

An integrated approach for the effective management of water pollution risks from emerging contaminants



Perfluorinated compounds
HOlistic ENvironmental
Interinstitutional eXperience

GREENHOUSE EXPERIMENT OF EDIBLE PLANT EXPOSITION TO PFAS UNDER A CONTROLLED ENVIRONMENT

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Preventing, Ensuring, Promoting

LIFE PHOENIX Project

COORDINATOR



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- Italy has the highest use of water for irrigation in Europe, while agriculture is among the most important economic sectors (fruits, vegetables, cereals and wine production)
- Red chicory (radicchio) was chosen as the model crop because of its significance and widespread cultivation in Veneto (more than 7400 ha)
- Towards better mechanistic understanding of PFAAs uptake in crops → Set of experiments with and without soil was performed → Hydroponics is presented in this work

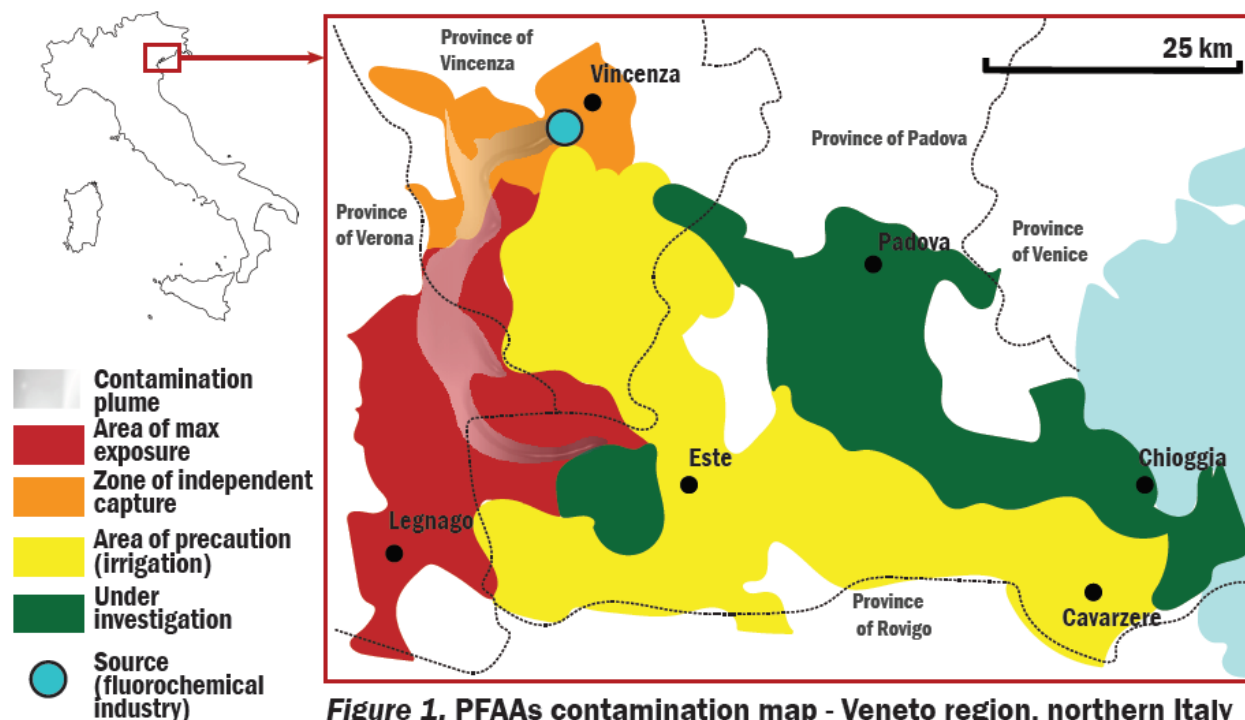
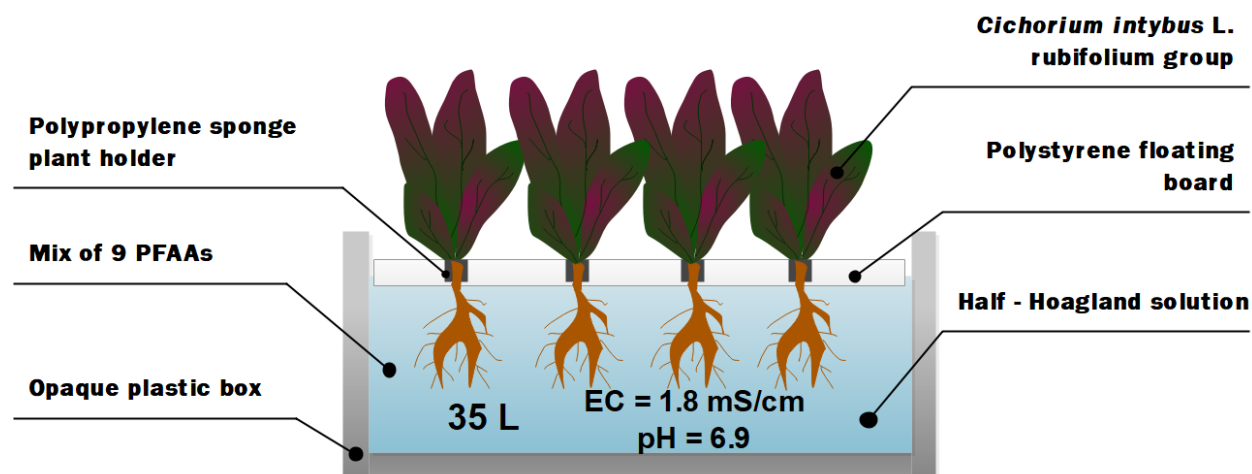


Figure 1. PFAAs contamination map - Veneto region, northern Italy (LIFE PHOENIX project)

- Radicchio var. Chioggia (*Cichorium intybus* L., rubifolium group) was grown in a greenhouse for a period of 38 days
- Experimental hydroponic system with a nutrient solution containing 9 perfluoroalkyl acids (PFAAs)*
- Evapotranspiration was measured by weighing on a weekly basis
- Clean water was added weekly to account for the lost nutrient solution



Nutrient solution concentrations were analyzed for PFAAs on the beginning and the end of experiment by LC-MS/MS

- After the exposure period, radicchio plants were harvested, separated into roots and shoots, extracted with acetonitrile and analyzed for the PFAAs concentrations by HPLC-MS/MS

Table 1. List perfluoroalkyl acids used in the experiment with no. of C-atoms*

Short - chained PFAAs ($< C6$ PFSA, $< C7$ PFCA):	Long - chained PFAAs ($\geq C6$ PFSA, $\geq C7$ PFCA):
Perfluoroalkyl carboxylic acids (PFCAs):	
Perfluorobutanoic acid (PFBA) (C3)	Perfluorooctanoic acid (PFOA) (C7)
Perfluoropentanoic acid (PFPeA) (C4)	Perfluorononanoic acid (PFNA) (C8)
Perfluorohexanoic acid (PFHxA) (C5)	Perfluorodecanoic acid (PFDA) (C9)
Perfluoroheptanoic acid (PFHpA) (C6)	
Perfluorosulfonic acids (PFSAs):	
Perfluorobutanesulfonic acid (PFBS) (C4)	Perfluorooctanesulfonic acid (PFOS) (C8)

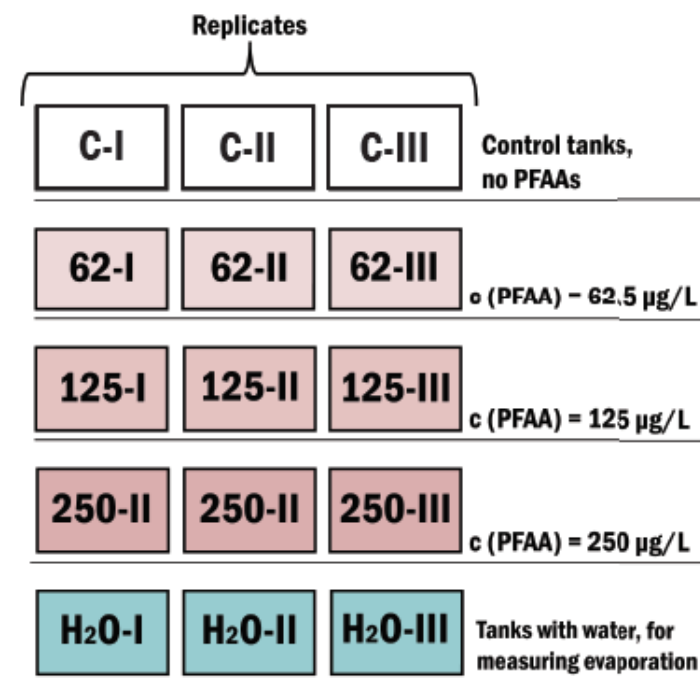


Figure 3. Experimental set-up with nominal concentrations of each PFAA

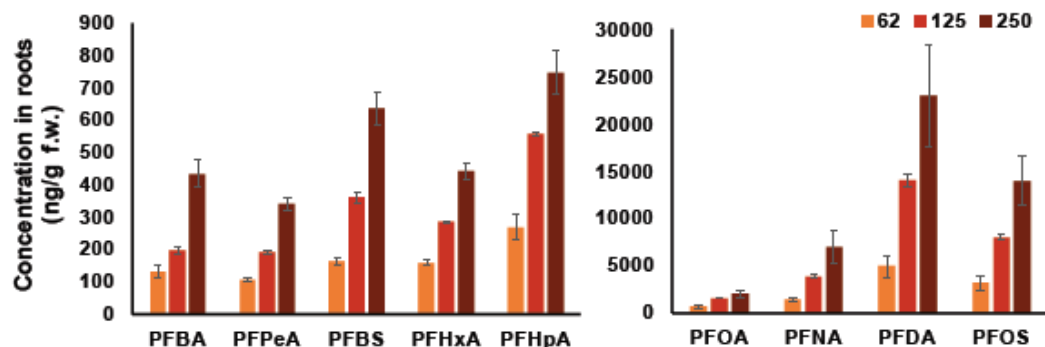


Figure 4. Measured concentrations of PFAAs in roots across treatments (mean ± st.err.)

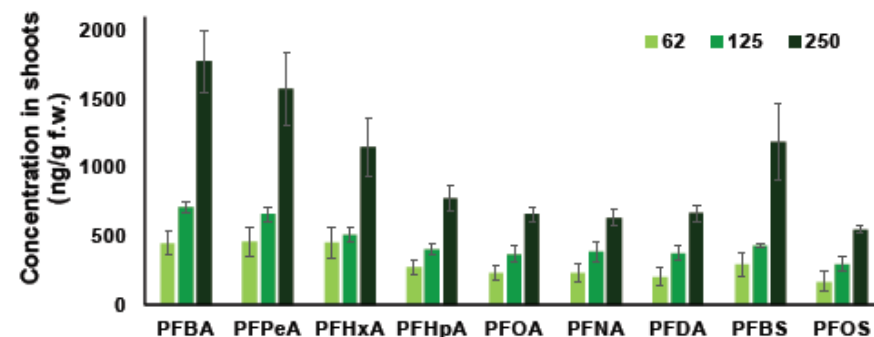
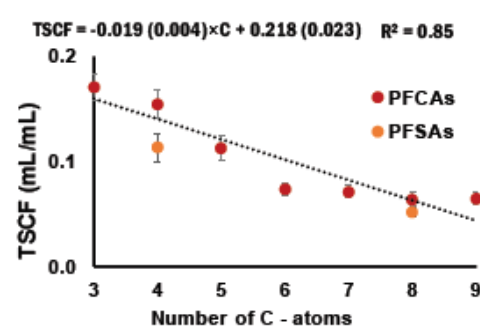
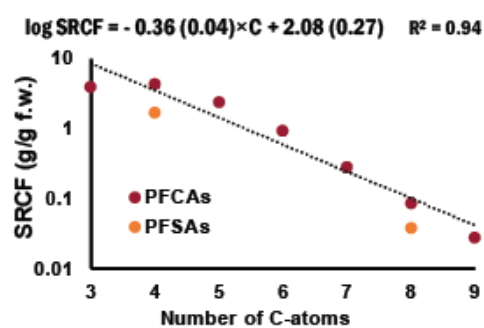
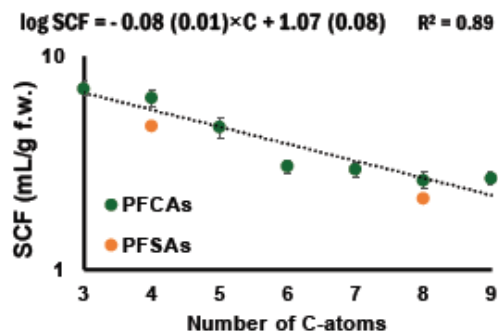
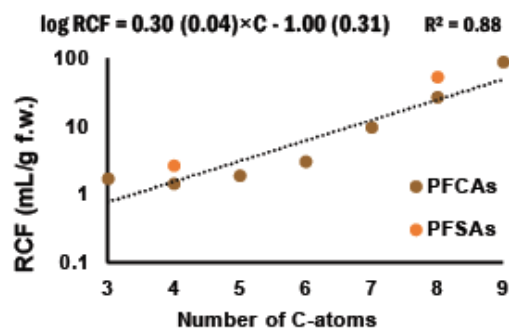


Figure 5. Measured concentrations of PFAAs in shoots across treatments (mean ± st.err.)



PHYSIOLOGICAL CHANGES DUE TO EXPOSURE TO PFAAs

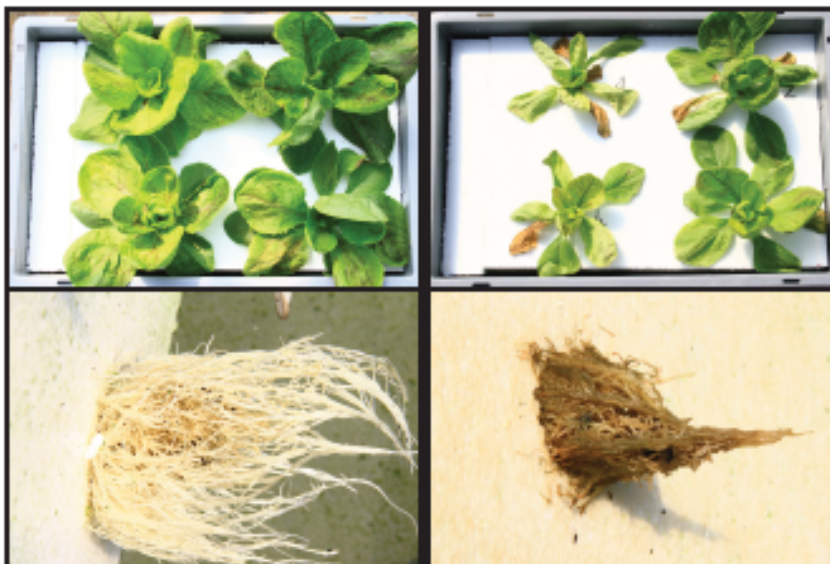
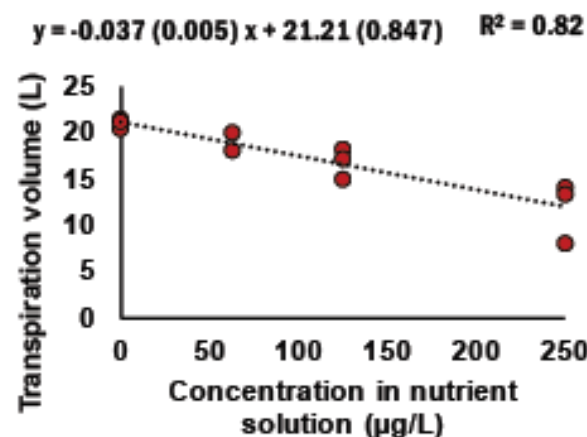
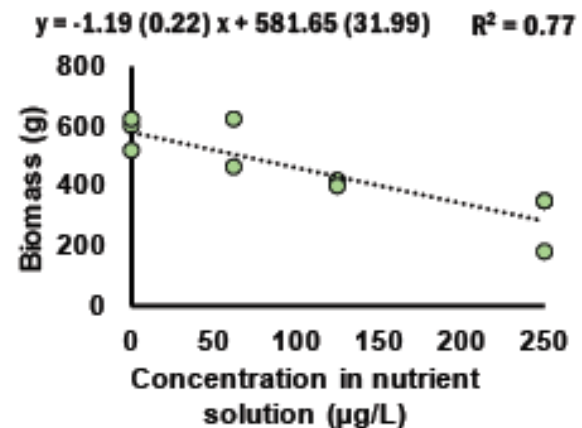
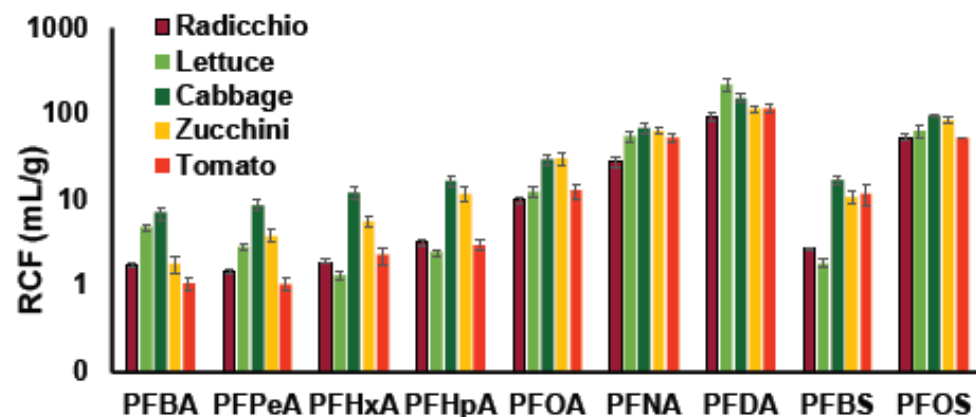


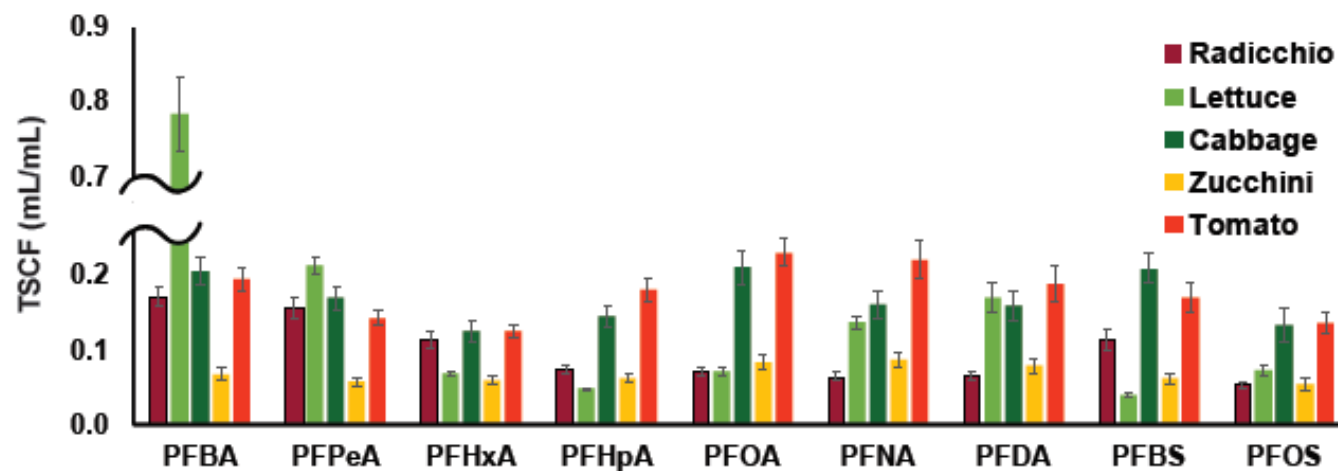
Figure 8. Shoots and roots of the control (left) compared to the treatment 250 (right), 16th day of the experiment

Figure 9. Correlations between nominal concentration in nutrient solution and total plant biomass and nominal concentration and total transpired volume of water



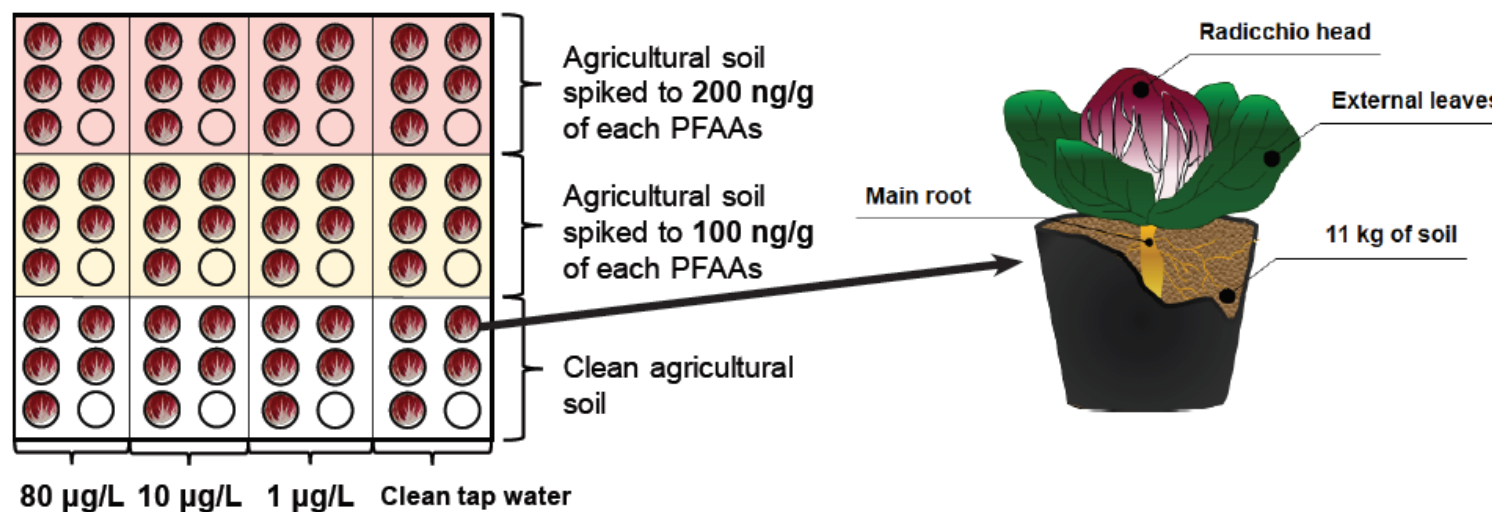


Comparison with other hydroponics experiments

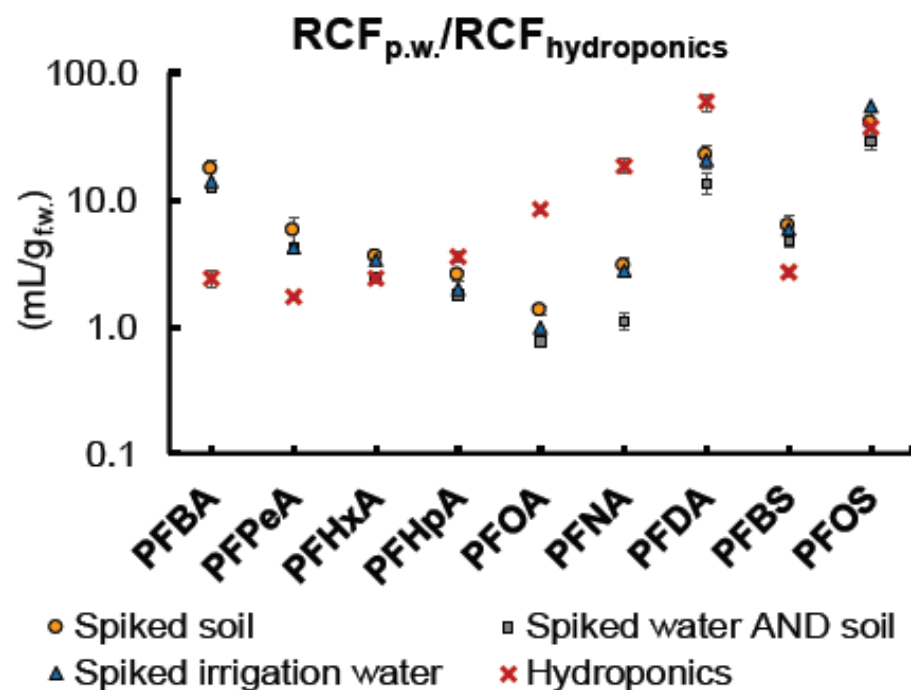


- Long-chained PFAAs mainly accumulate in the crop roots (among 65% and 90% of their mass remained in the roots in this study), while short-chained PFAAs (particularly C3 and C4) are readily transferred to the shoots (80-97% of their mass in this study).
- Compared to carboxylates, sulfonates with the same perfluoroalkyl chain length sorb more strongly to the roots and are transferred less to shoots
- RCFs for the long-chained PFAAs have similar values among crops, while short-chained PFAAs' sorption to roots is more crop dependent
- Generally, TSCFs for PFAAs are low, in the case of radicchio showing only very small decrease between C6 and C9, opposed to most of the other crops where its increase was reported

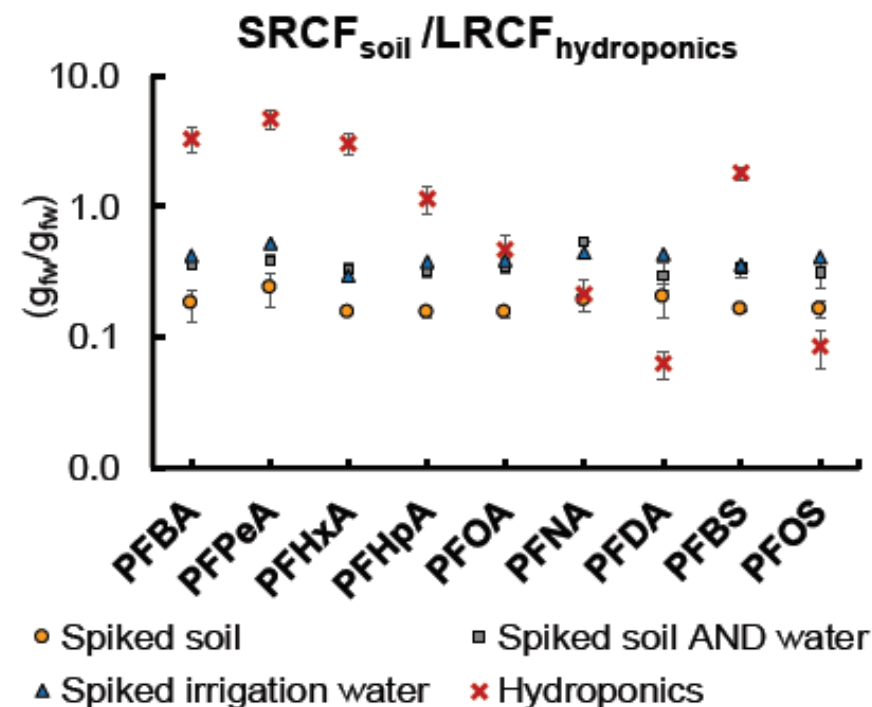
- Radicchio var. Chioggia (*Cichorium intybus* L.) was grown in a greenhouse for a period of 38 days (in hydroponic system) and 87 days (soil experiment)
- Soil experiment was performed in 12 treatments with spiked irrigation water, spiked soil and their combinations
- 9 perfluoroalkyl acids (PFAAs)*
- Kd/Kdes were derived from the batch test for used agronomic soil



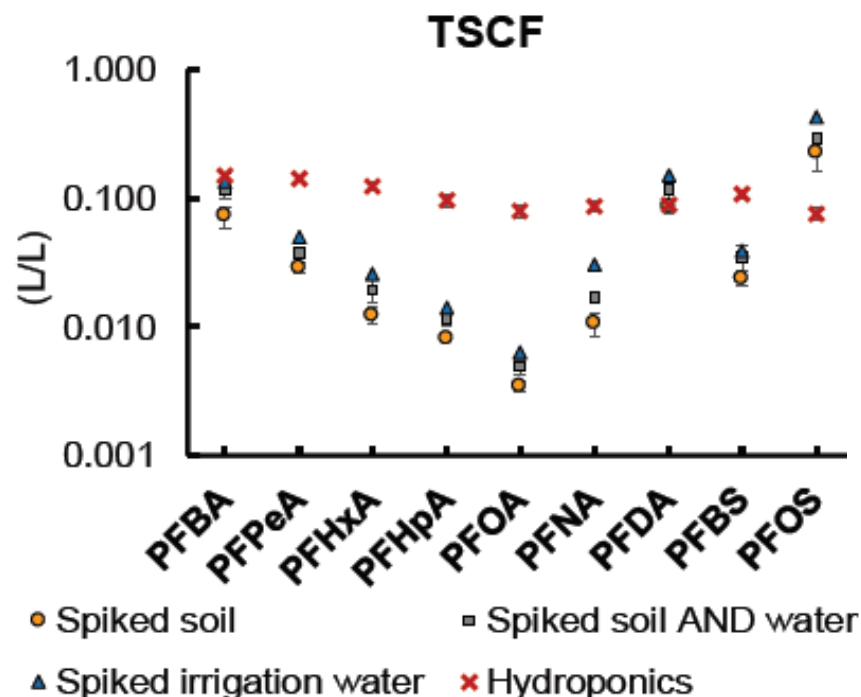
Soil experiment scheme



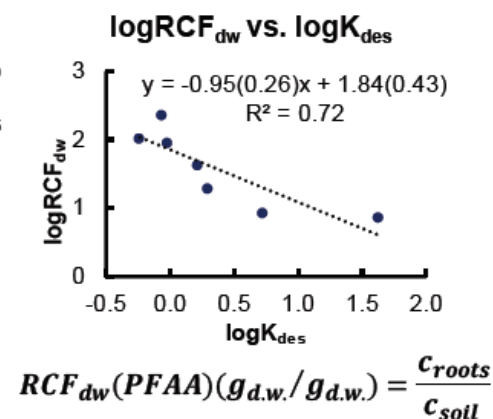
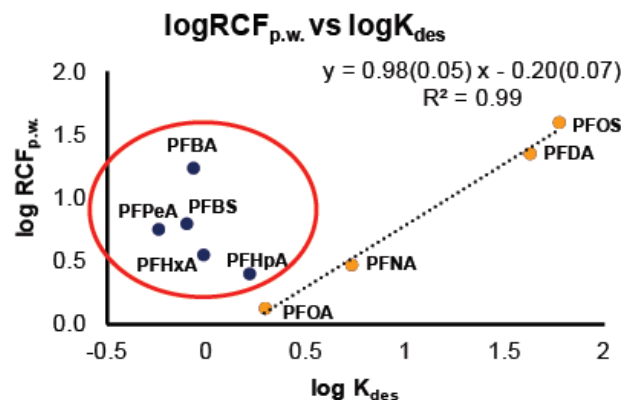
Comparison of the roots concentration factors (RCF)₁ from soil experiment and hydroponics.



Comparison of the shoots (leaves) to roots concentration factors (SRCF/LRCF) from soil experiment and hydroponics.



Comparison of transpiration stream concentration factors (TSCF) from soil experiment and hydroponics.



Correlations of root concentration factors⁴ with soil to water desorption coefficient (K_{des}) for treatments with pre-contaminated soil (in average).

Regression coefficients are shown with standard errors and coefficient of determination of the regression line.

- Clear differences can be seen in the patterns of PFAAs accumulation in roots from hydroponics solution and from the soil pore water
- Transfer of PFAAs from roots to leaves in hydroponics decreases with the PFCAs' chain length increase, while it is mostly constant for radicchio plants grown in soil
- TSCFs were mostly constant in hydroponics and they had a V pattern (min. for PFOA) for the radicchio grown in soil
- Soil is making the difference not only by reducing bioavailability of PFAAs in the pore water by sorption, but also for the roots development (much larger root system was developed in soil, with greater surface)
- Different transpiration volumes were measured for plants from soil experiment (total volume of about 8.6 L in 87 days) and hydroponics (total volume of 19 L in 37 days).
- K_d and K_{des} are very low for the short-chained PFAAs, sorption having almost no influence on bioavailability

- Paper

- Gredelj A., Nicoletto C., Valsecchi S., Ferrario C., Polesello S., Lava R., Zanon F., Barausse A., Palmeri L., Guidolin L., Bonato M. Uptake and translocation of perfluoroalkyl acids (PFAA) in red chicory (*Cichorium intybus* L.) under various treatments with pre-contaminated soil and irrigation water. Science of the Total Environment (2019). STOTEN 134766, doi: <https://doi.org/10.1016/j.scitotenv.2019.134766>
- Gredelj A., Nicoletto C., Polesello S., Ferrario C., Valsecchi S., Lava R., Barausse A., Zanon F., Guidolin L., Palmeri L., Bonato M. Uptake and translocation of perfluoroalkyl acids (PFAAs) in hydroponically grown red chicory (*Cichorium intybus* L.): Growth and developmental toxicity, comparison with growth in soil and bioavailability implications. Science of the Total Environment (2020). STOTEN 137333, doi: <https://doi.org/10.1016/j.scitotenv.2020.137333>