Sources, Fate and Effects of PFAS

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September 09, 2020

Biogeochemistry of Global Contaminants HARVARD

1) Effects 2) Sources 3)Fate of PFAS

Harvard John A. Paulson School of Engineering and Applied Sciences

HARVARD | SCHOOL OF PUBLIC HEALTH

Department of Environmental Health

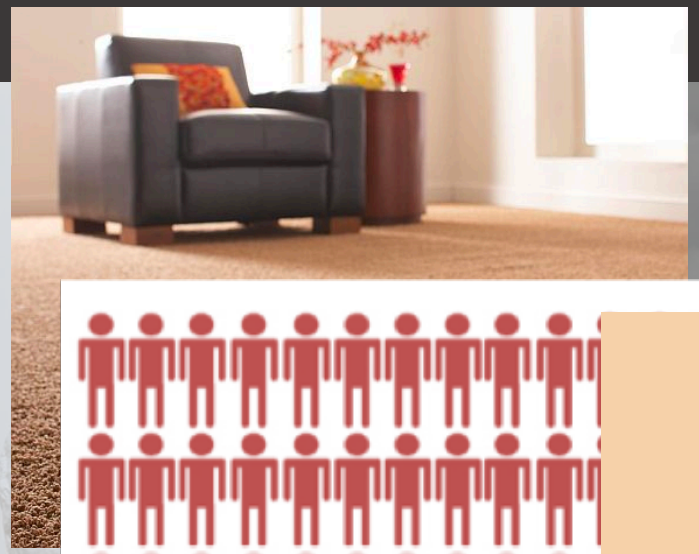
STEEP Sources, Transport, Exposure & Effects of PFASs

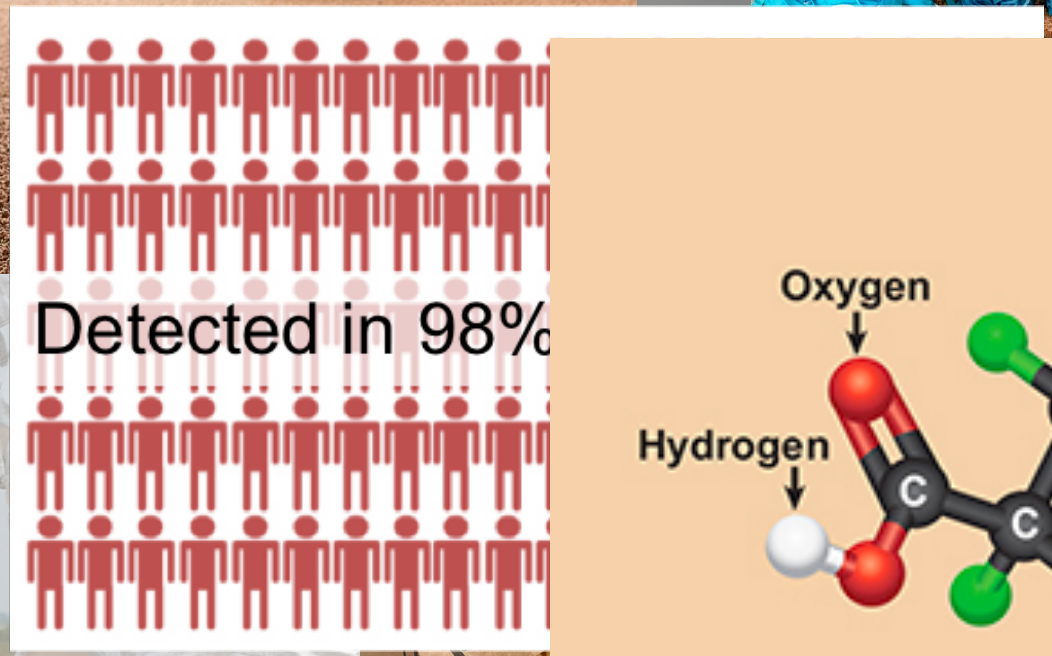
UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

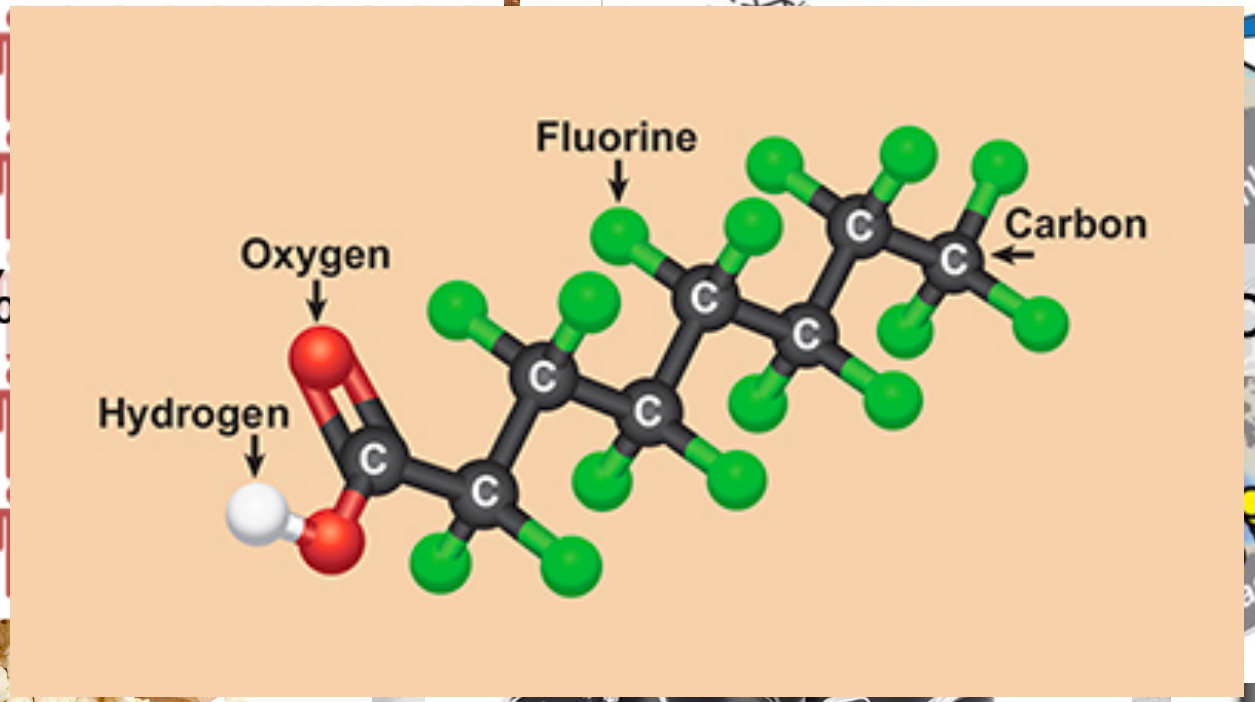
SERDP DOD · EPA · DOE

NIEHS National Institute of Environmental Health Sciences

Poly- and Perfluoroalkyl Substances (PFAS)







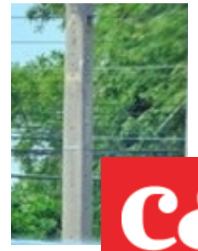
Toxic PFAS Found In 21 Places In Massachusetts

Nearly 200,000 Massachusetts residents have been exposed to toxic PFAS found in drinking water, environmental advocates said.

PFAS Contamination of Drinking Water Far More Prevalent Than Previously Reported

New Detections of 'Forever Chemicals' in New York, D.C., Other Major Cities

Reply



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U.S.

Air Contamination From 'Forever' Chemicals Sparks Concern

Groups sue to stop incineration of compounds linked to cancers

By Kris Maher | Photographs by Kristian Thacker for The Wall Street Journal

March 21, 2020 8:00 am ET

PRINT TEXT 20

EAST LIVERPOOL, Ohio—From her backyard, Sandy Estell can see an incinerator—a white complex of buildings along the Ohio River—owned by a company with a Defense Department contract to burn more than 800,000 gallons of firefighting foam and related waste.

RECOMM

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Debate Over Science And Risks Shapes 3M's Lawsuit Against N.H.'s PFAS Water Standards

Latest Issues SCIENTIFIC AMERICAN 175 Cart 0 Sign In | St

'Forever Chemicals' Are Building Up in the Arctic—and Likely Worldwide

c&en CHEMICAL & ENGINEERING NEWS TOPICS MAGAZINE COLLECTIONS VIDEOS JOBS

PERSISTENT POLLUTANTS

Chemours must keep PFAS from North Carolina river

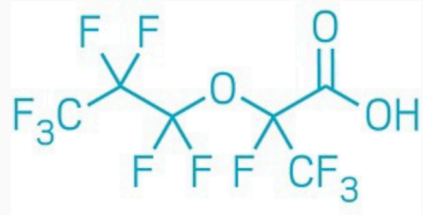
State requires company to clean up groundwater and runoff

*by **Cheryl Hogue***

AUGUST 17, 2020

Chemours must prevent highly persistent fluorinated compounds from seeping from or washing off its factory site near Fayetteville, North Carolina, the state has ordered.

The North Carolina Department of Environmental Quality (DEQ) this month **added conditions** to a 2019 consent order requiring Chemours to halt releases of **per- and polyfluoroalkyl substances** (PFAS) from manufacturing operations, such as from stack emissions or wastewater discharge. The new requirements address residual PFAS pollution at the property, including **hexafluoropropylene oxide dimer acid** (HFPO-DA), a



HFPO-DA

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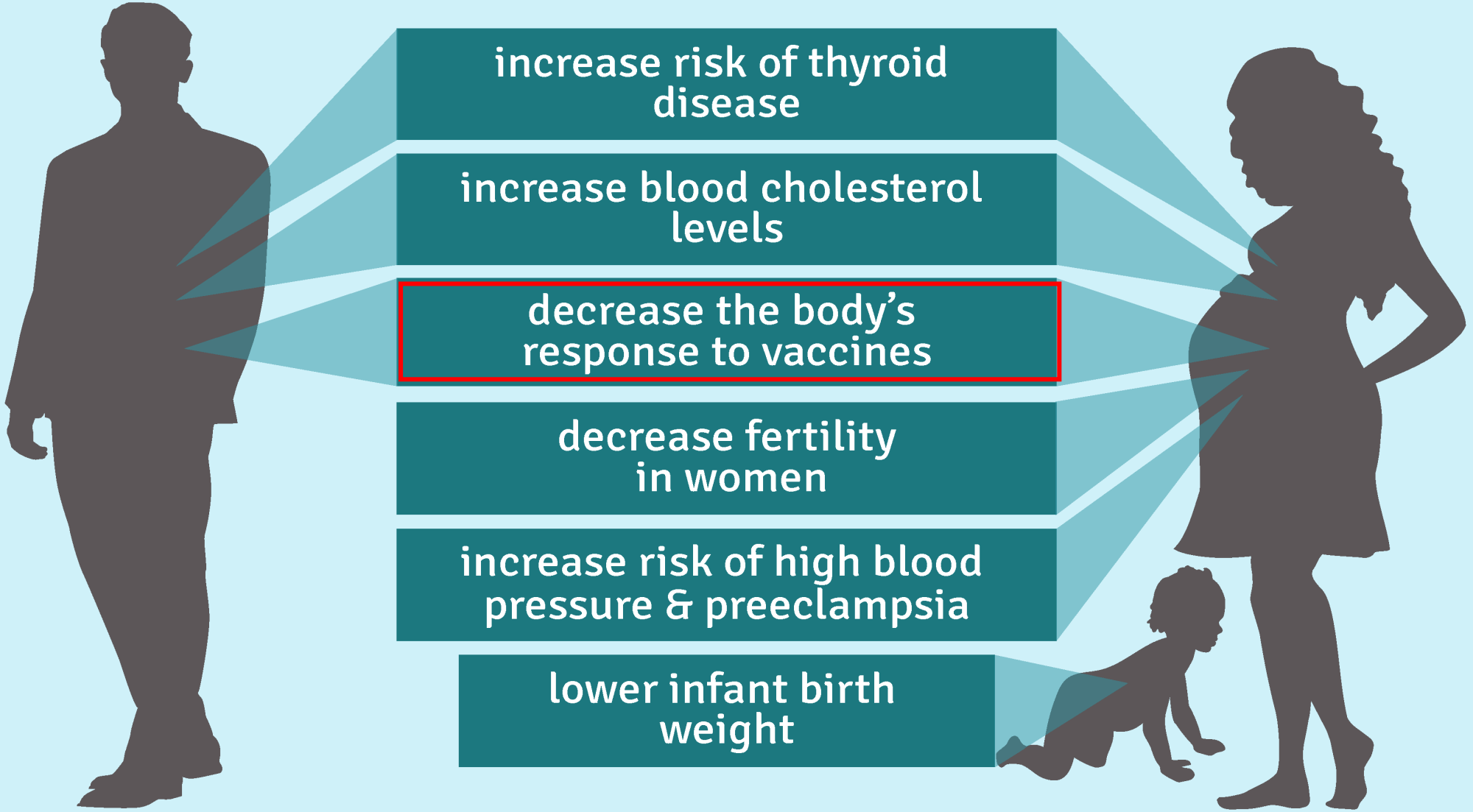
1) Effects: PFAS exposure has been linked to diverse adverse health effects on humans

No consistent mode of action across compounds studied – raising questions about how to regulate (compound specific or as a class?)

Human studies suggest PFAS exposure may...

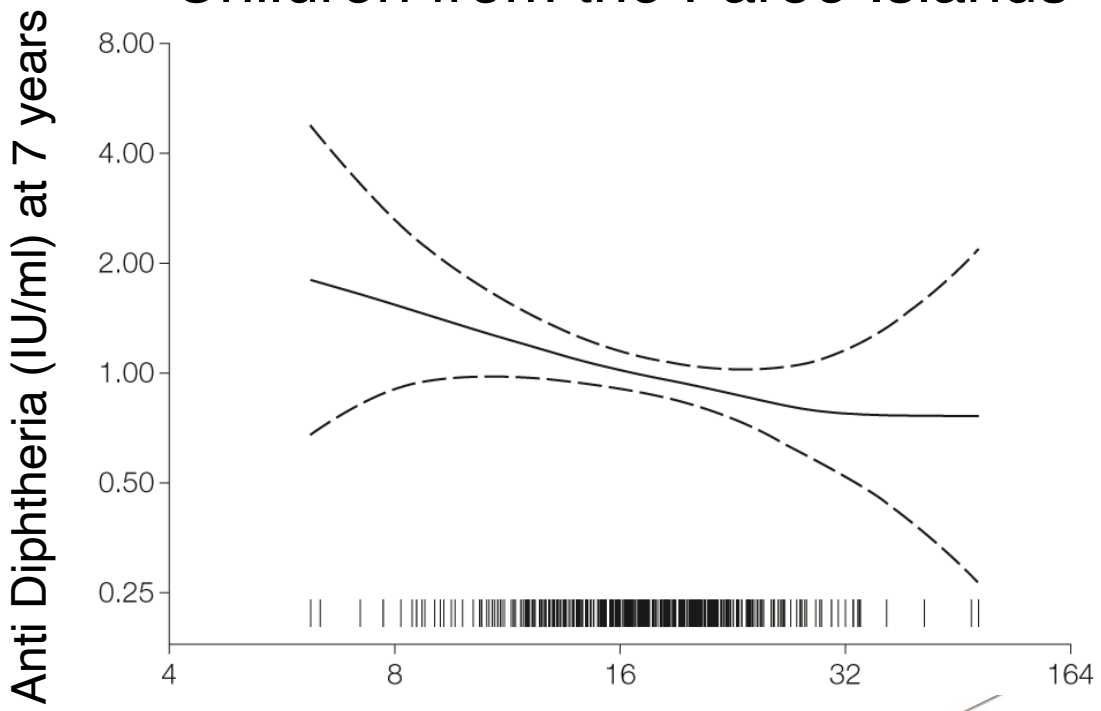


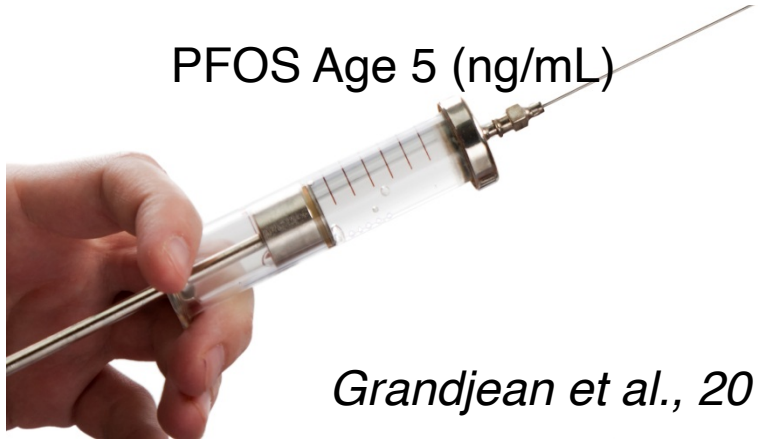
Information sourced from Agency for Toxic Substances and Disease Registry

Slide from: https://ncpfastnetwork.com/printed-materials/

PFAS suppresses immune response following vaccination in Faroese birth cohort

Children from the Faroe Islands





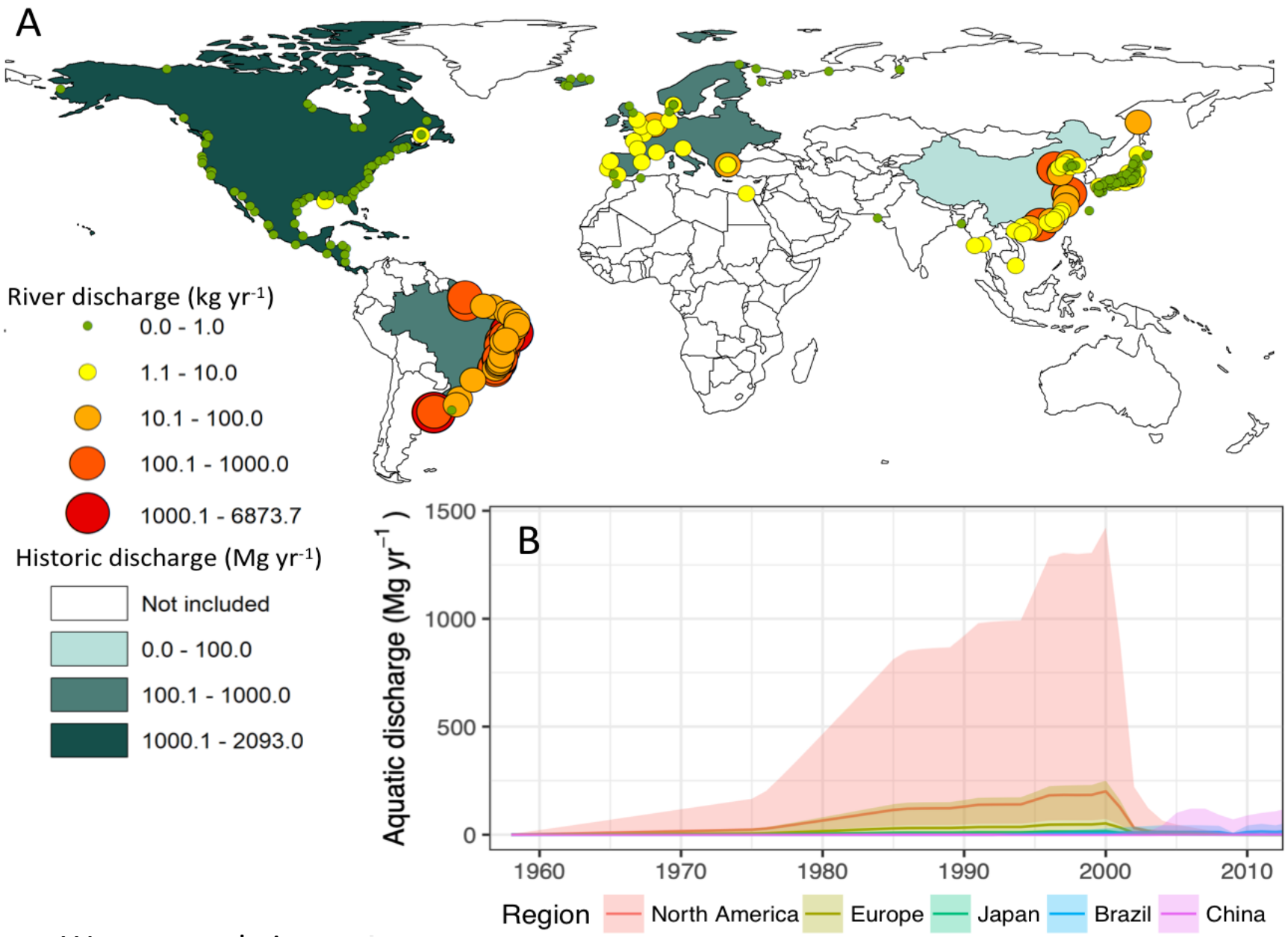
Grandjean et al., 2012

50% Reduction in antibody concentrations for each doubling of PFAS

2) Sources: Chemical production is changing rapidly and we are not able to detect most PFAS in use today using traditional techniques

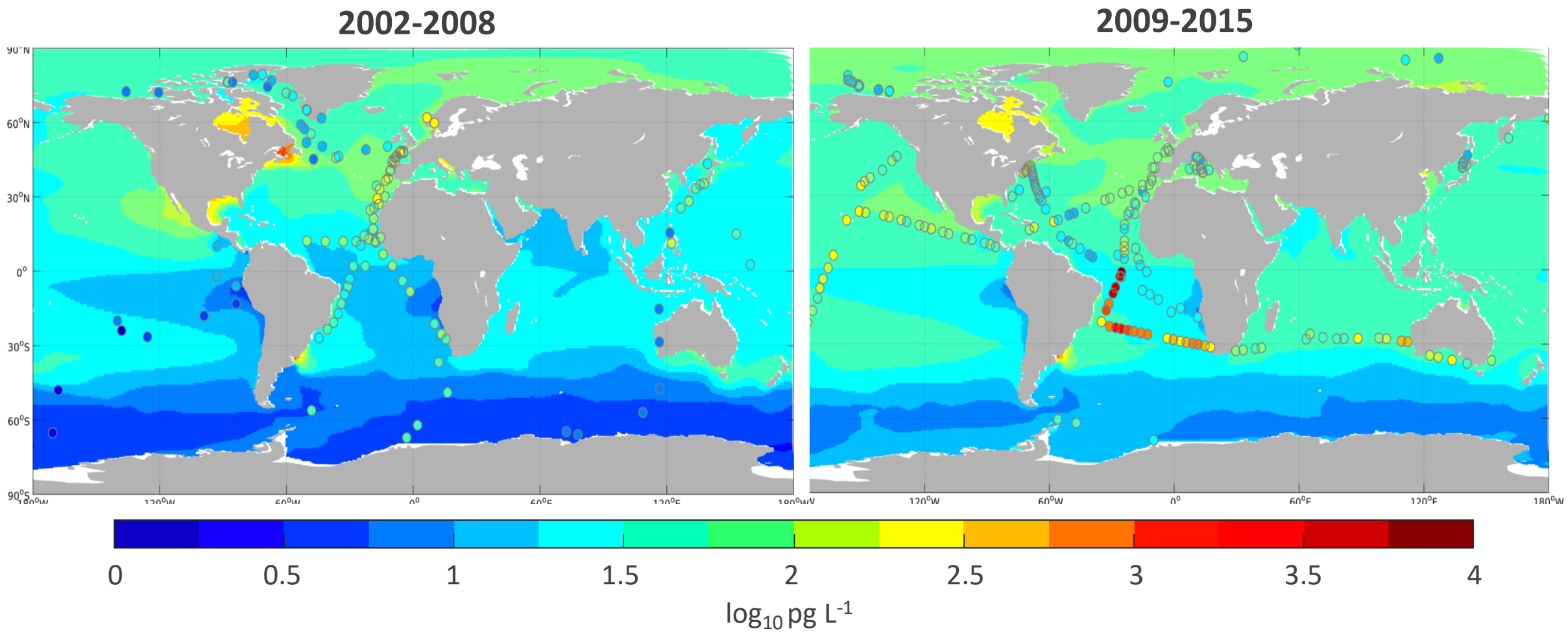
Focus of research on aqueous discharges next to contaminated sites; understanding of atmospheric sources and fate huge gap right now!

Large declines in global PFOS discharges from rivers to the oceans since the year 2000



Wagner et al., in prep

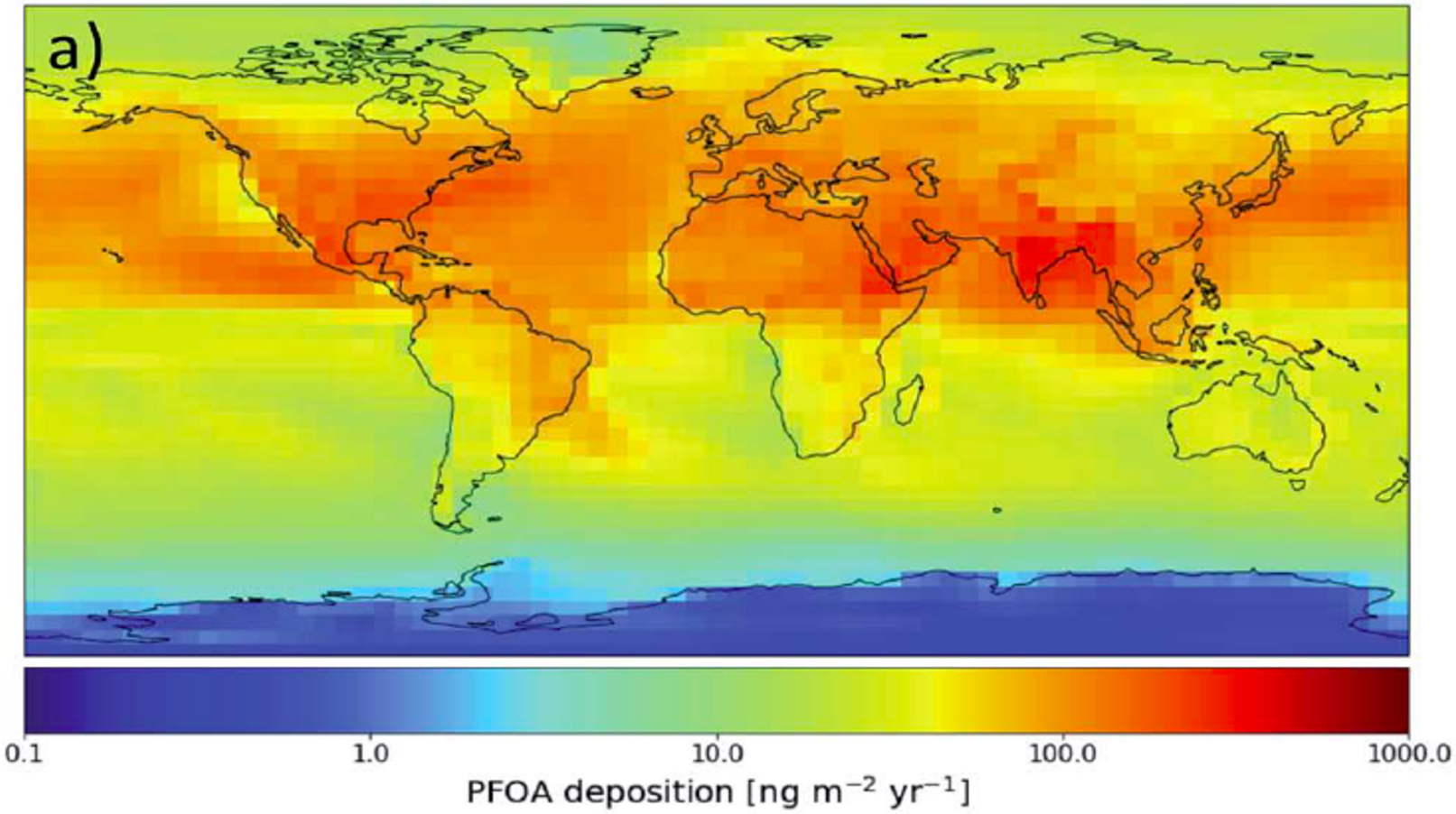
Global modeling underestimates Southern Ocean concentrations – likely due to missing atmospheric sources



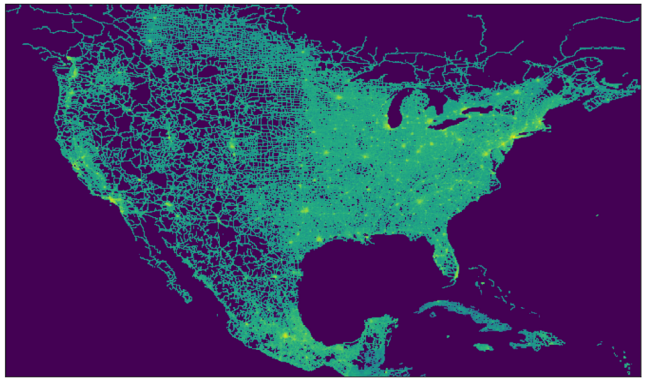
Wagner et al., in prep

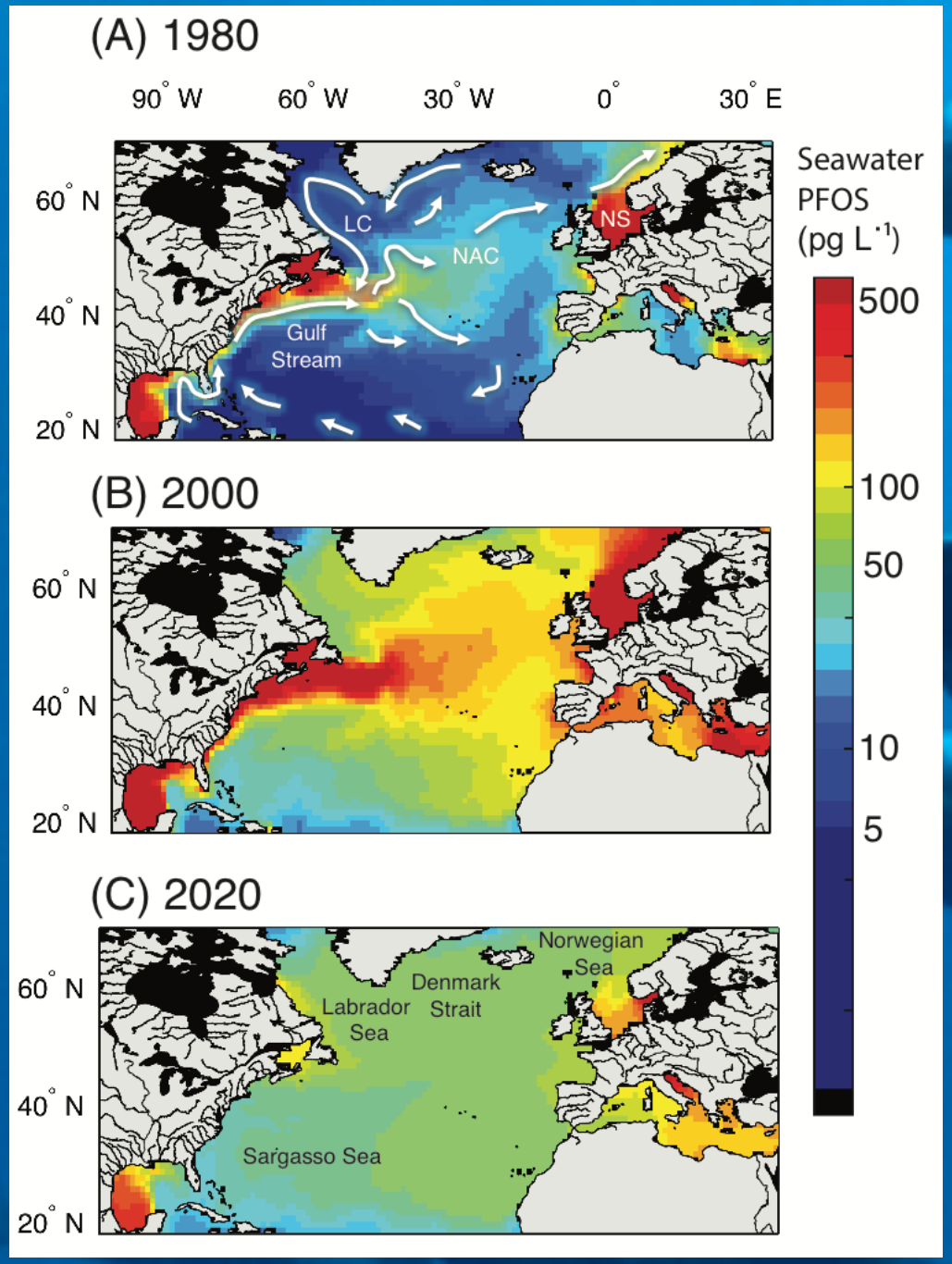
We are developing an improved atmospheric simulation for PFAS in GEOS-Chem: Need more measurements!

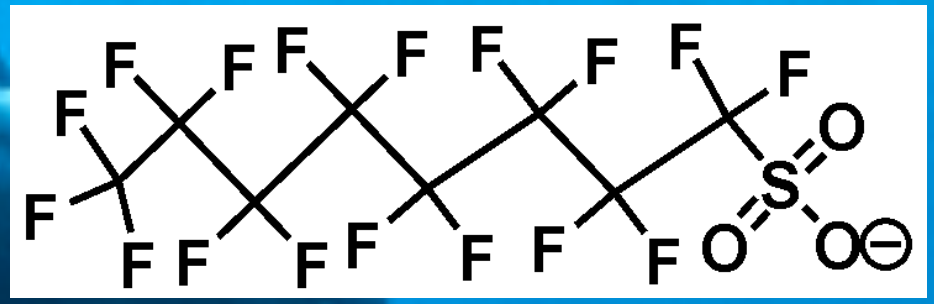
GEOS-Chem 2015 annual average PFOA deposition using a high emissions scenario. (Thackray et al, 2020)



- Global emissions of precursor compounds based on Wang et al. (2014) production/composition estimates
- Spatial distribution of emissions was previously assumed to follow the same pattern as NOx (originally used a 4x5 degree grid)



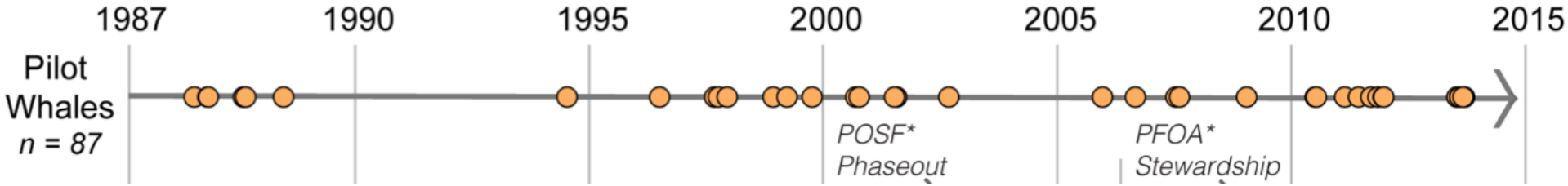




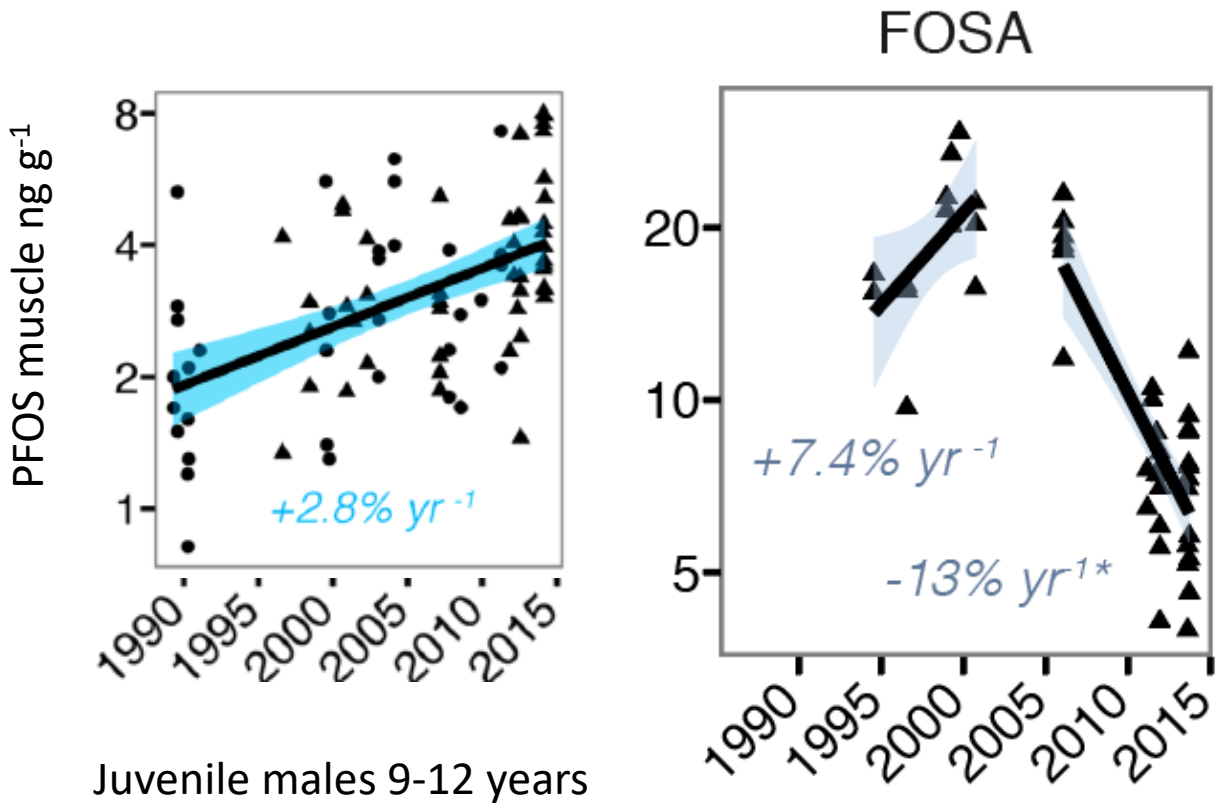
Large and rapid declines in modeled North Atlantic seawater PFOS (10 m)

X. Zhang et al., 2017, Global Biogeochemical Cycles

Measured targeted PFAS concentrations in North Atlantic pilot whales shows a rapid decline in FOSA, a PFOS precursor since 2000

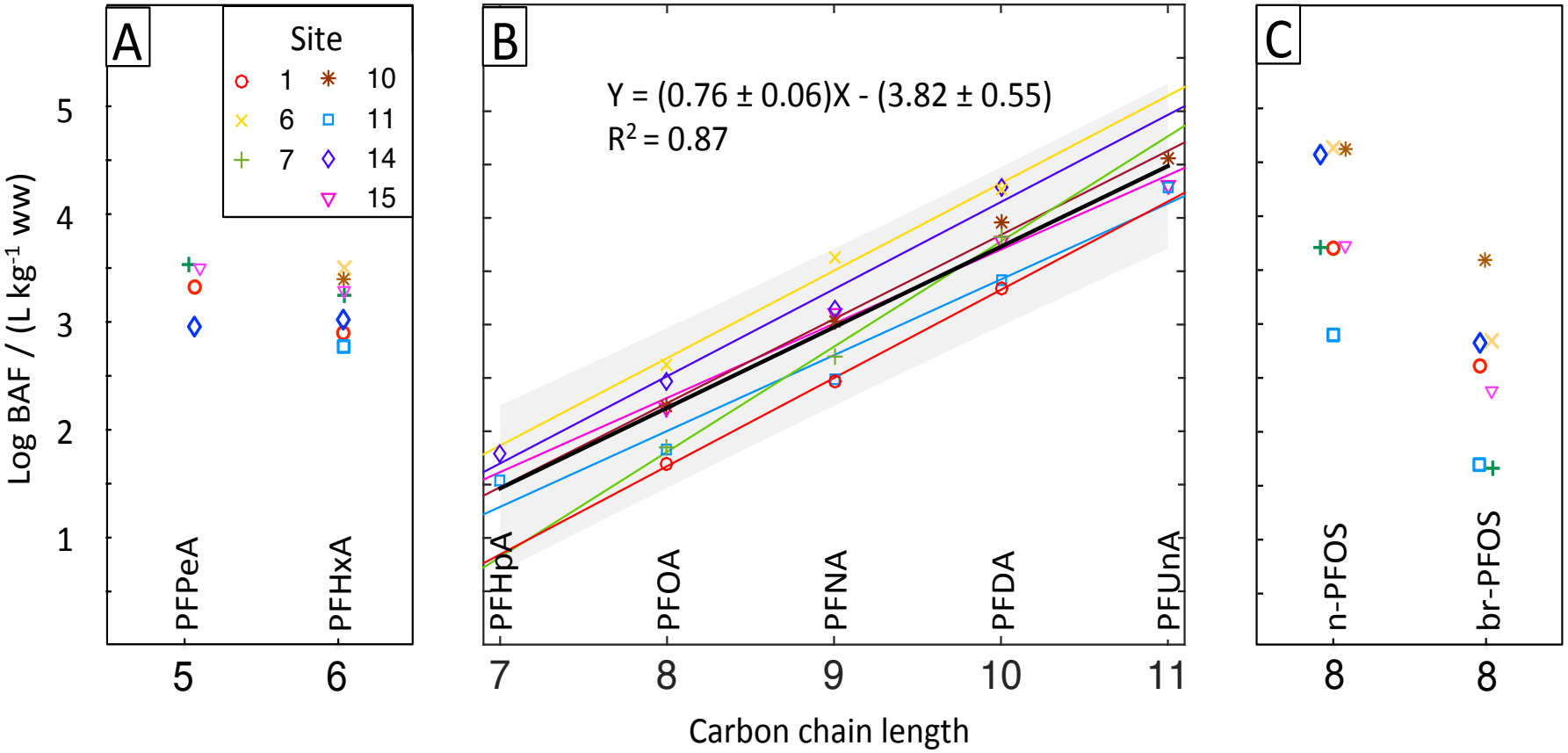


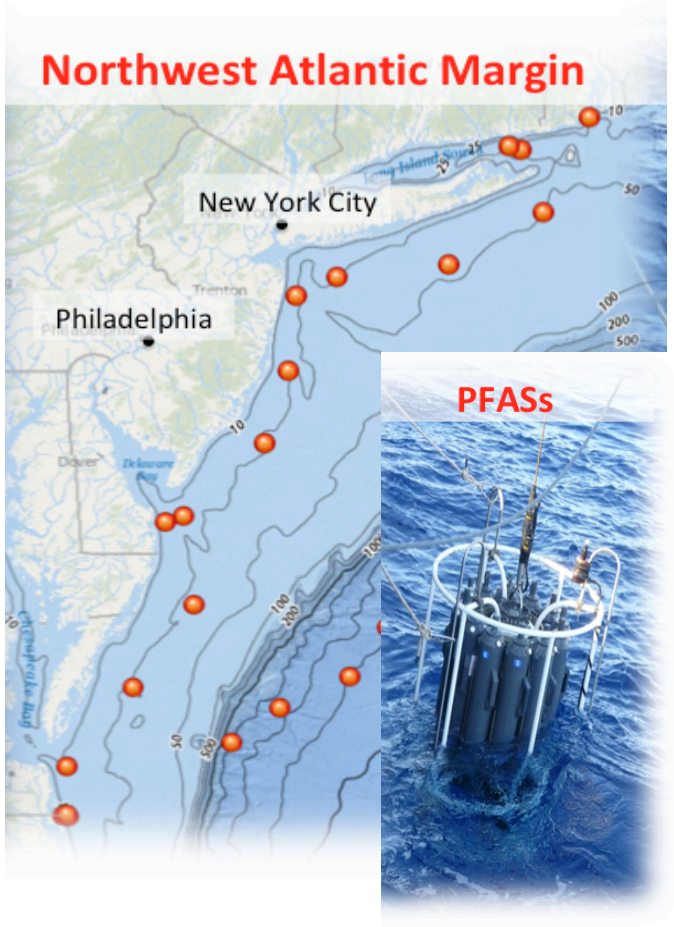
Dassuncao et al., 2017, ES&T



Juvenile males 9-12 years

PFAS measurements in plankton suggest some precursors and linear isomers may bioaccumulate more than the terminal PFAA

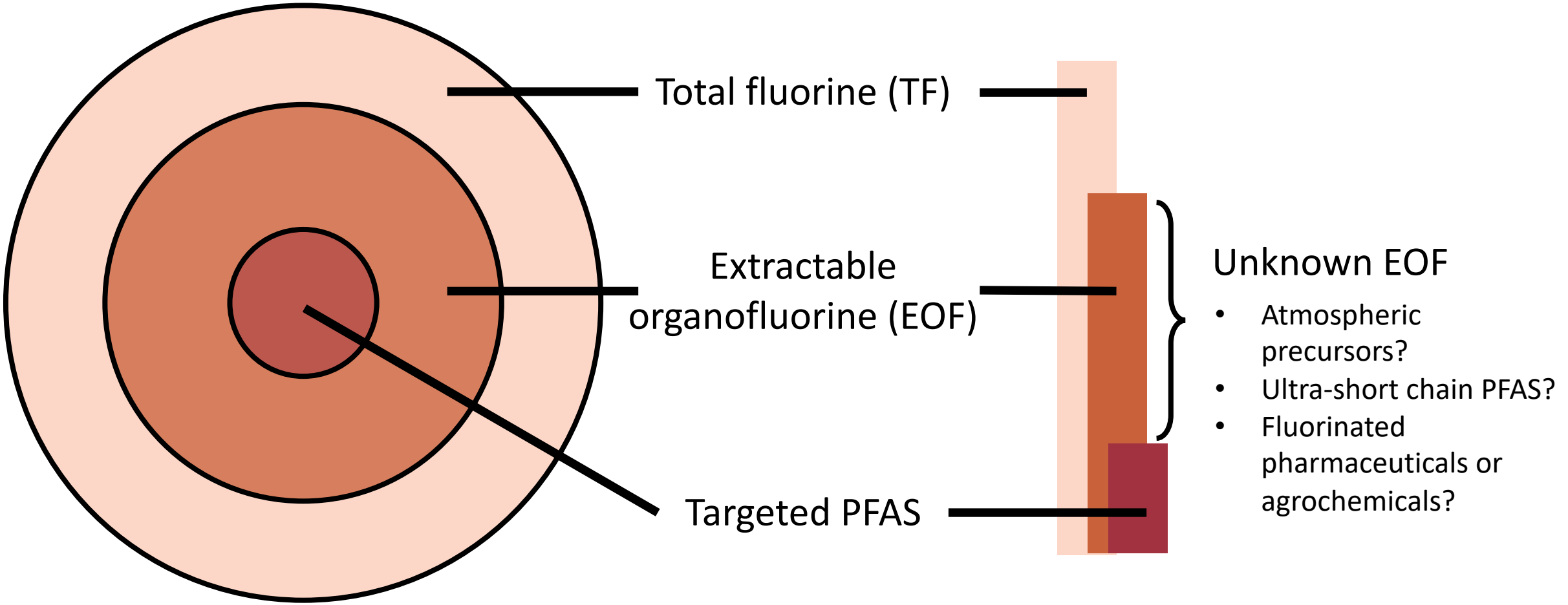




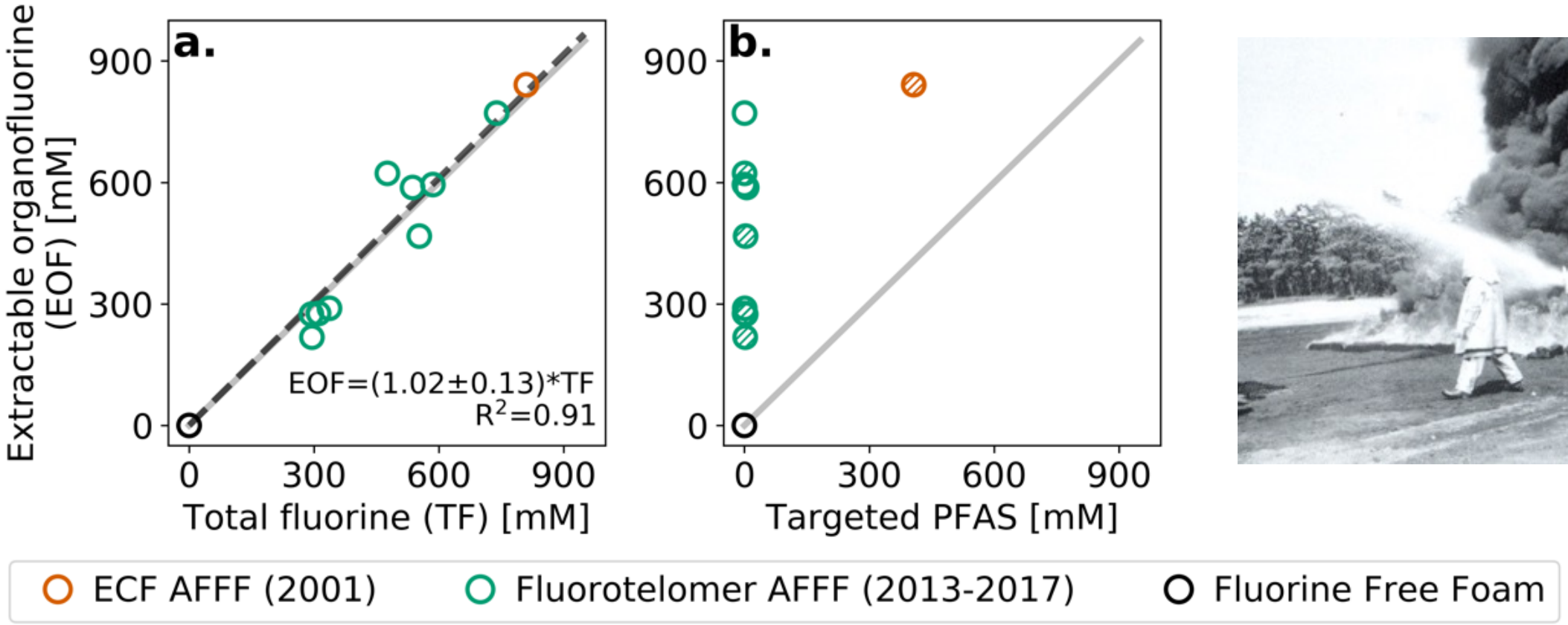
Zhang et al., 2019, Environmental Science & Technology

Gap in analytical methods for PFAS detection:
Most PFAS in AFFF and other media are not detected by targeted analysis

Targeted analysis is limited to a few dozen PFAS with analytical standards



Targeted analysis underestimates PFAS by 50% in ECF AFFF (legacy) and >99% in FT AFFF (contemporary)

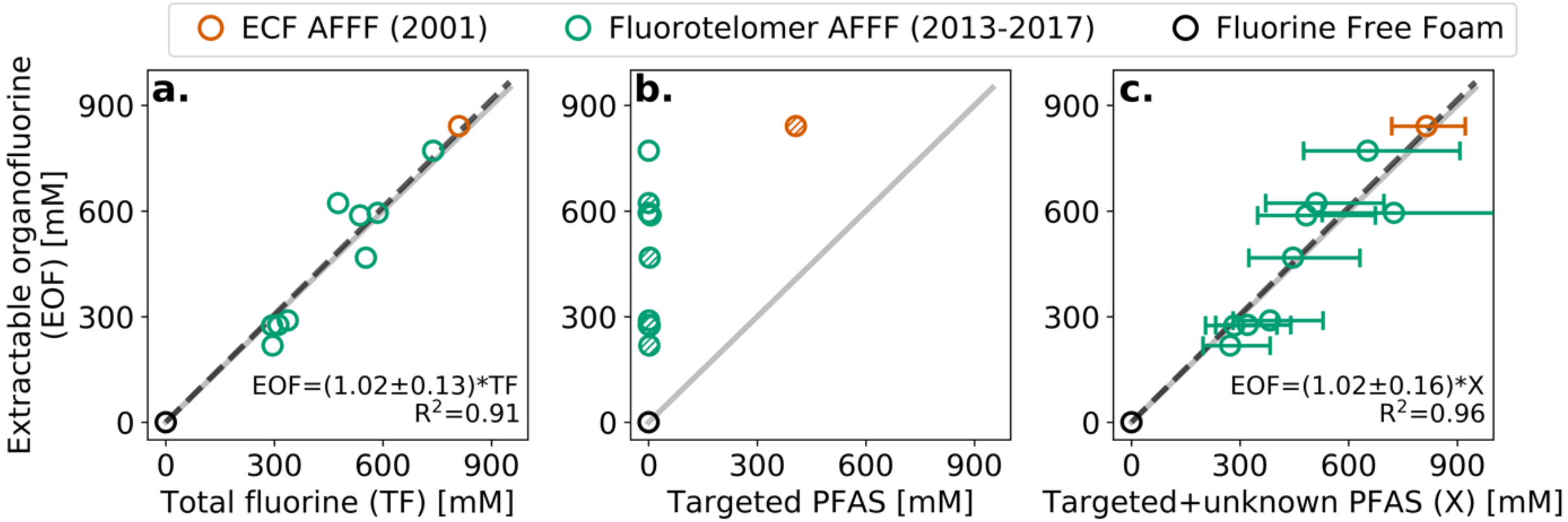


United States Environmental Protection Agency

National Institute of Environmental Health Sciences

Ruyle BJ, Thackray CP, McCord JP, Strynar MJ, Mauge-Lewis KA, Fenton SE, Sunderland EM. Reconstructing the composition of PFAS in contemporary AFFF. In review.

We developed a method for *quantifying* unknown compounds using the total oxidizable precursor (TOP) assay and Bayesian inference that closes PFAS mass budget



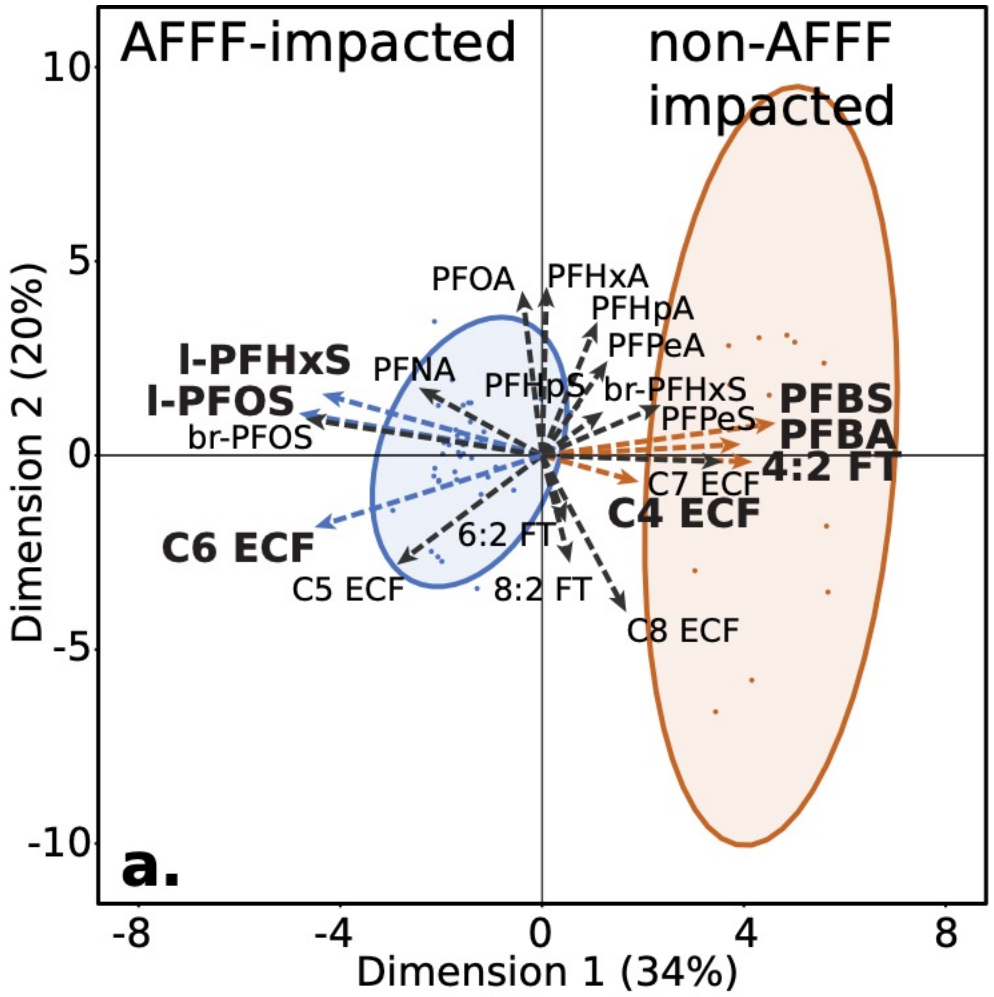
EPA United States Environmental Protection Agency

NIH National Institute of Environmental Health Sciences

Ruyle BJ, Thackray CP, McCord JP, Strynar MJ, Mauge-Lewis KA, Fenton SE, Sunderland EM. Reconstructing the composition of PFAS in contemporary AFFF. In review.

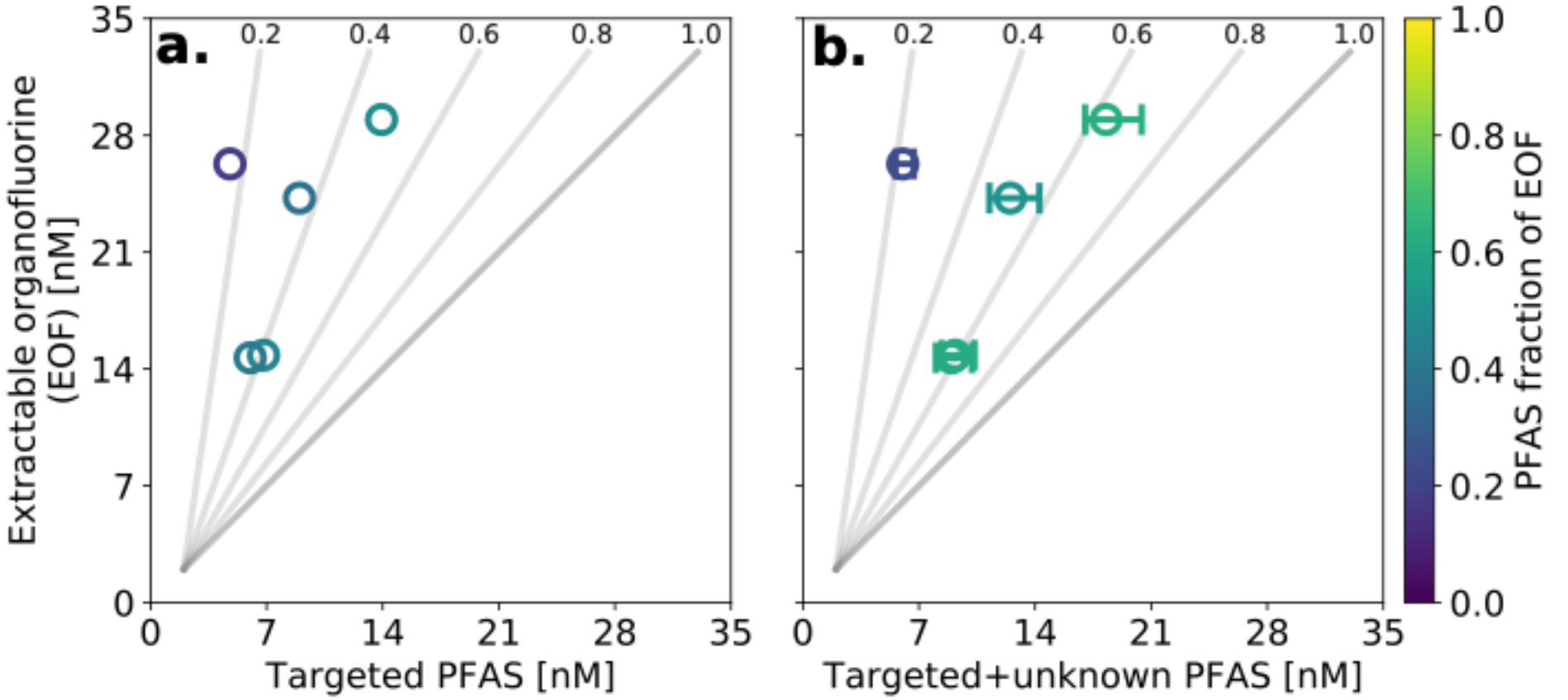
PFAS signature from AFFF in Cape Cod coastal watersheds is distinct from other background sources

AFFF signature is enriched in C6 PFAS



Ruyle BJ, Pickard HM, LeBlanc DR, Tokranov AK, Thackray CP, Hu XC, Vecitis CD, Thackray, CP, Sunderland EM. PFAS Precursor Transformations and Unexplained EOF in AFFF-Impacted Coastal Watersheds. In revision.

There is a large unidentified PFAS signature (~50% EOF) in Cape Cod coastal watersheds – unlikely to have originated from AFFF use



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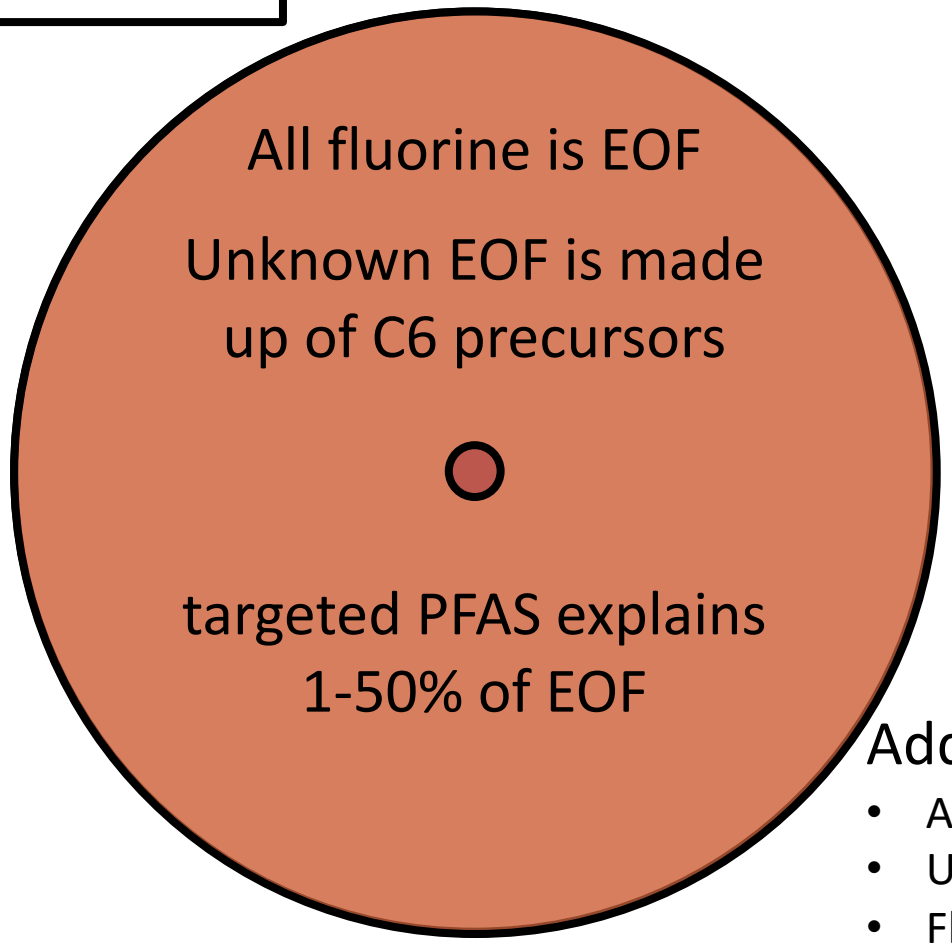
Downstream environment reflects AFFF signature (C6 PFAS) with substantial additional sources that are overlooked in routine site assessment

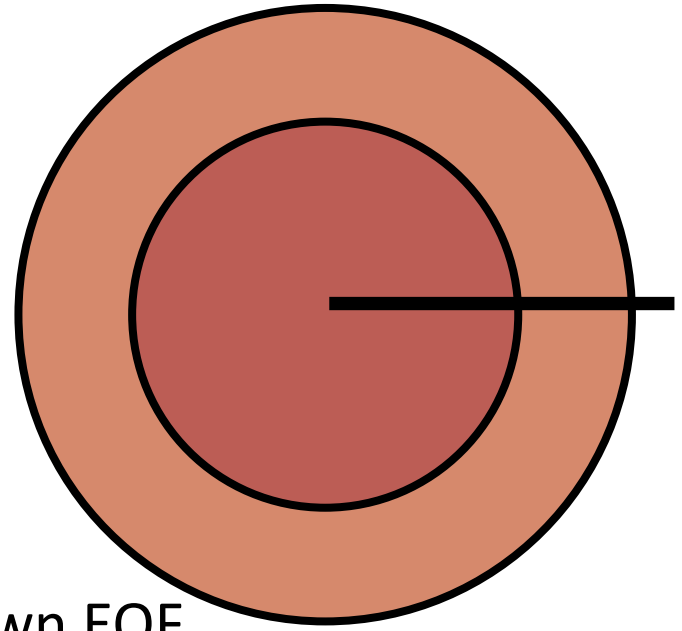
EOF
Targeted PFAS

AFFF



AFFF-impacted surface water
Cape Cod

Targeted PFAS+TOP assay explains half of EOF

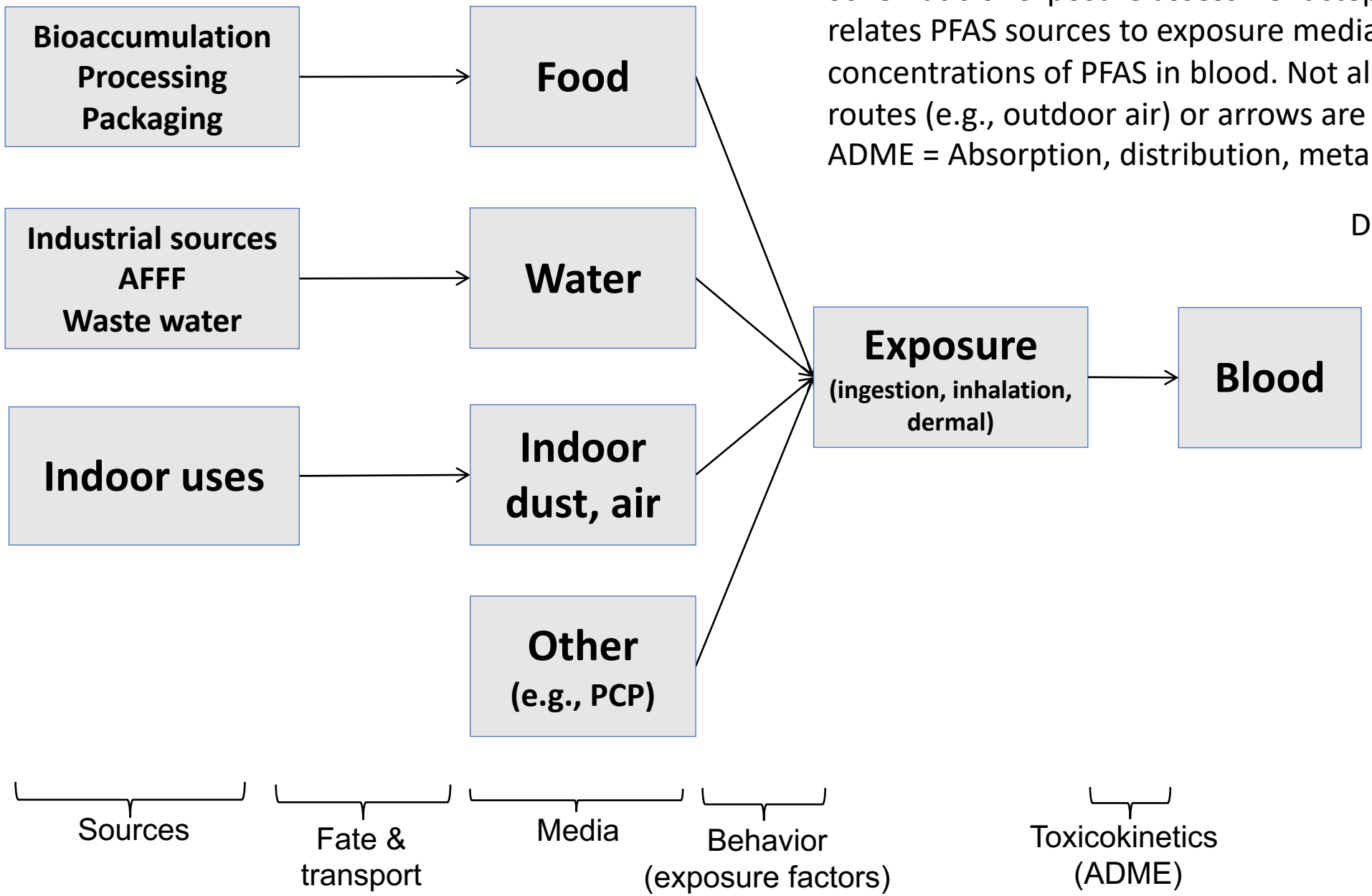


Additional unknown EOF

- Atmospheric precursors?
- Ultra-short chain PFAS?
- Fluorinated pharmaceuticals or agrochemicals?

3) Fate: Endpoints of concern for PFAS are humans and wildlife

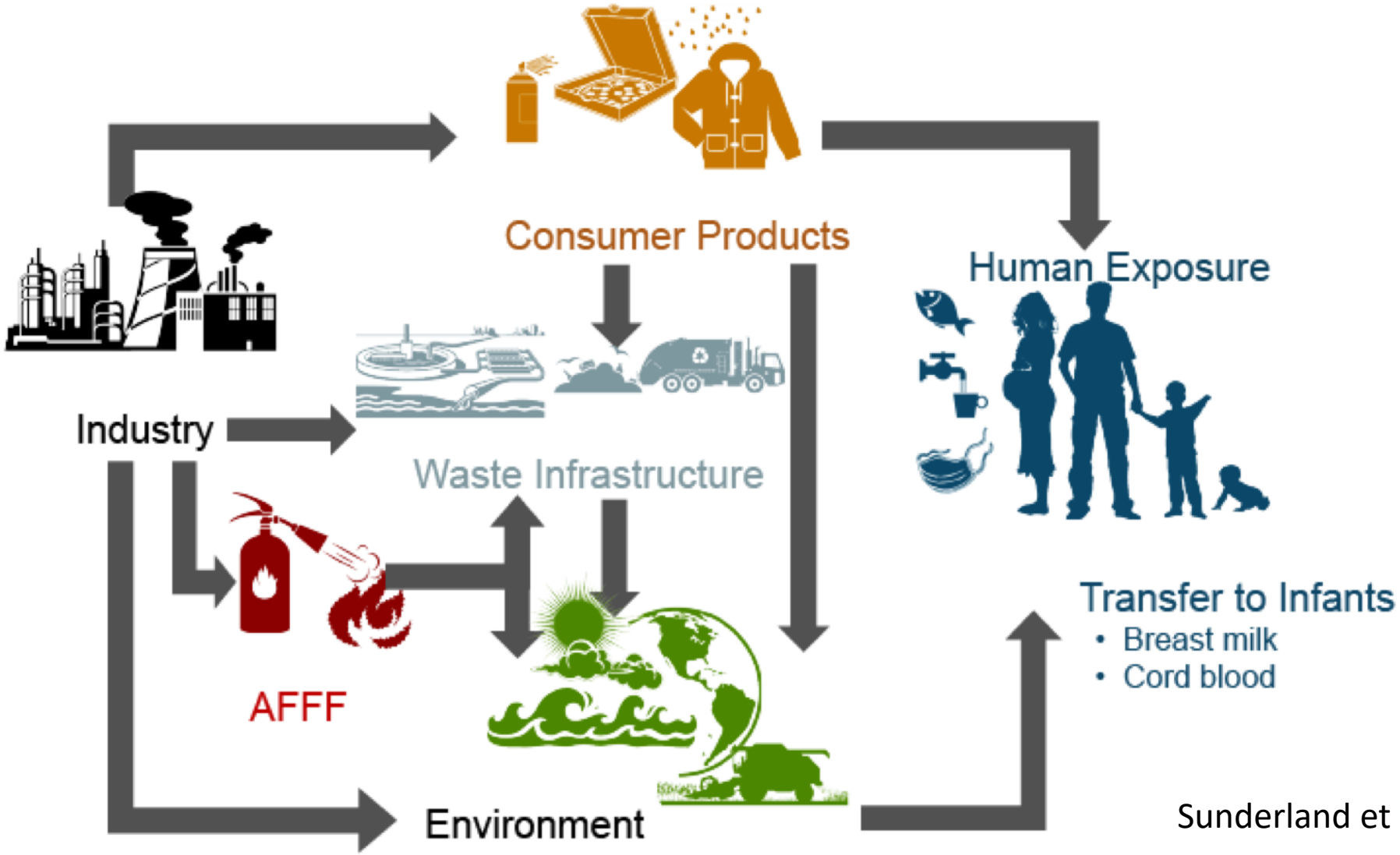
Human exposures at contaminated sites are dominated by contaminated drinking water. For the general population the relative importance of different exposure pathways is extremely uncertain.



Schematic of exposure assessment steps for humans that relates PFAS sources to exposure media, and internal concentrations of PFAS in blood. Not all possible exposure routes (e.g., outdoor air) or arrows are shown.
ADME = Absorption, distribution, metabolism and excretion.

De Silva et al., in review

Human exposures to PFAS are diverse: Some can be addressed/mitigated faster than others



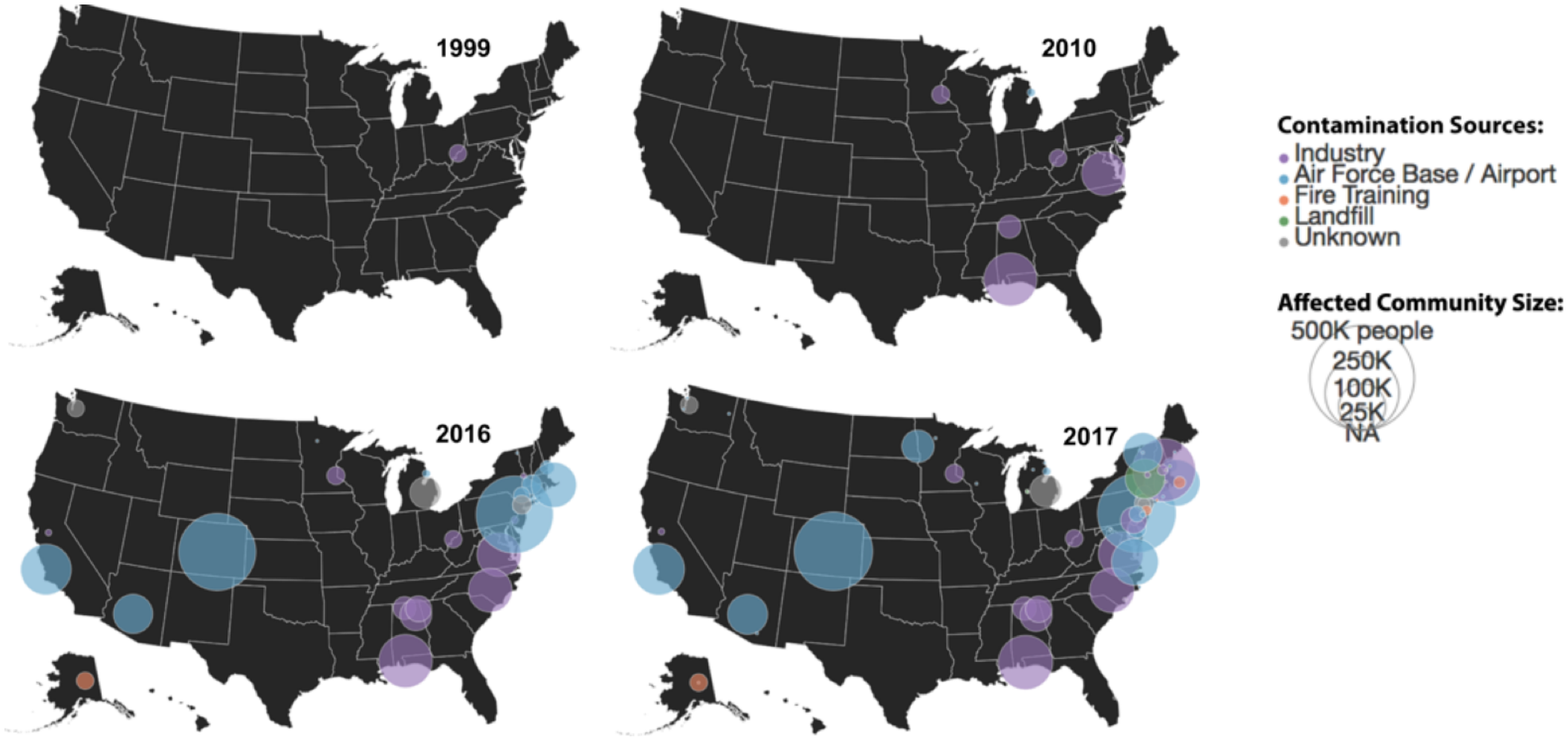
Our focus:

1. **Drinking water**
2. **Seafood**
3. **Consumer Products**

TIMESCALES

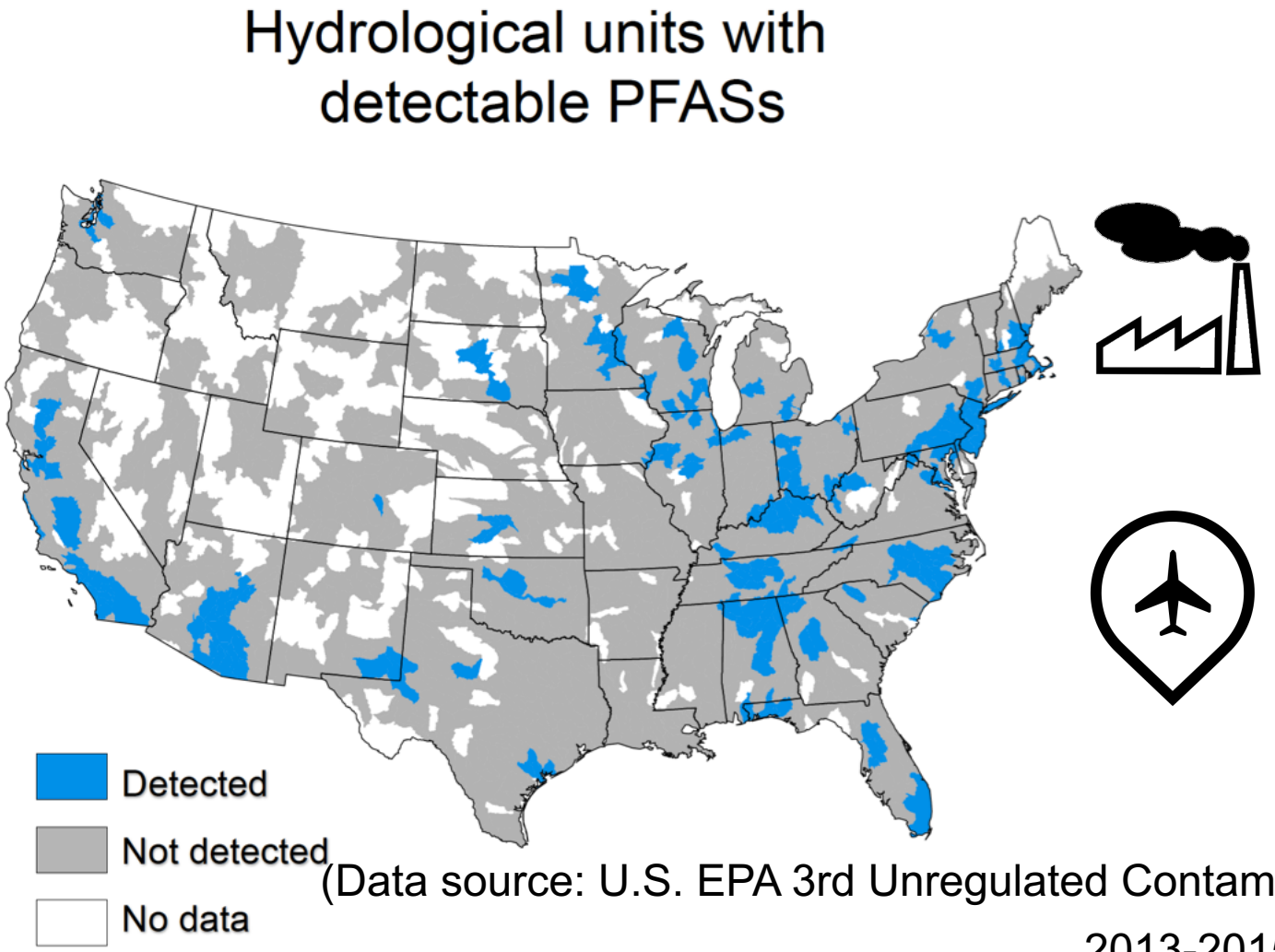
Sunderland et al., 2019, JESEE

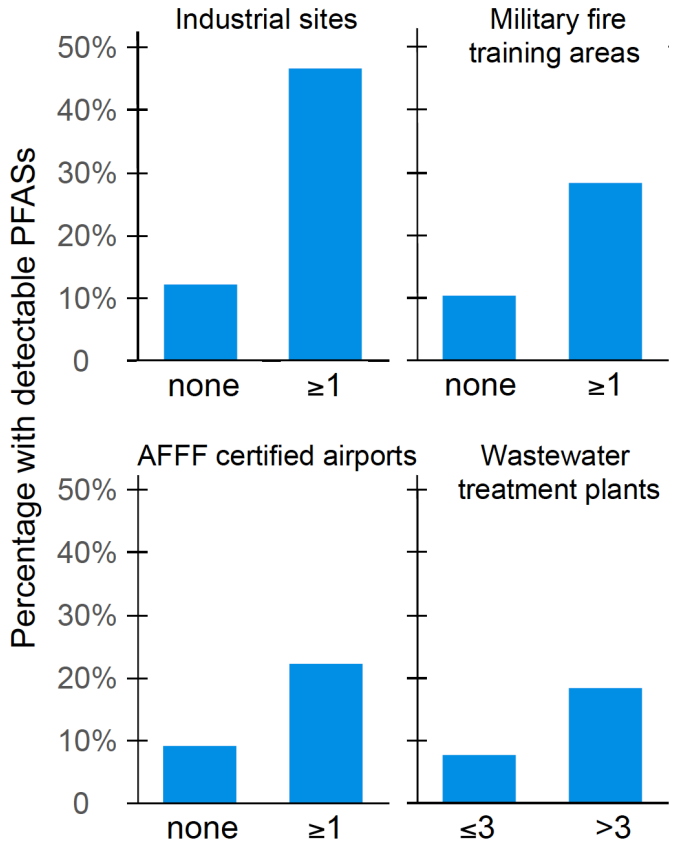
Drinking water is the primary pathway of PFAS exposure next to many contaminated sites



Source: Sunderland et al., 2019 adapted from Northeastern SSERHI data

Detection of PFAS in U.S. drinking water statistically increased with higher point source abundance





(Data source: U.S. EPA 3rd Unregulated Contaminants Monitoring Rule (UCMR3), 2013-2015) (Hu et al., *ES&T Letters*, 2016)

Nurses Health Study, HSPH, a large prospective study of US women est. 1976

1976

Enrollment

n = 121,319

1989/1990

Serum and tap water collection

n = 32,826

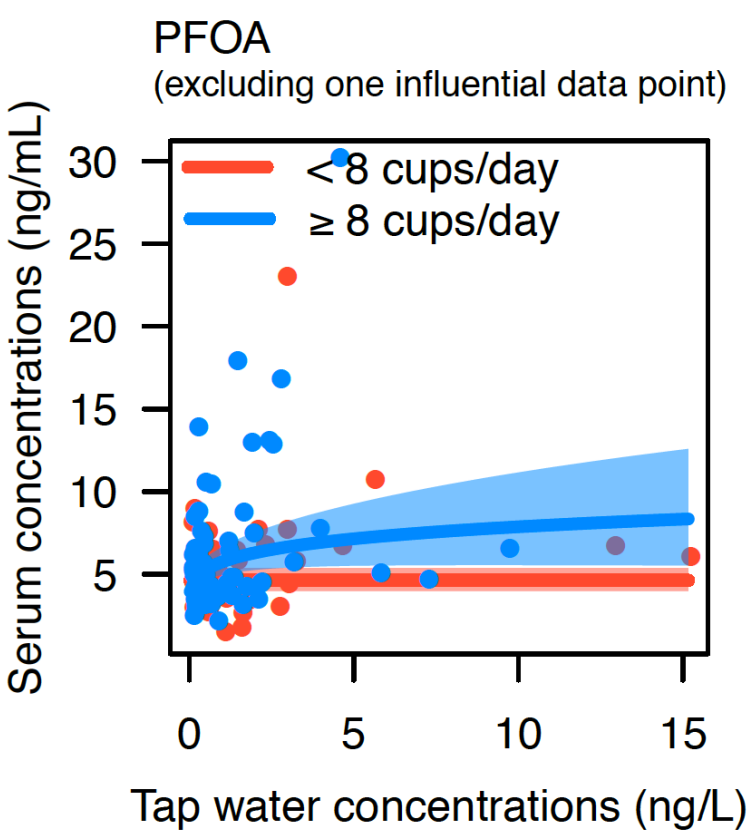
Dietary

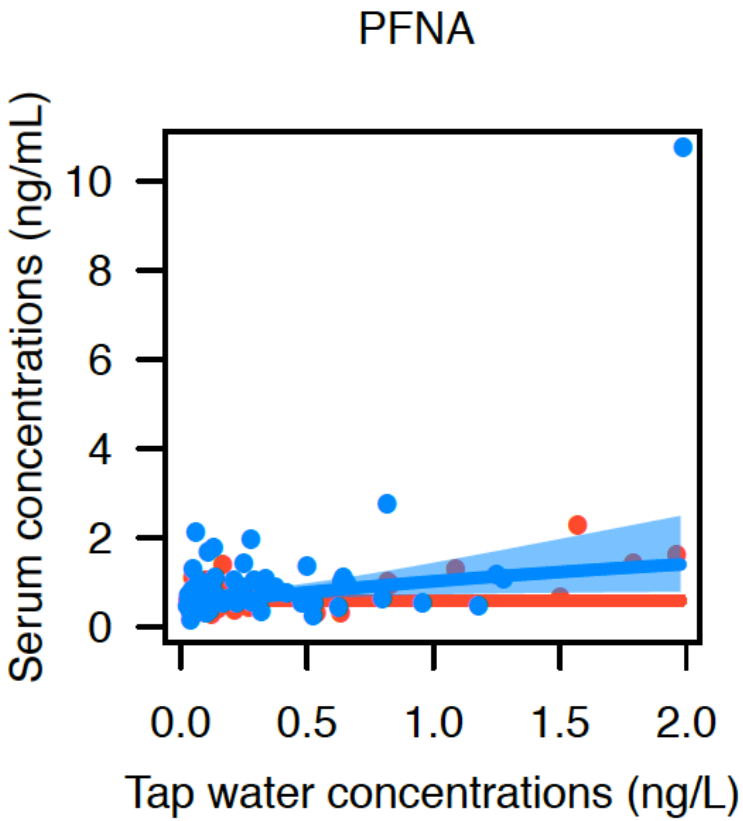
Life style

Residential location

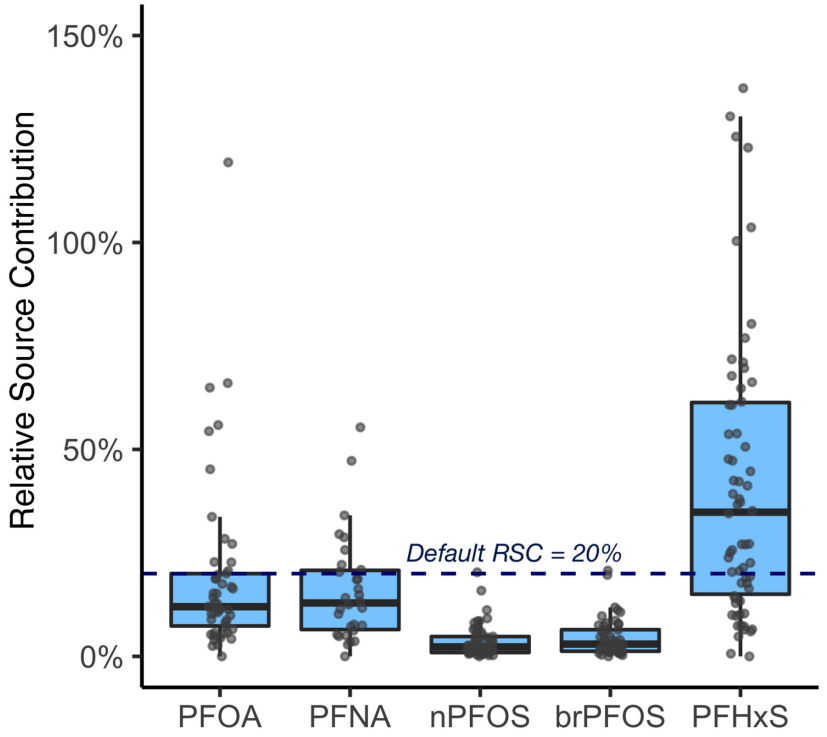
What are exposures now?

Tap water PFOA and PFNA are statistically significant predictors of serum in 1990





RSC = 2% - 34%



Hu et al., 2019, EHP

Pilot data suggest large increase in unidentified PFAS in drinking water: Consistent with production trends

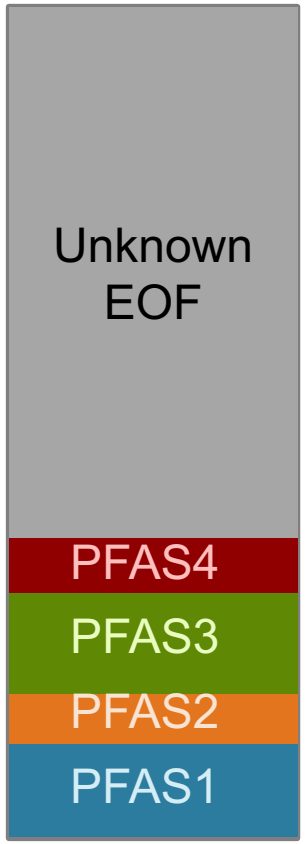
Extractable organic fluorine (EOF)

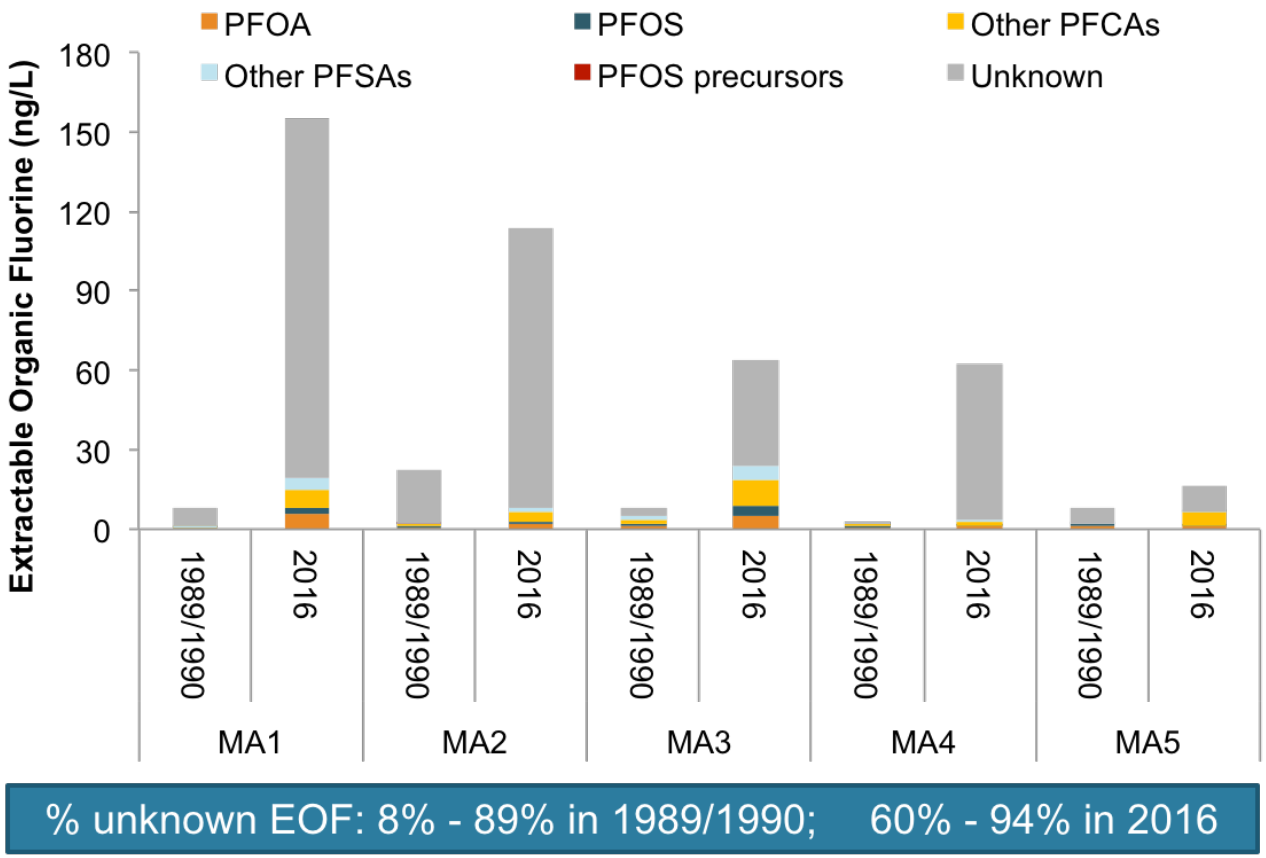
4700 PFASs

>200 detected

Toxicity of alternative PFASs

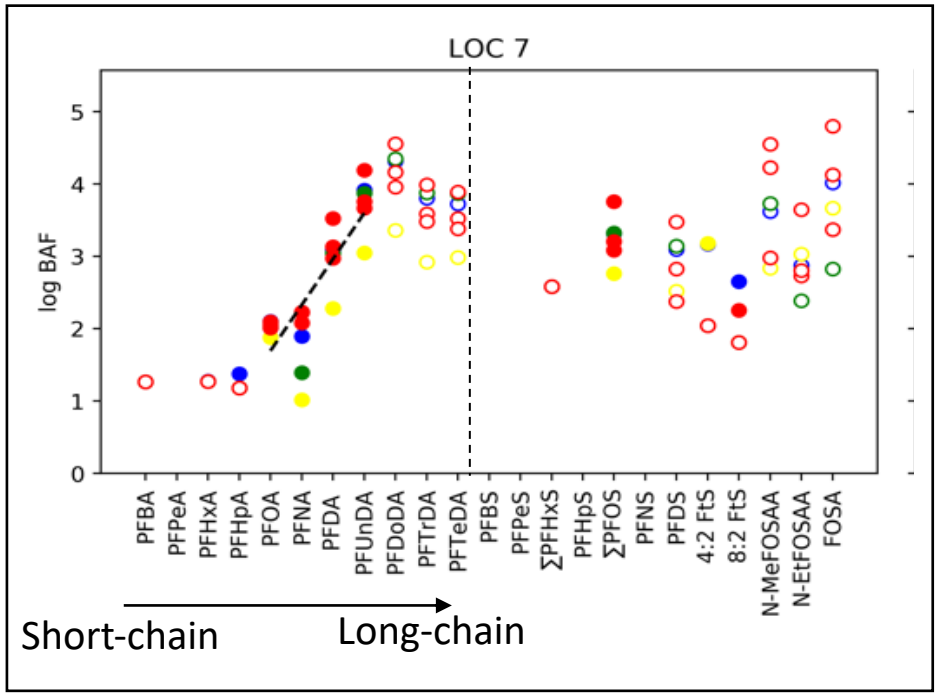
not well understood





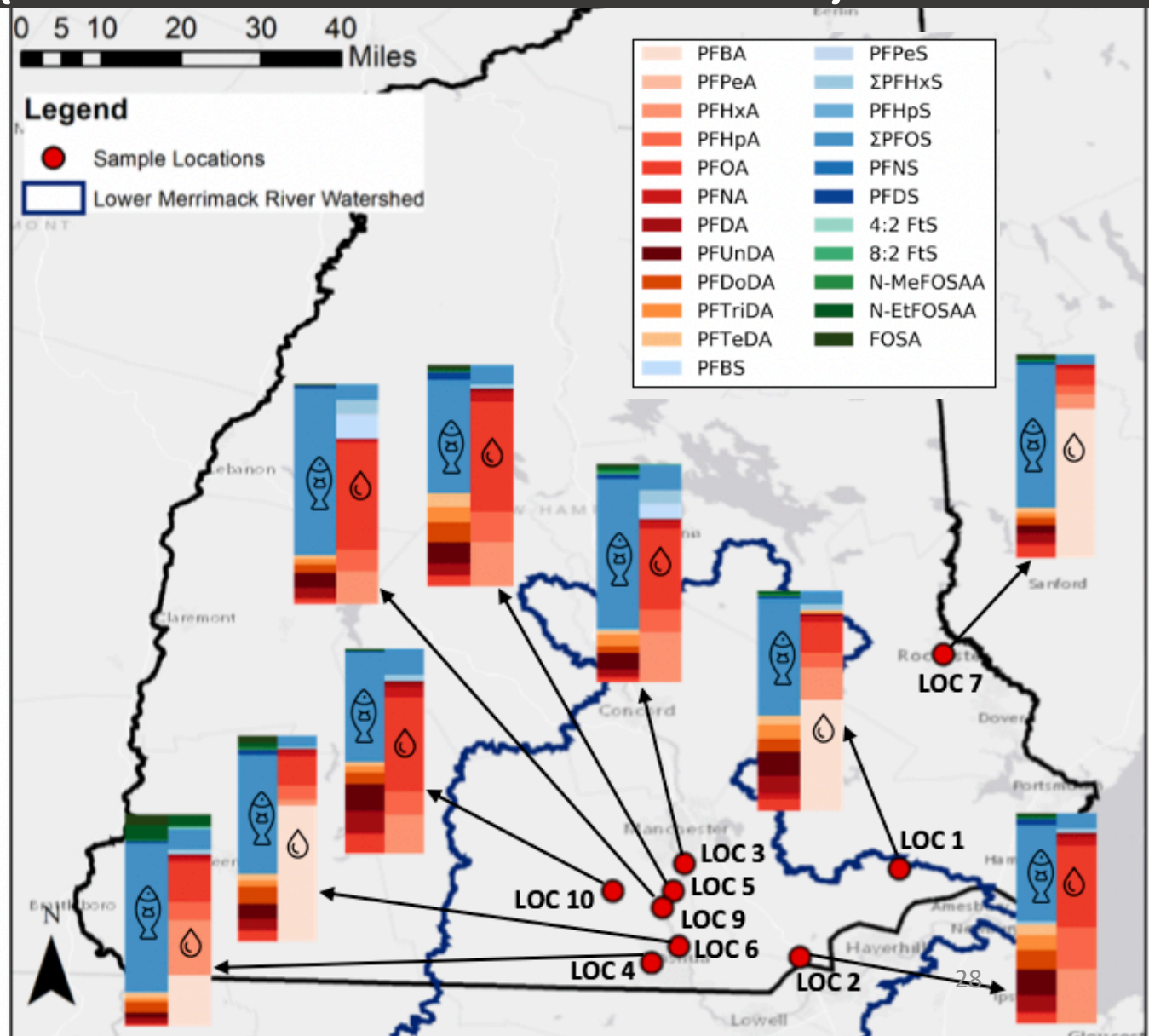
Hu et al., 2019, EHP

PFAS composition in fish differs significantly from those found in the water (NH surface water data)



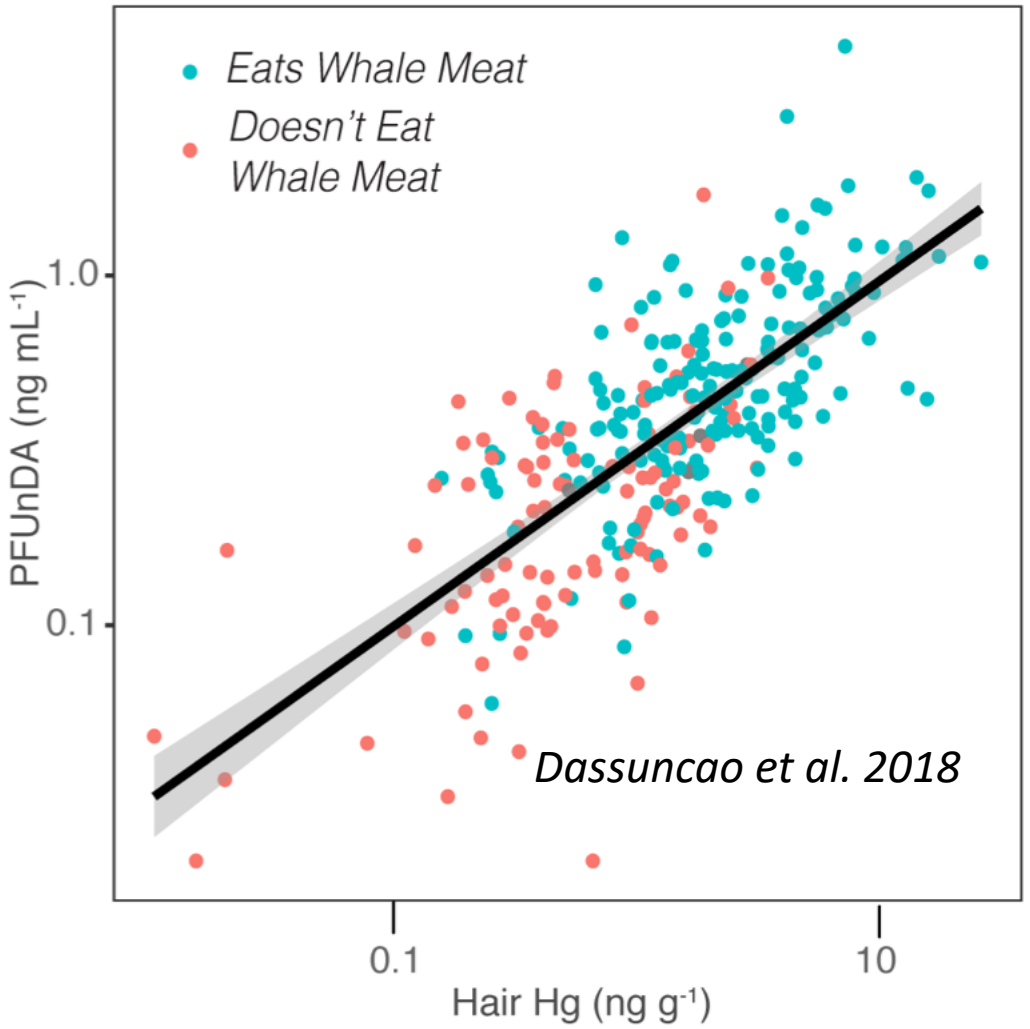
Bioaccumulation factor (BAF) increases with PFAS chain-length

Pickard et al., in prep.



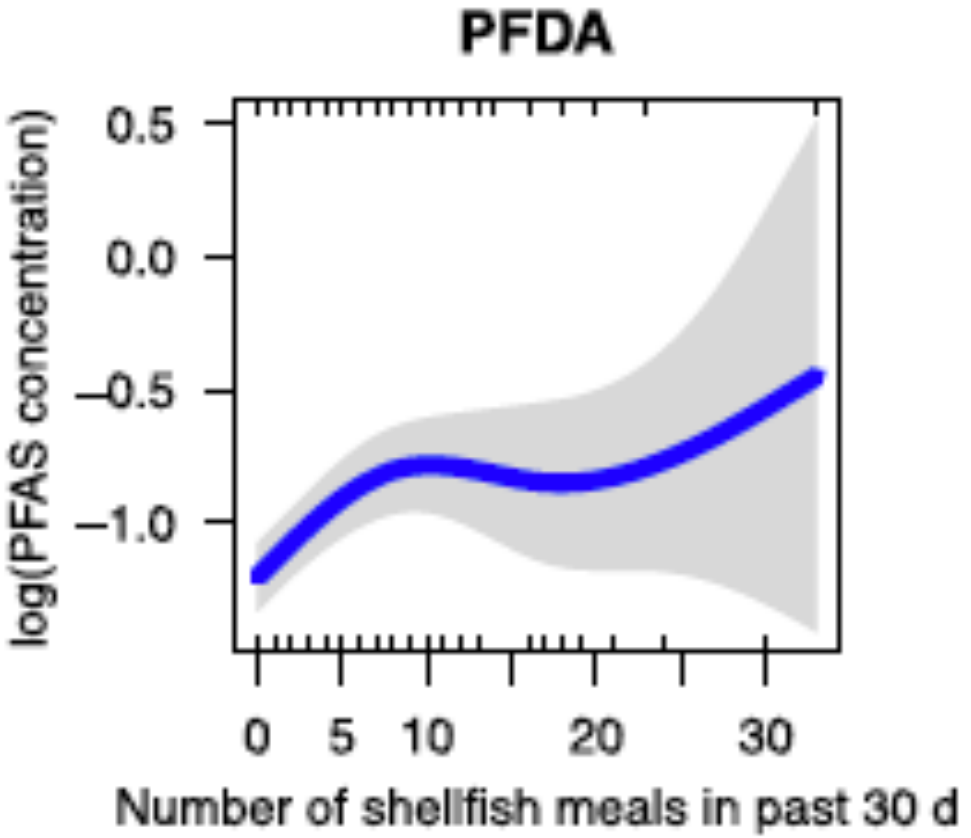
In human serum: Long-chain PFCA strongly associated with seafood consumption

Faroese Children



Dassuncao et al. 2018

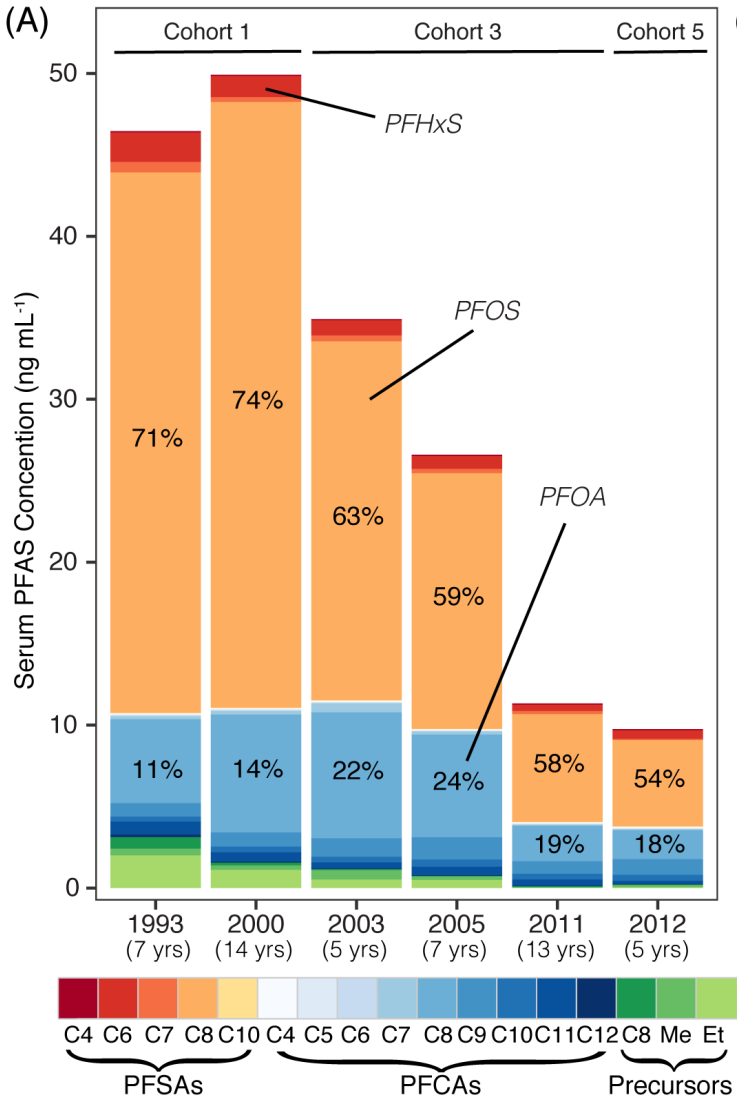
NHANES 2005-2006

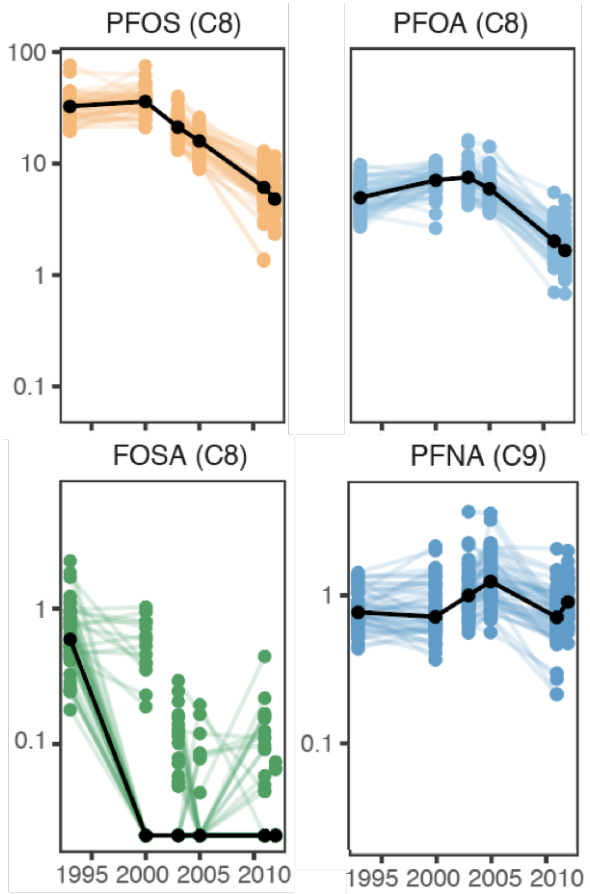


Hu et al. 2018

Rapid declines in targeted PFAS in children's serum driven mainly by PFOS, PFOA, and FOSA

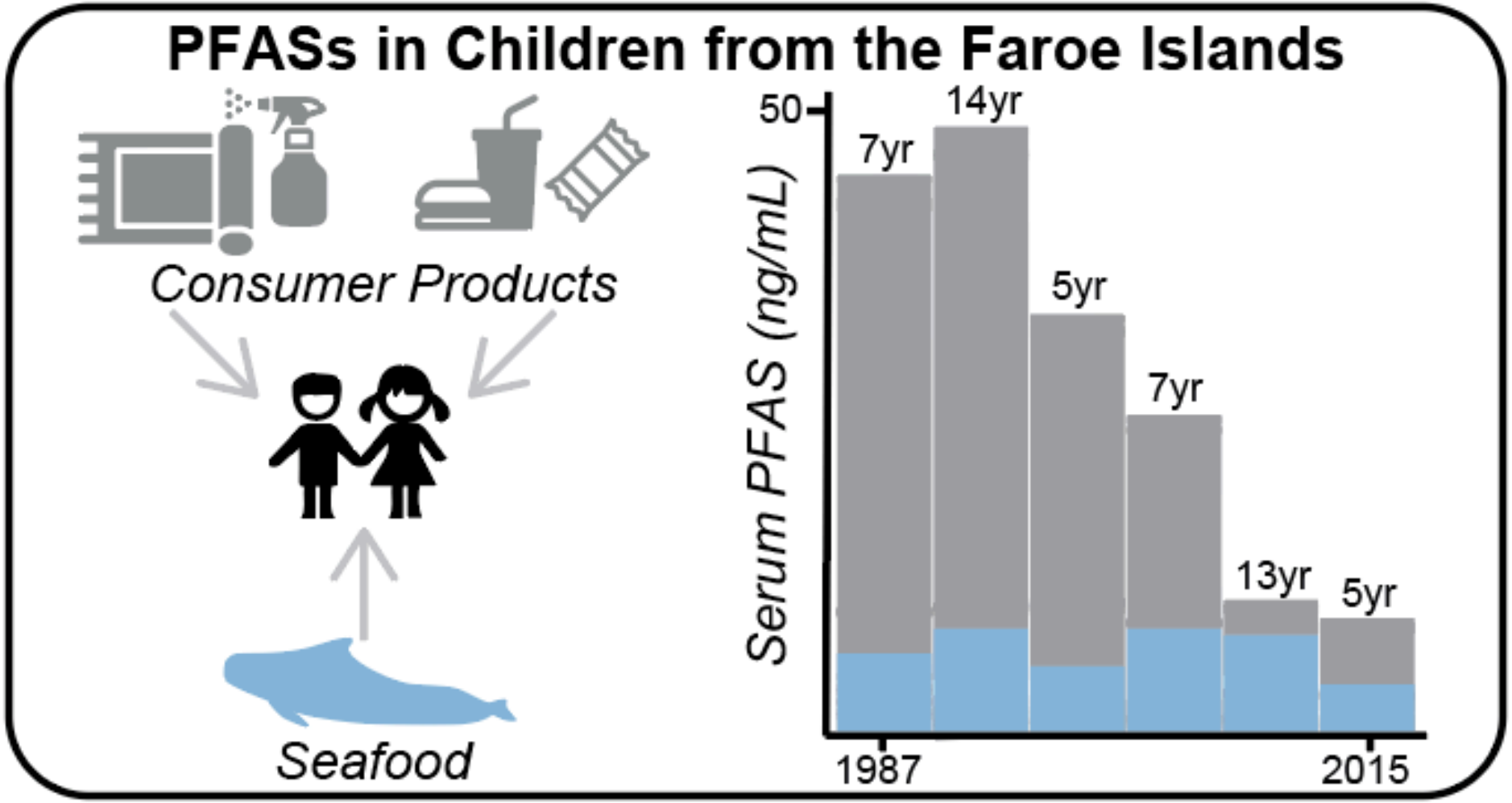
Some long chain PFAS (i.e., PFNA) stable or increasing





Dassuncao et al., 2018

Decline in serum PFAS concentrations can not be explained by shifts exposure from seafood consumption: Indoor air or diet?



Even in the Faroe Islands (remote high seafood consuming population), diverse consumer products appear to have accounted for the majority of exposures for children in the 1990-2000s.

Dassuncao et al. 2018

Targeted LC-MS/MS measurements make up SMALL fraction of total PFAS in consumer products

ENVIRONMENTAL Science & Technology LETTERS

Letter

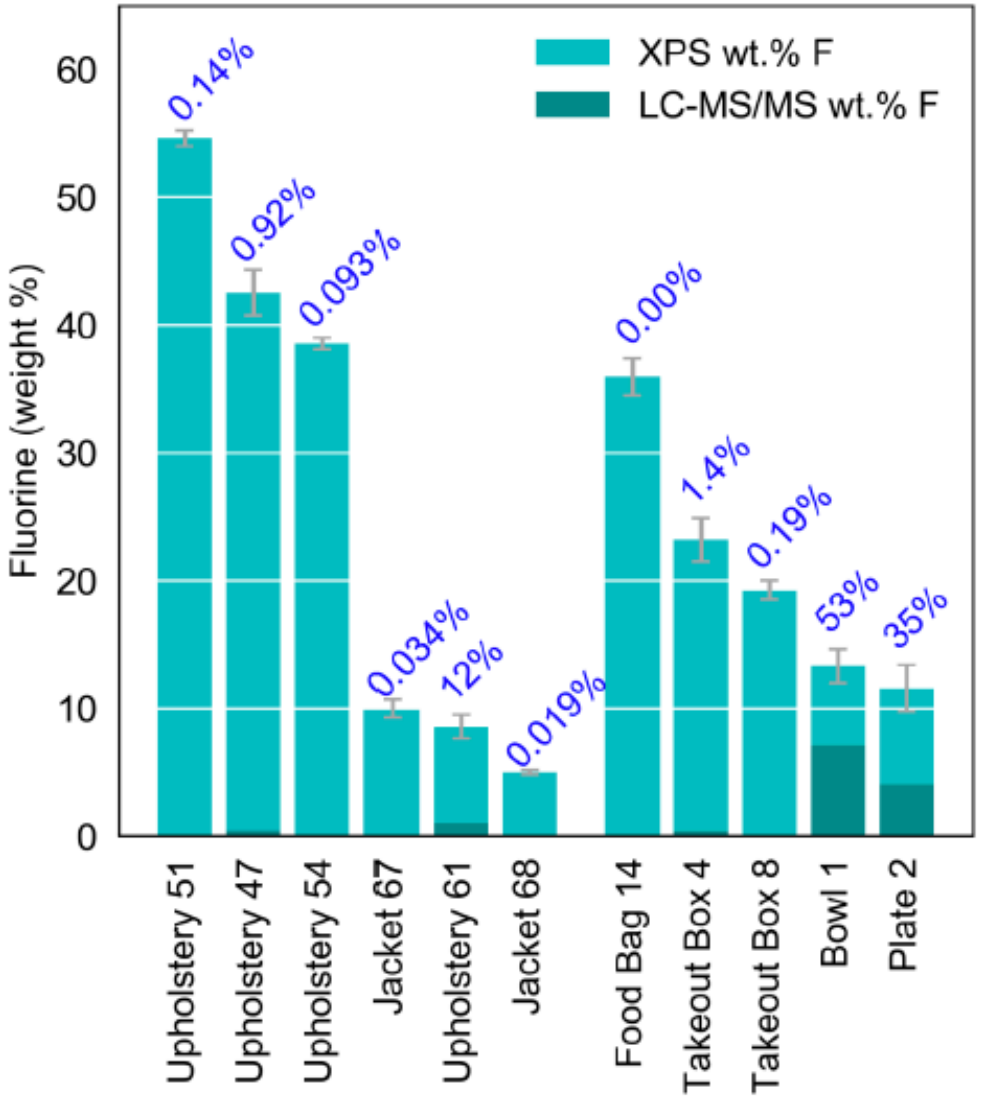
Cite This: *Environ. Sci. Technol. Lett.* 2019, 6, 38–43

pubs.acs.org/journal/estlcu

How Do We Measure Poly- and Perfluoroalkyl Substances (PFASs) at the Surface of Consumer Products?

Andrea K. Tokranov,*[†] Nicole Nishizawa,[†] Carlo Alberto Amadei,[†] Jenny E. Zenobio,[‡] Heidi M. Pickard,[†] Joseph G. Allen,[§] Chad D. Vecitis,[†] and Elsie M. Sunderland[†,§]

Tokranov et al., 2019, ES&T



Summary

- **Health Effects: Diverse adverse effects; No consistent mode of action across compounds studied – raising questions about how to regulate (compound specific or as a class?)**

- **Sources: Chemical production is changing rapidly and we are not able to detect most PFAS in use today using traditional techniques; understanding of atmospheric sources and fate huge gap right now!**

- **Fate and Exposure: Human exposures at contaminated sites are dominated by contaminated drinking water. For the general population the relative importance of different exposure pathways is extremely uncertain. This information is essential for informing risk mitigation measures.**