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Environmental risk assessment of perfluoroalkyl substances and halogenated flame retardants released from biosolids-amended soils

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HIGHLIGHTS

- The ecotoxicological risk of PFASs and HFRs due to biosolid amendment was studied.
- PECs for soil and aquatic compartments and for secondary poisoning were estimated.
- RCR_{soil}, $RCR_{oral,\ worm}$, RCR_{water}, RCR_{sed} and $RCR_{oral,\ fish}$ were <1 (negligible risk).
- HRs based on the consumption of tomato were <1 (negligible risk to human health).

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ABSTRACT

Biosolid application is considered a sustainable management tool as it positively contributes to recycle nutrients and to improve soil properties and fertility. Nevertheless, this waste management technique involves an important input source of emerging organic pollutants in soil. To evaluate the environmental potential risk related to perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) due to the biosolid application to soil, a quantitative ecotoxicological risk assessment was conducted. The analyte concentrations were employed to perform an estimation of the exposure levels to contaminants in the receiving media, defining predicted environmental concentrations (PECs) for terrestrial and aquatic compartments (PEC_{soil}, PEC_{water}, PEC_{sed}) and for secondary poisoning via the terrestrial and aquatic food chain ($PEC_{oral,\ predator\ (T)}$, $PEC_{oral,\ predator\ (Aq)}$). The risk characterization ratios (RCRs) were calculated based in the comparison of the PEC values obtained with concentrations with no effect (PNECs) on terrestrial and aquatic ecosystems. Based on the chosen scenarios and experimental conditions, no environmental risk of PFASs and HFRs released from biosolid amended soils to different environmental compartments was detected (RCR_{soil}, $RCR_{oral,\ worm}$, RCR_{water}, RCR_{sed} and $RCR_{oral,\ fish}$ were below 1 in all cases). Besides, the potential health risk of PFASs and HFRs to local people who live in the scenario studied and are fed on horticultural crops grown in biosolid amended soil was also below 1, indicating that the risk is not considered significant to human health in the conditions studied. This approach provides a first insight of the risks relative to biosolid amendments to further research based on fieldwork risk assessment.

1. Introduction

Wastewater treatment plants (WWTPs) which treat biosolids largely from domestic/industrial inputs have been identified as sources of emerging organic compounds such as perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) (Filipovic and Berger, 2015; Lindstrom et al., 2011; Weinberg et al., 2011). The structure of PFASs consists of a fully fluorinated hydrophobic alkyl chain attached to a hydrophilic end group, then, adsorption mechanisms onto sludge can occur due to both hydrophobic and electrostatic interactions. The hydrophobic property of PFASs increases with the increase of the perfluorocarbon chain length (Arvaniti and Stasinakis, 2015). In the case of HFRs, due to the hydrophobic character of these compounds, the hydrophobic

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interactions are predominant in their retention in biosolids (Rivas et al., 2012). Then, the persistent nature of these chemicals in combination with their hydrophobicity (mainly in the case of HFRs) and their surface properties (PFASs) may mean that their concentration in biosolids can become important (PFASs: 1–3120 ng/g d.w., Clarke and Smith, 2011; <0.01–287 ng/g d.w., Navarro et al., 2011; PBDES: 5–4690 ng/g d.w., Clarke and Smith, 2011; 57.5–2606 ng/g d.w., de la Torre et al., 2011a; Dechlorane Plus (DP): 2.45–93.8 ng/g d.w., de la Torre et al., 2011b).

The biosolid agricultural application has been adopted worldwide. Recycling biosolids on soil is internationally recognized as the most sustainable option for biosolid managing and it improves the physico-chemical soil properties or reduces the need for chemical fertilizers (European Economic Community, 1991). The recycling rates of biosolids to agriculture vary greatly among European Union (EU) Member States. For example, about 1,835,000 t (dry solid) of biosolid were produced in Germany during 2012–2015, and about 484,800 t (dry solid) were recycled to agriculture, equivalent to 26% of the biosolid produced. On the opposite side is Spain, whose agricultural soils mostly present a low organic matter content, and therefore, they are more susceptible to receive biosolid amendements (70% of the biosolid produced during 2012–2015 were recycled to agriculture; Eurostat, 2018). However, the direct application of biosolids as soil amendments is one of the main inputs of pollutants, such as PFASs and HFRs, to the soil compartment (Eljarrat et al., 2008; Gorgy et al., 2012; Sepulvado et al., 2011). The current European Sewage Sludge Directive 86/278/EEC (CEC, 1986) regulates the use of sewage sludge on agricultural land and provides limit values for heavy metals. The Working Document on Sludge 3rd Draft (CEC, 2000) on the revision of the Directive proposed limit values for several persistent organic pollutants (POPs), but did not suggest guidelines for PFASs or HFRs. Some European countries have fixed limit concentrations for some organic pollutants but the limits fixed and the pollutants regulated vary from one country to another. In the case of PFASs, 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 (Grümping et al., 2007). Besides, some Member States have prohibited the application of sludge to grassland due to the potential for grazing animals to directly ingest sludge solids with the possible risk of transfer of organic contaminants into the human food chain through milk and meat (Schowanek et al., 2004). The United States Environmental Protection Agency also set in 1993 the framework for biosolid regulations and established pollutant limits (heavy metals), management practices, and operational standards, for the final use or disposal of sewage sludge generated during the treatment of domestic sewage in a treatment works (USEPA, 1993).

Then, there can be a risk of the pollutant exposure to humans or wildlife from biosolid application. Some potential exposure pathways could be: i) the direct or indirect contact of the organisms feeding and living on agricultural land treated with the contaminated biosolids; ii) the consumption of these organisms by others of higher trophic level; iii) the pollutant release from agricultural soils, where biosolids were applied, to streams, rivers and surface water bodies; iv) the uptake of the compounds by plants, which can be consumed by humans and/or animals. In the case of PFASs and HFRs, their transfer from biosolid amended soils to soil organisms (Gaylor et al., 2014; Navarro et al., 2016; Sellström et al., 2005; Wen et al., 2015), plants (Blaine et al., 2013; Navarro et al., 2017) or aquatic system (Gorgy et al., 2011; Grümping et al., 2007; Navarro et al., 2018) has been demonstrated. Therefore, the redistribution of these compounds in the different environmental compartments could facilitate a probable entry pathway into the food chain, with the subsequent risk for terrestrial and aquatic organisms.

In previous works, the distribution and fate of the PFASs and HFRs from four biosolids used as amendment in agricultural soils were studied in different environmental compartments. These compounds were detected in the amended soils and earthworms exposed to the soil treated (Navarro et al., 2016), in crop plants grown in these biosolids-amended soils (Navarro et al., 2017) and in leachate and runoff water generated by natural rainfall in a semi-field simulated runoff experiment applying biosolid fortified to soils (Navarro et al., 2018).

In the present study, a quantitative ecotoxicological risk assessment was conducted to evaluate the environmental potential risk related to PFASs and HFRs due to the biosolid application to agricultural soil, considering different exposure routes. The concentrations measured in the previous experiments were employed to perform an estimation of the exposure levels to contaminants in the receiving media, defining predicted environmental concentrations (PECs) for soil and aquatic compartments and for secondary poisoning via the terrestrial and aquatic food chain. Then, the risk characterization ratios (RCRs) were calculated based on the comparison of the PEC values obtained with predicted no effect concentrations (PNECs) on terrestrial and aquatic ecosystems. Afterwards, the evolution of the risk for soil organisms due to the biosolid annual application to soil was also studied. Finally, the potential health risk of the pollutants to local people who live in the scenario studied and are fed on horticultural crops grown in biosolid amended soil was assessed.

2. Material and methods

2.1. Study design

Four different organic wastes were selected for the study: an aerobically digested municipal solid waste (MSW) compost (B-1), an anaerobically digested thermal drying sludge (B-2), an aerobically digested composted sewage sludge (B-3) and an anaerobically digested MSW compost (B-4). These biosolids were applied to soil in different experiments to study the transfer and fate of the selected emerging compounds to different environmental compartments (Navarro et al., 2016, 2017, 2018; see also Supplementary material). The concentrations measured for perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), pentabrominated diphenyl ether (penta-BDE: sum of BDE-85, -99 and −100), decabrominated diphenyl ether (Deca-BDE: BDE-209), Declorane Plus (DP: sum of *anti*- and *syn*-DP isomers) and decabromodiphenyl ethane (DBDPE) in the different environmental compartments were used in the exposure assessment (Table 1 and Table S1). The concentrations measured in biosolids, runoff water and tomato fruit are in accordance with those found in other studies performed worldwide (Table S10), what reflects the representativeness of the data selected. The maximum concentrations of the compounds studied are in the range of values detected in other sites, in some cases are close to extreme values but not in all cases. Although the maximum values considered in our study could not represent worst-case scenarios, the data selected could represent other scenarios because those are comparable to other concentrations found in other locations, in real conditions, where biosolid amendments have been performed.

To determine the required amount of biosolid to be added to soil and guarantee agronomic conditions, an equivalent of 150 kg of the available nitrogen form ($N_{available}$)/ha was considered appropriate. Then, N_{org}, $N{-}NH_4^+$ and $N{-}NO_3^-$ were determined in the biosolids and $N_{available}$ was calculated following the EPA recommendations (USEPA, 1995) (see Supplementary material). The estimation of the $N_{available}$ in each biosolid was used to calculate the application rates ($APPL_{waste}$) employed in the amendment (Table S2).

Table 1
Concentrations of the compounds studied in each different environmental compartment.

	Biosolid (ng/g)[a]	Runoff water (ng/L)[b,c]	Tomato fruit (ng/g w.w.)[d]
PFOS	27.0 ± 27.4	408 ± 277	0.002 ± 0.002
	(21.4)	(297)	(0.002)
	0.65–64.4	219–819	N.D. - 0.003
PFOA	6.11 ± 3.52	22.7 ± 7.68	0.01 ± 0.01
	(6.28)	(20.3)	(0.01)
	2.52–9.35	16.8–33.2	N.D. - 0.014
Penta-BDE	11.0 ± 6.92	0.40 ± 0.06	0.01 ± 0.002
	(12.4)	(0.41)	(0.01)
	1.82–17.3	0.34–0.46	0.007–0.01
Deca-BDE	184 ± 136	233 ± 115	0.67
	(179)	(237)	(0.67)
	29.3–347	92.4–364	0.67
DP	8.62 ± 5.71	18.6 ± 7.57	0.01 ± 0.003
	(8.80)	(15.5)	(0.01)
	2.28–14.6	13.6–29.8	0.007–0.011
DBDPE	0.09 ± 0.07	2.14 ± 2.53	N.D.
	(0.11)	(1.46)	N.D.
	N.D. - 0.15	0.06–5.58	N.D.

N.D.: not detected. Mean ± SD (n = 4); (median); min-max.
Concentrations detected in the individual scenarios are detailed in Supplementary material.
[a] Navarro et al., 2016.
[b] Navarro et al., 2018.
[c] Concentrations of Penta-BDE, Deca-BDE, DP and DBDPE have been normalized to ng/L.
[d] Navarro et al., 2017.

2.2. Environmental exposure assessment for the different compartment

Exposure-assessment case studies related to PFOS, PFOA, penta-BDE, deca-BDE, DP and DBDPE, were conducted by simulating the application of four biosolids to soil. The environmental risk in the terrestrial and aquatic ecosystems was estimated following the recommendations of the European Chemicals Bureau at Technical Guidance Document on Risk Assessment (European Commission, 2003) and recommendations of European Chemicals Agency at Guidance on information requirements and chemical safety assessment (ECHA, 2008, 2016a; 2016b).

2.2.1. Calculation of the predicted environmental concentration (PEC)

The predicted environmental concentrations in the different environmental compartments (PEC_{soil}, $PEC_{oral,\ predator\ (T)}$, PEC_{water}, PEC_{sed}, $PEC_{oral,\ predator\ (Aq)}$) were estimated covering direct exposure of organisms and exposure via the food chain for predators (ECHA, 2016a). The application of WWTP biosolids to agricultural soil is considered a direct source of pollutants for the soil at local scale (ECHA, 2016a) and, therefore, the calculations have been conducted at local scenario, that represents a worst-case situation. In cases where the local assessment does not indicate a potential risk, there is no reason for concern. For all pollutants, atmospheric-soil deposition input has been dismissed due to its low influence compared to the biosolid amendment.

PEC for the soil compartment was estimated by the following equation (ECHA, 2016a):

$$PEC_{soil}\ (n) = C_{soil}\ (0) \times \left[1 + \sum_{n=1}^{n-1} Facc^{n}\right] \quad (1)$$

where $PEC_{soil}(n)$ is the initial concentration in soil after n biosolid applications, $C_{soil}(0)$ is the initial concentration after the first biosolid application and Facc is the fraction accumulation of pollutant in one year.

The assessment of secondary poisoning via the terrestrial food chain was estimated by $PEC_{oral,\ predator\ (T)}$ (ECHA, 2016a):

$$PEC_{oral,\ predator\ (T)} = \frac{BCF_{earthworm} \times PEC_{porewater} + PEC_{soil} \times F_{gut} \times CONV_{soil}}{1 + F_{gut} \times CONV_{soil}} \quad (2)$$

where $PEC_{oral,\ predator\ (T)}$ represents the total concentration of the substance in the earthworm as a result of bioaccumulation in the worm tissues and the adsorption of the substance to the soil present in the gut. $BCF_{earthworm}$ is the bioconcentration factor for earthworms on wet weight basis, $PEC_{porewater}$ is the concentration in porewater, PEC_{soil} is the predicted environmental concentration in soil, F_{gut} is the fraction of gut loading in worm and $CONV_{soil}$ is a conversion factor for soil concentration wet-dry weight soil.

In the case of the aquatic compartment, the runoff water originated in several rainfall events occurring after the biosolid application was considered the effluent source released to the surface water (Table 1). For the calculations, it was considered that the runoff water was diluted into the surface water and a complete mixing was assumed as a representative exposure situation for the aquatic system. The volatilization and degradation were ignored because a short distance between the point of the release or source and the exposure location was established (ECHA, 2016a):

$$PEC_{water} = \frac{C_{eff}}{\left(1 + Kp_{susp} \times SUSP_{water} \times 10^{-6}\right) \times DILUTION} \quad (3)$$

where PEC_{water} is the predicted environmental concentration in surface water during the release episode, C_{eff} is the concentration of the substance in the effluent (runoff water), Kp_{susp} is the solids-water partitioning coefficient of suspended matter, $SUSP_{water}$ is the concentration of suspended matter in the river and DILUTION is a dilution factor.

PEC for the sediment compartment was derived as the concentration in sediment during the release episode (ECHA, 2016a):

$$PEC_{sed} = \frac{Kp_{susp-water}}{RHO_{water}} \times PEC_{water} \times 1000 \quad (4)$$

where $K_{susp\text{-}water}$ is a suspended matter-water partitioning coefficient, RHO_{susp} is the bulk density of suspended matter and PEC_{water} is the predicted environmental concentration in surface water during the release episode.

The assessment of secondary poisoning via the aquatic food chain was estimated by $PEC_{oral,\ predator\ (Aq)}$ (ECHA, 2016a):

$$PEC_{oral,\ predator\ (Aq)} = PEC_{water} \times BCF_{fish} \times BMF \quad (5)$$

where PEC_{water} is the predicted environmental concentration in water, BCF_{fish} is a bioconcentration factor for fish on wet weight basis and BMF is a biomagnification factor in fish.

The parameters used in the calculations are indicated in Tables S3 and S4.

2.2.2. Estimation of the predicted no effect concentration (PNEC)

The quantitative assessment of the effects of a substance on the environment is conducted by determining the concentration of the substance below which adverse effects in the environment are not expected to occur, the predicted no effect concentration (PNEC).

$PNEC_{soil}$, $PNEC_{oral}$, $PNEC_{water}$, $PNEC_{sed}$ values were obtained from laboratory toxicity tests (Table S6). In some case, $PNEC_{sed}$ was derived from $PNEC_{water}$ (ECHA, 2008):

$$PNEC_{sed} = \frac{K_{susp-water}}{RHO_{susp}} \times PNEC_{water} \times 1000 \quad (6)$$

2.2.3. Calculation of risk characterization ratios (RCR)

The risk characterization for the four biosolids was calculated by dividing the PEC by the PNEC for the single compounds. It is accepted that RCR values higher than 1 represent a significant risk while RCR values lower than 1 are considered negligible risks (ECHA, 2016b).

$$RCR = \frac{PEC}{PNEC} \quad (7)$$

2.3. Human exposure and healthy risk assessment

The potential health risk of the selected pollutants to local people who live in the scenario studied and are fed on horticultural crops grown in biosolid amended soil was assessed based on the average daily intake (ADI; g/kg body weight/d) and reference dose (RfD). The hazard ratio (HR) value was calculated according to the following equation (Pan et al., 2018):

$$HR = \frac{ADI}{RfD} \quad (8)$$

where ADI of the pollutants was obtained following the equation described by Pan et al. (2018).

$$ADI = Pollutant\ concentration\ x\ tomato\ consumption \quad (9)$$

HR value greater than 1 indicates that the risk is considered significant to human health.

2.4. Statistical calculations

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 and one-way analysis of variance (ANOVA) were performed to evaluate differences between compound and risk ratio groups. Mann-Whitney U-tests were performed to evaluate differences between environmental compartments. Statements regarding differences in this study are based on a significance level of $p < 0.05$.

3. Results and discussion

3.1. Environmental exposure assessment for the different compartments

3.1.1. Terrestrial environmental compartment

The PEC values obtained for soil compartment as a result of the biosolid application are detailed in Table 2. The PEC_{soil} for PFOS ranged between 7.55×10^{-6} mg/kg to 1.49×10^{-4} mg/kg, for PFOA between 1.39×10^{-6} mg/kg to 2.36×10^{-6} mg/kg, penta-BDE (2.69×10^{-5} - 1.61×10^{-4} mg/kg), deca-BDE (4.42×10^{-4} - 2.23×10^{-3} mg/kg), DP (3.47×10^{-5} - 9.50×10^{-5} mg/kg) and DBDPE (6.63×10^{-7} - 3.35×10^{-7} mg/kg). The PEC_{soil} values obtained for deca-BDE showed statistically significant differences ($p < 0.05$; Student's t-test), due to the significant higher concentrations found in the biosolids. Higher PEC_{soil} values than those obtained in this study have been reported for PFOS (3.02×10^{-2} mg/kg, Jensen et al., 2012, or 1.08×10^{-3} mg/kg, Yan et al., 2012) and PFOA (2.33×10^{-3} mg/kg, Yan et al., 2012). However, similar PEC_{soil} have been estimated for penta-BDE (1.9×10^{-4} mg/kg, Yang et al., 2011, or 6.0×10^{-5} mg/kg, Cincinelli et al., 2012) and deca-BDE (3.99×10^{-4} mg/kg, Cincinelli et al., 2012). In the case of DP, values obtained were lower than PEC_{soil} resulting from biosolid applications to land (1.4×10^{-4} mg/kg - 5.9×10^{-2} mg/kg) (ECCC, 2016).

$PEC_{oral,\ predator}$ is used to estimate the toxic effects in the higher members of the food chain, either living in the aquatic ($PEC_{oral,\ predator\ (Aq)}$) or terrestrial ($PEC_{oral,\ predator\ (T)}$) environment, which result from ingestion of organisms from lower trophic levels that contain accumulated substances. The terrestrial food chain considered was soil - earthworm - worm-eating birds or mammals, then the exposure of the predators may be affected by the amount of pollutant that is in the soil.

The $PEC_{oral,\ predator\ (T)}$ calculations depend on the log K_{ow} value (ECHA, 2016a), therefore compounds with higher log K_{ow} presented higher $PEC_{oral,\ predator\ (T)}$ values (Table 2 and Table S5). $PEC_{oral,\ predator\ (T)}$ for PFOS ranged between 1.12×10^{-4} mg/kg to 2.25×10^{-3} mg/kg, values very similar to PEC in worms estimated in areas with chromium plating use (1.94×10^{-3} mg/kg - 9.99×10^{-3} mg/kg), some areas related to aviation (9.3×10^{-3} mg/kg) or areas with fire-fighting foam use (9.38×10^{-4} mg/kg - 8.99×10^{-3} mg/kg) (Brooke et al., 2004). $PEC_{oral,\ predator\ (T)}$ values

Table 2
Predicted environmental concentrations in the different environmental compartments: PEC_{soil} (mg/kg), $PEC_{oral,predator\ (T)}$ (mg/kg), PEC_{water} (mg/L), PEC_{sed} (mg/kg), $PEC_{oral,\ predator\ (Aq)}$ (mg/kg).

	PEC_{soil} (mg/kg)	$PEC_{oral,\ predator\ (T)}$ (mg/kg)	PEC_{water} (mg/L)	PEC_{sed} (mg/kg)	$PEC_{oral,\ predator\ (Aq)}$ (mg/kg)
PFOS	$1.02 \times 10^{-4} \pm 6.75 \times 10^{-5}$	$1.51 \times 10^{-3} \pm 9.98 \times 10^{-4}$	$4.06 \times 10^{-5} \pm 2.76 \times 10^{-5}$	$3.21 \times 10^{-4} \pm 2.18 \times 10^{-4}$	$2.57 \times 10^{-4} \pm 1.75 \times 10^{-4}$
	(1.25×10^{-4})	(1.84×10^{-3})	(2.96×10^{-5})	(2.34×10^{-4})	(1.87×10^{-4})
	7.55×10^{-6}–1.52×10^{-4}	1.12×10^{-4}–2.25×10^{-3}	2.18×10^{-5}–8.15×10^{-5}	1.72×10^{-4}–6.45×10^{-4}	1.38×10^{-6}–5.16×10^{-4}
PFOA	$1.90 \times 10^{-6} \pm 3.99 \times 10^{-7}$	$2.24 \times 10^{-4} \pm 4.72 \times 10^{-5}$	$2.26 \times 10^{-6} \pm 7.67 \times 10^{-7}$	$6.21 \times 10^{-6} \pm 2.10 \times 10^{-6}$	$1.43 \times 10^{-5} \pm 4.85 \times 10^{-6}$
	(1.92×10^{-6})	(2.27×10^{-4})	(2.03×10^{-6})	(5.56×10^{-6})	(1.28×10^{-5})
	1.39×10^{-6}–2.36×10^{-6}	1.65×10^{-4}–2.79×10^{-4}	1.68×10^{-6}–3.32×10^{-6}	4.61×10^{-6}–9.10×10^{-6}	1.06×10^{-5}–2.10×10^{-5}
Penta-BDE	$8.12 \times 10^{-5} \pm 5.72 \times 10^{-5}$	0.08 ± 0.06	$3.71 \times 10^{-8} \pm 5.22 \times 10^{-9}$	$5.86 \times 10^{-6} \pm 8.24 \times 10^{-7}$	$2.35 \times 10^{-3} \pm 3.30 \times 10^{-4}$
	(6.84×10^{-5})	(0.07)	(3.76×10^{-8})	(5.94×10^{-6})	(2.38×10^{-3})
	2.69×10^{-5}–1.61×10^{-4}	0.03–0.16	3.14×10^{-8}–4.19×10^{-8}	4.96×10^{-6}–6.61×10^{-6}	1.99×10^{-3}–2.65×10^{-3}
Deca-BDE	$1.27 \times 10^{-3} \pm 7.33 \times 10^{-4}$	41.8 ± 24.2	$3.20 \times 10^{-7} \pm 1.58 \times 10^{-7}$	0.04 ± 0.02	$1.34 \times 10^{-5} \pm 6.60 \times 10^{-6}$
	(1.20×10^{-3})	(39.6)	(3.26×10^{-7})	(0.04)	(1.36×10^{-5})
	4.42×10^{-4}-2.23×10^{-3}	14.6–73.4	1.27×10^{-7}-5.01×10^{-7}	0.02–0.07	5.31×10^{-6}–2.09×10^{-5}
DP	$6.23 \times 10^{-5} \pm 2.85 \times 10^{-5}$	0.29 ± 0.13	$2.54 \times 10^{-8} \pm 1.04 \times 10^{-8}$	$3.30 \times 10^{-3} \pm 1.35 \times 10^{-3}$	$2.73 \times 10^{-6} \pm 1.11 \times 10^{-6}$
	(5.97×10^{-5})	(0.28)	(2.12×10^{-8})	(2.75×10^{-3})	(2.28×10^{-6})
	3.47×10^{-5}–9.50×10^{-5}	0.16–0.45	1.86×10^{-8}–4.07×10^{-8}	2.42×10^{-3}–5.29×10^{-3}	2.00×10^{-6}–4.38×10^{-6}
DBDPE	$1.19 \times 10^{-6} \pm 1.21 \times 10^{-6}$	26.5 ± 26.9	$4.64 \times 10^{-8} \pm 5.49 \times 10^{-8}$	$3.01 \times 10^{-4} \pm 3.57 \times 10^{-4}$	$3.45 \times 10^{-6} \pm 4.08 \times 10^{-6}$
	(6.63×10^{-7})	(14.7)	(3.16×10^{-8})	(2.05×10^{-4})	(2.35×10^{-6})
	3.35×10^{-7}–2.58×10^{-6}	14.7–74.3	1.24×10^{-9}–1.21×10^{-7}	8.09×10^{-6}–7.87×10^{-4}	9.24×10^{-8}–8.99×10^{-6}

Mean ± SD (n = 4); (median); min-max.
PEC_{soil}: Predicted Environmental Concentration in soil (mg/kg). $PEC_{oral,predator\ (T)}$: Predicted Environmental Concentration of contaminant in the food (earthworm) of worm-eating birds or mammals (mg/kg $_{wet\ earthworm}$). PEC_{water}: Predicted Environmental Concentration in surface water during release episode (mg/L). PEC_{sed}: Predicted Environmental Concentration in sediment (mg/kg). $PEC_{oral,predator\ (Aq)}$: Predicted Environmental Concentration of contaminant in the food (fish) of fish-eating predators (mg/kg $_{wet\ fish}$).

for deca-BDE and DBDPE were significantly higher ($p < 0.05$; Student's t-test) than those obtained for the rest of compounds. In the case of deca-BDE, the values ranged between 14.6 mg/kg to 73.4 mg/kg, similar to other concentrations estimated in earthworms for secondary poisoning in areas related to polymer processing and textile application (40.3 mg/kg - 81.0 mg/kg; European Chemicals Bureau, 2002). However, values obtained for DP were higher (0.295 mg/kg, average) than those reported for industrial areas (0.0716 mg/kg; ECCC, 2016).

The $PNEC_{soil}$ and $PNEC_{oral}$ for each substance were obtained from laboratory toxicity tests (Table S6). $PNEC_{oral}$ is used in the secondary poisoning assessment to represent all predatory organisms. In the case of DP, due to lack of experimental data, read-across from closely related substances (chlordane and mirex) was used for obtaining $PNEC_{soil}$ and $PNEC_{oral}$ (ECCC, 2016).

The risk characterization ratios for soil organisms (RCR_{soil}) were obtained by comparing the concentration of the substance in soil (PEC_{soil}) with the no effect concentration for terrestrial organisms ($PNEC_{soil}$). $RCR_{oral,\ worm}$ were determined for worm eating predators by division of the concentration of the chemical in earthworms ($PEC_{oral,\ predator\ (T)}$) with the no effect concentration for birds and mammals ($PNEC_{oral}$) (Table 3).

The average RCR_{soil} were 1.02×10^{-3} for PFOS, 1.19×10^{-5} for PFOA, 2.14×10^{-4} for penta-BDE, 1.29×10^{-5} for deca-BDE, 8.31×10^{-4} for DP and 7.64×10^{-9} for DBDPE. As observed, RCR_{soil} are much lower than 1 in all cases, suggesting that the concentrations of perfluoroalkyl substances and halogenated flame retardants in soil infer a low potential risk on soil organisms following the first biosolid application. As biosolid application is a periodically repeated practice, and some organic contaminants studied are considered persistent (COP, 2010), which can remain in soil for long time, RCR_{soil} values were estimated after repeated biosolid applications (Tables S7, S9 and Fig. S1). The steady-stage level RCR_{soil} for PFOS and PFOA was reached after 10 years of

Table 3
The risk characterization ratios estimated for soil organisms (RCR_{soil}), for worm-eating predators ($RCR_{oral,worm}$), for freshwater (RCR_{water}) and sediment (RCR_{sed}) organisms and for fish-eating predators ($RCR_{oral,fish}$).

	RCR_{soil}	$RCR_{oral,worm}$	RCR_{water}	RCR_{sed}	$RCR_{oral,fish}$
PFOS	$1.02 \times 10^{-3} \pm 6.75 \times 10^{-4}$	0.09 ± 0.06	$1.62 \times 10^{-3} \pm 1.11 \times 10^{-3}$	$4.79 \times 10^{-3} \pm 3.26 \times 10^{-3}$	0.02 ± 0.01
	(1.25×10^{-3})	(0.11)	(1.18×10^{-3})	(3.49×10^{-3})	(0.01)
	7.55×10^{-5}–1.52×10^{-3}	0.01–0.14	8.72×10^{-4}–3.26×10^{-3}	2.57×10^{-3}–9.62×10^{-3}	0.01–0.03
PFOA	$1.19 \times 10^{-5} \pm 2.49 \times 10^{-6}$	$1.42 \times 10^{-3} \pm 2.98 \times 10^{-4}$	$1.13 \times 10^{-4} \pm 3.84 \times 10^{-5}$	$4.35 \times 10^{-5} \pm 1.48 \times 10^{-5}$	$9.06 \times 10^{-5} \pm 3.07 \times 10^{-5}$
	(1.20×10^{-5})	(1.44×10^{-3})	(1.01×10^{-4})	(3.90×10^{-5})	(8.11×10^{-5})
	8.71×10^{-6}–1.47×10^{-5}	1.04×10^{-3}–1.77×10^{-3}	8.41×10^{-5}–1.66×10^{-4}	3.23×10^{-5}–6.38×10^{-5}	6.73×10^{-5}–1.33×10^{-4}
Penta-BDE	$2.14 \times 10^{-4} \pm 1.51 \times 10^{-4}$	0.08 ± 0.06	$7.00 \times 10^{-5} \pm 9.84 \times 10^{-6}$	$1.89 \times 10^{-5} \pm 2.66 \times 10^{-6}$	$2.35 \times 10^{-3} \pm 3.30 \times 10^{-4}$
	(1.80×10^{-4})	(0.07)	(7.09×10^{-5})	(1.92×10^{-5})	(2.38×10^{-3})
	7.08×10^{-5}–4.24×10^{-4}	0.03–0.16	5.93×10^{-5}–7.90×10^{-4}	1.60×10^{-5}–2.13×10^{-5}	1.99×10^{-3}–2.65×10^{-3}
Deca-BDE	$1.29 \times 10^{-5} \pm 7.48 \times 10^{-6}$	0.02 ± 0.01	$1.60 \times 10^{-3} \pm 7.91 \times 10^{-4}$	$3.25 \times 10^{-4} \pm 1.61 \times 10^{-4}$	$5.34 \times 10^{-9} \pm 2.64 \times 10^{-9}$
	(1.22×10^{-5})	(0.02)	(1.63×10^{-3})	(3.32×10^{-4})	(5.44×10^{-9})
	4.51×10^{-6}–2.27×10^{-5}	0.01–0.03	6.36×10^{-4}–2.50×10^{-3}	1.29×10^{-4}–5.09×10^{-4}	2.12×10^{-9}–8.35×10^{-9}
DP	$8.31 \times 10^{-4} \pm 3.80 \times 10^{-4}$	$2.50 \times 10^{-4} \pm 1.14 \times 10^{-4}$	–	–	$3.28 \times 10^{-9} \pm 1.34 \times 10^{-9}$
	(7.96×10^{-4})	(2.40×10^{-4})	–	–	(2.73×10^{-9})
	4.63×10^{-4}–1.27×10^{-3}	1.39×10^{-4}–3.81×10^{-4}	–	–	2.40×10^{-9}–5.26×10^{-9}
DBDPE	$7.64 \times 10^{-9} \pm 7.77 \times 10^{-9}$	0.12 ± 0.12	$2.32 \times 10^{-4} \pm 2.75 \times 10^{-4}$	$3.01 \times 10^{-6} \pm 3.57 \times 10^{-6}$	$1.57 \times 10^{-8} \pm 1.85 \times 10^{-8}$
	(4.24×10^{-9})	(0.07)	(1.58×10^{-4})	(2.05×10^{-6})	(1.07×10^{-8})
	2.14×10^{-9}–1.65×10^{-8}	0.03–0.26	6.22×10^{-6}–6.05×10^{-4}	8.09×10^{-8}–7.87×10^{-6}	4.20×10^{-10}–4.09×10^{-8}

Mean ± SD (n = 4); (median); min-max.

repeated biosolid applications. The rest of compounds reached the steady-stage level later, after 70 (penta-BDE), 250 (deca-BDE) and 500 (DP and DBDPE) years of consecutive amendments. The results evidence that these substances might accumulate in soil for hundreds of years. However, the evolution of the risk characterization ratios for soil organisms for all compounds remained below 1 in all cases, indicating that the consecutive application of the biosolids studied did not present risk to the soil organisms at agronomic conditions.

The average $RCR_{oral,\ worm}$ were 0.090 for PFOS, 0.001 for PFOA, 0.078 for penta-BDE, 0.017 for deca-BDE, 0.0002 for DP and 0.120 for DBDPE. All risk quotients presented a value bellow 1, suggesting that there was not significant risk for worm eating predators.

3.1.2. Aquatic environmental compartment

The PEC values obtained for aquatic compartment as a result of the biosolid application and release of the runoff water to surface water are detailed in Table 2 and Table S5. The average PEC_{water} values obtained were 4.06×10^{-5} mg/L for PFOS, 2.26×10^{-6} mg/L for PFOA, 3.71×10^{-8} mg/L for penta-BDE, 3.20×10^{-7} mg/L for deca-BDE, 2.54×10^{-8} mg/L for DP and 4.64×10^{-8} mg/L for DBDPE. The highest values estimated were for the perfluoroalkyl substances due to the concentrations found in the runoff water and their physicochemical properties. The values for PEC_{water} for PFOS were comparable to values estimated for areas with chromium plating use (4.52×10^{-5} mg/L -9.46×10^{-5} mg/L) or areas related to aviation (9.12×10^{-5} mg/L -1.42×10^{-4} mg/L) (Brooke et al., 2004). In the case of deca-BDE, PEC_{water} values were lower than PEC_{water} estimated in areas related to production or textile applications (3.3×10^{-4} mg/L -3.8×10^{-3} mg/kg; European Chemicals Bureau, 2002). However, similar PEC_{water} values for DP have been reported in industrial scenarios (4.38×10^{-8} mg/L -2.85×10^{-7} mg/L; ECCC, 2016).

In aquatic environments the main compartments are the water column and the sediment. Sediments may act as both a sink for substances through sorption of contaminants to particulate matter, and a source of chemicals through resuspension or sedimentation. Based on the assumption that there is equilibrium of adsorption between solid and liquid phase, PEC_{sed} was also derived (Table 2 and Table S5) (European Commission, 2003). In contrast to results obtained for PEC_{water}, the highest PEC_{sed} values corresponded to halogenated flame retardants, mainly, deca-BDE (average PEC_{sed} of 0.041 mg/kg; showing statistically significant differences ($p < 0.05$; Student's t-test)), DP (3.30×10^{-3} mg/kg) and DBDPE (3.01×10^{-4} mg/kg), compounds which present higher suspended matter-water partitioning coefficients (Table S4). Sediments integrate the effects of surface water contamination over time and space, and may thus present a hazard to aquatic communities which is not directly predictable from concentrations in the water column. PEC_{sed} values for PFOS (1.72×10^{-4} mg/kg -6.45×10^{-4} mg/kg) were similar to values predicted in areas with chromium plating use (1.17×10^{-4} mg/kg -2.53×10^{-4} mg/kg), photography use (3.18×10^{-4} mg/kg -4.55×10^{-4} mg/kg) or related to aviation (2.44×10^{-4} mg/kg -3.80×10^{-4} mg/kg) (Brooke et al., 2004). Values obtained for DP were also similar to those reported for industrial areas (1.5×10^{-3} mg/kg -1.0×10^{-2} mg/kg; ECCC, 2016).

The aquatic food chain considered was water - aquatic organism - fish-fish-eating birds or mammals, then the concentration in fish is a result of uptake from the aqueous phase and intake of contaminated food (aquatic organisms). The average $PEC_{oral,\ predator\ (Aq)}$ was 2.57×10^{-4} mg/kg for PFOS, 1.43×10^{-5} mg/kg for PFOA, 2.35×10^{-3} mg/kg for penta-BDE, 1.34×10^{-5} mg/kg for deca-BDE, 2.73×10^{-6} mg/kg for DP and 3.45×10^{-6} mg/kg for DBDPE (Table 2). Values obtained for penta-BDE were statistically higher ($p < 0.05$; Student's t-test) than the rest of the compounds, that could suggest a higher bioconcentration potential in aquatic organisms. A significant bioavailability and bioaccumulation of penta-BDE (mainly BDE-99) have been reported in aquatic oligochaetes (Ciparis and Hale, 2005), and a significant biomagnification has been found in freshwater fishes (Zhou et al., 2016), what would be in accordance with our results. $PEC_{oral,\ predator\ (Aq)}$ values for deca-BDE were lower than concentrations estimated in fish for secondary poisoning in areas related to production or textile applications (2.27×10^{-4} mg/kg -4.4×10^{-3} mg/kg; European Chemicals Bureau, 2002). As expected, values obtained for DP were also lower than those reported for industrial areas (1.1×10^{-4} mg/kg; ECCC, 2016).

The $PNEC_{water}$ and $PNEC_{sed}$ for each substance were obtained from laboratory toxicity tests (Table S6). $PNEC_{sed}$ for PFOA was derived from $PNEC_{water}$. However, in the case of DP, there were no data available for estimating $PNEC_{water}$ and $PNEC_{sed}$.

The risk characterization ratios for freshwater organisms were determined by the comparison between the concentration of the substance in surface water (PEC_{water}) and the no effect concentration for aquatic organisms ($PNEC_{water}$). RCR_{sed} values were estimated for sediment organisms by division of the concentration of the chemical in sediment (PEC_{sed}) with the no effect concentration for sediment dwelling organisms ($PNEC_{sed}$). The risk to the fish and fish-eating predators (birds and/or mammals) ($RCR_{oral,\ fish}$) was calculated as the ratio between the concentration in their food ($PEC_{oral,\ predator\ (Aq)}$) and the no effect concentration for birds and mammals ($PNEC_{oral}$) (Table 3). Due to the scarce toxicological information of DP, it was not possible to estimate the corresponding RCR for freshwater and sediment organisms. The quotients calculated (RCR_{water}, RCR_{sed} and $RCR_{oral,\ fish}$) were below 1, suggesting that the input due to runoff water from biosolid amended soils to surface water did not involve a significant risk for the aquatic system. The highest average RCR_{water} and RCR_{sed} were for PFOS (1.62×10^{-3} and 4.79×10^{-3}, respectively) and deca-BDE (1.60×10^{-3} and 3.25×10^{-4}, respectively), which presented the highest concentrations in runoff water (4.08×10^{-4} and 2.33×10^{-4} mg/L; PFOS and deca-BDE respectively) as shown in Table 1. The highest average risk for the fish and fish-eating predators was estimated for PFOS (0.015) followed by penta-BDE (2.35×10^{-3}).

PEC and RCR values obtained in the different environmental compartments (terrestrial and aquatic) were also compared to evaluate the behavior of the different compounds. Penta-BDE, deca-BDE and DP presented PEC values significantly ($p < 0.05$; Mann-Whitney *U* test) higher in the terrestrial compartment than in the aquatic compartment. Besides, RCR values for penta-BDE and DP were also significantly higher in the terrestrial compartment. These halogenated flame retardants are more likely to be associated with solids and particulate matter (Gorgy et al., 2011; He et al., 2014), therefore results obtained suggest that these compounds are more easily incorporated by terrestrial organisms via solids or particulate matter ingestion. No statistically significant differences were found for the rest of the compounds. Differences between treatments were not observed either.

3.2. Human exposure: healthy risk assessment

Among the major pathways for human exposure to PFASs and HFRs, food consumption is the most important route of human exposure (Domingo, 2012; Domingo and Nadal, 2017). Human behavior related to food consumption shows variations between countries or individuals. The present assessment represents the worst-case situation, by assuming that people intake is totally based on food coming from biosolid amended soils.

Table 4
Average daily intake (ADI) and hazard ratio (HR) value estimated for local population under the exposure through tomato fruit consumption from plants grown in biosolid amended soils.

		ADI (ng/kg/d)	RfD (mg/kg/d)	HR
PFOS				
	B-2	0.002	2×10^{-5}[a]	9.58×10^{-5}
	B-4	–	2×10^{-5}[a]	–
PFOA				
	B-2	0.009	2×10^{-5}[b]	4.47×10^{-4}
	B-4	–	2×10^{-5}[b]	–
Penta-BDE				
	B-2	0.004	0.002[c]	2.23×10^{-6}
	B-4	0.006	0.002[c]	3.19×10^{-6}
Deca-BDE				
	B-2	0.428	0.007[c]	6.12×10^{-5}
	B-4	0.428	0.007[c]	6.12×10^{-5}
DP				
	B-2	0.007	5[d]	1.40×10^{-9}
	B-4	0.004	5[d]	8.94×10^{-10}

DBDPE was not detected in tomato fruit.
B-2: anaerobic-digested thermal drying sludge, B-4: anaerobic-digested MSW compost.
An average body weight of 60 kg (adult) was assumed.
[a] USEPA, 2016a.
[b] USEPA, 2016b.
[c] USEPA, 2017.
[d] Wang et al., 2013.

The potential health risk of PFASs and HFRs to local people was assessed based on the average daily intake (ADI) and reference dose (RfD) (Table 4). The RfD for PFOS was 0.00002 mg/kg/d, based on decreased neonatal rat body weight from the two-generation study (USEPA, 2016a), and for PFOA was also 0.00002 mg/kg/d, derived by reduced ossification of the proximal phalanges (forelimb and hindlimb) in male and female mice pups and accelerated puberty in male mice pups of dams (USEPA, 2016b). In the case of Penta-BDE, the RfD was 0.002 mg/kg/d associated with liver effects in rats (USEPA, 2017), for deca-BDE, the RfD value was 0.007 mg/kg/d related to neurobehavioral effects in mice (USEPA, 2017), and for DP, it was 5 mg/kg/d derived by reproductive toxicity for rats (Wang et al., 2013). The concentration of substance used in the calculations was the concentration found in tomato fruit from tomato plants grown in soils amended with biosolids B-2 and B-4 (Table 1 and Table S1). The tomato consumption was approximately 13.98 kg per person per year in Spain during 2016 (MAPAMA, 2017) and it was assumed an average body weight of 60 kg.

The HRs of non-cancer risk based on pollutant concentrations in tomato grown in biosolid amended soils were less than unity, then the risk is not considered significant to human health. This is due to the relatively small concentrations of these substances in the tomato fruit (Table 1). These findings suggest that prevalent concentrations of PFASs and HFRs in vegetables (tomato) are unlikely to cause harm to the population.

3.3. Limitations and uncertainties of the present risk assessment

Environmental risk assessment of emerging organic compounds such as PFASs and HFRs is currently hampered by the lack of important information, mainly related to toxicological assays, required to the environmental exposure assessment for the different compartments.

Limited toxicity studies on several of the compounds selected have been published in the peer-reviewed literature. For example, in the case of DP, due to lack of experimental data, read-across from closely related substances (chlordane and mirex) was used for obtaining $PNEC_{soil}$ and $PNEC_{oral}$ and then the estimation of the corresponding RCR values, assuming some uncertainty. The use of a read-across approach for filling data gaps has been applied in various substance regulatory programs (ECCC, 2016). Chlordane and mirex have been identified as structurally and functionally potential analogues to DP. Their use as analogues for toxicity is conservative, as they are more bioavailable and therefore likely more toxic than DP (at least to aquatic organisms) due to higher water solubility than DP. As a result, these analogues could be considered “worst-case” and protective in relation to ecological effects for sediment and soil organisms (ECCC, 2016). However, there were no data available for deriving $PNEC_{water}$ and $PNEC_{sed}$ to assess the risks associated to DP in the aquatic environmental compartment. It is important to consider that the most representative compounds among groups were selected to conduct the risk assessment, but there are more congeners and compounds related whose lack of toxicological data hampers the environmental exposure assessment.

The present study only considers the application of biosolids to soil as main and direct source of the pollutants. The calculations have been conducted at local scenario because the application of WWTP biosolids to agricultural soil is a recognized direct source of pollutants for the soil at local scale (ECHA, 2016a), and it represents the worst-case situation. No regional inputs were considered in the assessment to avoid dispersive sources of pollutants.

4. Conclusions

An environmental exposure assessment for different compartments (terrestrial and aquatic systems) based on the application of four biosolids in an agricultural soil has been conducted considering a single biosolid application rate and the nitrogen plant requirements. The RCRs for soil, freshwater and sediment organisms and the RCRs for earthworms and fish-eating predators were below 1, suggesting that the input due to the application of biosolids containing PFASs and HFRs to soil did not involve a significant risk for the terrestrial and aquatic systems. The estimation of the evolution of the risk characterization ratios for soil organism due to the annual application remained in all cases below the unity. The assessment of the human exposure based on the consumption of tomato fruit from plants grown in biosolids-amended soils showed HR values below 1 (no significant risk to human health). Then, it is necessary to point out that the biosolid application to soil at

agronomic conditions, at the levels considered for the substances evaluated, might not induce any risk. Further research based on environmental risk assessment of field study is still essential to deepen in the knowledge of the risks relative to biosolid application to soil.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.07.007.

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