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Investigating the uptake and fate of per- and polyfluoroalkylated substances (PFAS) in bean plants (*Phaseolus vulgaris*): comparison between target MS and sum parameter analysis via HR-CS-GFMAS

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Abstract

In this study, we present a screening method based on molecular absorption spectrometry to study PFAS uptake and fate in plants. To evaluate the suitability of this method we analyzed plant extracts with molecular absorption spectrometry (MAS) as well as liquid chromatography–tandem mass spectrometry (LC–MS/MS) for mass balance studies ($w(F)$). French bean plants (*Phaseolus vulgaris*) were grown on soil spiked using eight PFAS substances that vary in chain length and functional group composition. Specifically, these include three short-chained (C4–C5), five long-chained (C7–C10) carboxylic acids, one sulfonic acid and one sulfonic amide moieties. To investigate substance-specific PFAS uptake systematically, PFAS were spiked as single substance spike. Additionally, we studied one mixture of the investigated substances in equal proportions regarding $w(F)$ and four PFAS mixtures of unknown composition. After 6 weeks, the plants were separated into four compartments. We analyzed the four compartments as well as the soil for extractable organically bound fluorine (EOF) by high resolution-continuum source-graphite furnace-molecular absorption spectrometry (HR-CS-GFMAS) as well as for sum of ten target-PFAS by LC–MS/MS. All three short-chained PFAS perfluorobutanoic acid (PFBA), perfluorobutanoic sulfonic acid (PFBS) and perfluoropentanoic acid (PFPeA) were determined in high concentrations mainly in the fruits of the investigated plants while long-chained PFAS perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were mainly determined in roots. PFBS was determined in remarkably high concentrations in leaves compartment by both quantification methods. Overall, comprehensive results of single substance spikes were in good agreement for both methods except for a few cases. Hence, two phenomena were identified: for mixed PFAS spikes of unknown composition huge differences between EOF and sum of target PFAS were observed with systematically higher EOF values. Overall, both methods indicate comparable results with MS being more reliable for known PFAS contamination and MAS being more valuable to identify PFAS exposure of unknown composition.

Keywords Per- and polyfluorinated alkyl substances (PFASs), High resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMAS), Biota samples, Bioaccumulation, Method comparison, Solid-phase extraction (SPE)

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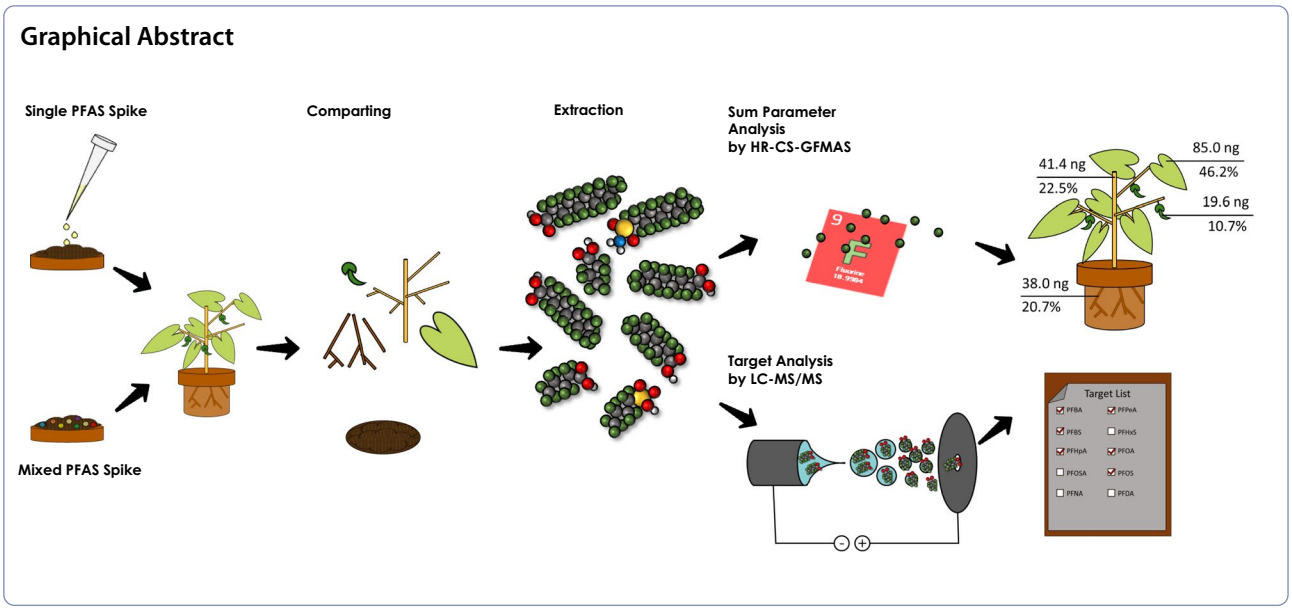

Introduction

Per- and polyfluoroalkyl substances (PFAS) are well known emerging pollutants with a broad field of application and uncountable entry pathways into the environment. Depending on the definition used, the number of individual substances included in this class of pollutants range from 4730 [1] with three or more perfluorinated carbon atoms to over 14,735 CAS-listed chemicals [2] with at least 1 perfluorinated carbon atom, up to several million substances listed on PubChem with at least one perfluorinated methyl or methylene carbon atom. The variety in the numbers can be explained by an updated definition of PFAS made by the OECD in 2021 [3]. Regardless of which number is used as a basis, all three exceed by far the capabilities of target MS-based analytical approaches to evaluate PFAS contamination comprehensively. But PFAS monitoring is highly needed, since all chemicals matching one of the definitions above can build persistent and toxic transformation products—such as trifluoroacetic acid as a final degradation product—or are persistent and/or toxic themselves [4, 5]. Therefore, public concern began to arise recently and regulatory measures were taken adding perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA) to the annexes of the Stockholm Convention on Persistent Organic Pollutants in 2009, 2019 and 2022, respectively [6]; reducing the tolerable concentrations of PFAS in drinking water guidelines over the last two decades (e.g., in the U.S. [7]) and establishing tolerable weekly intake (TWI) values for a sum of four PFAS [4].

These regulations seem to have had an impact: investigating a timeline of suspended particular matter (SPM) samples from German rivers, Göckener et al. found decreasing concentration for regulated PFAS, PFOS and PFOA, whereas the concentrations of non-regulated PFAS increased [8]. The former main producer of PFAS, 3 M, announced in December 2022 to exit PFAS production and manufacturing by end of 2025 [9]. Nevertheless, PFAS are still used in various applications and due to their ubiquitous occurrence and their persistence they will remain relevant pollutants for many decades. Cousins et al. highlighted in 2022 that humankind is out of the safe operating space for the new planetary boundary for PFAS [10]. They investigated the four most studied PFAS (PFOA, PFOS, PFHxA and PFNA) in rainwater samples from all over the world and found relevant PFAS concentrations in all samples even from remote locations. This is corroborated by investigations on PFAS in rain water samples from the U.S. by Kim et al. [11] and on PFAS in blood serum samples from European teenagers by Richterová et al. [12].

In the above-mentioned study Cousins et al. conclude that the background PFAS contamination in soil originates from atmospheric deposition and will increase by common practice of fertilizing with sewage sludge or biosolids [10]. This describes two major exposure pathways for humans to PFAS: (i) Direct uptake via water either by direct exposure to atmospheric deposition or by contamination of drinking water sources such as ground water through leaching from soil. (ii) Uptake by plants from soil and thereby directly into humans' food web or indirectly via forage crops into livestock. Therefore, in order

to ensure food safety and public health, it is important to deepen the understanding of PFAS uptake pathways and distribution in crop plants.

Despite better understanding the fate of PFAS in food webs, new techniques for PFAS remediation must be investigated. One possible way could be phytoremediation [13]. Blaine et al. investigated PFAA-uptake from municipal and industrial soil into lettuce and tomato plants. For lettuce they found bioaccumulation of PFCA up to C8 carbon chain length and for PFSA up to C7 in plants grown on municipal soil and bioaccumulation of PFCA up to C9 and PFSA up to C8 for plants grown on industrial soil. For tomato plants bioaccumulation was only found for PFCA up to C6 [14]. Therefore, PFAS uptake seems to be both PFAS-species as well as plant species specific.

Even though the fluorine–carbon bonds in PFAS are chemically inert, the single substance itself can undergo transformation processes. This leads to a further increase in the number of substances that may require monitoring. These additional transformation products might not be revealed by suspect screenings of crop plants using LC–MS/MS [15] or HRMS [16] (referred to as 'target analytical approaches').

Taking the possibility of transformation into account combined with the enormous number of PFAS species, target analytical approaches (e.g., MS based target or suspect screenings) might not be the most suitable tool to investigate PFAS uptake and fate in plants. The number of available isotope-labeled analytical standards—which are needed for reliable quantification using target MS approaches—is limited and transformation products have to be identified beforehand. Also, the chemical identity of new PFAS first must be determined before analytical standards can be synthesized. The determination of new structures is further complicated, because new PFASs are often developed as technical mixtures.

As an addition to target analytical approaches, sum parameter approaches can be used to investigate the gap between the sum of target substances and the sum of all (also unknown) substances of interest. Hence, it is to note, that in the case of PFASs also all available sum parameter approaches are not capable to determine the entirety the PFAS class, as compromises have to be accepted developing a sum parameter for such a divers substance class. A recently published study of our group based on PFAS sum parameter approaches revealed huge gaps between extractable organically bound fluorine (EOF), PFAS total oxidizable precursor assay (TOPA) and sum of target PFAS determined by means of LC–MS/MS [17]. In this work, we used molecular absorption spectrometry (MAS) to determine EOF in SPM and compared resulting data with TOPA as well as non-target MS qualification and target MS quantification. Over 90% of EOF was unidentified and the EOF–TOPA ratio even increased within the investigated timeframe from 2005–2019. Similar results were found by Aro et al. who compared EOF determined by combustion ion chromatography (CIC) and sum of 37 target PFAS in various environmental samples resulting in more than 70% of EOF unidentified [18]. Part of the unidentified EOF might originate from fluorinated organic compounds which do not match one of the above noted definitions of PFAS, but it is likely that the majority of unidentified EOF is made up of unknown PFAS such as transformation products.

Therefore, this study uses a comprehensive analytical approach based on MAS as a sum parameter method and LC–MS/MS as a target PFAS method to compare the uptake and fate of selected PFAS as well as unknown PFAS mixtures in French bean plants (*Phaseolus vulgaris*). Determined EOF and sum of ten target PFAS (ΣMS) will be compared as fluorine mass fractions ($w(F)$). With this the comparability of both methods as well as individual advantages and disadvantages will be studied. Plant samples will be comparted into fruits, leaves, stem, and roots to investigate the influence of sample matrices with both analytical approaches. In addition, their suitability as screening tools to study fate of PFAS in biosolids will be investigated.

Materials and methods

Study design

Single PFAS spikes

To systematically investigate PFAS uptake and distribution of various PFAS species into different plant compartments, French beans (*Phaseolus vulgaris*) were grown and analyzed. After the first sprouts grew, all plants were separated into single pots with 250 g soil (wet weight) each. For the spiking experiments with different single substances (PFBA, Merck KGaA, Darmstadt, Germany; PFBS, Merck KGaA, Darmstadt, Germany; PFPeA, Thermo Fisher Scientific GmbH, Dreieich, Germany; PFHpA, J&K Scientific Ltd., California, USA; PFOA, J&K Scientific Ltd., California, USA; PFOSA, abcr GmbH, Karlsruhe, Germany; PFNA, J&K Scientific Ltd., California, USA; PFDA; J&K Scientific Ltd., California, USA), stock solutions in pure MeOH (hypergrade for LC–MS; LiChrosolv®, Merck KGaA, Darmstadt, Germany) were prepared. All spiked PFAS were used as linear isomers. To obtain the spiked soils, 250 g of carefully homogenized wet soil and the prepared stock solutions of the respective chemicals used were mixed. The mass fraction for all single PFAS

spike experiments was adjusted to $w(F) = 400$ µg/kg wet soil.

Mixed PFAS spikes

Additionally, five mixed spikes of known and unknown PFAS compositions were used to model PFAS uptake under realistic PFAS exposure conditions. Mix 1 contained soil from a contaminated fire-fighting area which replaced the 250 g of potting soil. For mix 2 all 8 PFASs used as single substance spike (see above) were mixed in equal percentages regarding fluorine mass fraction and applied to 250 g of potting soil resulting in a theoretical $w(F)$ of 400 µg/kg based on soil wet weight. Mixes 3, 4 and 5 were prepared as a dilution series from a commercially available fire-fighting foam (fff) concentrate of 3/3 (mix 3), 2/3 (mix 4) and 1/3 (mix 5) the concentration of the original fff-concentrate.

Growing conditions

All spike experiments were performed in biological triplicates under artificial sunlight for 12 h/d, watering every 2–3 days with 50 mL tap water and addition of fertilizer on day 22 and 29 after PFAS spike. All added substances were tested for EOF before usage and a biological triplicate of French beans were grown under same conditions using pure MeOH as blank spike.

Sample preparation

Harvesting

All plants were harvested on day 30 after spiking. All specimens were directly comparted into fruits, leaves, stem, roots and soil. Compartments were freeze-dried for further sample preparation. The biological triplicates of each compartment were pooled, weighted, and milled for 30 s at 30 Hz in a liquid nitrogen-cooled ball mill using zircon balls. Pooling of samples was necessary to obtain a sufficient quantity of biomass—especially for the fruits compartment.

Primary solid–liquid extraction

Defined mass of resulting sample powders was extracted following an extraction protocol from Simon and Gehrenkemper et al. [19] using acidified MeOH. A more detailed description can be found in Additional file 1: S1.

Digestion of biosolids

For all plant samples residues after evaporation of the extraction solvent were digested following a modified protocol of Blaine et al. [14] using basic H_2O_2-solution [980 µL H_2O_2-solution (30%, (*v/v*)] (per analysis, Merck KGaA, Darmstadt, Germany) + 20 µL NH_3-solution [p.a., 25% (*v/v*), Merck KGaA, Darmstadt, Germany)] and an ultra-sonic bath at 30 °C until clear solutions were obtained (3–5 h). Resulting solutions were diluted with 2 mL H_2O and 1 mL MeOH, acidified to pH = 2 (using double sub-boiled HNO_3) cooled and stored for 24 h at 4 °C in the dark. Resulting white precipitates were separated from supernatants via centrifugation for 10 min at 4800 rcf. Supernatants were collected for following solid-phase extraction (SPE). For residues digestion were repeated as described above. Resulting clear solutions were combined with corresponding supernatants and pH was adjusted to pH = 2.

Solid-phase extraction

To separate organically bound fluorine from possible inorganic fluorine in plant samples, digested extracts of plant compartments were cleaned and enriched following a modified SPE protocol from Metzger et al. [20] using Oasis HLB cartridges (6 cc, 150 mg, *Waters GmbH,* Eschborn). Cartridges were rinsed with 3 × 5 mL MeOH and 3 × 5 mL nitric acid in water (pH = 2). Cartridges were covered with 5 mL nitric acid in water (pH = 2). Digested extracts were loaded onto cartridges, washed with 2 × 3 mL nitric acid in water (pH = 2) and dried for 0.5 h at 3–5 mbar. Analytes were eluted using 2 × 4 mL MeOH. The solvent was evaporated in a gentle nitrogen stream and samples were redissolved in 1 mL H_2O:MeOH [1:1 (*v/v*)] for comprehensive measurements by means of HR-CS-GFMAS and HPLC–MS/MS.

HR-CS-GFMAS quantification

MAS quantification followed a protocol from Metzger et al. [20] using a zirconium-coated graphite furnace with PIN platform (from Analytic Jena, Jena) and gallium as molecule forming agent and detecting in situ-generated GaF molecular absorption at a wavelength of 211.248 nm using a ContrAA800 system (Analytik Jena).

For EOF quantification via HR-CS-GFMAS individual calibrations for each compound (PFBA, PFBS, PFPeA, PFHpA, PFOA, PFOSA, PFNA and PFDA) were prepared. For mixed PFAS spikes, a PFOA calibration was used.

Since triplicates of blank plants showed no relevant molecular absorption for in situ-generated GaF, no blank correction was done. The limit of quantification (LOQ_{MAS}) for the used extraction and quantification method was published in a previous study by Simon and Gehrenkemper et al. [19] as 10.3 µg/L. Therefore, EOF concentrations in investigated extracts below LOQ were set to zero.

LC–MS/MS quantification

Complementary PFAS target quantification utilizing LC–MS/MS was based on German DIN 38414-14 [21] using a *1260* LC system (*Agilent Technologies,* Santa

Clara) coupled to a *Triple Quad 6500* Mass Spectrometer (*AB Sciex Instruments,* Toronto). HPLC separation was performed using gradient elution (see Additional file 1: Table S1) and a *Luna Omega 3 µm PS 100 Å* LC–MS/MS-column (*Phenomenex,* Torrance) with corresponding guard column at 35 °C with 350 µL/min flow rate and 20 µL injection volume. MS/MS was operated in ESI negative mode (−4.5 kV) at a source temperature of 300 °C using nitrogen as nebulizer gas, turbo gas (both 62 psi) curtain gas 35 psi and as collision gas (8 psi).

Quantification of investigated PFAS targets followed German DIN 38414-14 [21] using external one-point calibration and isotope-labeled internal standards for correction of ionization efficiency pairing as followed: $^{13}C_4$-PFBA for PFBA; $^{13}C_2$-PFHxA for PFPeA, PFBS, PFHxA; $^{13}C_4$-PFOA for PFHpA, PFOA, PFNA, PFDA; $^{13}C_4$-PFOS for PFOS, PFOSA. Ionization efficiency was calculated as quotient of detected intensity of internal standards in sample and in external calibration using equal concentrations.

PFAS were quantified via integrated intensity of mass transfer 1 "quantifier" when also a signal for mass transfer 2 "qualifier" was detected (see Additional file 1: Table S2) and $S/N > 10$ was given (corresponding N was conducted using 6 blank measurements injecting pure methanol).

For better comparability resulting target PFAS concentrations were converted into fluorine mass fractions which were summed up.

Bioaccumulation factors

Bioaccumulation factors (BAF) were calculated based on fluorine mass fractions in soil samples determined by MAS quantification following Eq. 1. Determined $w(F)$ values in samples were divided by those of corresponding soil samples, sampled on the same day. It is to note, that for soil samples no SPE clean-up step was needed, since no relevant amount of co-extracted fluoride was determined [19]. Therefore, determined $w(F)$ values in soil may represent higher fractions of the EOF than determined $w(F)$ values in plant samples, since recovery rates of digestion and SPE clean-up are accepted to < 1.

$$\mathrm{BAF} = \frac{w(F)_{\text{plant compartment } i;\text{quantification method } j}}{w(F)_{\text{soil; HR - CS - GFMAS}}}. \quad (1)$$

i is the roots, stem, leave, fruits or whole plant; j is the HR-CS-GFMAS or LC–MS

Results and discussion

Quality control

All tested blanks showed no relevant EOF and none of the PFAS investigated were detected in LC–MS/MS.

PFAS in potting soils

To evaluate substance uptake into plants and calculate ecotoxicological parameters as BAF, we used concentrations of the substances of interest in surrounding soil. Therefore, fluorine mass fractions ($w(F)$) in corresponding potting soils of eight single PFAS spike experiments and five mixed PFAS spike experiments were determined by HR-CS-GFMAS (see Fig. 1). Fluorine mass fractions were determined for each potting soil individually and averaged for soils with the same spike composition ($n = 3$).

Determined fluorine mass fractions in the soil samples varied between 320–1520 µg/kg with highest $w(F)$ in soil spiked with PFAS Mix 3 and lowest in soil from single PFAS spike experiment spiked with PFHpA. Highest value for a single substance spike with $w(F) = 1160$ µg/kg was determined for the PFNA spiked soil.

Relative standard deviations (RSD) of $w(F)$ for biological triplicates grown in individual pots ranged from 4% for PFNA spiked soil up to 33% for PFBS-spiked soil with a mean RSD of 15%. Since spiking took place in wet soil and the used potting soil was not homogenized before aliquoting it for the different experiments, determined RSDs are relatively low and therefore, pooling the samples from the biologically triplicates to obtain a sufficient amount of biosolides can be justified.

For all single substance spike experiments the PFAS spikes were normalized to $w(F) = 400$ µg/kg wet weight of the potting soil. Determined $w(F)$ corresponded to the soils dry weight after harvesting. Since the potting soil was not homogeneous, neither during potting the bean plants nor during sampling, varying fluorine mass

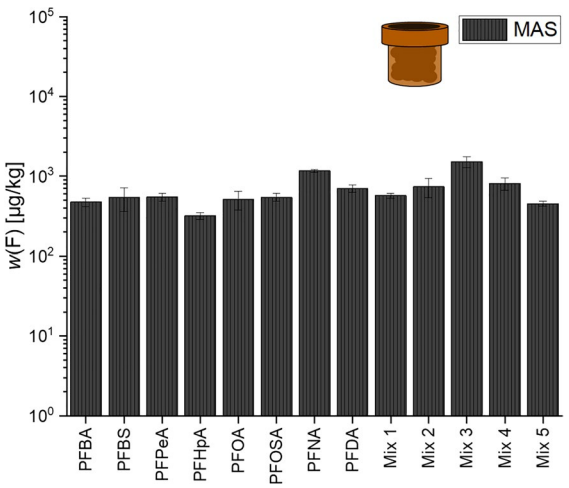

Fig. 1 Comparison of mean fluorine mass fractions $w(F)$ determined by MAS for soil samples of eight single substance spikes and five mixed PFAS spikes collected on day of plant harvesting. Error bars representing the standard deviation based on $n = 3$

fractions were expected, even though potting soil from same batch was used. In addition to inhomogeneity of the soils as well as varying porosity and water content in samples during spiking, substance-dependent behavior of the different PFAS might enhance differences in *w*(*F*) determined in soil samples: short-chained PFAS as PFBA, PFBS and PFPeA are known to be more mobile and a faster wash-out or higher PFAS uptake into the plants could be possible, and consequently a lower *w*(*F*) would be expected for those samples. This hypothesis is consistent with *w*(*F*) values of the short-chained PFAS spikes varying between 470–550 µg/kg while PFNA and PFDA—the two spikes with longest carbon chain length—showed values for *w*(*F*) of 1160 µg/kg, respectively, 700 µg/kg. For PFOA and PFOSA similar values to the short-chained PFAS spikes were determined, while PFHpA spike resulted in lowest *w*(*F*) with 320 µg/kg. Various processes in soil–plant–water interface may be the reason for this. But further interpretation of determined soil values would be speculative due to above-mentioned inhomogeneity of the soil samples both during spiking and sampling.

It is to highlight that *w*(*F*) for all mixed PFAS spikes in corresponding soils were comparable to those values determined for single PFAS spiked soils regarding *w*(*F*). Hence, comparability of observed effects is given. Additionally, for mix 4 and mix 5—which were diluted from mix 3—decreasing *w*(*F*) were determined.

PFAS in plant compartments after single PFAS exposure

To investigate substance-dependent PFAS uptake and fate in bean plants besides various moieties as sulfonic acid, carbonic acid and sulfonic amid, also various chain lengths of linear ionic PFAS were spiked which resulted in 3 short-chain PFAS and 5 long-chain PFAS according to classification by Buck et al. [22].

Determined *w*(*F*) varied among the different single substance PFAS spikes as well as among the four investigated

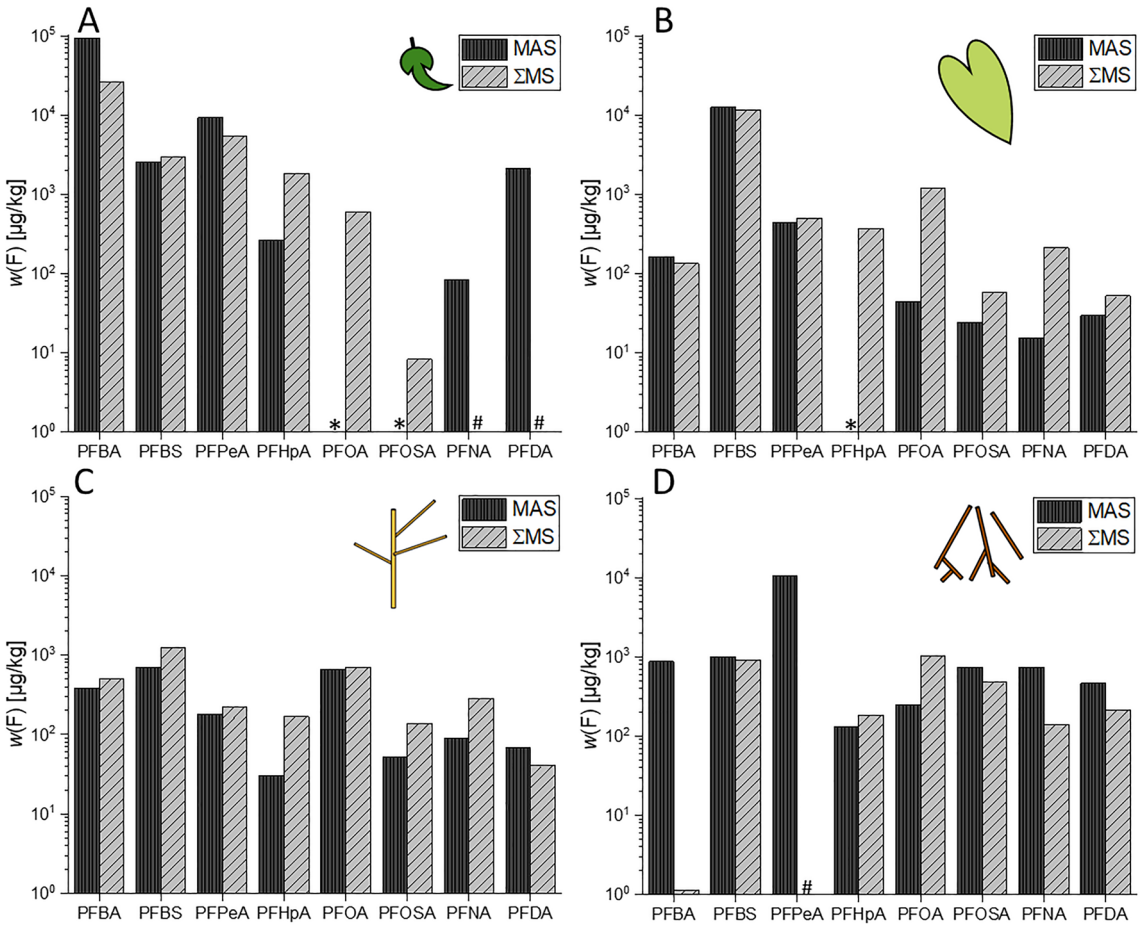

Fig. 2 Comparison of fluorine mass fractions *w*(*F*) determined by means of MAS (dark grey, vertical stripes) and by summarizing fluorine mass fraction of ten target PFAS (ΣMS) quantified by means of LC–MS/MS (light grey, oblique stripes) for eight pooled samples of plant compartments (A: fruits; B: leaves; C: stem; D: roots) grown on single substance PFAS spikes. *: *w*(*F*) determined by MAS < LOQ_{MAS}; #: *w*(F) determined by MS < LOQ_{MS}

plant compartments (see Fig. 2). Also, the amount of organically bound fluorine determined with the two compared quantification methods lead to differing $w(F)$ values. However, for most investigated single-spike samples $w(F)$ values were within the same order of magnitude.

Three phenomena were identified by comparing the $w(F)$-values of each sample determined with the two comprehensive quantification methods:

1. MAS and MS values were in good agreement/within the same order of magnitude.

   This would be expected for PFAS spike experiments using single substance spikes of known composition assuming that no metabolization during or after plant uptake and no transformation during sample preparation takes place.
2. $w(F)$ values determined with MAS were decisively higher than respective MS values.
   As observed for PFBA and PFPeA: the most obvious reason for this difference might be a transformation process which could have taken place either during PFAS uptake or during sample preparation. Another possible explanation for this phenomenon could originate from ionization efficiency correction factors used in this study according to DIN 38414-14 [21] calculated based on the intensity of the corresponding internal standard in the sample normalized to the intensity of this internal standard in external calibration. Hence, internal standard and corrected PFAS are not (inevitable) chemically identical and (can) have differing retention times in LC (see Additional file 1: Table S2), ionization conditions can differ and over- or underestimation can occur: e.g., PFPeA with a retention time $t_R = 7.2$ min is corrected based on the ionization efficiency of $^{13}C_2$-PFHxA with $t_R = 7.8$ min.
   An extreme of this phenomenon was observed for PFNA and PFDA where MS values were below LOQ while MAS values were decisively higher. Most probably, transformation of those PFAS took place. As other samples of the same spike experiments showed comparable MS signals, this transformation might have happened during PFAS uptake and could be compartment-specific. Furthermore, in literature barriers for particular within plant compartments were described—however, if transformation takes place barriers could be overcome and thus detected by our MAS method.
3. $w(F)$ values determined with MS were decisively higher than respective MAS values.
   Similar explanations can help for the third phenomenon: for PFHpA $w(F)$ values determined with MS were decisively higher than respective MAS values. PFHpA with $t_R = 8.2$ min was corrected via $^{13}C_4$-PFOAwith $t_R = 8.5$ min. It is to mention, that $w(F)$ values for all samples spiked with PFHpA determined by means of MAS are systematically lower than corresponding MS values.
   An extreme of this phenomenon was observed for PFOA and PFOSA where $w(F)$ values were both determined as below LOQ for MAS-quantification, while MS-quantification led to quantifiable results. For the PFOSA, the corresponding fluorine concentration in the final extract determined by MS was below the methodical LOQ of MAS ($c(\Sigma PFAS) = 1.5$ µg/L < $LOQ_{MAS} = 10.3$ µg/L), while the fluorine concentration of the corresponding PFOA samples extract determined via MS was higher than the methodical LOQ of MAS ($c(\Sigma PFAS) = 75.0$ µg/L > $LOQ_{MAS} = 10.3$ µg/L). Hence, a quantifiable amount of fluorine would have been expected. Therefore, for this sample the MAS quantification probably underestimated the PFOA mass fraction. A possible explanation for this could be a matrix effect causing signal suppression during MAS quantification.

Fruit compartment

For fruit compartment samples (see Fig. 2A) determined fluorine mass fractions varied between below LOQ (for MAS-quantification of PFOA and PFOSA; for MS-quantification for PFOSA, PFNA and PFDA) and over 92,750 µg/kg (for MAS-quantification for PFBA). Only for the PFBS-spiked sample determined $w(F)$ in fruits were in good agreement for both quantification methods: 2560 µg/kg (MAS) and 2950 µg/kg (MS). Both quantification methods led to highest $w(F)$-values in the fruit compartments for the PFBA-spike with 93,800 µg/kg utilizing MAS and 26,000 µg/kg utilizing MS, representing the overall highest $w(F)$-values determined in this study. Also, the two other short-chained PFAS PFBS and PFPeA were determined in high mass fractions valuing multiple times the $w(F)$ values in corresponding soil samples (compare Fig. 1), which indicates high bioaccumulation potential. For PFOA and PFOSA w(F) values determined by means of MAS were below the LOQ—hence, the fluorine concentration in the final extract was determined as below 10.3 µg/L—while corresponding values determined by means of MS were 590 µg/kg for PFOA and 10 µg/kg for PFOSA, respectively. For fruit samples from plants spiked with PFNA and PFDA it was the other way around: values determined via MS were below LOQ, while MAS quantification revealed $w(F)$ values of 80 µg/kg and 2110 µg/kg, respectively. This result is quit surprising since most studies on PFAS distribution in plants showed decreasing PFAS uptake with increasing

perfluorinated carbon chain length [14, 23, 24]. These studies were all based on MS quantification and are consistent with the $w(F)$ values determined via MS shown in Fig. 2A resulting in no or no relevant concentrations for PFNA and PFDA in fruits. As described above, transformation of long-chain PFAS could be a possible explanation for decisively higher MAS values for the fruits compartment after PFNA and PFDA spikes, since MAS quantification is not distinguishing between different PFAS species and therefore includes also unknown PFAS species as transformation products. For further interpretation deep characterization of resulting extracts with, e.g., non-target MS would be needed.

Leave compartment

For leave compartment samples of single PFAS spike experiments determined $w(F)$ values quantified by MAS ranged from below LOQ for PFHpA up to 12,400 µg/kg for PFBS (see Fig. 2B). Also, the highest $w(F)$ value quantified by MS was determined in the PFBS sample at comparable level (11,700 µg/kg), while the lowest value was determined for the PFDA sample. Comparing MAS and MS values for the leave compartment $w(F)$ were in good agreement for 5 out of 8 investigated samples. Fluorine mass fractions of PFHpA, PFOA and PFNA samples determined via MS-quantification were decisively higher than values determined via MAS-quantification. Therefore, MAS-quantification seems to underestimate these values. Hence, no matrix-matched calibration was used to determine MAS-quantification signal suppression due to matrix effects could be the reason for the underestimation. It cannot be excluded that this signal suppression also happened during the quantification of the other PFASs leading to underestimated values.

Remarkably high values were determined for PFBS in the leave compartment. A compartment-specific uptake of PFBS therefore seems likely.

Stem compartment

In the stem compartment $w(F)$ values were quantifiable for all samples of the single PFAS spike experiments for both quantification methods. Via MAS quantification $w(F)$ ranged from 30 µg/kg (PFHpA) to 700 µg/kg (PFBS) and MS-quantified values ranged from 40 µg/kg (PFDA) to 1220 µg/kg (PFBS) (see Fig. 2C). Comparing MAS and MS values, fluorine mass fractions were in good agreement, while those determined via MS were systematically higher—except for the stem sample from the PFDA spike experiment. Again, signal suppression could be the explanation for this systematic underestimation.

Root compartment

For the root samples from single PFAS spike experiments $w(F)$ determined by means of MAS were systematically higher than those determined via MS, ranging from 130 µg/kg (PFHpA) to 10,400 µg/kg (PFPeA) and from below LOQ (PFPeA) to 1040 µg/kg (PFOA) (see Fig. 2D). Exceptions are samples of PFHpA and PFOA spikes: for the PFHpA sample both values were still in good agreement, but with the MS value slightly higher than the MAS one, while for the PFOA sample the MS value was decisively higher.

Comparison of fluorine mass fractions in the four plant compartments

Comparing all four compartments with each other (Fig. 2A–D) and with determined fluorine mass fractions in corresponding soil (Fig. 1) it can be stated that investigated PFAS caused increased $w(F)$ values especially in the fruits compartment. Here, 9 out of 16 determined $w(F)$ were higher than determined values in corresponding soil samples. For the other compartments enrichment was found for 4 out of 16 for leaves, 5 out of 16 for stem and 6 out of 16 for root compartment samples. Highest values were determined for the three short-chained PFAS investigated, with fluorine mass fractions at least once higher than 10,000 µg/kg—PFBA in fruits, PFBS in leaves and PFPeA in roots. For one spike substance—PFNA—determined mass fractions in each compartment were lower than those in the corresponding soil sample. Reduced uptake or bioavailability may be a possible explanation for this. Nevertheless, discrimination of PFNA during sample preparation—especially during SPE—could also be a reason. Regarding this it is to mention that PFOA and PFDA which have similar chemical properties like PFNA, were determined in relevant mass fractions in various samples. Due to the limitations of an EOF-based sum parameter study isotope-labelled PFNA surrogate standard spikes were not a viable option to verify this hypothesis.

Comparing the two quantification methods, we noticed that $w(F)$ values determined by MS were higher than corresponding values determined by MAS in 19 out of 32 samples. This observation was expectable, because EOF determined by MAS is a sum parameter-based approach and therefore not optimized for each single PFAS. Additionally, while for target PFAS analysis by means of MS internal standards were used to correct matrix interferences, EOF was quantified using an external calibration without any matrix correction due to the lack of PFAS-free material for matrix-matched calibration and no possibility to use internal standards. Main exception for this observation was found for samples of the root compartment. Here, 6 out of 8 $w(F)$

values determined by means of MAS were higher than corresponding MS values. This could indicate negative matrix effects in root compartment on MS analysis. Hence, separating roots and soil without any residue of one compartment in the sample of the other was impossible. Therefore, higher complexity of the matrix is to be expected during ionization, possibly causing signal suppression in LC–MS/MS analysis.

PFAS in whole plants after single PFAS exposure

Values of all four compartments combined with dry weight of each compartment were used to calculate fluorine mass fractions for corresponding whole plants to compare the overall PFAS uptake depending on spiked substance. Resulting $w(F)$ based on whole plant dry weight are shown in Fig. 3.

Sum of $w(F)$ values taking into account the proportions of each compartment based on MAS-quantification ranged from 50 µg/kg (PFHpA) to 7120 µg/kg (PFBS), and 60 µg/kg (PFDA) to 6910 µg/kg (PFBS) for MS-quantification. Highest values were found for the three short-chained PFAS and in case of MS-quantification additionally for PFOA and PFHpA. For those three, respectively, five substances, whole plants bio accumulation factors (BAF) above 1 are reached when comparing mass fraction in the whole plant and corresponding soil (see Fig. 1)—ranging from 1.3 to up to 13. This indicates bioaccumulation of various PFAS in whole bean plants. Combined with data from Fig. 2, it seems that destination of PFAS in bean plants regarding

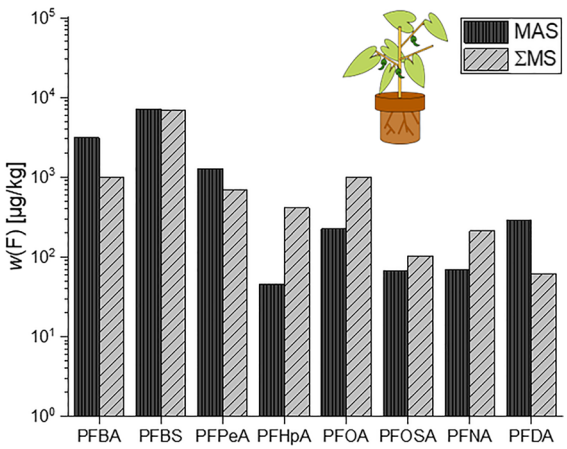

Fig. 3 Comparison of calculated fluorine mass fractions $w(F)$ in whole plants grown on single PFAS spiked soil. Calculations were based on dry weight of each compartment and $w(F)$ determined by means of MAS (dark grey, vertical stripes) and by summarizing fluorine mass fraction of 10 target PFAS (ΣMS) quantified by means of LC–MS/MS (light grey, oblique stripes) for 8 pooled samples of plant compartments

plant compartments is substance dependent. As an overall trend PFAS uptake decreases with increasing perfluorinated carbon chain length. This trend is consistent with results from comparable studies based on MS-quantification [14, 23, 24].

PFAS in plant compartments after mixed PFAS exposure

Besides the single substance spike experiments bean plants were exposed to 5 different mixtures of PFAS (see Table 1), cultivated, harvested, and comparted in the same way as described above. Pooled samples of the biological triplicates were quantified by means of MAS as well as MS. MS data were converted into fluorine mass fractions and compared with mass fractions determined via MAS quantification and PFOA calibration. Resulting data are summarized in Fig. 4. Due to sample loss, no mass fractions were obtained for stem samples of the bean plants exposed to mix 3 and mix 4.

Fruit compartment

Fluorine mass fractions determined in the fruit compartment by means of MAS ranged between 1120 and 4600 µg/kg (see Fig. 4A), with highest values for mix 1 and lowest for mix 5. Those determined via MS quantification were below LOQ for mix 1 while highest mass fractions were determined for mix 2 valuing 4500 µg/kg.

For fruit samples from plants spiked with mix 2, which was a mixture of known composition, four out of eight spiked PFAS were qualified via LC–MS/MS: PFBA, PFBS, PFPeA and PFHpA, which is consistent with results from single-spike experiments (compare Fig. 2A). Hence, those 4 PFAS were determined with highest $w(F)$. For all fruit samples from mixed spike experiments except for mix 2, $w(F)$s determined via MAS were higher than corresponding MS values. Largest difference between MAS and MS values was found for mix 1, where the highest $w(F)$ over all mixed spike samples was determined with MAS quantification, while no PFAS were quantifiable by means of MS. It is to note, that for those mixes with higher MAS values the spike composition was unknown and only 10 PFAS were quantified via MS.

For fruit samples from all mixed PFAS spikes, BAF were calculated as higher than 1—except for fruit sample of mix 2 determined via MS since this value was below LOQ. Therefore, for all investigated PFAS mixtures bioaccumulation of organically bound fluorine in the fruits compartment was observed.

Leave compartment

Determined $w(F)$ by means of MAS in leave compartments from mixed PFAS spike experiments ranged from 250 µg/kg for mix 5 up to 4040 µg/kg for mix 2 (see Fig. 4B). Corresponding MS values were determined in

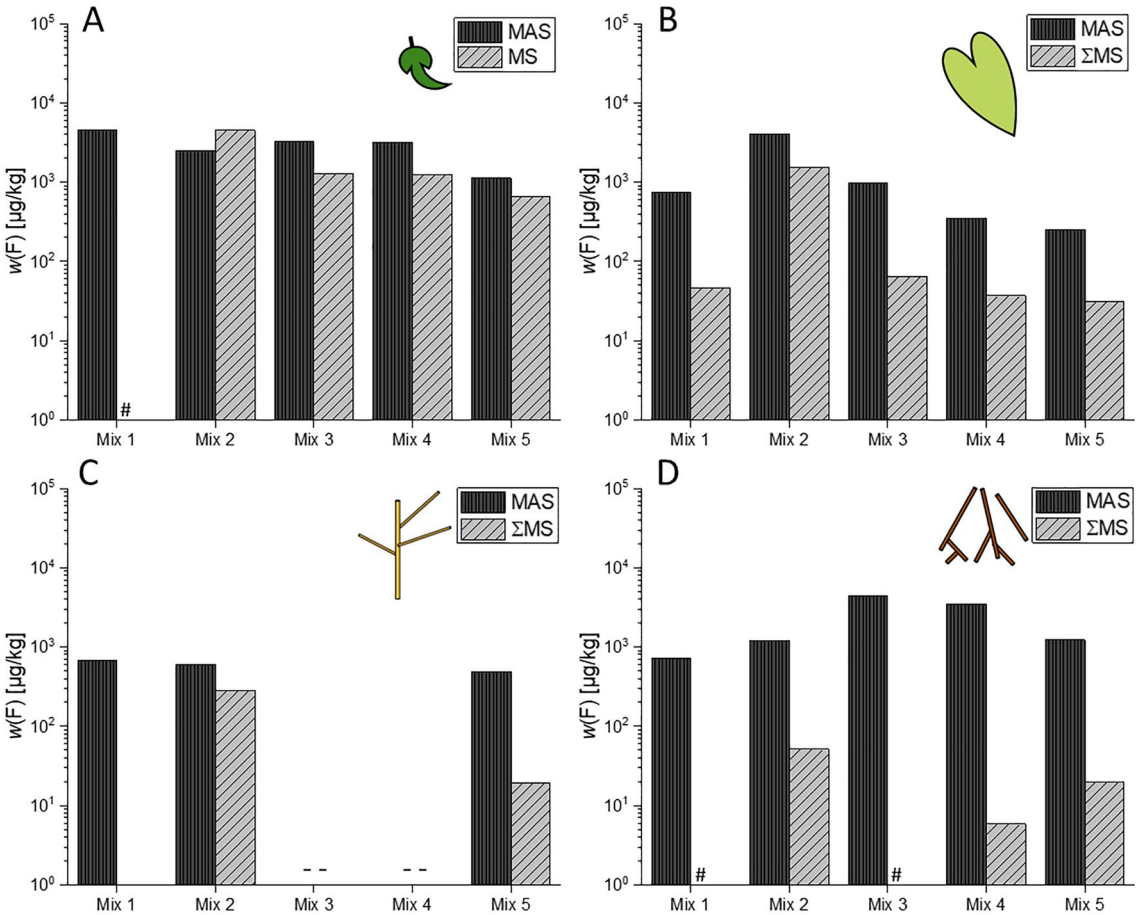

Fig. 4 Comparison of fluorine mass fractions *w*(*F*) determined by means of MAS (dark grey, vertical stripes) and by summarizing fluorine mass fraction of ten target PFAS (ΣMS) quantified by means of LC–MS/MS (light grey, oblique stripes) for five pooled samples of plant compartments (**A**: fruits; **B**: leaves; **C**: stem; **D**: roots) grown on mixed PFAS spikes. *w* (*F*) values for stem samples grown on spike mix 3 and 4 could not be determined due to loss of the corresponding stem sample extracts. #: *w*(*F*) determined by MS < LOQ_{MS}; –: no measurement possible due to sample loss

the range of 30 µg/kg (mix 1) to 1530 µg/kg (mix 2). For all leave samples values determined via MAS were systematically higher than corresponding MS values.

In the sample from mix 2 only PFBA and PFPeA were qualified by means of LC–MS/MS. Based on results from single substance spikes we expected to determine also PFBS, PFOA and PFHpA. Those were determined in higher or equally high *w*(*F*) as PFBA and PFPeA in leave compartment samples from single PFAS spike experiments.

Stem compartment

In stem compartment samples, all *w*(*F*) determined by means of MAS were systematically higher than corresponding MS values (see Fig. 4C). MAS values ranged from 490 µg/kg (mix 5) to 690 µg/kg (mix 1), while MS values were below LOQ for mix 1 and highest MS values were determined for mix 2. Here, four out of eight spiked PFAS were qualified and quantified: PFBS, PFPeA, PFHpA and PFOSA. In single-spike experiments investigating this compartment PFBA and PFOA spikes led to higher *w*(*F*) compared to PFPeA and PFOSA spikes (compare Fig. 2C). Therefore, it would have been expected to also find quantifiable amounts of those two PFAS in stem compartment after mixed PFAS spikes. For stem samples from mixed PFAS spike experiments 3 and 4 no data could be evaluated due to loss of the samples during sample preparation.

Root compartment

For root samples MAS values ranged from 720 µg/kg (mix 1) up to 4430 µg/kg (mix 3) and were systematically higher than corresponding MS values (see Fig. 4D). While for all extracts of the root compartment *w*(*F*) was quantifiable by means of MAS, using MS analysis *w*(*F*) values were only determined for 3 out of 5 samples with highest fluorine content in mix 2 (50 µg/

kg). This is in good agreement with results from single PFAS spikes. Hence, also MAS values were systematically higher than MS values (see Fig. 2D). Again, signal suppression caused by the complex matrix of the roots–soil interface might be a possible explanation.

PFAS in whole plants after mixed PFAS exposure

Whole plant EOF values for bean plants grown on mixed PFAS spiked soil were calculated by summing up $w(F)$ of each compartment multiplied with the compartment's mass fraction of the whole plant (see Fig. 5). For plants grown on mix 3 and 4 no EOF values could be determined since mass fractions for stem compartments were missing.

Determined MAS values were systematically higher than corresponding MS values for all whole plant samples with $w(F)$ ranging from 550–2590 µg/kg for MAS and from 20–1290 µg/kg for MS, respectively. Comparing MAS values for whole plant samples and corresponding MAS values for soil (compare Figs. 1 and 5) bioaccumulation of organically bound fluorine can be observed with bioaccumulation factors of 1.21 for mix 5, 1.44 for mix 1 and 3.51 for mix 2, respectively. Determined BAFs based on MS values in whole plant samples would only for mix 2 result in a BAF > 1 and thus indicate bioaccumulation. This means, only for the mixed spike of known composition MS quantification would have been sufficient to indicate bioaccumulation but not for any of the mixes with unknown composition.

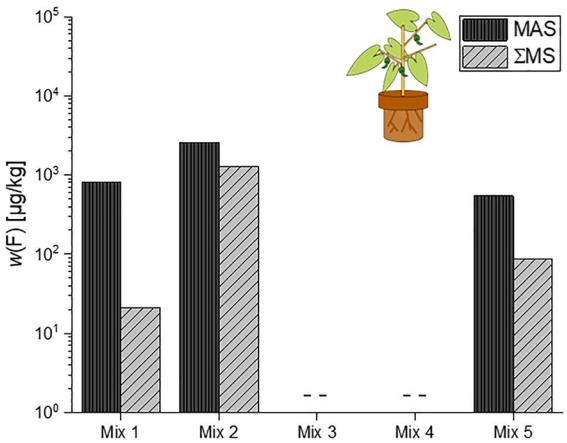

Fig. 5 Comparison of calculated fluorine mass fractions $w(F)$ in whole plants grown on mixed PFAS spiked soil. Calculations were based on dry weight of each compartment and $w(F)$ determined by means of MAS (dark grey, vertical stripes) and by summarizing fluorine mass fraction of ten target PFAS quantified by means of LC–MS/MS (light grey, oblique stripes) for five pooled samples of plant compartments. Whole plant values could not be calculated for mix 3 and mix 4 due to loss of the corresponding stem sample extracts. –: no calculation possible due to missing data for the stem compartment

Conclusion

In this study, PFAS uptake of plants grown on spiked soil as well as PFAS distribution into plant compartments was investigated using a comprehensive analytical approach of LC–MS/MS and MAS. Only by using single substance spikes it was possible to reveal substance-dependent PFAS uptake by applying a sum parameter method, hence MAS. By comparing $w(F)$ values determined with both methods in the different experimental settings, we identified three phenomena whereas (i) corresponding values were in good agreement; (ii) MAS values were decisively higher than sum of target-MS; (iii) MS values were decisively higher than MAS values. We discussed possible reasons for the different phenomena with different limits of quantification, PFAS transformation, matrix induced signal suppression and correction factors based on mismatching internal standards as main reasons for differences in corresponding data. Nevertheless, for most of the investigated samples, fluorine mass fractions determined with both analytical approaches were in good agreement.

Comparing results from the single PFAS spike experiments (Fig. 2A–D) and those from mixed (unknown) PFAS spike experiments (Fig. 4A–D), we observe that LC–MS/MS is the more powerful analytical method for known PFAS composition and matching isotope-labeled internal standards as it has lower limits of quantification and provides additional information regarding PFAS qualification. However, when it comes to unknown PFAS contamination, MAS is the more sensitive method yielding higher $w(F)$ values for investigated unknown PFAS compositions (mix 1, 3, 4 and 5). Therefore, MAS can be a highly valuable tool for screening of PFAS contamination and PFAS monitoring as well as to identify plants with high PFAS accumulation potential for, e.g., remediation purposes.

Comparing the two quantification methods, we noticed that $w(F)$ values determined using LC–MS/MS were higher than corresponding values determined via MAS in 19 out of 32 samples—this is mostly true in target analysis as well as lower LOQ of LC–MS/MS method; furthermore, correction factors in LC–MS/MS possibly overestimate some target PFAS. An exception for this observation was found for samples of the root compartment. Here, 6 out of 8 $w(F)$ values determined by MAS were higher than corresponding MS values. This could indicate negative matrix effects in roots compartment on MS analysis. Yet, separating roots and soil without any residue of one compartment in the sample of the other

was impossible. Therefore, higher matrix complexity is to be expected during ionization, possibly causing signal suppression in LC–MS/MS analysis.

Single substance spikes revealed a substance- and compartment-dependent PFAS uptake of French bean plants with varying bioaccumulation factors in both compartments and whole plants.

For the unknown mixed PFAS spikes $w(F)$ values determined by MAS were systematically higher than corresponding MS values resulting in contrary results regarding bioaccumulation of PFAS in investigated bean plants. MS values indicated no bioaccumulation for the PFAS spikes of unknown composition while MAS values clearly indicated bioaccumulation in whole plants for all tested PFAS mixtures.

Therefore, we conclude, that MAS is the superior tool to investigate uptake and fate of unknown PFAS mixtures from soil to plants. It can help to, e.g., identify potential candidates for PFAS phytoremediation of contaminated soils.

Additionally, investigated French bean plants showed high PFAS accumulation for some PFAS species—mainly for short-chained PFAS, especially in the fruits compartment. This opens up the possibility to use plants as markers for PFAS contamination in soils. The bioaccumulation can help to decrease limits of quantification to identify PFAS pollution sources—holding the species dependency of PFAS uptake in mind.

The bioaccumulation for investigated short-chained PFAAs in fruits and for PFBS also in leaves is alarming. If this finding can be reproduced for other plant species, even low PFAS soil contamination could end up in high PFAS exposure for humans due to enrichment via the food web. Therefore, besides PFAS monitoring and continuous reduction of PFAS usage, a better understanding of PFAS fate/bioavailability as well as efficient PFAS remediation strategies is needed.

With regard to the analytical methods used, it became clear in this study that PFAS analysis is diverse and powerful. Nevertheless, some questions have been raised that make further development desirable. MAS showed a species-specific response as described in Additional file 1: SI. The mechanics of GaF formation and defluorination of PFAS in the graphite furnace should be investigated and a species-unspecific EOF method should be developed. Furthermore, PFNA showed low mass fractions in all plant samples compared to all other PFAS investigated. Further studies based on target analysis should use isotope-labelled PFNA surrogate standards to investigate this phenomenon. Such surrogate standards interfere with sum parameter methods. Therefore, it was not possible to investigate it within in this study.

Supplementary Information

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Additional file 1. Chemicals and Methods.

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Author contributions

IR performed the planting study, sample preparation, and analyses at HR-CS-GFMAS. All authors read and approved the final manuscript. TW performed the LC–MS/MS measurements and the evaluation of the chromatograms. FS and MvdA assisted with data analysis and participated in the preparation of the manuscript. BM did the conception of the study and was involved in the creation of the manuscript. He contributes as corresponding author. LG did the conception of the study and analyzed target and sum parameter data comparatively. He contributes as first author.

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Availability of data and materials

Data and material are available upon request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Approved.

Competing interests

The authors declare that they have no conflict of interest.

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