# State of the Science: Firefighting Foam Transition Challenges and Solutions

Vision, Initiatives and Paradigm Shift

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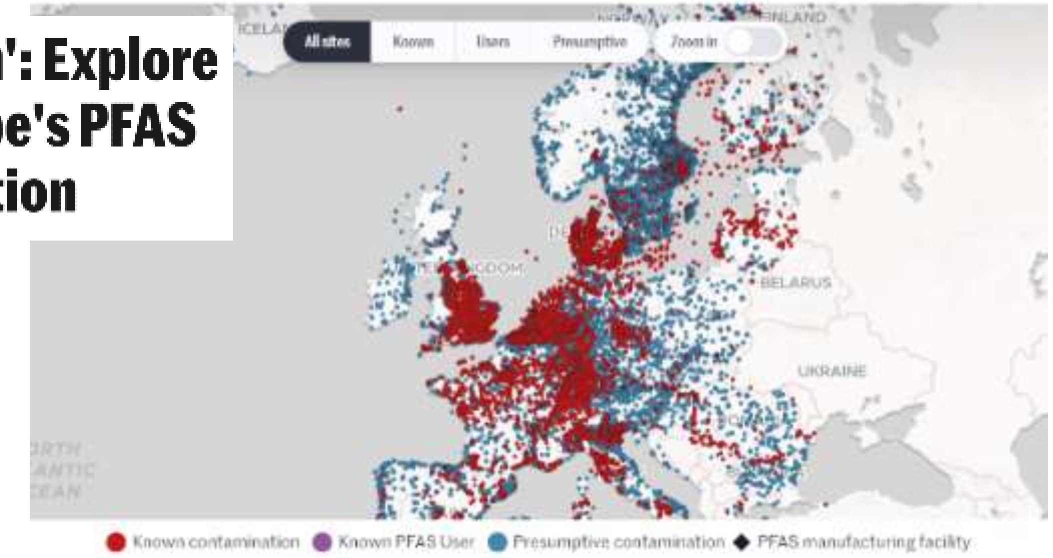
CDM Smith

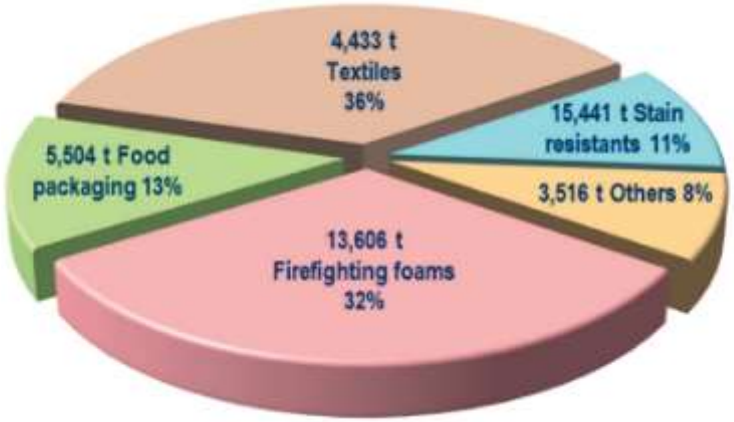
# Overview

- What are PFAS?
- What PFAS are in firefighting foams
- Chemical Analysis – how to comprehensively measure PFAS in solution
- Why do PFAS stick to surfaces?
- What's working to remove supramolecular PFAS from surfaces?
- Proving decontamination
- How to measure PFAS on surfaces
- Conclusions

**'Forever pollution': Explore the map of Europe's PFAS contamination**




https://www.lemonde.fr/en/les-decodeurs/article/2023/02/23/forever-pollution-explore-the-map-of-europe-s-pfas-contamination_6016905_8.html




**Projected fluorotelomer production in 2019 of 42,500 tonnes.**
After Global Market Insights, 2016. Projected compound annual growth rate of 12.5% from 26,500 tonnes in 2015.



https://ipen.org/sites/default/files/documents/the_global_pfas_problem-v1_5_final_18_april.pdf

# Safety Moment: Foam “Disposal”

Fire Fighting Foam

Free

Darwin, NT

Steve (11 listings)
MEMBER SINCE 2015

13 x 20 litre drums of fire fighting foam

all out of date

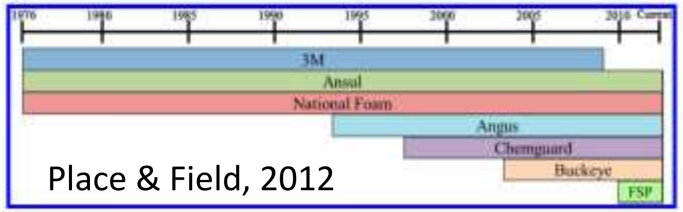
good for fire training

sell as one lot

# Class B Firefighting Foams

**Fluorinated Foams**

- **FP** foams (fluoroprotein foams) and **AR-FP / FP-AR** used for hydrocarbon storage tank protection and marine applications.
- **AFFF** (aqueous film forming foams) used for aviation, marine and shallow spill fires and **AR-AFFF** (alcohol resistant aqueous film forming foams),
- **FFFP** foams (film forming fluoroprotein foams) used for aviation and shallow spill fires and **AR-FFFP** (alcohol resistant film forming fluoroprotein foams)




Timeline of AFFF addition to the DoD Qualified Products Listing (certified to MIL-F-24385 specifications).

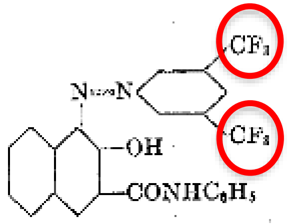
**High Expansion Foams –Hi-Ex**

- Not generally considered to contain deliberately added PFAS


https://nationalfoam.com/foam-concentrates/high-expansion-foams/high-expansion/

PFAS-containing foams contains both polyfluoroalkyl and perfluoroalkyl PFAS

# History of PFAS, Fluorinated and Fluorine Free Firefighting Foams




Naphthol AS red dye

**1930's** PFAS mass production (>100 tonnes p.a.) of azo dye TFA precursors

**1949** Simons describes extreme persistence of fluorocarbon molecules

Summer **1962** 3M field tests PFAS foams at Marinette, WI

**1967** 3M AFFF supplied to five US Naval stations

29th July **1967** USS Forrestal Fire

**1968** Dr. Donald Taves, New York, finds PFOS in blood samples from humans, including in his own blood.

15th May **1970**; US DoD QPL lists 3M Light Water FC-196

24th October **1973** US DoD QPL lists National Foam Aer-O-Water 6

3rd June **1976**; US DoD QPL lists Ansul AFFF

**1982** AFFF Product Environmental Datasheet state AFFF is biodegradable '*if AFFF products were pure chemicals instead of mixtures, OECD guidelines would classify them as "readily biodegradable"*'

**1985** Fluorine Free Training Foams developed

**2001** High Molecular Weight Fluoropolymers introduced to AFFF

**2002** 3M formulated F3 foam with comparable performance to PFOS-based AFFF foams meeting the ICAO Level B specification

**2003** 3M phases out sales of PFOS, PFOA and PFHxS in their production.

**2009** The Stockholm Convention establishes restriction on PFOS uses.

**2010** USEPA PFOA Stewardship program starts

**2010:** First observation of PFAS in Swedish drinking water resulting in the closure of 3 water supply wells.

**2014** Solberg Rehealing F3 Foam wins USEPA Presidential Designing Greener Chemicals Award

**2014** Testing of Danish groundwater finds elevated PFAS at multiple locations.

**2016** National Foam F3 Jetfoam ICAO B wins Green Apple Award

# Research Work – Rational Progression - more than 500 tests

Small scale
Simulated tank
Critical applica

Subsurface tests

Spill fire
Critical application rates

LARGE SCALE TEST PROGRAMME FOR STORAGE TANK FIRES

PRESS RELEASE

- From the samples tested, some concentrates of both C6 and FF formulations demonstrated adequate levels of fire performance for bund spill fires and small tank fires using standard NFPA application rates although generic conclusions cannot be drawn from this. The performance capability is very specific to the particular formulation and also to the type of application equipment used.
- There are different levels of performance within each generic type of foam. It is not possible to state, for example, that all C6 foams demonstrate better performance than all FF foams or vice versa. This emphasises the need for batch testing.

Self expanding foam

Vapour suppression

Hybrid Medium Expansion

Further obstructed spill fire testing

Polar solvent fires

# Use of F3 Foams – Oil & Gas

- Equinor (formerly Statoil) **completely switched to fluorine-free firefighting (F3) foam from 2013** for both its onshore and offshore (North Sea) operations
- AMPOL (formerly CALTEX) Australia transitioned to F3 foams


APPENDIX III

GOING FLUORINE-FREE IN THE PETROCHEMICAL INDUSTRY – ONSHORE AND OFFSHORE IN THE NORWEGIAN NORTH SEA SECTOR


https://ipen.org/sites/default/files/documents/the_global_pfas_problem-v1_5_final_18_april.pdf

# Civil Aviation: F3 Foams Users

airservices connecting australian aviation


Airservices Australia. : Re-Healing Foam is in use on all 27 airports

Stuttgart Airport

Dubai Airports

Dubai World Central

Dubai International

Billund Airport - West Denmark direct

Allgäu Airport Memmingen

Dortmund Airport 21

PARIS AÉROPORT

norwegian

Blackpool International Airport

nqy newquay airport

Bristol Airport Amazing journeys start here

MAG Manchester Airport

SAS Scandinavian Airlines

Köln Bonn Airport

Guernsey Airport YOUR GATEWAY TO THE CHANNEL ISLANDS

Copenhagen Airports CPH

## APPENDIX I

### LONDON HEATHROW GOES FLUORINE-FREE

**Statement from Graeme Day, Fire Service Regulation and Oversight Manager Operations, London Heathrow Airport (LHR).**

Heathrow Airport Fire & Rescue Service took the decision in mid-2012 after a 15-month evaluation period to change from an AFFF firefighting foam concentrates to a fluorine and organo-halogen free concentrate for the following reasons:

- Foam concentrates containing fluorine and organo-halogen components continue to represent an unacceptable risk to the airport infrastructure because of their chronic environmental impact and the size of infrastructure investment required to contain and mitigate that risk. Fluorine and organo-halogen free foam (F3) concentrates were found to be suitable for discharge into Heathrow Airport's foul sewer as they did not contain chemicals that were of concern to Thames Water and environmental regulators. On that basis, Heathrow Airport Limited was no longer prepared to approve foam concentrates containing these materials. This decision was made as a result of discussions with environmental regulators and was in line with UK CAA thinking and best practice. The decision also took compliance with ICAO requirements, the impact of F3's acute environmental pollution and the UK Environment Agency's guidance to Fire & Rescue Services i.e. that fluorosurfactant-free foam products should be considered where performance meets the needs of the organisation, into account.
- The change to an F3 concentrate meant that Heathrow Airport Ltd could deploy an ICAO Performance Level B compliant firefighting foam if required during an

Performance Level B compliant and offered the best value for money was subsequently purchased.

- Since attending the UN POPRC meeting in Rome in September 2018, I have received many enquiries about the use of fluorine-free firefighting foams from both end-users and regulators in numerous countries from New Zealand to the West Coast of the United States of America.

INTERNATIONAL Airport REVIEW

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## Is the burst of the AFFF bubble a precursor to long term environmental liabilities?

Ian Ross from Arcadis explains how the use of new generation Fluorine Free foams are not only playing a key part in aviation fire extinguishment, but also helping to mitigate the widespread environmental concerns surrounding PFASs.

284

# Danish Defence use of F3 Foams

FORSVARET
FORDI NOGET ER VÆRD AT KÆMPE FOR

**"Train as you Fight"**

Lars Andersen, Fire Chief, Royal Danish Airforce:

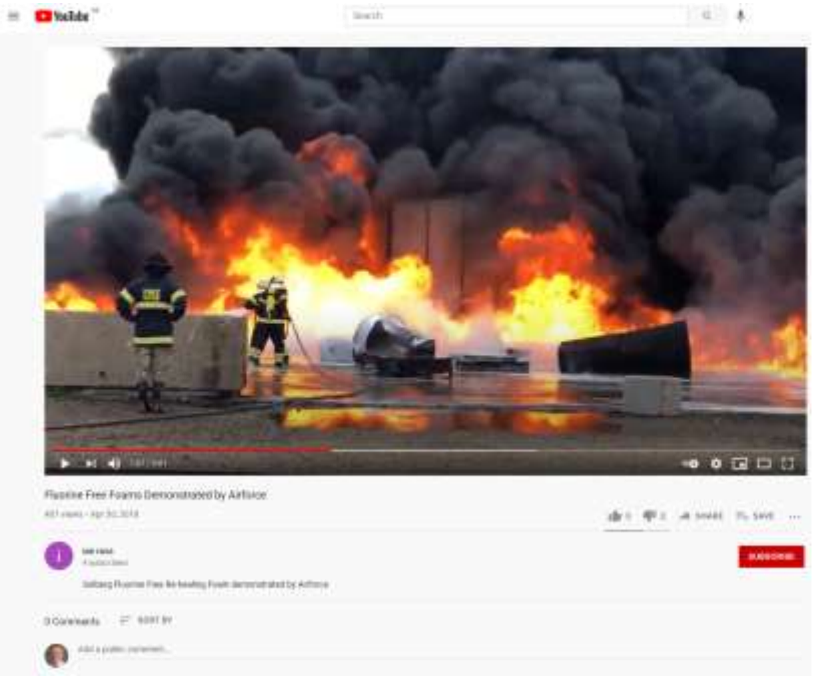
*"Put you self in the place of a crewmember trapped in a fuselage engulfed in flames. Ask yourself a question; would I trust the fluorine free foam? I would."*

https://www.linkedin.com/pulse/high-flow-fluorine-free-foam-lars-andersen/

*"My experience is that fluorine free foam works flawlessly. We have used it in two major incidents, and we are using it for training purposes"*

*"When it comes to the extinguishing capability of the fluorine free foam, there are, from my point of view, no difference compared to the old AFFF foam containing PFAS. It works exactly as good as the old stuff."*

https://www.linkedin.com/pulse/how-fluorine-free-foam-does-work-practice-lars-andersen/



https://www.youtube.com/channel/UCvG4n2UNuIuRcny0ASdYOmw

# GreenScreen Certified™

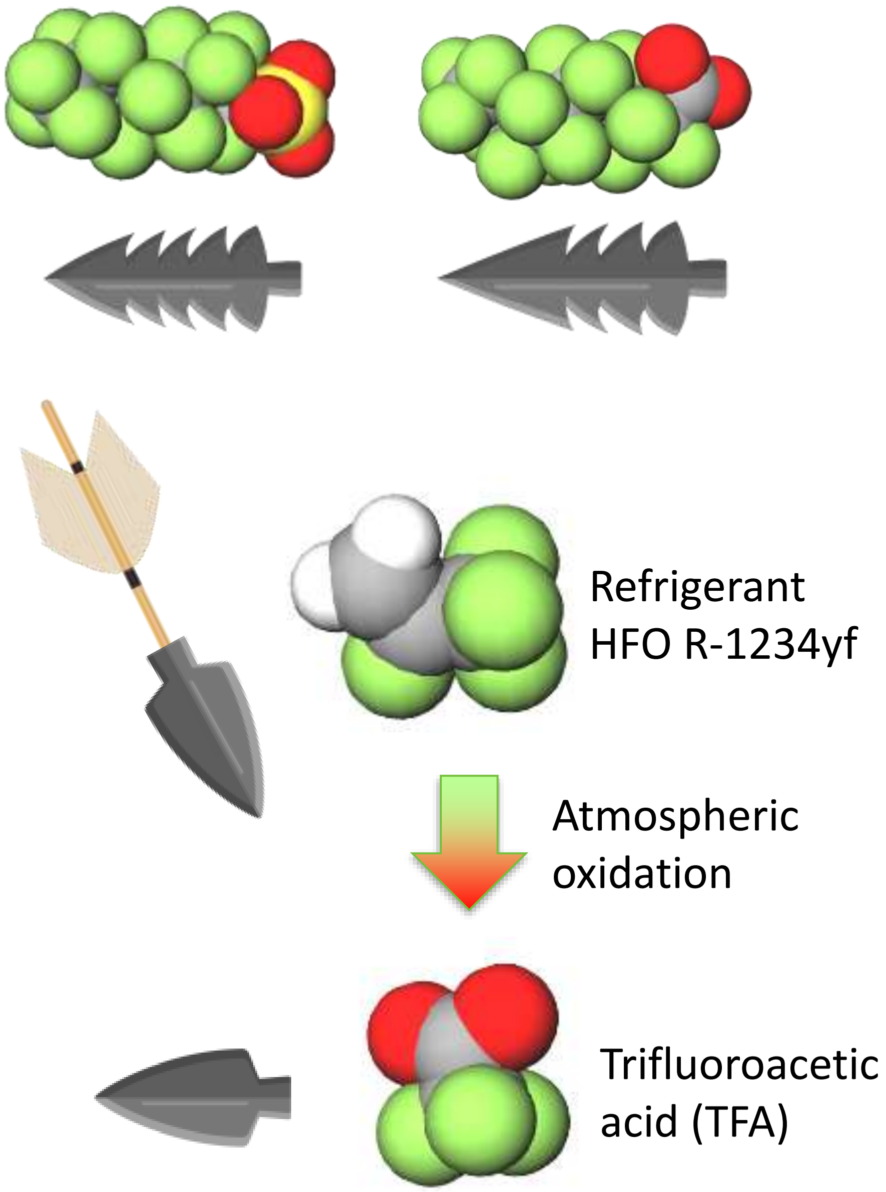
Independent Certification of Environmental Profiles of F3 Foams
https://www.greenscreenchemicals.org/certified/fff-standard

Similar to HOCNF – The Harmonised Offshore Chemical Notification Format used to assess the environmental impact of F3 foams in Europe

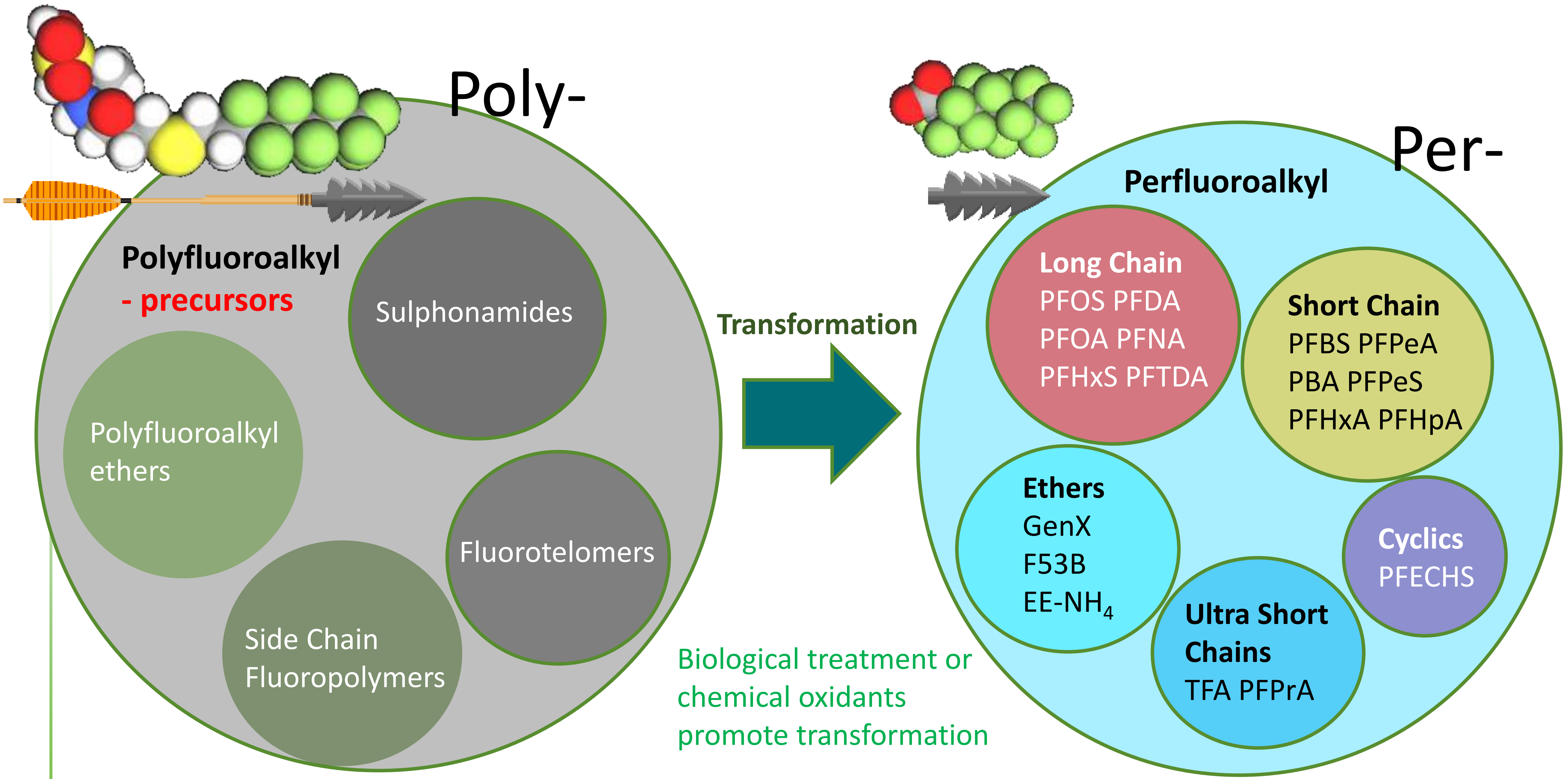

https://www.greenscreenchemicals.org/images/ee_images/uploads/resources/GSC_Foam_Webinar_2020_0225_final.pdf

# Characteristics of PFAS

- **Extreme Persistence**
  PFAS show no sign of biodegradation and have been termed “forever chemicals” –due to multiple robust C-F bonds which also protect C-C bonds from attack
- **Mobility**
  PFAS tend to be very mobile in the environment as they are soluble in water (unlike most other POPs)
- **Bioaccumulation**
  Some PFAS bioaccumulate and biomagnify - long chain PFAS concentrate humans via renal reabsorption, other mammals can excrete at much faster rates
- **Toxicity**
  There are very low (<10 ng/L) and diminishing regulatory acceptance criteria (drinking water standards) as more is known about the toxicity of specific PFAS
- **Surfactants**
  Amphiphilic PFAS stick on surfaces / interfaces when at higher concentrations



# Per- & Polyfluoroalkyl Substances

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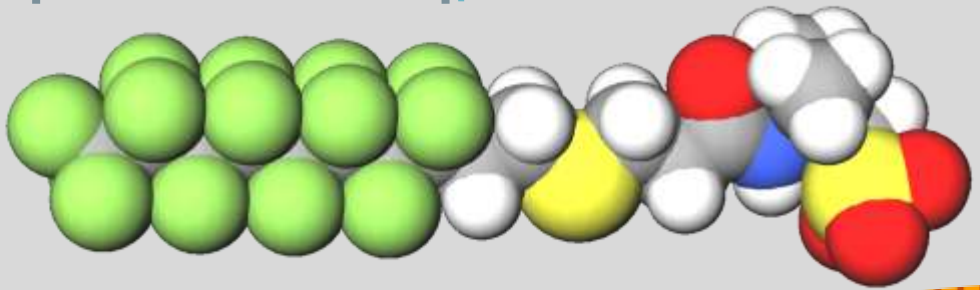
# Per- & Polyfluoroalkyl Substances

Poly-

(Precursors)

Persistent perfluorinated

Non-fluorinated - Biologically/Chemically removed



8:2 FTAoS

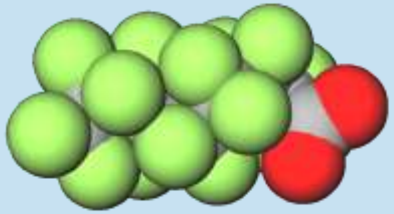
Stone arrowhead, like perfluorinated section of molecule, persists forever

Wooden shaft, like non-fluorinated section of molecule, is degraded so rots away in ground / in vivo

Biotransformation / Abiotic Oxidation

Per-

(Terminal products)



PFOA

Perfluoroalkly acid formed from precursor persists indefinitely as “chemical rocks”, like stone arrowheads that last forever in the environment

Stone arrowhead

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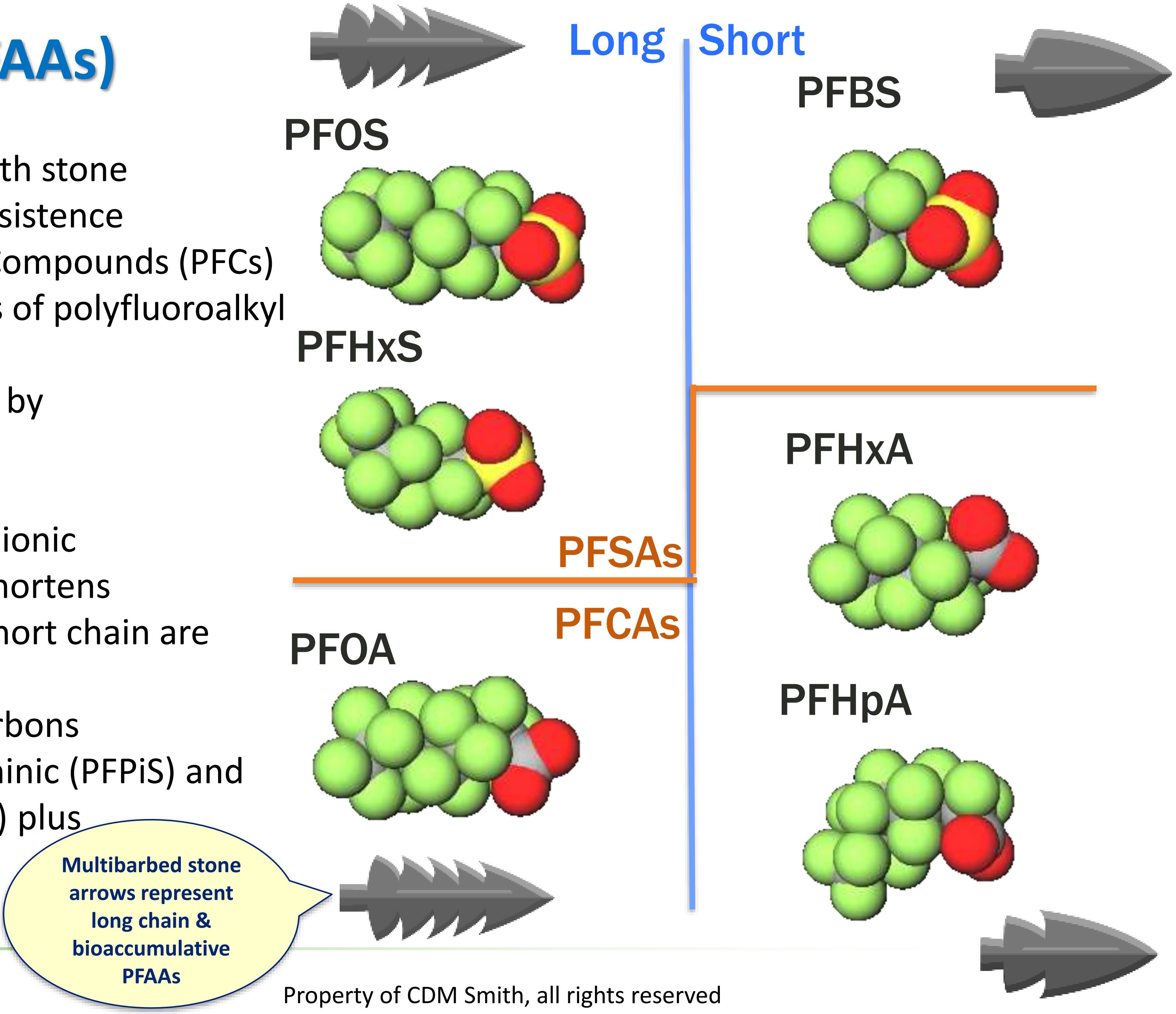
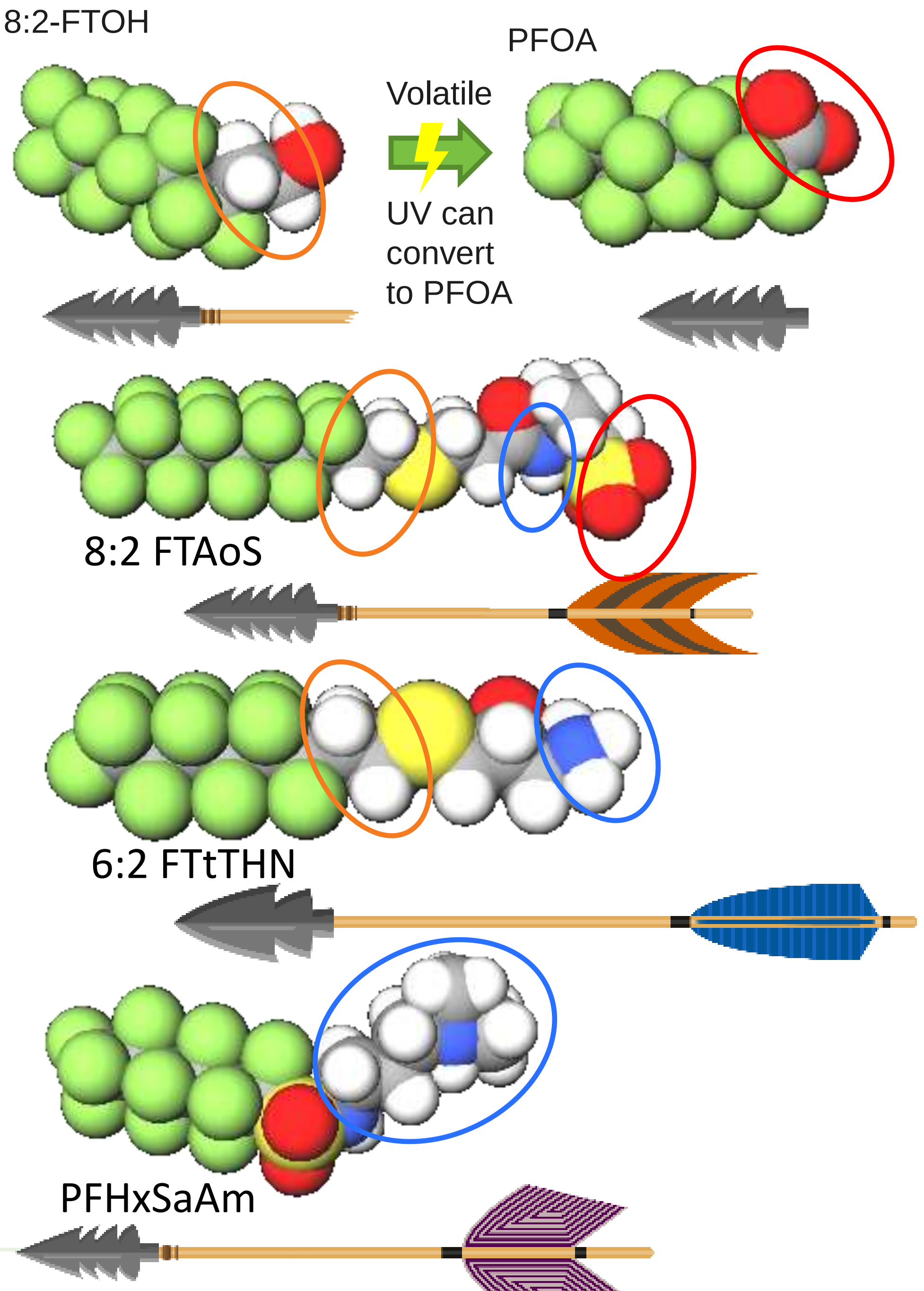
# Perfluoroalkyl Acids (PFAAs)

- Were termed “chemical rocks” with stone arrowhead analogy –extreme persistence
- Previously called Perfluorinated Compounds (PFCs)
- Terminal transformation products of polyfluoroalkyl substances
- Long chain vs short chain defined by bioaccumulation potential
- Generally, C1 – C20+ PFAAs
- Lipo- and hydrophobic, usually anionic
- Higher water solubility as chain shortens
- Long chain more regulated, but short chain are focus of increasing regulation
- Amphiphiles ≥4 perfluoroalkyl carbons
- Also includes perfluroalkylphosphinic (PFPiS) and phosphonic acids (PFPAs) (PFPiAs) plus perfluoroalkyl ethers (e.g. GenX)

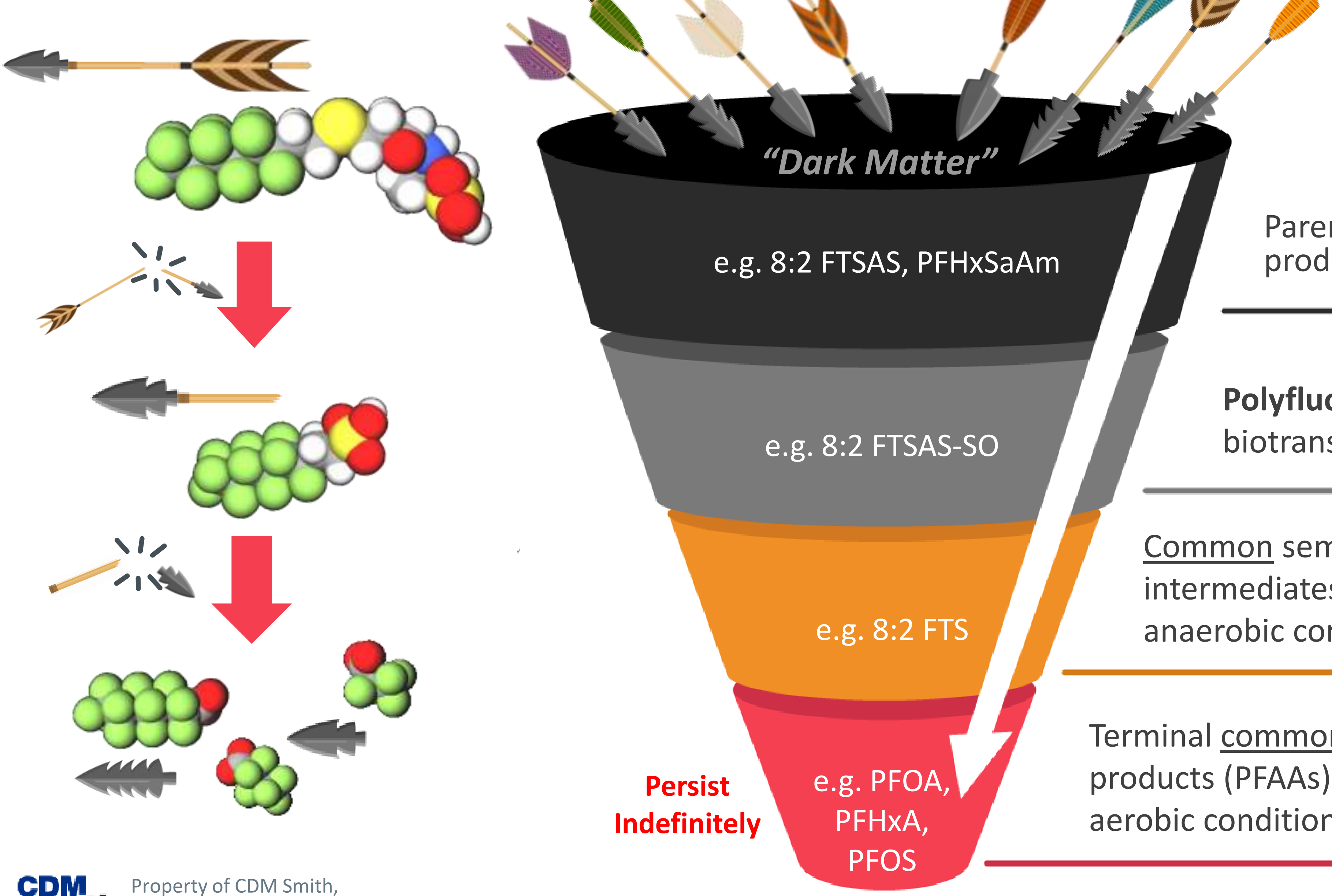


# Polyfluoroalkyl Substances –PFAA Precursors

- Polyfluorinated precursors will **biotransform** to make PFAA's as persistent "dead end" daughter products, some are anionic
- Fluorotelomer precursors form PFCAs i.e. PFOA, PFHxA
- Some precursors are cationic (positively charged) or zwitterionic (mixed charges)
- Environmental fate and transport will be complex as PFAS in AFFF comprise multiple chain lengths and charges
- Proprietary polyfluorinated precursors to PFAAs dominate most firefighting foams –there are a very limited number of  analytical standards, so they largey go undetected using conventional analyses



# PFAS Biotransformation Funnel



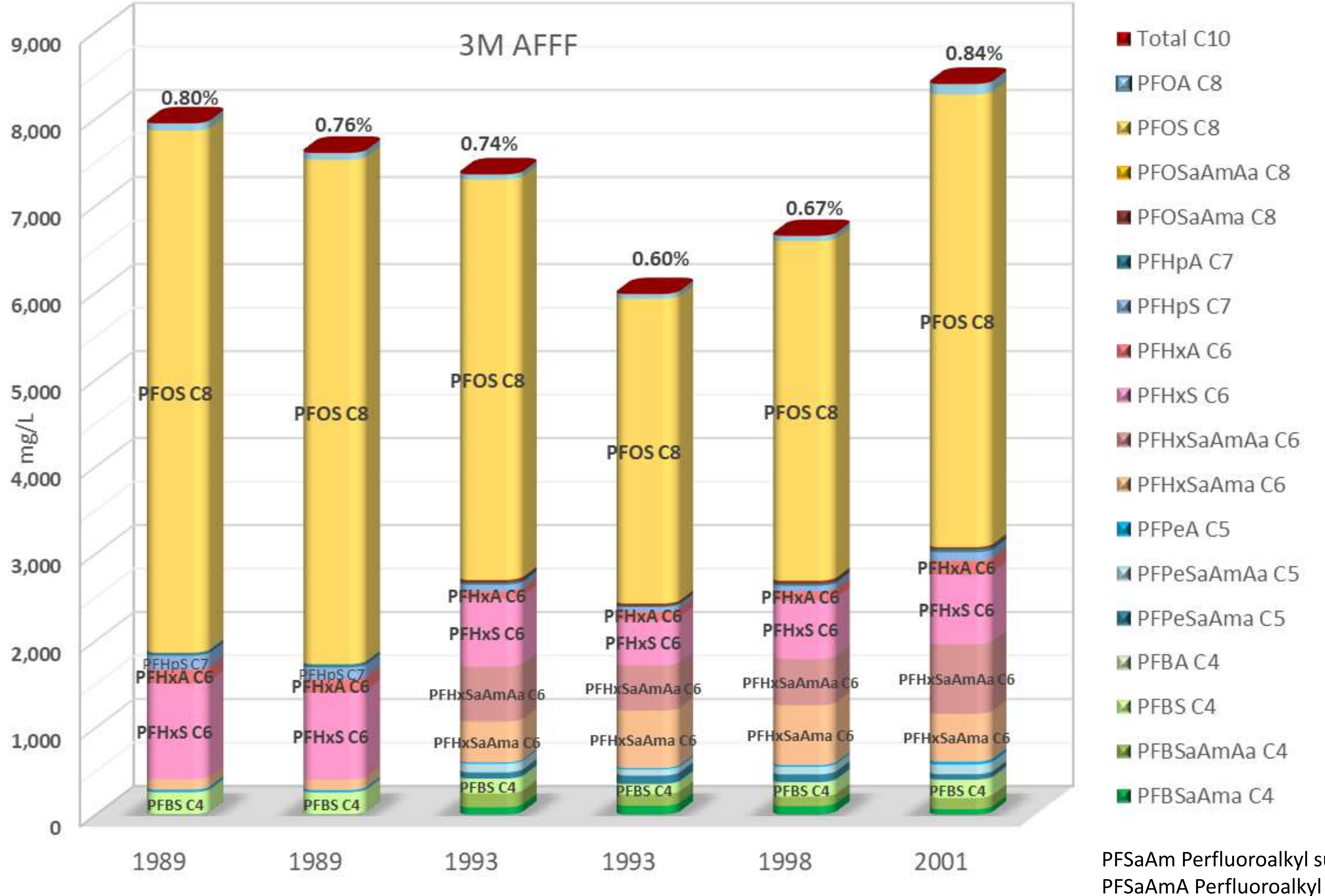

Parent **polyfluorinated** precursors in products e.g. in AFFF

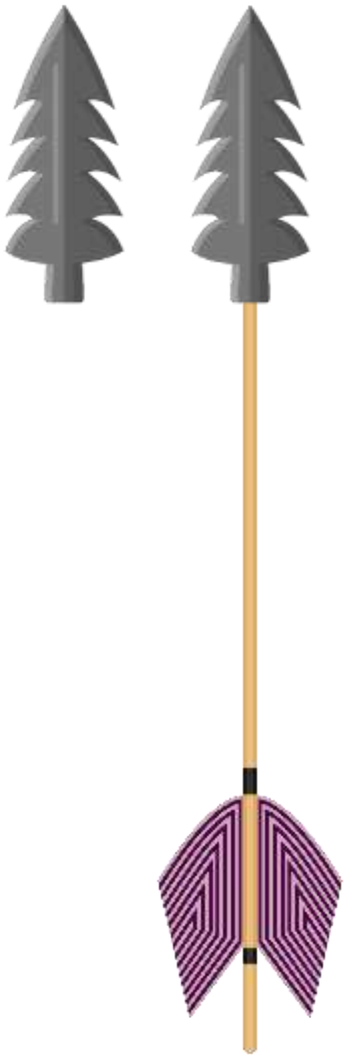
**Polyfluorinated** daughter biotransformation intermediates

<u>Common</u> semi-stable **polyfluorinated** daughter intermediates accumulating (especially under anaerobic conditions)

Terminal <u>common</u> **perfluorinated** daughter products (PFAAs) (formation favored under aerobic conditions)

Adapted from Ross et al., 2016



PFSaAm Perfluoroalkyl sulfonamido amine
PFSaAmA Perfluoroalkyl sulfonamide amino carboxylate

Field & Sedlak 2017. SERDP.

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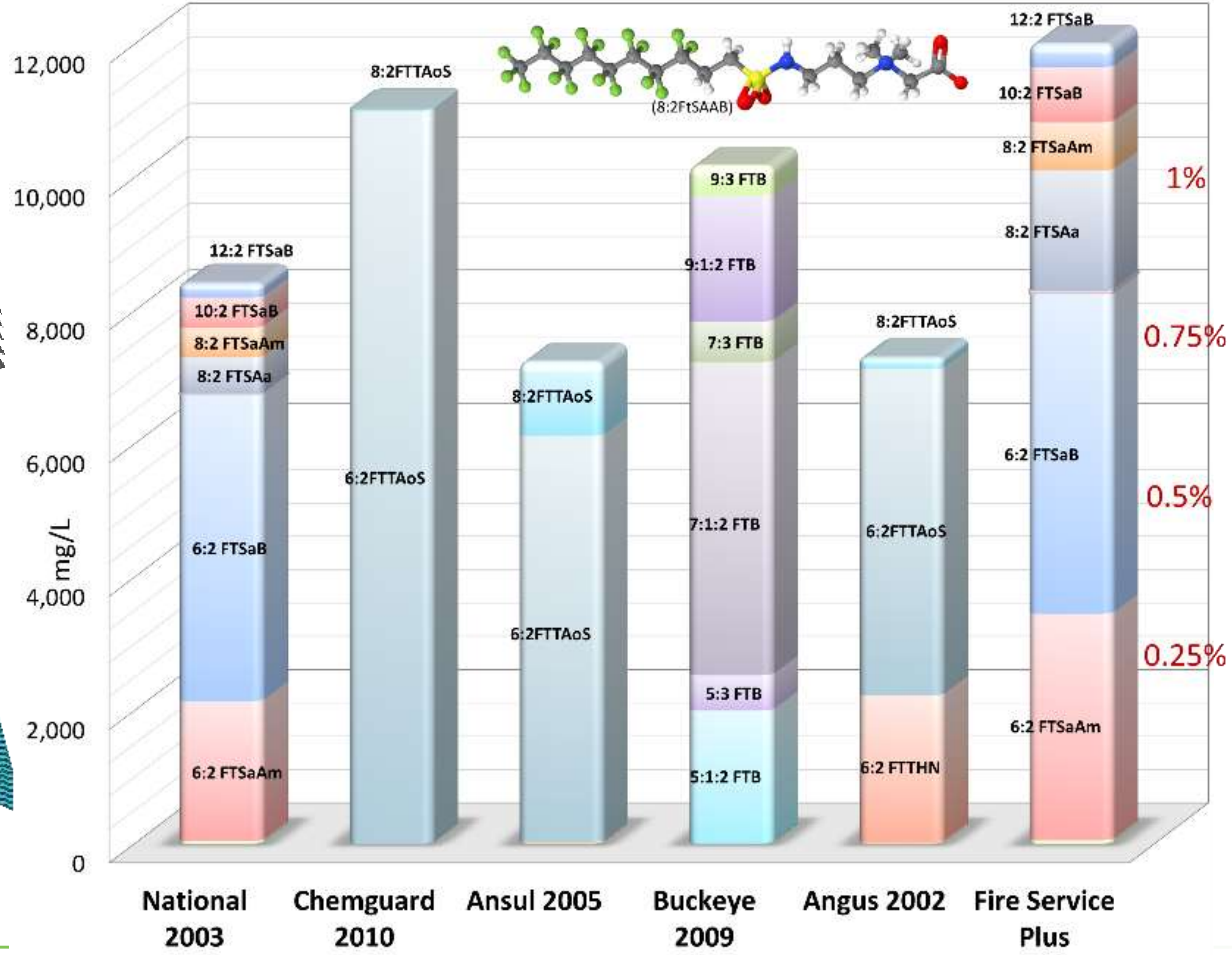
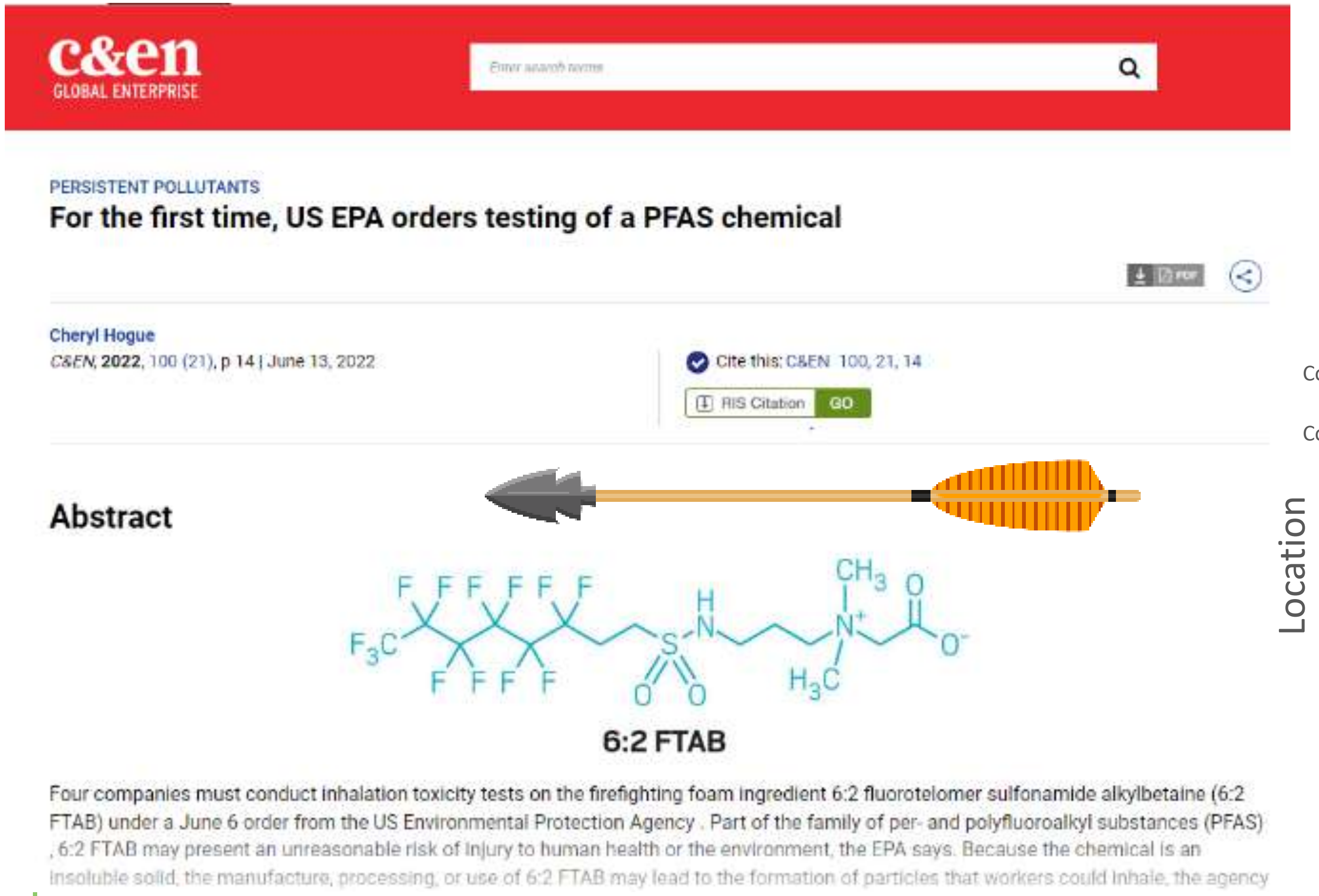







Field & Sedlak 2017, SERDP

# Polyfluoroalkyl substances under scrutiny



c&en
GLOBAL ENTERPRISE

PERSISTENT POLLUTANTS

For the first time, US EPA orders testing of a PFAS chemical

Cheryl Hogue

C&EN, 2022, 100 (21), p 14 | June 13, 2022

Cite this: C&EN 100, 21, 14

RIS Citation GO

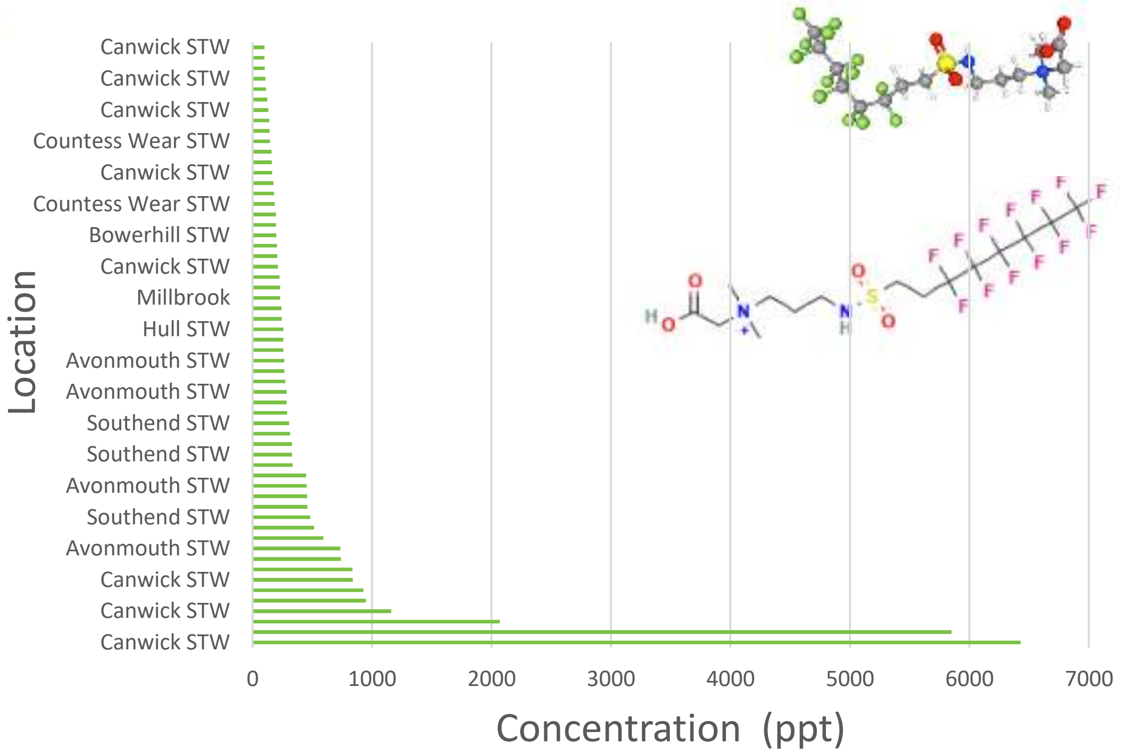
Abstract

6:2 FTAB

Four companies must conduct inhalation toxicity tests on the firefighting foam ingredient 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) under a June 6 order from the US Environmental Protection Agency . Part of the family of per- and polyfluoroalkyl substances (PFAS) , 6:2 FTAB may present an unreasonable risk of injury to human health or the environment, the EPA says. Because the chemical is an insoluble solid, the manufacture, processing, or use of 6:2 FTAB may lead to the formation of particles that workers could inhale, the agency

https://pubs.acs.org/doi/full/10.1021/cen-10021-polcon1

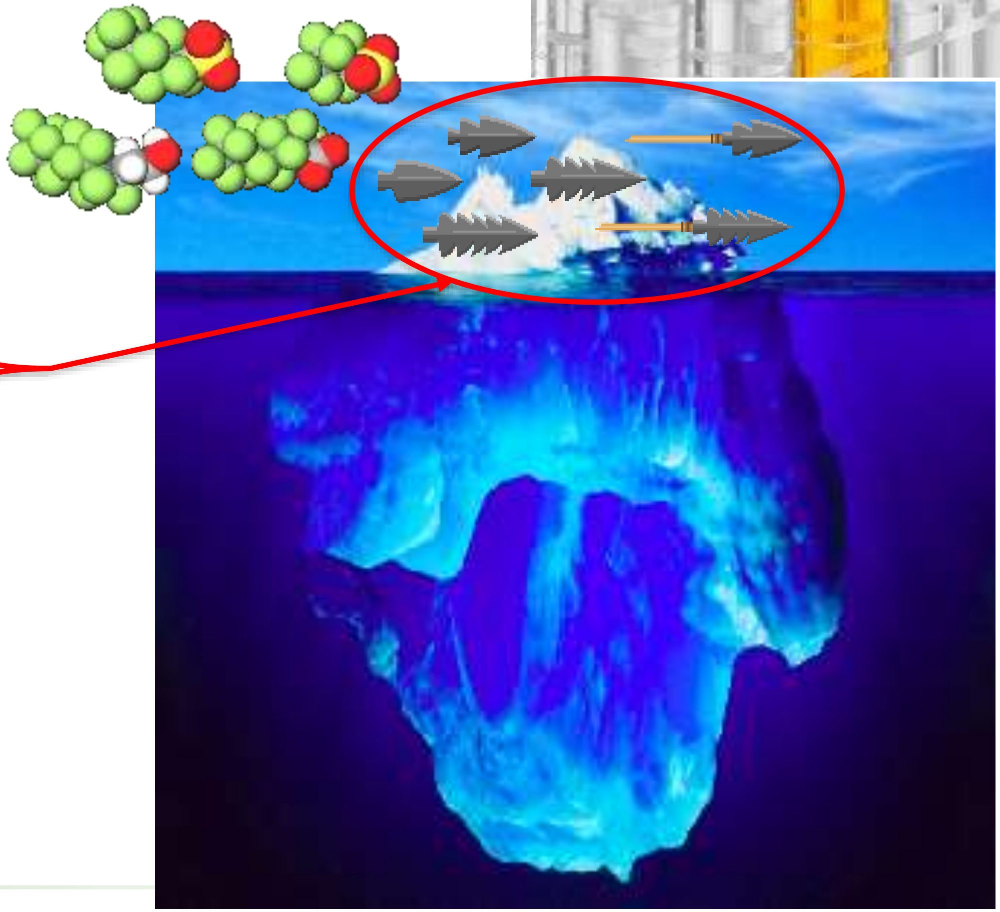
## 6:2 FTAB in UK waters - post sewage treatment



# Laboratory Analysis

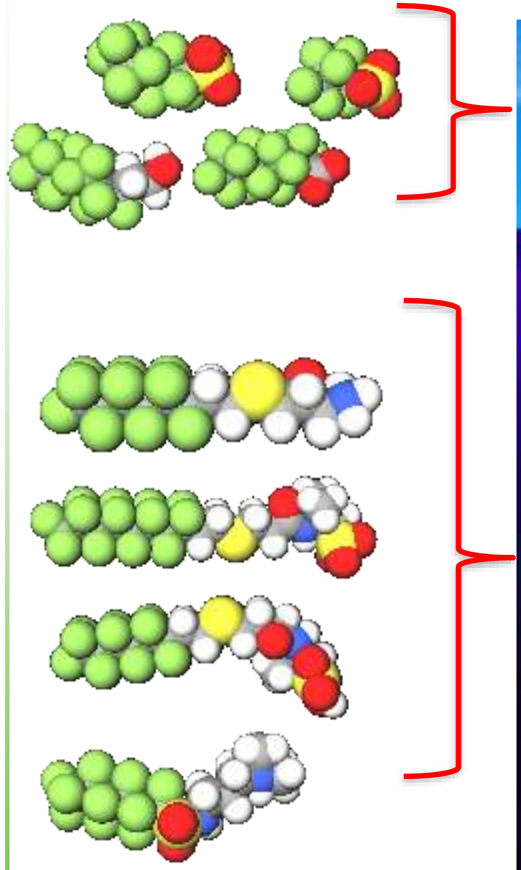
**Targeted Analysis**

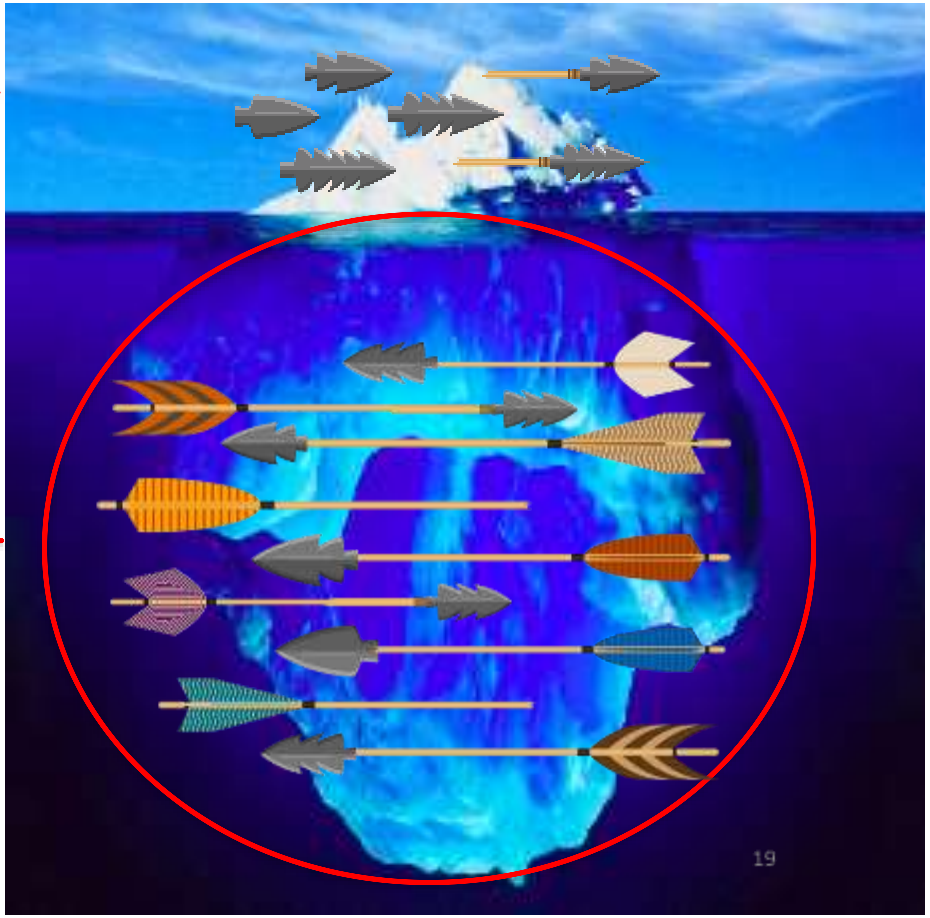
- USEPA Method 537.1
  - 18 PFAS (12 PFAAs + 6 Other PFAS Including GenX)
- USEPA Method 533
  - 25 PFAS (16 PFAAs + 9 Other PFAS Including GenX)
  - Focuses on Short Chain
- Draft Method 1633 (2021) for 40 PFAS
- DWI 47 PFAS



# Laboratory Analysis

## Non-Target Analysis





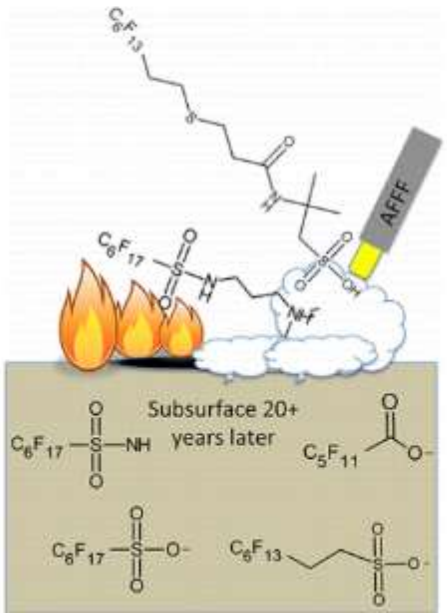
**Methods to Detect Non-Target Polyfluoroalkyl Substances**

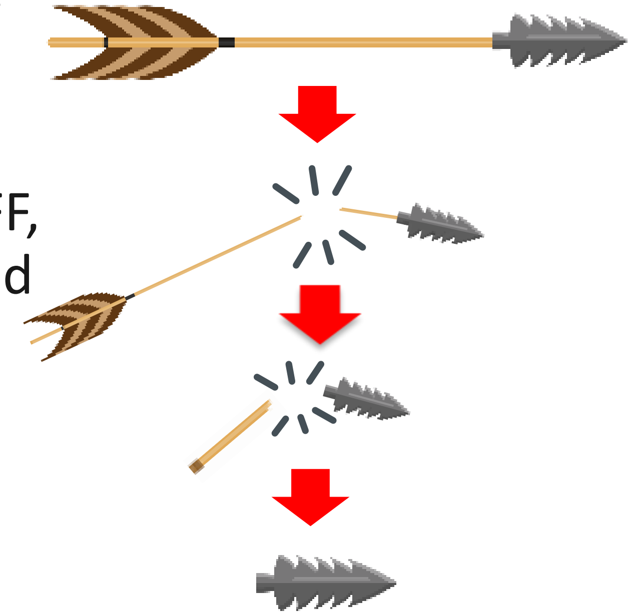
- Total Oxidizable Precursor (TOP) Assay
  - Converts Precursors to PFAAs so can detect chain lengths of precursors
- Total/Adsorbable/Extractable Organic Fluorine by combustion ion chromatography (e.g. USEPA 1621)
  - Mutiple organofluorine compounds that can be present / extracted
- High Resolution Mass Spectrometry
  - Orbitrap / Time of Flight
  - Identify PFAS based on high resolution molecular weight / transitions
- $^{19}F$ Nuclear Magnetic Resonance (NMR)
  - Identifies functional groups impacting F atoms chemical shift

# TOP Assay

- All PFAS-containing firefighting foams (AFFF, FFFP, FP) contain proprietary polyfluorinated PFAA precursors for which analytical standards are not available ’Dark matter’
- Converts ‘Dark Matter’ polyfluoroalkyl PFAS into detectable PFAAs –to provide some quantification of precursors
- Used to identify source areas of AFFF, FFFP, FP impacts and essential to find PFAS in firefighting foams

Series 1



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

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

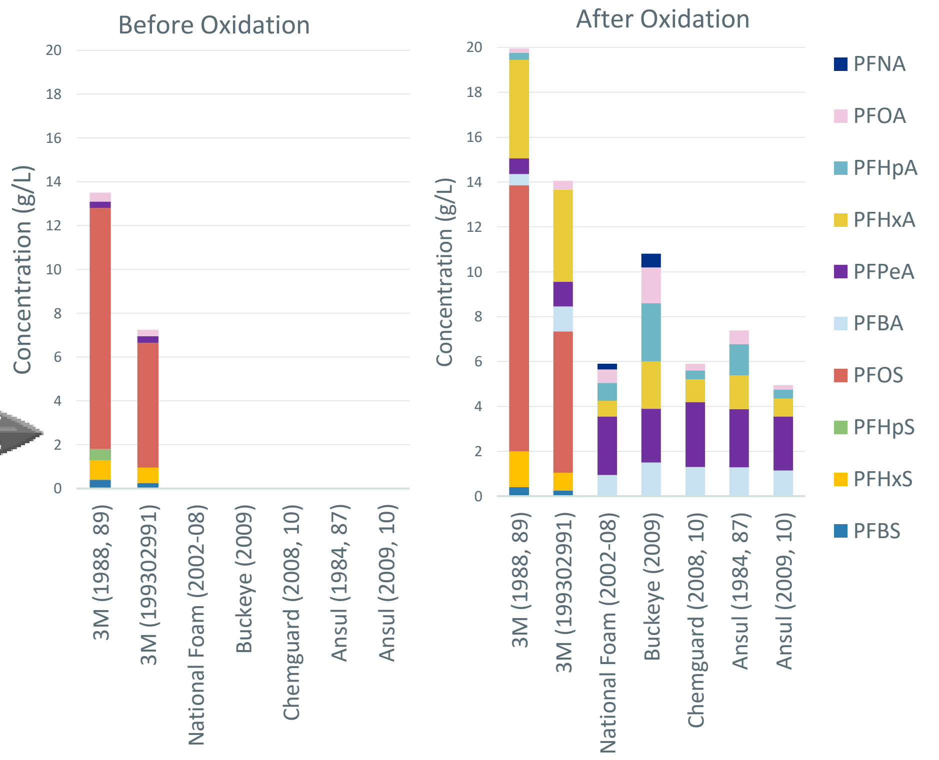


Figure 1. After concentrations of perfluorinated suflonates and carboxylates in AFFF formulations analyzed before (a) and after oxidation (b). Dates represent the years of manufacture of AFFF formulations analyzed in each category.

https://pubs.acs.org/doi/10.1021/es4018877

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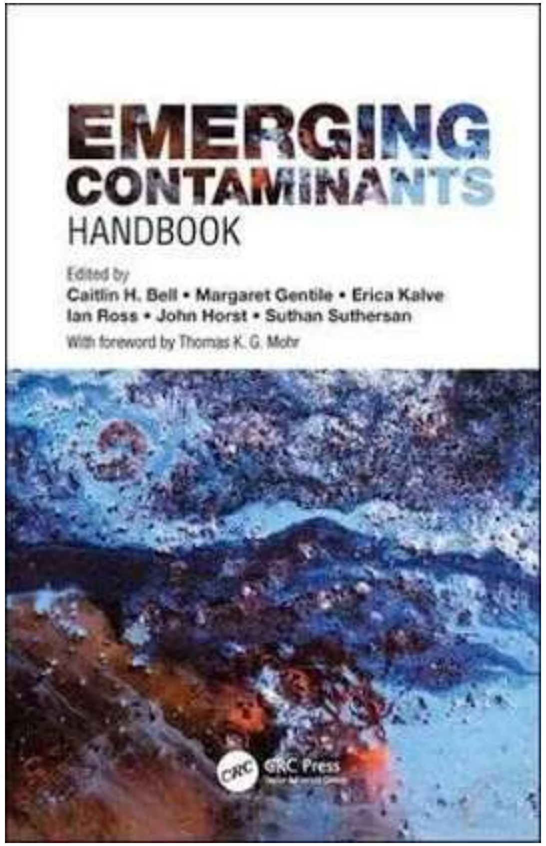
# Data Quality Objectives

Don't Overcook or Undercook TOP assay

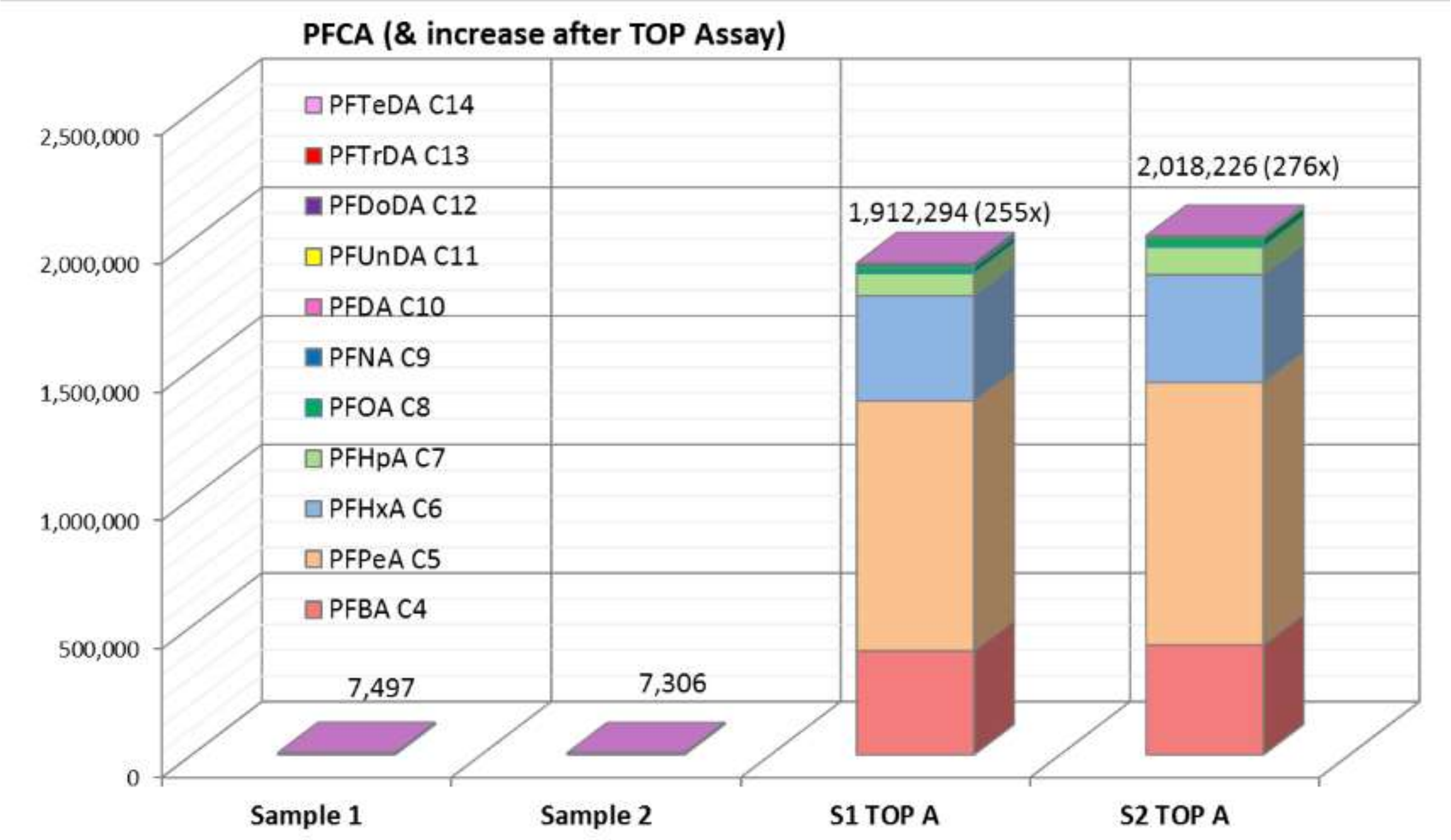
- Measured PFAA precursors have been (i.e., 6:2 FtS, FOSA, etc. <0) have been oxidized –undercook test
- If Σ[Perfluoroalkyl carboxylates] post-TOP < Σ[Perfluoroalkyl carboxylates] pre-TOP, this may suggest that the digest conditions have become acidic and carboxylates were destroyed - overcook test
- [Perfluoroalkyl sulphonates] post-TOP ≈ [Perfluoroalkyl sulphonates] pre-TOP; concentrations should not go down, but they may rise slightly.




Guidance on Use and Interpretation of the TOP assay
Erika Houtz PhD and Ian Ross PhD

# TOP Assay Applied to Surface Water from Recent C6 Fluorotelomer Foam Loss

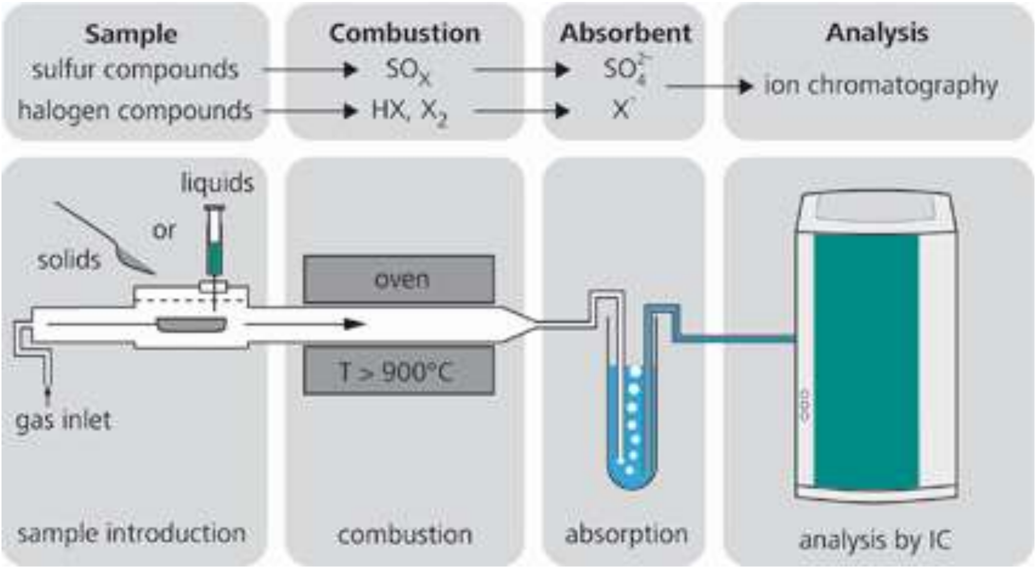
Assay Applied



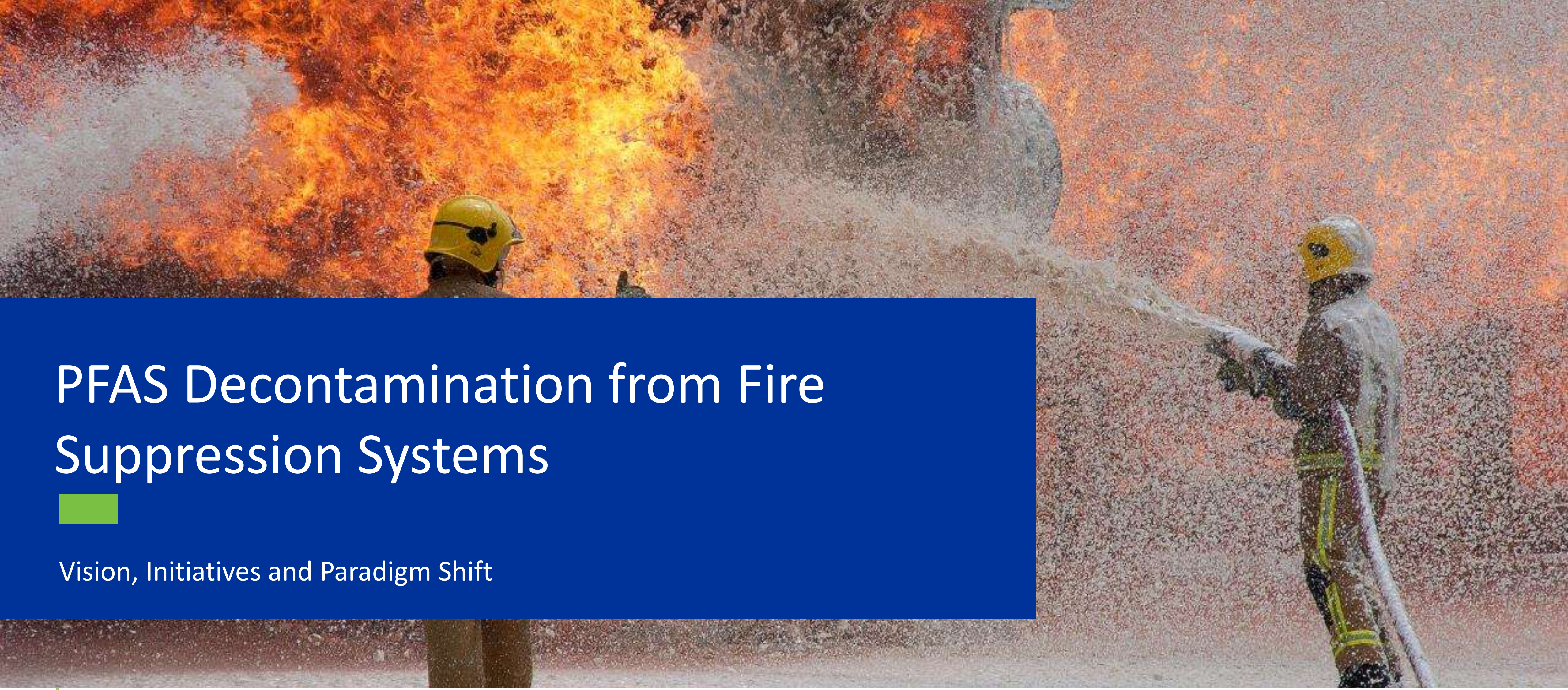

Data Courtesy of Nigel Holmes Queensland DEHP

# Organofluorine Detection via Combustion Ion Chromatography

- Potential to detect all organofluorine compounds
- Rapid screening for PFAS, but higher detection limits vs LCMSMS
- No speciation of PFAS chain length, reports total fluorine in sample
- Burn either samples, adsorbent or extractant and measure fluoride released using ion chromatography
  - Total Organic Fluorine (TOF)
  - Adsorbable Organic Fluorine (AOF) ~0.4 ppb detection limits
  - Extractable Organic Fluorine (EOF) ~0.2 ppb detection limit
- AOF with USEPA 1621 will not detect ultrashort PFAS as not extracted
- Mixed mode extraction cartridges (WAX, WAX, HLB. WAX/GCB) more comprehensive for PFAS extraction




https://www.metrohm.com/en_us/discover/blog/20-21/history-of-metrohm-ic---part-6.html



# PFAS Decontamination from Fire Suppression Systems

Vision, Initiatives and Paradigm Shift

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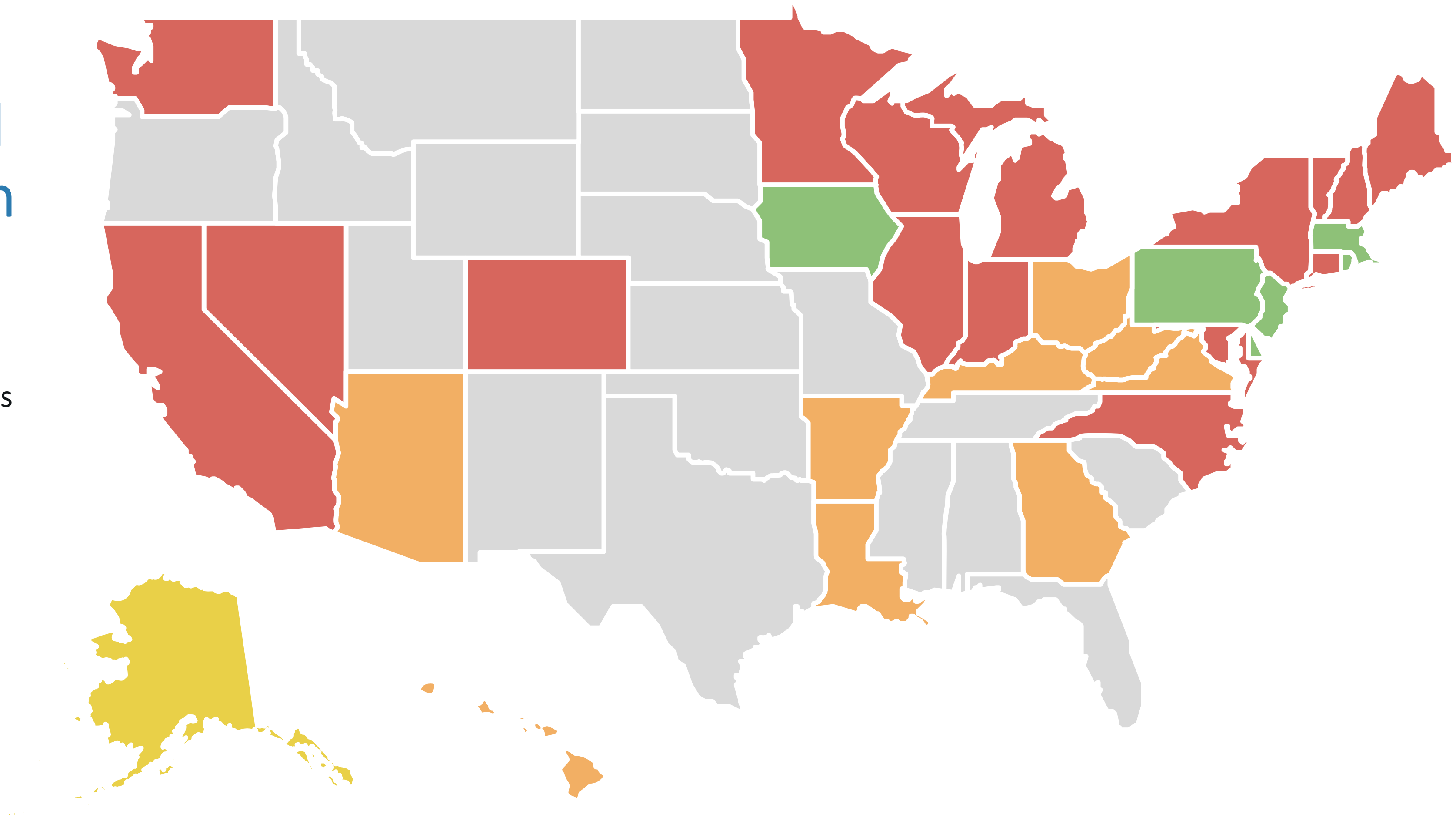
# US Fluorinated Foam Restrictions

(15th Dec 2023)

## Enacted and Proposed PFAS Firefighting Foam Regulations

- Use or Discharge Requirements, such as Training or Testing Requirements
- Notification or Reporting Processes
- Proposed
- Multiple Categories
- No Regulations

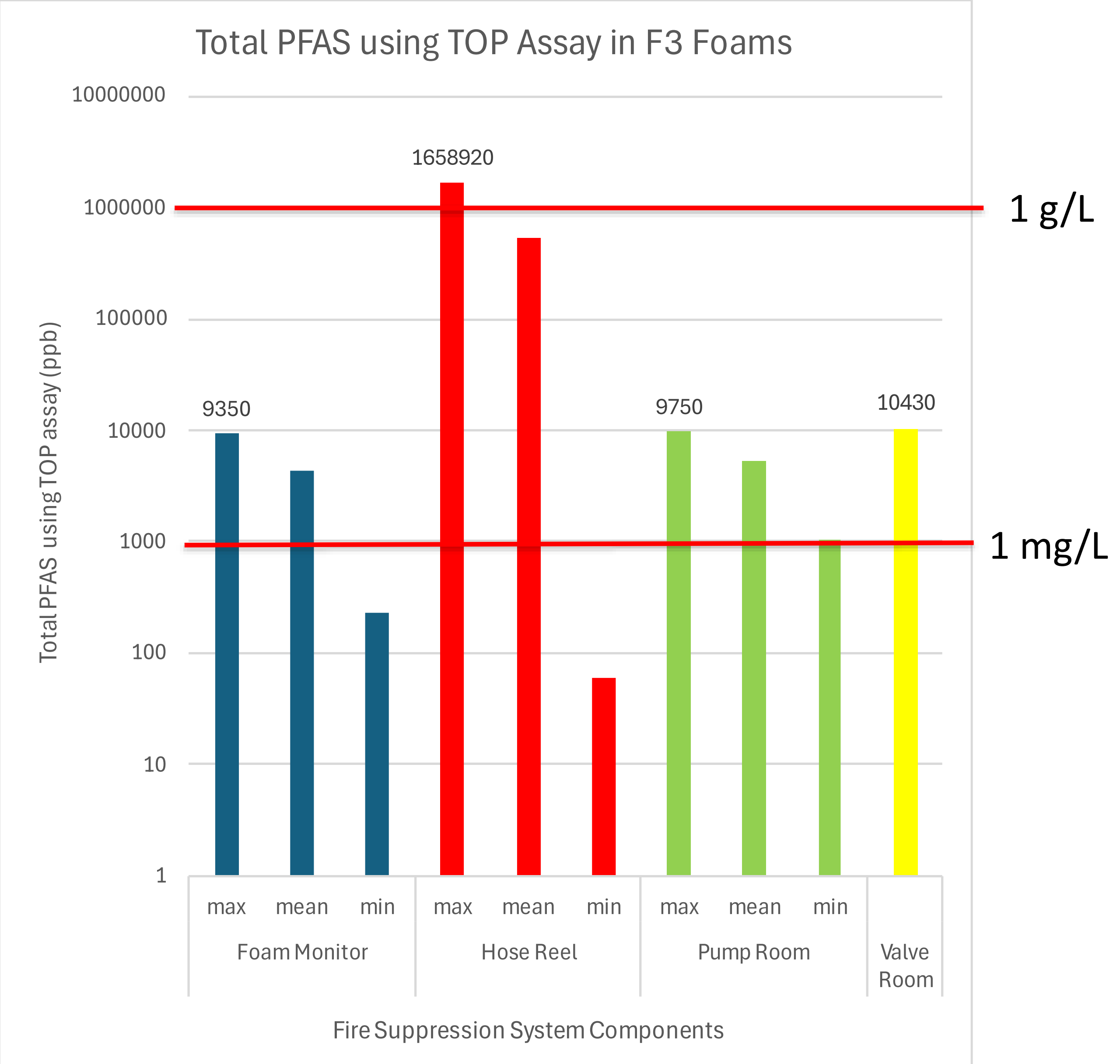


https://www.bclplaw.com/en-US/events-insights-news/pfas-in-firefighting-foam-afff-and-equipment-state-by-state-regulations.html#:~:text=Use%20and%20Discharge%3A%20A%20person%2C%20local%20government%2C%20fire%20department,subject%20to%20a%20few%20exceptions.

# PFAS Rebound into SFFF Foams

**One year after changeout of hangar to Synthetic Fluorine Free Firefighting (SFFF) Foam using dual water flush for decontamination:**

- PFAS residual up to 1.6 g/L in F3 foam lines
- F3 Foam now classed as a fluorinated foam under local regulations




Adapted from Ross et al., 2020 FOAM TRANSITION: IS IT AS SIMPLE AS "FOAM OUT / FOAM IN"? https://joiff.com/wp-content/uploads/2020/05/JOIFF-Catalyst-Q2-Foam-Supplement-13May20.pdf

CDM Smith

**Significant rebound of PFAS into F3 Foams after two water flushes**

# Regulatory Criteria: PFAS in Firefighting Foams

| EU Directive | Date | Requirements | Criteria |
| --- | --- | --- | --- |
| EU 2020/784   | 2023 (100% containment)<br>2025 (cannot be used) | C8 i.e. PFOA & PFOA precursors | 25 ppb PFOA<br>1,000 ppb PFOA-precursors (C8) |
| EU 2021/1297  | January 2023 (derogation to July 2025) | C9-C14 PFCAs:<br>PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA | 25 ppb sum of C9-C14<br>260 ppb sum of C9-C14 precursors |
| US NDAA  | Military applications –Oct 2024 | Total PFAS | 1 ppb |
| Queensland Australia  | 2021 | Sum PFSAs and precursors C4-C12<br>Sum PFCA precursors C4-C14 | 10,000 ppb<br>50,000 ppb (as fluorine) |

# How is so much PFAS stored on surfaces?

- Fluorosurfactants reported to produce stable, heat-sterilizable multilayered supramolecular assemblies
  - Vesicles
  - Flexible fibres
  - Rigid tubules
  - Lamellar sheets
- Liquid crystal PFAS structures in multiple layers can form when fluorosurfactants concentrate on surfaces

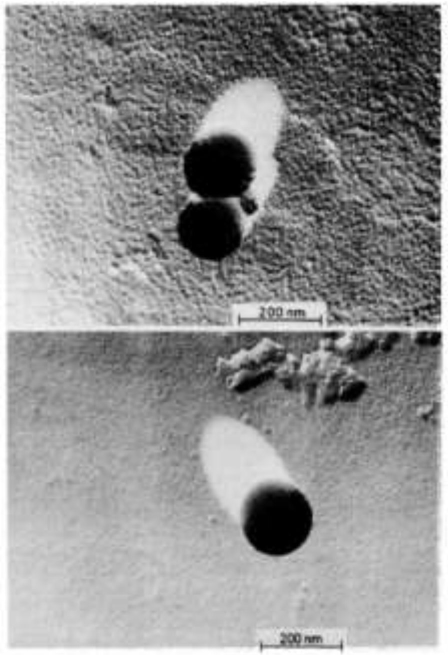
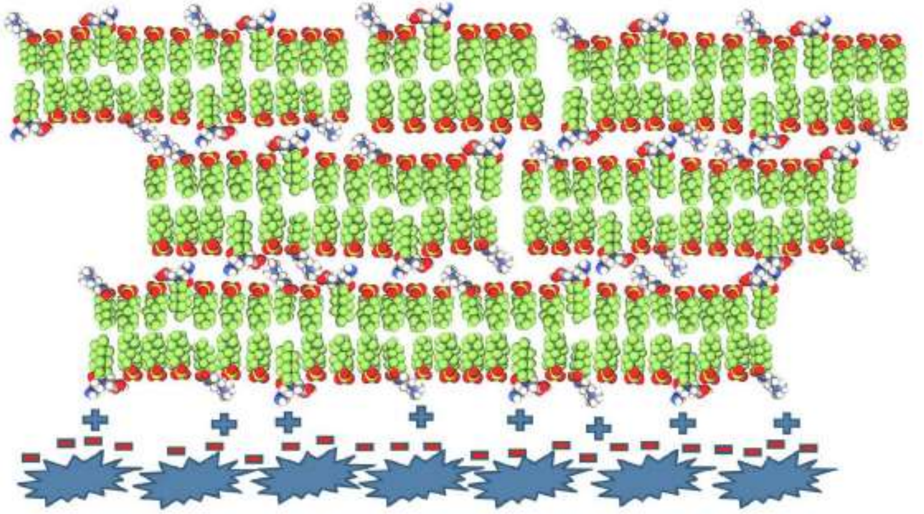
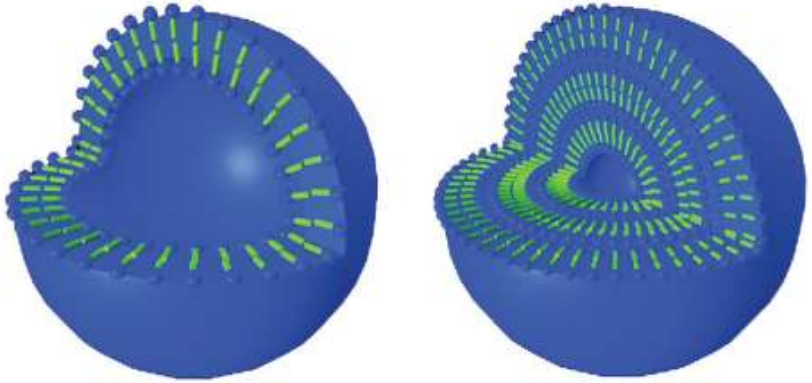



**Figure 6.** Electron micrograph of liposomes from 6: (a) monomeric, (b) polymeric (after 15 min of UV irradiation).

*J. Am. Chem. Soc.* **1984**, *106*, 7687–7692



*Schematic of PFAS Supramolecular Assembly Structures*




Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 10580

# Bulky and Rigid Perfluoroalkyl Chains

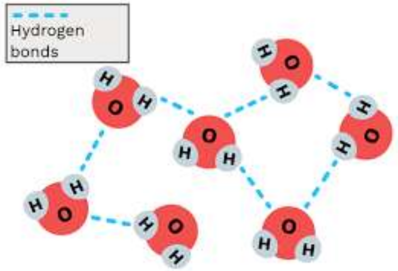
- Linear fluoroalkyl chains have a 50% larger cross-section area than an alkyl chain
- The "hydrophobic“ effect of the chain is roughly proportional to its area in contact with water
- Fluoroalkyl chain have diminished association with water as a result of reduced van der Waals interactions – imparting increased hydrophobicity

Punches a larger hole in water which increases surfactant properties

| | | Fluorine | Hydrogen |
|---|---|---|---|
| Electronegativity | | 3.98 | 2.2 |
| Ionisation potential | kJ/mol | 1676 | 1312 |
| Electron affinity | kJ/mol | 328 | 73 |
| Covalent radius | Å | 0.57 | 0.31 |
| van der Waals radius | Å | 1.35-1.47 | 1.2 |

| | | F-alkyl chain | Alkyl chain |
|---|---|---|---|
| Cross-section area | Å2 | 27–30 | 18–21 |
| Van der Waals diameters | Å2 | 5.6 | 4.2 |

| | | F-alkly chain | Alkyl chain |
|---|---|---|---|
| Volumes Occupied | Å3 | CF2 ~38 | CH2 27 |
| | Å3 | CF3 ~92 | CH3 54 |



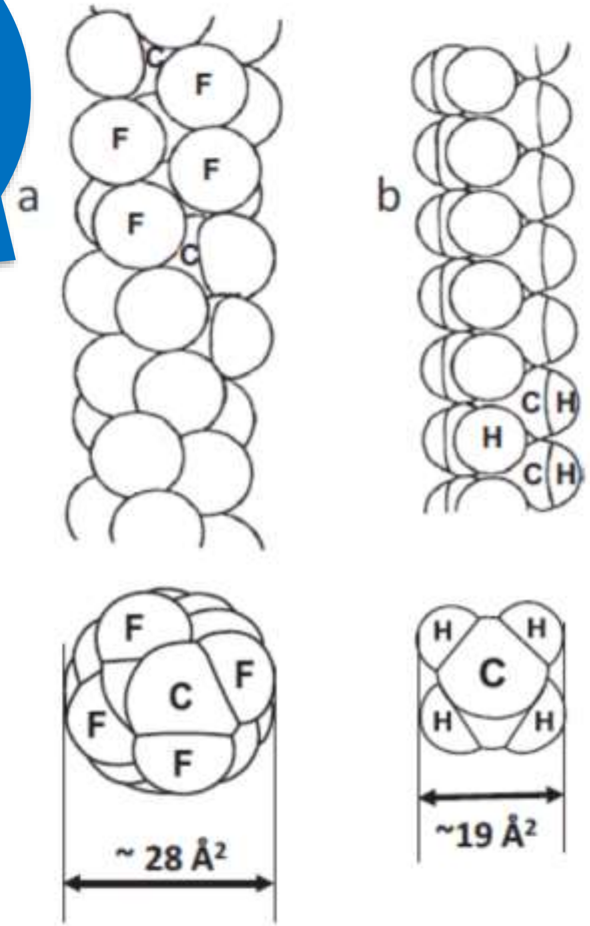
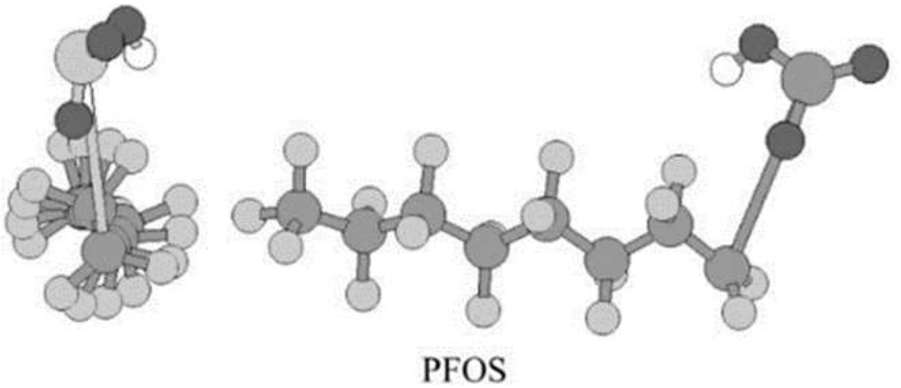
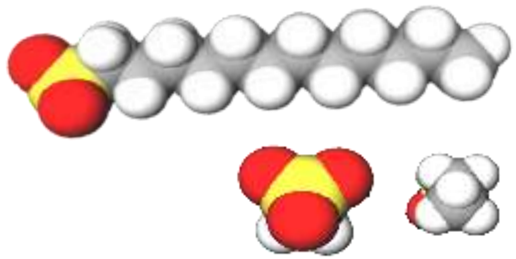




**Fig. 1.** Comparative hard-sphere model representations of *F*-alkyl and alkyl chains and their cross-sections. Adapted from Krafft and Riess (2009).

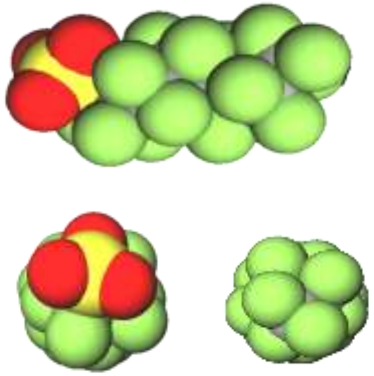
# Surfactant Tail Shape Determines Critical Packing Parameters



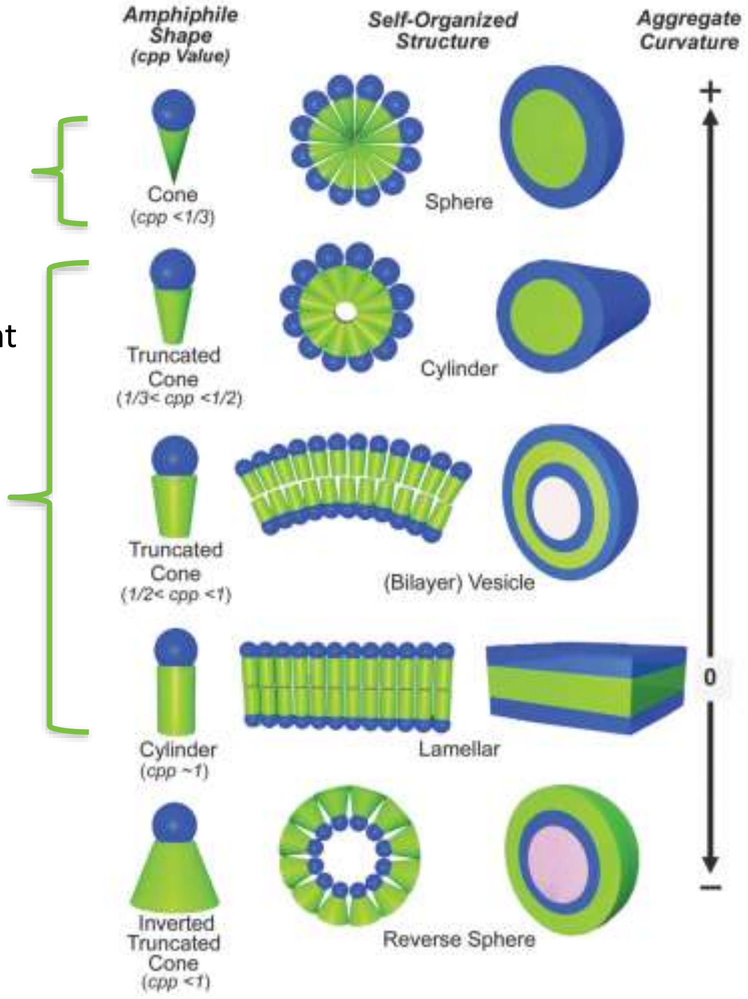

Erkoc et al., 2001 Journal of Molecular Structure (Theochem) 549 (2001) 289-293



SDS – C12 hydrocarbon surfactant



PFOS C8 fluorosurfactant




Ramanathan et al., Phys.Chem.Chem.Phys., 2013, 15, 10580

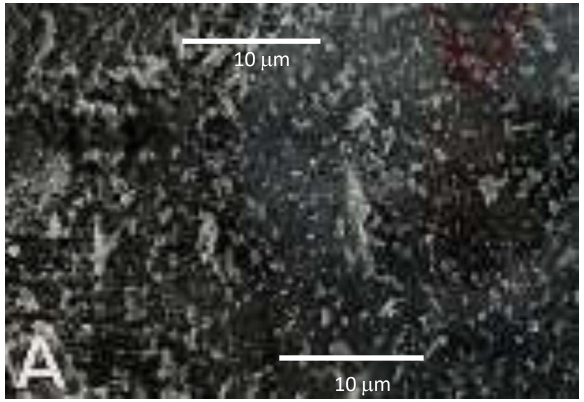
- Fluorine has high electronegativity which imparts a **rigid** helical fluorocarbon structure to perfluoroalkyl groups leading to the formation of **bulky, rigid, rod-shaped fluorosurfactant tails**
- The bulky, rigid, rod shape of the fluoroalkyl chains tends to decrease the curvature of the aggregates they form in solution
- This results in a strong tendency to form vesicles and lamellar phases rather than micelles

Gladysz, Curran, Horváth 2004 DOI:10.1002/3527603905

# Supramolecular Assemblies - PFAS retained on surfaces

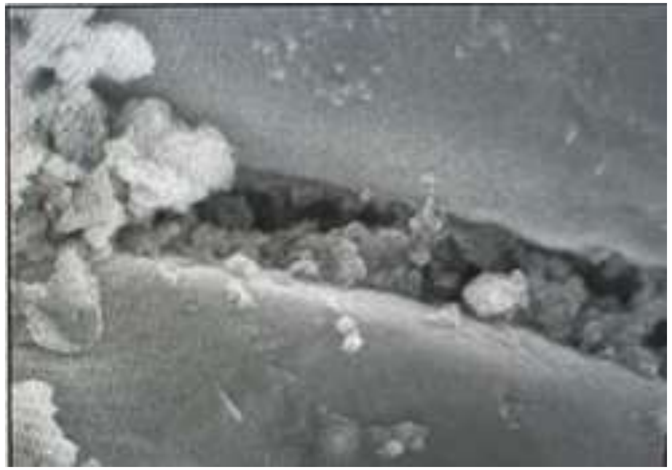
- Storage of AFFF within fire suppression systems causes a significant mass of PFAS to be retained on the inner surfaces of fire suppression system.
- Sorption of amphiphilic PFAS (fluorosurfactants) on surfaces often does not conform to conventional sorption theories.
- Formation of supramolecular assemblies is predicted and has been observe and provides a credible mechanism for PFAS retention within fire suppression systems.

***PFAS supramolecular assemblies detected on interior walls of fire suppression systems***



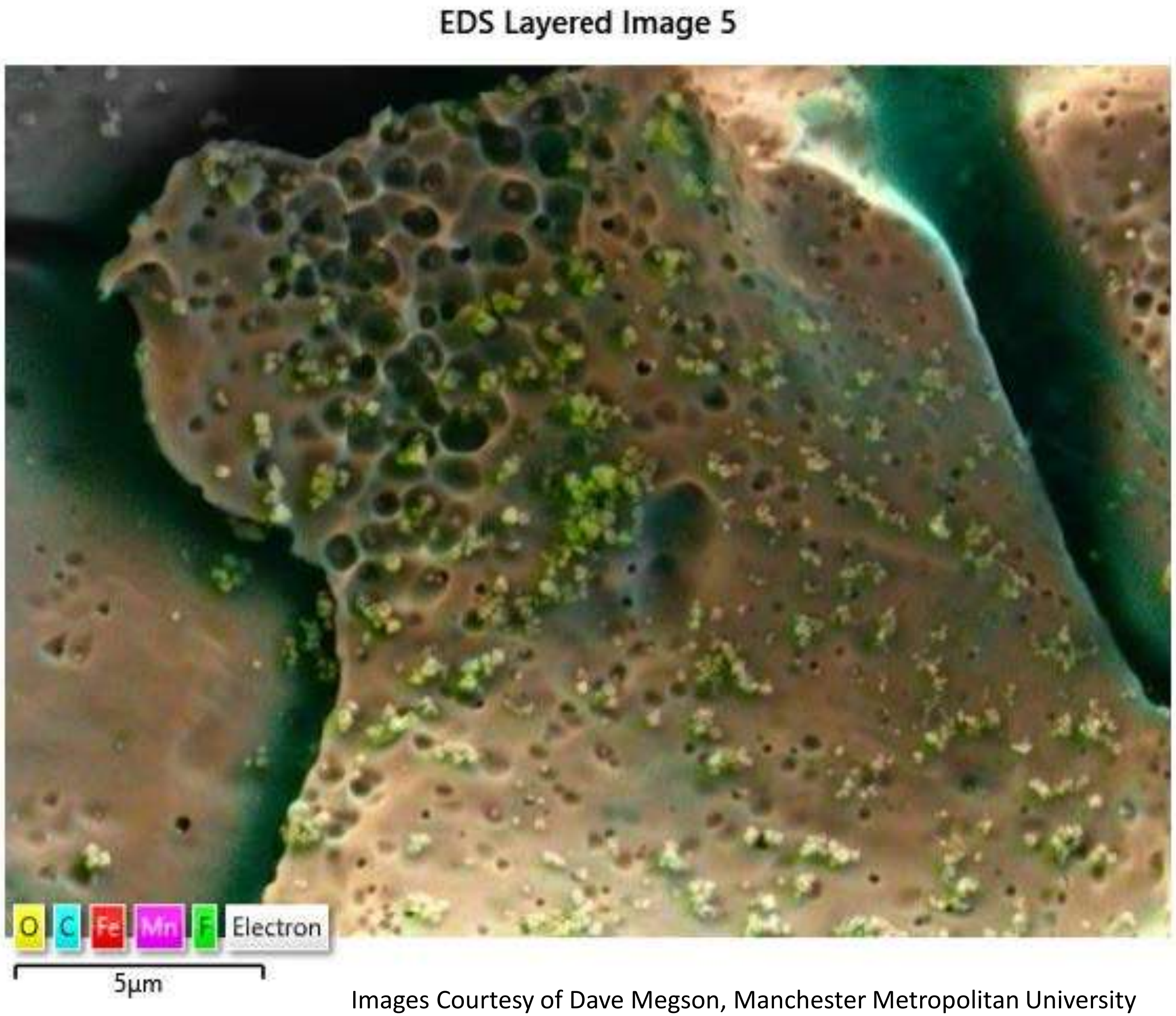

Pipe Interior


Pipe Exterior

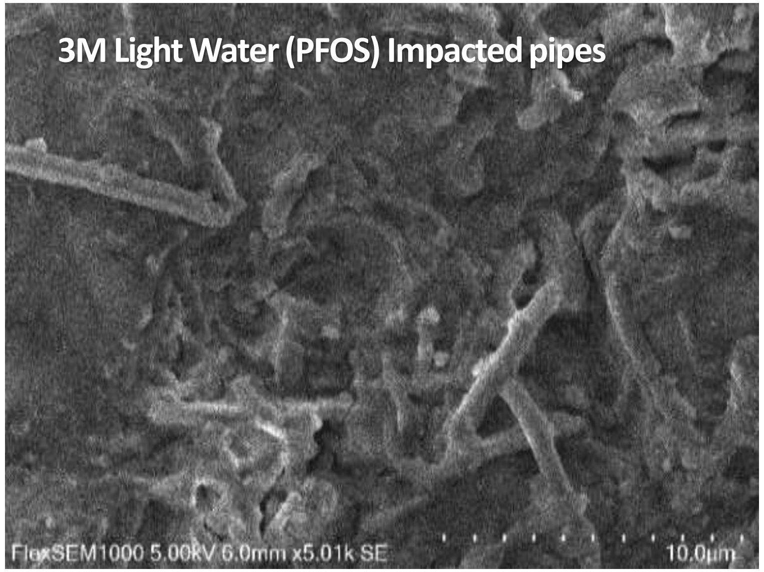


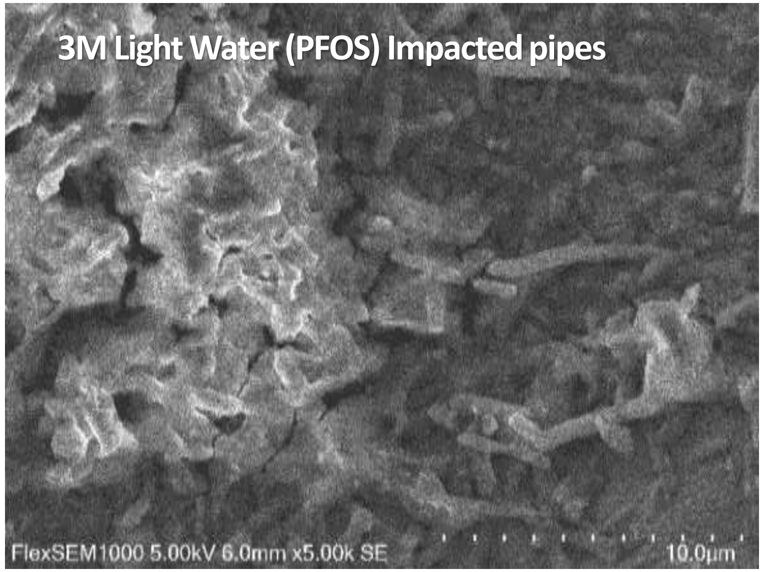
PFAS aggregates on the interior of fire suppression system pipework (Lang et al., Chemosphere, 308, (2), 2022)

# PFAS Retained on Surfaces




Images Courtesy of Dave Megson, Manchester Metropolitan University




Images Courtesy of Bjorn Bonnet, Swedish University of Agricultural Sciences (SLU)

# US DoD-Funded ESTCP Projects

## Sustainable Firefighting System Cleanout and Rinsate Treatment Using PerfluorAd

ER20-5370


POINT OF CONTACT

**Dung (Zoom) Nguyen**

**Principal Investigator**
CDM Smith
**Phone:** (425) 519-8325
nguyendd@cdmsmith.com


RELATED CONTENT

**Feature Story**

Environmentally Sustainable Methods Demonstrations to Clean Firefighting Delivery Systems

9/30/2020

### Objective

The overall technical objective of this demonstration is to provide a proven and sustainable solution to cleaning per- and polyfluoroalkyl substances (PFAS) out of firefighting delivery systems. The process will include the use of PerfluorAd as a functional precipitate (Cornelsen and Verena, 2018) to enhance the cleanout of the delivery system and reduce the volume of water required to reach a desired endpoint. The rinsate produced will be further treated with PerfluorAd as necessary to maximize PFAS removal from the rinsate. The small volume of concentrated filtrate will then be subject to further destruction or offsite disposal.

The specific technical objectives include the following:

- Demonstrate enhanced cleaning of a laboratory surrogate system with residual aqueous film forming foam (AFFF)
  - Reduce volume of waste requiring disposal or expensive destruction
  - Increase PFAS removal effectiveness from AFFF delivery systems
  - Determine optimal PerfluorAd dosage
  - Demonstrate effective rinsate treatment using PerfluorAd (with optional polishing)
- Demonstrate solution using a government-furnished Aircraft Rescue and Firefighting Vehicle
- Assess life cycle costs and sustainability
- Assuming all objectives are met, facilitate technology transition by developing a recommended general procedure for applying the technology, including any necessary treatability studies for different systems

## Remediation of AFFF-Impacted Fire Suppression Systems Using Conventional and Closed-Circuit Desalination Nanofiltration

ER20-5369


POINT OF CONTACT

**Christopher Bellona, Ph.D.**

**Principal Investigator**
Colorado School of Mines
**Phone:** (303) 273-3061
cbellona@mines.edu


PRODUCTS

**Webinar**

Environmentally Sustainable Methods to Remove AFFF from Firefighting Delivery Systems

3/23/2023

RELATED CONTENT

**Feature Story**

Environmentally Sustainable Methods Demonstrations to Clean Firefighting Delivery Systems

9/30/2020

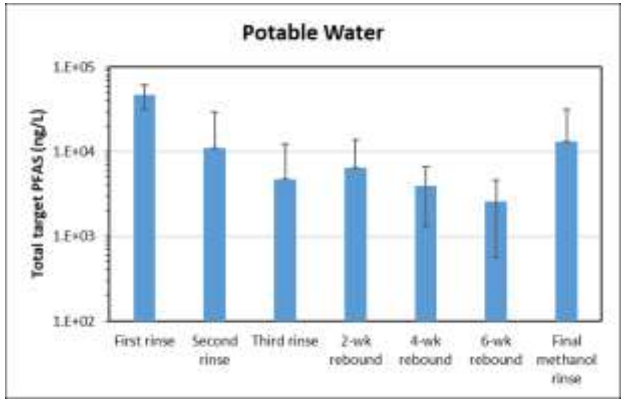
### Objective

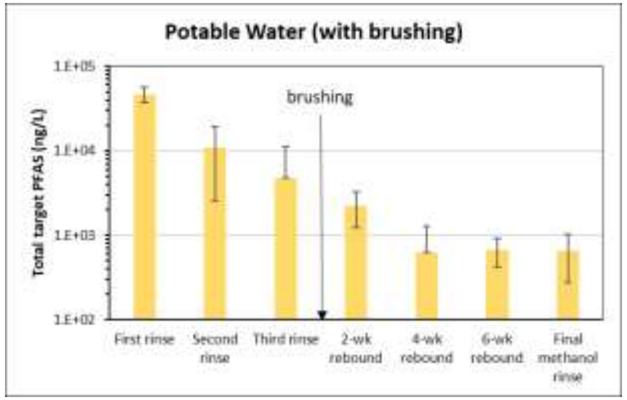
Research on soils and waters impacted by per- and polyfluoroalkyl substances (PFAS) over the past several years have produced important findings and highlighted many of the challenges associated with treatment and elimination of these compounds from the environment. Among these challenges are the large number of PFAS species in aqueous film forming foam (AFFF) (i.e., anionic, cationic, and zwitterionic compounds), many of which may strongly sorb to surfaces and are not readily rinsed with water. PFAS treatment is difficult and most treatment approaches generate a PFAS residual requiring further treatment and/or disposal that is costly. These challenges apply to the cleaning of firefighting delivery systems; thorough cleaning is critically important before new PFAS-free firefighting agents can be used in these systems.

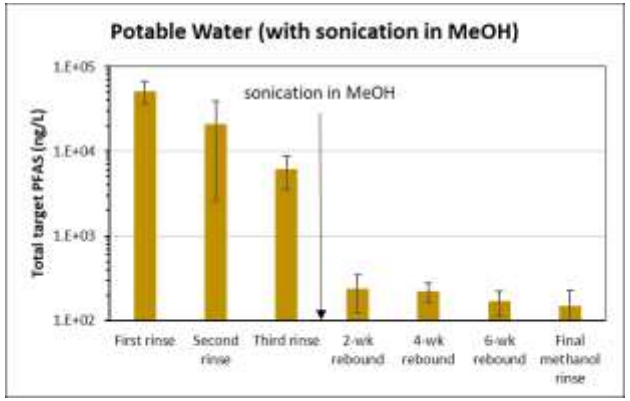

The first challenge is effectively removing AFFF residuals from the tanks and lines of the delivery systems. As simple water flushing will likely not be efficient for dissolving/desorbing all the AFFF constituents, the use of co-solvents may provide a promising solution. This demonstration will use water and a co-solvent to remove the residual AFFF constituents. The specific objectives of this project include:

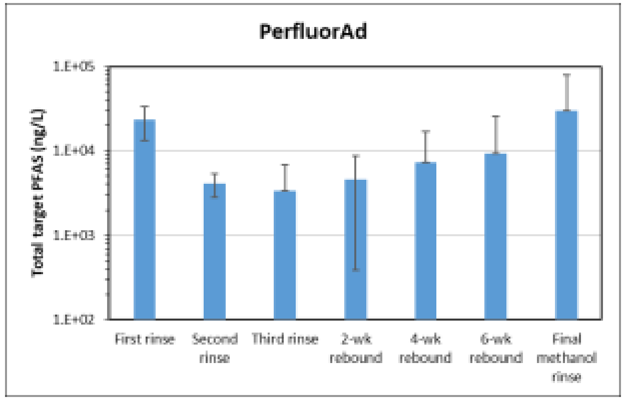
- Develop procedures for cleaning of equipment used to convey and transport AFFF,
- Optimize water–co-solvent ratios and number of cleaning cycles needed to remove AFFF from equipment and produce minimal volumes of cleaning wastewater,
- Optimize (maximize water recovery and solute rejection, and minimize energy demand) a nanofiltration process for separation of PFAS and co-solvent mixtures, and
- Assess overall system performance with respect to energy demand and cost, and provide recommendations for treatment system modifications.

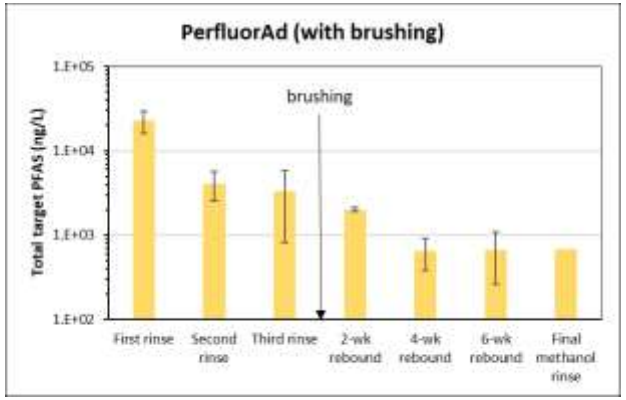
# PFAS Rebound Following Triple Water Rinse, PerfluorAd, and Methanol (Bench Study)

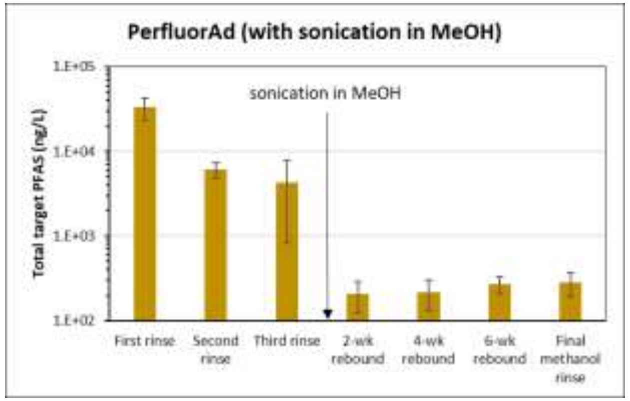


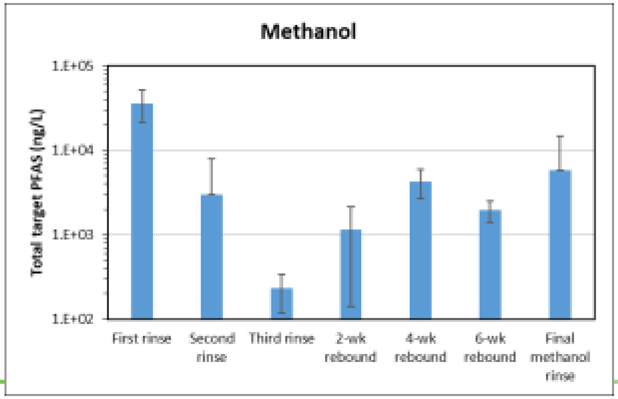



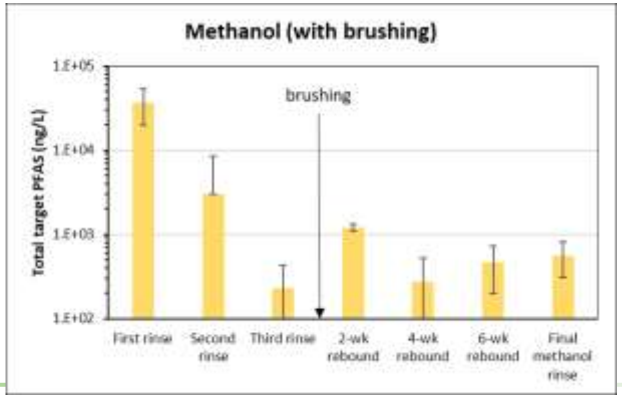



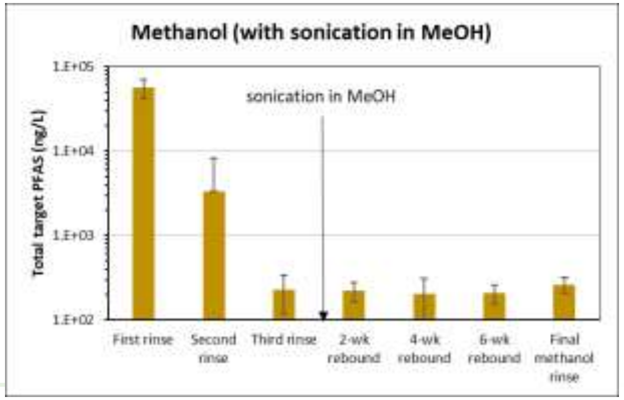



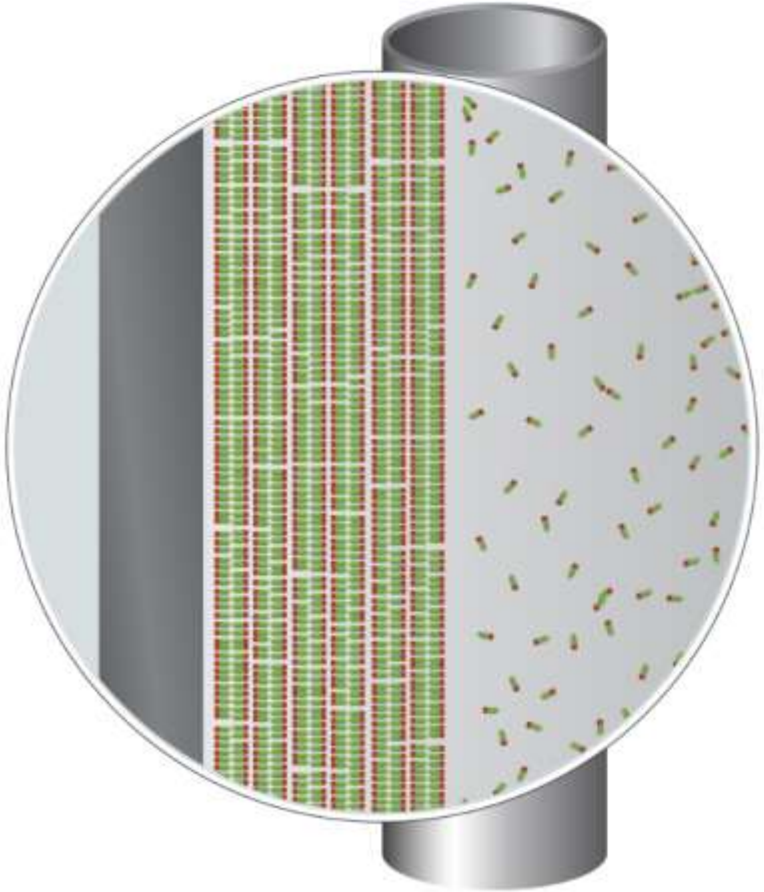



# Key Findings – ESTCP projects

- Target PFAS represents only a small fraction of PFAS-driven organic fluorine → TOP assay and AoF should be employed where possible
- Significant PFAS rebound observed in laboratory (batch + flow-thru) & field demos
  - Even with methanol
  - Proprietary reagent was no more effective than water
- Mild heating was effective in enhancing PFAS desorption
- Surface scrubbing and long-term (30 days) methanol sonication were the only means to minimize PFAS rebounds
- PFAS concentrations in rinse agents don't reflect the PFAS mass remaining on surfaces – expect long term rebound
- Membrane and proprietary reagents were very effective in treating the PFAS-laden rinsate solutions generated during firetruck cleanout



# Time of Flight-Elastic Recoil Detection (TOF-ERD)

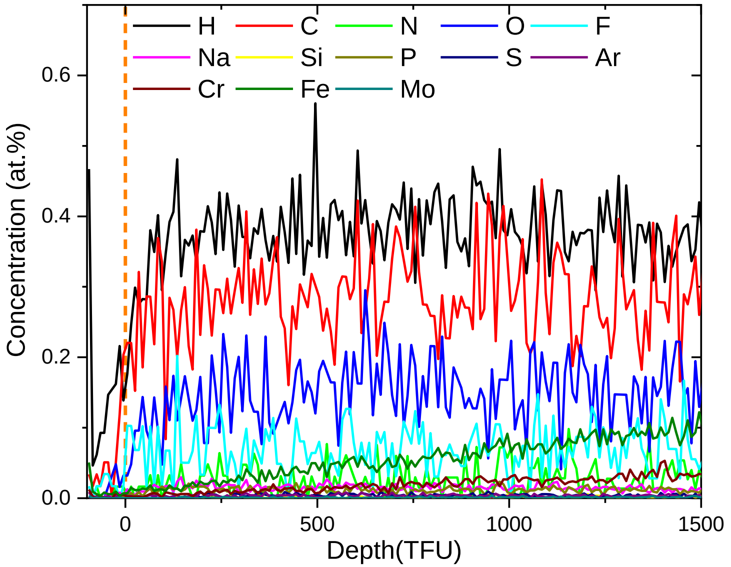

- Not a table-top instrument
- Staff (group) of highly skilled physicists and engineers to operate
- <5 machines in the world
- Expensive

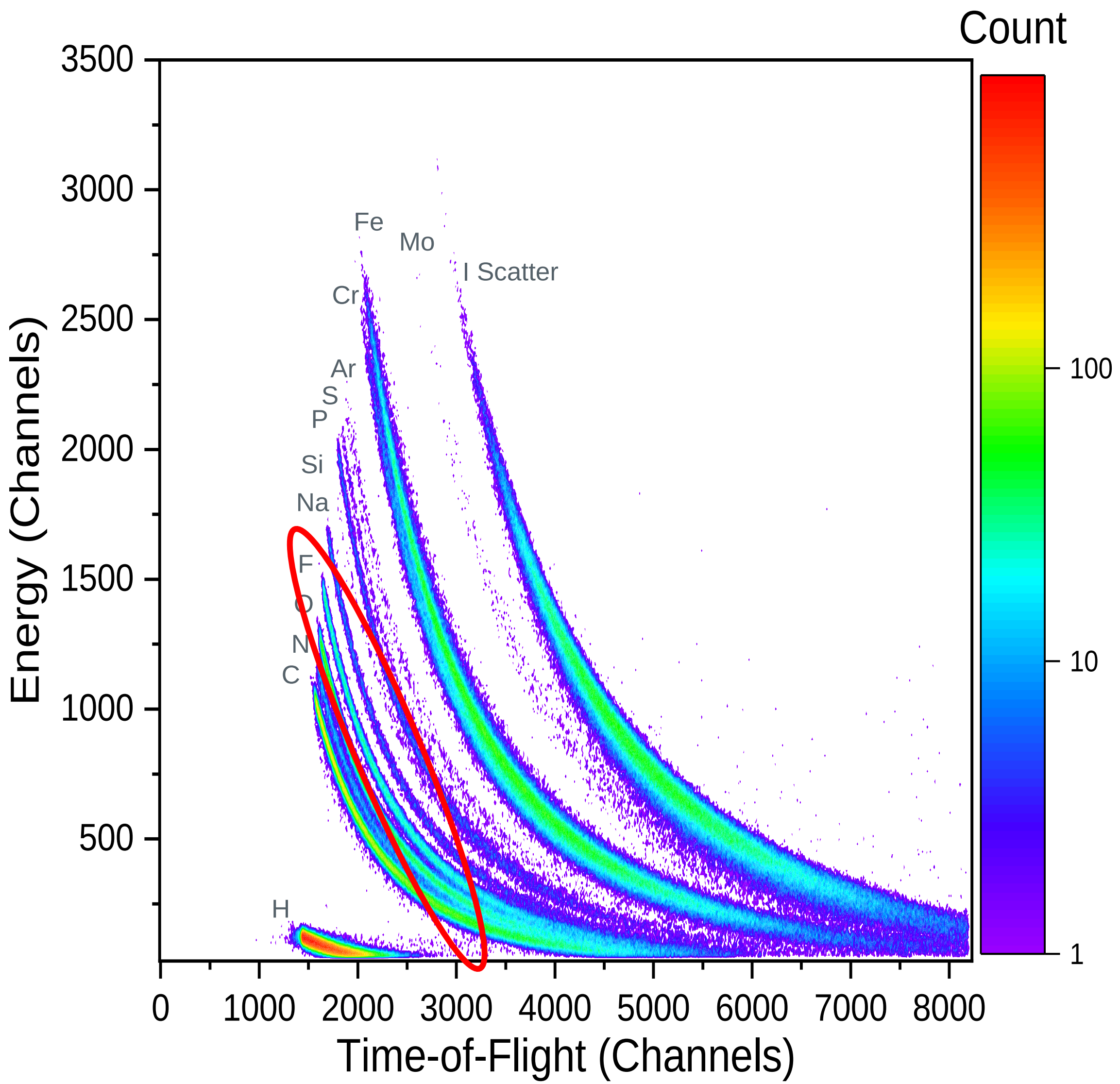
→ Not commercially available!

# TOF-ERD reveals surface F content of PFAS impacted pipe- before swab

Analysed to maximum depth (180 nm) possible to separate Cr and Fe

- Unswabbed surface: in top 120 nm around 8.1% F




Data courtesy of Eurofins

| Depth /TFU | Depth /nm | H /at.% | C /at.% | N /at.% | O /at.% | F /at.% | Na /at.% | Si /at.% | P /at.% | S /at.% | Ar /at.% | Cr /at.% | Fe /at.% | Mo /at.% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0-1000 | 0-120 | 27.8 | 29.3 | 2.98 | 15.3 | 8.1 | 1.41 | 0.2 | 1.29 | 0.337 | 0.325 | 2.87 | 9.9 | 0.159 |

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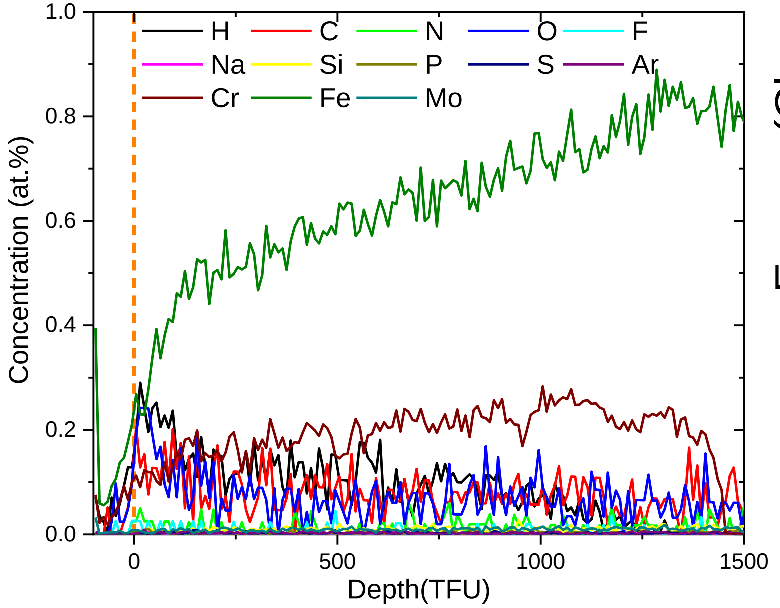
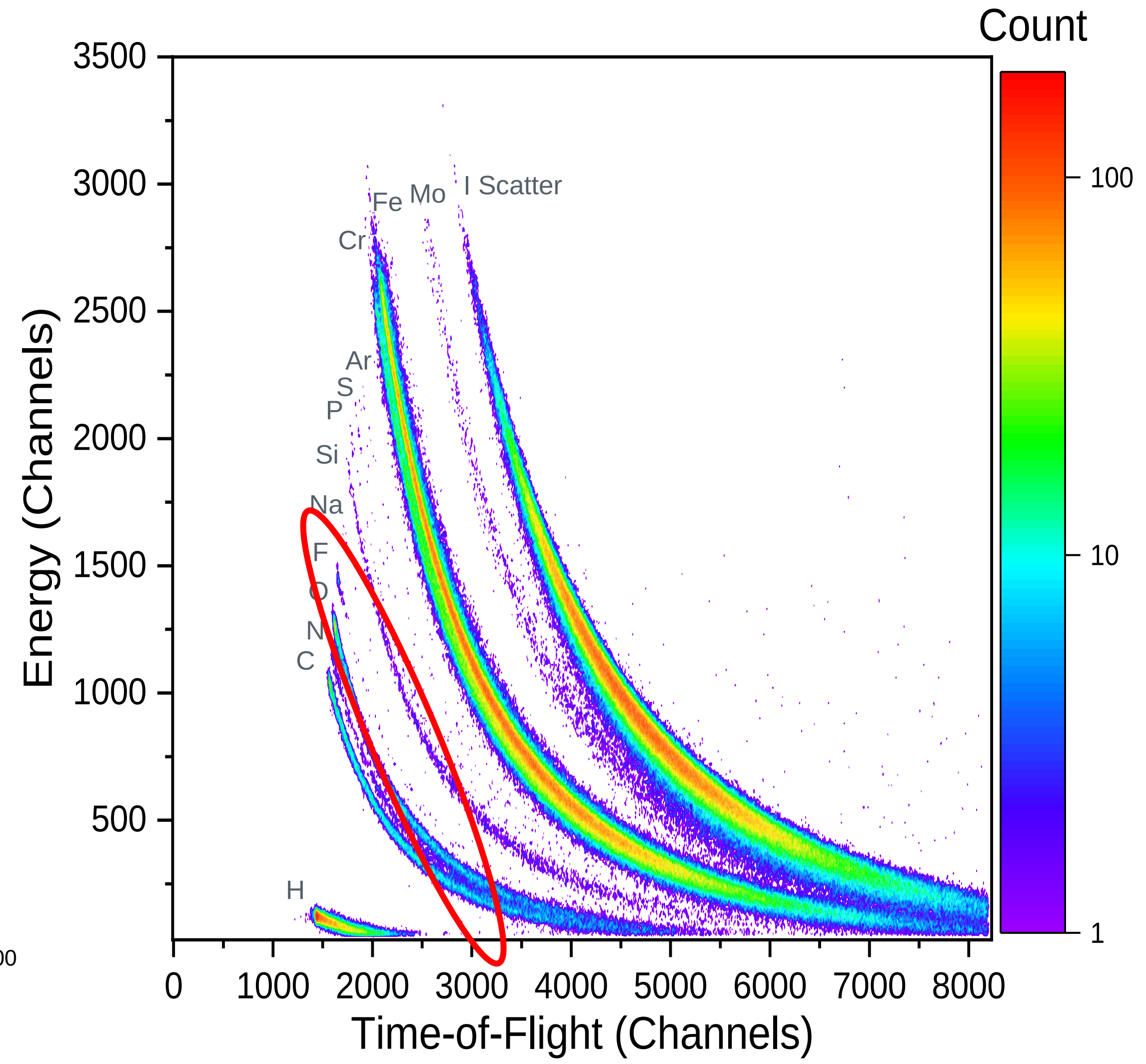
# TOF-ERD reveals surface F content following swab – after swab

Compare with swabbed surface:

- In same depth, now only 0.42% F – 95% decrease over unswabbed
- F present to maximum depth 22nm




Data courtesy of Eurofins

| Depth /TFU | Depth /nm | H /at.% | C /at.% | N /at.% | O /at.% | F /at.% | Na /at.% | Si /at.% | P /at.% | S /at.% | Ar /at.% | Cr /at.% | Fe /at.% | Mo /at.% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0-1000 | 0-120 | 11.2 | 7.9 | 1.14 | 7.3 | 0.42 | 0.13 | 0.82 | 0.27 | 0.22 | 0.23 | 17.1 | 52.5 | 0.79 |

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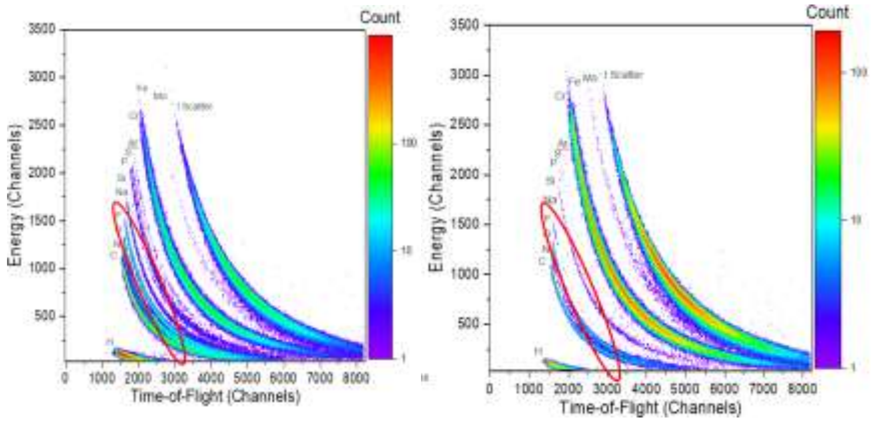
# Proving Decontamination

- Liquid phase data on PFAS concentrations in rinsing solutions not reflective of PFAS remaining on walls of fire suppression systems
- Multi-swab method developed and validated using:
  - Alcohol with pH adjustment
  - Cotton swabs
  - Specific swab time and pressure
- PFAS extracted from swabs at high-low pH and TOP assay applied to extract
- Evaluated using full elemental surface testing (to 200 nm) using Time of Flight – Elastic Recoil Detection (TOF-ERD)
- Swabs removed >95% surface Fluorine
- Swabs with non-target analysis (TOP assay/AOF) applied to quantitatively assess PFAS on surfaces




| Fe /at.% | F /at.% |
|---|---|
| 9.9 | 8.1 |

| Fe /at.% | F /at.% |
|---|---|
| 52.5 | 0.42 |

# Decontamination of PFAS contaminated fire suppression system pipes – Treatment verification with time-of-flight elastic recoil detection analysis (ToF-ERD)

Björn Bonnet[1], Matthew Sharpe[2], Ian Ross[3], Geraint Williams[4] and Lutz Ahrens[1]

[1]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden

[2]Surrey Ion Beam Centre, University of Surrey, Guildford GU2 7XH, UK

[3]CDM Smith, 2300 Clayton Rd #950, Concord 94520, USA

[4]ALS Laboratories, Units 7-8 Hawarden Business Park, Deeside, Flintshire Ch5 3US, UK

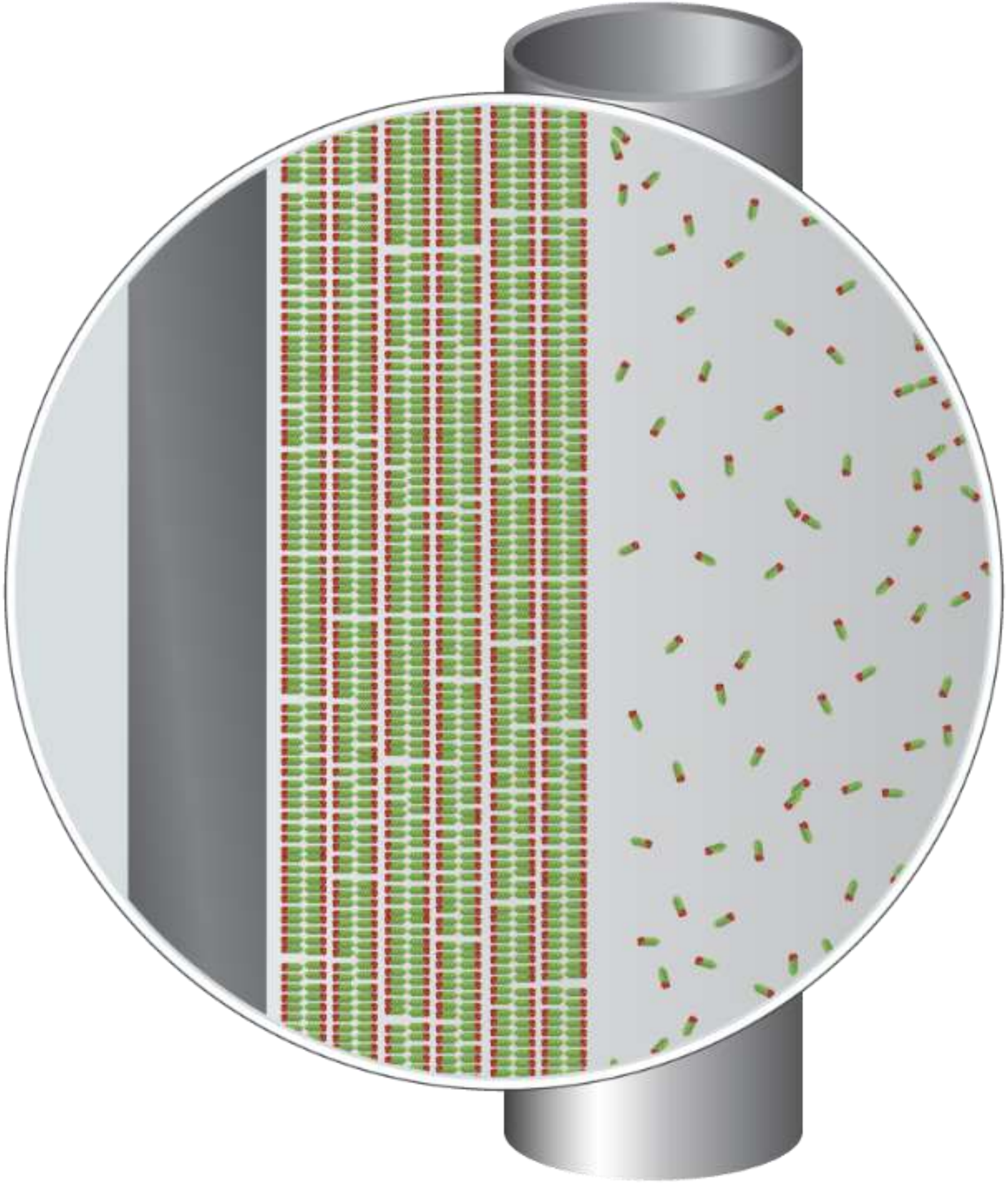
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860665 and No.824096

# Implications of Research

- Examining PFAS concentrations in cleaning solutions does not reflect concentrations of PFAS remaining on surfaces
- Surface PFAS analysis is required to demonstrate that decontamination has been successful
- Swab methods can assess PFAS mass on surfaces
- Most effective decontamination:
  - Solvents (Glycols)
  - Heat
  - Attrition (i.e. pressure washing, sonication, rubbing)
- Commercial vendors of PFAS decontamination technologies have generally not examined PFAS on surfaces to demonstrate effectiveness

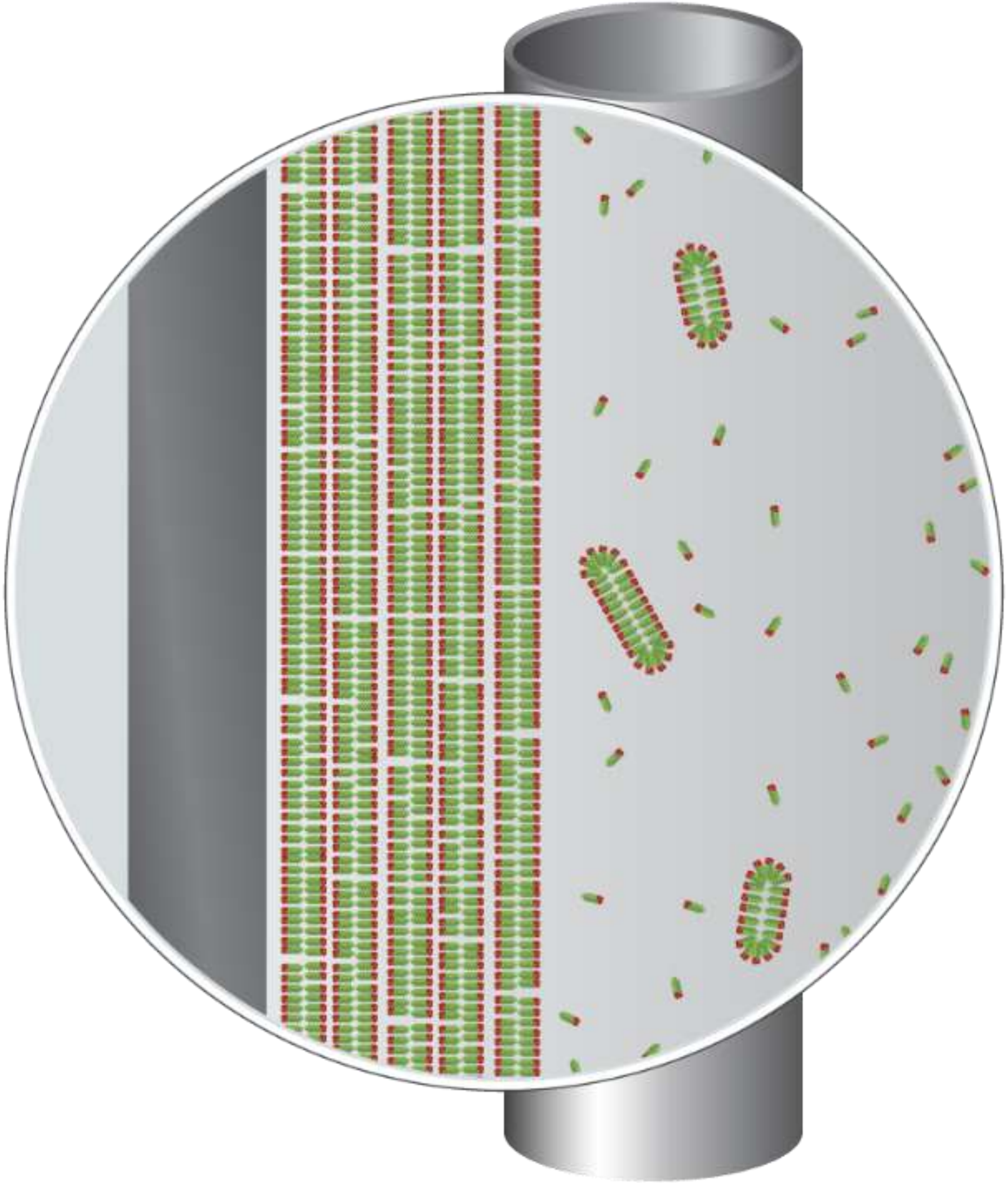
# Fire Suppression System Wall

Layers of PFAS adhere to the pipe wall



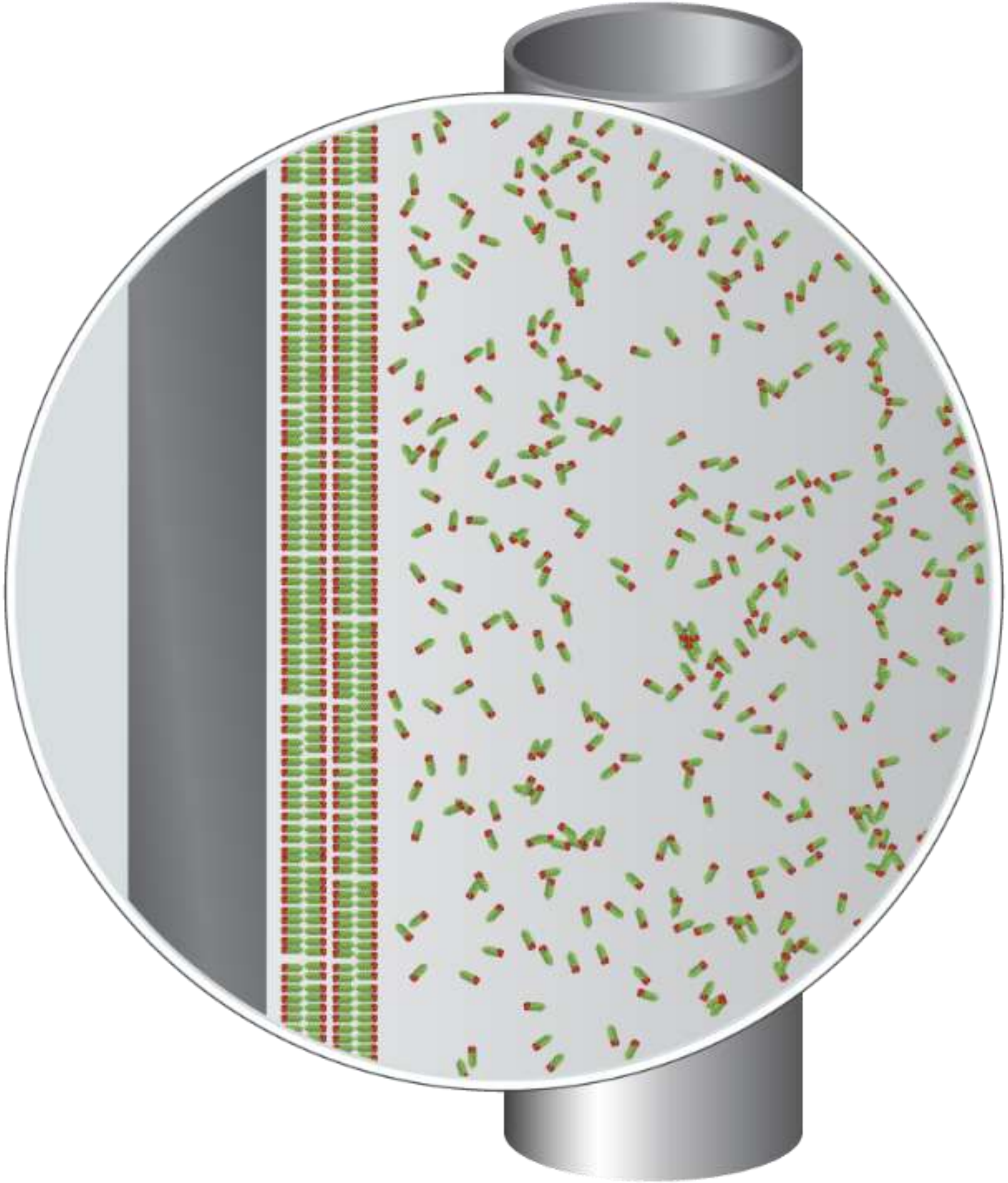
# Water Soak

Following a cold or hot water soak, layers remain adhered to the pipe wall and some come away into solution



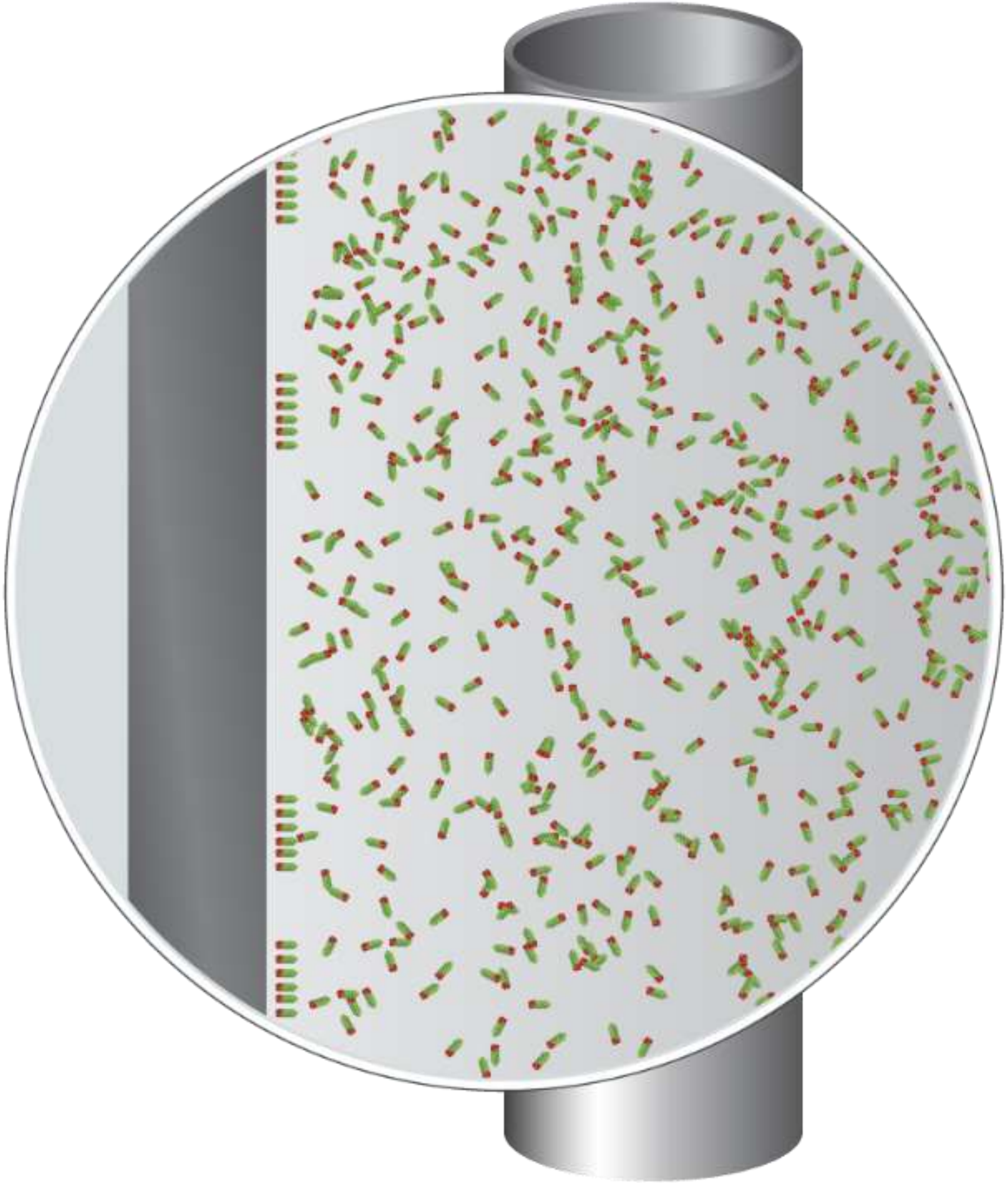
# Hot Glycol Soak

Significantly more PFAS removed using hot glycol soak, but residual layers remain attached to surfaces

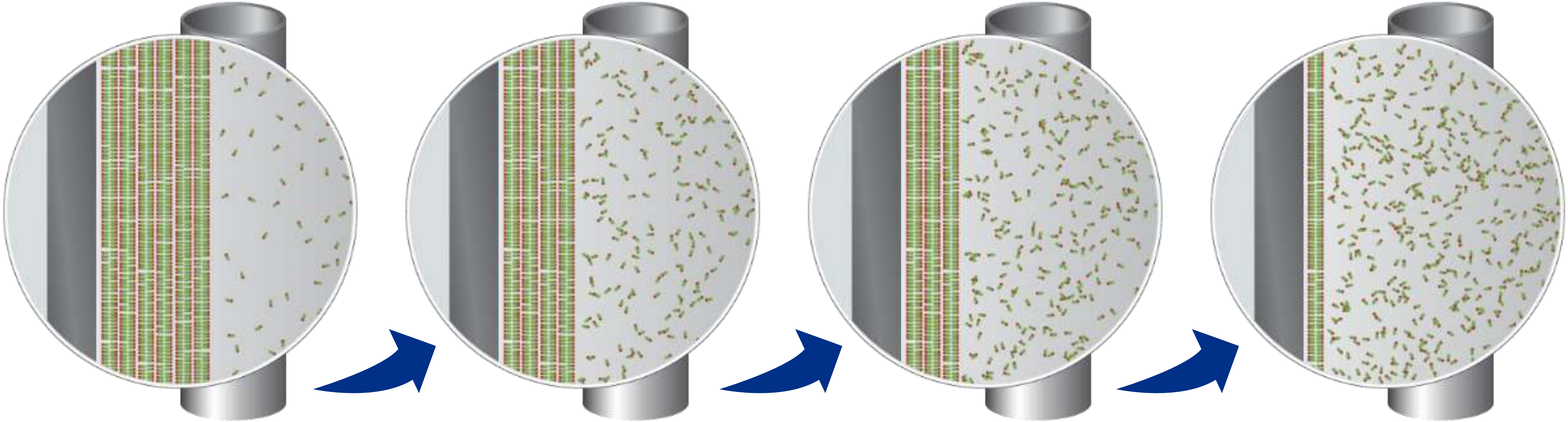


# Hot Glycols With Attrition

In a similar process to the swab sampling, hot glycols with continued attrition are expected to remove the vast majority of  PFAS from surfaces



# Projected Rebound of PFAS into F3 Foams



3 months | 1 year | 2 years | 3 years

# Fluorinated Foam Concentrate Disposal

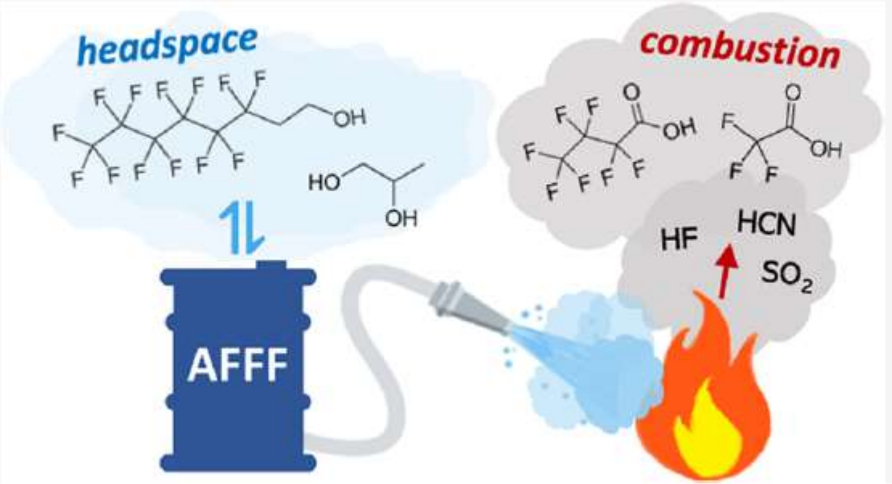
- 1,000 to 1,200 ºC required to completely degrade PFOS but residence time and turbulence are also critical parameters
- Lower temperature treatment of PFAS can produce toxic intermediates (e.g. perfluoroisobutylene)
- Incineration is not proven effective for liquid wastes, as potential for steam expansion i.e. AFFF concentrates
- Incineration of AFFF concentrates at 760 ºC / 820 ºC reported to generate emissions of PFCAs (C2-C8) with mg $m^{-3}$ of trifluoracetic acid (TFA) formed
- Potent greenhouse gases ($CF_4$, $C_2F_6$ etc.) form and require 1,400 $^{o}C$ for destruction –above incineration temperatures
- Comprehensive analysis of all gaseous emissions required for any PFAS thermal treatment
- Incinerator ash pits source of PFAS to groundwater
- Potential treatment solutions:
  - Cement kilns - Australia
  - Supercritical water oxidation (SCWO) available -Revive, MI
  - Hydrothermal Alkaline Treatment (HALT), in development by Aquagga, WA


DISPOSAL OF AFFF, FFFP AND FP:
CHALLENGES AND EMERGING SOLUTIONS
Ian Ross Ph.D. Arcadis, Leeds, West Yorkshire, UK

Monitoring&Remediation Advances in Remediation Solution

Understanding and Managing the Potential By-Products of PFAS Destruction

by John Horst, Jeffrey McDonough, Ian Ross, and Erika Houtz




Mattila et al, 2024 DOI: 10.1021/acs.est.3c09255

https://joiff.com/wp-content/uploads/2020/11/Catalyst-Q4-FINAL.pdf

https://earthjustice.org/sites/default/files/files/filed_complaint_-_pfas_incineration_suit.pdf

https://toxnet.nlm.ni.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7708

https://www.epa.gov/sites/production/files/2019-09/documents/technical_brief_pfas_incineration_ioaa_approved_final_july_2019.pdf

# CDM Smith's Total Solution

**Fire Engineering**
- Hazard Identification
- Risk Assessment
- Alternative Protection Analysis
- Cost Benefit Analysis
- Foam Selection
- System Design
- Accreditation of Modifications (UL, FM, NFPA etc.)


**Fire Service Contracting (Siron)**
- Foam Removal/Recharge
- Equipment Removal/Replacement
- System modifications
- Decontamination
- Proportioner Calibration
- Commissioning
- Acceptance testing

**Environmental Engineering**
- Transition Planning
- PFAS Management Strategy
- Decontamination Planning
- Verification Sampling
- Regulatory Approvals
- Environmental Management Plans
- Waste Characterization and Disposal
- Site Investigation/Remediation


CL:AIRE technical bulletin

TB 22

An overview of the uses of PFAS to assist with identification of sites of concern

1. INTRODUCTION

2. FIREFIGHTING FOAMS


2 Fluorine Free Foams Transitioning Guide

Ian Ross
Tetra Tech, United Kingdom

Peter Storch
Arcadis, Australia

Ted Schaefer
Energy and Resources Institute, Charles Darwin University, Australia

Niall Ramsden
ENRg Consultants, Monks Risborough, United Kingdom

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2


How clean is clean?

by Ian Ross

Pragmatism During Foam Transition

'Dark Matter' Fluorosurfactants as PFAA-Precursors

56 | The Catalyst


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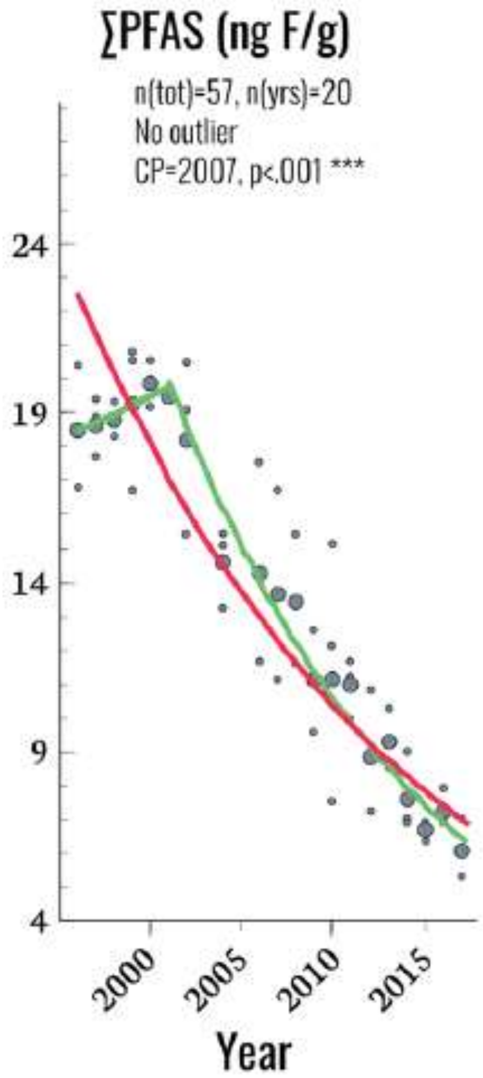
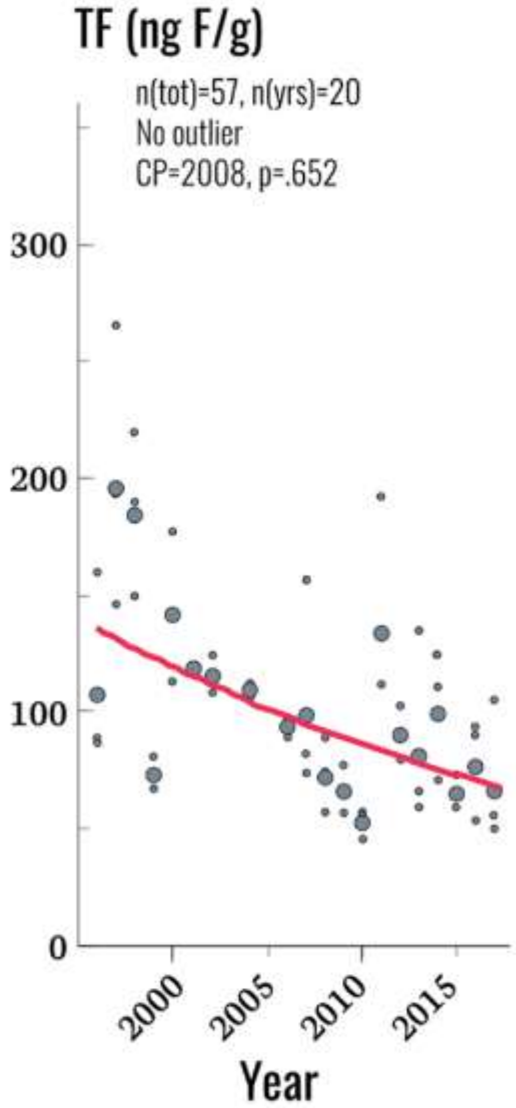
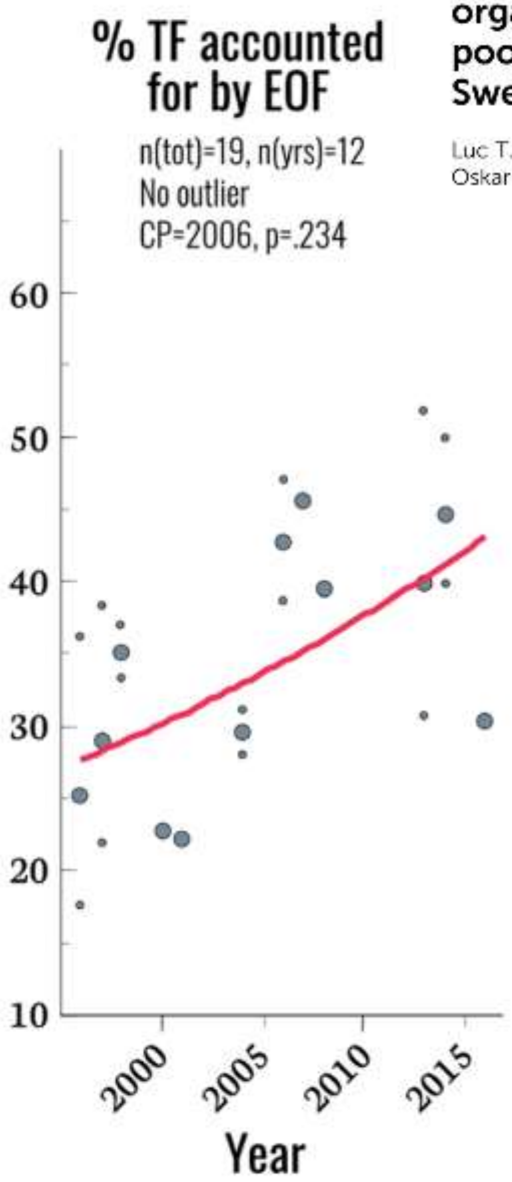
## Standard analytes e.g. PFOS, PFOA




## Total Fluorine




## Unknown PFAS




**Temporal trends of suspect- and target-per/polyfluoroalkyl substances (PFAS), extractable organic fluorine (EOF) and total fluorine (TF) in pooled serum from first-time mothers in Uppsala, Sweden, 1996–2017†**

Luc T. Miaz,[*a] Merle M. Plassmann,[a] Irina Gyllenhammar,[b] Anders Bignert,[c] Oskar Sandblom,[a] Sanna Lignell,[b] Anders Glynn[d] and Jonathan P. Benskin[*a]

## Regulatory concerns with increasing use of alternative PFAS

pooled serum from first-time mothers

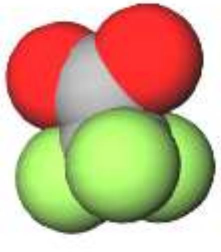
Miaz et al., 2020

# Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People

Guomao Zheng*, Stephanie M. Eick, and Amina Salamova*

Refrigerant
HFO R-1234yf

Atmospheric oxidation



TFA

Table 2. [illegible] rt-, and Long-Chain PFAAs and PFAA Precursors Detected in Paired Dust (ng/g), Drinking Water (ng/L), Serum (ng/mL), and Urine[a] Samples (ng/mL), and Contribution (Contr., %) of Each PFAA or Precursor to the Total Concentrations

| | dust | | | drinking water | | | serum | | | urine[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DF | Med (Min-Max) | Contr. | DF | Med (Min-Max) | Contr. | DF | Med (Min-Max) | Contr. | DF | Med (Min-Max) | Contr. |
| Ultrashort-Chain | | | | | | | | | | | | |
| TFA (C2) | 84 | 220 (ND,[b] 1400) | 75 | 95 | 79 (ND, 210) | 84 | 74 | 6.0 (ND, 77) | 57 | 31 | ND (ND, 290) | |
| PFPrA (C3) | 99 | 26 (ND, 200) | 9.1 | 95 | 6.9 (ND, 19) | 7.4 | 99 | 1.0 (0.14, 2.9) | 9.5 | 56 | 0.051 (ND, 6.8) | 1.4 |
| PFPrS (C3) | 3.7 | ND (ND, 53) | | 64 | 0.10 (ND, 0.40) | 0.11 | 4.9 | ND (ND, 0.013) | | 1.2 | ND (ND, 0.85) | |
| **∑ ultrashort-chain** | **100** | **290 (37, 1400)** | **85** | **100** | **86 (9.3, 220)** | **92** | **100** | **6.9 (2.3, 78)** | **66** | **100** | **0.13 (0.02, 290)** | **2.0** |
| Short-Chain | | | | | | | | | | | | |
| PFBA (C4) | 94 | 14 (ND, 410) | 5.0 | 98 | 2.4 (ND, 7.8) | 2.6 | 84 | 0.19 (ND, 2.5) | 1.8 | 60 | 0.33 (ND, 26) | 9.2 |
| PFBS (C4) | 54 | 0.40 (ND, 210) | 0.14 | 86 | 1.3 (ND, 0.16) | 1.4 | 85 | 0.05 (ND, 0.38) | 0.47 | 3.7 | ND (ND, 0.028) | |
| PFPeA (C5) | 10 | ND (ND, 120) | | 70 | 2.5 (ND, 7.7) | 2.6 | 25 | ND (ND, 2.2) | | 88 | 3.2 (ND, 34) | 89 |
| PFPeS (C5) | 22 | ND (ND, 15) | | 59 | 0.035 (ND, 22) | 0.038 | 69 | 0.0076 (ND, 0.034) | 0.071 | 23 | ND (ND, 0.022) | |
| PFHxA (C6) | 89 | 4.3 (ND, 290) | 1.5 | 85 | 0.42 (ND, 6.1) | 0.45 | 83 | 0.034 (ND, 0.10) | 0.32 | 2.5 | ND (ND, 0.09) | |
| PFHpA (C7) | 81 | 1.7 (ND, 460) | 0.60 | 83 | 0.15 (ND, 1.2) | 0.16 | 79 | 0.016 (ND, 0.10) | 0.15 | 23 | ND (ND, 0.0093) | |
| **∑ short-chain** | **100** | **27 (1.4, 1100)** | **7.3** | **100** | **8.5 (0.12, 38)** | **7.2** | **100** | **0.41 (0.058, 3.6)** | **3.0** | **100** | **4.6 (0.021, 41)** | **98** |
| Long-Chain | | | | | | | | | | | | |
| PFHxS (C6) | 73 | 2.7 (ND, 2200) | 0.93 | 88 | 0.17 (ND, 1.1) | 0.18 | 99 | 0.78 (ND, 5.4) | 7.3 | 0 | | |
| PFHpS (C7) | 23 | ND (ND, 12) | | 15 | ND (ND, 0.071) | | 96 | 0.099 (ND, 0.73) | 0.93 | 0 | | |
| PFOA (C8) | 98 | 5.9 (ND, 1900) | 2.1 | 93 | 0.46 (ND, 3.6) | 0.49 | 99 | 0.63 (ND, 4.9) | 5.9 | 14 | ND (ND, 0.051) | |
| PFOS (C8) | 95 | 10 (ND, 1100) | 3.5 | 84 | 0.22 (ND, 1.6) | 0.23 | 99 | 1.5 (ND, 33) | 14 | 7.4 | ND (ND, 0.019) | |
| PFECHS (C8) | 2.5 | ND (ND, 7.5) | | 44 | ND (ND, 0.67) | | 85 | 0.011 (ND, 0.079) | 0.11 | 0 | | |
| PFNA (C9) | 64 | 0.65 (ND, 27) | 0.23 | 65 | 0.11 (ND, 0.47) | 0.11 | 98 | 0.21 (ND, 1.2) | 2.0 | 30 | ND (ND, 8.9) | |
| PFNS (C9) | 7.4 | ND (ND, 1.4) | | 2.5 | ND (ND, 0.015) | | 1.2 | ND (ND, 0.0031) | | 0 | | |
| PFDA (C10) | 70 | 1.8 (ND, 39) | 0.62 | 49 | ND (ND, 0.28) | | 93 | 0.051 (ND, 0.21) | 0.48 | 0 | | |
| PFDS (C10) | 36 | ND (ND, 100) | | 0 | | | 7.4 | ND (ND, 0.019) | | 0 | | |
| PFUdA (C11) | 58 | 0.30 (ND, 15) | 0.11 | 15 | ND (ND, 0.093) | | 79 | 0.037 (ND, 0.16) | 0.35 | 0 | | |
| PFDoA (C12) | 70 | 1.1 (ND, 22) | 0.38 | 25 | ND (ND, 0.14) | | 42 | ND (ND, 0.034) | | 0 | | |
| PFTrDA (C13) | 57 | 0.25 (ND, 16) | 0.089 | 14 | ND (ND, 0.13) | | 37 | ND (ND, 0.079) | | 0 | | |
| PFTeDA (C14) | 58 | 0.52 (ND, 13) | 0.18 | 26 | ND (ND, 0.21) | | 36 | ND (ND, 0.043) | | 0 | | |
| PFHxDA (C16) | 42 | ND (ND, 8.6) | | 44 | ND (ND, 1.0) | | 70 | 0.023 (ND, 0.13) | 0.21 | 0 | | |
| **∑ long-chain** | **100** | **33 (0.45, 3300)** | **8.1** | **98** | **1.4 (ND, 5.8)** | **1.0** | **99** | **3.8 (ND, 35)** | **31** | **49** | **ND (ND, 8.9)** | |
| **∑ PFAAs** | **100** | **360 (11, 4000)** | **100** | **100** | **100 (12, 250)** | **100** | **100** | **13 (3.5, 81)** | **100** | **100** | **8.0 (0.041, 300)** | **100** |

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# PFAS Publications