Multivariate Analysis of PFAS in AFFF Contaminated Soil

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Contaminated land management of PFAS polluted sites is complicated with its composition, distribution, risk assessment and remedial actions. The use of aqueous film forming foam (AFFF) is one of the major sources. Also environmental forensics and source tracking are complex given the absence of different isotopes of F and specific additives. Thus statistical/chemometric methods are becoming an important tool in the evaluation of sources. Moreover, most legacy and all new AFFFs contain PFAS precursors, which are substances with the potential to degrade to perfluorinated carboxylic and sulfonic acids (PFCA and PFSA). For environmental risk assessment and forensics there may be a need to distinguish between different AFFF and how these many unknown precursor compounds are mirrored in the PFAS fingerprint obtained.

Table 1. Average concentrations (µg/kg DM) of PFAS4 + 6:2 FTS (n=1-3), PFAS (tot) (excl 6:2 FTAB, N-TAmP/N-AP-FHxSA) and sum of PFCA increase after TOP assay. L = linear, Br = Branched

sample no	sample id	L-PFOA	Br-PFOA	PFNA	L-PFHxS	Br-PFHxS	L-PFOS	Br-PFOS	6:2 FTS	PFAS (tot)	ΔPFCA
1-2	site 1, soil 1	9	<0.3	2	1	<0.5	20	2	12	88	1023
3-4	site 1, soil 2	10	<0.3	7	1	<0.5	48	5	134	366	12423
5-6	site 1, soil 3	42	3	9	30	3	3016	224	35	3794	2269
7-8	site 1, soil 4	54	7	8	1513	164	16548	4165	192	23236	2871
9-10	site 1, soil 5	2	<0.3	1	12	1	150	35	7	251	53
11-12	site 1, soil 6	2	<0.3	1	2	<0.5	43	5	1	68	11
13-14	site 1, soil 7	3	<0.3	4	0,5	<0.5	12	1	12	75	595
15-16	site 1, soil 8	1	<0.3	<0.5	1	<0.5	23	2	1	53	6
17-18	site 1, soil 9	2	<0.3	2	2	<0.5	138	8	1	170	8
19-20	site 1, soil 10	2	<0.3	<0.5	7	<0.5	164	28	<0.5	209	1
21-23	site 2, soil 1	3,7	0,7	0,6	2,5	0,2	723	22	11	847	679
24-26	site 2, soil 2	1,5	0,2	1,4	0,9	0,1	17	3	0,4	32	41
27-29	site 2, soil 3	0,7	0,1	<0.1	4,1	0,5	187	15	0,6	243	253
30-32	site 2, soil 4	0,3	<0.05	<0.1	2,3	0,3	197	9	<0.1	237	177
33	site 3, soil 1	0,4	<0.05	<0,1	4,9	0,5	68	9,5	<0.1	121	31
34	site 4, soil 1	0,8	<0,1	<0,2	3,7	0,3	340	27	0,3	392	19

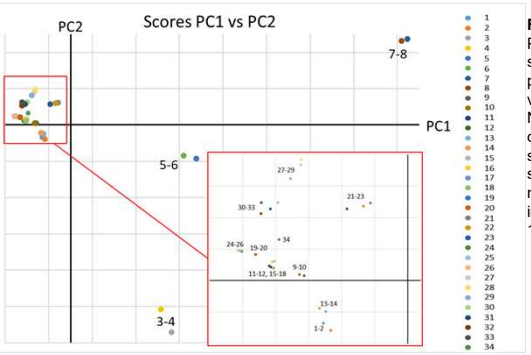

Fig 1. PCA scores plot PC1 vs PC2. Numbers correspond to sample number in Table 1.

Aim

The purpose of this project was to apply multivariate statistics (principal component analysis (PCA) and partial least square regression (PLS)) on a data set from 16 well characterized AFFF polluted soils to elucidate underlying "patterns" explaining the variance, study co-variance of variables and how "regular" PFAS could correlate to AFFF constituents. As input variables major PFCA/PFSA/FTSA plus three known AFFF constituents (and precursors) were used. Another intention was to include TOP (total oxidizable precursors) assay i.e. PFCAs formed after oxidation. Linear and sum of branched isomers (L/Br) were considered for PFCA/PFSA C4-C8 before/after TOP. Results were evaluated by assessing variance explained, no. of principal components (PCs), loadings/weights and scores.

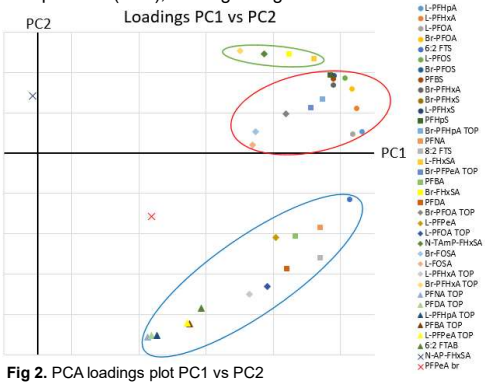

Fig 2. PCA loadings plot PC1 vs PC2

Material and Methods

The data set consisted of 16 previously analyzed soils from four AFFF polluted Swedish airports (sites 1-4): site 1: 10 soils with 2 repl.; site 2: 4 soils, 3 repl.; site 3 and 4, 1 soil, 1 repl. (n=34 in total). Approx 40 PFAS were determined using UPLC-MS/MS following alkaline methanol extraction. Br and L isomers of PFAS were separated and quantified. The procedure for TOP assay was slightly modified from Houtz et al. (2013).

PCA and PLS were performed using Tanagra 1.4.50 (R. Rako-Tomalala, Lumière University Lyon 2). As PCA variables, 36 PFAS (see legend in Fig 2) were selected on the basis of occurrence in soil. For PLS TOP results were excluded (n=22). Values <LOQ and any missing data were replaced by ½LOQ. Five PCs/factors were computed.

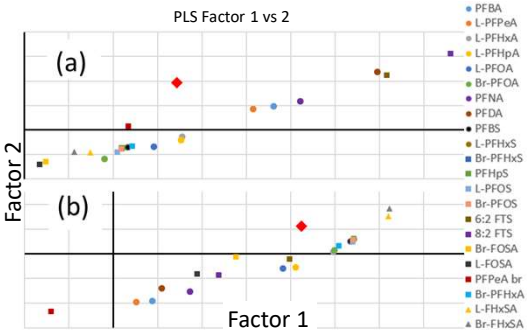

Fig 3. PLS factor plot with x weights (w*/r). Large red diamond denotes y-weight (c), (a) 6:2 FTAB and (b) N-TAmP-FHxSA

Results

Sum of PFAS ranged between 30-23000 µg/kg DM (Table 1). The composition and concentrations of PFAS both before and after TOP varied. PFOS was the major PFAS in all but site 1, soil 2 where 6:2 FTSA dominated. Substantial increases in PFCA (C4-C9) concentrations after TOP was found for most soils. The variation between the replicates for PFAS (tot) was <20% (s.d.) for all soils.

The PCA showed that PC1 explained 55%, PC2 25% and all five 98% of the total variance, proposing significant underpinning trends. The scores plot (PC1-PC2; Fig 1) was largely defined by the wide range of PC1 scores. Three soils that showed the highest scores (3-8) were left out as a test. This changed the loadings but resulted in lower variance explained and thus they were kept. PC2 hinted at a division between more PFSA plus sulphonamide (SA) and more fluorotelomer (FT) based soils (see below).

From the loadings plot (Fig 2) it was interpreted that the first PC showed a "pollution gradient"" trend with high loadings for common C6-8 PFCAs/PFSAs but also 6:2 FTSA; while PC2 demonstrated a split between FT and ECF (electrochem. fluorination) produced PFAS. The latter was represented by PFSA and SA, but also Br+L C6-C8 PFCAs. The plot suggested three groups: one smaller associated with C6-SA/ECF parameters (green), one for "general" ECF (red) and a third for FT (e.g. 6:2, 8:2) related (blue). This group also included C4-C5 + C9-C10 PFCAs. After TOP, Br- and L-PFCA formed differed in PC2 with the latter found among FT variables.

The PLS with 6:2 FTAB as y-variable (fig 3a) showed a poor degree of y-variance explained (31%) for the first factor while the two first summed up to 73%. The largest x weight was seen for 8:2 FTSA followed by 6:2 FTSA and PFDA. For N-TAmP-FHxSA (Fig 3b) the first factor accounted for 62% and the 2nd 19% of the y-variance. The highest coefficients were found for the degradation product FHxSA and thereafter a group of C4-C8 PFSA.

Discussion

Earlier efforts with multivariate statistics have mainly dealt with source tracking. In this work all samples were AFFF polluted but instead the scope of variables were extended to study co-variance among the original PFAS and after TOP. The loadings pattern may also shed light on potential precursors i.e. AFFF and intermediate compounds. PC1 suggested an underlying "pollution gradient", a feature sometimes seen for PCA of environmental data. For PC2 a split ECF vs FT was found which was also reflected in Br/L PFCA after TOP.

The methods employed here largely mirrors the forensic, tiered, approach described by Charbonnet et al (2021) where a conceptual site model is linked to PFAS fingerprinting and subsequent multivariate, exploratory statistics. A common assumption is (Kibbey et al, 2021) that AFFF sites are dominated by PFSA. This is to some extent supported but the results show that PFCA may explain the same variance as PFSA or represent FT based AFFF.

The PLS indicated that the AFFF compounds were related to degradation products (6:2 FTSA, FHxSA), but for 6:2 FTAB also 8:2 FTSA, which likely points to the 8:2 FT AFFF known to co-exist in these soils (Wang et al, unpubl). Any direct quantitative relationship between AFFF and intermediates should be interpreted with care, but FTSA/FHxSA are here shown to be important indicators.

For PFAS4, in the PCA, PFNA correlated with assumed FT (e.g. 8:2FTSA) while the others linked to the ECF group. Further work may be needed to elucidate this since C6-C8 could form at FT degradation too.

Conclusions

- Overall – PCA/PLS can be a useful tools in evaluating PFAS AFFF soil contamination to elucidate co-variance, possible precursors and anticipated classes of AFFF. PCA/PLS can also assist environmental forensics
- In the PCA two PCs explained 80% of total variance suggesting significant underlying patterns where PC1 was interpreted as a general "pollution gradient" and PC2 as an ECF (PFSA/SA) vs FT (6:2, 8:2 etc) division
- Three groups were identified in the loadings plot, one ECF, one FT and one smaller C6-SA (ECF)
- Br/L isomers, before/after TOP were significant parameters assisting interpretation (especially for PFCA)
- PLS with 6:2FTAB and N-TAmP-FHxSA as y-variables pointed to the importance of degradation products (FTSA, FHxSA) as x-variables and thus indicators.
- Among PFAS4, PFNA seemed linked to the FT variables while the others were associated with ECF.

References

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