Per- and Polyfluoroalkyl Substances (PFAS) in North Carolina Drinking Water Sources:
Analytical Techniques and Challenges

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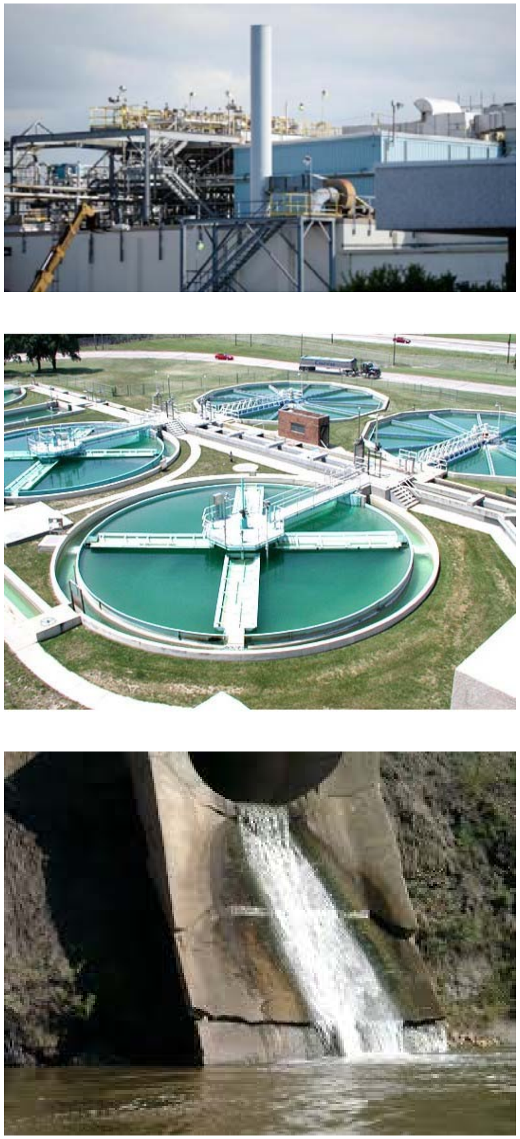
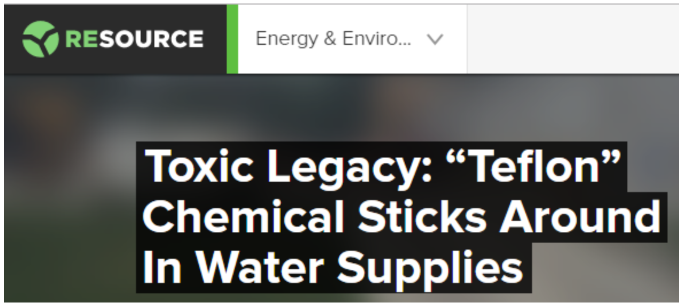
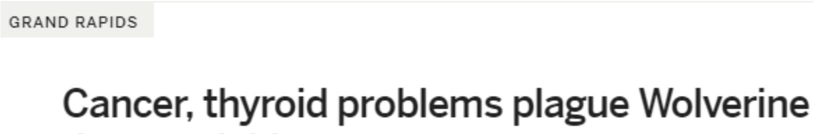
PFAS Background:
What is it and why do we care?



PFAS are gaining attention – news media and Google searches



Toxic Legacy: "Teflon" Chemical Sticks Around In Water Supplies



Cancer, thyroid problems plague Wolverine dump neighbors

Updated Oct 1, 2017; Posted Oct 1, 2017

LAWSUITS CHARGE THAT 3M KNEW ABOUT THE DANGERS OF ITS CHEMICALS

Study: High levels of toxic chemicals in drinking water of 6 million Americans

BY MARY BROPHY MARCUS
AUGUST 9, 2016 / 11:42 AM / CBS NEWS

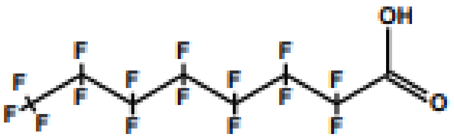
Scientists advise Michigan to set tougher PFAS standards

David Eggert, Associated Press Published 2:27 p.m. ET June 28, 2019 | Updated 5:25 p.m. ET June 28, 2019

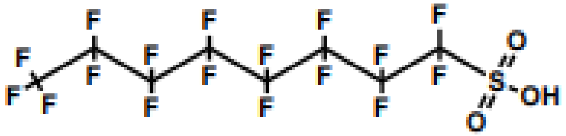
Per- and Polyfluoroalkyl Substances

- Per- and Polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals

Legacy PFASs:

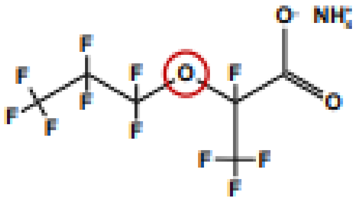


Perfluorooctanoic acid **(PFOA)**

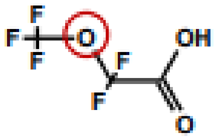


Perfluorooctane sulfonic acid **(PFOS)**

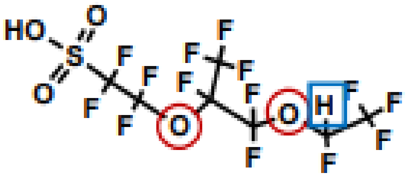
Fluorinated Alternatives:



ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate **(GenX)**

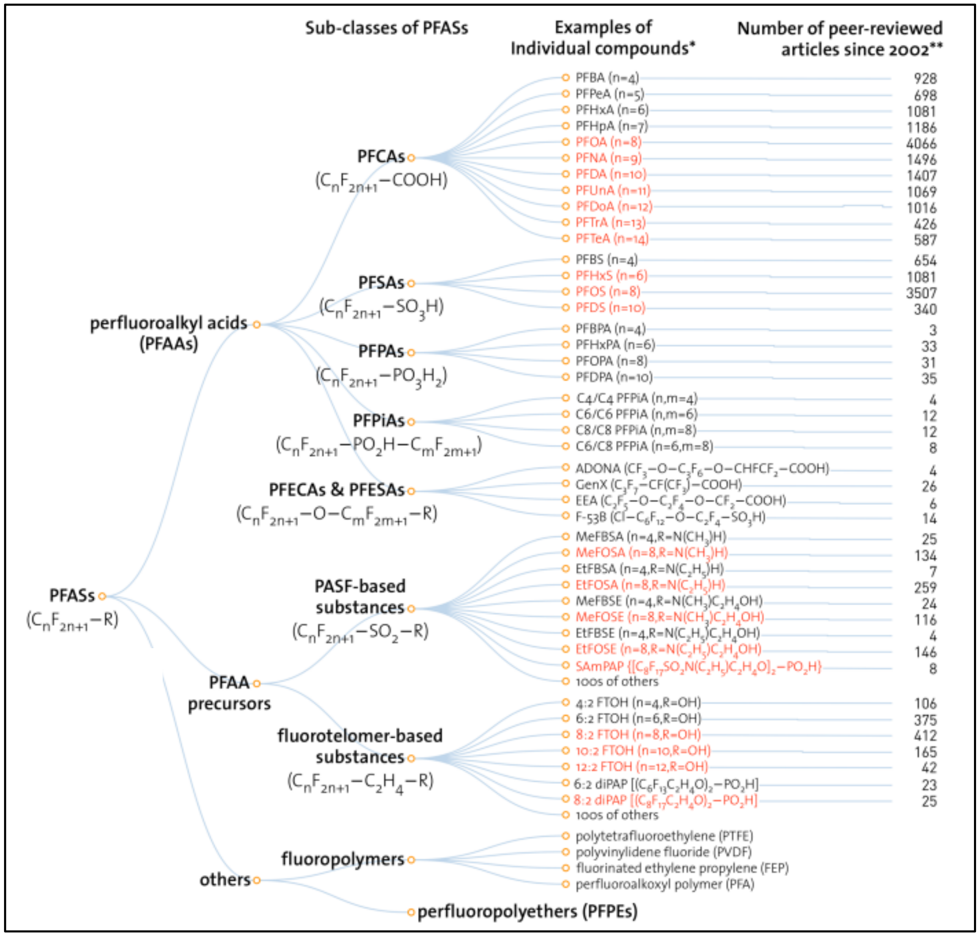


Perfluoro-2-methoxyacetic acid **(PFMOAA)**



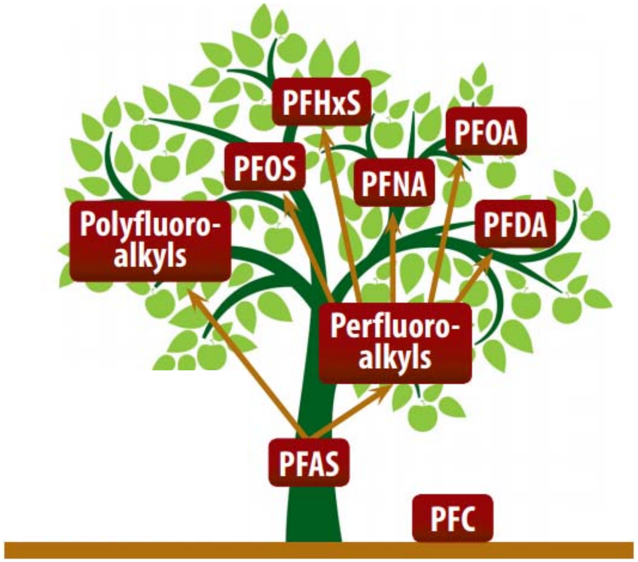
Nafion By-product 2

PFAS include many sub-classes and thousands of individual compounds



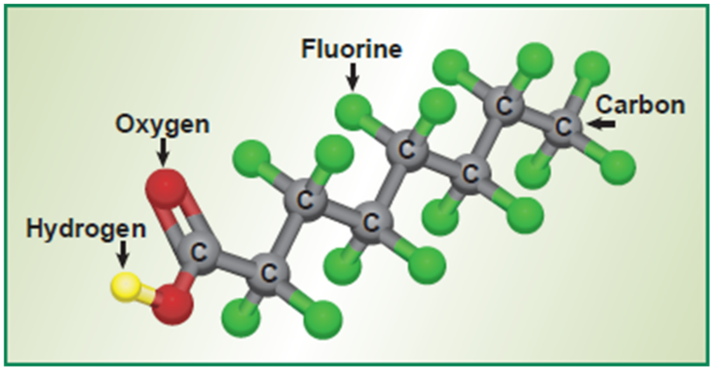
Wang et al., 2017, ES&T

- ➢ PFAS have been commercially produced since the 1950's
- ➢ > 3,000 may have been on the global market
- ➢ > 5,000 named on the EPA master list



https://www.atsdr.cdc.gov/docs/17_278160-A_PFAS-FamilyTree-508.pdf

Molecular properties of PFAS: the “forever chemicals”

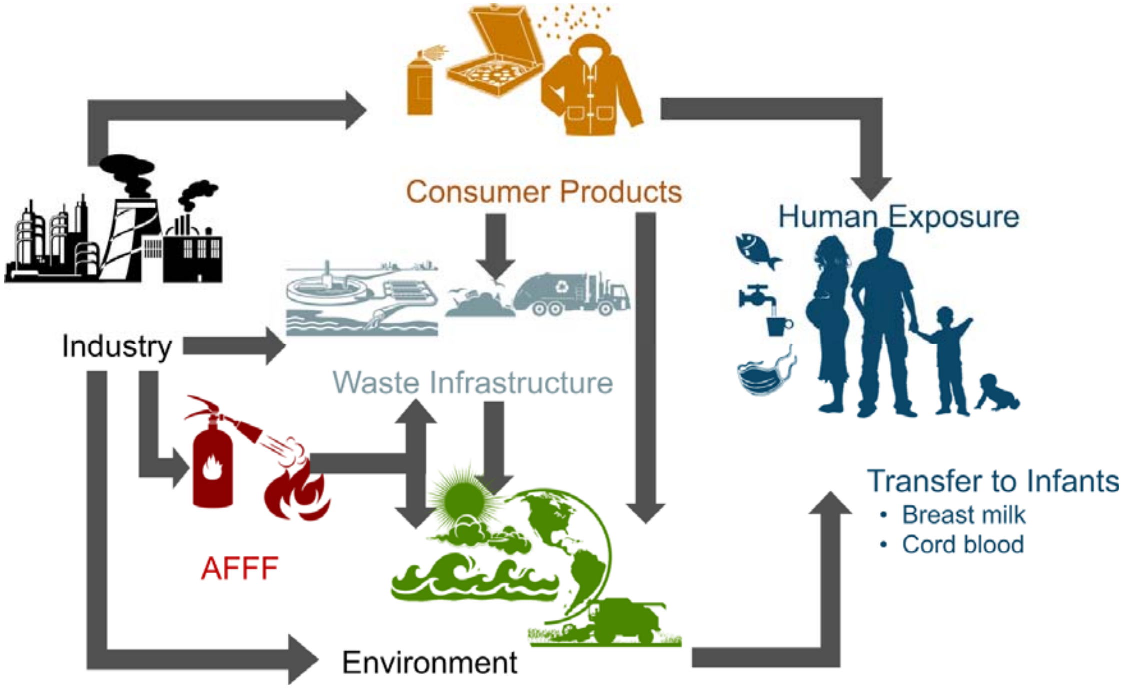


PFAS properties:

- Strong, electronegative polar covalent C-F bond
- Thermally & chemically stable
- Surfactant behavior
- Persistent in the environment
- Resistant to degradation
- Bioaccumulative
- Some PFAS are globally ubiquitous

Human Exposure and Health Effects

- PFOS, PFOA, PFNA and PFHxS are detected in humans globally
- PFOS and PFOA are "likely carcinogenic" (US EPA, 2016) and immunotoxic to humans (US DHHS, 2019)
- Health effects associated with exposure to many other PFAS are poorly understood



Sunderland et al., 2019, Nature

Current Federal and State PFAS Drinking Water Health Advisories

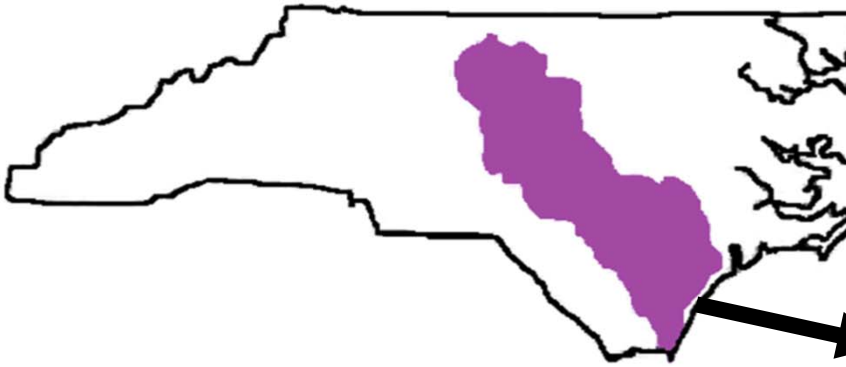
- Federal regulations have not been established for PFAS!

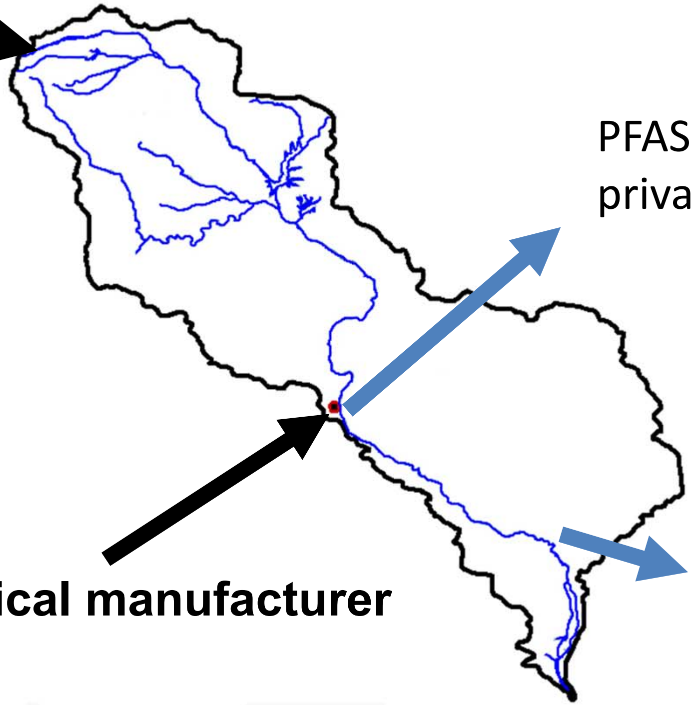
Health advisory = non-enforceable health goal

Maximum contaminant level (MCL) = enforceable standard

Agency / State	PFAS Name	Conc. (ng/L)	Status
US EPA, Maine, West Virginia	Σ PFOA + PFOS	70	advisory
Vermont	Σ PFOA + PFOS	20	advisory
Connecticut	Σ PFOA, PFOS, PFNA, PFHxS, PFHpA	70	advisory
New Jersey	PFOA PFOS PFNA	14 13 13	proposed proposed MCL
Minnesota	PFOA PFOS	35 27	advisory advisory
North Carolina	GenX	140	advisory

PFAS are contaminants in North Carolina surface and groundwater



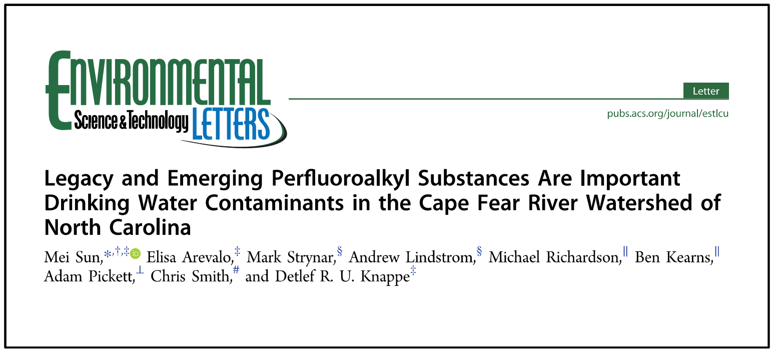


Cape Fear River basin

PFAS-impacted private wells

Fluorochemical manufacturer

PFAS-impacted surface water treatment plants



ENVIRONMENTAL Science & Technology LETTERS

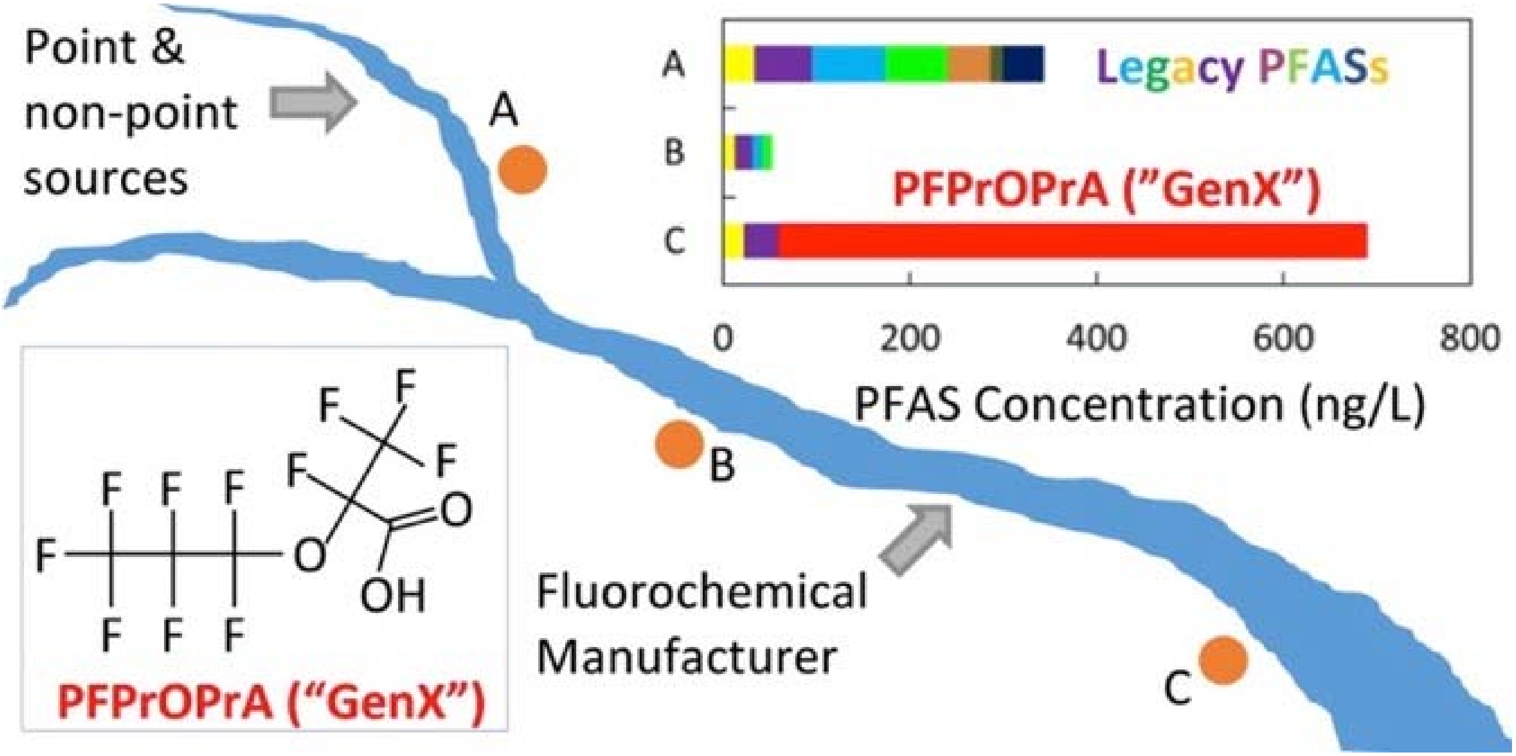
Letter

pubs.acs.org/journal/estlcu

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

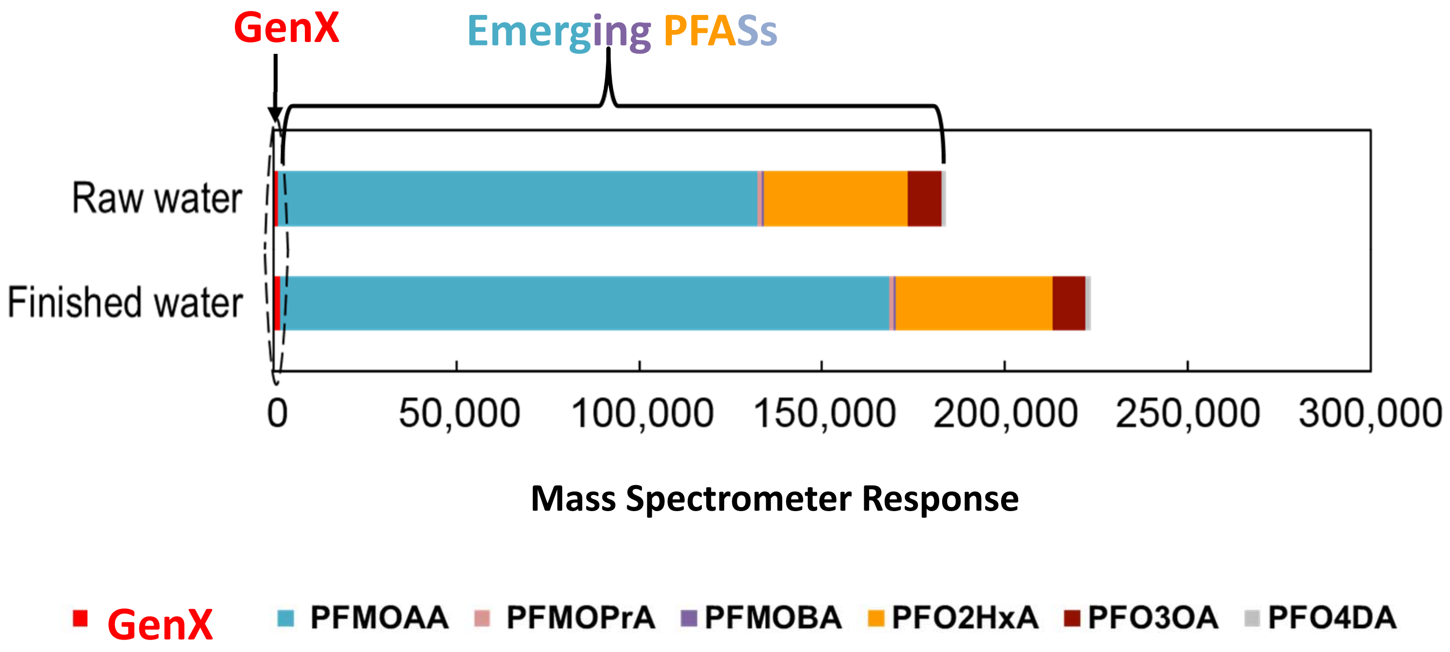
Mei Sun,[*,†,‡] Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,[∥] Ben Kearns,[∥] Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

Elevated concentrations of "GenX" were detected in drinking water sources downstream of a fluorochemical manufacturer



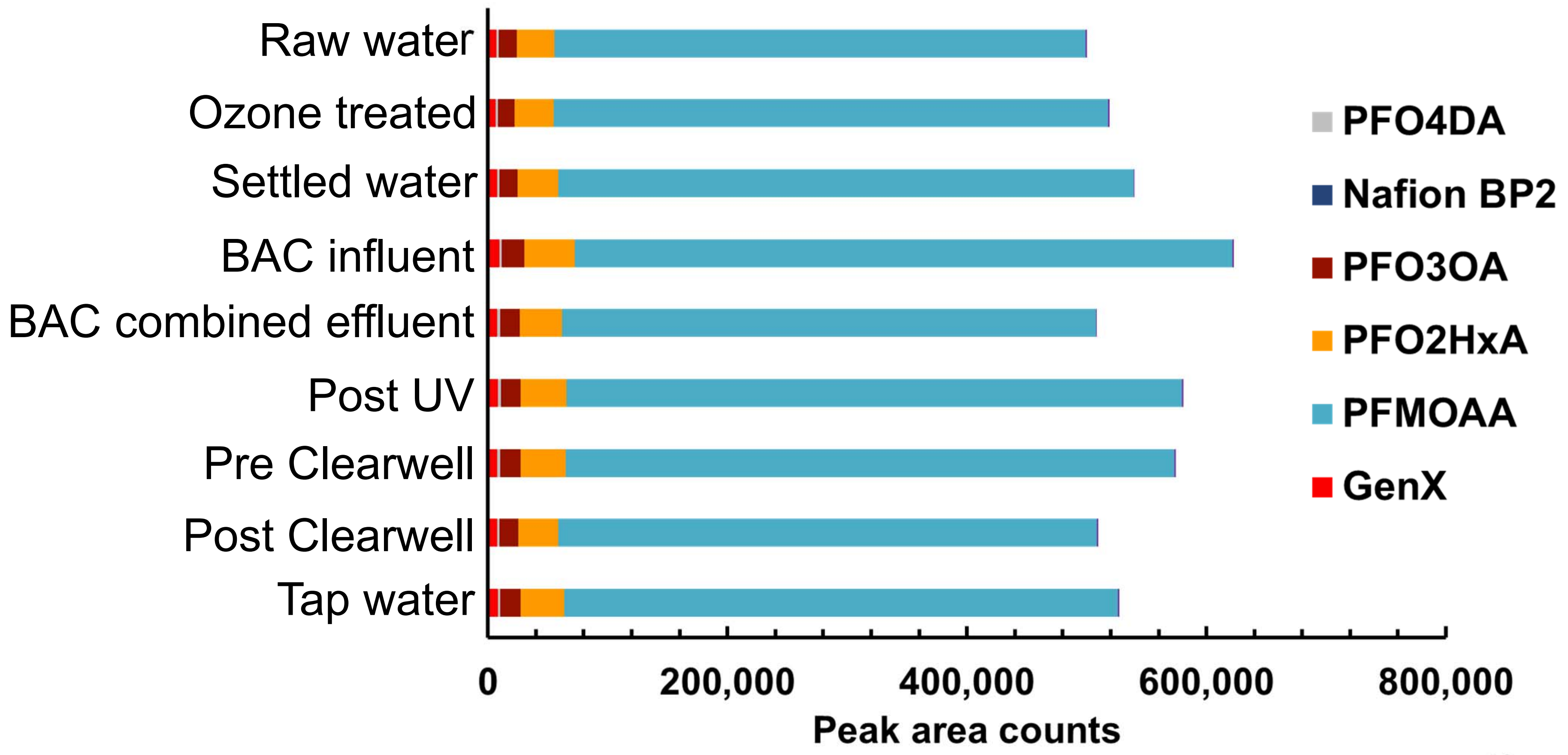
Sun et al., 2016, ES&T

GenX was only a small fraction of the total mass spectrometer response associated with PFAS in Wilmington, NC



Sun et al., 2016, ES&T

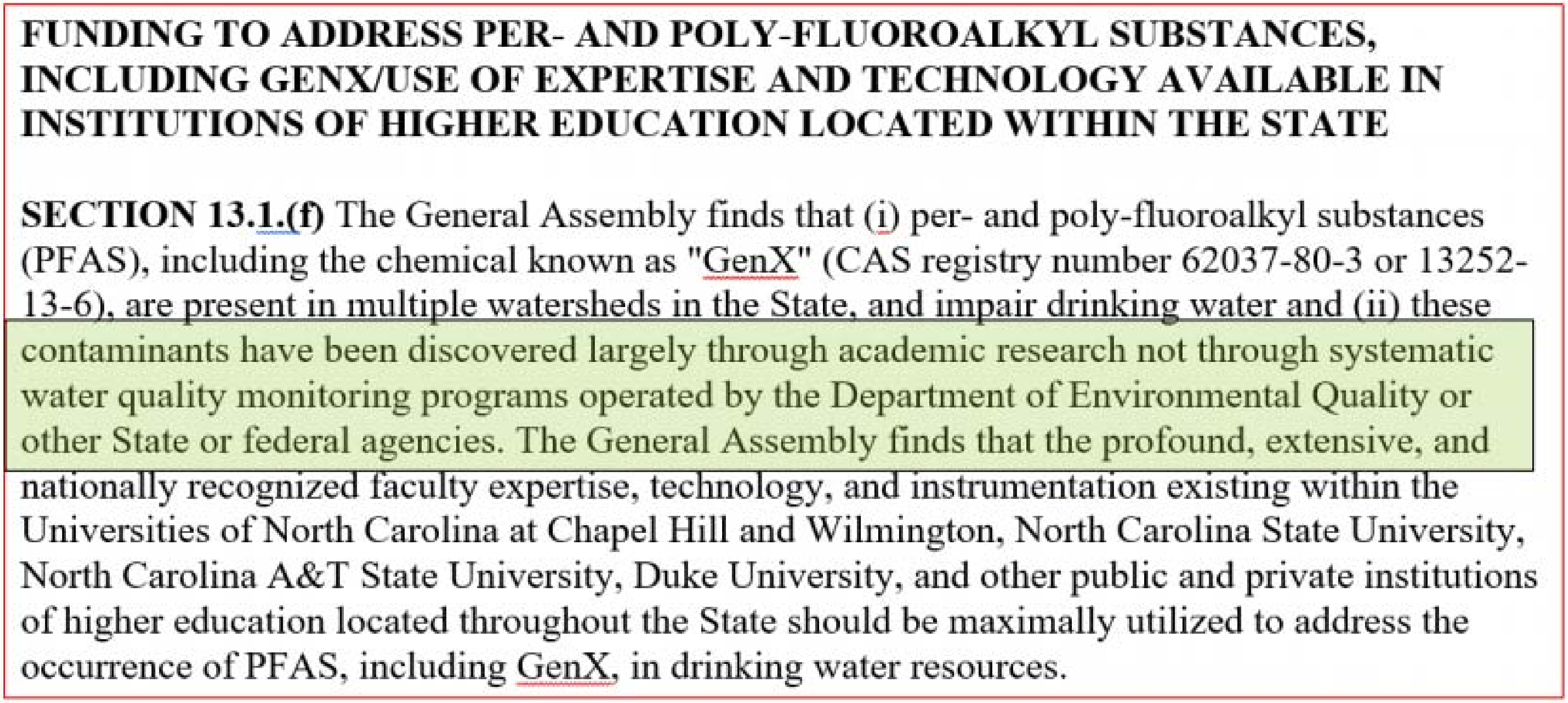
Conventional and advanced treatment options at the Sweeney WTP were ineffective for PFAS control in May 2017



Research Questions

- What are the concentrations of targeted legacy and emerging PFAS in North Carolina public drinking water sources?
- What unanticipated and untargeted PFAS occur in North Carolina public drinking water sources?
- How much of the total organic fluorine in North Carolina public drinking water sources can be accounted for by targeted PFAS analyses?

Legislative Mandate: 2018 Appropriations Act (*S99; SL 2018-5*)



FUNDING TO ADDRESS PER- AND POLY-FLUOROALKYL SUBSTANCES, INCLUDING GENX/USE OF EXPERTISE AND TECHNOLOGY AVAILABLE IN INSTITUTIONS OF HIGHER EDUCATION LOCATED WITHIN THE STATE

SECTION 13.1.(f) The General Assembly finds that (i) per- and poly-fluoroalkyl substances (PFAS), including the chemical known as "GenX" (CAS registry number 62037-80-3 or 13252-13-6), are present in multiple watersheds in the State, and impair drinking water and (ii) these contaminants have been discovered largely through academic research not through systematic water quality monitoring programs operated by the Department of Environmental Quality or other State or federal agencies. The General Assembly finds that the profound, extensive, and nationally recognized faculty expertise, technology, and instrumentation existing within the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions of higher education located throughout the State should be maximally utilized to address the occurrence of PFAS, including GenX, in drinking water resources.

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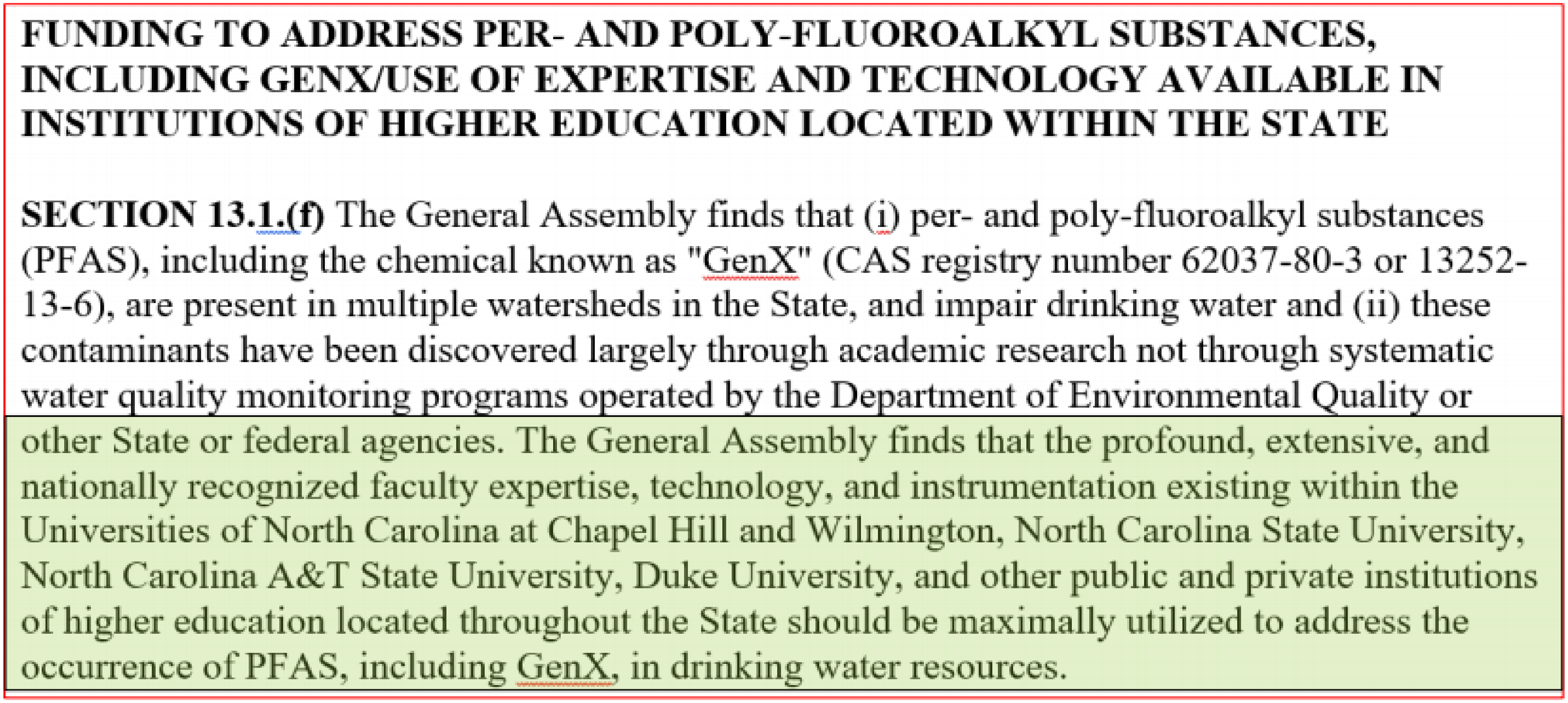

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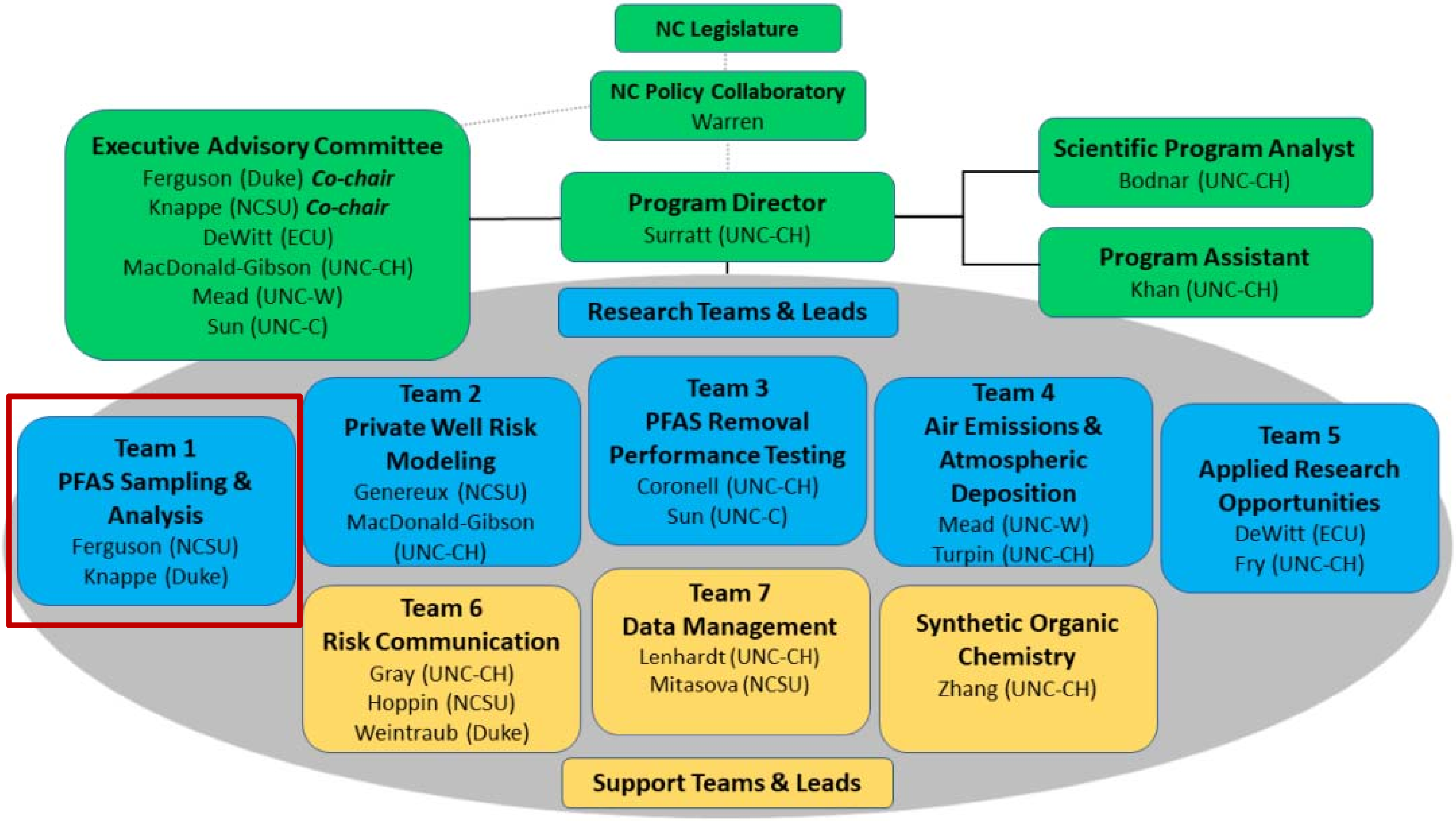
The NC Policy Collaboratory forms the PFAST Network in response to legislative mandate

NORTH CAROLINA PFAS Testing Network

Website:
ncpfastnetwork.com



NC Legislature

NC Policy Collaboratory
Warren

Executive Advisory Committee
Ferguson (Duke) ***Co-chair***
Knappe (NCSU) ***Co-chair***
DeWitt (ECU)
MacDonald-Gibson (UNC-CH)
Mead (UNC-W)
Sun (UNC-C)

Program Director
Surratt (UNC-CH)

Scientific Program Analyst
Bodnar (UNC-CH)

Program Assistant
Khan (UNC-CH)

Research Teams & Leads

Team 1
PFAS Sampling & Analysis
Ferguson (NCSU)
Knappe (Duke)

Team 2
Private Well Risk Modeling
Genereux (NCSU)
MacDonald-Gibson (UNC-CH)

Team 3
PFAS Removal Performance Testing
Coronell (UNC-CH)
Sun (UNC-C)

Team 4
Air Emissions & Atmospheric Deposition
Mead (UNC-W)
Turpin (UNC-CH)

Team 5
Applied Research Opportunities
DeWitt (ECU)
Fry (UNC-CH)

Team 6
Risk Communication
Gray (UNC-CH)
Hoppin (NCSU)
Weintraub (Duke)

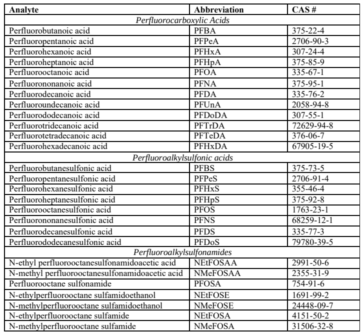
Team 7
Data Management
Lenhardt (UNC-CH)
Mitasova (NCSU)

Synthetic Organic Chemistry
Zhang (UNC-CH)

Support Teams & Leads

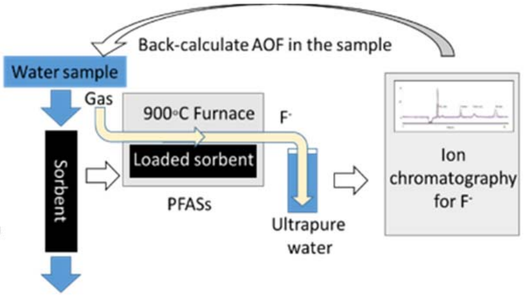
PFAS Analysis Strategy

Triple Quadrupole MS/MS
(target quantitation)



Analyte	Abbreviation	CAS #
Perfluorocarboxylic Acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoDA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
Perfluoroalkylsulfonic acids		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Perfluoroalkylsulfonamides		
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-ethylperfluorooctane sulfamidoethanol	NEtFOSE	1691-99-2
N-methylperfluorooctane sulfamidoethanol	NMeFOSE	24448-09-7
N-ethylperfluorooctane sulfamide	NEtFOSA	4151-50-2
N-methylperfluorooctane sulfamide	NMeFOSA	31506-32-8

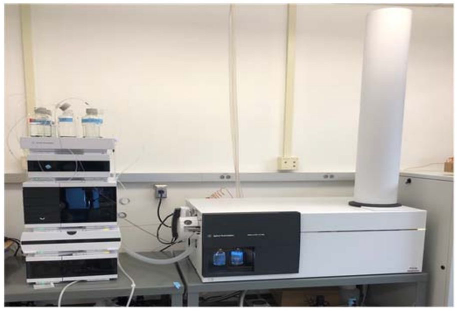
Sample Collection

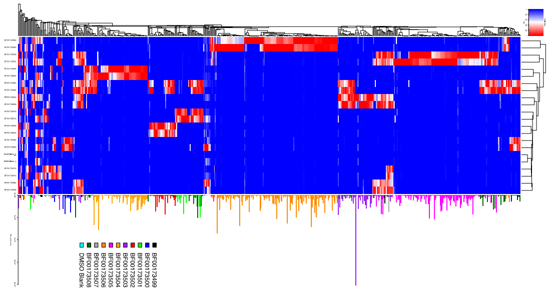


Adsorbable organic fluorine analysis

PFAS mass balance

High-resolution MS/MS
(nontarget & suspect screening)





Targeted PFAS: Analytical methods & challenges

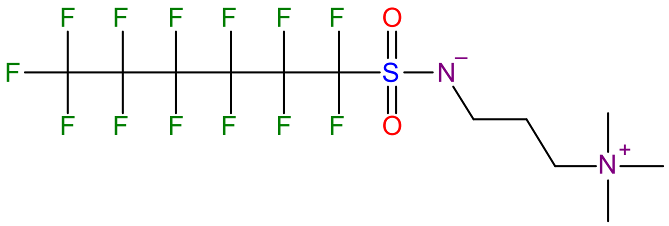
Standardized method for PFAS in drinking water:
Is EPA 537.1 adequate?

EPA 537.1	
Analytes	18 targets
Sample volume	250 mL
Sample prep	SPE
Injection volume	10 uL
ESI polarity	negative
Gas temperature	350 °C

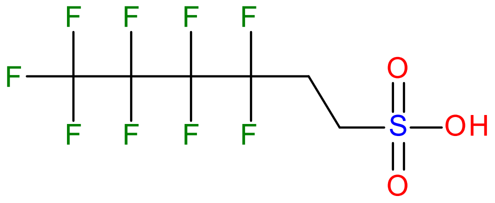
NCSU Analytes:
55+ targets

Can one method apply to all PFAS classes?

Zwitterions



Fluorotelomers



Challenges in PFAS method development: Background and Losses

Background:

- PFAS are everywhere!
- Contamination sources include:
  - PEEK tubing
  - PTFE filters, septa, fittings
  - Solvents (Optima, LC/MS grade)
  - Personnel / consumer products
- Caution and blanks are essential

Losses:

- Many PFAS are surfactants!
- Losses due to adsorption onto:
  - Vessel walls (plastic and glass)
  - Filtration materials
  - Sampling equipment
- Considerations:
  - Subsampling
  - Solvent rinsing
  - Spike recoveries

Challenges in PFAS method development: Solid Phase Extraction Media

- Many PFAS are strongly acidic
- Must consider pH and salinity in matrix

- EPA Method 537.1 relies on HLB
- WAX is more effective for short-chain PFAS

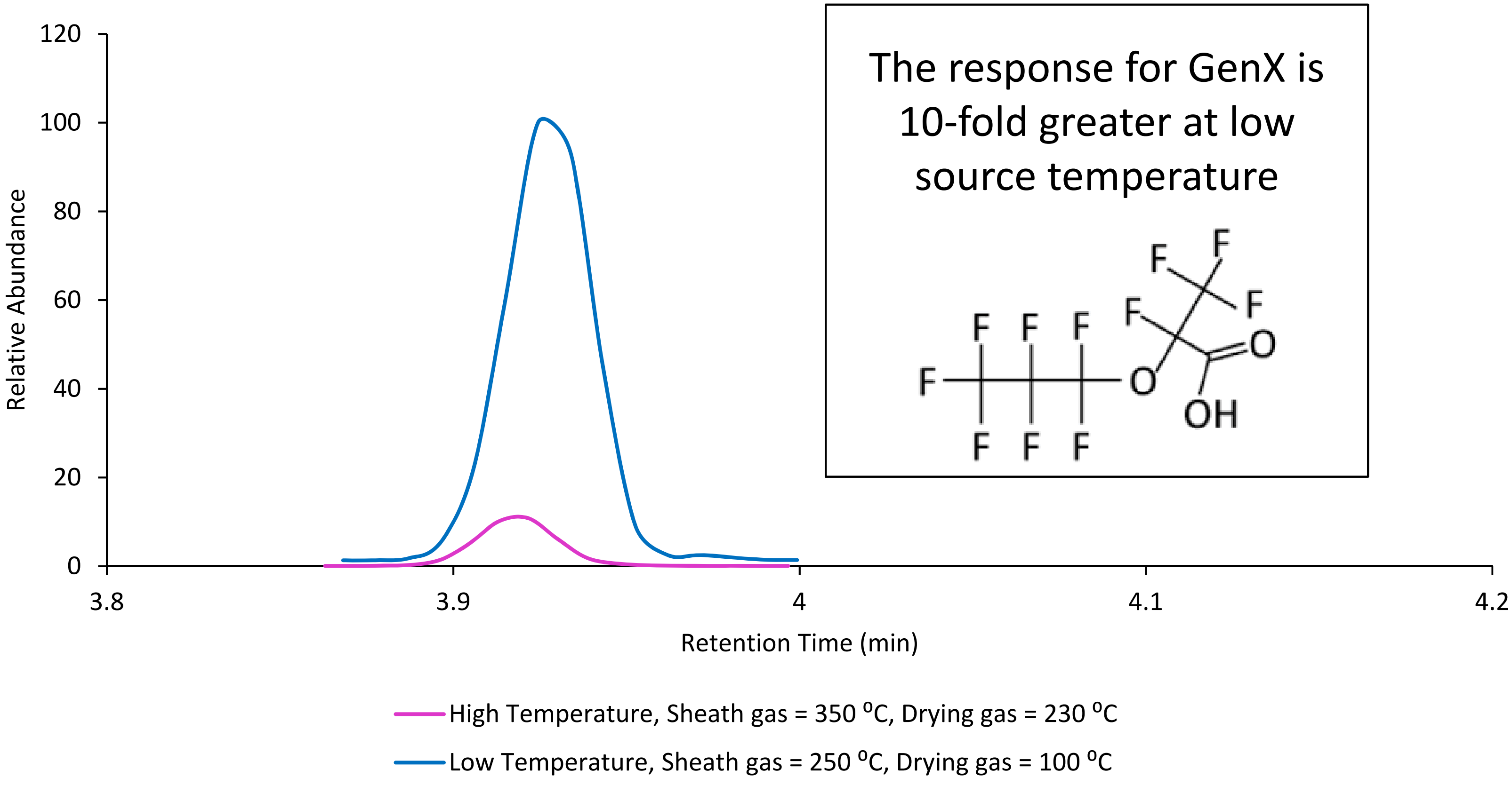
- Questions remain about capturing cationic and zwitterionic PFAS

SPE Phase Types:

Weak anion exchange (WAX)
Strong anion exchange (SAX)
Hydrophilic-lipophilic balance (HLB)
Mixed-mode (WAX + C18)
Fluorous SPE (F-SPE)

Challenges in PFAS method development: MS Source Temperature

- Ether compounds - stronger signal at lower source temperature
- Alkyl acid compounds - stronger signal at higher source temperature

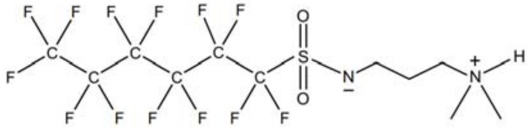


The response for GenX is 10-fold greater at low source temperature

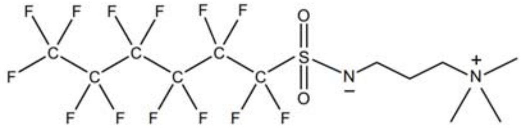
Challenges in PFAS method development: ESI Polarity

- Most PFAS are anionic and ionize in negative ESI
- Cationic and zwitterionic PFAS ionize in positive ESI

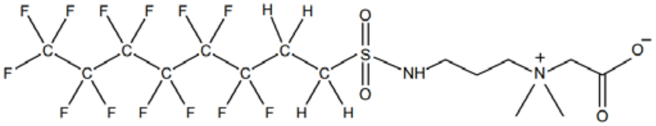
N-AP-FHxSA

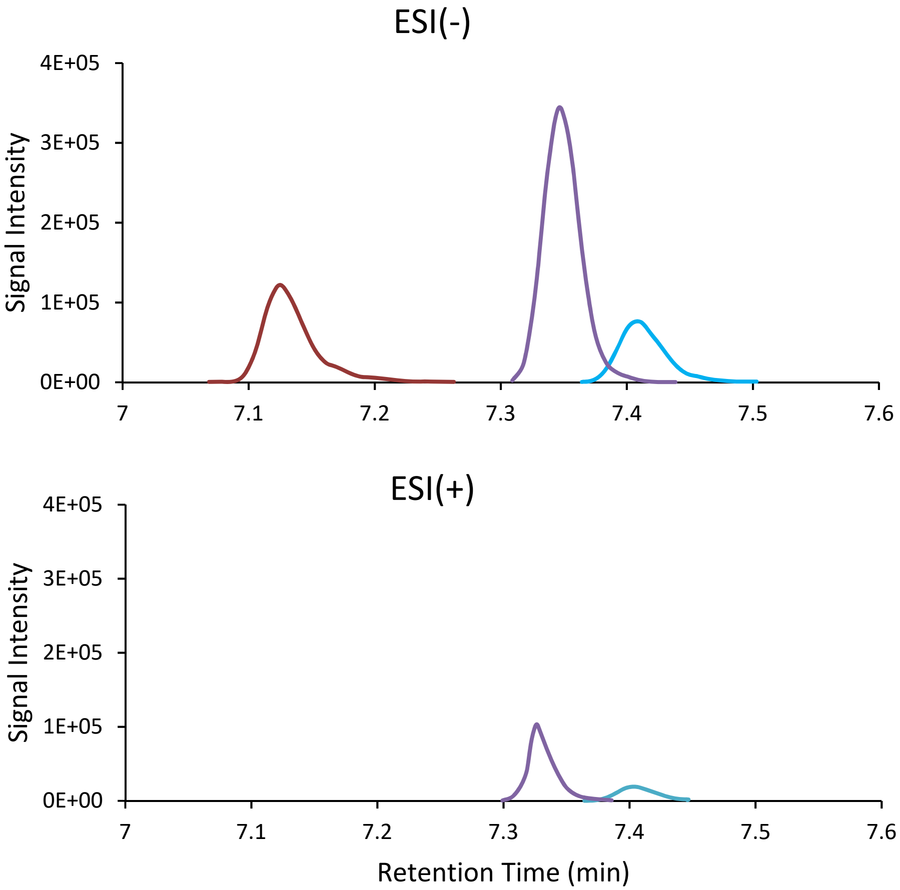


N-TAmP-FHxSA



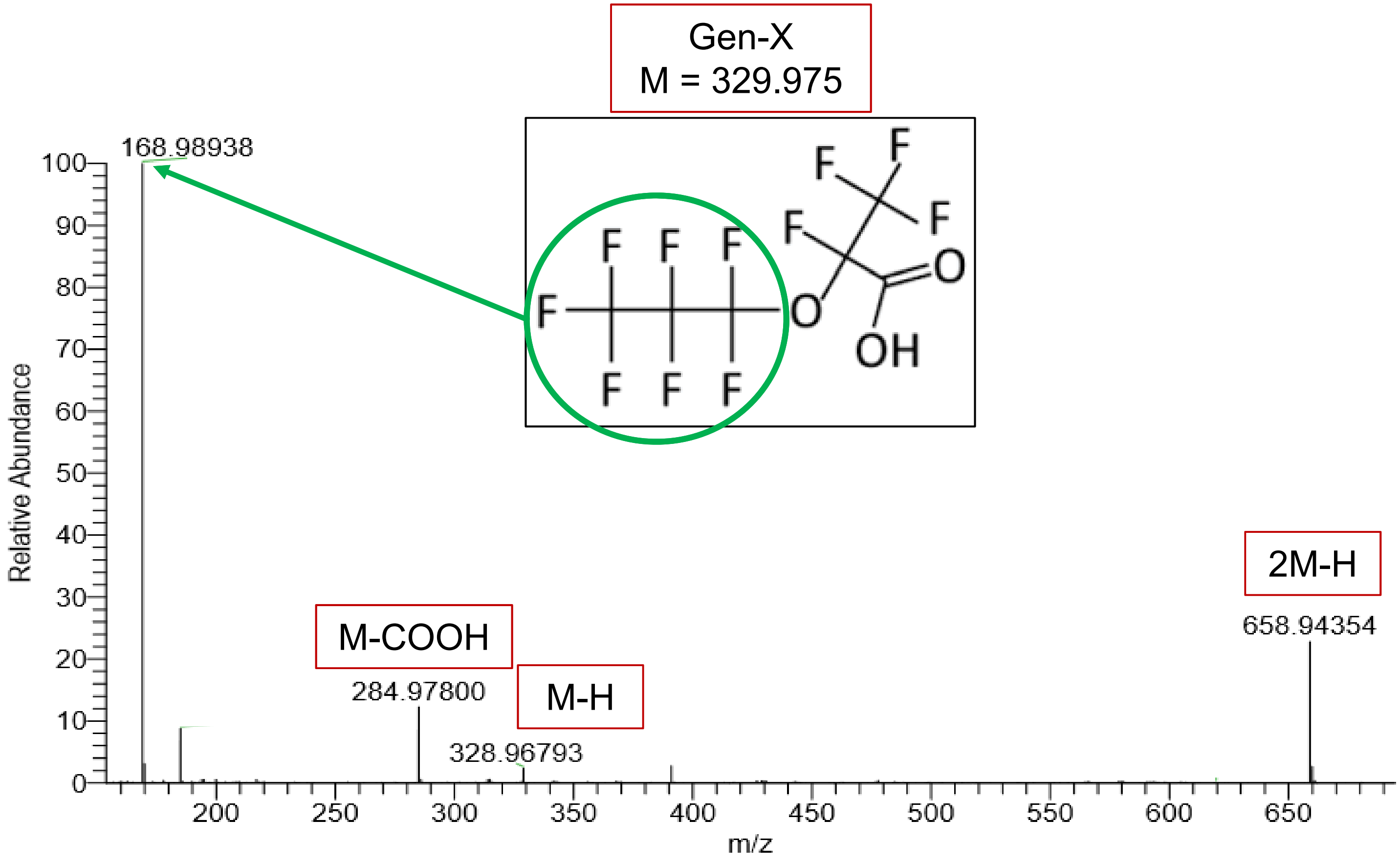
N-CMAmP-6:2FOSA (6:2 FTAB)





Challenges in PFAS method development: In-Source Fragmentation

- Some PFAS lack a strong molecular ion signal
- Need to anticipate in-source behavior



NCSU Modified EPA 537.1 Method

Sample Prep

Syringe filtration through Whatman 0.45 µm GD/X glass microfiber membrane

LC Conditions

LC System: Agilent 1260 Infinity HPLC
Analytical column: Agilent Eclipse Plus C18, 4.6 x 50mm, 3.5 µm
Column compartment temperature: 50 ºC
Injection volume: 200 uL
Flow rate: 0.5 mL/min
Eluent A: DI water with 5 mM ammonium acetate
Eluent B: 95:5 methanol:DI water with 5 mM ammonium acetate
Gradient: 10-95% B over 8 minutes, held for 5 minutes, return to initial conditions for 7 minutes post-run

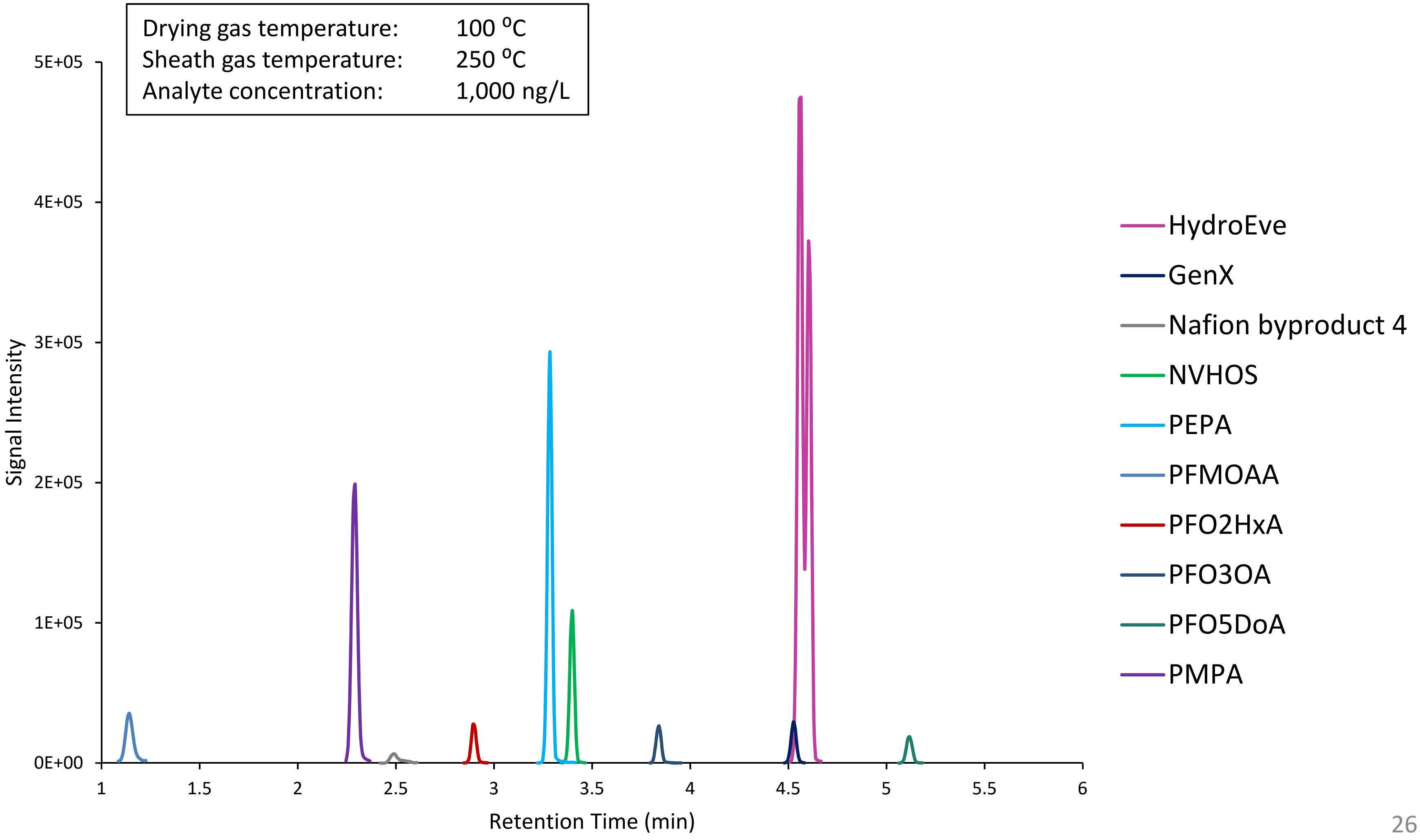
MS Conditions

MS System:	Agilent Ultivo triple quadrupole
Spray Voltage:	Static
Positive Ion:	3500 V
Negative Ion:	2200 V
Sheath Gas (arb):	25
Aux Gas (arb):	6
Sweep Gas (arb):	0
Nebulizer pressure (psi):	20

Drying gas temperature:
Sheath gas temperature:

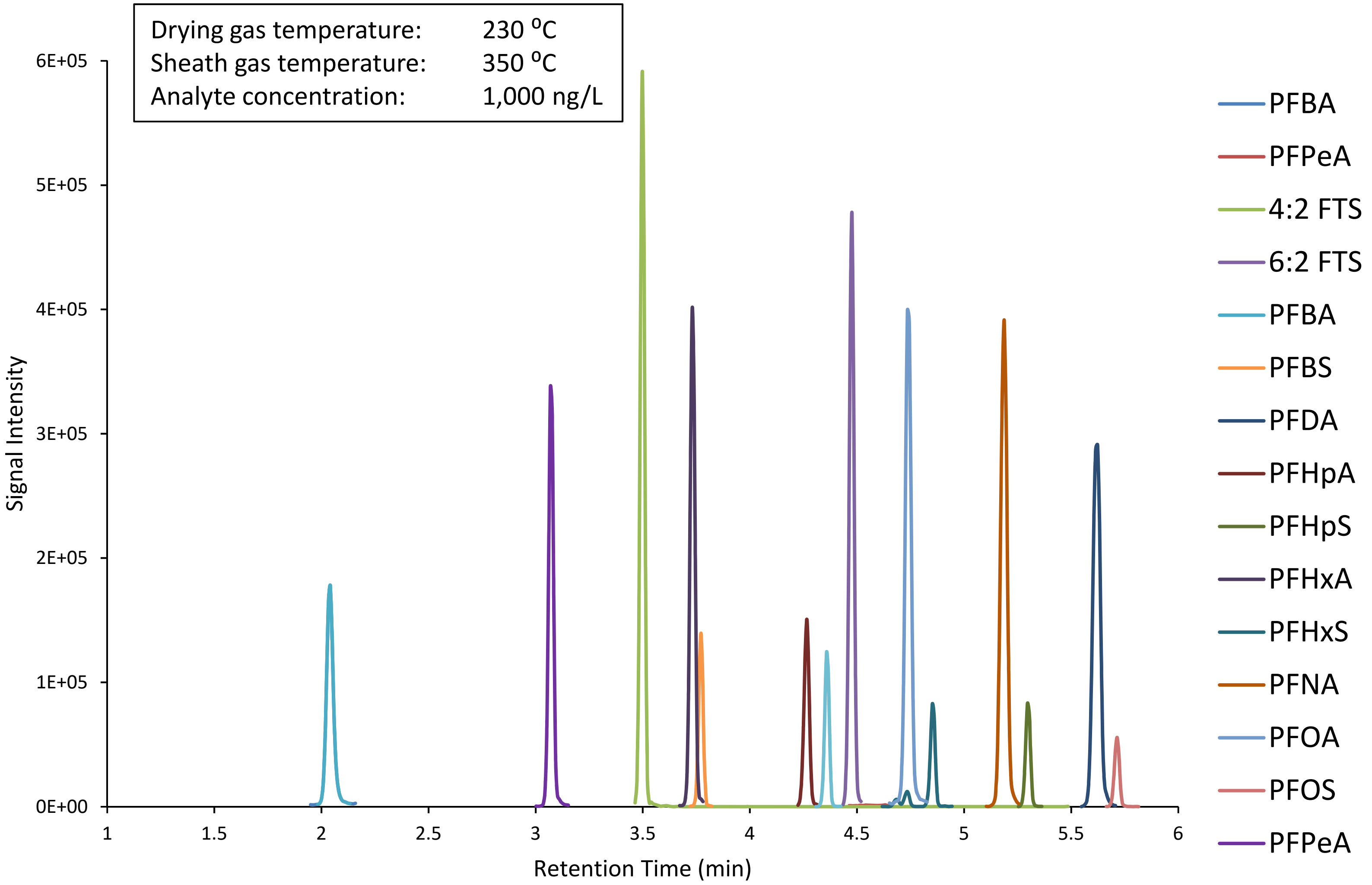
2 temperature methods required for best response

NCSU Modified EPA 537.1 Method: Low Temperature



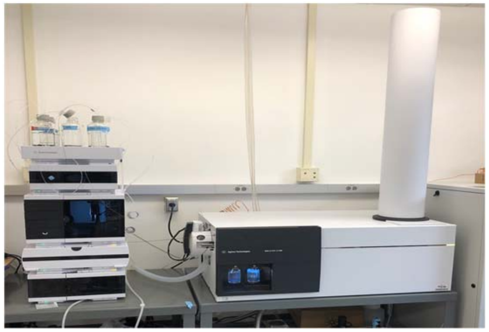
Drying gas temperature:	100 °C
Sheath gas temperature:	250 °C
Analyte concentration:	1,000 ng/L

NCSU Modified EPA 537.1 Method: High Temperature



Drying gas temperature: 230 °C
Sheath gas temperature: 350 °C
Analyte concentration: 1,000 ng/L

Complimentary PFAS Analyses: Nontarget HRMS and Total Fluorine



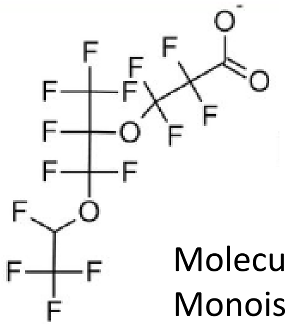
Non-targeted analysis by high resolution mass spectrometry (HPLC-HRMS)

- **Targeted Analysis**: Quantifying known PFAS
- **Suspect Screening:** Identifying PFAS against a database (EPA PFAS Master List)
- **Non-targeted Analysis:** Identifying true unknowns

Method development still in progress!

- ✓ **Agilent 6546 LC/Q-TOF**
- ✓ **Resolution >45,000**
- ✓ **Mass Accuracy <1 ppm**
- ✓ **Polarity Switching in 1.5 s**

Why do we need HRAM for nontargeted compound identification?



Hydro-EVE

Molecular Formula: $C_8HF_{14}O_4^-$

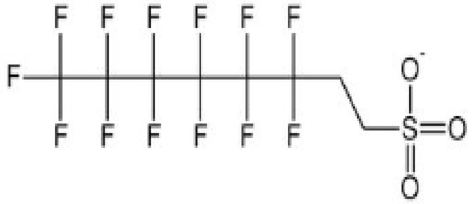
Monoisotopic Mass: $426.96\underline{57}$ Da

Mass Difference
+/- 5.15 ppm

6:2 FTS

Molecular Formula: $C_8\,H_4\,F_{13}\,O_3S^-$

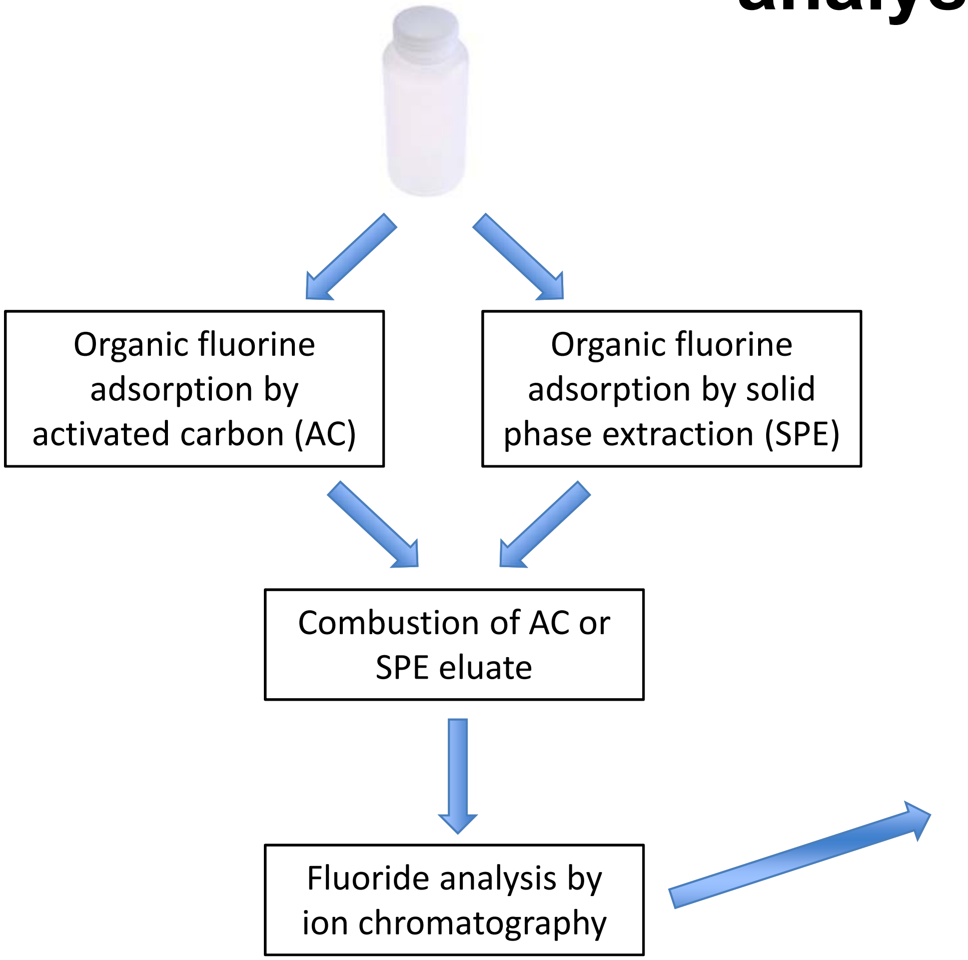
Monoisotopic Mass: $426.96\underline{79}$ Da



- As **resolution** increases:
  - Sharper separation of peaks with similar m/z
- As **mass accuracy** increases:
  - observed mass → exact mass
- Higher confidence in compound identification

$$R = \frac{M}{\Delta M} \qquad \Delta M = \frac{M}{R}$$

Adsorbable and extractable organic fluorine analysis



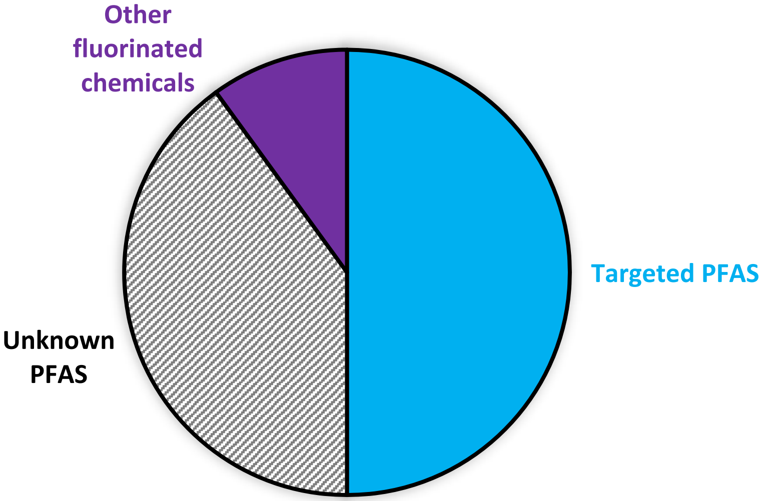
Organic fluorine adsorption by activated carbon (AC)

Organic fluorine adsorption by solid phase extraction (SPE)

Combustion of AC or SPE eluate

Fluoride analysis by ion chromatography

Do our methods detect all PFAS in samples?



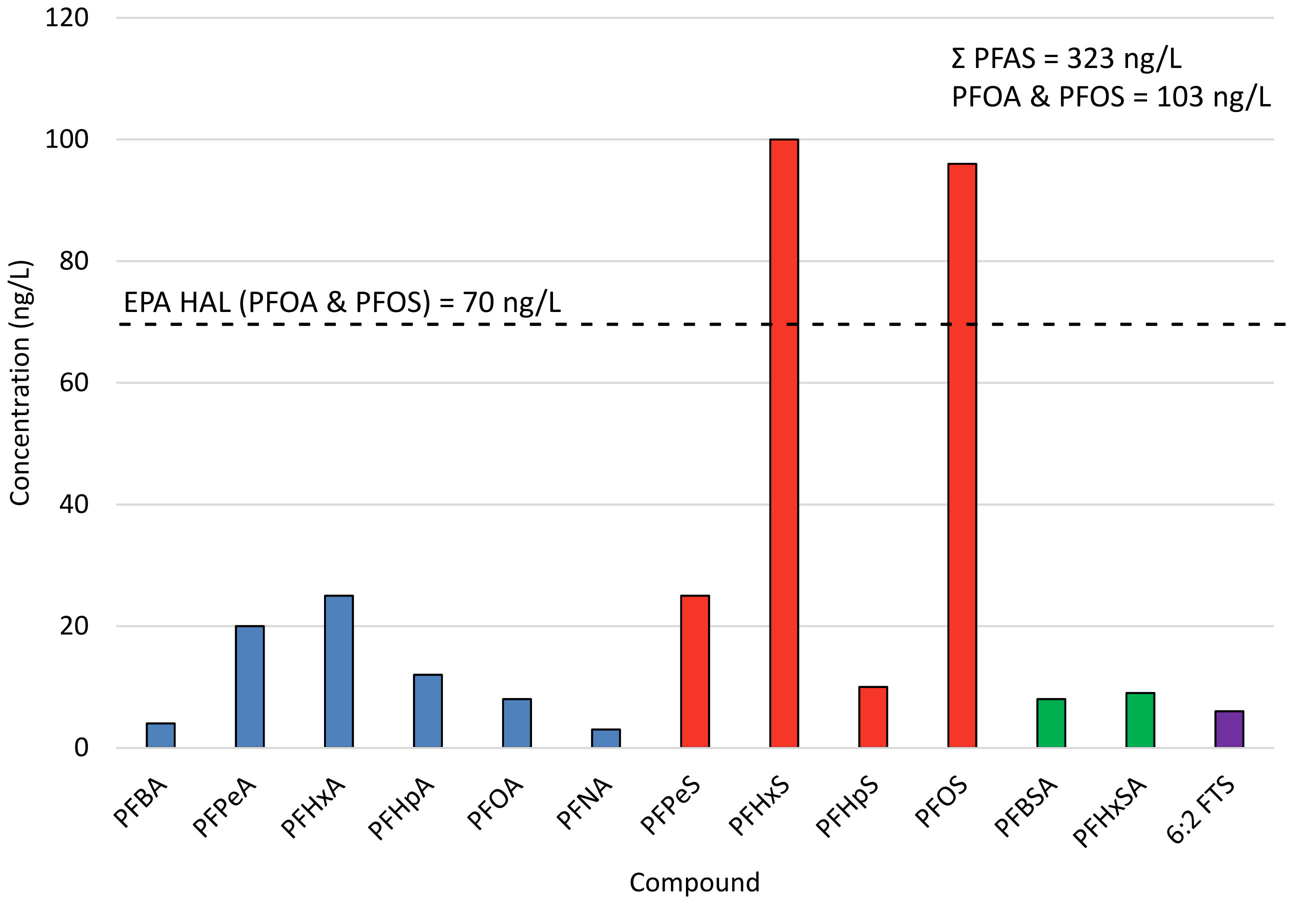
Case Study: Detecting PFAS in a NC drinking water source

The Town of Maysville, NC

- Maysville has a population of 1,019 residents
- Drinking water is provided by a groundwater well system
- The well was sampled on May 7, 2019 as part of the PFAST Network
- Targeted quantitation was performed for PFAS

MAYSVILLE
FOUNDED
1897
TOWN of
Maysville
NORTH CAROLINA

The sum of PFOA and PFAS in Maysville raw drinking water exceeded the EPA HAL



- ➢ Results were verified between two PFAST labs
- ➢ The town was notified within 10 days
- ➢ A second analysis was performed on raw and finished drinking water by a hired lab, confirming initial findings
- ➢ The town ultimately switched to an alternative water source

Take-Home Messages

- Standardized methods are needed for high-throughput analysis of PFAS in environmental samples
- A single analytical method is not sufficient to capture all PFAS classes
- Complimentary analyses (nontarget HRMS, total fluorine) support PFAS discovery
- Additional techniques are being investigated, including:
  - Online SPE (triple quad, IDX)
  - Direct aqueous injection (IDX)
  - SPE phases (F-SPE)

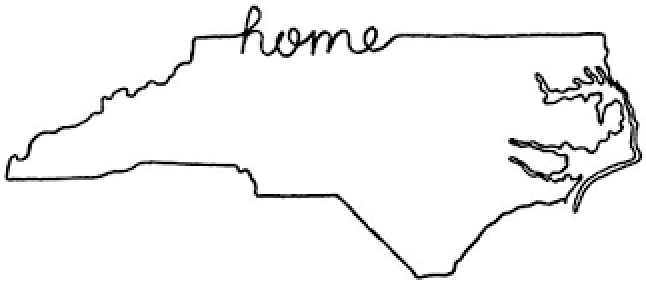
Acknowledgements

- Knappe Lab, North Carolina State University
- Ferguson Lab, Duke University
- NC Policy Collaboratory

www.collaboratory.unc.edu

NC Policy Collaboratory

Questions?



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