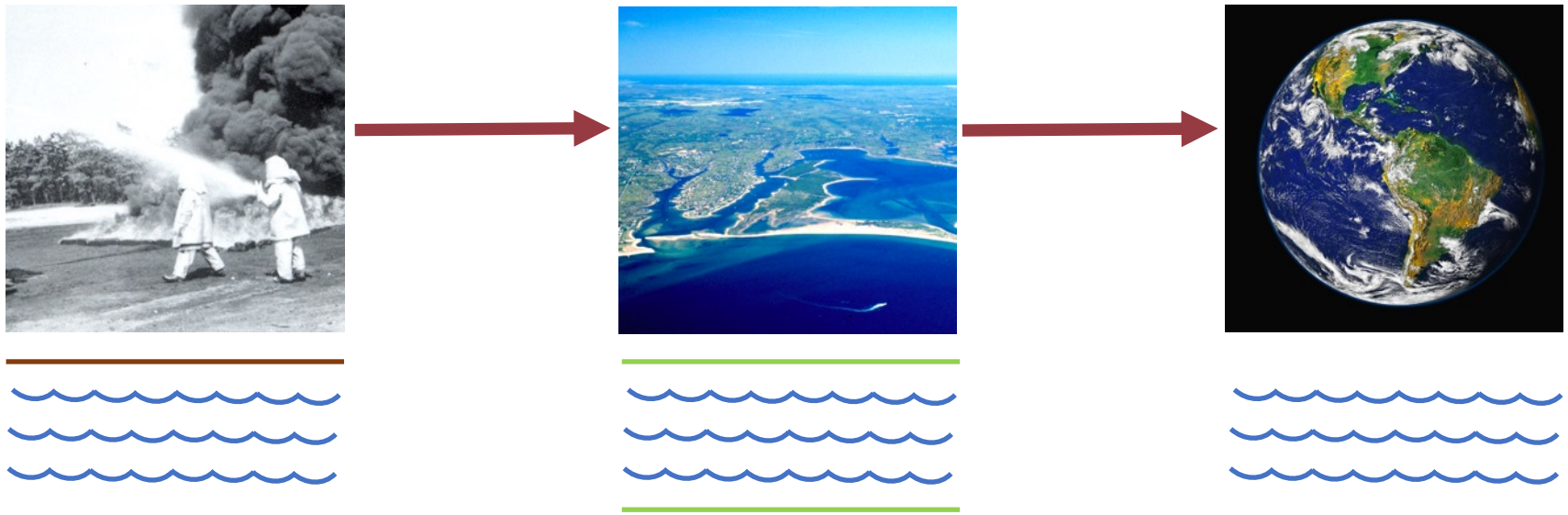
Using EOF and the TOP Assay to Understand PFAS Biogeochemistry Downstream of Historical Fire-fighting Training



Bridger Ruyle

The Science of PFAS: Public Health and the Environment

April 5, 2022

STEEP
Sources, Transport, Exposure & Effects of PFASs
UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

Biogeochemistry of Global Contaminants
HARVARD

Acknowledgements

Dr. Elsie Sunderland
Heidi Pickard
Dr. Colin Thackray
Dr. Cindy Hu

Dr. James McCord
Dr. Mark Strynar

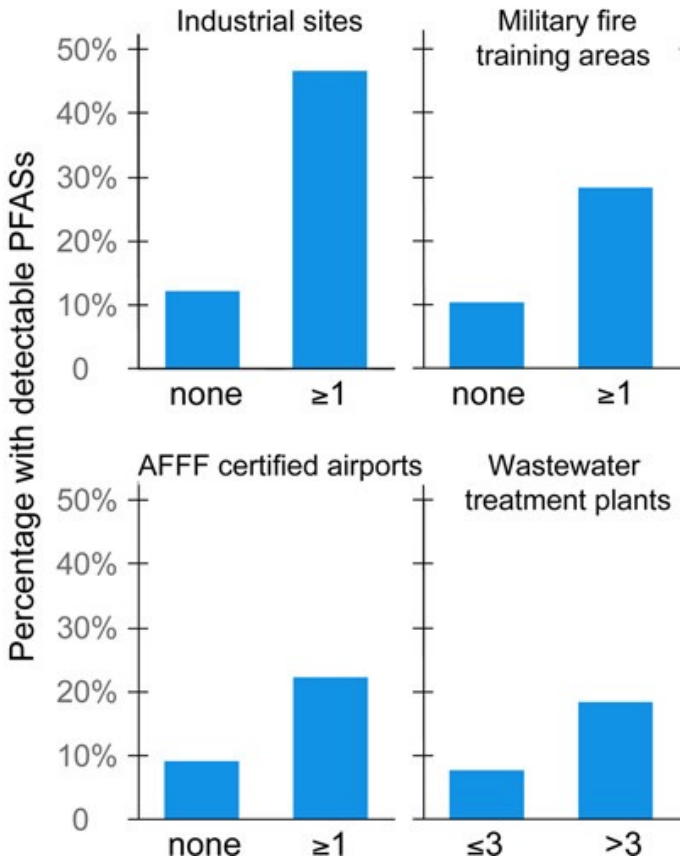
Denis LeBlanc
Dr. Andrea Tokranov

Dr. Suzanne Fenton
Kevin Mauge-Lewis

Dr. Craig Butt

Dr. Chad Vecitis

AFFF are major sources of PFAS to the environment



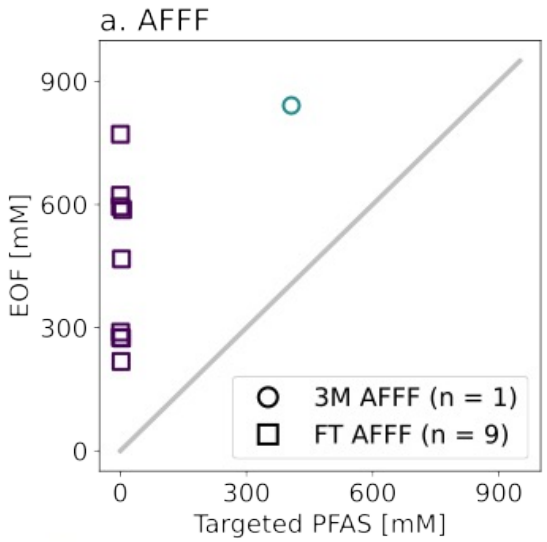
UCMR 3: Data from Hu et al. 2016

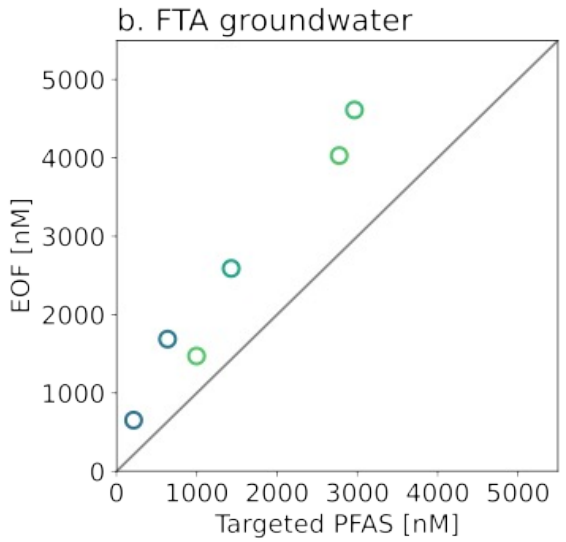
CAS	Component Name	Percent
Not available	Non-hazardous ingredients	60-90
112-34-5	Diethylene glycol butyl ether	10-20
142-31-4	Sodium octyl sulfate	1-10
64-17-5	Ethyl alcohol	1-5
107-21-1	Ethylene glycol	1-5

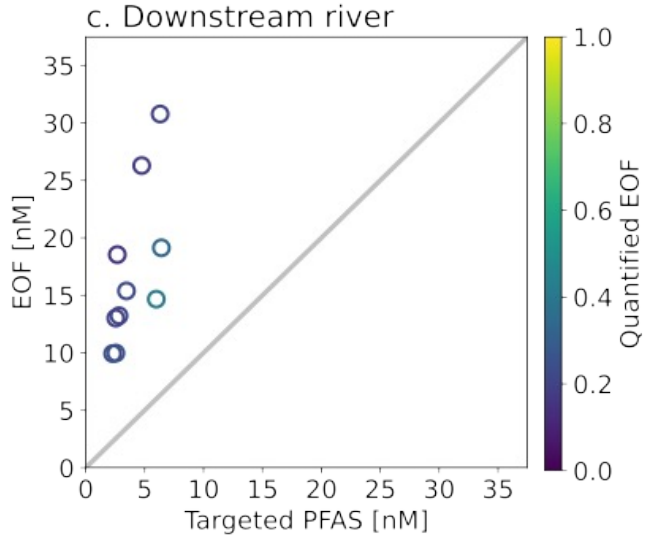
Example MSDS from AFFF currently approved on MILSPEC

Targeted analyte panels fail to capture AFFF pollution

The lack of analytical grade standards for precursors limits the ability to conduct site/exposure assessments







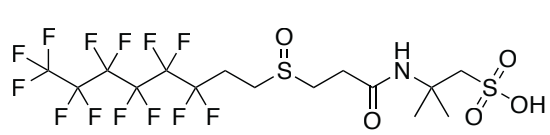
Data from

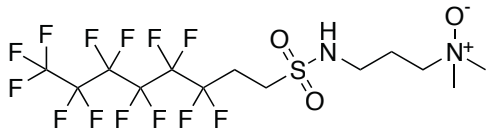
a. Ruyle et al. ES&T Letters 2021
b. Ruyle et al. in prep
c. Ruyle et al. ES&T 2021 & in progress

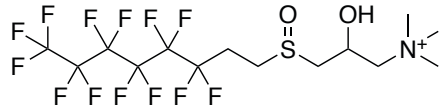
High resolution mass spectrometry can qualitatively identify untargeted precursors

However, semiquantitation based on HRMS peak area counts inconsistently reproduces quantitative approaches and lacks formalized assessment of uncertainty

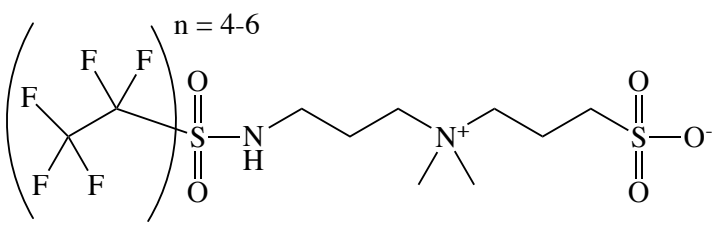
Fluorotelomer AFFF examples

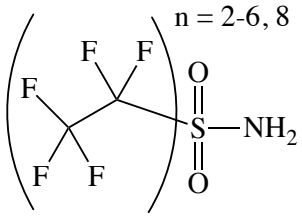






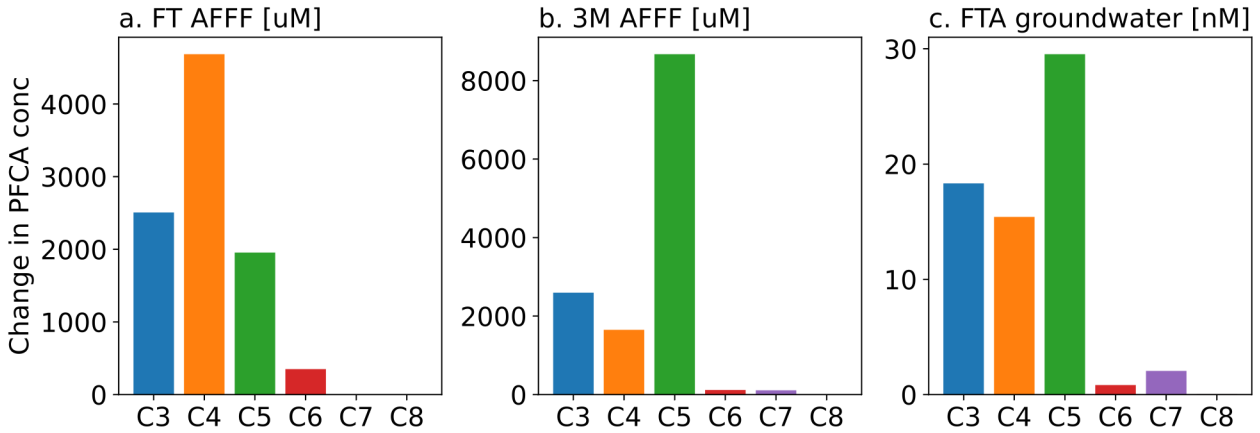
FTA Groundwater examples





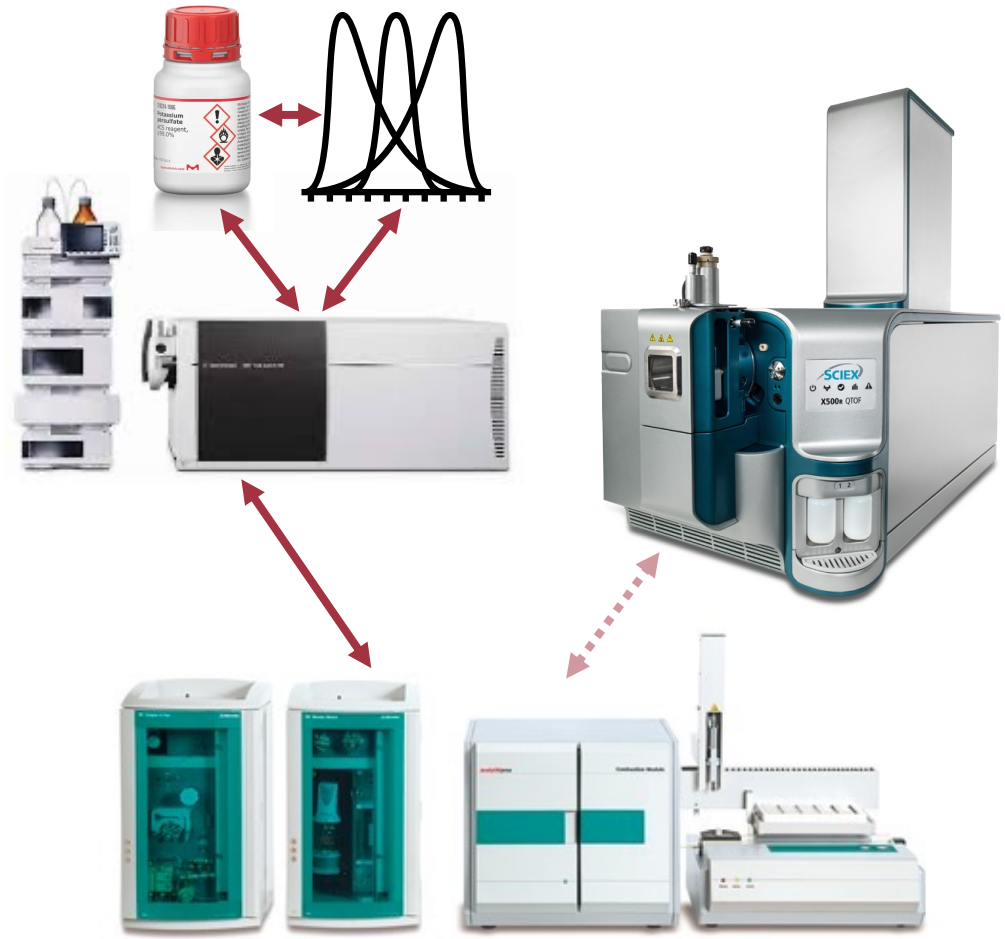
The TOP assay provides quantitative estimates of bulk precursor concentrations

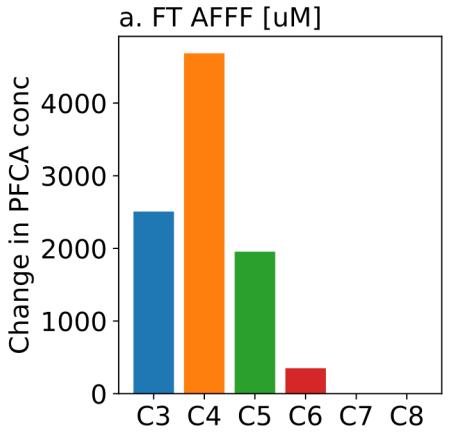
Using the sum of PFCA produced by the TOP assay underestimates actual precursor concentrations due to incomplete oxidation and production of ultrashort PFCA or fluoride



Data from
a., b. Ruyle et al. ES&T Letters 2021
c. Ruyle et al. in prep

Optimizing original precursor concentrations from TOP assay measurements





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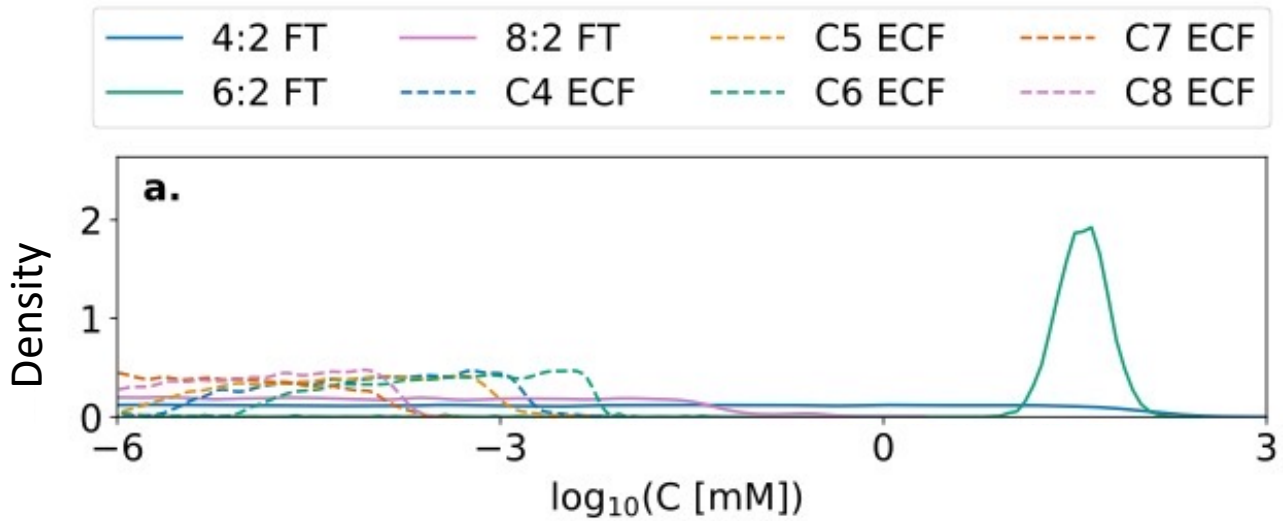
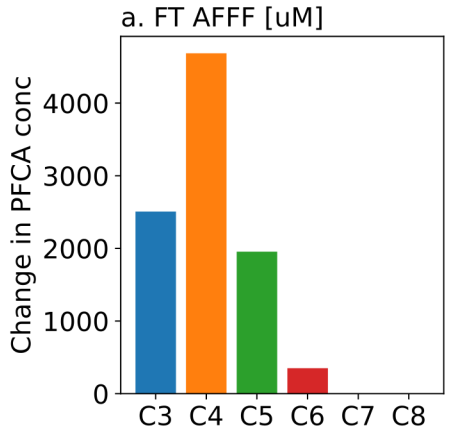


Optimizing original precursor concentrations from TOP assay measurements

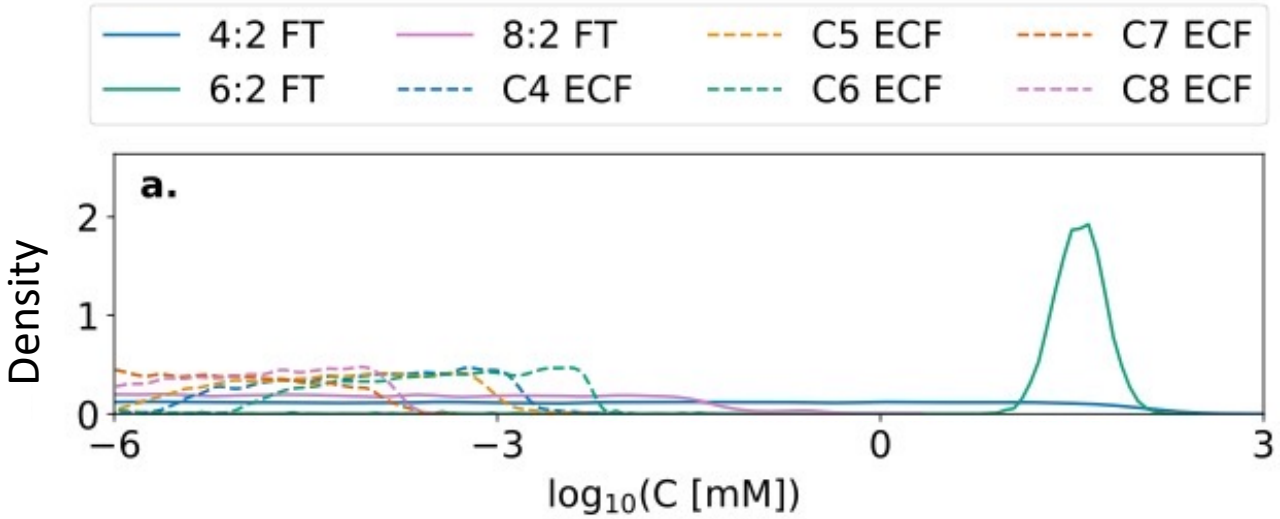
Background:
Precursors produced by fluorotelomerization (FT) and electrochemical fluorination (ECF) have unique yields in the TOP assay

Goal:
Optimize observations of ΔPFCA in the TOP assay based on yields reported in the literature using Bayesian inference

Outcome:
Quantitative estimates of original precursor concentrations grouped by the number of perfluorinated carbons and manufacturing origin



Data from Ruyle et al. ES&T Letters 2021

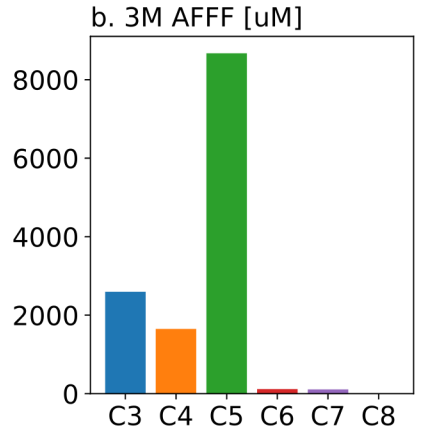


Optimizing original precursor concentrations from TOP assay measurements

x-axis = concentration
- Higher concentrations are further to the right
- Lower concentrations are further to the left

y-axis = density
- Higher densities are more likely
- Lower densities are less likely

Results
- Distribution of potential precursor concentrations
- Can be summarized by point estimates such as the mean and interquartile range



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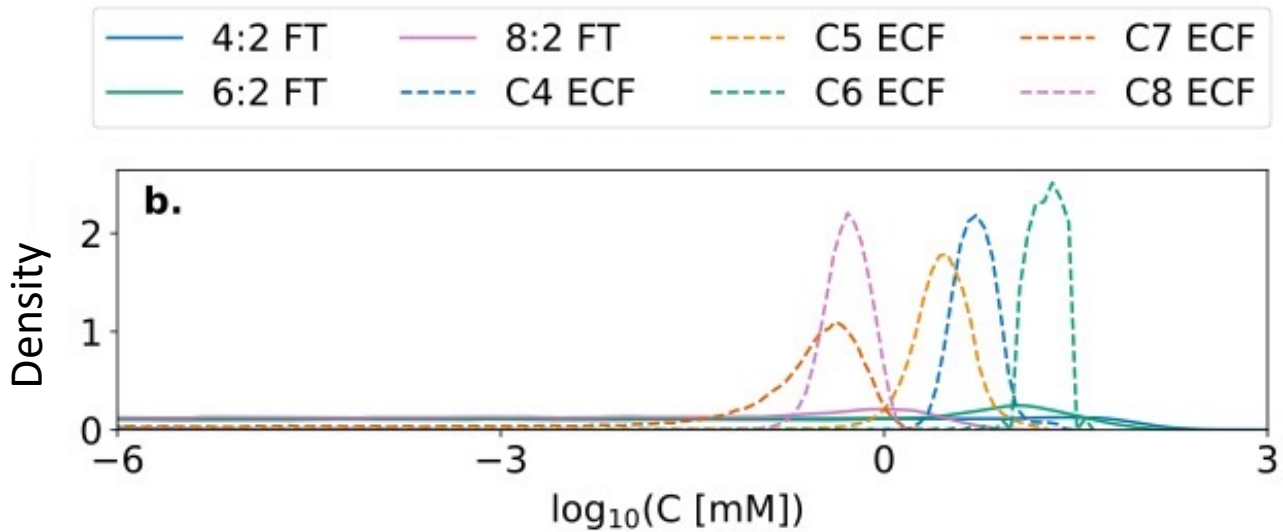
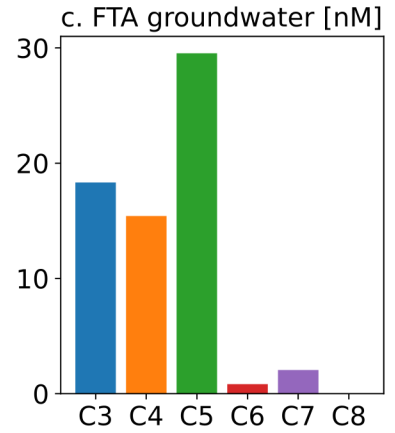
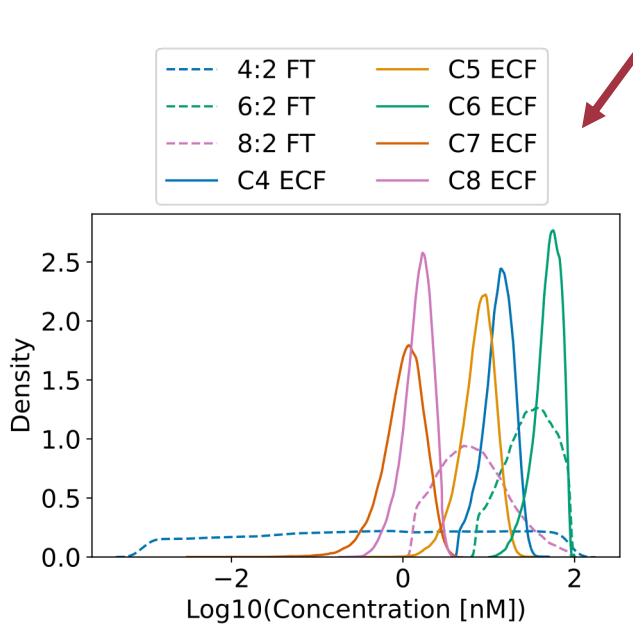


Distinguishing mixed sources in environmental samples

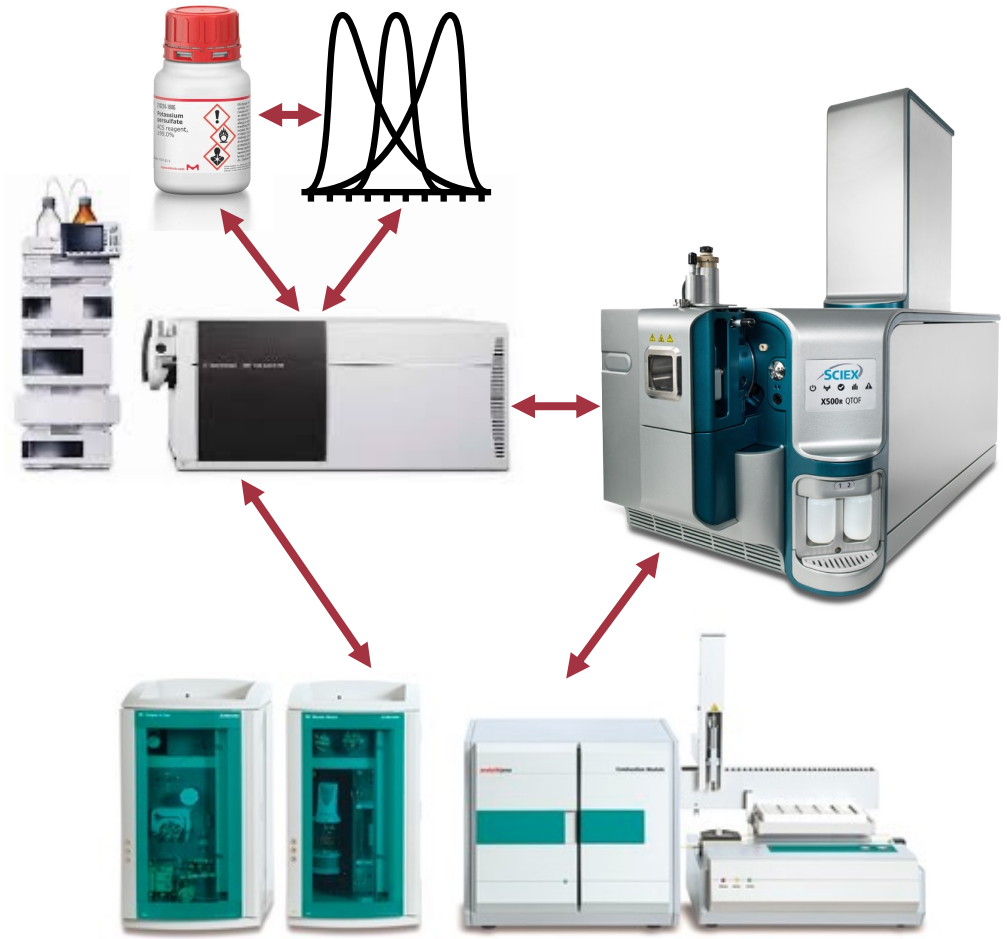
The relative abundance of ECF vs. FT precursors suggests a 3:1 usage of 3M AFFF at a former fire training area

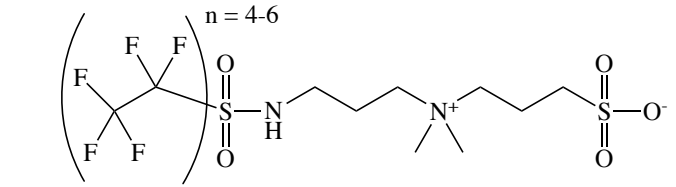
Data from Ruyle et al. in prep

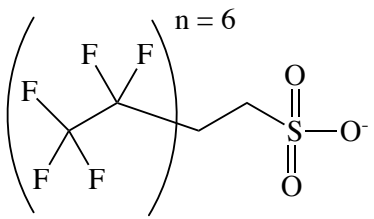


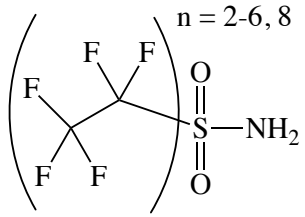


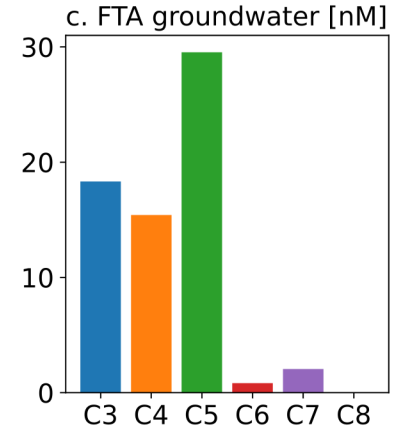
An analytical and statistical toolbox to measure precursors originating from AFFF

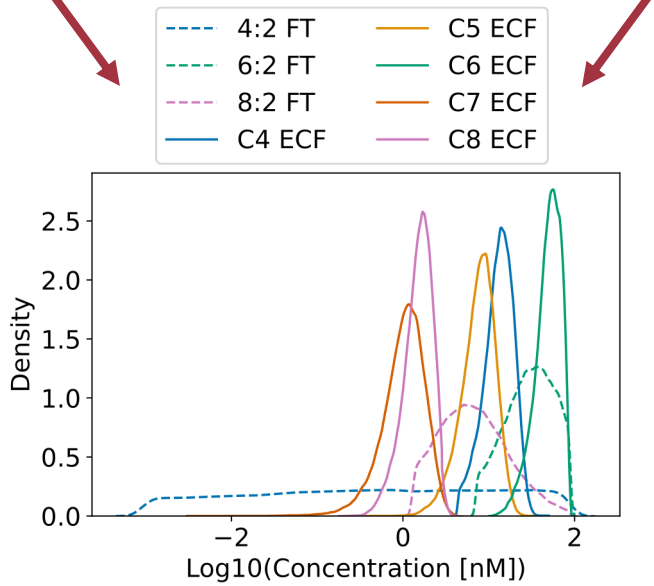






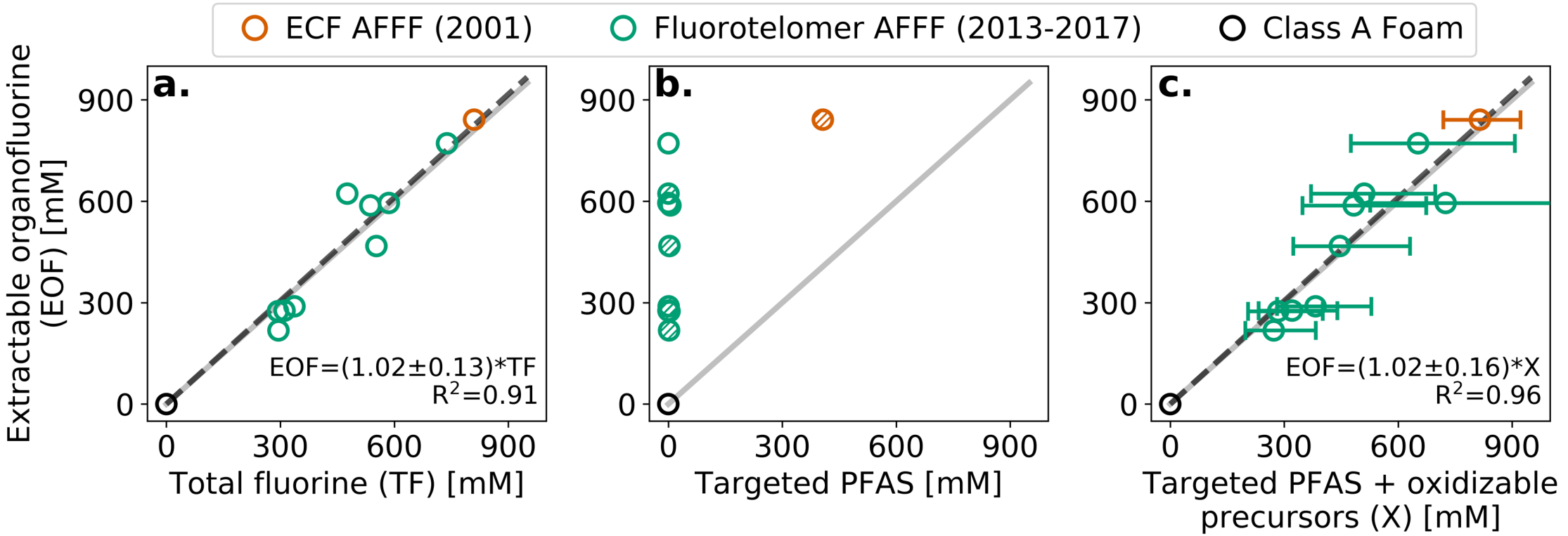






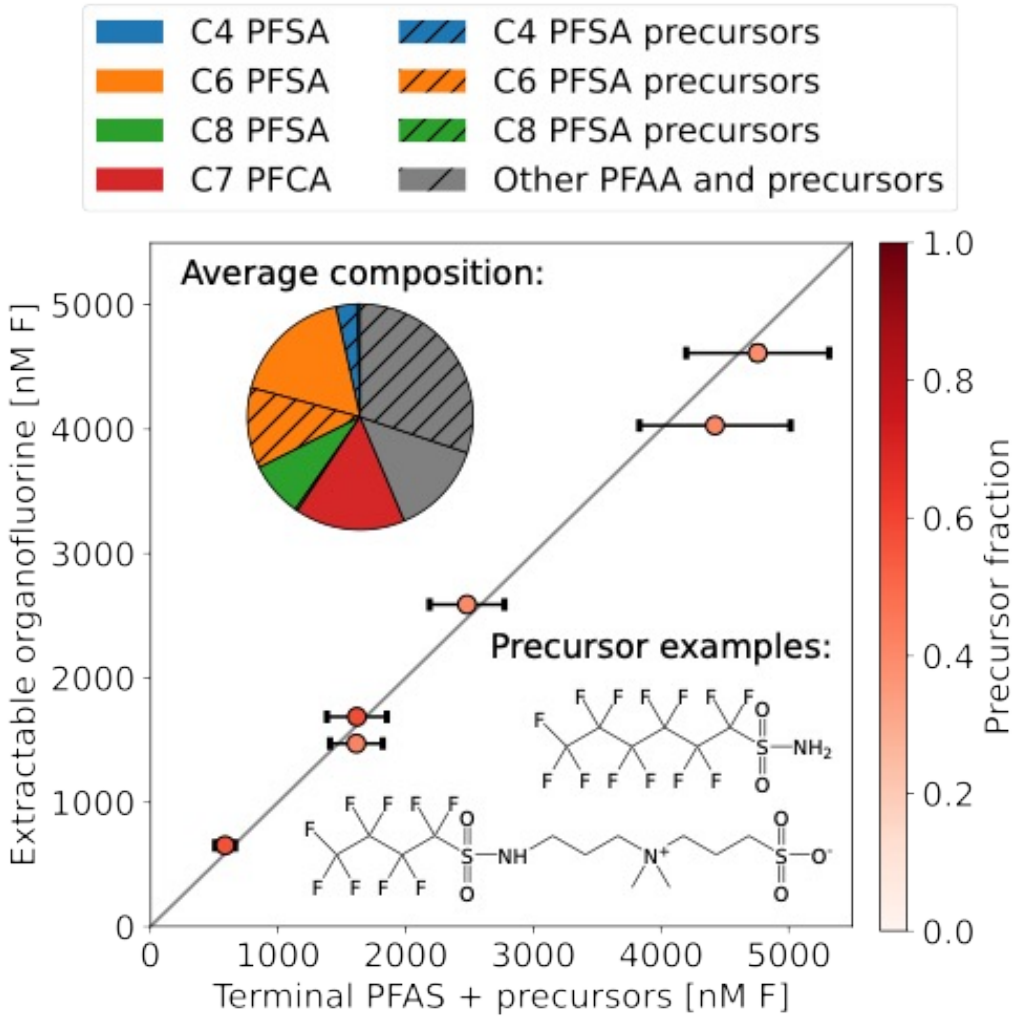
All PFAS originating from AFFF are captured by analytical and statistical toolbox

14 6:2 fluorotelomer precursors identified using HRMS in contemporary AFFF



Ruyle et al. ES&T Letters 2021

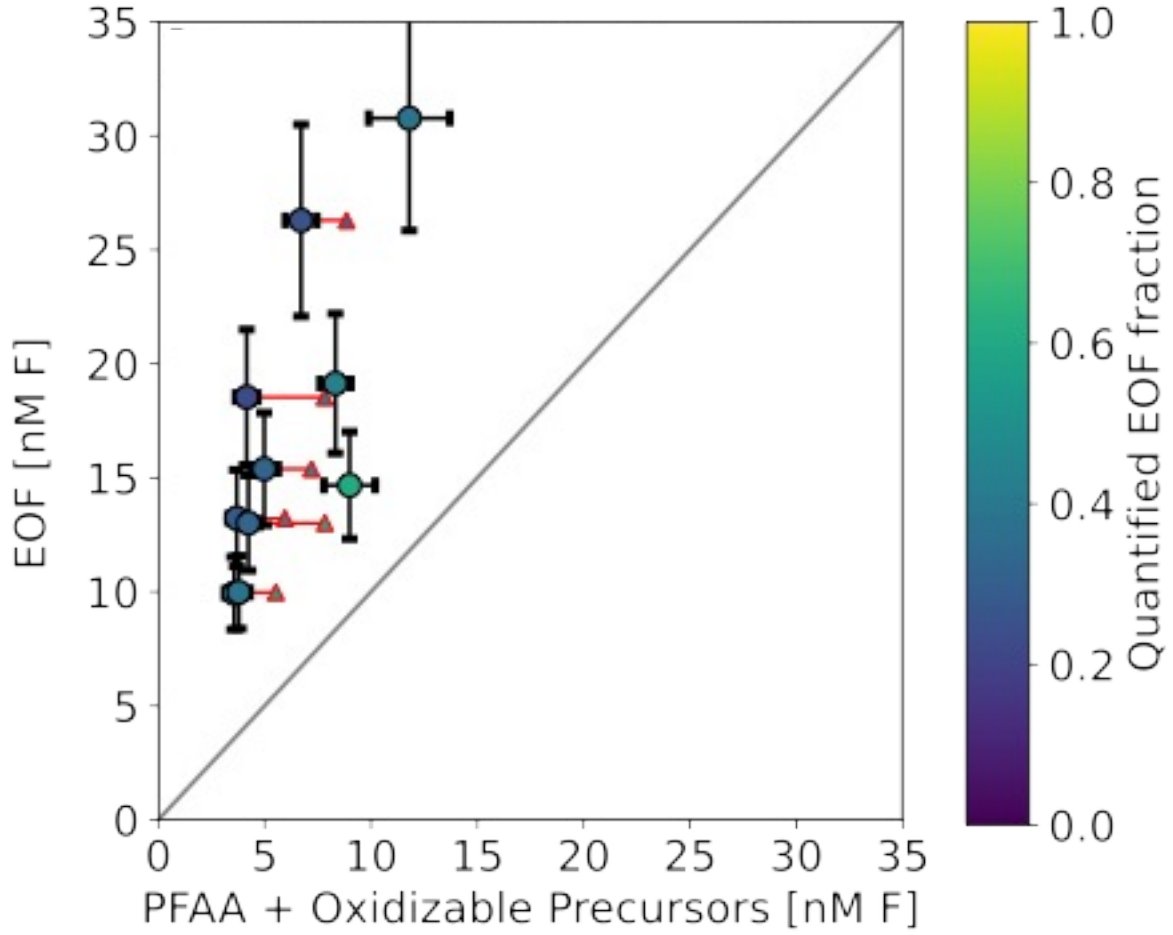
Precursors comprise half of total PFAS in groundwater at a former fire training area



Analytical and statistical toolbox completes PFAS mass balance in environmental samples for the first time

Ruyle et al. in prep

Unknown organofluorine compounds equally abundant in downstream river



Addition of oxidizable precursors and ultrashort chain PFAA (triangles) cannot complete fluorine mass balance

Ruyle et al. ES&T 2021 &
Ruyle et al. in progress

Ongoing work

- Explore unknown EOF fraction in the downstream river with suspect screening for PFAS and organofluorine pharmaceuticals and agrochemicals
- EOF interlaboratory comparison for groundwater and biota
- Expanding the use of the TOP assay + Bayesian inference to additional non-aqueous matrices (see Heidi Pickard in the Biosolids and Fish Tissue Sampling session tomorrow)