TRANSFER OF EMERGING POLLUTANTS FROM BIOSOLID AMENDED SOILS TO TERRESTIAL ECOSYSTEMS

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Introduction

Socio-economic changes during recent decades together with the development of the industry in different sectors and the exorbitant increase of human population and its highly consumer practices, have resulted in a significant increase of organic waste production that, in certain situations, can generate environmental problems. Much of this organic pollution ends up in wastewater and in the municipal solid waste (MSW) compost, however, its low concentration or availability to be metabolized by microorganisms does not necessarily cause a threat to the environment. Nevertheless, there are some organic compounds that do not break down easily during wastewater treatment and / or MSW composting and tend to accumulate in sludge and compost which if used for agricultural purposes, can originate problems due to toxicity, bioaccumulation and transfer trough the food chain.

Responding to this concern, the EU published in 2010 the third draft of future sludge directive for land application proposing cut-off values of different contaminants[1]. Since then, scientific community have made important efforts to characterize waste, being the presence of well known (polybrominated diphenyl ethers; PBDEs)[2], and emerging pollutants (perfluorinated chemicals PFCs, decabromodiphenyl ethane or Dechloranes)[3-5] well documented. Nonetheless, there is still a lack of knowledge regarding their fate, transfer or potential bioaccumulation after soil amendment. For this reason the aim of this study was to evaluate the potential for bioaccumulation of PBDEs, PFCs and Dechloranes and their transfer through food chains in terrestrial ecosystems.

Materials and methods

Three horticultural crop tests (spinach, tomato and corn) were conducted. Spinach (*Spinaca oleracea*) and tomato (*Solanum lycopersium*) were cultivated in soils amended with two different organic wastes: an anaerobically digested thermal drying sludge (Treatment A) and an anaerobically digested municipal solid waste (MSW) compost (Treatment B). Waste application rates were calculated by considering the N requirement of plants (150 and 120 kg N/ha for tomato and spinach). Spinach growth period was 28 days, while tomato plants were exposed to amended soils for six months, time needed to reach fruiting. In addition, seeds of corn (Zea mays) were cultivated during 28 days in soils fortified by the addition of DecaBDE (~5 mg DecaBDE/Kg), PFOS (~50 mg/Kg), and a mixture of both commercial mixtures (~5 and ~50 mg/Kg for DecaBDE and PFOS, respectively). After sowing, all seedlings from each pot (30) were harvested to analyse emerging pollutants.Then, earthworms (10 per treatment) were added to the soils, and a 28 days exposure study was conducted. A total of 66 pots (24, 24, and 18; spinach, tomato and corn experiments) were used. Control pots (not amended soils) were also prepared.

Presence of target analytes was evaluated in the soils (at the beginning t=0, and the end t=end of the experiments), spinach (whole plant), tomato (root, stem, leaf and ripe fruit), corn (root and leaf) and earthworms. All samples were processed according to previously published analytical procedures[2-5]. In brief, for PFOS determination samples were extracted by a combination of agitation, sonication and centrifugation and then purified with EnviCarb cartridges. PBDEs and Dechloranes were Soxhlet extracted and purified with an automated Power Prep System (FMS) including silica, alumina and carbon columns. Instrumental analyses were conducted by HPLC-MS/MS (Varian LC212 - 320MS) and HRGC-qMS (Agilent 6890N – 5973MSD) for PFOS and halogenated flame retardants, respectively. Procedural blanks were processed and analyzed under the same conditions. Concentrations obtained were used to correct those for the samples analysed. In this way, the final result of each sample is obtained by subtracting the blank values.

Results and discussion

Concentrations (ng/g) of PBDEs, DP and PFCs obtained in crop experiments are summarized in Figures 1 (spinach), 2 (tomato), and 3 (corn).

As mentioned previously, waste application rates were calculated considering N requirement of plants, resulting in low pollution input from wastes in the spinach and tomato experiments. However, important differences could be observed in terms of accumulation between analytes and horticultural crops.

Spinach data show accumulation of PBDEs of low bromination degree, mainly BDE 47 and 99, in the plants while BDE 209 levels were below detection limits in both treatments. This result is not strange considering molecular weight of BDE 209, and correlates well with the fact that DBDPE was not detected either. In addition, spinach results demonstrate DP transfer and reveal interesting differences in F*syn* ratios (ratio of *syn* DP isomer to total DP) between soils (~0.30) and plants (~0.12) which could suggest a stereospecific bioaccumulation of DP isomers. Considering PFCs, results showed accumulation of PFOS, PFPeA and PFOA.

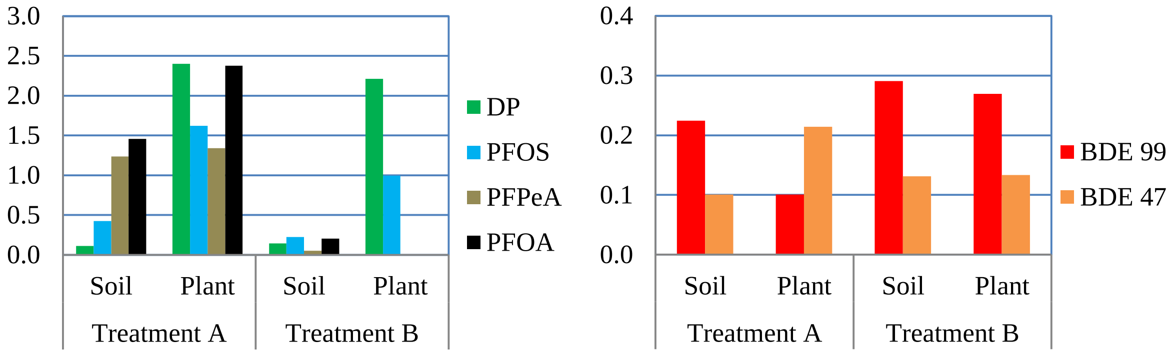

Figure 1. Mean concentrations (ng/g) obtained in the soils and plants from spinach experiments.

In the tomato experiments, root, stem, leaf and ripe fruit were analyzed separately. On contrary to what happened in the spinach, levels of BDE 209 could be found in some parts of the tomato plants (leaf and fruits), while BDE 47 and 99 were detected also in the root, see Figure 2. Levels of DP were detected in the root, stem, leaf and ripe fruit, and as for spinach samples, a stereospecific behavior could be observed between soil and plant parts. Treatment A revealed accumulation of PFCs (mainly PFPeA, PFBA and PFHxA, but also PFOS, PFOA, and PFDA to a lesser extent). Long chain PFCs (octa-, decanoic acids) meanly accumulate in the roots, whereas short chain compounds (buta-, penta-, hexanoic acids) do in the aerial parts (leaf and ripe fruit) of tomato plants.

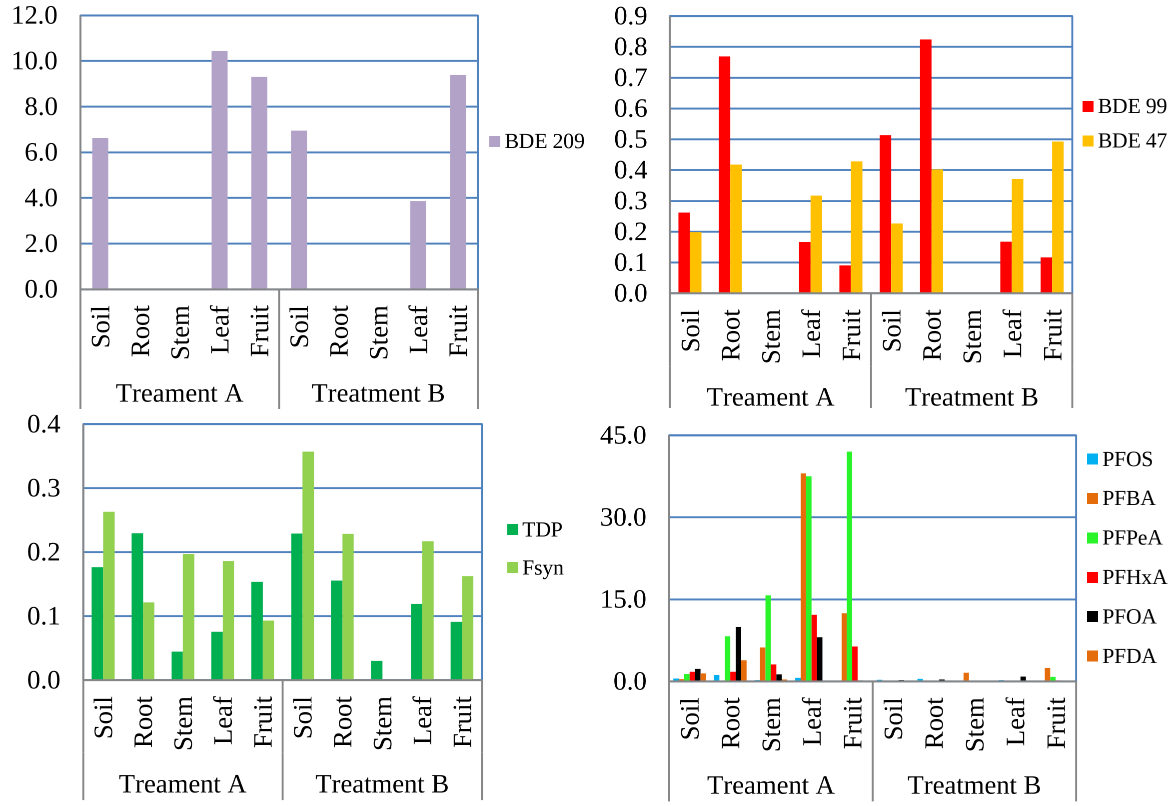

Figure 2. Mean concentrations (ng/g) obtained in the soils, root, stem, leaf and ripe fruit from tomato experiments.

Corn experiment produced interesting data. Presence of BDE 209 in root and corn leaves demonstrated its accumulation, however this is not clear in earthworm case, where BDE 209 concentrations were lower compare to those measured in individuals from control pots. Similar levels of BDE 100, 99 and 47 were found in earthworms from DecaBDE amended soils and from control pots.

Similarly to BDE 209, the presence of PFOS in the corn roots and leaves evidence its accumulation in this crop. In addition, it is important to note that PFOS concentrations in corn roots are five to nine times higher than the ones obtained in the leaves, which is in agreement with tomato results, which evidenced higher levels of long chain PFCs in the not aereal part of the plant.

On contrary to the behavior observed for BDE 209, PFOS bioaccumulation in earthworms seems to play an important role. As Figure 3 shows, PFOS concentrations found in individuals exposed to polluted soils present much higher concentration compared to control earthworms.

Results obtained in this study provide evidence of transfer of PBDEs, DP and PFCs from biosolid amended soils to terrestrial ecosystems. These data will be useful to include new chemicals in the European Directives relating to waste agricultural application and to establish their corresponding permissible limits.

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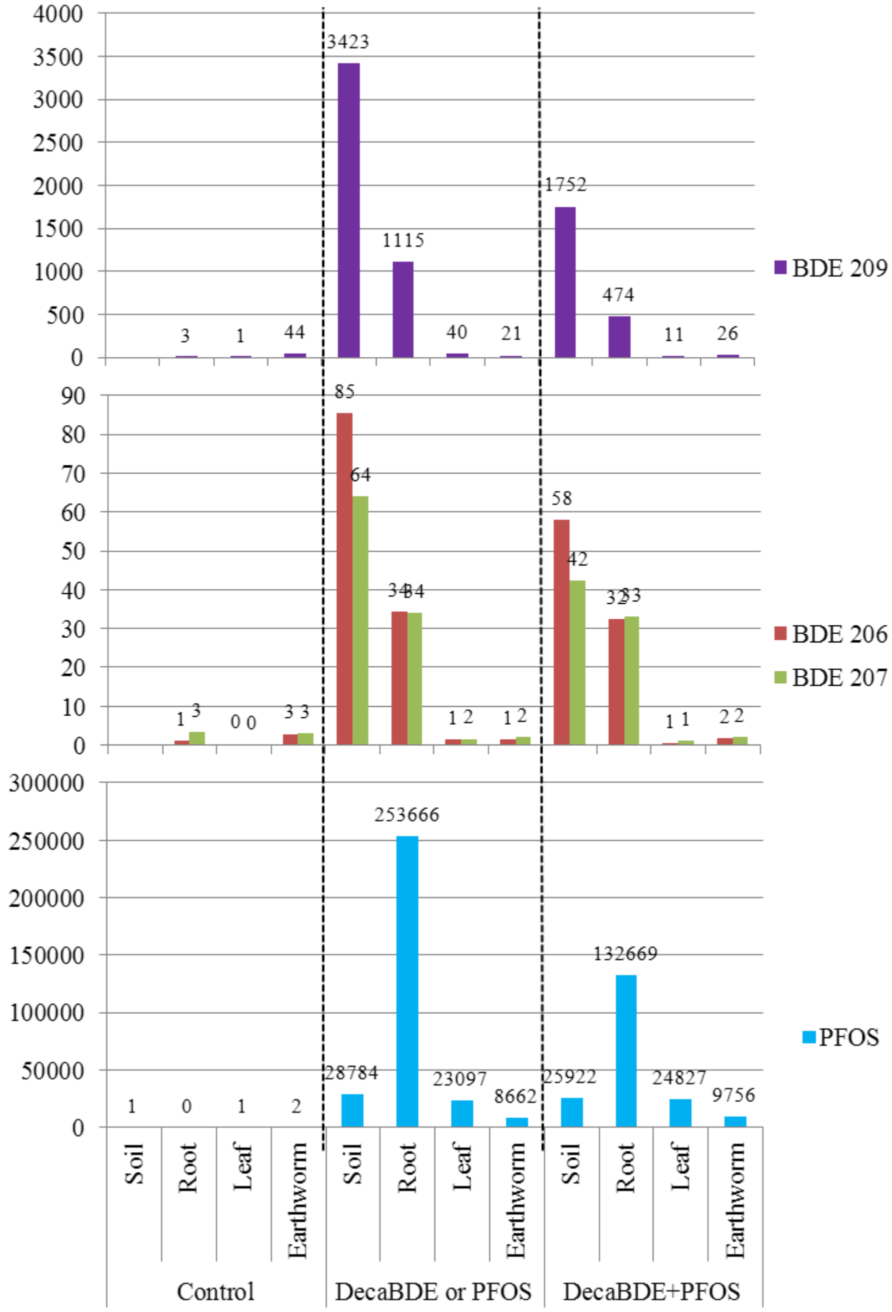

Figure 3. Mean concentrations (ng/g) obtained in the soils, root, leaf and earthworms from corn experiments.

References:

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