

# Leaching and Transformation of Perfluoroalkyl Acids and Polyfluoroalkyl Phosphate Diesters in Unsaturated Soil Column Studies

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**Abstract:** Per- and polyfluoroalkyl substances (PFAS) are environmentally ubiquitous, anthropogenic substances with adverse effects on organisms, which shows the need to study their environmental fate and leaching behavior. In the present soil columns study, the leaching behavior and fate of nontransformable and transformable (precursors) were investigated. Ten nontransformable PFAS in two different soils, two precursors and two field soils, which were already contaminated with a mixture of PFAS, and two uncontaminated controls, were set up for a time span of 2 years. At the end of the study, the molecular balance could not be closed for nontransformable PFAS. This effect was positively correlated to the fluorinated carbon chain length. The precursors, which were both polyfluoroalkyl phosphate diesters (diPAP), had different transformation products and transformation rates, with a higher rate for 6:2 diPAP than 8:2 diPAP. After 2 years, amounts of diPAP were still found in the soil with no significant vertical movement, showing high adsorption to soils. Transformation products were estimated to be simultaneously formed. They were predominantly found in the percolation water; the amounts left in soil were negligible. Up to half of the initial precursor amounts could not be balanced and were considered missing amounts. The results of contaminated field soil experiments showed the challenge to estimate PFAS leaching without knowing all occurring precursors and complex transformation dynamics. For this purpose, it was shown that a broad examination of contaminated soil with different analytical methods can help with qualitative estimations of leaching risks. For a better quantitative estimation, analytical determination of more PFAS and a quantification of the missing amounts are needed. *Environ Toxicol Chem* 2022;41:2065–2077. © 2022 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

**Keywords:** PFAS; Fate and transport; Biotransformation

## INTRODUCTION

In recent decades, emerging contaminants have been found increasingly in the environment, which has introduced new challenges for environmental management such as remediation of contaminated sites. One group of emerging contaminants

are per- and polyfluoroalkyl substances (PFAS), the so-called forever chemicals. The term relates to the persistency of some PFAS (Bell et al., 2019; Buck et al., 2011) which belong to the subgroup of perfluoroalkyl acids (PFAA), including the group of perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSA; Buck et al., 2011). The PFAS include several thousand compounds (Wang et al., 2017) with varying physicochemical properties. This creates a lot of research potential regarding their behavior in the environment. They have been detected in many environmental matrices such as soil (Göckener et al., 2021), air (Bell et al., 2019), ocean and coastal water (Muir & Miaz, 2021), food webs (Koch, Jonsson, et al., 2020b), and humans (Göckener, Weber, et al., 2020) because of their

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Published online 25 June 2022 in Wiley Online Library

(wileyonlinelibrary.com).

DOI: 10.1002/etc.5417

wide-ranging use and persistence as well as bioaccumulative behavior. These detections are connected to possible adverse impacts (persistent, bioaccumulative, toxic, carcinogenic, teratogenic), which were already identified for some compounds such as perfluorooctanoic acid (PFOA) in the Stockholm Convention (2019) and by the European Chemicals Agency (2020). The path of the solely anthropologically manufactured substances into the environment can be associated with the complete life cycle, starting with their industrial production, their subsequent use, and ending with their disposal. Especially their strong C–F bond-related stability, their amphiphilic character, as well as their surface tension reduction behavior are related to approximately 200 different industrial uses, including well-known applications such as surface treatment in the paper production industry, firefighting foams, household applications, as well as minor uses such as ammunition, guitar strings, and soil remediation (Glüge et al., 2020).

Knowledge about the sorption behavior of PFAS in soils is required, for example, to perform groundwater risk assessment. For a better understanding, the behavior of different PFAA is often attributed to the number of  $CF_x$  groups ( $x = 2, 3$ ), especially the adsorption potential. In addition, PFAA are categorized as short-chained for PFCA with  $CF_x < 7$  as well as PFSA with  $CF_x < 6$  and long-chained for PFCA  $CF_x \geq 7$  and PFSA  $CF_x \geq 6$  (Buck et al., 2011). In a study of Fabregat-Palau et al. (2021) a multiparameter regression was presented, showing that the number of  $CF_x$  groups, mineral content (clay, silt), and organic carbon content of soils are the parameters with the highest influence on PFAA sorption in soils. Studies dealing with sorption and leaching behavior of PFAS in soil were performed within different kinds of study setups, including field lysimeter studies (McLachlan et al., 2019; Stahl et al., 2013), soil column studies (Gellrich et al., 2012; Lyu et al., 2018; van Glubt et al., 2021), and batch studies (Knight et al., 2019; Miao et al., 2017; van Glubt et al., 2021).

In past studies, however, it has been observed that other processes in soil must also be relevant, leading to retention or, in some cases, to the disappearance of substances from the mass balance. There are two evidential approaches for explanation: (1) the formation of nonextractable residues (NERs; Liu & Liu, 2016; McLachlan et al., 2019), and (2) the sorption on additional interfaces such as the air–water interface (AWI; Brusseau, 2018; Lyu et al., 2018; Silva et al., 2021). According to a study with PFOA (Lyu et al., 2018), the AWI is the main reason for retention in soil, which is related to PFOA being a tenside.

Unlike sorption on additional interfaces, the process of NER formation is still very little understood and is often treated as a “black box” (Schäffer et al., 2018). The presence of NERs was already suggested to constitute a sink for other organic contaminants such as pesticides (Loeffler et al., 2020) and can be divided into three types: (1) strong adsorption with desorption potential, (2) covalent binding without desorption potential, and (3) biogenic NER (bioNER), which are formed through contaminant degradation (Schäffer et al., 2018). For some PFAS, including PFAA (Gassmann et al., 2021; McLachlan et al., 2019; Milinovic et al., 2015), polyfluoroalkyl phosphate esters

(PAPs; Liu & Liu, 2016), and fluorotelomer alcohols (FTOHs; Liu et al., 2010; Wang et al., 2009), NERs have been found to be relevant. Chen et al. (2016) concluded a positive correlation between NER formation and PFAA carbon chain length, with an almost complete desorption irreversibility of perfluorodecanoic acid (PFDA) and subsequent substances.

Lately, also precursors, which include PFAS with the potential to transform into PFAA, are focused because of their associated persistency caused by persistent transformation products. Polyfluoroalkyl phosphate esters are considered to be precursors (Bell et al., 2019) and can be found with a varying number of fluorinated tails: one, two (diPAP), and three (triPAP; Bizkarguenaga et al., 2016). Those with two tails, diPAPs, were found in soil after application of compost contaminated with paper sludge (Biegel-Engler et al., 2017), in residential indoor dust (de Silva et al., 2012), and in sludge of wastewater-treatment plants (Lee et al., 2010). Transformation behavior may also differ largely, even in case of similar molecule structures, such as 6:2 diPAP and 8:2 diPAP, with reported half-life times of 12–60 days and >1000 days, respectively (Lee et al., 2014; Liu & Liu, 2016). The maximum size of transformation products depends on the molecular structures of the precursors. For 6:2 and 8:2 diPAPs, the length of the perfluorinated alkyl chain is the limiting factor of possible PFCA products: perfluoroheptanoic acid (PFHpA;  $CF_x = 6$ ) and perfluorononanoic acid (PFNA;  $CF_x = 8$ ), respectively. Many intermediates after diPAP transformation, which are precursors to PFCA, are also known, such as FTOH, fluorotelomer secondary alcohol (sFTOH), fluorotelomer unsaturated carboxylates (FTUCA), and fluorotelomer ketone (ketone), which are summarized in Lee et al. (2010).

In the present study, we focused on the behavior of PFAS (PFAA and diPAP) in soil including leaching, sorption, and precursor transformation within similar surrounding conditions in a laboratory soil column study. So far, we are aware of only one study in which sorption behavior of PFAA in unsaturated soil columns was investigated (Gellrich et al., 2012). Furthermore, the mobility and transformation of diPAP have not been studied in soil columns before and will expand the knowledge about their environmental behavior when found in soil such as in the used field soils from a contamination case.

## MATERIALS AND METHODS

### Study design

A soil column study was set up with eight variants (variants 1–8; see Table 1) of soils and substances with three replications each, that is, 24 columns in total (Supporting Information, Figure S1). Basic information about column structure and parts of experimental design were taken from Gellrich et al. (2012), in which a comparable experiment was performed. The polyethylene columns had an internal diameter of 4.6 cm and were filled with one type of uncontaminated subsoil (25–50 cm) and different topsoils (0–25 cm). The bottom of the columns was equipped with a polyester net, operating as a soil barrier. All soils were sieved to a grain size <2 mm and were filled into the columns with a density of  $1.5 \text{ kg L}^{-1}$ . The top of the

**TABLE 1:** Description of study variants

Variant	Topsoil	Topsoil type	Contamination	Substances	Amount
PFAA-A	A	Sandy loam	Surface	10 PFAA <sup>a</sup>	623 µg, each
PFAA-B	B	Loam	Surface	10 PFAA <sup>a</sup>	623 µg, each
6:2 diPAP	C	Sandy loam	Topsoil	6:2 diPAP	1160.16 µg
8:2 diPAP	C	Sandy loam	Topsoil	8:2 diPAP	1160.16 µg
Field soil-D	D	Loamy sand	Topsoil	PFAS	1.0–166.9 µg/kg dry wt <sup>b</sup>
Field soil-E	E	Silt loam	Topsoil	PFAS	1.1–116.9 µg/kg dry wt <sup>b</sup>
Control-A	A	Sandy loam	None	–	–
Control-B	B	Loam	None	–	–

For a description of soil properties, see Supporting Information, Table S1. Amounts of substance (*n*) prior to study start are listed in Supporting Information, Table S10, for field soil-D and field soil-E. For surface contamination, a methanol-PFAS mixture was applied on the surface of the topsoil, which is already filled in the soil columns. Application corresponds to the start of experiment. For topsoil contamination, PFAS were present in the topsoil prior to being filled in the soil columns. In 6:2 diPAP and 8:2 diPAP variants, diPAP were mixed into soil. In field soil-D and field soil-E, soil samples from two different sites, which were affected by a contamination case, were taken.

PFAA = perfluoroalkyl acids; diPAP = polyfluoroalkyl phosphate diesters; PFAS, per- and polyfluoroalkyl substances.

<sup>a</sup>Perfluorobutanoic acid, perfluorobutanesulfonic acid, perfluoropentanoic acid, perfluorohexanoic acid, perfluorohexanesulfonic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorooctanesulfonic acid, perfluorononanoic acid, perfluorodecanoic acid.

<sup>b</sup>Each of the quantified 16–17 PFAS were in the given range.

columns was covered with watch glasses for evaporation protection.

Topsoil of variant 1 (PFAA-A) was a sandy loam soil from the location Forchheim (Baden-Württemberg, Germany, 48°57'N, 8°20'E), and topsoil of variant 2 (PFAA-B) was a loam soil from the location Augustenberg (Baden-Württemberg, Germany, 49°0'N, 8°29'E). A methanol solution with a concentration of 100 mg/L for each of the 10 PFAAs (perfluorobutanoic acid [PFBA], perfluorobutanesulfonic acid, perfluoropentanoic acid [PFPeA], perfluorohexanoic acid [PFHxA], perfluorohexane sulfonic acid [PFHxS], PFHpA, PFOA, perfluorooctane sulfonic acid [PFOS], PFNA, PFDA) was applied on the surface of the topsoil with a total input mass of 623 µg each. Thus, a topsoil concentration of 1 mg/kg<sub>wet</sub> soil for each PFAA was achieved, which is at least 10 times above background levels of individual compounds (Brusseau et al., 2020). To examine retardation, a nonretarding tracer (sodium chloride [NaCl]) was also added to both variants. Variants 7 and 8 (control-A and control-B) served as control treatments and to rule out background contaminations. They were filled with the same soil composition as PFAA-A and PFAA-B but without PFAS input or contamination. The subsoils of all columns and topsoil A (topsoil of PFAA-A) are the same.

Columns of 6:2 diPAP and 8:2 diPAP variant were filled with a sandy loam topsoil (Table 1) mixed with PFCA precursors 6:2 diPAP and 8:2 diPAP variant. Because of the poor solubility of the diPAPs, it was decided to mix them into the soil, rather than to apply them on the surface as was done in PFAA-A/PFAA-B. The applications of both substances were done by preparing a methanol solution with diPAP powder. The solution was applied to the soil with the target concentration of 2 mg/kg dry weight and then homogenized in a mixer. No PFAS were found in the soil during analytics prior to application. The soil was taken from the upper 30 cm of a field with classified soil properties (Refesol 01\_A; <https://www.refesol.de/boden01a.shtml>), recognized as an official standard soil by the German Federal Environment Agency.

For field soil-D and field soil-E, soils from two PFAS-contaminated sites of agricultural land in southwest Germany

were used (Regierungspräsidium Karlsruhe, 2018). The loamy sand of the topsoil used in field soil-D was collected at the location Hügelsheim (Baden-Württemberg, Germany, 48°47'N, 8°6'E), and the silt loam topsoil used in field soil-E was collected at the location Steinbach (Baden-Württemberg, Germany; 48°43'N, 8°8'E). The concentration of PFAS, which was determined prior to the start of our study, was within the range of approximately 1–170 µg/kg dry weight (field soil-D) and 1–120 µg/kg dry weight (field soil-E) for each quantified substance. Therefore, the total concentrations of quantified PFAS were 0.41 mg/kg dry weight (field soil-D) and 0.25 mg/kg dry weight (field soil-E). The majority of the PFAS masses was related to PFDA and 8:2 diPAP with approximately 20%–30% each.

The columns were irrigated three to five times a week using an Eppendorf pipette and demineralized water. The watering rate of 35 ml per week was determined using the 4-year average precipitation in southwestern Germany (Statista, 2021), where the contaminated soils (field soil-D/field soil-E) originated. The percolation water was collected in a sample bottle via a funnel (polyethylene). The collected water was frozen at –18 °C in 2-week intervals, and the sample bottles were changed. The measurements shown correspond to a cumulation of the 2 prior weeks; for example, a value in week 3 includes weeks 1 and 2. At the start of week 105, the last samples (weeks 103 and 104) were taken, followed by 2 weeks with no watering. At the start of week 107 the experiment was finished, and no percolation water was analyzed because of negligible percolation amounts.

The water was filtered using a regenerated cellulose filter (0.45 µm pore size) because few soil particles were found in the samples. Columns 2 and 3 from field soil-E were excluded partially from the experiment because of the emergence of silting, which caused ponding of water on top of the soils, partially obstructing the irrigation process. This exclusion was done from weeks 85 to 99. After this week, mean values and standard deviations were calculated using one observation or two observations depending on the number of excluded observations.

At the end of our study (105 weeks), soil columns were stored in a freezer at  $-23^{\circ}\text{C}$ . Every column was cut into four pieces with a targeted length of 12.5 cm with a multifunction tool equipped with a segment saw blade. Pieces were then thawed separately in polypropylene laboratory trays, and the soil was scooped out with sampling spoons (polypropylene). The soil trays were inserted into a drying cabinet and dried at  $40^{\circ}\text{C}$  with a targeted moisture content of maximal 5%. A total of 72 soil samples were produced. The samples were then pooled within a variant and soil depth; for example, all upper 12.5 cm of PFAA-A were pooled and named soil Layer 1, which resulted in 24 soil samples. Prior to analytics, pooled samples were homogenized in a kitchen machine. Approximately 1 g of each soil type was used to analyze the organic carbon content. Between steps in which mass loss could occur, samples were weighed with a precision of 1 g, to monitor mass loss of soil or water. To minimize contaminations among variants and samples, surfaces were cleaned with ethanol before using materials.

### Standards and reagents

All PFAS standards and isotope-labeled internal standards were purchased from Wellington Laboratories (see Supporting Information). Both 6:2 and 8:2 diPAPs were custom-synthesized by the University of Giessen, Germany (purity  $>98\%$ ). Water (liquid chromatography–mass spectrometry [LC-MS] grade) and concentrated hydrochloric acid (37%) were obtained from Chemsolute. Methyl *tert*-butyl ether (MTBE;  $\geq 99.7\%$ ) from Honeywell was used. Both sodium carbonate ( $\text{Na}_2\text{CO}_3$ ;  $\geq 99.5\%$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ;  $\geq 99.0\%$ ) as well as a concentrated ammonia solution (25%) were obtained from Merck. Potassium persulfate ( $\geq 99\%$ ) from Acros and LC-MS-grade methanol from Fisher Scientific were used. Ethanol, which was used to clean surfaces against contaminations, was purchased from Th. Geyer ( $>99.8$  vol.% pure). Tetrabutylammonium hydrogen sulfate (TBA;  $\geq 99\%$ ) and ammonium acetate for LC-MS were obtained from Sigma-Aldrich. Sodium hydroxide ( $\text{NaOH}$   $\geq 99.5\%$ ) microgranules from Th. Geyer were used. Nitrogen gas (Grade 5.0) was obtained from Messer. Sodium chloride ( $\geq 99.5\%$ ), which was used as a tracer, was purchased from Carl Roth. Both diPAP (6:2 diPAP, 8:2 diPAP;  $>98\%$ ) were provided and synthesized by the University of Giessen, Germany.

### Analytical methods

In the present study, a target analysis was performed to determine the levels of known PFAS in the percolation water and soil samples. Furthermore, the sum parameter analysis direct Total Oxidizable Precursor (dTOP) assay was carried out as described by Gökener, Eichhorn, et al. (2020). It is based on the transformation of oxidizable PFAS substances into stable PFAA using an alkaline potassium persulfate solution, as described by Houtz and Sedlak (2012). This method allows us to include known and unknown precursors of PFAA and thereby

to yield a more comprehensive overview on the total PFAS burden in both matrices.

For the target analysis of PFAS, 1 ml of water or 1 g of homogenized soil were put into a 15-ml polypropylene tube; 100  $\mu\text{L}$  of a mixture of isotopically labeled PFAS standards (100  $\mu\text{g/L}$ ; see Supporting Information) were added as internal standards. After addition of 2 ml of a carbonate buffer ( $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ , 0.25 M each), 1 ml of a 0.5 M TBA solution (pH 10), and 5 ml of MTBE, the tube was closed and shaken for 10 min (2000 rpm; Vortex), followed by a 10-min treatment in an ultrasonic bath and another 10 min of shaking. Afterward, the samples were centrifuged (4700 r/min, 5 min), and the organic supernatant was transferred into a new 15-ml polypropylene tube. The supernatant was then evaporated to dryness under a nitrogen stream ( $40^{\circ}\text{C}$ ) and resuspended in 1 ml of methanol. After 10 min of shaking and a 5-min treatment in an ultrasonic bath, the samples were centrifuged again. The methanolic solution was transferred into a polypropylene LC vial and analyzed by ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HRMS).

For the quantification of unknown oxidizable PFAS precursors in soil, the dTOP assay was used as a sum parameter, as described by Gökener, Eichhorn, et al. (2020). For the quantification of PFAS precursors in water samples, the method was adapted to the aqueous matrix. For this purpose, 100  $\mu\text{L}$  of a mixture of several isotopically labeled PFCA and PFSA standards (100  $\mu\text{g/L}$ ; see Supporting Information for details) were pipetted into a 15-ml polypropylene tube and evaporated to dryness under a stream of nitrogen ( $40^{\circ}\text{C}$ ). Afterward, 1 ml of the water sample was added as well as 1 ml of an alkaline potassium persulfate solution (200 mM  $\text{K}_2\text{S}_2\text{O}_8$  and 500 mM  $\text{NaOH}$ ). The tube was closed, manually shaken, and heated to  $85^{\circ}\text{C}$  for 7 h in a drying cabinet. After cooling to room temperature, 3 ml of a carbonate buffer ( $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ , 0.25 M each), 1 ml of a 0.5 M TBA solution (pH 10) and 5 ml of MTBE were added. The sample was shaken (2000 r/min, 10 min; Vortex), treated in an ultrasonic bath (10 min), and shaken again (10 min). After centrifugation (4700 r/min, 5 min), the organic supernatant was transferred into a new 15-ml polypropylene tube and evaporated to dryness under a stream of nitrogen ( $40^{\circ}\text{C}$ ). The residue was resuspended in 1 ml of methanol, shaken once again (10 min), and treated in an ultrasonic bath (5 min). The solution was then centrifuged (4700 r/min, 5 min) and transferred into a polypropylene LC vial. The analysis was performed by UHPLC-HRMS.

### UHPLC-HRMS analysis

The parameters used for the UHPLC-HRMS analysis are presented in Supporting Information, Tables S3 and S4. The quantification was performed using a linear calibration curve with 10 concentrations (0.1–10  $\mu\text{g/L}$ ) per substance in methanol and an internal standard level of 10  $\mu\text{g/L}$ . A coefficient of determination ( $r^2$ ) of at least 0.99 was required for the calibration curves of all substances for the quantification. Xcalibur Quan Browser software (Ver 4.0.27.19) was used for data evaluation.

## Method validation

All analytical methods were validated using similar guidance values as described in guideline SANCO/3029/99 (European Commission, 2000) for method validation in pesticide analysis. Samples of PFAS-free soil and water were spiked five times at the limit of quantification (LOQ) level and at the 10-fold LOQ, respectively. Furthermore, two noncontaminated samples of both matrices were not spiked, to observe any possible background contamination. All samples were then analyzed using the methods described above. The mean substance recoveries of a triplicate were in a range between 70% and 120% for each substance, with a relative deviation not exceeding 30% for being accepted. The LOQ for the target analysis was determined to be 0.5 µg/kg (or 0.5 µg/L for aqueous samples) for each surveyed PFAS (see Supporting Information, Table S5), as well as for the dTOP assay for water samples. Given an LOQ of 0.5 µg/L for aqueous samples, a percolate volume of approximately 40 ml per sample and a total of 48 samples in the 2-year experimental time, a total mass of <1 µg could have been eluted without being detected. In the case of LOQ of 0.5 µg/kg, approximately <0.4 µg of each PFAA could be in the soil column without being detected. The dTOP assay method for solid samples resulted in an LOQ of 5 µg/kg for all PFCA and PFSA.

## Calculations of mass, amount balances, and retardation

Calculations and preparation of data were done in two different ways: (1) In the case of nontransformable PFAA (PFAA-A, PFAA-B), masses were used to calculate substance balances, to gain a better comparison among the substances. The focus was set on relative masses in soil and percolation water. (2) If precursors and their final transformation products (PFCA) were in the same system, such as in diPAP and field soil variants, masses were converted to molar amounts ( $n$ ). The conversion was needed for calculating a substance balance independent of mass changes by transformation processes.

According to Lee et al. (2010), one molecule of diPAP can be transformed into two molecules of PFCA as a maximum. So, molar amounts of PFCA were divided by 2 ( $\tilde{n}_{PFCA}$ ) to match the initial molar amounts of diPAP, presuming a complete diPAP transformation. However, a molar balance can be made by doing this standardization.

The dissipation time (DT50) represents the half-life of precursors after which 50% of the initial substance cannot be measured. In the present study, DT50 includes all dissipation processes leading to missing amounts to close the molecular balance. The missing amount can cover the process of NER formation, but also other processes can be included such as adsorption on vessels, formation of intermediate transformation products, and ultra-short-chain PFCA. The DT50 (days) is calculated by implying a first-order degradation (Equation 1) considering the study duration  $t$  of 733 days using the initial mass  $m_0$  (micrograms) and the mass at the end of the study  $m(t)$ ; (micrograms).

$$DT50 = \frac{\ln(2) \times t}{\ln\left(\frac{m_0}{m(t)}\right)} \quad (1)$$

Retardation ( $R$ ) was calculated, comparing the times between study start and the peaks of PFCA  $t_{\max,PFCA}$  and the tracer  $t_{\max,tracer}$  in the percolation water:

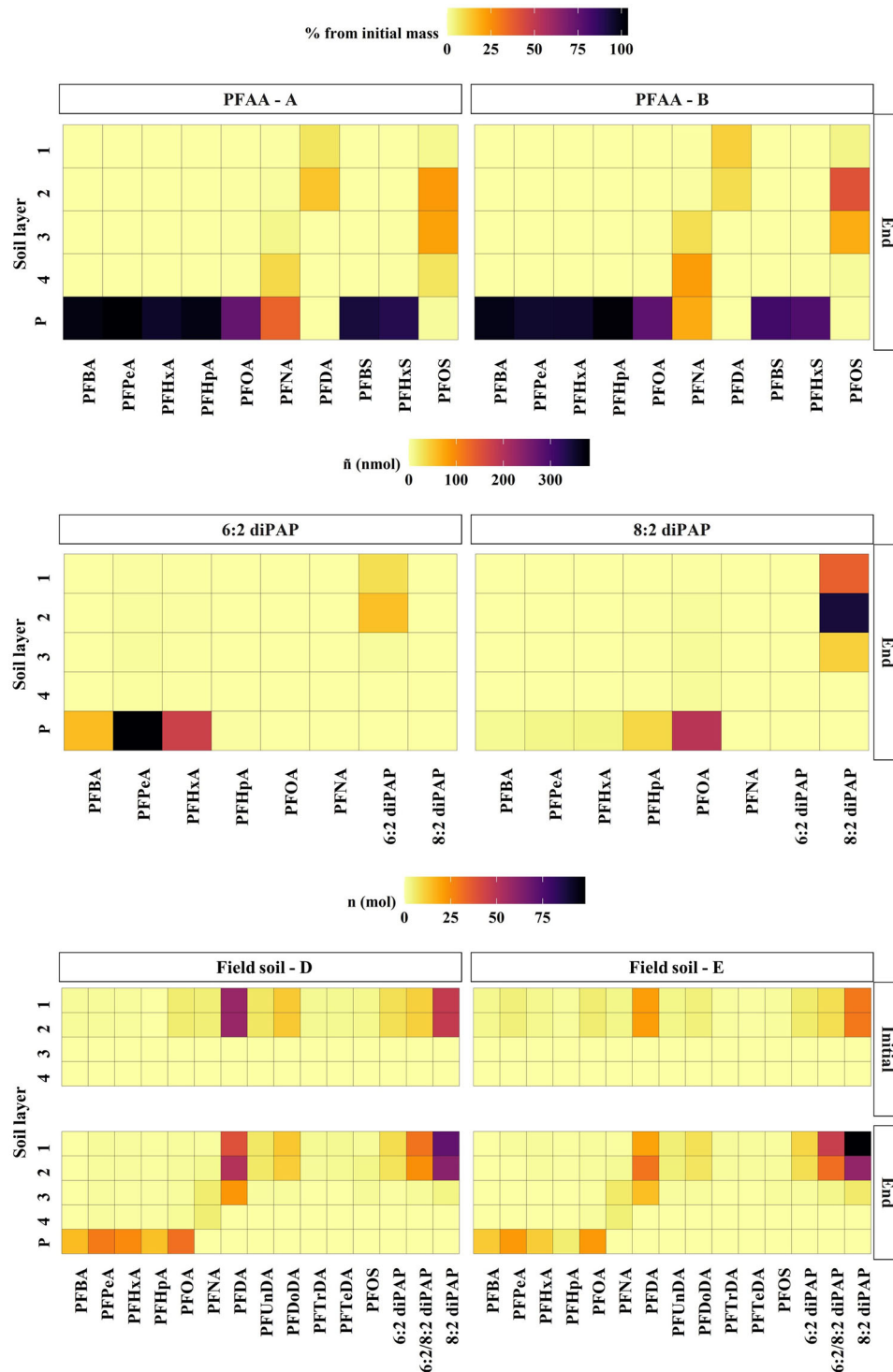
$$R = \frac{t_{\max,PFCA}}{t_{\max,tracer}} \quad (2)$$

## Results and Discussion

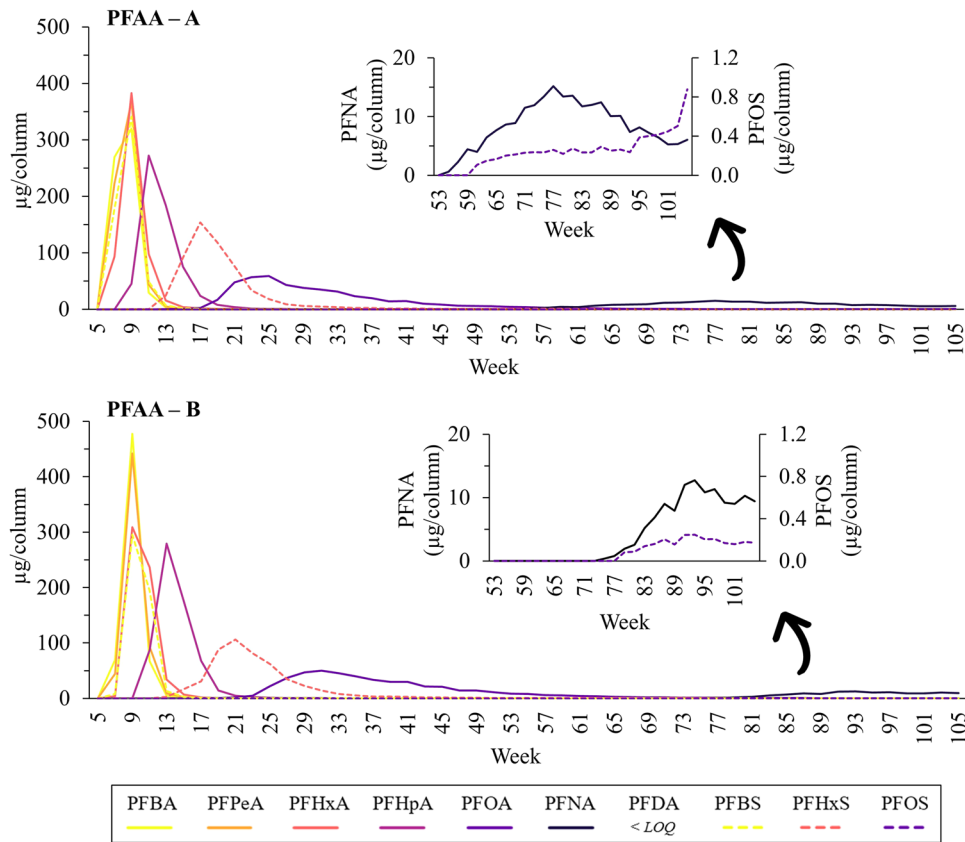
### PFAA mixture (PFAA-A, PFAA-B)

During 104 weeks of percolation analysis, nine of the 10 applied PFAA were found. With the largest number of CF<sub>X</sub> groups among the PFAA used, PFDA was not detected above the LOQ, which matches the results of the soil analysis (Figure 1), where it was solely found in the upper 25 cm of the soil columns. The peak of the NaCl tracer was found in week 5 (PFAA-A) and week 7 (PFAA-B) with the first percolation water. First detections of PFAA were found 2 weeks after (PFAA-A) and together with (PFAA-B) the tracer peak. The breakthroughs of short-chained PFAA were dominantly found between weeks 7 and 21 for both variants (Figure 2). In week 7, water discharge of PFAA-A (56 ml) was 18 ml above that of PFAA-B (38 ml) because of hydraulic conductivity differences, which is an explanation for the PFAA-B mass output delay compared to PFAA-A. However, leaching behavior changed in transition from PFOA to PFNA and from PFHxS to PFOS. High deviations of masses between triplicates were found for short-chain PFAA in both variants around breakthrough peaks. This can be related to high gradients of mass outputs around breakthrough events. After 104 weeks, the cumulative mass output was low for PFNA (19%–36%) and PFOS (0.40%–1.1%), compared with shorter-chain compounds of their PFAA group (Figure 3). However, their breakthrough was not yet finished by the end of the experiment. Mass recovery in the percolation water was >82.9% for all short-chain PFAA and both variants. A decreased recovery in the percolation water and a temporal delay were found with increasing number of CF<sub>X</sub> groups, which corresponds to results given in the literature (Fabregat-Palau et al., 2021; Gellrich et al., 2012). In the control columns (control-A and control-B) no PFAS were found in percolate. Therefore, no significant background contamination was detected in soils A and B.

The results of the soil analysis (Figure 1) support the results of the percolation analysis. A visible difference was found between PFOA/PFNA and PFHxS/PFOS, where PFAA with a larger CF<sub>X</sub> group were found in higher soil layers. Soil residues >1% of the initial mass were solely found for PFNA, PFDA, and PFOS for both variants. The slow leaching of these PFAA, which was already shown in the percolation water, was also visible in the substance distribution between the soil layers. The time until the majority of the substances was leached out could not be determined because our study ended before the breakthrough was over.



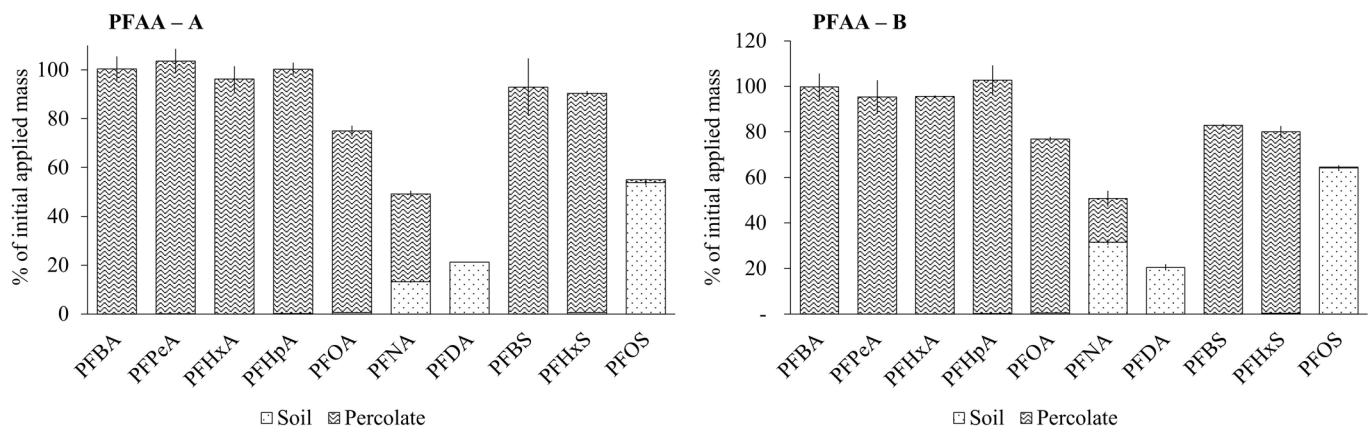
**FIGURE 1:** Perfluoroalkyl acids A (PFAA-A) and PFAA-B: Distribution of per- and polyfluoroalkyl substance (PFAS) relative masses related to initial mass in soil layers (percentage per layer). 6:2 Polyfluoroalkyl phosphate diesters (diPAP) and 8:2 diPAP: Distribution of the PFAS amount of substance ( $\bar{n}$ ) in soil layers (nanomoles per layer). Molar conversion. Field soil-D and field soil-E: Distribution of the amounts of PFAS in soil layers (moles per layer) prior to and at the end of our study. No molar conversion. Depths were approximately 12.5 cm each. Mean of triplicate. Layer 1 = upper topsoil; Layer 4 = lower subsoil. PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFDA = perfluorodecanoic acid; PFBS = perfluorobutanesulfonic acid; PFHxS = perfluorohexanesulfonic acid; PFOS = perfluorooctanesulfonic acid; PFUnDA = perfluoroundecanoic acid; PFDoDA = perfluorododecanoic acid; PFTTrDA = perfluorotridecanoic acid; PFTeDA = perfluorotetradecanoic acid; P = cumulated value in the percolation water.



**FIGURE 2:** Biweekly masses of 10 perfluoroalkyl acids (PFAA) in percolate of PFAA-A (sandy loam topsoil) and PFAA-B (loam topsoil). Average of triplicates. PFNA = perfluorononanoic acid; PFOS = perfluorooctanesulfonic acid; PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid; PFDA = perfluorodecanoic acid; PFBS = perfluorobutanesulfonic acid; PFHxS = perfluorohexanesulfonic acid.

Almost no retardation ( $R$ ) of PFAA with fewer than five  $\text{CF}_x$  groups was observed for both variants (Table 2). Retardation coefficients of substances were found to be slightly higher in PFAA-B than in PFAA-A for  $\text{CF}_x > 5$ . Organic carbon content, which was slightly lower in PFAA-B compared to PFAA-A (0.8% vs. 1.1%), and a higher pH value (7.0 vs. 5.4) rather point to a lower adsorption in PFAA-B (Gellrich & Knepper, 2012; Higgins

& Luthy, 2006). The significantly higher clay content in PFAA-B compared to PFAA-A (19.5% vs. 7.7%), however, might have been the dominant factor, outcompeting the other parameters (Fabregat-Palau et al., 2021). A proportion of the retardation can be related to the sorption on the AWI (Lyu et al., 2018), as a result of not having saturated flow conditions, which affects all PFAA similarly.



**FIGURE 3:** Mass balance of perfluoroalkyl acids (PFAA)-A and PFAA-B (percentage of initial applied mass, 623 µg) with fractions of soil and percolate. Mean values with standard deviation ( $n = 3$ ). PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFDA = perfluorodecanoic acid; PFBS = perfluorobutanesulfonic acid; PFHxS = perfluorohexanesulfonic acid; PFOS = perfluorooctanesulfonic acid.

**TABLE 2:** Retardation coefficients ( $R$ ) (–) of perfluoroalkyl acids (PFAA: PFAA-A, PFAA-B) based on maximum of curves for NaCl tracer and PFAA:  $R_{\text{Tracer}} = 1$  (no retardation)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
$R_{V1}$ (–)	1.3	1.3	1.3	1.6	3.6	11.0	n.d.	1.3	2.4	n.d.
$R_{V2}$ (–)	1.3	1.3	1.3	1.9	4.4	13.3	n.d.	1.3	3.0	n.d.

PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFDA = perfluorodecanoic acid; PFBS = perfluorobutanesulfonic acid; PFHxS = perfluorohexanesulfonic acid; PFOS = perfluorooctanesulfonic acid; n.d. = not determined.

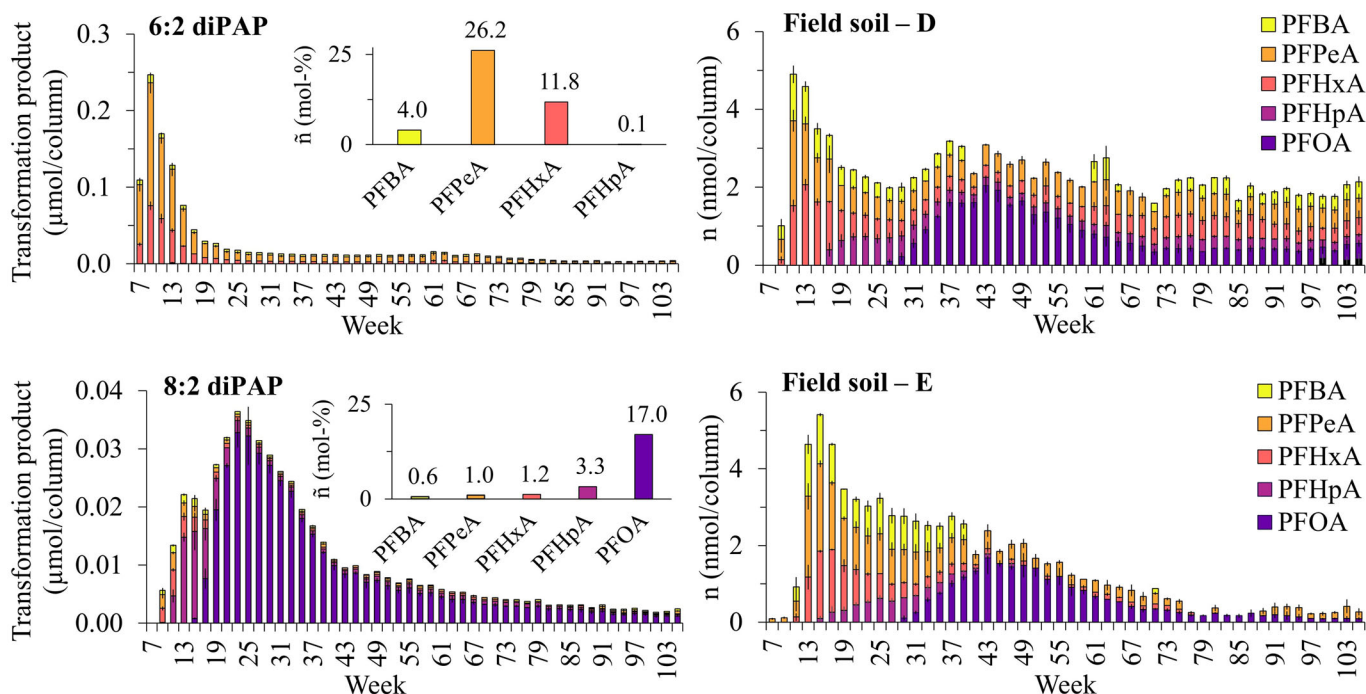
The distribution patterns of mass balances (Figure 3) were similar for both variants, PFAA-A and PFAA-B. Perfluorobutanoic acid to PFHpA predominantly leached after 20 weeks (Figure 2). A highly significant decrease of the PFAA recovery rate with increasing number of  $\text{CF}_x$  groups was determined (Spearman rank correlation test,  $r = 0.82$ ,  $p < 0.001$ ). In general, recovery rates were lower for PFSA than for PFCA homologs. These results deviate from those of McLachlan et al. (2019), in which recovery rates increased with increasing chain length, but are in line with those of Chen et al. (2016).

In the present study, PFOA was found 10 weeks earlier in percolation water compared to a similar soil column study by Gellrich et al. (2012; MIX100 variant), using a soil similar to our soil A (topsoil PFAA-A, control-A). Furthermore, PFNA/PFOS eluted in our study within 2 years, which was not the case in Gellrich et al. (2012), even though water input was higher (100 ml/week) than in the present study (35 ml/week). Compared to Gellrich et al. (2012), the total applied mass of PFAA (6230  $\mu\text{g}$ ) was a factor of 220 higher in the present study. This underlines

the findings of Gellrich et al. (2012), who suggested that a higher PFOA input mass resulted in accelerated leaching. This might further indicate that PFAA input masses might be a more important factor than water input, which would be a consequence of limited sorption sites. The influence of concentrations should be a subject of further investigations.

### 6:2 diPAP and 8:2 diPAP

Detected final transformation products in percolation water of 6:2 diPAP columns (Figure 4) are in line with other studies (Liu & Liu, 2016; Liu et al., 2010; Zhao et al., 2013), with PFPeA and PFHxA being the major products (Table 3). In weeks 101–105 of the present study, low but almost constant amounts of 1–2 nmol/water sample were found for PFBA, PFPeA, and PFHxA (each) in the percolation water, which corresponds to 0.02–0.07 mol-% of  $n_{\text{max}}$ . A possible reason is the ongoing transformation process of diPAPs. In accordance with other transformation studies (Bizkarguenaga et al., 2016; Liu & Liu,



**FIGURE 4:** Left: Biweekly cumulated amounts of perfluorocarboxylic acids (PFCA) in percolate (micromoles per column) and  $\bar{n}_{\text{PFCA}}$  relative to initial amount (mole percentage) of 6:2 polyfluoroalkyl phosphate diesters (diPAP) and 8:2 diPAP. Mean and standard deviation ( $n = 3$ ). Right: Biweekly amount of substance ( $n$ ) of perfluoroalkyl acids in percolation water of field soil-D and field soil-E. No molar conversion. Mean of triplicate, duplicate or single value. PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid.



**TABLE 3:** Relative amount of substance ( $\bar{n}_{\text{PFCA}}$ ) related to precursors of 6:2 polyfluoroalkyl phosphate diesters (diPAP) and 8:2 diPAP variants

Precursor	PFBA (mol-%)	PFPeA (mol-%)	PFHxA (mol-%)	PFHpA (mol-%)	PFOA (mol-%)
6:2 diPAP	4.0	26.2	11.8	0.1	—
8:2 diPAP	0.6	1.0	1.2	3.3	17.0

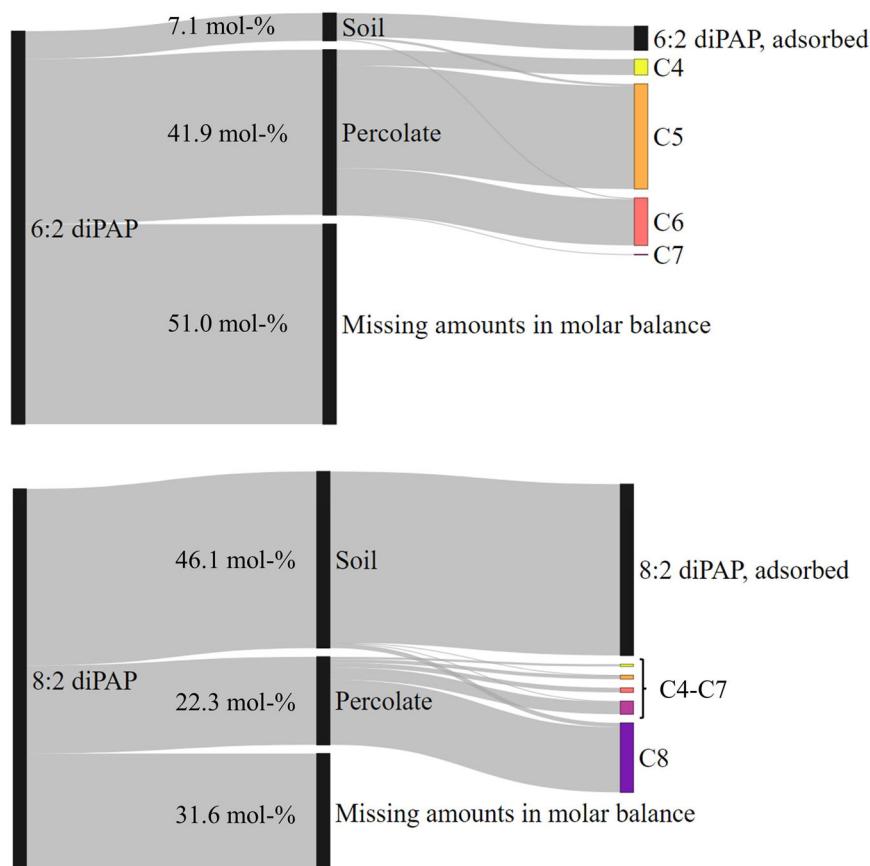
Mean ( $n = 3$ ).

PFBA = perfluorobutanoic acid; PFPeA = perfluoropentanoic acid; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid.

2016; Wang et al., 2009), PFOA was found to be the major transformation product of 8:2 diPAP (Figure 4) with 17.0 mol-% in the percolate. Also, short-chained PFCA were found in soil and percolate with much lower amounts compared to PFOA (Table 3), which is in accordance with several studies (Bizkarguenaga et al., 2016; Butt et al., 2014; Liu & Liu, 2016; Liu et al., 2007). In contrast to our study, short-chained PFCA were often not detected above the LOQ (Bizkarguenaga et al., 2016; Liu et al., 2007; Wang et al., 2009). The longest possible PFCA final transformation product of 8:2 diPAP, PFNA was solely detected during dTOP analysis (Supporting Information, Table S9). This corresponds to the statements of Butt et al. (2014) and D'eon and Mabury (2011) that PFNA is a transformation product of 8:2 diPAP which is predominantly found in animals and is not likely to occur in microbial systems. However,

Bizkarguenaga et al. (2016) found PFNA in the soil environment as a transformation product as well. First detections of PFCA in percolate were found depending on the precursor and  $\text{CF}_x$  group in the same order as found in PFAA-A and PFAA-B. This suggests that all PFCA were formed simultaneously. During our whole study, diPAP above LOQ were not detected in the percolation water, either through target analysis or through TOP analysis (Supporting Information, Table S9). This could be expected, because of the low predicted water solubility (Wang et al., 2011) and therefore a presumed high sorption to soil. To the best of our knowledge, sorption values of diPAP were not experimentally determined yet.

After 105 weeks, 6.1 mol-% of initially applied 6:2 diPAP and 44.7 mol-% of initially applied 8:2 diPAP were still adsorbed in the upper soil layers, into which they were mixed prior to the start of the present study; 42.1 mol-% (6:2 diPAP) and 23.0 mol-% (8:2 diPAP) were detected as PFCA in the percolation water, and 0.9 mol-% (6:2 diPAP) and 1.4 mol-% (8:2 diPAP) were present as PFCA in soil (Table 3 and Figure 5). The higher missing amount fraction in the 6:2 diPAP variant (51.0 mol-%) compared to the 8:2 diPAP variant (31.6 mol-%) is in accordance with studies conducted by Liu et al. (2010) and Wang et al. (2009) using 6:2 FTOH and 8:2 FTOH, which are intermediate metabolites of 6:2 diPAP and 8:2 diPAP (Lee et al., 2010). In these variants, missing amounts can be related to NER fractions of diPAP as well as their transformation

**FIGURE 5:** Molecular fluxes of 6:2 polyfluoroalkyl phosphate diesters (diPAP) and 8:2 diPAP and transformation products relative to initial amount of substance within our study duration.

products, unquantified intermediates (e.g., fluorotelomer carboxylic acid, FTUCA, ketones), loss through volatile intermediates (e.g., FTOH), and loss through sorption on vessels (Sanan & Magnuson, 2020). In the 6:2 diPAP variant, missing amount fractions are expected to consist of molecules other than the short-chain PFCAs according to results from PFAA-A and PFAA-B, in which negligible levels of missing amounts were observed. As a transformation product in the 8:2 diPAP variant, PFOA has a demonstrated potential to cause missing amounts (Figure 3). Taking the results of missing amounts and leaching amounts of 8:2 diPAP transformation products in PFAA-A and PFAA-B, it can be expected that the majority of the 8:2 diPAP missing amount fraction cannot be assigned to PFAA-related missing amounts. Furthermore, a recovery experiment with diPAP would be needed for both matrices, soil and water, similar to Göckener, Eichhorn, et al. (2020), to differ between amounts emerging from diPAP and intermediates with the aim to assign some parts of missing amounts to intermediates.

Liu and Liu (2016) concluded that missing amount are a result of biotransformation and therefore that higher transformation rates increase missing amounts, based on the results of an aerobic biotransformation in soil experiment with 6:2 and 8:2 diPAP. In addition, losses through volatile compounds such as n:2 FTOH or n:2 sFTOH are likely to occur more extensively for 6:2 diPAP than for 8:2 diPAP when looking at the results of headspace measurements of Liu and Liu (2016). Approximately 4 mol-%–6 mol-% of the initial applied 6:2 diPAP amount would be a potential loss of volatile compounds, assuming a conversion (Equation 1) and using the results of Liu and Liu (2016).

In the present study, calculated DT50 values of 6:2 diPAP and 8:2 diPAP are 182 and 630 days, respectively, using Equation 1. The DT50 values which were taken from other studies, such as 14.5 days (6:2 diPAP) and 114 days (8:2 diPAP) conducted by Liu and Liu (2016) and approximately 60 days (6:2 diPAP) conducted by Lee et al. (2014), were all based on first-order kinetics. Even though our DT50 results differ greatly from those of other studies, the order of DT50 is consistent among all studies when comparing 6:2 and 8:2 diPAP. Differences in reported DT50 values could be related to varying study conditions such as soil composition, soil moisture, targeted concentration, and special study characteristics like use of plants. A selection of conditions for the above-described studies is provided in Supporting Information, Table S12. Connections seen in the present study are not statistically significant because of the small number of three studies but can show potential relations, which should be further investigated. An increase of sorption sites attributable to an increase of mineral fractions (silt and clay), according to Fabregat-Palau et al. (2021), could be also connected to an increase of missing amounts. This would be a result of covalent binding (NER type II [Schäffer et al., 2018]) and/or bioNER formation (NER type III [Schäffer et al., 2018]). Another connection could be drawn between differences in soil moisture, which has an influence on biodegradation of other organic contaminants (Cho et al., 2000; Tao & Yang, 2011). In Tao and Yang (2011) DT50 decreased with increasing soil moisture in the range 20%–80%,

and Cho et al. (2000) found the lowest biodegradation rate at 25% and an increase at lower as well as higher soil moistures in a studied range of 10%–40%. Therefore, the relationship between soil moisture and biodegradation rate could be a potential reason for the different reported DT50 values. In the present study as well as in the study of Lee et al. (2014) soil moisture content was not determined, so a connection can only be assumed. In addition, in Lee et al. (2014) plants were part of the study, which could have enhanced microbial activity due to the ability of plants to influence microbial communities (Chaudhry et al., 2005). Furthermore, Liu and Liu (2016) showed that a double first-order in parallel equation was a better fit than the first-order equation with a slightly different DT50 value for 6:2 diPAP (11.5 days) and a big difference in the DT50 value of 8:2 diPAP (>1000 days), which was even higher than in our study.

### Contaminated field soil (field soil-D, field soil-E)

Within the experimental duration, five PFCAs (PFBA to PFOA) were quantified in the percolation water (Figure 1) with an accumulated amount of substance ( $n$ ) of approximately 5–30 nmol each for both variants. These amounts were found to be higher than the initial amounts in soil (Supporting Information, Table S10), which can be related to the transformation of determined diPAP. The distributions of leached PFCA in field soil-D and field soil-E were different from those of the 6:2 diPAP and 8:2 diPAP variants, especially for C <6, which might be a result of an unknown precursor mixture. Also, the amounts of PFCA found in the percolation water were higher for field soil-D than for field soil-E, which might be the result of higher initial amounts of precursors (Supporting Information, Table S10). The high amounts of PFHpA in percolation water of field soil-D up to 104 weeks was not observed in the 6:2 diPAP or in the 8:2 diPAP variants, which could be caused by different precursors. This statement was supported by the dTOP assay (Supporting Information, Table S11), according to which the amount of emerging PFCA in soil was four times (field soil-D) and five times (field soil-E) higher than the amount of measured diPAP (6:2, 6:2/8:2, 8:2 diPAP). During the whole study, no indication for the presence of precursors was found in the percolation water through dTOP analysis considering standard deviations of both methods (Supporting Information, Table S11). High amounts of PFCA were still found in percolation water of field soil-D after 104 weeks (Figure 2). Each PFCA up to PFOA was found with approximately 20%–30% of their peak, taking the mean of the last three samples (weeks 101–105). Using the same comparison for field soil-E gives approximately 0%–10% for each PFCA. Perfluorononanoic acid was solely found in field soil-D (percolation water) during target analysis with a cumulated amount of 0.4 nmol.

Amounts of 16 and 17 different PFAS were quantified in field soil-D and field soil-E, respectively, at the beginning of the experiment (Supporting Information, Table S10). The amounts of all measured diPAP homologs (6:2, 6:2/8:2, 8:2) increased during the present study, which can possibly be related to unknown diPAP precursors. A likely group of precursors is

triPAP, which can be transformed into diPAP (Trier et al., 2011) and was already found in soils with a similar contamination source (Bugsel & Zwiener, 2020). In field soil-D, PFDA and 8:2 diPAP accounted for the largest fraction with approximately 30% each on the total amount of quantified PFAS prior to and at the end of the experiment. A significant change in PFDA amounts was not determined, but 8:2 diPAP as well as 6:2/8:2 diPAP had an increase of 42 and 34 nmol, respectively. In field soil-E, PFDA and 8:2 diPAP were also the main substances found prior to the start of the present study, with approximately 20% and 30%, respectively. After the end of the experiment, 6:2/8:2 diPAP (21%) and 8:2 diPAP (43%) accounted for most of the total amount of substance in field soil-E. The increased PFDA amount can be related to precursors such as longer-chain diPAP, which were not analyzed. A reason for the constant PFDA amount in soil (field soil-D) could be a completed transformation of its precursor or a formation of missing amounts and an ongoing transformation.

Taking solely concentrations in percolation data and soil data prior to the start of the experiment, field soil-D would be classified as more highly contaminated than field soil-E. But soil analysis at the end of the present study showed that this conclusion would have been not quite correct because of a significant increase of the three quantified diPAPs, which shows an unpredictable risk when the masses of additional precursors are unknown.

## CONCLUSIONS

In the present study, we investigated three different spectra of PFAS contamination in soil columns with increasing complexity. Mass balances of PFAA showed a significant correlation between the number of CF<sub>x</sub> groups and recovery rates, including NER formation or losses due to adsorption on vessel walls. Furthermore, it was confirmed that the sorption behavior of PFAA might be more influenced by mineral soil fractions (silt and clay) than by organic carbon or pH. Transformation products of diPAPs were formed simultaneously during dissipation of 6:2 diPAP (DT50 = 182 days) and 8:2 diPAP (DT50 = 630 days). Considering all available data, we conclude that the dissipation of diPAPs and their transformation products includes transformation of diPAPs and the formation of missing amounts of both diPAPs and their degradation products (PFAA). Components of missing amounts need further investigations such as NER research and quantification of intermediates and ultra-short-chain PFAA. In addition, sum parameters such as the total extractable organically bound fluorine (Koch, Aro, 2020a) or the total adsorbable organically bound fluorine (Abercron et al., 2019) could be used to determine the total fluorine mass in a sample. While losing any structural information, this could help to identify missing amounts in different matrices.

The results of contaminated field soils show that PFAS can be found years after contamination. Taking solely concentrations in percolation data and soil data prior to the start of the experiment, contaminated field soils (field soil-D, field soil-E)

would have been classified differently, with a higher risk coming from field soil-D. Not until the soil analysis at the end of our study did it become apparent that this conclusion would not have been quite correct because of a significant increase of the three quantified diPAPs. This shows the unpredictable risk of not knowing the masses of additional precursors. Currently, leaching of PFAS can give some hints on the approximate type of contamination and leaching potential, but target analysis combined with dTOP analysis can give more insights into the estimated number of substances in a qualitative way. Therefore, a quantitative estimation about the remaining substances in soils, desorption potential, and therefore risks for future discharge needs further investigation.

**Supporting Information**—The Supporting information are available on the Wiley Online Library at <https://doi.org/10.1002/etc.5417>.

**Acknowledgment**—Special thanks to U. Telgmann, A. Brandl, and M. Degenhardt from the Laboratory for Urban Water Management and Water Quality (University of Kassel) for 2 years of experiment supervision; P.R. Schreiner and his group at the University of Giessen for providing diPAP; as well as M. Zoska, W. Sauer, and W. Heisel of the Agricultural Technology Centre Augustenberg for obtaining contaminated soil for the experiments. The present study was funded by the Ministry of the Environment, Climate Protection and the Energy Sector Baden-Württemberg (Germany) through the Project “PROSPeCT—PFAA and Precursors Soil Plant Contamination” (FKZ BWPFC19002, FKZ BWPFC19004, FKZ BWPFC19005, FKZ BWPFC19006). Open Access funding enabled and organized by Projekt DEAL.

**Author Contribution Statement**—**Eva Weidemann**: Writing—original draft; Visualization; Conceptualization; Formal analysis; Investigation. **René Lämmer**: Investigation; Writing—original draft; Writing—review & editing. **Thorsten Stahl**: Resources; Supervision; Writing—review & editing. **Bernd Göckener**, **Mark Bücking**, **Hildegard Just**: Writing—review & editing. **Jörn Breuer**, **Runa S. Boeddinghaus**: Resources; Writing—review & editing. **Janine Kowalczyk**: Funding acquisition; Writing—review & editing. **Matthias Gassmann**: Supervision; Writing—review & editing.

**Data Availability Statement**—The data sets generated and/or analyzed during the present study are included in this published article and its Supporting Information and available from the corresponding author ([eva.weidemann@uni-kassel.de](mailto:eva.weidemann@uni-kassel.de)).

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