Extraction of poly- and perfluorinated alkyl substances (PFAS) from solid matrices

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✍ABSTRACT

Recent studies suggest that toxic and highly persistent poly- and perfluorinated alkyl substances (PFAS) are much more prevalent in tissue and soil than in water. The increasing length of perfluoroalkyl chain in PFAS is correlated strongly to lower solubility/higher adsorption behaviour of a particular PFAS molecule in the environment. This poses a significant challenge to developing analytical methods, especially for the extraction of PFAS from solid matrices. The adsorption and mobility of PFAS (perfluoroalkyl chain length C6-C14) through soil were investigated by rinsing a soil column with 60 mL spiked rainwater at pH 4, pH 10 and pH 5.3. PFAS which adsorbed onto the soil column were extracted using a conventional vortex/sonication method. Aqueous eluate and extracts were analyzed using LC-MS/MS and quantified using an internal standard method. PFAS with chain length C6-C9 migrated completely or partially through the column and were effectively extracted from soil with 100% recovery. However, long-chain PFAS (C12-C14) did not appear to migrate through the column and had less than 50% recovery from the soil. The same extracted soil was then subjected to high-pressure accelerated solvent extraction (ASE) which yielded 100% recovery for long-chain PFAS. By extension, the application of ASE for the extraction of PFAS from mussel tissue and cooking oil was also investigated. Oil samples were spiked at 10 ng/g and tissue samples spiked at 25 ng/g. These samples were incubated and then subject to ASE. Recoveries of PFAS from these matrices were acceptable for all analytes and were highest for C11-C14. Blanks contained no significant amounts of PFAS. The use of ASE for extraction of longer chain perfluoroalkyl acids (C16, C18), sulfonates and sulfonamides from solid matrices was also investigated. The results of this study will inform our understanding of how to evaluate the transport of PFAS through soil and the assessment of PFAS bioaccumulation in tissue and food.

METHODS

SPIKING

↳ SOIL

10 g soil was washed through with 60 mL water at pH 4, pH 5.3 and pH 10, spiked at 10 ng PFAS. 4 spikes and 4 blanks were processed.

↳ MUSSEL TISSUE

2 g mussel tissue was spiked with 50 ng PFAS. 4 spikes and 4 blanks were processed and analyzed.

↳ COOKING OIL

2 g canola oil was spiked with 20 ng PFAS. 4 spikes and 4 blanks were processed and analyzed.

EXTRACTION

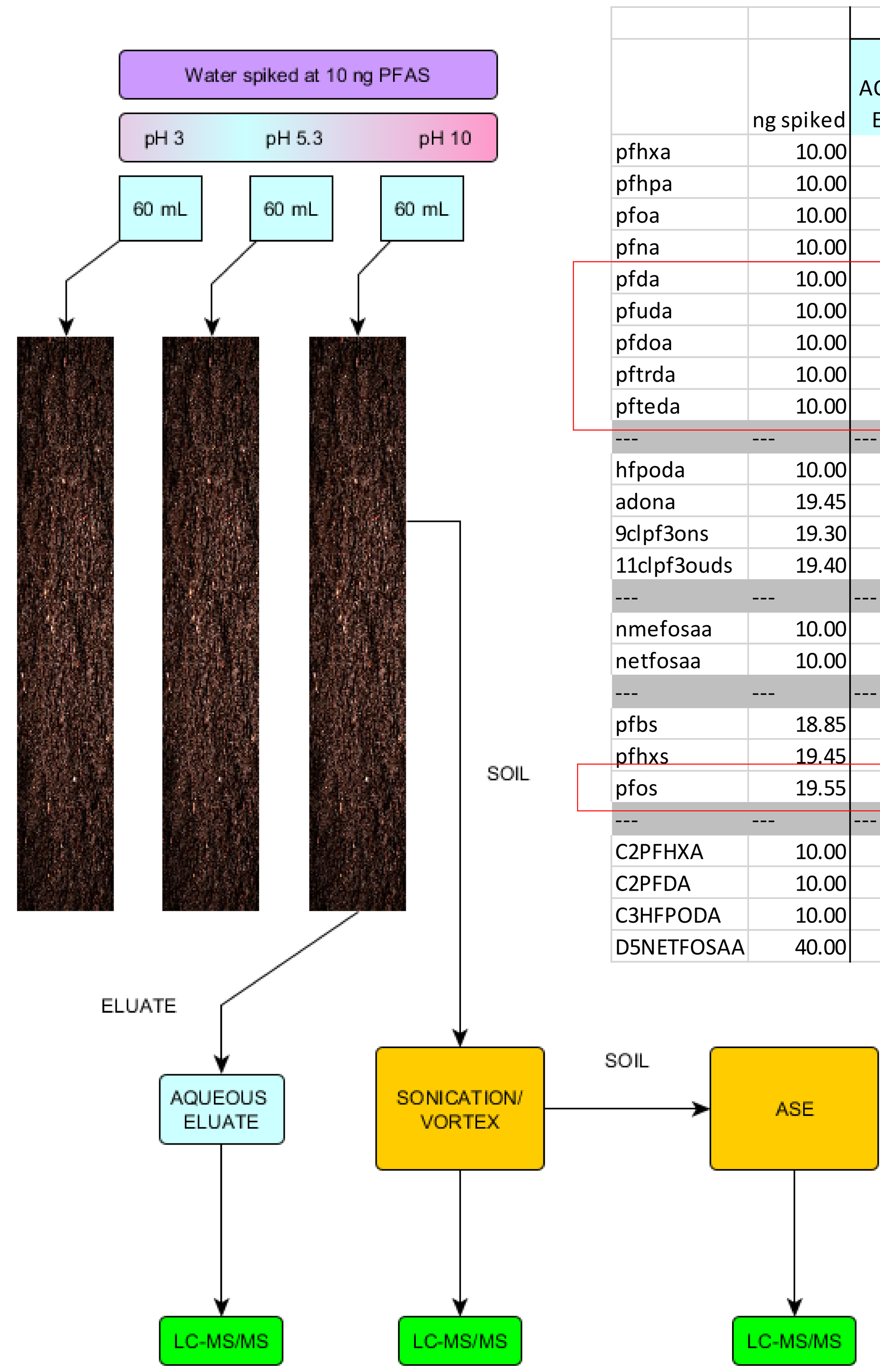
↳ 1. SONICATION/VORTEX

Solid sample is mixed with 1:1 methanol:water, sonicated and vortexed for 5 minutes.

↳ 2. ACCELERATED SOLVENT EXTRACTION

Solid sample is mixed with methanol and subject to methanol extraction under high pressure and temperature.

"SEARCHING FOR LONG-CHAIN PFAS" IN SOIL



		% RECOVERY		
	ng spiked	AQUEOUS ELUATE	AFTER SONIC/ VORTEX	AFTER ASE
pfhxa	10.00	98%	3%	10%
pfhpa	10.00	225%	0%	5%
pfoa	10.00	188%	14%	9%
pfna	10.00	92%	98%	24%
pfda	10.00	9%	192%	43%
pfuda	10.00	1%	106%	61%
pfdoa	10.00	0%	44%	67%
pftrda	10.00	0%	38%	80%
pfteda	10.00	0%	0%	92%
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hfpoda	10.00	78%	2%	0%
adona	19.45	194%	2%	4%
9clpf3ons	19.30	9%	121%	35%
11clpf3ouds	19.40	0%	33%	51%
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nmefosaa	10.00	4%	82%	57%
netfosaa	10.00	1%	60%	84%
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pfbs	18.85	106%	5%	6%
pfhxs	19.45	196%	6%	4%
pfos	19.55	29%	163%	54%
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C2PFHXA	10.00	68%	0%	2%
C2PFDA	10.00	9%	86%	26%
C3HFPODA	10.00	54%	0%	0%
D5NETFOSAA	40.00	2%	42%	50%

ANALYSIS

Extracts were analyzed via LC-MS/MS (SRM) using a Thermo Vanquish LC and TSQ Quantis MS.

RESULTS

1. pH has no significant effect on the adsorption of PFAS to soil under the conditions investigated.
2. C6 to C8 PFAS migrated completely or partially out of the soil column and were present in the aqueous eluate
3. C10 to C14 PFAS did not appear to migrate through the soil under the conditions investigated and were not present in the aqueous eluate.
4. C11 to C14 PFAS were extracted in under 50% recovery from the soil using a conventional sonication/vortex method
5. C11 to C14 PFAS were extracted fully from soil using accelerated solvent extraction (ASE)
6. All PFAS tested, including C10-C14 PFAS, were also extracted in high yield from tissue and cooking oil using ASE.

ASE of PFAS from oil, mussel tissue and soil

Matrix = 2 g oil

4 spikes, 4 blanks

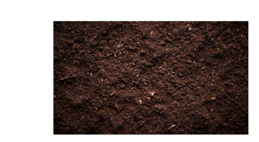
	ng spike	AVERAGE RECOVERY	AVERAGE RECOVERY BLANK
pfhxa	20	85%	0%
pfhpa	20	71%	0%
pfoa	20	104%	0%
pfna	20	116%	0%
pfda	20	93%	0%
pfuda	20	79%	0%
pfdoa	20	161%	0%
pftrda	20	319%	0%
pfteda	20	247%	0%
hfpoda	20	70%	0%
adona	38.9	74%	0%
9clpf3ons	38.6	79%	0%
11clpf3ouds	38.8	94%	0%
nmefosaa	20	116%	0%
netfosaa	20	92%	0%
pfbs	37.7	70%	0%
pfhxs	31	66%	0%
pfos	30.4	101%	0%
surrogates			
C2PFHXA	10	75%	114%
C2PFDA	10	86%	62%
C3HFPODA	10	64%	71%
D5NETFOSAA	40	90%	107%

Matrix = 2 g Mussel tissue

4 spikes, 4 blanks

	ng spike	AVERAGE RECOVERY	AVERAGE RECOVERY BLANK
pfhxa	50	75%	6%
pfhpa	50	69%	1%
pfoa	50	93%	2%
pfna	50	110%	1%
pfda	50	101%	0%
pfuda	50	89%	0%
pfdoa	50	112%	0%
pftrda	50	117%	1%
pfteda	50	151%	2%
hfpoda	50	68%	0%
adona	97.26	64%	1%
9clpf3ons	96.5	88%	0%
11clpf3ouds	97	63%	0%
nmefosaa	50	84%	0%
netfosaa	50	106%	0%
pfbs	94.26	78%	2%
pfhxs	97.26	85%	0%
pfos	97.76	89%	2%
C2PFHXA	10	74%	125%
C2PFDA	10	106%	84%
C3HFPODA	10	66%	91%
D5NETFOSAA	40	125%	94%

Matrix = 10 g soil



1 spike, 4 blanks

	ng spike	AVERAGE RECOVERY
pfhxa	10	10%
pfhpa	10	5%
pfoa	10	9%
pfna	10	24%
pfda	10	43%
pfuda	10	61%
pfdoa	10	67%
pftrda	10	80%
pfteda	10	92%
hfpoda	10	0%
adona	19.45	4%
9clpf3ons	19.3	35%
11clpf3ouds	19.4	51%
nmefosaa	10	57%
netfosaa	10	84%
pfbs	18.85	6%
pfhxs	19.45	4%
pfos	19.55	54%
C2PFHXA	10	2%
C2PFDA	10	26%
C3HFPODA	10	0%
D5NETFOSAA	40	50%

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CONCLUSIONS

Accelerated solvent extraction (ASE) is an effective technique for extracting a variety of PFAS, most notably long-chain PFAS >C11, from several solid matrices. The use of ASE for extraction of longer chain perfluoroalkyl acids (C16, C18), sulfonates and sulfonamides from solid matrices was also investigated and continued the trend of high extraction of long-chain PFAS using ASE. The results of this study will inform our understanding of how to evaluate transport studies of PFAS through soil and the assessment of PFAS bioaccumulation in tissue and food.