



PFAS and Precursors in soil and leachates - How can total oxidizable precursor (TOP) assay reveal the unknowns?

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Overall objectives and methodology

- Analysis of 10 soils and leaching tests of 5
 - Known “regular” PFAS (about 30), soil and leachate
 - Total Oxidizable Precursor (TOP) assay (measurement of known PFAS after oxidation), soil and leachate
- One-step leaching test L/S=10 (EN12457-2; batch test, “shaking”)
- Use TOP as a tool for “visualizing” precursors and yield information on their (basic) structures
- Calculation of leached amounts, before and after TOP
- Use PFCA pattern plus branched and linear isomers (ECF - electrochemical fluorination and fluorotelomerization) before/after TOP to estimate fluorotelomer and sulfonamide precursors

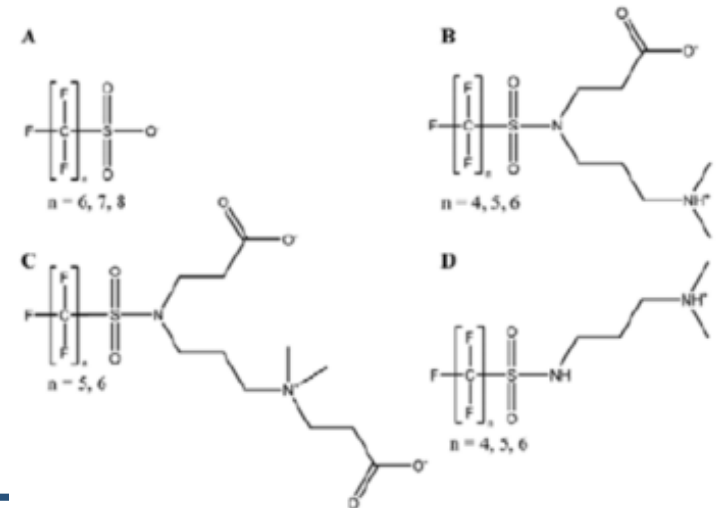


- Thousands of PFAS compounds
 - impossible to analyse all
- Pool of known as well as unknown precursors
- In nature precursors may degrade to PFCA and PFSA
 - Sulfonamides form PFSA (eg PreFOS to PFOS)
 - Telomers form PFCA
 - (eg 8:2 FTSA to PFOA, PFHpA, PFHxA)
 - Substances with ester, ether, urethane, ethoxylate, phosphate bounds (eg FTAC, FTMAC, FTEO and PAP), most frequently telomers
 - FTSAS, FTAA, FTAB – common in modern AFFF
- Numerous questions on time aspects, degradation rates, "final" yields of perflourinated substances, soil conditions etc
- To what extent do precursors leach from soil?



PFAS Precursor Oxidation - TOP

- **Oxidation of precursors can form perfluorinated compounds**
 - TOP – method developed by Houtz och Sedlak (Environ Sci Tech 2012, 46, 9342-49).
 - Chemical oxidation of precursors to PFCA
 - 85°C persulfate ($S_2O_8^{2-}$) at high pH (12)
 - Sulfonamides also form PFCA
 - Telomers form a series of PFCAs
 - Highest conc. for C(n-1) (eg 8:2 FTSA to PFHpA) followed by C(n) and C(n-2)
 - The method has been applied to various kinds of water, soil, products and firefighting foam



PFAS Results Soil – before and after TOP

sample id	PFBA	(TOP) PFBA	PFPeA	(TOP) PFPeA	PFHxA	(TOP) PFHxA	PFHpA	(TOP) PFHpA	L-PFOA	Br-PFOA	(TOP) L-PFOA	(TOP) Br-PFOA	PFNA	(TOP) PFNA
PFCA	C4	C4	C5	C5	C6	C6	C7	C7	C8	C8	C8	C8	C9	C9
Soil 1	4	222	14	353	5	173	2	177	9	<0,3	78	<1	2	56
Soil 2	10	2660	32	4240	14	2200	5	1860	10	<0,3	924	<1	7	618
Soil 3	13	338	46	469	16	379	11	301	42	3	736	99	9	87
Soil 4	10	544	31	860	83	1020	21	145	54	7	408	74	8	31
Soil 5	3	20	22	38	6	19	4	7	2	<0,3	7	1	1	<2
Soil 6	3	6	7	9	1	4	1	2	2	<0,3	4	<1	1	<2
Soil 7	6	162	20	279	6	106	2	55	3	<0,3	23	<1	4	12
Soil 8	2	5	11	13	7	7	3	3	1	<0,3	1	<1	<0,5	<2
Soil 9	1	<5	3	5	1	4	1	2	2	<0,3	4	<1	2	2
Soil 10	2	<5	2	2	1	2	<0,5	1	2	<0,3	2	<1	<0,5	<2

sample id	L-PFHxS	Br-PFHxS	(TOP) L-PFHxS	(TOP) Br-PFHxS	L-PFOS	Br-PFOS	(TOP) L-PFOS	Br-PFOS (TOP)	6:2 FTSA	(TOP) 6:2 FTSA	8:2 FTSA	(TOP) 8:2 FTSA
PFSA/FTSA	C6	C6	C6	C6	C8	C8	C8	C8	C8	C8	C10	C10
Soil 1	1	<0,5	2	<1	20	2	21	4	12	2	11	<5
Soil 2	1	<0,5	2	<1	48	5	43	6	134	3	83	<5
Soil 3	30	3	34	3	3020	224	2260	133	35	<1	39	<5
Soil 4	1510	164	1450	166	16500	4165	15200	3290	192	<1	66	<5
Soil 5	12	1	11	1	150	35	130	23	7	<1	1	<5
Soil 6	2	<0,5	2	<1	43	5	35	3	1	<1	<0,5	<5
Soil 7	0,5	<0,5	1	<1	12	1	11	3	12	2	6	<5
Soil 8	1	<0,5	1	<1	23	2	15	2	1	<1	<0,5	<5
Soil 9	2	<0,5	3	<1	138	8	109	5	1	2	1	<5
Soil 10	7	<0,5	7	<1	164	28	129	15	<0,5	<1	<0,5	<5



- Range and levels of known PFAS before TOP varied considerably
- PFOS most common, dominated soil 3 and 4
- 6:2 and 8:2 FTSA highest in soil 2
- Presence of PFCAs C4-C9, incl PFOA
- Significant branched PFOS and PFOA (=ECF)
- Increases in C4-C9 PFCAs after TOP, especially C4-C6 PFCAs

PFAS Results Leachate – before and after TOP



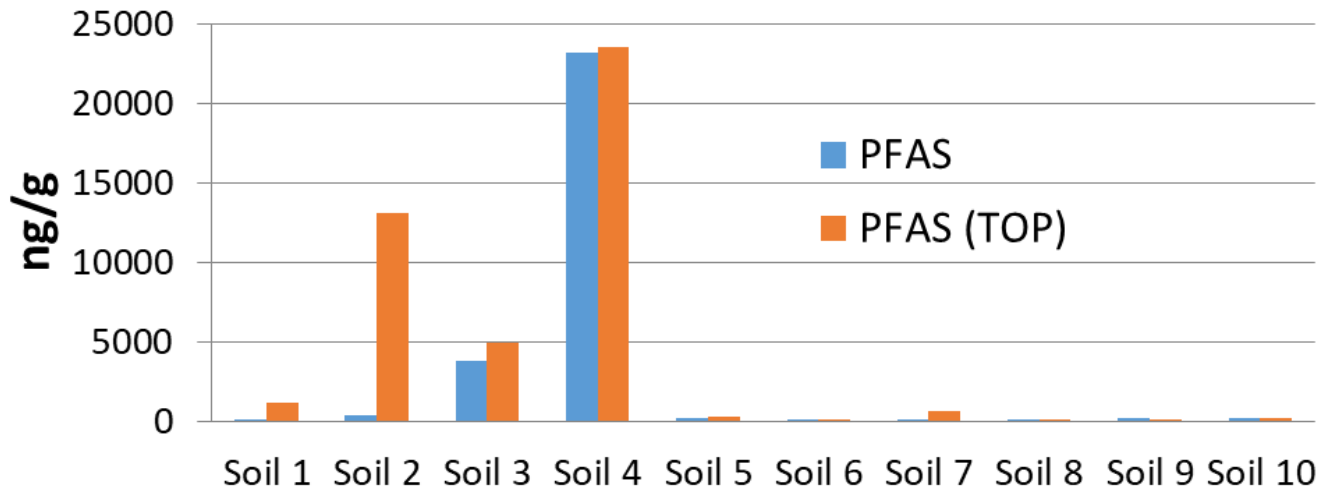
Soil no	PFBA	PFBA TOP	L-PFPeA	Br-PFPeA	TOP L-PFPeA	TOP Br-PFPeA	L-PFHxA	Br-PFHxA	TOP L-PFHxA	TOP Br-PFHxA	L-PFHpA	Br-PFHpA	TOP L-PFHpA	TOP Br-PFHpA	L-PFOA	Br-PFOA	TOP L-PFOA	TOP Br-PFOA
1	282	3984	1026	<10	7219	<10	508	<10	3095	<10	152	<10	830	<10	578	<10	761	<10
2	869	38843	2594	12	57978	<10	1122	<10	23337	<10	424	<10	4864	<10	622	<10	1317	<10
3	1022	4006	3233	280	7712	<10	1236	<10	4115	53	650	21	1523	<10	1520	152	2731	379
4	587	6879	1717	11	9943	52	3027	57	15906	903	1068	52	1670	29	1779	306	2493	552
6	252	243	523	<10	661	<10	110	<10	264	<10	79	<10	119	<10	125	<10	204	<10

Soil no	L-PFHxS	Br-PFHxS	TOP L-PFHxS	TOP Br-PFHxS	L-PFOS	Br-PFOS	TOP L-PFOS	TOP Br-PFOS	6:2 FTSA	TOP 6:2 FTSA	8:2 FTSA	TOP 8:2 FTSA
1	23	<10	20	<10	256	44	341	32	813	18	108	<10
2	62	<10	98	<10	281	55	242	42	14290	138	522	12
3	1035	144	1104	125	10958	1176	9186	1082	1161	10	122	41
4	31614	3827	34166	4005	76518	32012	66077	29929	11131	<10	364	14
6	71	<10	83	<10	1160	124	1174	130	19	<10	<10	<10



- 1-step leaching test L/S=10 (EN12457-2)
- Range and levels of known PFAS before TOP varied considerably
- PFOS dominated soil 3 and 4, high PFHxS in soil 4
- PFCAs C4-C9 in all leachates
- 6:2 FTSA highest in soil 2
- Significant branched PFOS, PFOA and PFHxS (=ECF)
- Increases in C4-C9 PFCAs after TOP, especially C4-C6

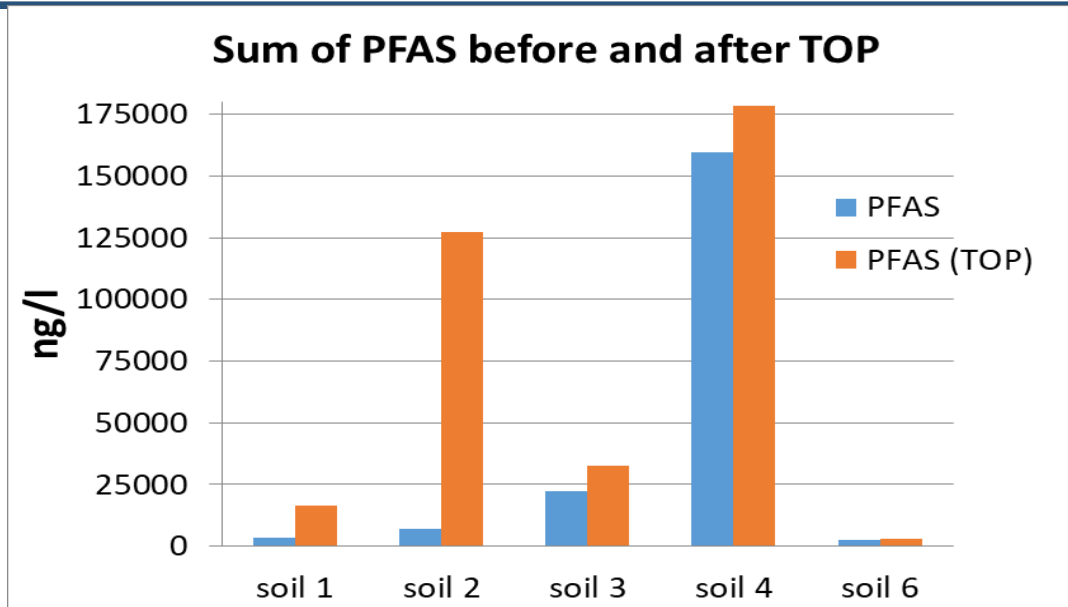
Sum of PFAS before and after TOP



- "Original" PFAS comprised 3-100% of sum after TOP

- Five soils (1-4, 7) showed sig. increases in PFCA (C4-C9)
- After TOP soil 2 became second highest
- Largest increases for C4-C6 PFCAs, the greatest for PFPeA
- Almost no Br C4-C5, limited C6 formed sugg. mainly telomer origin
- Consistent with degradation pattern of 6:2 precursors
- In soil 1-4 raised levels of linear C7-C9 PFCAs too, indicating 8:2 precursors
- In soil 3 and 4 Br-PFHxA and PFOA after TOP suggested ECF C6-/C8-sulfonamide precursors

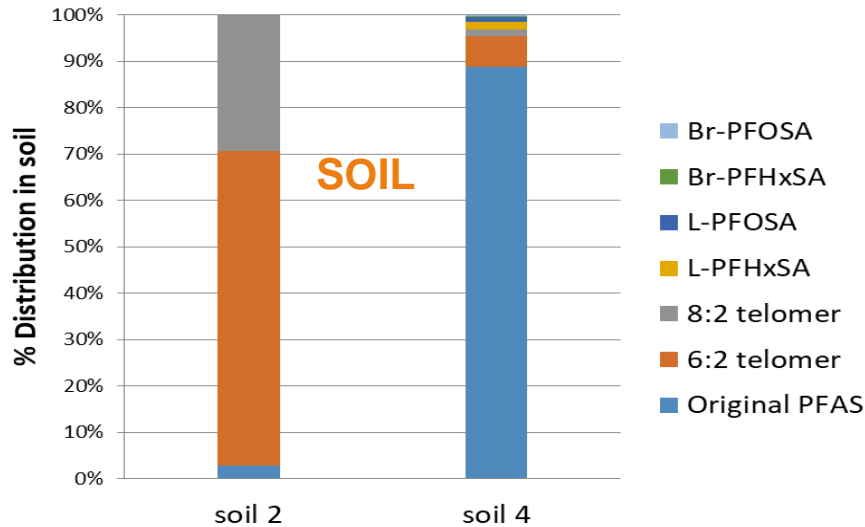
TOP Results Leaching



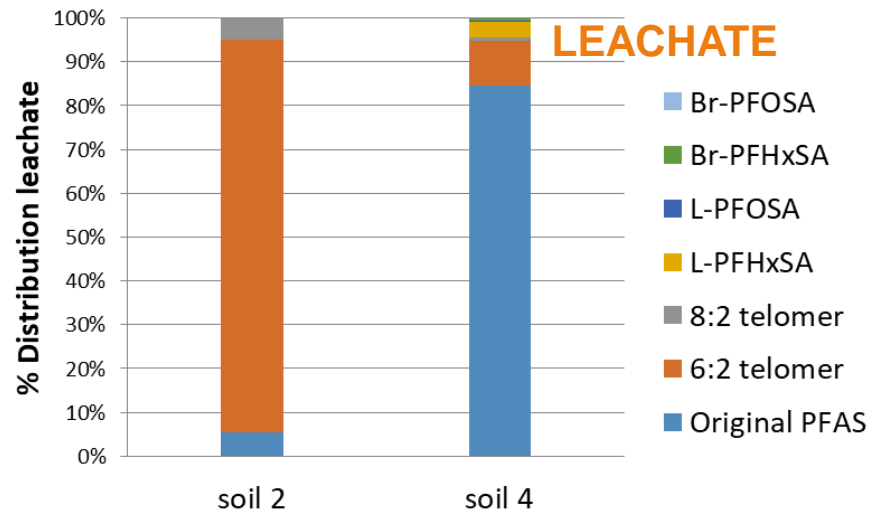
- Soil 1-4 showed increases in PFCA (C4-C9), +10000-120000 ng/l
- Overall leaching pattern similar to soils
- After TOP soil 2 became second highest
- Largest increases for C4-C6 PFCAs, the greatest for PFPeA
- Leached "original" PFAS made up 5-90% of sum after TOP assay

- Almost no branched C4-C5 and limited C6 formed suggesting mainly telomer origin
- Data consistent with degradation pattern of 6:2 precursors
- In soil 1-4 raised levels of linear C7-C9 PFCAs too, indicating 8:2 precursors
- In soil 3 and 4 Br-PFHxA and PFOA after TOP suggested ECF C6-/C8-sulfonamide precursors

Original PFAS and calc. precursors TOP



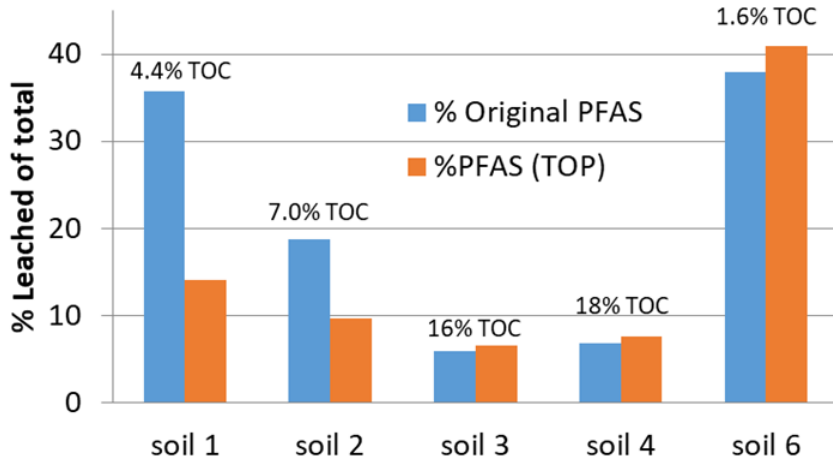
Original PFAS and calc. precursors TOP



- 6:2 and 8:2 telomers calculated based on TOP pattern and molar ratios published by Houtz et al
- C6 and C8 sulfonamide precursors estimated from fraction Br of PFOSA and PFHxS
- In both soils and leachates 6:2 precursors contributed most
- Significant 8:2 precursor in soil 2, both soil and leachate
- In soil 4, both C6 and C8 sulfonamides were present

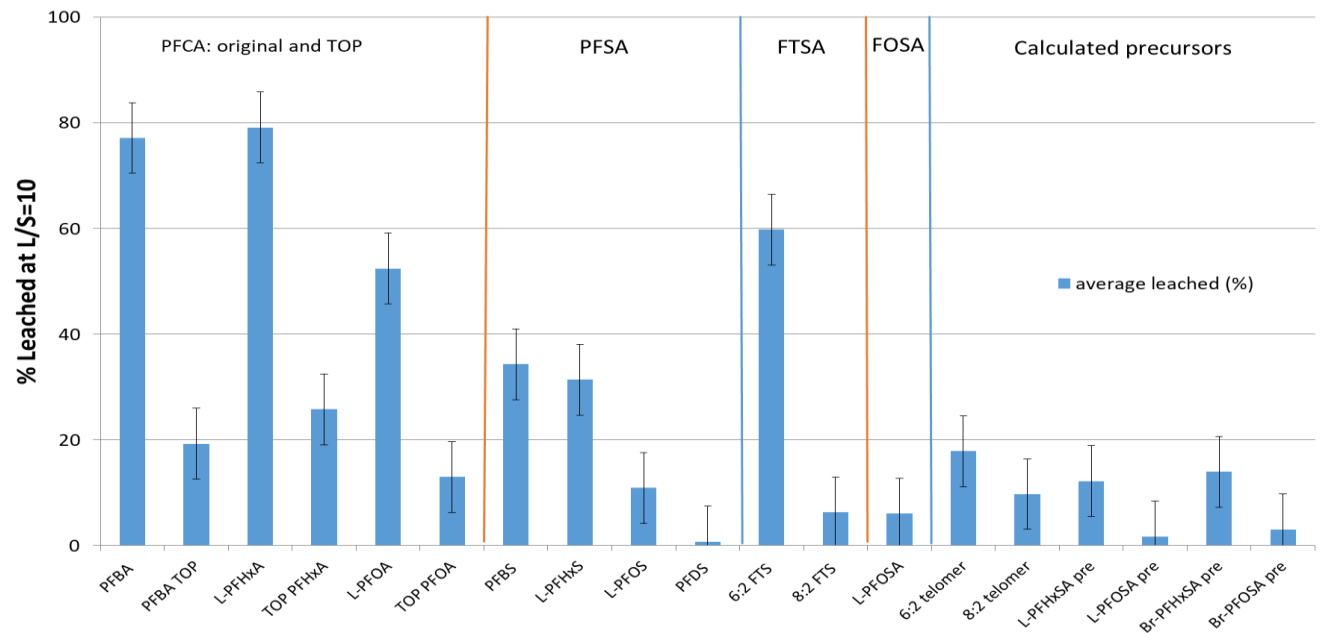
Results Leaching – PFAS and TOP

% PFAS Leached (L/S=10)



- The % leached of the total soil PFAS content varied between 6-41%
- Lower % leached at higher TOC
- Fraction leached could after TOP both decrease or slightly increase
- Besides TOC, composition of both original PFAS and precursors affect

- % Leached 1-79% for diff. PFAS
- Generally lower % leached for longer PFAS, esp. >6C
- Calc. precursors leach less than corr. PFCA, PFSA, FTSA (besides 8:2 FTS)



- Range and levels of known PFAS showed large variation among AFFF polluted sites, both in soil and leachate
- TOP “visualized” unknown precursors in both soil and leachate
- After TOP assay substantial increases were observed for C4-C9 PFCAs, especially C4-C6 with the greatest level for C5
 - Consistent with the degradation pattern of 6:2 precursors/structures, the backbone of more modern AFFF
 - Determination of branched/linear PFAS before/after TOP underpinned reasoning on structures and sources of precursors
 - TOP pattern and branched/linear levels used for calculation of various types of precursors
- Between 6-41% of the total PFAS was released into leachate.
 - The fraction varied between soil (TOC), type and size of PFAS
 - Range of % leached among different PFAS between 1-80%
- Just analysing a defined set of known PFAS in soil and leachate is likely to underestimate the PFAS load due to precursors
 - Might be difficult to judge impact in advance. In this study, original PFAS comprised 3-100% in soil and 5-90% in leachate, of TOP results
 - EOF (TOF) and TOP are of a complimentary nature



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- **Thanks to KKS for financial support!**

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