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Quantitative Determination of Perfluorochemicals and Fluorotelomer Alcohols in Plants from Biosolid-Amended Fields using LC/MS/MS and GC/MS

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Supporting Information

ABSTRACT: Analytical methods for determining perfluorochemicals (PFCs) and fluorotelomer alcohols (FTOHs) in plants using liquid chromatography/tandem mass spectrometry (LC/MS/MS) and gas chromatography/mass spectrometry (GC/MS) were developed, and applied to quantify a suite of analytes in plants from biosolid-amended fields. Dichloromethane−methanol and ethylacetate were chosen as extracting solutions for PFCs and FTOHs, respectively. Nine perfluorocarboxylic acids (PFCAs), three perfluorosulfonic acids (PFSAs), and ten FTOHs were monitored. Most PFCAs and perfluorooctanesulfonate (PFOS) were quantifiable in plants grown in contaminated soils, whereas PFCs went undetected in plants from two background fields. Perfluorooctanoic acid (PFOA) was a major homologue (∼10−200 ng/g dry wt), followed by perfluorodecanoic acid (∼3−170 ng/g). [PFOS] in plants (1−20 ng/g) generally was less than or equal to most [PFCAs]. The site-specific grass/soil accumulation factor (GSAF = $[PFC]_{Grass}/[PFC]_{Soil}$) was calculated to assess transfer potentials from soils. Perfluorohexanoic acid had the highest GSAF (= 3.8), but the GSAF decreased considerably with increasing PFCA chain length. Log-transformed GSAF was significantly correlated with the PFCA carbon-length ($p < 0.05$). Of the measured alcohols, 8:2*n*FTOH was the dominant species (≤1.5 ng/g), but generally was present at ≥10× lower concentrations than PFOA.

INTRODUCTION

Over the course of the past decade, perfluorochemicals (PFCs) and their precursors (e.g., fluorotelomer alcohols; FTOHs) have generated serious concern within the public sector, government, and the scientific community alike.[1−3] These concerns have grown as new findings have accumulated regarding PFC environmental persistence, trophic-transfer potential, and toxicity to animals.[4−7] Given that PFC precursors, including polymers, are being used in a wide range of consumer products every day, recent findings that these chemicals can degrade to form PFCs[8,9] has provoked still more concern. In response to these findings, in January 2006 the U.S. Environmental Protection Agency (EPA) initiated the 2010/15 PFOA Stewardship Program with eight major fluorochemical companies to work toward elimination of select PFC emissions and content in products by 2015. This voluntary initiative action is expected to reduce environmental levels of PFCs over the coming years. Beyond addressing possible sources related to manufacturing, however, quantitative knowledge regarding the PFC source-to-exposure continuum largely remains lacking.

In a general sense, the migration of organic contaminants (OCs) from soil and water to plants and their subsequent consumption by animals is a likely pathway for OCs to enter the human food chain.[10] Many studies have shown that absorption by roots is not a significant pathway for lipophilic OCs (typically $K_{ow} > 104$) into plant tissues; instead, for these compounds, accumulation via aerial transport (gaseous phase for higher vapor-pressure and particulate phase for lower vapor-pressure OCs) is the dominant route.[11−13] In contrast, other studies have shown that plants can uptake certain halogenated OCs.[14−16] Plant OC-uptake studies of long-chain OCs with fluorine as the halogen, however, remain rare. In perhaps the only existing peer-reviewed study on plant uptake of PFCs, Stahl et al.[17] found that perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were translocated from spiked soils into various agricultural crops in a dose-dependent manner.

An essential component of risk assessment is the establishment of reliable analytical measurements of environmental samples. While there are a number of peer-reviewed publications reporting analytical methods for PFCs in air, water, and animal-tissue matrices, methodological studies remain sparse for PFCs in plant material. In this paper, we report on the development of analytical methods to quantify PFCs and FTOHs in plant samples. This effort follows recent publications,[18,19] wherein we reported elevated levels of a wide array of organic fluorochemicals in the

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Table 1. Year 2009 Plant Samples Collected from near Decatur, AL [a]

field/sample	common name	field description
09Bgdp	tall fescue	background field, no biosolids
09Hp	barley	one biosolid application historically
09F1p	tall fescue	biosolid-applied field
09D1p	tall fescue	biosolid-applied field
09G1p	bermuda grass	biosolid-applied field
09E1p	tall fescue	biosolid-applied field
09C1p	Kentucky bluegrass	biosolid-applied field

[a] These sample numbers are consistent with the system used for our earlier papers reporting upon PFCs and FTOHs in the soils[18,19] from which these plant samples were harvested; the "p" used for these samples designates "plant sample".

sludge-applied agricultural soils from which we collected the plants reported here. Integrating these new plant results with the earlier soil results, we also report site-specific PFC plant/soil accumulation factors. To our knowledge, this is the first peer-reviewed report on the enrichment of PFCs in plants grown in contaminated fields and serves as a starting point for assessing the potential contribution of biosolid soil applications to environmental and human food chains.

EXPERIMENTAL SECTION

Sample Collection/Preparation. Grass samples (Table 1) from fields near Decatur, AL that had received applications of sludge were collected by EPA regional personnel simultaneously with, and immediately above, soil samples that we reported upon in earlier papers[18,19] including (1) two sludge-applied fields in September 2007, and (2) six sludge-applied fields and one background field in March 2009, several months (the winter season) to more than a year subsequent to the last sludge application. The above-ground portion of grasses was collected by cutting the plants immediately above the ground surface with stainless-steel scissors that had been washed three times in Optima-grade methanol and then storing the samples in certified-clean, plastic bags, which we had spot checked to ensure they were not contaminated with our analytes. Upon return to the laboratory, samples were inspected for dust, dirt, or stains on the plant exteriors with the intent of discarding contaminated material if found; no exterior contamination was found. The plants were not washed for fear of contamination with FTOHs by sorption from laboratory air.[20] The plant samples then were homogenized by grinding using a methanol-washed mortar and pestle while adding liquid nitrogen. Homogenized samples were stored in 40-mL glass vials in a freezer until chemical extraction.

Extraction Methods. All chemicals used were of the highest purity offered by the suppliers, uniformly ≥97% purity; they are identified in the Supporting Information (SI1.1).

LC/MS/MS Analytes. In the absence of a peer-reviewed comparison of solvent efficacies for extracting PFCs from plants, we tested four general schemes for extracting PFCs from plants (Figure SI1), each consisting of a chemical-pretreatment step (HCl, dichloromethane (DCM), or 1% acetic acid (HAc)) in a hot bath with sonication for 30 min followed by an extraction step (methanol (MeOH) or methyl *tert*-butyl ether (MTBE)) with moderate shaking for 1 h. The following "pretreatment + extractant" combinations were evaluated: (1) 2.5 mL of 1 M HCl + 7.5 mL of MeOH; (2) 5 mL of DCM + 5 mL of MeOH, previously used for organochlorines in plant tissue;[13] (3) 3 mL of tetrabutylammonium mixture (TBA-mix; SI1.1) + 10 mL of MTBE, previously used for PFCs in biological matrices;[21] and (4) 2.5 mL of 1% HAc + 7.5 mL of MeOH, previously used for PFCs in sludge.[22] For each treatment, we prepared four approximately 1-g samples in 16-mL polypropylene carbonate (PPCO) centrifuge tubes which we spiked with 5 ng of $^{13}C_8$-PFOA as a recovery internal standard. Upon completion of solid−liquid extraction, solvents were separated using a Sorvall RCSC centrifuge at 10,000*g* for 30 min and transferred to preweighed 12-mL glass vials. Informed by exploratory efforts (Figure SI2), this two-step extraction was repeated once and the extracts (∼20 mL) were combined for further analysis. For the 2.5 mL/HCl + 7.5 mL/MeOH treatment, equimoles of NaOH were added to neutralize the HCl. Test extracts were cleaned up using an ion-pairing method [23] and prepared for LC/MS/MS analysis (SI1.2).

GC/MS Analytes. Three solvents (MTBE, ethyl acetate (EtOAc), and DCM) were compared for extracting FTOHs from plants (SI1.3). Based on recovery results, an extractant was selected (EtOAc) and used for extraction to analyze plants. In brief, 1 g of homogenized plant sample in a centrifuge tube received 5 ng of $^2H_4$,$^{13}C_2$-8:2*n* FTOH in MTBE as a recovery internal standard which was allowed to dry for 1 min. Five milliliters of polished 18-MΩ water (SI1.1) and 2 mL of EtOAc were added sequentially. The prepared plant-water-extractant mixture was rotated overnight on a Labquake rotisserie (Barnstead International, Dubuque, IA). The centrifuged EtOAc fraction was recovered with a disposable glass Pasteur pipet and transferred to a preweighed 12-mL glass vial. Informed by exploratory efforts evaluating cumulative recoveries (Figure SI3), this extraction step was repeated twice and the extracts were combined for each sample. Informed by exploratory efforts showing satisfactory recoveries upon blow-down ranging from 92% to 103% (Table SI6), combined extracts (5−6 mL) were blown down to 1 mL under a gentle stream of N_2 gas and were stored at −20 °C until analysis. Immediately prior to injection on GC/MS, 1 mL of extract was pipetted into a GC vial and 1 ng of $^2H_4$,$^{13}C_2$-10:2*n*FTOH was added as a matrix internal standard.

Extraction QA/QC. As part of our method development, supplementary tests were performed to ensure analytical performance. Extraction recovery statistics were determined using the chosen extractants, i.e., DCM + MeOH for PFCs and EtOAc for FTOHs. We inspected two common ion-transitions to evaluate potential effects of unknown coeluting components for PFCs quantitation (Table SI1). Both quantitation and qualification ion-transitions were used to construct calibration curves and measure the sample concentration. For FTOHs, we confirmed target peaks in plant extracts (SI1.7; Figure SI4) using derivatization with trimethylsilylimidazole (TMSI) and authentic FTOH standards (Table SI2).[20] Also, qualification ions were monitored. The effect of sample blow-off (5−6 mL to 1 mL extract) on potential losses of volatile analytes was evaluated as well (SI1.4).

Instrumental Analysis. PFCs in the extracts were separated and analyzed on a Waters Acquity ultraperformance liquid chromatograph (UPLC) interfaced with a Waters Quattro Premier XE tandem mass spectrometer that had been modified to optimize PFC analytical capabilities (SI1.5). FTOHs in plant extracts were separated and quantified on an Agilent Technologies 6890N GC system equipped with a 5973N mass-selective detector (MSD). Detailed information on the instrumental conditions and quantitation is provided in the Supporting Information.

Table 2. Results of Extractant Selection for PFC analysis in Plants (n = 4 using sample 09F1p; ng/g, wet wt)

treatment	C6	C7	C8	C9	C10	C11	C12	C13	C14	S4	S8	% rec[a]
(1) 25:75 1 M HCl−MeOH (v/v)												
mean	7.2	3.0	4.7	3.0	22.8	6.1	8.8	0.6	0.4	3.6	3.2	71
CV (%)[b]	6.3	3.8	3.4	5.4	4.3	5.5	4.0	2.1	5.3	33.3	3.5	6
(2) 50:50 DCM−MeOH (v/v)												
mean	9.2	4.9	6.9	4.2	42.4	11.5	15.7	1.1	0.5	3.1	5.1	109
CV (%)	7.7	6.7	6.2	8.8	6.0	3.5	10.7	13.4	14.8	24.0	16.2	6
(3) MTBE ion-pairing												
mean	10.1	4.2	4.9	3.0	23.6	6.8	10.7	0.7	0.5	2.4	2.3	78
CV (%)	4.9	6.1	8.5	16.5	12.8	15.6	22.0	16.5	10.8	28.1	12.9	10
(4) 25:75 1% acetic acid−MeOH (v/v)												
mean	8.9	4.2	6.0	3.7	32.6	9.0	13.4	0.9	0.5	3.1	3.7	97
CV (%)	12.9	8.2	10.6	5.4	4.9	7.1	10.0	4.9	8.8	40.3	2.7	3

[a] $^{13}C_8$-PFOA was spiked before extraction to assess extraction efficiency. [b] Coefficient of variation (%).

Method-detection limits (MDLs) were defined as the concentration corresponding to the mean peak area plus three standard deviations ($x + 3 \times \sigma$) [24] of extract from the plant sample from the uncontaminated site. The limit of quantitation (LOQ) was defined as the $x + 10 \times \sigma$ [24] for the uncontaminated-plant extract. Mean sample concentrations less than the calculated MDLs were reported as <MDL. For the calculation of mean values and modeling work, <MDL was treated as zero and <LOQ values were assigned 1/2LOQ. The LOQs for PFCs ranged from 0.2 to 1.0 ng/g dry weight (dw) except PFBS (26.0 ng/g). The LOQs for FTOHs ranged from 0.5 to 1.0 ng/g dw.

RESULTS

Selection of Extractant for Target Analytes. Table 2 summarizes the results for each extraction scheme including (1) 1 M HCl−MeOH and (2) 1% HAc−MeOH, (3) DCM−MeOH, and (4) a conventional ion-pairing extractant (MTBE). Extraction recoveries of $^{13}C_8$-PFOA were 71 ± 6% for HCl−MeOH, 109 ± 6% for DCM−MeOH, 78 ± 10% for MTBE−IP, and 97 ± 3% for HAc−MeOH treatment. At a glance, the binary combination of less-polar DCM and polar MeOH appeared to generate the greatest PFC yields among the test extractants. More rigorously, the extractability of DCM−MeOH also was statistically more effective than other extractant schemes for most PFCAs (C7 − C12), but not so for PFSAs (Table SI3). The acetic-acid and MTBE extractions followed the DCM−MeOH treatment in efficacy, while the HCl treatment resulted in the lowest extractions for PFCs in plant material (Table SI3).

As demonstrated in Table SI4, the EtOAc extraction generated greatest yields of target FTOHs in plants among extractants tested. In previous studies for air samples,[25,26] the EtOAc extraction method was developed to determine volatile polyfluorinated chemicals including FTOHs. The DCM extraction method also showed a comparable extractability for some analytes, but withdrawing DCM after centrifugation was difficult due to its high density relative to water. Additionally, we observed mild fatiguing of the test tube and loss of DCM at the end of overnight extraction. Given all the above considerations, we chose the EtOAc extraction for FTOHs analysis in plant samples. Further results of extraction QA/QC including number of repeated extractions, compound identification, and sample blow-down, are presented in Supporting Information (SI1.7).

Concentrations of PFCs and FTOHs in Vegetation. Concentrations of nine PFCAs and three PFSAs are summarized in Table 3. These are the only data in the peer-reviewed literature reporting PFC concentrations in field-grown plants of which we are aware. Sample 09Bgdp is from the background field, which received no sludge application, and 09Hp is from a dairy field that received only one sludge application in the distant past. In these fields, levels of all analytes were <LOQs; generally less than 1 ng/g dw except PFBS. Extraction efficiencies for all plant analysis were acceptable based on recoveries (96−112%) of $^{13}C_8$-PFOA spiked prior to extraction and the small standard deviations of replicated extractions. Most PFCA analytes were detected quantitatively in plants from the five fields that received multiple sludge applications (09C1p, 09D1p, 09E1p, 09F1p, and 09G1p),[18] while only PFOS exceeded its LOQ among PFSAs (Table 3). Sample 09D1p was the most contaminated with short- to midlength PFCAs (C6−C9). In contrast, longer chain PFCAs (≥C10) and PFOS occurred in the greatest concentrations in sample 09F1p. The highest PFOA contamination was found in sample 09D1p at almost 10-fold greater concentrations than other samples. Following PFOA, PFDA was the second-most loaded PFC in this study (168.8 ng/g in 09F1p). In general, plants collected in 2007 had PFC concentrations comparing closely with 2009-study samples 09E1p and 09G1p.

Concentrations of PFOS in plants ranged from 1.2 (09E1p) to 20.4 ng/g (09F1p). It is noteworthy that these PFOS levels were relatively less than PFOA and other PFCAs because in animal samples of blood and liver PFOS levels typically are high relative to PFCA levels.[5,6,27] The salient pharmacokinetic differences in animals are well-known for PFOA and PFOS; whereas both compounds are readily absorbed, PFOA has much faster depuration rates from the body than does PFOS, commonly resulting in much greater PFOS residue.[7,28] In contrast, the virtually nonvolatile nature of PFCs would seem to exclude depuration as a significant loss mechanism except perhaps by seasonal leaf fall in deciduous plants.

In contrast to acids, FTOHs were quantifiable in only a few plant samples and only at very low concentrations compared to their PFC degradation products (Table SI7). Of the alcohols, 8:2nFTOH generally was the dominant species, but it was

Table 3. Concentrations of PFCs in Plants (n = 3) from near Decatur, AL (ng/g dw)

sample ID		C6	C7	C8	C9	C10	C11	C12	C13	C14	S4	S6	S8	% rec[a]
09Bgdp (background)	mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.8	<MDL	104
	SD													4
09C1p	mean	22.9	10.4	23.2	8.9	48.9	22.9	43.5	3.5	2.5	<MDL	<LOQ	16.8	103
	SD	1.5	0.4	1.1	0.6	5.0	0.9	0.9	0.1	0.2			2.3	5
09D1p	mean	182.2	165.1	202.7	27.4	81.1	15.1	17.1	1.2	1.2	<MDL	2.9	13.1	112
	SD	4.2	15.6	16.2	1.8	3.5	1.1	0.4	0.1	0.1			0.5	10
09E1p	mean	30.2	12.5	9.9	1.5	3.3	0.5	0.5	<LOQ	<LOQ	<MDL	0.9	1.2	96
	SD	1.8	0.1	0.3	0.3	0.6	0.0	0.1					0.2	4
09F1p	mean	36.7	19.4	27.6	16.8	168.8	45.6	62.5	4.2	1.8	13.0	<MDL	20.4	109
	SD	2.8	1.3	1.7	1.5	10.1	1.6	6.7	0.6	0.3			3.3	6
09G1p	mean	26.3	8.2	12.1	2.9	9.8	3.3	4.3	0.5	0.3	ND	1.3	4.1	98
	SD	2.7	0.5	0.5	0.9	2.1	0.7	0.3	0.0	0.0			0.6	7
09Hp (single app.)	mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	109
	SD													3
07Ap	mean	38.1	8.9	21.1	6.1	19.9	3.6	3.7	0.4	0.8	<MDL	<MDL	11.2	104
	SD	3.0	1.0	1.8	0.6	1.6	0.2	0.3	0.0	0.0			2.1	7
07Bp	mean	181.7	17.3	11.7	1.3	1.9	0.4	0.7	<MDL	<LOQ	<MDL	0.7	2.5	97
	SD	9.7	0.3	0.9	0.3	0.3	0.1	0.1				0.0	0.6	8
MDL		0.4	0.3	0.8	0.3	0.3	0.1	0.2	0.1	0.1	17.0	0.4	0.4	
LOQ		1.0	0.5	1.4	0.5	0.5	0.2	0.3	0.2	0.2	36.0	0.6	0.8	

[a] $^{13}C_8$-PFOA was spiked before extraction to assess extraction efficiency.

present at about 10-fold lower concentrations than PFOA, ≤1.5 ng/g (Table SI7).

DISCUSSION

Inferences Regarding Possible Modes of Accumulation in Plants. Literature studies of PFCs uptake by plants remain sparse with only a single peer-reviewed paper describing a laboratory study of PFOA and PFOS uptake (Stahl et al.)[17] In this study, the investigators found that each of the five plant species they studied (i.e., wheat, oats, corn, ryegrass, and potatoes) accumulated PFOA and PFOS via uptake from the soil through the roots. These researchers found (1) the plant PFC concentrations were directly proportional to the PFC concentration of the irrigation water; (2) PFOA tended to accumulate at higher concentrations than did PFOS; and (3) the PFCs tended to accumulate more in the plant stalks and leaves than in the seed and potato vegetative bodies. The results of Stahl et al.[17] strongly suggest that at least some of the plant PFCs we observed in this study are from soil via transpiration of soil-water through the roots. However, it is important to acknowledge other possible mechanisms for PFC accumulation for the plants of our study as well. One possible alternative accumulation pathway is via aerial transport of volatile PFCA precursors[29] (e.g., FTOHs) with subsequent oxidation of the plant-bound FTOHs to form PFCAs. While the partitioning behavior of FTOHs might allow for this possibility,[30,31] our observation of nondetectable to very-low concentrations of FTOHs in the plants (Table SI7) is not strongly supportive of this pathway. Another alternative PFC pathway to grass tissue is contact transfer of sludge-based PFCs to the plants. In our study, however, all plant samples were collected several months to years after the last sludge application. Furthermore, we excluded any plant tissue with visible nonplant material from our analytical samples, so this pathway does not seem highly likely either. Given that our results are for plants from fields having no laboratory-type controls, and that only a single laboratory study has been published,[17] further laboratory controlled studies are appropriate to improve our understanding of PFC soil-to-plant transfer mechanisms.

Grass/Soil Accumulation Factor. Accumulation factors commonly are used to assess the bioavailability and bioconcentration of chemicals from media such as water, soil, and sediment. Because the grasses reported upon herein were collected immediately above the soils we have reported upon previously,[18] we can calculate grass/soil accumulation factors (GSAFs), i.e., the ratio of PFC concentrations (dw) in grasses to that in the soils from which they grew. These GSAFs are tabulated in Table SI8 and plotted against carbon chain-length in Figure 1A. In surface soils, PFCs likely are concentrated in organic matter;[32] implicitly assuming our measured soil PFCs all are present in the soil organic matter, we calculate grass/organic-matter accumulation factors (GOMAFs) in Table SI8 as well to facilitate comparison with, or use in, other studies.

The shortest PFCA in this study, C6, had the highest GSAF values (mean = 3.8) and accumulation potentials decreased considerably over the homologue range of C6 to C9 with a mean decrease of 32-fold. In contrast, for C9−C14, GSAFs decreased only about 2-fold. With log-transformation, the GSAFs are linearly correlated with chain length (Figure 1B), indicating lower transfer potential from soil to plants for long-chain PFCAs. GSAF values did not vary much among grass species in our study (Table SI8). For example, GSAFs for C7 were 0.75 for Kentucky blue grass, 0.47 for Bermuda grass, and ranged from 0.43 to 2.1 for tall fescue.

Comparison to Other PFC Accumulation Factors. Stahl et al.[17] did not report accumulation factors, but they provided the data needed to calculate GSAFs for corn, oat, and wheat. Taking the straw values of Stahl et al. as comparable to our above-ground grass samples, our PFOA GSAF (0.25 ± 0.23; Table SI8) equates to the corn GSAF (0.25 ± 0.08), and is

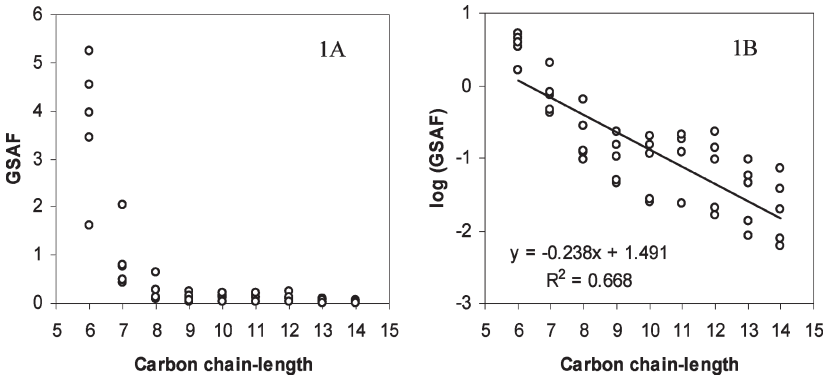

Figure 1. Relationship between GSAF and chain-length of PFCA. Rapid decrease of GSAF was found from PFHxA to PFNA (A). Log-transformed GSAF (B) was significantly correlated with number of carbons for PFCAs ($p < 0.05$).

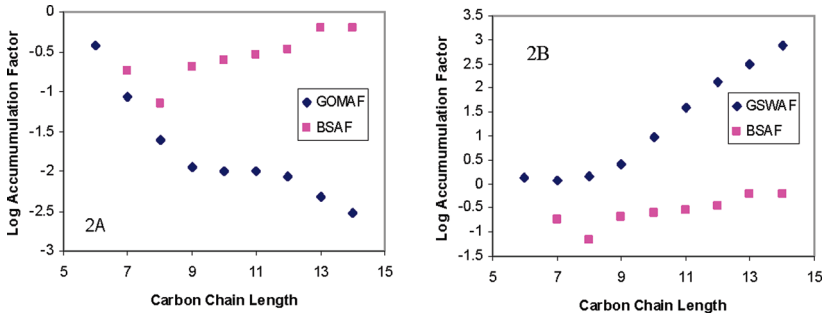

Figure 2. (A) Accumulation factor vs carbon chain-length in oligochaetes (BSAF)[33] and grasses (GOMAF; data from this study) normalized to sediment organic matter. When the grass accumulation factor is normalized to estimated soil-water (B; GSWAF), accumulation factors for both oligochaetes and grasses plot against chain length with positive slopes. See text for discussion.

less than that for oat (1.95 ± 1.90) and wheat (3.99 ± 1.81). Our PFOS GSAF (0.07 ± 0.04; Table SI8), falls a little below the range we calculate for Stahl et al. of 0.16 ± 0.04 for corn to 0.77 ± 0.55 for wheat.

Lasier et al.[33] recently reported PFC concentrations for aquatic worms (*Lumbriculus variegatus*) grown in contaminated sediments. Using these data, the researchers calculated biota/sediment accumulation factors (BSAFs) which they defined as PFC concentrations in the worms divided by the sediment PFC concentration normalized to the sediment organic matter. As such, the BSAF of Lasier et al.[33] is analogous to the GOMAF of our study in that both statistics are defined as the ratio of PFC concentrations in the organism (above-ground fraction for the plants) to the sediment (soil) concentration normalized to the organic-matter fraction. These accumulation factors are plotted against carbon-chain length in Figure 2. PFC accumulation from organic matter is greater in the worms (BSAF) than the grasses (GOMAF) for all homologues (Figure 2), possibly owing partly to PFC accumulation in fatty tissue present in worms that is absent in grasses. In addition, the grasses and worms exhibit opposing habits in accumulation of PFC homologues from organic matter; whereas the worm accumulation factor increases with lengthening chains, the grasses accumulate in short chains preferentially over long chains (Figure 2). These opposing trends for worms and grasses might reflect that PFCs accumulate in the worms by direct ingestion of PFC-laden organic matter, whereas plants presumably uptake the PFCs with soil-water into which PFCs have dissolved from the organic-matter reservoir. If this is correct, then the grasses might be expected to exhibit higher accumulation factors for the long-chained PFCs when normalized to soil-water concentration, i.e., concentration in the plant divided by concentration in the soil-water. Estimating water concentrations using K_{ow} values[34] as proxy for K_{oc}, we can estimate grass/soil-water accumulation factors (GSWAFs). When GSWAFs are plotted against homologue length they exhibit a positive slope with increasing chain length, consistent with the accumulation factors for the worms (Figure 2) supporting the idea that sorption to organic matter is the reason for the negative relationship between GOMAFs and chain-length. Regardless of the cause for the opposing slopes between the grass/and worm/organic-matter accumulation factors when plotted against chain length, a possible consequence of this is that food chains based on direct ingestion of sediments contaminated with PFCs might tend to accumulate long-chained PFCs more so than food-chains in which rooted plants serve as the basal trophic level and vice versa for the short chains.

■ ASSOCIATED CONTENT

Supporting Information. Text, tables, and figures referred to in this article with the designation SI. This information is available free of charge via the Internet at http://pubs.acs.org/.

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