Long-term behavior of per- and polyfluorinated alkyl substances (PFAS) on contaminated agricultural sites in Germany

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Abstract

Per- and polyfluorinated alkyl substances (PFAS) are an anthropogenic group of chemicals that have been used in many different products (e.g., paper coatings, fire-fighting foams, textiles) since the 1950s. PFAS are water and grease-repellent and also have high chemical and thermal stability. Some PFAS can be degraded in the environment to perfluorinated carboxylic acids (PFCAs) and sulfonic acids (PFSAs). These degradable compounds are also known as precursors. However, the resulting PFCAs and PFSAs are persistent in the environment and thus can be detected in even the most remote environmental compartments.

In 2006, PFAS were detected in the Ruhr River and its tributaries which are also used for drinking water production. The origin of the contamination was traced to agricultural fields that had been impacted by a so-called soil conditioner mixed with PFAS-containing waste material. A particularly heavily contaminated 10 ha area near Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW), was equipped with a drainage system and an activated carbon filter system to purify any leachate produced before the water was discharged back into a surface water body. In 2013, PFAS were also detected in groundwater near the city of Rastatt, Baden-Württemberg. This contamination could be traced back to a large-scale contamination of agricultural land in the region of Rastatt where presumably compost containing paper sludges was applied to the fields. PFAS-contaminated areas were also detected in Mannheim. In addition to PFCAs and PFSAs, precursors were found in Rastatt/Mannheim.

Surface and groundwater are both important sources of drinking water in Germany. Thus, it is of high relevance to accurately evaluate the release behavior of PFAS from contaminated agricultural soils. Therefore, several agricultural soils from the Rastatt/Mannheim area were sampled in this work to investigate the release behavior of PFAS in laboratory experiments. The aim was to assess as accurately possible time periods of PFAS release from soils for groundwater risk assessment. In addition, long-term monitoring data from BS-NRW were evaluated.

In the first part of the work, 14 soil samples from the Rastatt/Mannheim area were used to investigate the release behavior of PFCAs and PFSAs in extensive column percolation tests up to a liquid/solid ratio (LS) of 10 l/kg. It was found that PFCAs of chain length C4-C8 are rapidly mobilized and released from the soil. With increasing chain length (PFCAs > C8), the leaching slows down and larger quantities remain in the soil. The average recovery of C4-C8 PFCAs in column eluate was 104-111% while for the longer chain PFCAs the recoveries decreased down to 7%. However, relatively constant concentration levels were observed for C4-C8 PFCAs at LS >4 rather than dropping below the limit of quantitation. It was suspected

that this may be due to the degradation of precursors in the column that leads to the continuous production and thus tailing of the C4-C8 PFCAs.

In the long-term field monitoring data collected in BS-NRW, similar observations to the column experiments were made. PFCAs and PFSAs showed a continuous discharge over a 12-year period with only a slowly decreasing trend. A statistical analysis of the data revealed seasonal influences on the discharge behavior of most compounds.

A consecutive investigation using the direct total oxidizable precursor (TOP) assay that chemically converts PFAS precursors into PFCAs, on two soil samples from the Rastatt area revealed a higher load of PFCAs than estimated with standard methanolic soil extraction. The formation potential of PFCAs from precursors was analyzed by so-called microcosms or batch-tests. A linear increase in C4-C8 and partially C9 PFCAs was observed in the 60-day batch tests in both soils. This indicates aerobic biotransformation of precursors to PFCAs. Qualitatively, the PFAS distribution patterns from the batch tests resemble those found in groundwater. Therefore, it can be assumed that the transformation of precursors in the upper soil layers to mobile PFCAs caused the groundwater contamination. It further implies that groundwater exposure to PFCAs will continue until the reservoir of precursors is exhausted.

Using the rates from the batch tests as well as the results of the TOP assay, rate constants could be calculated, allowing to estimate time periods until concentrations decrease to legal limit levels. These indicated that it is likely to take several decades before the reservoir of precursors is exhausted and no significant further C4-C8 PFCAs are produced. However, these time periods should be considered a "best-case scenario" since the rates were conducted in laboratory experiments under optimal conditions. Seasonal influences, as observed in the long-term data from BS-NRW, indicate that the periods are further extended due to weather conditions.

In Germany, the application of recycling material to agricultural fields in the circular economy can cause the pollution of soil with a diverse and often unknown mix of PFAS. This can lead to a continuous release of PFAS as PFAS precursors are transformed into more mobile transformation products (TPs). Therefore, agricultural soils may act as a long-term source of groundwater pollution. To evaluate PFAS release time scales, several different investigation methods have to be combined.

Zusammenfassung

Per- und polyfluorierte Alkylsubstanzen (PFAS) sind eine anthropogene Stoffgruppe, die seit den 1950ern in vielen verschiedenen Produkten (z.B. in Papierbeschichtungen, Feuerlöschschäumen, Textilien) verwendet werden. PFAS sind wasser- und fettabweisend und besitzen darüber hinaus eine hohe chemische sowie thermische Stabilität. Einige PFAS können in der Umwelt unter anderem zu perfluorierten Carboxylsäuren (PFCAs) und Sulfonsäuren (PFSA) abgebaut werden. Diese abbaubaren Verbindungen werden auch als Präkursoren bezeichnet. Die entstehenden PFCAs und PFSAs sind in der Umwelt jedoch persistent und können so auch in den entlegensten Umweltkompartimenten nachgewiesen werden.

Im Jahr 2006 wurden in der Ruhr und ihren Nebenflüssen PFAS entdeckt. Der Ursprung der Kontamination wurde auf landwirtschaftliche Flächen zurückgeführt, die mit einem sogenannten Bodenverbesserer, der PFAS-haltige Abfälle enthielt, beaufschlagt wurden. Eine besonders stark belastete, 10 ha große Fläche bei Brilon-Scharfenberg, Nordrhein-Westfalen (BS-NRW), wurde mit einem Drainagesystem und einer Aktivkohlefilteranlage ausgerüstet, um anfallendes Sickerwasser zu reinigen, bevor das Wasser wieder in ein Oberflächengewässer eingeleitet wird. Im Jahre 2013 wurden in der Nähe von Rastatt ebenfalls PFAS im Grundwasser nachgewiesen. Diese Belastung konnte auf eine großflächige Verunreinigung landwirtschaftlicher Flächen in der Region Rastatt, Baden-Württemberg, mit mutmaßlich mit Papierschlämmen versetztem Kompost zurückgeführt werden. Auch in Mannheim konnten mit PFAS belastete Flächen festgestellt werden. Neben den PFCAs und PFSAs wurden in Rastatt/Mannheim auch Präkursoren nachgewiesen.

Oberflächen- und Grundwasser stellen in Deutschland bedeutende Trinkwasserquellen dar. Daher ist es von gesellschaftlicher Relevanz, das Freisetzungsverhalten von PFAS aus kontaminierten Ackerböden genau zu evaluieren. Aus diesem Grund wurden in dieser Arbeit mehrere Ackerböden aus dem Raum Rastatt/Mannheim beprobt, um in Laborversuchen das Freisetzungsverhalten von PFAS zu untersuchen. Ziel ist es, möglichst genaue Vorhersagen über die Zeiträume der PFAS-Freisetzung aus Böden für den Pfad Boden-Grundwasser zu machen. Außerdem wurden Langzeit-Monitoring-Daten aus Brilon-Scharfenberg ausgewertet.

Im ersten Teil der Arbeit wurde mit 14 Bodenproben aus dem Raum Rastatt/Mannheim das Freisetzungsverhalten von PFCAs und PFSAs im ausführlichen Säulenversuch bis zu einem Wasser-Feststoffverhältnis (WF) von 10 l/kg untersucht. Dabei konnte festgestellt werden, dass PFCAs der Kettenlänge C4-C8 schnell mobilisiert und aus den Böden ausgetragen werden. Mit zunehmender Kettenlänge (PFCAs >C8) verlangsamt sich die Freisetzung und es

verbleiben immer größere Anteile im Boden. So betrug die durchschnittliche Wiederfindung der C4-C8 PFCAs im Säuleneluat 104-111% (vollständige Austragung), während für die längerkettigen PFCAs die Wiederfindung auf 7% sinkt. Es wurde jedoch auch festgestellt, dass bei C4-C8 PFCAs ab einem WF >4 die Konzentrationen im Eluat nicht weiter abfallen und sich ein relativ konstantes Konzentrationsniveau einstellt. Vermutet wird, dass dies möglicherweise auf den kontinuierlichen Abbau von Präkursoren in der Säule zurückführen ist, das zu dem anhaltenden Tailing der C4-C8 PFCAs führt.

In den Langzeit-Monitoring-Daten aus BS-NRW konnte ein ähnliches Verhalten wie in den Säulenversuchen beobachtet werden. Auch dort wurden kontinuierliche PFCAs- und PFSAs-Austragungen beobachtet. Eine statistische Auswertung der Daten ergab saisonale Einflüsse auf das Austragungsverhalten der meisten Verbindungen.

Um diesen Beobachtungen nachzugehen, wurden im zweiten Teil der Arbeit zwei Böden aus dem Raum Rastatt sogenannten Mikrokosmen- (Batch-) Tests unterzogen. Über einen Summenparameter, total oxidizable precursor (TOP) assay, der chemisch Präkursoren in PFCAs umwandelt, wurde eine deutlich höhere Belastung der zwei Böden mit PFCAs festgestellt, als durch methanolische Extraktion des Bodens ersichtlich war. In den 60-tägigen Batch-Tests konnte eine lineare Zunahme von C4-C8 und teilweise C9 PFCAs festgestellt werden. Dies deutet auf eine aerobe biologische Transformation von Präkursoren zu PFCAs hin. Qualitativ ähneln die Verteilungsmuster aus den Batch-Tests den im Grundwasser hauptsächlich gefundenen PFAS. Es ist daher davon auszugehen, dass durch die Transformation der Präkursoren in den oberen Bodenschichten zu mobilen PFCAs die Kontamination des Grundwassers verursacht wurde. Dies bedeutet, dass die Kontamination des Grundwassers mit PFCAs so lange anhält, bis das Reservoir an Präkursoren erschöpft ist.

Mit den Raten aus den Batch-Tests sowie den Ergebnissen des TOP assays konnten Ratenkonstanten berechnet werden, um Zeiträume bis zum Ende der PFCA Nachlieferung aus Präkursoren abzuschätzen. Diese ergaben, dass es wahrscheinlich mehrere Jahrzehnte dauern wird, bis das Reservoir an Präkursoren erschöpft sein wird und keine weiteren C4-C8 PFCAs gebildet werden. Allerdings sind diese Zeiträume als „best-case scenario“ anzusehen, da die Raten in Laborversuchen unter optimalen Bedingungen durchgeführt wurden. Saisonale Einflüsse, wie sie in den Langzeitdaten aus Brilon-Scharfenberg zu beobachten sind, deuten darauf hin, dass sich witterungsbedingt die Zeiträume noch weiter verlängern werden.

In Deutschland kann die Ausbringung von Recyclingmaterial auf landwirtschaftliche Flächen im Rahmen der Kreislaufwirtschaft zu einer Verunreinigung der Böden mit einer vielfältigen und oft unbekannten Zusammensetzung von PFAS führen. Dies kann eine kontinuierliche

Freisetzung von PFAS zur Folge haben, da PFAS-Vorläufer zu mobileren Transformationsprodukten (TPs) umgewandelt werden. Daher können landwirtschaftliche Böden eine langfristige Quelle für die Verschmutzung des Grundwassers darstellen. Um die Zeitskalen der PFAS-Freisetzung zu bewerten, müssen verschiedene Untersuchungsmethoden kombiniert werden.

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Abbreviation

•OH	Hydroxyl radicals
AC	Activated carbon
AFFF	Aqueous fire-fighting foams
BS-NRW	Brilon-Scharfenberg, North Rhine-Westphalia
diPAP	Polyfluorinated dialkylated phosphate ester
diSAmPAP	N-ethyl perfluorooctane sulfonamide ethanol– based phosphate diester
ESI	Electrospray ionization
EPA	Environmental protection agency
FTCA	Fluorotelomer carboxylic acid
GFO	German fertilizer ordinance
HPLC	High-performance liquid chromatography
HRMS	High-resolution mass spectrometry
LS	Liquid-to-solid ratio
MS	Mass spectrometer / mass spectrometry
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluorinated alkyl substances
PFCA	Perfluorinated carboxylic acid
PFSA	Perfluorinated sulfonic acid
PFBS	Perfluorobutanesulfonic acid
PFBA	Perfluorobutanoic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFNA	Perfluorononanoic acid
PFOS	Perfluorooctanesulfonc acid
PFOA	Perfluorooctanoic acid
PFPeA	Perfluoropentanoic acid
PP	Polypropylene

QS	Quotientensumme
TOP	Total oxidizable precursor
TP	Transformation product
TQ	Triple quadrupole
UBA	Umweltbundesamt (federal german environmental protection agency)
WWTP	Wastewater treatment plant

List of Publications and Author Contributions

This thesis includes published and submitted papers. Chapter 8 presents the published article "*Long-term behavior of PFAS in contaminated agricultural soils in Germany*" by Klaus Röhler, Alexander Arthur Haluska, Bernd Susset, Binlong Liu, and Peter Grathwohl. Chapter 9 contains the submitted article "Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments." by Klaus Röhler, Bernd Susset, and Peter Grathwohl. As the content of chapter 9 was submitted to a scientific journal, the published article may contain modifications after revision.

Chapter 8

Klaus Röhler, Alexander Arthur Haluska, Bernd Susset, Binlong Liu and Peter Grathwohl. "Long-term behavior of PFAS in contaminated agricultural soils in Germany." *Journal of Contaminant Hydrology*, Volume 241,2021,103812.

Authors contributions

Klaus Röhler, Alexander Arthur Haluska, Bernd Susset, and Peter Grathwohl planned the study. Klaus Röhler, Alexander Arthur Haluska, and Bernd Susset generated the data. Binlong Liu ran model simulations. Klaus Röhler, Alexander Arthur Haluska, and Peter Grathwohl evaluated the data, and wrote the main part of the manuscript.

Chapter 9

Klaus Röhler, Bernd Susset, and Peter Grathwohl. „*Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments.*" Submitted to Environmental Science & Technology.

Klaus Röhler, Bernd Susset, and Peter Grathwohl planned the study. Klaus Röhler collected the samples, generated and evaluated the data, and had the main role in writing the manuscript. Peter Grathwohl provided constructive criticism and helped shape the manuscript.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a vast group of anthropogenic chemicals with more than 4700 individual compounds (OECD, 2018). PFAS are characterized by their carbon (C) chain and substitution of hydrogen (H) atoms with fluorine (F) atoms. They are either fully (perfluorinated) or partially fluorinated (polyfluorinated). The C-F bond is one of the strongest bonds in chemistry and bond stability increases with the degree of fluorination at the C-atom, giving PFAS high thermal and chemical stability as well as hydrophobic and lipophobic properties (Buck et al., 2011). The non-fluorinated part of the molecule allows for the addition of further desired features (e.g. increasing water-solubility or incorporation of fluorinated side-chains in polymers) and leads to a diversification of the PFAS subclasses (Krafft and Riess, 2015). PFAS are labeled as long-chain, if the number of fluorinated C equals or exceeds six ($n_{CF} \geq 6$) in perfluorosulfonic acids (PFSA) and if $n_{CF} \geq 7$ in perfluorocarbonic acids (PFCA), two important subclasses in PFAS (Buck et al., 2011). However, PFCA and PFSA only cover a small fraction of many compounds compared to the entirety of the whole PFAS class.

Broad application of PFAS began in the 1950s and since then they can be found in a variety of industrial and consumer products including, but not limited to automotive industry applications, aqueous film forming foams (AFFFs), textiles, biocides, paper coatings and non-stick cookware (Buck et al., 2011; ITRC, 2020). As a consequence, PFAS are detected in numerous environmental compartments, such as air (Morales-McDevitt et al., 2021; Vento et al., 2012), water (Ahrens, 2011; Schmidt et al., 2019), soil (Rankin et al., 2016; Röhler et al., 2021) and biota (Langberg et al., 2020; Routti et al., 2015). However, it was not until the early 2000s that an effort was made to prevent further emissions of two of the most prominent PFAS, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), which are both considered long-chained. Pressured by the Environmental Protection Agency (EPA) of the United States of America (USA), companies voluntarily phased out the production of PFOA and PFOS (Dean et al., 2020). Studies have shown that PFOA and PFOS bioaccumulate and can have adverse health effects (e.g., increased risk of thyroid disease, decreased antibody response to vaccine, or increased risk of decreased fertility) (Langenbach and Wilson, 2021). Due to intensified regulations of PFOA, PFOS, and other long-chain PFAS manufacturers around the world have simply shifted their production to short-chain PFAS, leading to a continuous exposure of the environment (Brendel et al., 2018).

1.1. PFAS Subsets

The term PFAS includes a diverse set of compounds with vastly different properties and are therefore grouped into several PFAS subclasses. The main focus of this thesis is on one of the most studied PFAS subclasses, the so-called perfluoroalkyl acids (PFAA), which can be further subdivided into PFCAs, PFSAs, and several others (see Figure 1) (Wang et al., 2017). PFCAs and PFSAs can be released either directly into the environment or can be produced by the degradation of so-called precursor substances (Houtz and Sedlak, 2012; Lee and Mabury, 2014). They are often referred to as "forever" chemicals since no further breakdown of these compounds is expected in the environment (Cousins et al., 2020; Lee and Mabury, 2014; Miner et al., 2021). A brief overview of important physical-chemical properties of selected representatives of the PFCAs and PFSAs group is provided in Table 1. Generally, PFCAs and PFSAs are water soluble, due to their hydrophilic head group, which is negatively charged under ambient environmental conditions (Vierke et al., 2013). The two opposing functional parts (hydrophilic head group vs. hydrophobic perfluoroalkyl chain) give PFCAs and PFSAs properties of a surfactant. Surfactants are compounds that, when dispersed in water, aggregate in an orderly fashion at interfaces depending on concentration (e.g. air-water interface) (Krafft and Riess, 2015). The tendency to accumulate at interfaces increases with an increasing chain length of the perfluoroalkyl moiety (Higgins and Luthy, 2006; Reth et al., 2011).

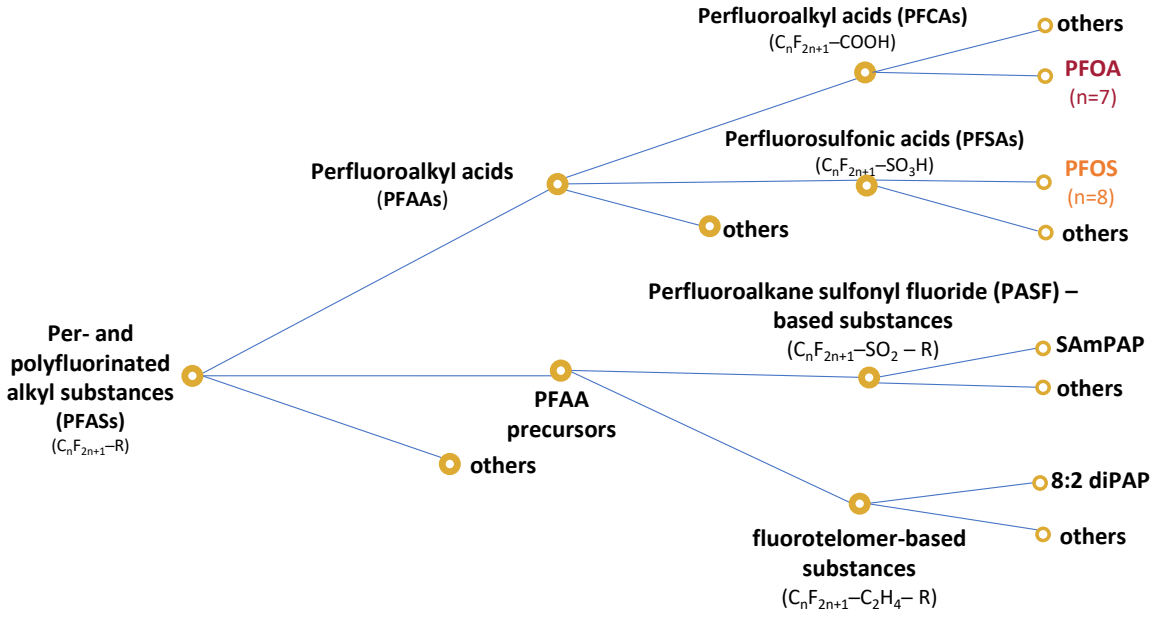

Figure 1. A brief overview of PFASs and their different subclasses including examples of individual compounds. PFOA = perfluorooctanoic acid, PFOS = perfluorooctanesulfonic acid, SAmPAP = N-Ethyl perfluorooctane sulfonamide ethanol–based phosphate ester. 8:2 diPAP = 8:2 polyfluorinated dialkylated phosphate ester.

Table 1. Overview of physio-chemical properties of selected PFAS. n_{CF} = number of fluorinated C-atoms; PFBA = perfluorobutanoic acid, PFHxA = perfluorohexanoic acid; PFOA = perfluorooctanoic acid, PFDA = perfluorodecanoic acid; PFBS = perfluorobutanesulfonic acid, PFHxS = perfluorohexanesulfonic acid; PFOS = perfluorooctanesulfonic acid.

Compound	Compound class	n_{CF}	log K_{AW} (m)	log K_{OW}	log K_{OC} (l/kg)	S_w (g/l)
PFBA	PFCA	3	-4.2[a]	2.8[b]	1.88[c]	563[b]
PFHxA	PFCA	5	-3.7[a]	4.1[b]	1.31[c]	22[b]
PFOA	PFCA	7	-2.9[a]	5.3[b]	1.89[c]	0.77[b]
PFDA	PFCA	9	-1.3[b]	6.5[b]	2.96[c]	0.025[b]
PFBS	PFSA	4	-3.6[a]	3.9[b]	1.79[c]	30[b]
PFHxS	PFSA	6	-2.7[a]	5.2[b]	2.05[c]	2.3[b]
PFOS	PFSA	8	-2.2[a]	6.4[b]	2.8[c]	0.06[b]

a: Schaefer et al. (2019); b: Wang et al. (2011); c: Guelfo and Higgins (2013)

Important classes of precursor substances for PFCAs and PFSAs in this thesis are polyfluorinated dialkylated phosphate esters (diPAPs) and N-ethyl perfluorooctane sulfonamide ethanol–based phosphate ester (SAmPAP). The 8:2/8:2 diPAP can act as a precursor for different PFCAs among PFOA, while SAmPAP can be degraded to PFOS (Figure 2) (Benskin et al., 2012; Lee et al., 2014). SAmPAP and diPAPs were used in food contact paper to make them grease-proof (Benskin et al., 2013; Trier et al., 2011). While diPAPs as well as SAmPAPs are relatively immobile, it has been shown that they can be microbially degraded to form mobile PFAAs, which then can pose a risk for ground- and surface waters due to their increased mobility (Benskin et al., 2013; Lee et al., 2014).

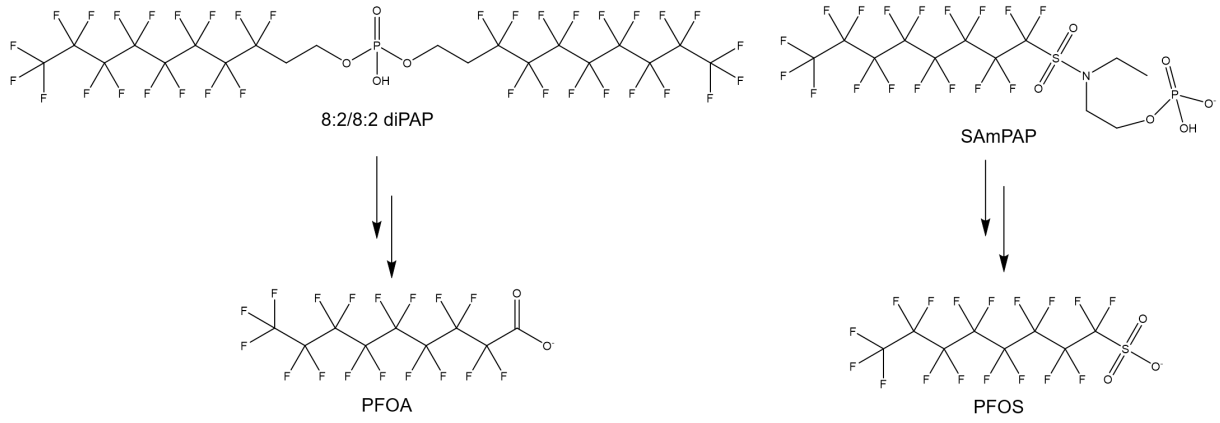

Figure 2. PFAS precursor compounds and their final transformation products (Benskin et al., 2012; De Silva et al., 2012).

1.2. PFAS Analytics

Non-volatile PFAS can be measured using high-performance liquid chromatography (HPLC) coupled to a mass spectrometer (MS). For a couple of PFCAs, PFSAs, and selected other PFASs, standardized methods exist e.g. from the EPA (Shoemaker and Tettenhorst, 2018) or the Deutsches Institut für Normung (DIN 38414-14:2011-08, 2018) and they are part of routine analysis. However, these target methods only capture a small fraction of the PFAS spectrum. For the majority of PFAS, no commercial reference standards and methods are available and therefore, these compounds cannot be quantified and often go unnoticed. Sum parameters such as the total oxidizable precursor (TOP) assay can be used to assess the extent of PFAS pollution by converting unknown precursors to measurable PFAS (Houtz and Sedlak, 2012). In the TOP assay, PFAS precursor substances are chemically oxidized using a strong oxidant (persulfate) and elevated temperatures to produce OH-radicals, which can degrade a certain spectrum of precursors to measurable PFCAs (Houtz and Sedlak, 2012). The TOP assay can be applied to solid and aqueous samples and gives an estimate of the potential PFAS reservoir. However, no information on the identity of the precursor substances is gained by sum parameters.

1.3. PFAS Transformation

PFAS are virtually found in every compartment on earth (Falk et al., 2019; Washington et al., 2019). In the environment, PFAS are exposed to several transformation processes (biotic and abiotic). Polyfluorinated substances (e.g. diPAPs) can be transformed biotically as well as abiotically to perfluorinated transformation products (e.g. PFCAs) which are reluctant to these processes and continue to persist in the environment (Benskin et al., 2013; Lee et al., 2014; Zweigle et al., 2021). Only a few examples in the literature have shown the biodegradation of perfluorinated substances like PFOA and PFOS under laboratory conditions with pure and enriched bacteria cultures (Huang and Jaffé, 2019; Kwon et al., 2014).

Zweigle et al. (2021) showed the electrochemical transformation of the polyfluorinated substance 6:2 diPAP with $^{\bullet}OH$ radicals to form the intermediate transformation products (TPs) 6:2 fluorotelomer carboxylic acid (FTCA), and 6:2 fluorotelomer unsaturated carboxylic acid (FTUCA) as well as the C5-C7 PFCA end-products. The results demonstrate that a single precursor compound can form several TPs with different rate constants. The 6:2 diPAP can also undergo photolytic degradation on TiO_2 particles in synthetic air (Yao et al., 2021). Similar to Zweigle et al. (2021), 6:2 diPAP formed 6:2 FTCA and 6:2 FTUCA as intermediates and the final products were C5-C7 PFCAs during photodegradation. However, the major PFCA formed

was PFHxA in Yao et al. (2021) compared to PFHpA in the study of Zweigle et al. (2021). This shows that different reaction mechanisms and conditions can alter the formation of TPs. A schematic overview of the transformation of 6:2 diPAP is given in Figure 3. Lee et al. (2010) investigated the microbial degradation of 6:2 diPAP in sludge from wastewater treatment plants (WWTP) to form FTOHs which can further be microbially transformed into PFCAs (Dinglasan et al., 2004; Wang et al., 2009). Similar results were observed in soil, where diPAPs were finally transformed into PFCAs (Lee et al., 2014). Also, biodegradation by bacteria, fungi, and phyto-microbial (plant-assisted degradation) can lead to the breakdown of polyfluorinated compounds (Zhang et al., 2022). So polyfluorinated parent compounds can act as a long-term source for the continuous emission of perfluorinated transformation products in the environment.

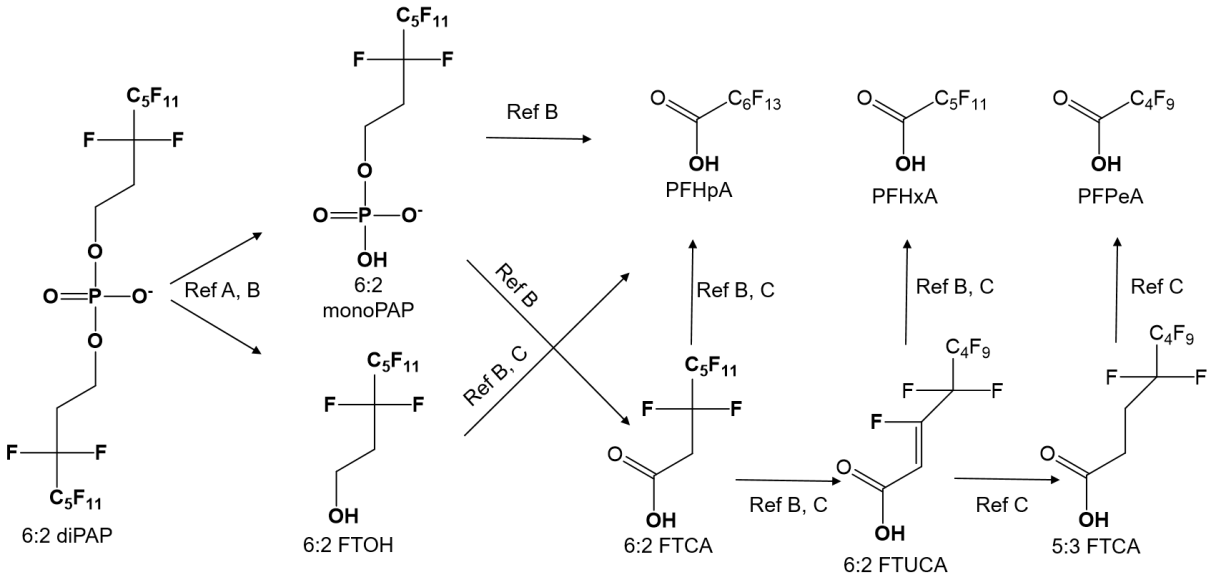

Figure 3. Proposed degradation pathway of 6:2 diPAP in the literature. Ref A: Lee et al. (2010), Ref B: Zweigle et al. (2021), Ref C: Martin et al. (2005).

1.4. PFAS Regulations in Germany

In Germany, PFAS are not uniformly regulated. In 2012, a limit of 100 µg/kg dry weight (∑PFOA+PFOS) was introduced in the German Fertilizer Ordinance (GFO), which regulates the use of fertilizers, soil conditioners, culture substrates, and plant aids (DüMV, 2012). In 2017, the German Federal Environmental Agency (UBA) proposed a list, including 7 PFAS with sufficient toxicological evidence to derive drinking water limits and assigned precautionary limits for 6 PFAS where further investigation is needed. (Table 2) (Umweltbundesamt, 2017).

The state of Baden-Württemberg enforced these limits with a ministerial decree in 2018 and additionally introduced a parameter the so-called "*Quotientensumme (QS)*", which is calculated according to equation Eq. 1

$$QS = \sum_{i=1}^{n} \frac{C_i}{DWL_i} \quad \text{(Eq. 1)}$$

C_i and DWL_i refer to the measured concentration and the drinking water limit of the compound, respectively. Only compounds listed with a DWL in Table 2 are considered in the QS. If the QS exceeds a value of 1 in an aqueous eluate, it is an indication of soil contamination with PFAS.

In late 2020, the EU introduced two PFAS parameters into their new Drinking Water Directive that either set the limit for the sum of C4-C13 PFCAs and PFSAs to 0.1 µg/l or the total PFAS to 0.5 µg/l, which is yet to be determined on how to analytically measure (EU Directive 2184, 2020).

Table 2. Recommended drinking water and precautionary limits for different PFAS by the Federal German Environmental Agency (UBA); n_{CF} = number of fluorinated carbons.

Analyte	n_{CF}	Drinking water limit (µg/l)	Precautionary limit (µg/l)
PFBA	3	10	
PFPeA	4		3
PFHxA	5	6	
PFHpA	6		0.3
PFOA	7	0.1	
PFNA	8	0.06	
PFDA	9		0.1
PFBS	4	6	
PFHxS	6	0.1	
PFHpS	7		0.3
PFOS	8	0.1	
6:2 FTS	6		0.1
FOSA	8		0.1

1.5. Contaminated Agricultural Sites in Germany

In Germany, two prominent cases of PFAS-contaminated agricultural land are known. The first to be detected is located near the city of Brilon-Scharfenberg in North Rhine-Westphalia and is further referred to as BS-NRW. The second case is located in the area of Rastatt and Mannheim in Baden-Württemberg. A brief introduction of the two cases is given below.

Brilon-Scharfenberg. NRW (BS-NRW)

In 2006, C4-C12 PFCAs and C4, C6, and C8 PFSAs were detected in drinking water and several rivers in the Ruhr area with PFOA concentrations of up to 33.6 µg/l, leading to elevated PFAS concentrations in human blood compared to control groups (Exner and Färber, 2006; Hölzer et al., 2008). The surface water contamination was backtracked to agricultural fields in the Hochsauerland region, where one particular 10 ha site was heavily contaminated with an estimated 390 kg of ∑PFOA+PFOS (Arenholz et al., 2011). In 2007, a drainage system was installed to collect the seepage water before it is pumped through an activated carbon (AC) filtration unit to reduce PFAS loads before the water is discharged into the adjacent River Steinbecke. The inflow of the AC plant is continuously monitored. Initially, only PFOA and PFOS concentrations were monitored, but since 2008, PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFBS and PFHxS, and since 2017, PFUnA, PFDoA, and PFDS were included into routine analysis. The origin of this pollution was compost mixed with PFAS-containing industrial waste material, which has been applied presumably between 2004 and 2006. However, no information on the identity of PFAS precursor substances is known at the site. This probably represents the longest data set on PFAS release from an agricultural field.

The Rastatt Case

In 2013, PFAS were analyzed in a drinking water well in the Rastatt Region (Regierungspräsidium Karlsruhe, 2022). The origin of this now large-scale groundwater pollution was backtracked to agricultural fields, where supposedly compost mixed with paper sludge had been applied between 2000 and 2008 (Regierungspräsidium Karlsruhe, 2022; Söhlmann et al., 2018). Until 2021, 1746 ha are considered contaminated with PFAS in the Rastatt and Mannheim area (Regierungspräsidium Karlsruhe, 2022). Bugsel and Zwiener (2020) identified 12 different PFAS compound classes in the Rastatt and Mannheim area with diPAPs (from 4:2/6:2 to 12:2/14:2) and diSAmPAPs (only C8/C8) accounting for the major fraction of precursors at the site. Janda et al. (2019) showed with discreet soil cores that

precursor substances such as diPAPs mainly remain in the top 30 cm of the soil, which corresponds to the plough horizon. The results indicate that a large fraction of the PFAS contamination (precursors) resides in the upper soil layers, where it potentially acts as a long-term source for the production of mobile PFAAs.

1.6. Saturated Column Percolation Test

Saturated column leaching tests according to (DIN 19528, 2009) are a common tool to characterize the leaching potential of organic and inorganic pollutants from solid materials (Grathwohl and Susset, 2009). Column tests are closer to natural conditions as they have a lower liquid-to-solid ratio (*LS*) (*LS* ≈ 0.3 l/kg) compared to batch tests, which usually have a LS of 2-10 l/kg (Grathwohl, 2014). In between two quartz layers, to allow for uniform flow, the solid material is percolated in an upstream flow regime in a column. Eluate fractions are sampled at certain LS, which is the amount of water that has been in contact with the solid material. Normalizing eluate concentrations on *LS* ratios facilitates the comparison between different tests (Grathwohl and Susset, 2009). The *LS* ratio is a proxy for time as saturated column leaching tests act as a time loop, trying to predict seepage water concentrations provided equilibrium conditions apply. The *LS* ratio can be back-calculated into time following Eq. 2:

$$t = LS \frac{x * \rho}{GWR} \quad \text{Eq. 2}$$

with soil layer thickness x (m), dry bulk density ρ (kg l^{-1}), and the groundwater recharge rate *GWR* (m y^{-1}). Extensive column tests are usually performed until a *LS* ratio of 10 and describe the long-term release behavior of contaminants from the solid material. Therefore, column leaching tests only consider the release behavior of already existing contaminants from solid materials into water, while lysimeters may also include the transport part (see Figure 4). For compliance testing, a one-point cumulative leaching test until *LS* of 2 l/kg is conducted and compared to regulatory threshold limits. In Germany, the point of compliance (POC) for the regulatory threshold limits usually is set to the transition point of the unsaturated to the saturated.

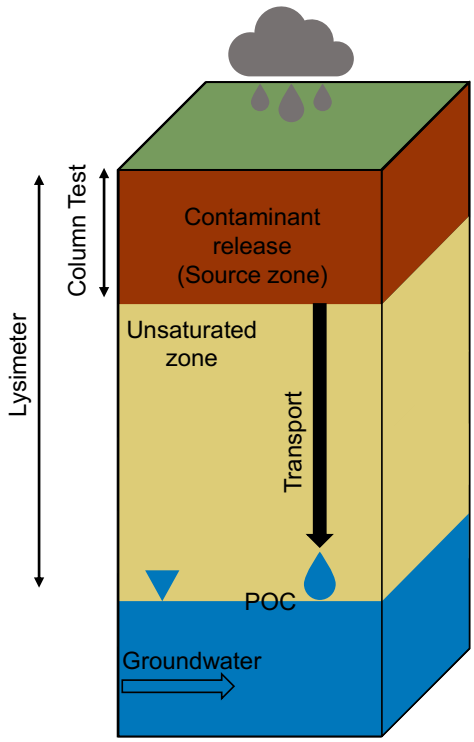

Figure 4. Schematic overview of the fate of contaminants in the subsurface. POC = point of compliance.

1.7. Microcosm Studies or Batch Incubations

Microcosms are laboratory-scale experimental setups (ecosystems) to investigate specific environmental processes under simplified and controlled conditions (Harding-Marjanovic et al., 2015; Lee et al., 2014). They can be used for the investigation of biotic and abiotic processes and allow for continuous observation and enable to identify key pathways or species. Processes of interest are e.g., the development of microbial communities or chemical composition. Microcosms are often performed under idealistic conditions (e.g. constant temperature) and therefore only approximate the environment.

2. Aim of this Thesis

In recent years, an increasing number of publications in the scientific literature report the contamination of soils with PFAS (Guelfo and Higgins, 2013; Rankin et al., 2016; Washington et al., 2010). However, the majority focuses on aqueous film-forming foams (AFFF) impacted sites, which are often located at military sites, airports, or industrial sites. In Germany, the application of biosolids mixed with waste materials has led to the pollution of two large-scale agricultural sites in Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW), and Rastatt/Mannheim, Baden-Württemberg. PFAAs are leaching into surface and groundwater affecting the drinking water quality of several million people in the area.

For groundwater risk assessment, it is crucial to characterize the leaching behavior of regulatory-relevant PFAS as the EU drinking water directive (2020/2184) sets a limit for the sum of 20 PFCAs and PFSAs. This raises the question of appropriate tools to describe the leaching behavior and estimate time scales for groundwater pollution. Furthermore, studies have shown that at the Rastatt/Mannheim site a significant amount of PFAS are precursors, which can degrade to mobile PFAAs (Bugsel and Zwiener, 2020). However, precursor identity and degradation rates are often unknown. Therefore, it is necessary to develop tools to derive production rates of PFAAs from precursor substances to estimate further exposure of groundwater by precursor degradation.

Therefore, the major aims of this thesis were to

1. Characterize the leaching behavior of regulatory-relevant PFCAs and PFSAs from different contaminated agricultural soils.
2. Evaluate the applicability of column percolation tests to estimate leaching time scales at PFAS-impacted agricultural soils.
3. Develop a method to estimate production rates of PFCAs and PFSAs from precursors and time scales until their depletion (and decline of transformation products).

3. Methods & Materials

In the following sections, the procedure to answer the research aims is summarized (for further details see chapters 8 and 9).

3.1. Soil Samples and Concentration

14 soil samples were taken from the Rastatt/Mannheim site. Soil samples were homogenized using a riffle splitter. PFAS concentrations in soils were determined by methanolic soil extraction as it has shown to be a suitable extraction solvent for PFAS (Ahmadireskety et al., 2021). Details on the exact extraction procedure are given in chapter 9. The TOP assay was performed on two soil samples from the Rastatt/Mannheim area and BS-NRW as described by Göckener et al. (2020). The TOP assay is a sum parameter that chemically transforms PFAS precursor substances to measurable PFAAs. Under basic conditions and elevated temperatures, persulfate ($S_2O_8^{2-}$) forms sulfate radicals ($SO_4^{-\bullet}$), which are then converted into $^{\bullet}$OH radicals:

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-\cdot} \qquad \text{(Reaction 1)}$$

$$SO_4^{-} + OH^{-} \rightarrow SO_4^{2-} + {}^{\cdot}OH \qquad \text{(Reaction 2)}$$

The $^{\bullet}$OH radicals then oxidize the precursor to PFAAs (Zweigle et al., 2021). The TOP assay does not allow for any conclusions about the identity of the precursor. For example, both 6:2 and 8:2 diPAP produce PFCAs of chain-length C4-C7 and sulfonamide-based compounds (e.g. FOSA) are converted to PFOA and not PFOS (Houtz and Sedlak, 2012). Therefore, the TOP assay is only suited to estimate a potential reservoir of precursors that can be transformed into PFAAs.

3.2. Saturated Column Percolation Test

Up-flow column leaching tests are a common tool to investigate the leaching of organic and inorganic compounds from solid materials (Grathwohl and Susset, 2009). The column tests were performed according to the German DIN 19528 (2009) for all soil samples. Details on the procedure are given in chapter 9.

3.3. Batch Incubations (Microcosms)

Microcosm studies were carried out to estimate production rates of PFAAs from precursors present in PFAS-impacted agricultural soils. Prior to the microcosms, column tests until a *LS* ratio of 10 l/kg were conducted to remove already existing PFAA background concentrations.

The soil was transferred into 2.5 l glass bottles and filled with deionized water until a *LS* ratio of ≈ 2.5 l/kg was reached. Control samples were autoclaved to inhibit microbial activity. The bottles were placed on a horizontal shaker for 60 days. The aqueous phase was sampled regularly. Further detail of the experimental setups is provided in chapter 9.

3.4. LC-MSMS

Leachate samples from column tests and microcosm experiments as well as soil extraction and TOP assay samples were analyzed using a 6470 triple quadrupole (TQ) or 6490 TQ from Agilent Technologies (Santa Clara, USA). The TQs were coupled with either a 1260 or 1290 high-performance liquid chromatographic system from Agilent Technologies (Waldbronn, Germany). Further information on acquisition parameters, columns used, and more is provided in chapter 9.

4. Results

In this chapter, the results of individual publications and manuscripts (Chapters 8 and 9) are summarized. The first publication (chapter 8) investigated long-term monitoring data of a PFAS-contaminated site located in BS-NRW. It was the first known case of PFAS pollution on agricultural soils in Germany and was discovered in 2006 as high concentrations of selected PFAAs were measured in rivers (Arenholz et al., 2011). In order to reduce PFAS loads into the rivers, a drainage system was installed at a 10 ha field site where the seepage water is collected before it passes through an activated carbon filtration unit. The inflow concentrations of PFOA and PFOS were monitored since 2007 and additional PFAAs were included in 2008 and are shown in Figure 5. PFAA concentrations were relatively stable throughout the monitoring from 2008 to 2019. Fluctuations in concentration were analyzed by seasons using the Kruskal-Wallis test. If there were statistically significant differences between the populations, a Seasonal Mann-Kendall test was performed, otherwise, a Mann-Kendall test was used for trend analysis. A seasonality was observed for PFBA, PFPeA, PFHxA, PFOA, PFDA, PFBS, and PFHxS, but not for PFHpA, PFNA and PFOS. The concentration of PFAAs was higher in fall and winter, potentially indicating the production and accumulation of these compounds during spring and summer and mobilization during fall and winter (Figure 6). Further, the trend analysis showed fairly stable concentrations for C4-C7 and C10 PFCAs, while the other PFAAs showed decreasing trends. Other observations from the literature suggest that especially short-chain PFAAs are not well retained in the soil and readily washed out of soils (Gellrich et al., 2012; McLachlan et al., 2019; Weidemann et al., 2022). For example, Stahl et al. (2013) conducted lysimeter experiments with soil spiked with PFOA and PFOS technical products, which had short-chain PFAAs as impurities but evidently, no precursors present, and short-chain PFAAs could not be detected in the leachate after one year of operation. This shows the rapid movement of the short-chain PFAAs through the unsaturated zone and that a continuous emission of these compounds is likely caused by precursor transformation.

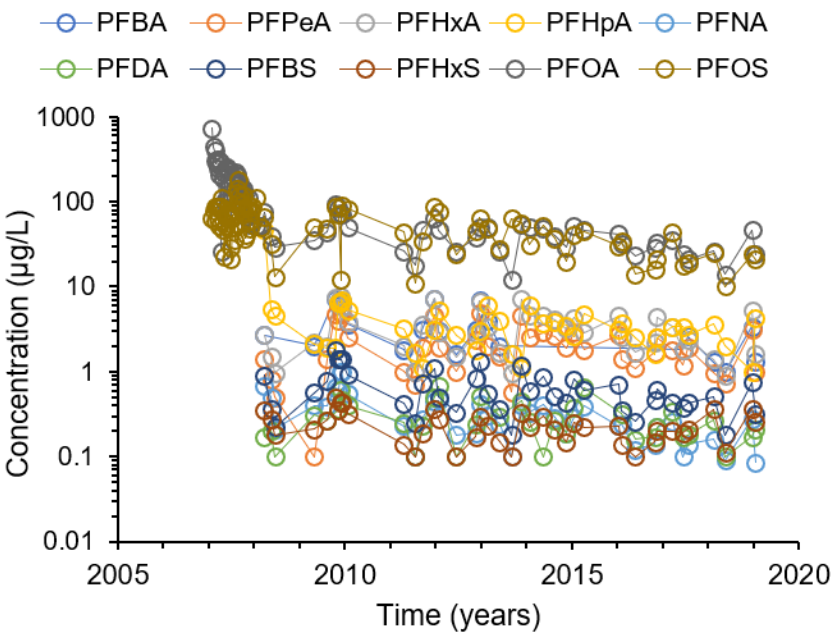

Figure 5. Long-term monitoring for PFAS concentration data at the 10 ha Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW) site. Data for PFOS and PFOA was collected from January 2007 to January 2019. Data for PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFBS, and PFHxS was collected from March 2008 to January 2019. Modified from Röhler et al. (2021).

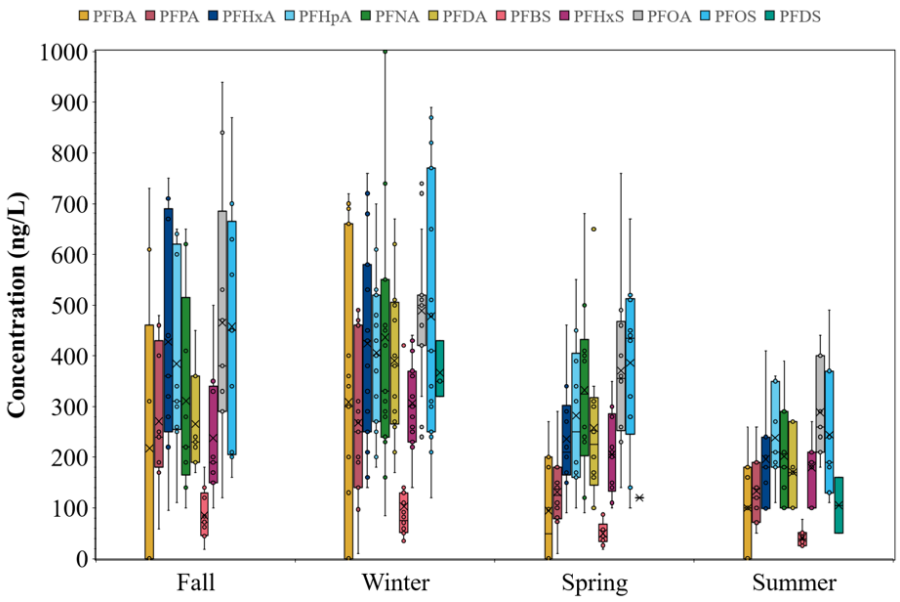

Figure 6. Variations of PFAS concentrations across seasons at the 10 ha Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW) site using data collected from February 2008 to January 2019. PFBA, PFPeA, PFBS, PFHxA, and PFHpA concentrations were divided by 10 and PFOS and PFOA by 100 to allow for comparison. Adapted from Röhler et al. (2021).

In chapter 9, samples from PFAS-contaminated agricultural soils from the Rastatt/Mannheim area in Baden-Württemberg were investigated using column percolation tests and batch tests (microcosms). The Rastatt/Mannheim case was discovered in 2013 and until 2021 1 746 ha were considered polluted (Regierungspräsidium Karlsruhe, 2022). This study aimed to estimate the release time scales of PFAAs from different soils. Therefore, column percolation tests were conducted in combination with batch tests, which were used to investigate further production of PFAAs by precursors. Leaching concentrations from column percolation tests are plotted versus *LS* to facilitate comparison between different tests. The *LS* ratio can be converted into time if the recharge rate is known (Eq. 1). Considering a soil depth of 0.3 m, bulk density of 1.3 kg l^{-1}, porosity of 0.4, and, a seepage velocity of 0.3 m y^{-1}, *LS* = 1 reflects roughly 3 years in the field.

The results show that C4-C8 PFCAs were readily washed out of soils, while leaching slows down with increasing chain length (Figure 7a). At a *LS* of 10 l/kg, C4-C8 PFCAs were recovered on average between 104-111% in the column effluent, while the recovery rate dropped from 89% for PFNA to 7% for PFDoA. For compounds ≥C10, leaching potential is significantly reduced compared to C4-C9 PFCAs. Therefore, these compounds will remain in soils for decades.

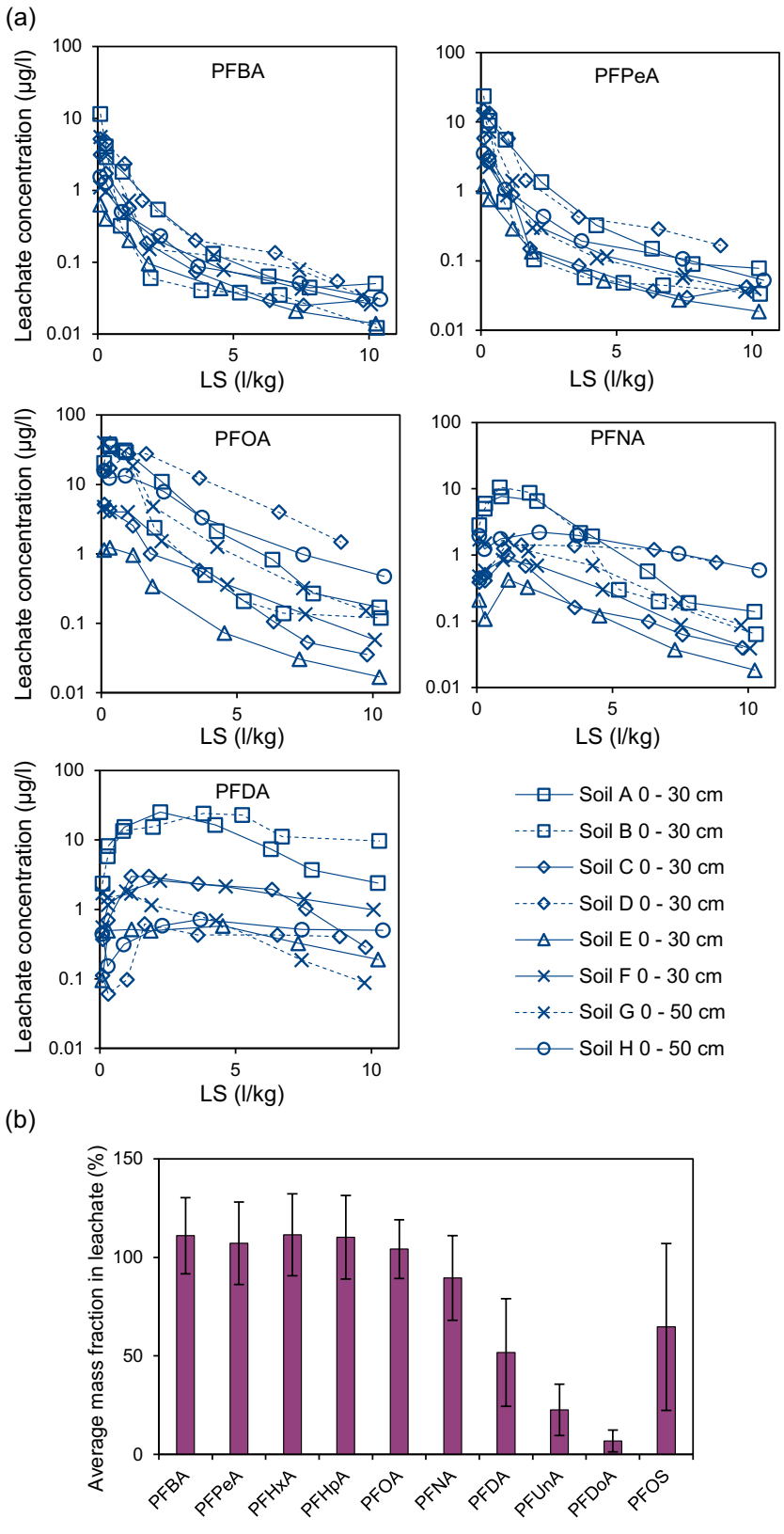

Figure 7. (a) Leaching behavior of selected PFCAs in column percolation tests with contaminated agricultural soils samples; (b) average mass fractions recovered in the column effluent until *LS* = 10. Error bars indicate standard deviations from 14 column percolation tests.

After a rapid decline in leachate concentrations, short-chain PFCAs like PFBA and PFPeA remained relatively stable at *LS* > 4 l/kg instead of declining further. This tailing was further investigated using batch tests, where soil material after column percolation tests was used to track the aqueous concentration of PFAAs over time. After 60 days, a linear increase in the aqueous concentration of C4-C8 PFCAs and partially PFNA in two soil samples from the Rastatt/Mannheim area was observed. While no increase in sterile controls was detected, the increase in the live (active microbiology community) setups indicates the aerobic biotransformation of precursors to PFCAs.

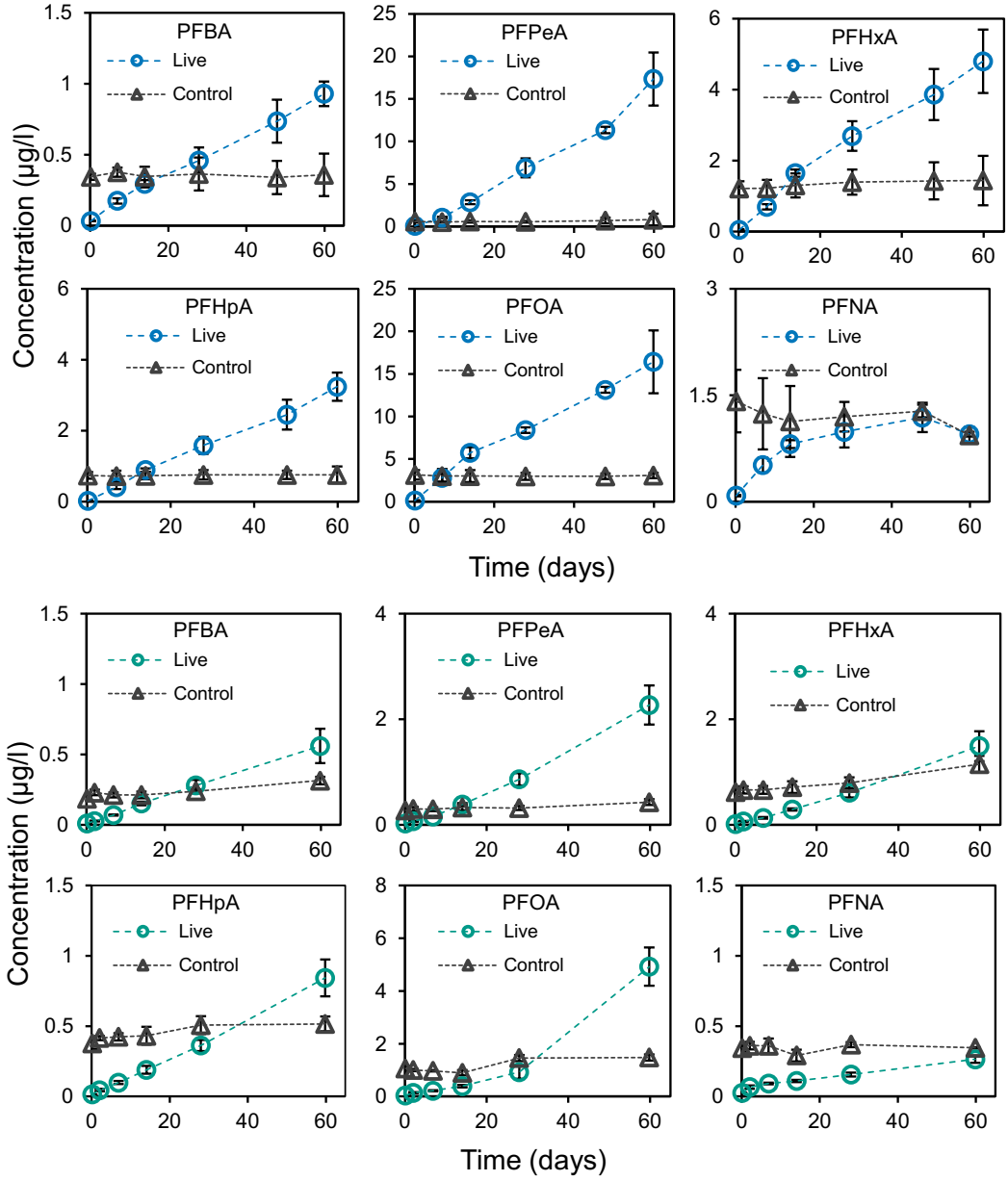

Figure 8. Aqueous concentrations of C4-C9 PFCAs during the 60 days batch experiments. Top: soil A 0 - 30 cm, bottom: soil B 0 - 30 cm. Error bars indicate standard deviations from triplicates.

As the exact composition of precursor substances is difficult to obtain, a sum parameter like the TOP assay can be used to estimate the potential reservoir of PFAAs from precursors. TOP assay results from the two soil samples (Soil A 0-30 cm and Soil B 0-30 cm) showed a reservoir of PFCAs 10-100-fold compared to methanolic soil extraction. By combining the results from the TOP assay and production rates obtained in the batch experiments, it is possible to calculate rate constants and estimate time scales for the complete removal of PFAAs. Depending on the soil sample and compound, depletion of the PFCA reservoir can take a couple of years to several decades.

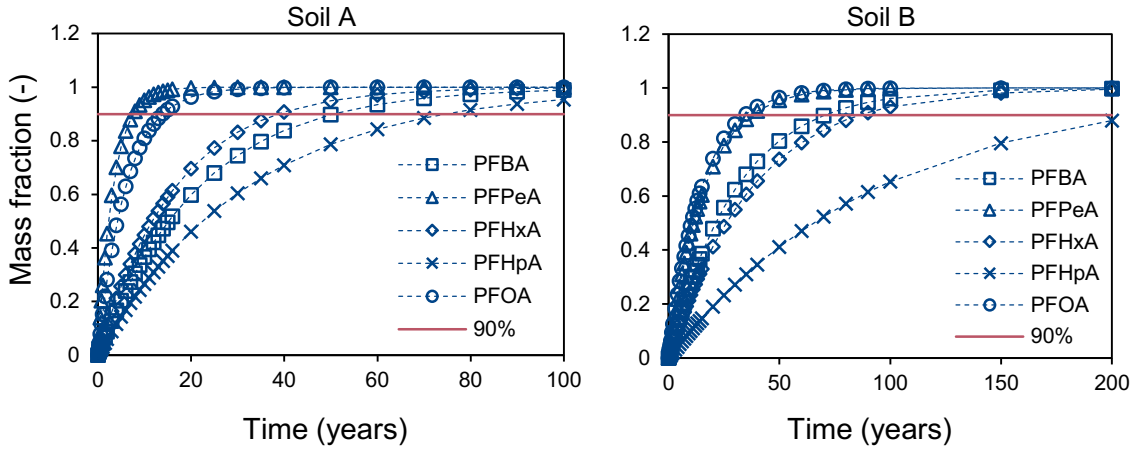

Figure 9. Time scales for the depletion of PFCA production from precursors by first-order production for two contaminated agricultural soils from southwest Germany.

5. Summary & Discussion

The abundance and potential risks of PFAS require their thorough investigation in groundwater risk assessment. Characterizing the leaching behavior of contaminants is crucial in order to estimate the time scales of groundwater pollution. Therefore, it is necessary to apply the right tools for laboratory results to approximate field conditions as close as possible. The aim of this work was to investigate the leaching potential of PFAAs from contaminated agricultural soils and develop a method to predict time scales for the leaching and production of PFAAs by precursors. These goals were achieved by combining different methods such as column percolation with batch tests and with sum parameters like the TOP assay. These methods allow to estimate the lower end (best case scenario) of leaching time scales for PFAAs from polluted agricultural soils. A brief summary of the most important findings is as follows:

- The leaching behavior of PFAAs from soils is mainly governed by their fluorinated chain length and the hydrophilic head group. Short-chain PFAAs show rapid mobilization, while for long-chain PFAAs leaching slows down with increasing chain length, and PFSAs are retained stronger than their PFCA counterparts with the same number of fluorinated C atoms.
- Column percolation tests alone cannot reliably predict leaching time scales of PFAAs if precursors are present. The production rates of PFAAs from unknown precursors can be estimated in batch tests (microcosms). Patterns received in the batch tests qualitatively match those found in groundwater.
- Laboratory setups, combining column percolation tests with batch tests and TOP assays, indicated that contamination of soils and groundwater will last several decades. However, these time scales need to be viewed as minimal time scales (best-case scenario), as these setups are conducted under optimal conditions.
- Long-term monitoring data of PFAAs from an aged agricultural site in BS-NRW show seasonal fluctuations, indicating that production of PFAAs from precursors is influenced by e.g. wet/dry phases and temperature. This can further extend time scales for groundwater pollution.

6. Further Research and Outlook

The above results highlight the necessity to combine several different methods to estimate leaching time scales of PFAAs from agricultural soils. They indicate consecutive research routes to improve the reliability of the laboratory predictions made in this thesis and to better understand the mechanisms involved in the release of PFAS from contaminated soil material. The following steps are suggested to further improve the knowledge of PFAS-contaminated sites:

- Batch tests proved to be a valid tool to determine production rates of C4-C8 PFCAs from contaminated soils when precursor composition is not exactly known. However, production of longer-chained PFAAs (≥C10) was not observed during the 60-day period, although TOP assay results indicate that long-chained PFAAs and precursors are present at the site as well. The duration of the setup needs to be extended in order to track the development of long-chained PFAAs. The setup potentially requires modifications to reduce the sorption of produced long-chained PFAAs.
- Batch tests for determination of PFAA production should be performed with solid material from other PFAS-impacted sites (e.g. AFFF sites) to investigate if different PFAS formulations affect leaching time scales. These investigations should further be coupled with HR-MS in order to elucidate transformation pathways and products that are missed in routine analysis.
- Analysis of long-term monitoring data in BS-NRW has shown seasonal fluctuations. Further investigations should target the effect and extent of environmental conditions on PFAS transformation in the field.
- Biodegradation is one crucial transformation pathway of PFAS precursors as the results of this thesis and the literature have shown. However, there is little knowledge about the microorganisms responsible for PFAS transformation and the corresponding mechanisms behind it. Further research about these processes is key for site remediation in terms of how these processes can either be promoted or inhibited in order to mitigate PFAS contamination.
- Sum parameters such as the TOP assay can convert precursors into measurable PFAAs. However, it is not clear how effective the TOP assay is when the exact composition of a complex contamination is not known. There can still be significant amounts of precursors left that are either not oxidized by the TOP assay or their transformation products differ slightly from the routinely analyzed PFAAs and are also missed in the evaluation of the total PFAS contamination.

- As PFAS-impacted sites often contain a complex mixture of different and often unknown PFAS subclasses, it is important to improve screening methods and increase the number of authentic reference standards to correctly assess the extent of the PFAS burden.
- While PFAS precursors can be transformed, their final TPs are very persistent in the environment, therefore posing wildlife and human health risks. In order to properly remediate PFAS-impacted sites, treatment technologies should aim for the complete mineralization of these compounds rather than a relocation of contaminated material (e.g. to landfills).
- PFAS have been detected in virtually every environmental compartment. Therefore, more studies are needed to investigate the environmental distribution and the long-term effects of low-concentration exposure to PFAS on biota and human health.

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Chapter 8 – personal contributions

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Bernd Susset	3	10	10	5	5
Binlong Liu	4	0	10	10	10
Peter Grathwohl	5	30	0	15	15
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8. Long-term behavior of PFAS in contaminated agricultural soils in Germany

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8.1. Abstract

Per- and polyfluoroalkyl substances (PFAS) contaminated compost materials have been applied over the last few decades to agricultural fields in Germany, resulting in large-scale diffuse PFAS plumes. The leaching behavior of PFAS from the first two identified contaminated agricultural sites in Germany were investigated, one at Brilon- Scharfenberg, North Rhine-Westphalia (BS-NRW), and the other at Rastatt/Mannheim, Baden-Württemberg. The specific objectives of this study were to assess the longevity of the PFAS agricultural sources and compare standardized column percolation tests to long-term leaching of PFAS from contaminated sites. The advection- dispersion model (ADM) was used to compare the leaching behavior of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) from standardized column percolation tests and long-term field leaching data from the BS-NRW site. Column leaching tests conducted with PFOS and PFOA contaminated soil simulated the initial rapid decline but did not predict the long-term behavior (tailing) observed at the field site over 12 years. Trend analyses of the PFAS field data from the BS-NRW showed that concentrations had stabilized and that individual PFAS exhibited distinct seasonal fluctuations; the latter is likely due to the ongoing transformation of precursors and a seasonal influence on production rates of mobile PFAS. Mass balances conducted at both sites indicate that complete removal of these compounds will likely take years to decades to occur, which is expected from the results of the column leaching tests.

8.2. Introduction

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic contaminants that comprise over 3,000 individual compounds and are likely widespread in the environment (OECD, 2018). Degradable PFAS (e.g., N-Ethyl perfluorooctane sulfonamide ethanol-based phosphate diesters (diSAmPAP)) are often referred to as precursor substances that are transformed to final transformation products, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) (Benskin et al., 2013). These final transformation products are persistent against further breakdown and appear to be widespread within the environment (Chen et al., 2019; Falk et al., 2019; Routti et al., 2015). Primary sources of PFAS in the environment are fire-fighting training grounds, industrial sites, landfills, and wastewater treatment plants (WWTPs) (ITRC, 2018). However, the historical application of biosolids/compost has led to known large-scale diffuse contamination of agricultural land and adjacent bodies of water in the states of Baden-Wuerttemberg, Germany and North Rhine-Westphalia, Germany, and has likely occurred in other regions worldwide (Delschen et al.,

2007; Rastatt, 2016). Currently, only a few studies have characterized the extent of PFAS contamination at agricultural sites and their long-term fate in the environment (Lindstrom

et al., 2011; Washington et al., 2010; Yoo et al., 2010; Gellrich et al., 2012; Stahl et al., 2018; Söhlmann et al., 2018).

Washington et al. (2010) and Yoo et al. (2010) reported the first PFAS contaminated agricultural fields in the United States of America (USA). In Decatur, Alabama, PFAS contaminated sludges from a WWTP had previously been applied to an agricultural area of approximately 20 km^2 for over a decade, leading to the pollution of both surface and groundwater (Lindstrom et al., 2011; Washington et al., 2010). Soil analyses of the polluted agricultural areas showed levels of precursor substances, such as fluorotelomer alcohols (FTOHs), up to 166 µg/kg and final transformation products, such as C6-C14 perfluorocarboxylic acids (PFCAs) and PFOS with perfluorodecanoic acid (PFDA), up to 990 µg/kg (Washington et al., 2010; Yoo et al., 2010). They found that long-chain PFCAs resided predominantly in the topsoil, while C6-C8 migrated to deeper soil layers. Lindstrom et al. (2011) investigated surface and groundwater for PFAS in the vicinity of the agricultural fields in Decatur, Alabama. They detected PFCAs from C4-C9 and perfluorosulfonic acids (PFSAs) between C4-C8, showing the mobility of these compounds in soils, while C10-C14 PFCAs remained in the soil and were not detected in groundwater. This observation is consistent with the findings of Washington et al. (2010) and other studies investigating perfluoroalky acids (PFAAs) mobility in soil (Br¨aunig et al., 2019; Gellrich et al., 2012).

Two of the first known PFAS contaminated agricultural sites, similar to the one described in Washington et al. (2010), were discovered in Germany in 2006 and 2013, after the application of compost and fertilizers mixed with PFAS-containing waste materials (e.g., paper sludge). During the time of application, no regulatory limits for PFAS existed in the German Fertilizer Ordinance (GFO), which regulates the use of fertilizers, soil conditioners, culture substrates, and plant aids. In 2012, the GFO was updated to include a limit of 100 µg/kg dry weight (ΣPFOA+PFOS) to limit the spread of PFAS in the environment (DüMV, 2012). While the use of PFOS and PFOA are regulated for fertilizing materials, Germany still has no binding limits for PFAS in drinking water and groundwater. In 2017, the German Federal Environmental Agency (UBA) released a list with 13 PFAS, recommending regulatory limits for 7 of these compounds in drinking water (Table S1). In 2020, the European Union (EU) included PFAS into their drinking water directive, setting a limit value for the sum of 20 distinct PFAS of 0.1 µg/l and total PFAS of 0.5 µg/l (EU Directive 2184, 2020). The contaminated agricultural sites discovered in Germany triggered laboratory studies, combined with clean-up and monitoring programs, to reduce PFAS loads from contaminated agricultural soils to surface and

groundwater. The primary objective of this study was to assess the long-term behavior of PFAS in agricultural soils. Specific objectives of the study were to: (1) evaluate the ability of standardized column percolation tests to predict long-term leaching of PFAS from contaminated agricultural sites; (2) to assess the seasonality of PFAS-leaching behavior in agricultural soil; and (3) quantify the longevity of PFAS agricultural sources. Field leaching PFAS data of a 10 ha site in Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW) site, monitored over a period of more than 12 years, were compared to laboratory column studies conducted after the contamination was detected in 2006. Earlier studies showed that data from column leaching tests from various types of material (e.g., contaminated soil, demolition waste, and waste incineration ash) for different compounds (e.g., heavy metals and polyaromatic hydrocarbons) compared well to lysimeters and could be fitted reasonably well with the advection-dispersion model (ADM) (Grathwohl and Susset, 2009). As such, soil column and field leaching data were fitted with the ADM to understand the short- and long-term leaching behavior. Trend analyses were also performed using the Seasonal Kendall test, Mann-Kendall test, and exponential decay functions to estimate rate constants. Data from this site are compared with another case of a 1000 ha contamination of agricultural land detected more recently in Rastatt/Mannheim, Baden-Württemberg, Southern Germany, which will further be referred to as the Baden site.

8.3. Sites and methods

8.3.1. Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW) site – Column tests and field data

8.3.1.1. Site history

Details of the site history and treatment system were previously reported by Delschen et al. (2007), but a summary is provided here (Fig. 1). A soil screening campaign of agricultural land in the vicinity of the Ruhr River, around the city of Olsberg, North Rhine-Westphalia, was conducted by the State Office for Nature, Environment, and Consumer Protection (LANUV) in 2006, looking specifically for the source of PFOA and PFOS in the Ruhr River (LANUV, 2011). The LANUV soil campaign results showed that 1802 ha of farmland were likely contaminated with around 420 kg PFAS, with the 10 ha BS-NRW site being the primary source of PFAS leaching into the Ruhr River (Fig. 2). PFAS detected at the BS-NRW site primarily resides in the first 0.6 m of topsoil, and the maximum PFAS concentration detected within the soil was approximately 6,300 µg PFOS+PFOA/kg, which would result in an estimated 390 kg PFOS+PFOA being applied to 90,000 tons of soil (Delschen et al., 2007). The suspected PFAS

contamination at the site was the result of the application of PFAS-containing compost, which had been applied at the BS-NRW site from 2004 to 2006 (LANUV, 2011).

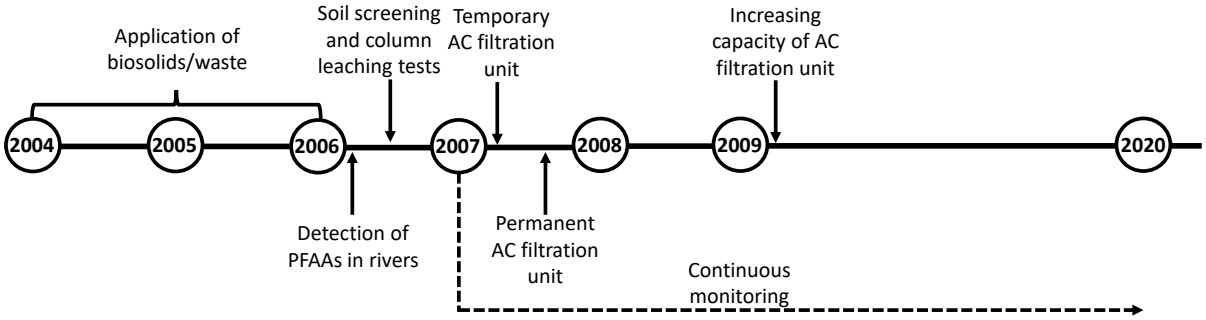

Fig. 1. Timeline of fieldwork completed at the Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW) site in Germany.

In early 2007, a drainage system connected to an activated carbon (AC) filtration plant with a capacity to handle 28 m3/h of contaminated water, was installed at the 10 ha BS-NRW site to remove PFAS from the seepage water before being discharged into Steinbecke and Bermecke, which are tributaries of the river M¨ohne (H¨olzer et al., 2008) (Fig. 3). In January 2009, the water capacity was increased to 80 m3/h (LANUV, 2011). The monitoring of PFOA and PFOS inflow concentrations of the AC-filtration plant began in January 2007, whereas monitoring of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), PFDA, perfluorobutanesulfonic acid (PFBS), and perfluorohexanesulfonic (PFHxS) started in February 2008. Agricultural activity at the BS-NRW site ceased in 2007.

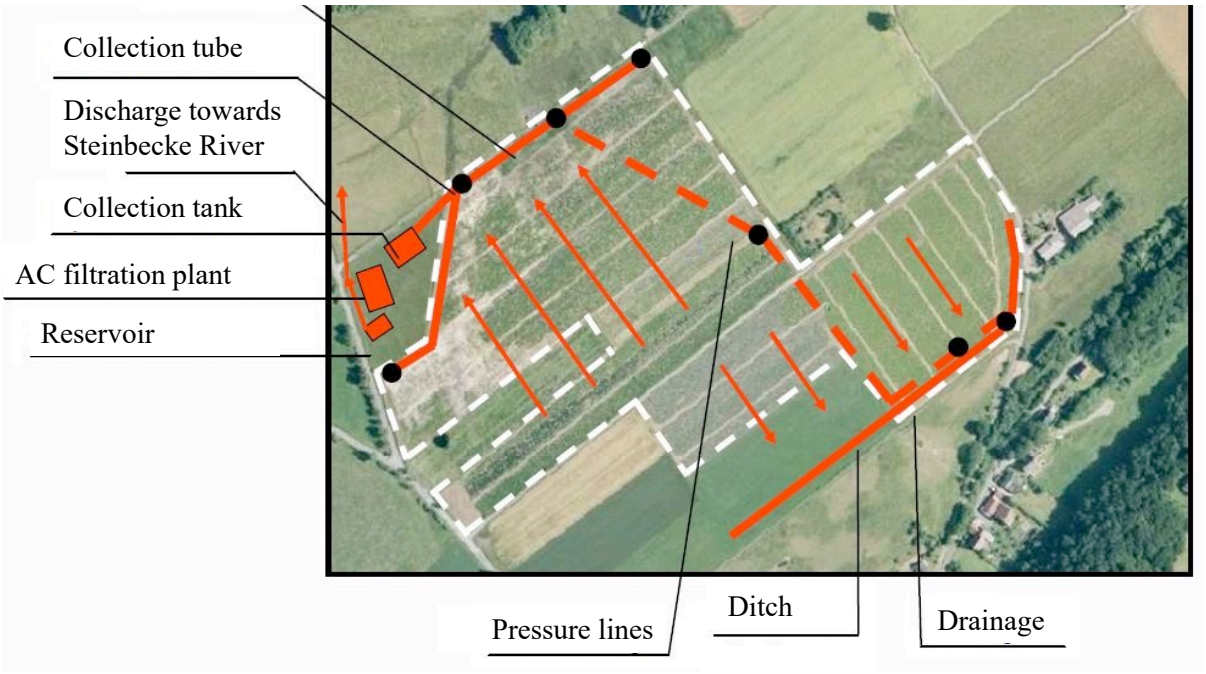

Fig. 2. Plan view of the 10 ha PFAS contaminated agricultural field site in Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW), Germany. Note that the drains and collection channels are shown in red, and the contaminated area is highlighted in white. Adapted from (LANUV, 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

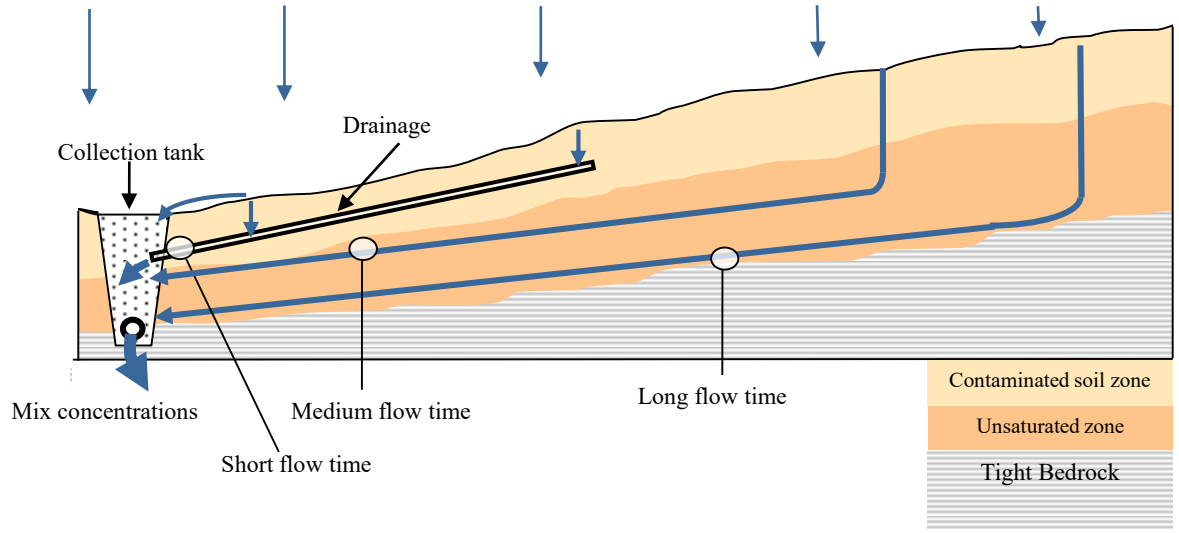

Fig. 3. Conceptualized cross-section of the PFAS contaminated agricultural field site in Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW), Germany, after the installation of the drainage system and collection tank to capture and filter seepage water in an AC-filtration plant, not to scale, length approximately 300 m.

8.3.1.2. Column leaching tests for PFOA and PFOS

Column leaching tests, according to German standards, are used to characterize the release behavior of inorganic and organic target compounds from solid materials (DIN 19528, 2009). Compared to lysimeters, which run in real-time, column leaching tests are conducted as a time-lapse. Material is packed into a column and percolated with water in the up-flow mode under saturated conditions. Samples are taken at the defined liquid to solid (*LS*) ratios. The *LS* ratio is the amount of water that has been in contact with the solid material. Up-flow, water-saturated, column leaching tests were conducted in September 2006 before the installation of the AC-filtration plant, using previously described methods (Grathwohl and Susset, 2009; DIN 19528, 2009). The columns had a diameter of 5.5 cm and a length of 30 cm. Contaminated topsoil (0.0–0.30 m) and subsoil (0.30–0.60 m) were obtained from the BS- NRW site. Topsoil PFOA and PFOS initial concentrations were 700 µg/kg and 6,600 µg/kg, respectively. Subsoil PFOA and PFOS initial concentrations were 400 µg/kg and 1,500 µg/kg, respectively. Both contaminated subsoil and topsoil were packed in layers up to a height of 25 cm and covered with a 2 cm thick quartz sand layer at the upper and lower section of the column to ensure that water flows in and evenly across the entire width of the column and to pre-filter the eluate. The column was flooded from bottom to top within 2 h, and the flow rate was adjusted to ensure a contact time of at least 10 h for equilibration. Control columns were set up and performed in parallel and consisted of only quartz sand. Leachate was collected at liquid LS-ratios of 0.1, 0.5, 1, 2, 3, 4, 4.5, 5, 6, and 7 L/kg and analyzed only for PFOA and PFOS by the LANUV laboratory using an Agilent 1100 Model LC system coupled to a QuattroMicro triple quadrupole instrument (Waters, Milford, MA, USA). The limit of quantification for both PFOA and PFOS was 0.1 µg/L. The *LS* is the amount of water that has been in contact with the solid material and can be used to compare field and column data provided that equilibrium conditions apply during leaching and groundwater recharge rates are known:

$$t = LS\frac{x}{v}\frac{\rho}{n} \qquad (1)$$

where t is the time [T], x is the column length [L], v is the seepage velocity [L T^{-1}], ρ_b is bulk density [M L^{-3}], and n is the porosity [-]. The analytical solution of the advection-dispersion model (ADM) accounting for the initial condition in the column after first flooding was used to fit the PFOA and PFOS leaching behavior as a function of the *LS* (Grathwohl and Susset, 2009):

$$\frac{C_w}{C_{w,ini}} = 1 - 0.5\left[erfc\left(\frac{K_d - LS}{2\sqrt{\frac{\alpha}{x}\left(\frac{n}{\rho_b} + K_d\right)LS}}\right) + exp\left(\frac{x\left(1-\frac{1}{R}\right)}{\alpha}\right)erfc\left(\frac{K_d + LS}{2\sqrt{\frac{\alpha}{x}\left(\frac{n}{\rho_b} + K_d\right)LS}}\right)\right] \quad (2)$$

where *erfc* is the complementary error function, C_w is the solute concentration in aqueous phase [M L^{-3}], $C_{w,ini}$ is the initial solute concentration in equilibrium with the solid phase [M L^{-3}], x is the length of the column [L], and α is the longitudinal dispersivity [L]. K_d is the distribution coefficient of solute [L^3 M^{-1}]. $R = \left(1 + K_d \frac{n}{\rho_b}\right)$ is the retardation factor [-]. For column data, the ADM was fit to the data by treating $C_{w,ini}$, K_d, and α as fitting parameters to minimize the difference between the modeled and measured data. For the field- leaching data, K_d values fitted from the column data were assumed to be the same as those in the field. $C_{w,ini}$, and α were used as fitting parameters as previously described. The coefficient of efficiency (E) was used to determine the goodness of fit of the ADM equation to both column and field data (Nash and Sutcliffe, 1970).

8.3.1.3. Field monitoring data

Long-term leaching data was obtained from the “collection tank” at the BS-NRW site before the water was treated in the AC-filtration plant. Samples were taken regularly and analyzed for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS by the LANUV laboratory, as previously described (Fig. 4). The limit of quantification for all PFASs detected after 2008 was 0.05 µg/L (Bergmann, 2021).

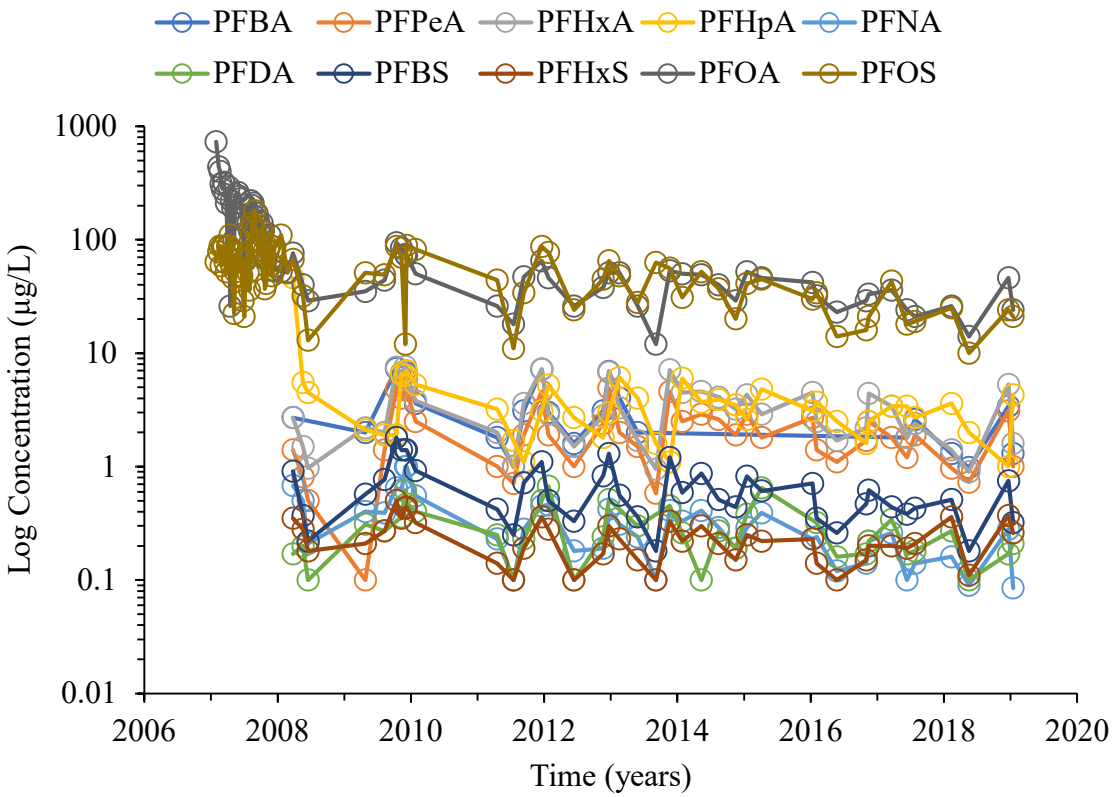

Fig. 4. Long-term monitoring for PFAS concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site. Data for PFOS and PFOA was collected from January 2007 to January 2019. Data for PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFBs, and PFHxS was collected from March 2008 to January 2019.

8.3.1.4. Statistical analysis

Kruskal-Wallis tests, Mann-Kendall tests, Seasonal Kendall tests, and regression analysis were performed using Microsoft® Excel for Windows (Microsoft®, Redmond, Washington, USA). The Kruskal-Wallis tests were performed, as per Chan and Walmsley (1997), to assess the seasonality of individual PFAS detected at the BS-NRW. The Kruskal-Wallis test statistic (H) and probability-value are reported in Appendix A. The Mann-Kendall and Seasonal Kendall tests are non-parametric statistical tests that were performed to assess if there were any temporal trends within the data (e.g., decreasing, stable/no trend or increasing) using the GSI Mann-Kendall Toolkit (https://gsi-net.com/en/software/free -software/gsi-mann-kendall-toolkit.html), a Microsoft Excel Spreadsheet previously developed for the MAROS Software (Aziz et al., 2003; Connor et al., 2012; Meals et al., 2011; Naidu et al., 2012; U.S. EPA, 2009a, 2009b). The Seasonal Kendall test was performed when the Kruskal-Wallis test indicated that the data was seasonally affected; otherwise, the Mann-Kendall was performed. The test statistic, confidence levels, and a qualitative description were determined for each individual

PFAS. As described by Connor et al. (2012) and Meals et al. (2011), the test statistic from each season was summed, and the confidence factor was determined for the Seasonal Kendall Test. First-order decay constants were determined for each individual PFAS detected at the site using data collected from March 2008 to January 2019 using the Regression package in Microsoft® Excel (Naidu et al., 2012).

8.3.2. Rastatt/Mannheim, Baden-Württemberg, southern Germany (Baden site) – Batch shaking test and soil extraction

8.3.2.1. Site history

In 2013 PFAAs were detected in a drinking water well near Rastatt, Germany (RP Karlsruhe, 2018). The source of the PFAAs was determined to be an upgradient agricultural area (~644 ha) where PFAS-contaminated compost was repeatedly applied to topsoils between 2000 and 2008 (S¨ohlmann et al., 2018). The compost mixture likely consisted of a broad spectrum of PFAS, including, but not limited to, PFAAs and precursors (e.g., polyfluorinated dialkylated phosphate ester (diPAPSs), diSAmPAPs) used in paper coatings (Bugsel and Zwiener, 2020). Bugsel and Zwiener (2020) identified 12 PFAS classes in soil samples from the agricultural soils, while the majority were diPAPs (from 4:2/6:2 to 12:2/ 14:2) and diSAmPAPs (only C8/ C8). The extent of the PFAS pollution for each field can vary due to different application rates and loads of PFAS contaminated compost and different mixtures at the time of application. For further characterization of the groundwater contamination, the state initiated a monitoring campaign, analyzing 970 groundwater samples for PFAAs (Rastatt, 2016). These data showed that 98% of PFAAs in groundwater were C4-C8 PFCAs (Rastatt, 2016). It should be noted that PFAS are ultimately discharged into the River Rhine.

8.3.2.2. Extraction/batch-shaking tests of top- and subsoil samples

Soil extraction and LS 2:1 batch shaking data sets were obtained from Arcadis GmbH to assess the distribution of C4-C14 PFCAs and C4-C8 and C10 PFSAs in the topsoil and subsoil at the Baden site. The soil extraction data was obtained in accordance with DIN 38414–14, whereas LS 2:1 batch shaking studies were conducted in accordance with DIN 19529. In total, over 2,000 diferent soil samples were analyzed.

8.4. Results & discussion

8.4.1. Brilon-Scharfenberg, North Rhine-Westphalia (BS-NRW): Comparison of column to field data

Column tests were conducted according to the German standards DIN 19528 (2009) and DIN 19528 (Table 1). K_d values, dispersivity (α), and initial concentration in the soil ($C_{s,o}$) were used as fitting parameters for the ADM. Curve fitting was carried out with the MATLAB tool "lsqcurevefit" to fit the measured data. The application of the ADM relies on the local equilibrium assumption, which is confirmed by the good fit of the column leaching data by the model (Fig. 5, Table 2) with a model efficiency coefficient of E >0.97, except for the PFOS topsoil column which had a E =0.43. The topsoil initially shows variable PFOS concentrations, and the model was fitted to average concentration. K_d values and arithmetic mean α values fitted in the column tests were used in the ADM equation to fit the PFOA and PFOS field leaching data with the assumption that the mean annual seepage recharge rate was 600 mm/year at the BS-NWR site (Delschen et al., 2007). Since the PFAS concentrations measured in soil samples from the site showed large variability, the initial concentration in the soil ($C_{s,o}$) was taken as the only fitting paramater for the field models (Delschen et al., 2007).

Table 1. Column and field characteristics for the BS-NRW site used in the advection dispersion; ρ_b: bulk density (density of the solids 2.57 kg/L), L_c: lengths of the packed column, t_c: contact time of water in the column (fully saturated) or contact time of the seepage water with the soil in the field (50% water saturation).

Symbol (unit)	Column Inputs			Field Inputs
	Topsoil	Subsoil 1	Subsoil 2	
L_c (m)	0.25	0.25	0.25	0.60
n (-)	0.56	0.50	0.50	0.50
ρ_b (kg/L)	1.13	1.28	1.28	1.28
n (m/d)	0.29	0.32	0.33	0.0064[a]
t_c (days)	0.86	0.78	0.76	94

[a]Estimated from field Darcy velocity of 0.0016 m/d = 600 mm/a (Delschen et al., 2007).

Table 2 Fitting parameters for the ADM for column leaching and field data for the BS-NRW site.

Soil Type	PFOA					PFOS				
	Column			Field		Column			Field	
	Top	Sub #1	Sub #2	Top	Sub	Top	Sub #1	Sub #2	Top	Sub
α (m)	0.050	0.080	0.070	0.18	0.18	0.04	0.030	0.17	0.18	0.18
K_d (L/kg)	1.6	0.57	0.60	1.6[a]	0.60[a,b]	5.7	0.78	1.7	5.7[a]	1.3[a,b]
$C_{s,0}$ (µg/kg)	310	250	230	310	170	3800	710	780	430	110
R (-)	4.2	2.5	2.5	9.2	4.1	13	3.0	5.4	30	7.7
E (-)	0.97	0.99	0.99	0.41	0.6	0.43	0.97	0.99	0.28	- 0.37

[a] K_d inputs derived from column leaching tests

[b] Mean of subsoil 1 column and subsoil 2 column

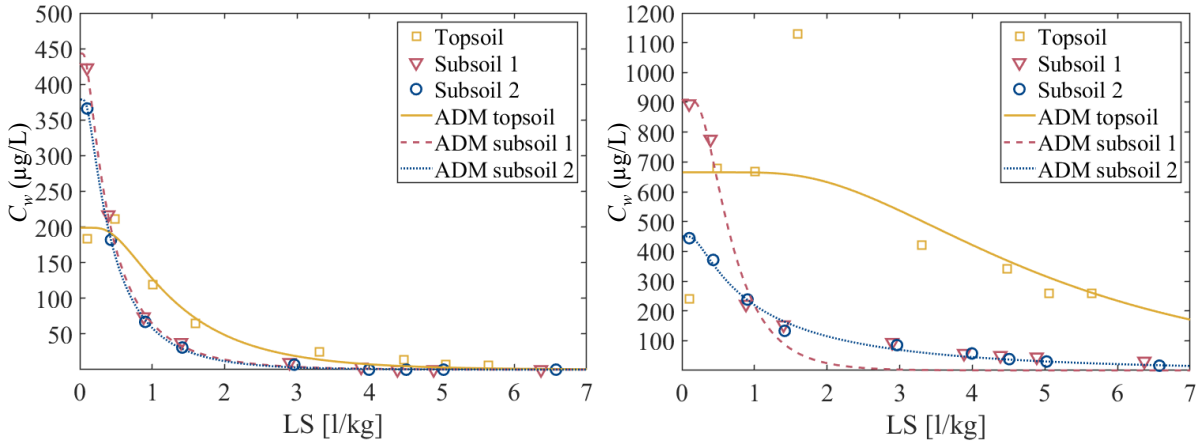

Fig. 5. PFOA (left) and PFOS (right) leaching concentrations (C_w) vs. time expressed as the liquid to solid ratio (LS) for column leaching tests (according to DIN 19528, 2009) fitted with the advection-dispersion model (ADM) equation (parameters shown in Tables 1 and 2).

As Fig. 6 shows, the model fits the field data reasonably well but fails to predict the long-term tailing observed in the field. Reasons for that may be manifold (e.g., heterogeneous distribution of pollutants, back diffusion from low permeability zone, etc.), but this might also come from the slow but ongoing transformation of precursor substances into the target compounds. The

model shows that the removal of 90% PFOA takes about five years (*LS* = 3.5), and approximately nine years (*LS* = 6.5) are needed for the removal of 99% PFOA. In terms of PFOS, *LS* = 10 was not long enough to capture the long-term behavior of PFOS. Although the ADM is in good agreement with column tests, it is a simplistic model that does not account for potential PFAS retention processes as described by Brusseau (2018) (e.g., adsorption at the air- water interface), which can additionally increase PFAS retention in the vadose zone.

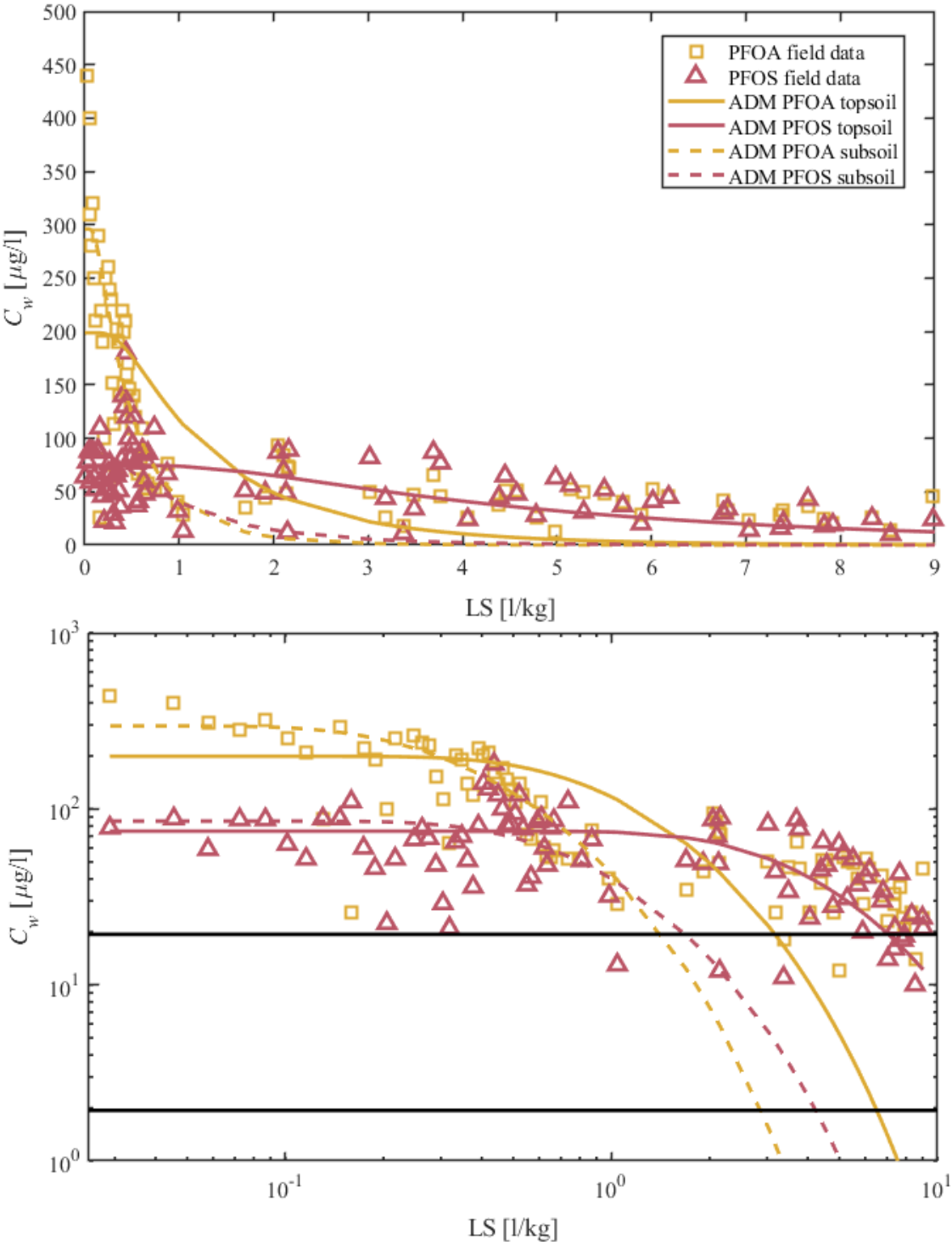

Fig. 6.Concentration from the field vs. the liquid to solid ratio (*LS* =10 corresponds to approx. 1 decade); colored lines calculated with advection-dispersion model (ADM) using K_d and α obtained in the column experiments (Fig. 5) and $C_{s,o}$ fitted to the 10 ha Brilon-Scharfenberg (BS-NRW) site data; the lower plot shows in log-log scale how long it would take to remove 90% and 99% of PFOA from the topsoil (black lines), e.g., at *LS* =3.5 (5 years) and *LS* =6.5 (9 years), respectively.

8.4.2. Seasonal analysis of field data (BS-NRW)

To assess the seasonality of the individual PFAS at the site, the data were categorized according to the season of the year in which they were measured (Fig. 7). The monitoring period to construct Fig. 7 for PFOA and PFOS ranged from July 2007 to January 2019, whereas the monitoring period ranged from March 2008 to January 2019 for all other PFAS identified at the site. The seasonality of the individual PFAS detected at the site for the monitoring period were assessed using the Kruskal-Wallis comparison test (Table S3). The Kruskal-Wallis comparison test confirmed a statistical difference among the seasonal data for all detected PFAS, except for PFHpA and the long-chain compounds: PFNA and PFOS. In general, concentrations of the short-chain PFAS were higher in the fall and winter, suggesting production and accumulation of these compounds during the spring and summer and mobilization during recharge in fall and winter. For long-chain PFAS, seasonal concentration changes might be buffered by sorption in the soil.

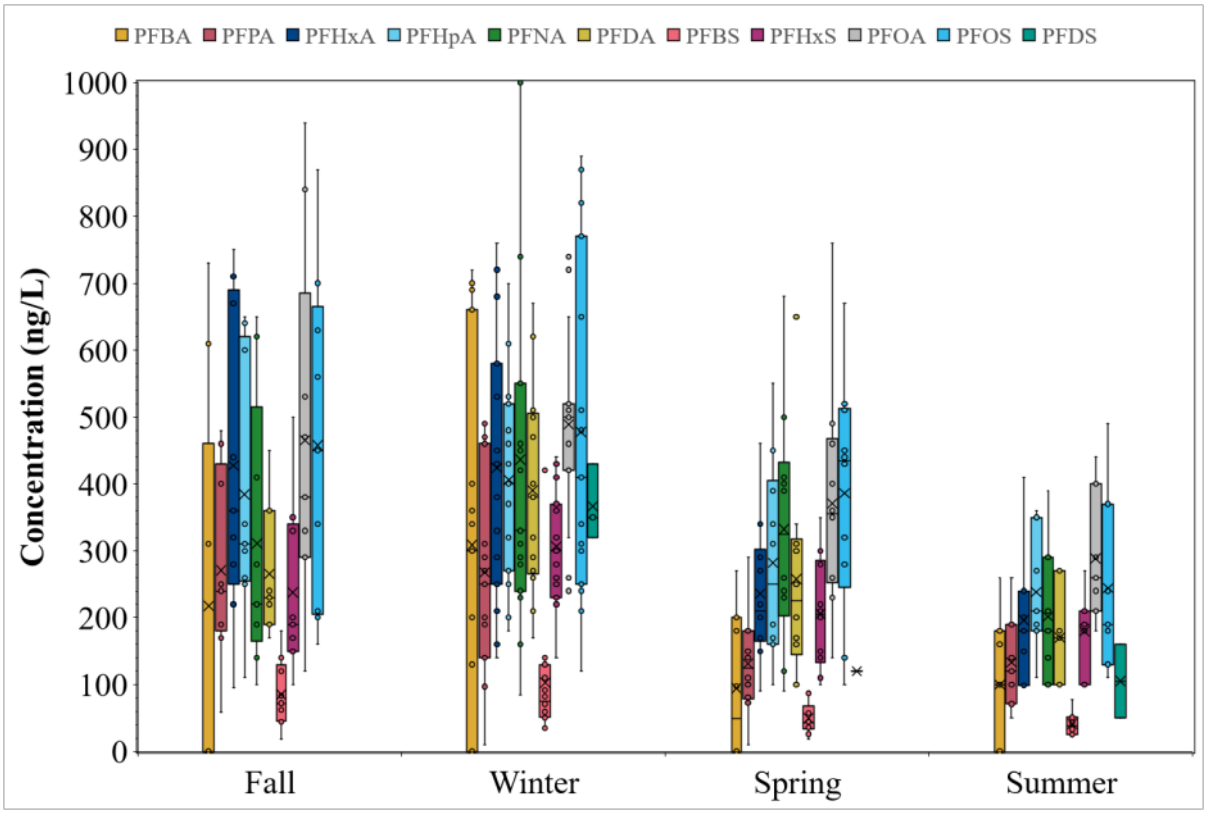

Fig. 7. Variations of PFAS concentrations across seasons at the 10 ha Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW) site using data collected from February 2008 to January 2019. PFBA, PFPeA, PFBS, PFHxA, PFHpA concentrations were divided by 10 and PFOS and PFOA by 100 to allow for comparison.

8.4.3. Assessment of trends at the BS-NRW site

The individual PFAS species data collected from February 2008 to January 2019 at the BS-NRW site were considered for analysis. Although data collection for PFOA and PFOS began in January 2007, it was not until February 2008 when additional PFAS species were analyzed. Table 3 shows results for both the Seasonal Kendall and the Mann- Kendall tests to obtain PFAS trends, indicating that PFBA, PFPeA, PFHxA, and PFDA are relatively stable, whereas PFHpA, PFOA, PFNA, PFBS, PFHxS, and PFOS demonstrate a decreasing trend. Perfluorodecanesulfonic acid (PFDS) was not analyzed since limited data (n =6) exists for this compound, as monitoring did not begin until July 2017. Additionally, Microsoft® Excel was used to fit simple exponential decay functions to PFAS data to predict k of PFAS (Table 3, Fig. S1 to S10), which ranged from -0.13 yr^{-1} to 0.012 yr^{-1}. Overall, the results of the trend analysis and k calculations suggest that short-chain PFAS have stabilized, most likely caused by the continuous production from unknown precursors at the site. Long-chain PFAS seem to decrease, possibly reflecting retardation of these compounds initially present in soil compared to short-chain PFAS.

Table 3. Temporal trend analysis and rate calculations for individual PFAS at the 10 ha Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW) site. All other PFAS data was collected from March 2008 to January 2019. Rates for PFAS were determined from exponential regressions (Appendix). The Mann-Kendall test was applied to PFHpA, PFNA, and PFOS, and the Seasonal Kendall test to all other PFAS. Note that a "-" indicates a removal rate and a "+" indicates a generation rate.

	Mann-Kendall and Seasonal Kendall test		Rate constants (k)			
PFAS Type	Trend	Confidence level (%)	Estimated k (yr^{-1})	Lower 95% k (yr^{-1})	Upper 95% k (yr^{-1})	p-value
PFBA	Stable	86	-0.094	-0.17	-0.019	0.016
PFPeA	Stable	65	0.012	-0.068	0.091	0.77
PFHxA	Stable	69	-0.024	-0.087	0.039	0.44
PFHpA	Decreasing	>99	-0.040	-0.092	0.011	0.12
PFOA	Decreasing	>99	-0.071	-0.11	-0.029	7.2×10^{-3}
PFNA	Decreasing	>99	-0.13	-0.18	-0.082	4.2×10^{-6}
PFDA	Stable	90	-0.031	-0.088	0.027	0.28
PFBS	Decreasing	>99	-0.064	-0.12	-0.0075	0.027
PFHxS	Decreasing	>99	-0.038	-0.081	-0.0054	0.084
PFOS	Decreasing	>99	-0.085	-0.14	-0.027	5.0×10^{-3}

8.4.4. Baden site

After the discovery of PFAS contamination at the Baden site, several hundred agricultural fields were sampled at different depths, and LS 2:1 batch shaking tests were conducted to determine potential PFAS concentrations in the leachate. To compare the BS-NRW site and the Baden site, a relative composition profile was created using the mean aqueous phase concentrations derived from the inflow of the AC-filtration plant (BS-NRW site) and samples from two different depths from the Baden site. Table S4 contains the values used to determine relative compositions at both sites. PFOA and PFOS accounted for up 70% and around 44% of the leachate composition at BS-NRW site and at the Baden site, respectively (Fig. 8). At the Baden site, the composition is more diverse compared to the BS-NRW site, which could be due to the application of different waste materials and the relatively higher abundance of other precursors as discussed by Bugsel and Zwiener (2020). The leachate composition between the topsoil and subsoil at the Baden site is similar. C4-C10 PFCAs and PFOS dominate the leachate. Compounds with ≥C11 represent only a minor fraction of PFAS found in the seepage water and tend to reside in the topsoil (Fig. S11). This is further supported by groundwater monitoring data from the Baden site, which showed that 98% of PFAS detected were C4-C8 PFCAs (Rastatt, 2016). Samples for soil extraction and 2:1 batch shaking data were collected between 2014 and 2019 and showed that a major fraction of PFAS still resides in topsoils, even though the last application of PFAS contaminated fertilizer occurred in 2008. This is likely caused by the slow and continuous degradation of precursors at the site as described by S¨ohlmann et al. (2018). Short-chain PFAAs move relatively quickly to deeper soil layers, while long-chain PFAAs will stay in the topsoil due to lower mobility caused by sorption. Based on the BS-NRW column tests, BS-NRW field leaching data, Baden site soil extraction data, and groundwater monitoring data from the Baden site, it is expected time scales for the complete leaching of PFAS from agricultural soils at both the Baden site and BS-NRW site will be similar. Aqueous leachate concentrations of short-chain PFCAs are higher than for long-chain PFCAs, suggesting that short-chain PFCAs leach more readily from the soil than long-chain PFCAs after the application of PFAS contaminated material or after short-chain PFAS have been produced by precursors present within the topsoil. Additionally, these data suggest that long-chain PFCAs tend to accumulate in topsoils until the degradation of precursors has ceased, and transport to groundwater will be retarded compared to short-chain PFAS.

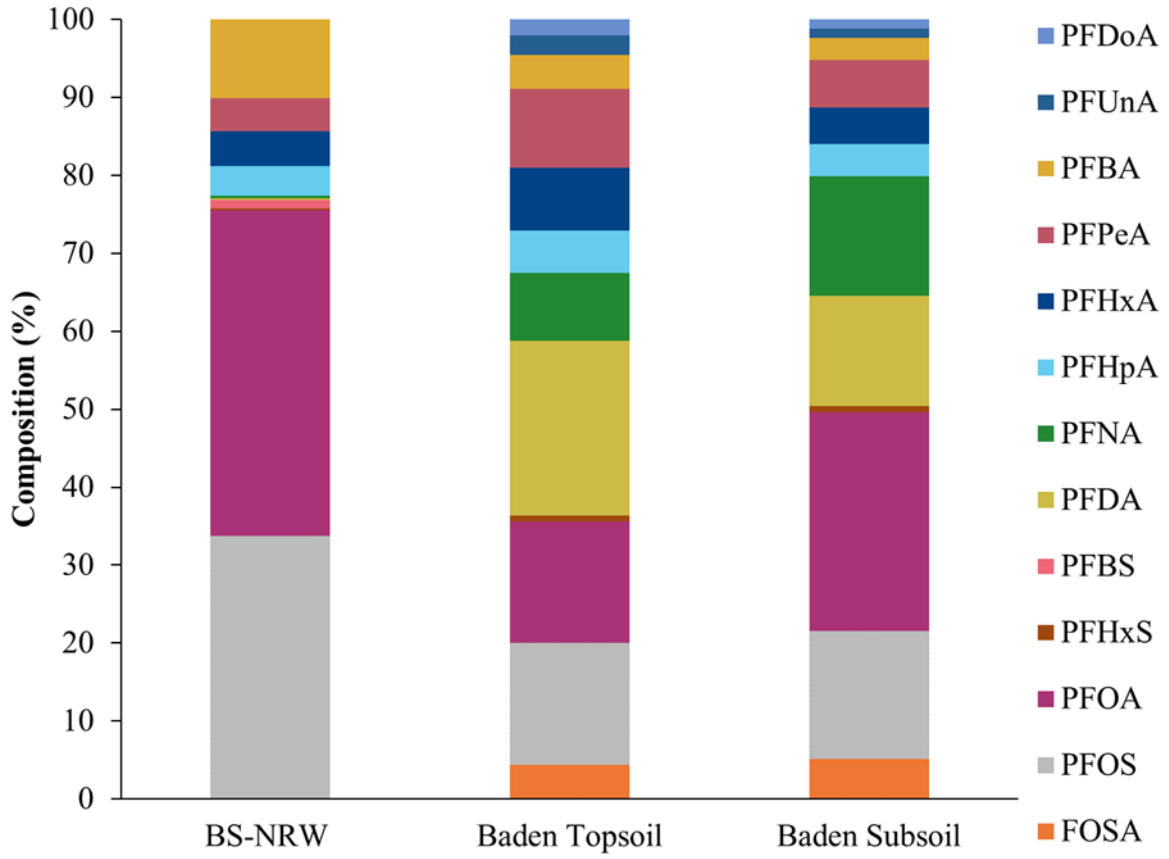

Fig. 8. Comparison of PFAS composition patterns in aqueous leachate at the 10 ha Brilon-Scharfenberg North Rhine-Westphalia (BS-NRW) site and Rastatt/ Mannheim, Baden-Württemberg, southern Germany (Baden) site; compounds with less than 20 data points were excluded, which for the BS-NRW were PFDS, and for the Baden site, PFBS and PFDS. Topsoil and subsoil refer to samples taken from 0–30 cm and 30–60 cm, respectively (see Table S4 for original data).

The time scales for the degradation of PFAA precursors depend on the type of precursors and their chain length (Benskin et al., 2013; Lee et al., 2014). PFCA precursors 6:2 diPAP and 8:2 diPAP have an estimated half-life in soil of around 12 days to >1,000 days, whereas the PFOS precursor SAmPAP has an estimated half-life of more than 380 days in sediments (Benskin et al., 2013; Lee et al., 2014). While biodegradation is considered one of the primary transformation pathways for precursors, the increasing half-life for long-chain PFAA precursors have been linked to a decreased solubility of the precursors, resulting in reduced bioavailability (Benskin et al., 2013; Liu and Avendano, 2013).

8.4.5. PFAS mass fluxes and time scales for leaching

As previously described, the total amount of ΣPFOA+PFOS estimated in topsoil and subsoil at the BS-NRW site was around 390 kg ΣPFOA+PFOS, and a ratio of 6:1 PFOS:PFOA, suggest that initial reservoir masses were about 56 kg PFOA and 334 kg PFOS (LANUV, 2011). Mass flux data for the AC-filtration plant obtained from the LANUV (Fig. S12) suggest that 95 kg ΣPFOA+PFOS has been leached from the site as of January 2019. This agrees reasonably well with the ADM results, which estimated around nine years for 99% removal of PFOA. However, PFOA is still observed in the µg/L range in the AC- filtration plant at the BS-NRW site, indicating that a precursor reservoir for PFOA exists at the site. It would take approximately 76 years to remove the remaining 295 kg, assuming a constant mass flux of 3.9 kg/a ΣPFOA+PFOS as observed in 2018. Thus, it will take many decades under current conditions to achieve complete removal of PFAS from the site. As long as precursor reservoirs in the field are not known, leaching time scales are likely to exhibit high uncertainty. At the Baden site, total PFAS fluxes could only be determined by estimating discharges into the River Rhine. Möller et al. (2010) investigated the PFAS distribution pattern along the River Rhine from Lake Constance to the North Sea in 2010. Their study included sampling stations up- and downstream of the polluted area in Rastatt, Baden- Württemberg. Between the upstream (Rheinmünster, Germany) and downstream station (Karlsruhe), an increase in the total PFAS mass flux of around 40 kg/a could be observed (using an average annual discharge at Karlsruhe of 1100 m^3/s). Compounds that had increased at the downstream station were C4-C6 and C9 PFCAs. As described by Söhlmann et al. (2018), the Baden area's contamination occurred between 2000 and 2008, suggesting that mobile PFAS, such as C4-C6 PFCAs, could already have leached into the River Rhine when Möller et al. (2010) conducted their study. By 2019, PFAS that reached the River Rhine from the Rastatt area included C4-C9 PFCAs, C4, C6, and C8 PFSAs and 6:2 fluorotelomer sulfonic acid (6:2 FTSA), and the mass flux had increased to 95 kg/a ΣPFAS (Rastatt, 2019).

8.5. Conclusions

Being the first of its kind in Germany, the PFAS contaminated agricultural land discovered in the state of North Rhine-Westfalia in Germany (e.g., BS-NRW site) was considered "exotic" in 2006. However, it seems that PFAS contamination occur much more frequently than initially expected (Washington et al., 2010; Rastatt, 2016; Stahl et al., 2018). While the BS-NRW site covered a contaminated area of just 10 ha, the second case in Baden, discovered in 2013, revealed a soil and groundwater contamination of an area of about 644 ha. For the BS-NRW site, bench-scale column leaching tests compare reasonably well to the 12-year long field-

collected seepage water data for PFOA and PFOS but underpredict the long-term tailing observed in the field. Even short- chain PFAS concentrations stay at high levels in the field in contrast to a fast decline expected from the column leaching tests. This may be due to the transformation of precursor substances into more mobile PFAS, such as PFOA and PFOS. Precursor transformation is not captured in laboratory flow-through tests since time scales are relatively short compared to the field (days vs. months). To assess the remaining PFAS reservoir preserved in the form of precursors of a contaminated site, a total oxidizable precursor (TOP) assay needs to be applied (Houtz and Sedlak, 2012). 12-years of BS-NRW PFAS site data suggest a distinct seasonal pattern for short-chain PFAS, potentially suggesting production and accumulation of these compounds during the spring and summer and mobilization during recharge in fall and winter. For long-chain PFAS, seasonal concentration changes seem buffered by sorption in the soil. Comparison of the 2006 case in North Rhine Westphalia with the more recent case in Southern Germany showed some similarities (e.g., higher concentrations of long-chain PFAS in the topsoil) but a different distribution pattern of PFAS in leaching tests. According to the experience gained since 2006 in the BS-NRW case, it will take many decades to completely leach PFAS from the topsoil. Prediction of the long-term fate of PFAS and time scales of potential seepage water and groundwater contamination requires knowledge of the type and concentrations of precursor substances, which needs to be further investigated.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2021.103812.

8.6. References

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8.7. Appendix

Table S1. Recommended drinking water limits in Germany. (UBA, 2017).

Substance	Drinking water limit [µg/l]	Preliminary limit [µg/l]
PFBA	10	—
PFPeA	—	3
PFHxA	6	—
PFHpA	—	0.3
PFOA	0.1	—
PFNA	0.06	—
PFDA	—	0.1
PFBS	6	—
PFHxS	0.1	—
PFHpS	—	0.3
PFOS	0.1	—
6:2 FTS	—	0.1
FOSA	—	0.1

Table S2. Cas-numbers of PFAS discussed in this study.

Analyt	Cas No.
PFBA	375-22-4
PFPeA	2706-90-3
PFHxA	307-24-4
PFHpA	375-85-9
PFOA	335-67-1
PFNA	375-95-1
PFDA	335-76-2
PFUnA	2058-94-8
PFDoA	307-55-1
PFBS	375-73-5
PFHxS	355-46-4
PFOS	1763-23-1
PFDS	335-77-3
FOSA	754-91-6

Table S3. Results of Kruskal-Wallis Tests for individual PFASs at the BS-NRW site using data collected from February 2008 to January 2019 and categorized by season as displayed in Figure 6. Microsoft Excel was used to conduct the Kruskal-Wallis Test. H is the Kruskal-Wallis test statistic.

Contaminant	Difference among populations?	H	p-value
PFBA	Yes	94	3.6×10^{-20}
PFPeA	Yes	84	5.3×10^{-18}
PFHxA	Yes	11	1.3×10^{-2}
PFHpA	No	7.2	6.4×10^{-2}
PFOA	Yes	9.3	2.6×10^{-2}
PFNA	No	6.1	0.11
PFDA	Yes	11	1.0×10^{-2}
PFBS	Yes	83	6.1×10^{-18}
PFHxS	Yes	11	1.1×10^{-2}
PFOS	No	5.5	0.14

Table S4. Concentration of individual PFAS in ng/l, mean±standard deviation, and the number of samples analyzed at the BS-NRW and Baden site. The BS-NRW site summarizes time series data collected from February 2008 to January 2019. The Baden Site is a summary of the aqueous concentration from a large-scale soil batch study (*LS* of 2:1) where PFAS contaminated topsoil (0-0.3 m), and subsoils (e.g., 0.3-0.6 m) were used to assess the desorption properties of the PFAS at the Baden site.

	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOA	PFOS	PFDS	FOSA
NR-BWR														
Range	0.98-7.3	0.1-4.9	0.9-7.6	1.0-7.0	0.085-1.0	0.1-0.67	—	—	0.18-0.42	0.9-7.6	12-730	10-89	0.5-4.3	—
Mean±Stdv	3.43±2.18	2.12±1.39	3.4±2.0	3.42±1.63	0.34±0.23	0.29±0.16	—	—	0.76±0.67	0.25±0.1	42.07±18.94	41.12±23.08	2.38±1.49	—
N	25	42	42	42	42	38	—	—	42	42	42	42	7	—
Baden														
0-30 cm														
Range	0.01-6.25	0.01-1.680	0.01-1.3	0.01-8.24	0.01-5.5	0.01-22	0.01-1.7	0.01-2.64	0.01-0.03	0.01-0.21	0.01-28.8	0.01-26.2	0.01-1.07	0.01-1.78
Mean±Stdv	0.21±0.33	0.49±0.89	0.39±0.73	0.26±0.51	0.42±0.66	1.09±2.04	0.12±0.20	0.10±0.25	0.02±0.01	0.03±0.05	0.75±1.62	0.76±2.4	0.22±0.32	0.21±0.29
N	1090	1024	1068	951	727	711	210	122	14	41	1262	832	12	85
Baden														
30-60 cm														
Range	0.01-1.52	0.01-3.34	0.01-3.25	0.01-4.15	0.01-1.47	0.01-8.8	0.01-0.32	0.01-0.28	0.01-0.02	0.01-0.24	0.01-11.9	0.01-28	0.01-0.53	0.01-2.2
Mean±Stdv	0.15±0.18	0.33±0.39	0.26±0.34	0.23±0.34	0.84±1.54	0.78±1.45	0.07±0.07	0.06±0.07	0.016±0.007	0.04±0.05	1.54±5.4	0.9±2.84	0.14±0.19	0.28±0.44
N	646	565	634	566	407	347	66	33	6	40	710	445	13	34

Temporal trend analysis at the BS-NRW site

The following figures show the tailing regression analysis for PFAS obtained at the inflow of the AC-filtration plant in BS-NRW site from March 2008 to January 2019.

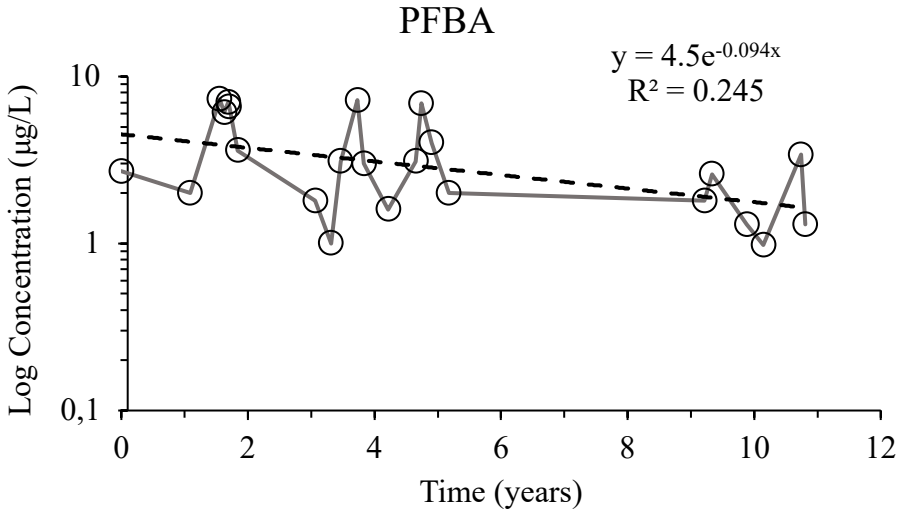

Fig. S1. Long-term monitoring PFBA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

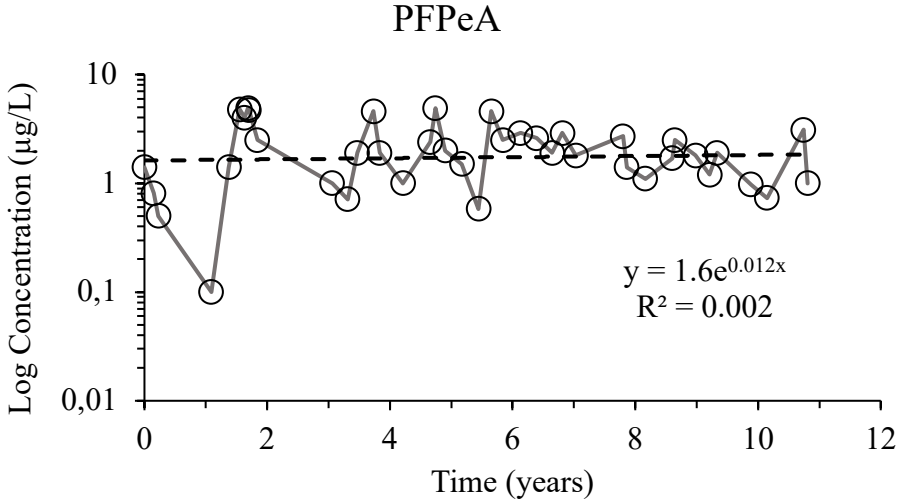

Fig. S2. Long-term monitoring PFPeA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

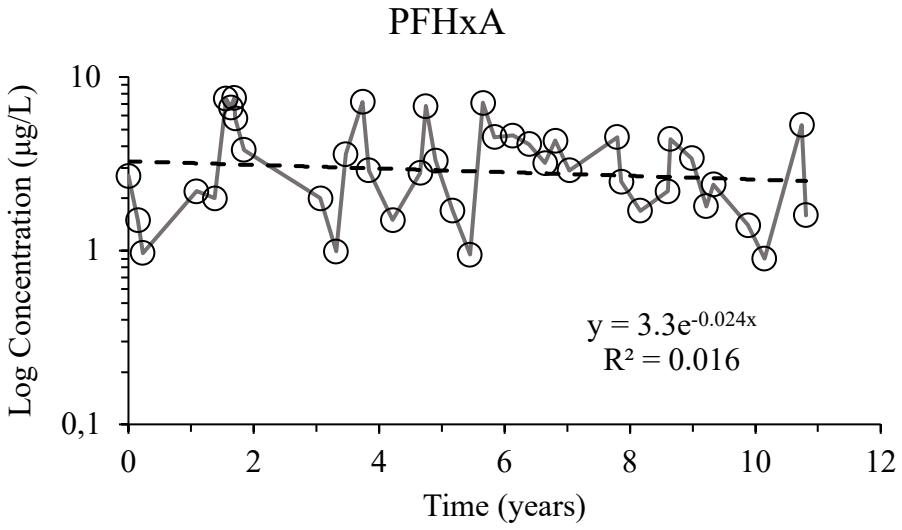

Fig. S3. Long-term monitoring PFHxA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

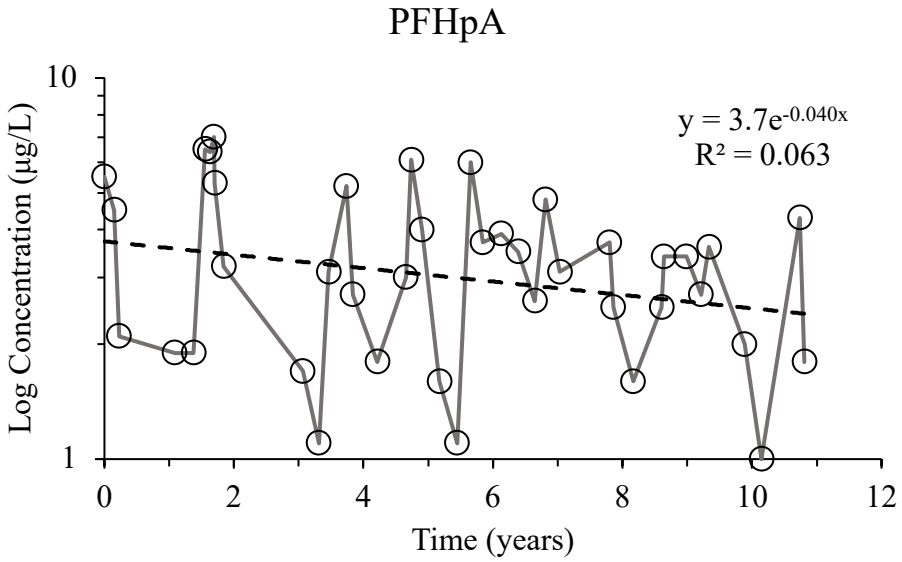

Fig. S4. Long-term monitoring PFHpA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

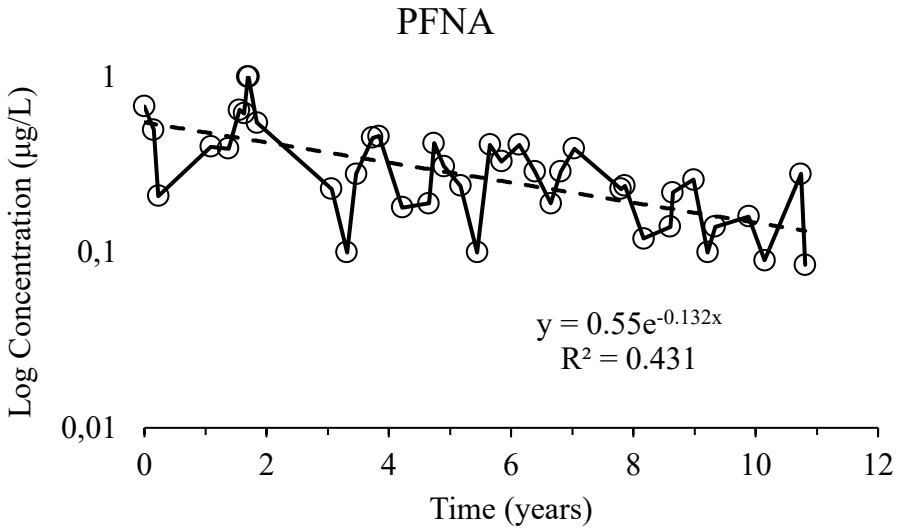

Fig. S5. Long-term monitoring PFNA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

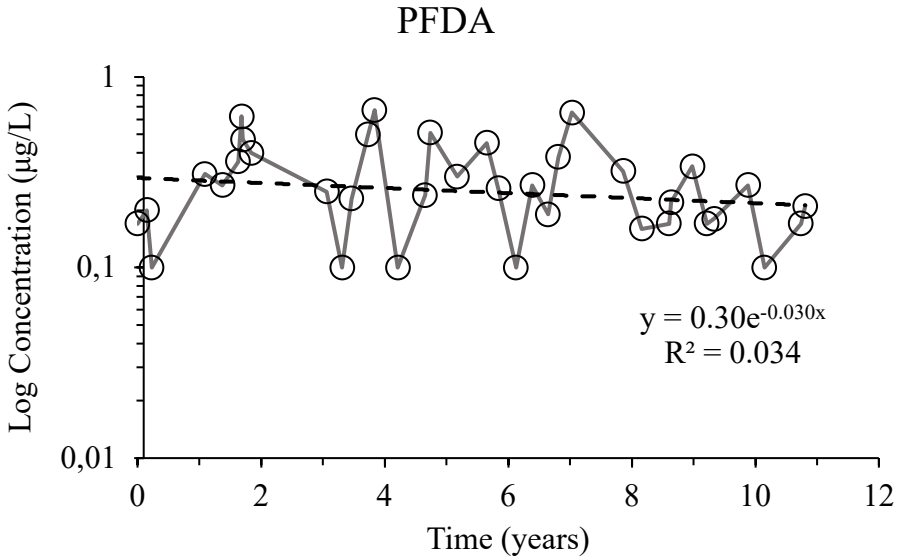

Fig. S6. Long-term monitoring PFDA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

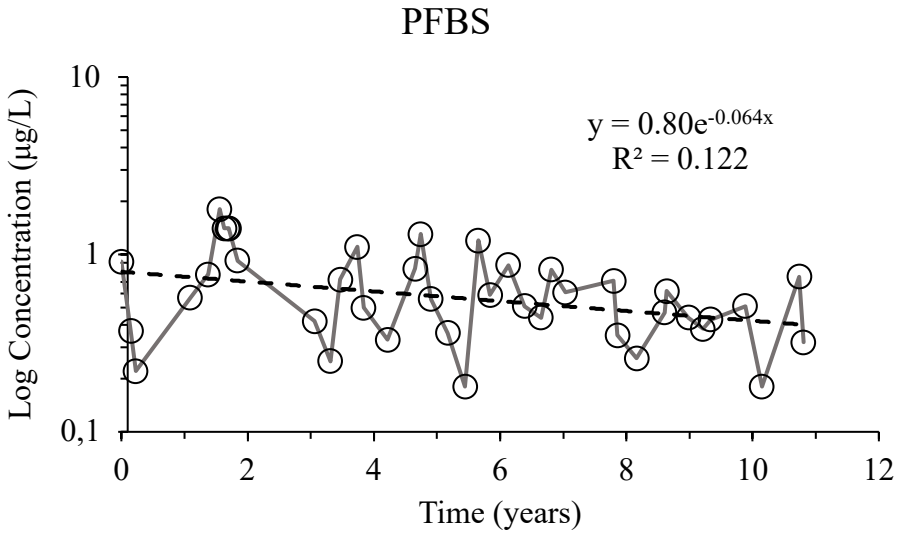

Fig. S7. Long-term monitoring PFBS concentration with time at the 10 ha agricultural site in Brilon-Scharfenberg using data collected from February 2008 to January 2019.

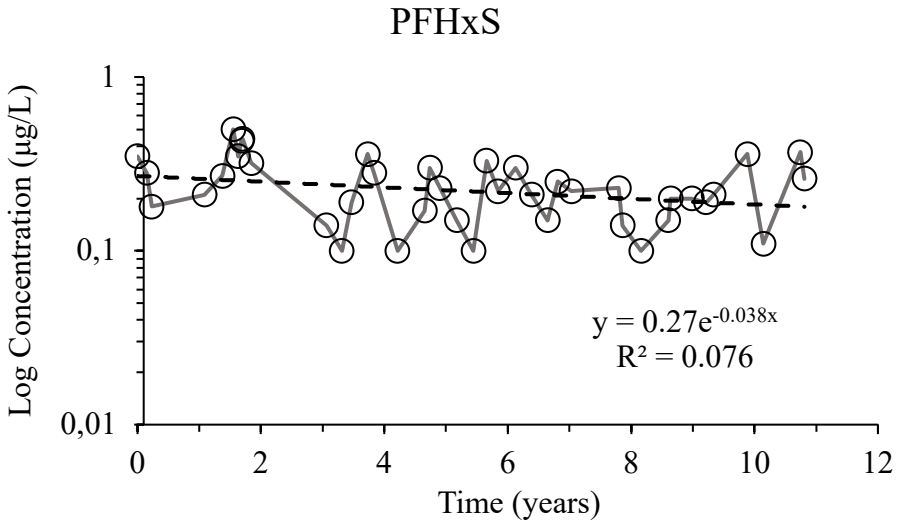

Fig. S8. Long-term monitoring PFHxS concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from February 2008 to January 2019.

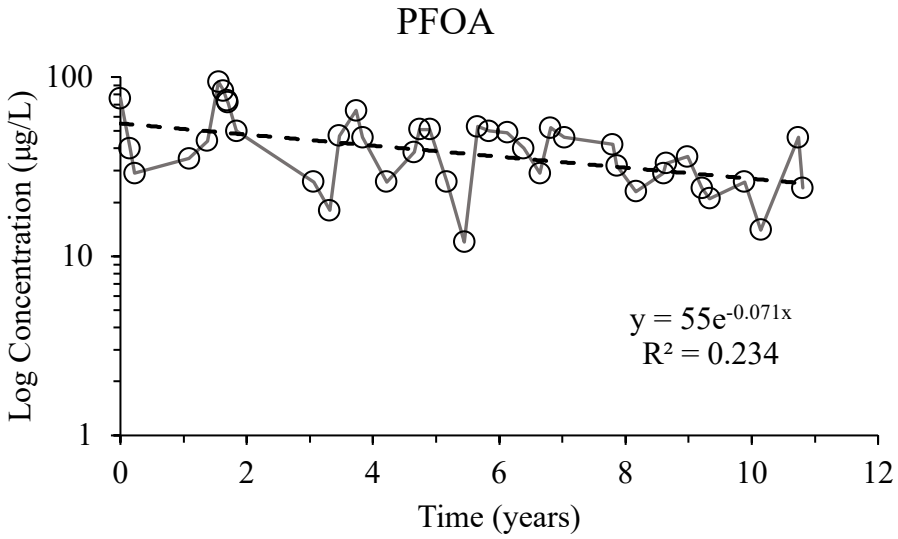

Fig. S9. Long-term monitoring PFOA concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from January 2007 to January 2019.

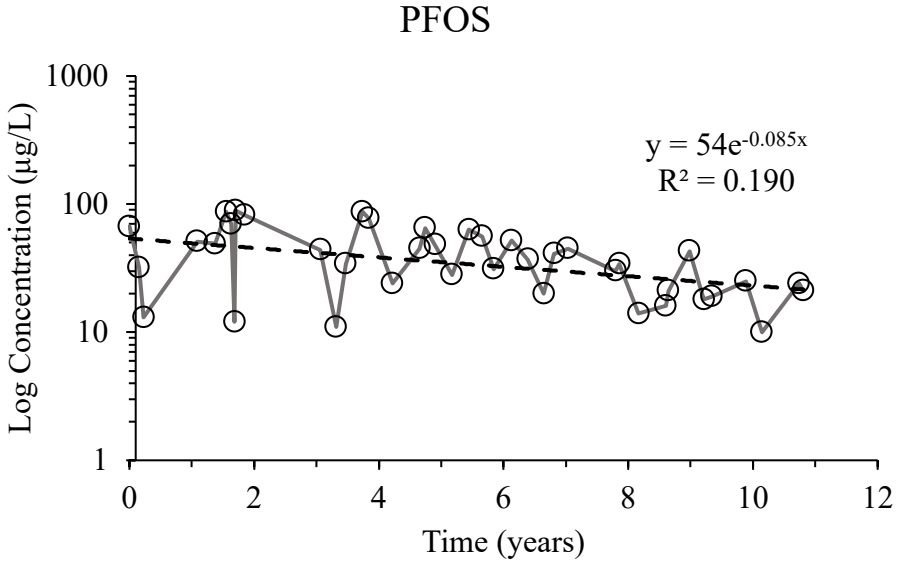

Fig. S10. Long-term monitoring PFOS concentration data at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data collected from January 2007 to January 2019.

Extraction of top- and subsoil samples at the Baden site

The dataset from Arcadis GmbH comprises soil extraction results (DIN 38414-14) for different depths. For our analysis of the dataset only results from 0-0.3 m and 0.3-0.6 m depth were used. Only results where the analyte concentration was ≥ 1 µg/kg in the topsoil and subsoil from the same field were considered. Comparison of topsoil to subsoil solid concentrations allow for the assessment of the mobility of the compounds, e.g.by calculating the ratios of the topsoil to the subsoil concentration. If the concentrations are equal in the top- and subsoil is equal, then the compound is evenly distributed between the top- and subsoil. Results are shown in Fig. S14.

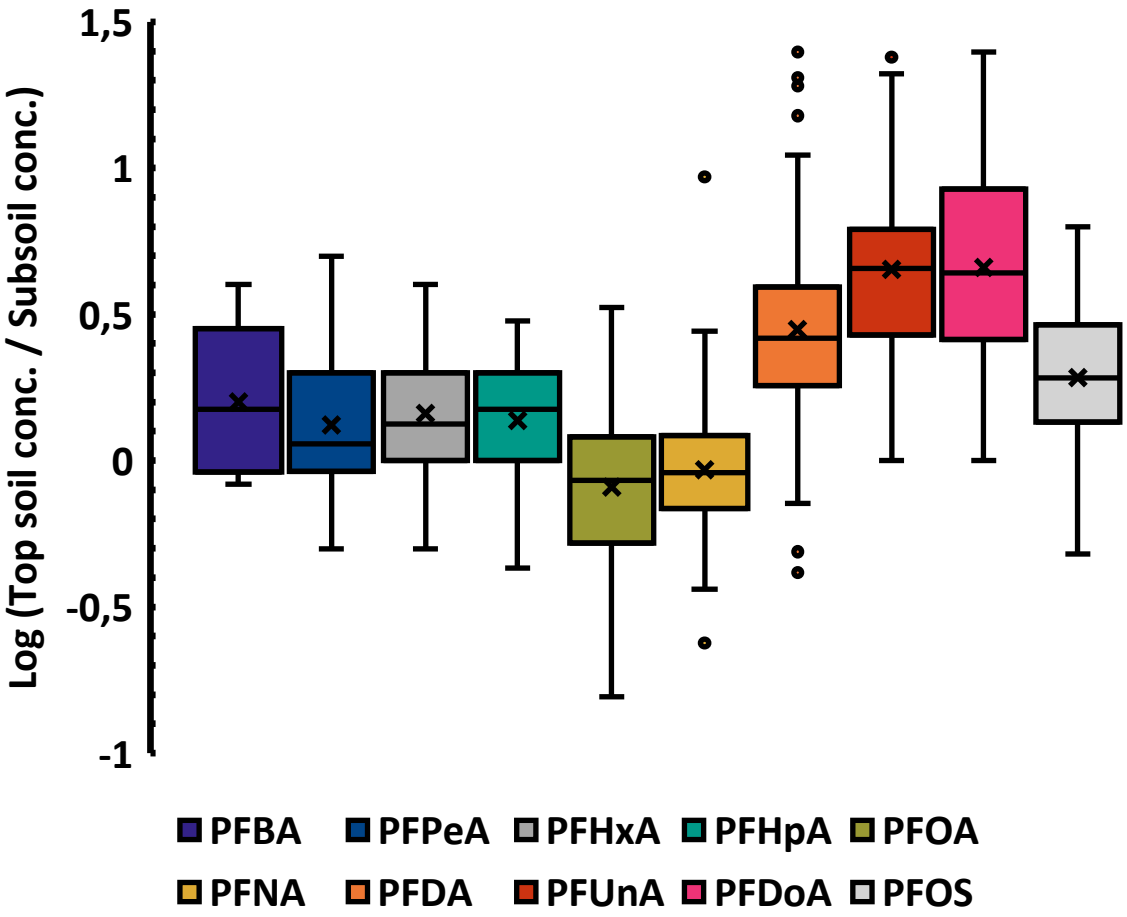

Fig. S10. Concentration ratios (CRs) for PFAAs in topsoils (0-0.3 m) and subsoils (0.3-0.6 m) in soil extracts from the Baden site. PFBA (n=5), PFPeA (n=27), PFHxA (n=19), PFHpA (n=15), PFOA (n=150), PFNA (n=105), PFDA (n=188), PFUnA (n=25), PFDoA (n=39), PFOS (n=91).

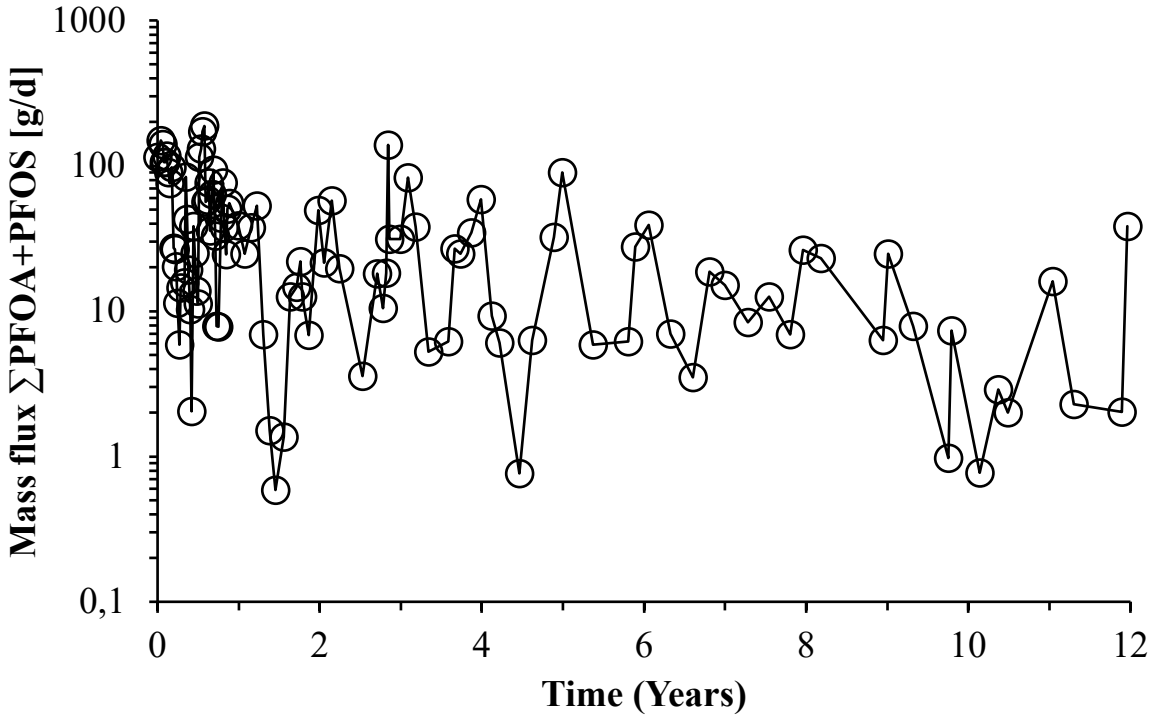

Fig. S11. Mass flux of ∑PFOA+PFOS at the inflow of the AC filtration plant at the 10 ha Brilon-Scharfenberg (BS-NRW) site using data from January 2007 to January 2019.

Chapter 9 – personal contribution

Author	**Author position**	**Scientific ideas %**	**Data generation %**	**Analysis & interpretation %**	**Paper writing %**
Klaus Röhler	1	80	100	80	90
Bernd Susset	2	5	0	0	0
Peter Grathwohl	3	15	0	20	10
Title of paper:		Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments.			
Status in publication process:		Submitted for publication in Environmental Science & Technology			

9. Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments

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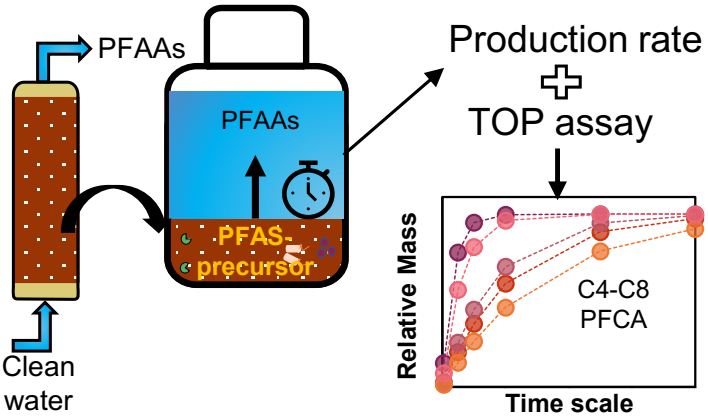
Manuscript submitted for publication to: *Environmental Science & Technology*

9.1. Abstract

Contamination of soils with per- and polyfluoroalkyl substances (PFAS) (e.g., aqueous film forming foams (AFFFs) or PFAS containing biosolids applied to agricultural soils) can lead to large scale groundwater pollution. For site management, knowledge about the extent and time scales of PFAS contamination is crucial. At such sites, often persistent perfluoroalkyl acids (PFAAs) and so-called precursors, which can be transformed into PFAAs, co-occur. In this study, the release of PFAAs from 14 soil samples from an agricultural site in southwest Germany contaminated via compost/paper sludge was investigated. Rapid leaching of C4-C8 perfluoroalkyl acids (PFCA) was observed in saturated column tests, while it slows down with increasing chain-length (≥ C9 PFCAs). After the column pretreatment, two selected samples were incubated in batch-tests and a linear increase of C4-C8 PFCAs in water by a factor of 29-222 was observed within 60 days, indicating their continuous production by precursors. The potential precursor reservoir was estimated by the direct total oxidizable precursor (dTOP) assay and about 10-100-fold larger than PFCAs in original soil extracted with methanol. Production rates determined in batch-tests combined with the results of dTOP assay allowed to estimate time scales for the continuous emission of C4-C8 PFCAs from the contaminated agricultural soils which likely will last for several decades.

Graphical abstract



9.2. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of anthropogenic chemicals that have been applied in numerous industry and consumer products such as firefighting foams, food contact paper, textiles and many more.[1] Broad application of PFAS began already in the 1950s and due to their chemical stability and longevity, they are now found in virtually every environmental compartment e.g. water[2-4] air[5, 6], soil[7-9] and biota[10, 11].

In the last decade reports of PFAS impacted soils by e.g. aqueous film forming foams (AFFF),[12-14] biosolid or industrial waste application to agricultural fields increased.[2, 15-17] Contaminated agricultural sites have led to large scale groundwater contamination.[15, 16] Often, a complex mixture of so-called PFAS-precursors and their persistent transformation products (TPs), the perfluoroalkyl acids (PFAAs) co-exist at these sites.[7, 12, 14, 15, 18] Saturated and unsaturated column tests, batch-tests and lysimeters have been used to study the release and transport behavior of PFAS in soils.[12, 16, 19-23] They showed that short-chain PFAAs (perfluorinated carboxylic acids (PFCAs) with <C8 and perfluorinated sulfonic acids (PFSAs) with <C6) are readily mobilized from soils and reach groundwater with little retardation, while precursors and long-chain PFAAs remain mostly in the upper soil horizon.[12, 17, 19, 23-25] In a critical literature review Li et al. (2018)[26] analyzed different soil properties and their impact on PFAS sorption. They concluded that organic carbon (OC) content, pH and clay content have significant effect on PFAS sorption in soils. In addition, accumulation at the air-water interface further impacts the transport of PFAAs in the unsaturated soil zones (especially affecting long-chain PFAAs).[22, 27-29]

Precursors in the upper soil layers are susceptible to degradation process, leading to the formation of PFAA and their subsequent transport to groundwater.[24, 30] To evaluate the transformation potential of precursors, microcosm or batch-test studies were used.[24, 30-36] Liu and Liu (2016)[36] and Lee et al. (2014)[24] investigated the biodegradation of polyfluoroalkyl phosphate diesters (diPAPs) in aerobic soil incubations and greenhouse microcosms and found degradation half-lives times of a few weeks to several years for 6:2 and 8:2 diPAP, respectively. Major TPs for 6:2 diPAP were C4-C7 PFCAs and in addition perfluorooctanoic acid (PFOA) for 8:2 diPAP.[24, 36] Further, Chen et al. (2020)[32] showed that also abiotic processes can degrade perfluorooctane-amido and -sulfonamido amine oxides (PFOANO and PFOSNO) which produce similar TPs as biotic processes.

At PFAS impacted agricultural sites the identity (and quantity) of precursors is often unknown. For example, Schaefer et al. (2022)[21] showed during a 6-month mesocosm study that the mass of PFAAs recovered in aqueous leachate form soils applied with biosolids containing PFAS was typically one order of magnitude greater than the mass initially present. Röhler et al. (2021)[16] analyzed long-term (12 years) monitoring data of PFAAs from a 10 ha contaminated agricultural site in North Rhine-Westphalia, Germany and observed continuous release of C4-C6 PFCAs, which they attributed to on-going transformation of unknown precursors.

This study addresses a second site in Germany located in the area of Rastatt/Baden-Baden and Mannheim, Baden-Württemberg, where 1650 ha of arable land were polluted in the 2000s by the application of compost presumably mixed with paper-sludge, which led to large-

scale PFAA groundwater pollution.[17, 37] Soil samples from the site were incubated in 60-day microcosm (batch) experiments to calculated PFCA production rates. Additionally, a direct total oxidizable precursor (dTOP) assay was conducted to estimate the potential reservoir for PFCAs production. By combining results from the batch-tests and dTOP assay times scales of precursor transformation and thus groundwater exposure to PFCAs may be estimated.

9.3. Methods & Materials

Standard and reagents

Chemicals used in the study are listed in section S1.1. Analytical standards and internal standards are presented in Table S1.

Soil sampling and site description

In the state of Baden-Württemberg, 16.5 km² of arable land is considered to be polluted with PFAS.[37] Most of the contamination occurs in an area of 11.05 km² in Rastatt/Baden-Baden. The remaining 5.45 km² are located in Mannheim ~80 km north. A groundwater monitoring and modeling study, covering 377 km² in the Rastatt/Baden-Baden area provided data on PFAS concentrations in groundwater monitoring wells and seepage water (leaching tests).[38] The PFAS distribution reported in groundwater on average was: 8% PFBA, 24% PFPeA, 28% PFHxA, 11% PFHpA, and 29% PFOA.[38]

For our study 10 soil samples were taken from the Rastatt/Baden-Baden and 4 from the Mannheim area between October 2019 and January 2020. Soils A, B, C, E, and F were collected from the Rastatt area. The maximum distance between fields A and B was ~15 km and sites C, E and F were located in between. Soil samples D, G, and H were collected in the Mannheim area and within a distance of 1.5 km to 4.5 km. Details on the sampling, sample preparation, and determination of soil properties (organic carbon (OC) content, pH, and grain size distribution) are described in section S1.2; soil properties are listed in Table S2. Soil textures indicate mostly sandy clay loams, loamy sands, sandy clays (soil A, B, E, and F) or clays (soil C). The soils from Mannheim include clays (soil D, and G) and loam (soil H). The OC content of the soils covered a range from 0.4 % (soil A 30 – 50 cm) to 6.6% (soil D 0 – 30 cm), while pH was between 5.5 and 7.5.

Soil extraction

For PFAS extraction 500 g of the soil sample was sieved <2 mm and dried in an oven at 40 °C. A ball mill was used to pulverize and homogenize the sample. 5 ml of methanol (MeOH) were added to 1 g of soil in a 50 ml polypropylene tube. After vortex mixing for 20 s, the sample

was sonicated for 30 min and placed on a horizontal shaker for another 30 min. The samples were then centrifuged at 7000 relative centrifugal force (rcf) and the supernatant was transferred into a 12 ml glass vial. The extraction procedure was repeated once. The combined extracts were evaporated to dryness under a gentle N_2 stream at 40 °C and reconstituted in 1 ml H_2O/MeOH (1/1, v/v). Internal standard in MeOH was spiked to the reconstituted sample by the high-performance liquid chromatograph (HPLC) autosampler before injection to account for matrix effects. Results from recovery experiments were > 85% and are presented in Table S3. To check for the presence of diPAPs and diSAmPAPs in soil A and B, 5 g soil were extracted as described above and analyzed using high-resolution mass spectrometry (HRMS) (further details in section 1.6).

Direct total oxidizable precursor (dTOP) assay

The dTOP assay was conducted similarly to the method described by Göckener et al. (2020).[39] Briefly, 0.1 g of soil was placed into 100 ml glass bottles, and 100 µl internal standard (100 µg/l) of PFCAs and PFSAs was added. Afterward, 100 ml of a 0.5 M NaOH and 0.2 M $K_2S_2O_8$ solution were added before the bottles were put into an oven at 85 °C for 7 h. After the samples cooled down to room temperature, pH was adjusted to 7 ± 0.5 using hydrochloric acid. Subsequent cleanup and enrichment were done with solid phase extraction (SPE), using cartridges with weak anion exchange material (Chromabond HR-XAW, 3 ml, 200 mg, Macherey-Nagel) pre-conditioned with 6 ml of 0.1 % NH_4OH in MeOH, and 3 ml of MeOH and 6 ml H_2O. The samples were passed through the cartridge using a vacuum at approximately 1 drop per second. Afterwards, the cartridges were washed with 6 ml H_2O and dried. Elution was achieved with 3 ml MeOH followed by another 6 ml of MeOH with 0.1 % NH4OH. The combined extracts were evaporated under a gentle stream of N_2 at 40 °C until dryness and reconstituted in 1 ml MeOH/H_2O (1/1, v/v). Results from recovery experiments were >75% for C4-C10 PFCAs and C4-C9 PFSAs and are presented in Table S4.

Column leaching tests

Up-flow column leaching tests were conducted according to the German DIN 19528 (2009).[40] The homogenized soil sample was packed into glass columns with a diameter of 5 cm and a length of 30 cm. The soil was packed in layers up to a height of 26 cm and covered with a 2 cm thick quartz sand layer at the upper and lower section of the column to ensure equal distribution of water flow and to pre-filter the eluate. The column was flooded from bottom to top within 2 h, then the flow rate was adjusted to ensure a contact time of 5 h. Samples were taken at certain liquid/solid ratios (*LS*), which accounts for the amount of water that has been in contact with the dry solid material inside the column. *LS* can be converted into time.[30]

$$t = LS\frac{x}{v}\frac{\rho}{n} \quad (1)$$

x, *v*, *ρ* and *n* denote the length of the column (m), the seepage velocity (m yr^{-1}), dry bulk density (kg m^{-3}) and porosity (-). Control columns containing only quartz sand were set up and performed in parallel to check for background contamination. Information on the quartz sand is provided in section S1.4. The column eluates were stored at 4 °C until further analysis. The sample preparation procedure for subsequent HPLC-MS analysis is described in section S1.4.

Long-term tailing in column leachate, suggesting transformation of precursors was used to estimate production rates for soil A and B according to Equation S1.

Precursor transformation experiments (batch-tests)

For the batch experiments, column tests until a *LS* ratio of 10 l/kg were carried out first to remove existing PFAAs in the soil. After column leaching, the soil of four columns was pooled and equally distributed into 2 l glass bottles (~500 g dry soil). For sterile controls, the soil in the bottles was autoclaved at 120 °C within 120 minutes. The bottles were then filled with deionized, autoclaved water until a *LS* ratio of around 2.5 l/kg was reached. The bottles were placed onto horizontal shakers at 200 rpm at 20 °C and protected from light. The bottles were opened regularly to ensure a sufficient supply with oxygen. Sterile controls were opened next to a flame. Oxygen levels were tracked non-invasively using a Fixbox 3 Minisensor Oxygen Meter from PreSens (Regensburg, Germany). At each sampling point, an aliquot of 18-20 ml was sampled (controlled by weight) which was considered in mass balances (losses in solid mass were negligible as only 1-3 mg of soil per sampling point were lost). Dry soil mass, water volumes and *LS* for the individual set-ups are given in Table S11.

Time scales for PFAA production from precursors

For time scale calculations a simple exponential decay function was assumed to describe the decrease of precursors (C_{PC} e.g., in µg kg^{-1} or mol kg^{-1}, λ is a rate constant e.g., in $days^{-1}$):

$$\frac{dC_{PC}}{dt} = -\lambda\, C_{PC} \tag{2}$$

integration ➔

$$\int_{C_{PC,0}}^{C_{PC}} \frac{dC_{PC}}{C_{PC}} = \int_{0}^{t} -\lambda\, dt$$

$$\frac{C_{PC}}{C_{PC,0}} = \exp(-\lambda\, t)$$

The relative concentration of the transformation product (C_{TP}) thus would increase with time:

$$\frac{C_{TP}}{C_{TP,\infty}} = 1 - \exp(-\lambda\, t) \tag{3}$$

$C_{TP,\infty}$ denotes the final yield of transformation product (total conversion of $C_{PC,0}$) per mass of soil solids. For short time periods (negligible precursor depletion) this reduces to a linear part:

$$C_{TP} = C_{TP,\infty}\,\lambda\,t \tag{4}$$

The term $C_{TP,\infty}\,\lambda$ denotes the initial production rate (µg kg^{-1} day^{-1}) and thus a linear increase of C_{TP} may be observed in short-term laboratory tests. The unknown $C_{TP,\infty}$ may be estimated by the dTOP assay soil concentration (C_{dTOP}) (µg kg^{-1}), thus λ may be determined by:

$$\lambda = \frac{C_{TP}}{C_{dTOP}}\frac{1}{t} = \frac{P}{C_{dTOP}} \tag{5}$$

P denotes the production rate (µg kg^{-1} day^{-1}) of the transformation product (= C_{TP}/t). Average P values and their 95% confidence intervals from triplicates in batch-tests were determined using Microsoft Excel®'s regression tool package.

Instrumental analysis

Details on the instrumental analysis (HPLC and MS systems used, source parameters, MS acquisition and limits of quantification (LOQ)) are provided in section S1.6.

9.4. Results & Discussion

PFAS in soil solids

C4-C12 PFCAs and C4-C10 PFSAs concentrations varied between individual agricultural fields ranging from 12 to 348 µg/kg of ∑PFAAs (Figure S2). A detailed list of individual PFAA soil concentrations is provided in Table S9 and S10. In all soils C4-C12 PFCAs could be detected. PFOS was the most frequently detected PFSA and was present in all soil samples except for soil A 30 - 50 cm. PFHpS could only be the detected in samples soil F 0 - 30 and 30 - 50 cm in low concentrations (< 1 µg/kg). Concentrations were dominated by long-chain PFAAs (PFCAs ≥C8 and PFOS), which account for 65 – 98 % of PFAAs in the soil (Figure 1). Single species with the highest concentration in soils were PFDA (n = 8, $C_{s,max}$ = 195 µg/kg), PFOA (n = 4, $C_{s,max}$ = 61 µg/kg) and PFOS (n = 2, $C_{s,max}$ = 282 µg/kg).

PFAA distribution patterns in soils from the Rastatt/Baden-Baden (soil A, B, C, E and F) and the Mannheim area (soil D, G and H) were similar except for soil F, where PFOS accounted for >80% of PFAAs while all other soil samples are dominated by PFCAs (PFOA and PFDA ≥50%). This suggests that different types of paper sludges could have been applied to individual fields.

HRMS conducted on 14 soil samples from the same region by Bugsel et al. (2022)[17] revealed diPAPs (from 4:2/6:2 to 12:2/14:2) and their TPs (including PFCAs) to be the major

contaminants in addition to fluorotelomer mercapto alkyl phosphates (FTMAP), the C8-based N-ethyl perfluorooctane sulfonamide ethanol–based phosphate diester (diSAmPAP) and their TPs. They found average chain lengths of diPAPs and PFCAs between 8-9 (for diPAPs) and 10 (for PFCAs) which confirms our results. Sources of PFAAs in soil may be due to a combination of PFAAs from impurities or aiding substances used during the paper coating process and by transformation of PFAA-precursors as PFAA chain-length (PFCAs C4-C12) matches the chain-length of precursors (diPAPs from 4:2/6:2 to 12:2/14:2).

Non-target screening (NTS) analysis by Bugsel and Zwiener (2020)[7] report concentrations of PFOA, PFOS, 6:2/8:2 diPAP and diSAmPAP for one soil from Rastatt/Baden-Baden and three soils from the Mannheim area. PFOA and 6:2/8:2 diPAP concentrations were between 60 – 250 µg/kg and 20 – 210 µg/kg, respectively. PFOS and diSAmPAP were only observed in the soil from the Rastatt/Baden-Baden area and were 100 and 630 µg/kg, respectively. These results match well with our study. This confirms that individual fields may have been contaminated with different types of paper sludges as soil F shows a distinct PFAA distribution compared to the rest.

Soil samples A and B, which were later used in batch-tests to investigate potential precursor transformation, were screened using HRMS to verify the presence of precursors previously reported by Bugsel and Zwiener (2020)[7]. Results confirmed the presence of diPAPs (from 6:2/6:2 to 10:2/12:2) in both soils and additionally 4:2/6:2 diPAP in soil A (Figure S3 and S4), but no diSAmPAP was found (in both soils).

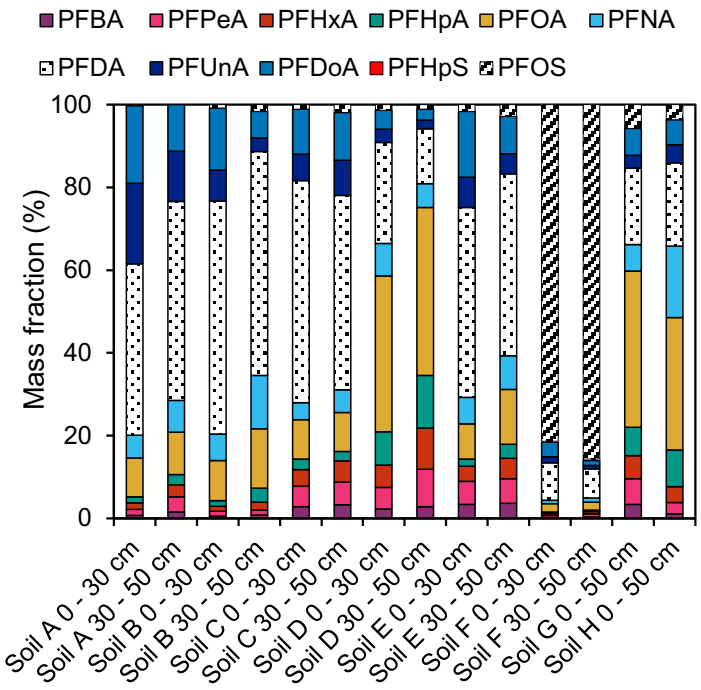


Figure 1. Mass fraction of C4-C12 PFCAs and PFOS in soil samples (A – H) from the Rastatt/Baden-Baden and Mannheim area.

Direct total oxidizable precursor (dTOP) assay

Screening of soils A and B (both 0 – 30 cm) qualitatively confirmed the presence of diPAPs. The dTOP assay was performed to quantify the production potential of PFAAs after column leaching to *LS* of 10 l/kg (to remove previously accumulated TPs). It also confirmed negligible leaching of precursors.

Figure 2 shows the PFCA concentrations before and after the dTOP assay. PFSAs concentrations after the dTOP assay were below the LOQ in soil A and 7 µg/kg (PFOS) in soil B, indicating no or only minor PFSA precursors. PFCA concentrations in both soils increased by a factor of 10 - 100 after the TOP assay, which indicates transformation of a significant number of precursors and which compares well to estimates by Bugsel and Zwiener (2020)[7]. They report 6:2/8:2-diPAP concentrations in a soil sample from Rastatt/Baden-Baden of around 210 µg/kg. Assuming similar concentrations apply to the other diPAPs found in soil A and B, PFCA concentrations of about 1000 µg/kg after the dTOP assay seem reasonable.

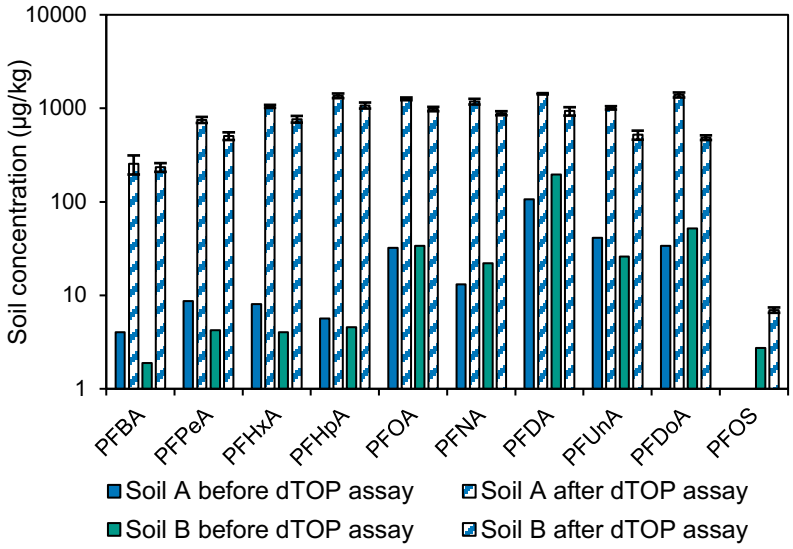


Figure 2. Comparison of PFCAs concentrations before and after the dTOP assay for two soil samples; error bars indicate standard deviation of triplicates (after dTOP assay: soil samples after leaching in columns until *LS* 10; before dTOP assay: without column leaching).

PFAA column leaching

Saturated column leaching tests according to German DIN 19528[40] were conducted to investigate the release potential of PFAAs from soils and as pre-treatment step for batch-experiments. These column leaching tests do not address fate and transport of solutes in the vadose zone and other processes relevant to contaminant migration in the subsurface.

Results on leaching of PFBA, PFPeA, PFOA, PFNA and PFDA in soils from 0 - 30 cm in column tests are shown in Figure 3a. Leaching from subsoils (30 - 50 cm) and other PFAAs are shown in Figures S5 and S6. C4-C10 PFCAs and PFOS were detected in the leachate of all soils with a maximum concentration of PFOA of 67 µg/l. PFUnA was detected in at least one eluate sample from all soils except for soil D (30 - 50 cm) and PFDoA concentrations were below the LOQ (0.01 µg/l) in eluates from soil D (0 - 30/30 - 50 cm), soil E (0 - 30/30 - 50 cm) and soil H (0 - 50 cm). The PFSAs PFHxS and PFHpS were only occasionally detected (Figure S5 and S6), whereas PFPeS, PFNS and PFDS were not found. PFBS was only detected in the initial two sampling points of one soil sample and concentrations were <0.04 µg/l (data not shown).

Overall, C4-C7 PFCAs showed rapid leaching from soils similar to conservative tracers as observed in other studies.[19, 25] High initial concentrations ($C_{w,max}$ = 11.6 - 27.6 µg/l) dropped around 1-2 orders of magnitude until *LS* 2 l/kg. Only soil D with a high OC content of 6.6% (0 - 30 cm) and 4.2% (30 - 50 cm) showed slower leaching confirming that hydrophobic interactions with OC are important for PFAA sorption in soil.

The release of long-chained PFAAs from soil decreased with increasing chain-length, which is in accordance with the literature.[19, 21, 25] PFOA and PFNA ($C_{w, max}$ = 30 µg/l) effluent concentrations decreased 1-2 orders of magnitude until *LS* 10 l/kg, while PFDA, PFUnA and PFDoA showed relative stable effluent concentrations, indicating stronger sorption and thus more retardation. The initial increase of long-chained PFAAs observed in the column tests, likely is an artifact due to small water volumes sampled at early times with losses of PFAS at large water/air surface areas (more elaborated in section S2.2).

In general, no differences were observed in the leaching of PFAAs from soil 0 – 30 (or 0 – 50) cm and 30 – 50 cm. Average recoveries (Figure 3b) for C4-C8 PFCAs were between 104-111%. Recoveries of >120% (Figure S7) and extensive tailing of C4-C8 PFCAs also indicates production by precursors as already observed by Bräunig et al. (2019)[20]. Average recoveries in column leachate of C9-C12 PFCAs dropped with increasing chain length from 89 % to 7%. PFOS average recovery was around 65% and therefore lower compared to the PFCA homologue PFNA. These results show that C4-C8 PFCAs are readily washed out of the soil, while it would take decades for PFCAs >8 and PFOS to be leached from soil, assuming that LS = 1 equals ≈ 4 years in the field (eq. 1, assuming soil depth of 0.3 m, porosity 0.4[41], dry bulk density of 1.6 kg/l[41] and a seepage velocity of 0.3 m/yr[38]).

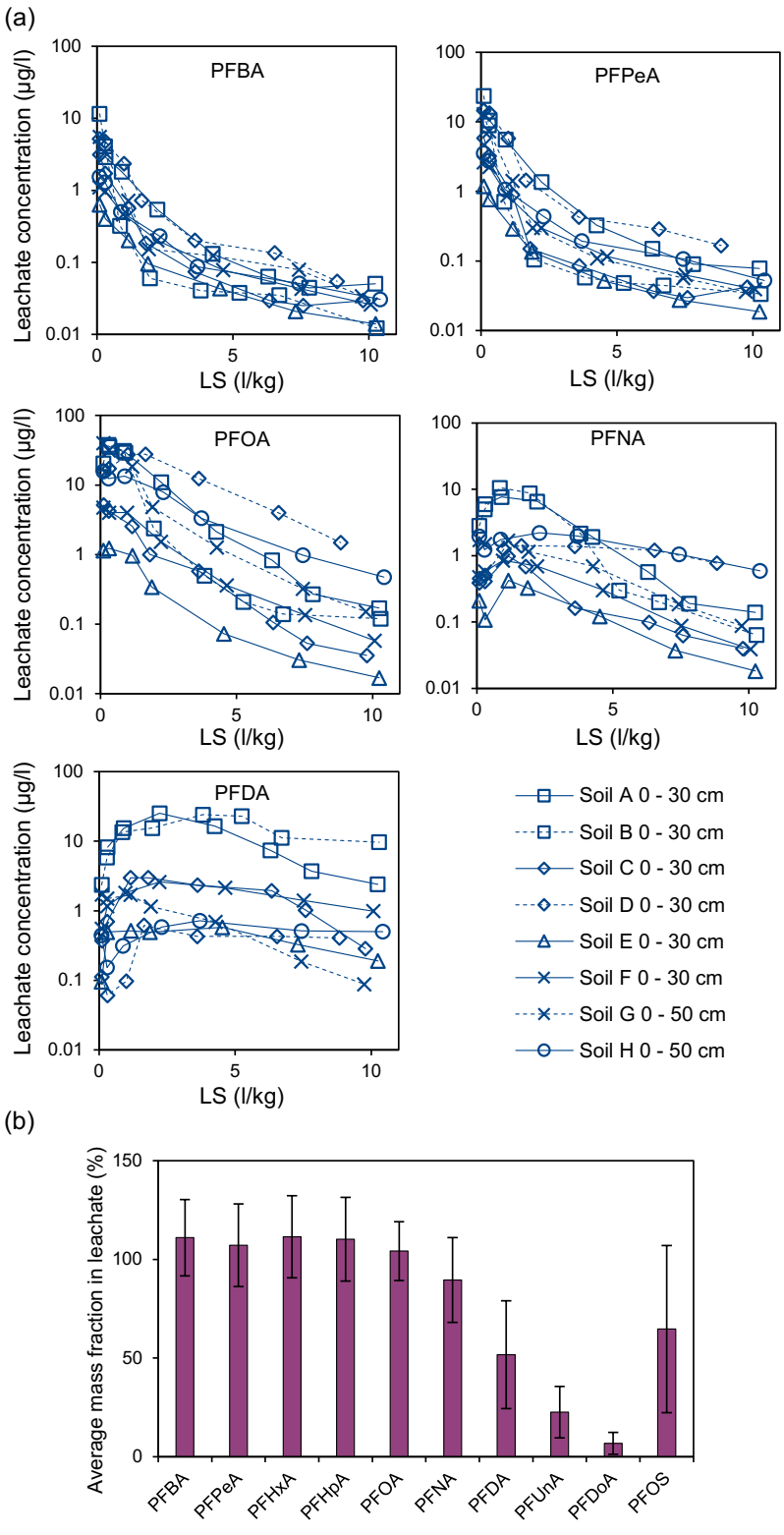


Figure 3. (a) Release of selected PFCAs in column leaching tests with contaminated agricultural soils samples (A – H); (b) average mass fractions recovered from samples in column leachates until *LS* = 10; error bars indicate standard deviation from numbers of soil samples.

Batch-tests for precursor transformation and release of transformation products

To further investigate the potential production of PFCAs from precursors, well controlled batch experiments were set up with soil A and B. In both soils, diPAPs (Figure S3 & S4) were detected and showed a high reservoir of PFCAs in the dTOP assay (Figure 2). During incubation aerobic conditions were maintained (>5 mg/l O_2 see Figure S9). A linear increase in aqueous concentration of C4-C8 PFCAs was observed for both batch setups as shown in Figure 4. Initial concentrations of C4-C7 PFCAs were between 0.02 - 0.08 µg/l in soil A and 0.01 - 0.02 µg/l in soil B and increased after 60 days to concentrations between 0.93 – 17 µg/l and 0.56 – 2.3 µg/l, respectively. PFOA increased linearly in soil A from 0.13 µg/l initially to 16 µg/l after 60 days and in soil B from 0.04 µg/l to 4.9 µg/l. In soil B a slow linear increase of PFNA from 0.02 µg/l to 0.26 µg/l was observed, while the increase in soil A for PFNA leveled off after 48 days at ~1 µg/l. These results show that during aerobic incubation of PFAS-impacted soils, precursors can be transformed into PFCAs. Anaerobic transformation of precursors is expected to be minimal.[32] Agricultural soils experience regular turn-over (when fields get cultivated) and therefore, aerobic conditions in the field will likely apply.

C10-C12 PFCAs and PFOS (Figure S10) concentrations did not increase and no PFOS was detected in soil B during the batch-test, although a potential reservoir was indicated for C10-C12 PFCAs and PFOS in soil B by the dTOP assay. This might have several reasons. First, C10-C12 PFCAs are not completely removed during the column leaching, causing relatively high initial concentrations in batch tests.

Secondly, C9-C12 PFCAs have K_d values larger than the *LS* ratio (≈2.5 l/kg) in the batch-test.[33] This leads to a significant amount of produced mass to be sorbed to the solid phase, thus reducing the aqueous concentrations (see section S2.3. for further explanation). Furthermore, decreasing bioavailability of precursors with increasing chain length (e.g. 6:2 diPAP and 8:2 diPAP) as reported by Liu and Liu (2016)[30] may result in low amounts of PFCA ≥C9 produced during the test period of 60 days.

As no concentration increase in the autoclaved controls was observed, production of PFCAs was likely caused by aerobic biodegradation of precursors. Controls showed elevated background concentrations (10 -100 times compared to initial concentrations in not autoclaved samples), which did not further increase during 60 days of incubation. This is likely caused by abiotic/chemical precursor transformation during autoclavation of moist samples at temperatures of 120 °C.

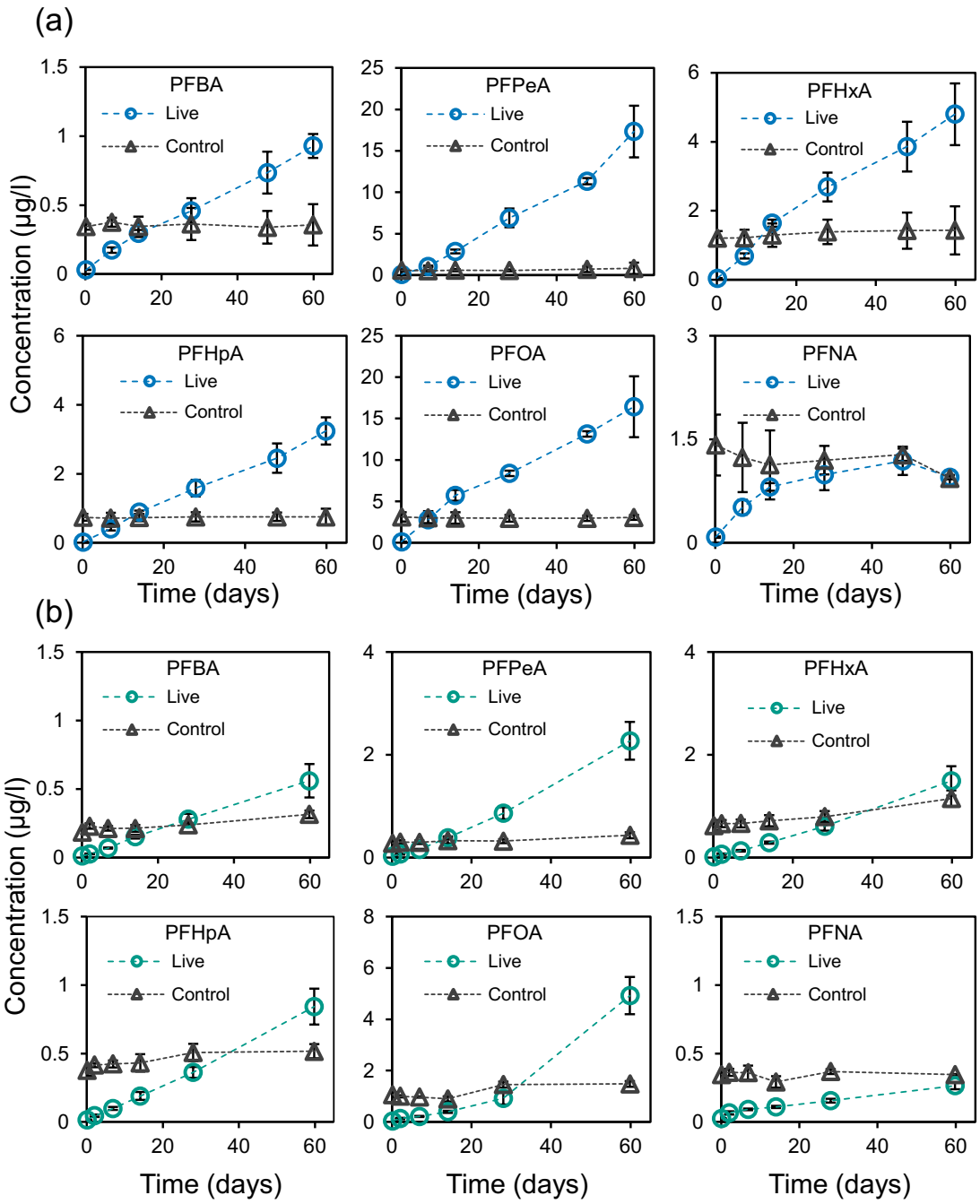


Figure 4. Aqueous concentrations of C4-C9 PFCAs for (a) soil A 0 - 30 cm, (b) soil B 0 - 30 cm in batch incubations. Error bars indicate standard deviations from triplicates.

Increases in concentrations of C4-C8 PFCAs allow for the calculation of production rates using Microsoft Excel®'s regression tool package. Production rates from batch-tests were also compared to data in the literature. For example, 6:2 and 8:2 diPAP degradation experiments reported by Liu and Liu (2016)[36] allowed to calculate C4-C8 PFCA production rates (see Fig. 5a). For PFBA, the rates compared well between our two samples and the results from Liu and Liu (2016)[36], while the production rates differ between soil A and B for C5-C8 PFCA. PFHxA

was a major TP in the degradation experiment from Liu and Liu (2016)[36], whereas in soil from Rastatt/Baden-Baden PFPeA and PFOA were the major TPs.

Differences in the rate of PFCA production may arise from different precursor mixes, their quantities and specific transformation kinetics including potential (unknown) intermediate TPs. For example, 4:2/6:2 diPAP as potential precursor for PFPeA was only detected in soil A. Furthermore, microbial communities and environmental conditions (e.g., temperature, moisture content, oxygen) can influence the production of PFAAs. Chen et al. (2020)[32] found that inherent differences in soil characteristics can largely influence the transformation of precursors. Therefore, transformation rates and patterns are not just dependent on the precursor type but may also be site specific.

The rates derived in the batch experiments have to be viewed as a result of the superposition of transformation of various precursors (and intermediate TPs). In Figure S11 the production rates derived from batch experiments are compared to production rates calculated for C4-C8 PFCAs in the tailing part from column leaching tests. Batch-test derived production rates of PFPeA and PFOA in soil A were significantly higher compared to results obtained in column tests. This may be due to turbulent vs. laminar flow conditions, and the higher likelihood of anaerobic conditions in columns limiting biodegradation. In addition, *LS* ratios control TP and precursor mass distribution between solid and liquid which has to be considered. All that may influence TP rates and bioavailability of precursors. Furthermore, continuous agitation of batch tests reduces aggregate sizes and finally may even increase temperatures.

Figure 5b compares the distribution pattern of TPs from batch experiments to the major PFAS species found in the groundwater in the Rastatt/Baden-Baden area.[38] The pattern from the batch experiments qualitatively matches the pattern in the groundwater, again indicating that the groundwater contamination most likely is caused by the production of PFCAs from precursors in top soils.

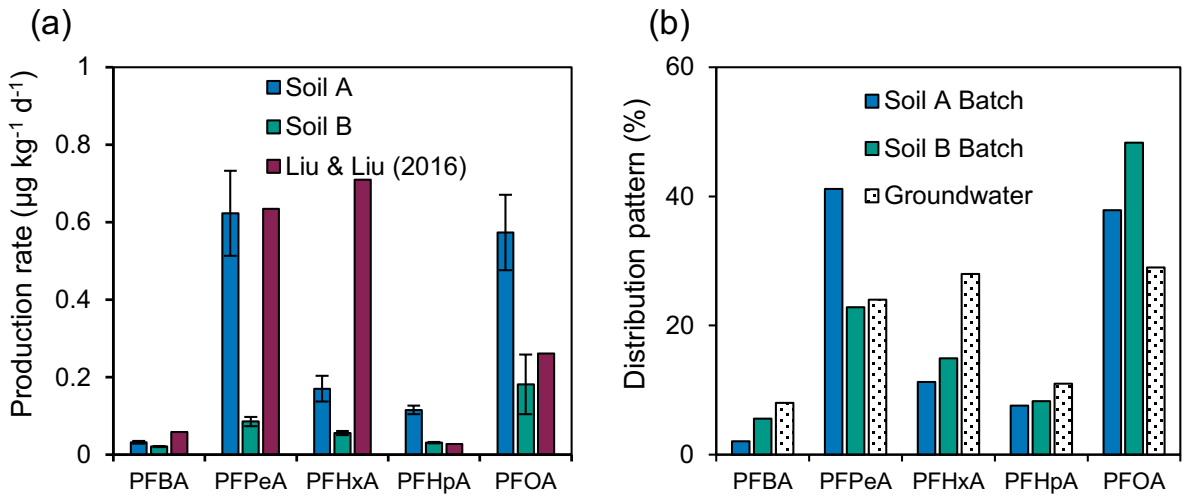


Figure 5. (a) Production rates of C4-C8 PFCAs calculated from batch experiments and from data from Liu and Liu (2016)[36] (C4-C6 PFCA rates were calculated from 6:2 diPAP and C7-C8 PFCA rates from 8:2 diPAP degradation experiments by Liu and Liu (2016)[36]); error bars indicate the lower and upper margins of 95% confidence interval. (b) Comparison of the distribution pattern of PFCAs produced in batch experiments und major PFCAs found in the groundwater[38] from the contaminated area in Rastatt/Baden-Baden.

Time scales for PFAAs production from precursors

While column leaching tests have shown that C4-C8 PFCAs are washed out of soils quickly with almost no retardation (meaning that they likely reach groundwater with no further retardation), extended tailing is observed indicating ongoing production of PFCAs from precursors. Hence, column leaching tests alone do not allow to predict time scales for the exposure of groundwater to mobile PFAAs. By the combination of the batch incubation results and the dTOP assay minimum time scales may be estimated until production of PFAAs has ceased (or precursors are exhausted).

Assuming that production will continue linearly as observed during the 60 days batch experiments, it will take less than 20 years in soil B and less than 10 years in soil A until PFPeA and PFOA production ceases. For other compounds (PFBA, PFHxA, PFHpA) it would take one to three decades until production stops. If we account for continuous degradation of precursors following 1st order decay (as observed for several PFAAs in field data by Röhler et al. (2021)[16] (equation 2 - 5) and by Lee et al. (2014)[24]), then time scales will stretch out to several decades as shown in Figure S12 (rate constants are given in Table S13) and legal limits are reached only after many decades.

These time scales have to be seen as best-case scenario since the production rates were determined under laboratory conditions (20 °C, sufficient oxygen supply, well mixed, etc.).[30] Schaefer et al. (2022)[21] did not observe any decreasing trend in release of PFCAs from

diPAP contaminated soil during a 6-month mesocosm study. Similar trends were reported in Röhler et al. (2021)[16] report trends and seasonal changes in field leaching data of PFAAs at a contaminated agricultural site in BS-NRW over a time period of 12 years. They also observed seasonal concentration changes, which may indicate different seasonal microbial activity.

A critical factor for the time prediction is the correct estimate of the total potential PFAA precursor reservoir. In the TOP assay PFAA precursors are converted and this may be used to estimate the potential PFAA reservoir. However, the TOP assay also has its limitations. For example, Schaefer et. al (2022)[21] notices significant differences between the total fluorine measured by direct precursor analysis and by the TOP assay. They associated this discrepancy to incomplete oxidation of precursors due to the chemical nature of precursors and matrix effects of the sample (biosolids). Further, during the TOP assay a reduction in chain-length of the produced PFAA is observed.[42] This becomes relevant if ultra-short-chained (C2 and C3) PFCAs are produced, since these compounds are challenging to analyze.[42] An alternative may be a photocatalytical conversion of precursors as described by Zweigle et al. (2022)[43] which better preserves the chain-length of TPs (mostly n-1 chain-length reduction).

Environmental implications

At PFAS-impacted sites, often a mix of TPs and their precursors co-occur. The characterization of precursors is challenging as only a limited amount of analytical reference standards are available. Therefore, it is helpful to combine established methods (column and batch-tests as well as the TOP assay) to estimate the minimum time scale of the contamination for site management strategies.

Column leaching tests are frequently used to assess the release of contaminants from solid materials in a time-lapse (as concentrations are plotted versus the *LS*), but they fail to predict the long-term release of transformation products if precursors are present. This affects especially leaching of C4-C8 PFCAs which show extended tailing in column tests not expected for low sorbing compounds.

Our results demonstrate that simple, but well-controlled aerobic batch-tests provide a reasonable estimate of production rates of C4-C8 PFAAs released from transformation of unknown precursors. In combination with the potential reservoir of PFAAs obtained by the dTOP assay, minimum time scales for PFAA release from PFAS-impacted sites may be estimated. This method can likely be applied to similar PFAS-impacted sites with precursors (e.g., AFFF sites) but further research is needed to elucidate effects of changing environmental conditions (temperature, moisture, sorption and microbial communities) to improve time scale estimates of PFAS soil contaminations.

Supporting Information

Chemicals, reagents soil samples and properties and PFAA concentrations, Sample preparation, Recovery experiments, Instrumental analysis; Precursors; Column leaching of PFAAs including depths 30 - 50 cm; Theoretical explanations; Batch-test set-ups; Production rates.

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Notes

The authors declare no competing financial interest.

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9.6. Appendix

SUPPORTING INFORMATION

TITLE: Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments.

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Section 1. Materials & Methods

S.1.1. Chemicals and reagents

PFCA and PFSA standards, including stable isotope standards were purchased from Wellington Laboratories (Ontario, Canada; **Fehler! Verweisquelle konnte nicht gefunden werden.**). Ammonium acetate (NH_4Ac) (Thermo Fisher Scientific), ammonium hydroxide (NH_4OH) (Thermo Fisher Scientific), calcium chloride ($CaCl_2$) (Thermo Fisher Scientific), hydrochloric acid (HCl) (Thermo Fisher Scientific), methanol (MeOH) (Thermo Fisher Scientific, Optima LC/MS grade), potassium persulfate (Fisher Scientific), sodium hydroxide (NaOH) (Thermo Fisher Scientific), and water (Thermo Fisher Scientific, Optima LC/MS grade) were used in this study.

Table S1. PFAS standards and internal standards used in the targeted analysis.

Chemical Name	Acronym	Molecular Formula	Internal Standard
Perfluoroalkyl carboxylic acids			
Perfluoro-n-butanoic acid	PFBA	C4HO2F7	MPFBA
Perfluoro-n-pentanoic acid	PFPeA	C5HO2F9	M5PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	M5PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	M8PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	M9PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	M6PFDA
Perfluoro-n-undecanoic acid	PFUnA	C11HO2F21	M7PFUdA
Perfluoro-n-dodecanoic acid	PFDoA	C12HO2F23	MPFDoA
Perfluoroalkane sulfonates			
Perfluorobutane sulfonate	L-PFBS	C4HO3SF9	M3PFBS
Perfluoropentane sulfonate	L-PFPeS	C5HO3SF11	M3PFHxS
Perfluorohexane sulfonate	L-PFHxS	C6HO3SF13	M3PFHxS
Perfluoroheptane sulfonate	L-PFHpS	C7HO3SF15	M8PFOS
Perfluorooctane sulfonate	L-PFOS	C8HO3SF17	M8PFOS
Perfluorononane sulfonate	L-PFNS	C9HO3SF19	M8PFOS
Perfluorodecane sulfonate	L-PFDS	C10HO3SF21	M8PFOS

S1.2. Soil sampling and properties

Depending on the size, the fields were subdivided into several 10x10 m patches and samples were taken along the diagonals in equal spacing using an Edelman driller. Soil samples from depth horizons of 0 - 30 cm and 30 - 50 cm or 0-50 cm were collected and stored in

polypropylene buckets. The soil was homogenized using a riffle splitter according to the scheme shown in Figure S1.

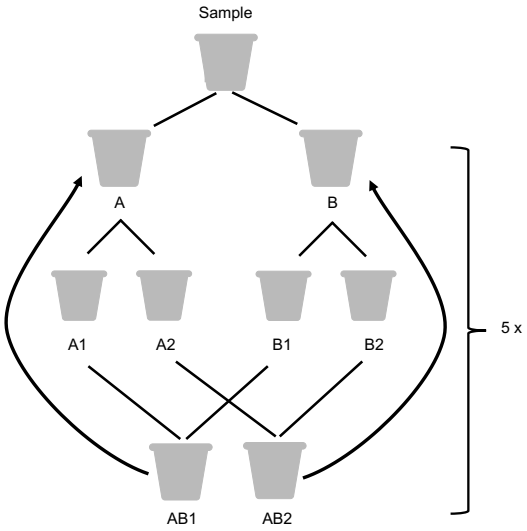

Figure S1. Schematic overview of the mixture procedure. The original sample was divided into two buckets using a riffle splitter.

The soil samples were characterized for their grain size distribution, organic carbon content (OC) and pH (Table S2). The grain size distribution analysis was carried out according to DIN 19683-1 and DIN 19683-2. OC was determined by using 1 g of dried (40 °C) and pulverized soil. Inorganic carbon was removed with 16% HCl. Subsequently the sample was rinsed with deionized water until a pH 6 was reached. The sample was dried (60 °C) before thermal oxidation using a vario EL from Elementar (Langenselbold, Germany) with infrared detection (IR). The pH was measured using 10 g of soil dispensed in 25 ml 0.01 M $CaCl_2$ solution after 2 h and 24 h and the average value was taken.

Table S2. Properties of soil samples.

Soil / Sample	Depth (cm)	pH ($CaCl_2$)	OC (%)	Grain size distribution			Soil typ
				Sand (% 2-0.06 mm)	Silt (% 63-2 µm)	Clay (% <2 µm)	
Soil A	0 - 30	5.5	0.8	63.5	27.8	9.1	Luvisol
	30 - 50	5.6	0.4	64.0	25.2	10.6	
Soil B	0 - 30	6.9	2.3	76.0	19.4	4.7	Luvisol
	30 - 50	6.8	0.8	86	10.2	3.4	
Soil C	0 - 30	6.5	1.2	29.6	54.8	15.9	Luvisol
	30 - 50	6.4	0.6	27.1	50.0	23.0	
Soil D	0 - 30	7.1	6.6	40.0	45.2	14.9	Gley
	30 - 50	7.5	4.2	29.5	47	23.4	
Soil E	0 - 30	6.4	1.7	60.7	30.4	9	Gley
	30 - 50	6.5	0.9	60.3	27.6	12.4	
Soil F	0 - 30	6.7	2.8	48.4	40.5	11.1	Peat
	30 - 50	6.4	1.9	49.6	29.5	20.9	
Soil G	0 - 50	7.2	1.6	34.95	42.5	22.7	Luvisol
Soil H	0 - 50	7.0	3.9	44.4	24.5	30.9	Luvisol

A standard soil (2.4. sandy loam) obtained from the Landwirtschaftliche Untersuchungs- und Forschungsanstalt (Speyer, Germany) was used to check recovery rates from methanolic extraction. In a 15 ml polypropylene tube 1 g of soil was spiked with 40 µl of a 10 µg/l standard in methanol which was allowed to evaporate overnight. Then the soil was extracted two times as described in the main text. Procedural blanks (in triplicates) were performed in parallel to check for PFAS background concentrations. PFBA, PFOA and PFOS were found in the procedural blanks (~0.2 µg/kg) and were subtracted from spiking experiments. Recovery rates are displayed in Table S3.

Table S3. Recovery of PFCAs and PFSAs in soil during methanolic extraction (in triplicates).

Analyte	Recovery ± STD (%)
PFBA	85 ± 20
PFPeA	102 ± 11
PFHxA	106 ± 10
PFHpA	101 ± 8
PFOA	93 ± 12
PFNA	101 ± 9
PFDA	94 ± 13
PFUnA	93 ± 12
PFDoA	90 ± 4
PFBS	98 ± 8
PFPeS	88 ± 9
PFHxS	92 ± 9
PFHpS	94 ± 8
PFOS	104 ± 14
PFNS	90 ± 9
PFDS	95 ± 9

S1.3. Direct total oxidizable precursor (dTOP) assay

For dTOP assay recovery rates 40 µl of standard solution mix (10 µg/l) was spiked to the oxidation solution without additional matrix. Recoveries are displayed in Table S4. Recoveries <70% indicate loss to adsorption to laboratory vessels as described by Göckener et al. (2020).[1]

Table S4. Recovery rates of PFAAs during TOP assay (in triplicates).

Analyte	Recovery ± STD (%)
PFBA	94 ± 15
PFPeA	87 ± 9
PFHxA	84 ± 8
PFHpA	99 ± 4
PFOA	90 ± 8
PFNA	88 ± 7
PFDA	75 ± 13
PFUnA	69 ± 8
PFDoA	64 ± 16
PFBS	105 ± 5
PFPeS	84 ± 6
PFHxS	98 ± 6
PFHpS	82 ± 15
PFOS	106 ± 3
PFNS	94 ± 17
PFDS	63 ± 21

S1.4. Column percolation tests

Quartz sand used in control columns and in upper and lower 2 cm sand layers in column tests was purchased from Gebrüder Dorfner GmbH & Co (Hirschau, Germany). The grain size of the quartz sand was between 0.6 – 1.2 mm.

Column leachate and water samples from batch-tests that did not require enrichment using solid-phase extraction (SPE), were centrifuged at 7500 rcf for 10 minutes using an Eppendorf Centrifuge 5430 R. An aliquot of the supernatant was diluted with MeOH to achieve a final composition of 1/1 H_2O/MeOH (v/v). Internal standard (dissolved in MeOH) was spiked by the HPLC autosampler before injection to account for matrix effects. Aqueous samples undergoing SPE were centrifuged at 3400 rcf for 10 minutes using a Thermo Megafuge 1.OR. Chromabond HR-XAW 30 mg cartridges from Macherey-Nagel, Germany were used after conditioning with 3 ml 0.1 % NH_4OH in methanol, 2 ml methanol and 2 ml H_2O. 10 ml of sample were spiked with 40 µl internal standard and loaded on the cartridge using gravimetric flow. The cartridge was washed with 2 ml of H_2O. Elution was achieved with 2 ml methanol and 4 ml 0.1 % NH_4OH in methanol. The extract was evaporated to dryness at 40 °C under a gentle nitrogen stream and the residue reconstituted in 1 ml of 1/1 H_2O/MeOH (v/v).

Recovery experiments for aqueous samples was done by spiking 40 µl of standard solution (concentration 10 µg/l) to 10 ml H_2O and SPE was conducted as described above. Recovery rates are displayed in Table S5.

Table S5. Recovery rates of PFAAs in H_2O in spiking experiments (in triplicates).

Analyte	**Recovery ± STD (%)**
PFBA	98 ± 7
PFPeA	98 ± 7
PFHxA	93 ± 4
PFHpA	86 ± 1
PFOA	105 ± 8
PFNA	98 ± 3
PFDA	97 ± 1
PFUnA	88 ± 5
PFDoA	76 ± 7
PFBS	100 ± 3
PFPeS	102 ± 9
PFHxS	98 ± 1
PFHpS	109 ± 7
PFOS	102 ± 2
PFNS	87 ± 9
PFDS	83 ± 9

Air/water interfaces loses during sampling

To elucidate the tendency of PFAAs to accumulate at the air/water-interface in sample vessels, recovery experiments were conducted. To test this, 50 ml glass and polypropylene (PP) vessels were filled with an aqueous stock solution of PFAAs at 20 ml and 5 ml. After 4 days the vessels were sampled and analyzed; results are compared in Figure S7.

Production rates from column tests

Production rates from the tailing part of C4-C8 PFCAs in column percolation tests were calculated by Equation S1:

$$P_C = \frac{m_{PFAS}}{t_{LS} * m_{soil}} \quad \text{S1}$$

P_c, m_{PFAS}, t_{LS} and m_{soil} denote the production rate of PFAS in the column (µg kg^{-1} d^{-1}), the mass of PFAS produced between *LS* 4 and 10 (µg), the time between the sampling points at *LS* 4 and 10 (days) and the dry mass of soil in the column (kg).

S1.5. Precursor transformation experiments (batch-tests)

Samples from batch-tests were treated as described in section S1.4.

S.1.6. Instrumental analysis

Samples were analyzed by HPLC-MSMS using either a 1290 HPLC (Agilent Technologies, Waldbronn, Germany) coupled to a 6470 triple quadrupole mass spectrometer (QqQ-MS) (Agilent Technologies, Santa Clara, USA) or a 1260 HPLC (Agilent Technologies, Waldbronn, Germany) coupled to a 6490 QqQ-MS (Agilent Technologies, Santa Clara, USA). A waters Acquity UPLC BEH C_{18} (1.7 µm; 2.1 x 100 mm) column equipped with an Acquity UPLC BEH C_{18} VanGuard Pre-column (1.7 µm; 2.1 x 5 mm) was used on the 1290 HPLC and a Poroshell 120 EC-C_{18} column (2.1 mm × 100 mm) with a particle size of 2.7 µm on the 1260 HPLC to separate the analytes. The majority of the samples were measured using the 1290 HPLC and 6470 QqQ-MS system. Eluent A (95:5 H_2O/MeOH) and eluent B (5:95 H_2O/MeOH), both with 2 mM NH_4Ac, were used for gradient elution (Table S6). The column was heated to 60 °C. The QqQ-MS were equipped with an electrospray ionization (ESI) source operated in negative mode and dynamic multiple reaction monitoring (dMRM). For instrument parameters see Table S7 and S8. An external calibration curve with seven concentration levels between 0.1 and 5

µg/l were used. Concentration levels were prepared from a methanolic PFAS stock solution (10 µg/l) and diluted with Optimal LC/MS grade H_2O to achieve a 1/1 solution of H_2O/MeOH (v/v). Internal standard was spiked to calibration points prior to analysis by the HPLC autosampler. Data evaluation was performed using Agilent MassHunter software (Quantitative Analysis for QQQ – Version 10.1 Build 10.1.733.0). Linear calibration curves generally had R^2 >0.98. Limit of quantification was defined as the lowest calibration point (0.1 µg/l), where the signal to noise-ratio was ≥10 and the quantifier/qualifier ion ratio within ±30% of the highest calibration point.

For aqueous samples from column and batch-tests the LOQ was 0.01 µg/l. Due to stronger matrix effects in soil extractions and dTOP assay samples the LOQ were set to 0.2 µg/kg and 4 µg/kg respectively.

Table S6. HPLC gradient for PFAS analysis. A = 95:5 H_2O/MeOH with 2 mM NH_4Ac and B = 5:95 H_2O/MeOH, both with 2 mM NH_4Ac.

HPLC 1290 – 6470 QqQ				HPLC 1260 – 6490 QqQ			
Time (min)	A (%)	B (%)	Flow (ml/min)	Time (min)	A (%)	B (%)	Flow (ml/min)
0	60	40	0.4	0	85	15	0.3
1	30	70	0.4	8	0	100	0.3
3.5	0	100	0.4	16	0	100	0.3
6	0	100	0.4	16.1	85	15	0.3
6.1	60	40	0.4	23	85	15	0.3
7.5	60	40	0.4				

Table S7. Instrument parameters for the HPLC-QqQ-MS measurements.

Instrument parameters	**6470 QqQ**	**6490 QqQ**
Gas Temp (°C)	230	150
Gas Flow (l/min)	4	16
Nebulizer (psi)	15	45
Sheath Gas Heater (°C)	350	380
Sheath Gas Flow (l/min)	12	12
Capillary voltage (V)	2500	3200

Table S8. Parameters used during dynamic multiple reaction monitoring (dMRM) for the target compounds: precursors and the corresponding product ions with respective collision energies (CE) and fragmentor voltages (FV).

			6470 QqQ		6490 QqQ	
Compound name	**Precursor ion**	**Product ion**	**FV (V)**	**CE (V)**	**FV (V)**	**CE (V)**
PFBA	213	169	60	8	380	5
PFPeA	262.9	219	60	8	380	5
PFPeA	262.9	68.8	-	-	380	45
PFHxA	313	269	70	8	380	5
PFHxA	313	119	70	18	380	25
PFHpA	363	319	72	0	380	5
PFHpA	363	169	72	12	380	15
PFOA	413	369	69	4	380	5
PFOA	413	169	69	12	380	20
PFNA	463	419	66	4	380	5
PFNA	463	169	66	17	380	15
PFDA	513	469	81	4	380	10
PFDA	513	219	100	16	380	15
PFUnA	563	519	73	5	380	5
PFUnA	563	219	100	20	380	15
PFDoA	613	569	79	5	380	10
PFDoA	613	269	100	20	380	15
PFBS	299	80	100	29	380	30
PFBS	299	80	100	45	380	40
PFPeS	349	99	135	40	380	30
PFPeS	349	80	135	40	380	25
PFHxS	399	99	100	45	380	45
PFHxS	399	80	100	49	380	45
PFHpS	449	99	100	44	380	45
PFHpS	449	80	100	52	380	50
PFOS	499	99	100	50	380	50
PFOS	499	80	100	50	380	55
PFNS	549	99	165	40	380	50
PFNS	549	80	165	40	380	50
PFDS	599	99	100	60	380	55
PFDS	599	80	100	80	380	55

HRMS

Screening of soil A 0 – 30 cm and B 0 – 30 cm was performed using a 1290 HPLC coupled to a 6550 quadrupole time-of-flight (QTOF) MS from Agilent Technologies (Santa Clara, USA) using the method described by Bugsel and Zwiener, 2020[2]. For data analysis the MassHunter software from Agilent Technologies (version 10.0 build 10.0.10305.0) was used by extracting the ion chromatogram for the exact mass-to-charge (m/z) ratio of diPAPs and diSAmPAPs with a deviation of ±10 ppm.

Section 2. Results & discussion

2.1. PFAS in soil solids

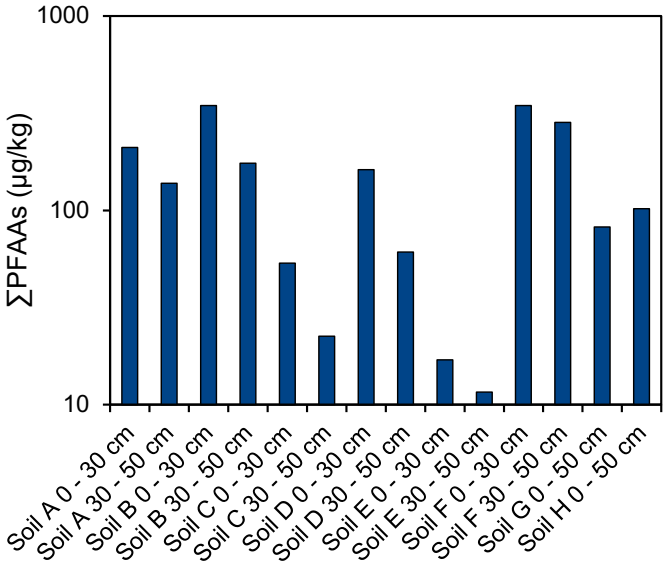

Figure S2. Concentration of the sum of C4-C12 PFCAs and C4-10 PFSAs in soil samples (A – H) from Rastatt/Baden-Baden and Mannheim.

Table S9. Soil concentration (µg/kg) of PFAAs in solids from depth 0 – 30 cm and 0 - 50 cm.

	Soil A	Soil B	Soil C	Soil D	Soil E	Soil F	Soil G	Soil H
Depth (cm)	0 – 30	0 – 30	0 – 30	0 – 30	0 – 30	0 – 30	0 – 50	0 – 50
PFBA	1.5	1.9	1.5	3.7	0.6	0.9	2.7	1.1
PFPeA	3.1	4.2	2.7	8.4	0.9	1.9	5.2	2.8
PFHxA	3.3	4.1	2.1	8.8	0.6	1.5	4.6	4.0
PFHpA	3.0	4.6	1.4	13.1	0.3	1.1	5.7	9.0
PFOA	20	34	5.1	61	1.4	6.9	31	33
PFNA	12	22	2.2	13	1.1	2.8	5.3	18
PFDA	88	195	29	40	7.8	31	15	21
PFUnA	41	26	3.4	5.2	1.3	5	2.6	4.4
PFDoA	39	52	5.8	7.3	2.7	13	5.3	6.2
PFBS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHxS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.4	<LOQ	<LOQ
PFOS	0.6	2.7	0.6	2.2	0.3	282	4.7	3.7
PFNS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFDS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table S10. Soil concentration (µg/kg) of PFAAs in solids from depth 30 – 50 cm.

	Soil A	Soil B	Soil C	Soil D	Soil E	Soil F
Depth (cm)	30 – 50	30 – 50	30 – 50	30 – 50	30 – 50	30 – 50
PFBA	2.1	1.4	0.7	1.7	0.4	1.0
PFPeA	5.0	2.1	1.2	5.6	0.7	2.0
PFHxA	4.1	3.2	1.2	6.1	0.6	1.6
PFHpA	3.3	6.0	0.5	7.8	0.4	1.2
PFOA	14	25	2.1	25	1.5	5.3
PFNA	11	23	1.2	3.5	0.9	2.8
PFDA	66	95	11	8.1	5.1	20
PFUnA	17	5.7	1.9	1.3	0.6	2.1
PFDoA	16	11.2	2.6	1.7	1.1	3.5
PFBS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHxS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.9
PFOS	<LOQ	2.8	0.4	0.6	0.3	243
PFNS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFDS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

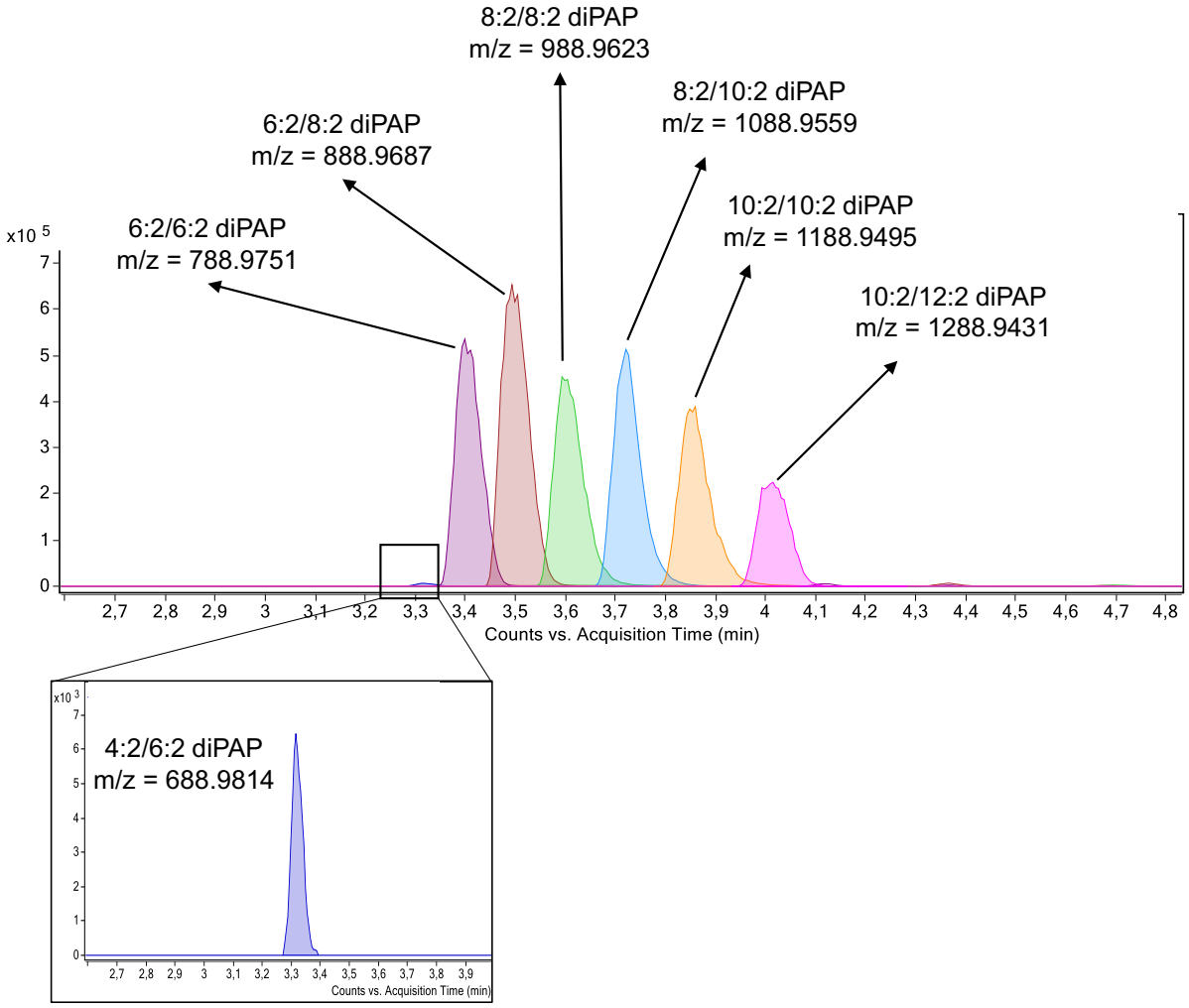

Figure S3. Extracted ion chromatogram (EIC) of diPAPs and their exact mass-to-charge (m/z) ratio in soil A. The m/z from the EIC were extracted with a deviation of ±10 ppm.

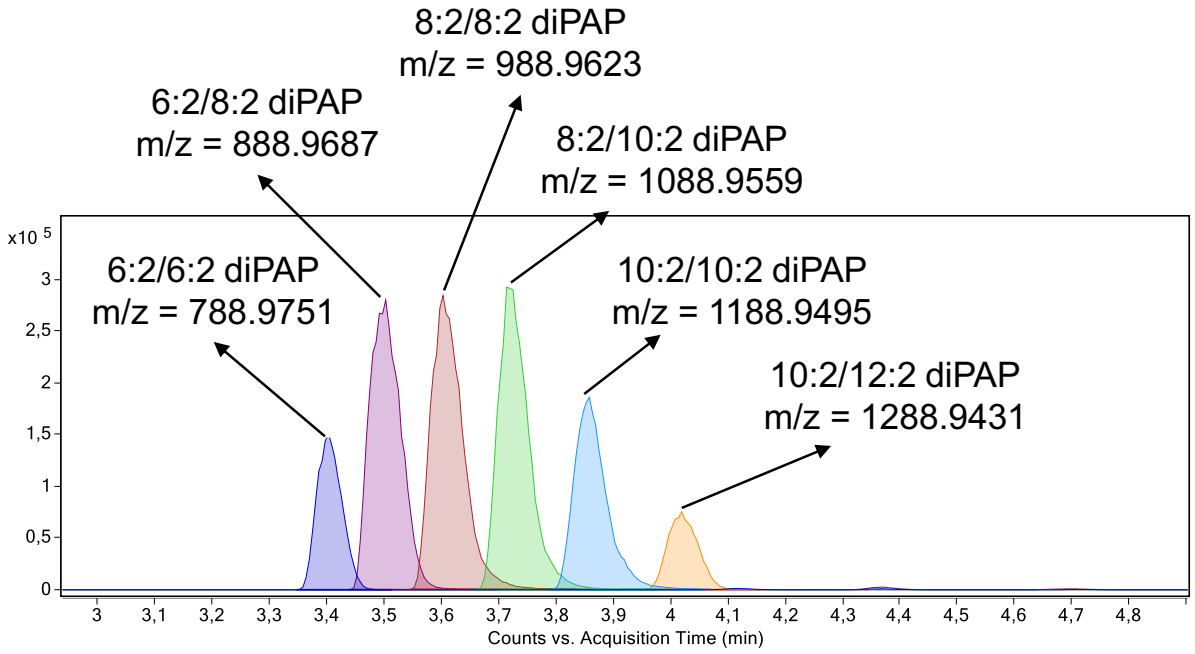

Figure S4. Extracted ion chromatogram (EIC) of diPAPs and their exact mass-to-charge (m/z) ratio in soil B. The m/z from the EIC were extracted with a deviation of ±10 ppm.

2.2. PFAA column leaching

Figure S5 and S6 show column percolation data for all additional compounds for all soil samples. The blank column containing quartz sand only showed no detectable levels of PFAS.

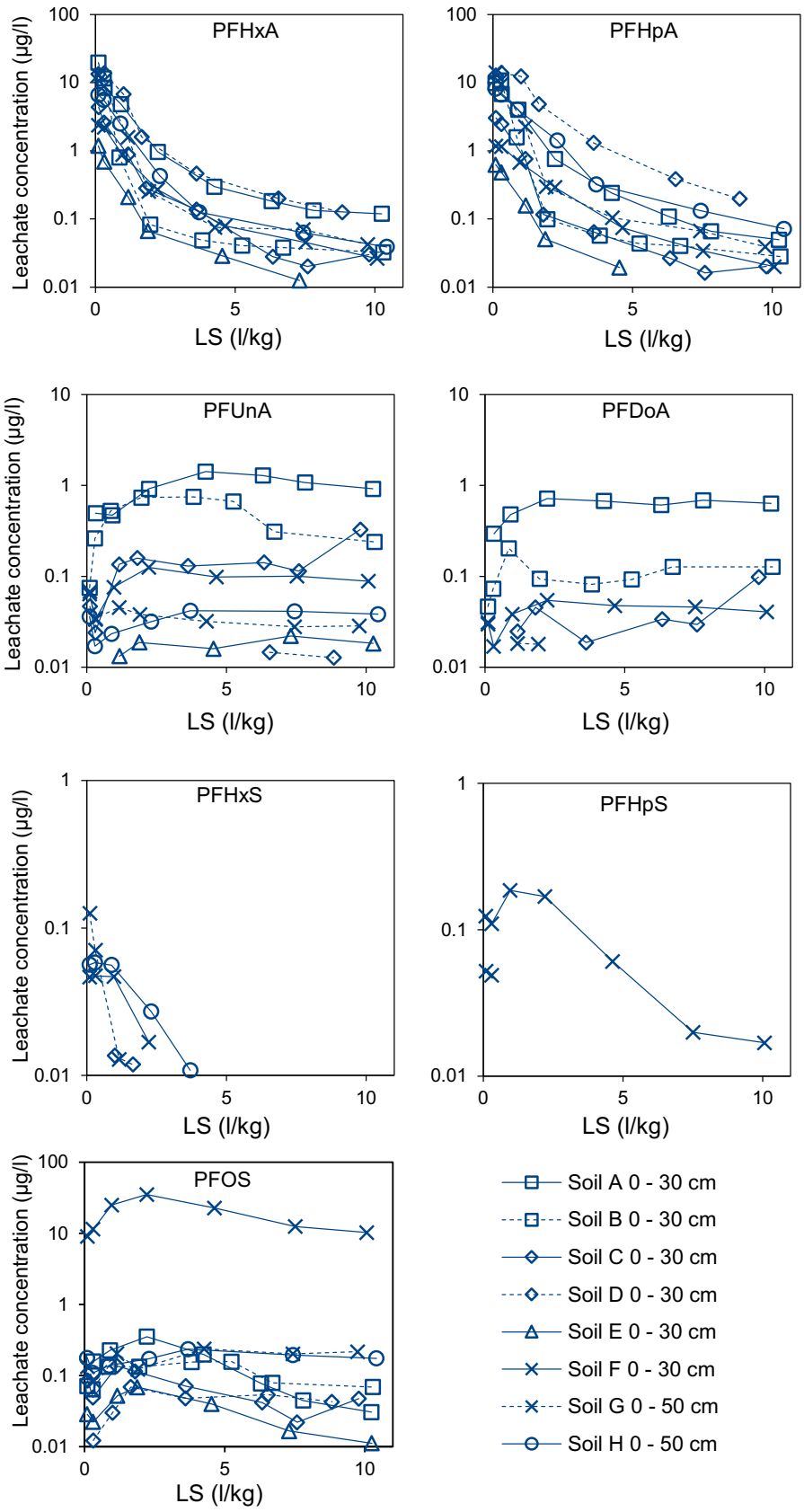

Figure S5. Leaching behavior of PFAAs in saturated column percolation tests with contaminated agricultural soil from 0 - 30 cm and 0-50 cm depth.

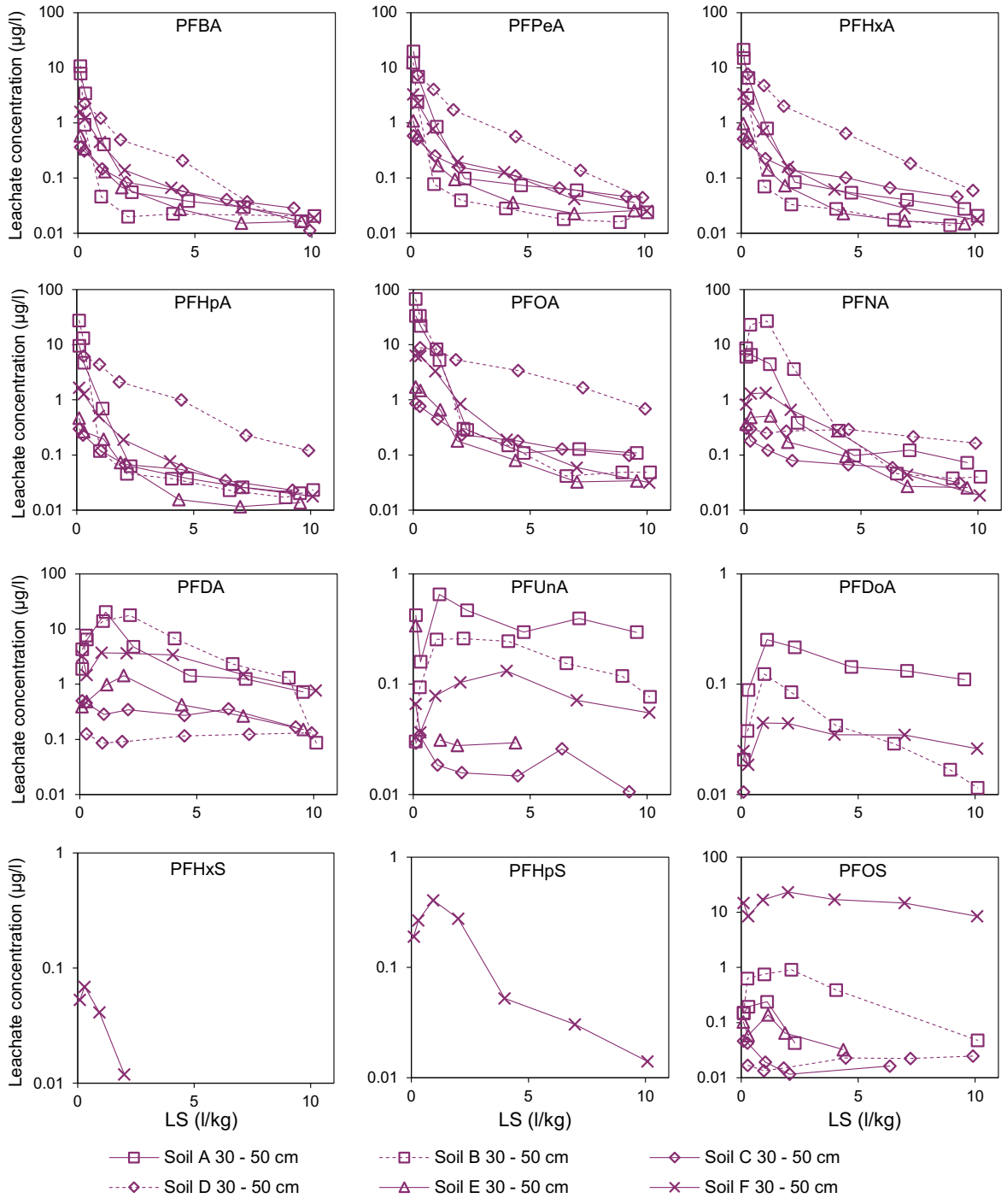

Figure S6. Leaching behavior of PFAAs in saturated column percolation tests with contaminated agricultural soil from 30 - 50 cm depth.

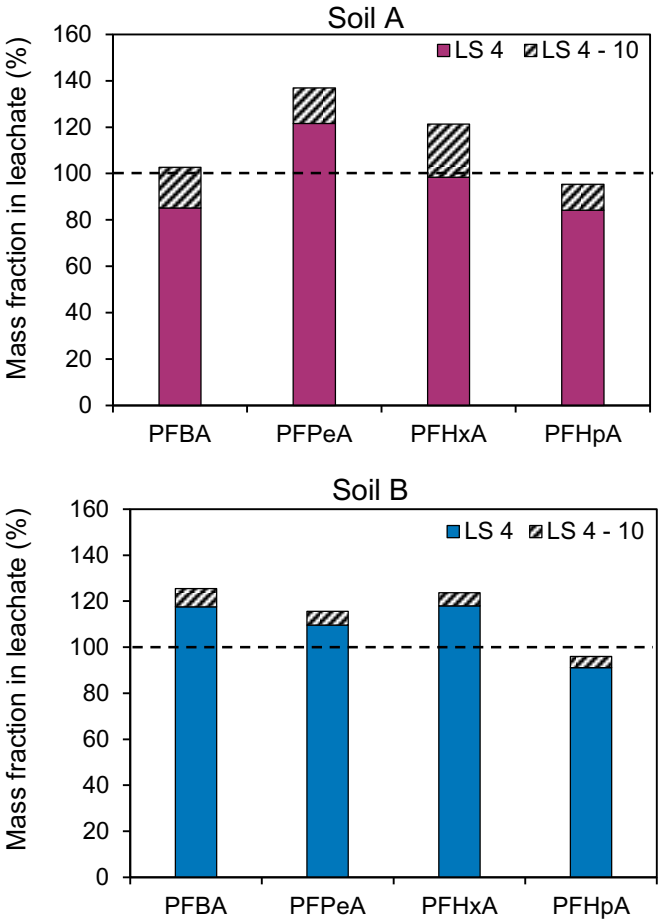

Figure S7. Mass fraction of C4-C7 PFCAs recovered in the column leachate after different *LS* ratios for soil A and B, which were later used for batch-tests.

During saturated column percolation tests, long-chain PFAAs showed an initial increase in concentration, which is likely an artifact due the accumulation of long chain PFAAs at interfaces (water/air, water/vial). This affects water samples with low volumes which were collected at the beginning of the column tests. Recoveries from both set-ups are shown in Figure S7 and confirm increased losses of long-chain PFAAs with lower water volumes; the effect is more pronounced for PP.

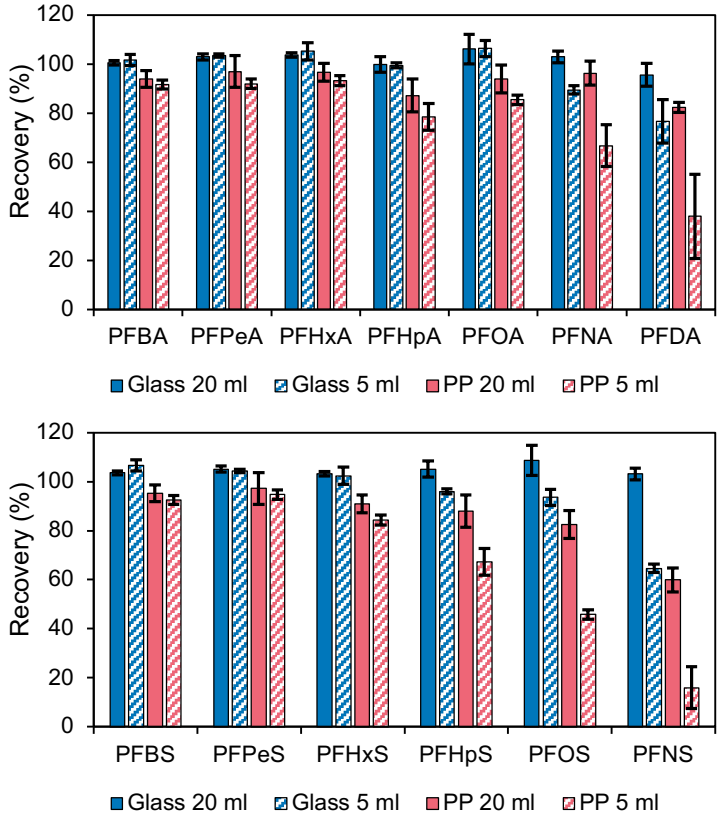

Figure S4. Recoveries of PFAAs at different water volumes samples for glass and polypropylene vials (initial concentrations approx.:1.5 µg/l).

2.3. Batch-test setup: Generation of transformation products

During the 60-day batch-test, no additional formation of long-chain PFAAs (≥C10 and PFOS) was observed. Sorption of the produced PFAS to soil solids may have led to low aqueous PFAS concentrations. The mass produced in the batch-tests will be distributed between solid and aqueous phase as follows:

$$\frac{X_W}{X_S} = \frac{C_W\,V_W}{C_S\,m_d} = \frac{C_W\,V_W}{C_W\,K_d\,m_d} = \frac{LS}{K_d} \qquad \text{(S2)}$$

X_W, X_S, C_W, V_W, C_S, m_d, K_d and LS denote the mass in aqueous and solid phase, aqueous concentration, water volume, concentration in the solids, mass of solids, distribution coefficient and the liquid-to-solid ratio. With a constant LS ratio increasing K_d would lead to a decrease of the mass fraction in aqueous phase which likely further reduces with increasing chain-length.

Table S2. Soil mass and water volumes used in triplicate batch experiments for the two soils.

Soil A	**Natural (live) soil**			**Autoclaved controls**		
	A1	A2	A3	Aa1	Aa2	Aa3
Dry soil mass (g)	520	510	502	466	456	473
Total water vol. (ml)	1237	1216	1208	1108	1133	1150
LS (l/kg)	2.4	2.4	2.4	2.4	2.5	2.4
Soil B	**Natural (live) soil**			**Autoclaved controls**		
	B1	B2	B3	Ba1	Ba2	Ba3
Dry soil mass (g)	518	510	553	532	462	497
Total water vol. (ml)	1250	1240	1364	1291	1295	1219
LS (l/kg)	2.4	2.4	2.5	2.4	2.8	2.5

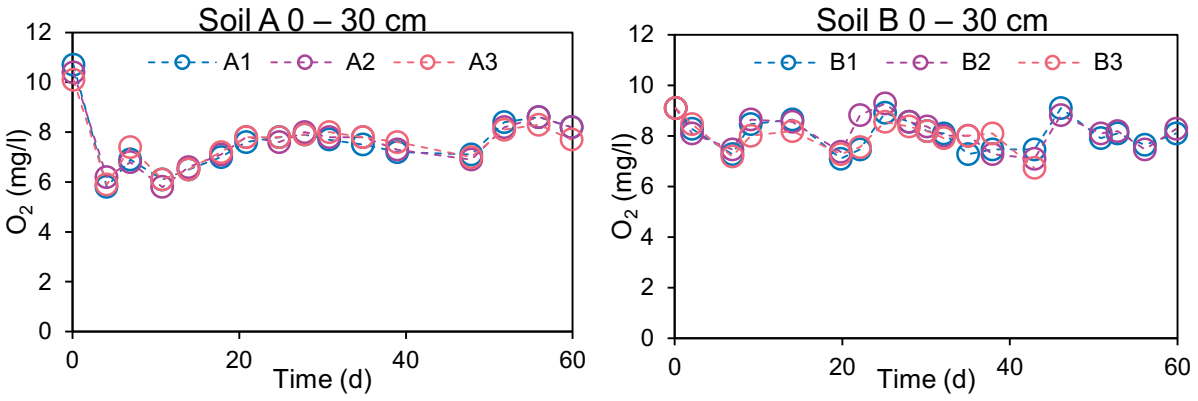

Figure S9. Oxygen concentrations during batch experiments with the natural samples measured by fiber optic sensors. B3 of soil sample B was damaged after 46 days and was continued in a new bottle without oxygen sensor.

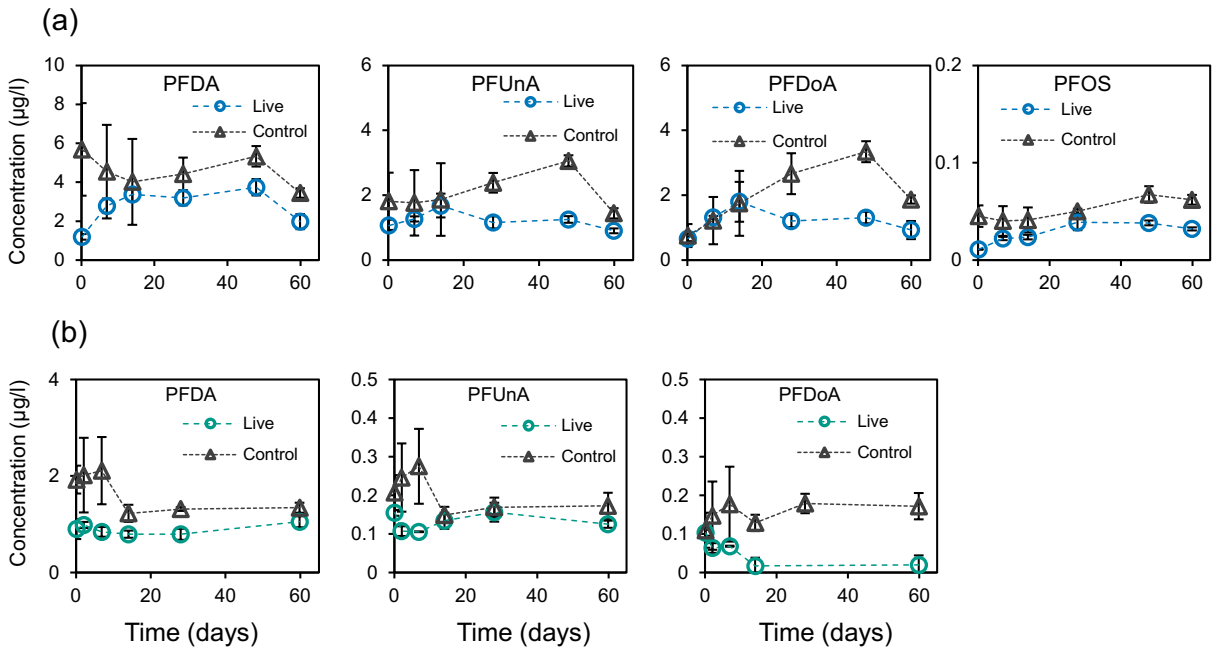

Figure S10. Aqueous concentrations of C10-C12 PFCAs and PFOS during 60 days batch-tests (a) soil A: 0 - 30 cm, (b) soil B: 0 - 30 cm. In set-ups with soil B no PFOS was detected.

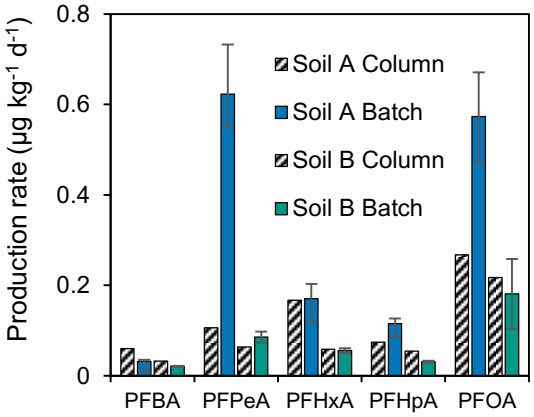

Figure S11. Comparison of production rates derived in 60 days batch experiments and calculated from the tailing part (*LS* > 4) in column tests.

Table S3. Production rates *P* of PFCAs calculated from 60 days batch experiments with two selected soil samples.

	Soil A 0 - 30 cm				Soil B 0 - 30 cm			
		Production rate (µg kg^{-1} d^{-1})				Production rate (µg kg^{-1} d^{-1})		
	R^2	Average	Lower 95%	Upper 95%	R^2	Average	Lower 95%	Upper 95%
PFBA	0.99	0.03	0.03	0.04	1.00	0.02	0.02	0.02
PFPeA	0.98	0.62	0.51	0.73	0.99	0.09	0.07	0.10
PFHxA	0.98	0.17	0.14	0.20	1.00	0.06	0.05	0.06
PFHpA	1.00	0.12	0.10	0.13	1.00	0.03	0.03	0.03
PFOA	0.99	0.57	0.48	0.67	0.91	0.18	0.10	0.26

Table S4. Rate constants (λ) for PFCAs calculated from 60 days batch experiments.

	Soil A 0 - 30 cm				Soil B 0 - 30 cm			
		λ (yr^{-1})				λ (yr^{-1})		
	C_{TOP} (µg kg^{-1})	Average	Lower 95%	Upper 95%	C_{TOP} (µg kg^{-1})	Average	Lower 95%	Upper 95%
PFBA	255	0.05	0.04	0.05	234	0.03	0.03	0.03
PFPeA	752	0.3	0.25	0.36	506	0.06	0.05	0.07
PFHxA	1045	0.06	0.05	0.07	765	0.03	0.02	0.03
PFHpA	1363	0.03	0.03	0.03	1072	0.01	0.01	0.01
PFOA	1262	0.17	0.14	0.19	984	0.07	0.04	0.10

2.4. Time scales for PFAAs production from precursors

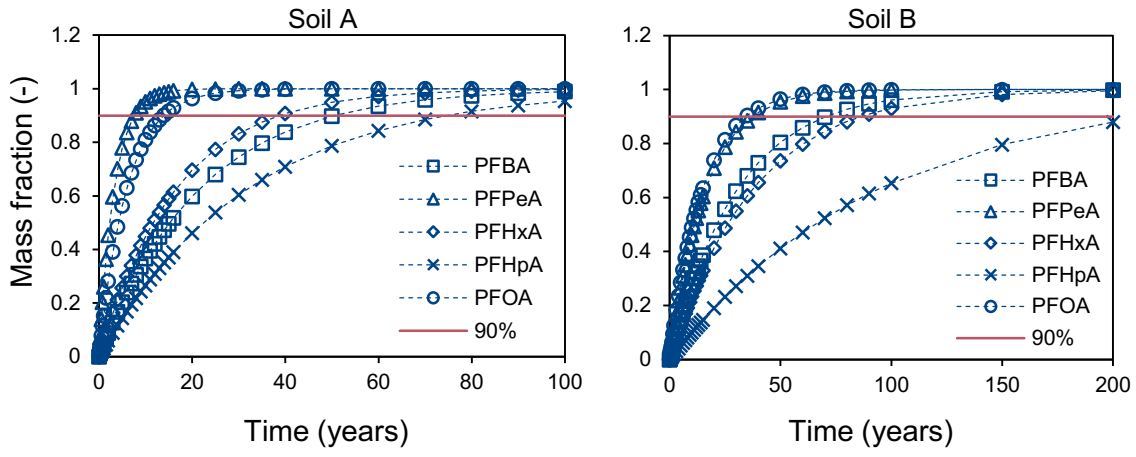

Figure S12. Time scales for depletion of C4-C8 PFCA production from precursors by first order production for soil A and B from the Rastatt/Baden-Baden area.

Reference

1. Göckener, B.; Eichhorn, M.; Lämmer, R.; Kotthoff, M.; Kowalczyk, J.; Numata, J.; Schafft, H.; Lahrssen-Wiederholt, M.; Bücking, M., Transfer of Per- and Polyfluoroalkyl Substances (PFAS) from Feed into the Eggs of Laying Hens. Part 1: Analytical Results Including a Modified Total Oxidizable Precursor Assay. *Journal of Agricultural and Food Chemistry* **2020,** *68*, (45), 12527-12538.

2. Bugsel, B.; Zwiener, C., LC-MS screening of poly- and perfluoroalkyl substances in contaminated soil by Kendrick mass analysis. *Analytical and Bioanalytical Chemistry* **2020,** *412*, (20), 4797-4805.