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

TEAM LEADS: P. LEE FERGUSON[1], DETLEF KNAPPE[2] AND MEI SUN[3]

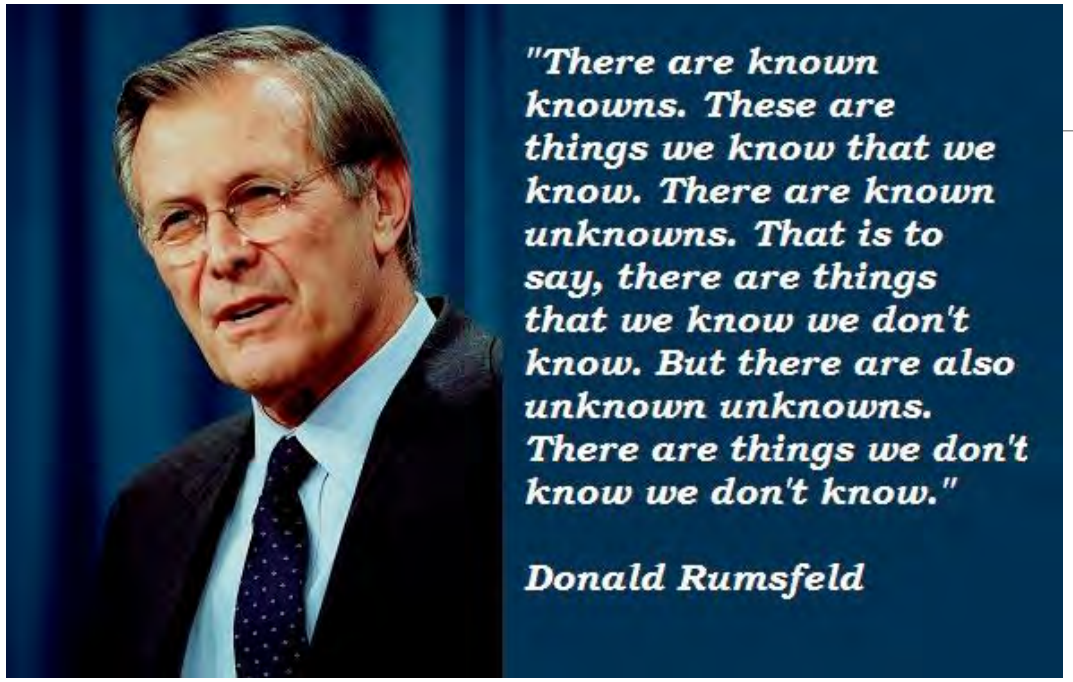
POSTDOCS: ABIGAIL JOYCE[1], NOELLE DESTEFANO[2]

[1]DUKE UNIVERSITY, [2]NC STATE UNIVERSITY, [3]UNC-CHARLOTTE

Key Motivating Question

IS MY WATER SAFE TO DRINK?

What do we know?



?

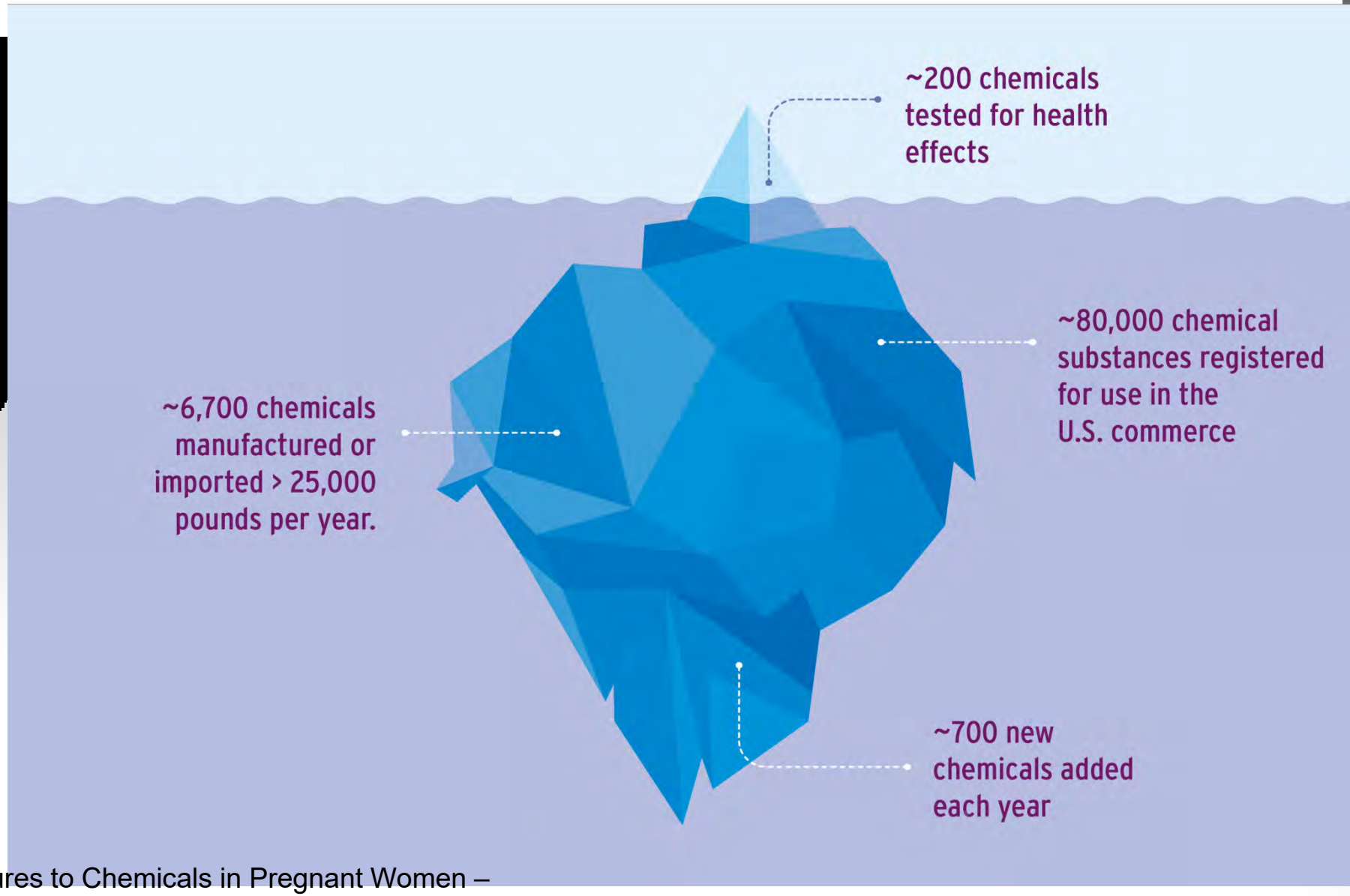
Regulated contaminants (known knowns)

Unregulated contaminants on our radar (known unknowns)

The universe of chemicals (unknown unknowns)

We only know the tip of the i

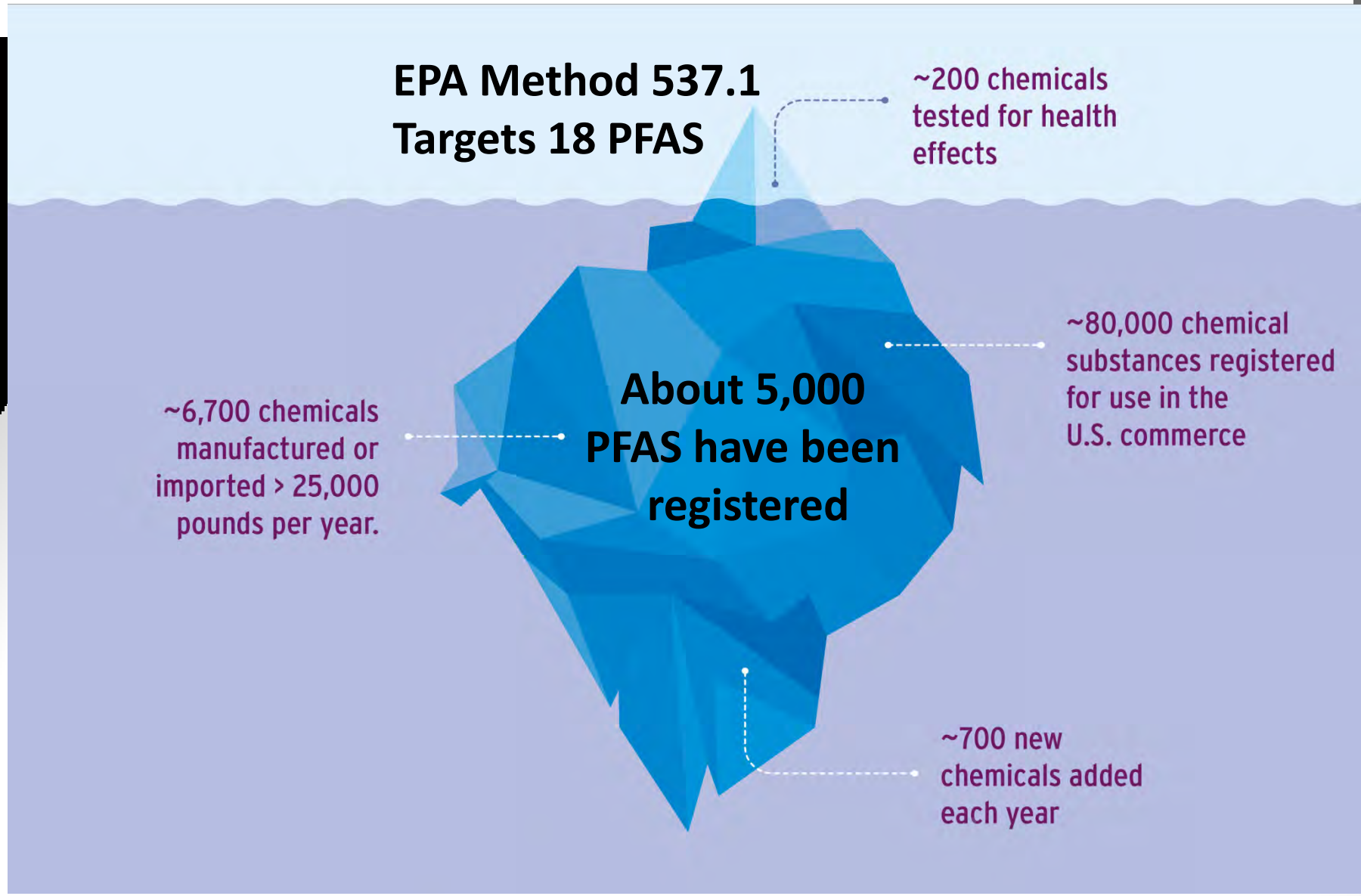
Majority of Chemicals Not Tested Before Entering the Market



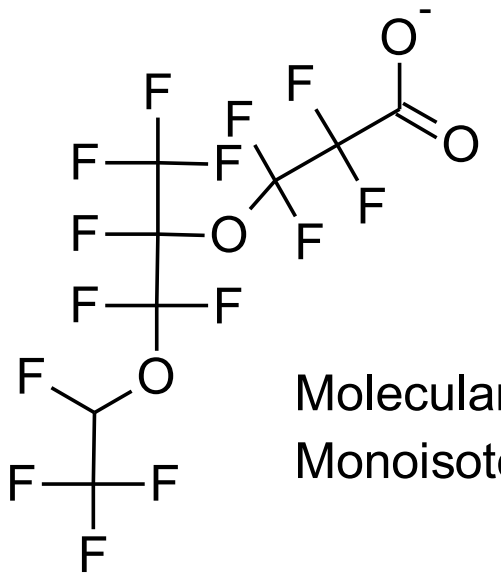
Woodruff, T. Identifying Cumulative Exposures to Chemicals in Pregnant Women – Non-targeted Screening of Environmental Chemicals. PPTOX IV, Boston, MA, Oct. 26-29, 2014.

Similar situation with PFAS

Majority of Chemicals Not Tested Before Entering the Market



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

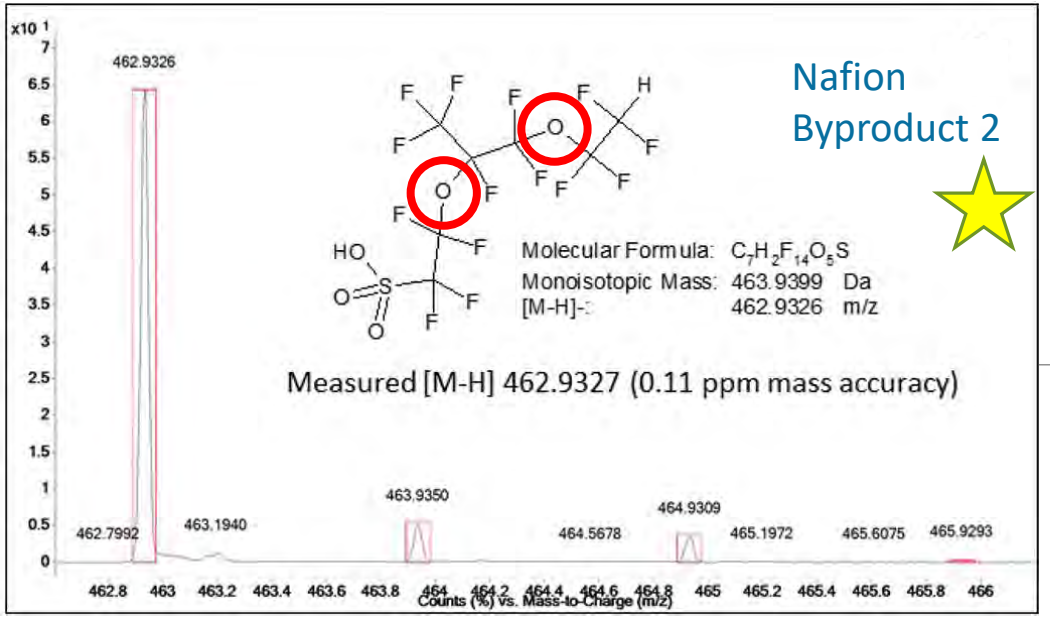


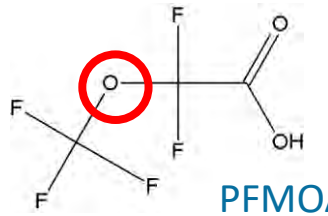
Hydro-EVE Acid

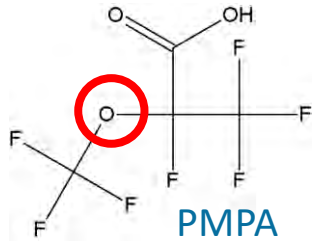
Molecular Formula: $C_8HF_{14}O_4^-$

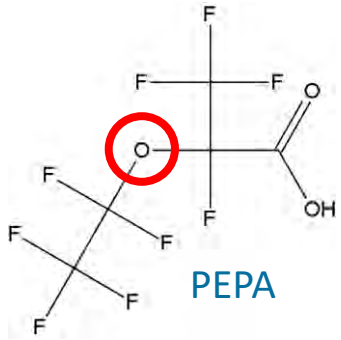
Monoisotopic Mass: 426.9657 Da

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

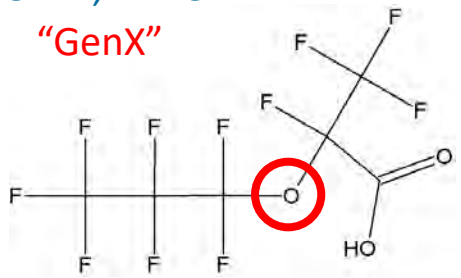


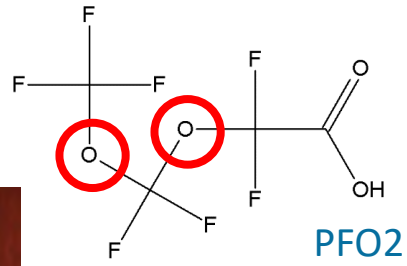

PFMOAA

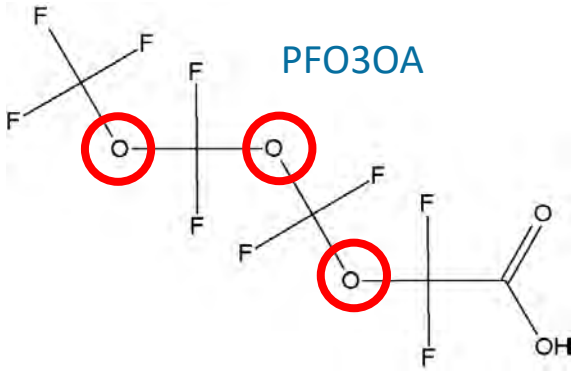

PMPA

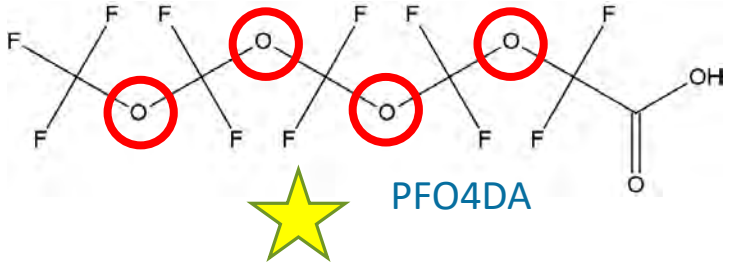

PEPA

PFPrOPrA, HFPO-DA
"GenX"




PFO2HxA


PFO3OA


PFO4DA

Strynar et al. ES&T (2015)

Jane Hoppin,
CHHE, NCSU

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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Research Questions

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

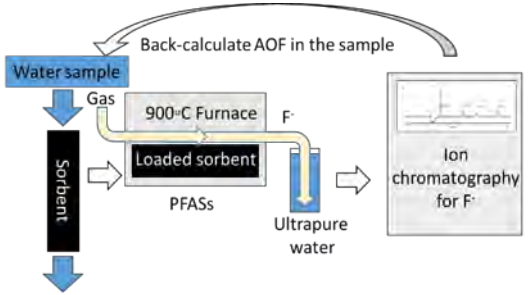
PFAS analysis strategy

Triple Quadrupole MS/MS (target quantitation)

Analyte	Abbreviation	CAS #
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

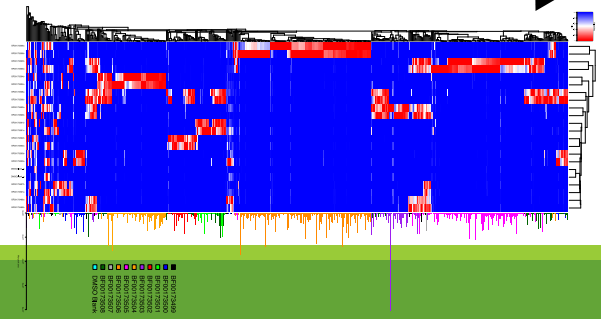
Sample Collection

Solid Phase Extraction



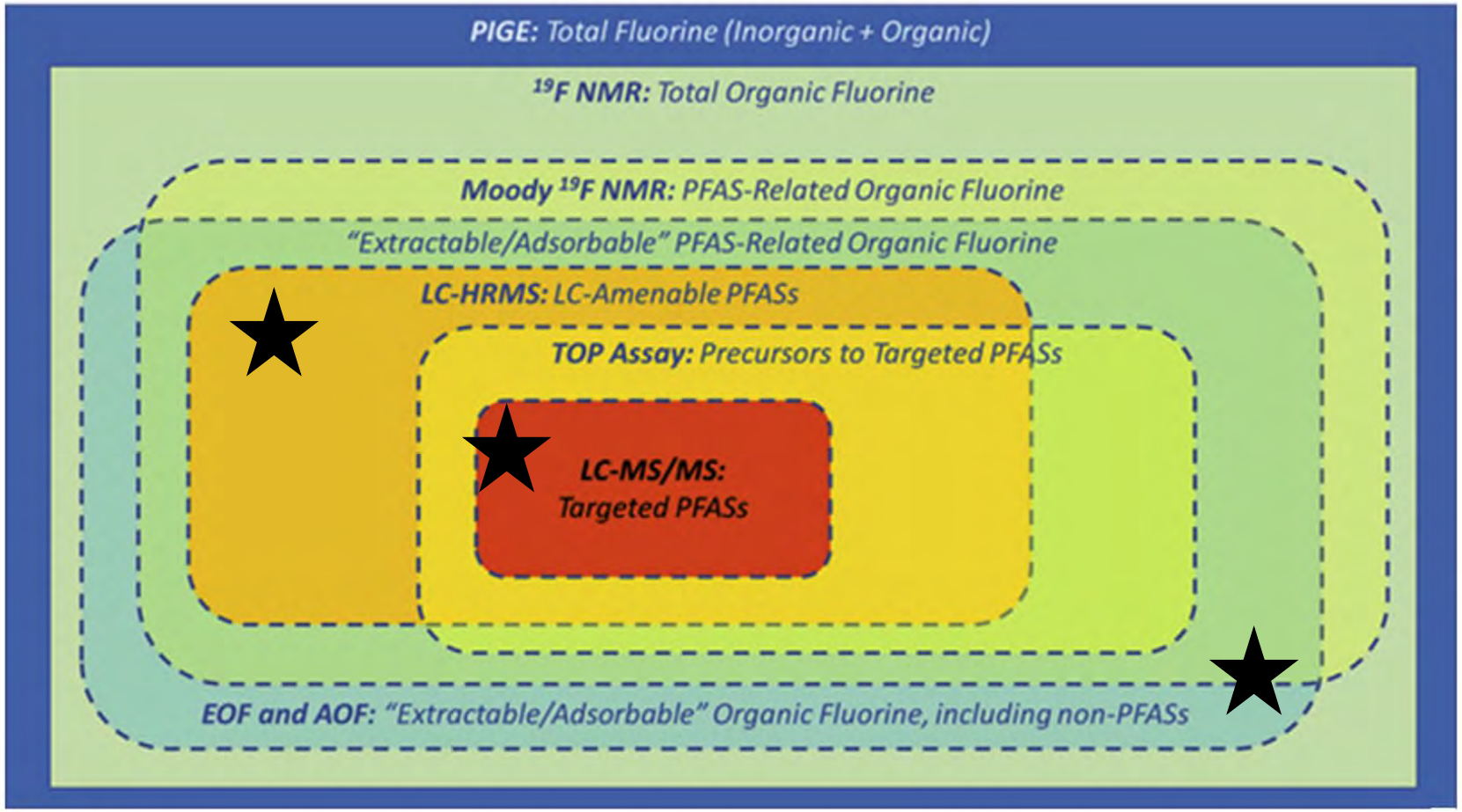
Adsorbable organic fluorine analysis

PFAS mass balance



High-resolution MS (suspect screening)

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



McDonough et al. (2018)

PFAS target compounds (quantitative measurements) – 55 compounds

Analyte	Abbreviation	CAS #
Perfluorocarboxylic Acids		
Perfluorobutanoic acid	PFBA	375-22-4
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Perfluorohexanoic acid	PFHxA	307-24-4
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Perfluoroalkylsulfonamides		
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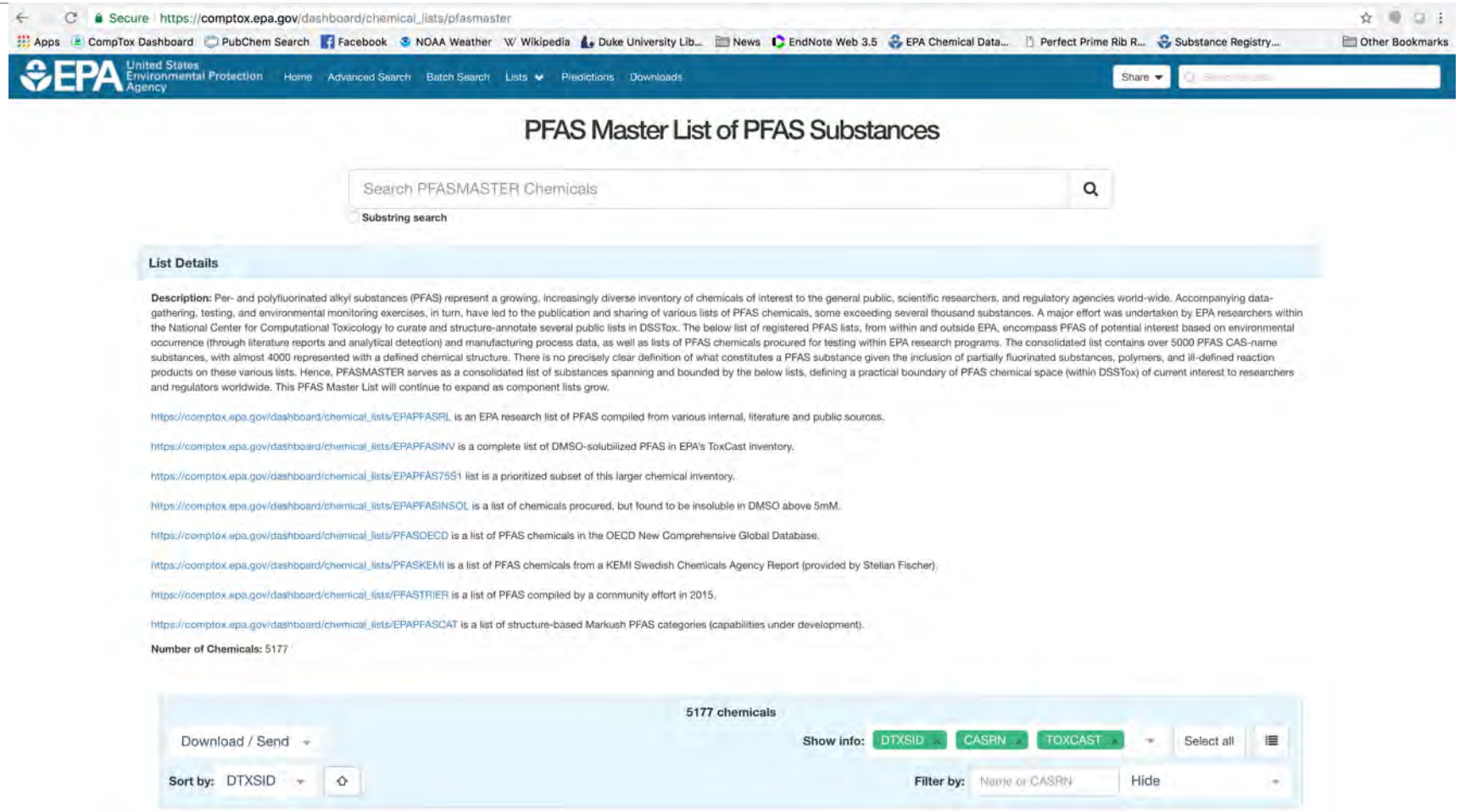
N-ethylperfluorooctane sulfamide	NEtFOSA	4151-50-2
N-methylperfluorooctane sulfamide	NMeFOSA	31506-32-8

Analyte	Abbreviation	CAS #
Fluorotelomer sulfonic acids		
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
Perfluoroalkyl ether carboxylic and sulfonic acids		
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-chloroeicosafluoro-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-tetrafluoro-ethoxy)ethane sulfonic acid	NVHOS	N/A

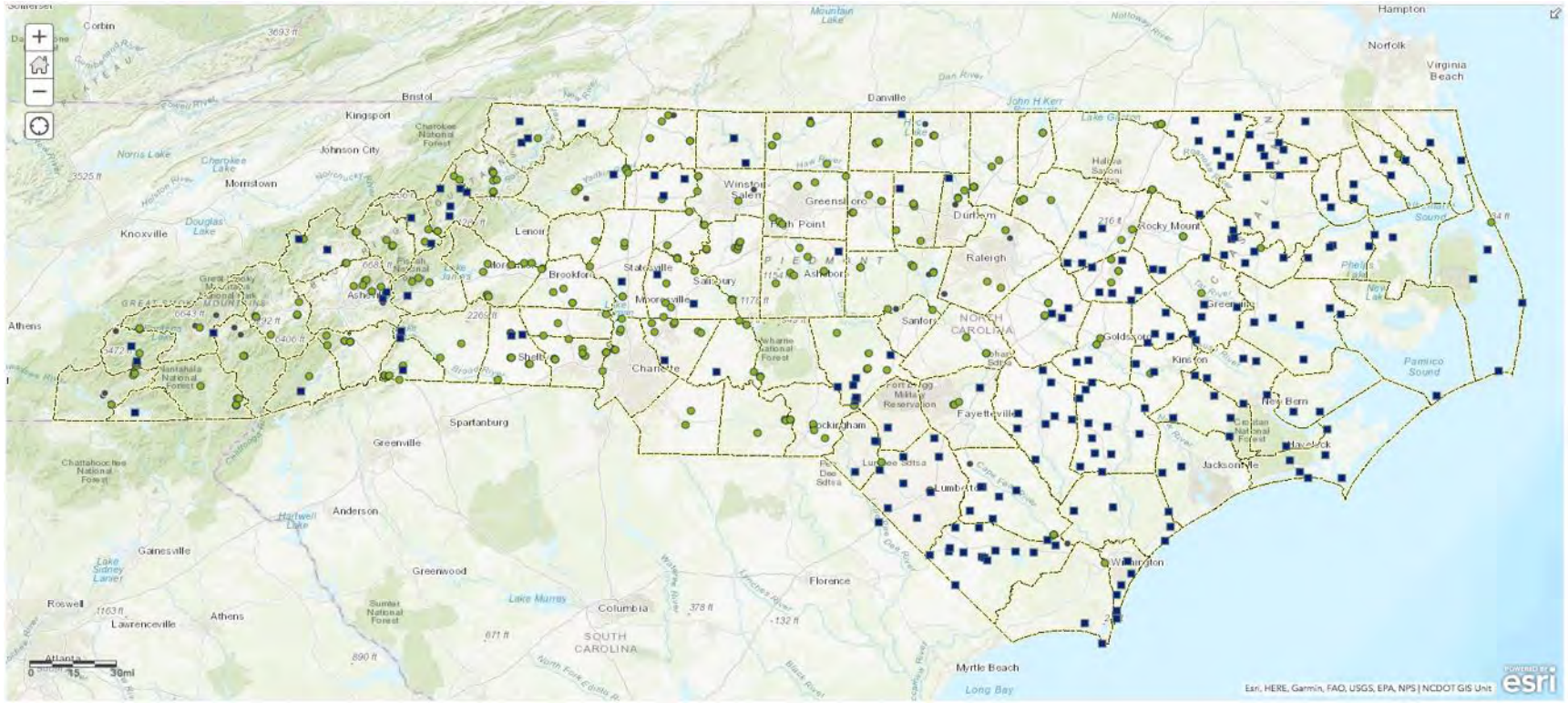
“Semi-Targeted” high-resolution MS screening for PFAS

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



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

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

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

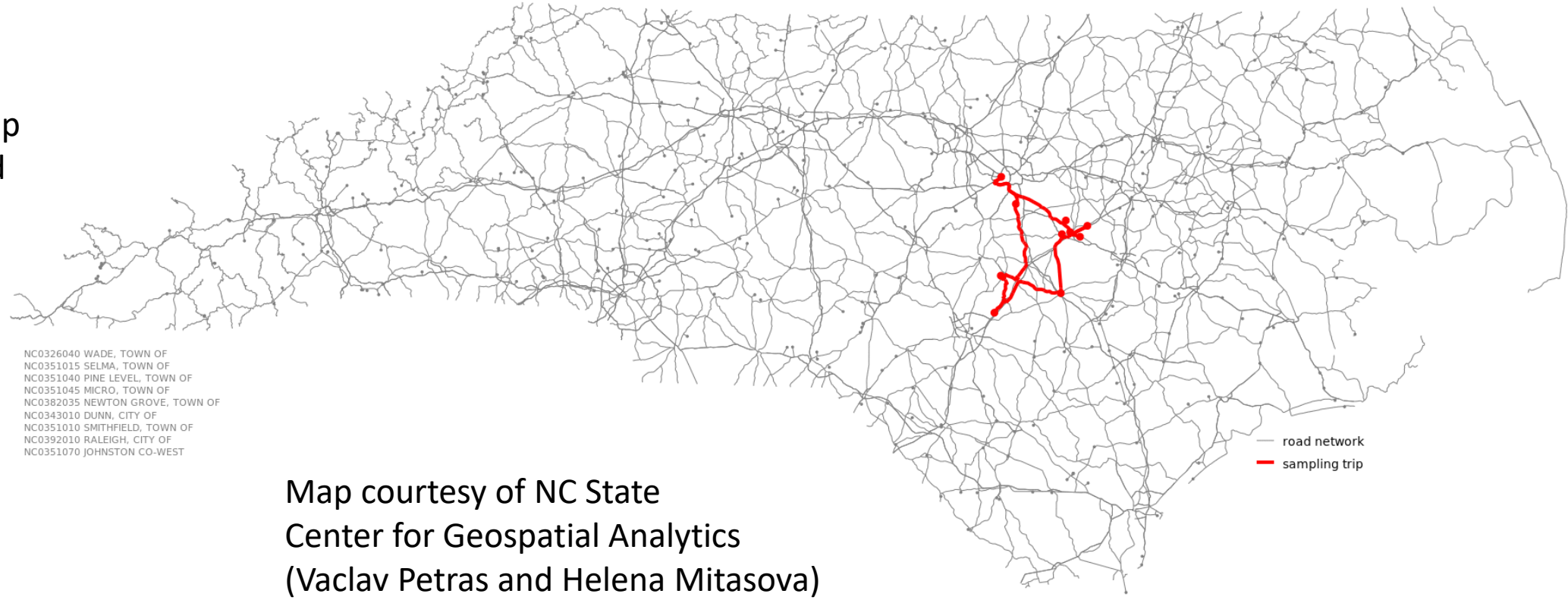
UNC - Charlotte

Mei Sun, PhD
Co-Investigator

Yuling Han, PhD
Vivek Pulikkal
- Adsorbable organic fluorine (AOF) measurements
- Extractable organic fluorine (EOF) measurements

Sampling trip design

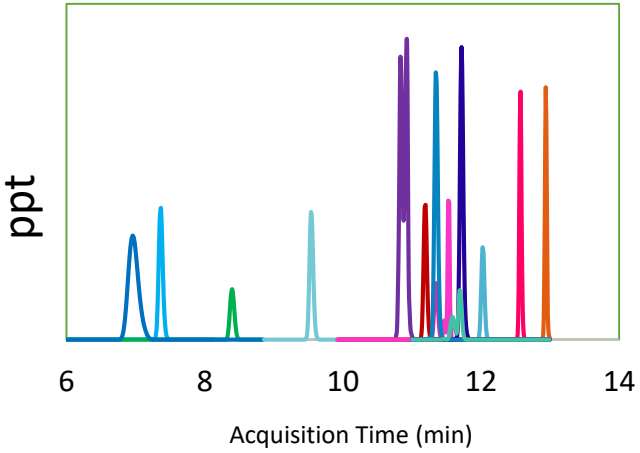
- 27 total trips
- 1-3 day trips
- 6-17 sites per trip
- 58 sites sampled to date

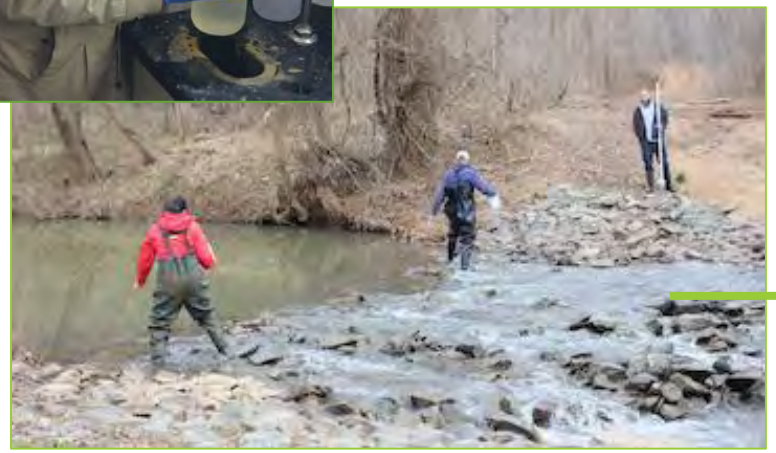


Map courtesy of NC State
Center for Geospatial Analytics
(Vaclav Petras and Helena Mitasova)

Sample Processing – LC/MS

48 hours





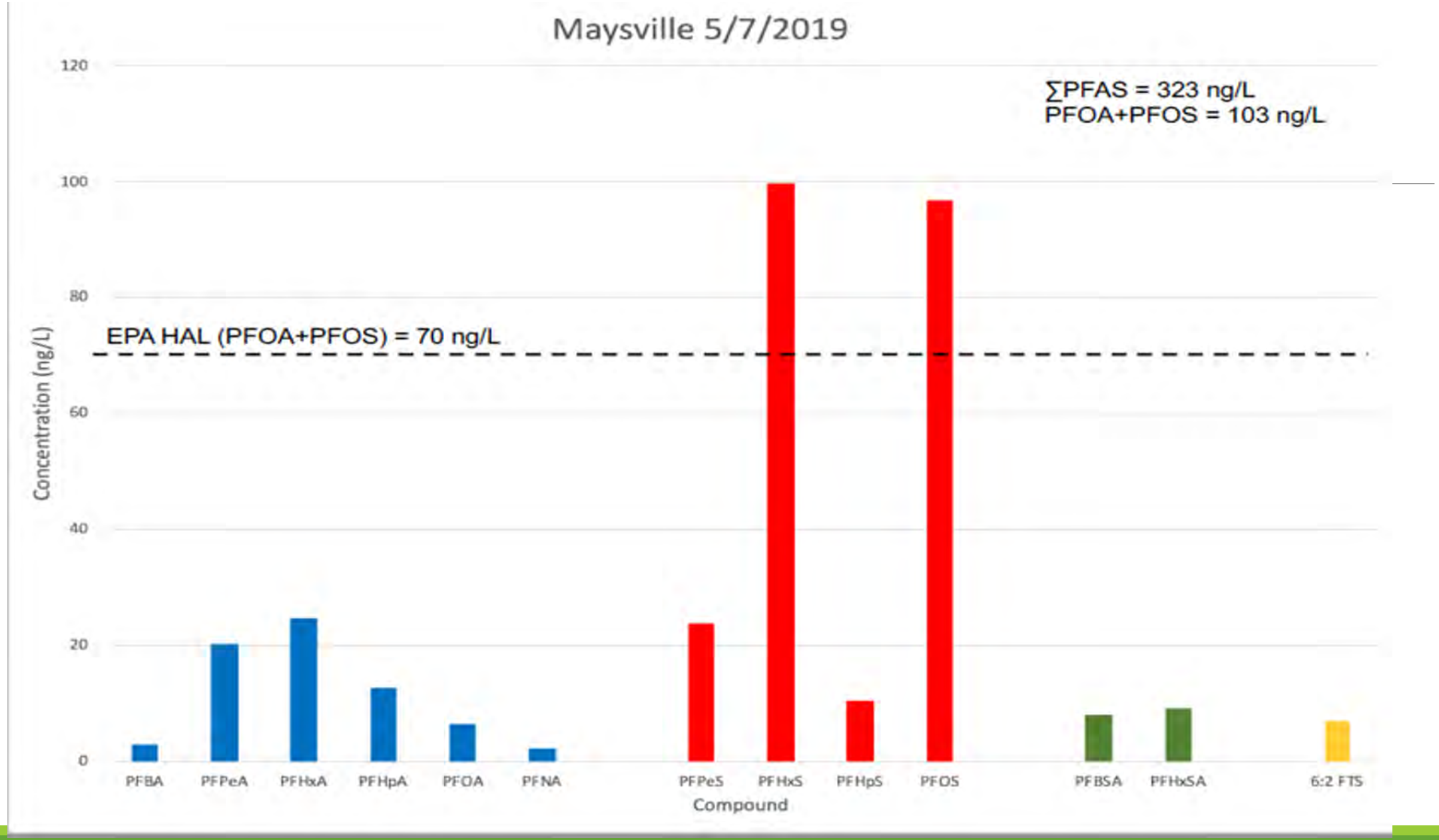
Sample Processing – AOF/EOF

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
∑PFAS = 323 ng/L
PFOA+PFOS = 103 ng/L
EPA HAL (PFOA+PFOS) = 70 ng/L
Concentration (ng/L)
120
100
80
60
40
20
0
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFPeS
PFHxS
PFHpS
PFOS
PFBSA
PFHxSA
6:2 FTS
Compound

Acknowledgements

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