ADVANCES IN POLY- AND PERFLUORALKYL SUBSTANCES (PFAS) ANALYTICAL TECHNIQUES

Implications for Conceptual Site Models

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Background: Precursors - The Hidden PFAS Mass

Multiple and Varied PFAS Sources

Some Typical:

- Fire Training Areas (FTA)/Large Scale Historical Fires: Fluorosurfactant Firefighting foams for Class B (liquid hydrocarbon) fires e.g. Aqueous Film Forming Foams (AFFF) represent point sources for PFAS.
- AFFF Storage Areas
- Manufacturing and electroplating mist suppressants: coating/chromium plating/Tank related manuf./retrofitting
- Landfills (diffuse background PFAS)
- WWTP Discharge/Sludges: more concentrated PFAS
- Some Pesticides –Insecticides and Herbicides
- Photo Processing/Development






PFOS/PFOA Nature and Extent Implications

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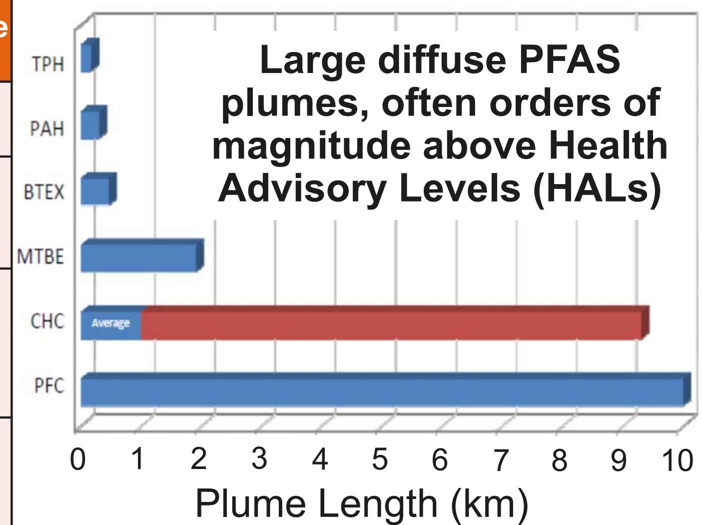
PFAS plumes are generally longer than other common contaminants

- Highly soluble
- Low sorption to organic materials (Low K_{OC})
- Recalcitrant – extreme persistence
- Mostly Anionic

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility (@20-25°C), mg/L	0.0027	3,400 – 9,500	519	1,100	1,780
Vapor Pressure (@25°C), mmHg	4.05×10^{-5}	0.5-10	2.48×10^{-6}	77.5	97
Henry's Constant, atm-m^3/mol	4.6×10^{-3}	1.01×10^{-4}	3.05×10^{-9}	0.01	0.0056
Log K_{oc}	5 – 7	2.06	2.57	2.473	2.13



Large diffuse PFAS plumes, often orders of magnitude above Health Advisory Levels (HALs)

Mobile Large, Diffuse Plumes Present a Cost Saving Opportunity using Real Time Investigations/Mobile Labs.

Perfluorinated compounds (PFCs)

- Perfluorinated Compounds (PFCs) generally are the **Perfluoroalkyl acids (PFAAs)**
- PFAAs include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluoroalkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluoroalkyl phosphinic acids (PFPiS); perfluoroalkyl phosphonic acids (PFPAs)
- There are many PFAAs with differing chain lengths, PFOS and PFOA have 8 carbons (C8) - octanoates

C1 **M**ethane
C2 **E**thane
C3 **P**ropane
C4 **B**utane
C5 **Pe**ntane
C6 **Hex**ane
C7 **Hep**tane
C8 **O**ctane
C9 **N**onane
C10 **D**ecane
C11 **Un**odecane
C12 **Do**decane
C13 **Tr**idecane
C14 **Te**tradecane

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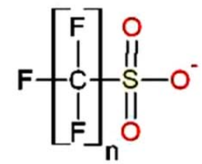
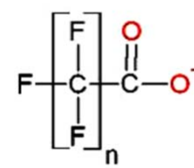
Perfluoroalkyl Sulfonates[L]



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Perfluoroalkyl Carboxylates[L]



PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS
Will J. Backe,† Thomas C. Day,† and Jennifer A. Field*,‡

PFAAs totally resist biodegradation & biotransformation so are extremely persistent

Polyfluorinated Compounds - Precursors

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Thousands of polyfluorinated precursors to PFAAs have been commercially synthesized for bulk products

The common feature of the precursors is that they will **biotransform** to make PFAA’s as persistent “dead end” daughter products

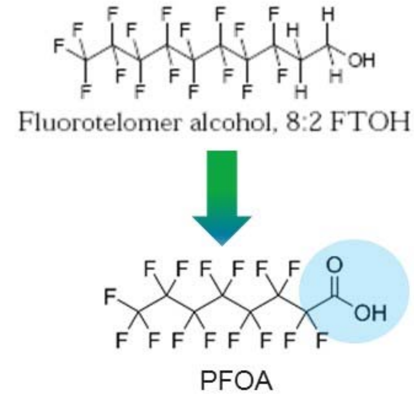
PFAS do not biodegrade i.e. mineralise

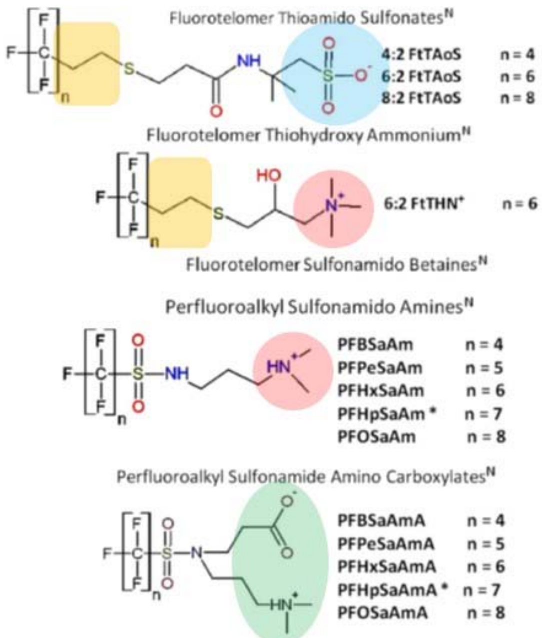
Some precursors are fluorotelomers

Some are cationic (positively charged) or zwitterionic (mixed charges) –this influences their fate and transport in the environment

Cationic / zwitterionic PFAS tend to be less mobile than anionic PFAAs and so can potentially be retained longer in “source zones”

Environmental fate and transport will be complex as PFAS comprise multiple chain lengths and charges





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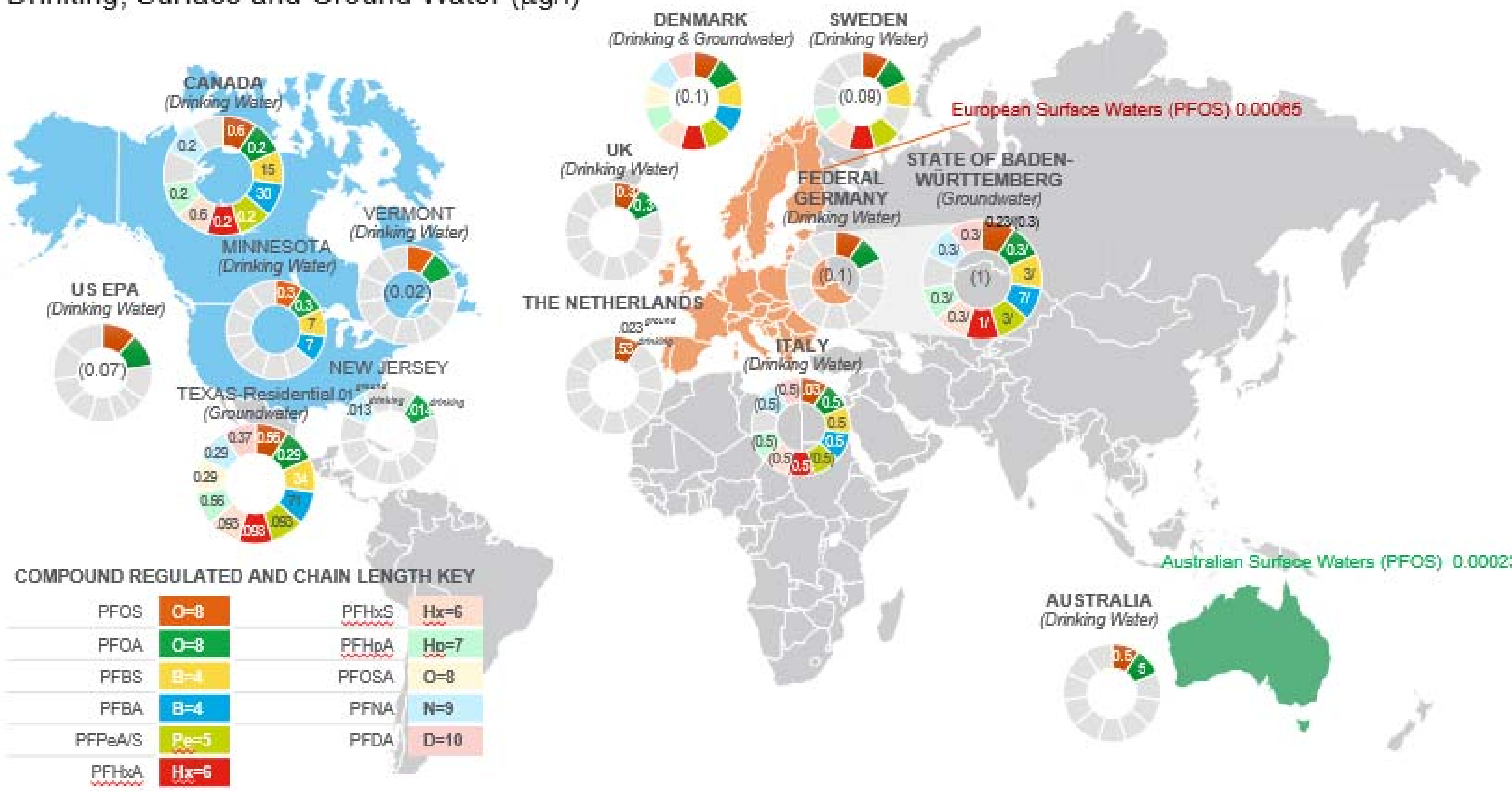
Regulatory Perspective – Outside the U.S.

Evolving Regulatory PFAS Values – Overview

Drinking, Surface and Ground Water (µg/l)



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Evolving Regulatory PFAS Values

	O=8	O=8	O=8	B=4	B=4	Pe=5	Hx=6	Hp=7	N=9	D=10		Hp=7	Hx=6	Pe=5
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Drinking Water Criteria in µg/l in European Countries														
Denmark[1]	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
Germany[2]	(0.1)	(0.1)	-	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	0.53	-	-	-	-	-	-	-	-	-	-	-	-	-
Sweden[3]	(0.09)	(0.09)	-	(0.09)	-	(0.09)	(0.09)	(0.09)	-	-	-	-	(0.09)	-
U.K.[4]	0.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-
Italy[5]	0.03	0.5	-	0.5	0.5	(0.5)	(0.5)	(0.5)	(0.5)	(0.5)	-	-	(0.5)	-
Australia	0.5	5												
Drinking Water Criteria in µg/l U.S.[6]														
Minnesota	0.3	0.3	-	7	7	-	-	-	-	-	-	-	-	-
New Jersey	-	0.014	-	-	-	-	-	-	0.013	-	-	-	-	-
Vermont[7]	(0.02)	(0.02)												
U.S. EPA[8]	(0.07)	(0.07)	-	-	-	-	-	-	-	-	-	-	-	-
Canada	0.6	0.2	-	15	30	0.2	0.2	0.2	0.2	-	-	-	0.6	-
Groundwater Criteria in µg/l in European Countries														
Denmark[1]	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
State of Bavaria[9]	0.23/(0.3)	(0.3)	-	3	7	3	1	0.3	0.3	0.3	-	-	(0.3)	-
State of Baden-Württemberg[10]	0.23/(0.3)	0.3/(1)	-	3/(1)	7/(1)	3/(1)	1/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	1/(1)
The Netherlands	0.023*	-	-	-	-	-	-	-	-	-	-	-	-	-
Groundwater Criteria in µg/l in U.S.														
New Jersey	-	-	-	-	-	-	-	-	0.01	-	-	-	-	-
Texas, Residential	0.56	0.29	0.29	34	71	0.093	0.093	0.56	0.29	0.37	-	-	0.093	-
Soil Criteria in mg/kg in European Countries, U.S.														
Denmark[1]	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	-	(0.4)	-
Norway	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	0.0023	-	-	-	-	-	-	-	-	-	-	-	-	-
Italy (Resi & Ind)	-	0.5/5	-	-	-	-	-	-	-	-	-	-	-	-
Texas, Residential	1.5	0.6	0.058	73	150	5.1	5.1	1.5	0.76	0.96	-	-	4.8	-

Values in parentheses indicate the analytes are considered as a sum concentration

Notes:

1 = Σ12 PFAS = 0.100 µg/L, includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA

2 = Σ PFOS and PFOA = 0.100 µg/; Composite precautionary guidance value for long term exposure

3 = Σ7 PFAS = 0.090 µg/L, includes PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA

4 = Tier 1 values

5 = Σ8 PFAS = 0.500 µg/L, includes PFHxS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA; Separate standards for PFBA, PFBS, PFOA, PFOS

6 = Alaska Department of Environmental Conservation published chemical toxicity parameters to support development of PFOS and PFOA cleanup levels on May 15, 2016.

7 = Σ PFOS and PFOA = 0.020 µg/L

8 = Σ PFOS and PFOA = 0.070 µg/L

9 = Σ PFOS, PFOA, PFHxS = 0.3 µg/l

10 = Σ12 PFAS < 1 µg/L, includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFB, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA; PFOS standard changes to 0.3 µg/L if multiple PFAS present

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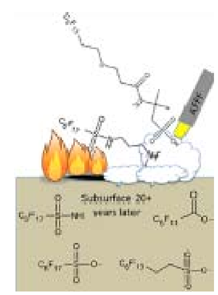
Next Generation Analytical Techniques

Advanced Analytical Techniques
Expanding analytical tool box to assess total PFAS

- **Total oxidizable precursor (TOP) Assay**
  - Initial LC-MS/MS analysis with re-analysis following oxidative digest
  - Detection limits to ~ 2 ng/L (ppt)
  - Commercially available in UK, Australia, under development in US
- **Particle-induced gamma emission (PIGE) Spectroscopy**
  - Isolates organofluorine compounds on solid phase extraction, measures total fluorine
  - Detection limits to ~ 15 ug/L (ppb) F
  - Commercially available in US
- **Adsorbable organofluorine (AOF)**
  - Isolates organofluorine compounds with activated carbon and measures F by combustion ion chromatography
  - Detection limits to ~ 1 ug/L (ppb) F
  - Commercially available in Germany, Australia
- **Time of Flight MS (LCQTOF) MS**
  - Identifies multiple precursors via mass ions capture and accurate mass estimation (to 0.0001 of a Dalton) to give empirical formulae (e.g. $C_{10}F_{21}O_3N_2H_4$)
  - Semi quantitative



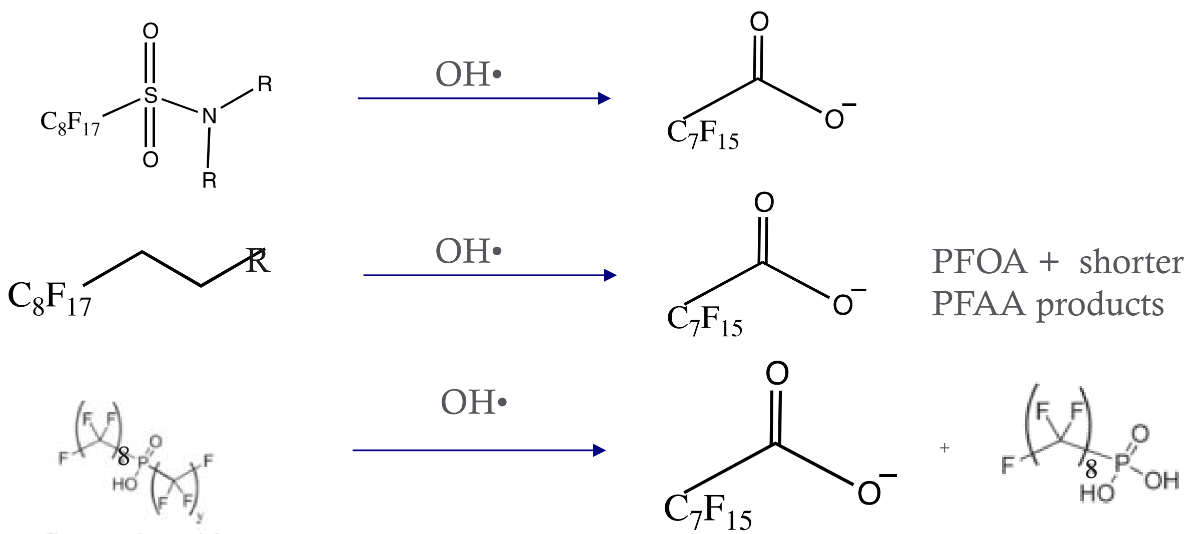
Total Oxidizeable Precursor Assay (TOP)

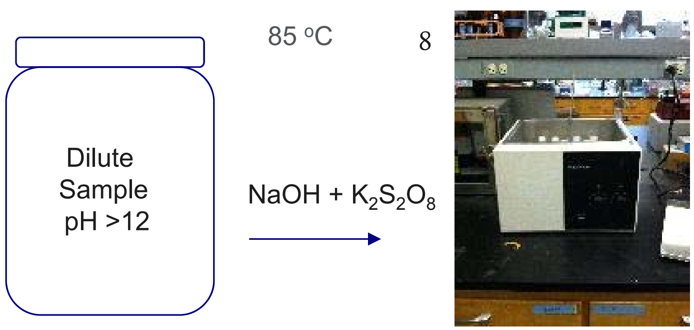
Oxidation of Precursors to PFAAs with OH•

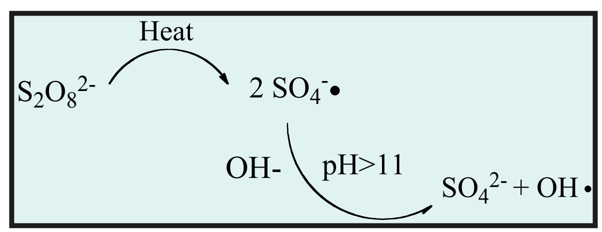
PFSA Precursors

PFCA Precursors

PFPA Precursors







Approach described in Houtz and Sedlak, *ES&T*, 2012

Digest AFFF precursors and measure the hidden mass: TOP Assay

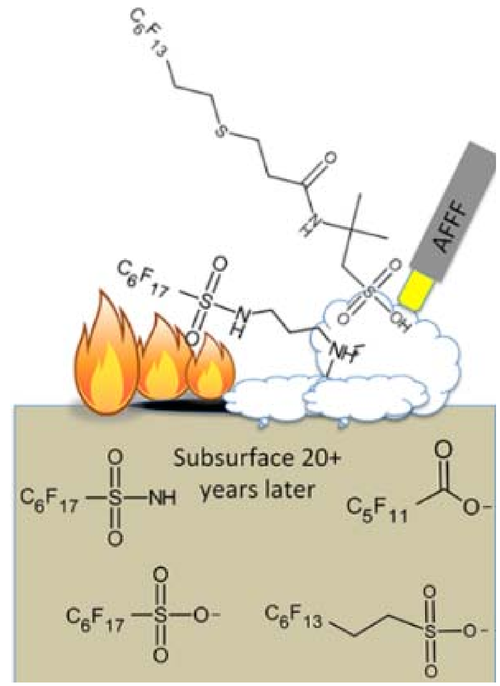
Microbes slowly make simpler PFAA's (e.g. PFOS / PFOA) from PFAS (PFAA precursors) over 20+ years

Need to determine precursor concentrations as they will form PFAAs

Too many PFAS compounds and precursors –so very expensive analysis

Oxidative digest convert PFAA precursors to PFAA's

Indirectly measure precursors as a result of the increased PFAAs formed



Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

Erika F. Houtz,[†] Christopher P. Higgins,[‡] Jennifer A. Field,[§] and David L. Sedlak[†,*]

Analytical tools fail to measure the hidden PFAS precursor mass, the TOP assay solves this

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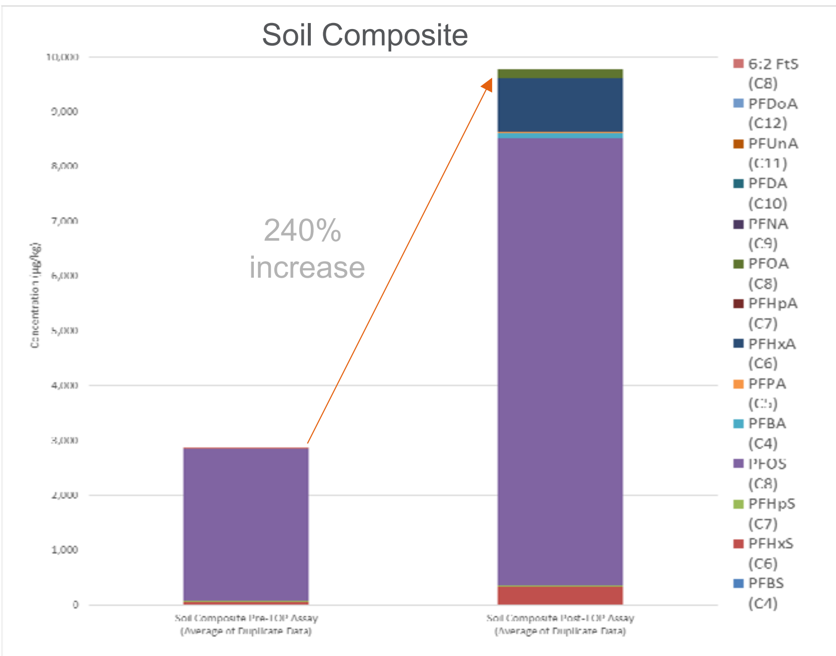
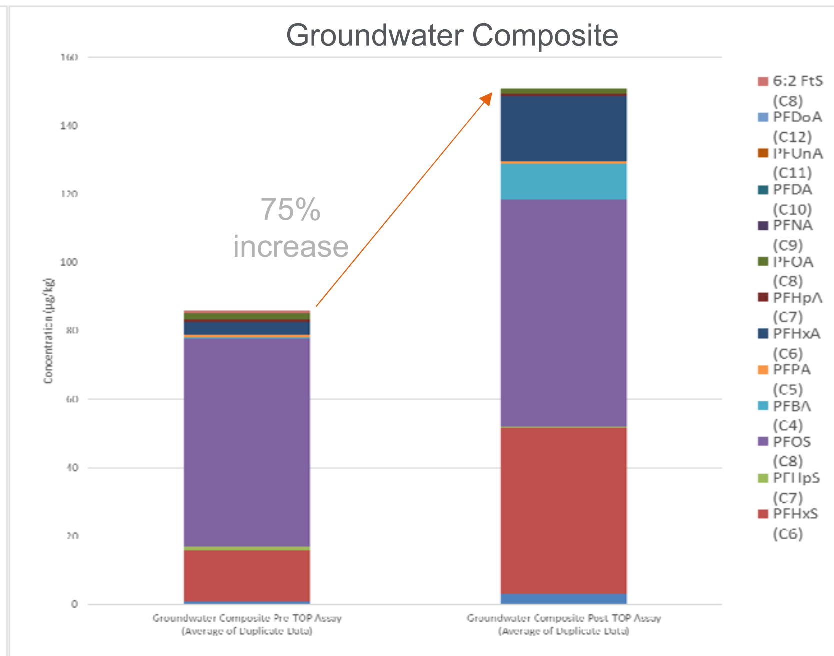
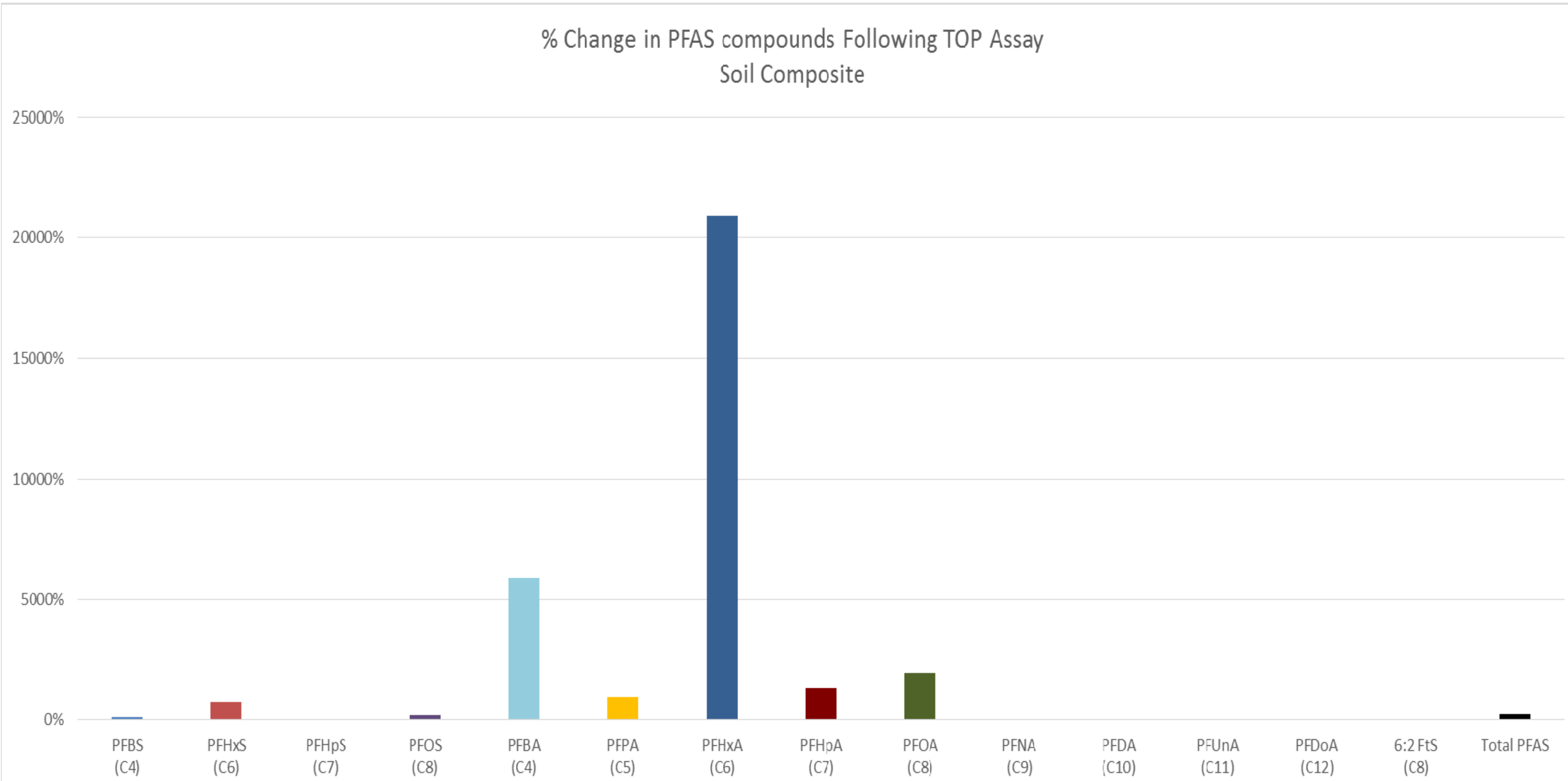
Total Oxidisable Precursor (TOP) Assay



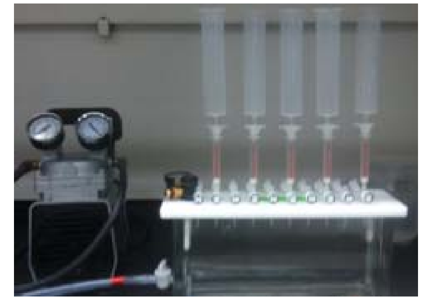


TOP Assay –Fire Training Area



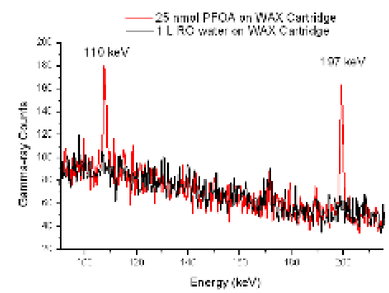
Particle-induced Gamma Ray Emission (PIGE) Spectroscopy

- Solid-phase extraction of PFAS via commercial extraction disks; analysis of surface by PIGE.
- Measures total F values, with a limit of detection of ~15 ppb for ~80 mL aqueous sample
- Uses nuclear science to quantitatively determine elemental concentrations
- Fluorine produces a unique gamma ray signature (when bombarded with protons
- Rapid screening for PFASs
- No speciation of PFAS chain length, reports total fluorine in sample



SPE extraction

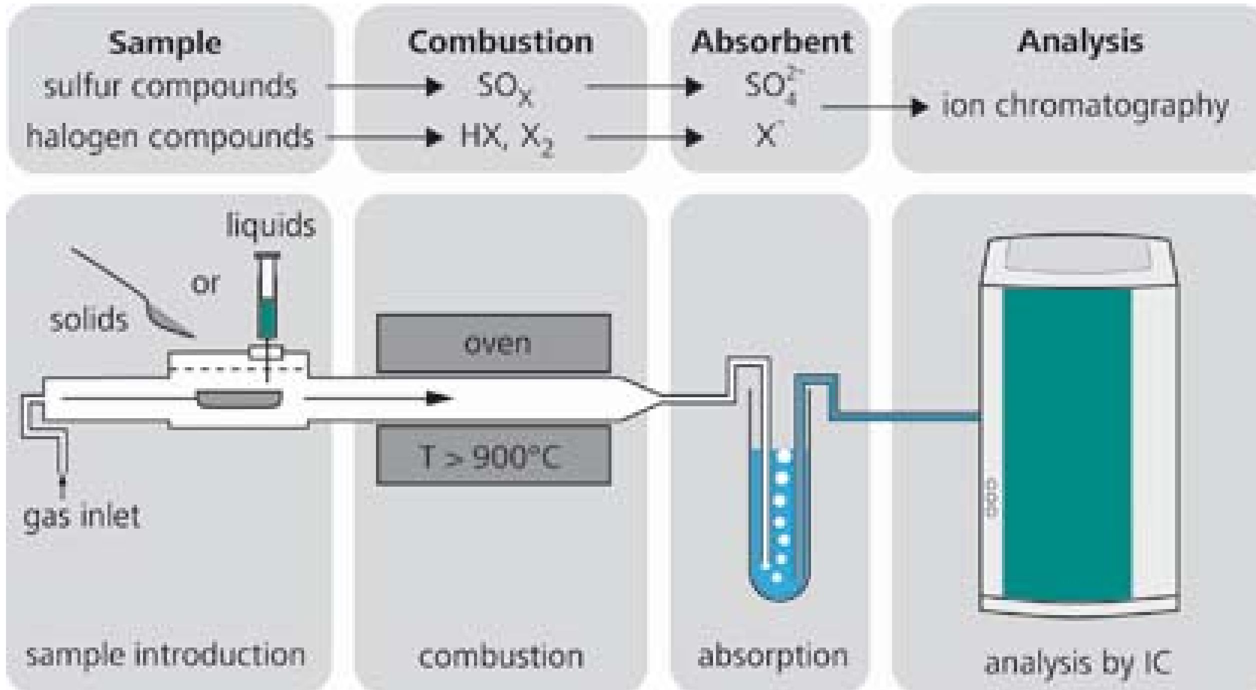
ex vacuo PIGE analysis



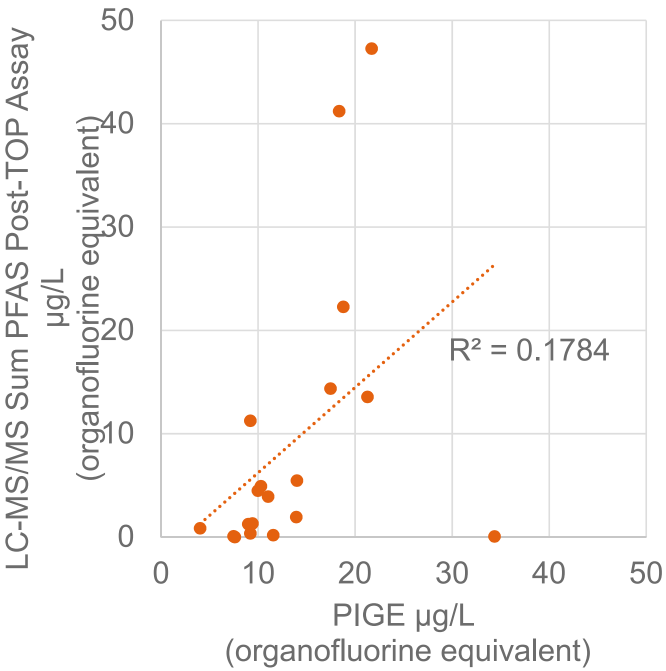
Typical PIGE spectrum

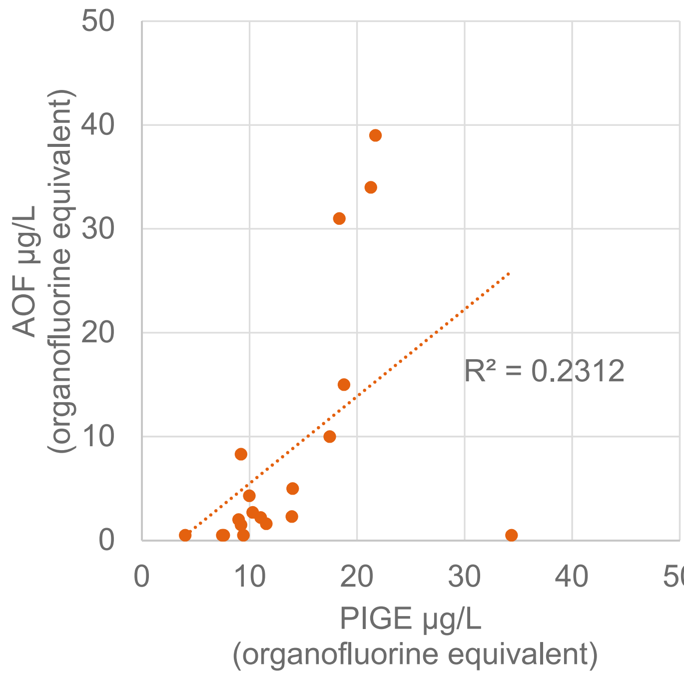
Absorbable Organo-Fluorine (AOF) Combustion Ion Chromatography

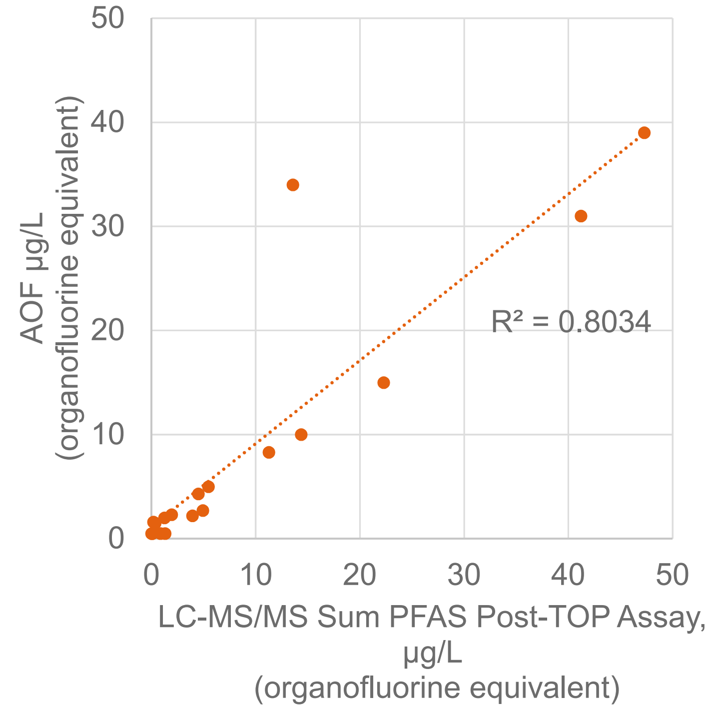
- Measures total F, with a limit of detection of 1 ppb
- Rapid screening for PFASs
- No speciation of PFAS chain length, reports total fluorine in sample



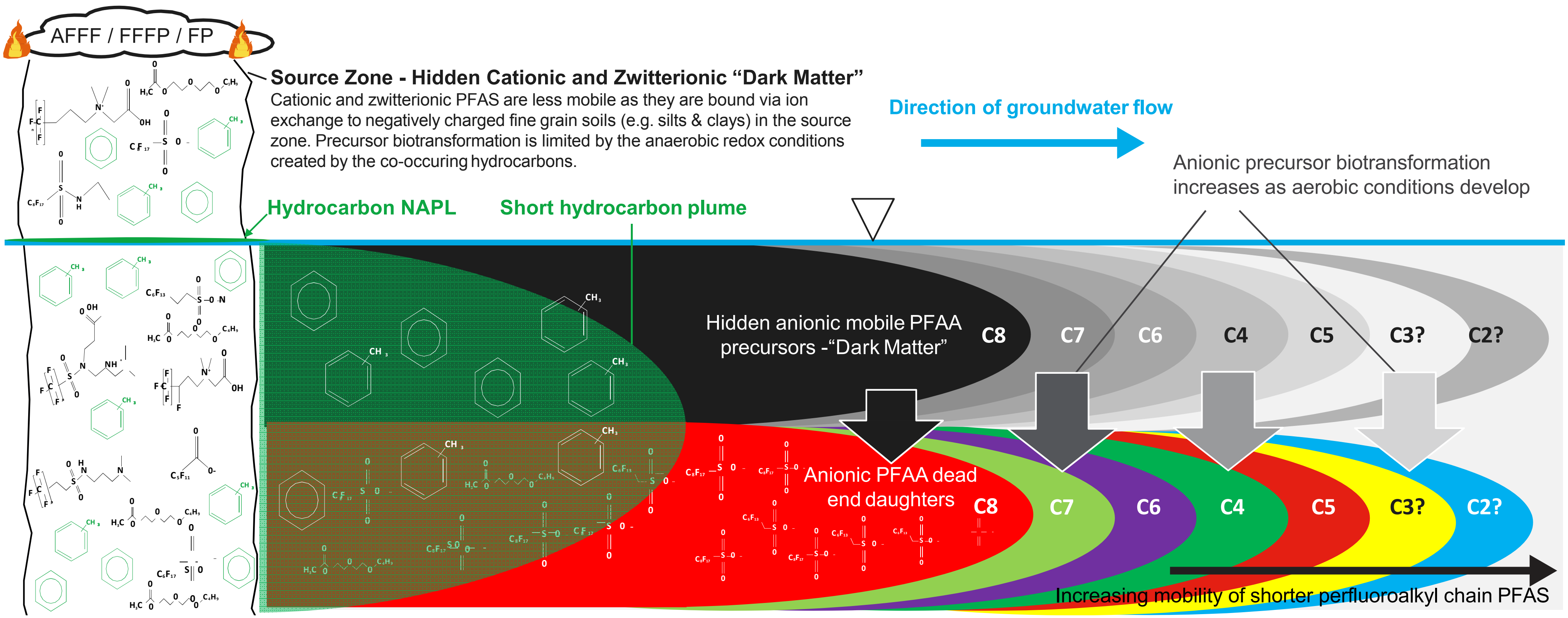
Comparison of Analytical Techniques - AFFF Impacted Groundwater







PFAS Source Zones, a CSM



Summary

Pre-design and the CSM for a PFAAs remediation project should consider broader PFAS chemistry and pre-cursor loading:

- Nature and extent of sourcing
- Fate and transport
- Informed and appropriate remedial designs
- Support future risk based and more cost efficient remedial strategies

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Download at:
https://www.concawe.eu/publications/558/40/Environmental-fate-and-effects-of-poly-and-perfluoroalkyl-substances-PFAS-report-no-8-16