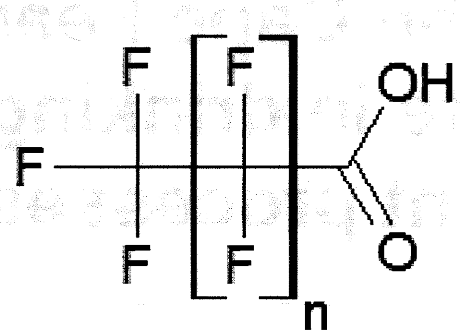
Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

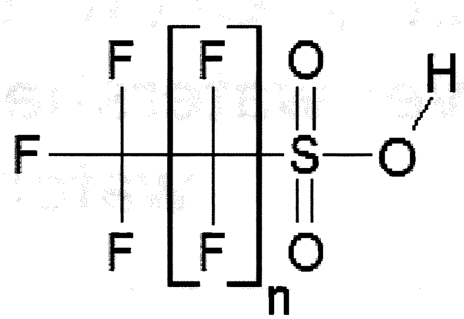
Mei Sun, Elisa Arevalo, Leigh-Ann Dudley,
Andrew Lindstrom, Mark Strynar, Detlef Knappe

NC STATE UNIVERSITY

Wilmington, April 19, 2017

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

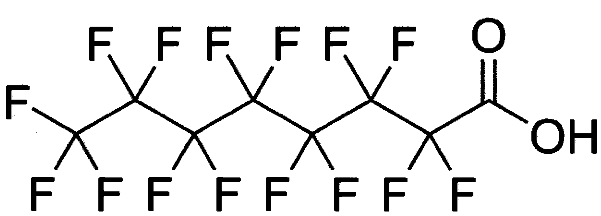


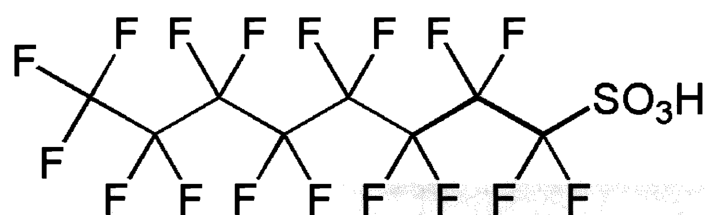


Long-chain PFASs:

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

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

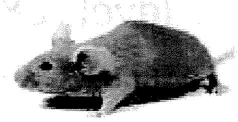




Long-chain PFASs have long half-lives in humans

- Half-lives in humans
  - PFOA: 3.8 years
  - PFOS: 5.4 years
  - PFBS: 4 months

- Toxicokinetic differences for PFOA
  - 17-19 days in mice
  - 4 hours in female rats



To protect the public from adverse health effects, health based guidelines have been established

EPA Health Advisory (chronic exposure) →	PFOS + C8: 70 ng/L
New Jersey guidance level (C8) and recommended MCL (C9) →	C8: 40 ng/L C9: 13 ng/L

Are PFASs a concern in US drinking water?

Six PFASs were included in the third Unregulated Contaminant Monitoring Rule (UCMR3)

Compound	MRL (ng/L)
Perfluoroheptanoic acid (PFHpA, C7)	10
Perfluorooctanoic acid (PFOA, C8)	20
Perfluorononanoic acid (PFNA, C9)	20
Perfluorobutanesulfonic acid (PFBS)	90
Perfluorohexanesulfonic acid (PFHxS)	30
Perfluorooctanesulfonic acid (PFOS)	40

Samples collected from January 2013 – December 2015
Public Water Systems (PWSs) serving >10,000 people

At first glance, UCMR3 data suggest low PFAS detection frequency

UCMR3 requires monitoring for six PFASs in US drinking water.
Monitoring began in 2013, and latest data release was January 2017.

PFAS	MRL (ng/L)	Occurrence (%)	Max. Concentration (ng/L)	Locations with high concentrations
C7	10	0.64	410	Saipan, PA, NY, DE, CO
C8	20	1.03	349	PA, MN, Saipan, DE, WV
C9	20	0.05	56	NJ, DE, PA, MA, NY
PFBS	90	0.05	370	GA, Saipan, CO, AL, PA
PFHxS	30	0.56	1,600	Saipan, AZ, DE, CO, PA
PFOS	40	0.79	7,000	Saipan, DE, CO, PA, WA

36,972 samples from 4,920 PWSs
PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)
Of samples with PFAS detects: 23.4% derived from surface water

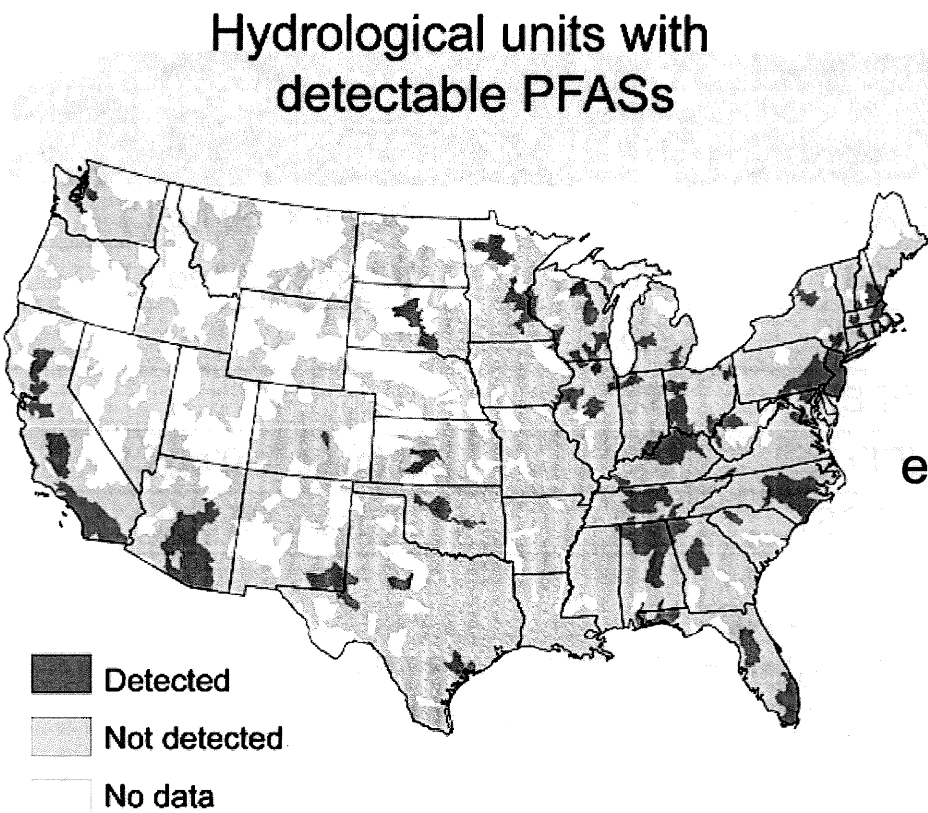
Some drinking water samples had PFOA+PFOS levels well above the HAL

UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

Compound	MRL (ng/L)	NC Detects
Perfluoroheptanoic acid (PFHpA, C7)	10	29 (max. 60 ng/L)
Perfluorooctanoic acid (PFOA, C8)	20	10 (max. 30 ng/L)
Perfluorononanoic acid (PFNA, C9)	20	0
Perfluorobutanesulfonic acid (PFBS)	90	0
Perfluorohexanesulfonic acid (PFHxS)	30	5 (max. 110 ng/L)
Perfluorooctanesulfonic acid (PFOS)	40	8 (max. 90 ng/L)

1,320 samples from 151 PWSs in NC
PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)
Of samples with PFAS detects: 79% derived from surface water

Elevated PFAS levels affect a sizeable number of US residents



PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

Hu et al. ES&T Letters (2016)

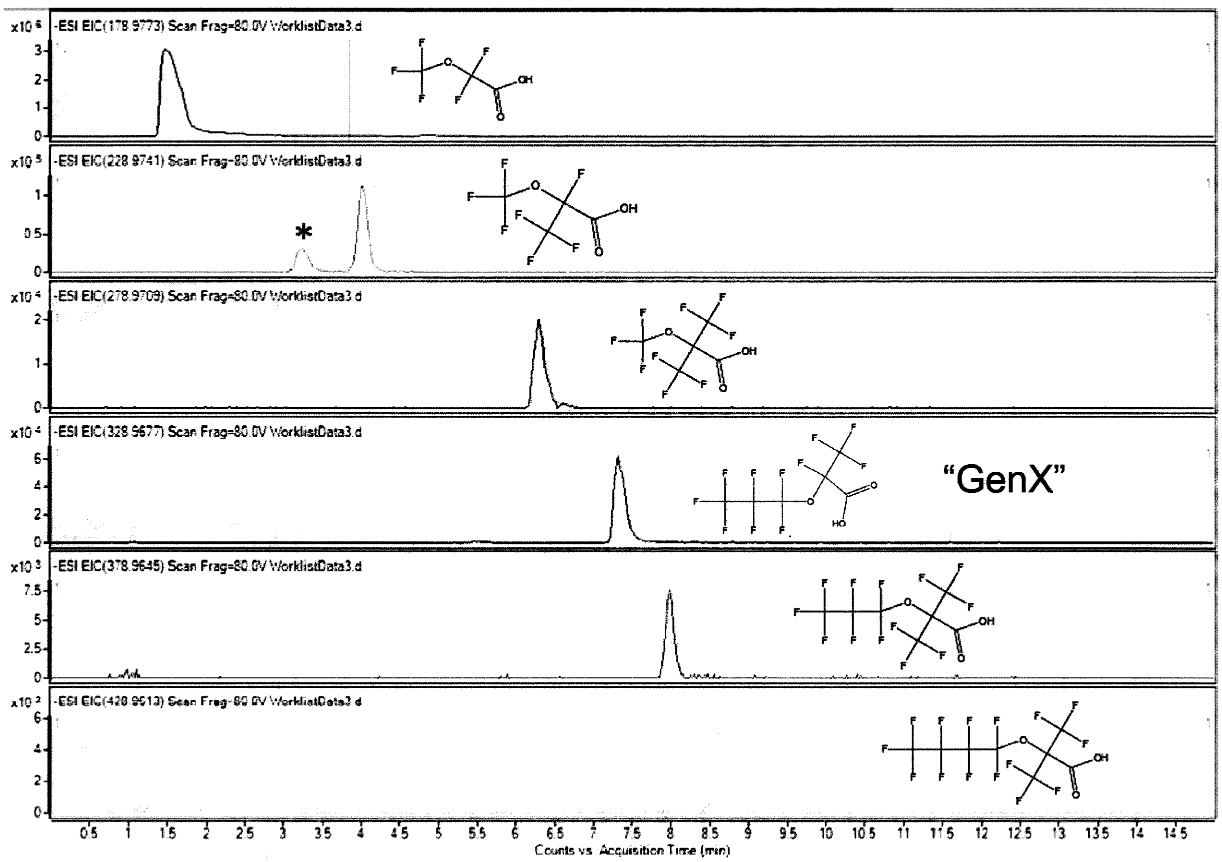
…but are we seeing the complete picture?

Many PFASs are used in commerce

PFASs	Class	Sub-classes of PFASs	Examples of Individual compounds*	Number of peer-reviewed articles since 2002**
PFASs ($C_nF_{2n+1}-R$)	perfluoroalkyl acids (PFAAs)	PFCAs ($C_nF_{2n+1}-COOH$)	PFBA (n=4)	928
			PFPeA (n=5)	698
			PFHxA (n=6)	1081
			PFHpA (n=7)	1186
			PFOA (n=8)	4066
			PFNA (n=9)	1496
			PFDA (n=10)	1407
			PFUnA (n=11)	1069
			PFDoA (n=12)	1016
			PFTrA (n=13)	426
			PFTeA (n=14)	587
		PFSAs ($C_nF_{2n+1}-SO_3H$)	PFBS (n=4)	654
			PFHxS (n=6)	1081
			PFOS (n=8)	3507
			PFDS (n=10)	340
		PFPAs ($C_nF_{2n+1}-PO_3H_2$)	PFBPA (n=4)	3
			PFHxPA (n=6)	33
			PFOPA (n=8)	31
			PFDPA (n=10)	35
		PFPiAs ($C_nF_{2n+1}-PO_2H-C_mF_{2m+1}$)	C4/C4 PFPiA (n,m=4)	4
			C6/C6 PFPiA (n,m=6)	12
			C8/C8 PFPiA (n,m=8)	12
			C6/C8 PFPiA (n=6,m=8)	8
		PFECAs & PFESAs ($C_nF_{2n+1}-O-C_mF_{2m+1}-R$)	ADONA ($CF_3-O-C_3F_6-O-CHFCF_2-COOH$)	4
			GenX ($C_3F_7-CF(CF_3)-COOH$)	26
			EEA ($C_2F_5-O-C_2F_4-O-CF_2-COOH$)	6
			F-53B ($Cl-C_6F_{12}-O-C_2F_4-SO_3H$)	14
> over 3000 PFASs may have been on the global market	PFAA precursors	PASF-based substances ($C_nF_{2n+1}-SO_2-R$)	MeFBSA (n=4,R=$N(CH_3)H$)	25
			MeFOSA (n=8,R=$N(CH_3)H$)	134
			EtFBSA (n=4,R=$N(C_2H_5)H$)	7
			EtFOSA (n=8,R=$N(C_2H_5)H$)	259
			MeFBSE (n=4,R=$N(CH_3)C_2H_4OH$)	24
			MeFOSE (n=8,R=$N(CH_3)C_2H_4OH$)	116
			EtFBSE (n=4,R=$N(C_2H_5)C_2H_4OH$)	4
			EtFOSE (n=8,R=$N(C_2H_5)C_2H_4OH$)	146
			SAmPAP {$[C_8F_{17}SO_2N(C_2H_5)C_2H_4O]_2-PO_2H$}	8
			100s of others	
		fluorotelomer-based substances ($C_nF_{2n+1}-C_2H_4-R$)	4:2 FTOH (n=4,R=OH)	106
			6:2 FTOH (n=6,R=OH)	375
			8:2 FTOH (n=8,R=OH)	412
			10:2 FTOH (n=10,R=OH)	165
			12:2 FTOH (n=12,R=OH)	42
			6:2 diPAP [$(C_6F_{13}C_2H_4O)_2-PO_2H$]	23
			8:2 diPAP [$(C_8F_{17}C_2H_4O)_2-PO_2H$]	25
			100s of others	
	others	fluoropolymers	polytetrafluoroethylene (PTFE)	
			polyvinylidene fluoride (PVDF)	
			fluorinated ethylene propylene (FEP)	
			perfluoroalkoxyl polymer (PFA)	
		perfluoropolyethers (PFPEs)		

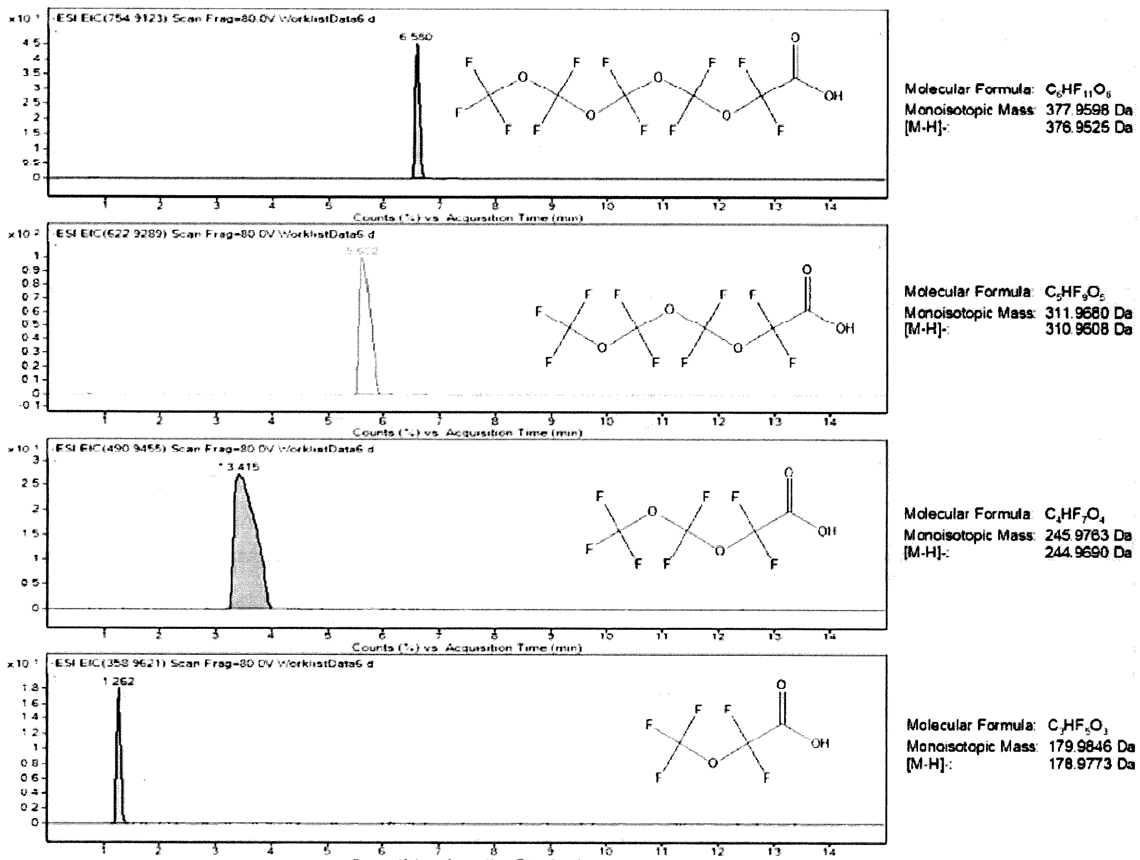
Wang et al. ES&T (2017)

Two series of PFECAs were recently discovered in the Cape Fear River



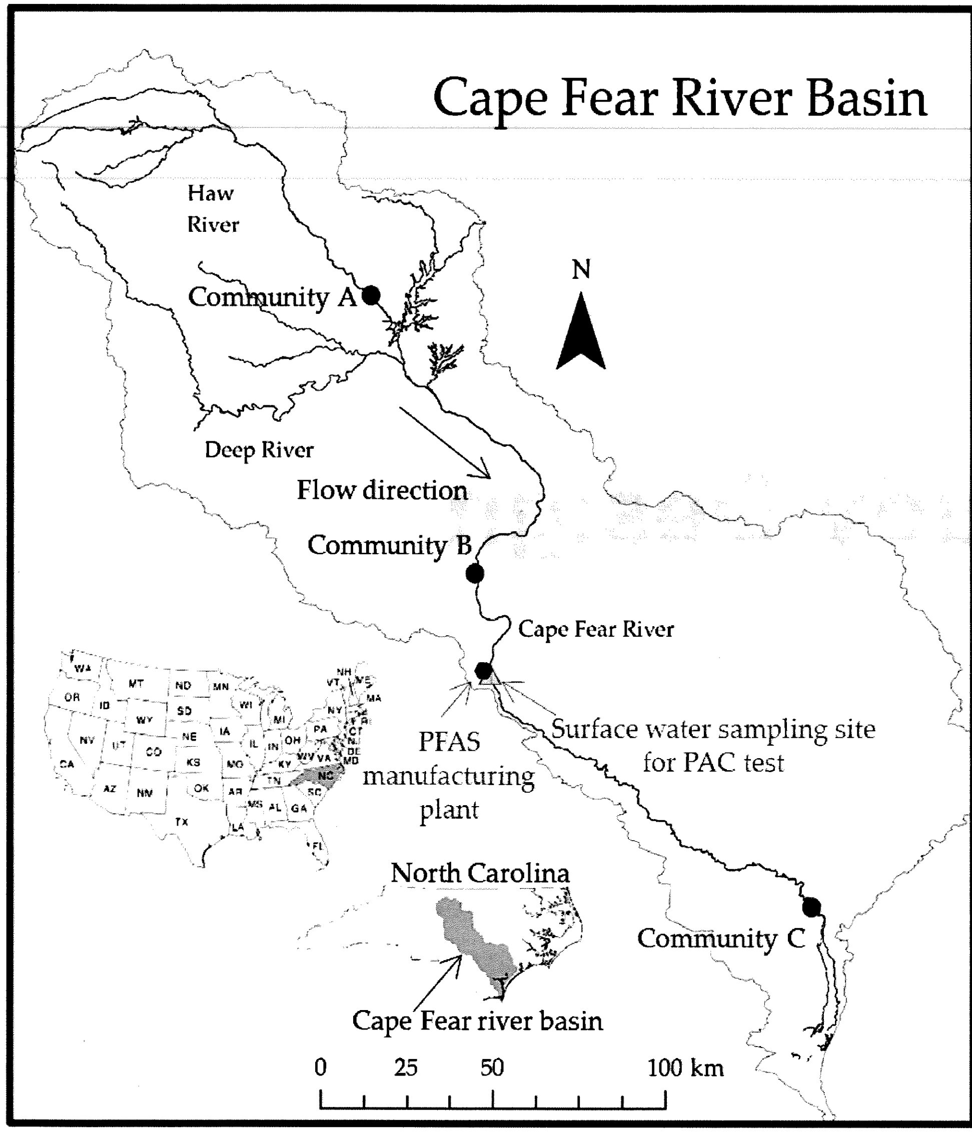
Strynar et al. ES&T (2015)

Two series of PFECAs were recently discovered in the Cape Fear River



Strynar et al. ES&T (2015)

Study Design



- Largest watershed in NC
- Supplies ~1.5M people with drinking water

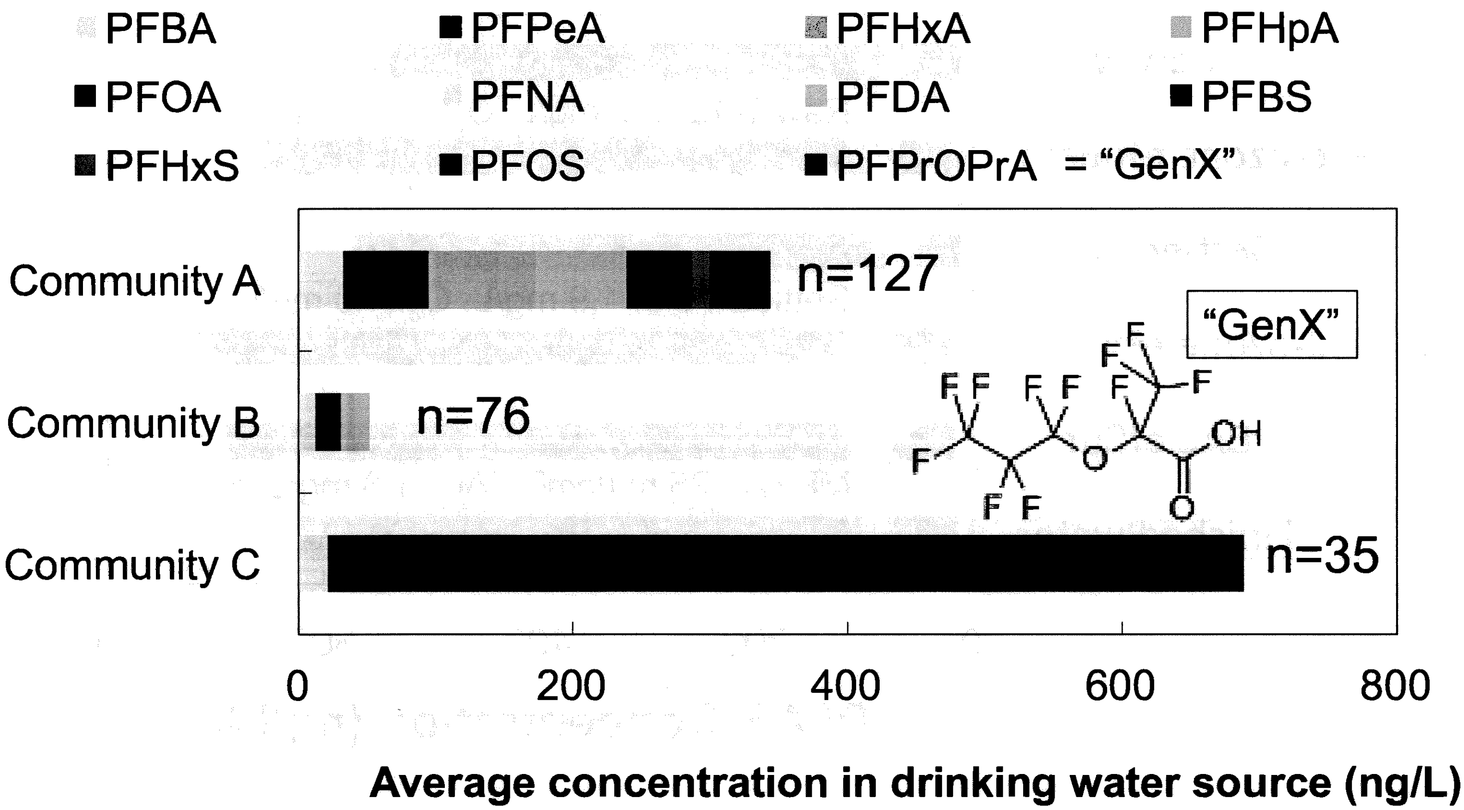
Sampling Protocol

- Samples collected in 1-L HDPE bottles
- Two sampling approaches
  - Daily composite samples of source water at three drinking water treatment plants
  - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection

PFAS Analytical Method

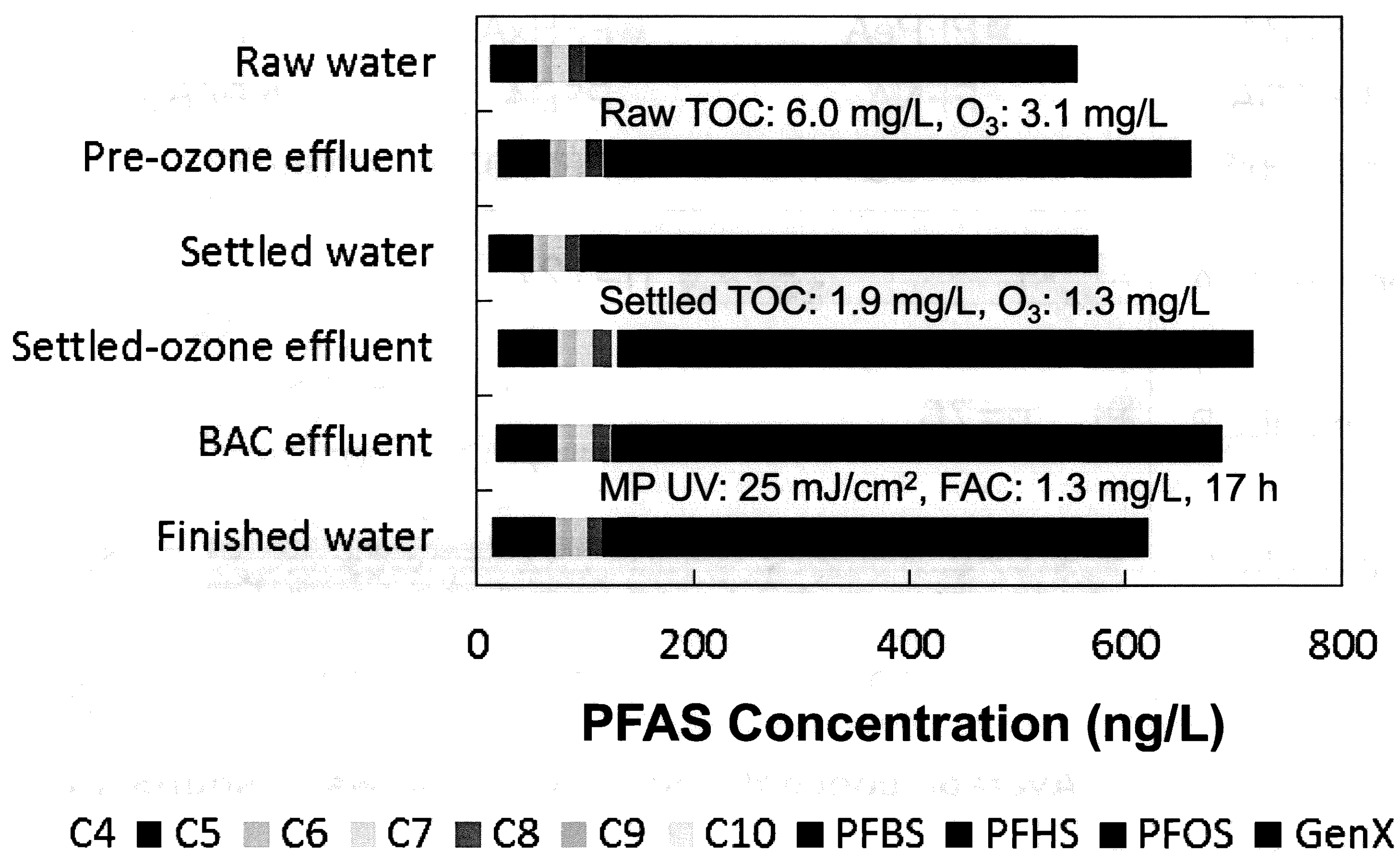
- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 µL)
- Sample and standard preparation:
  - filtration with a 0.45-µm glass fiber filter
  - addition of mass-labeled internal standards
  - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)

PFAS Occurrence in the CFR Watershed

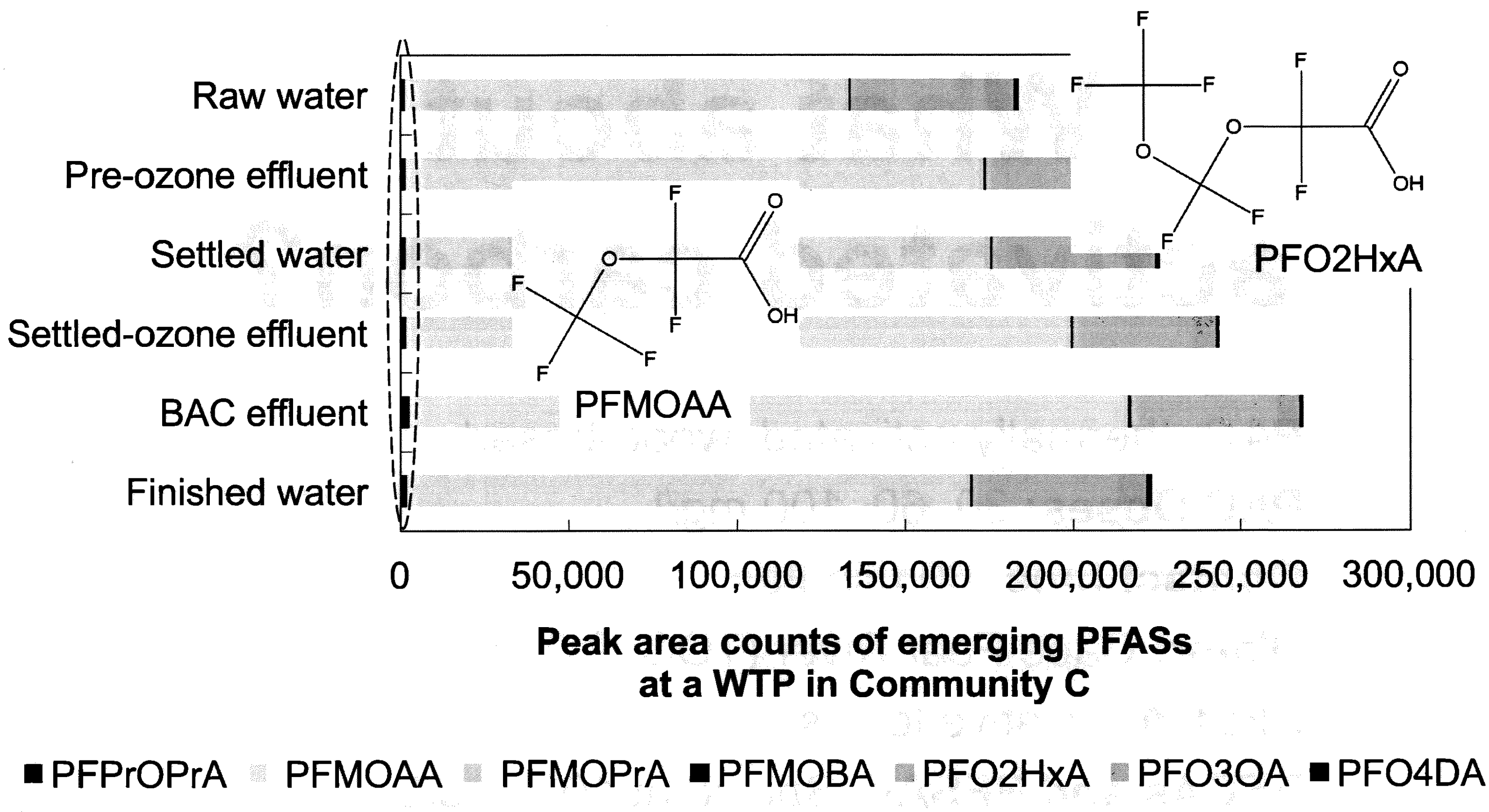


Sun et al. (2016) ES&T Letters

No measurable PFAS removal by conventional and advanced treatment



Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX

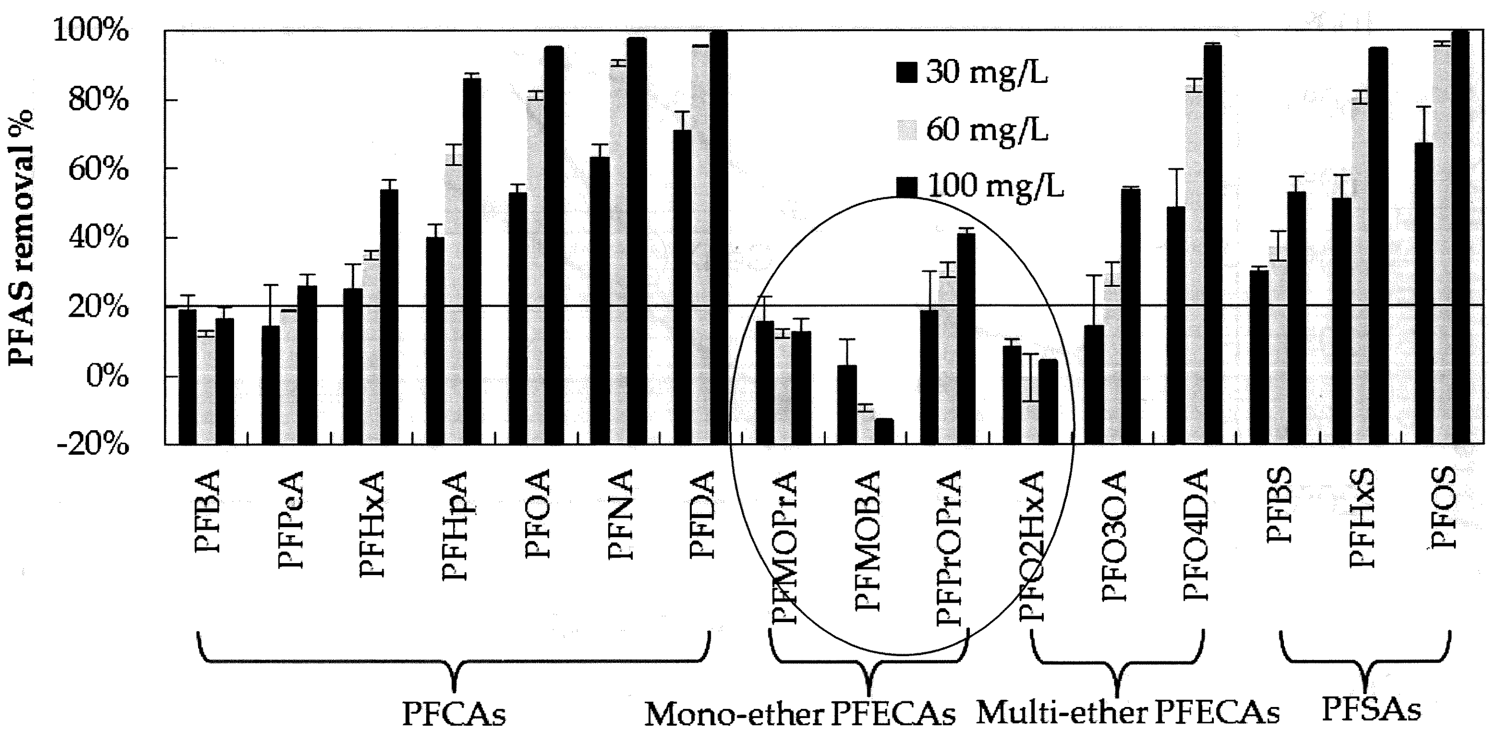


Sun et al. (2016) ES&T Letters

What about activated carbon?

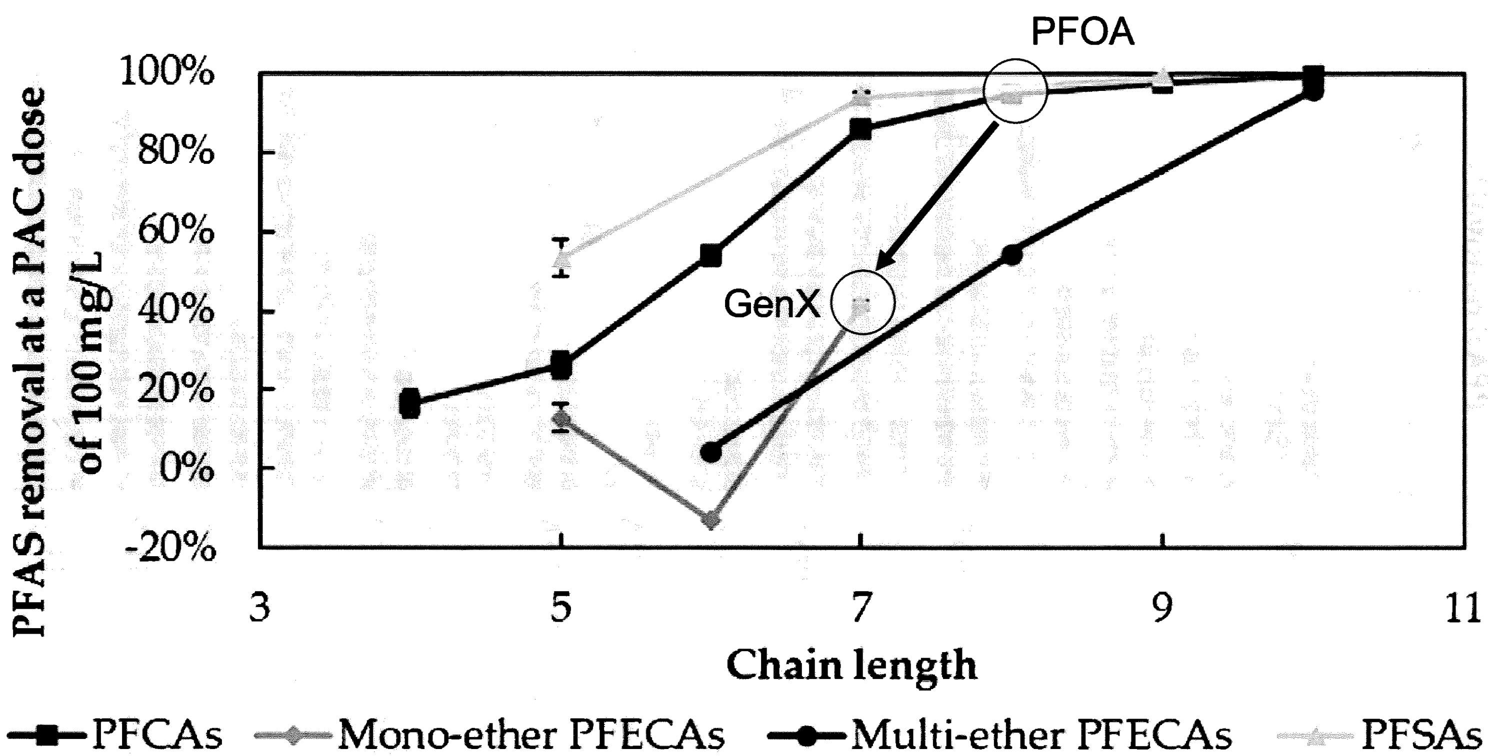
PAC: thermally activated, wood-based
PAC Doses: 30, 60, 100 mg/L
Contact time: 60 minutes
Water: Cape Fear River (TOC: 9.0 mg/L)
PFECAs: Native levels
PFCAs and PFSAs: Spiked at 1000 ng/L

Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable



Sun et al. (2016) ES&T Letters

PFAS adsorbability: PFSA>PFCA>PFECA

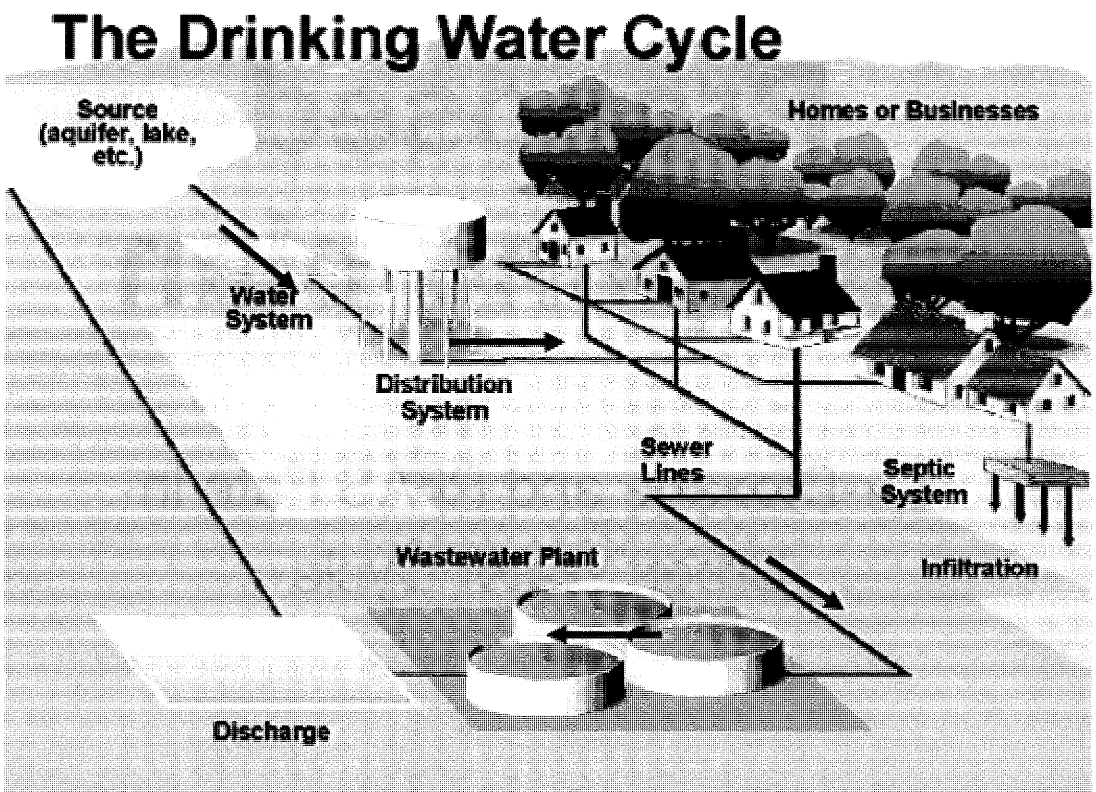


Sun et al. (2016) ES&T Letters

Proposed sampling plan

1,4-Dioxane and PFAS Fate in Urban Water Cycle

Objective 1: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle



Identify residence times/water ages at suitable sampling points to trace a parcel of water through the water/wastewater system

Objective 2: Determine fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR)

Sample monthly for one ASR cycle (ASR and monitoring wells)

- Recharge
- Storage
- Recovery

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV_{254} absorbance

Objective 3: Determine possible association of 1,4-dioxane and PFASs with biosolids

Measure 1,4-dioxane and PFAS concentrations in aqueous and solid phases of biosolids. Determine partition coefficients.

Target Audiences for Results

- CFPUA staff
  - Data expected to illustrate treatment/ operational challenges associated with PFASs and 1,4-dioxane
  - Demonstrate need for source control – eliminate PFASs and 1,4-dioxane at upstream NPDES discharge locations
- North Carolina DEQ
  - Raise awareness about treatment challenges with emerging contaminants
  - Expand scope of current 1,4-dioxane working group to start looking at possibilities for controlling PFAS sources

Acknowledgments

- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson, Ben Kearns at participating utilities

NC STATE UNIVERSITY

Shehee, Mina
Thursday, June 08, 2017 3:54 PM
'Cris Harrelson'
Moore, Zack; Staley, Danny
GenX detected in Cape Fear River

Dear Cris,

Currently, there is little health effect literature on the chemical making up "GenX" (2,3,3,3 -tetrafluoro-2-(heptafluoropropoxy)propionic acid, ammonium salt CAS # 62037-80-3). In the U.S. there are no regulatory levels for GenX in drinking water and no health guidelines. However, Dr. Risen found an assessment by the European Chemical Agency (https://echa.europa.eu/registration-dossier/-/registered-dossier/2679/7/1) which calculated a derived no effect level for oral exposure of 0.01 mg/kg/day.

I used the mean value cited in Sun et al 2016, 631 parts per trillion, as the concentration in drinking water and calculated reasonable maximum exposure doses for people drinking the water. The maximum dose was 0.00009 mg/kg/day, more than 100 times lower than the derived no effect level. Please note the samples taken for the Sun et al 2016 paper were collected in 2013-2014, so the concentrations of GenX in the waterway may be different now. This is an emerging contaminant so the OEEB toxicologists will continue to monitor the latest scientific literature.

We asked the cancer registry to look at likely cancers of the kidney, liver, testicular, and pancreas that could be expected in a similar compound (e.g. C8) in Brunswick and New Hanover Counties compared to the state rate. The rate and confidence interval comparisons do not show elevated rates of the selected cancers in these counties. Caution - this is only 6 years of data. Development of cancer can take decades.

Please let me know if you need any further from us.
Mina

Mina Shehee, PhD
Branch Head
Division Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

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1912 Mail Service Center
Raleigh, NC 27699-1912

Nothing Compares

Environmental
Quality

ROY COOPER
Governor

MICHAEL S. REGAN
Secretary

June 9, 2017

Mr. James Flechtner, PE
Executive Director
Cape Fear Public Utility Authority
235 Government Center Drive
Wilmington, N.C. 28403

Dear Mr. Flechtner:

Thank you for your June 7 letter regarding the presence of poly-fluoroalkyl substances present in the Lower Cape Fear River. We certainly understand the public concerns surrounding this issue and are working with the EPA and others to better understand the chemical compound and any potential impacts it may have.

It iss important that people know that drinking water from the Cape Fear Public Utility Authority and other utilities supplying consumers in the Lower Cape Fear Region meets all state and federal drinking water standards. Thank you for reinforcing that message with your customers and the media in the recent articles on this topic.

The EPA is the sole agency responsible for establishing drinking water standards nationwide. The federal agency has extensive resources necessary to determine the nature, extent and potential impacts of chemicals such as GenX. As such, the North Carolina Department of Environmental Quality is awaiting guidance from the EPA that will provide our agency with the information needed to begin developing regulatory limits for GenX.

We recognize that the regulatory process can sometimes take considerable time. While we are awaiting guidance from the EPA, staff in DEQ will be working with Chemours to assess waste streams containing GenX and determine if the company can reduce the amount of the chemical compound being discharged to the river. I am also working closely with staff and health experts at the N.C. Department of Health and Human Services to stay abreast of any new developments from the numerous interested stakeholders so we will can take swift action to address public health concerns.

Our No. 1 priority in DEQ is to protect public health and the environment. That is the mission that guides us. Please feel free to reach out to me at Sheila.Holman@ncdenr.gov or 919-707-8619 if you have questions, concerns or suggestions. I look forward to working with you.

Sincerely,

Sheila Holman
Assistant Secretary for the Environment

Roy Cooper, Governor

Michael S. Regan, Secretary

Environmental Quality

Release: IMMEDIATE
Date: June 13, 2017

Contact: Jamie Kritzer; Chris Mackey
Phone: 919-707-8602; 919-855-4840

DEQ leading investigation of reports of unregulated chemical in Cape Fear River

RALEIGH – The N.C. Department of Environmental Quality is leading a state investigation into reports of an unregulated chemical in the Cape Fear River.

Staff in DEQ ~~and~~ with assistance from the state Department of Health and Human Services are investigating the reported presence of a compound known as GenX and the company, Chemours, that produces the chemical for industrial processes at its facility in Fayetteville.

State environmental regulators will start collecting water samples from the Cape Fear River and will send those to the nation's only laboratory capable of detecting GenX in water. After meeting with DEQ staff this week, Chemours agreed to pay for the water collection and testing.

"We are seeking answers and solutions to a problem that has prompted understandable concern among people who live and work in Wilmington and the lower Cape Fear region," said Michael Regan, secretary of the state Department of Environmental Quality. "We are taking a hard look at the quality of the region's source of drinking water and pushing the company to find ways to limit how much of this chemical makes its way to the river."

Mandy Cohen, the secretary of the N.C. Department of Health and Human Services, said XXXX

There are no U.S. regulatory guideline levels for GenX. However, as part of the European chemical registration, a 2-year chronic toxicity and cancer study with rats was performed. They reported a Derived No Effect Level of 0.01 mg/kg bw/day. Based on U.S. risk assessment calculations, this corresponds to a concentration in drinking water of 70,909 ng/L of GenX- more than 100 times greater than the mean value of 631 ng/L detected in the Cape Fear River. Based upon these data, the GenX levels detected in 2013-2014 would be expected to pose a low risk to human health.

Leadership in DEQ have reached out to staff with the Environmental Protection Agency seeking information about GenX. The EPA, which is the sole agency responsible for establishing drinking water standards, is working to establish guidance on GenX that North Carolina and other states can use to develop regulations for the chemical compound.

At the same time, DEQ staff are also pushing Chemours officials to limit the amount of GenX making its way into the river. A Chemours official said during a meeting this week with state environmental regulators that officials with the company were working to assess waste streams containing GenX and determine if the company can reduce the amount of the chemical compound being discharged to the river.

# # #

③

DS Burton
Director Strategy

Level Set

① Ummunhon waste stream
and points down stream

② DW Supplies
near-term data
to be collected

| 2 weeks turn around
| time 3-4 weeks
TOTAL

another 3 weeks of Poly Prop
production sample
once a week and
After producing Poly prop.

Tarheel too

Michael Scott

↓

Gen X?
Chechonit
(Dupont)

polypropylene
vinyl ether → Process

6 weeks @ a time

small amount
waste stream ← seed stock

Make
Ether
6 months out of
year

under subpoena
Sheila Holman
Jamie Kritzer

EPA: Region 4
HQ order Consent
Agreement - Global
WVA INC no data
submitted by Company.

• TSCA reports
self reporting
from Industry

Mike Johnson
NO one asked
Fay Chemours for
data → will
get the data

50 lbs

HFPO
↑
Gen X
Family
byproduct
Vinyl ether
production

Roy Cooper, Governor

Michael S. Regan, Secretary

Environmental
Quality

Release: IMMEDIATE
Date: June 14, 2017

Contact: Jamie Kritzer; Chris Mackey
Phone: 919-707-8602; 919-855-4840

DEQ, DHHS investigating reports of unregulated chemical in Cape Fear River

RALEIGH – The N.C. Department of Environmental Quality is leading a state investigation regarding reports of an unregulated chemical in the Cape Fear River.

Staff in DEQ, in consultation with state Department of Health and Human Services, are investigating the presence of a compound known as GenX. DEQ is strongly encouraging Chemours, the company that produces the chemical for industrial processes at its facility in Fayetteville, to identify any measures that can be taken to reduce the discharges of the chemical to the river until the state completes its investigation. DEQ is also pushing the Environmental Protection Agency to provide regulatory guidance on GenX.

State environmental regulators will collect water samples from the Cape Fear River in the coming days and will send those to a laboratory capable of detecting GenX in water at low concentrations. The laboratory has indicated that the materials the state is required to use for the water collection and testing should arrive next week. DEQ staff are prepared to mobilize as soon as the sample materials arrive from the lab. After meeting with DEQ staff this week, Chemours agreed to bear all costs for the water collection and testing. The laboratory, which is in Colorado, has indicated that the first test results will likely be available four weeks from when they are received, but multiple rounds of testing and analysis will be necessary for a meaningful evaluation of the water quality.

"We are seeking answers and solutions to a problem that has prompted understandable concern among citizens who live and work in Wilmington and the lower Cape Fear region," said Michael Regan, secretary of the state Department of Environmental Quality. "We are taking a hard look at the quality of the region's source of drinking water and pushing the company to find ways to limit how much of this chemical makes its way to the river."

Mandy Cohen, the secretary of the N.C. Department of Health and Human Services, said: "The department has a history of close collaboration with DEQ to protect the health of North Carolinians. We are working closely with DEQ to understand and communicate the potential health risks of GenX."

Staff at DHHS also have initiated daily conference calls with local health departments in the lower Cape Fear region to share the latest information on this issue.

There are no U.S. regulatory guideline levels for GenX. However, based on available published research, the levels of GenX that were detected in the Cape Fear River in 2013-14 are at levels that pose a minimal health risk. This is a relatively new chemical, and the health effects are not fully understood at the current time.

"A sampling event from 2014 is the most recent data that shows GenX present in the Cape Fear, which makes obtaining new data critical," Regan said.

Leadership in DEQ have reached out to staff with the Environmental Protection Agency seeking information about GenX. The EPA, which is the lead agency responsible for establishing drinking water standards, is working to establish guidance

-more-

on unregulated compounds such as GenX that North Carolina and other states can use to develop potential regulations for the chemical compound.

More recent data will be available for analysis following the water sampling underway in the coming days.

DEQ staff are pushing Chemours officials to limit the amount of GenX making its way into the river. A Chemours official told state environmental regulators this week that the company is working to assess waste streams containing GenX and determine whether the company can reduce the amount of GenX discharged to the river under current production levels.

DEQ and DHHS leadership plan to participate in a meeting convened by local officials on Thursday to establish the next steps in addressing this issue.

###

Shehee, Mina

From: Langley, Rick
Sent: Thursday, June 15, 2017 8:45 PM
To: Shehee, Mina; Holt, Kennedy; Moore, Zack; Risen, Amy J
Subject: Fw: GenX and Cape Fear River

fyi

From: Langley, Rick
Sent: Thursday, June 15, 2017 8:43 PM
To: Lea, Suzanne
Subject: Re: GenX and Cape Fear River

ok, thanks for info. Will let you know

From: Lea, Suzanne <LEAC@ecu.edu>
Sent: Thursday, June 15, 2017 3:19:54 PM
To: Langley, Rick
Subject: GenX and Cape Fear River

Hi Rick,

Greg Kearney mentioned today that you were answering questions about the GenX exposure issue.
Detlef Knappe asked me two weeks ago to help him design a study to sample people in Wilmington to measure PFOA/GenX family compounds.
Let me know if I can help DPH/DEQ.
-Suzanne Lea

C. Suzanne Lea, PhD, MPH
Associate Professor, Epidemiology
Department of Public Health | Brody School of Medicine | East Carolina University
Greenville, NC 27834
Office. 252-744-4036 | Email. Leac@ecu.edu

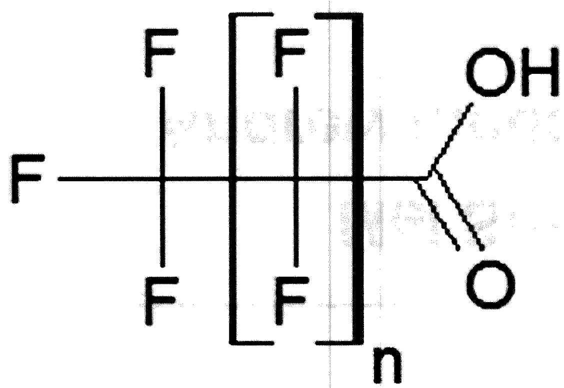
Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

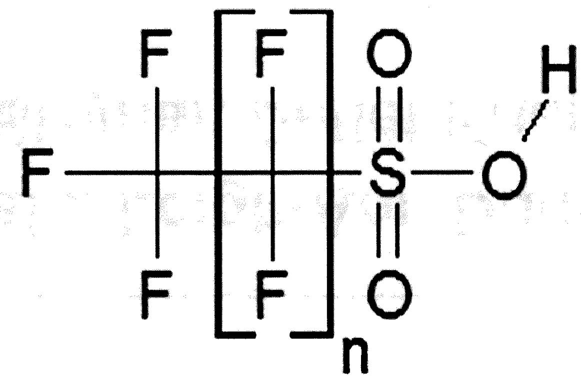
Mei Sun, Elisa Arevalo, Leigh-Ann Dudley,
Andrew Lindstrom, Mark Strynar, Detlef Knappe

NC STATE UNIVERSITY

NC DEQ
Raleigh, June 16, 2017

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

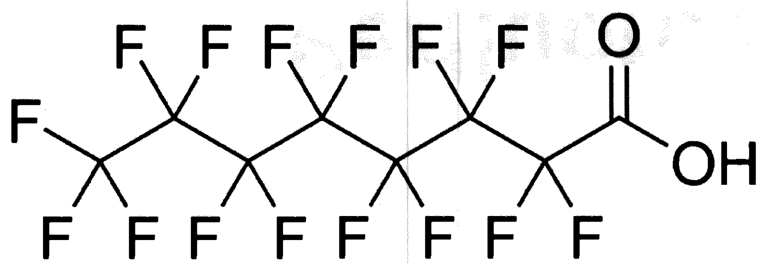


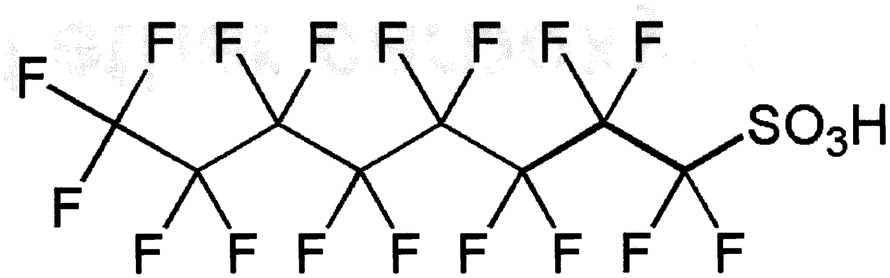


Long-chain PFASs:

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

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





To protect the public from adverse health effects, health based guidelines have been established

EPA Health Advisory (chronic exposure)	→	PFOS + C8: 70 ng/L
New Jersey recommended MCLs	→	C8: 14 ng/L C9: 13 ng/L

At first glance, UCMR3 data suggest low PFAS detection frequency

UCMR3 requires monitoring for six PFASs in US drinking water.
Monitoring began in 2013, and latest data release was January 2017.

PFAS	MRL (ng/L)	Occurrence (%)	Max. Concentration (ng/L)	Locations with high concentrations
C7	10	0.64	410	Saipan, PA, NY, DE, CO
C8	20	1.03	349	PA, MN, Saipan, DE, WV
C9	20	0.05	56	NJ, DE, PA, MA, NY
PFBS	90	0.05	370	GA, Saipan, CO, AL, PA
PFHxS	30	0.56	1,600	Saipan, AZ, DE, CO, PA
PFOS	40	0.79	7,000	Saipan, DE, CO, PA, WA

36,972 samples from 4,920 PWSs
PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)
Of samples with PFAS detects: 23.4% derived from surface water

Some drinking water samples had PFOA+PFOS levels well above the HAL

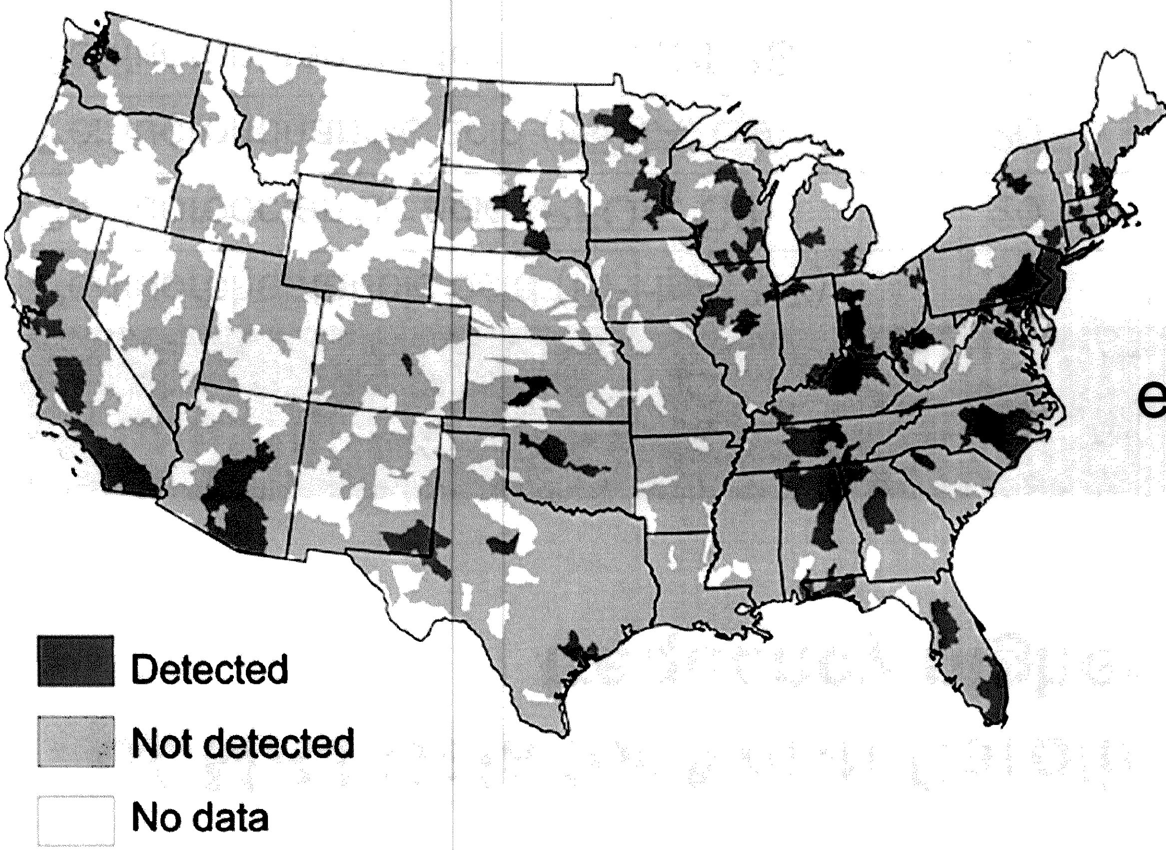
UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

Compound	MRL (ng/L)	NC Detects
Perfluoroheptanoic acid (PFHpA, C7)	10	29 (max. 60 ng/L)
Perfluorooctanoic acid (PFOA, C8)	20	10 (max. 30 ng/L)
Perfluorononanoic acid (PFNA, C9)	20	0
Perfluorobutanesulfonic acid (PFBS)	90	0
Perfluorohexanesulfonic acid (PFHxS)	30	5 (max. 110 ng/L)
Perfluorooctanesulfonic acid (PFOS)	40	8 (max. 90 ng/L)

1,320 samples from 151 PWSs in NC
PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)
Of samples with PFAS detects: 79% derived from surface water

Elevated PFAS levels affect a sizeable number of US residents

Hydrological units with detectable PFASs

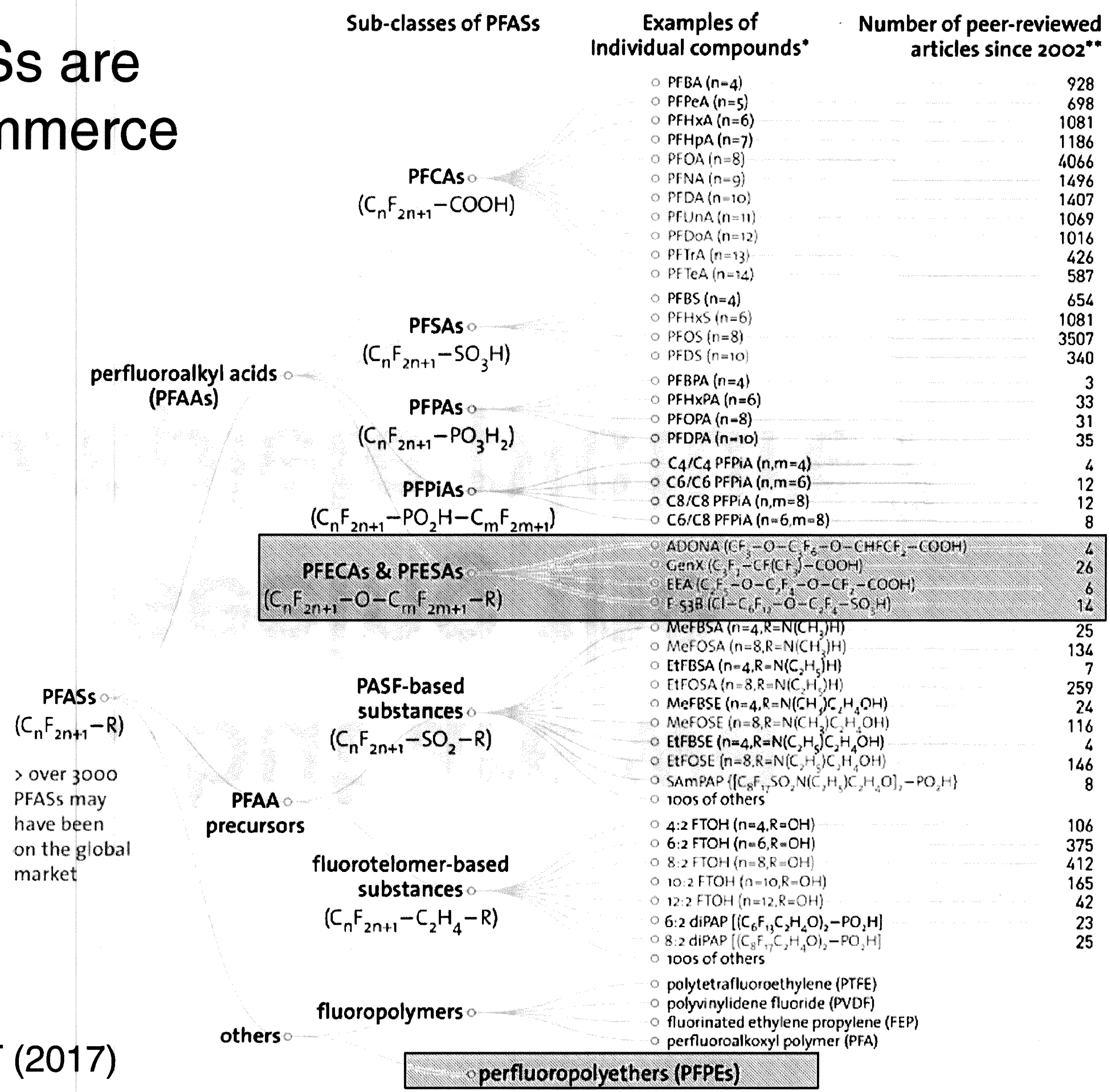


PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

Hu et al. ES&T Letters (2016)

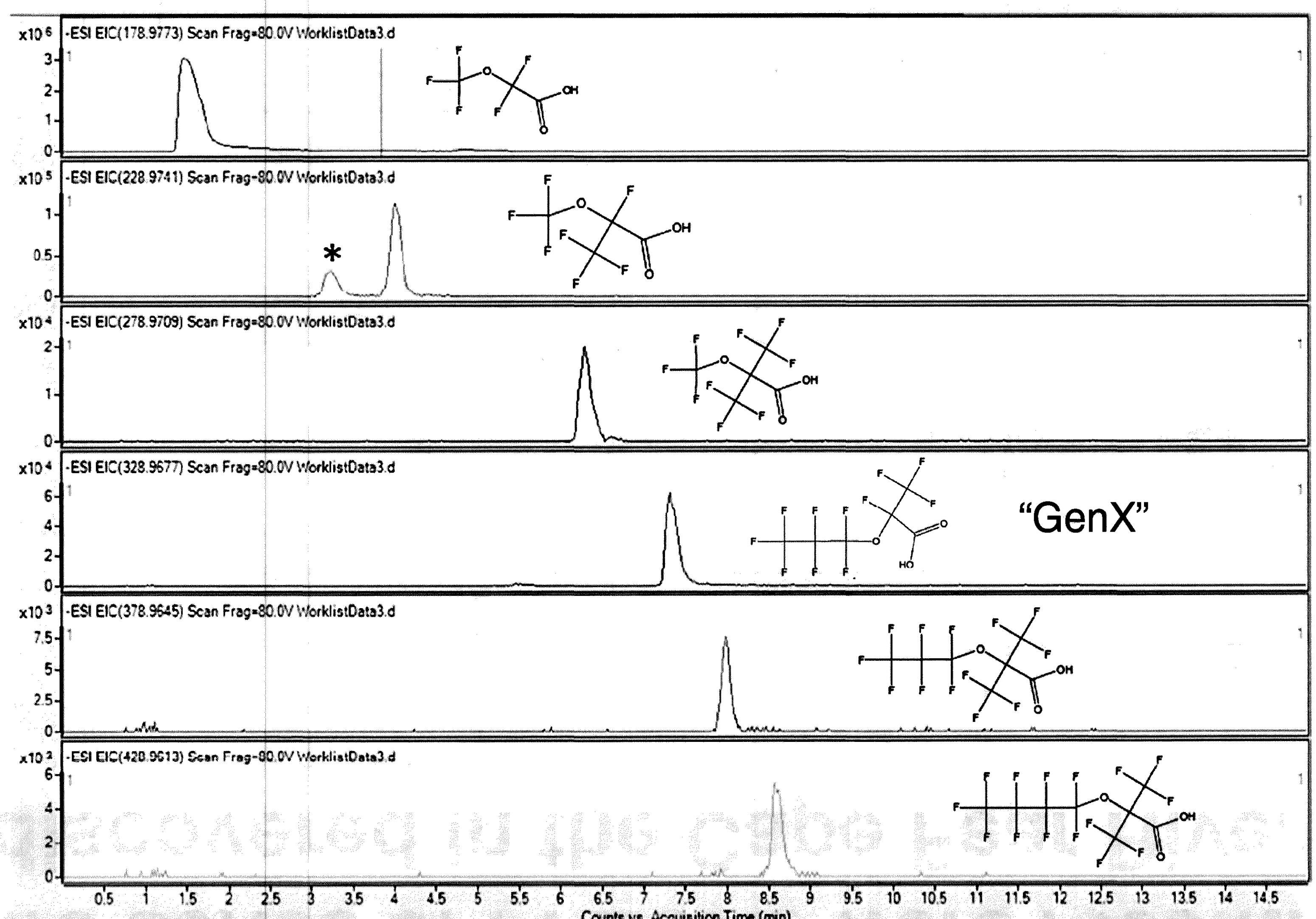
…but are we seeing the complete picture?

Many PFASs are used in commerce



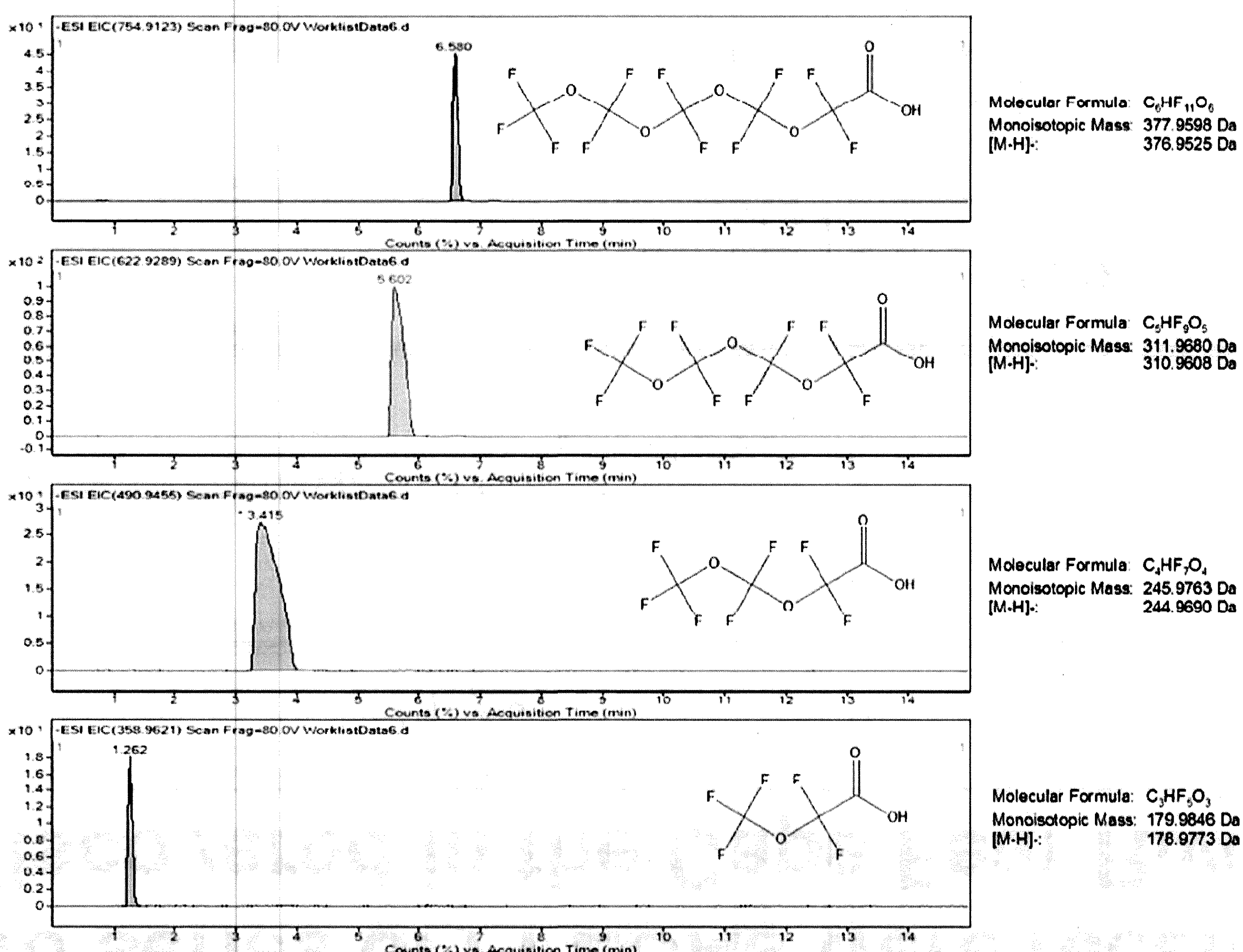
Wang et al. ES&T (2017)

Two series of PFECAs were recently discovered in the Cape Fear River



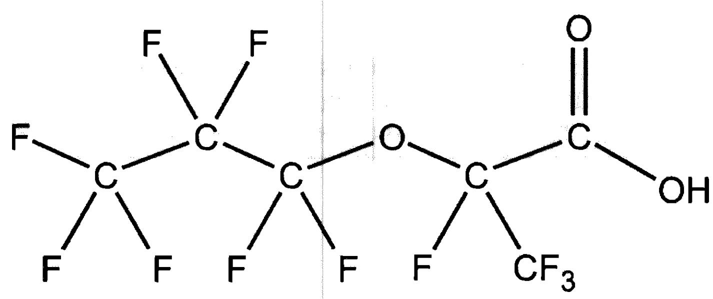
Strynar et al. ES&T (2015)

Two series of PFECAs were recently discovered in the Cape Fear River



Strynar et al. ES&T (2015)

GenX



- Commercially produced polymer processing aid (ammonium salt) to replace PFOA
- By-product of “vinyl ether process” – hexafluoropropylene oxide (HFPO) gas can form a stable dimer (GenX)

Serum Elimination Half-Lives

Table 4
Serum elimination half-lives ($t_{1/2}$) of GenX, ADONA, PFBA, PFHxA, and PFOA in male (M) and female (F) rats, mice and humans. In some cases, half-life is expressed in the form of "arithmetic mean ± standard deviation", while in other cases when the standard deviation is less than 15% of the arithmetic mean only the arithmetic mean is provided. Notes on studies on rats and mice and monkeys provide information on dosing method (e.g. single oral dose or single intravenous (IV) dose) and dosage (in ppm: mg substance/kg bw); notes on studies on humans provide sample numbers (n) of humans involved. "–" means no data available.

	Rats				Mice				Humans	
	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes
GenX (F)	<12 h	Oral[a] 30 ppm	–	–	>12 h, <7 d	Oral[a] 3 ppm	–	–	–	–
GenX (M)	<12 h		–	–	>12 h, <7 d		–	–	–	–
ADONA (M)	44 h	5× oral[b]	–	–	–	–	–	–	23 ± 11 d	3[h,m]
PFBA (F)	1 h	IV[c] 30 ppm	2 h	Oral[c] 30 ppm	3 h	Oral[c] 10 ppm	3 h	Oral[c] 30 ppm	87 ± 31 h	2[c,m]
PFBA (M)	6 h		9 h		13 ± 5 h		16 ± 7 h		68 ± 35 h	7[c,m]
PFHxA (F)	0.4 h	IV[d] 10 ppm	1.2 h	IV[c] 15 ppm	<72 h	Gastric[f] 50 ppm	–	–	–	–
PFHxA (M)	1 h		2.4 h		<72 h		–	–	<28 days	8[g,m]
PFOA (F)	2 h	IV[e] 20 ppm	–	–	17 days	–[h]	–	–	3.3 years	2[i,m]
PFOA (M)	6 days		–	–	19 days		–	–	3.8 ± 1.7 years	24[i,m]
PFOA (all)	–	–	–	–	–	–	–	–	3.26 years	138[j,n]
PFOA (all)	–	–	–	–	–	–	–	–	2.3 years	200[k,n]
PFOA (all)	–	–	–	–	–	–	–	–	2.9 years	643[l,n]
PFOA (all)	–	–	–	–	–	–	–	–	8.5 years	1029[l,n]

[a] ECHA (2014). [b] EFSA (2011a). [c] Chang et al. (2008). [d] Chengelis et al. (2009). [e] Ohmori et al. (2003). [f] Iwai (2011). [g] Nilsson et al. (2010). [h] Lau et al. (2007). [i] Olsen et al. (2007). [j] Brede et al. (2010). [k] Bartell et al. (2010). [l] Seals et al. (2011). [m] These studies focus on samples from people who were occupationally exposed to these substances and the levels in serum were high. [n] These studies focus on samples from people who were exposed to PFOA mainly through highly contaminated drinking water.

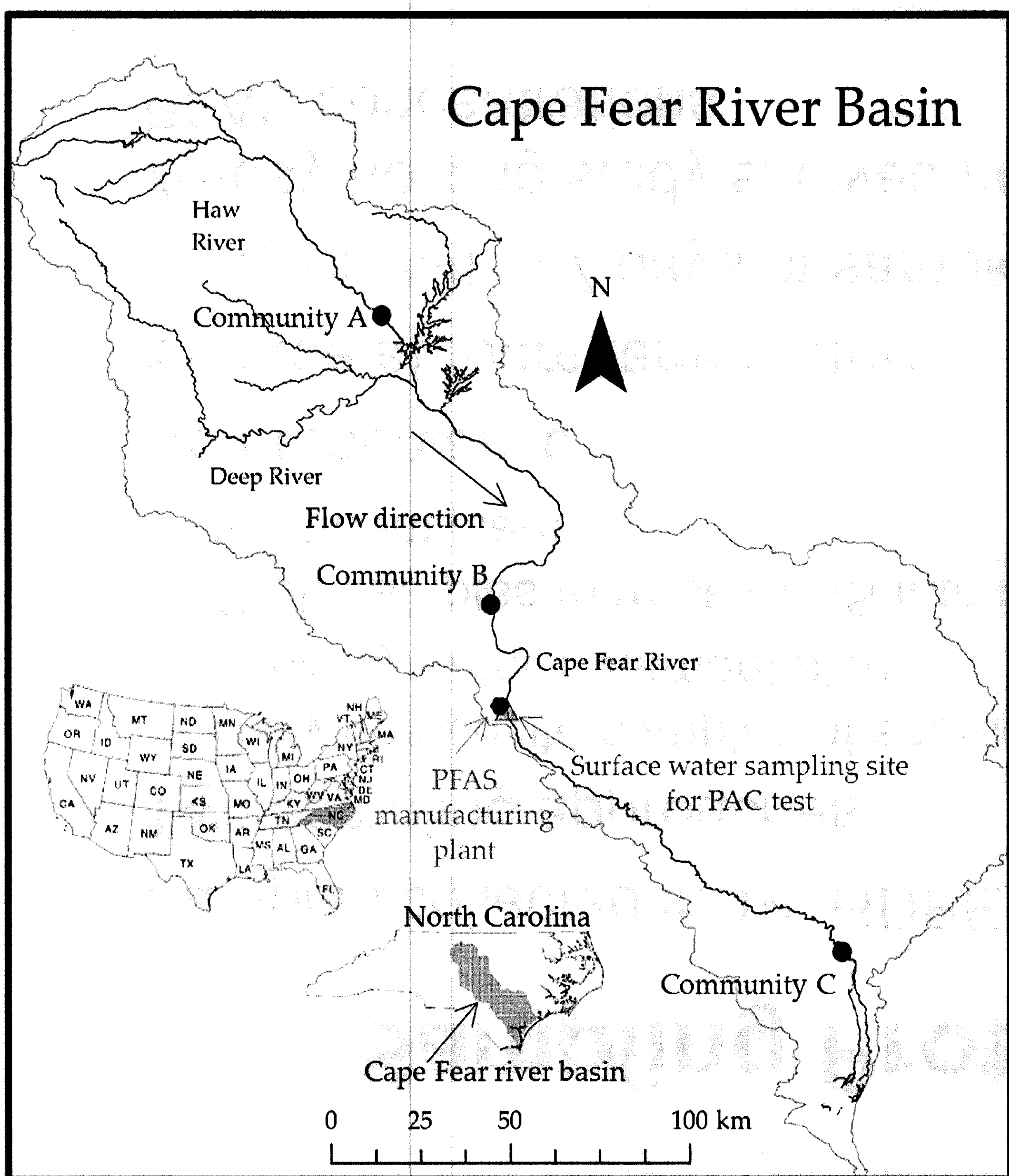
Comparing the potency in vivo of PFAS alternatives and their predecessors

Gomis Ferreira, Melissa Ines; Vestergren, Robin; Borg, Daniel; Cousins, Ian T.

Abstract

Since the year 2000, a number of per- and polyfluoroalkyl substances (PFASs) have been introduced onto the market to replace long-chain perfluoroalkyl acids (e.g. perfluoroctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)) and their respective precursors. The main rationale for this industrial transition is that the PFAS alternatives are less bioaccumulative and toxic than their predecessors. Here, we evaluated to what extent differences in toxicological effect thresholds for PFASs, expressed as an administered dose, were confounded by differences in their distribution and elimination kinetics. Increased liver weight was selected as the investigated endpoint based on the availability of sufficient toxicological and toxicokinetic data to enable a comparison of sub-chronic effects. Converting administered doses into equivalent serum and liver concentrations significantly reduced the variability in the dose-response curves for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononaoic acid (PFNA) and ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX). The toxicity ranking using serum (PFNA>GenX>PFOA>PFHxA>PFBA) and liver (GenX>PFNA≈PFOA≈PFHxA≈PFBA) concentrations also indicated that some PFAS alternatives may have a higher toxic potency than their predecessors when correcting for differences in toxicokinetics. For PFOS and perfluorobutane sulfonic acid (PFBS) the conversion from administered dose to serum concentration equivalents did not change the toxicity ranking which, however, could be due to the internal dose of PFBS being too low to allow a correct comparison. This study illustrates the importance of taking toxicokinetics/internal dose into account in substitution of hazardous chemicals for independent evaluation of bioaccumulation and toxicity criteria.

Study Design



- Largest watershed in NC
- Supplies ~1.5M people with drinking water

Sampling Protocol

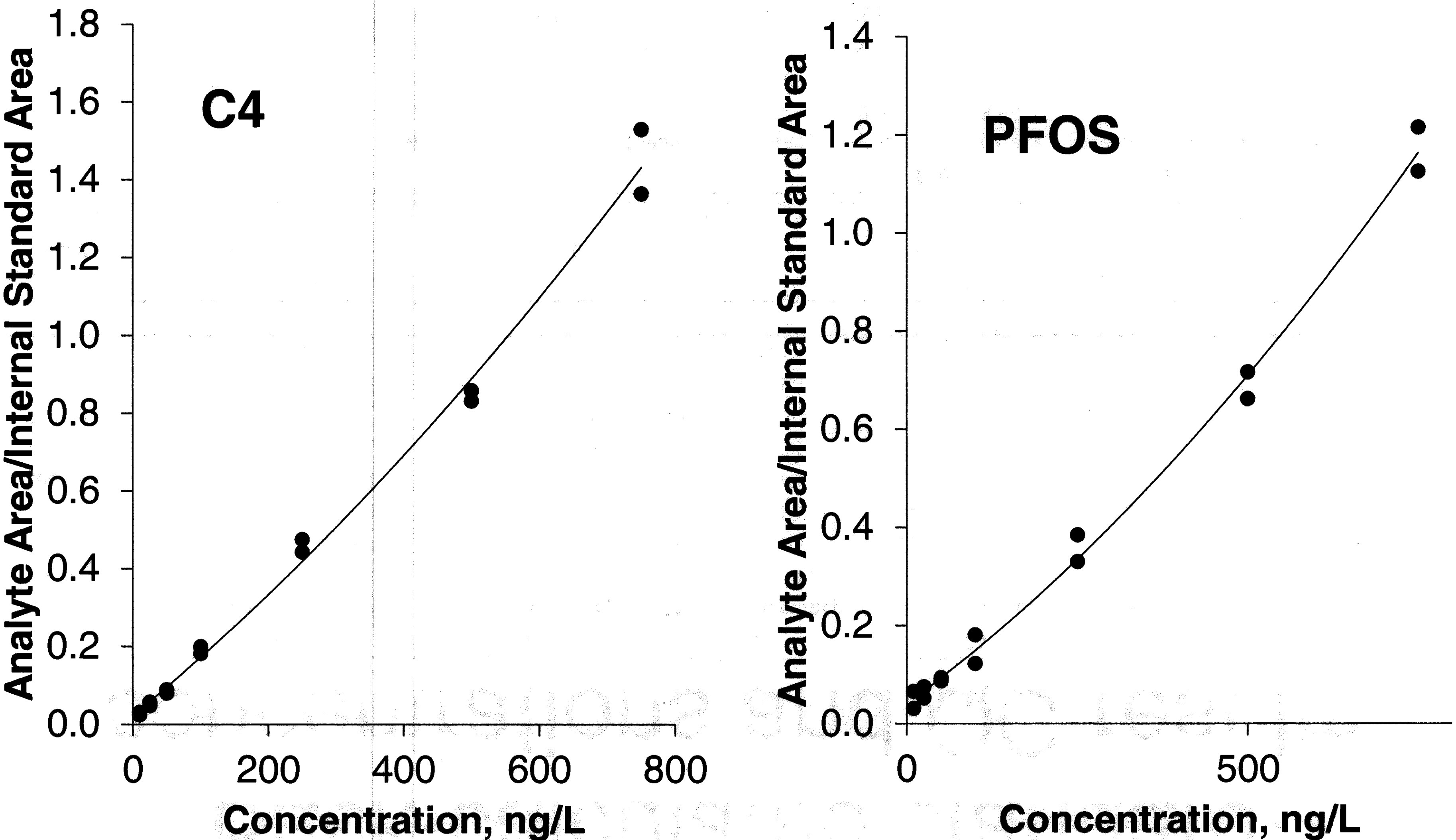
- Samples collected in 1-L HDPE bottles
- Two sampling approaches
  - Daily composite samples of source water at three drinking water treatment plants
  - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection
- 70-day holding study showed no changes in PFAS concentrations

PFAS Analytical Method

- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 µL)
- Sample and standard preparation:
  - filtration with a 0.45-µm glass fiber filter
  - addition of mass-labeled internal standards
  - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)
- Acceptance criterion: QCs within 30%

	Compound	MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4-$^{13}C_2$]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

Representative calibration curves



Back-calculated standard concentrations and QC results

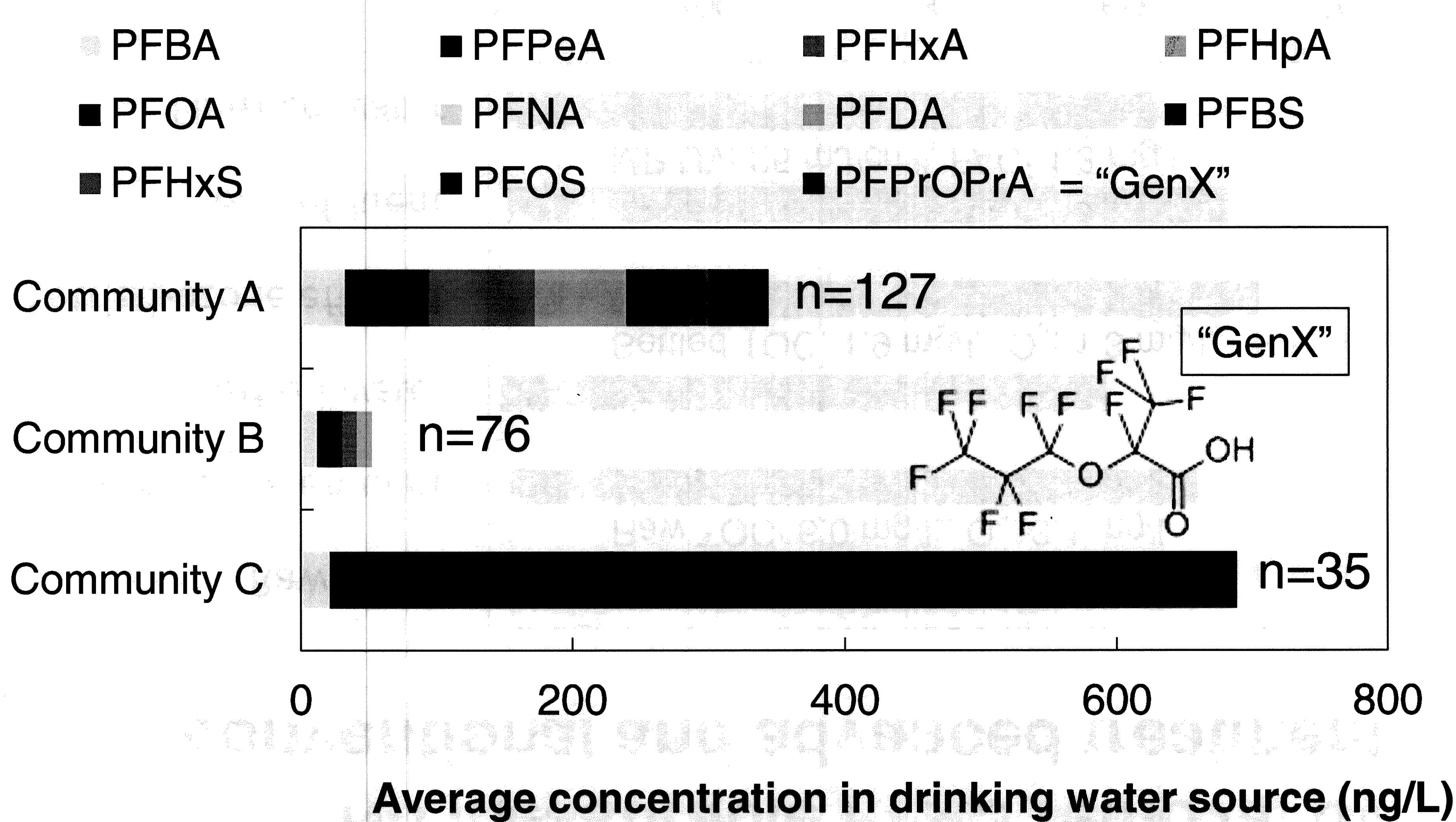
	GenX		C4		C5		C6		C7	
Sample Name	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**
10 ng/L	7.4	73.9	8.3	81.7	10.1	99.5	8.3	80.5	7.6	70.7
25 ng/L	28.5	114.1	27.7	110.5	23.3	91.2	29.7	115.2	29.6	110.4
50 ng/L	56.5	112.9	54.4	108.2	52.2	102.2	54.0	104.6	64.5	120.6
100 ng/L	104.1	104.1	103.1	102.1	112.5	110.3	107.9	104.7	110.6	103.4
250 ng/L	240.0	96.0	242.3	96.6	252.6	99.0	245.6	95.2	260.5	97.2
500 ng/L	488.0	97.6	503.1	100.0	496.0	97.1	517.6	100.1	511.0	95.5
750 ng/L	760.6	101.4	755.8	100.2	773.1	100.9	777.8	100.4	819.9	102.1
r	0.9975		0.9991		0.9927		0.9978		0.9975	

Sample Name	**GenX**		**C4**		**C5**		**C6**		**C7**	
100QC	98.1	90	101	104	105	111	98	96.9	113	101
500QC	462	441	497	511	526	540	512	478	412	485

C8		C9		C10		PFBS		PFHS		PFOS	
Mean	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**	**Mean**	**Accuracy**
8.2	80.3	7.4	73.7	7.8	76.1	7.44	73.63	7.2	71.1	8.7	86.5
28.5	111.7	28.1	111.2	27.8	109.0	28.25	111.66	29.0	115.0	25.5	101.6
56.1	109.8	60.5	119.9	56.7	111.3	57.76	114.16	57.3	113.4	58.1	115.7
105.3	103.2	99.4	98.4	110.1	108.0	108.95	107.88	107.0	105.9	99.9	99.9
243.1	95.3	246.9	97.6	250.7	98.3	237.15	93.74	241.8	96.0	244.3	97.3
511.3	100.1	494.4	97.9	482.1	94.7	497.59	98.34	491.4	97.3	496.5	98.9
769.4	100.5	765.6	101.0	781.6	102.3	768.91	101.31	767.4	101.4	758.8	100.8
0.9987		0.9982		0.998		0.9972		0.9981		0.9985	

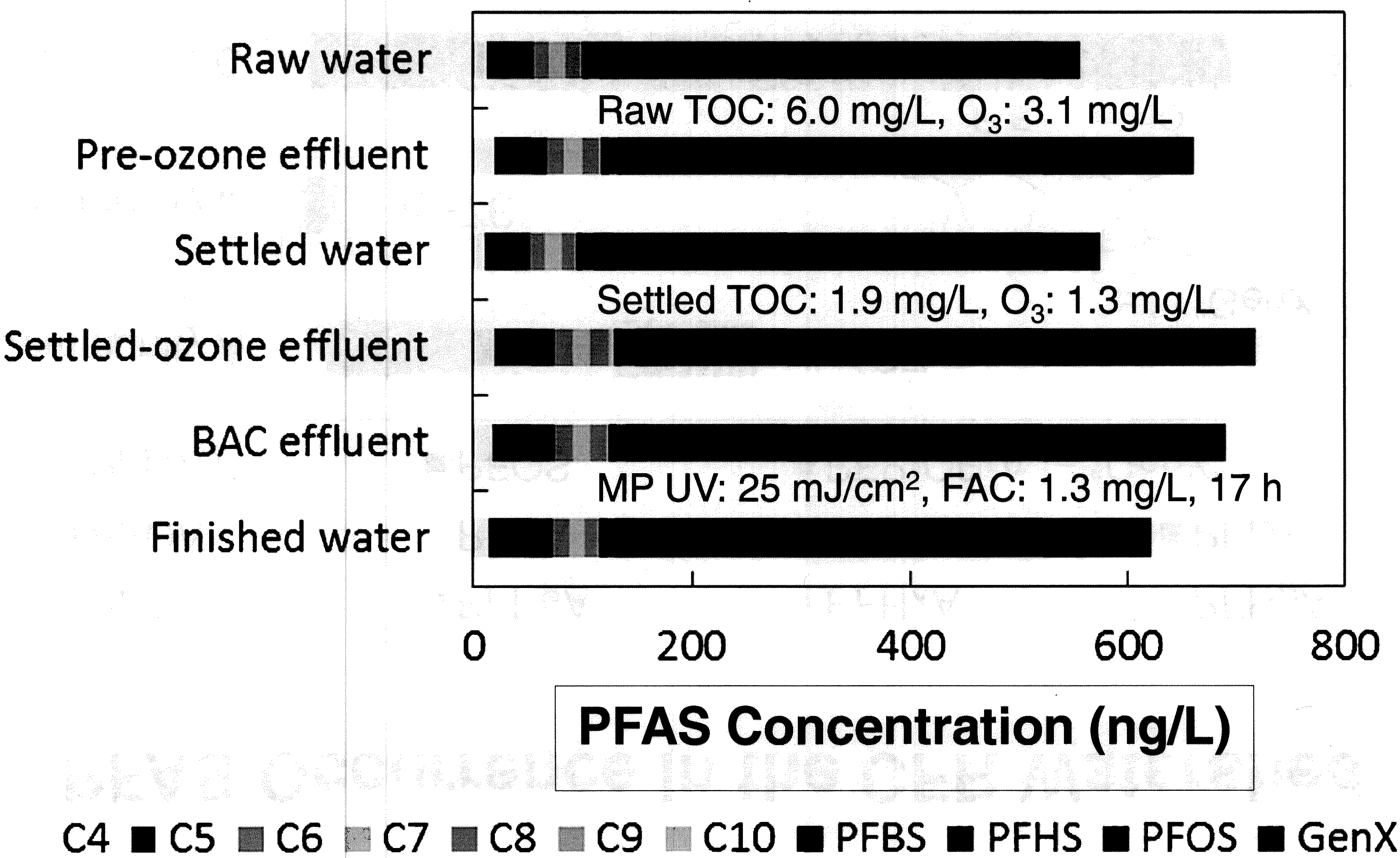
C8		**C9**		**C10**		**PFBS**		**PFHS**		**PFOS**	
117	103	109	98.5	110	102	105	105	106	101	98.5	85.8
528	509	415	422	501	434	507	493	463	449	462	426

PFAS Occurrence in the CFR Watershed

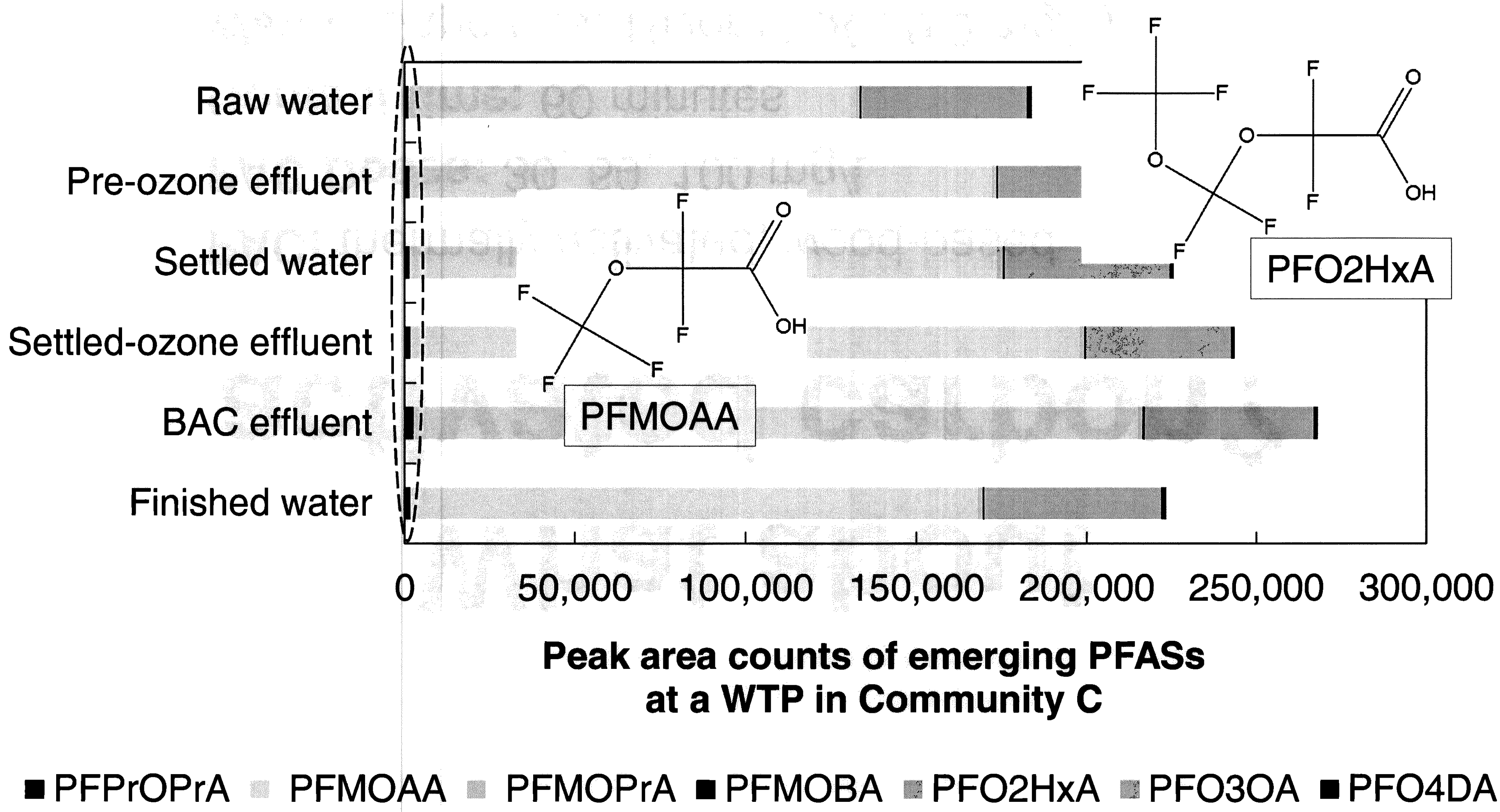


Sun et al. (2016) ES&T Letters

No measurable PFAS removal by conventional and advanced treatment



Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX



Sun et al. (2016) ES&T Letters

What about activated carbon?

PAC: thermally activated, wood-based

PAC Doses: 30, 60, 100 mg/L

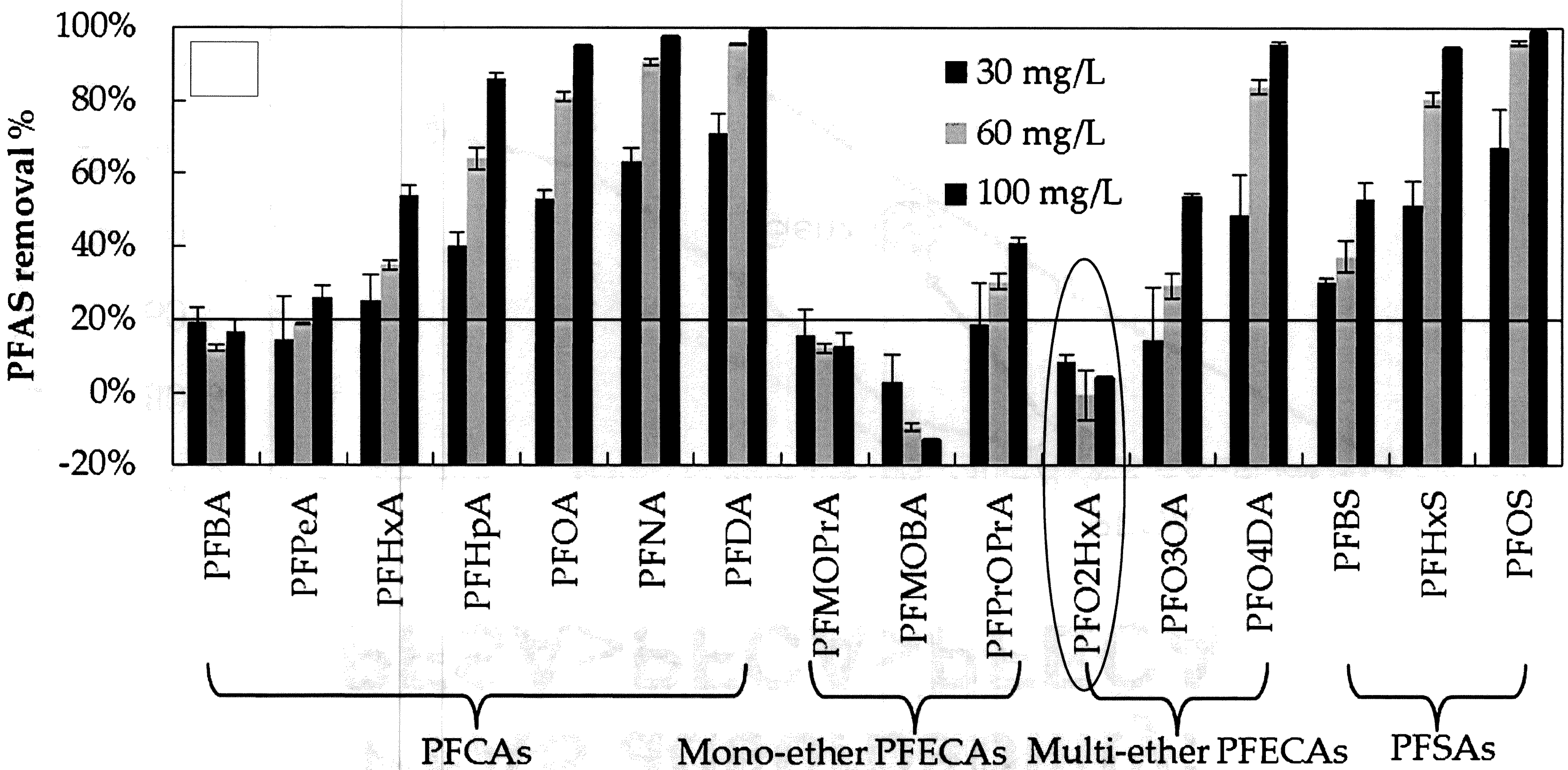
Contact time: 60 minutes

Water: Cape Fear River (TOC: 9.0 mg/L)

PFECAs: Native levels

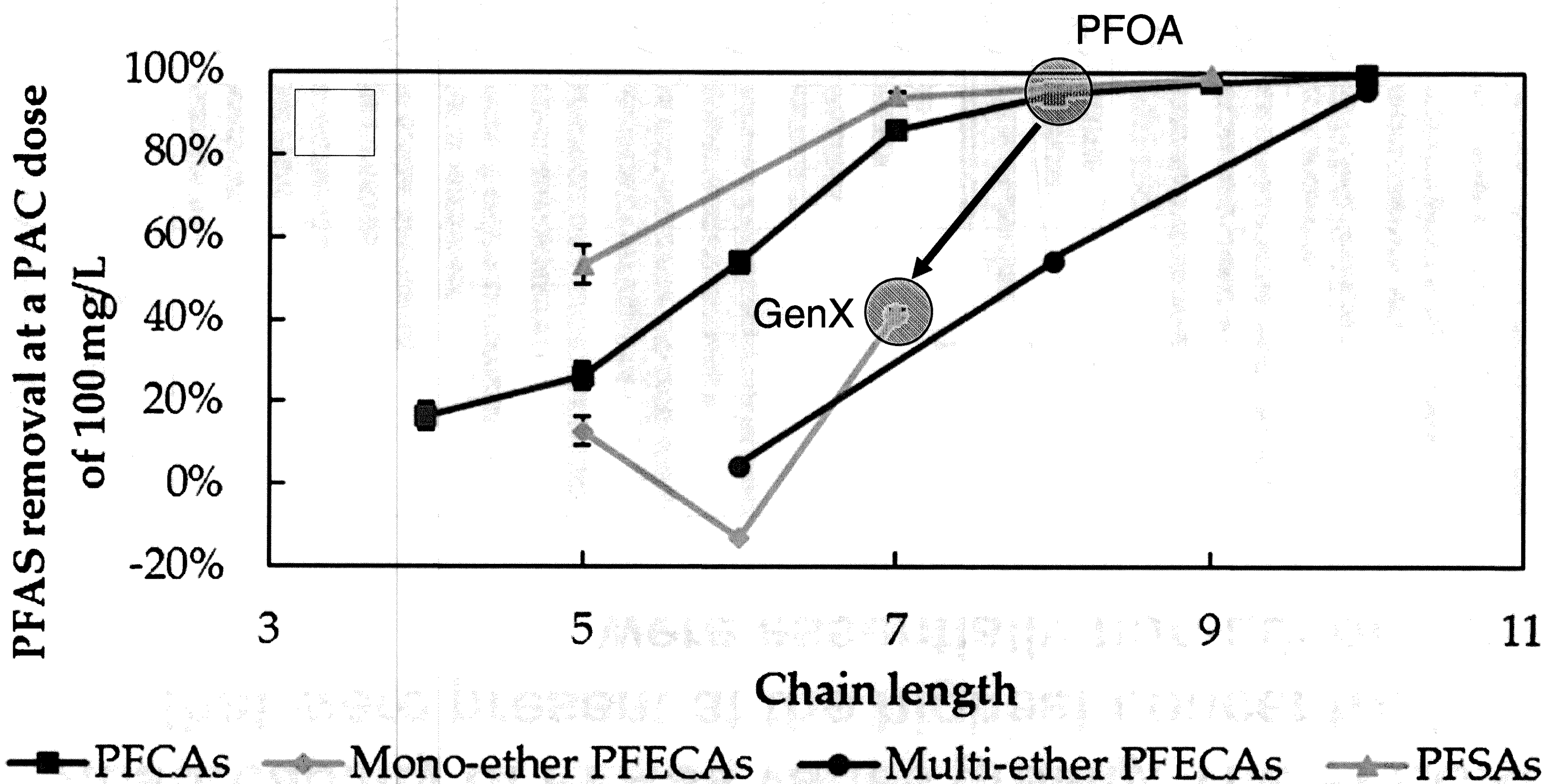
PFCAs and PFSAs: Spiked at 1000 ng/L

Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable



Sun et al. (2016) ES&T Letters

PFAS adsorbability: PFSA>PFCA>PFECA



Sun et al. (2016) ES&T Letters

Conclusions

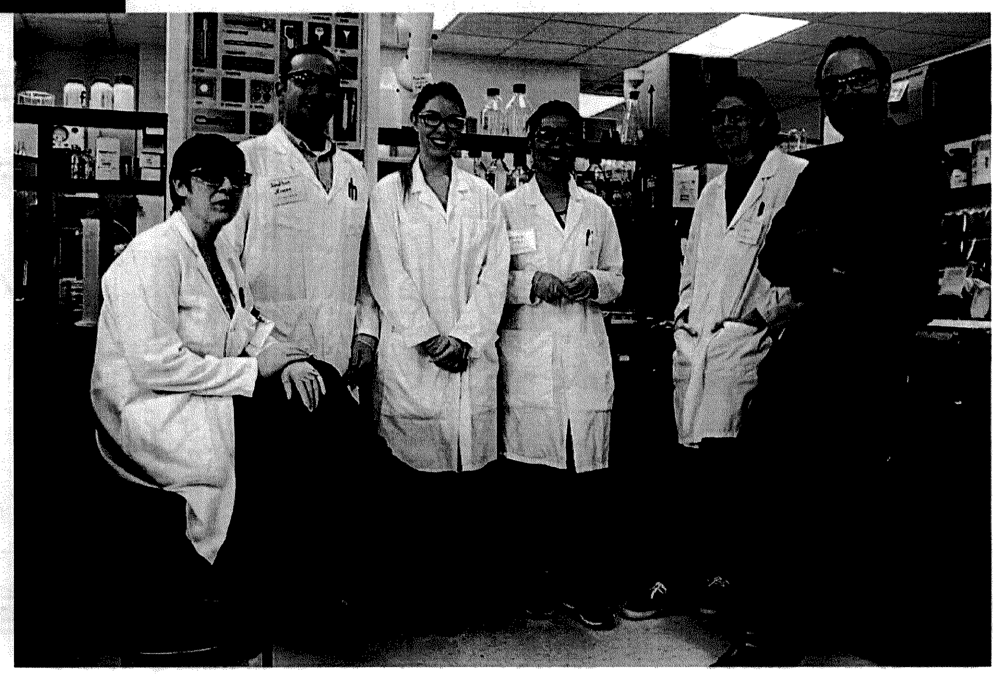
- Legacy PFASs dominant in upstream river reaches
- PFOA+PFOS levels exceeded 70 ng/L in community A on 57 of 127 sampling days
- PFECAs dominated PFAS signature downstream of a fluorochemical manufacturer
- PFECA concentrations were not attenuated by:
  - Conventional treatment
  - Ozonation
  - Biofiltration
  - Disinfection by medium pressure UV lamps and free chlorine
- Activated carbon adsorption only effective for long-chain PFASs

Acknowledgments

- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson, Ben Kearns at participating utilities

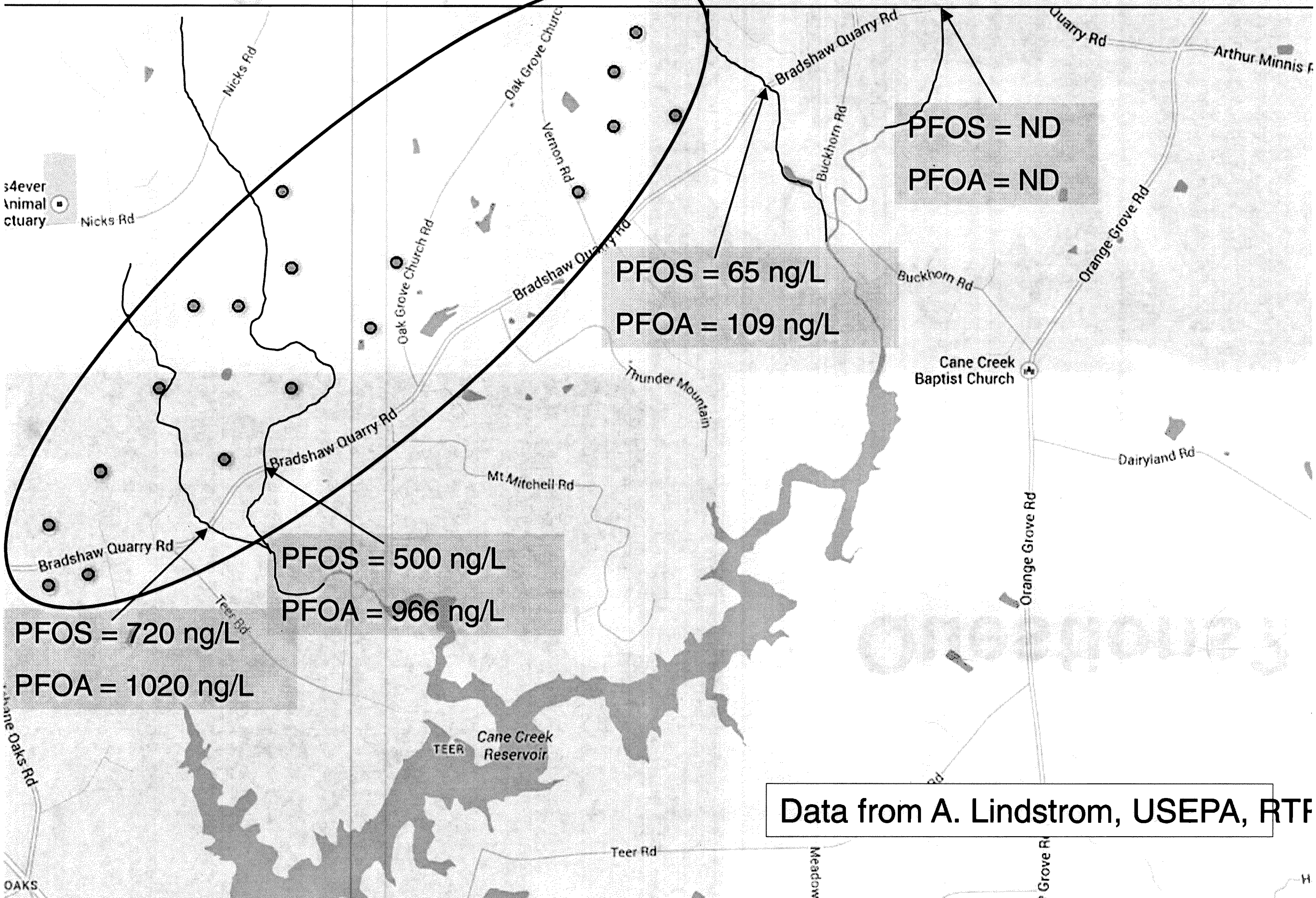
NC STATE UNIVERSITY

Questions?



knappe@ncsu.edu

Land application of biosolids in watershed of a NC drinking water reservoir



Emerging Per- and Polyfluoroalkyl Substances (PFAS)

Andrew B. Lindstrom[1], Jason E. Galloway[2], Mark J. Strynar[1], Detlef Knappe[3], Mei Sun[4], Seth Newton[1], Linda K. Weavers[2]

[1]U.S. Environmental Protection Agency, [2]The Ohio State University, [3]North Carolina State University, [4]University of North Carolina Charlotte

Northeastern University
Social Science Environmental Health Research Institute

Highly Fluorinated Compounds
Social and Scientific Discovery
Northeastern University Social Science
Environmental Health Research Institute
June 14 – 15, 2017

Overview

- Sources and exposure pathways of legacy PFAS (PFOS & PFOA) somewhat known

- USEPA's Stewardship Program has reduced legacy PFAS but has also resulted in the development of many new "emerging" PFAS

- New analytical capabilities (high resolution mass spectrometry) allow detection of many new PFAS

- Emerging PFAS almost completely uncharacterized with regard to sources, environmental fate, human exposure implications

- Discussion of some recent research on sources of emerging PFAS, human exposure pathways, overall implications

US Environmental Protection Agency
PFOA Stewardship Program

- In January 2006, USEPA started this program to help minimize impact of PFOA in the environment

- Eight major international companies have agreed to participate (including 3M, DuPont, Asahi Glass, Daikin)

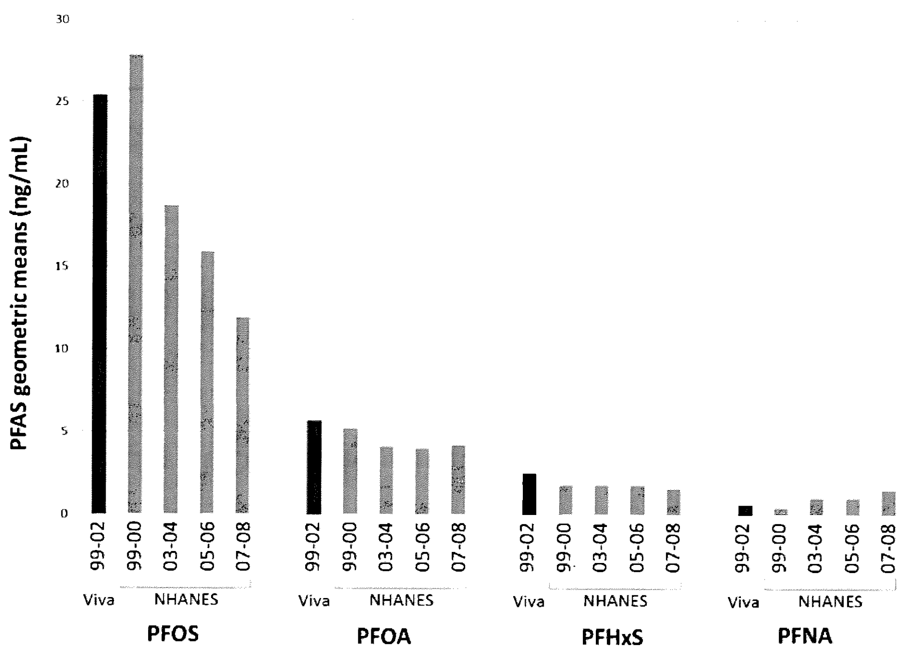
- Agreement to voluntarily reduce factory emissions and product content of PFOA and related compounds* on a global basis by 95% no later than 2010

- Agreement to work toward total elimination of emissions and product content of these compounds by 2015

- Based on emissions and content determinations made for 2006

* Includes PFOA, precursor chemicals that can break down to PFOA, higher homologues (C9 and larger)

Trends in PFAS Serum Levels in US

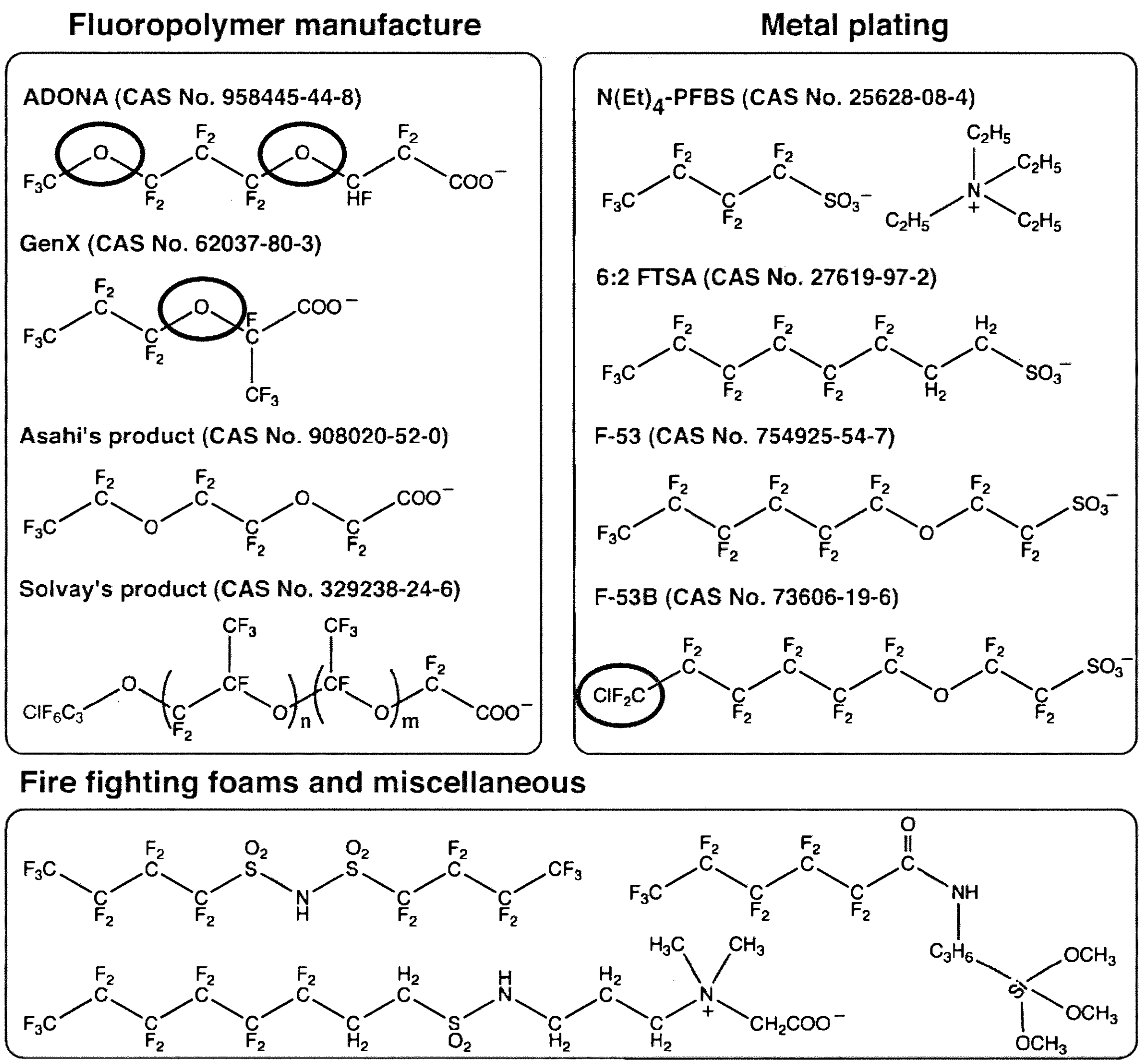


Sagiv et al. *Environmental Science & Technology* 2015, 49, 11849−11858

Table 2. Geometric mean and 95% confidence interval and selected percentiles of PFOS, PFOA, PFHxS, and PFNA serum concentrations (ng/mL) for the U.S. population 12 years of age and older: Data from NHANES 2011-2012 [a]

	Geometric Mean (95% Confidence Interval)		Selected Percentiles			
			50th	75th	90th	95th
PFHxS	1.28	1.15-1.43	1.27	2.26	3.81	5.43
PFOS	6.31	5.83-6.82	6.51	10.48	15.62	21.68
PFOA	2.08	1.95-2.22	2.08	3.02	4.35	5.67
PFNA	0.88	0.80-0.97	0.86	1.30	1.95	2.54

[a] CDC (2015)


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)
Fire fighting foams and miscellaneous

Unknown Characteristics of “Emerging” Fluorinated Compounds

- Actual identities of alternatives unknown in industrial sectors and geographical regions that are not well regulated

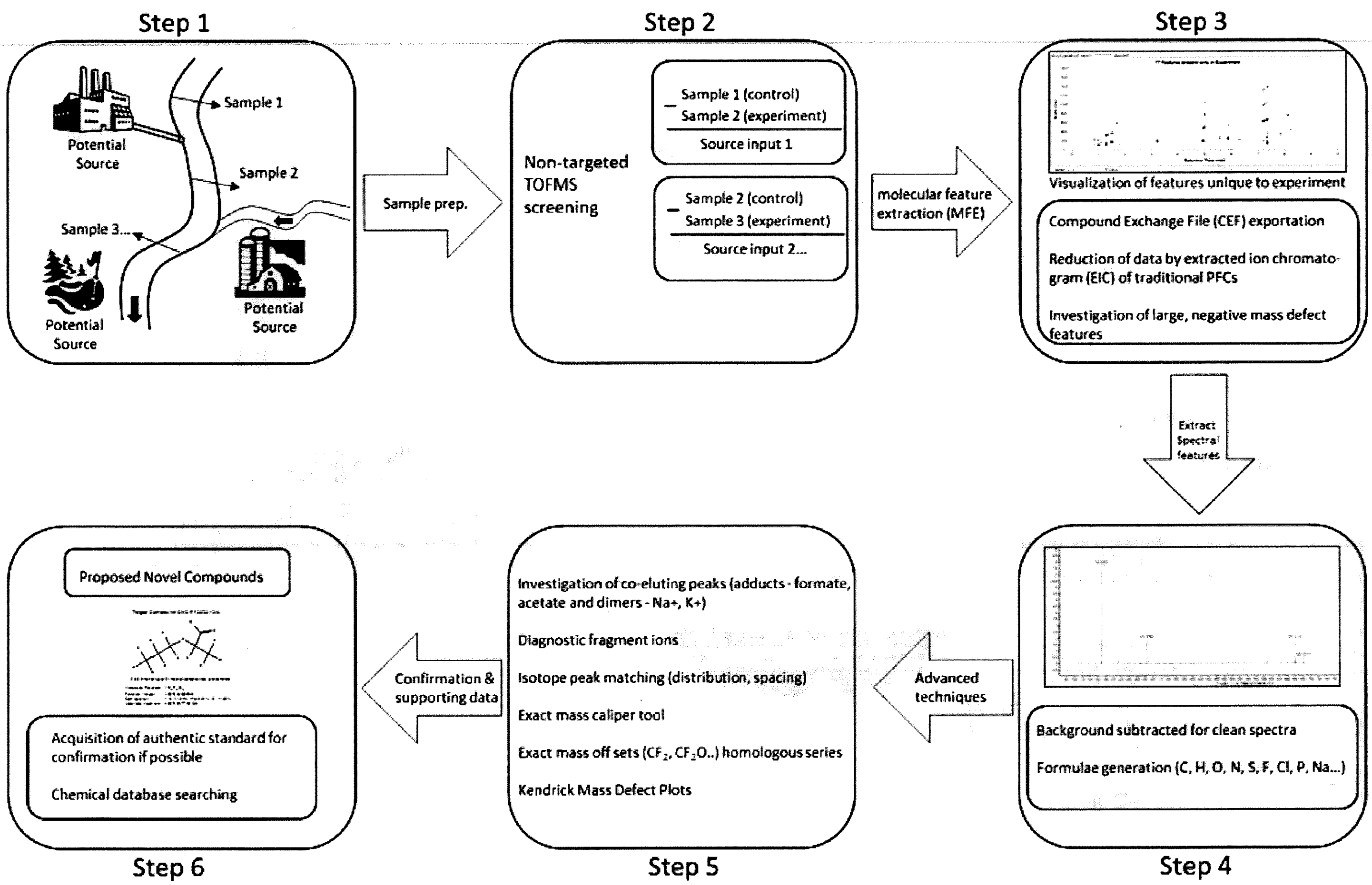
- Data on environmental and human health effects are incomplete (at best) and more often nonexistent

- Data on degradability, bioaccumulation, and toxicity (environmental and human) are incomplete (at best) or completely lacking

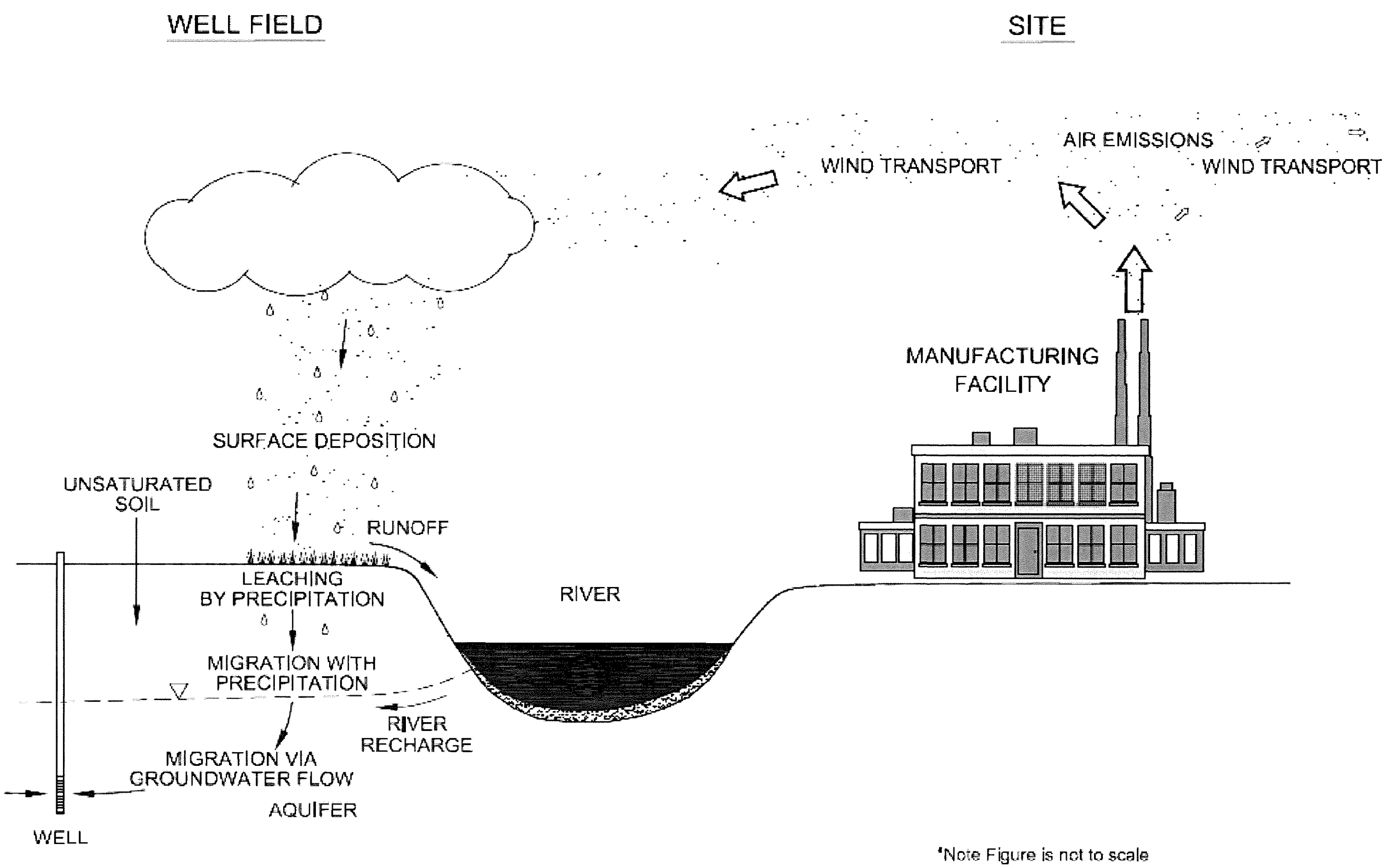
- Information on production volume and environmental emissions not available

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

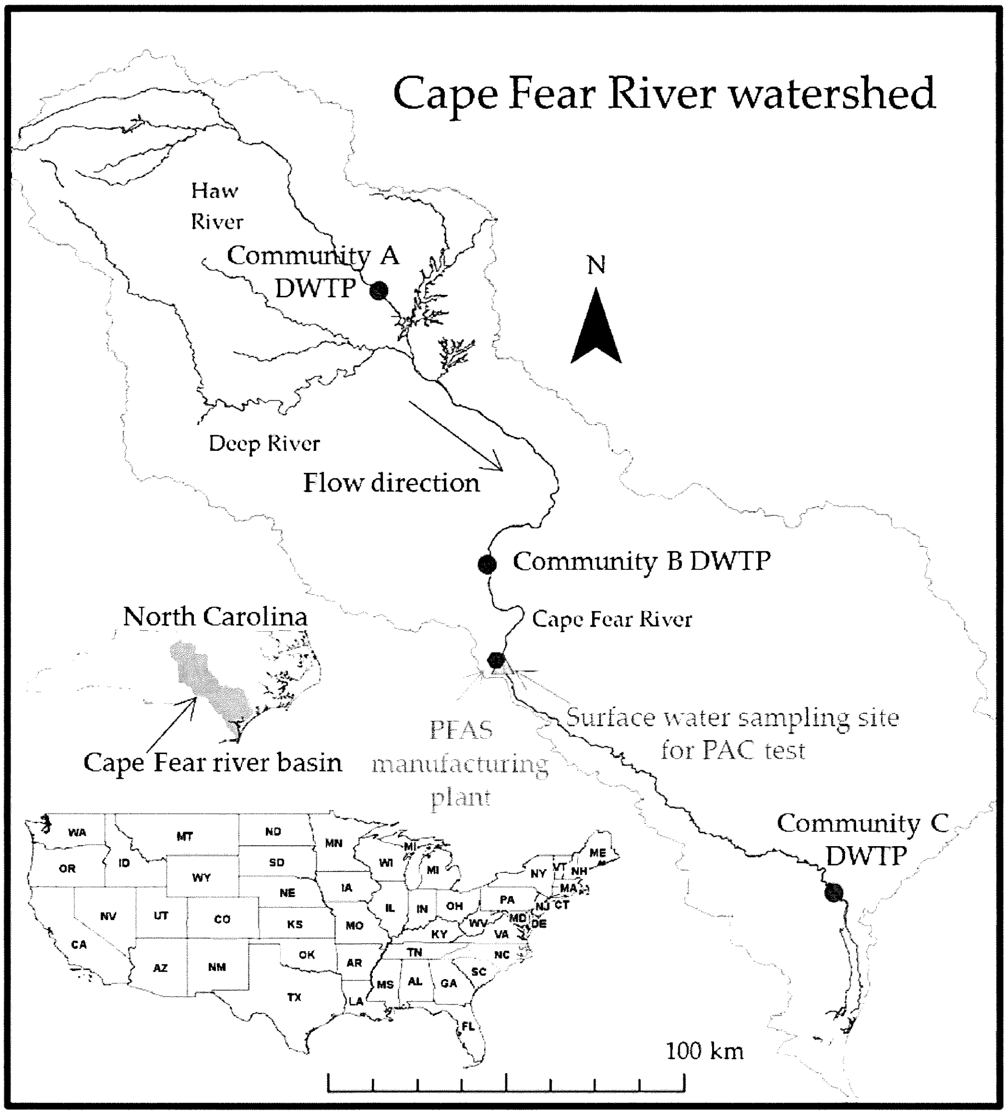
High Resolution Mass Spectrometry to Find "Emerging" PFAS



Strynar et al. *Environmental Science & Technology* 2015, 49, 11622−11630

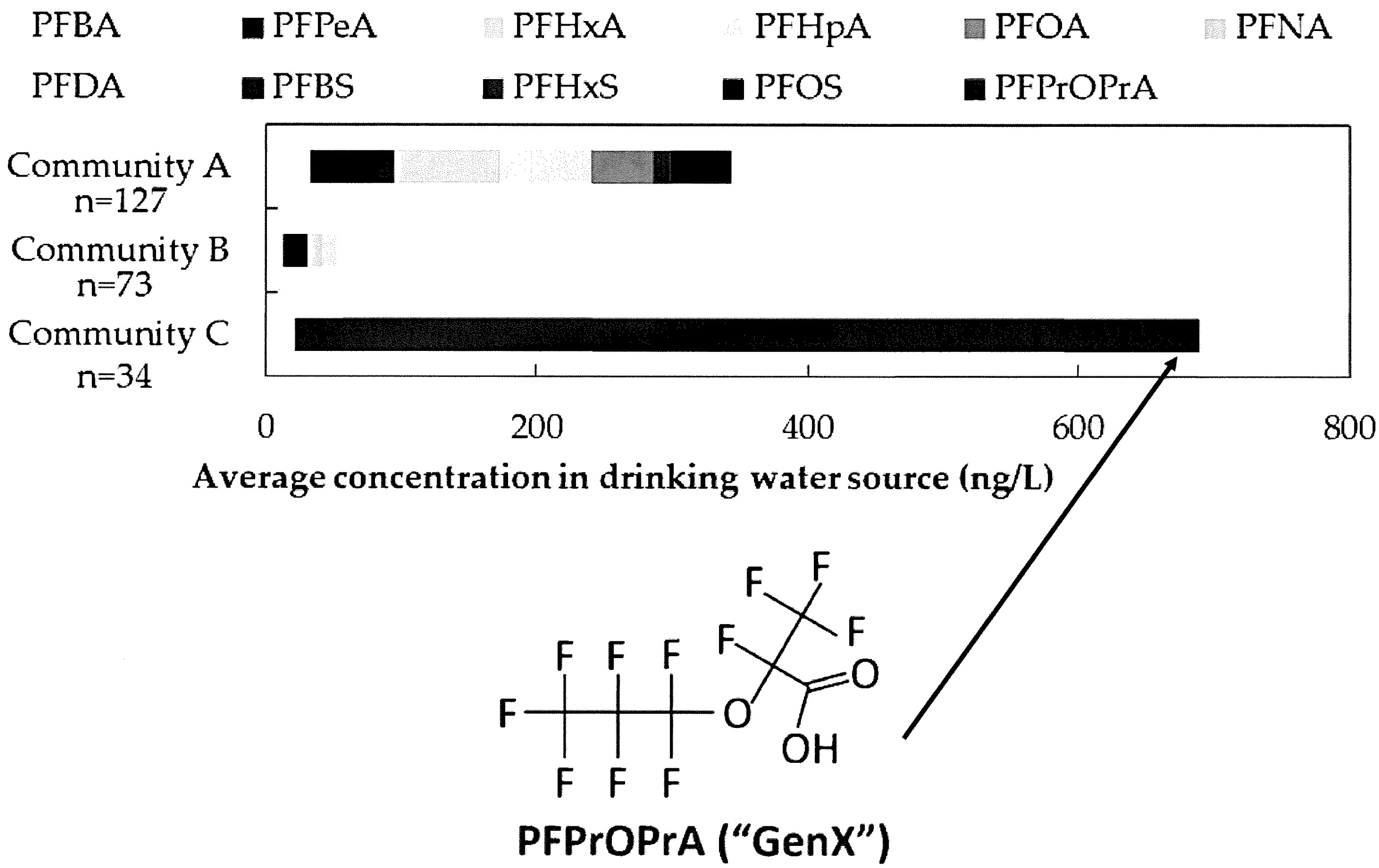


Davis et al. *Chemosphere* 2007, 67, 2011–2019



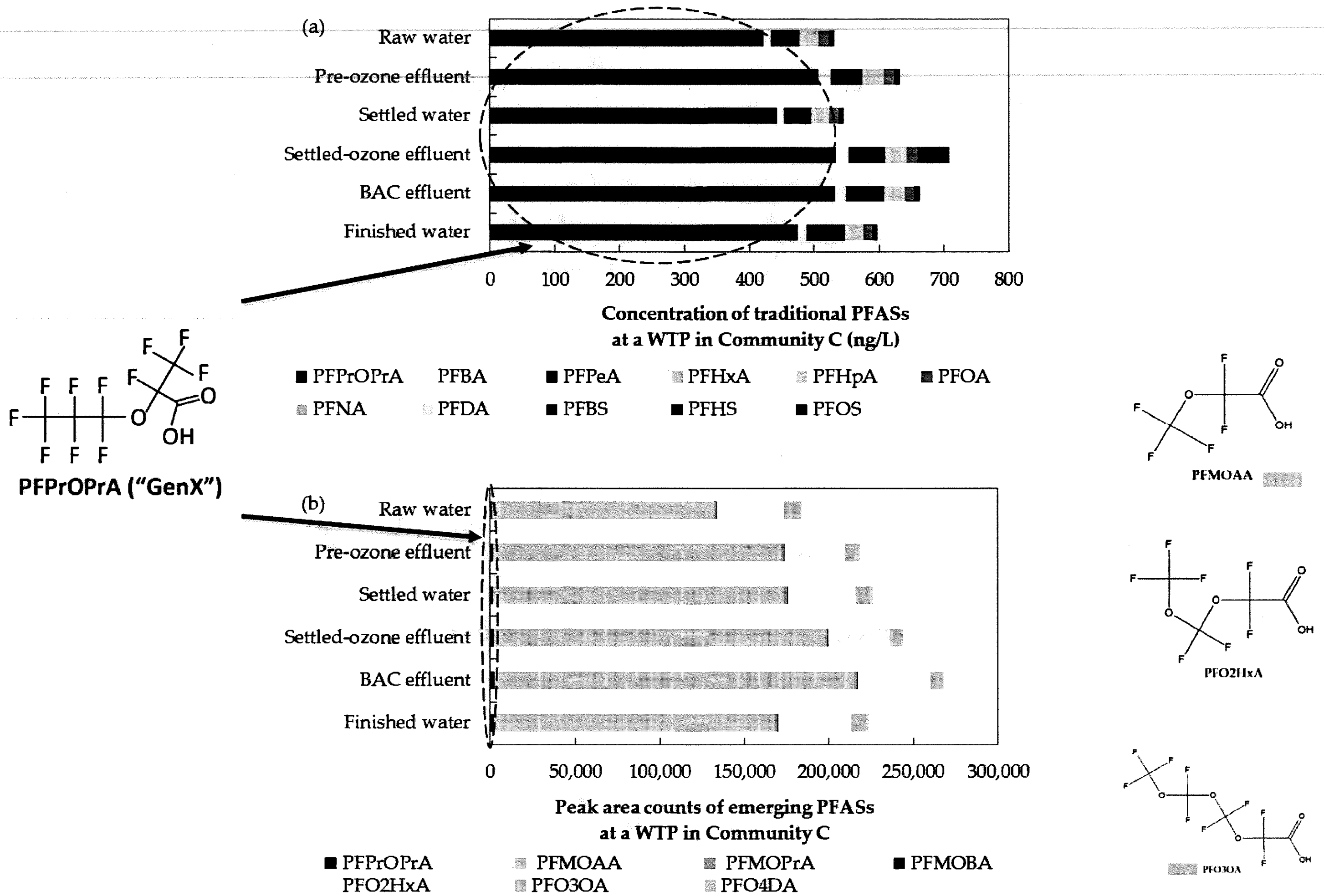
Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419

Legacy PFAS with GenX in Cape Fear River Basin

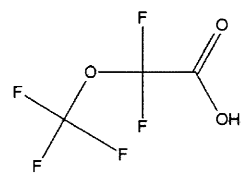


Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415–419

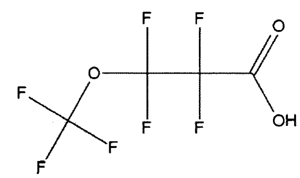
Emerging PFAS in Cape Fear River Basin



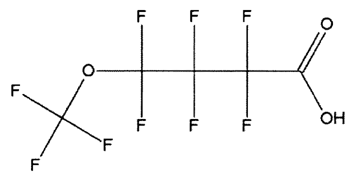
Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419



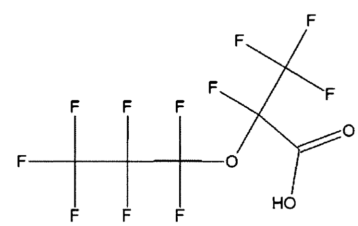
PFMOAA



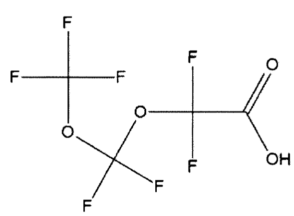
PFMOPrA



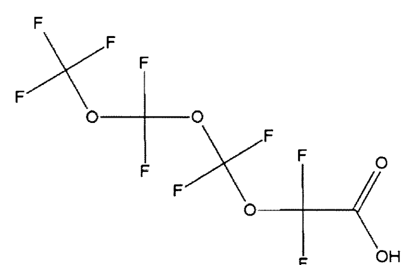
PFMOBA



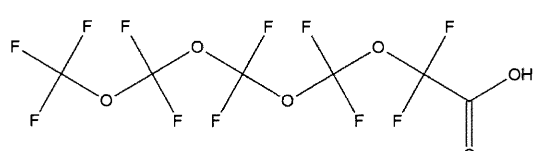
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

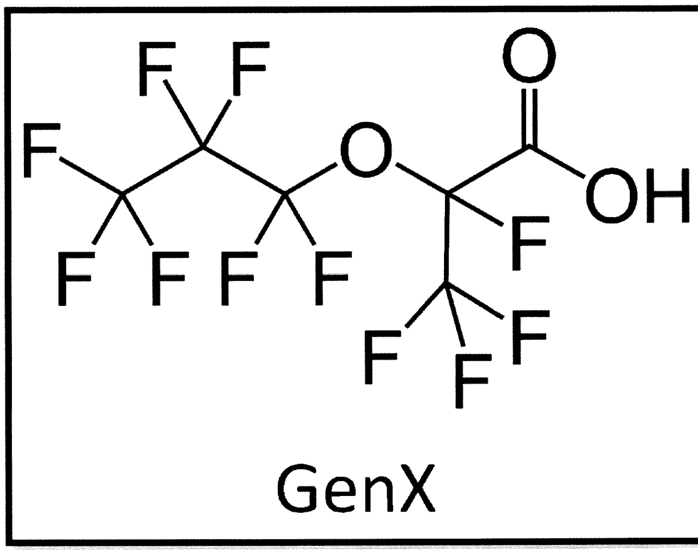
Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419

GenX

- Identity originally protected as Confidential Business Information (CBI)

- Still persistent, still toxic, but less bioaccumulative than C8

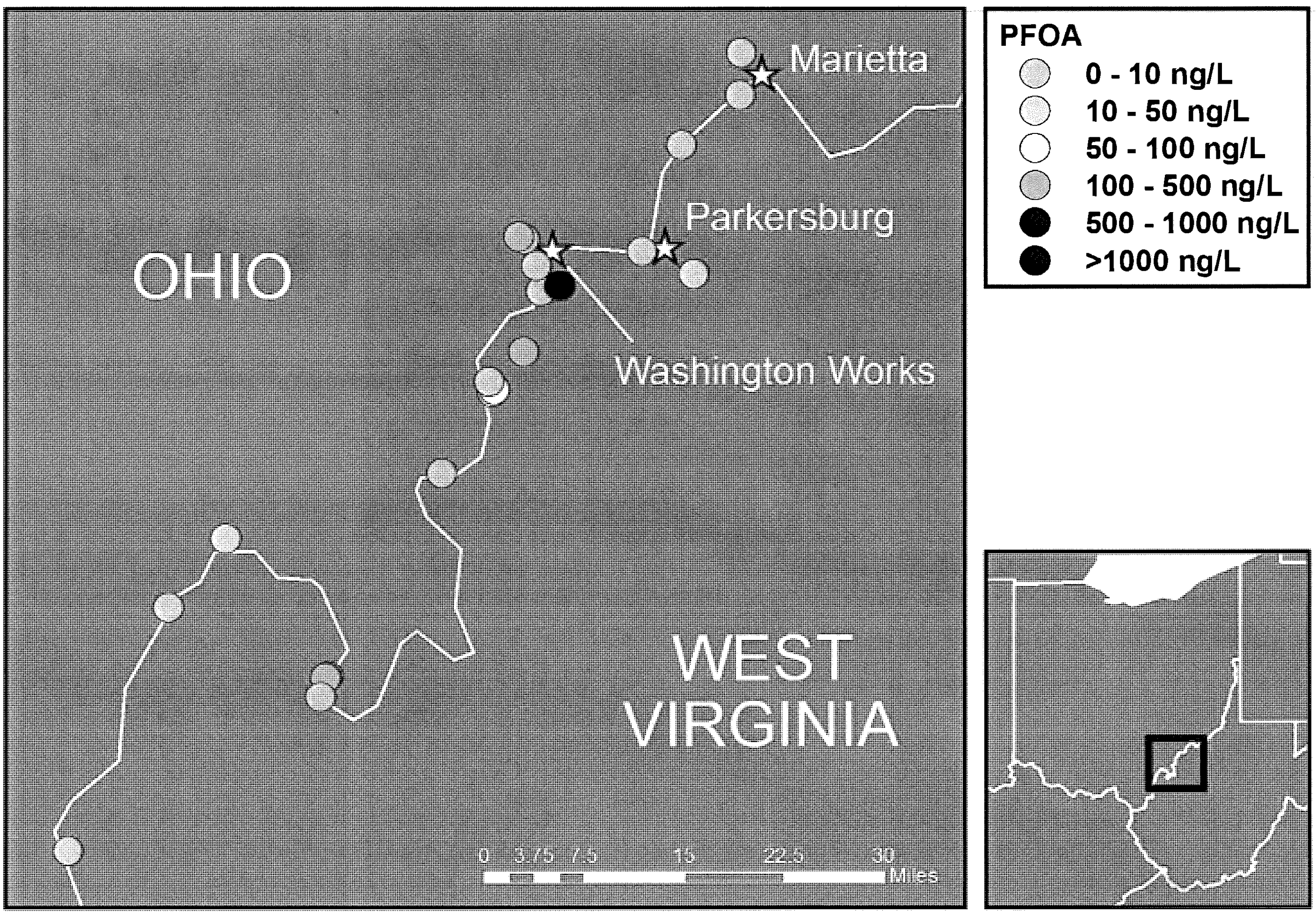
- DuPont studies found effects on rats similar to C8, including possible endocrine/immune disruption, enlarged livers and kidneys, and cancer



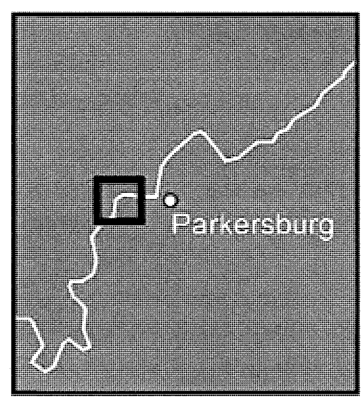
- Approved by the EPA, no further testing required

Trip #1 – Ohio River

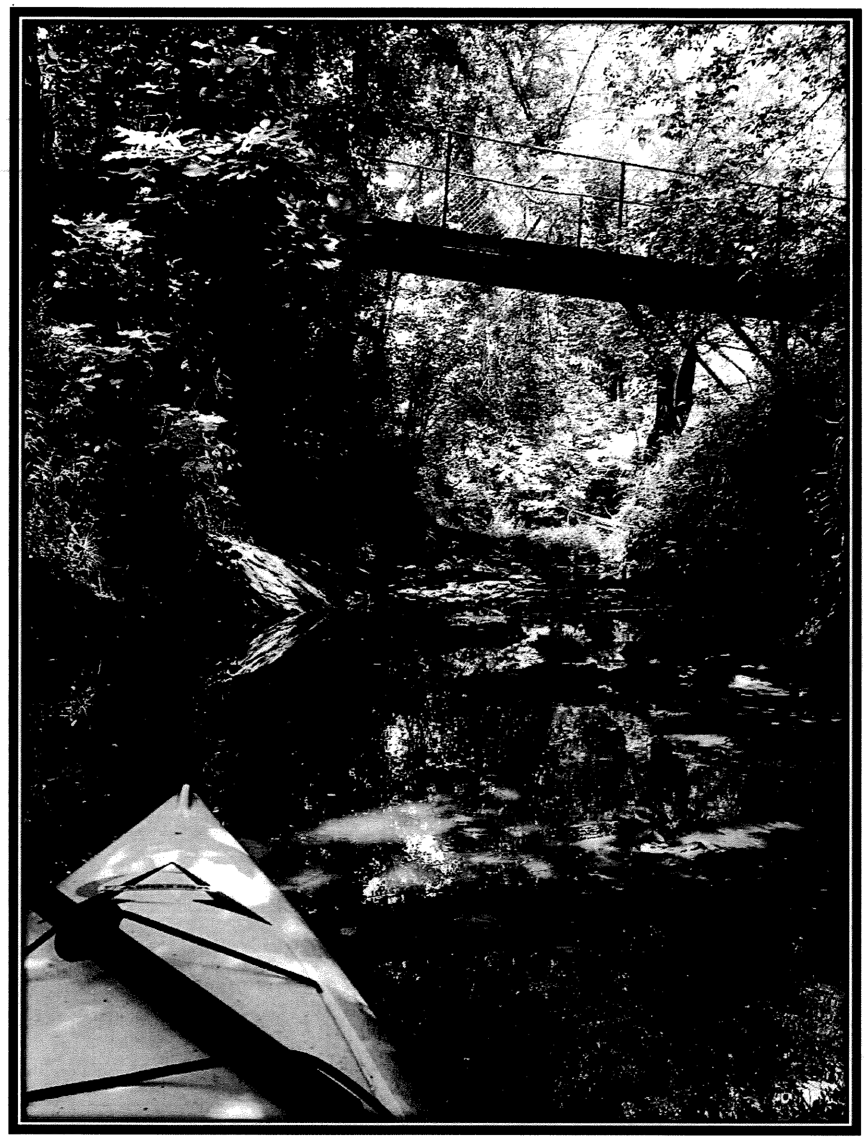
Ohio River Results



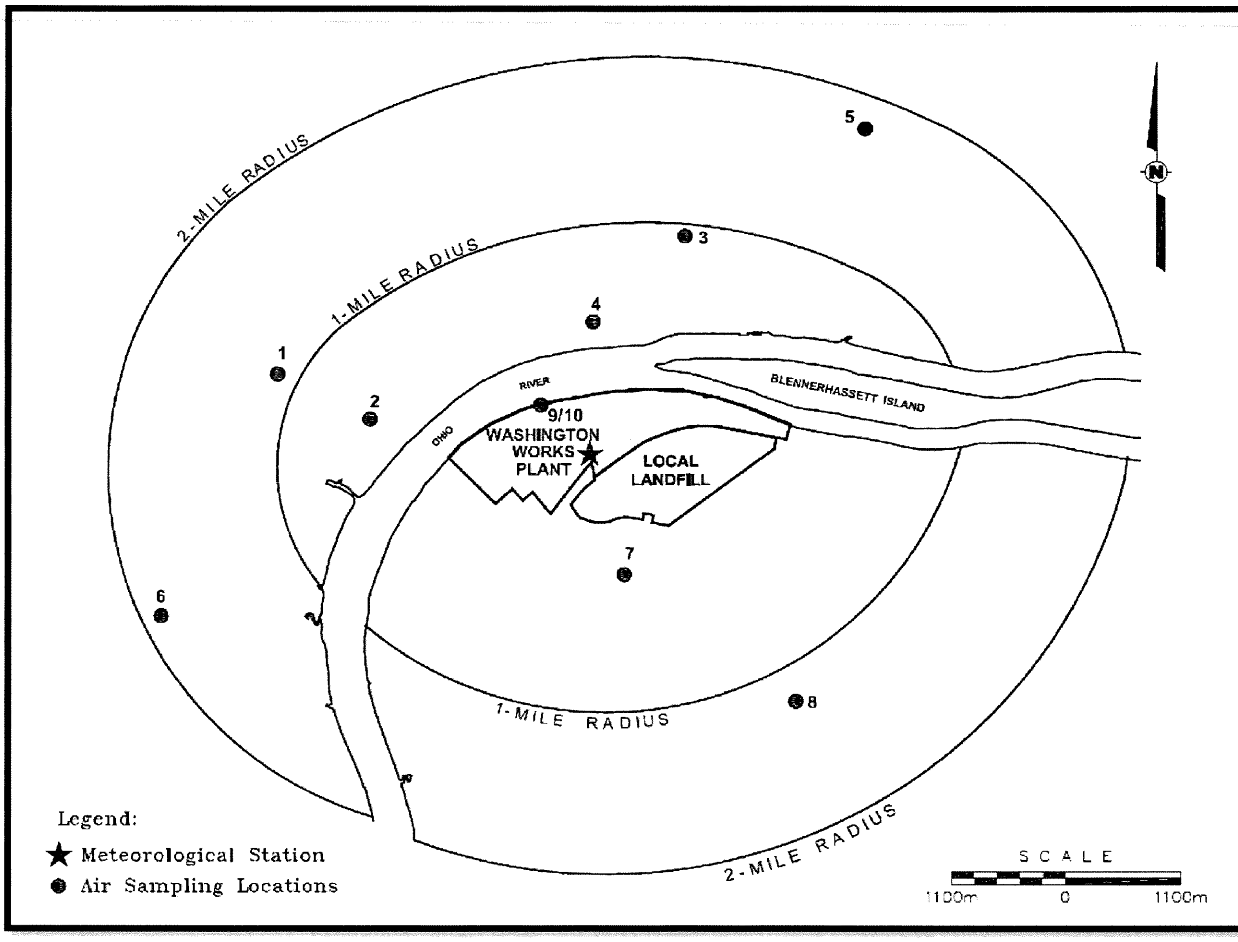
Ohio River Results (Detail)



Trip #2 – Little Hocking River

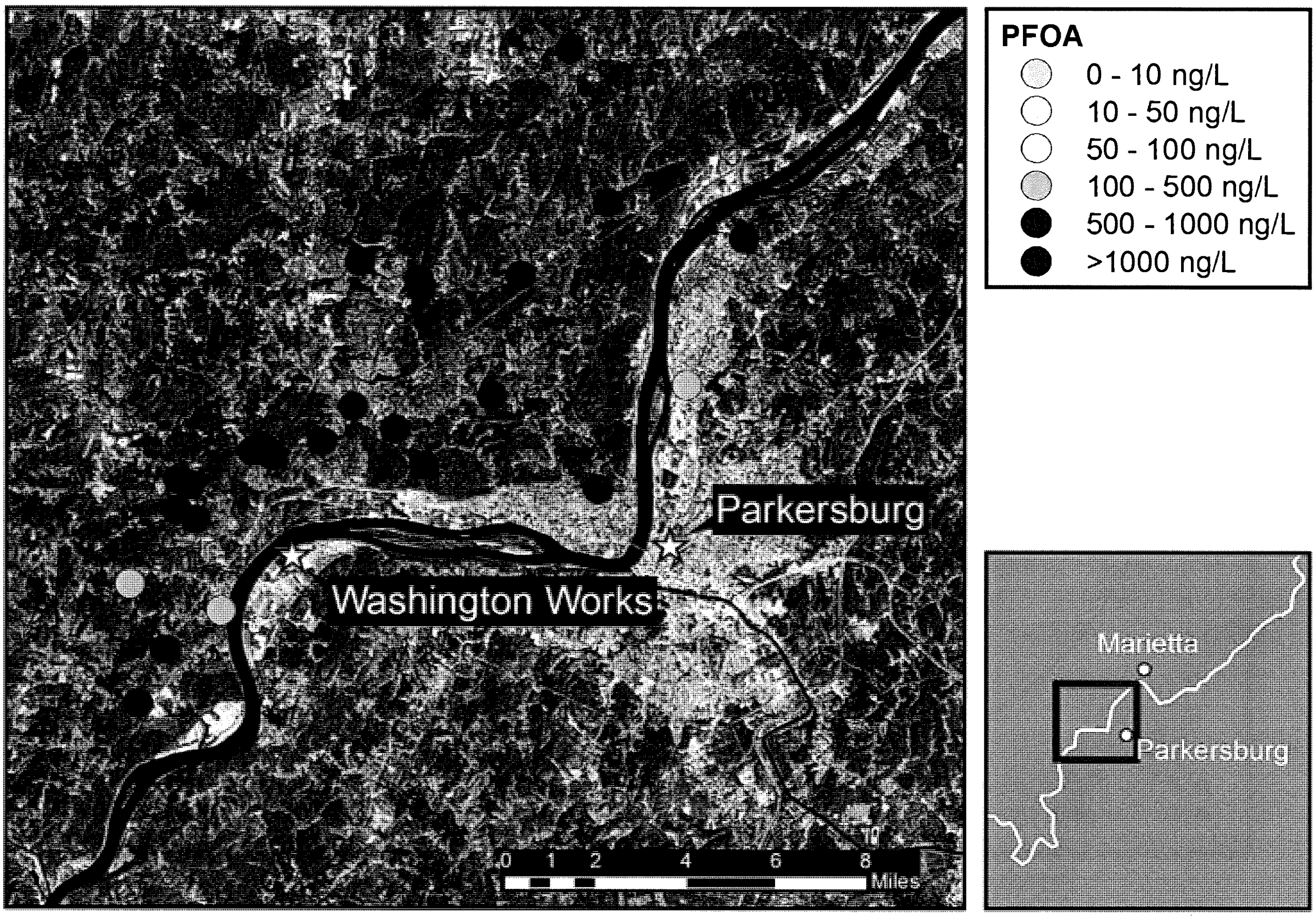


Air Monitoring Around Washington Works



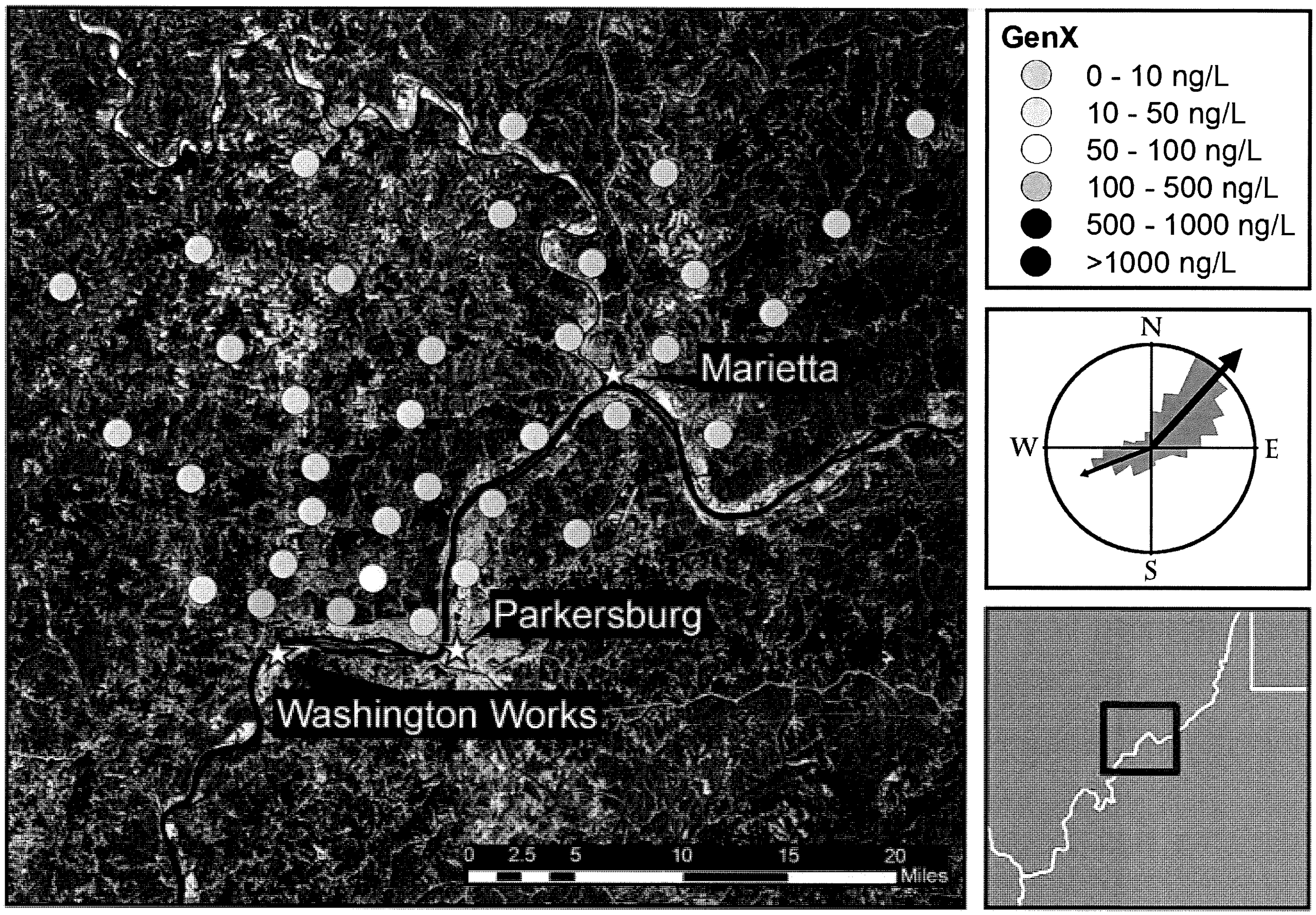
Barton et al. *Journal of the Air & Waste Management Association* 2010, 60, 402–411

Little Hocking Results



Trip #3 – Little Hocking and Beyond

Extended Sampling Results



Conclusions

- The presence of significant levels of PFOA (>100 ng/L) in surface water more than 15 miles from the facility and quantifiable levels (>10 ng/L) more than 25 miles away suggest local contamination may be more extensive than originally thought

- The discovery of GenX at many of the collection sites suggests the replacement PFAS is contaminating the local environment via air deposition as well

- More testing is needed – especially private well water between the boundaries of the Little Hocking Public Water district and the Muskingum River

Questions?

Email: lindstrom.andrew@epa.gov
galloway.18@osu.edu

Call

(6/14)

distribute to group

O Invite

[redacted]

Deeb follow up.

O - deliverables / Next Steps

DHHS

+ DEQ Communication Meeting

Working on a joint DEQ/DHHS press release

+ DPH
Working on FAQ for health departments

O DPH Communication Call 6/16/17 9:30 Am

O 11:00 DEQ/DHHS meeting

11:00 NHC meeting

2 participant list

- 1:00pm EPA Call

C 252 671 4778

O 910 796 7386

WATER TESTING:

DEQ

Wilmington

Jim Gregson Regional Office

ASR

Michael Johnson

Michael / Knappe

MACK

1

published Reports (2) - Pender

phone conversation

Meet

Julie Gribe

Stephen

→ CASE Study c GAC (C8)

on Pender

Cape Fear

Public Utilities

Heidi Cox

New plant 2012

(Source Water Flexibility 79%)

AWWA 79%

Jim Gregson

Gregson

3

O calls

summations

Stephens + Sites

funding

Jud:

Update to info More

Smithfield
up and down River plus wells.

#4 call 8 May

DWM Plant → ground water monitor

Chemours · One Sample 2014
water scrubber
gas permeator → look at current DATA
are put in NOV 2013
post Dr Knappe's study

Contact other labs.

POC Luda

(26)

6/14

DEQ | DHHS

Plan on having.
Press release out by Noon

FORMAT of Tomorrow's Meeting
Ruth Smith — NHC
Be there 10:30 — Governmental Center
premeeting — START
10:45

MC Woody White
Chair County Commission → New
JUST Local County Commissioners

[STAR News Wagner pool reporter]
US Congressman STAFF too.

Who will Evaluate New Sampling data? → Other unregulated contaminants?

Ruth Smith → ASK About
public Meetings
Consult c̄ County Attorneys.
yeah!

/ Going over agenda
/ County to ASK Chemours (3-4 reps)

Jessica Godreau
Linda Sink
Connie Brown
Jeff
Julia Gribs
Zack Moon
Michael Scott
Scott Coleman
Mark Shuler
Kennedy Holt
Sarah Young
Chris Mosely
Jamie Kanak
Bridgette Morgan
Linda Culpepper
Jay Zimmerman
Mark Burton
Amy Rose
Rich Fogle
Secretary Regan
Danny Smalley
Jim Gregson
Heidi
Bob Midgette
Trent

Time line

Scope and bounds of testing? TRI?
How much do we test for???

11:30 – 12:45 [ ] 1:00 pm – 1:30 pm / 2:30 PM

Live: County / City TV
Facebook
Web site

We are available to the media

Sec Regan
DS MARK Benton
AS Shute Holman.

How to answer is this water safe TO drink.

ZM: 2013 – 2014 (safe?)
Speak about it
Convey uncertainty

Analytical done by EPA (ask Knappe)

Fy

⊛ Fish Consumption Contribution

Triennial review
• unregulated contaminants

DWM || at the site
14 wells
6/Hits on C8 ||

|| Background
put Story
into Context

⊛ FAQ's | 2016 Hx data

No impact to surface waters

2 potential receptors on property

40-

50 lbs air

396 Water 2 lbs/day @ 180 days

Sampling Plan

Effluent M/T/W 24 hr Composite (Test America) 6/16 get the stuff Fri

4 intakes

King Bluff
Lower Capefear
five Facilities

CFPUA · ASR
Bladen · well
Pender
Bruns.
Int Paper / Riegelwood

3-4 weeks

1 set (10) 3 intake
5 WTP
1 ASR
1 WB well

— per week

10 location

Wrightsville Beach well = connection = them.

Next 3 week
Starting R
Next well 6/22

2 week TAT

dermal

Wait 1 month

another round of Sampling

B/A
Brunswick Contaminant
Render Samples (3)

More Samples.

HFPF dimer

Chairman
NH Woody White

9/14/17

EPA Call 1:00PM

Federal
STATE

TSCA — Permit

Current permit doesn't monitor
Gen X; it does regulate PFOA/PFOS
(not delegated to STATE); 99% Effluent; EPA oversees.
2009 – 2017

EPA
2009
Re Chemours order Report
Self test
Chemours
EPA → budget

Chairman White

How is that measured
* All effluents @ WVA not NC

DATA meet federal mandate
Annual; doesn't require INFORMATION

EPA — looking at DATA
Michael Johnson
Sampling locations
air emissions: 40-50lbs/year
water - 2.2lbs/day operation 180days 396lbs/year

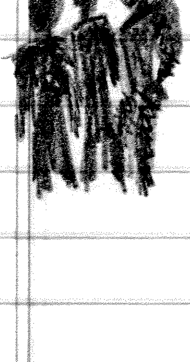
MAKE SURE
FOCUS ON what HSL
[scribbled] means

EPA TOXICOLOGIST AND
RISK ASSESSORS

who are they
and what are
they ASSESSING.

2013
GAS permeator
at Plant site

— emission



Control Technology

Consent Agreement.

GEORGE HOUCH

Find out who
it is

EPA
ORD
Testing
available?

HFPO dimer acid
WVA incinerator.

6/15 (1)

Kelly O'Keef
Shawn Gannon
Mike Johnson
Andrew Barton

• 300 people employed
•

Is the water Safe
• GenX in drinking water IS safe
no harm in human health
why → health and Safety
data
replacement for PFOA
EPA → TSCA new chemical
Approval
withdrawl
limitations
consent order – mitigate concerns
health & Safety Studies
[illegible] / nine studies → EPA
releases into the environ.
99% Control
|| Manufacture GenX ok but
Vinyl ethers → GenX by product
unregulated chemical
diffrent / un intended
Site
Not under consent order

EPA Toxicologist → Amy (Mina) (UTA Sheela) ②

Controls 2013 put into place (Abatement)

June - Dec 2013 / + 2014
631 ng/L

Models 80% reduction
2016 → 100 ng/L calculation
(Models only)
not Actual Sampling
Sampling needed and committed.

70909 ng/L DHHS HSL
Can Chemours share these studies ??

Vinyl Ether process → Did they know prior to 2013 ?? And could of done something → Measure ports Steam ??

WWTP
↓
Lock 3
Lock 1 3 days

MASS discharge

USGS flow

Good Stewardship?

MASS/disch / Flow (96 ppt) 2016

Air → emissions
water →

Vinyl ether {1980 → 2013} November ← Abatement
3 TANKERS pending

80% reduction | 20% process changes operation changes

Compound level 15,000

pronounce

Chimours "Chim" "oars"

1 second 32K years.

| Trivializing the concentration |

rate (constant / variable ?) of waste flow ?

24 hour composite sample at site

100 drops (3)

10 pools

10 drops
1 pool

Answer:
Both
(Surfactant)

PVE made during ETL study.
on each sampling event

Air emission
40-80 lbs/year
2.2 lbs/day

Does
The Vinyl Ether
process have
Same lenbyar [?]
emissions ?

1 million gallon waste

12 million gallons

20ppb
+ River
↓
100 ppt

(dilution)

| Provisional |

Record keeping
for Consent
order process and
Vinyl ether
process.
↓
was there anything

Combined toxicity test ?
Tell later
me

chronic health
C4
effects at same time

(C3 diamine
ethics [?])

④

- other 6 are not ruled out on the 10 State Study →

Pittsboro
Fayetteville
Bladen Bluff

① Hx record of discharge
water
air

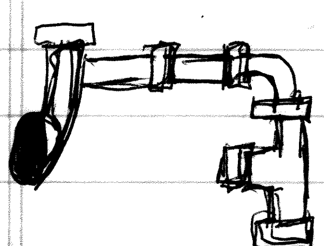
[redacted]

② Provisional non Regulatory / non enforcement Health Screening value

EPA Toxicologist
SAB / DEQ

Yes

③ 7 Health Studies → Availability



④ up date what is GenX an intentional by-product of Vinyl ether process

"Emotional Issue"
Assumes Irrational response, [redacted]

[redacted]

⑤ Community Meetings next ?
NHC
Chemours ?

But no less important. The public has a right to be emotional!
Let them speak out

6/15

Carol Kemker   Linda Culpepper

INFORMATION

POC

2 year Study Maria/Tala / Ken Mitchell

Increased

EPA → 0.1 (*)

OCC ↗ 1.0 .1 .5 .3

< 28 day

Reproduction

OCC → ENV exposure

|| Guidance (Tuesday)

(2-3)

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

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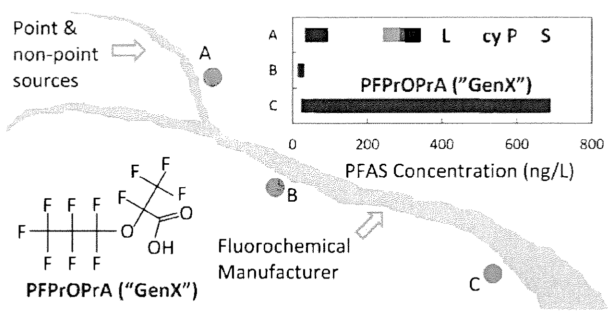
[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.[1] Until 2000, long-chain perfluoroalkyl sulfonic acids [$C_nF_{2n+1}SO_3H$; $n \geq 6$ (PFSAs)] and perfluoroalkyl carboxylic acids [$C_nF_{2n+1}COOH$; $n \geq 7$ (PFCAs)] were predominantly used.[2] Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs[3,4] has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.[5,6] Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.[7−10] Some fluorinated alternatives were recently identified,[8,11] but others remain unknown[12−14] because they are either proprietary or manufacturing byproducts.

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One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA), and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative[15] that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,[15] and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),[16−20] little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C−F bond makes PFASs refractory to abiotic and biotic degradation,[21] and most water treatment processes are ineffective for legacy PFAS removal.[22−27] Processes capable of removing PFCAs and PFSAs include nanofiltration,[28] reverse osmosis,[25] ion exchange,[28,29] and activated carbon adsorption,[28,29] with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

■ MATERIALS AND METHODS

Water Samples. Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10−800% of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm_v) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μm, BET surface area of 1460 m^2/g)[30] proven to be effective for PFAS removal in a prior study[29] was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography−tandem mass spectrometry (LC−MS/MS) methods for PFAS quantification is provided in the Supporting Information.

■ RESULTS AND DISCUSSION

Occurrence of PFASs in Drinking Water Sources. Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

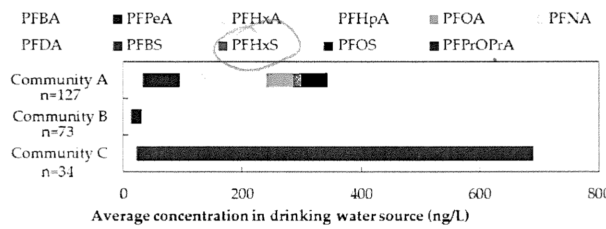

Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean ∑PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,[31] suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80−85% $C_nF_{2n+1}COOH$; n = 7−9) in 2006 to short-chain (76% $C_nF_{2n+1}COOH$; n = 5−6) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

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