IV Reunión Nacional de Dioxinas, Furanos y Compuestos Orgánicos Persistentes Relacionados

Alicante, 26-28 Junio 2013
IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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CARRYOVER OF PERFLUORINATED COMPOUNDS FROM WASTE-AMENDED SOILS TO PLANTS

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Introduction

The presence of perfluorinated compounds (PFCs) in waste material has been documented in some countries.1–3 Recycling biosolids on land is recognized internationally as the most sustainable option for managing the residual sludge from urban wastewater treatment.4,5 The organic matter and nutrients contained in sludges make the spreading of this waste material on land as a fertilizer or an organic soil improver suitable. While PFCs are known to be present in biosolids, the potential PFC-related risks for human and ecological health due to the application of municipal biosolids to agricultural soil remain unclear.6

Once PFCs are introduced to the environment, two of the primary concerns for human health are the capacity for contamination of water and food. The migration of chemicals from soil to plants could facilitate a probable entry pathway into the food chain.7,8 The study of PFCs in plants grown in waste-amended soils provides a starting point for assessing the possible risks related to applications of biosolids to agricultural soils.

There is still a lack of data regarding transfer rates of PFCs from soil into different vegetables. Accumulation or transfer factors (TF) commonly are used to assess the bioavailability and bioconcentration of chemicals from media such as water, soil and sediments. The knowledge of these factors could help to deduce the potential toxicological risk related to vegetables grown in soils with PFC content.

The aim of the present study was the evaluation of the possible transfer of perfluorinated compounds from waste-amended soil to vegetables.

Materials and Methods

Sample Collection

Two sort of plants were chosen to assess the transfer of PFCs from soils to different plant compartments: spinach (Spinacia oleracea) and tomato (Solanum lycopersicum L.).

Waste samples were kindly provided by Spanish waste management companies and wastewater treatment plants. Two different organic wastes were applied to soil in each transfer assay: anaerobically digested thermal drying sludge (W1) and anaerobically digested municipal solid waste compost (W2). Wastes application rates were calculated by considering the nitrogen requirement of plants and restrictions established in the Council Directive 91/676/EEC9: spinach (120 kg N/ha) and tomato (150 kg N/ha).

The assays were performed in a greenhouse with temperature and irrigation controlled conditions. Spinach assay was carried out during April and May 2012: after seedbed preparation, 7 seedlings were transplanted in each pot (27 kg soil/pot). Due to the sparse espinach biomass harvested, a pool sample of 8 replicates of each treatment was analyzed without plant compartment separation. Tomato assay was performed from April to December 2012: 3-4 seedlings were transplanted in each pot. After harvesting, the tomato plant material was separated according to its respective plant compartment: root, stalk, leaf and ripe fruit. In this case, 3 pool samples were obtained of 8 replicates for each treatment. Apart from control pots, fertilizer-free plant material was also analyzed to determine base levels. Waste-amended soil in two stages (t=0 and t=final) of each treatment was also studied.
Sample Preparation and Extraction

Waste (1 g) and soil (5 g) samples were extracted and purified according to the analytical procedure previously described. Plant material samples (1 - 8 g) spiked with $^{18}$O$_2$-PFHxS, $^{12}$C$_4$-PFOS, $^{13}$C$_4$-PFOA, $^{12}$C$_2$-PFDA, N-d3-MeFOSA and N-d5-EtFOSA solutions were extracted with 9 ml of acetonitrile in PP tubes. Samples were vortex-mixed, shaken for 10 min, ultrasonicated at 40º C for 30 min and centrifuged for 15 min at 3000 rpm. The extraction process was repeated with fresh acetonitrile. Extracts of each sample were then combined and evaporated to 2 ml under nitrogen. 100 µl of acetic acid was added before this solution was centrifuged for 5 min at 2000 rpm and passed through EnviCarb SPE cartridges (500 mg, 6 ml). The purified extract was reduced to 140 µl under a gentle stream of nitrogen. 240 µl of methanol and 240 µl of 2 mM ammonium acetate in Milli-Q water were added to the final extract which was spiked with $^{13}$C$_9$-PFNA solution prior to HPLC-MS/MS injection. Procedural blanks were processed and analyzed with every batch of samples under the same conditions.

HPLC-MS/MS Analysis

Samples extracts were analyzed on a Varian LC 212 liquid chromatograph interfaced with a Varian 320 MS triple quadrupole mass spectrometer. The chromatographic separation was carried out in an ACE C18-PFP (50 x 2,1 mm, 3 µm) analytical column. Analytical details have been described elsewhere.

Results and Discussion

Different PFCs were detected in the two distinct treatments studied in the spinach assay: concentrations of PFOS in plants ranged from 0.99 ng/g d.w. to 1.72 ng/g d.w. (Figure 1). PFPeA (1.34 ng/g d.w.) and PFOA (2.37 ng/g d.w) were found only in the spinaches from Treatment -2 (W2). Apart from control pots, spinaches from seedbed were analyzed as control and any compound was detected.

The presence of PFOS in the spinaches indicates its possible transfer from soil to plant: PFOS transfer factor (TF) was calculated by division of the amount found in the plant material (ng/g d.w.) by the concentration determined in the soil (ng/g d.w.). The average PFOS TF was 4.76 ± 1.12. This value corresponds well with other PFOS TF reported in literature for potato vegetative compartments (3.85) and for carrot foliage (2.94).

Levels of PFOS found in soils and plants from control were close to those detected in Treatment -1 (W1) and -2 (W2). The low PFOS content in the wastes chosen and the nitrogen requirements of plants considered for a proper waste application to soil could explain these similar results. According to those results, the application into soil of the wastes chosen (W1 and W2) has not apparently contributed to PFC increase in spinaches. However, additional investigations implicating other wastes and/or repeated waste applications would be necessary to assess chemical carryover in soil-plant system.

![Figure 1](image.png)

*Figure 1. Concentration of PFOS (ng/g d.w.) in waste, soil and spinach in the different treatments studied.*
Table 1. Concentrations of PFOS and PFOA (ng/g d.w.) measured in waste, soil and the different compartments of the tomato plants.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Waste (n=3)</th>
<th>Soil t=0 (n=3)</th>
<th>Soil t=final (n=3)</th>
<th>Root (n=3)</th>
<th>Stalk (n=3)</th>
<th>Leaf (n=3)</th>
<th>Tomato (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PFOS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer-free plant</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>N.A.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Control</td>
<td>---</td>
<td>0.28 ± 0.07</td>
<td>0.20 ± 0.04</td>
<td>1.10 ± 0.35</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Treatment-1</td>
<td>28.20 ± 2.19</td>
<td>0.47 ± 0.10</td>
<td>0.57 ± 0.12</td>
<td>1.17 ± 0.84</td>
<td>0.24 ± 0.10</td>
<td>0.65 ± 0.39</td>
<td>0.03 ± 0.05</td>
</tr>
<tr>
<td>Treatment-2</td>
<td>0.65 ± 0.30</td>
<td>0.30 ± 0.03</td>
<td>0.30 ± 0.02</td>
<td>0.44 ± 0.40</td>
<td>0.02 ± 0.04</td>
<td>0.11 ± 0.27</td>
<td>N.D.</td>
</tr>
<tr>
<td><strong>PFOA</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer-free plant</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>N.A.</td>
<td>N.D.</td>
<td>0.34</td>
<td>N.D.</td>
</tr>
<tr>
<td>Control</td>
<td>---</td>
<td>0.20 ± 0.05</td>
<td>0.15 ± 0.02</td>
<td>0.45 ± 0.15</td>
<td>0.06 ± 0.10</td>
<td>0.65 ± 0.19</td>
<td>N.D.</td>
</tr>
<tr>
<td>Treatment-1</td>
<td>8.90 ± 0.13</td>
<td>1.20 ± 0.24</td>
<td>3.36 ± 0.46</td>
<td>9.96 ± 9.01</td>
<td>1.26 ± 0.41</td>
<td>8.10 ± 2.16</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>Treatment-2</td>
<td>2.52 ± 0.24</td>
<td>0.24 ± 0.05</td>
<td>0.23 ± 0.07</td>
<td>0.37 ± 0.12</td>
<td>0.08 ± 0.08</td>
<td>0.99 ± 0.13</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

N.D.: not detected
N.A.: not available

Conclusions
The presence of PFCs in the spinach and tomato plants cultivated in waste-amended soils indicates the carryover of these compounds from the soil system to the plant. To the best of our knowledge, this is the first study reporting PFOS and PFOA transfer factors for spinach (Spinacia oleracea) and tomato (Solanum lycopersicum L.). Besides, the concentrations of PFOS and PFOA observed in the tomato assay suggest a different plant compartment distribution and an accumulation tendency in roots and leaves.

The present work is a preliminary study, it would be necessary to perform more assays with different wastes and repeated applications in soil to assess the PFC fate and transport in the soil-plant system.

Acknowledgments
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References


