PFPrA Analytical Capabilities and Environmental Occurrence

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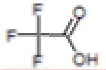
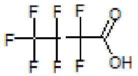
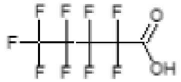
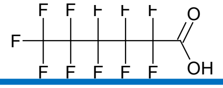
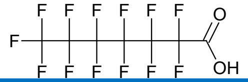
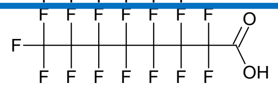
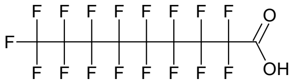
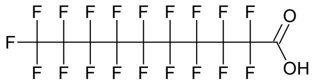
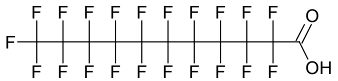
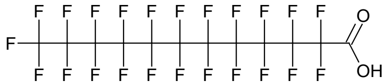
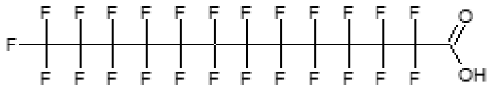
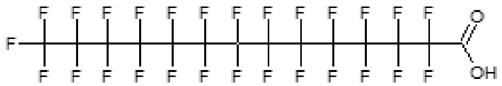
October 4, 2023

PFPrA Topics

- Background information
- Analytical challenges and approaches
- Data considerations
- Statewide measurement data
- SE NC measurement data

Homologous series of perfluorinated carboxylic acids

	Acronym	Structure	MW	Ions (m/z)
Trifluoroacetic acid	TFA – C2		114	113 → 69
Perfluoropropanoic acid	PFPrA– C3		164	163 → 119
Perfluorobutanoic acid	PFBA – C4		214	213 → 169
Perfluoropentanoic acid	PFPeA – C5		264	263 → 219
Perfluorohexanoic acid	PFHxA – C6		314	313 → 269
Perfluoroheptanoic acid	PFHpA – C7		364	363 → 319
Perfluorooctanoic acid	PFOA - C8		414	413 → 369
Perfluorononanoic acid	PFNA – C9		464	463 → 419
Perfluorodecanoic acid	PFDA – C10		514	513 → 469
Perfluoroundecanoic acid	PFUnDA – C11		564	563 → 519
Perfluorododecanoic acid	PFDoA – C12		614	613 → 569
Perfluorotridecanoic acid	PFTriA – C13		664	663 → 619
Perfluorotetradecanoic acid	PFTA – C14		714	713 → 769

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Sources of PFPrA

- PFPrA forms in the atmosphere from breakdown of compounds such as replacement refrigerants (HFCs and HCFCs) and is subsequently deposited
- Breakdown of longer chain PFAS
- Can be found near manufacturing facilities
- Chemours appears to be the main source of PFPrA in the SE part of NC

Origins of Table 3+ Compounds- Onsite Offsite Assessment

4.1.2 Laboratory Analytical Methods

EPA method 537 is a commercial analytical method to analyze for PFAS compounds, including PFOA and PFOS. EPA method 8321A is a commercial analytical method for HFPO-DA. Through non-targeted mass spectrometry analyses of water and soil samples collected at Site, Chemours has identified 24 PFAS not currently quantified by EPA Method 537 or 8321A. In 2019, a commercial analytical method, referred to as the Table 3+ SOP method, was developed (Table 2-1). An analytical method for four of these PFAS is still under development. These PFAS are Difluoro-sulfo-acetic acid (DFSA), Difluoromalonic acid (MMF), Perfluoro-2-methoxypropanoic acid (MTP) and Perfluoropropionic acid (PPF Acid).

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Determination of Table 3 *Plus* Compounds by LC/MS/MS

Chemours Fluoroproducts Analytical Method

Revision date 1/10/2019

QQQ Acquisition Parameters:

Compound Name	MRM Transition	RT (mins)	Dwell (msec)	Frag (V)	CE (V)	Cell Accelerator (V)
DFSA	175.0 -> 131.0	0.268	50	72	12	2
MMF	139.0 -> 95.0	0.271	50	93	8	1
MTP	175.0 -> 97.0	0.370	50	78	12	1
PPF acid	163.0 -> 118.9	0.394	50	58	8	5
PFMOAA	179.0 -> 84.9	0.437	50	54	12	1
R-EVE	405.0 -> 217.0	0.420	50	100	16	4
Byproduct 4	440.9 -> 241.0	0.509	50	114	28	1
Byproduct 5	439.0 -> 343.0	0.510	50	126	30	1
PMPA	229.0 -> 184.9	0.662	50	55	4	5
PFO2HxA	245.0 -> 85.0	1.046	50	60	8	1
NVHOS	297.0 -> 135.0	1.655	50	123	28	1
PEPA	279.0 -> 234.9	1.702	50	58	4	4
PFECA B	295.0 -> 201.0	3.027	50	55	8	3
PFO3OA	310.9 -> 85.0	3.298	50	54	12	3
PES	314.9 -> 135.0	3.388	50	109	20	5
HFPO-DA	329.0 -> 284.9	3.386	50	75	0	4
HFPO-DA_qualifier	329.0 -> 169.0	3.386	50	75	12	1
PFECA_G	378.9 -> 184.9	3.702	50	87	16	4
PFO4DA	376.9 -> 85.0	3.794	50	66	20	3
Hydro-EVE Acid	427.0 -> 282.9	3.825	50	90	12	3
EVE Acid	407.0 -> 262.9	3.825	50	78	8	2
Byproduct 6	397.0 -> 217.0	3.951	50	122	27	1
Byproduct 2	463.0 -> 262.9	4.072	50	160	32	1
Byproduct 1	443.0 -> 146.9	4.084	50	143	30	1
PFO5DoA	442.9 -> 85.0	4.085	50	66	8	1

Origins of Table 3+ Compounds - Corrective Action Plan Executive Summary

The PFAS that originate from the Site are referred to as Table 3+ PFAS. The Table 3+ analytical method was developed to analyze PFAS specific to the Site that were identified through non-targeted chemical analyses. Currently the Table 3+ method can quantitate for 20 PFAS compounds including HFPO-DA, i.e. "GenX". When examining PFAS at the Site, the sum of these compounds, i.e. total Table 3+ PFAS compounds, is often used to evaluate concentration trends and distributions.

The Table 3+ PFAS compounds are found onsite and offsite. The highest Table 3+ PFAS concentrations (by two to three orders of magnitude - i.e. 100 to 1000 times higher) are found onsite. Onsite the PFAS in many of the wells and surface water drainage features have a PFAS signature indicating the PFAS in these wells or surface water features originated from historical direct releases of process water. Onsite the process water signature is found over an area of approximately one square mile. Offsite Table 3+ PFAS in groundwater have an aerial deposition signature and a much lower and diffuse concentration of PFAS over a much larger area (70+ square miles) than the onsite process water signature. The Cape Fear River as it flows past the Site gains a process water PFAS signature indicating that transport pathways comprised of process water signature PFAS loading dominate the mass loading in the Cape Fear River.

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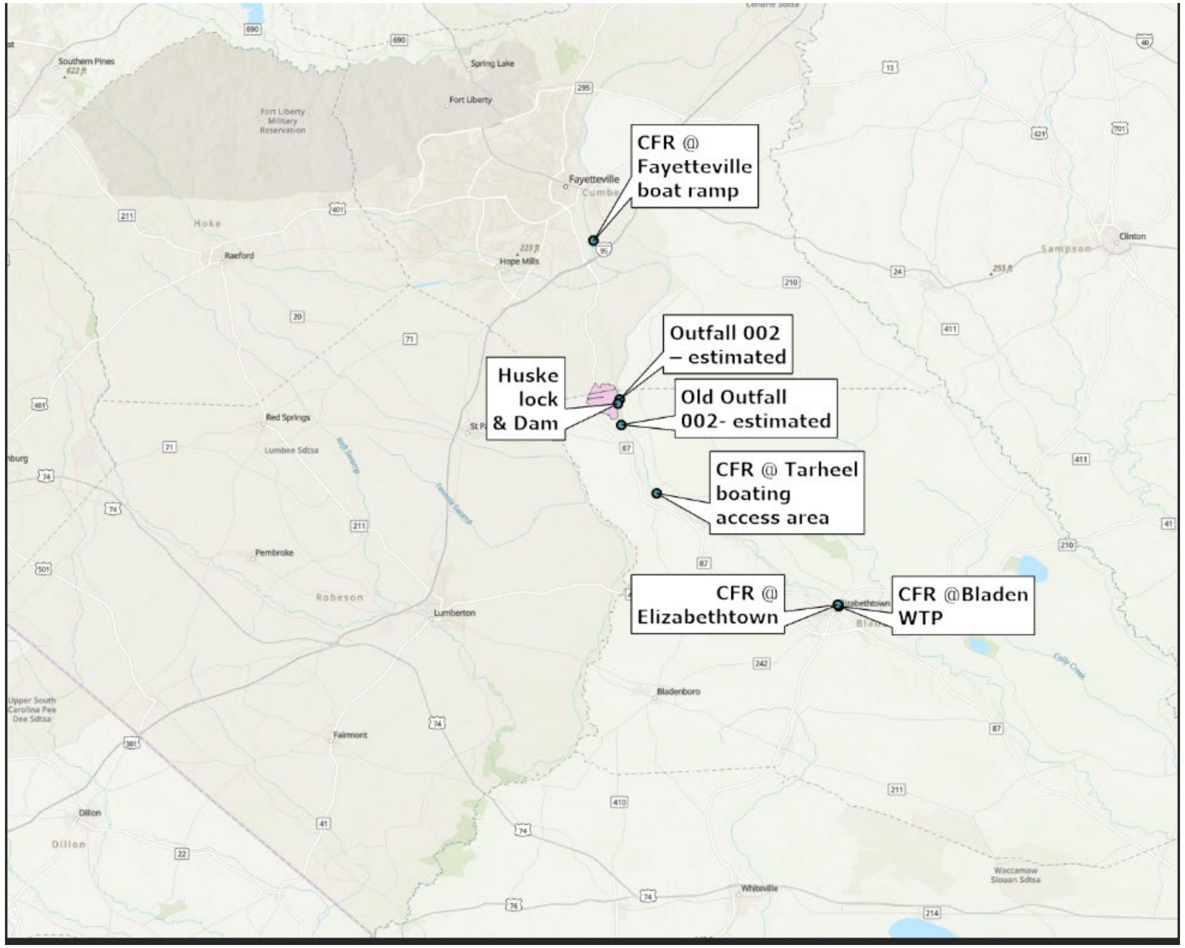
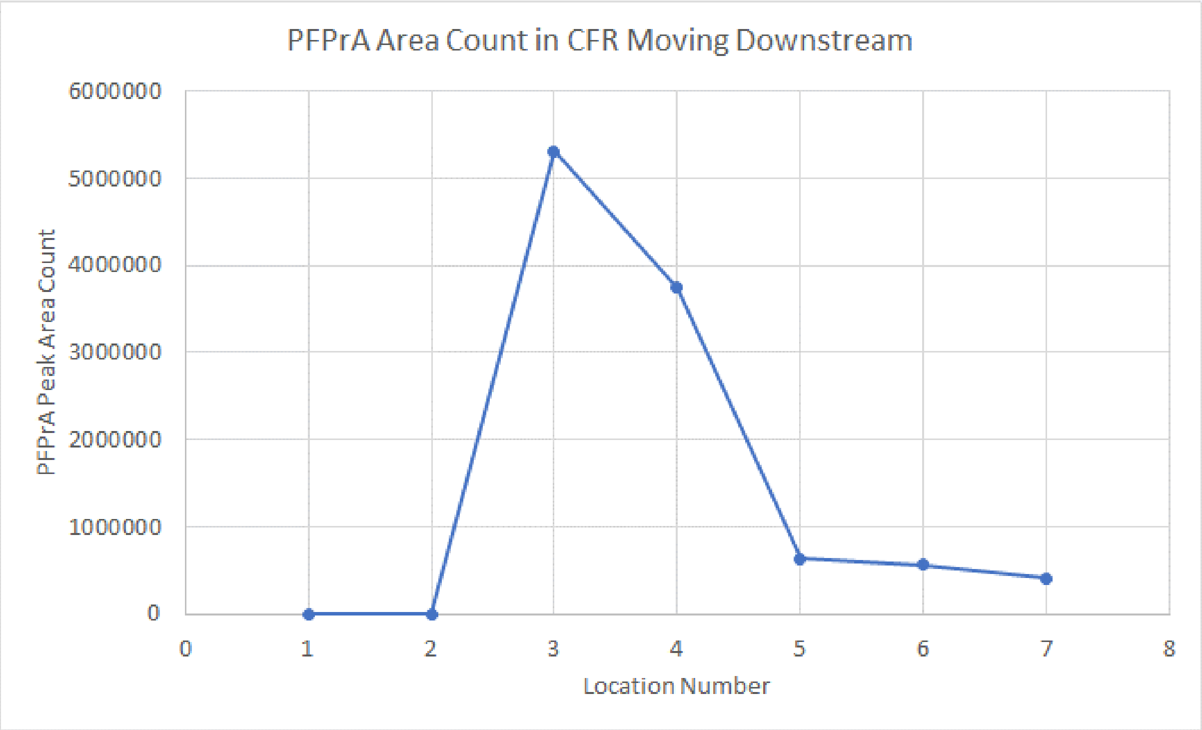
EPA ORD Non-Targeted Analysis

- Using Non-targeted Analysis, EPA ORD as part of their research effort has found PFPrA in the following:
  - DuPont effluent (2012-2013)
  - Chemours effluent (2017-2022)
  - Chemours onsite groundwater (2022)
  - Cape Fear River (2012-2017)

EPA ORD Non-Targeted Analysis Data





	Upstream		Site Adjacent		Downstream		
	1	2	3	4	5	6	7
	CFR Hoffer WTP raw	CFR Fayetteville	Old DuPont Effluent	CFR Huske L&D	CFR Bladen WTP raw	CFR at Tarheel	CFR at Elizabethtown
PFPrA- C3 Peak Area	0	0	5305900	3742298	632264	562838	408334

Targeted Analytical Methods

<u>Analytical Challenges</u>

- Contamination of lab consumables → high reporting limit
    - Solvents
    - Solid phase extraction (SPE) cartridges
- Early eluting compound (but has good performance relative to other early eluters)
- No labeled internal standard

<u>Strategies to Address Analytical Issues</u>

- Use of solvents and SPE cartridges with minimal contamination
- Adjust HPLC (chromatography) method
    - Alter conditions with existing method
    - Use HPLC column that better retains early eluting PFAS
- Labeled internal standard now available from Cambridge Isotope Labs

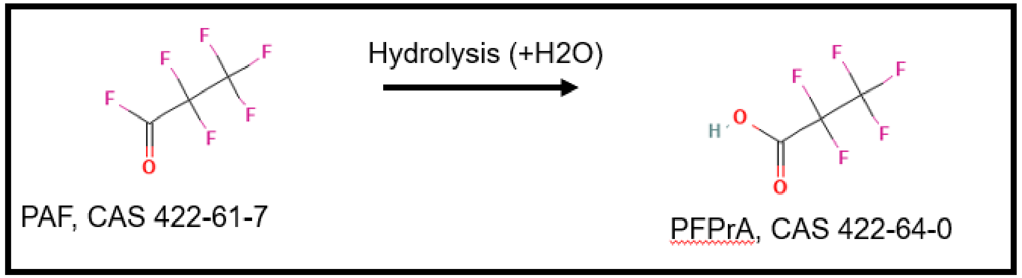
Analytical Methods for Air

- Current air method (OTM-45) does not detect PFPrA because
  1) PFPrA is a liquid at ambient conditions
  2) This method is best suited for compounds with 4 or more carbons

- Chemours process chemistry produces acyl fluorides, which form carboxylic acids upon reaction with water (including moisture in the atmosphere)

- OTM methods would detect perfluoro propionyl fluoride (PAF), the acyl fluoride form of PFPrA

- OTM-50 may be able to detect smaller compounds, including the acyl fluoride form of PFPrA (PAF)



Current Analytical Capabilities and Data Considerations

Analytical Capabilities

- Contamination is now better understood and avoided
  - Quantitation limit of 50 ng/L, 20 ng/L, or lower depending on lab
- PFPrA is sufficiently retained on HPLC columns
- Internal standard is available
- OTM-50 may help analyze smaller compounds in air
- NTA an option

Data Considerations

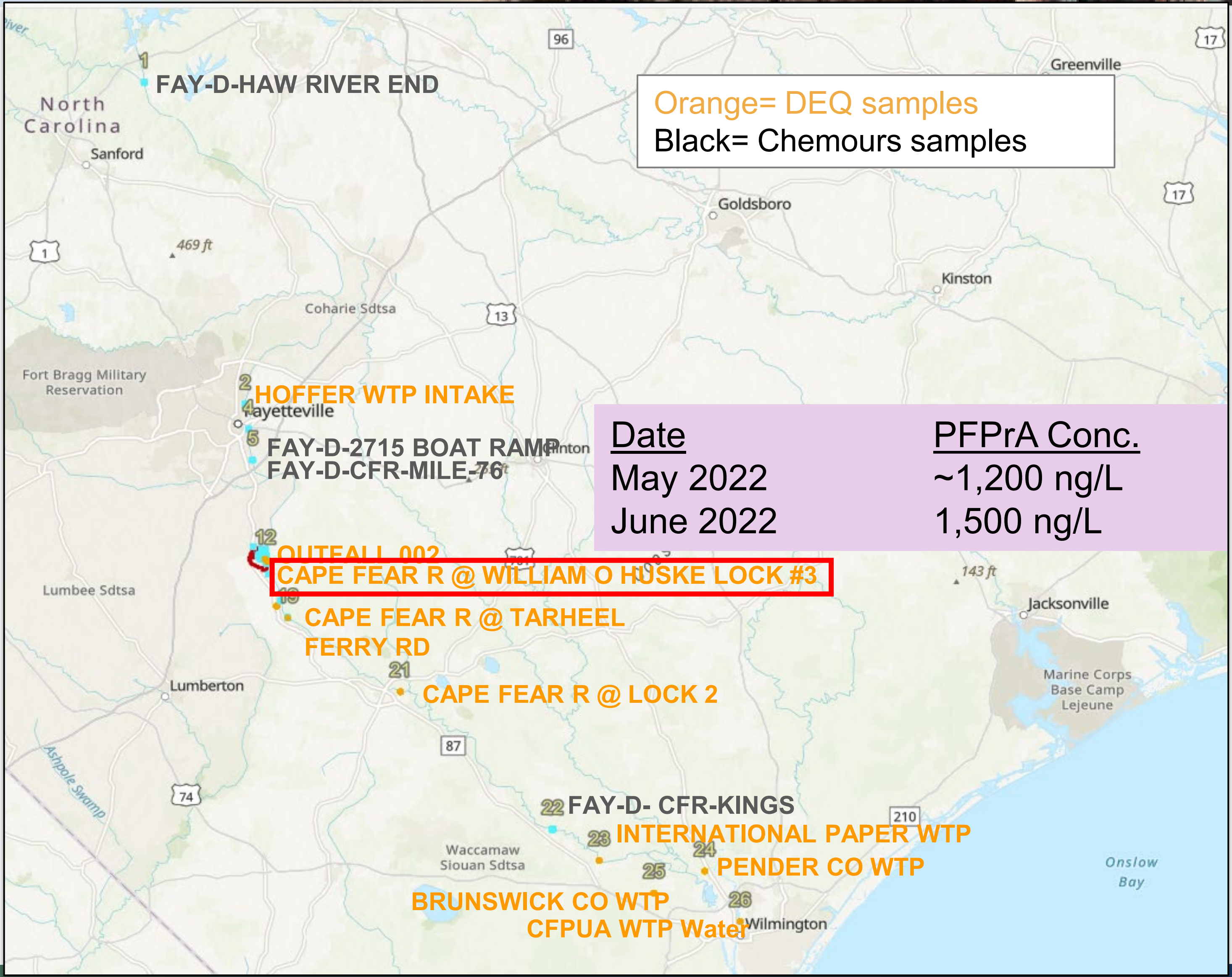
- DEQ data presented on following slides has higher confidence due to:
  - Analysis after April 6, 2023 (when there was certainty in LOQ due to better handle on lab contamination)
  - Earlier results if sample concentrations were over 1000 ng/L

Statewide Data

NC DEQ Surface Water Sampling Stations

Station Key (from upstream to downstream)

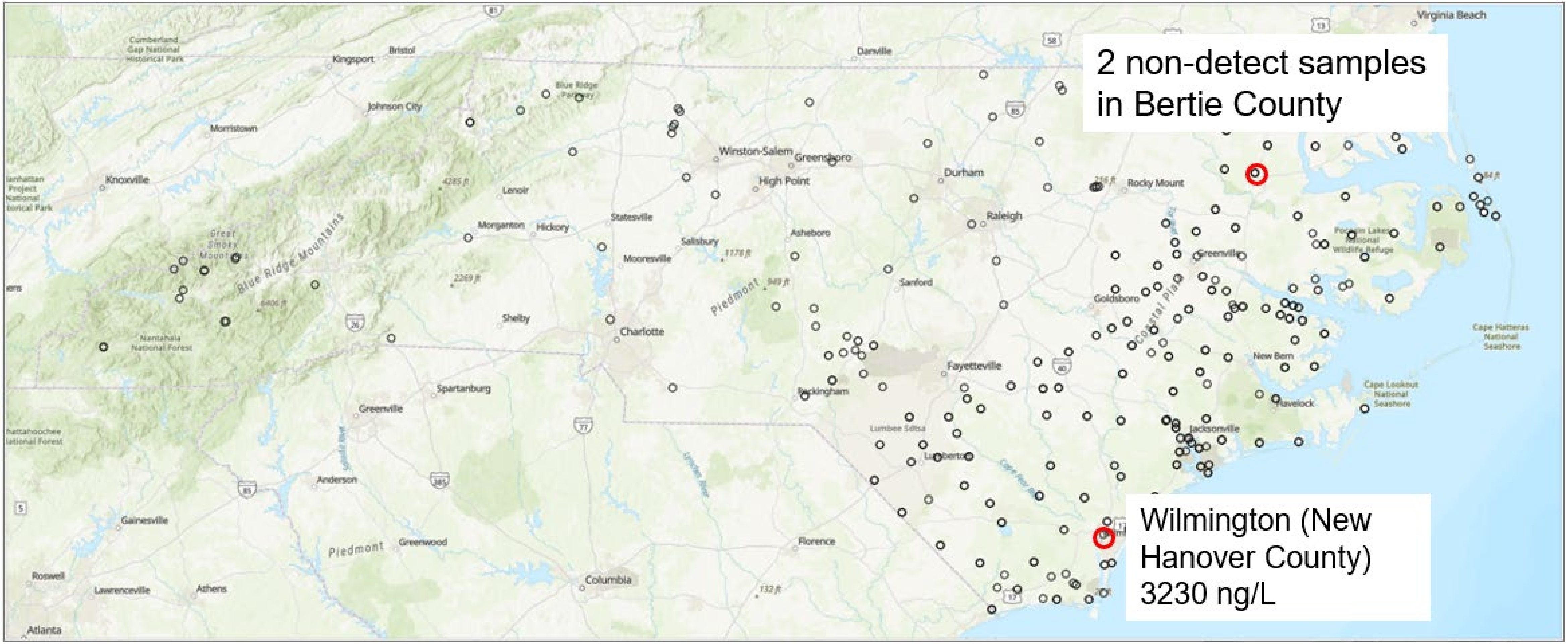
1. FAY-D-HAW-RIVER-END
2. FAY-D-CFR-MILE-54
3. CAPE FEAR RIV AT HOFFER WTP INTAKE
4. FAY-D-CFR-DCO
5. FAY-D-2517BOATRAMP
6. FAY-D-CFR-MILE-76
7. FAY-D-WC-5
8. FAY-D-WC-2
9. FAY-D-WC-1-TR2
10. FAY-D-WC-1
11. RIVER WATER INTAKE 2
12. Chemours Outfall 002
13. Cape Fear R at William O Huske Lock #3
14. FAY-D-OLDOF-2
15. OUTFALL 002
16. FAY-D-OLDOF-1
17. FAY-D-CFR-BLADEN
18. Bladen Bluff WTP Finished Water
19. FAY-D-CFR-TARHEEL
20. Cape Fear R @ TarHeel Ferry Rd
21. CAPE FEAR RIV AT LOCK 2 NR ELIZABETHTOWN
22. FAY-D-CFR-KINGS
23. International Paper WTP Water
24. Pender County WTP Water
25. Brunswick County WTP Water
26. CFPUA WTP Water



Date	PFPrA Conc.
May 2022	~1,200 ng/L
June 2022	1,500 ng/L

PFPrA in DWR Groundwater Monitoring Wells

Samples collected after April 2023



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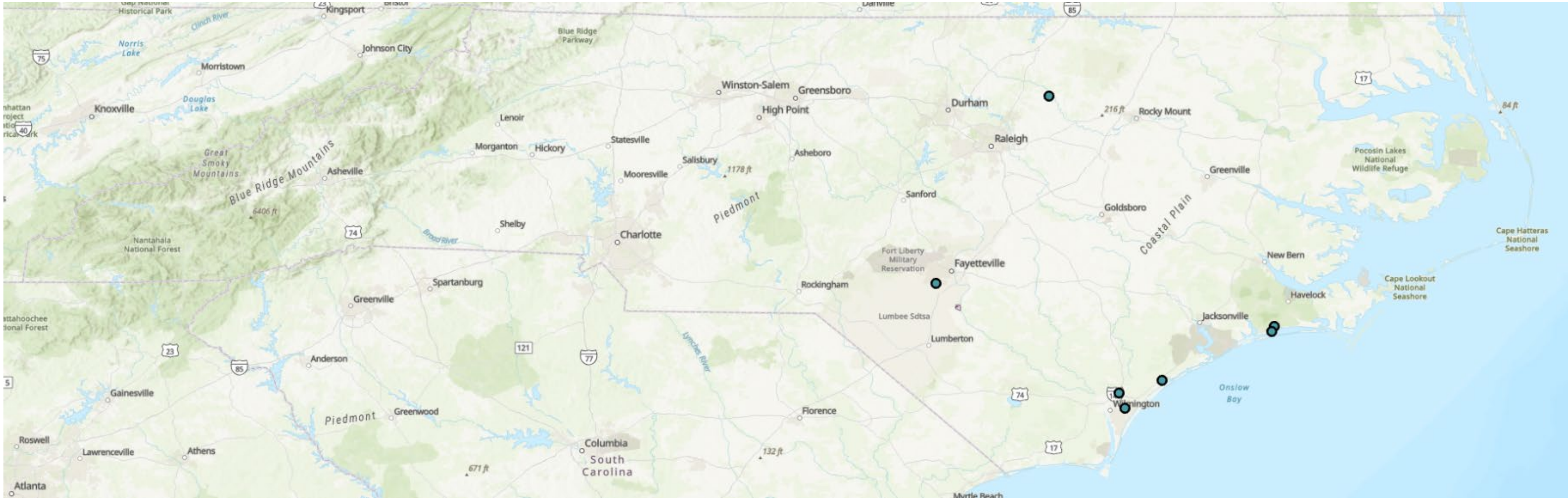
PFPrA in DWR Public Water Supply Sampling

Year	Sample Type	Concentration (ng/L)	n	Frequency of Quantifiable Results
2023	Public Water Supply (Groundwater)	<20 to 31.8	286	2.4%



PFPrA was detected above 20 ng/L in:

- 7 water systems
- 5 counties (New Hanover, Pender, Cumberland, Carteret, and Franklin)
- 3 river basins (Cape Fear, White Oak, Tar Pamlico)

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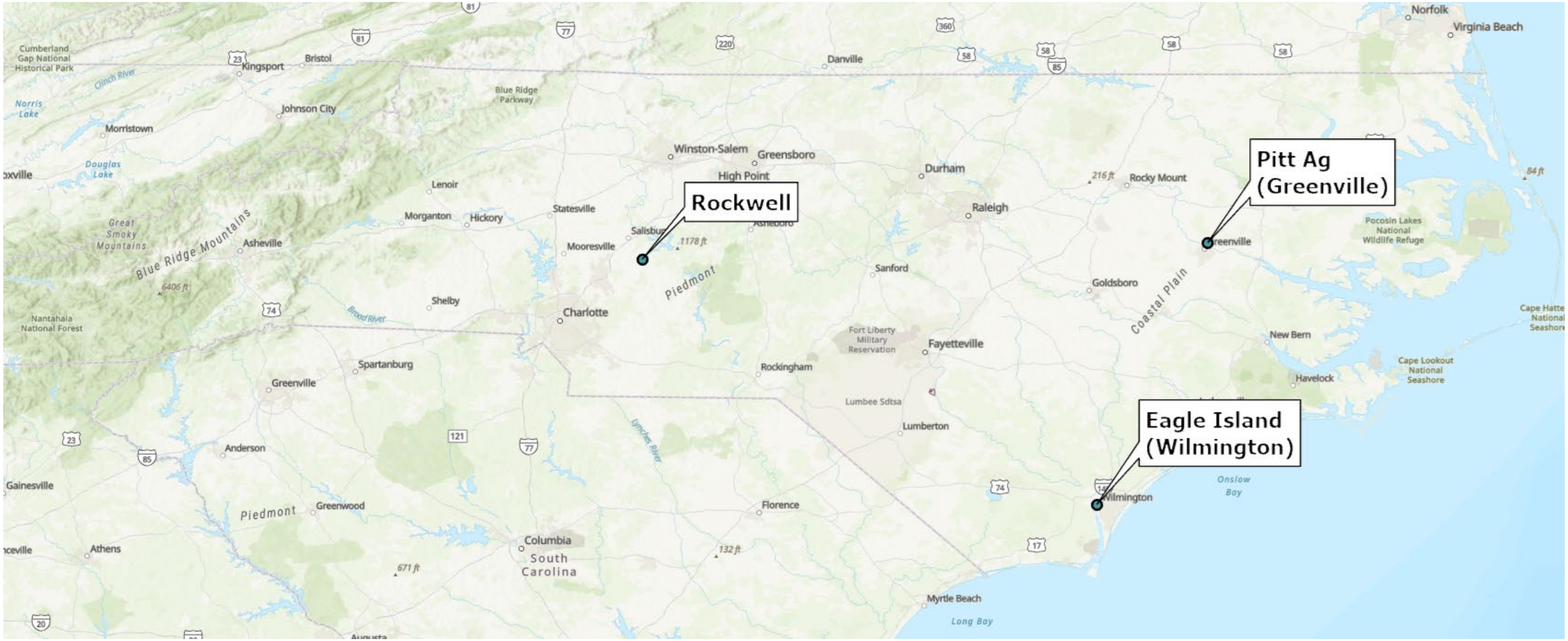
PFPrA in Wet and Dry Deposition Samples

2023 Wet Deposition Perfluoropropionic acid concentrations (ng/L)				
April to present				
Station	min	max	range	n
2	<RL	<RL		
21	<RL	<RL		
21C	<RL	<RL		
32	<RL	<RL		
33	<RL	<RL		
MB	<RL	<RL		
AS	<RL	<RL		
EG	<RL	26.4	<RL - 26.4	1
CD	<RL	<RL		
RK	<RL	26.2	<RL - 26.2	1
PG	<RL	19.8	<RL - 19.8	1

2023 Dry Deposition Perfluoropropionic acid concentrations (ng/L)		
April to present		
Station	min	max
2	<RL	<RL
21	<RL	<RL
21C	<RL	<RL
32	<RL	<RL
33	<RL	<RL
MB	<RL	<RL
AS	<RL	<RL
EG	<RL	<RL
CD	<RL	<RL
RK	<RL	<RL
PG	<RL	<RL

PFPrA detected in wet deposition at 3 air stations, not detected in dry deposition samples

Location of Air Stations with PFPrA



PFPrA found at 3 air sampling stations in Rowan, Pitt, and New Hanover Counties

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Chemours Site Data

PFPrA Occurrence Data from DWM

Year	Location	Concentration (ng/L)	Median DetectedConc. (ng/L)	n	Frequency of Quantifiable Results (%)
2021	CFR at Huske Lock and Dam Boat Ramp	1020	NA	1	100
2022	Chemours Onsite Groundwater Wells	3,120 -288,000	13,600	41	97.6
2023	Private Wells Surrounding Chemours	<17 to 128	24.8	58	48.2

GAC Data- PFPrA Concentrations (ng/L)

Location	Before Filtration	After Filtration
Residence 1	9.7	8.64
Residence 2	64.1	82.2

PFAS Concentrations in Chemours Onsite Monitoring Wells –

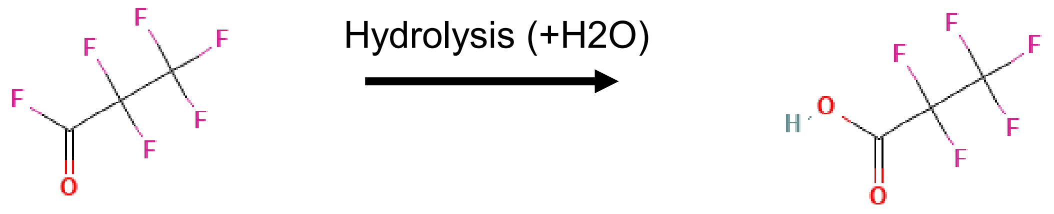
Split Samples Analyzed by DEQ

Concentrations in ng/L

			Results (ng/L)					
	cas_rn	Short Name	FTA-02-20220727	NAF-02-20220727	NAF-08A-20220727	BCA-03R-20220729	NAF-06-20220801	SMW-12-20220804
Chemours PFAS Attachment C	674-13-5	PFMOAA	3,750	451,000	2,000	289,000	610,000	4,360
	13140-29-9	PMPA	5,900	19,100	103,000	25,500	25,900	2,170
	267239-61-2	PEPA	1,800	9,980	58,300	6,080	13,700	461
	13252-13-6	GenX/HFPO-DA	17,100	531,000	39,000	11,200	353,000	1,350
	39492-88-1	PFO2HxA	31,200	202,000	11,500	60,800	293,000	1,400
	39492-89-2	PFO3OA	25,800	79,900	4,250	15,500	121,000	84
	39492-90-5	PFO4DA	1,900	35,400	1,860	1,680	52,000	--
	39492-91-6	PFO5DA	430	23,600	1,650	18	33,300	--
	801212-59-9	PFECA-G	3	--	3	1	--	--
	29311-67-9	Nafion Byproduct 1 (PS Acid)	765	6,810	855	154	22,000	--
	749836-20-2	Nafion Byproduct 2 (Hydro-PS Acid)	547	3,980	907	330	11,600	1
Chemours PFAS Paragraph 11 Research	2416366-18-0	Nafion Byproduct 4 (R-PSDA)	965	2,800	1,160	389	954	104
	2416366-19-1	Nafion Byproduct 5 (Hydrolyzed PSDA)	741	19,600	5,110	3,960	6,830	3
	2416366-21-5	Nafion Byproduct 6 (R-PSDCA)	33	270	32	18	410	--
	151772-58-6	PFECA-B (NFDHA)	1	--	--	1	--	--
	2416366-22-6	R-EVE	401	1,390	640	52	--	82
	69087-46-3	EVE	7,150	14,000	1,260	14	5,510	--
	773804-62-9	Hydro-EVE	483	3,530	901	137	3,590	0
	801209-99-4	NVHOS	1,160	9,980	101	2,320	8,070	22
	113507-82-7	PFEESA (PES)	--	--	--	2	--	0
Legacy PFAS Carboxylic Acids (PFCAs)	422-64-0	PFPrA (PPF Acid)	13,600	243,000	31,900	62,200	288,000	3,140
	375-22-4	PFBA	216	1,690	2,960	181	1,580	22
	2706-90-3	PFPeA	476	1,920	1,100	561	3,150	45
	307-24-4	PFHxA	108	239	61	25	255	2
	375-85-9	PFHpA	110	312	135	71	501	--
	335-67-1	PFOA	89	60	42	11	189	--
	375-95-1	PFNA	10	65	31	1	253	--
	335-76-2	PFDA	--	--	--	--	16	--
	2058-94-8	PFUnA	--	--	--	--	32	--
	307-55-1	PFDoA	--	--	--	--	3	--
	72629-94-8	PFTriA	--	--	--	--	--	--
	376-06-7	PFTA	--	--	--	--	--	--
	67905-19-5	PFHxDA	--	--	--	--	--	--
	16517-11-6	PFODA	--	--	--	--	--	--
Legacy PFAS Sulfonic Acids (PFSAs)	375-73-5	PFBS	4	--	--	6	--	--
	2706-91-4	PFPeS	6	--	--	--	--	--
	355-46-4	PFHxS	17	--	--	5	1	--
	375-92-8	PFHpS		--	--	--	--	--
	1763-23-1	PFOS	41	--	9	2	7	--
	68259-12-1	PFNS	--	--	--	--	--	--
	335-77-3	PFDS	--	--	--	--	--	--
	79780-39-5	PFDoS	--	--	--	--	--	--
Other PFAS	919005-14-4	ADONA	--	--	--	--	--	--
	756426-58-1	9-ClPF3ONS/ F53 Major	--	--	--	--	--	--
	763051-92-9	11-ClPF3OUdS/F 53 Minor	--	--	--	--	--	--
	757124-72-4	4:2 FTS	--	--	--	--	--	--
	27619-97-2	6:2 FTS	206	--	--	--	2	--
	39108-34-4	B	--	--	--	--	--	--
	754-91-6	PFOSA	--	--	--	--	--	--
	31506-32-8	N-MeFOSA	--	--	--	--	--	--
	4151-50-2	N-EtFOSA	--	--	--	--	--	--
	2355-31-9	N-MeFOSAA	--	--	--	--	--	--
	2991-50-6	N-EtFOSAA	--	--	--	--	--	--
	24448-09-7	N-MeFOSE	--	--	--	--	--	--
	1691-99-2	N-EtFOSE	--	--	--	--	--	--

PFPrA in Air Emissions

- **Potential** sources of PFPrA include the following:
  - Process emissions as acyl fluoride (perfluoro propionyl fluoride, PAF, CAS 422-61-7) with subsequent hydrolysis upon exposure to moisture in atmosphere to form PFPrA + HF



PAF (or acyl fluoride form of PFPrA), CAS 422-61-7

PFPrA, CAS 422-64-0

  - Processes that **may** result in PFPrA include the following:

Conversion of hexafluoropropylene to hexafluoropropylene oxide (HFPO) and other partial oxidation products	Reaction of HFPO in presence of catalyst to form intermediate due to incomplete reaction while forming acyl fluoride ether in vinyl ethers operations (VEN and VES)	Thermal degradation of HFPO trimer and tetramer, which are byproducts of VEN reaction of HFPO with itself. Trimer used to produce E-2 for polymerization. E-2 process area may be a source.	Loss of vinyl ethers either as a direct release or through maintenance or decontamination procedures

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Questions?

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