Development of a New Surface Testing Method to Comprehensively Assess PFAS on Surfaces

Vision, Initiatives and Paradigm Shift

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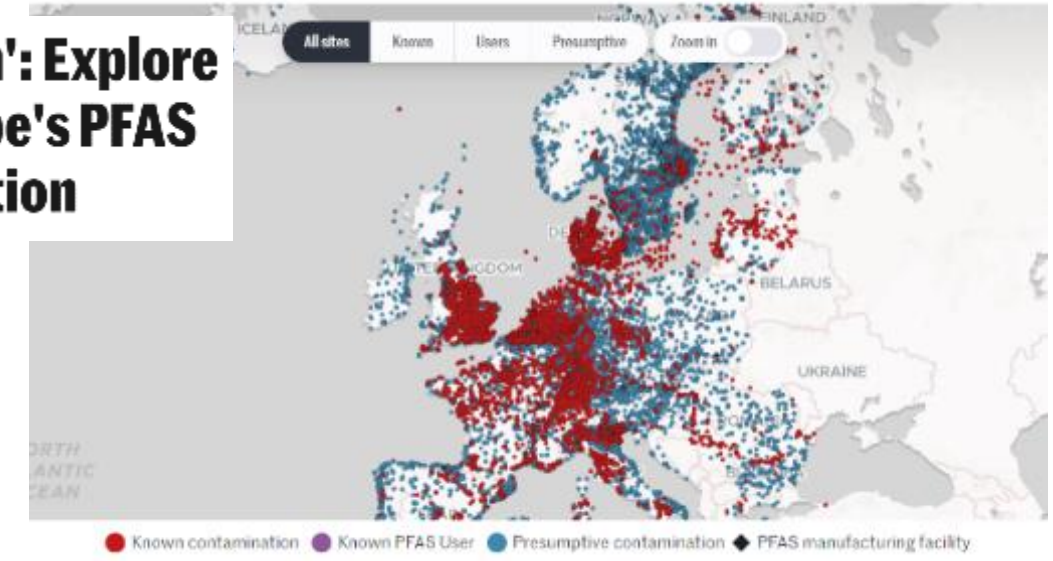
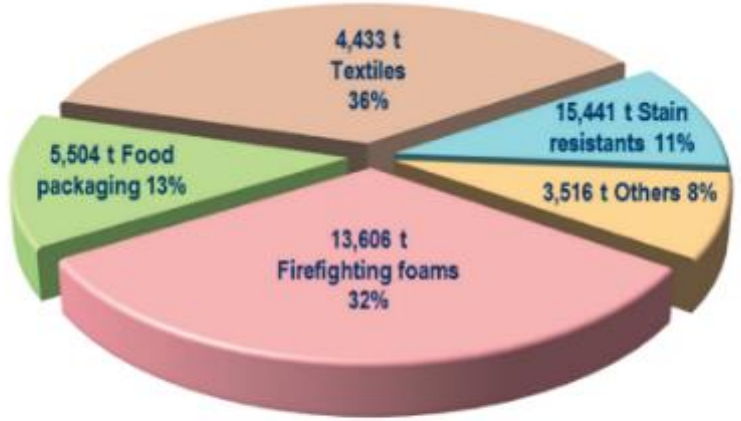
Overview

- Firefighting Foam History
- Decontamination Challenges- How to measure PFAS on surfaces
- PFAS chemistry and precursor transformation
- Which PFAS are in firefighting foams?
- Why do PFAS stick to surfaces?
- Proving decontamination
- Conclusions



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

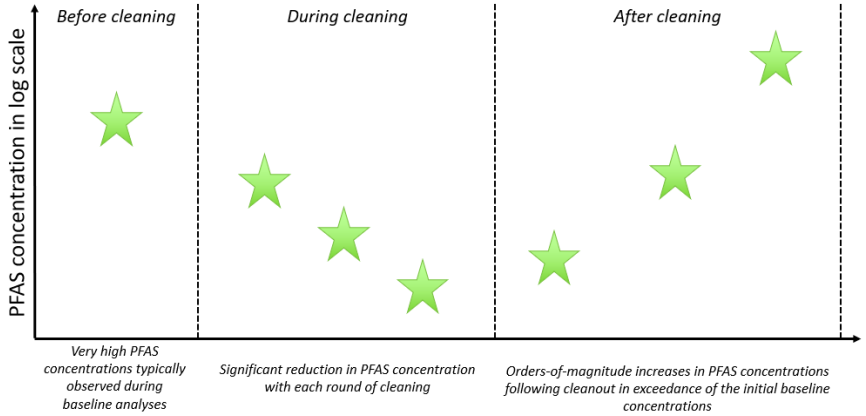


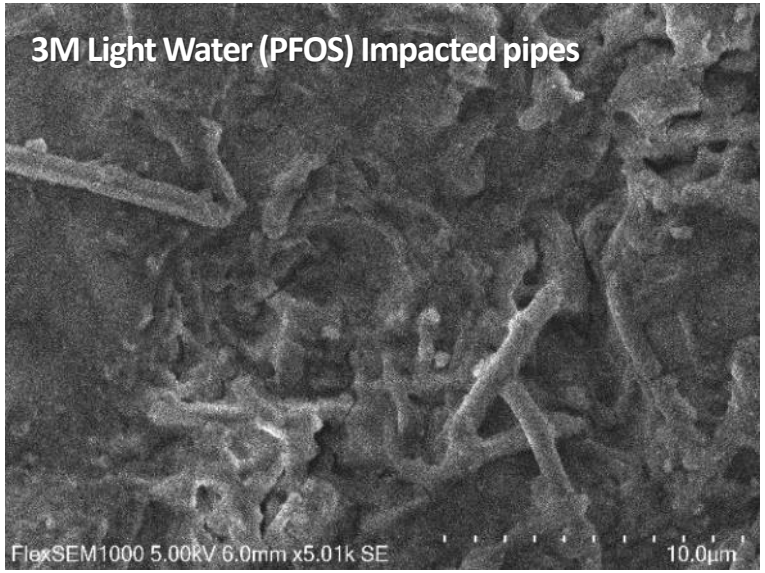
Projected fluorotelomer production in 2019 of 42,500 tonnes.
After Global Market Insights, 2016. Projected compound annual growth rate of 12.5% from 26,500 tonnes in 2015.

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

PFAS Decontamination

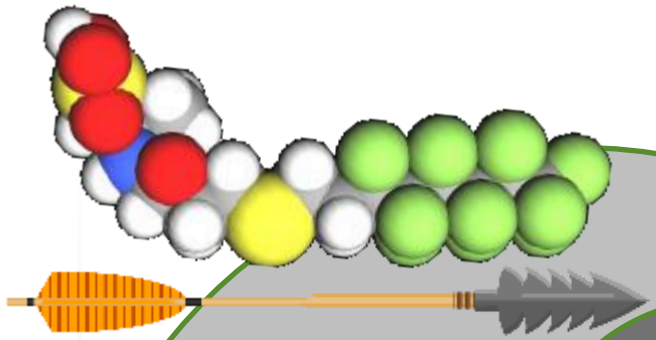
- Proprietary PFAS ‘cleaning agents’ litter the decontamination market
- Claims of success generally don’t include any scientific evidence to show PFAS have been removed from surfaces
- Data showing PFAS in the liquid phase is erroneously used to claim that surfaces have been decontaminated
- A method to quantitatively assess PFAS mass on surfaces is required to determine whether decontamination has been successful





Per- & Polyfluoroalkyl Substances

>7 Million PFAS – OECD Definition



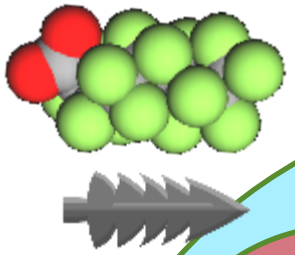
Poly-

Polyfluoroalkyl
- precursors

- Sulphonamides
- Polyfluoroalkyl ethers
- Fluorotelomers
- Side Chain Fluoropolymers

Transformation

Biological treatment or chemical oxidants promote transformation



Per-

Perfluoroalkyl

- **Long Chain**
  PFOS PFDA
  PFOA PFNA
  PFHxS PFTDA
- **Short Chain**
  PFBS PFPeA
  PBA PFPeS
  PFHxA PFHpA
- **Ethers**
  GenX
  F53B
  EE-NH_4
- **Cyclics**
  PFECHS
- **Ultra Short Chains**
  TFA PFPrA

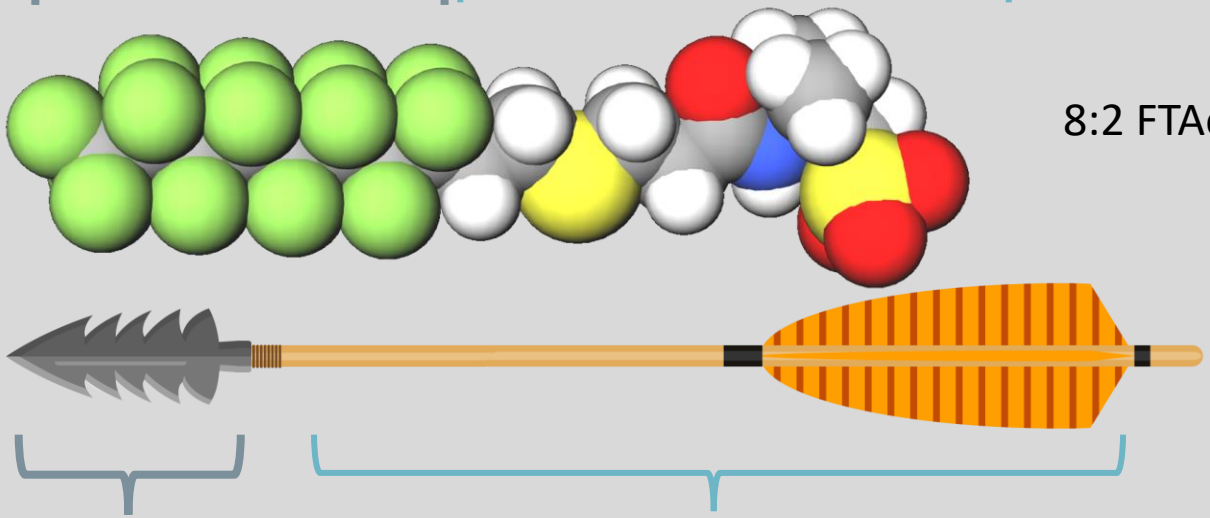
Per- & Polyfluoroalkyl Substances

Poly-

(Precursors)

Persistent perfluorinated

Non-fluorinated - Biologically/Chemically removed



8:2 FTAoS

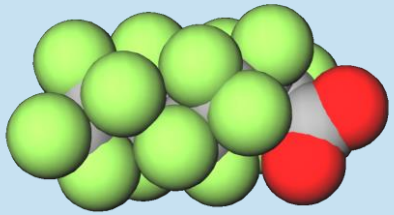
Stone arrowhead, like perfluorinated section of molecule, persists forever

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

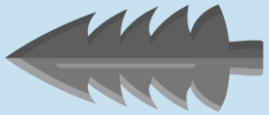
Biotransformation / Abiotic Oxidation

Per-

(Terminal products)



PFOA



Stone arrowhead

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

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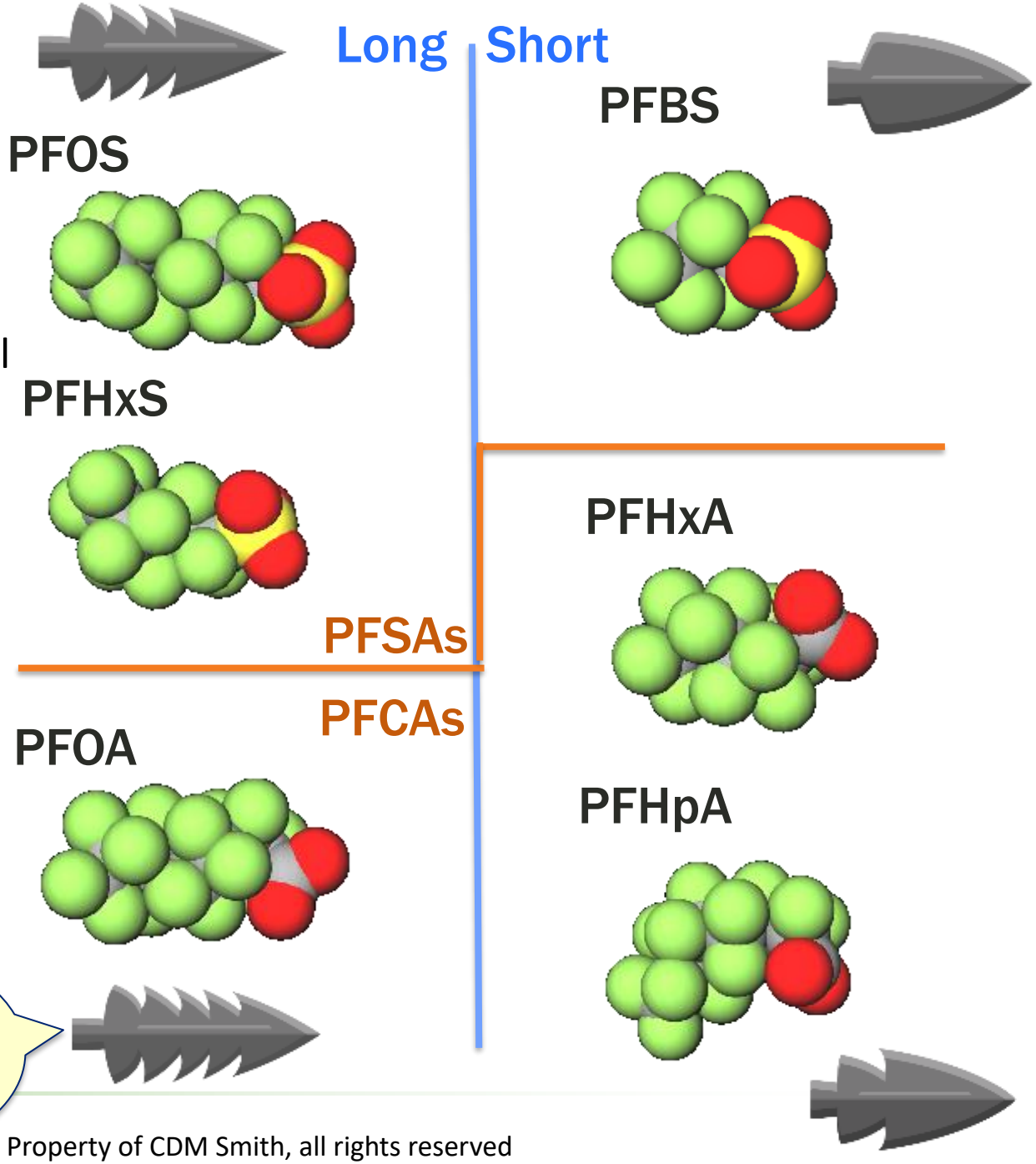
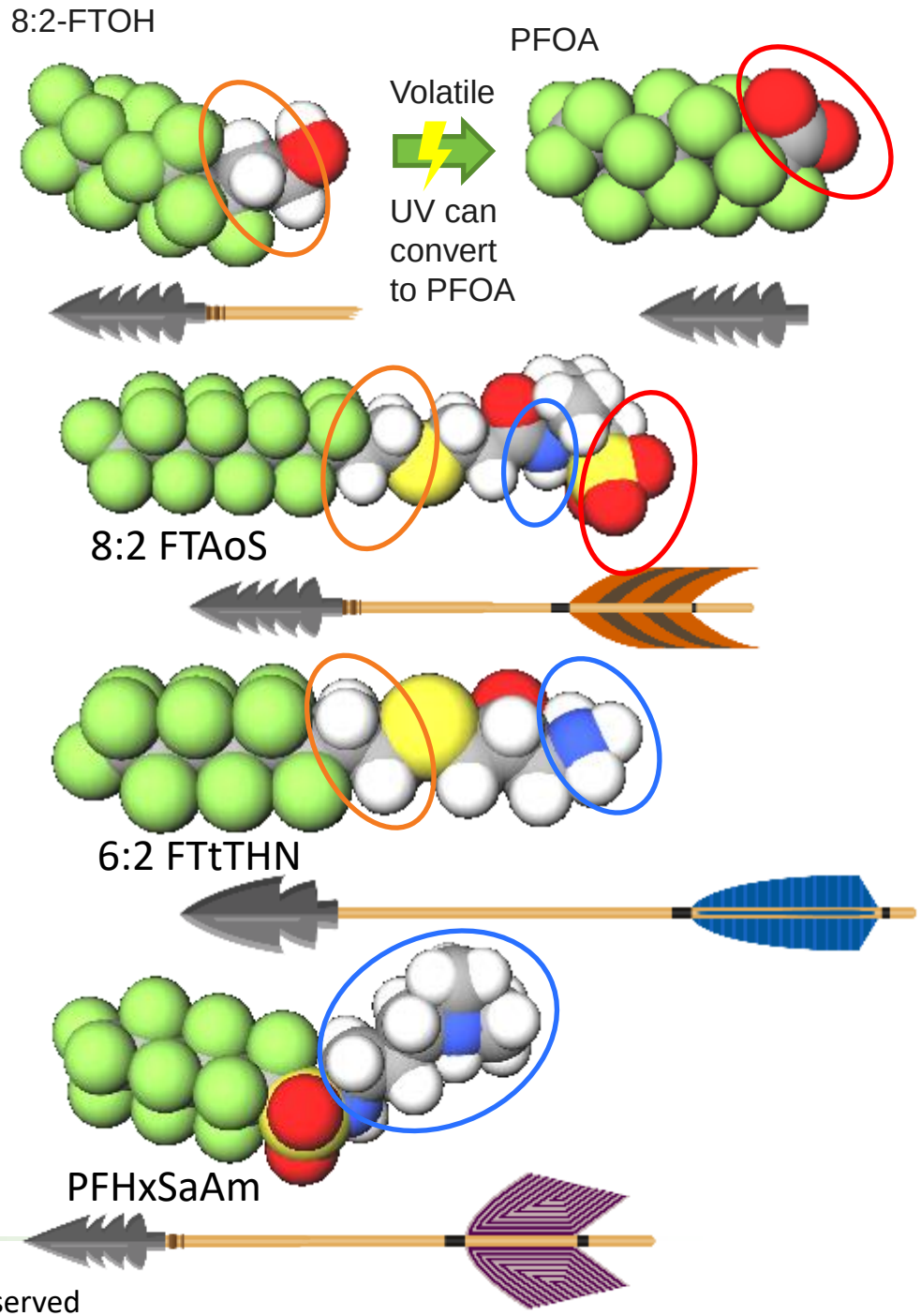
Perfluoroalkyl Acids (PFAAs)

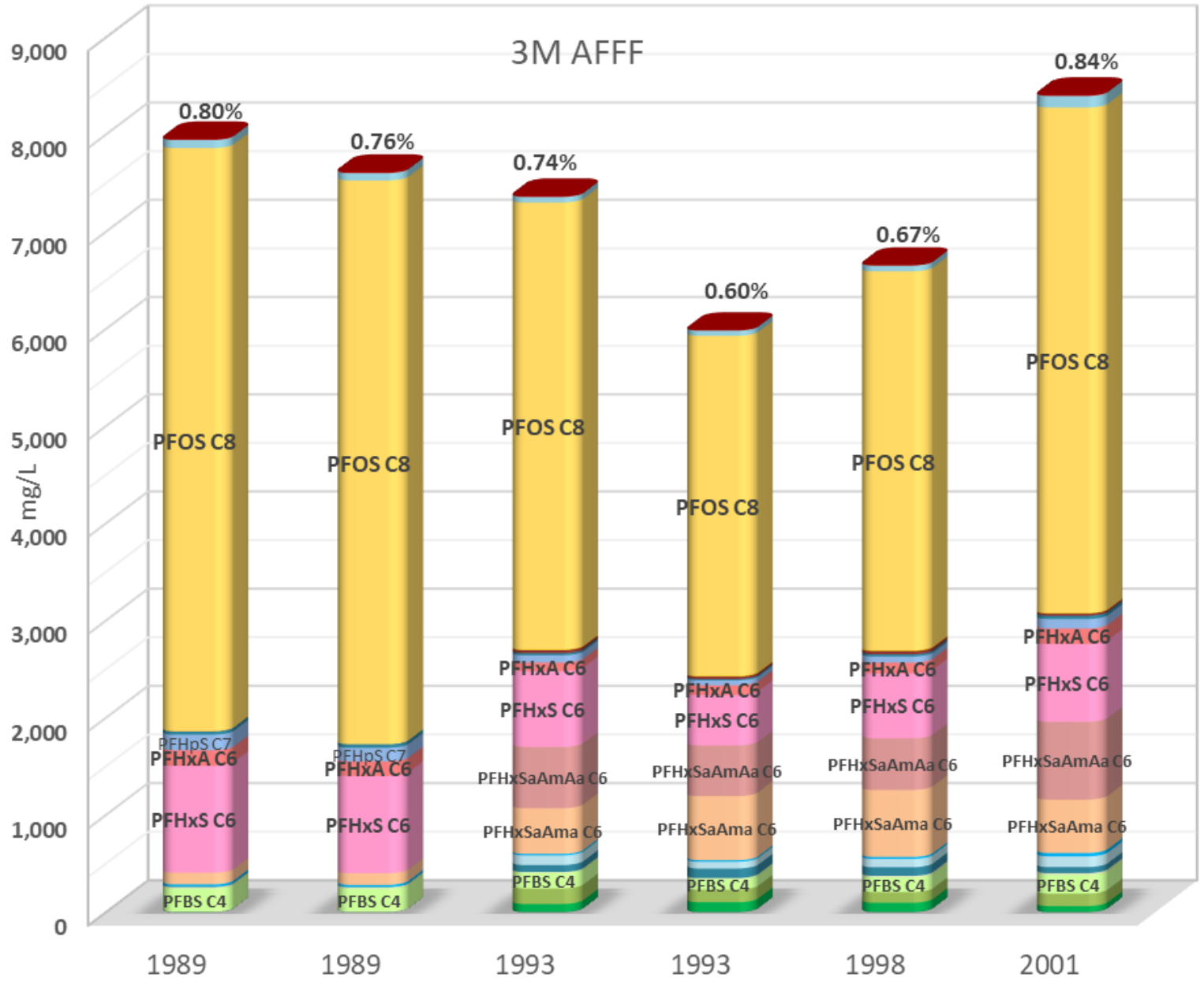
- Were termed “chemical rocks” with stone arrowhead analogy –extreme persistence
- Previously called Perfluorinated Compounds (PFCs)
- Terminal transformation products of polyfluoroalkyl substances
- Long chain vs short chain defined by bioaccumulation potential
- Generally, C1 – C20+ PFAAs
- Lipo- and 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)

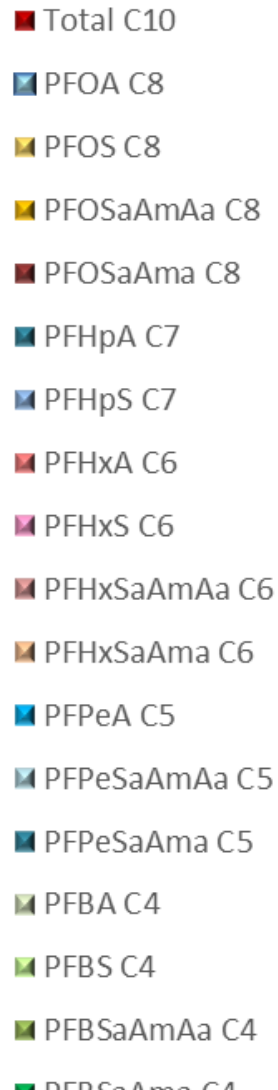


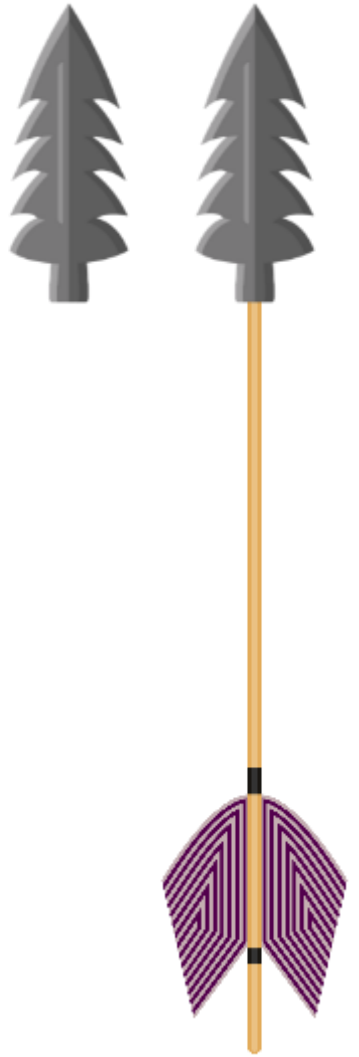
Polyfluoroalkyl Substances –PFAA Precursors

- 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



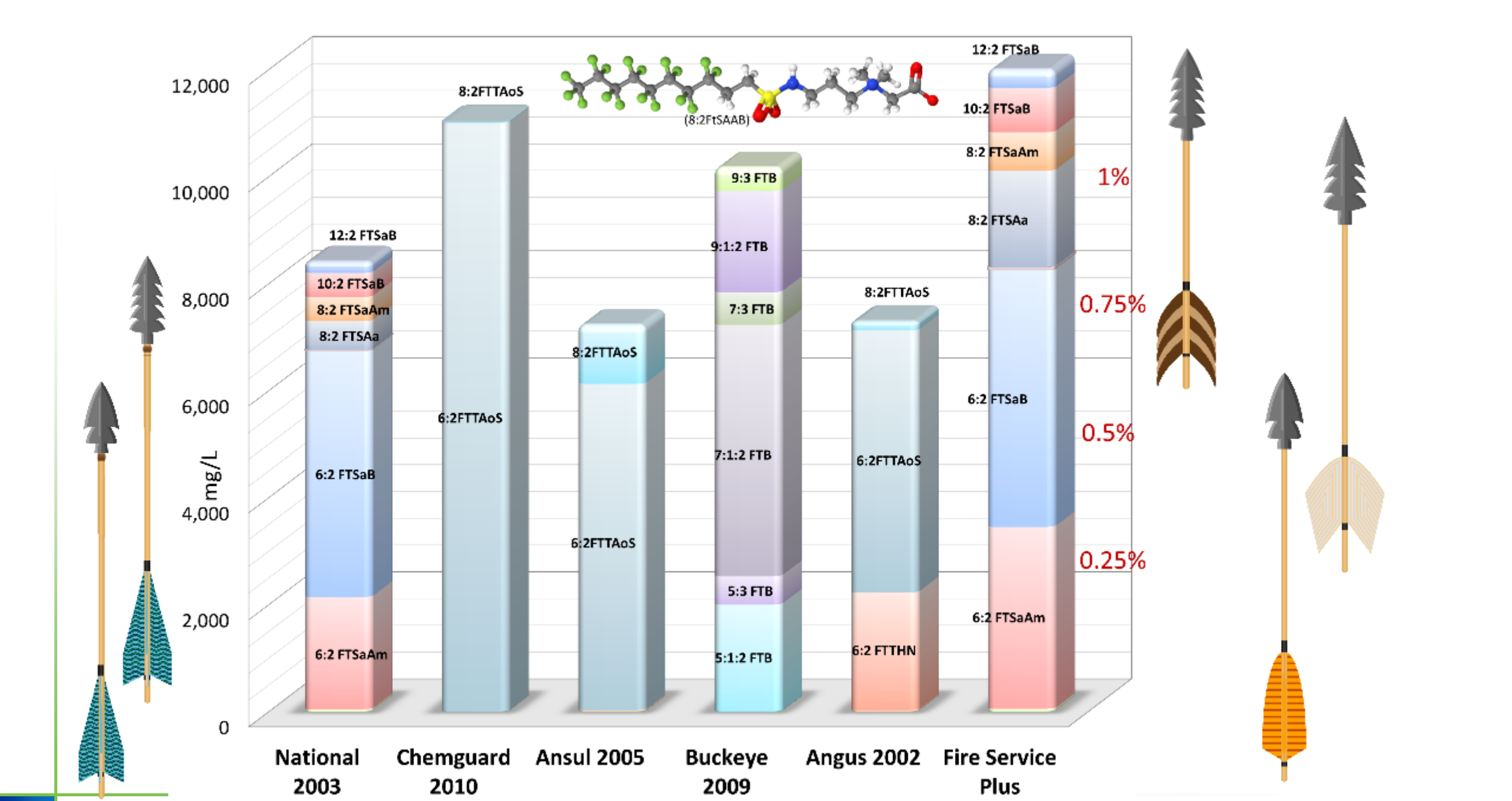






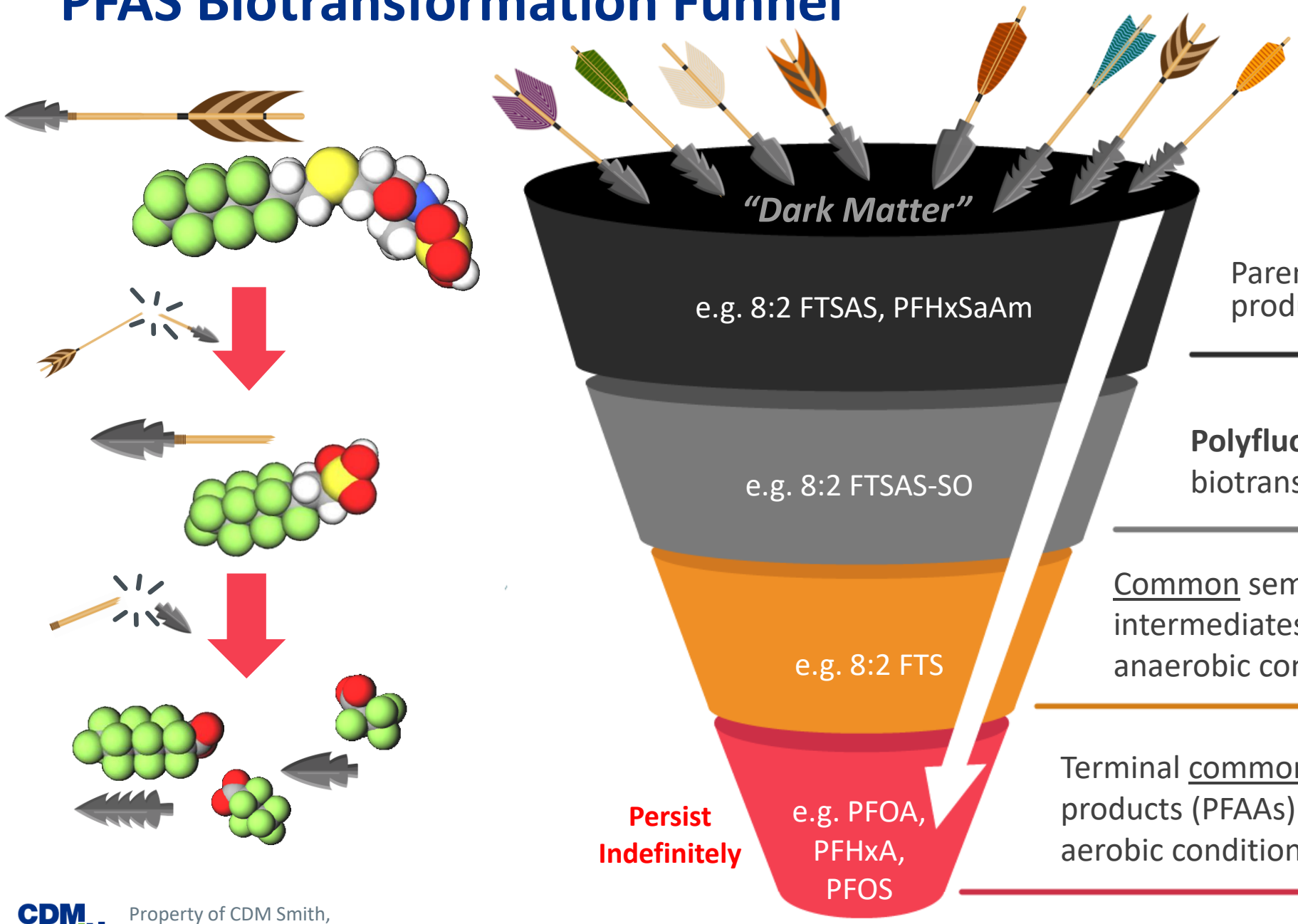
PFSaAm Perfluoroalkyl sulfonamido amine
PFSaAmA Perfluoroalkyl sulfonamide amino carboxylate

Field & Sedlak 2017. SERDP.



Field & Sedlak 2017, SERDP

PFAS Biotransformation Funnel



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

Polyfluorinated daughter biotransformation intermediates

Common semi-stable **polyfluorinated** daughter intermediates accumulating (especially under anaerobic conditions)

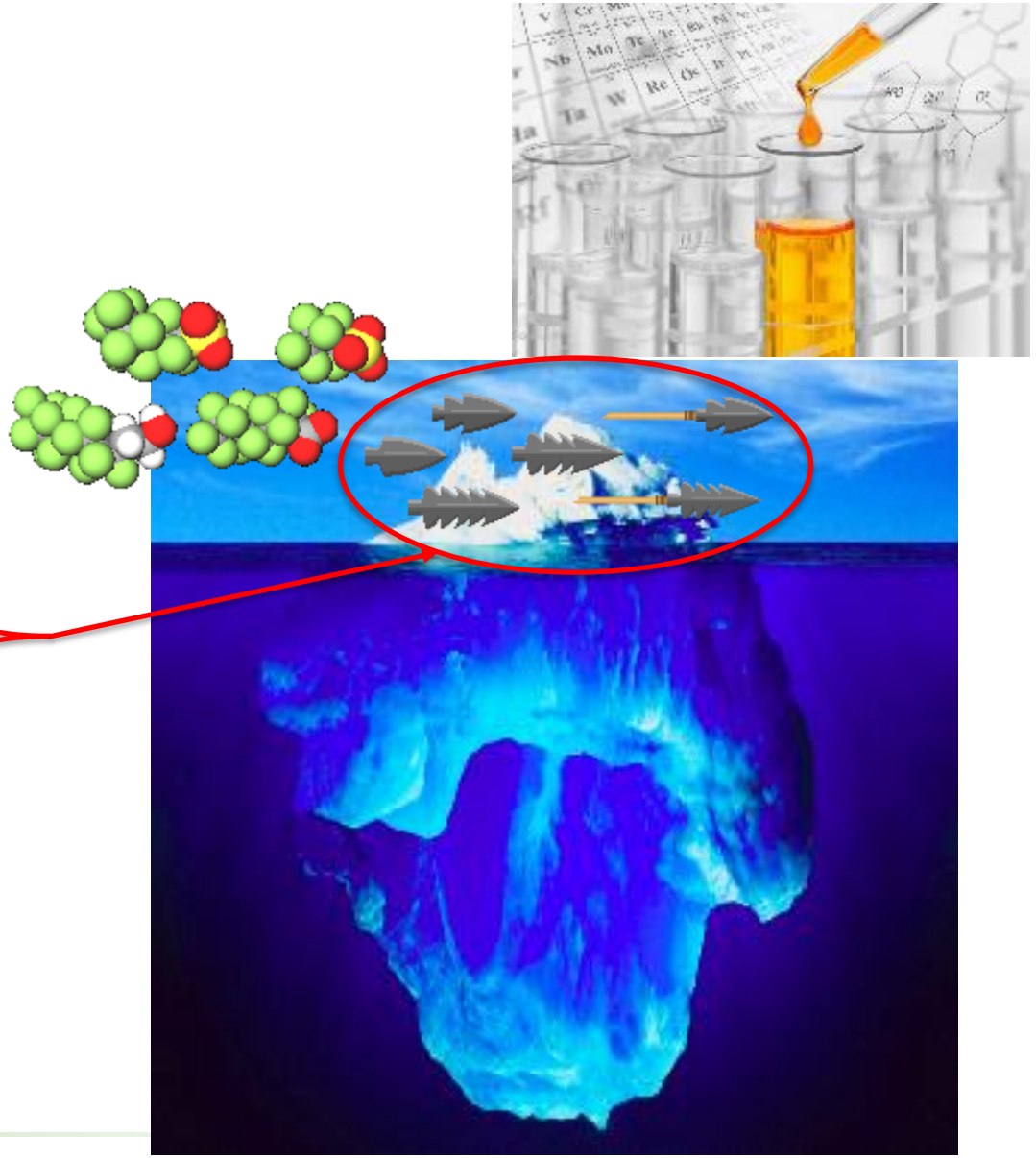
Terminal common **perfluorinated** daughter products (PFAAs) (formation favored under aerobic conditions)

Adapted from Ross et al., 2016

Laboratory Analysis

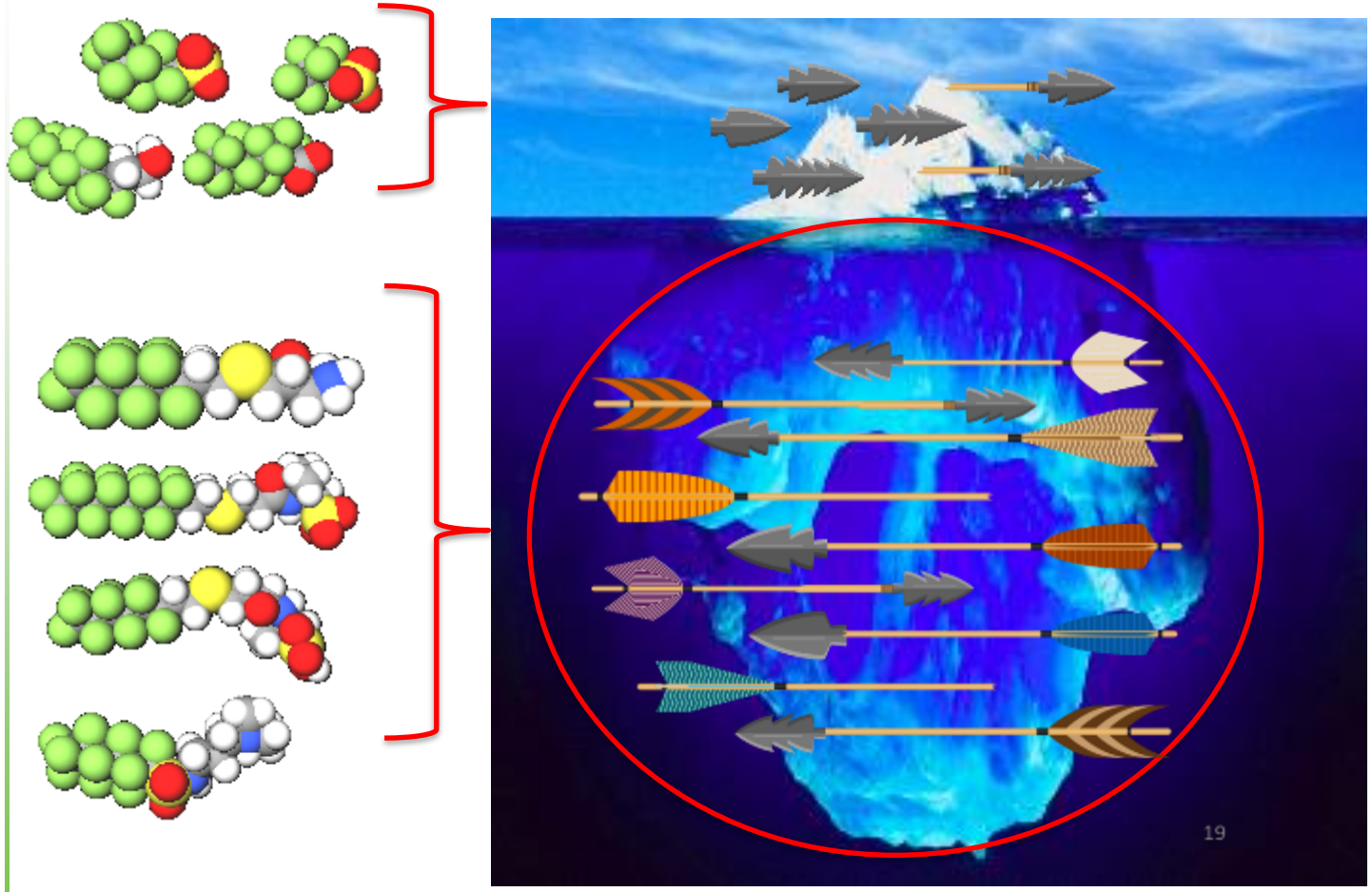
Targeted Analysis

- 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

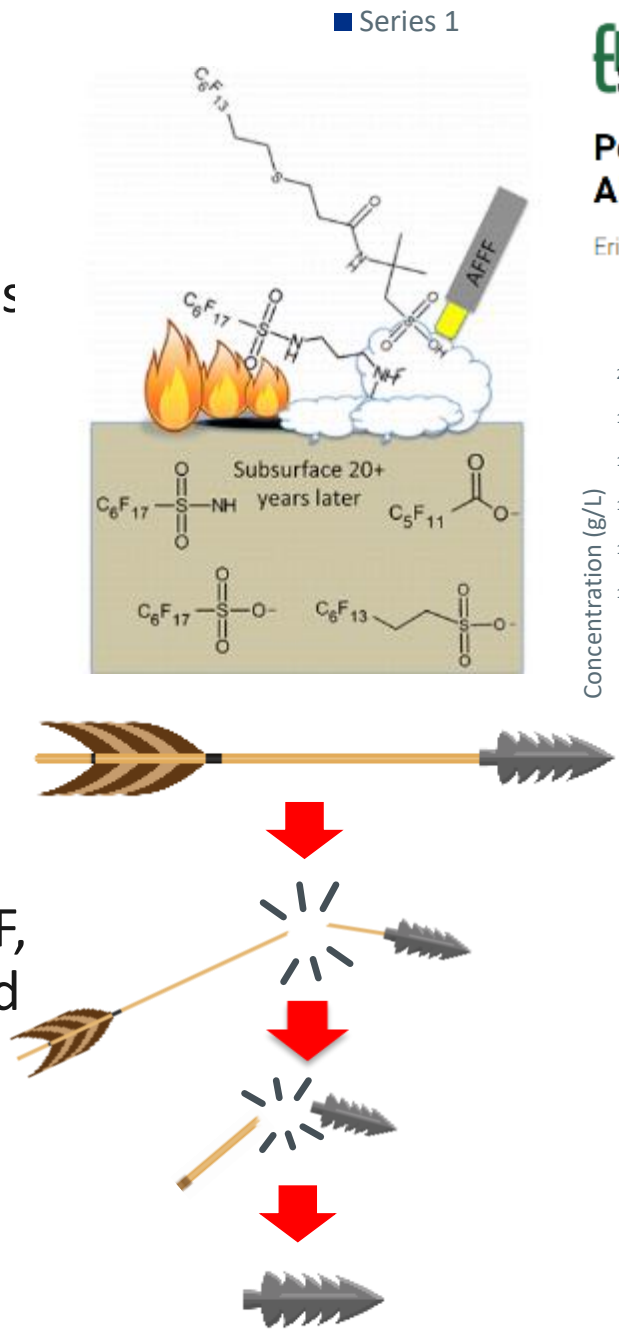


Methods to Detect Non-Target Polyfluoroalkyl Substances

- 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 F atoms chemical shift which is impacted by adjacent functional groups

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



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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[†,*]

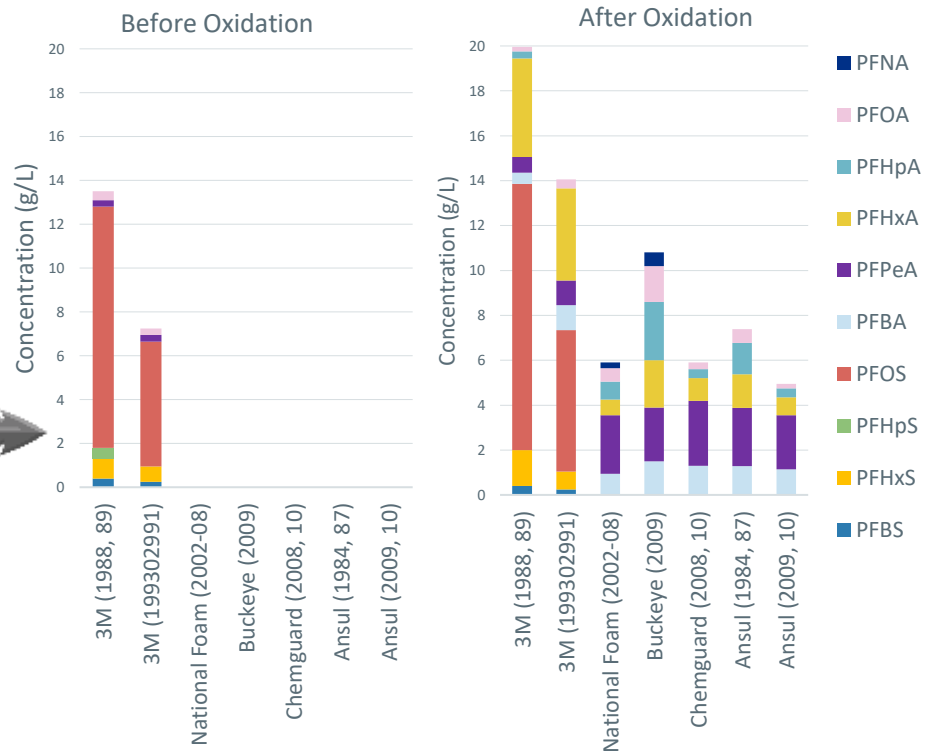
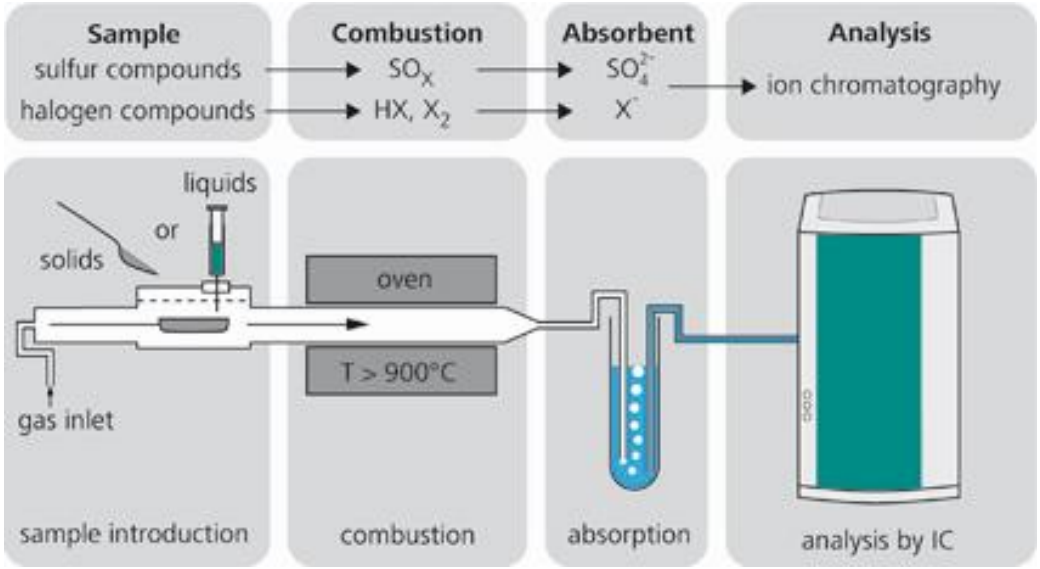


Figure 1. After concentrations of perfluorinated suflonates and carboxylates in AFFF formulations analyzed before (a) and after oxidation (b). Dates represent the years of manufacture of AFFF formulations analyzed in each category.

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

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

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PFAS Decontamination from Fire Suppression Systems

Vision, Initiatives and Paradigm Shift

Zoom Nguyen, CDM Smith

US DoD-Funded ESTCP Projects

Sustainable Firefighting System Cleanout and Rinsate Treatment Using PerfluorAd

ER20-5370

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

POINT OF CONTACT

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RELATED CONTENT

Feature Story

Environmentally Sustainable Methods Demonstrations to Clean Firefighting Delivery Systems

9/30/2020

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

ER20-5369

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.

POINT OF CONTACT

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PRODUCTS

Webinar

Environmentally Sustainable Methods to Remove AFFF from Firefighting Delivery Systems

3/23/2023

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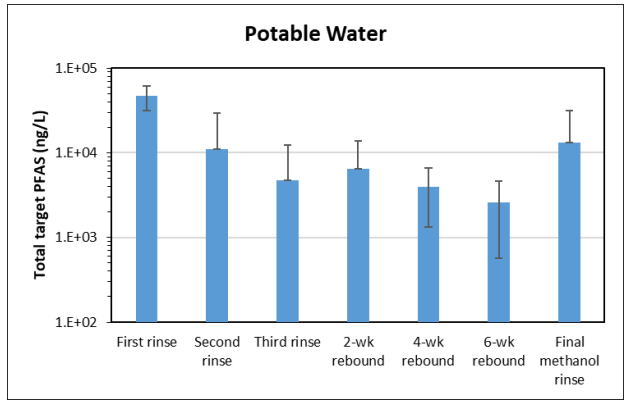
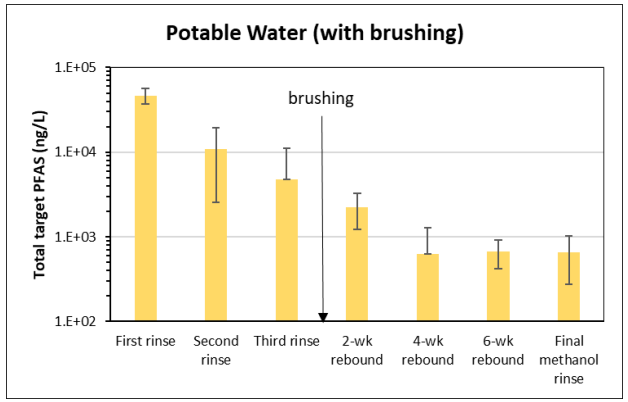
Feature Story

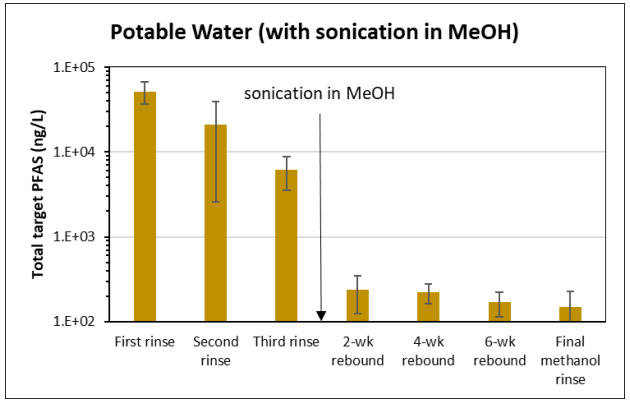
Environmentally Sustainable Methods Demonstrations to Clean Firefighting Delivery Systems

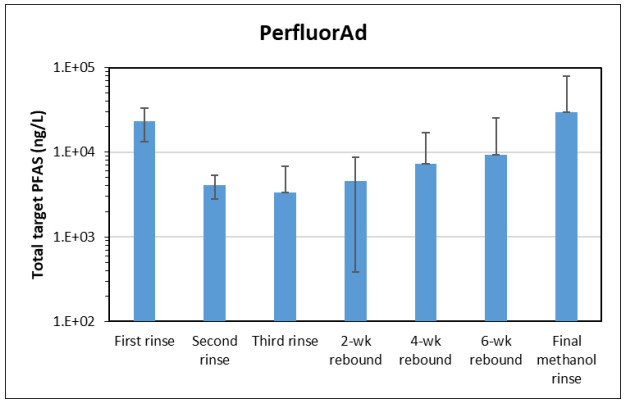
9/30/2020

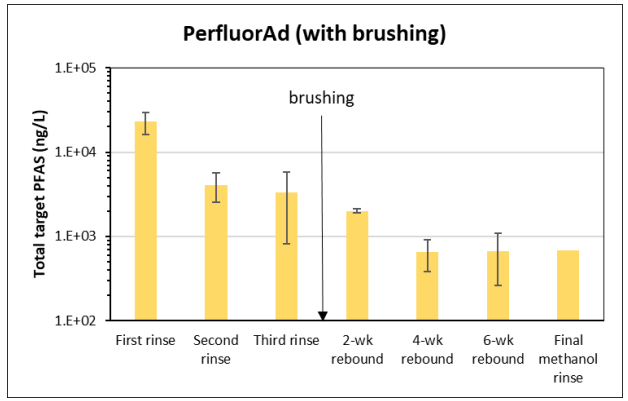
PFAS Rebound Following Triple Water Rinse, PerfluorAd, and Methanol (Bench Study)

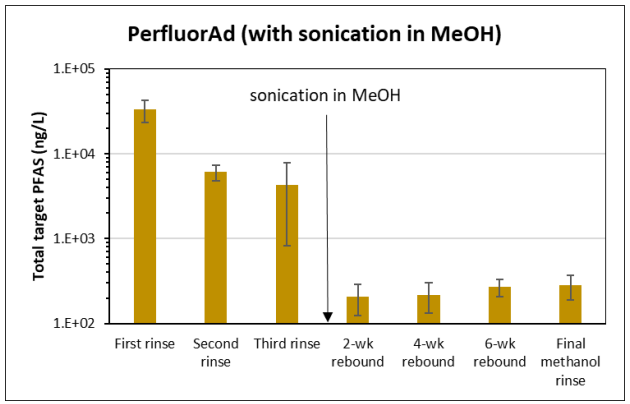


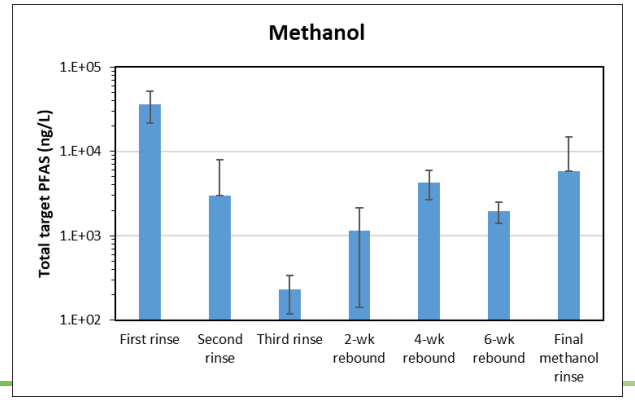


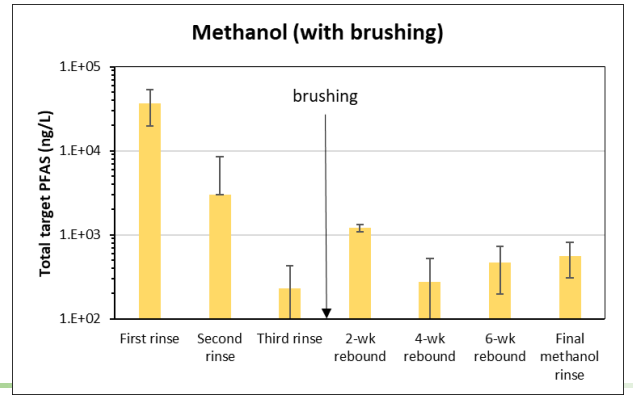


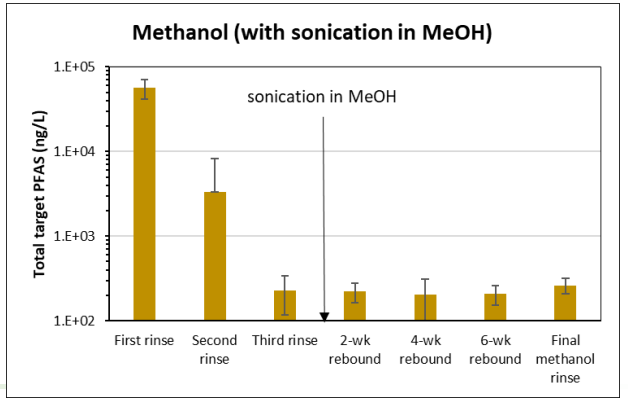




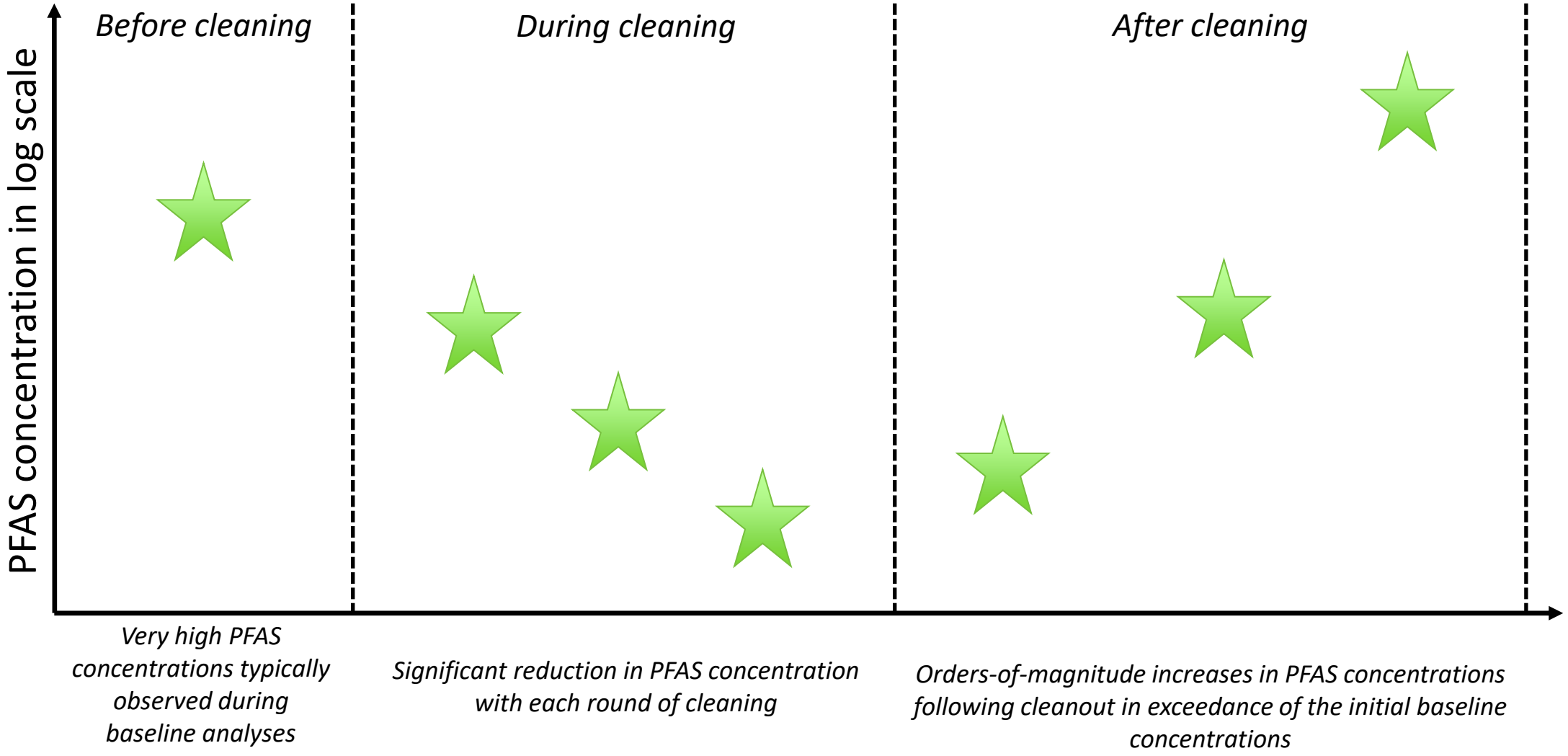








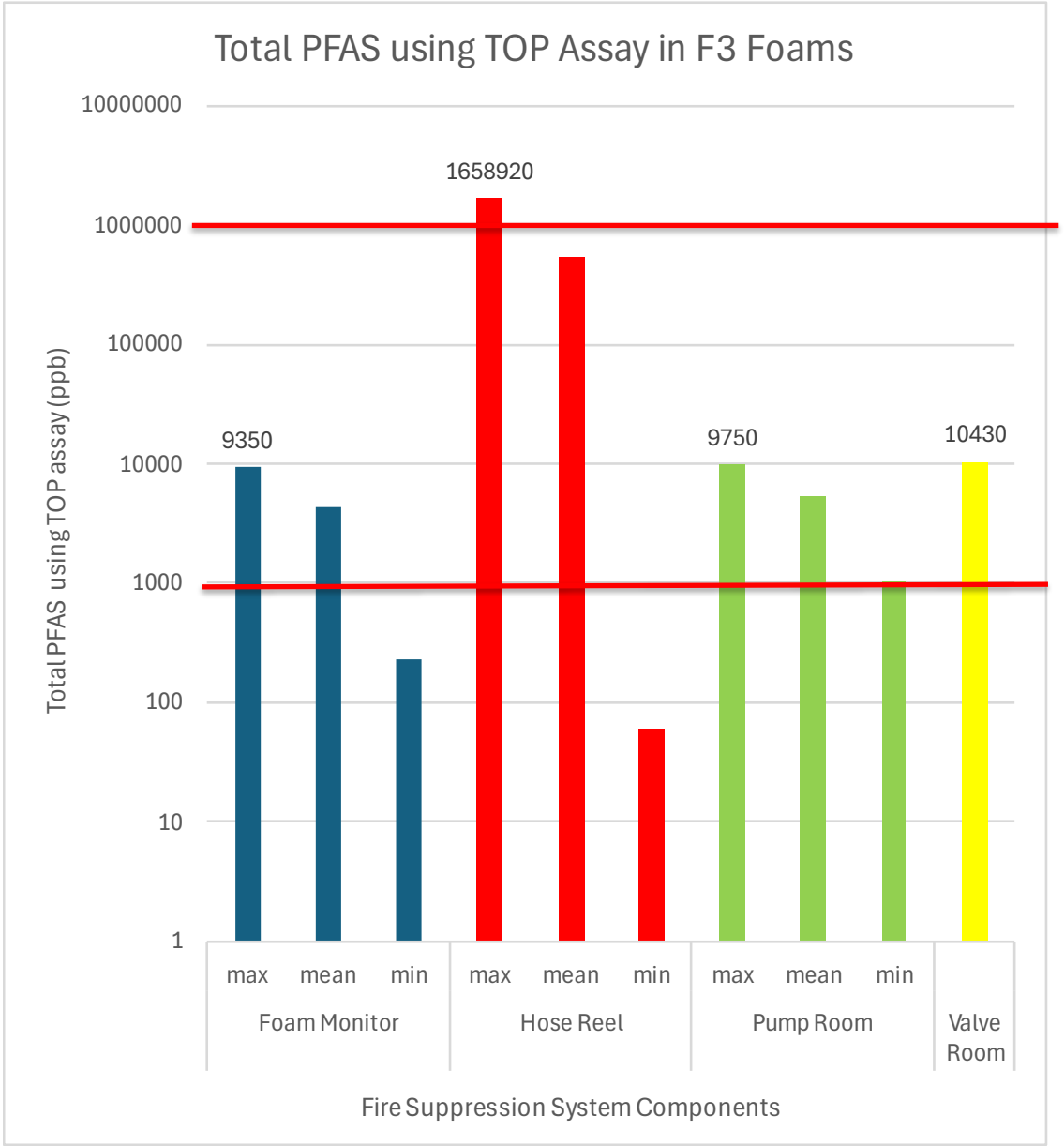
Technical Challenges



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

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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) 2025 (cannot be used)	C8 i.e. PFOA & PFOA precursors	25 ppb PFOA 1,000 ppb PFOA-precursors (C8)
EU 2021/1297 	January 2023 (derogation to July 2025)	C9-C14 PFCAs: PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA	25 ppb sum of C9-C14 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 Sum PFCA precursors C4-C14	10,000 ppb 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

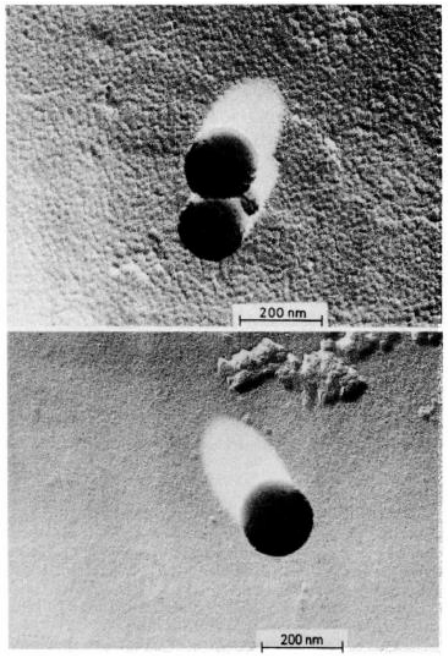
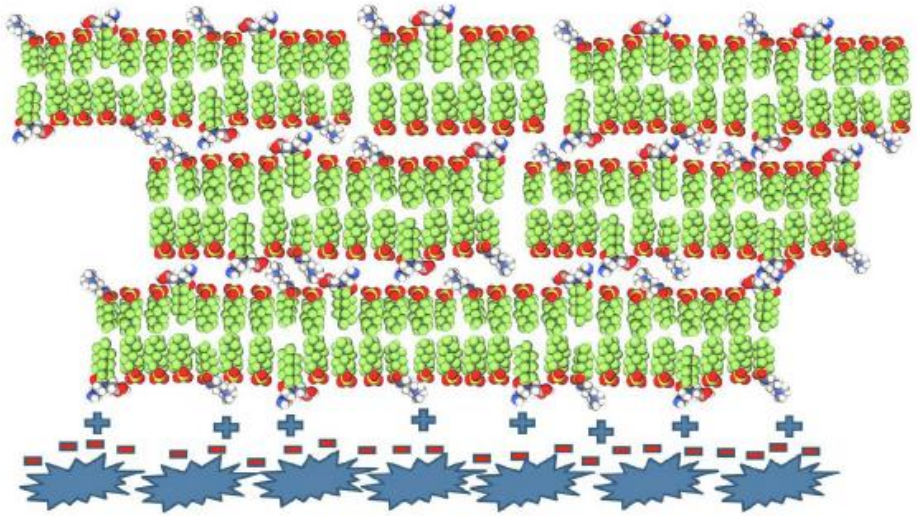
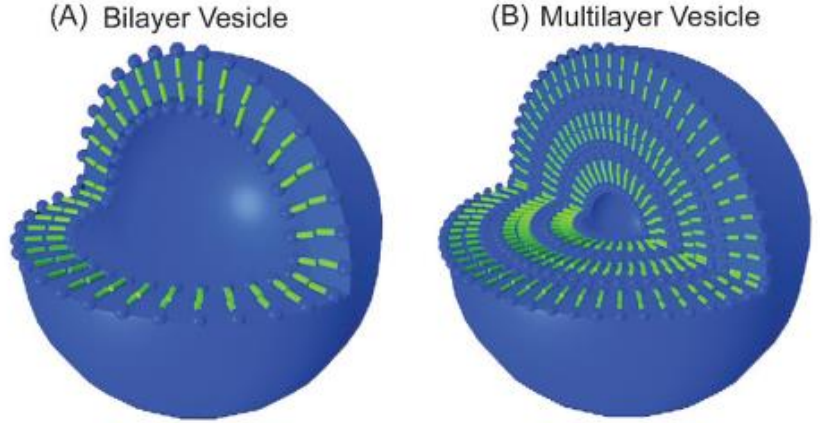


Figure 6. Electron micrograph of liposomes from **6**: (a) monomeric, (b) polymeric (after 15 min of UV irradiation).

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



Schematic of PFAS Supramolecular Assembly Structures

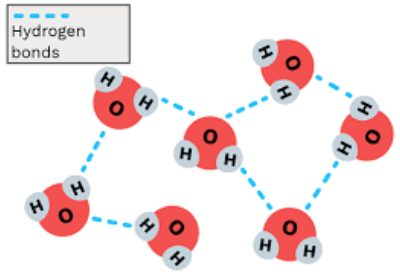


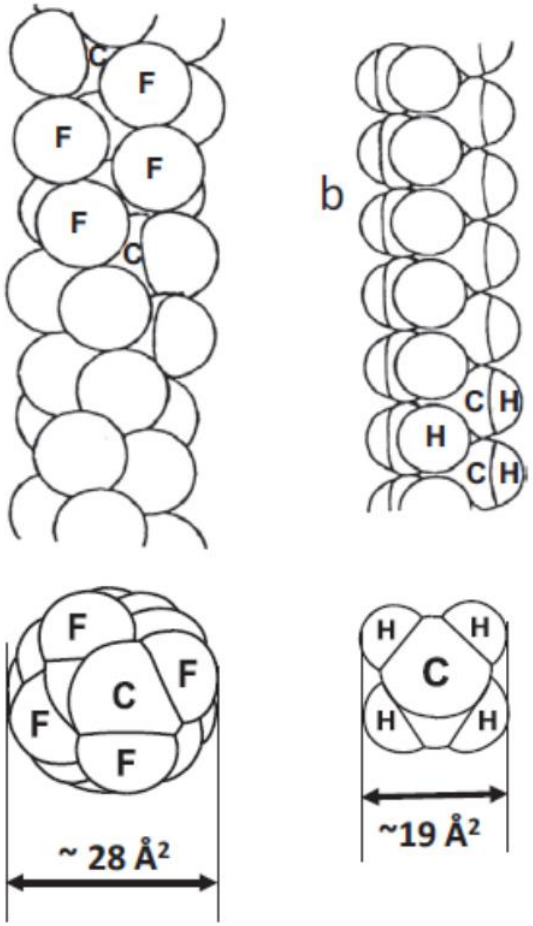
Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 10580

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).

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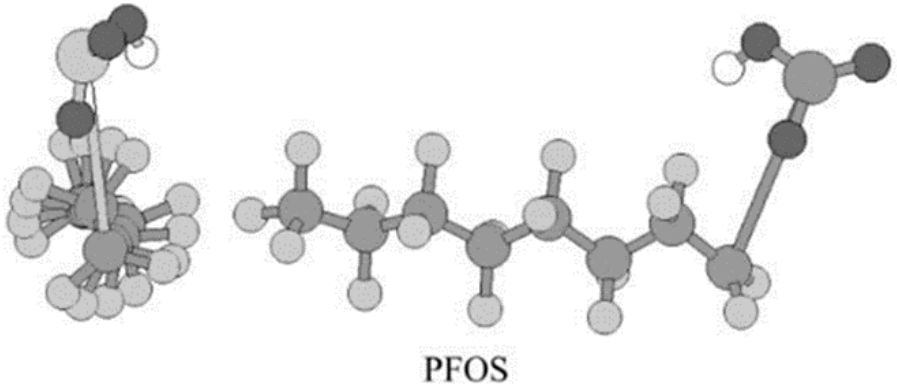
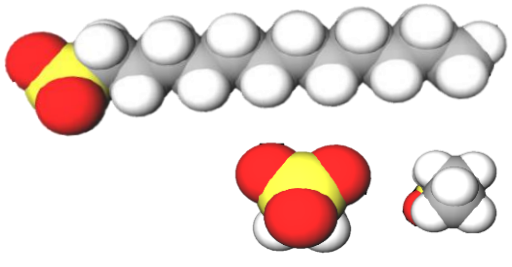
Surfactant Tail Shape Determines Critical Packing Parameters

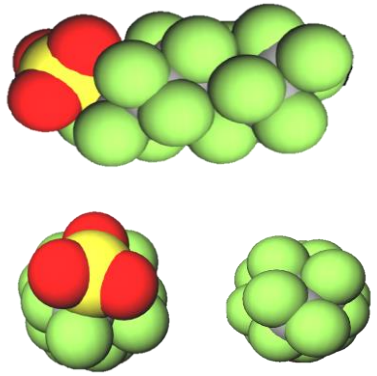


Erkoc et al., 2001 Journal of Molecular Structure (Theochem) 549 (2001) 289-293

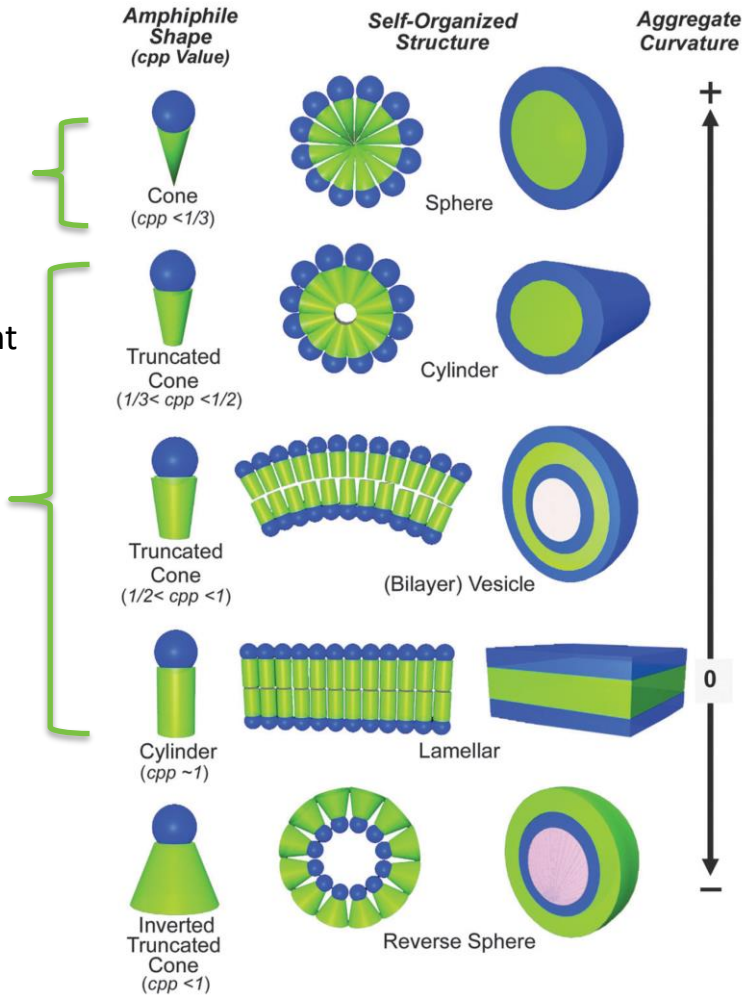
- Fluorine has high electronegativity which imparts a **rigid** helical fluorocarbon structure to perfluoroalkyl groups leading to the formation of **bulky, rigid, rod-shaped fluorosurfactant tails**
- The bulky, rigid, rod shape of the fluoroalkyl chains tends to decrease the curvature of the aggregates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



SDS – C12 hydrocarbon surfactant



PFOS C8 fluorosurfactant



Gladysz, Curran, Horváth 2004 DOI:10.1002/3527603905

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

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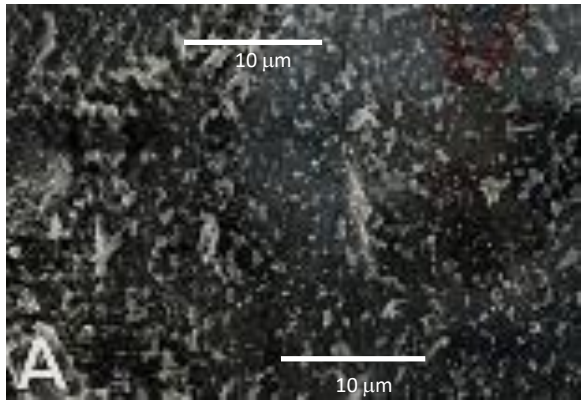
Supramolecular Assemblies - PFAS retained on surfaces

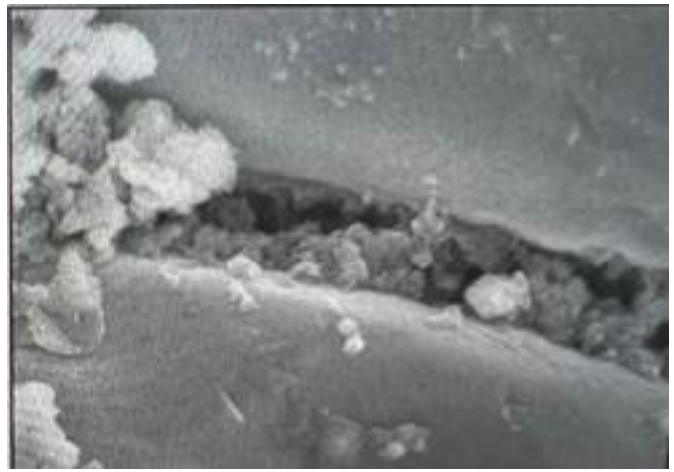
- Storage of AFFF within fire suppression systems causes a significant mass of PFAS to be retained on the inner surfaces of fire suppression system.
- Sorption of amphiphilic PFAS (fluorosurfactants) on surfaces often does not conform to conventional sorption theories.
- Formation of supramolecular assemblies 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

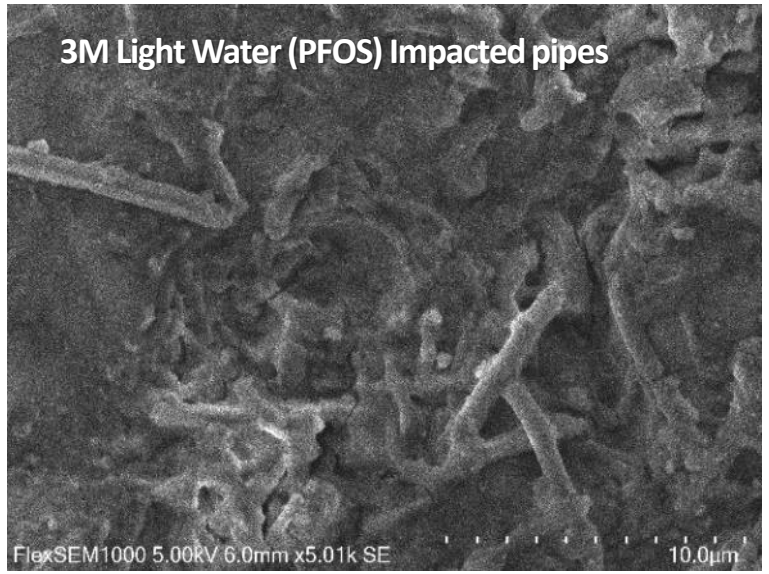
Pipe Exterior

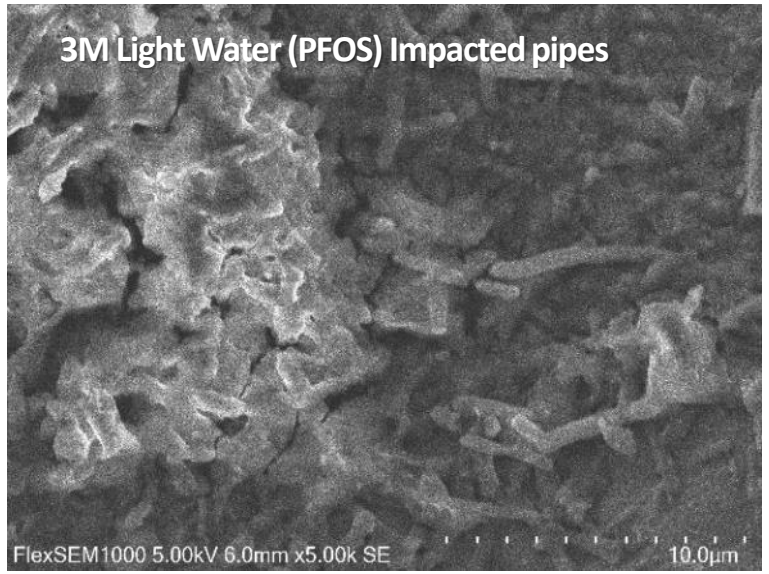


PFAS aggregates on the interior of fire suppression system pipework (Lang et al., Chemosphere, 308, (2), 2022)

PFAS Retained on Surfaces

Images Courtesy of Dave Megson, Manchester Metropolitan University





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

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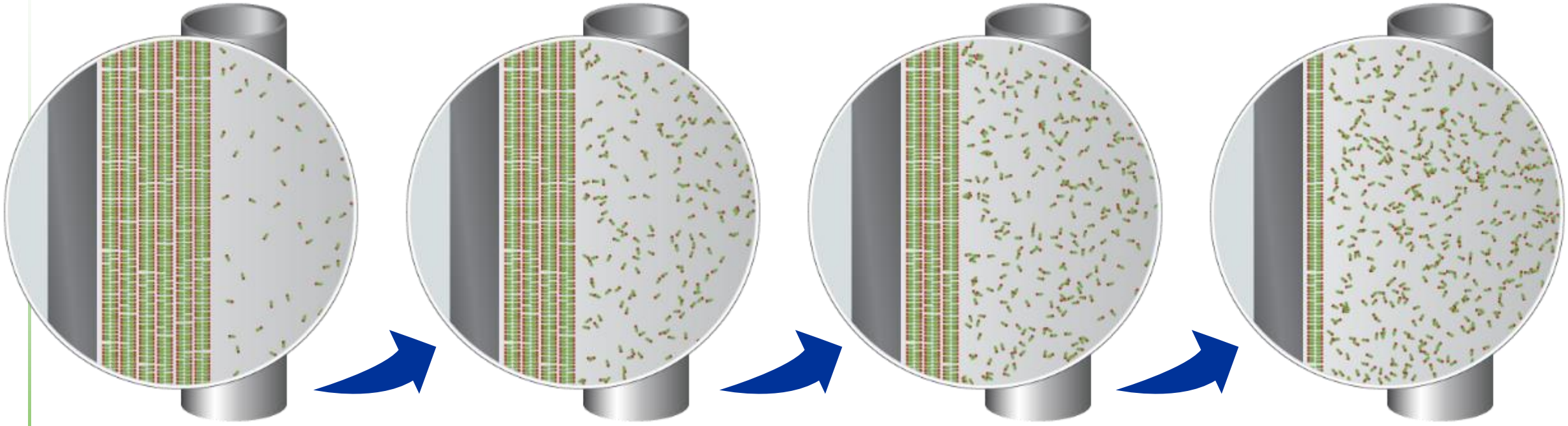
Projected Rebound of PFAS into F3 Foams



3 months

1 year

2 years

3 years

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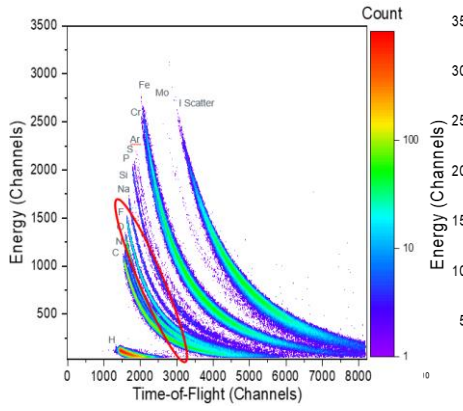
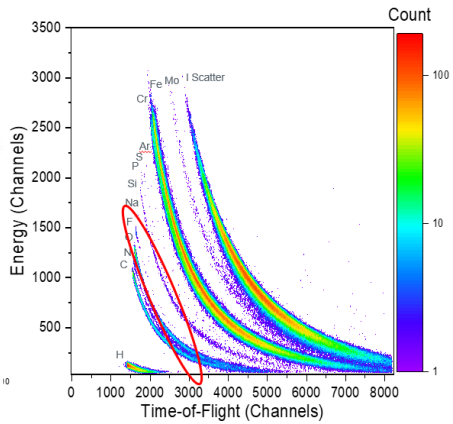
Proving Decontamination

- 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



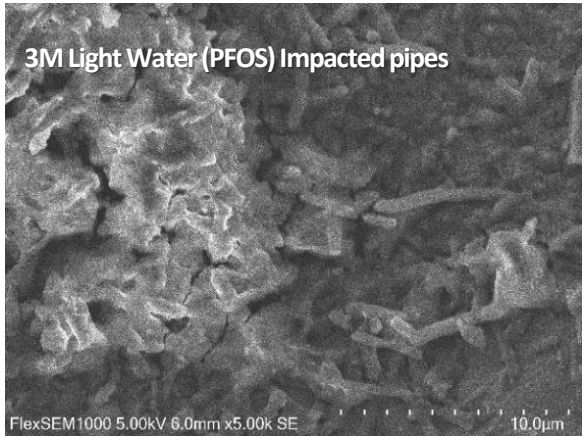


Fe /at.%	F /at.%
9.9	8.1

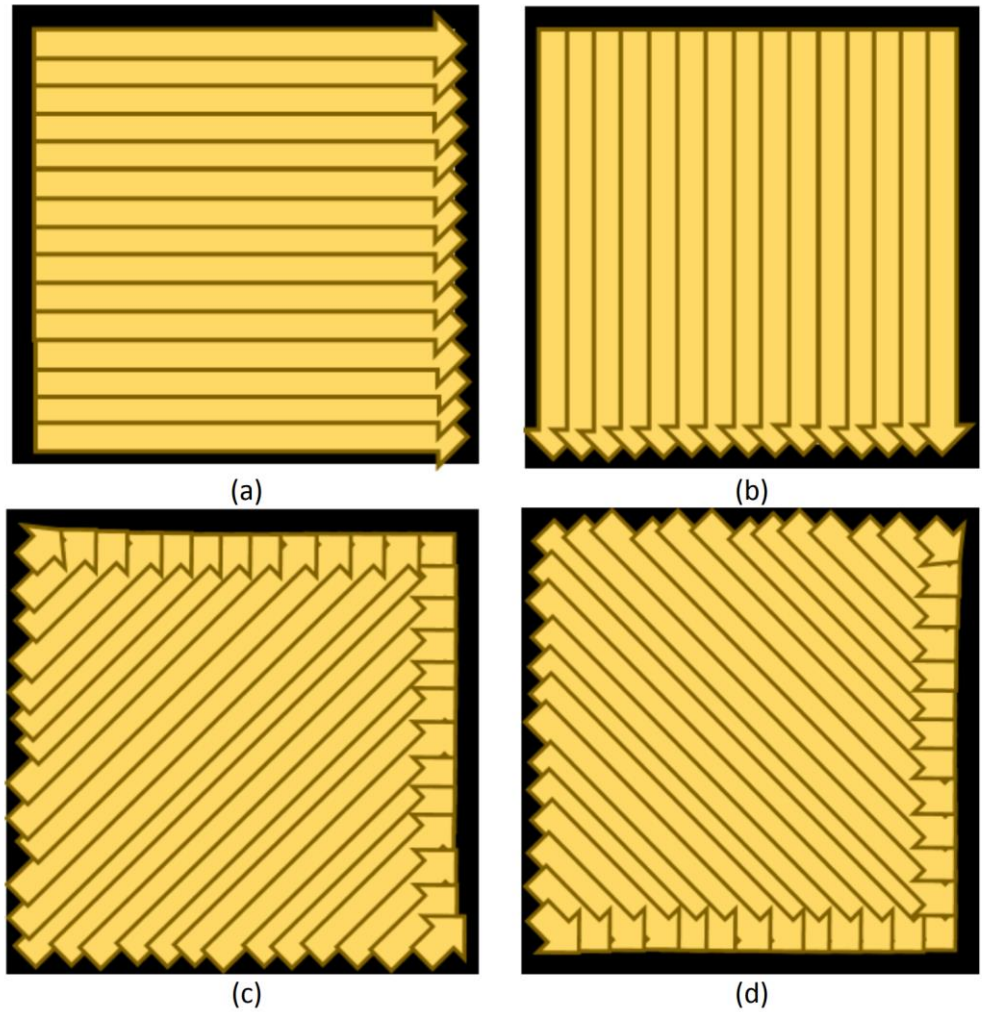
Fe /at.%	F /at.%
52.5	0.42

Swab sampling method

- We want to assess efficacy of treatment - How effective was the removal of PFAS into the cleaning solution?
- How much toal PFAS mass is present on pipe surfaces?
- Swab sampling method:
  - Cotton gauze swab (medical supply)
  - Sequential swabbing of pipe surface with
    in basic MeOH (0.4% KOH) and
    in acidic MeOH (0.1 M HCL)
    soaked cotton swab, time of application: 5 min each
  - Inspired by soil extractions using sequential basic-acidic extraction of AFFF
  - Analysis of pipe section before and after treatment with ToF-ERD
  - Standardised methology followed i.e. swab time and pressure required



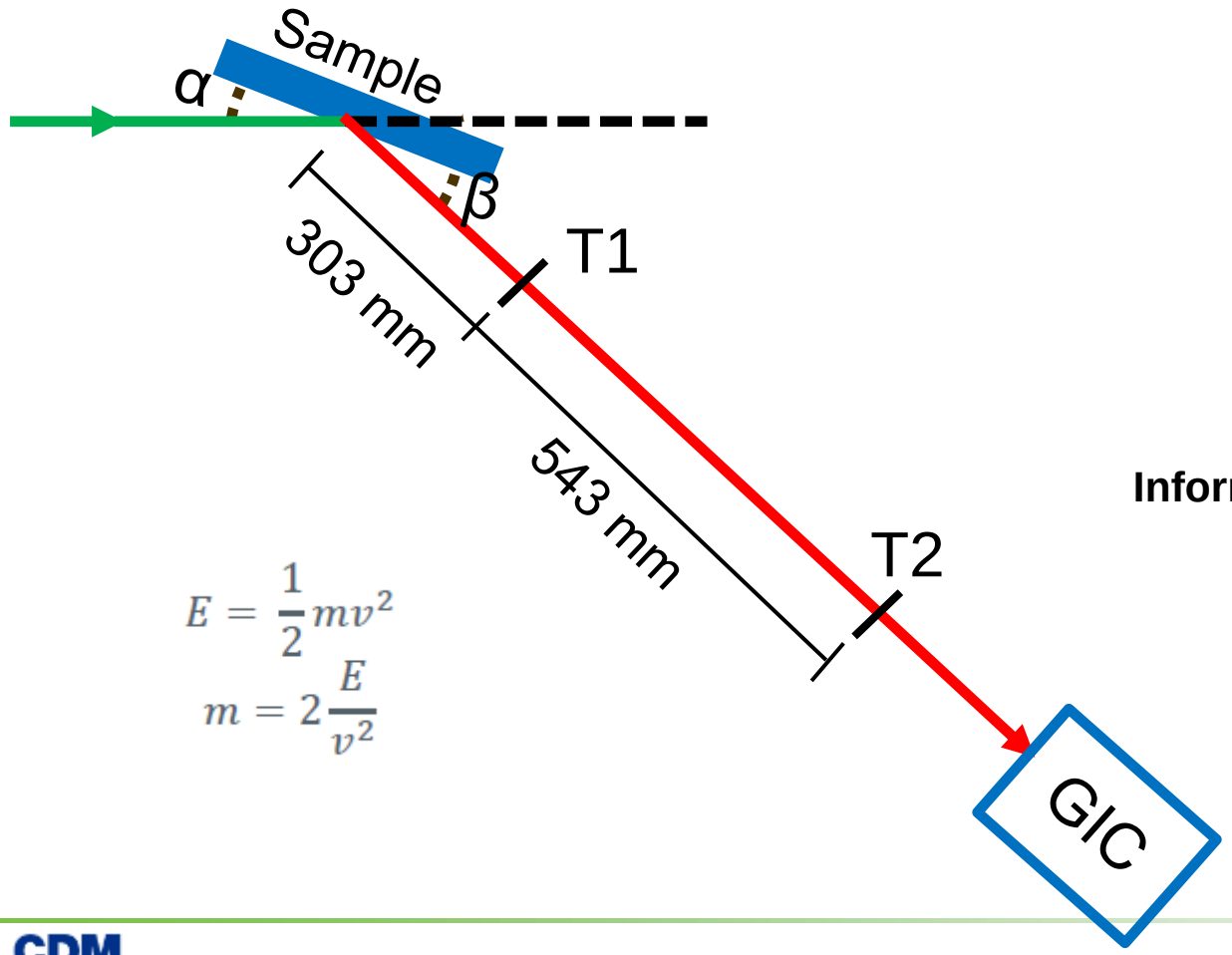
Swabbing procedure



- Use template to set uniform surface area to swab within
- Wipe the whole surface left to right
- Re-wipe again top to bottom
- Re-wipe again bottom left to top right
- Re-wipe again top left to bottom right

Surface Analysis – ToF-ERD

Time-of-Flight Elastic Recoil Detection Analysis



$$E = \frac{1}{2}mv^2$$

$$m = 2\frac{E}{v^2}$$

- Primary beam of Iodine ions enter the sample and cause atoms on the surface to be forward recoiled
- Recoiled atoms pass two timing foils → velocity v
- Then, Gas ionization chamber (GIC) → Energy E
- → determination of elemental mass
- → Accuracy 0.1 at(omic)%

Information:

- Elemental composition of the pipe surface
- → Fluorine F, Iron Fe
- Assumption F = PFAS
- Depth information

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

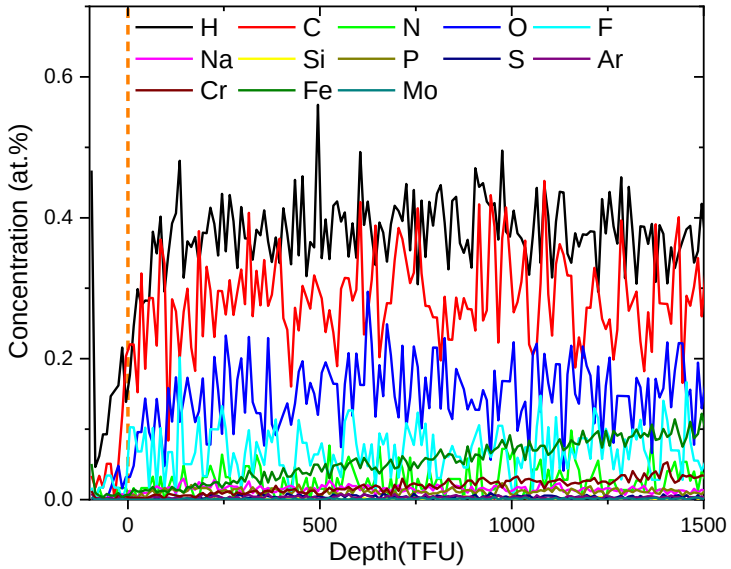
- Not a table-top instrument
- Staff (group) of highly skilled physicists and engineers to operate
- <5 machines in the world
- Expensive

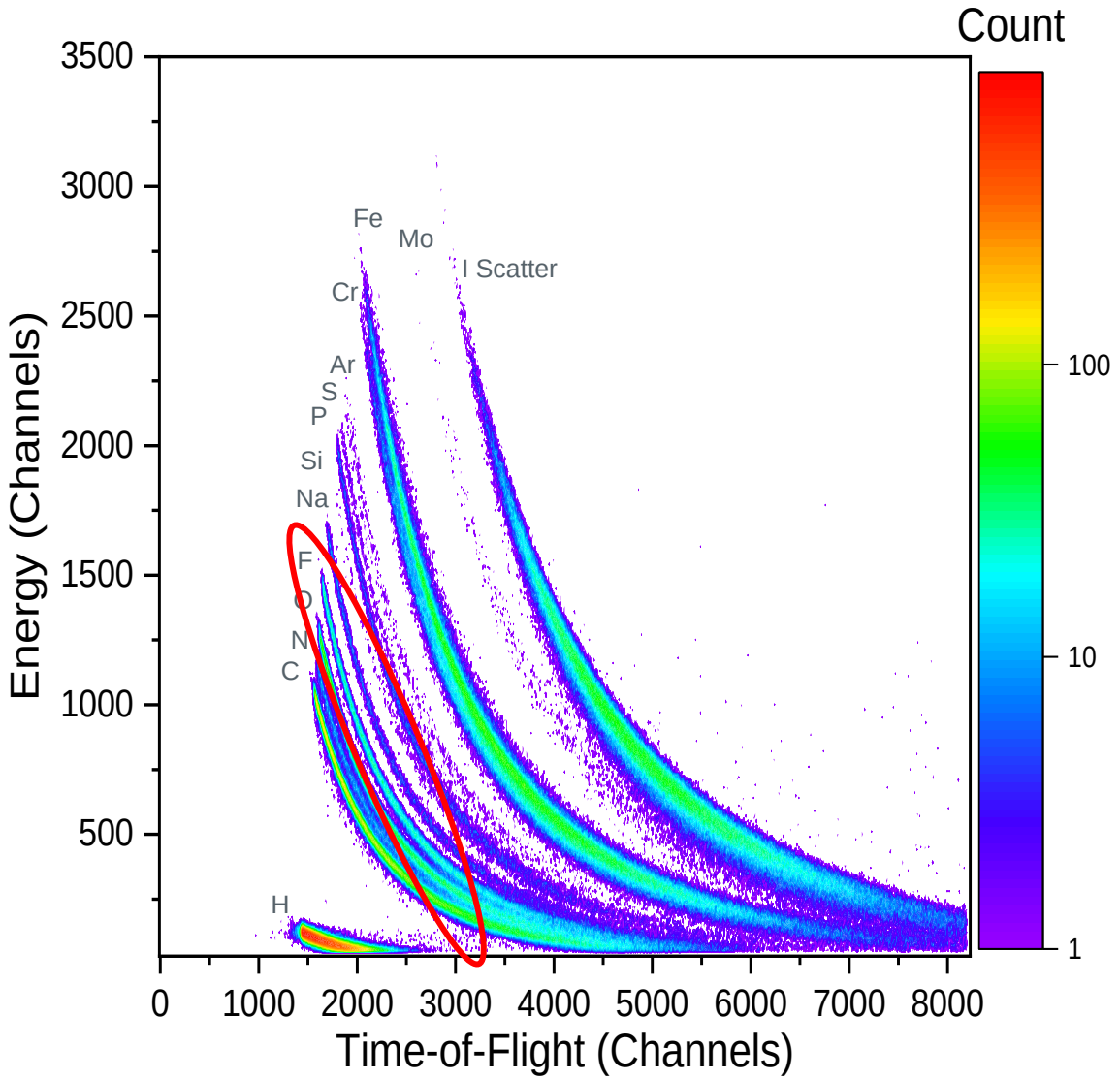
→ Not commercially available!

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



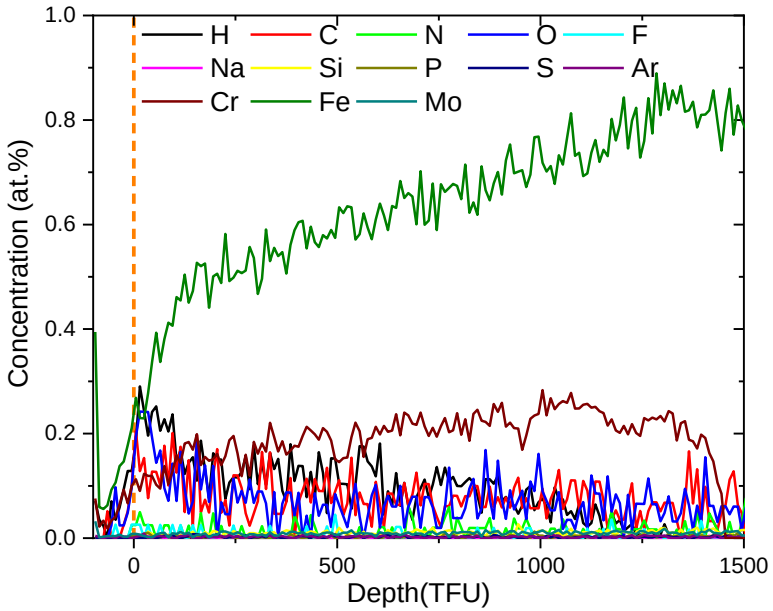


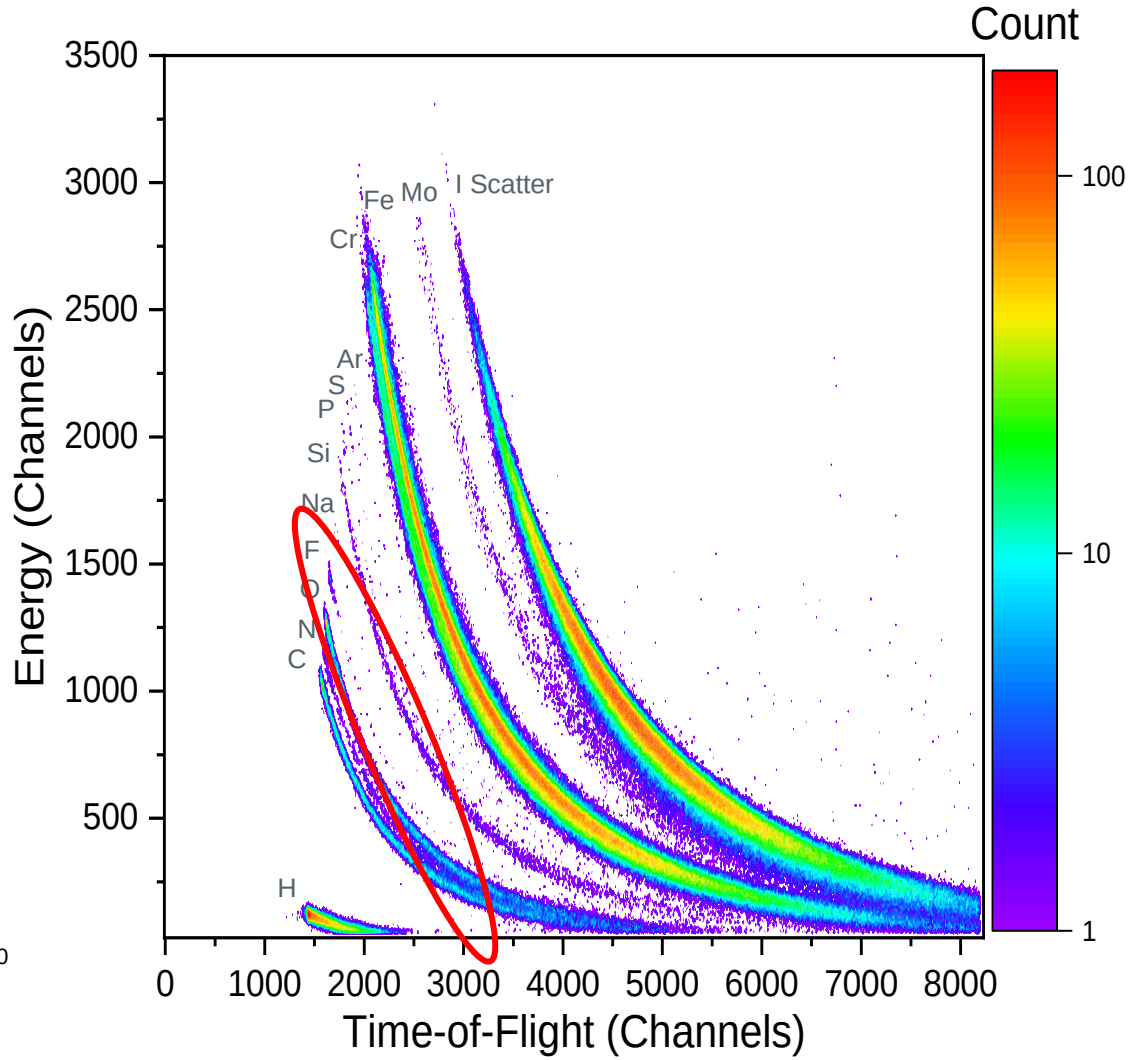
Depth /TFU	Depth /nm	H /at.%	C /at.%	N /at.%	O /at.%	F /at.%	Na /at.%	Si /at.%	P /at.%	S /at.%	Ar /at.%	Cr /at.%	Fe /at.%	Mo /at.%
0-1000	0-120	27.8	29.3	2.98	15.3	8.1	1.41	0.2	1.29	0.337	0.325	2.87	9.9	0.159

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





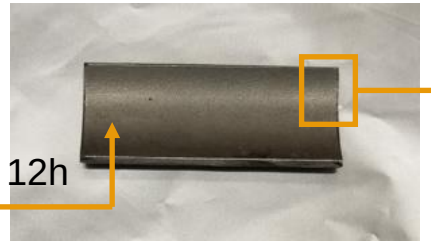
Depth /TFU	Depth /nm	H /at.%	C /at.%	N /at.%	O /at.%	F /at.%	Na /at.%	Si /at.%	P /at.%	S /at.%	Ar /at.%	Cr /at.%	Fe /at.%	Mo /at.%
0-1000	0-120	11.2	7.9	1.14	7.3	0.42	0.13	0.82	0.27	0.22	0.23	17.1	52.5	0.79

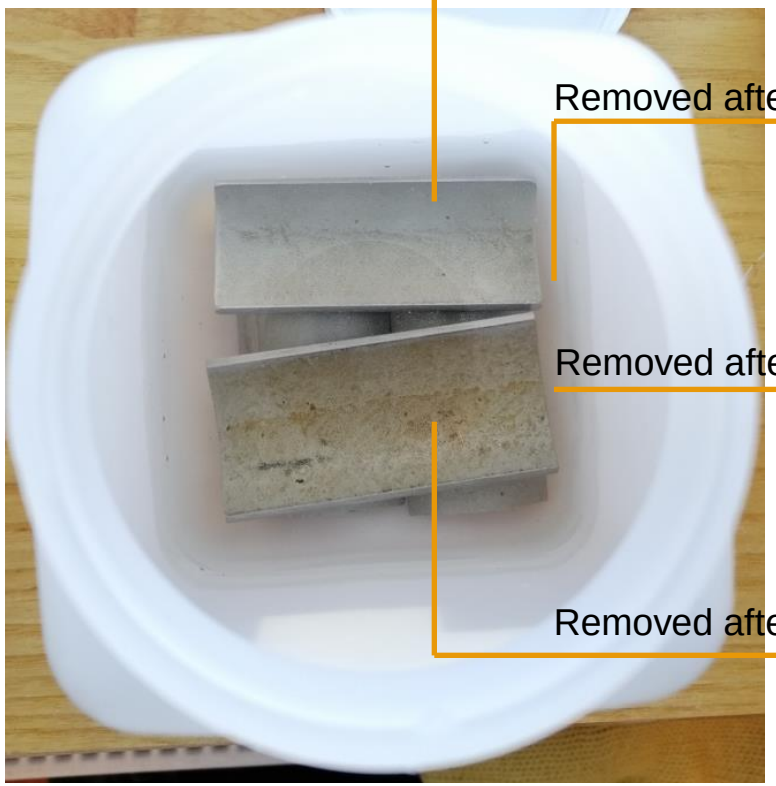
Surface analysis – Sample Preparation

1 cm x 1 cm

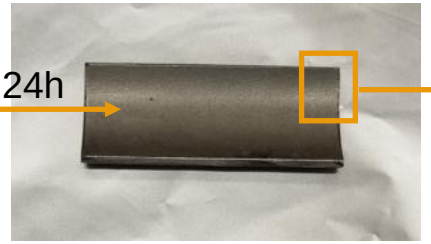
No treatment

Removed after 12h

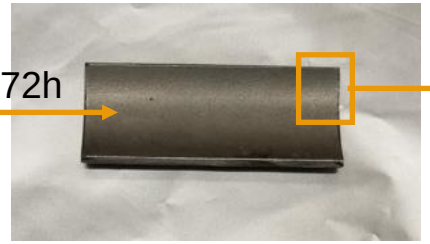




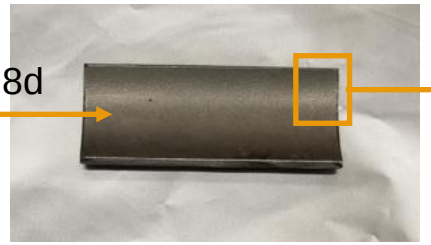
Removed after 24h

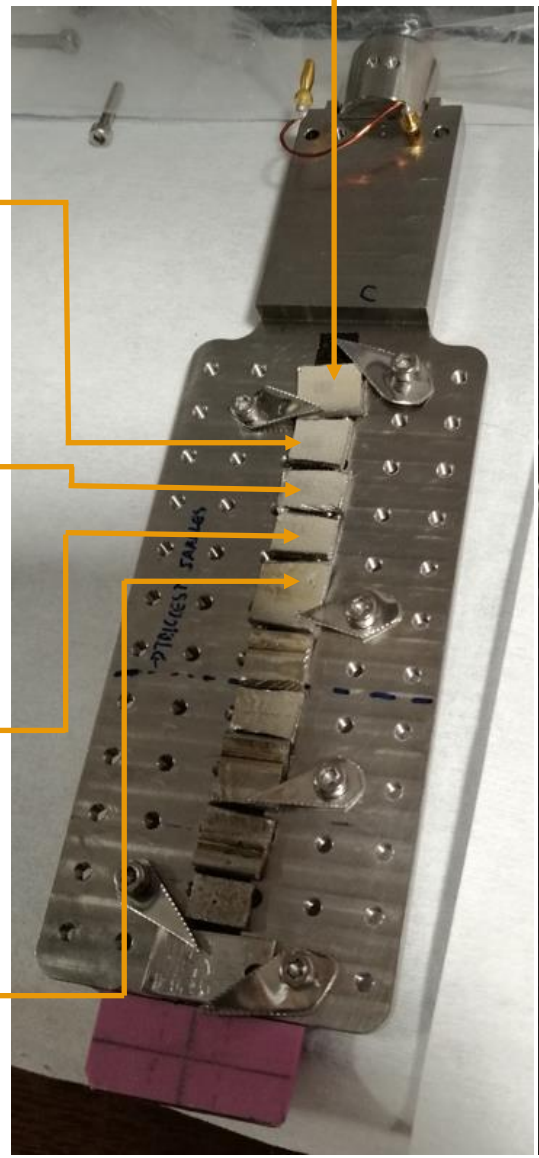


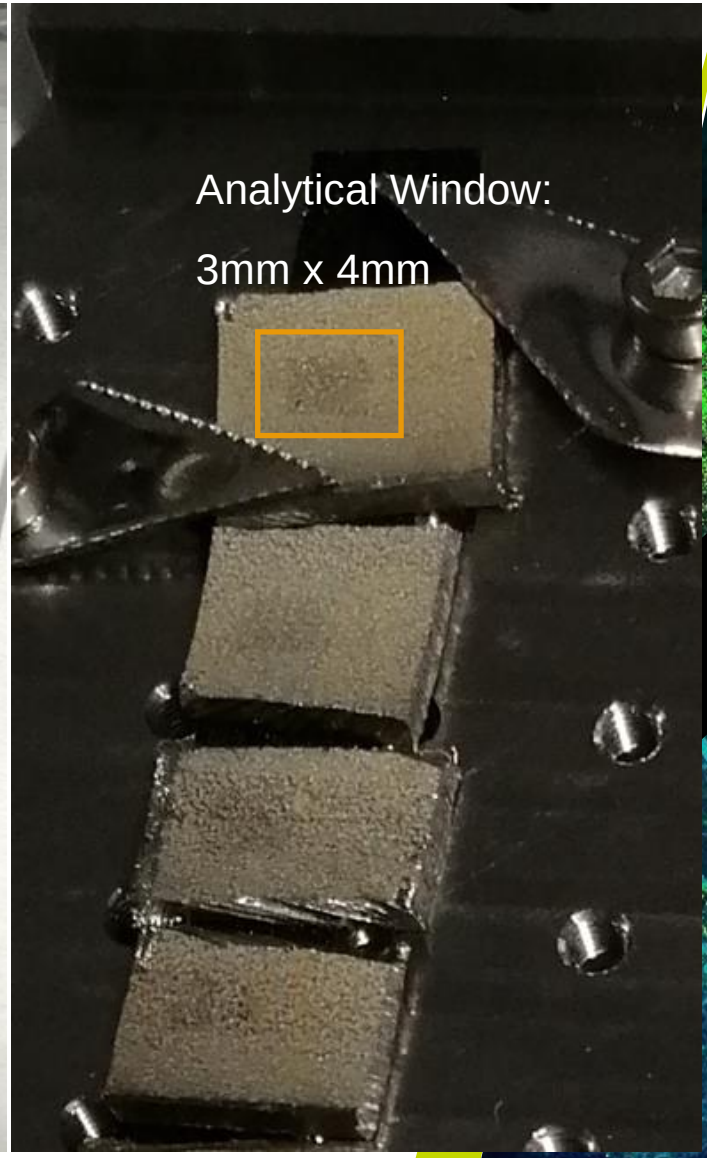
Removed after 72h



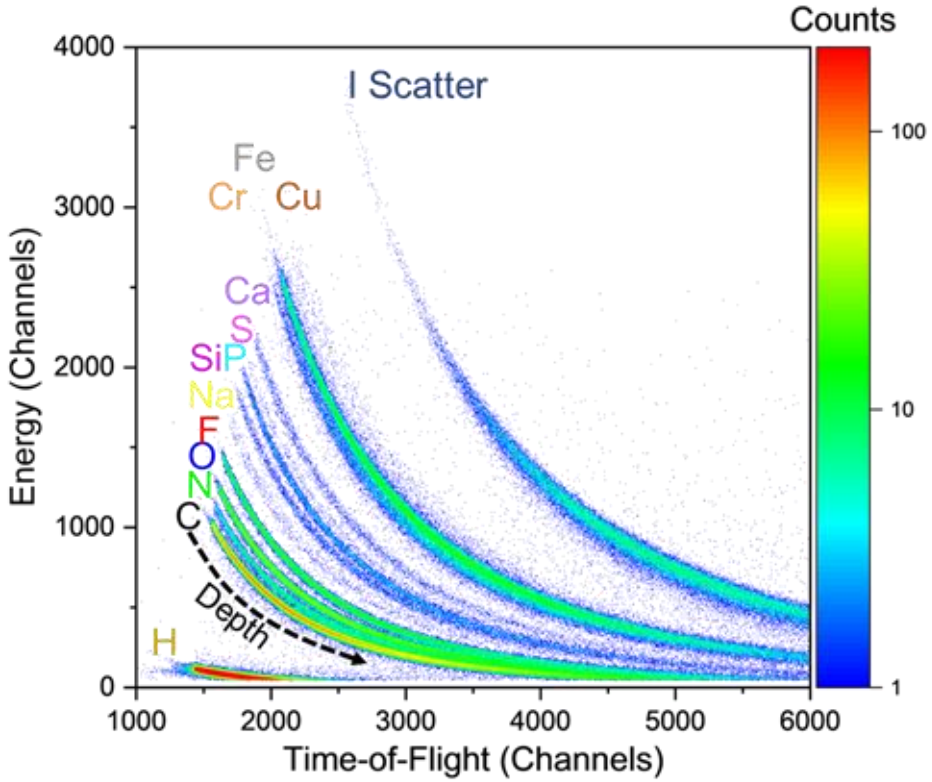
Removed after 8d

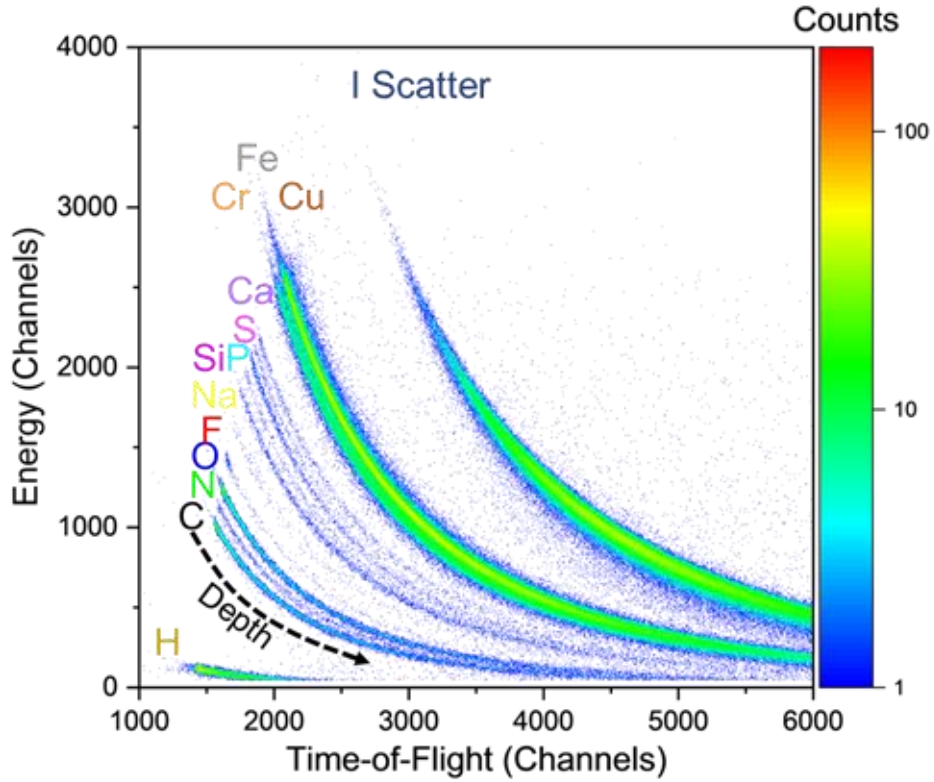






Results – Swab sampling method

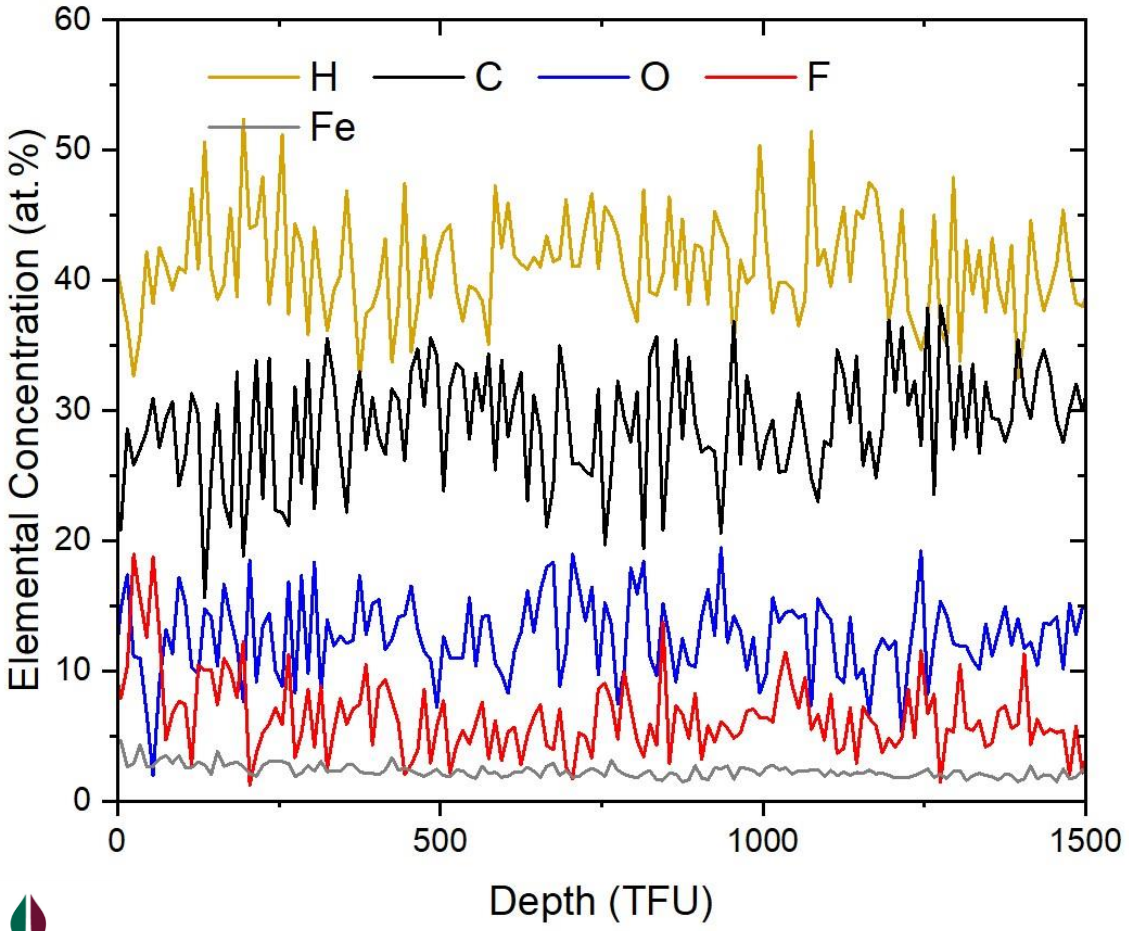




	Untreated PIpe	Swabbed Pipe
Fluorine [at.%]	6.3	0.3
Iron [at.%]	2.2	44.3

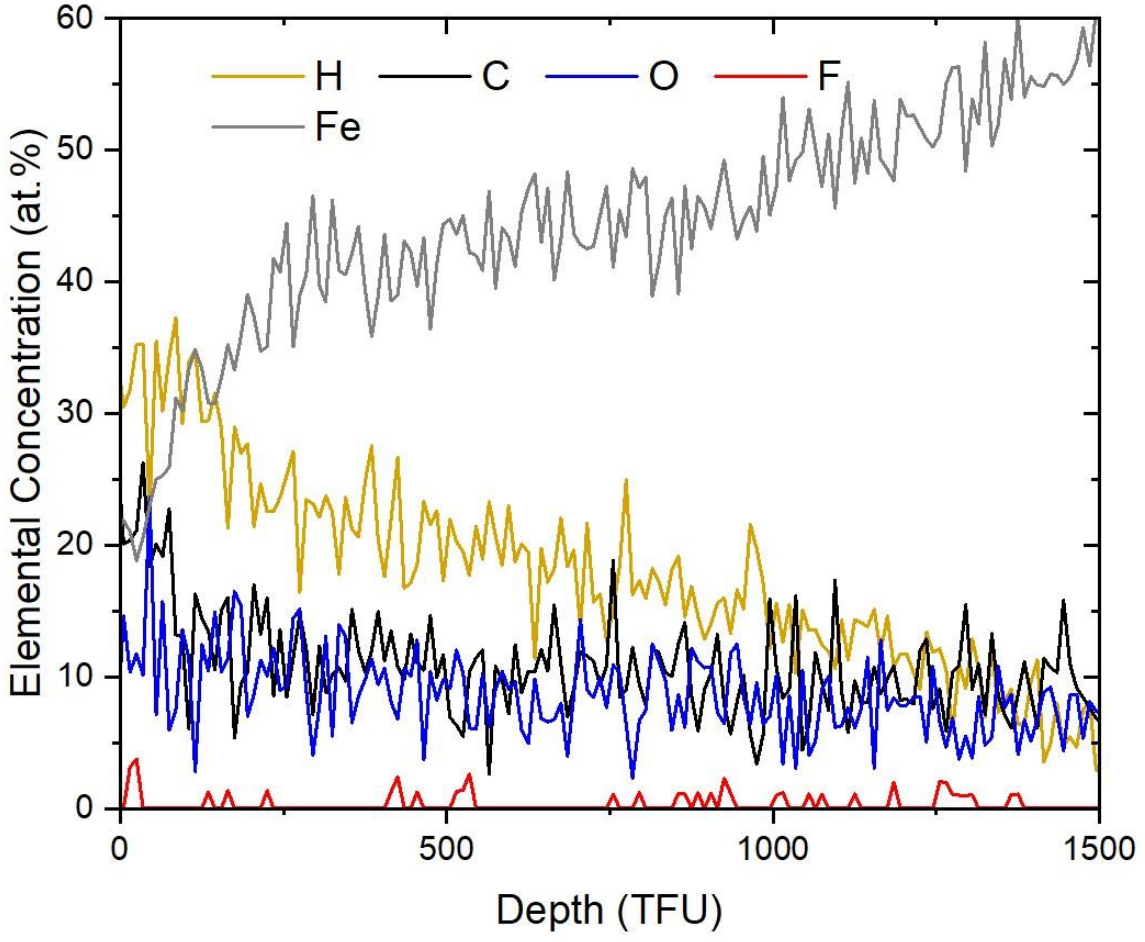
Results – Swab sampling method

Pre swabbing



Fluorine -Layer Steel

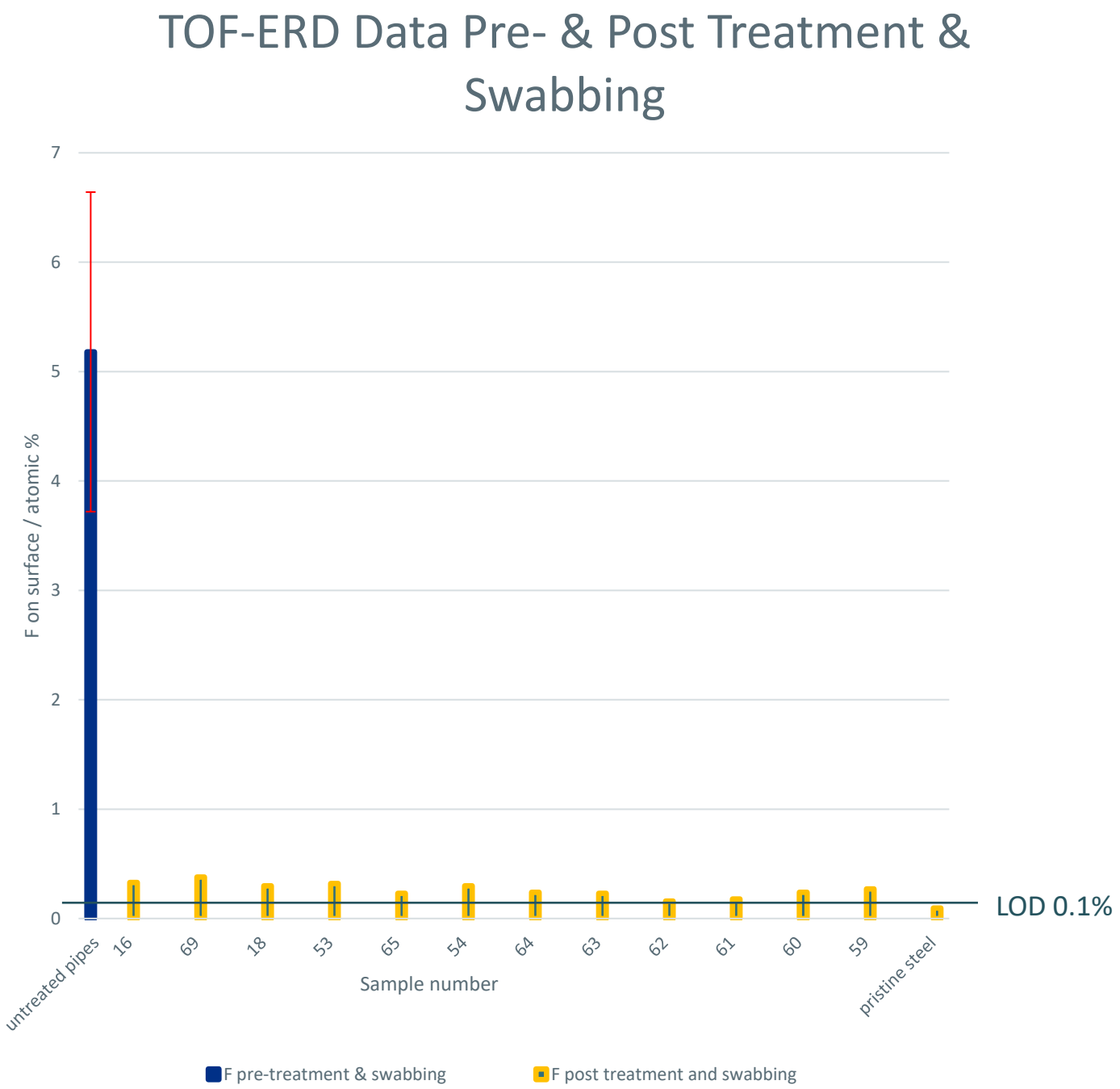
Post swabbing



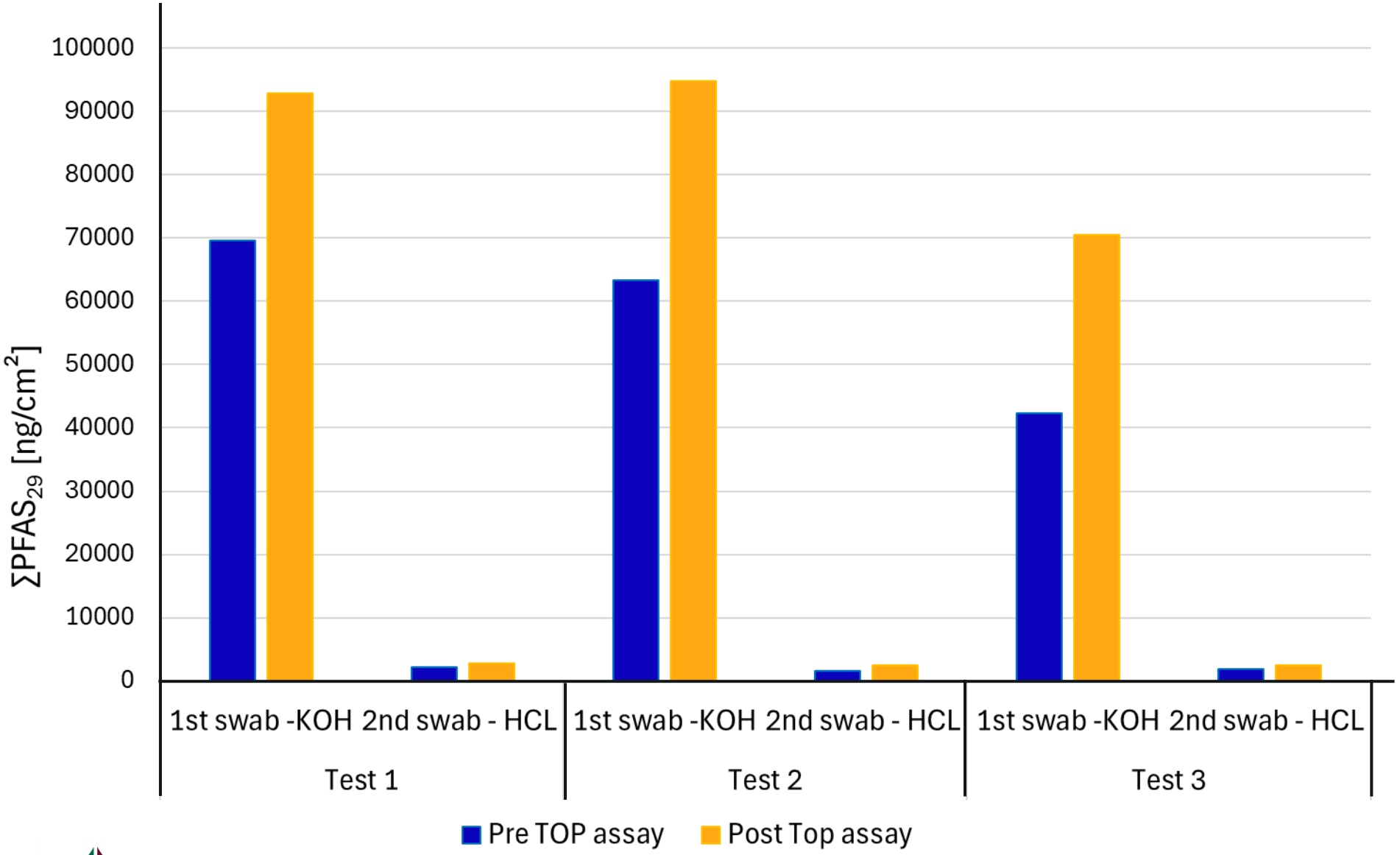
Fluorine Steel

Results

- Swab sampling methodology is usally removing >90% of PFAS from surfaces
- Low level of fluorine (baseline: 0.2-0.3 at.%) remains on surfaces after swabbing
- Pristine steel contained 0.97 at% F
- Limit of Detection is 0.1% at%F



Results – Extraction of swabs



Swab Sampling Implementation

Important for performing the swab sampling:

- Consistency
- Apply significant pressure (rub hard)
- Do not oversoak the swab, solvent will run off and be lost (let solvent drip off the cotton swab before application)
- Repeat swabs to ensure long enough application
  - standardization progressing
  - applicable in practice and good method to determine total PFAS mass on surfaces
- Commercially available using sampling protocol via ALS laboratories

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Summary

- PFAS if firefighting foams cannot be detected using targeted analysis i.e. USEPA 1633
- PFAA-precursors in foams require assessment to prove decontamination
- Solid surface PFAS analysis required to assess if PFAS remain attached
- A swab test methodology has been developed to quantitatively determine the mass PFAS remaining on surfaces and is commercially available

Ian Ross

Bjorn Bonnet

Lutz Ahrens

Matthew Sharpe

Geraint Williams

Thank You!!

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