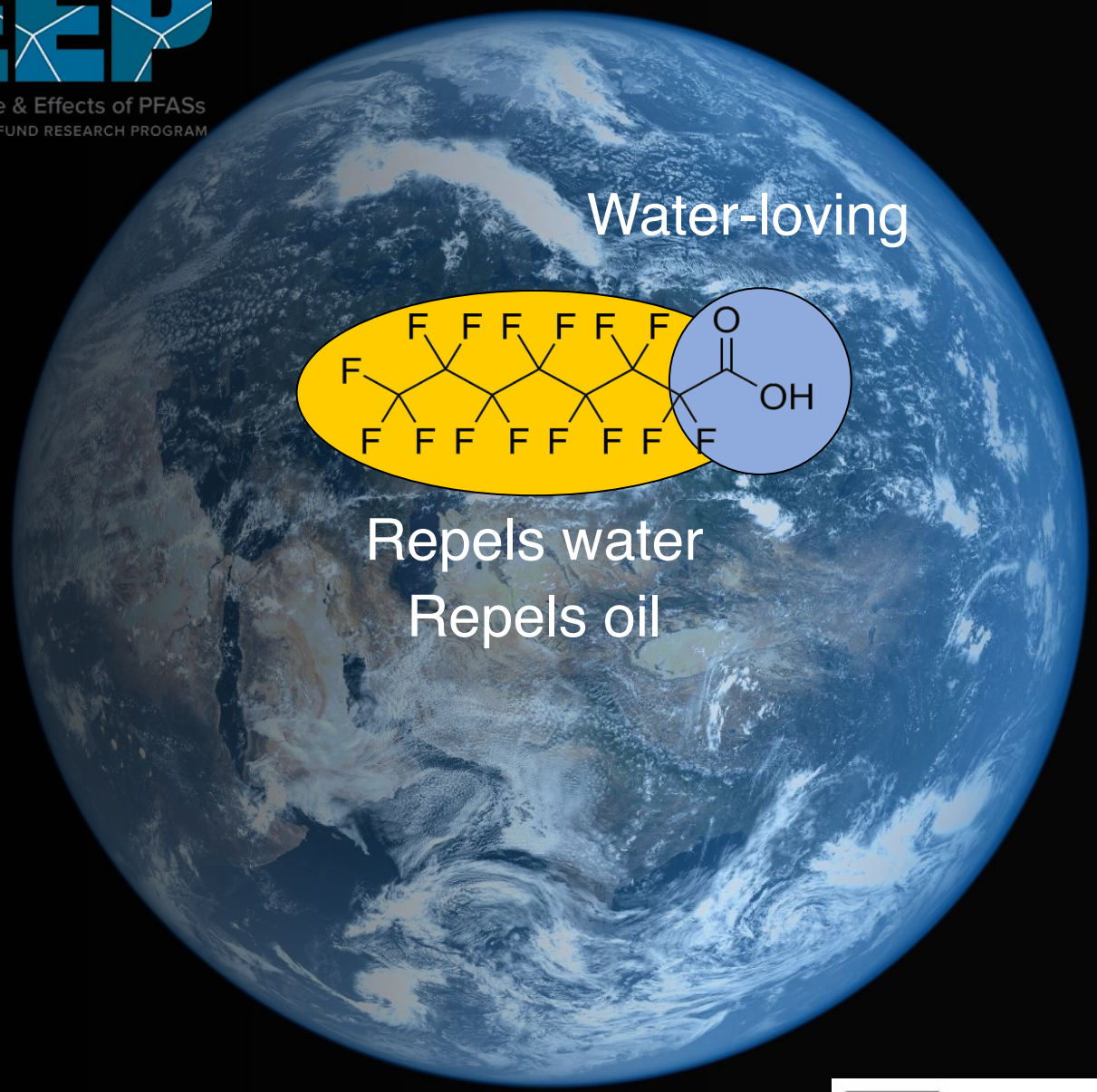
Biogeochemistry of Global Contaminants HARVARD

STEEP
Sources, Transport, Exposure & Effects of PFASs
UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

# PFAS In Our World: Understanding Exposures in a World Full of PFAS




Elsie M. Sunderland (ems@seas.harvard.edu)
October 3, 2021

HARVARD T.H. CHAN SCHOOL OF PUBLIC HEALTH

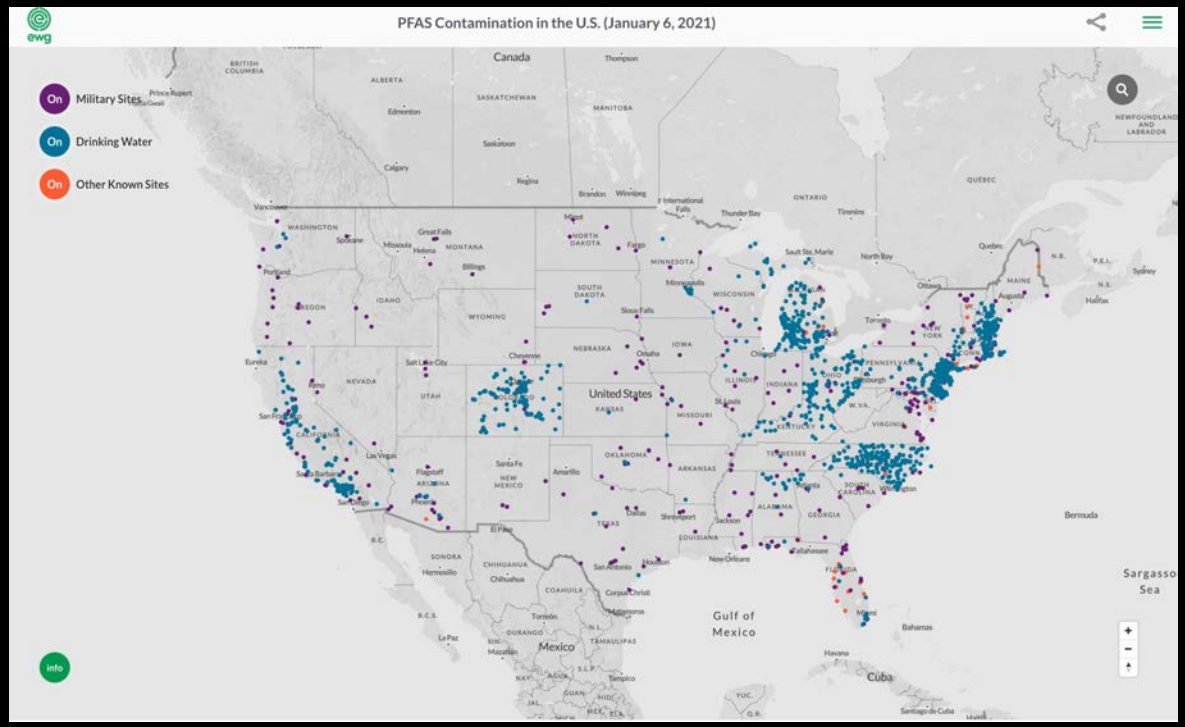
HARVARD John A. Paulson School of Engineering and Applied Sciences

# Why are we concerned about PFAS exposures?


Impacts on communities

Nathaniel Brooks The New York Times

## Continued Discovery of Contaminated Sites

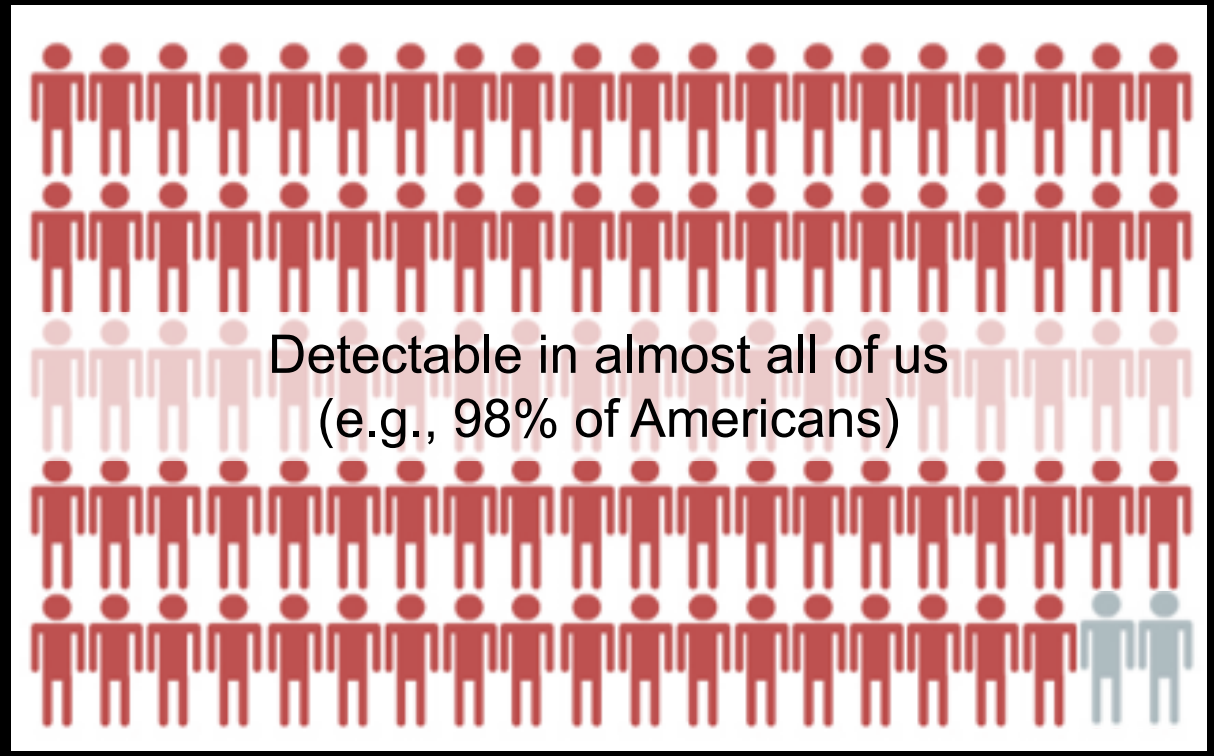



Source: Environmental Working Group (EWG)

# Why are we concerned about PFAS exposures?

Use in our everyday products

Gluge et al., 2020, ESPI

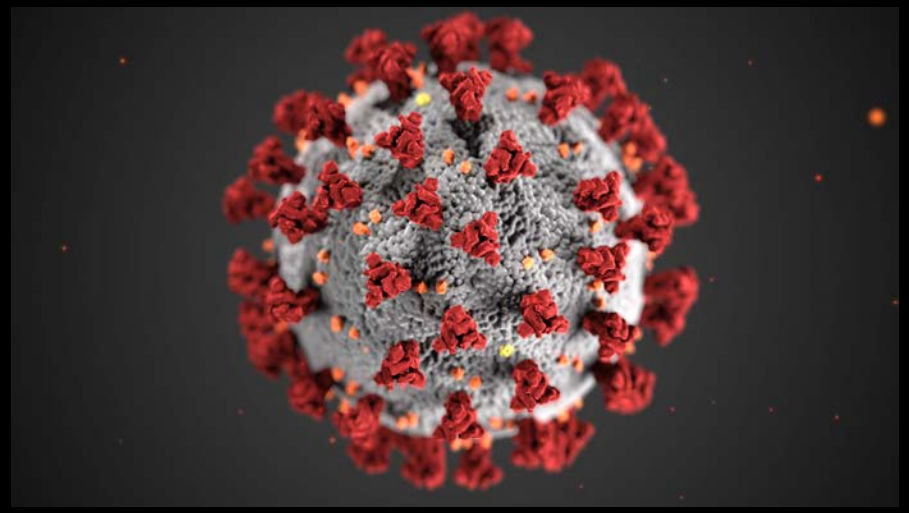


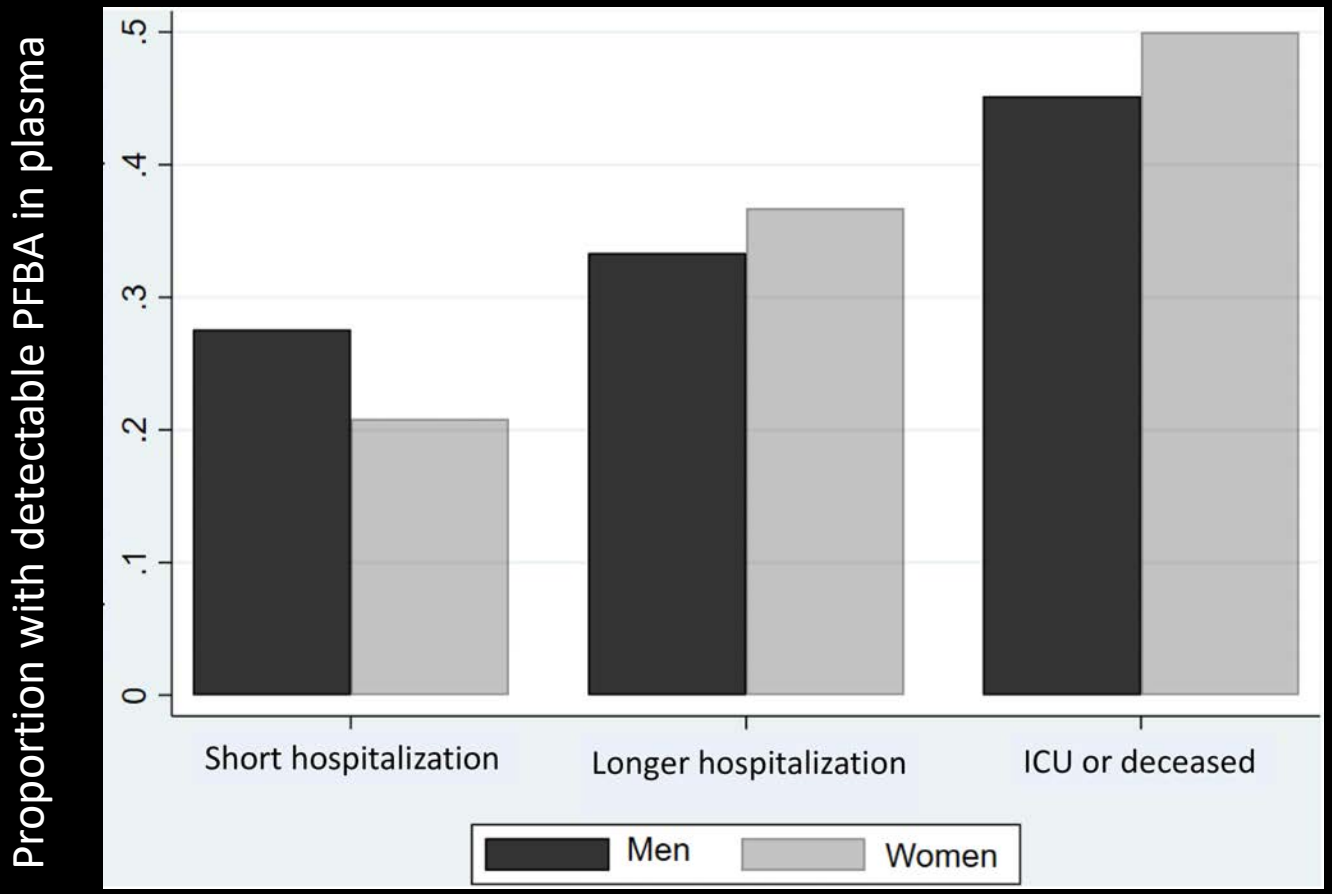

Khalil et al., 2016

# Rapid Discovery of New Health Effects Associated with PFAS Exposure

## PFBA exposure linked to COVID-19 severity

- Grandjean et al., 2020
- https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0244815





# A Few Grand Challenges for PFAS Exposure Research

1. Targeted methods for analysis underestimate total PFAS exposure

2. Incomplete data on pollution/exposure sources for developing risk mitigation strategies

3. Incomplete understanding of how and why exposures are changing in response to shifts in chemical production and regulation

# 1. We need to understand the organofluorine mass budget in different exposure matrices

**Organofluorine**: C-F Bond (rare in nature)

**PFAS**: $C_nF_{2n+1}$ moiety

*Thousands of structures listed by OECD*

F-C

FOREVER CHEMICALS

**Precursors**

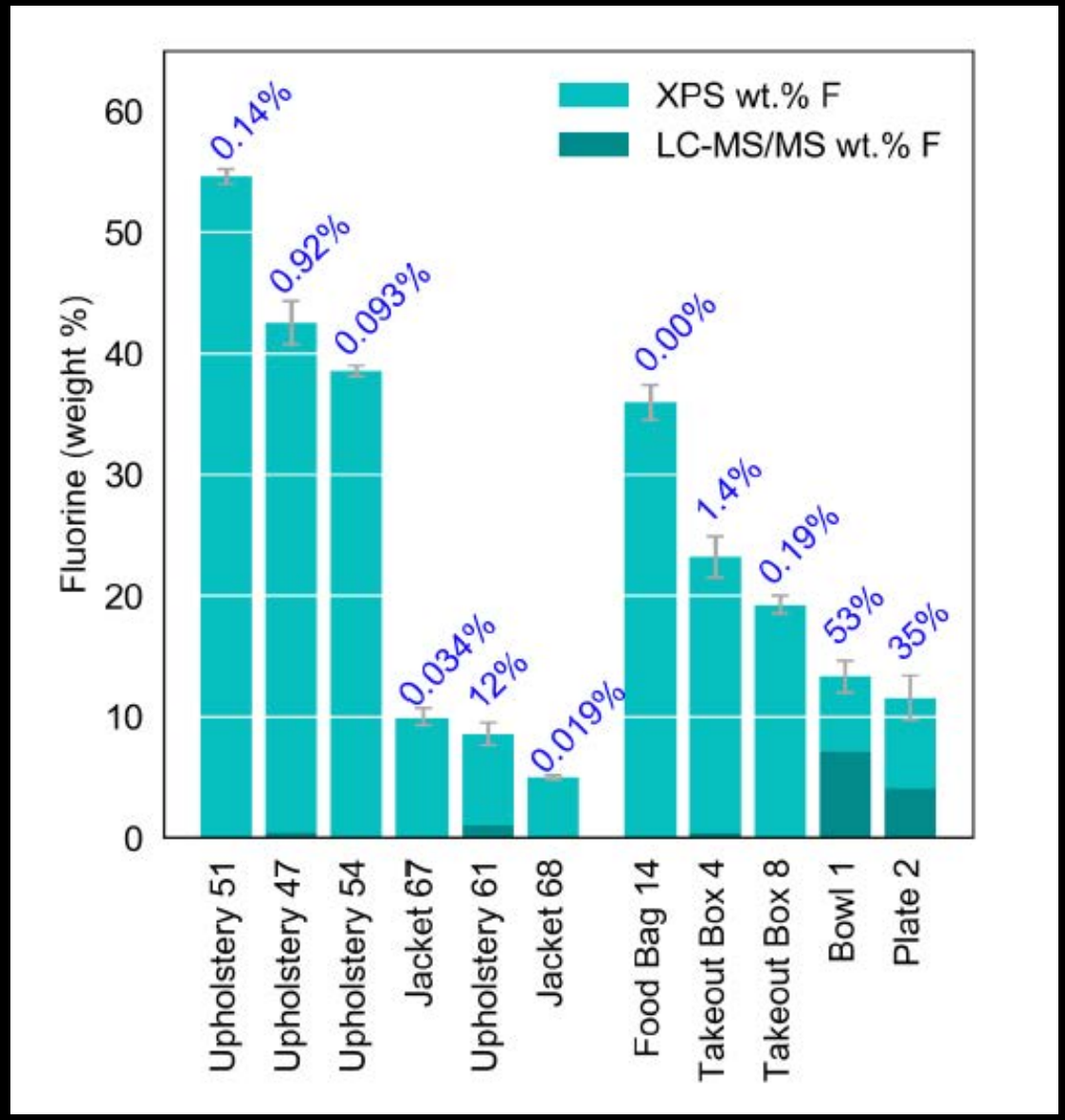
(most organofluorine in many commercial products)

**Terminal Compounds**

e.g., PFCAs like PFOA, PFHxA

These are the real “forever chemicals”

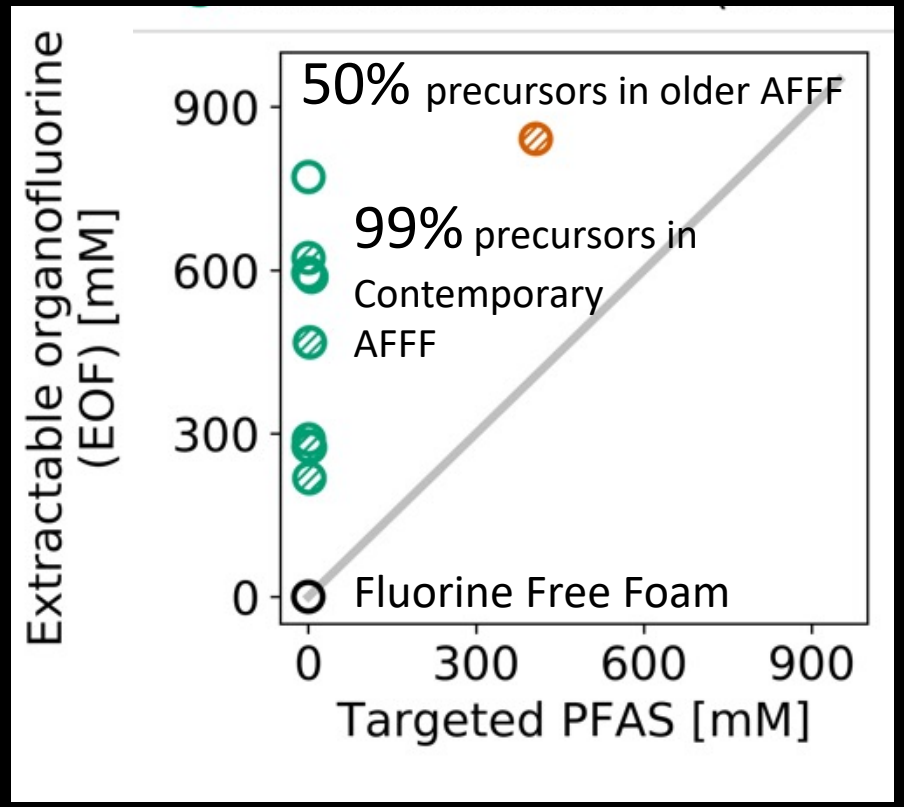
Example: Targeted LC-MS/MS measurements make up SMALL fraction of organofluorine (XPS) in consumer products

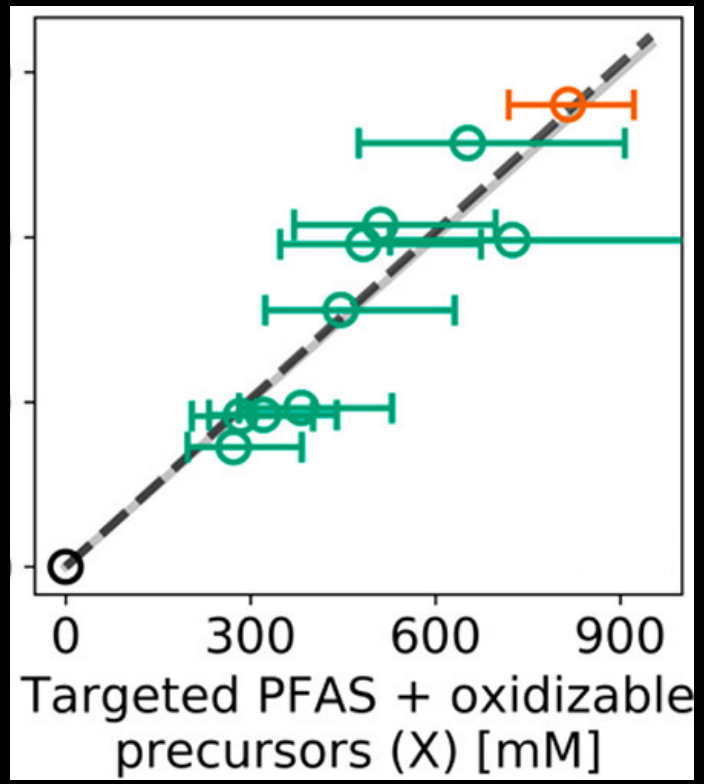



Tokranov et al., 2019, ES&T

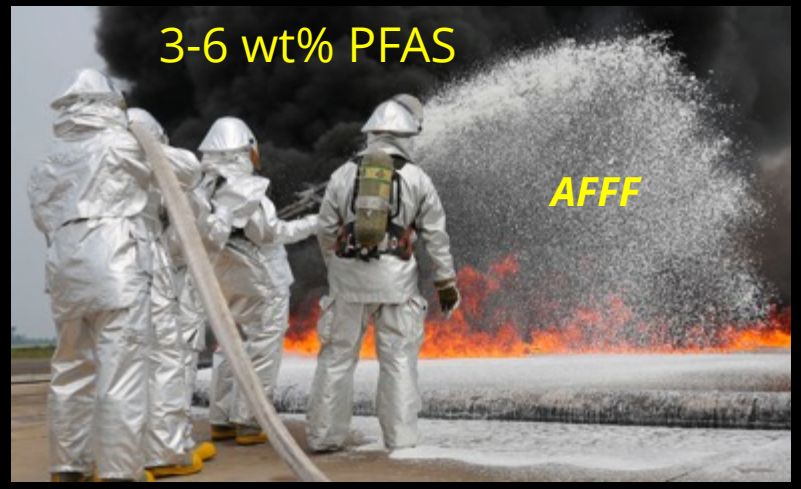
# Example: Many sites have been contaminated by use of aqueous film forming foams (AFFF)

Most organofluorine (EOF) in AFFF not detected by standard EPA method



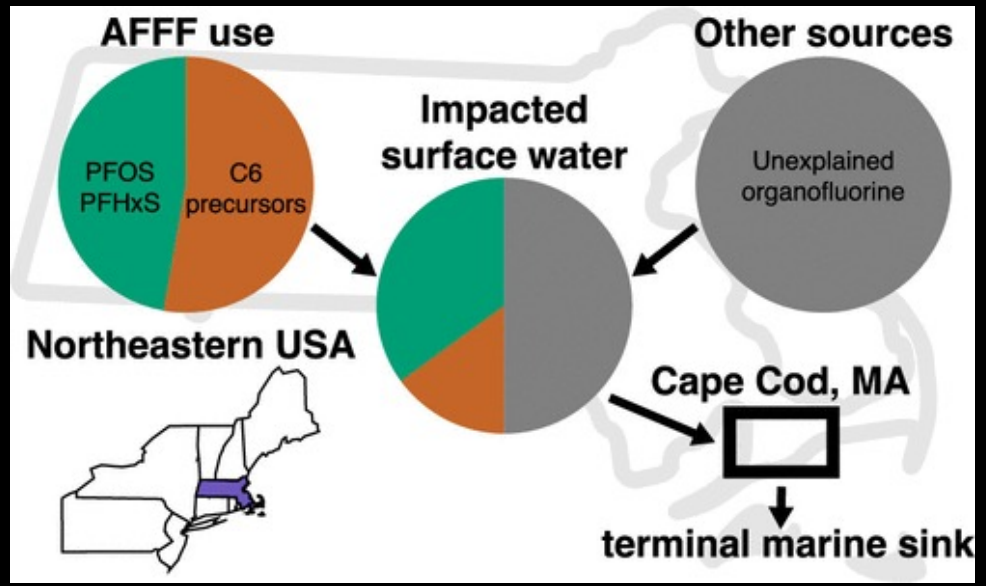

100% of the EOF in AFFF can be reproduced using the total oxidizable precursor (TOP) assay + statistical inference



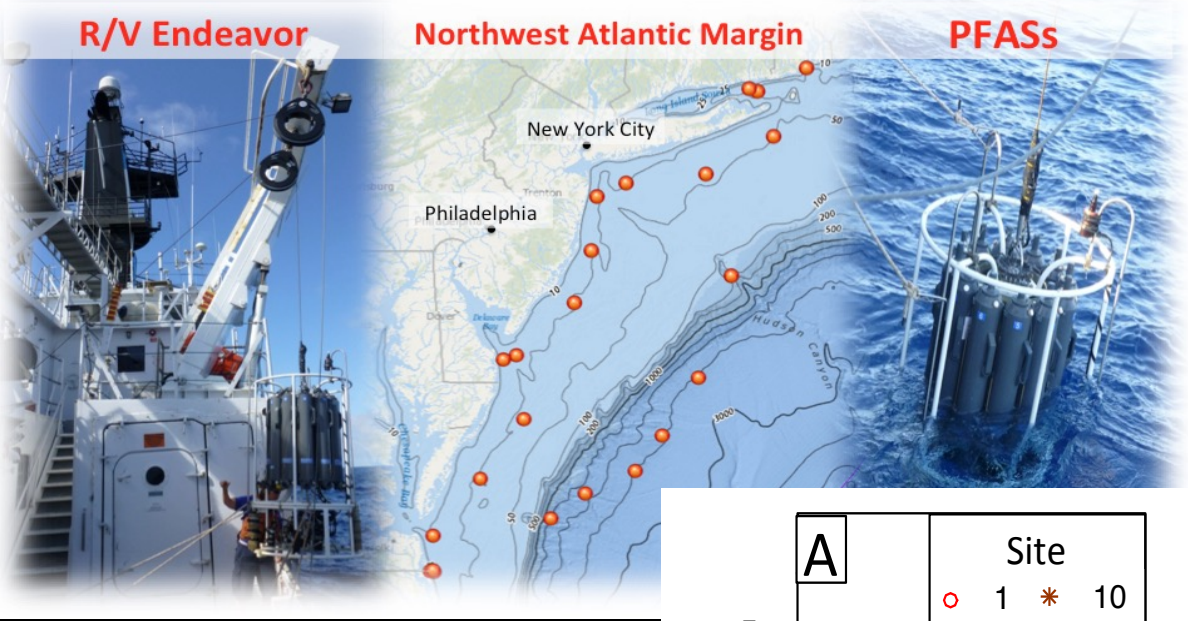

Ruyle et al., 2021a, ES&T Letters

# Large fraction of unidentified organofluorine in Cape Cod, MA rivers: Likely fluorinated pharmaceuticals from septic systems

24-63% of EOF in coastal watersheds with a known AFFF source explained by targeted PFAS + oxidizable precursors

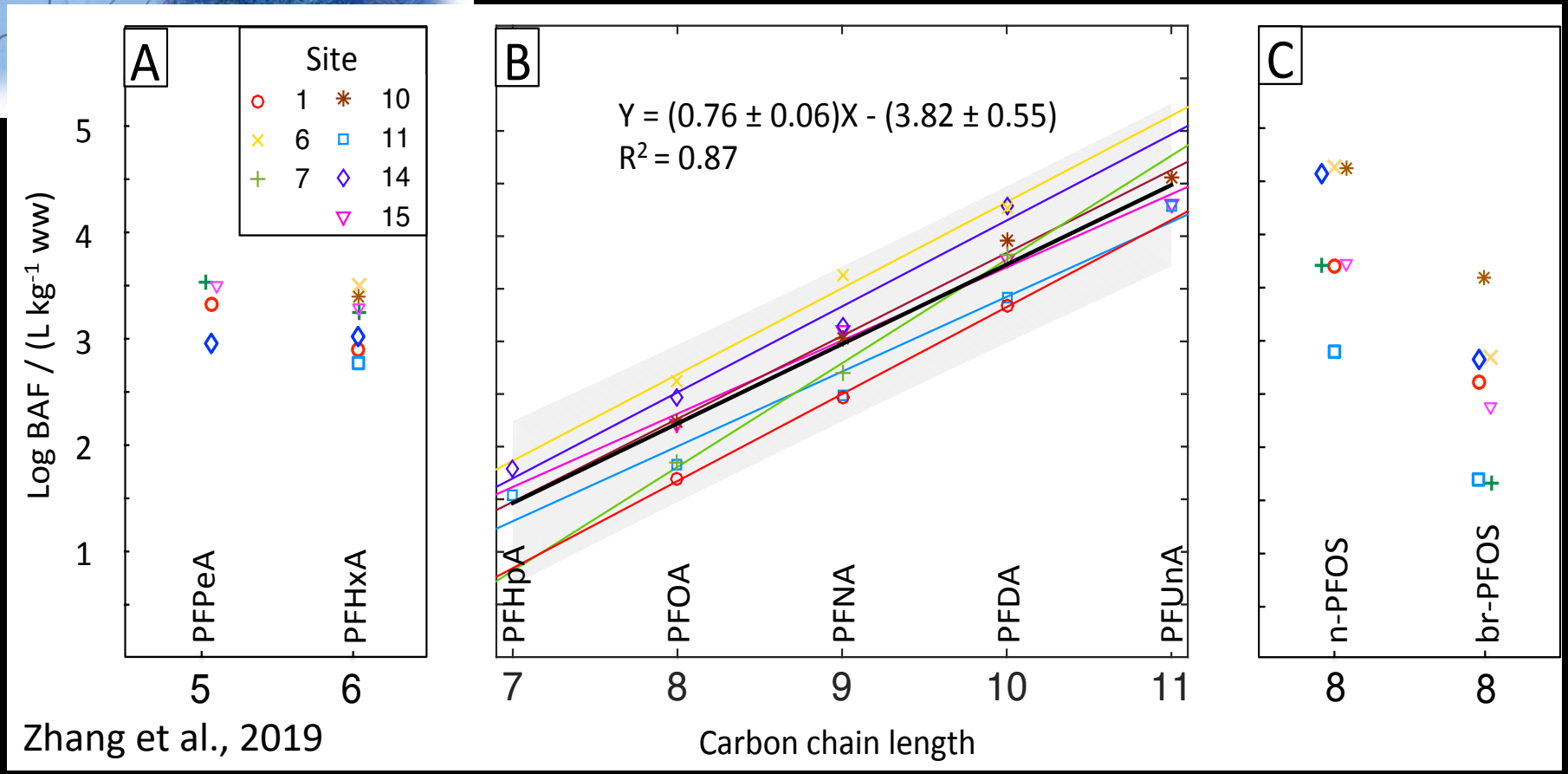



Ruyle et al., 2021b, ES&T




# Empirically derived Bioaccumulation Factors ($C_{plankton}/C_{water}$) from the Northwestern Atlantic Shelf and Slope

Higher than expected concentrations of C-5 and C-6 PFCAs in plankton – evidence of precursor uptake?




Zhang et al., 2019

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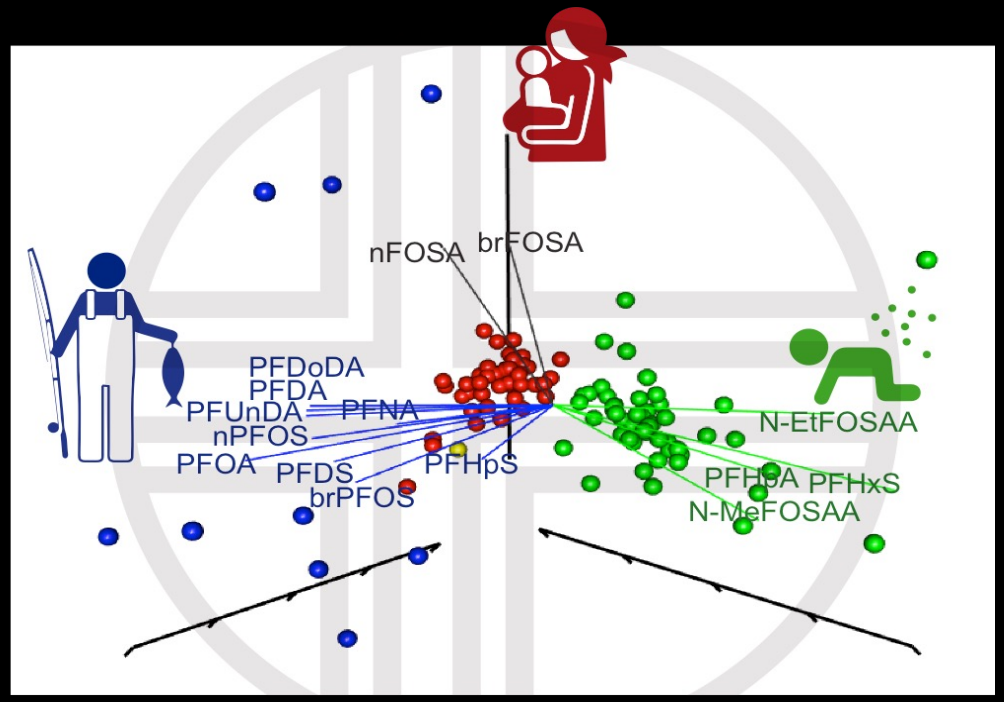
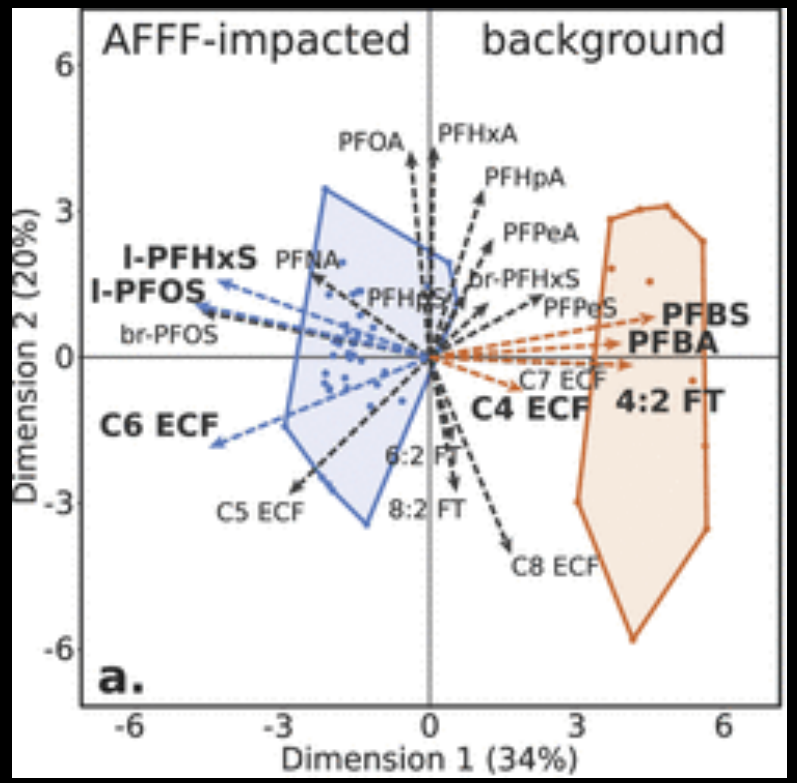
# Chemometrics approach to source identification: Exposure information can be derived from the composition of PFAS

Human serum




Long-chain PFAA in serum (i.e., C>9) good tracer for seafood consumption (Hu et al., 2018; Dassuncao et al., 2018)

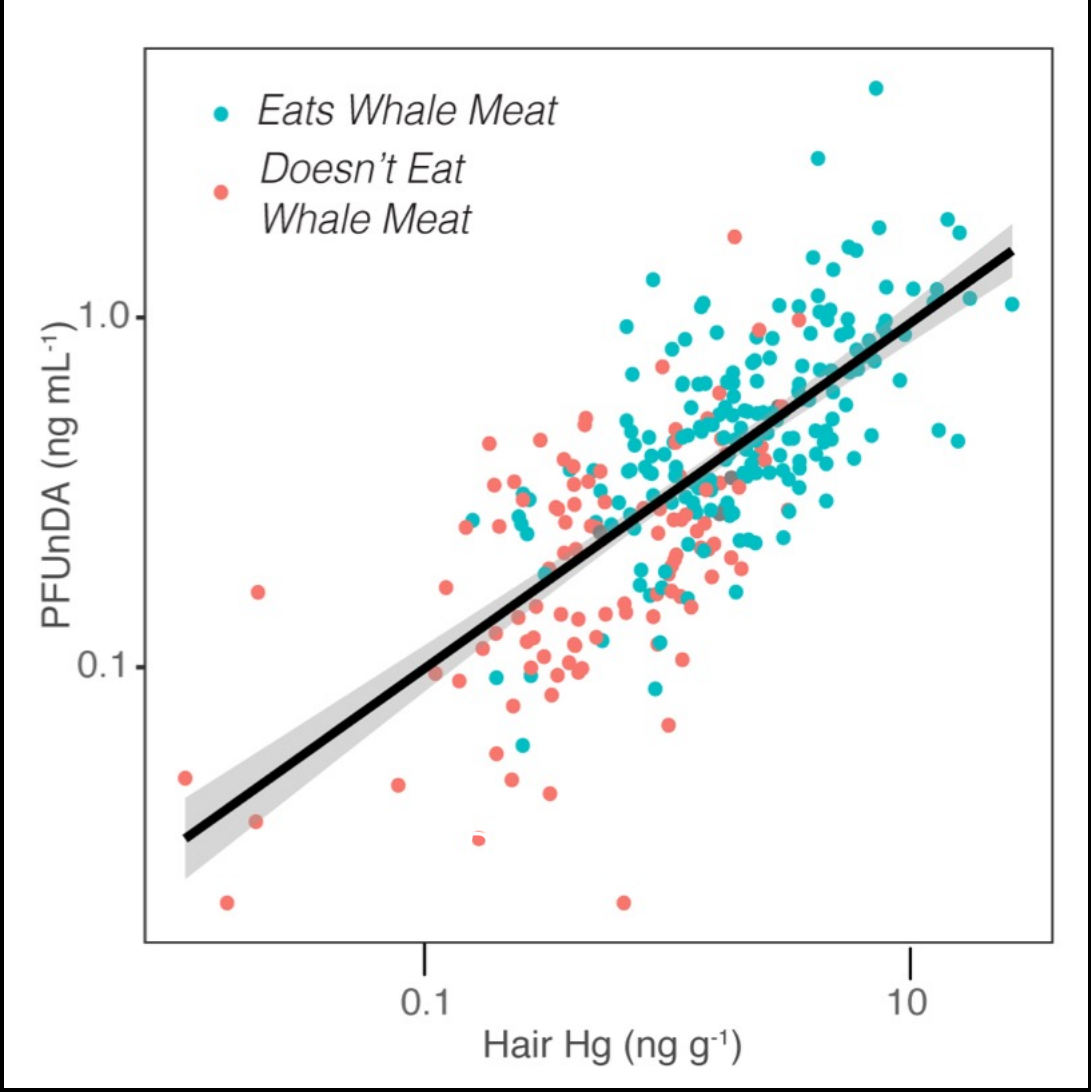
Surface water



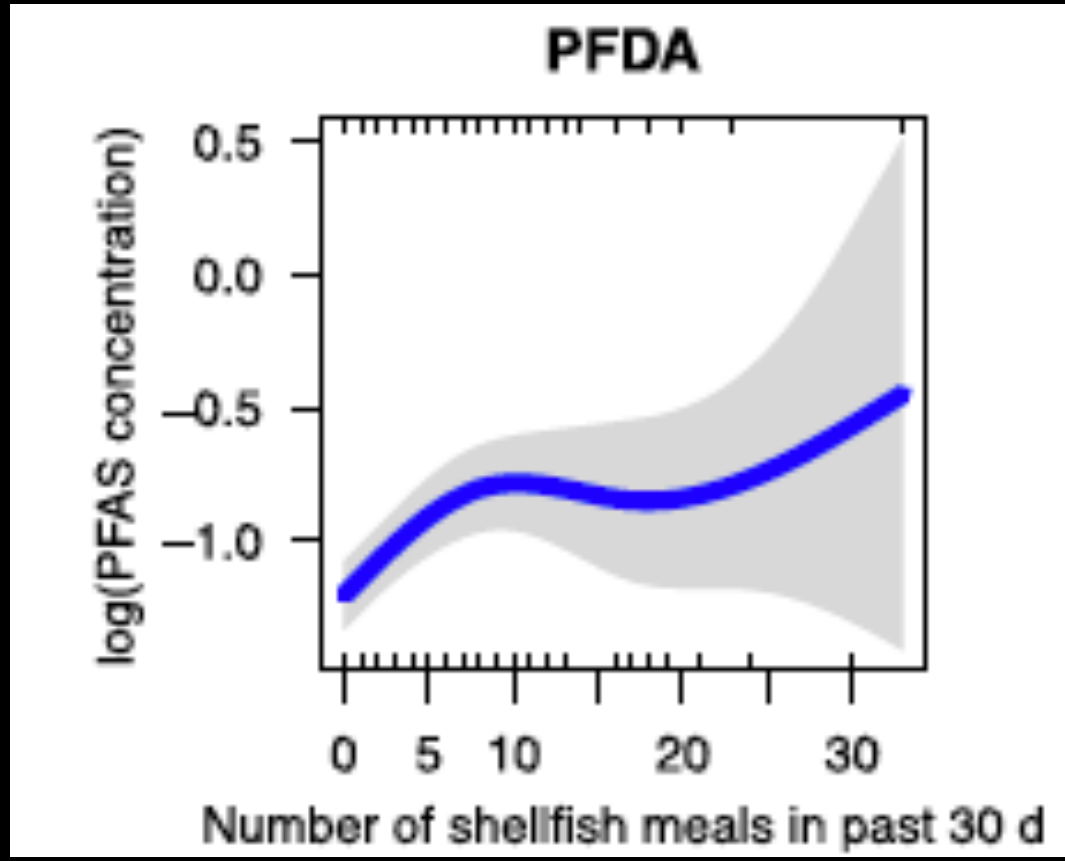

Also useful for source identification of AFFF on Cape Cod (Ruyle et al., 2021)

# Human data can be validated by identifying associations with exposure using survey data on behavior

Faroese Children



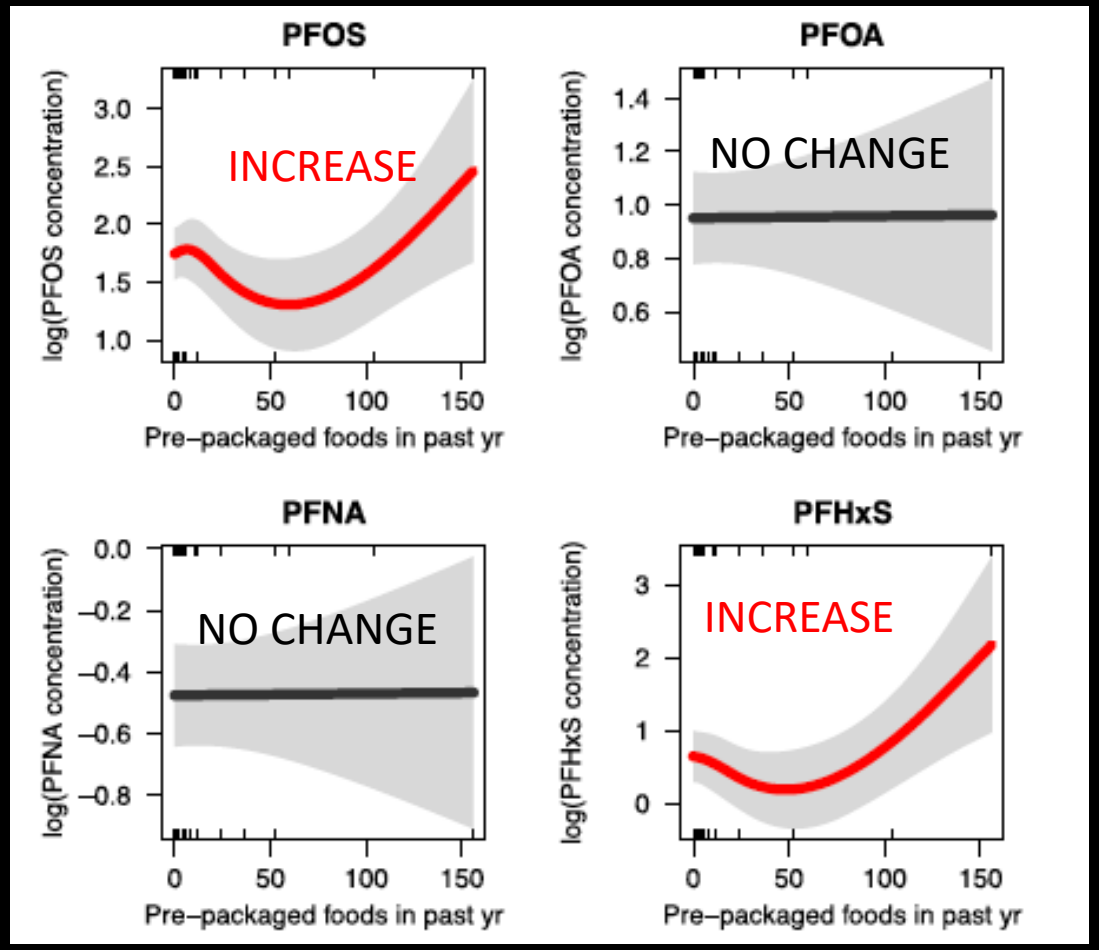

NHANES 2005-2006




*Hu et al. 2018*

# Human data can be validated by identifying associations with exposure using survey data on behavior

Cohort of pregnant women in Vancouver, Canada




Hu et al., 2018, Environmental Health

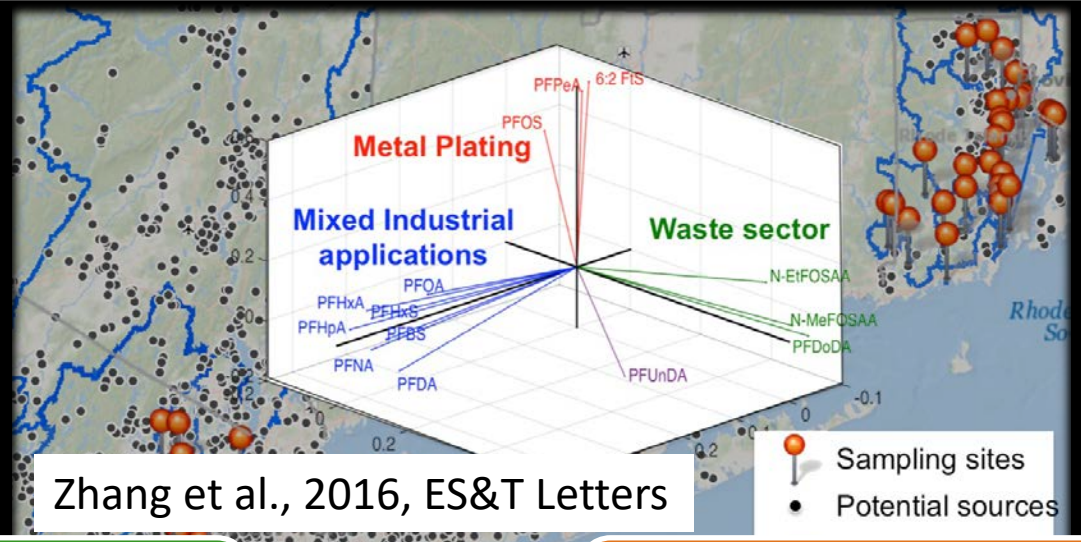
BY SARAH GIBBENS 10 OCTOBER 2019

## FAST FOOD INCREASES EXPOSURE TO A FOREVER CHEMICAL CALLED PFAS

Used in fast food packaging, the long-lasting chemicals can seep into food—and build up in our bodies.

FOLLOW SHARE TWEET

# Summary of chemometric approach




Zhang et al., 2016, ES&T Letters

## Measure

- Quantify the broadest suite of PFAS feasible

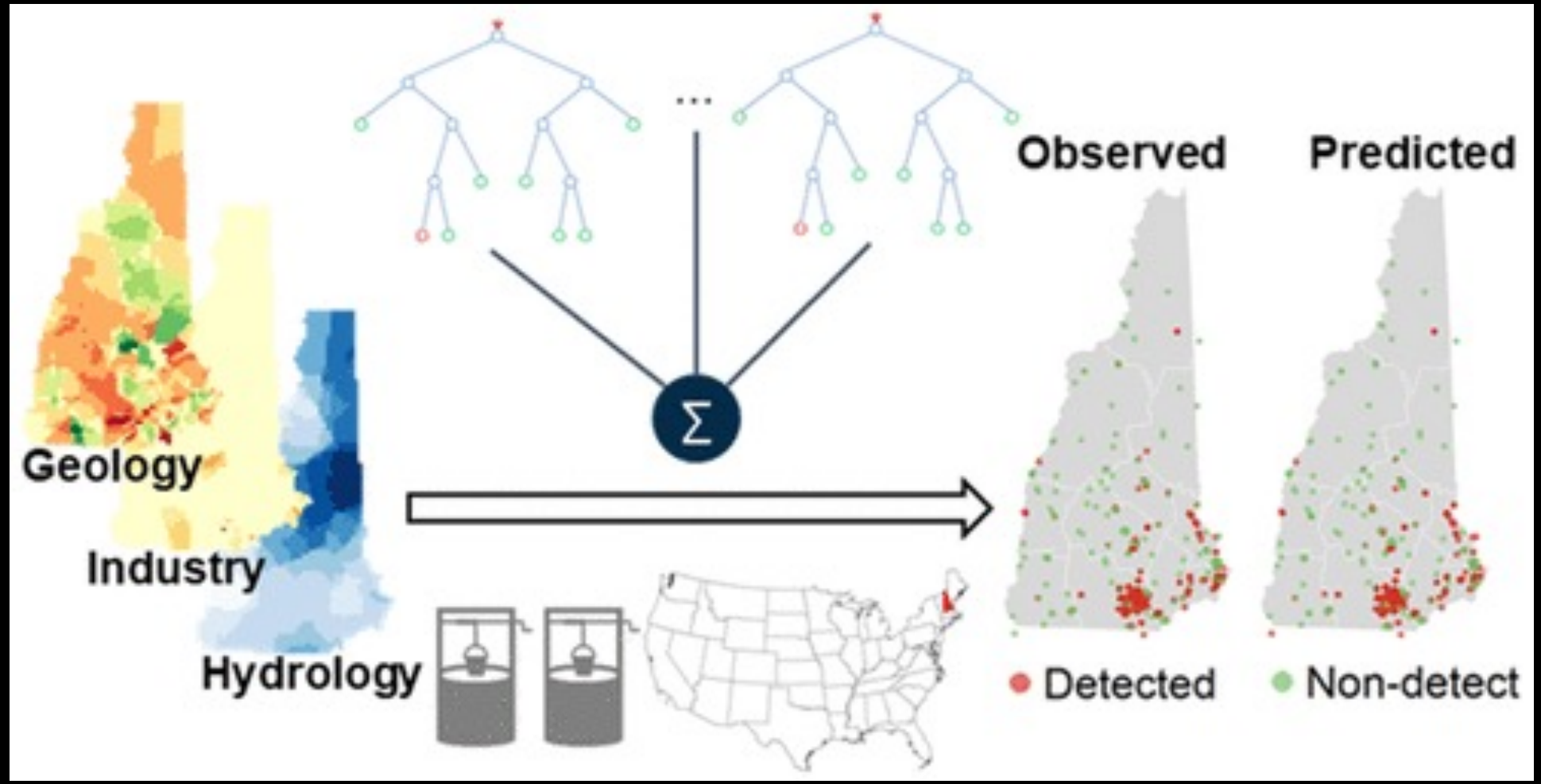
## Derive source profile

- Principal Component Analysis (PCA) and Hierarchical Clustering

## Interpret and identify

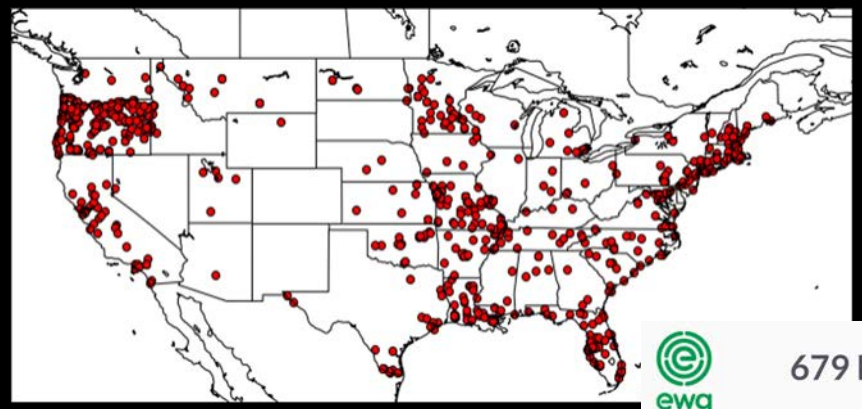
- Geospatial analysis
- Source information
- Environmental transformation and toxicokinetics

# Extension of approach to model likelihood of detecting PFAS in private wells in the state of NH, USA: Good data on sources needed



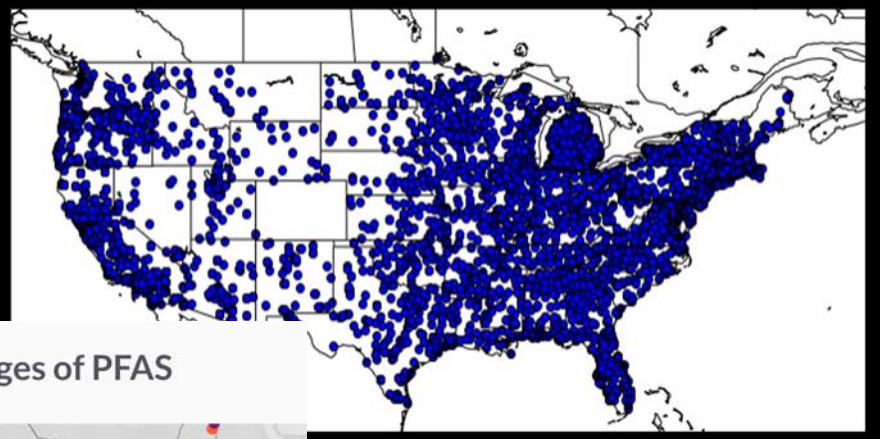

Hu et al., 2021, ES&T Letters

# Still large gaps in data on PFAS releases: Present methods for inferring sources has limited accuracy and require ground-truthing

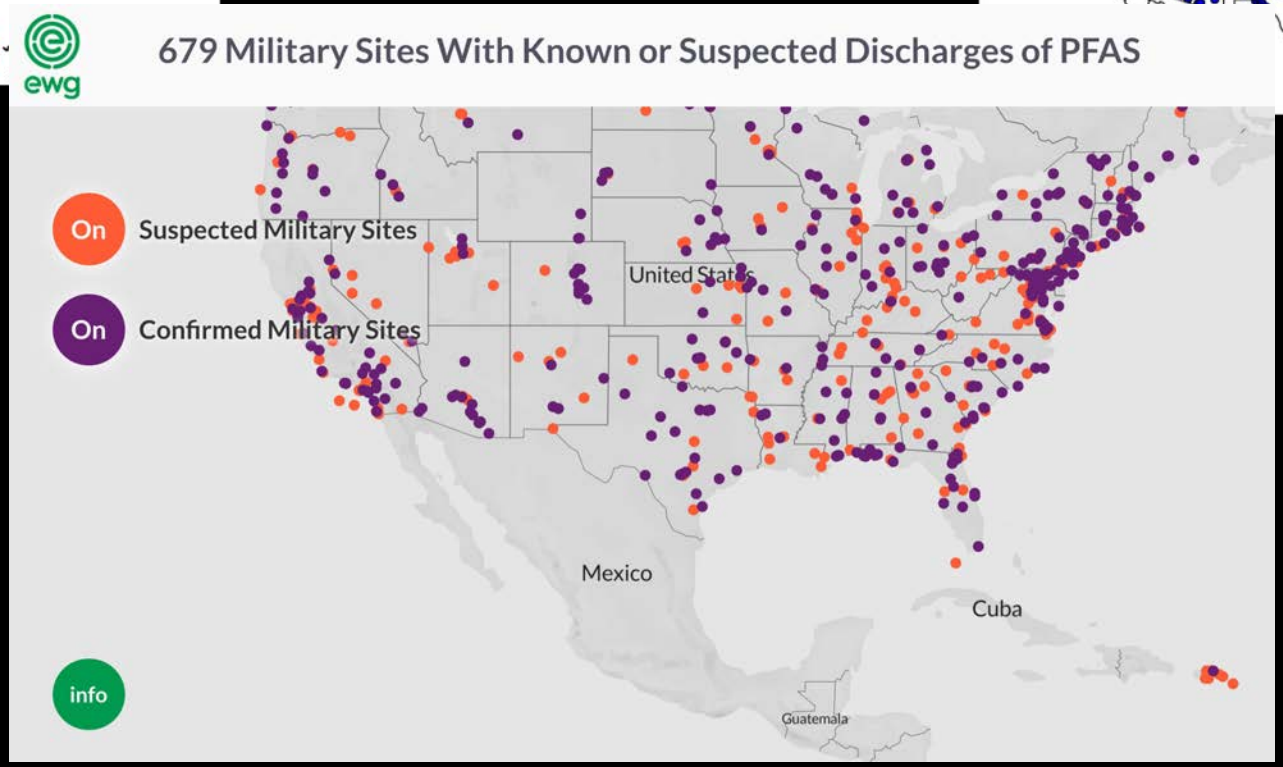


Incinerators

Facility Registry Service (FRS) code queries identify locations

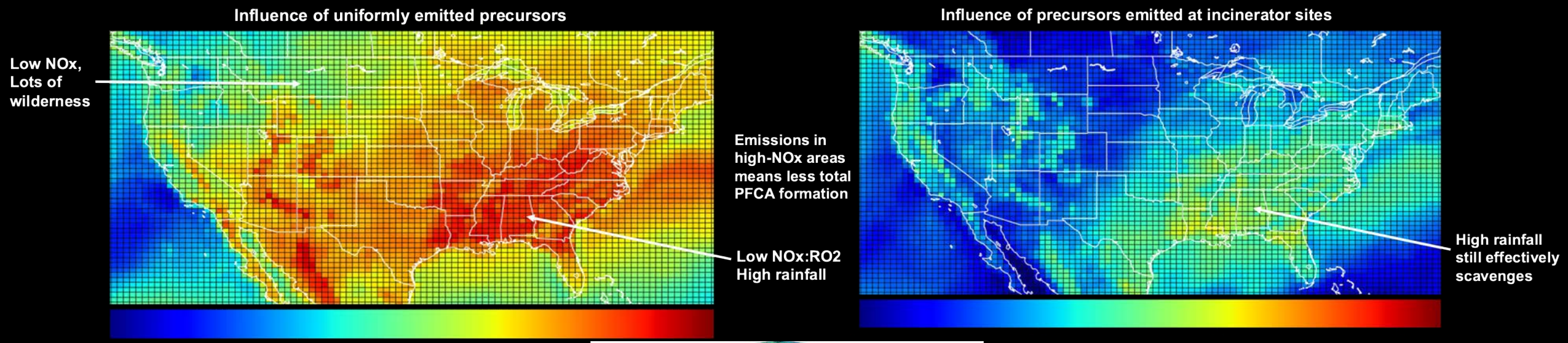


Landfills

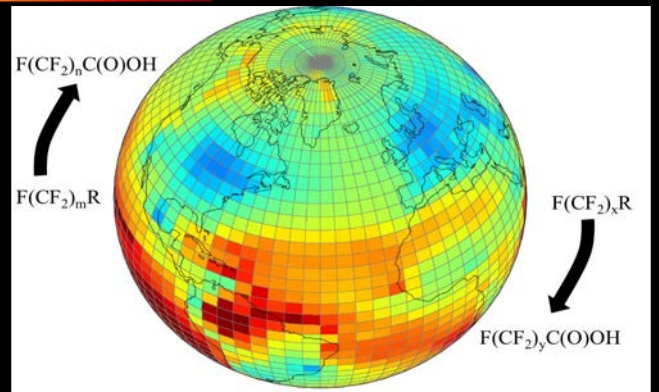


# Example: Redistribution of atmospheric precursor emissions results in 4x lower modeled PFCA deposition

Modeled PFCA deposition (ng $m^{-2}$ $yr^{-1}$ per tonne emitted)




Sun, Thackray et al. (in prep.)



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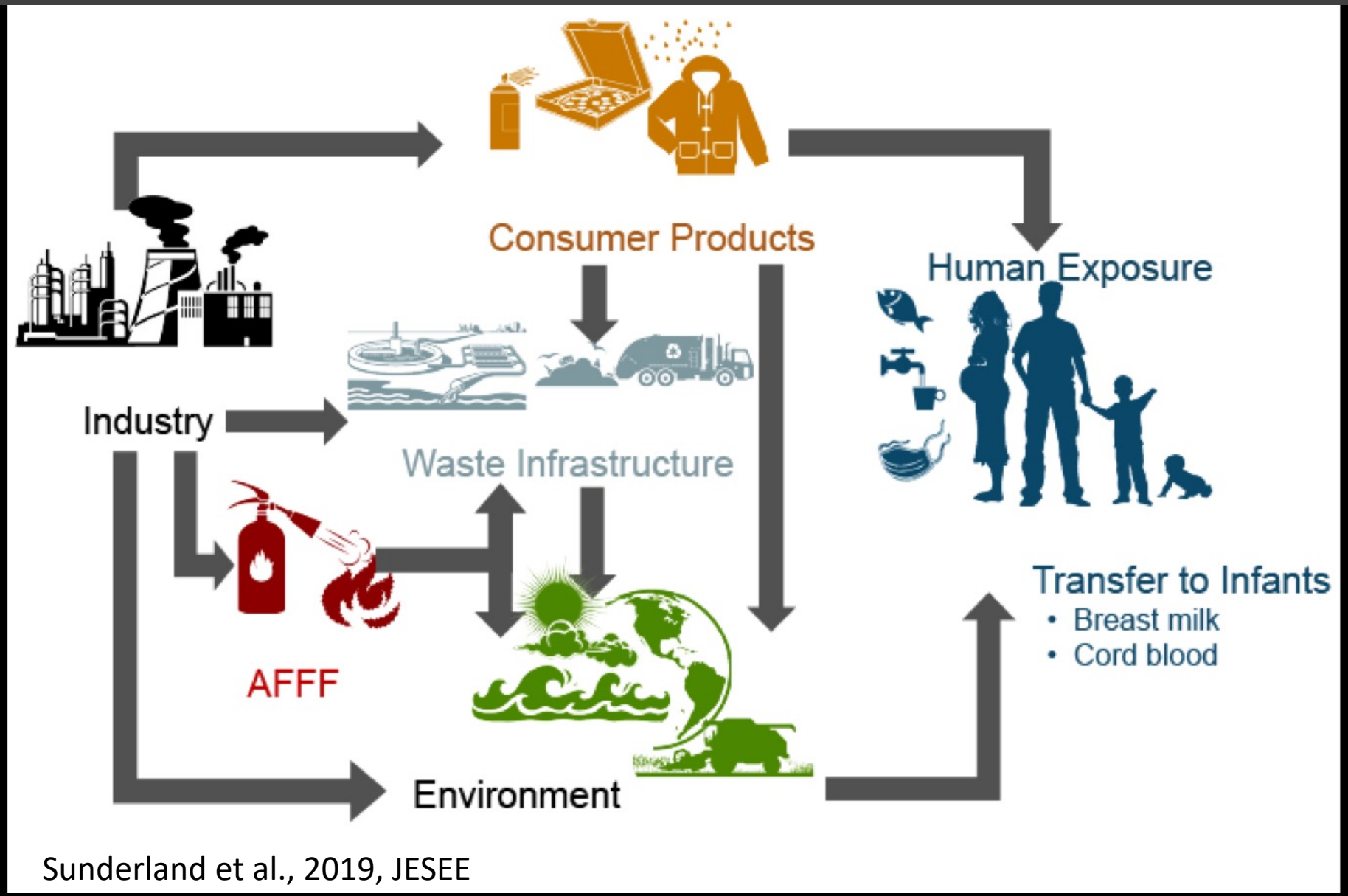
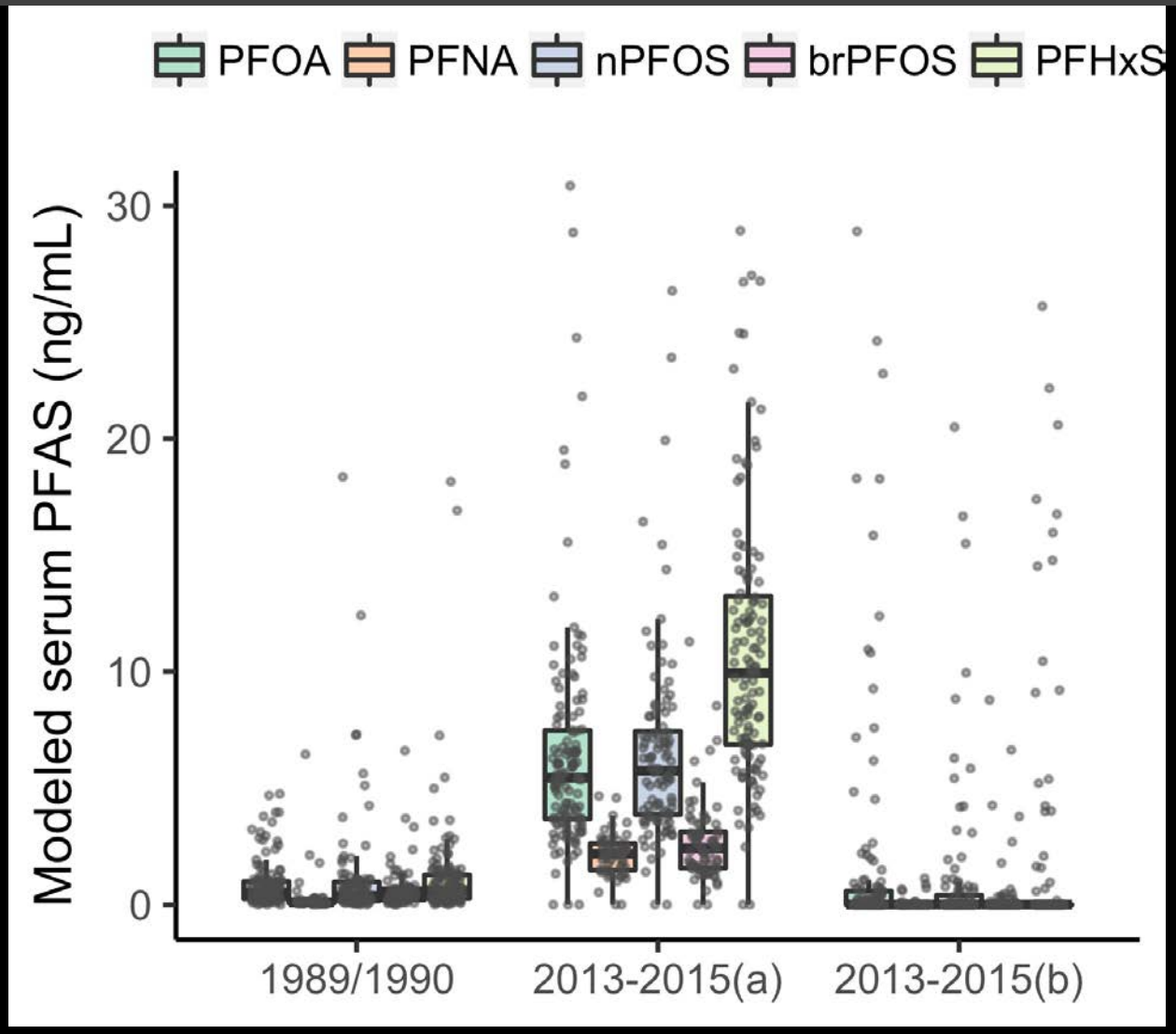
# Two timescales of human exposures with different solutions: 1) Contemporary production of new compounds; 2) Legacy contamination




Sunderland et al., 2019, JESEE

# Suggestive increases in general population exposures from drinking water between 1989/1990 and 2013-2015




Hu et al., 2019, EHP

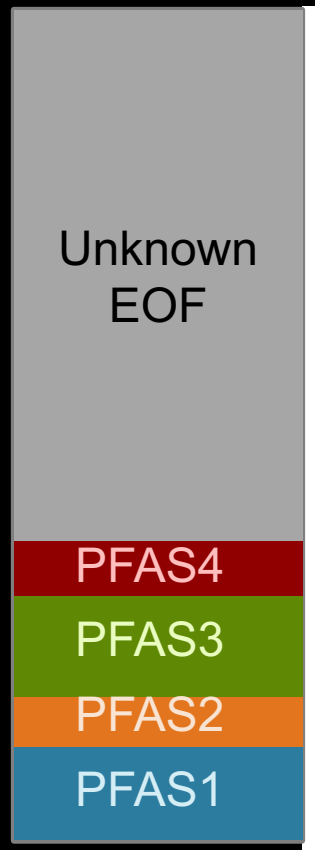
# Pilot data suggest large increase in unidentified PFAS in drinking water: Consistent with production trends

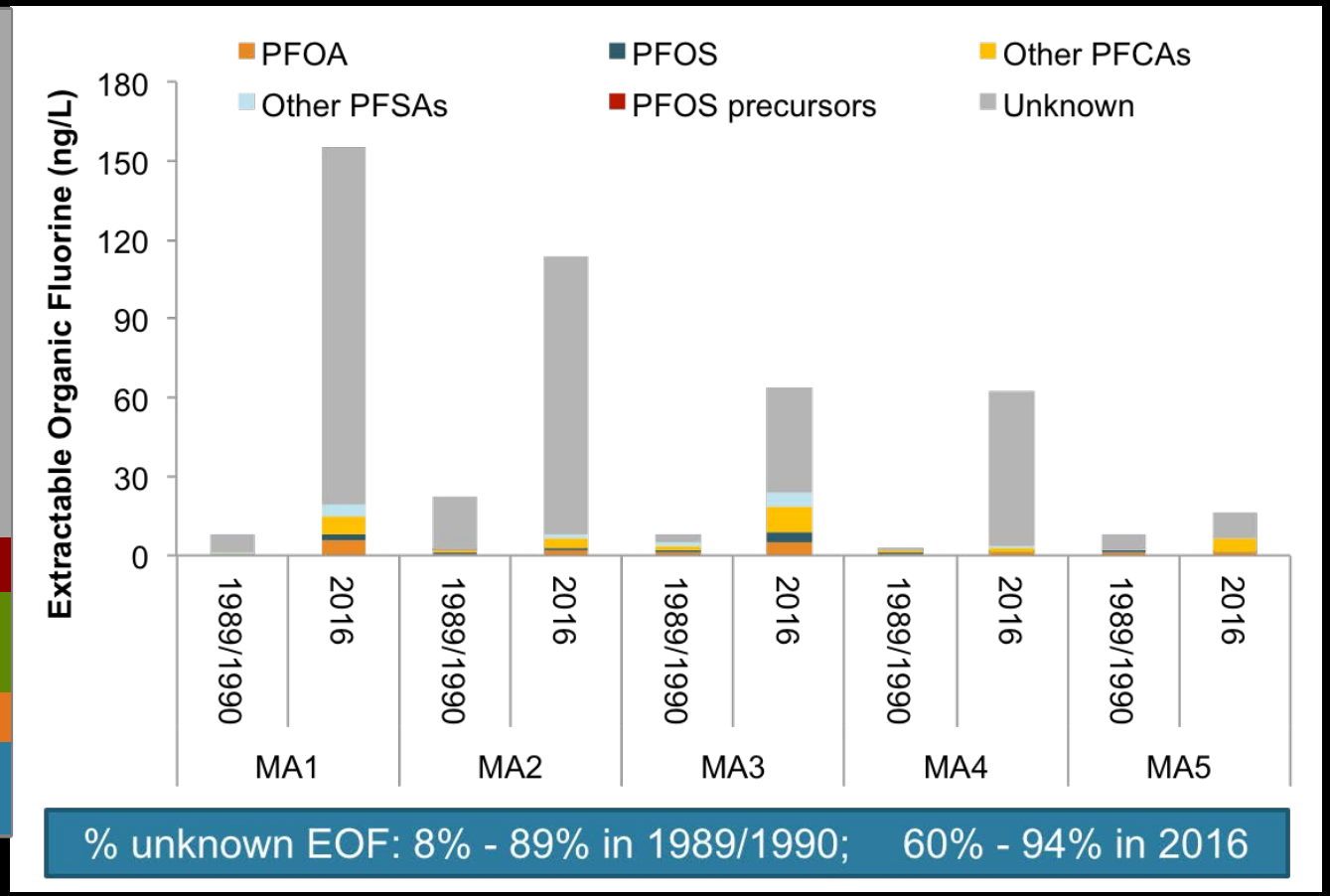
Extractable organic fluorine (EOF)

Thousands of chemical structures registered

>200 detected

Toxicity of alternative PFASs not well understood

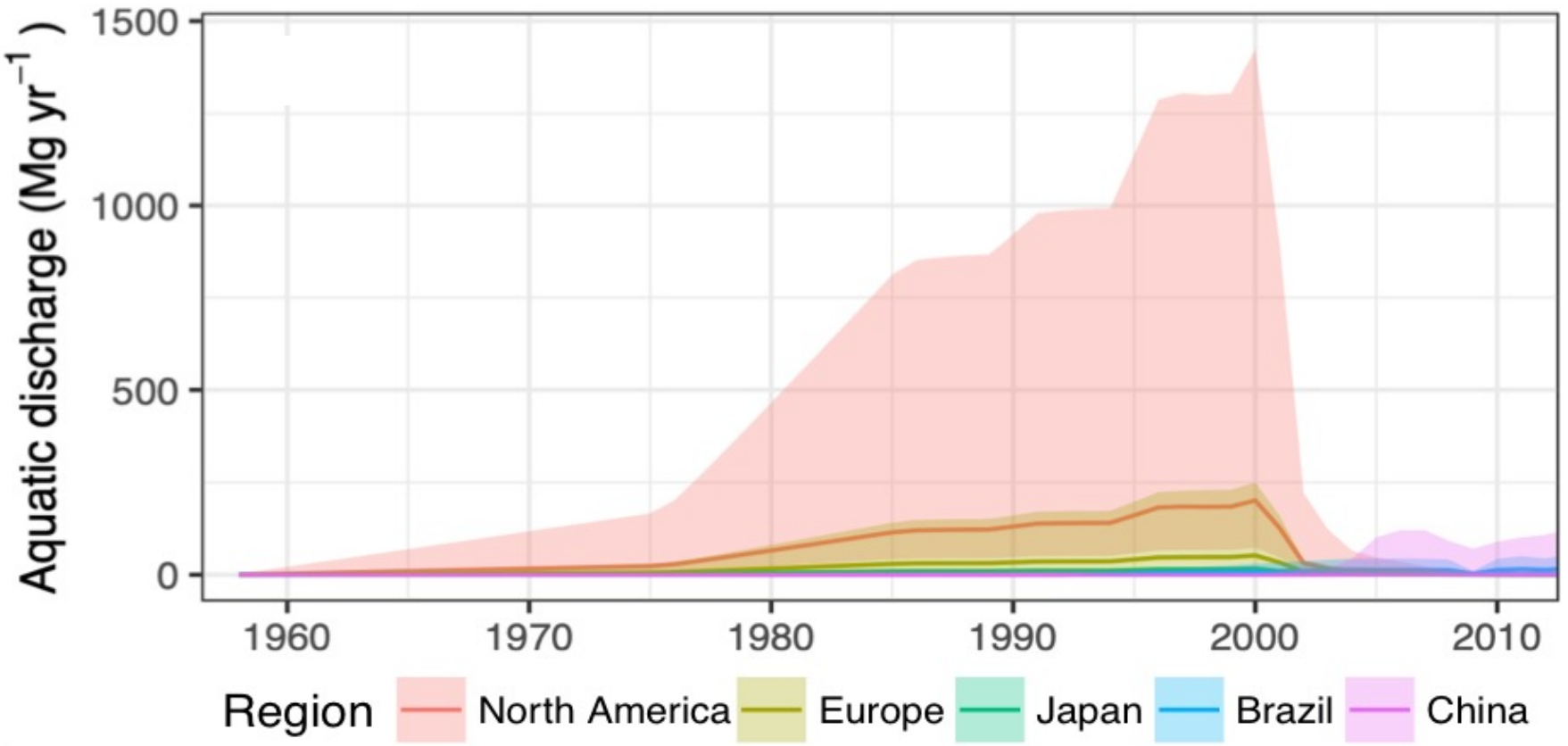



Hu et al., 2019, EHP

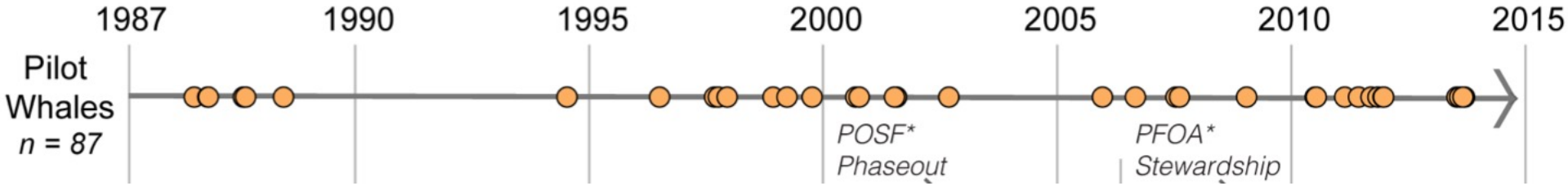
Production changes: What has happened following the phase out of POSF production ca. 2000?

Modeled PFOS discharges from rivers to the global oceans

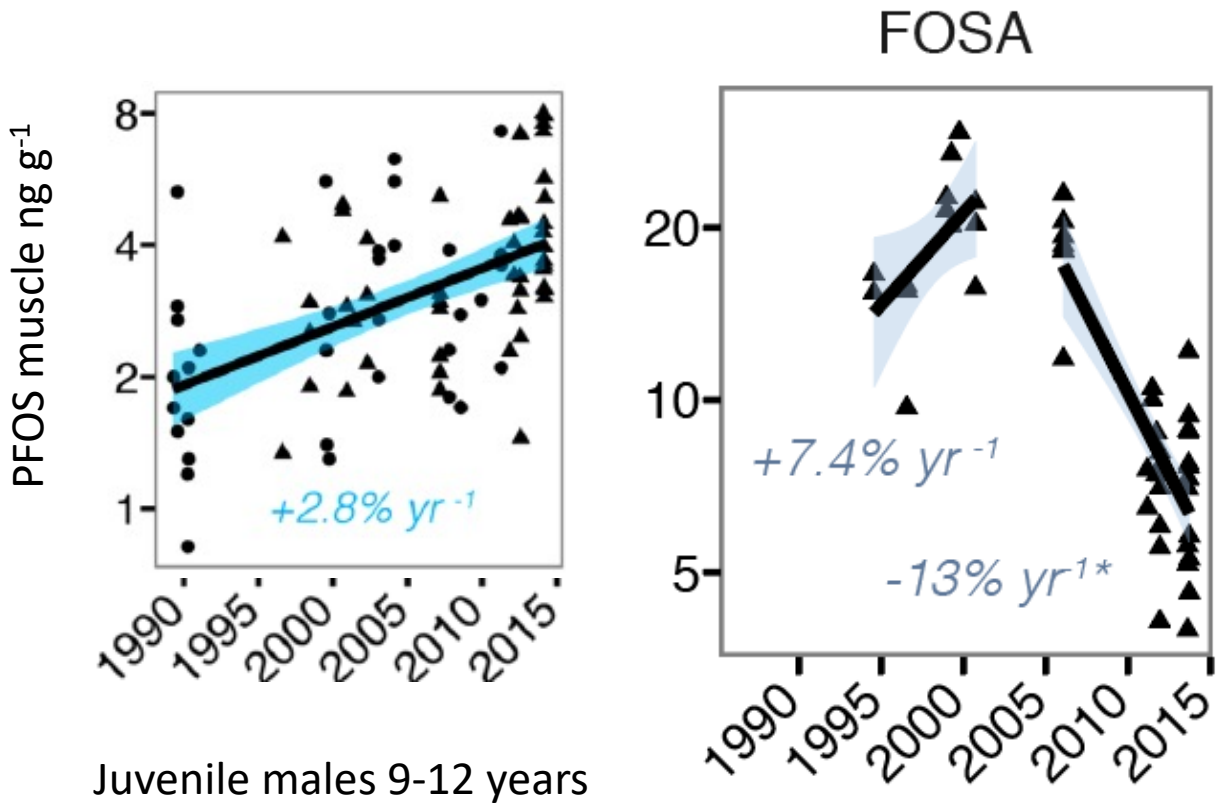



Wagner, 2021

# Declining atmospheric FOSA (a PFOS precursor) drives declines in pilot whale PFAS exposures since 2000



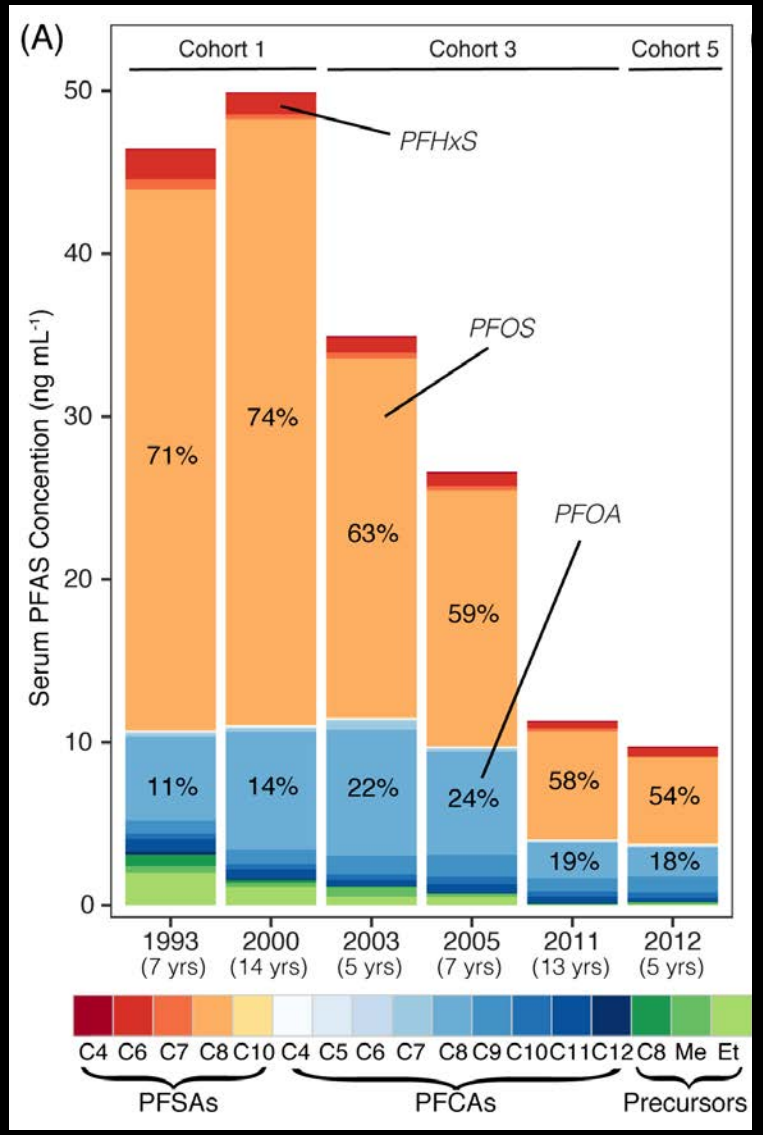

Dassuncao et al., 2017, ES&T

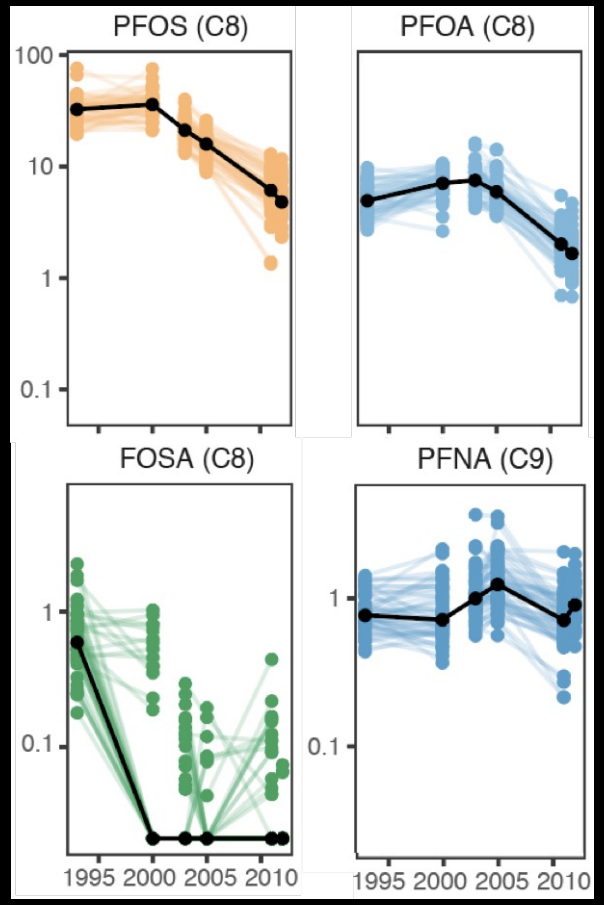



Juvenile males 9-12 years

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

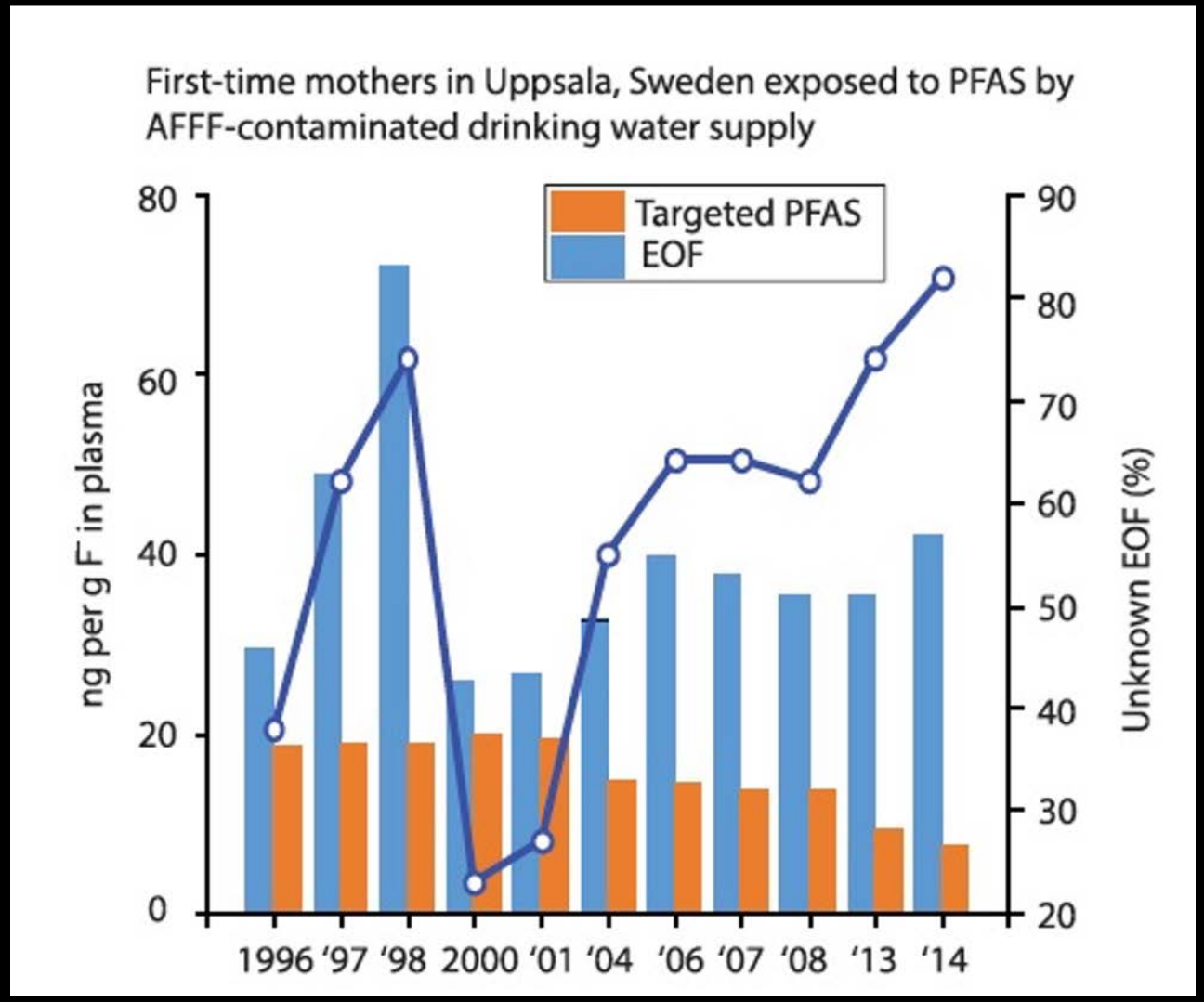
**Some long chain PFAS (i.e., PFNA) stable or increasing**




Dassuncao et al., 2018

# Large quantities of organofluorine in human serum




Data from Miaz et al., 2020, ESPI

# Summary: Better understanding of predominant exposure sources for different populations is needed for risk mitigation

## Present Gaps

- Simple analytical techniques for closing PFAS mass budget
- Incomplete information on pollution sources
- Limited data on impacts of changes in production and regulation on exposure

## Solutions

- Toolbox of available techniques; analytical innovation and standardization of methods needed
- Chemometric methods; data science and modeling using available observations; more systematic exposure studies
- Longitudinal human/wildlife data; total PFAS measurements

# Acknowledgements


- **Contributions**
- **Trainees**: Clifton Dassuncao, Cindy Hu, Heidi Pickard, Bridger Ruyle, Lara Schultes , Jennifer Sun, Andrea Tokranov, Colin Thackray, Charlotte Wagner, Xianming Zhang
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STEEP Sources, Transport, Exposure & Effects of PFASs

SERDP DOD • EPA • DOE

NIEHS National Institute of Environmental Health Sciences

RICHARD AND SUSAN SMITH FAMILY FOUNDATION