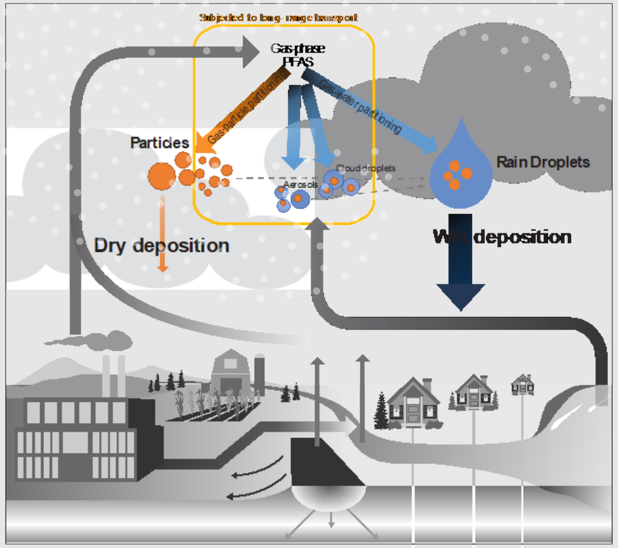
Atmospheric Deposition of PFAS Update
SSAB Meeting
December, 2023

Ralph Mead

Department of Earth and Ocean Sciences

UNCW

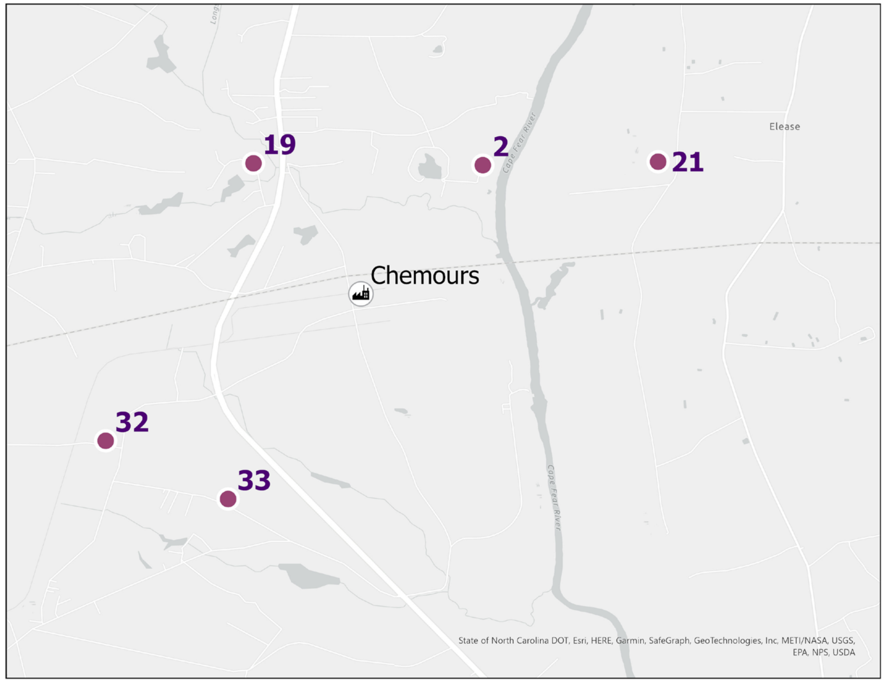
meadr@uncw.edu



Tasks Developed in Conjunction with DAQ

1. Data analysis – Review and analyze the DAQ near-field atmospheric deposition data set (2018 – present) for all PFAS analytes. Examine whether any trends exist such as seasonal trends, relational trends between compounds or groups of PFAS. Explore reasons for any such trends existing.
2. Data analysis – As part of the review and analysis in #1 above, determine whether any correlations exist between the near-field atmospheric deposition data and meteorological parameters collected in the area. Explore whether there are trends or correlations in the wet vs. dry deposition data and examine why these correlations exist.
3. Data analysis – Review and analyze whether any correlations exist between the atmospheric deposition data and groundwater and surface water results nearby.
4. Share results of ongoing forensic PFAS research with DEQ that is focused on the distribution and molecular traits of specific compounds in the environment.

Wet/Dry Deposition Stations and Collection



Sample Stations near field to Fayetteville Works Facility

- Dry deposition refers to the removal of particles by collision with terrestrial or hydrological surfaces by gravitational settling, impaction, interception, and/or diffusion

- Wet deposition refers to the scavenging of particles from the atmosphere by solid or liquid water and their subsequent removal by precipitation

N-Con Wet/Dry Deposition Collector at UNCW Campus, same as DAQ Collector. National Atmospheric Deposition Trends Network approved sampler

National Atmospheric Deposition Program

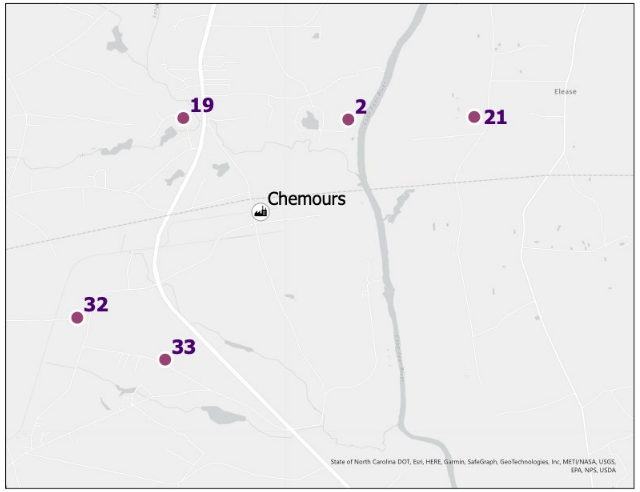
Monitoring precipitation chemistry since 1978

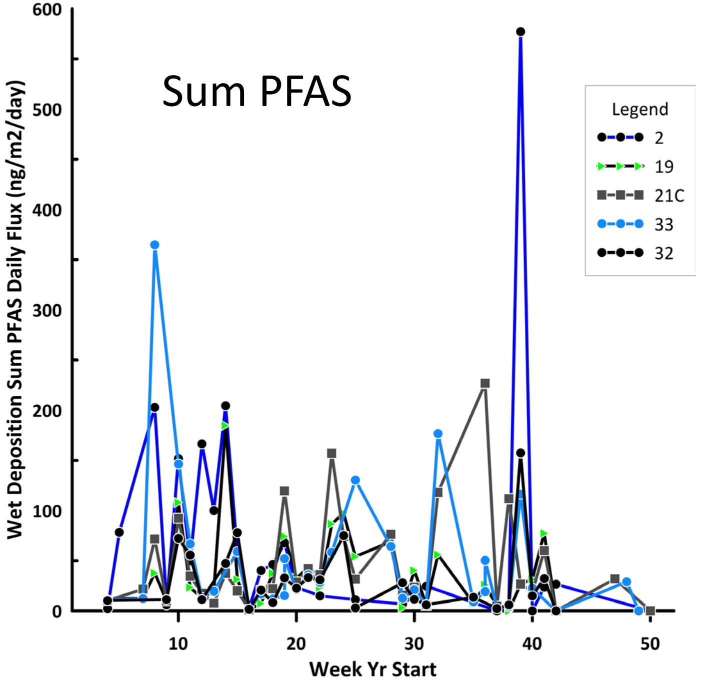
Analysis Workflow

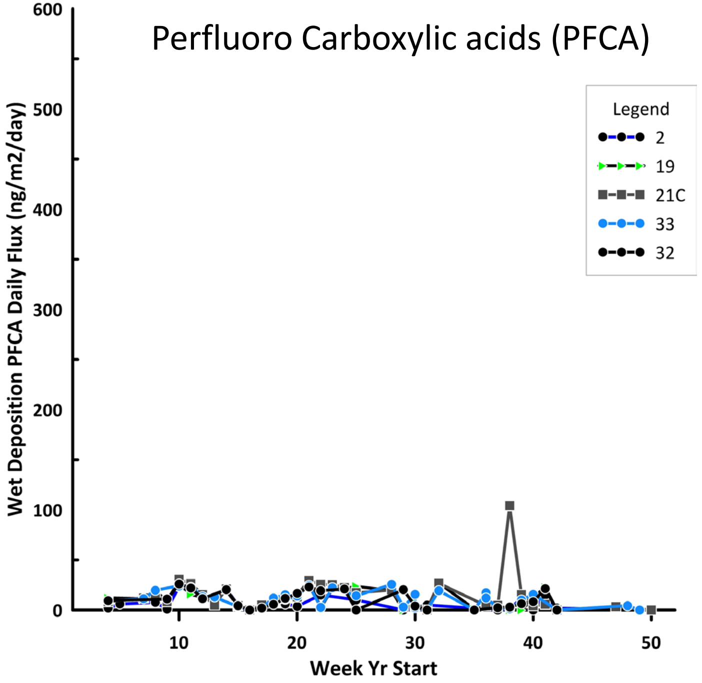
- 2022 Data set for this discussion
- Wet and dry deposition samples were collected for one week
- 0.5 L of wet deposition sent for targeted PFAS; 0.1 L archived
- For dry deposition, 0.6 L of PFAS free water was added to container and collected, 0.5 L saved for targeted analysis, 0.1 L archived

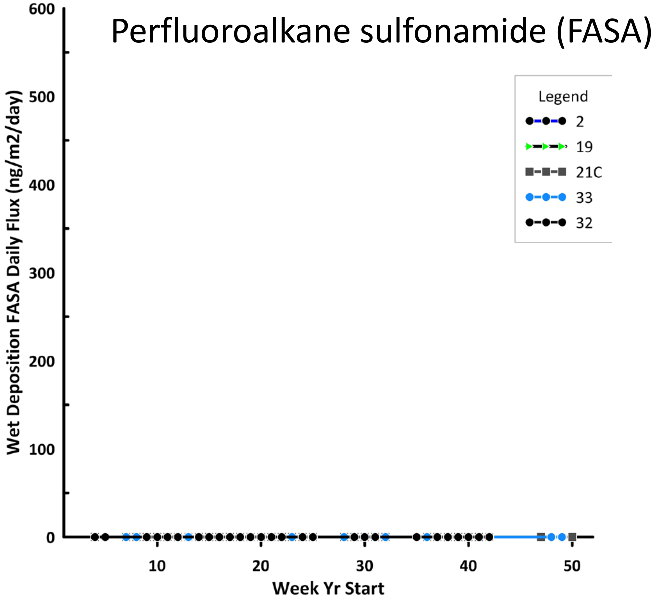
2022 **Wet** Deposition

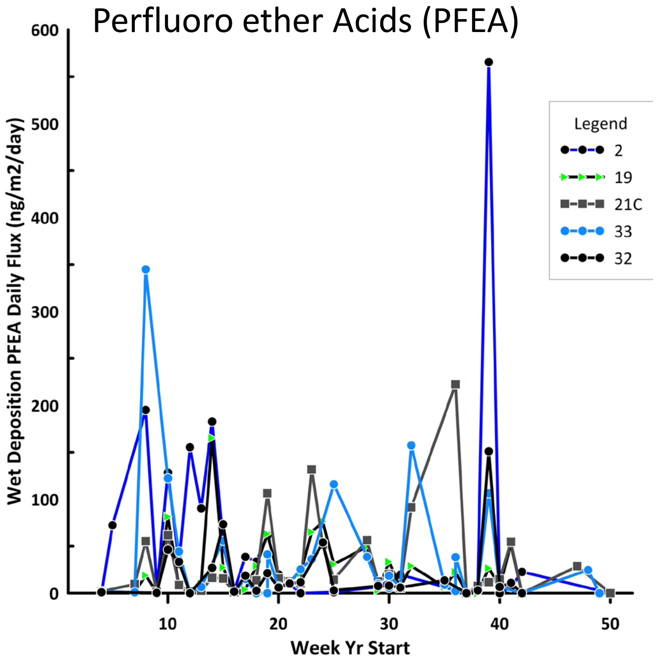
- 1 Week sample collection for each station

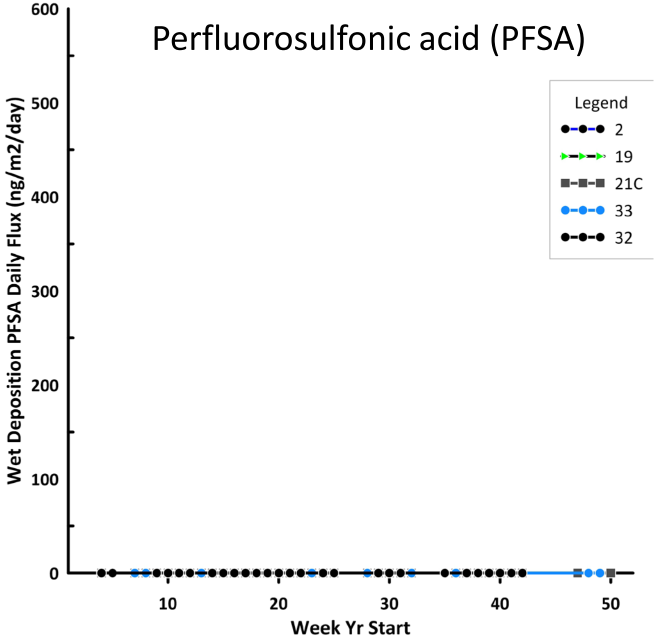






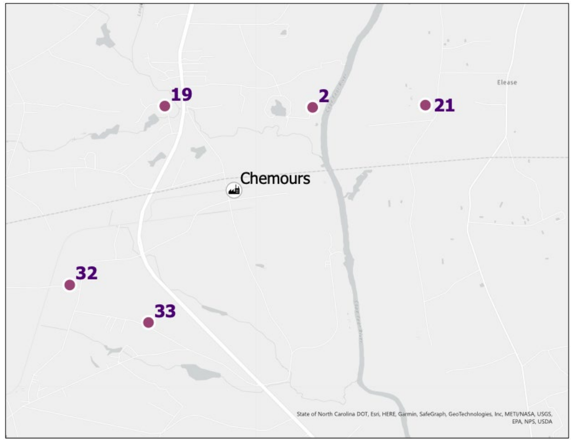


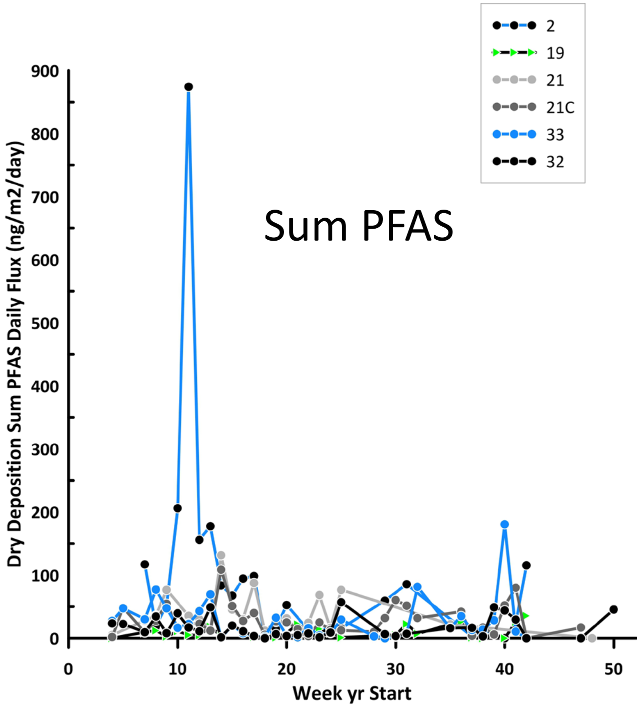


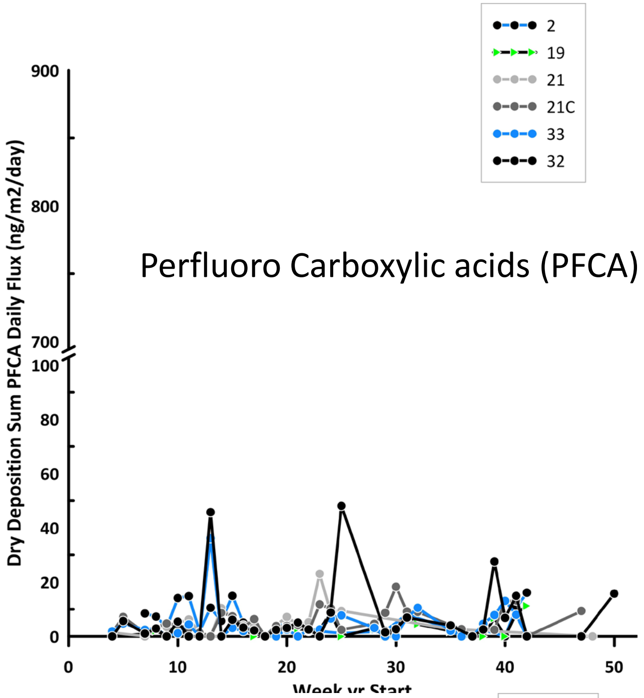


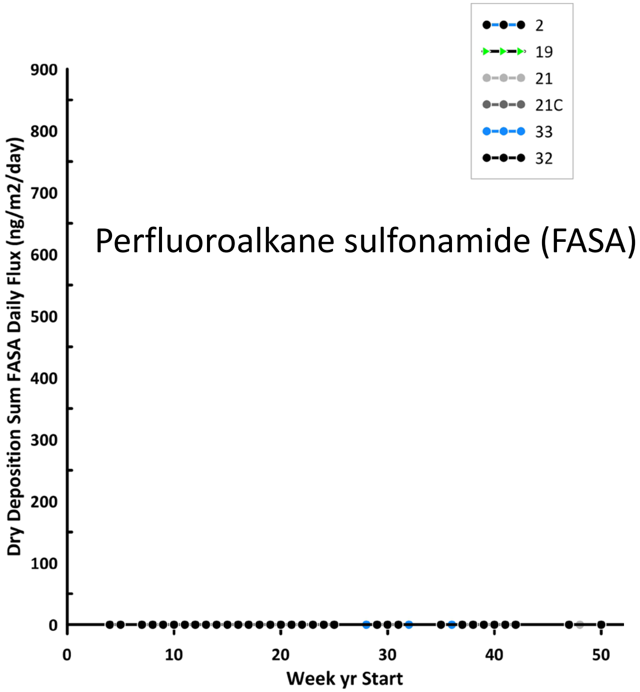
2022 **Dry** Deposition

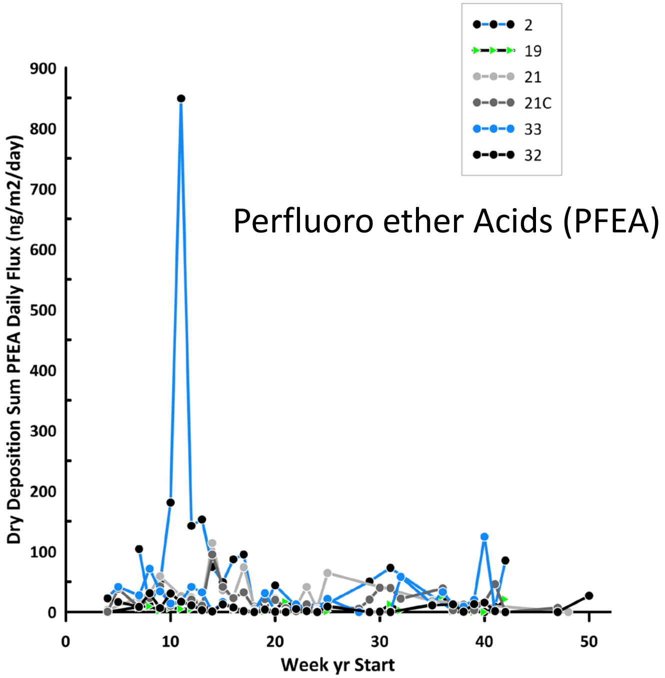
- 1 Week sample collection for each

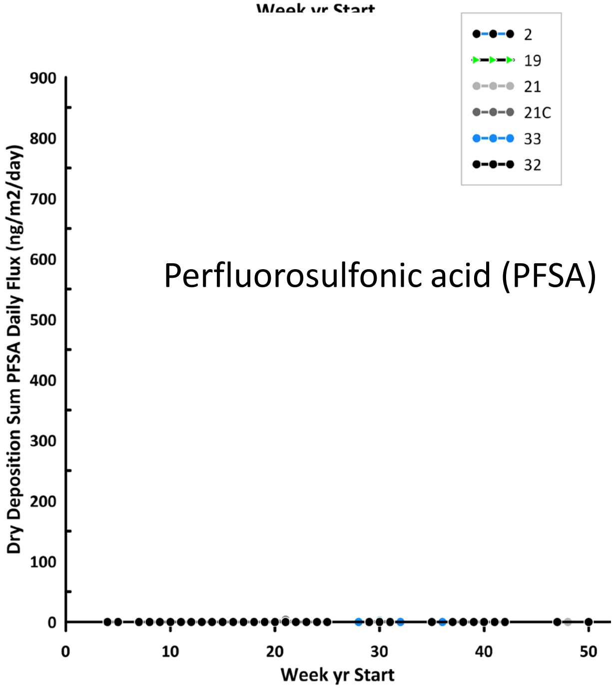






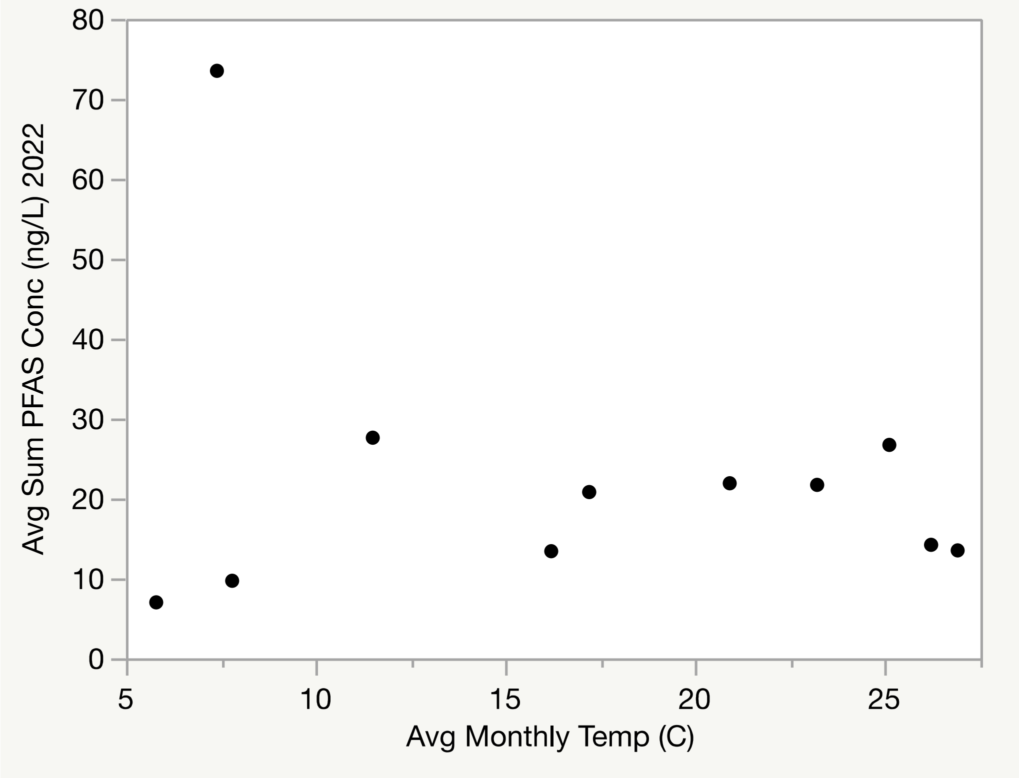






Is there a significant relationship between **wet** deposition PFAS and ambient air temperature?

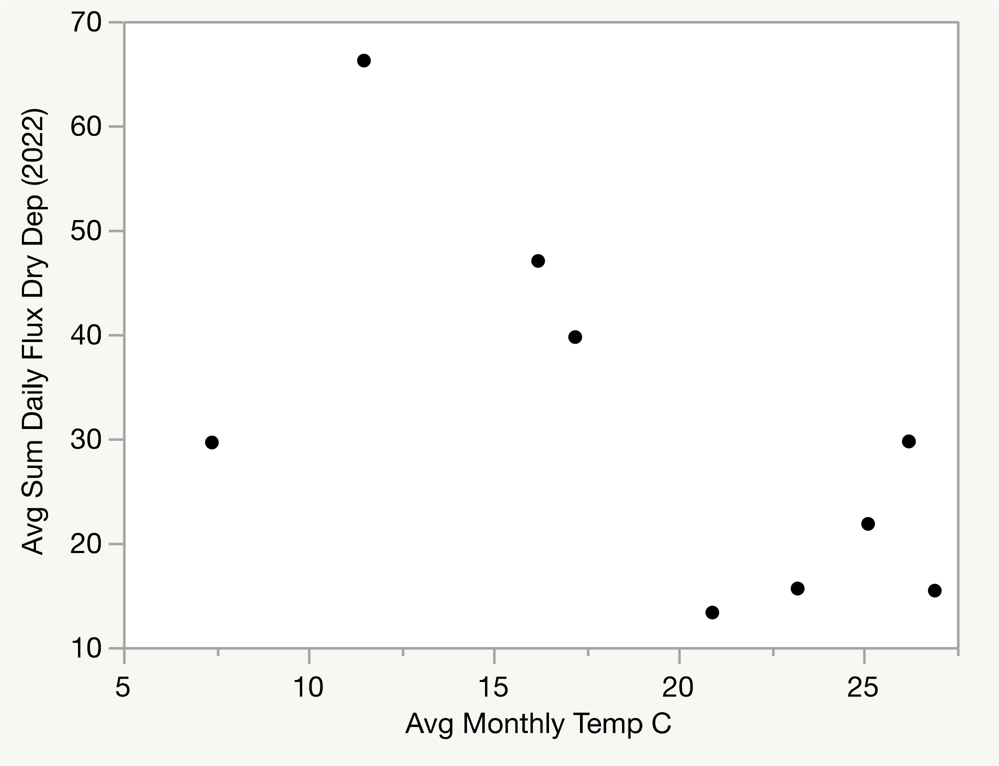
Answer is no…. but relationship has been found in colder climates



No significant relationship of average PFAS sum with average monthly temperature

	Value	Lower 95%	Upper 95%	Signif. Prob
Correlation	-0.24814	-0.73814	0.413246	0.4619
Covariance	-35.8363			
Count	11			

Pooled all stations and treated as one for each month
Months not included either not sampled or sample period was greater than one week



Is there a significant relationship between PFAS **dry** deposition flux and ambient air temperature?

Answer is no at $p < 0.05$

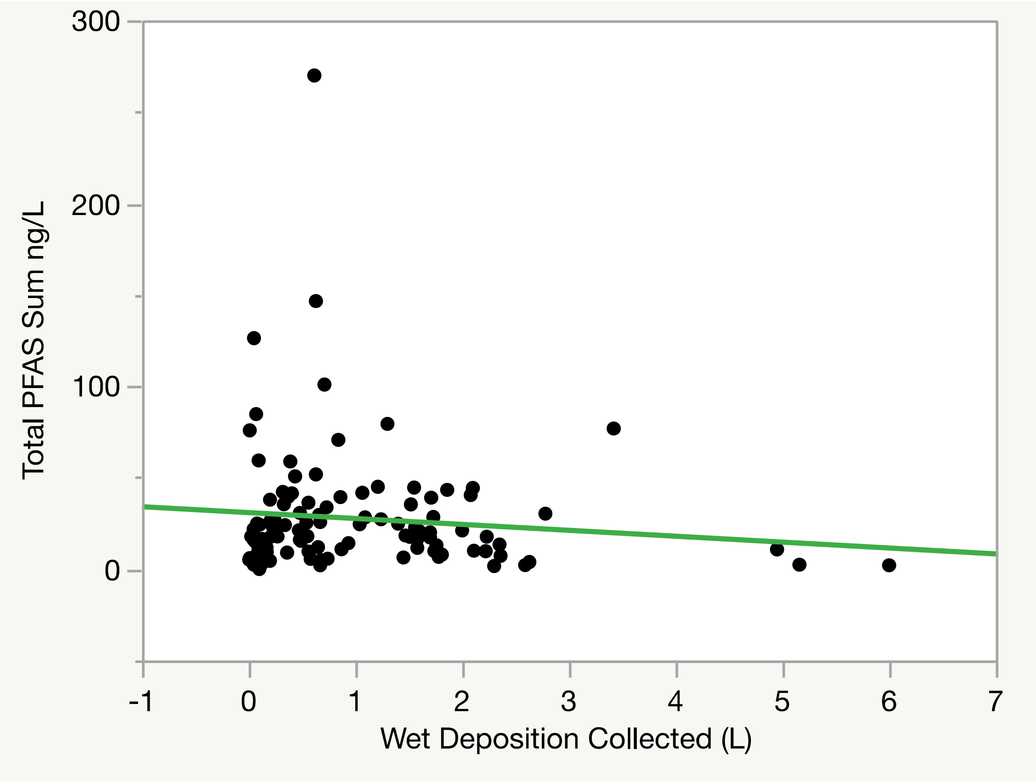
	Value	Lower 95%	Upper 95%	Signif. Prob
Correlation	-0.6219	-0.91012	0.071935	0.0737
Covariance	-74.3713			
Count	9			

Pooled all stations and treated as one for each month

Months not included either not sampled or sample period was greater than one week

2022 Wet Deposition (pooled all stations and treated as one)

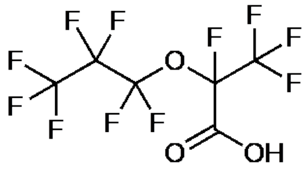
Is there a significant relationship between PFAS and wet deposition collected?



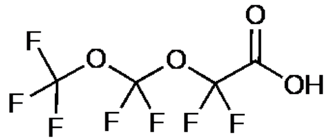
Answer is no…. But would like to include 2018-2023 data as well and rerun test

	Value	Lower 95%	Upper 95%	Signif. Prob
Correlation	-0.10341	-0.28432	0.084613	0.2801
Covariance	-3.78465			
Count	111			

2022 **Wet** Deposition: Correlations between PFAS Compounds (Pooled all station data)



HFPO-DA
13252-13-6



PFO2HxA 39492-88-1

Relationship: Closer to 1, stronger

Significance of relationship

Variable	by Variable	Kendall τ	Signif Prob
HFPO-DA	PFBA	0.3100	0.0115*
PFO2HxA	PFBA	0.3127	0.0194*
PFO2HxA	HFPO-DA	0.7436	<.0001*
PFPrA	PFBA	0.4354	<.0001*
PFPrA	HFPO-DA	0.3943	0.0025*
PFPrA	PFO2HxA	0.4391	<.0001*

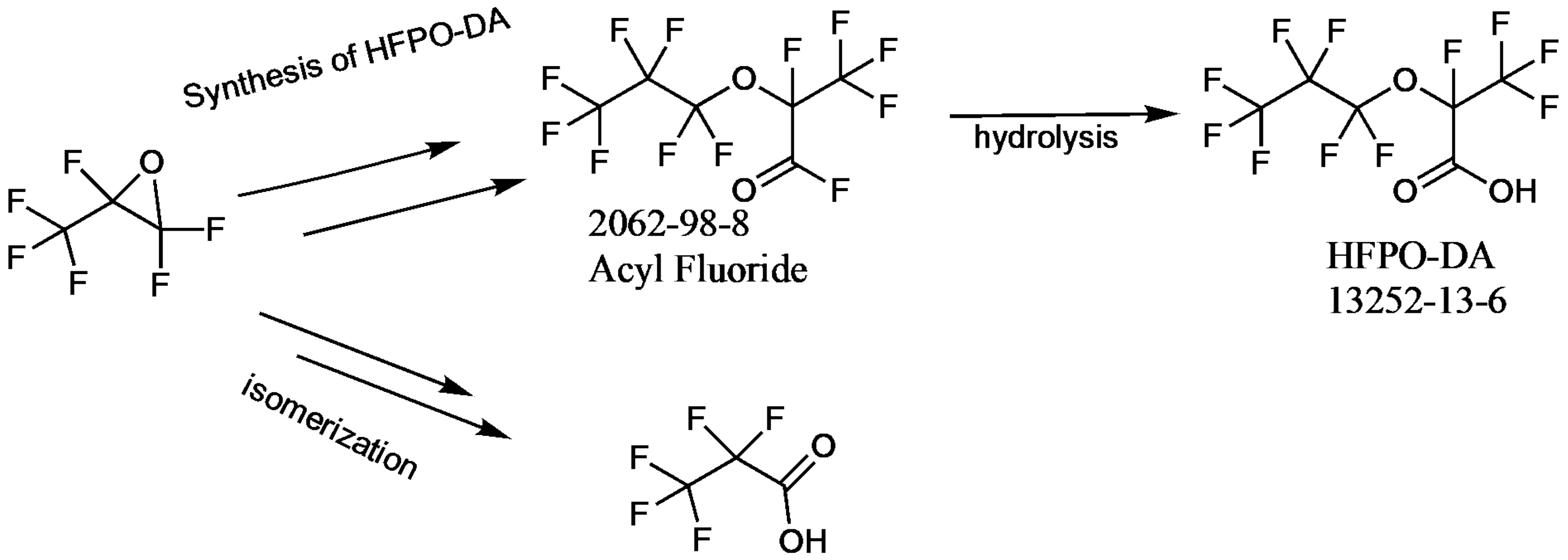
	>LOQ %
PFBA	56
HFPO-DA	57
PFO2HxA	50
PFPrA (PPF Acid)	77

- All pairwise correlations significant ($p < 0.05$ at 95% confidence)
- PFO2HxA and HFPO-DA is the strongest relationship
- Why does PFBA correlate with HFPO-DA and PFO2HxA?
  - *Is PFBA used in any Chemours process?*
- Why does PFPrA correlate with HFPO-DA and PFO2HxA?

Kendall's rank correlation was chosen to explore the ordinal relationship between two quantities where t of +/- 1 is indicative of correlation between two variables.

Why does PFPrA correlate with HFPO-DA?

One possible route is explained below



- *PFPrA is an isomerization product of HFPO through nucleophilic rxn (Angew. Chem. Int. Ed. (1985 (24) 161-179 ; J. Org. Chem.* 1966, 31, 7, 2312–2316; Journal of Fluorine Chemistry 2018, 211, 109-118*)*
- *In other words PFPrA is a degradation product from synthetic reactions that involve HFPO…*

Key Take Aways so Far and Running tasks

- PFESA dominate wet and dry deposition
- No correlation with temperature for either wet or dry deposition
- Continue working on 2022 dry dep data analysis
- Combine 2022/2023 data sets for statistical analysis
- Explore further PFAS compound relationships, what are the controlling mechanisms?
- Continue working through metrological data and correlate with PFAS

Comparison to Literature

PFAS concentrations and deposition in precipitation: An intensive 5-month study at National Atmospheric Deposition Program – National trends sites (NADP-NTN) across Wisconsin, USA

David Pfotenhauer [a,*], Emily Sellers [b], Mark Olson [b,1], Katie Praedel [a], Martin Shafer [b]

[a] Wisconsin Department of Natural Resources, Air Management Program, Madison, WI, USA
[b] University of Wisconsin-Madison, Wisconsin State Laboratory of Hygiene, Madison, WI, USA

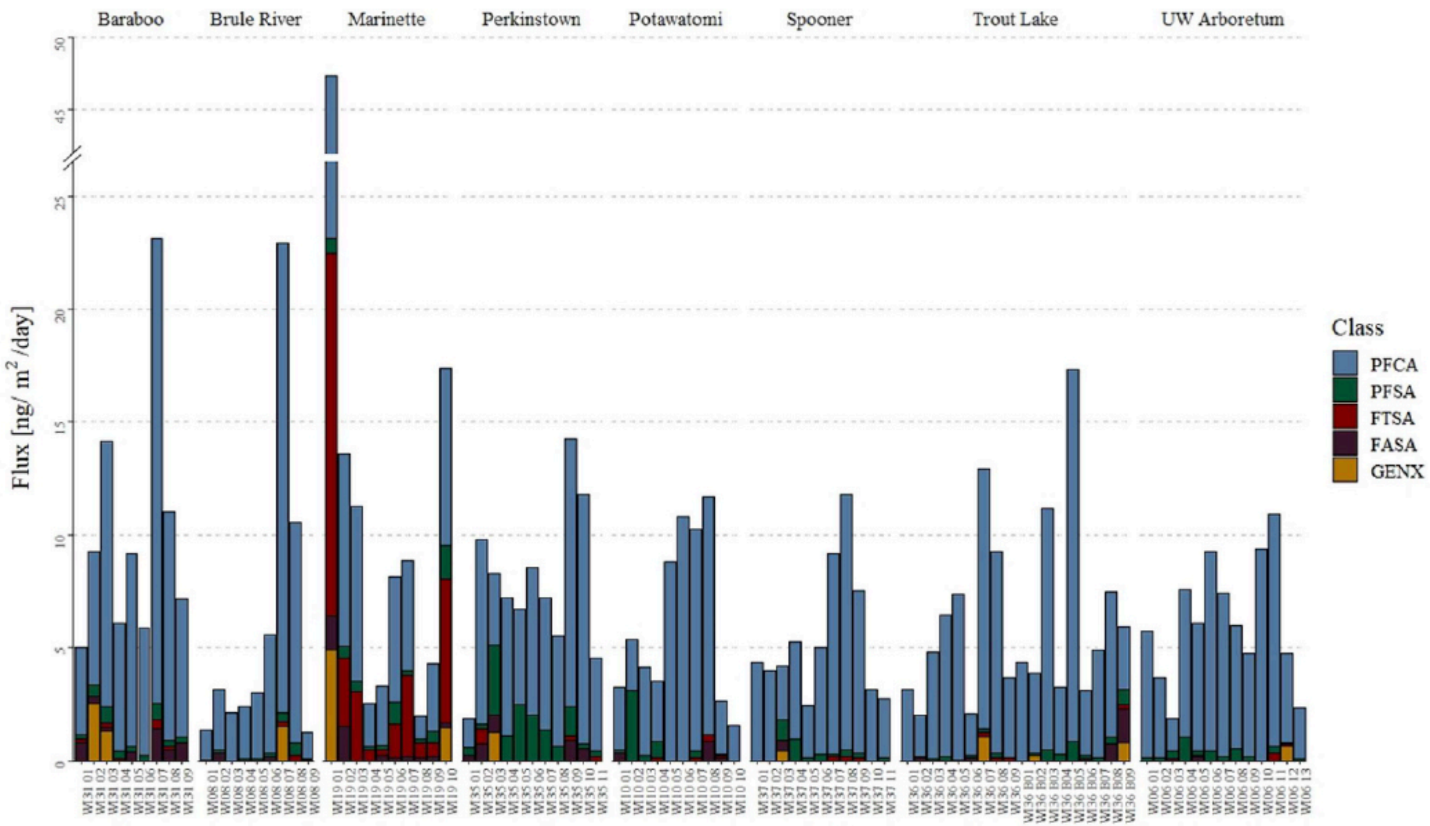


Fig. 4. Bar chart of PFAS daily flux estimates across all samples. Samples are grouped by site, and individual PFAS are aggregated based on chemical classification and represented by specific colors. Scale is broken to account for outlying flux value from sample WI19 01. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Comparisons of wet deposition flux of PFAS at Chongqing with other places worldwide. (NA: not calculated as targeted species are under method detection limit.)

region(time)	ΣPFAS	PFOA	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFUdA	References
This study (ng/m^2/season)											
2020 summer	1375.8	1007.3	54.9	81.9	61.2	54.8	48.8	32.6	13.6	1.2	–
2020 autumn	368.5	130.4	57.1	51.3	19.7	21.6	20.5	46.1	9.5	5.4	–
2020 winter	80.2	23.8	1.7	12.7	8.6	7.4	5.2	3.3	6.9	4×10^{-4}	–
2021 spring	211	104.6	1.1	0.03	12.3	36.9	16.3	7.5	2.2	0.2	–
Wet deposition flux (ng/m^2/day)											
This study	NA-175.5	NA-121.2	NA-41.5	7×10^{-8}-7.8	3×10^{-5}-12.6	NA -19.6	2×10^{-5}-11.6	6×10^{-6}-10.1	NA-2.9	NA-1.3	
Xiamen(2016)	872	170	240	NA	NA	170	130	120	42	–	Chen et al. (2019)
Shenzhen(2016)	1162.7	690	83	94	130	12	110	34	9.7	–	
Hefei(2016)	595	48	280	87	60	57	20	25	18	–	
Chengdu(2016)	270.7	48	59	41	–	50	29	34	9.7	–	
Nanjing(2016)	446	100	160	1.0 × 102	50	70	40	20	6	–	
Northern Germany (2007.10–2008.05)	2.0–91	0.8–13.9	0.1–11.9	1.3–10.7	–	0.3–2.7	0.2–2.4	0.1–11.9	0.1–2.8	–	Dreyer, et a., 2010
Canada (1998–2003)	540–5158	3–726	–	6–295	–	6–441	12–386	1–789	–	–	Scott et al. (2006)
Lake Ontario (2018.05)	6.8–36.8	2.0–5.0	3–5.5	2.2–5.2	0.1–4.1	0.4–3.9	0.3–4.2	1.0–4.2	NA-3.5	–	Gewurtz et al. (2019)

Source apportionment and wet deposition of atmospheric poly- and per-fluoroalkyl substances in a metropolitan city centre of southwest China

Fengwen Wang [a,*], Weiru Wang [a,b], Daiyin Zhao [a], Jiaxin Liu [c], Peili Lu [a], Neil L. Rose [d], Gan Zhang [b]

[a] State Key Laboratory of Coal Mine Disaster Dynamics and Control, Department of Environmental Science, Chongqing University, Chongqing, 400030, China
[b] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[c] Chongqing University Cancer Hospital, Chongqing University, Chongqing, 400030, China
[d] Environmental Change Research Centre, University College London, Gower Street, London, WC1E 6BT, United Kingdom

Atmospheric Environment 273 (2022) 118983

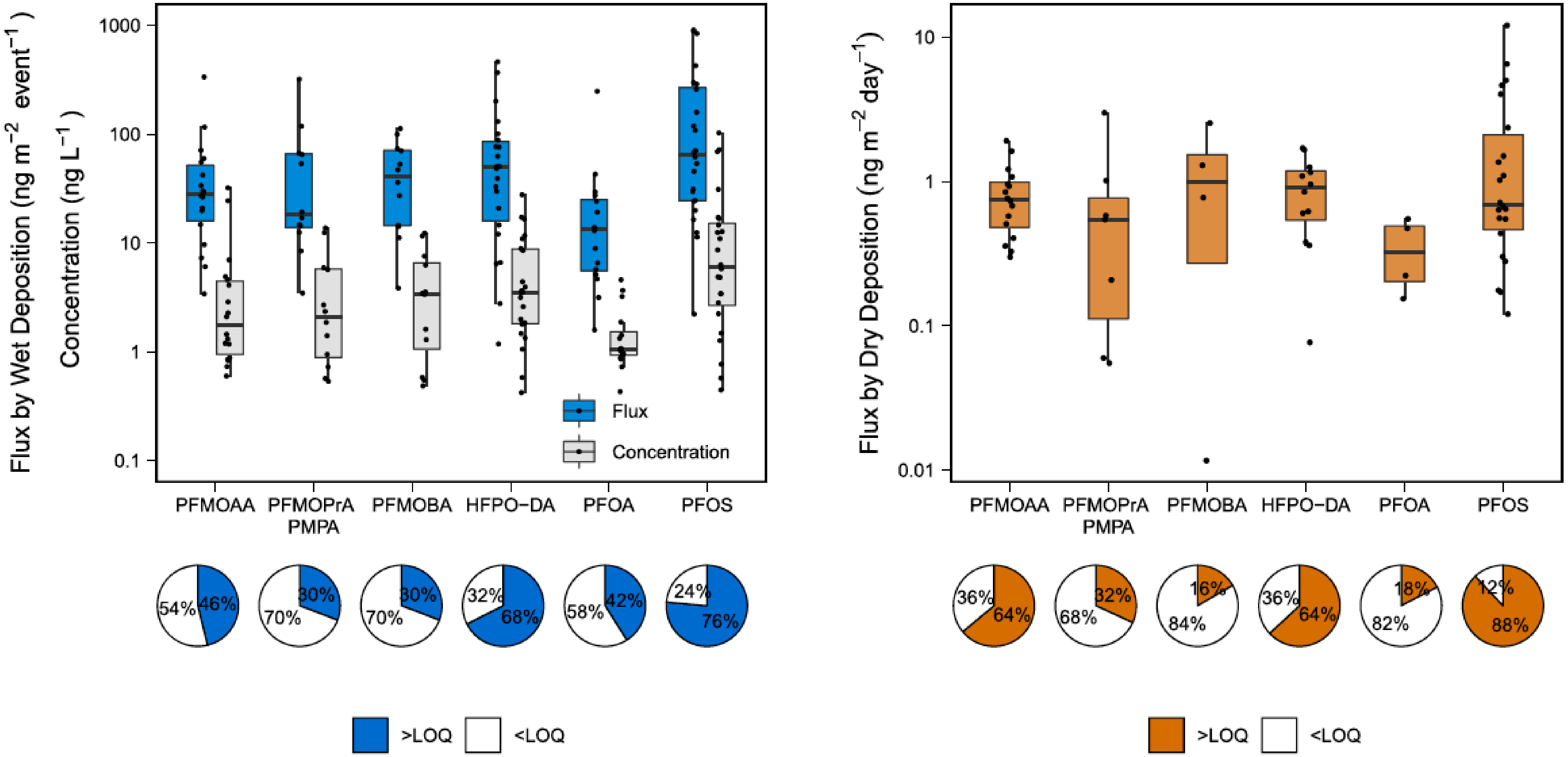
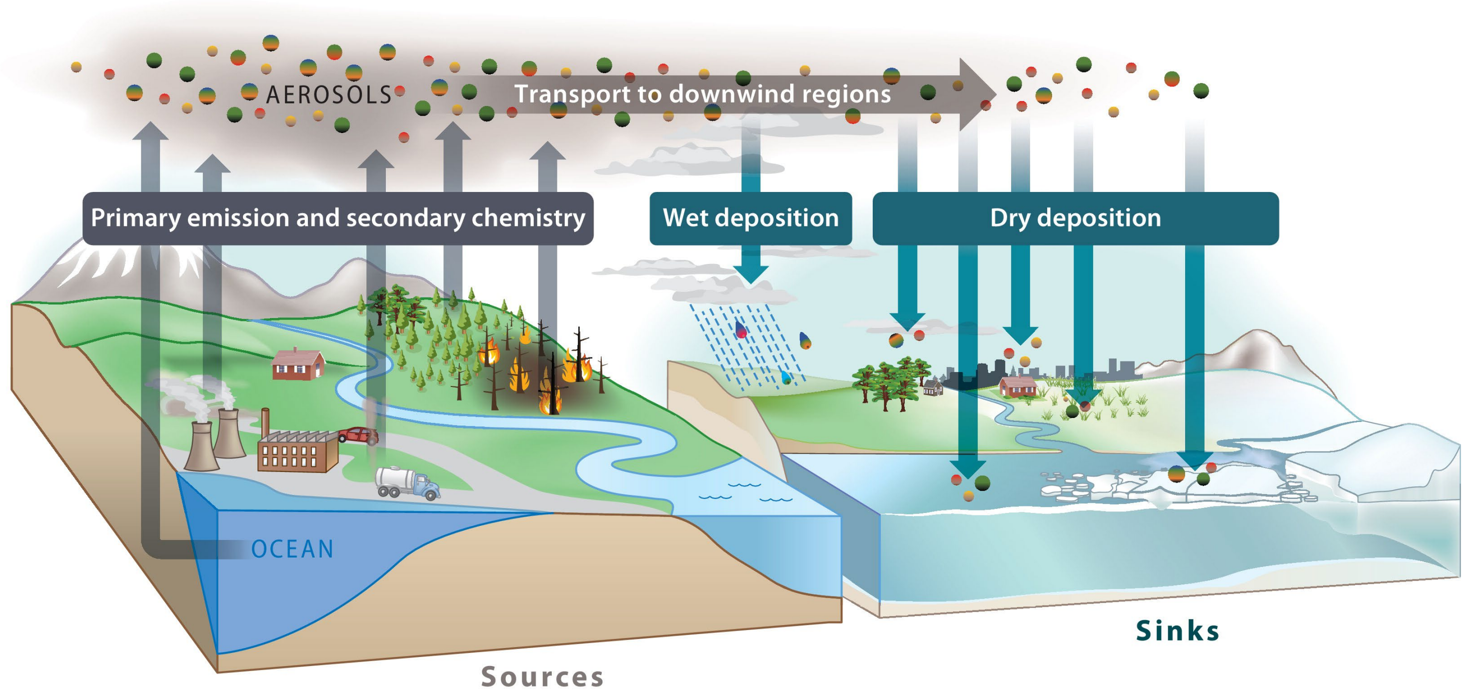
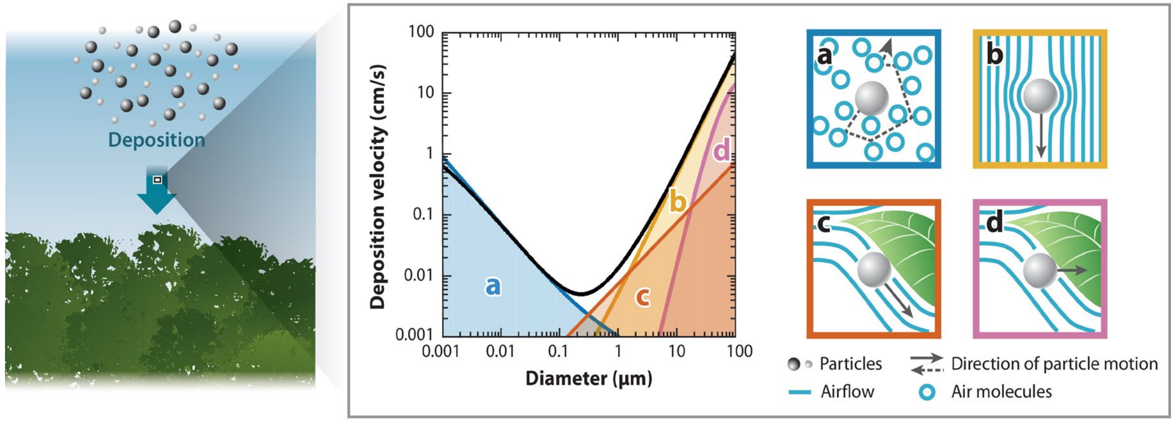


Figure 1. Detection frequencies of targeted analytes and detected concentration and flux in wet (left) and dry (right) deposition. LOQ stands for the limit of quantification. Note that *y*-axis scales and units are different between wet and dry deposition. The structures of the measured compounds are shown in Figure S1.



Farmer DK, et al. 2021
Annu. Rev. Phys. Chem. 72:375–97

Dry deposition velocities of particles are a function of particle diameter and are driven by a combination of processes, including (a) Brownian diffusion (blue), (b) gravitational settling (yellow), (c) interception (orange), and (d) impaction (purple). The relative importance of these processes varies with particle size and surface type, with the graph providing an example of these processes and the total calculated deposition velocity (thick black line) for a conifer forest. The direction of airflow in panels a–d is indicated by solid blue lines; the direction of particle motion is indicated by gray arrows. In the case of Brownian diffusion, particle movement is random, as indicated by the dashed gray arrow. The size of particles relative to gases is not drawn to scale.



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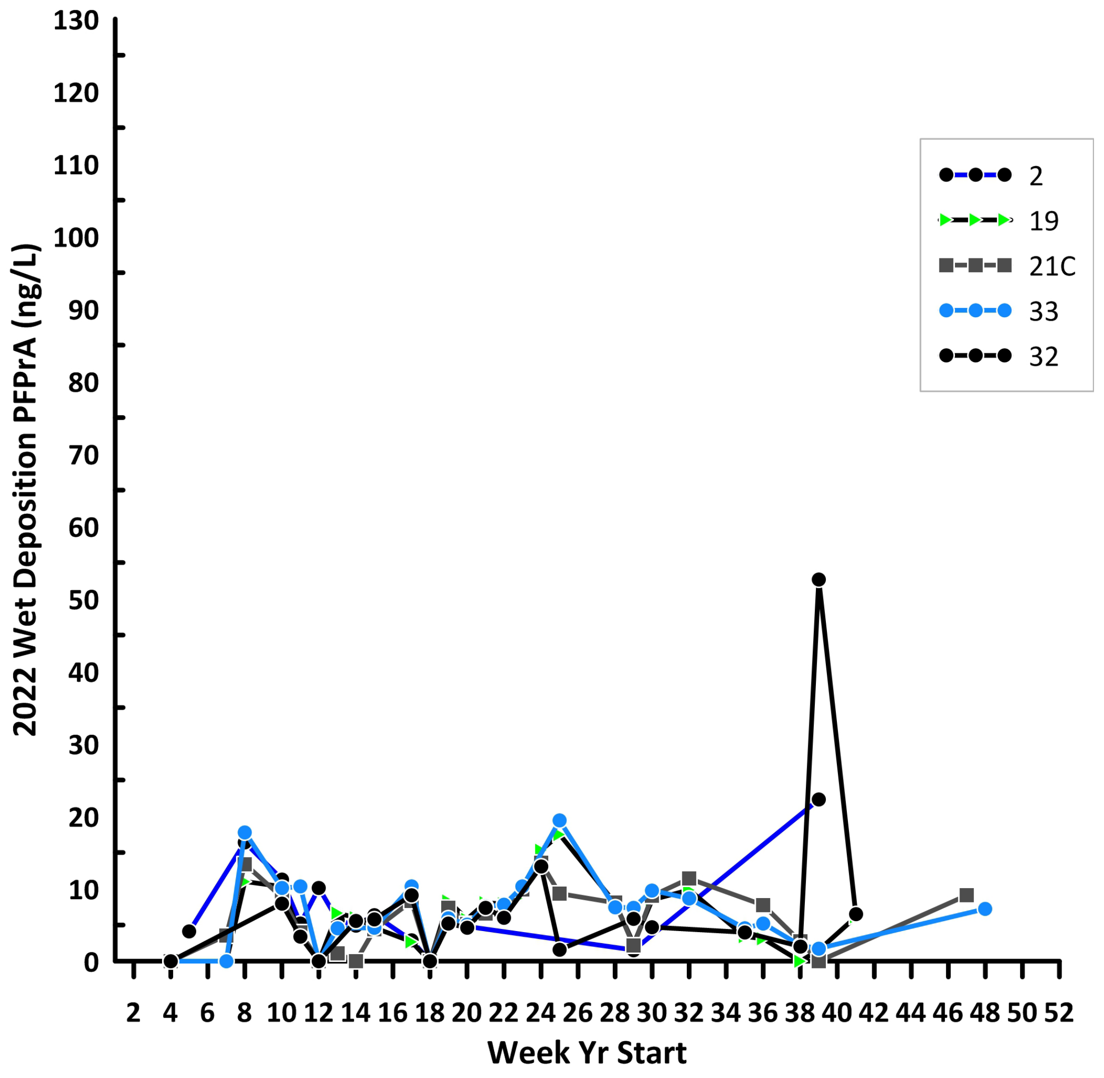
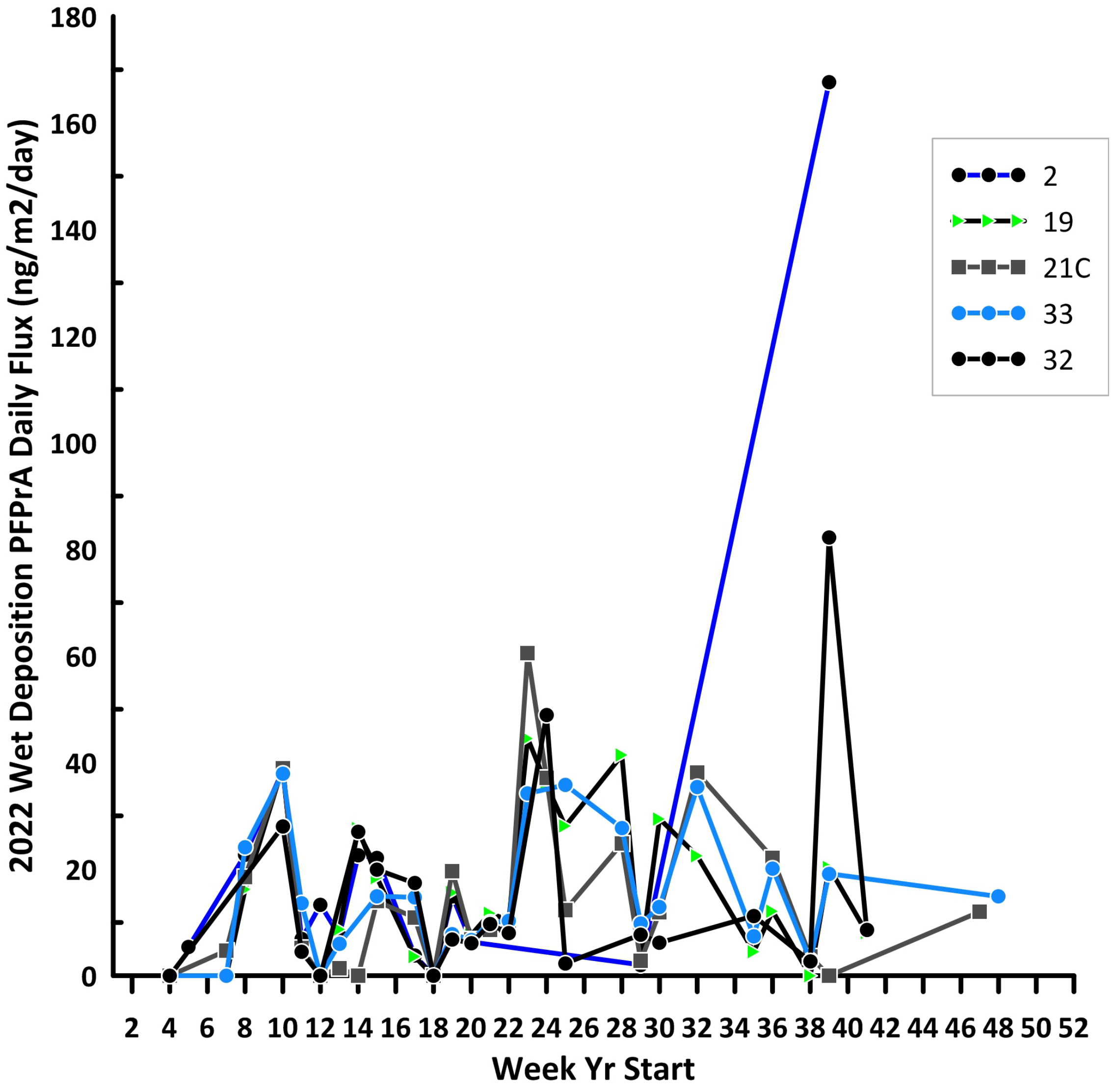
2022Perfluoropropionic Acid Wet Deposition




2022 Wet Deposition PFPrA Daily Flux (ng/m2/day)
180
160
140
120
100
80
60
40
20
0
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52
Week Yr Start
2
19
21C
33
32