

PFAS Enrichment in Naturally Occurring Foams on a Northern U.S. Freshwater Lake



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Outline

- Introduction
- Materials and Methods
- Results and Discussion
- Implications



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Introduction

More PFAS foam found in Twin Cities' Battle Creek

Kirsti Marohn May 4, 2020 11:38 p.m.



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- Media reports from Michigan, Wisconsin and Minnesota

News

Don't touch toxic PFAS foam, Michigan officials now warn

Updated Apr 30, 2019; Posted Apr 30, 2019



PFAS foam gathers along a beach shoreline along Van Etten Lake on June 7, 2018 in Oscoda Township near Wurtsmith Air Force Base. (Jake May | MLive.com) Jake May



State of Michigan Brochure



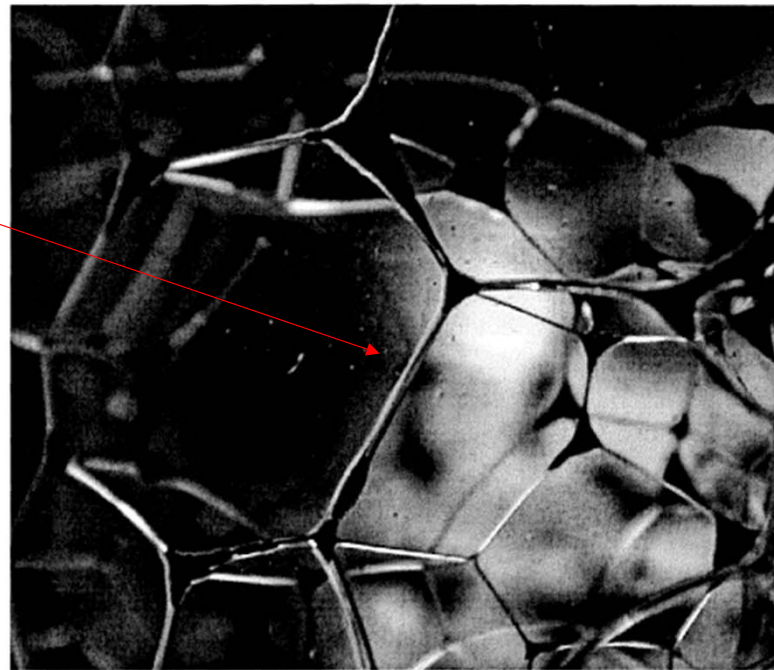
Introduction

- Liquid component of foam is called the **lamella**

- Pressure differential across curved surface:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

- Leads to drainage towards border regions, collapsing foam





Introduction

- Foam can occur in pristine and contaminated systems¹
- Contaminants like PCBs and metals are enriched in foam²
- Foam-like matrices (sea-spray aerosols, surface microlayer) are enriched in PFAS³⁻⁵
 - Is the surface microlayer the lamella of foam?

1. Schilling, K.; Zessner, M., Foam in the aquatic environment. *Water Res* 2011, 45 (15), 4355-66.

2. Napolitano, G. E.; Richmond, J. E., Enrichment of Biogenic Lipids, Hydrocarbons and PCBs in Stream-Surface Foams. *Environmental Toxicology and Chemistry* 1995, 14 (2), 197-201.

3. Johansson, J. H.; Salter, M. E.; Acosta Navarro, J. C.; Leck, C.; Nilsson, E. D.; Cousins, I. T., Global transport of perfluoroalkyl acids via sea spray aerosol. *Environ Sci Process Impacts* 2019, 21 (4), 635-649.

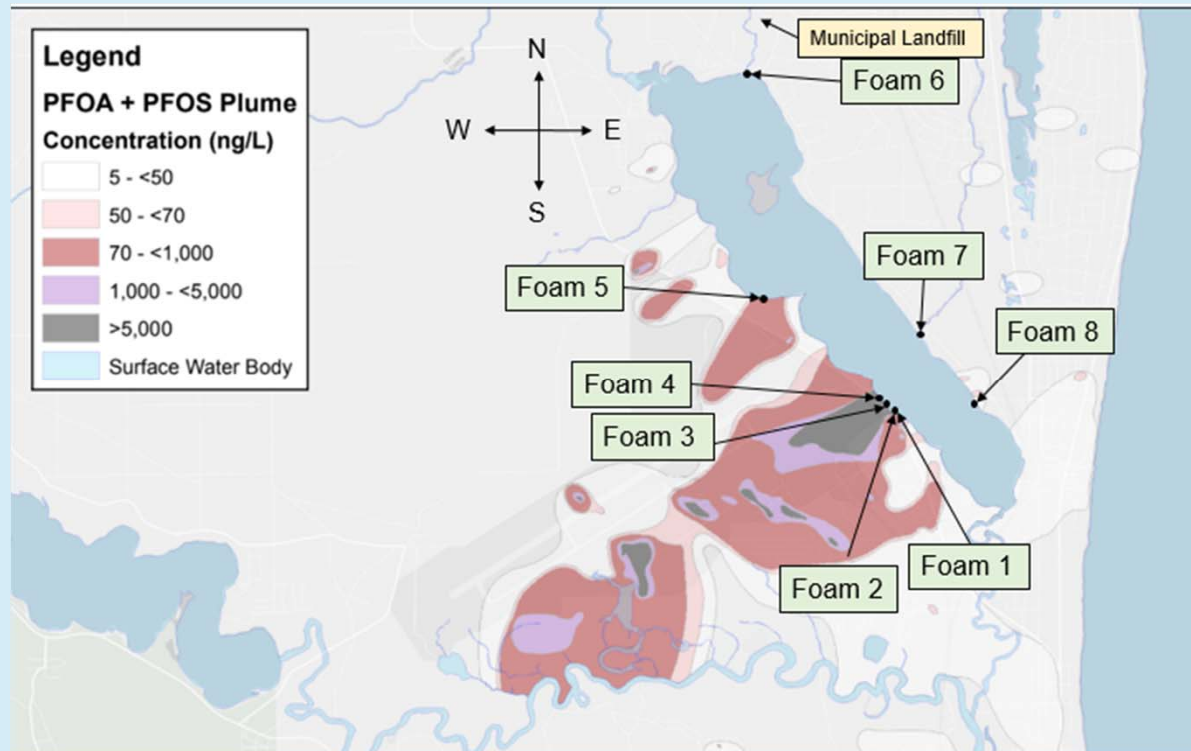
4. Wang, S. L.; Wang, H.; Zhao, W.; Cao, Y. X.; Wan, Y., Investigation on the distribution and fate of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in a sewage-impacted bay. *Environmental Pollution* 2015, 205, 186-198.

5. Ju, X. D.; Jin, Y. H.; Sasaki, K.; Saito, N., Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian Coastal waters in China. *Environ. Sci. Technol.* 2008, 42 (10), 3538-3542.



Introduction

- 8 pairs of foam and underlying bulk water





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Sample Collection Bulk Water

- Submerge a closed 250 mL HDPE bottle 30 cm below surface
- Open underwater for sample collection
- Close underwater before bringing up through the surface

Sample Collection Foam

EGLE Michigan Department of Environment, Great Lakes, and Energy

SURFACE WATER FOAM PFAS SAMPLING

Guidance

- PFAS-free nitrile gloves
- PFAS-free plastic bags





Sample Prep - Bulk Water

- Bulk Water done using a micro liquid-liquid extraction
 - Will Backe 2013
- 6 mL of sample + 31 isotopically labeled PFAS + 6M HCL + 2.0 g NaCL
- Extracted 3x with 10% TFE in Ethyl Acetate (w/w)
- Add 1 mL of Methanol + 2 different isotopically labeled PFAS
- Yield 3 mL extract

ENVIRONMENTAL
Science & Technology


Article
pubs.acs.org/est

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

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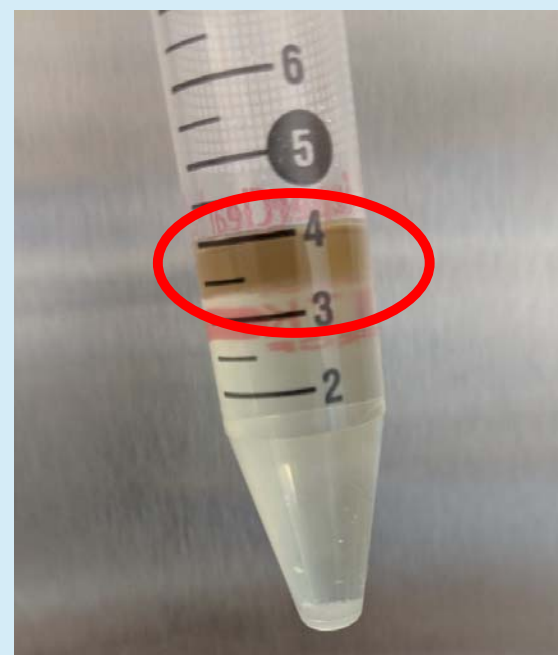
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 Supporting Information



Sample Preparation

- Originally treated like groundwater (Backe 2013)
 - Liquid-liquid extraction using salt and organic solvent (TFE/Ethyl acetate)
- This formed a gelatinous extract not compatible with LC methods
- Extraction was not possible





Sample Preparation cont.

- 1:5 dilution factor into methanol was chosen for better sensitivity, peak shape, and data quality
- Centrifuge after dilution to remove particles
- Spiked with 50 native standards, 33 mass-labeled internal standards



Particles prevented from being injected



PFAS Analysis by LC-QToF

- Liquid Chromatography using ion-exchange onto C18 analytical
 - Ion-exchange acts as wash step done in SPE
- TFE/Ethyl Acetate matrix for bulk waters
- Methanol matrix for foams



PFAS Analysis by LC-QToF

- Quadropole Time-of-Flight Mass Spectrometry
- Quantitation based on accurate mass of the parent ion
 - MRM transition for PFBA and MPFBA to reduce background
- Collection in SWATH mode allows for suspect screening
 - Anastasia Nickerson at Colorado School of Mines





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DOC Analysis

- Central Analytical Laboratory (CAL) at Oregon State University
 - Foams were diluted 1:10 v/v into DI water
 - Bulk waters ran undiluted
- Both Bulk Water and Foam were filtered through a Wattman no.1 paper filter
- Shimadzu TOC-V_{cph/cpn}



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Foam Method Validation

- LC did not show any clogs in pressure profile
- Internal standard area counts across calibration curve (CC), continuing-calibration verification (CCV every 10 samples), and samples
- **25 of 31** internal standards were **<30%** different in samples from CC and CCV



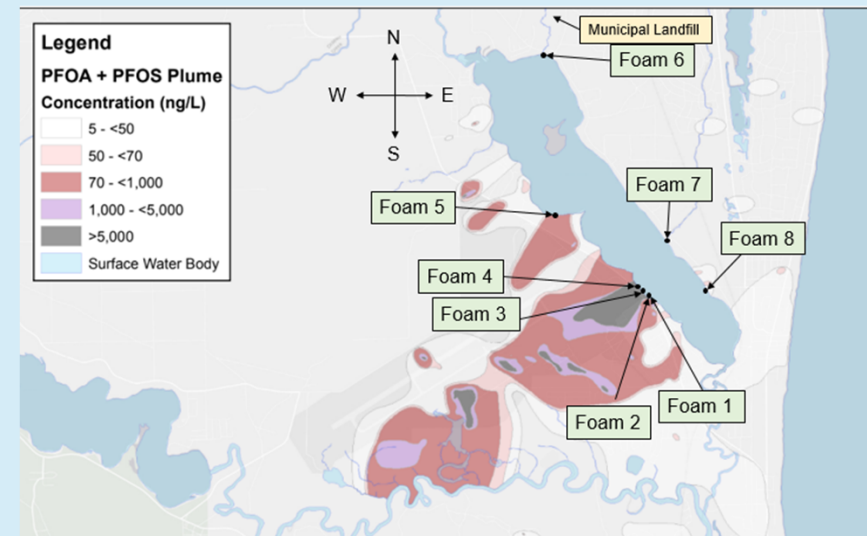
PFAS Composition

- Foam
 - Of the 50 target analytes, 16 analytes comprising 8 PFAS classes were found
- Bulk Water
 - 5 analytes comprising 3 PFAS classes
- Highest detection in bulk water was PFHxS: 59 ng/L
- Highest detection in foam was PFOS: 97,000 ng/L
 - PFOS + PFOA in that foam was 1,400 times greater than EPA HAL of 70 ng/L



PFAS Composition

- Long-chained carboxylates in Foams 1-5 (up to **C11**, 100s ng/L)
- ECF (e.g., 3M) analytes included **PFEtCHxS**, **FHxSA**, **EtFOSAA**, and **Spr-FHxSA** (suspect screening)
- Fluorotelomers also found
- **5:3 FTCA** in Foam 6 indicates landfill leachate





Dissolved Organic Carbon Composition

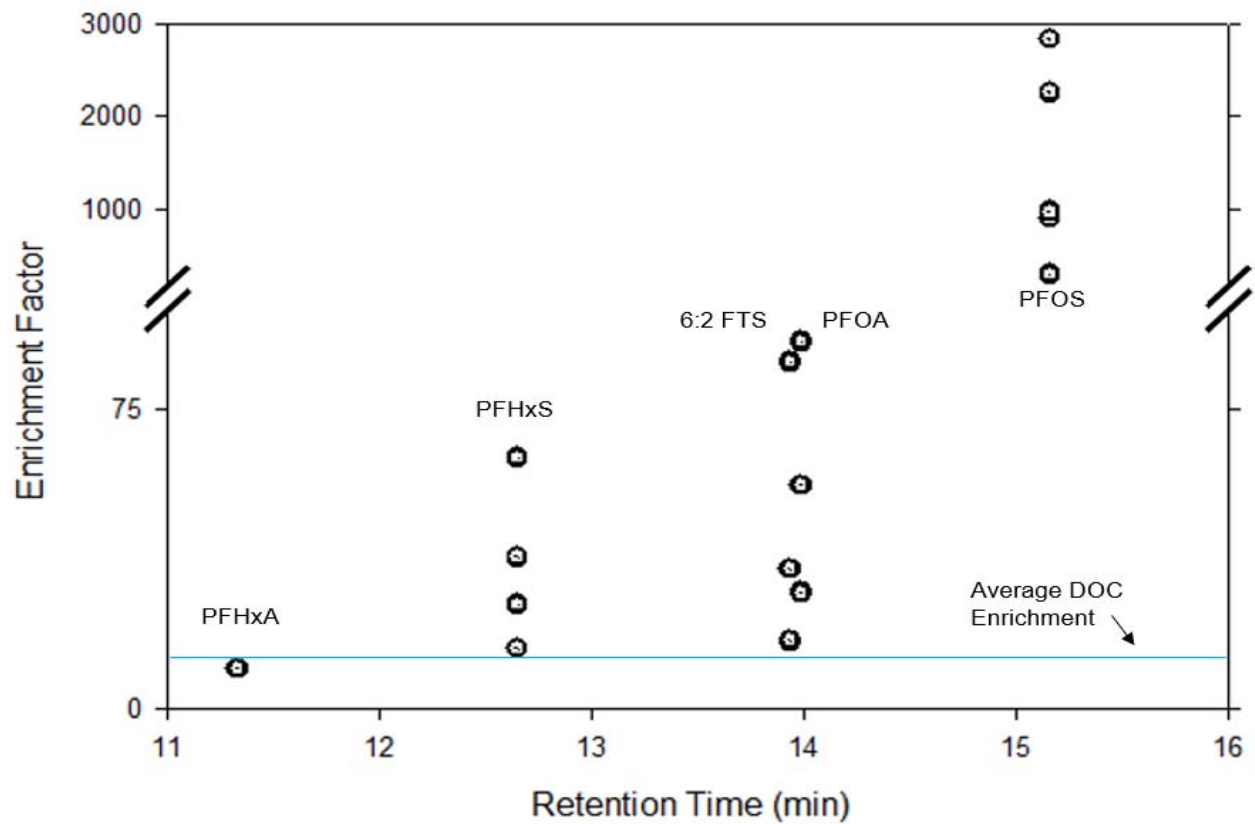
- DOC concentrations were fairly uniform and enriched in foam
 - Foam average **250,000,000 ng/L**
 - Bulk Water average **15,000,000 ng/L**
- Total PFAS constitute <0.1% of DOC
- Foam is largely driven by **uncharacterized DOC**
 - Color/shape/smell driven by DOC
 - Humic/fulvic acids, lipids, proteins from decaying organic matter



Enrichment Factors

- Enrichment factors in water

- EFs

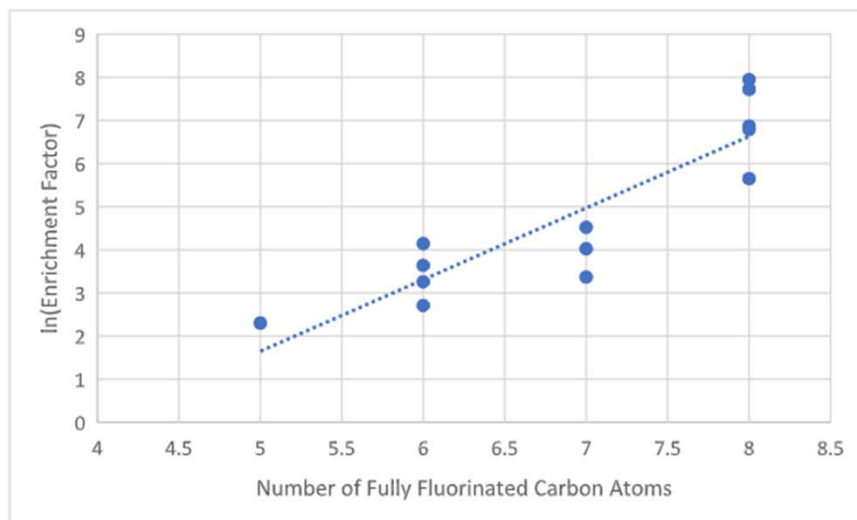


Enrichment Factors



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Simple linear regression was performed on the log transformed enrichment factors as a function of the number of fully fluorinated carbons present on each molecule.



- $\ln(\text{EF})$ vs # Fluorinated Carbons gives r^2 of 0.795



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Implications

- Foam is largely driven by DOC
- However, foam provides a route of exposure to high concentrations (PFOS) and long-chain carboxylates
- Surface microlayer also may be providing a route of exposure
- Avoid foam when sampling and during sample prep

Acknowledgements



- Field Lab
- Strategic Environmental Research and Development Program (SERDP) ER19-1205



Questions?