



THE UNIVERSITY  
of NORTH CAROLINA  
at CHAPEL HILL



# Atmospheric Concentrations and Deposition of PFAS

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TEAM 4:CO-LEADS: RALPH N. MEAD (UNCW; [MEADR@UNCW.EDU](mailto:MEADR@UNCW.EDU))  
BARBARA TURPIN (UNCCH; [BJTURPIN@EMAIL.UNC.EDU](mailto:BJTURPIN@EMAIL.UNC.EDU))

INVESTIGATORS: M. SUN (UNCC); R. KIEBER, G.B AVERY, S. SKRABAL, J. WILLEY (UNCW); J. SURRATT, K. BAUMANN, W. BODNAR, Z. ZHANG (UNCCH)

The Chemours facility in Fayetteville produces GenX for industrial processes.

Cape Fear; Contaminated well water near Chemours - some > 140 ppt

DEQ measured GenX in rain water near Chemours (starting Late 2017 )  
sometimes hundreds of ppt

Chemours estimated their air emissions of GenX to be 67 lb/yr (2016)

DEQ ordered emissions measurements (2018)

Revised emissions estimates were 2300 lb/yr - consent order requiring reduction

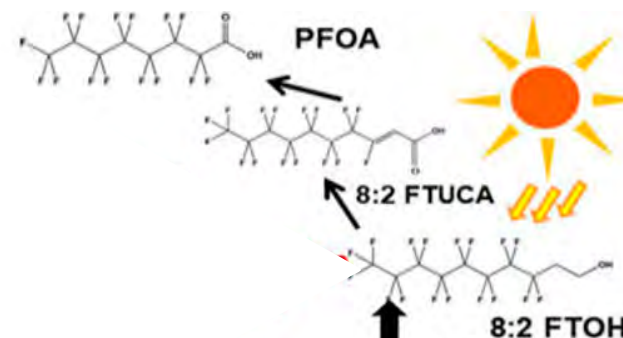
May to Dec 2018 – control technology installed to reduce air emissions by 92%

Dec 2019 - installation of thermal oxidizer expected to reduce to 99%

# Motivation

## • Atmospheric Sources:

- PFAS is emitted into atmosphere from stack at Chemours,
- It can be chemically altered in the atmosphere
- Atmospheric wet/dry deposition can be a source of PFAS to local and remote locations
- PFAS have been measured in wet deposition (near Chemours by DAQ)



**Non- Point source emission**  
(regional transport, contaminated soil, landfill)

**Multi-Phase Chemistry**

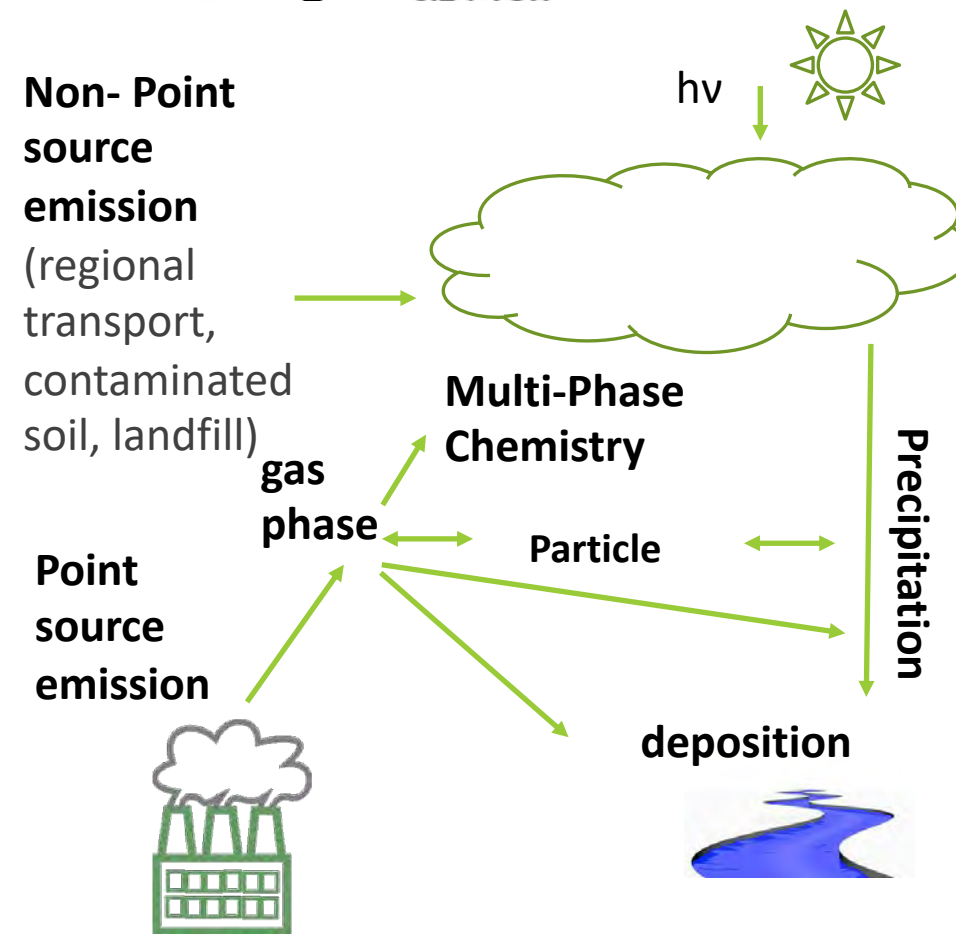
**Point source emission**

gas phase

Particle

deposition

Precipitation



# Motivation

- **Atmospheric Sources:**

- PFAS is also emitted indoors and outdoors because of the use of PFAS-containing products (e.g., firefighting foams; household products),
- And from waste streams (e.g., contaminated soil, wastewater, landfills)



# Motivation

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**However, the concentrations, transformations, and fate of atmospheric PFAS are poorly understood**

How widespread is air contamination now? What other PFAS compounds? Sources?

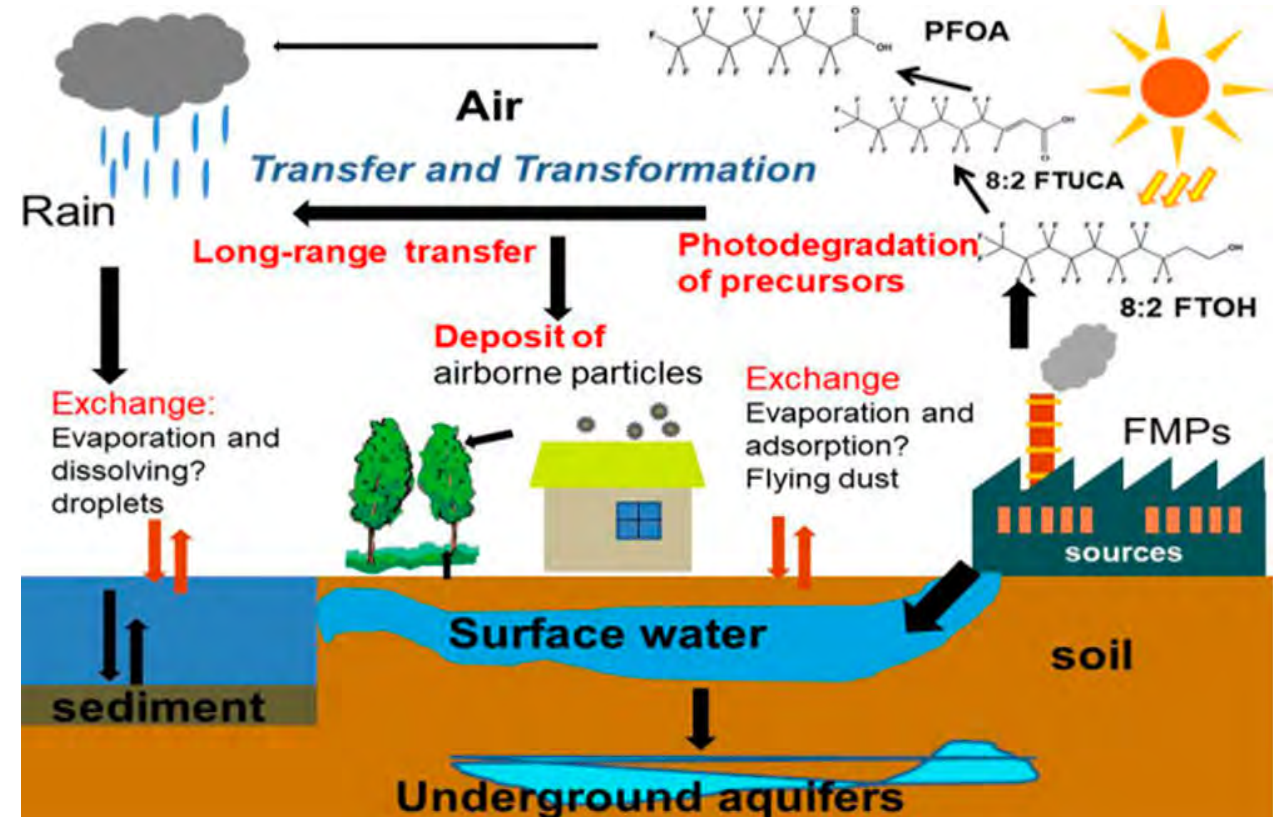
# Research Questions

*What PFAS compounds are present in ambient NC air? in wet/dry deposition?*

*What is the geographic distribution and what does this tell us about sources?*

*What is the contribution of wet/dry deposition to the Cape Fear watershed?*

*How does gas-to-particle conversion (multiphase atmospheric chemistry) during air mass transfer alter the fate of certain PFAS species?*

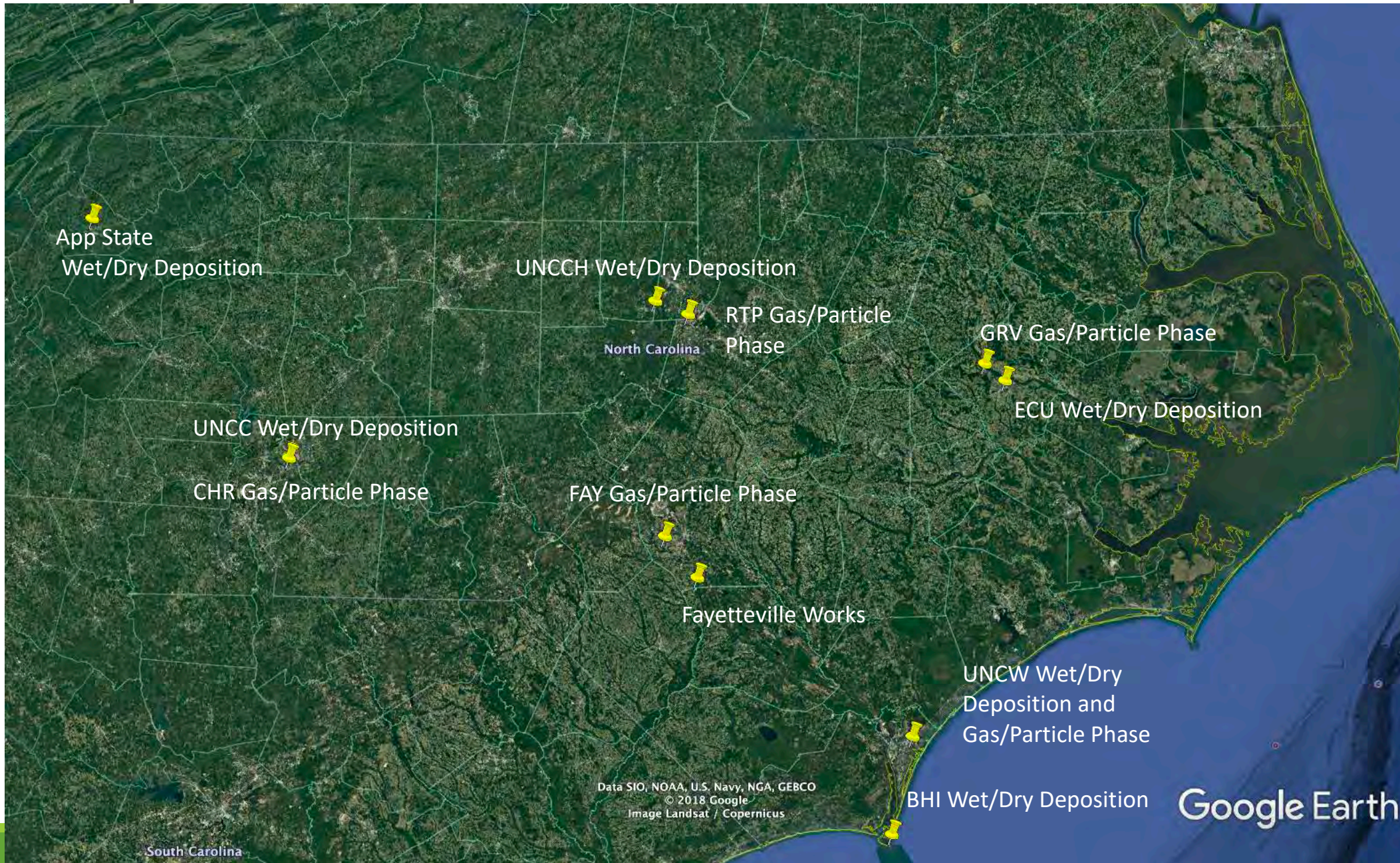


# Approach

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- 1. Event-based wet/dry deposition sampling:** in Wilmington and selected other stations
- 2. Integrated gas and particle sampling:** Weekly 6 day periods; seasonal composites for one year. Wilmington, RTP, Charlotte, Greenville, Fayetteville
- 3. Chemical analysis:** Isolation and analysis by UPLC-ESI-HR-QTOF-MS. UPLC-ESI-QqQ-MS
- 4. Calculate:** deposition to Cape Fear watershed
- 5. Examine:** influence of back trajectory, geography, season, sources
- 6. Real-time measurement of highly polar gases:** with exact mass chemical ionization mass spectrometry) and **Controlled Laboratory experiments:** to examine multiphase chemistry, hexafluoropropylene oxide (HFPO)

# Sample Stations



Data SIO, NOAA, U.S. Navy, NGA, GEBCO  
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Image Landsat / Copernicus

Google Earth



# Sample Collection Personnel

## **FAY**

1). **NC Department of Environmental Quality-  
-Division of Air Quality**

Joette Steger & Mitchell Revels

2). Sample collection: **UNC-Chapel Hill**

**Karsten Baumann, Ph.D**

**Jiaqi Zhou, Ph.D**

## **GRV**

**East Carolina University**

**Jamie C. DeWitt, Ph.D.**

**Samuel Alan Vance, M.S**

## **WIL**

**UNC-Wilmington**

**Stephen Skrabal, Ph.D.**

**Robert Kieber, Ph.D**

**Brooks Avery, Ph.D.**

## **CHR**

**UNC-Charlotte**

**Mei Sun, Ph.D.**

**Isabel Srivoraphan**

**Dave Tilley**

## **RTP**

**UNC-Chapel Hill**

**Karsten Baumann,  
Ph.D.**

**App State**

**Bob Swarthout, Ph.D.**

## **BHI**

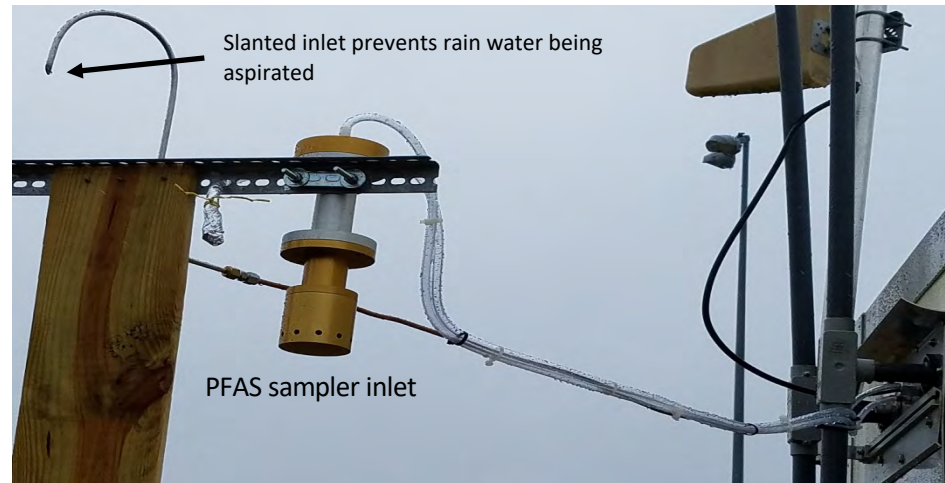
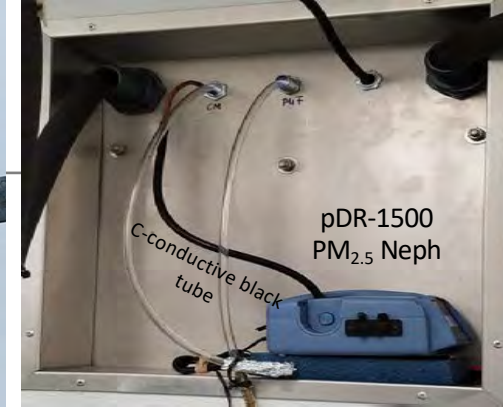
**Chris Shank, Ph.D.**

**Beth Darrow, Ph.D.**

# Example Aerosol Station

## FAY

Operational since  
11/16/2018



NC Department of Environmental Quality

Division of Air Quality

Thanks to

**Joette Steger & Mitchell Revels**

Fayetteville Regional Office

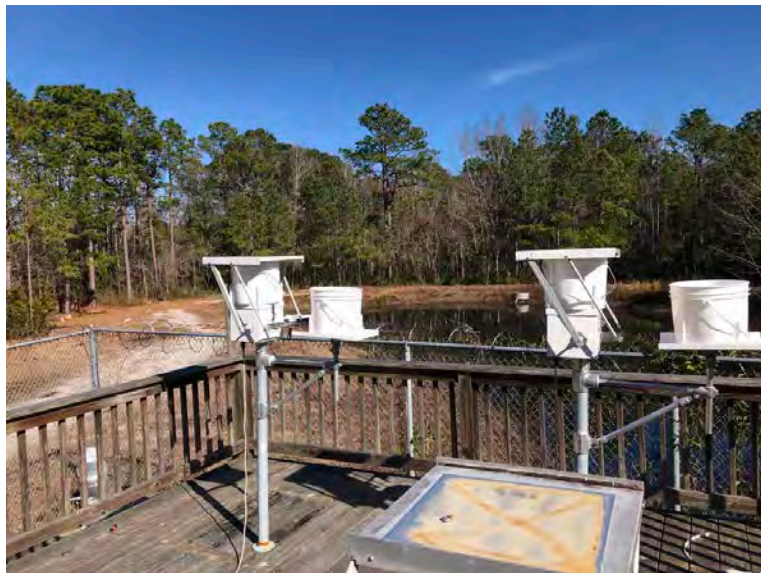
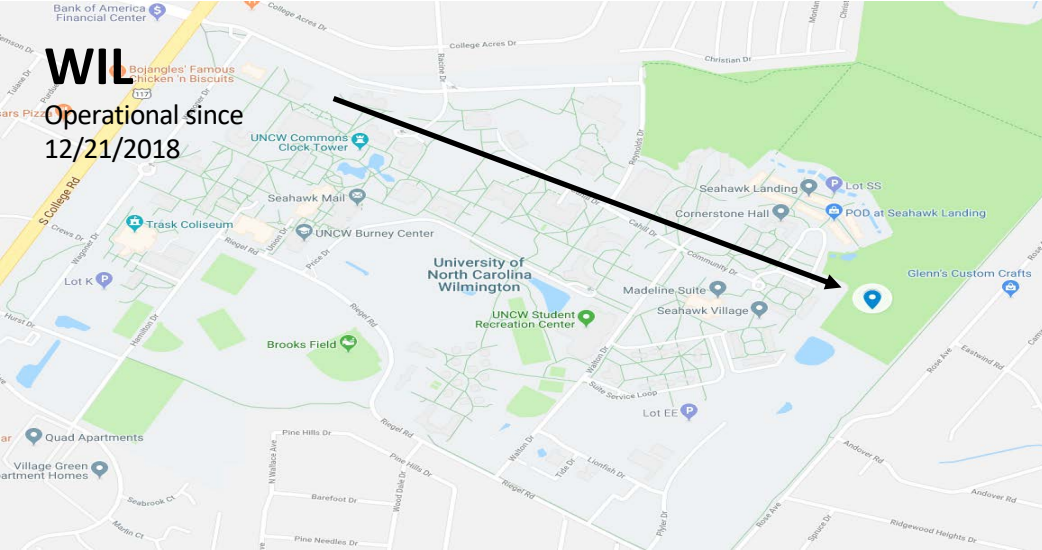
Site Address

John Griffin Middle School

8943 Fisher Road

Fayetteville, NC 28304

# Example Aerosol and Wet/Dry Deposition Station



UNIVERSITY of NORTH CAROLINA WILMINGTON

Department of Chemistry & Biochemistry

Drs. Kieber & Skrabal  
Center for Marine Science  
5600 Marvin Moss Lane  
Wilmington, NC 28409-5928



# Sample Collection Schedule



<b>Air Samples</b>		2019											
Site	Sampling starts	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
GRV	12/05/18												
WIL	12/21/18												
FAY	11/23/18												
RTP	01/11/19												
CHR	02/08/19												

<b>Wet/dry deposition</b>		Dec 18 - Mar 19	April 19 - May 19	May 19 – Sept 19	Oct 19 – Dec 19
Wilmington		xxxx	xxxx	xxxx	xxxx
Other locations		3 collections		3 collections	

# Wet/Dry Deposition Samples



	Wet Deposition	Dry Deposition
Wilmington	57 samples (Oct 2018-) Air mass back trajectories <ul style="list-style-type: none"> <li>• 5 coastal</li> <li>• 7 terrestrial</li> <li>• 41 mixed</li> <li>• 4 marine</li> </ul>	18 samples (Dec 2018 - ) 2- week continuous collection with wet-dry sampler.
Other sites (App State, UNCC, BHI, ECU, UNCCH)	3 rain events in each site (Dec – March) 3 rain events in each site (May – Sep)	3 dry events in each site (Dec – March) 3 dry events in each site (May – Sep)

## Sample Collection Timeline

	Dec 18 - Mar 19	April 19 - May 19	May 19 – Sept 19	Oct 19 – Dec 19
Collect wet/dry deposition at Wilmington site	xxxx	xxxx	xxxx	xxxx
Collect wet/dry deposition at other locations	3 collections		3 collections	

# Toward Selection of Targeted PFAS

- 1). NC DAQ modeled PFAS emissions for Chemours
- 2). NC water measurements
- 3). Availability of PFAS analytical standards
- 4). Literature on PFAS atmospheric measurements

# List of Targeted PFAS in air --- 41 Compounds (28 Legacy +13 Emerging)

Analyte	Abbreviation	CAS#	Analyte	Abbreviation	CAS#
<b>Perfluorocarboxylic acids (PFCAs)</b>			<b>Fluorinated vinyl ethers</b>		
Perfluoro-n-butanoic acid	PFBA	375-22-4	Trifluoromethyl trifluorovinyl ether	PMVE	1187-93-5
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	Pentafluoroethyl trifluorovinyl ether	PEVE	10493-43-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Perfluoropropoxyethylene	PPVE	1623-05-8
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	<b>Fluorotelomer alcohols</b>		
Perfluoro-n-octanoic acid	PFOA	335-67-1	1H,1H,2H,2H-Perfluoro-1-hexanol	4:2 FTOH	2043-47-2
Perfluoro-n-nonanoic acid	PFNA	375-95-1	1H,1H,2H,2H-Perfluoro-1-octanol	6:2 FTOH	647-42-7
Perfluoro-n-decanoic acid	PFDA	335-76-2	1H,1H,2H,2H-Perfluoro-1-decanol	8:2 FTOH	678-39-7
Perfluoro-n-undecanoic acid	PFUDA	2058-94-8	1H,1H,2H,2H-Perfluoro-1-dodecanol	10:2 FTOH	856-86-1
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	<b>Perfluoroalkyl ether carboxylic and sulfonic acids</b>		
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Perfluoro-2-propoxypropanoic acid	GenX	13252-13-6
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonate	NVHOS	801209-99-4
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	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	HydroEve	773804-62-9
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5
<b>Perfluorosulfonic acids (PFSAs)</b>			Perfluoro-4-methoxybutanoic acid	PEPA (PFMOBA)	267239-61-2
Potassium perfluoro-1-butanesulfonate	PFBS	375-73-5	Perfluoro-3-methoxypropanoic acid	PMPA (PFMOPrA)	13140-29-9
Sodium perfluoro-1-pentanesulfonate	PFPeS	2706-91-4	Perfluoro (3,5-dioxahexanoic) acid	PFO2HxA	39492-88-1
Sodium perfluoro-1-hexanesulfonate	PFHxS	355-46-4	Perfluoro (3,5,7-trioxaoctanoic) acid	PFO3OA	39492-89-2
Sodium perfluoro-1-heptanesulfonate	PFHpS	375-92-8	Perfluoro (3,5,7,9-tetraoxadecanoic) acid	PFO4DA	39492-90-5
Sodium perfluoro-1-octanesulfonate	PFOS	1763-23-1	Perfluoro3,5,7,9,11-pentaoxadecanoic acid	PFO5DoA	39492-91-6
Sodium perfluoro-1-nonanesulfonate	PFNS	68259-12-1	2-[1-[Difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonic acid	Nafion Byproduct 1	29311-67-9
Sodium perfluoro-1-decanesulfonate	PFDS	335-77-3	Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-	Nafion Byproduct 2	749836-20-2
Sodium perfluoro-1-dodecanesulfonate	PFDoS	79780-39-5	2,2,3,3,4,5,5,5-4-(1,1,2,2-tetrafluoro-2-sulfoethoxy) pentanoate	Nafion Byproduct 4	N/A



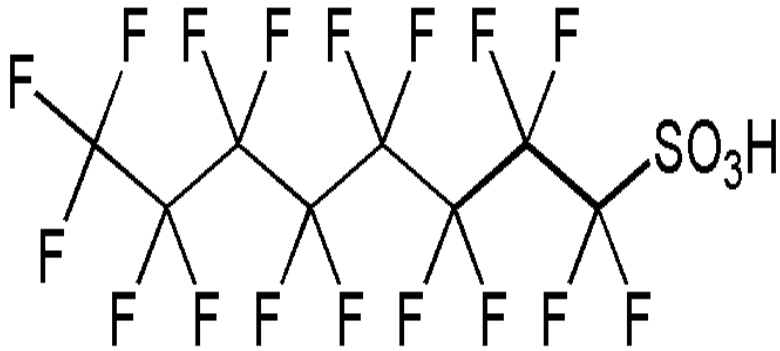
# Particle Samples – 27 compounds can be measured with high confidence/ low DL

Analyte	Estimated Air Conc. (pg/m <sup>3</sup> )	Analyte	Estimated Air Conc. (pg/m <sup>3</sup> )
<b>Perfluorocarboxylic acids (PFCAs)</b>		<b>Perfluoroalkyl ether carboxylic and sulfonic acids</b>	
PFPeA		GenX	
PFHxA		HydroEve	
<b>PFHpA</b>	Perfluoro-n-heptanoic acid		
<b>PFOA</b>	Perfluoro-n-octanoic acid	PEPA (PFMOBA)	
PFNA	0.002 – 0.02	PMPA (PFMOPrA)	
PFDA			
<b>PFUdA</b>	Perfluoro-n-undecanoic acid	PFO2HxA	0.005 - 0.03
<b>PFDoA</b>	Perfluoro-n-dodecanoic acid	PFO3OA	
PFTTrDA		Nafion Byproduct 1	pg/m <sup>3</sup>
PFTeDA		<b>Nafion Byproduct 2</b>	
		Nafion Byproduct 4	

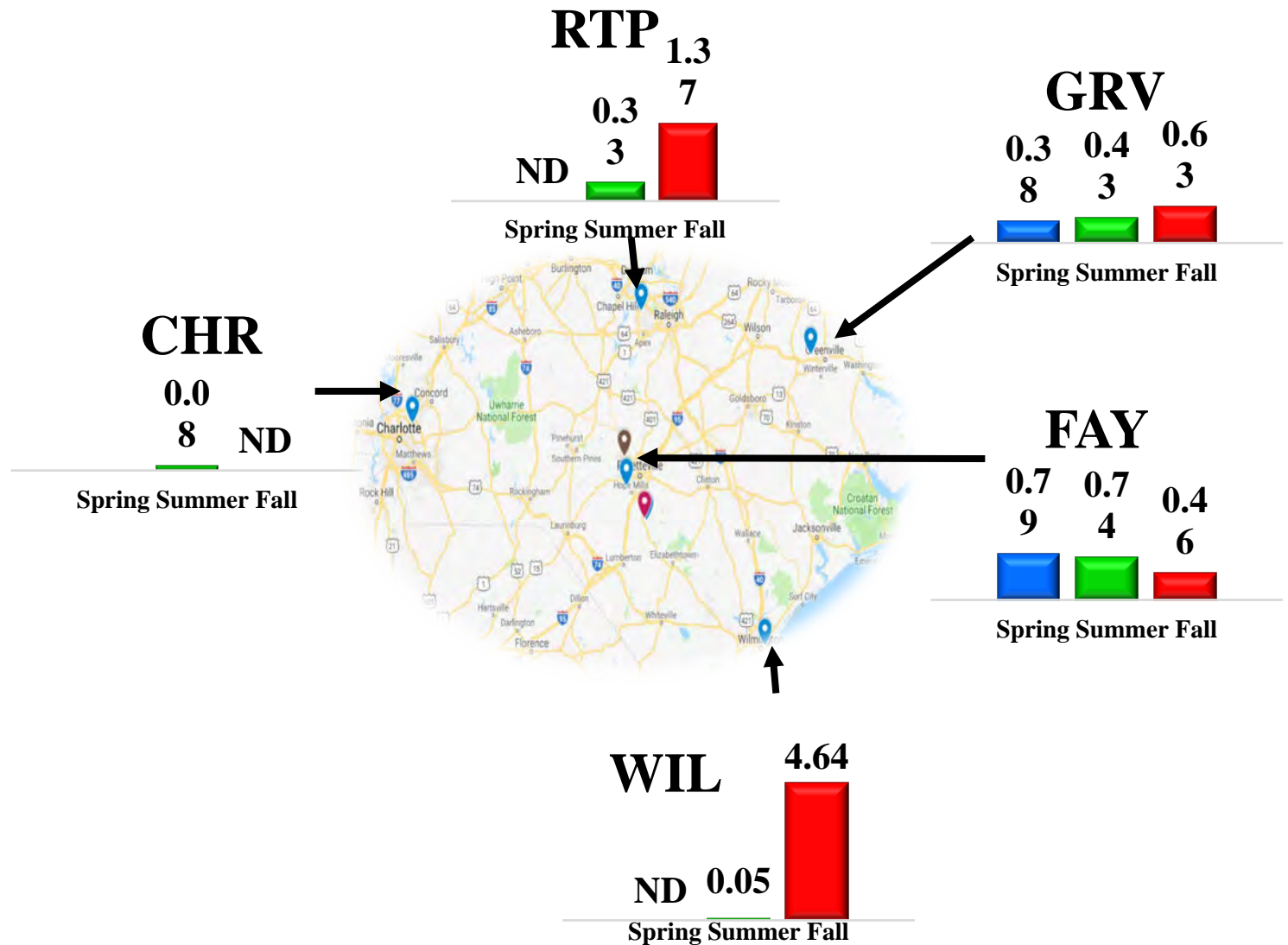
## Perfluorosulfonic acids (PFSAs)

PFBS			
PFPeS			
PFHxS			
<b>PFHpS</b>	perfluoro-1-heptanesulfonate	0.005 – 0.05	
<b>PFOS</b>	perfluoro-1-octanesulfonate		
PFNS		pg/m <sup>3</sup>	
PFDS			
PFDoS			

# Preliminary: Particle Phase-**PFOS** seasonal average air concentrations (pg/m<sup>3</sup>)



Name: Sodium perfluoro-1-octanesulfonate  
CAS#: 1763-23-1



# Indoor and outdoor PFAS air concentrations (Indoor>>Outdoor)



<b>Indoor</b> PFAS air concentration (pg/m <sup>3</sup> )	PFOS	PFOA	PFHxS
Homes, Birmingham, UK (n=20), Goosey et al. (2012)	38	52	36
Offices, Birmingham, UK (n=12), Goosey et al.(2012)	56	58	94
Vancouver, Canada (homes),(n=59, for PFOS and PFOA n=39), Shoeib et al. (2011)	<0.02	113	
<b>Outdoor</b> PFAS air concentration (pg/m <sup>3</sup> )			
Birmingham UK (n=10), Goosey et al. (2012)	2.3	3.5	7
Vancouver, Canada (n=6), Shoeib et al. (2011)	<0.02	2.5	
Hamburg, Germany (Barbüttel, n=117), Dreyer et al. (2009)	1.3	0.3	
Hamburg, Germany,(GKSS, n=121), Dreyer et al. (2009)	0.6	0.2	

# Wet/Dry Deposition Compound List – 22 compounds



abbreviation	CAS	abbreviation	CAS
perfluoro carboxylic acid		<i>Perfluoro alkyl ether carboxylic and sulfonic acids</i>	
TFA	76-05-1	PFMOAA	674-13-5
PFA	422-64-0	PMPA	13140-29-9
PFBA	375-22-4	PEPA	267239-61-2
PFPePA	2706-90-3	PFPPrOPrA	13252-13-6
PFHxA	307-24-4	NBP1	29311-67-9
PFOA	335-67-1	NBP2	749836-20-2
		NBP4	852187-01-8
Perfluoro sulfonic acids		NVHOS	80129-99-4
PFBS	375-73-5	PFO2HxA	39492-88-1
PFHxS	432-50-7	PFO3OA	39492-89-2
PFOS	1763-23-1	PFO4DA	39492-90-5
		PFO5DoA	34942-91-6
		HydroEve acid	773804-62-9

- Focused on compounds that have reliable standard source and have been reported in literature and can be reliably quantified.

# QA/QC Wet Deposition

	PFMOAA	PMPA	PEPA	PFProPrA	PFOA	PFOS	
Recovery	70%	88%	89%	86%	87%	65%	
Precision %RSD, n=4	15%	14%	8%	18%	10%	4%	
Accuracy	104%	108%	106%	101%	112%	92%	
n=	3	3	3	1	4	3	
LOD (pg on column)	6.38	0.68	1.54	2.14	0.05	0.55	LOD = (3*std)/slope
LOQ (pg on column)	21.26	2.27	5.14	7.12	0.15	1.83	LOQ = (10*std)/slope
LOD (ng/L=ppt)*	1.28	0.14	0.31	0.43	0.01	0.11	
LOQ (ng/L=ppt)*	4.25	0.45	1.03	1.42	0.03	0.37	

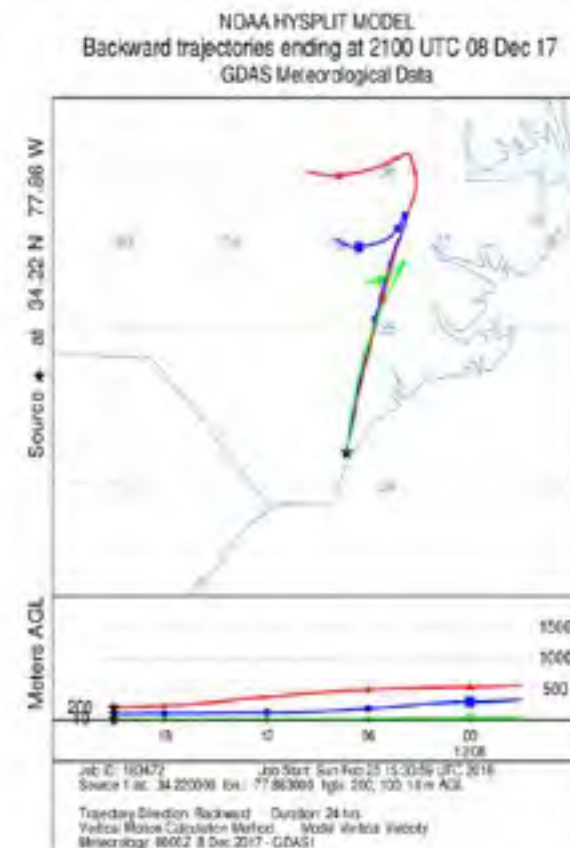
\*assuming extraction of 1L water, blowdown to 0.5mL, 50uL sample diluted to 200uL in LC vial, and 10uL injection

PMPA quantified against PFMOPrA

PEPA quantified against PFMOBA

# Wet Deposition Concentration Range in Wilmington

Wilmington Wet Deposition		
Storm Type	PFOA	PFOS
ng/L		
Terrestrial (n=3)	<LOQ	<LOQ – 1.0
Marine (n=3)	<LOQ	n.a.
Coastal (n=2)	<LOQ	n.a.
Mixed (n=3)	<LOQ	n.a.

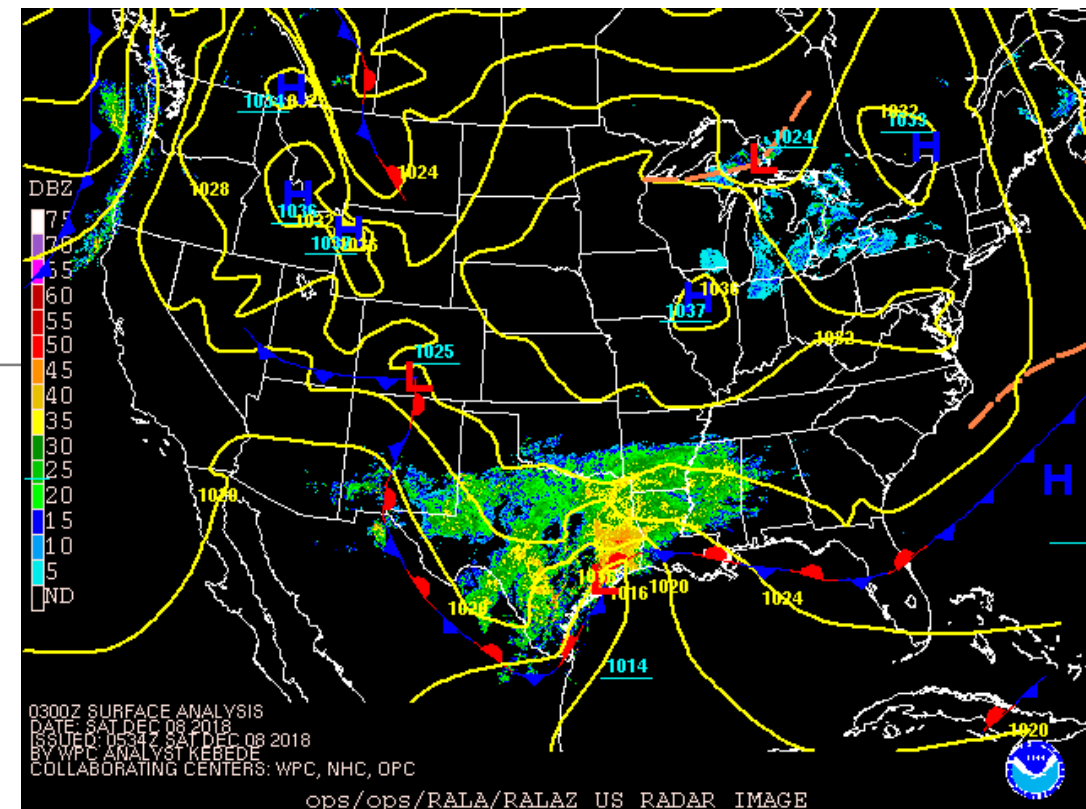


Example of a terrestrial airmass back trajectory

# State Wide Wet Deposition

Coordinated sampling event December 8, 2018

Station	PFOA	PFOS
UNCCH	<LOQ	<LOQ
ECU	<LOQ	<LOQ
APP State	<LOQ	<LOQ
UNCC	1	1.7
BHI	1.5	2.7



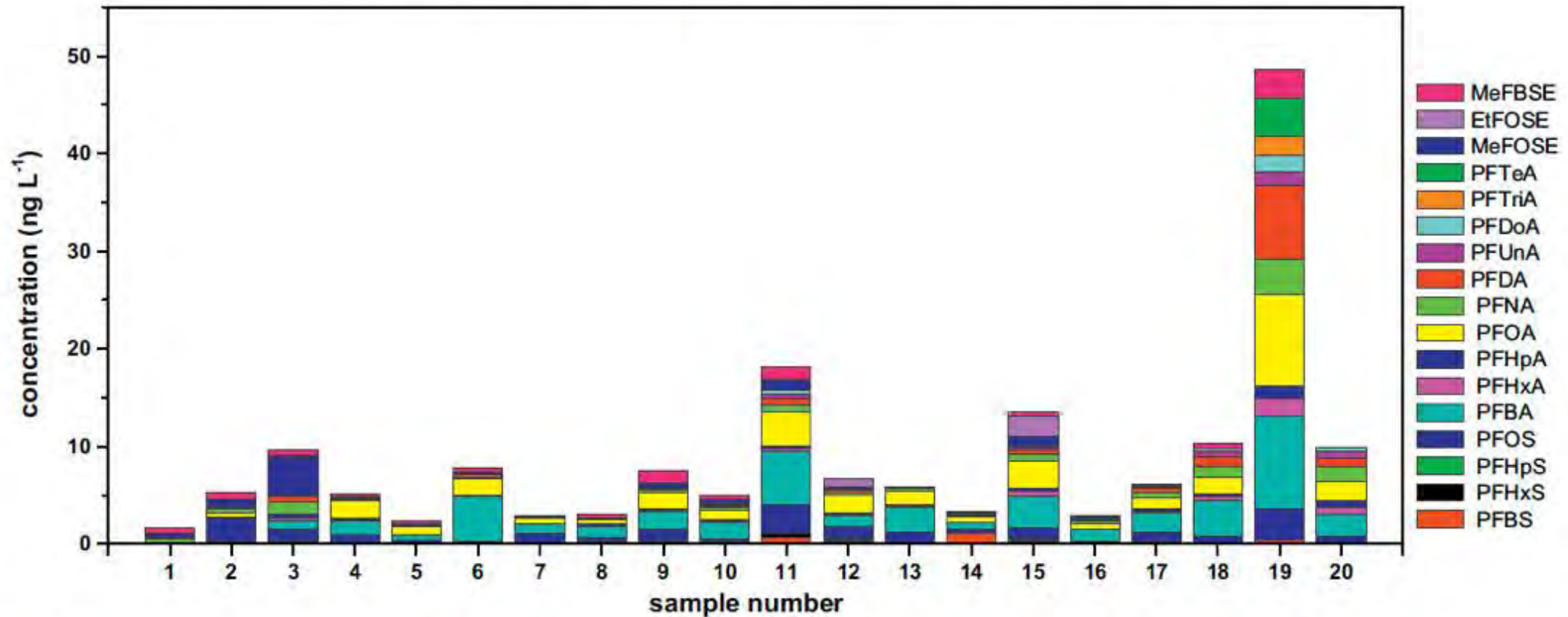


Fig. 1. Daily total precipitation ( $0.1 \text{ mm} = 0.1 \text{ L m}^{-2}$ ), wet deposition rates ( $\text{ng m}^{-2} \text{ d}^{-1}$ ), and rain water concentrations ( $\text{ng L}^{-1}$ ) of detected PFC. Note: PFOA concentration samples BAR-R1 and BAR-R3 were below the corresponding blank. Daily total precipitation was obtained from the nearby German Weather Service station Reinbek.



# Wet deposition of poly- and perfluorinated compounds

**Table 1**  
PFC rain water concentrations (ng L<sup>-1</sup>) as reported in literature.

site	Smith Is., MD, USA	Lewes, DE, USA	Ithaca, NY, USA	Underhill, VT, USA	Kejimikujik, NS, Canada	Algoma, ON, Canada	Saturna Is., BC, Canada	Egbertt, ON, Canada	Toronto, ON, Canada	Dalian, China	Winnipeg, MB, Canada	Albany, NY, USA	Tsukuba City, Japan	Kawaguchi City, Japan	Scandinavia	Barsbüttel, Germany
n	20	42	43	18	19	23	16	8	7	2	3	11	4	4	5	20
category	near urban	near urban	rural	rural	remote	remote	rural	near urban	urban	urban	urban	urban	urban	urban	rural/ urban	semi- rural
PFBS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.6–2.1	n.a.	n.a.	<0.1	<0.1	<LOQ	n.d.–1.1
PFHxS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.49	n.a.	n.d.–0.4	<0.1	<0.1	0.2–0.6	n.d.–0.5
PFOS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.9–113	0.6 ± 0.04	<0.1–1.5	0.1–0.2	0.5–1	0.2–3	0.1–3.3
PFBA	<0.1–23	<0.1–26	<0.1–4.6	<0.1–0.9	<0.1–2.9	0.5–11	<0.1–5	0.1–0.8	0.1–2.1	n.a.	n.a.	n.a.	1–2.2	0.8–2	n.a.	n.d.–9.4
PFFPA	<0.1–39	<0.1–10	<0.1–17	<0.1–3.6	<0.1–1.9	0.6–13	<0.1–6.1	0.1–0.4	0.2–1.1	n.a.	n.a.	n.a.	0.2–1.1	0.6–0.8	n.a.	n.d.
PFHxA	<0.1–42	<0.1–4.7	<0.1–10	<0.1–1.9	<0.1–2.3	<0.1–3	<0.1–3.2	<0.1–0.5	0.2–0.9	n.a.	n.a.	n.a.	0.5–1.5	0.9–2.7	n.a.	n.d.–1.9
PFHpA	<0.1–31	<0.1–5.3	<0.1–11	<0.1–2.9	<0.1–5.4	<0.1–3.1	<0.1–10	0.1–2.4	<0.1–1.7	4.8–23.5	n.a.	<0.1–2.3	0.5–1.2	0.7–3.1	n.a.	n.d.–1.2
PFOA	<0.1–37	<0.1–89	<0.1–10	<0.1–7.6	<0.1–3.1	<0.1–6.1	<0.1–2	0.7–3.8	1.0–11	32.9–40.8	n.d.	<0.1–7.3	1–1.7	1.3–3.8	8.2–17	0.4–9.3
PFNA	<0.1–20	<0.1–77	<0.1–3.2	<0.1–1.9	<0.1–3.3	<0.1–7.6	<0.1–2.8	0.4–4.1	0.5–9.7	n.a.	n.d.	<0.1–3.5	1.7–4.2	1–2.4	0.7–1.4	0.1–3.7
PFDA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–1.1	<0.07–1.0	n.a.	n.d.	n.d.–1.1	0.6–0.8	0.5–0.7	n.a.	n.d.–7.5
PFUnDA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–1.2	<0.07–3.7	n.a.	n.d.	<0.1–0.9	0.6–0.8	0.5–0.7	n.a.	n.d.–1.4
PFDODA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–3.3	<0.07–5.2	n.a.	n.d.	<0.1–0.7	0.1–0.2	0.1–0.2	n.a.	n.d.–1.7
8:2 FTCA	<0.07–0.4	<0.07–5.1	<0.07–1.1	<0.07–0.3	<0.1	<0.1	<0.1	<0.07–8.6	<0.07–5.6	n.a.	1 ± 0.08	n.a.	1.1–1.9	1–1.9	n.a.	n.d.
10:2 FTCA	<0.07–0.1	<0.07–0.7	<0.07–1.3	<0.07–0.2	<0.1	<0.1	<0.1	<0.07–0.5	<0.07–0.6	n.a.	0.3 ± 0.04	n.a.	n.a.	n.a.	n.a.	n.d.
8:2 FTUCA	<0.07–0.9	<0.07–0.7	<0.07–0.2	<0.07–0.6	<0.1	<0.1	<0.1	<0.07–0.5	<0.07–0.4	n.a.	0.12 ± 0.02	n.a.	0.03–0.18	0.04–0.23	n.a.	n.d.
10:2 FTUCA	<0.07–0.1	<0.07–0.08	<0.07–0.5	<0.07–0.3	<0.1	<0.1	<0.1	<0.07–0.8	<0.07–0.7	n.a.	0.12 ± 0.01	n.a.	<0.1	<0.1	n.a.	n.d.
Reference	(Scott et al., 2006)									(Liu et al., 2009)	(Loewen et al., 2005)	(Kim and Kannan, 2007)	(Taniyasu et al., 2008)	(Berger et al., 2004)	this study	

# Future work

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- 1. Event-based wet/dry deposition sampling:** *in Wilmington and selected other stations*
- 2. Integrated gas and particle sampling:** *Weekly 6 day periods; seasonal composites for one year. Wilmington, RTP, Charlotte, Greenville, Fayetteville*
- 3. Chemical analysis:** *Isolation and analysis by UPLC-ESI-HR-QTOF-MS. UPLC-ESI-QqQ-MS*
- 4. Calculate:** *deposition to Cape Fear watershed*
- 5. Examine:** *influence of back trajectory, geography, season, sources*
- 6. Real-time measurement of highly polar gases:** *with exact mass chemical ionization mass spectrometry) and **Controlled Laboratory experiments:** to examine multiphase chemistry, hexafluoropropylene oxide (HFPO)*

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Questions?