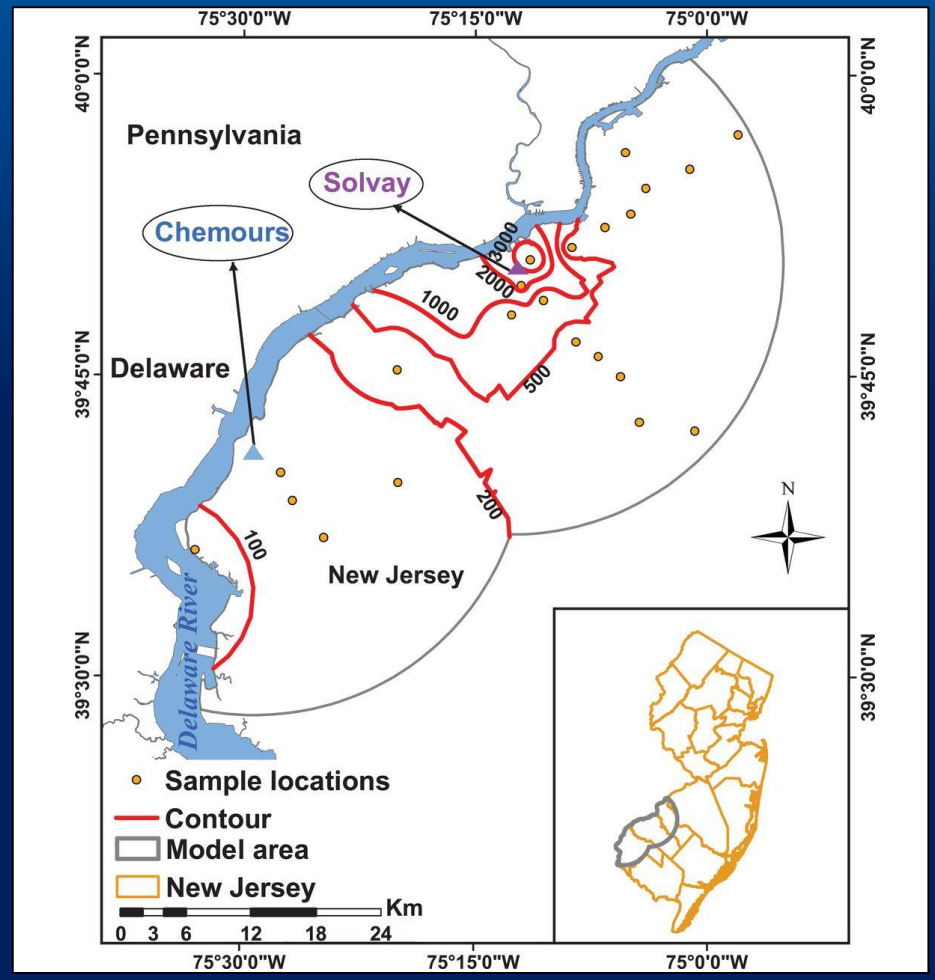
Multimedia Exploration of Emerging PFASs and Their Sources

James McCord - ORD/CEMM/WECD/MMB

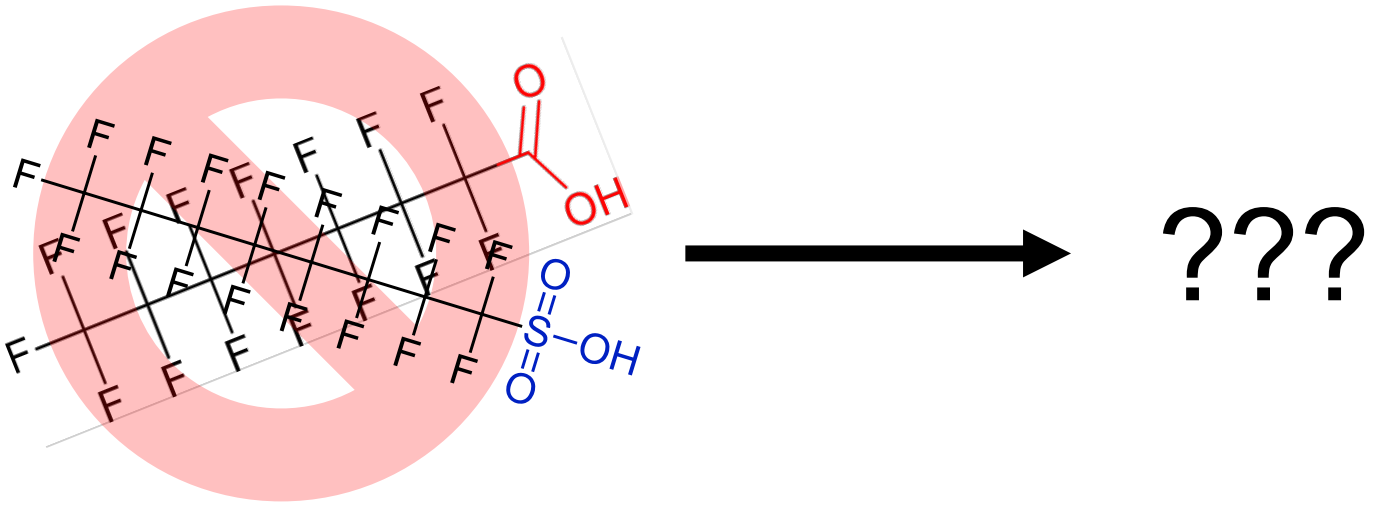


July 14, 2020
Biomonitoring California Scientific Guidance Panel

The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. EPA

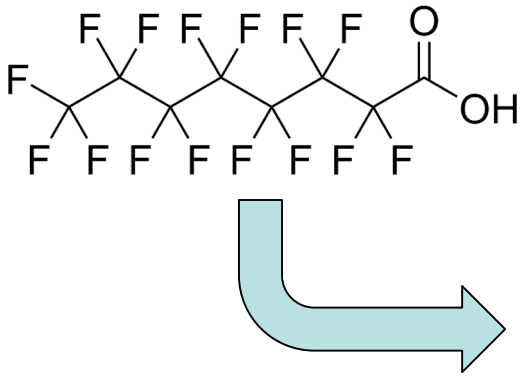
PFAS and Non-Targeted Analysis Approaches

- Historical PFAS usage continues to be investigated and monitored with traditional techniques (Targeted LC-MS)
- Post-PFOA stewardship agreement / PFOS phaseout there is a proliferation of replacement species

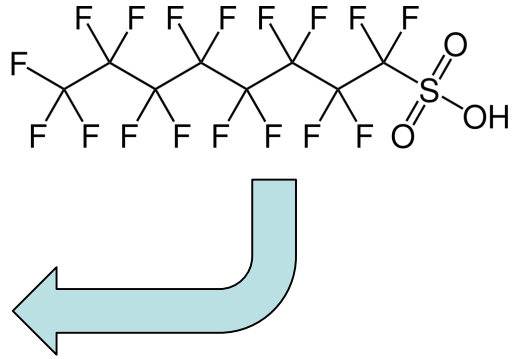


Proliferation of Replacement Species

PFOA

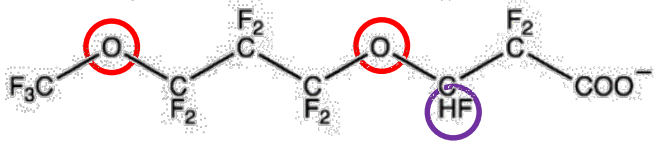


PFOS

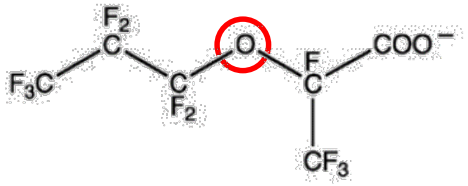


Fluoropolymer manufacture

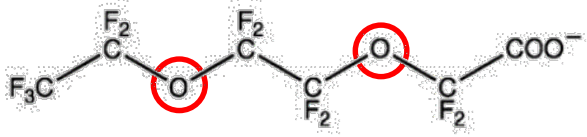
ADONA (CAS No. 958445-44-8)



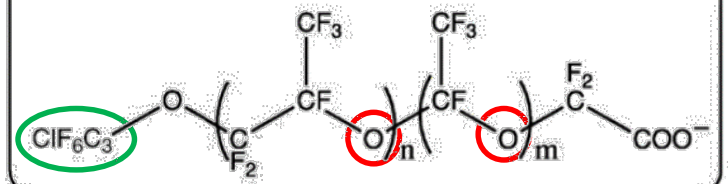
GenX (CAS No. 62037-80-3)



Asahi's product (CAS No. 908020-52-0)

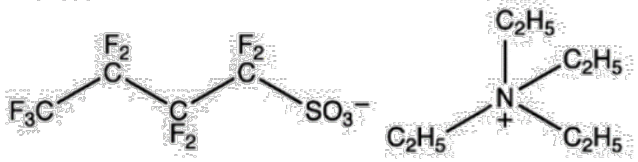


Solvay's product (CAS No. 329238-24-6)

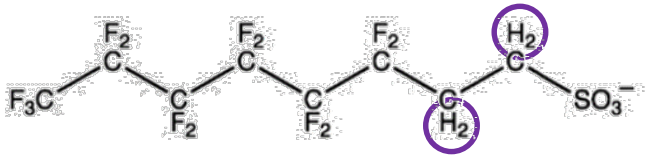


Metal plating

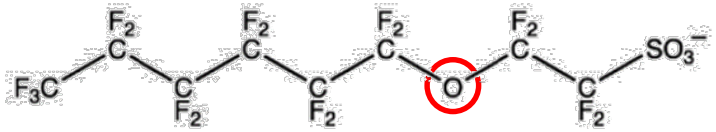
$N(Et)_4$-PFBS (CAS No. 25628-08-4)



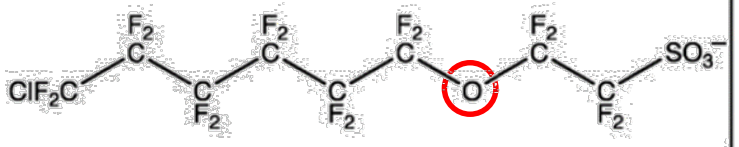
6:2 FTSA (CAS No. 27619-97-2)



F-53 (CAS No. 754925-54-7)



F-53B (CAS No. 73606-19-6)



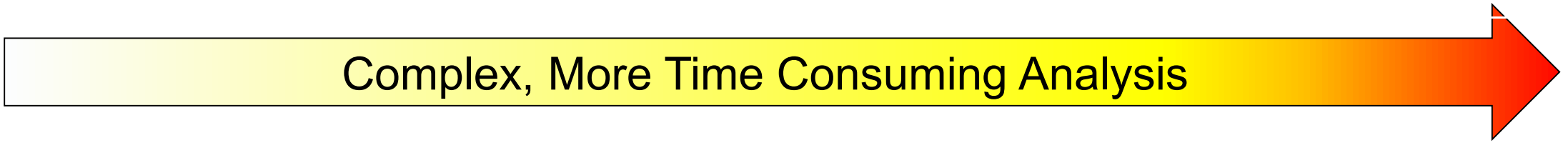
Wang et al., **2013** *Environment International* 60, 242–248

PFAS and Non-Targeted Analysis Approaches

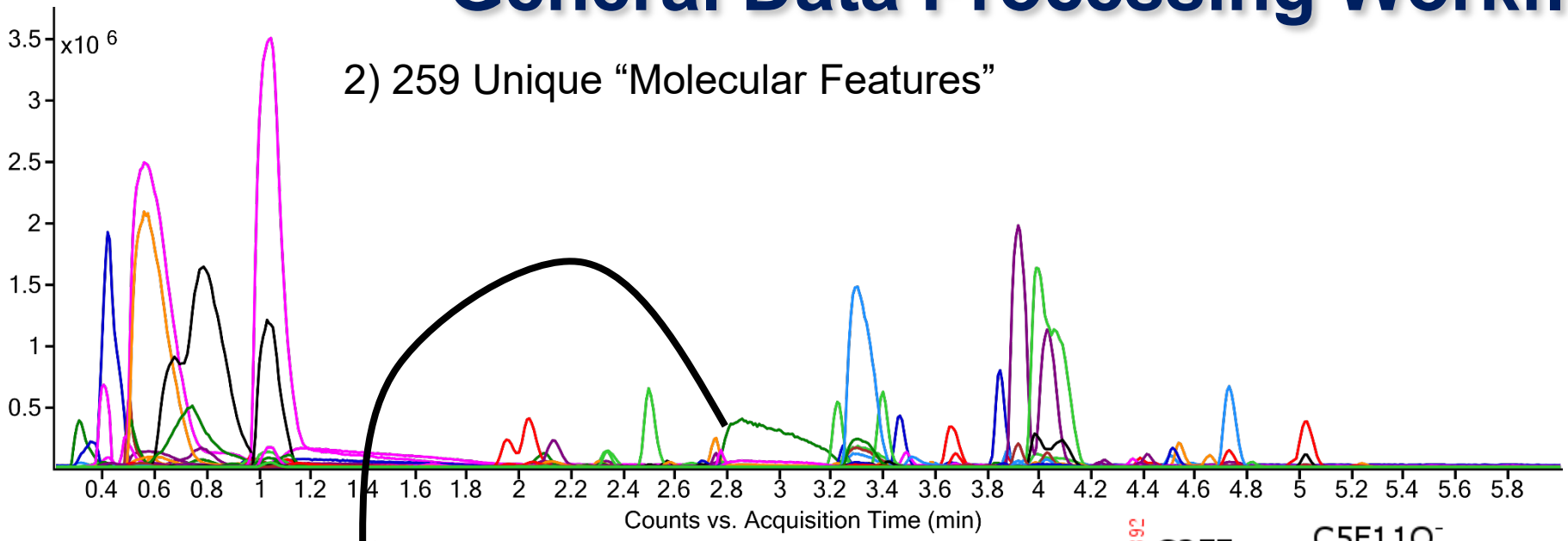
- Historical PFAS usage continues to be investigated and monitored with traditional techniques
- Post-PFOA stewardship agreement / PFOS phaseout there is a proliferation of replacement species
- Driving research questions for States/EPA Regions
  - Is there environmental contamination from new “replacement” PFAS used as substitutes for historical PFOA/PFOS and related species?
  - Can we develop ways to identify and monitor legacy and emerging PFAS to help with source attribution?

Approaches to Chemical Measurements

	Targeted	Screening	Discovery
Chemical Targets	Few, selected chemicals	100s – 100,000s per library	Any chemical
Method of Analysis	Focused method	Non-Targeted Method	Non-Targeted Method
Chemical Structure	Known	Known in library	Unknown
Reference Data	Available	Some, maybe simulated	Some, maybe simulated
Standards	Available	For common compounds	Unlikely



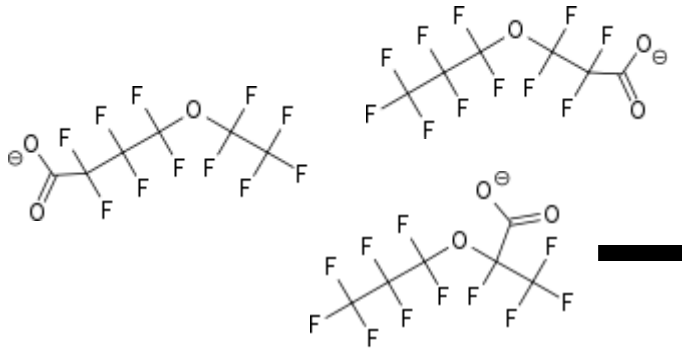
General Data Processing Workflow



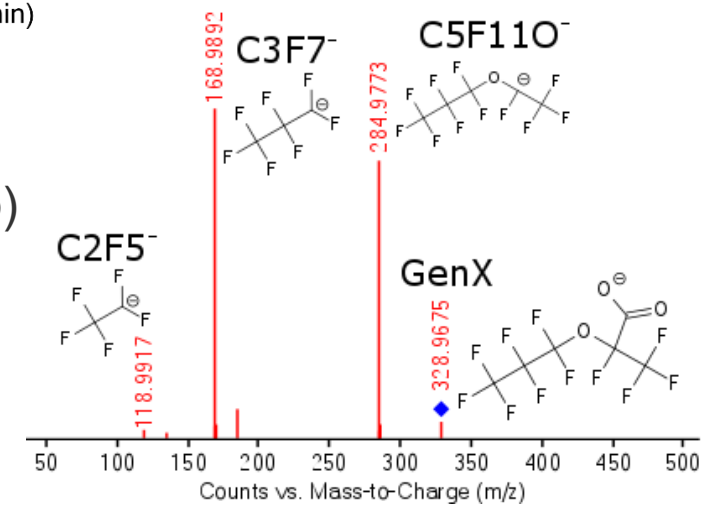
2) 259 Unique "Molecular Features"

3) C6HF11O3

3a)

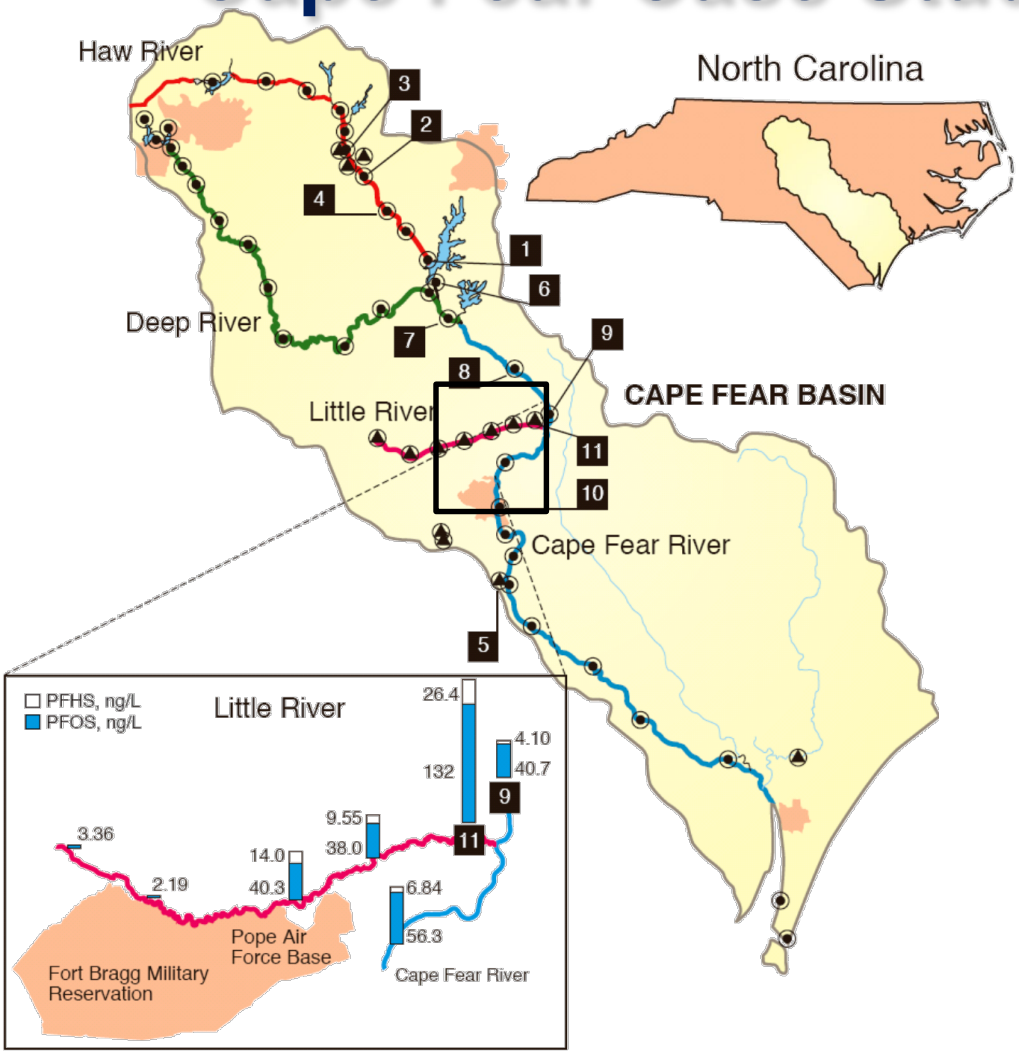


3b)



1) Data Generation
2) Feature Finding
3) Formula Assignment
   - 3a) Tentative Structures
   - 3b) Structure Confirmation
4) Quantitation?
   - 4a) Relative Quant
   - 4b) Absolute Quant

Cape Fear Case Study: Historical PFAS in Watershed



Surface Water PFAS Concentrations (circa 2007)

Site	River	C10 ng/L	C9 ng/L	C8 ng/L	C7 ng/L	C6 ng/L	PFOS ng/L
1	Haw	***120***	***194***	***287***	118	22	127
5	Cape Fear*	20	71	59	***329***	***23***	30.0
7	Cape Fear	13	35	70	24	8	67
11	Little	2	2	13	3	3	***132***

Haw River: performance fabrics, bio-solids, AFFF, industrial waste

*Cape Fear Tributary: Fluoropolymer manufacturing

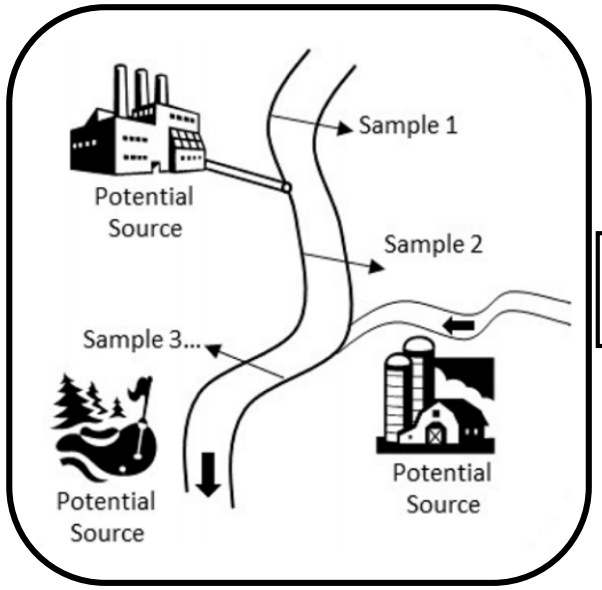
Little River: Airport, DOD, AFFF

Nakayama et al. **2007.** *ES&T* 41:5271-5276

Cape Fear Case Study: Water NTA

Environmental Science & Technology
November 2015
Article
pubs.acs.org/est

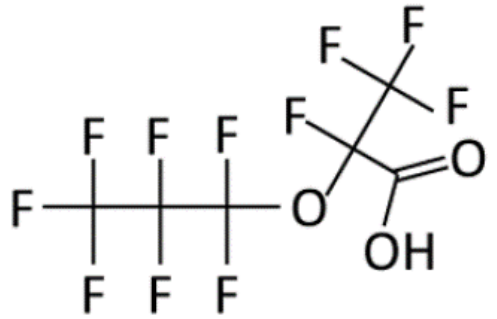
Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)



Sample Prep

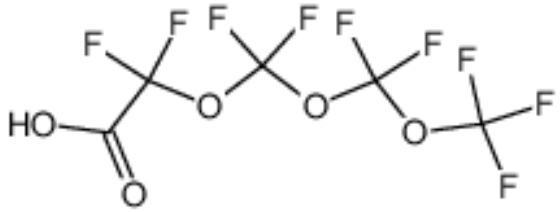
$$\frac{Sample\ 2\ (Experiment)}{Sample\ 1\ (Control)} = \text{Source 1}$$

$$\frac{Sample\ 3\ (Experiment)}{Sample\ 2\ (Control)} = \text{Source 2}$$



PFPrOPrA ("GenX")

monoethers (6)
polyethers (4)
sulfonates (2)

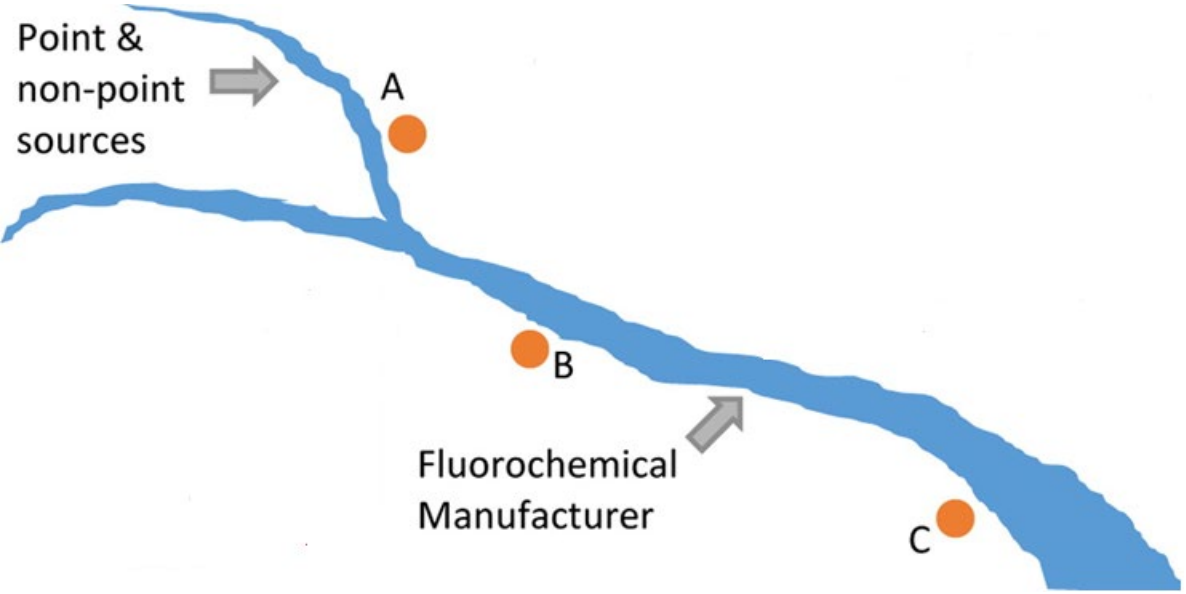


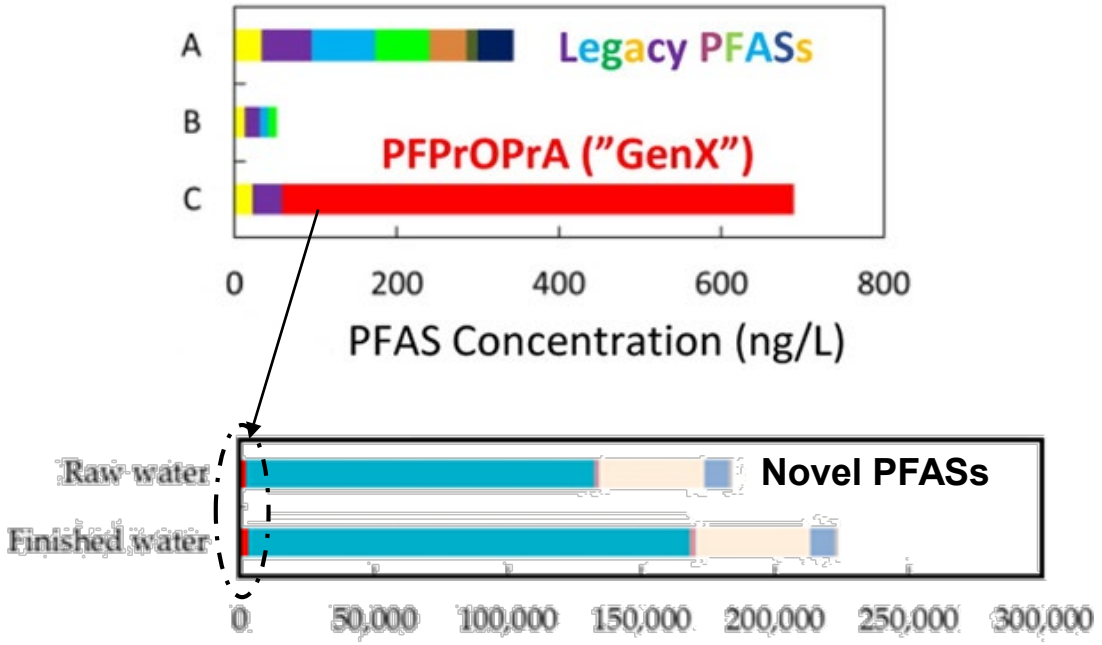
Strynar et al. **2015.** *ES&T* 49(19);11622–11630

Cape Fear Case Study: Water NTA

ENVIRONMENTAL Science & Technology LETTERS December 2016

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





Peak Area Counts of Emerging PFASs at Community C

Sun et al. **2016** *ES&T Letters* 3(12):415–419

NORTH CAROLINA
Environmental Quality

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Home » News » Key Issues » GenX Investigation

GenX Investigation

The N.C. departments of Environmental Quality (DEQ) and Health and Human Services (DHHS) began investigating the presence of a compound known as GenX in the Cape Fear River in June 2017. The Chemours facility in Fayetteville was identified as the company that produces the GenX chemical for industrial processes.

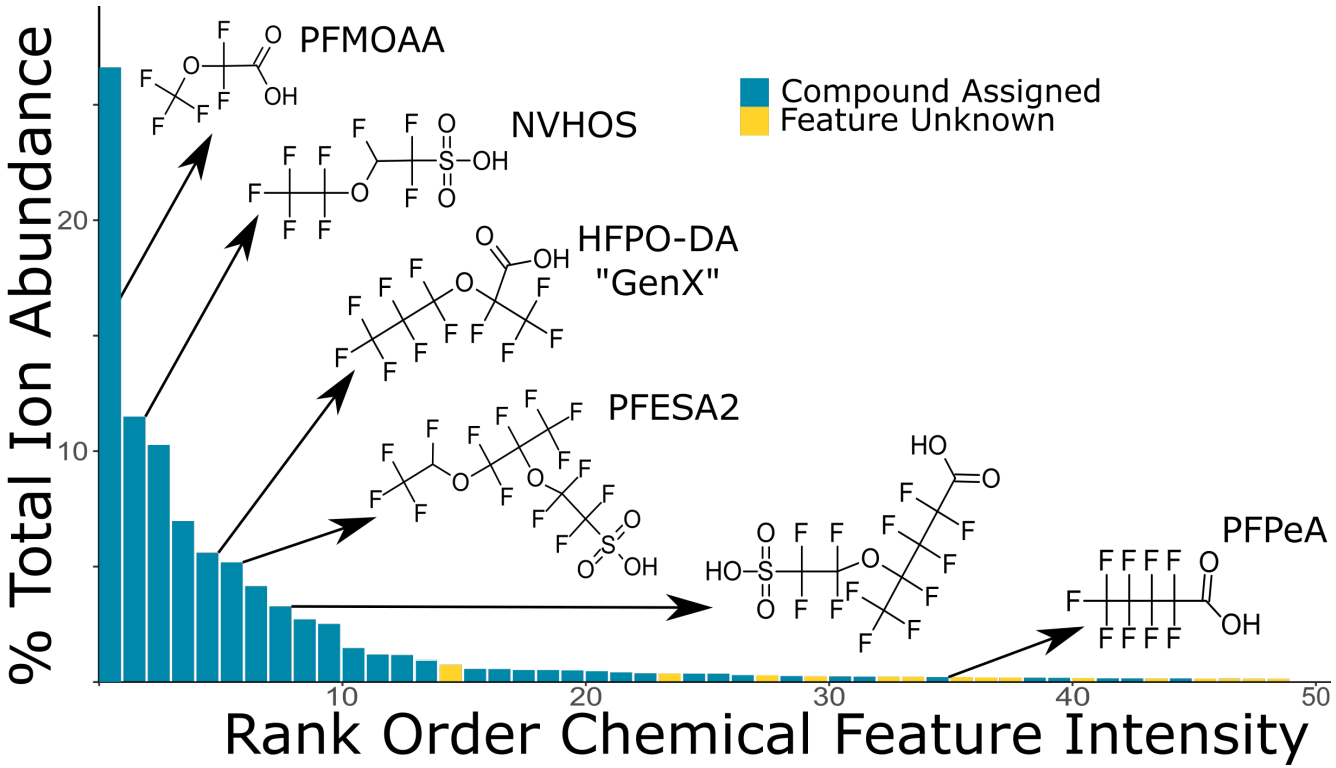
Key Issues

- DEQ Orders Coal Ash Closures
- GenX Investigation
  - Chemours Consent Order (February 2019)

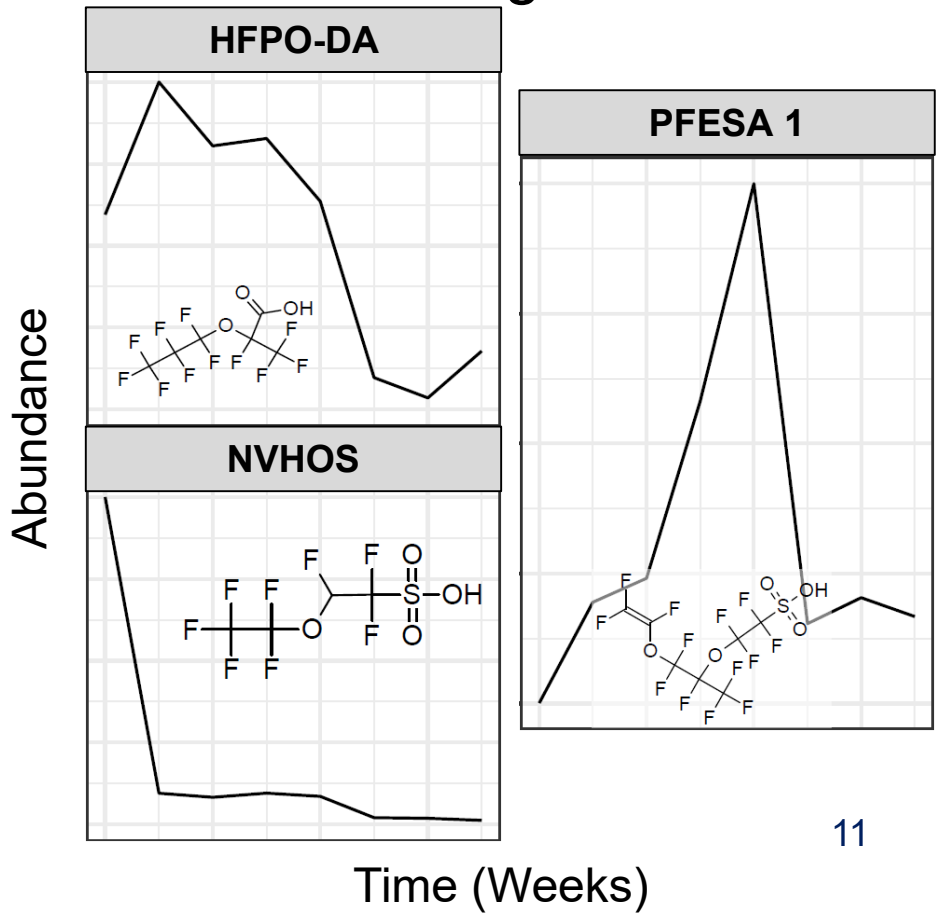
https://deq.nc.gov/news/key-issues/genx-investigation

Cape Fear Case Study: Water NTA Follow-up

37 Unique Chemical Formulae ID'd



Abundance Following Effluent Shutoff

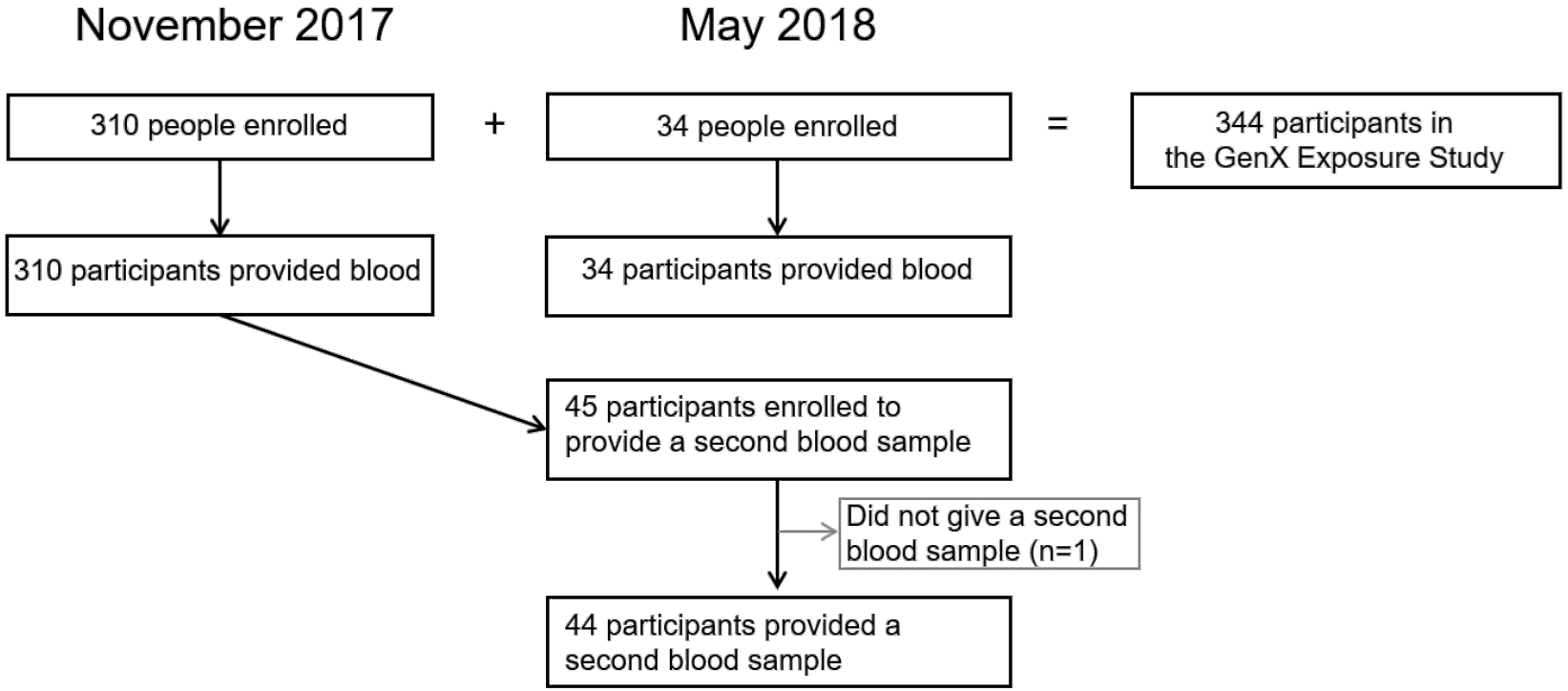


McCord et al. **2019**, *ES&T*, 53(*9*):4717-4727

Cape Fear Case Study: Serum Biomonitoring

NC State led GenX Exposure Study collected serum from Wilmington, NC Residents in 2017/2018. Analyzed at EPA

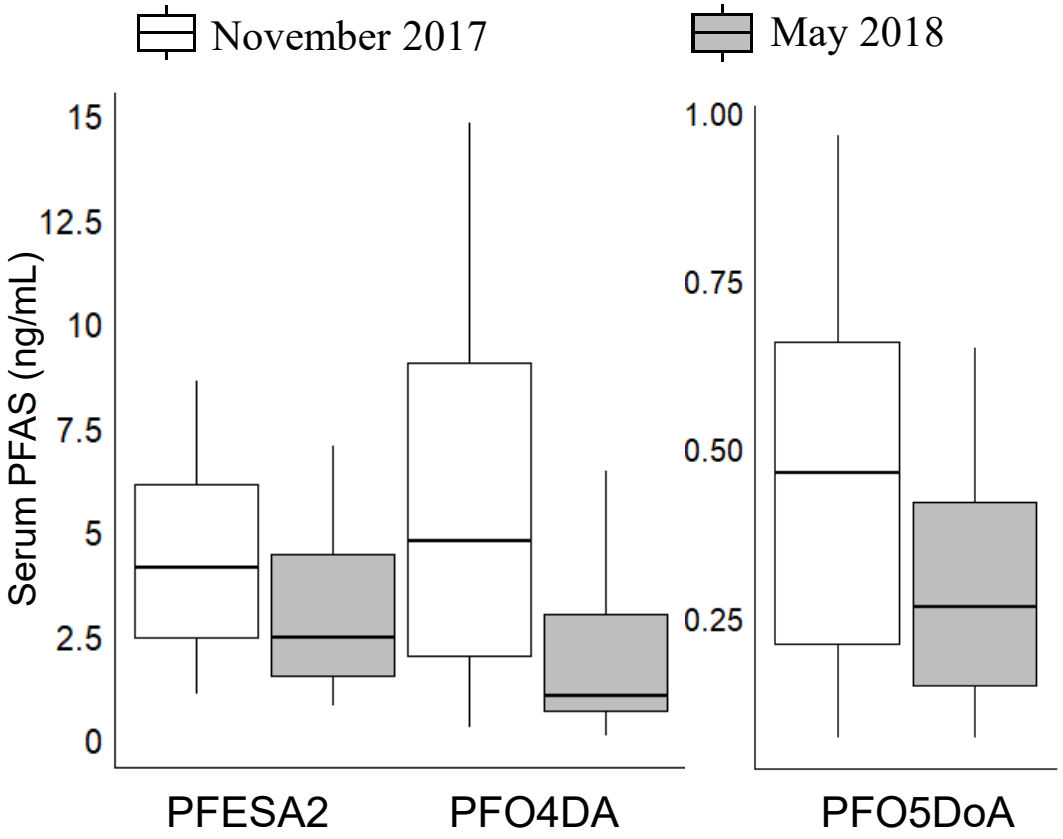
Are emerging PFAS detectable in exposed populations?



Kotlarz et al. **2020** *EHP – DOI 10.1289/EHP6837*

Cape Fear Case Study: Serum Biomonitoring

- No GenX detected in human serum
- Three emerging Chemours compounds detected in serum
- Decreasing serum levels after emissions shutoff, half-lives on the scale of months



Kotlarz et al. **2020** *EHP – In Press*

Cape Fear Case Study: Outcomes

- Chemours provided 12 novel compound standards to EPA, NC State University, NCDEQ based on Strynar 2015 & McCord 2019 NTA identifications
- NCDHHS GenX drinking water health target set @ 140 ppt[1]
  - Benchmark dose modeling from repeated oral dose studies in mice
- Feb 2019 consent order requires Chemours to monitor Strynar/McCord compound list monthly and show 99% reduction in PFAS emissions[2]
- Installation of air emission controls (thermal oxidizer), effectiveness study with NTA ongoing

1 - 10-30-2018-GenX-Report.pdf
2 - 2019-02-25-Consent-Order.pdf

NJ Case Study: Historical PFAS in West Deptford

New Jersey vs. National PFAA Detections in 2013-15
USEPA Unregulated Contaminated Monitoring Rule 3 (UCMR3)

Compound	Reporting Level (ng/L)	New Jersey PWS		National PWS other than NJ	
		# Detects*	% Detects	# Detects**	% Detects
PFOA (C8)	20	**19/175**	**10.9%**	**98/4745**	**2.1%**
PFNA (C9)	20	**4/175**	**2.3%**	**10/4745**	**0.2%**
PFOS (C8-S)	40	6/175	3.4%	89/4745	1.9%
PFHxS (C6-S)	30	2/175	1.1%	53/4745	1.1%
PFBS (C4-S)	90	0/175	0%	8/4745	0.2%
PFHpA (C7)	10	6/175	3.4%	80/4745	1.7%

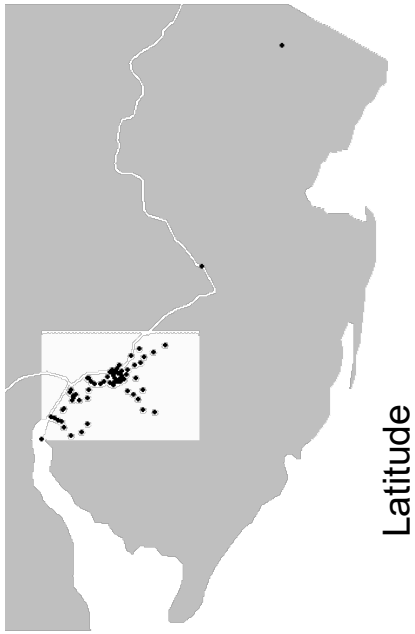
** New Jersey UCMR3 data. **USEPA data, Jan 2017.*

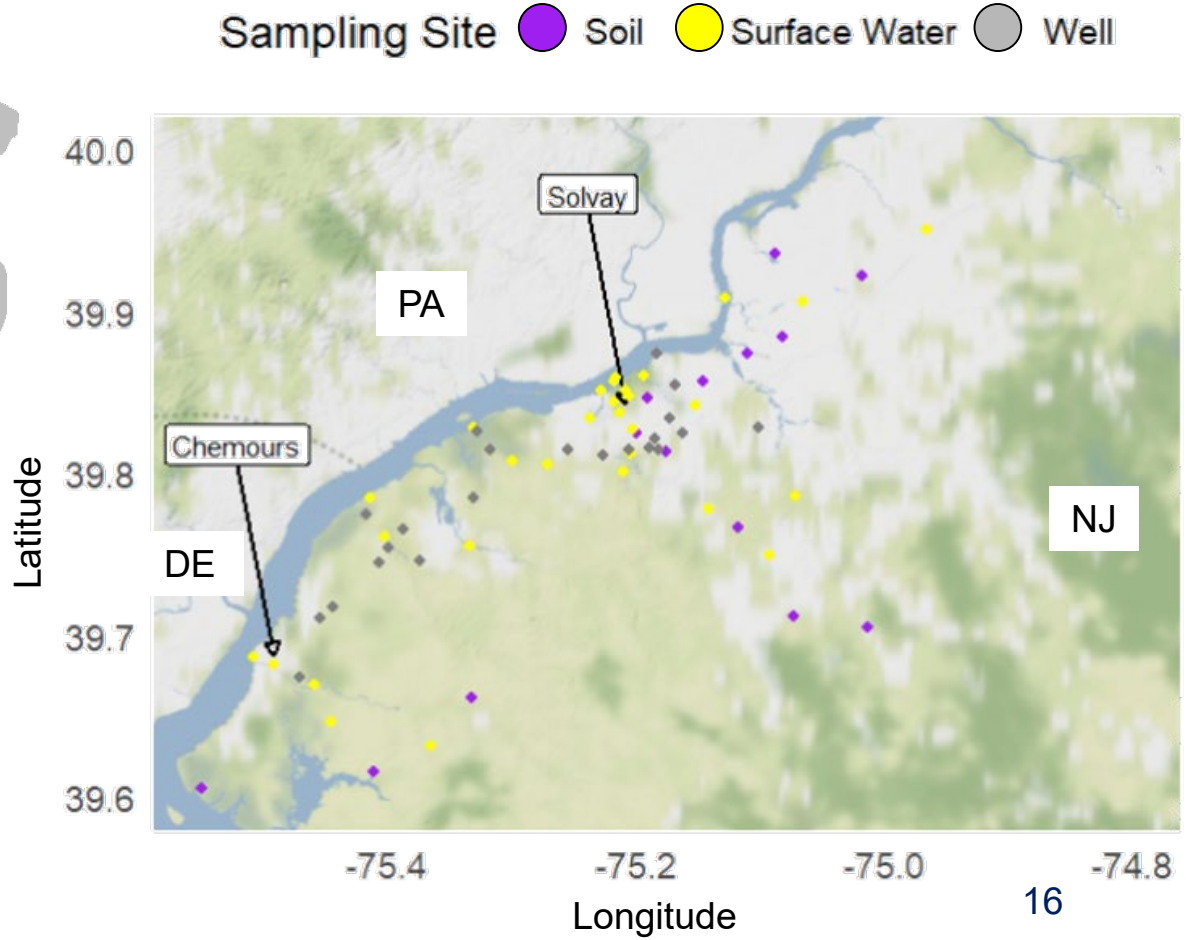
Industrial site(s) in West Deptford a primary source, with widespread contamination of water resources, and longstanding questions related to impact of airborne releases

Courtsey of Sandra Goodrow, NJDEP

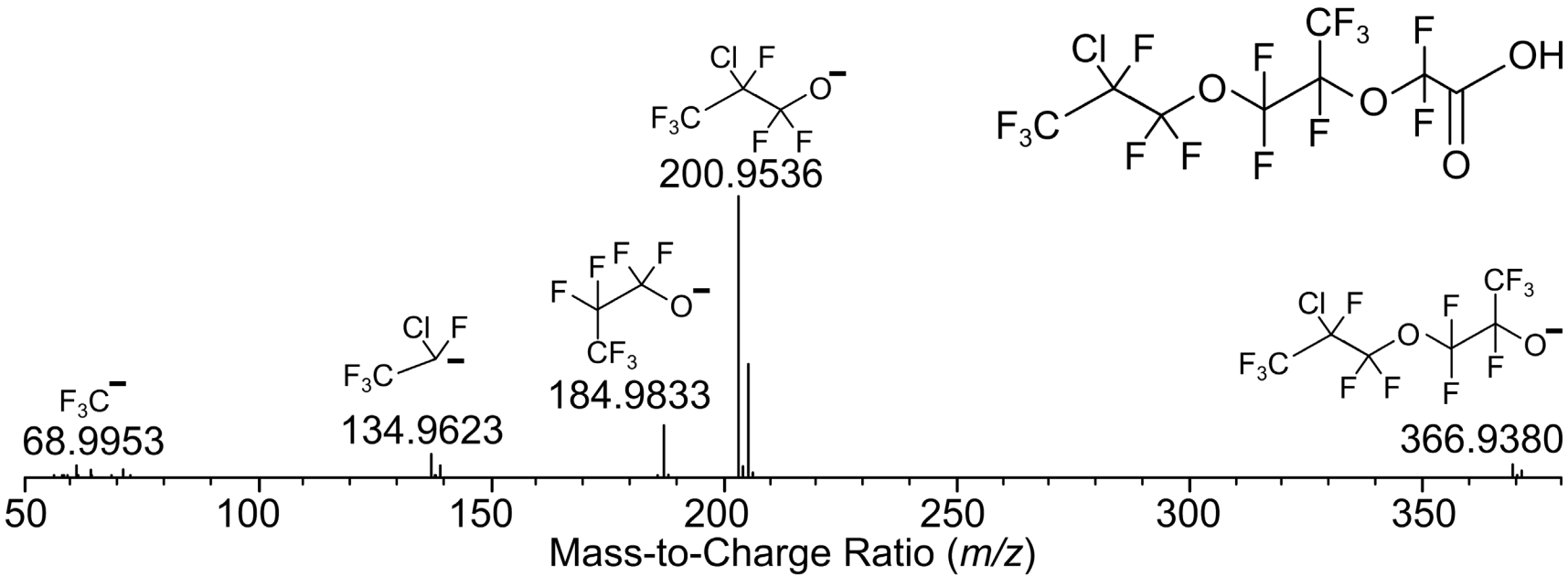
NJ Case Study: Multimedia Sampling in Southwest NJ

- NJDEP led collection of soil, surface, and groundwater
  - Is there contamination from new "replacement" PFAS since 2010?
  - Can we identify legacy and emerging PFAS source "fingerprints"?



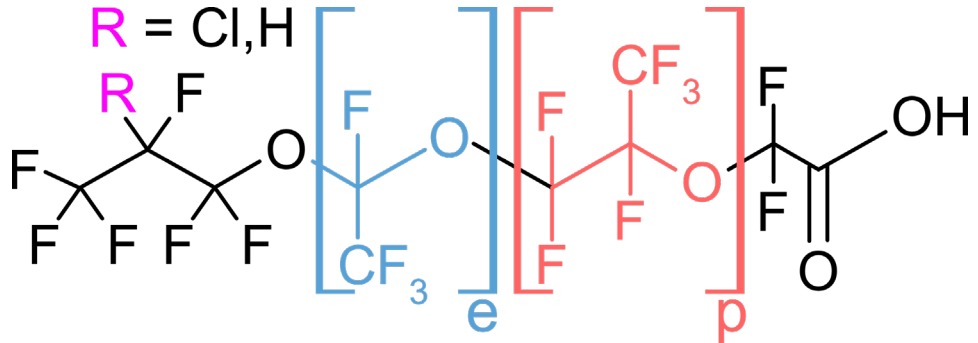


NJ Case Study: Structural Elucidation by MS/MS



Observed mix of e + p = 1 – 4
Chlorinated and dechlorinated analogs
Quantified ***as PFNA*** due to lack of standard

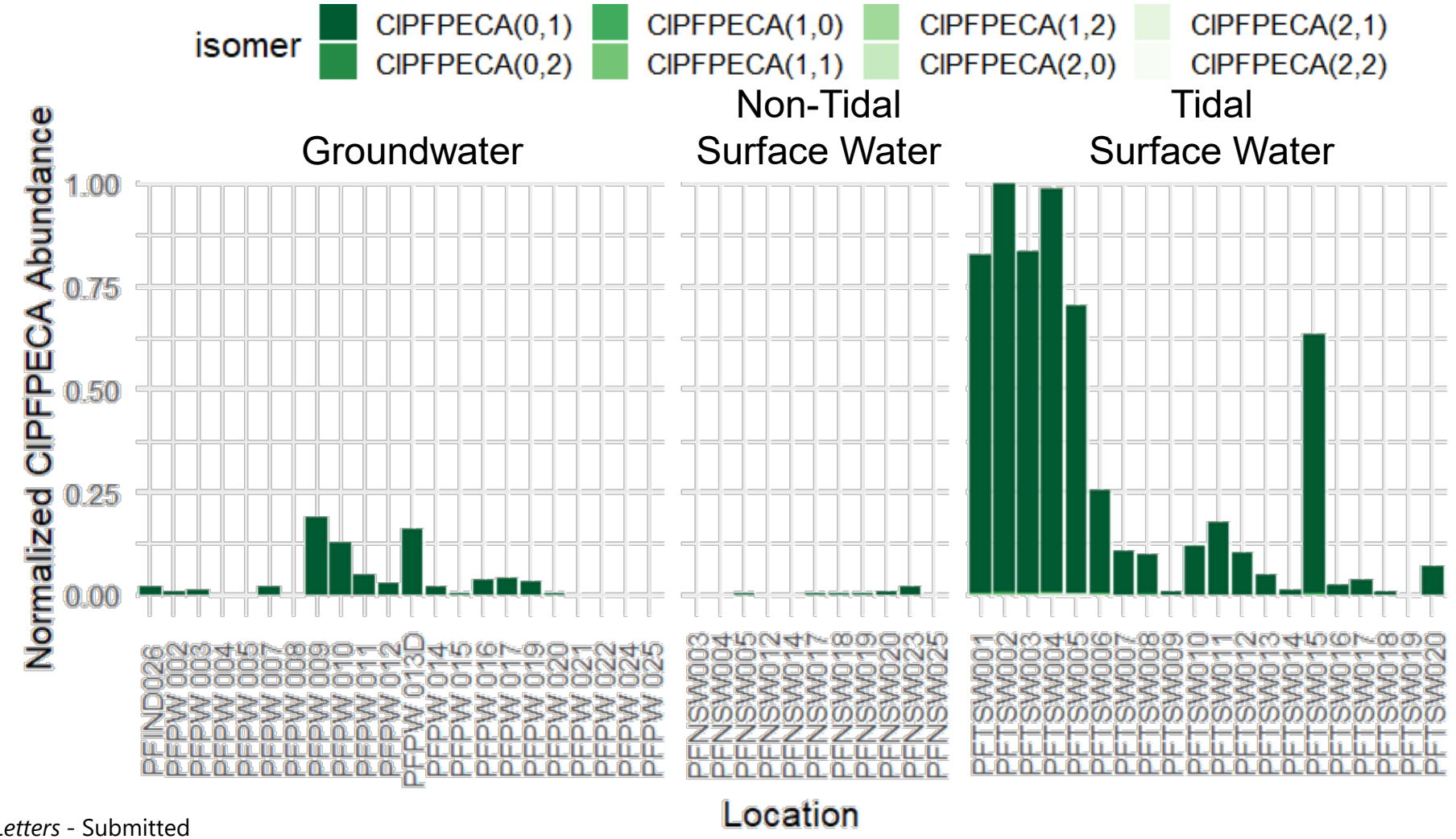
Perfluorochloroether carboxylic acid - ClPFPECA(e,p)



Washington et al. **2020**, *Science*, *368*(6495), 1103-1107

McCord et al. *ES&T Letters* - Submitted

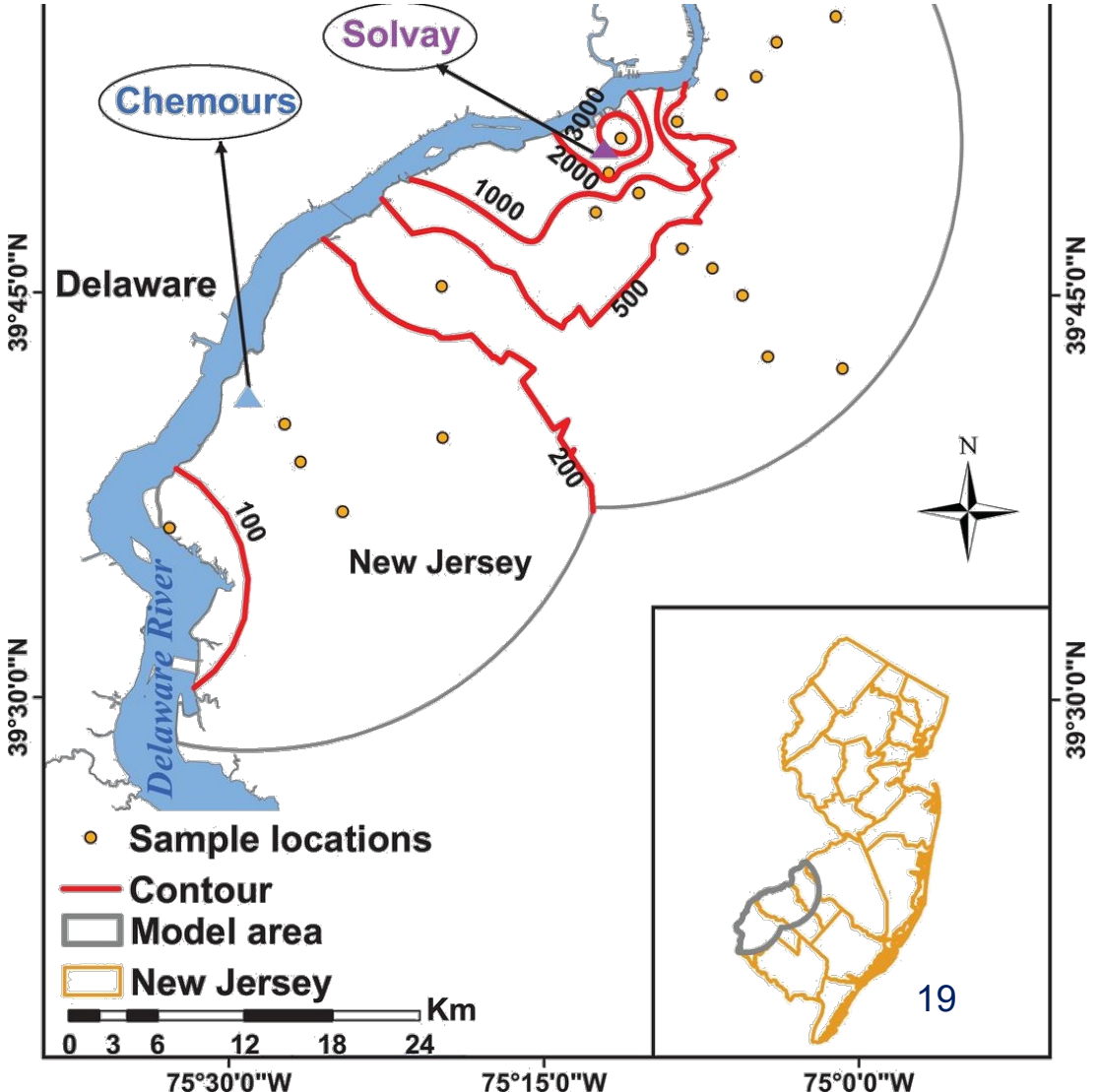
NJ Case Study: Surface and Groundwater Contamination



McCord et al. *ES&T Letters* - Submitted

NJ Case Study: Source Identification

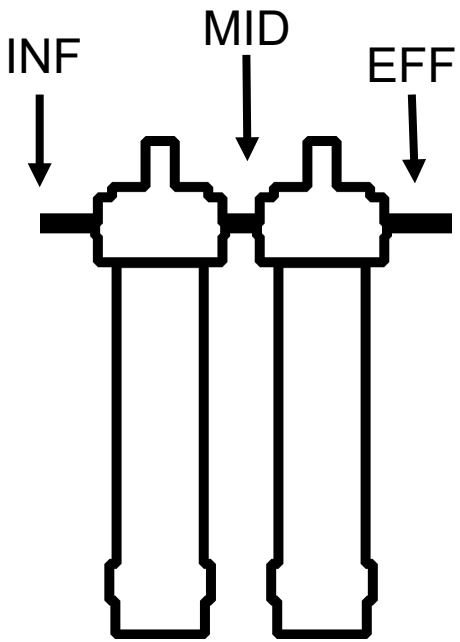
- Geographic trend in ClPFPECA abundance in soil indicating Solvay as chemical source
  - Contours from ∑ClPFPECAs in surface soils (pg/g) shown (right)
- Similar trends toward high abundance near Solvay seen in water sampling

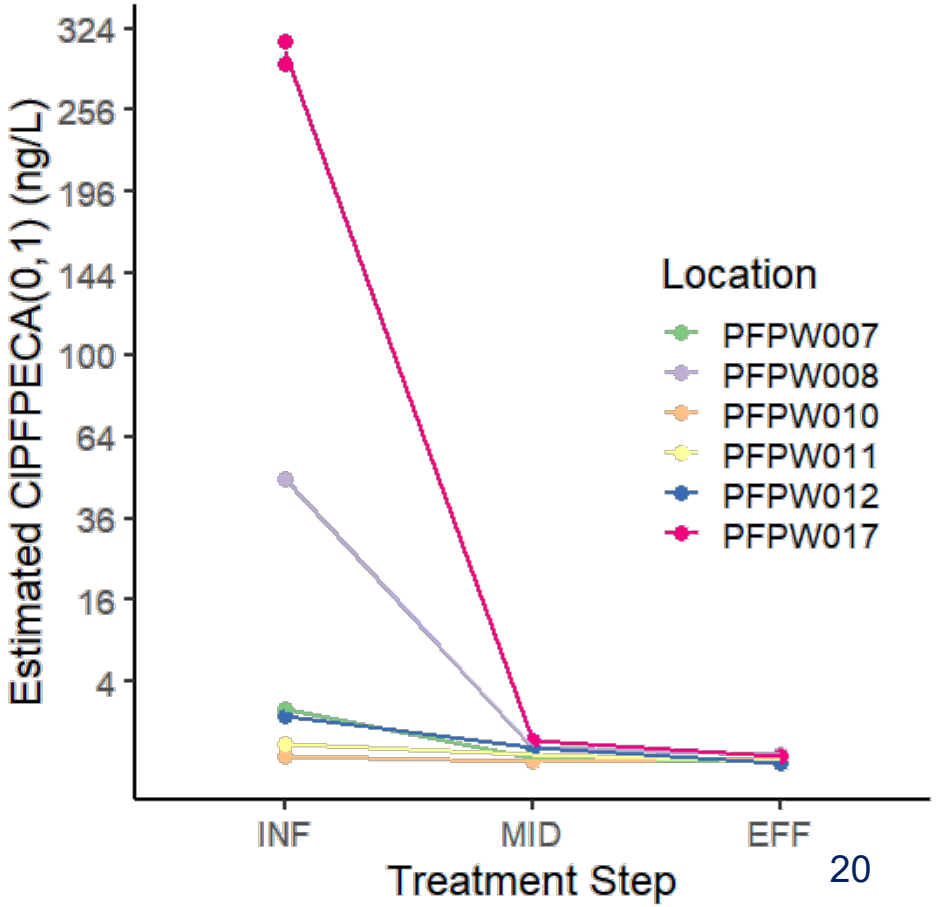


Washington et al. **2020**, *Science*, *368*(6495):1103-1107

NJ Case Study: POET Effectiveness

- Measured concentrations across two-stage point-of-entry treatment
- Reduction of emerging PFAS equivalent to legacy PFAS (95+%)





McCord et al. *ES&T Letters* - Submitted

NJ Case Study: Outcomes

- In-place treatment systems for PFNA seem effective at controlling emerging compounds
- Active request for ClPFPECA standards/stock materials for quantification
- Ongoing litigation between NJDEP and Solvay over PFAS emissions, cleanup, etc.; outcomes currently unclear
- Addition of emerging compound(s) to serum monitoring panel proposed for affected population

Conclusions

- NTA allows straightforward exploratory investigation of wide ranges of environmental media
- NTA is critical in the discovery and characterization of emerging PFAS
- Non-targeted data can support early stage monitoring and treatment experiments in absence of absolute quantitation
- Chemical standards and quantification methods remain necessary for risk assessment purposes

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- EPA/ORD
  - Mark Strynar
  - Andy Lindstrom
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  - Zack Hopkins
  - Jane Hoppin
- UNC Charlotte
  - Mei Sun
- NC DEQ
  - Chris Johnson
  - Linda Culpepper
- NJ DEP
  - Sandra Goodrow
  - Gloria Post
  - Erica Bergman
- Delaware River Basin Commission
  - Ron MacGillivray

Questions?

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