Supporting Information of:

PFOS Dominates PFAS Composition in Ambient Fine Particulate Matter ($PM_{2.5}$) Collected Across North Carolina Nearly 20 Years After the End of Its US Production

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1. Targeted Per- and Polyfluoroalkyl Substances (PFASs)

Table S1. List of Targeted PFASs

Analyte	Formula	Abbreviation	CAS#	Mass-labeled standard
Perfluorocarboxylic acids (PFCAs)				
Perfluoro-n-butanoic acid	$C_4HF_7O_2$	PFBA	375-22-4	$^{13}C_4$-PFBA
Perfluoro-n-pentanoic acid	$C_5HF_9O_2$	PFPeA	2706-90-3	$^{13}C_5$-PFPeA
Perfluoro-n-hexanoic acid	$C_6HF_{11}O_2$	PFHxA	307-24-4	$^{13}C_5$PFHxA
Perfluoro-n-heptanoic acid	$C_7HF_{13}O_2$	PFHpA	375-85-9	$^{13}C_4$-PFHpA
Perfluoro-n-octanoic acid	$C_8HF_{15}O_2$	PFOA	335-67-1	$^{13}C_8$-PFOA
Perfluoro-n-nonanoic acid	$C_9HF_{17}O_2$	PFNA	375-95-1	$^{13}C_9$-PFNA
Perfluoro-n-decanoic acid	$C_{10}HF_{19}O_2$	PFDA	335-76-2	$^{13}C_6$-PFDA
Perfluoro-n-undecanoic acid	$C_{11}HF_{21}O_2$	PFUdA	2058-94-8	$^{13}C_7$-PFUdA
Perfluoro-n-dodecanoic acid	$C_{12}HF_{23}O_2$	PFDoA	307-55-1	$^{13}C_2$-PFDoA
Perfluoro-n-tridecanoic acid	$C_{13}HF_{25}O_2$	PFTrDA	72629-94-8	$^{13}C_2$-PFDoA
Perfluoro-n-tetradecanoic acid	$C_{14}HF_{27}O_2$	PFTeDA	376-06-7	$^{13}C_2$PFTeDA
Perfluoro-n-hexadecanoic acid	$C_{16}HF_{31}O_2$	PFHxDA	67905-19-5	$^{13}C_2$PFTeDA
Perfluoro-n-octadecanoic acid	$C_{18}HF_{35}O_2$	PFODA	16517-11-6	$^{13}C_2$PFTeDA
Perfluorosulfonic acids (PFSAs)				
Perfluorobutane sulfonic acid	$C_4HF_9O_3S$	PFBS	375-73-5	$^{13}C_3$-PFBS
Perfluoropentane sulfonic acid	$C_5HF_{11}O_3S$	PFPeS	2706-91-4	$^{13}C_3$-PFBS
Perfluorohexane sulfonic acid	$C_6HF_{13}O_3S$	PFHxS	355-46-4	$^{13}C_3$-PFHxS
Perfluoroheptane sulfonic acid	$C_7HF_{15}O_3S$	PFHpS	375-92-8	$^{13}C_3$-PFHxS
Perfluorooctane sulfonic acid	$C_8HF_{17}O_3S$	PFOS	1763-23-1	$^{13}C_8$-PFOS
Perfluorononane sulfonic acid	$C_9HF_{19}O_3S$	PFNS	68259-12-1	$^{13}C_8$-PFOS
Perfluorodecane sulfonic acid	$C_{10}HF_{21}O_3S$	PFDS	335-77-3	$^{13}C_8$-PFOS
Perfluorododecane sulfonic acid	$C_{12}HF_{25}O_3S$	PFDoS	79780-39-5	$^{13}C_8$-PFOS
Perfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs)				
Perfluoro-2-methoxyacetic acid	$C_3HF_5O_3$	PFMOAA	674-13-5	$^{13}C_4$-PFBA
Perfluoro-2-methoxypropanoic acid	$C_4HF_7O_3$	PMPA	13140-29-9	$^{13}C_4$-PFBA
Perfluoro (3,5-dioxahexanoic) acid	$C_4HF_7O_4$	PFO2HxA	39492-88-1	$^{13}C_3$-PFPrOPrA
Perfluoro-2-ethoxypropanoic acid	$C_5HF_9O_3$	PEPA	267239-61-2	^{13}C3-PFPrOPrA
Perfluoro (3,5,7-trioxaoctanoic) acid	$C_5HF_9O_5$	PFO3OA	39492-89-2	$^{13}C_3$-PFPrOPrA
Hexafluoropropylene oxide-dimer acid (HFPO-DA), parent acid of "GenX"	$C_6HF_{11}O_3$	GenX	13252-13-6	$^{13}C_3$-PFPrOPrA
Perfluoro (3,5,7,9-tetraoxadecanoic) acid	$C_6HF_{11}O_6$	PFO4DA	39492-90-5	$^{13}C_3$-PFPrOPrA
Perfluoro 3,5,7,9,11-pentaoxadecanoic acid	$C_7HF_{13}O_7$	PFO5DoA	39492-91-6	$^{13}C_9$-PFNA

2,2,3,3-tetrafluoro-3-((1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl)oxy)propanoic acid	$C_8H_2F_{14}O_4$	HydroEve	773804-62-9	$^{13}C_3$-PFPrOPrA
1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonate	$C_4H_2F_8O_4S$	NVHOS	801209-99-4	$^{13}C_3$-PFBS
2-[1-[Difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonic acid	$C_7HF_{13}O_5S$	Nafion Byproduct 1	29311-67-9	$^{13}C_3$-PFHxS
Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-	$C_7H_2F_{14}O_5S$	Nafion Byproduct 2	749836-20-2	$^{13}C_3$-PFHxS
2,2,3,3,4,5,5,5-4-(1,1,2,2-tetrafluoro-2-sulfoethoxy) pentanoate	$C_7H_2F_{12}O_6S$	Nafion Byproduct 4	2416366-18-0	$^{13}C_4$-PFBA

2. Characteristics of Selected Monitoring Sites

The site selection followed general criteria to meet monitoring objectives and spatial scales described in EPA's network design criteria for ambient air quality monitoring. [1] The main objective for the PFAS Testing Network was to capture urban background at a neighborhood scale for representative population exposure. The Honeycutt site operated by North Carolina Department of Environmental Quality's (NC DEQ) Division of Air Quality (DAQ) in Fayetteville was established in May 2015 to meet exactly this objective. DAQ kindly provided access to this site and allowed us to establish our Network's Fayetteville site (FAY). Its location in terms of geographic latitude, longitude, elevation, and physical address is listed in Table S2. Since population exposure- focused monitoring requires siting in an urban to sub-urban environment, a compromise had to be made between representing urban background and influence from potential PFAS sources such as wastewater treatment plants (WWTP) and landfills. Therefore, Table S2 also lists the distance of each Network site to the nearest WWTP and landfill. For all five sites, landfills were located at similar distances in transitions of sub-urban to rural areas, and mostly downwind or perpendicular to the main wind directions of SW and NE. At all five locations the sampling inlet was between 2 and 3 m above ground. Site specific details and differences are described in the following.

The Charlotte site (CHR) was located on the campus of UNC-Charlotte ca. 12 km NE from the city center at the edge of a grass recreational field in the university's track and field sporting center. The nearest city highway is over 900 m away in a sub-urban area with office buildings (libraries, lecture halls and research laboratories) and residential buildings (dormitories and student living) mixed in many green spaces. Noteworthy is the presence of an artificial turf field at about 320 m to the north, which might be the source of PFASs during high temperatures.[2] The RTP site was located in a residential subdivision of the Town of Morrisville in the heart of the Research Triangle Park of North Carolina. The site is 410 m away from the nearest highway (I-540 expressway) to the north and two city highways at over 1 km distance to the east and west. Nearest restaurants are also over 1 km away. The FAY site was in a sub-urban residential area over 10 km southwest from downtown Fayetteville. The location was generously made available by the DAQ within the NC DEQ. The site is located at the edge of a softball field between the EM Honeycutt Elementary School and the John Griffin Middle School. Fisher Road, a 2-lane road with ~16,000 vehicles per day is 60 m to the north. There are no restaurants or fast food places nearby. The site is located between the Chemours fluorochemical manufacturing plant and the Fort Bragg military installation, which are ~34 km apart, although not predominantly downwind of either. The GRV site was located on the West Research Campus (WRC) of the East Carolina University, ca. 11km west from the Greenville city center. This site is the most rural of all, surrounded by forested and cultivated lands. The NC State Highway 264 passes 2.6 km to the south. Formerly a Voice of America Site, the WRC hosts a meteorological station on its 240 ha poorly drained flat land, where we were allowed to setup and operate the GRV site. The WIL site was located on the SE edge of the Wilmington campus, ca. 6 km from the Atlantic coast. The immediate surroundings of the site are wooded with the nearest University of North Carolina Wilmington campus buildings at ~400 m to the north and residential areas starting ~160 m to the southeast bordered by the nearest road. Our sampler was installed on a wooden deck used by UNCW researchers for wet and dry deposition measurements.

Table S2. Network site locations and distances to nearest waste water treatment plants (WWTP) and landfills.

Site ID	Latitude, deg N	Longitude, deg E	Elevation, Metres above sea level	Nearest WWTP	Nearest Landfill
CHR	35.303828	-80.741579	190	5.4 km to NE	8.6 km to NE
RTP	35.842151	-78.874155	101	4.7 km to NNW	18.2 km to S
FAY	35.001653	-78.990737	58	11.5 km to NE	11.6 km to ESE
GRV	35.633628	-77.484751	24	16.6 km to ESE	6.3 km to SE
WIL	34.220333	-77.863250	7	7.1 km to NNW	11.2 km to NW

3. UHPLC/ESI-MS/MS Parameters

Table S3. 9-Min Gradient Elution Method for UHPLC/ESI-MS/MS.

Time (min)	A	B	Curve
0.0	75	25	initial
0.5	75	25	6
5.0	15	85	6
5.1	0	100	6
6.0	0	100	6
6.5	75	25	1
9.0	75	25	1

Table S4. UHPLC/ESI-MS/MS Parameters.

Column	Waters BEH C18 reverse-phase, 2.1×50 mm, 1.7-µm particle size
Column temperature	50°C
Injection Volume	20 µL
Mobile phase	A: 2 mM ammonium acetate in Milli-Q water with 5% methanol B: 2 mM ammonium acetate in 100% methanol
Flow rate	500 µL min^{-1}
Ion source	Turbo spray ion Drive
Curtain gas (CUR)	30 psi
Collision gas (CAD)	12 psi
IonSpray Voltage (IS)	-4500 V
Temperature (TEM)	400 °C
Ion source gas 1 (GS1)	40 psi
Ion source gas 2 (GS2)	30 psi

Table S5. Ion Quantification Parameters for UHPLC/ESI-MS/MS.

Analyte	Mass transitions (m/z)	Decluster potential (DP, volts)	Collision Energy (CE, volts)
PFMOAA	178.9→85.0	-35	-12
PFBA	212.9→168.9	-35	-10
$^{13}C_4$-PFBA	216.9→171.9	-35	-10
PMPA	228.9→184.9	-35	-10
PEPA	234.9→118.7*	-35	-10
	278.9→234.9	-35	-10
PFO2HxA	244.9→85.0	-35	-10
PFPeA	262.9→218.9	-35	-10
$^{13}C_5$-PFPeA	268.0→223.0	-35	-10
NVHOS	296.9→135.1	-70	-30
PFBS	298.9→79.9*	-35	-68
	298.9→98.9	-35	-36
$^{13}C_3$-PFBS	301.9→79.9	-35	-68
PFO3OA	310.9→84.9	-35	-12
PFHxA	312.9→118.9	-35	-12
	312.9→268.9*	-35	-12
$^{13}C_5$-PFHxA	318.0→273.0	-35	-12
GenX	329.0→285.0	-35	-10
$^{13}C_3$-PFPrOPrA	332.0→287.0	-35	-10
PFPeS	349.0→80.0*	-45	-34
	349.0→99.0	-45	-30
PFHpA	362.9→168.9	-35	-12
	362.9→318.9*	-35	-12
$^{13}C_4$-PFHpA	367.0→322.0	-35	-12
PFO4DA	376.9→84.9	-70	-30
PFHxS	398.9→79.9	-70	-30
	398.9→98.9*	-70	-30
$^{13}C_3$-PFHxS	402.0→99.0	-70	-30
PFOA	412.9→168.9	-15	-18
	412.9→368.9*	-15	-11
$^{13}C_8$-PFOA	420.9→375.9	-15	-11
Hydro Eve	426.9→282.9	-35	-10
Nafion BP4	440.9→197.0	-35	-32
Nafion BP1	442.9→146.9	-35	-32
PFO5DoA	442.9→84.8	-35	-10
PFHpS	448.9→79.9*	-70	-70
	448.9→98.9	-70	-70
PFNA	462.9→218.9	-30	-24
	462.9→418.9*	-30	-24
$^{13}C_9$-PFNA	472.0→427.0	-70	-24
Nafion BP2	463.0→213.0	-35	-30
	462.3→262.9*	-35	-42
PFOS	498.9→79.9*	-60	-122
	498.9→99.0	-60	-98
$^{13}C_8$-PFOS	507.0→99.0	-60	-98
PFDA	512.9→218.9	-25	-16
	512.9→468.9*	-25	-16
$^{13}C_6$-PFDA	519.0→474.0	-25	-16
PFNS	549.0→80.0*	-70	-70
	549.0→99.0	-70	-70
PFUdA	562.9→268.9	-35	-10

	562.9→518.9*	-35	-10
$^{13}C_7$-PFUdA	570.0→525.0	-35	-10
PFDS	598.9→79.9*	-70	-70
	598.9→98.9	-70	-70
PFDoA	612.9→168.9	-35	-10
	612.9→568.9*	-35	-10
$^{13}C_2$-PFDoA	615.0→570.0	-35	-10
PFTrDA	662.9→168.9	-35	-10
	662.9→618.9*	-35	-10
PFDoS	699.0→99.0	-70	-70
PFTeDA	712.9→318.9	-35	-10
	712.9→668.9*	-35	-10
$^{13}C_2$-PFTeDA	715.0→670.0	-35	-10
PFHxDA	813.0→769.0	-230	-38
PFODA	913.0→869.0	-230	-38

*Used for quantification.

4. Sample Extraction Efficiency

Table S6. PFASs extraction efficiency of quartz fiber filters (recovery, %). Each target analyte was corrected for the extraction efficiency using the mass-labeled standards spiked on each filter prior to extraction.

Analyte	Recovery (%)
Perfluorocarboxylic acids (PFCAs)	
PFBA	133
PFPeA	98
PFHxA	112
PFHpA	104
PFOA	105
PFNA	97
PFDA	95
PFUdA	107
PFDoA	98
PFTrDA	92
PFTeDA	102
PFHxDA	31
PFODA	41
Perfluorosulfonic acids (PFSAs)	
PFBS	175
PFPeS	96
PFHxS	69
PFHpS	71
PFOS	89
PFNS	75
PFDS	63
PFDoS	N/A*
Perfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs)	
GenX	110
NVHOS	165
HydroEve	85
PFMOAA	177
PEPA	N/A*
PMPA	79
PFO2HxA	82
PFO3OA	94
PFO4DA	55
PFO5DoA	113
Nafion Byproduct 1	N/A*
Nafion Byproduct 2	85
Nafion Byproduct 4	N/A*

*: at spiked concentrations, no recovery can be calculated due to high detection limit and low recovery.

5. Analytical Detection Limit

Analytical detection limits were determined as per Environmental Protection Agency protocol[3]. In brief, 7 lowest detectable concentrations of PFASs standards were prepared and analyzed in a sequence to estimate the analytical detection limits.

Table S7. Analytical Detection Limit for Targeted PFASs

Analyte	Extract Conc. (ng mL^{-1})	Estimated Air Conc. (pg m^{-3})
Perfluorocarboxylic acids (PFCAs)		
PFBA	0.13	0.0121
PFPeA	0.08	0.0074
PFHxA	0.05	0.0045
PFHpA	0.07	0.0067
PFOA	0.07	0.0067
PFNA	0.05	0.0050
PFDA	0.05	0.0048
PFUdA	0.08	0.0081
PFDoA	0.06	0.0060
PFTrDA	0.10	0.0092
PFTeDA	0.02	0.0015
PFHxDA	0.23	0.0224
PFODA	0.20	0.0193
Perfluorosulfonic acids (PFSAs)		
PFBS	0.25	0.0237
PFPeS	0.20	0.0197
PFHxS	0.26	0.0248
PFHpS	0.10	0.0098
PFOS	0.05	0.0047
PFNS	0.12	0.0114
PFDS	0.09	0.0087
PFDoS	0.54	0.0521
Perfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs)		
GenX	0.32	0.0307
NVHOS	0.21	0.0201
HydroEve	0.05	0.0052
PFMOAA	0.18	0.0171

PEPA	0.30	0.0288
PMPA	0.04	0.0042
PFO2HxA	0.23	0.0224
PFO3OA	0.17	0.0164
PFO4DA	0.13	0.0125
PFO5DoA	0.09	0.0090
Nafion Byproduct 1	0.05	0.0052
Nafion Byproduct 2	0.05	0.0050
Nafion Byproduct 4	0.06	0.0062

Note: The detection limits, expressed as air concentrations, were estimated using the analytical method detection limit, multiplying by a final extract volume of 100 µL, and dividing by a sample air volume of 1,036.8 m^3 (the average air volume calculated by a sampling flow rate of 10 L min^{-1}, sampling duration of 6 days per week, 12 weeks per quarter).

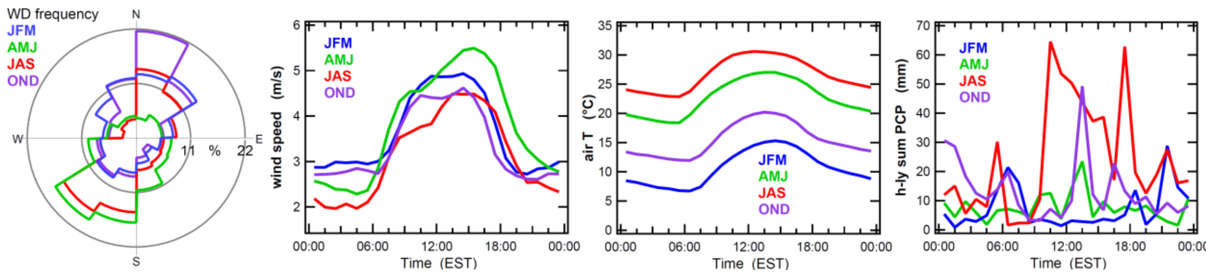
6. Quarterly PFAS Concentrations Normalized by $PM_{2.5}$ concentrations

Table S8. Quarterly PFAS concentrations normalized by $PM_{2.5}$ concentrations[a] (pg PFAS/µg $PM_{2.5}$)

Location	Date	PFOA	PFOS	PFHpS	PFDoA	PFHpA	PFUdA	Nafion Byproduct 2
Fayetteville	Jan.-Mar.	<0.0009	**0.1160**	<0.0013	<0.0007	<0.0009	<0.0010	<0.0006
	Apr.-Jun.	<0.0008	**0.1086**	0.0106	<0.0007	<0.0008	<0.0009	<0.0005
	Jul.-Sept.	<0.0006	**0.0436**	<0.0008	<0.0005	<0.0006	<0.0007	<0.0004
	Oct.-Dec.	<0.0005	0.0498	<0.0009	0.0130	<0.0005	<0.0006	<0.0004
Research Triangle Park	Jan.-Mar.	0.0314	0.0008	<0.0017	<0.0010	<0.0012	<0.0013	<0.0008
	Apr.-Jun.	0.0286	**0.0546**	<0.0012	<0.0007	<0.0008	<0.0009	<0.0007
	Jul.-Sept.	<0.0007	**0.1314**	<0.0008	<0.0006	<0.0007	<0.0007	<0.0005
	Oct.-Dec.	0.0022	0.0173	<0.0009	0.0087	<0.0006	<0.0006	<0.0004
Greenville	Jan.-Mar.	0.0550	**0.0674**	<0.0018	0.0071	<0.0012	<0.0014	<0.0009
	Apr.-Jun.	<0.0008	**0.0707**	<0.0011	<0.0007	<0.0008	<0.0010	<0.0005
	Jul.-Sept.	<0.0007	**0.0756**	0.0036	<0.0006	<0.0007	<0.0008	0.0007
	Oct.-Dec.	0.0333	**0.0683**	<0.0017	0.0167	<0.0012	<0.0013	<0.0008
Wilmington	Jan.-Mar.	0.0688	<0.0013	<0.0026	<0.0016	**0.0370**	<0.0021	<0.0013
	Apr.-Jun.	<0.0020	0.0367	<0.0024	<0.0017	<0.0020	<0.0022	<0.0012
	Jul.-Sept.	0.0551	**1.0064**	0.0424	<0.0019	<0.0021	0.0085	<0.0015
	Oct.-Dec.	0.0064	**0.1535**	<0.0017	0.0128	<0.0013	<0.0013	<0.0009
Charlotte	Apr.-Jun.	0.0761	0.0196	<0.0011	<0.0006	<0.0007	<0.0009	<0.0005
	Jul.-Sept.	**1.4421**	<0.0004	<0.0008	<0.0005	<0.0005	<0.0006	<0.0004
	Oct.-Dec.	0.0491	**0.0379**	<0.0009	0.0089	<0.0007	<0.0008	<0.0004

[a]: NC DAQ Federal Reference Method $PM_{2.5}$ mass concentrations were available from the NC Department of Air Quality sites at Charlotte, Fayetteville, Raleigh, Castle Hayne (near Wilmington) and near Greenville (https://deq.nc.gov/about/divisions/air-quality/air-quality-monitoring/historical-data-summaries/design-value-0).

7. Quarterly Meteorological Conditions at Wilmington 2019



Note: JFM: Jan.-Mar.; AMJ: Apr.-Jun.; JAS: Jul.-Sept.; OND: Oct.-Dec.

Figure S1. Quarterly wind direction (WD) frequency, wind speed, air temperature and accumulated rainfall at Wilmington 2019

References

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2. DC Report, Nov. 8, 2019. https://www.dcreport.org/2019/11/06/new-health-concerns-over-artificial-turf/#:~:text=The%20PFAS%20substances%20that%20the (accessed November 2020).
3. U.S. Environmental Protection Agency (EPA), Method Detection Limit (MDL) procedure. Title 40 Code of Federal Regulations Part 136 (40 CFR 136, Appendix B, revision 1.11).