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Fate of a perfluoroalkyl acid mixture in an agricultural soil studied in lysimeters

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HIGHLIGHTS

- K_d for C4-C14 PFCAs increased by 0.39–0.48 log units per perfluorinated carbon atom.
- C4-C7 PFAAs were almost completely removed from the 60 cm deep lysimeter after 72 days.
- Leaching (%) increased with the initial concentration of the PFAA mixture in the soil.
- Modeling using measured K_d values underestimated observed loss of PFAAs from soil.
- Accelerated leaching was attributed to competition with other PFAS for sorption sites.

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ABSTRACT

Perfluoroalkyl acids (PFAAs) are environmental contaminants of concern in both food and drinking water. PFAA fate in agricultural soil is an important determinant of PFAA contamination of groundwater and crops. The fate of C4-C14 perfluorinated carboxylic acids (PFCAs) and two perfluorinated sulfonic acids (PFSAs) in an agricultural soil was studied in a field lysimeter experiment. Soil was spiked with PFAAs at four different levels and crops were planted. PFAA concentrations in soil were measured at the beginning and end of the growing season. Lysimeter drainage water was collected and analysed. The concentrations of all PFAAs decreased in the surface soil during the growing season, with the decrease being negatively correlated with the number of fluorinated carbons in the PFAA molecule. PFAA transfer to the drainage water was also negatively correlated with the number of fluorinated carbons. For the C11-C14 PFCAs most of the decrease in soil concentration was attributed to the formation of non-extractable residues. For the remaining PFAAs leaching was the dominant removal process. Leaching was concentration dependent, with more rapid removal from the soils spiked with higher PFAA levels. Model simulations based on measured K_d values under-predicted removal by leaching. This was attributed to mixture effects that reduced PFAA sorption to soil.

1. Introduction

Perfluoroalkyl acids (PFAAs) are a group of highly persistent environmental contaminants (Moody and Field, 2000; Prevedouros et al., 2006). Some PFAAs have been shown to have toxic effects (Domingo, 2012; Lau et al., 2007; Saikat et al., 2013). As a result, the European Food Safety Authority has established tolerable daily intakes (TDIs) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) (Johansson et al., 2009, TDIs now under revision) and is considering establishing them for other PFAAs. Human exposure to PFAAs occurs primarily via food and drinking water (Fromme et al., 2009; Klenow et al., 2013). PFAAs enter the agricultural food chain via root uptake from soil (Stahl et al., 2009). Agricultural soil can become contaminated with

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PFAAs via atmospheric deposition, the application of pesticides, or the addition of material for soil improvement such as sewage sludge or industrial waste (Scott et al., 2006; Gilljam et al., 2016; Sepulvado et al., 2011; Wilhelm et al., 2008). The fate of PFAAs in agricultural soil is therefore an important determinant of the PFAA contamination of groundwater and crops, and thereby of the potential for human exposure.

To understand the fate of PFAAs in soil, a variety of laboratory studies have been conducted. One focus has been on batch sorption experiments, which have been used to quantify the soil-water distribution coefficient K_d and to understand the soil and chemical properties that influence it (Higgins and Luthy, 2006; You et al., 2010; Ferrey et al., 2012; Guelfo and Higgins, 2013; Milinovic et al., 2015; Chen et al., 2012, 2013; 2015; Zhang et al., 2015). There has also been considerable research with soil column experiments to study the leaching and persistence of PFAAs under controlled conditions (Gellrich et al., 2012; Vierke et al., 2014; McKenzie et al., 2015, 2016). This work has shown PFAAs to be persistent in soil and provided insight into how leaching is influenced by the PFAA's structure (perfluoroalkyl chain length and functional group) and by soil properties (e.g., organic carbon content and pH). However, there have been comparatively few studies of PFAA behaviour under field conditions. A notable exception is a long term lysimeter experiment in which PFOA and PFOS were applied to the surface of 1.5 m deep soil columns in outdoor lysimeters and their concentrations in leachate were monitored. After 42 months only 3.1% of the PFOA and 0.013% of the PFOS had eluted (Stahl et al., 2013).

In this work the fate of PFAAs in an agricultural soil was studied in a field lysimeter experiment that provided a close approximation of environmental conditions. In parallel, K_d was measured in the laboratory in order to assess whether the leaching behaviour it predicts is consistent with that observed in the field experiment. A broad spectrum of PFAAs consisting of C4-C14 perfluorinated carboxylic acids (PFCAs) and two perfluorinated sulfonic acids (PFSAs) was included in the experiment in order to explore the impact of chemical structure on fate. The soil was spiked at four different levels, and the chemicals were uniformly mixed throughout the whole soil column, as this approximates agricultural situations where contaminants are mixed into soil via tilling. The lysimeters were planted with different crops and the chemical concentrations in soil, drainage water and plant parts were studied. Here we report on the results for the soil system (soil and drainage water).

2. Materials and methods

2.1. Chemical reagents and lab materials

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA), perfluorotetradecanoic acid (PFTeA), perfluorobutane sulfonic acid (PFBS) and perfluorooctane sulfonic acid (PFOS) were purchased. Each had a purity >95%. The suppliers and purities of these chemicals, their molecular formulas and the ^{13}C-labeled internal standards used for their quantification are listed in Tables S1 and S2 of the Supporting Information (SI) along with details about the other chemicals used.

Materials used for extraction and clean-up of the samples included Acrodisc LC13 GHP Pall 0.2 μm filters from Pall Corporation (Port Washington, NY, USA), 15 mL polypropylene (PP) tubes with screw caps from Sarstedt (Nümbrecht, Germany), centrifugation filter tubes (50 mL, 0.2 μm nylon filter) from Grace (Breda, Netherlands), and 2.0 mL PP vials from VWR International (Amsterdam, Netherlands).

2.2. Lysimeter experiment

The lysimeter experiment was conducted at the Fraunhofer Institute for Molecular Biology and Applied Ecology IME in Schmallenberg, Germany. A total of 20 lysimeters were employed. The soil of 16 of the lysimeters was spiked with equal concentrations of the 13 PFAAs studied to give four lysimeters at each of five different PFAA contamination levels: background concentrations (unspiked), 0.1 mg/kg, 1 mg/kg, 5 mg/kg, and 10 mg/kg of each PFAA. For comparison, PFOA and PFOS concentrations of ~1 mg/kg were measured in contaminated agricultural soil in Arnsberg, ~30 km from Schmallenberg (Wilhelm et al., 2008). Each lysimeter had a surface area of 1 m^2 and a total depth of 60 cm. Drainage water was collected in a stainless steel container. The lysimeters were outdoors and unprotected. Precipitation was measured at the site.

The lysimeters were each filled with 450 kg of sand (30–60 cm depth, pH 5–5.5, organic carbon content 0.3–0.5%, hereafter called the lower soil layer) and 450 kg of loamy sand (0–30 cm depth; 71% sand, 24% silt, 5% clay, pH 5.67, organic carbon content 0.93%, upper soil layer). 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 soil used for the lower layer is the soil that naturally occurs under the soil used for the upper layer.

The spiking of the soil was done stepwise. First a stock solution was prepared containing all PFAAs in methanol. Then 2 kg of soil were spiked with the stock solution and homogenized. Afterwards the 2 kg of spiked soil was mixed with 90 kg of soil in a cement mixer to achieve the desired concentration. This was repeated 5 times for each layer in each lysimeter. Samples were taken from each 90 kg batch, combined, and stored at −20 °C for later determination of the initial PFAA concentration in the soil of each lysimeter. The filled lysimeters were covered until planting, which occurred within one week.

The lysimeters were planted with onion (*allium cepa*), carrot (*daucus carota*), radish (*rapahnus sativus*), lettuce (*lactuca sativa*), pea (*pisum sativum*), or maize (*zea mays*). Each crop was planted in one lysimeter from each soil contamination level with the exception of onion, carrot and radish, which were planted together in one lysimeter from each soil contamination level. On June 21, 2011, ca. 20 onion seeds, 20 carrot seeds, 20 radish seeds, 6 pea seeds, 20 lettuce seedlings or 9 maize seedlings (pre-grown in uncontaminated soil) were planted. The lysimeters were watered after planting, and kept humid by rain events and additional watering as needed (see Table S3 for water inputs to the lysimeters). When a significant quantity of drainage water had accumulated in the drainage container it was retrieved, weighed, and a sub-sample of approx. 10 mL was transferred to 15 mL centrifugation tubes and stored at 4 °C until analysis.

Radish, lettuce, pea and maize were harvested at maturity on Aug. 9, Sept. 1, Oct. 4 and Oct. 19, respectively, and soil samples were taken. This corresponds to lysimeter exposure periods of 49, 72, 105, and 120 days. For lettuce, pea and maize the soil samples were collected with a corer. The soil core was divided into two 30 cm lengths to provide average concentrations in the two soil types used. The soil was packed in freezer bags and stored at −20 °C until analysis. Onion and carrot did not germinate. For radish a sample of the top 1–2 cm of the soil was collected, as at the time of radish harvest it was still hoped that the onions and carrots seeded in the same lysimeters would germinate. PFAA concentrations were measured in the upper layer for lettuce, pea and maize, the surface layer for radish, and the lower layer for lettuce.

2.3. Determination of K_d

Soil-water distribution coefficients (K_d) were determined for each of the two soils according to OECD guideline 106 using 2 g of soil and 10 mL of water (OECD, 2000). A mixture containing equal concentrations of the 13 PFAAs was tested. Seven different initial concentrations were used: 1, 5, 10, 50, 100, 500, and 1000 ng/mL. Each concentration level was measured in duplicate. PFAAs were analysed in both soil and water. An equilibration time of 3 days was used based on a preliminary experiment. Only results showing a PFAA mass balance between 70% and 140% were retained.

2.4. PFAA analysis

The soil was dried in an oven at 40 °C until no further weight loss was recorded. After homogenization, 1 g of 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 a Rapidvap (Labconco, Kansas City, US). The extraction was repeated twice with 5 mL MeOH. In a pre-experiment it was found that the third extraction contained only ~5% of the mass of PFAAs in the first extraction, so it was decided that three extractions were sufficient. The extracts were combined and concentrated in the Rapidvap to a final volume of 1 mL. They were diluted 1:1 with water prior to analysis to match the injection conditions of the HPLC.

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. Drainage water and water from the K_d determination was filtered and then treated like the pore water. The solutions were stored at 4 °C until instrumental analysis.

An HPLC system (LC-20AD XR pump, SIL-20A autosampler and SCL-10A 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-C18 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.

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. A volume of 20 μl was injected. The gradient used for separation and the mass transitions as well as other mass spectrometer settings can be found in the Supporting Information (Text S1). 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.

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

2.5. Quality assurance of PFAA analysis

Each soil sample was extracted twice and each soil extract was injected in duplicate. The relative standard deviation of the concentrations derived from these four 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.

Recoveries from the analytical procedure for soil 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 91% (PFPeA) and 112% (PFDoA) (Table S4 in the Supporting Information).

Limits of quantification (LoQs) for soil (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. The LOQ for leachate was 0.5 μg/L for all substances. It was validated by replicate (five-fold) determination of fortified blank samples at the LOQ and at 10 x LOQ level.

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 represent the sum of non-branched and branched isomers.

2.6. Model of PFAA fate in soil

The fate of PFAAs in soil was simulated using the one-dimensional model PELMO (Pesticide Leaching Model, Klein, 1995). PELMO calculates the vertical transport of chemicals in the unsaturated soil system within and below the plant root zone. PELMO considers various environmentally relevant processes (run-off, erosion, plant uptake, sorption, leaching, degradation in soil and on plants, and volatilisation of pesticides). However, the model has been mainly used to estimate the leaching potential (described in more detail in e.g. FOCUS, 2000, 2002, 2009), and this is the context in which it was employed here. PELMO is presently officially used in European and national registration of pesticides (EFSA, 2017).

To calculate the soil water regime, PELMO uses the field capacity approach (Carsel et al., 1984). For the simulations the soil was divided into different compartments (layers) of 5 cm each. All properties (e.g. soil density, soil moisture, temperature, but also the concentration of the chemical) are considered to be uniform within these compartments. Dependent on the soil depth, different processes determining the water content are considered. The model distinguishes between the surface layer, the segments in the root zone, and the compartments below the root zone. A time step of one day was considered for the simulations.

Since data on potential evapotranspiration were not available, it was estimated internally by the model using daily air temperature. Plants are characterised in the model by their maximum rooting depths and seasonal Kc-factors. The Kc-factors are used to calculate crop specific potential evapotranspiration. Plant growth is assumed to be linear. Actual evapotranspiration was calculated based on daily plant growth, the soil moisture at the current rooting depth, and the crop specific potential evapotranspiration.

Solute transport is calculated with the Convection-Dispersion-Equation (CDE). In the model non-linear sorption is implemented using a Freundlich isotherm. However, as the experimental data did not indicate any non-linear behaviour the Freundlich exponent was set to 1.0 for all PFAS. Sorption was described using the measured K_d values for the top and the bottom layer. Transformation was switched off.

3. Results and discussion

3.1. Quality assurance of the experiment

The initial concentrations in the soil were close to the nominal concentrations for all chemicals (98 ± 12%, Fig. 1, Table S6). This indicates that the soil contamination procedure was successful and that the soil analytical method was accurate. An exception was PFHxA, for which a deficit in initial concentrations was observed in the upper layer. This deficit increased with increasing contamination level, being negligible at the lowest spiking level and ~50% at the highest spiking level. We have no explanation for this observation.

At the end of the lettuce and peas experiments the concentrations in the uncontaminated soil were at least a factor of 10 less than the concentrations in the upper soil layer with the lowest spiking level with the exception of PFPeA (factor 5 less) and PFHxA (factor 8 less) in the pea experiment. In the maize experiment the smallest differences were a factor of 4–5 (for PFNA, PFDA, PFUnA, and PFOS), while in the radish experiment (where only the top 1–2 cm of soil was sampled) the differences were less than a factor of 4 for 10 of the analytes. This indicates that the influence of the surrounding environment on the PFAA concentrations in the contaminated soils was in all cases small or negligible. When quantifiable, PFAA concentrations from the non-spiked lysimeters were subtracted from the concentrations in the spiked lysimeters.

The different plant crops had an influence on the amount of evapotranspiration from the lysimeter. The amount of drainage water generated was markedly greater for lettuce (mean of 129 L) than for radish (99 L), pea (83 L) or maize (80 L). However, the crops did not play a significant role in the sequestration of PFAAs out of the soil. The quantity of PFAAs in the vegetation at harvest did not exceed 1% of the amount added to the soil with the exception of PFBA, which had a maximum sequestration of 12% from the lowest spiking level with maize.

3.2. Measured loss of PFAAs from soil

The concentrations of all of the chemicals decreased in soil during the 49–120 days from the start of the experiment to the end of the experiment (Fig. 1, Table S7). There was a clear relationship between the final concentration in the soil as a fraction of the initial

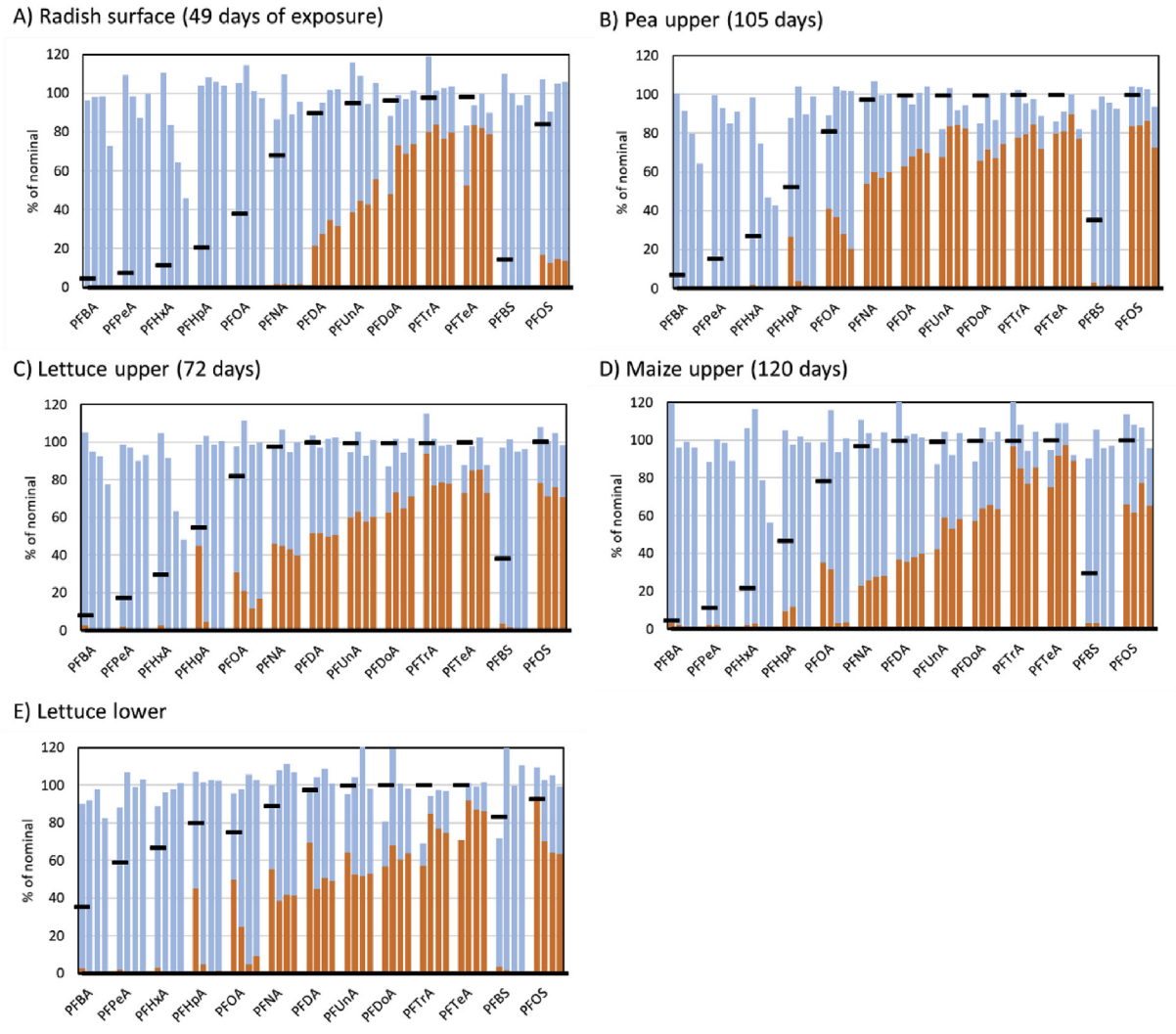

Fig. 1. PFAA concentrations in the soil expressed as a percent of the nominal concentration at the start of the experiment. Blue bar = Measured initial concentration; Red bar = Measured final concentration (at harvest); Black symbol = Modeled final concentration. For each chemical the results are shown for spiking levels 1–4 (in order from left to right). For radish the final soil concentration refers to the surface layer (top 1–2 cm measured and top 2 cm modeled). The exposure period of the lysimeters is given in the panel headings. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

concentration and the number of perfluorinated carbon atoms in the molecule, with the median final fraction remaining in the upper soil layer increasing from <1% for PFBA to ~90% for PFTeA (Figure S1).

The spiking level could potentially influence the fate of the PFAAs in soil. In this study the decrease in soil concentration was similar between the different spiking levels for most chemicals in the upper soil layer (Fig. 1), suggesting that this was not the case. However, for those chemicals with high removal rates from the upper soil layer (PFBA, PFPeA, PFHxA, PFHpA, PFBS), a dependency on the spiking levels was observed. The fraction of the nominal soil concentration remaining in the soil at the end of the experiment decreased as the spiking level increased, often by more than a factor of 10 between the lowest and the highest spiking level (Table S8). In other words, the removal of these chemicals became more efficient as the spiking level increased. A similar trend was observed in the lower soil layer, whereby it affected longer chained PFAAs (up to PFDA). Gellrich et al. (2012) observed interactions between PFAAs in soil. In laboratory soil column experiments they found that the addition of longer chained PFAAs increased the mobility of shorter chain PFAAs already in soil columns. Their explanation was that the longer chained PFAAs are able to displace the shorter chained PFAAs from their binding sites.

For the lysimeters growing lettuce, pea, and maize, the loss of the PFAAs from the soil was comparable. This indicates that the crop did not have a major influence on the PFAA fate in the soil. The lysimeters growing radish showed a greater loss of many chemicals, especially the C7-C11 PFCAs and PFOS. For radish, only the top 1–2 cm of the upper soil layer was sampled, whereas for the other crops the full 30 cm of each soil layer was sampled. Given that the length of the experiment was shorter for radish than for the other crops, this indicates that the loss of PFAAs was greater in the top 1–2 cm of the soil than in the top 30 cm. This can be explained by leaching removing a larger fraction of the PFAAs from the top 1–2 cm (see below).

3.3. PFAAs in drainage water

Three drainage samples were collected on July 29, August 11 and August 19. Not all of the results of the PFAA analysis of the drainage water could be used quantitatively. The extracts had to be diluted prior to analysis due to high concentrations of some analytes, which introduced uncertainty into the quantification. We therefore present only the results for Level 1, which had the lowest concentrations and thus were most proximate to the analyte:internal standard ratios in the calibration curve.

The drainage water data were used together with the concentrations in the soil at the beginning and the end of the experiment to assemble a mass balance of PFAAs in the lysimeter growing lettuce in soil with Level 1 contamination (Fig. 2). The contribution of the residual in soil to the mass balance at the end of the experiment increased with PFAA chain length, in agreement with Fig. 1. The drainage water made a major contribution to the mass balance, accounting for 30–40% of the original amount present in the lysimeter for PFBA, PFPeA, PFHxA, PFHpA and PFBS. For the remaining PFAAs the contribution of drainage water decreased with increasing chain length. There was also a strong correlation between the concentration in drainage water and the number of perfluorinated carbons in the PFAA molecule (nFC) for nFC > 5 (Figure S2), confirming that leaching of the PFAA was dependent on chain length. Finally, the mass balance did not close (Fig. 2). Possible explanations include the fact that not all drainage water was analysed and the uncertainty in the drainage water analysis.

Evidence for chain length dependence of PFAA leaching has been reported previously. In soil plots to which sewage sludge

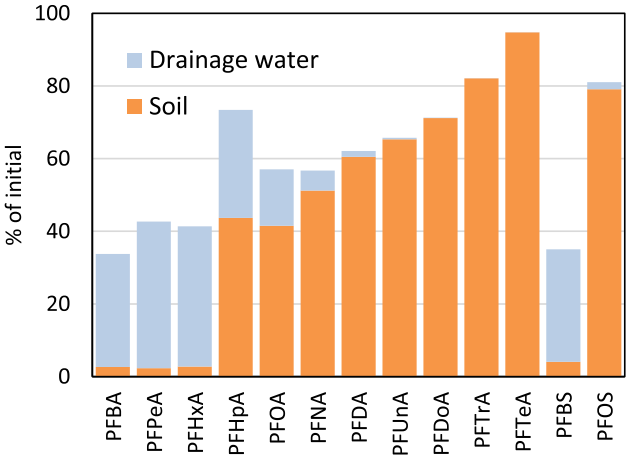

Fig. 2. Quantity of PFAA in soil at harvest and in the accumulated leachate for the level 1 lysimeter planted with lettuce. The results are expressed as a percentage of the initial quantity of PFAA in the lysimeter.

contaminated with PFAAs had been applied, the ratio of the PFAA concentration at depth (60–120 cm) to that in surface soil decreased with increasing perfluoroalkyl chain length (Sepulvado et al., 2011). In a laboratory study in which PFAAs were applied to the top of 60 cm soil columns and then eluted with water for >100 weeks, PFAAs with nFC <6 eluted with or shortly after the conservative tracer, while the elution of PFHpA, PFHxS, PFOA and PFOS took progressively longer with increasing nFC (Gellrich et al., 2012). Retardation factors for PFBA, PFPeA, PFHxA, PFOA and PFNA applied to the top of a column containing water saturated aquifer material increased with increasing nFC (Vierke et al., 2014). Similarly, retardation factors of C6-C11 PFCAs increased with increasing chain length in laboratory column studies (McKenzie et al., 2015). In a long term lysimeter experiment, the time trend for the concentrations of PFHxA, PFHpA, PFBS and PFHxS in drainage water indicated that these chemicals had largely eluted from the soil column after 27 months, while the concentrations of PFOA in drainage water peaked after 6 months, continuing at that level for 36 months, and the PFOS concentrations continued to increase over the 42 month monitoring period (Stahl et al., 2013). In that study, 3.1% of the PFOA applied to the soil eluted during the 42 months, while in our study only 20–30% was left determinable in the soil after < 4 months. This can be at least partly explained by the method of PFAA application (to the whole soil column in this study versus to the soil surface in Stahl et al., 2013).

3.4. Soil-water partition coefficients (K_d)

The measured K_d values ranged from 0.11 L kg^{-1} for PFBA to 330 L kg^{-1} for PFTeA in the upper layer soil and 3700 L kg^{-1} in the lower layer soil (Table S9). K_{OC} values were calculated, and they lay within the range of K_{OC} values reported in the literature (see Table S10). There was a strong positive correlation between K_d and nFC. A linear regression of log K_d for the PFCAs against nFC gave correlation coefficients of 0.97 and 0.96 for the upper and lower layer soils, respectively (Fig. 3). The slope of the regression line was 0.48 for the lower layer soil and 0.39 for the upper layer soil; at a first approximation the addition of two CF_2 groups to the PFCA chain increased K_d by an order of magnitude. Higgins and Luthy observed this chain length dependence in batch sorption experiments of PFOA, PFNA, PFDA AND PFUnA to sediments. This relationship was confirmed for sorption of these chemicals to soil in later studies (Guelfo and Higgins, 2013; McKenzie et al., 2015).

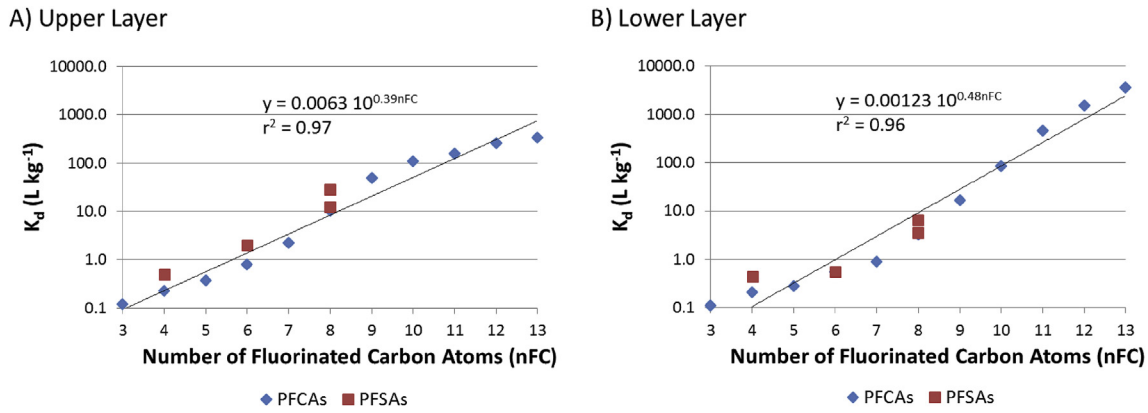

Fig. 3. Soil water distribution coefficients K_d of the PFAAs versus the number of fluorinated carbon atoms in the PFAA molecule for the two soils studied. The line and equation show the linear regression of K_d against nFC for the PFCAs.

Both soils show a clearly weaker influence of nFC for shorter chain PFCAs (nFC < 7), with the addition of two CF_2 groups increasing K_d by only half an order of magnitude. Higgins and co-workers have reported K_d values for PFBA and PFPeA that were similar or higher than PFHxA, based on batch sorption experiments and soil column retention studies (Guelfo and Higgins, 2013; McKenzie et al., 2015). On the other hand, K_d values derived from breakthrough times of PFAAs in sediment columns showed an increase from PFBA through PFPeA and PFHxA of more than an order of magnitude (Vierke et al., 2014). We observed a behaviour intermediate between these reports, with a K_d dependence on nFC that was positive but markedly weaker than reported by Vierke et al.

The PFSAs showed a similar dependence of K_d on nFC. From PFHxS to PFOS (i.e., nFC from 6 to 8), K_d increased by 1 order of magnitude in both soils, while the increase between PFBS and PFHxS was markedly smaller (Fig. 3). K_d for the PFSAs was a factor of ~2 larger than K_d for the PFCA with the same nFC, with the exception of PFHxS in the lower layer soil (Fig. 3, Table S9). Exchanging the carboxylic functional group for a sulfonate functional group thus had an influence on K_d. The literature provides contrasting reports on this subject. In their pioneering work, Higgins and Luthy (2006) concluded that K_d was on average a factor of 1.7 higher for PFSAs than for PFCAs with the same nFC, but a later reanalysis of their data indicated that there was no difference (Rayne and Forest, 2009 review). Follow-up work by Higgins' group found that K_d values of PFSAs were 0.49 log units greater (McKenzie et al., 2015).

K_d was larger for the upper layer soil than for the lower layer soil for all PFSAs and the PFCAs with $6 \leq$ nFC ≤ 11. The difference was largest for PFNA, PFDA, and PFOS (a factor of 3–4). The upper layer soil was a loamy sand with an organic carbon content of 0.93% whereas the lower layer soil was sand with an organic carbon content of 0.3–0.5%. A range of studies have reported that these PFAAs sorb primarily to the organic matter in soil (Higgins and Luthy, 2006; Chen et al., 2012, 2013; Milinovic et al., 2015), and it was recently shown that PFOA selectively binds to soil microbial protein (Masoom et al., 2015). Therefore the larger K_d values in the upper layer soil were expected.

In contrast, K_d was smaller for the upper layer soil than for the lower layer soil for the PFCAs with nFC ≥ 11. For PFTeA the difference was more than an order of magnitude. Although organic carbon is believed to dominate sorption of PFAAs to soil, they have also been shown to sorb to soil minerals (Zhang et al., 2015). This sorption can be strong. A K_d value of 2.81 L kg^{-1} was measured for PFOS to organic carbon free Ottawa River sand (Johnson et al., 2007), which is similar to the K_d value measured for PFOS to the lower layer soil in this study (3.15 L kg^{-1}). The much stronger sorption of the longer chain PFCAs to the lower layer soil suggests that sorption to soil minerals may be a comparatively more important process for long chain PFCAs. A recent review concluded that at least organic carbon content, pH, and clay content influence PFAS sorption to soil (Li et al., 2018).

K_d was compared with soil/pore water distribution coefficients calculated from the PFAA concentrations measured in soil and soil pore water in the lettuce and maize lysimeters at the time of harvest. For the upper layer soil, the average soil/pore water distribution coefficient across all exposure levels agreed within a factor of 2.6 with the exception of PFPeA. For the lower layer soil good agreement was obtained for the shortest and longest chained compounds, while PFNA, PFDA, PFUnA and PFOS had average soil/pore water distribution coefficients that were about one order of magnitude greater than the K_d values. However, there was considerable variability between exposure levels, with the lower exposure levels tending to have higher soil/pore water distribution coefficients, particularly for the PFAAs with nFC $\geq$ 7 in the lower layer soil (Figure S3).

3.5. Modeled behaviour of PFAAs in the lysimeter

The model predicted the removal of the PFAAs from the lysimeter via the drainage water. It assumed that losses due to volatilisation and transformation are negligible, assumptions which are consistent with current understanding of the environmental chemistry of PFAAs. It was also assumed that the formation of non-extractable residues was negligible. The modeled concentration in the upper soil layer at the end of the experiment increased with increasing chain length (Fig. 1). Since removal via drainage water was the only modeled loss process, removal via drainage water decreased with increasing chain length. This is consistent with the measured concentration trend in the drainage water (Figure S2). However, the modeled and measured residual concentrations in soil differ greatly. Whereas the measurements indicated <5% of PFBA, PFPeA, PFHxA, PFHpA (except Level 1) and PFBS was left in the soil at the end of the experiment in all lysimeters, the model indicated the amount remaining was much higher (as high as 64% in the upper layer and 90% in the lower soil layer for PFHpA in lettuce (Fig. 1)). Similarly, the PFAAs with nFC >7 were predicted by the model to be fully retained (>90%) in the soil, while the measurements indicated that just 80% of the PFTeA and as little as 25%

of PFNA were left in the soil at the end of the experiment (Fig. 1). The model results changed little when the model was rerun using realistic worst case assumptions in the water mass balance that maximized leachate generation. Possible explanations for this inconsistency between theory and observations are discussed below.

3.6. Fate of longer chained PFAAs in soil

The loss of PFUnA, PFDoA, PFTrA and PFTeA from the soil ranged from 14% to 40% (Fig. 1). Given the high persistence and low volatility of PFAAs, the only mechanisms expected to have a major impact on their fate in soil are leaching and the formation of non-extractable residues. As noted above, a negligible fraction of the chemicals in the soil was sequestered into the crops.

The concentrations of PFUnA, PFDoA, PFTrA and PFTeA in drainage water were <5% of the concentrations of the short chained PFCAs and PFBS (Figure S2). This indicates that only a small fraction of these chemicals was removed from the soil column by leaching. This is consistent with the high K_d values of these chemicals. Furthermore, for PFDoA, PFTrA and PFTeA the loss from the surface soil (top 1–2 cm) in the radish lysimeters was not greater than the loss from the upper soil layer (30 cm) in the other lysimeters. This indicates that downward displacement of these chemicals via leaching was negligible, and would suggest that the formation of non-extractable residues was a major loss process for the longer chained PFAAs. Since the initial concentrations in the soil were close to the nominal concentrations, the non-extractable residues would not have been primarily formed immediately after contamination of the soil. It is possible that they were formed during the experiment, perhaps as a result of natural weathering processes. We note that it may have been possible to extract more of these chemicals from the soil using a more aggressive extraction; non-extractable is relative to the extraction method employed.

3.7. Fate of shorter chained PFAAs in soil

The removal of the PFAAs with nFC <7 was much more rapid than predicted by the model, most particularly for the lower soil layer. This cannot be attributed primarily to the formation of non-extractable residues, as large fractions of these chemicals were found in the drainage water (Fig. 2). Approximately equal concentrations of the PFAAs with nFC $\leq$ 6 were found in the leachate (Table S11), whereas the model predicted a pronounced dependency on chain length, with concentrations of PFHpA that were 3.2 times less than concentrations of PFBA in drainage water. This indicates that leaching of the chemical was apparently much more rapid than predicted by the model.

One possible explanation for the underestimation of leaching by the model is that the K_d values used were too high. We employed K_d values that had been measured with the same chemical mixture and the same soils as used in the study. However, the maximum PFAA concentrations in soil for the K_d measurements were at the lower end of the PFAA concentration range in the lysimeter experiment. Furthermore, the composition of the PFAA mixture sorbed to the soil was different as a result of the higher water:soil ratio in the K_d measurement. While the laboratory measurements showed no evidence that K_d decreases with increasing concentration (Table S9), the soil/pore water distribution coefficients measured at harvest tended to increase with increasing contamination level, and they were generally smaller than K_d for the shorter chained PFAAs (Figure S3). Hence the measured K_d may have overestimated soil/water distribution in the lysimeters.

Replacing the K_d values with the soil/pore water distribution coefficients yielded model predictions that agreed somewhat better with the observations, but the model continued to severely underpredict leaching (results not shown). As already noted, the loss of chemical from the soil increased with increasing level of soil contamination. This suggests that the process causing more rapid leaching of the chemicals is concentration dependent. Gellrich et al. (2012) showed that when PFBA was applied to a soil column that only about 80% could be eluted with water. However, when PFHxA and PFHxS were then added the remaining PFBA eluted immediately. They attributed this to the longer chained PFAAs outcompeting PFBA for strong sorption sites in the soil. Such a mechanism could explain the concentration dependence observed in this study as well as the discrepancy between model predictions and observations. The longer chained PFAAs may have occupied sorption sites preferred by the PFAAs and reduced the sorption capacity of the soil for the shorter chained PFAAs. These PFAAs would have been more rapidly eluted from the lysimeters. For higher concentrations in the soil, the displacement would have been greater and would have affected PFAAs with longer chain lengths. As the experiment progressed and the concentrations of many of the PFAAs were depleted, the competition for sorption sites would be less intense and soil/pore water distribution coefficients would increase. This explanation is generally consistent with the observations. Interestingly, there was no time trend in the soil concentrations between the harvest dates for lettuce and maize (Figure S4), which could suggest that the accelerated leaching was largely over by the time of the lettuce harvest. However, there was comparatively little leachate produced after the lettuce harvest, so little loss of chemical by leaching would be expected.

3.8. Implications of the findings

This study shows that the shorter chained PFCAs (PFBA, PFPeA, PFHxA) and PFBS are readily transported with water through soil. As a consequence, if these chemicals are introduced to agricultural soil with significant downward transport of water, they will reside in the surface soil for only a short period. The exposure of crops to the chemicals will be only transient. On the other hand, a large portion of these chemicals will be bioavailable for uptake by the roots. Furthermore, they will be rapidly transported to and with groundwater, where comparatively high concentrations will occur.

The longer chained PFCAs (PFDoA, PFTrA, PFTeA) sorb strongly to soil and there is very limited transport with water. When introduced to agricultural soil, these chemicals will largely stay put. The exposure of crops to these chemicals will continue for many years, albeit with a low bioavailability; they will be a long-term contamination problem. In addition, repeated inputs of these chemicals will result in their accumulation in soil; while the concentrations arising from one season's input may be of little concern, after several years or more of inputs they could become problematic. On the positive side, the transport of these PFAAs to and with groundwater will be limited, and the chemical concentrations in groundwater will be comparatively low. The slow rate of transport to groundwater will offer more time for remediation of surface soils before the groundwater becomes contaminated. In contrast to the shorter chain PFAAs such as PFBA and PFBS, there are water treatment technologies that efficiently remove longer chained PFCAs from water (Eschauzier et al., 2012). However, groundwater contamination can be expected to persist for a much longer period of time.

This work suggests that non-extractable residues of PFAAs can form in soil under environmental conditions. In this study the PFAAs were applied to the soil using a solvent carrier. It is unknown whether non-extractable residues are also formed when the PFAAs enter the soil via other means more commonly encountered in the environment, such as atmospheric deposition or sewage sludge

application. Sepulvado et al. (2011) conducted a mass balance of soil that had received PFAAs via sewage sludge over 3 years, but their study was not designed to identify losses of the PFAAs of the order of 20% via, e.g., formation of non-extractable residues.

Finally, this work highlights the necessity of measuring K_d values under conditions that closely approximate those in the environment of interest. Where the chemical contamination is a mixture, it can also be important that K_d is measured for the mixture, as mixture components can interact to influence sorption. For PFAAs, firefighting foams are mixtures that may warrant this treatment. Thereby it may not be sufficient to employ the mixture composition present in bulk soil in the K_d experiment; one should instead strive to have the same mixture composition in the sorbed phase in the K_d experiment and in the soil of interest.

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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.2019.02.012.

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