PFAS analysis – What are the options?

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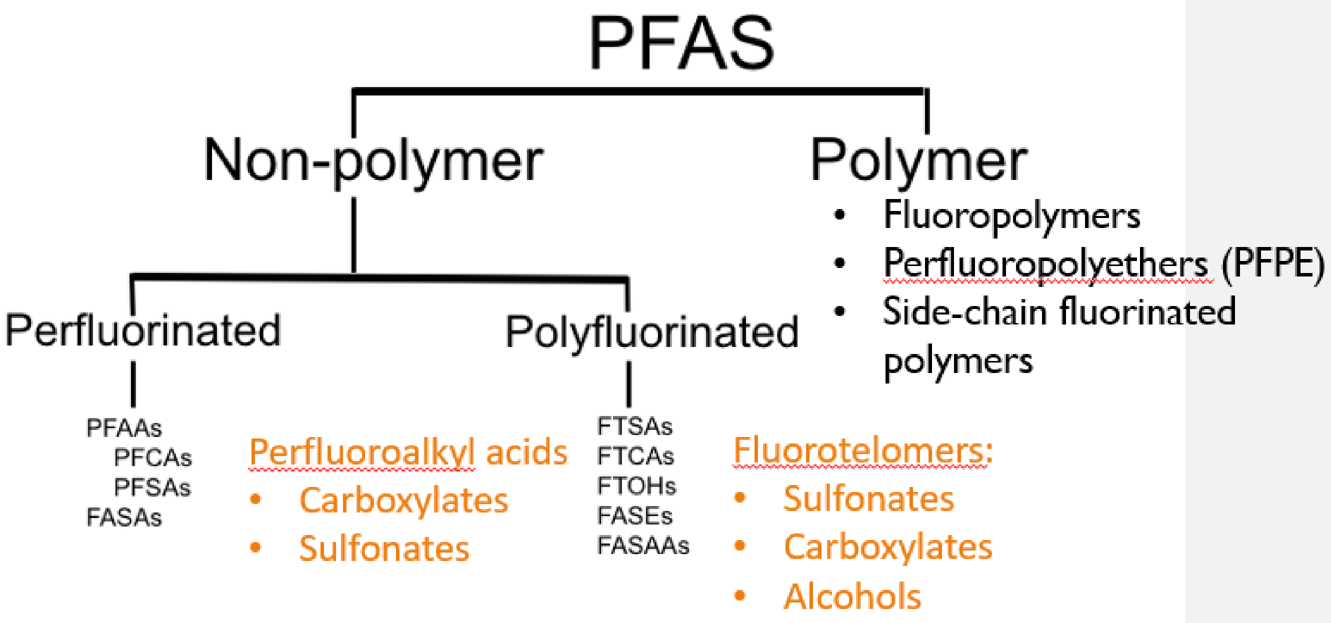
Outline:

- PFAS classes and organic fluorine
- Analytical methods
- Environmental Forensics
- Some challenges
- PFAS analysis – Summary

PFAS and Organic Fluorine - Classes

PFAS chemistry and classes



- **PFAS is "unique" as many classes of the group can be relevant in the risk assessment**
- **OECD definition from 2021 – a perfluorinated methyl or methylene group is sufficient**
  - **Includes eg ultrashort PFAS**

PFAS Classes

1 Polymers e.g. PTFE (teflon), PVDF (Polyvinylidene fluoride), PFPE (perfluorinated polyether), PVF (polyvinylfluoride)

Exposure often linked to production (PFOA, GenX, ADONA) than polymer itself
Analysis: FTIR, TOF, PY-GC-MS

2 Side-chain co-polymers e.g. poly/perfluorinated (meth)acryl (C2-20), fluorinated urethanes (C4-18), alkyl sulfonamide derivatives (C4-9; Scotchgard), alkyl ammonium (C4-7), alkyl alcohols (C3-14)

May break down over time (100y?) to intermediates such as FTOH, FT-acrylates, sulphonamides and eventually PFCA + PFSA
Analysis: FTIR, TOF, TOP (qual)

3 ”Large precursors” – e.g. PFAAB, FTSAB, FTSAS, FTAB, FTB, FTHSA, PFASAC, PFASNO, diPAP, diSAmPAP (C3-C10)

Typical AFFF constituents (but also other uses) can degrade to PFSA and PFCA. 1-6% in AFFF concentrate.
Analysis: HR-LC-MS, LC-MS-MS, TOP (standard available for 6:2 FTAB and 2 C6-SA)

4 ”Small measurable precursors” – 6:2, 8:2 FTS, PFOSA, PFHxSA, 5:3 FTCA, 6:2, 8:2 FTOH

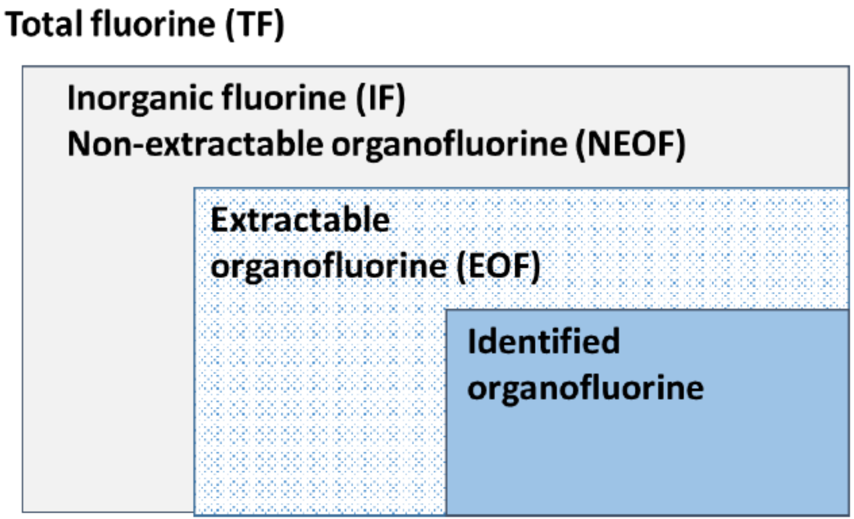
Degradation intermediates, sometimes primary products
Analysis: LC-MS/MS, TOP

5 ”Regular” and ”novel” PFAS” – PFSA , PFCA, PFEAS (e.g. F53B), PFECA (e.g. GenX)

Mostly perflourinated compounds
Analysis: LC-MS/MS

Kemi 7/15
Env Sci Tech 14, 48, 121

Organofluorine Classes



- Definition of organo-F is dependent upon both chemical nature and analysis
- Identified organo-F = LC-MS/MS and GC-MS (MS/MS) (approx. 100 PFAS)
  - Frequently just a few % of EOF/TOF/TF
- Nature of NEOF uncertain
- TF can be determined in different ways
- AOF alternative to EOF for water
- TOF may be relevant for products

TemaNord 2019:515

Analytical Methods

Target Analysis – LC-MS/MS

- Liquid chromatography coupled to mass spectrometric detection
- Electrospray (ESI) ionization
- MS/MS = "triple-quad"
- Collision cell (quadropole) in between produce molecular fragments
- Detection in two steps = very high selectivity and sensitivity
- Quantification
- ppb – ppt (ppq) level
- The "workhorse" of PFAS analysis

“Total Methods” - Total Oxidizable Precursors (TOP) and TF/TOF

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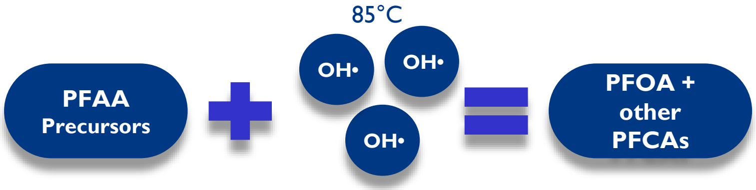
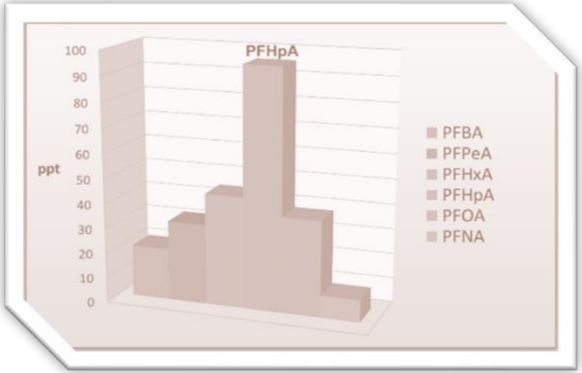
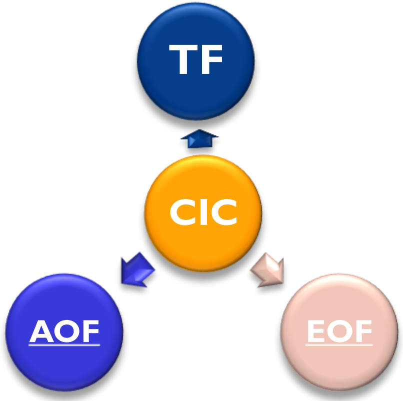
TOP Assay





TOP Conversion of 8:2 FTS

Total Organic Fluorine Analysis



CIC: Combustion Ion Chromatography

Total Organic Fluorine Analysis

Combustion Ion Chromatography (CIC)

Marriage of TOX and IC. Sample (or treated sample) is combusted in a furnace at 900°C – 1100°C

Effluent collected in buffer and injected into ion chromatograph (IC)

Quantify fluorine (as fluoride) content

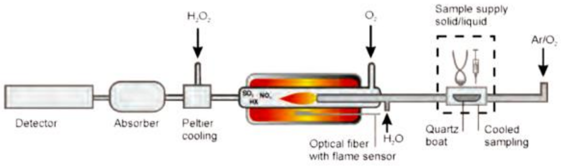
Compare ratio of total (or extractable) fluorine to total PFAS

Oxidative pyrohydrolytic combustion

Handling of the sample prior to F determination determines result and evaluation

EOF – Extractable Organic Fluorine

AOF – Absorbable Organic Fluorine



Total Organic Fluorine Analysis in Water

Adsorbable Org. F (AOF)

- **Sample Prep**
  - 100mls sample pass thru activated charcoal bed(s)
  - Final wash with nitrate solution to remove inorganic fluoride
- **Combustion of Charcoal into CIC to measure F^- by IC**

Extractable Org. F (EOF)

- **Sample Prep**
  - 100mls sample pass thru weak anion exchange (WAX) SPE
  - Elute PFAS with methanol
  - Concentrate methanol to final 1mL
- **Combustion of extracted sample into CIC to measure F^- by IC**

Total Org. F (TOF)

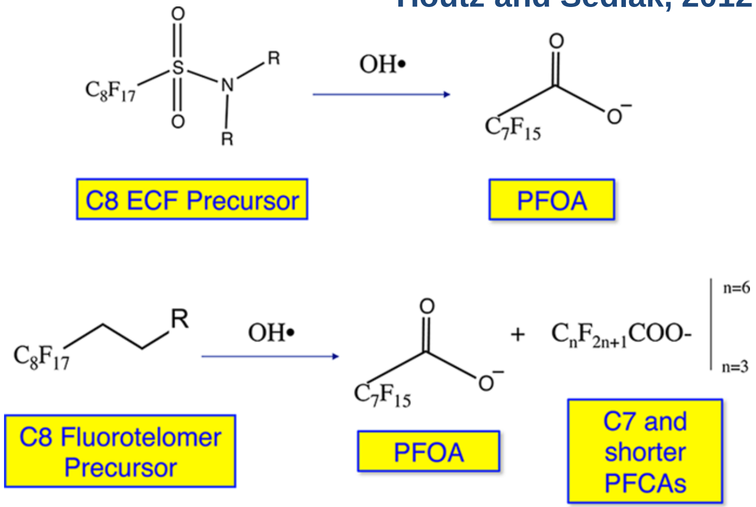
- **Sample Prep (water samples)**
  - No Sample Prep
- **Direct injection of aqueous sample into CIC system to measure both Inorganic F^- and Organic F^- simultaneously**

Courtesy of Dr. Jayesh Ghandi - Metrohm

TOP – Total Oxidizable Precursors

- TOP – method developed by Houtz and Sedlak (Environ Sci Tech 2012, 46, 9342-49)
- Chemical oxidation of precursors to PFCA
  - 85°C persulphate ($S_2O_8{}^{2-}$) at high pH (12)
- Sulfonamide precursors forms the corresponding PFCA (Ex. MeFOSE are oxidized to PFOA).
- Telomers form a series of PFCAs where the highest concentration is for C(n-1) (ex 8:2 FTS – PFHpA) followed by C(n) and C(n-2) and so on.
  - 6:2 FTS: C4:C5:C6 = 1:1.2:1 (molar ratio)
  - 8:2 FTS: C4:C5:C6:C7:C8 = 1:1.1:1.7:2.5:1.9 (molar ratio)
  - C4:PFBA, C5:PFPeA, C6:PFHxA, C7:PFHpA, C8:PFOA
  - Forms the basis for equations to calculate contributions from different telomer precursors (Houtz and Sedlak, 2012, suppl mtrl)
- It can be discussed whether these "ideal" molar ratios always are obtained during oxidation of natural samples

Houtz and Sedlak, 2012



Suspect Screening and Non-Target Analysis

Targeted Analysis

Suspect Screening Analysis

Non-Targeted Analysis

- **High Resolution MS (HR-MS)**
  - **Q-TOF and Orbitrap**
- **Suspect screening: detecting known structures in a sample from (often) user-built databases (mass accuracy, retention time, isotopic patterns etc)**
- **Non-target: No inital info on the compounds contained in the sample. Elemental composition derived from accurate mass of the ions. Database searches to give plausible structures**
- **Qualitative (initially) and time consuming**

Problems?
Accurate mass solves a variety of PFAS problems

No More Limitations
Precursors without TOP Assay
No LIMS constraints

Byproducts?
Can capture all byproducts

Environmental Forensics

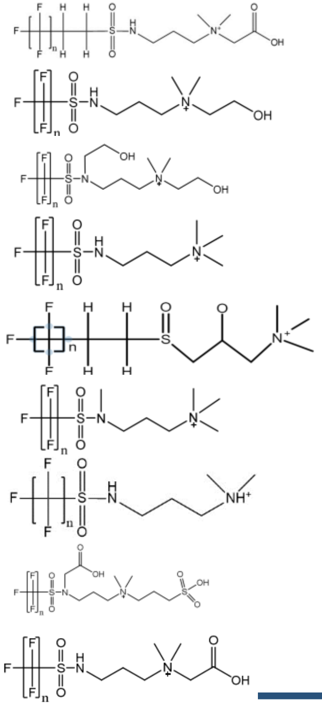
Example of Suspect Screening

Suspect screening-Positive data (HRMS confidence Level 3 or above)

Semi-quantification (ng/g dw)

Based on the intensity and concentration of PFHxS or PFOS

Name	Observed m/z	Detection in fraction	CF2	Site A	Site B	Site C
4:2 FTAB	471.1016	Alkaline	4			3
6:2 FTAB	571.0933	Both	6	43	880	157
8:2 FTAB	671.0859	Both	8		568	11
10:2 FTAB	771.0783	Both	10		188	3
12:2 FTAB	871.0749	Both	12		57	
14:2 FTAB	971.0696	Alkaline	14		11	
N- HOEAmP - FHxSA	529.0823	Both	6	4	32	19
N- HOEAmP - FHxSE	573.1077	Both	6		24	6
N- TAmP -N- FHxSA	513.0888	Both	6		163	17
N- TAmP -N-FOSA	613.0819	Alkaline	8		25	2
6:2 FTSHA-sulfoxide	512.0935	Both	6		59	
N- TAmP - MeFHxSA	499.0731	Both	6		174	30
N- TAmP - MeFOSA	599.0665	Both	8	6	76	13
PFHxSaAm	485.0572	Both	6		7	14
PFOSaAm	585.0504	Alkaline	8		4	
N-SPAmP-FHxSA	607.0589	Both	6		7	3
N-SPAmP-FOSA	707.0519	Alkaline	8			3
N-CMAmP-FHxSA	543.0623	Both	6			30
N-CMAmP-FOSA	643.0558	Alkaline	8		19	10



19 PFASs from 9 classes were additionally identified through suspect screening;

Based on semi-quantification result, the total concentration up to 880 ng/g dw;

High levels of C6 based PFASs found, followed by C8 based compounds;

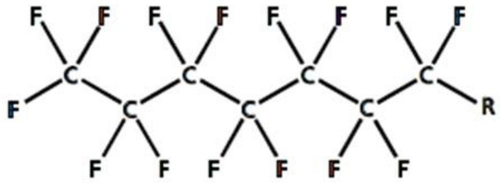
In line with the EOF and TOP results;

More cationic and zwitterionic in site B.

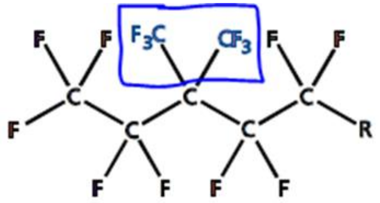
Yeung, Wang, Karlsson, Filipovic, van Hees, unpubl

PFAS – Branched and Linear Isomers

- PFAS produced using the ECF method (electrochemical fluorination) contain different isomers
  - PFOS approx. 70% linear , 30% variously branched
  - PFOA approx. 78% linear , 22% variously branched
- Small but significant differences in physico-chem characteristics
  - Branched slightly less hydrophobic, slightly higher water solubility
  - Less adsorption capacity and lower bioaccumulation for branched
- 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 active carbon (86 vs 78%)
  - PFOS foods and biota: <10% branched
  - Same tendency for PFOA, PFHxS , PFOSA
- Source tracking and environmental forensics
  - PFOS and Sulfonamide based AFFF typically produced using the ECF method

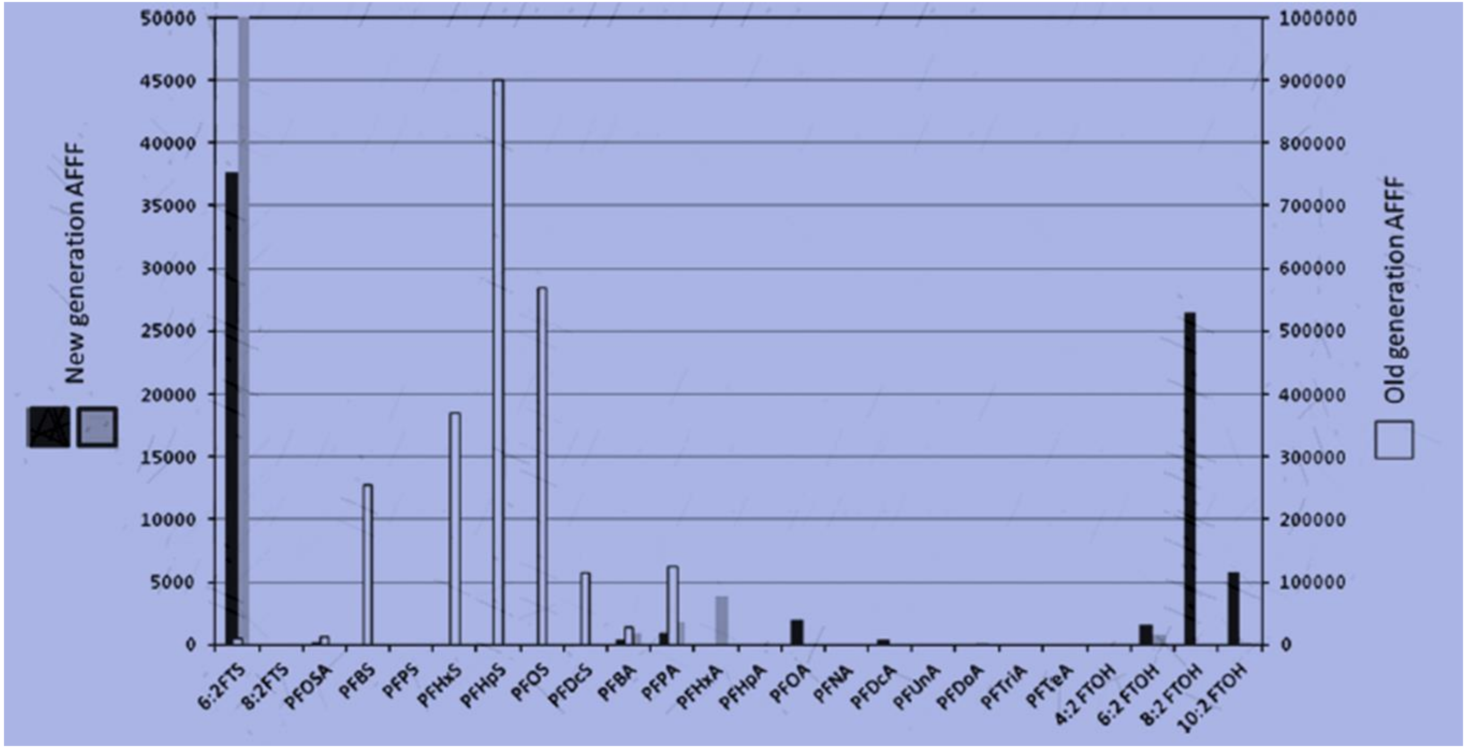


Linear Isomers



Branched Isomers

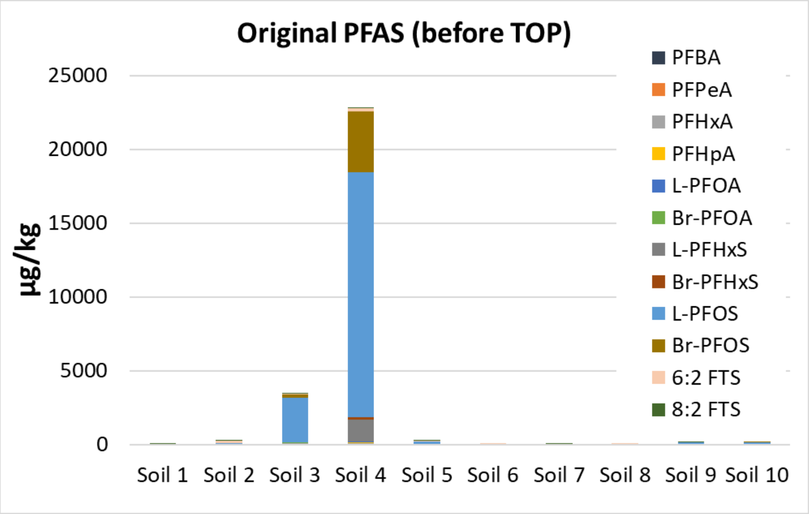
PFAS fingerprinting

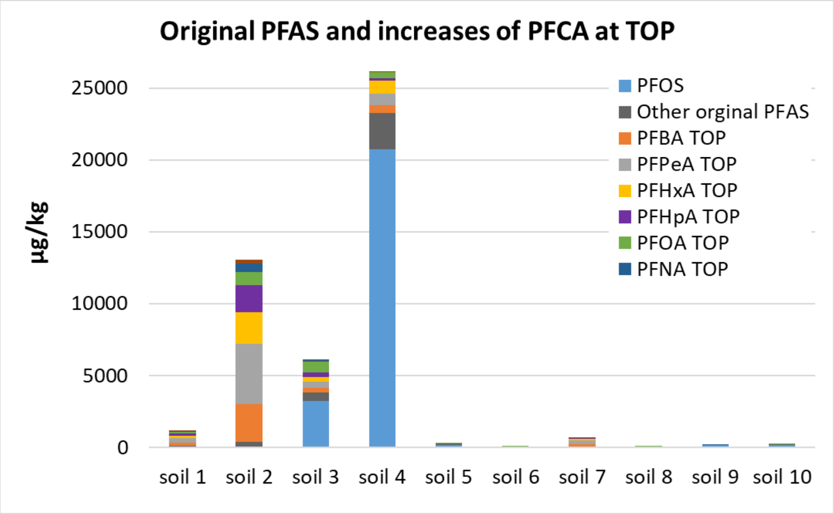


Herzke, et al., 2012, Chemosphere, 88, 980-987

- Older foams are dominated by C4-C10 PFSA (sulfonic acids)
- Newer ones are dominated by 6:2 FTS, 6:2-10:2 FTOH
- Certain levels of PFCA for all types of foam
- Significantly higher levels in older foam
- Probable presence of precursors especially in newer foams

PFAS Results Soil – Before/after TOP





- **PFAS34 before TOP <100-23000 µg/kg**
- **Soil no 2 becomes second highest**
- **Significant branched PFOS, PFOA and PFHxS (=ECF)**
- **Pattern of PFCA formed after TOP indicated primarily 6:2 and 8:2 FT precursors**

- **Branched PFHxA and PFOA indicated minor contributions of C6 and C8-sulphonamides (SA) in soil 3 and 4**
- **Measured precursors could explain 25-35% of those C6/C8-SA estimated**

PFAS - Multivariate Analysis

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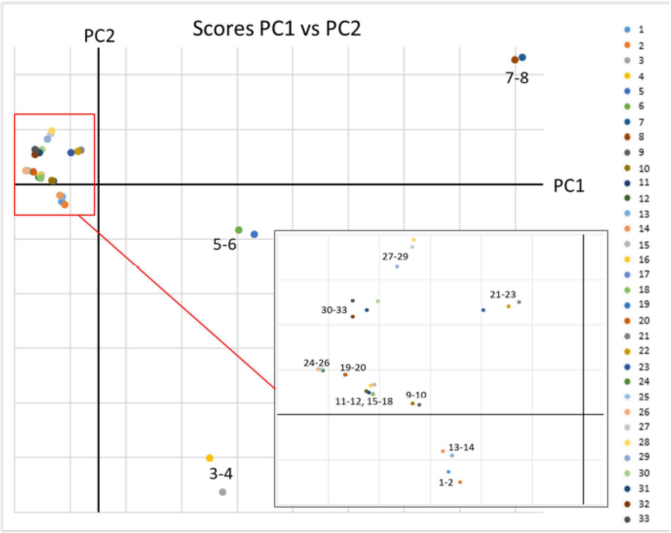
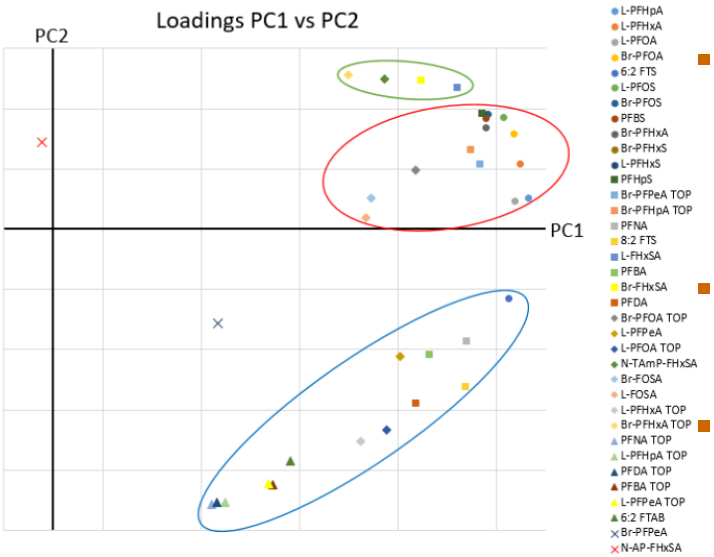
- PCA (Principal Component Analysis) evaluation of PFAS composition before/after TOP in 33 AFFF polluted soils





- Two PC (Principal Components) explained 80% of tot variance, sugg. underlying patterns.
- From Loadings plot: 1st PC interpreted as a general ”pollution gradient” and PC2 as an ECF vs Fluoro-telomer (FT) division
- Three groups in the loading plot: ECF, FT and C6-SA
- Branched/Linear isomeres before/after TOP assisted interpretation
- TOP correlated to measured precursors
- PFNA linked to FT, rest of PFAS4 to ECF produced

van Hees, Karlsson, Filipovic, Törneman, Thureson, Sjölund, Yeung

PFAS Analysis - Challenges

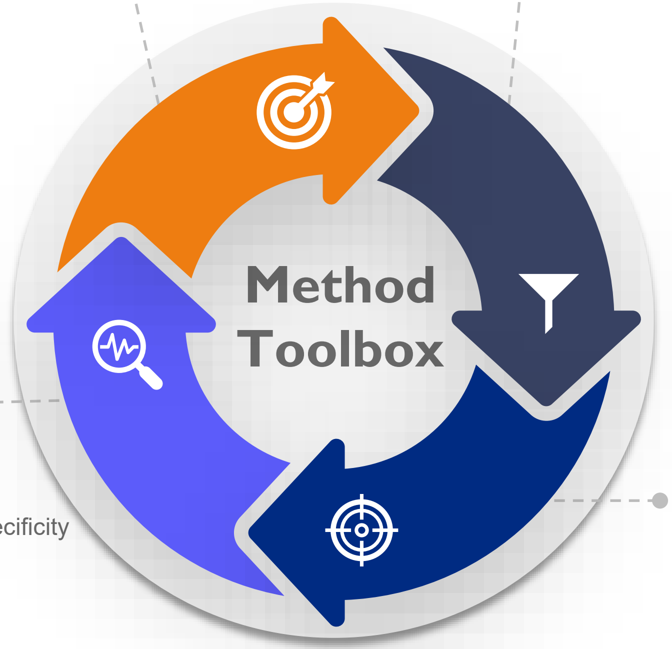
PFAS analysis - Challenges

- Definition of organo-F is dependent upon both chemical nature and analysis i.e. there is no “clear cut”
- How to close the (organo)-F mass balance in a sample do we need to get – quantitatively and qualitatively?
- Future LOQ requirements? Limits are frequently at environ backgrounds
- The need for online/on-site/in-field measurements?
  - Lab-on-a-chip: claims to detect 0.5 ng/l PFOS (see ref)
  - PIGE has also been suggested (but requires 2 lit of water)
  - But as for other devices of this kind, factors such as price, robustness, selectivity, matrix effects, accreditation, standards need to be addressed
- Case: ”Total PFAS” in the drinking water directive (DWD; 500 ng/l)
  - Method not decided upon, ongoing work. Group led by IWW (DE) (incl Örebro Univ). Is going to give a recommendation to the commission by the end of 23
  - How many member states will apply ”total PFAS” vs ”sum of PFAS” (i.e. PFAS20)?
  - Possibilties: EOF/AOF, TOP + ultrashort, Non-target + target
  - Key question is how TFA should be regarded, but also pesticides/pharmaceuticals

https://www.wateronline.com/doc/detecting-toxic-pfas-with-a-chip-sized-sensor-0001

PFAS Analysis - Summary

Summary PFAS Methods



Targeted PFAS

All Matrices – Up to 100 Compounds

Strengths: Selectivity, Sensitivity at ~1 ppt

Can be used for risk assessment

Weaknesses: Limited list of compounds

TOP Assay

All Matrices – Oxidizable Precursors

Strengths: Sensitivity at ~1-5 ppt

Specific to ‘unknowns’ with potential to convert to risk drivers

Weaknesses: Not specific

Does not complete a mass balance

Non-Target Analysis

All Matrices – Unknowns

Strengths: Ability to identify ‘unknowns’ with specificity

Ability to conduct novel compound identification

Weaknesses: Limited to current libraries

Limited quantitation, Time consuming

Total Organic Fluorine

All Matrices – Organic Fluorine

Strengths: Closest to a mass balance

Weaknesses: Sensitivity at ~1ppb

No selectivity

PFAS Methods - Conclusions

- PFAS is a broad and complex group of substances
  - One method is rarely enough to get a complete picture
  - The exception is direct comparison against reference values
- Target analysis (LC-MS/MS) most common
  - Individual substances, quantification, comparison to limit values
  - Selective and high sensitivity (= low reporting limit)
- Total methods
  - TOP – some structural info but not full identity and mass balance
  - TOP – linear and branched isomers can contribute to interpretation
  - EOF/AOF/TOF: "Most total" for mass balance, but only gives F/lit or F/kg
  - EOF/AOF: Fairly selective but not completely problem-free
- Suspect and Non-target Screening
  - HR instrumentation – detection of known/unknown structures
  - Time consuming, more costly
  - Limited possibilities for quantification
- Do not limit investigations to PFAS4!

Thanks!

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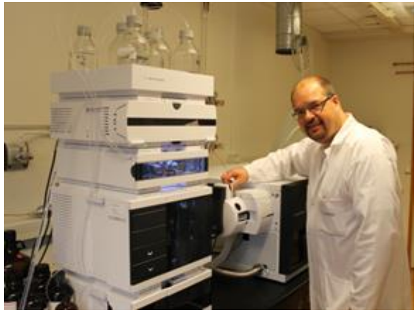
Thanks for listening!

Welcome to contact me!

Eurofins in Lidköping has become an EU PFAS competence center within the group!

Questions?

Meet us in Almedalen 27/6-1/7 (week 26) !



	Stockholm Tap Water	ng/l
	PFOS	2.0
PFAS4	PFOA	1,0
	PFHxS	1,1
	PFNA	0,3
	PFAS4	4,3
Sums	PFAS20 (DWD; NO)	9,2
	PFAS21 (SE)	9,2
	PFAS22 (DK)	9,2
	TFA	420
Ultra-	TFMS	1,6
short	PFPrA	<3
	PFEtS	<3
	PFPrS	<0.3