Atmospheric Concentrations and Deposition of PFAS

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NC PFAS Testing (PFAST) Network, a research program funded by the NC Policy Collaboratory

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

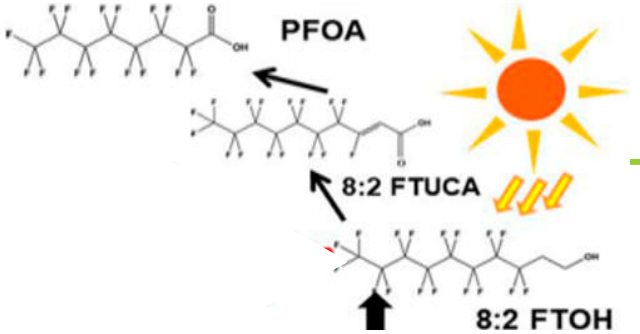
- **Atmospheric Sources:**

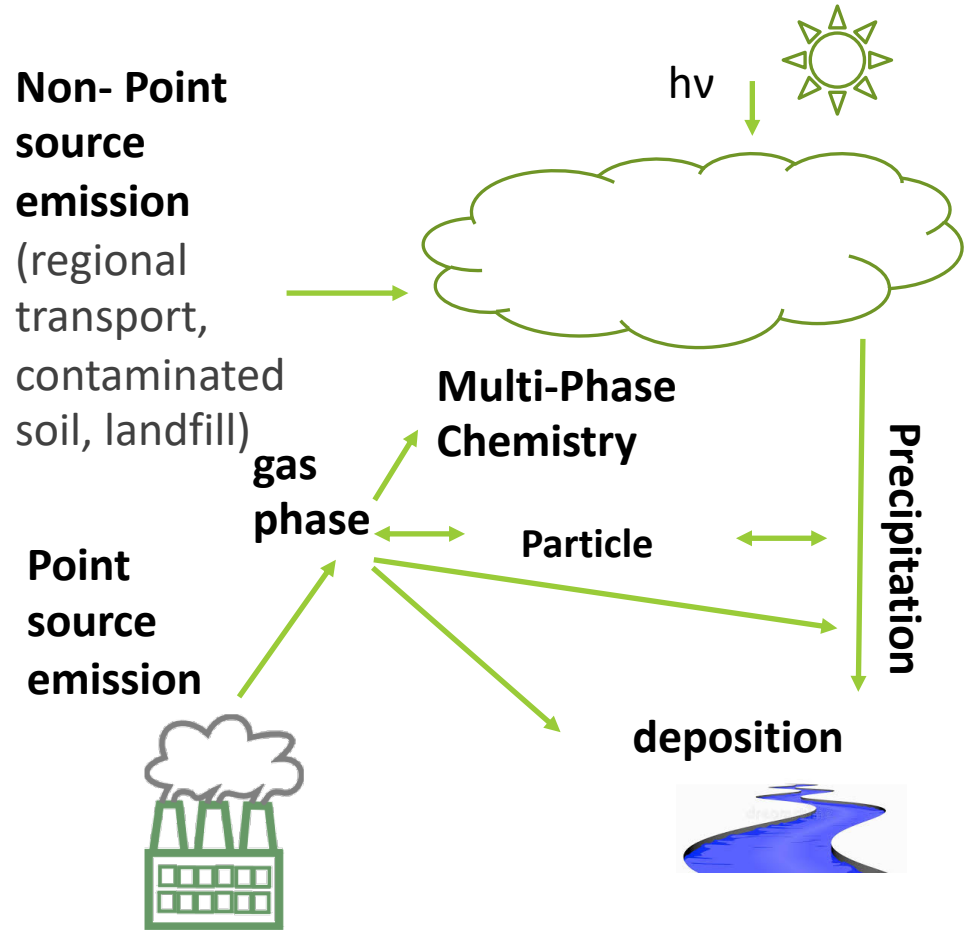
  - PFAS is emitted into atmosphere from stack at Chemours,

  - 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)





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

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

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

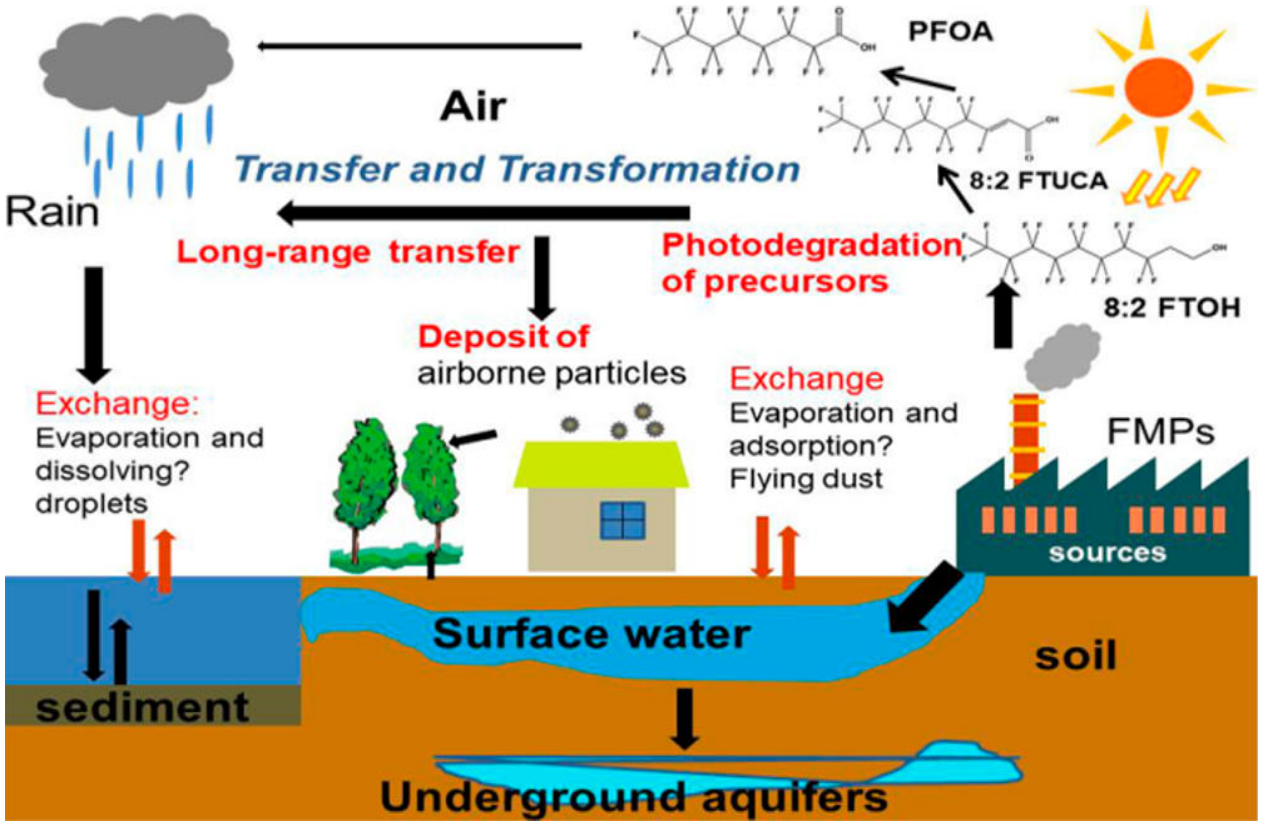
Research Questions

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?

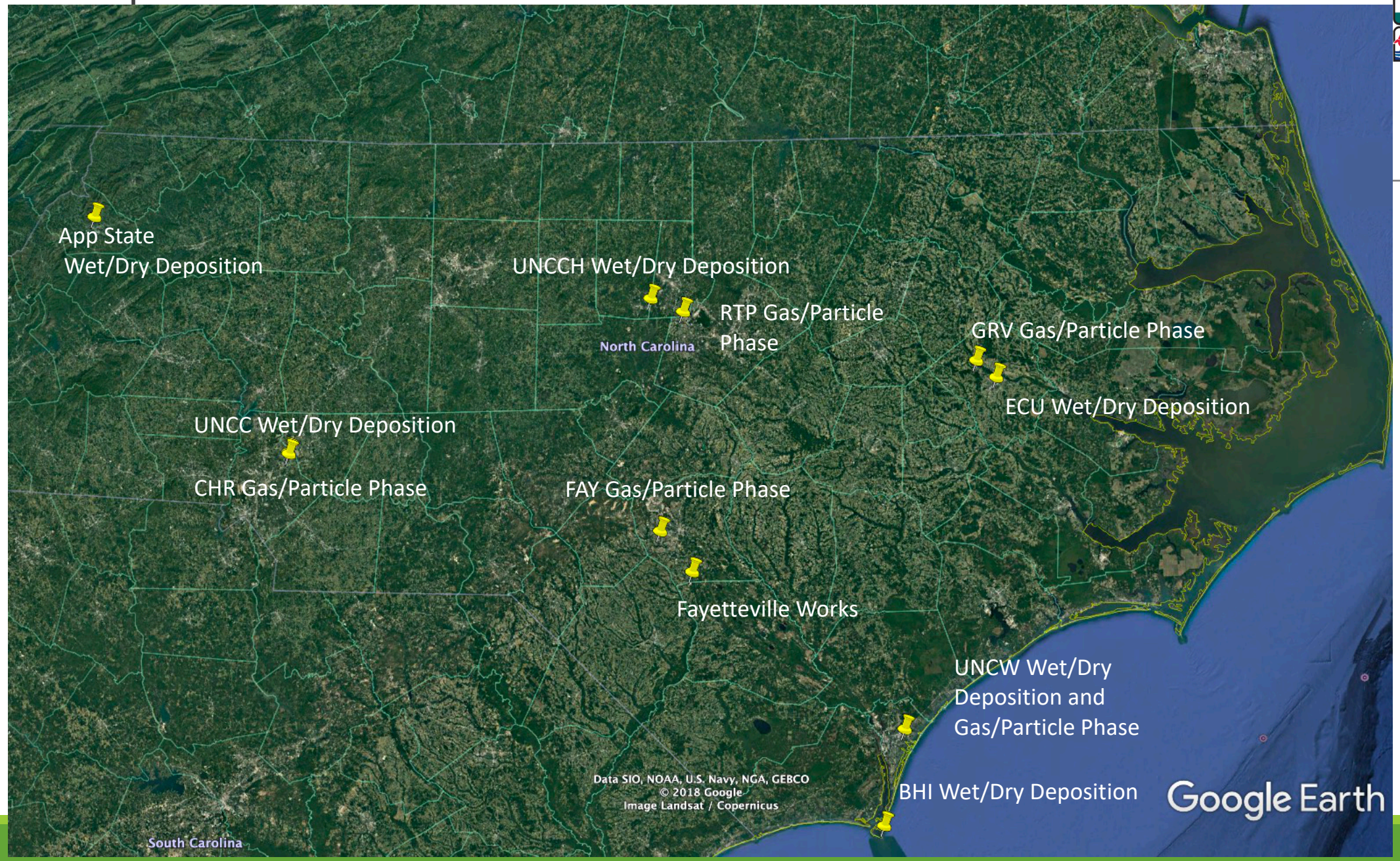
How does gas-to-particle conversion (multiphase atmospheric chemistry) during air mass transfer alter the fate of certain PFAS species?



Approach

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



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

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UNC-Wilmington

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Isabel Srivoraphan

Dave Tilley

RTP

UNC-Chapel Hill

Karsten Baumann, Ph.D.

App State

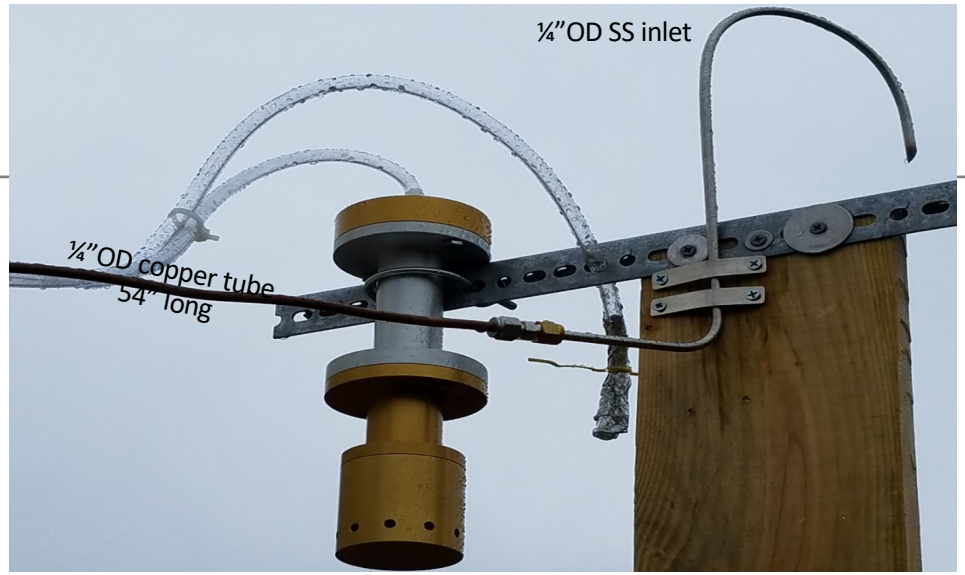
Bob Swarthout, Ph.D.

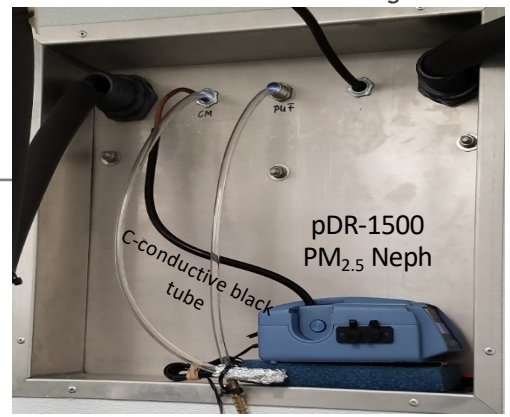
BHI

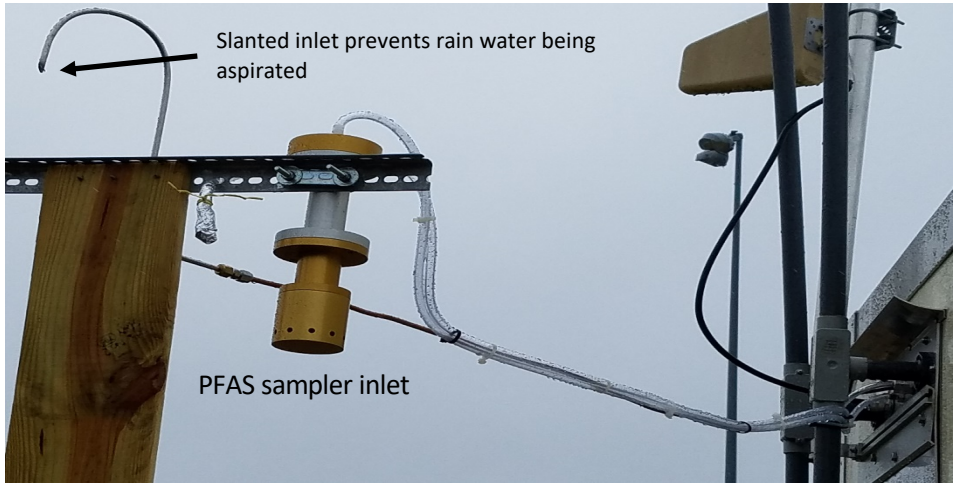
Chris Shank, Ph.D.

Beth Darrow, Ph.D.

Example Aerosol Station

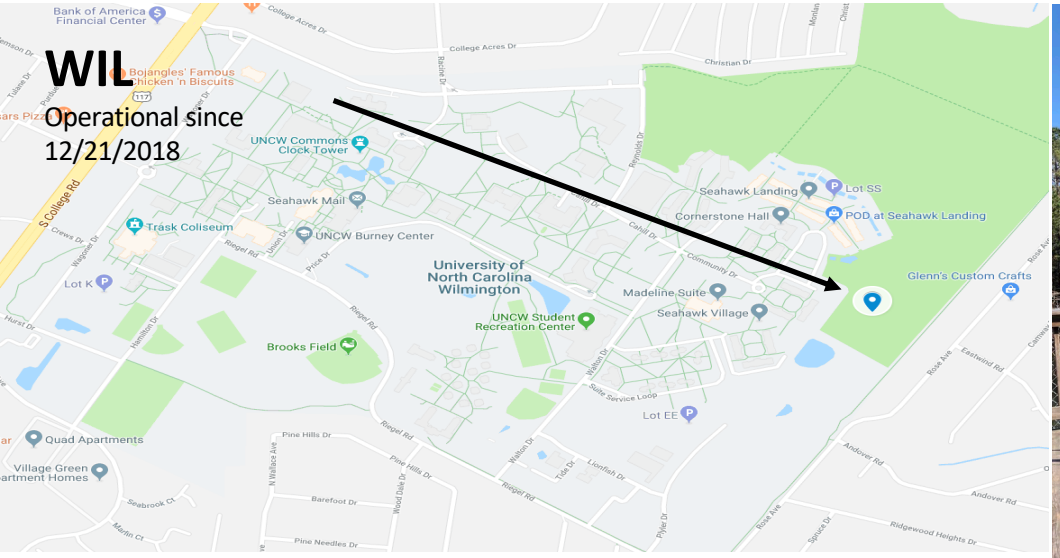






NC Department of Environmental Quality
Division of Air Quality
Thanks to
Joette Steger & Mitchell Revels
Fayetteville Regional Office
Site Address
John Griffin Middle School
8943 Fisher Road
Fayetteville, NC 28304

Example Aerosol and Wet/Dry Deposition Station



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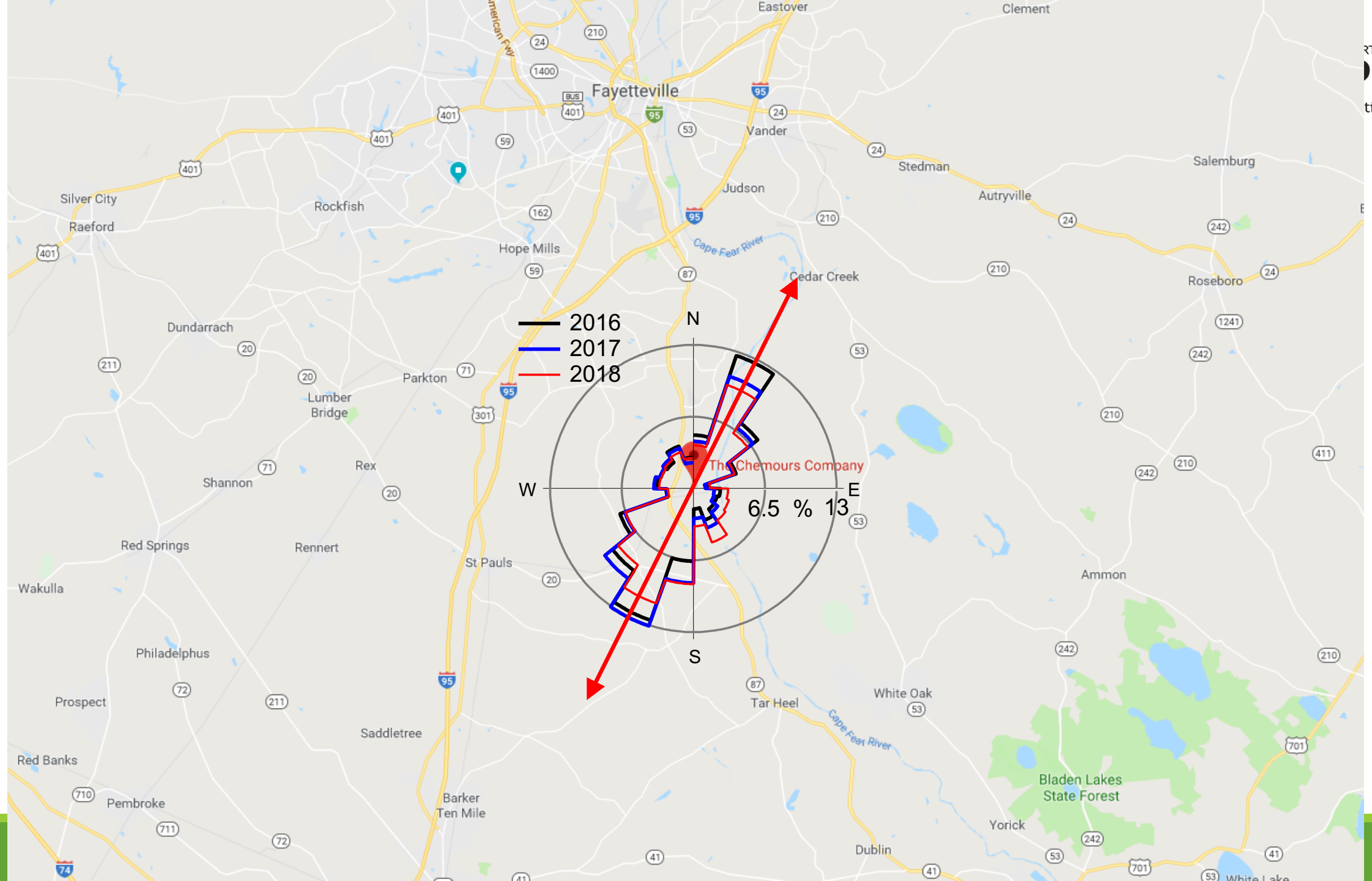

2016
2017
2018
N
W
E
S
6.5 % 13
The Chemours Company
Fayetteville
Eastover
Clement
Vander
Stedman
Salemburg
Autryville
Roseboro
Judson
Cedar Creek
Hope Mills
Rockfish
Silver City
Raeford
Dundarrach
Lumber Bridge
Parkton
Shannon
Rex
Red Springs
Rennert
St Pauls
Wakulla
Philadelphus
Prospect
Saddletree
Red Banks
Pembroke
Barker Ten Mile
Tar Heel
White Oak
Ammon
Bladen Lakes State Forest
Yorick
Dublin
Cape Fear River

Sample Collection Schedule

Air Samples	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												

Wet/dry deposition	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 • 5 coastal • 7 terrestrial • 41 mixed • 4 marine	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#
Perfluorocarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6
Perfluorosulfonic acids (PFSAs)		
Potassium perfluoro-1-butanesulfonate	PFBS	375-73-5
Sodium perfluoro-1-pentanesulfonate	PFPeS	2706-91-4
Sodium perfluoro-1-hexanesulfonate	PFHxS	355-46-4
Sodium perfluoro-1-heptanesulfonate	PFHpS	375-92-8
Sodium perfluoro-1-octanesulfonate	PFOS	1763-23-1
Sodium perfluoro-1-nonanesulfonate	PFNS	68259-12-1
Sodium perfluoro-1-decanesulfonate	PFDS	335-77-3
Sodium perfluoro-1-dodecanesulfonate	PFDoS	79780-39-5

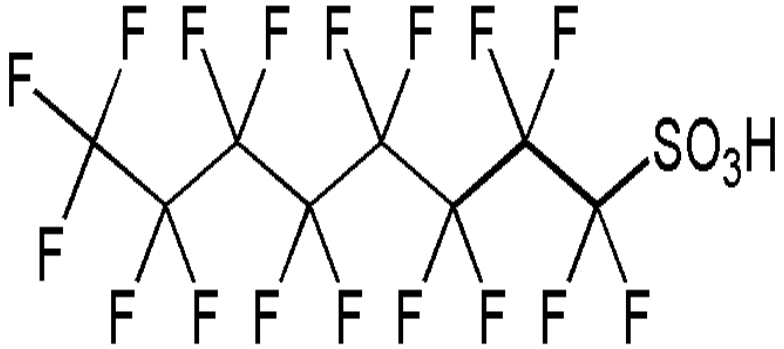
Analyte	Abbreviation	CAS#
Fluorinated vinyl ethers		
Trifluoromethyl trifluorovinyl ether	PMVE	1187-93-5
Pentafluoroethyl trifluorovinyl ether	PEVE	10493-43-3
Perfluoropropoxyethylene	PPVE	1623-05-8
Fluorotelomer alcohols		
1H,1H,2H,2H-Perfluoro-1-hexanol	4:2 FTOH	2043-47-2
1H,1H,2H,2H-Perfluoro-1-octanol	6:2 FTOH	647-42-7
1H,1H,2H,2H-Perfluoro-1-decanol	8:2 FTOH	678-39-7
1H,1H,2H,2H-Perfluoro-1-dodecanol	10:2 FTOH	856-86-1
Perfluoroalkyl ether carboxylic and sulfonic acids		
Perfluoro-2-propoxypropanoic acid	GenX	13252-13-6
1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonate	NVHOS	801209-99-4
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-2-methoxyacetic acid	PFMOAA	674-13-5
Perfluoro-4-methoxybutanoic acid	PEPA (PFMOBA)	267239-61-2
Perfluoro-3-methoxypropanoic acid	PMPA (PFMOPrA)	13140-29-9
Perfluoro (3,5-dioxahexanoic) acid	PFO2HxA	39492-88-1
Perfluoro (3,5,7-trioxaoctanoic) acid	PFO3OA	39492-89-2
Perfluoro (3,5,7,9-tetraoxadecanoic) acid	PFO4DA	39492-90-5
Perfluoro3,5,7,9,11-pentaoxadecanoic acid	PFO5DoA	39492-91-6
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
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
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

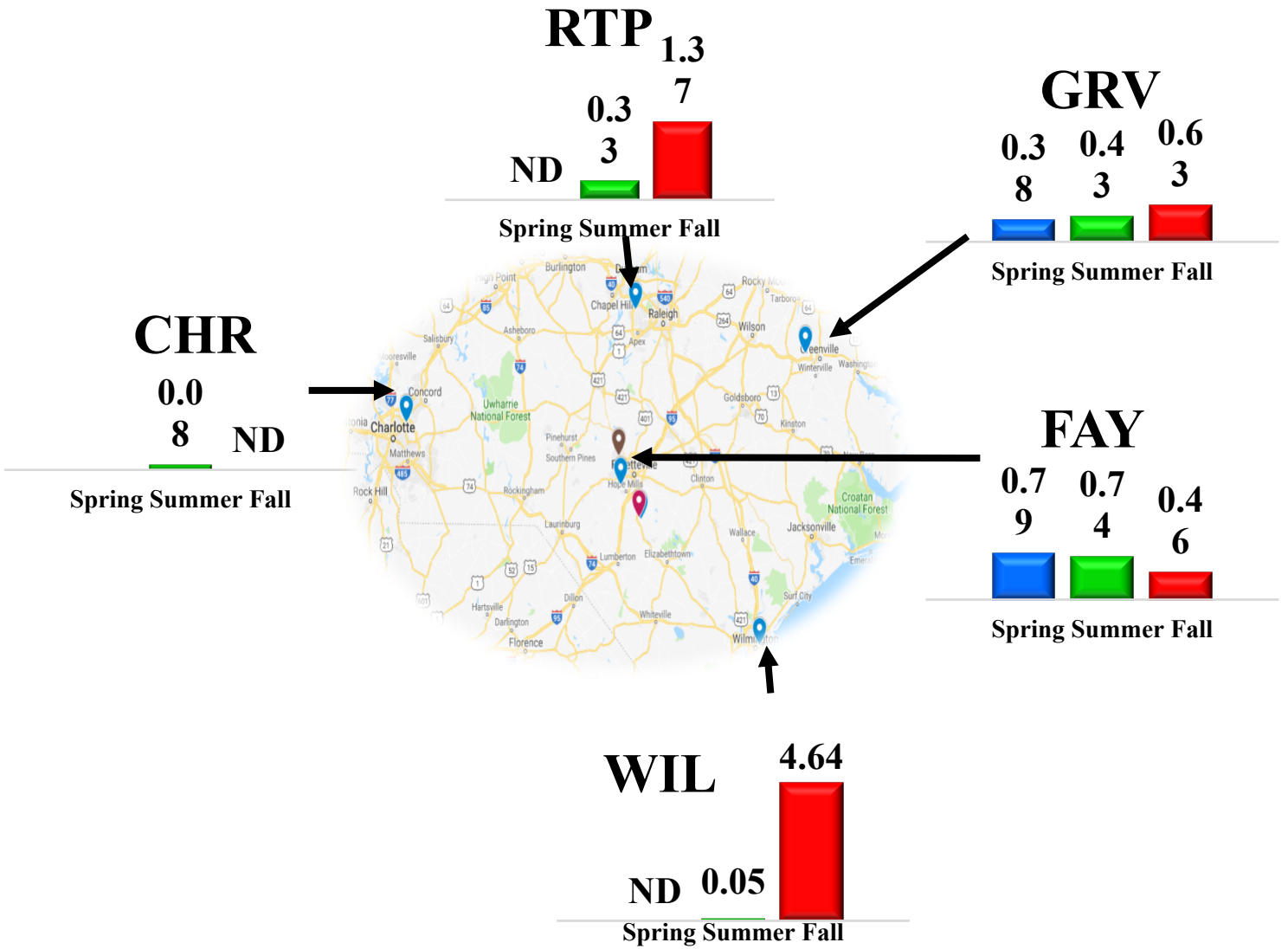
Analyte		Estimated Air Conc. (pg/m^3)
Perfluorocarboxylic acids (PFCAs)		
PFPeA		0.002 – 0.02 pg/m^3
PFHxA		
PFHpA	Perfluoro-n-heptanoic acid	
PFOA	Perfluoro-n-octanoic acid	
PFNA		
PFDA		
PFUdA	Perfluoro-n-undecanoic acid	
PFDoA	Perfluoro-n-dodecanoic acid	
PFTrDA		
PFTeDA		
Perfluorosulfonic acids (PFSAs)		
PFBS		0.005 – 0.05 pg/m^3
PFPeS		
PFHxS		
PFHpS	perfluoro-1-heptanesulfonate	
PFOS	perfluoro-1-octanesulfonate	
PFNS		
PFDS		
PFDoS		

Analyte	Estimated Air Conc. (pg/m^3)
Perfluoroalkyl ether carboxylic and sulfonic acids	
GenX	0.005 - 0.03 pg/m^3
HydroEve	
PEPA (PFMOBA)	
PMPA (PFMOPrA)	
PFO2HxA	
PFO3OA	
Nafion Byproduct 1	
Nafion Byproduct 2	
Nafion Byproduct 4	

Preliminary: Particle Phase-**PFOS** seasonal average air concentrations (pg/m^3)



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



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

Indoor PFAS air concentration (pg/m^3)	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	
Outdoor PFAS air concentration (pg/m^3)			
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		*Perfluoro alkyl ether carboxylic and sulfonic acids*	
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	PFPrOPrA	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
LOQ (pg on column)	21.26	2.27	5.14	7.12	0.15	1.83
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

LOD = (3*std)/slope

LOQ = (10*std)/slope

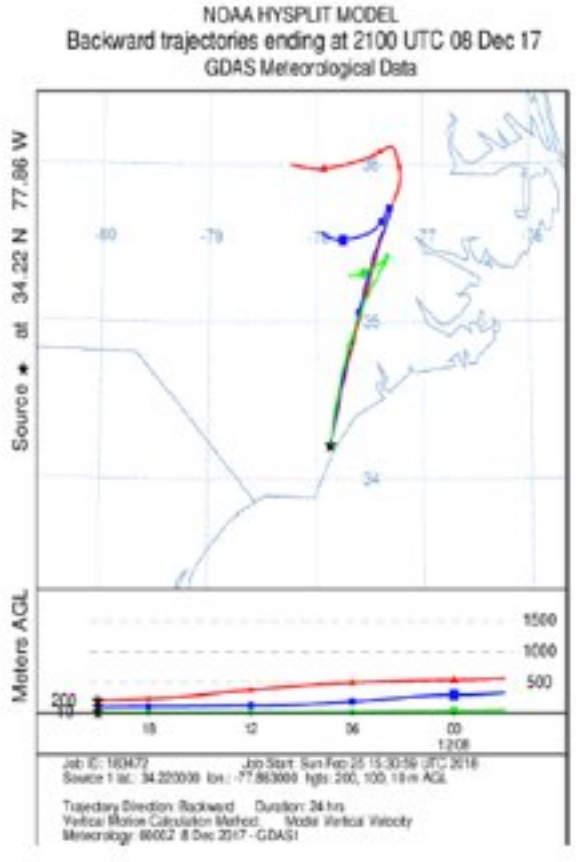
*assuming extraction of 1L water, blowdown to 0.5mL, 50uL sample diluted to 200uL in LC vial, and 10uL injection

PMPA quantified against PFMOPrA

PEPA quantified against PFMOBA

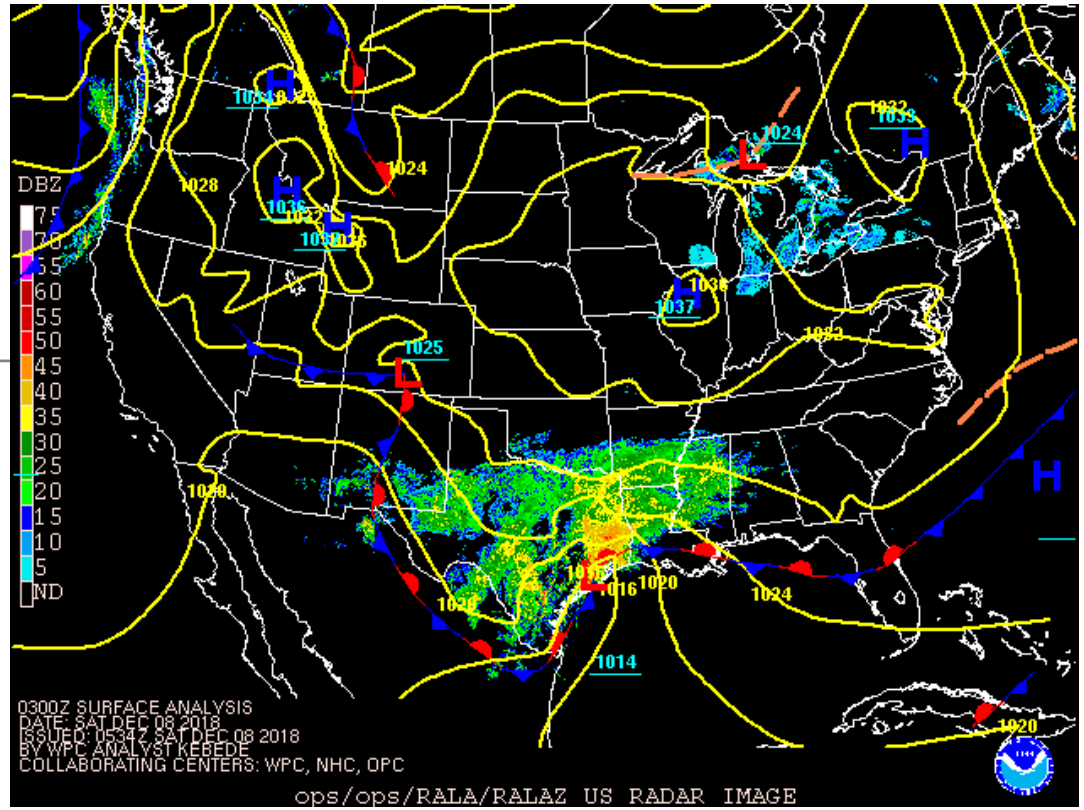
Wet Deposition Concentration Range in Wilmington

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

Wet deposition of poly- and perfluorinated compounds in Northern Germany

Rainwater PFAS Concentration in Literature

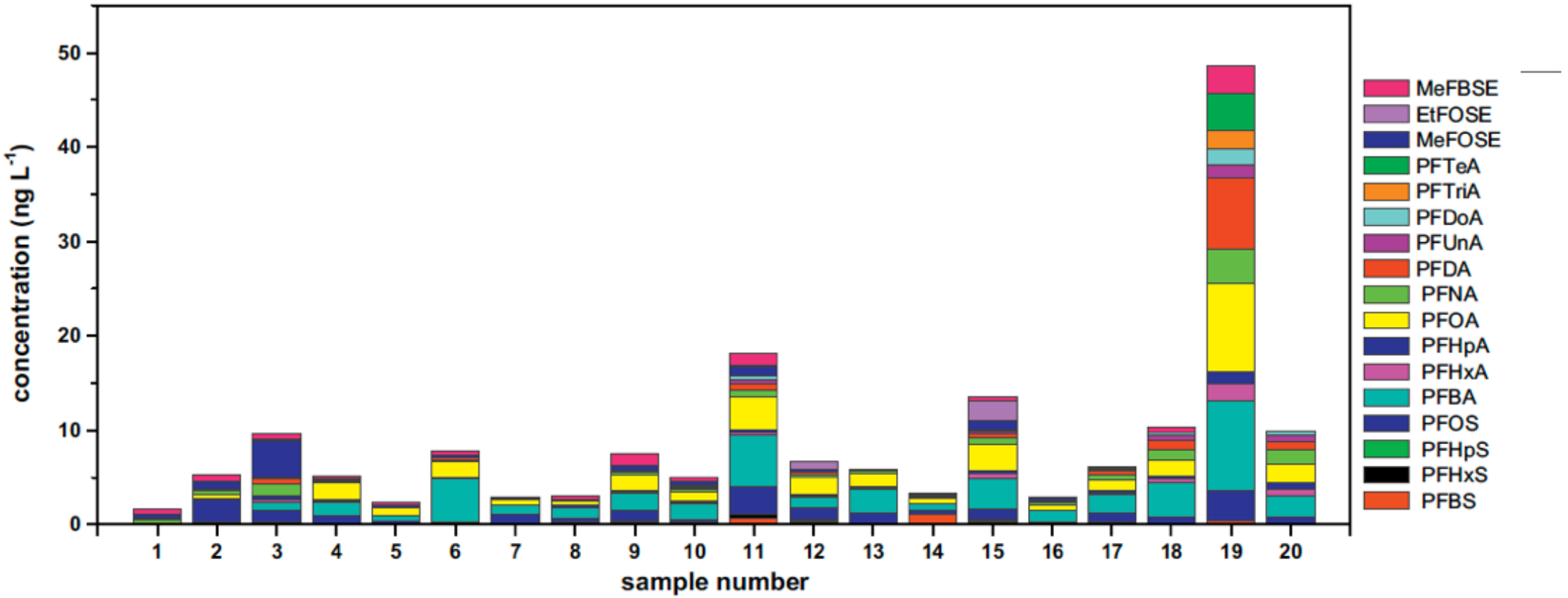


Fig. 1. Daily total precipitation (0.1 mm = 0.1 L m^{-2}), wet deposition rates (ng m^{-2} d^{-1}), and rain water concentrations (ng L^{-1}) of detected PFC. Note: PFOA concentration samples BAR-R1 and BAR-R3 were below the corresponding blank. Daily total precipitation was obtained from the nearby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

Dreyer et al.
Environmental Pollution 158 (2010) 1221–1227

Wet deposition of poly- and perfluorinated compounds

Table 1
PFC rain water concentrations (ng L^{-1}) as reported in literature.

site	Smith Is., MD, USA	Lewes, DE, USA	Ithaca, NY, USA	Underhill, VT, USA	Kejimkujik, 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
PFPA	<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

Dreyer et al. Environmental Pollution 158 (2010) 1221–1227 and references there in

Future work

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?