The known unknowns: What are we are currently overlooking related to PFAS exposures?

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HARVARD | SCHOOL OF PUBLIC HEALTH
Department of Environmental Health

Harvard John A. Paulson School of Engineering and Applied Sciences

SERDP DOD • EPA • DOE

NIEHS National Institute of Environmental Health Sciences

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

Biogeochemistry of Global Contaminants HARVARD

By way of background: I lead STEEP Project 1 on the impacts of geochemistry and transport on PFAS exposure from drinking water and fish

Aims:

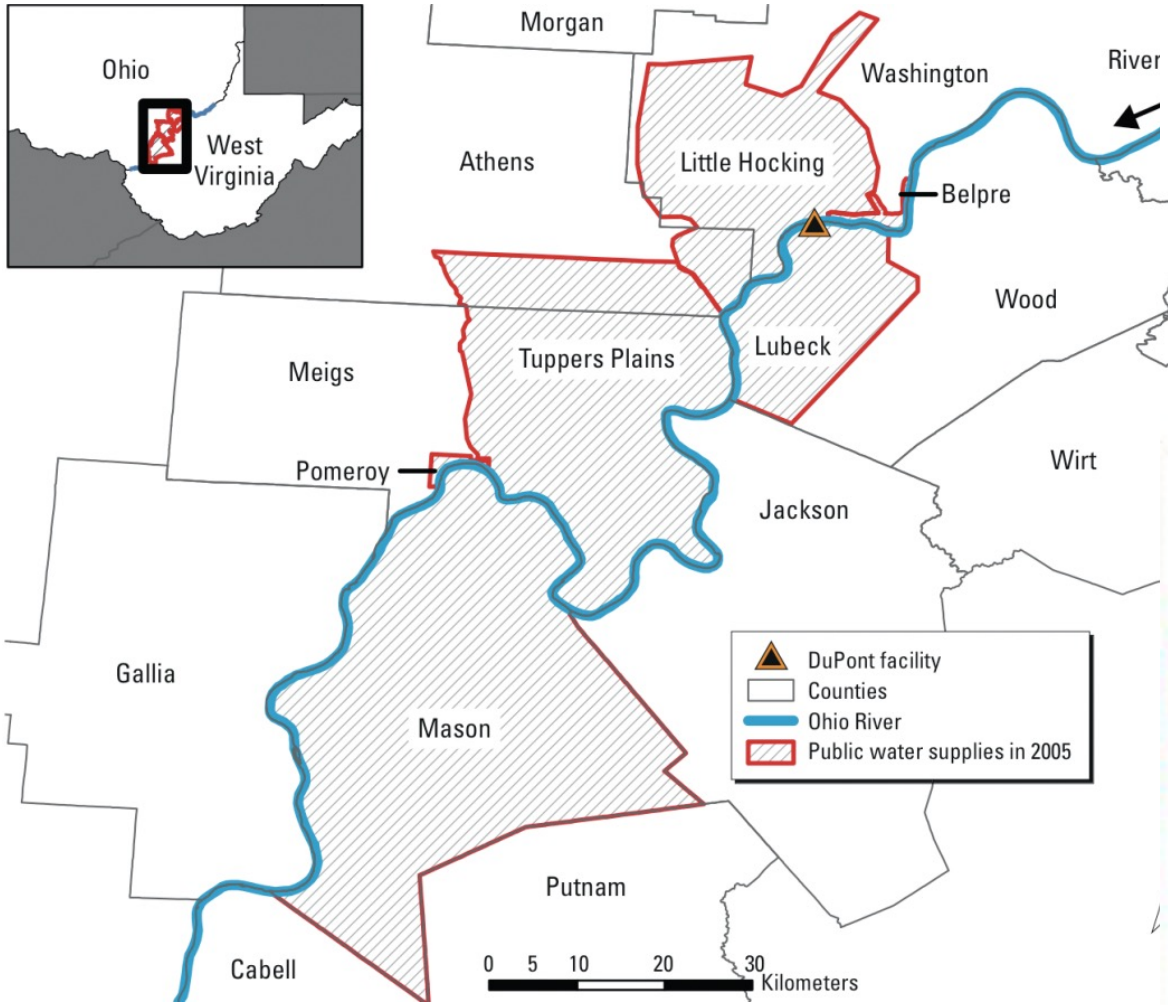
- Aim 1: Fingerprinting PFAS exposure sources (several methods published)
- Aim 2: Geochemical factors affecting PFAS transport and transformation at AFFF contaminated site
- Aim 3: USGS mobile fish lab (now integrated with Rainer Lohmann/URI research)

Relevance to SRP Mandate:

- Improved detection methods
- Better characterization of exposure sources for risk assessment

- Renewal application: Focus on PFAS precursors

Why do we care so much about PFAS exposure: Diverse adverse health effects



C8 Science Panel

http://www.c8sciencepanel.org

cross-sectional study ~ 70,000 people (2005-2013)

Probable links for <u>PFOA</u> in this community included:

Cancer - kidney and testicular

Diagnosed elevated cholesterol

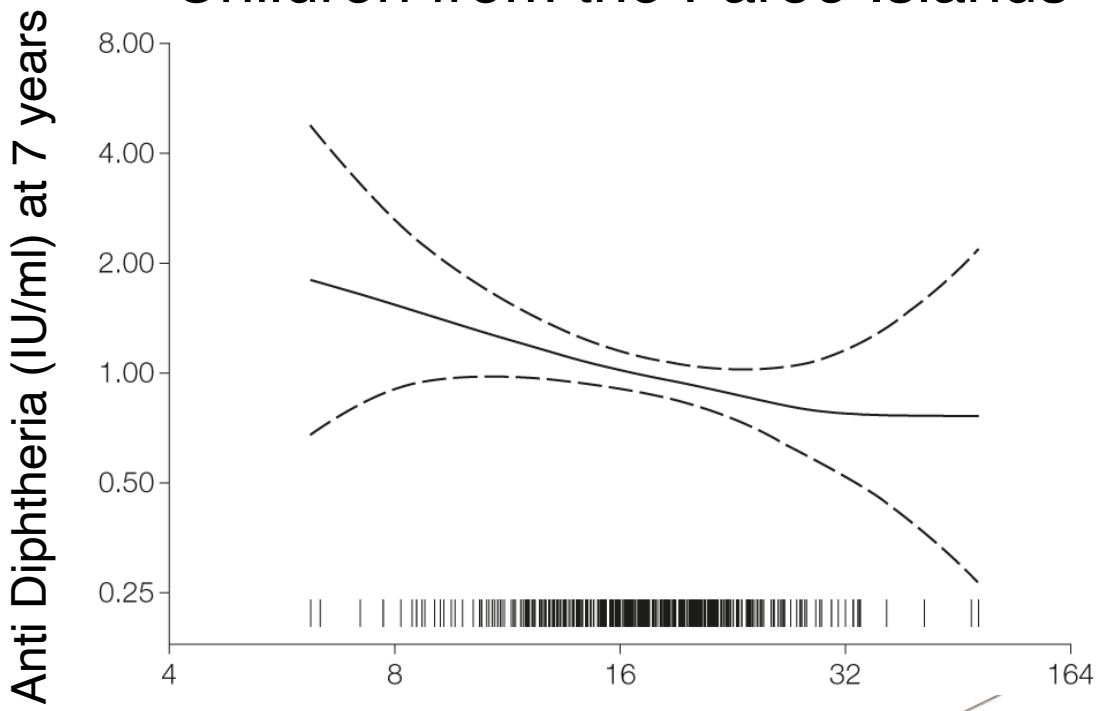
Pregnancy-induced hypertension and preeclampsia

Thyroid Disease

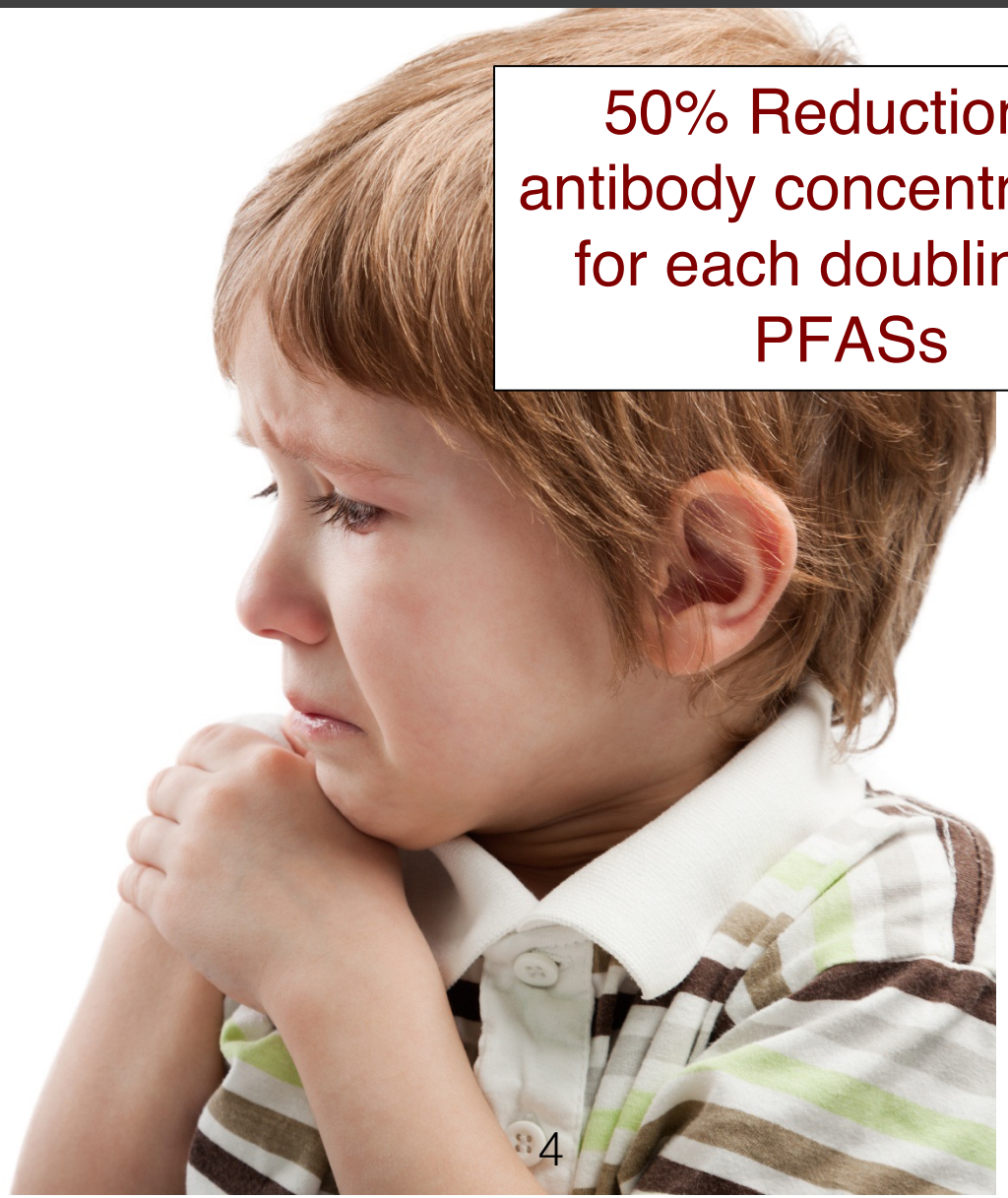
Ulcerative colitis

Potent immunotoxic response following vaccination in Faroese birth cohort

Children from the Faroe Islands

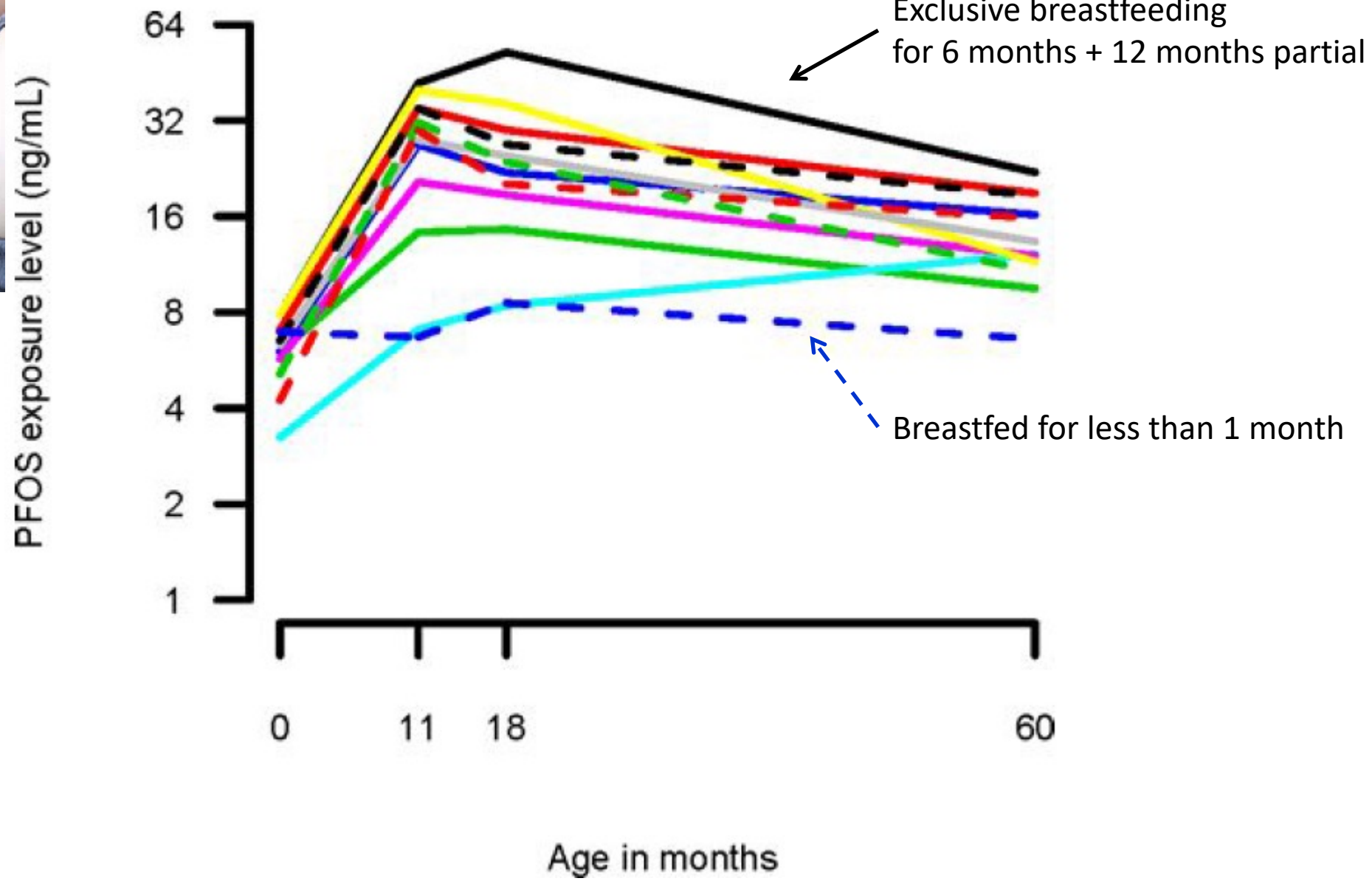


Grandjean et al., 2012



50% Reduction in antibody concentrations for each doubling of PFASs

Infancy is critical for risk assessment due to peak PFAS exposure and crucial development of the adaptive immune system



Mogensen et al., ES&T, 2015

High certainty

Lower certainty

Developmental effects affecting the unborn child

Delayed mammary gland development

Reduced response to vaccines

Lower birth weight

Obesity

Early puberty onset

Increased miscarriage risk (i.e. pregnancy loss)

Low sperm count and mobility

Thyroid disease

Increased cholesterol levels

Breast cancer

Liver damage

Kidney cancer

Inflammatory bowel disease (ulcerative colitis)

Testicular cancer

Increased time to pregnancy

Pregnancy induced hypertension/pre-eclampsia (increased blood pressure)

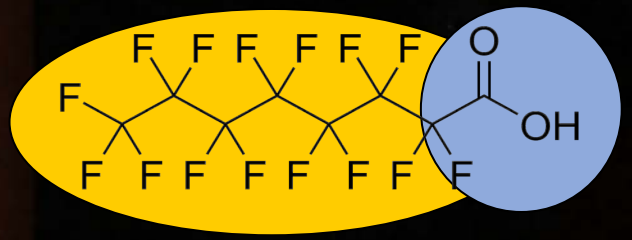
Image source: https://www.eea.europa.eu/themes/human/chemicals/emerging-chemical-risks-in-europe

PFAS: Delayed insight or delayed public access

Research finding	*First*	*Public*
PFASs in general population	1976	2001
PFASs in cord blood	1981	2004
PFAS transfer into milk (goats)	1993	2008
PFOS immunotoxicity (monkeys)	1978	2000
Immune cell changes in workers	1992	2018

22 years lag

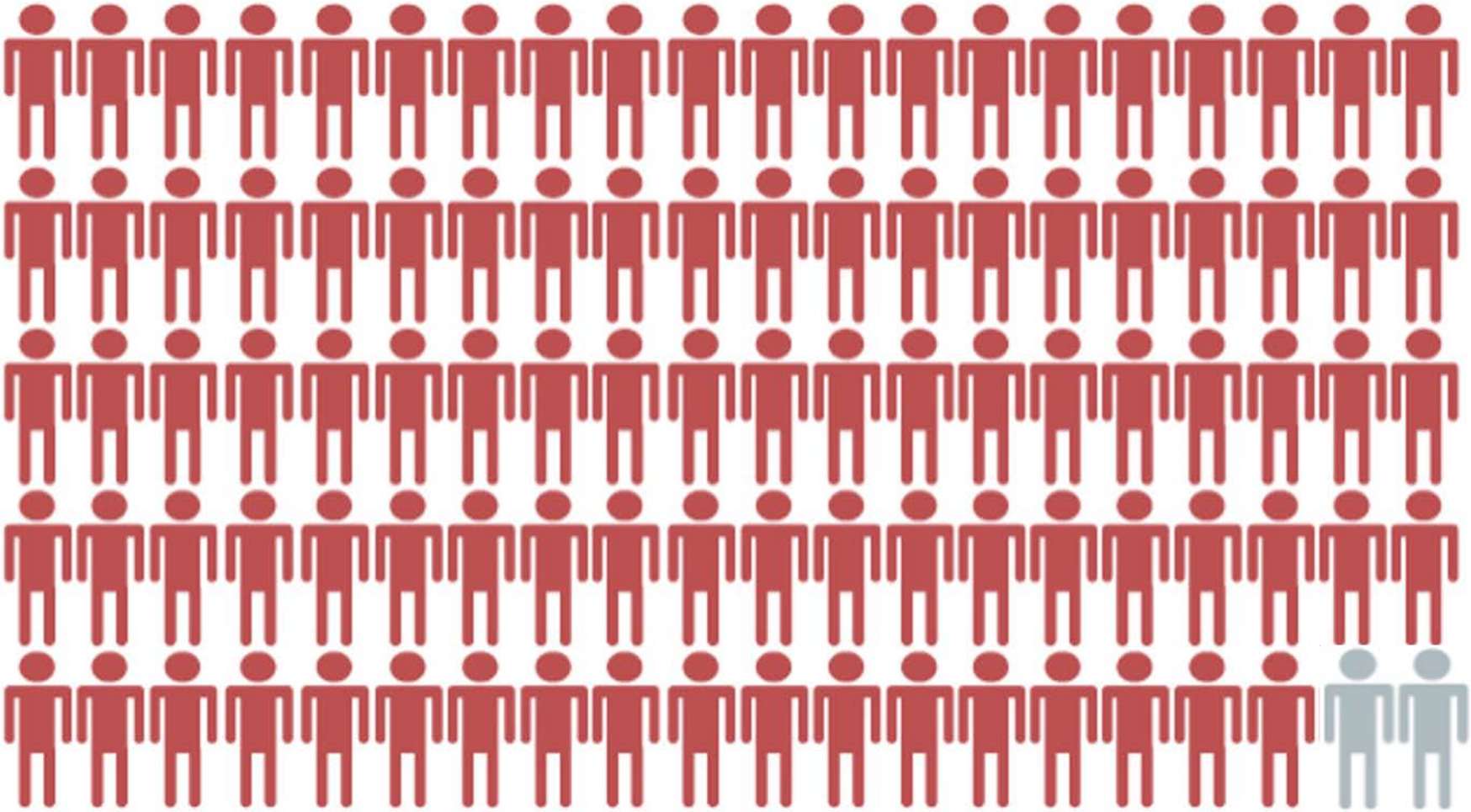
Water-loving



Repels water
Repels fat

F-C
FOREVER CHEMICALS

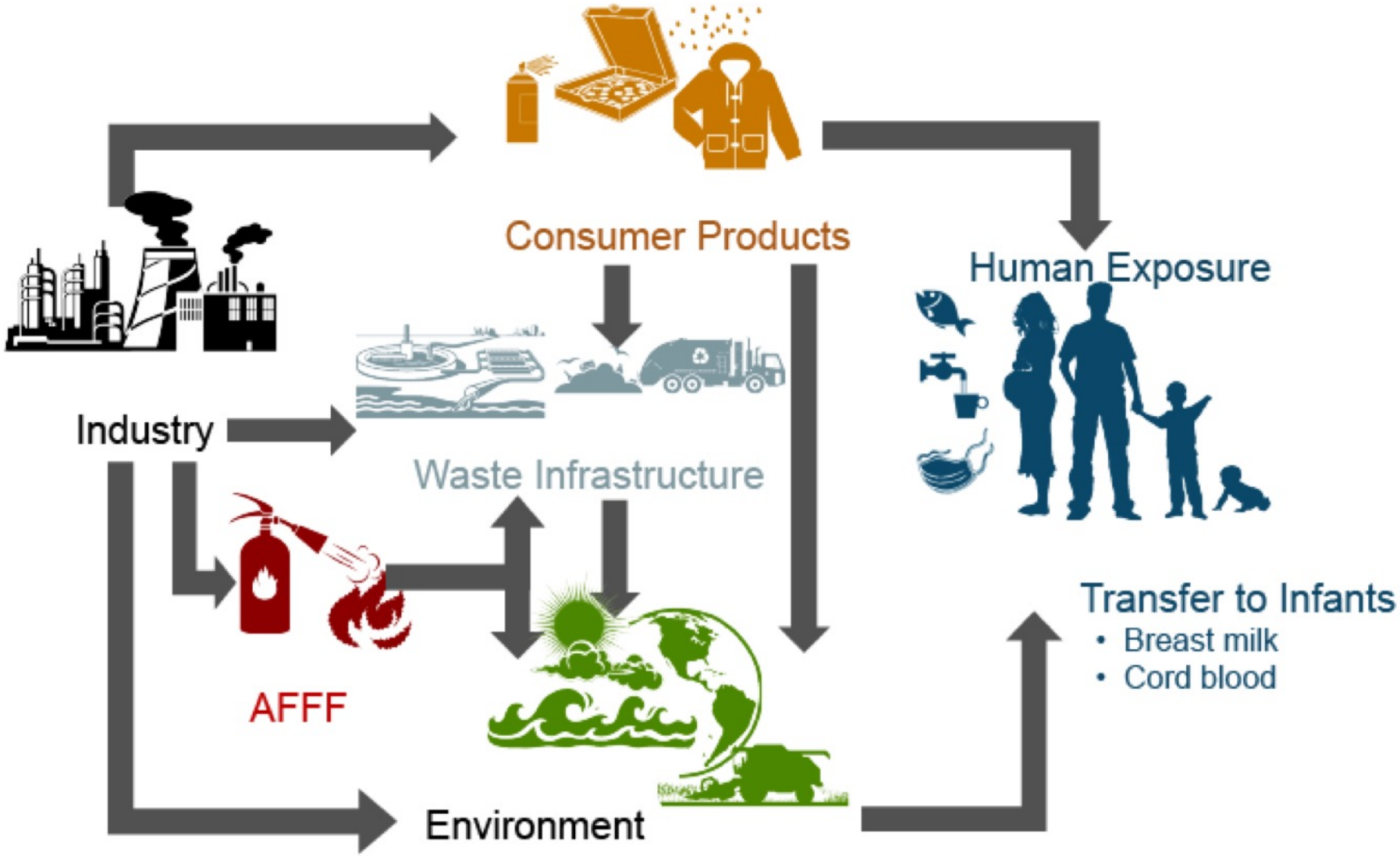
98-99% of Americans have detectable blood PFAS: Who are the 1-2%?



Detectable PFAS in serum

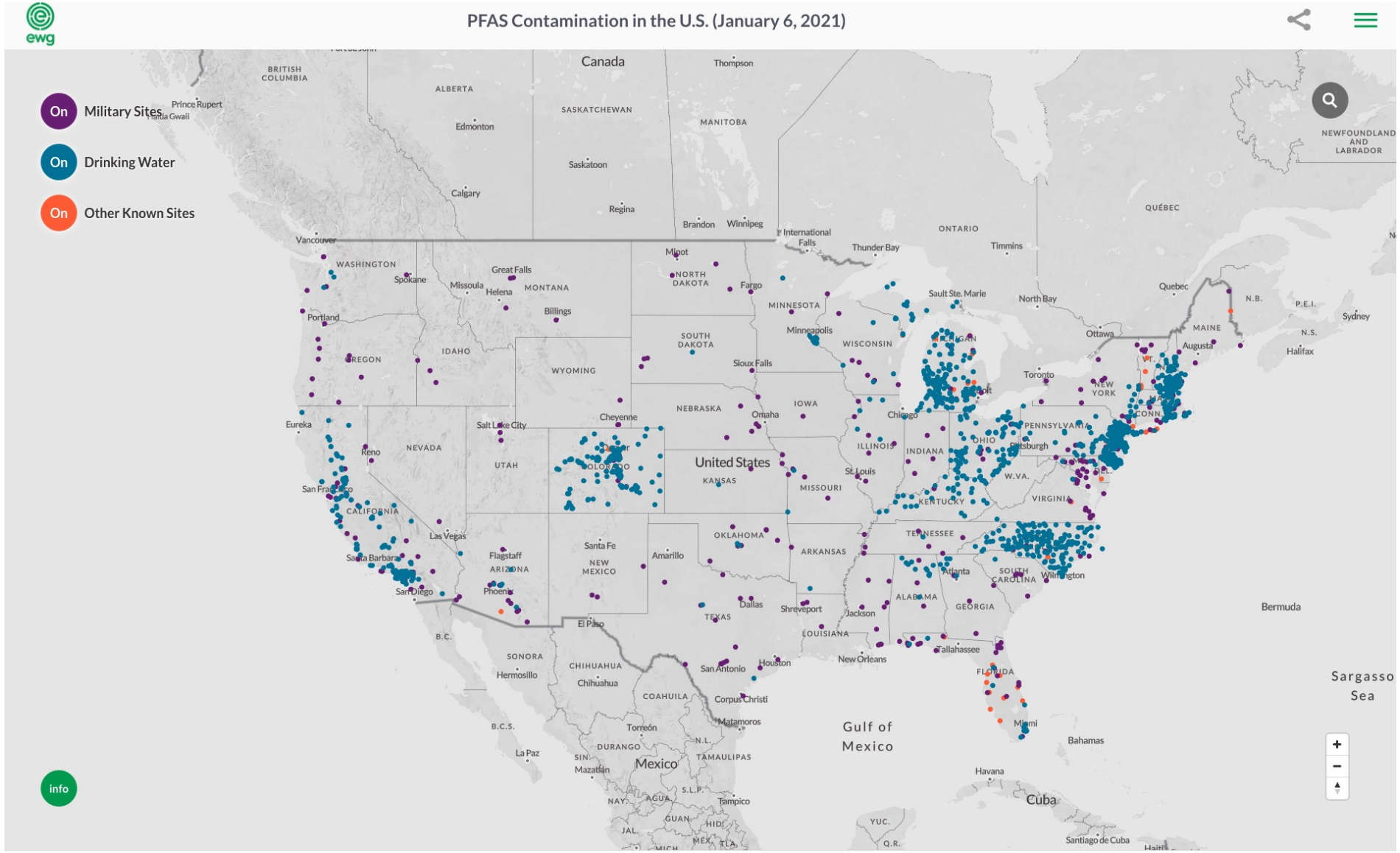
Below detection

Diverse human exposures to PFAS:
Can we characterize the relative importance of different sources?

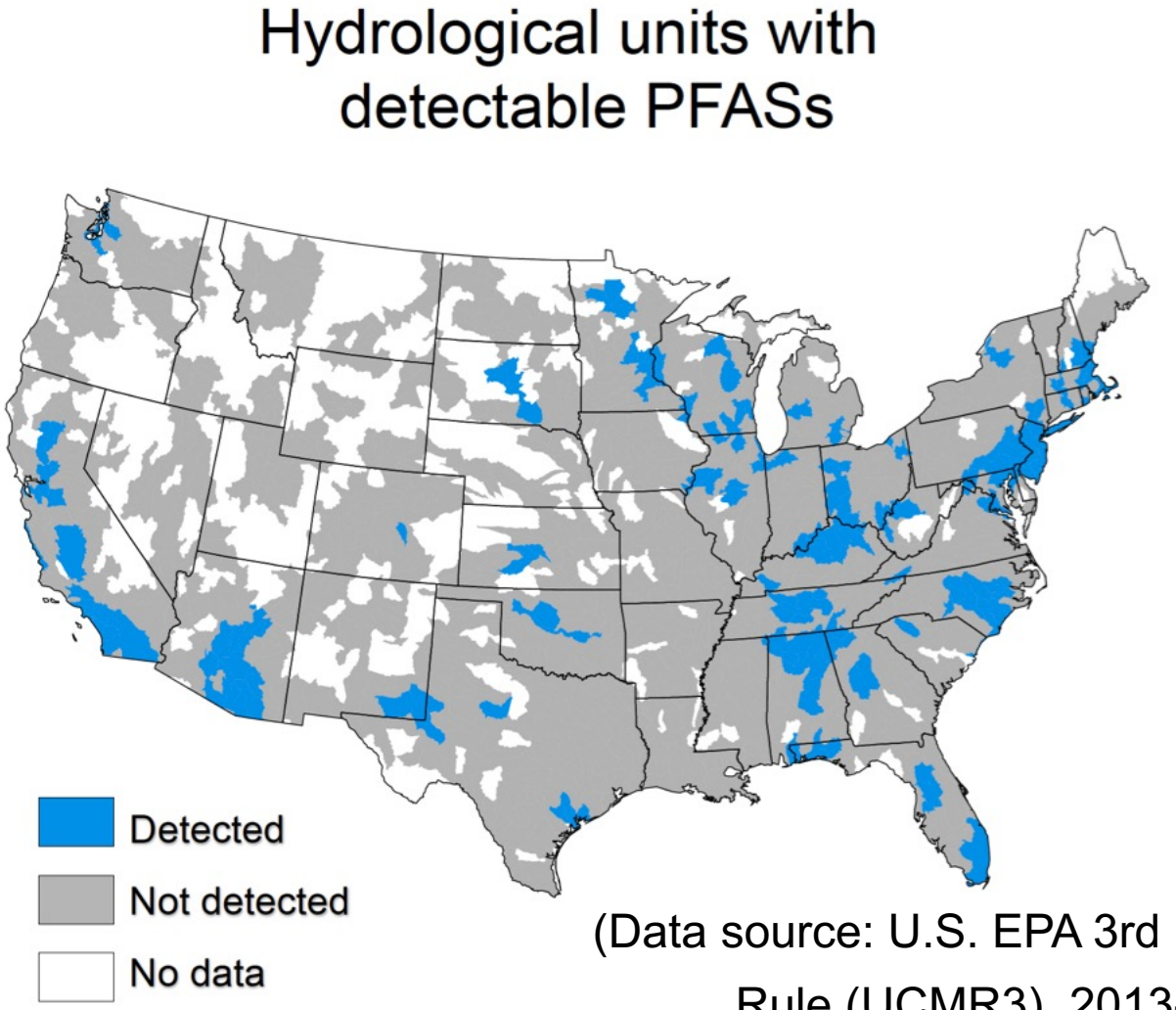


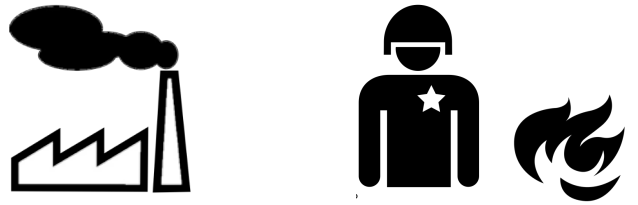
Sunderland et al., 2019, JESEE

Drinking water is the predominant PFAS exposure source near contaminated sites

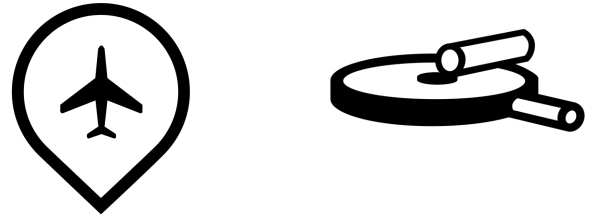


No good national databases for environmental releases to characterize general population exposures





Industrial sites Military fire training areas



AFFF
Certified airports

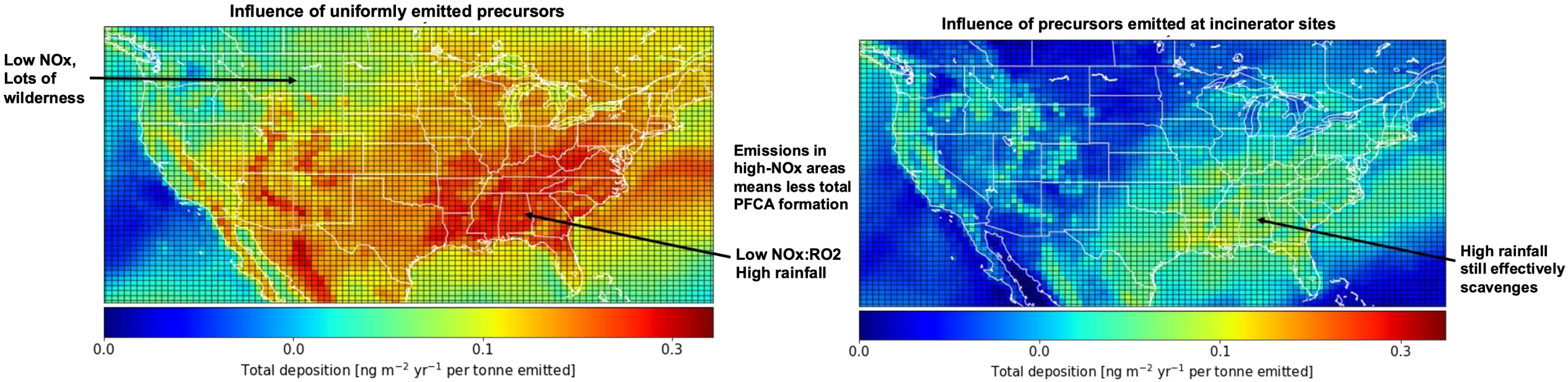
Wastewater treatment plants

Biogeochemistry of Global Contaminants
HARVARD

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

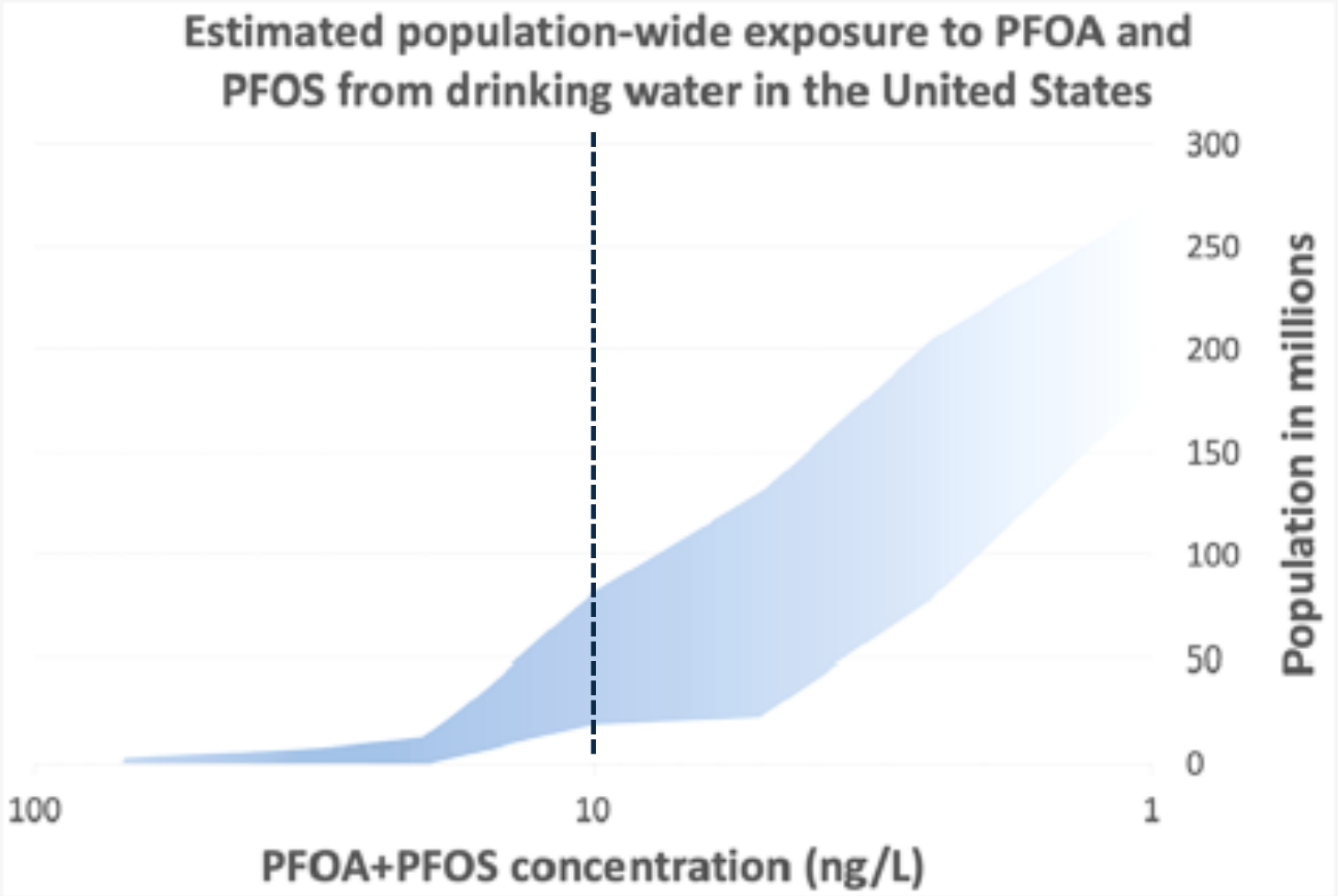
Importance of atmospheric PFAS emissions and deposition increasingly recognized

Modeled PFCA deposition (ng m^{-2} yr^{-1} per tonne emitted) with differing assumptions regarding source locations



Sun, Thackray et al. (in prep.)

Estimated **18-80 Million** U.S. Residents have **>10 ng/L PFAS** in their tap water



Andrews and Naidenko, 2020, EST Letters

Cambridge tap water:
Current information about PFAS testing (Feburary 2021)
Test Results

PFAS Analyte PFAS6 (regulated)	Result ng/L (ppt)
Perfluorooctane Sulfonic Acid (PFOS)	Trace*
Perfluorooctanoic Acid (PFOA)	6.0
Perfluorohexane Sulfonic Acid (PFHxS)	2.3
Perfluorononanoic Acid (PFNA)	Not Detected
Perfluorohepatanoic Acid (PFHpA)	3.0
Perfluorodecanoic acid (PFDA)	Not Detected
Sum of PFAS6 - compare to MassDEP MCL of 20 ng/L	**11.3**

*Trace amounts are present, but below the minimum concentration that can be reported as a quantified value.
MCL = Maximum Contaminant Level
ng/L = nanogram per liter
ppt = parts per trillion

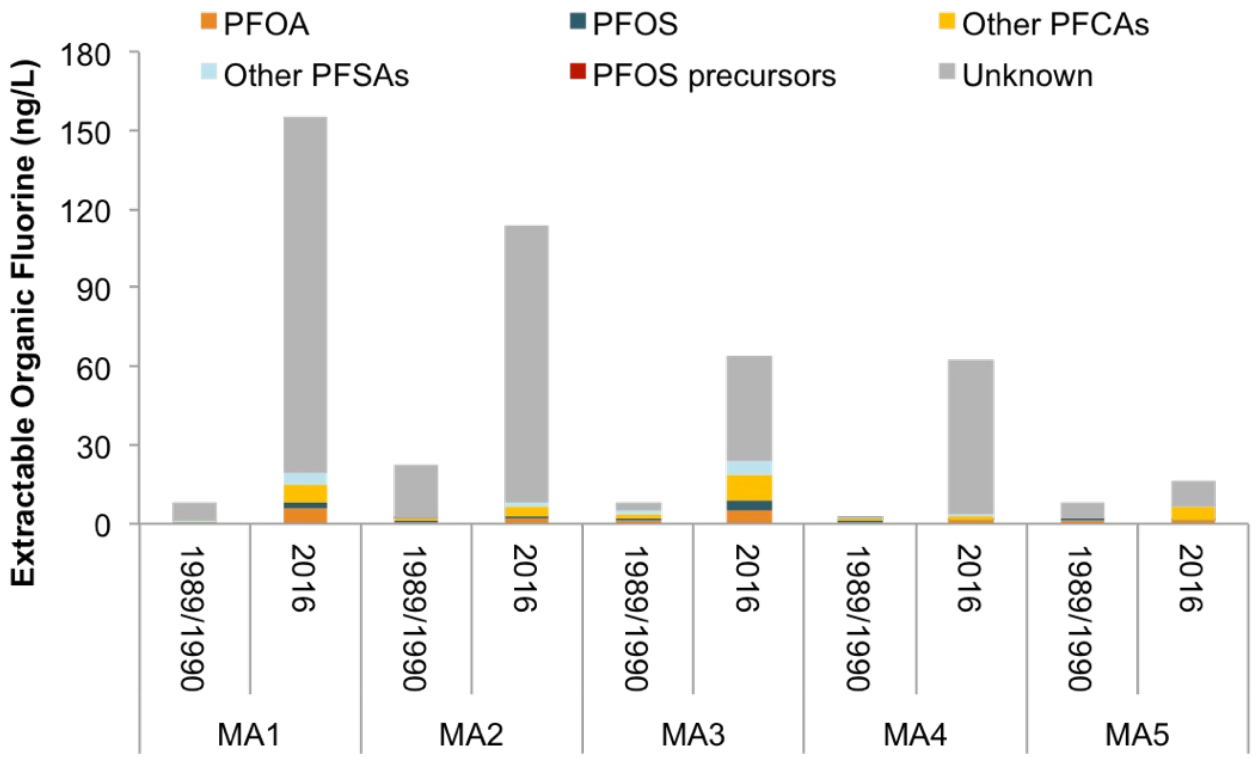
PFAS = Per and Poly Fluoroalkyl Substances

There are thousands of PFAS. Large amounts of unidentified organofluorine in surface & drinking waters

AFFF impacted watersheds in Cape Cod MA

Ruyle et al. (2021) ES&T

Drinking Water in MA



% unknown EOF: 8% - 89% in 1989/1990; 60% - 94% in 2016

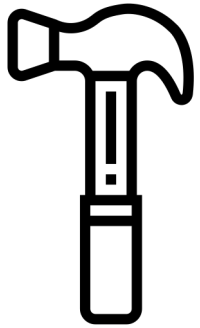
Hu et al. (2019), Environmental Health Perspectives

NIH National Institute of Environmental Health Sciences
EPA United States Environmental Protection Agency

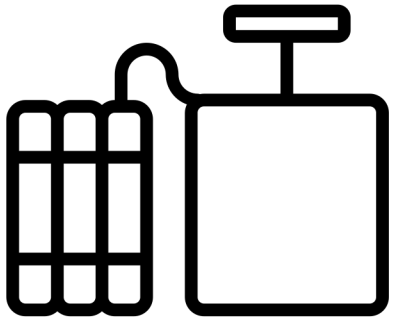
14

Need to better leverage the full analytical toolbox for PFAS measurements

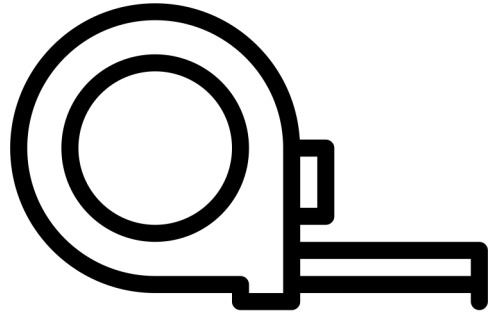
Targeted analysis
"the go to"



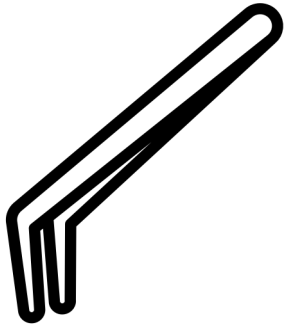
TOP assay
"the oxidizer"



Extractable organofluorine
"the total"



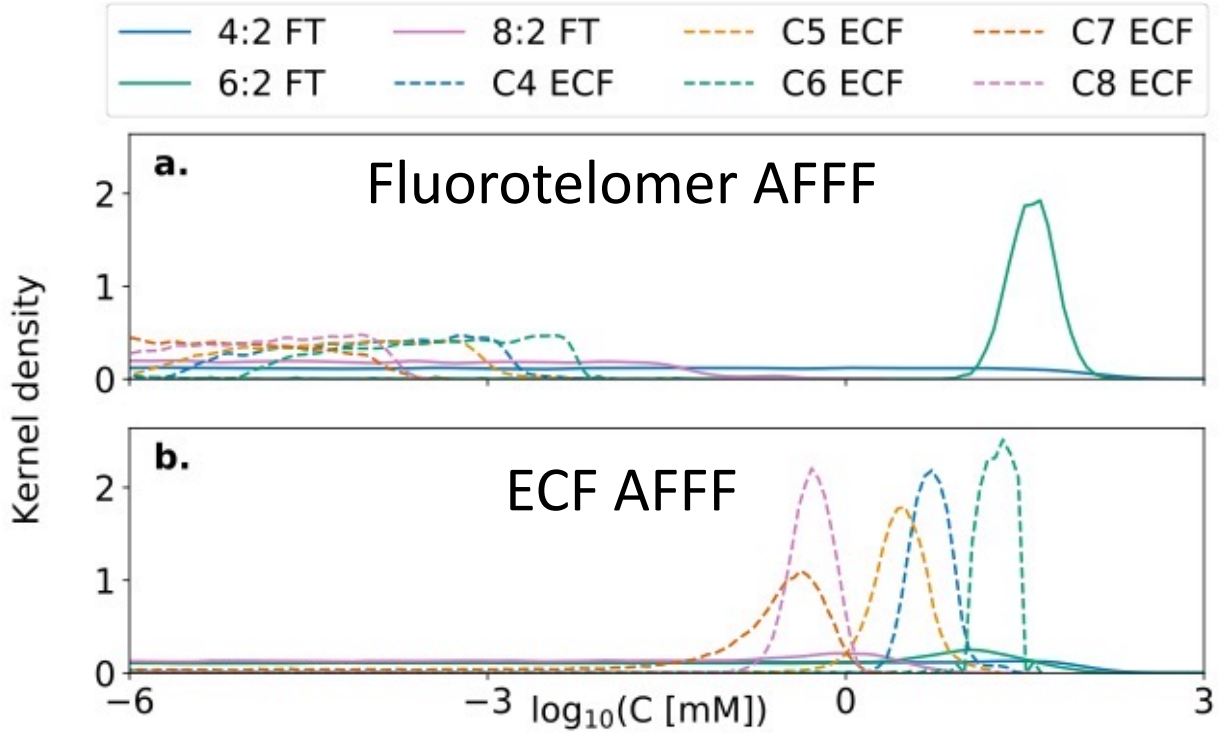
Ion chromatography
mass spectrometry
"the mini"



Non-targeted analysis/
suspect screening
"the discoverer"

Precursors are the majority of PFAS in AFFF

Source and chain length can be inferred from the TOP assay

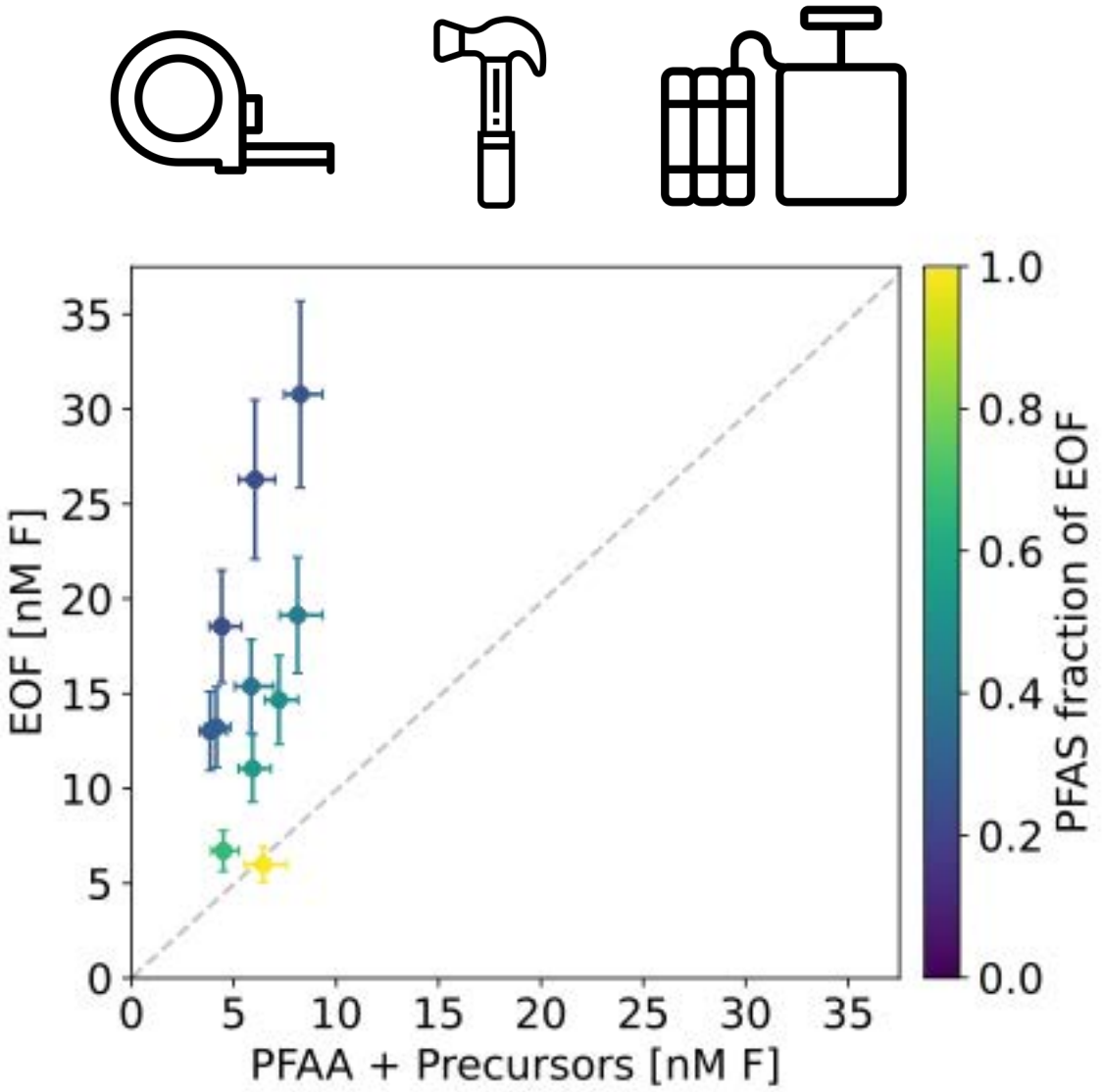


EPA United States Environmental Protection Agency

NIH National Institute of Environmental Health Sciences

Ruyle, B. J.; **Thackray, C. P.**; McCord, J. P.; Strynar, M. J.; Mauge-Lewis, K. A.; Fenton, S. E.; **Sunderland, E. M.** *Environ. Sci. Technol. Lett.* **2021**, *8* (1), 59–65.

PFAS suspect screening and ultra-short chain PFAA do not account for unexplained EOF in MA surface waters



TFA < 3 nM F consistent with HFC degradation

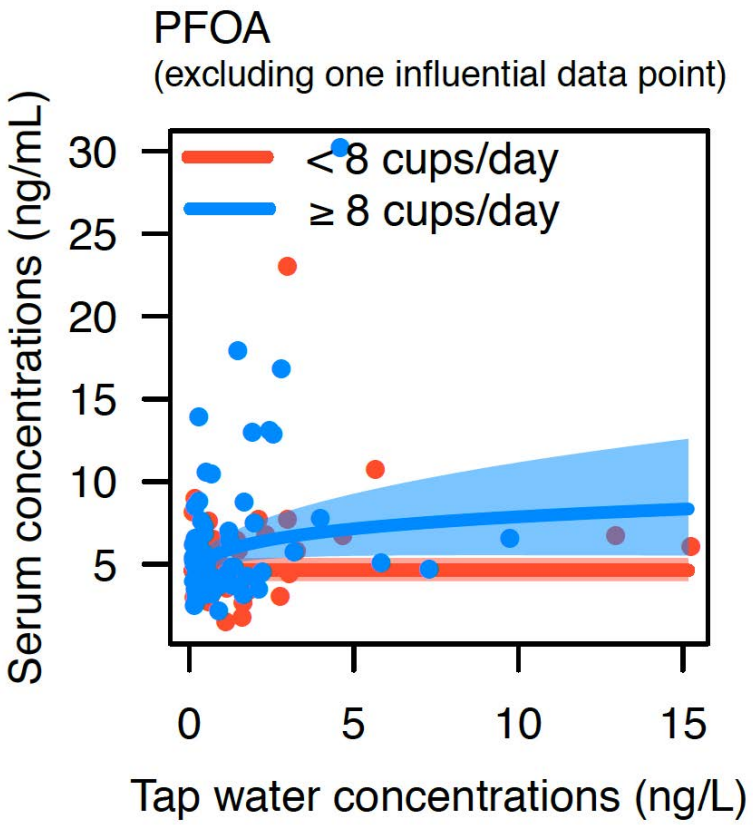
Suspect screening did not identify any PFAS beyond targeted compounds

Several library matches to fluorinated pharmaceuticals

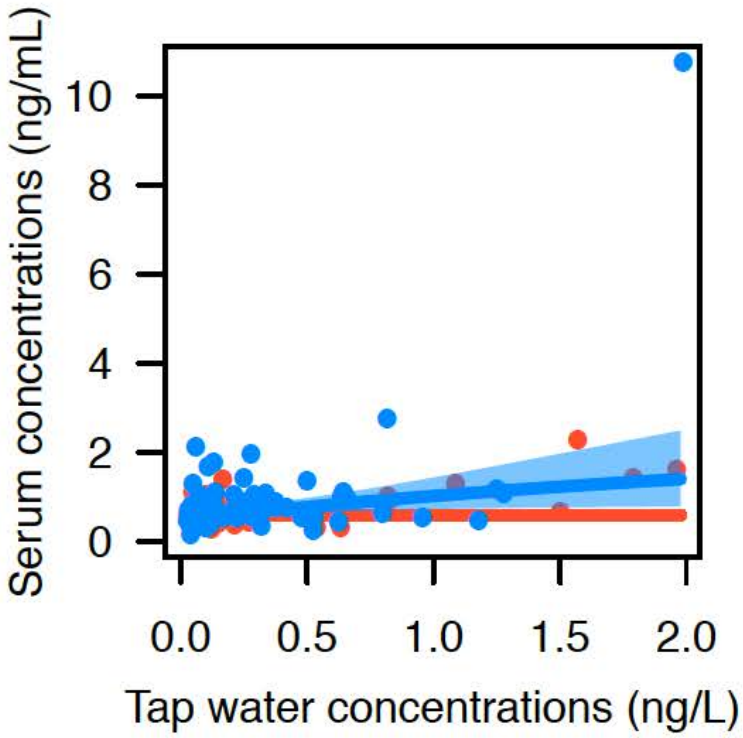
For much of the general U.S. population drinking water may only account for ~20% total PFAS exposure

Tap water PFOA and PFNA are statistically significant predictors of serum in 1990 for the NHS cohort

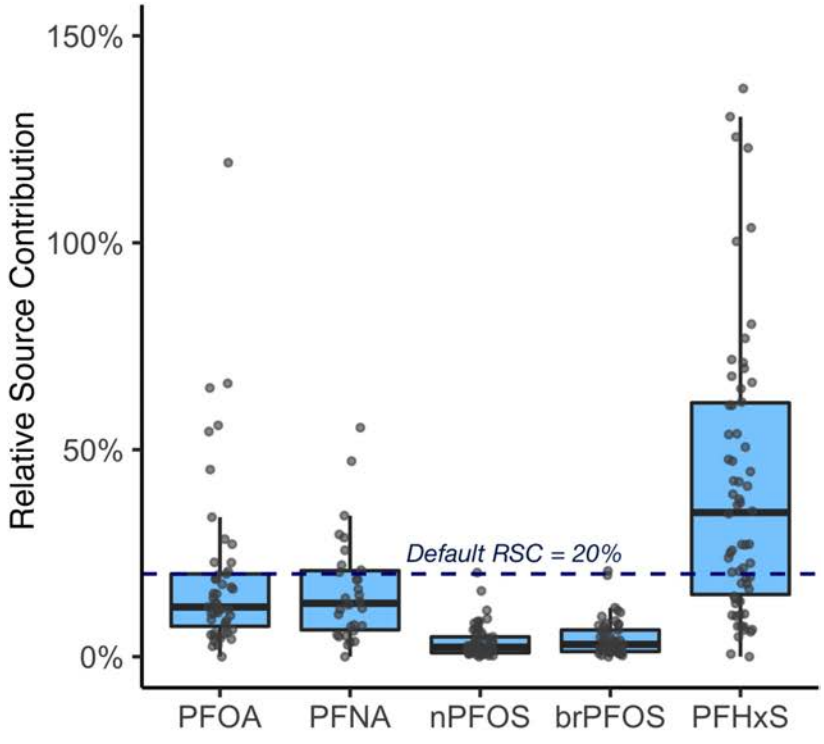
PFOA



PFNA



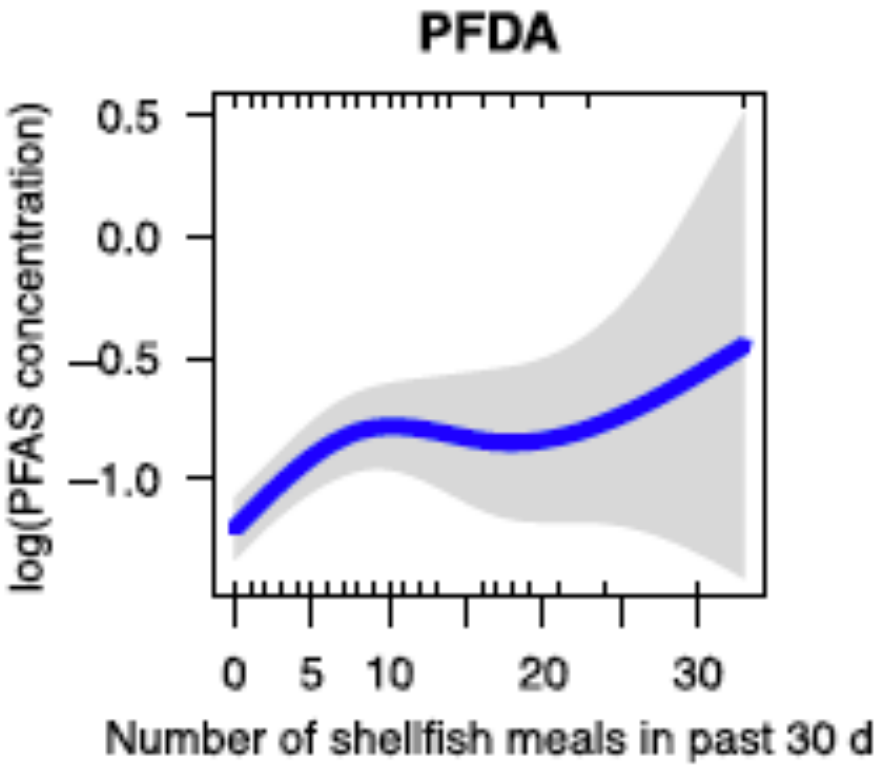
RSC = 2% - 34%



Hu et al., 2019, EHP

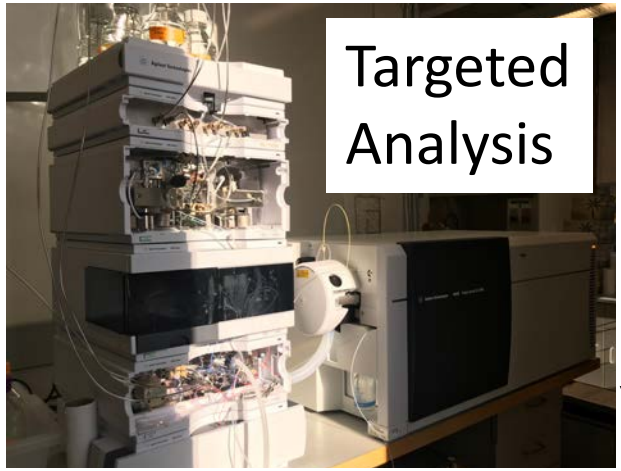
Some PFAS accumulate in food webs & seafood: an important human exposure source

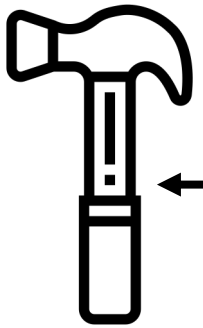
NHANES 2005-2006



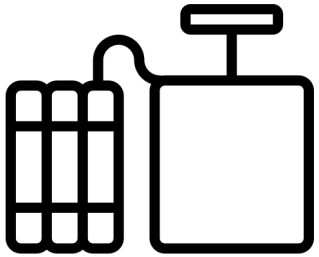
Hu et al. 2018, Environmental Health

Expanding the Analytical Toolbox to Biological Tissues





TOP Assay



Suspect Screening/Non-target

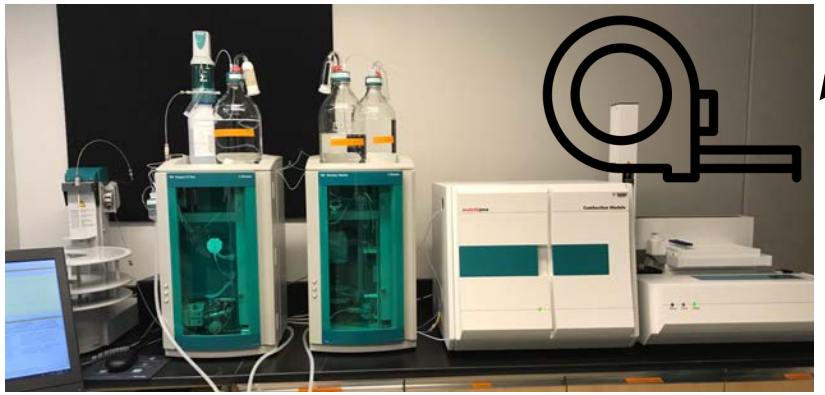
Sample Clean-Up

1. Ion-Pairing Extraction

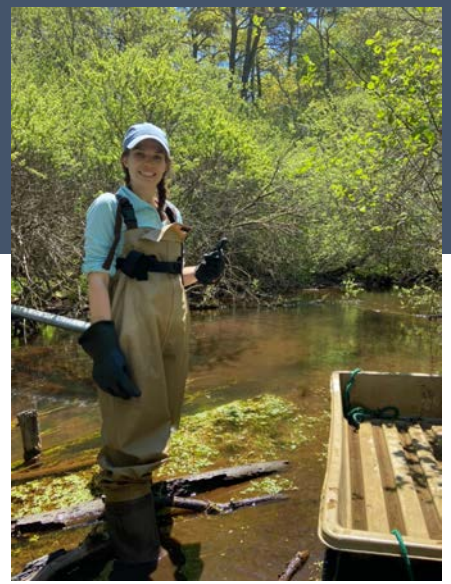
2. Acetonitrile Extraction

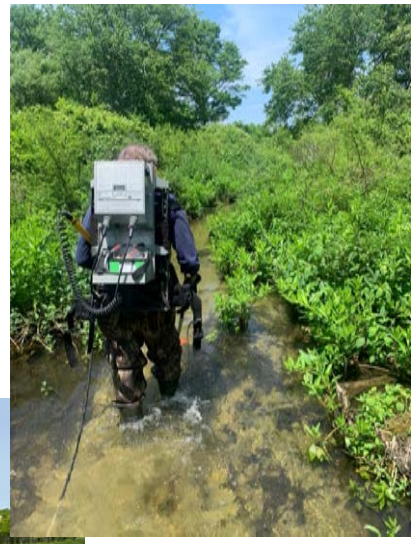
Biotic Tissues
(e.g. fish, shellfish, whale)

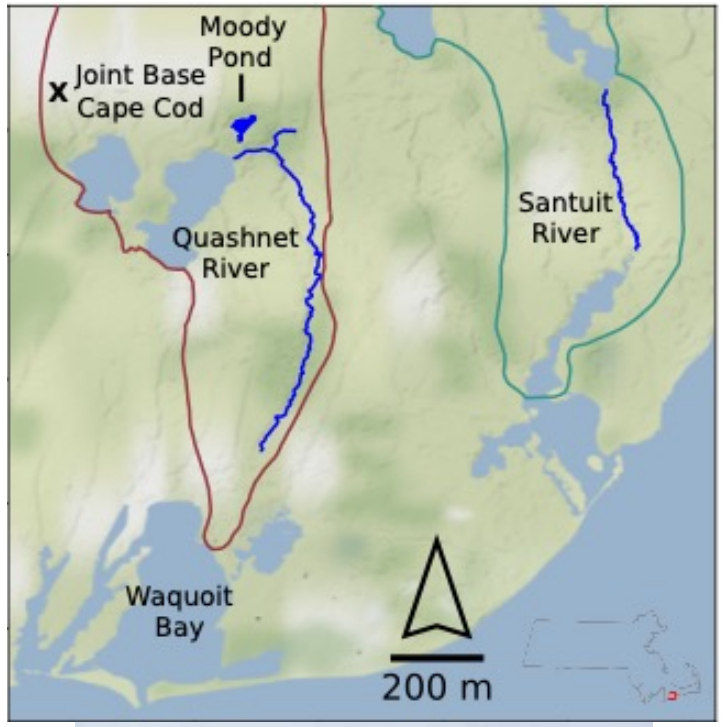
Extractable Organofluorine

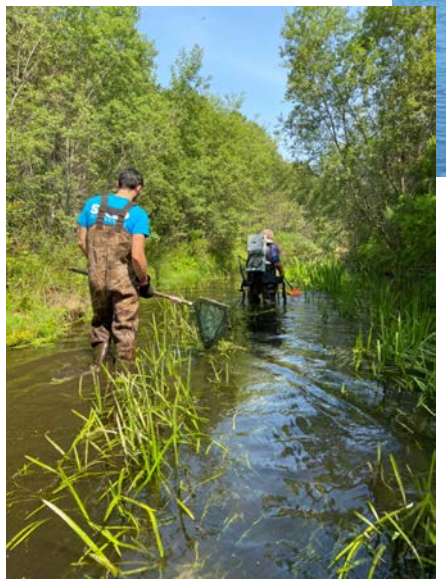


Various sampling techniques were used to collect multiple species from different ecosystems









Agronomic exposure pathway for PFAS

The curious case of tainted milk from a Maine dairy farm

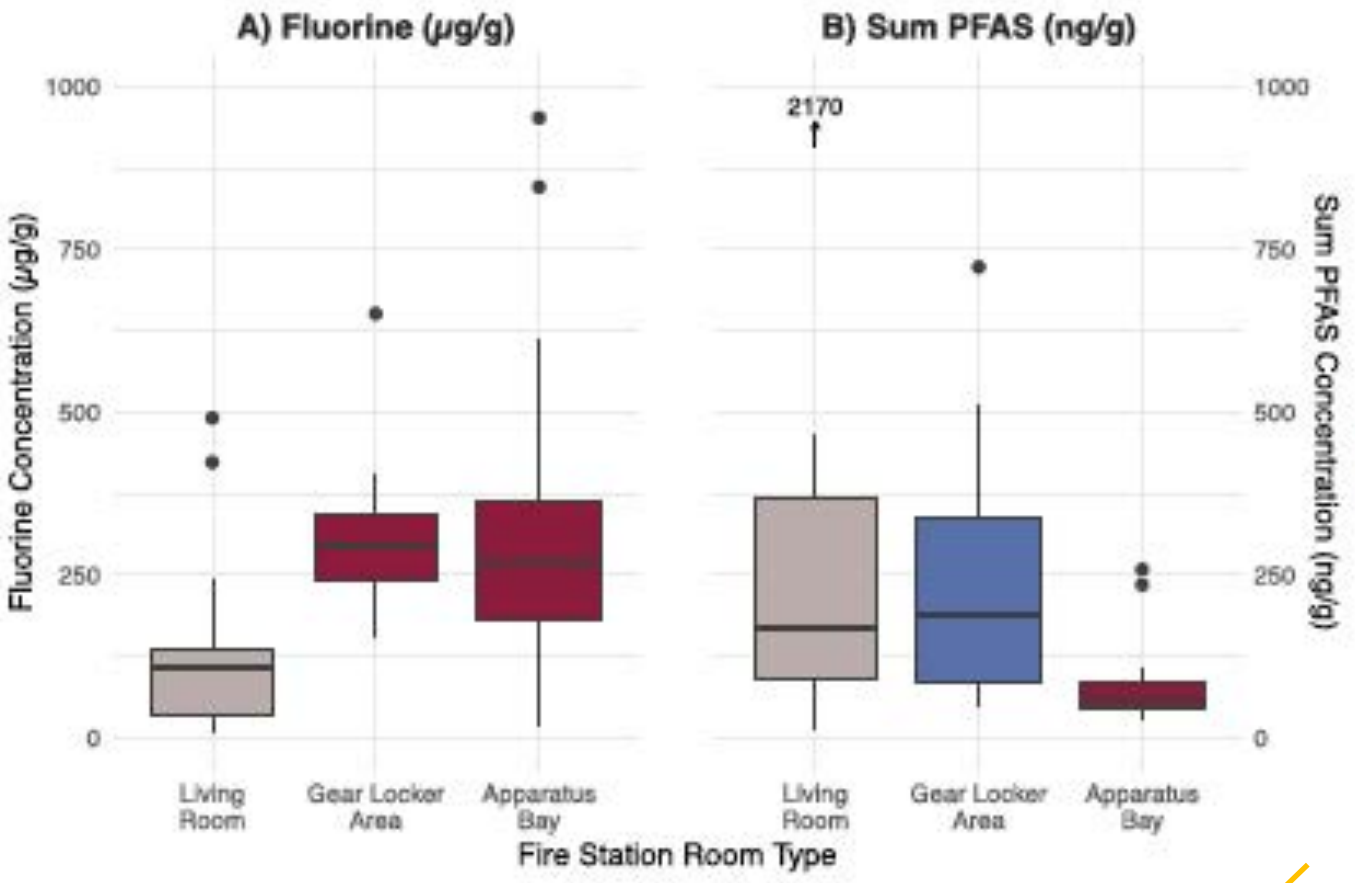
Richard Valdmanis, Joshua Schneyer

6 MIN READ

ARUNDEL, Maine (Reuters) - For Maine dairy farmer Fred Stone, the discovery in 2016 that his cows were producing tainted milk has since brought financial ruin and threatened to shut down a century-old family business.

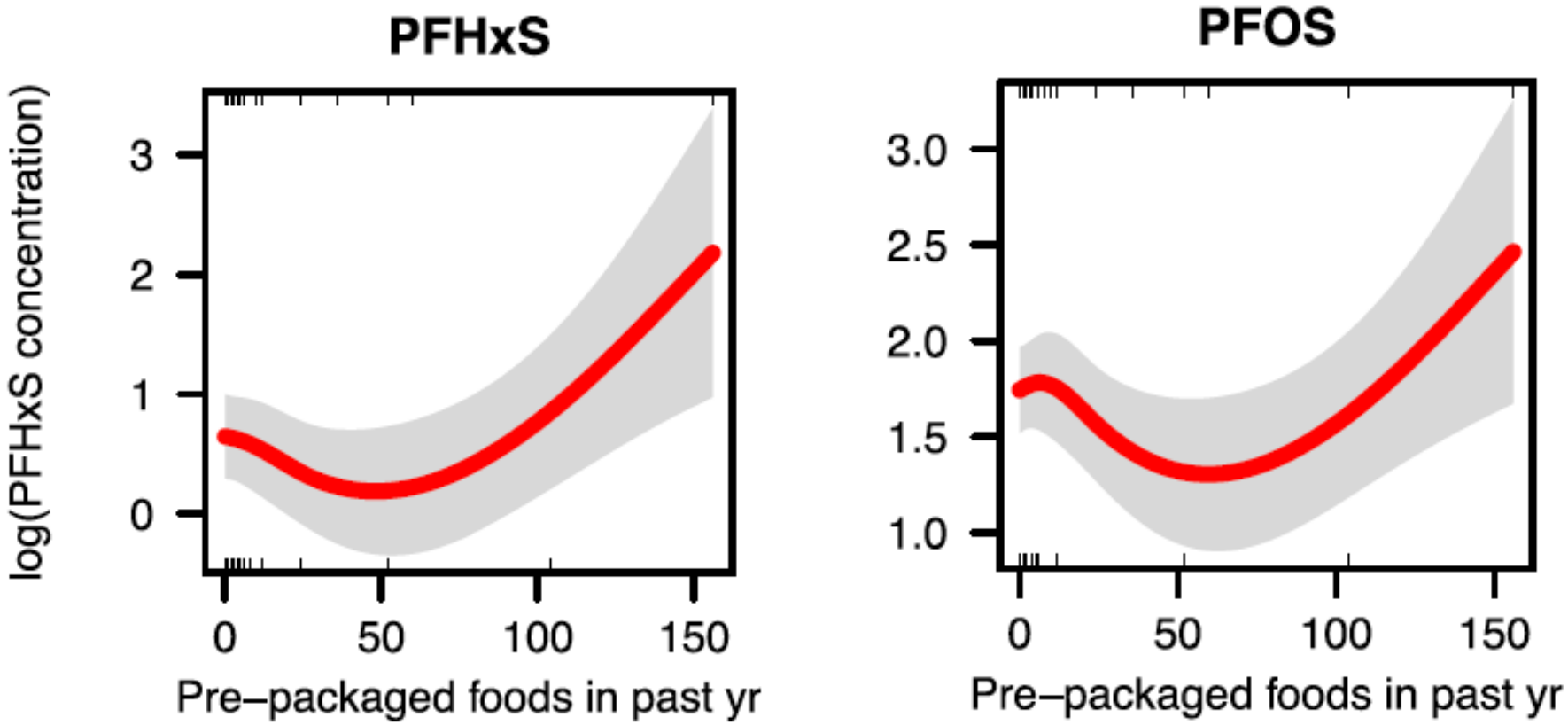
PFAS in many consumer products: Indoor environment and dust

Example: 15 Fire Stations in MA



Young et al., 2020, JESEE

Associations between use of packaged food and serum PFAS (Vancouver, Canada cohort)



Hu et al., 2018, Environmental Health

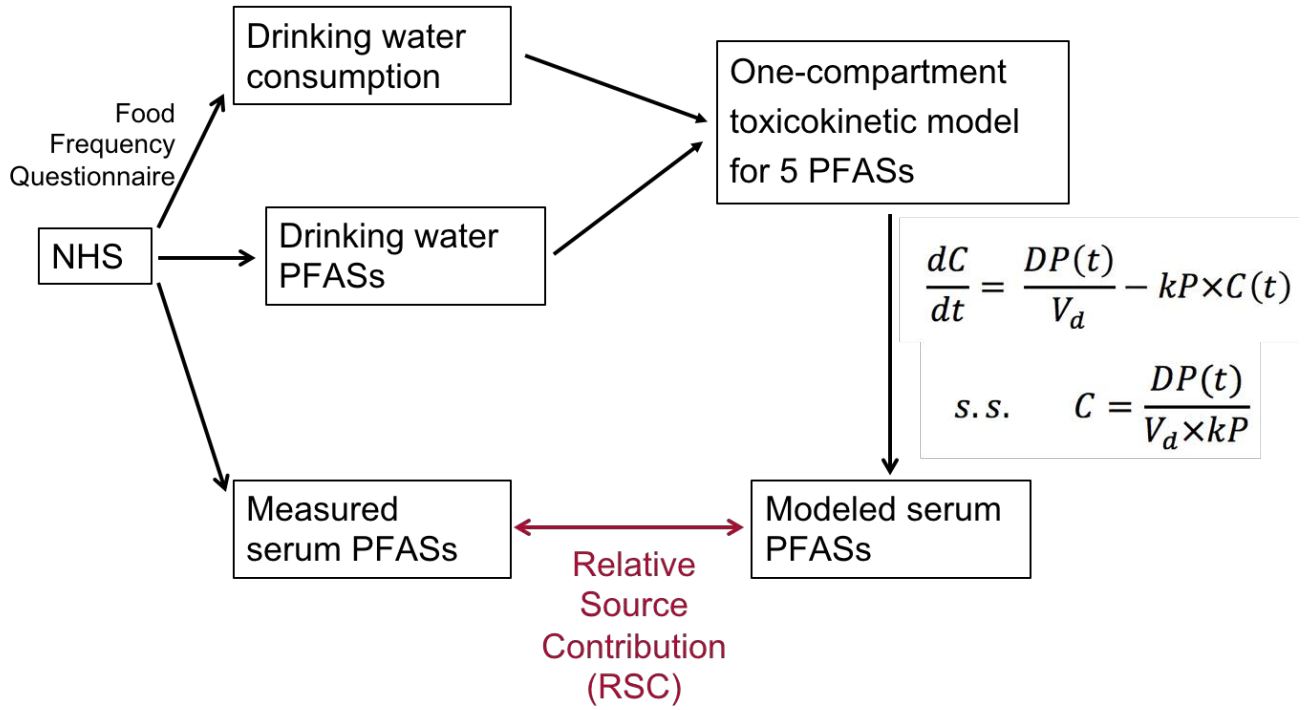
2021 FDA announcement on dietary PFAS sources in the U.S. food supply

"The U.S. food supply is among the safest in the world, and the available scientific evidence does not support avoiding particular foods because of concerns regarding PFAS exposure," said Acting FDA Commissioner Janet Woodcock, M.D. "Since we began testing foods from the general food supply for PFAS in 2019, only four samples out of the nearly 300 tested have had detectable levels of PFAS and none have been determined to be at levels of concern for human health. The FDA remains committed to sharing further updates as our work in this important space progresses."

https://www.fda.gov/news-events/press-announcements/fda-provides-update-ongoing-efforts-better-understand-occurrence-pfas-food-supply

More paired serum & environmental exposure measurements are needed!

- Systematic rather than ad hoc study design to assess patterns for different populations
- Ranking of exposure sources would aid risk mitigation
- Chemometric tools that use the serum PFAS profile may aid in interpretation of exposure data



Example for tap water from Hu et al., 2019, EHP

Summary

- **<u>Diverse adverse health effects associated with PFAS Exposure:</u> PFAS are particularly problematic because they affect every major organ system in the human body!**

- **<u>Many human exposure sources – some</u> : We have the most data on drinking water as an exposure source but the importance of others (diet, consumer products, seafood) is poorly understood.**

- **<u>The importance of PFAS precursors for human exposures needs to be better understood</u>: Our standard analytical techniques have been limited by commercially available standards and are not keeping pace with industrial production of new PFAS. Innovation is needed (HRMS + total fluorine metrics).**