Case Study of PFAS in Waste Water Influent and Effluent

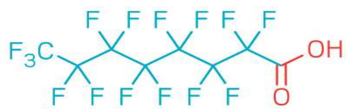
ENTHALPY ANALYTICAL
a Montrose Environmental Group company

Lindsay Boone, M.Sc, Technical Program Manager

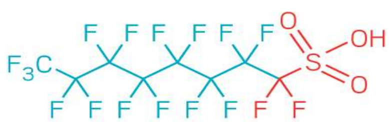
PFAS (Per & Polyfluorinated Alkyl Substances)

Longer Chains & Strong Bonds C8

Perfluorinated

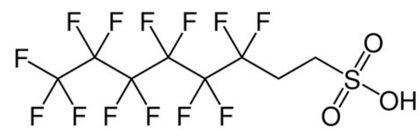


**Perfluorooctanoic acid,
PFOA,
CAS 335-67-1**



**Perfluorooctane
sulfonic acid,
PFOS,
CAS 1763-23-1**

Polyfluorinated

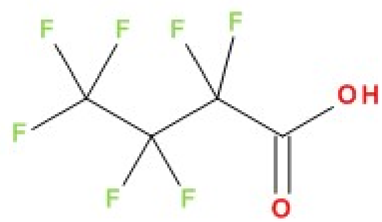


6:2 FTS

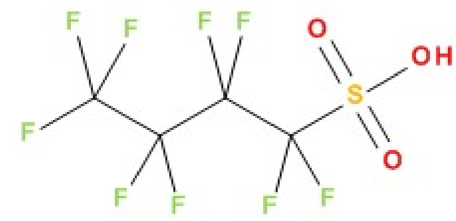
Replacement Compounds

C4 & C6

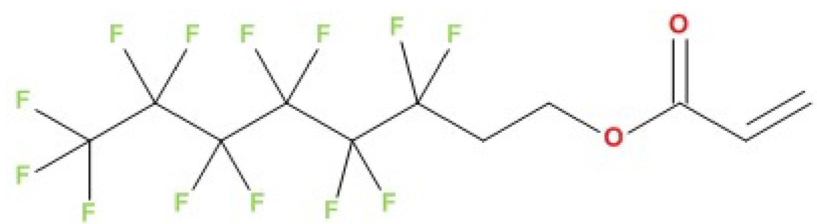
- Industry Claims they are safer
- Precursors are still longer chain C8
- PFBA-food packaging and film
- PFBS-surfactants/repellents, metal plating, pesticides, and flame retardants



PFBA



PFBS



6:2 Fluorotelomer acrylate

PFAS
Uses

- AFFF
- Household Products(Teflon)
- Cosmetics
- Food Wrappers (PFPeA)
- Stain Resistant/Water Proofing

PFOA C8

PFOS (perfluorooctane sulfonate)

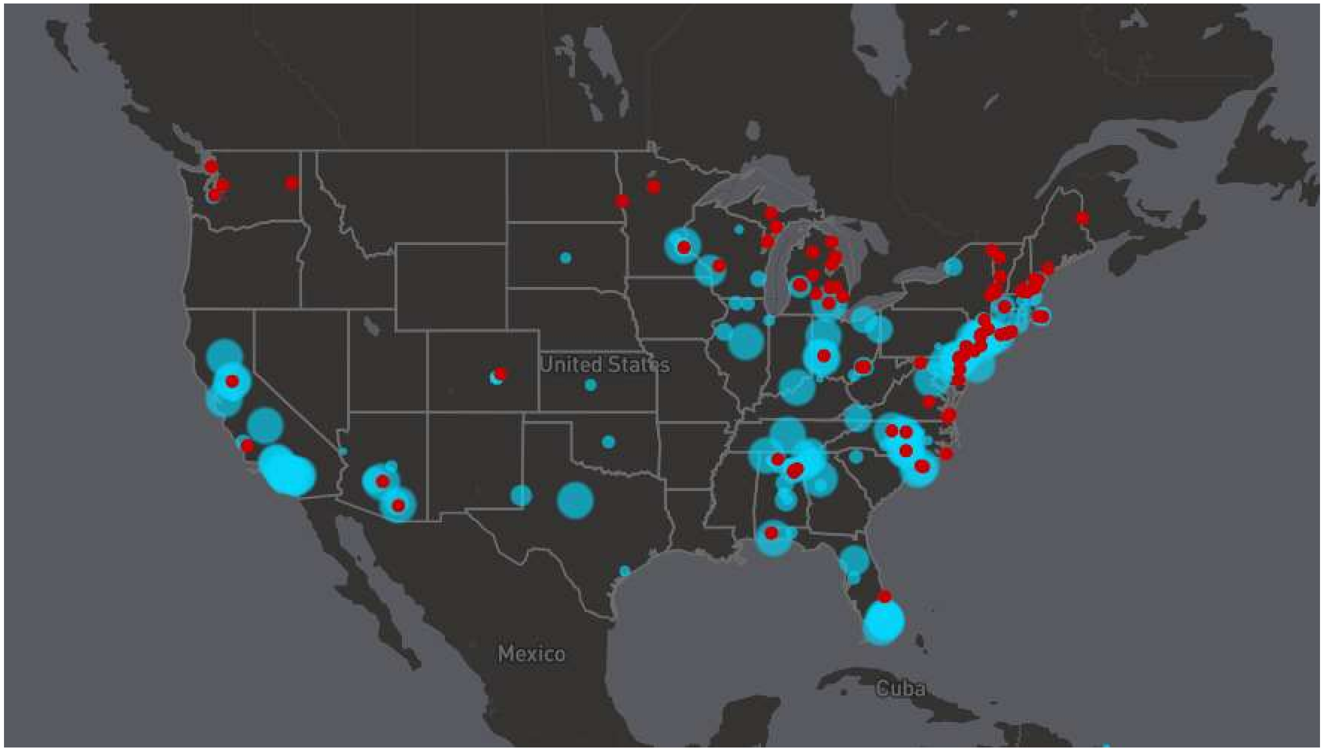
Health Concerns

PFOA/PFOS most studied…

- Reproductive/development issues
- Increased Cholesterol
- Infant birth rate
- Cancer (PFOA)
- Thyroid hormone effects (PFOS)

Where are they....

April 2018



https://www.northeastern.edu/environmentalhealth/mapping-the-expanding-pfas-crisis/

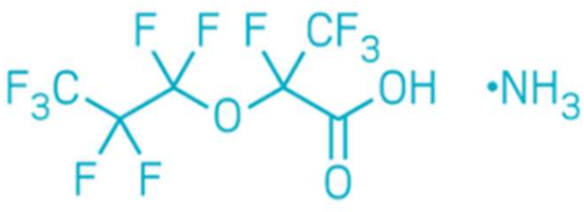
NC DEQ Influent Study

April 2019

- 20 plus WWTPs
- 21 PFAS compounds
- 3 month study
- Influent grab sampling
- DOD compliant

Gen X 2009 Dupont

PFOA Replacement Compound



GenX

Method Options

Matrix Dependent

- EPA 537/537.1-Drinking Water, Required for demonstrating compliance, 18 compounds, but only a few states accredit
- EPA 533-Drinking Water, Isotope Dilution, 25 compounds
- EPA 8327-direct inject, screening method water high RL, poor accuracy/precision, few calibration points, 24 compounds
- Isotope Dilution, largest number of quality requirements, wide variety of matrices/compounds, and most accurate.

Isotope Dilution

And its many names

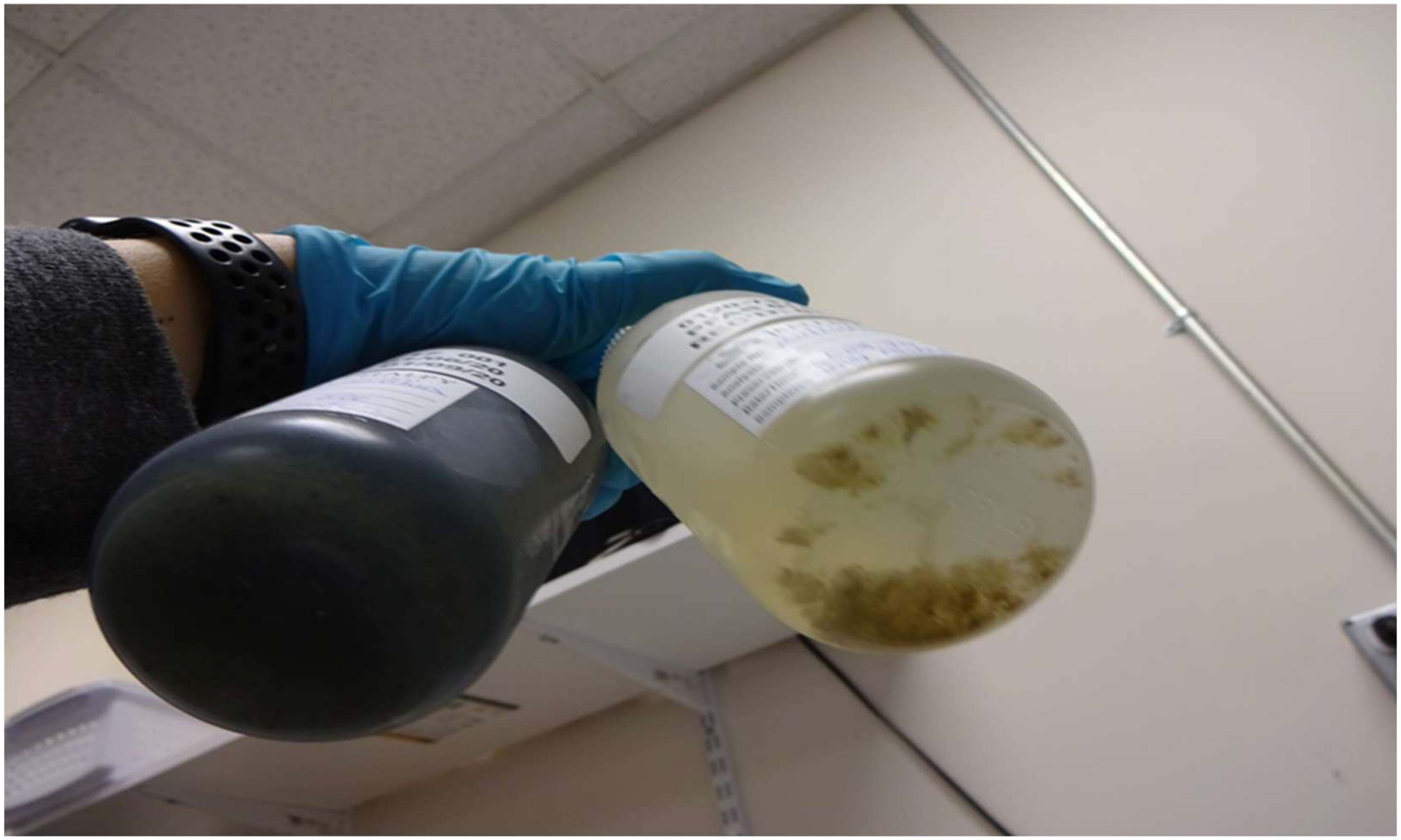
- Modified 537/537.1
- PFAS by LC/MS/MS
- PFAS by Table B-15
- PFAS by DOD QSM Table B-15

DOD QSM Table B-15

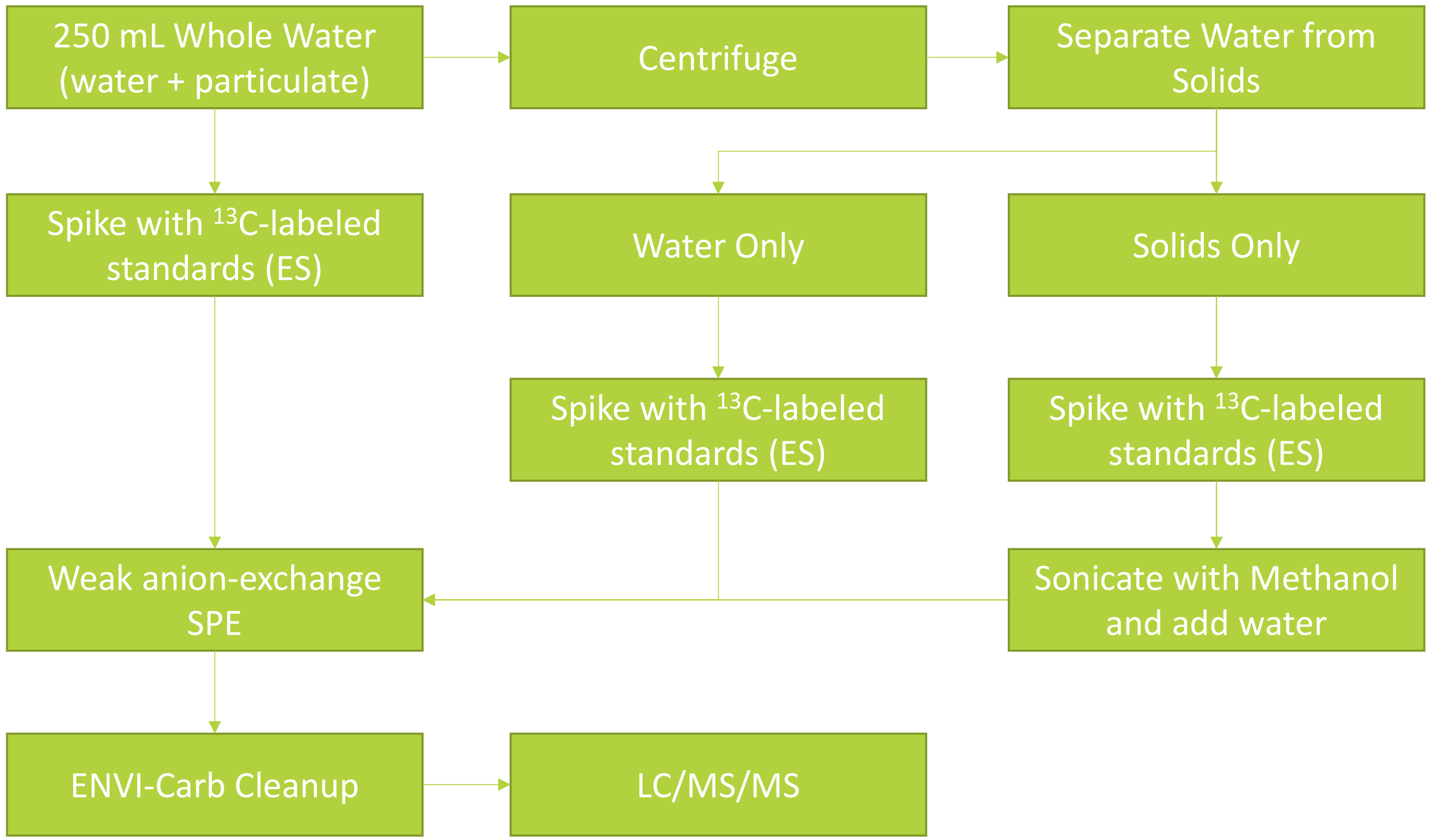
Highlights of Quality Requirements

- Requirements that Improve PFAS Analysis
  - Two ions monitored for each compound – reduces false positives
  - Method blanks to ensure a lack of contamination in sample results
  - Instrument blanks assess and prevent carryover to ensure a lack of contamination in sample results
  - Calibration criteria to ensure accuracy within ~30% of reported values
  - Low level accuracy confirmation with each analytical sequence
- Requirements that work against Isotope dilution
  - Labeled standard recoveries measured by area and required to be within 50% of calibration – why use isotope dilution?
  - Matrix spikes & matrix spike duplicates – not necessary in isotope dilution

Waste Water Influent

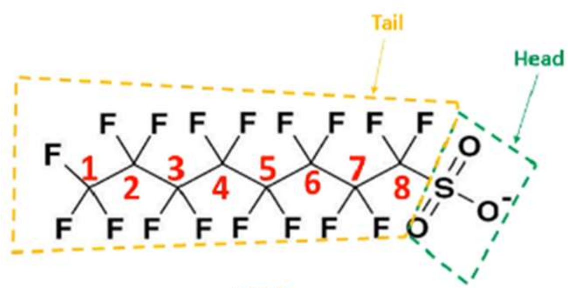


Partitioning of PFAS between Water and Particulate

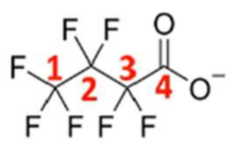


PFAS Measurable in Study

- PFNA (C9)
- PFOS (C8)
- PFOA (C8)
- 6:2 FTS (C8)
- PFHpA (C7)
- PFHxS (C6)
- PFHxA (C6)



PFOS



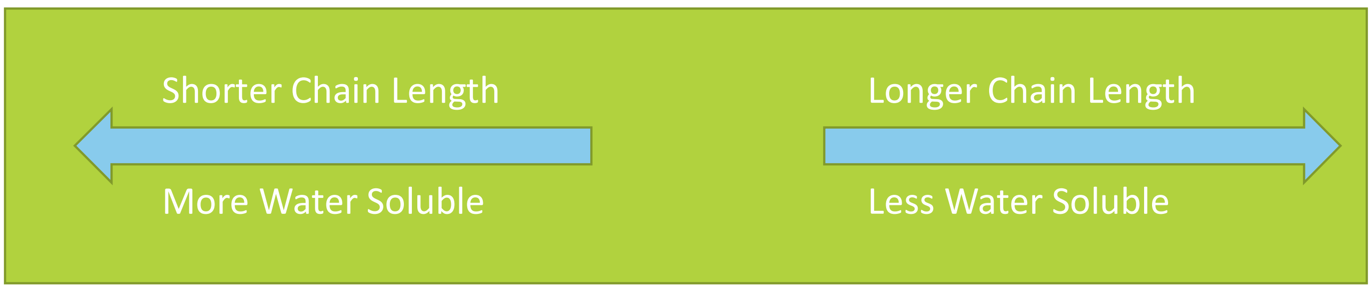
PFBA

- Hydrophobic fluorinated carbon chain – "tail"
- Anionic sulfonate or carboxylate group – "head"

Expected Outcomes

Less Soluble Compounds Stick to Solids

PFHxA PFHxS PFHpA 6:2 FTS PFOA PFOS PFNA



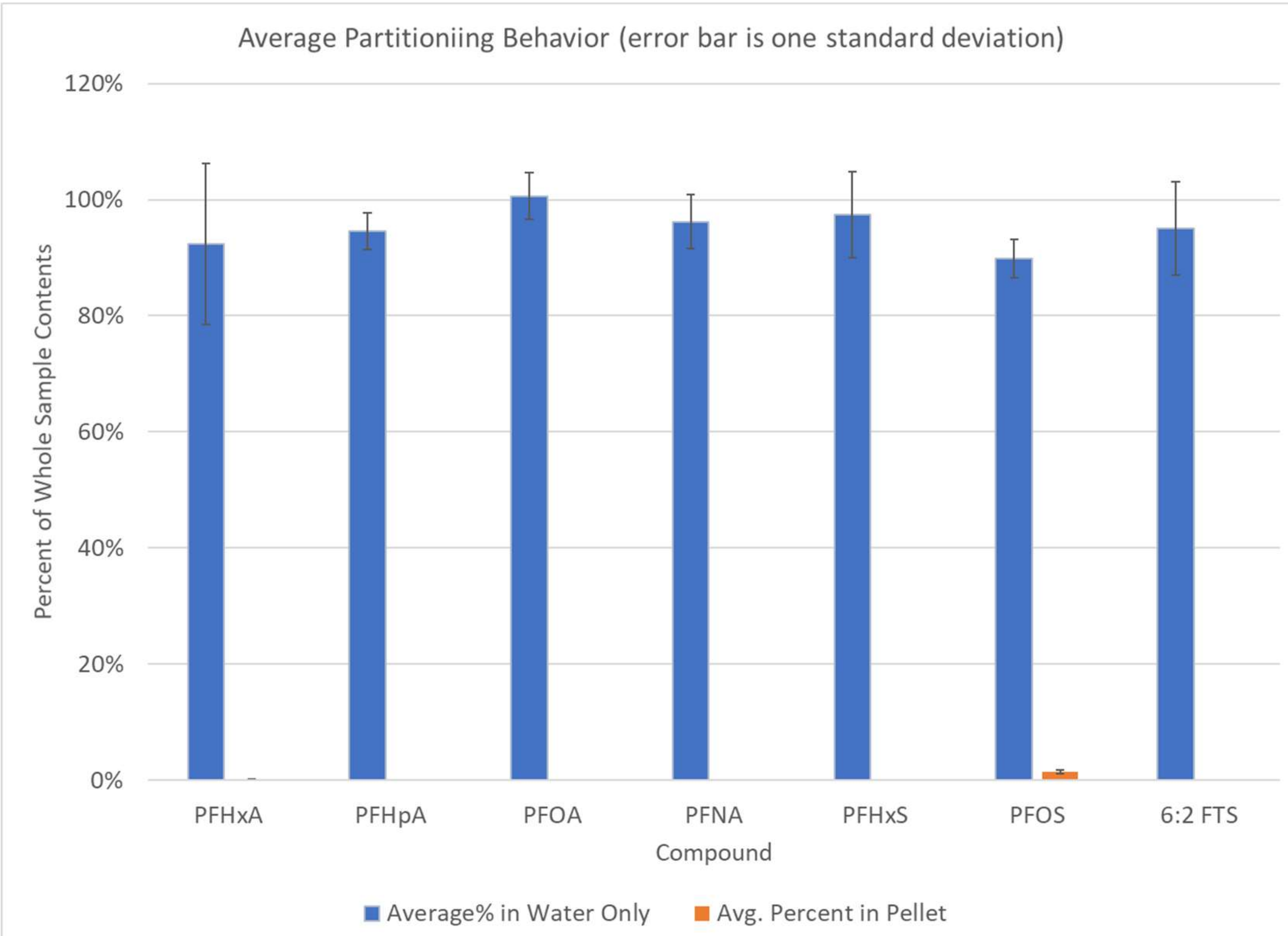
C6 C8 C9

Results and Reproducibility

(N=3 for each Site)

	Results in Whole Water Samples (ng/L)					
	PFHxA	PFHpA	PFOA	PFNA	PFHxS	PFOS
Site 1	31.2 ± 6.00%	19.7 ± 6.15%	11.1 ± 6.13%	1.60 ± 0.00%	7.20 ± 4.24%	24.2 ± 4.42%
Site 2	21.8 ± 11.0%	11.1 ± 1.38%	10.7 ± 1.43%	1.80 ± 3.21%	5.70 ± 6.64%	13.5 ± 4.08%

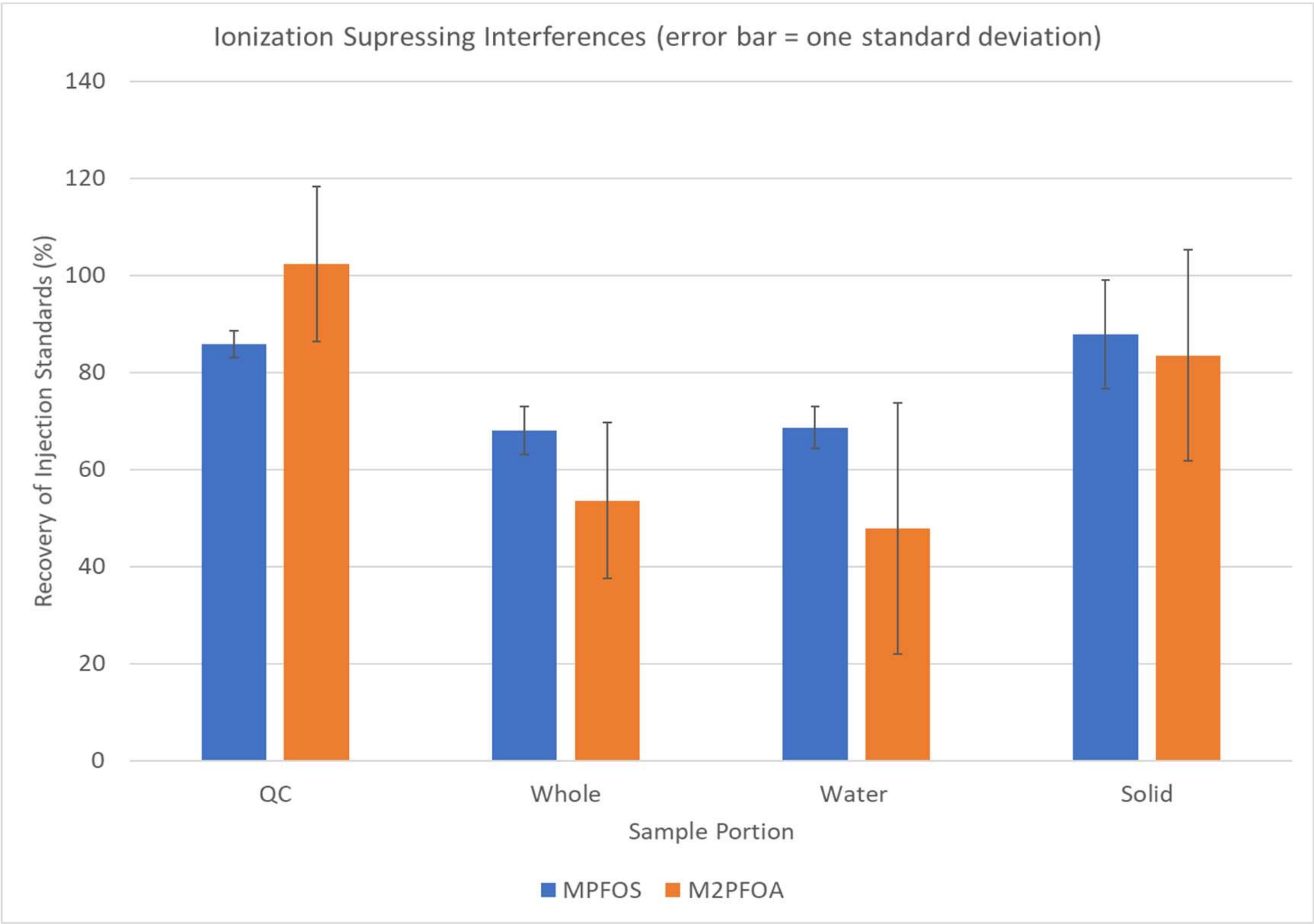
Under 10% for PFAS is good!
But what about the particulate?


Average Partitioniing Behavior (error bar is one standard deviation)
120%
100%
80%
60%
40%
20%
0%
Percent of Whole Sample Contents
PFHxA
PFHpA
PFOA
PFNA
PFHxS
PFOS
6:2 FTS
Compound
Average% in Water Only
Avg. Percent in Pellet

Ionization Suppression

What is it?-Anything in the sample that causes an instrument’s signal to be reduced.

- Interferences co-extracted with the PFAS cause the instrument signal to be reduced
- Very Important when looking at ppt level
- Our original thought was more complex/dirty sample matrices would have an increased level of Ionization Suppression
- Does the particulate matter contribute?


Ionization Supressing Interferences (error bar = one standard deviation)
Recovery of Injection Standards (%)
140
120
100
80
60
40
20
0
QC
Whole
Water
Solid
Sample Portion
MPFOS
M2PFOA

Partitioning Conclusion

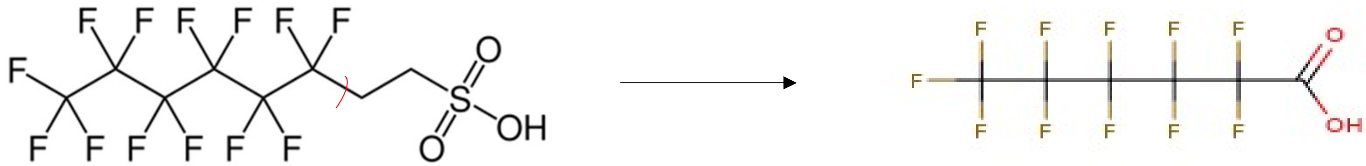
It is not what we thought….

- In this study PFAS that we measured does not significantly adsorb to particulate matter
- Ionization Suppressing compounds do not adsorb to particulate matter either
- Overall variability of particulate in a Influent sample should not greatly effect the results when running duplicates due to partitioning

TOPS Influent and Effluent Study in Waste Water

Degradation Products

Common in Waste Water & Chemically Rich Environments



6:2 FTS (C8)

PFHxA (C6)

Liver and Kidney Toxicity
Skin Irritation

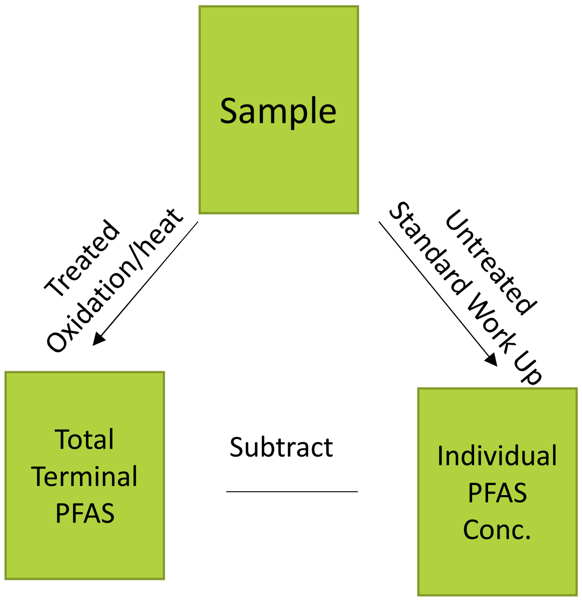
Compounds	Influent	Effluent	Δ
6:2 FTS	1840 ppt	105 ppt	- 1735
PFHxA	19.9 ppt	70.8 ppt	+ 50.9

Mass Balance….Where did it go?

https://nasf.org/wp-content/uploads/2019/04/Summary-of-Toxicology-Studies-on-6-2-FTS-and-Detailed-Technical-Support-Documents.pdf

TOPS (Total Oxidizable Precursor Assay)

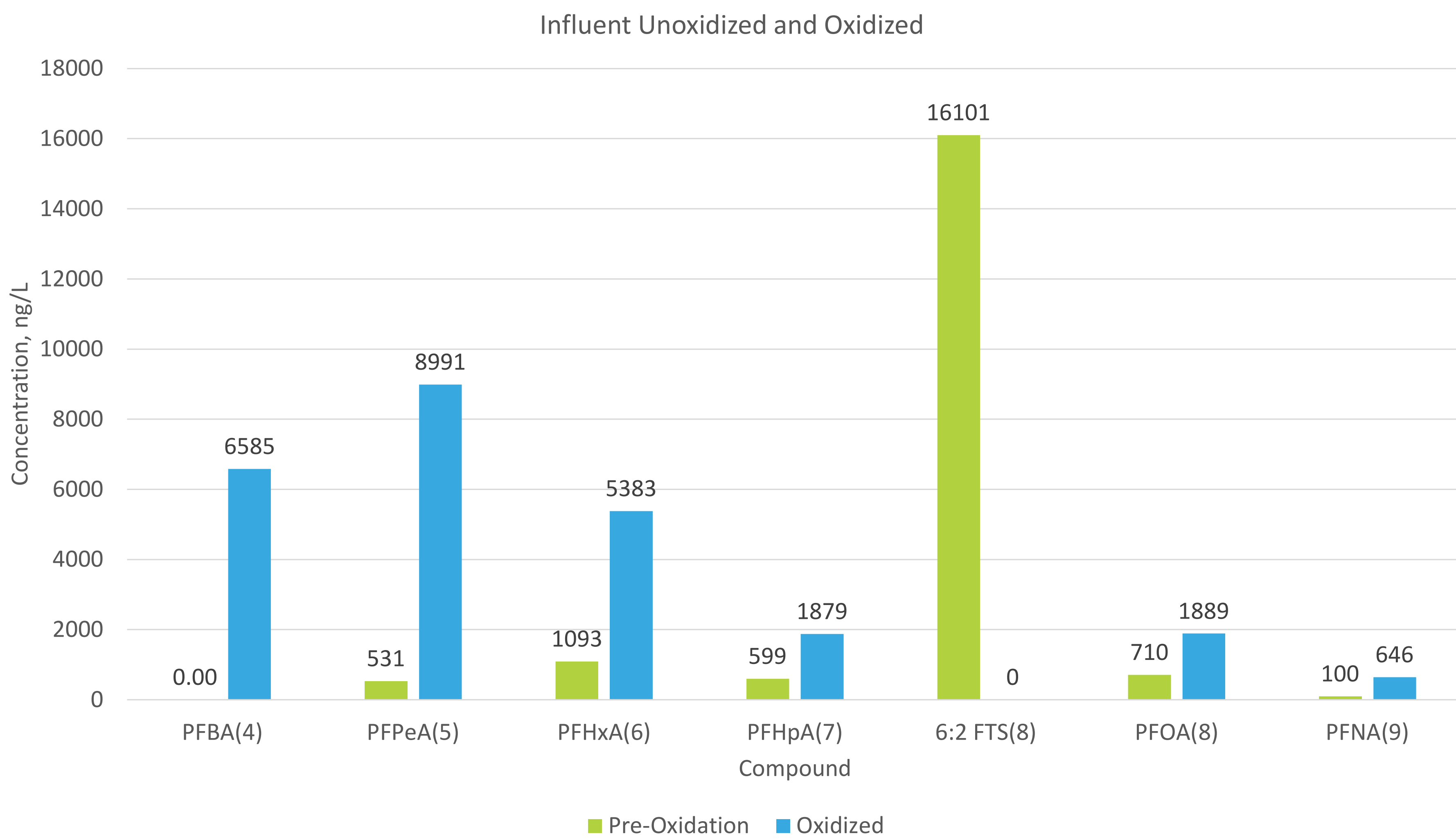
- Max Value of Estimated PFAS Composition
- Speeds up potential environmental oxidation that might occur over many years. Lab oxidation takes less than a day.
- Helpful in remediation testing as well as waste water treatment facilities.
- Used in AFFF analysis frequently.
- Assumptions are made-1) all non-targeted PFAS will be converted to targeted PFAS 2) 100% of the PFAS will be oxidized 3) all compounds oxidize similarly



The difference if any is presumed to be due to the oxidation of precursors

Study Outline

- We collected Influent and Effluent samples in which we wanted to compare the magnitude of PFAS precursors
- Samples were collected from the same WWTP at the same time points.
- A 24 hr lag time was given for effluent collection as to be more representative of the corresponding influent sampled



Influent Unoxidized and Oxidized
Concentration, ng/L
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0.00
6585
531
8991
1093
5383
599
1879
16101
0
710
1889
100
646
PFBA(4)
PFPeA(5)
PFHxA(6)
PFHpA(7)
6:2 FTS(8)
PFOA(8)
PFNA(9)
Compound
Pre-Oxidation
Oxidized

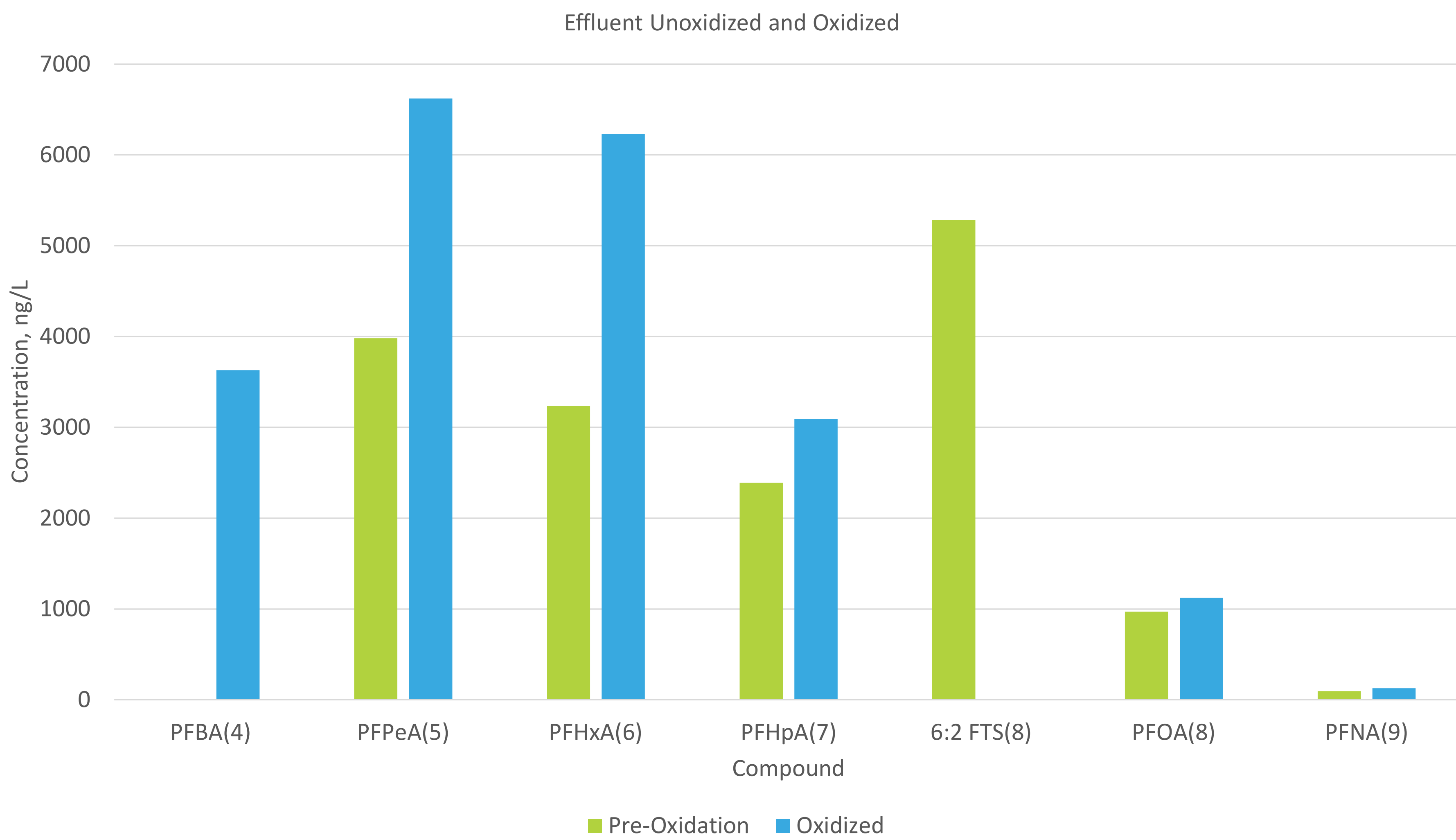
Tabulated Influent Results

	Pre-Oxidation			
	Influent 1	Influent 2	Influent 3	Average
Compounds	ng/L	ng/L	ng/L	ng/L
PFBA(4)	0.00	0.00	0.00	0.00
PFPeA(5)	0.00	792	802	531
PFHxA(6)	1073	1100	1107	1093
PFHpA(7)	669	574	553	599
6:2 FTS(8)	17465	16596	14243	16101
PFOA(8)	765	697	668	710
PFNA(9)	100	85	116	100
ΣPFAS	20072	19843	17490	19134

	Post-Oxidation			
	Influent 1	Influent 2	Influent 3	Average
Compounds	ng/L	ng/L	ng/L	ng/L
PFBA(4)	7963	5736	6056	6585
PFPeA(5)	10753	7987	8233	8991
PFHxA(6)	6361	4929	4861	5383
PFHpA(7)	3070	2568	0	1879
6:2 FTS(8)	0	0	0	0
PFOA(8)	2270	1748	1649	1889
PFNA(9)	759	631	548	646
ΣPFAS	31177	23598	21347	25373

Average Difference = 6,239 ppt
Represents unknown precursors and it is a lower limit on the precursor content (This assumes that 100% of 6:2 FTS converted to a measured PFAS)

The complete removal of 6:2 FTS also indicates oxidation was driven to completion


Effluent Unoxidized and Oxidized
7000
6000
5000
4000
3000
2000
1000
0
Concentration, ng/L
PFBA(4)
PFPeA(5)
PFHxA(6)
PFHpA(7)
6:2 FTS(8)
PFOA(8)
PFNA(9)
Compound
Pre-Oxidation
Oxidized

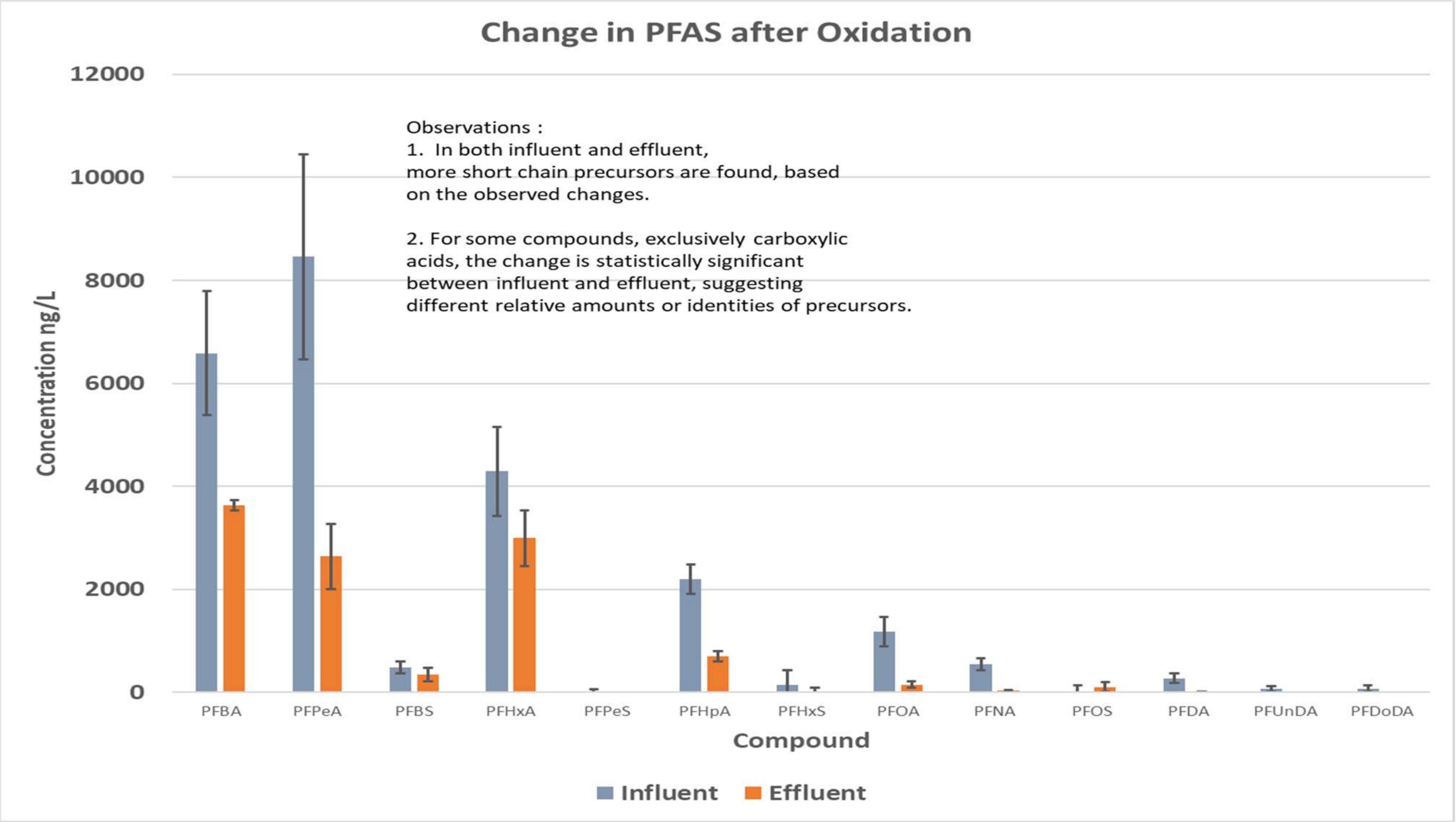
Tabulated Effluent Results

	Pre-Oxidation			
	Effluent 1	Effluent 2	Effluent 3	Average
Compounds	ng/L	ng/L	ng/L	ng/L
PFBA(4)	0.00	0.00	0.00	0.00
PFPeA(5)	4176	3901	3865	3981
PFHxA(6)	3431	3103	3174	3236
PFHpA(7)	2496	2310	2362	2390
6:2 FTS(8)	6035	5181	4630	5282
PFOA(8)	999	951	960	970
PFNA(9)	88	101	99	96
ΣPFAS	17226	15547	15090	15955

	Post-Oxidation			
	Effluent 1	Effluent 2	Effluent 3	Average
Compounds	ng/L	ng/L	ng/L	ng/L
PFBA(4)	3517	3707	3670	3631
PFPeA(5)	7549	6242	6074	6622
PFHxA(6)	7039	5811	5836	6229
PFHpA(7)	3154	2943	3170	3089
6:2 FTS(8)	0	0	0	0
PFOA(8)	1194	1127	1049	1124
PFNA(9)	139	127	117	128
ΣPFAS	22592	19957	19916	20823

Average Difference = 4,868 ppt
The overall concentration of oxidizable precursors is smaller than that in the influent.

TOPS Influent and Effluent Conclusion



TOF (Total Organic Fluorine)

- What is it? Measurement of all fluorine in a sample that can be attributed to organic chemicals. There are nearly zero naturally occurring chemicals with organic fluorine. The mast majority of organic fluorine is PFAS.
- There are 3 common ways to measure combustion-Ion Chromatography is the most common
- The measurement is very non-specific. You will get an amount of organic fluorine but it does not tell you what chemical it specifically came from. Total Organic Fluorine can't be used to correlate toxicity.
- How do we measure it? Combustion Ion Chromatography. We measure Total Fluorine by combustion. Then we measure inorganic fluorine per a common IC procedure. This is done on the same instrument. Then the organic fluorine is obtained by subtracting inorganic from the total fluorine.

Questions?

- Lindsay Boone
  - lboone@enthalpy.com
  - 910.544.6077

NC Policy Collaboratory Statewide Study: PFAS Occurrence in North Carolina Drinking Water Sources

Noelle DeStefano[1], Abigail Joyce[2], Lee Ferguson[2], Detlef Knappe[1]

[1]Civil, Construction & Environmental Engineering, North Carolina State University
[2]Civil & Environmental Engineering, Duke University

PFASs have gained widespread attention

GRAND RAPIDS

Cancer, thyroid problems plague Wolverine dump neighbors

Updated Oct 1, 2017; Posted Oct 1, 2017

Scientists advise Michigan to set tougher PFAS standards

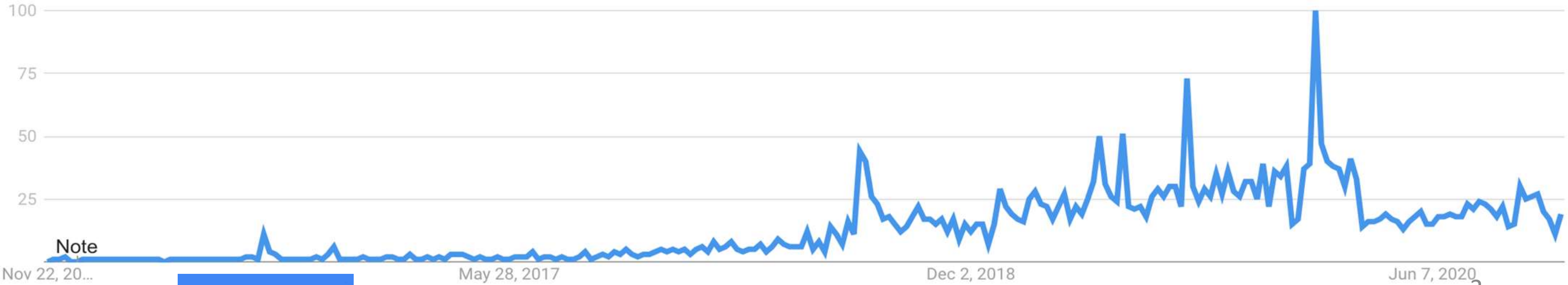
David Eggert, Associated Press Published 2:27 p.m. ET June 28, 2019 | Updated 5:25 p.m. ET June 28, 2019

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

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

Sharon Lerner

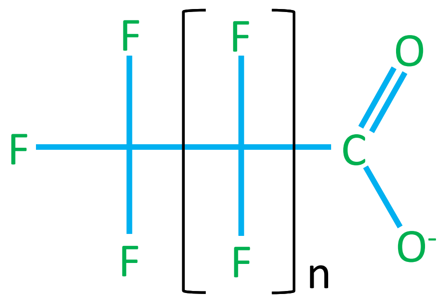


Google Trends

PFAS Terminology & Structure

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

Perfluoroalkyl substances:
fully fluorinated alkyl tail



Perfluoroalkyl Carboxylic Acids (PFCAs)

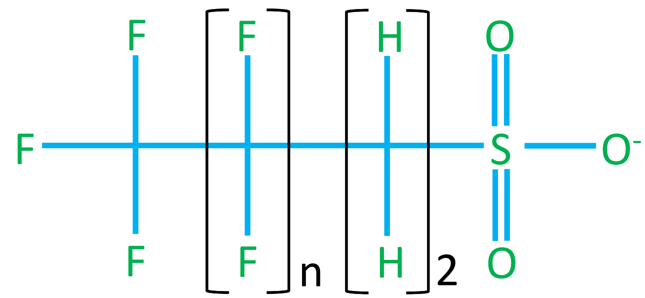
n = 2 PFBA

n = 4 PFHxA

n = 5 PFHpA

n = 6 PFOA

Polyfluoroalkyl substances:
partially fluorinated alkyl tail



Polyfluorotelomer Sulfonic Acids (FTSAs)

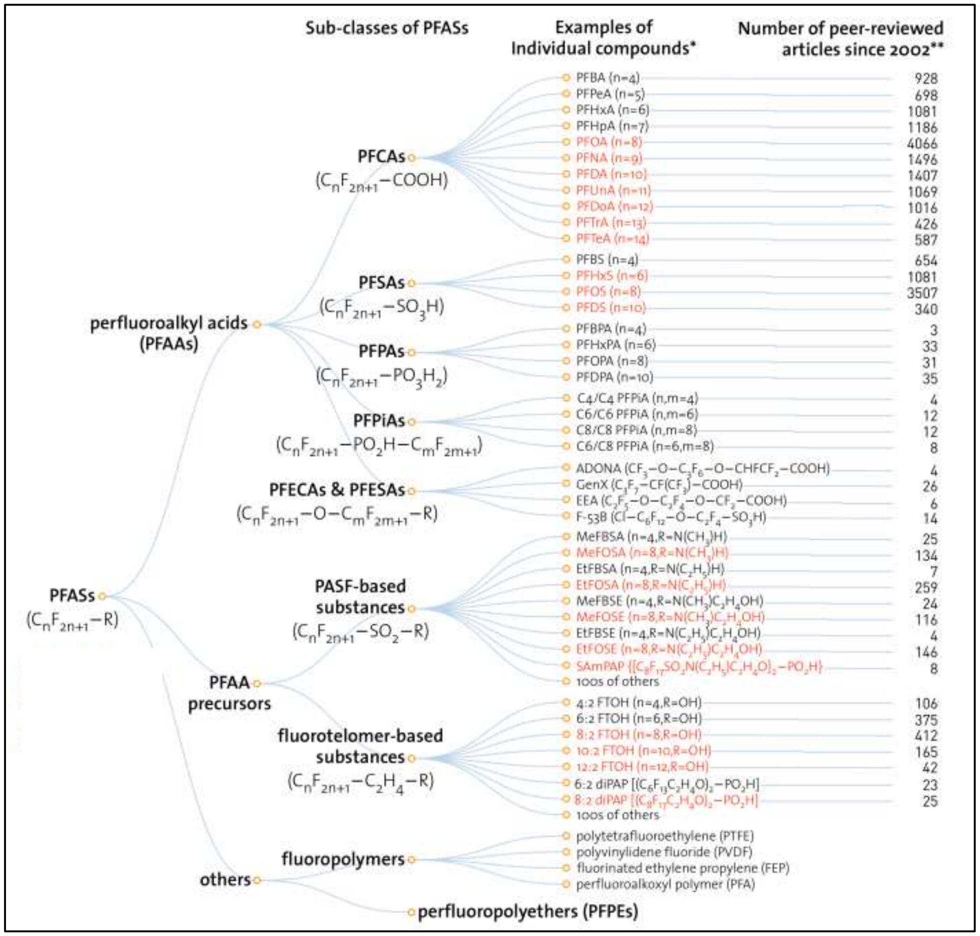
n = 3 4:2 FTS

n = 5 6:2 FTS

n = 7 8:2 FTS

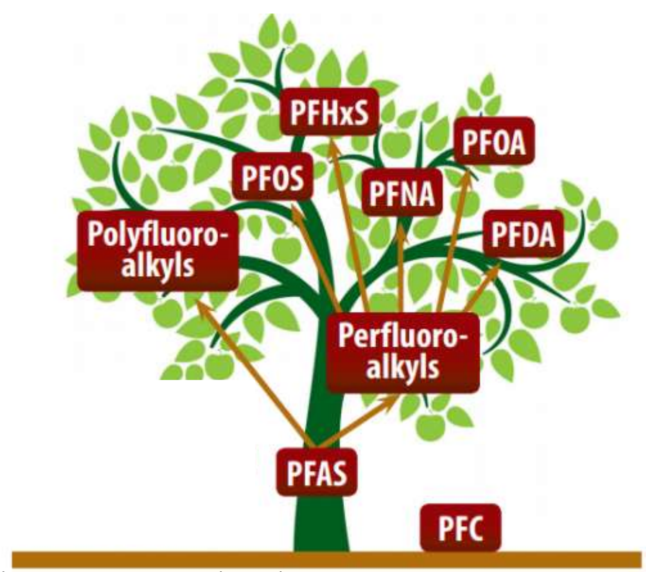
n = 9 10:2 FTS

PFAS include many sub-classes and thousands of individual compounds



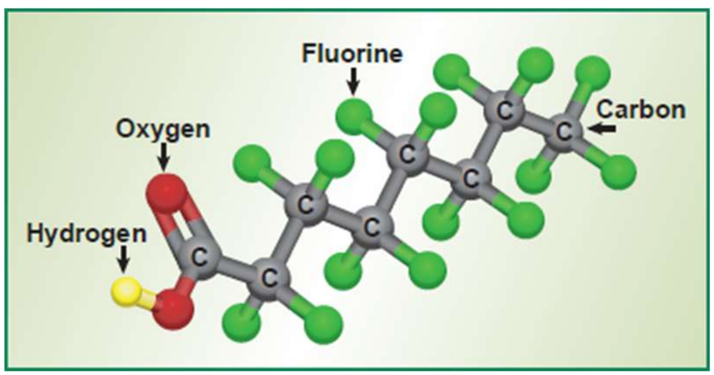
Wang et al., 2017, ES&T

- 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"

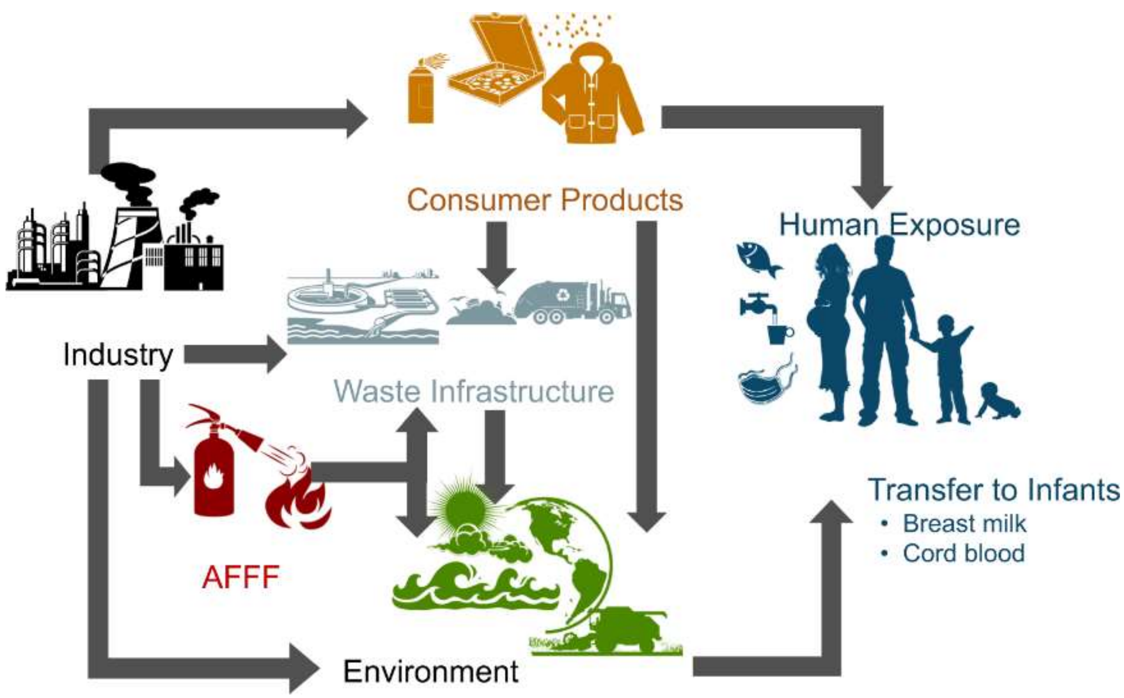


PFAS properties:

- 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

Drinking water guidelines/standards for PFASs are designed to limit exposure

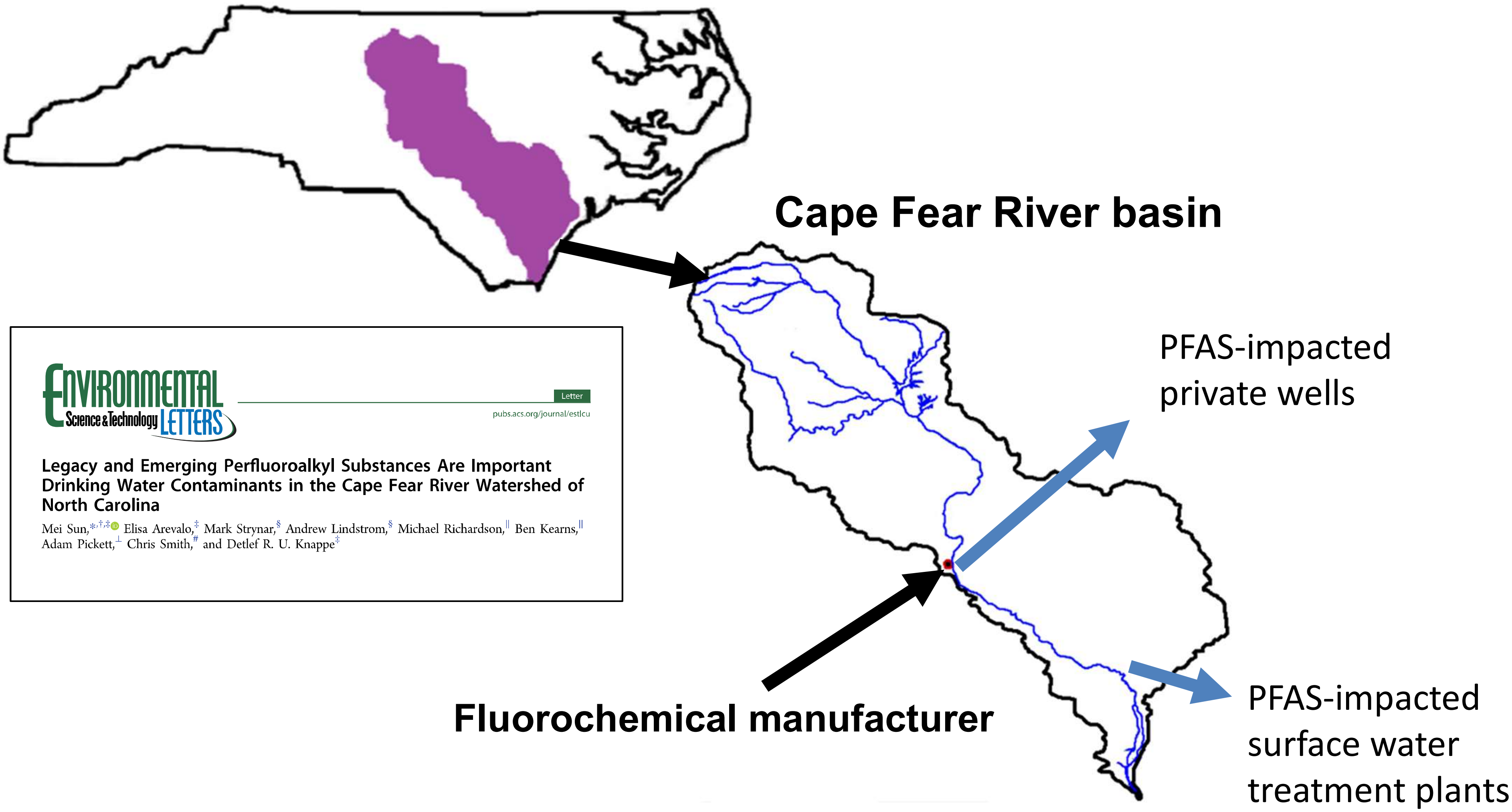
National

EPA Health Advisory (chronic exposure) →	PFOS + PFOA: 70 ng/L

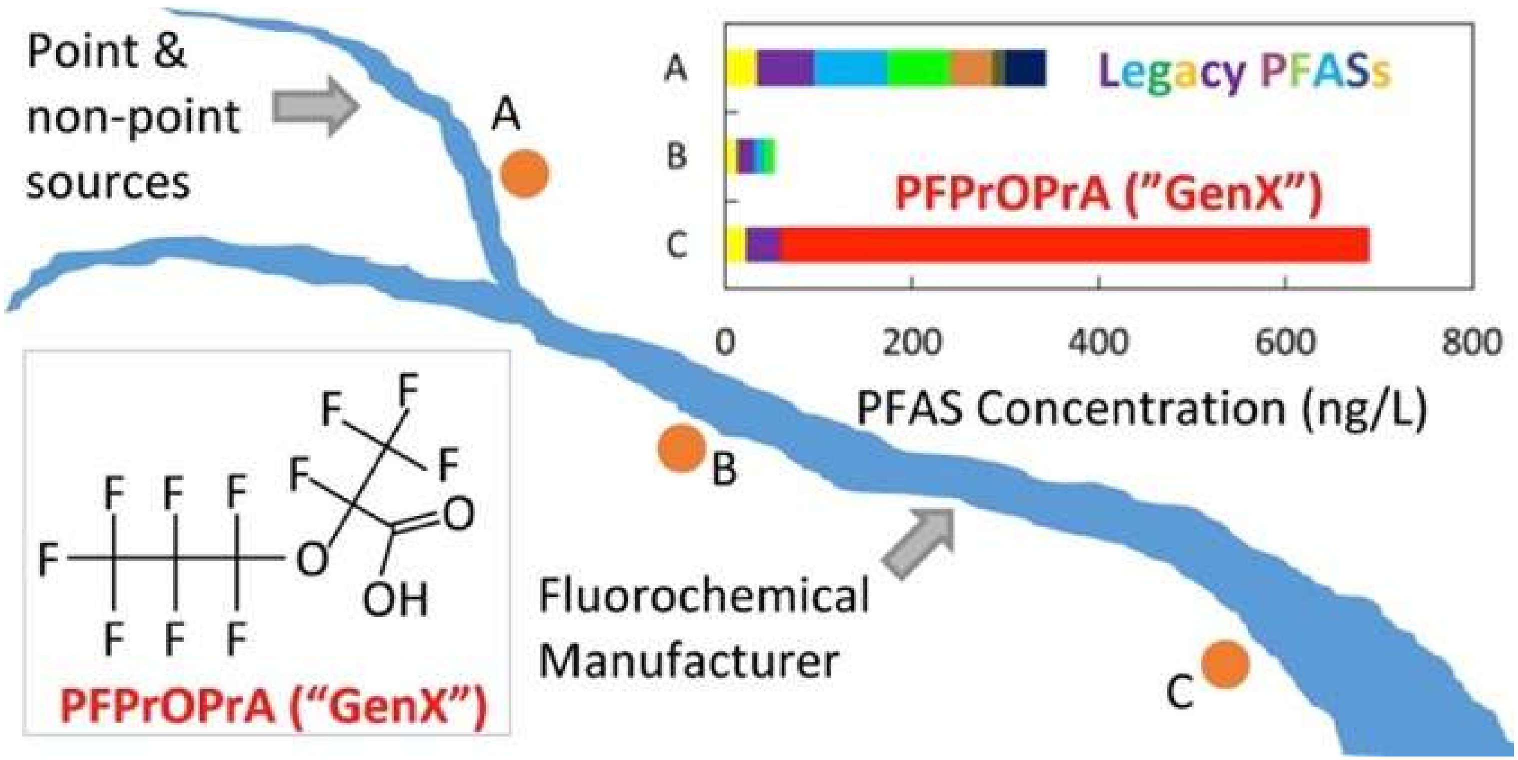
State

New Jersey maximum contaminant level →	PFOS, PFNA: 13 ng/L PFOA: 14 ng/L
Michigan maximum contaminant level →	PFOA: 8 ng/L PFNA: 6 ng/L PFOS: 16 ng/L PFHxA: 400,000 ng/L PFBS: 420 ng/L PFHxS: 51 ng/L GenX: 370 ng/L
Vermont maximum contaminant level →	PFHxS + PFHpA + PFOA + PFOS + PFNA: 20 ng/L
North Carolina health goal →	GenX: 140 ng/L

PFAS are contaminants in North Carolina surface and groundwater

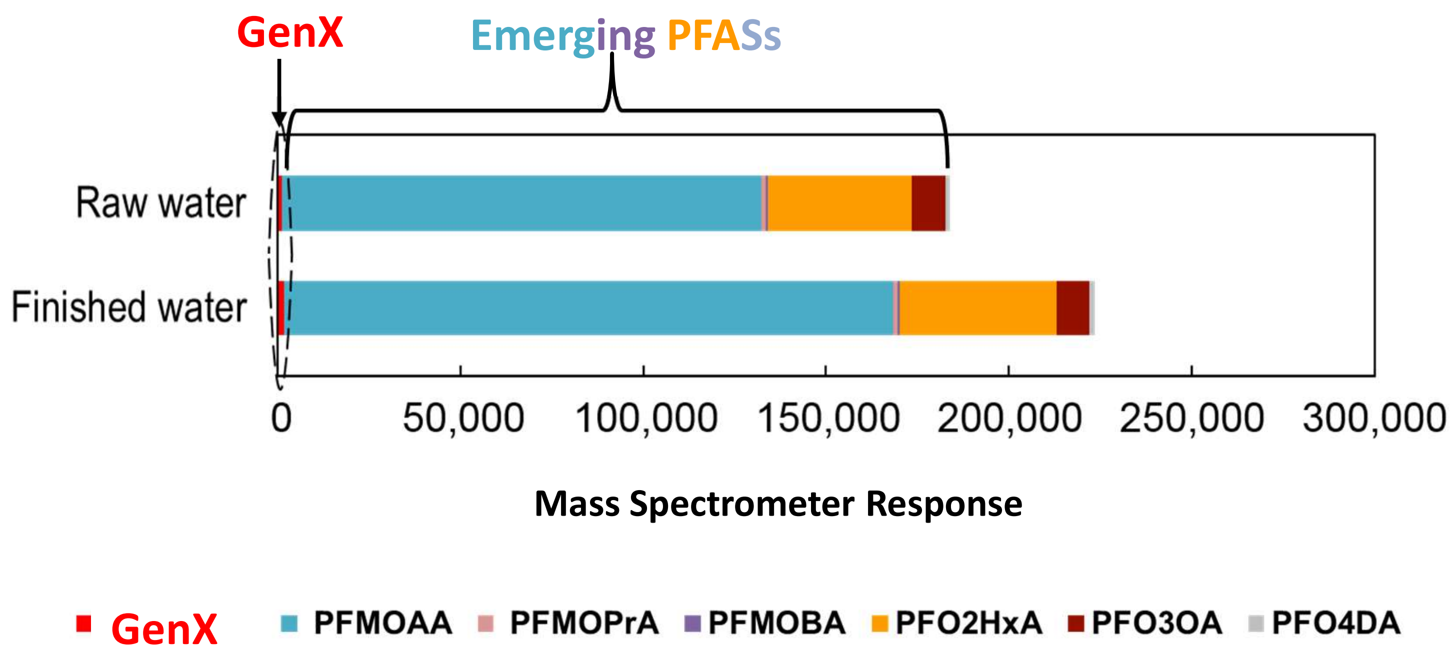


Elevated concentrations of “GenX” were detected in drinking water sources downstream of a fluorochemical manufacturer



Sun et al., 2016, ES&T

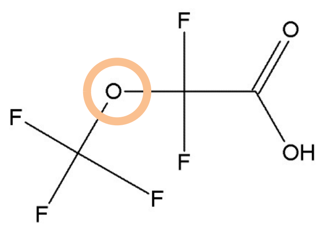
GenX was only a small fraction of the total mass spectrometer response associated with PFAS in Wilmington, NC



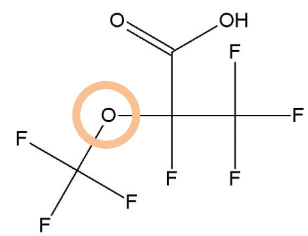
Sun et al., 2016, ES&T

Non-targeted analysis led to the identification of per- and polyfluoroalkyl ether acids (PFEA) in the Cape Fear River

- **(1) Mono-ether carboxylic acids with three to six carbon atoms – all perfluorinated**

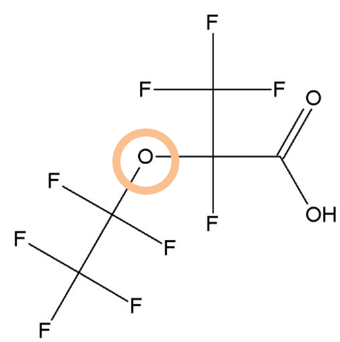


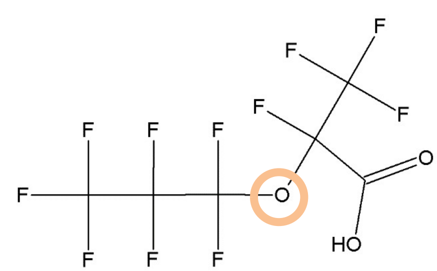
PFMOAA



PMPA

PEPA



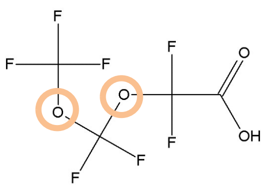


HFPO-DA ("GenX")

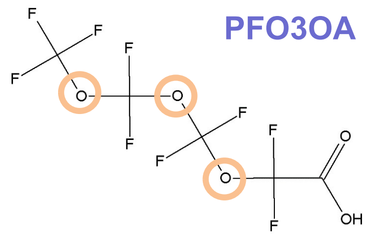
Strynar et al. (2015) *ES&T*
Hopkins et al. (2018) *JAWWA*

Non-targeted analysis led to the identification of per- and polyfluoroalkyl ether acids (PFEA) in the Cape Fear River

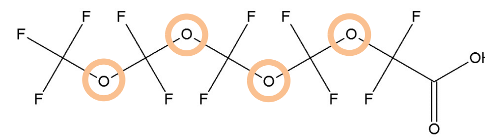
- **(2) Multi-ether carboxylic acids with up to five ether oxygen atoms – all perfluorinated**



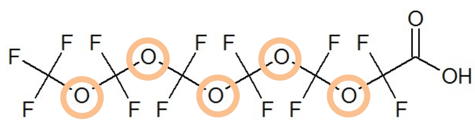
PFO2HxA



PFO3OA



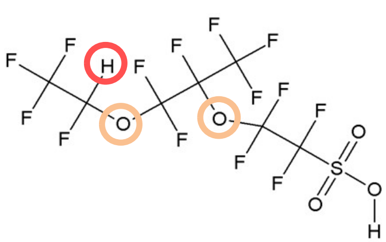
PFO4DA



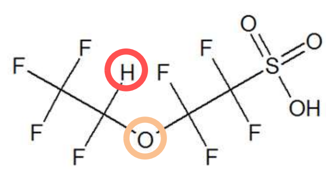
PFO5DoA

Strynar et al. (2015) *ES&T*
Hopkins et al. (2018) *JAWWA*
McCord et al. (2019) *ES&T*

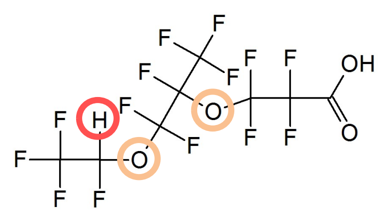
- **(3) Polyfluorinated ether acids**



Nafion by-product 2

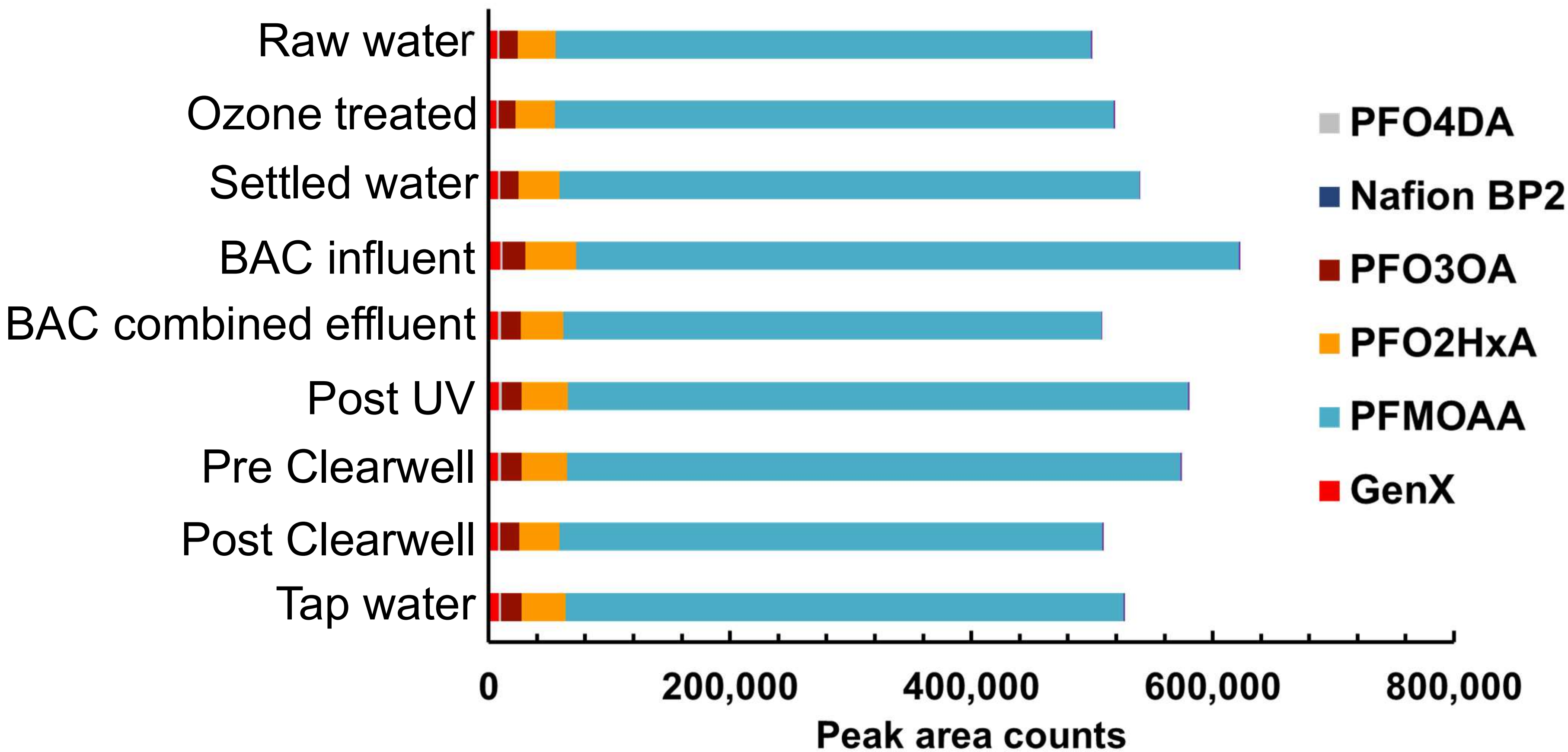


NVHOS

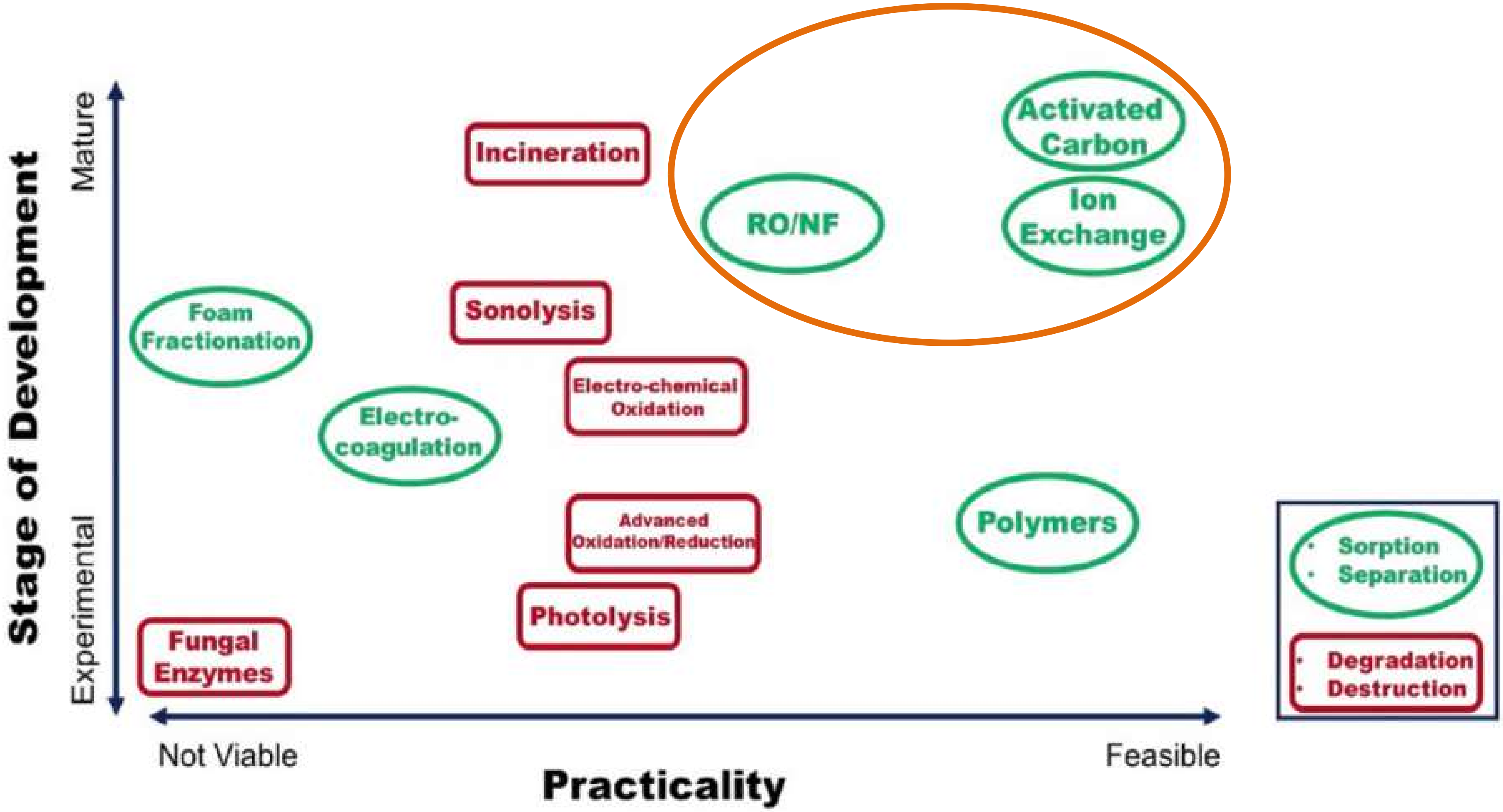


HydroEVE

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



Current PFAS water treatment technologies



T. Karanfil, Clemson University, 2018

PFAS are known contaminants in North Carolina waters

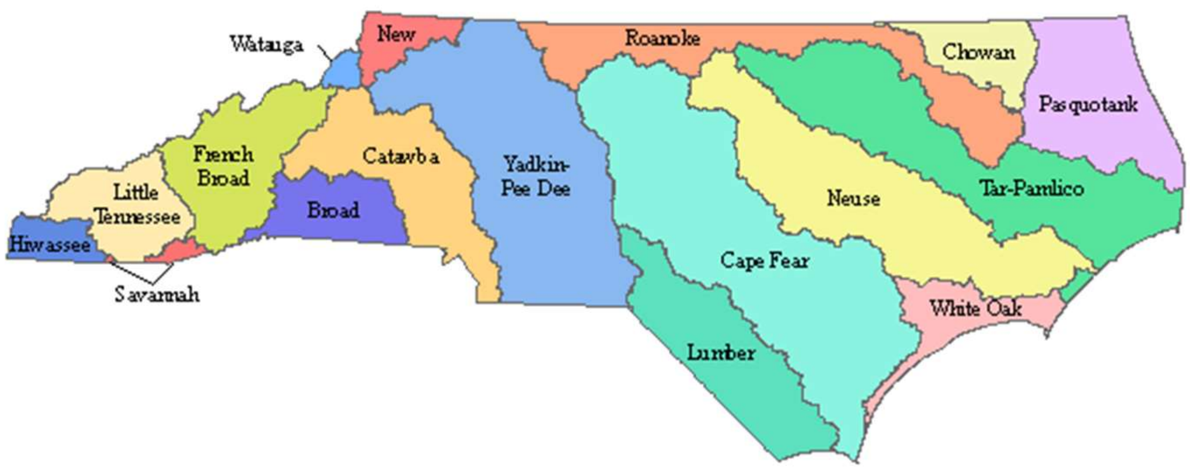
Sources:

- Manufacturing
  - Fluorochemicals (Chemours plant)
- Use of AFFF
  - Cherry Point MCAS
  - Seymour Johnson AFB
  - Local fire departments
  - Airports
- Wastewater disposal
  - Textile Industry
  - Commercial & domestic use

Is MY drinking water impacted by PFAS?

Impacts:

- PFAS-impacted private wells
- PFAS-impacted surface water
- Water treatment burden
- Community anger



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.

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

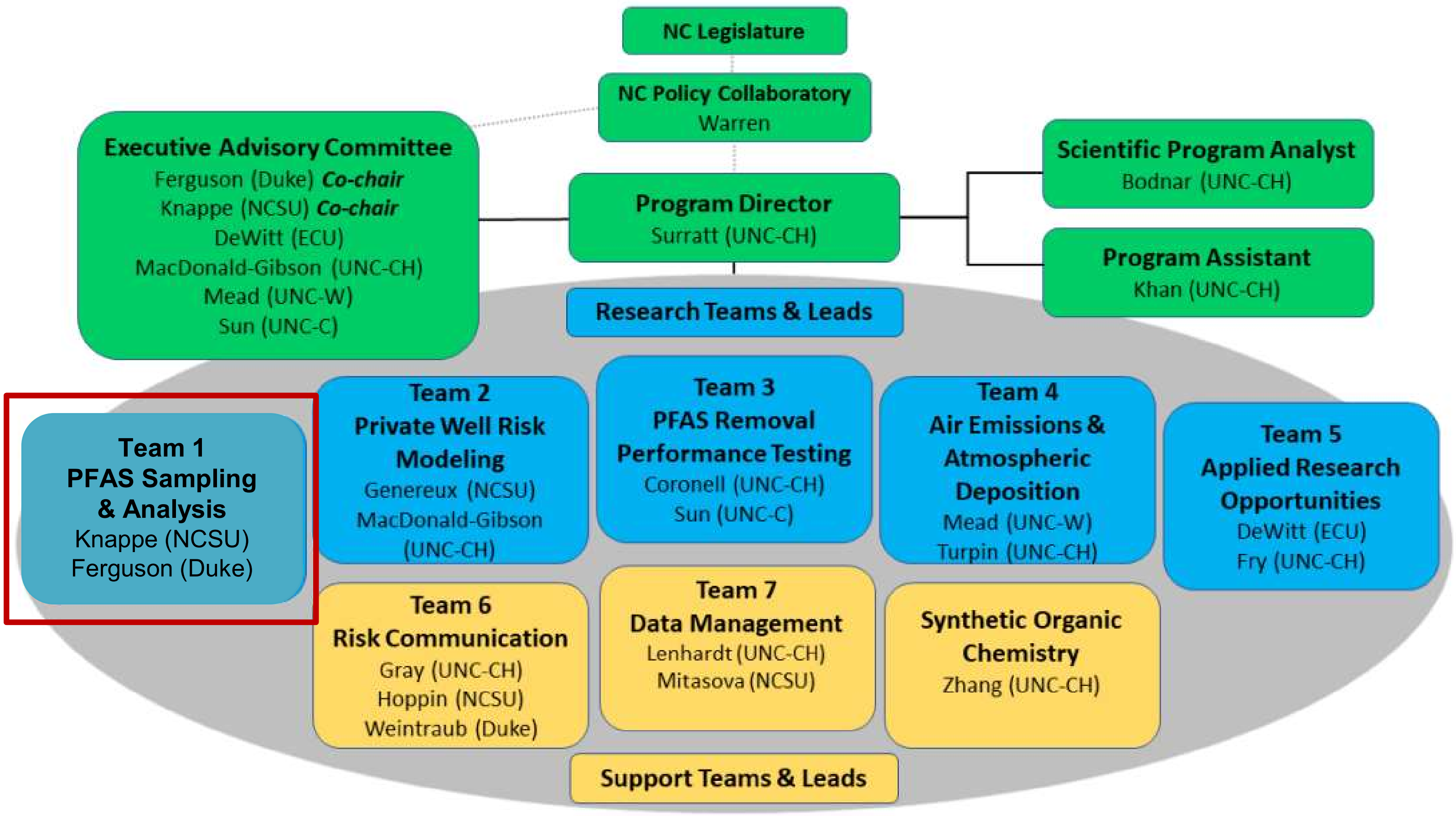
FUNDING TO ADDRESS PER- AND POLY-FLUOROALKYL SUBSTANCES, INCLUDING GENX/USE OF EXPERTISE AND TECHNOLOGY AVAILABLE IN INSTITUTIONS OF HIGHER EDUCATION LOCATED WITHIN THE STATE

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.

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

NORTH CAROLINA PFAS Testing Network

ncpfastnetwork.com



PFAST Team 1 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?**

Statewide sample acquisition

405 total municipal & county drinking water providers

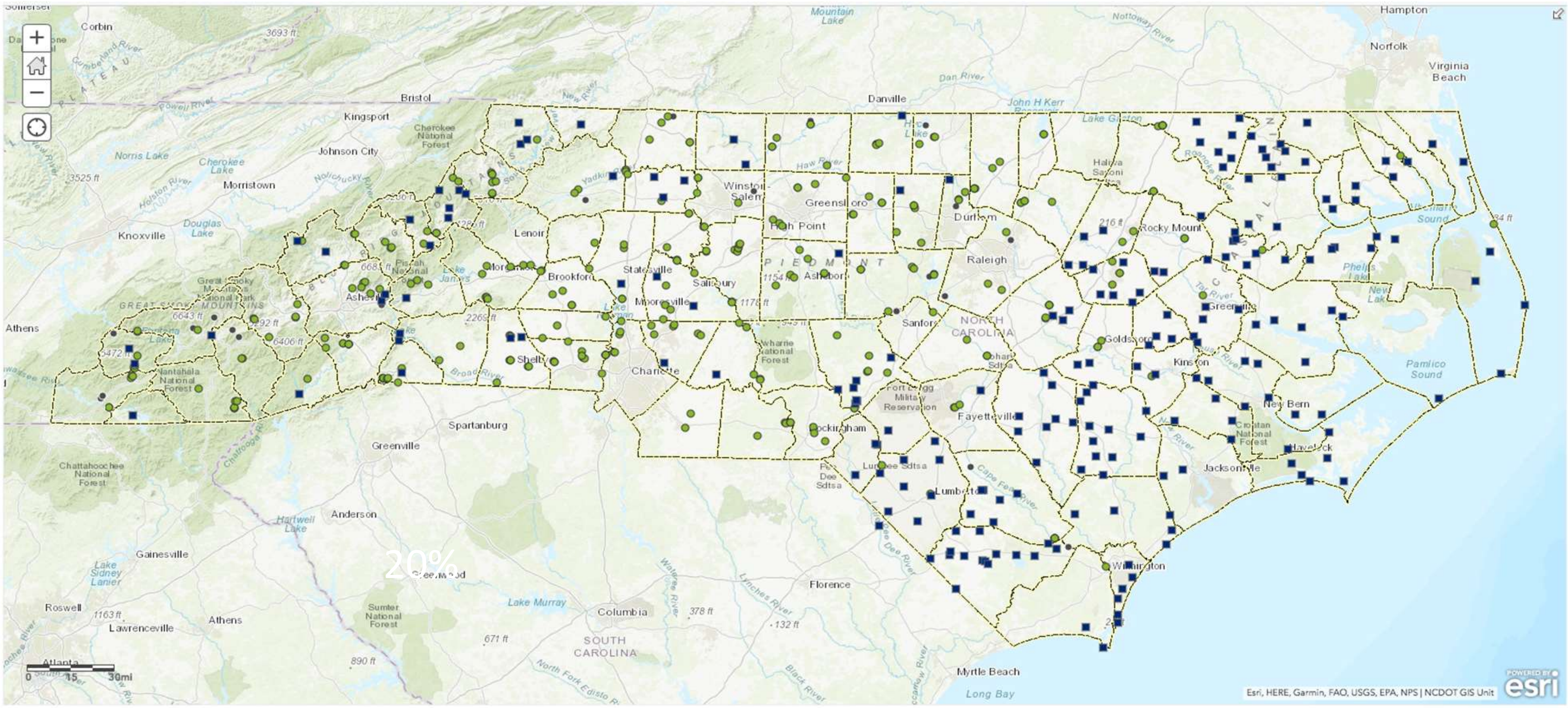


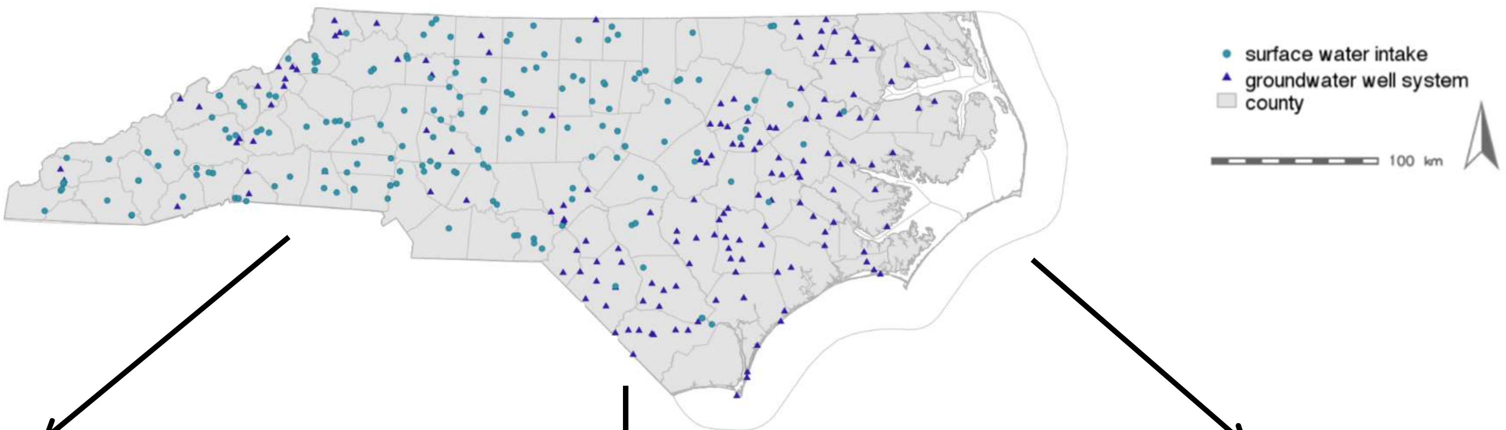
Figure 1. Surface (green circle) and groundwater (blue square) sampling sites for drinking water sources to be analyzed for PFAS compounds.

- 191 municipal surface water sites
- 149 municipal ground water sites
- 58 county water sites

Round 1 : COMPLETED (2019)

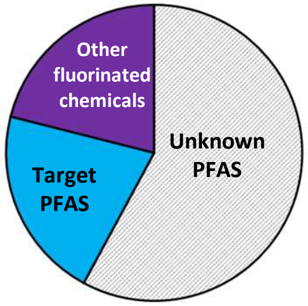
Round 2: In Progress (~15% remaining)

Complementary Analyses Help Answer the Question: Are PFAS in my Drinking Water?



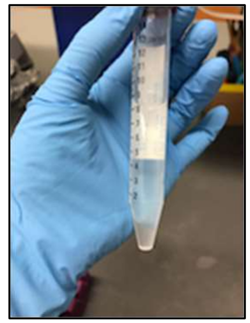
Target Quantitation:
"How much known PFAS?"

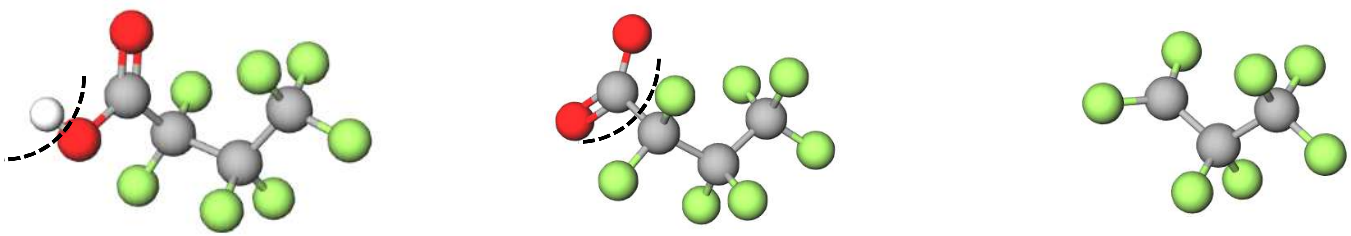
Adsorbable Organic Flourine (AOF) Quantitation:
"How much PFAS is unexplained by target methods?"

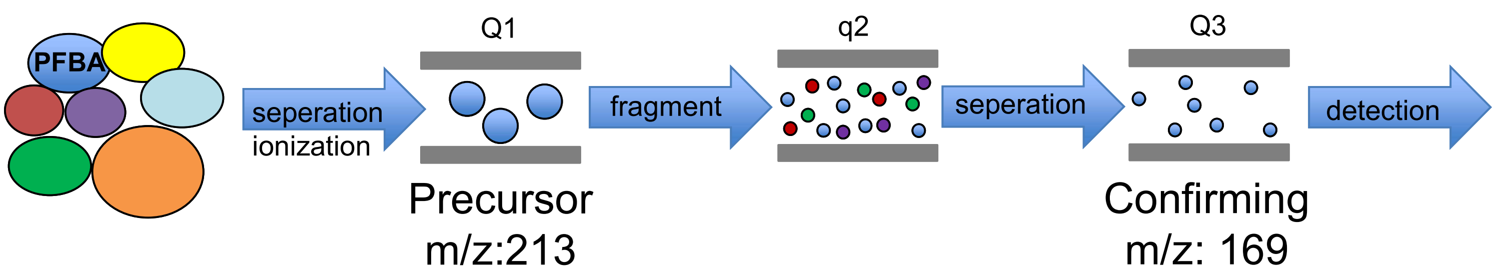


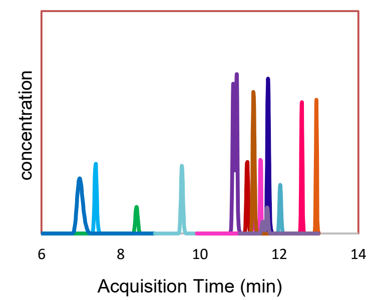
Suspect / Non-target Analysis:
"Which unknown PFAS?"

Targeted analysis by liquid chromatography – triple quadrupole mass spectrometry (LC-TQMS)





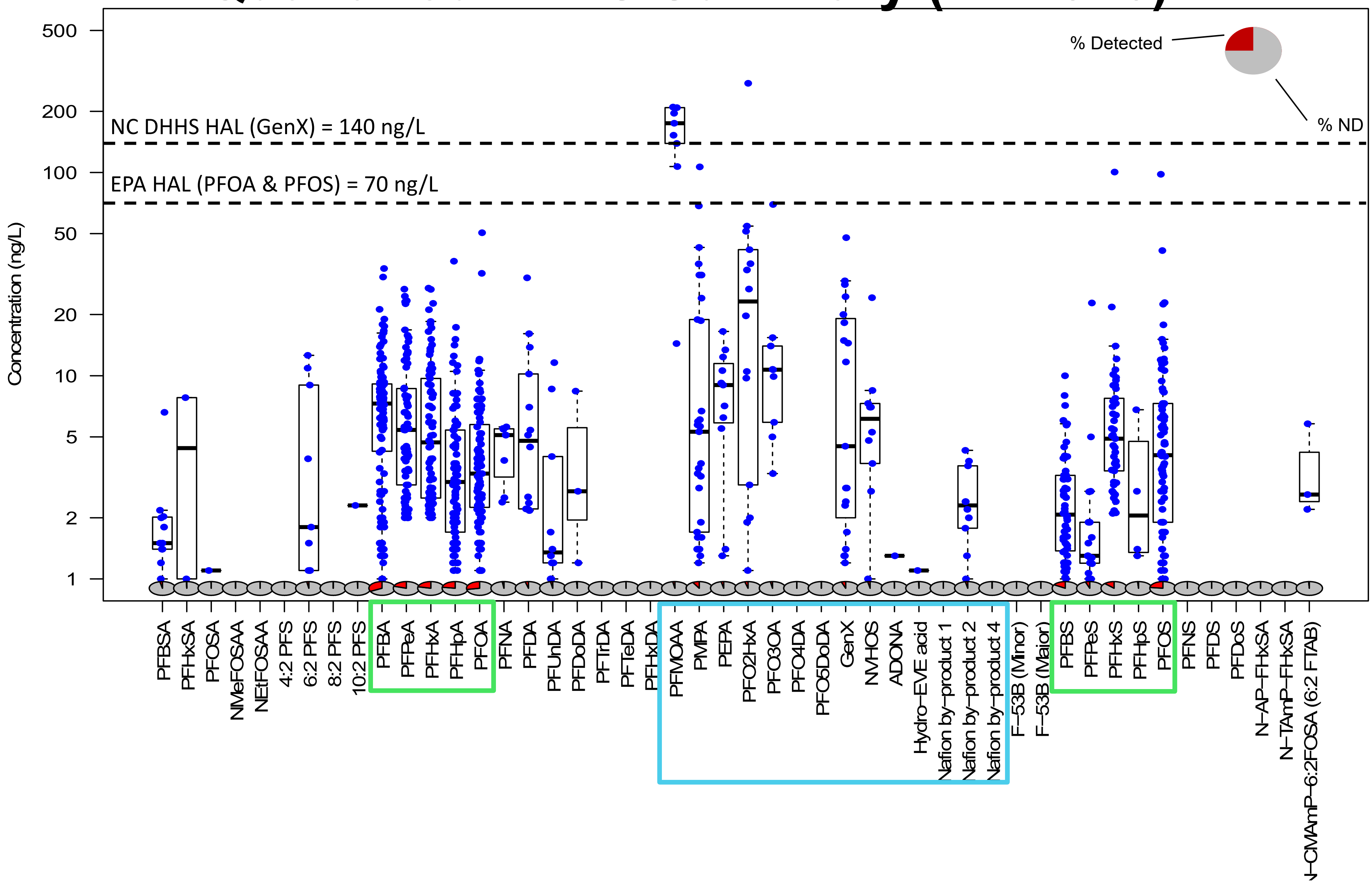




Targeted PFAS list:
>50 authentic standards

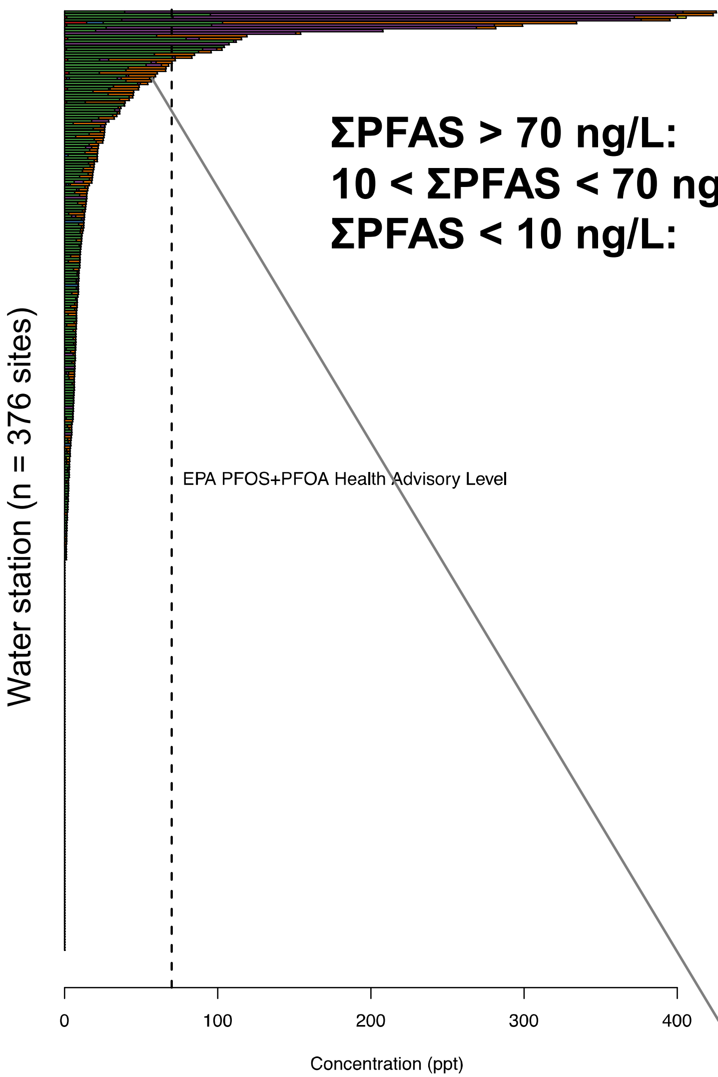
NC STATE UNIVERSITY

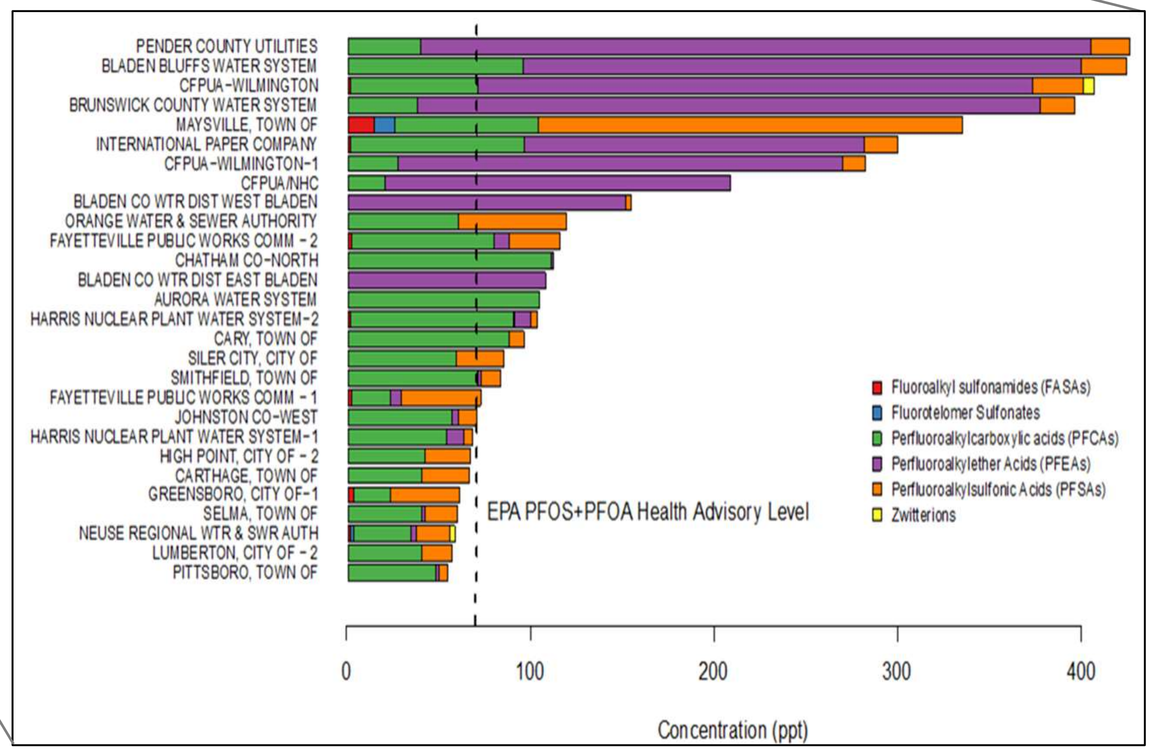
Round 1 Results: Quantified PFAS Summary (n = 376)



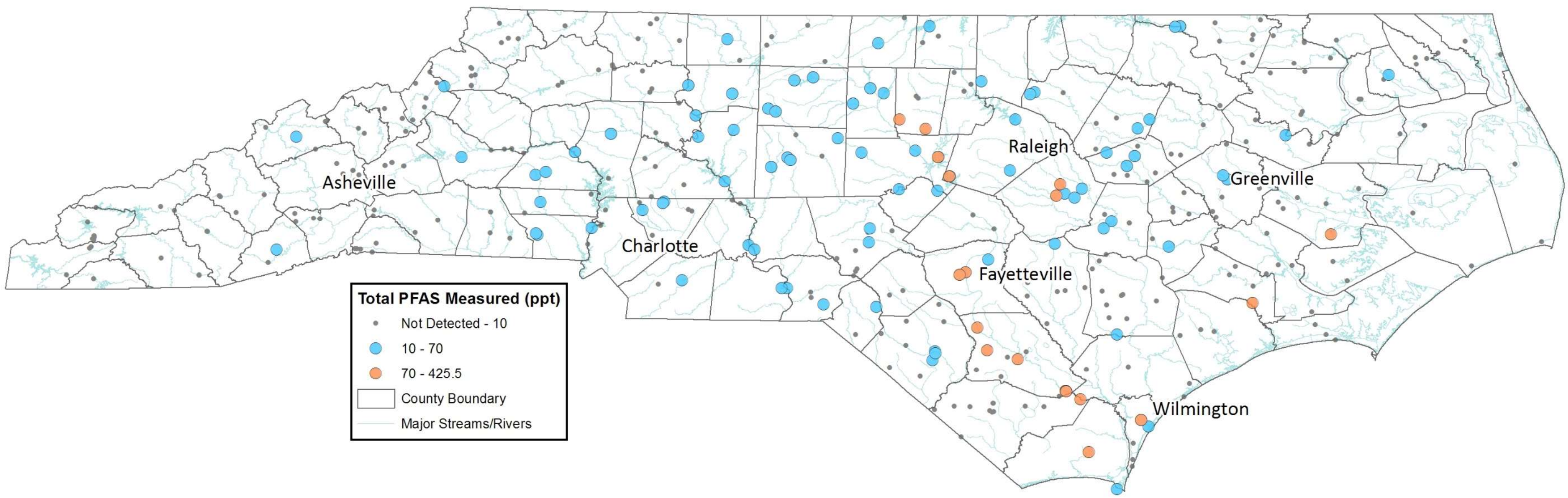
Round 1 Results Summary
n = 376

ΣPFAS > 70 ng/L: 20 (5%)
10 < ΣPFAS < 70 ng/L: 71 (19%)
ΣPFAS < 10 ng/L: 285 (76%)





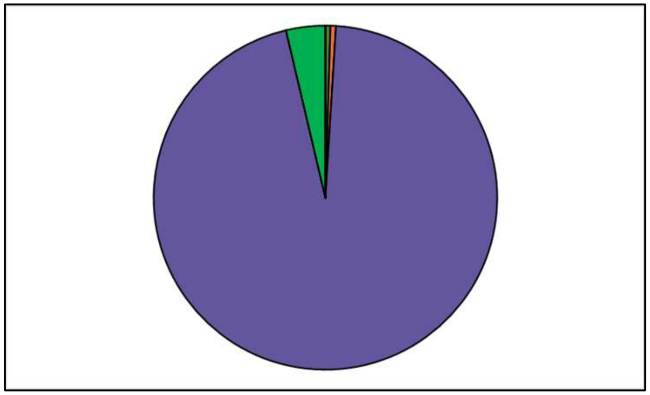
The majority of water sources with sum PFAS > 70 ng/L were in the Cape Fear River basin



PFAS Class Profiles are Unique to Contamination Sources

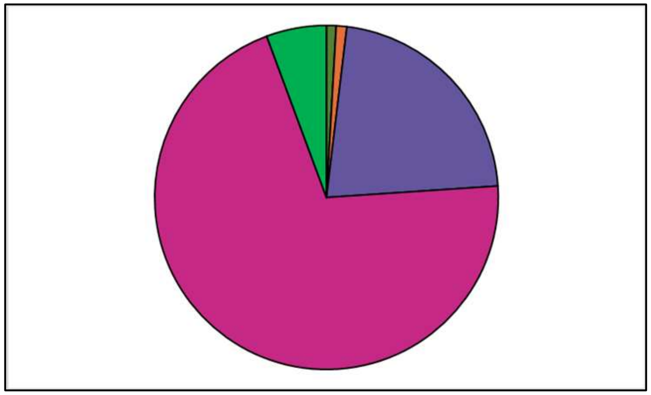
Pittsboro / Haw River:

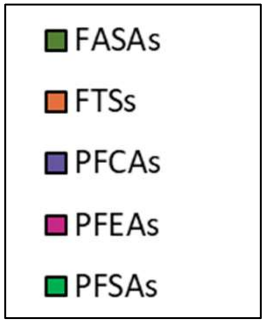
WWTPs, Textiles, Industrial Waste



Bladen Bluffs / Cape Fear River:

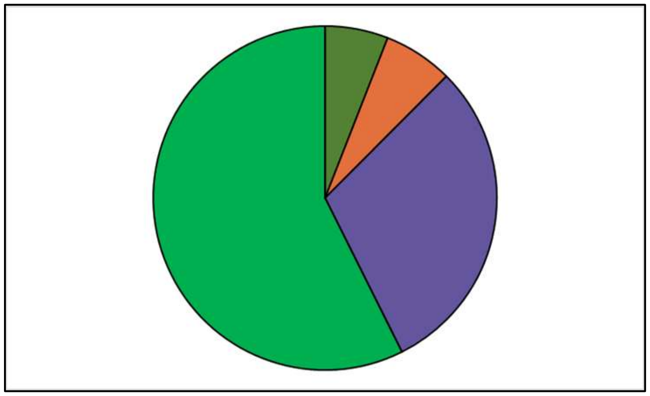
Fluorochemical Manufacturing, AFFF





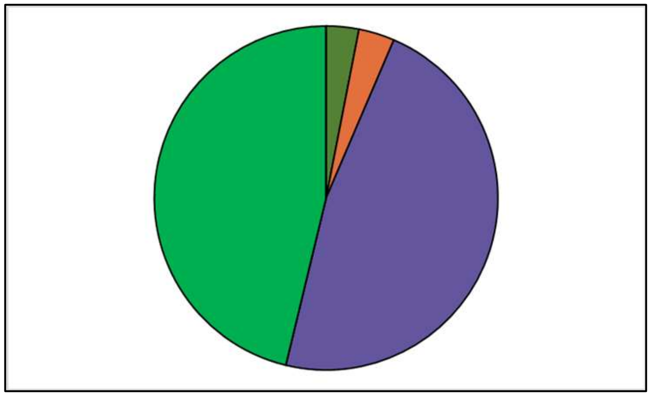
Greensboro / Lake Brandt:

Textiles, Industrial Waste



OWASA / Cane Creek:

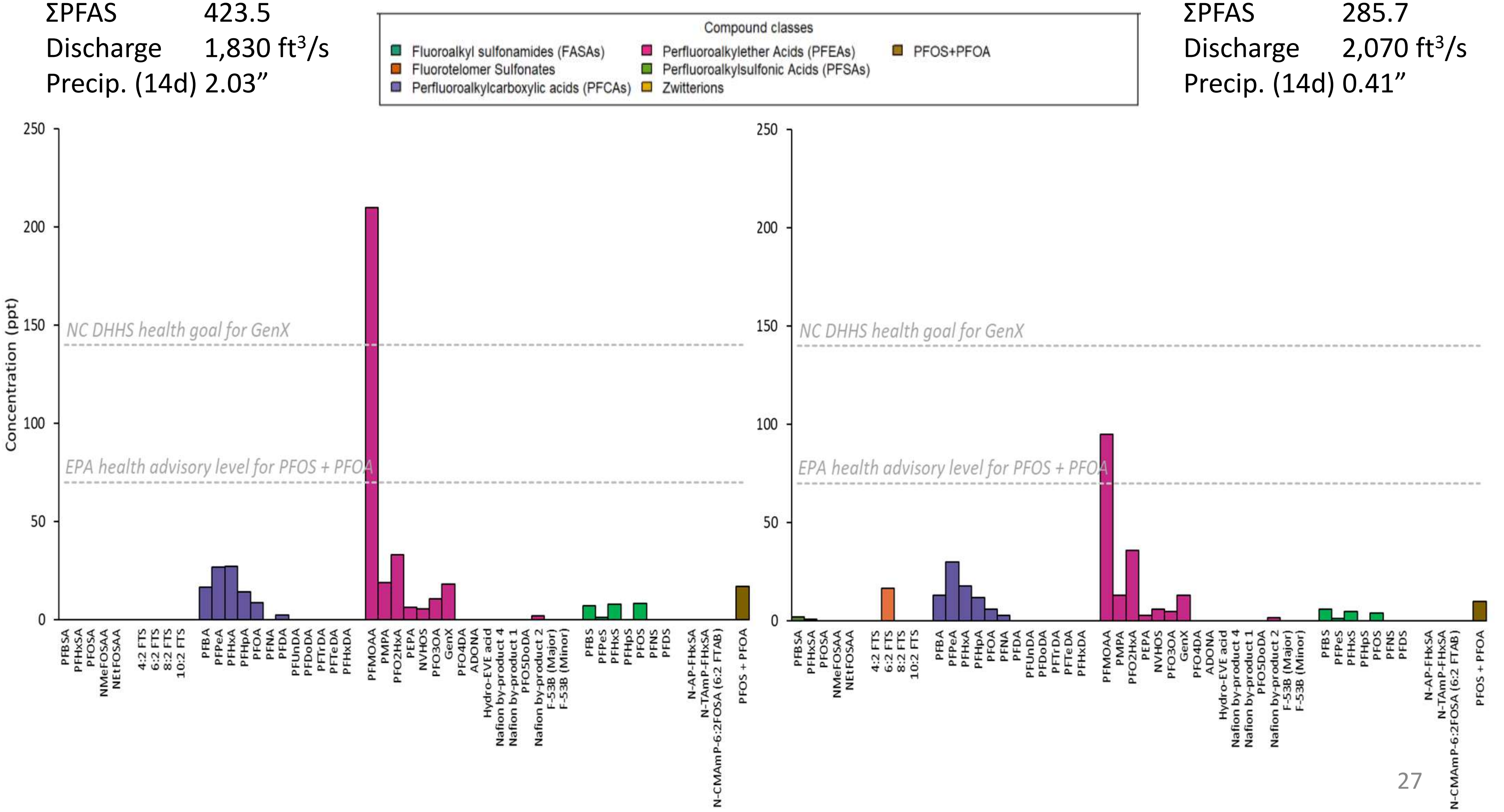
Biosolids Applications



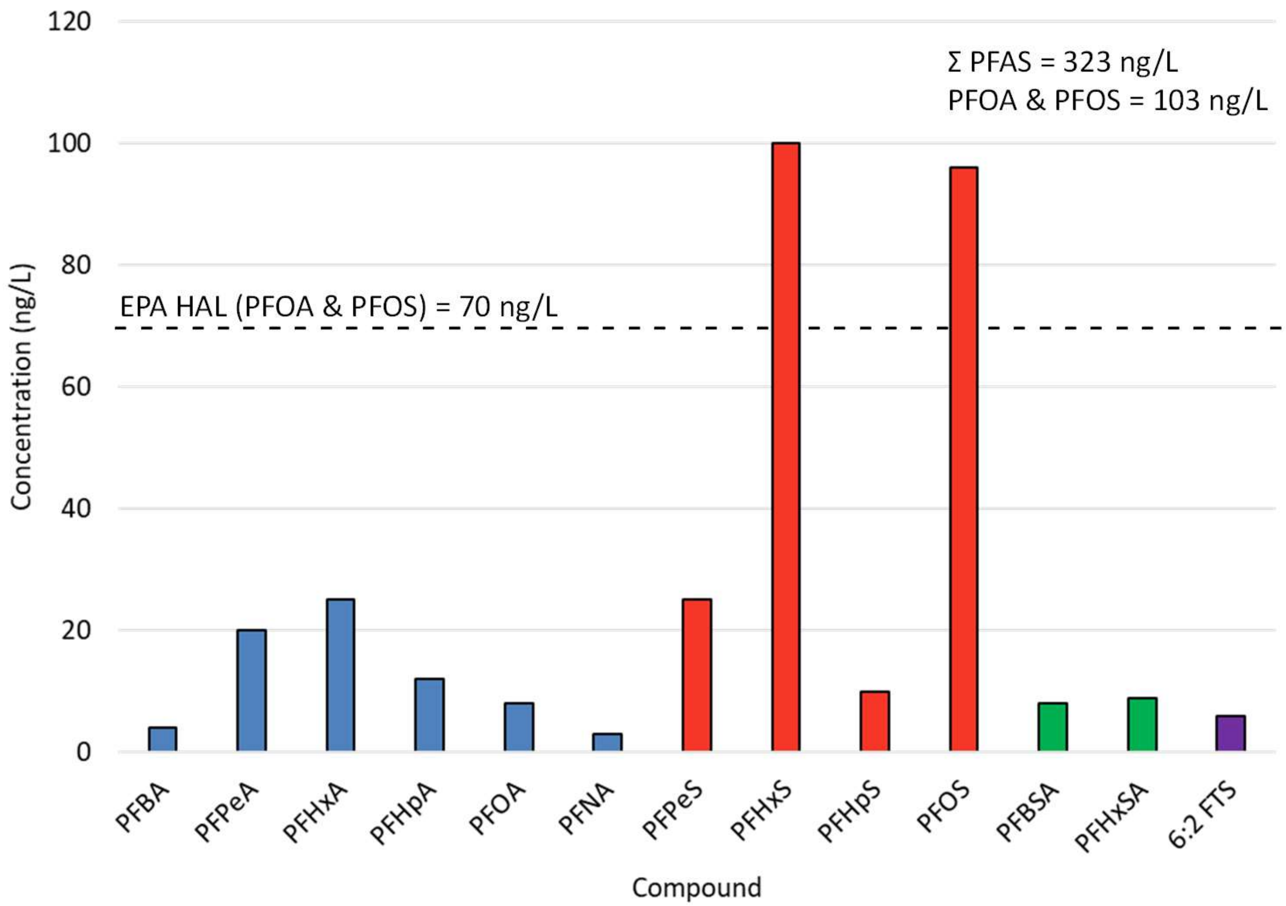
Round 2 Comparison: PFAS in the Lower Cape Fear River at Bladen Bluffs

Round 1 8/22/19
ΣPFAS 423.5
Discharge 1,830 ft^3/s
Precip. (14d) 2.03”

Round 2 11/5/19
ΣPFAS 285.7
Discharge 2,070 ft^3/s
Precip. (14d) 0.41”



Case Study: Small Town in Jones County The sum of PFOA and PFAS in raw ground water exceeded the EPA HAL



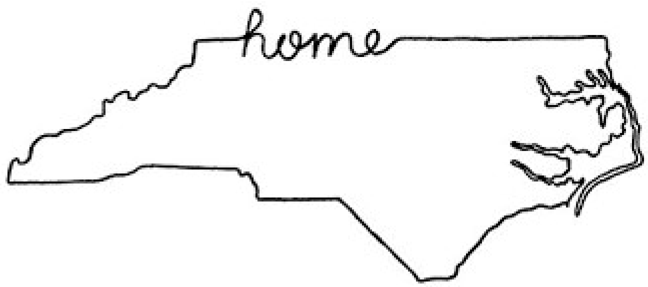
- Results were verified between two PFAST labs
- The town was notified within 10 days
- A second analysis was performed on raw and finished drinking water by a hired lab, confirming initial findings
- Within a month, the town switched to an alternative water source

Take-Home Messages

- Of the 376 water sources tested in Round 1:
  - 20 had ΣPFAS > 70 ng/L (max 425 ng/L)
  - 71 had ΣPFAS 10-70 ng/L
  - 285 had ΣPFAS < 10 ng/L
- The majority of systems with ΣPFAS above 70 ppt were in the Cape Fear and Haw River Basins
- GenX was not detected above 140 ng/L, but 3 fluoroethers were (PFMOAA, PFO2HxA, PMPA)
- Important PFAS sources are the Fayetteville Works site (Chemours), AFFF, and runoff from fields that received biosolids
- Testing should be expanded to include additional groundwater sources to capture spatial variability among wells
- Testing should continue to capture temporal variability of impacted sources

Questions?

Noelle DeStefano
njdestef@ncsu.edu



Acknowledgment:
Funding: North Carolina Policy Collaboratory