.92	0.99
BDE-17	0.01	0.01	N.D.	N.D.	0.09	0.01	0.01	0.01	0.05	0.01	0.01	0.01
BDE-28	0.01	N.D.	N.D.	N.D.	0.22	N.D.	0.01	0.01	0.30	N.D.	0.01	N.D.
BDE-47	0.11	0.06	N.D.	0.14	7.19	0.09	0.15	0.21	3.44	0.11	0.15	0.13
BDE-66	0.01	N.D.	N.D.	N.D.	0.24	0.01	N.D.	N.D.	0.28	0.01	N.D.	N.D.
BDE-85	N.D.	N.D.	N.D.	N.D.	0.42	0.01	0.01	N.D.	0.29	0.01	0.01	N.D.
BDE-99	0.26	0.17	N.D.	0.06	12.42	0.23	0.31	0.10	7.87	0.27	0.31	0.27
BDE-100	0.06	0.04	N.D.	0.01	2.36	0.05	0.06	0.02	1.36	0.06	0.06	N.D.
BDE-138	N.D.	N.D.	N.D.	N.D.	0.10	0.01	N.D.	N.D.	0.18	N.D.	N.D.	N.D.
BDE-153	0.12	0.09	N.D.	0.05	1.55	0.11	0.12	0.04	1.61	0.13	0.12	0.01
BDE-154	0.09	0.08	N.D.	N.D.	1.01	0.07	0.08	0.02	0.73	0.08	0.08	0.02
BDE-183	0.17	0.15	N.D.	N.D.	1.91	0.18	0.22	0.07	3.29	0.23	0.22	N.D.
BDE-184	0.02	0.03	N.D.	N.D.	N.D.	0.02	0.03	N.D.	0.06	0.03	0.03	N.D.
BDE-191	0.03	0.05	N.D.	N.D.	N.D.	0.04	0.03	N.D.	0.21	0.04	0.03	N.D.
BDE-196	0.29	0.26	N.D.	N.D.	1.96	0.26	0.31	N.D.	1.75	0.33	0.31	N.D.
BDE-197	0.21	0.47	N.D.	N.D.	0.90	0.22	0.56	N.D.	2.18	0.26	0.56	N.D.
BDE-206	0.37	0.45	N.D.	N.D.	14.78	0.35	0.43	N.D.	5.79	0.71	0.43	N.D.
BDE-207	0.40	0.47	N.D.	N.D.	10.38	0.49	0.60	N.D.	8.60	0.80	0.60	N.D.
BDE-209	8.63	8.07	N.D.	N.D.	277.8	10.44	5.63	N.D.	129.99	7.92	5.63	N.D.
Σ PBDEs	10.81	10.41	N.D.	0.27	333.33	12.59	8.56	0.48	167.98	11.00	8.56	0.43
DBDPE	N.D.	N.D.	N.D.	N.D.	125.83	1.39	0.88	N.D.	149.46	0.58	0.88	N.D.
***anti*-DP**	0.04	0.19	N.D.	1.91	10.68	0.10	0.05	2.15	4.1	0.15	0.05	1.90
***syn*-DP**	0.03	0.11	N.D.	0.36	3.89	0.04	0.03	0.25	1.35	0.06	0.03	0.32
Σ DP	0.07	0.31	N.D.	2.27	14.57	0.14	0.08	2.40	5.45	0.20	0.08	2.21
f_{syn}	0.42	0.37	–	0.16	0.27	0.28	0.36	0.10	0.25	0.29	0.36	0.14
Dec 604	0.18	0.21	N.D.	N.D.	N.D.	N.D.	0.27	N.D.	N.D.	N.D.	0.27	N.D.

N.D.: not detected.
PFHxS, PFDS, PFTrDA, PFTeDA, PFHxDA, PFODA, FOSA, N-MeFOSA, N-EtFOSA, BDE-77, -119, -156, Dec 602, Dec 603, CP and Mirex were not detected in any sample.

PFBA, PFPeA, PFHxA tended to be translocated to above-ground tissues (leaf: 31–56%, and fruit: 32–48%). This predominant accumulation of long-chain PFASs in the roots and shorter-chain compounds in the vegetative compartments has also been detected in other studies conducted in tomato, zucchini and cabbage (Felizeter et al., 2014), corn (Krippner et al., 2014), wheat (Wen et al., 2014) and lettuce (Felizeter et al., 2012). Similar to the short-chain PFCAs, DBDPE (96%) and DP (65%) show higher preference for above-ground parts.

Transfer factors are detailed in Table S9. In general, TF values in tomato plants were higher for PFASs than HFRs. TF mean values for the root, stem, leaf and fruit were: 3.44–5.48–22.2–12.6 for PFASs, 2.50–0.16–0.89–1.76 for PBDEs and 1.44–0.38–0.48–0.59 for DP. TFs in roots showed values >1, indicating that the uptake and accumulation in roots by the plant are effective. Besides, most of the compounds, except PFBA, PFPeA and PFHxA, show TF values in roots higher than in above-ground plant parts (Fig. S3). This could indicate that the transport of these three substances from the roots to aerial plant parts is more efficacious (Felizeter et al., 2012; Blaine et al., 2013; Krippner et al., 2014). TF values for PFASs calculated in fruit ranged from 0.06 to 51.5. The highest values were obtained for PFBA and PFPeA. This result is in agreement with that reported by Blaine et al. (2013) in the same species.

Transfer factors between plant parts (LCF and ECF) were also calculated for each compound to evaluate their translocation and distribution within the tomato plant (Table S10). PFPeA, PFHxA, PFOA and DBDPE exhibited mean LCF values >1 and PFPeA, BDE-17, BDE-28, BDE-47, BDE-154, BDE-206, BDE-207, BDE-209 and *anti*-DP showed mean ECF values >1. These values could indicate a higher translocation of these compounds from other plant parts to leaves or fruits. To compare with the literature data, PFAS ECFs on fresh weight basis were calculated: the mean ECF was 0.01 for PFOS, 0.02 for PFBA, 0.09 for PFPeA and 0.04 for PFHxA. Felizeter et al. (2014) reported ECF values for PFASs in tomato: 0.03 for PFOS, 0.14 for PFBA, 0.48 for PFPeA and 0.46 for PFHxA. Although ECF values in our study were lower, ECF for PFOS was very similar. The highest ECF value obtained by Felizeter et al. was reported for PFPeA, which is also consistent with our results, indicating a higher uptake and translocation for this compound. To the best of our knowledge, no other studies have measured the uptake of HFRs in tomato.

Taking into account that K_{ow} could be considered as the main physicochemical property related to the uptake and bioaccumulation of these compounds by plants (McKone and Maddalena, 2007), the relationship between the translocation of the compounds in the plant (TF) and their hydrophobicity were examined (Fig. S4). In general, inverse relationships between transfer factors and log K_{ow} were observed. Significant correlations between TF and log K_{ow} were found

Table 2
Concentrations of ΣPFASs, ΣPBDEs and ΣDP (ng/g d.w.) in wastes, soils and tomato plants.

	Waste	$Soil_{t=0}$	$Soil_{t=final}$	Root	Stem	Leaf	Fruit
Σ PFASs							
Fertilizer-free plant	–	0.43	–	N.A.	1.78	35.97	0.03
Control	–	0.58 ± 0.19	0.40 ± 0.02	1.67 ± 0.36	0.06 ± 0.86	0.64 ± 0.19	2.74 ± 2.23
Treatment-1	105.43 ± 8.34	7.82 ± 1.60	9.17 ± 0.90	26.75 ± 15.88	26.84 ± 4.17	96.50 ± 41.35	61.30 ± 8.04
Treatment-2	17.54 ± 1.11	0.88 ± 0.02	0.92 ± 0.21	0.83 ± 0.55	0.89 ± 0.85	1.10 ± 0.24	3.47 ± 1.55
Σ PBDEs							
Fertilizer-free plant	–	3.89	–	N.A.	0.01	0.07	N.A.
Control	–	5.38 ± 1.01	12.95 ± 1.38	4.26 ± 1.00	0.003 ± 0.001	5.56 ± 4.22	0.55 ± 0.17
Treatment-1	333.33 ± 21.22	10.47 ± 0.62	8.99 ± 2.44	0.92 ± 0.85	0.002 ± 0.001	11.57 ± 12.03	10.77 ± 6.61
Treatment-2	167.98 ± 9.37	10.88 ± 0.93	10.49 ± 0.65	0.88 ± 0.81	0.01 ± 0.01	3.28 ± 2.87	11.27 ± 0.89
Σ DP							
Fertilizer-free plant	–	N.D.	–	N.A.	N.D.	N.D.	N.A.
Control	–	0.13 ± 0.01	0.08 ± 0.01	0.28 ± 0.09	0.06 ± 0.01	0.07 ± 0.03	0.07 ± 0.04
Treatment-1	14.57 ± 1.43	0.24 ± 0.02	0.16 ± 0.03	0.23 ± 0.22	0.04 ± 0.01	0.08 ± 0.03	0.15 ± 0.16
Treatment-2	5.45 ± 0.14	0.18 ± 0.03	0.24 ± 0.05	0.05 ± 0.09	0.03 ± 0.01	0.12 ± 0.01	0.09 ± 0.03
f_{syn}							
Fertilizer-free plant	–	–	–	N.A.	–	–	N.A.
Control	–	0.26 ± 0.02	0.32 ± 0.02	0.10 ± 0.08	0.25 ± 0.16	0.04 ± 0.03	0.09 ± 0.06
Treatment-1	0.27 ± 0.02	0.29 ± 0.03	0.25 ± 0.06	0.12 ± 0.01	0.20 ± 0.01	0.19 ± 0.08	0.09 ± 0.09
Treatment-2	0.25 ± 0.01	0.33 ± 0.01	0.36 ± 0.08	0.23 ± 0.01	–	0.22 ± 0.07	0.16 ± 0.05

Mean ± SD (n=3); N.D.: not detected; N.A.: not available.
ΣPFASs: sum of PFBS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA and PFDoA. ΣPBDEs: sum of BDE-17, -28, -47, -66, -99, -100, -153, -154, -183, -184, -191, -196, -197, -206, -207 and -209. ΣDP: sum of anti-DP and syn-DP. Concentrations of individual compounds are detailed in Supplementary material.

for PFASs in stem (N=28, R^2=−0.837, $p < 0.01$, Spearman test), leaf (N=26, R^2=−0.682, $p < 0.01$) and fruit (N=30, R^2=−0.929, $p < 0.01$), and for PBDEs in root (N=58, R^2=−0.910, $p < 0.01$) and stem (N=14, R^2=−0.802, $p < 0.01$). The results suggest that more hydrophobic compounds preferentially remained in roots and less hydrophobic compounds tended to be translocated from roots to above-ground tissues.

3.3. Uptake and distribution of compounds in corn

Concentrations of PFOS and BDE-209 in corn plants cultivated in spiked soils: T1 (~50 mg PFOS/kg soil), T2 (~5 mg Deca-BDE/kg soil), and T3 (~50+~5 mg/kg for PFOS and Deca-BDE) are detailed in Table 3 and Table S11. High levels for PFBS, PFHxS, BDE-207 and BDE-206 were also detected. The presence of nonabrominated diphenyl ethers in Deca-BDE commercial mixtures has been well documented: 2% and 3% for BDE 207 and 206, respectively (La Guardia et al., 2006). The composition of BDE 207 and 206 in the soils was 2% and 2% for BDE 207 and 206, respectively, at the beginning of the experiment and 2% and 3% at the end of the experiment. This congener composition resembles that of the Deca-BDE formulation. These results also highlight that BDE-209 degradation is low under the experiment conditions. Presence of PFBS and PFHxS in PFOS technical mixture has been documented as sum of both compounds, approximately 1.5%, (Stahl et al., 2013). PFBS and PFHxS contribution to the total PFASs content in soils did not varied greatly from the beginning to

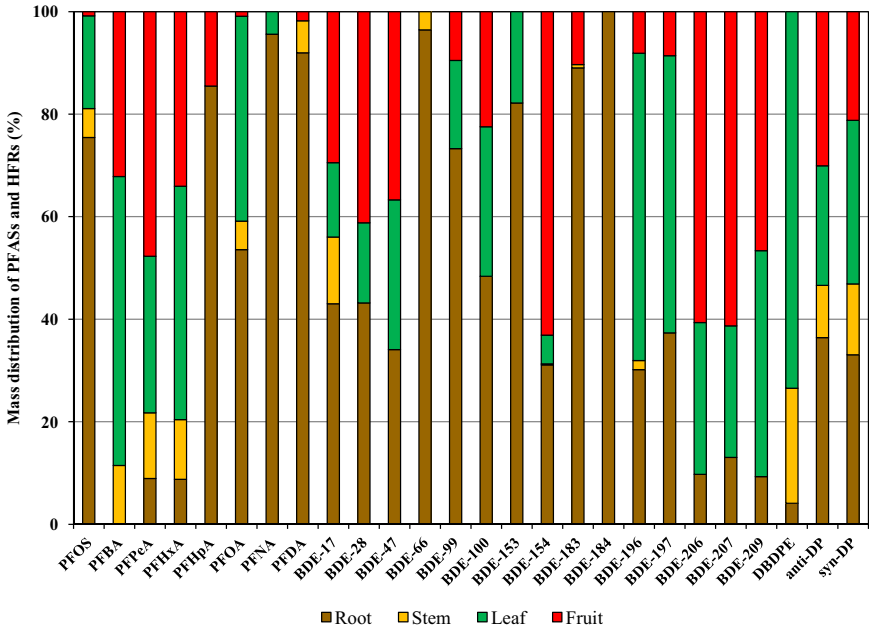

Fig. 1. Mass distribution (percentage of the total amount taken up by the plants) of PFASs and HFRs in different tissues of tomato plants.

Table 3
Concentrations of PFASs and PBDEs (μg/g d.w.) in spiked soils, corn plants and earthworms. Accumulation factors in corn and earthworms.

	$Soil_{t=0}$	$Soil_{t=final}$	Root	Leaf	Earthworm	TF_{Root}	TF_{Leaf}	$BAF_{Earthworm}$
Treatment-1 (PFOS)								
PFBS	0.02 ± 0.01	0.04 ± 0.01	0.15 ± 0.05	0.12 ± 0.03	0.11	5.00 ± 1.03	4.00 ± 1.21	2.75
PFHxS	0.76 ± 0.16	0.94 ± 0.27	2.23 ± 0.24	7.98 ± 0.99	3.18	2.62 ± 0.28	9.39 ± 1.17	3.38
PFOS	38.5 ± 7.24	19.1 ± 8.49	254 ± 72.3	23.1 ± 6.13	74.3	8.82 ± 2.51	0.80 ± 0.21	3.89
Treatment-2 (Deca-BDE)								
BDE-206	0.07 ± 0.01	0.09 ± 0.01	0.03 ± 0.01	0.001 ± 0.001	0.001	0.38 ± 0.08	0.01 ± 0.01	0.01
BDE-207	0.05 ± 0.01	0.07 ± 0.02	0.03 ± 0.01	0.002 ± 0.001	0.002	0.50 ± 0.08	0.03 ± 0.01	0.03
BDE-209	3.76 ± 0.53	3.31 ± 0.41	1.12 ± 0.14	0.04 ± 0.01	0.021	0.32 ± 0.04	0.01 ± 0.01	0.01
Treatment-3 (PFOS+Deca-BDE)								
PFBS	N.D	0.03 ± 0.02	N.D.	0.98 ± 0.42	0.07	–	–	2.33
PFHxS	0.53 ± 0.17	0.83 ± 0.20	1.28 ± 0.39	8.29 ± 2.86	2.93	1.88 ± 0.57	12.19 ± 4.21	3.53
PFOS	37.9 ± 5.34	13.9 ± 3.95	133 ± 52.6	24.8 ± 7.37	84.7	5.14 ± 2.03	0.96 ± 0.28	6.09
BDE 206	0.07 ± 0.02	0.05 ± 0.04	0.03 ± 0.01	0.001 ± 0.001	0.002	0.50 ± 0.20	0.02 ± 0.01	0.04
BDE 207	0.05 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.001 ± 0.001	0.002	0.67 ± 0.27	0.02 ± 0.01	0.05
BDE 209	2.19 ± 0.40	1.61 ± 0.61	0.47 ± 0.07	0.01 ± 0.01	0.03	0.25 ± 0.04	0.01 ± 0.01	0.02

Mean ± SD (n=3); N.D.=not detected. Treatment-1:~50 mg PFOS/kg soil, Treatment-2: ~5 mg Deca-BDE/kg soil and Treatment 3: ~50+~5 mg/kg PFOS and Deca-BDE.
TF_{Root}: Ratio between concentration in root and soil (mean soil t=0 and t=final). TF_{Leaf}: Ratio between concentration in leaf and soil (mean soil t=0 and t=final).
$BAF_{Earthworm}$: Ratio between concentration in earthworm and soil (soil t=final).

the end of the experiment (< 1% in both cases for PFBS and from 2% to 5% for PFHxS). Then, PFOS degradation to PFBS and PFHxS was considered negligible.

Reduction rates of the PFOS and BDE-209 in the soils (comparing the concentrations in the soils before and after planting) ranged from 48% to 64% and 12% to 26%, respectively. The reduction of the latter corresponds well with values previously published for higher brominated PBDEs in contaminated soils in which corn plants were planted (from 13% to 18%) (Huang et al., 2011). The dissipation of PFOS and BDE-209 in the soils can be caused by several factors as degradation, volatilization and plant uptake. As in the spinach and tomato cases, corn experiments were conducted in closed enclosures (no wind) and under regulated temperature (21 ± 1 °C) and humidity (55 ± 5%) conditions. Considering this, influence of volatilization could be assumed low. Planting processes have been described as potential contributors to the pollutants dissipation in soils due to the microbial metabolism and bioestimulation of microbial communities (Huang et al., 2011). Accumulation of PFOS and BDE-209 in leaves may result from a combination of uptake through the soil-to-plant pathway and foliar uptake from the air. Leaf concentrations of plants growing in nonspiked soils were about 0.001 μg/g for PFOS and BDE-209, accounting for less than 1% and 8% of the concentrations in the plants growing in spiked soils, respectively. This implies that there was no appreciable contribution from foliar uptake to leaf accumulation of PFOS and BDE-209 for this experiment.

The mass distribution of PFASs and PBDEs (percentage to total plant content) in different plant tissues was calculated to evaluate the translocation in the plant. Most of compounds presented a higher accumulation in roots: PFOS (89%), BDE-206 (97%), -207 (97%) and -209 (97%). However, PFBS (88%) and PFHxS (82%) were preferentially found in leaves. Transfer factors within corn plant were calculated for characterizing the distribution of compounds in the plants (see Table 3). TF mean values in roots considering all treatments ranked as follows: 6.98 (PFOS), 5.00 (PFBS), 2.25 (PFHxS), 0.58 (BDE-207), 0.44 (BDE-206) and 0.28 (BDE-209). TF mean values in leaves were: 10.79 (PFHxS), 4.00 (PFBS), 0.88 (PFOS), 0.03 (BDE-207), 0.01 (BDE-206) and 0.01 (BDE-209). TF values were also calculated based on the concentration of the compounds in spiked soils at the beginning and the end of the experiment (28 days). The TFs in roots of PFBS and PFHxS decreased 55% and 27% respectively, suggesting that the bioavailability of these pollutants in soil decreased as the time of their residence increased. Nevertheless, the effect of the aging time on the bioavailability of PFOS, BDE-206, BDE-207 and BDE-209 was not observed.

TF values were higher for PFASs than PBDEs, these results indicate a higher translocation and bioaccumulation for PFOS from soil to the plant. In general, small and more apolar molecules can be dissolved in the lipid phase of the cell membrane and pass through it more easily. Several properties are decisive so as to a molecule could diffuse through a membrane: polarity, molecular size, functional groups and the position of the functional groups within the molecule (Krippner et al., 2014). Organic compounds could be taken up via passive (i.e apoplastic) process, which involves simple and facilitated diffusion, and/or active (i.e. symplastic) process, depending on the properties, the concentration of the compounds and the plant species (Zhan et al., 2010). The mechanism of PFOS and PFOA uptake by corn was examined by Wen et al. (2013). According to that, uptake of PFOS is carrier-mediated passive process, which may be conducted via aquaporins and anion channel in root cell membranes. They demonstrated that corn absorption of PFOS and PFOA may follow different pathways. PFOS and PFOA are PFASs, with similar perfluoroalkyl tail of varying chain length and different polar head group (sulfonate for PFOS and carboxylate for PFOA). Nevertheless, PBDE chemical structure is based on two aromatic rings where hydrogen atoms have been substituted by bromine atoms in different position. Due to their different chemical structures, properties and transfer factors obtained, it might be expected that PFOS and BDE-209 did not share a common uptake transport mechanism by the corn roots, but further studies should be conducted to clarify that.

3.4. Bioaccumulation in earthworms

Bioaccumulation in earthworm is detailed in the Table 3. High levels were also found in earthworms: PFBS (0.09 ± 0.03 μg/g d.w., mean ± SD), PFHxS (3.06 ± 0.18 μg/g d.w.), PFOS (79.50 ± 7.35 μg/g d.w.), BDE-206 (0.002 ± 0.001 μg/g d.w.), BDE-207 (0.002 μg/g d.w.) and BDE-209 (0.03 ± 0.01 μg/g d.w.). Mean BAFs ranked as follows: 4.99 (PFOS), 3.46 (PFHxS), 2.54 (PFBS), 0.04 (BDE-207), 0.03 (BDE-206), and 0.01 (BDE-209). A calculation for the PBDE BAF on lipid weight basis for comparison with the literature data shows that the mean accumulation factors for earthworm were 0.43 (BDE-207), 0.26 (BDE-206), and 0.12 (BDE-209). These values are in accordance with data previously reported for earthworms: 1.54–4.12 (Wen et al., 2015) and 2.94–4.19 (Zhao et al., 2014) for PFOS and 0.07 (Gaylor et al., 2014) and 0.30 (Sellström et al., 2005) for BDE-209. Similar to PFAS behavior in corn plant, BAF values for PFASs are higher than those for

PBDEs, indicating a higher uptake and bioacummulation for PFASs by earthworm.

The effect of the aging (28 days) on the bioavailability of the pollutants to earthworms in the spiked soils was also assessed. Similar to TFs calculated on soil basis at the beginning and the end of the experiment, the BAFs of PFBS and PFHxS declined 71% and 28% respectively. No evidences of the aging effect on the bioavailability of PFOS and the rest of PBDEs to earthworms were detected. Previously, the effect of aging (21 days) on the bioavailability of PFOS and BDE-209 to earthworms in biosolid amended soils was studied (Navarro et al., 2016). No significant differences on the bioavailability of PFOS, BDE-207 and BDE-209 were observed, which is consistent with that computed here.

4. Conclusions

Altogether 49 target emerging compounds, 29 HFRs and 20 PFASs, were determined to study the behavior and distribution in the soil-plant and soil-biota systems. To the best of our knowledge, this study is the first to look at PFAS uptake in spinach, PBDEs in spinach and tomato and DP uptake in crops from biosolids-amended soils, following recommended agronomic application rates. This study has demonstrated that the contamination of the soil with the emerging compounds studied, as a result of the biosolid application or pollution accident (worst case scenario), could be transferred to the plants via the roots into different plant tissues and to invertebrates in direct contact with the polluted soil. Transfer and bioaccumulation factors were higher for PFASs than PBDEs in all crop plants and earthworms, indicating a higher and more efficacious uptake, transport from the roots to aerial plant parts and bioaccumulation for the former. Regarding the translocation behavior of PFASs, a predominant accumulation of long-chain compounds in the roots and shorter-chain ones in the aerial plant organs was detected. The difference in uptake patterns of the crop assessed (spinach, tomato and corn) suggests that the type of crop and consequently, their vegetative structure, could have a significant importance in PFASs and HFRs transport through the tissues of the plant and bioaccumulation.

Further monitoring of these compounds is very important due to their bioaccumulation in different environmental compartments, including food chains, which could result in potential risks and organism exposure.

Acknowledgements

The present work has been funded by the Spanish Ministry of Economy and Competitiveness (Project numbers CTM2010-19779-C02-01 and CTM2010-19779-C02-02).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envres.2016.10.018.

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