The STEEP Challenge of Dealing with PFAS

Rainer Lohmann

(<u>rlohmann@uri.edu</u>) University of Rhode Island

THE UNIVERSITY OF RHODE ISLAND

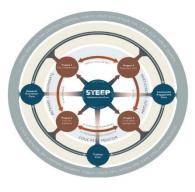


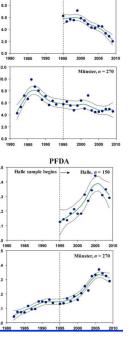






STEEP is funded by the Superfund Research Program, National Institute of Environmental Health Sciences under award number P42ES027726. More information about STEEP is available at: https://web.uri.edu/steep/ and https://booksniehs.nih.gov/stp/programs/Program_detail.cfm?Project_D=P42ES027706





PFASs: Challenging compounds

- Widespread human and environmental exposure
 - 100s of contaminated sites in U.S.
 - PFAS production sites, industrial users
 - Fire training sites, airports •

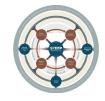


- Everyday exposure for all
 - Contaminated drinking water; Consumer products/dust, diet
- Wide range of adverse effects (humans/animals)
 - Immunosuppression (Grandjean et al., 2013)
 - More PFOA, higher risk of being overweight (Haldersson et al., 2012)
- Unique physical-chemistry, unlike traditional hydrophobic POF_
 - Amphiphilic compounds, ionized in solution; bind to proteins
- Regulatory action
 - PFOS withdrawal and PFOA action plan; novel chemistries (e.g., Gen X)









The known unknowns are getting us

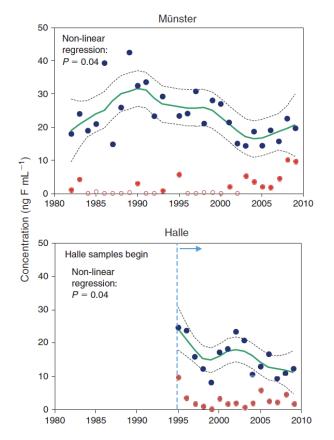


Fig. 3. Temporal trends of extractable organofluorine (EOF) and unidentified organofluorine concentrations (ng F mL⁻¹) in German plasma. (Blue dot indicates the mean value of EOF, dotted line indicates the 95 % confidence interval of the trend and green line indicates the trend generated using locally weighted regression smoother (LOESS); red dot indicates the mean value of unidentified organofluorine; open red dots indicates no unidentified organofluorine.)

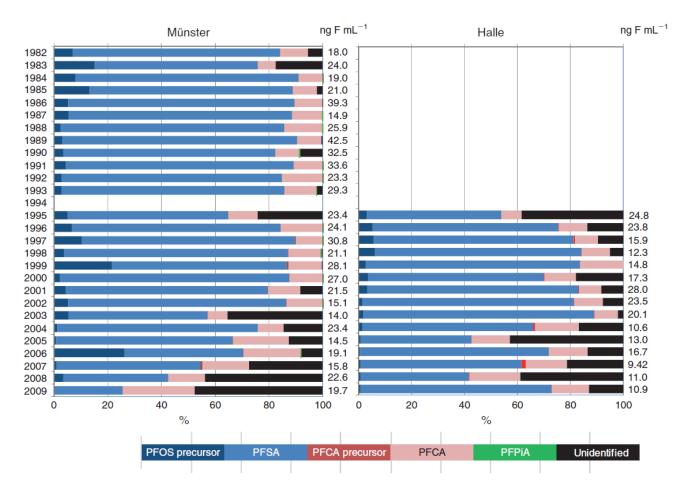
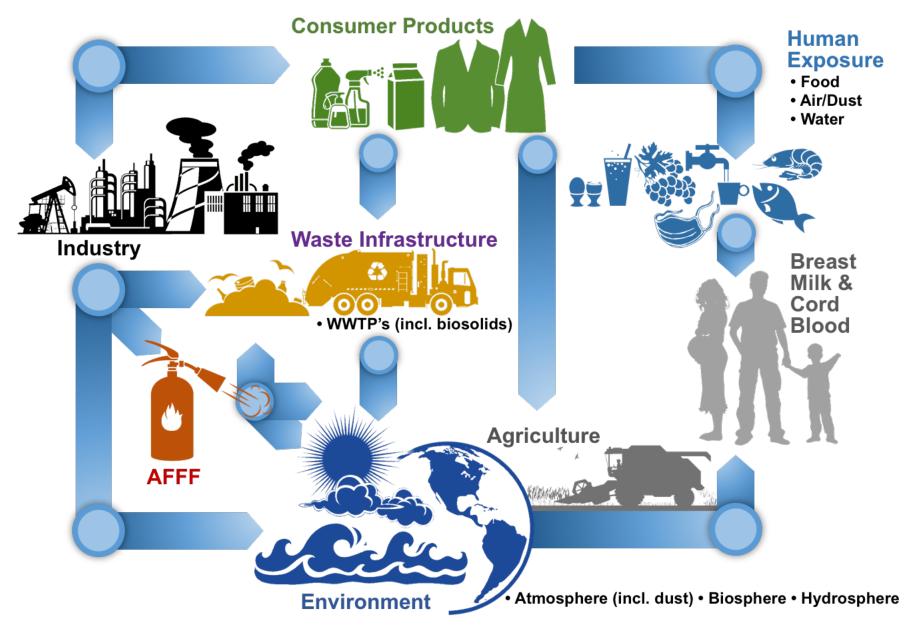


Fig. 4. Composition and concentrations (ng F mL⁻¹) of extractable organofluorine (EOF) in German blood plasma samples (perfluoroctane sulfonate, PFOS; perfluoroalkyl sulfonate, PFSA; perfluorinated carboxylates, PFCAs; perfluorinated phosphinates, PFPiAs).

(Yeung and Mabury, 2016)



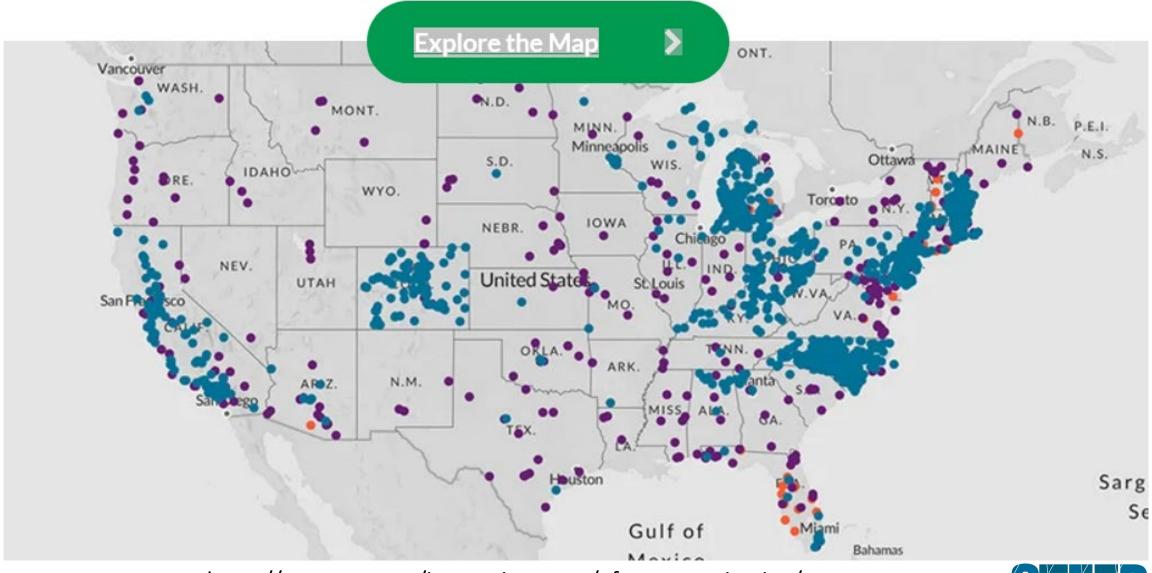
Human Exposure Pathways





What has changed since 2015 in the US?

2015	2021
2015	2021
2015	2021
2015	2021
2015	2021
2015	2021
	2021

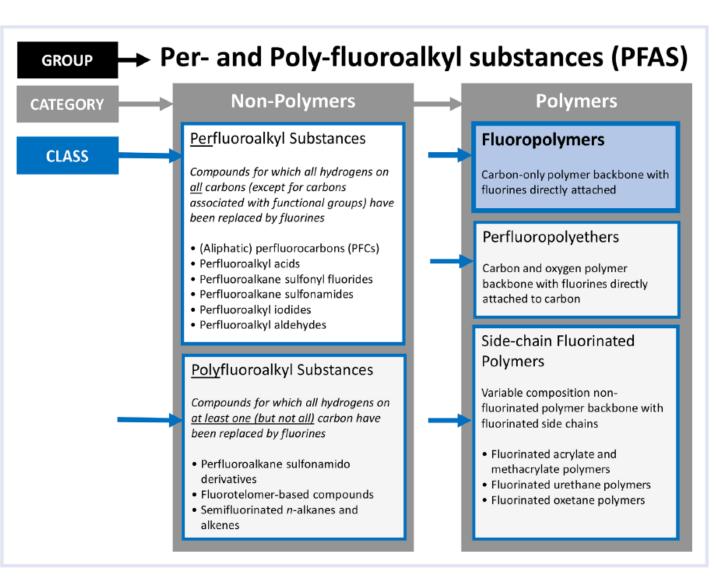


Sources, Transport, Exposure & Effects of PFASs

https://www.ewg.org/interactive-maps/pfas_contamination/

1000s of PFAS 100s produced * 10s monitored 2 targeted (EPA)

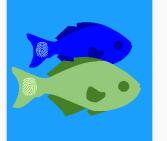
• Categories:





Sources, Transport, Exposure & Effects of PFASs

Connecting science and people



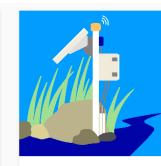
STEEP Research: Environmental Fate & Transport



STEEP Research: Childhood Risk



STEEP Research: Metabolic Effects



STEEP Research: Detection Tools



STEEP Core: Next Generation



STEEP Core:

Research Translation



STEEP Core: Community Engagement



STEEP Core: Administrative



Project 1: Sources, fate and transport

PI: Elsie Sunderland (HU) Collab: Dennis LeBlanc (USGS); Alan Vajda (CU)

Biogeochemistry of

Global Contaminants

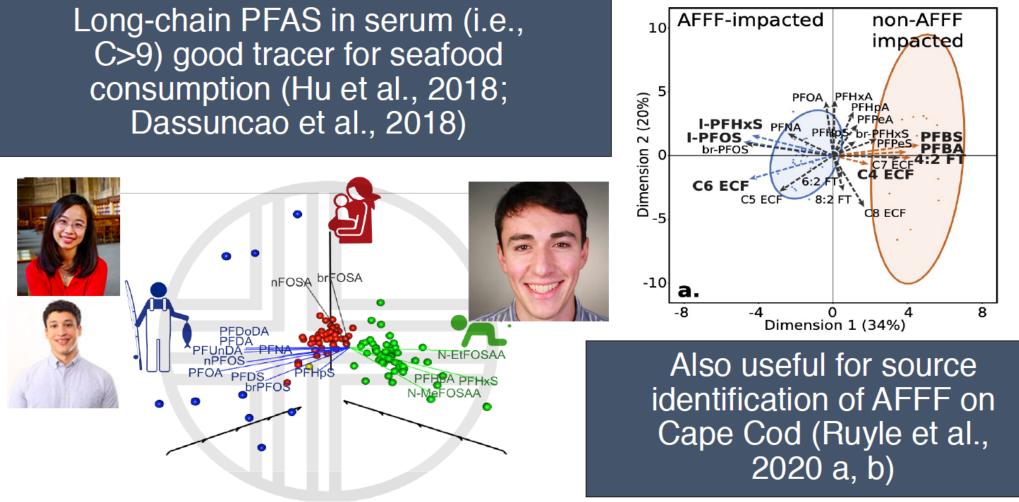
HARVARD

Cape Cod: Linking local sources to global systems

Total: 666 ppt Total: 9.12 ppt Total: 314 ppt PFOA: 2.06 ppt PFOA: PFOS: 86.3 pp PFOS: 0.89 ppt PFOS: 46 Total: 7.86 ppt PFOA: 1.49 ppt PFOS: 0.43 ppt Total: 185 ppt Legend PFOS: 55.4 08/2017 Sampling 07/2018 Sampling 70°30'0"W 70°28'0"W 70°24'0"W 70°22'0"W 70°18'0"W 70°16'0"V 70°32'0"W 70°26'0*W 70°20'0*V



Aim 1: Statistical fingerprinting of PFAS

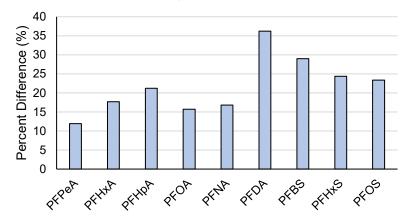




Project 4: Detection tools-A passive sampler for water

- 6 caged vs 6 "naked" deployments in the Bay.
- No sign. difference

Reproducibility Percent Difference

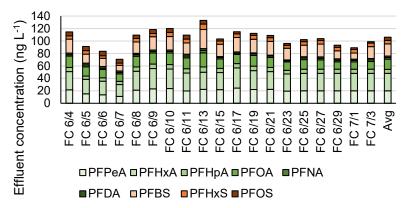


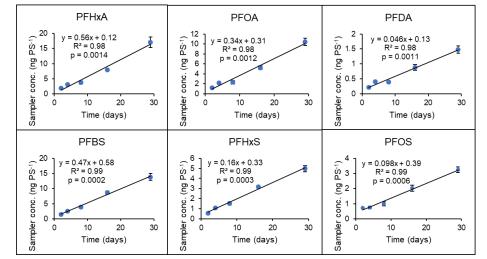


(Gardiner, 2019)



Fields Point Effluent



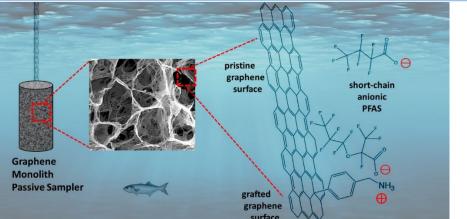


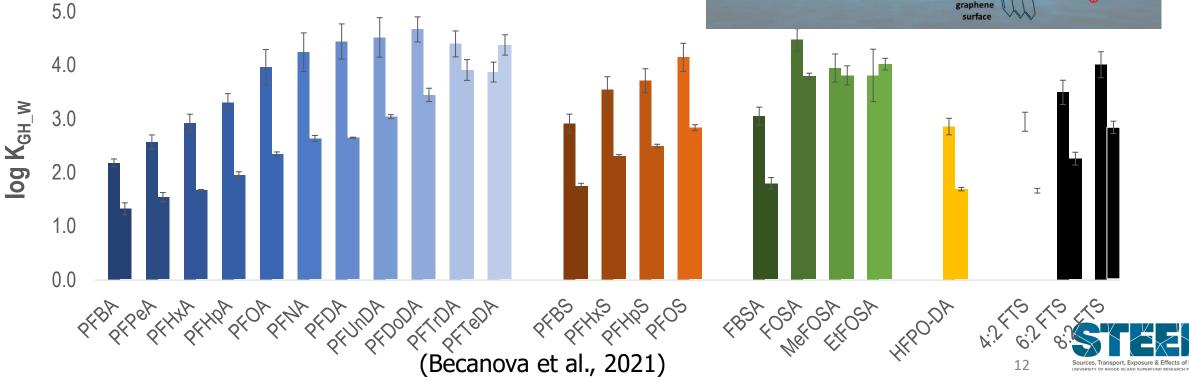


Graphene monolith sampler (fast, equilibrium)



- modified/functionalized graphene oxide
- SPE sorbents weak anion exchange STRATA X
- 4-Aminobenzylamine (4-ABA) \rightarrow positively charged GO

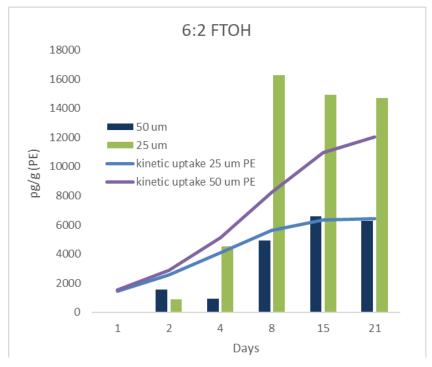


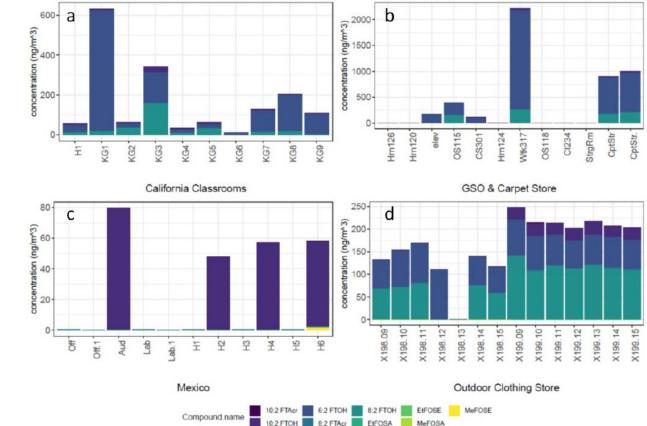


Indoor air sampling tools



• PE-sheets, and 2 weeks





SOURCES, TRANSPORT, EXPOSURE & Effects of PFASS

(Morales-McDevitt, 2021)

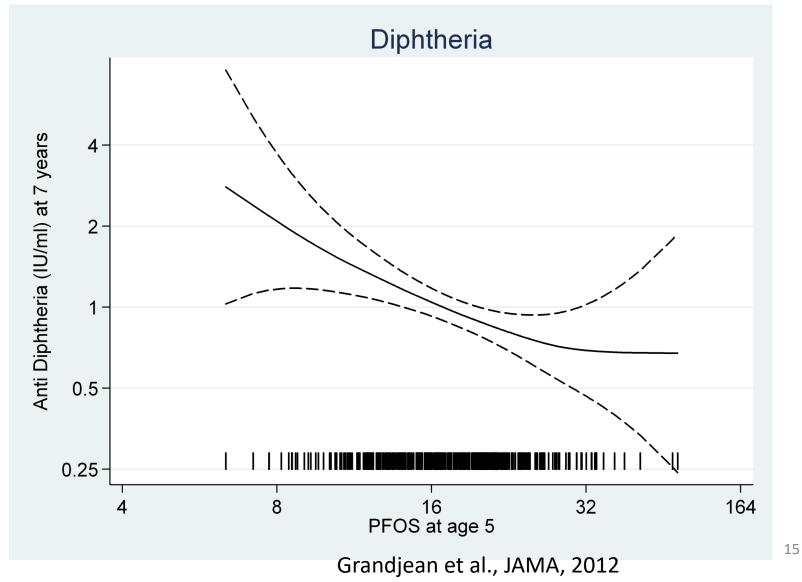
Project 2: Inflammation and Metabolic Changes in Children Developmentally Exposed to PFASs PI: Philippe Grandjean (HU), w/Pal Weihe (Faroese Hospital)





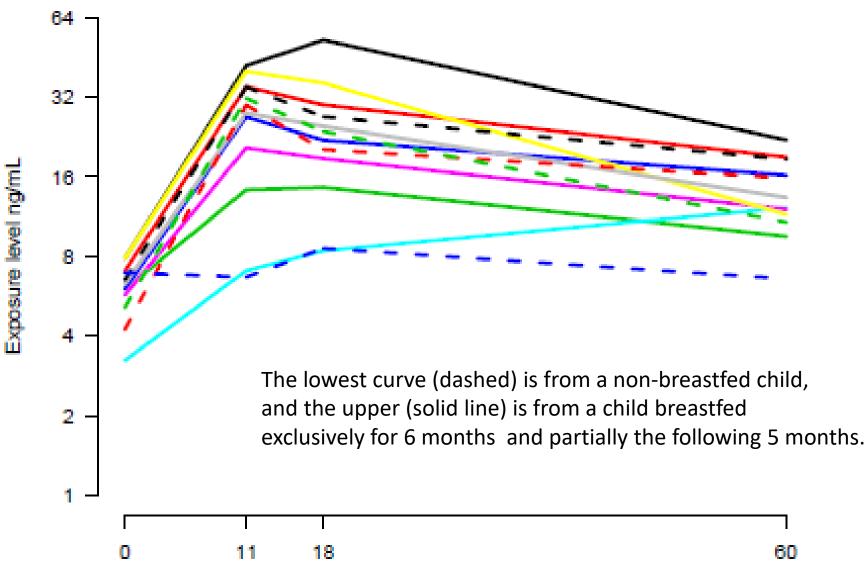


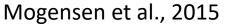
Childhood risks of PFAS





PFOS transfer via human milk impacts infant serum levels

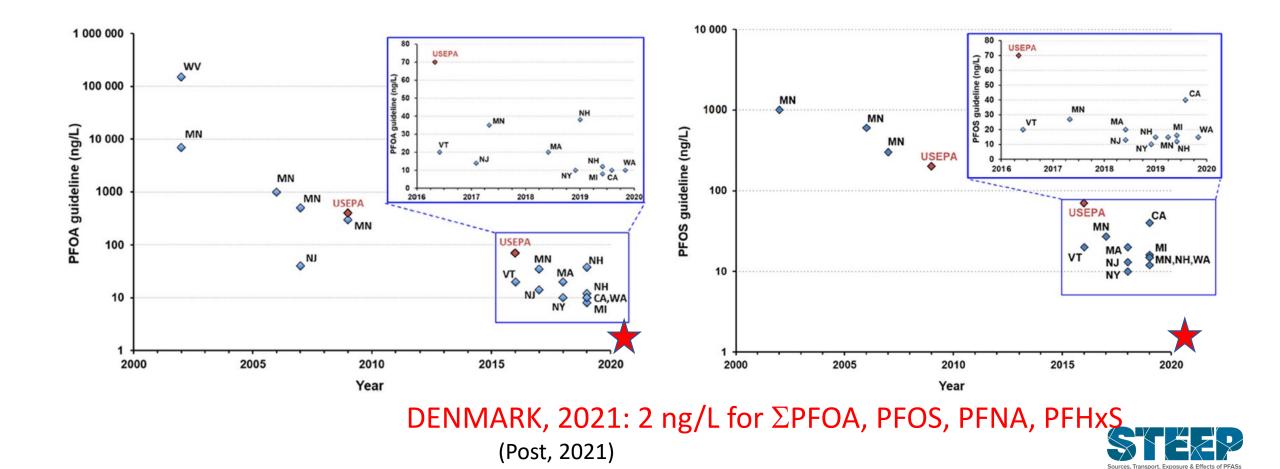




Age in months

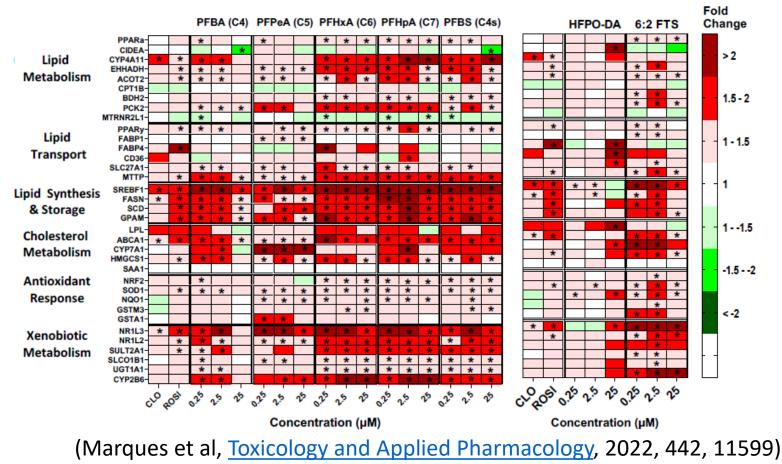


What is safe? It depends on where, when, which.



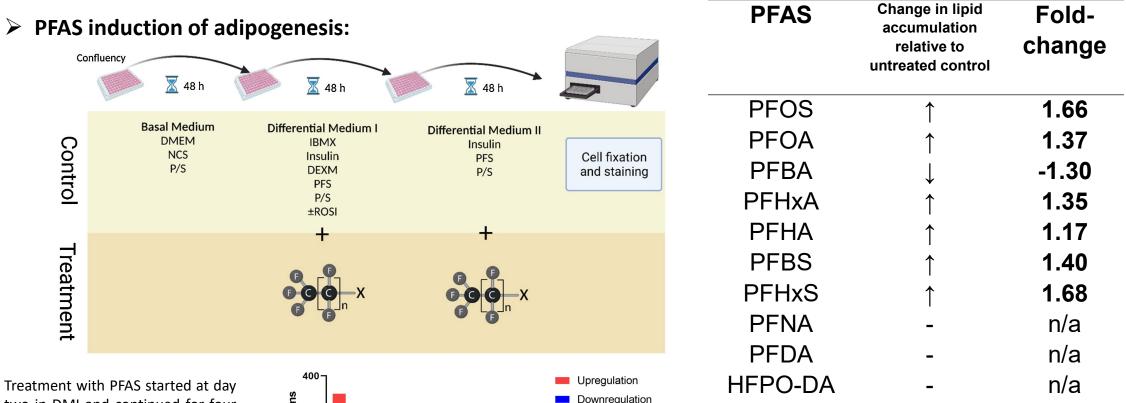
Project 3: Using Cell Based Assays to learn more about "emerging PFASs" PI: Angela Slitt (URI); co-PI: Geoff Bothun (URI)

• Gene expression in human hepatocytes exposures

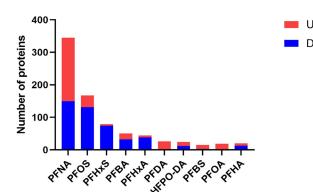




PFAS augment adipogenesis and shift the proteome in murine 3T3-L1 adipocytes*



two in DMI and continued for four days. Ten different PFAS with 3 different concentrations each was added along with three different concentrations of the cocktail differentiation the in of presence or absence rosiglitazone.



*Modaresi SMS, Wei W, Emily M, DaSilva NA, Slitt AL. Toxicology 2022; 465:153044.

Summary of lipid accumulation results at the 25 μ M PFAS along with rosiglitazone made 6 out of 10 PFAS to significantly increase lipid content.

In this study, lipid content of cells exposed to 3 dilutions of the differentiating cocktail along with 10 different PFAS at 0.25, 2.5, and 25 μ M with or without rosiglitazone was determined using Nile Red staining (all data not shown).



How else to explain PFAS to the public?

• "forever chemicals"



NO DEFENSE

More than 650 towns contaminated.

Millions of Americans affected.

The largest-known polluter of chemicals that are nearly indestructible ...

... is also the **regulator** that has failed to act.

This is the story of the war on water.

THE TRUTH HAS A MAN ON THE INSIDE.



Research Translation Core PI: Judith Swift; co-PI Nicole Rohr, Amber Neville (URI)



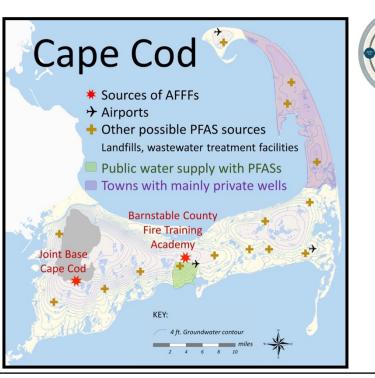


STEEP website: www.uri.edu/steep

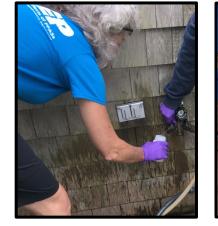
Sources, Transport, Exposure & Effects of PFASs UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

RSVP: superfundsteep@etal.uri.edu

- STEEP's focus on Cape Cod
- Vulnerable sole-source aquifer
- AFFF contamination of public and private drinking water wells
- Prior studies of septic systems as PFAS sources
- Community concerns about water quality and health



Community engagement Core PI: Alyson McCann (URI) Laurel Schaider (SSI)





Private well testing









Community events and presentations



Based on these definitions, how many use categories can we define for PFAS?

Based on the Montreal Protocol, which defined the concept of essential use for chlorofluorocarbons (CFCs).

- An essential use is a use necessary for health or safety or for the functioning of society.
- An essential use is a use for which there are no available technically and economically feasible alternatives.



Essential use concept for PFAS

Table 1 Three essentiality categories to aid the phase out of non-essential uses of chemicals of concern, exemplified with PFAS uses

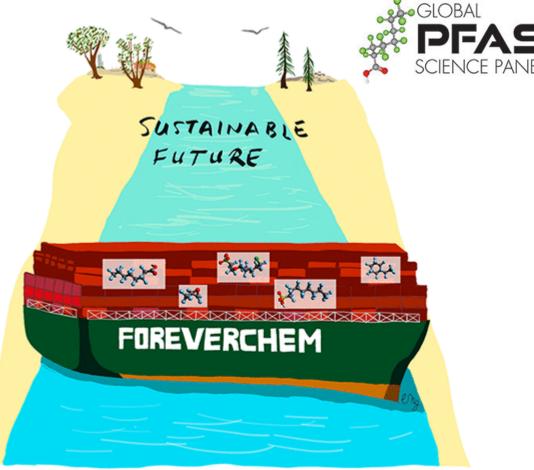
Category	Definition	PFAS examples
(1) "Non-essential"	Uses that are not essential for health and safety, and the functioning of society. The use of substances is driven primarily by market opportunity	Dental floss, water-repellent surfer shorts, ski waxes
(2) "Substitutable"	Uses that have come to be regarded as essential because they perform important functions, but where alternatives to the substances have now been developed that have equivalent functionality and adequate performance, which makes those uses of the substances no longer essential	Most uses of AFFFs, certain water-resistant textiles
(3) "Essential"	Uses considered essential because they are necessary for health or safety or other highly important purposes and for which alternatives are not yet established ^{<i>a</i>}	Certain medical devices, occupational protective clothing

^a This essentiality should not be considered permanent; rather, a constant pressure is needed to search for alternatives in order to move these uses into category 2 above.



Outlook: Addressing Urgent Questions for PFAS in the 21st Century





Carla Ng,* Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Sharyle Patton, Martin Scheringer, Xenia Trier, and Zhanyun Wang







QUESTION 1: WHAT ARE THE GLOBAL PRODUCTION VOLUMES OF PFAS AND WHERE ARE PFAS USED?

Importance.

• Underlies effective measurements, assessment, and management strategies

Barriers.

- Regulations, CBI
- Producer interests
- Complexity of production chains

Potential Paths Forward.

- New rules/regulations (TSCA)
- Consumer pressure; industry pushback



What are global production volumes of PFAS, and where are PFAS used?



QUESTION 2: WHERE ARE THE UNKNOWN PFAS HOTSPOTS IN THE ENVIRONMENT?



Importance.

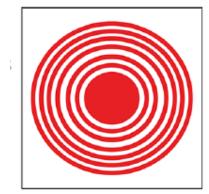
• Unknown sites (biosolids, etc)

Barriers.

- Country-specific uses (leaf ant control)
- Lack of capabilities

Potential Paths Forward.

- Country-specific inventories
- Emission reporting
- Testing, testing, testing



Where are the unknown PFAS hotspots in the environment?



QUESTION 3: HOW CAN WE MAKE MEASURING PFAS GLOBALLY ACCESSIBLE?



Importance.

- Lack of methods
- Lack of testing

Barriers.

- Lack of cheap/simple screening tests
- Lack of standards and affordable tools

Potential Paths Forward.

- Simpler tools (EOF/XRF) for totals
- Collaboration and exchange
- Capacity building



How can we make measuring PFAS globally accessible?



QUESTION 4: HOW CAN WE SAFELY MANAGE PFAS-CONTAINING WASTES?



- Stockpiles, landfills, WWTPs
- Problem of persistence

Barriers.

- Pump and treat etc creates waste/rejects
- (In situ) destruction not widely used
- Incineration as panacea?

Potential Paths Forward.

- Turn off the tap
- R&D for mineralization; interim storage.



How can we safely manage PFAS-containing waste?





QUESTION 5: HOW CAN WE UNDERSTAND AND DESCRIBE THE HEALTH EFFECTS OF PFAS EXPOSURE?

Importance.

- Too many (unknown) understudied PFAS
- On-going exposures

Barriers.

- causality
- Many pathways
- Divers structures

Potential Paths Forward.

- Class-based approach
- Precautionary approach
- Combine different approaches



How do we describe the health effects of PFAS exposure?



QUESTION 6: WHO PAYS FOR THE IMPACTS OF PFAS CONTAMINATION?



Importance.

- Testing, treatment costs. (1-2 Bio EUR/yr Nordic)
- Health costs (10s Bio EUR /yr Nordic)

Barriers.

- Polluter pays??
- Responsible party
- Effects delay

Potential Paths Forward.

- Internalize costs
- PFAS in CERCLA
- PFAS-tax?



How do we deal with the costs of PFAS contamination?



Much progress, much more is needed

• EPA's decisions on MCLs (PFOA + PFOS+?); CERCLA, testing

- Progress in the EU, DC, and some states on
 - essential use, MCLs, PFAS restrictions
- Remediation, treatment, atmosphere?

• Health implications



Thanks, again

- Tides Foundation (grant 1907-59084 for GPSP).
- NIEHS, of course (P42ES027706)
- RI STAC for passive sampling tube work
- SERDP ER 18-1280 (Sunderland, Harvard U)
- SERDP 20-2538 (Lohmann, URI)
- Partners/collaborators, grad students







SCHOOL OF PUBLIC HEALTH Department of Environmental Health





National Institute of Environmental Health Sciences Superfund Research Program

STEEP is funded under award number P42ES027706. More information about STEEP is available at: www.uri.edu/steep/



Thank you.

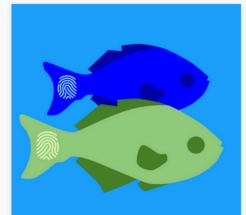
Questions?



Research Translation Core PI: Judith Swift; co-PI Nicole Rohr, Amber Neville (URI) **STEEP website: www.uri.edu/steep**



Social media



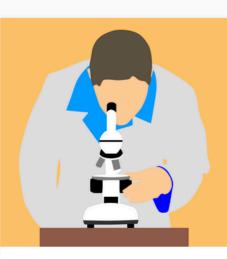
Environmental Fate & Transport

Environmental Engineering: Exposure assessment and chemometrics of PFASs.



Childhood Risk

Epidemiological Study: Inflammation and metabolic changes in children exposed to PFASs.



Metabolic Effects

Laboratory Study: PFAS compound effects on metabolic abnormalities in rodents.



Detection Tools

Environmental Engineering: Develop passive samplers for the detection and bioaccumulation of PFASs.









Faroes community

- The Faroe Islands are comprised of a dozen islands located between the Shetland Islands and Iceland
- Unique epidemiological setting, where birth cohorts have been formed and followed-up with minimal attrition
- The marine diet results in a wide range of PFAS exposures
- The Faroese are of Nordic and Irish origin and comparable in many ways to other Western populations.



Can consumers identify products containing PFAS? Products that do or did contain PFAS





Something in the air..



... and in your blood



Airborne Precursors Predict Maternal Serum Perfluoroalkyl Acid Concentrations



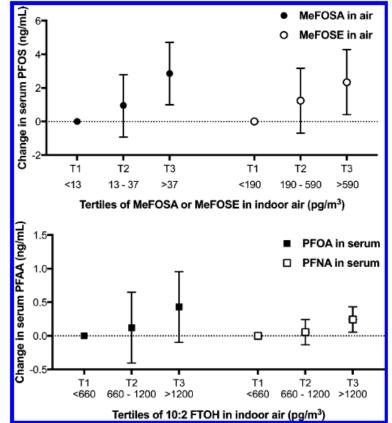


Figure 1. Exposure categories [low (n = 17), medium (n = 16), and high (n = 16)] of PreFAA in air predicting serum PFAA levels in 50 women.

(Makey et al. 2017)

Article

pubs.acs.org/est



Table 2 Essentiality of PFASs in selected use categories

Use	Table 1 Category
Personal care products including cosmetics	1
Ski waxes	1
Fire-fighting foams (commercial airports)	2
Fire-fighting foams (military)	2 or 3
Apparel (medical: long operations)	3
Apparel (protective clothing oil and gas industry)	3
Apparel (medical: short operations, everyday)	2
Apparel (military: occupational protection)	2 or 3
Waterproof jacket (general use)	2
Easy care clothing	1
Food contact materials	1, 2 or 3
Non-stick kitchenware (fluoropolymers)	1 or 2
Medical devices (fluoropolymers)	1, 2 or 3
Pharmaceuticals	2 or 3
Laboratory supplies, equipment and instrumentation	1, 2 or 3
Perfluorosulfonic membranes in fuel cells	2
Perfluorosulfonic membranes in	3
chlor-alkali process	

^{*a*} Note that the categories in the above table represent the current evaluation and may change in the future.

Essential use concept for PFAS

"When considering chemical alternatives for PFASs, the focus should be on the service the product should deliver. The compound should therefore be evaluated for performance using the specifications required for the product as opposed to comparing directly to the PFAS being replaced...

Additionally, the potential for health hazard and potential for exposure...must be conside

Concern about PFASs

How do impacted communities contaminated with many different PFAS raw materials and byproducts manage and/or mitigate public and environmental health risks?

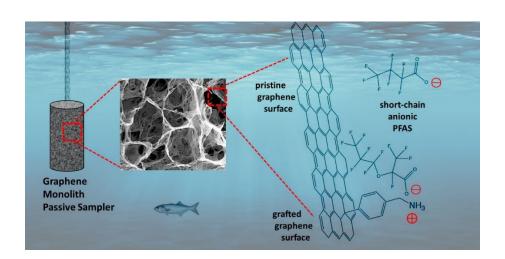


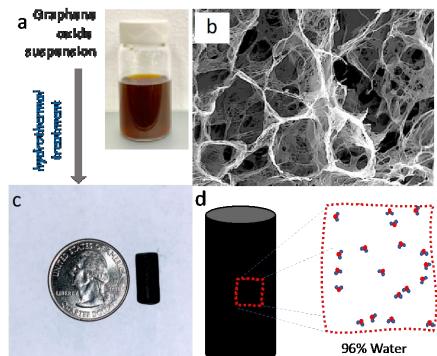
THE SPREAD OF TOXIC PFAS POLLUTION SITES



A graphene-based hydrogel monolith with tailored surface chemistry for PFAS passive sampling

 Jitka Becanova¹*, Zachary Saleeba²*, Aidan Stone², Robert H. Hurt², Rainer Lohmann¹





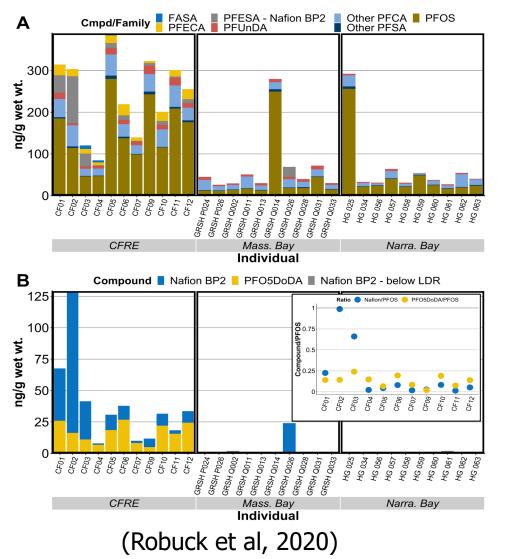


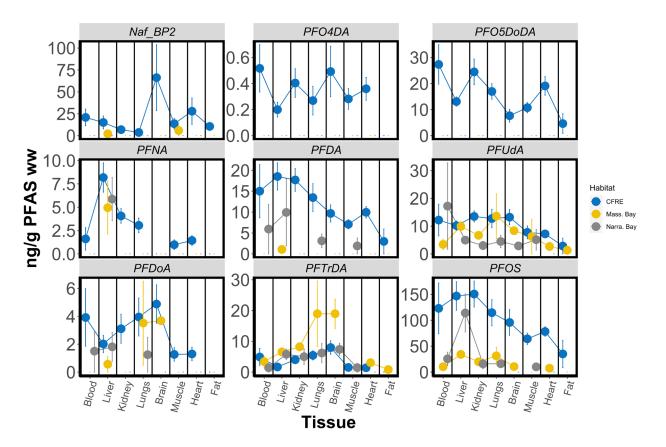
41

(Becanova et al., 2021)



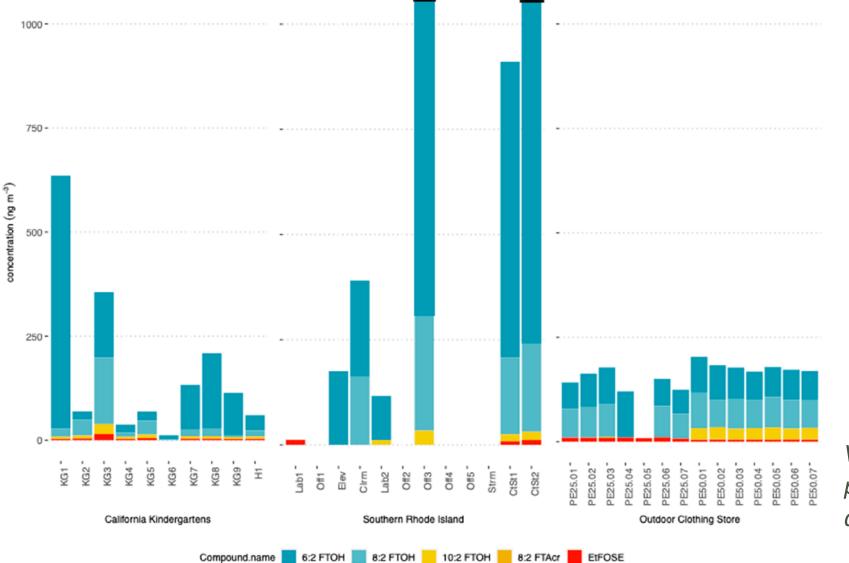
Legacy and novel PFAS in birds





(Robuck et al, 2021)





Volatile and neutral PFAS were present at most locations, dominated by FTOHs

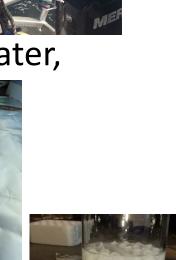
43

Figure 1. Indoor air concentrations measured in California kindergarten classrooms, an outdoor clothing store, university classrooms, offices and laboratories, and a carpet store in southern Rhode Island. Abbreviations: H, home; KG, kindergarten classrooms; Lab, laboratory; Off, office; Elev, elevator; Clrm, classroom; Ctst, carpet store; Strm, storage room. Numbers (i.e., KG7) are indicative of separate/individual samples. Off3 (2220) and CtSt2 (1040) have concentrations of >1000 ng m

(ME Morales-McDevitt et al., 2021)



- **Project 4: Novel Detection tools PI: Rainer Lohmann (URI)** Collab: Laurel Schaider (SSI); Barry Kim (U Guam)
- Develop novel sampling tools for PFASs and precursors in air, water, sediment and biota
- Support site characterization
- Enable stakeholder to deploy/use these samplers
- Aim 1: A thin fiber sampler for hotspots
- Aim 2: A passive sampler for water
- Aim 3: A sampler for (volatile) precursor PFASs









Community engagement Core Alyson McCann (URI), Laurel Schaider (SSI) Project scope:

- Analyze samples from 250 wells
- 101 samples collected to date
- Analytes:
 - 25 PFASs (PFCAs, PFSAs, FtSs, FOSAAs)
 - Septic system markers (nitrate, boron)
- Questionnaires including well depth
- Report-back to participants using DERBI

Insights from meeting well owners:

- Perceptions of water quality challenges
- Barriers to water testing and treatment
- Common questions and concerns
 - Is my water safe to drink?
 - What do I do if my well is contaminated?
 - Are high cancer rates linked to water quality?







Co-exposures to 5 main PFAS.. PFOS, PFOA, PFHxS, PFNA and PFDA

 BMDL of ~ 0.1 ng/mL serum for both PFOS and PFOA

RESEARCH ARTICLE

Application of benchmark analysis for mixed contaminant exposures: Mutual adjustment of perfluoroalkylate substances associated with immunotoxicity

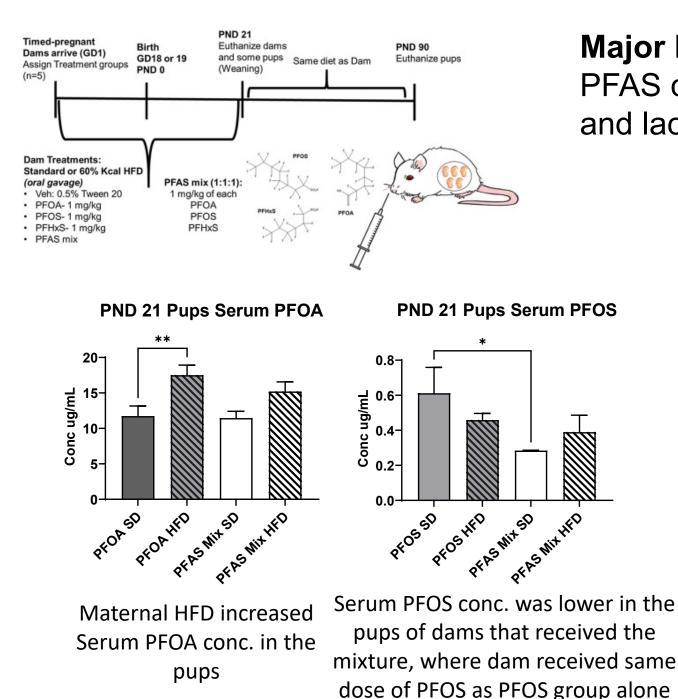
Esben Budtz-Jørgensen¹, Philippe Grandjean^{2,3}*

 Department of Biostatistics, Institute of Public Health, University of Copenhagen, Copenhagen, Denmark,
Department of Environmental Medicine, University of Southern Denmark, Odense, Denmark,
Department of Environmental Health, Harvard T.H. Chan School Public Health, Boston, Massachusetts, United States of America

* pgrand@hsph.harvard.edu

Our BMDL results, both before and after adjustment are generally below current exposure levels and therefore suggest that all five perfluorinated substances should attract regulatory attention, at least until additional evidence shows otherwise.





Major Finding: Maternal diet and other PFAS can impact PFAS transfer (placental and lactational) from dam to pup.

Check out the full Paper!



Symposium: PFAS Sum versus Some? The Science and Policy of Mixtures

(Thurs. March 31 in CC Room 7) Dr Angela Slitt will be presenting some of this work in her talk entitled "Understanding PFAS-PFAS interaction in hepatocyte and Mouse Models of Steatosis

Sources, Transport, Exposure & Effects of PEAS