Per- and Poly-fluorinated compounds Analysis:

Case Study Cape Fear Drainage Basin

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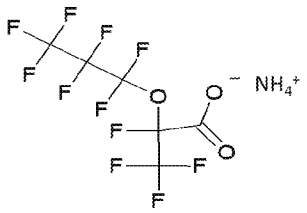
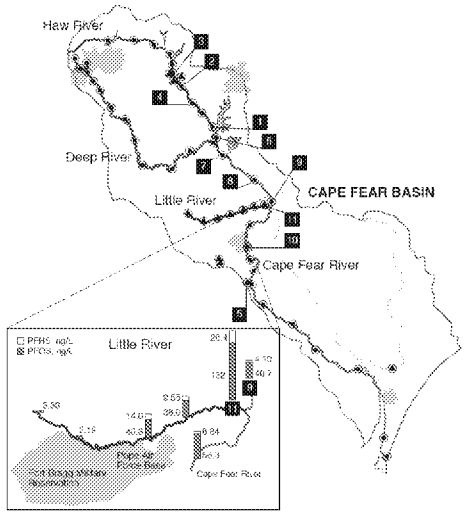


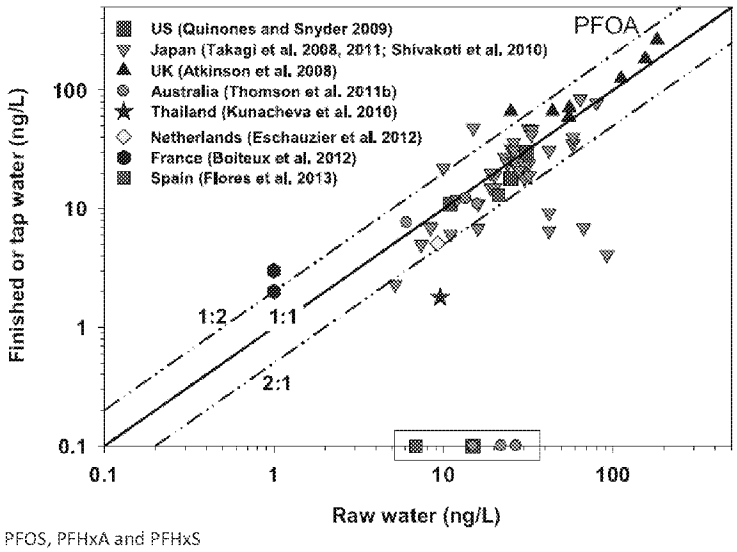


R4 State Labs Presentation
October 17th, 2017

Presentation Content

- Background
- Timeline
- Methods
- Nakayama et al., 2007 findings
- Strynar et al., 2015 findings
- Sun et al., 2016 findings
- Current efforts and findings

PFAS Generally Not Removed During Conventional Drinking Water Treatment



Similar for PFOS, PFHxA and PFHxS

Rahman et al., (2014) *Water Research,* 50:318-340

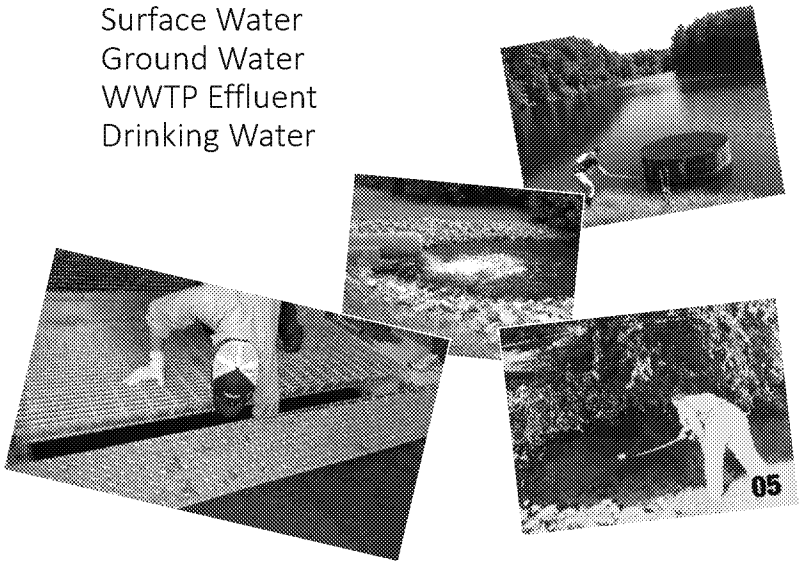
Work approached for detection not quantification

Timeline: US EPA/NERL Water PFAS Efforts

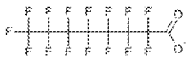
- 2007 Nakayama et al., PFAS in Cape Fear Watershed
- 2007-2008 Decatur, AL discovery of PFAS in bio-solids, soil, surface water, groundwater
- 2009 (January) Provisional Health Advisory (PHA) for PFOA and PFOS established 400 and 200 ng/L
- 2011-2012 Sampling of Cape Fear River for determination of replacement chemistries
- 2012 (November) Presentation at SETAC Long Beach CA – Identification of novel polyfluorinated compounds in natural waters using accurate mass TOFMS (GenX)
- 2013-2014 Collaborative study with NCSU with sampling of Cape Fear River and three municipalities (Pittsboro, Fayetteville, Wilmington, NC) for legacy and PFECA determination
- 2014 (November) Presentation at SETAC Vancouver, BC - Determination of perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in North Carolina surface water using high resolution mass spectrometry (GenX and eleven other novel chemicals)
- 2015 (August) Publication of Strynar et al., *"Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)"* ES&T
- 2016 (May) OW Health Advisory for PFOS and PFOA set at 70 ng/L
- 2016 (November) Publication of Sun et al., *"Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina" ES&T Letters*
- 2017 (June) Reporting of PFECAs in CFR and Wilmington drinking water – Star News Online

NERL/EMMD Water Analysis Method

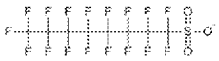
Surface Water
Ground Water
WWTP Effluent
Drinking Water



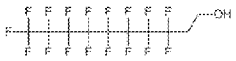
Some Typical PFAS



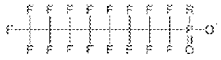
Perfluorocarboxylic acids
(ex. PFOA)



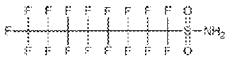
Perfluorosulfonic acids
(ex. PFOS)



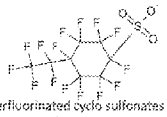
Fluorotelomer alcohol
(ex. 8:2 FTOH)



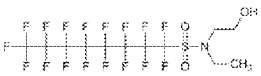
Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPi)



Perfluorosulfonamide
(ex. FOSA)

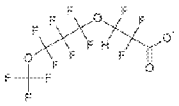


Perfluorinated cyclo sulfonates
(ex. PFECHS)

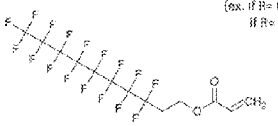


Perfluorosulfonamidoethanol
(ex. N-EtFOSE)

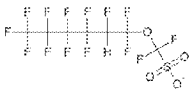
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
If R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

Analytes (n=24 native; n=19 isotope labeled)

Wellington PFAC-24PAR (2 ng/uL) $250/1.2 mL

	Analyte Name	Acronym	CAS Number
N-1	Perfluorotetradecanoic acid	PFTreA	376-06-7
N-2	Perfluorotridecanoic acid	PFTriA	72629-94-8
N-3	Perfluorododecanoic acid	PFDoA	307-55-1
N-4	Perfluoroundecanoic acid	PFUnA	2058-94-8
N-5	Perfluorodecanoic acid	PFDA	335-76-2
N-6	Perfluorononanoic acid	PFNA	375-95-1
N-7	Perfluorooctanoic acid	PFOA	335-67-1
N-8	Perfluoroheptanoic acid	PFHpA	375-85-9
N-9	Perfluorohexanoic acid	PFHxA	307-24-4
N-10	Perfluoropentanoic acid	PFPeA	2706-90-3
N-11	Perfluorobutanoic acid	PFBA	375-22-4
N-12	Perfluorodecanesulfonate	PFDS	335-77-3
N-13	Perfluorononanesulfonate	PFNS	68259-12-1
N-14	Perfluorooctanesulfonate	PFOS	1763-23-1
N-15	Perfluoroheptanesulfonate	PFHpS	375-92-8
N-16	Perfluorohexanesulfonate	PFHxS	355-46-4
N-17	Perfluoropentansulfonate	PFPeS	2706-91-4
N-18	Perfluorobutanesulfonate	PFBS	375-73-5
N-19	Perfluorooctanesulfonamide	PFOSA	754-91-6
N-20	Fluorotelomer sulfonate 8:2	FtS 8:2	39108-34-4
N-21	Fluorotelomer sulfonate 6:2	FtS 6:2	27619-97-2
N-22	Fluorotelomer sulfonate 4:2	FtS 4:2	NA
N-23	N-ethyl-N-((heptadecafluorooctyl)sulfonyl)glycine	NEtFOSAA	2991-50-6
N-24	N-(Heptadecafluorooctylsulfonyl)-N-methylglycine	NMeFOSAA	2355-31-9

Analytes (n=24 native; n=19 isotope labeled)

Wellington MPFAC-24ES (1 ng/uL) $700/1.2 mL

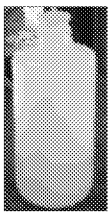
	Analyte Name	Acronym
	PERFLUOROALKYLCARBOXYLATES (PFCAs)	
L-1	Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid	M2PFTeDA
L-2	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	M2PFDoA
L-3	Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	M7PFUdA
L-4	Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	M6PFDA
L-5	Perfluoro-n-[$^{13}C_9$]nonanoic acid	M9PFNA
L-6	Perfluoro-n-[$^{13}C_8$]octanoic acid	M8PFOA
L-7	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	M4PFHpA
L-8	Perfluoro-n-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	M5PFHxA
L-9	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	M5PFPeA
L-10	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	MPFBA
	PERFLUOROALKYLSULFONATES (PFASs)	
L-11	Sodium perfluoro-[$^{13}C_8$]octanesulfonate	M8PFOS
L-12	Sodium perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonate	M3PFHxS
L-13	Sodium perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	M3PFBS
	PERFLUOROOCTANESULFONAMIDES (FOSAs)	
L-14	Perfluoro-1-[$^{13}C_8$]octanesulfonamide	M8FOSA-I
	TELOMER SULFONATES	
L-15	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]decane sulfonate (8:2)	M2-8:2FTS
L-16	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]octane sulfonate (6:2)	M2-6:2FTS
L-17	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]hexane sulfonate (4:2)	M2-4:2FTS
	PERFLUOROOCTANESULFONAMIDOACETIC ACIDS	
L-18	N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	d5-N-EtFOSAA
L-19	N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid	d3-N-MeFOSAA

Quality Assurance – Quality Control

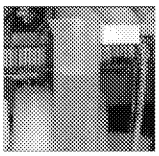
- Trip spike(s) (ex. 50 ng/L) MOST PEOPLE DO NOT DO THIS
- Trip blank (DI)
- Replication (>10%)
- Occasionally standard addition
- Extracted calibration curves

Method Summary – Sample Processing

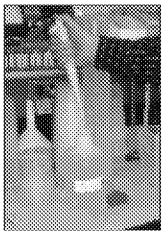
Nakayama et al., 2009, Strynar et al., 2015; Sun et al., 2016, Newton et al., 2017



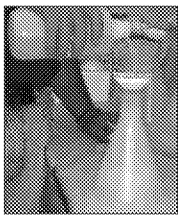
1 L HDPE bottles
5 mL 1:1 HNO_3 (35%):DI
Shipped ambient



Pour water out of sample bottle for volume measurement

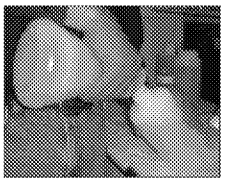


Wash bottle with 10 mL MeOH, add water back to bottle, add IS Shake



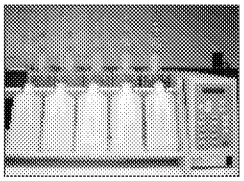
Filter entire contents
Whatman GF/A 1.7 um

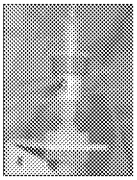
All samples Treated same way
- Trip Spike
- Blanks
- Unknowns
- Calibration



Add filtered water back into original bottle

Subsample 500 mL
Store 500 mL

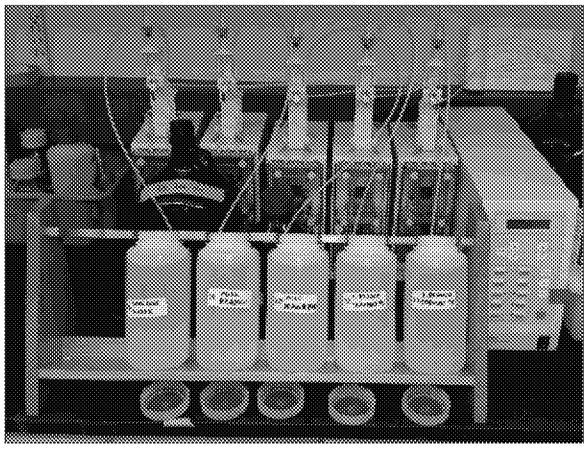




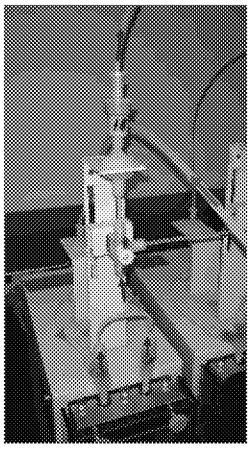
Load onto SPE tube
Waters Plus style WAX

Elute for LC/MS-MS analysis

Positive Displacement Sample Concentration



CHRATEC Sep-Pak Concentrator
SPC 10-C (10 ml/min)



Waters Oasis WAX-plus

Sample Elution

Note: Rack modified to fit 15 mL BD Falcon tubes

Wash:
4 mL pH 4.0 buffer
(Acetate/Acetic Acid water)

4 mL methanol

Elute:
4 mL NH_4OH/MeOH

Evaporate:
~15-20 minutes 40°C N_2
TurboVap concentrator

~ 0.5 – 1.0 mL

Sample prep for analysis:
Prepare sample to match
starting conditions of UPLC
gradient (75:25 aqu:MeOH)

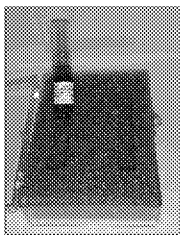
Samples That Exceed Calibration Curve

- Estimate concentration based on exceedance analysis
- Dilute sample (analyte and IS presence) with DI lab water (IS added) (ex 1:1, 2:1, 5:1 10:1) aiming for midpoint of calibration curve.

Example: Standard curve 10 – 1000 ng/L PFOA
Sample estimated to be 1600 ng/L

- Dilute sample into new HDPE bottle:
  1 part (250 mL prepared water sample with IS spike and analytes)
  1 part(250 mL) DI water with IS spike at same level as real sample
  Re-extract, elute and analyze.
- Calibrate against existing calibration curve.

Source of Analytical Standards



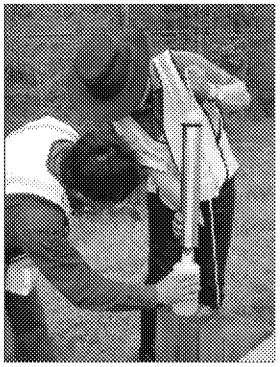
Stable Isotope Labeled (^{13}C, ^{18}O, D):
Wellington Labs
Cambridge Isotopes Labs

Native:
Wellington Labs (Mixtures – 1-2 ng/uL; Individual 50 ng/uL)

Sigma-Aldrich
Synquest Labs
Oakwood Products
Manufacturer (industrial mixtures 3M, DuPont, Mason Chemicals)

Method Summary – Water Sample Collection

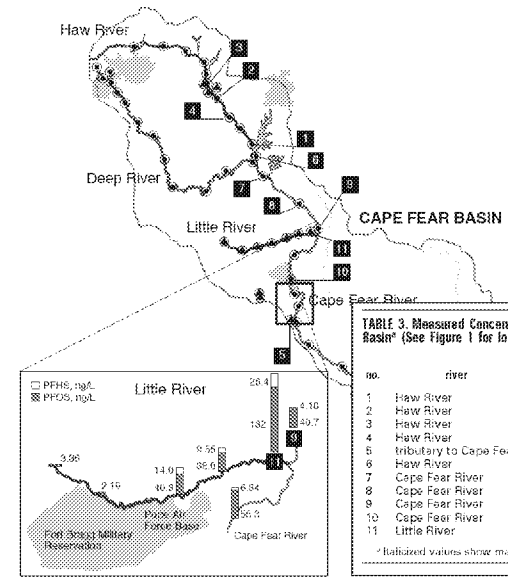
SS Kemmerer sampler



Lab-made dip sampler

Nalgene 1L HDPE bottles: PFAS free; Prefer wide mouth bottles

Water Sampling Cape Fear River, NC
Nakayama et al., 2007



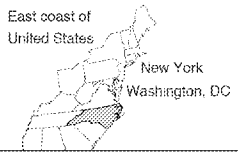


TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin* (See Figure 1 for locations)

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	*4.95*	*52.1*	*128*	*159*	*287*	116	21.7	127	8.43	*9.41*	942
2	Haw River	3.20	23.7	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	86.2	151	201	59.2	13.2	31.5	7.49	2.36	574
5	Tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	229	*23.0*	30.5	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	6.98	17.2	35.7	71.5	25.9	9.36	55.4	4.82	ND	228
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.16	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	3.36	3.23	*132*	*26.4*	3.20	185

* Italicized values show maximal concentrations of each compound.

{DateTime}

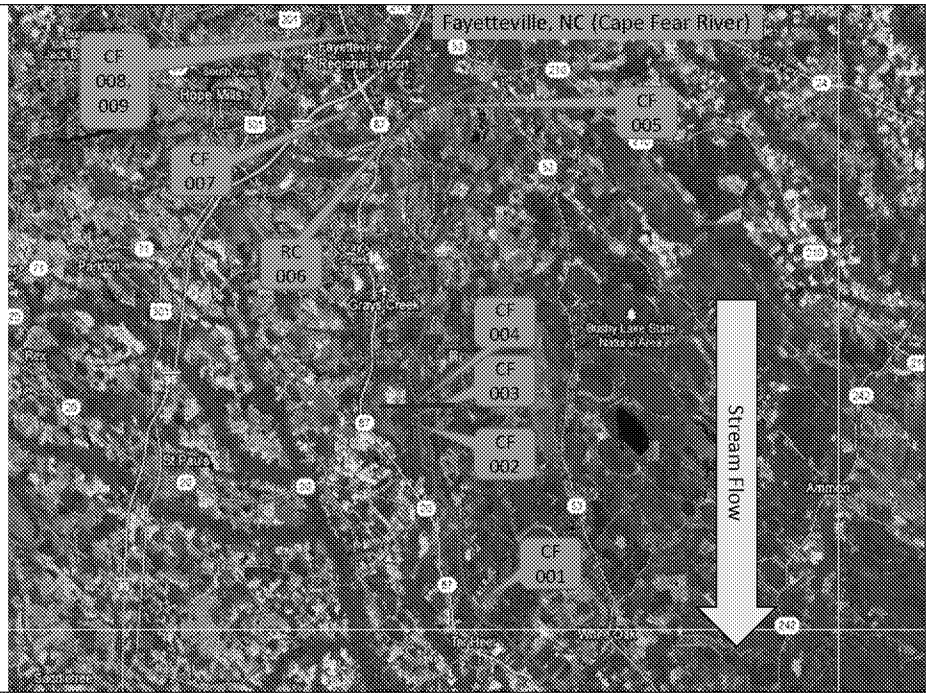
Framed talk in terms of defining the problem
Why this is important at NERL

First Sampling 2011-2012

Presented at SETAC 2012

Follow-up sampling 2013-2013

Presented at SETAC 2014



Legacy PFAS found in Cape Fear Water

Stream Flow

Analyte	001	002	003	004	005	006	007	008	008	009
C4	23	502	3761	6	4	0	8	7	5	3
C5	441	5607	43590*	17	9	1	32	46	12	9
PFBS	4	5	3	4	5	2	9	5	6	4
C6	17	90	434	18	12	2	27	16	18	14
C7	37	599	3873	14	17	0	11	20	21	9
PFHS	7	12	10	9	7	4	9	10	9	22
C8	32	39	71	33	25	2	38	36	41	18
C9	13	34	127	7	11	1	6	8	11	5
PFOS	19	27	26	17	23	0	0	16	18	14
C10	10	17	12	11	0	3	3	8	10	5

items in red exceed the standard curve high end of 500 ng/L; 10x diluted and re-analyzed; * still exceed curve and are estimated

Negative Mass Defect: Per- and Poly- fluorinated Compounds

Formula	Mass	C	H	N	O	P	S	Cl	F
		12.000000	1.007825	14.003074	15.994915	30.973762	31.972071	34.968853	18.998403
C_8H_{18}	114.1408506	8	18						
$C_8H_{16}O_2$	144.1150298	8	16		2				
$C_8HO_2F_{15}$	413.9737023	8	1		2				15
$C_8HO_3F_{15}$	429.9686169	8	1		3				15
$C_8HO_3SF_{17}$	499.937494	8	1		3		1		17

Octane	114.1408506
Octanoic acid	144.1150298
PFOA	413.9737023
Perfluoro-4-ether-octanoic acid	429.9686169
PFOS	499.937494

Mass fragments of per and poly fluorinated compounds conserve negative mass defect

Environmental Science & Technology

November 2015

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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[‡]

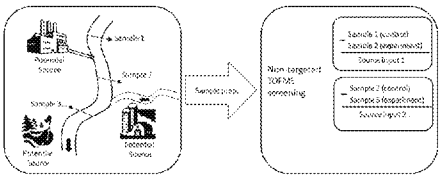
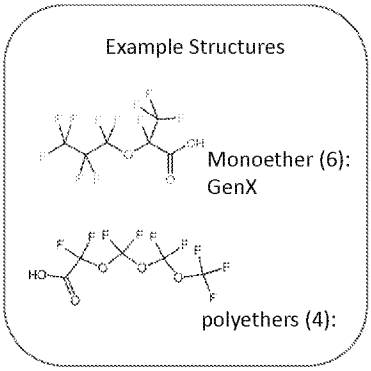
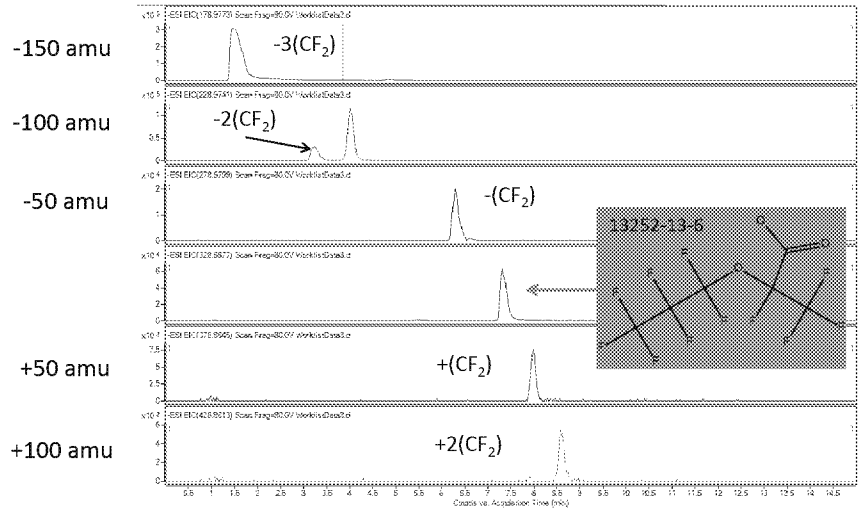


Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

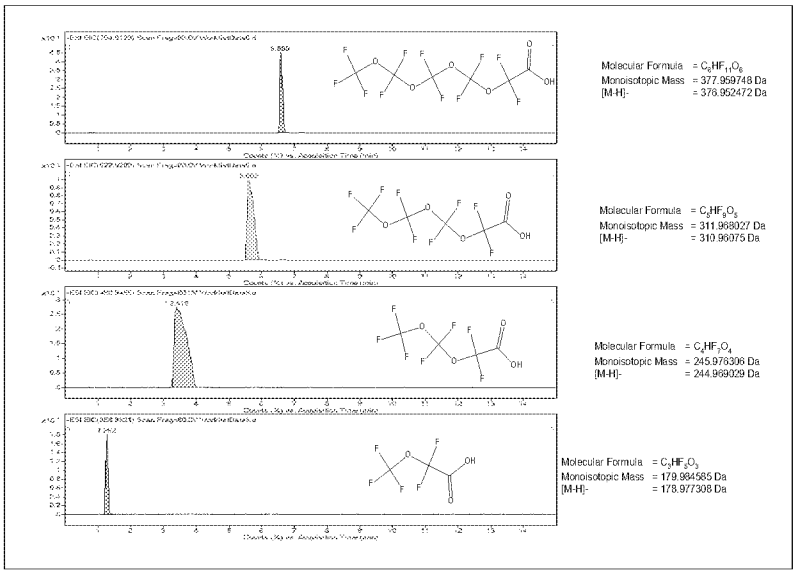
number	formula	CAS no.	name	$[M]^a$	$[M - H]^+$ m/z	$[2M - 2H + Na]^+$ m/z	$[2M - H]^+$ m/z
Monoether PFECAs							
1	$C_4HF_7O_3$			179.9846	178.9773	380.9438	358.9619
2	$C_6HF_9O_3$			329.9813	228.9740	480.9372	458.9553
3	$C_6HF_9O_3$	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	$C_8HF_{13}O_3$	13252-13-6	nudecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
5	$C_8HF_{13}O_3$			379.9718	378.9645	780.9182	758.9363
6	$C_8HF_{13}O_3$			429.9686	428.9613	880.9118	858.9299
Polyether PFECAs							
7	$C_7HF_{14}O_3$	39492-91-6	perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	445.9515	442.9442	908.8776	886.8957
8	$C_8HF_{15}O_3$	39492-90-5	perfluoro-3,5,7,9-butaoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	$C_9HF_{17}O_3$	39492-89-2	perfluoro-3,5,7-propaoxaoctanoic acid	311.9681	310.9608	644.9108	622.9289
10	$C_9HF_{17}O_3$	39492-88-1	perfluoro-3,5-diethaxanoic acid	245.9764	244.9691	512.9274	490.9455
PFESAs							
11	$C_7HF_{14}O_3S$	66796-30-3[b]		445.9337	442.9264		
12	$C_7H_2F_{14}O_3S$			463.9399	462.9326		



m/z Extracted Ion Chromatograph (EIC) Suspected polyfluorinated compound homologous series



Homologous series NOT offset by CF_2 BUT CF_2O



November 2016

Environmental Science & Technology Letters

Letter

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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[‡]

June 7, 2017 story on in Wilmington Star Online News basis

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StarNews

Toxin taints CFPUA drinking water

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OUR PICKS

By Vaughn Hagerty Starkines Correspondent

Utility can't filter out chemical produced upriver

Cape Fear River
Fayetteville to Wilmington, NC

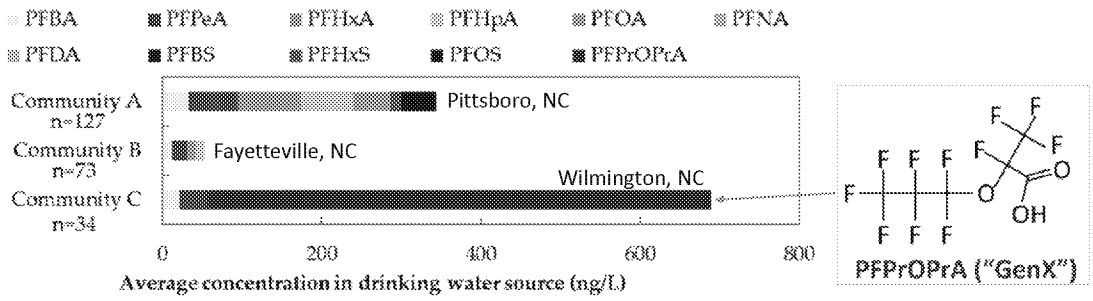
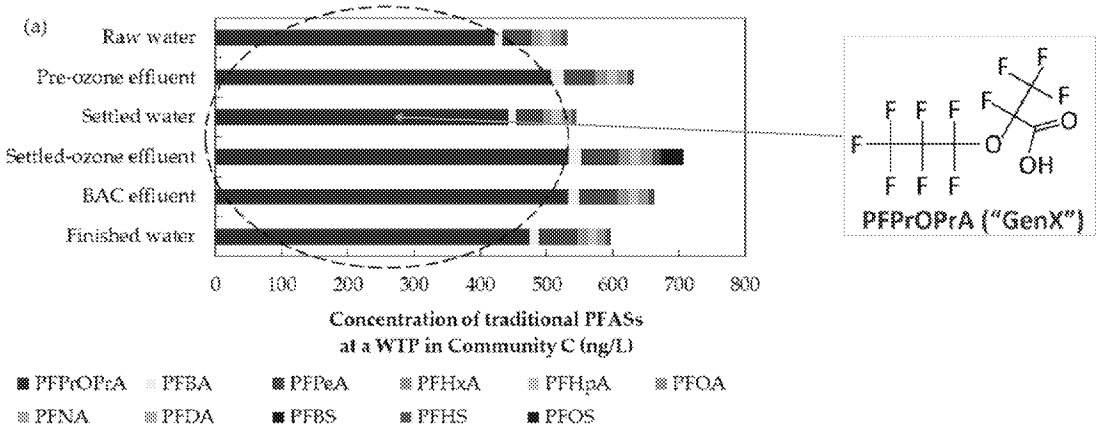


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations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

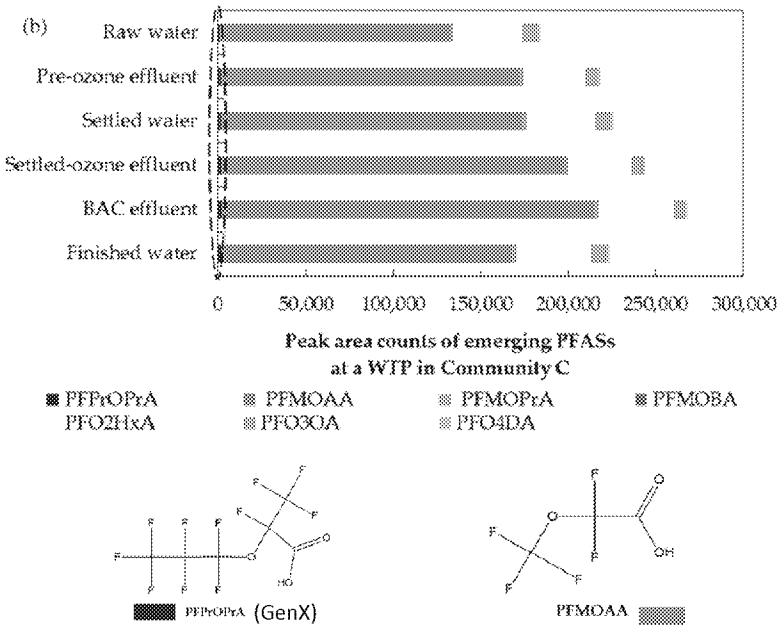
Sun et al., 2017

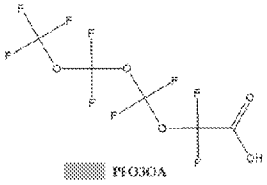
PFAS removal at Sweeney WTP

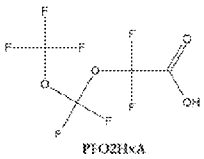


Sun et al., 2017

Other PFECAS Sweeney WTP







PFPrOPrA (GenX)

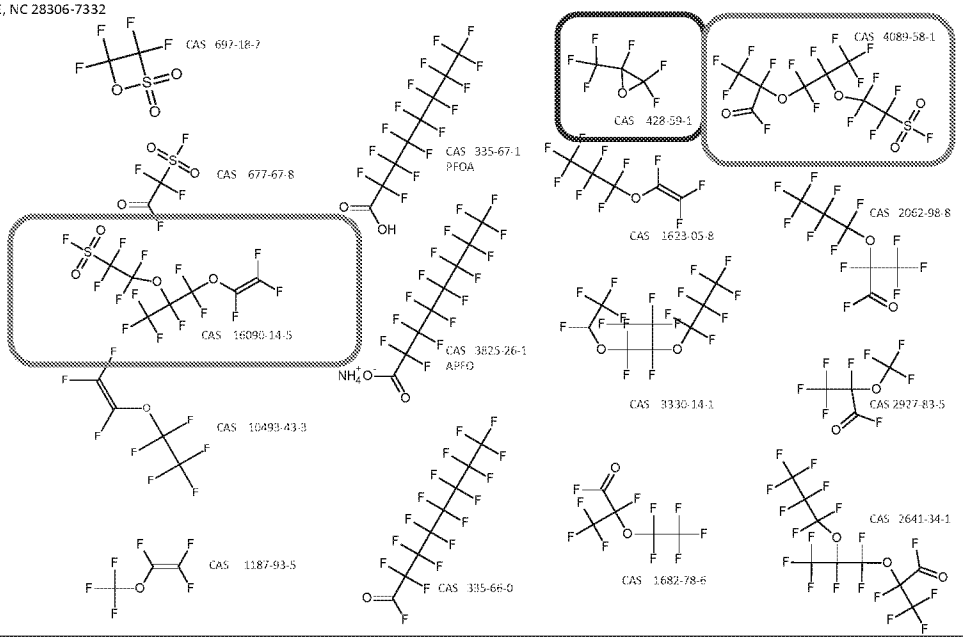
PFMOAA

Current Efforts: EPA/NERL/EMMD

- Completed method validation of PFAS (EPA 24 analyte list) in surface water, waste water and DI water
- Working with NC DEQ and EPA R4 for sample analysis CFR contamination GenX, Nafion by-products and related
- Full method validation GenX and 4 other PFECAs in tap water, surface water, waste water.
- Monitoring well and facility process sample analysis (ongoing)

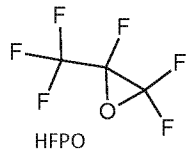
DUPONT FAYETTEVILLE PLANT
22828 NC HIGHWAY 87 WEST
FAYETTEVILLE, NC 28306-7332

http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609



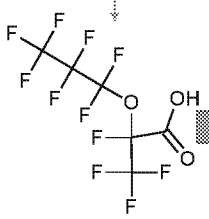
Hexafluoropropylene oxide (HFPO)

- an intermediate used in industrial organofluorine chemistry
- a monomer for fluoropolymers.
- colourless gas is the epoxide of hexafluoropropylene
- produced by DuPont and 3M and as a precursor to the lubricant Krytox and related materials
- generated by oxidation of perfluoropropylene, e.g. with oxygen as well as other oxidants



HFPO

CAS 428-59-1

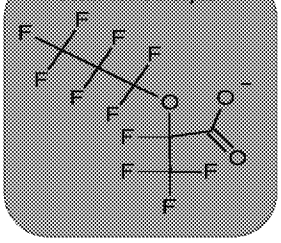


HFPO DA

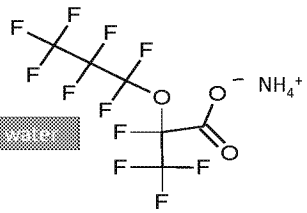
CAS 13252-13-6

in water

Common Analyte

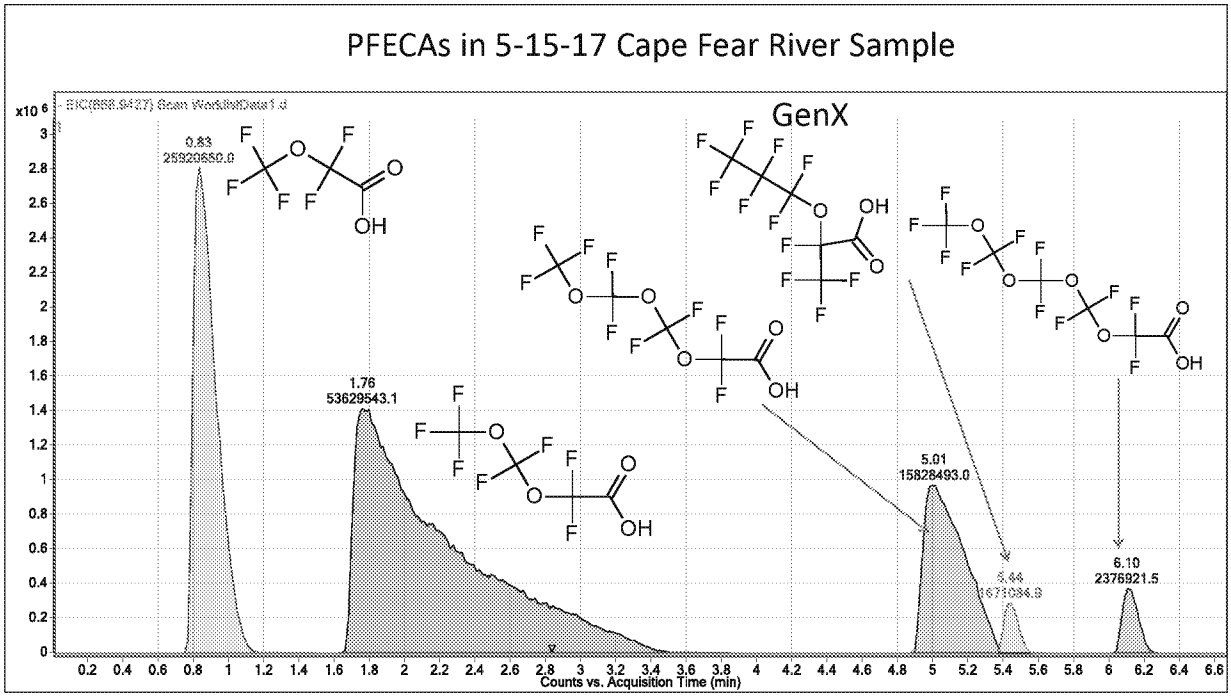


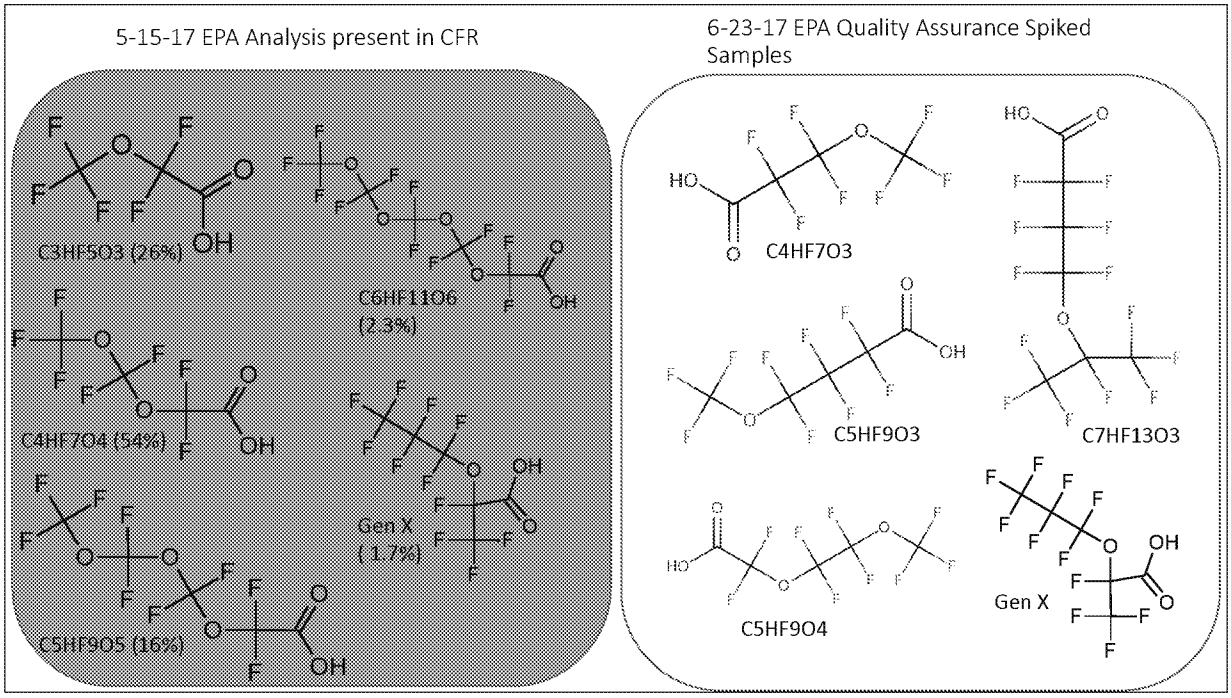
in water



GenX

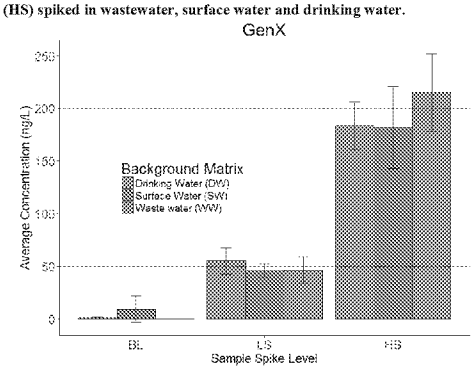
CAS 62037-80-3

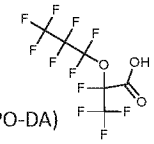

PFECAs in 5-15-17 Cape Fear River Sample
GenX
0.83
25920650.0
1.76
53629543.1
5.01
15828493.0
5.44
1671084.0
6.10
2376921.5
x10 6
Counts vs. Acquisition Time (min)


5-15-17 EPA Analysis present in CFR
C3HF5O3 (26%)
C6HF11O6 (2.3%)
C4HF7O4 (54%)
Gen X (1.7%)
C5HF9O5 (16%)
6-23-17 EPA Quality Assurance Spiked Samples
C4HF7O3
C5HF9O3
C7HF13O3
C5HF9O4
Gen X

PFECAs Method Validation McCord et al., 2017 draft

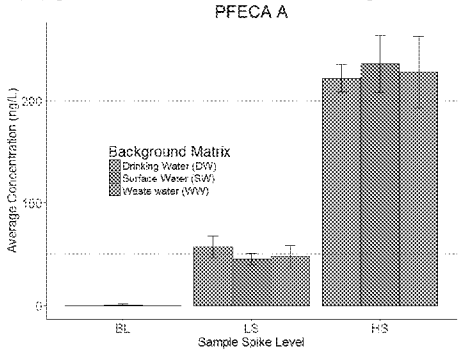
Figure 1. GenX Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.

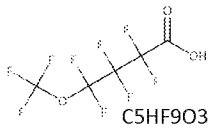




Gen X (HFPO-DA)

Figure 2. PFECA A Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.

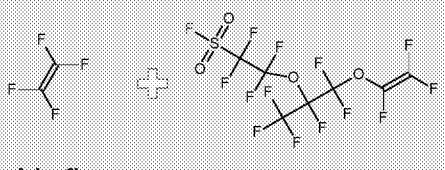




C5HF9O3

“Nafion Like” Compounds

CAS 16090-14-5



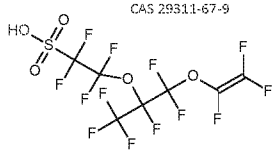
Nafion

http://www.chemspider.com/Chemical-Structure.55751.html?rid=adf15395-d088-4a3b-9df8-3298ea7c800b

- Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer.
- proton conductor for proton exchange membrane (PEM) fuel cells

Molecular Formula: $C_7HF_{13}O_5S$
Monoisotopic Mass: 443.93371 Da
[M-H]-: 442.926433 Da

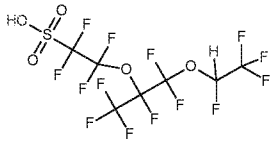
CAS 293111-67-9



Nafion BP1

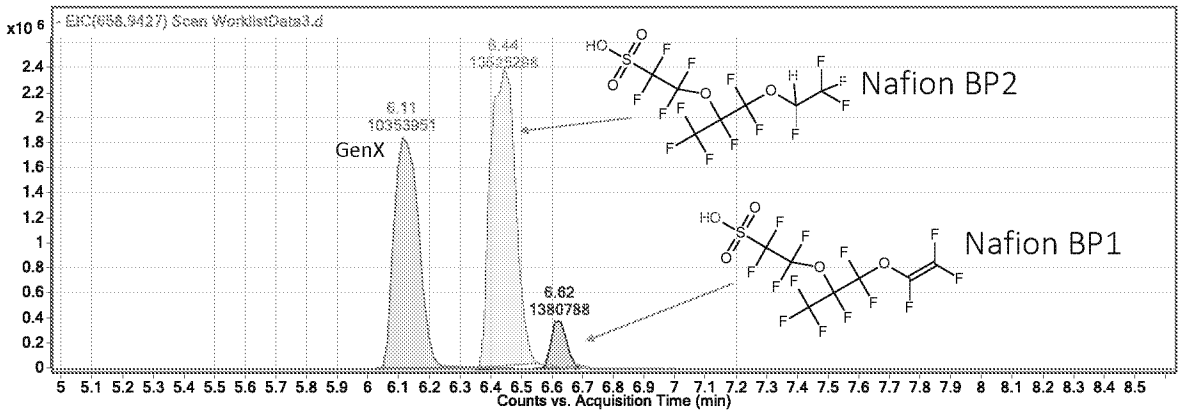
Molecular Formula: $C_7H_2F_{14}O_5S$
Monoisotopic Mass: 463.939938 Da
[M-H]-: 462.932662 Da

CAS 749836-20-2

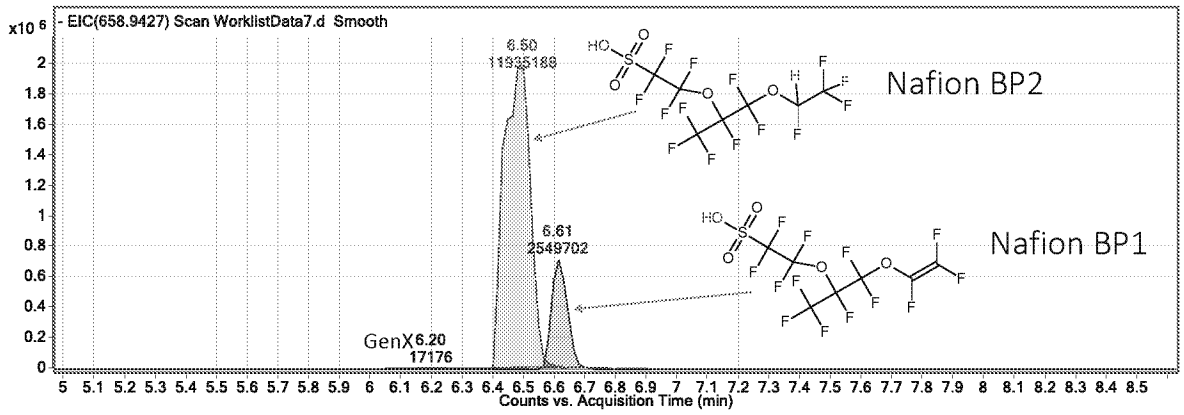


Nafion BP2

Nafion Like Compounds –
Week#1 Chemours outfall



Nafion Like Compounds
Week#6 Chemours outfall



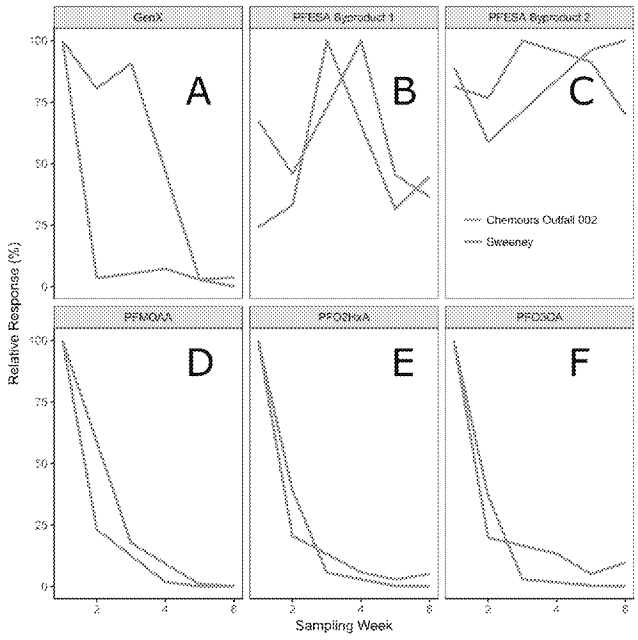
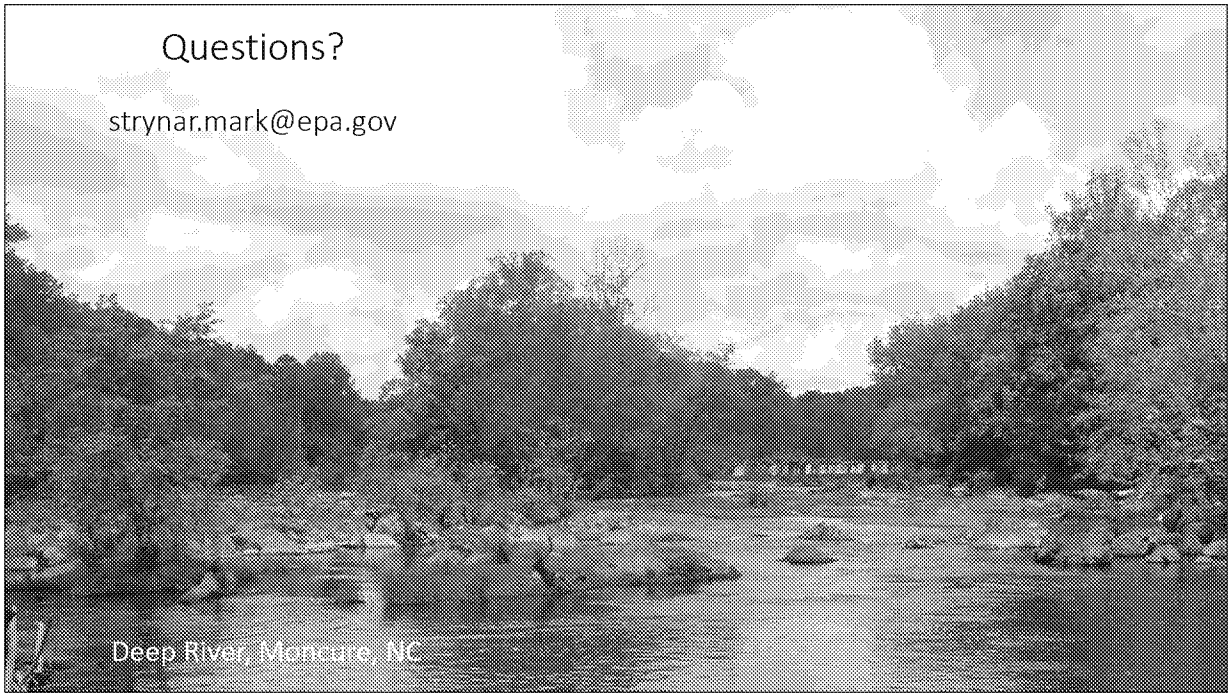


Figure 7. Relative change (compared to highest measured value) in PFAS concentration over weeks 1 – 6 for GenX and NTAs at the Chemours outfall and Sweeney Finished Drinking Water. GenX and NTAs in Panels A,D,E, & F show a consistent decreasing profile. The PFESA Byproduct concentrations are variable and do not show a clear trend.


Questions?
strynar.mark@epa.gov
Deep River, Moncure, NC