Perfluoroalkyl Substances (PFAS) – Current Insights on the Collection and Analysis of Environmental Samples

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Why so complicated?

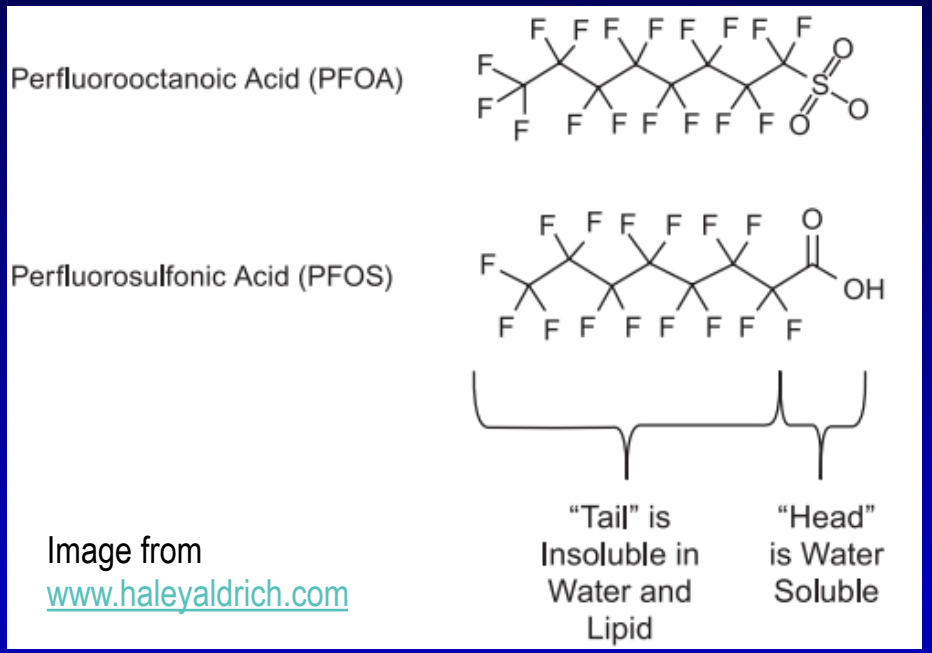
1. PFAS are complex analytes with unusual properties.
2. PFAS have interesting peculiarities in terms of distribution in the environment.
3. Our sampling supplies and equipment can be sources or have "active" surfaces.
4. Laboratory best practices and quality assurance are needed.
5. There is a tension between standardization of methods vs. changes that could result in improvement.

Basis for this presentation

- Past and present PFAS studies in the USGS
  - DOD, USEPA, and States (DE, NJ, VT, NY, etc.)
  - Monitoring & occurrence studies
  - Comprehensive fate & transport (e.g., Cape Cod)
  - Biodegradation and effects of mixtures
- Sampling protocols by Jerry Casile & others
- Laboratory method development by James Gray
- USGS PFAS Collaboration workgroup

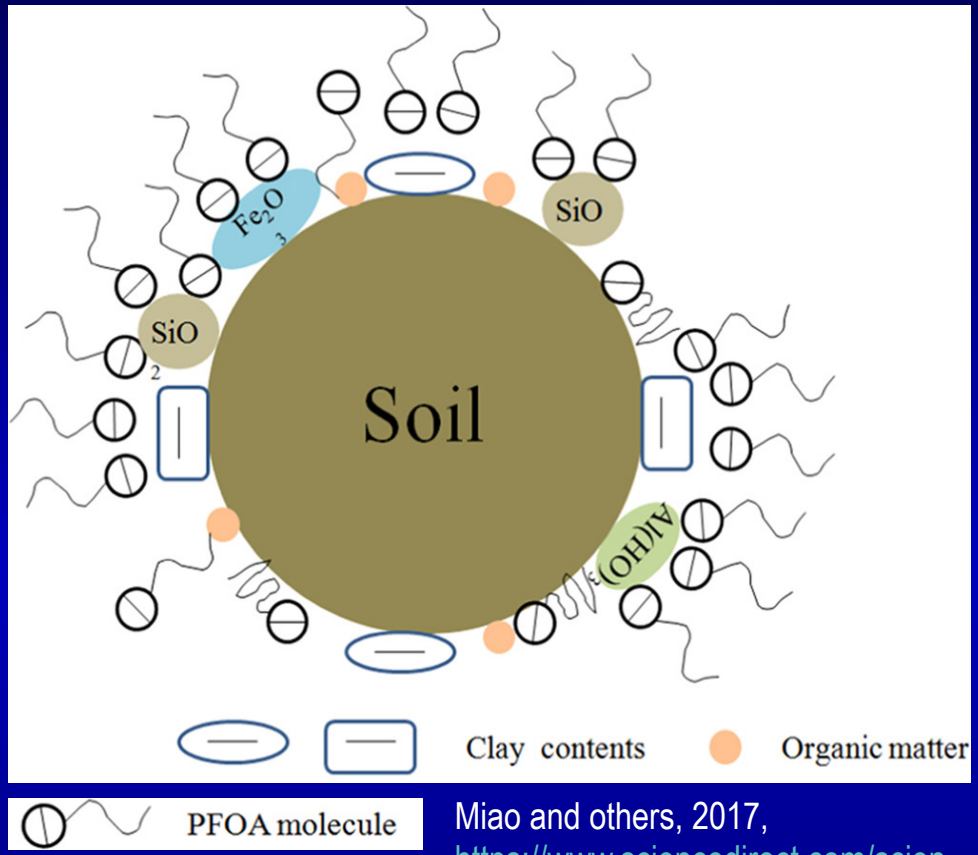
1. PFAS are complex analytes with unusual properties.

- PFAS compounds tend to be stable, resistant to breakdown, owing to the strength of the C-F bonds
- Many PFAS molecules act as surfactants, with a water-soluble "head" …but the "tail" end is insoluble in water or oils
- ***Repulsion***, not just sorption.



1. PFAS are complex analytes with unusual properties.

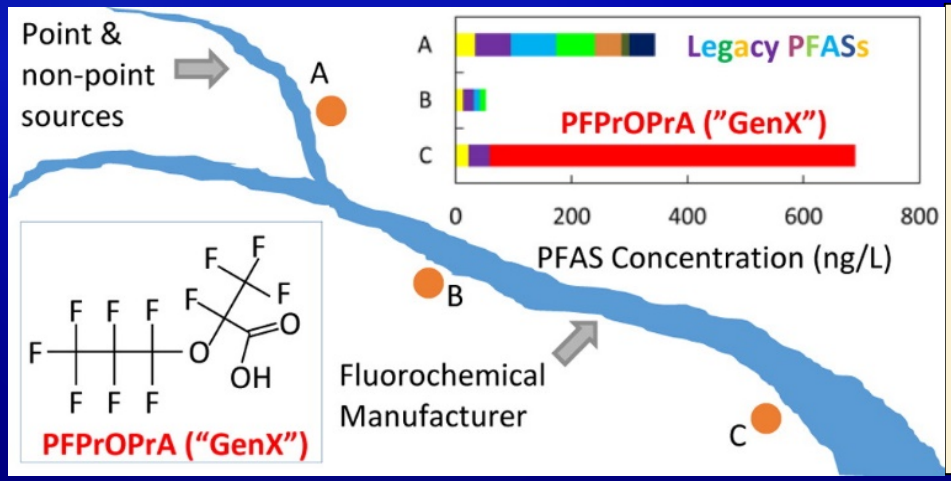
- Don't fit traditional K_{OC}-based sorption isotherms
- Entropy-driven sorption in spite of anionic structure
- Simultaneously highly water soluble and highly particle reactive
- Tend to accumulate at interfaces



Miao and others, 2017, https://www.sciencedirect.com/science/article/pii/S0147651317300222

1. PFAS are complex analytes with unusual properties.

- Long-chain (6 or more carbons)
  - perfluoroalkyl carboxylic acids (PFCAs) with ≥8 carbons, including PFOA
  - perfluoroalkane sulfonates (PFSAs) with ≥6 carbons, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonic acid (PFOS).
- Short-chain (< 6 carbons)
  - Precursors, including fluorotelomer alcohols
- Branched vs. straight-chain isomers
- Precursors and degradates

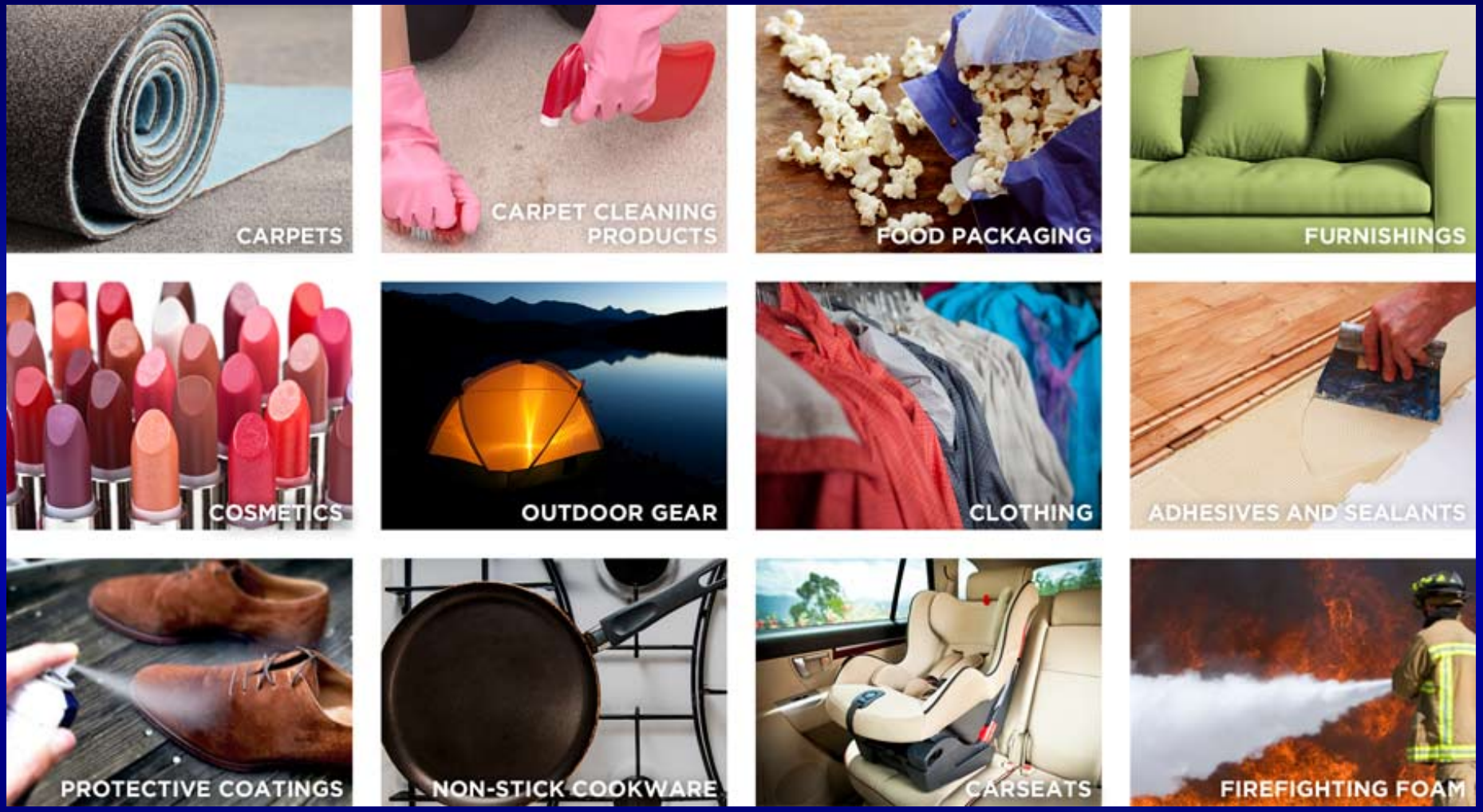


Sun and others (2016)

"The number of PFAS compounds that might be a cause of concern is thought to be in the hundreds and continues to grow." Since the phase-out of PFOA and PFOS, companies have shifted to short-chain PFAS such as GenX, which is now a significant concern in the Cape Fear Watershed in North Carolina.

-- https://www.asdwa.org/pfas/

2. PFAS have interesting peculiarities in terms of distribution in the environment..

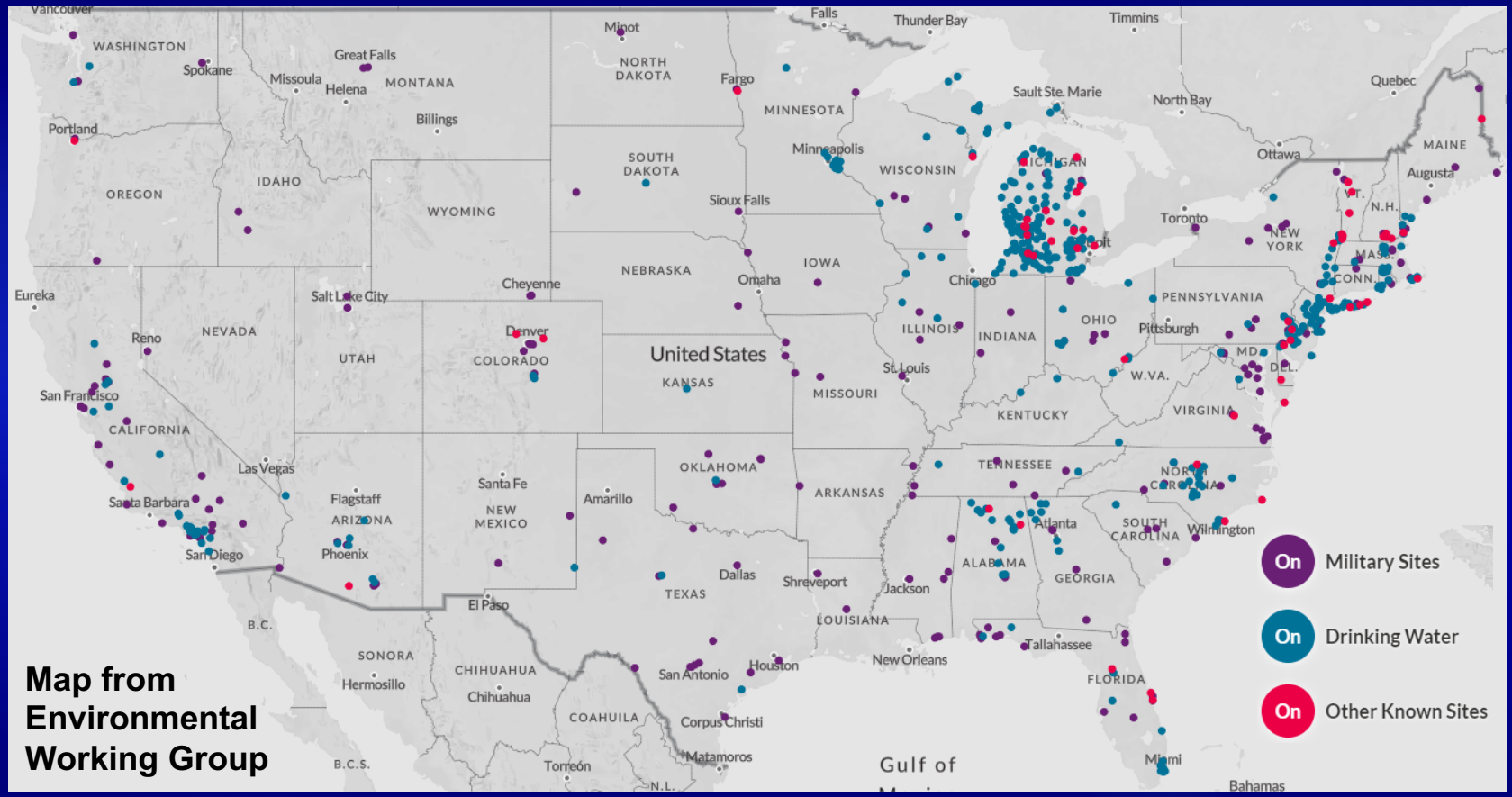


2. PFAS have interesting peculiarities in terms of distribution in the environment..

- Major sources of PFAS compounds include industrial and municipal wastewater treatment plants (WWTPs), fire-fighting incidents/training areas, and landfills (Eschauzier et al., 2012; Ahrens and Bundschuh, 2014; Hu et al., 2016)
- Point releases vs. areal releases vs. nonpoint
- Concentration thresholds relevant to human heath are very small: USEPA lifetime health advisory level for PFOS and PFOA (8-carbon homologues) is **0.070 micrograms per liter**

2. PFAS have interesting peculiarities in terms of distribution in the environment..

- Spills can have high concentrations (>2,000 µg/L)



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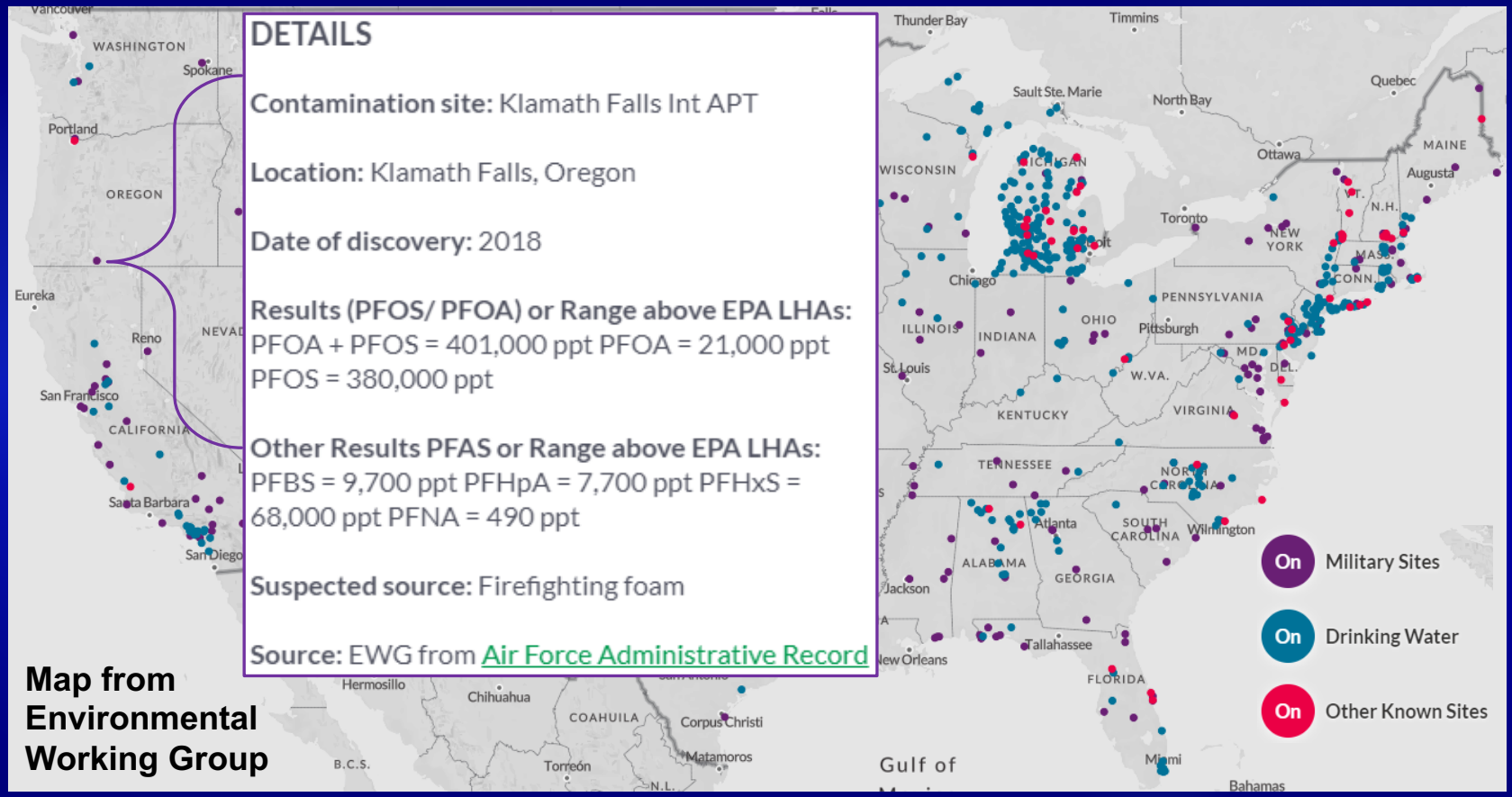
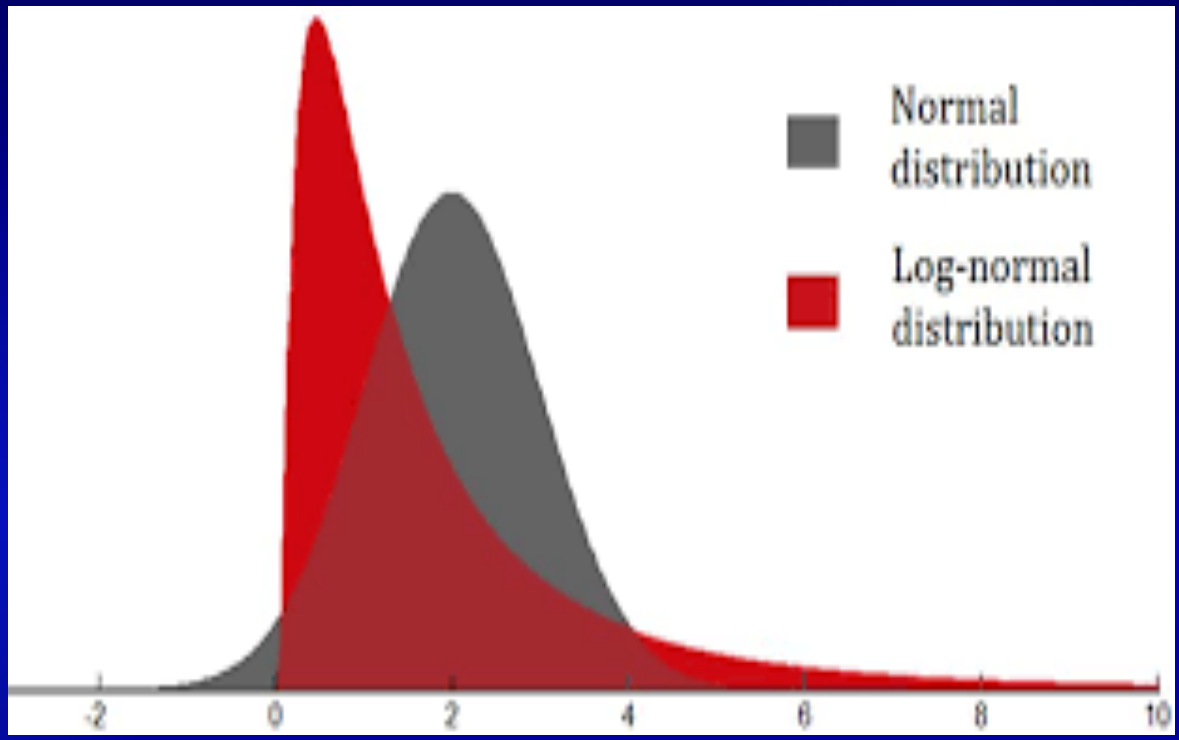


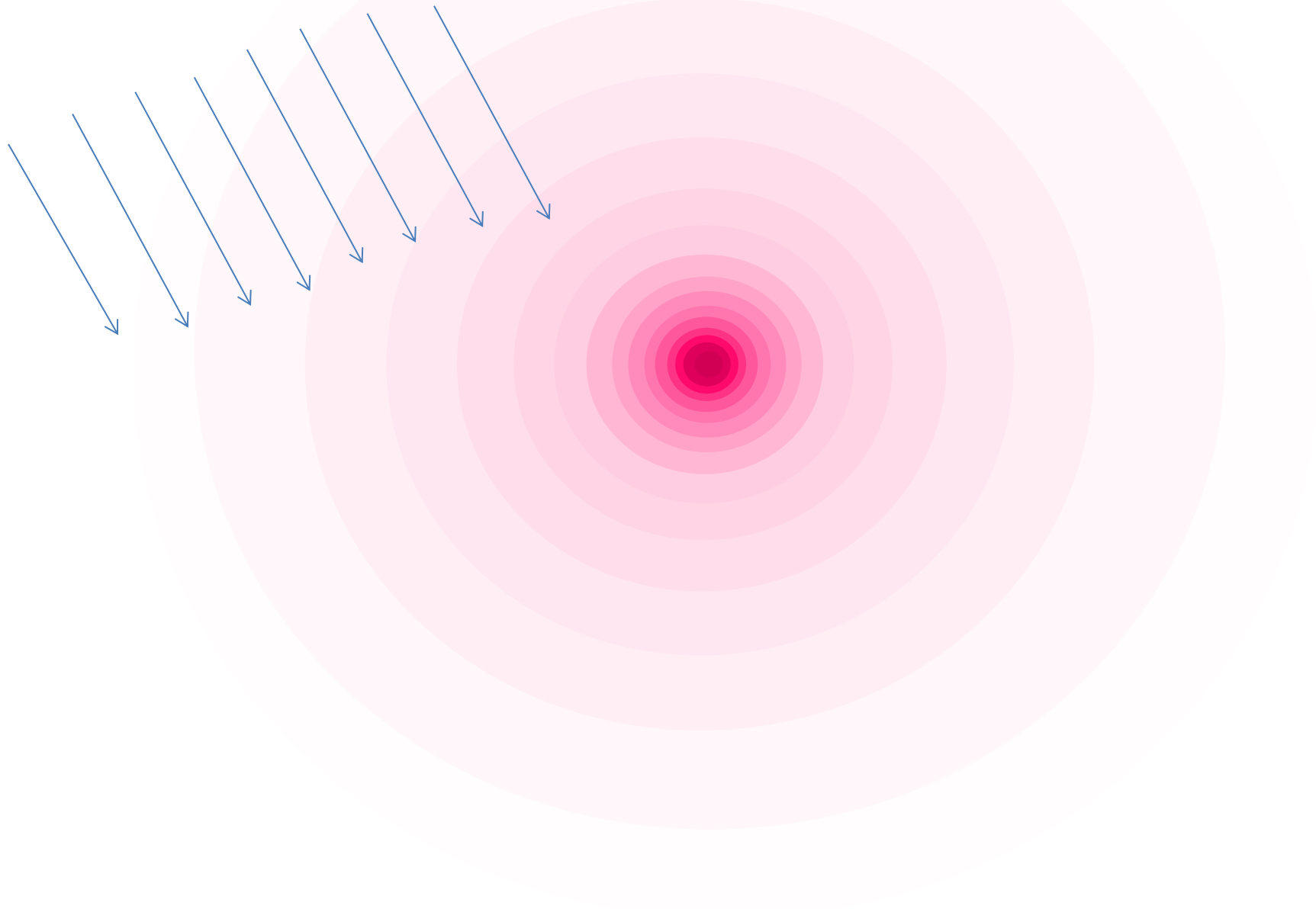
Map from Environmental Working Group

2. PFAS have interesting peculiarities in terms of distribution in the environment..

Contaminants from point sources usually don't follow a normal distribution.



Contaminants that emanate from a point source:



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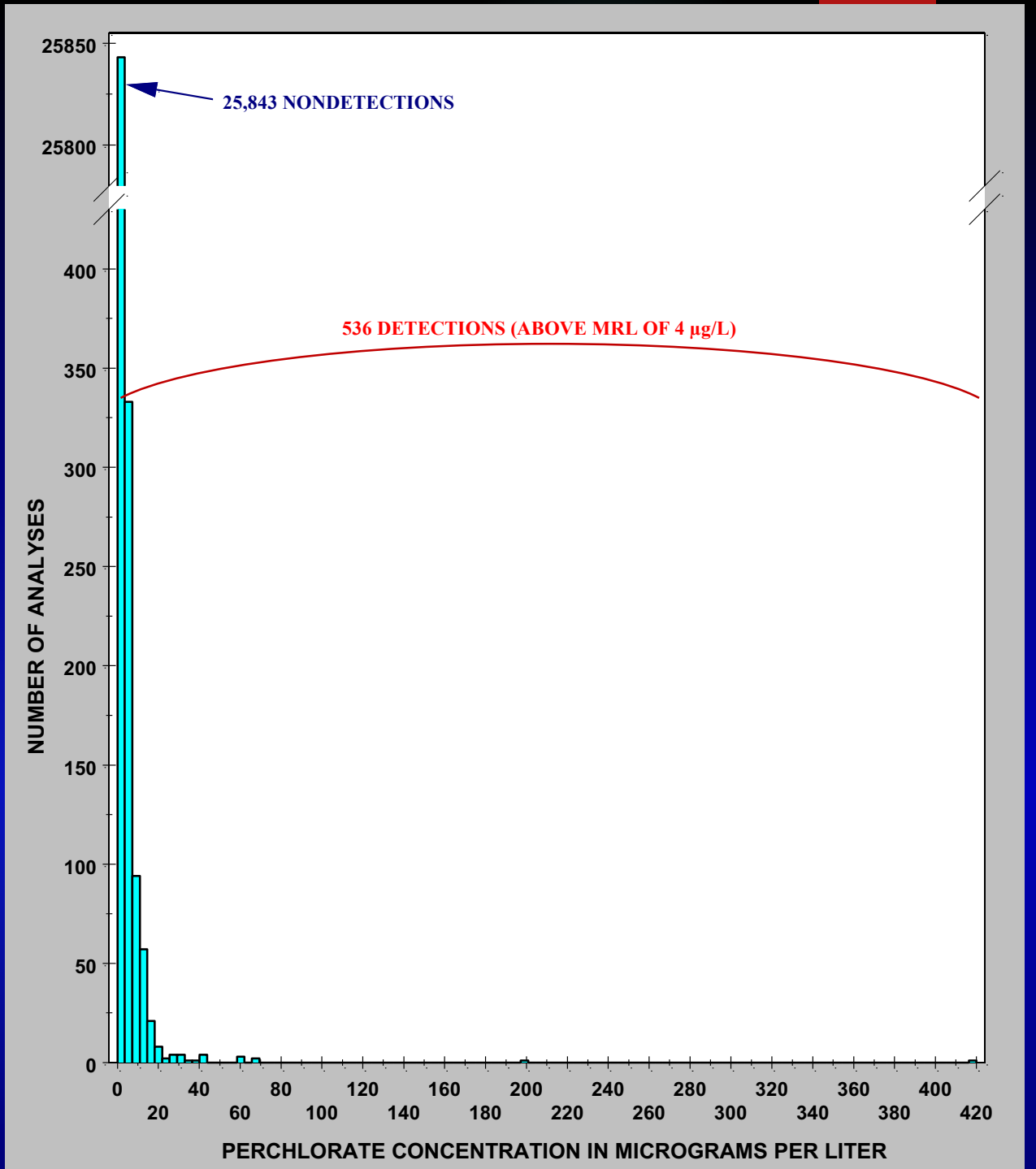
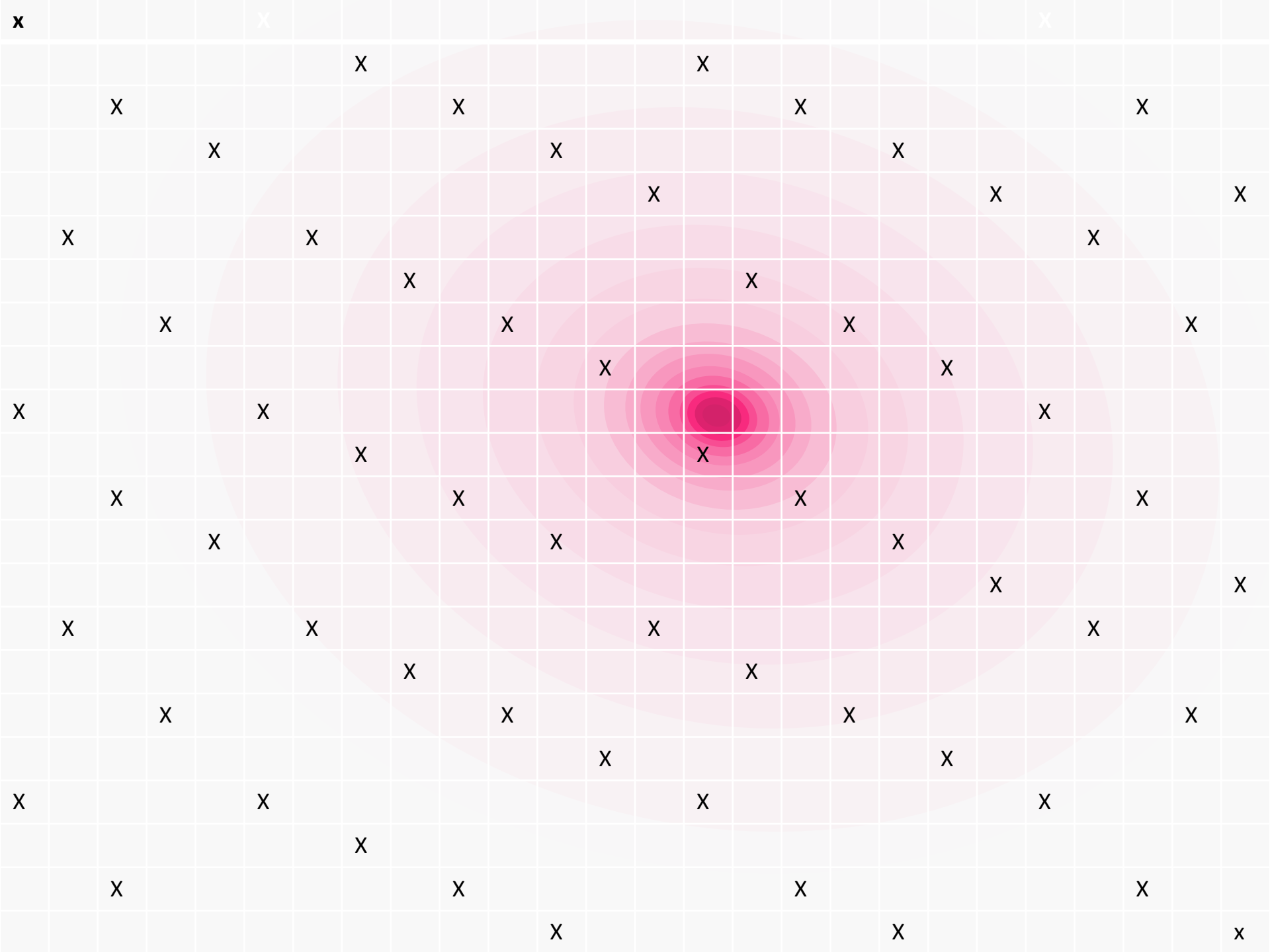


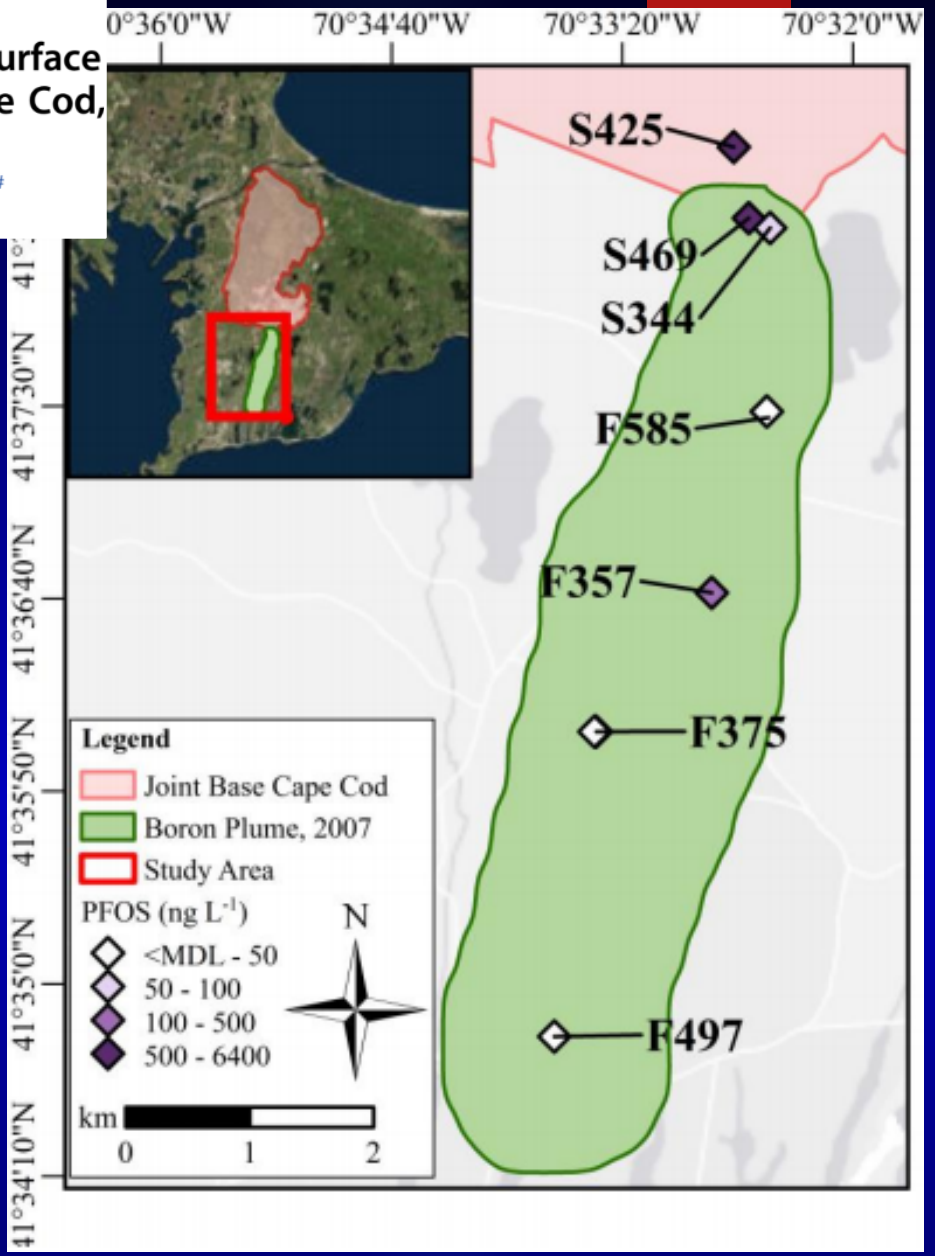


Environmental Science & Technology

Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts

Andrea K. Weber,[†] Larry B. Barber,[‡] Denis R. LeBlanc,[§] Elsie M. Sunderland,[†,#] and Chad D. Vecitis*[,†]

U.S. Geological Survey data release, https://doi.org/10.5066/F7Z899KT



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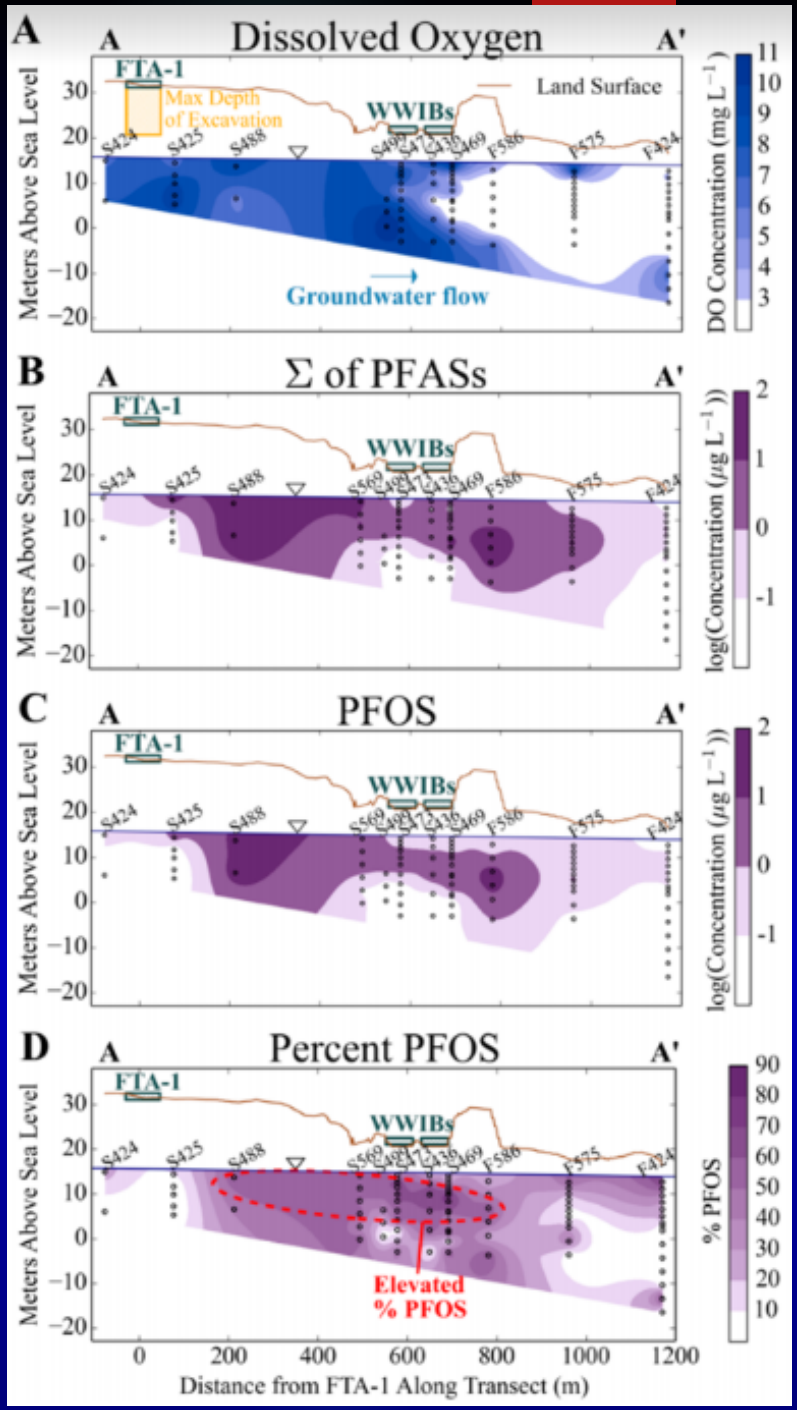
As a result of geochemical and hydrologic factors, PFAS have interesting peculiarities in terms of distribution in the environment.



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3. Our sampling supplies and equipment can be sources or have “active” surfaces..

- Repulsions and attractions, not just “sorption”
- Materials that can sorb PFAS
  - Glass
  - Low-density polyethylene (LDPE) plastic
  - Polypropylene (depending on chain length of the molecule)
- Most commonly used filters use these materials.
- Centrifugation vs. filtering to remove particles.

3. Our sampling supplies and equipment can be sources or have “active” surfaces..

- Materials that can leach PFAS
  - Fluoropolymers: Teflon, PTFE, FEP, etc.
  - Anything with “fluoro” in its name.
  - Any material that sorbed PFAS and is reused.
- Blank water and reagents should be PFAS-free and freshly opened.
  - Fisher “Optima” LC/MS-grade blank water
  - If in doubt, test it.

3. Our sampling supplies and equipment can be sources or have “active” surfaces..

- Protocols in the literature
  - USEPA Method 537 & USEPA Technical Brief
  - DOD (https://www.denix.osd.mil/army-pfas/home/)
  - States (for example, Massachusetts DEP)
  - NGWA, ITRC, TetraTech, etc.

3. Our sampling supplies and equipment can be sources or have “active” surfaces..

- Waterproof items – clothing, boots, treated fabrics in vehicles, waterproof labels, paper, etc.
- New clothing / washed with fabric softener.
- Personal care items – Some cosmetics, insect repellant, sunscreen.
- Unwashed hands

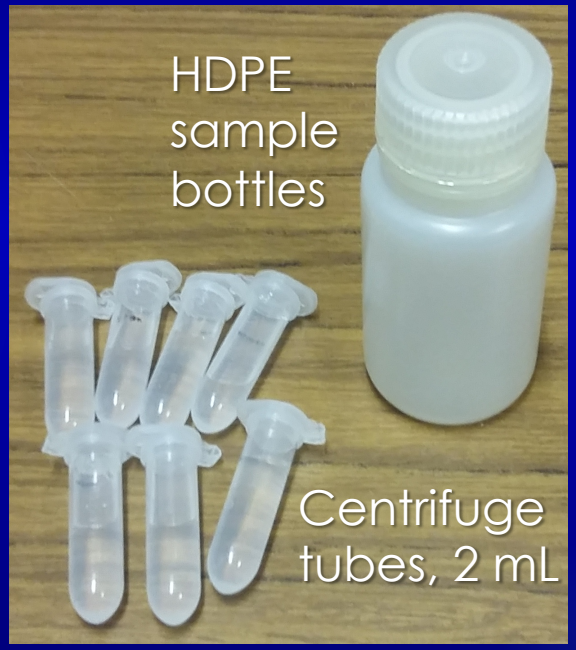
What’s in contact with the sample?

Materials that can be used

- Stainless steel, brass, copper
- HDPE plastic, silicone
- Nitrile or polyethylene (for gloves)
- Bennett pump (as produced)
- Materials that are tested prior to use

Stainless-steel Swagelok fitting (reusable)

Tufflite adapter (disposable)



Copper tubing (reusable)

HDPE tubing (disposable)

4. Laboratory best practices and quality assurance are needed.

- Field QC
  - Equipment blanks for supplies and materials (or combinations thereof)
  - Field blanks to assess effectiveness of SOPs at preventing contamination (especially at low levels)
  - If contamination is identified, need enough field blanks for characterizing the frequency and magnitude of the contamination.
  - Replicates and spare samples are particularly important when working in difficult matrixes, such as wastewater effluent, sediment, or tissue.

4. Laboratory best practices and quality assurance are needed.

- Laboratory Practices
  - Method in validation testing at USGS National Water Quality Laboratory (NWQL) for >24 compounds.
  - LC/MS/MS with negative electrospray ionization conditions (Agilent 6495 triple-quadrupole)
  - Direct aqueous injection, except where SPE needed
  - All consumables are polypropylene or similar plastic (no PTFE or glass). Removed all PTFE tubing from LC flow path, replaced with PEEK or stainless steel
  - Eliminated filtration — Using centrifugation for particle removal

4. Laboratory best practices and quality assurance are needed.

- Laboratory Practices
  - New NWQL method will be extensively tested prior to making it available for USGS studies.
  - Weber & others (ES&T 2017) method used for Cape Cod study

Photo credit:
Denis LeBlanc, USGS

5. There is a tension between standardization vs. changes that could result in improvement.

- Monitoring for regulatory compliance? Use labs and methods approved by the regulatory entity.
  - USEPA Method 537 from a laboratory accredited for UCMR.
  - Department of Defense (DOD) PFAS laboratory accreditation program
- Modifications of EPA 537 for additional matrixes, compounds, etc.

"EPA is not aware of a standardized description of the modified methods, nor is the Agency aware of studies that have validated the performance of these modified methods across multiple laboratories. Therefore, EPA cannot address the performance of "Modified Method 537" in a general manner. If you are considering using a modified method 537 to analyze a sample, EPA recommends that you evaluate its appropriateness relative to your goals for the data and data-quality objectives."

5. There is a tension between standardization vs. changes that could result in improvement.

- Targeted vs. broad-spectrum analysis
  - MS/MS vs. high-resolution MS
  - Trade-off between robust quantitation and getting the "whole picture"
- Total organic fluorine (TOF), total oxidizable precursors (TOP)

How to balance needs:

- Combine multiple complementary methods.
- Ensure that the laboratory provides sufficient QC (e.g., use of isotopically labeled standards, etc.)
- Use field QC to supplement the laboratory QC.

Thank you!!

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