



# PFAST Team 1 – Occurrence of PFAS in North Carolina’s drinking water sources

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POSTDOCS: ABIGAIL JOYCE<sup>1</sup>, NOELLE DESTEFANO<sup>2</sup>

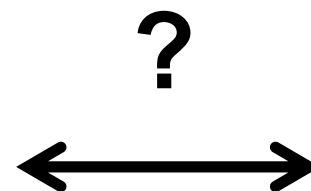
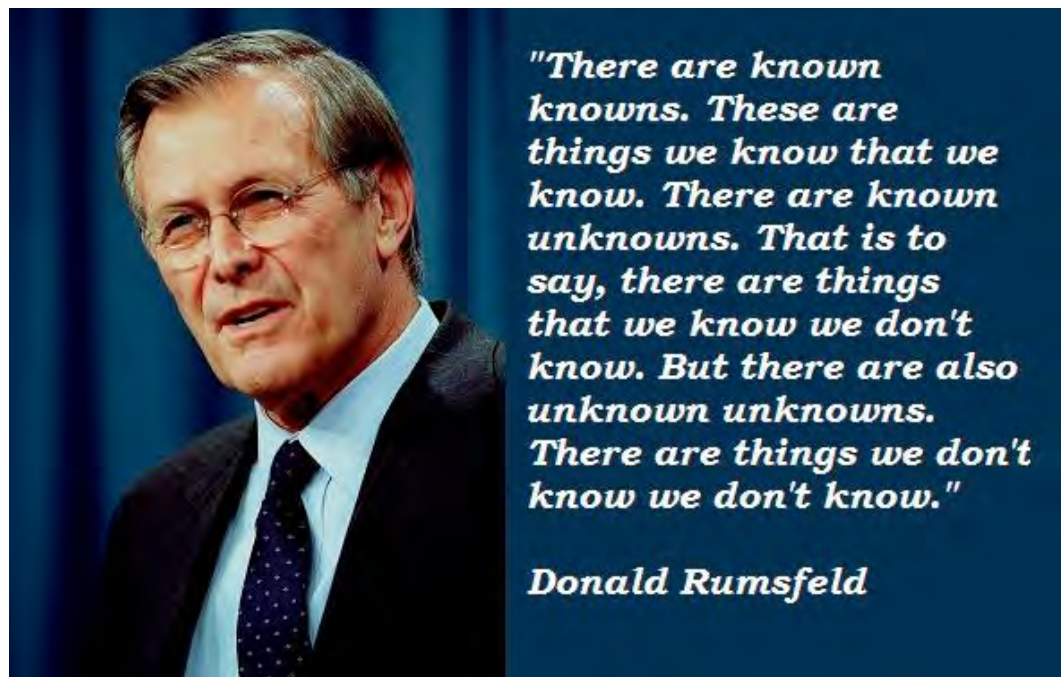
<sup>1</sup>DUKE UNIVERSITY, <sup>2</sup>NC STATE UNIVERSITY, <sup>3</sup>UNC-CHARLOTTE

Key Motivating Question

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**IS MY WATER SAFE TO DRINK?**

# What do we know?



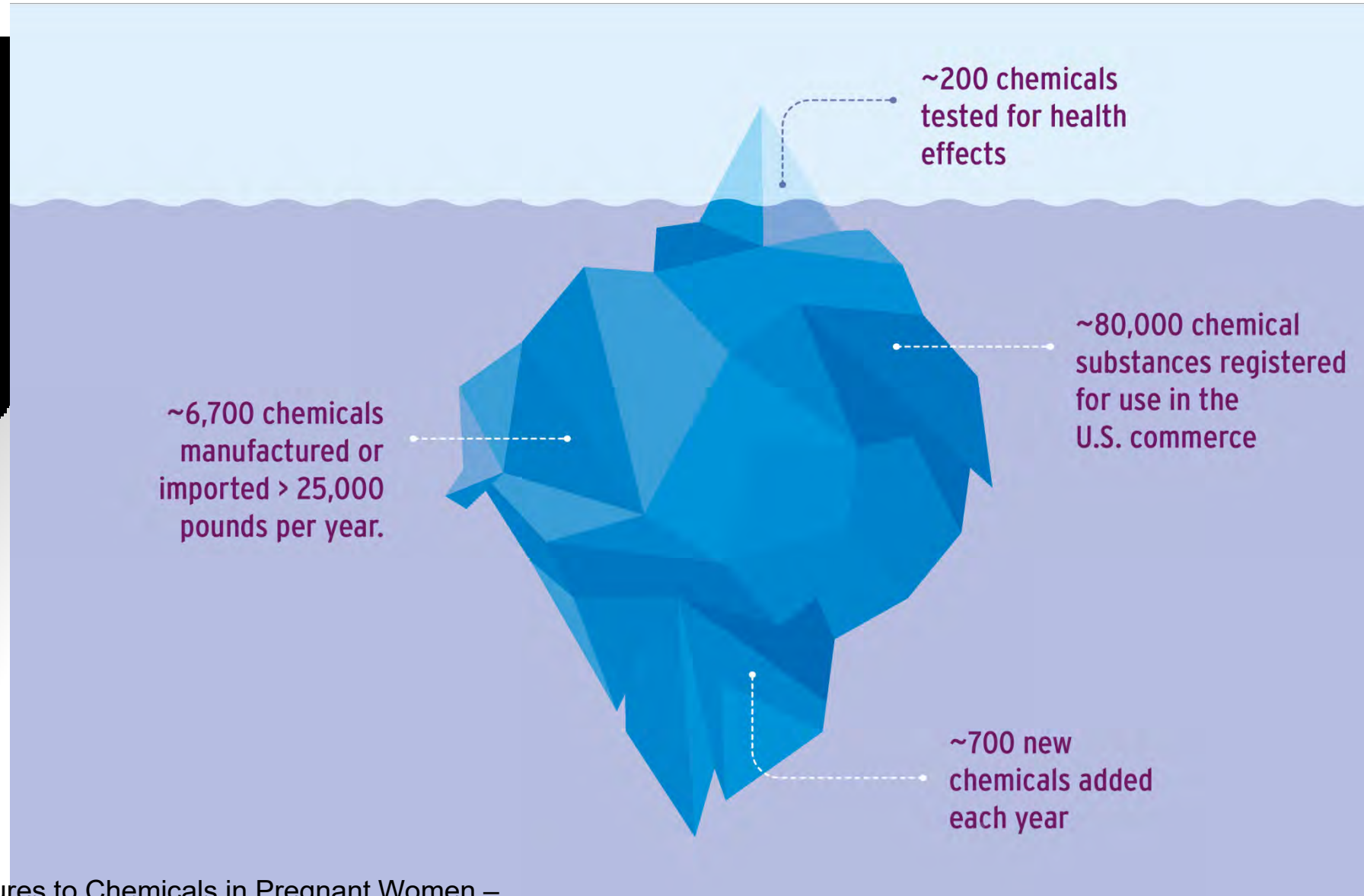
Regulated contaminants (known knowns)

Unregulated contaminants on our radar (known unknowns)

The universe of chemicals (unknown unknowns)

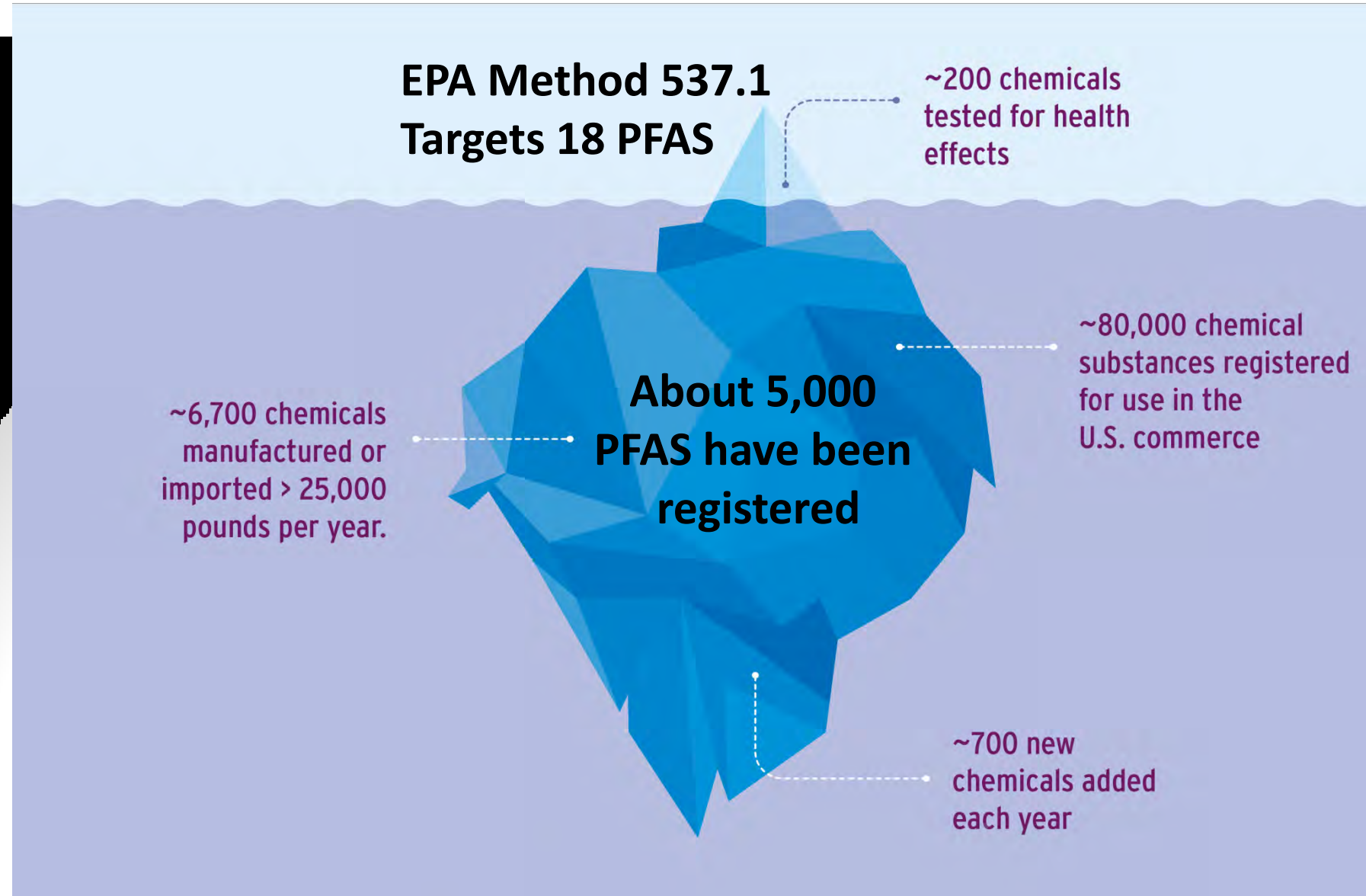
# Majority of Chemicals Not Tested Before Entering the Market

We only know the tip of the iceberg

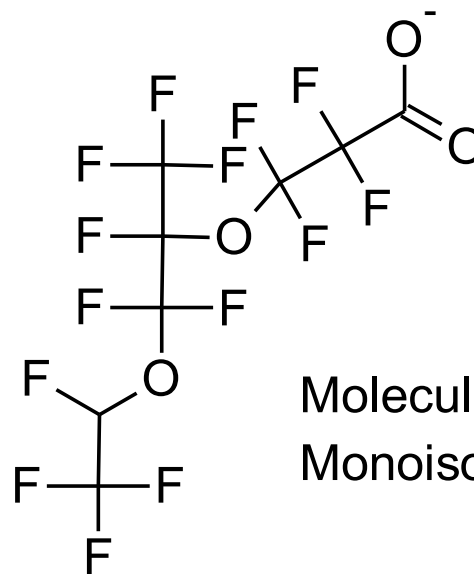


# Majority of Chemicals Not Tested Before Entering the Market

Similar situation with PFAS



# Non-targeted analysis is an emerging approach in environmental analytical chemistry to identify unknown unknowns



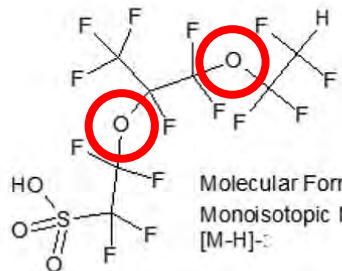
**Hydro-EVE Acid**

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

Monoisotopic Mass: 426.9657 Da

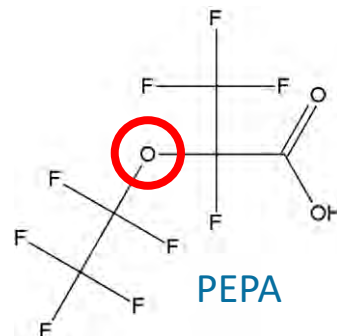
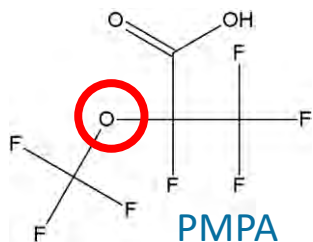
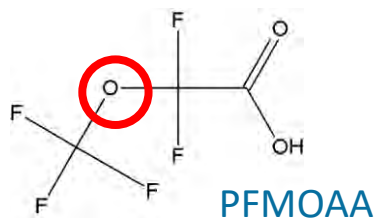
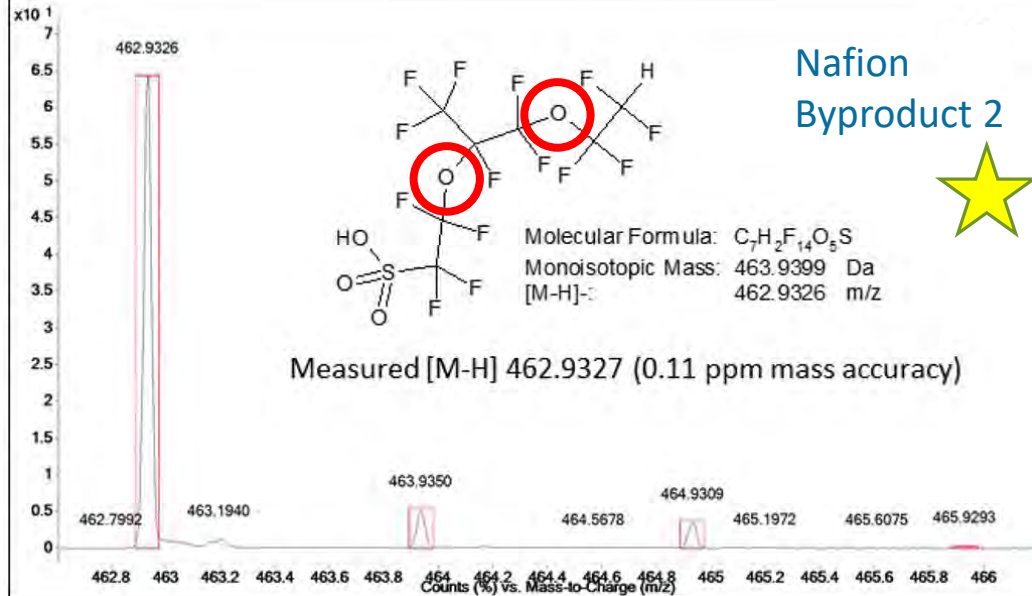
# Per- and polyfluoroalkyl ether acids identified by high resolution mass spectrometry

Nafion  
Byproduct 2

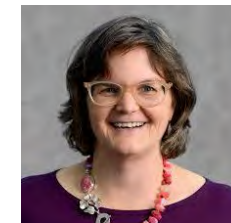
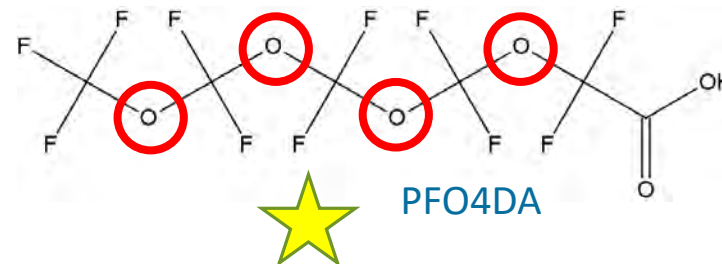
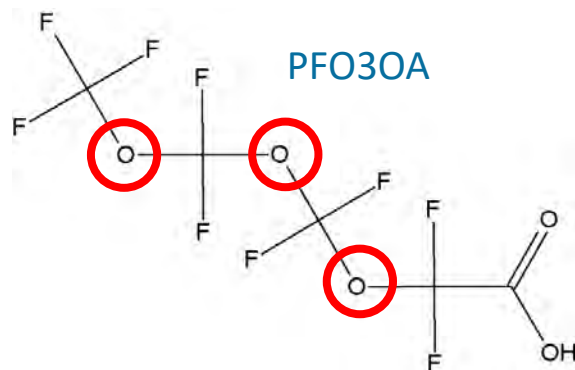
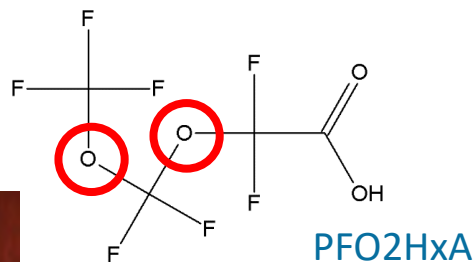
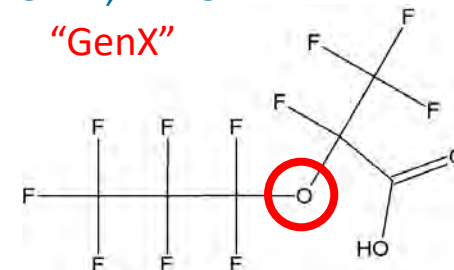


Molecular Formula:  $C_7H_2F_{14}O_5S$   
 Monoisotopic Mass: 463.9399 Da  
 $[M-H]^-$ : 462.9326 m/z

Measured  $[M-H]$  462.9327 (0.11 ppm mass accuracy)



PFPrOPrA, HFPO-DA  
"GenX"



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

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## **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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# Research Questions

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## **What are the concentrations of targeted legacy and emerging PFAS contaminants in North Carolina public drinking water sources?**

- Collect and analyze raw water samples during two consecutive quarters of 2019 at all 191 municipal surface water intakes and all 149 municipal drinking water systems treating groundwater in NC for PFAS measurement
- Repeat this sampling for systems with detectable PFAS in the third quarter of 2019

## **What unanticipated and untargeted PFAS compounds occur in North Carolina public drinking water sources?**

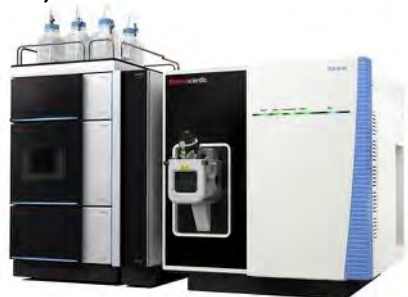
- Apply high-resolution mass spectrometry methods to screen samples collected above for presence of > 5,100 known PFAS compounds as well as for unknown fluorinated organic compounds

## **How much of the total organic fluorine in North Carolina public drinking water sources can be accounted for by targeted PFAS quantitation?**

- Utilize adsorbable organic fluorine (AOF) measurements in concert with the quantitative PFAS measurements outlined above to assess fluorine “mass balance” in water samples

# PFAS analysis strategy

Triple Quadrupole MS/MS (target quantitation)



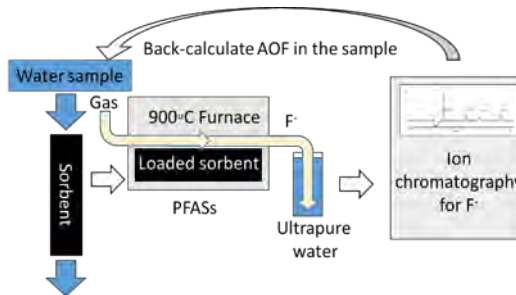
Analyte	Abbreviation	CAS#
<i>Perfluorocarboxylic acids</i>		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPA	2706-99-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-83-9
Perfluorooctanoic acid	PFOSA	375-07-1
Perfluorononanoic acid	PFNA	375-05-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUdA	2028-24-8
Perfluorododecanoic acid	PFDDA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTEdA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67908-19-5
<i>Perfluoroalkylsulfonic acids</i>		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	335-66-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecane sulfonic acid	PFDS	335-77-5
Perfluorododecane sulfonic acid	PFDoS	79780-39-5
<i>Perfluoroalkylsulfonamides</i>		
N-ethyl perfluorooctanesulfonamide	NEPFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamide	NMFPoSAA	3355-31-9
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-ethylperfluorooctane sulfonamide	NEPFOSF	1691-99-2
N-methylperfluorooctane sulfonamide	NMFPoSF	2448-06-7
N-ethylperfluorooctane sulfonamide	NEPFOSA	4151-50-2
N-methylperfluorooctane sulfonamide	NMFPOSA	3156-32-8

PFAS mass balance

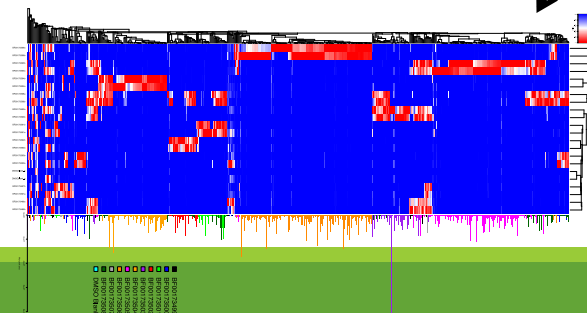
Sample Collection



Solid Phase Extraction

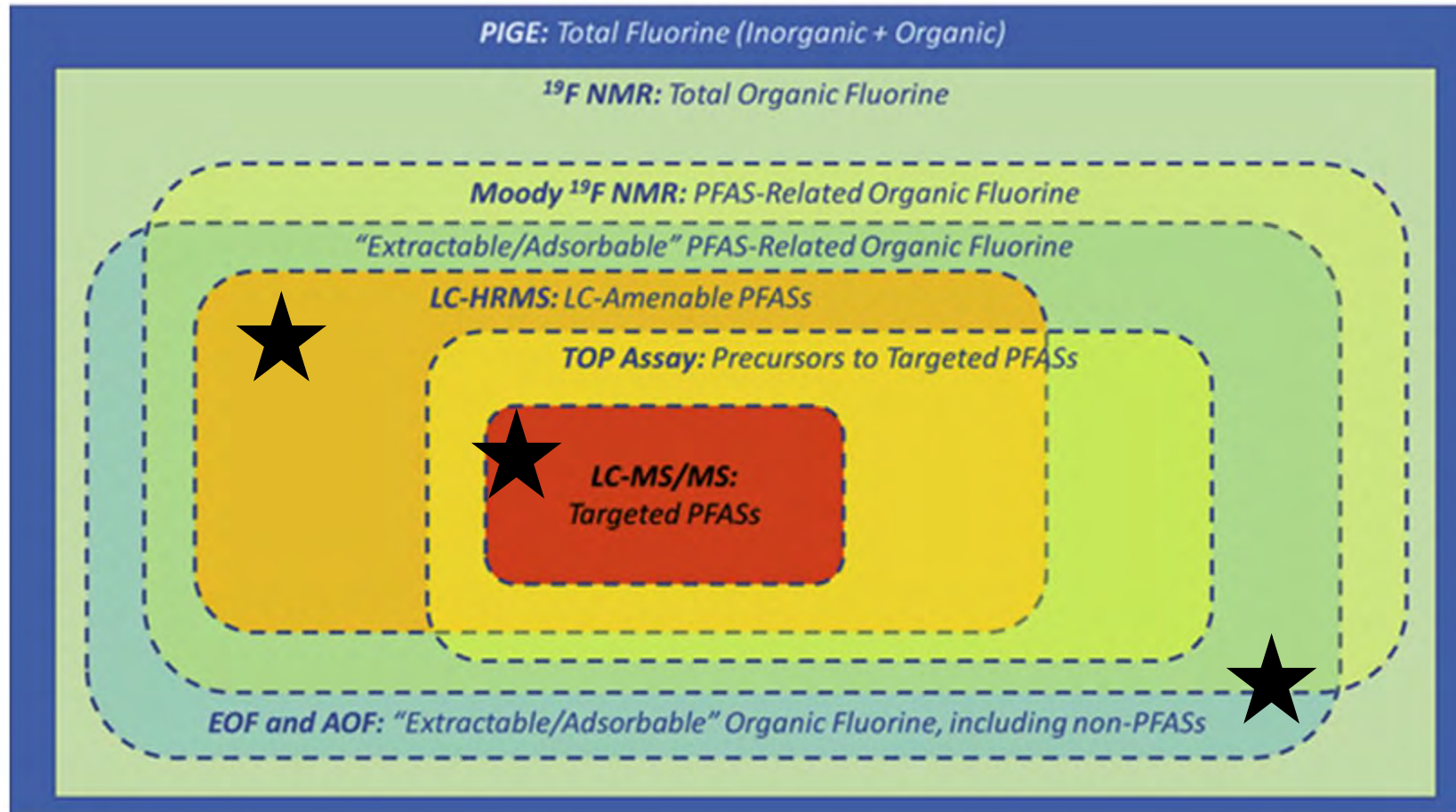


Adsorbable organic fluorine analysis



High-resolution MS (suspect screening)

We are using complementary methods to obtain a comprehensive understanding of PFAS occurrence in NC drinking water sources



# PFAS target compounds (quantitative measurements) – 55 compounds

Analyte	Abbreviation	CAS #
<i>Perfluorocarboxylic Acids</i>		
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	PFTriDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
<i>Perfluoroalkylsulfonic acids</i>		
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
<i>Perfluoroalkylsulfonamides</i>		
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

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Analyte	Abbreviation	CAS #
<i>Fluorotelomer sulfonic acids</i>		
4:2 Fluorotelomer sulfonic acid	4:2 PFS	757124-22-4
6:2 Fluorotelomer sulfonic acid	6:2 PFS	27619-97-2
8:2 Fluorotelomer sulfonic acid	8:2 PFS	39108-34-4
10:2 Fluorotelomer sulfonic acid	10:2 PFS	120226-60-0
<i>Perfluoroalkyl ether carboxylic and sulfonic acids</i>		
Perfluoro-2-propoxypropanoic acid	GenX	13252-13-6
Dodecafluoro-3H-4,8-dioxanonanoic acid	ADONA	958445-44-8
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	F-53B (Major)	73606-19-6
11-chloroicosadecafluoro-3-oxanonane-1-sulfonate	F-53B (Minor)	83329-89-9
Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5
Perfluoro-2-methoxypropanoic acid	PMPA	13140-29-9
Perfluoro-2-ethoxypropanoic acid	PEPA	N/A
Perfluoro(3,5-dioxahexanoic) acid	PFO2HxA	39492-88-1
Perfluoro(3,5,7-trioxaoctanoic) acid	PFO3OA	39492-89-2
Perfluoro(3,5,7,9-tetraoxadecanoic) acid	PFO4DA	39492-90-5
Perfluoro(3,5,7,9,11-pentaoxadodecanoic) acid	PFO5DoDA	39492-91-6
Ethanesulfonic acid, 2-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-	Nafion by-product 1	29311-67-9
Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-	Nafion by-product 2	749836-20-2
2,2,3,3,4,5,5,5-4-(1,1,2,2-tetrafluoro-2-sulfoethoxy)pentanoic acid	Nafion by-product 4	N/A
Propanoic acid, 3-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoro-	Hydro-EVE acid	773804-62-9
1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoroethoxy)ethane sulfonic acid	NVHOS	N/A

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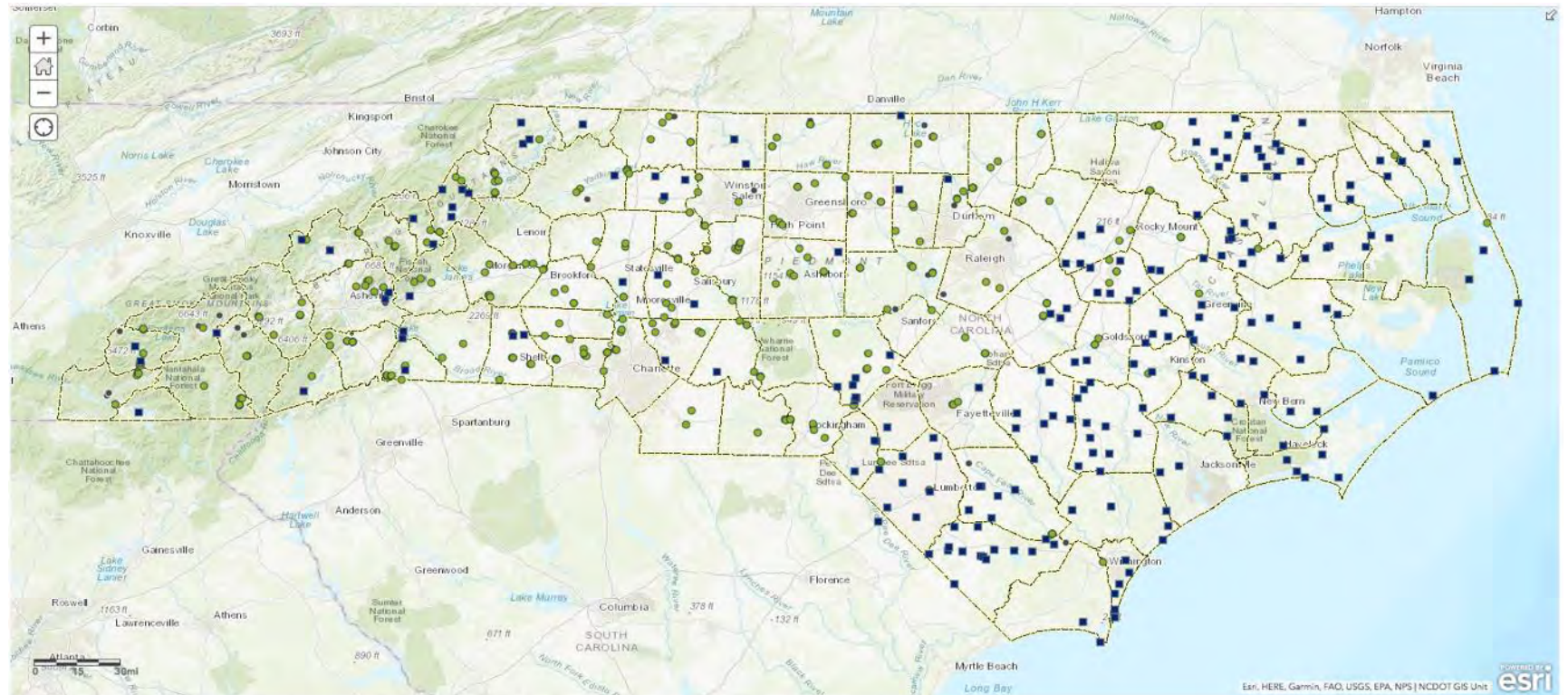
# “Semi-Targeted” high-resolution MS screening for PFAS

- “Master List” of > 5,000 PFAS compounds
- Data will be non-quantitative (relative abundances among water samples)
- Potential to discover novel PFAS contaminants

The screenshot displays the EPA's PFAS Master List of PFAS Substances. The page title is "PFAS Master List of PFAS Substances". A search bar is present with the text "Search PFASMASTER Chemicals". Below the search bar, there is a "List Details" section. The description states: "Description: Per- and polyfluorinated alkyl substances (PFAS) represent a growing, increasingly diverse inventory of chemicals of interest to the general public, scientific researchers, and regulatory agencies world-wide. Accompanying data-gathering, testing, and environmental monitoring exercises, in turn, have led to the publication and sharing of various lists of PFAS chemicals, some exceeding several thousand substances. A major effort was undertaken by EPA researchers within the National Center for Computational Toxicology to curate and structure-annotate several public lists in DSSTox. The below list of registered PFAS lists, from within and outside EPA, encompass PFAS of potential interest based on environmental occurrence (through literature reports and analytical detection) and manufacturing process data, as well as lists of PFAS chemicals procured for testing within EPA research programs. The consolidated list contains over 5000 PFAS CAS-name substances, with almost 4000 represented with a defined chemical structure. There is no precisely clear definition of what constitutes a PFAS substance given the inclusion of partially fluorinated substances, polymers, and ill-defined reaction products on these various lists. Hence, PFASMASTER serves as a consolidated list of substances spanning and bounded by the below lists, defining a practical boundary of PFAS chemical space (within DSSTox) of current interest to researchers and regulators worldwide. This PFAS Master List will continue to expand as component lists grow." Below the description, there are several links to specific lists: [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFASRL](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASRL) is an EPA research list of PFAS compiled from various internal, literature and public sources. [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFASINV](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINV) is a complete list of DMSO-solubilized PFAS in EPA's ToxCast inventory. [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFAS75S1](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFAS75S1) list is a prioritized subset of this larger chemical inventory. [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFASINSOL](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINSOL) is a list of chemicals procured, but found to be insoluble in DMSO above 5mM. [https://comptox.epa.gov/dashboard/chemical\\_lists/PFASOECD](https://comptox.epa.gov/dashboard/chemical_lists/PFASOECD) is a list of PFAS chemicals in the OECD New Comprehensive Global Database. [https://comptox.epa.gov/dashboard/chemical\\_lists/PFASKEMI](https://comptox.epa.gov/dashboard/chemical_lists/PFASKEMI) is a list of PFAS chemicals from a KEMI Swedish Chemicals Agency Report (provided by Stellan Fischer). [https://comptox.epa.gov/dashboard/chemical\\_lists/PFASSTRIER](https://comptox.epa.gov/dashboard/chemical_lists/PFASSTRIER) is a list of PFAS compiled by a community effort in 2015. [https://comptox.epa.gov/dashboard/chemical\\_lists/EPAPFASCAT](https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASCAT) is a list of structure-based Markush PFAS categories (capabilities under development). The number of chemicals is 5177. At the bottom, there is a table with 5177 chemicals. The table has columns for DTXSID, CASRN, and TOXCAST. The table is sorted by DTXSID. There are filters for Name or CASRN and Hide.

# Sample acquisition strategy

- 191 Municipal surface water sources
- 149 Municipal well water sources



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

# PFAS analysis strategy

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## Sample collection:

- Coordinated between NCSU and Duke
- ~25-30 samples per week, organized in geographic sectors
- Samples collected in polypropylene bottles and stored on ice during transport

## QA/QC and replication:

- Trip blanks included with every sampling
- Trip spikes (50 ng/L analyte addition) included with every sampling
- Duplicate samples for 10% of sites
- NCSU & Duke will split sample analyses evenly, with 20% samples analyzed by both labs



# Team 1

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## Duke University

Lee Ferguson, PhD  
Co-Lead

Abigail Joyce, PhD

- Sampling
- Quantitative Analysis

Gordon Getzinger, PhD

- Non-target Analysis

## NC State University

Detlef Knappe, PhD  
Co-Lead

Noelle DeStefano, PhD

- Sampling
- Quantitative Analysis
- Non-Target Analysis

Zachary Hopkins

- Quantitative Analysis

## UNC - Charlotte

Mei Sun, PhD  
Co-Investigator

Yuling Han, PhD

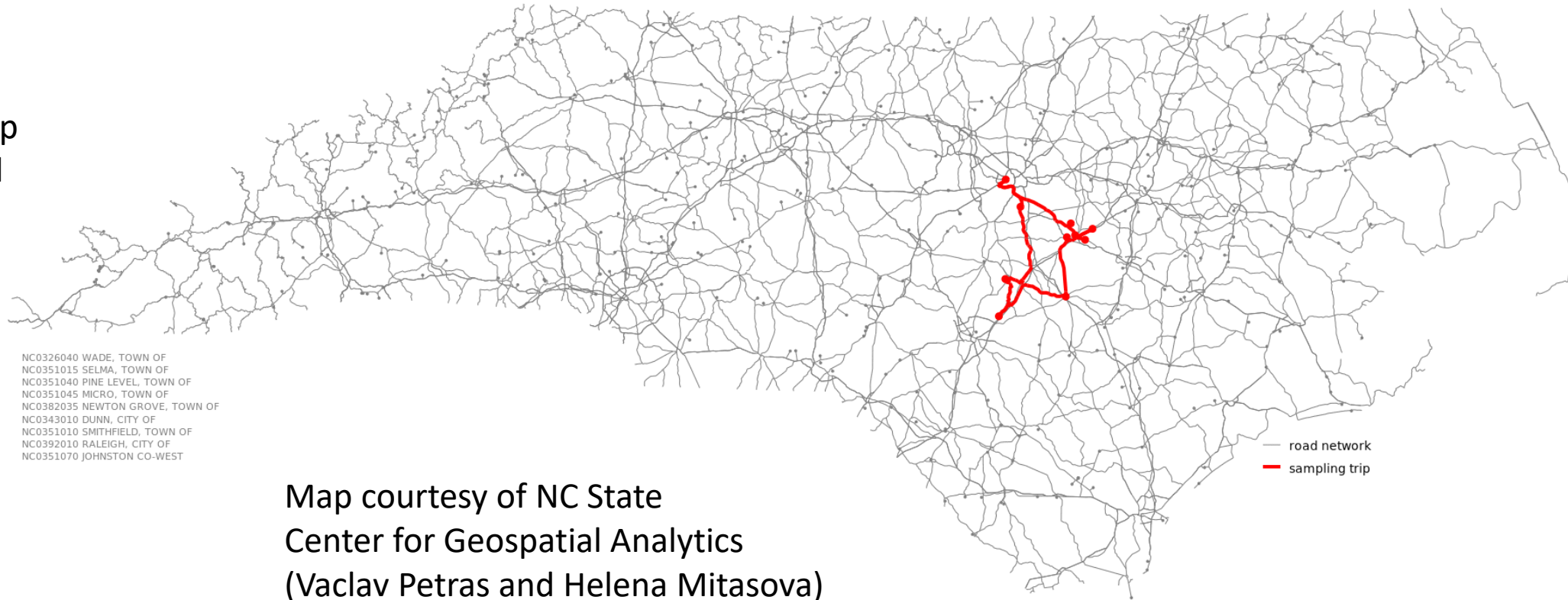
Vivek Pulikkal

- Adsorbable organic fluorine (AOF) measurements
- Extractable organic fluorine (EOF) measurements

# Sampling trip design

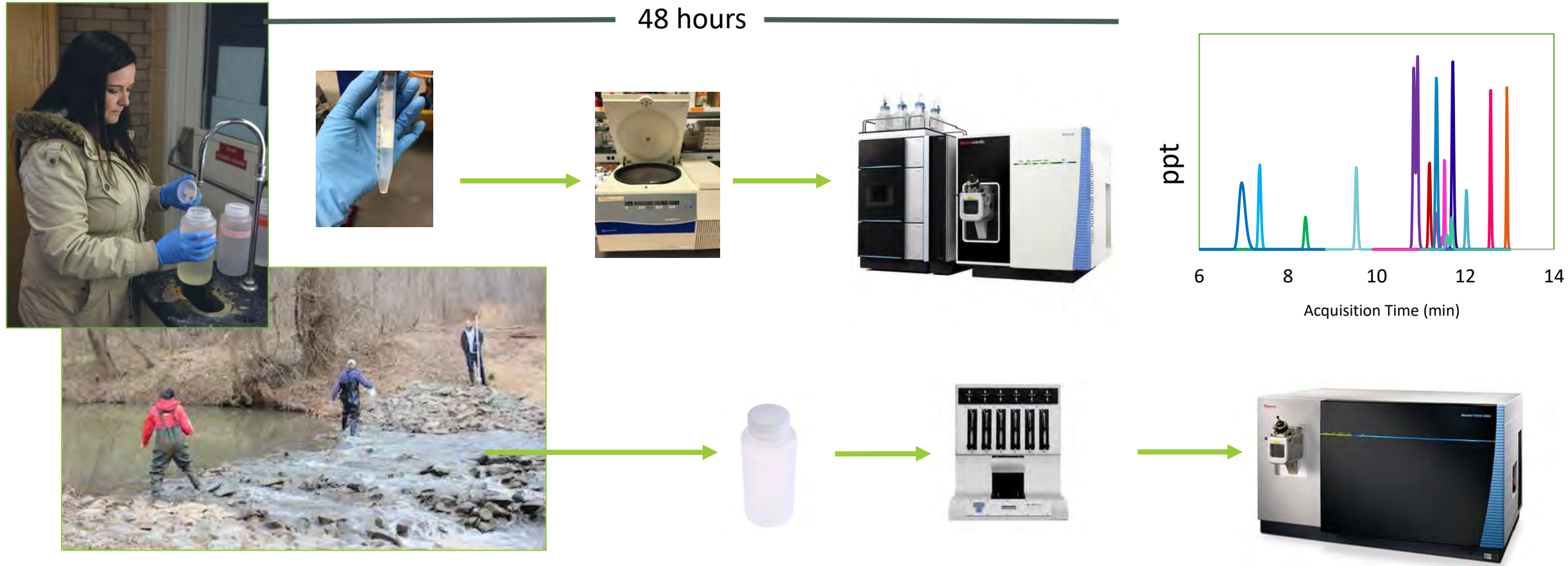
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- 27 total trips
- 1-3 day trips
- 6-17 sites per trip
- 58 sites sampled to date



Map courtesy of NC State  
Center for Geospatial Analytics  
(Vaclav Petras and Helena Mitasova)

# Sample Processing – LC/MS



# Sample Processing – AOF/EOF



Organic fluorine  
adsorption by  
activated carbon (AC)



Organic fluorine  
adsorption by  
solid phase  
extraction (SPE)

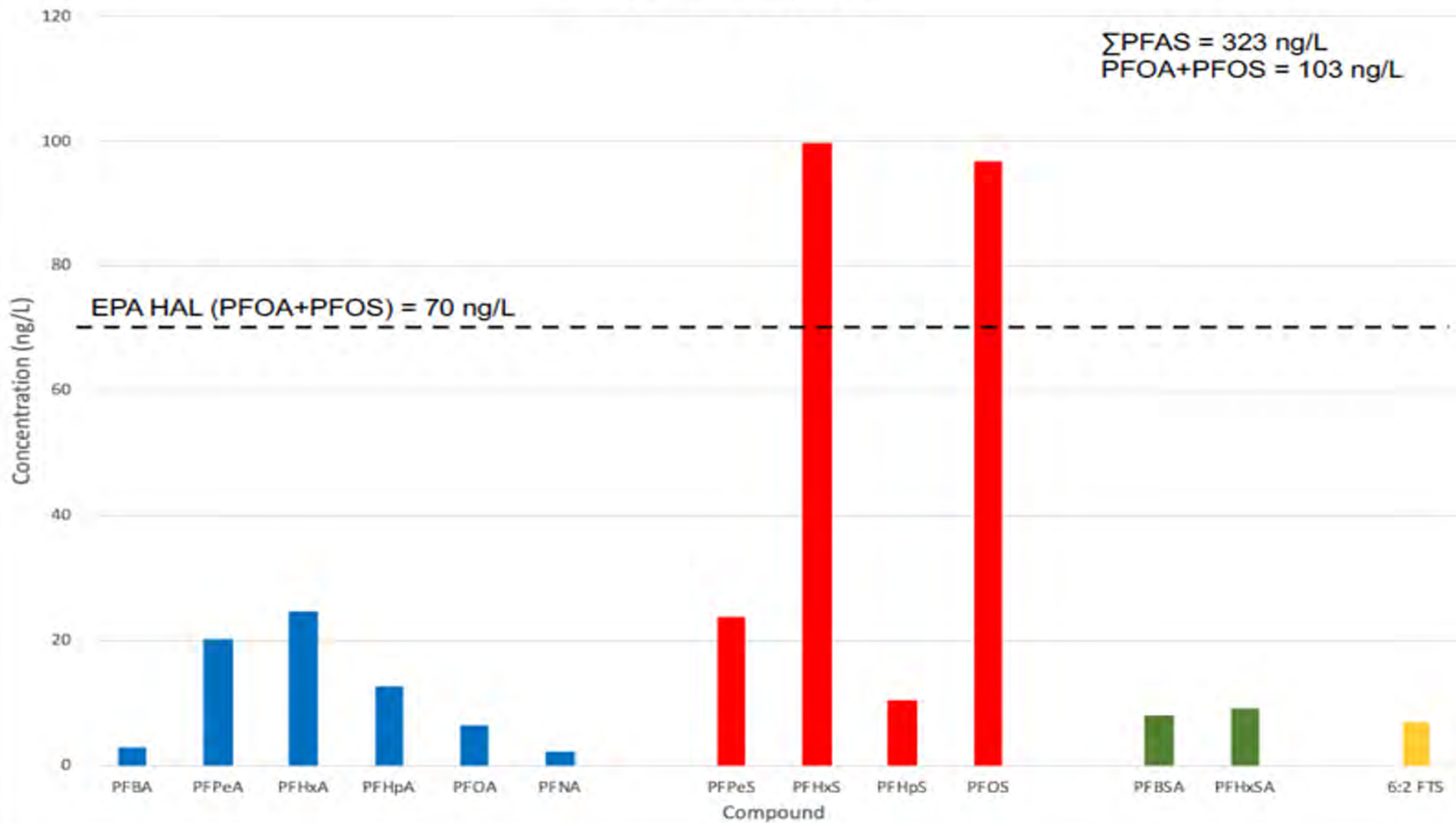


Combustion of AC or  
SPE concentrate



Fluoride analysis  
by ion  
chromatography

# Maysville 5/7/2019



# Acknowledgements

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- NC Policy Collaboratory
- PFAST Management Team
- Knappe Lab
  - Lan Cheng
  - Julia Harrison
  - Gavin Mouat
- Ferguson Lab
  - Jake Ulrich
- Sun Lab
  - Yuling Han
  - Vivek Pulikkal

