CECAREA PROJECT: MOBILITY AND FATE OF POLLUTANTS FROM ORGANIC WASTE USED AS AGRICULTURAL SOIL AMENDMENTS

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Introduction

In 2010, Spain was situated in the ninth position in waste material production among the European Union Member States (535 Kg/inhabitant, above the European average: 502 Kg/inhabitant)[1,2]. This waste material can be deposited in landfill (58%), recycled (15%), incinerated (9%) or managed as compost (18%)[3] for agricultural purposes. Similarly, there are several sewage sludge management options, but spreading it on land has been increased considerably, reaching 70%, from 2005 to 2010[4].

Considering the fertilizing characteristics and the potential as organic amendment of sewage sludge and municipal solid waste (MSW) compost, the application of biosolids in agricultural soils is recommended. In fact, the use of the organic fraction of this waste as agricultural amendment, offering benefits and acceptable risks to both soil and plants is one of the best outings environmentally sustainable waste[5]. Nevertheless, it is important to emphasize that contaminants like heavy metals, pathogenic microorganisms and much of the organic pollution ends up in wastewater and in the MSW compost. The pathogens can be removed by various tretaments, but there are some organic compounds that do not break down easily during wastewater treatment and / or MSW composting, and tend to accumulate in biosolids. Consequently, if they are used for agricultural purposes, could 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[6]. Since then, scientific community have made important efforts to characterize waste, by detecting some emerging pollutants, EPs (halogenated flame retardants and perfluorinated chemicals) in this kind of biosolids[7,8,9,10]. Nonetheless, there is still a lack of knowledge regarding their fate, transfer or potential bioaccumulation after soil amendment. For this reason, Spanish Ministry of Economy and Competitiveness funded the "CECAREA" project to evaluate environmental consequences of utilizing organic waste as agricultural soil amendments and determine the fate, potential for transfer and accumulation and risks related to polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane (DBDPE), decloranes and perfluorinated componds (PFCs). This work aims to include and summarize the different experiments performed under the frame of CECAREA project from 2011 to 2013.

Materials and methods

In order to achive CECAREA objetives, the following tasks were performed: 1) analytical characterization, specially on EPs (PBDEs, DBDPE, Dechloranes and PFCs, among others), of WWTP sludge and MSW compost samples, 2) evaluation of potential transfer of chemicals from waste containing them both to abiotic (surface and ground water; *semi field studies*) and biotic (horticultural crops and terrestrial invertebrate organisms; *multi species soil systems (MS·3)* and *horticultural crop studies*) environmental compartments, and 3) evaluation of the potential for bioaccumulation of these pollutants and their transfer through food chains in terrestrial ecosystems. Pollutant characterization was conducted in 16 waste (4 MSW compost and 12 WWTP biosolids) which were kindly provided by Spanish waste management companies and wastewater treatment plants. Then, those with a higher burden of facing contaminants were selected for the subsequent experiments.

Semi field studies: leachate and runoff

A semi-field test was conducted to determine the leaching and runoff capacity of EPs, following the implementation of agricultural organic waste. This experiment was carried out in 15 trays (2.5 m length and 2 m width), containing a 5 cm of soil layer (sieved < 6 mm) supported by a metal frame with a 10 % slope. Four biosolids (two MSW compost and two sewage sludge) were fortified by the addition of Deca BDE (~10 mg

Deca BDE/Kg waste), DP (~0.26 mg/Kg) and PFOS (~1 mg/Kg). Next, fortified biosolids were applied at the top of the trays (0.5 m length and 2 m width). Two individual systems were connected to each tray for collecting independently leachate and runoff water after rainfall events. Leachate and runoff samples were collected in three stages: i) first rainfall event (October 28th 2011), ii) second rainfall event (November 7th 2011), iii) sum of all rainfall from November 23rd 2011 to May 7th 2012. After the rainfall events, two soil pool samples were taken from each tray: one obtained from the top level (0.5 m length to the top) and the other from the remaining surface (0.5 m to bottom). The assay was carried out in triplicate using three trays for each treatment. A pool sample resulting of the combination of the three trays for each treatment was used in the analysis.

Multi species soil systems (MS·3)
MS·3 were used as rapid tests for assessing the presence of pollutants, both in waste-soil mixtures and in the exposed earthworms. MS·3 is a terrestrial microcosm that has already been used with the antibiotic doxycycline in aged spiked pig manure[11] or sewage sludge amended soil[12]. In the present study, PVC cylinders (20 cm internal diameter and 30 cm high) covered by a fine nylon mesh at the bottom to avoid soil loss were used. The leachates were collected in a glass bottle by means of a funnel in each MS·3. The MS·3 columns were saturated with spring water; after that, 30 plant seeds (*Triticum aestivum*, *Brassica rapa* and *Vicia sativa*) and 20 eathworms (*Eisenia andrei*) were introduced. During the exposure period, 21 days, the MS·3 columns were daily irrigated (100 ml/day) to simulate 1000 mm rainfall/year. Four MS·3 experiments were performed using the same four organic waste than the ones used in the semi-field studies. Each MS·3 was filled with 8 kg of the waste-amended soil (0.120 - 0.5 Kg of waste in each treatment). The four treatments and the control were performed in triplicate, although due to small sample size (especially for earthworms) chemical analyses were conducted with pooled samples.

Horticultural crop tests
Considering that one of the principal routes of pollutants uptake in vascular plants is the roots from the soil solution[13], three horticultural crop tests (spinach, tomato and corn) were performed. Spinach (*Spinaca oleracea*) and tomato (*Solanum lycopersium*) were cultivated in soils amended with two different organic waste: an anaerobically digested thermal drying sludge and an anaerobically digested municipal solid waste (MSW) compost. 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 in plants.Then, earthworms (10 per treatment) were added to the soils, and a 28 days exposure study was conducted.

In all cases waste application rates were calculated by considering the N requirement of plants and in no case exceed the levels set out in Directive 91/676/EEC on the contribution of N fertilizers. Presence of target analytes was evaluated according to previously published analytical procedures[6,7,8]. 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 results are obtained by subtracting the blank values.

Results and discussion
Waste characterization
Waste presented a similar chemicals pattern being PBDEs the predominant chemicals (ranging from 31.4 to 1414.1 ng/g d.w.) following in decreasing order by DBDPE (N.D. to 149.5 ng/g d.w.) and DP (2.3 to 51.8 ng/g d.w.).Concentrations of Dec 603, Dec 602, and CP were also quantified but at three order of magnitude lower than DP (~ pg/g d.w.). Mirex levels were below method detection limits (MDLs) in all cases. Concentrations of perfluoro alkyl substances were in the same order of magnitud (from N.D. to 121.4 ng/g d.w.) than major FR (PBDEs, DBDPE, and DP).

A similar PBDE pattern was obtained both in sewage sludge and MSW compost, being BDE-209 the major congener (accounting 78 ± 4% to the total PBDEs; mean ± SD), following in decreasing order by BDE-207 (5 ± 1%), BDE-206 (6 ± 3%), BDE-99 (4 ± 1%), BDE-47 (2 ± 1%), and BDE-100, 183, 196, and 197 (≤ 1%). This result proves the use of DecaBDE commercial mixtures in Spain. The four waste also presented a similar dechlorane pattern (DP>> Dec 603 > Dec 062). PFC concentrations are in the same order of magnitud than major FR (PBDEs, DBDPE and DP, ng/g d.w.). Besides, PFC content in MSW compost is lower than that obtained in sewage sludge.

Semi field studies: Leachate and runoff

Considering physicochemical differences between target analytes (water solubility= 519 mg/L for PFOS[9], 44 ng/L- 249 µg/L for DP[6] and < 0.1 µg/L for BDE 209[10]), water samples were filtered prior analysis. The content of PFOS was determined in the liquid phase while BDE 209 and DP levels were evaluated in the particulate matter obtained.

The presence of BDE 209, DP and PFOS in soil at the beginning (t=0 day) and the end (t=293 days) was evalutated. Pollutant concentrations in the < 0.5 m soil area at the end of the semi-field study decrease in the most of the cases. However levels found in the remaining surface of the tray (0.5-2.5 m) are notably lower than values of the top area in the different treatments and very similar to those detected in the control tray. At first this result could indicate that there is not an observable mobility of these compounds through the soil. Nevertheless, data from leachate and runoff suggest other hypothesis.

Levels of PFOS in the runoff water (33.8- 415.1 ng/L) are higher than those found in the leachate (3.1-23.9 ng/L) in the four treatments and in all rainfall events. Besides, a significant decrease is observed from the first to the third rainfall event, indicating rainfall water could mobilise this soluble compound out of soil. In the same manner, BDE 209 concentrations in the suspended particulate matter of the runoff (surface water 115.5 ± 244.7 ng/L; mean ± SD) were higher than those found in leachate (43.8 ± 25.5 ng/L groundwater) but they increase from the first rainfall event (7, 9, 17 and 3 ng/g d.w. ;T1, T2, T3 and T4) to the third one (805, 300, 154, and 447 ng/g d.w), being the latter values similar to those obtained in the amended soils at the beginning of the assay (799, 301, 216 and 815 ng/g d.w.). DP behaviour seems to stay betwwen PFOS and BDE 209. As found for PFOS, concentrations in the suspended particulate matter of the leachate samples decrease from the first to the third rainfall event. However, similarly to BDE 209, concentrations detected in the runoff samples increase as the rain water mobilizes particulates from the top part of the trays.

Multi specie systems (MS.3)

As mentioned before, the amount of waste added to the soil was determined by considering the agronomic requirenment of the plants. Therefore, relative low amounts of waste (0.120 - 0.5 Kg) were added. Concentrations in the waste amended soils are low; however presence of all these organic pollutants evidences their transfer during waste application and allows bioaccumulation studies. Chemical pattern in the waste amended soil reflect the one obtained in the waste selected. Nevertheless, pollutant pattern varies when it comes to earthworms, where PBDEs, DP, Dec 602 and Dec 603 were quantified, but levels of DBDPE and CP were below MDLs. Consequently, it can be inferred that these chemicals present important differences in terms of bioacumulation.

Considering PBDEs, an enrichment in lower brominated congeners (BDE-47 (7 ± 2%), BDE-99 (7 ± 1%), and BDE-100 (2 ± 1%)) in earthworms compare to amended soils could be observed. Bioaccumulation differences could be also distinguished when Dec 602 and 603 levels are compared. While levels of Dec 603 in the amended soil are higher than those found for Dec 602, bioaccumulation of the former appears to be lower than the latter. PFC levels in earthworms are also higher than those related to waste amended soils, indicating bioaccumulation has taken place. In this case, results suggest higher bioaccumulation rates for longer chain perfluorinated carboxylic acids.

Horticultural crop tests

Spinach data show accumulation of PBDEs of low bromination degree, mainly BDE 47 and 99, in the plants while BDE 209 levels were below MDLs. 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.

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. 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. Results revealed accumulation of long chain PFCs (octa-, decanoic acids) in the roots, whereas short chain compounds (buta-, penta-, hexanoic acids) do in the aerial parts (leaf and ripe fruit).

Presence of BDE 209 and PFOS in corn seedlings demonstrated their accumulation, however important differences could be found between them in the earthworms. Thus, no evidendes of BDE 209 bioacumulation could be found but PFOS concentrations found in individuals exposed to polluted soils presented much higher concentration compared to control earthworms.

In summary, leaching and runoff capacity of emerging pollutans following the implementation of agricultural organic waste was evaluated and results showed important differences. Solubility of PFOS in runoff waters seems to play and important role in ther mobility, while dragging of waste particles by rainfall waters are the major route of BDE 209 tranfer. Results from multi specie systems (MS·3) demostrate PFCs (PFOS, PFDA, PFDoA), PBDEs (mainly BDE 47, 99 and 100), DP, Dec 602 and Dec 603 transfer from waste amended soils to terrestial organisms (earthworms, *Eisenia andrei*). In addition, horticultural crop tests evidende acumululation of PBDEs, DP and PFCs, however important differences could be observed between species and plant parts.

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