

What is the total budget of PFAS in contaminated soil?

And how does total oxidizable precursor (TOP) assay help comprehend the picture?

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The problems of per/polyfluoroalkyl substances (PFAS) in the perspective of contamination of water and soil are of great concern. It is still common that only PFOS or a limited suite of PFASs are measured. However, it has become increasingly evident that a broader evaluation, including so-called precursors, is necessary in research and risk assessment. Precursors are compounds of known or unknown identities, which have the potential to form perfluorinated carboxylic and sulfonic acids (PFCAs/PFSAs) upon degradation in natural systems. Similarly it is of interest to study the total composition of fluorine to be able to achieve a complete picture.

Table 1. Known major PFAS concentrations before and after TOP assay (ng/g). L = linear, Br = Branched

sample id	PFBA (TOP)	PFPeA (TOP)	PFHxA (TOP)	PFHpA (TOP)	L-PFOA (TOP)	Br-PFOA (TOP)	PFNA (TOP)	L-PFHxS (TOP)	Br-PFHxS (TOP)	L-PFHxS (TOP)	Br-PFHxS (TOP)	L-PFOS (TOP)	Br-PFOS (TOP)	6:2 FTSA (TOP)	8:2 FTSA (TOP)											
Soil 1	4	14	5	173	2	177	9	<0.3	78	<1	2	56	1	<0.5	2	<1	20	2	21	4	12	2	11	<5		
Soil 2	10	2664	32	4238	14	2197	5	1859	10	<0.3	924	<1	7	618	1	<0.5	2	<1	48	5	43	6	134	3	83	<5
Soil 3	13	338	46	469	16	379	11	301	42	3	736	99	9	87	30	3	34	3	3016	224	2255	133	35	<1	39	<5
Soil 4	10	544	31	860	83	1023	21	145	54	7	408	74	8	31	1513	164	1446	166	16548	4165	15214	3293	192	<1	66	<5
Soil 5	3	20	22	38	6	19	4	7	2	<0.3	7	1	1	<2	12	1	11	1	150	35	130	23	7	<1	1	<5
Soil 6	3	6	7	9	1	4	1	2	2	<0.3	4	<1	1	<2	2	<0.5	2	<1	43	5	35	3	1	<1	<0.5	<5
Soil 7	6	162	20	279	6	106	2	55	3	<0.3	23	<1	4	12	0,5	<0.5	1	<1	12	1	11	3	12	2	6	<5
Soil 8	2	5	11	13	7	7	3	3	1	<0.3	1	<1	<0.5	<2	1	<0.5	1	<1	23	2	15	2	1	<1	<0.5	<5
Soil 9	1	<5	3	5	1	4	1	2	2	<0.3	4	<1	2	2	2	<0.5	3	<1	138	8	109	5	1	2	1	<5
Soil 10	2	<5	2	2	1	2	<0.5	1	2	<0.3	2	<1	<0.5	<2	7	<0.5	7	<1	164	28	129	15	<0.5	<1	<0.5	<5

Aim

The purpose of this project was to construct fluorine budgets in ten soil samples by measuring known PFAS and extractable organic F (EOF), and known PFAS in the same samples after subjected to total oxidizable precursor (TOP) assay. All samples were also being analyzed for total fluorine (TF) and inorganic water extractable fluoride (IF). Another aim was to use TOP as a tool for "visualizing" precursors and gain structural information. Study of the increase/decrease of branched and linear isomers may also give insight to the production method e.g. ECF (electrochemical fluorination) and telomerization.

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 1-10. Before analysis soils were dried at 35°C, sieved <2mm and milled. All analytical results thus refer to dry sample. Extraction and analyses of PFAS (alkaline digestion followed by methanol extraction and SPE cleanup), EOF and TF followed Yeung et al. (2013). EOF and TF were measured using CIC (combustion ion chromatography) from the SPE extracts and whole soil, respectively. The procedure for TOP assay was slightly modified from Houtz et al. (2013). Thirty PFASs originally present and after TOP assay were determined using UPLC-MS-MS. Branched and linear isomers of PFASs were separated and quantified. IF (fluoride) was extracted at L/S 1:5 in water; IF in the extract was analyzed using IC.

Results

The composition and concentrations of PFAS both before and after TOP varied among the samples (Tables 1 and 2). PFOS was the most commonly detected and dominant in soils 3 and 4. In contrast in soil 2, the highest concentrations were seen for 6:2 and 8:2 FTSA. Other PFASs (not shown) among the 30 determined were at low concentration or <LOQ. Anionic PFAS comprised >98% of the total PFAS except soil 3 (93%). Sum of PFASs ranged between 50-23000 ng/g (Table 2)

Five soils (1-4, 7) showed substantial increases in PFCA (C4-C9) concentrations after TOP assay, with the greatest increase in soils 1,2 and 7. After TOP the PFAS sum of soil 2 became the second highest in the set (Table 3). Generally measurable precursors such as 6:2, 8:2 FTSA and FOSA were reduced by 85% or more.

TF varied within a factor of three (Table 2), and by large exceeded all of the other fractions measured. The levels of neutral/cationic EOF fraction was greater than those of the anionic one with the exception of soil 4, dominated by PFOS. EOF could explain 0.1-13% of TF, while IF corresponded to 1.3% or less. Initial measurable PFAS could explain 1-80% and after TOP oxidation 7-78% of total EOF. As expected TOP assay raised the fraction explained for most soils.

Table 2. Fluor budgets. Mean values (n=2). RSD mostly <10% for PFAS, TOP and IF and <20% for TF See text for abbreviations

Instrumentation	Types of Fluoride	Unit	sample ID									
			Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10
CIC	TF	ng F/g	232000	202000	517000	296000	227000	256000	290000	371000	187000	331000
IC	dissolved IF	ng F/g	1620	1360	1170	873	2970	2790	1990	1600	1880	1780
CIC	EOF F1 (Neutral/cationic)	ng F/g	2710	22500	4490	5550	819	353	1990	265	288	78
LC-MS/MS	Neutral/Cationic PFAS	ng F/g	0,401	0,634	168	75,5	1,27	0,732	0,218	0,302	3,45	0,485
	Known neutral/EOF	%	0,015	0,003	3,75	1,36	0,15	0,21	0,01	0,11	1,20	0,62
CIC	EOF F2 (Anionic)	ng F/g	469	3170	3080	13700	724	314	590	285	304	287
LC-MS/MS	Anionic PFAS	ng F/g	56,4	226	2300	15400	163	43,6	47,8	34,3	108	137
	known anionic/EOF	%	12,0	7,1	74,7	112	22,5	13,9	8,1	12,0	35,4	47,9
CIC	Sum EOF	ng F/g	3179	25670	7570	19250	1543	667	2580	550	592	365
LC-MS/MS	Sum PFAS	ng F/g	57	227	2468	15475	164	44	48	35	111	138
	After TOP	ng F/g	769	8630	3250	15000	172	47	446	42	103	107
	Known PFAS/EOF	%	1,8	0,9	32,6	80,4	10,6	6,6	1,9	6,3	18,8	37,7
	TOP/EOF	%	24,2	33,6	42,9	77,9	11,1	7,1	17,3	7,6	17,3	29,2
	EOF/TF	%	1,4	12,7	1,5	6,5	0,7	0,3	0,9	0,1	0,3	0,1

sample id	PFAS	PFAS (TOP)
Soil 1	90 ± 5	1200 ± 65
Soil 2	370 ± 8	13100 ± 1400
Soil 3	3800 ± 320	4900 ± 160
Soil 4	23200 ± 800	23600 ± 1800
Soil 5	250 ± 15	270 ± 14
Soil 6	70 ± 2	74 ± 2
Soil 7	75 ± 3	680 ± 14
Soil 8	53 ± 2	56 ± 10
Soil 9	170 ± 9	160 ± 6
Soil 10	210 ± 11	170 ± 8

Table 3. Sums of known PFAS before and after TOP. Mean ± std dev (n=2)

Discussion

The range and levels of known PFAS before TOP reflect the variation for AFFF polluted sites (e.g. NV6709). After TOP oxidation especially C4-C6 PFCA increases were seen with the highest level for PFPeA. This is consistent with the pattern of 6:2 precursors (Houtz et al., 2012), and that 6:2 structures form the backbone of more modern AFFF (KEMI, 2015). In this study the identity of the precursors was further evidenced by the observation that no branched C4-C6 PFCAs were formed suggesting a telomer origin. In soil 1 and 2 raised levels of C7-C9 PFCAs were seen too, again linear substances only, indicating 8:2 besides 6:2 precursors. On the contrary, in soil 3 and 4 branched PFOA appeared after oxidation indicating a presence of ECF C8-sulfonamide precursors. This was also suggested by PFOSA found in these soils (not shown). The sum of PFAS after TOP varied from basically unchanged to about +3000% showing the importance of the nature of the precursors, e.g. for soils with, assumedly, 6:2 substances.

PFAS present. The F budget showed that the EOF and IF could only account for a small part of TF. However, to what extent this is caused by non-soluble inorganic fluoride salts and minerals have not been investigated. Water vs methanol as extract is most likely not the cause since IC runs of the latter showed values <5000 ng/g for all soils (not shown).

The PFAS/EOF quotient demonstrated that the degree of explanation is highly dependent upon the PFAS and precursor composition. The largest fraction explained was in soil 4, dominated by a high level of PFOS. The ratio is likely to be related to AFFF used but need to be further elucidated. TOP/EOF ratios were raised in accord with the PFAS increase seen for the particular soil, but a part of EOF could still not be explained. Also this observation deserves further attention, but to the best of our knowledge this is the first time this parameter has been reported for soil. Presence of compounds that are not oxidized could be one cause.

Similarly it is of interest to study the total composition of fluorine (F) to achieve a complete picture of

References

- 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
NV6709, 2016, Naturvårdsverket, Stockholm
Yeung, L. W. Y., De Silva, A. O. Loi, E. I. H., Marvin, C. H., Taniyasu, S., Yamashita, N., Mabury, S. A., Muir, D. C. G., Lam, P. K. S. Environ. Int., 2013, 59, 389-397