OCURRENCE AND FATE OF BDE 209, DP AND PFOS IN LEACHATE AND RUNOFF WATERS COMING FROM BIOSOLID AMENDED SOILS

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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. However, these biosolids could also contain harmful pollutants. The presence of several contaminants as heavy metals, pathogenic microorganisms or some organic compounds in sludge and composts for use on land has been regulated[5], but there are some emerging pollutants recently detected in this kind of biosolids[6-8], whose presence and fate after amendment require to be characterized.

Besides, water is presently considered one of the main pathways for propagation of some emerging compounds. Natural precipitation such as rain may wash water-soluble compounds out of soil or sludge or may carry suspended particulate matter from soil. Therefore, pollutants that are transported rapidly by water passing through the soil may reach the groundwater and surface water and find their way into water system, contributing to wildlife and human exposure.

This work aims to evaluate the transfer of emerging organic pollutants such as: decabromodiphenyl ether (BDE 209), dechlorane plus (DP) and perfluorooctanesulfonate (PFOS), after application of sewage sludge and municipal solid waste (MSW) compost as amendments in agricultural soils. To achieve this objective, a semi-field study was conducted to evaluate the behaviour of these pollutants, their transfer capability and subsequently, their fate from biosolid amended agricultural soils to groundwater (leachate) and surface water (runoff) generated during rainfall events.

Materials and methods

The semi-field study 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) coming from different Spanish urban waste treatment plants were first characterized and then fortified by the addition of Deca BDE (~10 mg Deca BDE/Kg waste), DP (~0.26 mg/Kg) and PFOS (~1 mg/Kg) commercial mixtures. 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, where fortified biosolids were added) and the other from the remaining surface (2 m to bottom). The assay was carried out in triplicate using three trays for each treatment (control, treatment 1, 2, 3 and 4). A pool sample resulting of the combination of the three trays for each treatment was used in the analysis.

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.

Biosolids, soils and leachate and runoff particulate matter were processed according to the analytical procedures previously described[6-8]. Leachate and runoff water samples (2 L) to determine PFOS were extracted with Oasis WAX (500 mg, 6 ml) and then purified with EnviCarb cartridges (500 mg, 6 ml). Procedural blanks were processed identically to samples. Concentrations obtained in blanks were used to correct those for the samples analyzed.

Results and discussion

Concentrations of BDE 209, DP and PFOS (ng/g d.w.) in fortified biosolids are detailed in the Table 1. Biosolid application rates and pollutant nominal concentrations in soil after amendment are shown in Table 2.

Table 1. Concentrations (ng/g d.w.) of BDE 209, DP and PFOS in fortified wastes.

Biosolid	BDE 209	DP	PFOS
B1 (MSW compost)	10207.8	196.2	300.6
B2 (sewage sludge)	9579.8	264.2	671.6
B3 (sewage sludge)	8025.1	232.0	1070.4
B4 (MSW compost)	11518.1	210.3	373.8

Table 2. Nominal concentrations (ng/g d.w.) in soils after amendment.

			Soil concentrations		
Treatment	Biosolid	Kg/tray	BDE 209	DP	PFOS
T1	B1	5.2	722.4	18.3	73
T2	B2	1.8	246.6	5.9	24.7
T3	B3	1.3	185.8	3.1	19.1
T4	B4	5.9	810.2	63.3	80.1

The presence of BDE 209, DP and PFOS in soil at the beginning (t=0 day) and the end (t=293 days) of the rainfall events is shown in the Table 3. Concentrations of the pollutants studied at the beginning of the assay in the area of the top of the tray (< 0.5 m), where fortified biosolids were applied, correspond well with nominal concentrations, mainly in the case of BDE 209; levels of DP and PFOS in the samples analyzed are close to the nominal values only in some cases, this variability could be explained by the different homogeneity and nature of the biosolids evaluated .

Pollutant concentrations in the < 0.5 m soil area at the end of the semi-field study decrease in the most of the cases, probably because of the effect of the rainfall events.

Table 3. Pollutant concentrations (ng/g d.w.) in the soil at the beginning (t=0 day) and the end (t=293 days) of the rainfall events.

	Control			Treatment 1			Treatment 2			Treatment 3			Treatment 4		
COMPOUND	t = 0	t = final		t = 0	t = final		t = 0	t = final		t = 0	t = final		t = 0	t = final	
	<0.5 m	<0.5 m	0.5-2.5 m	<0.5 m	<0.5 m	0.5-2.5 m	<0.5 m	<0.5 m	0.5-2.5 m	<0.5 m	<0.5 m	0.5-2.5 m	<0.5 m	<0.5 m	0.5-2.5 m
BDE 209	2.14	1.97	0.84	799.39	725.34	4.19	301.67	234.84	8.06	216.00	143.85	2.37	815.19	588.76	5.07
DP	N.D.	N.D.	N.D.	16.29	19.31	0.04	13.14	9.46	N.D.	12.38	7.67	0.04	23.88	23.31	N.D.
PFOS	0.11	0.16	0.29	41.81	84.65	0.59	44.96	36.12	0.41	37.98	30.06	0.33	94.32	47.24	0.49

(< 0.5 m= area of the top of the tray where fortified waste was applied; 0.5-2.5 m= remaining surface of the tray without amendment).

Concentrations of PFOS, BDE 209 and DP in leachate and runoff water samples are detailed in Figure 1. Levels of PFOS in the runoff water (ng/L) are higher than those found in the leachate 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.

BDE 209 concentrations in the suspended particulate matter of the runoff (surface water) were higher than those found in leachate (groundwater) and they increase from the first rainfall event to the third one. This behaviour is specially important in runoff water. More concretelly, BDE 209 levels in runoff water increase from 7, 9, 17 and 3 ng/g d.w. (T1, T2, T3 and T4) for the first rainfall event up to 805, 300, 154, and 447 ng/g d.w., for the third one. It is important to note these values are similar to those obtained in the amended soils at the beginning of the assay (799, 301, 216 and 815 ng/g d.w.), suggesting the mobility of particles of amended soils is preferently caused by the surface water.

In the case of DP, similarly to PFOS, concentrations in the suspended particulate matter of the leachate samples decrease from the first to the third rainfall event. However, concentrations detected in the runoff samples increase as the rain water mobilizes particulates from the top part of the trays, close to BDE 209 behaviour.

In general, levels of PFOS, BDE 209 and DP in surface water are higher than those obtained in the groundwater. This fact evidences the importance of the runoff water events as transfer route of these pollutants among different environmental compartments.

The presence of the emerging pollutants studied in the different environmental matrices assessed (biosolid amended soil - rainfall water) demonstrates the mobility and transfer of these compounds to the different environmental compartments due to the application of biosolids in agricultural soils.

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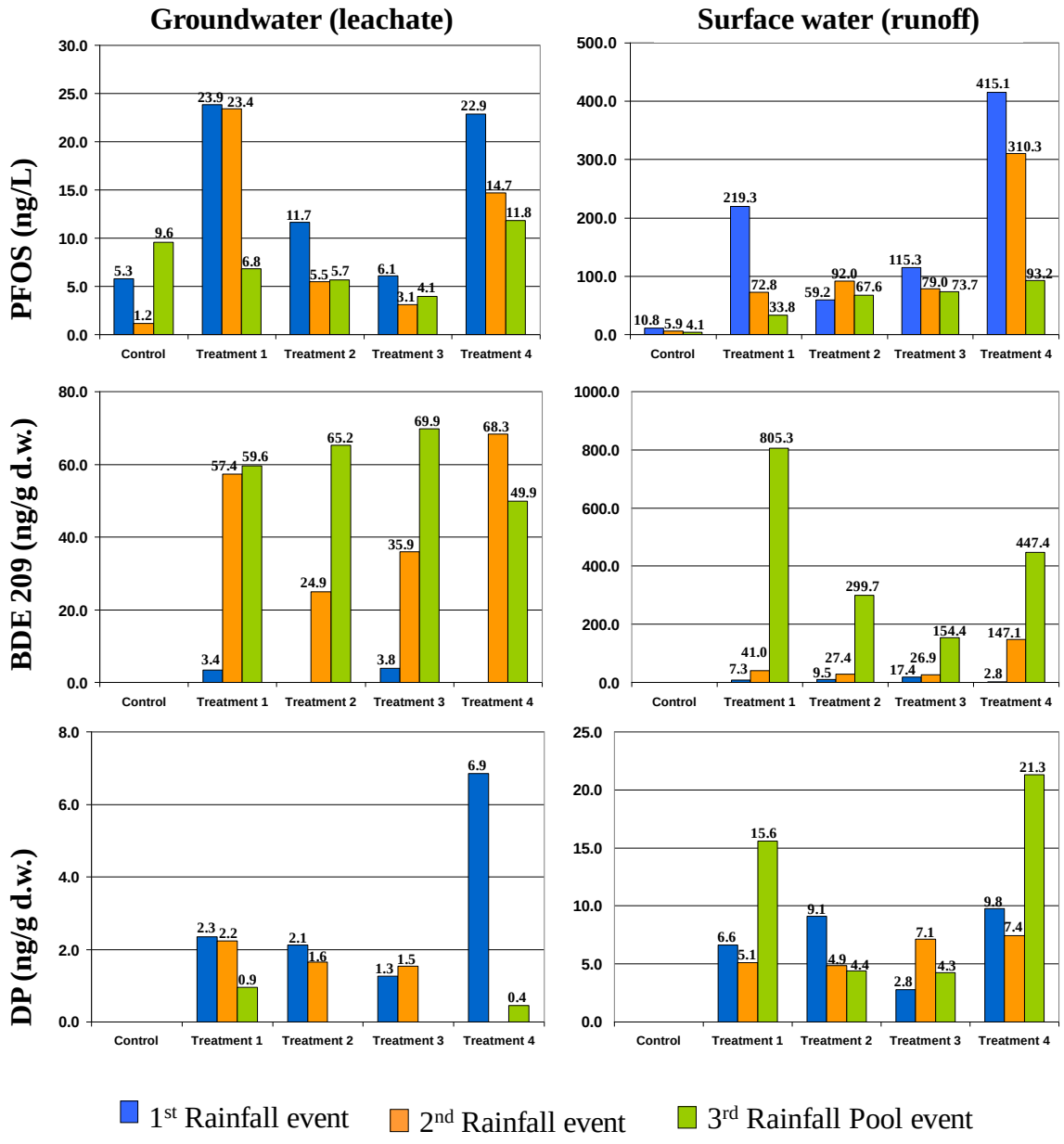

Figure 1. Concentrations of PFOS (ng/L; liquide phase), BDE 209 (ng/g d.w.; particulate matter) and DP (ng/g d.w.; particulate matter) in leachate and runoff samples.