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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).