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CRedit author statement

Andrea Gredelj: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization

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Retardation factor (R) for the slow uptake into roots

Model-based analysis of the uptake of perfluoroalkyl acids (PFAAs) from soil into plants

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Abstract

Perfluoroalkyl acids (PFAAs) bioaccumulate in crops, with uptake being particularly high for short-chain PFAAs that are constantly transported with transpiration water to aerial plant parts. Due to their amphiphilic surfactant nature and ionized state at environmental pH, predicting the partitioning behavior of PFAAs is difficult and subject to considerable uncertainty, making experimental data highly desirable. Here, we applied a plant uptake model that combines advective flux with measured partition coefficients to reproduce the set of empirically derived plant uptake and soil-partitioning data for nine PFAAs in red chicory, in order to improve the mechanistic understanding and provide new insights into the complex uptake processes. We introduced a new parameter for retarded uptake (R) to explain the slow transfer of PFAA across biomembranes of the root epidermis, which have led to low transpiration stream concentration factors (TSCFs) presented in literature so far. We estimated R values for PFAAs using experimental data derived for red chicory and used the modified plant uptake model to simulate uptake of PFAA into other crops. Results show that this semi-empirical model predicted PFAAs transport to shoots and fruits with good accuracy based on experimental root to soil concentration factors (RCF_{dw}) and soil to water partition coefficients (K_d) as well as estimated R

25 values and plant-specific data for growth and transpiration. It can be concluded that the
26 combination of rather low K_d with high RCF_{dw} and the absence of any relevant loss are the
27 reason for the observed excellent plant uptake of PFAAs.

28

29 **Keywords:** Plant Uptake; PFOS; PFOA; Membrane Permeability; Exposure Assessment;
30 Transpiration Stream

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a family of anthropogenic chemicals containing at least one perfluoroalkyl moiety ($-\text{C}_n\text{F}_{2n-}$). Due to their high stability and surfactant properties of some PFASs, PFASs have been used in a variety of industrial and commercial products and processes since the 1950s (Buck et al., 2011; DeWitt et al., 2018). It is estimated that more than 4000 individual PFASs are currently present on the market (Cheng and Ng, 2018). Wide-range emissions, high thermal and (bio)chemical stability and amphiphilicity determine their persistence and ubiquitous presence in the environment, from tropical to polar areas (Chen et al., 2017; Greaves et al., 2012).

The most commonly detected (and now “historical”) PFASs in environment, wildlife and humans are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Cheng and Ng, 2018; Krafft and Riess, 2015a). Substances containing a perfluoroalkyl moiety have the potential to be transformed abiotically or biotically through changes in the non-fluorinated part of the molecule into perfluoroalkyl acids (PFAAs), which are regarded as their final stable transformation products (Brendel et al., 2018; Buck et al., 2011; Ghisi et al., 2019). PFAAs are acidic surfactants that, within the group, differ in perfluoroalkyl chain length and in the terminal polar group (consequently forming carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic perfluoroalkyl acids). After their common detection in humans and biota, long-chain perfluorocarboxylic (PFCAs) and perfluorosulfonic (PFSAs) acids (defined as $\geq 7\text{C}$ for PFCAs, $\geq 6\text{C}$ for PFSAs) from C8 to C14 have been voluntarily phased-out by producers and are subject to the subsequent regulation (e.g. PFOS and its salts are restricted under the Stockholm Convention) (Buck et al., 2011). Precursors of short-chain PFAAs are broadly used as their alternatives (Brendel et al., 2018). Long- and short-chain PFAAs were originally distinguished with the assumption that short-chain PFAAs have a lower bioaccumulation potential and are less persistent compared to the long-chain ones (Buck et al., 2011). In animal and human body,

bioaccumulation was accordingly found to steeply increase with chain length (Krafft and Riess, 2015) and to be higher for PFSAAs than PFCAs. However, recent findings have shown the opposite pattern for crops and other plants, whereby short-chain PFCAs are accumulating to a high extent in aerial plant parts (Blaine et al., 2014a; Felizeter et al., 2014; Ghisi et al., 2019). Food of plant origin was identified as an important category contributing to dietary exposure to PFAAs (D'Hollander et al., 2015; Felizeter et al., 2014; Klenow et al., 2013).

PFAAs in the environment are present in anionic form, suggesting weak adsorption to soil (Franco et al., 2009), high water solubility and negligible vapor pressure. This combination of properties, together with their extreme persistence, imposes PFAAs as good candidates for high uptake and accumulation in crops, consequently making the exposure and fate assessment for the soil-plant pathway highly needed. Sorption to soil strongly depends on the soil type and it is not fully ascribable to the soil's organic carbon content (%OC) (Y. Li et al., 2018) but usually increases with the chain length (Guelfo and Higgins, 2013; McLachlan et al., 2019), with long-chain PFAAs adsorbing strongly to soil (McLachlan et al., 2019; Milinovic et al., 2015). Motivated by the contamination event caused by a fluorochemical plant in the Veneto Region, Northern Italy (WHO, 2016), and the significance of the area for the crop production and its extensive irrigation needs (Veneto Region, 2014), a previous study was conducted to measure uptake of 9 PFAAs into red chicory (*Cichorium intybus* L.) under simulated environmental conditions of contaminated soil and irrigation water (Gredelj et al., 2019). Differently from previous studies on PFAAs uptake in crops (Blaine et al., 2014a, 2014b, 2013; Navarro et al., 2017; Xiang et al., 2018), plant-specific data and sorption to soil and roots were also measured and served as input for the plant uptake model derived here.

A widely used plant uptake model is the so-called "standard model" (Trapp, 2015, 2007; Trapp and Matthies, 1995). It combines advective fluxes into and through the plant with partition processes to roots, stem and leaves with volatilization, degradation and dilution by growth as

loss processes. Its adaption to weak acids and bases is available as well (Trapp, 2009). This basic approach has been adopted in assessment tools for contaminated soils (CSOIL (Brand et al., 2007); CLEA (Jeffries and Martin, 2009)), in chemical risk assessment (European Commission, 2003) and in sustainability assessment (dynamicroP (Fantke et al., 2011b, 2011a)). Most, if not all, of these established assessment tools require knowledge of the equilibrium partitioning between environmental compartments, in particular for adsorption to soil (K_d -value) and to plant tissue (root concentration factor RCF). Only, the estimation routines for partitioning implemented in these exposure assessment tools are strictly restricted to neutral, nonpolar chemicals (Trapp et al., 2010). PFAAs do not have typical lipid partitioning mechanisms due to their ionic state and surfactant nature, showing low storage lipid accumulation and high affinity for proteins (Cheng and Ng, 2018; Droge, 2019; Ng and Hungerbühler, 2014) and resulting in great uncertainty of both experimentally and QSAR based K_{OW} -values (Droge, 2019). Therefore, the partition coefficients cannot be estimated from structure or from physico-chemical properties, but need to be determined empirically or by inverse modeling.

In this study, we used experimental soil-water partition coefficients and measured PFAA concentrations in red chicory grown in soil provided by (Gredelj et al., 2019), together with plant-specific input parameters to calibrate the standard plant uptake model for PFAAs. We introduced a new parameter for retarded uptake into roots and xylem, and estimated it for all tested PFAAs. We also evaluated the relationship between the chemical structure (perfluoroalkyl acid's chain length) and root to water, root to soil and water to soil partition coefficients. The model was then applied to other experimental PFAA uptake data presented in literature to validate the modelling approach used. Overall, the outcome of our investigation allows for an improved interpretation of the experimental results and for the comparison of

PFAAs with other chemicals, providing new insights into the uptake mechanisms of PFAAs into crops and being a step forward towards the prediction of the uptake of PFAAs into crops.

2. Methodology

2.1. Perfluoroalkyl acids

Physico-chemical properties of PFAAs differ with the functional group and are decreasing or increasing with the chain length (Smith et al., 2016). A list of the PFAAs used in this study together with their names, structures and relevant physico-chemical properties is shown in Table 1.

Abbreviation	Chemical (common) name	No. of perfluorinated carbons (CF _x)	CAS number	Molar mass (g/mol)	Dissociation constant (pK _a)	Structure
PFBA	Perfluorobutanoic acid	3	375-22-4	214.04	-0.2 to 0.7	
PFPeA	Perfluoropentanoic acid	4	2706-90-3	264.05	-0.06	
PFHxA	Perfluorohexanoic acid	5	307-24-4	314.05	-0.13	
PFHpA	Perfluoroheptanoic acid	6	375-85-9	364.06	-0.15	
PFOA	Perfluorooctanoic acid	7	335-67-1	414.07	-0.16 to 3.8	
PFNA	Perfluorononanoic acid	8	375-95-1	464.08	-0.17	
PFDA	Perfluorodecanoic acid	9	335-76-2	514.08	-0.17	
PFBS	Perfluorobutane sulfonic acid	4	375-73-5	300.1	-6.0 to -5.0	
PFOS	Perfluorooctane sulfonic acid	8	1763-23-1	500.13	-6.0 to -2.6	

Table 1. A list of investigated PFAAs with relevant physico-chemical properties (Smith et al., 2016)

2.2. Experimental data

Experimental uptake data for a mixture of nine PFAAs (Table 1) into red chicory plant compartments were taken from the study of (Gredelj et al., 2019). Only the data from experiments with pre-contaminated soil were considered to avoid non-equilibrium conditions resulting from the use of spiked irrigation water (Blaine et al., 2014b). Briefly, uptake experiments with red chicory (*Cichorium intybus* L.) were performed in a greenhouse located in Legnaro (Italy) from August to November 2018. Plants were grown in pots containing 11 kg of agricultural soil (loam), spiked to nominal concentrations of 100 ng/g_{dw} or 200 ng/g_{dw} of each PFAA. Concentrations of PFAAs in soil were analytically determined at the beginning and at the end of experimental period of 87 days, as well as final concentrations in roots, leaves and heads of the red chicory plants.

For determination of transpiration and growth rates, the pots were weighed before every irrigation. This was also done for non-planted controls to determine evaporative losses of water. The gravimetric water content of the soil was measured at the beginning (before planting) and at the end of the experiments. Moreover, plant biomass was measured at the beginning (by weighing the seedlings before planting) and at the end of the experiments for each plant compartment. Dry matter content of plant tissue was determined by oven drying at 65 °C (72 h).

Partitioning of PFAAs between soil and water was determined by a set of batch adsorption/desorption experiments (following the standardized OECD guideline 106 (OECD, 2000)), using concentration ranges relevant for the plant uptake experiments. For the long-chain PFAAs (i.e. PFOA, PFNA, PFDA, PFOS) both adsorption and desorption-based soil-water partition coefficients were derived, $K_{d,ads}$ (L/kg) and $K_{d,des}$ (L/kg), respectively, only $K_{d,des}$ being relevant for the used treatments with the pre-contaminated soil. For the other PFAAs, concentrations of PFBA, PFPeA, PFBS and PFHxA in solution could not be quantified precisely enough in the consecutive desorption tests performed with “decant-refill” technique, due to their

rather low adsorption to soil and their low concentrations in the desorption reactors (Gredelj et al., 2019). However, considering their low K_d values and the adsorption reversibility of the short-chain PFAAs (Chen et al., 2016; Milinovic et al., 2015), $K_{d,ads}$ values were applied in uptake calculations with the short-chain PFAAs.

Data from (Gredelj et al., 2019), including the measured PFAA concentrations in soil and plant compartments and soil-water partition coefficients are listed in the SI (Tables S1 and S4).

2.3. Model description

The main purpose of the model application here is the interpretation of measured PFAA uptake data. Chemical model input parameters, specific for the investigated PFAAs, were determined either directly from the experimental data or by model calibration. This enabled us to identify plant-specific factors that influence PFAAs uptake and allowed to transfer from the red chicory experiment to other experimental results, assuming that the chemical-specific parameters remain constant and only the environmental parameters vary.

2.3.1. Soil

Earlier plant uptake studies with PFAAs (Bizkarguenaga et al., 2016; Blaine et al., 2014a, 2013; Navarro et al., 2017) provided measured PFAA concentrations in dry soil and bioconcentration factors on a dry weight basis as descriptors for accumulation in plants. Thus, the model was modified to accommodate for dry weight-based root to soil bioconcentration factors (RCF_{dw}) and PFAA concentration in dry soil (c_o).

The gravimetric water content w (g/g) of soil was determined by weighing the wet soil and the soil after drying in the oven at 105°C for 72 h (AS TM International, 2019). The concentration of each PFAA in the pore water c_{pw} (µg/L) of soil is then:

$$c_{pw} = \frac{c_0}{K_d + \frac{w}{\rho_{H_2O}}} \quad (1)$$

161 where c_0 is the respective concentration in dry soil (ng/g_{dw}, measured before planting), K_d (mL/g)
 162 is the soil-water distribution coefficient determined in adsorption or desorption experiments, as
 163 described, and ρ_{H_2O} (g/mL) is the density of water. w is defined as ratio of the mass of water
 164 contained in soil and mass of dry soil.

165 Considering K_{WS} (g/mL) as the concentration ratio between pore water c_{pw} and bulk (wet) soil
 166 concentration c_{soil} (equal to $c_0 / (1 + w)$), the pore water concentration is given as:

$$c_{pw} = K_{WS} c_{soil} = K_{WS} \frac{c_0}{1 + w} = \frac{c_0}{K_d + \frac{w}{\rho_{H_2O}}} \quad (2)$$

167 2.3.2. Roots and shoots

168 PFAs are non-degradable and present in ionic form at environmental pH. Loss due to plant
 169 metabolism, photolysis (or other abiotic degradation processes) and volatilization can thus be
 170 safely neglected (Krafft and Riess, 2015; Liu and Avendaño, 2013). Moreover, in the case of red
 171 chicory, only the root and shoot compartments (later divided into leaves and head) need to be
 172 considered, while stem and fruits can be neglected, simplifying the model to two differential
 173 equations describing mass balances for roots and for shoots (leaves and heads), respectively.

174 The inflow of PFAA from soil pore water and the outflow via xylem lead to the mass balance for
 175 roots (Trapp, 2015, 2002):

$$\frac{dm_R}{dt} = R Q c_{pw} - Q c_{xy} \quad (3)$$

176 where m_R is the mass of contaminant in roots (μg), Q is the transpiration stream (L/d), c_{pw} is the
 177 concentration in pore water (μg/L) and c_{xy} is the concentration in xylem at the outflow of the root

($\mu\text{g/L}$). R is a new factor describing the retardation of uptake relative to water ($R \leq 1$, unitless) (more details are given in the section 2.4.).

Equation (3) can be modified:

- (i) by considering that $c_R = m_R/M_R$, where c_R is the concentration in roots ($\mu\text{g/kg}_{\text{fw}}$) and M_R is the mass of roots (kg),
- (ii) under the assumption of exponential plant growth and constant ratio of transpiration stream and root mass (Q/M_R), where k_R is growth dilution rate (1/d). The concentration in xylem at equilibrium c_{Xy} is c_R/K_{RX} , where K_{RX} is the partition coefficient xylem to root (Trapp, 2007).

The differential equation for the change of concentration in roots therefore becomes:

$$\frac{dc_R}{dt} = R \frac{Q}{M_R} K_{WS} c_{soil} - \frac{Q}{M_R K_{RX}} c_R - k_R c_R \quad (4)$$

The steady-state solution of this differential equation is:

$$c_R = \frac{\frac{R Q}{M_R} K_{WS} c_{soil}}{\frac{Q}{K_{RX} M_R} + k_R} \quad (5)$$

Accordingly, the change of concentration in shoots due to the inflow from roots and with exponential growth dilution is:

$$\frac{dc_S}{dt} = \frac{Q}{M_S K_{RX}} c_R - k_S c_S \quad (6)$$

where c_S is the concentration of contaminant in shoots ($\mu\text{g/kg}_{\text{fw}}$), c_R is the steady-state concentration in roots ($\mu\text{g/kg}_{\text{fw}}$), k_S is the growth rate of the shoots (1/d) and M_S their mass (kg_{fw}). The differential equation (6) was solved analytically for $t = 87$ days. The reader is referred to (Legind and Trapp, 2009; Trapp, 2009, 2007), where more detailed numerical and visual descriptions of the model are provided.

2.4. Model calibration

According to the equations of the standard plant uptake model, all of the chemical that is taken up into the roots partitions between root tissue and xylem water. The latter fraction is translocated upwards. The chemical reaching the shoots accumulates there, as no relevant loss processes occur for PFAAs. Thus, the equation system contains only two chemical-specific parameters, namely:

The **partition coefficient** K_{RX} is describing the equilibrium concentration ratio of the chemical between root tissue and water in the xylem. Xylem solution consists of water, and for neutral compounds, K_{RX} is identical to the partition coefficient between roots and water K_{RW} (also known as root concentration factor RCF) which can be estimated from the K_{OW} (Briggs et al., 1982). For partly ionized substances, additional effects like the ion trap need to be considered (Briggs et al., 1987; Trapp, 2009). For purely ionic substances (like PFAAs), no reliable estimation method has been provided so far. By considering root water content w_R and soil-water partition coefficient K_d (either adsorption or desorption based) it follows that the fresh-weight based partition coefficient K_{RX} (L/kg_{fw}) can be calculated as:

$$K_{RX} = RCF_{dw}(1 - w_R)(K_d + \frac{w}{\rho_{H2O}}) \quad (7)$$

where w_R is the water content of fresh roots, RCF_{dw} is the empirical root concentration factor, calculated as the ratio between measured root concentration of PFAA and total measured concentration in soil (accounting for all PFAA present in soil, not only the fraction that is adsorbed):

$$RCF_{dw} = \frac{\text{PFAA concentration in roots (ng/g}_{dw})}{\text{PFAA concentration in soil (ng/g}_{dw})} \quad (8)$$

The **retardation factor** R has been introduced to interpret the observed values of the transpiration stream concentration factor ($TSCF$), defined as the concentration ratio between

xylem sap and soil pore water (Trapp and Matthies, 1995). Parameter R describes the uptake velocity of a chemical relative to the water and is thus comparable to the plant uptake factor PUF (Gourlay, 2017; Lamshoeft et al., 2018). The underlying mechanism is the difference between root permeability for a chemical and water, so R can be defined as the ratio:

$$R = \frac{P_{R,Chem}}{P_{R,H_2O}} \quad (9)$$

with $R \leq 1$ (advective uptake is never faster than the flow with water), where $P_{R,Chem}$ (m/s) and P_{R,H_2O} (m/s) are the root membrane permeabilities towards chemical and water, respectively. For very polar chemicals (usually ionic, PFAAs included), uptake into the root is slower than that of water, while for other chemicals R equals 1. The effect of $R < 1$ is a slower uptake and thus a lower $TSCF$. For example, measured water permeabilities of barley roots ranged from 0.4 to 6 $\times 10^{-9}$ m/s (Steudle and Peterson, 1998). The membrane permeability for neutral compounds can be estimated with satisfying accuracy from K_{OW} (Trapp, 2004):

$$\log P_{R,Chem} = \log K_{OW} - 6.7 \quad (10)$$

which means that only chemicals with $\log K_{OW}$ less than about -2 (log L/L) would have a membrane permeability slower than water and consequently $R < 1$. For purely ionic substances like PFAAs, such estimates are unreliable.

The $TSCF$ (L/L) can be calculated from established empirical equations, but being also based on the K_{OW} , their applicability is restricted to neutral compounds (Briggs et al., 1982; Dettenmaier et al., 2009). Instead, $TSCF$ can be found from the measured data as:

$$TSCF = \frac{m_s}{c_{pw} \sum(Q t)} \quad (11)$$

where m_s (μg) is the mass of chemical in shoots at the harvest, $\sum(Q t)$ (L) is the total volume of the water transpired during the growth period (until the harvest) and c_{pw} ($\mu\text{g/L}$) is the

concentration of chemical in the pore water. Here, the dynamic solution of the standard uptake model equation (6) for shoots (including both leaves and head in the case of red chicory) was solved for $TSCF = c_{xy}/c_{pw}$:

$$TSCF = \frac{c_s}{(1 - e^{-k_s t})} \frac{M_{shoots} k_s}{C_{pw} Q} \quad (12)$$

The $TSCF$ was calculated with the measured concentrations of each PFAA in shoots c_s ($\mu\text{g}/\text{kg}_{fw}$) for $t = 87$ days.

Principally, the $TSCF$ can also be calculated with the root model equation (Trapp, 2007):

$$TSCF = \frac{c_{xy}}{c_{pw}} = \frac{R Q}{Q + K_{RX} k_R M_R} \quad (13)$$

Vice versa, if the $TSCF$ has been measured, the retardation factor can be calculated from $TSCF$ (as was done here):

$$R = TSCF \left(1 + \frac{K_{RX}}{Q} k_R M_R \right) \quad (14)$$

2.5. Plant parameters and model parametrization

Plant-specific parameters can have a very significant impact on the uptake of chemicals into plants (Trapp, 2015). In the present study, transpiration and growth rates, together with water contents of the soil and crops were measured, providing the site-specific data set for fitting the measured PFAA concentrations in crop compartments and soil. The average transpiration coefficient (volume of water transpired per mass of the plant weight) was $35.2 \text{ L}/\text{kg}_{fw}$. From the measured data, average daily transpiration rate and growth rates were calculated (Text S1) and the input parameters are shown in Table S2. All data were calculated and fitted to individual plants (pots) and the results are shown as average per each treatment (initially 12 treatments, each with 5 planted pots and one empty pot that included only soil and no plant (Gredelj et al., 2019)). As the shoot concentrations (calculated from the measured concentrations and masses

of heads and leaves) were used for calculation of R values, model performance was tested for the chicory leaves and heads separately by using the determined plant specific data listed in Table S2.

2.6. Applying the modeling approach to other crops

In order to test the semi-empirical model calibrated for PFAAs uptake into red chicory, the model and the calibrated values of R were used to estimate concentrations in roots, shoots and fruits of tomato, celery, pea and radish plants. In the respective studies, soil-water partition coefficient K_d and compartmental concentrations of the same set of PFAAs were determined (Blaine et al., 2013; Blaine et al., 2014a), but no plant specific input data except time to harvest and water content of plant material were available. Accordingly, for these experimental results, model calculations were made with the default plant dataset listed in (Trapp, 2015). To evaluate the significance of using the plant specific data (Table S5), red chicory uptake was additionally simulated with the default parameters and compared to simulations with chicory-specific plant data.

2.7. Statistical evaluation of the results

The performance of model calculations was evaluated by the means of least-squares linear regression between predicted and measured concentration values in the different plant compartments for all PFAAs. With axis intercept forced to zero, the slope is a measure of the accuracy of the model simulations, while R^2 is a measure of the calculations precision. All statistical analyses were performed using the Data Analysis ToolPak from MS Excel® add-in.

3. Results and discussion

3.1. Modeling results and measurements

Figure 1 shows measured and calculated concentrations of PFAAs in leaves and heads of red chicory, based on chicory-specific plant data and the nominal exposure concentrations of 100

and 200 ng/g_{dw} (namely, from (Gredelj et al., 2019), treatments S100W0 and S200W0). Data are shown from the lowest to the highest perfluoroalkyl chain length, including both PFCAs and PFSA. For both heads and leaves, the model expectedly reproduced the trend of PFAAs distribution in leaves and heads (R^2 -values of the regression lines between modeled and measured values being > 0.92, Table S8), always overestimating concentrations for leaves (slopes of the regression line were 1.26 and 1.32 for S100W0 and S200W0, respectively, Table S8). Overestimated modeled concentrations could be the consequence of the oldest leaves that withered and were, therefore, not extracted and analyzed. They transpired for the longest period and probably had higher concentrations (than those actually measured in the remaining leaves) of accumulated PFAAs, as stated in (Gredelj et al., 2019). The model performed generally better for the treatment S100W0 and performance was better for PFCAs than PFSAs (estimation statistics improved after neglecting PFBS and PFOS from regression of modeled and measured concentrations, Table S8).

Figure 1. Comparison of the calculated and measured PFAA concentrations in red chicory leaves and head for two exposure concentrations. Estimated standard errors are shown for the measured data. Measured values are taken from (Gredelj et al., 2019).

3.2. R values

Figure 2 shows the estimated R values for the two exposure concentrations used in the experiments. Values of R for PFCAs decline with chain length, from $3CF_x$ to $7CF_x$, but increase from $7CF_x$ to $9CF_x$, in an almost log-linear pattern.

Due to the relatively low K_{RX} -values, the numerical values of R are close to the values of the $TSCF$ (Table 3). Except for PFOS, PFDA and PFBA, all PFAA have $TSCF$ and R -values smaller than 0.1. Similarly, (Briggs et al., 1987) found $TSCF$ -values of weak acids with pK_a about 3 (pK_a 2.84 to 3.7) at pH 7 (thus, about 99.99% ionized) rather constant at 0.02 to 0.05 L/L, median 0.04 L/L. This is close to the lower R values observed here, obtained for the short-chain PFAAs (except PFBA), which were between 0.01 and 0.09.

PFAA	K_{RX} (L/kg)		$TSCF$ (L/L)		$K_{RX}/TSCF$ (L/kg)	
	S100W0	S200W0	S100W0	S200W0	S100W0	S200W0
PFBA	13.7	20.7	0.22	0.18	62.0	116.1
PFPeA	4.18	7.27	0.09	0.08	47.5	90.8
PFBS	5.16	7.42	0.06	0.08	81.1	98.7
PFHxA	3.15	3.97	0.04	0.04	88.7	102.2
PFHpA	2.28	2.78	0.02	0.03	95.1	94.4
PFOA	1.25	1.40	0.01	0.01	93.1	98.1
PFNA	3.47	2.47	0.04	0.04	82.3	70.4
PFDA	26.6	17.5	0.29	0.26	90.5	68.3
PFOS	50.2	28.7	0.54	0.34	93.6	84.5

Table 2. Calculated values of the root-xylem partition coefficient (K_{RX}), transpiration stream concentration factor ($TSCF$) and their ratio ($K_{RX}/TSCF$) for all modeled PFAAs

Trends for PFAA accumulation in shoots and roots were similar (increasing from $3CF_x$ to $9CF_x$ of PFCAs) (Gredelj et al., 2019), implying that PFAAs substantially entering the roots (and having the highest RCF_{dw}) will also be transferred into shoots with transpiration water. Conversely, residual mass accumulated in the root cortex or the apparent free space cannot be translocated upwards and could have been lost before extraction (as explained in Gredelj et al., (2019)), considering the conclusions of (Felizeter et al., 2012) that the longest PFAAs adsorb externally to root surfaces of the lettuce grown in a hydroponic system. In addition to our

hypothesis, the ratio of $K_{RX}/TSCF$ is almost constant, usually not being the case for other chemicals. When the $TSCF$ had been calculated from the original root model (Trapp, 2007) it gave a sigmoid curve, similarly to what had been observed by (Dettenmaier et al., 2009), with highest $TSCF$ values for polar compounds (low K_{RX}), while low $TSCF$ values had been calculated for strongly adsorbing lipophilic compounds (high K_{RX}) (Trapp, 2007). In other words, there was an inverse relation between adsorption to roots and translocation to shoots for neutral, lipophilic compounds. The low $TSCF$ -values found here for PFAAs, therefore, are not originating from the adsorption to root tissue and retention within the main root, but due to their deceleration in the epidermal cell membranes, here described by the new factor R . The increase in R , observed with chain length increase above $7CF_x$, may be a consequence of the pronounced surfactant nature of these PFAAs. They could have formed a film around the root cell membranes and either resided in the apparent free space (up to 40% of the root volume) (Mc Farlane and Trapp, 1994) or on the membrane surfaces, a possibility even when the cell interior is accessible for PFAAs.

Figure 2. a) Calculated retardation factor (R) values for two exposure treatments. Average R -values for both treatments are shown as numerical values above the bars. b) Treatment-averaged $\log R$ in relation to PFCA chain length. Standard error estimates of two averaged treatments are shown as error bars.

3.3. Partitioning

The currently unknown link between the structure of PFAAs and their adsorption behavior requires experimental determination of sorption to soils, sediments or tissues (Droge, 2019). Measured K_d values of short-chain PFAAs do not correlate well with the organic carbon content (%OC) (F. Li et al., 2018; Y. Li et al., 2018; Milinovic et al., 2015; Zhu et al., 2014), and observed K_d values for PFAAs in different soils and sediments can vary significantly (e.g. between 0.1 and > 3000 L/kg for PFOS), underlining the need for experimental determination (F. Li et al., 2018; Y. Li et al., 2018). Nonetheless, to our knowledge, only one plant uptake study of PFAAs (apart from (Gredelj et al., 2019)) included experimental determination of the K_d values of the growth medium (Blaine et al., 2014a, 2013).

The K_d values of PFCAs determined in these studies show a close relation to chain length, with almost log-linear increase with the number of carbon atoms of perfluoroalkyl chain (CF_x) (Figure 3c showing the relationship from (Gredelj et al., 2019)). The K_d values for PFCAs with less than 6 CF_x are below 1 L/kg, indicating very low adsorption to soil and a significant fraction of the chemical present in the soil pore water. On the contrary, RCF_{dw} values are the highest for short-chain PFCAs, being up to 260 kg/kg_{dw} (Figure 3a). Attempts to correlate the RCF_{dw} to octanol-water distribution coefficient, $\log D$ (estimated using ACD/i-Lab) were unsuccessful and are not shown. Similarly, estimated adsorption to human serum albumin K_{HSA} data were unsuccessful for the prediction of the adsorption to roots. However, RCF_{dw} shows a declining and K_d an increasing trend with the chain length (Figure 3 bc).

The combination of comparably low adsorption to soil (K_d) and rather high partitioning into roots leads to an unusually high ratio of RCF_{dw} to K_d for the short-chain PFAAs (Figure 3a). The measured ratio (average of both treatments) was from 263.5 kg/kg for PFBA to 11.4 kg/kg for PFHpA while it was lower for the long-chain PFAAs, ranging between 4.2 kg/kg (PFOA) and 0.1 kg/kg (PFOS). For other organic compounds, the opposite has been observed, i.e. adsorption to soil is typically similar or higher than adsorption to plant roots (Trapp, 1995). Usually, growth dilution and loss processes within the plant lead to concentrations below equilibrium in roots, and root-to-soil bioconcentration factors <0.01 kg/kg_{dw} have been observed for lipophilic compounds such as benzo(a)pyrene and PCBs (Trapp, 2002). Hence, the partitioning of PFAAs (PFCAs) in the soil-root environment differs very much from that of other organic compounds.

Figure 3. Regression analysis of logarithmically transformed dry weight-based root concentration factors ($\log RCF_{dw}$), soil-water partition coefficients ($\log K_d$) and PFCA chain length for red chicory (from Gredelj et al., (2019)). Standard error estimates ($n = 3$) are shown for measured values of RCF_{dw} . Regression lines are shown with standard errors in brackets and coefficients of determination.

3.4. Other crops

By adapting the plant specific input data (Tables S12 and S15), the model can be applied to other plant species when the retardation factor R of each PFAA remains the same. In order to test this assumption, the approach was applied to literature crop data-sets for PFAAs (Blaine et al., 2014a, 2013). Modeled concentrations in plant compartments of tomato, celery, pea and radish are shown in Figure 4, together with the measured values. Like before, measured RCF_{dw} was used to calculate K_{RX} (Eq. 7). For PFAAs with high K_{RX} (PFOS and PFDA), growth dilution leads to calculated root concentration somewhat below equilibrium (Table S9).

Concentration trends in shoots were estimated mostly accurately for all four crops, their values always being in the same order of a magnitude (slopes of the regression line between measured and modeled values ranging between 1.22 and 1.73), even though the R values were taken from the red chicory experiments and default plant data were used (Trapp, 2015). In particular, estimations were better for the short-chain PFAAs (improving of the model evaluation statistics was noticed after elimination of long-chain PFAAs, Table S9) and for the tomato and pea (R^2 values of 0.75 and 0.86, respectively). For radish and celery, modeled concentrations are not far from the measured ones (R^2 values of 0.78 and 0.52), despite of their overestimation (model evaluation slopes of 1.73 and 1.32) and similar trends are shown among them (e.g., lowest concentration for PFNA). Differences between measurements and simulation results could be attributed to the use of default data instead of the carefully determined plant-specific data in the case of chicory. This hypothesis was confirmed by comparing simulation results of the red chicory experiments using measured and default plant parameters sets, whereby worse model performance was observed in the latter case, with underestimation of PFOS and PFDA in roots and shoots, and overestimation in shoots for most of the other PFAAs (see Figure S1 and

accompanying evaluation statistics). Overestimation with the default plant data for red chicory is in consistence with observations of the model performance for the other crops.

Simulation results for fruits typically overestimated measured data (Table S9), except for short-chain PFAAs, and exhibited the poorest fit for PFDA and PFOS. Notably, the fruit compartment is very rudimentary described in the current version of the standard plant uptake model, being identical to the leaf but with reduced water flux (this is why calculated fruit concentrations follow very closely the trend of the shoots, but about one order of magnitude lower). Complex processes that lead to phloem loading and unloading are not adequately expressed in the equations.

Interestingly, except for celery, RCF_{dw} values of these experiments show no significant correlation with the PFAA chain length (Blaine et al., 2014a) and the calibrated RCF_{dw} values are lower than those reported in (Gredelj et al., 2019) (Figure S2). More data for root and soil concentrations are available for PFOS and PFOA than for the other PFAAs (Table S7). The experimental RCF_{dw} of PFOS found in literature ranged from < 0.1 to 8.38 kg/kg, with an average of 2.93 kg/kg (Bizkarguenaga et al., 2016; Blaine et al., 2014a; Lan et al., 2018; Navarro et al., 2017; Wen et al., 2016, 2014; Zhao et al., 2017) while for the red chicory treatments S100W0 and S200W0 they ranged from 6.14 to 11.35 kg/kg. For PFOA, experimental RCF_{dw} found in literature ranged from 0.8 to 10.34 kg/kg, with average 3.3 kg/kg (Bizkarguenaga et al., 2016; Blaine et al., 2014a; Lan et al., 2018; Navarro et al., 2017; Wen et al., 2016, 2014; Zhao et al., 2017) while the range for red chicory was from 8.10 to 10.31 kg/kg.

Figure 4. Comparison of modeled and measured PFAA concentrations in crops. Measured values are shown as means with standard errors and are taken from (Blaine et al., 2014a, 2013).

4. Conclusions

"Mathematical models provide a framework for understanding the cycling of compounds through environment" (Ramaswami et al., 2005). We thus applied a plant uptake model to interpret measured plant uptake data for PFAAs and gained new insights in uptake processes and accumulation mechanisms.

The high concentrations of perfluoroalkyl acids (and in particular short-chain PFAAs) in crops are neither due to rapid plant uptake, nor due to active or preferential transport, nor due to exceptionally high adsorption to plant material. We found two main reasons for the observed high accumulation potential of PFAAs in terrestrial crop plants:

i) Partition coefficients. The root-to-xylem partition coefficients K_{RX} , here derived from measured RCF_{dw} , ranged from < 1 to 54 L/kg_{fw} . The highest values were observed for the shortest PFAA ($3CF_x$, PFBA), PFDA and PFOS. At the same time, K_d values (expressing adsorption to soil) of the short-chain PFAAs are small, $< 1 \text{ L/kg}$. Thus, these PFAAs show very high bioavailability in soil and rapid transport with water. The combination of low K_d and relatively high K_{RX} (or RCF_{dw}) is rather unusual and has not been described before. The accumulation of chemicals in roots is determined by the ratio K_{RX}/K_d , and this leads to the observed very high concentrations of short-chain PFAAs in chicory roots and consequently leaves and head. For PFOA, PFNA, PFDA and PFOS, K_d is higher than RCF_{dw} , and less accumulation in roots and shoots was accordingly observed.

ii) System dynamics. PFAAs show no rapid uptake into roots. Possibly due to their unusual chemical properties (being hydrophobic and lipophobic at the same time), their biomembrane permeability is slow, in any case slower than that of water ($R < 1$), and the retardation factor appears to be independent of the type of crop. Slow transport across biomembranes is typical for very polar or highly charged compounds. However, there are no loss processes of relevance known within the plant. Neither biotic nor abiotic degradation nor volatilization lead to a decline of chemical mass once the chemical has been taken up. The permanent transport to and within the plant with the transpiration water over time leads to very high concentrations, and no steady-state is reached. This is the best seen from the solution of the underlying differential equation, $m(t) = I/k (1 - e^{-kt})$, where $m(t)$ is the mass in plant shoots at time t , I is the input (here with the transpiration water) and k is the sum of loss processes. With very small loss (k close to 0 d^{-1}),

chemical mass in the shoots increases steadily as long as the chemical is transported into plant and shoots with the water taken up. Thus, considerable accumulation can be reached with longer time periods provided that the input of chemical is constant (a reasonable assumption for long-term contamination events, such as the one in the Veneto Region, Italy).

Having in mind (a) the strong affinity of PFAAs (particularly short-chain) for crop uptake through roots, (b) the long maturation period of some crops, (c) crop-dependent uptake and particularly (d) soil-type dependency as the only way for decreasing the bioavailability of PFAAs to roots through the soil sorption, research is urgently needed to improve the mechanistic understanding and allow predicting PFAAs uptake in crops, eventually leading towards more reliable human health exposure and risk assessment for these substances.

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Highlights:

- Short-chain perfluoroalkyl acids (PFAAs) are highly bioaccumulative in edible crops
- Plant uptake model extended to interpret the uptake of nine PFAAs into red chicory
- New parameter R for slow transfer through root membranes estimated for red chicory
- The newly developed semi-empirical model was successfully applied for other crops
- High PFAA uptake in plants is the combination of persistence, low K_d and high RCF

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: