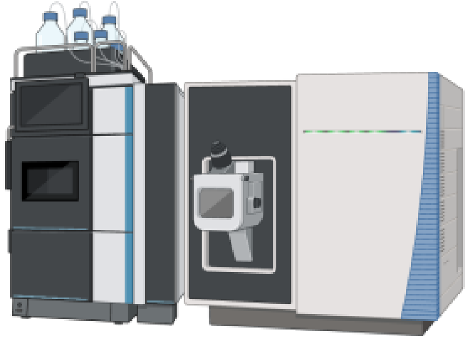


Application of Nontargeted Analysis During Hydrothermal Treatment of PFAS

Shilai Hao

Estelle Cronmiller, Juan Sanchez, Timothy Strathmann, Christopher Higgins

06/2/2024

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

PFAS@MINES

ThermoFisher SCIENTIFIC

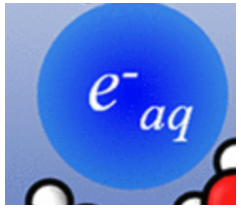
Outline

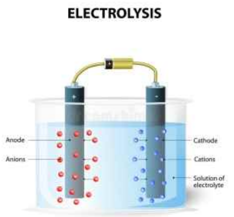
1. The need of nontargeted analysis for PFAS treatment technologies
2. Nontargeted analysis (NTA) **workflow**
3. NTA example 1: Identify the **nonfluorinated recalcitrant DOC** during hydrothermal treatment of foam fractionate
4. NTA example 2: Identify **fluorinated transformation products** during hydrothermal treatment of PFOS with Ru/C
5. Conclusions

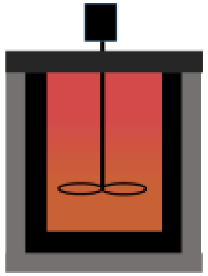
Not every treatment technology can fully defluorinate PFAS

Destructive technologies

1. Incineration
2. Hydrated electron
3. Electrochemical oxidation
4. Sonochemical
5. Supercritical water oxidation
6. **Hydrothermal treatment**
7. …

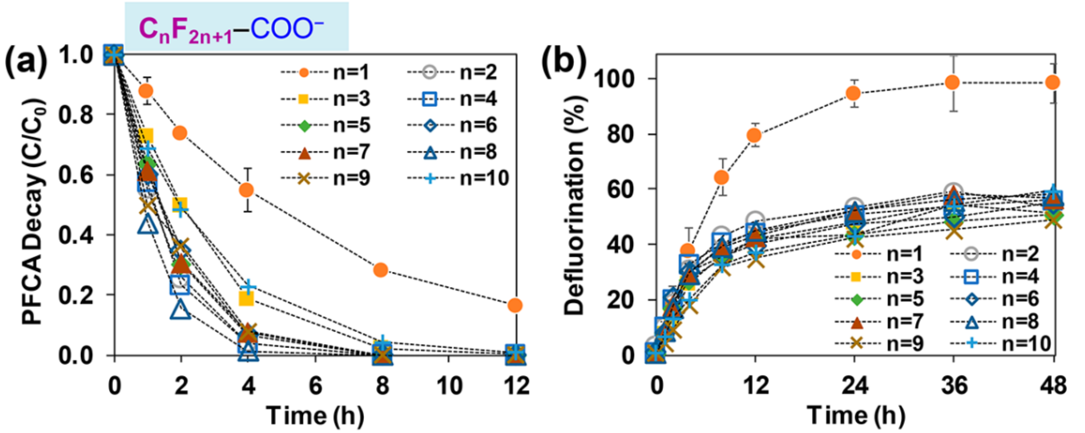







1. The lag between degradation and defluorination

UV/Sulfite of PFCAs

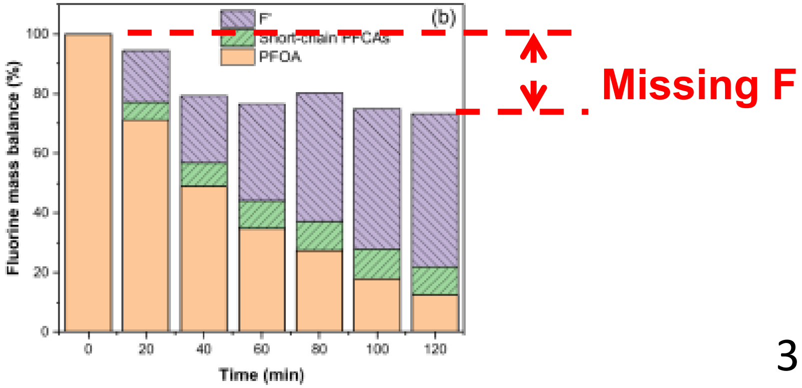


100% Degradation

60% Defluorination

2. The missing fluorine mass balance

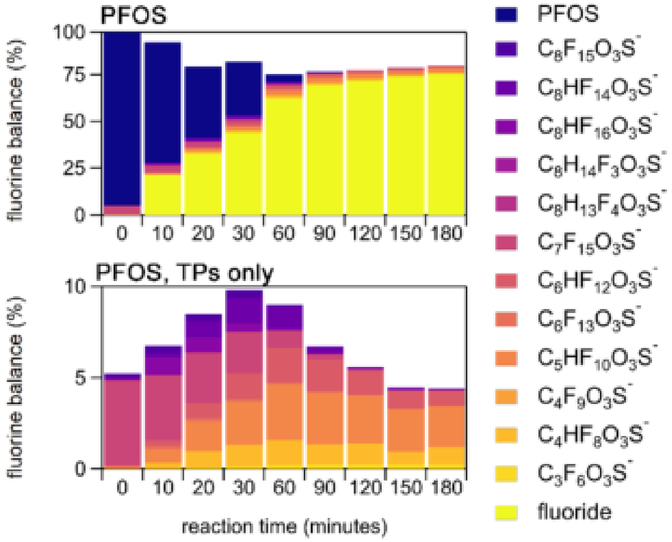
Plasma treatment of PFOA



Bentel et al, *Environ. Sci. Technol.* 2019, 53, 7, 3718–3728;
Zhang et al., *Environ. Sci. Technol.* 2021, 55, 23, 16067–16077

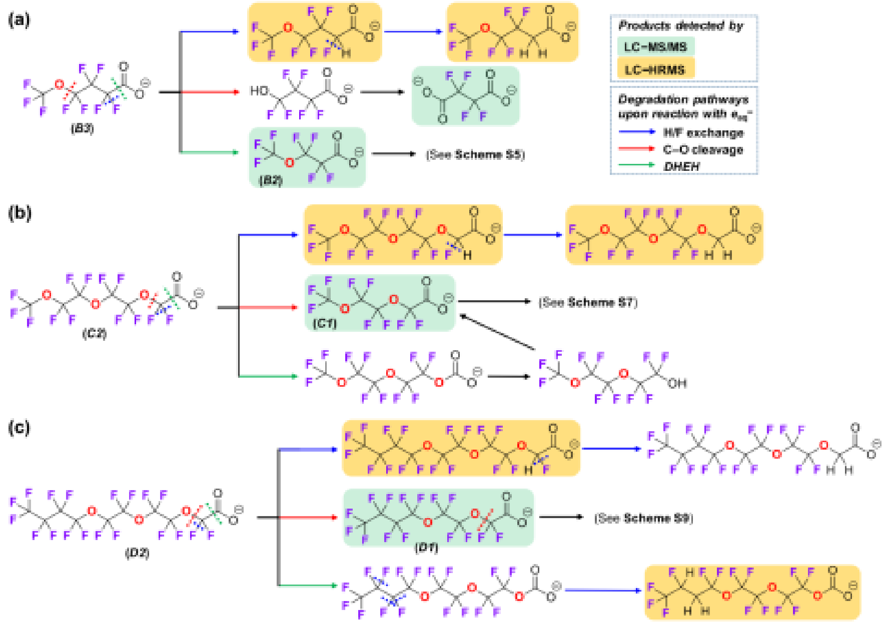
NTA is needed to help understand PFAS treatment technologies

1. **Identify PFAS transformation products during treatment**
2. **Close fluorine mass balance and confirm no products of incomplete destruction (PIDs)**
3. **Elucidate the reaction mechanism**



Bowers et al., Environ. Sci.: Processes Impacts, 2023, 25, 472-483

Bentel et al., *Environ. Sci. Technol.* 2020, 54, 4, 2489–2499



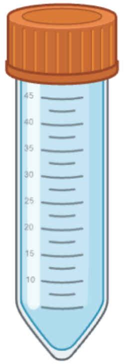
Transformation products from PFOS degradation

Degradation pathways for perfluoroalkyl ether carboxylate

HRMS data acquisition with LC-Orbitrap-MS

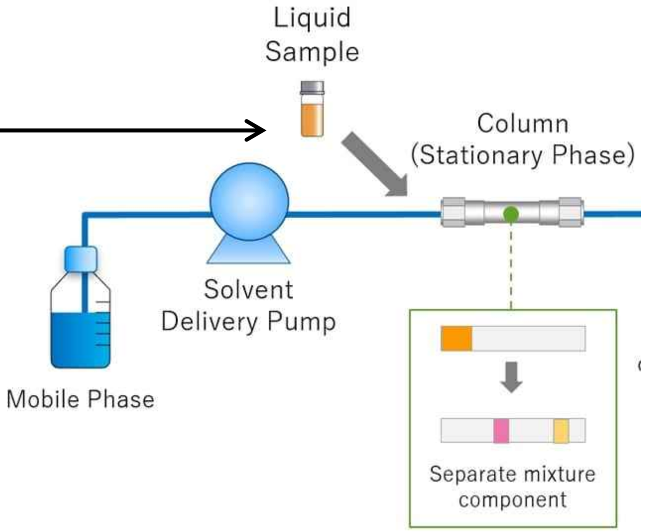
Sample preparation

100-1000X dilution



Mix with IS and methanol

HPLC Separation



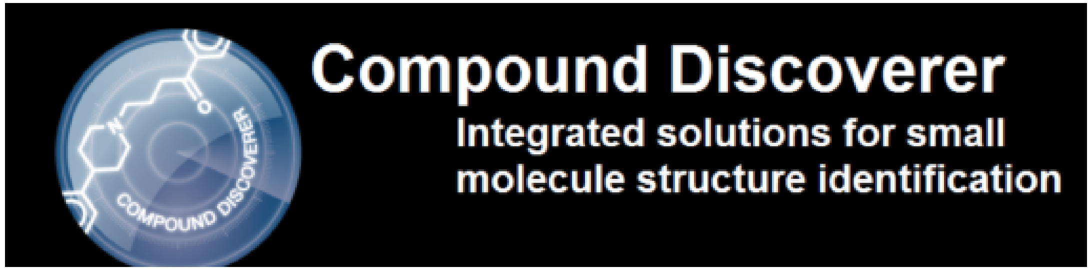
1. C18 column
2. 50 uL injection
3. Mobile phase: 20 mM ammonium acetate aqueous solution and methanol, gradient elution

Mass Spectrometry Detection

1. ESI NEG mode
2. Full scan-DDA mode

NTA workflow with Compound Discoverer

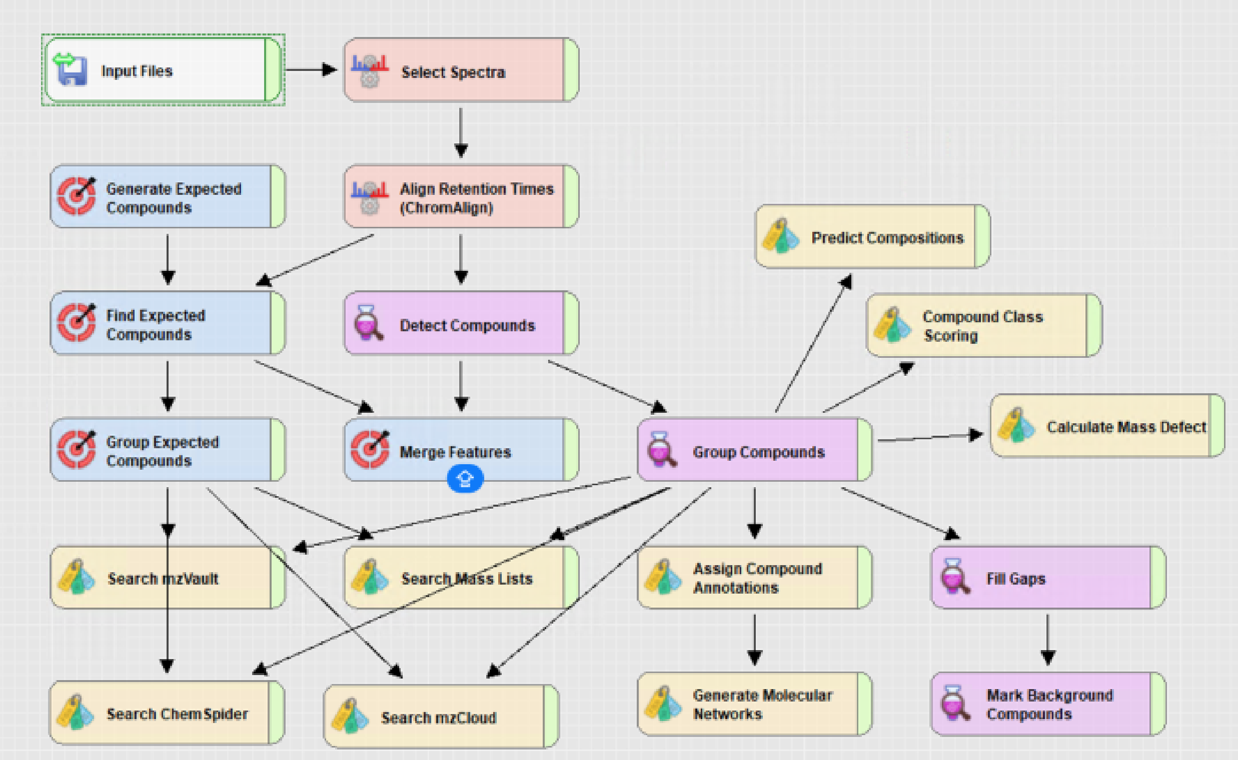
Compound Discoverer from Thermofisher



A comprehensive software workflow for non-targeted analysis of per- and polyfluoroalkyl substances (PFAS) by high-resolution mass spectrometry (HRMS)

Authors Goal

Nontargeted analysis workflow



NTA workflow for PFAS is available in the most updated CD 3.3

NTA workflow with Compound Discoverer (CD 3.3)

PFAS and hydrocarbon surfactant list and library that we used in the CD

1. PFAS list from NIST, Mines, and Duke University including 80 targeted + 4968 suspected structures. Some of them have MS2 library

2. AFFF hydrocarbon surfactant list from adapted Raymmah et al (Jenniffer Field group's publication)

NIST PUBLIC DATA REPOSITORY 1.11.2

Public Data Resource

Suspect List of Possible Per- and Polyfluoroalkyl Substances (PFAS)

Contact: Benjamin Place..

Identifier: doi:10.18434/mds2-2387

Version: 1.7 ... Revised: 2023-01-05

Description

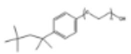
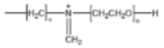
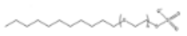
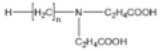
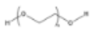
A list of structures (and other identifiers) of possible per- and polyfluoroalkyl substances (PFAS). The data provided in the PFAS Suspe
and users, including peer-reviewed literature, patent literature, and public websites. Therefore, the quality and accuracy of the compou
not been validated. The National Institute of Standards & Technology does not endorse or provide any assessment of confidence with

Environmental Science & Technology Article
Cite This: Environ. Sci. Technol. 2019, 53, 8068−8077 pubs.acs.org/est

Suspect Screening of Hydrocarbon Surfactants in AFFFs and AFFF-Contaminated Groundwater by High-Resolution Mass Spectrometry

Raymmah Aleyda García,[†] Aurea C. Chiaia-Hernández,[‡] Pablo A. Lara-Martin,[§] Martin Loos,[∥] Juliane Hollender,[⊥,#] Karl Oetjen,[∇] Christopher P. Higgins,[∇] and Jennifer A. Field*[,○]

Table 1. Hydrocarbon Surfactant Classes Classified by Repeating Units in 3M and Fluorotelomer-Based AFFFs (Buckeye, Ansul, Chemguard, National Foam)[a]

Class	Structure	3M 1993a	3M 1993b	3M 1988	3M 1989	Buckeye 2009	Ansul 2012	Chemguard 2010	National Foam 2003
Octylphenol polyethoxylate[a,b,c] EOn		ND	ND	3-16	ND	4-9	4-10	4-20	ND
linear alcohol ethoxylate[c] Cn / EOn		10/2-10	10/2-10	ND	ND	10/2 -7	ND	ND	ND
Ethoxylated Cocoamine[c] Cn / EOn		ND	ND	ND	ND	14,15,16/3	ND	ND	14,15,16,17/3
Alkyl ether sulfate[b] Cn / EOn		15,16,17/1 12/1-8	15,16,17/1 12/1-7	ND	15,16,17/1 12/1-6	14/1,2,3 12/1-7	15,16,17/1	14/1,2,3 12/1-10	15,16,17/1
Alkyl amido-dipropionates[b] Cn		ND	ND	ND	ND	12,13,14	ND	12,13,14	ND
linear alkyl benzene sulfonate[b] Cn		11,12,13	10,11,12,13	ND	10,11,12,13	10,11,13	10,11,12,13	ND	10,11,12,13
Alkyl sulfates[a,b,c] Cn		8,10,12	8,10,12	ND	8,10,12	8,9,10,11,12	ND	8,9,10,12	8,9,10,11,12
Polyethylene Glycol EOn		8-13	ND	8-13	8-13	8-13	10-13	ND	ND

[a]Multiple repeating units are separated by "/". ND = Not detected, which means that no homologous series matched that of the suspect list. Surfactants in AFFF literature listed by (a) Pabon et al. 2002, (b) Thomas Marin 2012, and (c) U.S. Patent No. 6,015,838.

Most mass lists and libraries are available in the most updated CD 3.3

General confidence level and PFAS confidence level (PCI)

General confidence level (Schymanski et al)

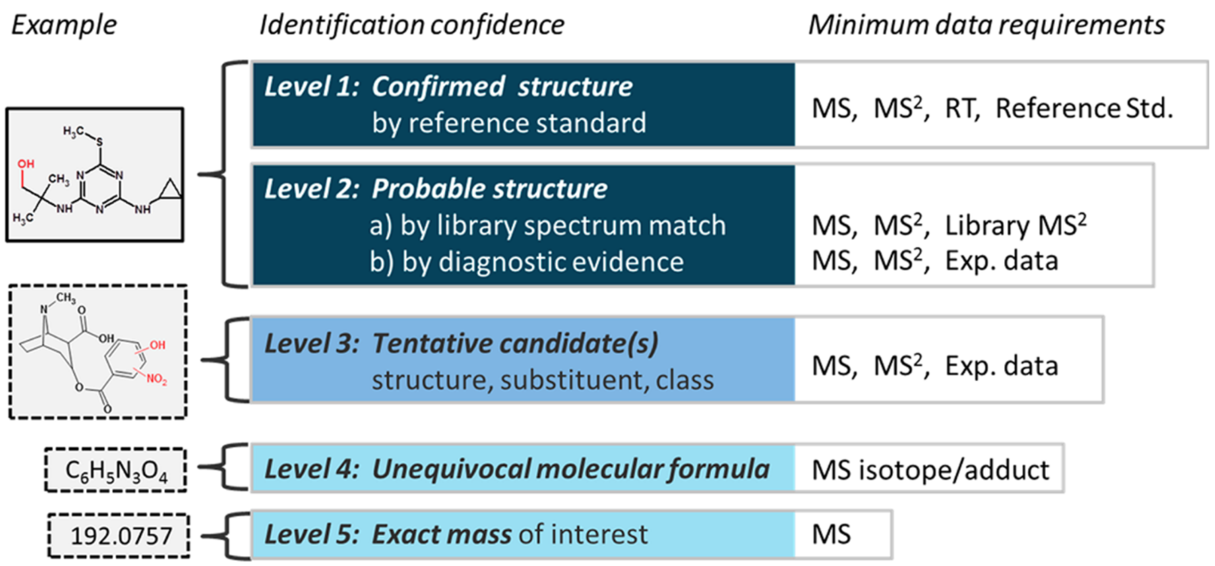


Figure 1. Proposed identification confidence levels in high resolution mass spectrometric analysis. Note: MS^2 is intended to also represent any form of MS fragmentation (e.g., MS^e, MS^n).

PFAS confidence level (Charbonnet et al)

Level	Identification Confidence	Accurate Mass	Mass Defect	Isotopic Pattern Match	Consistent RT
Level 1a	Confirmed by reference standard	✓	✓	✓	✓
Level 1b	Indistinguishable from reference standard	✓	✓	✓	✓
Level 2a	Probable by library spec. match	✓	✓	✓	✓
Level 2b	Probable by diagnostic fragmentation evidence	✓	✓	✓	✓
Level 2c	Probable by diagnostic homologue evidence	✓	✓	✓	✓
Level 3a	Positional isomer candidates	✓	✓	✓	✓
Level 3b	Fragmentation-based candidate	✓	✓	✓	✓
Level 3c	Circumstantial candidate with fragmentation evidence	✓	✓	✓	✓
Level 3d	Circumstantial candidate with homologue evidence	✓	✓	✓	✓
Level 4	Unequivocal molecular formula	✓	✓	✓	
Level 5a	PFAS suspect screening exact mass match	✓ (suspect list match)			
Level 5b	Nontarget PFAS exact mass of interest	✓	✓		

Schymanski et al., *Environ. Sci. Technol.* 2014, 48, 4, 2097–2098
Charbonnet et al., *Environ. Sci. Technol. Lett.* 2022, 9, 6, 473–481

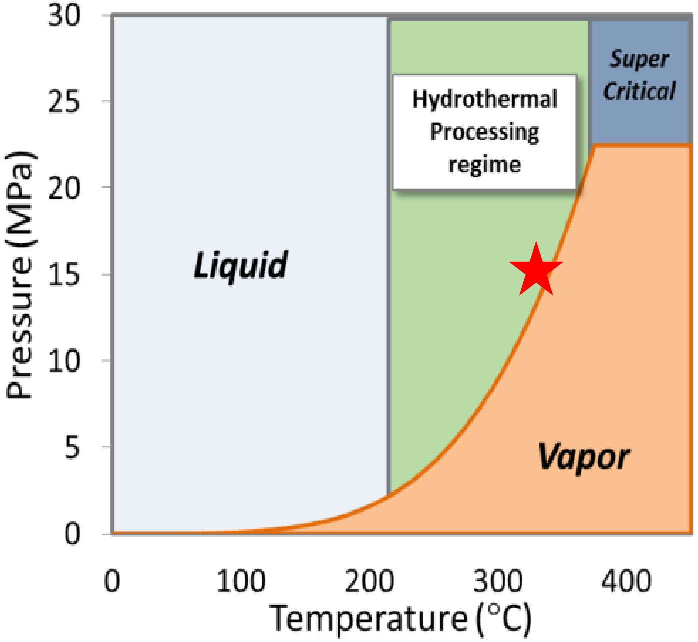
More criteria in the paper

The unique hydrothermal technology used for PFAS destruction

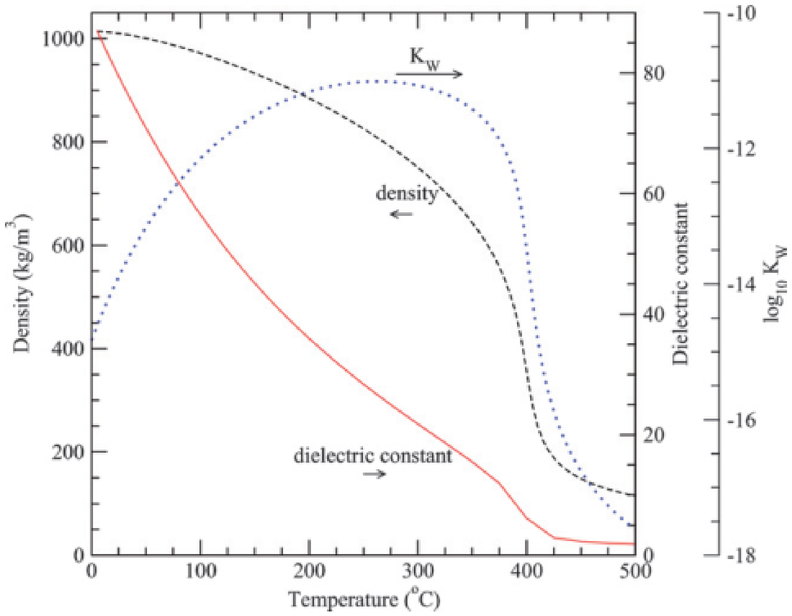
Hydrothermal Media

- Elevated temperatures and pressures (200 – 374 °C , 2-22 MPa)
- Water properties changed dramatically.
- Avoids parasitic energy losses associated with water vaporization
- Less energy required to heat liquid water to hydrothermal condition than to evaporate water at room temperature.

H_2O: $\Delta H_{25 \rightarrow 300} = 1.2$ MJ/kg
$\Delta H_{vap} = 2.5$ MJ/kg



High Temperature
High Pressure!



Peterson, Andrew A., et al. *Energy & environmental science* 1.1 (2008): 32-65.

Example 1: Hydrothermal alkaline treatment of foam fractionate

µg/L PFAS

Foam fractionation (FF)

mg/L – g/L PFAS

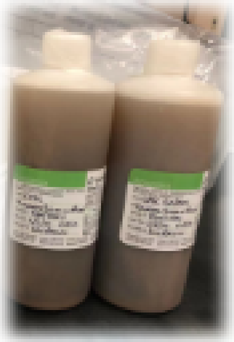
Foam concentrate
(200 kL – 0.6 L)

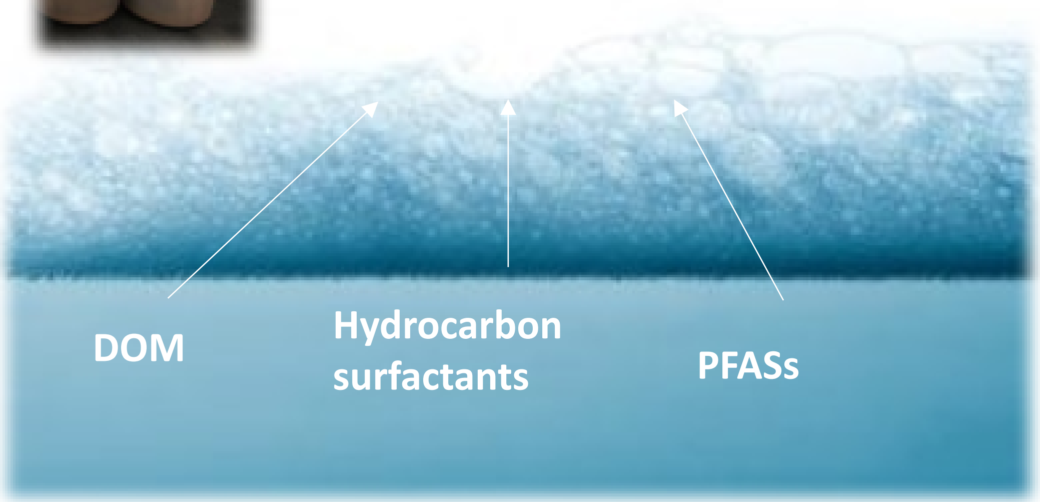
>99% destruction

Hydrothermal alkaline treatment (HALT)

The NTA of post-treatment samples did not show transformation products of PFASs other than targeted and suspected PFAS decay

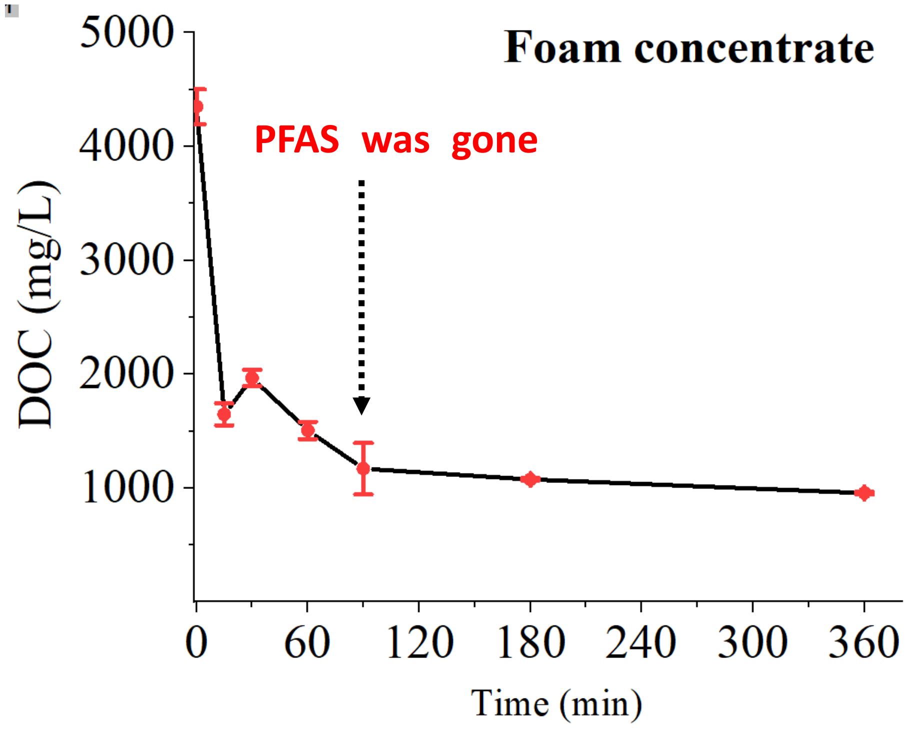
Example 1: Recalcitrant dissolved organic carbon during hydrothermal





HALT

DOC degradation over reaction time



PFASs contributed to TOC: **16%**

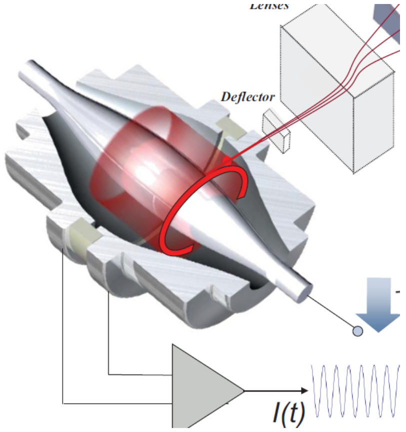
HALT-stable DOC is more recalcitrant than PFAS

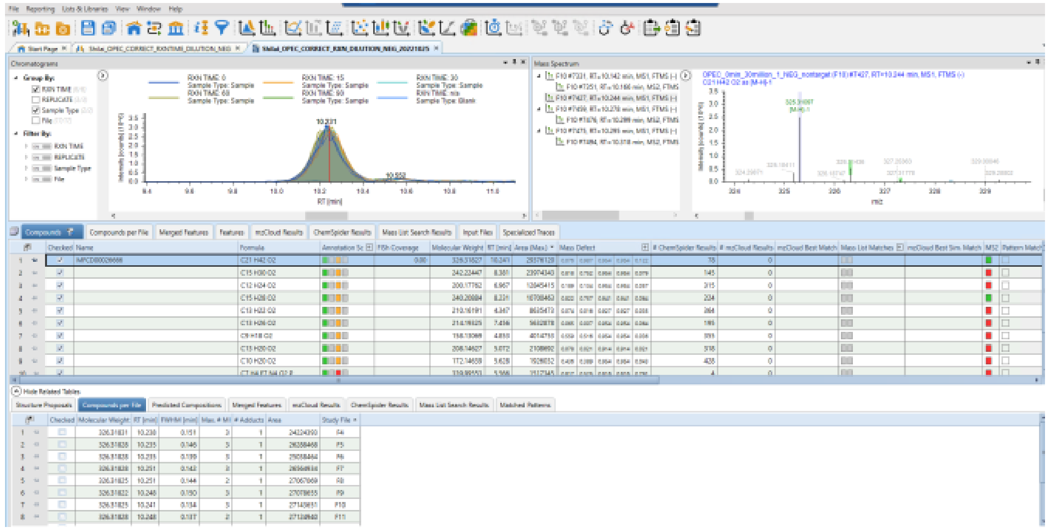
Hao et al., *Environ. Sci. Technol.* 2023, 57, 44, 17154–17165

Example 1: Homologs of $C_nH_{2n}O_2$ identified at confidence level 2

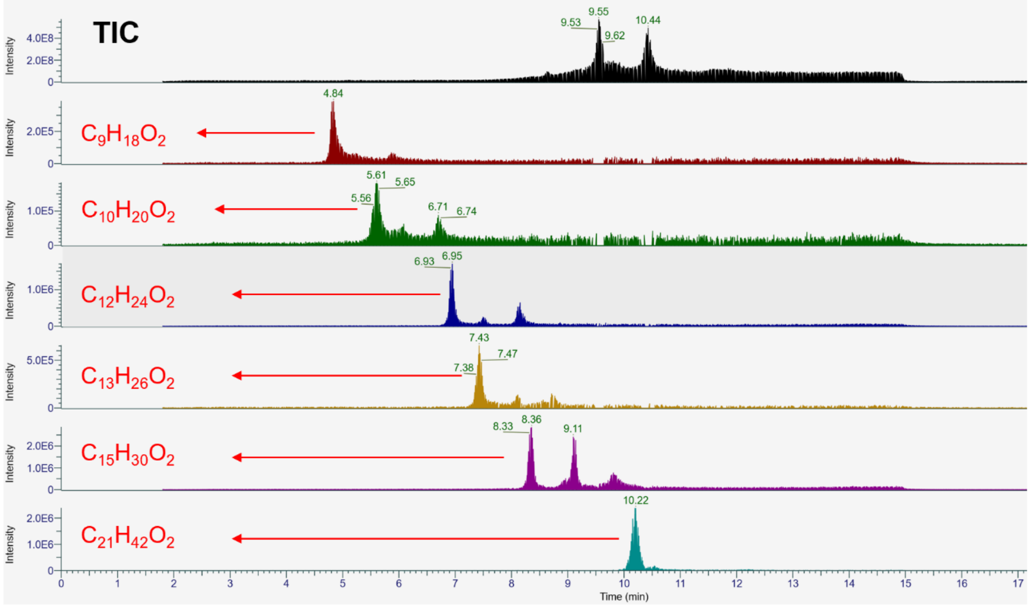
COLORADO SCHOOL OF MINES

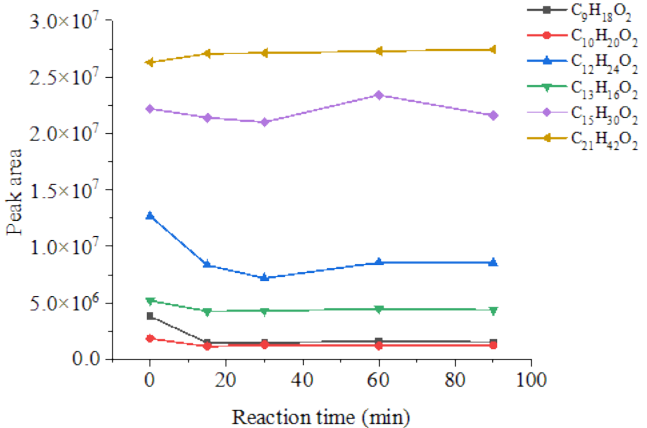
LC-Orbitrap-MS for non-targeted analysis

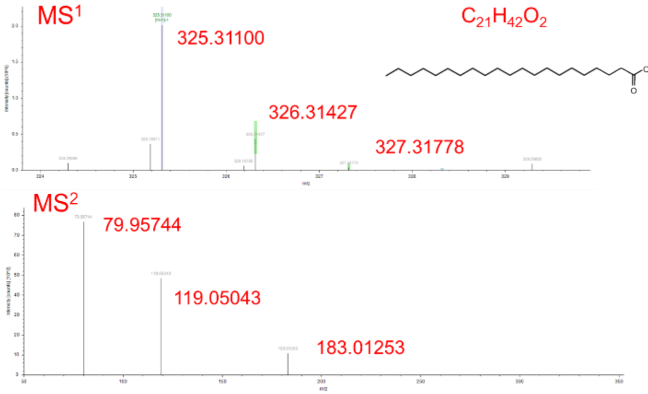




A series of homologs $C_nH_{2n}O_2$ identified



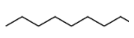
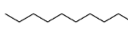
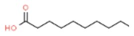
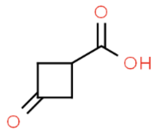
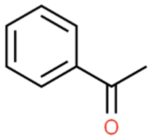
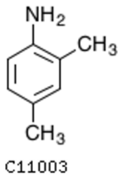
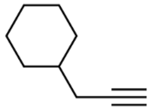




Example 1: Other hydrocarbon surfactants identified

A total of 129 molecules associated with different structures including aromatic and aliphatic functional groups were identified

Table 1 The HALT-stable molecules in foam concentrate sample detected by LC-Orbitrap-MS under both ESI+ and ESI- m

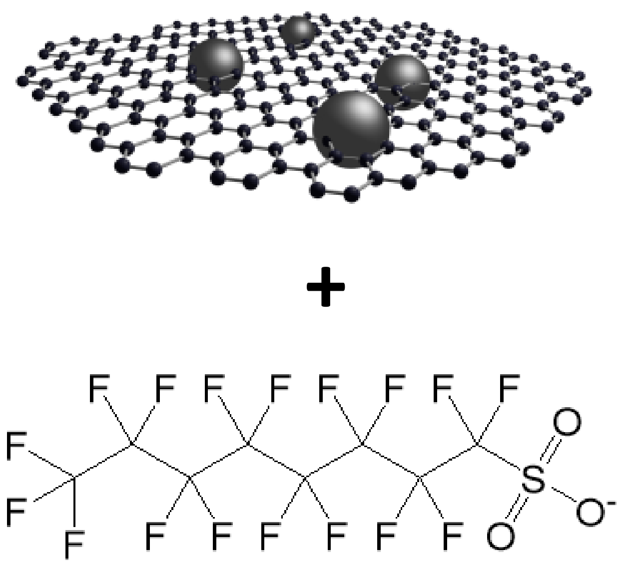
No.	Molecular formula	Molecular weight (Da)	Retention time (min)	Peak area	ESI mode	Confidence level	Suspect analyte	Structure	
1	C9H18O2	158.13069	4.853	4.01E+06	NEG	3	1-nonanoic acid		
2	C11H20O	168.15145	5.155	2.54E+06	NEG	3	10-Undecenal		
3	C10H20O2	172.14639	5.628	1.93E+06	NEG	3	Decanoic acid		
4	C12H24O2	200.17762	6.967	1.28E+07	NEG	3	lauric acid		
							cyclohexadien-1-one		
25	C21H35O8P	446.20667	6.29	1.18E+07	NEG	4	N/A	N/A	N/A
26	C5H6O3	114.03162	2.668	3.02E+07	POS	3	3-Oxocyclobutanecarboxylic acid		ChemSpider
27	C8H8O	120.05746	5.103	1.89E+06	POS	3	Acetophenone		ChemSpider
28	C8H11N	121.08908	4.083	6.35E+07	POS	3	2,4-Xylidine		mzCloud
29	C9H14	122.1095	5.126	5.63E+06	POS	3	2-Propyn-1-ylcyclohexane		ChemSpider

Hao et al., *Environ. Sci. Technol.* 2023, 57, 44, 17154–17165

Example 2: Hydrothermal reaction of PFOS with Ru/C

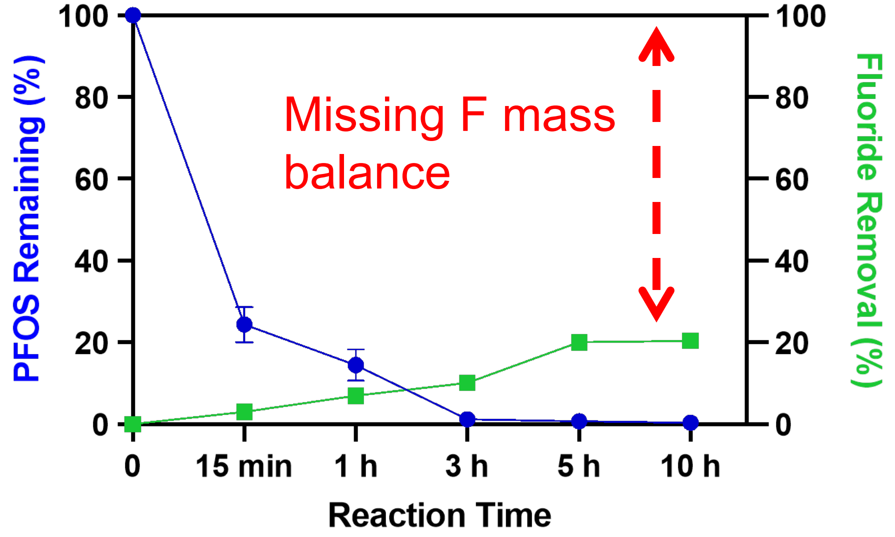
A study to explore the heterogeneous catalyst to degrade PFOS in hydrothermal reaction

Ru/C Catalyst (100 mg/mL)



PFOS (C8) 60 mg/L

Conditions: 350 °C, No NaOH



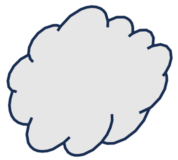
What products were PFOS transformed into other than fluoride?

More details in the poster presentation
(E5. Innovative Ex Situ PFAS Destruction Technologies)

Cronmiller et al., *manuscript in prep*

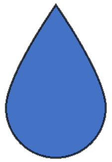
Example 2: Comprehensive approaches to identify TPs

Hydrothermal reaction of PFOS with Ru/C



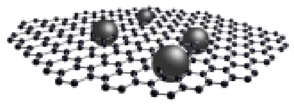
Gas phase

- GC-MS
- GC-TCD



Liquid phase

- Targeted analysis (PFOS decay)
- ISE Probe (defluorination)
- Nontargeted analysis (TPs identification)



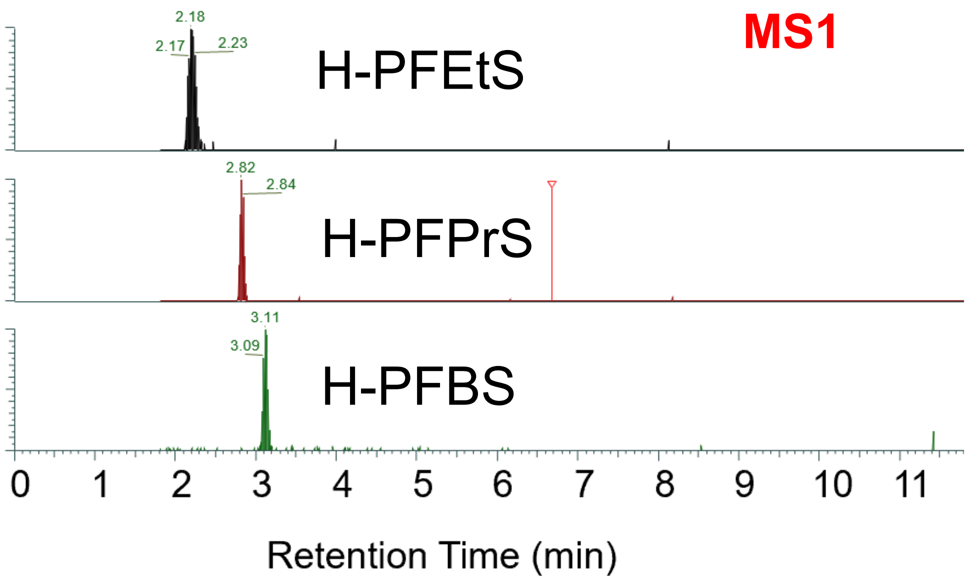
Solid phase

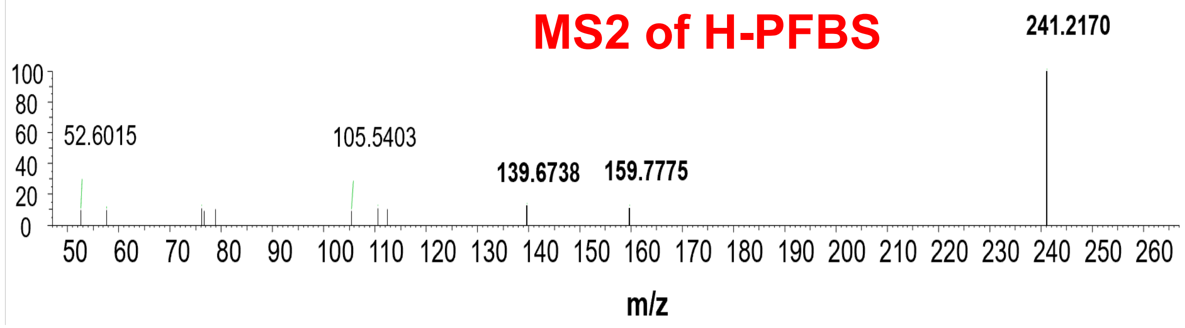
- Organic solvent extraction for further analysis

Cronmiller et al., *manuscript in prep*

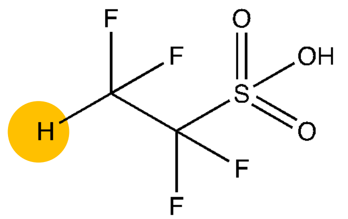
Example 2: Comprehensive approaches to identify TPs

Homologs of H-PFSAs

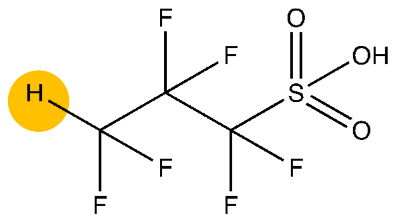




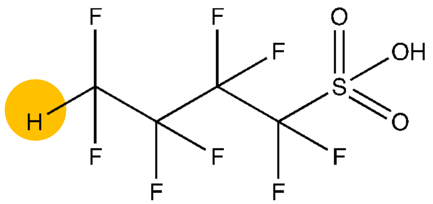
Molecular structures of H-PFSAs



H-PFEtS (C2)



H-PFPrS (C3)

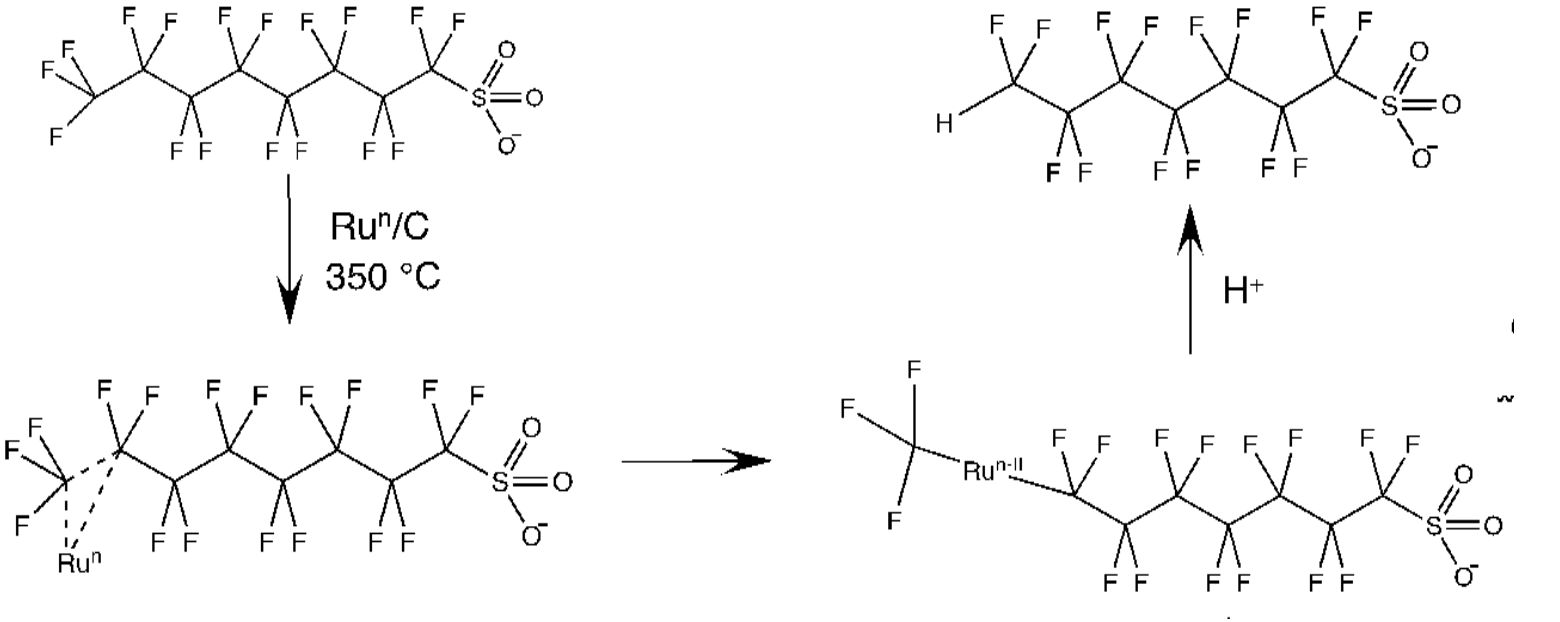


H-PFBS (C4)

Confirmed with standards

Example 2: Degradation pathway we proposed

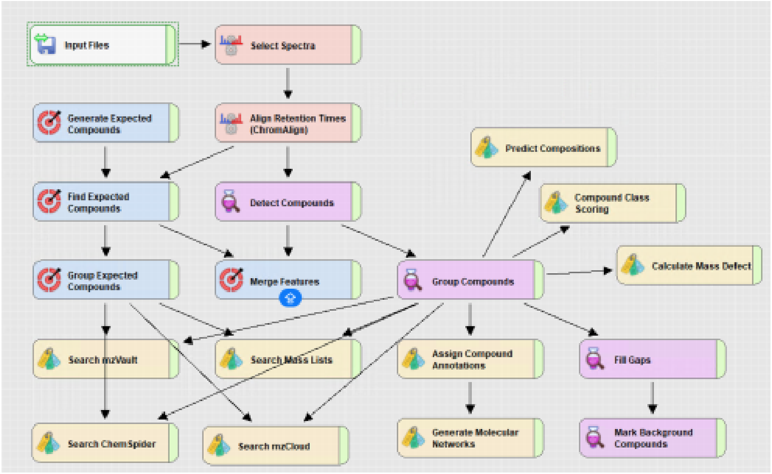
Semiquantitative analysis showed the total mass of H-PFSAs accounted for **~5% of total F** in post-treatment samples. We proposed a portion of the degradation pathway

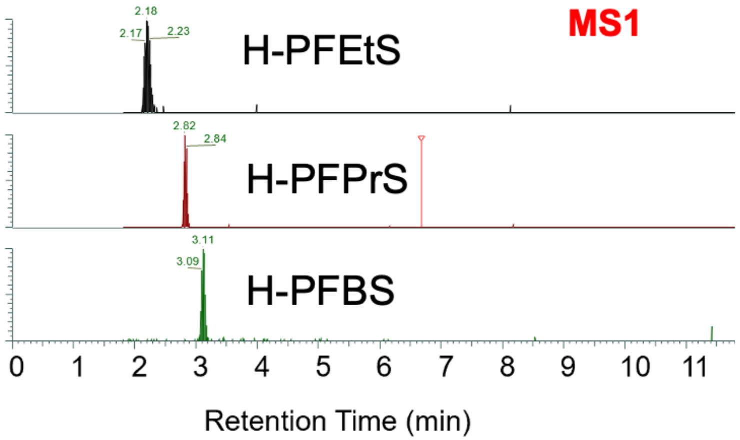


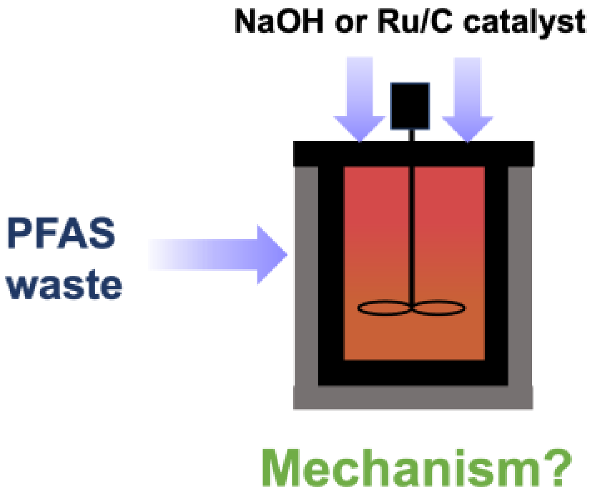
The complete mechanism for degradation and defluorination will be shown in the poster presentation

Conclusions

1. A NTA **workflow** for PFAS and hydrocarbon surfactant analyses was proposed
2. NTA revealed recalcitrant **hydrocarbon surfactants and PFAS transformation products during** hydrothermal treatment
3. NTA is a useful tool to **close fluorine mass balance and explore reaction mechanisms** for PFAS treatment technologies







PFAS@MINES

THANK YOU!

Prof. Higgins

Prof. Strathmann

Estelle Cronmiller

Juan Sanchez

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

SERDP ESTCP

ER23-8372
ER18-1501
ER24-4143