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Uptake of 8:2 perfluoroalkyl phosphate diester and its degradation products by carrot and lettuce from compost-amended soil

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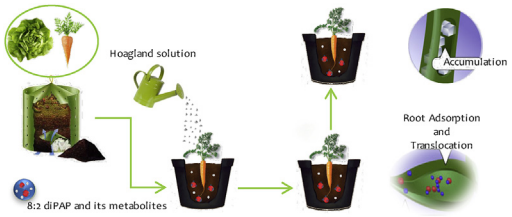
HIGHLIGHTS

- 8:2 diPAP was degraded in the presence and absence of crops (lettuce and carrot).
- PFOA was always the major metabolite both in the presence and absence of crops.
- Low accumulation in carrot and lettuce of 8:2 diPAP was observed.
- The higher the solubility of the metabolites, the higher the BCFs observed in carrot.
- PFOA was the only metabolite detected in lettuce uptake experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work studied the uptake of 8:2 perfluoroalkyl phosphate diester (diPAP) by two different crops (lettuce and carrot) and two different amended soils. Firstly, the possible degradation of 8:2 diPAP in the absence of crop was studied and 8:2 monoPAP (monophosphate), 8:2 FTCA (saturated fluorotelomer carboxylate), 8:2 FTUCA (unsaturated fluorotelomer carboxylate), 7:3 FTCA (saturated fluorotelomer carboxylate), PFHpA (perfluoroheptanoic acid), PFHxA (perfluorohexanoic acid) and PFOA (perfluorooctanoic acid) were detected. In the presence of crops, different degradation products were detected in the soil and, while PFNA (perfluorononanoic acid), PFHpA, PFHxA, PFPeA (perfluoropentacoic acid), PFBA (perfluorobutanoic acid), 7:3 FTCA and PFOA were determined in the cultivation media when carrot was grown, PFOA was the only degradation product detected in the case of lettuce experiments.

Regarding the uptake in carrot, all the degradation products except 7:3 FTCA were translocated from the soil to the carrot. Carrot core, peel and leaves bioconcentration factors, BCFs, were determined for 8:2 diPAP and its degradation products. Values lower than method detection limits for core and low BCFs in peel (0.025–0.042) and leaves (0.028–0.049) were achieved for 8:2 diPAP. Regarding to the degradation products, the higher their water solubility, the higher the plant translocation. In this sense, the lower the carbon chain length of PFCAs, the higher the BCFs determined (PFBA > PFHxA > PFHpA > PFOA > PFNA). In general, lower total BCFs were achieved when the total organic carbon of the soils increased. For lettuce experiments, 8:2 diPAP (0.04–0.18) and PFOA (0.28–1.57) were only determined in lettuce heart.

1. Introduction

During the last decades perfluoroalkyl acids (PFAAs) have been

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detected in different environmental compartments, including water (Villaverde-de-Sáa et al., 2012), sewage sludge (Zhang et al., 2010), food (Vazquez-Roig and Picó, 2015) and air (Jahnke et al., 2007). These chemicals present a wide range of applications in consumer products due to their biological and chemical stability, as well as their water and grease repellence and surface tension lowering properties. In this sense, PFAAs are commonly used in non-stick cookware, breathable membranes for clothing, stain-resistant carpets and fabrics, components for fire fighting foams, surfactants, shampoos, paints or inks, among others. The high concentrations of PFAAs often reported in effluents from wastewater treatment plants (WWTPs) (Llorca et al., 2011; Yoo et al., 2009), and their capacity to accumulate in the sludge (Zhou et al., 2010; Zhang et al., 2013), suggest that these matrices can contribute to their presence in the environment. However, the source and origin of PFAAs found in the environment are still not well known. Apart from the direct release of PFAAs from industrial emissions and commercial products, indirect sources such as the transformation of precursor compounds, including fluorotelomer alcohols (FTOHs), perfluorinated alkyl sulfonamides or polyfluoroalkyl phosphates (PAPs), through different reactions (i.e., atmospheric oxidation, metabolization or hydrolysis) can lead to the formation of PFAAs (Wallington et al., 2006; Nabb et al., 2007).

As mentioned before, PAPs are one of the families of compounds considered PFAA precursors. They belong to a group of hydrophobic phosphates attached to partially fluorinated alkyl chains and are commercially produced as a mixture of several polyfluorinated chain lengths (i.e., 4:2, 6:2, 8:2 and 10:2) and can have one (monoPAP), two (diPAP) or three (triPAP) polyfluorinated tails. In recent years, PAPs were primarily applied in food contact paper industries to replace the previously phased out levelling and wetting agent perfluorooctane sulfonate acid (PFOS) (UNEP/POPS/POPRC.6/13/Add.3/Rev.1, 2013). In the case of diPAPs, they have been reported to be present in matrices such as household dust (Eriksson and Kaerrman, 2015), human serum (Lee and Mabury, 2011; D'eon et al., 2009), drinking water (Ding et al., 2012) or even sewage sludge (D'eon et al., 2009; Liu et al., 2013).

Several works in the literature have reported concentrations for different PAPs. While Liu and co-workers (Liu et al., 2013) found 8:2 monoPAP (1H, 1H, 2H, 2H-perfluorodecylphosphate) and 10:2 monoPAP (1H, 1H, 2H, 2H-perfluorododecylphosphate) at the low ng/g but did not detect any diPAPs in sewage sludge, Deon and co-workers (D'eon et al., 2009) found mainly 6:2 diPAP (bis(1H, 1H, 2H, 2H-perfluorooctyl)phosphate) and 8:2 diPAP (bis(1H, 1H, 2H, 2H-perfluorodecyl)phosphate) at the ng/g levels. Loi et al. (2013) reported similar concentrations in sewage sludge samples from Hong Kong, where 6:2 diPAP and 8:2 diPAP were present at concentration levels as high as PFOS. Moreover, recent studies reported in the literature have shown that PAPs could be bio-transformed into PFAAs in sludge (Lee et al., 2010) and in biota, such as rat (D'eon and Mabury, 2011) and rainbow trout (Brandsma et al., 2011). In the experiments performed with rats, elevated levels of perfluorooctanoic acid (PFOA) were measured in blood and 7:3 FTCA (3-perfluoroheptyl propanoic acid), 8:2 FTCA (2-perfluorooctyl ethanoic acid), as well as 8:2 FTUCA (2H-perfluoro-2-decenoic acid) were also detected. Besides, Yoo et al. (2011) determined that PFOA was the major homologue followed by perfluorodecanoic acid (PFDA) when the determination of FTOHs and perfluoroalkyl substances (PFASs) in plants from a biosolid-amended field was performed. However, in rainbow trout exposure experiments, 8:2 FTCA, 10:2 FTCA (2-perfluorodecyl ethanoic acid), 8:2 FTUCA and 10:2 FTUCA (2H-perfluoro-2-dodecenoic acid) were the major products, while small amounts of PFOA and PFDA were also detected. Further experiments are therefore necessary in order to understand the degradation pathways of compounds such as PAPs in different matrices.

Sludge or sludge derived compost are used as soil fertilizers in agriculture since their application improves soil properties, such as the water capacity and the texture, and supplies nutrients. However, concerns about this practice continue rising mainly because biosolids contain a broad range of toxic organic and inorganic chemicals, as well as pathogens (Kinney et al., 2006). Therefore, the use of biosolids as fertilizers may present an exposure pathway of contaminants since translocation through the plant, accumulation in the edible part of vegetables and the transfer to the food chain exert a potential risk for humans. Therefore, uptake experiments to evaluate the risk of PFAAs due to the degradability of precursors such as PAPs, FTOHs and saturated (FTCAs) and unsaturated (FTUCAs) fluorotelomer carboxylates, among others, have gained scientific attention.

In the last years, several works have been carried out to determine FTOHs and their degradation products in biosolid-amended soils and plants. Yoo et al. (2011) reported a quantitative determination of PFAAs and FTOHs in grass plants from biosolid-amended fields. In the former work, most PFAAs were detected quantitatively in the grass plants cultivated in soil which received multiple sludge applications. However, FTOHs were quantifiable in a few grass plant samples and at very low concentration comparing with PFAAs. Moreover, it was observed that the shortest chain PFAAs showed the highest grass accumulation factor. Zhang et al. (2015) also found FTOHs and their possible degradation products, including PFAAs (C4–C9), FTCAs and FTUCAs in soils and plants. Besides, the concentrations of some intermediate degradation products in plants were higher than in soil. These concentrations of the intermediate products could be due to translocation and accumulation from the soil to the plant or by degradation of the original compound in the plant (Zhang et al., 2015). Lee et al. achieved the same conclusion (Lee et al., 2014) when the decline of 6:2 diPAP and its degradation products upon soil amendment with biosolids that had been sown with *Medicago truncatula* plants was evaluated. Authors reported that the decline of 6:2 diPAP concentration could be due to both plant uptake and transformation contribution over time. The latter one was further evidenced by the degradation of 6:2 diPAP to its corresponding FTOH intermediates and PFAAs.

Within this context, the main objective of the present work was to investigate the uptake and distribution of 8:2 diPAP and its degradation products by carrot (*Daucus carota* ssp *sativus, Chantenay* variety) and lettuce (*Lactuca sativa, Golden Spring* variety) from two different compost amended soils with different total organic carbon (TOC) content. Both crops were selected to see the differences between a root vegetable, where the fruit is underground in direct contact with polluted soil, and a leaf vegetable, where the edible part is not in direct contact with the polluted soil.

2. Experimental section

2.1. Chemicals, reagents and laboratory material

All chemical reagents are provided in the supporting information (SI).

In the case of vegetables, a Cryodos-50 laboratory freeze-dryer from Telstar Instrument (Sant Cugat del Valles, Barcelona, Spain) was used to freeze-dry the samples. For extraction, 50-mL polypropylene conical tubes (PP, internal diameter 27.2 mm × 117.5 mm length) obtained from Deltalab (Barcelona, Spain) and a Bandelin sonifier ultrasonic cell disruptor/homogenizer (20 kHz; Bandelin Electronic, Berlin, Germany) equipped with a 3-mm titanium microtip were used. After the extraction step, the supernatant was filtered through polyamide filters (0.45 μm, 25 mm, Macherey–Nagel, Germany). Evolute-WAX (primary/secondary amine