Transport and Transformations of PFAS precursors at legacy AFFF contaminated sites

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Acknowledgements

Most the work I will present today was part of the dissertation research by **Bridger J. Ruyle,** which includes the following papers (and many co-authors!):

- B.J. Ruyle, C.P. Thackray, J.P. McCord, M.J. Strynar, K.A. Mauge-Lewis, S.E. Fenton, E.M. Sunderland. 2021a. **Reconstructing the composition of poly- and perfluroalkyl substances (PFAS) in contemporary aqueous film forming foams**. Environmental Science & Technology Letters. 8(1): 59-65.

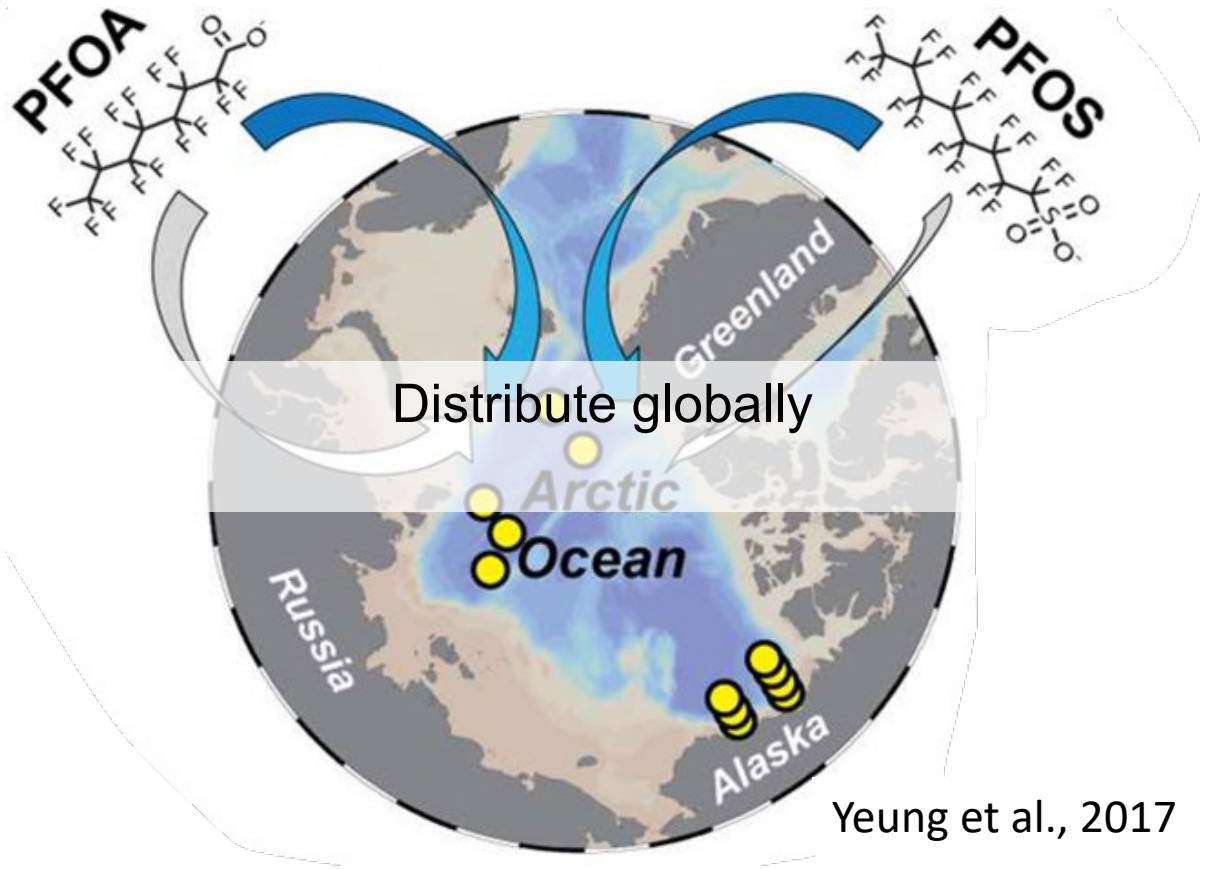
- B. Ruyle, H. Pickard, D. LeBlanc, A. Tokranov, C. Thackray, X.C. Hu, C.D. Vecitis, E.M. Sunderland. 2021b. **Isolating the AFFF signature in coastal watersheds using oxidizable PFAS precursors and unexplained organofluorine**. Environmental Science & Technology. 55(6): 3686-3695.

- B.J. Ruyle, L. Schultes, D.M. Akob, C.R. Harris, M.M. Lorah, S. Vojta, J. Becanova, S. McCann, H.M. Pickard, A. Pearson, R. Lohmann, C.D. Vecitis, E.M. Sunderland. **Nitrifying bacteria linked to biotransformation of perfluoroalkyl sulfonamido precursors from legacy aqueous film forming foams.** In-review.

- B.J. Ruyle, C.P. Thackray, C.M. Butt, D.R. LeBlanc, A.K. Tokranov, C.D. Vecitis, E.M. Sunderland. **Centurial persistence of forever chemicals at military fire training sites**. In-prep.

Poly- and perfluoroalkyl substances (PFAS) are both local and global contaminants

Impacts on communities



Distribute globally

Yeung et al., 2017

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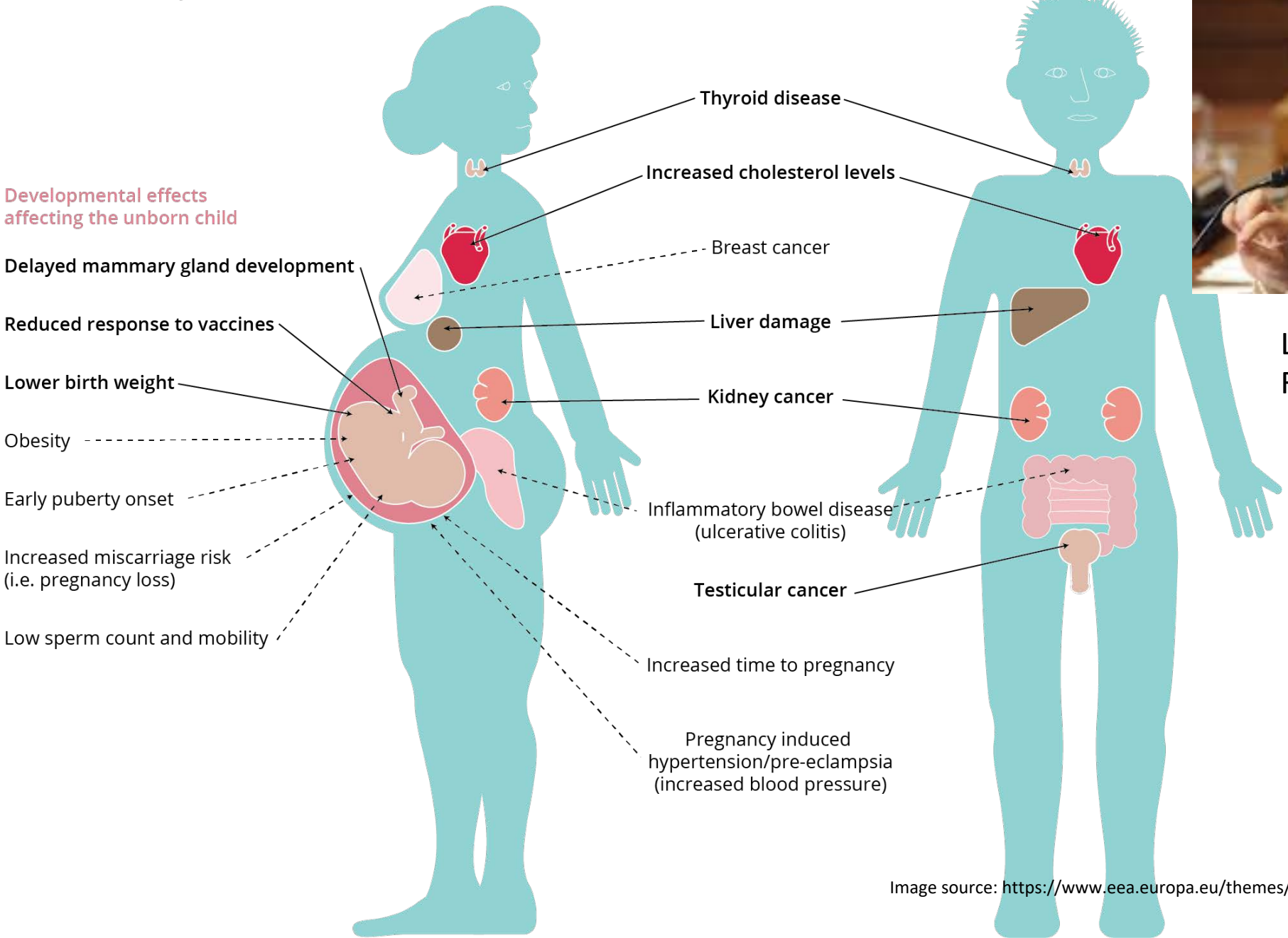
High certainty

Lower certainty



Linda Birnbaum,
Former Director, NIEHS

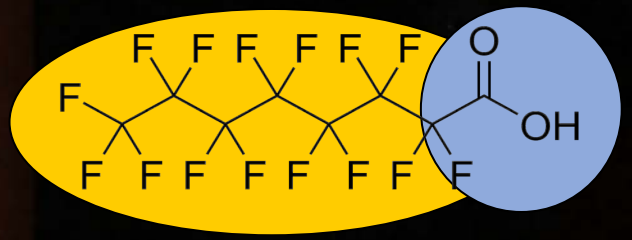
Image source: https://www.eea.europa.eu/themes/human/chemicals/emerging-chemical-risks-in-europe

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

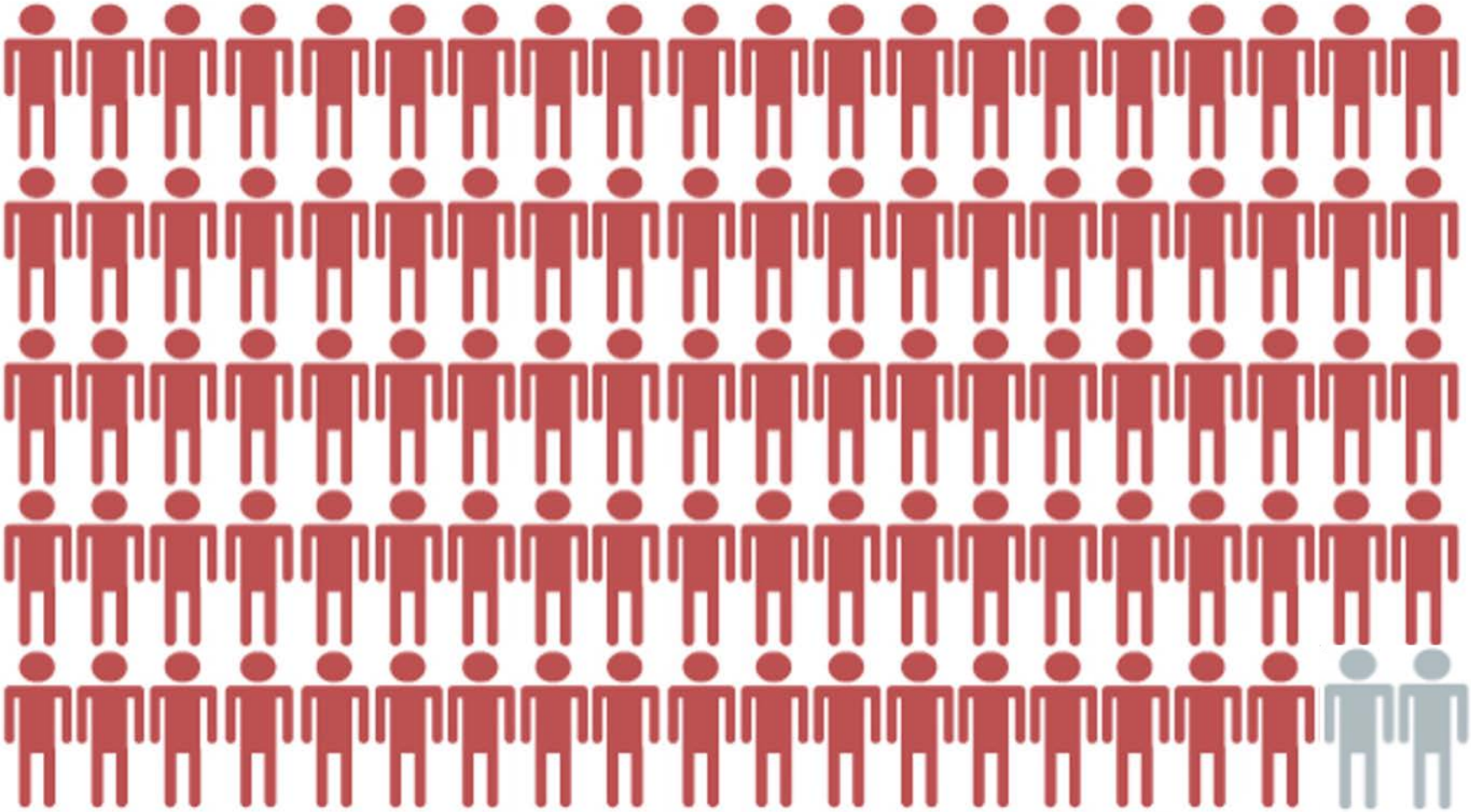


Repels water
Repels fat

Philippe Grandjean,
Professor HSPH

F-C
FOREVER CHEMICALS

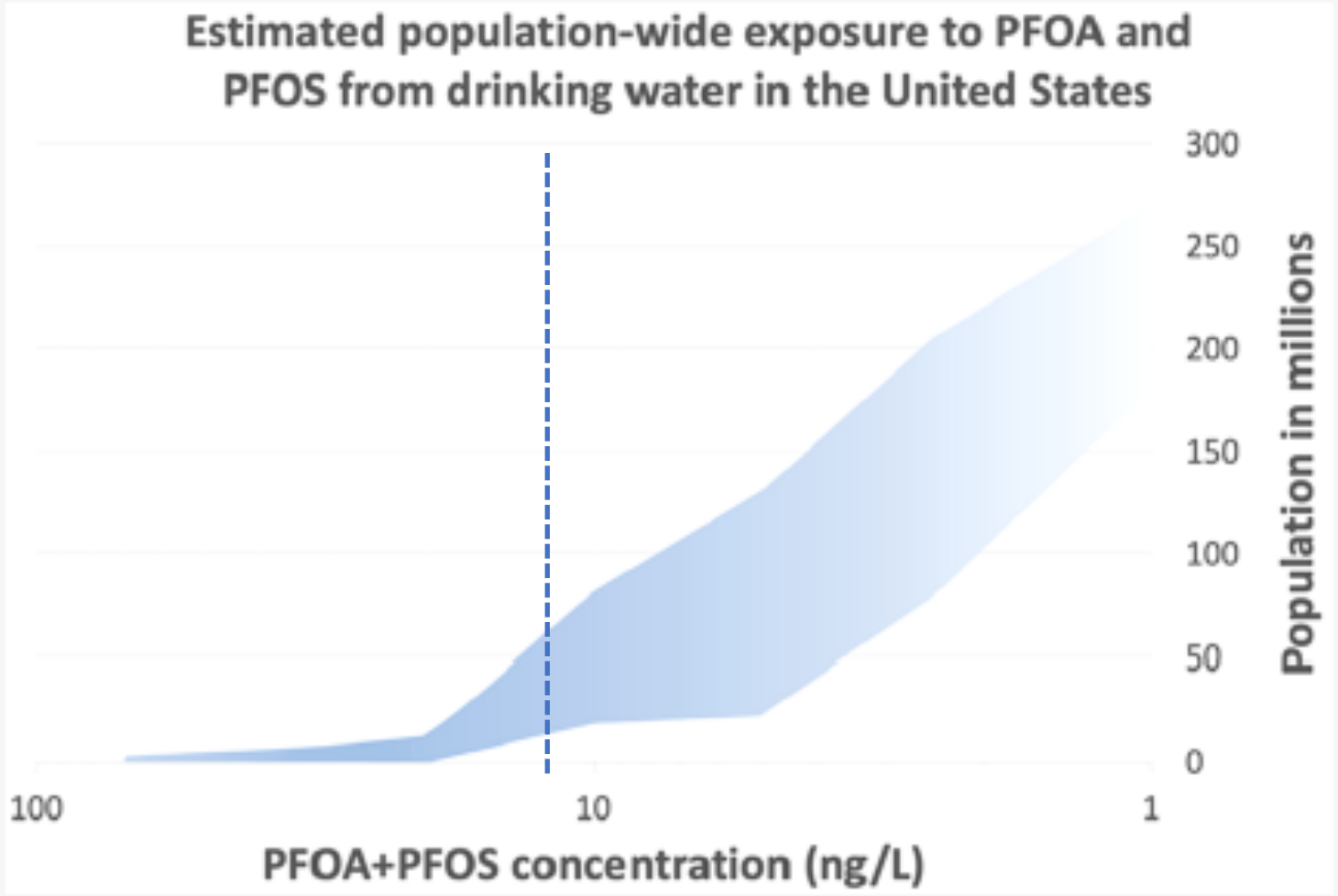
CDC data show 98-99% of Americans have detectable PFAS in their blood



Detectable PFAS in serum

Below detection

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

Hundreds of PFAS point sources across U.S. are from legacy (3M) AFFF use

3-6 wt% PFAS and 41-100% PFAA precursors

Used at hundreds fire training areas (FTAs) on military installations and airports

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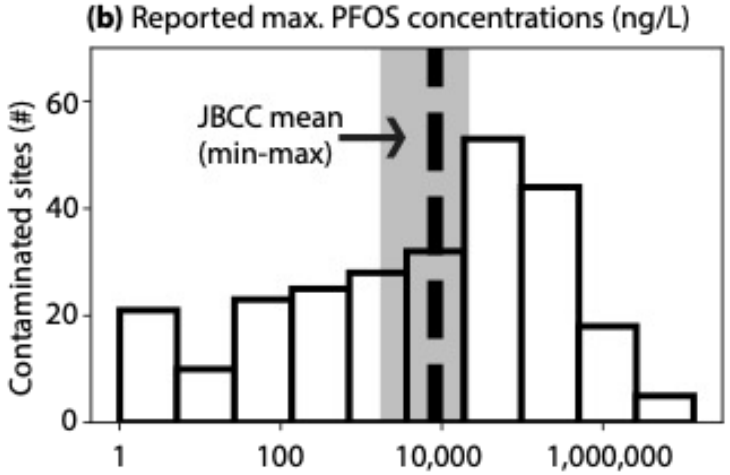


AFFF = aqueous film forming foam

Ruyle et al., in-prep.

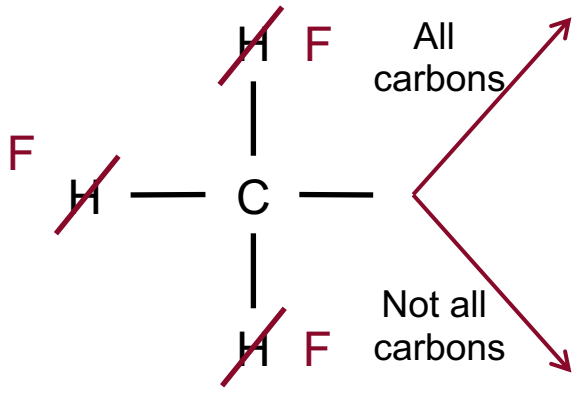
Cape Cod Field Site: Essential for Understanding Groundwater Transport

Photo courtesy of Denis LeBlanc

USGS science for a changing world

HARVARD John A. Paulson School of Engineering and Applied Sciences

F-C backbone of “Forever Chemicals”: Most research on a subset of PFAS known as PFAA



All carbons

Not all carbons

Perfluoroalkyl substances
(C_nF_{2n+1}-R)

Polyfluoroalkyl substances
(C_nF_m-R)

PFCAs
(C_nF_{2n+1}-COOH) → C4 – C14:
buta-, penta-, hexa-, hepta-, ***octa- (PFOA)****, nona-, deca-, etc.*

PFSAs
(C_nF_{2n+1}-SO_3H) → C4 – C10:
buta-, hexa-, ***octa- (PFOS)****, deca-*

Long-chain PFAS:
PFCAs, n ≥ 7
PFSAs, n ≥ 6

More bioaccumulative

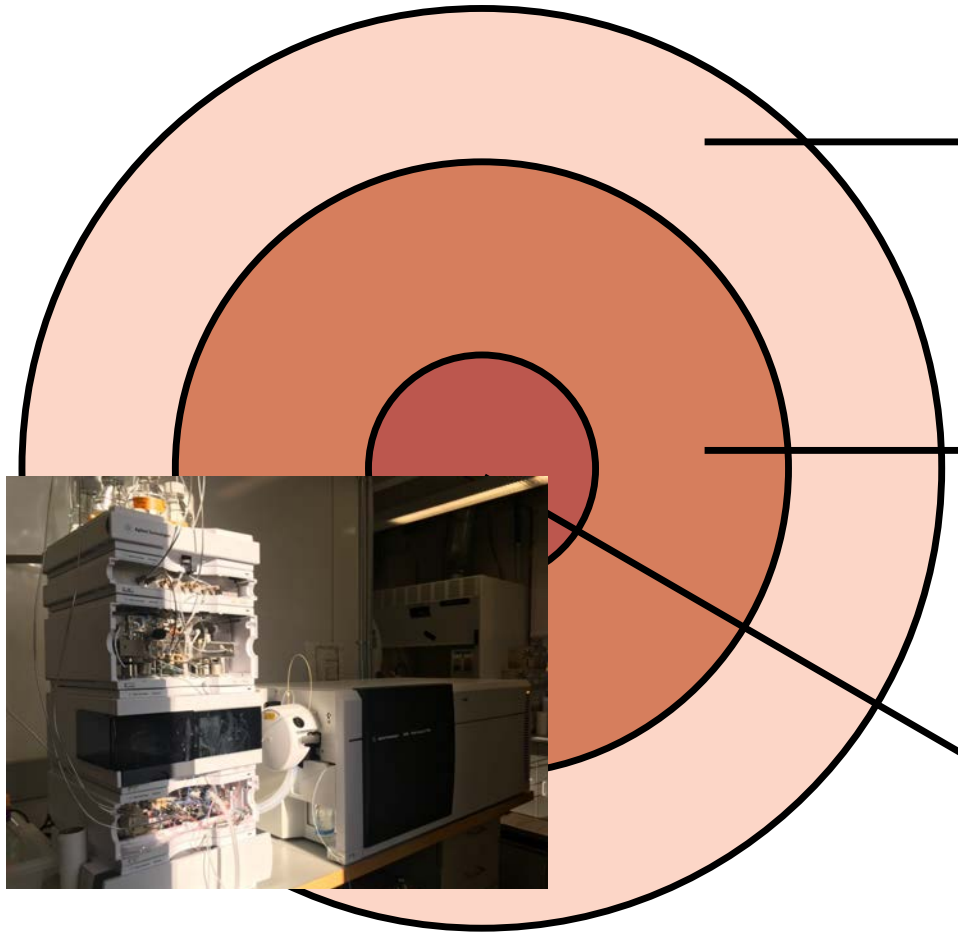
Certain classes of PFAS are **volatile or semi-volatile** and can be transported long distances

Some known as **precursors** can degrade into terminal PFAA (**PFOS, PFOA** etc.)

(Buck et al. 2011; Wang et al. 2017)

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

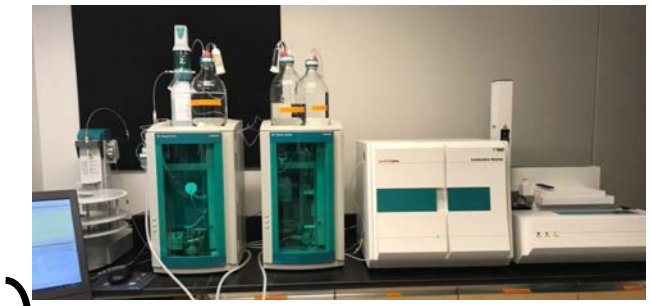
Targeted analysis is limited to a few dozen PFAS with analytical standards



Total fluorine (TF)

Extractable organofluorine (EOF)

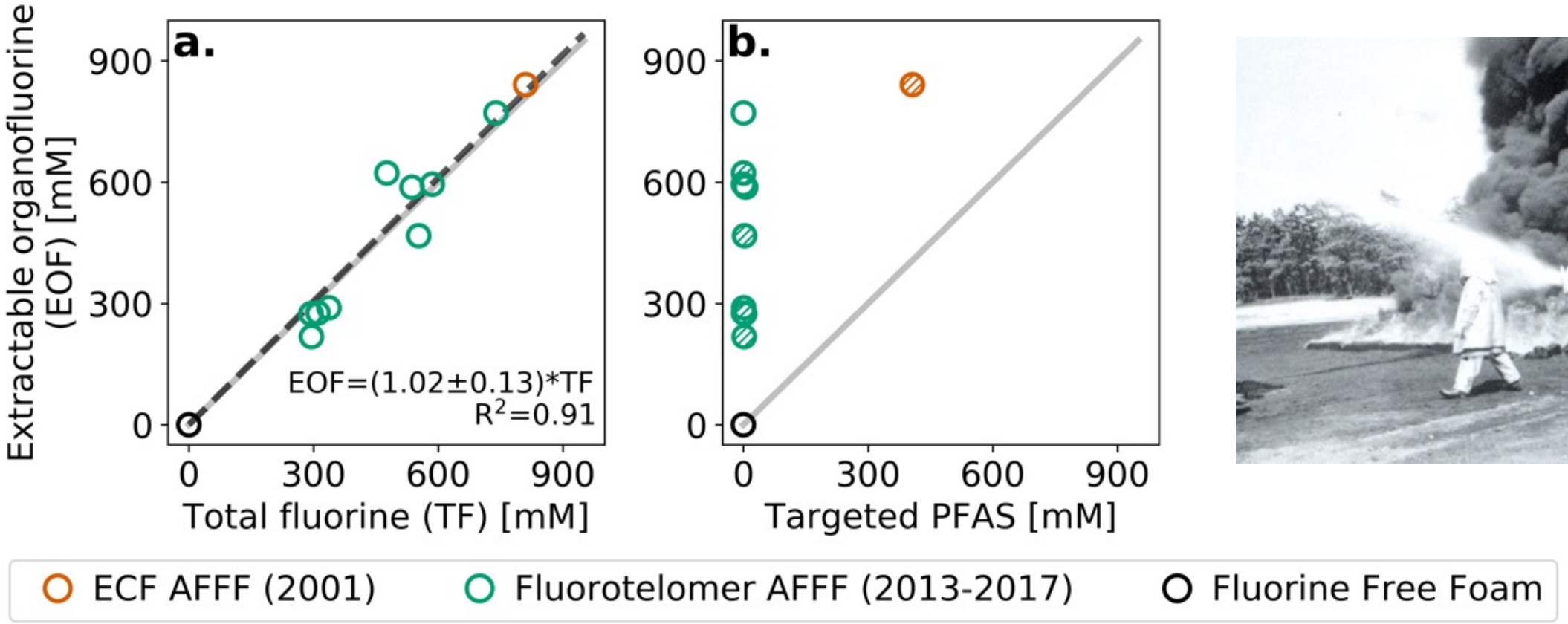
Targeted PFAS



Unknown EOF

- Precursors?
- Ultra-short chain PFAS?
- Fluorinated pharmaceuticals or agrochemicals?

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



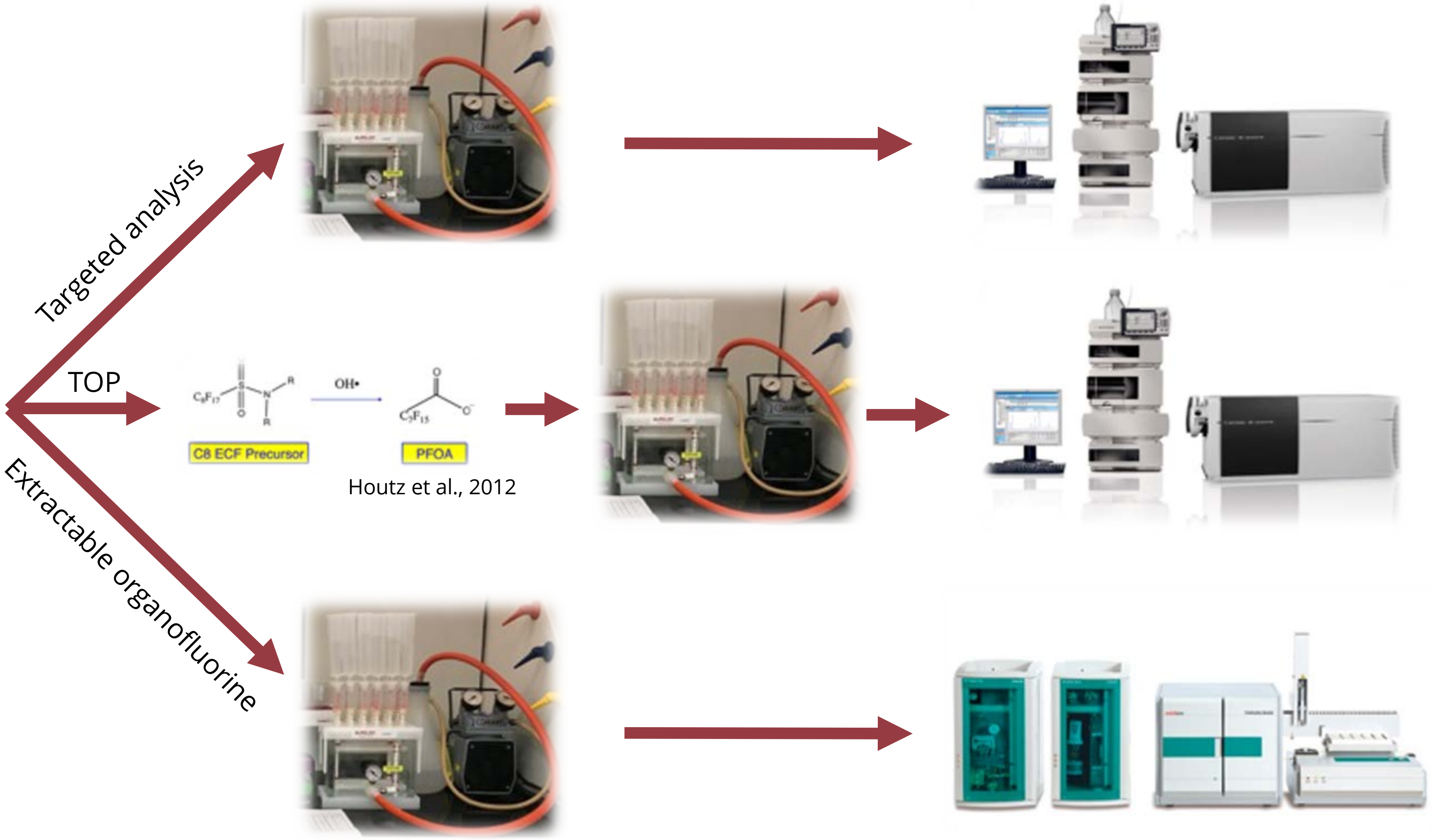
EPA United States Environmental Protection Agency

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. Environmental Science & Technology Letters. 8(1): 59-65.

Toolbox of analytical methods needed for PFAS mass budget in AFFF

TOP = total oxidizable precursor assay



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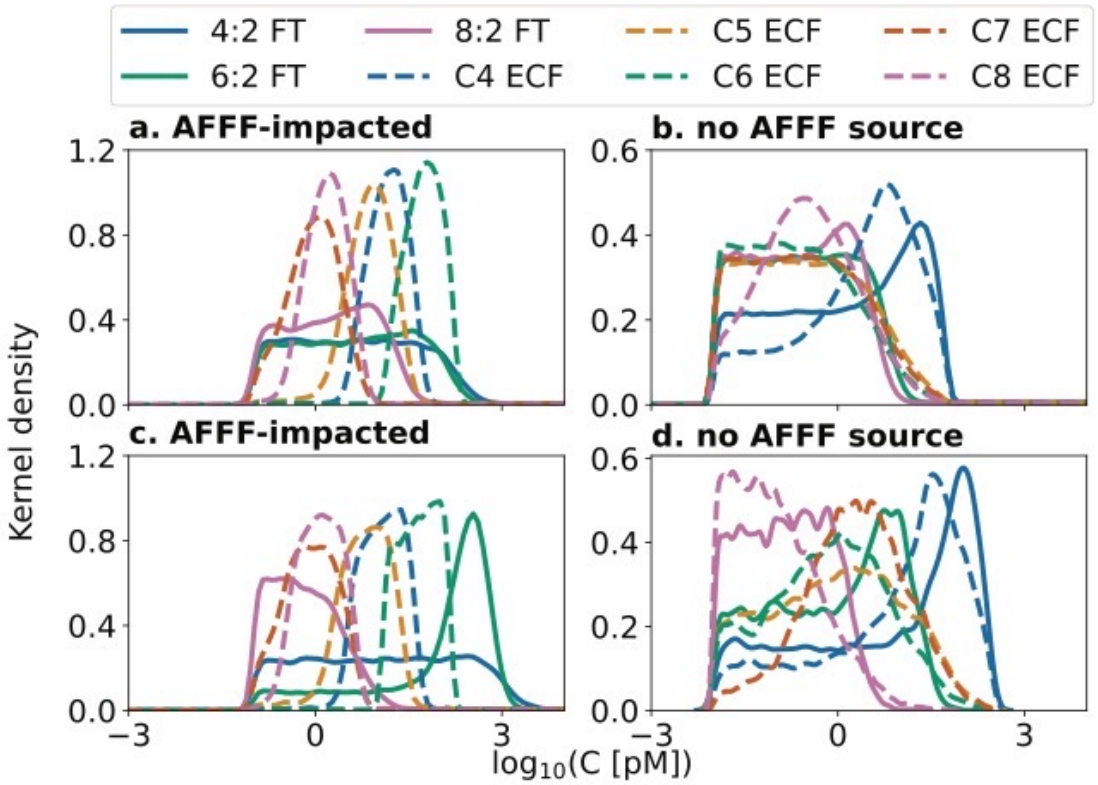
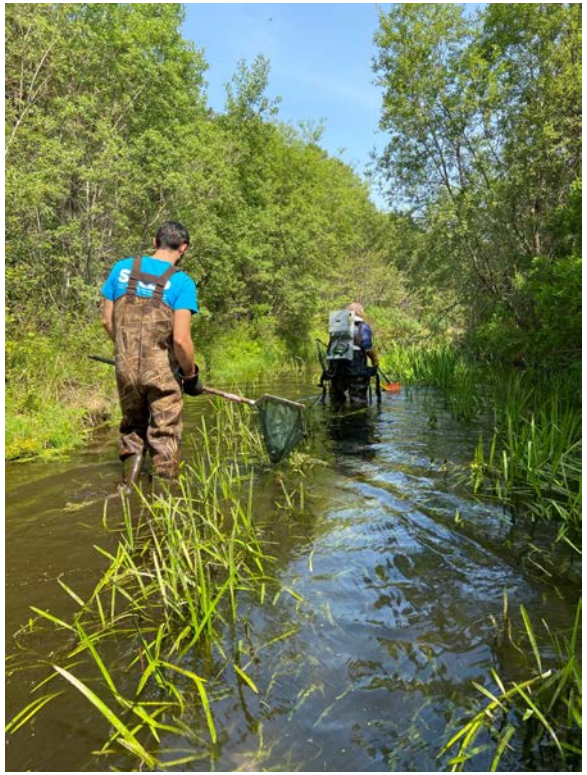
Example results from TOP+BI for surface waters on Cape Cod

Code available here: https://github.com/SunderlandLab/pfas-precursor-biotransformation



Ruyle et al., 2021a, b



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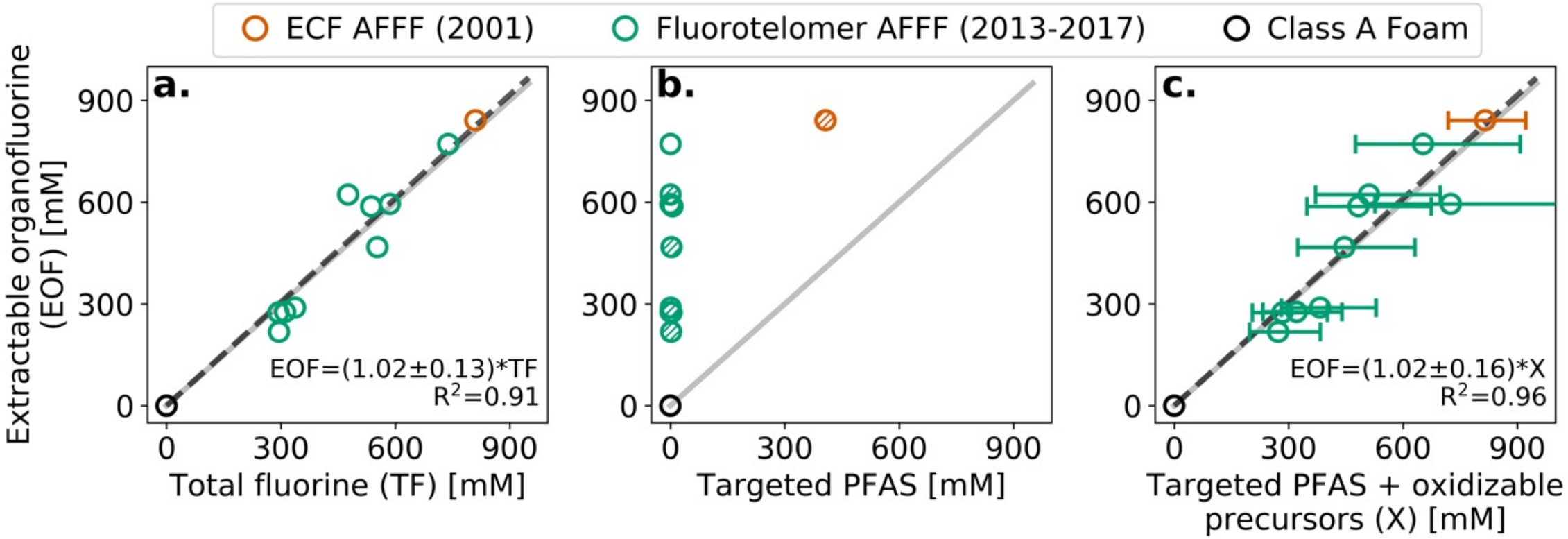
All of the PFAS can be detected using targeted analysis and TOP + BI (verified using extractable organofluorine: EOF)



Ruyle et al., 2021a

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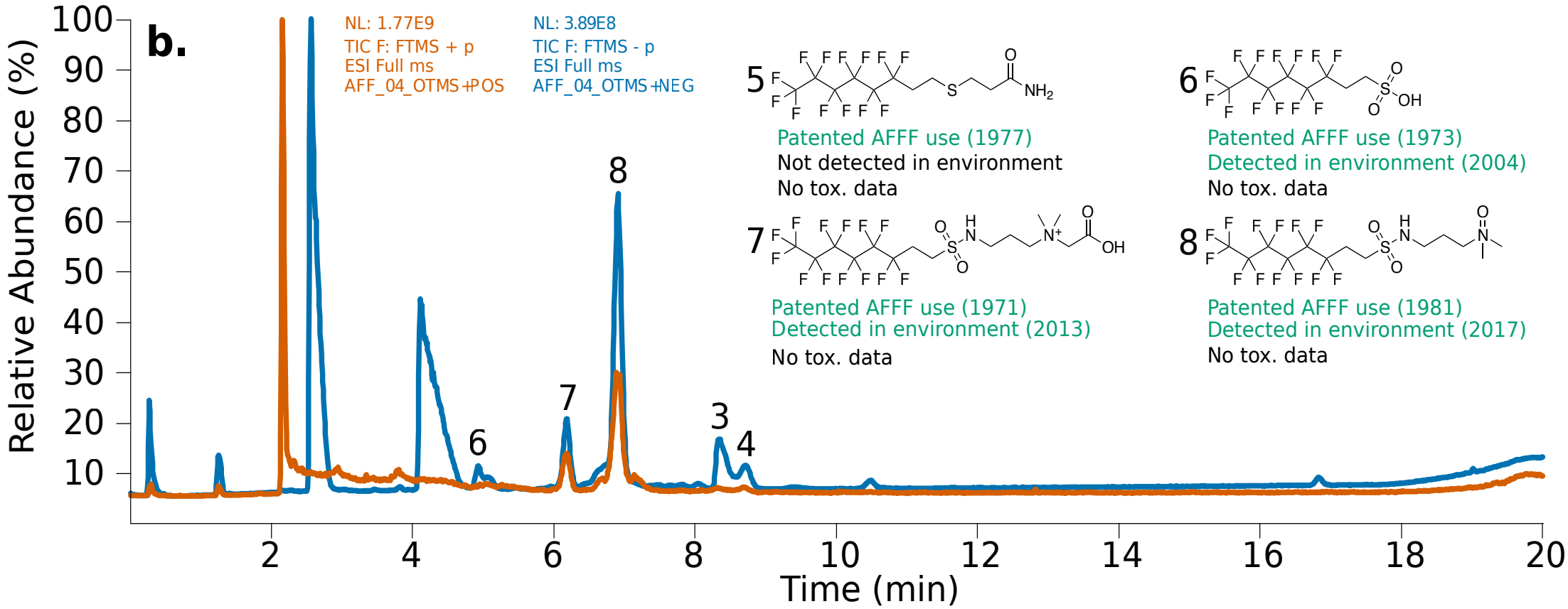
Time between patented use of PFAS and environmental detection using non-targeted techniques is 37±5 years: Too Long!



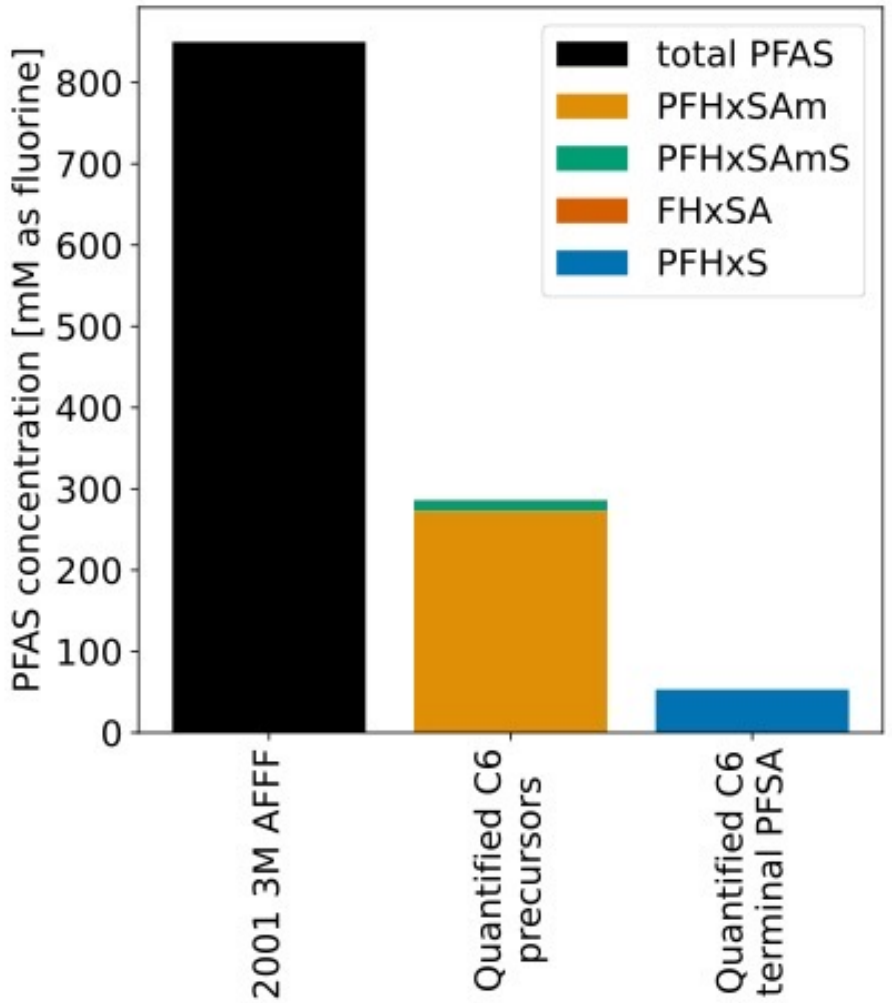
Non-targeted analysis *identifies* novel compounds (qualitative)

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. Environmental Science & Technology Letters. 8(1): 59-65.

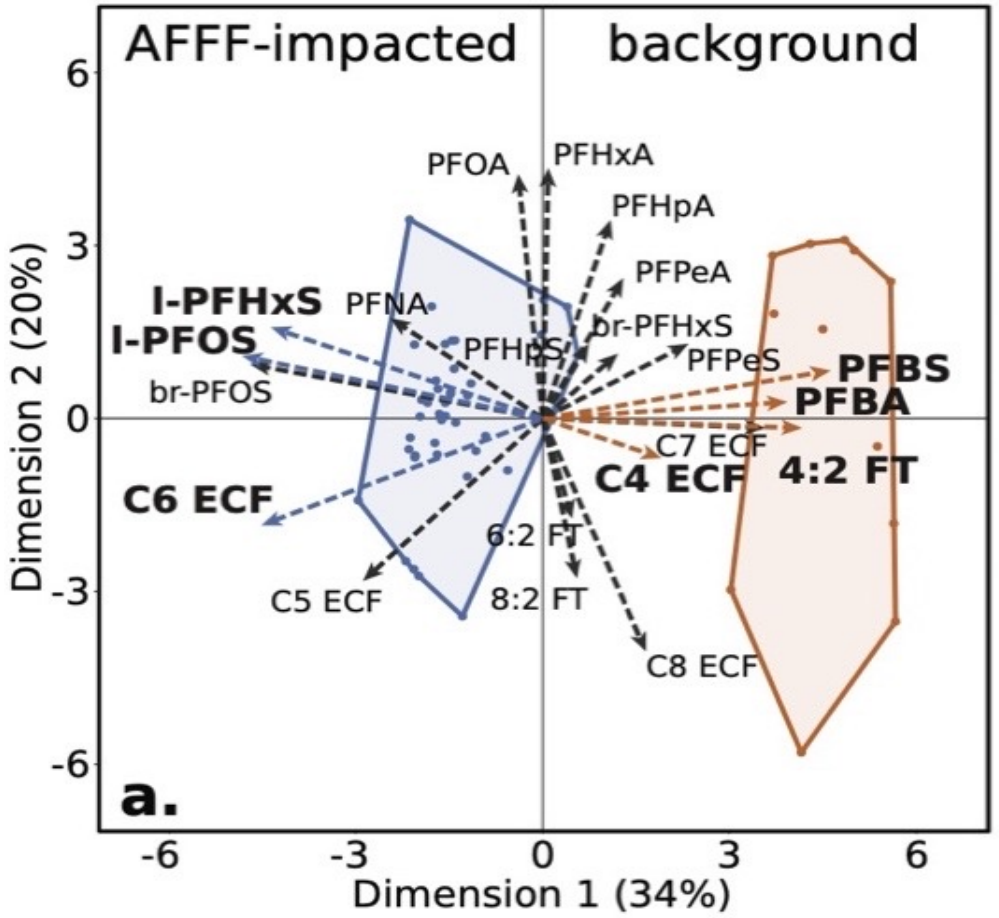
~50% of the PFAS in 3M AFFF are C4 and C6 sulfonamide precursors that eventually are transformed into PFBS (C4) and PFHxS (C6)



What is the role of microbes in this process?
How long will it take?
What is the transformation pathway?

Evidence of enrichment in PFHxS in AFFF impacted watersheds

AFFF signature is enriched in C6 PFAS



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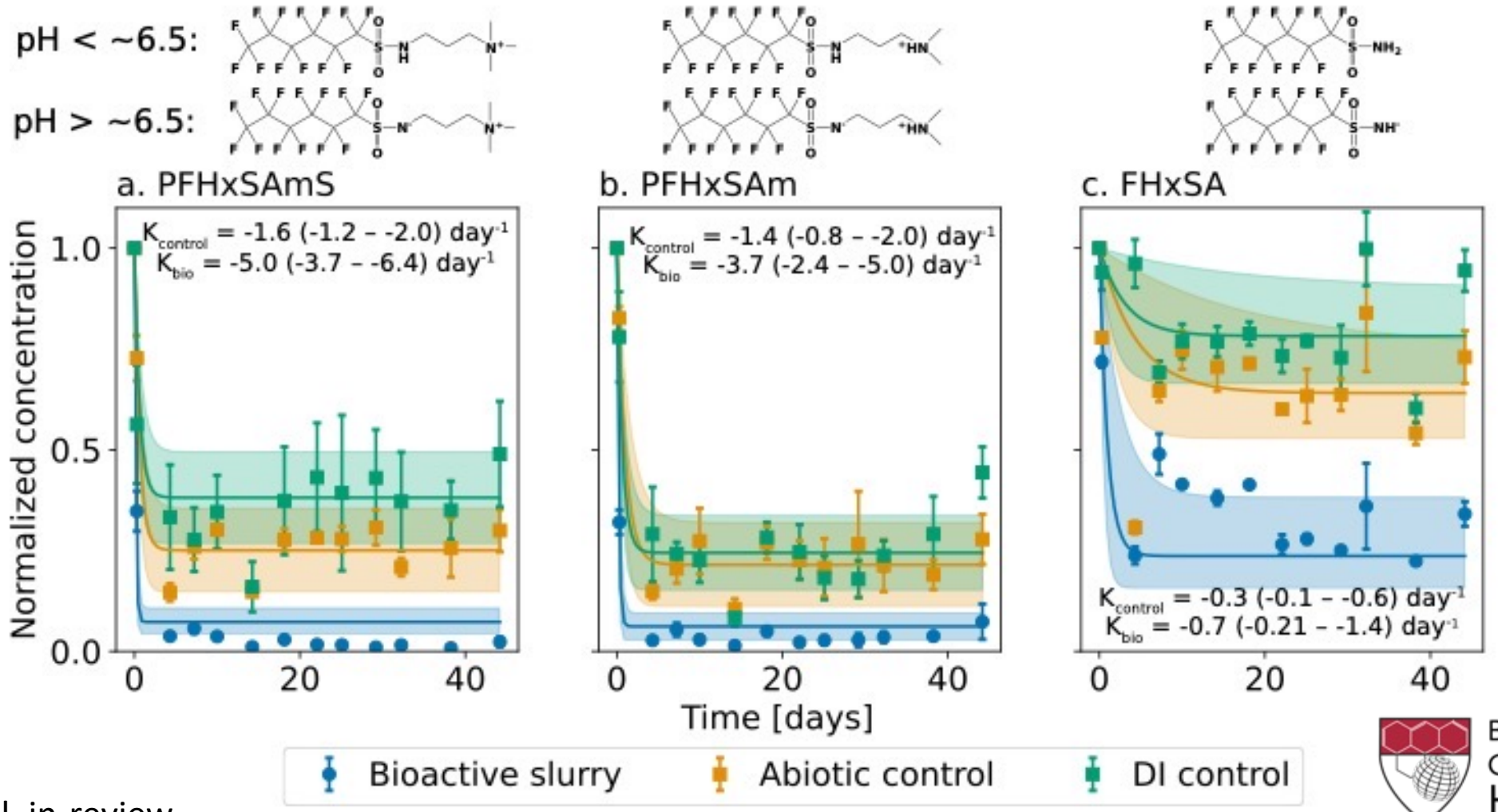
Ruyle, B.J., H. Pickard, D. LeBalnc, A. Tokranov, C.P. Thackray, X.C. Hu, E.M. Sunderland, 2021. Isolating the AFFF signature in coastal watersheds using oxidizable PFAS precursors and unexplained organofluorine. Environmental Science & Technology. 55(6): 3686-3695.

Biotransformation experiments show rapid biologically-associated sorption compared to autoclaved and DI controls: first-order kinetics



Ruyle et al, in-review

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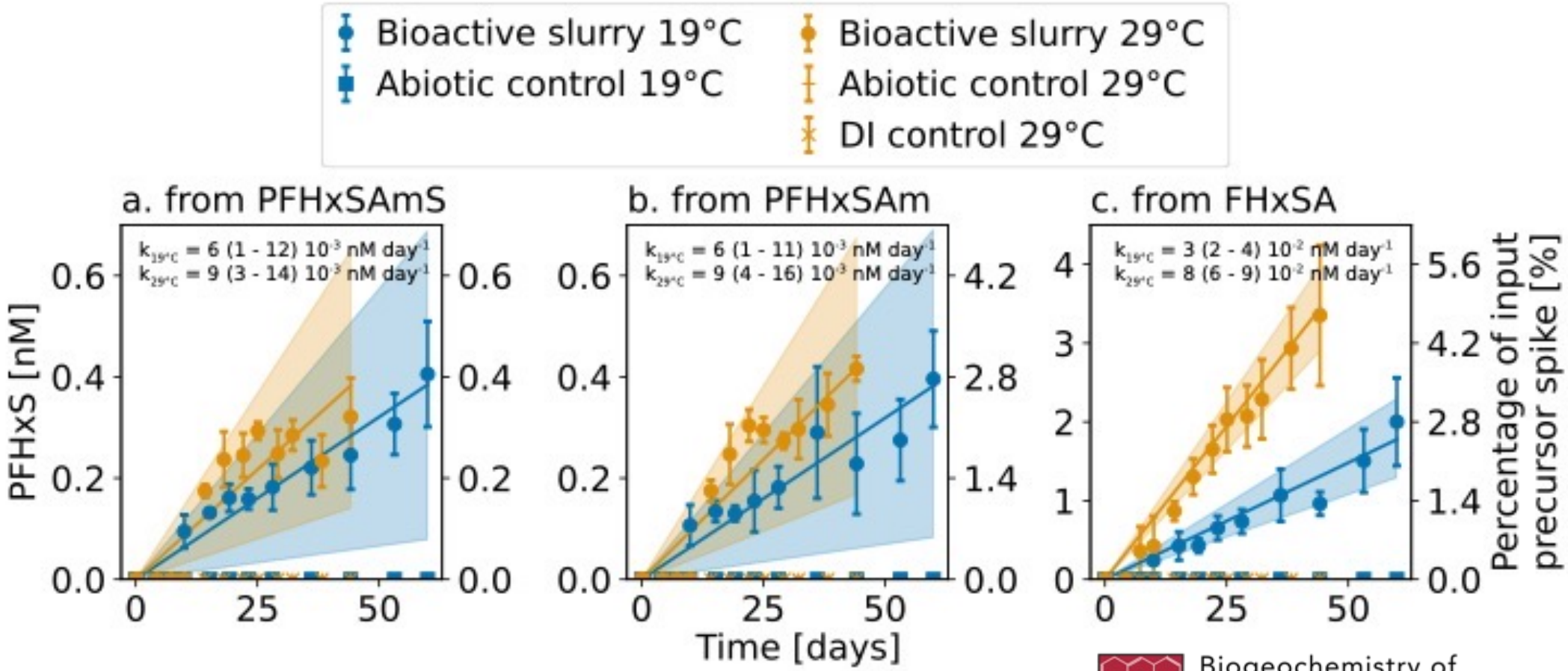
Biotransformation is inferred from time-dependent production of terminal compound PFHxS (C6 PFSA): Zero-order kinetics



Ruyle et al, in-review

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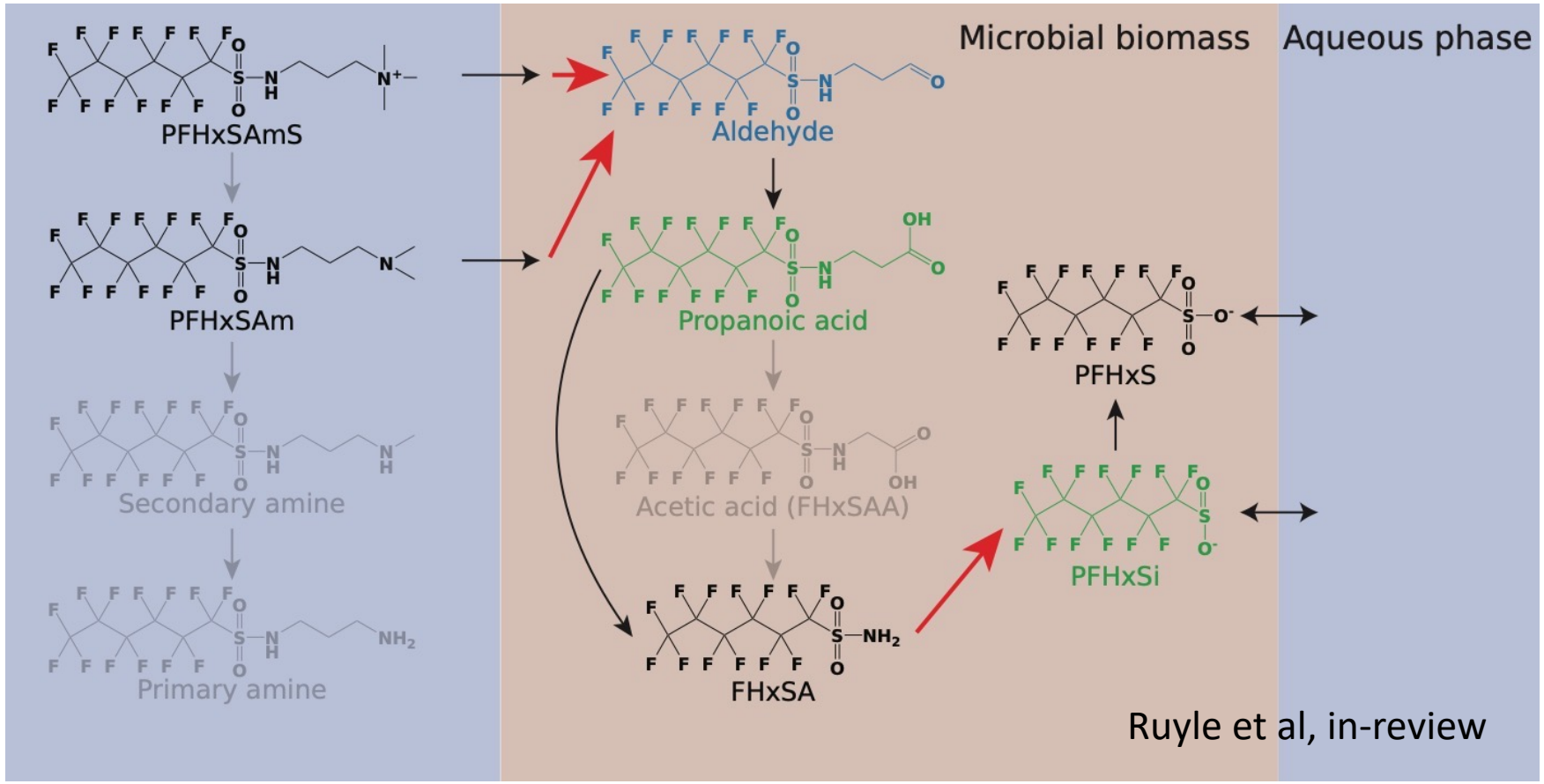
Potential biotransformation pathway of C6 precursors into PFHxS based on EAWAG Biocatalysis/Biodegradation database

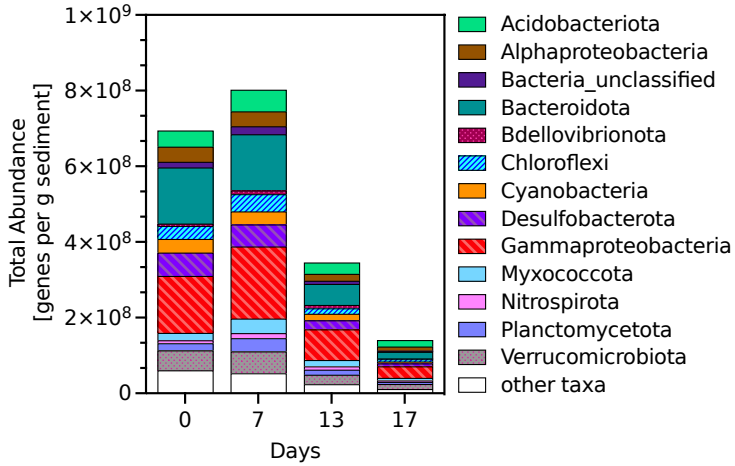


Red arrows show steps involving nitrification (microbial oxidation) of amine moieties

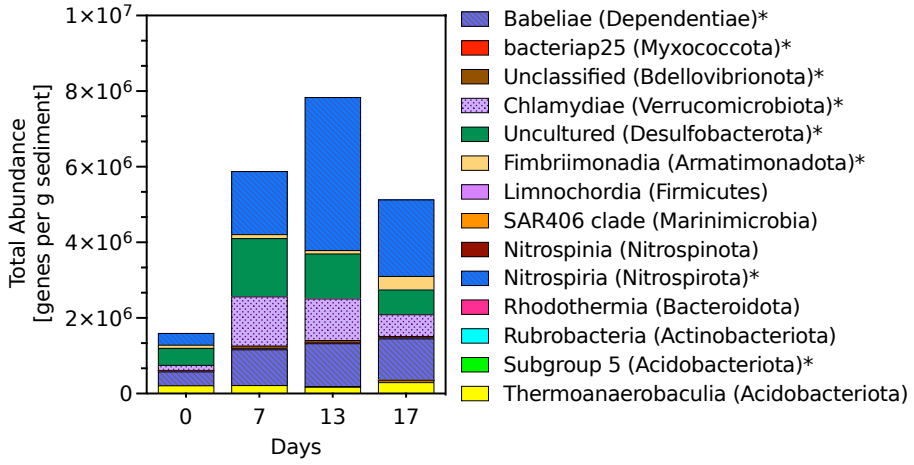
- Black = targeted compounds
- Blue = not amenable to LCMS detection
- Green = HRMS identified compounds
- Gray = proposed, but not detected w/ HRMS

Microbial community analysis shows increase in nitrifying taxa over duration of experiment

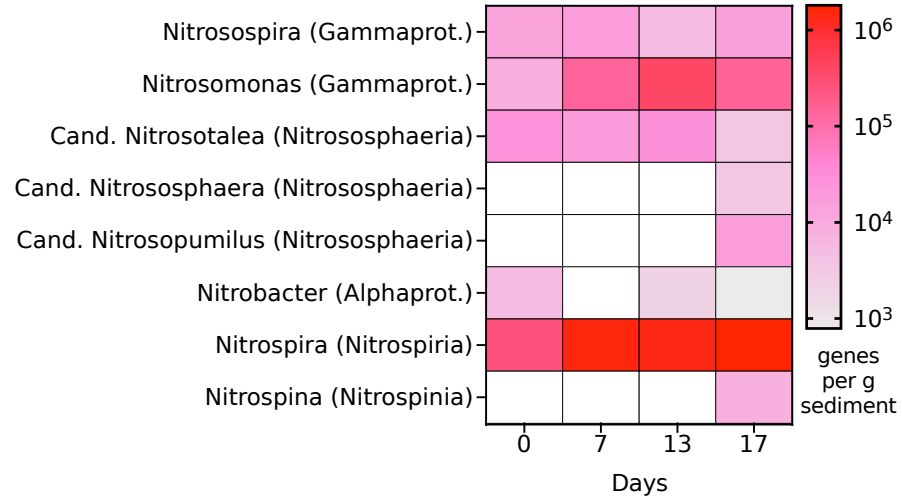
a. phyla level total abudance



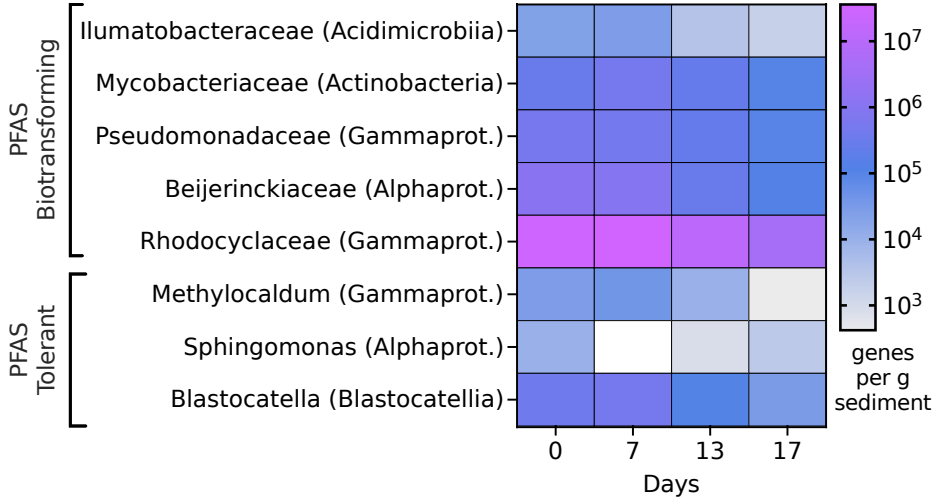
b. increasing microbial classes



c. nitrifying microbial taxa



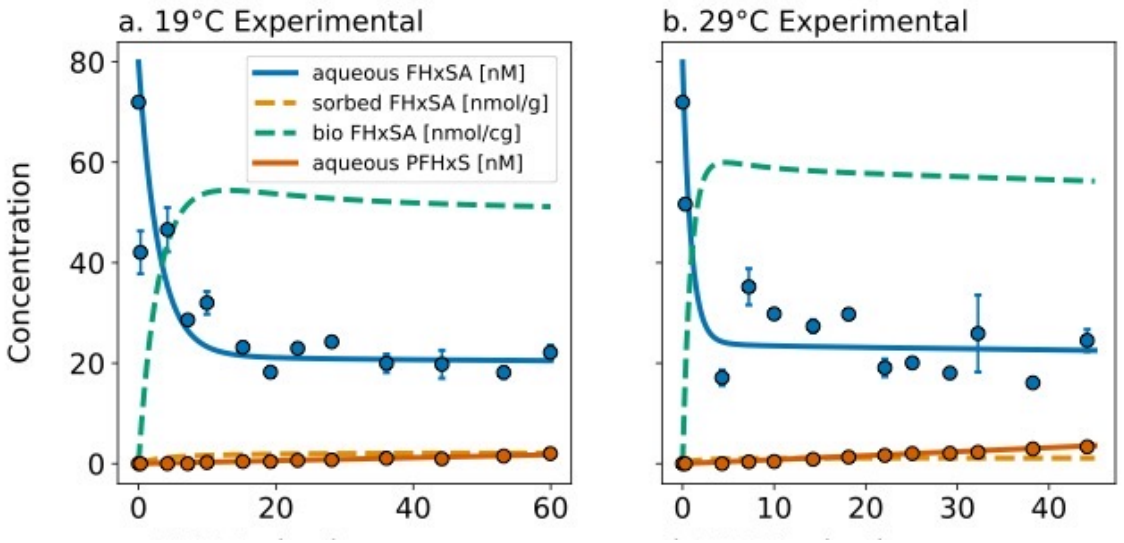
d. PFAS biotransforming/tolerant taxa



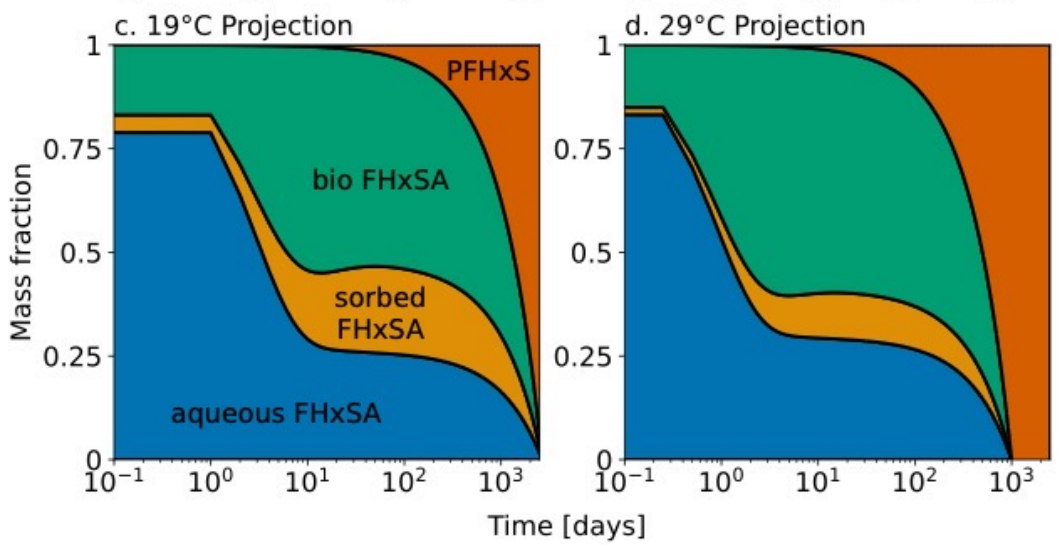
Complete transformation to terminal PFAA will take many years – explaining persistence of precursors in downgradient environment

Sediment-water slurries from JBCC field site

Modeled and measured concentration data



Modeled temporal evolution of precursors



Ruyle et al, in-review

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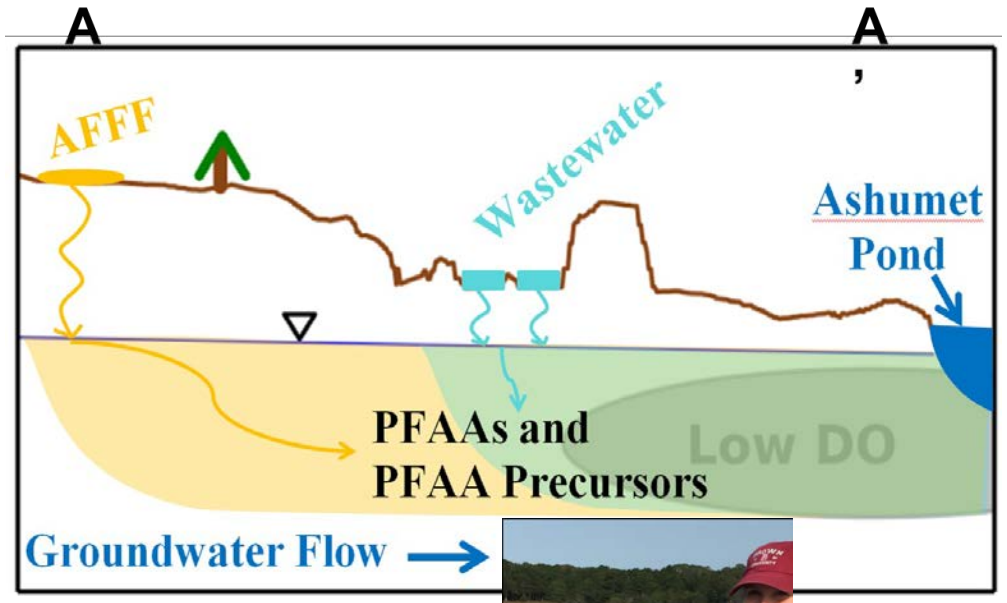
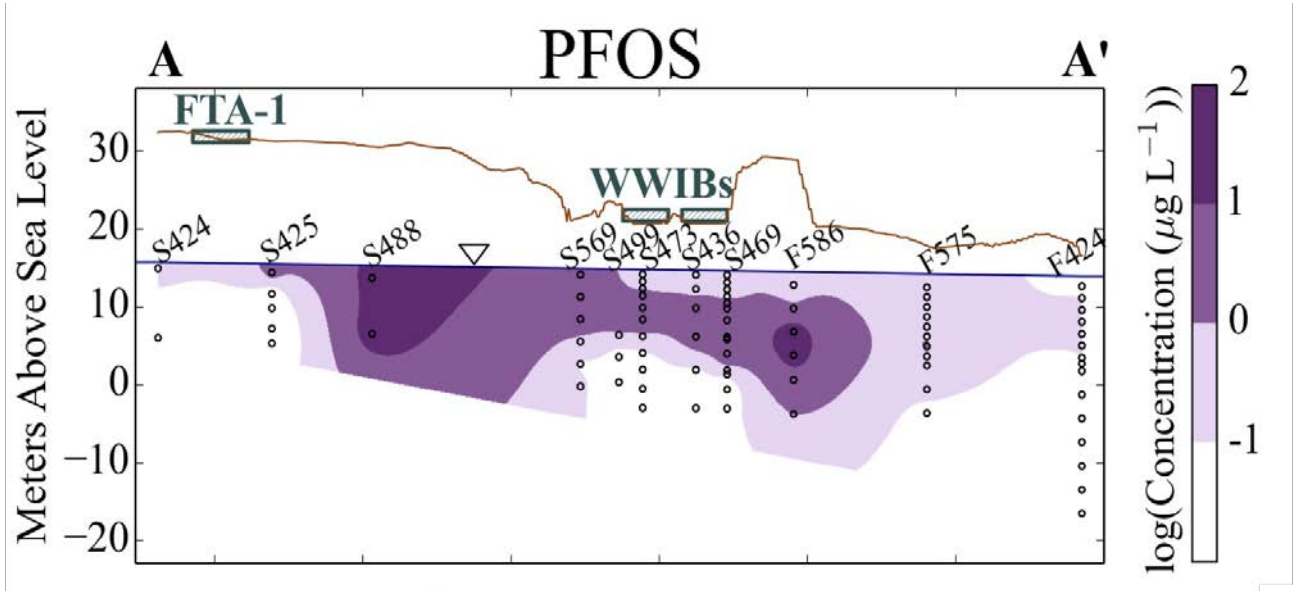
What are the implications of precursor biotransformation for groundwater PFAS concentrations?

Former fire training area at field site and downgradient groundwater PFAS plume



Tokranov et al., 2017



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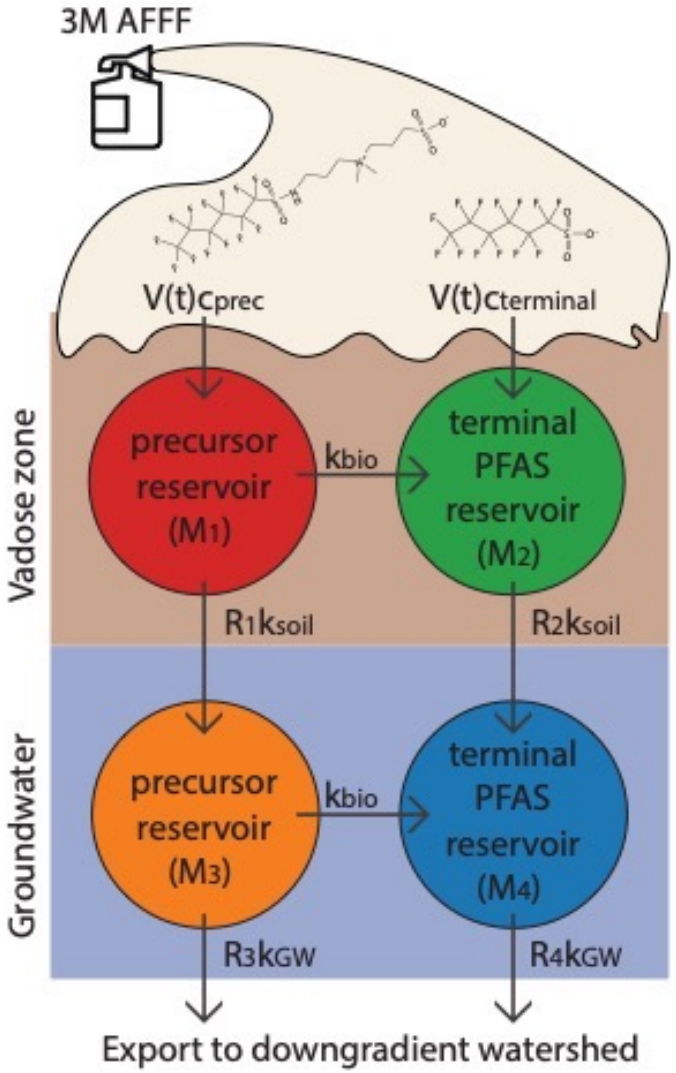
What are the implications of PFAS precursor transformation for ongoing groundwater contamination?

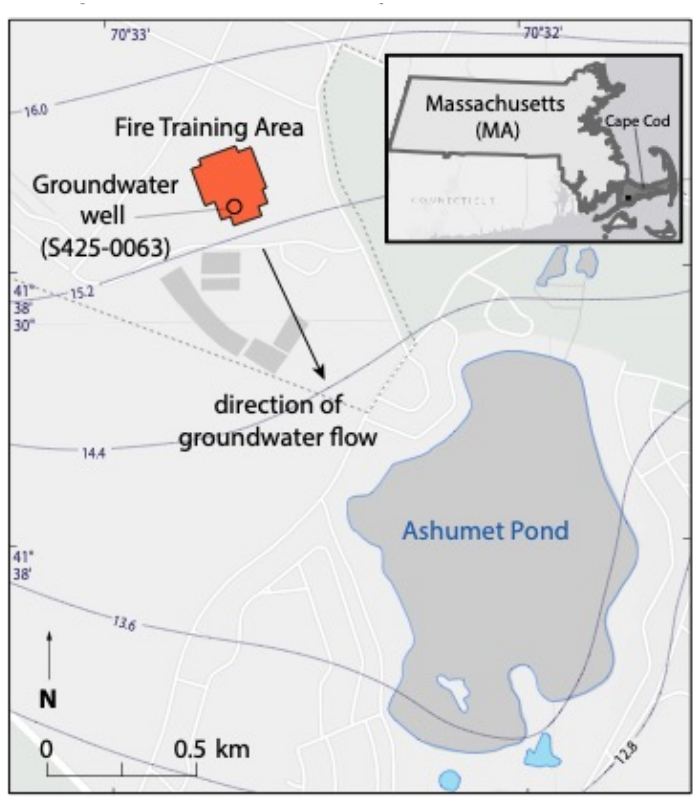
Volume of 3M AFFF inputs to field site:
1970-1985; 1997 (uncertain)

Concentrations of terminal PFAS and precursors in 3M AFFF (measured)

Concentrations in vadose zone (measured by Air Force for some terminal compound)

Concentrations in groundwater (measured 2007-2021)





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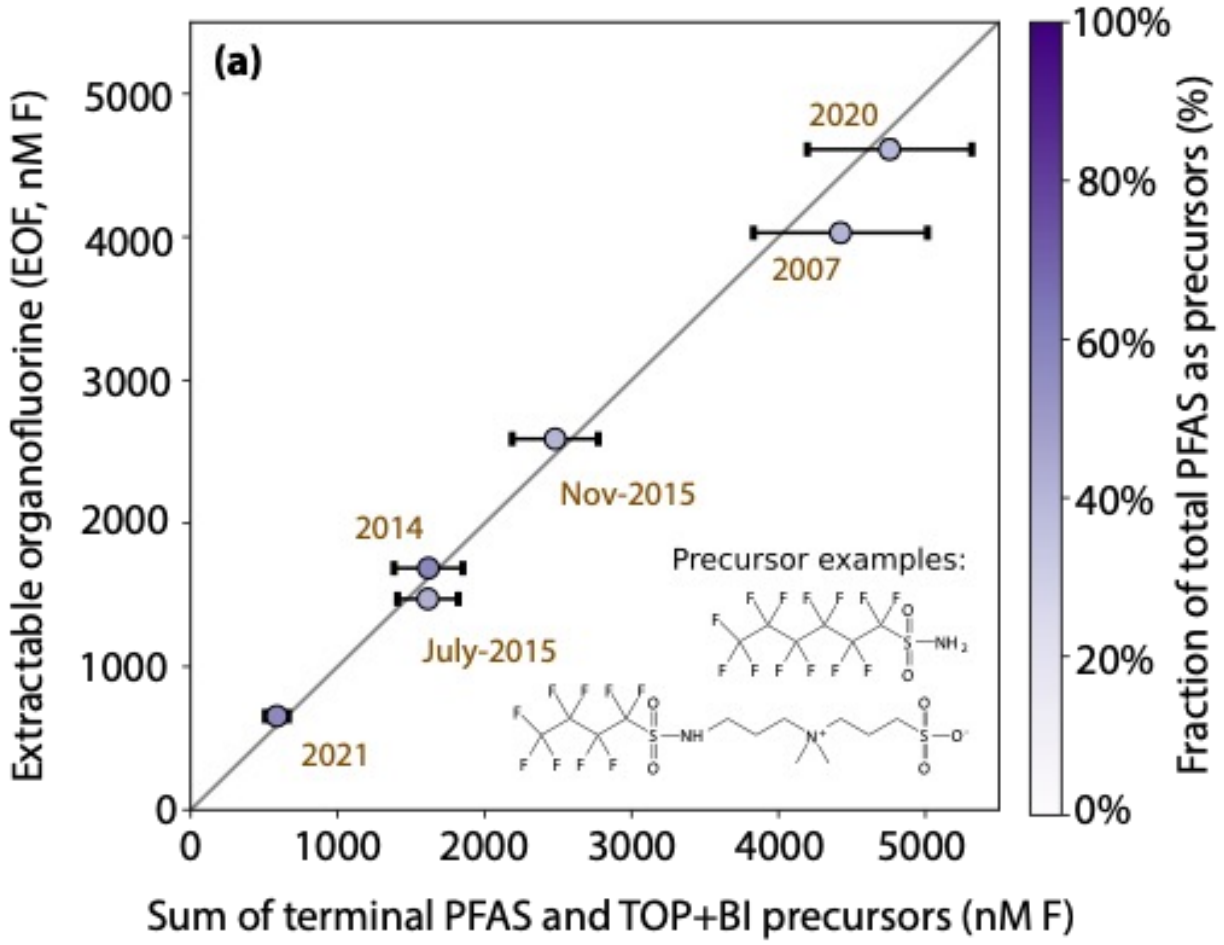
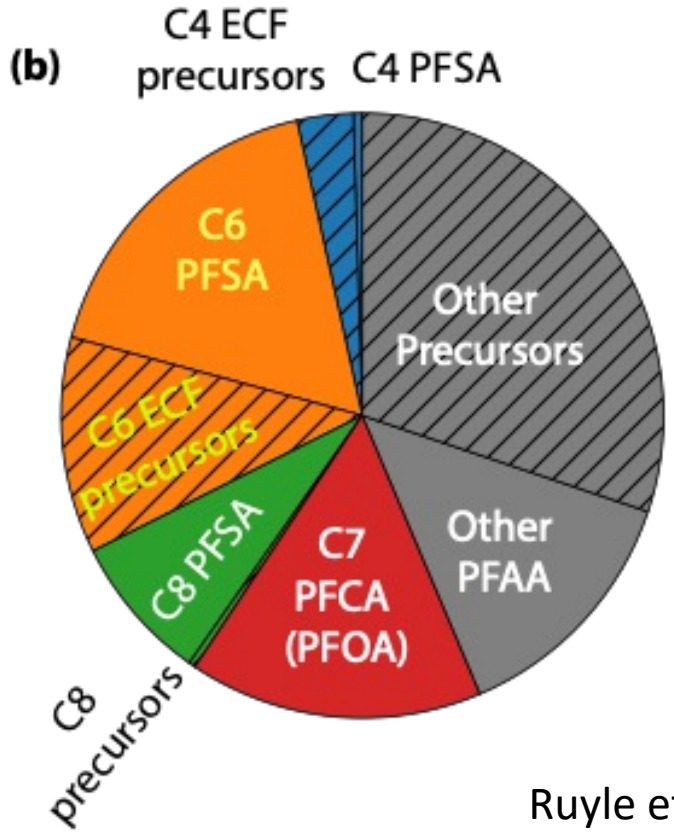
Ruyle et al, in-prep.

No clear temporal trends in groundwater PFAS below former fire-training area; Lots of C6 sulfonamide precursors

Total PFAS Mass Budget

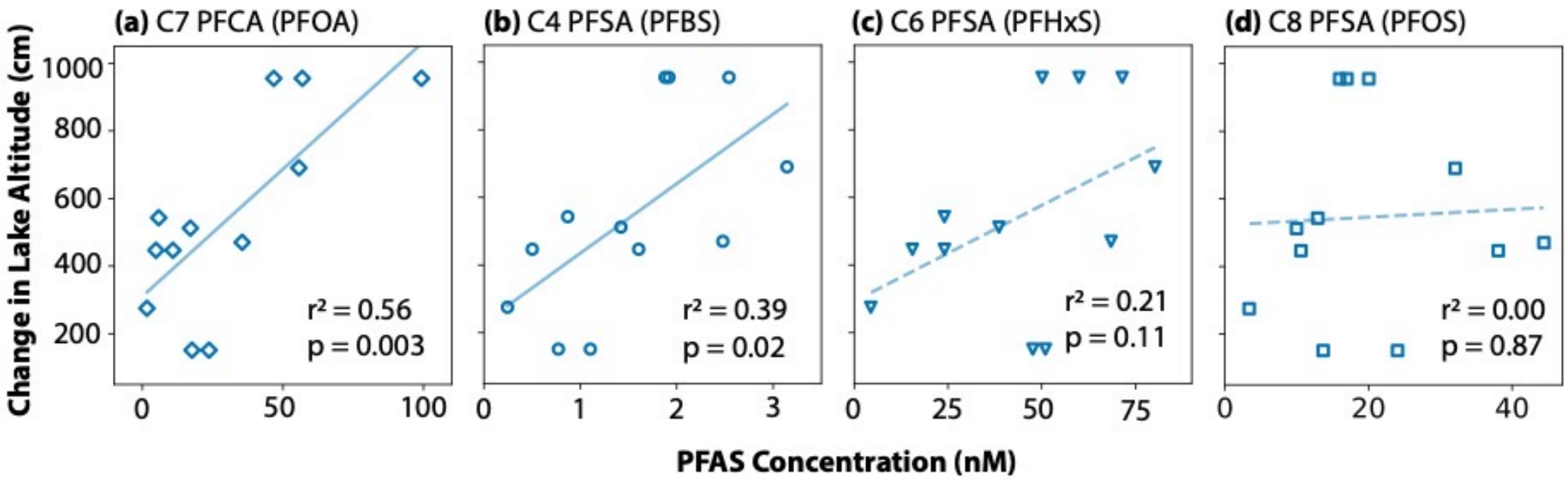


Average Composition in Groundwater



Ruyle et al, in-prep.

Temporal variability in PFOA and PFBS significantly associated with a proxy for soil moisture (groundwater-fed lake altitude)



Ruyle et al, in-prep.

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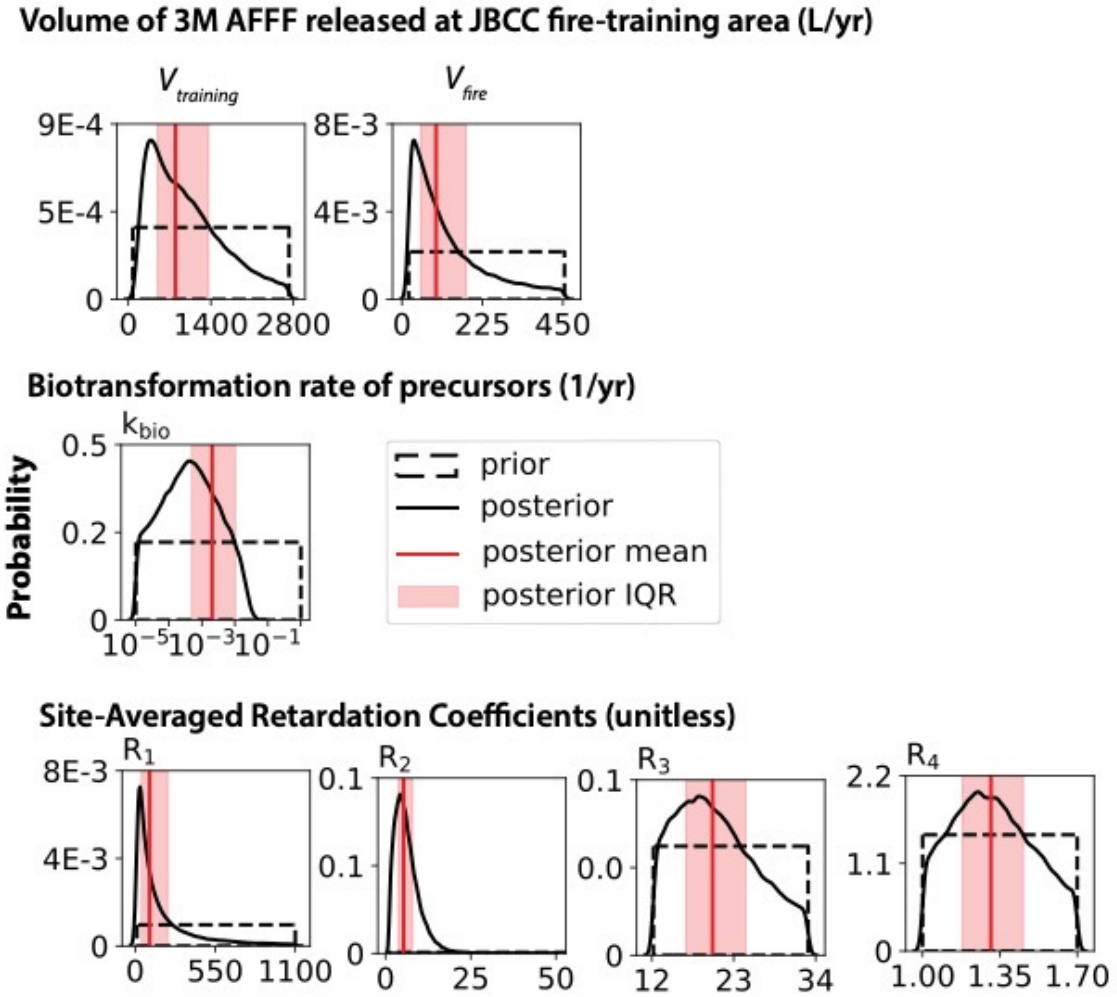
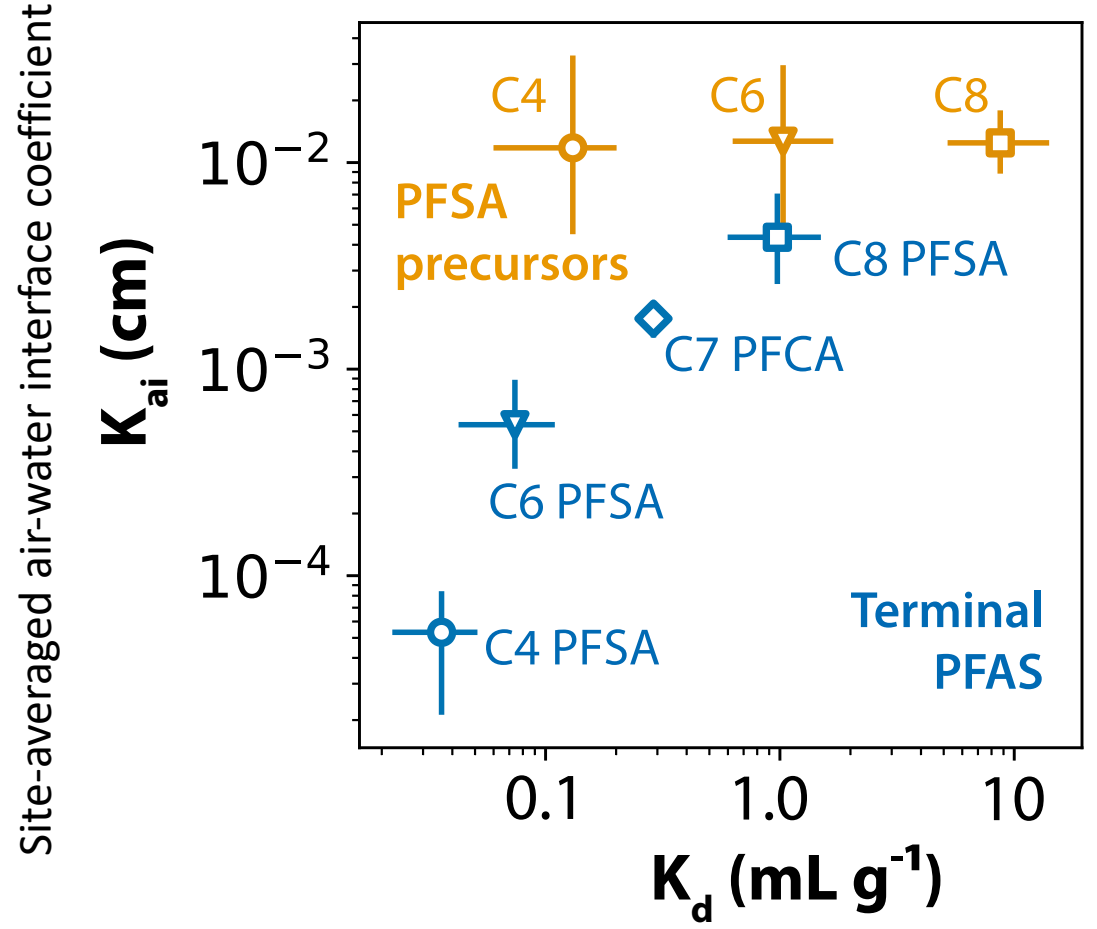
Statistically-optimized box-model for field site used to infer site-averaged partition coefficients that explain major controls on transport



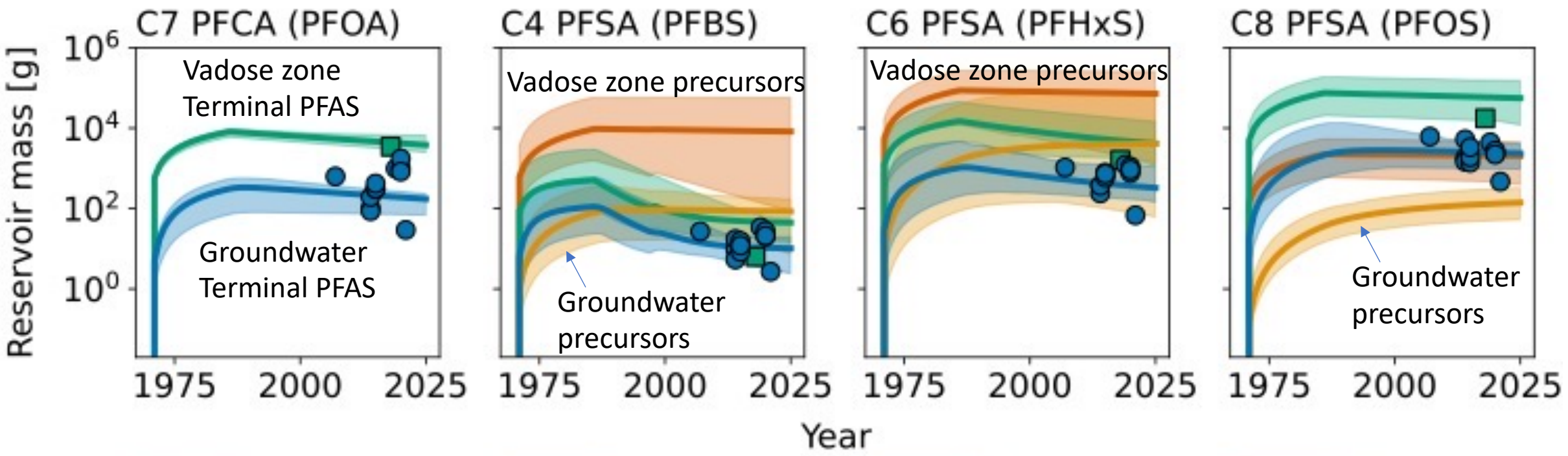
Ruyle et al, in-prep.



Site-averaged solids-water partition coefficient

Modeling suggests large vadose zone reservoir that is slowly leaching into groundwater but has not been substantially attenuated

No substantial attenuation of PFAS reservoirs decades after AFFF was actively used



Circles and squares show measurements

Ruyle et al, in-prep.

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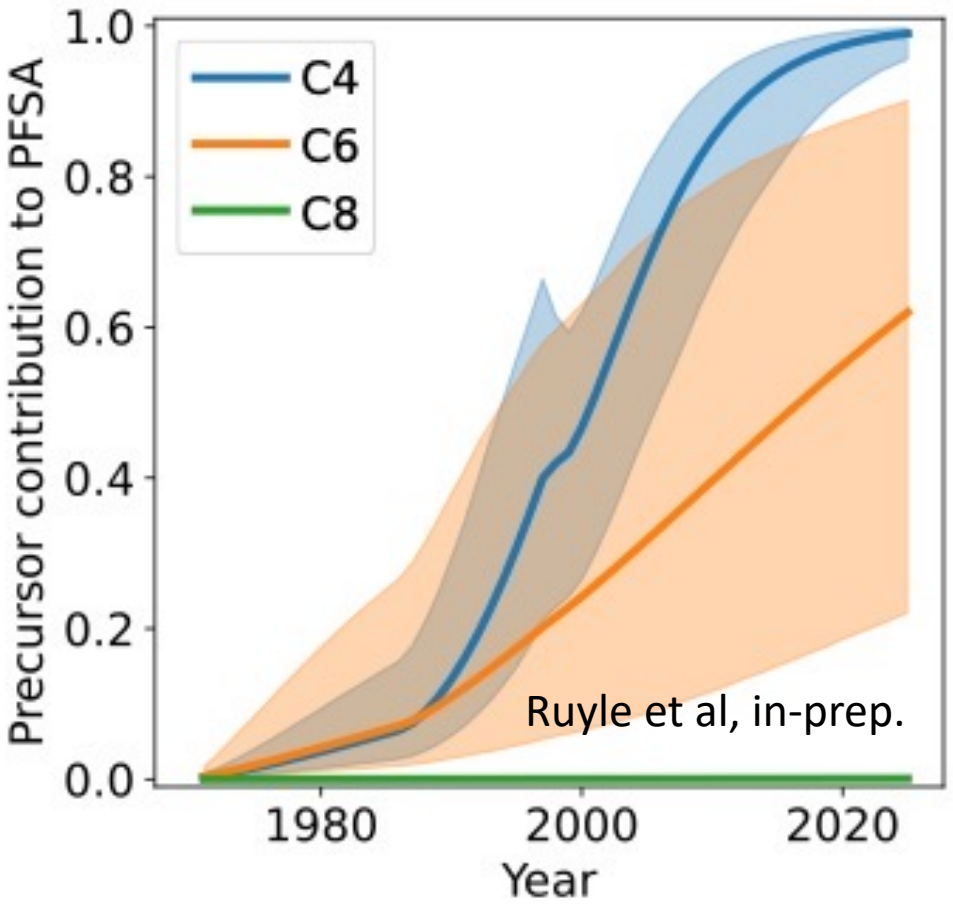
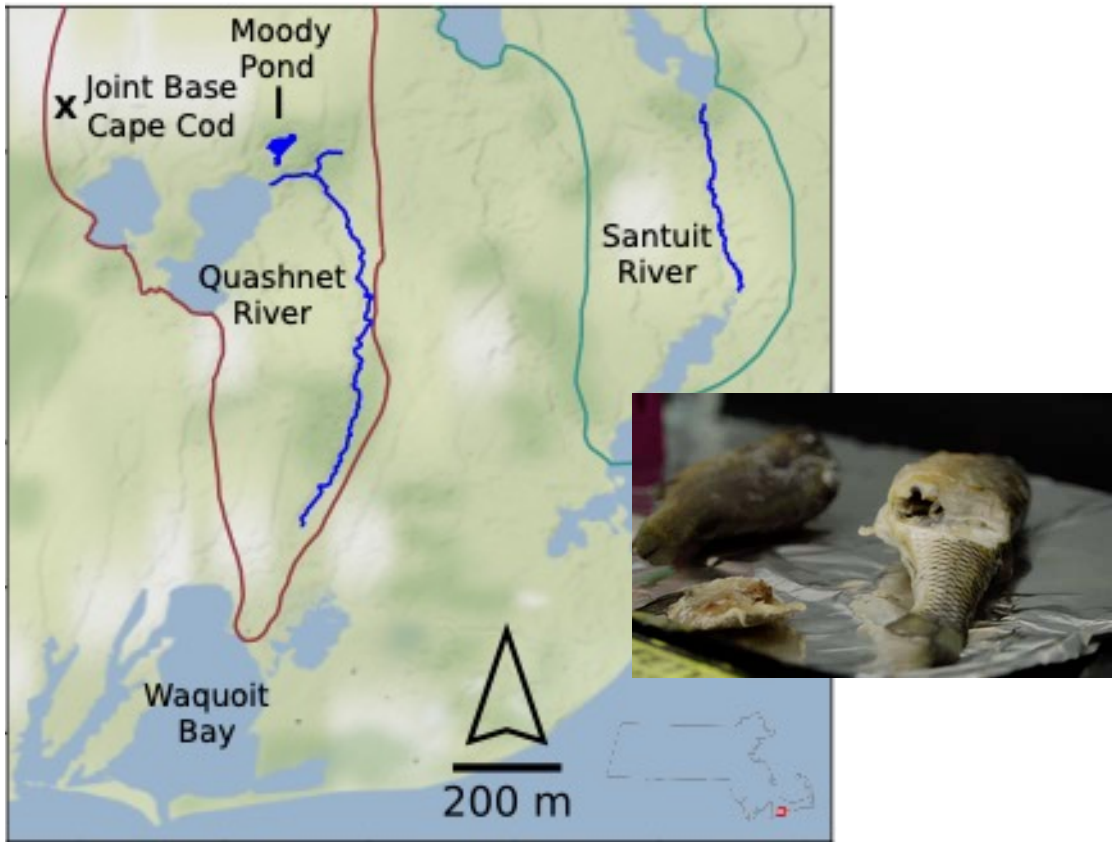
For PFBS and PFHxS the flux of PFAS into groundwater is being sustained by slow biotransformation of precursors in the vadose zone

Precursors detects in downgradient watersheds and marine areas; some have high propensity for bioaccumulation





Summary

- Many drinking water supplies have been contaminated by AFFF use
- Many of the legacy sources were 3M AFFF (more than 300 U.S sites identified)
- Mass budget for PFAS can be reconstructed for AFFF contaminated areas using targeted analysis, TOP+BI, EOF
- HRMS best for identifying structures without commercially available standards
- 3M AFFF contains ~50% precursors as a fraction of total PFAS, including lots of C6 sulfonamides that are likely biotransformed by nitrifying microbes, but it takes a long time…
- Timescales of PFAS contamination likely centuries without direct remediation of the vadose zone, including precursors!