Measuring PFAS- possibilities and challenges

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Disclosures

I have no financial, commercial, legal, or professional conflict of interest to disclose

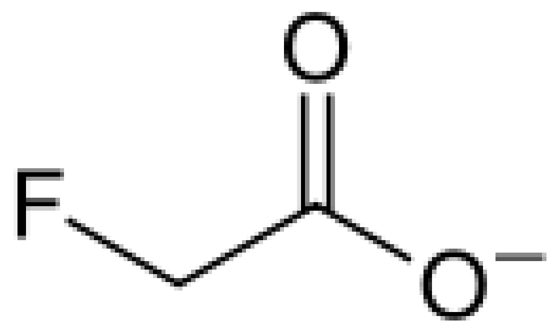
Content

- Introduction to analysis of PFAS as a whole group
    - Analytical possibilities
    - Analytical challenges
- Experiences from combustion ion chromatography (CIC) analysis
    - Target PFAS screening and EOF analysis of environmental and human matrices
    - Quality control
- Conclusions

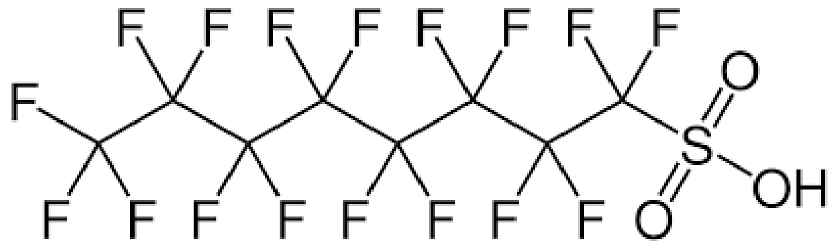
Introduction

F^{-}

most common form
found in nature



Example of natural
occuring organofluorine

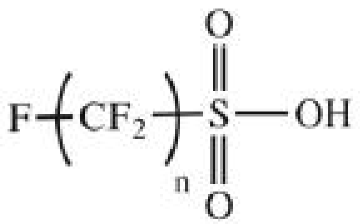


Antropogenic organofluorine

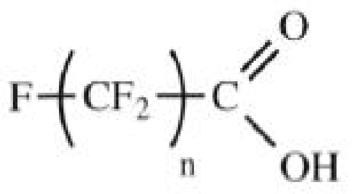
Per- and polyfluoroalkyl substances (PFAS) represent a class of substances containing at least one perfluorocarbon moiety (i.e. $–C_nF_{2n}–$)

PFAS groups

Perfluoroalkyl acids



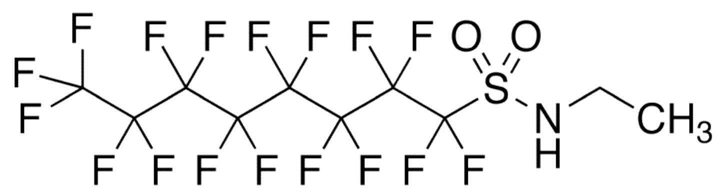
PFSAs



PFCAs

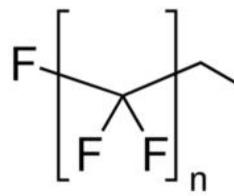
Precursors

Examples of precursors to PFSAs:

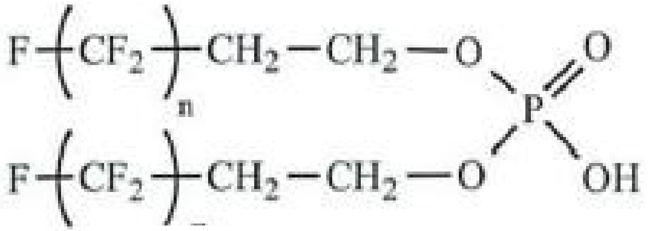


Et-FOSA

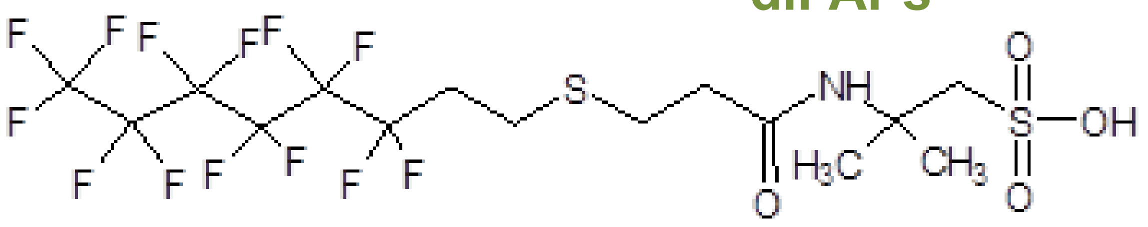
Examples of precursors to PFCAs:



FTOHs



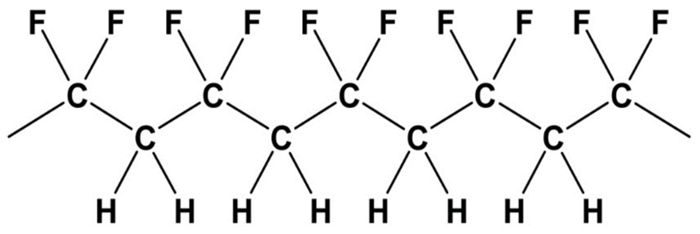
diPAPs

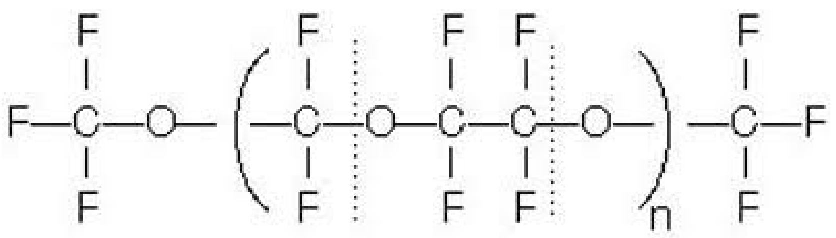


6:2 FTSAS

Others

Polymers:





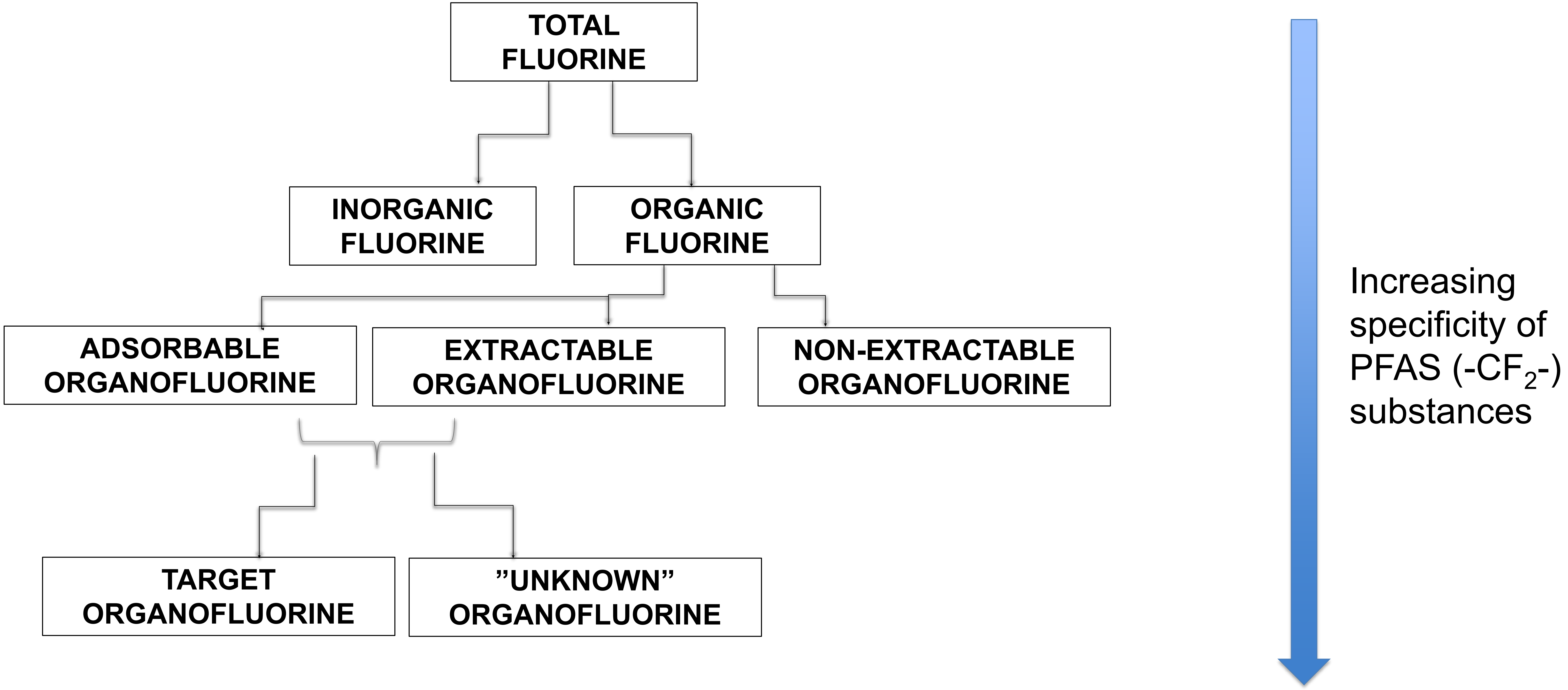
Wang et al. 2017

Monitoring PFAS

EU Drinking Water Directive (DWD) 2021: Group approach for "PFAS - Total" meaning the "totality of per- and polyfluoroalkyl substances" with the threshold concentration of 0.50 µg/L. To serve as a complement to the 100 ng/L limit based on the sum of 20 individual PFAS, as soon as the required method becomes available

The precautionary principle enables decision-makers to adopt precautionary measures when scientific evidence about an environmental or human health hazard is uncertain and the stakes are high

Analytical possibilities using fluorine as marker for PFAS



PFAS Total Assessment

- PFAS Total
  - Challenging
- Extractable/adsorbable organofluorine
  - Extraction methods suitable for the sample matrix together with a fluorine specific detection
- Total fluorine
  - Direct measurement of fluorine with fluorine specific detection

Group methods

Fluorine specific:

- Combustion ion chromatography (CIC) (Miyake et al. 2007, DIN 38409-59:2020-11)
- Particle Induced Gamma-ray Emission (PIGE) spectroscopy
- Inductively coupled plasma mass spectrometry (ICP-MS/MS) (Jamari et al. 2017)
- Continuum source graphite furnace molecular absorption spectroscopy (HR-CS-GF-MAS) (Gehrenkemper et al. 2021)

Specific for perfluorinated substances:

- X-ray photoelectron spectroscopy (XPS)
- ^{19}F NMR spectroscopy

Hydropyrolysis, specific for F. Total Fluorine or EOF/AOF

Specific for F

Common instrument for element analysis, measures BaF

Specific analysis of GaF (I_{GaF}: 211,248 nm)

High detection limits

Analytical challenges

- High standardization requirements may hinder data production of PFAS as a group, needed for hazard assessment
- Demand for low quantification levels
    - EFSAs TWI reduced with three orders of magnitude from 2008 to 2020 (currently 4.4 ng/kg.bw/wk for ∑PFOS, PFOA, PFHxS, PFNA)(EFSA 2020)
    - Miljøstyrelsen (Denmark) limit value for ∑PFOS, PFOA, PFHxS, PFNA in drinking water 0.002 ug/L

Analytical challenges for PFAS-Total assessment

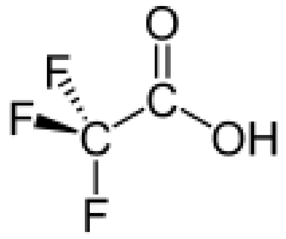
- Inorganic fluoride needs to be removed before fluorine detection

Drinking water	Up to 4 mg/L*
Ocean water	1.2-1.4 mg/L
Surface water	<0.5 mg/L- 2800 mg/L**
Ground water	<10 mg/L
Plasma	9.5-28.5 ug/L ***
Human milk	3.8-7.6 ug/L ***
Urine	0.2-3.2 mg/L ***

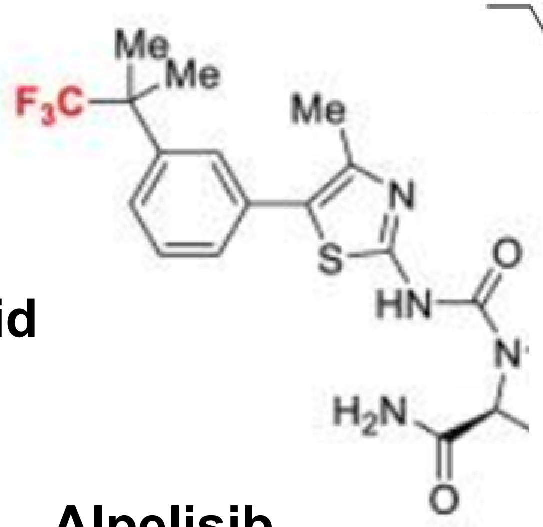
*recommended limit (EPA), ** upper range volcano affected water, *** ranges depend on intake

- Do we want to target all organofluorines?

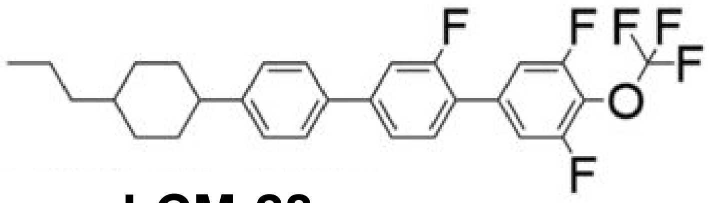
  Low-fluorinated pesticides, pharmaceuticals, etc.



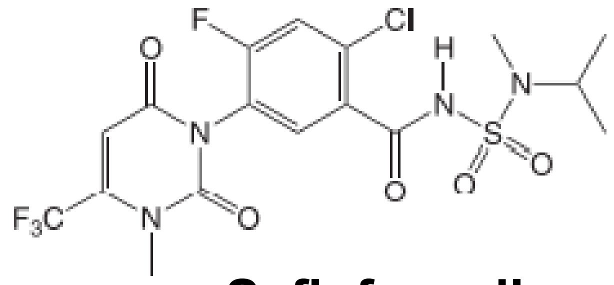
Trifluoroacetic acid



Alpelisib



LCM-28

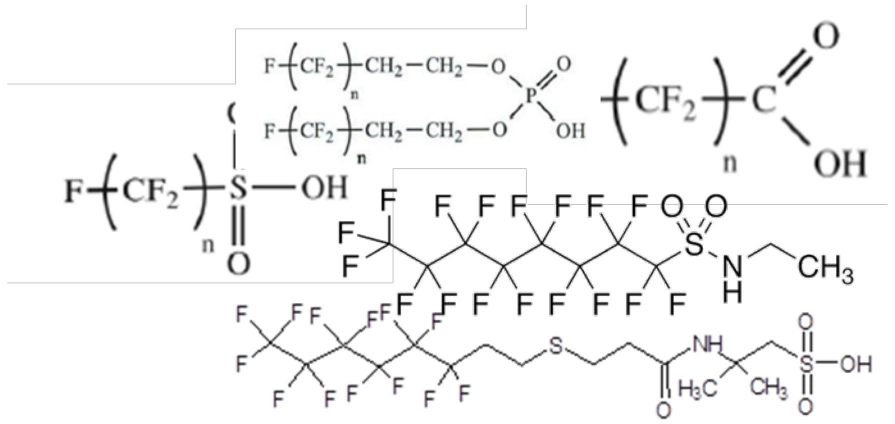


Saflufenacil

- Extraction methods

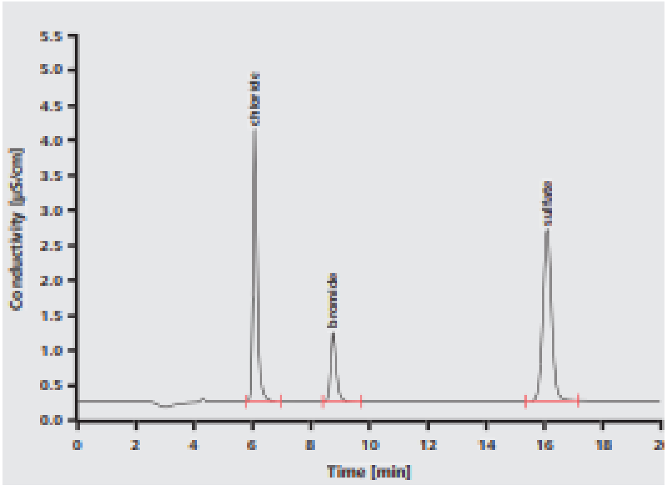
  Multiple approaches might be required for PFAS-Total

Combustion ion chromatography (CIC)



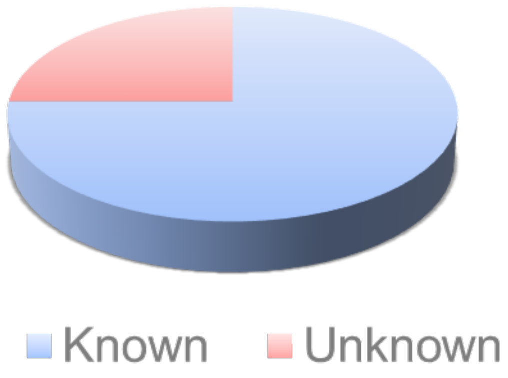
HF

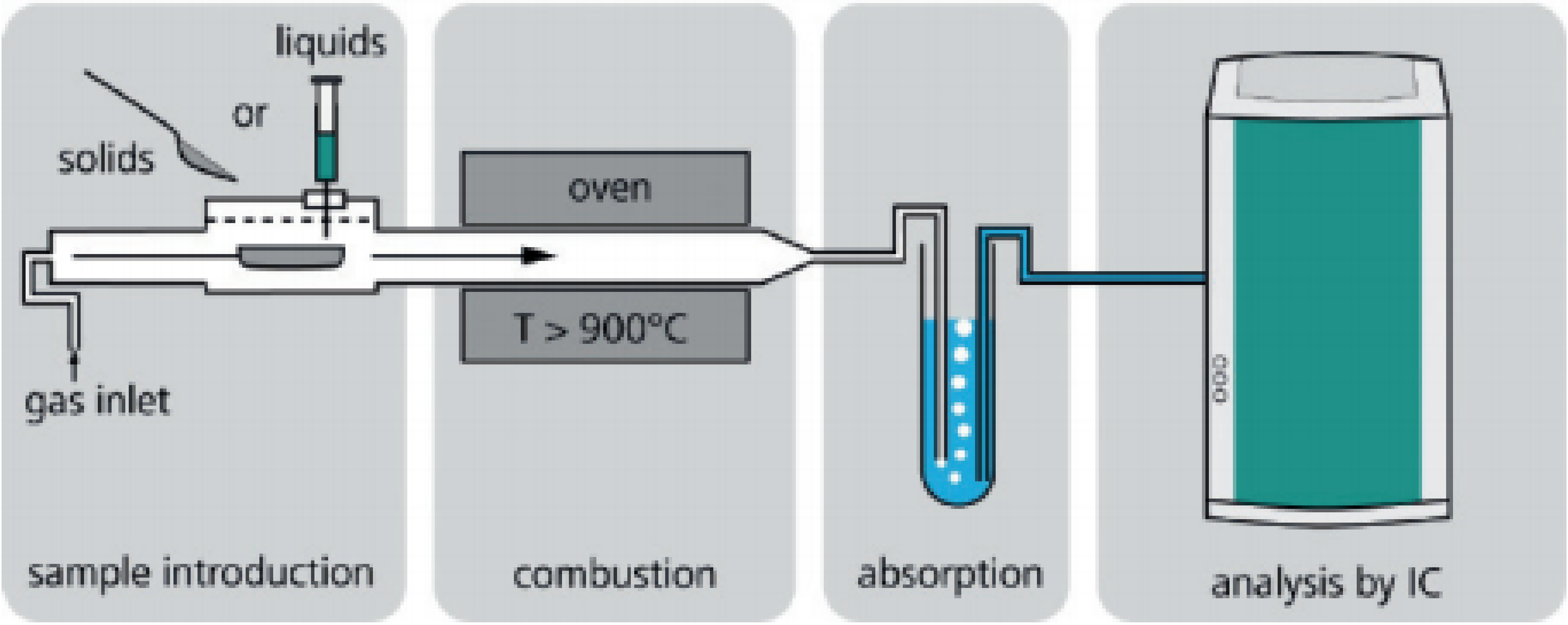
F-



+ target PFAS analysis

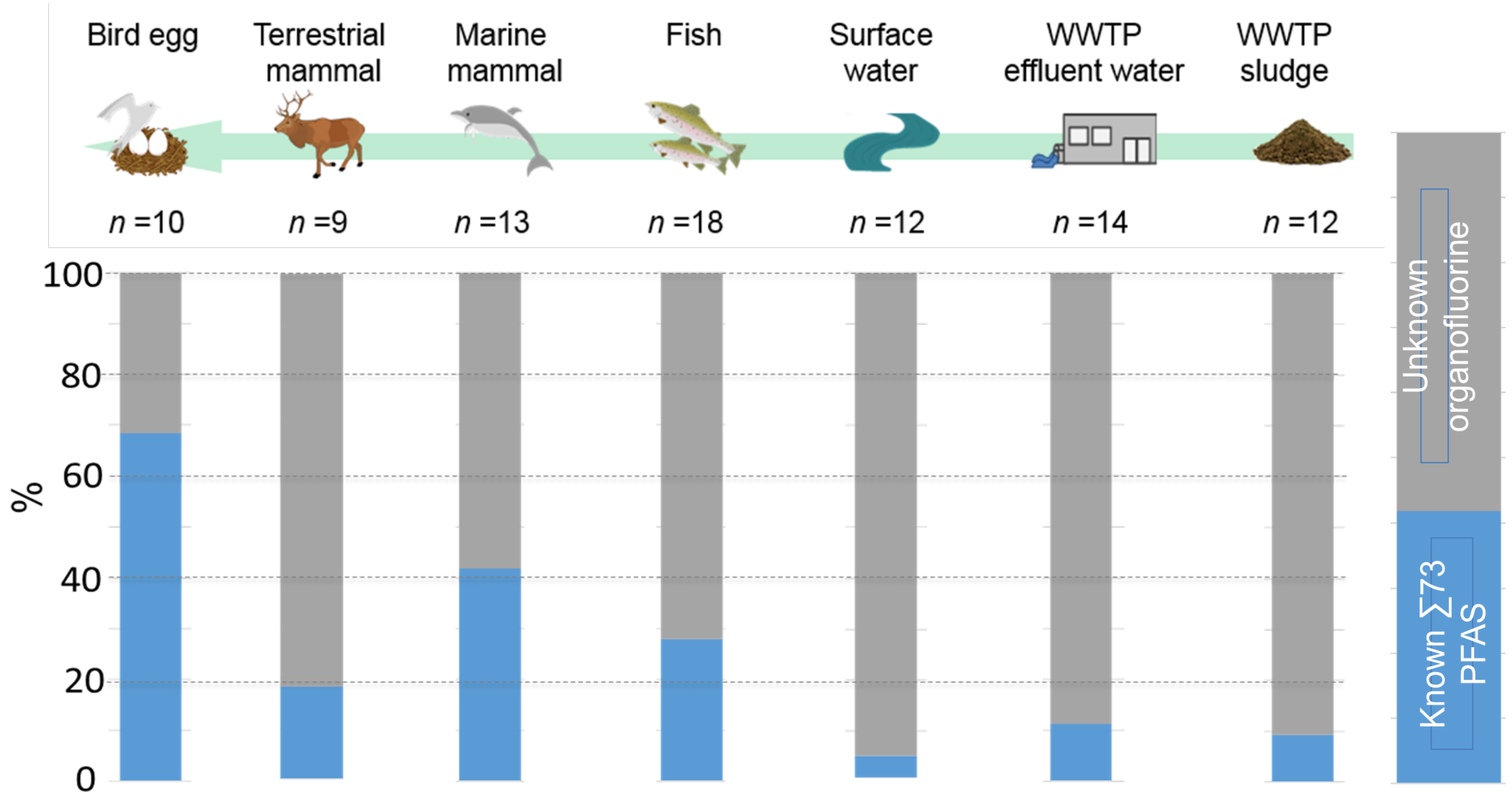
Fluorine mass balance





Extractable organofluorine (EOF) - fluorine mass balance to reveal unidentified PFAS

Comparing EOF-CIC with target PFAS can indicate presence of unknown PFAS



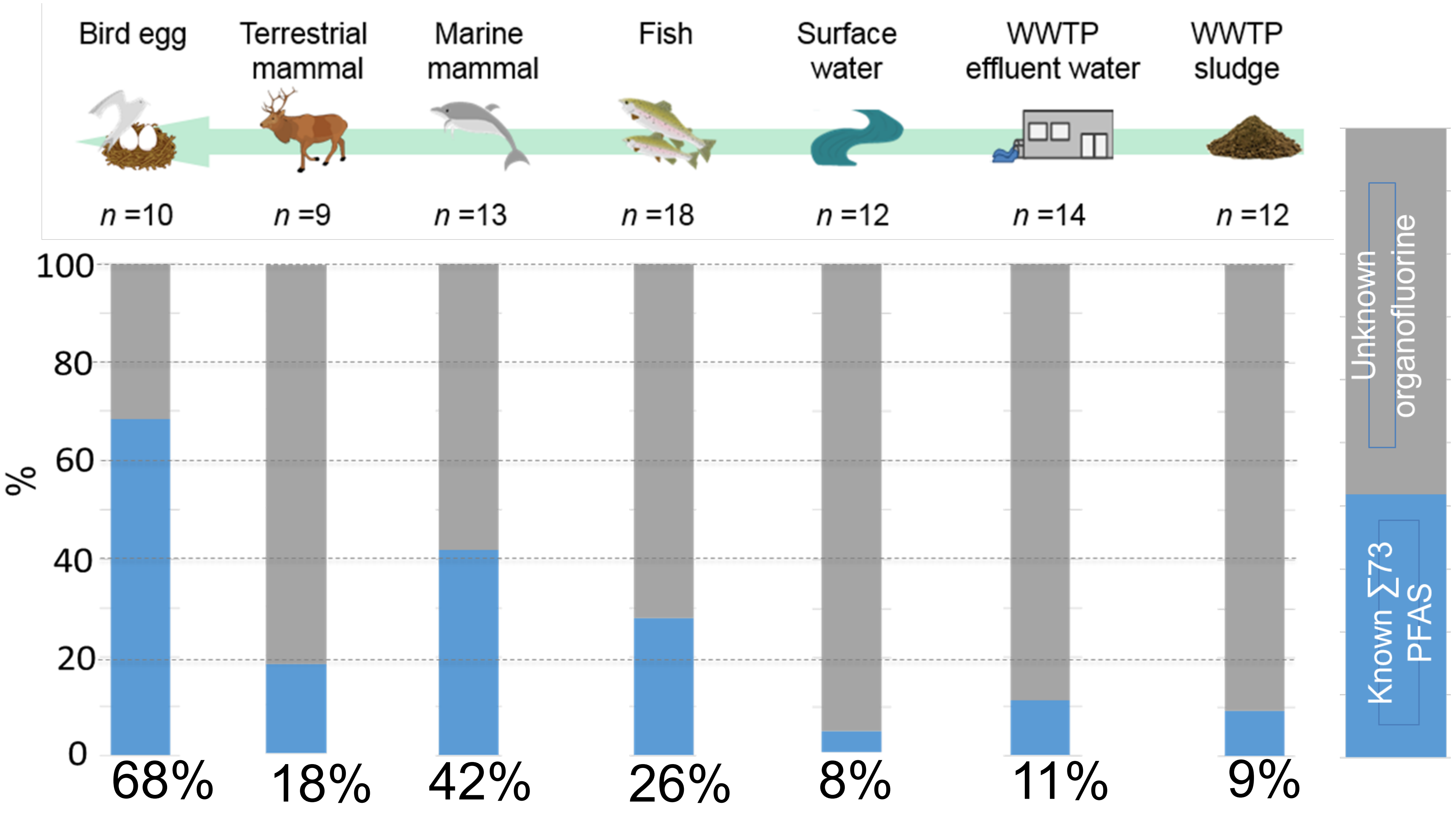
Kärrman et al. 2019. PFASs in the Nordic environment. TemaNord 2019:515

Extractable organofluorine (EOF) - fluorine mass balance to reveal unidentified PFAS

Comparing EOF-CIC with target PFAS can indicate presence of unknown PFAS

Average target PFAS of EOF (% showing in the graph)

- No information on the identity of unknowns
- Measuring F is less sensitive than target PFAS



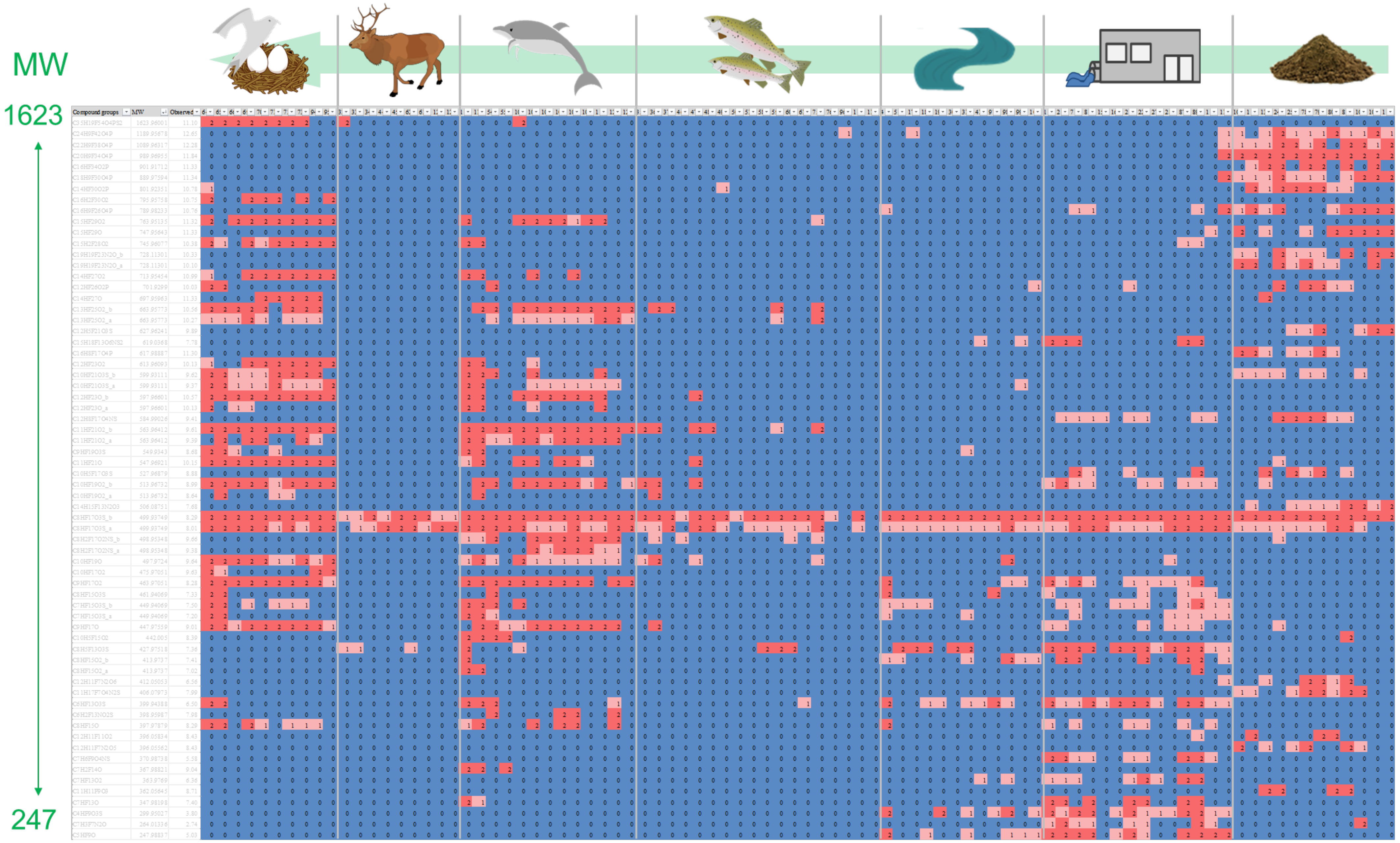
Kärrman et al. 2019. PFASs in the Nordic environment. TemaNord 2019:515

Suspect screening to identify unknowns

Norman suspect list exchange (no. 26 and No 46), n=3236

Challenges:

- Confidence in the identification
- Quantification using surrogate standards



0 : No EIC peaks

1) Low identification level

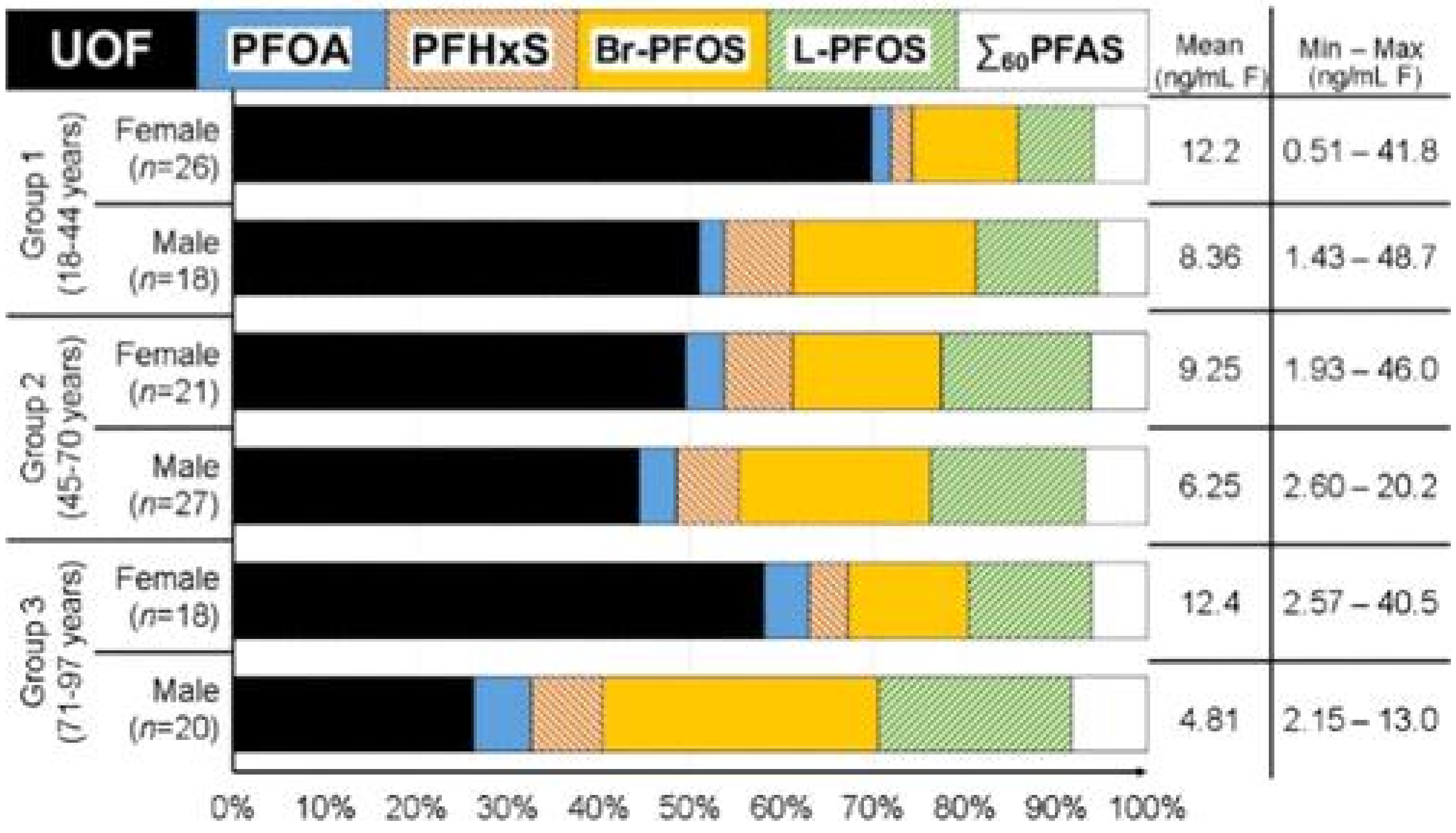
- Response: >=1000
- Mass error (ppm): ±5 ppm

2) High identification level

- Response: >=10000
- Mass error (ppm): ±5 ppm
- Isotope Match Intensity RMS Percent: =<20
- Isotope Match Mz RMS PPM: ±5

EOF-CIC in human blood

- Unidentified organofluorine in Swedish whole blood
  - women average 60%
  - men average 41%
- Large variations in and between groups
- Significant differences between men, women and age groups



Aro et al. 2021. Organofluorine Mass Balance Analysis of Whole Blood Samples in Relation to Gender and Age

Pre-validation of EOF-CIC (3 laboratories)

Ground water and fortified ultrapure water

SPE-(WAX[(1)])-CIC

- 500 mL
- pH 4
- Extended wash (total 38 mL)

WWTP effluent

SPE-(WAX[(1)])-CIC

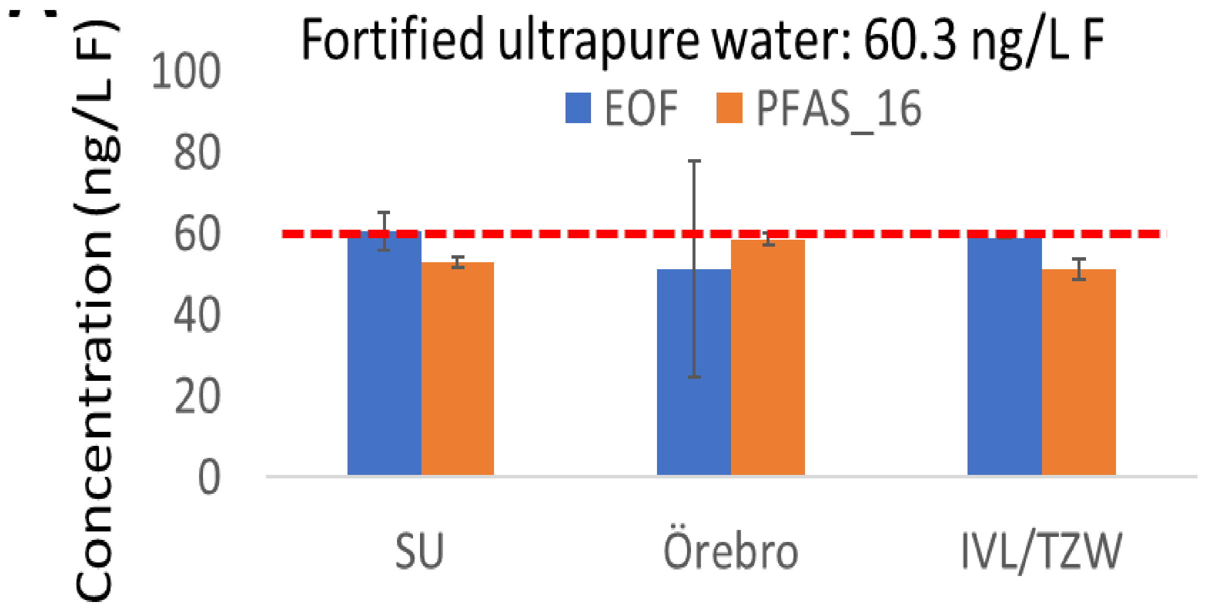
- 250 mL
- Filtration, pH 4
- Extended wash (total 38 mL)

Sludge

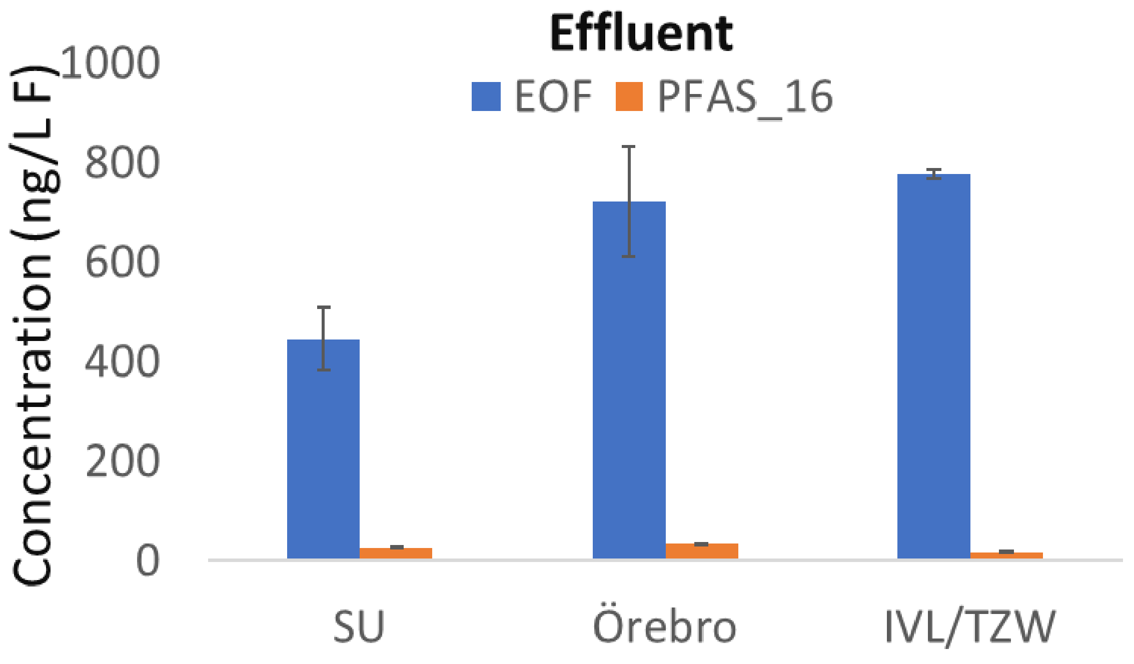
MeOH extraction-CIC

0,5 g dry weight

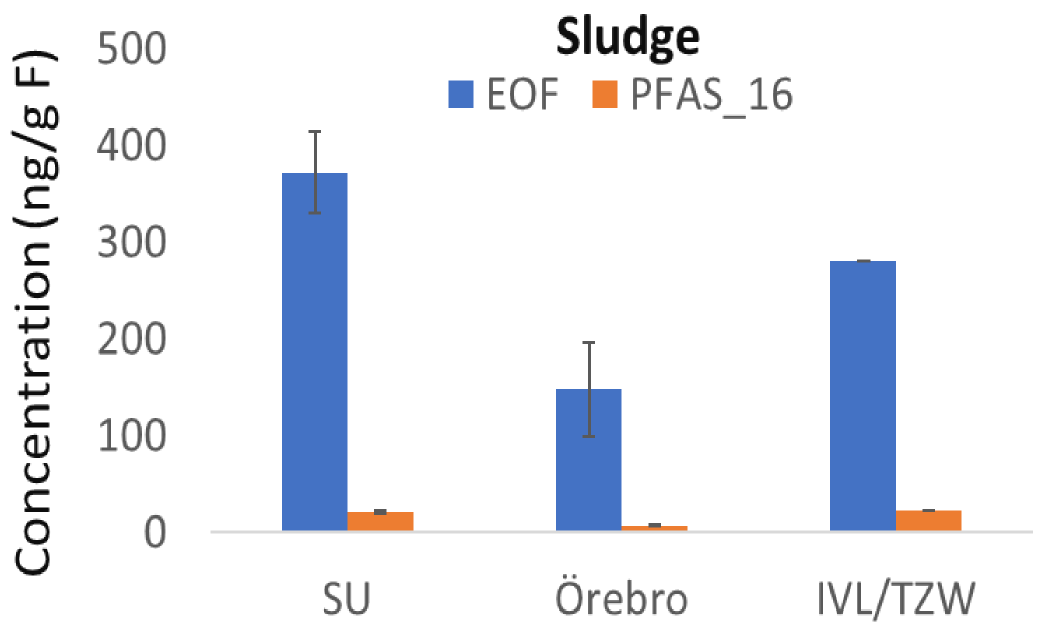
- ENVI-Carb clean-up



- Accuracy 85-101%
- Inter-lab variation 9%



- 445-785 ng/L F
- Inter-lab variation CV 27%
- ∑PFAS-16: 2-6% of EOF



- 148-372 ng/g F
- Inter-lab variation CV 43%
- ∑PFAS-16: 5-8% av EOF

(1) Based on ISO 21675

Validation results

- Samples range 60 ng/L F – 2500 ng/L F (water), 370 ng/g F (sludge)
- Specific for organofluorine
  - > 96-99% inorganic fluoride removal (tests adding NaF) for both aqueous and sludge extraction
- Promising results for the DWD requirements
  - <50% measurement uncertainty
  - The reporting limits varied between 22 and 232 ng/L PFOA-equivalents

Kärrman et al. 2021. Can determination of extractable organofluorine (EOF) be standardized? First interlaboratory comparisons of EOF and fluorine mass balance in sludge and water matrices

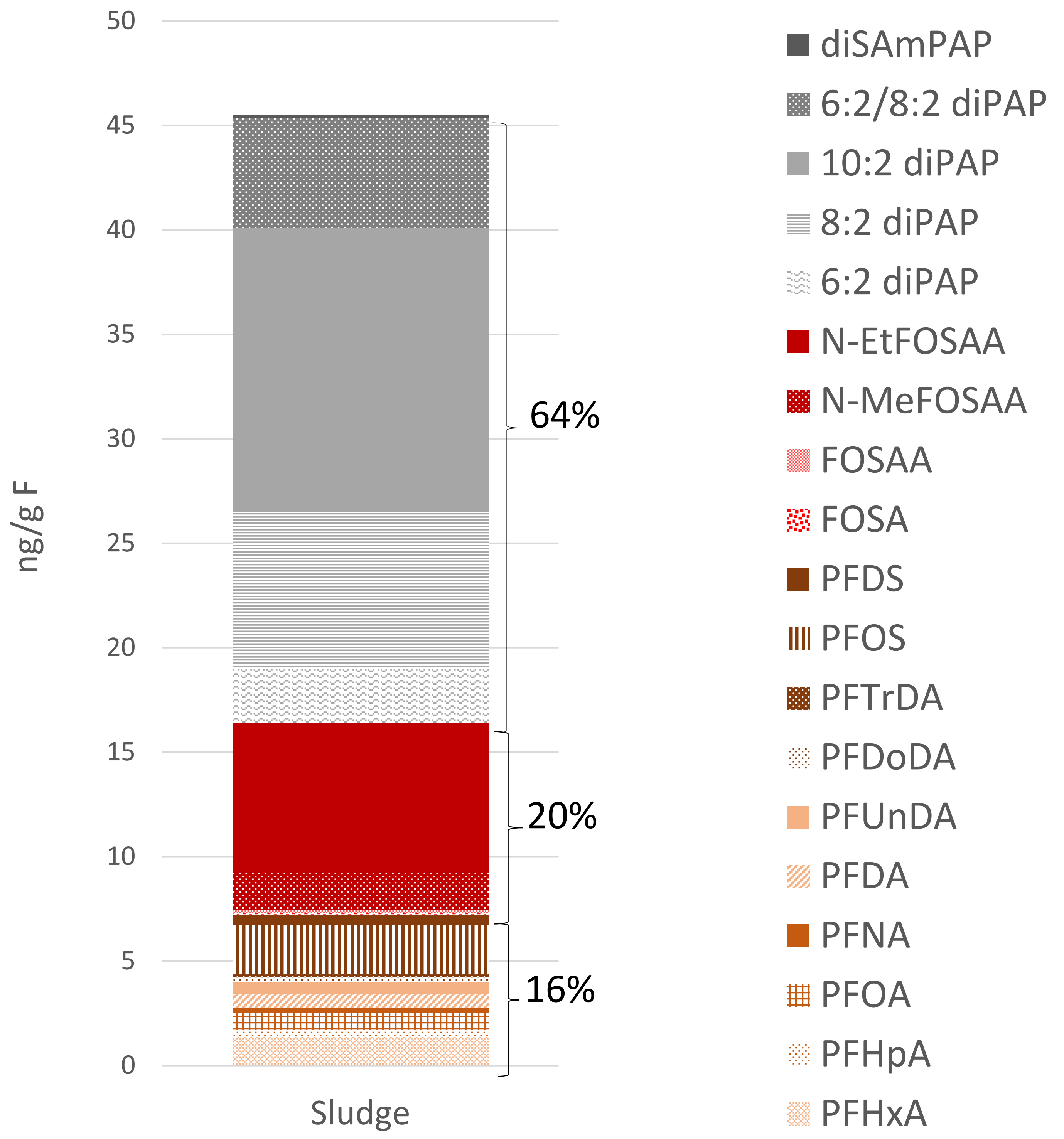
Extended PFAS target screening to close the mass balance

Sludge:

- Precursors (diPAPs and FOSA-derivatives) were major target PFAS
- Increasing the fluorine mass balance from 5-8% known, to 31% known

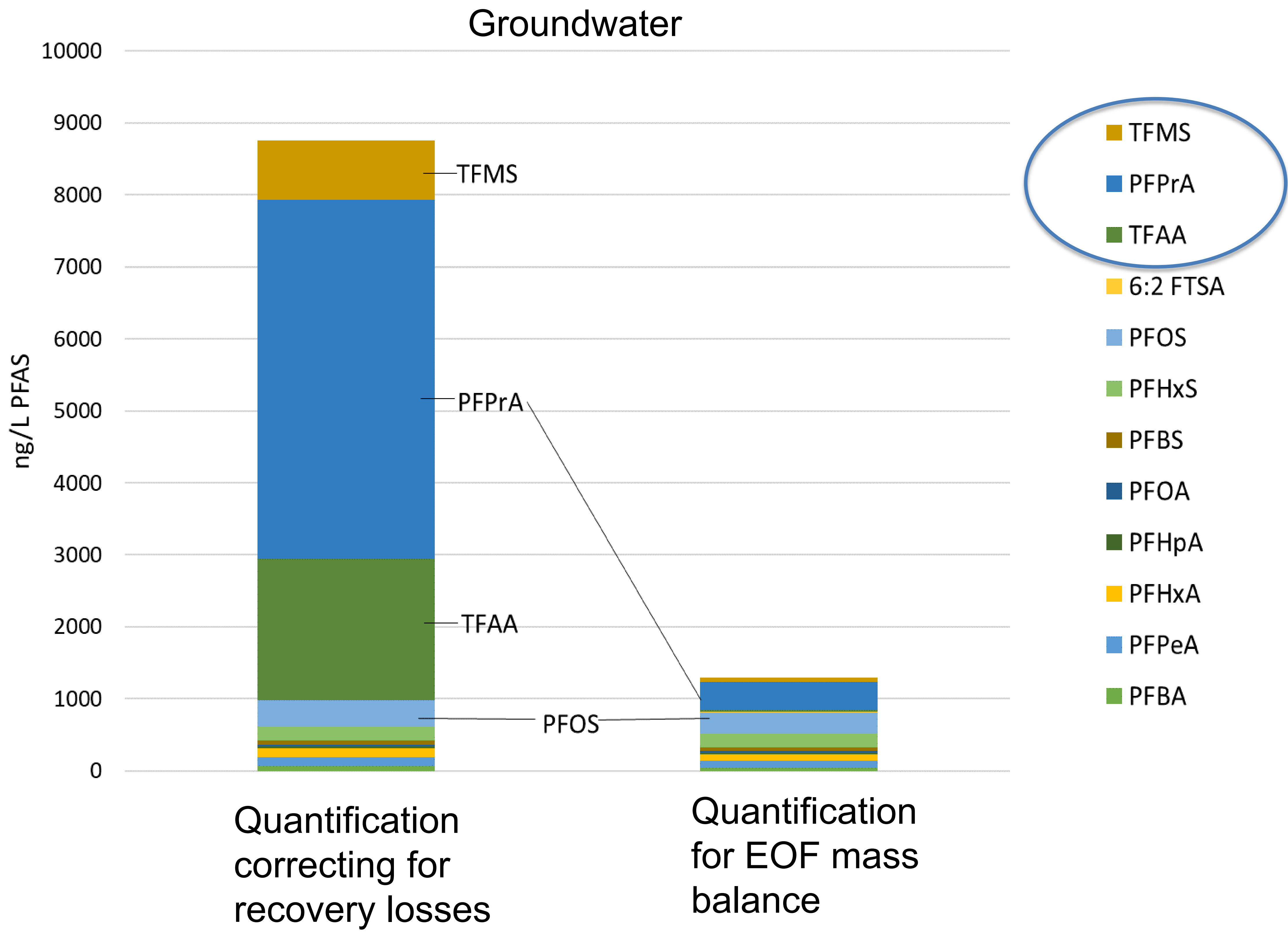
Groundwater and effluent:

- Ultra-short-chain (C1-C3) PFAS were major (46-87%) of target PFAS
- Only increased the fluorine mass balance with 0,6-10%



Extraction efficiency

- Ultra-short-chain PFAS showed low recovery in SPE (with extensive washing to remove fluoride)
- EOF-CIC does not correct for extraction losses



Conclusions

- Methods for assessing PFAS as a group (e.g. flourine detection) are available and EOF-CIC is a promising candidate for the EU DWD PFAS-Total limit value
    - Variation in procedural blank levels (background F levels) needs to be reduced
- Extraction methods are key aspects of a PFAS-Total assessment and needs to be further developed
- One single analytical approach will not fulfill all policy goals
- EOF-CIC shows that environmental and human samples contain large fraction of unknown organofluorine relative to the known, target PFAS

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Thanks for listening

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