Precursors, Novel and Ultrashort PFAS in Soils and Leachates

Patrick van Hees[1,2,*], Marko Filipovic[3], Patrik Karlsson[4], Bei Wang[2], Linn Lindblom[4], Leo Yeung[2]

[1]*Eurofins Environment Testing Sweden AB, Sjöhagsgatan 3, 531 17 Lidköping, Sweden*
[2]*Man-Technology-Environment (MTM) Research Centre, Örebro University, 701 82 Örebro, Sweden*
[3]*Niras Sweden AB, Fleminggatan 14, 112 26 Stockholm, Sweden*
[4]*Eurofins Food & Feed Testing Sweden AB, Sjöhagsgatan 3, 531 17 Lidköping, Sweden*
** patrickvanhees@eurofins.se*

Per/polyfluorinated substances (PFAS) is a group of contaminants for which further knowledge is essential. The picture is complex in terms of occurrence, composition, tools for risk assessment and remedial actions. As the historically most used PFAS e.g., PFOS and PFOA, have been banned and/or phased out, there has been a shift to shorter homologues. However, there are also other replacement products, often called "novel" PFAS. In this context "novel" may also refer to PFAS that so far has been (largely) overlooked. Among these various sulphonamides, telomer degradation products and ultrashort (C≤3) PFAS can be mentioned. Precursors are compounds that have the potential to transform into perfluorinated carboxylic and sulfonic acids (PFCAs and PFSAs). The need to include these has become more pronounced in evaluation of PFAS contamination. This can, in some cases, be through direct analysis or indirectly by using the total oxidizable precursor assay (TOPA). Also leaching of PFAS from soil is of interest in a broader assessment, not at least when considering groundwater protection.

Aim

The objective of this work was to perform a more comprehensive characterization of PFAS in five AFFF polluted soils. Analysis was performed including known "regular" PFAS (34) and a range of novel PFAS e.g. ethers, sulphonamides, ultrashort and some known AFFF constituents e.g. 6:2 FTAB. TOPA was used as a tool for determining precursors and gain information on their (basic) structures. Ultrashort PFAS were also analyzed after TOPA in the soils to measure its formation. Leaching tests were carried out; novel and PFAS34 were analyzed in leachates before TOPA and PFAS34 after. The pattern of formed PFCA and branched/linear isomers before/after TOPA were evaluated to distinguish between ECF (electrochemical fluorination) vs telomerization production, in order to estimate fluorotelomer (FT) and sulphonamide (SA) precursors.

Material and Methods

Soils were sampled from five different locations at a site in Sweden where AFFFs are and have been historically used. Each sample was collected from three test pits within a 10x10m grid, where topsoil (0-0.5m) was collected in HDPE-bottles; samples are denoted as Soil 1-4, 6. Before analysis, soils were dried at 35°C, sieved <2mm and milled. All analytical results thus refer to dry sample. Leaching with water was performed in batch tests with L/S=10 in accord with EN12457-2. Extraction of PFAS in soil was carried out with alkaline methanol. Leachates were centrifuged before analysis. The procedure for TOPA was slightly modified from Houtz et al. (2012; 2013). PFAS originally present and after TOPA were determined using UPLC-MS/MS, and ultrashort acc. to Björnsdotter et al (2019). Branched (Br) and linear (L) isomers of PFASs were quantified separately.

Results

∑PFAS34 (incl PFCA, PFSA, FTSA, PreFOS) showed between <100–23000 ng/g (Table 1; Fig 1) in soils and 2600-160 000 ng/l in leachates. PFOS was the most commonly detected and dominant in soil 3+4. In contrast in soil 2, the highest concentrations were found for 6:2 and 8:2 FTSA. The composition in the leachates was similar to the soils but with a small shift towards more short-chain PFAS (not shown). Telomer degradation intermediates (12 FTCA/FTUCA/FTOH) were frequently detected, but mostly with limited quantitative impact (Table 1). 5:3 FTCA was the major in the group. The amides FBSA and FHxSA were both identified, especially in soil 3+4. Ultrashorts were analyzed in soil and PFPrA was observed in all, while PFPrS in soil 3+4 mainly. Ethers incl ADONA and F53-B (6:2 Cl-PFAES) could not be detected in soil nor in the leachate (not shown).

(a)

Soil (ng/g)	Regular ∑PFAS34	ΣFTCA/ FTUCA/ FTOH	PFPrS	TFA	PFPrA	FBSA	FHxSA	N-TAmP-FHxSA	N-AP-FHxSA	6:2 FTAB
1	100	6.4	<0.02	< 5	13	0.02	0.2	0.02	<0.03	210
2	470	17	<0.02	< 5	31	0.05	0.3	0.02	<0.03	3660
3	3800	33	0.7	< 5	24	1.2	27	0.82	2.6	170
4	23300	10	22	< 5	32	4.6	120	19	4.0	1040
6	68	2.8	0.02	< 5	12	0.02	0.2	0.05	0.02	0.8

(b)

Leachate (ng/l)	Regular ∑PFAS34	ΣFTCA/ FTUCA/ FTOH	PFPrS	FBSA	FHxSA	N-TAmP-FHxSA	N-AP-FHxSA
1	3200	280	<5	3	16	<5	<5
2	6900	1350	<5	7	37	<5	<5
3	22500	590	27	140	650	17	8
4	162000	280	500	420	5100	180	6
6	2600	99	<5	3	11	<5	<5

Table 1. Regular PFAS-34, ultra-short, sulphonamides and 6:2 FTAB in **(a)** soil in [ng/g] and **(b)** leachate in [ng/l].

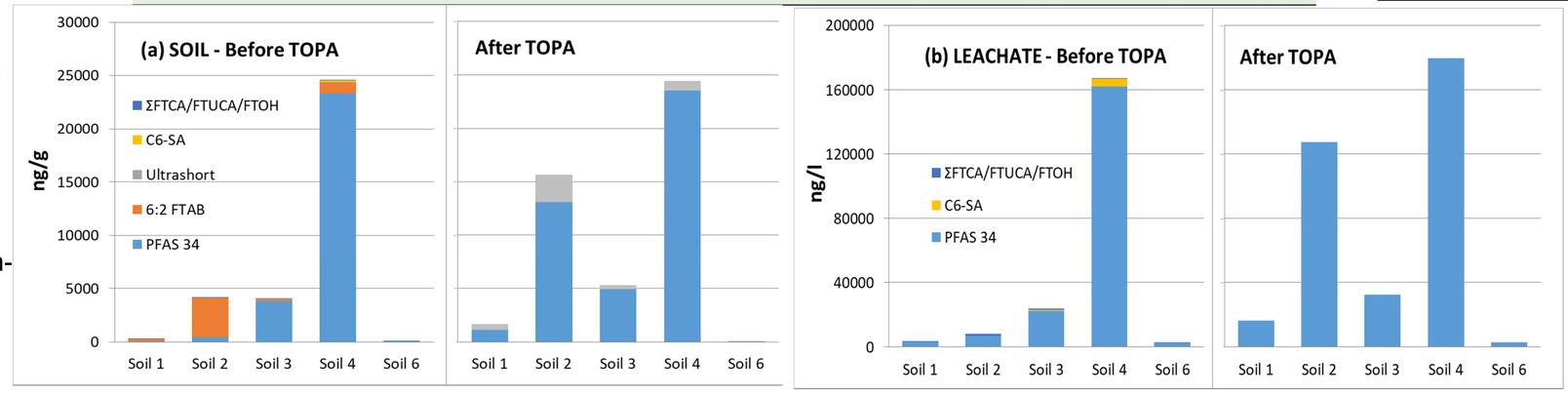

Fig 1. Composition of PFAS before and after TOPA **(a)** Soil, **(b)** Leachate. SA= sulphonamides

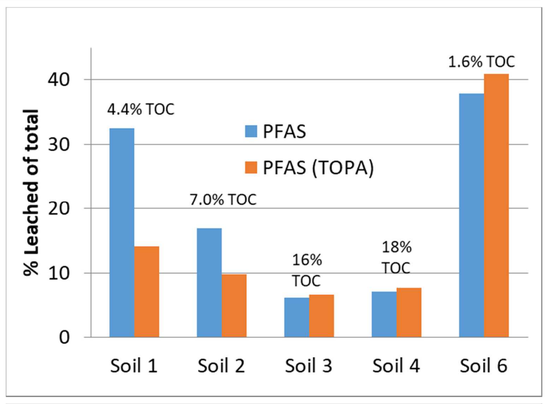

Fig 2. % leached PFAS (PFAS-34 + sulphonamides + ΣFTCA/ FTUCA/FTOH before and after TOPA**.** TOC values refer to soil samples

A minor level of PFECHS (0.05 ng/g) was found in soil 6. Among known AFFF substances, besides PFAS34, N-TAmP- and N-AP-FHxSA were identified in low concentrations. 6:2 FTAB was found in all soils, especially 2 and 4. PFAS34 before TOPA made up 4-100% (soil) and 5-90% (leachate) of the sum afterwards, a variation likely caused by the composition of AFFF used on site. Soils/ leachates 1-4 showed significant increases in PFCA (C4-C9) with the largest relative change observed for 1-2 (Fig 1). Ultrashort PFCA, up to 2500 ng/g (>96% PFPrA) was also formed after TOPA in soil (Fig 1). Measurable precursors were oxidized by >85%, frequently >99%.

The percentage leached of the total soil PFAS content varied between 6-41% and was generally less at higher soil TOC level (Fig 2). The fraction could after TOPA either decrease or slightly increase.

Discussion

The results of this work demonstrate that a wider scope of PFAS analysis yields additional knowledge when investigating AFFF contaminated soil. For example, the presence of FT acids/alcohols is likely to indicate degradation of telomer precursors, though levels are moderate. 6:2 FTAB is known to be present in modern AFFF products (KEMI, 2015), and is here shown to be a significant soil pollutant and major PFAS in two soils. Identification of C6-SA, in particular FHxSA, suggested that these amides can be important alongside PFHxS. Moreover, the outcome showed the occurrence of ultrashort PFAS, in particular PFPrA.

For TOPA, substantial amounts of especially C4-C6 PFCA (highest for C5) were formed. The sum of PFAS varied from largely unchanged to +2800% or +270% if 6:2 FTAB was taken into account.

Formation of C4-C6 PFCAs is consistent with the pattern of 6:2 precursors (Houtz et al., 2012), and that 6:2 FT constitutes the main structure of modern AFFF (KEMI, 2015). The identity of the precursors was further indicated by the fact that (almost) only linear C4-C6 PFCAs was produced, pointing to a telomere origin. In soil 1+2 levels of linear C7-C9 PFCAs implied 8:2 FT too. Another observation is that C2/C3 (mainly PFPrA) comprises an important part of the PFCAs after TOPA. In soil 1-4 the molar fraction was 23-47%. In comparison, yields of PFPrA for 6:2 FT substances ranged from 17-30% in the paper by Martin et al (2019). In two soil and leachate samples (3,4), some Br-PFHxA/PFOA were seen after TOPA indicating the presence of ECF C6/C8 SA precursors. This was also implied by the partly Br-C6 SA and FOSA (tot 110-250 ng/g) found in these soils. 6:2 FTAB corresponded to 3-12% on molar basis of the TOPA C2-C9 PFCAs.

Calculation of precursor "types" revealed by TOPA was performed for soil 2 and 4 (Fig 3) with 6:2/8:2 telomers estimated from TOP pattern and molar ratios published by Houtz et al (2012). All ultrashort was assigned to 6:2 FT. C6/C8 SA precursors were computed from the Br-fraction of FOSA/FHxSA. 6:2 precursors contributed the most followed by 8:2, with limited amounts of C6/C8 SAs in soil/ leachate 4. The 6:2/8:2 ratio in soil 2 is similar to the pattern of some AFFF in Houtz et al (2013), if ultrashort is left out. 6:2 FTAB contributed to about 15% (molar basis) of the calculated 6:2 precursors and measured C6-SA 26% of the total SA.

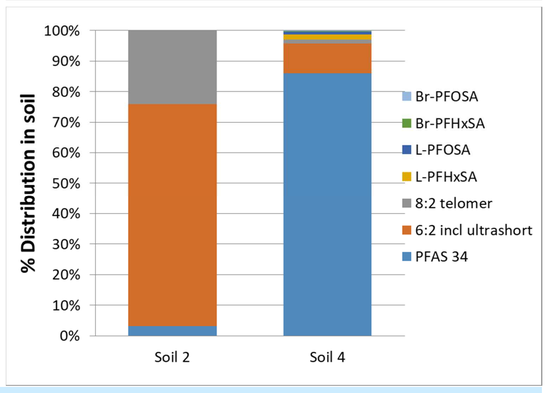

Fig 3. % (w/w) distribution after TOPA of PFAS-34 and calculated relative contributions of precursors for soil 2 and 4.

Conclusions

- PFAS composition in the 5 soils reflected AFFF used and was mirrored in both soils and soil leachates (L/S=10)
- Leaching tests showed that 6-41% of the total PFAS content was released with a tendency for shorter PFAS.
- TOPA revealed unknown precursors to a significant degree. Regular PFAS34 made up <5-100% in soil/leachate of the sum after TOPA, a fraction not possible to assess on beforehand.
- Determination of FTCA/FTUCA/FTOH indicated FT degradation, though concentrations were moderate
- Analysis of known AFFF substances yielded additional information. 6:2 FTAB was found in all soils and was the dominant PFAS in two. Also C6-SA could be identified.
- The prescence of PFPrA in soil was shown. Formation of ultrashort PFAS, especially PFPrA after TOPA was highly significant corresponding to 23-47% on a molar basis
- Patterns of PFCA formed indicated origin of the precursors, primarily 6:2 but also 8:2 FT based. Br forms suggested minor contributions of C6/C8 SAs
- Measured precursors, in particular 6:2 FTAB could explain some of total PFCA formed but the major part remained unknown, warrenting further studies

References

Björnsdotter, M.K, Yeung, L.W.Y., Kärrman, A,. Jogsten, I.E. Environ. Sci Tech. 2019, 53, 11093-11101

Houtz, E. F., Sedlak, D. L. Environ. Sci. Technol., 2012, 46, 9342−9349

Houtz, E. F., Higgins, C. P., Field, J. A., Sedlak D. L. Environ. Sci. Technol. 2013, 47, 8187−8195

KEMI PM 6/15, 2015, Stockholm

Martin, D., Munoz, G., Mejia-Avendano, S., Vo Duy, S., Yao, Y., Volcheck, K., Brown, C. E., Liu, J., Sauve, S. Talanta, 2019, 195, 533-542