Uptake and translocation of perfluoroalkyl acids (PFAAs) in red chicory grown under varying contamination conditions: A greenhouse study

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Abstract

In the past decade, significant concerns have been raised regarding the presence of perfluoroalkyl substances (PFASs) in northern Italy, with the Veneto Region as one of the contamination hotspots. Concentrations up to 700 µg/L (PFOA) were detected in the groundwater, up to 3.4 µg/L (PFOA) in the surface waters and 7.9 µg/L (PFOA) in the source waters of the Vicenza province (ARPAV, 2018; Valsecchi et al., 2015). Agriculture is traditionally among the most important economic sectors in Veneto, being one of the most significant producers of fruits, vegetables, cereals and wine in Italy and Europe. Concurrently, Italy has the highest use of water for agricultural purposes in Europe (Nicoletto, Maucieri, & Sambo, 2017). The most important routes of the human exposure to PFASs are drinking water and food consumption, among which, vegetables have been identified as the most important food category in terms of the PFASs exposure (Felizeter, McLachlan, & De Voogt, 2014). Even though elevated serum PFASs concentrations have been detected in the residents of the contaminated areas in Veneto, connected with contaminated drinking water ingestion (Ingelido et al., 2018) and associated to higher mortality levels for some causes of death (Mastrantonio et al., 2018), comprehensive health risk assessment and research considering the food consumption are still lacking. In the light of the global trends in the substitution of long-chained PFASs (as PFOA and PFOS) with their short-chained equivalents (as PFBA and PFBS), the scarcity of data on the environmental behaviour and pathways of short-chain PFAAs and their health impacts are another emerging issue (Ghisi & Vamerali, 2018). In this work, a typical Veneto crop - red chicory var. Chioggia (*Cichorium intybus L.* Rubifolium group), was cultivated in a greenhouse as model crop, under varying concentrations of pre-contaminated soil and irrigation water corresponding to 12 different treatments, with the final goal of developing a forecast model of PFAAs uptake to edible parts of the crops under environmentally representative contamination conditions. Even though PFAAs uptake in crops has been already studied providing some insights in their distribution and pathways in the plants, studies concentrating on mechanistic understanding are still scarce, usually including only one or several long-chained PFAAs (Ghisi & Vamerali, 2018). To our knowledge, this is the first study assessing the PFAAs plant uptake from both PFAAs contaminated agricultural soil and irrigation water in separation and in synergy.
Radicchio plants were grown in the greenhouse for a period of 87 days (from transplanting the seedlings to harvesting) in pots filled with 11 kg of soil per pot. Agricultural soil was spiked with nine short and long chained perfluoroalkyl acids (PFAAs) (Table 1) to the nominal concentrations of 100 ng/g and 200 ng/g each, and was irrigated with spiked drinking water with nominal concentrations of 1 µg/L, 10 µg/L and 80 µg/L, respectively, according to the following scheme, also including a control (clean soil and irrigation water) (Figure 1).

Table 1. List of PFAAs used in the experiments:

Short – chained PFAAs (≤ C6):	***Long – chained PFAAs (> C6):***
Perfluoroalkyl carboxylic acids (PFCAs):	
Perfluorobutanoic (PFBA) acid	Perfluoroheptanoic acid (PFHpA)
Perfluoropentanoic acid (PFPeA)	Perfluorooctanoic acid (PFOA)
Perfluorohexanoic acid (PFHxA)	Perfluorononanoic acid (PFNA)
	Perfluorodecanoic acid (PFDA)
Perfluorosulfonic acids (PFSAs):	
Perfluorobutanesulfonic acid (PFBS)	Perfluorooctanesulfonic acid (PFOS)

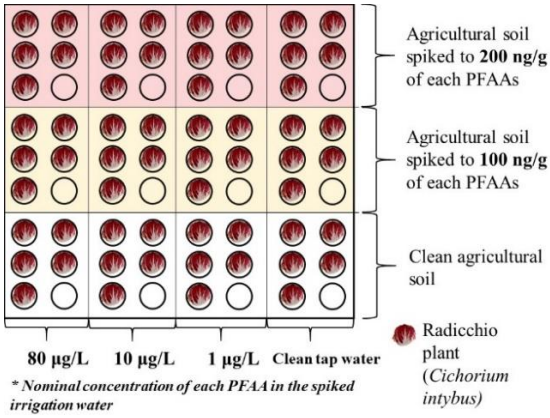

Figure 1: Experimental set-up

After the maturation (and reaching a marketable size), radicchio plants were harvested in triplicates, split into roots, leaves and heads and were analysed by HPLC-MS/MS for the determination of the PFAAs concentrations. Soil samples were taken and analysed by LC-MS/MS after the spiking activities (after the equilibration period of 10 days), to evaluate the homogeneity of the spike, and after the harvesting, as representative samples for the rhizosphere of each sampled radicchio plant. Estimates of the distribution of each PFAA inside the plant compartments with respect to the soil concentrations resulting from the pre-contaminated soil, contaminated irrigation water, and their combination, were evaluated to estimate the importance of the contamination sources (separately and synergistically). Also, to assess the importance of PFAAs soil sorption as a factor in decreasing bioavailability, laboratory batch tests were performed to estimate the soil-water distribution coefficient for both sorption ($K_{d,ads}$) and desorption ($K_{d,des}$). For all treatments, mass-balances for each PFAA were calculated as well as the root concentration factors (RCFs), leaves-to-root concentration factors (LRCF), leaves concentration factors (LCF), leaves-to-head concentration factors (LHCF) and transpiration stream concentration factors (TSCFs) as the basis for the uptake and bioaccumulation estimation and the development of essential chain-length and functional group correlations. Results throughout all the treatments showed that short-chained PFAAs, and PFBA particularly, are more prone to accumulate in all plant compartments, PFBA reaching concentrations up to 53(±13) $\mu g/g_{dw}$ in the roots, 27(±8) $\mu g/g_{dw}$ in the leaves and 12(±0.2) $\mu g/g_{dw}$ in the heads (the edible part) in the treatment with the highest contamination. Mass balance results indicate that the total PFAAs mass is mostly contained in roots in the treatments with only pre-contaminated soil, whereas most of the PFAAs mass passes to the leaves when contaminated irrigation water is applied on the clean soil. The highest mass percentages of PFAAs ending in the heads are detected in the treatments with highest contamination from both water and pre-contaminated soil. While short-chained PFAAs (PFBA, PFPeA, PFBS, PFHxA) were always detected in all plant compartments, and were primarily contained in the aerial plan parts, PFOA was detected in the radicchio head only twice, in the treatments with pre-contaminated soil irrigated with clean water. PFOS was generally detected in the lowest concentrations, and mainly it was stopped in the roots. The BCFs were calculated on dry weight basis, with the highest BCF calculated for PFBA (86.2 g_{dw}/g_{dw} on average among treatments) and the lowest for PFOS (2.6 g_{dw}/g_{dw}) The bioconcentration factors comparison indicated that in treatments with the PFAAs delivered through the irrigation water (having higher compartmental BCFs), all PFAAs were more readily uptaken in radicchio and also transferred to leaves and heads compared to the treatments where only pre-contaminated soil is used. This difference is particularly visible for the long-chained PFAAs that are more significantly adsorbed to the soil, especially PFDA and PFOS, having the highest K_d values. These results represent a valuable empirical base for the validation of the existing plant uptake models which, when adequately modified to account for the specific environmental behaviour of PFAAs, can support a mechanistic understanding of their transport from soil to crop and, in general, of inter-compartmental translocation of different PFAAs under realistic environmental conditions, all of immense importance in risk assessment.

Keywords: PFOA, PFOS, Chicorium intybus, crop uptake, bioconcentration factors

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Acknowledgements: This work was co-funded through the LIFE programme of the European Union, Grant Agreement number LIFE16 ENV/IT/000488 - project LIFE PHOENIX. Authors acknowledge Direzione Prevenzione, Sicurezza Alimentare, Veterinaria, Area Sanità e Sociale – Regione del Veneto for supporting activities in the experiment. Andrea Gredelj's PhD research was funded by the Fondazione CARIPARO's grant for foreign PhD students at the University of Padova.