

PFAS in Contaminated Land Management (CLM) – How Many Should Be Assessed?

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PFAS, per- and polyfluorinated substances, cover a wide range of chemicals from ultrashort PFAS (1-3C) to polymers such as PTFE and PVDF. New assessments are largely based on PFAS4 from EFSA's TWI (tolerable weekly intake), but the picture of exposure is at the same time broadened through e.g. PFAS 20/21/22 and PFAS24. The latter is applied for both water and biota in upcoming EU directives, which are already in part implemented in some Nordic countries. However, soil to some extent differs both when it comes to regulation and PFAS included in guidelines. A key question is which so-called precursors that are present and possible to determine in relation to CLM risk assessment, not at least given their ability to degrade to more mobile perfluorinated compounds. This is in particular important for soils contaminated with firefighting foam (AFFF) where, in the worst case current regulated PFAS may only correspond to a few percent of the total PFAS load.

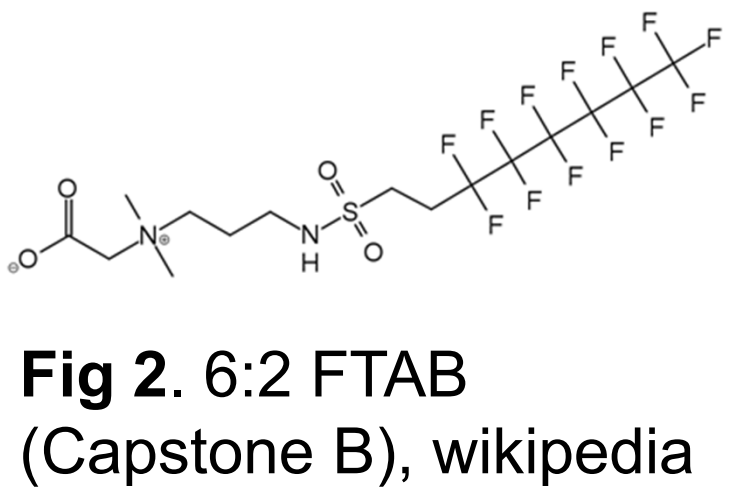
Background and Aim

PFAS show a number of challenges with it comes to their structure and chemistry, analytical possibilities and what risk they pose. Other things to address are that the composition (incl linear and branched forms) may differ in various matrices, precursors and that background levels in many cases start to approach limit values. In particular precursors that can break down to PFAS on the limit lists are only included to a minor degree. In this scenario the choice of a “relevant” number of PFAS to determine and include in CLM becomes an important issue. Moreover, the selection can potentially affect remediation goals and selection plus efficiency of remedial techniques.

The purpose is to address PFAS present in soil and should be assessed in CLM with focus on soil. The range of PFAS considered in the Nordic countries vary, from PFOS only up to PFAS22, but any range may not reflect the total content. Results from “regular” PFAS analysis together with TOP (total oxidizable precursors) will be related to limit values, in addition to a “selected” suspect screening. Precursors in AFFF hotspots/source zones found in the screening will be given special attention.

Table 1. PFAS concentrations and degree of explanation vs guidelines at Airport 1, location A, B, C. (a) Sum of PFAS (before), after TOP and increase, (b) percentage explained by different soil guideline sums

(a)	PFAS sum	PFAS TOP	ΔPFCA
Soil A	370	12600	12200
Soil B	23200	23600	2900
Soil C	53	56	6



(b)	Before TOP				After TOP	
	PFAS4	PFAS7	PFAS11	PFAS22	PFAS4	PFAS7
Soil A	18%	31%	75%	75%	0.5%	0.9%
Soil B	97%	98%	98%	100%	95%	96%
Soil C	49%	91%	95%	97%	46%	86%

Conclusions

- PFAS chemistry, analysis and thus risk assessment are complicated as shown for five AFFF polluted airport soils
- Knowledge of “total” content incl precursors (often AFFF components) in soil can be important for risk assessment and remedial actions
- Current guideline groups (PFAS4, 7, 11, 22) can only to a varying degree explain the “total” “regular” PFAS content (18-100%)
- TOP strengthens this picture and the sums may after TOP make up <1%
- PFAS4 does not take any intermediates or PFCA end-products of 6:2 FT precursors (i.e. common AFFF constituents) into account
- Both PFAS4 and 7 depends heavily on the PFOS level in the soil
- Suspect screening despite being largely semi-quantitative can be an important tool in a more detailed assessment of PFAS soil pollution
- Screening showed the presence of 23 different PFAS, many with 6:2/8:2 fluorotelomer (FT) and C6/C8-sulphonamide (SA) structures
- Concentrations of 6:2 FTAB, a common AFFF compound, exceeded PFOS in 3 of 4 soils
- TOP and suspect screening largely supported each other quant- and qualitatively
- Results show the necessity to extend assessment beyond guideline groups

References

Houtz et al. Environ. Sci. Technol. 2013, 47, 15, 8187
Koch et al. Chemosphere, 2021, 276, 130179
Miljöstyrelsen (MST), 2021. Kvalitetskriterier förurenat jord.
Nickerson et al. Environ. Sci. Technol. 2020, 54, 4952
SGI, 2015. Preliminära riktvärden för högfluorerade ämnen (PFAS) i mark och grundvatten.
SGI 2022. Vägledning 6 Riktvärden för PFAS i mark och grundvatten Remiss 2022-05-31

Sampling and Analysis

Sampling was made at three different Swedish airports, civilian and civilian/military. At Airport 1 soils were taken at three locations (A, B, C) and analysed separately. All soils (n=5) were polluted with fire fighting foam (AFFF).

Depending upon site 40-50 “regular” target PFAS were determined after alkaline methanol (MeOH) extraction and UPLC-MS-MS analysis. TOP was performed acc to Houtz et al (2013) with minor modification. A “selected” suspect screening was performed based on the work by Wang et al. (unpubl) where AFFF constituents were identified in a number of composite samples of polluted Swedish soils. The soils used in this study (Airport 1, A and B, Airport 2 and 3) were subjected to alkaline MeOH followed by acid MeOH extraction (Nickerson et al., 2020) before instrumental analysis. The screening was mainly semi-quantified using 6:2 FTAB, DPOSA, N-TAmP- and N-AP-FHxSA standards for calibration.

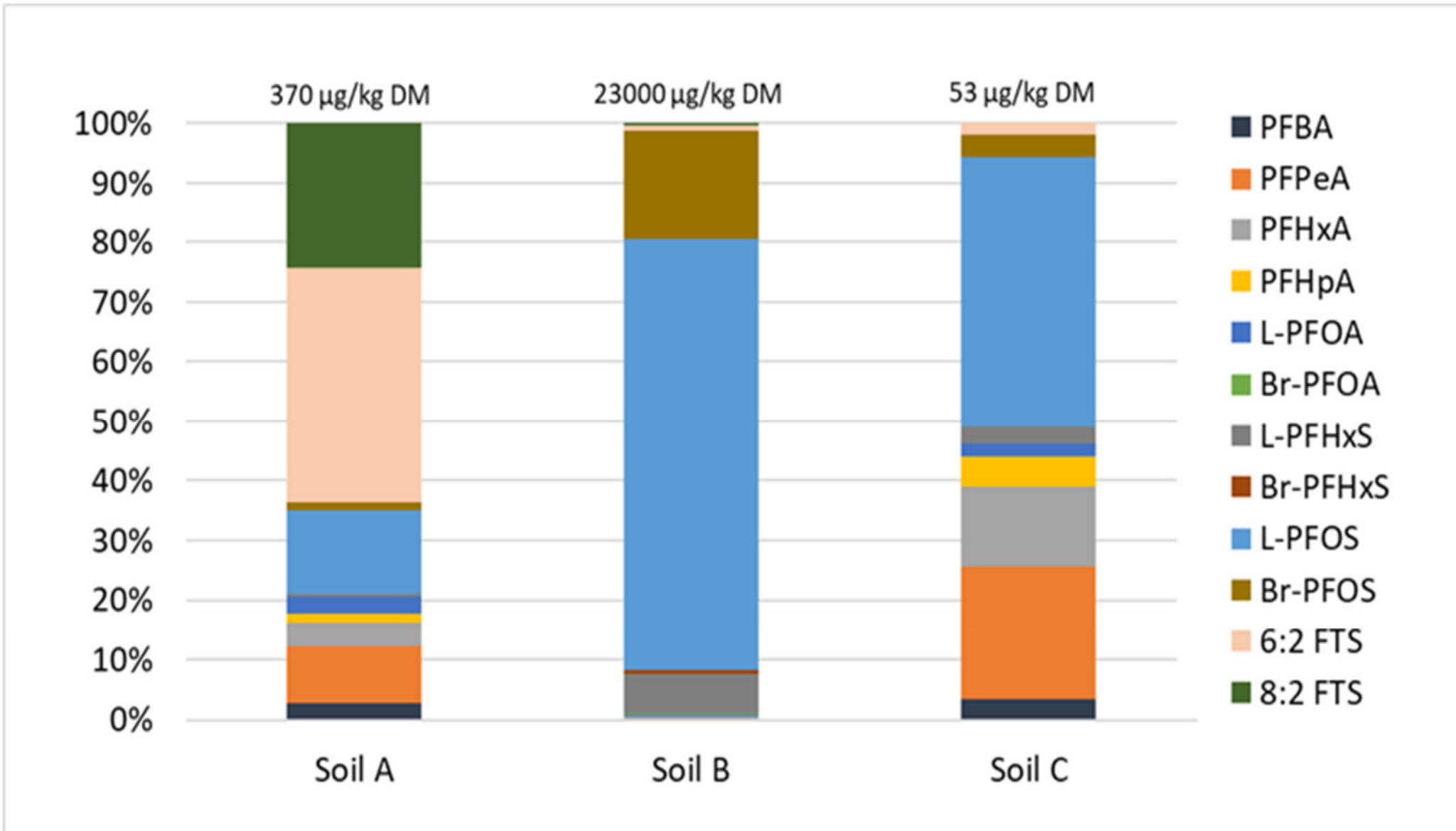


Fig 1. PFAS distribution in three locations (A, B, C) within Airport 1

Table 2. Suspect screening of soil from Airport 1 (A, B, 2 and 3. Structure refer to the molecular type of PFAS. PFAS4 (in italic) are given as reference. FT = fluorotelomer, SA = sulphonamide, PFSA = perfluorinated sulphonamic acid, PFESA = perfluoroether sulphonamic acid

Soil	Airport 1		Airport 2	Airport 3	Structure
	Soil A	Soil B			
µg/kg DM					
6:2FTAB	8100	5200	2000	900	6:2 FT
8:2FTAB	7900	99	n.d	59	8:2 FT
10:2FTAB	1200	18	n.d	7,3	10:2 FT
12:2FTAB	140	2,6	n.d	0,8	12:2 FT
14:2FTAB	4,2	n.d	n.d	n.d	14:2 FT
DPOSA	75	n.d	n.d	n.d	6:2 FT
5:1:2 FTB	1,4	n.d	n.d	n.d	FT
6:2 FTSHA-sulfoxide	400	740	n.d	n.d	6:2 FT
N-AmCP-FHxSA	210	5,1	n.d	1,9	C6-SA
N-AP-FHxSA	n.d	8,6	2,4	10	C6-SA
N-CMAmP-FHxSA	n.d	18	17	46	C6-SA
N-CMAmP-FOSA	n.d	55	n.d	210	C8-SA
N-HOEAmP-FHxSA	n.d	28	n.d	1,3	C6-SA
N-HOEAmP-FHxSE	1	66	4	11	C6-SA
N-HOEAmP-FPeSA	n.d	50	16	13	C5-SA
N-TAmP-FHxSA	n.d	35	21	17	C6-SA
N-TAmP-FOSA	n.d	26	n.d	7,7	C8-SA
Cl-PFOS	n.d	4,8	n.d	n.d	PFSA
Ether-PFNS	n.d	2,9	n.d	n.d	PFESA
F5S-PFHpS	n.d	3,2	n.d	n.d	PFSA
F5S-PFHxS	n.d	6,4	n.d	n.d	PFSA
F5S-PFNS	n.d	41	n.d	1,9	PFSA
F5S-PFOS	1,5	150	3	7,4	PFSA
PFOS	53	20700	640	750	PFSA
PFHxS	1,3	1700	1,8	2,8	PFSA
PFOA	10	61	0,3	4,3	PFCA
PFNA	7,2	8,2	0,6	4,4	PFCA

Results

The distribution and concentrations of “regular” PFAS differed among the three soils investigated at Airport 1 (Table 1; Fig 1a). Notably, PFOS varied, from 14% (A) - 50% (C) to 88% (B). In soil A 6:2 and 8:2 FTS showed the largest shares instead while in C there was a split between PFOS, PFHxS and PFPeA.

In DK there are guideline values for soil PFAS4 (10) and PFAS22 (400 µg/kg DM; MST, 2021) and in SE PFAS4, 7 and 11 are proposed or current groups (ranging from 0.25 to 20 µg/kg DM depending on report/referral and land use; SGI, 2015, 2022)). The fraction that could be explained by these guideline values varied considerably e.g. PFAS4 between 18-97%. The degree increased with the number of PFAS included. PFCA formed at TOP varied too with soil A showing a 34x increase and the “original” PFAS 4/7 could then explain <1% (PFAS11/22 not shown due to inclusion of precursors that are oxidized).

The “selected” suspect screening (Table 2) revealed 23 compounds, of which the majority were precursors. Among the “backbone” structures 6:2/8:2 fluorotelomers (FT) were major contributors but also a variety of C6/C8-sulphonamides was seen. The levels of 6:2 FTAB (Fig 2) exceeded PFOS in 3 of 4 soils. In soil A, 8:2 FTAB equaled the 6:2 but was a minor substance in the others indicating differences in AFFF composition. It can also be noted that in all but soil B, C6-SA precursors were found at higher concentrations than PFHxS. At Airport 3 soil C8-SA (incl PFOSA) corresponded to 34% of the PFOS level. Among other substances F5S-PFOS deserves to be mentioned. This PFAS has e.g. been identified in water, sediment, plants and insects at the Kallinge site in S:th Sweden (Koch et al., 2021).

Discussion

The 3 soils from the same airport (Fig 1, Table 1) showed a large difference in concentration and composition. Thus the amount of “regular” target PFAS explained by guideline sums, especially PFAS4/7, varied (18-98%). The fraction was much dependent upon the PFOS content. Further explanation was seen if 6:2 FTS was taken into account as for PFAS11/22. A shortcoming with PFAS4 is that it does not include any intermediate or final PFCA (mostly C4-C6), from 6:2 FT degradation. The inclusion of more PFAS can be a challenge regarding effects etc but it is also a risk not to address the “total” PFAS content and chemistry. This is not at least if leaching of intermediates and end products is of importance e.g. for drinking water quality or EQS. Moreover, the selection of and impact on remedial techniques will also be affected, a field that likely needs to be further developed in the future.

TOP can be used for assessment of precursors incl AFFF. This work demonstrated the big, relative and absolute increase that was found for soil A (Fig 1). As a result, the fraction covered by the PFAS sums was further reduced while the PFAS load was disclosed. Although not part of this work it should be mentioned that interpretation of the PFCA pattern incl linear/branched after TOP can yield insights into the structure of the precursors (AFFF).

Suspect screening is a way to directly assess PFAS content, but semi-quantification is required. The major AFFF compound found was 6:2 FTAB (in soil A also 8:2). 6:2 FTAB is a common PFAS in modern foams (KEMI 6/15). For other substances in the KEMI report, DPOSA was a minor analyte in soil A, while 6:2 FTSAS was not found at all. Levels in Table 2 are comparable to TOP results (partly not shown), considering that full recovery is not expected (especially 6:2 FT) and PFCA formed are lighter. The precursors found did also, overall, support the TOP pattern, though C6-SA seemed relatively lower at Airport 3 than indicated by TOP.

