Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP)

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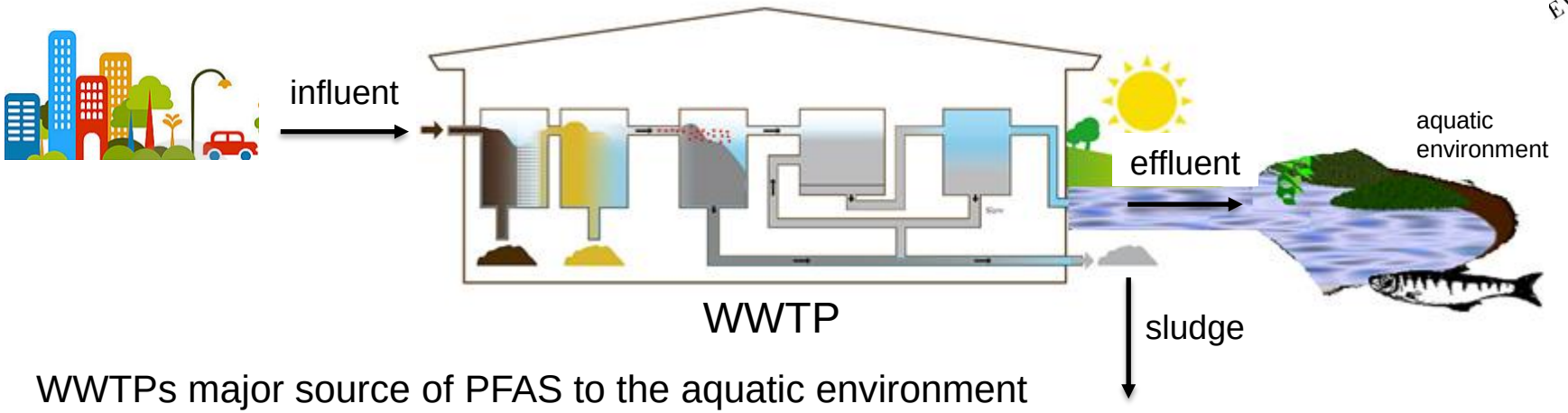
Introduction



- WWTPs major source of PFAS to the aquatic environment
- PFASs have been monitored in Swedish WWTPs for more than a decade by the Swedish Environmental Protection Agency (EPA)
- Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) has been shown to decline following the control measures taken to reduce these compounds.
- Production and usage pattern of PFASs have changed

What are the total amount of PFASs used today and released into the environment?

- Total extractable organofluorine (EOF) analysis allows for assessment of unknown PFASs

Samples

	Henriksdal (Stockholm)	Gässlösa (Borås)	Öhn (Umeå)	Bergkvara
	Municipal, industry	Municipal, hospital, industry	Municipal, hospital	Municipal
Number of people served	737000	82000	92000	5900
Amount sludge produced (t/year)	14400	2400	2300	110
Sludge samples (n)	12	12	2	1
Year of collection	2004-2005, 2015-2016	2004-2005, 2007-2016	2015-2016	2015
Water samples (n)	2	4	4	
Year of collection	2016	2015-2016	2015-2016	

Materials and methods

Sludge samples:[1-3]

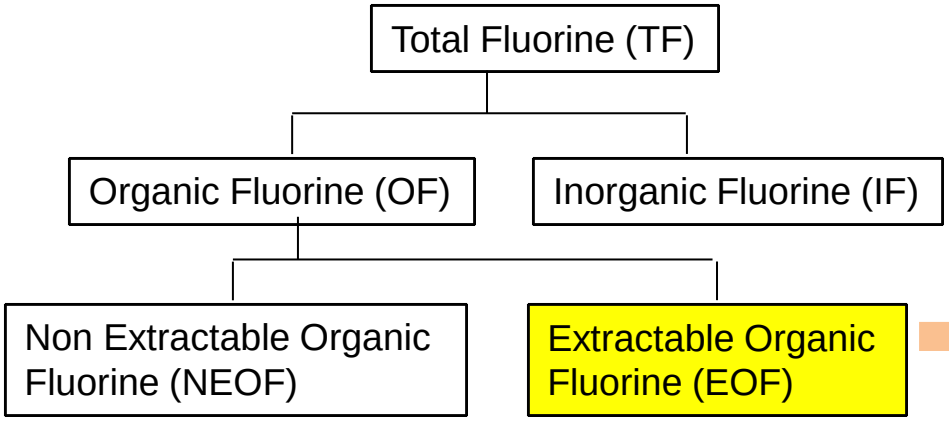
- freeze-dried
- digested with NaOH,
- followed by MeOH extraction.
- Ion pair cleanup with TBAS and MTBE

Water samples:[1]

- filtered with GF/B glass fiber filters before extraction (Whatman)
- SPE using WAX sorbents, according to ISO/DIS 25101 (ISO, 2009) with some modifications.

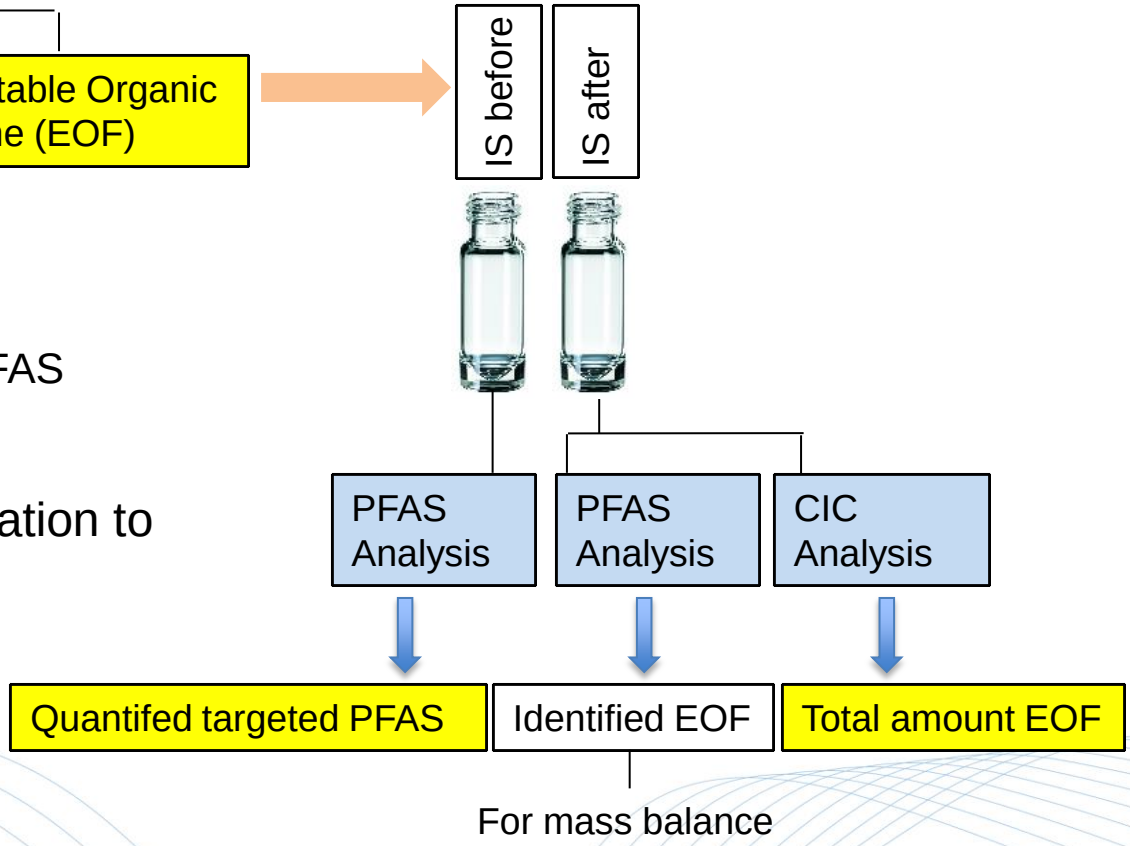
[1]ISO, 2009. ISO25101. Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry.
[2]Yeung, et al. 2013. Environ. Int. 59, 389–397.
[3]Yeung and Mabury, 2016. Environ. Chem. 13, 102.

Mass balance of fluorine

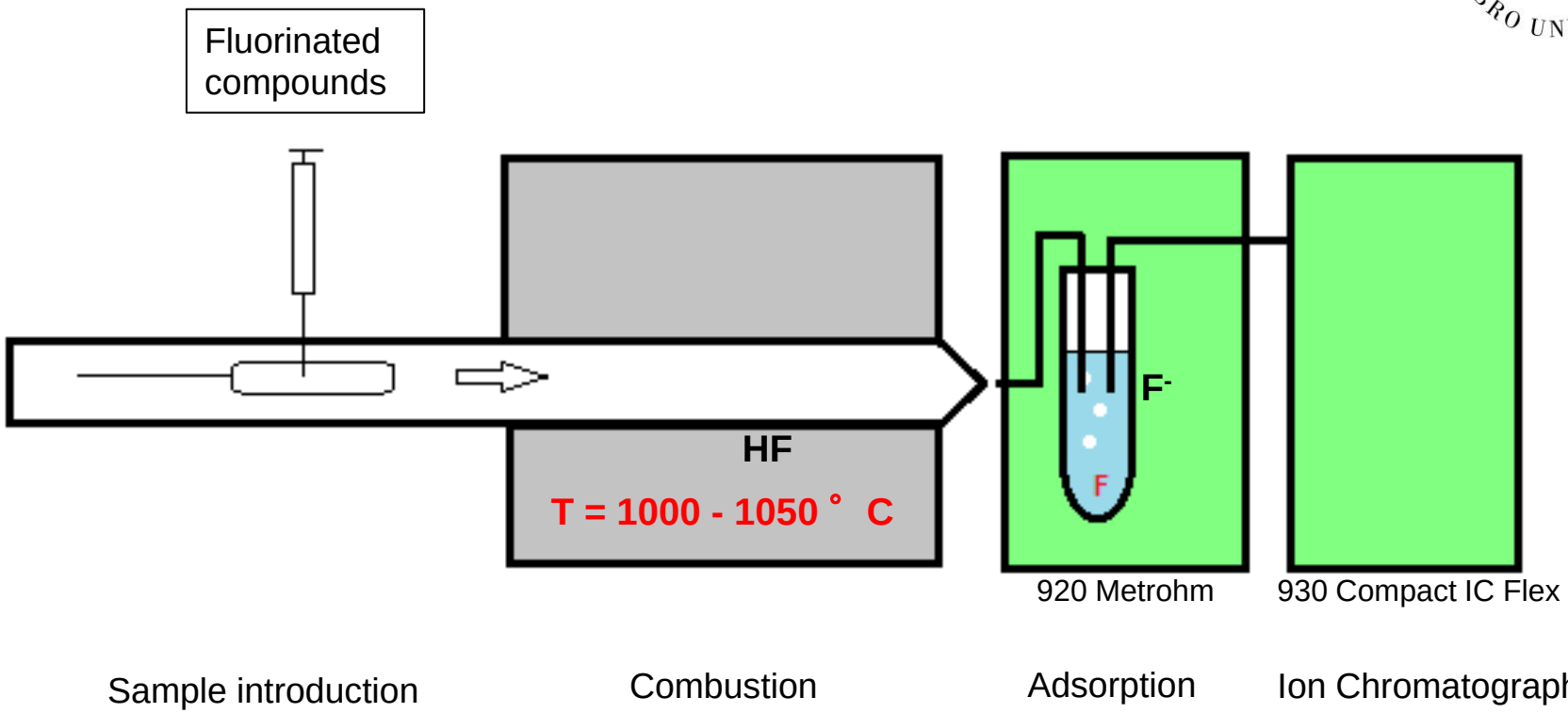


$$C_F = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS}$$

Conversion of PFAS concentration to fluoride concentration



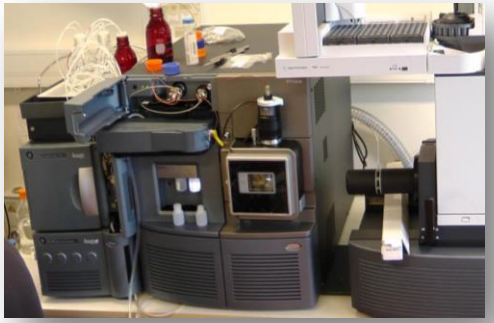
Combustion Ion Chromatography



- Solid or liquid sample is introduced on a quartz boat
- Sample is pyrolized with Ar, followed by burning with O_2
- Resulting gasueous compounds are passed into an adsorbtion solution (Milli-Q water)
- Separation of anions on an ion exchange column
- F^- concentration analyzed using ion chromatography

LC-MS/MS Analysis

Acquity UPLC system coupled to Xevo TQ-S triple quadropole in ESI^- mode (Waters)



Perfluoroalkylacids (PFCAs)
PFBA (C4)
PFPePA (C5)
PFHxA (C6)
PFHpA (C7)
PFOA (C8)
PFNA (C9)
PFDA (C10)
PFUnDA (C11)
PFDoDA (C12)
PFTrDA (C13)
PFTDA (C14)
PFHxDA (C16)
PFOcDA (C18)

Telomer acids
6:2 FTUCA
8:2 FTUCA
10:2 FTUCA
5:3 FTCA
7:3 FTCA

Perfluoroalkylsulfonic acids (PFSAs):
PFBuS (C4)
PFHxS (C6)
PFHpS (C7)
PFOS (C8)
PFNS (C9)
PFDS (C10)

Sulfonamides
PFOSA
Me-FOSA
Et-FOSA
Me-FOSE
Et-FOSE

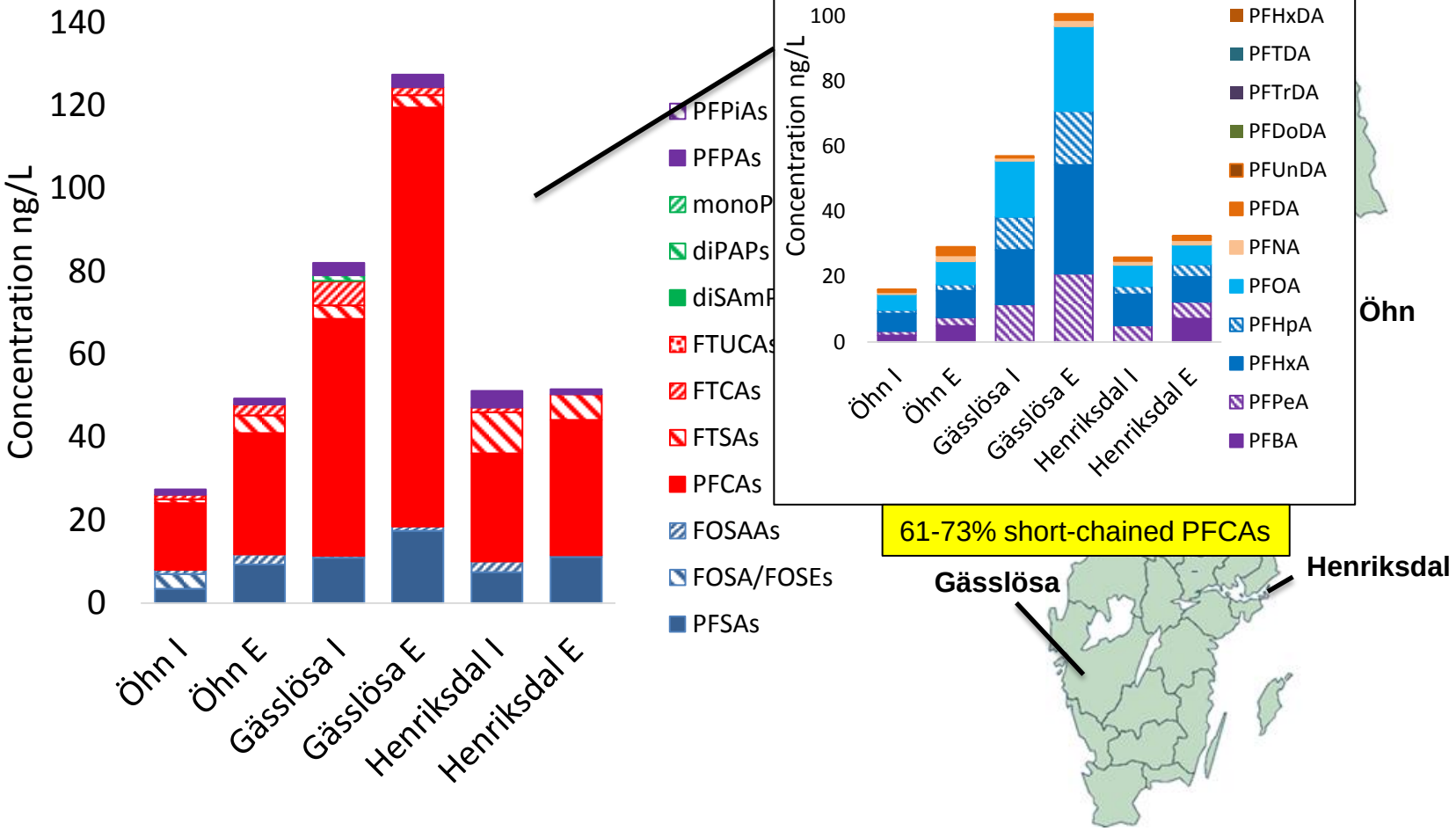
Sulfonamide acetates
FOSAA
Me-FOSAA
Et-FOSAA

Phosphate esters
6:2 diPAP (4:2/8:2)
8:2 diPAP (6:2/10:2, 4:2/12:2)
10:2 diPAP (8:2/12:2, 6:2/14:2)
6:2/8:2 diPAP (4:2/10:2)
8:2/10:2 diPAP (6:2/12:2)
10:2/12:2 diPAP (8:2/14:2, 6:2/16:2)
12:2 diPAP (10:2/14:2, 8:2/16:2)
SAmPAP (C8)
diSAMPAP (C8)

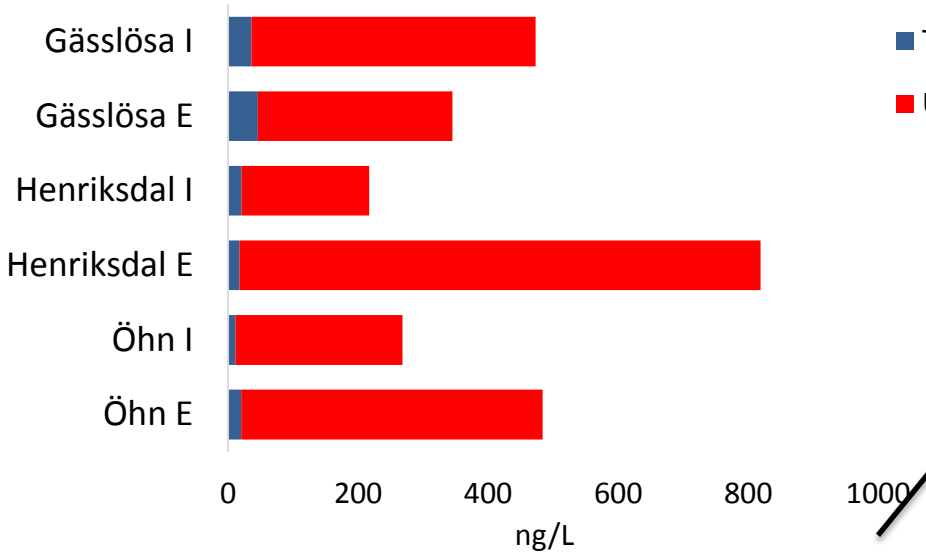
Perfluorophosphate esters
PFPA (C6, C8, C10, C12, C14, C16)
PFPiA (C6/C6, C6/C8, C8/C8, C8/C10, C10/C10, C10/C12, C12, C10/C14, C14)

Flurotelomer sulfonic acids
6:2 FTSA
8:2 FTSA

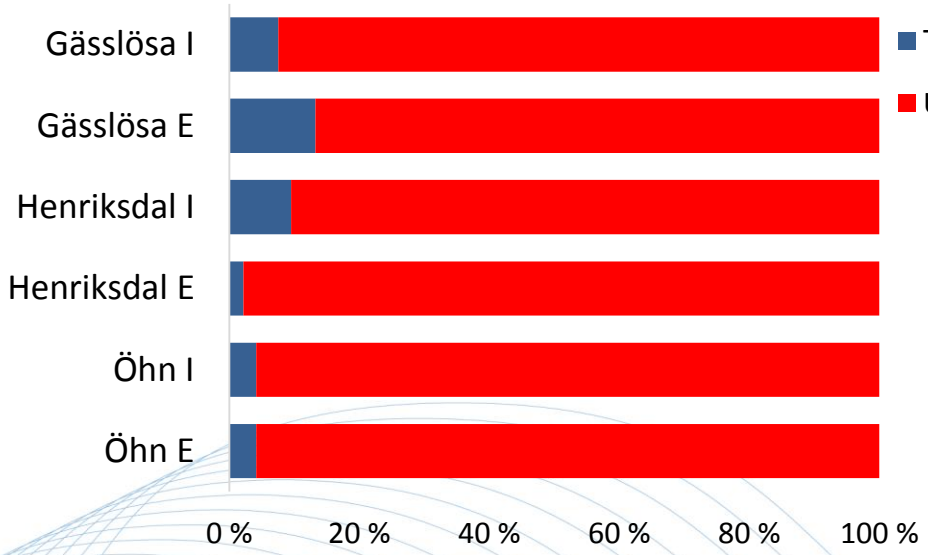
Targeted PFAS in water 2016

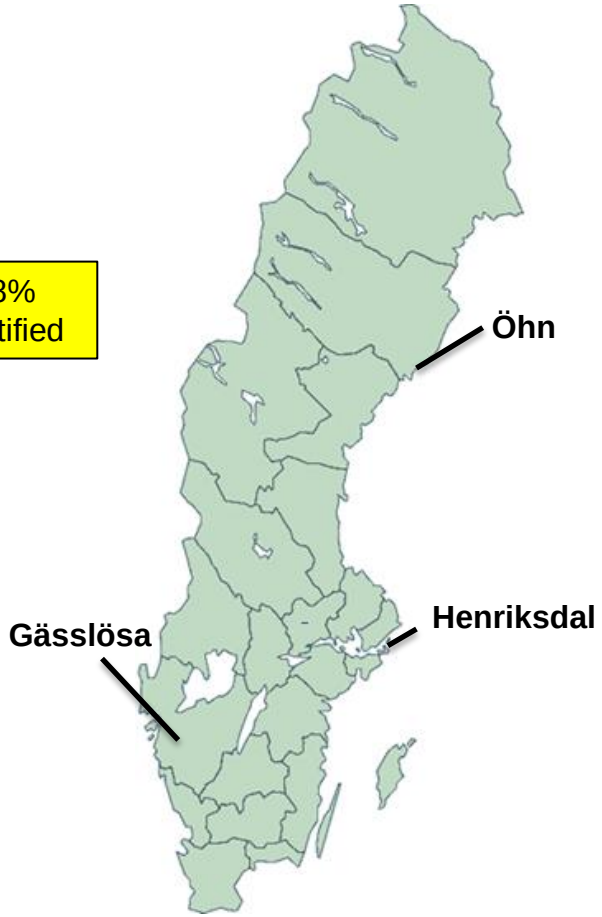


EOF in water 2016

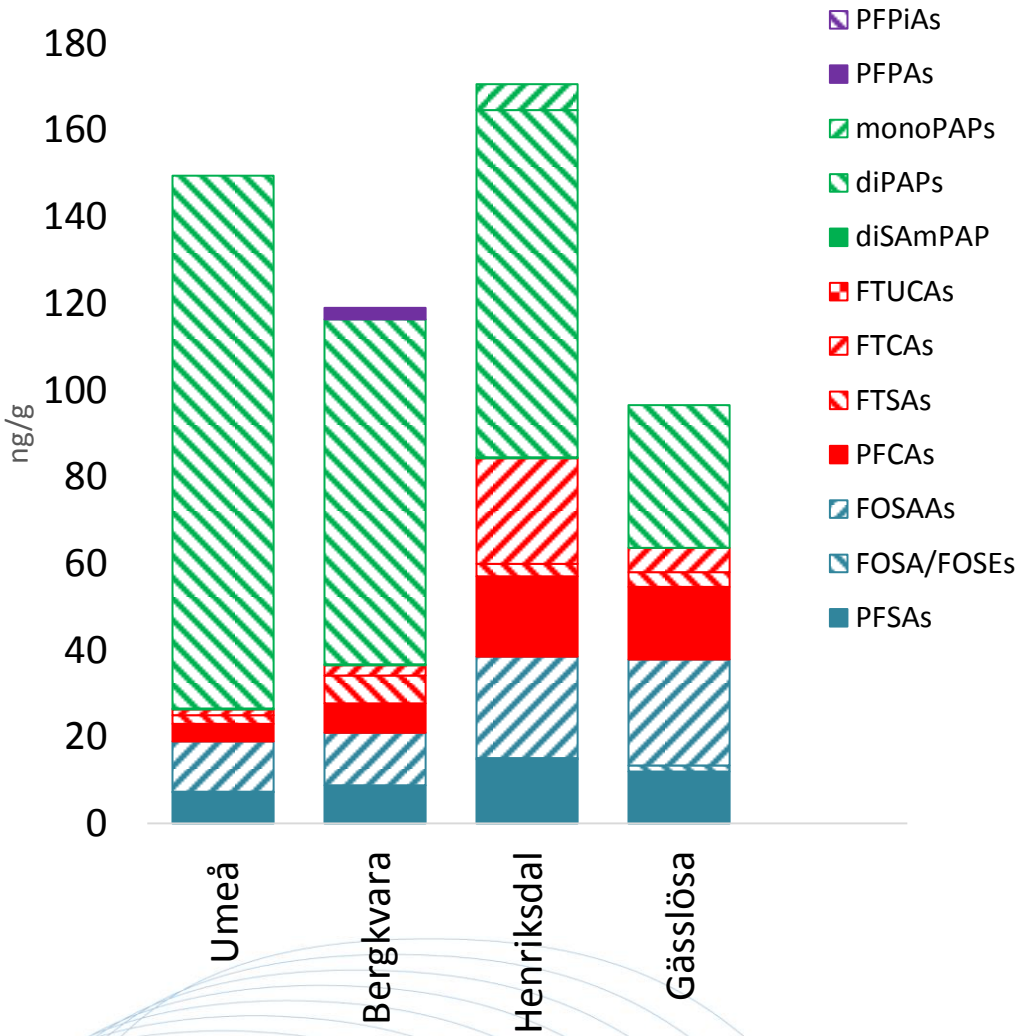


87 – 98% unidentified

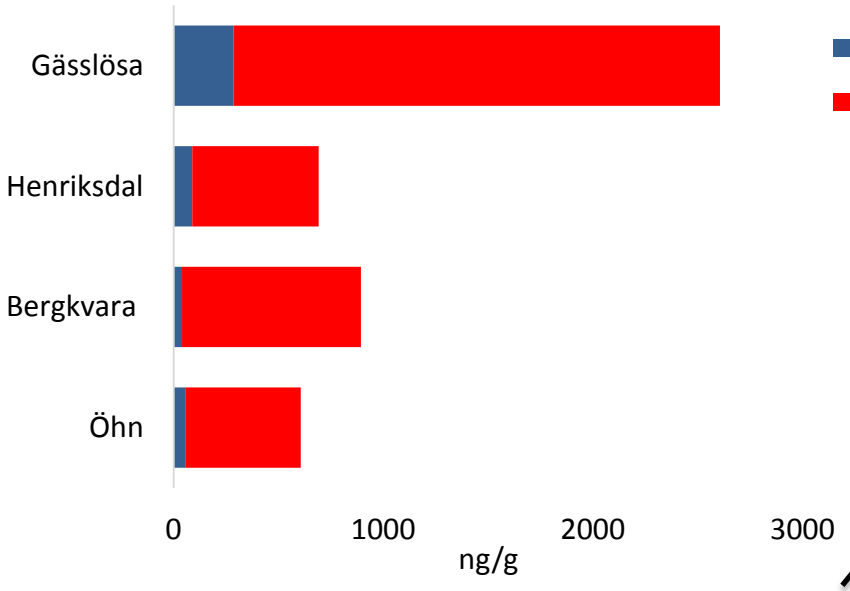




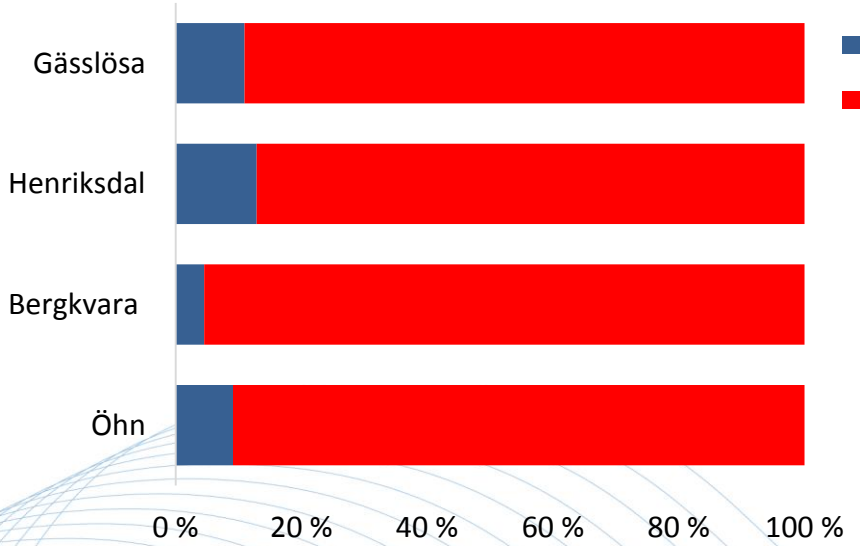
Targeted PFASs in sludge 2015

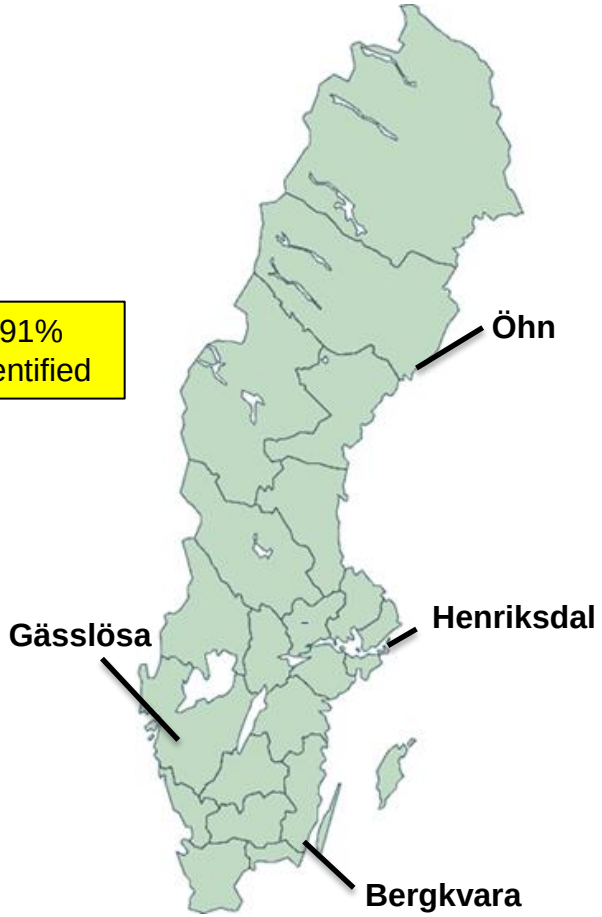


EOF in sludge 2015

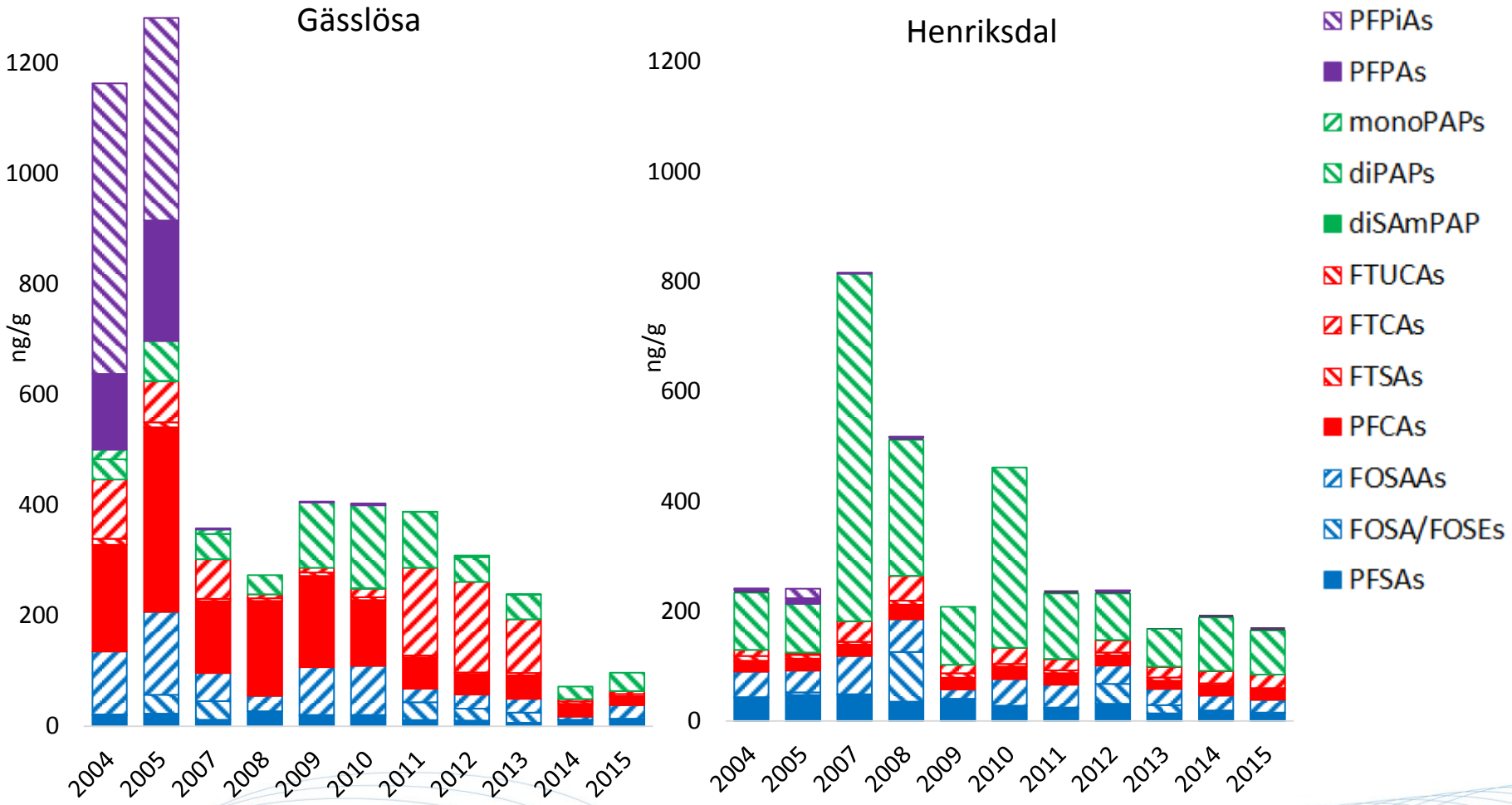


87 – 91% unidentified

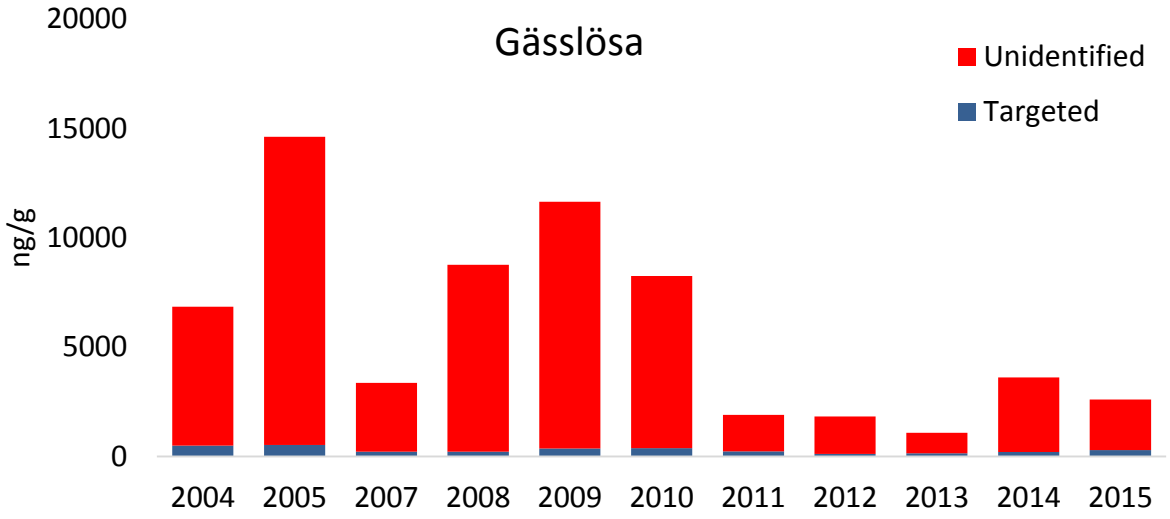


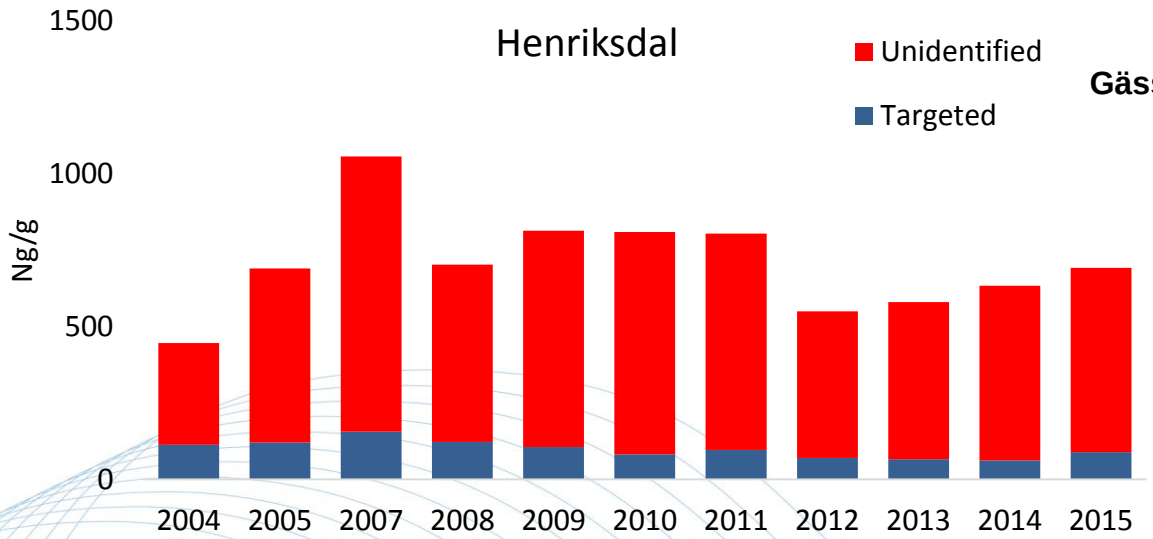


Temporal trend targeted PFAS in sludge

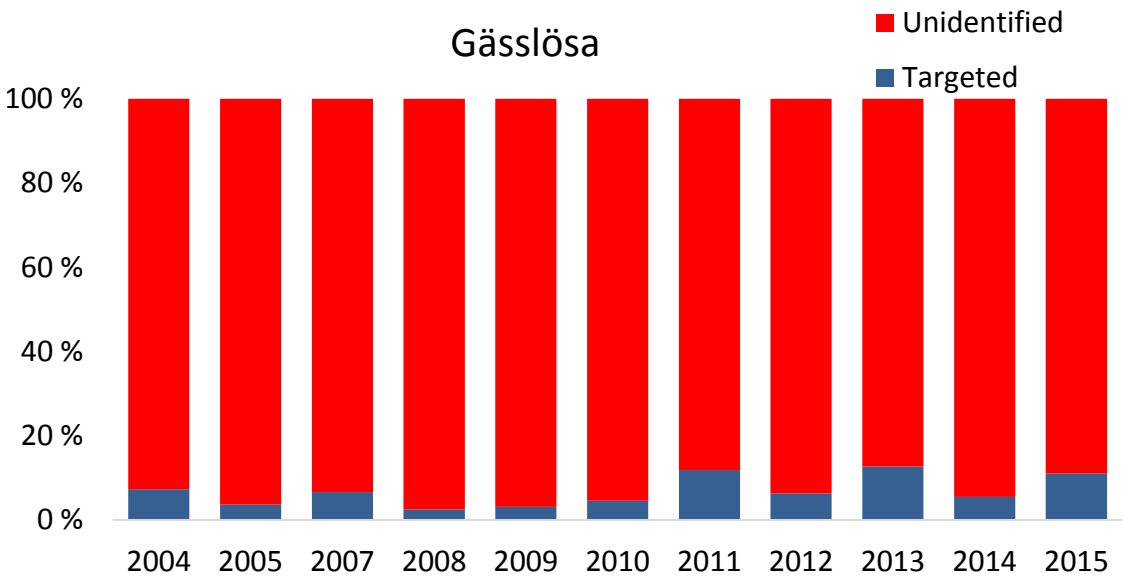


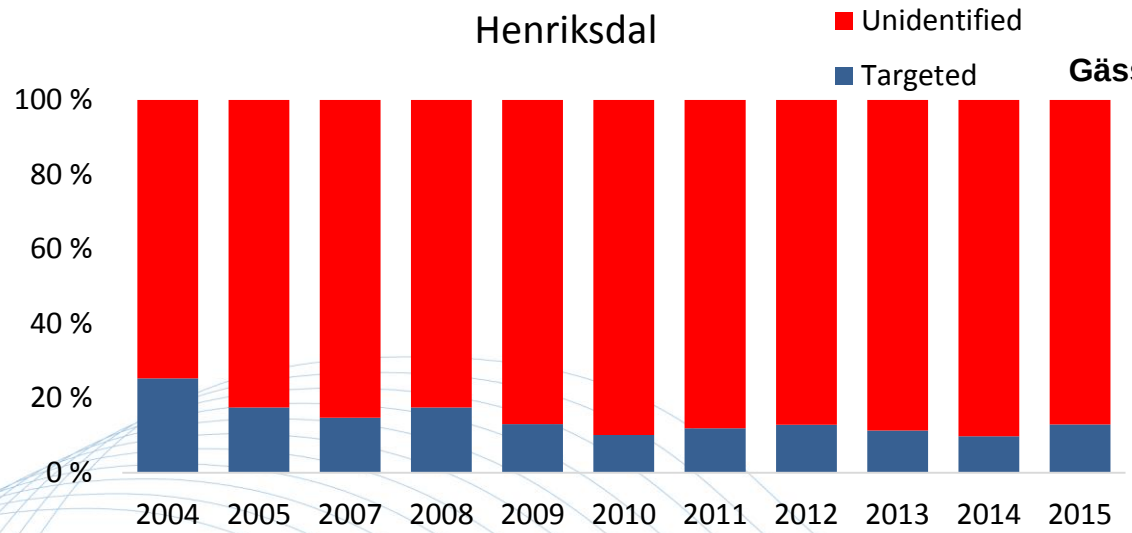
Temporal trend EOF in sludge





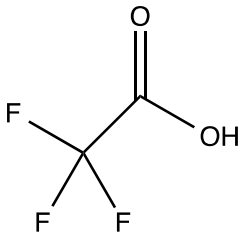
Temporal trend EOF in sludge



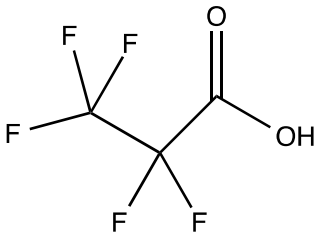


Unidentified PFASs

Short-chained PFCAs:

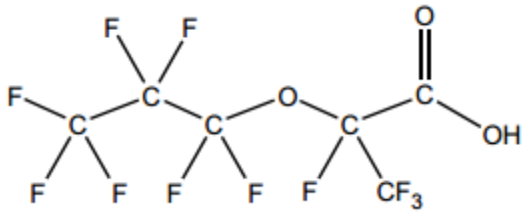


TFA

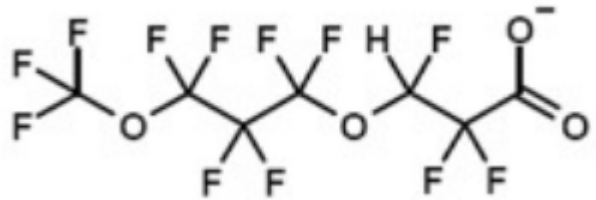


PFPrA

Polyfluoroalkyl ether acids:

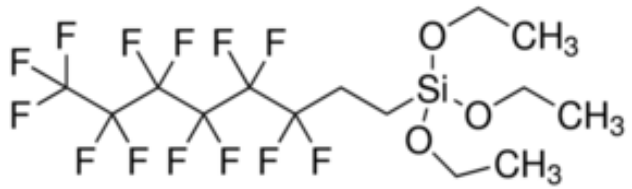


HFPO-DA (GenX)
Hexafluoropropylene oxide dimer acid



ADONA

Fluorinated silanes and siloxanes:



1*H*,1*H*,2*H*,2*H*-Perfluorooctyltrietoxysilane

Summary

- A large proportion of the EOF were unidentified –
  87 – 98% in water and 87 – 91% in sludge
  - total amount PFAS could not be explained by the targeted analytes
- Precursor compounds made a significant contribution to the total amount of PFAS in the sludge.
- Levels of short-chain PFCAs increased during the WWTP process
- The amounts of unknown PFASs have increased 2012 - 2015

Thank you!

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