



# PFAS analysis: TOP assay and leaching from soil

**Patrick van Hees**

**Eurofins Environment Testing Sweden AB,  
Man-Technology-Environment (MTM) Research Centre, Örebro University**

## ■ Questions to discuss

- Why analysis of branched and linear PFAS is of interest
- How TOP analysis can be used to assess PFAS contamination when it comes to presence of precursors and understanding of the source (AFFF)
- The importance of leaching from soil in risk assessment and remediation
- Presentation based on a set of 10 soils, all AFFF polluted, from an unknown airport and leaching tests on 5 of these (L/S=10; EN12457-2)
- Comprehensive characterization of soils and soil leachates
  - Known “regular” PFAS (34), soil and leachate
  - Branched (Br) and Linear (L) forms
  - Total Oxidizable Precursor (TOP) assay (measurement of known PFAS after oxidation), soil and leachate



- **Branched and linear PFAS**
  - PFAS produced by the ECF method (electrochemical fluorination) contain different isomers
    - PFOS about 70% linear, 30% different branched
    - PFOA about 78% linear, 22% different branched
    - Also precursor molecules can be linear and/or branched e.g. (older) sulphonamides highly likely to be ECF
  - **Small but significant differences in physicochemical properties**
    - Branched slightly less hydrophobic, slightly greater water solubility
    - Lower adsorption ( $K_d$ ) and lower bioaccumulation for branched
    - Faster biodegradation of some branched precursors (e.g. PreFOS)
    - Distribution in environmental matrices:
      - PFOS natural water: often 35-50% branched
      - PFOS in soil, sediment and sludge: 12-30% branched (<20% common)
    - Lower PFOS adsorption to activated carbon (86 vs 78%)
    - PFOS food and biota: <10% branched
    - Same trend for PFOA, PFHxS, PFOSA
  - **Source tracking and environmental forensics**
  - **Transport, degradation, adsorption and biotic uptake of precursors can give a more complex pattern (M-1318, NGI, 2019)**
  - **Mini review published on Eurofins.se**



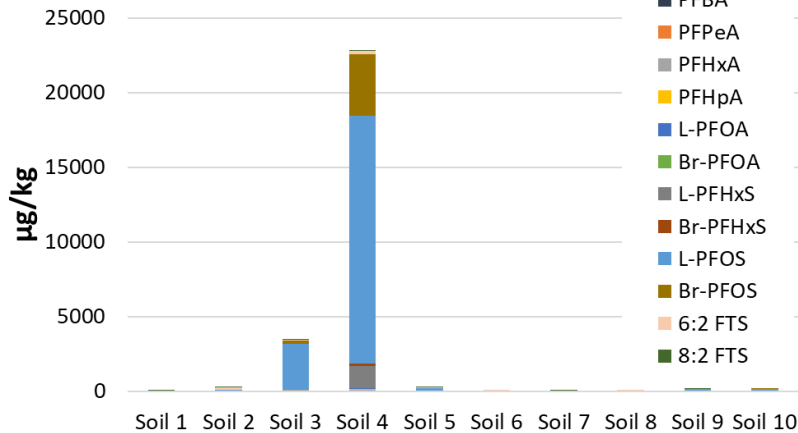
# PFAS Precursor Oxidation – TOP(A) eurofins

- Oxidation of precursors can form perfluorinated compounds
  - TOP (total oxidizable precursors) – method developed by Houtz and 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 form (a single) 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

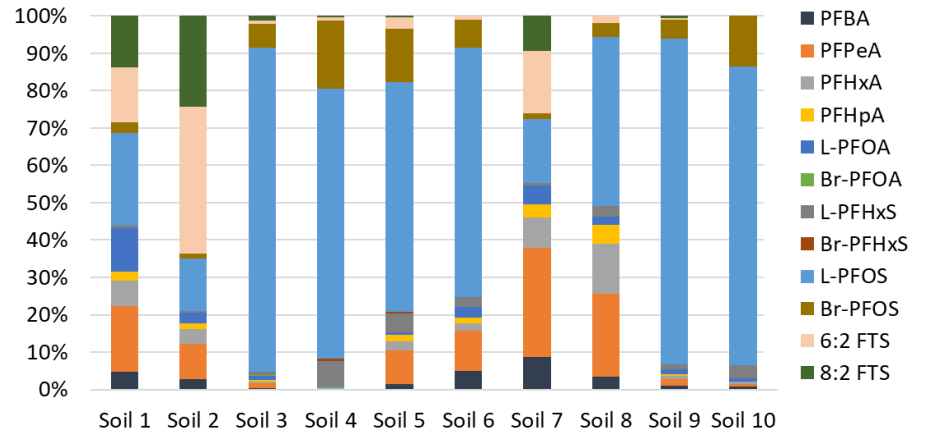


# PFAS Results Soil – Before/after TOP

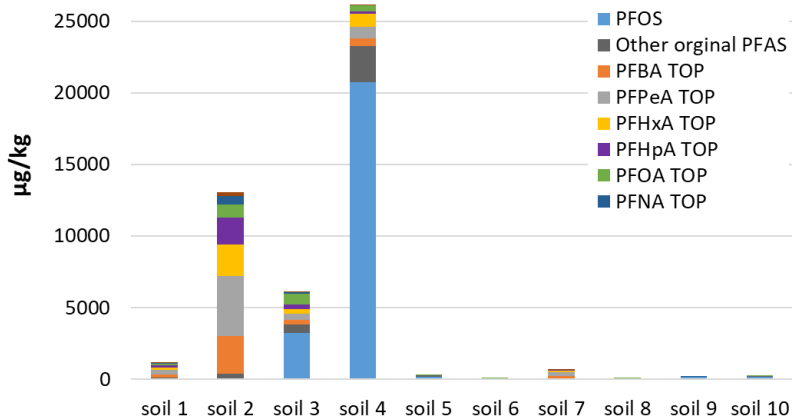
Original PFAS (before TOP)



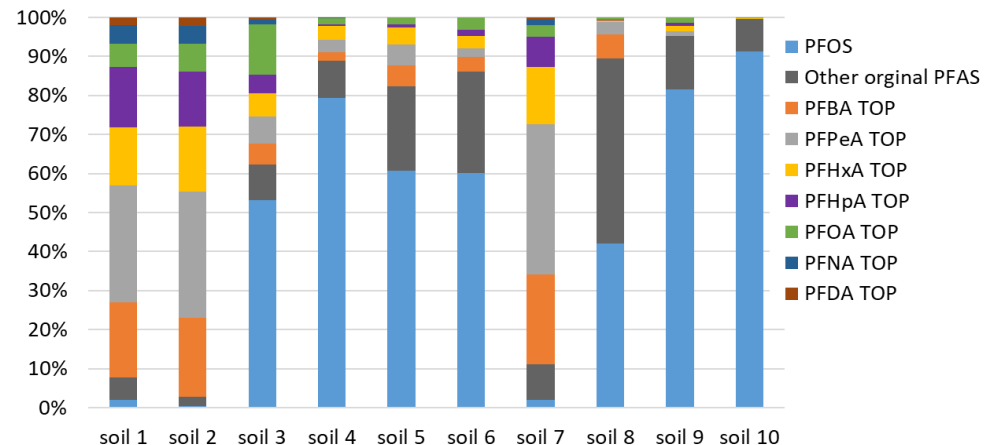
Original PFAS (before TOP)



Original PFAS and increases of PFCA at TOP

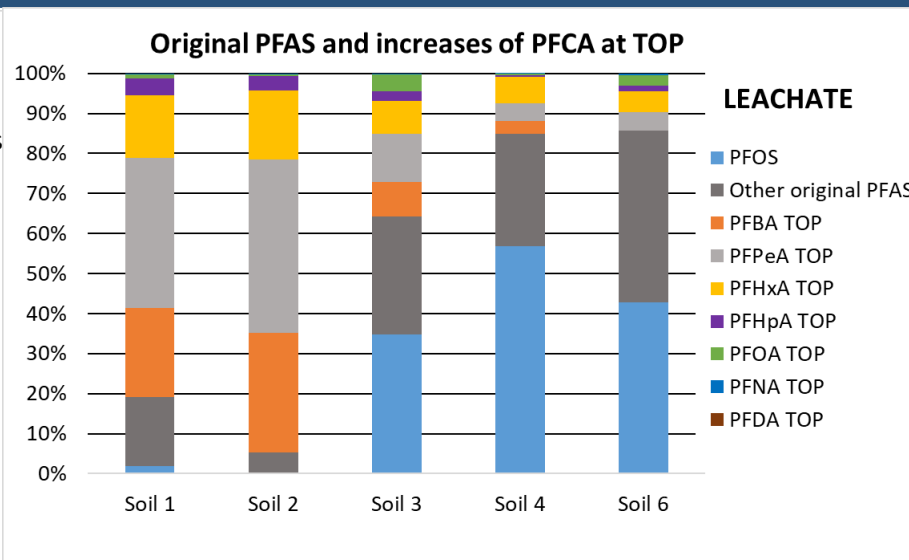
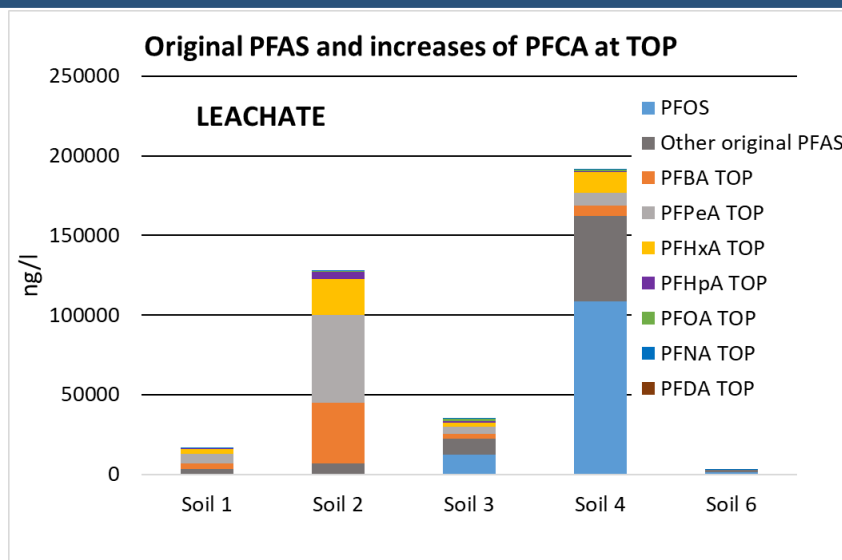


Original PFAS and increases of PFCA at TOP



- PFAS34 before TOP <100-23000 µg/kg
- 6:2 FTAB: 1-3700 µg/kg (soil 1-4, 6)

- Formation of PFPrA may be important in TOP of 6:2 FT

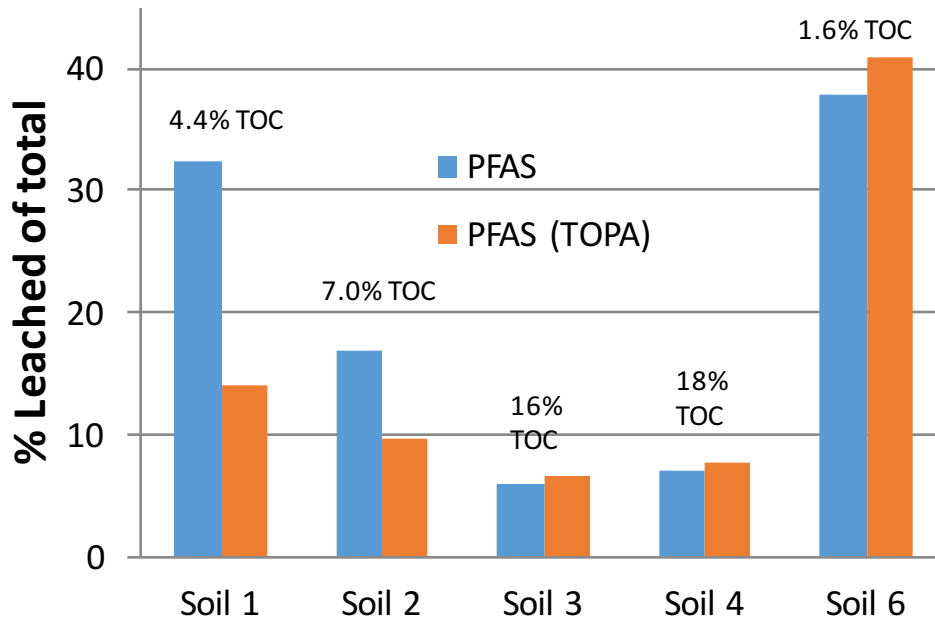


- PFAS34 before TOP 2600-162000 ng/l
- Significant branched PFOS, PFOA and PFHxS (=ECF)
- 6-38% of the total original PFAS content was leached
- Overall similar picture for leachate as for soil, but a shift towards shorter PFAS in leachate
- PFAS34 comprised 4-100% of sum after TOP, both for soil and leachate
- TOP PFCA pattern consistent with 6:2 and 8:2 FT precursors
  - Calculations indicated that 6:2 FT was most important, then 8:2
  - Small calculated amounts of C6/C8 ECF sulphonamides in 3+4
  - Both soil and leachates

% Branched	Soil	Leachate
PFHxS	9 ± 0.3	12 ± 1
PFOS	11 ± 2	16 ± 3
PFOSA	20 ± 2	32 ± 4
PFOA	10 ± 2	12 ± 3

Mean ± SEM (n=2-10)

- Higher fraction of branched in leachate
- Branched PFOA and PFOS appear depleted vs tech ECF product
- Highest Br-PFOS in soil 4, 20%
- Even lower fraction of branched PFCA <C8
- After TOP almost no Br C5, C7 and limited C6, C8 PFCA formed
- In soils 3 and 4 branched PFCA formed
  - PFHxA (3%), PFOA (14%)
  - Suggest (limited) ECF C6-/C8-SA precursors

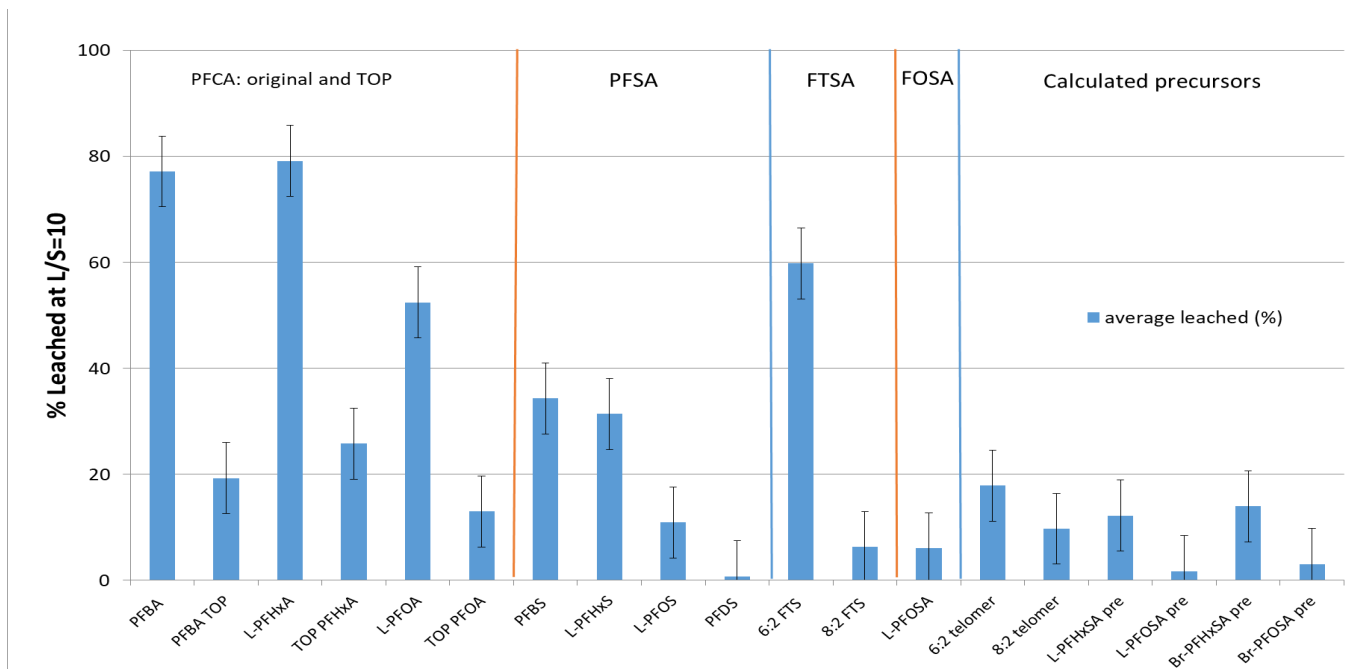


PFAS = PFAS34 +  $\Sigma$ FTCA/FTUCA/  
FTOH + sulphonamides (SA)

- 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
- Soils (3, 4) dominated by PFOS smaller diff before/after TOP
- Besides TOC, composition of both original PFAS and precursors affect leached amount (complex pattern)



# Results Leaching – PFAS and TOP



- % Leached 1-79% for major PFAS and calculated precursor types
- Generally lower % leached for longer PFAS, esp. >6C
- Calc. precursors leach less than corresponding PFCA, PFSA, FTSA (besides 8:2 FTS)
- Tendency for lower Koc for Br-PFSA, Br-FOSA and Br-SA precursors (scattered for PFCA)
- Log Koc values calculated for L and Br PFCA, PFSA, FTS and calc. precursors, range 1.1-3.9
- Corr. between no of C and log Koc above ≥C6, log Koc ~ +0.35-0.5 per C

## Soil levels giving equilibrium leachate conc 2 ng/l

Soil concentrations ( $\mu\text{g}/\text{kg DM}$ )			
	Log Koc	1% TOC	10% TOC
PFHxS	2.4	0.0054	0.054
PFOS	3.2	0.032	0.32
PFOA	2.1	0.0027	0.027
PFNA	2.5	0.0058	0.058

- Very low soil concentrations required ( $<0.1 \mu\text{g}/\text{kg}$  all but one)
- Log Koc given for linear form
- Log Koc 0.2-0.3 units lower for Br-PFHxS and Br-PFOS
- If assuming 0.5 ng/l for each substance, sum PFAS4 = 0.012-0.12  $\mu\text{g}/\text{kg DM}$
- If 2.5  $\mu\text{g}/\text{kg DM}$  assumed for each (i.e. sum PFAS4 = 10), sum in leachate equals 380-3800 ng/l
- If 0.75  $\mu\text{g}/\text{kg DM}$  assumed for each (i.e. sum PFAS4 = 3), sum in leachate equals 110-1100 ng/l
- Many uncertainties but computations suggest that 2 ng/l quickly becomes crucial

- PFAS34 reflected AFFF used and was seen in both soils/leachates
- TOP revealed unknown precursors to a significant degree, substantial increases were observed for C4-C9 PFCA
- Patterns of PFCA formed at TOP indicated origin of the precursors, primarily 6:2 but also 8:2 FT based. Br forms suggested minor contributions of C6/C8 SAs.
- 6:2 precursors is in line with findings that this structure forms the backbone of modern AFFF. Supported by 6:2 FTAB analysis
- Regular PFAS34 made up <5-100% in soil/leachate of the sum after TOP, a fraction not possible to assess on beforehand.
- Just analysing a defined set of known PFAS in soil and leachate is likely to underestimate the PFAS load due to precursors
- Leaching tests showed that 6-41% of the total PFAS content was released with a tendency for shorter PFAS
  - The fraction varied between soil (TOC), type and size of PFAS
  - Range of % leached among different PFAS between 1-80%
  - Slightly higher leaching for branched PFAS
  - Calculations indicate very low (<0.3 µg/kg DM) soil concentrations needed to reach 2 ng/l in leachate



# Thank you for your attention!



- **Thanks to co-workers**

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**EnForce**  
Environmental Forensics



- **EnForce profile at Örebro univ - Thanks to KKS for financial support!**

- **Lin/Br and TOP "mini-reviews" published on eurofins.se**

- **Welcome to contact me!**

- **Thanks PFOA!**

**NIRAS**

Patrik Karlsson

