Air and Atmospheric Deposition of PFAS in North Carolina

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

Motivation:

- **Measurements:** air and atmospheric 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 near industrial and military sources (e.g., military bases, household products), fugitive emissions from waste streams (contaminated soil, wastewater, landfills).
- **Atmospheric PFAS Transformations**: Limited knowledge regarding PFAS atmospheric abiotic reactions and drinking water impacts
- **Elevated concentrations:** indoors, near industrial sources, urban areas.

Fate and effects are poorly understood: depend on composition, gas-particle partitioning, atmospheric chemistry, water solubility.
Atmospheric PFAS research is quite limited

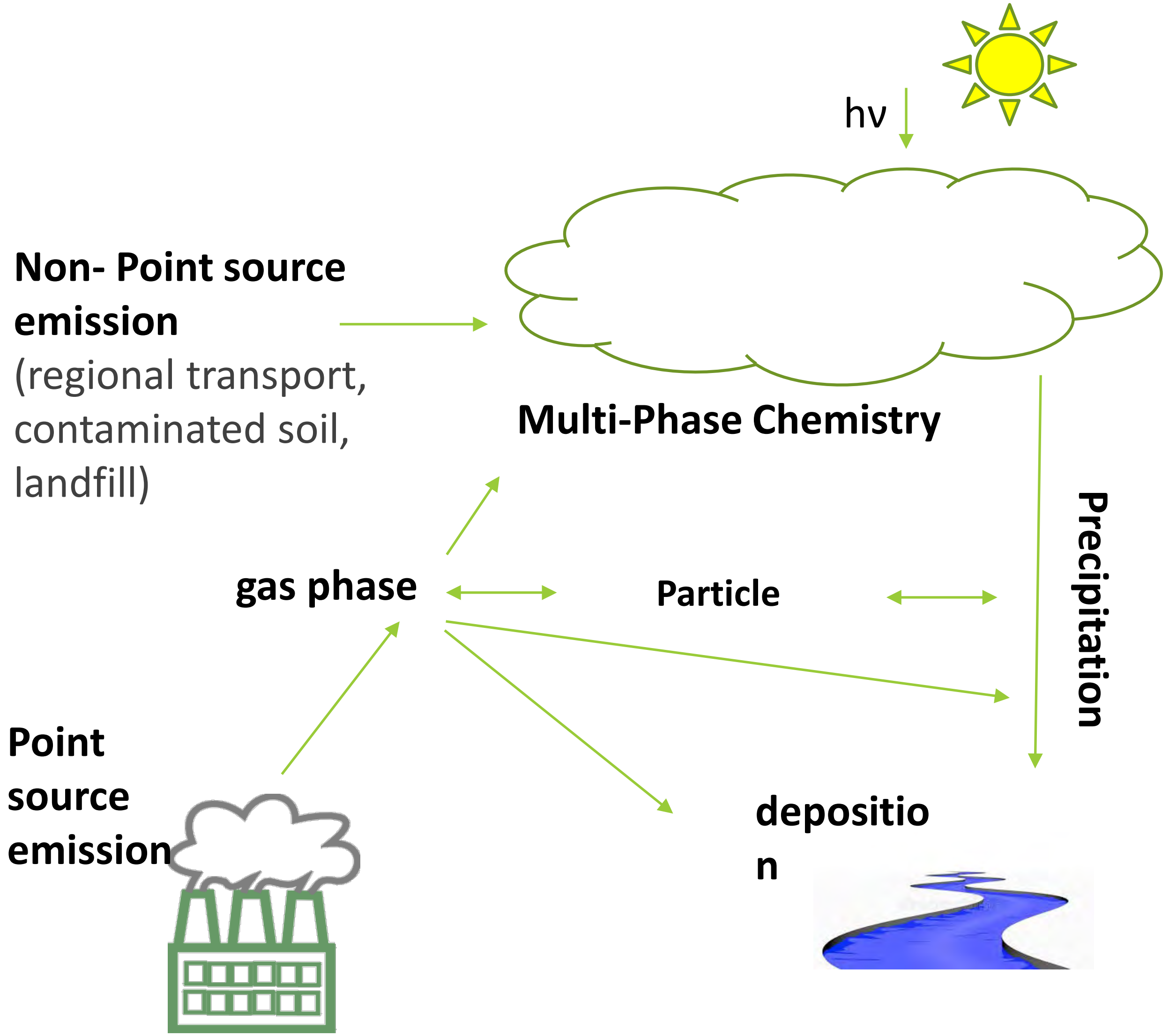
Research Questions

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

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

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

Does gas-to-particle conversion (multiphase atmospheric chemistry) alter the fate of small polar gaseous PFAS species, as we have seen for similar non-fluorinated organics?



Planned Approach

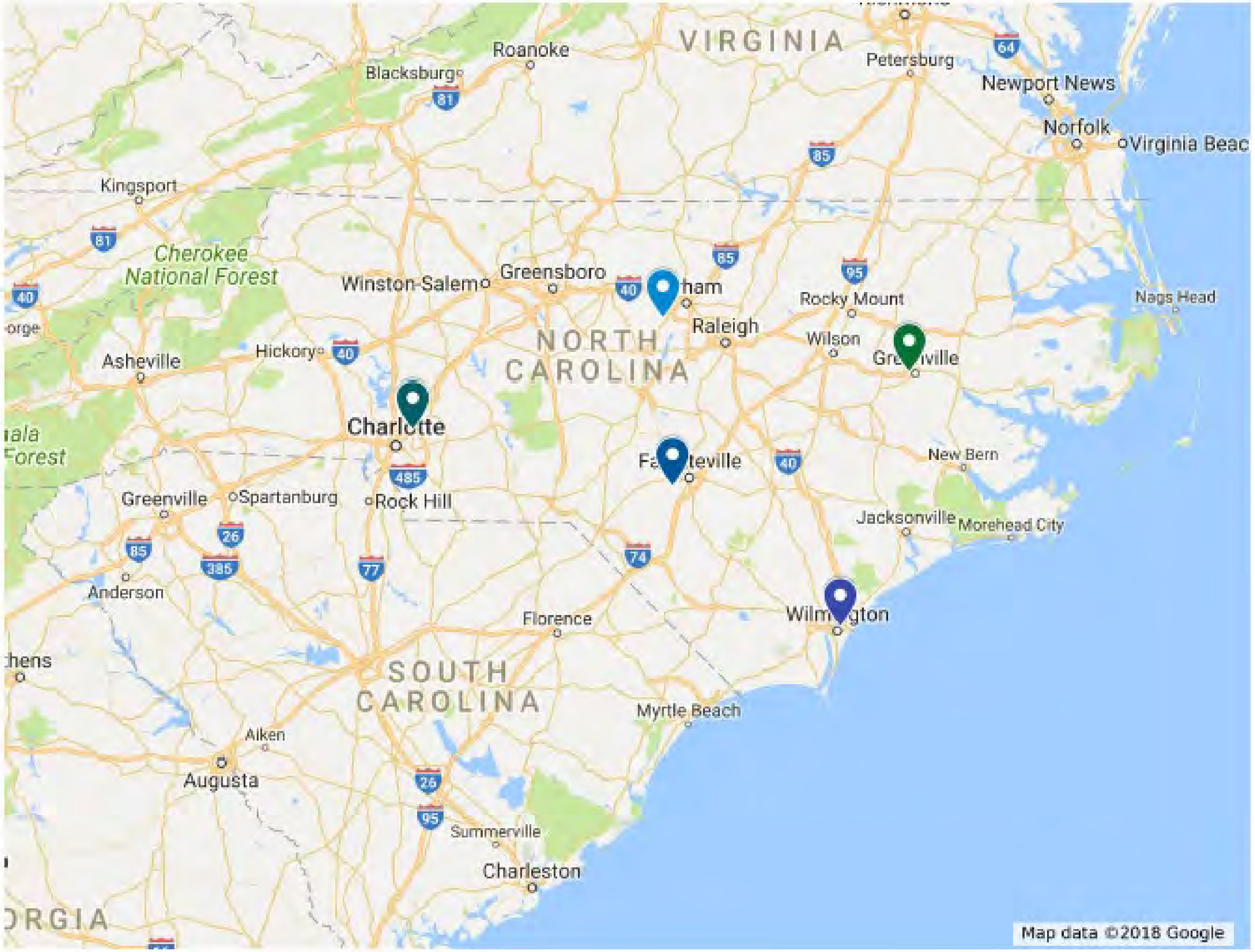
1. ***Event-based wet/dry deposition sampling**: in Wilmington and selected other*
2. ***Integrated gas and particle sampling:** every 6^{th} day for one year. Wilmington, Chapel Hill, Charlotte, Greenville, Fayetteville*
3. ***Intensive real-time measurement of highly polar gases:** 1-2 weeks. Wilmington (exact mass chemical ionization mass spectrometry)*
4. ***Chemical analysis:** UPLC-ESI-HR-QTOF-MS. OASIS WAX cartridges*
5. ***Calculate:** deposition to Cape Fear watershed*
6. ***Examine:** influence of backtrajectory, geography, season, sources*
7. ***Laboratory experiments:** of multiphase chemistry of hexafluoropropylene oxide (HFPO)*

PFAST Atmospheric network sites

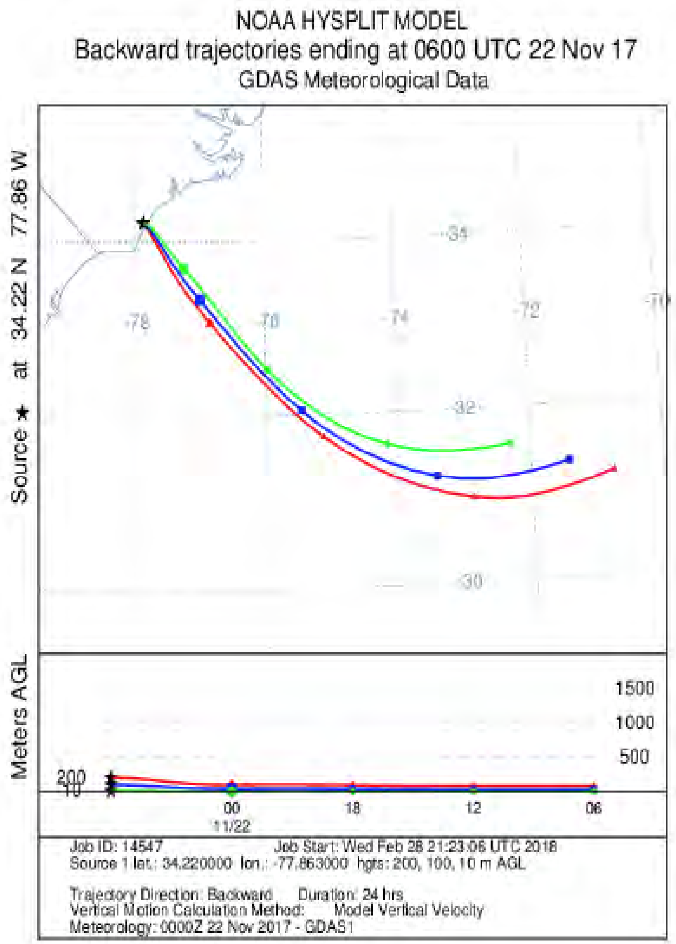
State-wide view

- 1 UNC-Chapel Hill
- 2 NCDEQ Fayetteville
- 3 UNC-Wilmington
- 4 UNC-Charlotte
- 5 ECU-Greenville

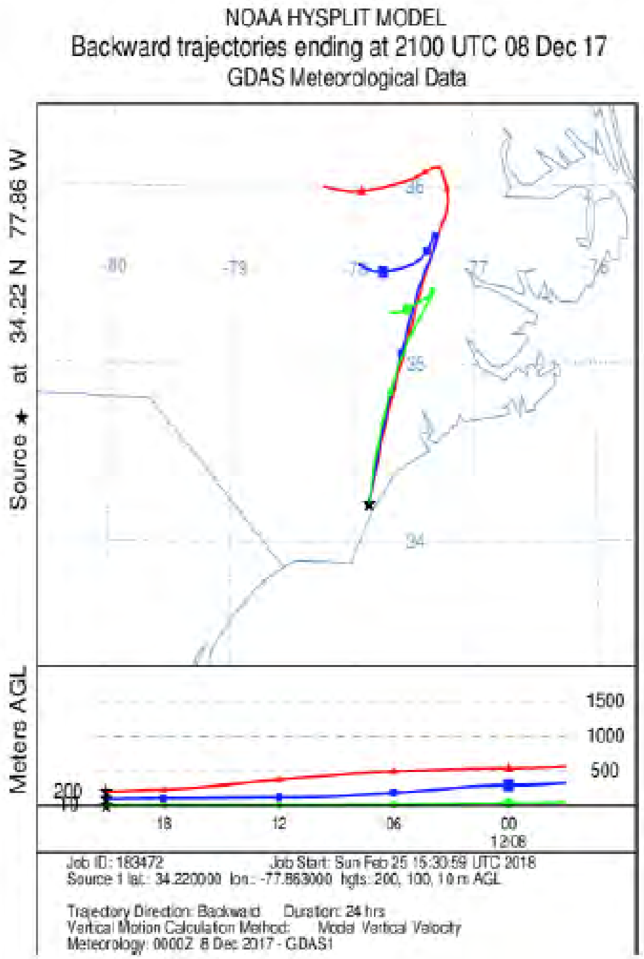
Locations for integrated 24h gas+PM sampling every 6th day. Event based collection of wet/dry deposition at Wilmington, non-automated collection at all other sites.



Air Mass Back Trajectory and GenX rainwater Concentration

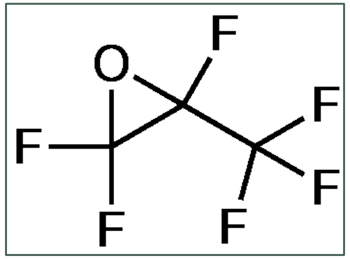


E 1775
11/21-22/17
GenX <3 ppt (ng/L)
0.26 inches at UNCW
pH not analyzed

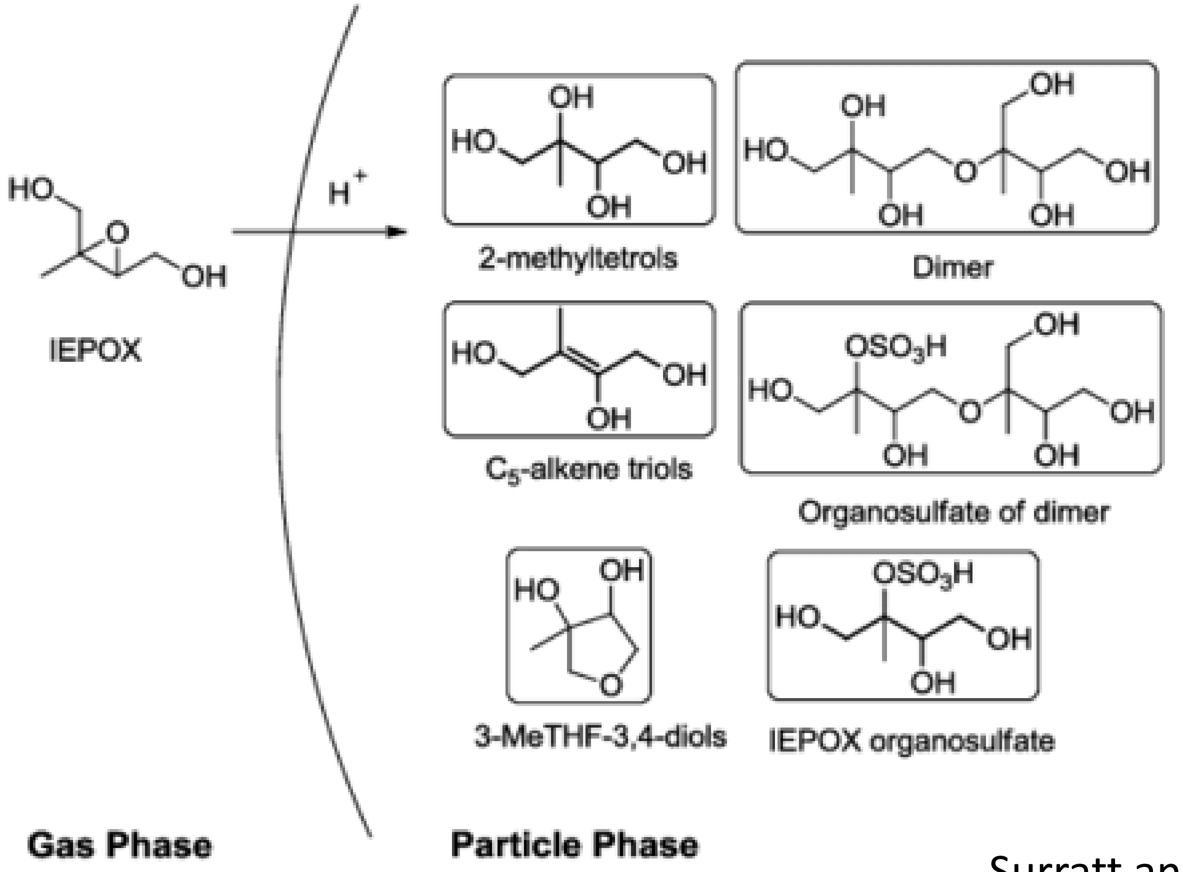


E 1781
12/8-9/17
GenX >500 ppt (ng/L)
1.8 inches at UNCW
pH4.68

Atmospheric multiphase chemistry of epoxides can alter the gas-particle partitioning, fate and effects.

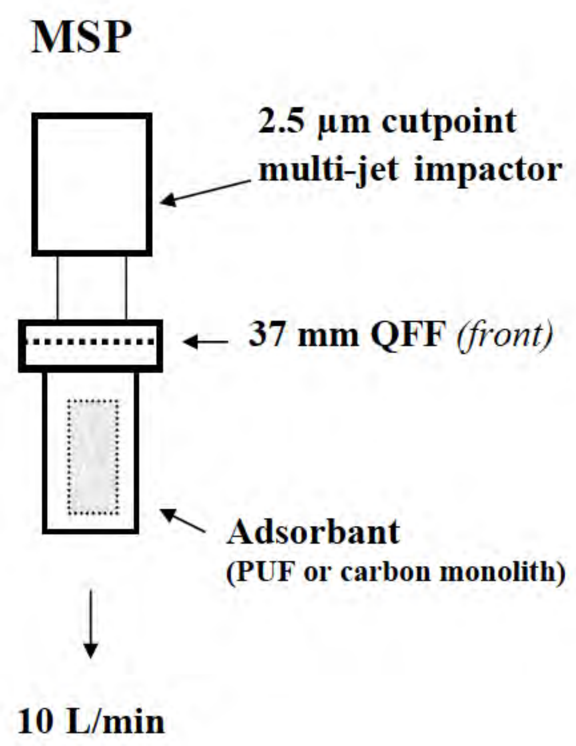


Hexafluoropropylene oxide
HFPO (C_3F_6O)

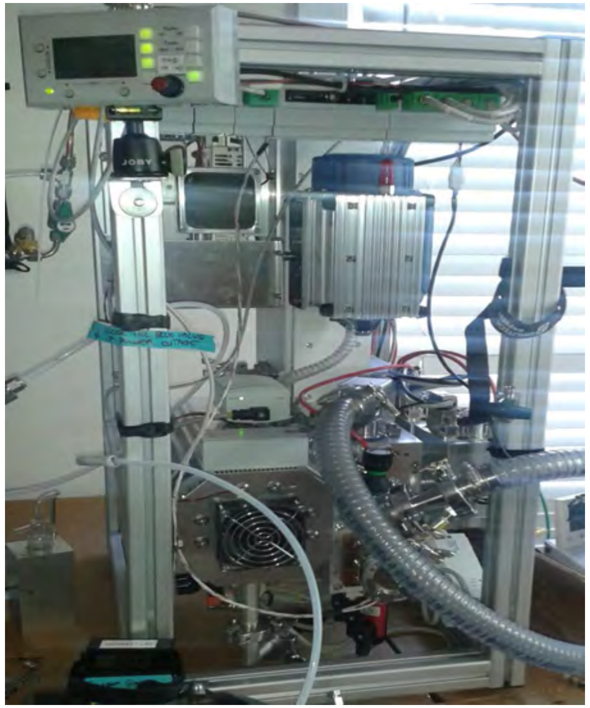


Surratt and colleagues

Questions?



Iodide CIMS



5 – 800 pg/m³

urban and rural European sites

Barber et al., *J. Environ. Mon.* 2007

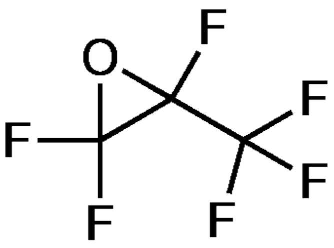
HILIC or RP UPLC-ESI-HR-QTOF-MS

Our DL: ~14 pg/m³

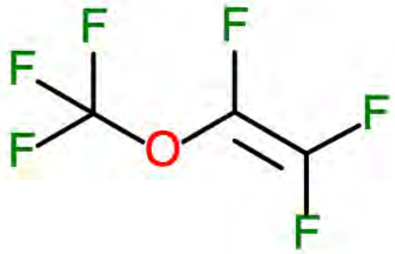
Real time (2 min)

Exact mass

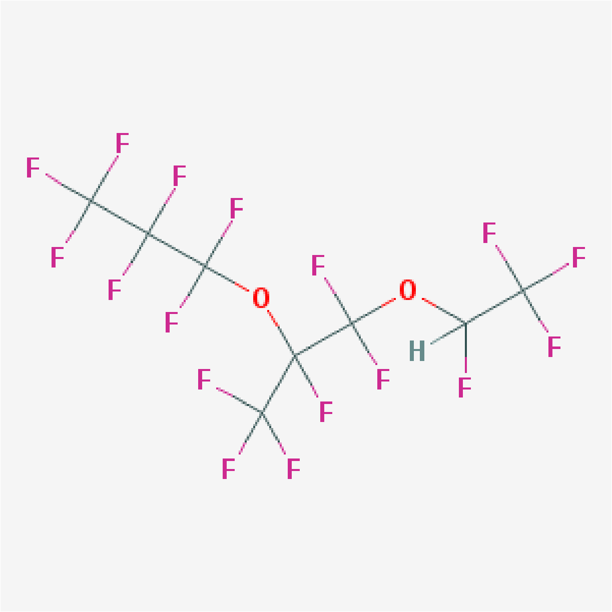
Small polar organic gases



Hexafluoropropylene oxide (HFPO)
C_3F_6O



Trifluoromethyl trifluorovinyl ether
C_3F_6O

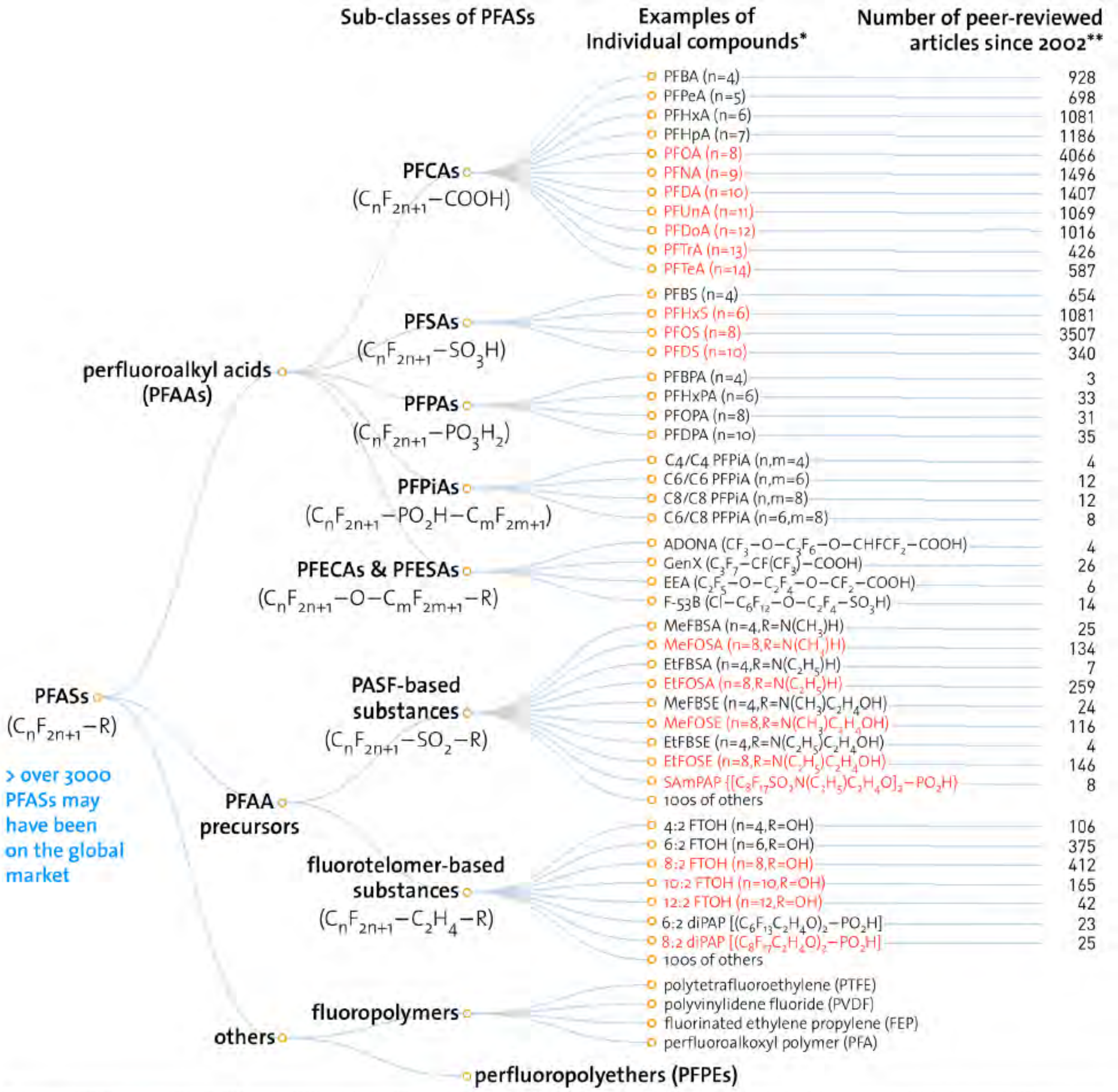


$C_8HF_{17}O_2$ (Fluoroether)

Chemours Fayetteville Works Facility Emissions of GenX

Chemours 2016 emissions estimates as originally reported to DAQ	Chemours revised 2016 emissions estimates as of October 2017	Latest calculations, including January through April 2018 stack test measurements
66.6 lb/yr	594 lb/yr	2758 lb/yr

Data from DAQ August 2018 update



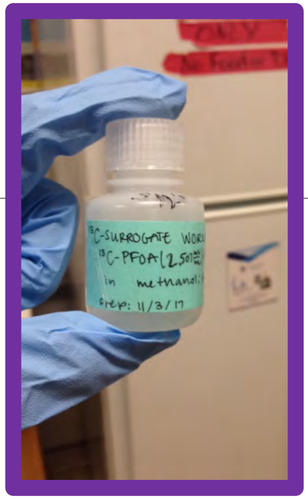
* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).
** The numbers of articles (related to all aspects of research)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

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?

Method Summary – Sample Processing

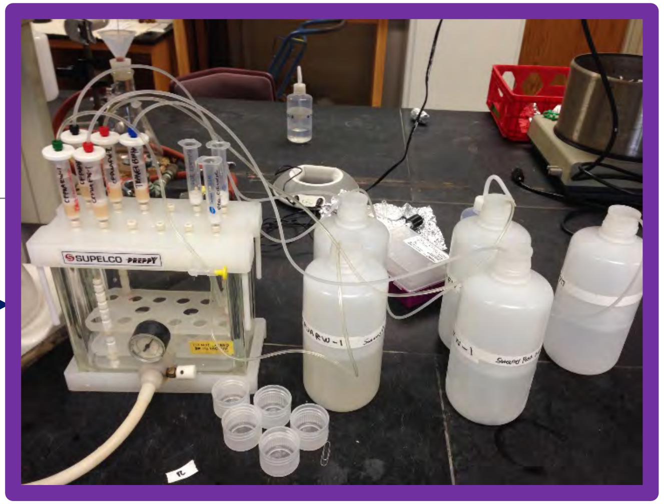
Collect water in 1 L HDPE bottles; Pour 500 ml of sample into graduated cylinders for volume measurement



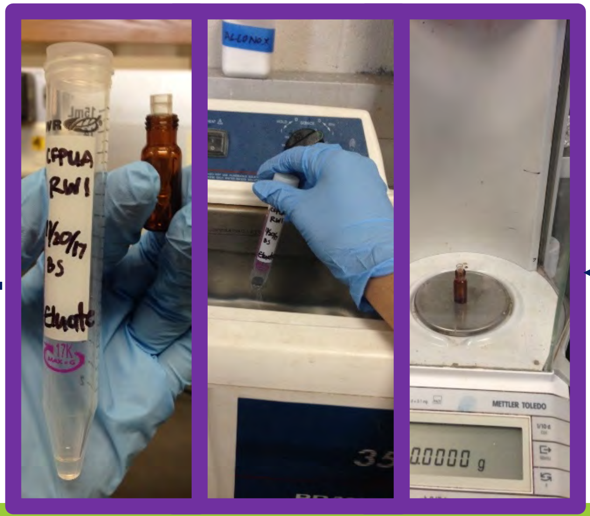
add 25 ul of surrogate to 500 mL of sample

Subsample 500 mL
Store 500 mL

Filter water samples with pre combusted GF/F glass fiber filter



Load onto SPE tube Waters Plus style WAX SPE bed



LC/MS-MS analysis

All samples Treated same way

- Trip Spike
- Blanks
- Unknowns
- Calibration

Wet deposition of poly- and perfluorinated compounds in Northern Germany

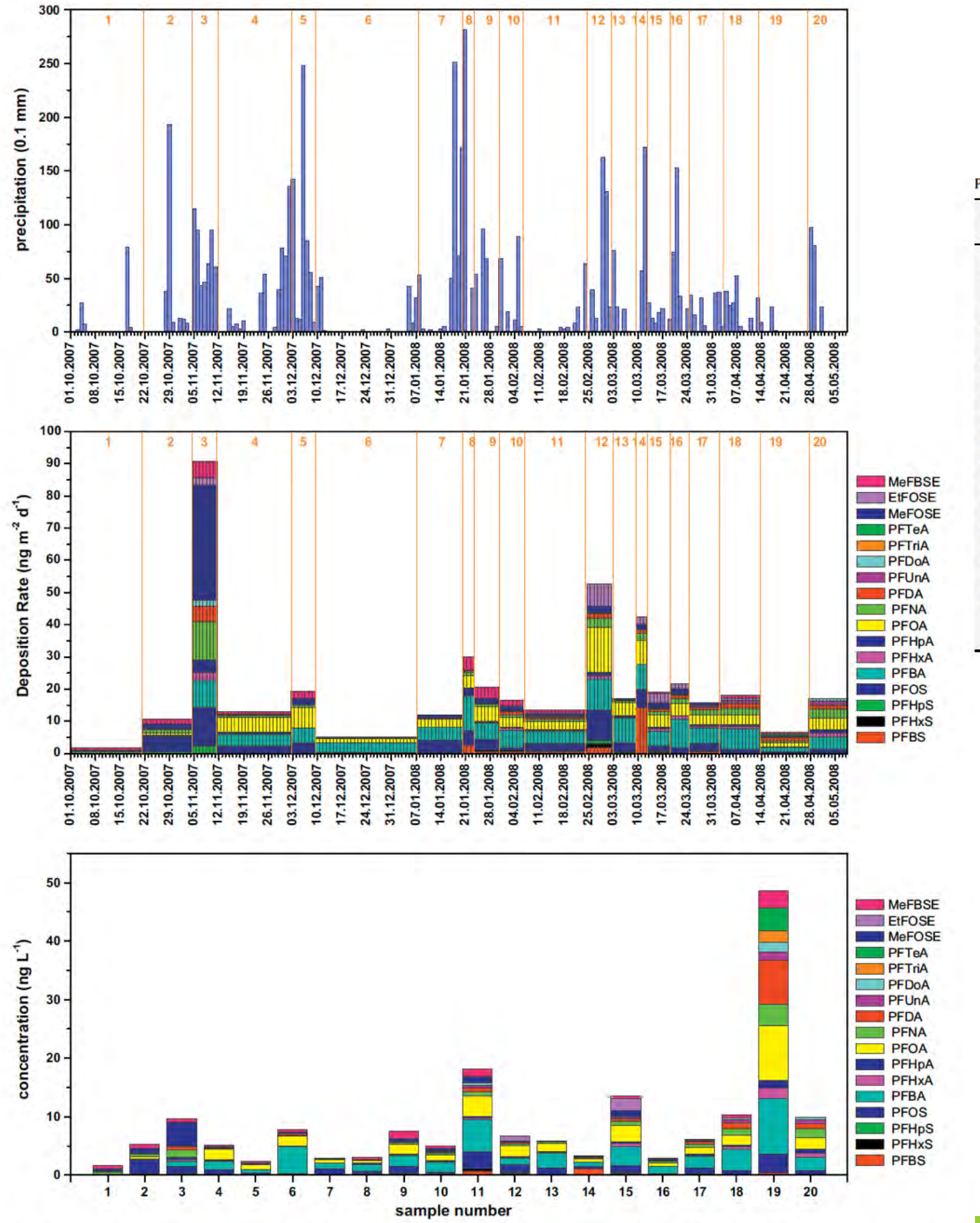


Fig. 1. Daily total precipitation (0.1 mm = 0.1 L m^{-2}), wet deposition rates (ng m^{-2} d^{-1}), and rain water concentrations (ng L^{-1}) of detected PFC. Note: PFOA concentration of samples BAR-R1 and BAR-R3 were below the corresponding blank. Daily total precipitation was obtained from the nearby 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
n	20	42	43	18	19	23	16	8
category	near urban	near urban	rural	rural	remote	remote	rural	near urban
PFBS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PFHxS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PFOS	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
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
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
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
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
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
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
PFDA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–1.1
PFUnDA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–1.2
PFDoDA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.07–3.3
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
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
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
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
Reference	(Scott et al., 2006)							

site	Toronto, ON, Canada	Dalian, China	Winnipeg, MB, Canada	Albany, NY, USA	Tsukuba City, Japan	Kawaguchi City, Japan	Scandinavia	Barsbüttel, Germany
n	7	2	3	11	4	4	5	20
category	urban	urban	urban	urban	urban	urban	rural/ urban	semi-rural
PFBS	n.a.	0.6–2.1	n.a.	n.a.	<0.1	<0.1	<LOQ	n.d.–1.1
PFHxS	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.	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	0.1–2.1	n.a.	n.a.	n.a.	1–2.2	0.8–2	n.a.	n.d.–9.4
PFPA	0.2–1.1	n.a.	n.a.	n.a.	0.2–1.1	0.6–0.8	n.a.	n.d.
PFHxA	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	<0.1–1.7	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	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	0.5–9.7	n.a.	n.d.	<0.1–3.5	1.7–4.2	1–2.4	0.7–1.4	0.1–3.7
PFDA	<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	<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	<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	<0.07–5.6	n.a.	1 ± 0.08	n.a.	1.1–1.9	1–1.9	n.a.	n.d.
10:2 FTCA	<0.07–0.6	n.a.	0.3 ± 0.04	n.a.	n.a.	n.a.	n.a.	n.d.
8:2 FTUCA	<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	<0.07–0.7	n.a.	0.12 ± 0.01	n.a.	<0.1	<0.1	n.a.	n.d.
Reference		(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)

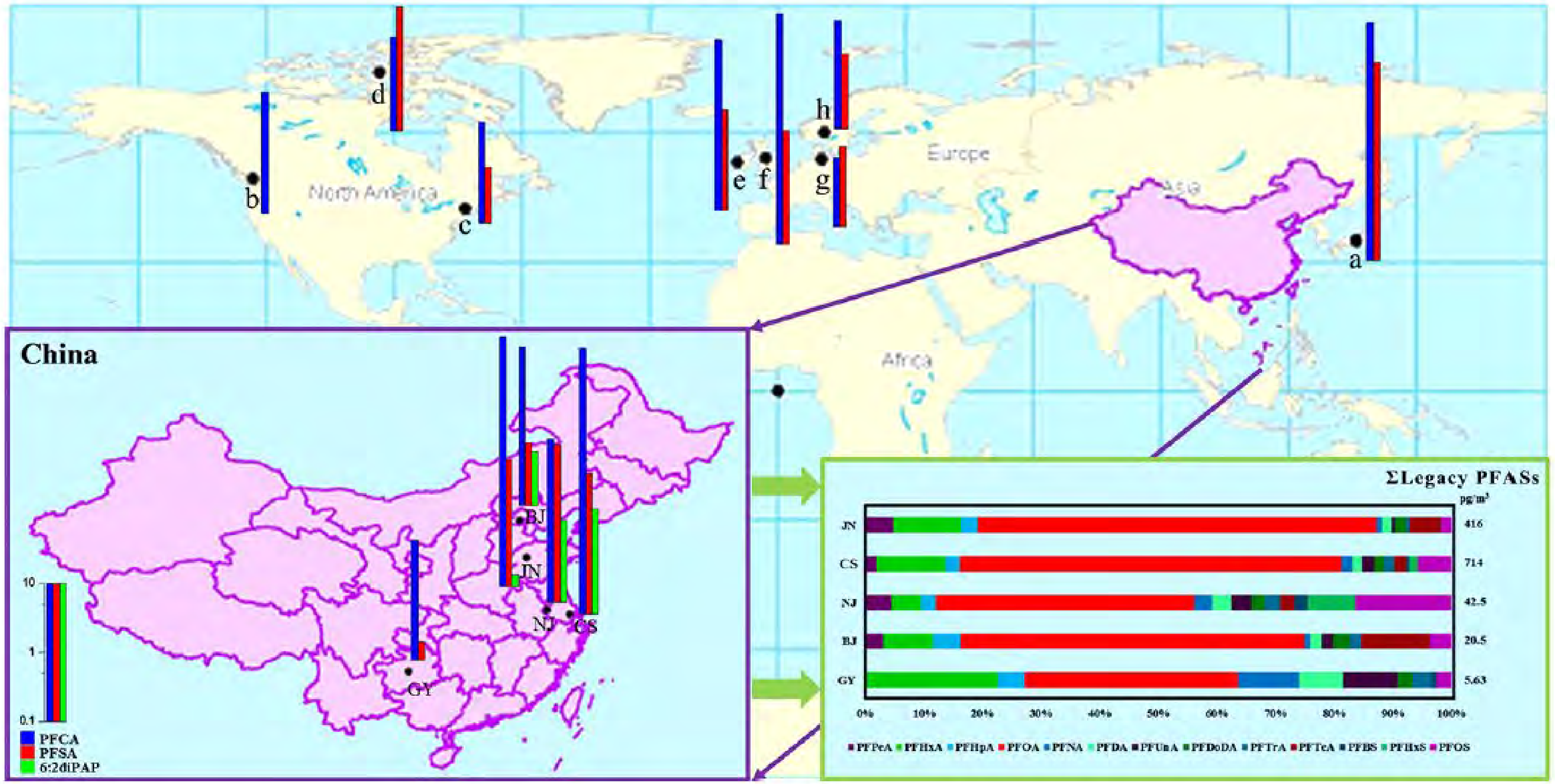


Figure 3. Distribution of PFCAs, PFSAs, and 6:2 diPAP in outdoor APM (data for China were obtained from this study, and those for other countries were obtained from previous studies; a: Japan,[76] b: Canada,[29] c: U.S.,[77] d: Arctic,[78] e: UK,[42] f: Ireland,[42] g: Germany,[79] h: Norway[42]) and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

PFAS in House Hold Dust

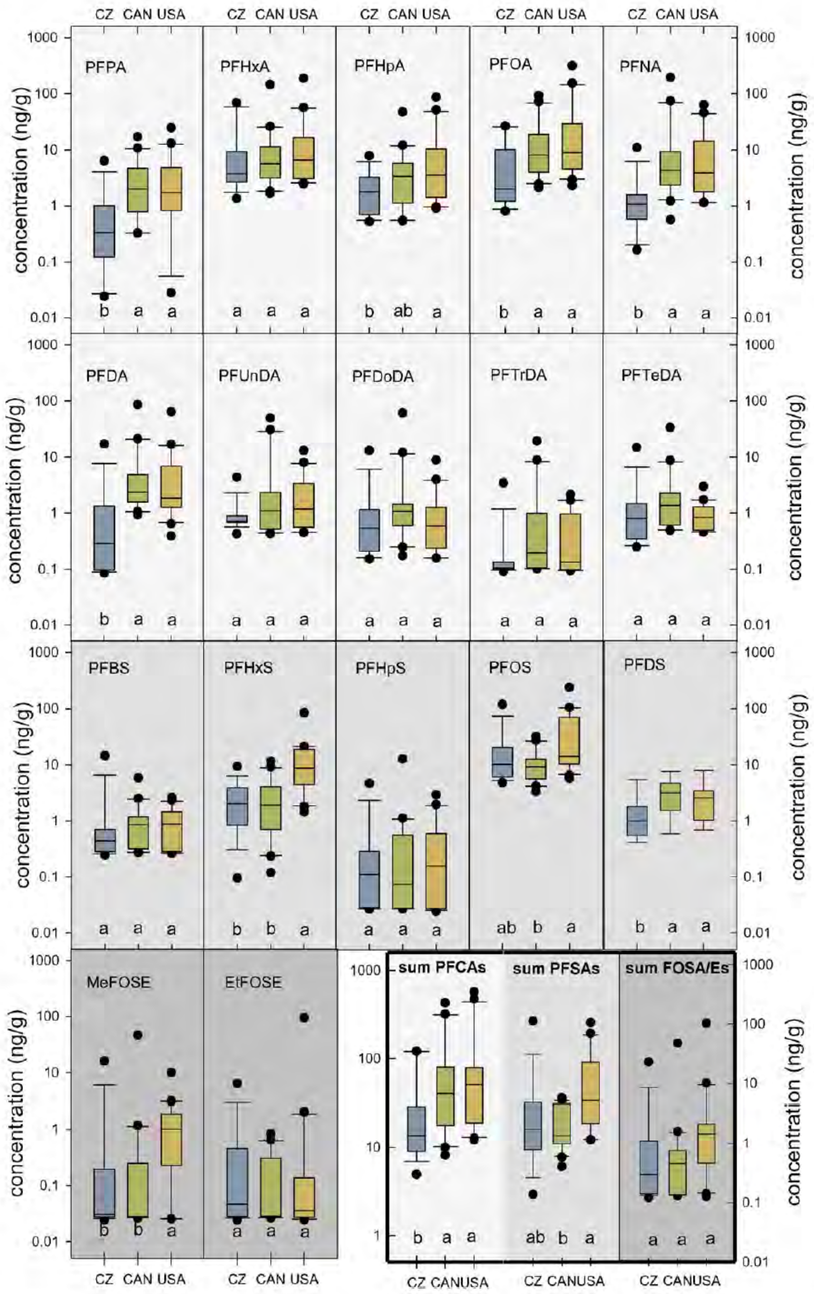


Fig. 1. Box and whisker plots of concentration (ng/g) showing the distribution of PFASs in dust samples from Czech Republic, Canada and USA. The lower and upper ends of the box are the 25th and 75th percentiles of data. The horizontal line within the box is the median value. The whiskers define the 5th 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.

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).

Kim and Kannan Environ. Sci. Technol. 2007, 41, 8328–8334

Landfill Atmospheric Emissions

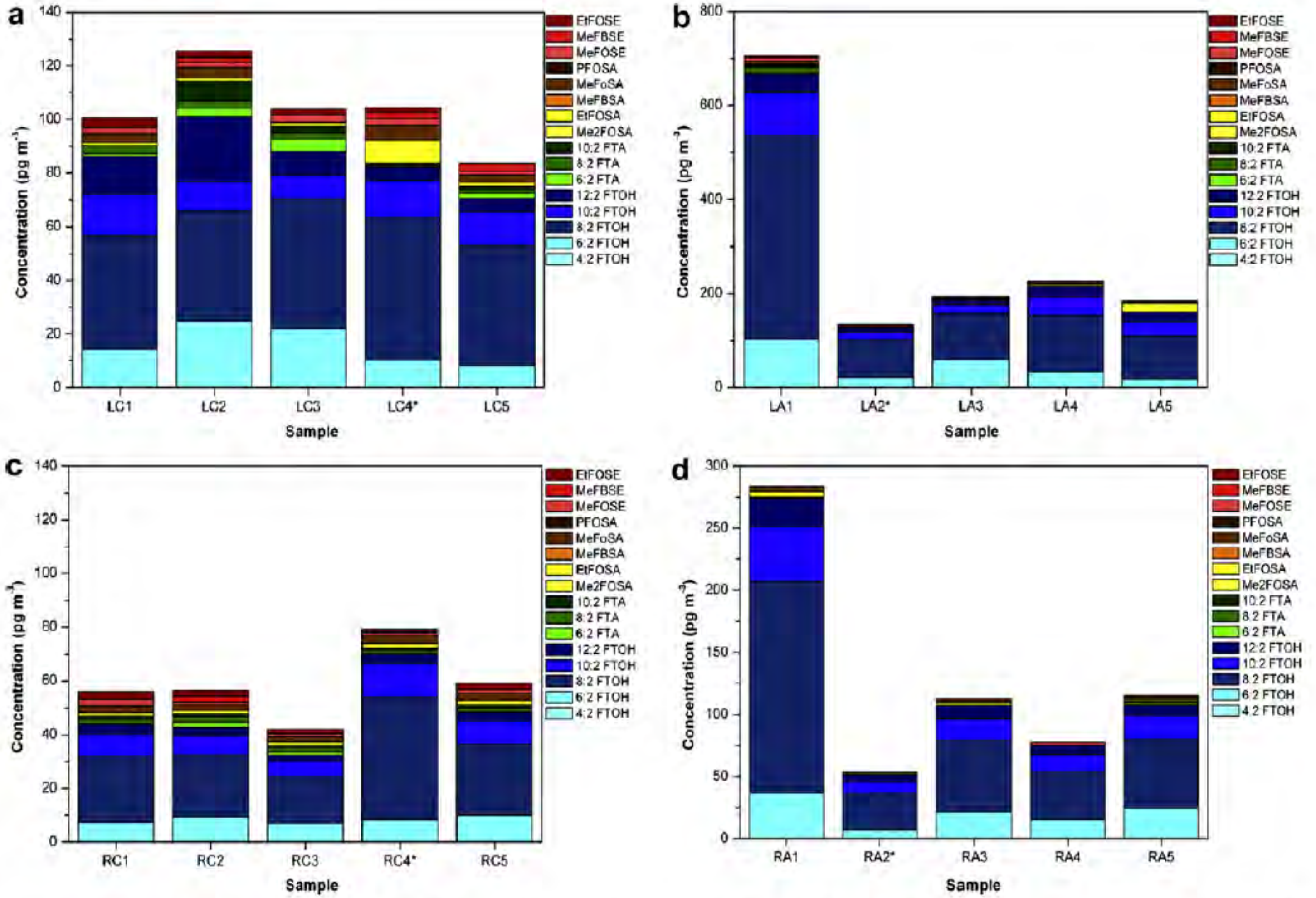


Fig. 1. Concentrations (pg m^{-3}) of semi-volatile and volatile PFCs in gas-phase samples taken at landfills (LC (a) and LA (b)) and at the corresponding reference sites (RC(c) and RA (d)). Sampling periods: 11.08.–18.08.2009 (LC) and 27.08.–02.09.2009 (LA). Note the different scales. Asterisks mark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

Atmospheric Environment 45 (2011) 935-941

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

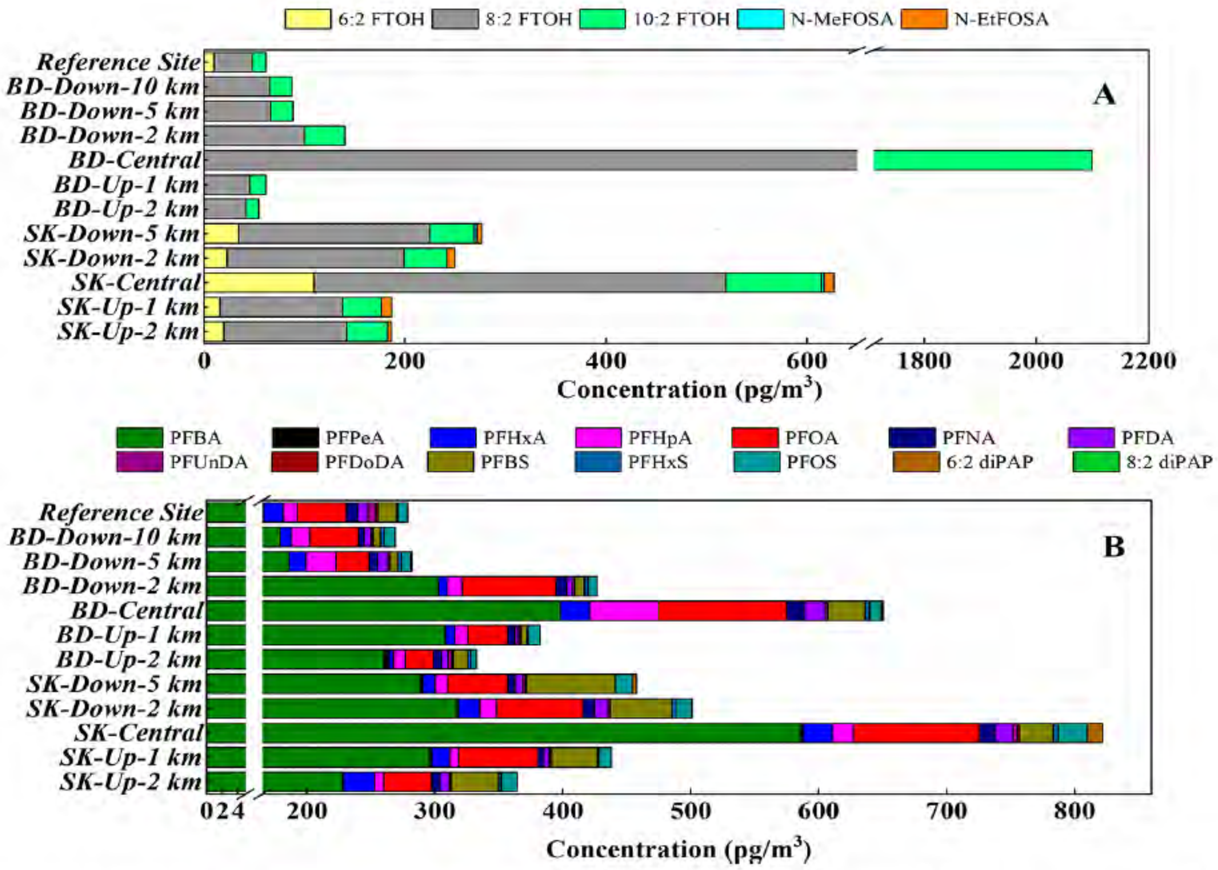


Figure 1. Concentrations and spatial distributions of neutral and ionizable PFASs in the air around two landfills (SK and BD) and the suburban reference site (JN) in Tianjin, China. SK-Central and BD-Central represents the central area of the two landfills, SK-Up and BD-Up represent upwind sites, SK-Down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

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