Atmospheric Concentrations and Deposition of PFAS

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

Motivation

- **Measurements**: aerosol concentrations, wet and dry deposition, even far from point sources
- **Human exposure:** Airborne PFAS contributes directly (through inhalation) and indirectly (through deposition to watersheds and water supplies)
- **Sources:** Production facilities (e.g., Chemours), use of PFAS-containing products (e.g., firefighting foams; household products), waste streams (e.g., contaminated soil, wastewater, landfills)
- Atmospheric PFAS Transformations: Limited knowledge regarding PFAS atmospheric reactions and drinking water impacts
- **Elevated concentrations:** indoors, near industrial sources, in urban areas

Fate and effects of atmospheric PFAS are poorly understood: they depend on PFAS chemistry and properties

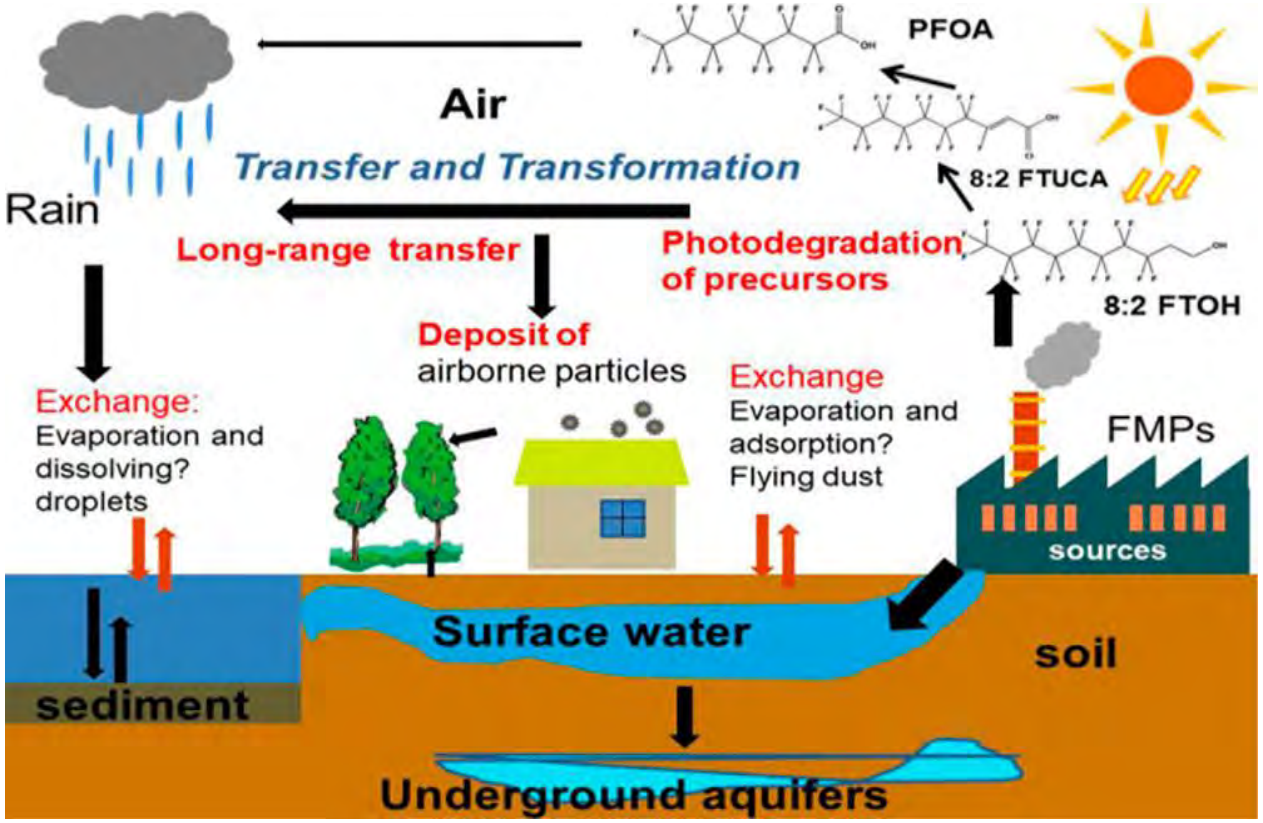
Research Questions

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?

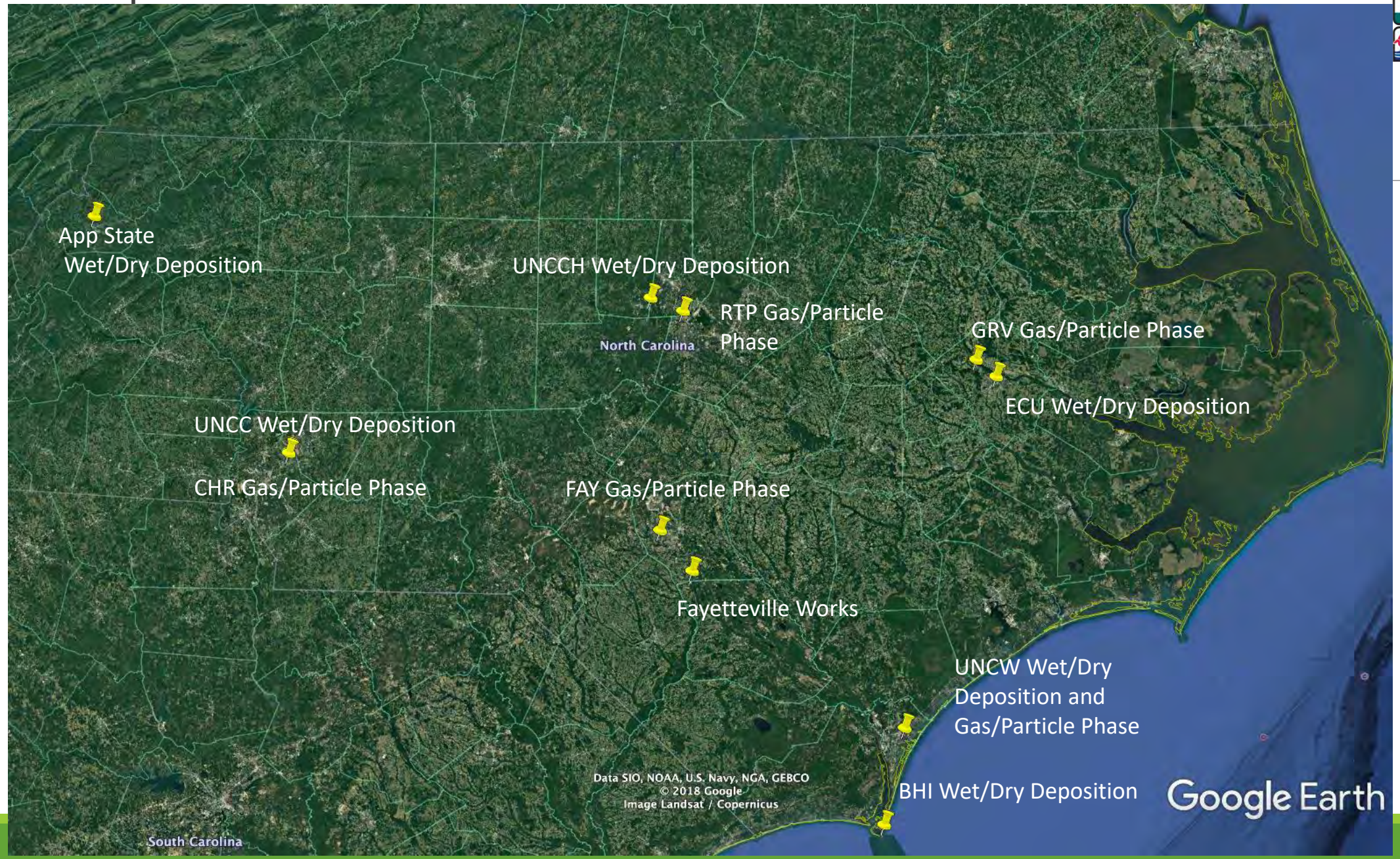
How does gas-to-particle conversion (multiphase atmospheric chemistry) during air mass transfer alter the fate of certain PFAS species?



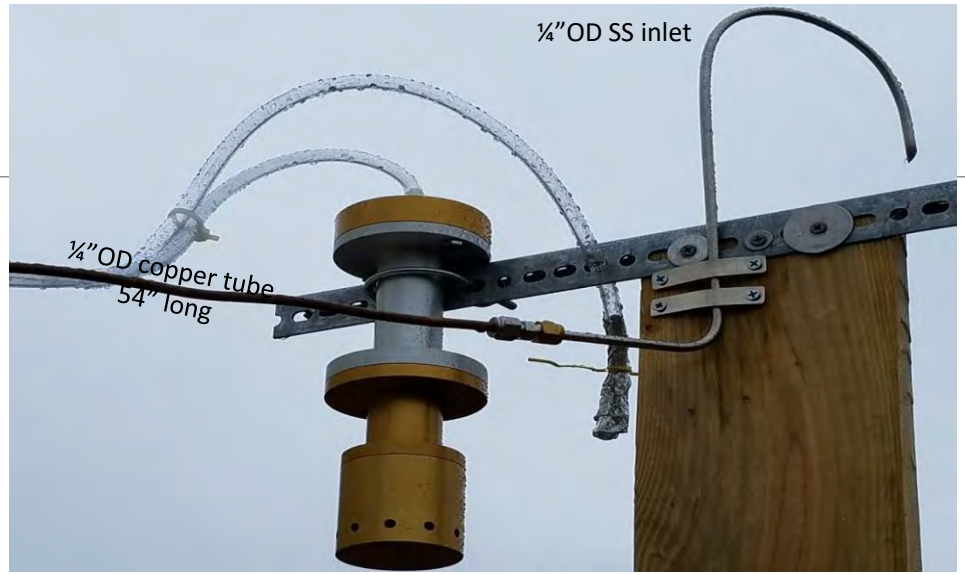
Planned Approach

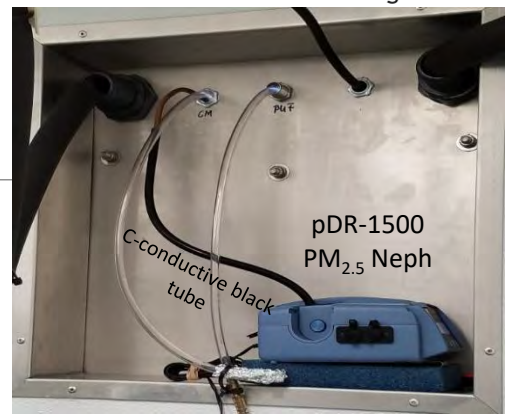
1. ***Event-based wet/dry deposition sampling***: *in Wilmington and selected other stations*
2. ***Integrated gas and particle sampling:*** *Weekly 6 day periods for one year. Wilmington, RTP, Charlotte, Greenville, Fayetteville*
3. ***Real-time measurement of highly polar gases:*** *1-2 weeks (exact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

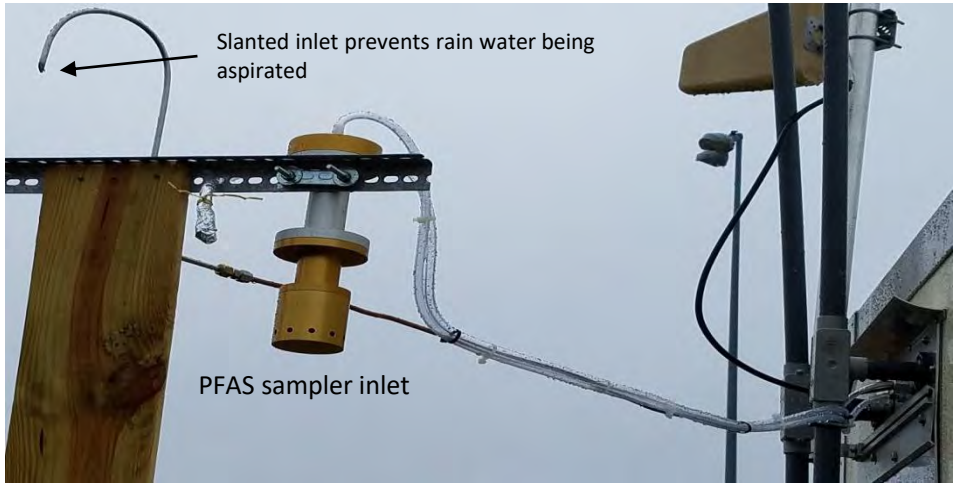
Sample Stations



Example Aerosol Station







NC Department of Environmental Quality
Division of Air Quality
Thanks to
Joette Steger & Mitchell Revels
Fayetteville Regional Office
Site Address
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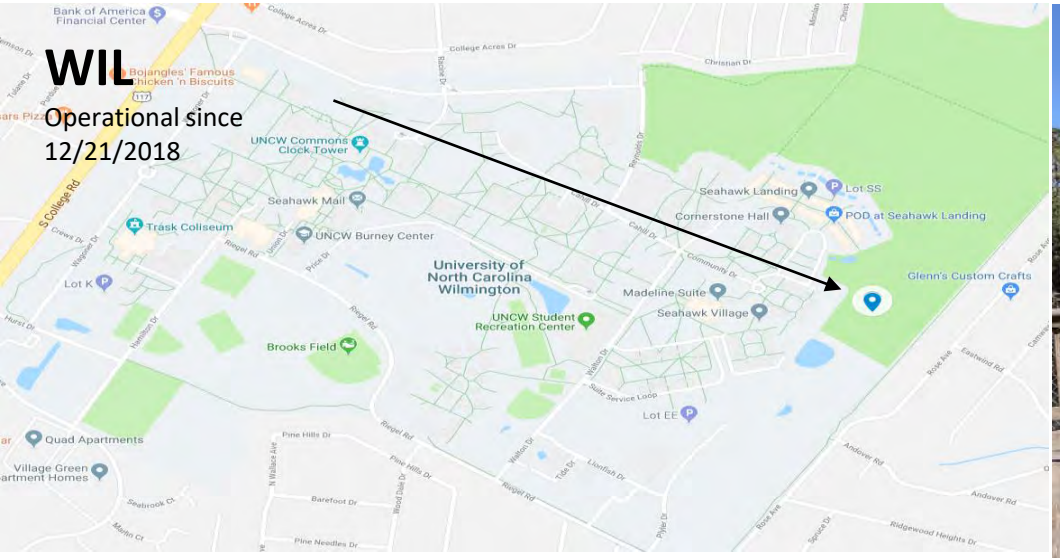
Example Aerosol and Wet/Dry Deposition Station



UNCW UNIVERSITY of NORTH CAROLINA WILMINGTON

Department of Chemistry & Biochemistry

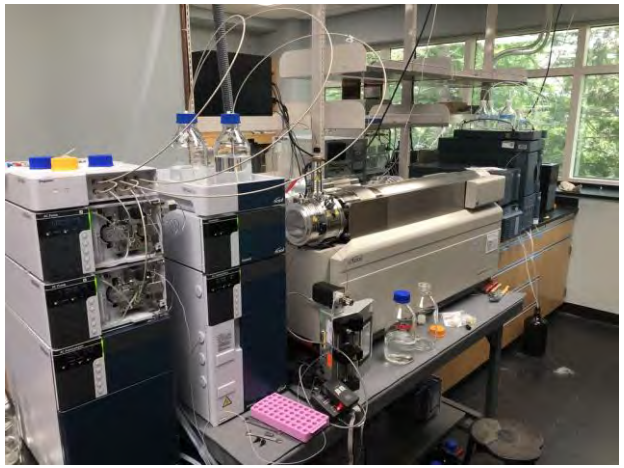
Drs. Kieber & Skrabal
Center for Marine Science
5600 Marvin Moss Lane
Wilmington, NC 28409-5928

Sample Collection and Analysis

Wet/Dry Deposition Collector

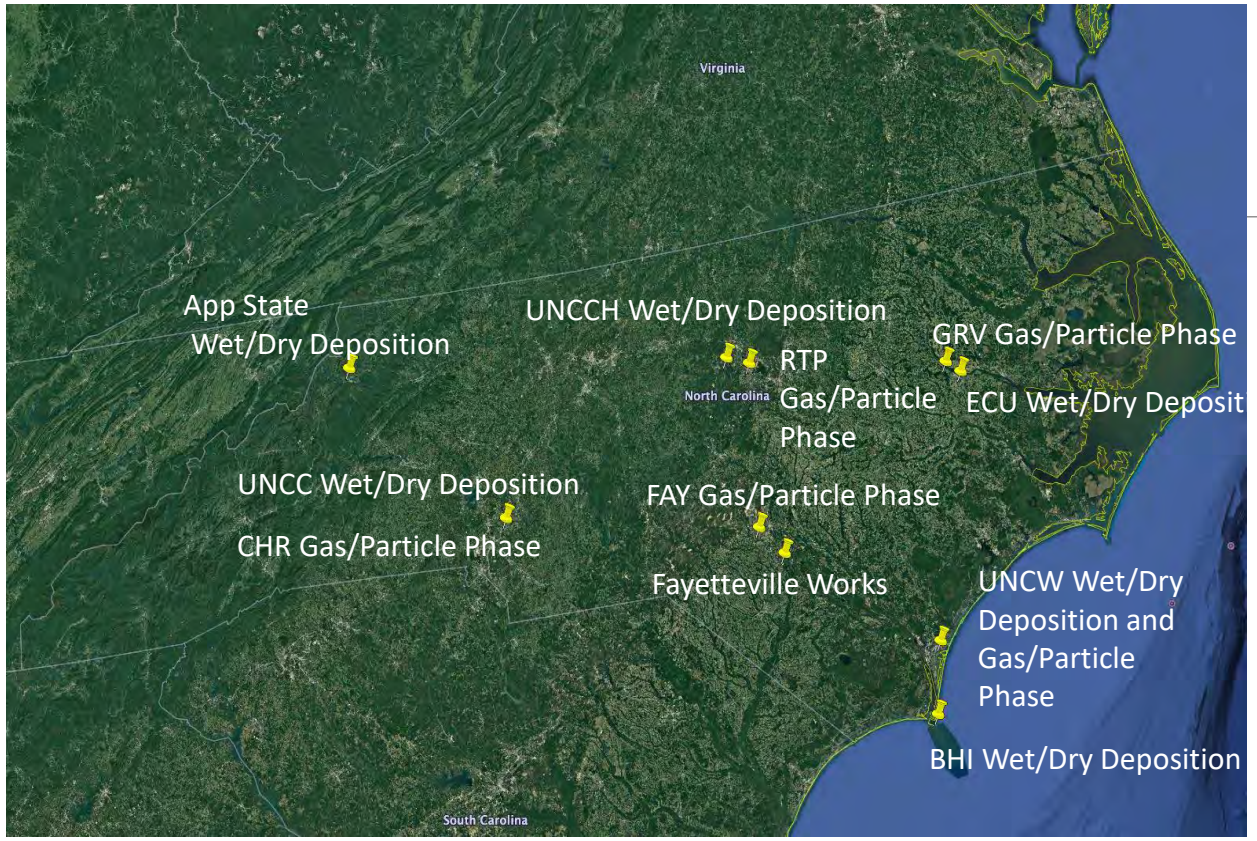
Gas/Particle Phase Collector

Extraction



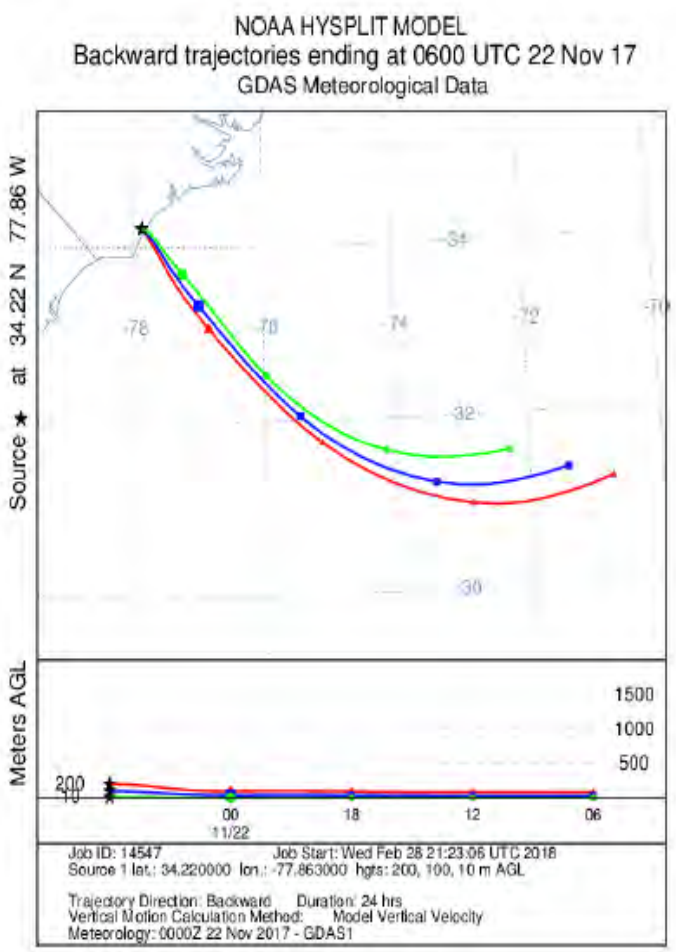
Analysis by mass spectrometry to identify compounds and report concentrations

Timeline of Sampling

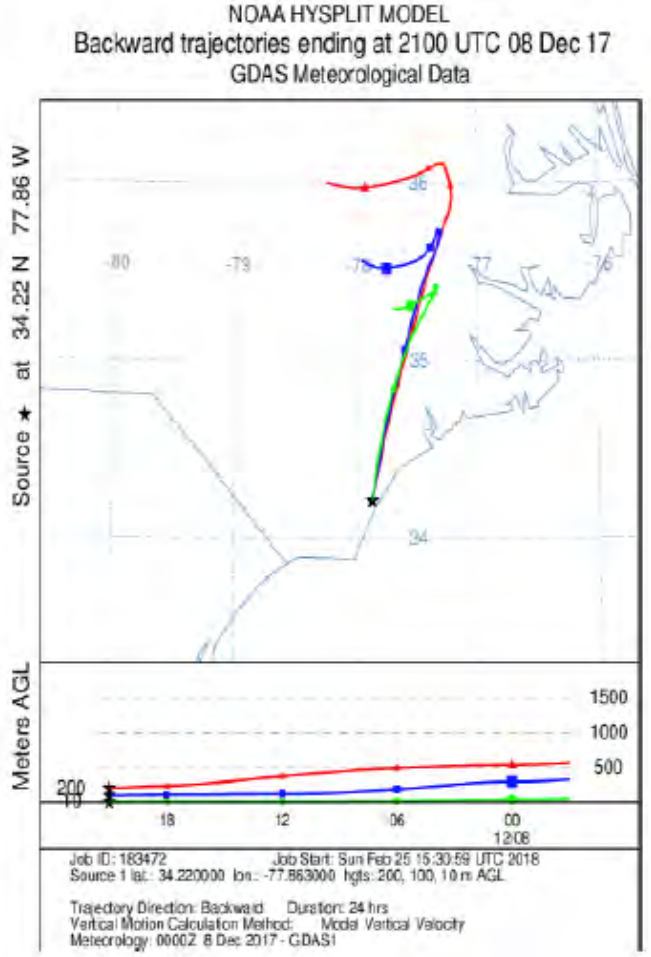


	Dec 18 - Mar 19	April 19 - May 19	May 19 – Sept 19	Oct 19 – Dec 19
Collect wet/dry deposition at Wilmington site	xxxx	xxxx	xxxx	xxxx
Collect wet/dry deposition at other locations	3 collections		3 collections	
Gas/Particle phase collection	xxxx	xxxx	xxxx	xxxx
Airborne gas/particle collection real time			xxxx	

Example of Data: Air Mass Back Trajectory and GenX Rainwater Concentration



E 1775
11/21-22/17
GenX <3 ppt (ng/L)
0.26 inches at UNCW
pH not analyzed



E 1781
12/8-9/17
GenX >500 ppt (ng/L)
1.8 inches at UNCW
pH4.68

Outcomes

- The proposed research will provide critical and transformative information regarding the atmospheric reactions, transport and deposition of PFAS to surface and ground waters that feed drinking water supplies.
- There is limited to no information on the atmospheric reactions these PFAS compounds undergo during long range transport influencing deposition.
- Ultimately, the knowledge gained from this research will benefit stakeholders within NC and beyond.
- Results will be presented in peer reviewed publications and shared with local, state and federal agencies

Acknowledgements

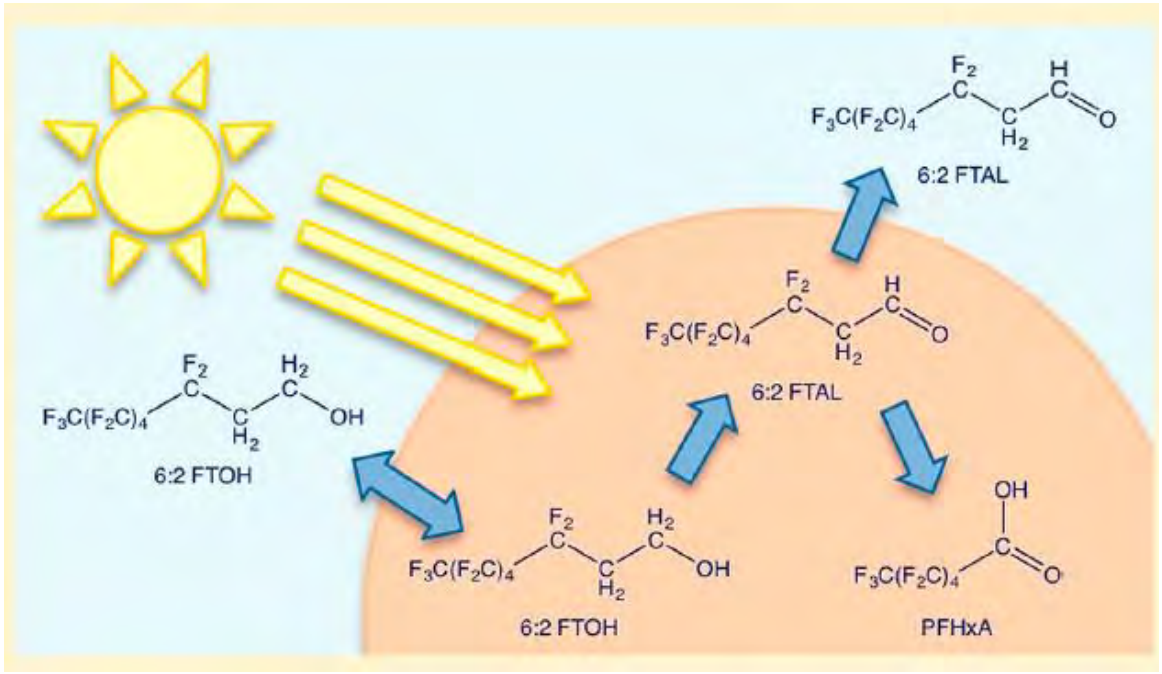
- Research funded by the North Carolina Policy Collaboratory through an appropriation from the North Carolina General Assembly

- NC DEQ and especially DAQ for access to FAY station

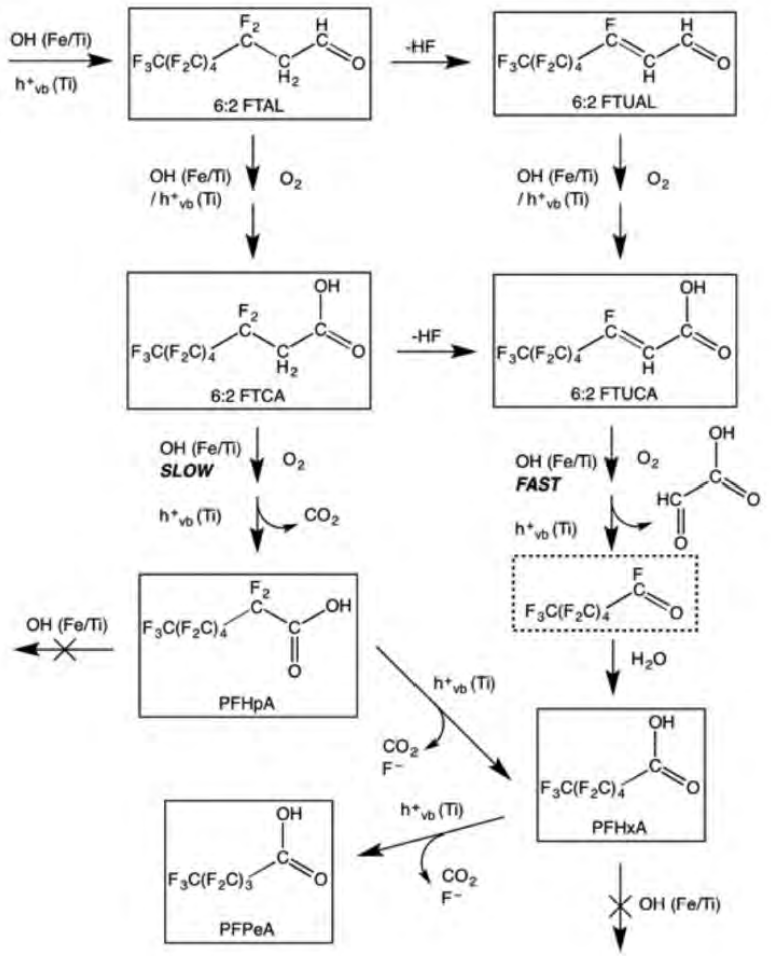
Questions?

Extra Slides

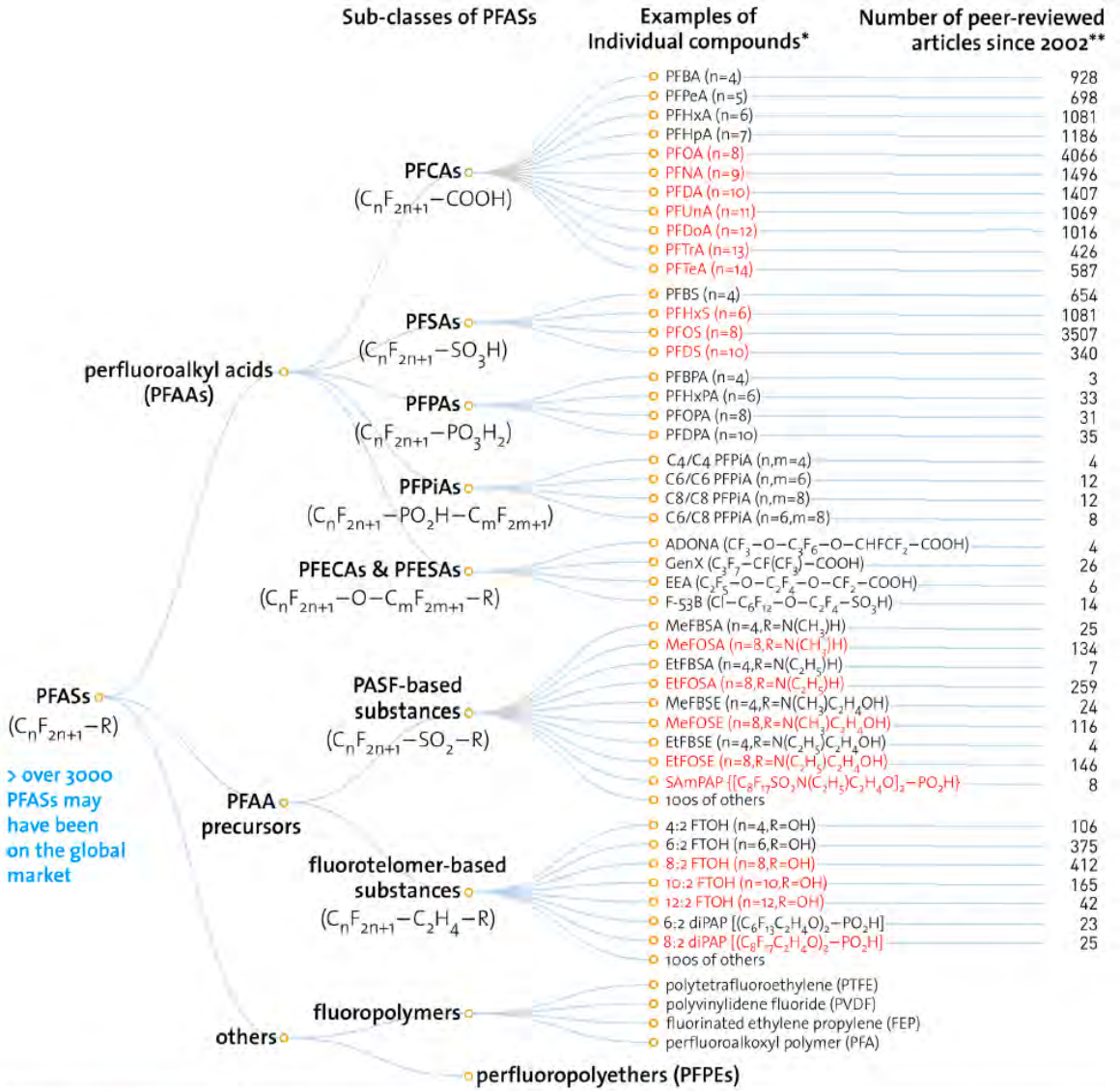
PFAS Atmospheric Transformations on Surfaces



Scheme 1. Suggested Mechanisms for Photoproduction of PFAS from Surface-Sorbed FTOHs. Species in Solid Rectan
Observed in the Present Experiments



Styler et al. Environ. Sci. Technol. 2013, 47, 6358−6367



* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

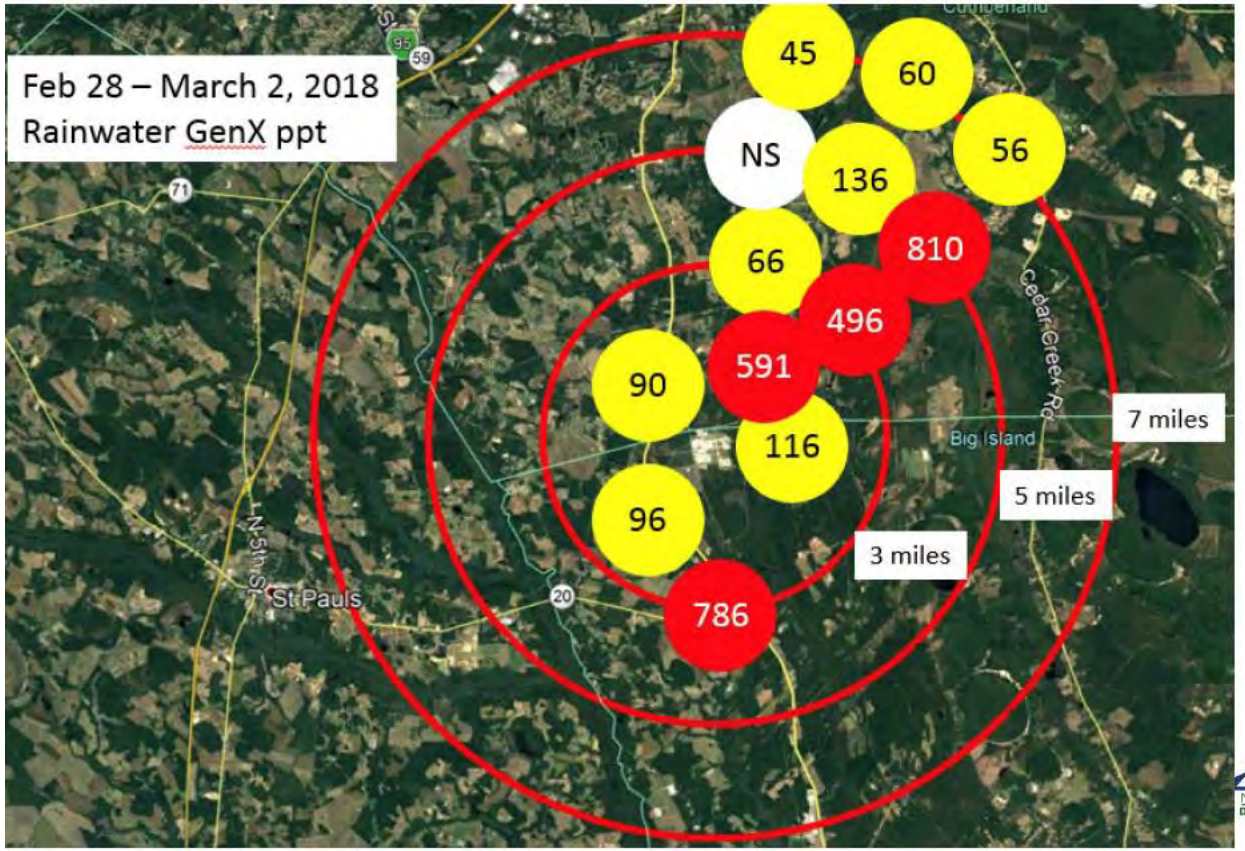
Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors.).

NORTH CAROLINA PFAS Testing Network

Several of these PFAS sub-classes have been detected in atmospheric samples. Do members of these classes decompose in the atmosphere or undergo other transformations? Do these compound(s) impact drinking water through wet/dry deposition?

Wang et al Environ. Sci. Technol. 2017, 51, 2508−2518

Wet/Dry Deposition of GenX near Fayetteville Works Facility



Data from NC DAQ

Wet deposition of poly- and perfluorinated compounds in Northern Germany

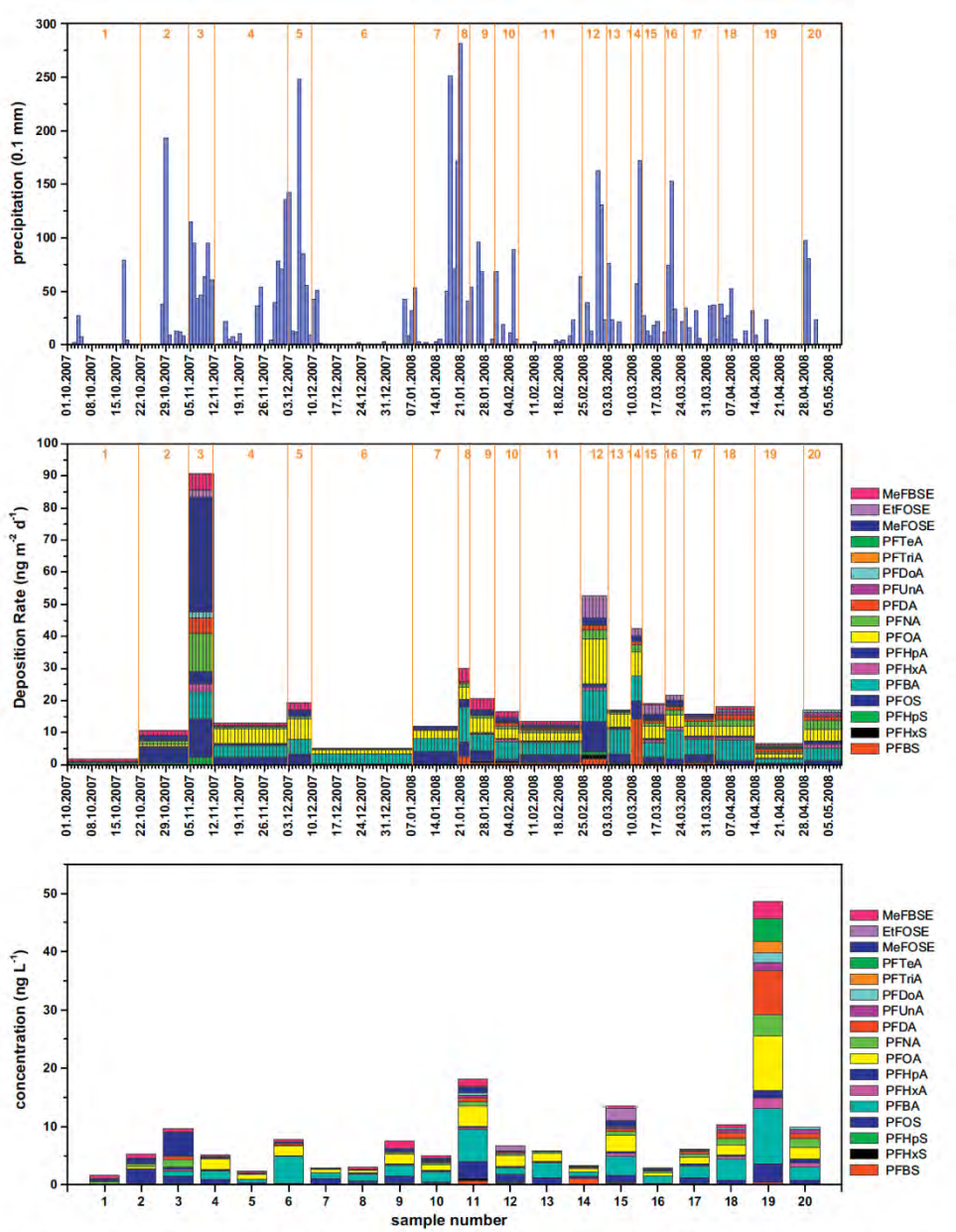


Fig. 1. Daily total precipitation (0.1 mm = 0.1 L m^{-2}), wet deposition rates (ng m^{-2} d^{-1}), and rain water concentrations (ng L^{-1}) of detected PFC. Note: PFOA concentration of samples BAR-R1 and BAR-R3 were below the corresponding blank. Daily total precipitation was obtained from the nearby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

Rainwater PFAS Concentration in Literature

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

Atmospheric Particulate Organic Matter (APM)

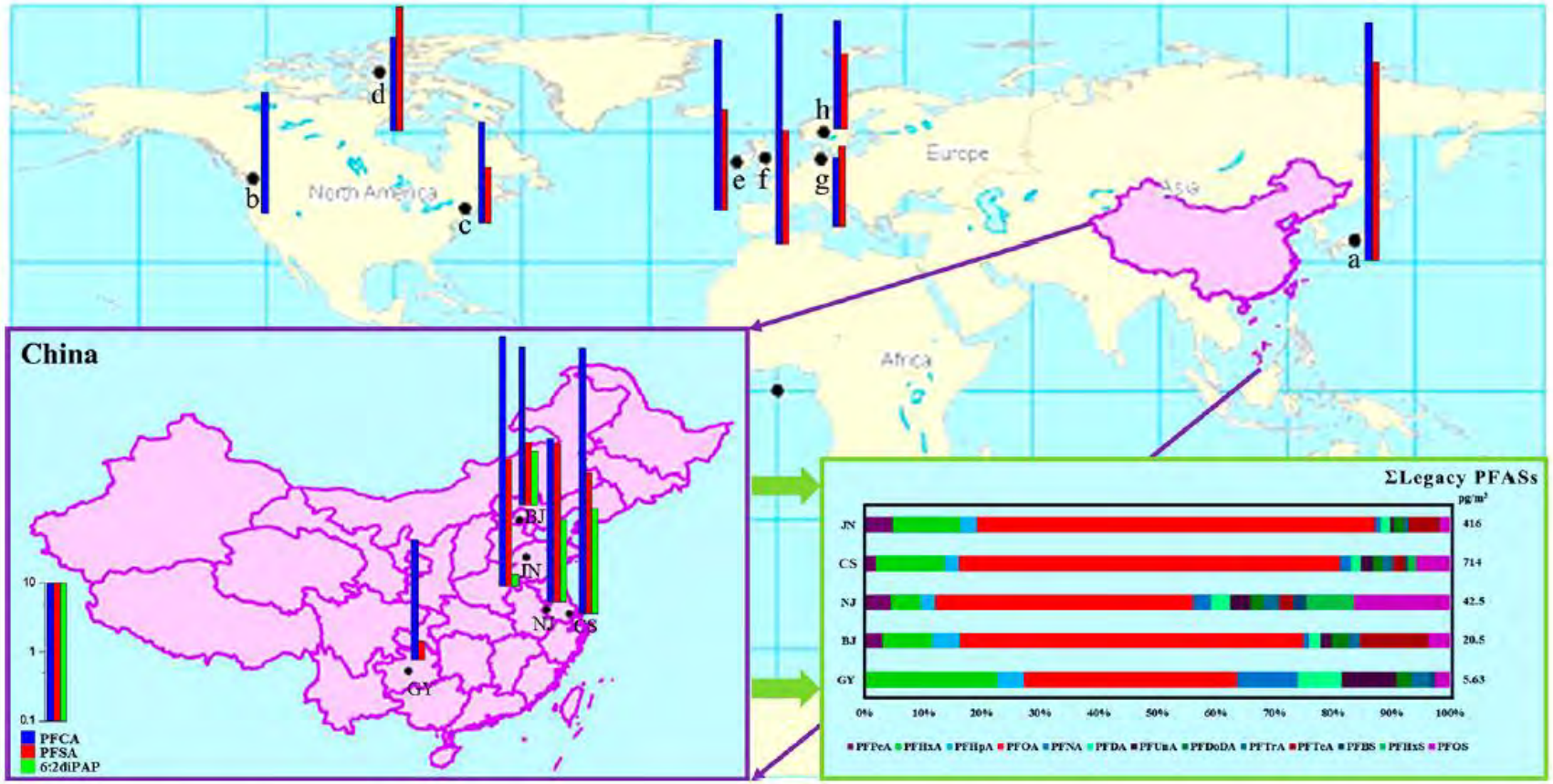


Figure 3. Distribution of PFCAs, PFSAs, and 6:2 diPAP in outdoor APM (data for China were obtained from this study, and those for other countries were obtained from previous studies; a: Japan,[76] b: Canada,[29] c: U.S.,[77] d: Arctic,[78] e: UK,[42] f: Ireland,[42] g: Germany,[79] h: Norway[42]) and proportional distribution of legacy PFASs in outdoor APM (value of legacy PFASs is arithmetic mean).

PFAS in House Hold Dust

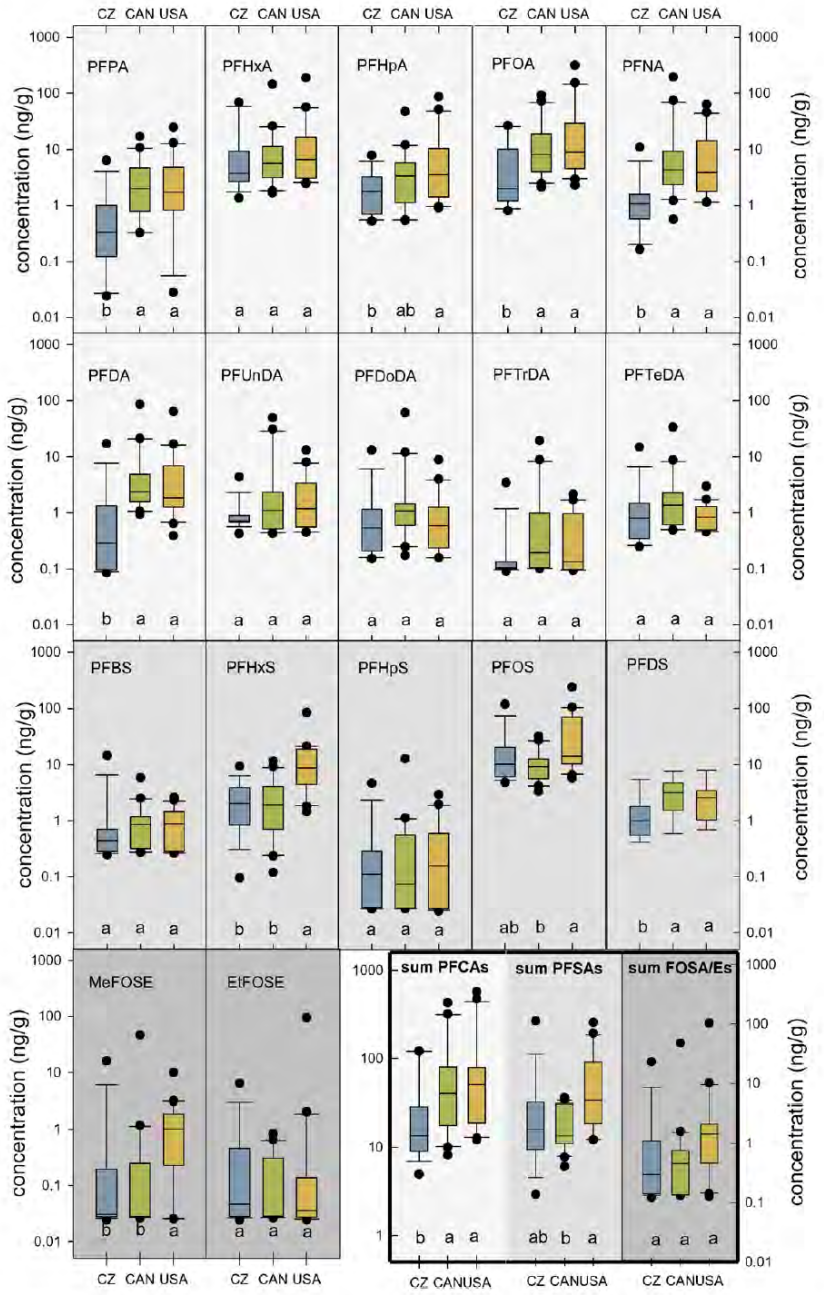


Fig. 1. Box and whisker plots of concentration (ng/g) showing the distribution of PFASs in dust samples from Czech Republic, Canada and USA. The lower and upper ends of the box are the 25th and 75th percentiles of data. The horizontal line within the box is the median value. The whiskers define the 5th and 95th percentiles and symbol ● illustrates outliers. Boxes that share the same letter are not significantly different at a 5% level in ANOVA analysis using Tukey's test.

Environment International 94 (2016) 315–324

Multiphase Environmental Concentrations of PFAS

TABLE 1. Concentration (Range, Median, and Average; pg/m³ or ng/L) of Perfluorinated Carboxylates (PFCAs), Perfluorinated Alkylsulfonates (PFAS), and Fluorotelomer Sulfonates (FtS) in Various Environmental Media in Urban Area (Albany, New York)

	sampling date	site	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	PFDS	PFOSA	6:2 FtS[a]	8:2 FtS[b]	ΣPFAs[c]
air (gas)	May, Jul/06	L2 ($n = 8$)	0.13–0.42 (0.23, 0.26)	1.89–6.53 (2.86, 3.16)	0.16–0.31 (0.20, 0.21)	0.24–1.56 (0.56, 0.63)	ND-0.16 (<LOQ)	0.14–0.43 (0.27, 0.27)	0.13–0.44 (0.34, 0.31)	0.94–3.0 (1.42, 1.70)	ND	0.22–2.2 6 (0.47, 0.67)	ND–<LOQ (<LOQ)	ND–<LOQ (<LOQ)	5.10–11.6 (6.26, 7.29)
air (particle)	May, Jul/06	L2 ($n = 8$)	<LOQ–0.81 (0.29, 0.37)	0.76–4.19 (1.57, 2.03)	<LOQ–0.40 (<LOQ, 0.13)	0.13–0.49 (0.22, 0.27)	ND	<LOQ–0.38 (<LOQ, 0.12)	<LOQ	0.35–1.16 (0.66, 0.64)	<LOQ–0.18 (<LOQ)	<LOQ–0.79 (0.23, 0.29)	ND–<LOQ (<LOQ)	ND–<LOQ (<LOQ)	2.05–6.04 (3.96, 4.03)
lake water	Feb–Nov/06	L2 & 3 ($n = 11$)	1.15–12.7 (4.09, 4.77)	3.27–15.8 (7.20, 8.61)	ND–3.51 (1.63, 1.70)	0.25–3.58 (1.38, 1.64)	ND–1.45 (<LOQ)	ND–<LOQ	<LOQ–4.05 (0.53, 1.58)	ND–9.30 (2.88, 4.14)	ND–0.34 (<LOQ)	ND–0.47 (<LOQ,)	ND–1.46 (<LOQ, 0.35)	<LOQ–0.32 (<LOQ)	9.49–35.9 (21.1, 21.8)
rain water	Aug/06-Mar/07	L1&2&3 ($n = 11$)	<LOQ–2.32 (0.56, 0.69)	<LOQ–7.27 (2.15, 2.53)	<LOQ–3.48 (1.04, 1.27)	ND–1.14 (<LOQ, 0.41)	<LOQ–0.86 (0.41, 0.44)	<LOQ–0.71 (<LOQ)	ND–0.36 (<LOQ)	<LOQ–1.51 (<LOQ, 0.36)	ND–0 0.41 (<LOQ)	ND–<LOQ	ND–0.41 (<LOQ)	<LOQ–3.19 (<LOQ, 0.56)	0.91–13.2 (6.60, 6.19)
snow	Feb/06, Jan–Mar/07	L1&2&3 ($n = 21$)	<LOQ–1.61 (0.39, 0.45)	<LOQ–19.6 (2.72, 4.89)	<LOQ–4.94 (0.55, 0.91)	ND–1.37 (0.32, 0.45)	ND–1.08 (<LOQ, 0.30)	ND–0.41 (<LOQ)	ND–0.35 (<LOQ)	<LOQ–1.93 (0.52, 0.62)	ND–<LOQ	ND–0.57 (<LOQ)	ND–0.34 (<LOQ)	ND–3.37 (<LOQ, 0.44)	0.91–23.9 (5.54, 7.98)
SRWs	Jan–Mar/07	all P&R ($n = 14$)	<LOQ–6.44 (1.13, 1.61)	0.51–29.3 (3.80, 6.58)	<LOQ–5.90 (0.71, 1.30)	ND–8.39 (0.46, 1.15)	ND–1.99 (<LOQ)	ND–1.60 (<LOQ, 0.30)	ND–13.5 (0.35, 1.40)	<LOQ–14.6 (0.81, 2.21)	ND	ND–2.14 (<LOQ, 0.33)	<LOQ–21.3 (1.22, 4.03)	<LOQ–5.84 (<LOQ, 1.09)	1.11–81.8 (9.85, 15.1)

[a] The number analyzed ($n = 11$ for lake water, $n = 10$ for rainwater, and $n = 15$ for snow). [b] The number analyzed ($n = 2$ for lake water, $n = 7$ for rainwater, and $n = 12$ for snow). [c] The sum of PFCAs and PFAS except for two FtS. The values in parentheses indicate "median" and "arithmetic mean" and LOQ was 0.25–0.75 ng/L for PFOA and 0.25 ng/L for others in aqueous samples. For air samples, LOQ was 0.12 pg/m³ for all gaseous and particulate compounds except for particulate PFOA (0.195 pg/m³) and PFOS (0.07 pg/m³).

Landfill Atmospheric Emissions

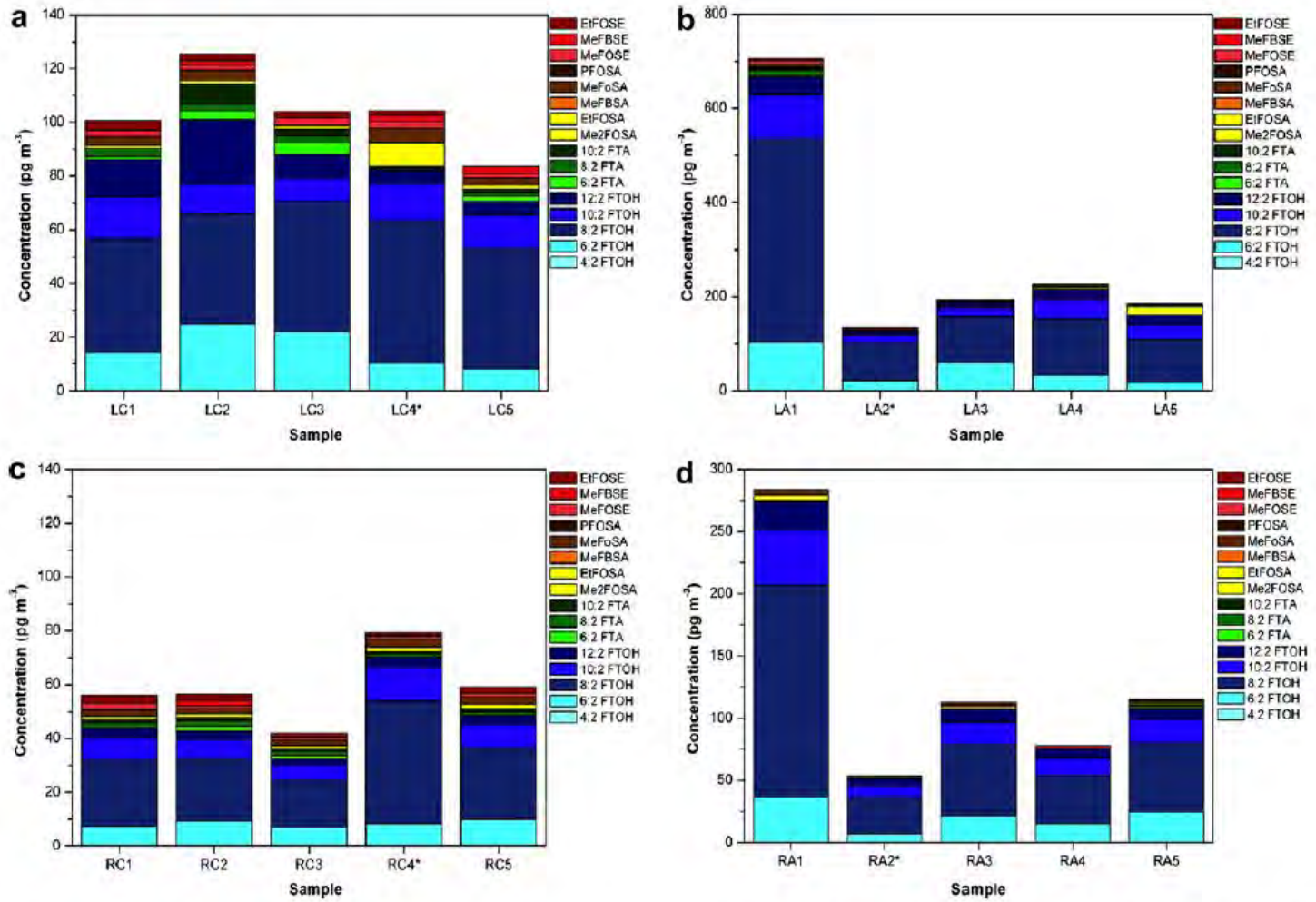


Fig. 1. Concentrations (pg m^{-3}) of semi-volatile and volatile PFCs in gas-phase samples taken at landfills (LC (a) and LA (b)) and at the corresponding reference sites (RC(c) and RA (d)). Sampling periods: 11.08.–18.08.2009 (LC) and 27.08.–02.09.2009 (LA). Note the different scales. Asterisks mark the 3-day samples.

Atmospheric Environment 45 (2011) 935-941

Landfill Emissions Impacts Atmospheric Concentrations of Neutral and Ionizable PFAS in China

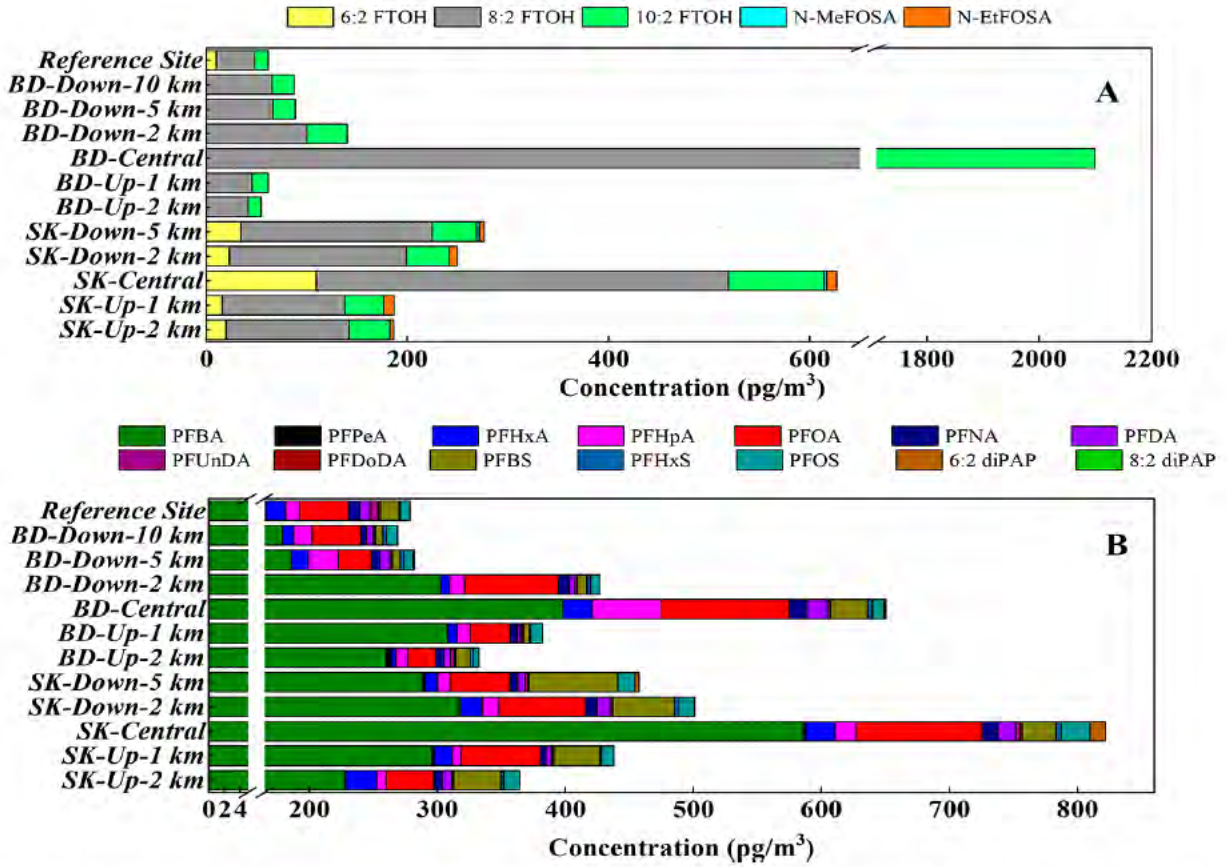
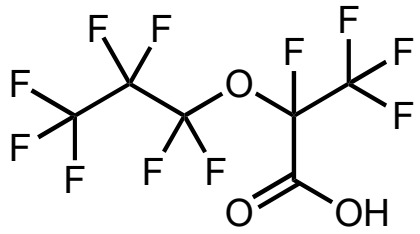
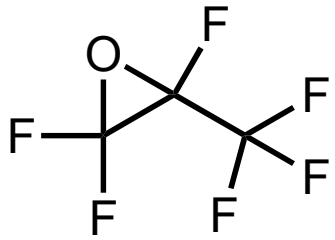


Figure 1. Concentrations and spatial distributions of neutral and ionizable PFASs in the air around two landfills (SK and BD) and the suburban reference site (JN) in Tianjin, China. SK-Central and BD-Central represents the central area of the two landfills, SK-Up and BD-Up represent upwind sites, SK-Down and BD-Down represent downwind sites. (A) neutral PFASs; (B) ionizable PFASs ($C \geq 4$).

Tian et al. Environ. Sci. Technol. 2018, 52, 1301−1310

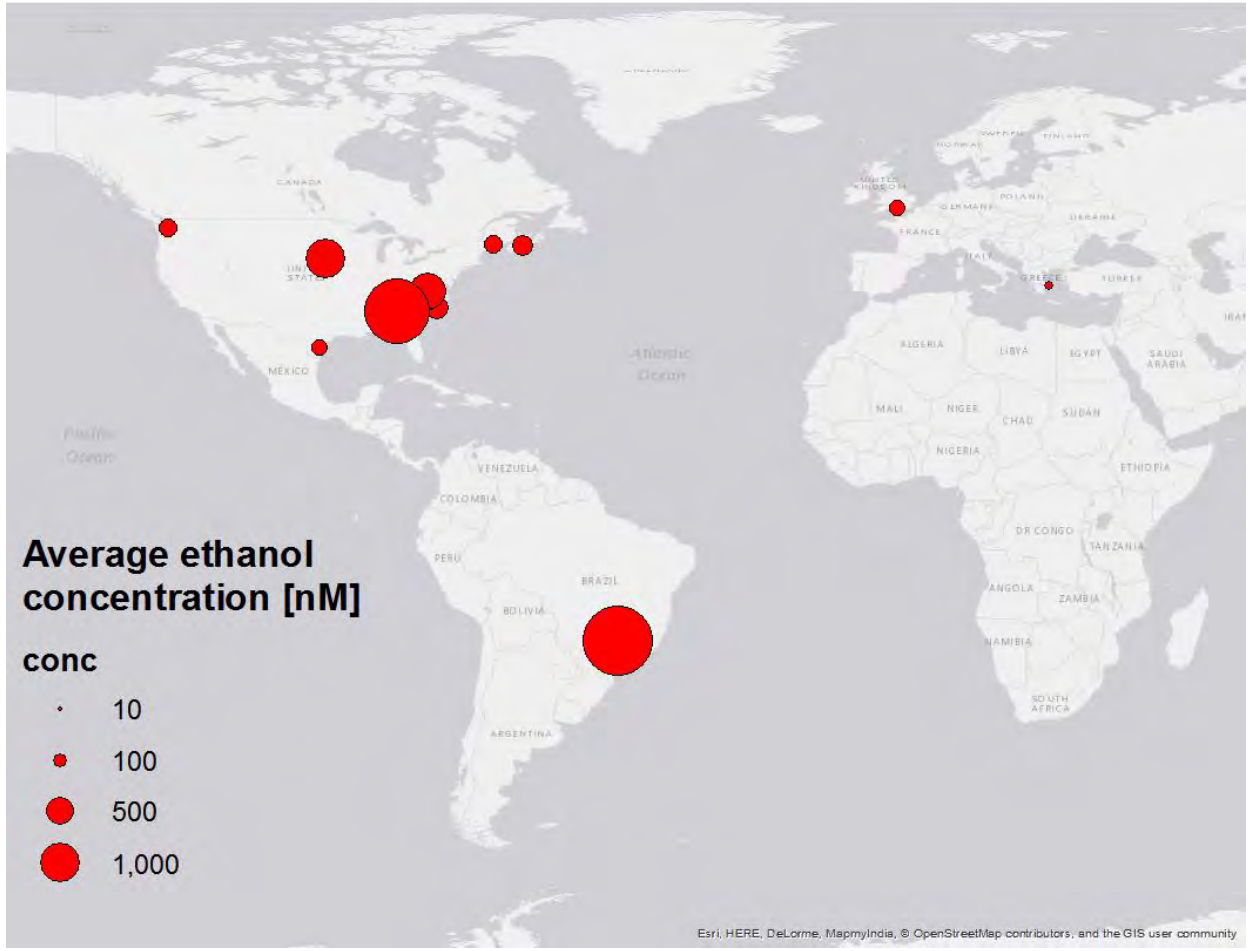


2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
CAS # 13252-13-6



Hexafluoropropylene oxide (HFPO)
CAS # 428-59-1

Example Research: Removal of Atmospheric Ethanol by Wet Deposition



- Wet deposition is estimated to remove 6%-16% of ethanol emitted to the atmosphere annually. The large range indicates uncertainty in global models with limited wet deposition concentrations
- Global wet deposition flux of ethanol from storms with terrestrial derived back trajectory 1.99 Tg/year and marine derived back trajectory 0.44 Tg/year
  Total flux: 2.43 Tg/year

Figure 2: Global wet deposition site collections and the volume weighted ethanol concentrations at each site represented by proportional red circles.

Felix et al., 2018