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Per- and Polyfluoroalkyl Substances in Cloud Water over the Northwestern Atlantic

Eva-Lou Edwards, Andrea Corral, Chris Olivares, Jialin Dong,
Armin Sorooshian, and the ACTIVATE Science Team

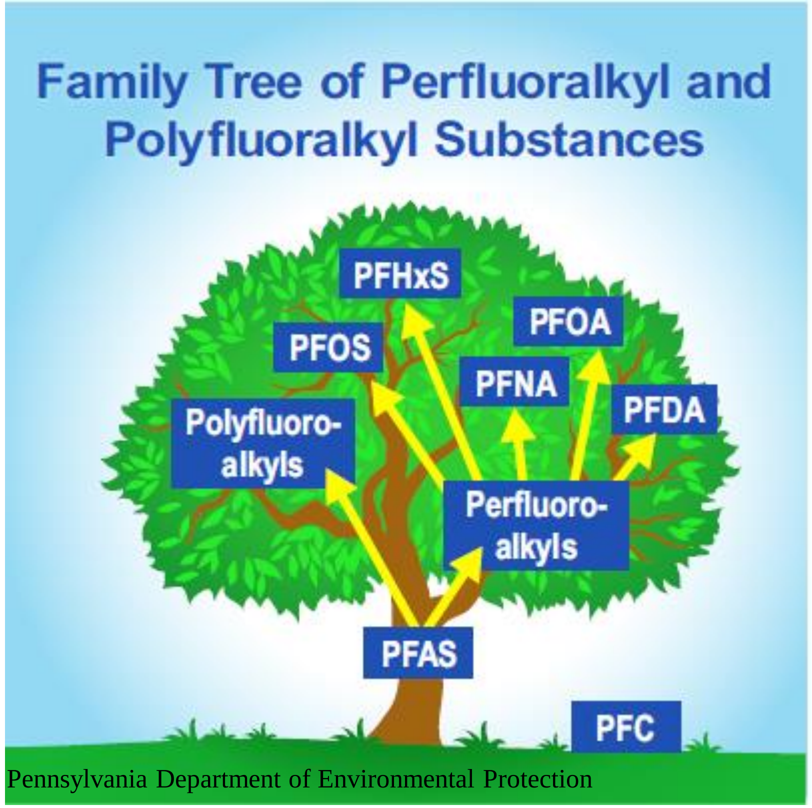
ACTIVATE STM
Tucson, AZ
13 – 15 November 2023

Image credit: JWH

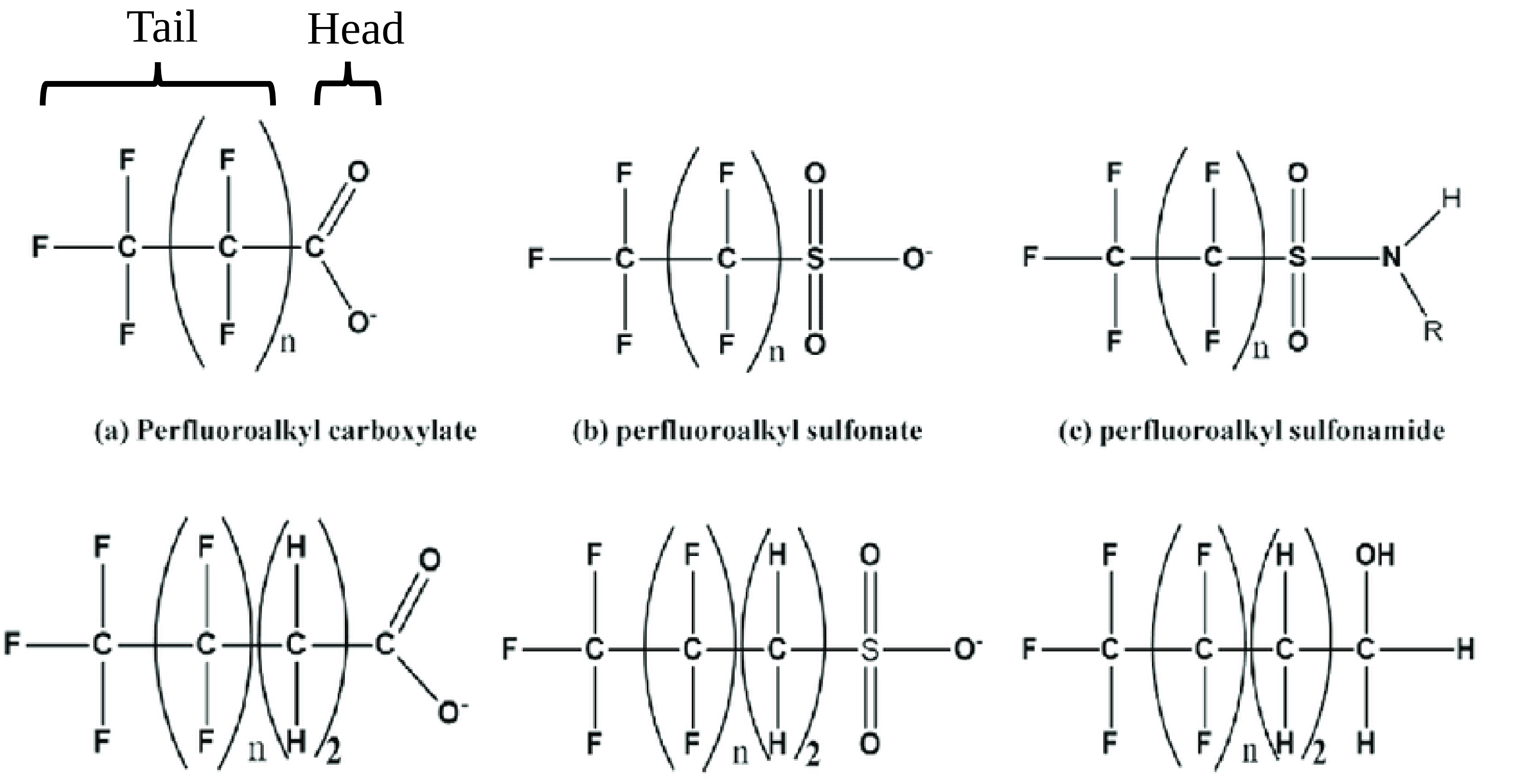
What are per- and polyfluoroalkyl substances (PFAS)?

PFAS are a group of 12,000+[1] man-made chemicals containing carbon-fluorine bonds that do not degrade easily in the environment or in living tissues, earning them the nickname "**forever chemicals**."

C-F bond = 466 kJ mol^{-1}



Pennsylvania Department of Environmental Protection



(a) Perfluoroalkyl carboxylate (b) perfluoroalkyl sulfonate (c) perfluoroalkyl sulfonamide

(d) Polyfluoroalkyl carboxylate (e) Polyfluoroalkyl sulfonates (f) Polyfluoroalkyl carboxylate

Olatunde et al. (2020), *Heliyon*

[1]USEPA (2021). *PFAS Master List of PFAS Substances (RETIRED).* CompTox chemicals dashboard. https://comptox.epa.gov/dashboard/chemical-lists/PFASMASTER

Sources of PFAS

PFAS are found in products we come in contact with everyday.

[PFAS: Last Week Tonight with John Oliver (HBO) - YouTube]

John Wiegand, MIT Technology Review

Progressive Charlestown

Toxic Carpet: We're Breathing Harmful Forever Chemicals in Homes, Offices, and Classrooms

TOPICS: Pollution Popular Public Health

By GREEN SCIENCE POLICY INSTITUTE AUGUST 31, 2021

SciTechDaily.com

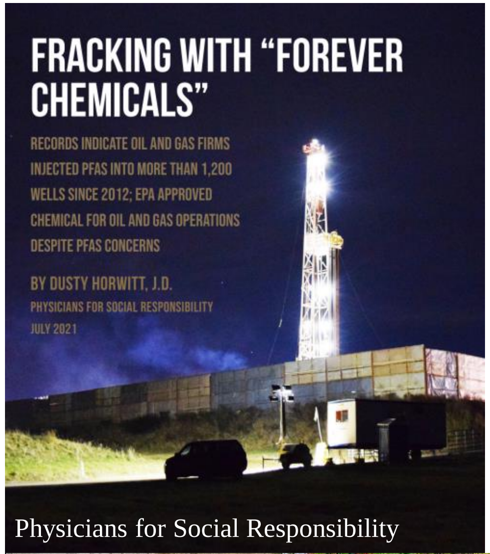
NEWS & INSIGHTS / NEWS / 2022 / 01

New tests find toxic 'forever chemicals' in bedding, yoga pants and other textiles

ewg.org

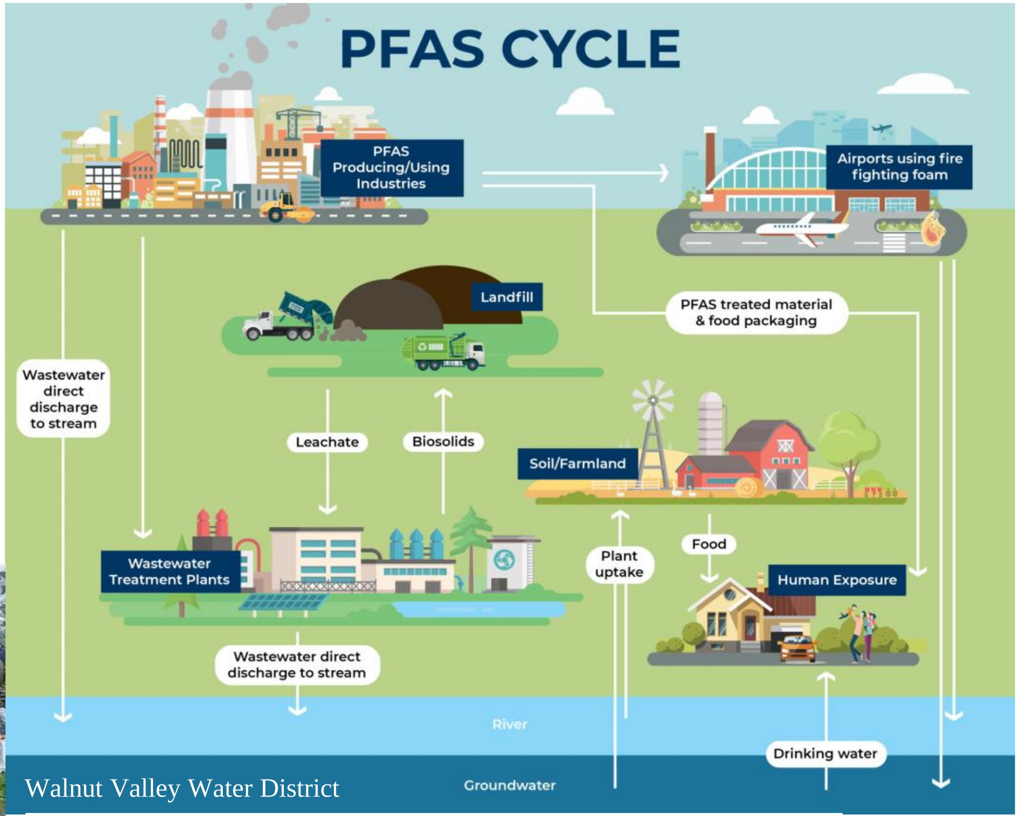
Sources of PFAS

PFAS can also be found in drinking water, fruits, vegetables, meat, lakes, rivers, and soil due to their resistance to degradation and tendency to accumulate in the environment.



Physicians for Social Responsibility


Alexander Schimmeck

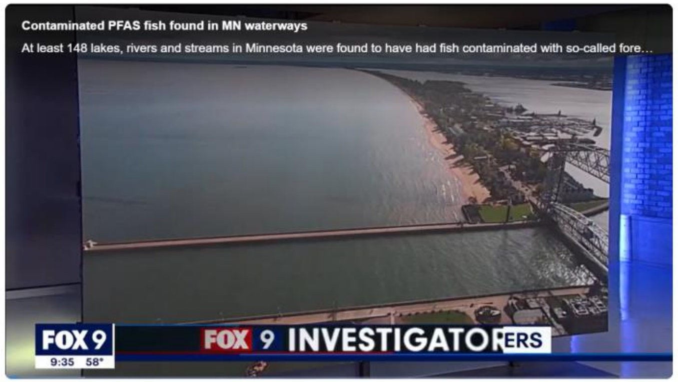


Walnut Valley Water District

FOX 9 MINNEAPOLIS

Contaminated PFAS fish found in MN waterways

KMSP
Sun, November 5, 2023 at 9:15 PM MST



Yahoo News

NEWS > WASHINGTON

PFAS is in the groundwater west of Spokane. What's known about the contamination is only growing

Nov. 1, 2023 | Updated Wed., Nov. 1, 2023 at 8:43 p.m.

The Spokesman Review

PUBLIC INTEREST

PFAS poisoning: Don't eat deer from near Clark's Marsh

Published: Nov. 06, 2023, 1:30 p.m.

MLive

WISCONSIN

PFAS 'forever chemicals' found in 71% of Wisconsin's shallow, private wells

450 shallow, private wells were sampled in study

Associated Press

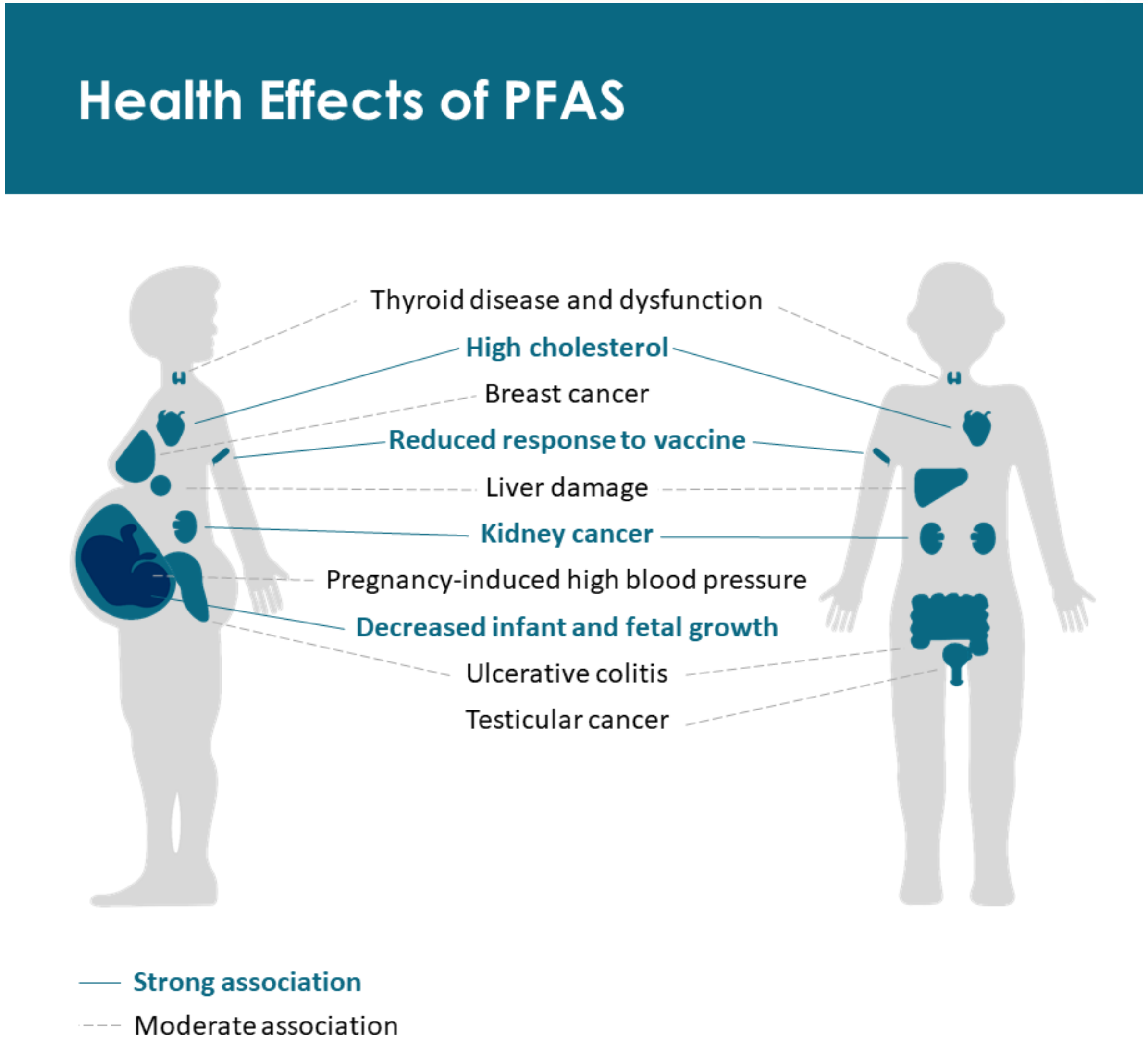
Published November 3, 2023 5:28pm EDT

Fox News

Motivation to quantify and monitor PFAS

Exposure to certain levels of PFAS may result in the following[1]:

- Decreased fertility
- Increased high blood pressure for pregnant women
- Developmental abnormalities in children
  - low birth weight
  - accelerated puberty
  - bone variations,
  - behavioral changes
- Increased risk of prostate, kidney, and testicular cancer
- Reduced immune system functioning
- Reduced response to vaccines
- Interference with the body’s natural hormones
- Increased cholesterol and/or obesity.

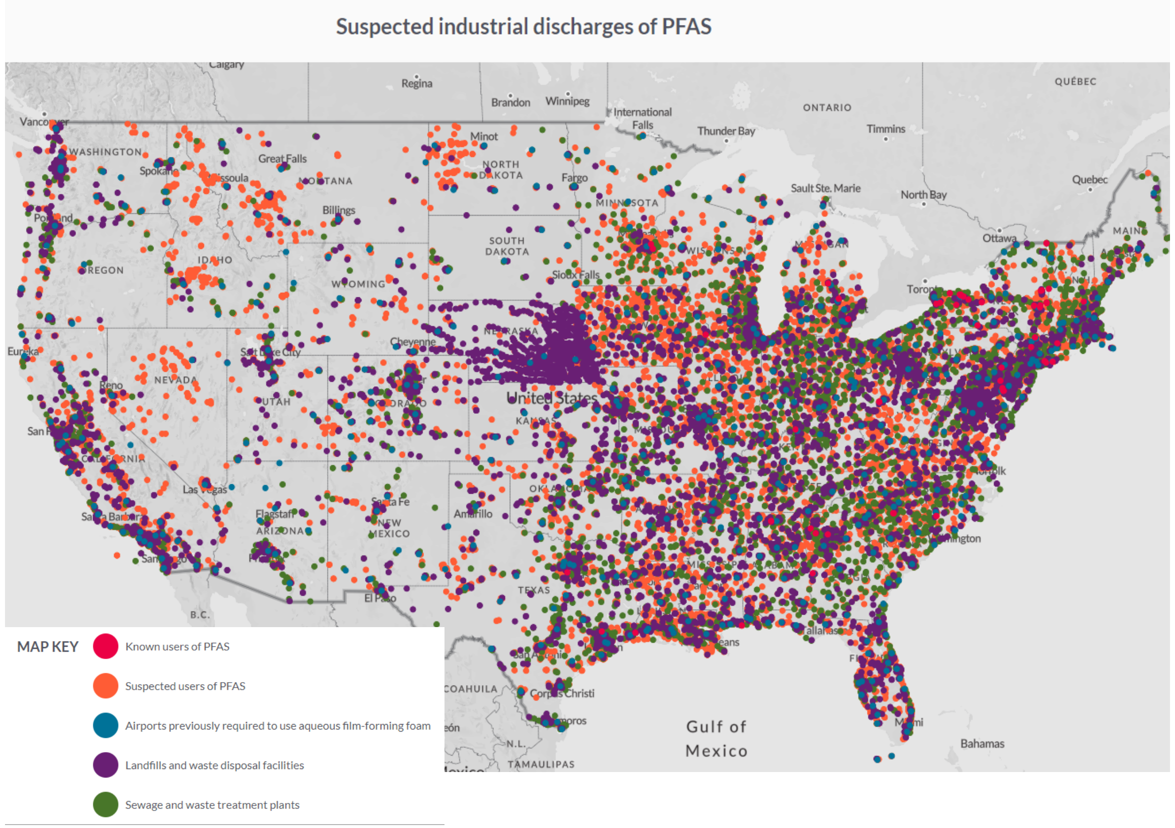


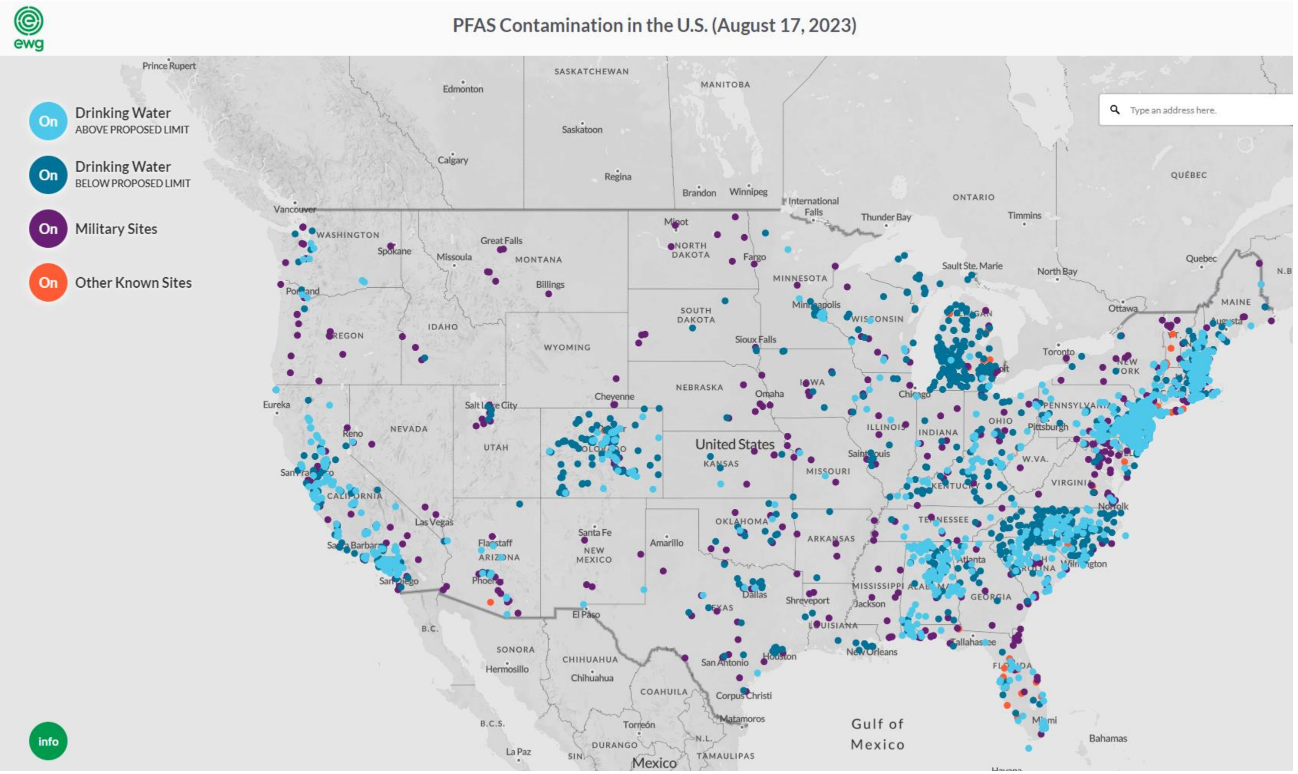
Madison and Dane Country Public Health

[1]USEPA (2023, June 03). *Our Current Understanding of the Human Health and Environmental Risks of PFAS*. United States Environmental Protection Agency. https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas

Sources of PFAS relevant to the ACTIVATE region

The United States East Coast has numerous suspected PFAS sources and instances of drinking water contamination.





Environmental Working Group

[Interactive Map: Suspected industrial discharges of PFAS (ewg.org)]

[Interactive Map: PFAS Contamination Crisis: New Data Show 3,186 Sites in 50 States (ewg.org)]

Atmospheric transport of PFAS

Airborne PFAS can come from three main sources.

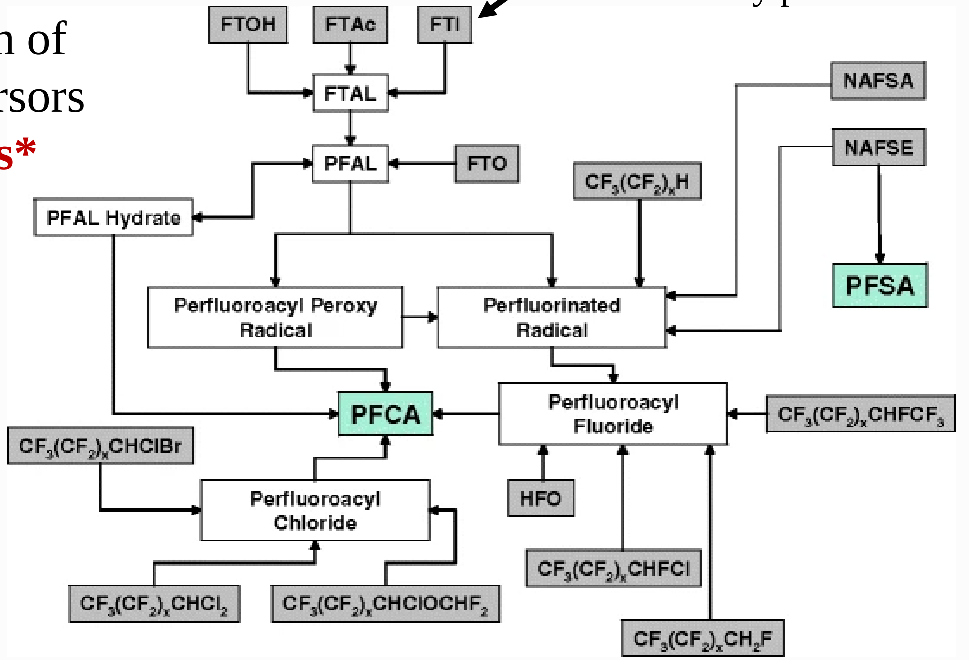
1. Direct emission from point sources

~Days – weeks*

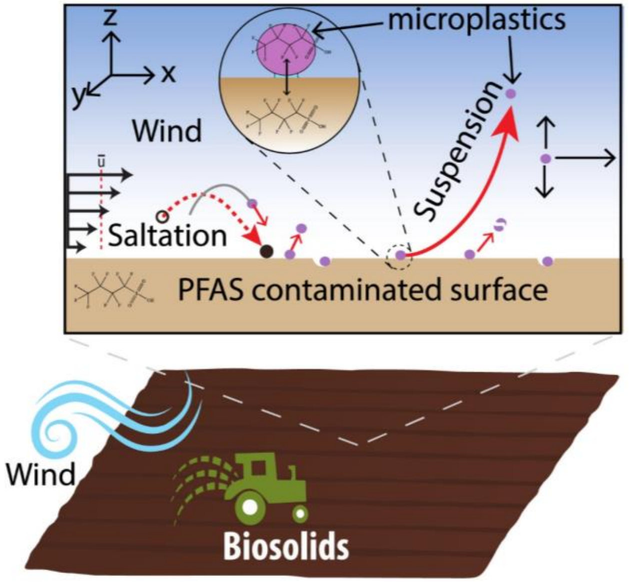
3. Degradation of volatile precursors

~Days – years*

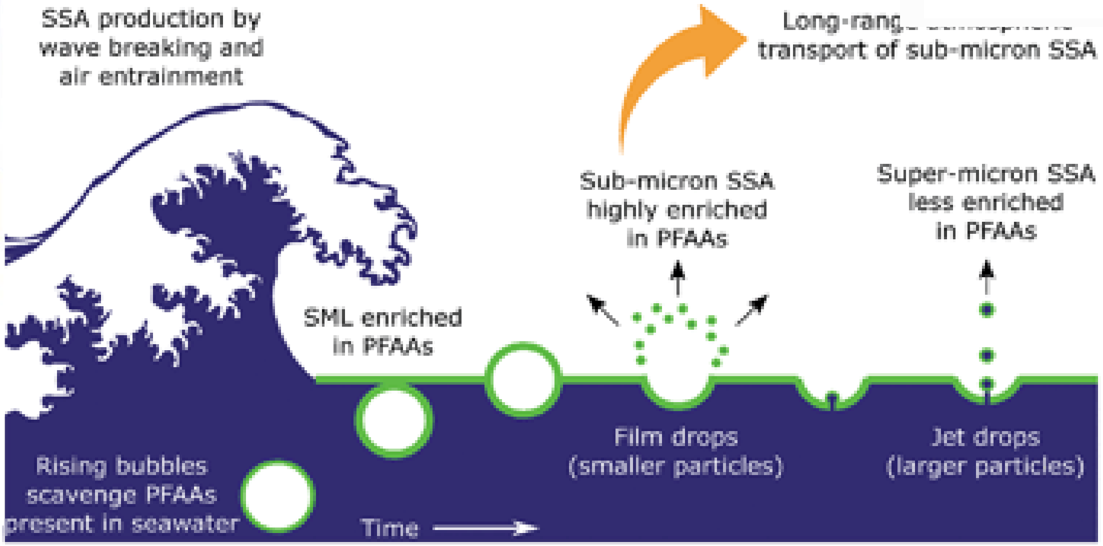
Grey shading = commercially produced



Young and Mabury (2010), *Reviews of Environmental Contamination and Toxicology*



Borthakur et al. (2022), *Current Opinion in Env. Sci. and Health*



2. Dust and sea spray aerosols emitted from soil and bodies of water contaminated with PFAS.

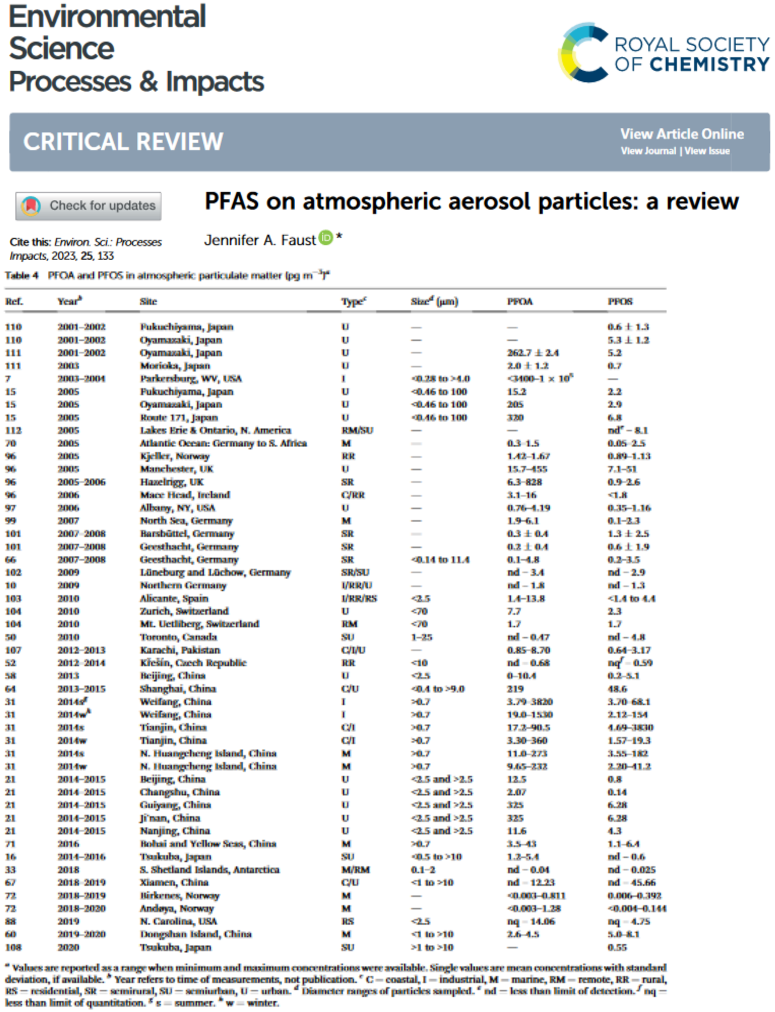
~Days – weeks*

***Atmospheric lifetime of relevant PFAS**

Existing literature on airborne PFAS

Several works have quantified PFAS in particles and wet deposition… but not in cloud water.

1. Atmospheric aerosol particles



Environmental Science Processes & Impacts

ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW

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PFAS on atmospheric aerosol particles: a review

Cite this: *Environ. Sci.: Processes Impacts*, 2023, 25, 133

Jennifer A. Faust *

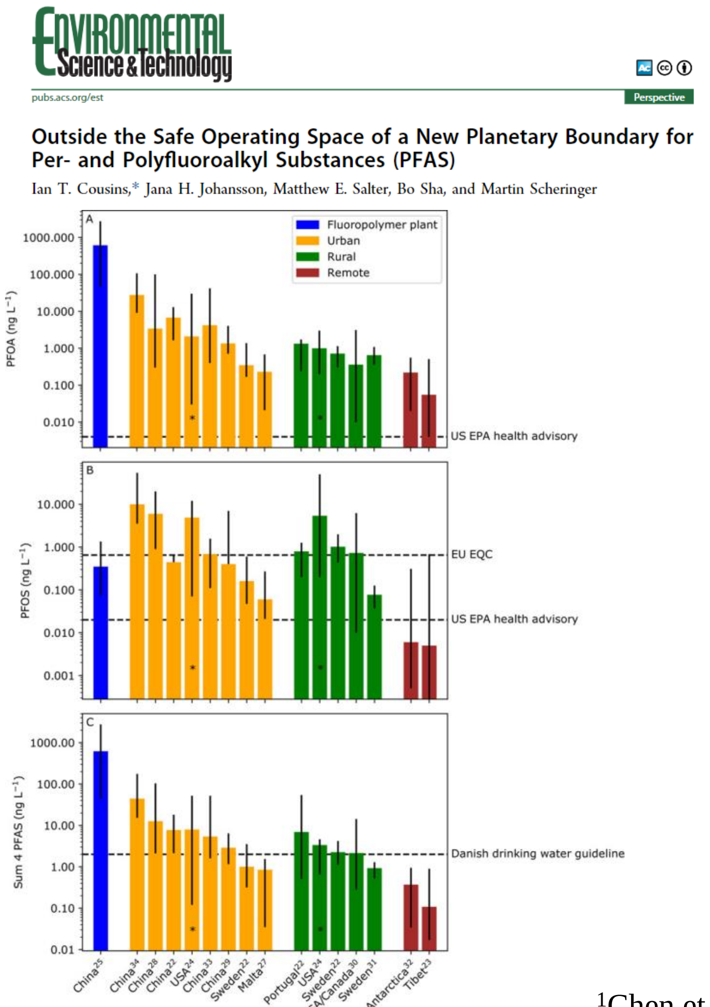
Table 4 PFOA and PFOS in atmospheric particulate matter (pg m^{-3})[a]

Ref.	Year[b]	Site	Type[c]	Size[d] (μm)	PFOA	PFOS
110	2001–2002	Fukuchiyama, Japan	U	—	—	0.6 ± 1.3
110	2001–2002	Oyamazaki, Japan	U	—	—	5.3 ± 1.2
111	2001–2002	Oyamazaki, Japan	U	—	262.7 ± 2.4	5.2
111	2003	Morioka, Japan	U	—	2.0 ± 1.2	0.7
7	2003–2004	Parkersburg, WV, USA	I	<0.28 to >4.0	<3400–1 × 10^5	—
15	2005	Fukuchiyama, Japan	U	<0.46 to 100	15.2	2.2
15	2005	Oyamazaki, Japan	U	<0.46 to 100	205	2.9
15	2005	Route 171, Japan	U	<0.46 to 100	320	6.8
112	2005	Lakes Erie & Ontario, N. America	RM/SU	—	—	nd[e] – 8.1
70	2005	Atlantic Ocean: Germany to S. Africa	M	—	0.3–1.5	0.05–2.5
96	2005	Kjeller, Norway	RR	—	1.42–1.67	0.89–1.13
96	2005	Manchester, UK	U	—	15.7–455	7.1–51
96	2005–2006	Hazelrigg, UK	SR	—	6.3–828	0.9–2.6
96	2006	Mace Head, Ireland	C/RR	—	3.1–16	<1.8
97	2006	Albany, NY, USA	U	—	0.76–4.19	0.35–1.16
99	2007	North Sea, Germany	M	—	1.9–6.1	0.1–2.3
101	2007–2008	Barsbüttel, Germany	SR	—	0.3 ± 0.4	1.3 ± 2.5
101	2007–2008	Geesthacht, Germany	SR	—	0.2 ± 0.4	0.6 ± 1.9
66	2007–2008	Geesthacht, Germany	SR	<0.14 to 11.4	0.1–4.8	0.2–3.5
102	2009	Lüneburg and Lüchow, Germany	SR/SU	—	nd – 3.4	nd – 2.9
10	2009	Northern Germany	I/RR/U	—	nd – 1.8	nd – 1.3
103	2010	Alicante, Spain	I/RR/RS	<2.5	1.4–13.8	<1.4 to 4.4
104	2010	Zurich, Switzerland	U	<70	7.7	2.3
104	2010	Mt. Uetliberg, Switzerland	RM	<70	1.7	1.7
50	2010	Toronto, Canada	SU	1–25	nd – 0.47	nd – 4.8
107	2012–2013	Karachi, Pakistan	C/I/U	—	0.85–8.70	0.64–3.17
52	2012–2014	Křešín, Czech Republic	RR	<10	nd – 0.68	nq[f] – 0.59
58	2013	Beijing, China	U	<2.5	0–10.4	0.2–5.1
64	2013–2015	Shanghai, China	C/U	<0.4 to >9.0	219	48.6
31	2014s[g]	Weifang, China	I	>0.7	3.79–3820	3.70–68.1
31	2014w[h]	Weifang, China	I	>0.7	19.0–1530	2.12–154
31	2014s	Tianjin, China	C/I	>0.7	17.2–90.5	4.69–3830
31	2014w	Tianjin, China	C/I	>0.7	3.30–360	1.57–19.3
31	2014s	N. Huangcheng Island, China	M	>0.7	11.0–273	3.55–182
31	2014w	N. Huangcheng Island, China	M	>0.7	9.65–232	2.20–41.2
21	2014–2015	Beijing, China	U	<2.5 and >2.5	12.5	0.8
21	2014–2015	Changshu, China	U	<2.5 and >2.5	2.07	0.14
21	2014–2015	Guiyang, China	U	<2.5 and >2.5	325	6.28
21	2014–2015	Ji'nan, China	U	<2.5 and >2.5	325	6.28
21	2014–2015	Nanjing, China	U	<2.5 and >2.5	11.6	4.3
71	2016	Bohai and Yellow Seas, China	M	>0.7	3.5–43	1.1–6.4
16	2014–2016	Tsukuba, Japan	SU	<0.5 to >10	1.2–5.4	nd – 0.6
33	2018	S. Shetland Islands, Antarctica	M/RM	0.1–2	nd – 0.04	nd – 0.025
67	2018–2019	Xiamen, China	C/U	<1 to >10	nd – 12.23	nd – 45.66
72	2018–2019	Birkenes, Norway	M	—	<0.003–0.811	0.006–0.392
72	2018–2020	Andøya, Norway	M	—	<0.003–1.28	<0.004–0.144
88	2019	N. Carolina, USA	RS	<2.5	nq – 14.06	nq – 4.75
60	2019–2020	Dongshan Island, China	M	<1 to >10	2.6–4.5	5.0–8.1
108	2020	Tsukuba, Japan	SU	>1 to >10	—	0.55

[a] Values are reported as a range when minimum and maximum concentrations were available. Single values are mean concentrations with standard deviation, if available. [b] Year refers to time of measurements, not publication. [c] C = coastal, I = industrial, M = marine, RM = remote, RR = rural, RS = residential, SR = semirural, SU = semiurban, U = urban. [d] Diameter ranges of particles sampled. [e] nd = less than limit of detection. [f] nq = less than limit of quantitation. [g] s = summer. [h] w = winter.

Summarizes results from 37 studies from 2001 - 2020.

2. Wet deposition



Environmental Science & Technology

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Perspective

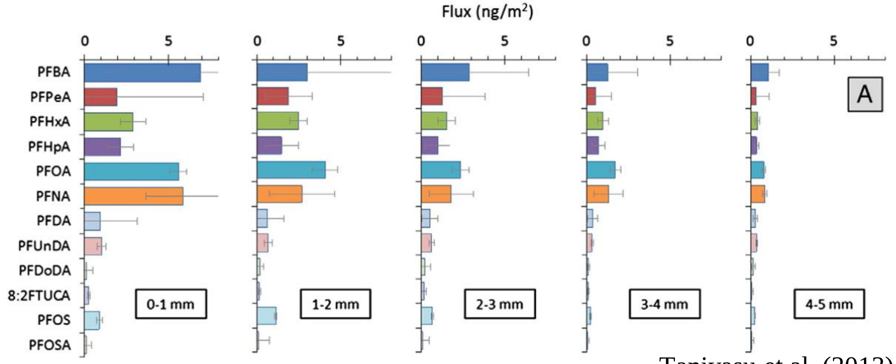
Outside the Safe Operating Space of a New Planetary Boundary for Per- and Polyfluoroalkyl Substances (PFAS)

Ian T. Cousins,* Jana H. Johansson, Matthew E. Salter, Bo Sha, and Martin Scheringer

Summarizes results from 11 studies from 2010 - 2022.

3. Cloud droplets? Here's what we know:

- Shorter chain PFAS are water soluble.[1]
- PFAS reduce surface tension[2] yet lower vapor pressure of water.[3]
- Lab studies show PFOA have ice nucleating ability.[4]
- PFAS concentrations in rainwater can vary with duration of the rain event.[5,6]
- Modeling studies have attempted to simulate nucleation and scavenging of PFAS-containing particles in clouds.[7,8]



Taniyasu et al. (2013)

[1]Chen et al. (2019), *Water Research*, [2]Buck et al. (2012), Faust et al. (2023), *Env. Sci.: Processes and Impacts*, [4]Schwidetzky et al. (2021), *J. Phys. Chem. Letters*, [5]Kwok et al. (2010), *Env. Sci. & Technology*, [6]Taniyasu et al. (2013), *Env. International*, [7]D'Ambro et al. (2023), *Sci. of the Total Env.*, [8]Franco et al. (2011), *Chemosphere*

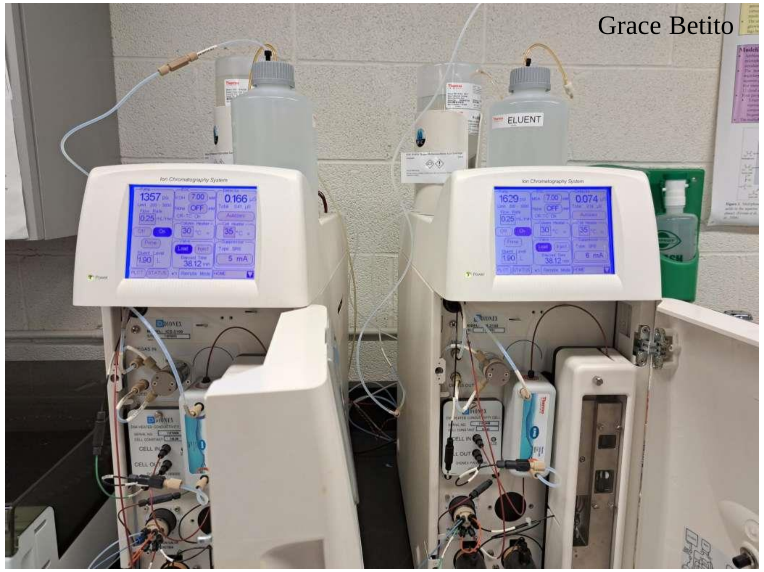
Methods

Cloud water samples from ACTIVATE 2020 and 2021 flights were analyzed for mass concentrations of water-soluble ions, elements, and PFAS.

1. Cloud water collected using the AC3.

Armin Sorooshian

Corning Inc.



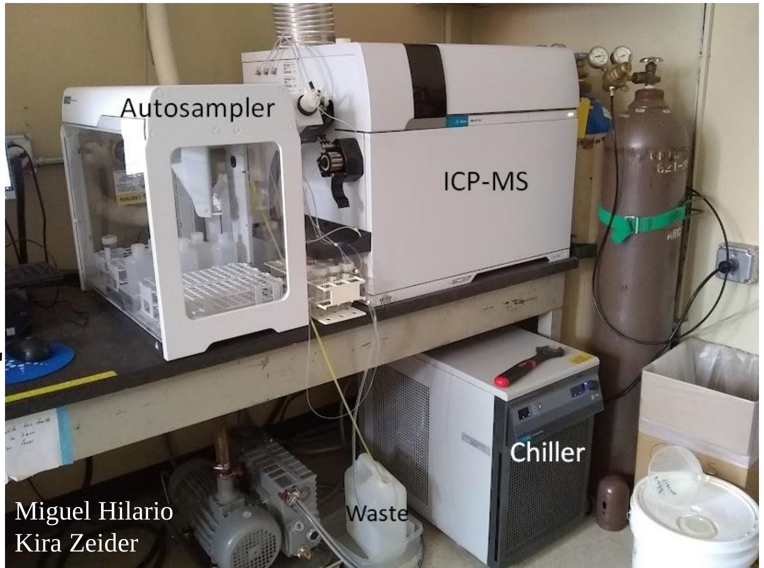
Grace Betito

2. IC system provided aqueous water-soluble ion mass concentrations.

IC = ion chromatography

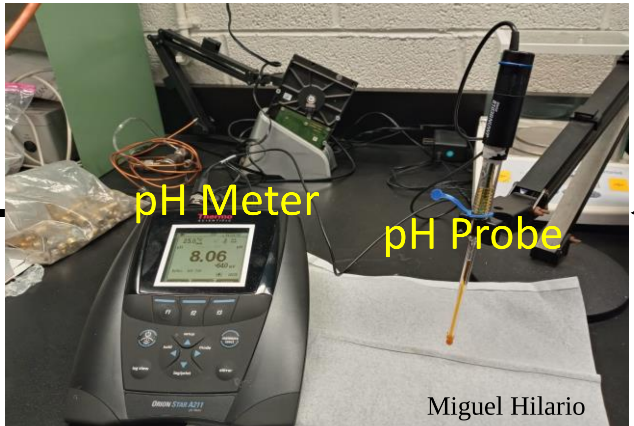
3. ICP-MS system provided aqueous water-soluble elemental mass concentrations.

ICP-MS = inductively coupled plasma mass spectrometry



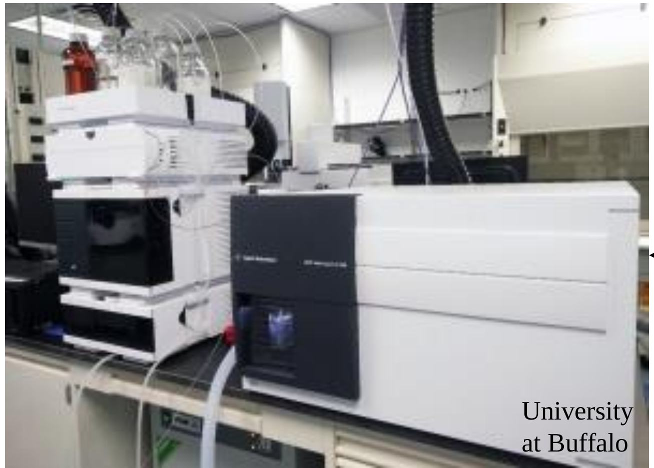
Miguel Hilario
Kira Zeider

4. pH analysis



Miguel Hilario

5. Agilent 6470 QQQ LC-MS/MS provided aqueous PFAS mass concentrations.

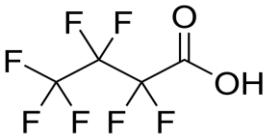


University at Buffalo

PFAS in ACTIVATE cloud water

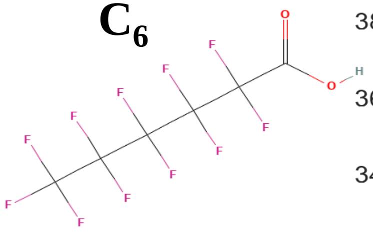
Aqueous mass concentrations of ions, elements, and PFAS were converted to air-equivalent using the mean total water content (TWC; FCDP + 2D-S) for periods when TWC > 0.02 g m^{-3} for each sample.

C_4

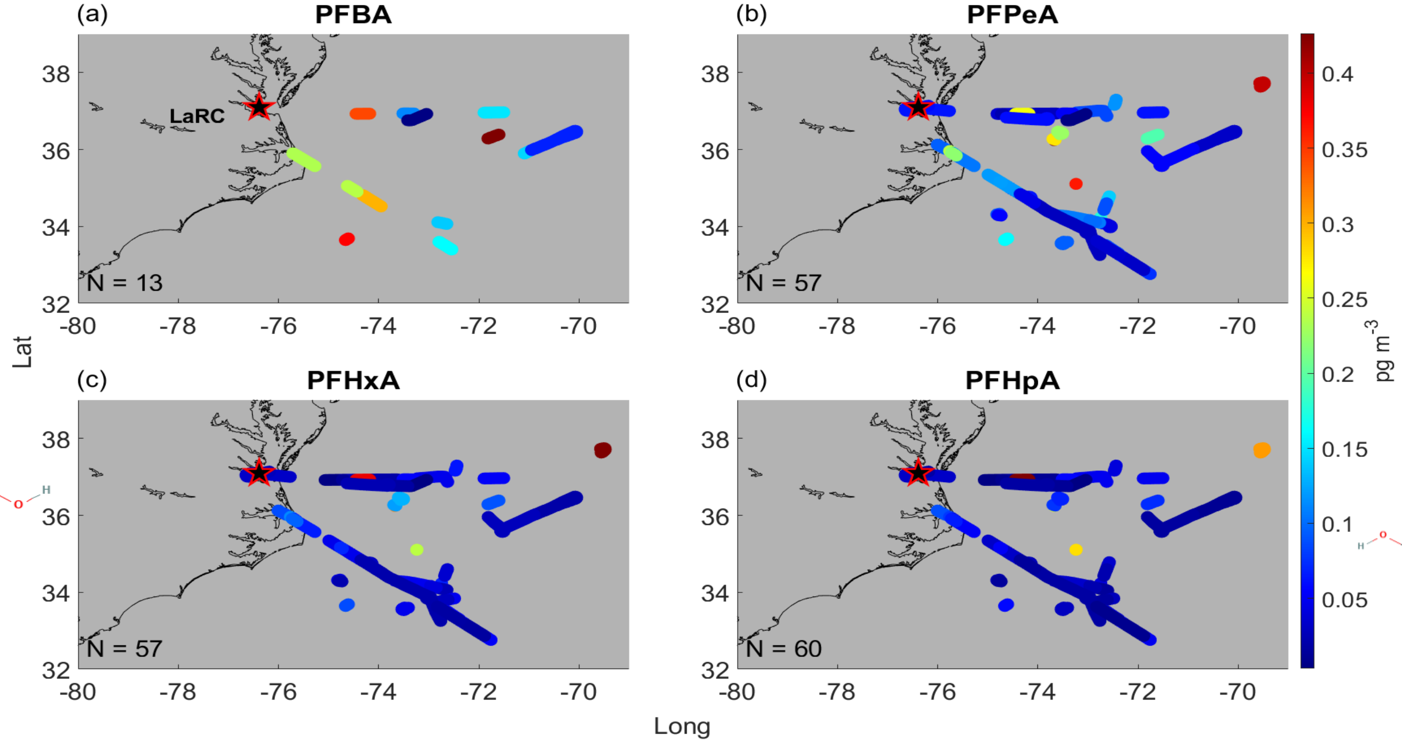


Wikipedia

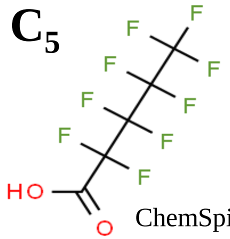
C_6



ChemSpider

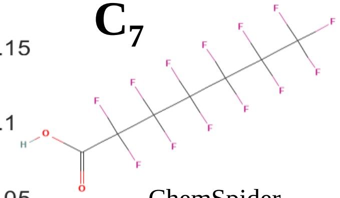


C_5



ChemSpider

C_7



ChemSpider

FCDP = fast cloud droplet probe

2D-S = two-dimensional stereo probe

- PFBA, PFPeA, PFHxA, and PFHpA detected in 13, 57, 57, and 60 samples (out of 62), respectively.
- PFBA mass concentrations typically higher than C_5 – C_7 PFAS, consistent with past works.[1,2]
- Mass concentrations for C_4 – C_7 PFAS are an order of magnitude lower than those reported **in aerosol particles** over China, India, Japan, and South Korea[3] as well as Toronto, Canada[1] and Northwest Europe[4].
- Values for PFHpA are an order of magnitude higher than those reported **in $PM_{2.5}$** over North Carolina, U.S.[5]

[1]Ahrens et al. (2012), *Env. Sci. & Technol.*, [2]Taniyasu et al. (2013), *Env. International*, [3]Lin et al. (2020), *Env. Sci. & Technol.*, [4]Barber et al. (2007), *Journal of Environmental Monitoring*, [5]Zhou et al. (2021), *Env. Sci.: Processes Impacts*

Sources/particle types associated with PFAS

	ssNa+	ssCa2+	Cl-	dust Na+	dust Ca2+	Al	Mn	Fe	NO3-	Oxalate	MSA	NH4+	K+	nssSO4 2-	V	Cr	As	PFBA	PFPeA	PFHxA	PFHpA
ssNa+		62	62	62	62	59	59	58	62	60	23	62	60	62	59	59	41	13	57	57	60
ssCa2+	0.99***		62	62	62	59	59	58	62	60	23	62	60	62	59	59	41	13	57	57	60
Cl-	0.98***	0.96***		62	62	59	59	58	62	60	23	62	60	62	59	59	41	13	57	57	60
dust Na+	-0.19	-0.07	-0.20		62	59	59	58	62	60	23	62	60	62	59	59	41	13	57	57	60
dust Ca2+	-0.19	-0.07	-0.20	1.00***		59	59	58	62	60	23	62	60	62	59	59	41	13	57	57	60
Al	0.29*	0.37**	0.25	0.51***	0.51***		59	58	59	57	23	59	57	59	59	59	41	13	54	54	57
Mn	0.36**	0.48***	0.34**	0.65***	0.65***	0.68***		58	59	57	23	59	57	59	59	59	41	13	54	54	57
Fe	0.38**	0.46***	0.38**	0.30*	0.30*	0.77***	0.46***		58	56	23	58	56	58	58	58	41	13	53	53	56
NO3-	0.45***	0.52***	0.46***	0.47***	0.47***	0.86***	0.78***	0.66***		60	23	62	60	62	59	59	41	13	57	57	60
Oxalate	0.09	0.12	0.08	0.33**	0.34**	0.68***	0.34*	0.43***	0.54***		22	60	58	60	57	57	39	12	55	55	58
MSA	0.43*	0.49*	0.40	0.32	0.32	0.49*	0.64**	0.13	0.60**	0.25		23	22	23	23	23	16	4	21	22	23
NH4+	0.34**	0.38**	0.34**	0.32*	0.32*	0.63***	0.59***	0.56***	0.76***	0.38**	0.36		60	62	59	59	41	13	57	57	60
K+	0.95***	0.93***	0.95***	-0.16	-0.16	0.28*	0.40**	0.33*	0.53***	0.10	0.59**	0.42**		60	57	57	41	13	55	55	58
nssSO4 2-	0.59***	0.63***	0.62***	0.22	0.22	0.57***	0.63***	0.44***	0.81***	0.37**	0.66***	0.68***	0.70***		59	59	41	13	57	57	60
V	0.22	0.31*	0.20	0.55***	0.55***	0.76***	0.59***	0.63***	0.68***	0.56***	0.43*	0.51***	0.18	0.51***		59	41	13	54	54	57
Cr	0.24	0.28*	0.18	0.35**	0.35**	0.71***	0.52***	0.34**	0.72***	0.39**	0.52*	0.48***	0.30*	0.42***	0.38**		41	13	54	54	57
As	0.07	0.20	0.07	0.60***	0.60***	0.74***	0.61***	0.65***	0.59***	0.48**	0.30	0.53***	0.01	0.37*	0.85***	0.28		12	37	39	40
PFBA	0.07	0.14	0.07	0.49	0.52	0.77**	0.62*	0.69*	0.75**	0.65*	-0.80	0.65*	-0.01	0.52	0.85***	0.78**	0.86***		13	13	13
PFPeA	0.02	0.11	-0.07	0.66***	0.66***	0.60***	0.59***	0.39**	0.46***	0.46***	0.27	0.36**	-0.01	0.20	0.57***	0.39**	0.74***	0.96***		53	55
PFHxA	0.06	0.18	-0.03	0.70***	0.70***	0.71***	0.74***	0.43**	0.65***	0.43***	0.55**	0.46***	0.09	0.34**	0.57***	0.60***	0.69***	0.91***	0.95***		57
PFHpA	0.10	0.21	0.02	0.71***	0.71***	0.69***	0.74***	0.38**	0.64***	0.38**	0.63**	0.42***	0.14	0.36**	0.56***	0.61***	0.63***	0.79**	0.86***	0.96***	

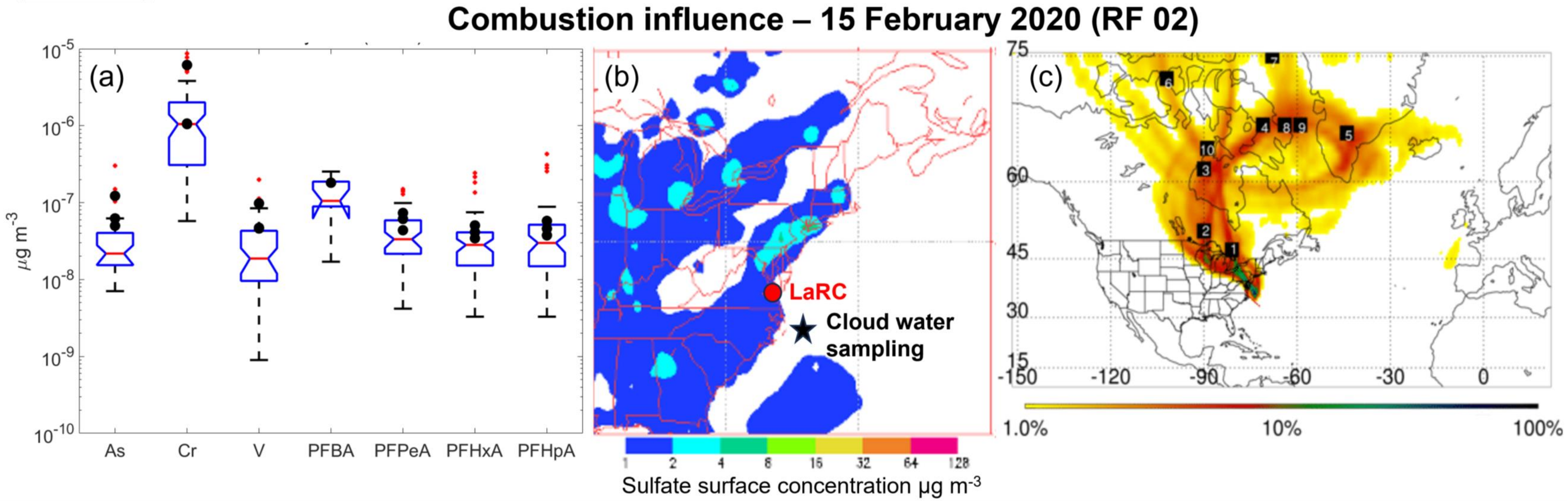
- $C_4 – C_7$ PFAS correlated with As, V, and Cr, suggesting combustion influence.[1]
- $C_5 – C_7$ PFAS correlated with dust Na^+, dust Ca^{2+}, Al, Mn, NO_3^-, oxalate, and MSA, indicating association with dust particles.[1,2,3,4]
- Weak correlations between $C_4 – C_7$ PFAS and $ssNa^+$, $ssCa^{2+}$, and Cl^- despite past works identifying relationships between PFAS and sea salt.[5,6]

Colored boxes show Spearman rho values, white boxes show number of samples considered for each correlation.

* = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$

[1]Stahl et al. (2020), *ACP*, [2]Dadashazar et al. (2019), *Sci. of the Tot. Env.*, [3]Ma et al. (2019), *Atmos. Env.*, [4]Hilario et al. (2021), *GRL*, [5]Sha et al. (2022), *Env. Sci. & Technol.*, [6]Johansson et al. (2019), *Env. Science: Processes & Impacts*

Case studies: combustion influence



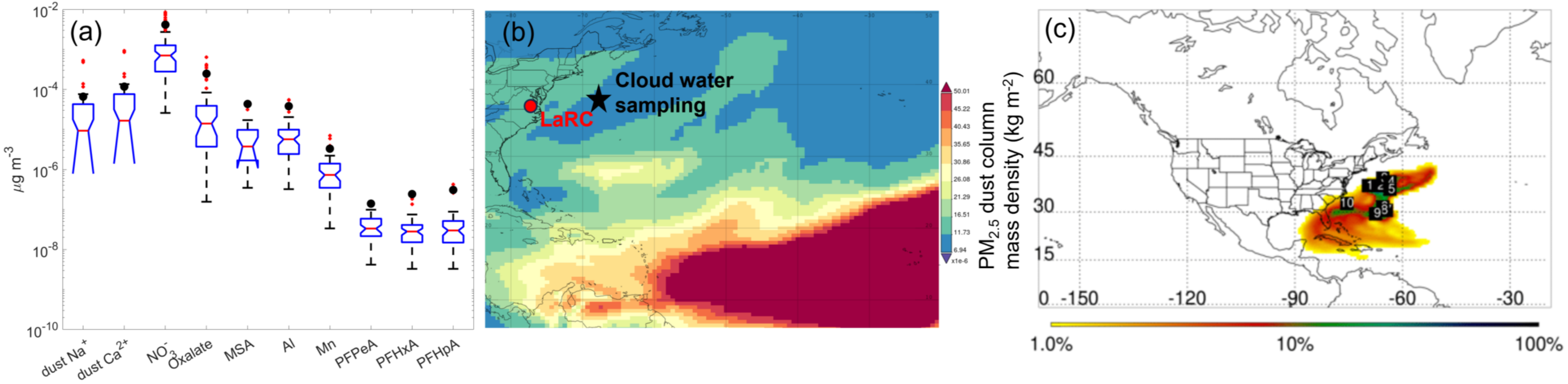
- As, Cr, V, and $C_4 – C_7$ PFAS mass concentrations are mostly above their respective medians.
- NAAPS simulates sulfate as the only particle type contributing to AOD over the Upper Midwest and Northeast where FLEXPART back trajectories come from.
- $C_4 – C_7$ PFAS in cloud water appear to be associated with combustion particles originating from these regions, consistent with past works.[1,2]
- PFAS can readily adsorb to organic matter and soot particles when they are protonated (i.e., at low pH).[1]

[1]Dreyer et al. (2015), *Chemosphere*, [2]MacInnis et al. (2019), *Env. Sci. & Technol.*

NAAPS = Navy Aerosol Analysis Prediction System; AOD = aerosol optical depth

Case studies: dust influence

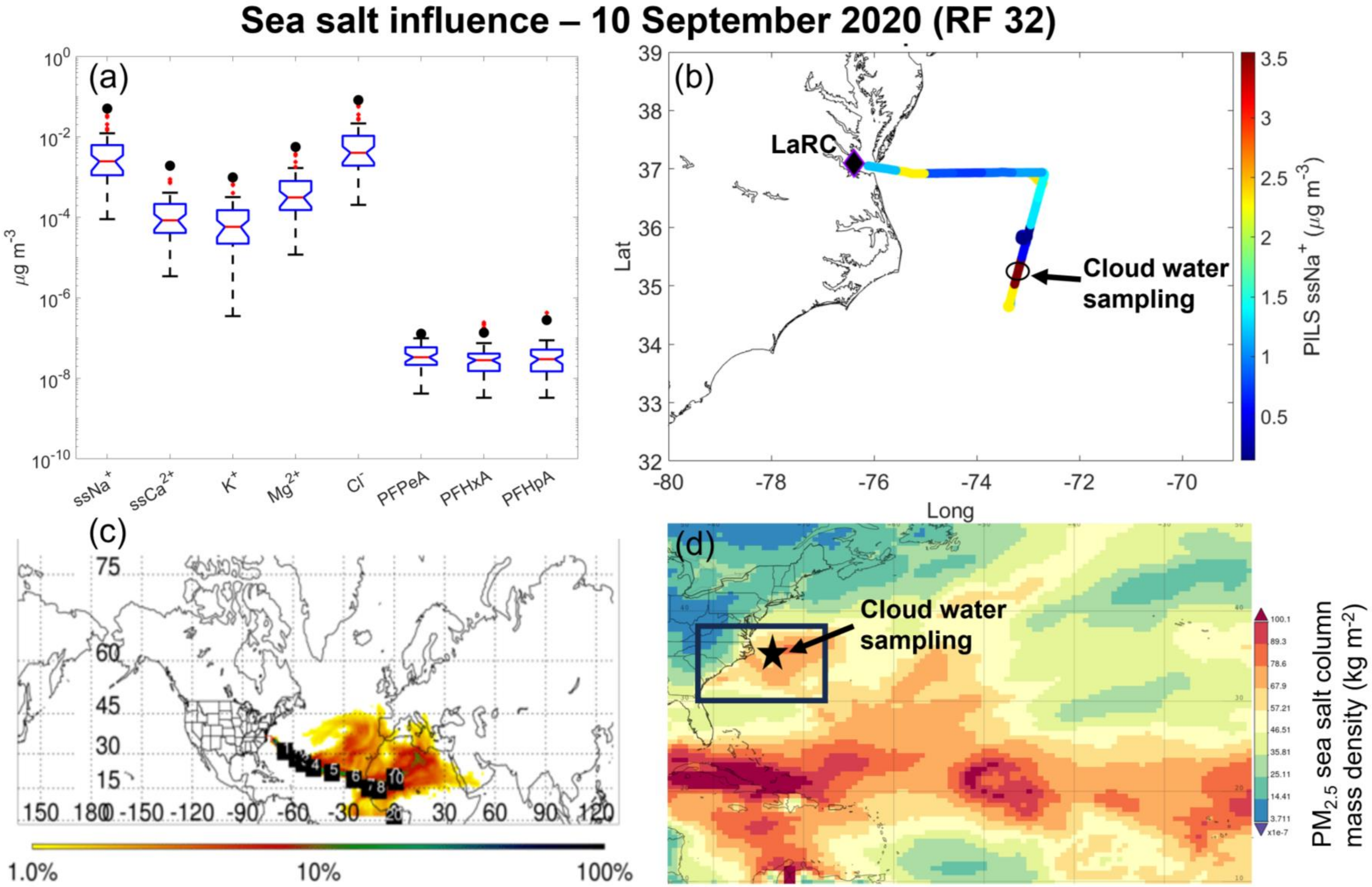
Dust influence – 28 June 2021 (RF 90)



- High mass concentrations observed for dust tracers and C_5 – C_7 PFAS.
- MERRA-2 shows African dust over Caribbean and Atlantic from June 19 – 28, 2021 where FLEXPART back trajectories come from.
- PFAS appear to be associated with African dust particles.
- There are currently no studies discussing PFAS in African dust plumes, yet past works have found PFAS to adsorb to the surface of dust particles and be transported long distances.[1,2]

[1]Ismail et al. (2023), *Toxics*, [2]MacInnis et al. (2019), *Env. Sci. & Technol.*

Case studies: sea salt influence



- High mass concentrations observed for sea salt tracers and $C_5 – C_7$ PFAS.
- PILS Na^+ also high where the sample was obtained.
- FLEXPART back trajectories show sampled air mass originated over the Atlantic where MERRA-2 $PM_{2.5}$ sea salt column density values are high.
- Many past works have found sea spray aerosols to contain and transport PFAS over long distances.[1,2]

[1]Sha et al. (2022), *Env. Sci. & Technol.*, [2]Johansson et al. (2019), *Environ. Sci.: Processes Impacts*

PILS = particle into liquid sampler

Conclusions and discussion

- This is the first study quantifying PFAS mass concentrations in cloud water.
- PFBA, PFPeA, PFHxA, and PFHpA are present at detectable levels.
- PFAS are most correlated with tracers for combustion and dust.
- Case studies show elevated PFAS associated with the following:
  - Combustion particles from the Upper Midwest and Northeastern U.S.
  - African dust
  - Marine air with relatively high sea salt mass concentrations
- These results have the following implications:
  - Demonstrate cloud droplets play a role in how PFAS are distributed globally.
  - Show PFAS in rainwater can come from both cloud droplets and below-cloud scavenging.
  - Provide validation data for past and future modeling studies simulating airborne PFAS life cycles and their influence on cloud droplet thermodynamics.

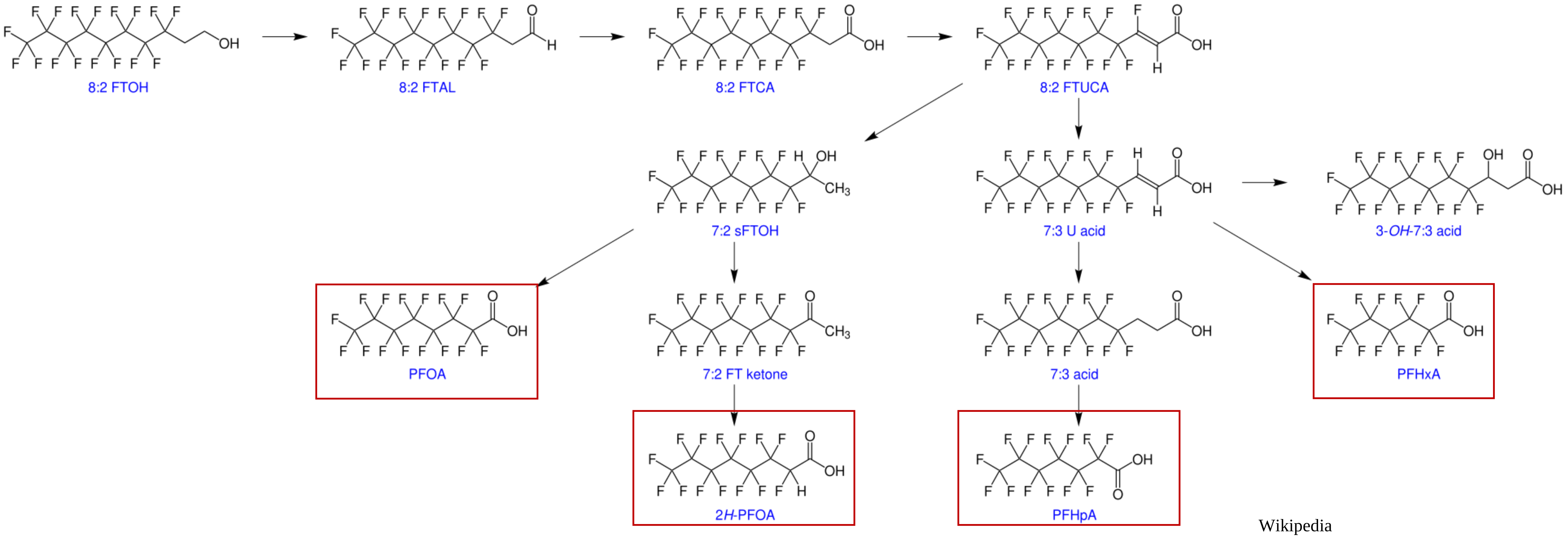
Questions?
evalouedwards@arizona.edu

Backup Slides

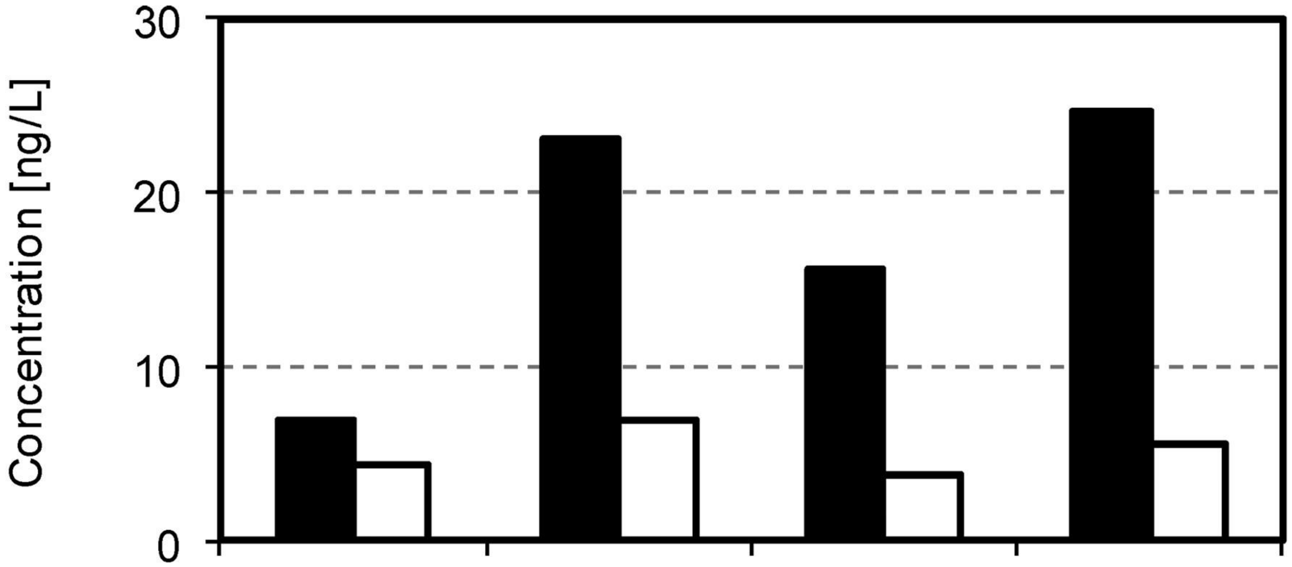
Atmospheric transport of PFAS

2. Degradation of volatile precursors (e.g., fluorotelomer alcohols [FTOHs])

At least 20 days

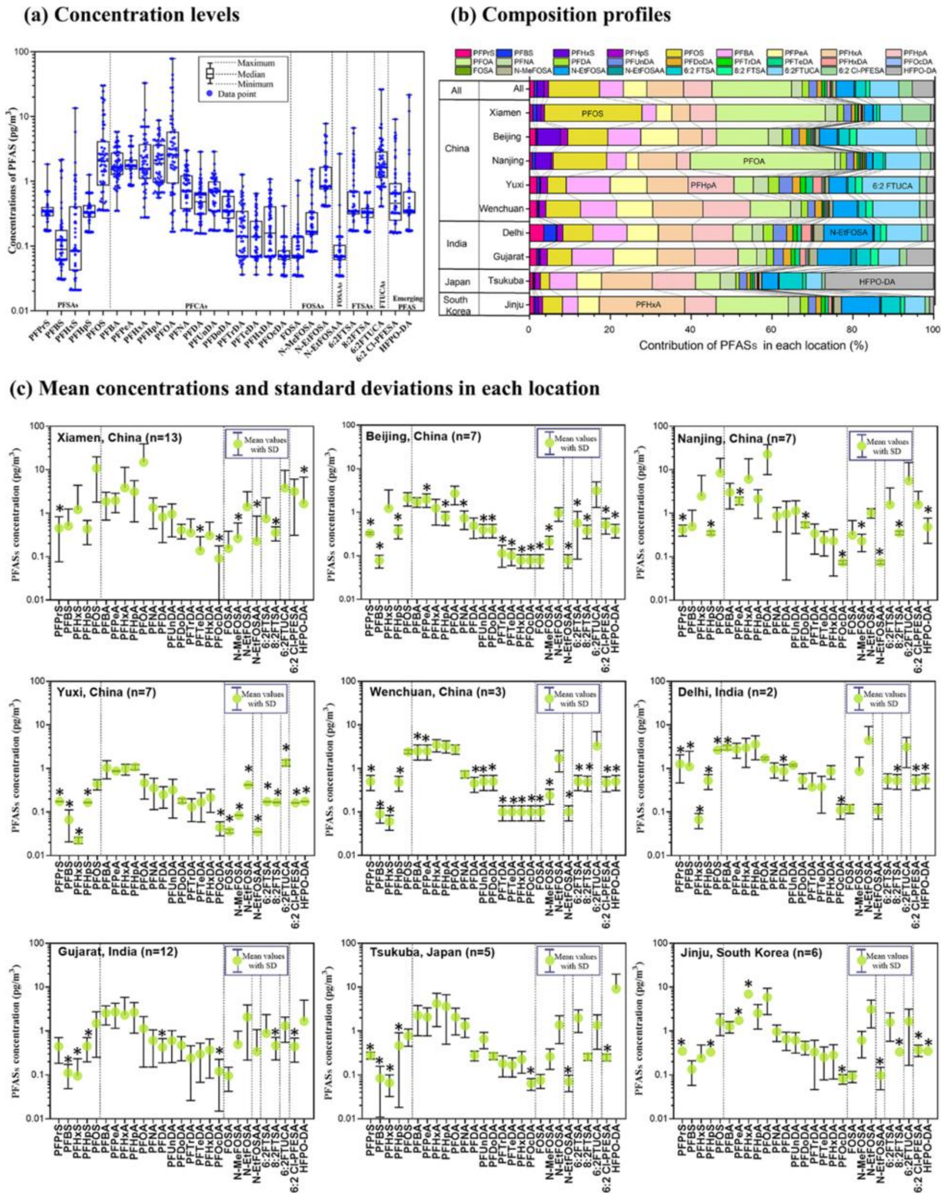


Wikipedia

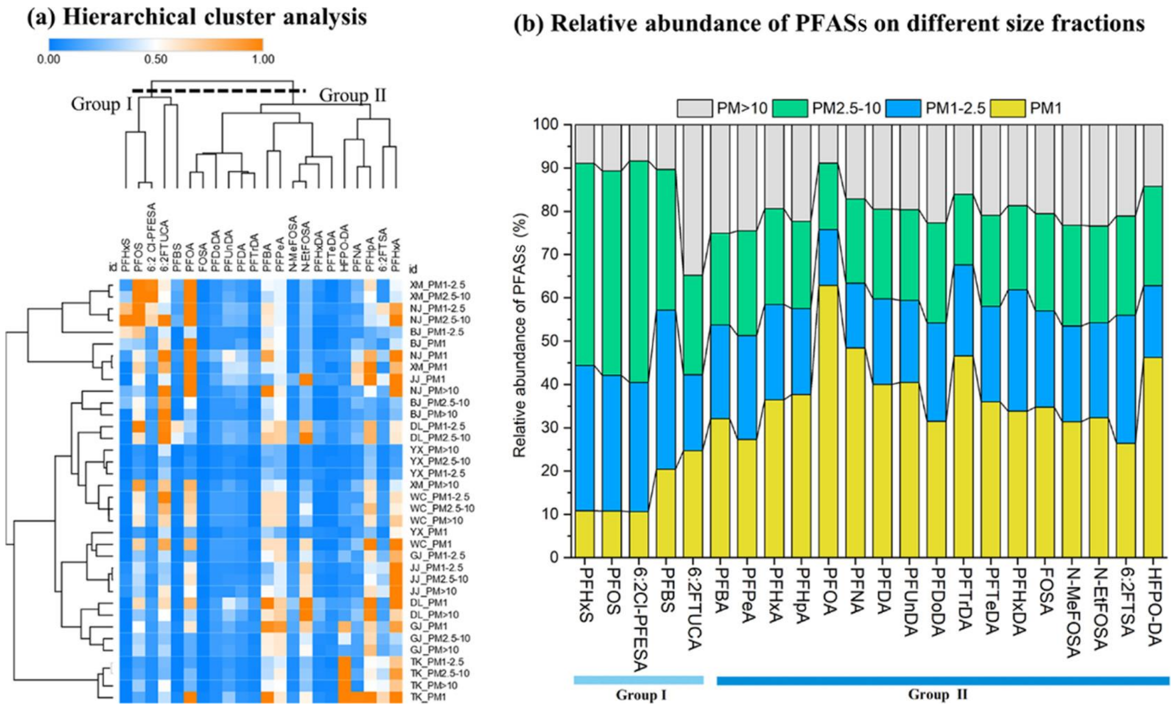


Day	23rd 24th	29th–30th 30th–31st	19th 19th–20th	11th–12th 12th–13th
Month Year	Oct 2006	Jul 2007	Oct 2007	Jan 2008
Location	Tsukuba	Tsukuba	Kawaguchi	Kawaguchi
Precipitation [mm]	22.4 9.6	37.4 20.1	7.4 9.6	5.7 4.5

Kwok et al. (2010)



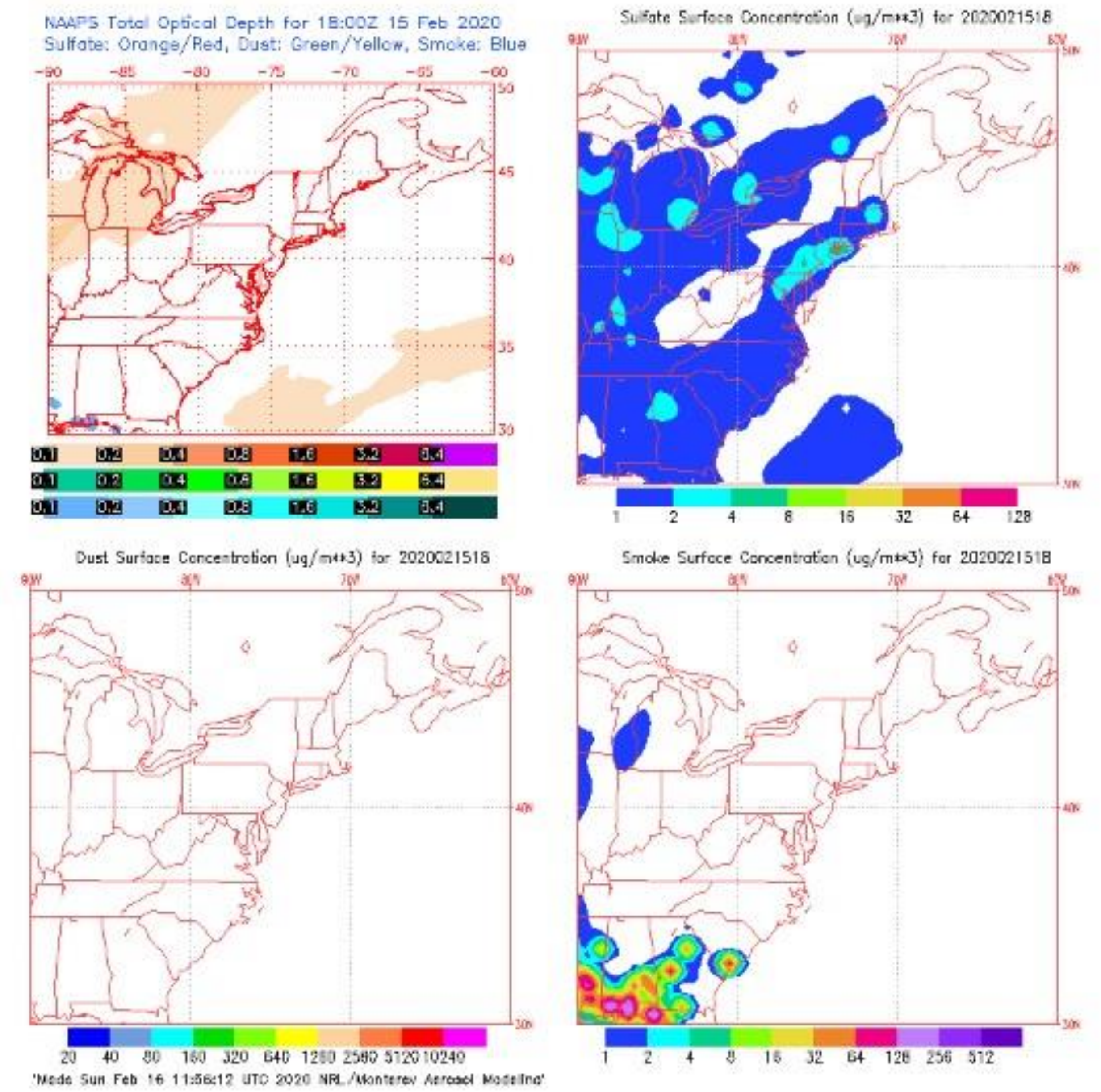
Lin et al. (2020)



Lin et al. (2020)

PFAS in ACTIVATE cloud water

Statistic	Units	PFBA	PFPeA	PFHxA	PFHpA
N samples		13	57	57	60
Median	pg m^{-3}	0.11	0.03	0.03	0.03
Mean		0.13	0.04	0.04	0.05
Std. Deviation		0.07	0.03	0.05	0.08
Minimum		0.02	0.004	0.003	0.003
Maximum		0.25	0.15	0.24	0.43


NAAPS Total Optical Depth for 18:00Z 15 Feb 2020
Sulfate: Orange/Red, Dust: Green/Yellow, Smoke: Blue
Sulfate Surface Concentration (ug/m**3) for 2020021518
Dust Surface Concentration (ug/m**3) for 2020021518
Smoke Surface Concentration (ug/m**3) for 2020021518
'Made Sun Feb 16 11:56:12 UTC 2020 NRL/Monterey Aerosol Modeling'

Agenda

- What are per- and polyfluoroalkyl substances (PFAS)?
- Sources of PFAS
- Motivation to quantify and monitor PFAS in the environment
- Current understanding of airborne PFAS
- Methods
- PFAS in ACTIVATE cloud water samples
- Sources/particle types associated with PFAS
- Case studies
- Conclusions and discussion