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Review

## Extending the knowledge about PFAS bioaccumulation factors for agricultural plants – A review

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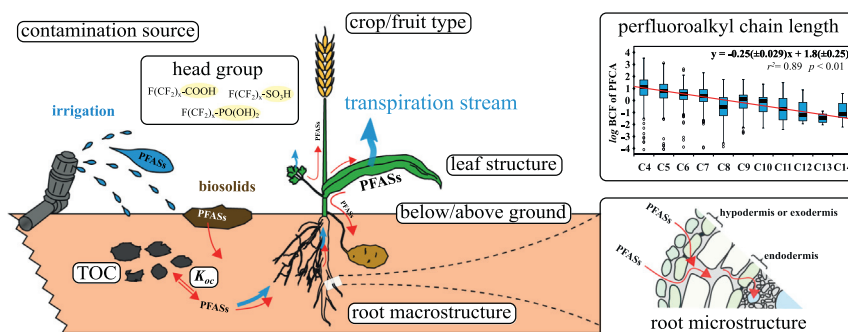
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## HIGHLIGHTS

- Scope & gaps of PFAS BAFs in agricultural plants, easy to grasp in chord diagram
- Suggests PFASs for future uptake studies (e.g., PFPAs, PFSAs  $\leq$  C3, GenX, DONA)
- First review to include plant uptake of ultra-short chain PFAAs ( $\leq$ C3)
- Showing ubiquitous presence of TFAA in plants, independent from other PFAAs
- Suggests to try aqueous soil leachates for future BAF calculations

## GRAPHICAL ABSTRACT



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## ABSTRACT

A main source of perfluoroalkyl and polyfluoroalkyl substances (PFASs) residues in agricultural plants is their uptake from contaminated soil. Bioaccumulation factors (BAFs) can be an important tool to derive recommendations for cultivation or handling of crops prior consumption.

This review compiles >4500 soil-to-plant BAFs for 45 PFASs from 24 studies involving 27 genera of agricultural crops. Grasses (Poaceae) provided most BAFs with the highest number of values for perfluorooctanoic acid and perfluorooctane sulfonic acid. Influencing factors on PFAS transfer like compound-specific properties (hydrophobicity, chain length, functional group, etc.), plant species, compartments, and other boundary conditions are critically discussed.

Throughout the literature, BAFs were higher for vegetative plant compartments than for reproductive and storage organs. Decreasing BAFs per additional perfluorinated carbon were clearly apparent for aboveground parts (up to 1.16 in grains) but not always for roots (partly down to zero). Combining all BAFs per single perfluoroalkyl carboxylic acid (C4-C14) and sulfonic acid (C4-C10), median log BAFs decreased by  $-0.25(\pm 0.029)$  and  $-0.24(\pm 0.013)$  per fluorinated carbon, respectively. For the first time, the plant uptake of ultra-short-chain ( $\leq$  C3) perfluoroalkyl acids (PFAAs) was reviewed and showed a ubiquitous occurrence of trifluoroacetic acid in plants independent from the presence of other PFAAs.

Based on identified knowledge gaps, it is suggested to focus on the uptake of precursors to PFAAs, PFAAs  $\leq$  C3, and additional emerging PFASs such as GenX or fluorinated ethers in future research. Studies

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regarding the uptake of PFASs by sugar cane, which accounts for about one fifth of the global crop production, are completely lacking and are also recommended. Furthermore, aqueous soil leachates should be tested as an alternative to the solvent extraction of soils as a base for BAF calculations.

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## 1. Introduction

Many industrial and commercial products contain perfluoroalkyl and polyfluoroalkyl substances (PFASs) (Buck et al., 2011) which encompass > 4700 chemical compounds (OECD, 2018). All of them are either persistent or can degrade into persistent transformation products. Consequently, PFASs have been found in several environmental compartments including humans (Brusseau et al., 2020; Eun et al., 2020; Ghisi et al., 2019; Xiao, 2017). The main exposure pathways to humans regarding PFASs are food, air, and dust. Solid foodstuffs can be considered as the dietary main uptake route (Sunderland et al., 2019). Recently, a low tolerable weekly intake (TWI) of 4.4 ng/kg bw per week for the sum of perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), and perfluorooctane sulfonic acid (PFOS) was established by the European Food Safety Authority (EFSA, 2020). Field crops and food of animal origin (e.g., meat, milk, and eggs) are the major constituents of the human diet. In a large part, the animals' feed determines the PFAS contamination of animal food products (Kowalczyk et al., 2012; Kowalczyk et al., 2013). Therefore, knowledge about PFAS levels in agricultural plants as well as understanding the uptake mechanisms is essential to fully understand their environmental fate.

A main source of PFAS residues in agriculturally grown products is the transfer of PFASs from contaminated soil into plants (Lechner and Knapp, 2011; Zhao et al., 2014). Regarding PFAS contamination of soils, different pathways are known, e.g., through amendment with sewage sludge or paper-fiber biosolids, use of PFAS-containing firefighting foams, and atmospheric deposition. However, the many factors influencing the subsequent transfer of PFASs from soil to agricultural plants are still not fully understood.

To indicate partitioning of PFASs from the environment to biota, bioconcentration factors (BCFs) or bioaccumulation factors (BAFs) can be used. In contrast to animal studies, for the uptake into plants, the terms BCF and BAF are used interchangeably in the literature (ITRC, 2020). Both are defined as the concentration in the plant divided by the concentration in the surrounding environment, i.e., soil or water. To prevent confusion, throughout the present article, the term BAF (mass/mass)

is used consistently as defined in Eq. (S1). The movement of substances within plants can be described with the translocation factor (TF), e.g., from roots to shoots ( $TF_{\text{shoot/root}}$ ). Furthermore, BAFs and TFs which consider the impact of different plant species, compartments and boundary conditions on the transfer of PFASs are an important tool to derive recommendations for cultivation of certain plants on PFAS contaminated fields or for handling crops, e.g., washing or peeling before consumption.

The present review compiles BAFs for agricultural plants and discusses the underlying transfer mechanisms and the role of boundary conditions for the PFAS transfer from soil into plants and their translocation within the plants. In addition to previous reviews, the present review also encompasses the soil-plant-transfer of the ultra-short-chain perfluoroalkyl acids (PFAAs) trifluoroacetic acid (TFAA) and perfluoropropionic acid (PFPrA), which haven't been considered in uptake studies with agricultural plants until recently. Furthermore, the role of precursors to PFAAs in the determination of BAFs from field studies is critically reviewed.

## 2. Scope

The scientific literature on PFAS soil-plant transfer was comprehensively reviewed. Despite the relatively small number of publications (24 articles), >4500 BAFs could be extracted or calculated from the given data. Thereof, about 2600 associated pairs of soil and plant concentrations allowed quantitative statements (concentrations of both values above their limit of quantification, LOQ).

In addition to studies on the transfer of PFASs from soil to plants, studies in hydroponic systems were evaluated. Because the two are not directly comparable, BAFs derived from hydroponic solutions were not compiled along with those from soil studies. This is because, on the one hand, BAFs from hydroponic cultures are at a different magnitude than BAFs derived from soil cultures due to developmental differences in plant organs and the missing interactions of PFASs and soil (Gredelj et al., 2020a). Furthermore, many studies in hydroponic solution were kinetic studies in which plants were only exposed to contaminated media for very short time periods (hours to a few days)

(e.g., Wen et al., 2013; Zhao et al., 2013; Krippner et al., 2014; Zhang et al., 2019; Lin et al., 2020). As such, these studies covered only a fraction of the plants' growth phase as opposed to typical uptake studies in soil, which usually investigate PFAS uptake within the total growth phase until harvest. Nevertheless, hydroponic studies were used to provide context and information about PFAS transport, partitioning, and degradation in plants throughout the review (e.g., pH-dependent transfer). The chord diagram in Fig. 1 summarizes the investigated scope in soil-to-plant transfer studies from which BAFs could be derived. Its aim is to display which areas are already well exploited and to highlight

research gaps. Note that Fig. 1 does not take into account BAFs from hydroponic studies and BAFs for which no traceable plant/soil value pairs were given. For example, Li et al. (2019) are providing additional BAFs for grapes, watermelon, honeydew melon, and pear, as well as values summarized under "leafy vegetables" and "melons and nightshade plants". However, these do not have comprehensible plant/soil pairs. Moreover, Eun et al. (2020) are providing PFAS concentrations in soils and plants, but no traceable value pairs to derive BAFs.

The entities on the circumference represent the columns (plant genera) and rows (PFASs) of a table containing the number of soil-plant

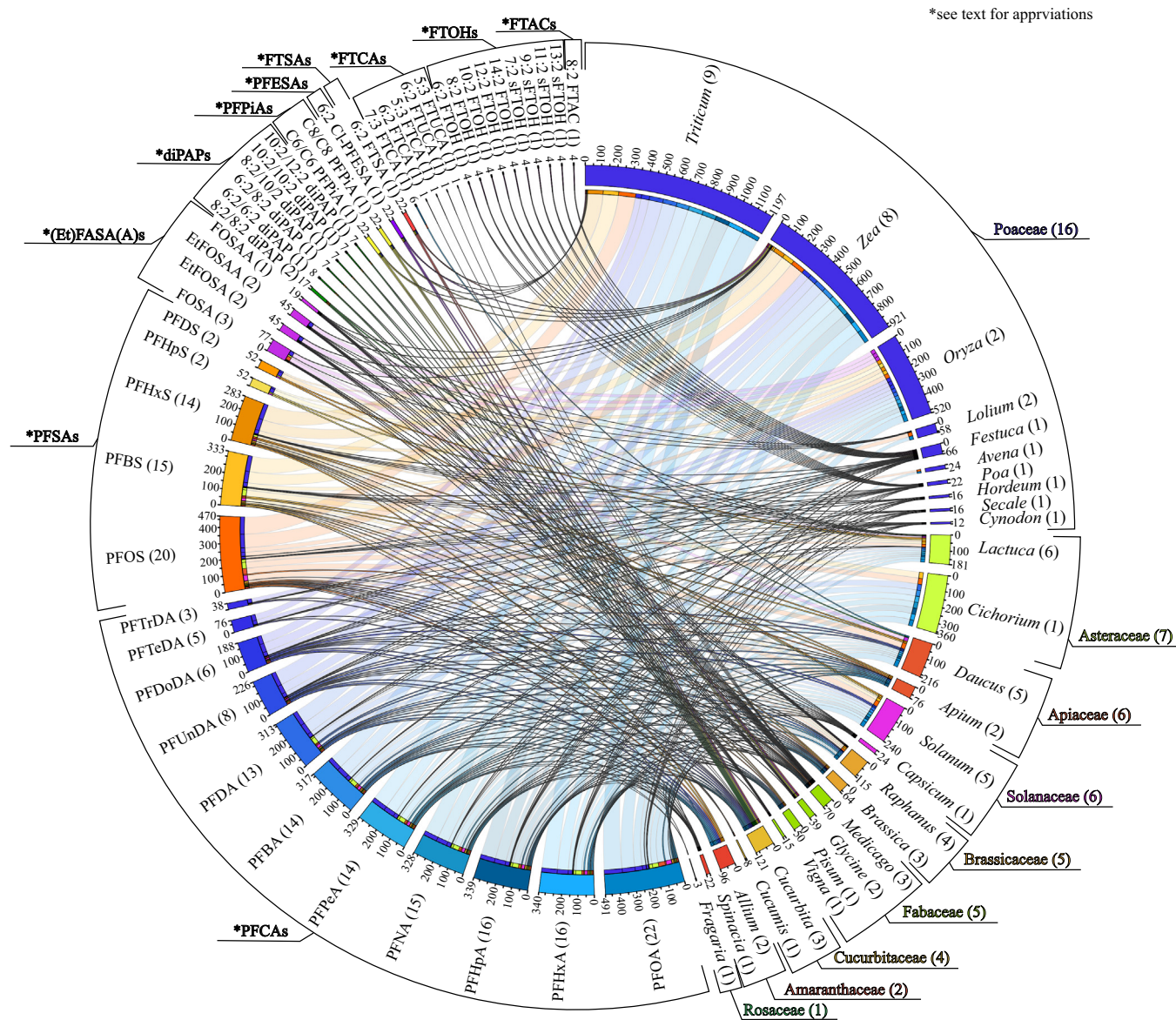


Fig. 1. Scope of reviewed or derivable soil-plant BAFs for PFASs from crops within previous international studies (as by April 2020). The thickness of ribbons indicates how many BAFs are reported for each pairing. Smaller numbers have been highlighted to indicate research gaps.

BAFs extracted from the literature for each pairing. The number of BAFs for each pair is displayed by a ribbon whose thickness is proportional to its relative value compared to the total number of BAFs. Because of this, the sum of all ribbons connected to an entity make up the sum of all BAFs found for that entity. The smallest quartile of values has been highlighted to better recognize research gaps. The fraction of each entity on the circumference is also proportionally sized to its relative contribution to the total number of BAFs. In this way, it is easy to see that the most BAFs (1197) existed for wheat (*Triticum* spp.) and the biggest proportion thereof (118) was coming from PFOA which in turn was the compound for which the most BAFs (491) have been found. To quickly grasp which areas have been studied the most, the entities are ordered in their number of studies (brackets after names) starting with the biggest number and continuing clockwise with the next smaller one. This is mostly also reflecting the order of the number of BAFs per entity and has firstly been done on the level of summarizing groups (i.e., plant families, compound classes) and then for each entity within a group. More information on the chord diagram is provided in the SI (Text S1).

Thus, the figure shows that, among agricultural plants, most soil-plant BAFs for PFASs could be derived for grasses (Poaceae) and the least for the rose family (Rosaceae). Regarding PFASs, most data were found for perfluoroalkyl carboxylic acids (PFCAs) lead by PFOA (22 Studies, 491 BAFs) followed by perfluoroalkane sulfonic acids (PFSA) lead by PFOS (20 Studies, 470 BAFs). Only few studies were available for precursors to PFAAs including perfluoroalkane sulfonamides (FASAs), such as *N*-ethyl perfluorooctane sulfonamide (EtFOSA) and perfluorooctane sulfonamide (FOSA), *N*-alkyl perfluoroalkane sulfonamidoacetic acids (MeFASAs, EtFASAs), e.g., *N*-ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), polyfluoroalkyl phosphoric acid esters (PAPs), perfluoroalkyl phosphonic acids (PFPIAs), perfluoroether sulfonic acids (PFESAs), and fluorotelomer compounds including fluorotelomer sulfonic acids (FTSAs), fluorotelomer carboxylic acids (FTCAs), fluorotelomer alcohols (FTOHs), and fluorotelomer acrylates (FTACs).

The high number of studies and BAFs for grasses reflects their important role in the human diet both for direct consumption and as fodder for livestock. In 2018, the production of wheat (*Triticum* spp.), maize (*Zea mays*), and rice (*Oryza* spp.) alone accounted for 3.8 billion tons, corresponding to over 40% of the global crop production (FAO, 2020). The individual global production volumes of these three crops were only surpassed by the one of sugar cane, which accounted for 21% of the global crop production and 1.9 billion tons in the same year. Hence studying BAFs for PFASs in sugar cane should be highly desired. However, to the authors' best knowledge, studies on this subject are still missing. Another striking feature is the distribution of studies on precursors to PFAAs within the Poaceae family. For example, fluorotelomer compounds have not been studied in the three most important of the displayed crops, wheat, maize, and rice. FTCAs and FTSAs have not been studied in grasses cultivated in soil at all. Only soil-plant BAFs for FTOHs in tall fescue (*Festuca arundinacea*) and Kentucky bluegrass (*Poa pratensis*) could be derived. Both are fodder plants and no food crops. The lack of knowledge about BAFs for fluorotelomer compounds in food crops is a gap that should be tackled in future research. Generally, several important food crops are missing investigations on their behavior for PFASs uptake when precursors are involved, i.e., rice (*Oryza* spp.), chicory (*Cichorium intybus*), tomato (*Solanum lycopersicum*), potato (*Solanum tuberosum*), pepper (*Capsicum annuum* L.), and the amaranth family (Amaranthaceae) such as garlic chives (*Allium tuberosum*), spring onions (*Allium fistulosum*), and spinach (*Spinacia oleracea*). On the other hand, there has been a relatively high proportion of BAFs for precursors to PFAAs for legumes (Fabaceae) and for the gourd family (Cucurbitaceae).

The scope of Fig. 1 also reveals that soil-plant BAFs in agricultural plants have only been investigated for 45 PFASs, thus covering a very small fraction of the >4700 chemical compounds on the OECD list (OECD, 2018). In addition to very few studies in the realm of precursors to PFAAs,

further categories of PFASs haven't been regarded at all so far. These include for example per- and polyfluorinated ether carboxylic acids such as GenX or perfluoro-4,8-dioxa-3-nonanoic acid (DONA), perfluoroalkane sulfonamidoethanols (FASEs), perfluorooctane sulfonamidoethanol-based phosphate esters (SAmPAPs), and perfluoroalkyl phosphonic acids (PFPA). PFPA are stable end products of PFPIAs which let assume a certain accumulation thereof in the environment (Wang et al., 2016). So far, they only have been regarded in a plant uptake study with hydroponically grown wheat (Zhou et al., 2019). In addition, investigations on the transfer of ultra-short-chain PFAAs ( $\leq C3$ ) from soil to agricultural plants are completely lacking. Indeed, also for TFAA and PFPrA exist first BAFs in hydroponic cultures (Zhang et al., 2019; Zhao et al., 2019). However, despite their presence in the environment (Björnsdotter et al., 2019; Schulze et al., 2019), information on uptake of ultra-short-chain PFASs such as trifluoromethane sulfonic acid (TFMS), perfluoroethane sulfonic acid (PFES) and perfluoropropane sulfonic acid (PFPrS) neither exist for agricultural plants cultivated in soil nor hydroponic media.

### 3. General aspects of PFAS uptake into plants

According to Buck et al. (2011), PFASs comprise aliphatic compounds containing at least one perfluoroalkyl moiety  $C_nF_{2n+1}$  which acts water- and oil-repellent. In addition, many PFASs contain polar non-fluorinated functional groups with hydrophilic properties. Moreover, the head groups of the persistent PFAA end-products (Buck et al., 2011; Lee and Mabury, 2014, 2017) are negatively charged in the environment due to low  $pK_a$ -values (i.e., carboxylic acids, sulfonic acids, phosphonic acids). Hence many PFASs, especially longer-chained PFAAs, possess amphiphilic properties (Ghisi et al., 2019).

Regarding environmental exposure, their low vapor pressure due to their anionic nature makes direct distribution of PFAAs via the gas phase unlikely (Lechner and Knapp, 2011). Though long range atmospheric transport of volatile precursors such as FTOHs and FASAs as well as distribution via aerosols are possible (Buck et al., 2011; Lee and Mabury, 2014; Martin et al., 2006; Schenker et al., 2008; Young and Mabury, 2010). These distribution pathways are likely the reason for a global background level of certain PFASs throughout environmental compartments (Ghisi et al., 2019; Lee and Mabury, 2014) and contamination at trace level even at sites without direct PFAS emission nearby (Eun et al., 2020).

Nearby point-sources such as a fluorochemical industrial park can increase the possibility of PFAS uptake into plants via air or deposition of particles on above-ground parts (Barton et al., 2006; Liu et al., 2017; Liu et al., 2019; Shan et al., 2014). However, absorption by roots from the soil or pore water is presumably the major uptake pathway in most cases for the majority of PFASs (Lechner and Knapp, 2011; Zhao et al., 2014).

Basically, for actual uptake into plant cells, dissolved compounds need to overcome cell membranes (Briskin, 1994). Overcoming the lipid bilayer by direct diffusion is easier for small uncharged and apolar substances (Briskin, 1994; Davson and Danielli, 1944; Raven et al., 2006). For ions and molecules with polar groups, membranes represent an important natural barrier. Transmembrane movement of these substances necessarily requires proteins to act as transport systems (Briskin, 1994). For phospholipids as representatives of amphiphilic substances, Kornberg and McConnell (1971) demonstrated a direct transversal transport through membranes via a "flip-flop" mechanism. It involves a reorientation of the polar head group from the outer to the inner lipid-water interface. This transport process was also assumed by Glatz et al. (2010) for long-chain fatty acids in animal cells. However, next to passive diffusion across the membrane by phospholipid vesicles, the study also considered carrier-mediated transport of the compounds. Wen et al. (2013) suggested a carrier-mediated process for the uptake of PFOA and PFOS in maize as well. This assumption fits well to a statement by Hankins et al. (2015) according to which transmembrane

transport of amphiphilic compounds mainly happens actively (flippases, floppases) or passively (scrambling) via protein carriers. According to Zhang et al. (2019), an energy-dependent active transport via protein carriers can be considered as the main mechanism for PFAA uptake in wheat. However the uptake of TFAA and PFPrA was inhibited by certain anion channel blockers and aquaporin inhibitors, respectively, indicating that they are involved in the uptake of ultra-short-chain PFAAs.

For neutral hydrophobic compounds, transport via vascular bundles is very unlikely due to their low water solubility (Fismes et al., 2002; Murano et al., 2010). According to Jing et al. (2009), the strong electron withdrawing effect of perfluoroalkyl groups to an adjacent oxoanion group results in a very high lipophilicity of perfluoroalkyl carboxylates and perfluoroalkyl sulfonates. Felizeter et al. (2012) pointed out that this could lead to a similar plant uptake behavior to neutral compounds. However, at 25 °C, PFCAs with alkyl chains <C7 seem to be miscible with water in any ratio, and even PFOA and PFDA with pronounced surfactant properties are, in their anionic form, water-soluble to a certain but very low extent (Kauck and Diesslin, 1951). Therefore, they can be transported in the aqueous phase of plant fascicles (Lechner and Knapp, 2011). In fact, their water solubility is probably the decisive factor making root uptake the main entry path for PFASs in plants.

#### 4. Hydrophobicity and effect of perfluoroalkyl chain length on BAFs

##### 4.1. The reference system

When determining BAFs for PFAS transfer, two issues are of major importance: a) have the plants been cultivated in soil or in a hydroponic medium; b) if plants have been cultivated in soil, are BAFs based on the concentration in the soil or in the pore water? Comparing hydroponic cultures to soil cultures, the interaction of PFASs soil particles leads to a decreasing availability to plants. In order to become available to plants from soil, PFASs need to dissolve in the pore water. Their water solubility and sorption tendency to soil particles determine their distribution between pore water and soil, and subsequently their mobility in the soil matrix and their availability at the plant roots (Zhao et al., 2014). Plant transpiration creates a concentration gradient causing an increased transport of more hydrophilic compounds in the interstitial water to plant roots compared to more hydrophobic compounds that undergo increased retardation in the soil matrix (Gellrich et al., 2012; Higgins and Luthy, 2006; Krippner et al., 2014). In hydroponic solution, no selective retardation takes place before reaching the plant roots. In addition, plants develop finer root structures in soil than in hydroponic solution which also influences the uptake. BAFs from hydroponic cultures are thus not directly comparable with BAFs from soil or pore water (Gredelj et al., 2020a). Most studies with soil cultures derived BAFs from the PFAS soil concentration. However, there are two studies that provided BAFs based on the pore-water concentration (Blaine et al., 2014a; Yoo et al., 2011). As PFAS pore-water concentrations cannot be determined directly, they have to be estimated from the PFAS soil concentration using the organic carbon-water partition coefficient  $K_{oc}$  (Blaine et al., 2014a) or the octanol/water partition coefficient  $K_{ow}$  (Yoo et al., 2011) instead as a proxy. Due to their surfactant nature, the  $K_{ow}$  of PFASs cannot be determined experimentally but needs to be predicted by models. Therefore, the  $K_{ow}$  is considered a quite uncertain parameter to predict pore water PFAS concentrations. The  $K_{oc}$ , on the other hand, can be determined experimentally using the soil/water distribution coefficient  $K_d$  and the soil organic carbon content  $f_{oc}$ .

However, it may seem questionable, if soil extraction by a certain organic solvent, such as methanol (e.g., according to DIN 38414-14, 2011), is appropriate for determining PFAS soil concentrations for the calculation of BAFs at all. Aqueous leachates might be a more realistic approach to predict their bioavailability to plants, even though the liquid-solid ratio (L/S) is larger in typical leaching procedures (e.g., L/S = 2 L/kg in ISO 21268-1, 2019) compared to the pore water volume. An additional

advantage of aqueous leachates are generally smaller LOQs for PFASs due to much higher sample amounts in the soil extraction step (typically several hundred grams) compared to organic solvent extraction (typically <1 g). To the authors' best knowledge, there haven't been any studies experimenting on or discussing that matter. Yet a closer inspection thereof could be valuable as this would allow to determine BAFs for lower PFAS soil concentrations. In addition, the aging of PFASs in the field might lead to bound residues of PFASs in soil, similar to the well-known effect of pesticide residues (Gevao et al., 2000). Hence, a higher bioavailability of PFASs can be assumed in greenhouse studies, when substances are spiked shortly before the start of the experiments.

##### 4.2. Chain length dependency

Despite the uncertainties mentioned above, in some studies, model-predicted  $\log K_{ow}$ -values were used and correlated well ( $p > 0.05$  where indicated) with BAFs for PFAAs (Lan et al., 2018; Navarro et al., 2017; Zhou et al., 2020). With increasing carbon chain length, the  $\log K_{ow}$  increased and the BAFs decreased. Other studies showed good correlations of  $\log K_d$  and  $\log K_{oc}$  with the PFAS transfer in the soil-plant microcosm with decreasing BAFs towards higher  $K_d$  and  $K_{oc}$  (Gredelj et al., 2020b; McLachlan et al., 2019; Zhao et al., 2014). In summary, most results suggest that BAFs of PFASs depend on the hydrophobicity of the compound.

##### 4.2.1. Root-BAFs

When BAFs were based on an aqueous solution (hydroponics, pore water), root-BAFs (C4–C11) either increased with increasing PFAA chain length (Felizeter et al., 2014; Zhao et al., 2018a) or showed a u-shaped dependency with minima for C6 or C7 PFASs (Blaine et al., 2014b; Felizeter et al., 2012; Krippner et al., 2014). The u-shape was most explicitly seen in a study with wheat which also included TFAA (C2) and PFPrA (C3) (Zhang et al., 2019). The root-BAFs of these two PFCAs were notably higher (one or two orders of magnitude) than for all other investigated PFCAs (C4, C6, C8). The smallest root-BAF was found for PFHxA and the one of PFOA was higher than the one of PFBA. This u-shape was explained by the sorption tendency of the single compounds to organic matter, including plant tissues (Blaine et al., 2014b; Felizeter et al., 2014). Generally, longer alkyl chains lead to increased hydrophobic interactions, but also short-chained PFAAs such as perfluorobutanoic acid (PFBA) have been reported to show a strong sorption tendency to organic matter (Gellrich et al., 2012; Guelfo and Higgins, 2013). To explain the observed high sorption tendency of PFBA, which was comparable to PFOA in batch sorption experiments including PFCAs (C4–C11) and different soils, Guelfo and Higgins (2013) assumed either a different sorption mechanism relatively more important for short-chained PFCAs (C4 and C5), such as ion exchange, or a subset of sorption sites that only smaller molecules could reach due to steric effects. The authors also observed a u-shaped curve when plotting the chain length against  $\log K_d$ . In the plant uptake studies, the u-shape was additionally explained by an increasing membrane permeability for short-chained PFASs (Blaine et al., 2014b; Felizeter et al., 2012). Felizeter et al. (2012) assumed that only the short-chained PFAAs were actually absorbed by the plant roots while for the longer-chained ones, adsorption to the root surface was the dominant sorption mechanism.

In contrast to the behavior in hydroponic cultures and pore water, root-BAFs based on soil concentrations were showing a very low or no chain length dependency (Blaine et al., 2014b; Navarro et al., 2017; Wen et al., 2014) or they decreased with increasing chain length (Bizkarguenaga et al., 2016b; Blaine et al., 2014b; Gredelj et al., 2020b; Zhao et al., 2014). In soil, the short-chained PFASs are more mobile as they sorb less to soil particles and dissolve better in the pore water than long-chained PFASs. Hence the selective transport along the transpiration stream gradient in the soil to the roots may result in increased

availability of short-chained PFASs in the rhizosphere (Lan et al., 2018). Paired with the selective passage through the root epidermis (absorption into the root), this could explain the decreasing tendency of root-BAFs with increasing PFAA chain length for plants cultivated in soil. Different observations, i.e., the lack of a significant decrease with increasing chain length as observed in some studies, could have two reasons: a) different root structures of various plants result in different interactions with PFASs (Blaine et al., 2014a); b) the above mentioned strong external adsorption of long-chained PFASs could not be distinguished from the stronger absorption of shorter-chained PFASs. Gredelj et al. (2020b) assumed that a less effective or insufficient cleaning procedure not being able to remove adsorbed proportions of longer-chained PFASs from roots could also explain the absent chain length dependency in some previous uptake studies with soil cultures. Based on the cited literature, it is not possible to decide which of the two factors (a or b) is more important.

#### 4.2.2. Shoot-BAFs

Regardless of the behavior in the roots, all studies found decreasing BAFs with increasing chain length for other vegetative compartments and reproductive organs both with cultures in hydroponic solution (e.g., Felizeter et al., 2012, 2014; García-Valcárcel et al., 2014; Krippner et al., 2014; Zhang et al., 2019; Zhao et al., 2018a) and in soil (e.g., Navarro et al., 2017; Wen et al., 2014; Zhao et al., 2014). This further supports the hypothesis that longer-chained PFAAs undergo a lower absorption into vascular bundles due to hampered membrane passage with increasing chain length (Felizeter et al., 2012; Gredelj et al., 2020b). Only an uptake into the symplast and the xylem allows translocation from roots to shoots and other plant compartments (Strasburger et al., 2008). Hence a lower absorption of long-chained PFAAs could explain their lower translocation into shoots (Lan et al., 2018; Zhang et al., 2019). Interestingly, when actual TFs were calculated from the PFAS concentration in the shoots divided by the concentration in the roots (not the soil), Zhao et al. (2014) found the highest TFs for perfluorohexanoic acid (PFHxA) (0.60 to 1.9) and not for the shortest investigated PFCA, perfluoropentanoic acid (PFPeA) (0.39 to 0.58) in wheat. This result was not further discussed by the authors.

In the field, a high mobility of compounds in the soil leading to increased transport to plant roots along the transpiration stream can be counteracted by their increased leaching into deeper soil layers. Batch sorption experiments with various soils let assume a better sorption and thus a lower mobility in the soil with increasing carbon chain lengths for PFAAs >C5 due to increasing hydrophobic interactions (Guelfo and Higgins, 2013). But also PFBA showed a similar sorption to soil as PFOA ( $\log K_{oc} = 1.88$ ) in that study. Gellrich et al. (2012) demonstrated that PFBA and PFPeA adsorbed well in soil column studies, but leached eventually in the presence of longer-chained PFAAs. Hence, the available PFAS depot in the root zone will consequently undergo a permanent change towards a higher proportion of longer-chained PFAAs (McLachlan et al., 2019; Washington et al., 2010). However, studies at real contaminated sites sometimes still observed higher concentrations of PFAAs in plants with shorter alkyl chain lengths compared to longer-chained ones (Liu et al., 2017; Liu et al., 2019; Yoo et al., 2011). This is indicating a continuous availability of these compounds in the rhizosphere. They could stem from direct aerial transport and deposition or deposition and degradation of precursors to these compounds. They could also stem from continuous degradation of largely immobilized precursors to PFAAs present in materials contaminating the soil such as industrial and municipal sewage sludge used as soil conditioners, landfill leachates or runoff from areas treated with firefighting foams (Ghisi et al., 2019). The degradation of precursors is subjecting the top soil of such sites to a continuous supply of bioavailable degradation products including shorter-chained PFAAs. This further complicates the assessment of BAFs.

BAFs decreased with increasing PFAA chain length in greenhouse and field studies (Liu et al., 2017; Liu et al., 2019; Yoo et al., 2011). As

a consequence, chain length dependent soil-plant BAFs derived from greenhouse experiments appear to be valid for agricultural practice in the field as well (references listed in Table 1).

4.2.2.1. PFAAs  $\geq$  C4. All BAFs from the literature combined revealed a decrease per perfluorinated carbon atom of  $-0.25 (\pm 0.029)$  for PFCAs and  $-0.24 (\pm 0.013)$  for PFSAs (Fig. 2). It has to be noted that the experimental conditions in the studies included in Fig. 2 were quite heterogeneous in terms of investigated plant species and compartments, soils, PFASs, etc. This resulted in an inhomogeneous data base for the considered compounds (e.g., PFOA: 376 values from 20 studies with 28 different plant species; perfluorotridecanoic acid (PFTTrDA): 26 values from 3 studies with 4 plant species). Furthermore, BAFs can also be expected to decisively vary depending on the type of physical and chemical interactions of PFASs with the respective contaminating material (e.g., sewage sludge, paper fiber biosolids, compost, organic solutions or contaminated irrigation water) (Bizkarguenaga et al., 2016a; Blaine et al., 2014b; Gredelj et al., 2020b; Lee et al., 2014). i.e., depending on their leachability and availability for plant uptake. For example, Gredelj et al. (2020b) found different uptake behaviors for PFAAs depending on whether the contamination originated in the soil or in the irrigation water (further discussed in Chapter 5). Moreover, it could be hypothesized that the plant uptake, of e.g., PAPs and their degradation products, might be very different in artificially spiked soils compared to soils contaminated by paper fiber biosolids from food contact material production. In such paper fibers, PFASs, such as PAPs, are used as water and oil repellents and are suggested to be bound by chemisorption, i.e., covalently to hydroxyl groups of cellulose (Trier et al., 2018). Because this issue is not well understood, the diversity of the data sets for the different compounds is leaving great room for uncertainties. The scattering of values by sometimes six log levels is relatively large. Despite all this, the regressions through the medians of the log BAFs from the literature result in good correlations with the chain length of PFCAs ( $r^2 = 0.89$ ;  $p < 0.01$ ) and PFSAs ( $r^2 = 0.99$ ;  $p < 0.01$ ) (Fig. 2 and statistical evaluation in Fig. S1, Tables S1 and S2). Since not all of the data sets are normally distributed (Fig. S2), it is straightforward to evaluate the data with the medians instead of the total scattered data (Fig. S3 and associated Tables S3 and S4).

The incremental decreases of the median log BAFs per perfluorinated carbon atom are remarkably close to the data found in single studies (Table 1) for both PFCAs (Fig. 2a) and PFSAs (Fig. 2b). Individual slopes of log BAFs per perfluorinated carbon for PFCAs indicated in literature ranged from not significant in roots of greenhouse grown tomatoes and peas (Blaine et al., 2014a) to  $-1.16$  in field grown soybeans (Liu et al., 2019). With regard to PFSAs, the smallest decrease was  $-0.1$  per perfluorinated carbon in shoots of greenhouse-grown carrots (Lasee et al., 2019). The most pronounced one was found in the same study for alfalfa shoots being  $-0.47$  per perfluorinated carbon. Medians and median absolute deviations for the combined literature values from Table 1 were  $-0.31 \pm 0.15$  per perfluorinated carbon for PFCAs and  $-0.23 \pm 0.089$  per perfluorinated carbon for PFSAs.

Interestingly, the slopes for PFCAs and PFSAs are very similar. The condensed data from Fig. 2 and Table 1 do not reveal a significant difference between the chain length dependency for PFCAs and PFSAs (Table S5,  $\alpha = 0.05$ ). However, when the values are only taken from one study, they are more comparable in terms of plant species, soil characteristics, etc. As such, the reported slopes from Lasee et al. (2019) result in a significantly smaller slope of log BAFs per perfluorinated carbon atom for PFSAs compared to PFCAs ( $p = 0.02$ , Table S5). Nevertheless, more comparative studies are needed to confirm this outcome.

Moreover, the slopes were different among various plant species (Blaine et al., 2014a; Lasee et al., 2019). However, the summary over various studies and plant species seems to reveal a general tendency that these slopes are steeper in regard to the transfer into shoots compared to roots (Blaine et al., 2013; Blaine et al., 2014a; Blaine et al.,

**Table 1**  
Incremental decreases  $\Delta \log$  BAFs per perfluorinated carbon atom from linear regression through  $\log$  BAFs as indicated in literature.

Reference	Culture	Compartment	$\Delta \log$ BAF (PFCAs)	Range	$\Delta \log$ BAF (PFASs)	Range	
Yoo et al., 2011	tall fescue+barley+Bermuda grass+Kentucky bluegrass	Shoot	-0.24	C6-C14			
Blaine et al., 2013	lettuce (greenhouse)		-0.32 <sup>a</sup> ; -0.31 <sup>b</sup>	C4-C10	-0.29 <sup>a</sup> ; -0.28 <sup>b</sup>	C4,C6,C8	
	lettuce (field)		-0.4	C4-C10			
	tomato (greenhouse)		-0.5 <sup>b</sup> to -0.9 <sup>b</sup>	C5-C10			
Blaine et al., 2014a	tomato (field)		-0.1 to -0.3	C4-C10			
	radish (greenhouse)	Shoot	-0.11	C4-C10			
		Roots	-0.12	C4-C10			
	celery (greenhouse)	Shoot	-0.36	C4-C10			
		Roots	-0.17	C4-C10			
	tomato (greenhouse)	Shoot	-0.20	C4-C10			
		Fruit	-0.54	C4-C10			
		Roots	not significant	C4-C10			
	pea (greenhouse)	Shoot	-0.30	C4-C10			
		Fruit	-0.58	C4-C10			
Blaine et al., 2014b	strawberry (greenhouse)	Roots	not significant	C4-C10			
		Fruit	-0.29	C4-C9			
		Shoot	-0.17	C4-C9			
		Roots	-0.31	C4-C9			
Liu et al., 2017	lettuce (greenhouse)		-0.43 to -0.70	C4-C9			
	wheat (field)	Grains	-0.52	C4-C8			
Liu et al., 2019	maize (field)	Grains	-0.52	C4-C8			
	Radish+Carrot (field)	Roots	-0.28 <sup>c</sup> ; -0.25 <sup>d</sup>	C4-C8			
	7 Shoot vegetables (field)	Shoot	-0.23 <sup>c</sup> ; -0.10 <sup>d</sup>	C4-C8			
	Cauliflower (field)	Edible part	-0.37 <sup>c</sup> ; -0.25 <sup>d</sup>	C4-C8			
	Pepper (field)	Fruit	-0.60 <sup>c</sup> ; -0.31 <sup>d</sup>	C4-C8			
	Wheat+Corn+Soybean (field)	Grains	-0.79 <sup>c</sup> ; -0.36 <sup>d</sup>	C4-C8			
	Celery (field)	Shoot	-0.34 <sup>c</sup>	C4-C8			
	Pumpkin (field)	Fruit	-0.71 <sup>c</sup>	C4-C8			
	Soybean (field)	Grains	-1.16 <sup>c</sup>	C4-C8			
	Lasee et al., 2019	Radish (greenhouse)	Shoot	-0.27	C7-C9	-0.21	C4,C6,C8
		Roots	-0.42	C7-C9	-0.35	C4,C6,C8	
carrot (greenhouse)		Shoot	-0.52	C7-C9	-0.10	C4,C6,C8	
		Roots	-0.66	C7-C9	-0.19	C4,C6,C8	
alfalfa (greenhouse)		Shoot	-0.87	C7-C9	-0.47	C4,C6,C8	
		Roots	-0.48	C7-C9	-0.23	C4,C6,C8	
Gredelj et al., 2020b	chicory (greenhouse)	Shoot	-0.27 <sup>e</sup> ; -0.28 <sup>f</sup> ; -0.31 <sup>g</sup>	C4-C10			
			Roots	-0.26 <sup>e</sup> ; -0.31 <sup>f</sup> ; -0.32 <sup>g</sup>	C4-C10		
			Roots	-0.26 <sup>e</sup> ; -0.31 <sup>f</sup> ; -0.32 <sup>g</sup>	C4-C10		

The table is only considering  $\log$  BAFs from soil to respective compartments, no translocation between different compartments or BAFs from hydroponic cultures. Radish: no actual investigation of the roots but rather of the hypocotyl (unclear for Lasee et al., 2019).

<sup>a</sup> soil impacted with industrial biosolids

<sup>b</sup> soil impacted with municipal biosolids

<sup>c</sup> 0.3 km distance from fluorochemical industrial park

<sup>d</sup> 10 km distance from fluorochemical industrial park

<sup>e</sup> spiked irrigation water

<sup>f</sup> spiked soil

<sup>g</sup> spiked soil and spiked irrigation water

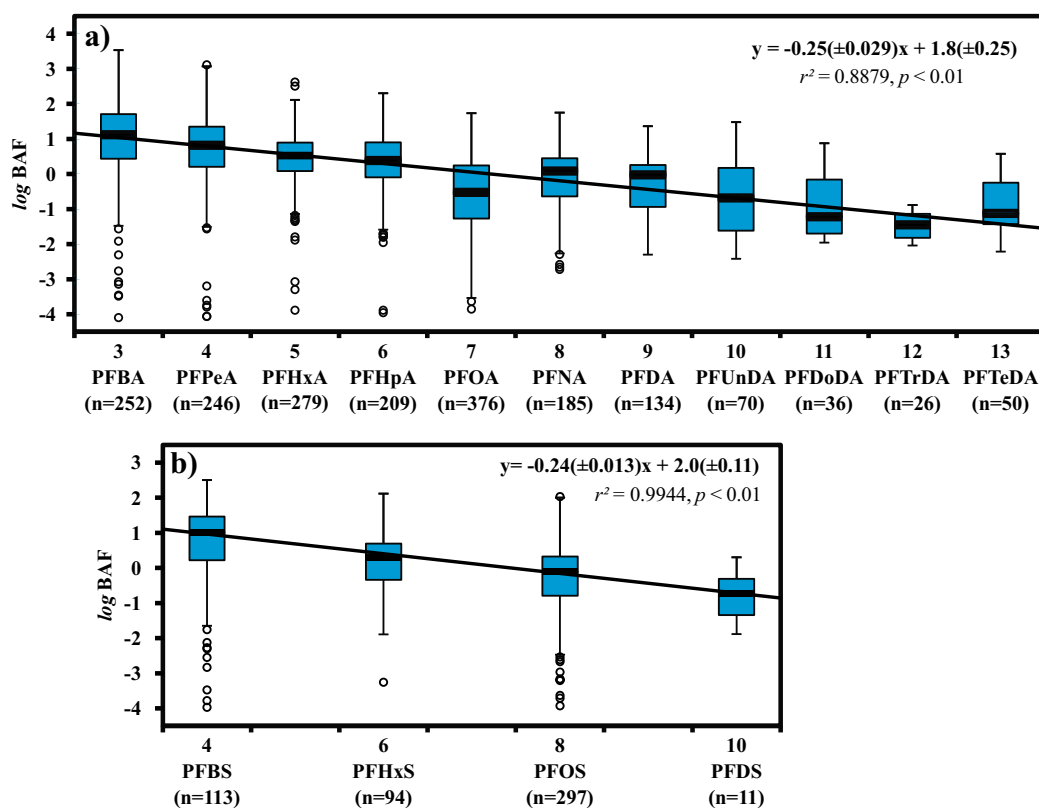
2014b; Gredelj et al., 2020b; Lan et al., 2018; Lasee et al., 2019; Wen et al., 2014). Both aspects are discussed in detail in Chapter 6.

**4.2.2.2. Ultra-short-chain PFAAs (C2 and C3).** The transfer of the ultra-short-chain PFCAs TFAA (C2) and PFPrA (C3) in agricultural plants has been very scarcely reported in scientific literature. In the light of the preferred transfer of short-chained PFASs, this can be considered as one of the most important knowledge gaps in understanding transfer mechanisms and total PFAS burden of plants.

The main reason is that TFAA and PFPrA are generally difficult to integrate in existing methods for PFAS analysis. As these are normally based on reversed phase (RP) liquid chromatography (LC), whereas ultra-short-chain PFASs elute with insufficient retention together with salt matrix components and require special analytical approaches. Furthermore, compared to other PFASs, only few published extraction methods for TFAA exist for soils or biological samples. In most of these older methods, extraction is followed by a derivatization of TFAA and subsequent measurement by gas chromatography coupled to mass spectrometry (GC-MS) (e.g., Cahill et al., 1999; Frank et al., 2002) instead of LC. However, recent developments in analytical chemistry, like ion chromatography-tandem mass spectrometry (IC-MS/MS),

supercritical fluid chromatography coupled with tandem mass spectrometry, or the design of RP columns for the retention of ionic compounds, allowed the inclusion of C2 and C3 PFAAs in analytical protocols (Björnsdotter et al., 2019; Scheurer et al., 2017; Schulze et al., 2019) and few results regarding the transfer of ultra-short-chain PFCAs into plants were published just recently. However, ultra-short-chain PFASs, i.e., TFMS, PFETs, and PFPrs have not been considered in plant uptake experiments yet.

The first publication addressing TFAA retention in soil and its theoretical uptake by plants was published by Berger et al. (1997) for a northern hardwood forest soil in the US. However, TFAA was only measured in the soil solution of two lysimeters and not in the soil or any plants. Nevertheless, plant uptake was modelled as the product of transpiration and soil matrix concentrations reduced by the flux in bypass water. An overall plant uptake of 5–35% was calculated for that particular soil. Twenty years later, the European Reference Laboratories for Residues of Pesticides (EURL-SRM) analyzed TFAA in > 1600 food samples of plant origin. In nearly every sample, TFAA was found at least in traces (EURL-SRM, 2017). The frequency of TFAA findings was higher in conventionally produced products compared to organic ones, but median values were similar. The highest mean concentrations were observed



**Fig. 2.** Linear regressions of log BAFs (medians) as a function of the number of perfluorinated carbon atoms  $x$  for a) PFCAs with  $x = 3-13$  and b) PFASs with  $x = 4, 6, 8,$  and  $10$ . For sources of values, see Text S3.

for dry pulses and leafy vegetables, respectively. Unfortunately, no calculation of BAFs was performed as plant products were bought on local markets and thus the analysis of corresponding soil samples was not possible.

Two very recently published studies dealt with the uptake of ultra-short-chain PFASs in hydroponic experiments. TFAA and PFPrA were found in roots and shoots of a hydroponically grown pumpkin culture spiked with 6:2 fluoroteleomer sulfonic acid (6:2 FTSA) (Zhao et al., 2019). The findings are surprising as neither TFAA nor PFPrA were found in the aqueous solution throughout the experiment and have not been assigned as biodegradation products of 6:2 FTSA. However, the applied spiking solution of 6:2 FTSA only had a purity of 98%. Hence it cannot be excluded that TFAA and PFPrA might have originated from the degradation of 4:2 FTSA present as impurity in the spiking solution.

Zhang et al. (2019) stated that an energy-dependent active transport via protein carriers is the main mechanism for PFAA uptake in general, but a significant uptake of ultra-short-chain PFAAs (C2, C3) would also take place via aquaporins and anion channels. Compared to PFPrA, TFAA had more than ten times higher shoot-BAFs in their study. Compared to PFCAs with longer chain lengths, the uptake of both TFAA and PFPrA was significantly higher.

The special role of TFAA among all PFCAs was shown for worst case scenarios (highly PFAS contaminated sites) but also for sites with no direct PFAS impact. Fluorochemical manufacturing facilities were identified to directly release TFAA (Chen et al., 2018; Scheurer et al., 2017). Around such a facility in China, concentrations of TFAA in soil, plants, surface water, and air were 1–2 orders of magnitude higher than those of all other PFASs including other short-chained ones (Chen et al., 2018). The here reported BAFs for all PFASs were even 2–3 orders of magnitude higher than those reported for greenhouse experiments, although the latter often represent worst case scenarios in terms of concentration and root density in the soil. However, it has to be noted that

precursors to PFAAs like FTOHs were also emitted and that the impact of their degradation, possibly even within the plants, was not investigated. Chen et al. (2018) also observed a significant correlation (Spearman's  $r = 0.714$ ;  $p < 0.05$ ) between air and leaf concentrations for PFAAs  $\geq C4$ , but not for TFAA or PFPrA. Thus, the authors concluded that root uptake was the dominant mechanism for the accumulation of these two PFASs and that in this case leaf uptake was negligible.

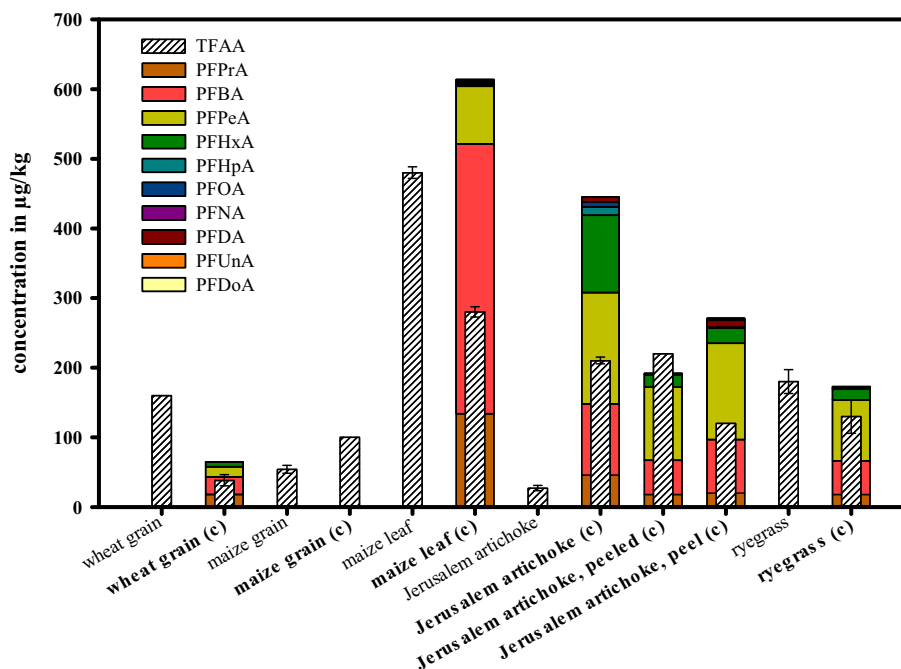
Apart from fluorochemical industry, a further source of TFAA in the environment is atmospheric photodegradation of novel refrigerants and deposition onto soil by precipitation (Chen et al., 2019; Freeling et al., 2020). Furthermore, it is a final biodegradation product of plant protection agents with C-CF<sub>3</sub> moiety (EFSA, 2014) and thus also present in elevated concentration at remote sites with no direct PFAS contamination. This was demonstrated by Sacher et al. (2019), who performed a comparison between background study sites and highly contaminated sites where PFASs containing paper fibers had been mixed with compost and deployed on agricultural fields. TFAA was detected in all plant samples irrespective of their origin, whereas other PFCAs were solely found in samples from the PFAS contaminated site (Fig. 3).

## 5. Effect of the functional group on BAFs

Since PFOA and PFOS represent indicator substances, many studies provided soil-to-plant-BAFs for these two compounds as representatives of PFCAs and PFASs, respectively. However, such a comparison needs to take into account that PFOA and PFOS have the same number of carbon atoms in the molecule but PFOS possesses one more perfluorinated carbon atom compared to PFOA. Considering the influence of the perfluoroalkyl chain length, as discussed in the previous chapter, this fact alone results in significantly different properties of the two compounds.

In order to better address the influence of the head group on the transfer, compounds with the same perfluoroalkyl chain length should





**Fig. 3.** Concentrations of TFAA and other PFCAs in plant samples from background and highly PFAS contaminated agricultural fields. Raw data published by Sacher et al. (2019): bold (c) = samples from contaminated site; n = 1, except for TFAA where n = 2; error bars represent relative percent difference.

be compared. For this reason, BAFs for PFPeA and perfluorobutan sulfonic acid (PFBS) were compared using values from Zhao et al. (2014) for wheat (*Triticum aestivum* L.) (Table 2). In this example, pronounced differences between these two PFAAs were observed with higher shoot-BAFs for PFPeA.

Generally, most studies found higher BAFs for PFCAs than for PFSAs (especially PFPeA vs. PFBS) in vegetative compartments and especially reproductive organs of various plant species (e.g., Blaine et al., 2014a; Blaine et al., 2014b; Krippner et al., 2015; Wen et al., 2014; Yamazaki et al., 2019). Yet in some of these studies, BAFs for PFBS in roots were greater than the BAFs for PFPeA (Blaine et al., 2014a; Zhao et al., 2014). Similarly, Felizeter et al. (2014) found significantly higher root-BAFs for PFSAs compared to PFCAs with the same perfluoroalkyl chain length in hydroponically grown cabbage, zucchini, and tomato (between factor 2 and 3), but uptake into vegetative plant compartments and edible plant parts were either not significantly different or higher for PFCAs. The authors concluded that the uptake in plant vascular tissues is independent of the functional group and that the enhanced contribution of the sulfonate group to root-BAFs may rather be due to higher sorption to the root surface. The same study also found a

significantly higher root uptake of linear PFOS than of branched PFOS for cabbage and tomato. This was attributed to the smaller molecular volume of the branched isomers which would lead to smaller root surface tissue/water sorption coefficients (Felizeter et al., 2014). However, the observation might as well be a result of higher adsorption of the more hydrophobic linear PFOS compared to the branched isomers to organic matter, in this case the roots, as observed for soil and sediment (Gellrich et al., 2012; Schulz et al., 2020).

Nevertheless, between transpiration stream concentration factors regarding leaves and edible parts, no significant differences (t-test,  $\alpha = 0.05$ ) were found between the different isomers (Felizeter et al., 2014). These results suggest that the distribution of PFSAs and PFCAs depends on the plant compartments. Mostly, vegetative compartments seem to take up more PFCAs than PFSAs. In addition, different species take up specific PFCAs and PFSAs to different amounts (Blaine et al., 2014a).

Another look at Table 2 reveals that with increasing chain length, differences between PFCAs and PFSAs seem to be less pronounced (comparison between perfluoroheptanoic acid, PFHpA, and perfluoroheptane sulfonic acid, PFHpS). Findings from another study that investigated the

**Table 2**  
BAFs for PFCAs and PFSAs with the same perfluoroalkyl chain length in wheat (pot experiments, differently spiked soil levels).  
Source of values: Zhao et al. (2014).

Number of perfluorinated carbons	PFAA soil concentration/(µg/kg)	PFAA shoot concentration/(µg/kg)		BAF <sup>a</sup>	
		PFPeA	PFBS	PFPeA	PFBS
4	200	2481 ± 449	643 ± 45.6	12	3.2
	500	3624 ± 595	1394 ± 32.6	7.2	2.8
	1000	5347 ± 127	2065 ± 253	5.3	2.1
Number of perfluorinated carbons	PFAA soil concentration/(µg/kg)	PFAA shoot concentration/(µg/kg)		BAF <sup>a</sup>	
		PFHpA	PFHxS	PFHpA	PFHxS
6	200	165 ± 9.27	147 ± 13.6	0.83	0.74
	500	285 ± 6.13	255 ± 8.72	0.57	0.51
	1000	493 ± 75.2	493 ± 45.8	0.49	0.49

<sup>a</sup> Calculated.

uptake of six PFAAs in three plant species (radish, carrot, alfalfa) in a maximum bioavailability scenario (sandy soil with very low organic carbon content) foster this assumption (Lasee et al., 2019). While with six fluorinated carbons in the molecule (PFHpA vs. PFHxS), BAFs were significantly ( $p < 0.05$ ) higher for PFHpA in most of the investigated plant tissues, with eight fluorinated carbons (PFNA vs. PFOS), radish was the only species with significantly higher uptake of PFNA. Referring to the increased significance of short-chained PFASs, Blaine et al. (2014a) pointed out that the larger size of the sulfonate moiety compared to the carboxylate moiety becomes more relevant with decreasing chain length. Also other studies have observed this phenomenon (Gredelj et al., 2020b; Lan et al., 2018; Lasee et al., 2019), but in most cases, explanations are merely suggested, not conclusively investigated or would need more data to be confirmed. Suggestions include for instance the influence of different physical-chemical properties of various head groups such as the decreasing water solubility and increasing  $\log K_{oc}$  from carboxylic acids to sulfonic acids and further to sulfonamides (Bizkarguenaga et al., 2016a).

Some authors also suggested different uptake mechanisms for PFAAs with various head groups (Blaine et al., 2013; Blaine et al., 2014a; Krippner et al., 2015; Wen et al., 2013; Wen et al., 2014) but no conclusive explanation was given. One of the most extensive studies on this subject was conducted in hydroponic culture with maize, in which Wen et al. (2013) experimented with different phosphorylation, phosphatase, and aquaporin inhibitors. Based on the non-competitive uptake of PFOA and PFOS, they concluded that PFOA uptake is likely energy-dependent and does not mainly take place through aquaporins. In contrast, PFOS uptake seems to mainly involve diffusion and at least partly transport through aquaporins. Though the uptake of both compounds seems to be carrier-mediated (Wen et al., 2013). The same group of authors also postulated different pathways for the uptake of PFCAs and PFSAs from soil and their translocation within plants. This assumption was based on the observation that concentrations of nine PFCAs (C4-C11, C14) in wheat grains increased logarithmically with increasing soil concentrations whereas concentrations of three PFSAs (C4, C6, C8) correlated linearly with increasing soil concentrations ( $p < 0.01$ ) (Wen et al., 2014). Furthermore, the study found that root-to-shoot translocation of PFOA in wheat exceeded that of PFOS. However, from the shoots, a larger proportion of PFOS entered the grains compared to PFOA. Though, it has to be noted that the study used soils with different biosolid application rates. As no pure substances had been applied, it remains unclear whether degradation and uptake of precursors to PFAAs was also involved, i.e., the degradation of EtFOSAA, EtFOSA, or FOSA to PFOS in the soil and/or in plants. Since this would likely influence the detected concentrations in the different compartments, these assumptions should be handled with care.

Recently, results from Gredelj et al. (2020b) indicated that the uptake ratio of PFCAs and PFSAs could also be influenced by the delivery medium (irrigation water vs. soil). The study demonstrated for leaves and shoots of chicory that when the source of PFBS and PFPeA in plants was only contaminated soil, PFPeA exhibited higher BAFs similar to the studies mentioned above, but when the compounds were additionally coming from contaminated irrigation water, BAFs for PFBS were higher. These results could indicate a better uptake of dissolved PFSAs compared to dissolved PFCAs. At lower concentrations, the proportion of PFSAs dissolved in the pore water is less due to their stronger sorption to soil. However, this assumption is not conclusive as Gredelj et al. (2020b) did not find significant differences (two-tailed student's *t*-test,  $\alpha = 0.05$ ) between PFCAs and PFSAs with four and eight fluorinated carbons in the roots for any of the treatments.

Despite the mentioned effects, there are indications that the influence of the fluorinated carbon chain length is stronger than differences resulting from the functional head group (e.g., Lan et al., 2018; Gredelj et al., 2020b). Furthermore, uptake and transport may vary between different plant species and different plant compartments, which is discussed in more detail in the next chapter.

## 6. Dependence of BAFs on plant-specific characteristics (species, compartment)

The entry points for PFASs into plants are usually the roots which take up substances from the pore water (Lechner and Knapp, 2011; Zhao et al., 2014). Rice cultivation represents a special case in which plants may also absorb substances (especially PFAAs  $\leq C9$ ) at the lower stalk sections due to their continuous exposure to possibly contaminated irrigation water (Yamazaki et al., 2019). After adsorption to plant tissues, compounds encounter the first plant barrier, the epidermis or rhizodermis in roots (Fig. S4). Young roots usually contain no apoplastic barriers (Casparian strip, suberin lamellae) between epidermis and endodermis (Kim et al., 2018). Because the main driving force is the hydrostatic pressure created by plant transpiration, dissolved compounds are mainly transported through the intercellular space, i.e., the apoplast (Fig. S4a), which is assumed to provide no selective transport of PFASs. The endodermis is the transition layer between root cortex and plant vascular bundles (stele). Its cell walls contain the Casparian strip which represents a barrier for apoplastic transport (Blaine et al., 2014a; Liu et al., 2019). At this point, dissolved substances need to overcome the cytoplasmic membranes of the endodermis and are thus subjected to the selective transport of the symplast. Only compounds reaching the vascular tissues are transported through the xylem to other plant parts (Kolattukudy, 1984; Raven et al., 2006). The Casparian strip as an early obstacle for the transfer between roots and shoot, promoting selective transport, likely contributes to the stronger decrease of BAFs with increasing chain length in shoots compared to roots (Table 1). Depending on the plant species and age of the roots, plants may also develop the root hypodermis into an exodermis (Kim et al., 2018). In this case, roots contain a second Casparian strip and thus an even earlier barrier for organic contaminants to enter the vascular system (Fig. S4b).

Furthermore, differences in root macro structure can influence the effectiveness of the selective compound accumulation and translocation (Blaine et al., 2014a; Liu et al., 2019). Blaine et al. (2014a) explained the absence of a chain length dependent accumulation of PFCAs in the roots of tomatoes and peas with their thicker taproots compared to the more finely branched root systems of radish and celery. Thick taproots could increasingly enable larger molecules to pass through the root epidermis and to remain in the apoplast without further transport (Taiz and Zeiger, 2010 cited from Blaine et al., 2014a). In contrast, finer roots result in a larger root surface enabling selective transfer in favor of short-chained PFASs via the Casparian strip at an earlier stage. The weaker dependency in radish compared to celery was explained with the absence of the Casparian strip in the hypocotyl tuber of radish. However, only the tuber was analyzed in the study, not the fine root system below. The authors assumed that the fine root system under the tuber allows a weak selection in favor of short-chained PFASs via its Casparian strip but at the same time, long-chained compounds could enter the hypocotyl tuber by other means, for example via aquaporins or diffusion through the hypocotyl endodermis (Suga et al., 2003 quoted from Blaine et al., 2014a). This would weaken the previous selection by chain length.

Some studies referred to Suga et al. (2003) to explain increased translocation of total PFASs from hypocotyl tubers of radish and carrot compared to celery roots to their respective shoots (Blaine et al., 2014a; Liu et al., 2019). The absence of the Casparian strip seems to allow a rather unimpeded transfer therefrom into the shoot. However, according to Blaine et al. (2014a), the greater surface area of the celery root system consisting of a fine root structure could also account for the higher overall root-BAFs and generally higher PFAS accumulation in celery compared to other investigated species. Yet the more likely factor for increased PFAS accumulation in celery may be its comparably longer growing season (224 d compared to 162 d of tomatoes and 129 d of peas). A longer growing season leads to a higher amount of total transpiration resulting in increased substance flow into the plant and

accumulation therein. Overall, transpiration seems to be the main driving force for the compound transfer in the soil/plant system (Blaine et al., 2013; Blaine et al., 2014a; Krippner et al., 2014).

Therefore, studies have also assigned differences in PFAS accumulation to different transpiration coefficients of various species, such as those of wheat compared to maize (Liu et al., 2017). The transpiration stream is considered the most prominent reason why transferable PFASs accumulate to a large extent in strongly transpiring plant parts, mainly the leaves (Blaine et al., 2013; Blaine et al., 2014a; Krippner et al., 2014). Liu et al. (2019) even showed that leaf blades of carrot (50; 19), celery (30), and spring onion (6.0; 6.1) were showing higher BAFs than their respective leaf stems (carrot: 11; 3.2, celery: 6.9) and pseudo stems (spring onion: 0.47; 1.4) growing on agricultural fields with 0.3 km and 10 km distance from a fluorochemical industrial park, respectively. Furthermore, the authors hypothesized that plants with a larger proportion of long leaf stems or pseudo stems, such as spring onion, store less PFASs in the shoot than those with larger proportions of leaf blades. Thus the size of the leaf surface could influence the strength of transpiration. Contradicting this assumption, Bizkarguenaga et al. (2016a) obtained higher BAFs for PFOA and PFOS in hearts (PFOA: 4.1–4.5; PFOS: 3.0–3.2), than in leaves (PFOA: 1.4–2.1; PFOS: <0.2) of lettuce, a plant with a comparatively large proportion of leaf blades. Therefore, in case of Liu et al. (2019), larger leaf blades could have represented an increased surface for the deposition of airborne dust particles from the fluorochemical industrial park nearby, or the length of the vegetation period and actual overall transpiration (Blaine et al., 2014a) may actually be a more decisive factor.

In fact many studies reported higher BAFs of the sum of all investigated PFASs in the vegetative plant compartments (e.g., Bizkarguenaga et al., 2016b; Blaine et al., 2014a; Liu et al., 2019). For wheat several authors have found the major amount of investigated PFASs to remain predominantly in the roots (Stahl et al., 2009; Wen et al., 2014; Zhou et al., 2016). However, it has to be noted that only Wen et al. (2014) investigated nine PFCAs and three PFASs with different chain lengths and could report on the sum of these twelve substances, while Stahl et al. (2009) and Zhou et al. (2016) only investigated PFOA and PFOS both having low shoot-BAFs by nature. In addition, the actual amount absorbed by roots may differ from the measured amount in some cases as the measurement may also have partly included the proportion of compounds only adsorbed to the root surface (no actual uptake and translocation) (Felizeter et al., 2012; Gredelj et al., 2020b).

Either way, transfer into reproductive and storage organs was comparatively low in all included studies (e.g., Blaine et al., 2013; Lechner and Knapp, 2011; Liu et al., 2019; Stahl et al., 2009; Stahl et al., 2013). To explain this, several authors mentioned a number of transfer barriers inside plants on the way from roots via shoots to generative compartments (Blaine et al., 2013; Blaine et al., 2014a; Liu et al., 2019; Yamazaki et al., 2019). As a result, only relatively small amounts of PFASs are transported to reproductive organs. Another important point of concern here is the transition from xylem to phloem. After substances have reached the leaves via the xylem, further transfer is only possible via the phloem. It mainly transports photosynthesis products from their production sites to growing plant parts, reproductive and storage organs (Lalonde et al., 2004). In dicotyledonous plants, compounds need to overcome the cambium as an additional boundary layer and barrier between xylem and phloem in order to reach fruits or stem tubers (e.g., potato tubers) (Strasburger et al., 2008). This could explain low findings of PFASs in fruits of tomatoes and peas (Blaine et al., 2014a) and potato tubers (Lechner and Knapp, 2011; Stahl et al., 2009) compared to other plant compartments. It could also explain lower findings in fruit vegetables such as peppers, pumpkins and tomatoes than in shoot vegetables such as Chinese cabbages, garlic-chives, and lettuce (Blaine et al., 2013; Liu et al., 2019). Nevertheless, despite the lack of a cambium in monocotyledonous plants

(Strasburger et al., 2008), also various Poaceae showed significantly less PFASs in ears, grains, and cobs than in corresponding vegetative compartments (stems, leaves, glumes, pods). These include wheat (Liu et al., 2019; Stahl et al., 2009; Wen et al., 2014; Zhao et al., 2014), maize (Blaine et al., 2013; Krippner et al., 2015; Liu et al., 2019; Navarro et al., 2017; Stahl et al., 2009; Wen et al., 2018), rice (Yamazaki et al., 2019), oats (Stahl et al., 2009), and barley (Stahl et al., 2013).

To explain differences between various vegetables, their biological function of the respective plant part has to be considered. For example, a carrot's taproot and potato tubers are both located in the soil. However, the carrot functions as root and storage organ while potatoes are merely storage organs at the end of a stem. PFAS uptake by roots therefore must take place through the carrot itself, while in order to reach the potato tuber through the plant, compounds first need to overcome several internal barriers (Lechner and Knapp, 2011). Consequently, Lechner and Knapp (2011) observed up to five times higher BAFs in carrots than in peeled potato tubers. In relation of peel to tuber and root, the two vegetables also behaved differently. BAFs of PFOA and PFOS for potato peelings (average 0.03 for PFOA; 0.04 for PFOS) exceeded the ones for the peeled tubers (PFOA: 0.01; PFOS: <0.01). However, no differences in concentration between peeled carrot roots and carrot peel were found (average BAFs for both substances in peel and root: 0.04). Likewise, Bizkarguenaga et al. (2016a) did not detect significant differences between BAFs for carrot and carrot peel, but Stahl et al. (2009) reported higher accumulation in potato peel compared to tubers for PFOS and PFOA. Interestingly, Eun et al. (2020) found micron-sized soil particles on potato peels that had not been washed off by cleaning the tubers with water. The contaminated soil particles were affecting detected PFAS concentrations in such a way that the tuber (including peel) was grouped together with soil in a principle component analysis. This result shows that not only the biological function but also the location (below or above ground) of a vegetable needs to be considered when studying PFAS accumulation. Interestingly though, although irremovable particles were also found on the surfaces of carrot and sweet potato, all other plant samples had been assigned to a group separate from soil (Eun et al., 2020). These results do not allow a general conclusion of how much residual soil particles on the plant surface influence the PFAS contamination and the analysis thereof. But they surely suggest to keep them in mind from a risk perspective.

Further additional plant characteristics might be important to explain different BAFs between species within the same set-up. For example, Lechner and Knapp (2011) explained increased BAFs for PFOA in cucumbers (average 0.88) compared to tomatoes (average 0.40) and carrots (average 0.53) with the presence of protein-like substances in the xylem sap of Cucurbitaceae (Murano et al., 2010). They also mentioned special oil channels in carrot (Wang and Jones, 1994) resulting in a higher lipid content in the root, and higher lipid contents of potato peel compared to the tuber (Fismes et al., 2002) that could explain increased accumulation therein. Likewise, several other studies used different protein and lipid contents of plant tissues to explain differences in accumulation of PFASs therein (Kim et al., 2019; Liu et al., 2017; Liu et al., 2019; Wen et al., 2016; Wen et al., 2018; Zhou et al., 2020). Wen et al. (2016) demonstrated a linear positive relationship between the protein content of seven plant species (maize, soy, radish, mung beans, lettuce, alfalfa, and ryegrass) and the accumulation of PFOA and PFOS in roots as well as root-to-shoot translocation (all correlation coefficients around 0.8;  $p < 0.05$ ). However, correlation with the lipid content was negative in this study, with a stronger inhibiting effect for the transfer of PFOA ( $r = -0.76$ ,  $-3.3$  per percent of lipid content on logarithmic scale) than for PFOS ( $r = -0.86$ ,  $-0.79$  per percent of lipid content on linear scale). A principal component analysis in a follow-up study revealed that the protein content could explain 55% of differences in EtFOSAA uptake ( $p > 0.05$ ). Adding the lipid content raised the factor to 85% (Wen et al., 2018).

On the one hand, some studies have shown only marginal variations in PFAS uptake between closely related plant species with similar structures. For example Yoo et al. (2011) did not find decisive differences in the BAFs for the Poaceae Kentucky bluegrass, Bermuda grass, and tall fescue. On the other hand, in other studies these differences were more pronounced, e.g., Liu et al. (2017) found notable differences for the accumulation of PFBA, PFHxA, and PFHpA in grains of wheat and maize, which likewise belong to the family of Poaceae. Even within varieties of the same species (carrot), some significant differences have been found (Bizkarguenaga et al., 2016a). Moreover, increased accumulation has been assumed to be related to stronger biomass production in certain plant sections (Yamazaki et al., 2019) and generally to enhanced plant growth (Blaine et al., 2014a; Zhao et al., 2013). The latter can be stipulated by growth-favoring conditions such as increased nutrient availability through fertilization (Blaine et al., 2014a). These results suggest that the degree of relation between species is not necessarily an indicator for a similar PFAS uptake, and more research is needed in that area.

## 7. Dependence of BAFs on non-plant-specific characteristics

### 7.1. Impact of PFAS soil concentration

Since the first systematic study on PFAS transfer in crops (Stahl et al., 2009), several studies have generally confirmed increasing accumulations of PFASs in plants or specific plant parts of numerous species with increasing PFAS soil concentrations in greenhouse pot experiments (Blaine et al., 2013; Blaine et al., 2014a; Blaine et al., 2014b; Krippner et al., 2015; Zhao et al., 2014) as well as in the field (Kim et al., 2019; Lee et al., 2014; Liu et al., 2017; Liu et al., 2019; Wen et al., 2014). The increase of the concentration in the plant with increasing PFAS soil concentration seems to be compound-specific and tends to be stronger with increasing chain length (Blaine et al., 2014b; Krippner et al., 2015; Liu et al., 2019). For example, a 4-fold increase of the amount of PFBA, PFPeA, and PFBS spiked to the soil lead to a 2-fold increase of the concentration found in maize straw (Krippner et al., 2015). In the same study, a 4-fold increase of the concentration of PFAAs  $\geq C6$  in the soil lead to a 4-fold increase of the PFAA plant concentration and a 4-fold increase of the PFOS soil concentration resulted in an 8-fold higher concentration in the straw.

The idea that PFAS accumulation could be limited due to active transport mechanisms such as a limited enzyme capacity was briefly mentioned by Blaine et al. (2013). However, the concentration dependency over a really large concentration range (up to concentrations in the g/kg-range) let assume that there is no practically relevant limit of PFAS accumulation in plants. Gredelj et al. (2020c) postulated that no steady state of PFAS accumulation is reached due to the direct relationship with the transpiration stream.

Nevertheless, general statements on how BAFs change with increasing PFAS soil concentrations cannot be made. The BAFs derived from Zhao et al. (2014) for wheat shoots (Table 2) may suggest decreasing values with increasing PFAS soil concentration. An even stronger trend is indicated for the roots. Similarly, decreasing BAFs with increasing PFAS soil concentration can be derived from Gredelj et al. (2020b) for shoots of chicory. However, for the majority of studies, given data indicated no trend regarding BAFs in different plants or plant parts and the PFAS soil concentration (Krippner et al., 2015; Lan et al., 2018; Lee et al., 2014; Liu et al., 2017; Wen et al., 2014). BAFs calculated with values from Stahl et al. (2009) even reveal the highest BAF in wheat straw (6.8) in the batch with the highest PFOA concentration applied to the soil (50 g/kg).

### 7.2. Impact of soil organic carbon and other factors

Besides compound-specific characteristics, plant species, and the concentration in the substrate, bioaccumulation of PFASs is also

dependent on soil characteristics (Blaine et al., 2013). Most prominently, an increasing amount of organic carbon present in the solid substrate (soil, compost, applied sewage sludge etc.) was associated with decreasing PFASs uptake into plants (Bizkarguenaga et al., 2016a; Blaine et al., 2013; Blaine et al., 2014b; Wen et al., 2014). Bizkarguenaga et al. (2016a) even asserted the total organic carbon (TOC) content of the soil to have a greater effect on the PFAS transfer (PFOA, PFOS) than the plant species (lettuce, carrot). Normalization of BAFs to the soil organic carbon content can mostly compensate for differences between experimental treatments with different soils for PFCAs and partly also for PFSAs (Blaine et al., 2013).

The interaction of PFASs with organic carbon in soil and sediment is chain length dependent (Ahrens et al., 2015; Campos Pereira et al., 2018; Higgins and Luthy, 2006; Milinovic et al., 2015). Increased hydrophobicity with longer chain lengths allows better sorption to soil particles and organic matter. This may impede the uptake by plants. As mentioned in Subchapter 3.2, even PFBA and PFPeA can exhibit a strong sorption to soil organic matter (Guelfo and Higgins, 2013). But they are desorbed and made available to plants when longer-chained PFAAs are present (Gellrich et al., 2012). In addition to the total amount, the composition of the organic carbon can be an essential factor. Blaine et al. (2013) assumed that the capacity of a soil to retain PFASs is smaller when the carbon is stemming from fresh compost compared to an aged soil which is richer in more stable clay-humic complexes.

Concerning retention in sediments, Higgins and Luthy (2006) identified increasing sorption of PFASs with decreasing pH (between 5.7 and 7.5) and increasing salinity ( $Ca^{2+}$  concentration) of the aqueous solution used in the experiments. In reality, this would reflect the conditions in the pore water. Plant uptake studies with wheat seedlings and maize in hydroponic solution did not lead to consistent results with regard to an influence of the pH (Krippner et al., 2014; Zhao et al., 2013). However, increasing the salinity in a hydroponic culture from 0 to 0.4‰ lead to increasing BAFs in wheat roots and shoots for PFBA, PFHpA, PFOA, and perfluorododecanoic acid (PFDoDA) (Zhao et al., 2013; Zhao et al., 2016). In soil, the interaction with soil components could interfere with this effect. Hence, also for salinity, more research is needed to gain further insight into the processes involved.

Besides abiotic factors, Zhao et al. (2014) found that the co-presence of wheat (*Triticum aestivum* L.) and earthworms (*Eisenia fetida*) increased the bioavailability of PFASs for both species. Specifically PFCAs  $\leq C7$  accumulated to a higher extent in wheat when earthworms were present. Longer-chained PFCAs and PFSAs in general showed lower accumulations than in the control treatments without worms. The authors considered several reasons for this. First, earthworms show a significantly higher bioaccumulation capacity for hydrophobic PFASs, (such as PFCAs with chain lengths  $>C7$  and PFSAs) compared to wheat due to larger protein and fat contents in the tissue. Therefore, the two species are competing in the bioaccumulation of these substances, which could lead to reduced uptake in wheat. On the other hand, short-chained PFCAs ( $<C7$ ) were enriched in earthworm excrements compared to organic soil material. This could have stimulated diffusion of short-chained PFCAs from worm excrements into the soil solution. Consequently, this would have increased the concentration of short-chained PFCAs available to plants from soil increasing their transfer into plants. In addition, bioturbation by earthworms could stimulate the activity of soil organic matter decomposing microorganisms. This would allow PFASs bound to organic matter to dissolve in pore water more often, increasing their bioavailability to wheat (Zhao et al., 2014). It could be interesting to see how this co-presence interacts with the PFASs uptake when precursors to PFAAs are present.

An important factor at real contaminated sites is, if the contamination is predominantly present in the soil or if contaminated irrigation water is applied to the field. Results from Blaine et al. (2014b) and Gredelj et al. (2020b) demonstrated that the uptake into plants is higher when the irrigation water is contaminated as the mobility and bioavailability is increased in these scenarios. As stated in Chapter 4.2.1, the

source of contamination in general can influence the availability of PFASs to the plants.

## 8. Precursors to PFAAs hampering the determination of BAFs

Inevitably complicating the interactions with and between different influencing factors for the uptake of PFASs into plants is the presence of precursors to PFAAs, which frequently occur at contaminated field sites (Janda et al., 2019; Lee and Mabury, 2014). Principally, all compounds containing a perfluoroalkyl moiety can be assumed to be degraded abiotically and/or biotically to PFCAs, PFSA, or PFPAs by changes in the non-fluorinated molecular moiety (Buck et al., 2011). The corresponding PFAAs can thereby be formed from numerous different precursors such as fluorotelomer alcohols (FTOHs), polyfluoroalkyl phosphoric acid (di)esters ((di)PAPs), sulfonamide derivatives, perfluorophosphinates (PFPIAs) etc. (Ghisi et al., 2019; Zhou et al., 2020). While most known PFAS contaminated sites are results of handling aqueous firefighting foams (applications, training, accidents), the most relevant input pathways for precursors to agricultural land are the application of sewage sludge and the atmospheric deposition of volatile compounds. In search for the cause of contamination with PFCAs and PFSA in different environmental matrices, the question will therefore always arise whether the compounds were introduced directly into the compartment under investigation or whether they were formed as a result of precursor degradation. This can alter their availability to plants as their uptake and/or accumulation in plant tissues additionally or solely (depending, if precursors are the only source) depends on degradation kinetics of their precursors.

Various precursors have already been investigated in soil-plant transfer studies. These include precursors to PFCAs such as FTOHs (Yoo et al., 2011), diPAPs (Bizkarguenaga et al., 2016b; Lee et al., 2014), fluorotelomer unsaturated carboxylic acids (FTUCAs) (Bizkarguenaga et al., 2016b; Eun et al., 2020; Lee et al., 2014), and precursors to PFSA such as EtFOSAA, EtFOSA, FOSA (Bizkarguenaga et al., 2016a; Eun et al., 2020; Wen et al., 2018; Yamazaki et al., 2019). Zhou et al. (2020) investigated four emerging PFOS alternatives: 6:2 FTSA, 6:2 chlorinated polyfluoroalkyl ether sulfonic acid (6:2 Cl-PFESA) and two PFPIAs (C6/C6 and C8/C8 PFPIAs) in a soil-plant system.

For some precursors, their hydrophobic character and relatively large molecular size may impede the transfer through plant membranes, which is why transfer to vegetative plant compartments was found to be low. Thus, most likely, a major amount of these precursors might be degraded already in the soil via microbial activity in the rhizosphere and plant-specific root exudates and not after their uptake into plants (Bizkarguenaga et al., 2016a; Wen et al., 2018). However, results indicate that precursors are at least partly degraded inside plants (Bizkarguenaga et al., 2016b; Bizkarguenaga et al., 2016a; Lee et al., 2014; Wen et al., 2018). For example, Wen et al. (2018) found a continuous increase of the PFOS concentration in seven plant species within 60 days while the concentrations of its precursors EtFOSAA, EtFOSA, FOSA, and perfluorooctane sulfonamido acetic acid (FOSAA) were decreasing throughout the second half of the experiment.

Especially hydroponic studies can provide insight into degradation processes and an increasing number of such involving precursors to PFAAs have emerged (Zhao et al., 2018b; Zhao et al., 2019; Zhou et al., 2019). These also provided sufficient evidence for the degradation of precursors inside the plants as the compounds itself as well as (intermediate) degradation products have been found in plant tissues. For example, Zhou et al. (2019) found perfluorohexyl phosphonic acid (C6-PFPA), perfluorooctyl phosphonic acid (C8-PFPA), 1H-perfluorohexane, and 1H-perfluorooctane as degradation products of C6/C6 and C8/C8 PFPIAs in wheat. PFPIAs seem to undergo phase I metabolism (e.g., oxidation) catalyzed by enzymes of the cytochrome P450 group in the roots. These enzymes have also been shown to be involved in the degradation of fluorotelomer sulfonic acids (FTSAs) (Zhao et al., 2019) and may also be involved in the degradation of FTOHs in plants

(Zhang et al., 2016). Although to the authors' best knowledge, it was not specifically tested so far, the involvement of cytochrome P450 in diPAP degradation in plants is very likely due to its role in the degradation of several organophosphorus esters (Wan et al., 2017). For the degradation of FTOHs, there are also hints for the involvement of alcohol dehydrogenases, aldehyde dehydrogenases, and glutathione S-transferase. This has been demonstrated for soybean roots during exposure to 8:2 FTOH (Zhang et al., 2016).

Results obtained so far indicate that the transfer of precursors depends on the same factors as transfer of PFAAs including the hydrophobicity of a compound, the plant species and compartments (root exudates, protein content etc.), and the soil organic carbon content (Bizkarguenaga et al., 2016b; Bizkarguenaga et al., 2016a; Wen et al., 2018; Zhou et al., 2020). Moreover, Bizkarguenaga et al. (2016b) found higher BAFs for lettuce (2.45–3.19) than for carrot (0.81–0.94) when PFOA was applied directly to the soil. But when PFOA was formed from applied 8:2 diPAP, carrot (0.86–1.43) exhibited higher BAFs than lettuce (0.089–0.093). Furthermore, for lettuce growing on soil with an organic carbon content of only  $2.3\% \pm 0.5\%$ , BAFs of directly applied PFOA resembled those of PFOA formed from 8:2 diPAP. But on soil with high organic carbon content ( $53\% \pm 9\%$ ), BAFs of PFOA formed from the precursor were only half as high as the ones from directly applied PFOA. Additionally, with higher organic carbon content, the final concentration of 8:2 diPAP in the soil was much lower while the PFOA concentration was much higher. The authors assigned the differences to plant-specific root exudates influencing precursor degradation that are not relevant when the final degradation product is directly applied to the soil. Supporting this assumption, the authors found different intermediate degradation products in the presence and absence of plants which also depended on which of the two plant species was present. The second example is showing that the higher soil TOC seems to retain the compounds better in the soil, but it also enhances the degradation of the precursor (Bizkarguenaga et al., 2016b).

Considering all these additional interactions, calculating BAFs from directly applied end-products from greenhouse experiments cannot be directly transferred to scenarios with precursors. Due to long half-lives (e.g., 0.85 a to 1.8 a for investigated FTOHs) and their low mobility in the soil (no leaching into deeper soil layers), known precursors such as FTOHs and PAPs represent long-lasting reservoirs for permanent PFCA replenishment (Janda et al., 2019; Lee et al., 2014; Washington et al., 2010; Yoo et al., 2010). Potentially present unknown precursors may complicate the assessment of meaningful BAFs even more. Because of its perfluoroalkyl chain specificity, application of the total oxidizable precursor (TOP) assay (Houtz et al., 2013; Janda et al., 2019) might help to address the impact of this "dark matter".

## 9. Conclusions

Root uptake represents the main mechanism for the PFASs uptake into plants where they need to overcome selective membrane barriers to be taken up and transported within plants leading to higher BAFs for vegetative compartments than for reproductive and storage organs. The selective transport to, into, and inside the plants leads to BAFs tending to decrease with increasing carbon chain length and  $|\Delta \log \text{BAFs}|$  to be higher for shoots compared to roots. The PFAS chain length seems to have greater impact on the transfer than individual differences resulting from the functional head group. However, the presence of known and unknown precursors to PFAAs can complicate the calculation of meaningful BAFs for individual compounds. It often remains unclear, if the precursor compound has been transformed in the soil or in the plants after uptake.

Some results from the reviewed literature are contradictory or inconclusive and require additional research. The observed different uptake behavior of PFCAs and PFSA, the smaller  $\Delta \log \text{BAFs}$  for PFSA, and the underlying mechanisms are inconsistent in the reviewed literature. In this context, also further investigations on linear vs. branched

isomers of PFOS and other PFAAs could be valuable. Results of some studies suggest that the degree of relation between species is not necessarily an indicator for a similar PFAS uptake, although specific traits and structures of organs (e.g., roots or leaf surface area) were mentioned as important features influencing the uptake in other publications. The fact that a higher organic carbon content seems to result in lower BAFs due to better sorption on soil components but seems to enhance the degradation of certain precursors at the same time further complicates the interpretation of results.

The literature evaluation identified knowledge gaps regarding the PFAS uptake into plants that qualify for being prioritized in future research. These can be divided in two thematic groups:

### 1. Tested species and compounds

Soil-plant BAFs in agricultural plants have only been investigated for 45 PFASs, thus covering a very small fraction of the compound class. There have been only few studies investigating PFASs uptake of precursors to PFAAs. Completely overlooked plant species in this context include rice, chicory, tomato, potato, pepper, garlic chives, spring onions, and spinach. Overlooked compounds with environmental importance include PFAAs  $\leq C_3$ , especially PFSAs, PFPAs, fluorotelomer compounds, and additional emerging PFAS categories such as perfluorinated (e.g., GenX) and polyfluorinated (e.g., DONA) polyethers, FASEs, SAMPAPs. Even more surprising is that no study about the PFAS uptake (even for PFAAs) for sugar cane as one of the most important grasses for food production is available.

### 2. Conceptual unknowns

The availability of PFASs for plant uptake is a crucial point for the setup of meaningful greenhouse and field experiments. However, besides the comparison of soil and irrigation water, there has been no systematic study investigating influences of different contamination sources. The role of possible bound-residues of PFASs in aged soil compared to recently spiked soil has not been addressed so far either. Furthermore, the applicability of aqueous soil leachates for BAF calculations for a better reflection of environmental plant uptake conditions compared to the solvent extraction of PFASs has not been discussed although this might lead to new insights regarding the general availability of PFASs and for cases when PFASs are present in plant tissues at 'unpolluted' sites.

It seems possible that BAFs can become an important tool to derive recommendations for cultivation or handling of crops prior consumption. At least this holds true for uncontaminated background sites with solely atmospheric PFAS deposition. The presence of known and unknown precursors to PFAAs, however, complicate the calculation of meaningful BAFs for individual compounds, as this can result in a constantly changing PFAS depot. In such cases, it often remains unclear, if the precursor compound has been transformed in the soil or in the plants after uptake.

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### Declaration of competing interest

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

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.142640>.

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