Analytical approaches for assessing sources, scope, and chemical identity of PFAS contamination

P. Lee Ferguson

Department of Civil & Environmental Engineering, Duke University

lee.ferguson@duke.edu

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CIVIL & ENVIRONMENTAL ENGINEERING

DIOXIN 2022, New Orleans, LA

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Per-and polyfluorinated Alkyl Substances (PFAS)

Non-stick coatings

"GenX"

C8 = PFOA

Grease- and oil- resistant coatings for paper products

Stain-resistant coatings for fabrics, carpets, and leather

Water repellent fabrics

Aqueous film forming foams

PFOS

Playing environmental "whack-a-mole" with PFAS compounds

Long-chain PFASs are being replaced by fluorinated alternatives...

"Legacy" perfluoroalkyls

Substituted by perfluoroalkyl ethers

Exploring PFAS chemical & geographic space in water

- <u>Assessing the problem scope</u>: Can we define the PFAS chemical universe, and how do we measure it in the environment?

   Advanced analytical chemistry and cheminformatics
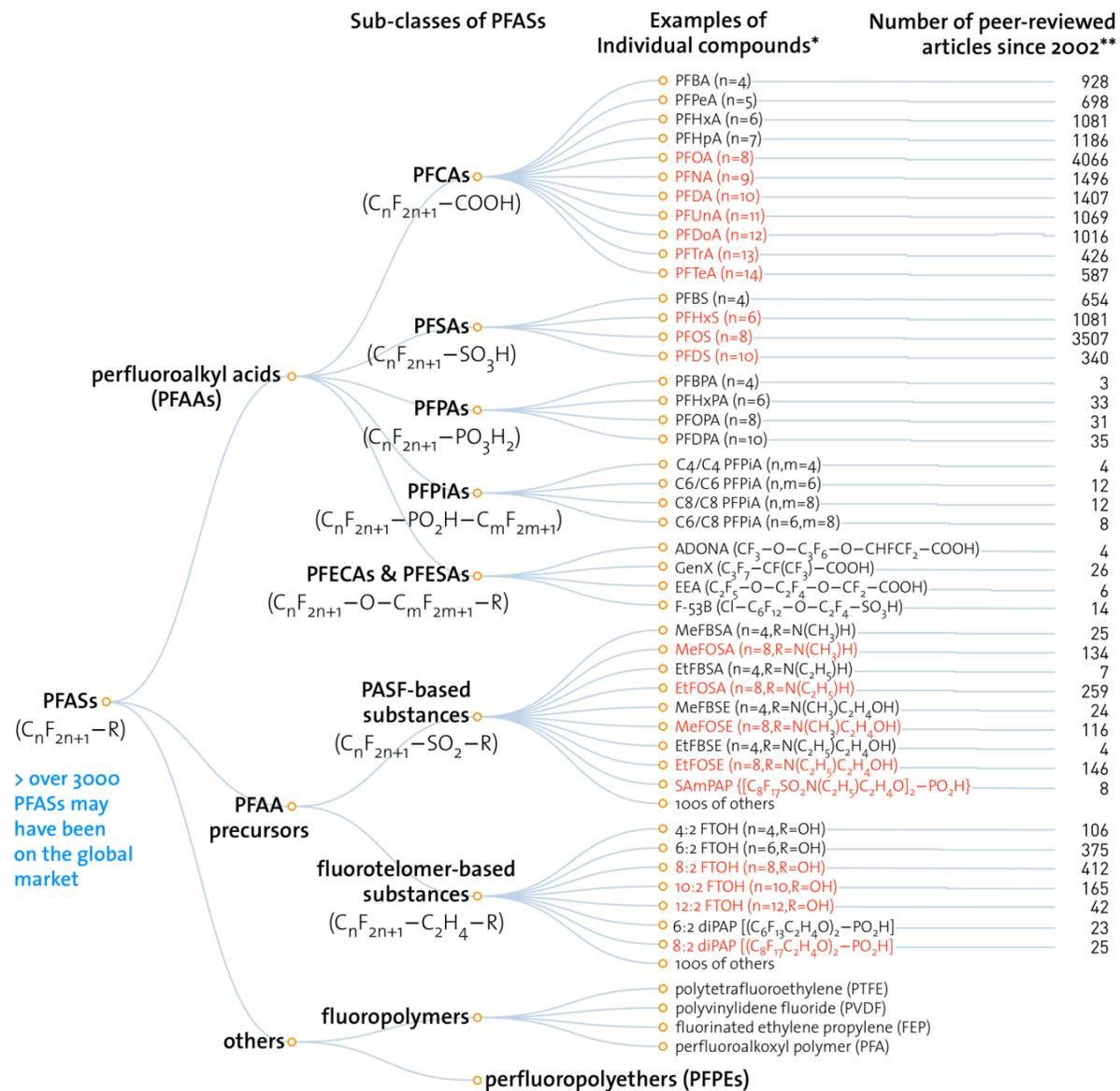
- <u>Surveying the extent of the problem</u>: Where does PFAS pollution pose a risk to human and environmental health, and what are the major sources?

   Case study in North Carolina waters

Exploring PFAS chemical & geographic space in water

- <u>Assessing the problem scope</u>: Can we define the PFAS chemical universe, and how do we measure it in the environment?

    Advanced analytical chemistry and cheminformatics

- <u>Surveying the extent of the problem</u>: Where does PFAS pollution pose a risk to human and environmental health, and what are the major sources?

    Case study in North Carolina waters

Alphabet soup: the PFAS chemical family

These compounds are characterized by numerous C-F bonds, lending them unique chemical characteristics:

- High chemical stability (strong C-F bond)

- Oleophobic + hydrophobic character (repel both water AND oil)

- Unique partitioning behavior in the environment and in biological systems (e.g. protein-binding)

- Extreme long lifetime in the environment (essentially non-biodegradable)

Sub-classes of PFASs	Examples of Individual compounds*	Number of peer-reviewed articles since 2002**
PFCAs $(C_nF_{2n+1}-COOH)$	PFBA (n=4)	928
	PFPeA (n=5)	698
	PFHxA (n=6)	1081
	PFHpA (n=7)	1186
	PFOA (n=8)	4066
	PFNA (n=9)	1496
	PFDA (n=10)	1407
	PFUnA (n=11)	1069
	PFDoA (n=12)	1016
	PFTrA (n=13)	426
	PFTeA (n=14)	587
PFSAs $(C_nF_{2n+1}-SO_3H)$	PFBS (n=4)	654
	PFHxS (n=6)	1081
	PFOS (n=8)	3507
	PFDS (n=10)	340
PFPAs $(C_nF_{2n+1}-PO_3H_2)$	PFBPA (n=4)	3
	PFHxPA (n=6)	33
	PFOPA (n=8)	31
	PFDPA (n=10)	35
PFPiAs $(C_nF_{2n+1}-PO_2H-C_mF_{2m+1})$	C4/C4 PFPiA (n,m=4)	4
	C6/C6 PFPiA (n,m=6)	12
	C8/C8 PFPiA (n,m=8)	12
	C6/C8 PFPiA (n=6,m=8)	8
PFECAs & PFESAs $(C_nF_{2n+1}-O-C_mF_{2m+1}-R)$	ADONA $(CF_3-O-C_3F_6-O-CHFCF_2-COOH)$	4
	GenX $(C_3F_7-CF(CF_3)-COOH)$	26
	EEA $(C_2F_5-O-C_2F_4-O-CF_2-COOH)$	6
	F-53B $(Cl-C_6F_{12}-O-C_2F_4-SO_3H)$	14
PASF-based substances $(C_nF_{2n+1}-SO_2-R)$	MeFBSA (n=4,R=N(CH_3)H)	25
	MeFOSA (n=8,R=N(CH_3)H)	134
	EtFBSA (n=4,R=N(C_2H_5)H)	7
	EtFOSA (n=8,R=N(C_2H_5)H)	259
	MeFBSE (n=4,R=N(CH_3)C_2H_4OH)	24
	MeFOSE (n=8,R=N(CH_3)C_2H_4OH)	116
	EtFBSE (n=4,R=N(C_2H_5)C_2H_4OH)	4
	EtFOSE (n=8,R=N(C_2H_5)C_2H_4OH)	146
	SAmPAP $\{[C_8F_{17}SO_2N(C_2H_5)C_2H_4O]_2-PO_2H\}$	8
	100s of others	
fluorotelomer-based substances $(C_nF_{2n+1}-C_2H_4-R)$	4:2 FTOH (n=4,R=OH)	106
	6:2 FTOH (n=6,R=OH)	375
	8:2 FTOH (n=8,R=OH)	412
	10:2 FTOH (n=10,R=OH)	165
	12:2 FTOH (n=12,R=OH)	42
	6:2 diPAP $[(C_6F_{13}C_2H_4O)_2-PO_2H]$	23
	8:2 diPAP $[(C_8F_{17}C_2H_4O)_2-PO_2H]$	25
	100s of others	
fluoropolymers	polytetrafluoroethylene (PTFE)	
	polyvinylidene fluoride (PVDF)	
	fluorinated ethylene propylene (FEP)	
	perfluoroalkoxyl polymer (PFA)	
	perfluoropolyethers (PFPEs)	

perfluoroalkyl acids (PFAAs)

PFASs $(C_nF_{2n+1}-R)$

> over 3000 PFASs may have been on the global market

PFAA precursors

others

* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors.).

Comprehensive data analysis pipeline for PFAS annotation by HRMS
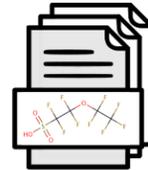

CompTox Chemicals Dashboard

882 Thousand Chemicals

Environmental Science & technology — Article — pubs.acs.org/est

Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson, Simon C. Roberts, Sarah Choyke, Karl Oetjen, Alan McAlees, Nicole Riddell, Robert McCrindle, P. Lee Ferguson, Christopher P. Higgins, and Jennifer A. Field

① PFAS in commerce

② prediction
- Hydrolysis
- Biotrans.
- MS/MS

③ *in silico* MS² library

④ HRMS(/MS) screening

Predicted
m/z
Experimental

CFM-ID
Competitive Fragmentation Modeling for Metabolite Identification
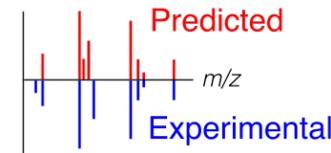
Djoumbou-Feunang *et al. J Cheminform* (2019) 11:2
https://doi.org/10.1186/s13321-018-0324-5

SOFTWARE — Open Access

BioTransformer: a comprehensive computational tool for small molecule metabolism prediction and metabolite identification

Yannick Djoumbou-Feunang[1], Jarlei Fiamoncini[2,3], Alberto Gil-de-la-Fuente[4], Russell Greiner[5,6], Claudine Manach[2] and David S. Wishart[1,5]

EPA United States Environmental Protection Agency

CTS: Chemical Transformation Simulator

$n_{Structures} = 39,369$
$n_{Formulas} = 17,047$

7
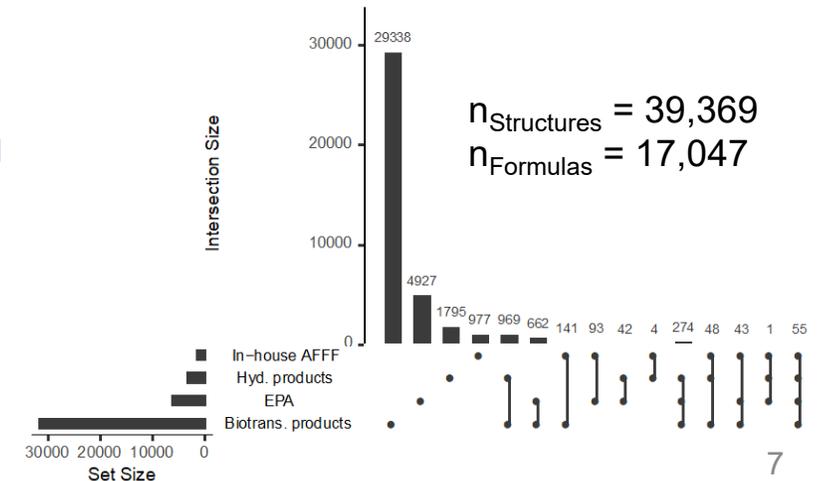
Example: Molecular transformation network for PFOA

Molecular network for structures within four predicted reactions of perfluorooctanoic acid (PFOA).

- Nodes represent unique chemical structures.
- Structures from PFAS molecular databases are depicted as **green** nodes, while those predicted by transformations are shown as **purple** nodes
- Structures both present in input molecular databases and predicted by in silico transformations are depicted in **orange**.
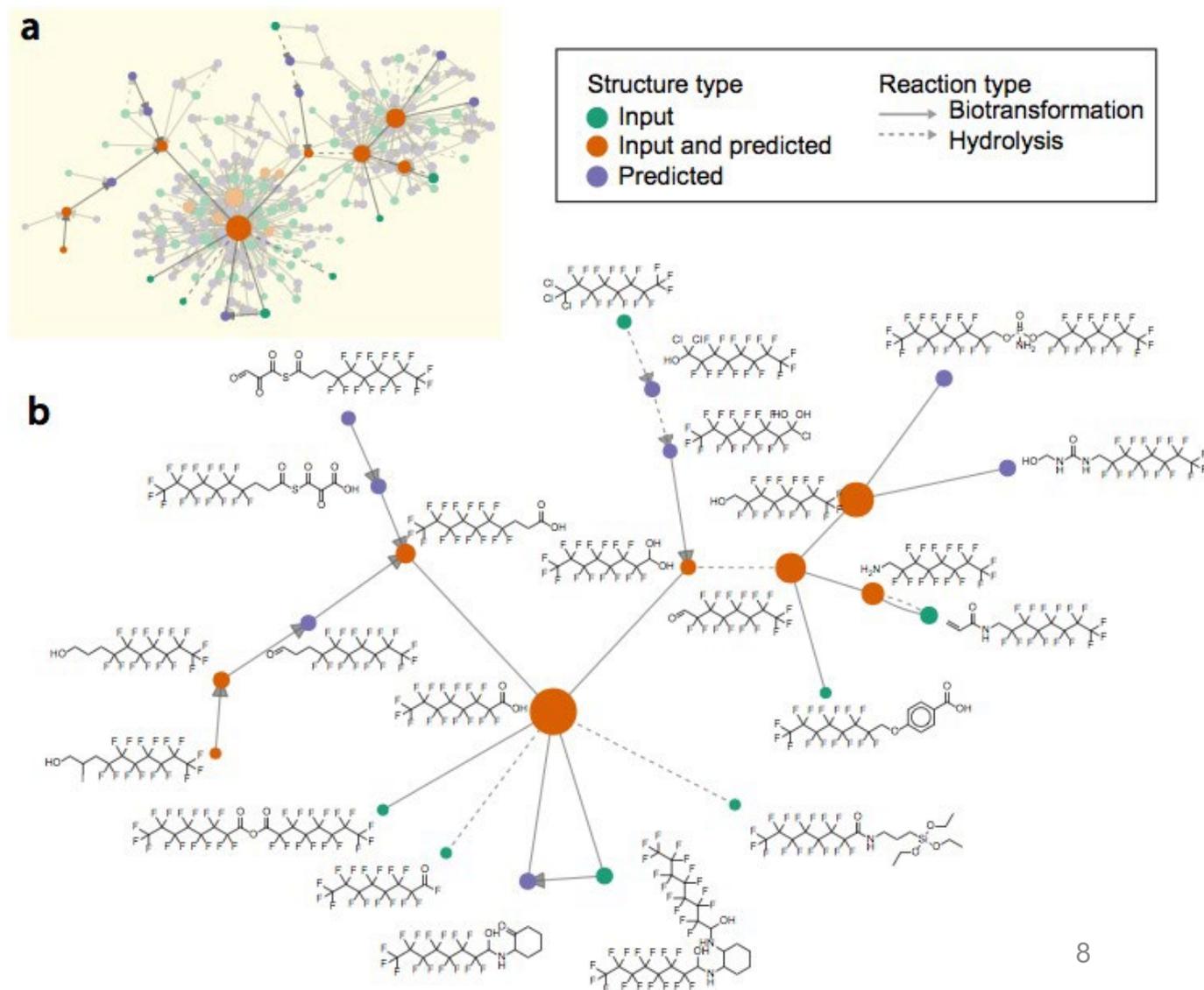
Ultra-high resolution mass spectrometry for PFAS detection/analysis

- Orbitrap Fusion Lumos mass spectrometer
- Critical resolution (500,000) and <u>mass accuracy</u> (< 1 ppm)
- Ultra-fast data-dependent MS/MS maximizes data acquisition rate
- MS^3 capability for structural characterization
- Ion funnel for maximum sensitivity

Ultra-High Field Orbitrap Mass Analyzer

Dual-Pressure Linear Ion Trap

Low Pressure Cell

Advanced Active Beam Guide

Advanced Quadrupole Technology

High Pressure Cell

EASY-ETD/IC Ion Source

Ion Routing Multipole

Electrodynamic Ion Funnel

C-Trap

High Capacity Transfer Tube
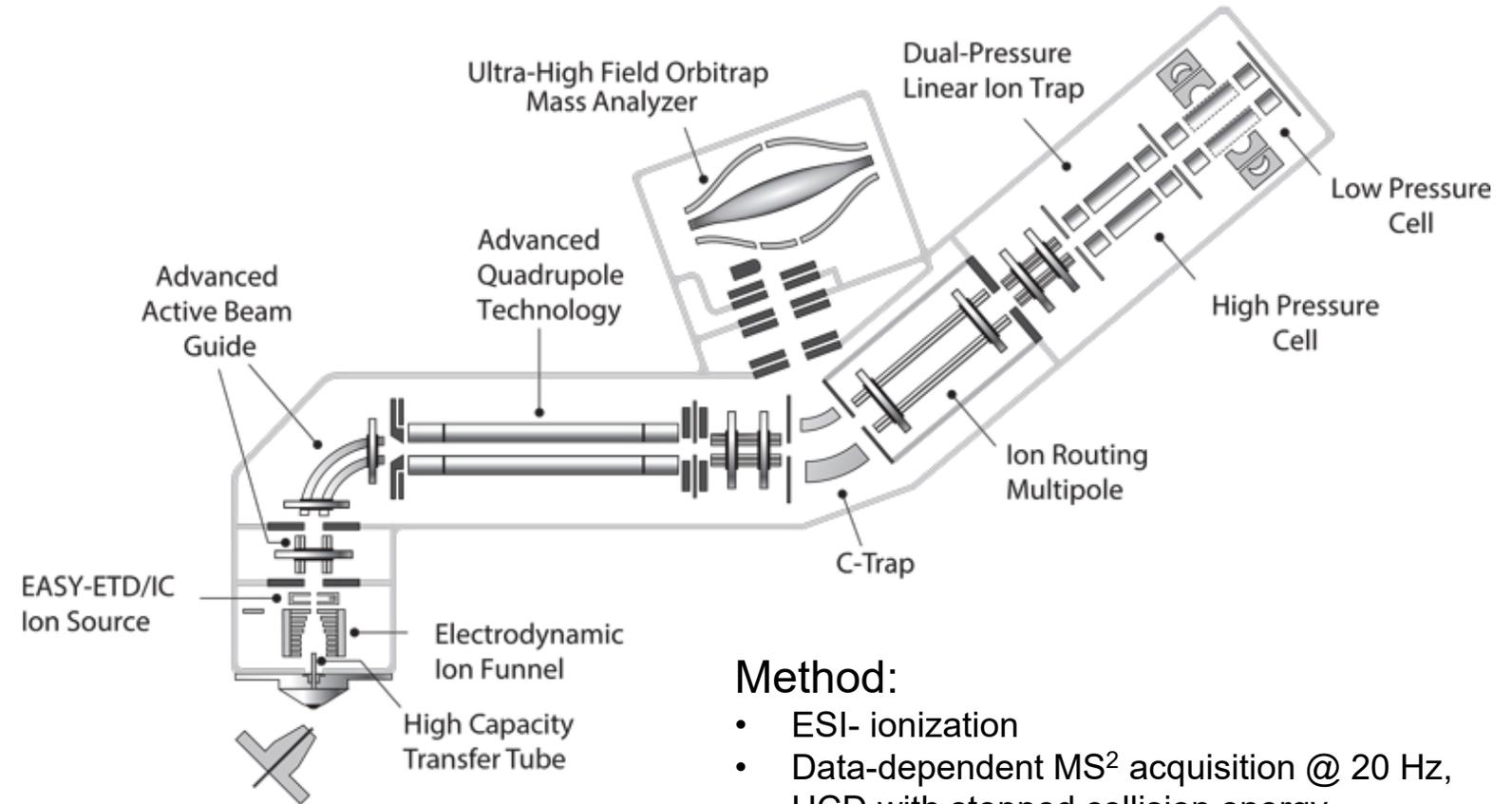
Method:
- ESI- ionization
- Data-dependent MS^2 acquisition @ 20 Hz, HCD with stepped collision energy
- Internal mass calibration

Increasing throughput in HRMS-based PFAS analysis using online solid-phase extraction

Excellent sensitivity and separation achieved for PFAS standards
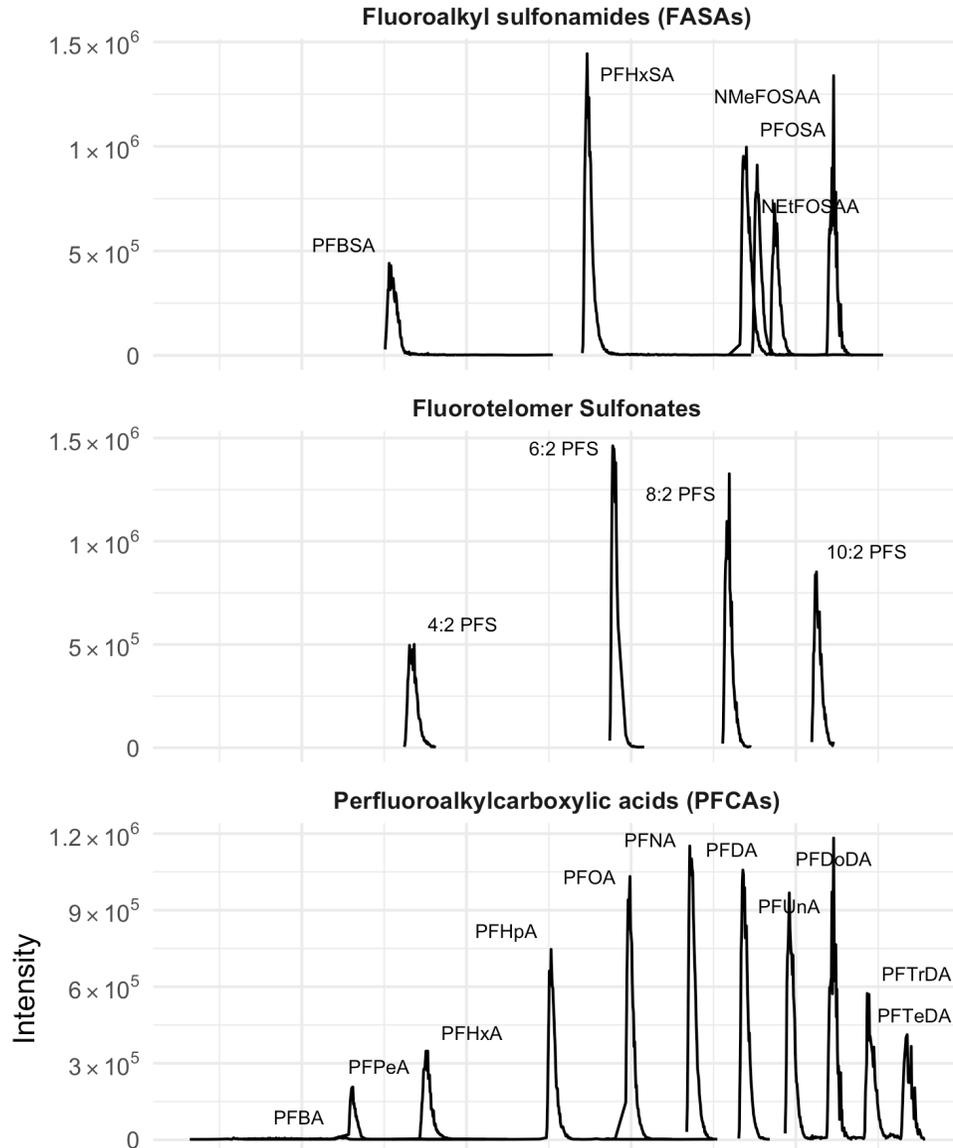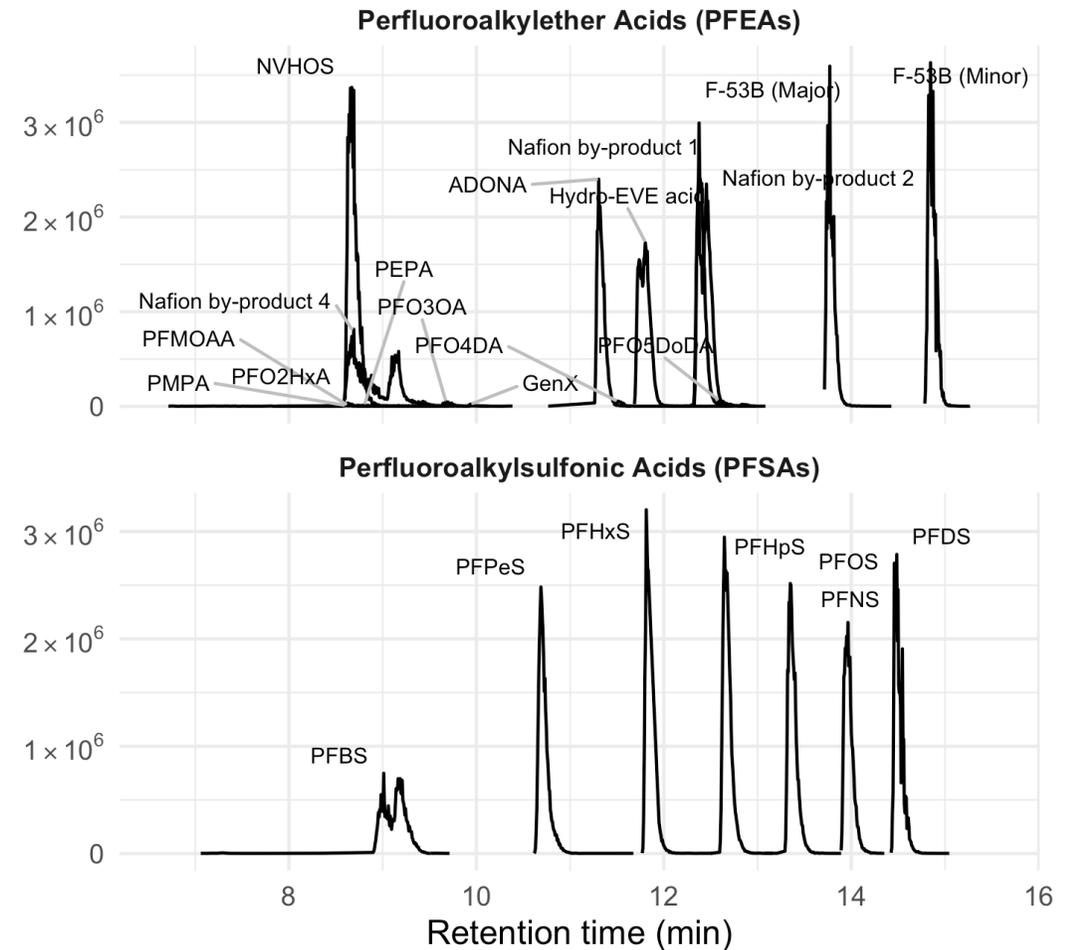
Method optimization and validation

- Total water volume enriched = **6 mL**

- Samples were diluted to 50% MeOH before online SPE

- Elution/transfer time & flow rate from WAX trap cartridge to analytical column were optimized

- Longer transfer times resulted in loss of small, hydrophilic PFAS, while short transfer times caused incomplete transfer of long-chain PFAS
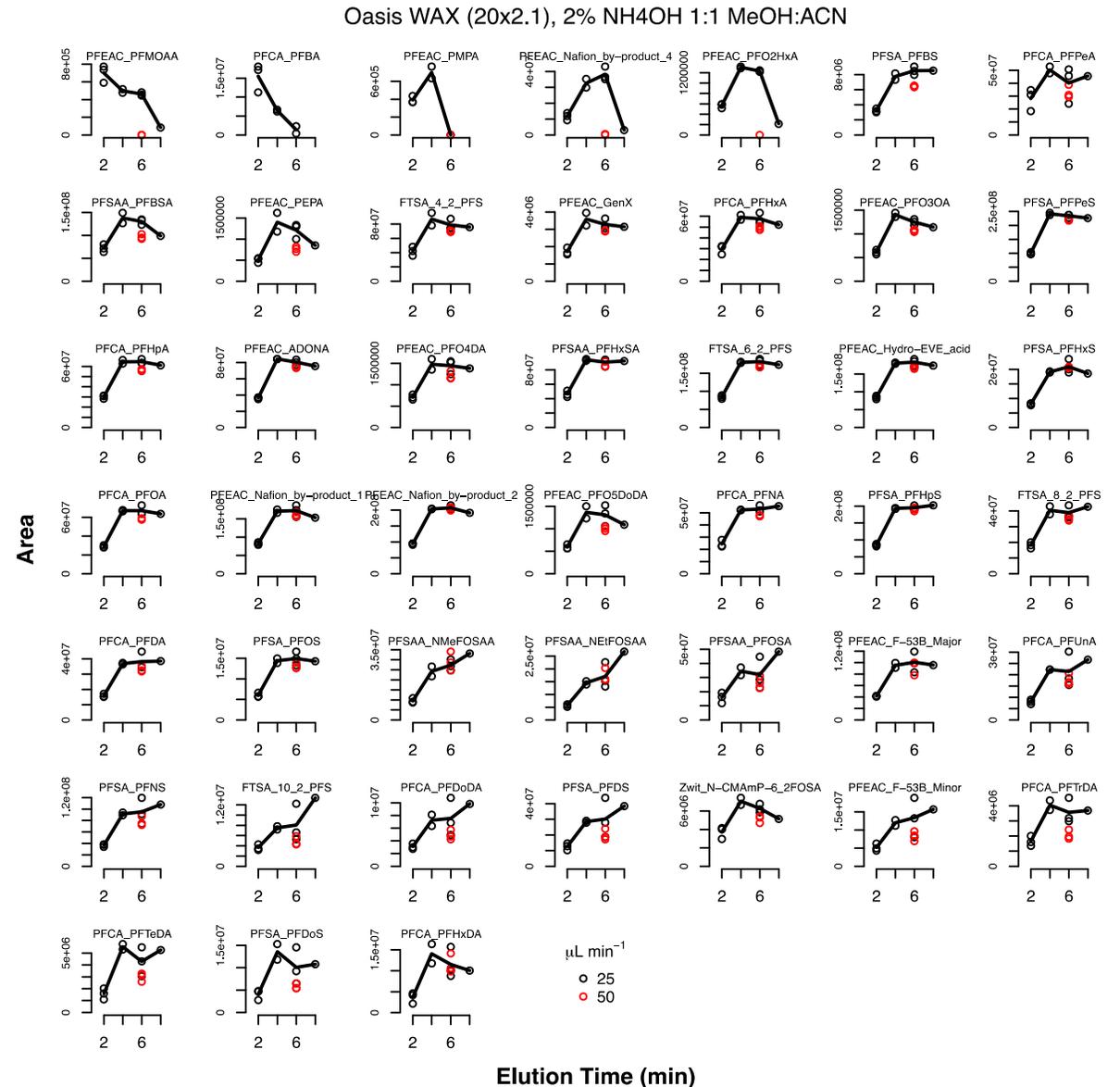
Oasis WAX (20x2.1), 2% NH4OH 1:1 MeOH:ACN

Method optimization and validation
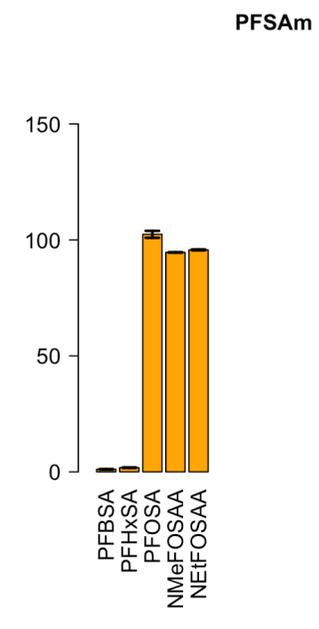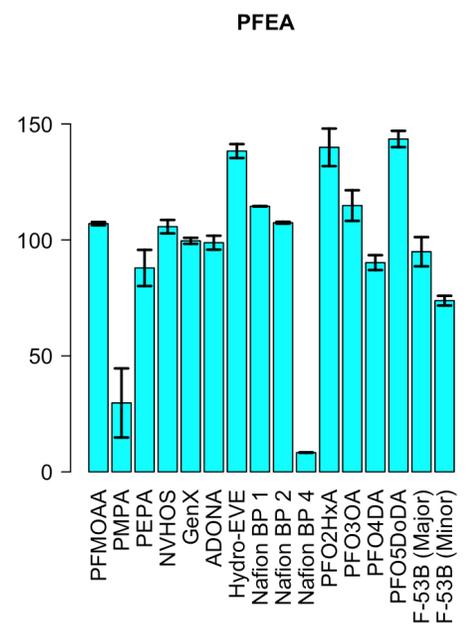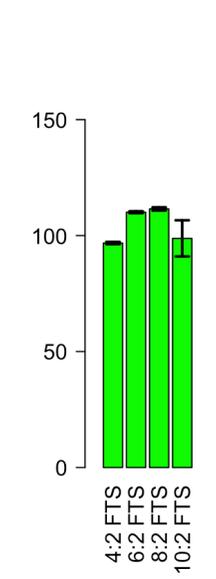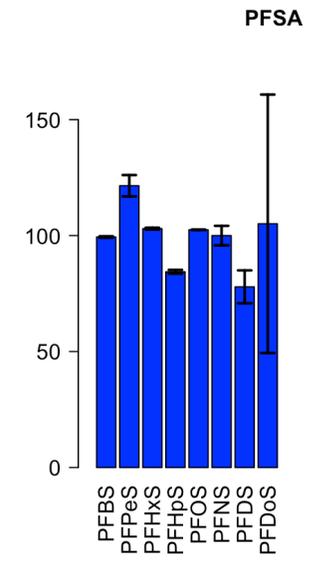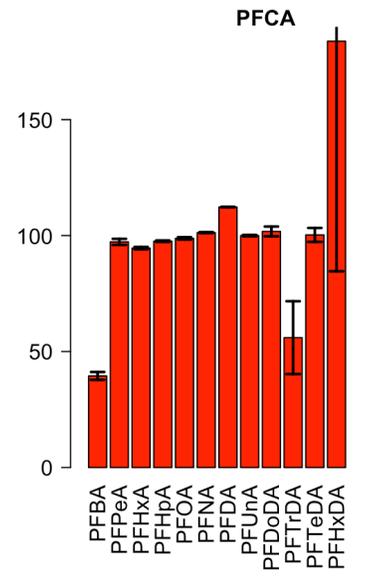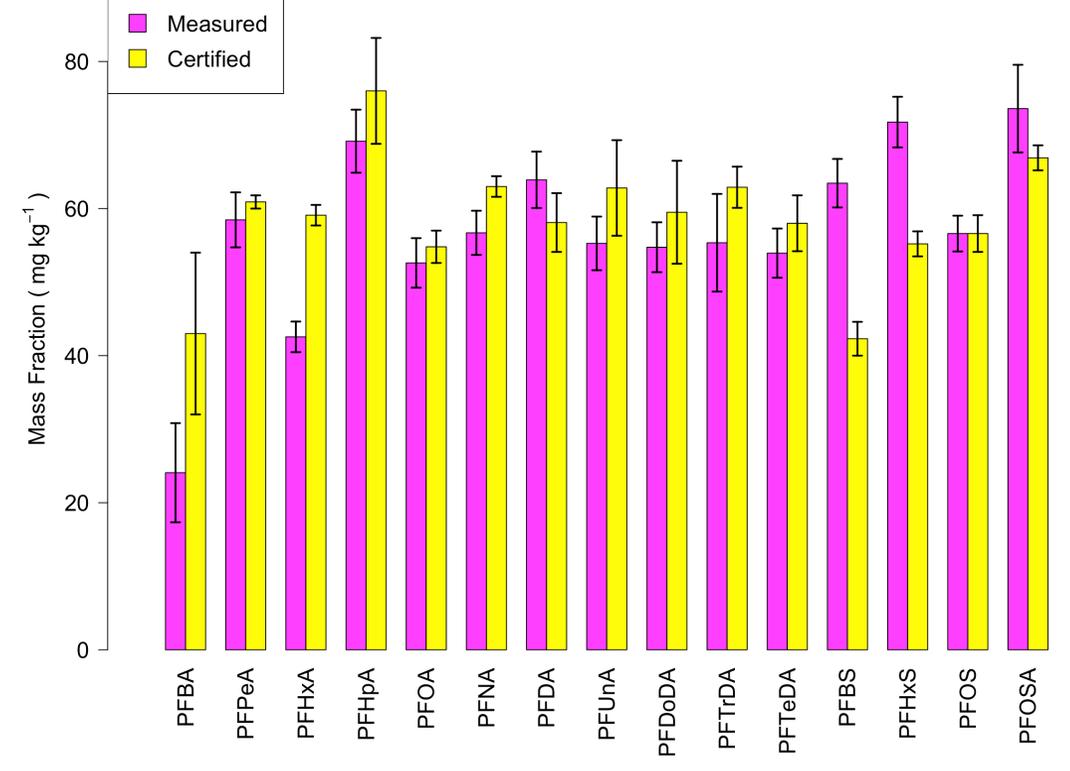
Test case: Assessing PFAS contamination in surface water following an AFFF release


Lincoln County, North Carolina

- Gasoline tanker accident near Denver, NC January 28, 2020 resulted in large release of AFFF to nearby creek
- Creek empties to Catawba River upstream of Belmont, NC drinking water treatment plant
- Surface water samples collected at spill site and downstream

SKY3

WBTV ON YOUR SIDE
1 KILLED IN FUEL TANKER CRASH, CREWS STILL CLEANING UP
HIGHWAY 16 - LINCOLN COUNTY
11:02 | 42°
3 WBTV ON YOUR SIDE

https://www.wbtv.com/2020/01/28/overturned-gasoline-tanker-closes-part-hwy/

Suspect-screening analysis of AFFF-impacted water revealed numerous PFAS compounds

- 92 of 1,388 detected compounds in samples were tentatively annotated as PFAS

- Van Krevelen and Kendrick Mass Defect (KMD) plots revealed likely PFAS transformations

- Fragmentation tree analysis allows for identification of distinct and diagnostic fragment ions for PFAS compound classes
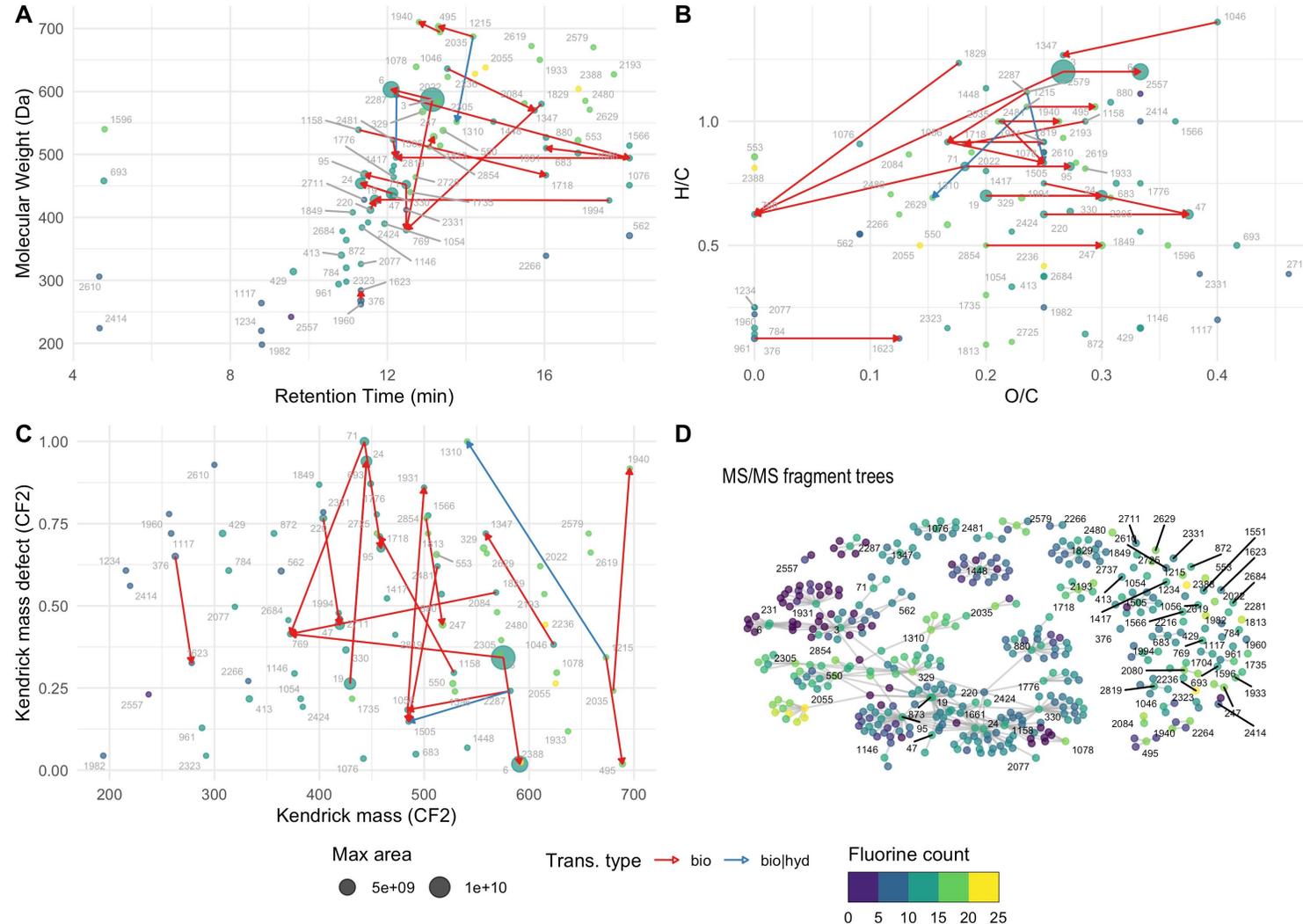
In silico MS/MS and computational mass spectrometry facilitated PFAS structure annotation

- CFM-ID[1]-predicted MS/MS spectra matched numerous fragment ions in HRMS analysis of PFAS

- The molecular formula annotation tool Sirius[2] increased confidence in elemental composition assignment from HRMS data

- MS/MS for several classes of PFAS were poorly predicted by CFM-ID and Sirius
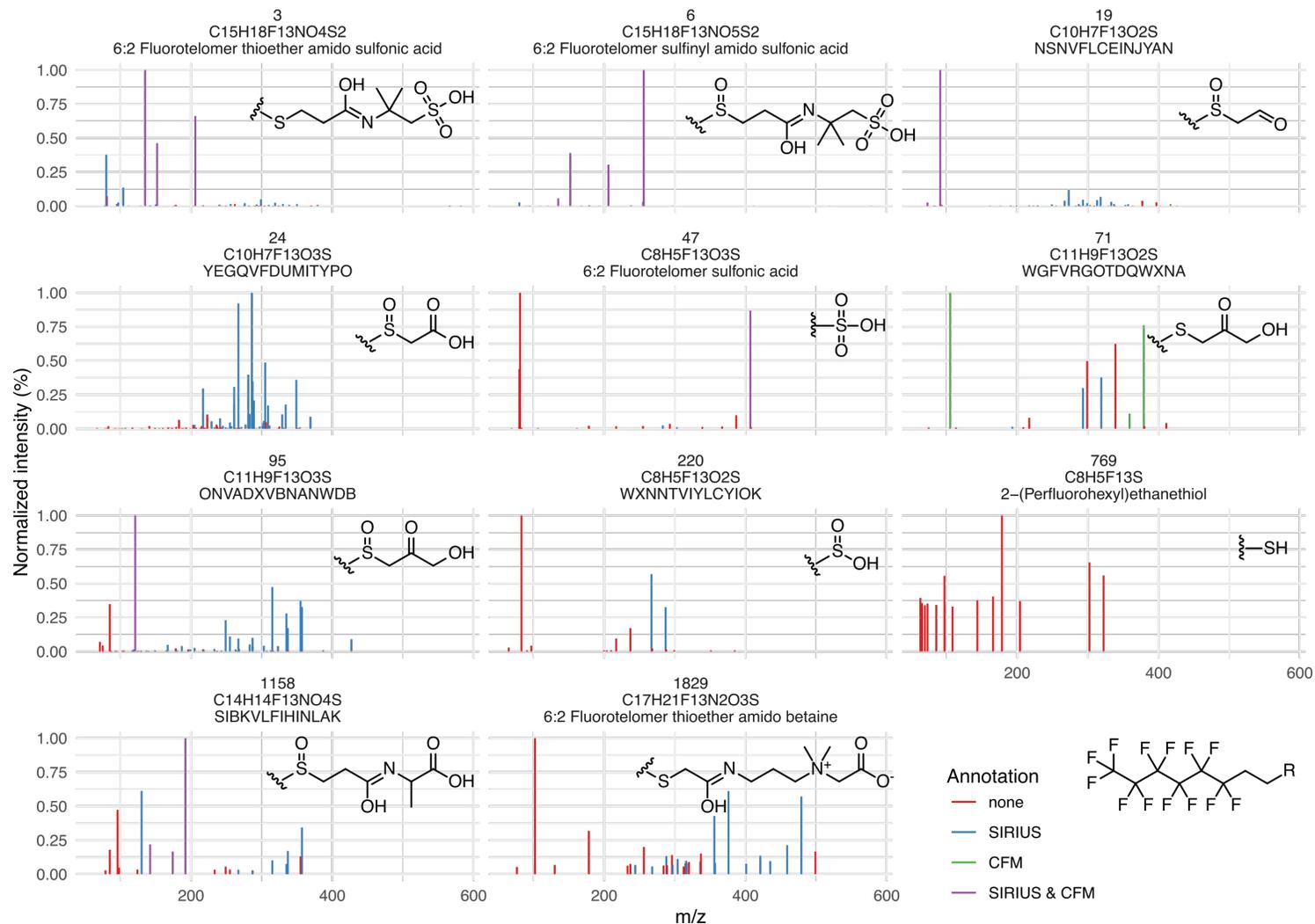
[1]Allen et al., CFM-ID: a web server for annotation, spectrum prediction and metabolite identification from tandem mass spectra. Nucleic Acids Res, 42, 2014

[2]Dührkop et al., SIRIUS4: a rapid tool for turning tandem mass spectra into metabolite structure information. *Nat Methods*, 16, 2019

A molecular network of 6:2 fluorotelomer species was revealed in AFFF-impacted water

- Transformation processes including hydrolysis, oxidation, and dealkylation produced 6:2 flurotelomer-based PFAS from precursors

- Several previously-known AFFF components were detected (e.g. 6:2 FTS, 6:2 FTSAS, 6:2 FTSAAB)

- Multiple novel (bio)transformation products of AFFF precursors were tentatively annotated in samples
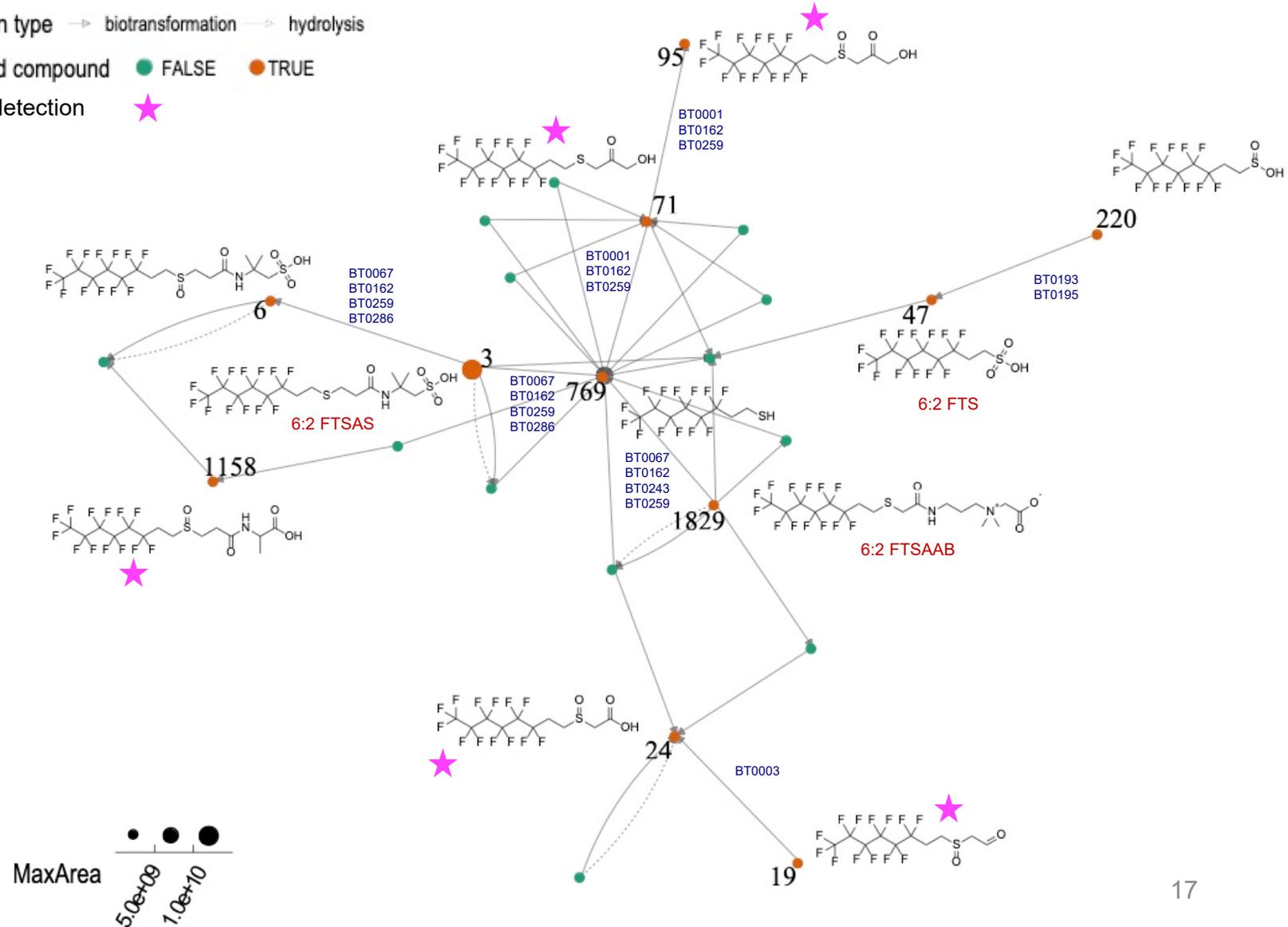
Direct-injection LC-MS/MS for rapid PFAS quantitation in water

Number of analytes	48 (legacy and emerging PFAS)
Injection volume	50 µL raw water
Run time	20 minutes
Reporting limits	1 – 10 ng/L
Spike recoveries	• 40-110% recovery • 38 of 48 compounds > 80% recovery • Trip spikes indicate 10 -20% loss for PFCA/PFSA > C_{10}

SRM Validation (n = 21 measurements)
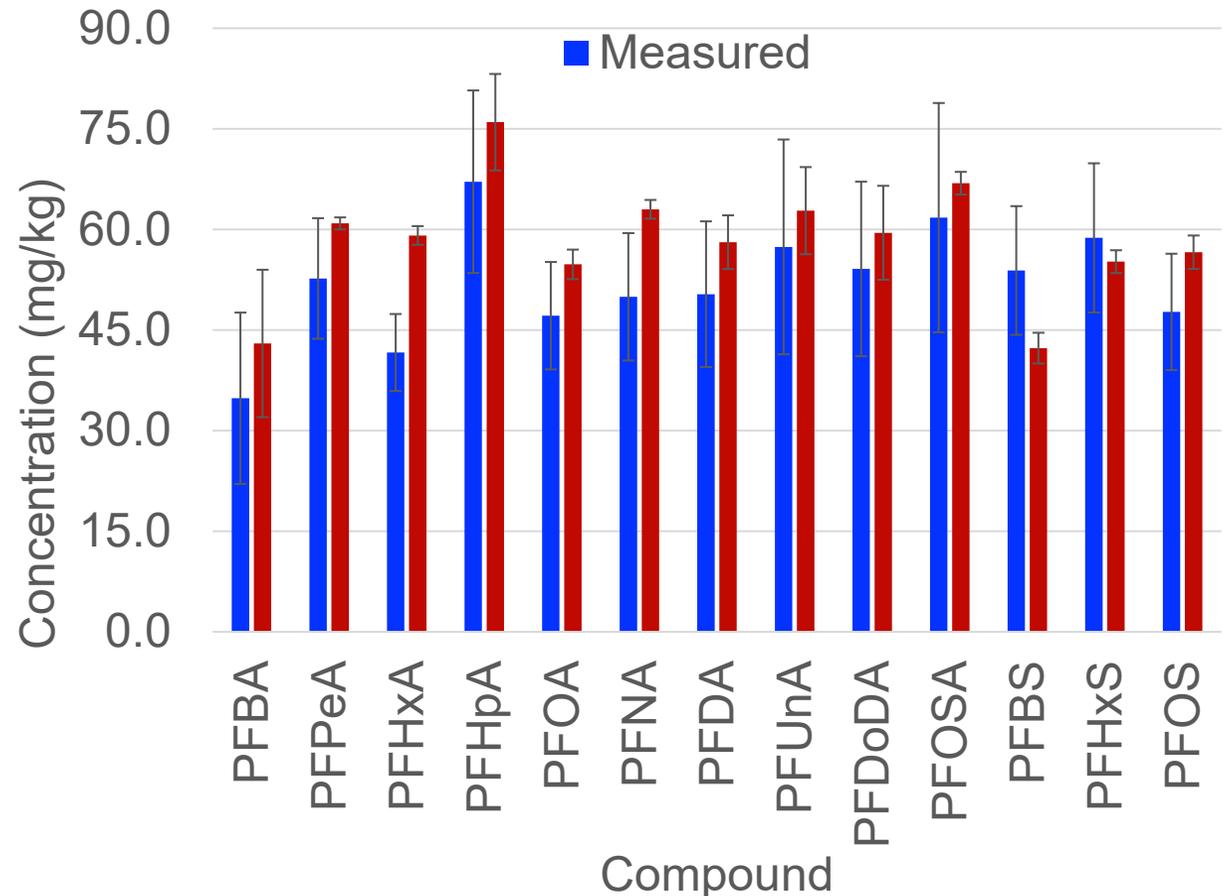
Comprehensive analytical strategy for PFAS measurement in water

Sample Collection

Triple Quadrupole MS/MS (target quantitation)

Online Solid-Phase Extraction

PFAS mass balance

Adsorbable organic fluorine analysis

High-resolution MS (suspect screening)
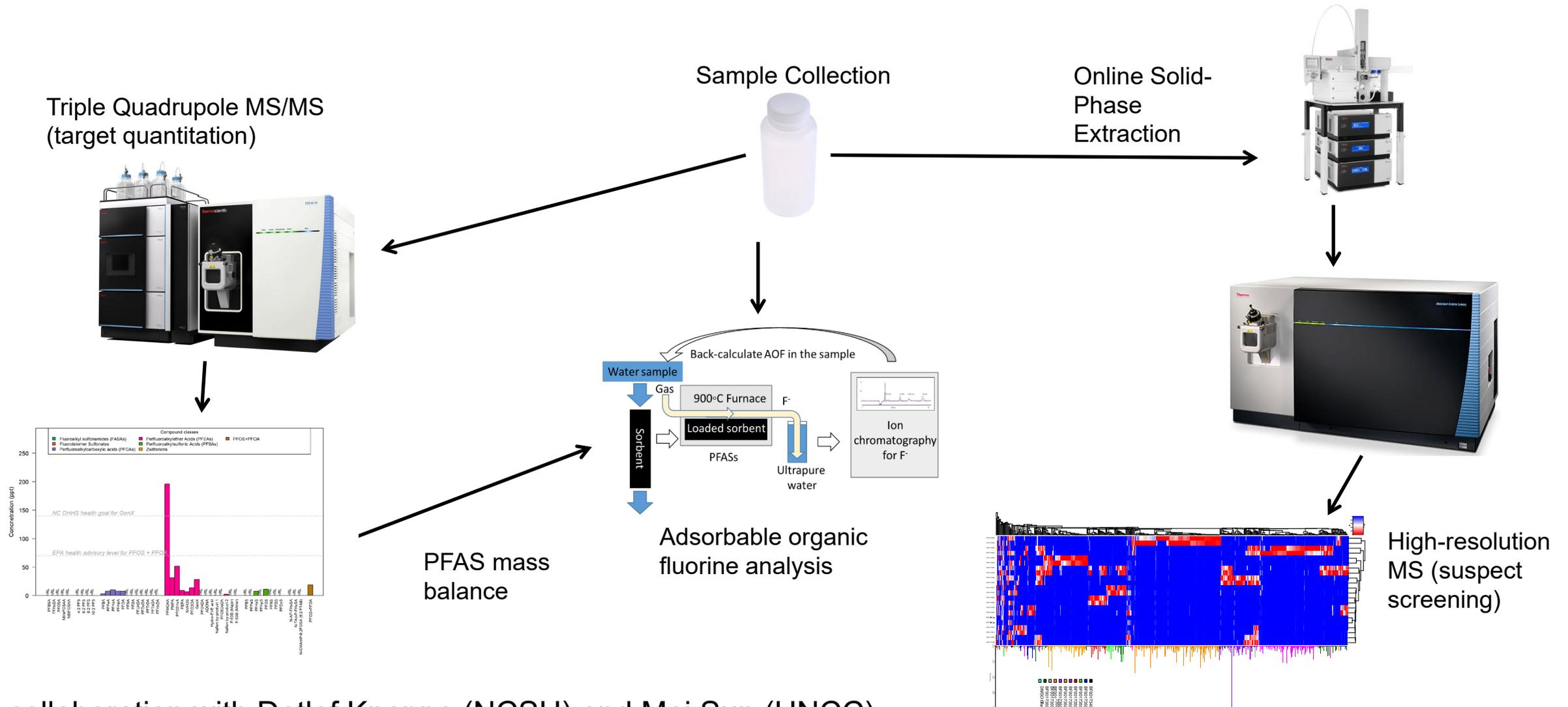
In collaboration with Detlef Knappe (NCSU) and Mei Sun (UNCC)

# Exploring PFAS chemical & geographic space in water

- Assessing the problem scope: Can we define the PFAS chemical universe, and how do we measure it in the environment?

  Advanced analytical chemistry and cheminformatics

- Surveying the extent of the problem: Where does PFAS pollution pose a risk to human and environmental health, and what are the major sources?

  Case study in North Carolina waters

PFAS in NC drinking water sources
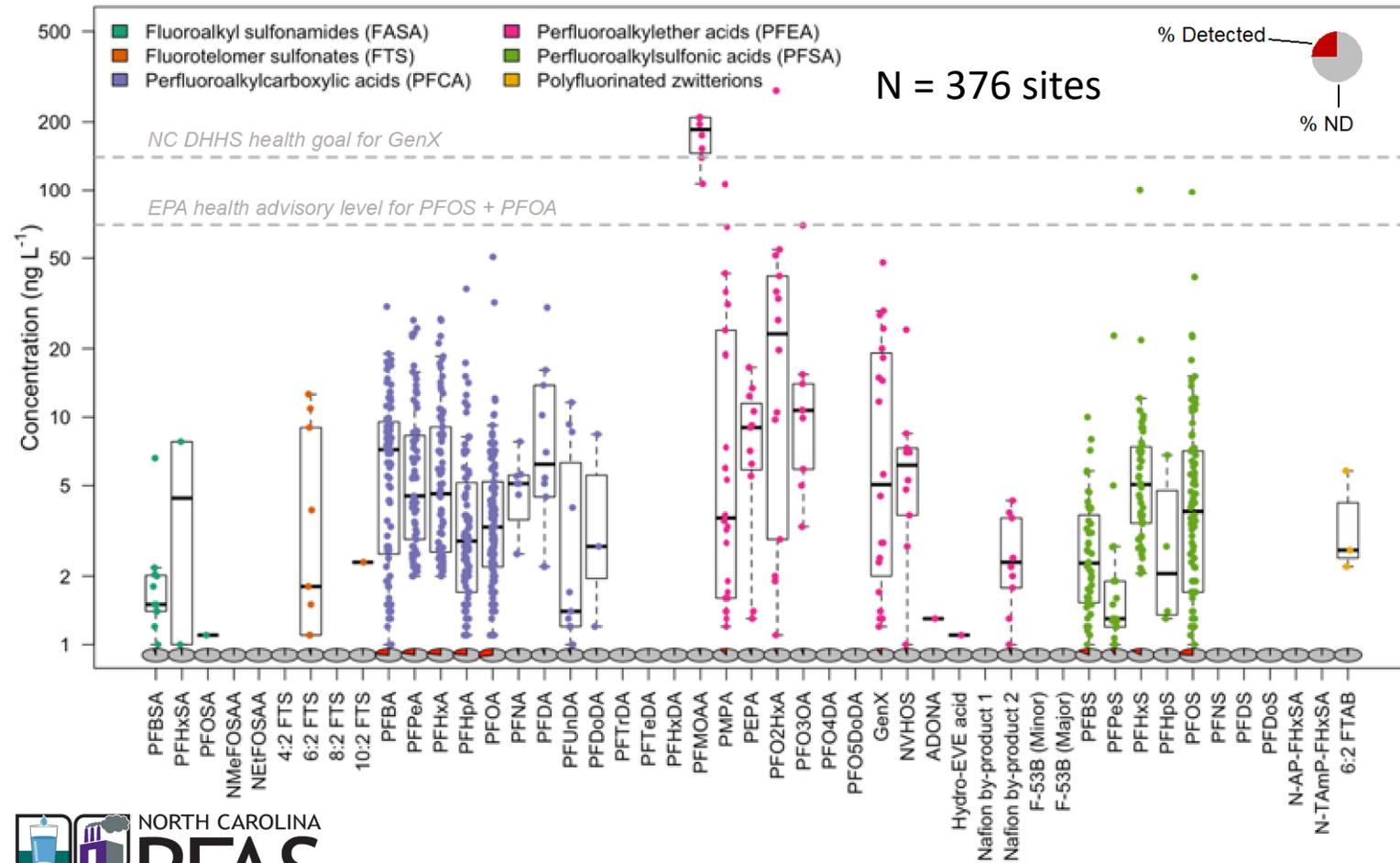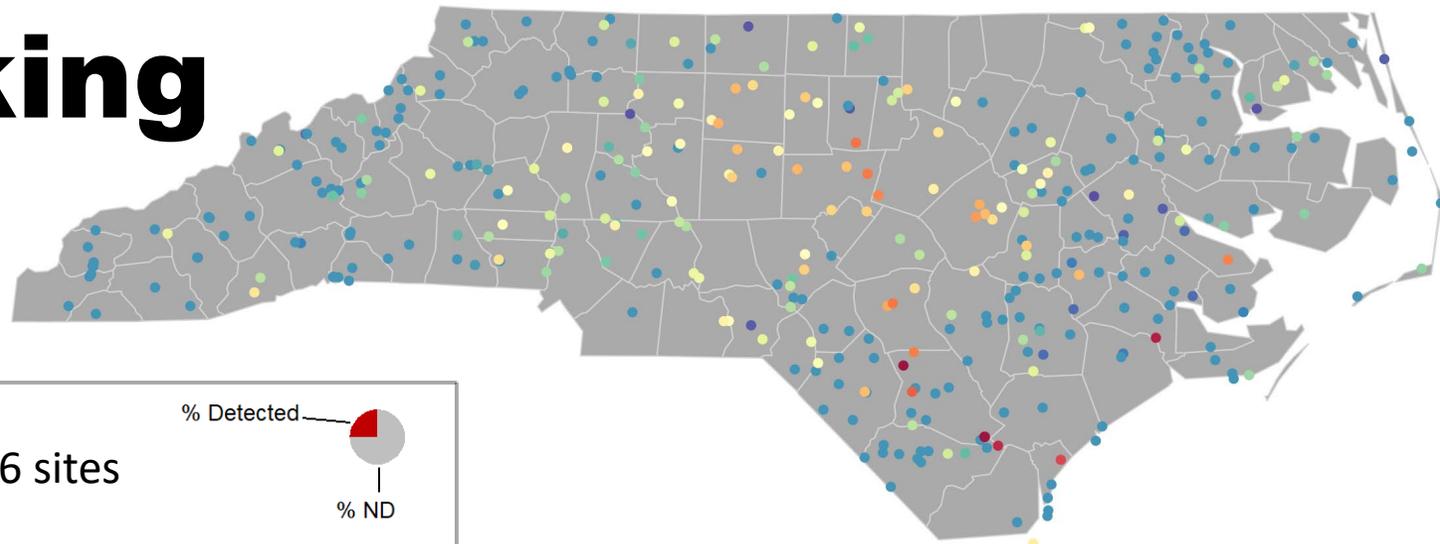
- Statewide drinking water monitoring in 2019 revealed PFAS mostly concentrated in central NC and along the Haw & Cape Fear river basin

- C4-C8 PFCAs and PFOS were the most frequently observed compounds

- Ether acids/sulfonates were only measured East of Chemours plant in Cape Fear water

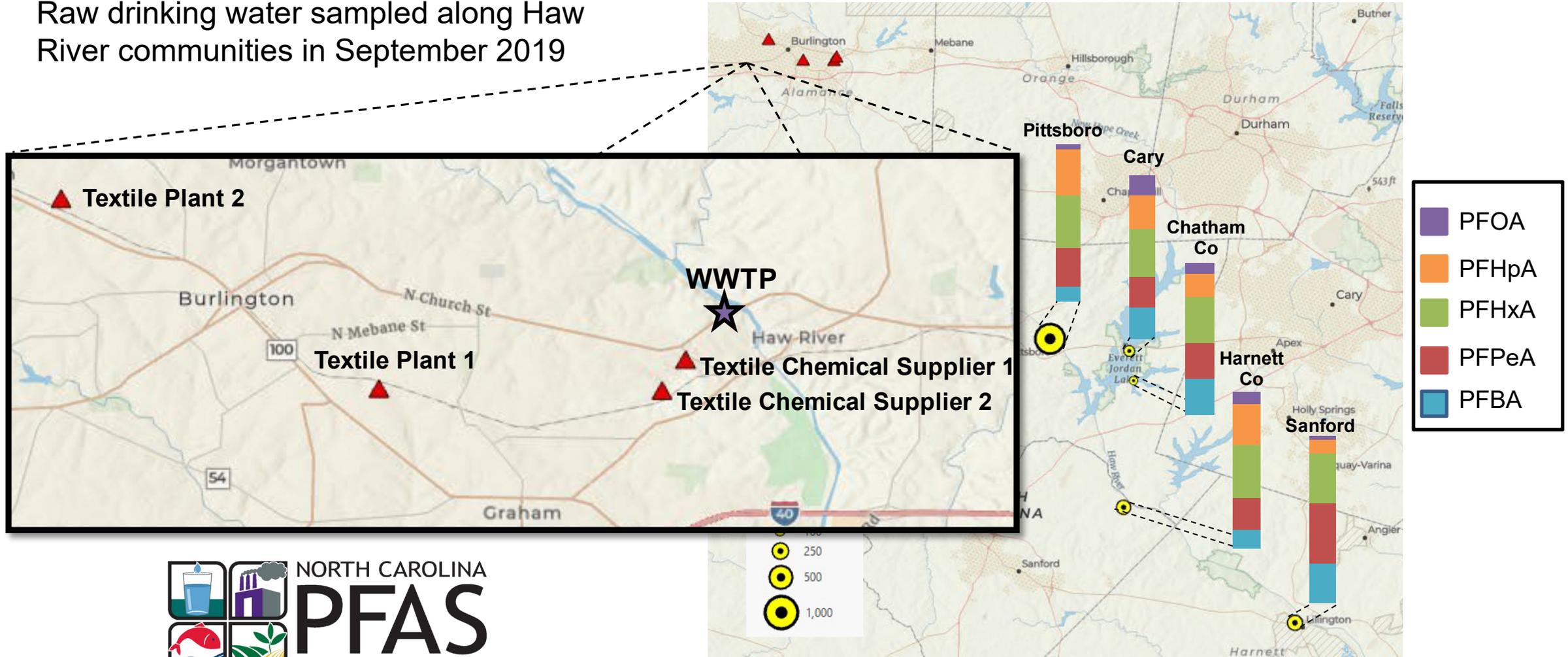# Sources near Burlington, NC contribute significant PFAS to the Haw River
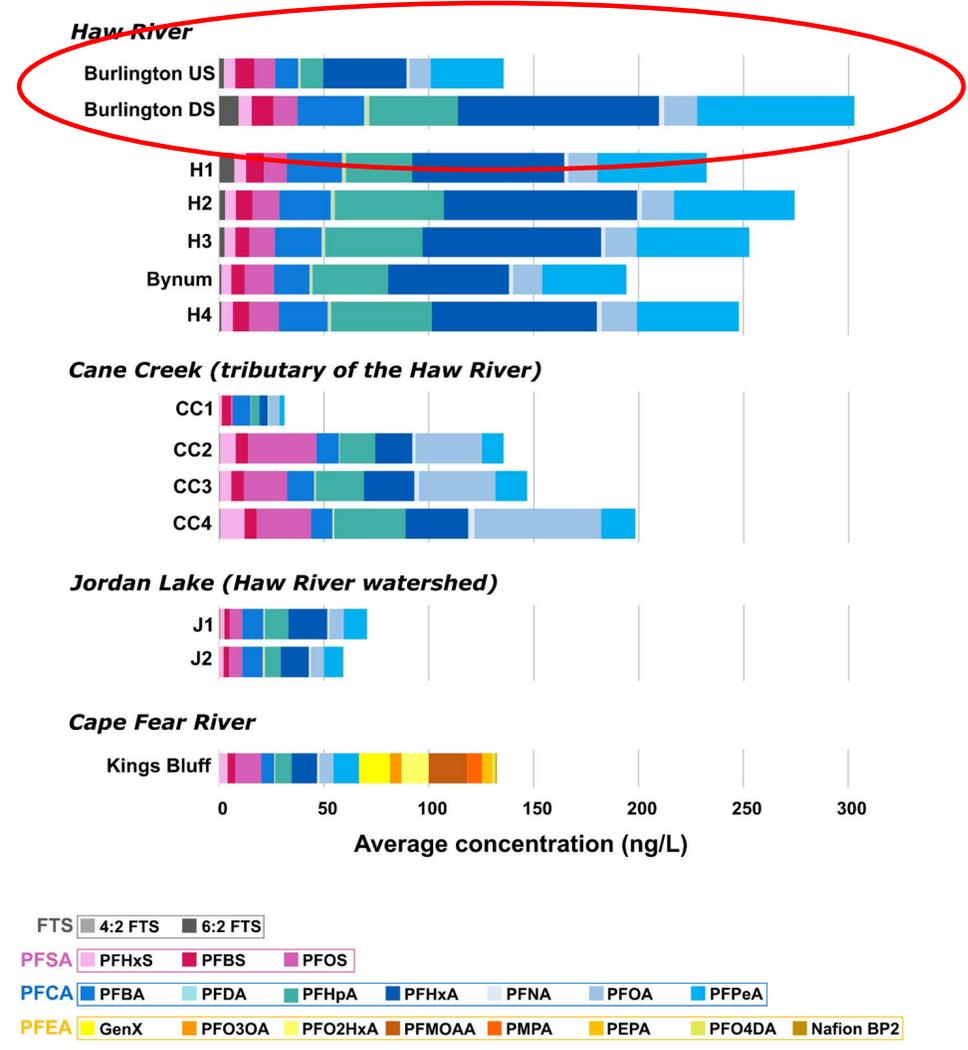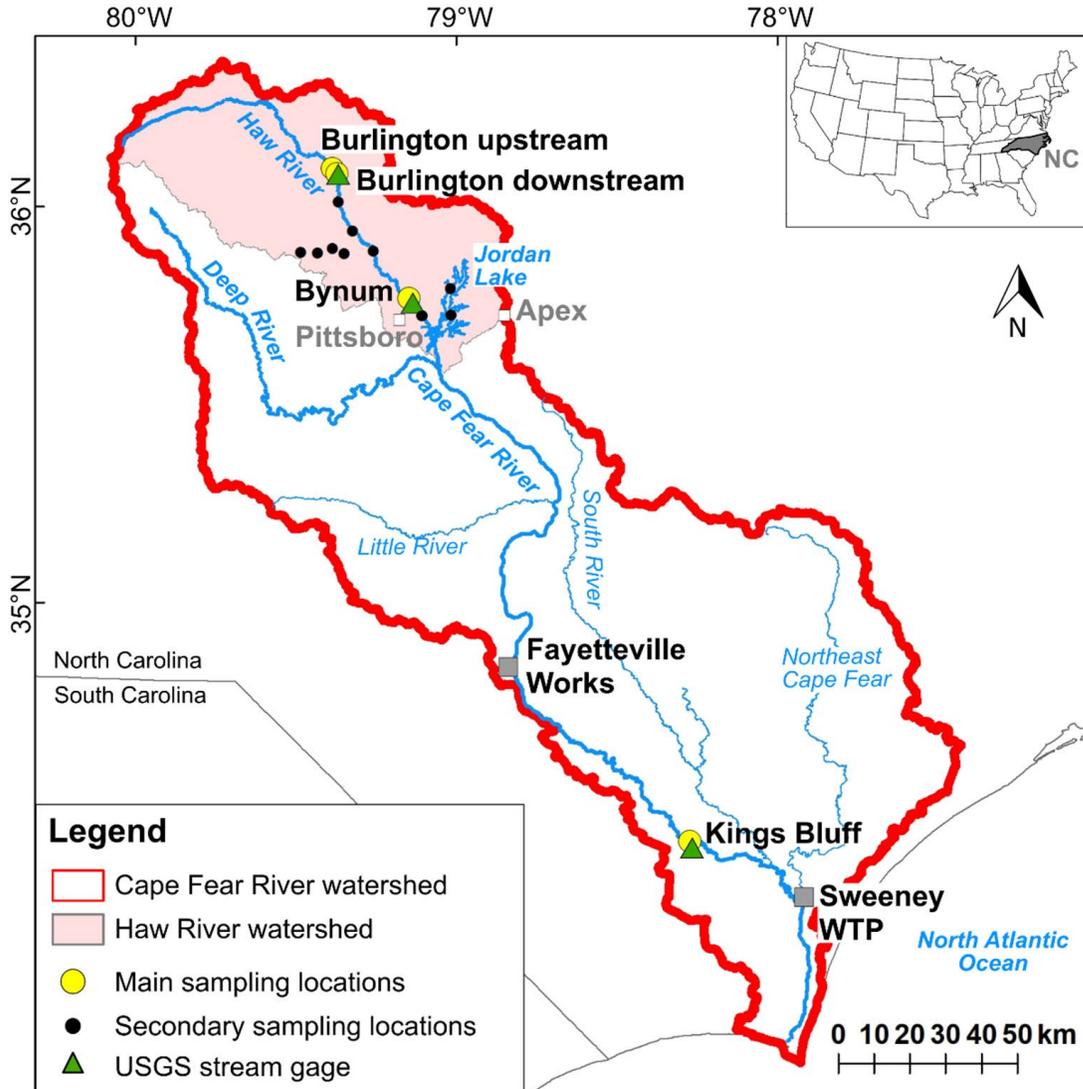
M.-A. Pétré, K.R. Salk, H.M. Stapleton, P.L. Ferguson, G. Tait, D.R. Obenour, D.R.U. Knappe, D.P. Genereux. 2022. Per- and polyfluoroalkyl substances (PFAS) in river discharge: Modeling loads upstream and downstream of a PFAS manufacturing plant in the Cape Fear watershed, North Carolina. *Sci. Total Environ.* 831, 154763.

Drinking water sources downstream from Burlington were impacted by PFAS discharges

Raw drinking water sampled along Haw River communities in September 2019

Burlington WWTP discharged elevated PFAS to the Haw River before May 2020

Zimpro® wet air sludge oxidation halted

Legend: ▲ Influent ● Effluent

Y-axis: Sum PFAS (ng/L), 0 to 35,000

X-axis: 10/12/19, 12/1/19, 1/20/20, 3/10/20, 4/29/20, 6/18/20, 8/7/20, 9/26/20, 11/15/20, 1/4/21, 2/23/21, 4/14/21, 6/3/21, 7/23/21, 9/11/21, 10/31/21, 12/20/21, 2/8/22

https://www.siemens.com/

Diagram labels: Air Compressor, Atmospheric Air, Feed Pump, Feed, Heat Recovery Heat Exchanger, Reactor, Steam Temperature Control Valve, Pressure Control Valve, Cooling Water, Process Cooler, Separator, Off-Gas, Treated Effluent
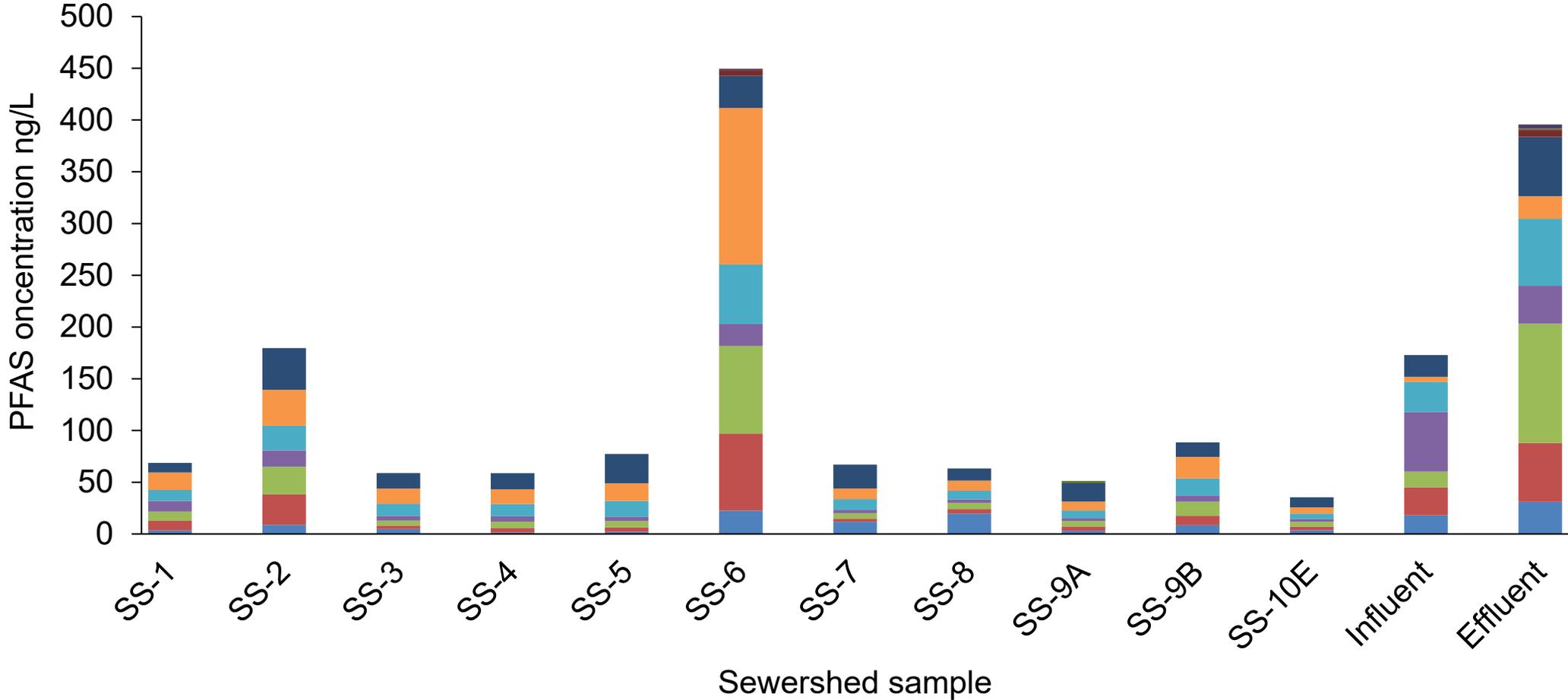
Data from City of Burlington

Sewershed monitoring for PFAS was initiated in cooperation with Burlington during 2021

Sewershed boundaries were designed to capture industries likely to use/discharge PFAS
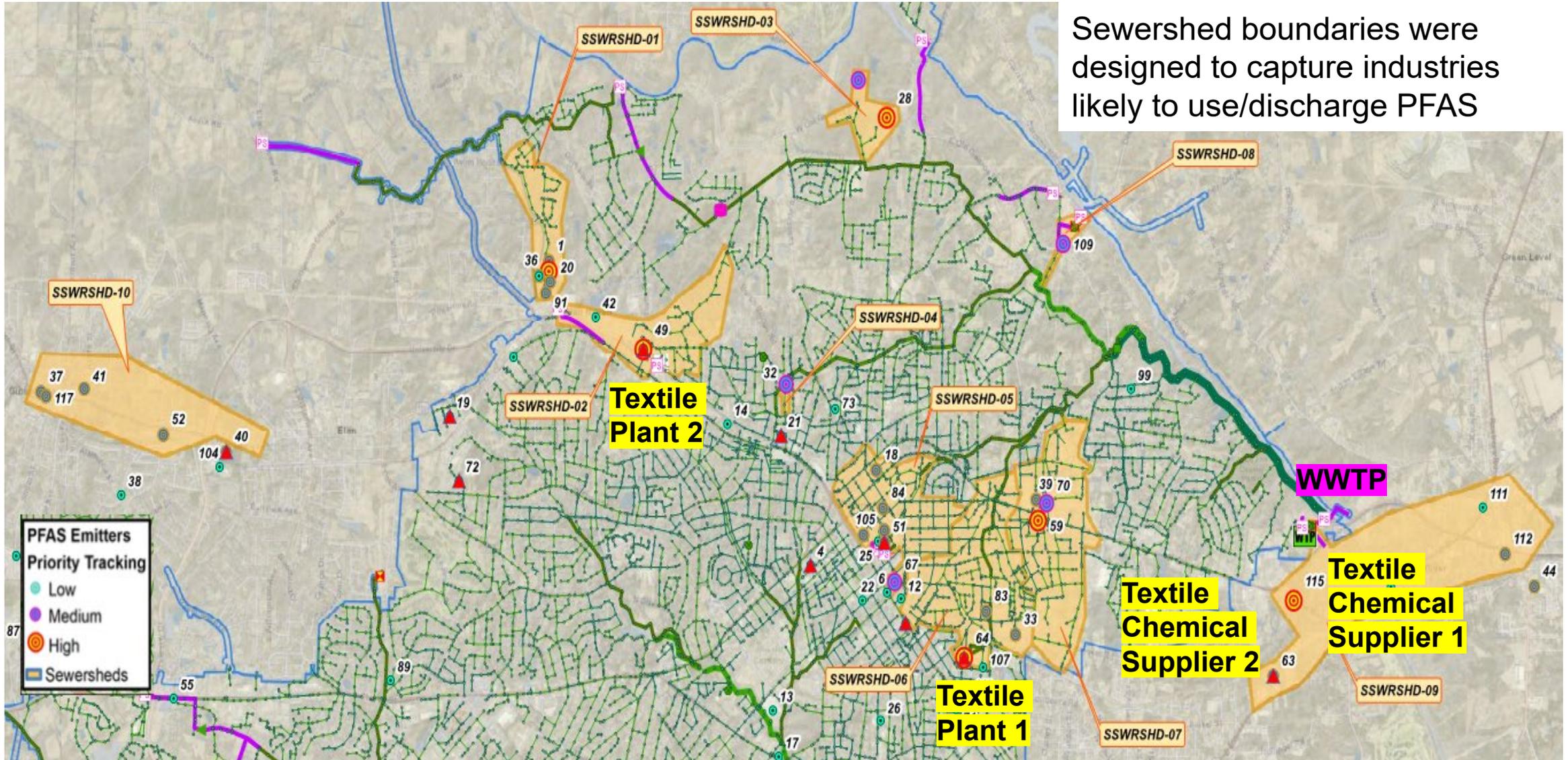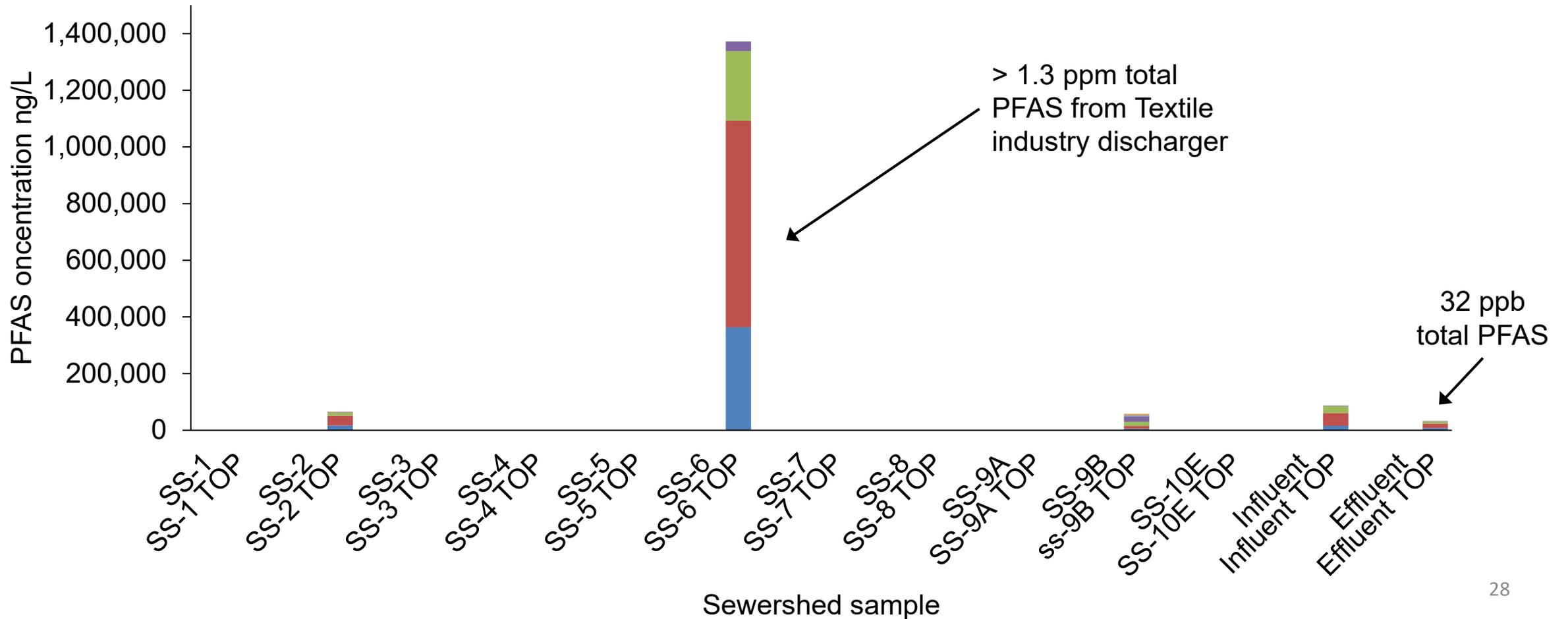
Targeted PFAS concentrations in raw wastewater did not explain pre-2020 effluent levels

Legend: PFBA, PFPeA, PFHxA, PFHpA, PFOA, Total long chain PFCA, Total sulfonic acid, Total sulfonamide, Total Zwitterion, Total FTS

Y-axis: PFAS oncentration ng/L (0 to 500)

X-axis (Sewershed sample): SS-1, SS-2, SS-3, SS-4, SS-5, SS-6, SS-7, SS-8, SS-9A, SS-9B, SS-10E, Influent, Effluent

Total oxidizable precursor (TOP) assay

Total Oxidizable Precursor (TOP) Assay

16 hours @85°C

200mM K₂S₂O₈
500mM NaOH

Unknown precursors
precursors
PFCAs
PFSAs

PFCAs
PFSAs

Non-oxidizable Precursors

Reversed-phase LC-MS/MS

HILIC LC-MS/MS

Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and David L. Sedlak*

Department of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, California, 94720-1710
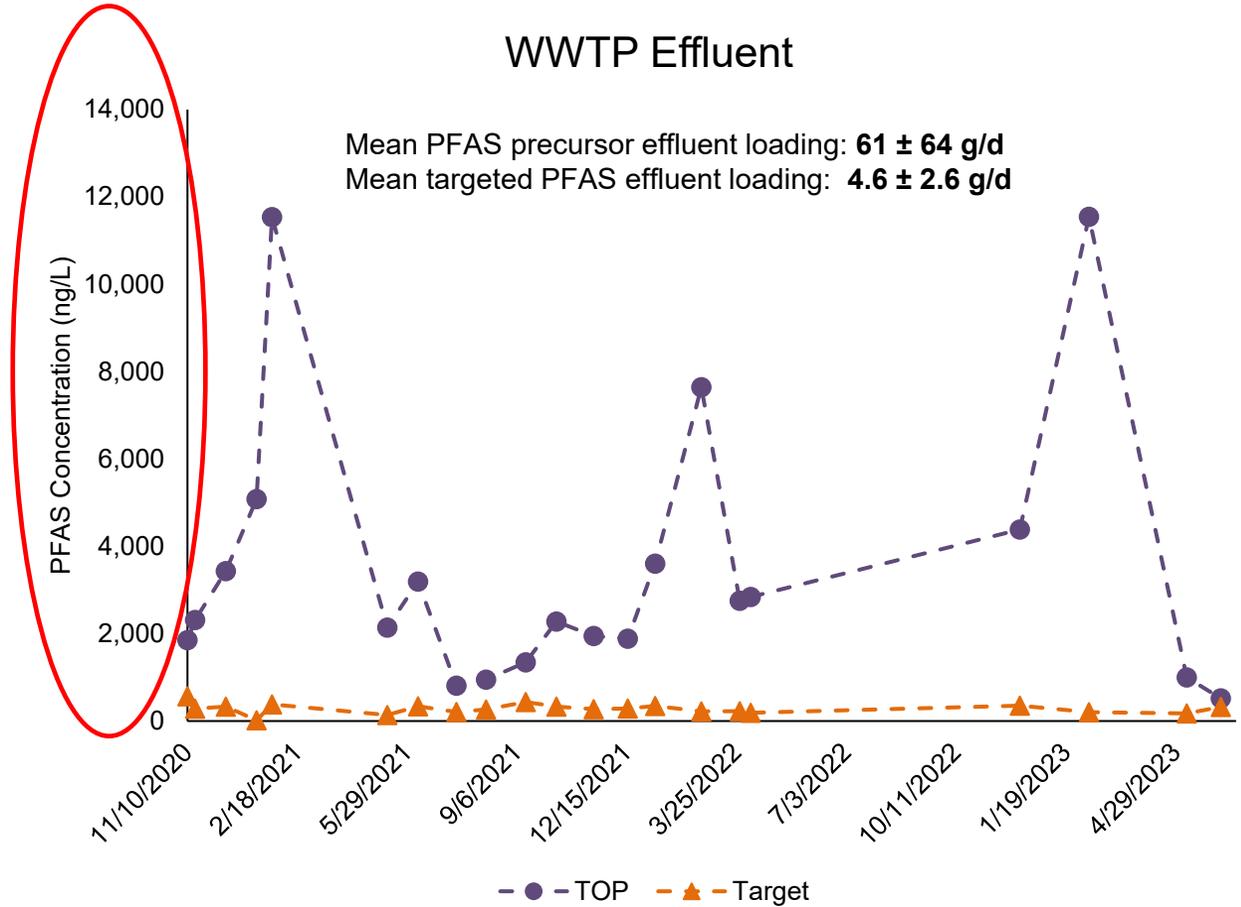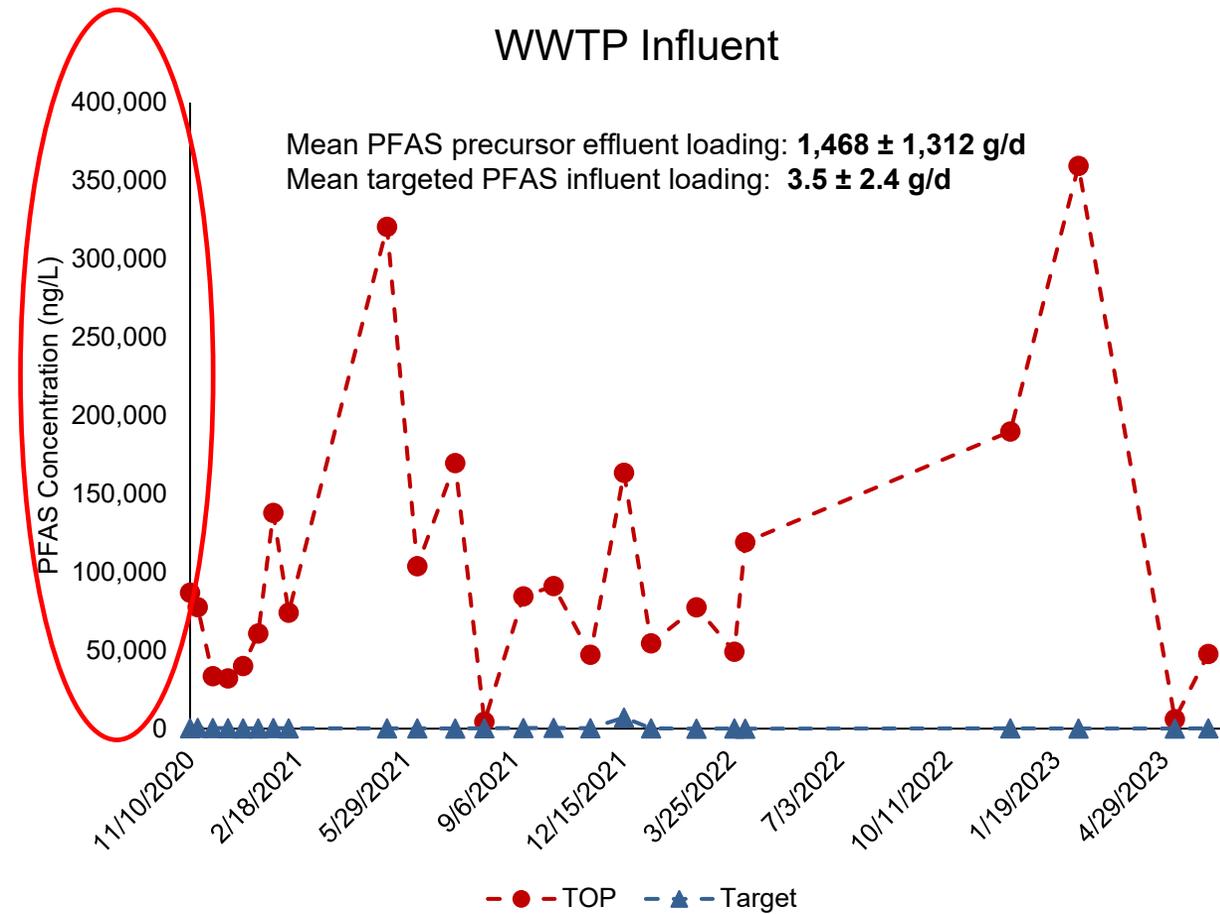
TOP assay revealed very high levels of PFAS precursors in one sewershed

Legend: PFBA, PFPeA, PFHxA, PFHpA, PFOA, Total long chain PFCA, Total sulfonic acid, Total sulfonamide, Total Zwitterion, Total FTS

Y-axis: PFAS oncentration ng/L

X-axis: Sewershed sample (SS-1, SS-1 TOP, SS-2, SS-2 TOP, SS-3, SS-3 TOP, SS-4, SS-4 TOP, SS-5, SS-5 TOP, SS-6, SS-6 TOP, SS-7, SS-7 TOP, SS-8, SS-8 TOP, SS-9A, SS-9A TOP, SS-9B, ss-9B TOP, SS-10E, SS-10E TOP, Influent, Influent TOP, Effluent, Effluent TOP)

> 1.3 ppm total PFAS from Textile industry discharger

32 ppb total PFAS

Textile-derived PFAS precursors constituted the majority of PFAS loadings to and from WWTP

WWTP Influent

Mean PFAS precursor effluent loading: **1,468 ± 1,312 g/d**
Mean targeted PFAS influent loading: **3.5 ± 2.4 g/d**

WWTP Effluent

Mean PFAS precursor effluent loading: **61 ± 64 g/d**
Mean targeted PFAS effluent loading: **4.6 ± 2.6 g/d**

Over 90% of textile-derived PFAS precursors were removed to sludge during municipal wastewater treatment, via agglomeration and settling – *implications for biosolids disposal*

Industrial textile wastewater contained > 10 part-per-million colloidal PFAS precursors
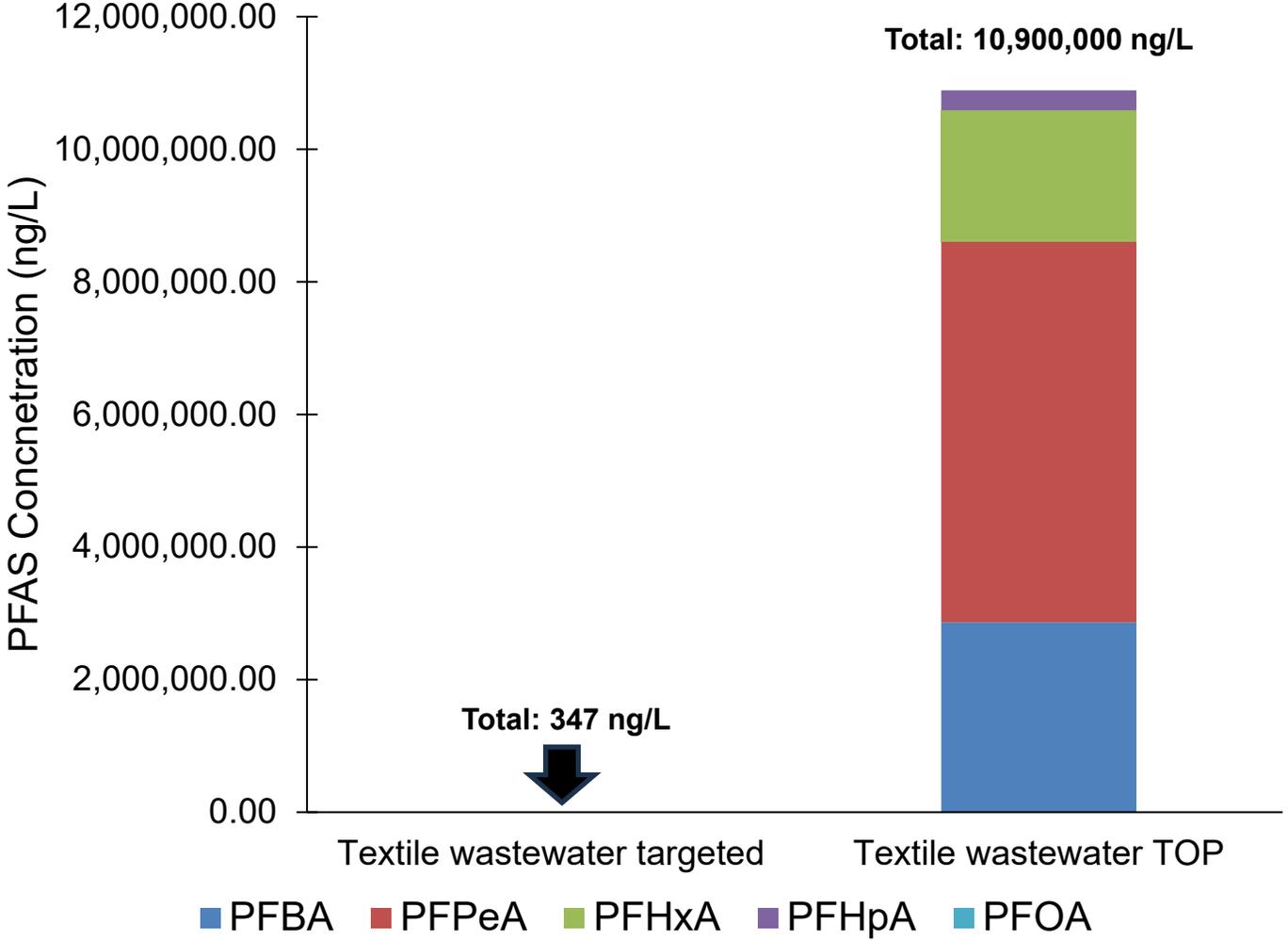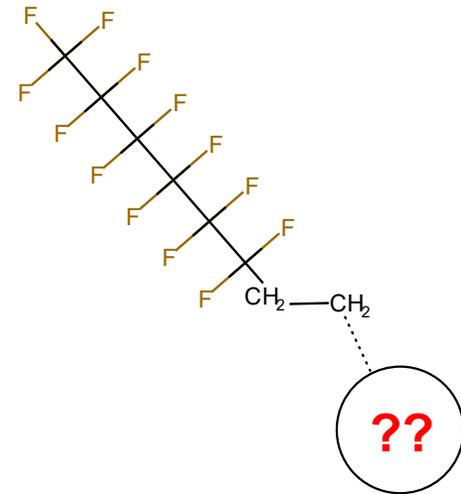

- Total oxidizable precursor (TOP) assay revealed 6:2 fluorotelomer precursors as the dominant PFAS in wastewater from textile plant #1

- Precursors could not be detected in targeted (48 analytes) or non-targeted (Orbitrap high-resolution MS) analysis

PFAS precursors could be quantitatively isolated by ultrafiltration on 30 kDa MWCO membrane
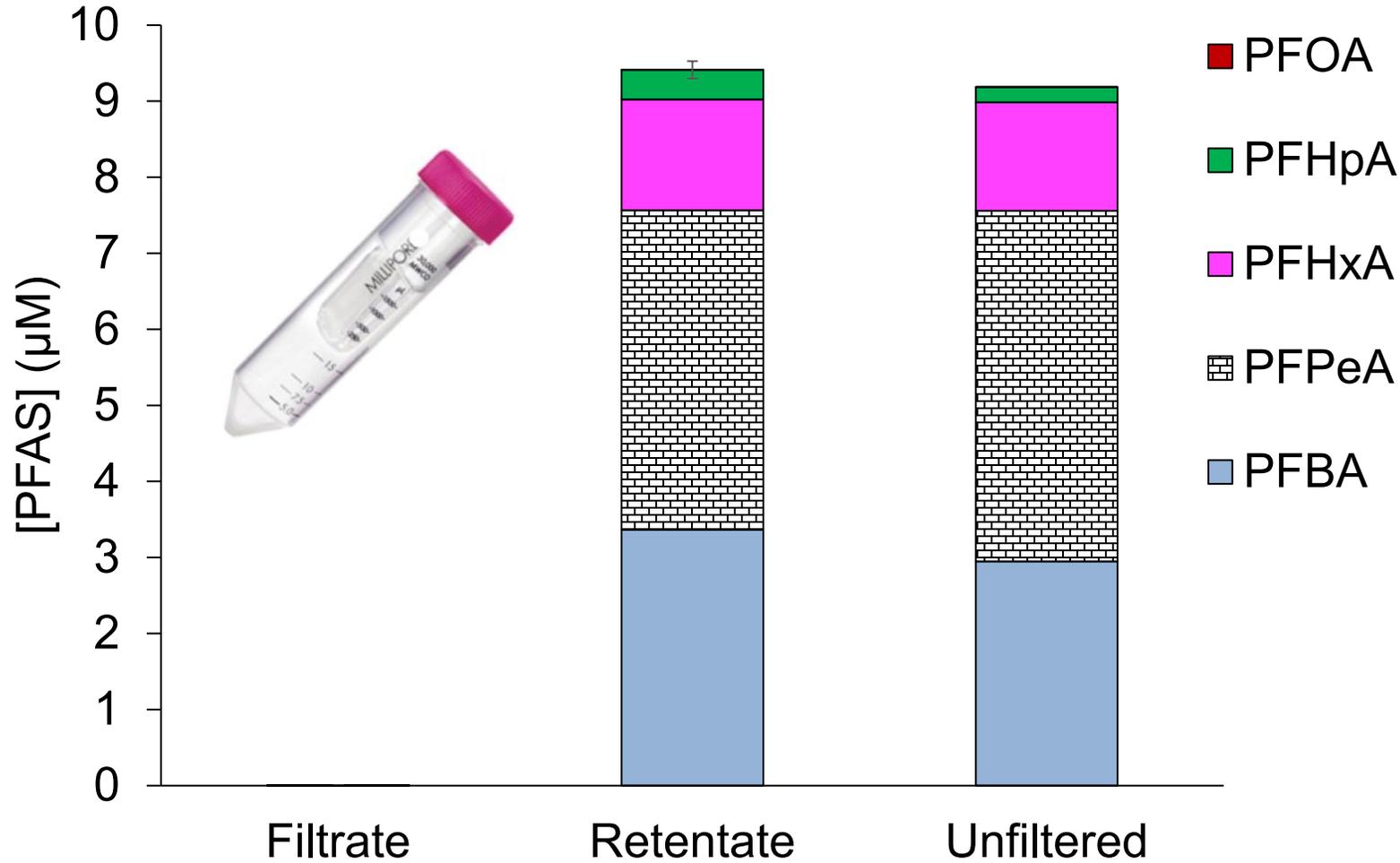
Ultrafiltration revealed that precursors were < 0.2 μm in diameter, and > 30,000 molecular weight (*colloidal/nanoparticulate size*)

Legend:
- PFOA
- PFHpA
- PFHxA
- PFPeA
- PFBA

X-axis: Filtrate, Retentate, Unfiltered
Y-axis: [PFAS] (μM)

Assymetric flow field flow fractionation (AF4) for colloid separation

- AF4 separates nanoparticulates via hydrodynamic flow

- Open channel separation avoids problems with particle attachment to packing surfaces

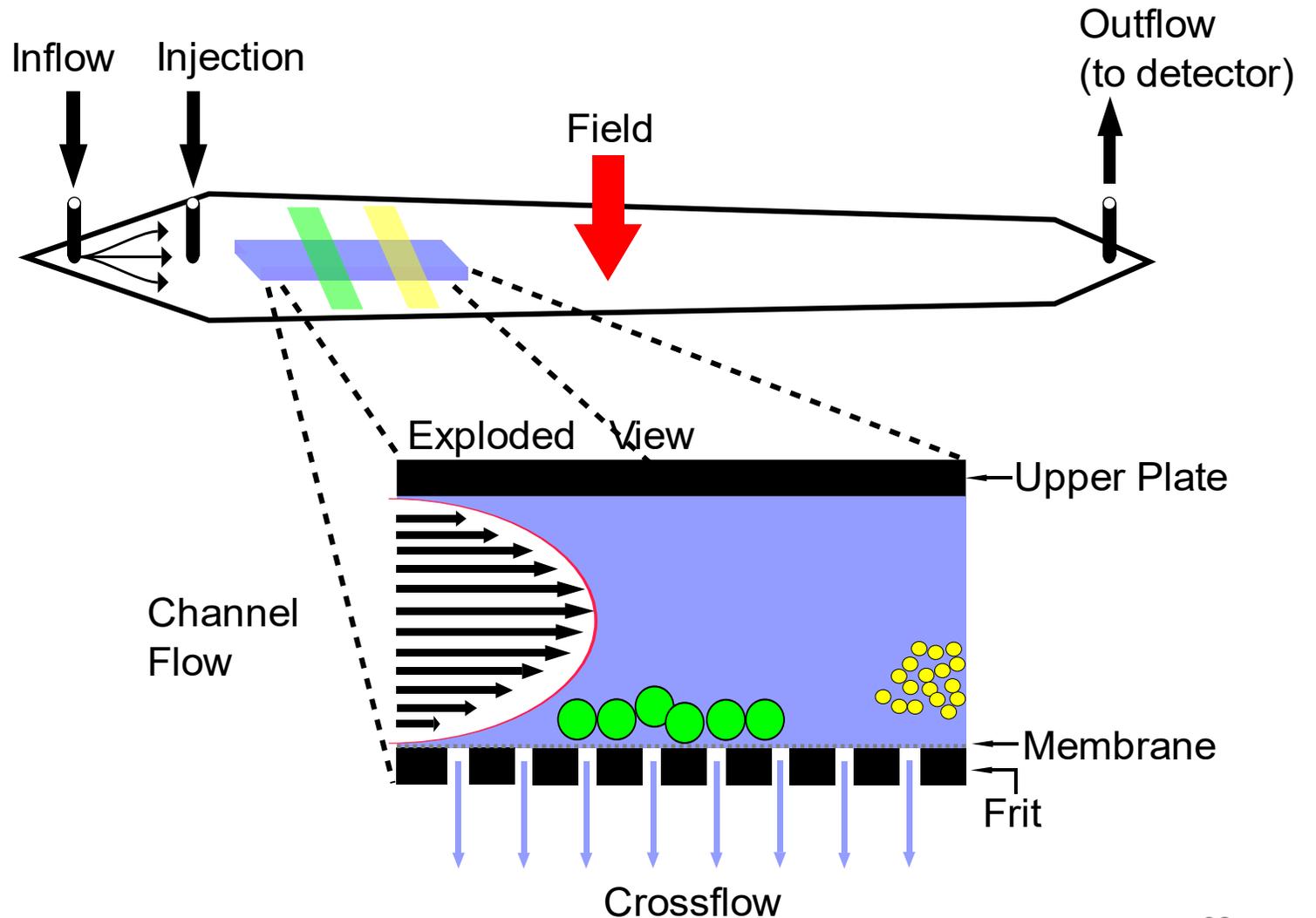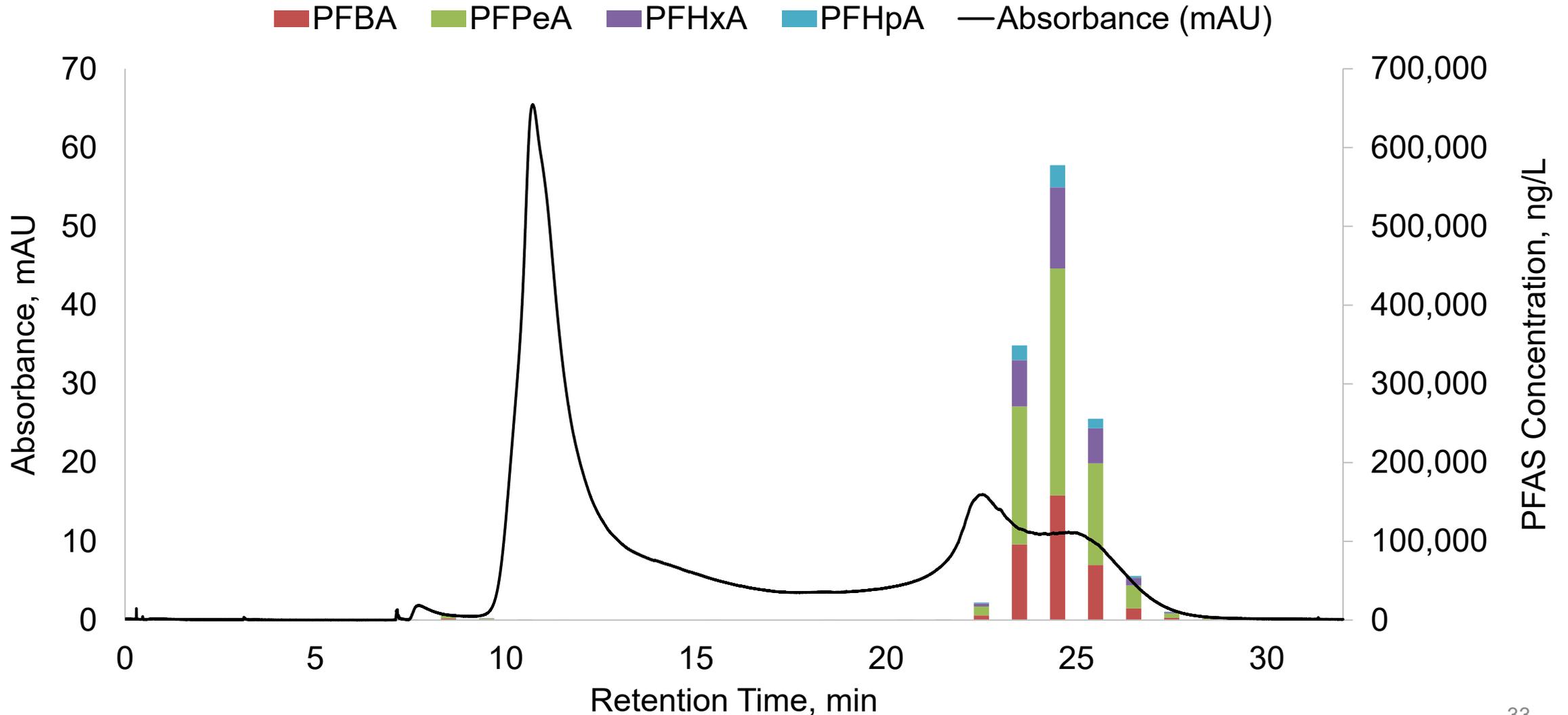- Separation mechanism intrinsically removes low MW compounds
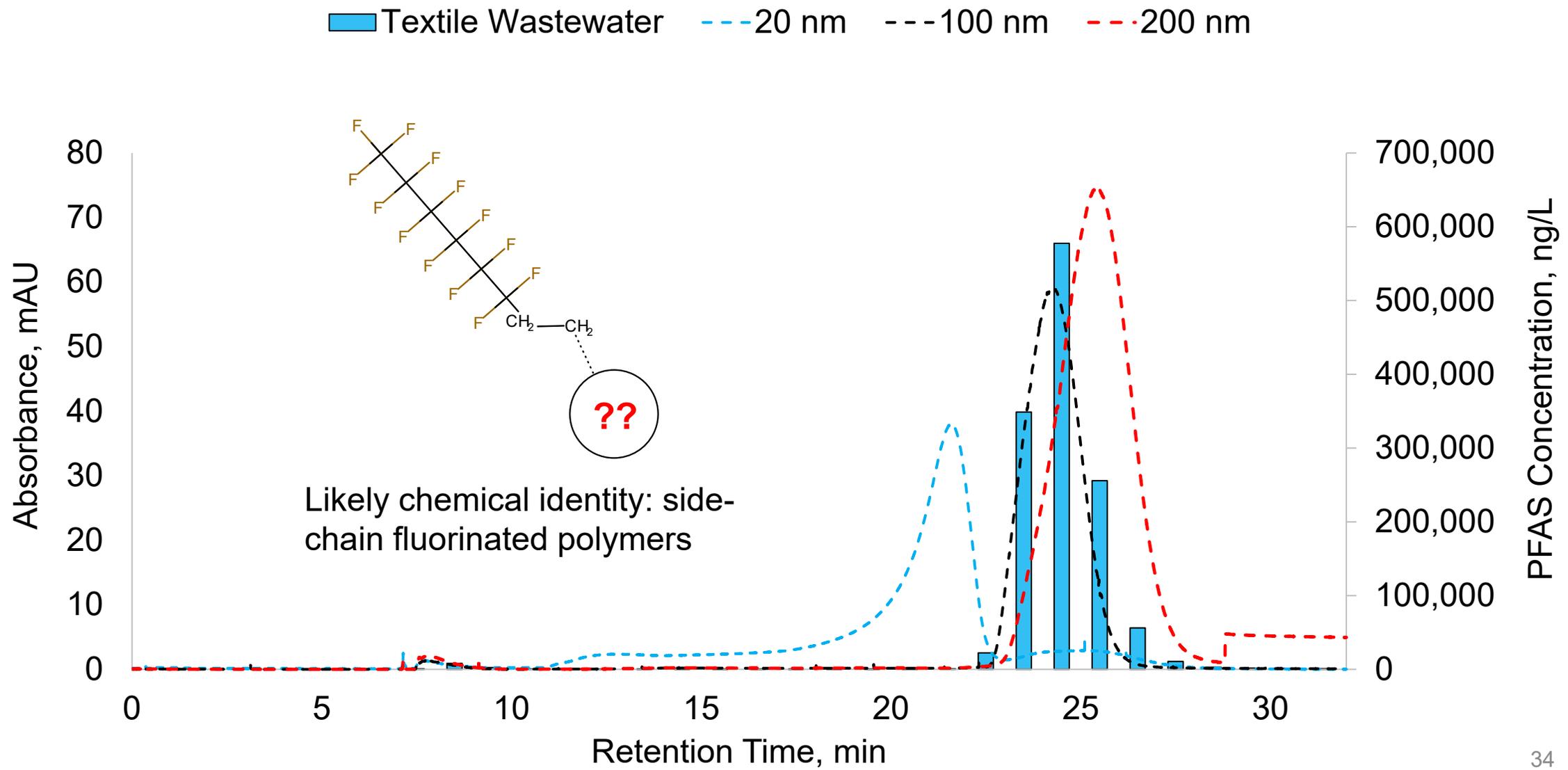
Inflow   Injection   Outflow (to detector)

Field

Exploded View

Upper Plate

Channel Flow

Membrane

Frit

Crossflow

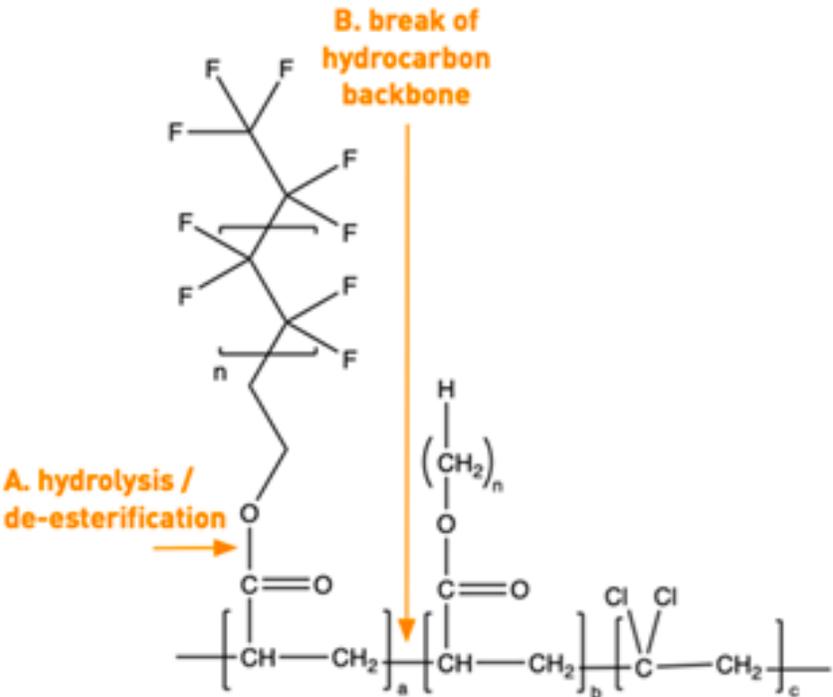Image courtesy of Wyatt Technology Gmbh

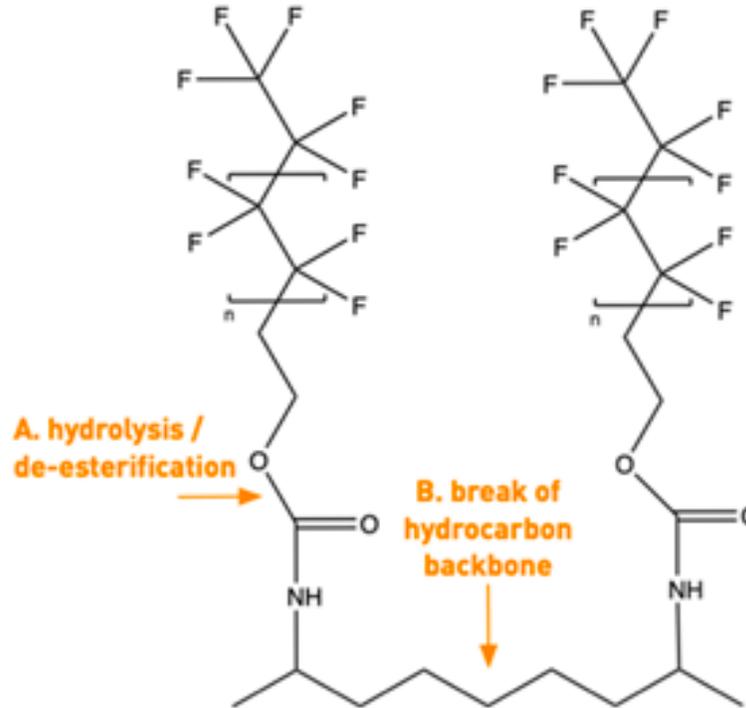# Textile wastewater separation using AF4 reveals colloidal PFAS precursors

Colloidal PFAS precursors in textile wastewater elute near 100 nm size standards

Hypothesis: the nanoparticulate PFAS in textile wastewater are polymeric residues

B. break of hydrocarbon backbone

A. hydrolysis / de-esterification

an example of fluorotelomer acrylate polymers

A. hydrolysis / de-esterification

B. break of hydrocarbon backbone

conceptual chemical composition of a fluorotelomer urethane polymer

Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle

OECD
BETTER POLICIES FOR BETTER LIVES

Side chain fluorinated polymers (SCFP) are performance coatings used in textiles and other applications to repel water, oil, and grease.

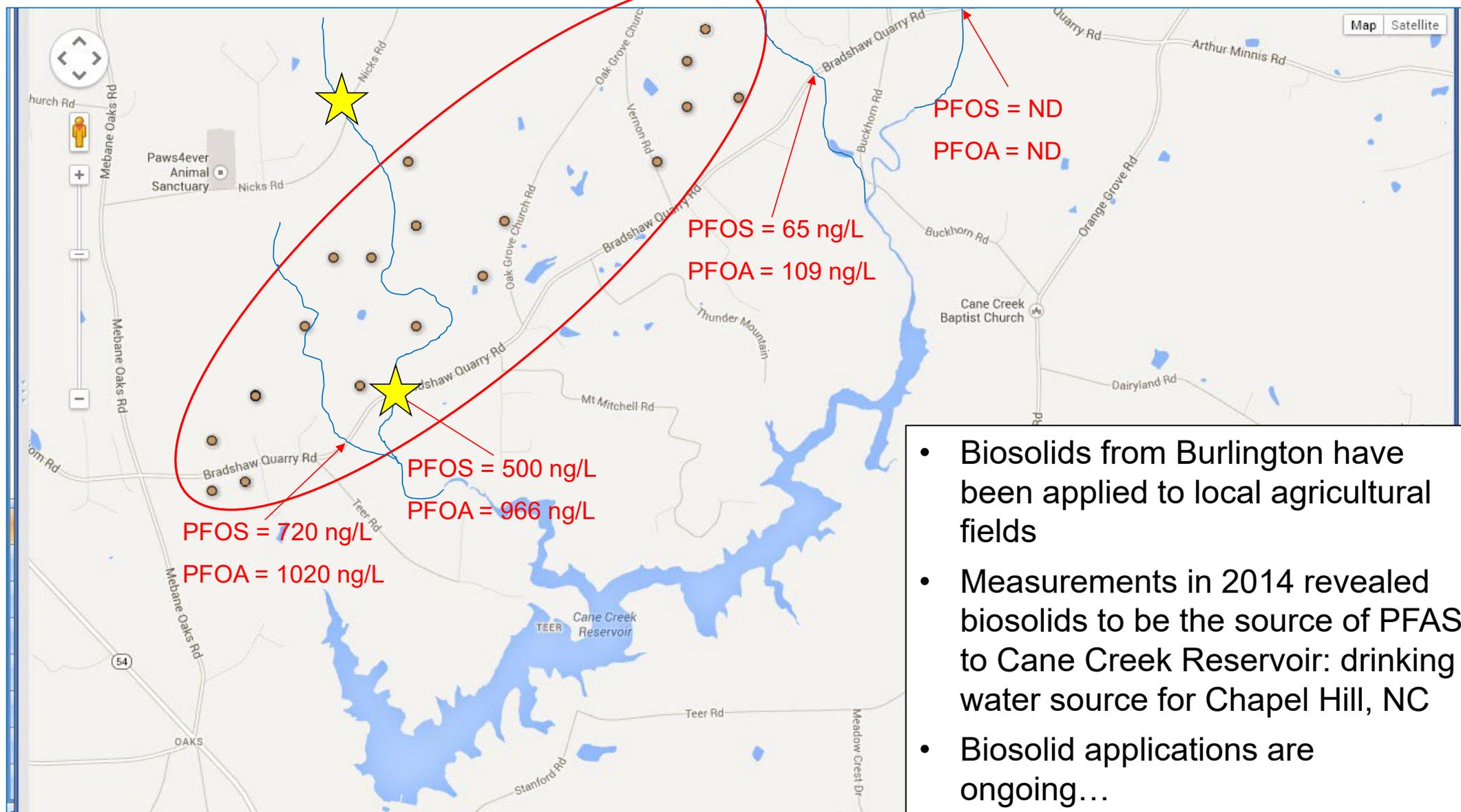These polymers can undergo slow degradation in the environment

Ongoing work: characterization of SCFP isolated from textile wastewater (NMR, FTIR, MALDI, chemical degradation)

Conclusions

- Analytical cheminformatics combined with online-SPE and high-resolution MS are enabling technologies for comprehensive PFAS analysis in the environment

- High concentrations of PFAS in the Haw River of NC were contributed by textile manufacturing facilities in Burlington, NC

- PFAS sources were characterized as 6:2 fluorotelomer-based precursors

- Combination of total oxidizable precursor assay with size separation techniques reveals novel colloidal PFAS contaminants in textile wastewater

Epilogue: what about the sludge??

- Biosolids from Burlington have been applied to local agricultural fields
- Measurements in 2014 revealed biosolids to be the source of PFAS to Cane Creek Reservoir: drinking water source for Chapel Hill, NC
- Biosolid applications are ongoing…

Data from Andy Lindstrom, Mark Strynar (USEPA), Detlef Knappe (NCSU), 2014 unpublished

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Ferguson Lab Group

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NORTH CAROLINA
PFAS
Testing Network

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