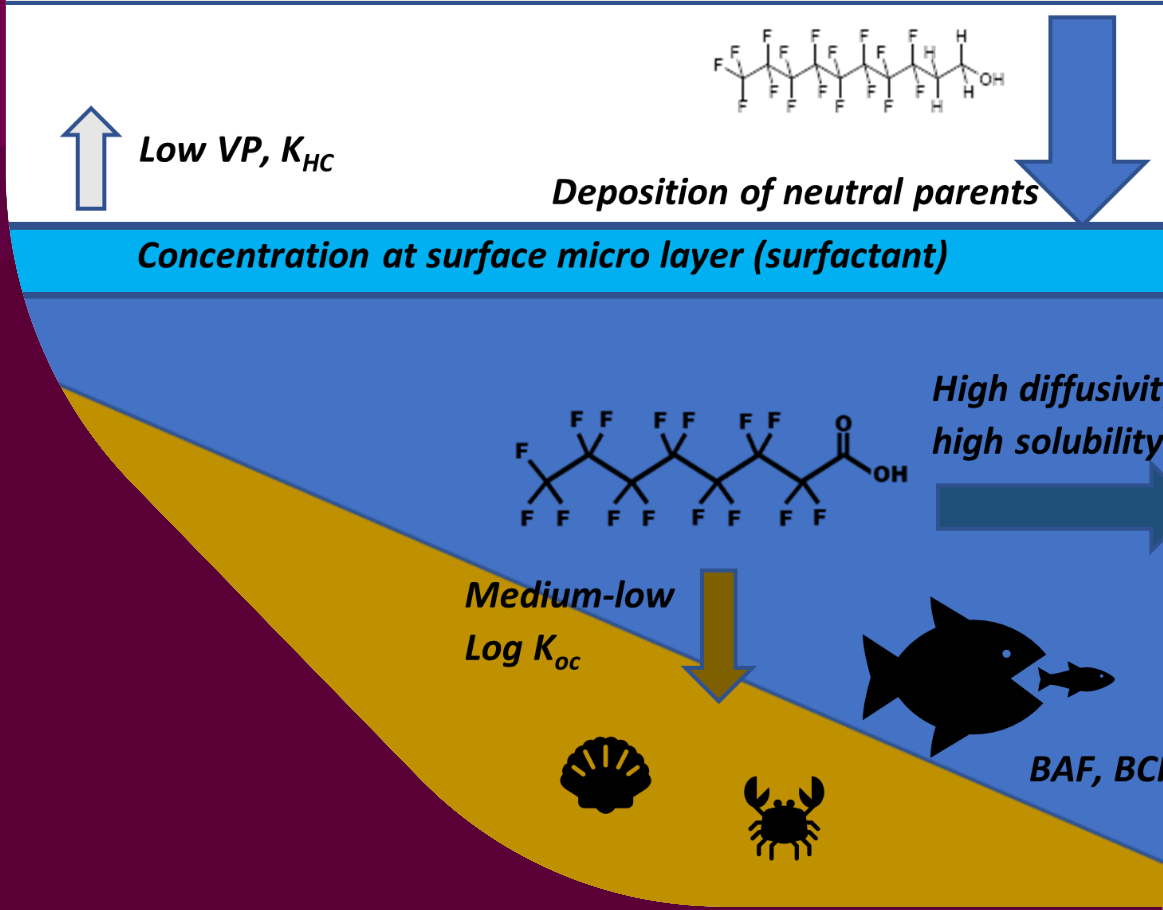
Precursor PFAS Present A New Fluorinated Feedback Loop



Matt Dunn, PhD

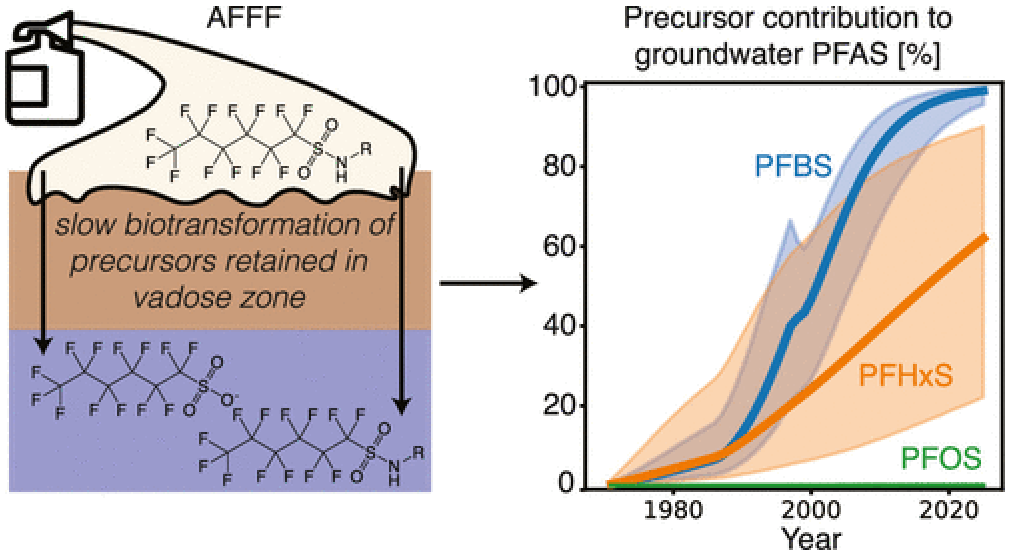
Northeast Conference on the Science of PFAS: Public Health & the Environment

rpsgroup.com

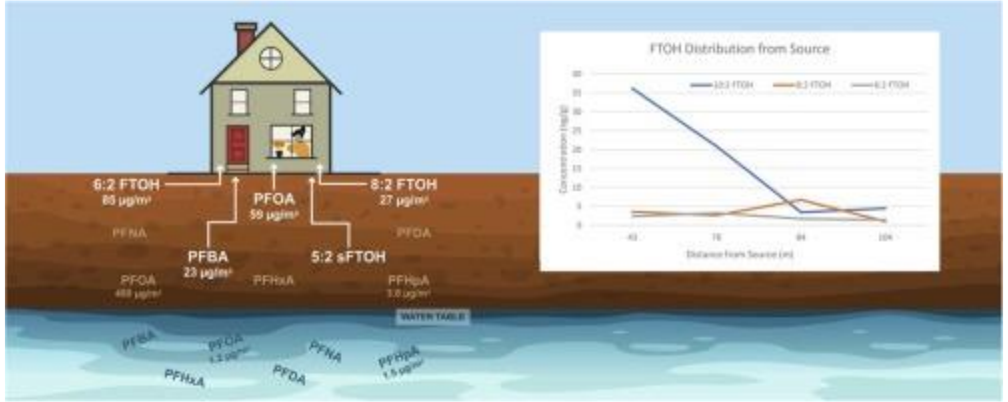
MAKING
COMPLEX
EASY

A TETRA TECH COMPANY

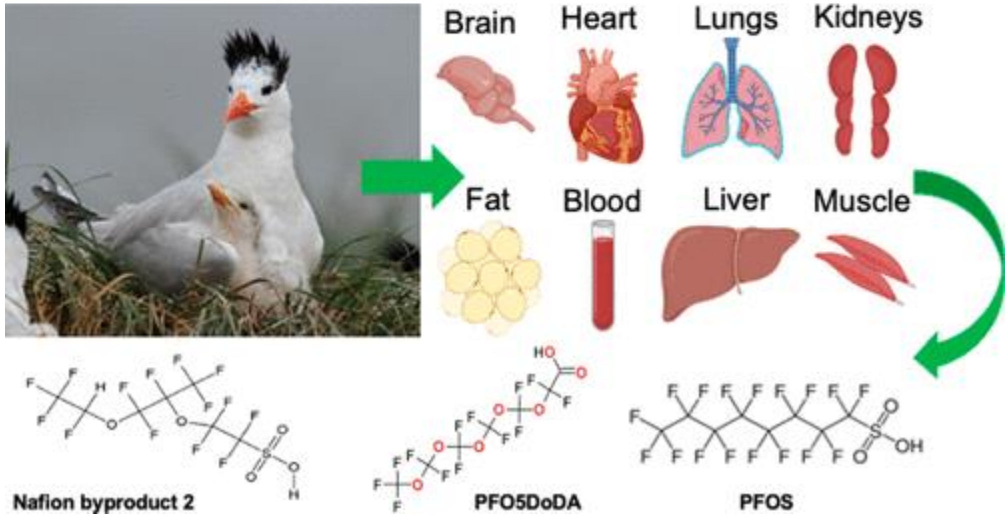
With So Many PFAS, There's No Shortage Of Fun



Ruyle et al. 2023

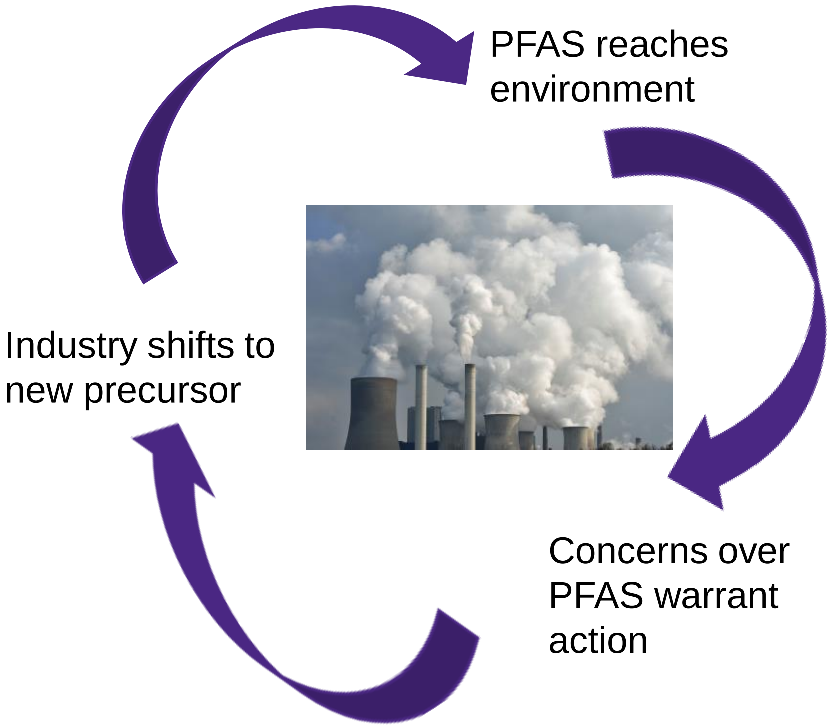


Schumacher et al. 2023



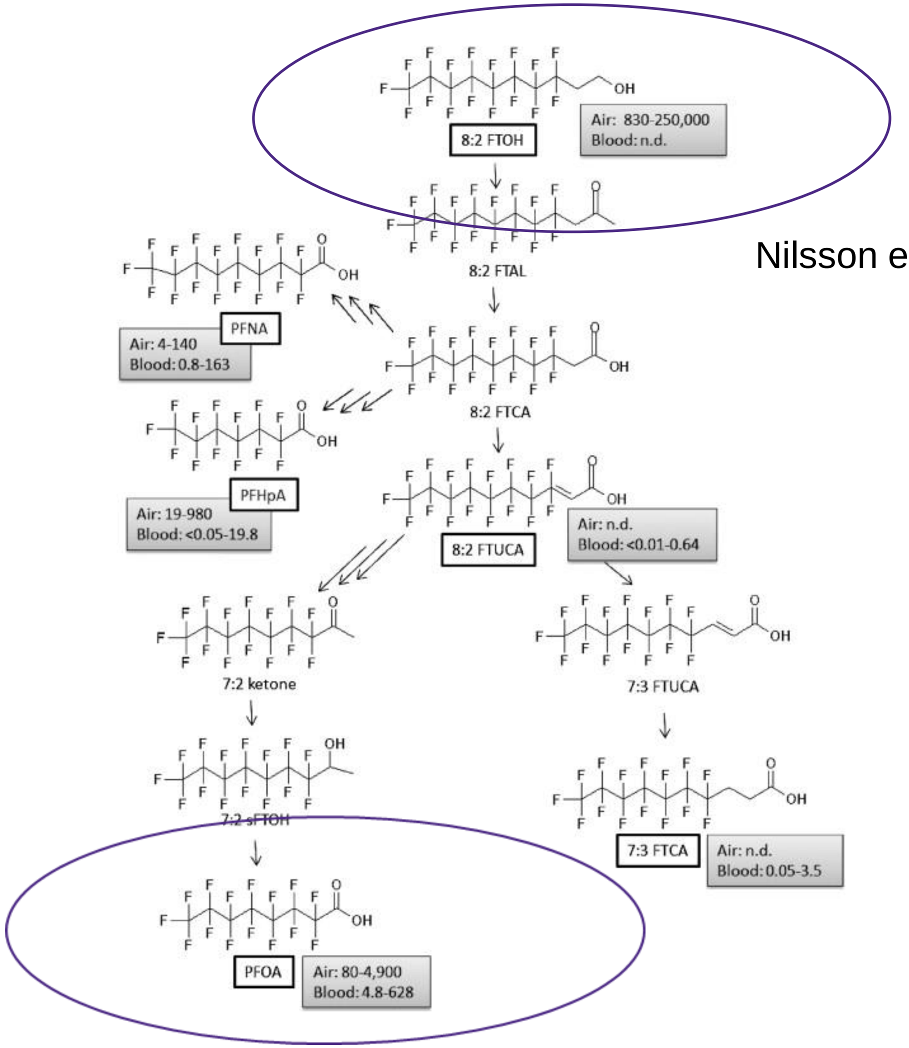
Robuck et al. 2021

Transformation processes can muddy the waters further


PFAS reaches environment

Concerns over PFAS warrant action

Industry shifts to new precursor



Nilsson et al. 2013

With new chemistry, comes new pathways

Forensics are only as good as your data; what constitutes good data?

Some questions to ask yourself:

- Are your measurements representative?
- What are your detection levels?
- What are your number of compounds detected above detection levels?
- What method are you using?
- How many PFAS are in the method?
- Do you already know of any potential sources?
- Are you trying to disentangle nearby sources?
- Or identify new sources?

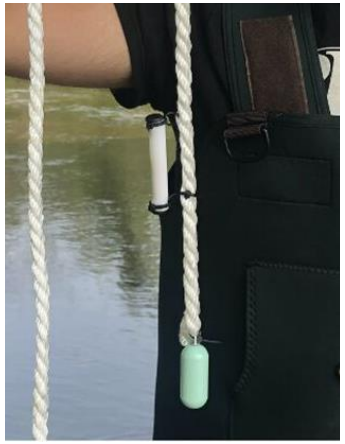


Image from Cyclopure Inc ,

That’s where passive samplers can help!

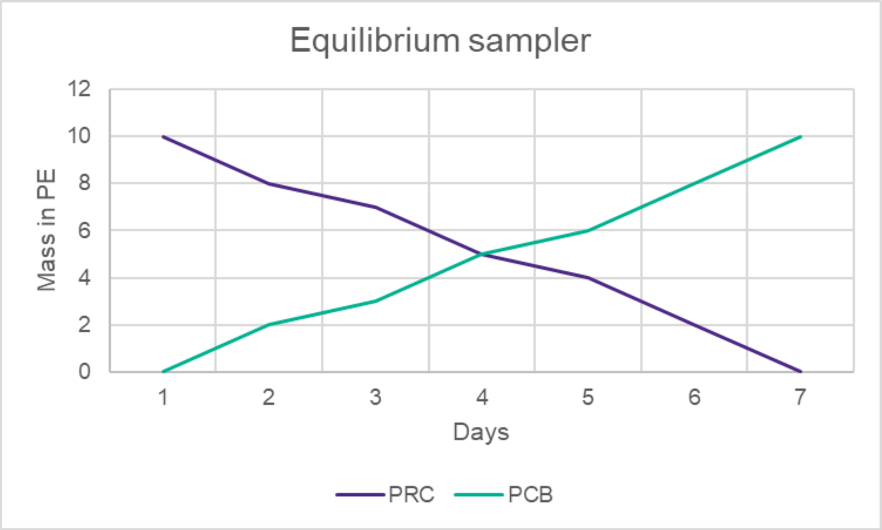
Each have varying levels of limitations that must be considered prior to use!

Images from dgtresearch.com, USGS, chemcatcher.ie, Cyclopure inc, Lohmann Lab @ URI, Thomas Scientific, ,

Equilibrium versus Integrated Passive Samplers

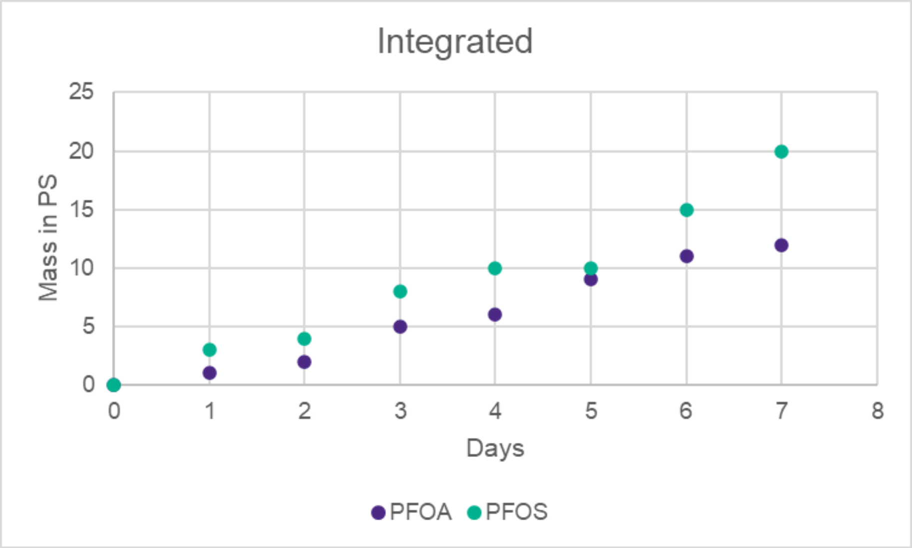
Equilibrium

- Traditionally used for non-polar POPs
- Performance reference compound
- Using Keq values to derive conc



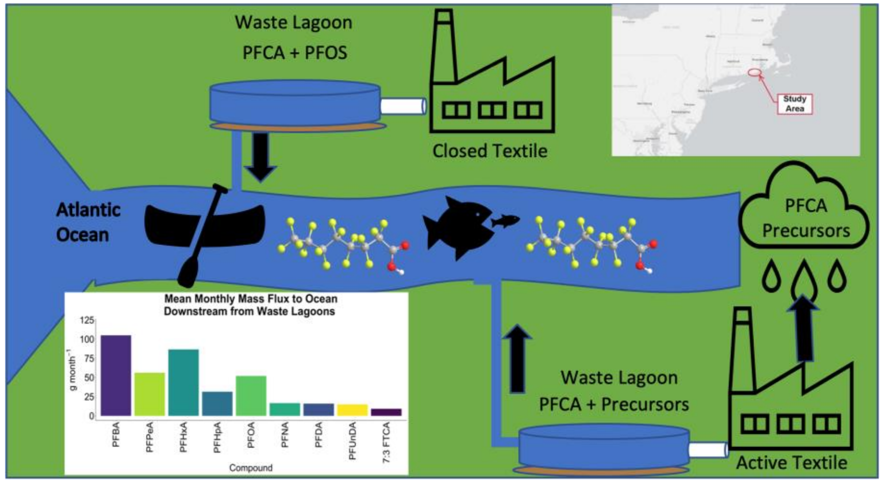
Integrated

- Traditionally used for polar POPs
- Constantly accumulating
- Need a sampling rate to derive conc



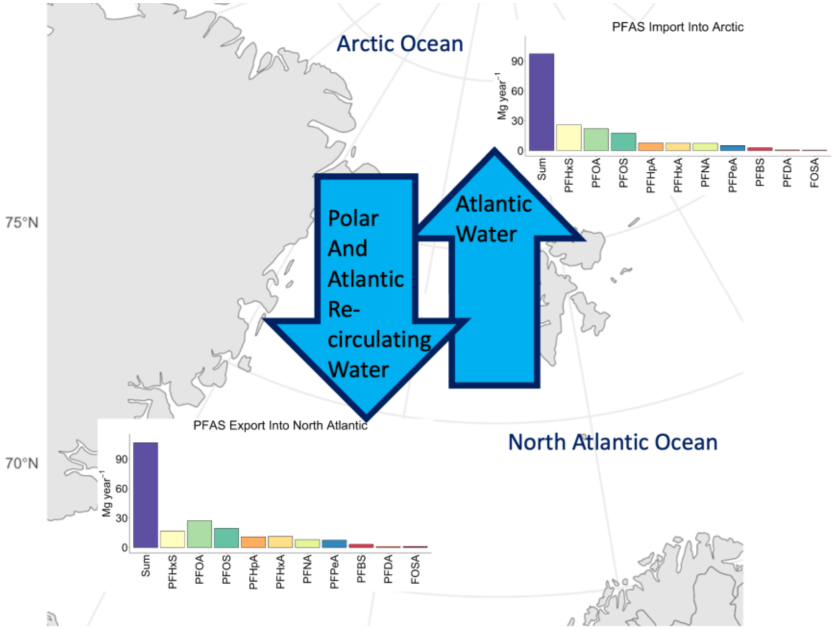
Forensic efforts require broad background info

- **Part I: Evidence of changing PFAS usage exhibited by active and closed textile mills**



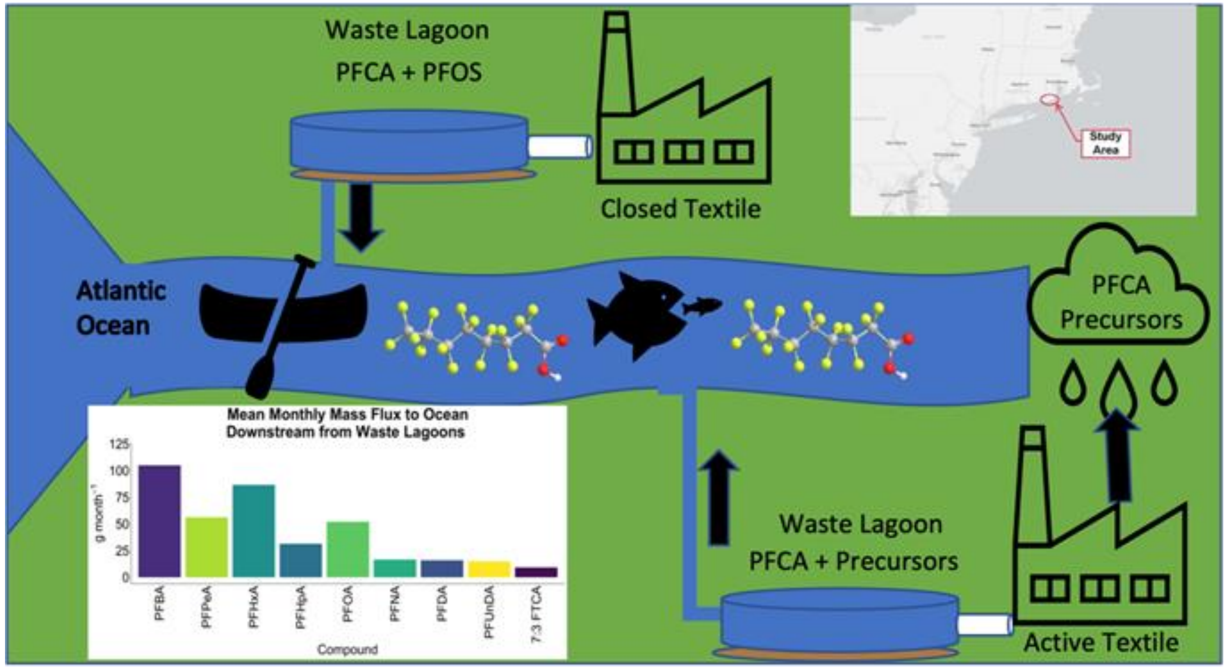
[Unregulated Active and Closed Textile Mills Represent a Significant Vector of PFAS Contamination into Coastal Rivers | ACS ES&T Water]

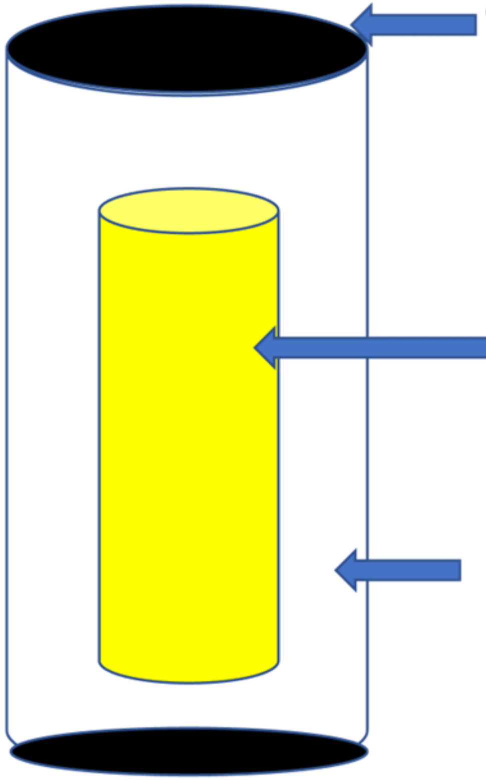
- **Part II: What goes in must come out of the Arctic Ocean according to passive sampler estimations in the Fram Strait**



Part I: Disentangling nearby sources

Dunn, M., Noons, N., Vojta, S., Becanova, J., Pickard, H., Sunderland, E.M., & Lohmann, R. 2023 ES&T Water



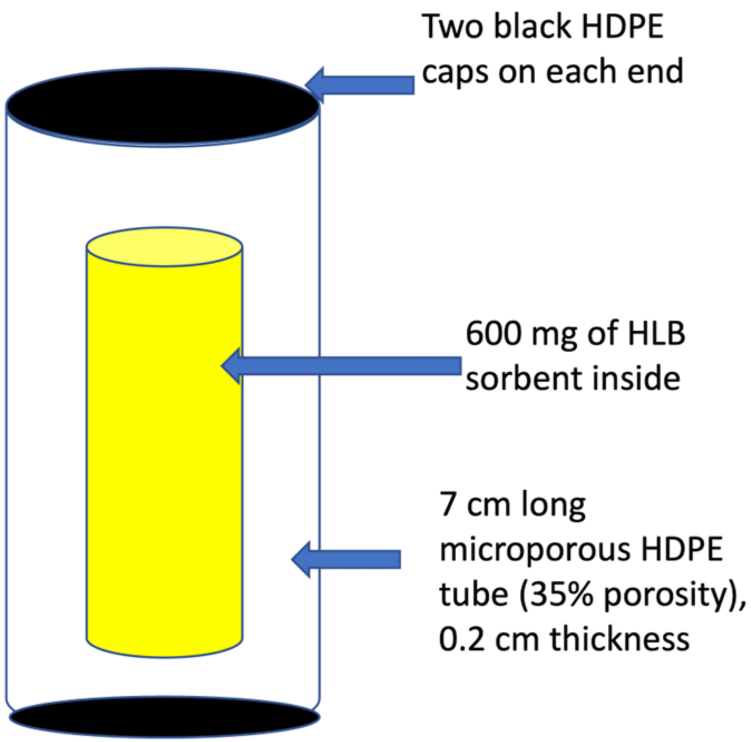


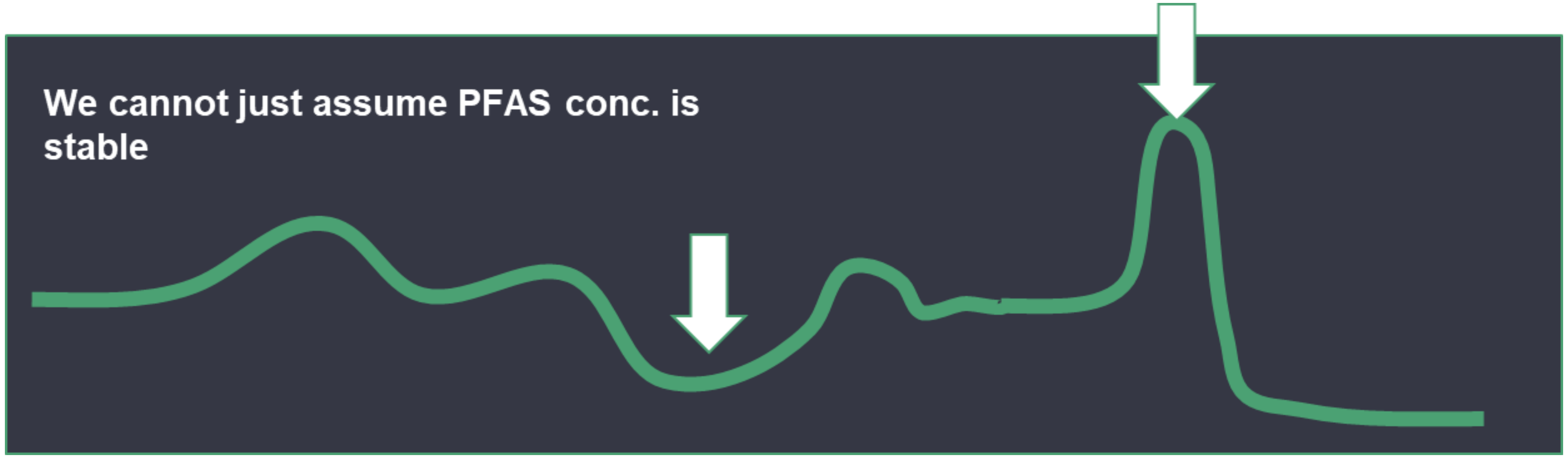
Two black HDPE caps on each end

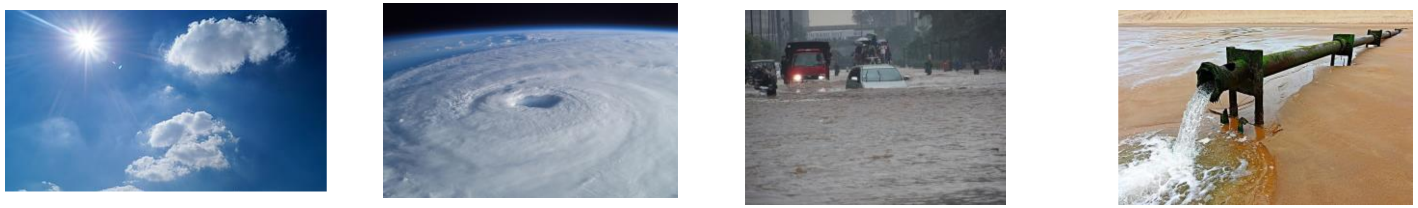
600 mg of HLB sorbent inside

7 cm long microporous HDPE tube (35% porosity), 0.2 cm thickness

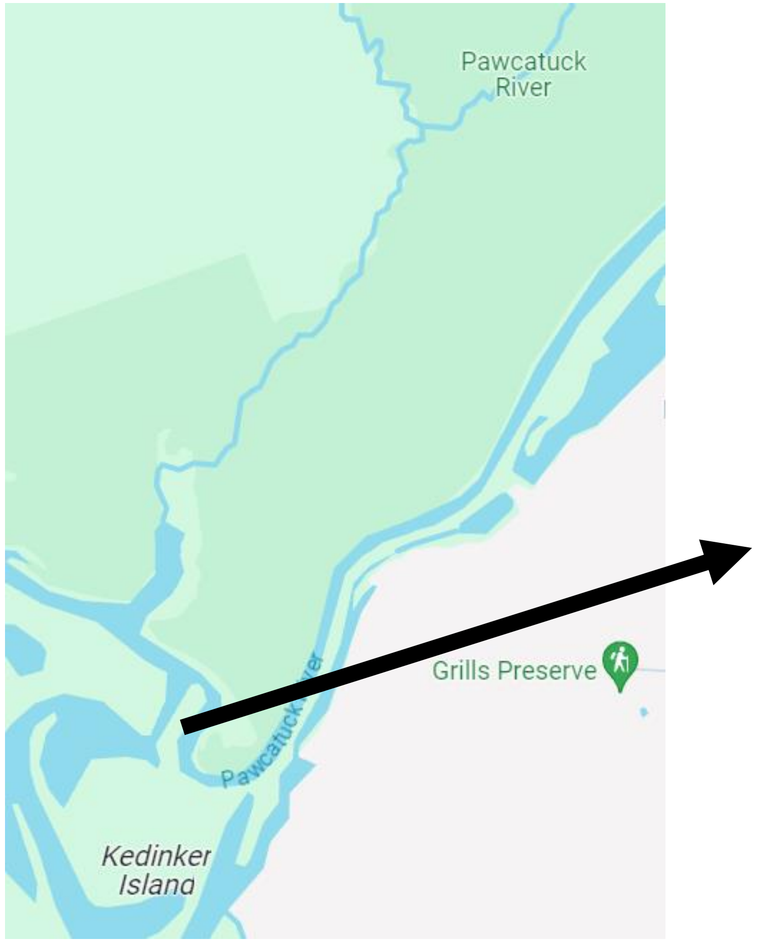
Quick foray into passive sampling




We cannot just assume PFAS conc. is stable



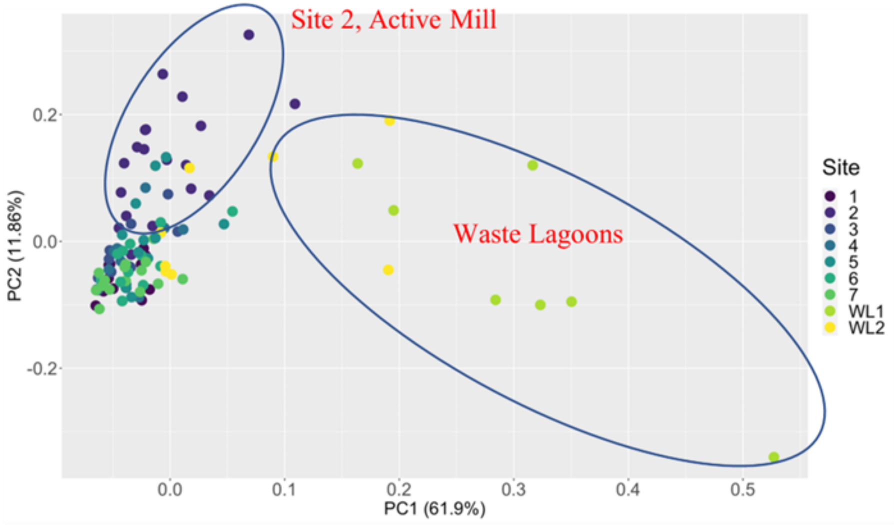
Textile-derived PFAS reaches waters from waste lagoons

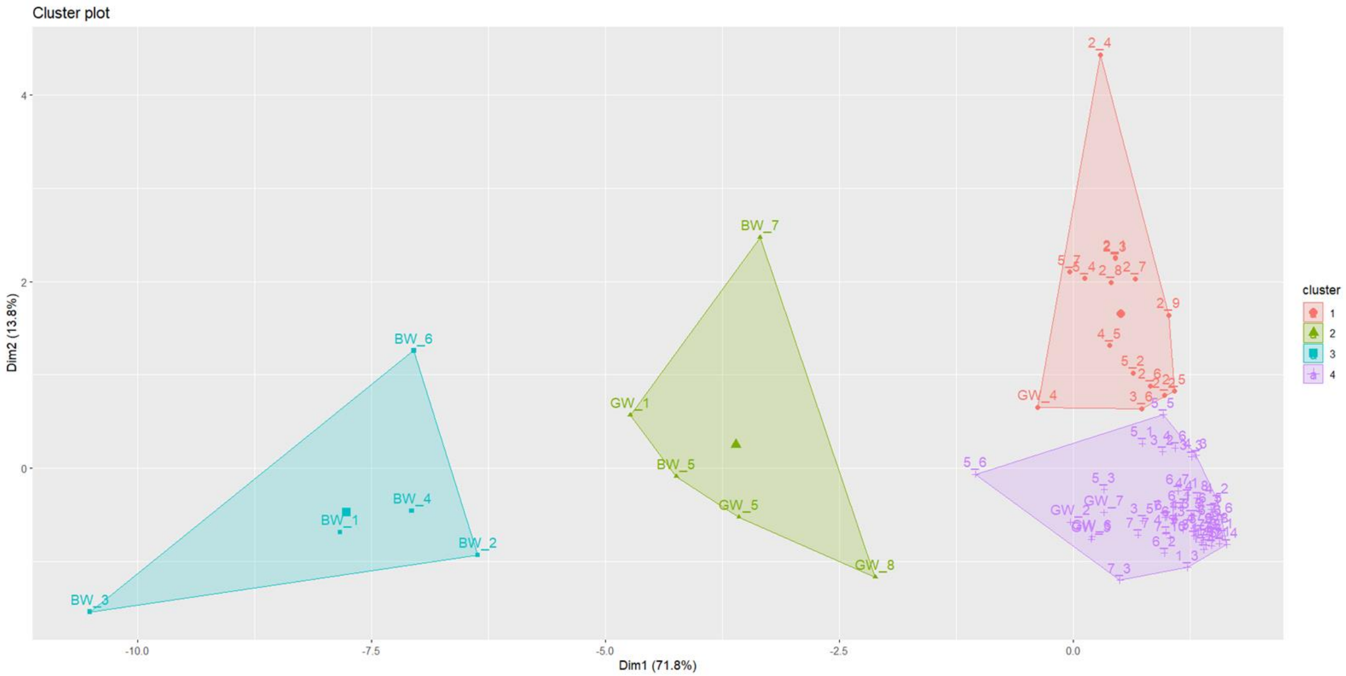


- Textile PFAS inputs generally understudied despite known use
- US EPA reports 93 active textile mills in US
- Distinct chemicals + transport compared to most AFFF studies

Sources: EPA TRI webpage, Gluge et al. 2020, Hill et al. 2017, and Peaslee et al. 2020

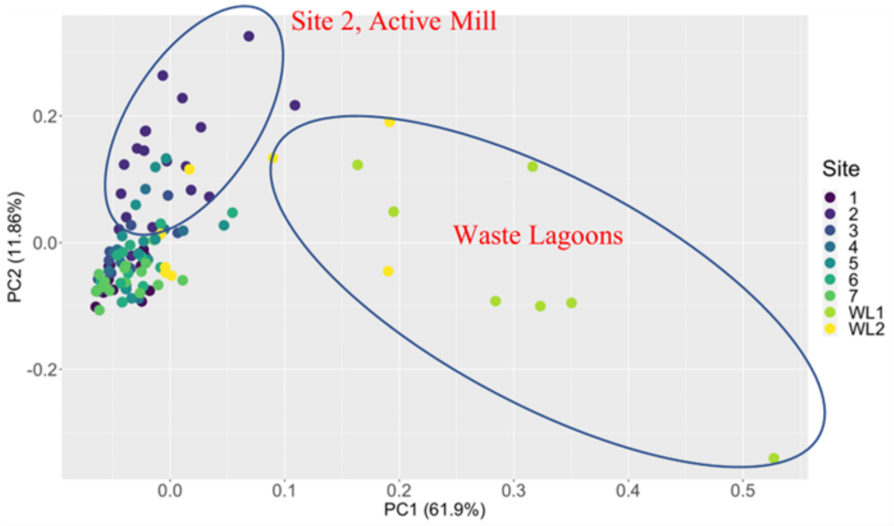
Part I: Textile Mill PFAS Contribution Tied To Age

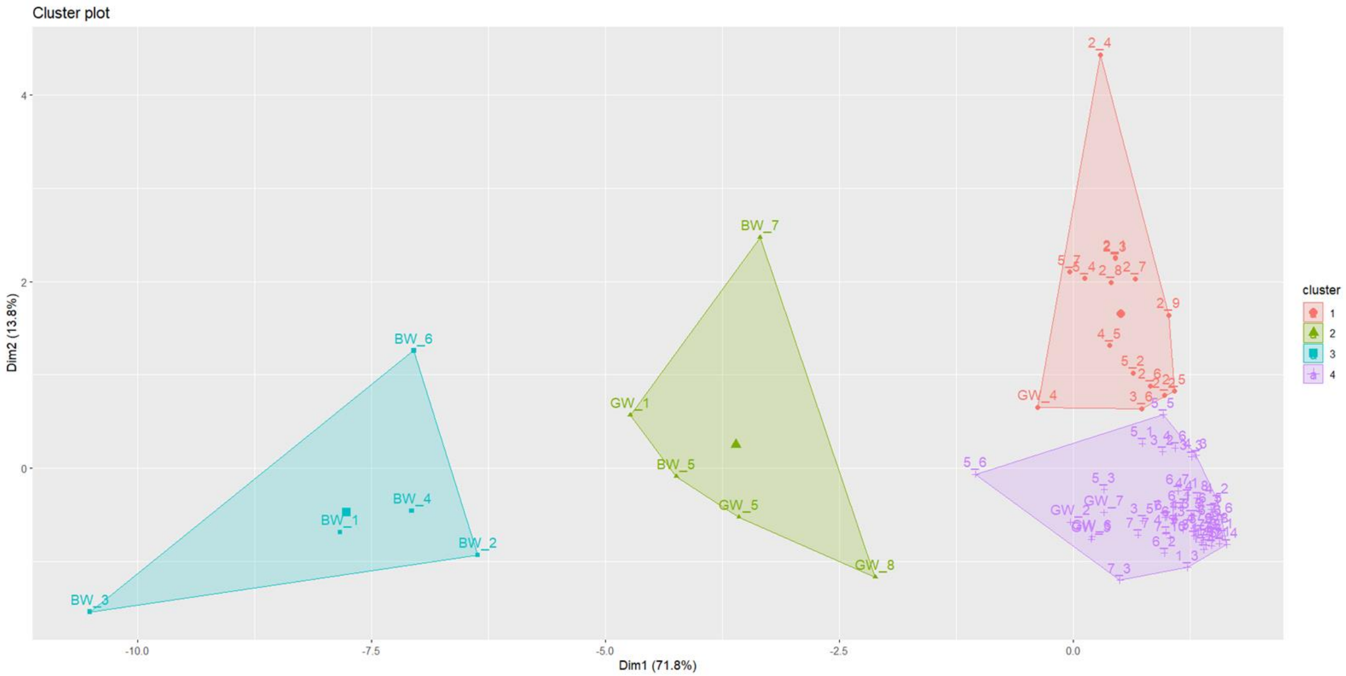




When it comes to assessing forensics using statistical approaches, I suggest using multiple approaches to compare & contrast

Part I: A note on statistical approaches

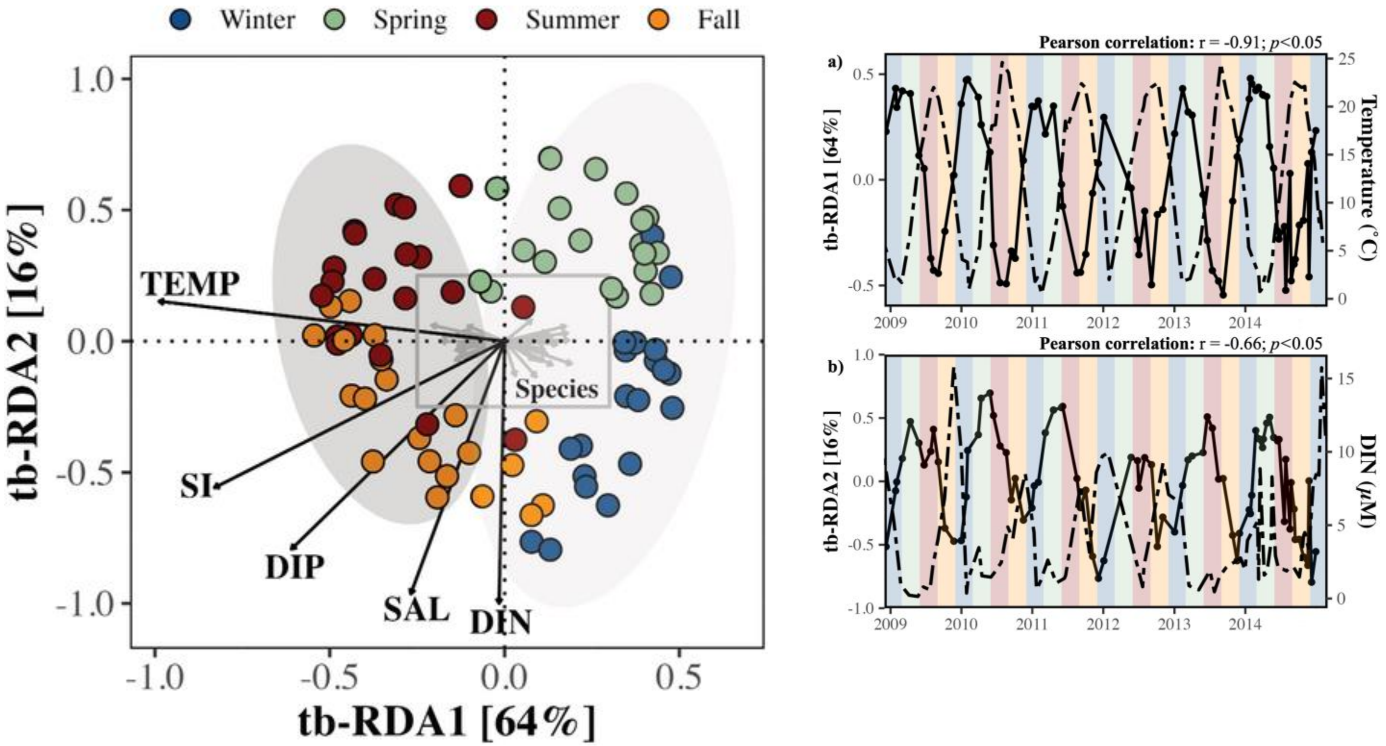




What do you do with zeros or non-detects?

- **In past, we have replaced with MDL/$\sqrt{2}$**

Part I: Can we learn from community composition studies?



Fontaine & Rynearson, 2023 in
Limnology and Oceanography

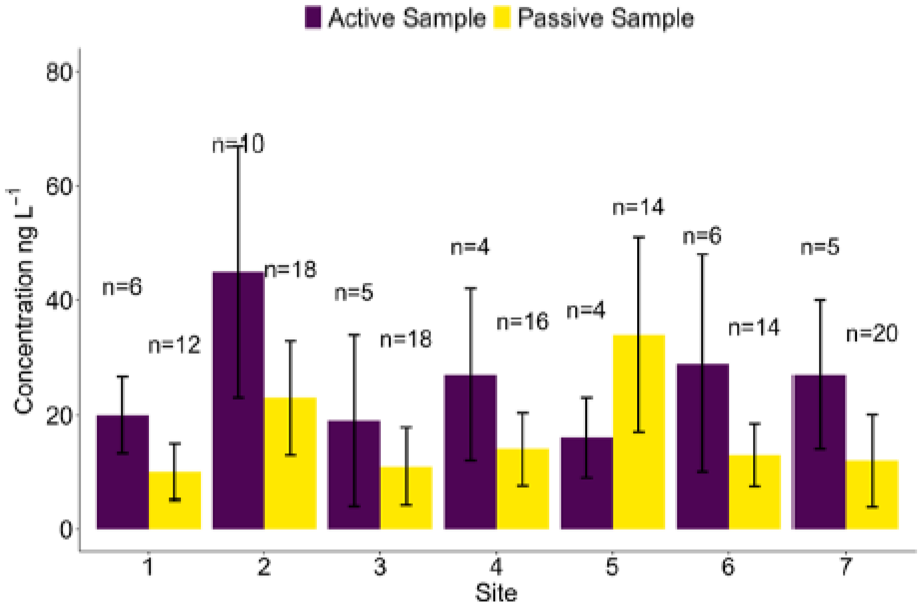
- Biologists deal with compositional data all the time!
  - Sometimes they have zeroes
  - Treat PFAS like presence/absence on large scales
  - Apply NMDS, RDA, PCA, K-means clustering
  - Obvious ML opportunities here
- But most importantly, biologists spend a lot of time thinking about WHY something is there
- **Now is the time to get creative!**

Part I: Replacement Compounds Highlight Sediment & Atmosphere Questions

- Differences in passive vs grab samples
  - Passives = month long average
  - Grabs = discrete
  - Hypothesis: disruption of surface microlayer

- Passive vs grab also raises sediment question
  - Is this FTCA reaching via atmospheric deposition and degradation?
  - Or, is it diffusion out of sediments as FTOH binds and transforms?

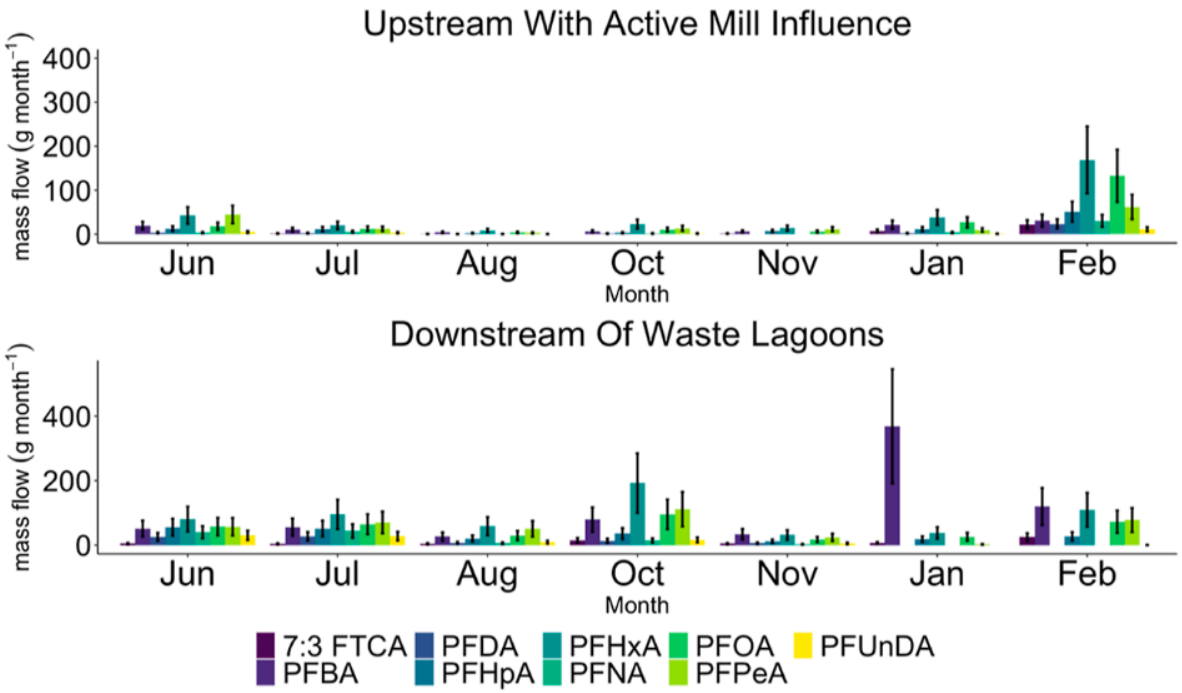
- Underscores complex path from industry to ocean, hard to capture via grab sampling



Big take away: using passive samplers can provide a better data set for forensic and assessment approaches due to creation of more representative sample

PFAS transport to sea isn't as straightforward

- Future questions/directions:
  - Identify degradation rates in environmental waters
  - Add air + sediment data into forensic mix
  - TRI to have expanded PFAS reporting from EPA, will help
- **Transformation/degradation of precursors enroute may make forensics more difficult in ocean/coastal waters**



Poll Question:
Do PFAS precursors always retain the same chemical characteristics (i.e. charge or functional group) when they break down?

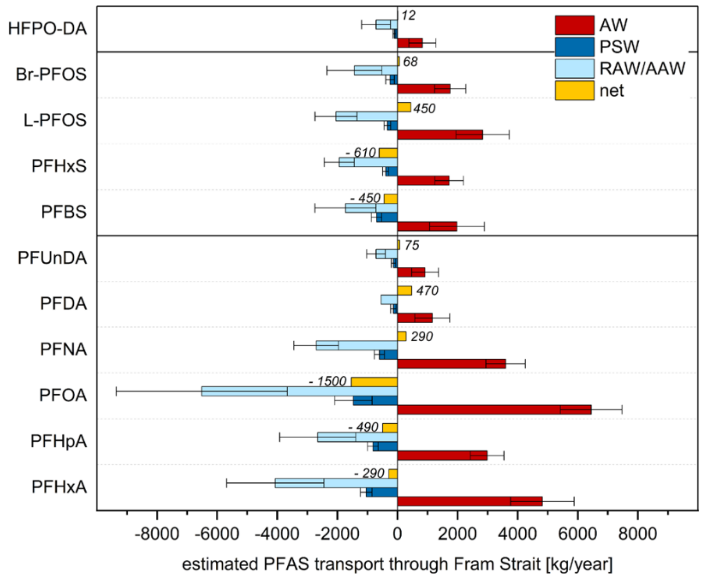
Lowering detection limits & looking at offshore profiles

Dunn, M., Vojta, S., Soltwedel, T., von Appen, W-J., & Lohmann, R. 2024 ES&T Letters

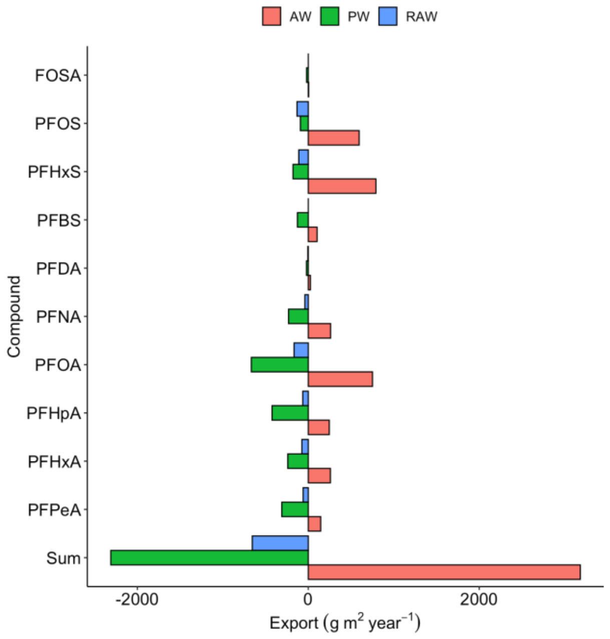
- Year long study of Fram Strait displays what goes around comes around
- Passive samplers accumulated PFAS from 2021-2022 at depth transects at 3 sites
- Depth range: 54 – 2532 m
- Water age range 0-250 years

Credit: AWI

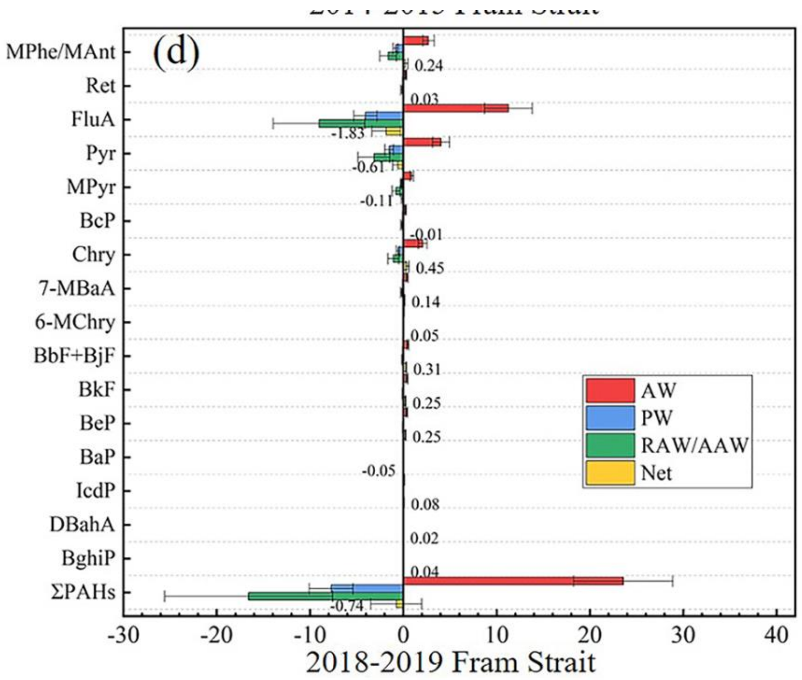
Part II: What goes to sea, stays at sea?



Joerrs et al. 2020



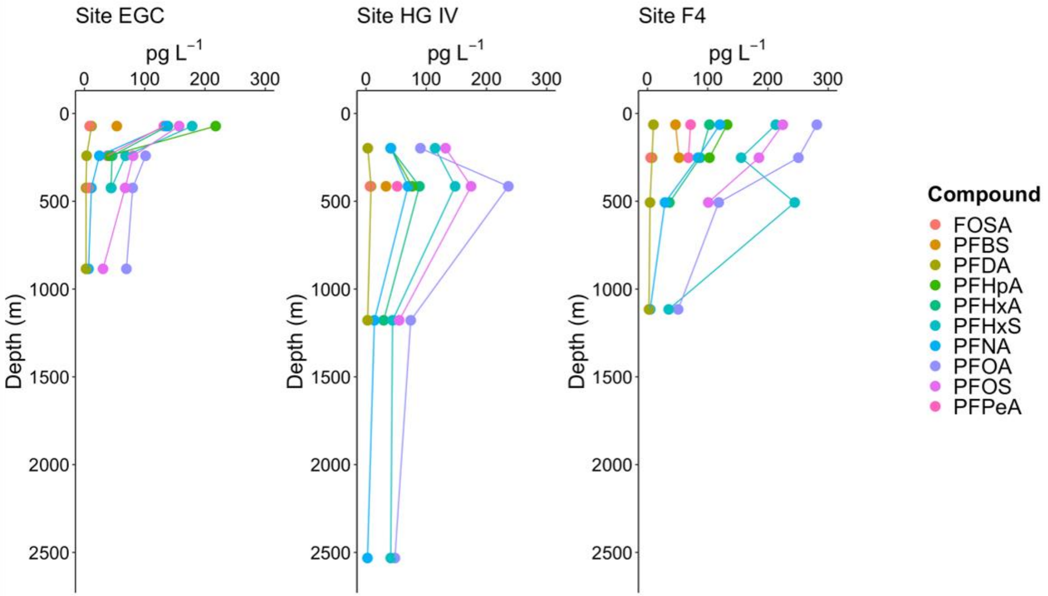
Dunn et al. 2024

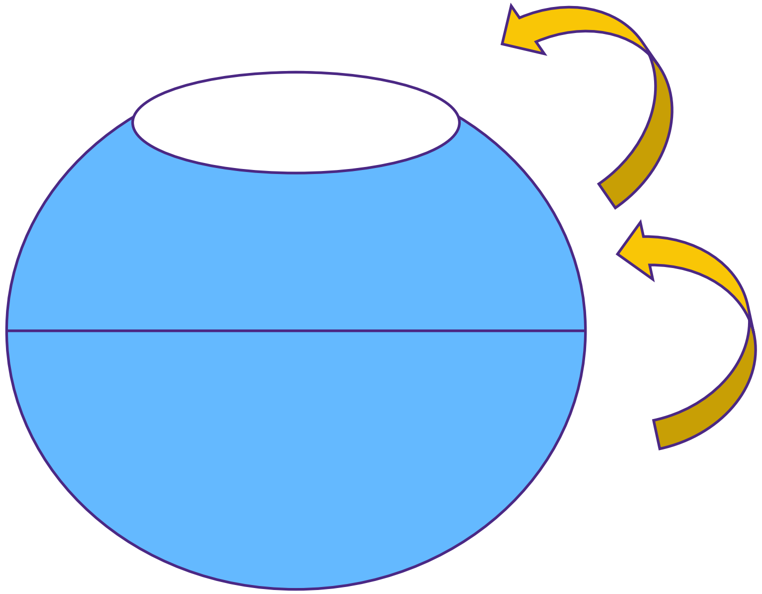


Zhang et al. 2023

- What goes in, seems to be coming out across PFAS + PAH
- It could be that there’s additional atmospheric sources compensating for what’s “sinking” out
- Suggest that most likely, we could re-exposed to contaminants of concern as they transit ocean

Part II: Difficult to apply forensics after the fact

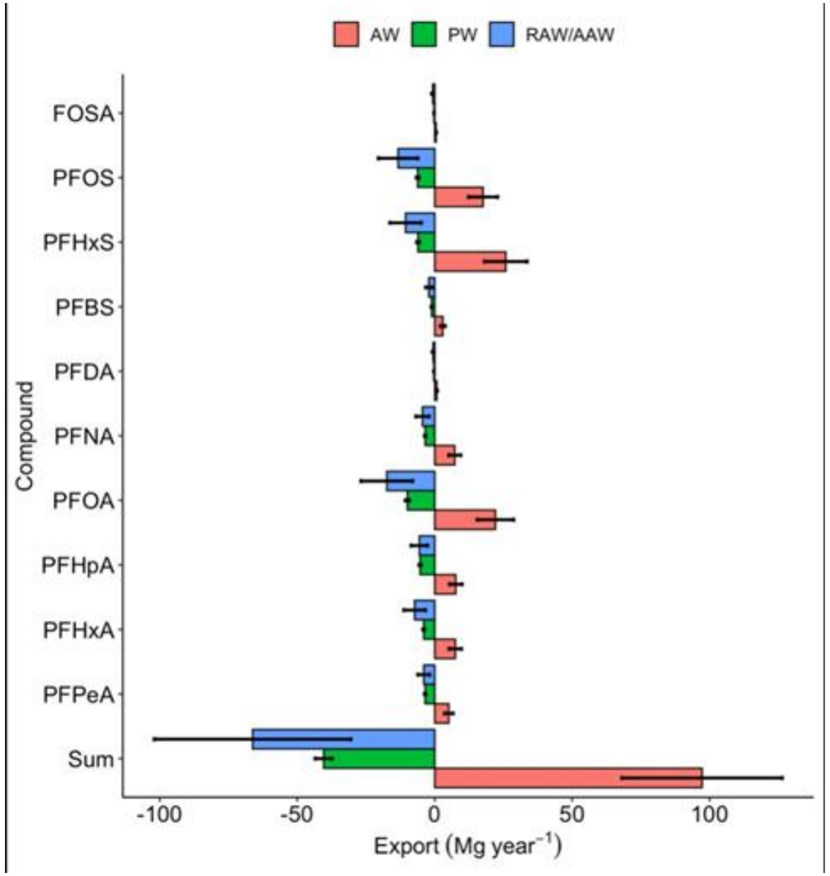




- **Passive derived concentrations below SPE MDL**
- Is PFHpA/PFOA ratio useful tool? Saw general decrease with depth at each site in ratio, but all ratios were <0.60

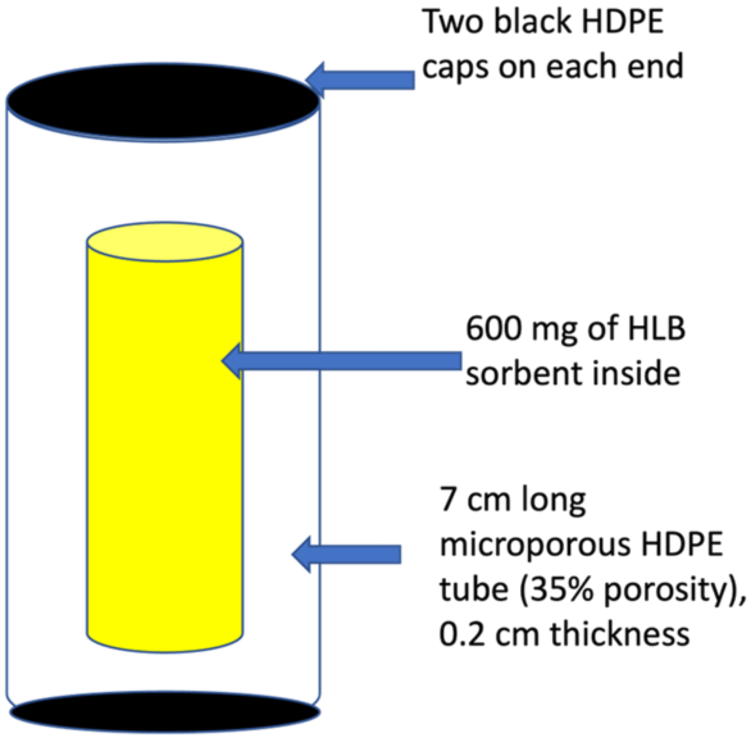
- Encourage use of tools like passive samplers to evaluate beyond SPE detection limits
- Forensics gets easier with more compounds in methods/analysis

Part II: What goes to sea, stays at sea?



- Is there ever really **a PFAS “sink”?**
  - Underscores importance of pathways to “turn the tap off”
  - Is it due to physical oceanography?
  - Or also their hydrophilic nature?
  - How do we distinguish re-circulated PFAS from sources in coastal systems?
- **precursors make this a challenge!**
  - Do we model atmospheric transport of FTOH/others to elucidate?
  - Or focus on terminal products with known chemistry
  - Lack of info on degradation rates

How do they “lower” detection limits?



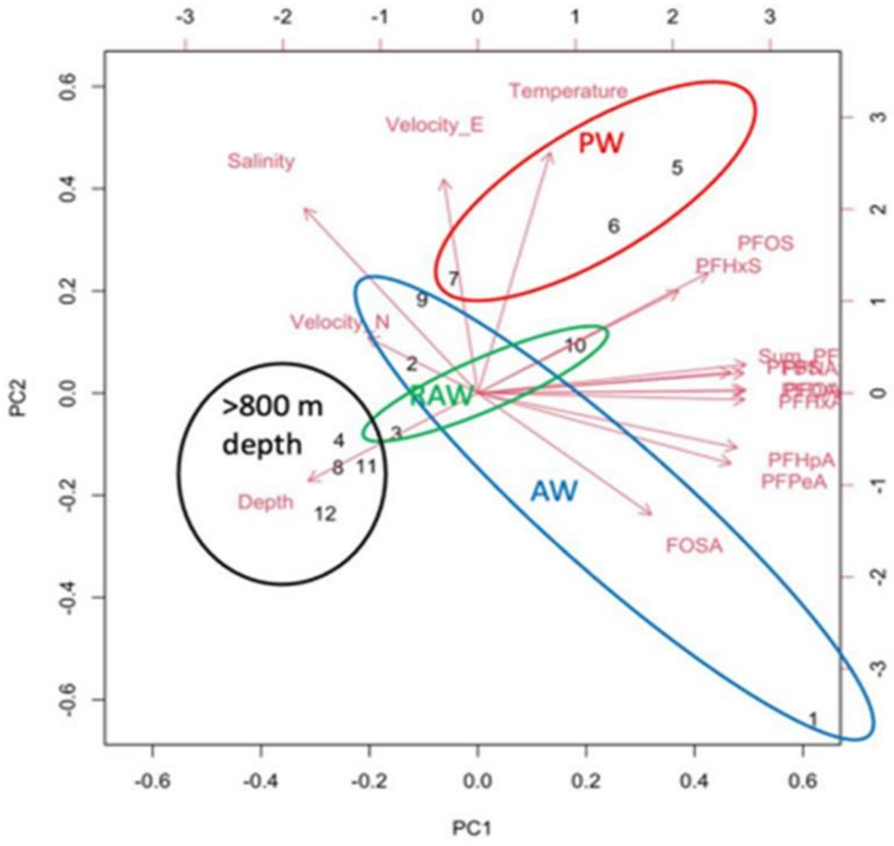
It’s like an SPE cartridge in the water

- You’re constantly sampling the water over 7+ days
- You just need to accumulate enough in the tube to be >MDL of tube
- Then you back calculate conc
- Example from Arctic:
  - SPE MDL for PFOA = 840 pg/L
  - Passive sampler MDL <48 pg/L
- **<u>More detections + more compounds = improved capabilities of statistical approaches</u>**

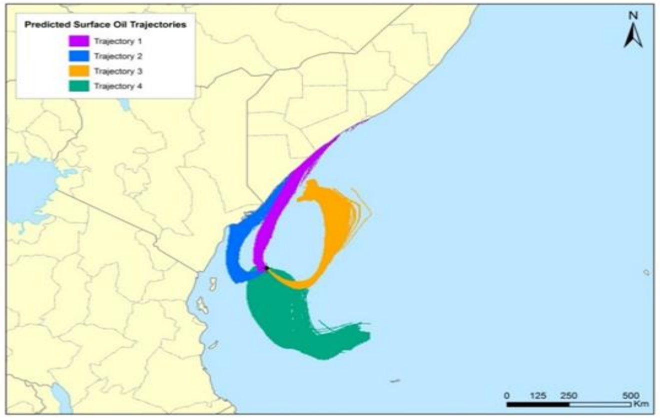
Environmental data is important

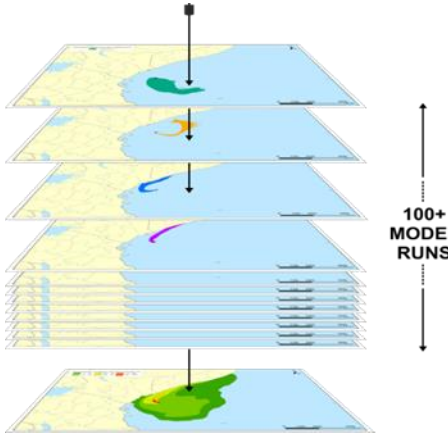
- To improve chances of determining transport & source dynamics think about
  - Salinity
  - Temperature
  - TSS
  - DOC/DO
  - Other tracers
  - Depth
  - Time scales

- This is where passive sampling can help or hurt forensic approaches based on the environment you wish to sample



How do passive samplers & models relate to forensics?



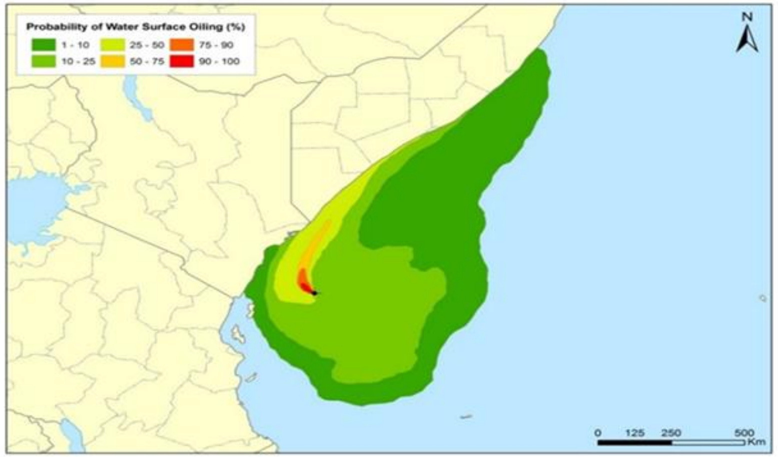


CHEMMAP MODES

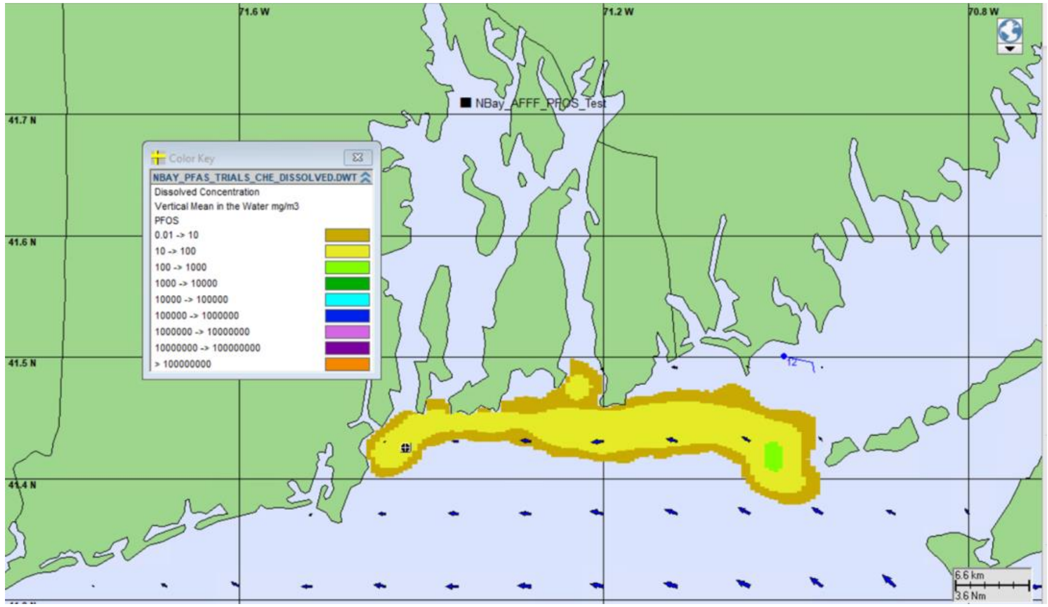
- We typically use **stochastic model**: large # of chemical simulations using different wind/current conditions over time.
- **Deterministic model**: tracks surface movement of a chemical at one discrete time and set of conditions
- **AIRMAP**: integrated air dispersion model (not yet investigated for PFAS)

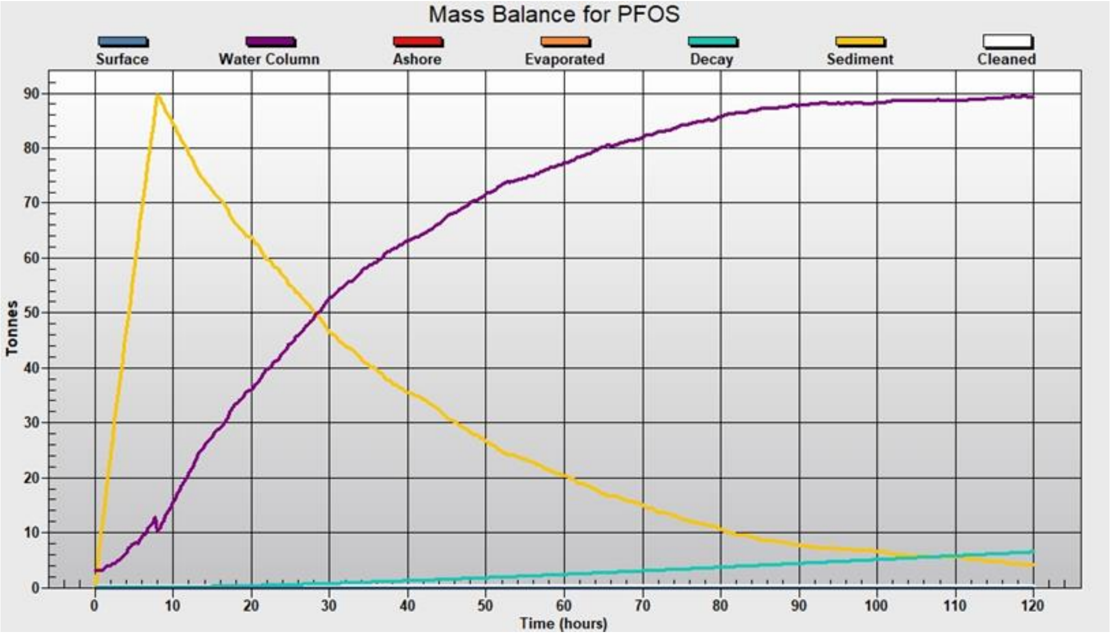
CHEMMAP Infrastructure

- Embedded GIS
- Input: winds, currents, chemical information, spill coordinates
- Lagrangian particles (spillets)
  - Total amount spilled is uniformly distributed between the number of spillets
  - More spillets = better results BUT more computing time/storage
  - Mapped onto concentration grid from GIS team



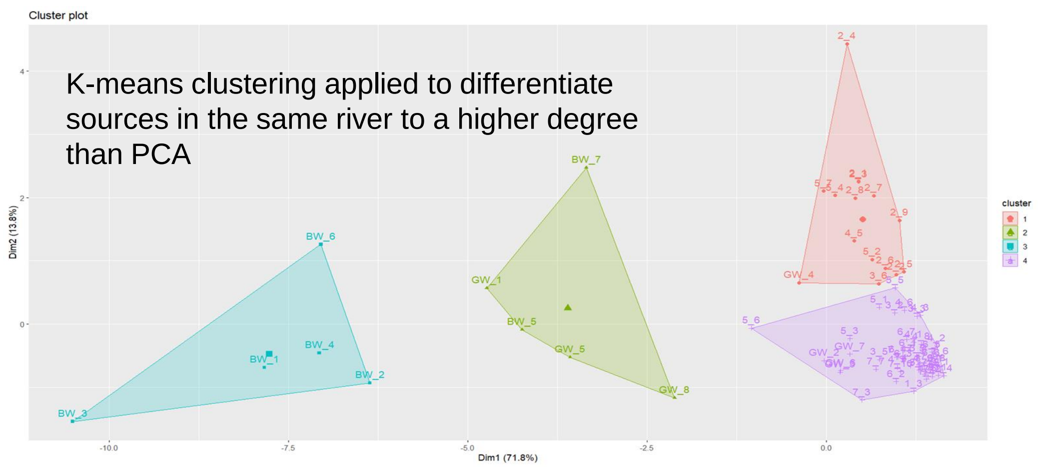
Both are tools for expanding forensic studies!



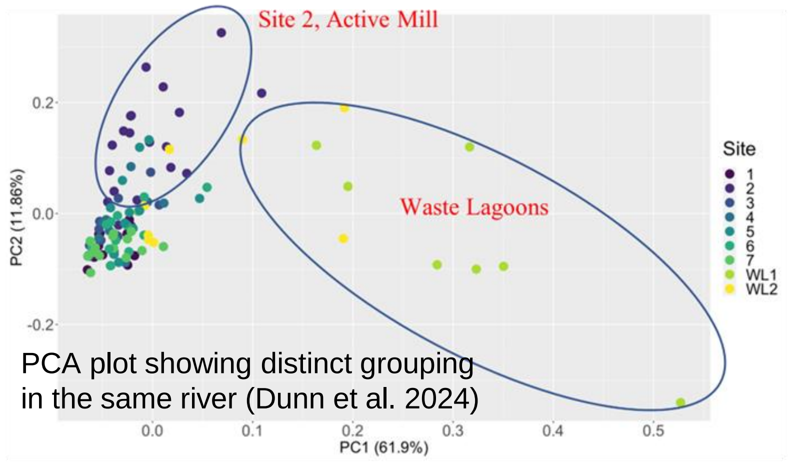


Goal: by pairing tools like passive samplers & forecasting models with forensic approaches, we can ascertain better concepts of PFAS fate in the environment across a multitude of factors

Paired approaches for comprehensive source investigation



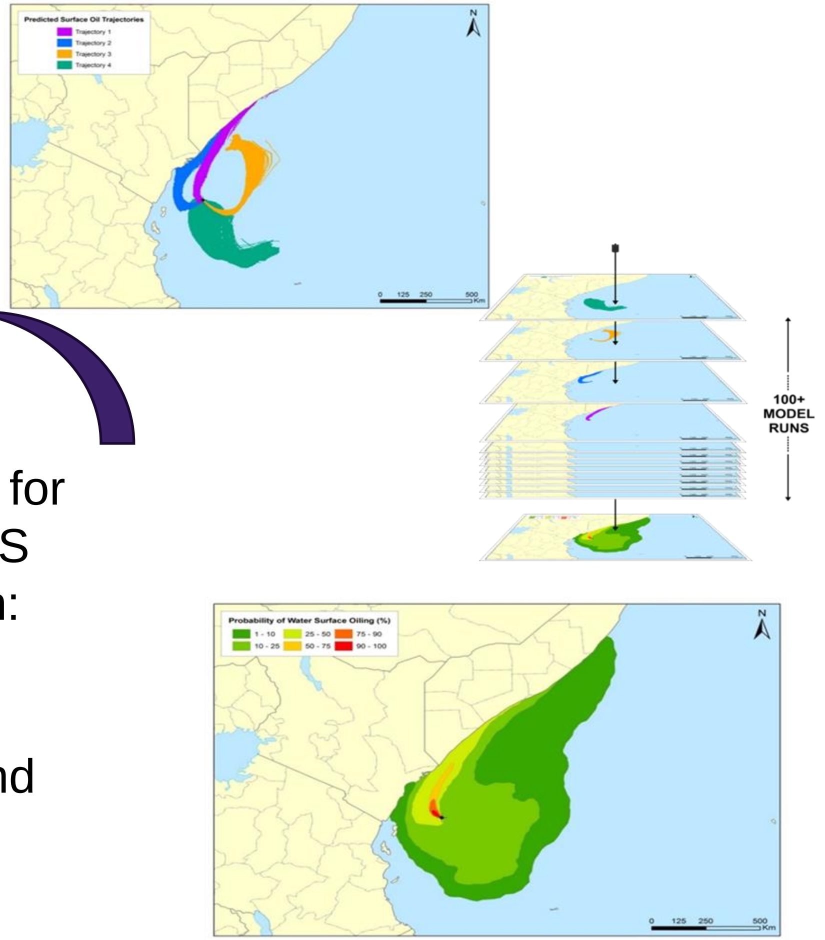
K-means clustering applied to differentiate sources in the same river to a higher degree than PCA



PCA plot showing distinct grouping in the same river (Dunn et al. 2024)

Our combined approach allows for thorough investigation of PFAS sources & transport based on:

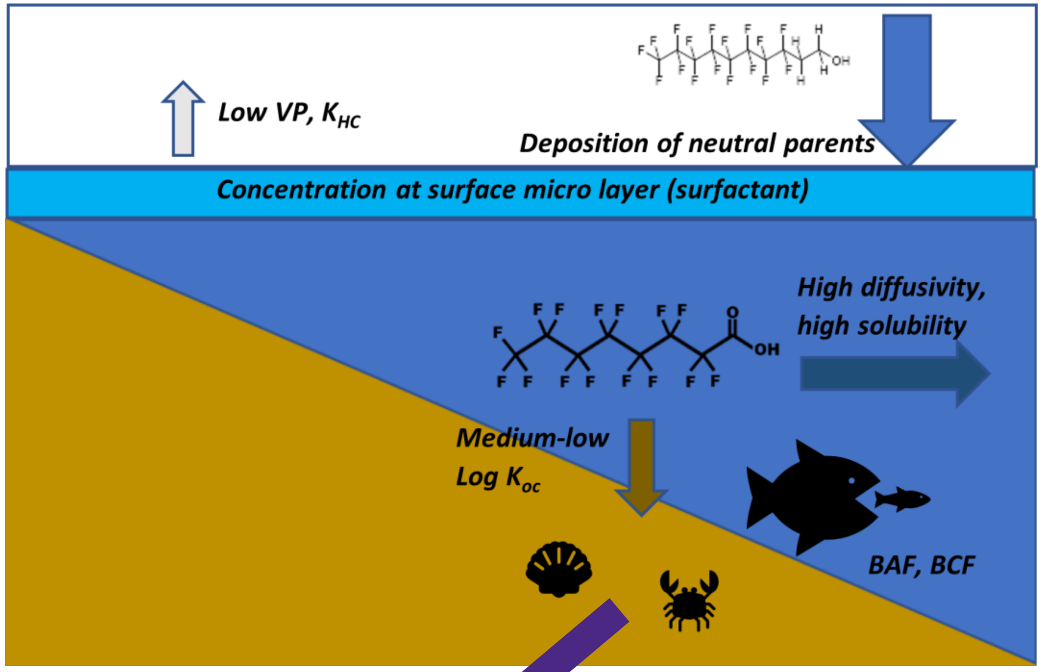
- PFAS chemistry
- Environmental conditions
- Expertise from both field and modeling studies



Using multiple statistical analysis together including k-means clustering, PCA, NMDS, and ratios of short-long chain PFAS

Apply CHEMMAP modeling over time to assess probability of transport based on winds/currents/chemistr

Forensics should always be based on fate & transport



Input degradation of specific precursors into terminal PFAS

Use algorithms for modeling surface area oiling to estimate PFAS concentration

Use outputs of predicted concentration to estimate chronic exposure for biota & C_{biota}

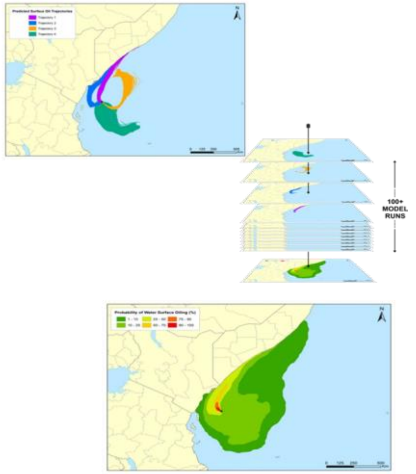
Estimate losses of PFAS to sediment

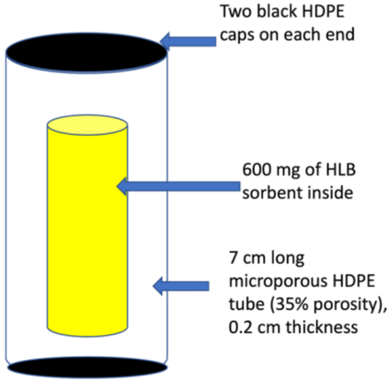
Lingering questions:

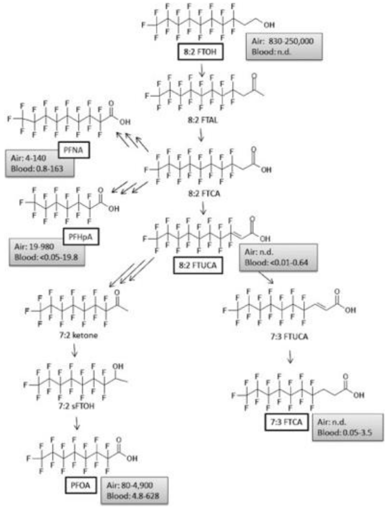
- How do we apply forensics to dilute/far away sites?
- How does the recycled PFAS return to us or complicate forensics?
- Need more “fingerprints” for non-AFFF contamination

Wrapping it all up

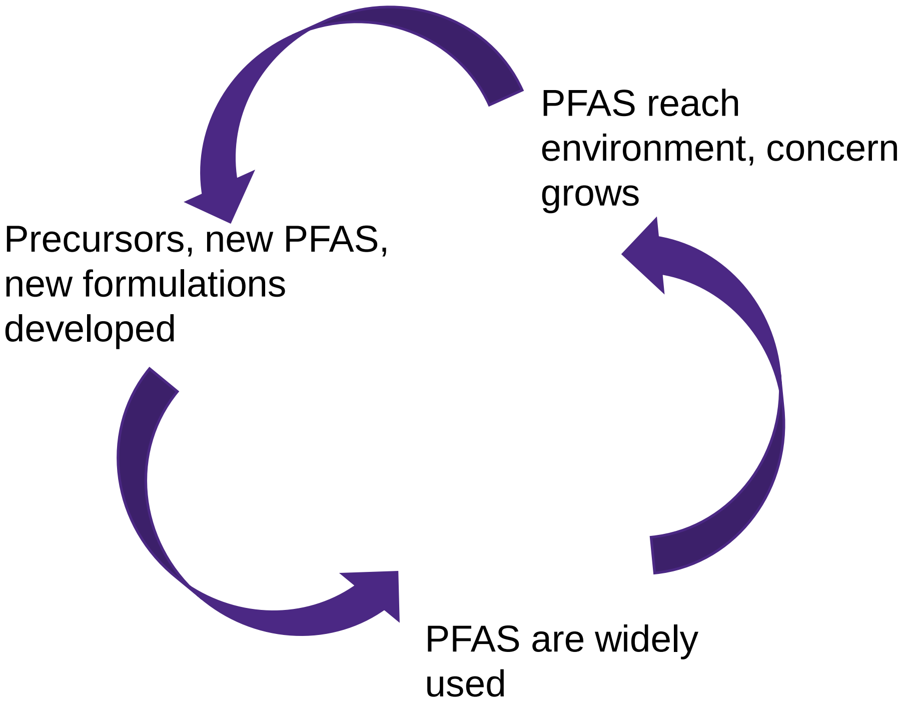
- **Precursors & transformation products!**
  - Hard to do this far away from sources
  - Need to know if releases are continuous or discrete
  - Consider multi directional sources!
- **Passive samplers are an asset for improving forensics**
  - Time weighted average profile
  - Lower detection limits = more data
- **Models can serve as “proof of concept”**
  - Would PFAS even reach there?
  - What concentrations and profiles could we expect to see?







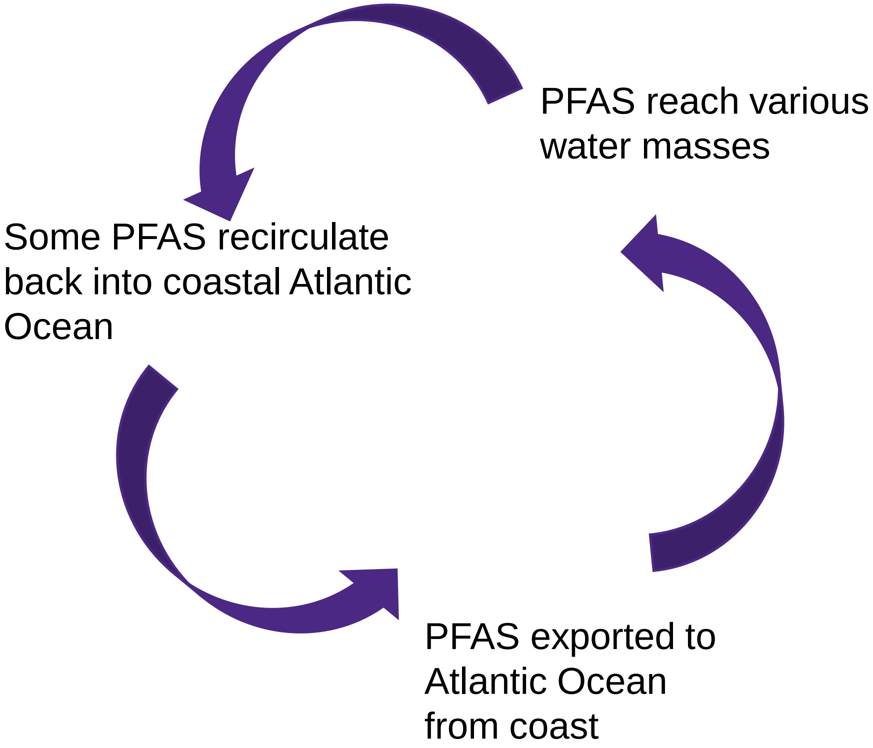
Fluorinated Feedback Loops



PFAS reach environment, concern grows

Precursors, new PFAS, new formulations developed

PFAS are widely used



PFAS reach various water masses

Some PFAS recirculate back into coastal Atlantic Ocean

PFAS exported to Atlantic Ocean from coast

Questions? Don’t be a stranger

Email:
Matthew.dunn@tetratech.com

Let’s chat about:
PFAS forensics
Passive sampling
Oceanography
Contaminant transport