# Possibilities and challenges for PFAS analysis

Anna Kärrman

MTM Research Centre, Örebro University, Sweden

PFAS Contaminated sites risk-assessment 2020-11-09

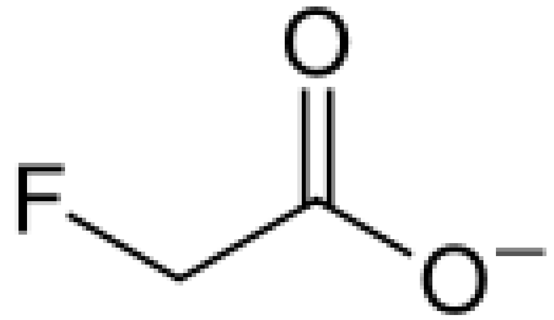
# Different forms of fluorine

$F^-$

most common form found in nature

*E.g.*

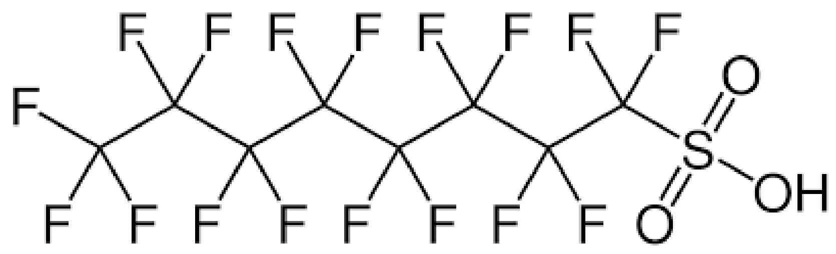
- *$CaF_2$*
- *NaF*
- *$Na_2PO_3F$*




Natural occuring organofluorine

*E.g.*

- *Trifluoromethane*
- *Fluoroacetate*
- *Fluorinated fatty acids*




Antropogenic organofluorine

*E.g.*

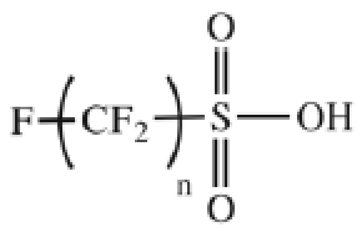
- *PFAS*
- *Pharmaceuticals*
- *Agrochemicals*

# Per- and polyfluoroalkyl substances (PFAS)

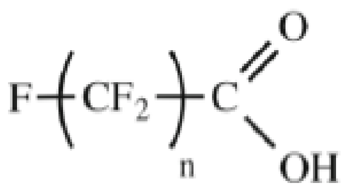
4730 PFASs (CAS-numbers, OECD definition 2018)

## Perfluoroalkyl acids (PFAA)

Examples:



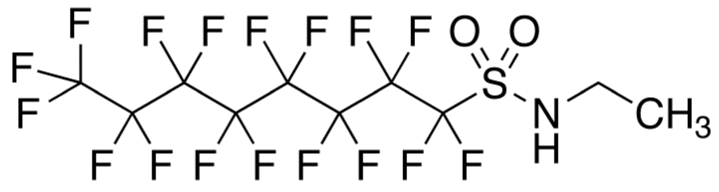
PFSA



PFCA

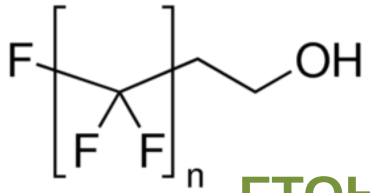
## Precursors

Examples of precursors to PFSA:

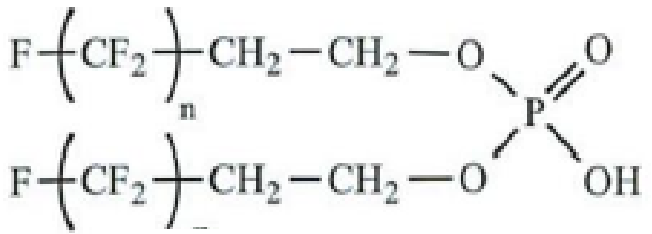


Et-FOSA

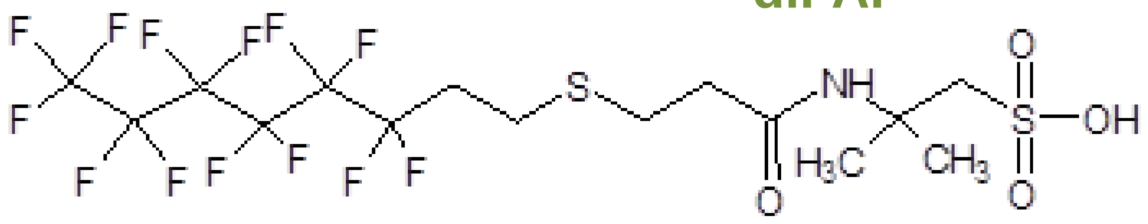
Example of precursors to PFCA:



FTOH



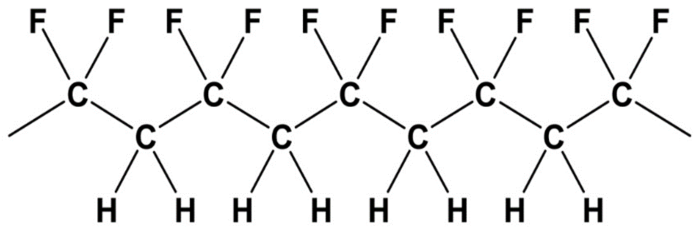
diPAP

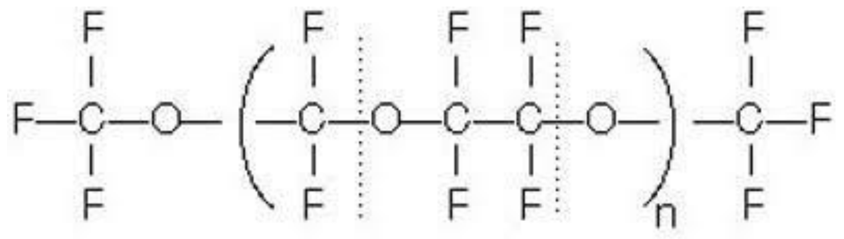


6:2 FTSAS

## Others

Polymers:



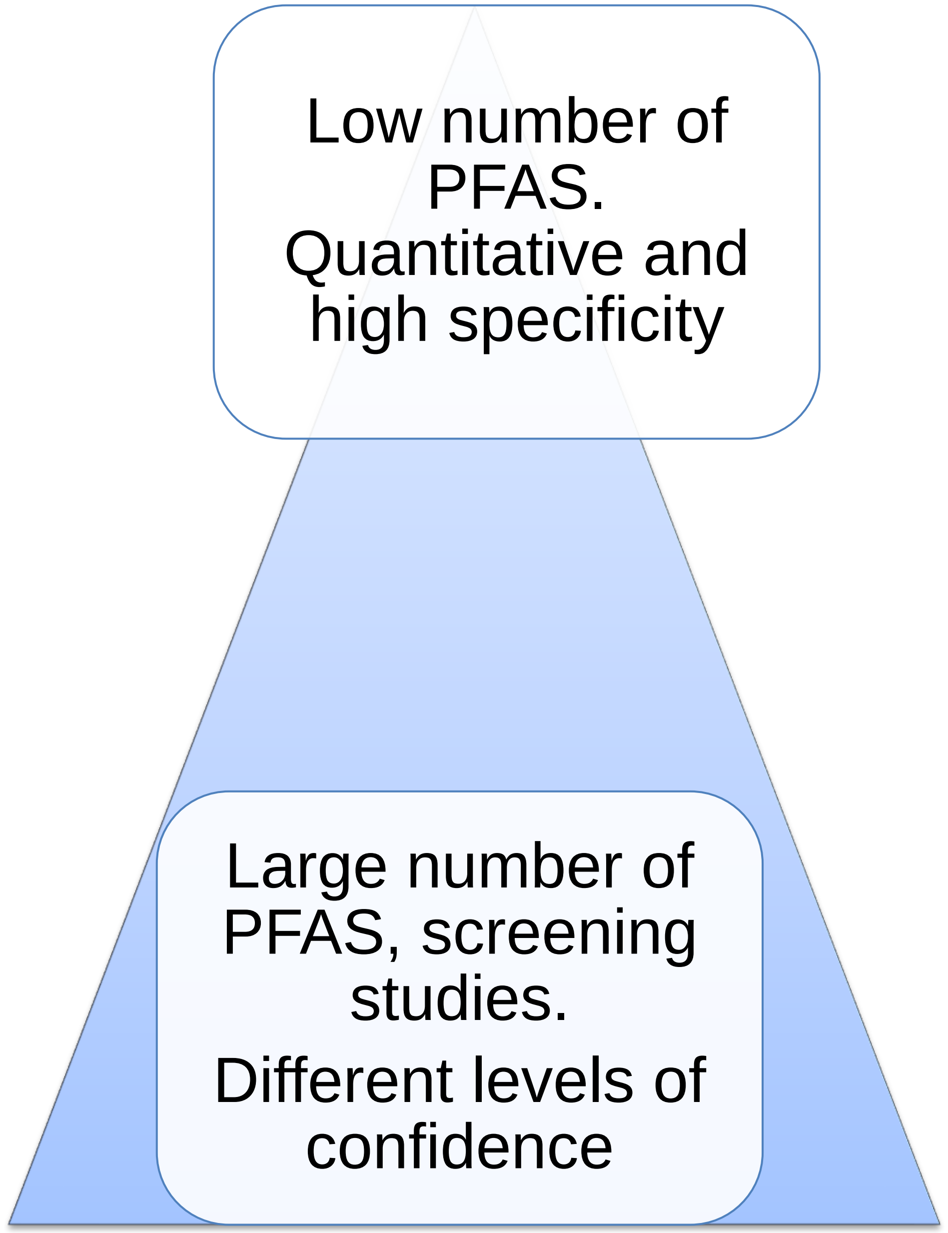


# What are being monitored, and why?

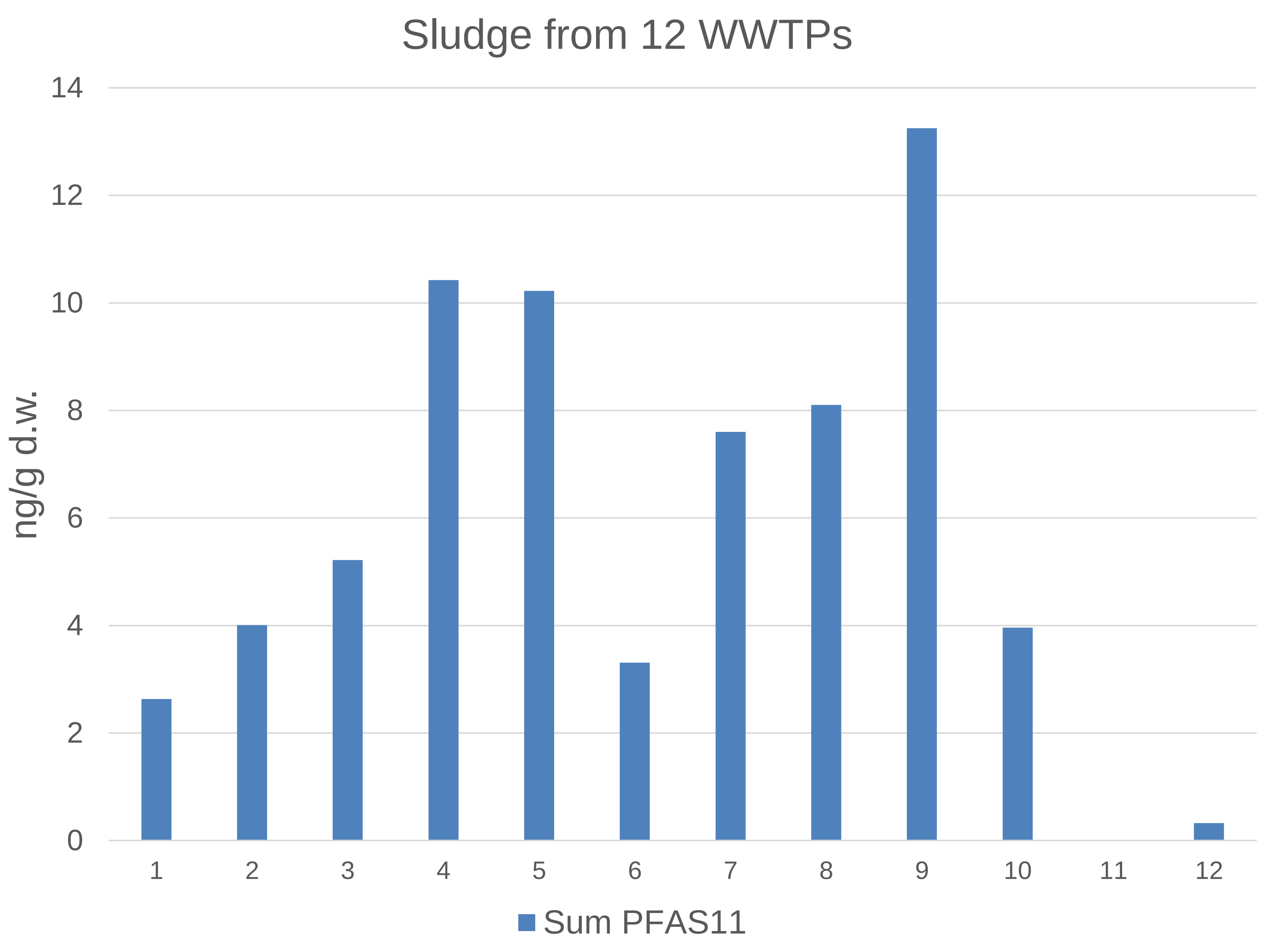
**Why?**

- Comply to regulations
- Study health effects and impacts
- Study removal efficiency in WWTP, drinking water, remediation,…
- Study environmental distribution and fate
- Occurrence of (new) PFAS in products, environment, humans,…

**What?**



# Example from waste water treatment




∑PFAS11:

PFBA

PFPeA

PFHxA

PFHpA

PFOA

PFNA

PFDA

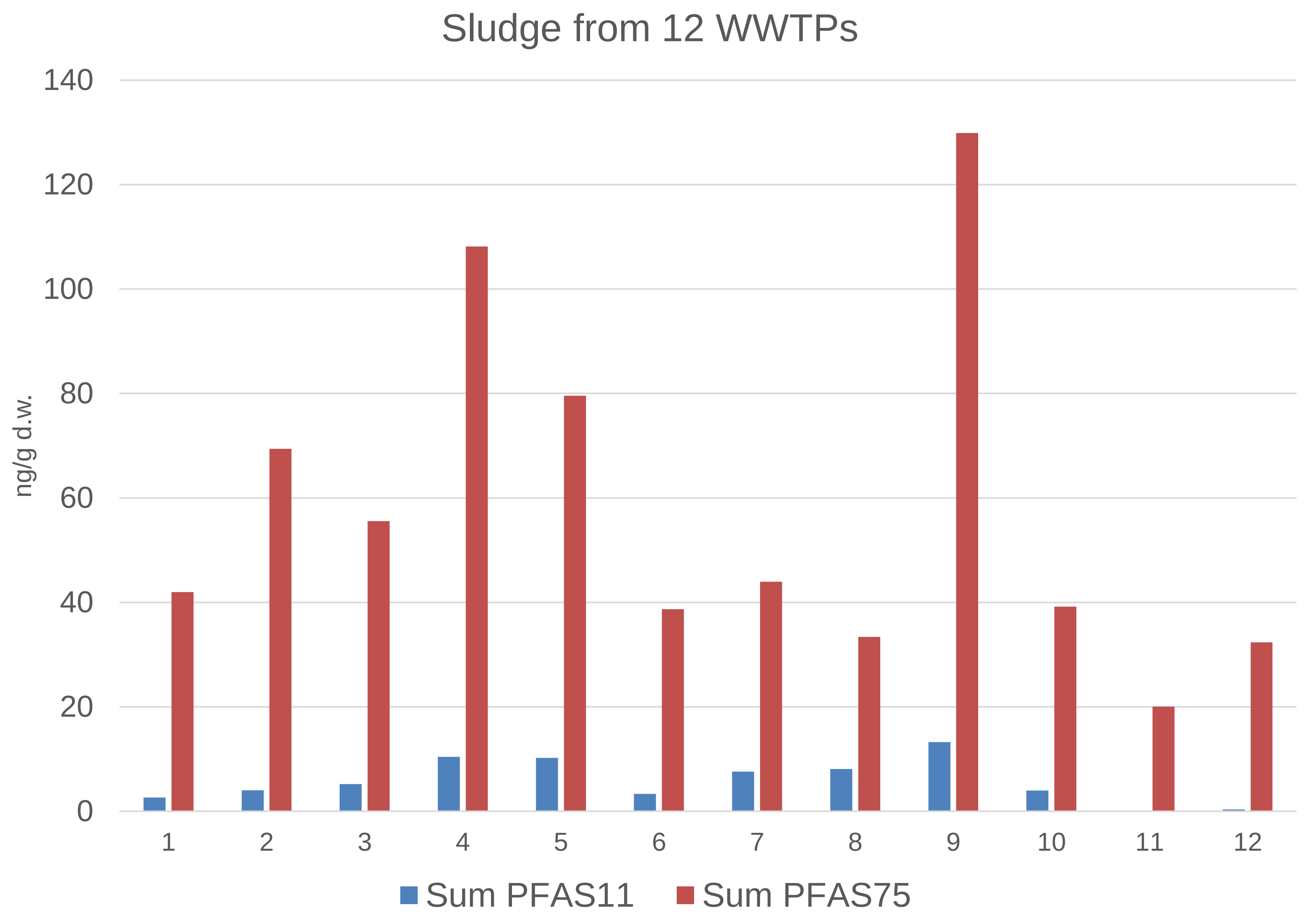
PFBS

PFHxS

PFOS

6:2 FTSA

# Example from waste water treatment




**Are there more PFAS?**

∑PFAS11:

PFBA

PFPeA

PFHxA

PFHpA

PFOA

PFNA

PFDA

PFBS

PFHxS

PFOS

6:2 FTSA

∑PFAS75:

PFCAs

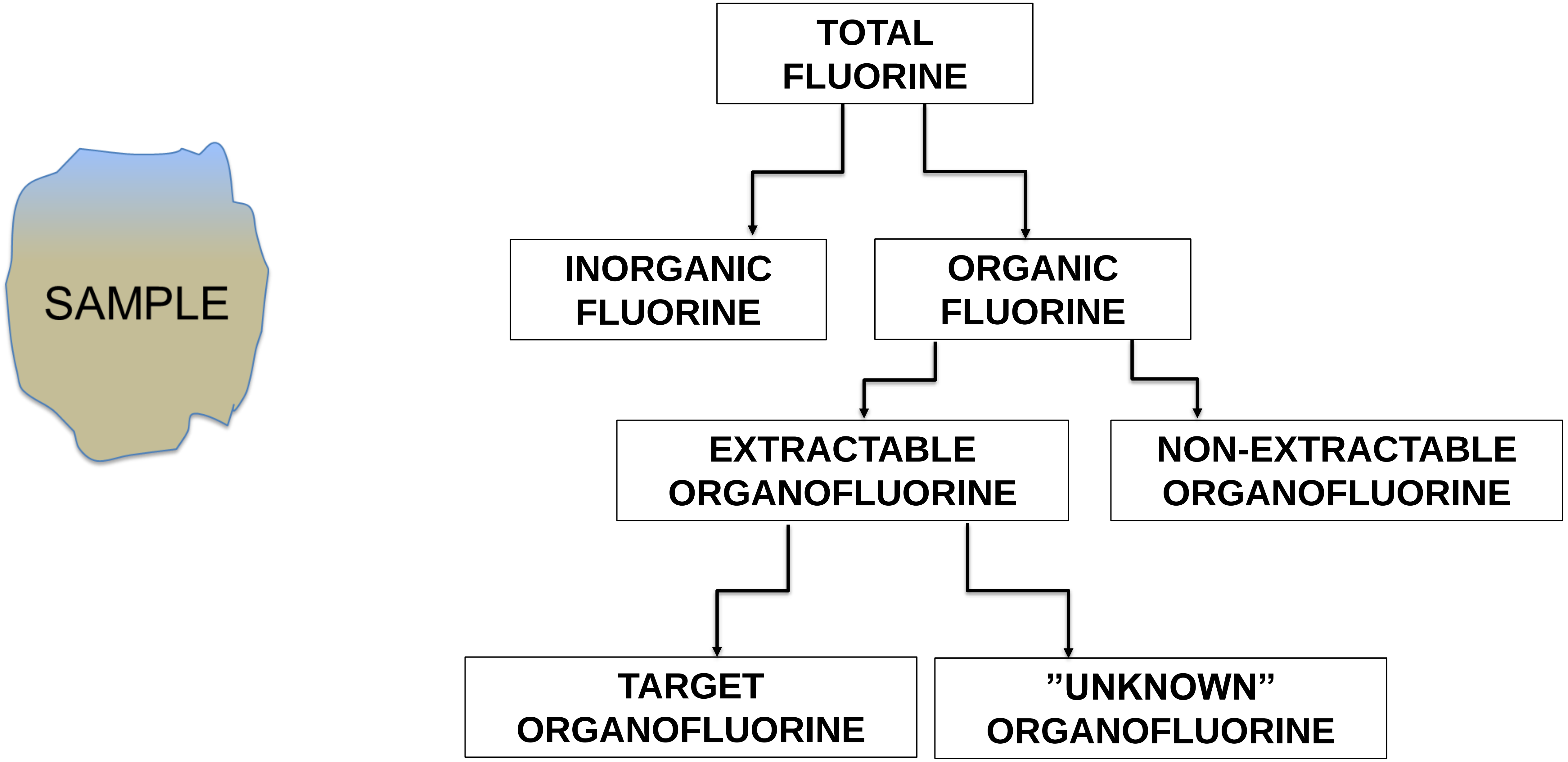
PFSAs

Precursors: PAPs, FTSAs, FTUCA, FTCA FOSA, FOSAA, diSamPAP,

PFPA/PFPiA

ADONA, HFPO-DA, PFECHS, F53B

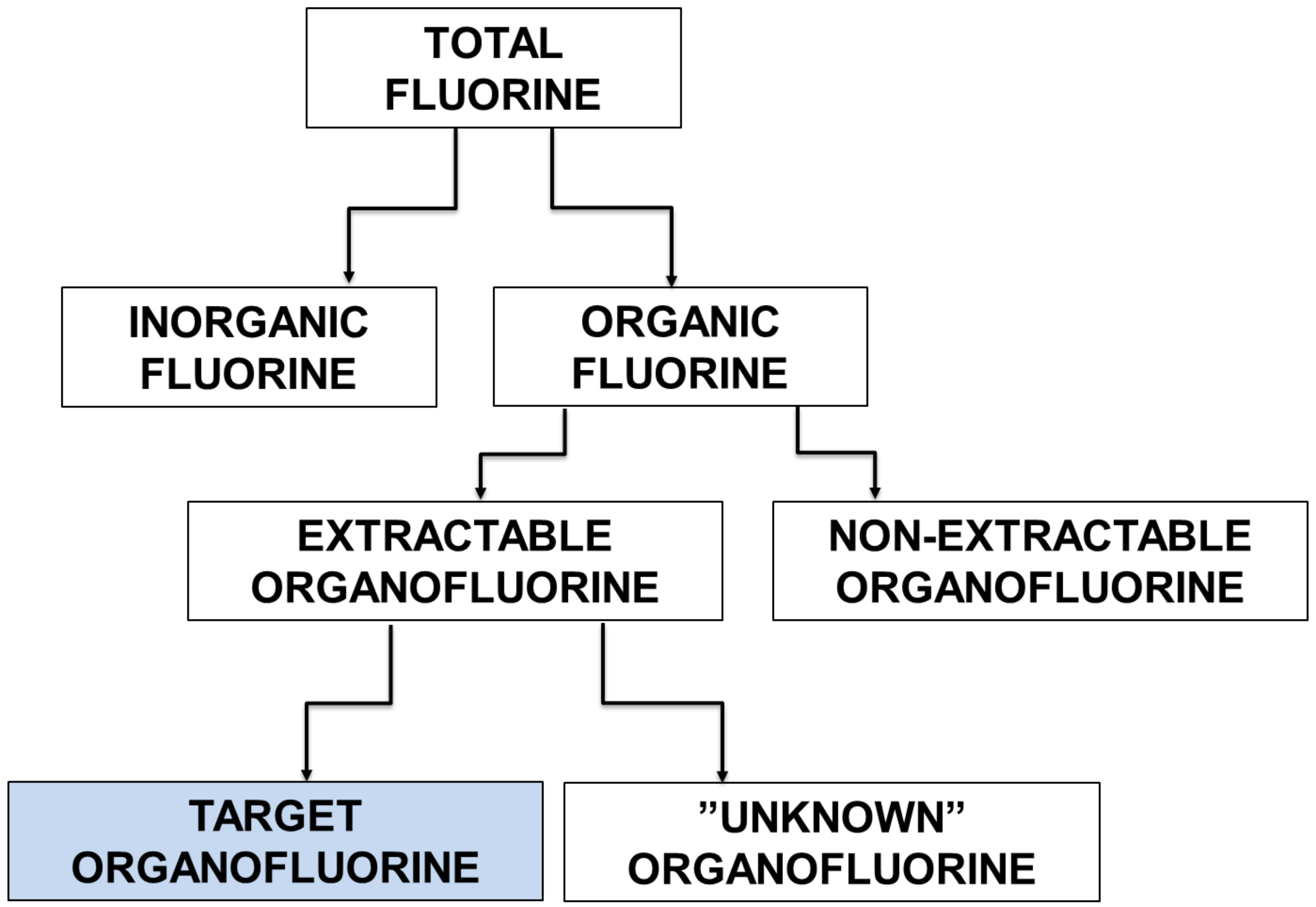
# Analytical possibilities



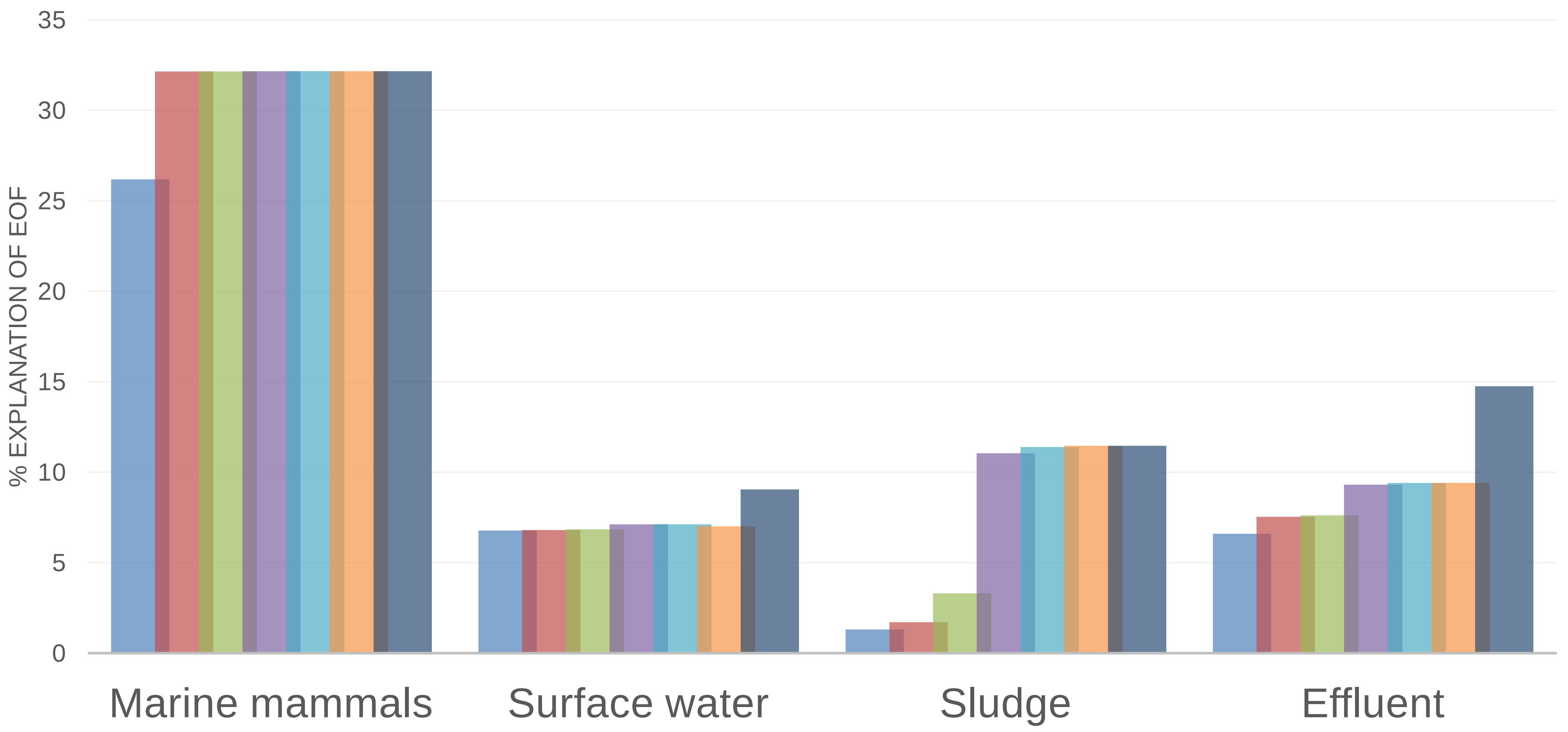
# Target analysis

PFAA and selected precursors:

- Sensitive (ppt-levels) and specific
- Routine measurement of ~40 PFAS
- Further challenges:
    - increase physicochemical range to be more inclusive
    - commercial standards
- Is it possible to target all PFAS?



# Profile analysis




| Largest contribution to Organofluorine: | PFCA + PFSA incl. long chain | PFCA + PFSA incl. C2-C3 | Precursors | PFCA + PFSA + Precursors |
|---|---|---|---|---|

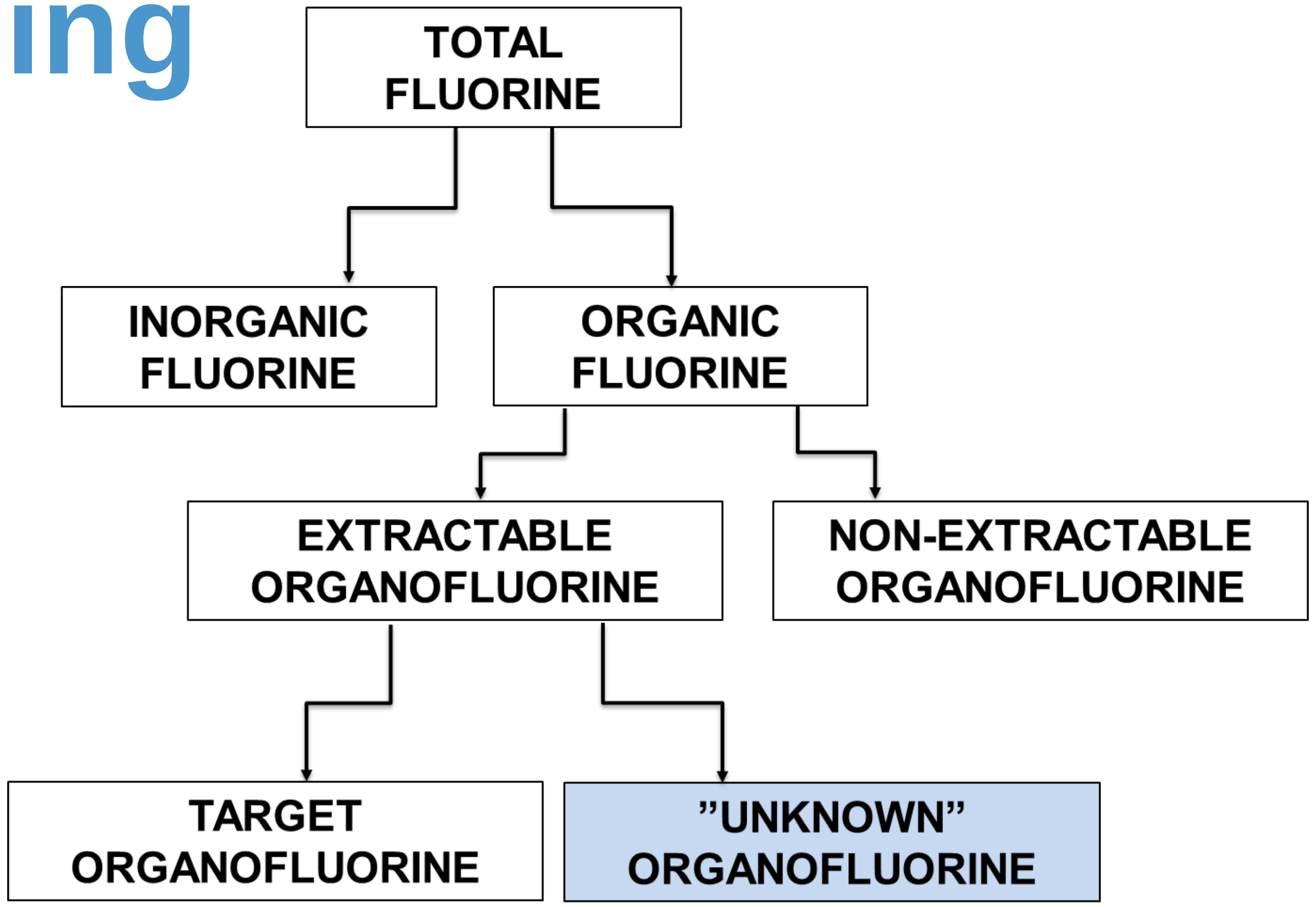
∑PFAS 11 ∑PFAS20 ∑PFAS25 ∑PFAS 54 ∑PFAS 64 ∑PFAS 70 ∑PFAS 73

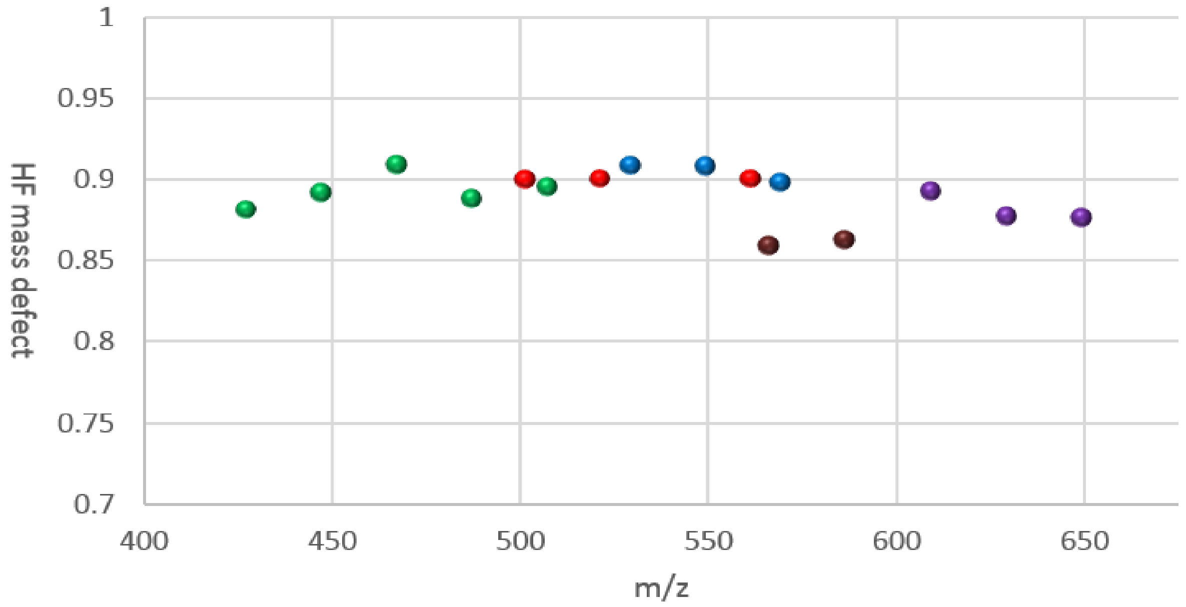
Profiles in environmental compartments
- surface water
- soil
- ground water
- Biota

Profiles from different contamination sources :
- historical AFFF
- recent AFFF
- ski wax
- paper treatment
- textile treatments
- etc.

# Suspect and nontarget screening

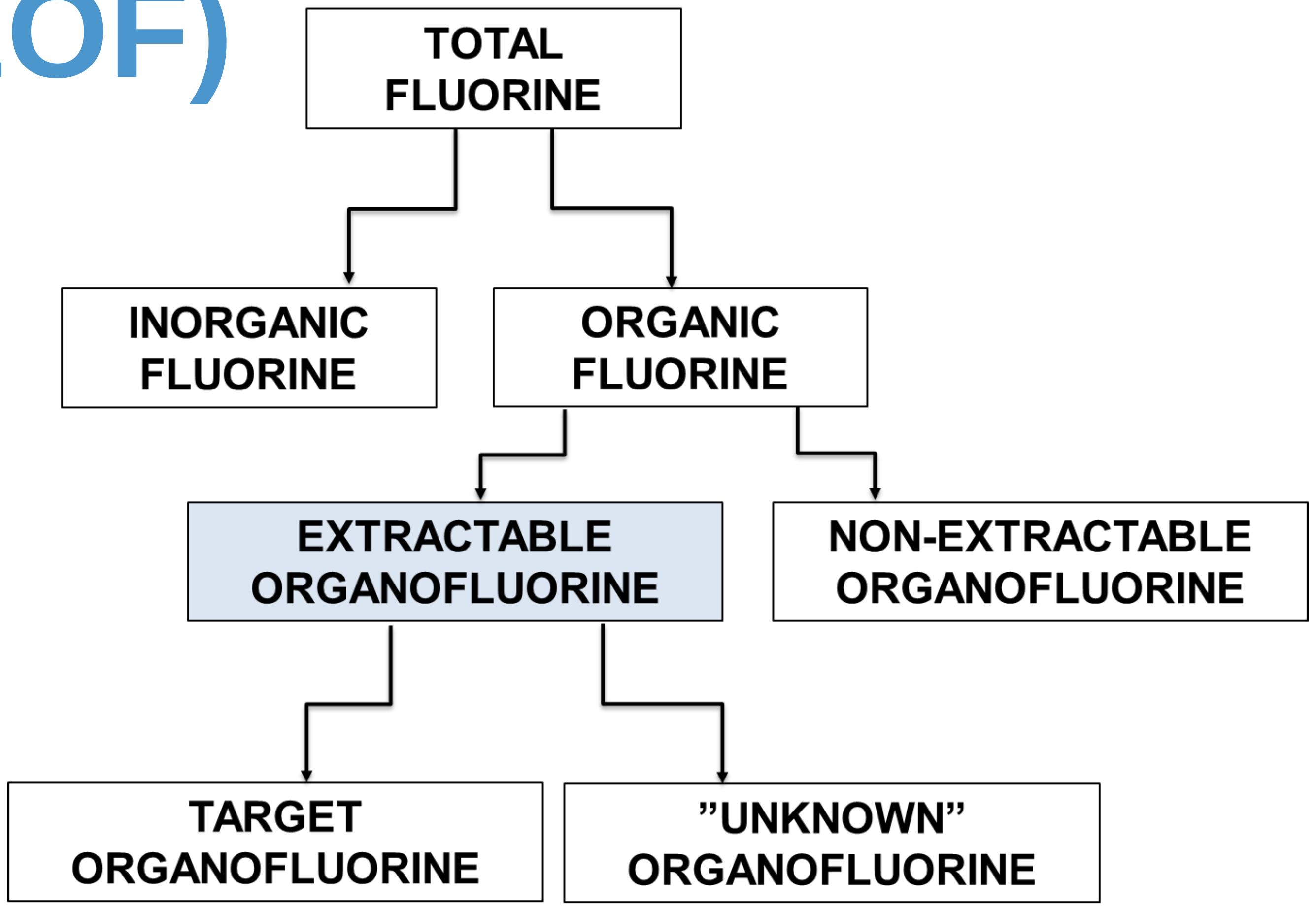
- Increasingly used to detect known unknowns (suspects), or unknowns (nontargeted)
- Limited possibilities for quantitative analysis
- Automation challenges for data mining and reduction
  - mass defects
  - fragment flagging
  - suspect lists



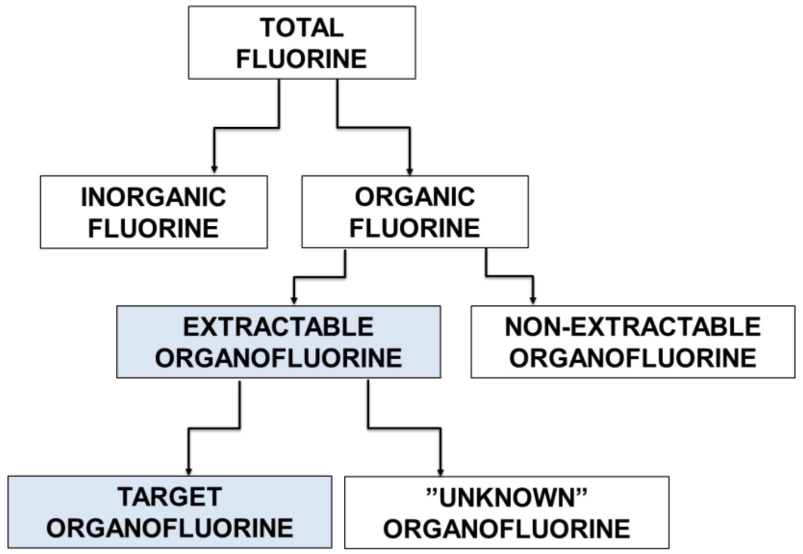



# Extractable organofluorine (EOF)

- Measure the elemental fluorine in an extract
- Possibilities to separate and fractionate different classes
    - High selectivity towards organofluorine after removing inorganic fluorine
- Results depends on the extraction method



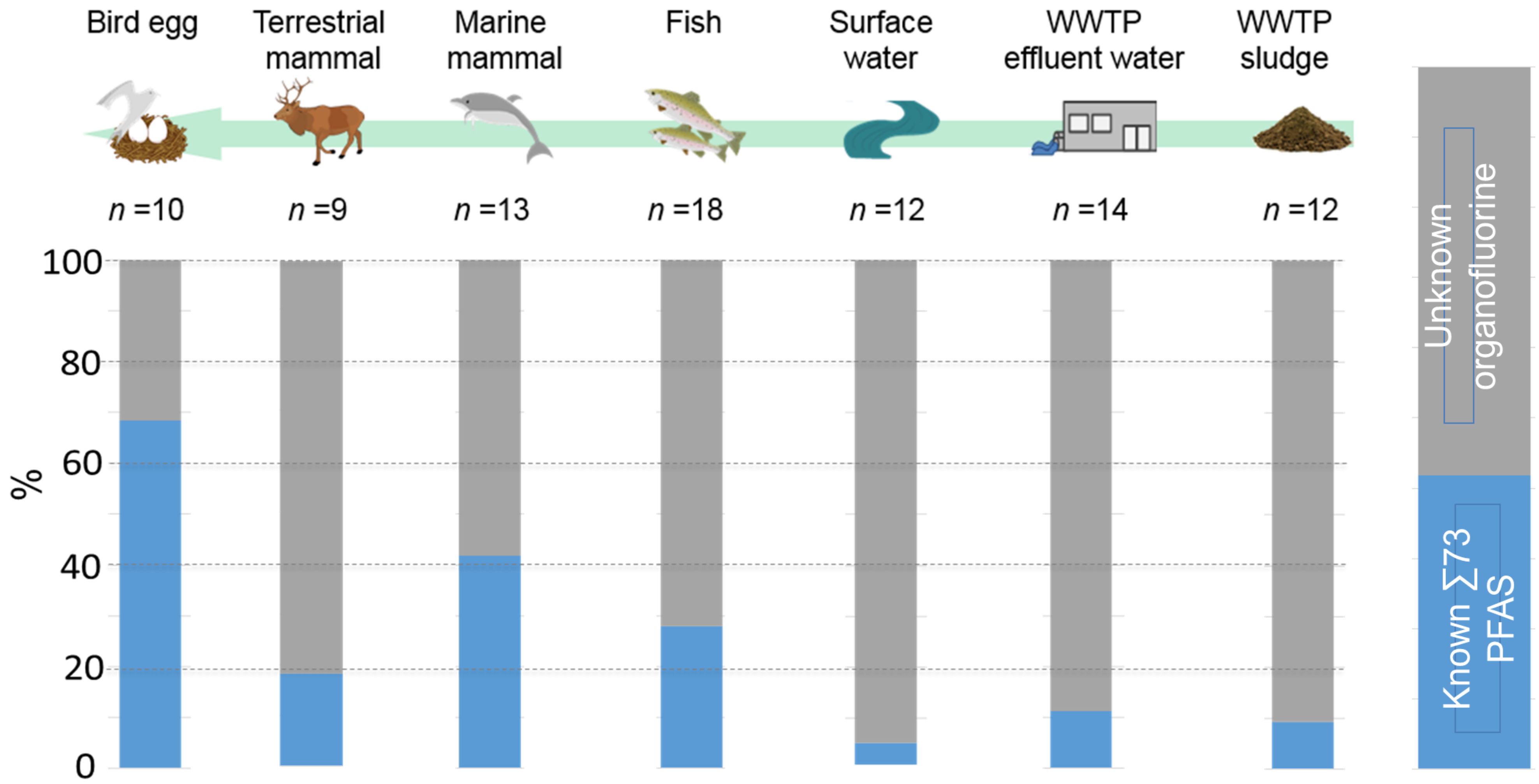
# Fluorine mass balance to show possible unidentified PFAS



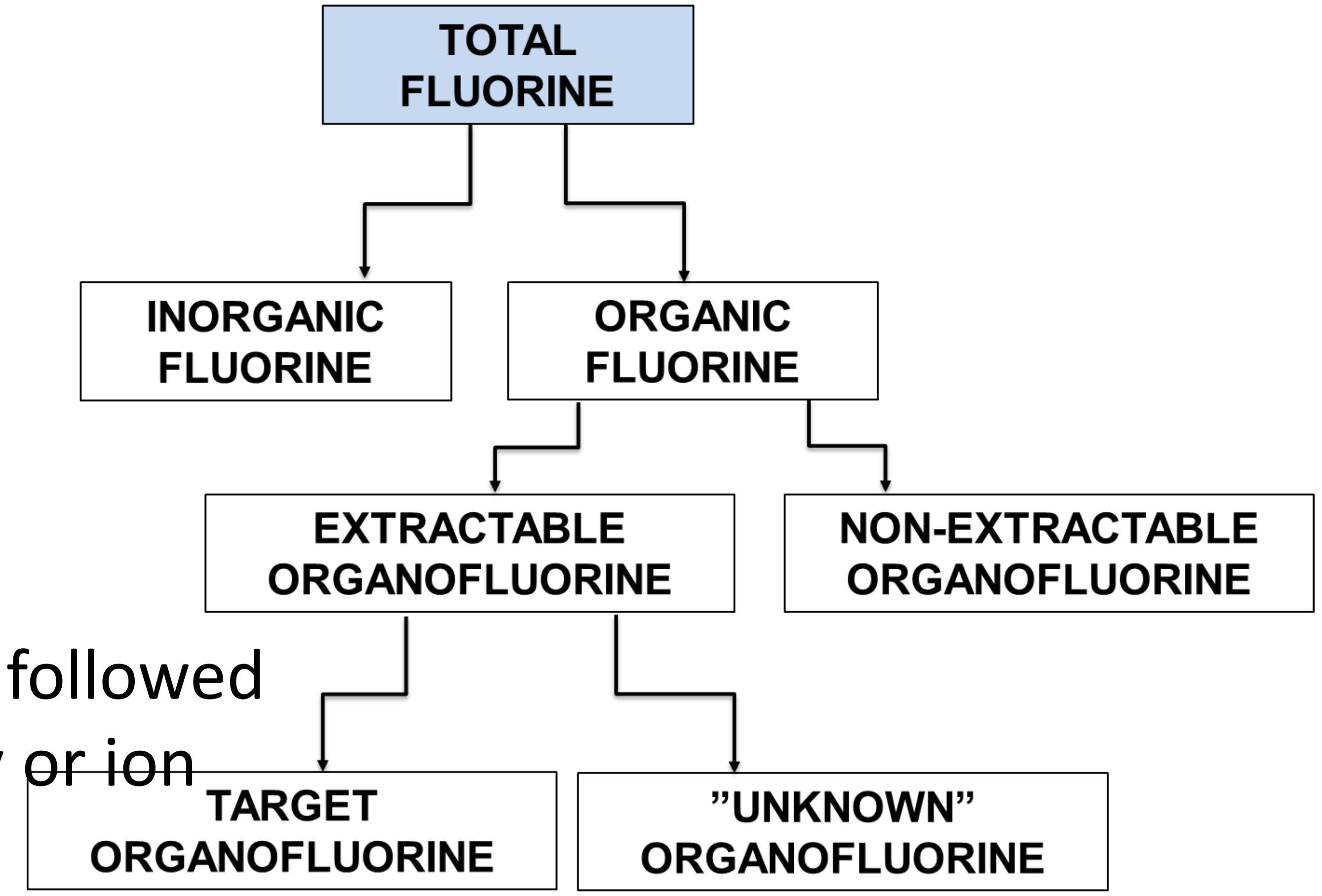

Comparing EOF with target PFAS can indicate presence of unknowns

**Mass balance = $C_F$ target / $C_F$ EOF**

- no information on identity of unknowns
- measuring F is less sensitive than target PFAS



# Total fluorine



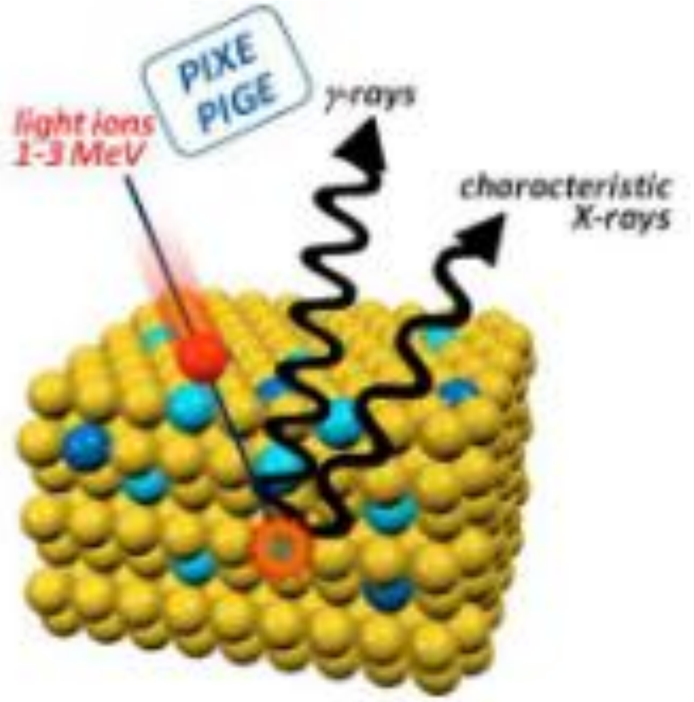

Indicates the presence of fluorine

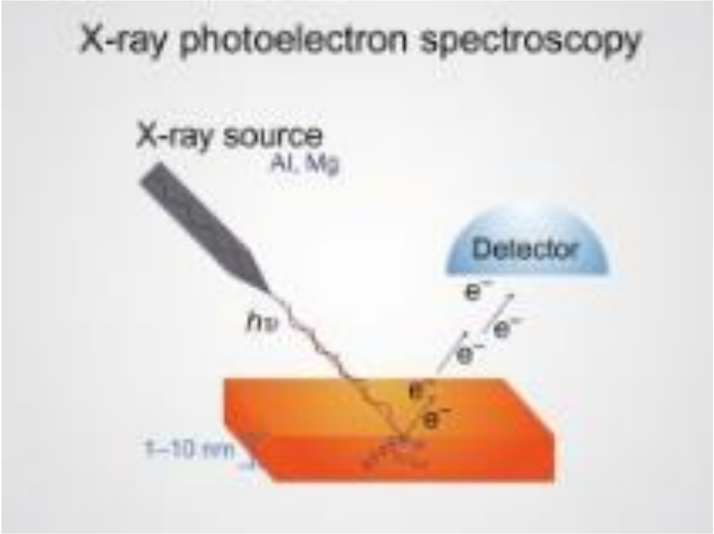
- Combustion
  - Pyrolysis (1000-1100 ° C) and thermal oxidation followed by fluoride measurement by ion chromatography or ion selective electrode
- Surface analysis
  - Particle Induced Gamma-ray Emission (PIGE) spectroscopy
    - surface 100–250 µm
  - X-ray photoelectron spectroscopy (XPS)
    - surface ≤0.1 µm

# Total fluorine

- Combustion
    - Inclusive for all elemental fluoride
    - Less sensitive (0.1-0.5 ppm F) than targeted analyses

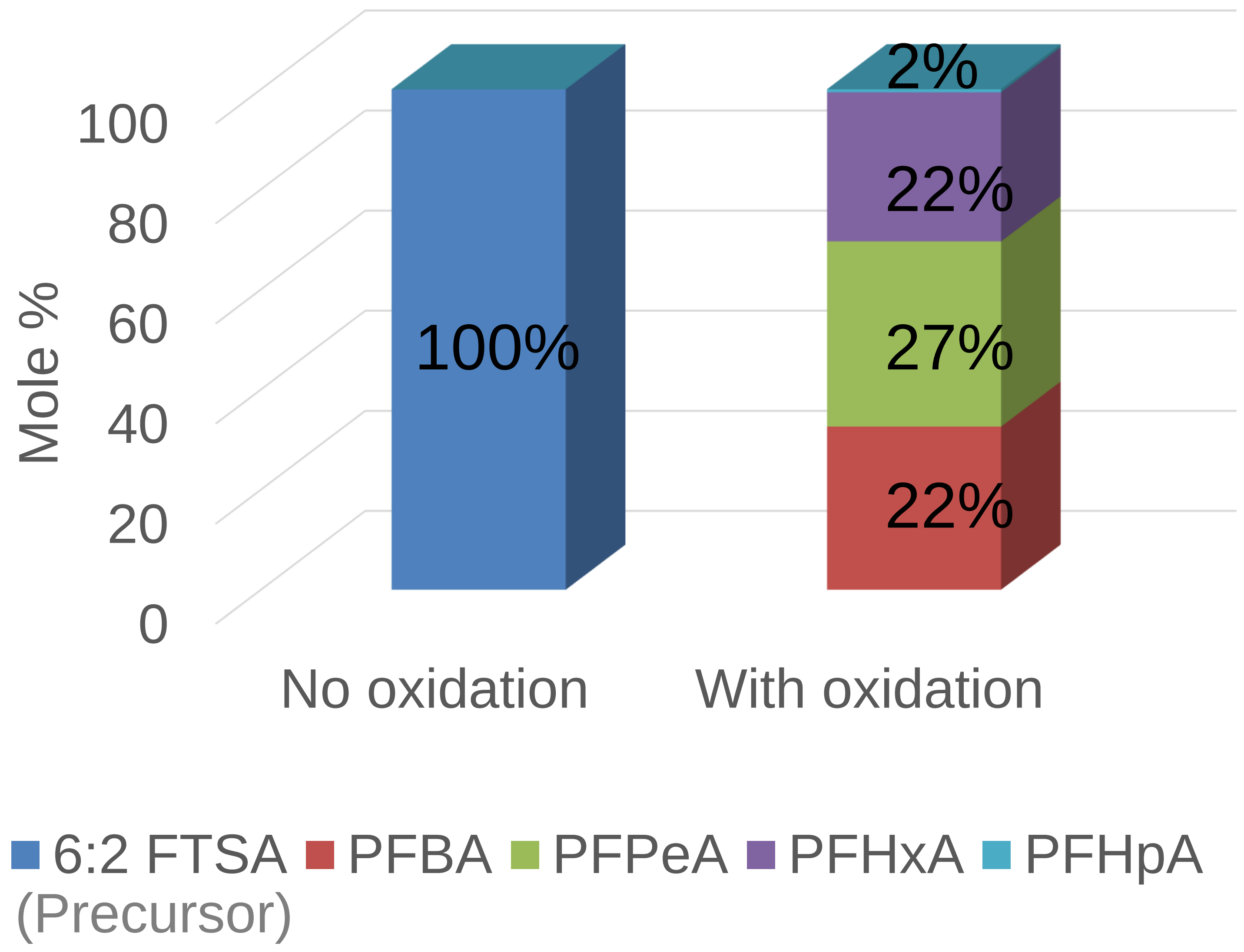
- Surface analysis
  - Particle Induced Gamma-ray Emission (PIGE) spectroscopy
    - High-throughput
    - Non-destructive
    - Less sensitive (50 nmol F/cm$^2$) than targeted analyses
  - X-ray photoelectron spectroscopy (XPS)
    - High-throughput
    - Widely-available instrumentation
    - Identification of perfluoroalkyl moiety
    - Detection limit 1%



# Total oxidizable precursor (TOP) assay

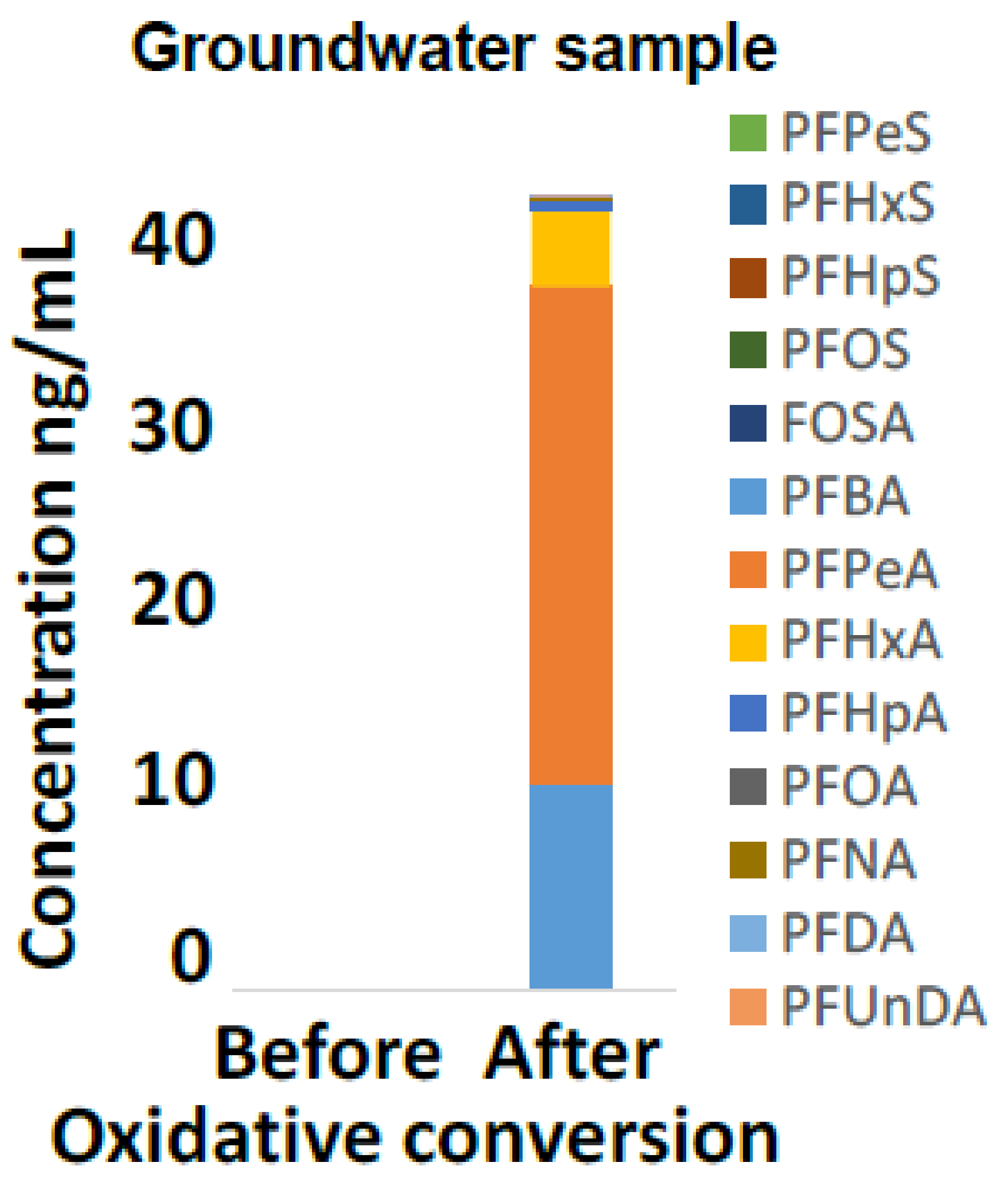
Chemical reaction of a *sample** or a *sample extract* converts precursors to perfluoroalkyl acids




*mainly aqueous samples

# Total oxidizable precursor (TOP) assay

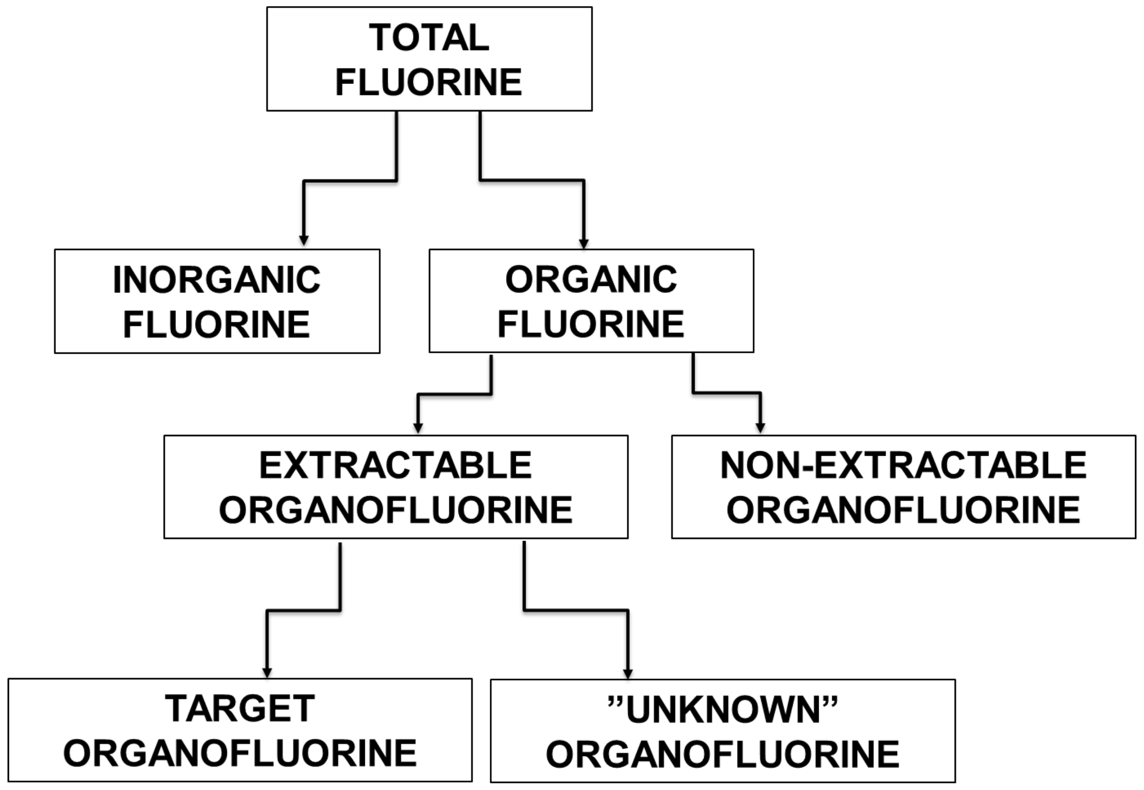
- Sensitive analysis (ppt-levels) after successful reaction
- Reaction products depends on structure of precursors (e.g. functional group and chain lengths)
- Reaction results depends on precursor stability towards hydroxyl oxidation



# Conclusion

Available inclusive methods for total fluorine, extractable organofluorine, and oxidizable precursors can act as triggers for further actions

- develop indicator values for background - and different contamination levels
- describe the method`s performances for different matrices and circumstances



# References


Gribble G. Naturally occurring organofluorines. In book: Organofluorines. Springer-Verlag Berlin Heidelberg. DOI: 10.1007/10721878_5

Houtz EF; Sedlak DL. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science & Technology* DOI: 10.1021/es302274g

Houtz EF, Sutton R, Park JS, Sedlak M. 2016. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Res* 95:142-149. DOI: 10.1016/j.watres.2016.02.055.

Koch A, Aro R, Wang T, Yeung LWY. 2020. Towards a comprehensive analytical workflow for the chemical characterisation of organofluorine in consumer products and environmental samples. *Trac-Trends in Analytical Chemistry* 123:9. DOI: 10.1016/j.trac.2019.02.024

Kärrman, A. , Wang, T. , Kallenborn, R. , Langseter, A. M. , Grønhovd, S. M. , Ræder, E. M. , Lyche, J. L. , Yeung, L. W. Y. & et al. (2019). PFASs in the Nordic environment: Screening of Poly- and Perfluoroalkyl Substances (PFASs) and Extractable Organic Fluorine (EOF) in the Nordic Environment. Copenhagen: Nordisk Ministerråd (TemaNord 2019:515). http://dx.doi.org/10.6027/TN2019-515

Liu, YN; D´Agostino, LA; Qu, GB; Jiang, GB; Martin, JW. 2019. High-resolution mass spectrometry (HRMS) methods for nontarget discovery and characterization of poly- and perfluoroalkyl substances (PFASs) in environmental and human samples. *Trac-Trends in Analytical Chemistry* DOI: 10.1016/j.trac.2019.02.021

Miyake Y, Kato M, Urano K. 2007. A method for measuring semi- and non-volatile organic halogens by combustion ion chromatography. *Journal of Chromatography A* 1139:63-69. DOI: 10.1016/j.chroma.2006.10.078.

Ritter EE, Dickinson ME, Harron JP, Lunderberg DM, DeYoung PA, Robel AE, Field JA, Peaslee GF. 2017. PIGE as a screening tool for Per- and polyfluorinated substances in papers and textiles. *Nucl Instrum Methods Phys Res Sect B-Beam Interact Mater Atoms* 407:47-54. DOI: 10.1016/j.nimb.2017.05.052

Tokranov AK, Nishizawa N, Amadei CA, Zenobio JE, Pickard HM, Allen JG, Vecitis CD, Sunderland EM. 2019. How Do We Measure Poly- and Perfluoroalkyl Substances (PFASs) at the Surface of Consumer Products? *Environmental Science & Technology Letters* 6:38-43. DOI: 10.1021/acs.estlett.8b00600.

Wang Z, Boucher J, Scheringer M, Cousins I, Hungerbühler K. 2017. Toward a Comprehensive Global Emission Inventory of C4–C10 Perfluoroalkanesulfonic Acids (PFSAs) and Related Precursors: Focus on the Life Cycle of C8-Based Products and Ongoing Industrial Transition. Environ Sci Technol 51:4482-4493. *Environmental Science & Technology* 51:4482-4493

Yeung LWY, Mabury SA. 2016. Are humans exposed to increasing amounts of unidentified organofluorine? *Environmental Chemistry* 13:102-110. DOI: 10.1071/en15041

Yeung LWY; Eriksson U; Kärrman A. 2017. Time trend of unidentified poly- and perfluoroalky substances in sludge from wastewater treatment plants in Sweden. S-EPA report urn:nbn:se:oru:diva-61515

Wang, J., et al., Fluorine in Pharmaceutical Industry: Fluorine-Containing Drugs Introduced to the Market in the Last Decade (2001–2011). Chemical Reviews, 2014. 114(4): p. 2432-2506.