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Influence of soil on the uptake of perfluoroalkyl acids by lettuce: A comparison between a hydroponic study and a field study

Sebastian Felizeter [a, 1], Heinrich Jürling [b], Matthias Kotthoff [b, 2], Pim De Voogt [a, c], Michael S. McLachlan [d, *]

[a] Universiteit van Amsterdam, Institute for Biodiversity and Ecosystem Dynamics, Science Park 904, 1098XH, Amsterdam, the Netherlands
[b] Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Schmallenberg, Germany
[c] KWR Water Research Institute, Nieuwegein, the Netherlands
[d] Department of Environmental Science (ACES), Stockholm University, Sweden

HIGHLIGHTS

- Root uptake of PFAAs was compared in lettuce grown hydroponically and in soil.
- Transfer to roots was 1–2 orders of magnitude greater under hydroponic conditions.
- Transfer to foliage was similar in lettuce grown hydroponically and in soil.
- Soil reduces sorption of PFAAs from pore water to root surfaces.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

This study explores whether mechanistic understanding of plant uptake of perfluoroalkyl acids (PFAAs) derived from hydroponic experiments can be applied to soil systems. Lettuces (*Lactuca sativa*) were grown in outdoor lysimeters in soil spiked with 4 different concentrations of 13 PFAAs. PFAA concentrations were measured in soil, soil pore water, lettuce roots, and foliage. The PFAA uptake by the lettuce was compared with uptake measured in a hydroponic study. The foliage:pore water concentration ratios in the lysimeter were similar to the foliage:water concentration ratios from the hydroponic experiment. In contrast, the root:pore water concentration ratios in the lysimeter were 1–2 orders of magnitude lower than in the hydroponic study for PFAAs with 6 or more perfluorinated carbons. Hence, hydroponic studies can be expected to provide a good quantitative measure of PFAA transfer from soil to foliage if one accounts for soil:pore water partitioning and differences in transpiration rate. However, hydroponic studies will be of little value for estimating PFAA transfer from soil to roots because sorption to the root surface is greatly enhanced under hydroponic conditions.

1. Introduction

Perfluoroalkyl acids (PFAAs) have been detected ubiquitously in water (Ahrens, 2011; Eschauzier et al., 2012; Xiao, 2017), biota (Giesy and Kannan, 2001; Langberg et al., 2018) and the atmosphere (Dreyer et al., 2008; Rauert et al., 2018) as well as in human

* Corresponding author.
E-mail address: michael.mclachlan@aces.su.se (M.S. McLachlan).
[1] Current address: Eurofins Dr. Specht International GmbH, Hamburg, Germany.
[2] Current address: Hamm-Lippstadt University of Applied Sciences, Department 2, Hamm, Germany.

blood serum and breast milk (Volkel et al., 2008; Winkens et al., 2017; Jin et al., 2020). They have known and suspected toxic effects (Lau et al., 2008; Anderko et al., 2020), and human exposure occurs via food (D'Hollander et al., 2010; Fromme et al., 2009; Klenow et al., 2013). In response to concerns about these chemicals, the European Food Safety Authority established tolerable daily intakes (TDIs) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), and they have recently presented a proposal to add perfluorononanoic acid (PFNA) and perfluorohexane sulfonic acid (PFHxS) while reducing the TDI for the sum of all four (Johansson et al., 2009; Knutsen et al., 2018). To ensure that the TDIs are not exceeded, we must understand the sources of PFAAs in food. Crops are one possible vector for PFAAs into the food supply. Crops have been shown to take up PFAAs from soil (Stahl et al., 2009; Zhao et al., 2013) and soils can be contaminated with PFAAs (Wilhelm et al., 2008; Rankin et al., 2016). This work aims to further our understanding of how PFAAs are transferred from soils into crops.

Plant uptake of PFAAs via the roots has been studied using several experimental designs. The first studies published were soil-based experiments. Stahl et al. (2009) and Lechner et al. (2011) showed that the concentration of PFOA and PFOS in several crops was linearly proportional to the concentration in the soil in which they were grown. Since then there have been several reports of uptake of a broad spectrum of PFAAs in vegetation growing in biosolids-amended soils. They show that the length of the perfluoroalkyl chain is the dominant variable influencing PFAA uptake in foliage. Foliage concentration factors (FCFs) are negatively correlated with chain length (Yoo et al., 2011; Blaine et al., 2013; Wen et al., 2014; Narvaro et al., 2017). For grasses, an average decrease in FCF of 0.24 log units per CF_2 group was observed (Yoo et al., 2011), while for lettuce and tomato plants the average decrease was 0.3 log units per CF_2 group (Blaine et al., 2013). Regarding PFAA accumulation in root tissue, a much weaker influence of chain length has been observed. For instance, the variation in root concentration factors (RCFs) for C5−C10 perfluoroalkyl carboxylic acids (PFCAs) was just 0.5 log units for radish, celery, tomato and pea (Blaine et al., 2014). A similarly small variation was found between PFHxA, PFOA, PFBS, PFHxS and PFOS in wheat (see Tables S1 and S2 in the Supporting Information for a list of the abbreviations of the different PFAAs and their full chemical names) (Lan et al., 2018). In contrast, root concentration factors in chicory showed a pronounced dependence on the chain length, suggesting that root accumulation is influenced by species and soil type (Gredelj et al., 2019).

Hydroponic experiments provide an opportunity to obtain a more systematic understanding of contaminant accumulation in plants. For instance, a hydroponic experiment was used to assess the influence of different metabolic inhibitors on the uptake of PFOA and PFOS in maize shoots (Wen et al., 2013). The influence of pH on PFAA uptake into maize roots was also elucidated in a hydroponic experiment, showing no effect in a pH range of 5−7 for nine of the ten PFAAs studied (Krippner et al., 2014). A hydroponic study was used to explore the effect of temperature and salinity on PFAA uptake in wheat, identifying a positive effect for both, which was attributed to increased evapotranspiration (Zhao et al., 2016).

Hydroponic experiments have also been used to study how perfluoroalkyl chain length influences uptake in plants. PFAAs with perfluoroalkyl chain lengths ranging from 3 to 13 were all transferred via the roots to the plant foliage in lettuce, tomato, cabbage and zucchini (Felizeter et al., 2012, 2014). Transpiration stream concentration factors (TSCFs, the quotient of the concentration in the xylem flow and that in the nutrient solution) for C4−C10 PFAAs ranged over just a factor of two for three of the four species. Relatively high TSCFs of 0.05−0.8 showed that the PFAAs were

clearly able to cross the Casparian strip and plasma membranes that prevent the passive entry of many polar molecules into the vascular tissue of the root (Felizeter et al., 2012). A weak influence of chain length on TSCF was also observed in grass (García-Valcárcel et al., 2014).

Hydroponic studies have also been used to study PFAA uptake into roots. In lettuce, the root-nutrient solution concentration factor decreased with chain length for C4−C6 PFCAs before increasing by almost 3 orders of magnitude from PFHxA to PFUnA. While the accumulation of the shorter chained compounds was explained by uptake with the transpiration stream, the uptake of the longer chained compounds was attributed to sorption to the surface tissue of the roots (Felizeter et al., 2012). Hydroponic experiments with tomato, cabbage and zucchini showed a strong positive relationship between root-hydroponic solution concentration factor and chain length for C4−C11 PFAAs, indicating that root-surface sorption was the dominant uptake mechanism for all of the PFAAs in these species (Felizeter et al., 2014). In detailed experiments with a hydroponic model plant system (*Arabidopsis thaliana*), Müller et al. (2016) also concluded that the root uptake of all but the shortest PFAAs was governed by sorption and observed that the dead root-hydroponic solution concentration factor increased by almost 3 orders of magnitude from PFBA to PFOS.

Comparing the results from hydroponic and soil experiments, there are clear differences in the chain length dependence of PFAA uptake. In foliage, the hydroponic studies show a weak dependence of uptake on chain length, while soil studies show a very strong dependence. The opposite is the case in roots; the hydroponic studies show a strong positive chain length dependence that is attributed to sorption to root surfaces, while the soil studies show a weak dependence.

It is unclear what the reasons for these differences are, and how and to what extent findings from hydroponic studies can be transferred to natural soil systems. Sorption of PFAAs to soil solids is certainly an important factor, as this reduces the fraction of chemical available for uptake by the roots. To be able to sorb to the root surface or be taken up with the transpiration stream, the compounds first need to be present in pore water. Long chain compounds sorb strongly to the soil; hence, for a long chain PFAA much higher concentrations in soil are required to generate a given concentration in pore water than for short chain PFAAs (Yoo et al., 2011; Zhao et al., 2013; Blaine et al., 2014; Wen et al., 2014). However, there may be other factors that affect the comparability of hydroponic and soil systems. For instance, some contaminants appear to be taken up through the action of root exudates (Campanella and Paul, 2000), which would be highly diluted or not present under hydroponic conditions. Another possibility is that differences in the nature of root tissue when grown under hydroponic conditions influence PFAA uptake and translocation. The uptake of the PFAAs could also be influenced by other solutes present in the soil.

To explore these questions, we conducted a lysimeter experiment in which lettuce was grown in soil containing PFAAs, and compared this with our previous hydroponic experiment conducted with the same plant species, chemicals, sample preparation and analysis. The lysimeter soil was spiked with 11 PFCAs and 2 perfluoroalkane sulfonates (PFSAs). Four lysimeters were used, each with a different spiking level. At maturity the lettuce was harvested and the roots and leaves were analyzed separately. Additionally, the PFAA concentrations in soil and pore water were determined. The measurement of concentrations in pore water facilitated comparison of this experiment with our earlier hydroponic greenhouse study, and thereby identification of differences in the uptake into roots and leaves between soil and hydroponic

growth environments.

2. Materials and methods

2.1. Chemical reagents and lab materials

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonic acid (PFBS) and perfluorooctane sulfonic acid (PFOS) were studied. All standards had a purity >95%. The suppliers and purities of the chemicals, their molecular formulas and the ^{13}C-labeled internal standards used for their quantification can be found in Tables S1 and S2.

Materials used for extraction and clean-up of the samples included Florisil SPE cartridges (1000 mg, 6 mL) from Applied Separations (Allentown, PA, USA); Acrodisc LC13 GHP Pall 0.2 μm filters from Pall Corporation (Port Washington, NY, USA); 50 and 15 mL polypropylene (PP) tubes with screw caps from Sarstedt (Nümbrecht, Germany); and Supelclean ENVI-Carb 120/140 from Supelco (Bellefonte, PA, USA). Tetrabutylammonium hydrogensulfate and sodium hydrogencarbonate were purchased from Merck (Darmstadt, Germany). Sodium carbonate and ammonium hydroxide a. c.s. reagent were from Sigma Aldrich; 2.0 and 0.3 mL PP vials were purchased from VWR International (Amsterdam, Netherlands). Centrifugation filter tubes (50 mL, 0.2 μm nylon filter) were obtained from Grace (Breda, Netherlands).

2.2. Field experiment

The field experiment was conducted at the Fraunhofer Institute for Molecular Biology and Applied Ecology IME in Schmallenberg, Germany. Lettuce plants (*Lactuca sativa*, var. attraction) were grown in 5 lysimeters, one containing soil with background concentrations of PFAAs (unspiked), and 4 with intended concentrations of individual PFAAs in soil of 0.1 mg/kg, 1 mg/kg, 5 mg/kg and 10 mg/kg (all soil concentrations on a dry weight basis). This compares with PFOA and PFOS concentrations of ~1 mg/kg measured in contaminated agricultural soil in Arnsberg, ~30 km from Schmallenberg (Vestergren et al., 2012). The results from the highest spiking level were not used because the lettuce plants were significantly smaller at the time of harvest than those growing in the lower exposure levels, indicating that PFAAs had phytotoxic effects (see Table S3). Phytotoxic effects of PFAAs have been reported elsewhere (Stahl et al., 2009; Qu et al., 2010; Zhao et al., 2011; Qian et al., 2019; Zhang et al., 2019; Chen et al., 2020; Lin et al., 2020).

Each lysimeter had a surface area of 1 m^2 and a total depth of 60 cm. The lysimeters were each filled with ~450 kg sand (30–60 cm depth) and ~450 kg of loamy sand (0–30 cm depth; 71% sand, 24% silt, 5% clay, pH 5.67, organic carbon content 0.93%). This resembled a typical soil from northwestern Germany. The soil used for the upper layer is available as a reference soil (Refesol 01-A) from Fraunhofer IME (www.refesol.de/boden01a.shtml).

The spiking of the soil was done stepwise. First a stock solution was prepared containing all PFAAs in methanol. With this stock solution 2 kg of soil were spiked. Afterwards the 2 kg spiked soil was mixed with approximately 90 kg of soil in a concrete mixer to achieve the desired concentration. This was repeated 5 times for each layer in each lysimeter. Samples were taken from each batch and combined to determine the initial PFAA concentration in the soil of each lysimeter.

The lettuce plants were pre-grown in a greenhouse for 2 weeks in non-spiked soil before they were transferred to the lysimeters. Within one week of preparing the spiked soil, 20 lettuce seedlings were put in each lysimeter (on June 21, 2011). The seedlings were watered after planting, and kept humid by rain events until harvest with supplementary watering when needed (a total of 17 L of tap water per lysimeter distributed over 5 occasions). After 72 days the lettuce plants were harvested (on September 1, 2011). The plants were divided into roots and foliage, packed in freezer bags and stored at −20 °C until analysis. Soil samples were taken with a soil corer when the plants were harvested. The soil core, which was taken from the top to the bottom of the lysimeter, was divided between the upper and lower soil layers, and the soil was packed in freezer bags and stored at −20 °C for later separation of pore water and analysis.

2.3. Extraction and clean-up

Before homogenization with a household blender (Braun Multiquick MX, 2050) the roots were rinsed with demineralized water to wash off residual soil and then carefully dried superficially with paper towels. As no residual soil was visibly apparent on the leaf samples, no cleaning was performed.

The extraction method used is based on the modification Vestergren et al. (2012) proposed for the method published by Hansen et al. (2001). Briefly, 10 g of the homogenate were weighed into a 50 mL PP tube and spiked with mass-labeled surrogate standards. After adding 5 mL of 0.4 M NaOH solution and vortex-mixing, the samples were left in the refrigerator (4 °C) over night to allow the internal standards to distribute in the slurry. Next, 4 mL of 0.5 M tetrabutylammonium hydrogensulfate solution and 5 mL of a carbonate buffer (0.25 M Na$_2$CO$_3$/NaHCO$_3$) were added to the samples and thoroughly mixed. After adding 10 mL MTBE and vortex-mixing for 1 min the samples were sonicated for 10 min. Phase separation was achieved by centrifuging for 10 min at 3000 rpm. The MTBE phase was transferred to a new 50 mL PP tube and the extraction repeated two times. The extracts were combined and concentrated to approximately 2 mL using a Rapidvap (Labconco Corp., Kansas City, MO, USA). After adding 1 g of sodium sulfate to Florisil SPE-cartridges to remove any remaining water in the extracts, the cartridges were conditioned with 10 mL MeOH and 10 mL MTBE before they were loaded with the extract. The elution of the non-polar matrix was done with 10 mL MTBE before the target compounds were washed off the cartridge with 10 mL MeOH/MTBE (30:70, v:v). This extract was again evaporated to 1 mL final volume. An additional clean-up step following the Powley method with ENVI-Carb (Powley et al., 2005) was added when the final extract was still strongly colored.

For the analysis of PFAAs in soil, the soil was dried in an oven at 40 °C until no further weight loss was recorded. After homogenization, 1 g of dried soil was weighed in a 15 mL PP tube and spiked with internal standards. The soil was then extracted with 10 mL MeOH by vortex mixing for 1 min and sonication for 10 min. Phase separation was achieved by centrifugation (10 min, 3000 RPM). The supernatant was transferred to a new 15 mL PP tube and concentrated in the Rapidvap. The extraction was repeated twice with 5 mL MeOH. The extracts were combined and concentrated in the Rapidvap to a final volume of 1 mL.

For pore water analysis 20 g of the soil was put in a 50 mL centrifugation filter tube with a 0.2 μm nylon filter. After 20 min of centrifugation at 2000 RPM, 0.5 mL of pore water was transferred to a vial. The internal standards and MeOH were added to achieve a final volume of 1 mL.

All final extracts were passed through an Acrodisc LC 13 GHP Pall nylon filter into 2 mL PP vials and stored at 4 °C until analysis.

2.4. Analysis

An HPLC system (LC-20AD XR pump, SIL-20 A autosampler and SCL-10 A VP system controller, Shimadzu, Kyoto, Japan) coupled with a tandem mass spectrometer (4000 QTrap, Applied Biosystems, Toronto, Canada) was used to analyze the samples for PFAAs. A pre-column (Pathfinder 300 PS-C$_{18}$ column, ID 4.6 mm; length 50 mm; 3 μm particle diameter; Shimadzu, Duisburg, Germany) prior to the injection valve was used to remove potential background contamination from the LC system.

Separation of the analytes was achieved using an ACE 3 C18-300 column (ID 2.1 mm; length 150 mm; 3 μm particle diameter; Advanced Chromatography Technologies, Aberdeen, Scotland) maintained at 30 °C with a mobile phase gradient consisting of two eluents A (40:60 MeOH:H2O, v:v) and B (95:5 MeOH:H2O; v:v), both containing 2 mM ammonium acetate. The gradient used for separation and the mass transitions as well as other mass spectrometer settings can be found in the Supporting Information. The mass spectrometer was equipped with an electrospray ionization interface operating in the negative ionization mode, and it was run in a scheduled MRM-mode.

The purified extracts were diluted 1:1 with water prior to analysis to match the injection conditions of the HPLC. A volume of 20 μl was injected.

Raw data were processed with the Analyst 1.5 software (Applied Biosystems).

2.5. Quality assurance and control

Each sample was extracted three times and each extract was injected in duplicate. The relative standard deviation of the concentrations derived from these six injections was <10% for all analytes in all samples.

Concentrations were quantified using a twelve-point calibration with fitted correlation lines that had r^2 values of >0.99 for all analytes; no weighting was applied. Further information on quality assurance and quality control is provided in our previous studies (Felizeter et al., 2012, 2014).

Recoveries were determined by comparison with a matrix free solution spiked with internal standard immediately prior to injection. Average recoveries of the internal standards in the samples were between 22% (PFBA) and 112% (PFDoDA). Since mass labeled internal standards were used for quantifying the analytes, no correction for recovery was necessary. See Table S4 in the Supporting Information for detailed information on recoveries.

Limits of quantification (LoQs) (Table S5 in the Supporting Information) were calculated on the basis of the lowest validated calibration standard (signal to noise ratio ≥10). They were derived from the amount injected back calculated to an extract volume of 1 mL and divided by the average extracted sample quantities. Method blanks were prepared repeatedly with the same extraction procedure as the samples, but showed no quantifiable contamination. Solvent blanks were injected every ten injections to check for contamination of the LC system and for memory effects, but no contamination or memory effects were observed during the study.

All PFAA concentrations from the non-spiked lysimeters (in plant parts as well as in soil or pore water) were subtracted from the concentrations in the spiked lysimeters. Any resulting concentrations below the LoQ were neglected.

Since PFOS is the only compound for which branched isomers were included in the standards used for the calibration curve, branched isomers could only be quantified for PFOS. All reported PFOS concentrations are sum concentrations of non-branched and branched isomers.

3. Results and discussion

3.1. PFAA fate in soil

The soil concentrations at the time of planting were generally within the intended concentration range (Fig. S1). The soil concentrations at the harvest date show that the shortest chain PFAAs, the C4−C6 PFCAs and PFBS, were depleted. Less than 3% of the initial mass was left in the soil (Fig. S1). Depletion occurred in both the upper and lower soil layers (see Tables S6 and S7). In contrast, some 80−90% of the longer chain PFCAs dosed were still present in the soil at the harvest date.

We analyzed the behavior of the PFAAs in the lysimeter soil in another paper in which we include data from 12 other lysimeters prepared in the same manner but planted with different crops (McLachlan et al., 2019). That work showed that the depletion of the shorter chained PFAAs was due to leaching, and that the leaching was greater than anticipated due to interactions between the PFAAs. This accelerated leaching increased with the initial PFAA contamination level of the soil. Lower precipitation towards the end of the growth period contributed to reduced leaching and more stable conditions; two weeks before harvest the lysimeters had already received 91% of the water input for the whole growth period (Fig. S2). Hence, although the lettuce was exposed to changing PFAA concentrations in soil, the evidence indicates that the concentrations were more stable towards the end of the growth period when the plants were largest and transpiring (and thus taking up PFAAs) most.

3.2. Uptake factors

To evaluate the plant uptake of the PFAAs, the PFAA concentrations in the plant tissues were compared with the PFAA concentrations in the sampled exposure media, soil and pore water, using uptake factors. Concentrations in soil were only available for the start of the experiment and at the time of harvest, and concentrations in pore water were only available at harvest. We chose to use the concentrations in exposure media measured at harvest because a much larger portion of the plant growth and transpiration occurred during the latter part of the growth period and because soil concentrations were judged to be more stable (see above). It is nevertheless possible that the uptake factors for the shortest chain PFAAs are somewhat overestimated due to the depletion of these chemicals in the soil over the course of the experiment.

3.3. Root uptake

Root uptake was assessed using RCFs, calculated as the ratio between the PFAA concentration in the roots (on a fresh weight basis) at the time of harvest and the concentration in the corresponding exposure medium (i.e., soil). Two RCFs were calculated, one using the PFAA concentration in the upper layer of the soil (on a dry weight basis) at the time of harvest (RCF$_{soil}$) to represent the exposure medium, and the other using the concentration in the pore-water in the upper soil layer at the time of harvest (RCF$_{porewater}$). For a given chemical, there was some variability between the RCFs from the different contamination levels, with relative standard deviations averaging 0.64 for RCF$_{porewater}$ and 0.35 for RCF$_{soil}$ (Table 1). The higher variability for RCF$_{porewater}$ could be due to a larger uncertainty in the determination of the PFAA concentration in pore water, which could have arisen from the separation procedure, small sample quantity and lower concentrations.

The variability in RCF between chemicals exceeded three orders of magnitude for both RCF$_{soil}$ and RCF$_{porewater}$, and was thus much

Table 1
Root concentration factors (RCFs) for PFAAs in lettuce roots from the three lowest exposure levels, calculated with respect to the concentration in soil pore water (RCF$_{porewater}$) and dry soil (RCF$_{soil}$).

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFOS
RCF$_{porewater}$ (L/kg root fresh weight)[a]													
Level 1	16.2	11.2	0.43	0.02	0.1	5.0						0.11	
Level 2	9.4	3.3	0.37	0.07	0.1	2.0	23				28	0.16	8.8
Level 3	5	1.14	0.14	0.09	0.24	1.57	8.1	61	61	27	9.5	0.28	3.6
Average	**10.2**	**5.2**	**0.31**	**0.06**	**0.14**	**2.9**	**15.5**	**61**	**61**	**27**	**18.8**	**0.18**	**6.2**
RSD[b]	0.56	1.02	0.49	0.60	0.58	0.65	0.68				0.70	0.49	0.60
RCF$_{soil}$ (kg dry soil/kg root fresh weight)[c]													
Level 1	152	68	1.51	0.04	0.08	0.36	0.55	0.51	0.41	0.09	0.07	0.15	0.21
Level 2	92	27	1.41	0.17	0.15	0.39	0.71	0.77	0.36	0.14	0.08	0.21	0.43
Level 3	40	8	0.6	0.17	0.14	0.64	0.84	0.89	0.36	0.15	0.08	0.24	0.38
Average	**95**	**34**	**1.17**	**0.13**	**0.12**	**0.46**	**0.70**	**0.72**	**0.38**	**0.13**	**0.08**	**0.20**	**0.34**
RSD[b]	0.59	0.89	0.43	0.58	0.32	0.33	0.21	0.27	0.08	0.25	0.07	0.23	0.34

[a] Concentrations in roots and pore water are given in Table S10 and Table S8, respectively.
[b] Relative standard deviation.
[c] Concentrations in roots and soil are given in Table S10 and Table S7, respectively.

greater than the variability due to the different contamination levels. The lowest and highest values of RCF$_{soil}$ were measured for PFTeDA (0.08) and PFBA (95), respectively, while the lowest and highest values of RCF$_{porewater}$ were measured for PFHpA (0.06) and PFUnA/PFDoDA (61) (Table 1). RCF$_{soil}$ was particularly elevated for PFBA and PFPeA, which is consistent with other reports for wheat, radish, celery, tomato and pea (Blaine et al., 2014; Lan et al., 2018). However, some of the elevation could be due to the uncertainty in the concentrations of these chemicals in soil (see above). No chain length dependence of RCF$_{soil}$ was observed in another study of wheat (Wen et al., 2014).

Mechanistic insight into the influence of soil on root uptake was obtained by comparing RCF$_{porewater}$ with the RCF values from our previous experiment in which lettuce was grown in a hydroponic solution (RCF$_{hydroponic}$) (Wen et al., 2014). Both RCF$_{porewater}$ and RCF$_{hydroponic}$ are referenced to water, which facilitates comparison. The maximum concentrations in the nutrient solution in the hydroponic experiment (~1 µg L^{-1}) were somewhat below the concentration range observed in pore water in the field experiment (2−900 µg L^{-1}). RCF$_{hydroponic}$ and RCF$_{porewater}$ show a similar pattern with PFAA carbon chain length, characterized by minimum values for PFHxA and PFHpA, with increasing values towards shorter and longer chain lengths (Fig. 1). For PFBA and PFPeA there
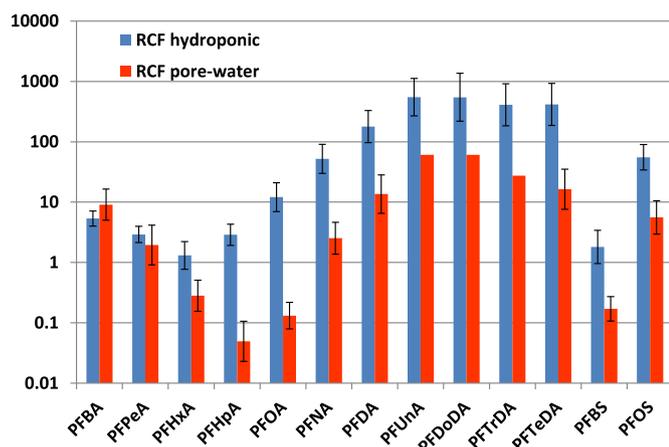
was good agreement between RCF$_{hydroponic}$ and RCF$_{porewater}$ (5.6/10.2 and 3.0/5.2, respectively). For the longer chain PFCAs and the PFSAs, RCF$_{porewater}$ was 1−2 orders of magnitude less than RCF$_{hydroponic}$. For these chemicals the hydroponic study greatly overestimated the root uptake under field conditions.

The similar chain length pattern for RCF$_{hydroponic}$ and RCF$_{porewater}$ suggests that similar processes govern the root uptake of PFAAs from these two media. In the hydroponic study it was concluded that PFBA and PFPeA readily crossed the Casparian strip and accumulated in the vascular tissue of the roots (Felizeter et al., 2012). The similar values of RCF$_{hydroponic}$ and RCF$_{porewater}$ for these two chemicals suggest that their transport from solution in pore water across the Casparian strip is similar under hydroponic and soil conditions.

In the hydroponic study it was further concluded that the uptake of the longer chain PFAAs was dominated by sorption to the root surface (Felizeter et al., 2012). In the soil experiment the RCF of PFAAs with perfluoroalkyl chain lengths of six and longer is 1−2 orders of magnitude lower than in the hydroponic experiment. It follows that there are marked differences between hydroponic and soil conditions with respect to sorption to the root surface. This cannot be attributed to differences in the preparation of the root samples, as the same procedure was used in both studies (rinsing with demineralized water, drying on paper towel, homogenization, extraction). One possible explanation is that a significant fraction of the chemical in the pore water was not freely dissolved but rather sorbed to colloidal matter. Since presumably only the freely dissolved PFAAs are available for sorption to the root surface, this would have reduced the root uptake. However, although this hypothesis is plausible for PFDoDA, PFTrDA and PFTeDA for which the concentrations in soil are more than two orders of magnitude greater that the concentrations in pore water (Tables S7 and S8), it cannot explain the differences between RCF$_{hydroponic}$ and RCF$_{porewater}$ for medium chain length PFAAs like PFHpA and PFOA for which the concentration in pore water is similar to or even higher than the concentration in soil. Wen et al. (2013) reported that uptake of PFOA and PFOS into maize roots is modulated by metabolic inhibitors, aquaporin inhibitors and anion channel blockers, but it is not apparent how an absorption model could explain the observed difference in RCF between soil and hydroponic exposure. Zhao et al. (2013) stated in their work that water chemistry variables such as pH and salinity can have an effect on the RCF. The pH dependence of root uptake was also investigated by Krippner et al. (2014). However, the effects that they reported (maximum a factor of 1.7 between pH = 5 and pH = 7) are much smaller than the discrepancy between RCF$_{hydroponic}$ and RCF$_{porewater}$ observed in the

Fig. 1. Comparison of PFAA root concentration factors: RCF$_{soil}$, based on concentrations in soil from this experiment; RCF$_{porewater}$, based on concentrations in pore water from this experiment; RCF$_{hydroponic}$, from a hydroponic experiment (Felizeter et al., 2012). Average values from experiments conducted at different exposure levels are shown. Error bars denote the standard error.

present study. This suggests that other soil pore water properties play a more important role for the sorption of PFAAs to roots.

The one plausible explanation that we have for the discrepancy between RCF$_{hydroponic}$ and RCF$_{porewater}$ is competitive sorption. The pore water contains a multitude of other solutes besides the PFAAs. If they successfully compete for sorption sites on the root surfaces, this would result in less sorption of the PFAAs. To explain inter-species differences in RCF of PFOS and PFOA of a factor 3.5 and 6, respectively, Wen et al. have proposed that lipids in plant root tissue compete with PFAAs for sorption sites in root proteins (Wen et al., 2016). Our results suggest that competition from other solutes in the soil may have an even stronger effect.

3.4. Foliage accumulation

Foliage uptake was assessed using FCFs that were calculated analogously to the RCFs using the PFAA concentrations in the foliage (on a fresh weight basis) at the time of harvest. For a given chemical, there was some variability between the FCFs from the different contamination levels, with relative standard deviations averaging 0.67 for FCF$_{porewater}$ and 0.45 for FCF$_{soil}$ (Table 2). As for RCF, the higher variability for FCF$_{porewater}$ could be due to a larger uncertainty in the determination of the PFAA concentration in pore water.

The variability in FCF$_{porewater}$ between chemicals was much less than for RCF, amounting to a factor of 26. The variability in FCF$_{soil}$, on the other hand, was a factor 8800 and exceeded the variability in RCF$_{soil}$. It showed a strong inverse correlation with chain length, with the lowest and highest values measured for PFTeDA and PFBA, respectively (Table 2). This pronounced inverse correlation for FCF$_{soil}$ with chain length is consistent with other reports in the literature (Yoo et al., 2011; Blaine et al., 2014; Krippner et al., 2015; Navarro et al., 2017; Lan et al., 2018). As with the roots, the properties of the PFAAs clearly have a strong influence on their transfer from the soil environment to lettuce foliage.

In analogy to the RCF, we first compared FCF$_{porewater}$ with FCF$_{hydroponic}$ to obtain mechanistic insight into the influence of soil on the uptake of PFAAs in foliage (Fig. 2). FCF$_{porewater}$ and FCF$_{hydroponic}$ show a similar pattern with chain length; minimum FCFs were obtained for PFHpA and PFOA, with increasing values towards shorter and longer chain lengths. The magnitudes of FCF$_{porewater}$ and FCF$_{hydroponic}$ were also similar; the standard deviations overlapped for all substances except for PFOS (no measure of uncertainty was available for FCF$_{porewater}$ for PFUnA, PFDoDA and PFTrDA), and the median difference was a factor 1.6 (Fig. 2).

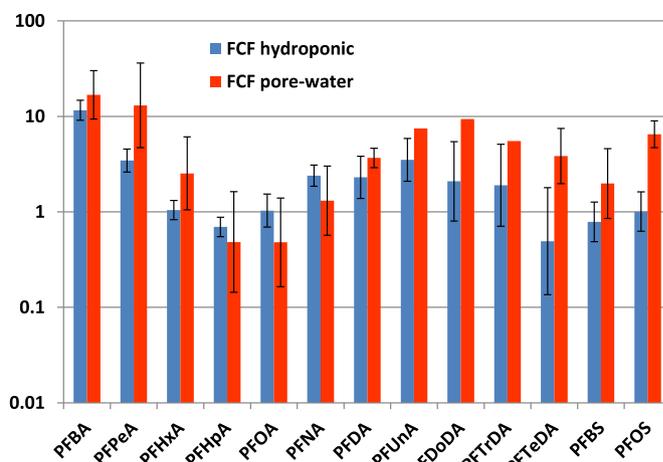Transport from the soil solution to the foliage requires that a

Fig. 2. Comparison of PFAA foliage concentration factors: FCF$_{soil}$, based on concentrations in soil from this experiment; FCF$_{porewater}$, based on concentrations in pore water from this experiment; FCF$_{hydroponic}$, from a hydroponic experiment (Felizeter et al., 2012). Average values from experiments conducted at different exposure levels are shown. Error bars denote the standard error.

chemical first crosses the Casparian strip in the root endodermis and then is translocated with the xylem flow through the roots to the foliage. Underway the chemical can be sequestered into the root tissue. In the hydroponic study the overall effectiveness of this transport was evaluated using TSCF, the quotient of the concentration in the xylem flow and that in the nutrient solution. This is equivalent to the fraction of the chemical originally in the water taken up by the roots that arrives in the foliage. It showed a maximum (0.8) for PFBA, decreasing values with increasing perfluoroalkyl chain length to a minimum (0.05) for PFHpA, followed by increasing values again to PFDoDA (0.3) and thereafter decreasing values to PFTeDA (0.06). It was concluded that the TSCF minimum for PFHpA was the result of lower efficiency of the transport across the Casparian strip (Felizeter et al., 2012). A similar U-shaped dependency of TSCF on perfluoroalkyl chain length was observed in chicory, and retardation factors for root uptake of different PFAAs were determined (Gredelj et al., 2020).

To calculate the TSCF for the lysimeter study, the amount of water transpired (Q_W, L) must be known in order to convert the concentration in the foliage (C_F, mol kg^{-1}) into the concentration in xylem flow (C_X, mol L^{-1}).

Table 2
Foliage concentration factors (FCFs) for PFAAs in lettuce from the three lowest exposure levels, calculated with respect to the concentration in soil pore water (FCF$_{porewater}$) and dry soil (FCF$_{soil}$).

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFOS
FCF$_{porewater}$ (L/kg foliage fresh weight)[a]													
Level 1	31	37	4.8	0.13	0.21	0.5						0.91	
Level 2	16.3	12.3	3.7	0.65	0.34	2.2	4.3				6.1	1.75	5.2
Level 3	9.6	4.9	0.93	1.38	1.59	2.1	3.1	7.5	9.4	5.5	2.4	4.9	8.2
Average	**18.8**	**18.1**	**3.1**	**0.72**	**0.71**	**1.58**	**3.7**	**7.5**	**9.4**	**5.5**	**4.3**	**2.5**	**6.7**
RSD[b]	0.57	0.94	0.63	0.87	1.07	0.59	0.22				0.61	0.83	0.32
FCF$_{soil}$ (kg dry soil/kg foliage fresh weight)[c]													
Level 1	290	230	16.8									1.22	
Level 2	161	99	14.1	1.58	0.51	0.41	0.13	0.09	0.05	0.04	0.02	2.4	0.19
Level 3	78	34	3.9	2.7	0.95	0.85	0.32	0.11	0.06	0.03	0.02	4.2	0.88
Average	**175**	**120**	**11.6**	**2.1**	**0.73**	**0.63**	**0.23**	**0.1**	**0.05**	**0.03**	**0.02**	**2.6**	**0.53**
RSD[b]	0.60	0.82	0.59	0.36	0.43	0.49	0.58	0.14	0.14	0.24	0.00	0.57	0.92

[a] Concentrations in foliage and pore water are given in Table S10 and Table S8, respectively.
[b] Relative standard deviation.
[c] Concentrations in foliage and soil are given in Table S10 and Table S7, respectively.

$$C_X = C_F \frac{Q_F}{Q_W} \tag{1}$$

where Q_F is the mass of the foliage (kg). However, Q_F is not known, so the TSCF cannot be calculated. Nevertheless, the TSCF is related to $FCF_{porewater}$ by a constant (Q_F/Q_W), and therefore the PFAA chain length pattern for $FCF_{porewater}$ corresponds to the PFAA chain length pattern for TSCF. The similarity in the chain length patterns for $FCF_{porewater}$ and $FCF_{hydroponic}$ (Fig. 2) indicates that the relative efficiency of transport across the Casparian strip and translocation through the roots was similar for lettuce grown in the soil and hydroponic environments. Consequently, and in contrast to the results for root uptake, the hydroponic experiment yielded information on PFAA uptake in foliage that could be transferred to field conditions.

With this finding, measurements of foliage accumulation from hydroponic experiments can be integrated in a simple and sensible structure to quantify foliage uptake in the field. In order to quantitatively transfer $FCF_{hydroponic}$ for a given PFAA to the field, two pieces of information are required. One is the ratio of the specific cumulative transpiration in the field to that in the hydroponic study, where the specific cumulative transpiration is defined as the total amount of water transpired during the period of exposure to the PFAAs per gram of foliage biomass. This ratio will vary with the duration of the exposure and the climate, as well as with the conditions in the laboratory experiment (in this study the ratio was ~1.6). The second important piece of information is the soil/pore water distribution coefficient. Since we generally only have information on contaminant levels in soil, we need to understand the soil/pore water distribution in order to employ FCF from hydroponic experiments to estimate levels in foliage in the environment.

Transferring FCF results from hydroponic experiments to other plant species is subject to larger uncertainty than transferring for the same species. Considerable interspecies variation in FCF_{soil} has been observed (Blaine et al., 2014; Gobelius et al., 2017). Some of this can be due to differences in the specific cumulative transpiration of different species. However, marked differences in relative FCF_{soil} for different PFAAs have also been reported. One explanation for this is species specific differences in the TSCF. For instance, the TSCF for lettuce varies widely as a function of chain length, with a very pronounced minimum for PFHpA (a factor of 5 and 4 lower than for PFPeA and PFDA, respectively) (Felizeter et al., 2012), while the TSCF for tomato, cabbage, and zucchini varied by less than a factor of 2 among the C3−C10 PFAAs (Felizeter et al., 2014). This suggests that there are chain length specific differences in the permeability of the Casparian strip barrier for lettuce. It is also conceivable that differences in sorption coefficients to viable root tissue could contribute to species differences in the relative FCFs of PFAAs, as this would create different chromatography-like retention effects during xylem (i.e., the mobile phase) transport through viable root tissue (i.e., the stationary phase) to the foliage. Despite these limitations, hydroponic experiments remain a useful tool for studying the accumulation of PFAAs in plant foliage.

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Declaration of competing interest

The authors declare no completing financial interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.127608.

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