NC STATE UNIVERSITY Center for Human Health and the Environment

NC STATE UNIVERSITY Center for Environmental and Health Effects of PFAS

NORTH CAROLINA PFAS Testing Network

Occurrence and Community Impacts of Per- and Polyfluoroalkyl Substances in North Carolina

Detlef Knappe

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NC State University
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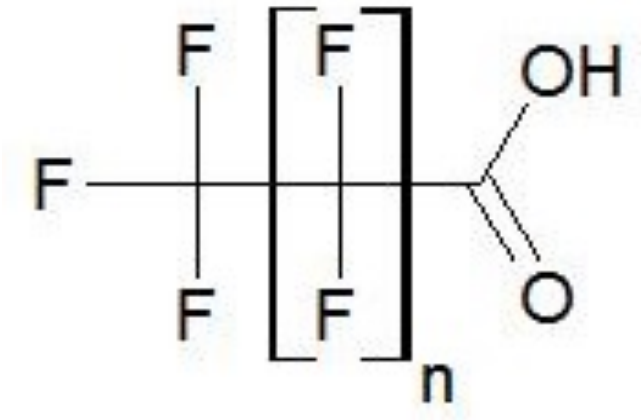
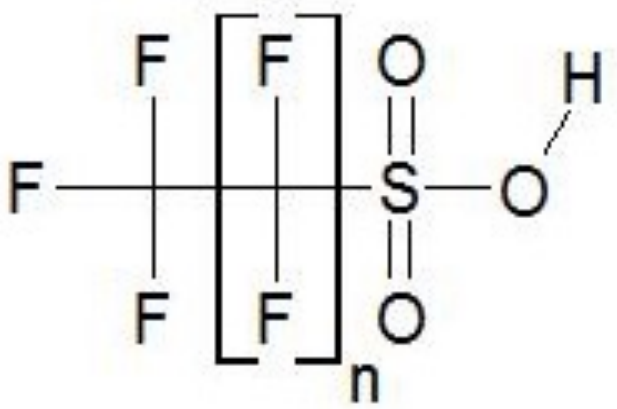
University of Kentucky – November 18, 2021

Perfluoroalkyl acids are organic compounds in which all C-H bonds are replaced with C-F bonds.

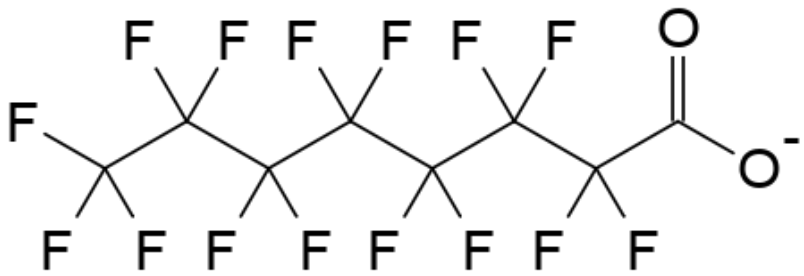


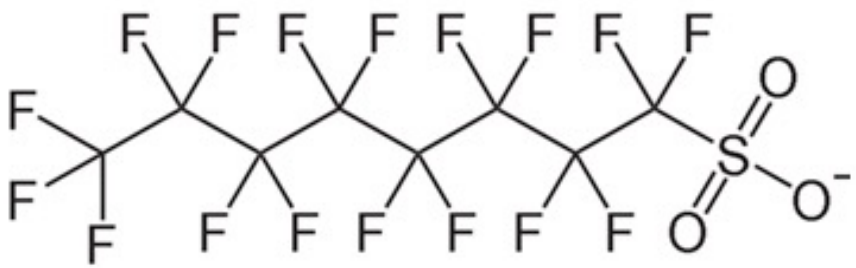


Long-chain PFASs:

PFCAs: $C_nF_{2n+1}COOH$, $n \geq 7$

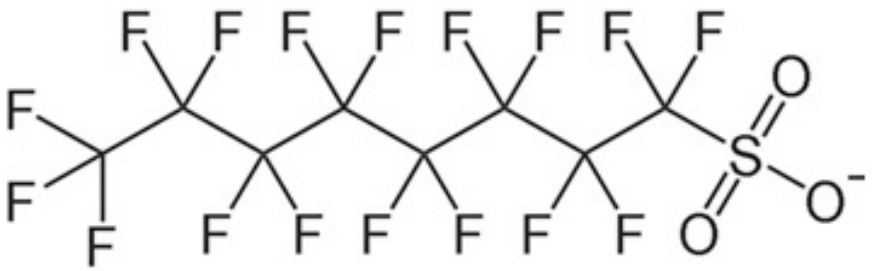
PFSAs: $C_nF_{2n+1}SO_3H$, $n \geq 6$





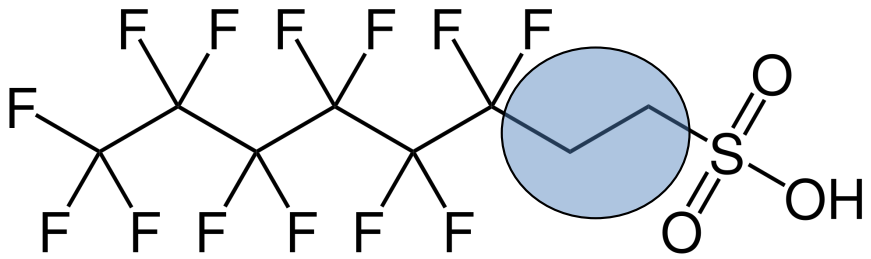
Polyfluoroalkyl acids contain C-F bonds and at least one C-H bond.

- Perfluorooctanesulfonate (PFOS)



Perfluorinated
(no C-H bonds)

- 6:2 Fluorotelomersulfonic acid (6:2 FtS)



Polyfluorinated
(contains C-H bonds)

PFASs are released into the environment by:

fluorochemical manufacturing processes, and

the production, use, and disposal of products containing PFASs

- **Non-stick coatings**

- **Grease- and oil-resistant coatings for paper products**

- **Water repellent fabrics**

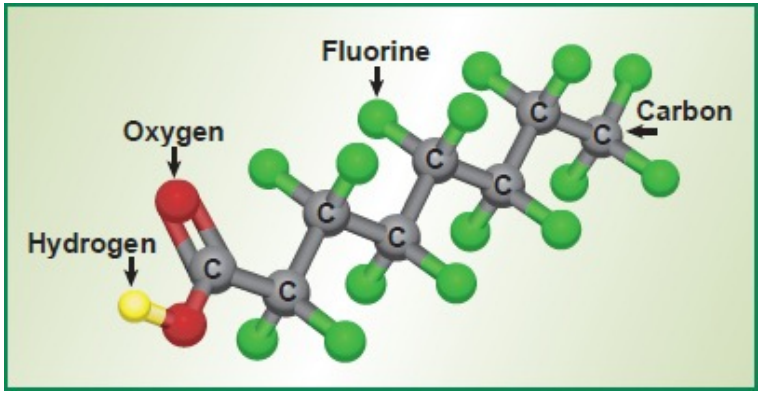
- **Stain-resistant coatings for fabrics, carpets, and leather**

SCOTCHGARD™ PROTECTOR 3M

- **Firefighting foams**

http://www.sixclasses.org/

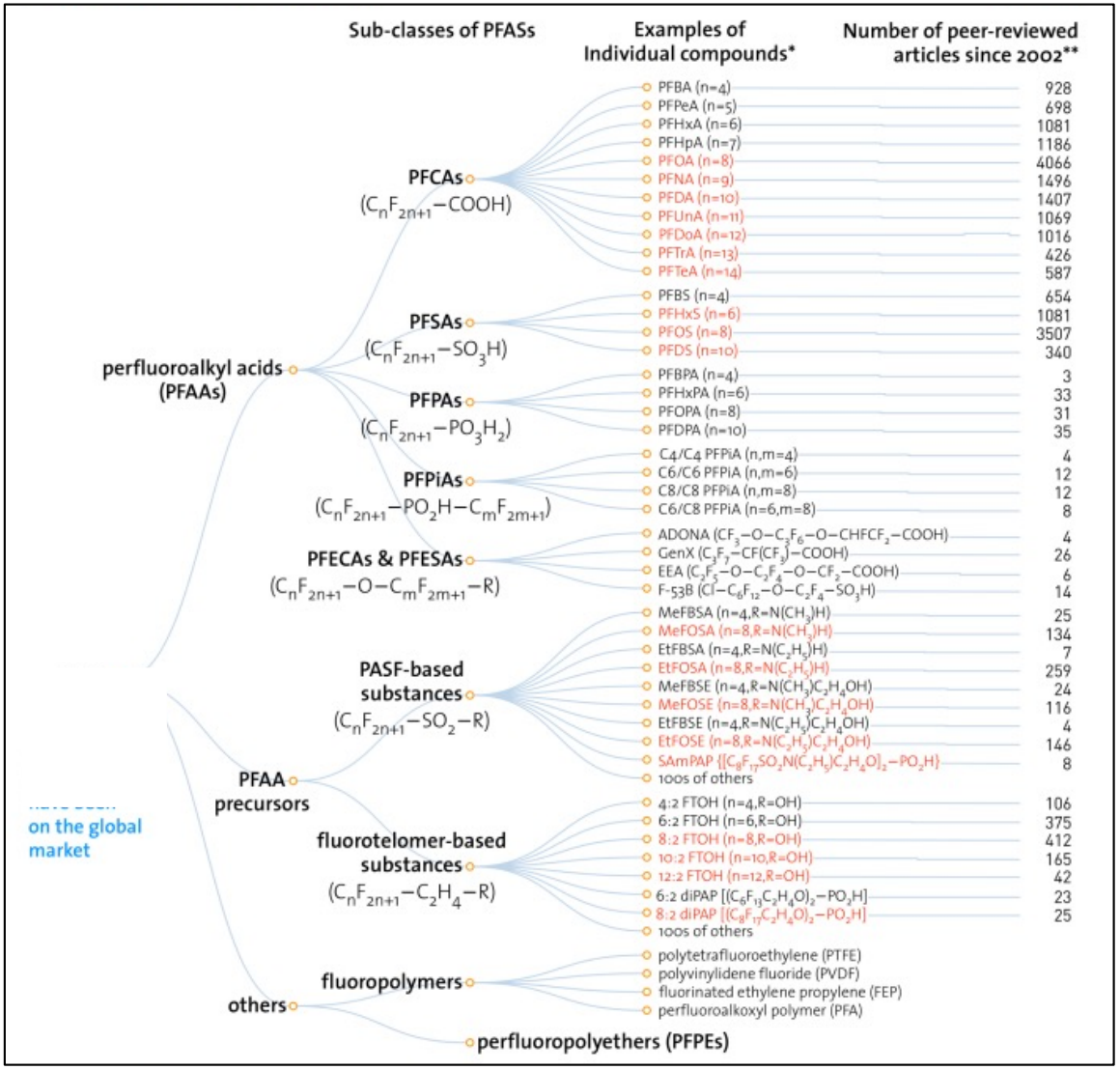
PFASs: Useful, but "forever chemicals"



PFAS properties:

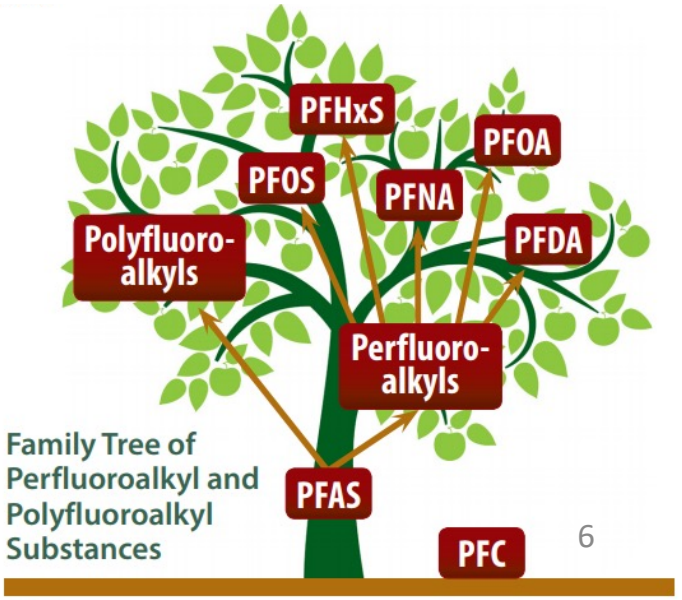
- Very strong covalent C-F bond
  - Persistent in the environment
  - Persistent in most engineered treatment systems
- Surfactant behavior
- Some PFASs bioaccumulate
- Other PFASs are very mobile
- PFASs are ubiquitous
- Adverse health effects

The PFAS class includes many sub-classes and thousands of individual compounds



Wang et al., 2017, ES&T

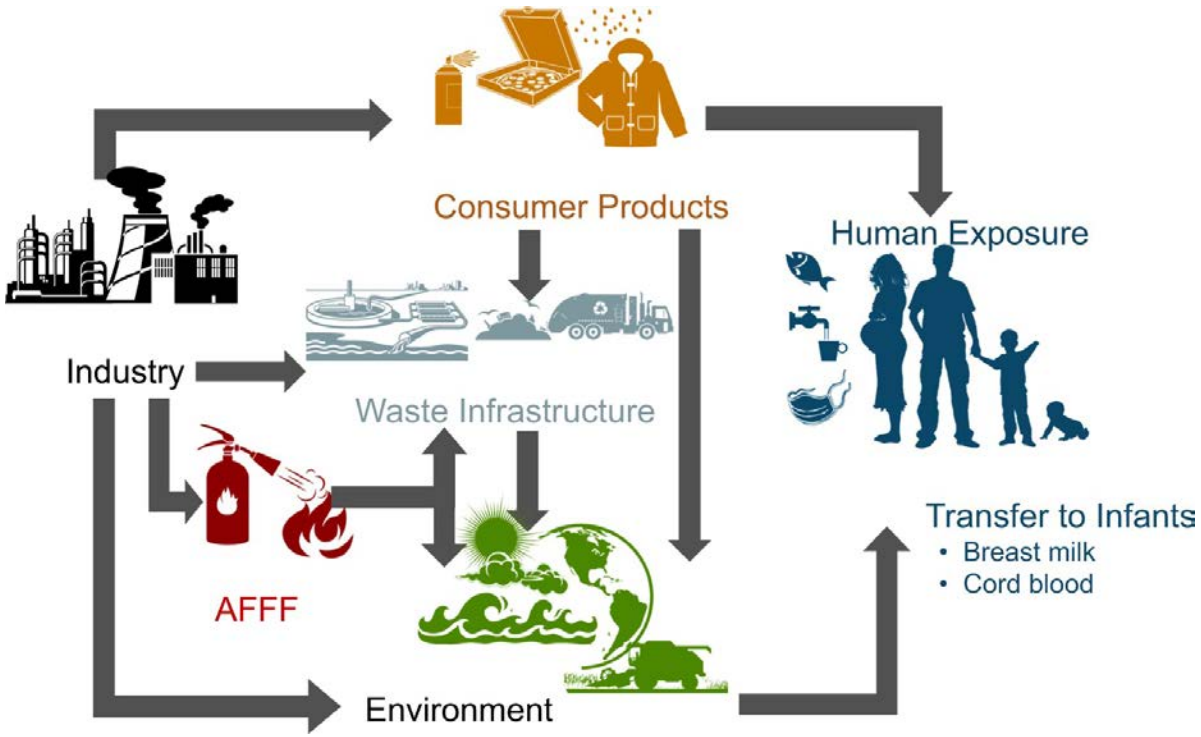
- PFAS have been commercially produced since the 1950's
- > 3,000 may have been on the global market
- > 5,000 named on the EPA master list



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

Human Exposure and Health Effects

- PFOS, PFOA, PFNA and PFHxS are widely detected in people 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 PFASs are poorly understood



Sunderland et al., 2019, Nature

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

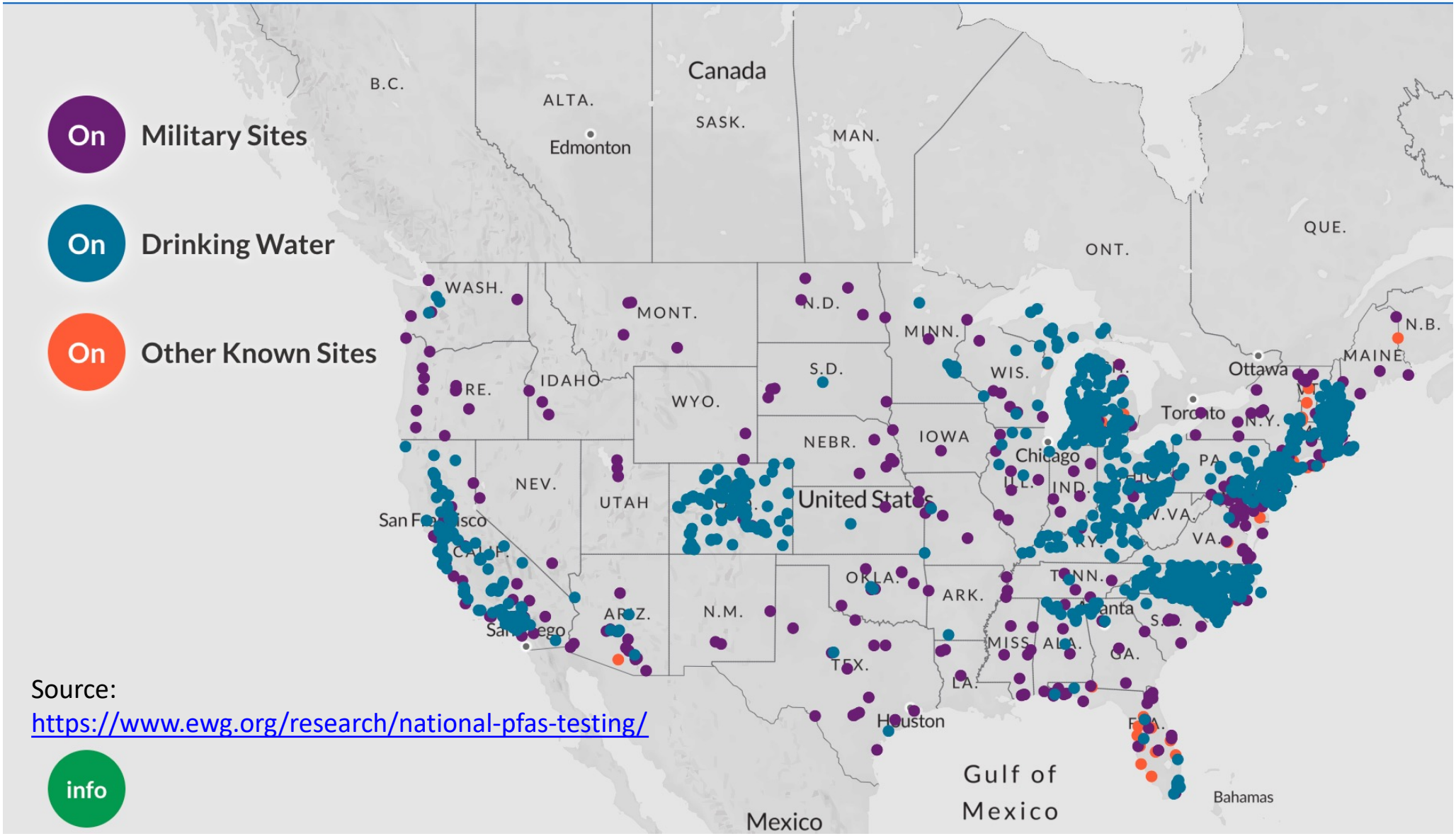
National

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

State

New Jersey maximum contaminant levels	PFOS, PFNA: 13 ng/L PFOA: 14 ng/L
Michigan maximum contaminant levels	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

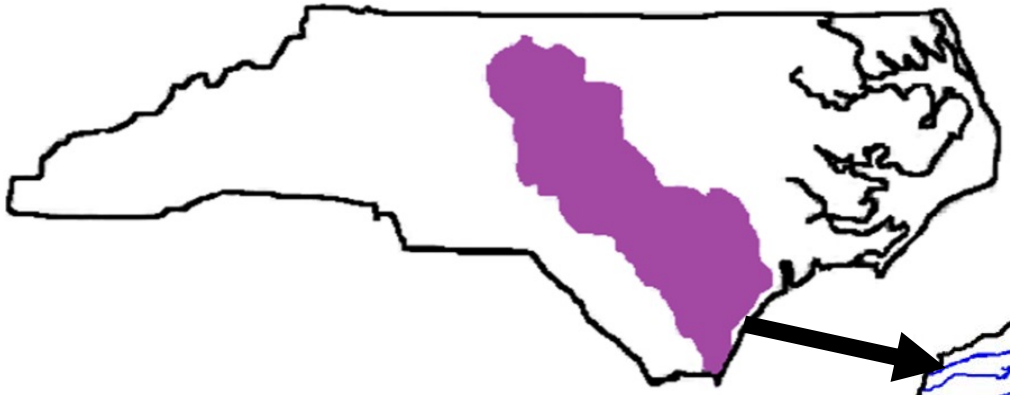
PFAS Contamination in the U.S. (January 6, 2021)



Source:
https://www.ewg.org/research/national-pfas-testing/

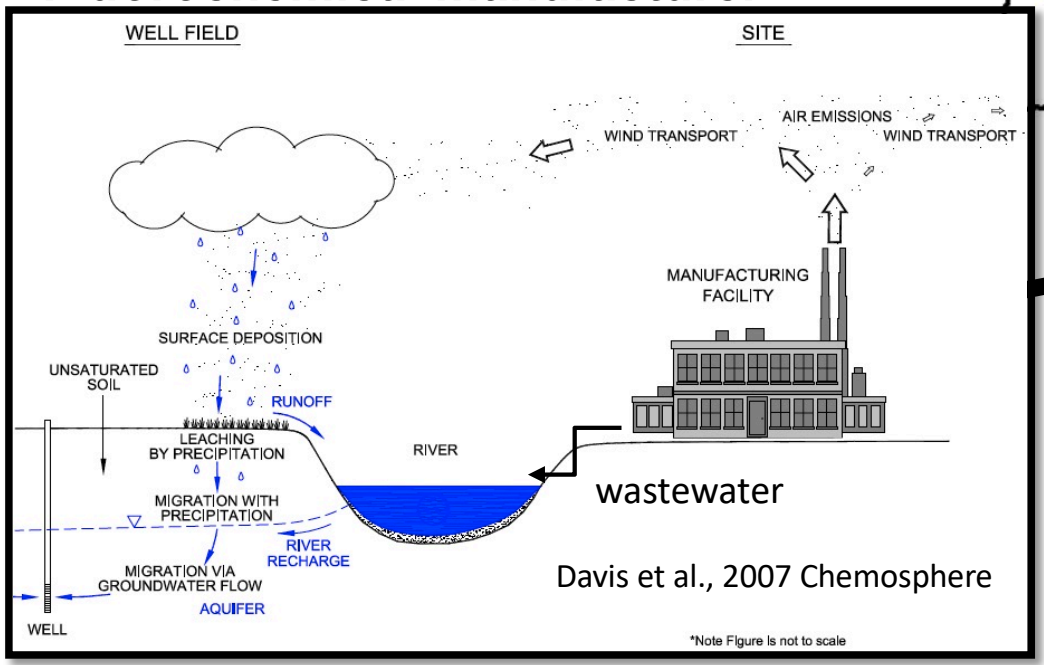
Water supplies for at least 110 million people in the US are contaminated with PFAS

In NC, both rural and urban communities are impacted by recently identified fluoroethers



Cape Fear River basin

Fluorochemical manufacturer



wastewater

Davis et al., 2007 Chemosphere

Impacted private well communities

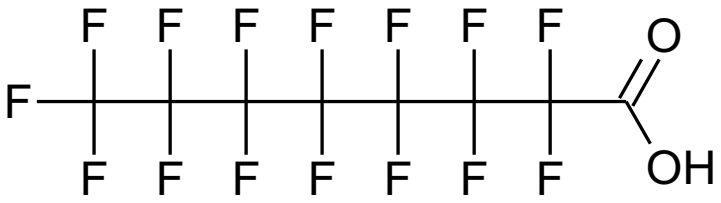
Impacted urban and rural communities

A brief history

Fluorochemical production begins at DuPont's Fayetteville Works

1980 2002 2007 2009 2012 2014 2015 2016

A brief history



Perfluorooctanoic acid (PFOA = C8)

Fluorochemical production begins at DuPont's Fayetteville Works

1980 2002 2007 2009 2012 2014 2015 2016

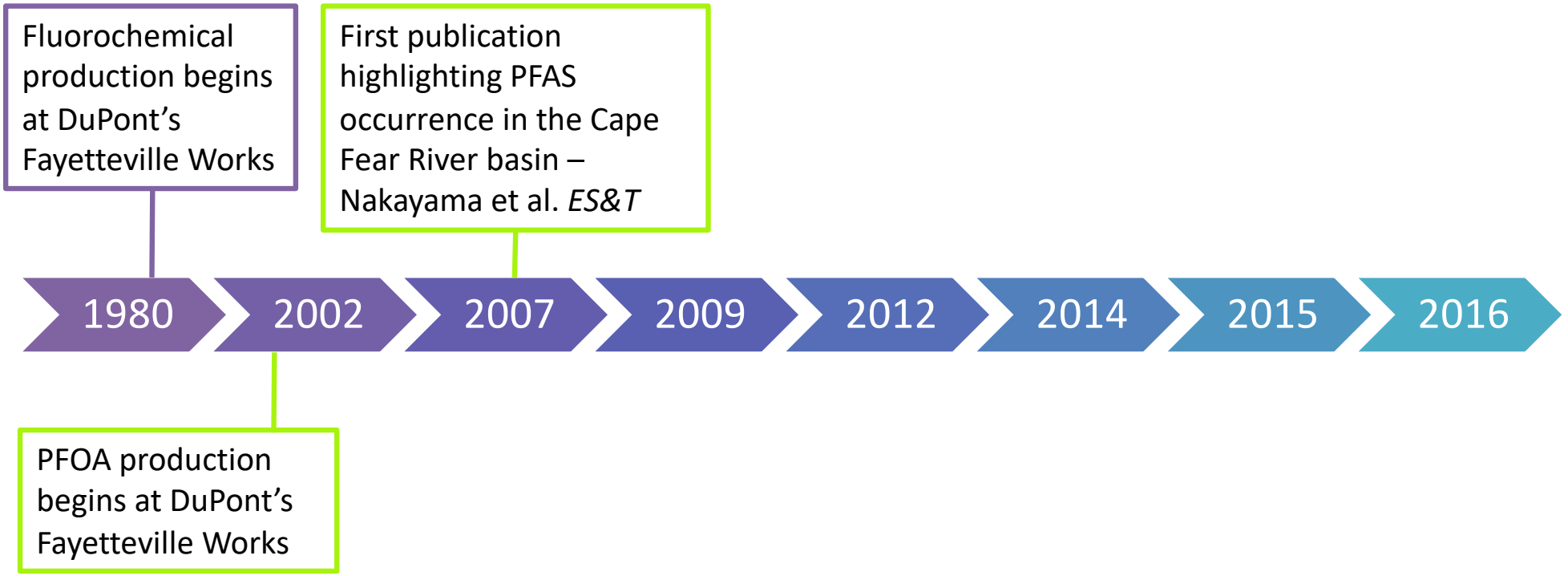
PFOA production begins at DuPont's Fayetteville Works

The Fayetteville Observer

By Greg Barnes
Staff writer
Posted Mar 25, 2018 at 6:07 PM
Updated Apr 24, 2018 at 6:37 PM

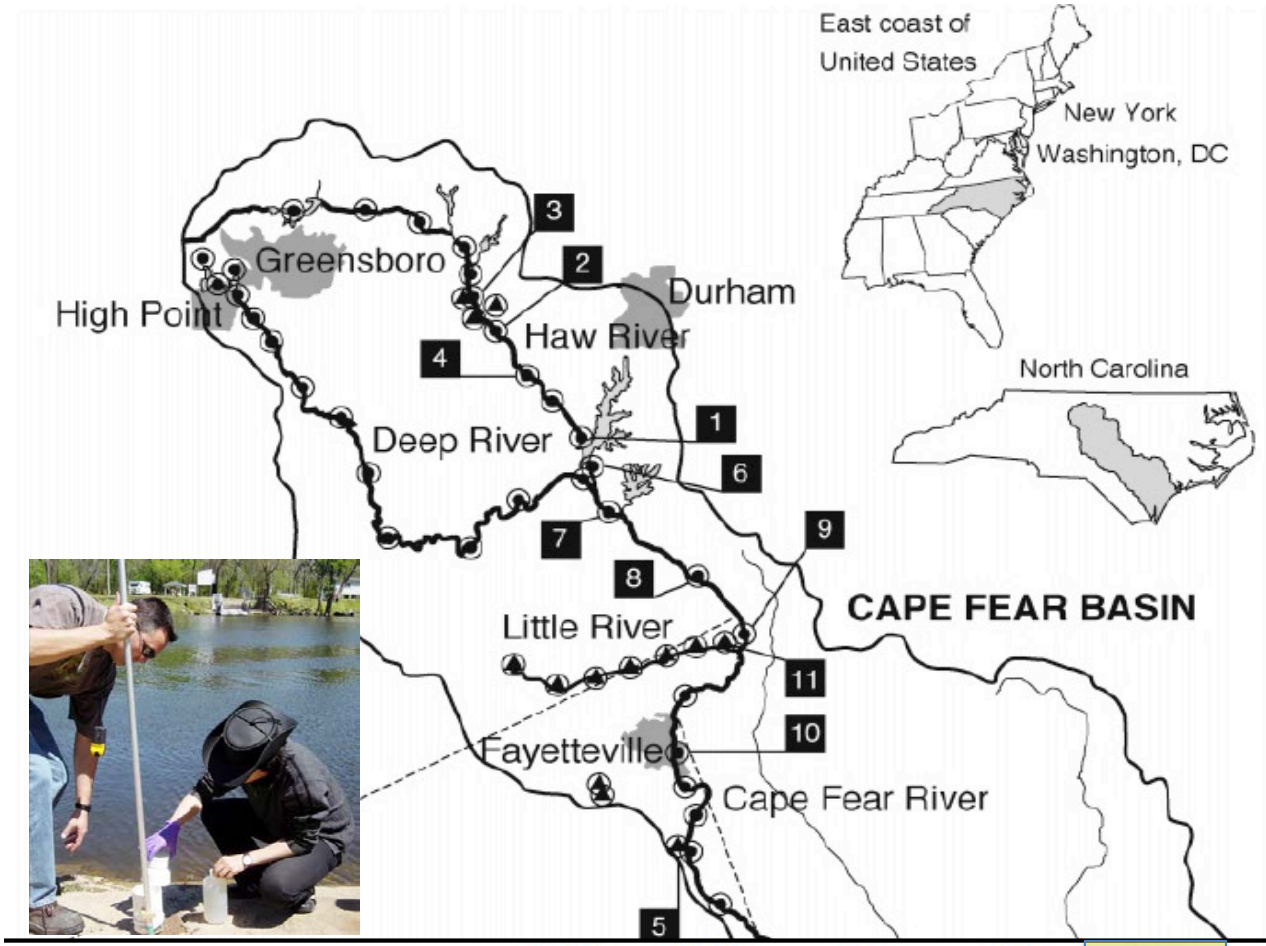
Soon after DuPont started making C8 at Fayetteville Works, the chemical turns up in a well under the plant. The public wouldn't find out for another two years.

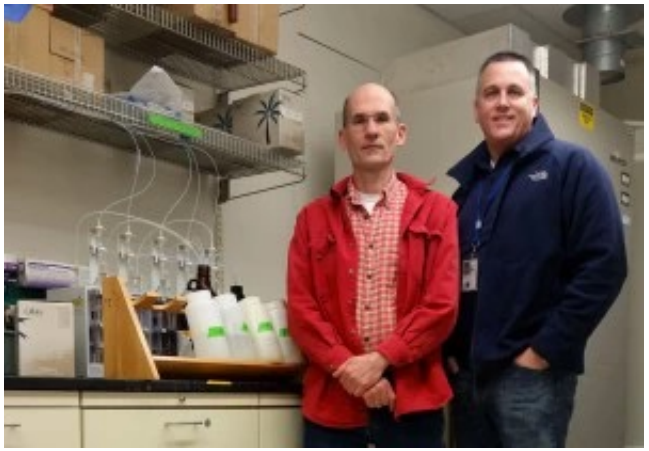
A brief history



Perfluorinated Compounds in the Cape Fear Drainage Basin in North Carolina

SHOJI NAKAYAMA, MARK J. STRYNAR, LAURENCE HELFANT, PETER EGEGHY, XIBIAO YE, AND ANDREW B. LINDSTROM*

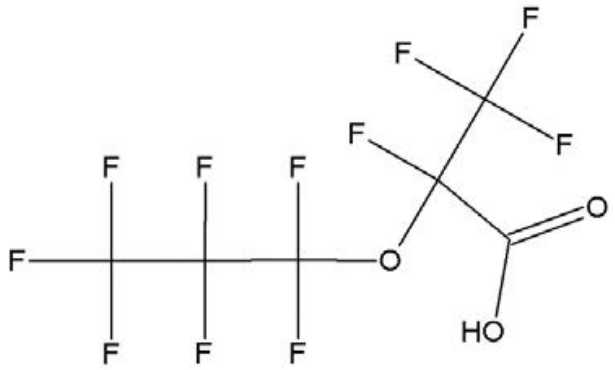




no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	*4.46*	*52.1*	*120*	*194*	*287*	118	21.7	127	8.43	*9.41*	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	88.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	*329*	*23.0*	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	*132*	*26.4*	3.20	185

[a] Italicized values show maximal concentrations of each compound.

A brief history



Hexafluoropropylene oxide dimer acid (HFPO-DA, "GenX")

Fluorochemical production begins at DuPont's Fayetteville Works

First publication highlighting PFAS occurrence in the Cape Fear River basin – Nakayama et al. *ES&T*

1980 | 2002 | 2007 | 2009 | 2012 | 2014 | 2015 | 2016

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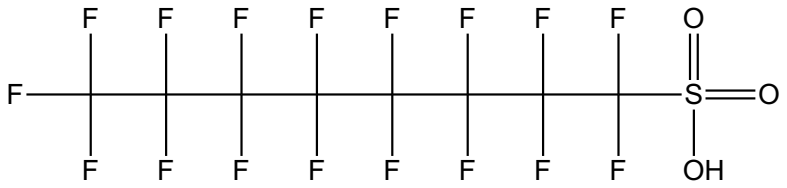
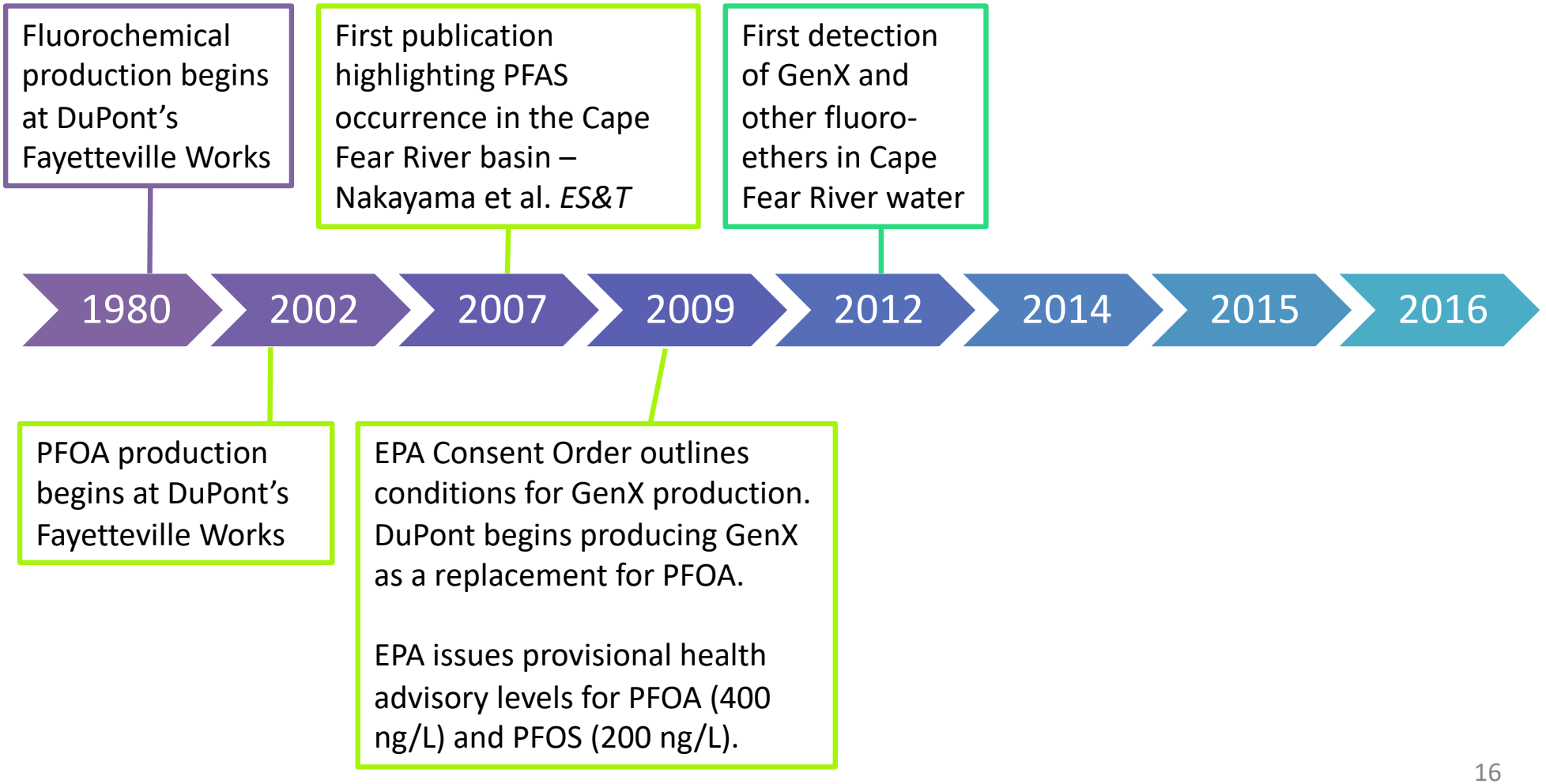


Perfluorooctane sulfonate (PFOS)

A brief history



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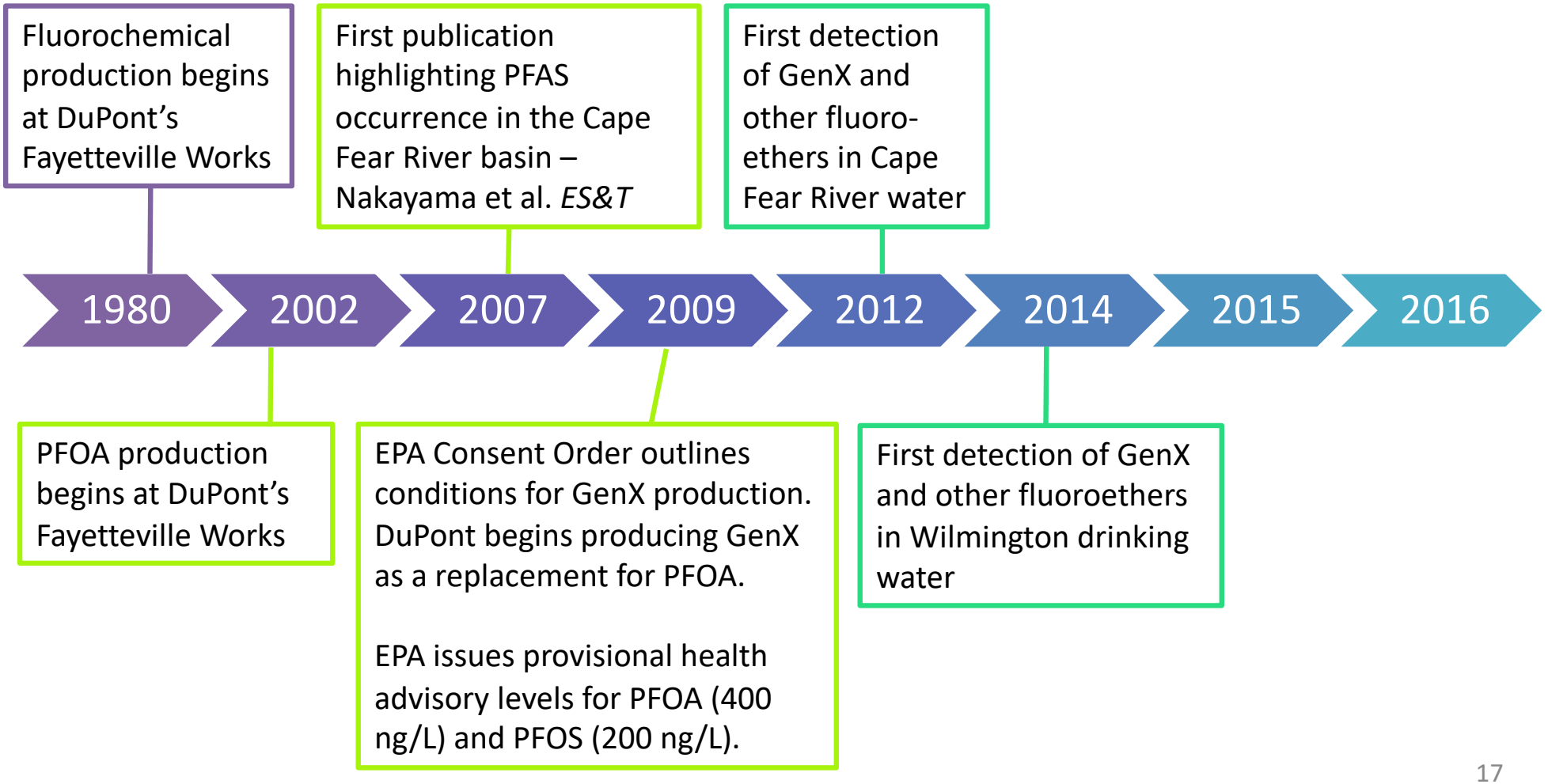

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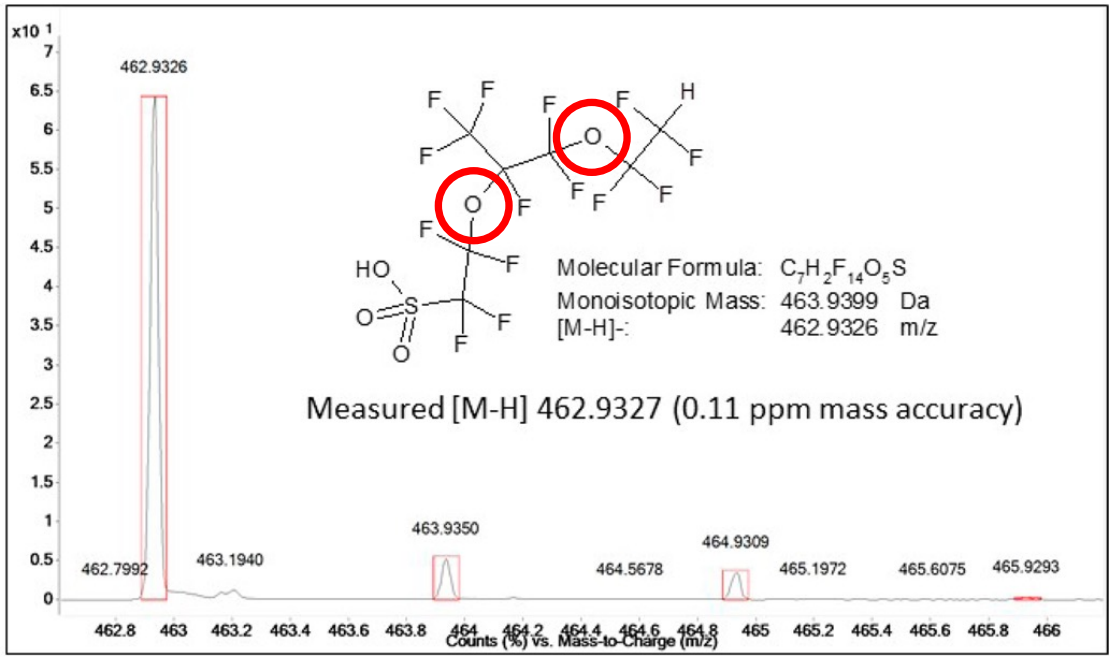
2016

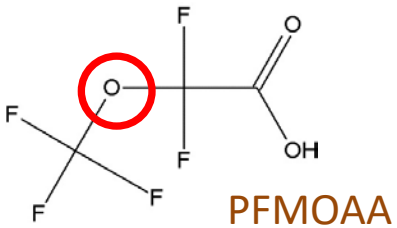


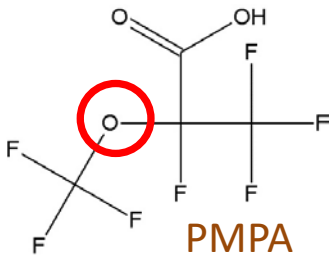
Environmental Science & Technology
Article
pubs.acs.org/est

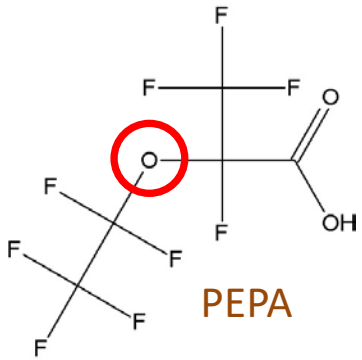
Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,[*,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Liang,[†,‡] Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[∥] Imma Ferrer,[∥] and Carol Ball[⊥]

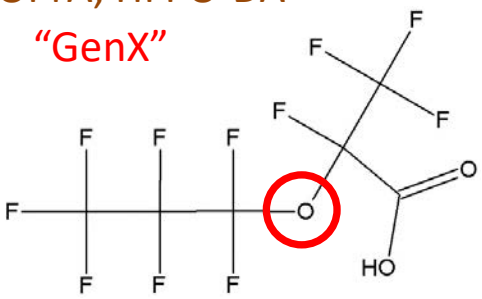
Per- and polyfluoroalkyl ether acids identified by high resolution mass spectrometry

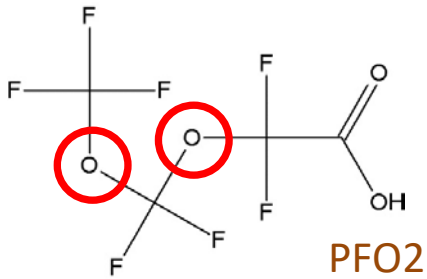

PFMOAA

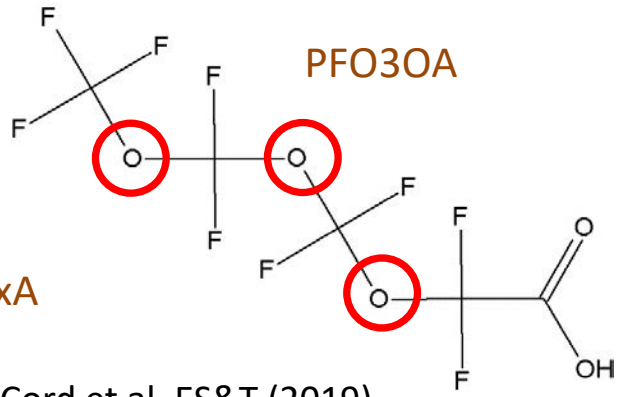

PMPA

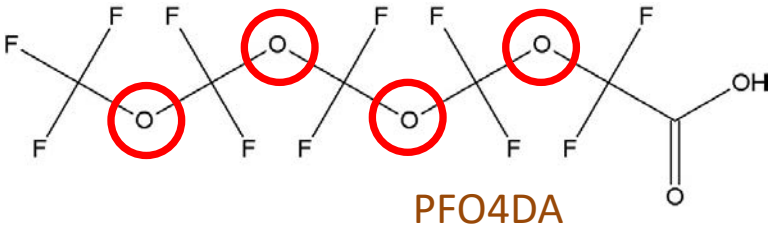

PEPA

PFPrOPrA, HFPO-DA
"GenX"



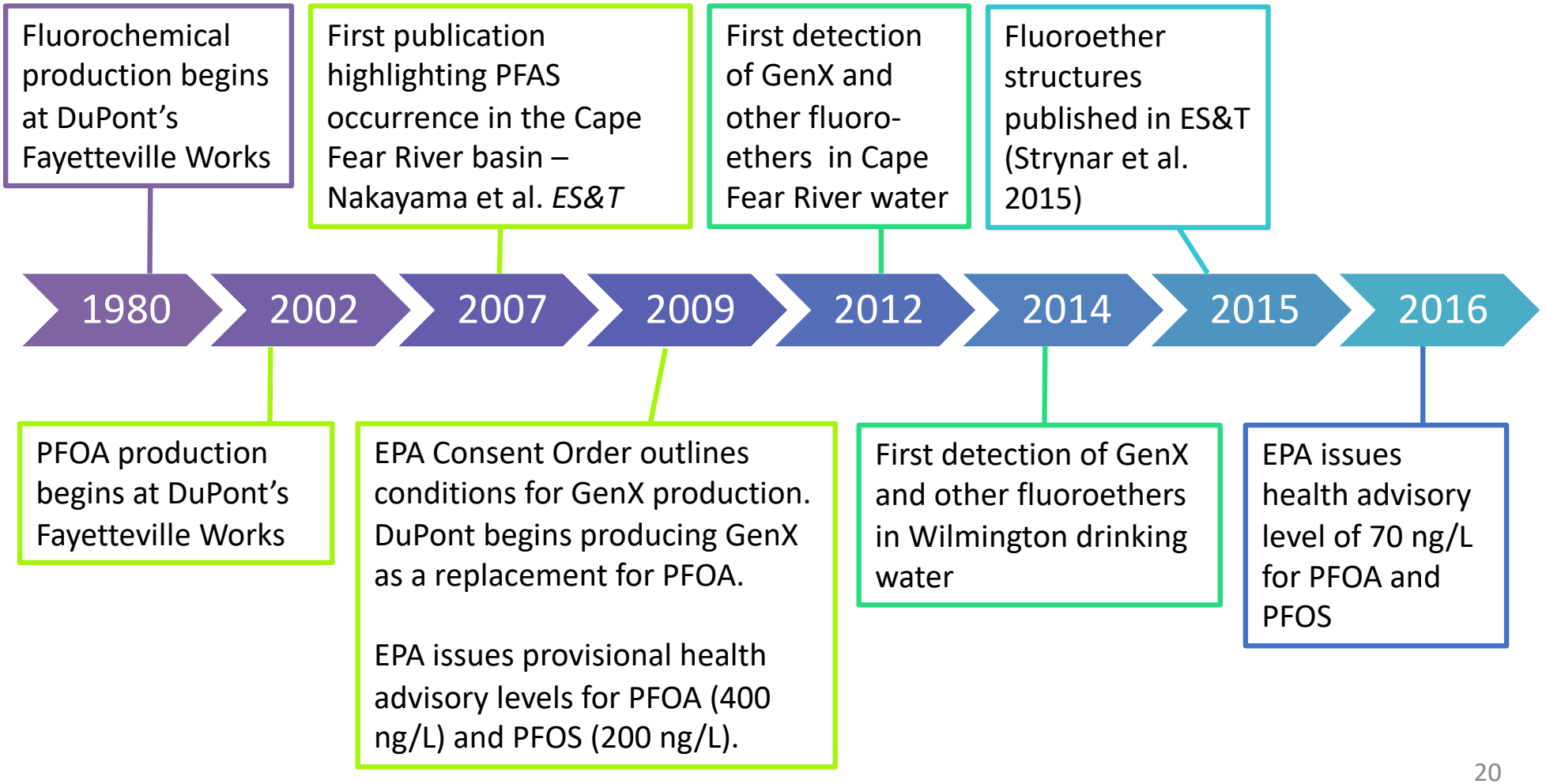

PFO2HxA


PFO3OA


PFO4DA

Strynar et al. ES&T (2015), McCord et al. ES&T (2019)

A brief history



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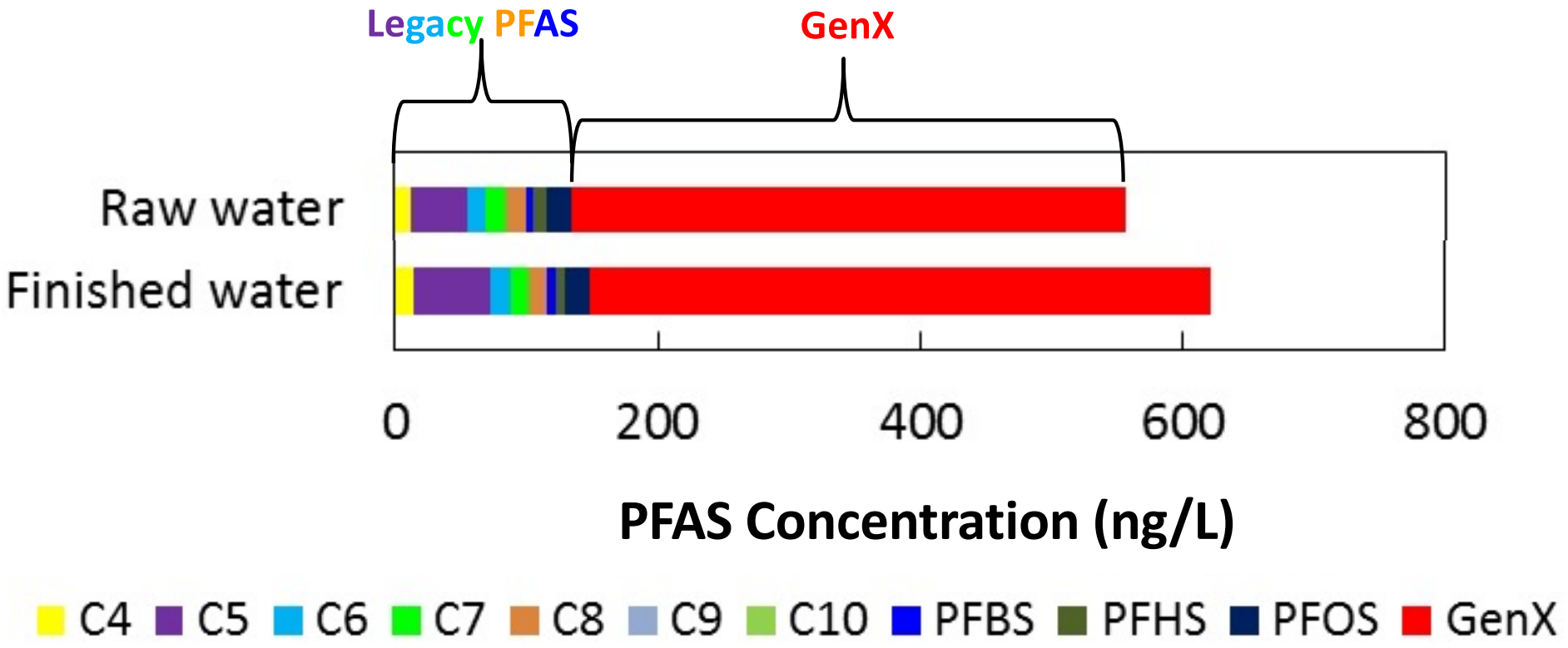
2014 — First detection of GenX and other fluoroethers in Wilmington drinking water

2015 — Fluoroether structures published in ES&T (Strynar et al. 2015)

2016 — ES&T Letters paper reports high levels of PFAS, including fluoroethers, in drinking water (Sun et al. 2016)

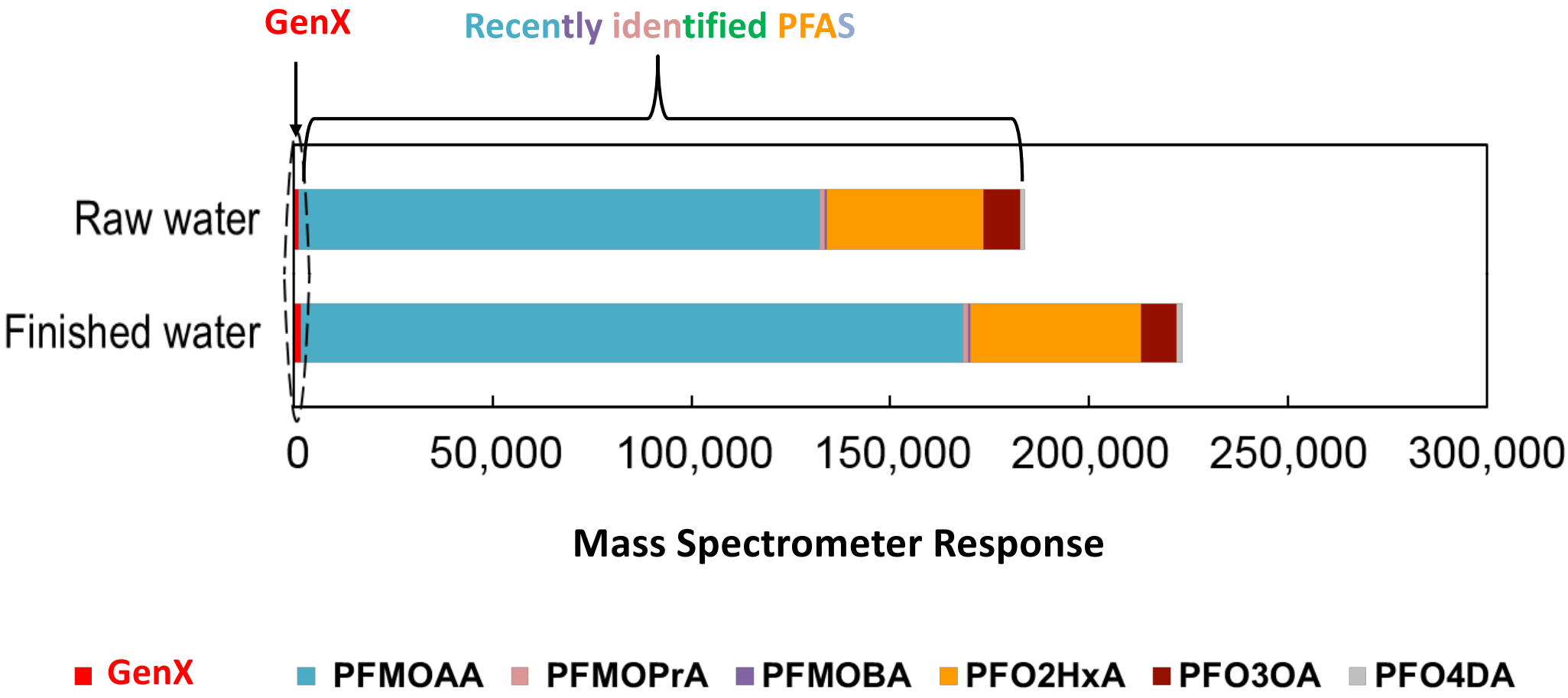
EPA issues health advisory level of 70 ng/L for PFOA and PFOS

In Wilmington, only PFHpA (C7) was detected in UCMR3 samples. C7 was only a very small percentage of the total PFAS concentration we could quantify



Sun et al. (2016) ES&T Letters

… and GenX was only a small fraction of the total mass spectrometer response associated with PFASs



Sun et al. (2016) ES&T Letters

Effecting change can be challenging

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[‡]

- Web Release: November 2016

Toxin taints CFPUA drinking water

MOST POPULAR

1 Toxin taints CFPUA drinking water
Jun 8 at 10:38 AM

2 WATER FAQs: What we know and what we don't know
Jun 8 at 3:35 PM

3 GenX fallout: Is my water safe to drink?
Jun 8 at 5:59 PM

4 Local officials respond to GenX report
Jun 8 at 5:30 PM

▲ HIDE CAPTION

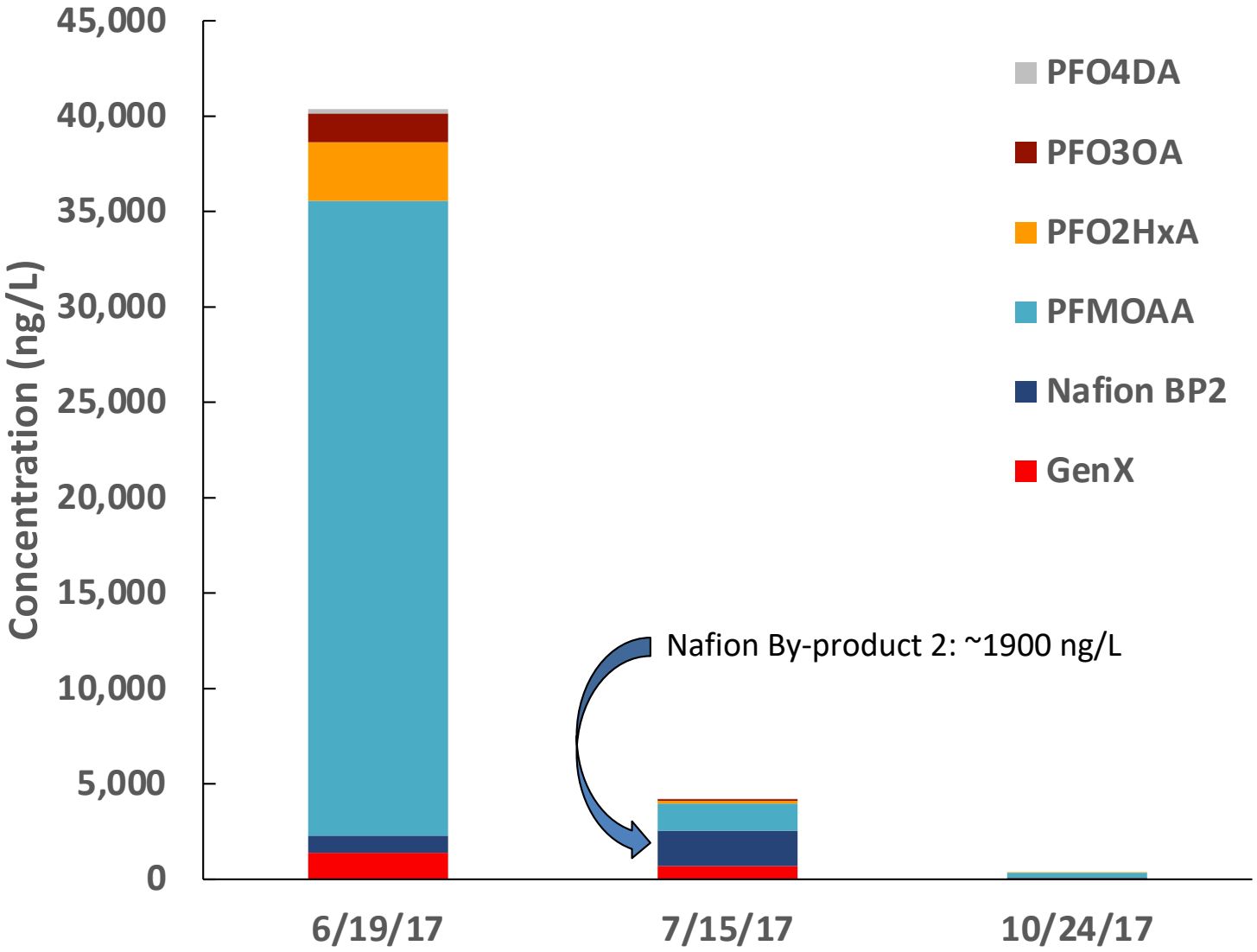
A 2000 aerial photo of Fayetteville Works on the Cumberland-Bladen county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

Utility can't filter out chemical produced upriver at Fayetteville plant

By Vaughn Hagerty StarNews Correspondent

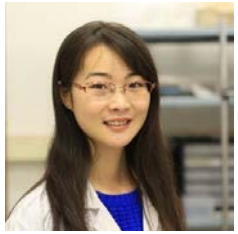
Posted Jun 7, 2017 at 10:31 AM
Updated Jun 8, 2017 at 10:38 AM

PFAS concentrations at drinking water intake have dropped dramatically since mid-June 2017

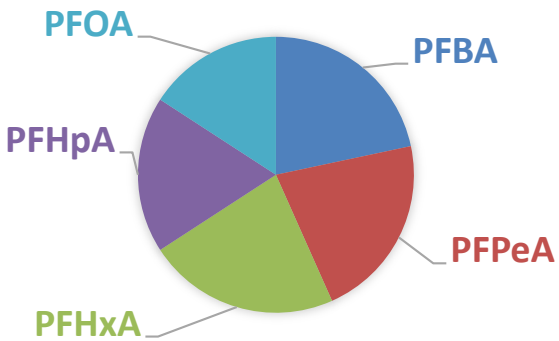


Hopkins et al. JAWWA 2018

2015 PFAS levels in Wilmington drinking water source

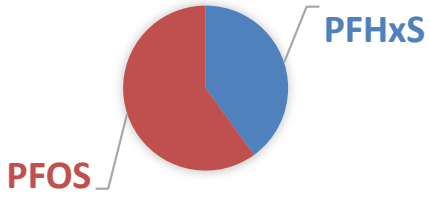


PhD student
Chuhui Zhang

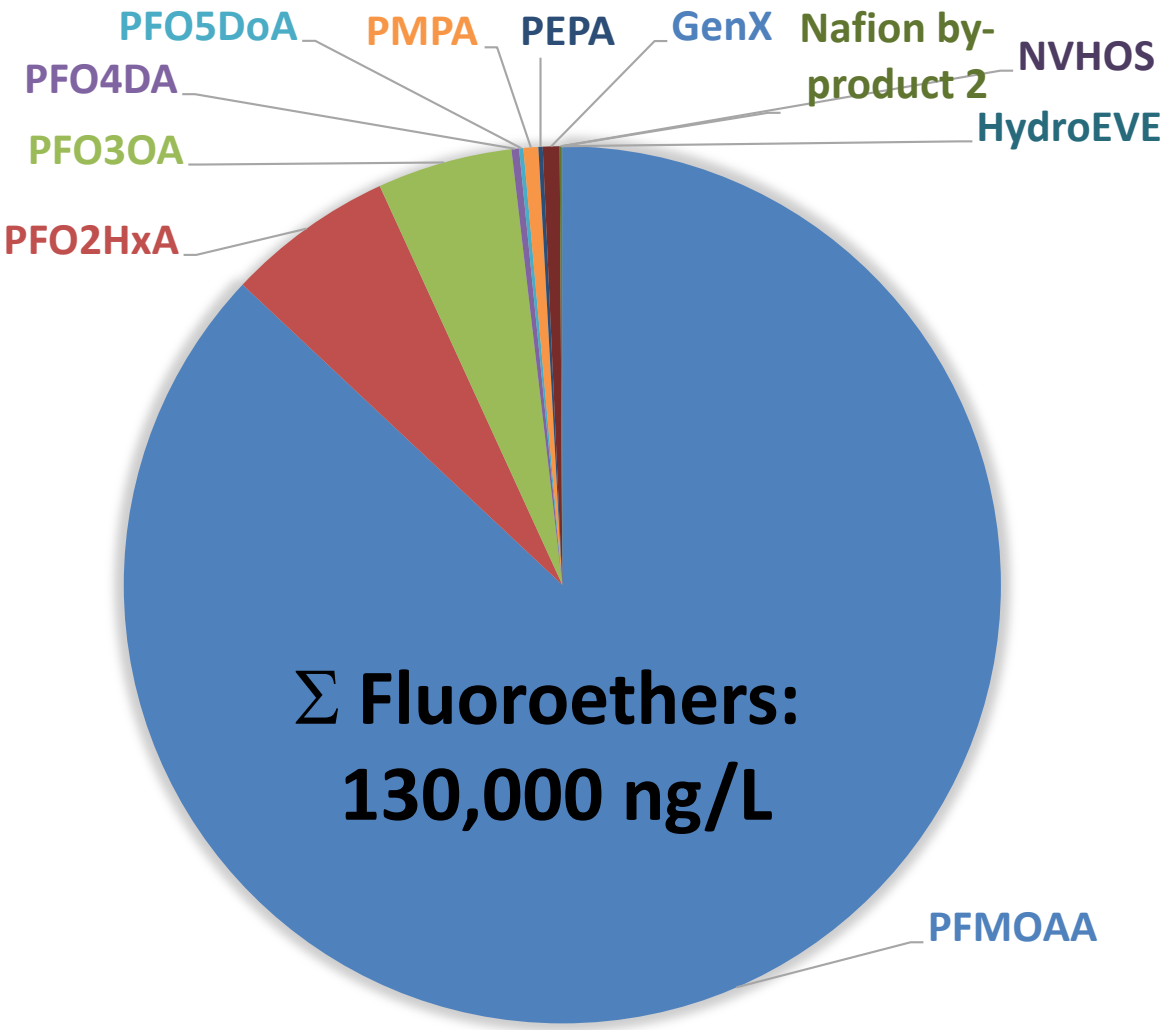


Σ PFCAs: 120 ng/L

July 2015 sample

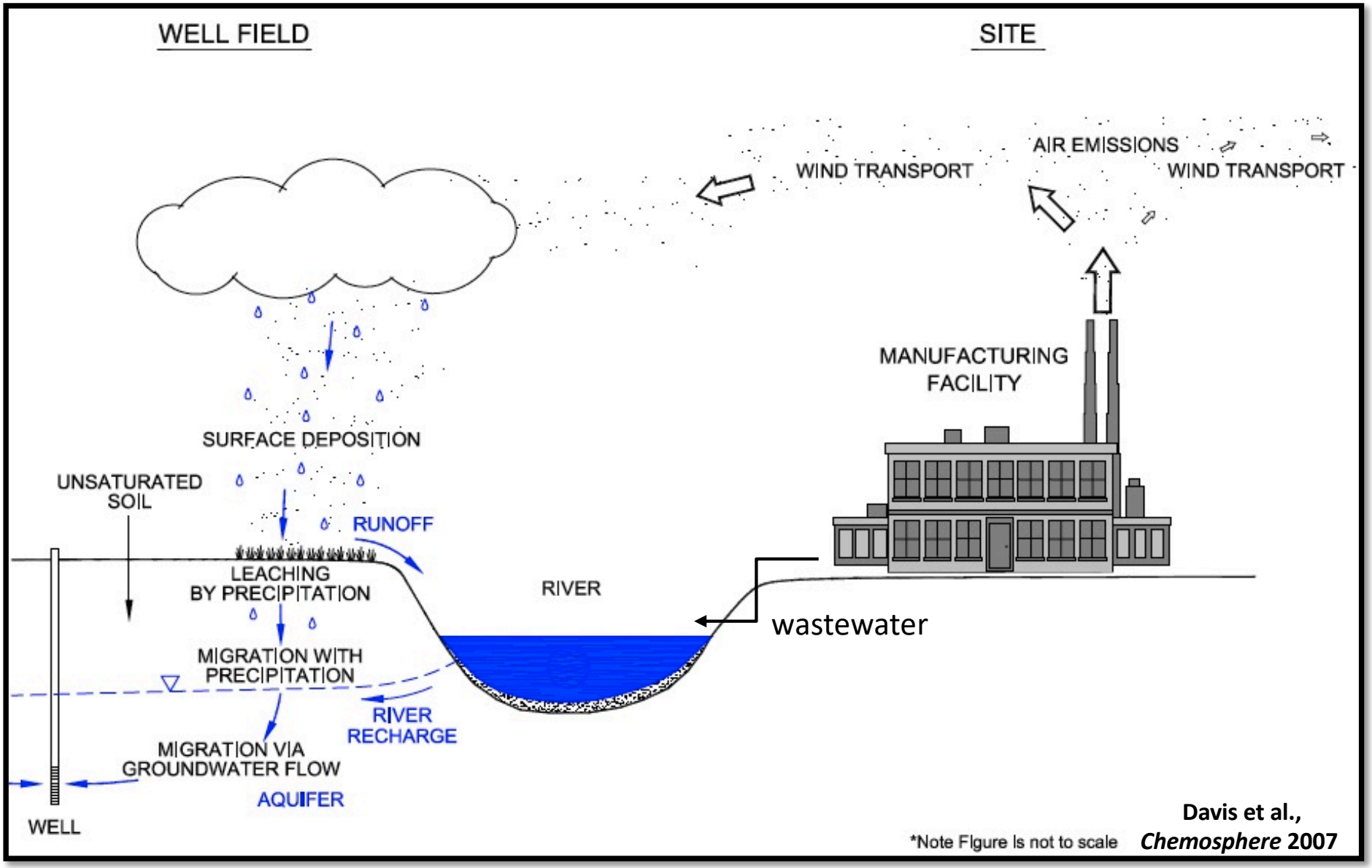


Σ PFSAs: 45 ng/L

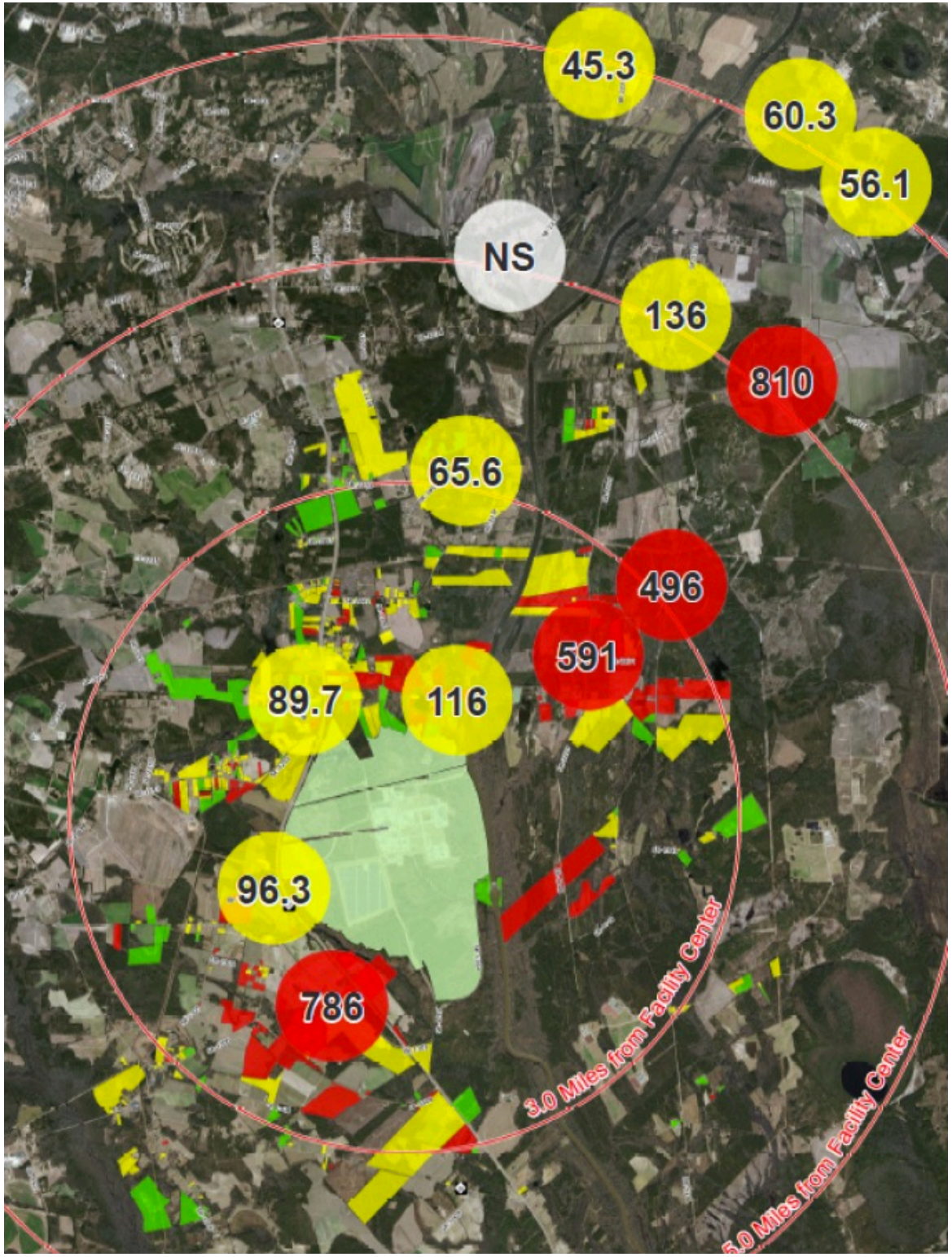


Zhang et al. (2019) ES&T Letters

Fluorochemical manufacturers and industries using fluorochemicals **emit PFAS to air and water**



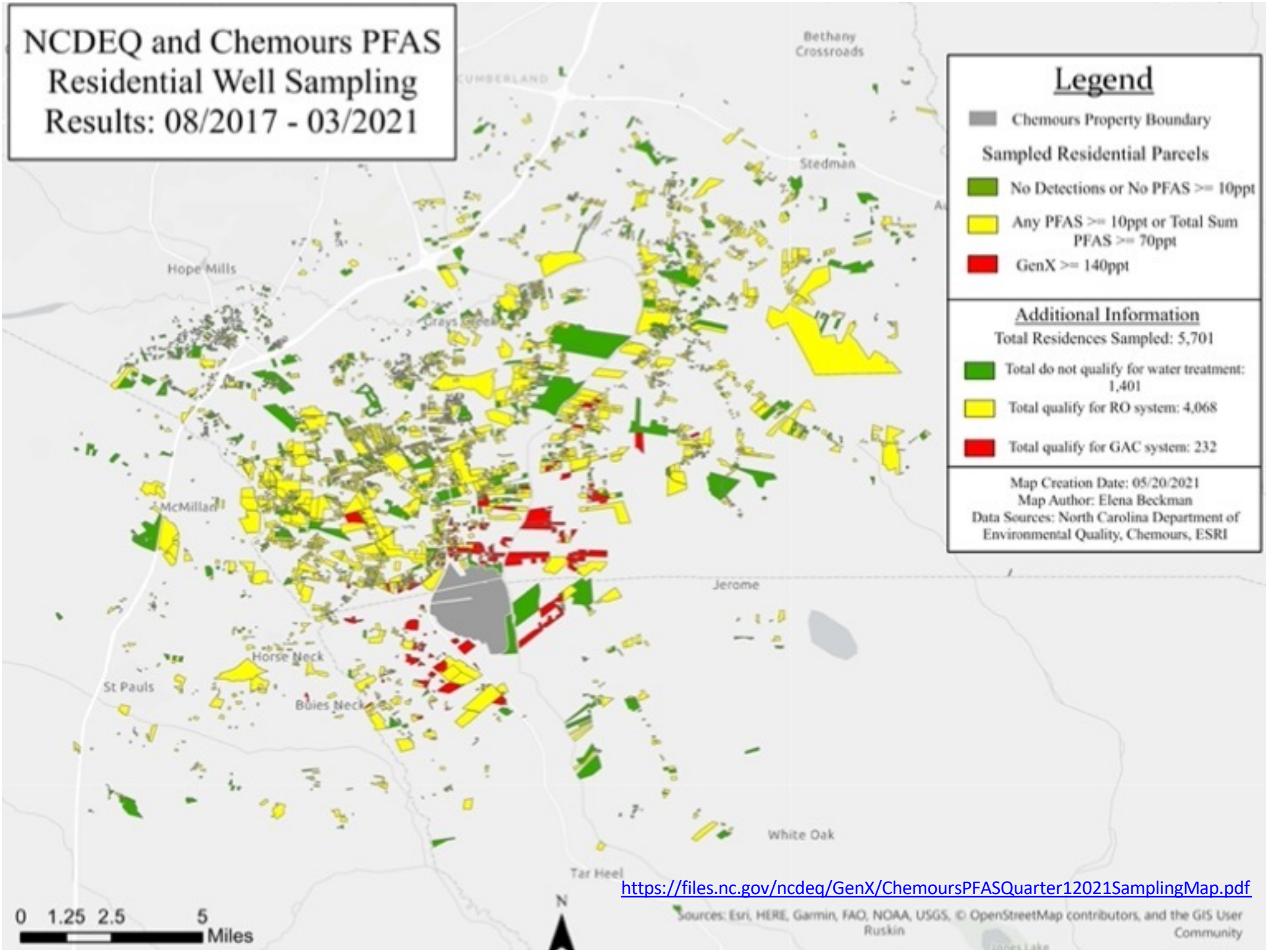
Davis et al., *Chemosphere* 2007



Rain events return GenX (and other PFAS) from the atmosphere to the land surface

Rain water collected February 28 – March 2, 2018

https://files.nc.gov/ncdeq/GenX/Presentation_May29InfoSession_StPaulsMiddleSchool.pdf



https://files.nc.gov/ncdeq/GenX/ChemoursPFASQuarter12021SamplingMap.pdf

The public has many questions

- Are PFAS in my drinking water? Are PFAS in my water that standard methods do not detect?
- Are PFAS in me? At what levels? What are the health effects?
- Are PFAS in the fish I catch? The food I grow in my garden?
- How can I get PFAS out of my water?

NC 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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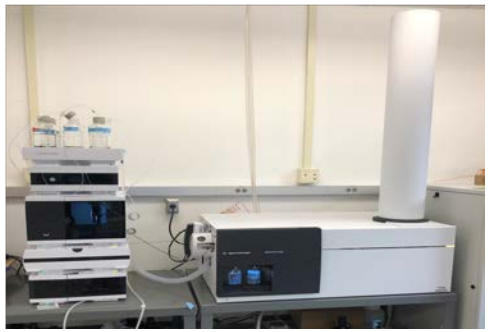
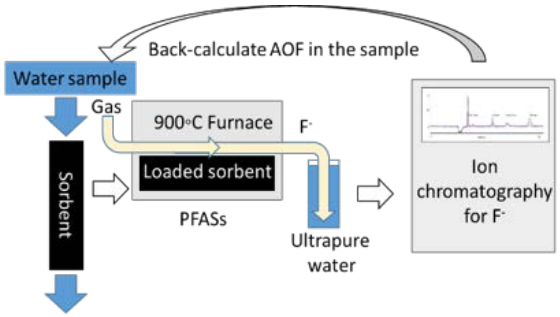
PFAS Analysis Strategy

Triple Quadrupole MS/MS (target quantitation)

Sample Collection

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

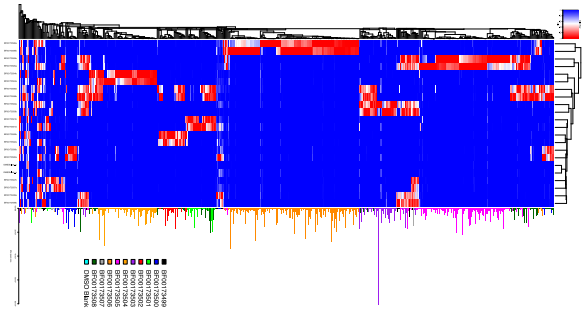




PFAS mass balance

Adsorbable organic fluorine analysis

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



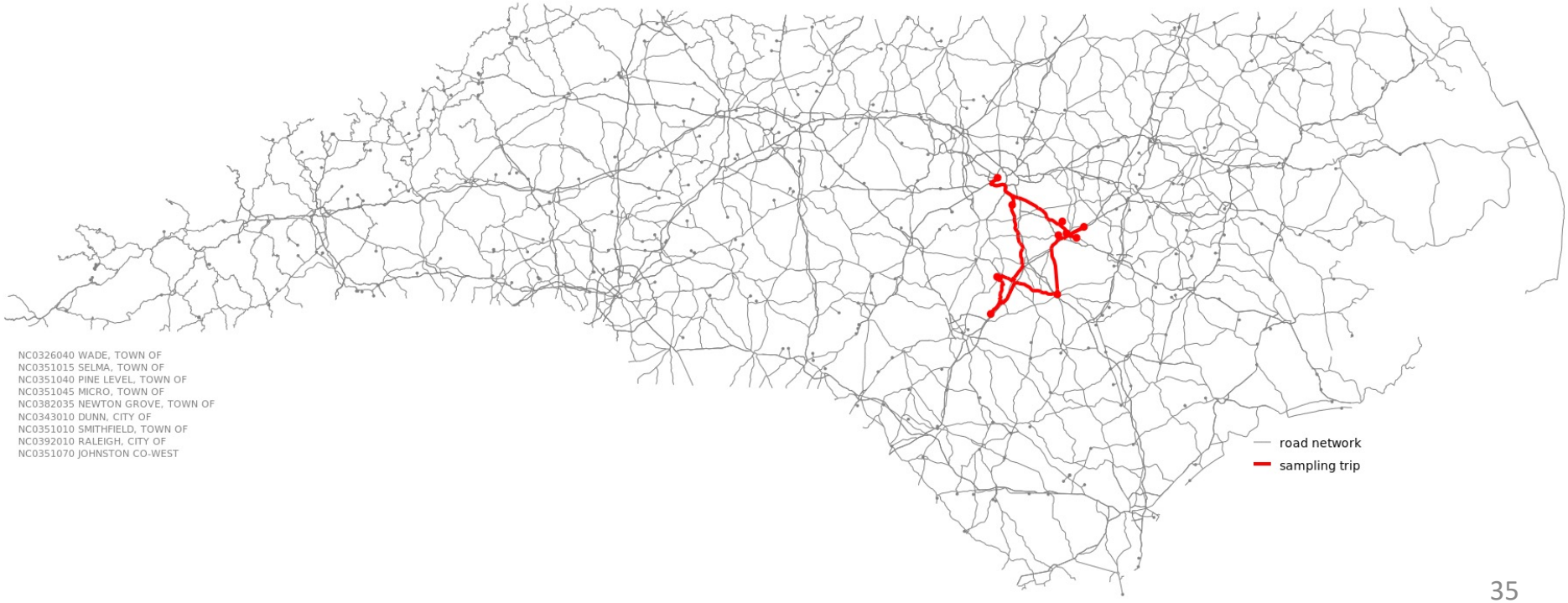
Statewide sample acquisition: Trip optimization

Raw drinking water sampled from every NC Public Drinking Water Provider for PFAS quantitation, 2 rounds

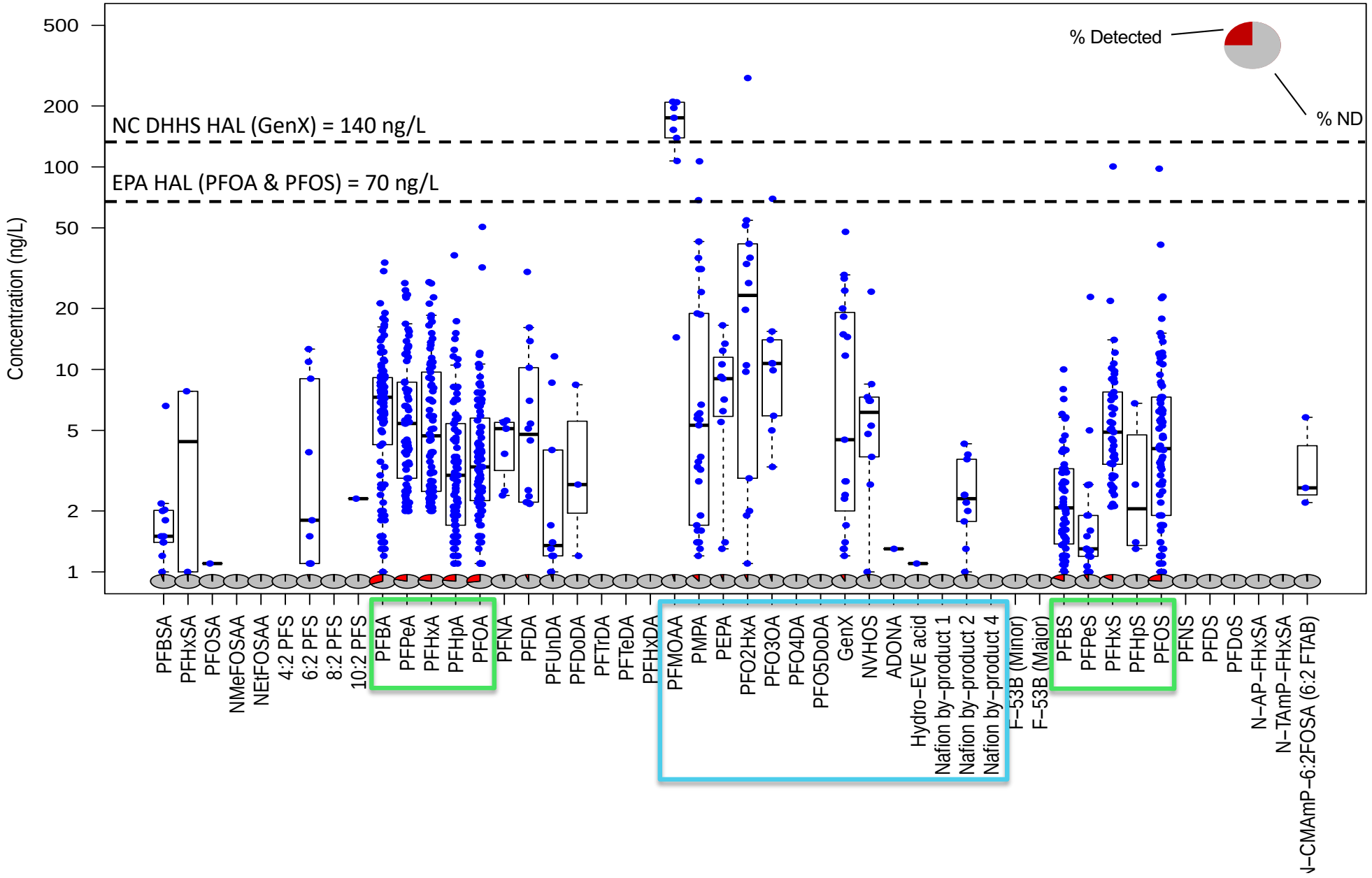
- 191 municipal surface water sites
- 149 municipal ground water sites
- 58 county water sites

Round 1 : **COMPLETED** ✓

Round 2: **In Progress**

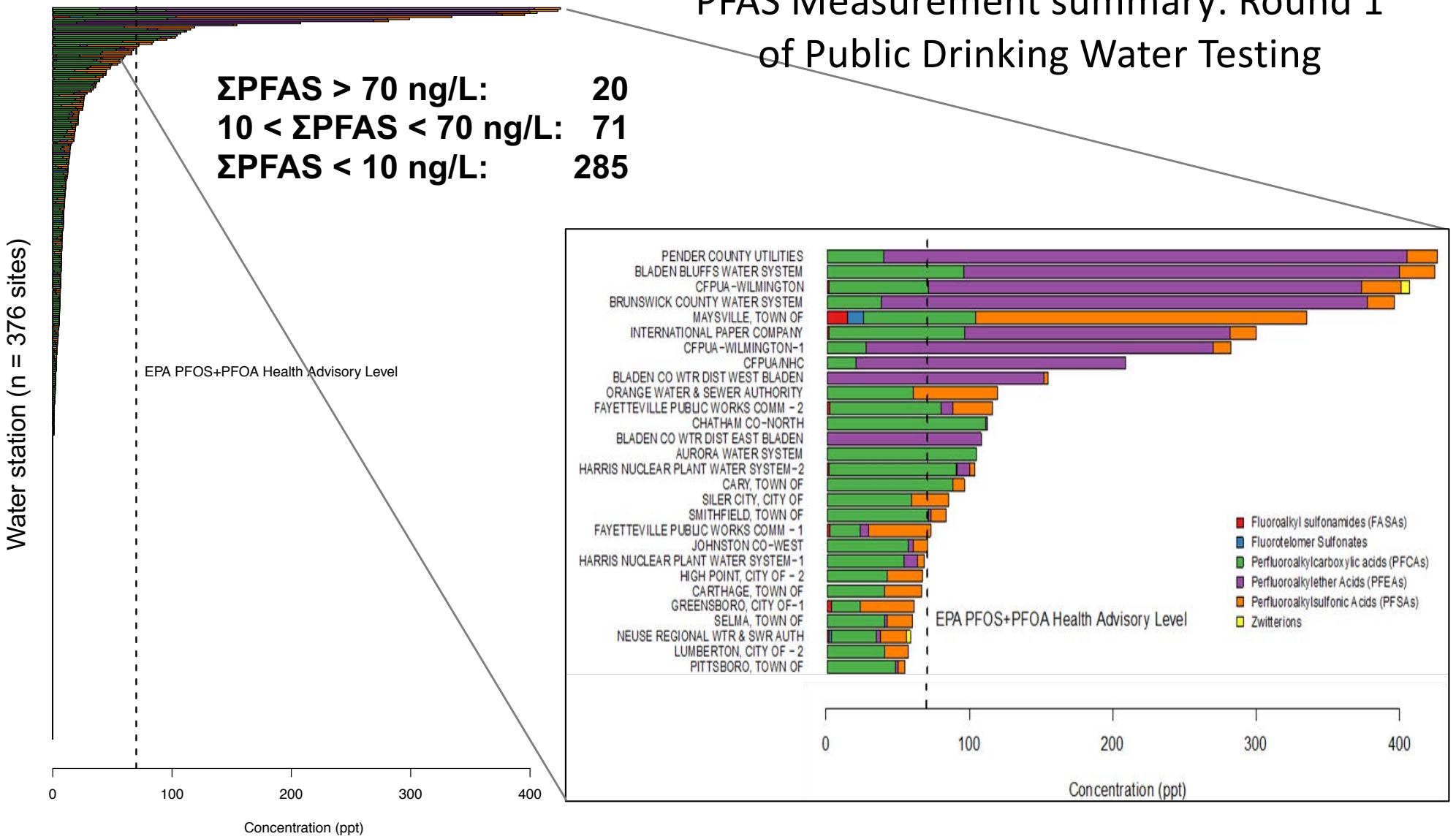


Occurrence of Individual PFASs (n = 376)



PFAS Measurement summary: Round 1 of Public Drinking Water Testing

ΣPFAS > 70 ng/L: 20
10 < ΣPFAS < 70 ng/L: 71
ΣPFAS < 10 ng/L: 285



NC STATE UNIVERSITY Center for Human Health and the Environment

The GenX Exposure Study:

Characterizing PFAS exposure in the Lower Cape Fear River Basin

Funding: NIEHS 1R21ES029353-01

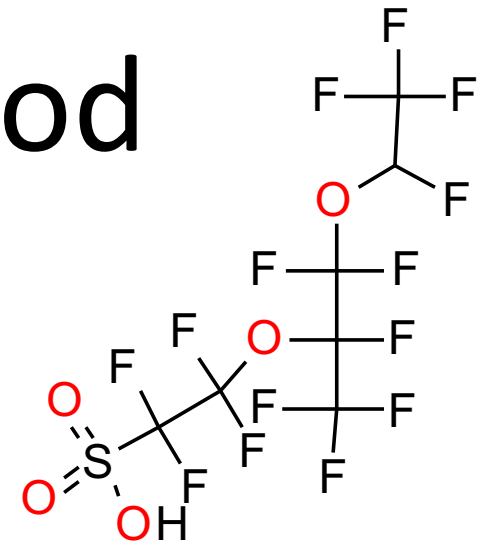

Jane Hoppin,
CHHE, NCSU


Detlef Knappe,
CCEE, NCSU

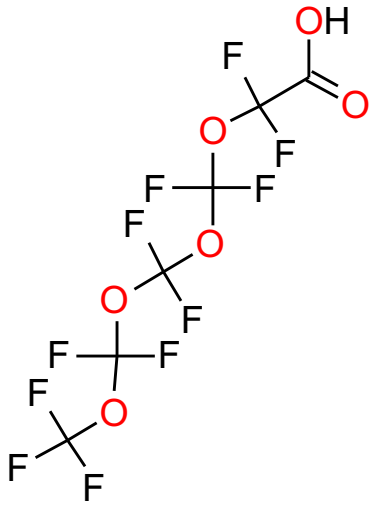

Nadine Kotlarz,
CHHE, NCSU

Long chain fluoroalkyl ether acids in Wilmington blood

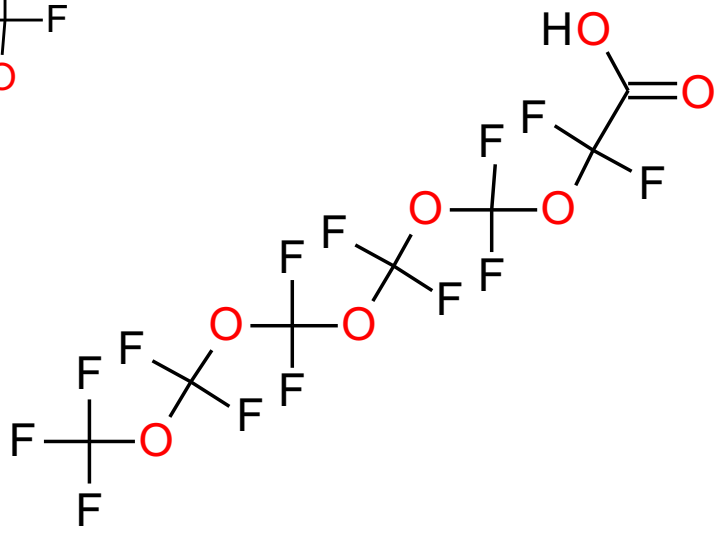
1. Nafion byproduct 2 (99%)



2. PFO4DA (98%)

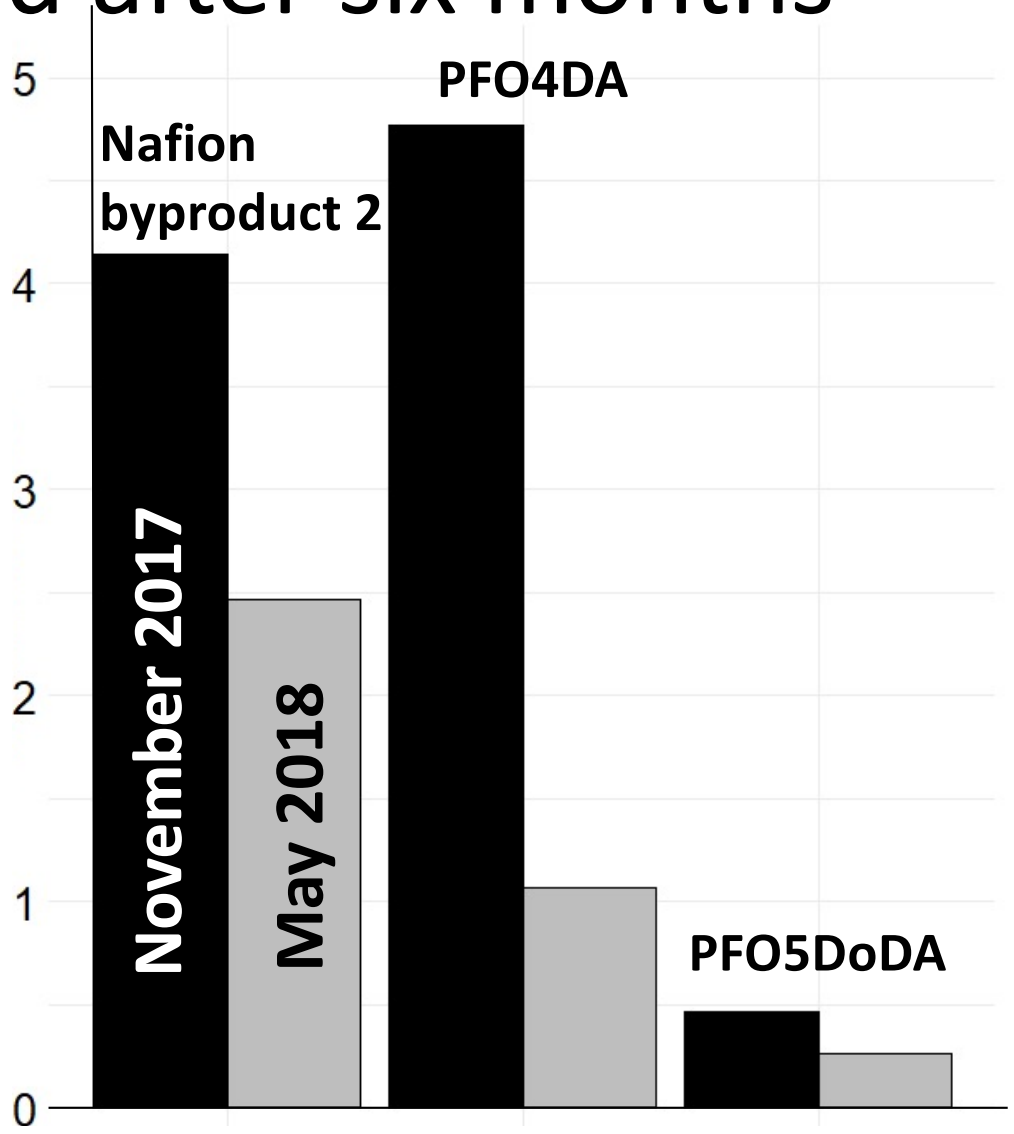


3. PFO5DoDA (87%)



Blood concentrations of newly identified PFAS decreased after six months

Median blood concentration for 44 participants (ng/mL)



The presence of PFAS in NC drinking water sources has operational and financial impacts

- Brunswick County: Installation of reverse osmosis plant
  - Capital cost: $99M
  - Operating cost: $2.9M/year
- Cape Fear Public Utilities Commission: Installation of post-filter granular activated carbon adsorbers
  - Capital cost: $46M
  - Operating cost: $2.7M/year
- Pittsboro: Started feeding powdered activated carbon
- Greensboro: Temporarily stopped using one of its water treatment plants, evaluating treatment options
- Cary/Apex, Fayetteville: Evaluating treatment options

Whole house granular activated carbon filters are one option to treat private wells

- 2 filters in series
- 200 pounds of activated carbon per filter
- Locked shed on property
- Water pressure and flow can be impacted

Common home filters

Pitcher filter

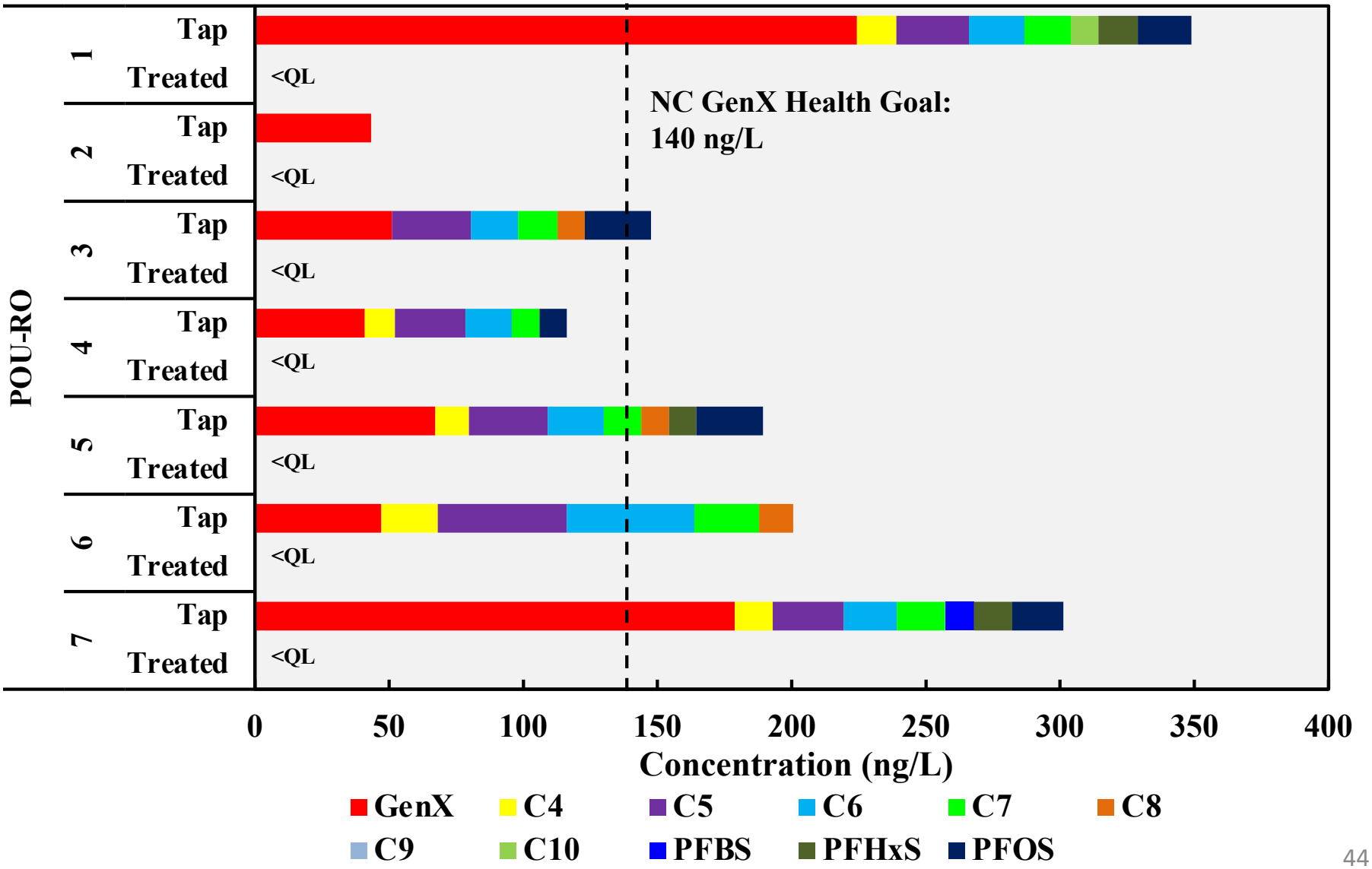
Faucet filter

Under-sink reverse osmosis filter

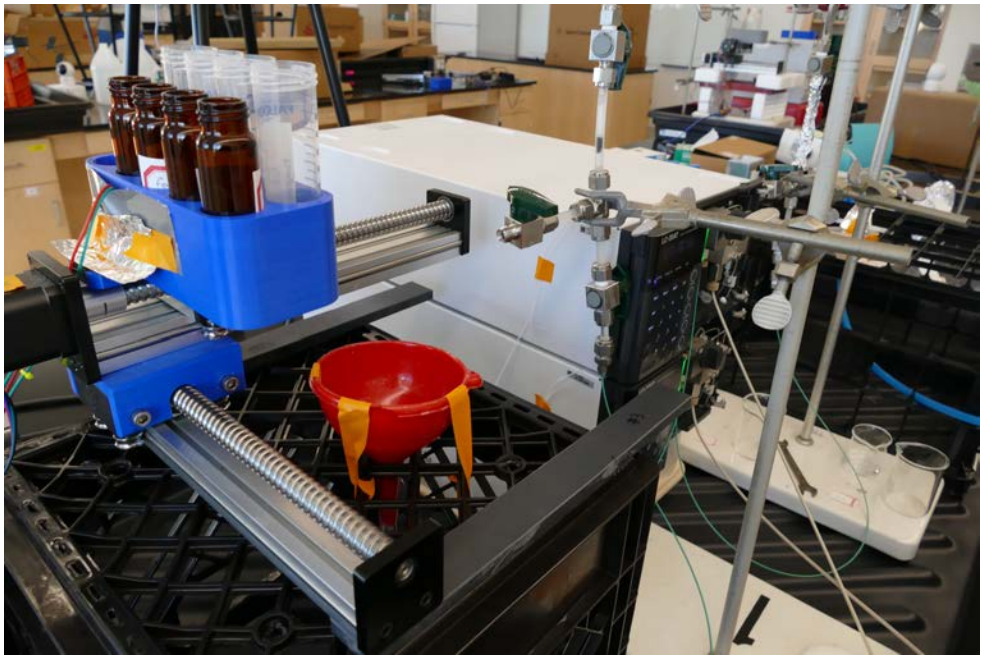
Refrigerator filter

2-stage under-sink filter

Under-Sink Reverse Osmosis Filters Effectively Removed PFAS



Come visit our brand-new labs!



NC STATE UNIVERSITY Center for Human Health and the Environment

NC STATE UNIVERSITY Center for Environmental and Health Effects of PFAS

NORTH CAROLINA PFAS Testing Network

Thank you!

Questions:

knappe@ncsu.edu