UNIVERSITY OF NOTRE DAME

Rapid Screening of PFAS in Real-World Water Samples Using Particle-Induced Gamma-Ray Emission Spectroscopy

Presenter: Yukun Jin (GSI)

Co-authors:

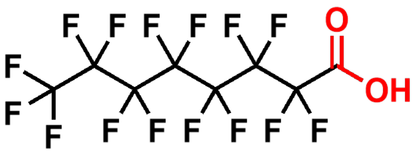
Alyssa Wicks, Daniele Miranda, Graham Peaslee

(University of Notre Dame)

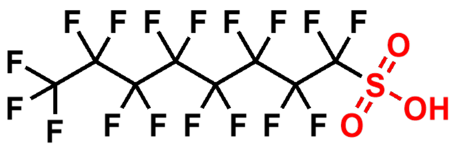
June 3rd, 2024

Battelle 2024 Chlorinated Conference

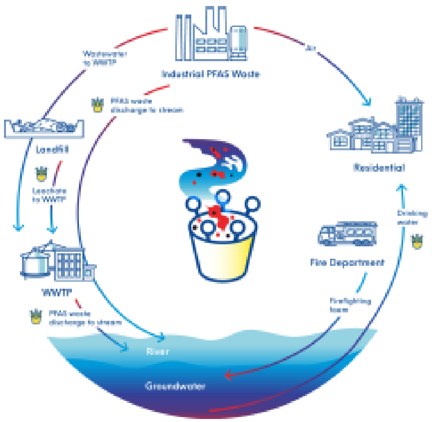
Per- and Polyfluoroalkyl Substances (PFAS)

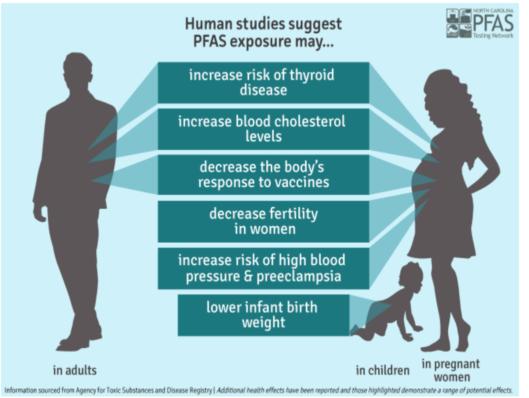


PFOA



PFOS



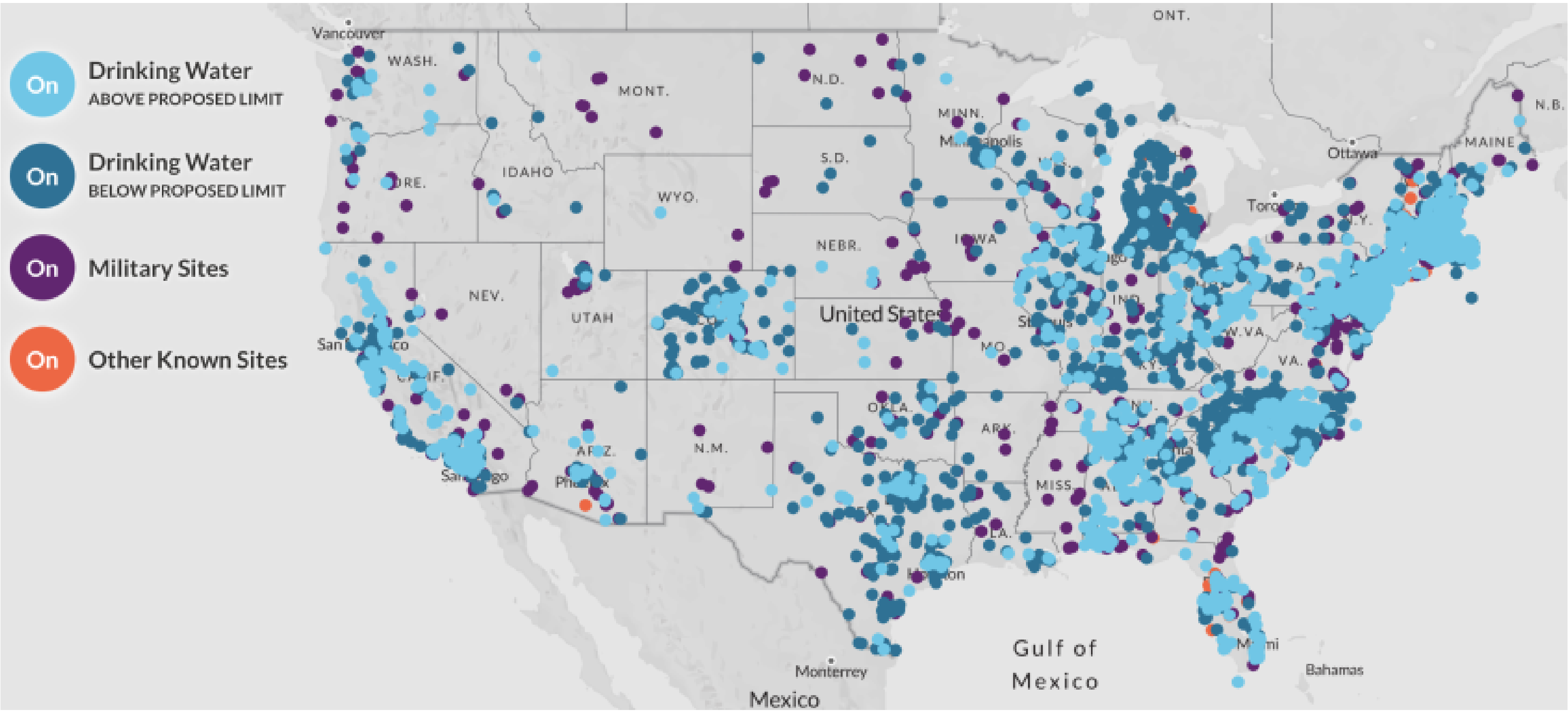


- Human Exposure:
  - ❑ Contaminated water
  - ❑ Contaminated food
  - ❑ Consumer products
  - ❑ Air and dust inhalation
  - ❑ Dermal sorption

1. https://cyclopure.com/environmental-applications/
2. https://hawriver.org/ongoing-research-for-pfas-contamination-and-impacts/

PFAS Dissolved in Water

- Primary Routes of PFAS Get into Water
  - Industrial discharges
  - Landfills
  - Sewage treatment plants
  - Aqueous film-forming foams (AFFF)
  - Biosolids
- Surface & Ground Water



PFAS Contamination in the U.S.
Source: https://www.ewg.org/interactive-maps/pfascontamination/map/

PFAS Dissolved in Water

NEW: EPA Maximum Contaminant Levels (MCLs) in Drinking Water

Compound	Proposed MCL (enforceable levels)
PFOA	4.0 ppt (or ng/L)
PFOS	4.0 ppt (or ng/L)
PFNA	1.0 (unitless) Hazard Index
PFHxS	
PFBS	
HFPO-DA (GenX)	

Previous health advisory guidelines (2016) for PFOA + PFOS were a total of 70 ppt (or ng/L)

Challenge: routinely monitor and detect PFAS below the new limit

https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

Traditional Analytical Technique

UNIVERSITY OF NOTRE DAME

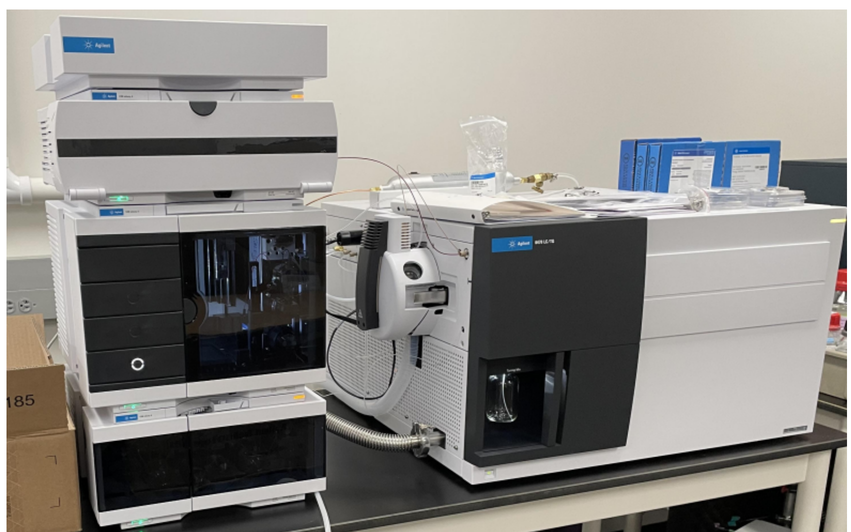
Liquid Chromatography with Tandem Mass Spectrometry

☺ Highly selective and sensitive analysis

☺ Using both EPA Method 533 and 537.1, 29 individual PFAS can be sensitively measured in water samples

☹ Limited targeted analyte coverage

☹ Extensive sample preparation and analysis time



Alternative Analytical Technique

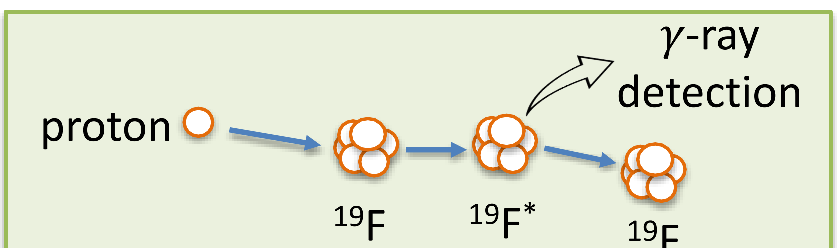
Particle-**I**nduced **G**amma-ray **E**mission

- Rapid and non-destructive screening tool
- Easy sample preparation
- Detection limit (solids): ppm (parts-per-million, mg/L)
- Total F analysis (inorganic fluoride and organic fluorine)

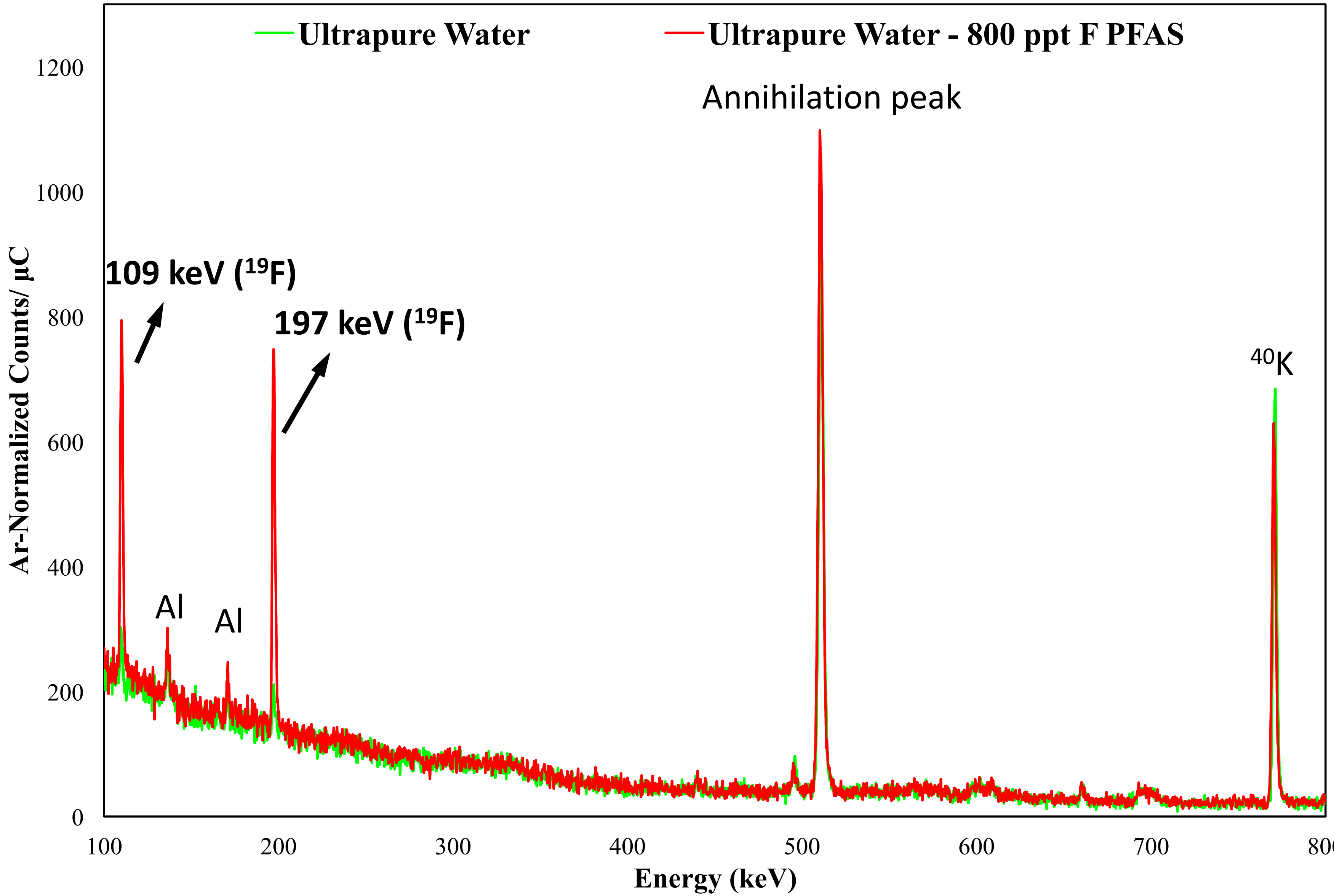
Ion source & Accelerator

Beamline

Target wheel & HPGe detector



PIGE Spectrum (180 s)



Method Development

Field Sampling Made Easy with Commercialization Potential

Solid-Phase Extraction (SPE) Method

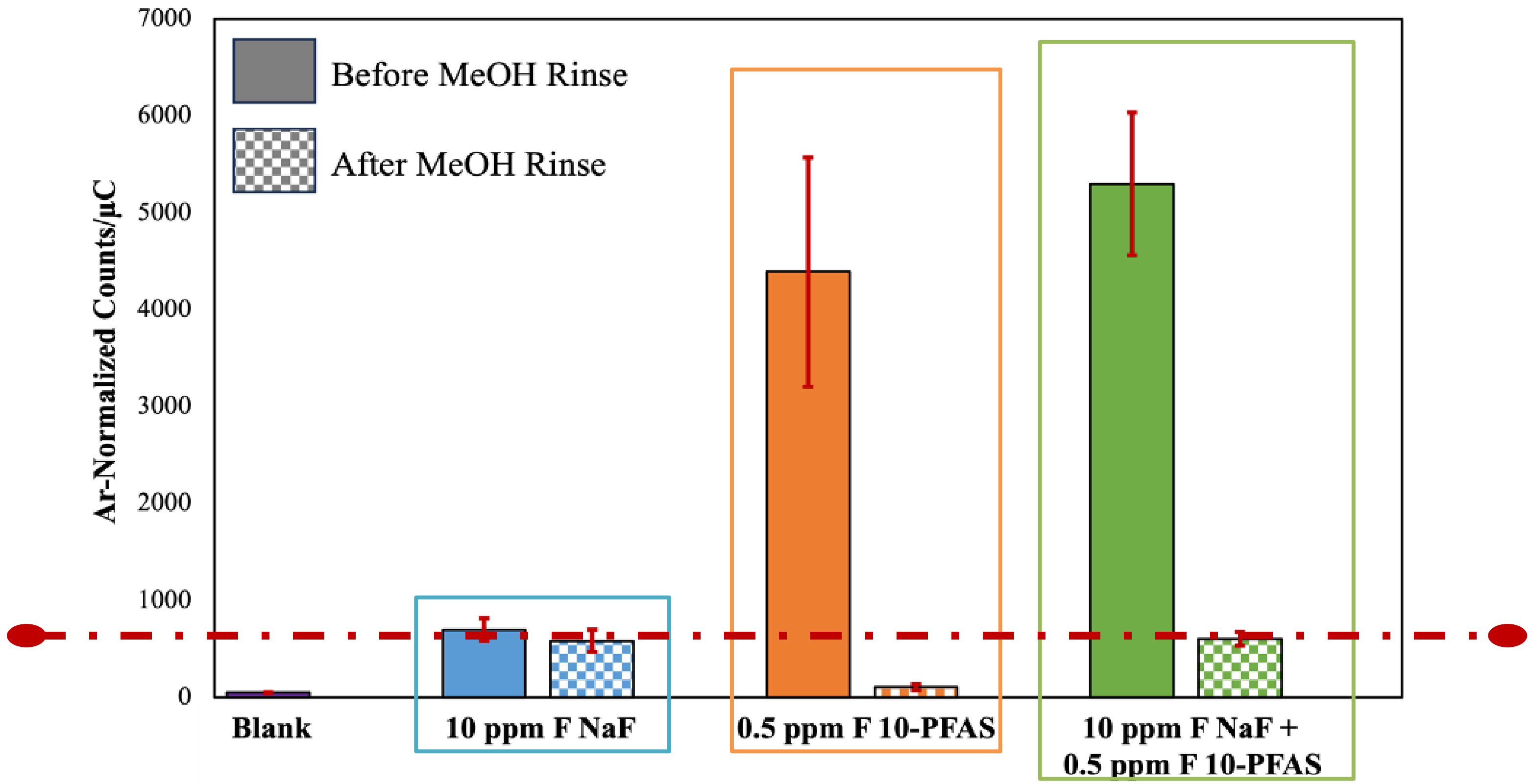
- Graphite Activated Carbon Fiber (GACF): $0.07
- 1-gallon water bag: $1
- 3D-print insert: $5

GACF Felt

Problem: Inorganic Fluoride Interference

- Inorganic fluoride (IF) is commonly found in environmental waters due to natural process and human activities.
- ≪1% adsorption efficiency on GACF felt

Solution: 10-mL methanol rinse post filtrations to distinguish inorganic fluoride and organic fluorine in PIGE



Ultrashort-Chain PFAS

UNIVERSITY OF NOTRE DAME

Environmental Science & Technology

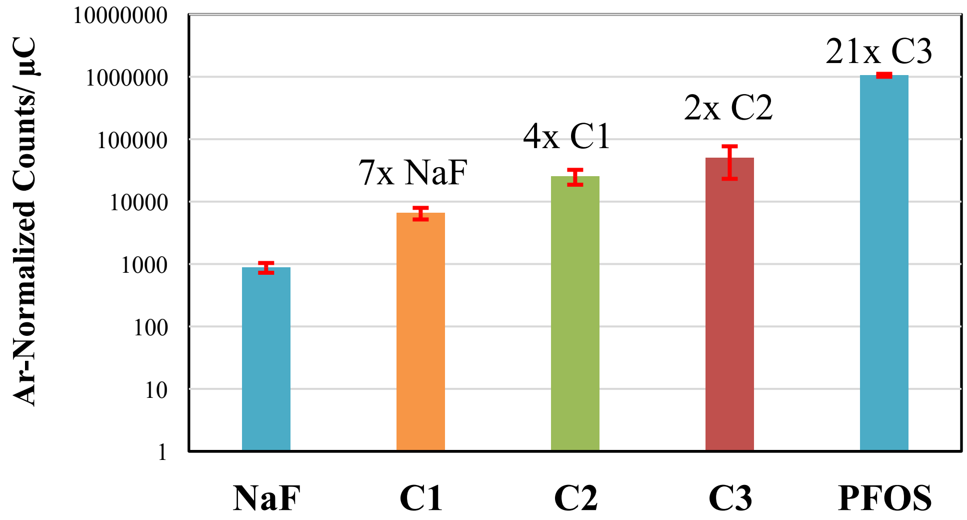
98% of PFAS measured were ultrashort-chain PFAS

pubs.acs.org/est Article

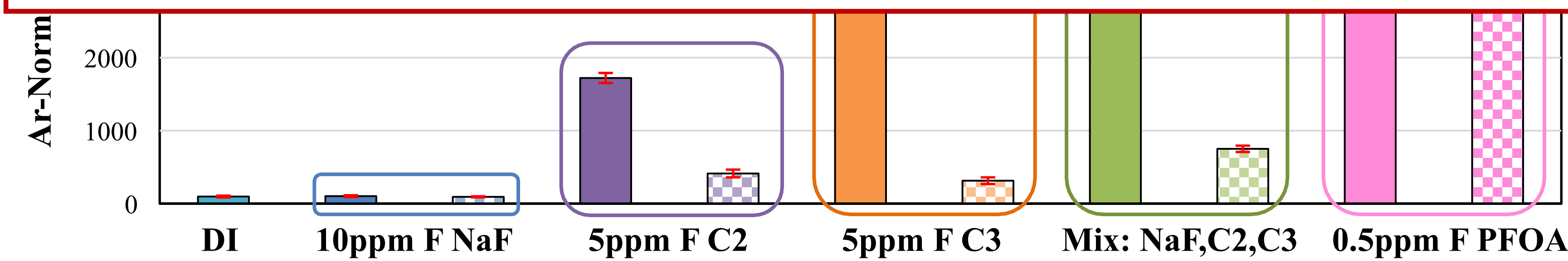
Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated

Isabelle J. Neuwald, Daniel Hübner, Hanna L. Wiegand, Vassil Valkov, Ulrich Borchers, Karsten Nödler, Marco Scheurer, Sarah E. Hale, Hans Peter H. Arp, and Daniel Zahn*

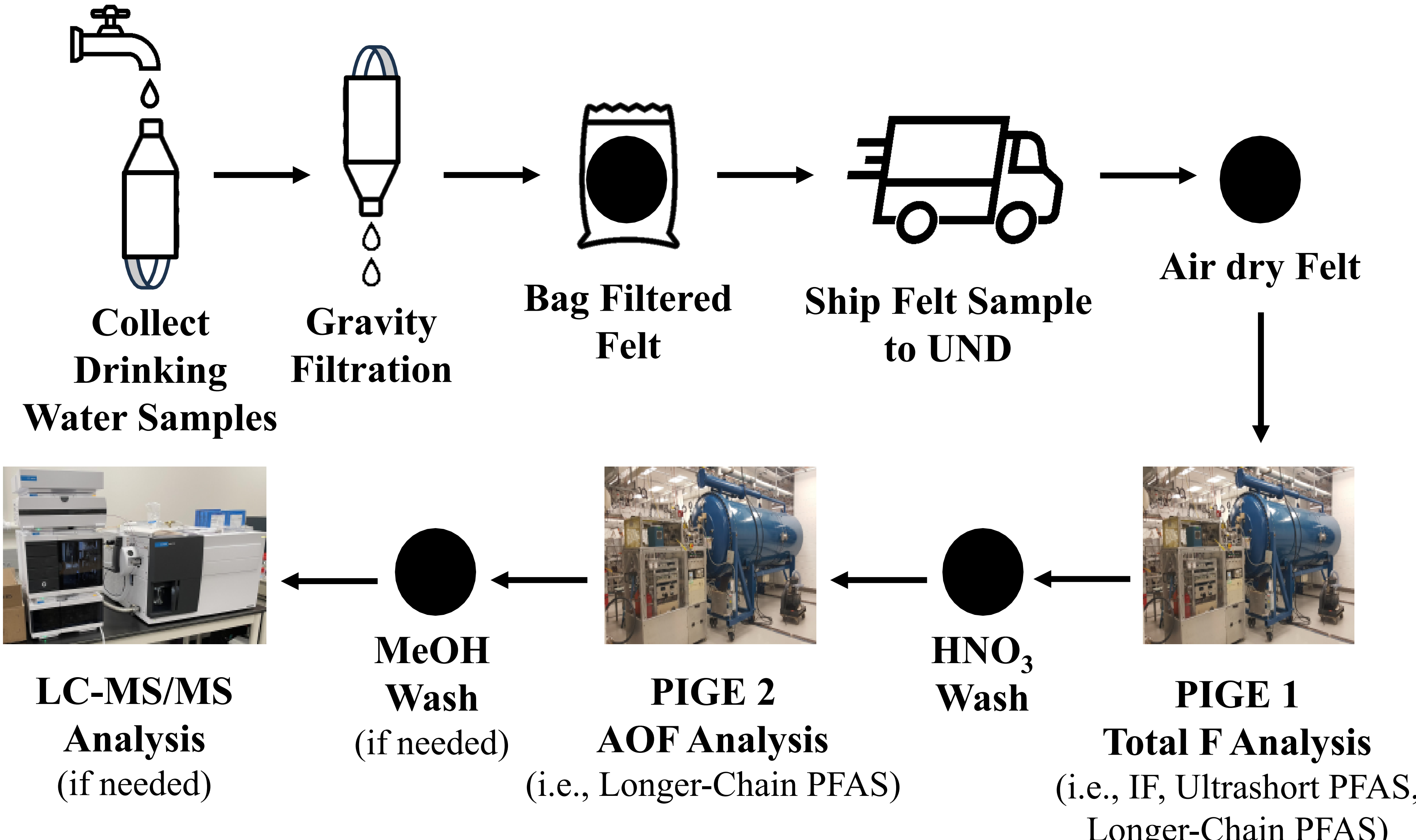
- <4 carbons on the alkyl chain
- C1 (sodium triflinate), C2 (TFA), C3 (PFPrA), all at same 5 ppm F



HNO_3 can remove ultrashort but not longer-chain PFAS



Workflow for Real-World Water Collections



Project 1: Drinking Water
(Northern IN)

PFAS in Indiana

UNIVERSITY OF NOTRE DAME

- Indiana Department of Environmental Management (IDEM)
  - Three-phase investigation across all Community Public Water Systems (CWS) in the state (2021-2023)
  - Elevated PFAS found in: Elkhart, Elkhart County and Columbus, Bartholomew County
  - 2 years to collect and expensive
  - Large Excel file, not user-friendly

	Population Served	Tentative Sampling Schedule
Phase 1	3,300 to 10,000	March 2021 - October 2021
Phase 2	<3,300	November 2021 - December 2022
Phase 3	>10,000	January 2023 - May 2023

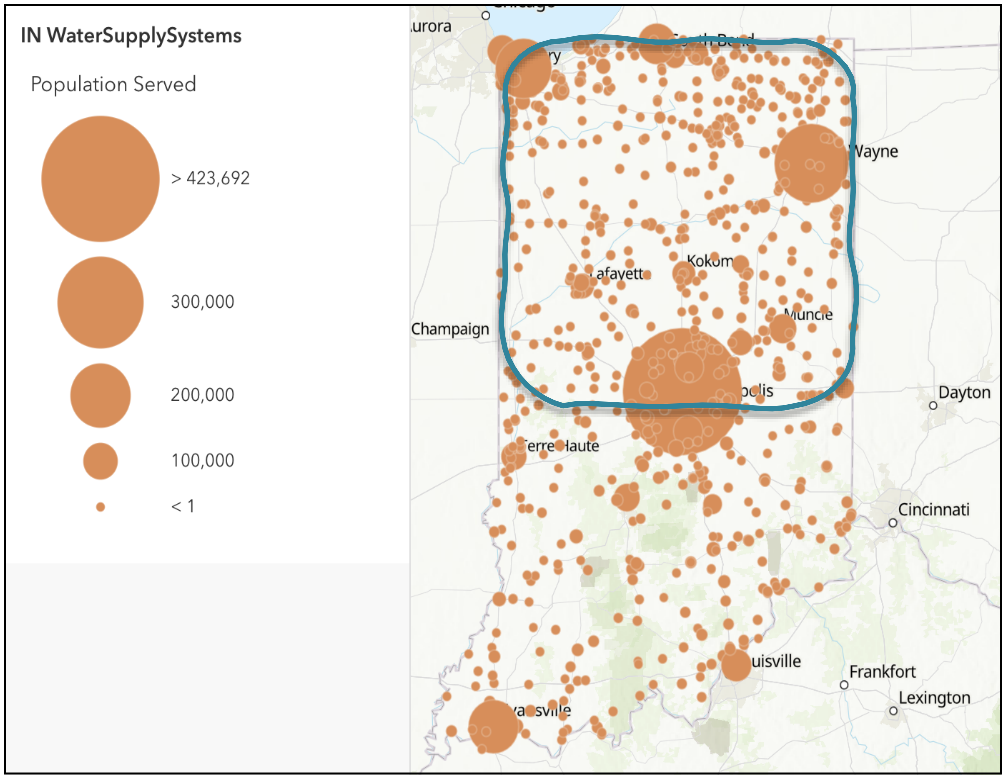
- Phase 1 Results [XLSX] - Updated May 2023
- Phase 1 Resample Results [XLSX] - Updated June 2023
- Phase 2 Results [XLSX] - Updated January 2024
- Phase 2 Resample Results [XLSX]
- Phase 3 Results [XLSX] - Updated November 2023
- Phase 3 Resample Results [XLSX] - Updated January 2024

- Other studies, such as Environmental Working Group, few PFAS results for drinking water have been reported within Indiana.

https://www.in.gov/idem/resources/nonrule-policies/per-and-polyfluoroalkyl-substances-pfas/

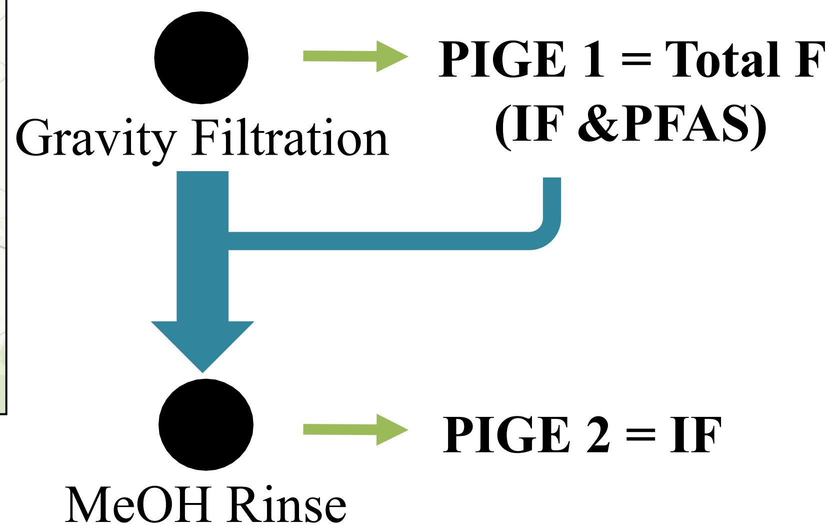
Northern Indiana Drinking Water

UNIVERSITY OF NOTRE DAME



Map made by Matthew Sisk

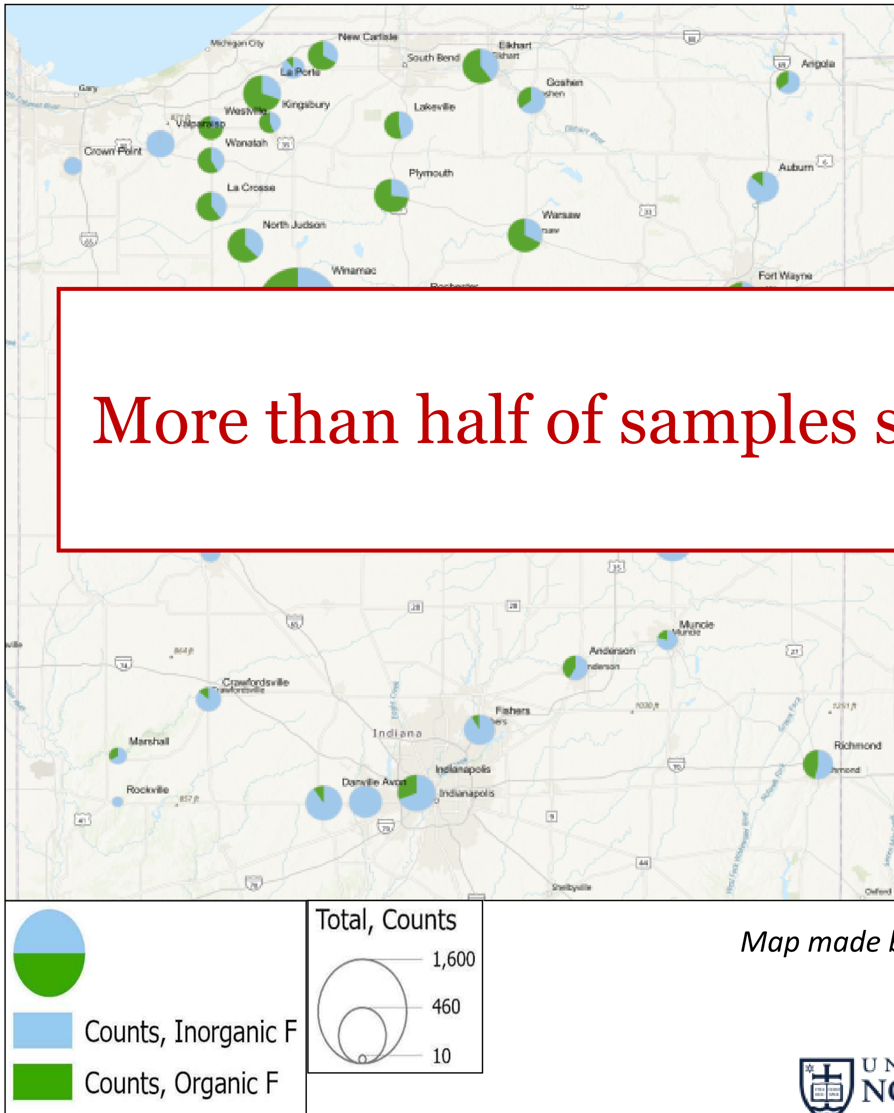
- 39 locations
- Public resources: libraries, parks, restaurants, gas stations
- Two PIGE analysis



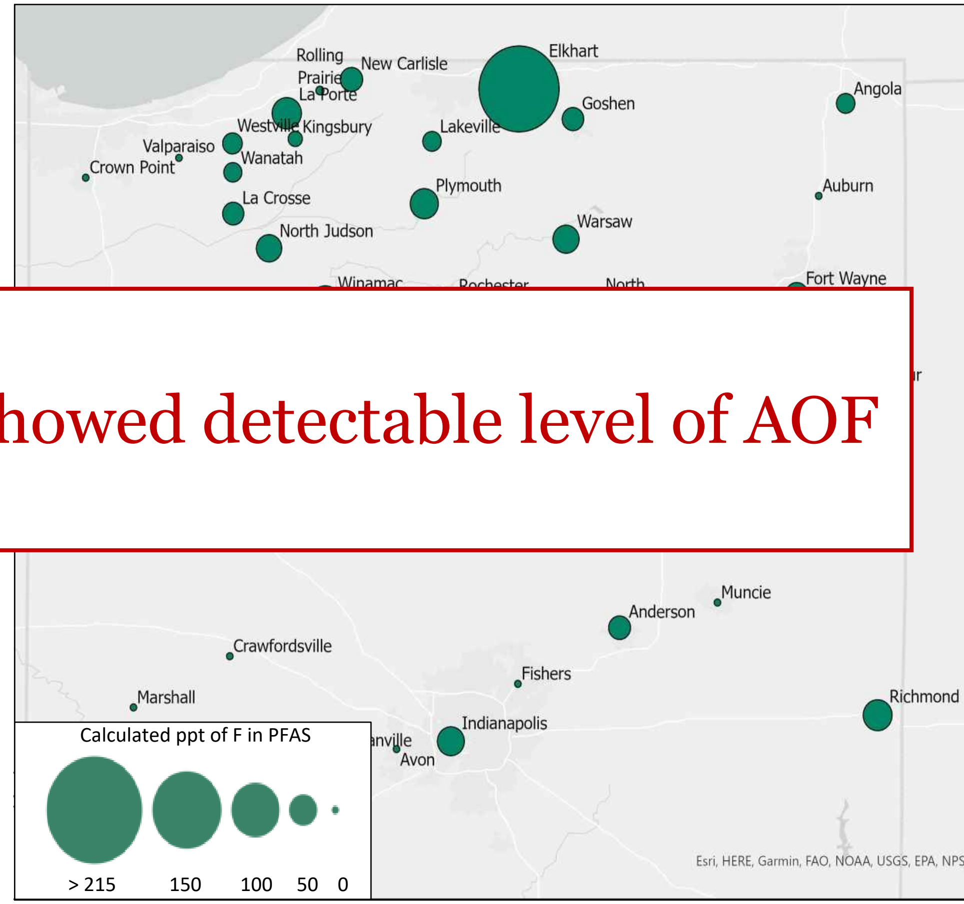
PIGE 1 – PIGE 2 = Adsorbable Organic Fluorine (AOF)

PFAS in Northern Indiana Drinking Water

Map of Detected Levels of AOF & F⁻



Map of Measured Levels of AOF



More than half of samples showed detectable level of AOF

Map made by Matthew Sisk

UNIVERSITY OF NOTRE DAME

Results: PIGE vs. LC-MS/MS

UNIVERSITY OF NOTRE DAME

Site #	PIGE AOF (ng/L, ppt F)	LC-MS/MS ∑F PFAS (ng/L, ppt F)
S.26	215	0.74
S.25	94	<LoD
S.9	73	0.31
S.3	67	0.04
S.32	66	<LoQ
S.12	63	0.09
S.36	63	0.06
S.23	60	0.33
S.11	58	0.51
S.8	55	0.07
S.39	52	0.06
S.1	46	0.07
S.30	46	<LoD
S.34	45	<LoQ
S.27	44	0.50
S.7	43	2.24
S.5	39	0.05
S.10	38	0.46
S.28	35	0.15
S.13	35	0.05
S.6	34	0.02

Site #	PIGE AOF (ng/L, ppt F)	LC-MS/MS ∑F PFAS (ng/L, ppt F)
S.14	<LoD	<LoD
S.16	<LoD	<LoD
S.19	<LoD	<LoD
S.20	<LoD	<LoD
S.21	<LoD	<LoD
S.29	<LoD	<LoQ
S.37	<LoD	<LoQ
S.38	<LoD	<LoQ
S.17	<LoD	0.36
S.15	<LoD	0.24
S.18	<LoD	0.21
S.31	<LoD	0.11
S.35	<LoD	0.11
S.4	<LoD	0.06
S.2	<LoD	0.04
S.24	<LoD	0.04
S.22	<LoD	0.04
S.33	<LoD	0.07

39 sites measured with both PIGE & LC-MS/MS

21 sites: PIGE AOF > LC-MS/MS PFAS

8 Sites: PIGE & LC-MS/MS both were <LoD

10 Sites: PIGE <LoD LC-MS/MS = very low PFAS

Highest PIGE result was from Elkhart, which agreed with IDEM's investigation

Capture Efficiencies on GACF Felt

PFAS Analytes	(Relative) Capture Efficiency
PFPeA (C5)	57% ± 9%
PFHxA (C6)	47% ± 11%
PFHxS (C6)	60% ± 7%
PFHpA (C7)	55% ± 9%
PFOA (C8)	61% ± 7%
PFOS (C8)	60% ± 8%
PFNA (C9)	59% ± 12%
PFDA (C10)	60% ± 11%
PFPrA (C3)	2.9%
TFA (C2)	1.4%
Sodium Triflinate (C1)	0.4%
NaF	0.05%

Average: 57% ± 5%

- 10-PFAS standard solutions (except PFBS & GenX)
- No observed increase with the chain length
- No obvious correlation between acids and sulfonates.
- C1 - C3 less than 3% of relative capture efficiency

Project 2：Surface Water
(Northern Lake County, IN)

Northern Indiana Surface Water

- The Laurentian Great Lakes constitute approximately 20% of the Earth's freshwater supply

Bunnell, David B. et al. "Changing Ecosystem Dynamics in the Laurentian Great Lakes: Bottom-Up and Top-Down Regulation." *BioScience* 64 (2014): 26-39.

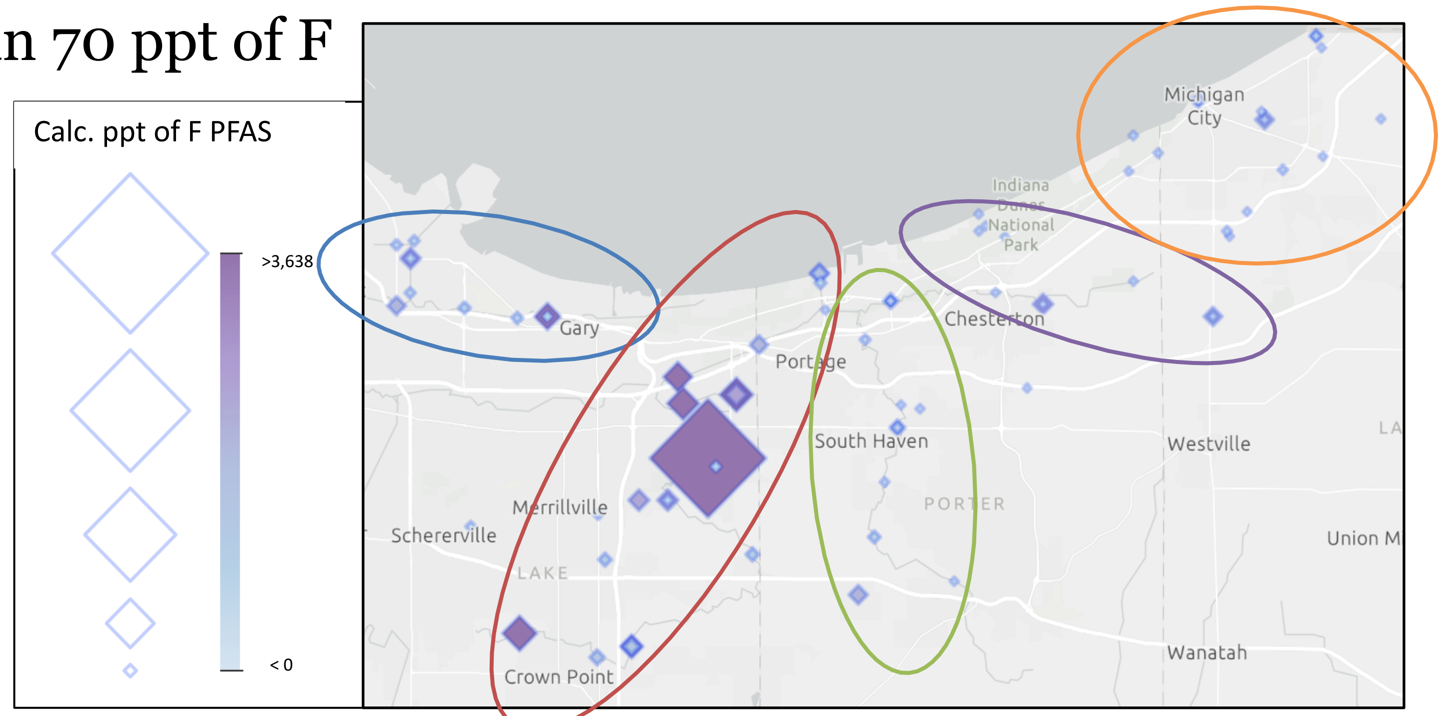
Phase I Sampling

- 60 sample sites were strategically selected from all major Indiana tributaries entering Lake Michigan, and verified for safe access
- 5 tributaries:
  Grand Calumet River watershed (GC)
  Deep River watershed (DR)
  Salt Creek watershed (SC)
  Little Calumet River (LC)
  Trail Creek watershed (TC)

AOF Results

Most locations showed elevated PFAS concentrations surpassing 160 ppt of F

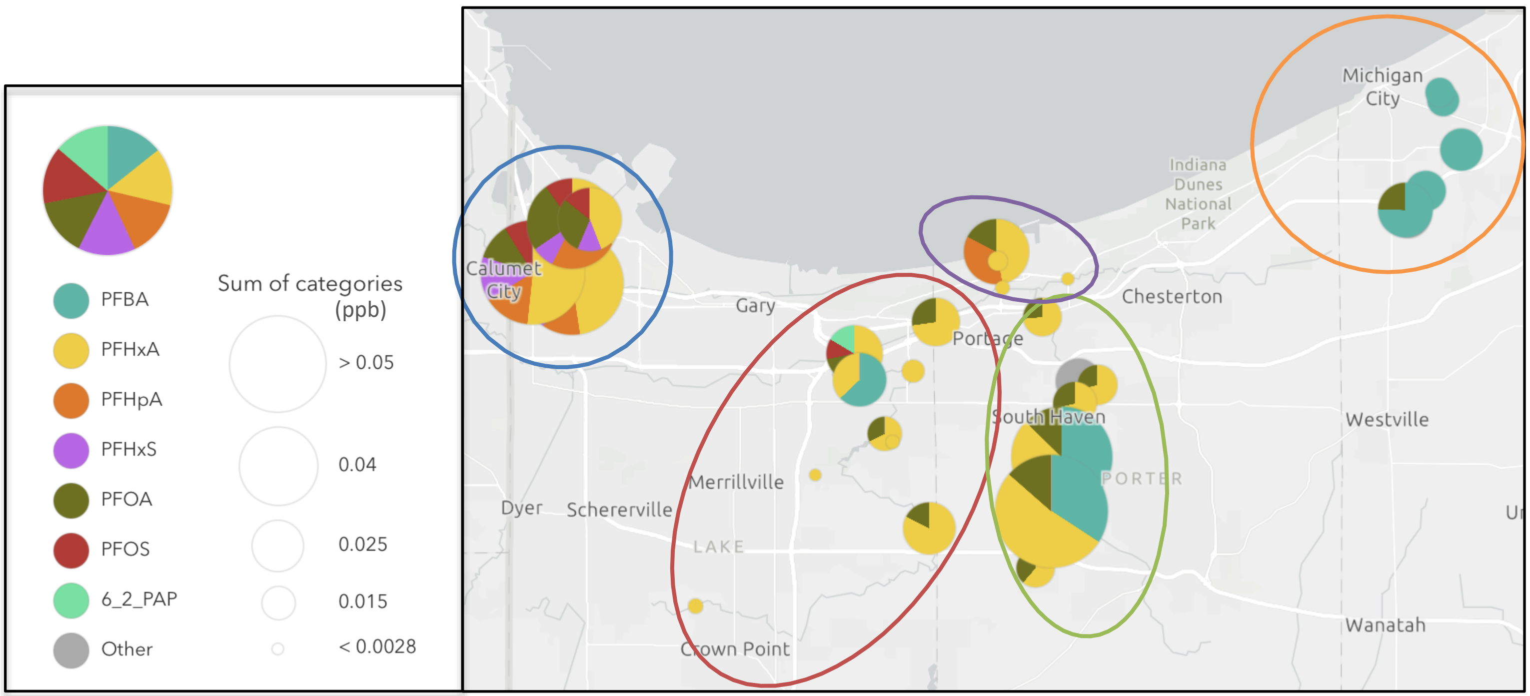
- DR sites were most elevated, especially “DR-5” significantly elevated with 3638 ppt of F
- GC most locations displayed AOF concentrations above 70 but below 160 ppt of F
- SC, LC, and TC had AOF concentrations either below LoD or less than 70 ppt of F



Targeted Results

15 of the 31 locations that underwent targeted analysis returned PFOA concentrations greater than the MCL of 4 ppt

- GC sites were among most elevated (range total PFAS: 18-46 ppt), and contained a mix of PFHxA, PFHpA, PFHxS, PFOA, and PFOS
- SC sites contained a mix of PFBA, PFHxA, and PFOA with total PFAS concentrations ranging from 0-50 ppt
- DR, LC, and TC ranged in total PFAS concentrations from 0-28 ppt



Conclusions

- The average capture efficiency of C5-C10 is 57% ± 5%, and the relative capture efficiency of C1-C3 is below 3%. Still significant likely because of high environmental concentrations of C1-C3.

- Half drinking water samples from northern IN showed detectable concentration of AOF; The high AOF value we identified in Elkhart corresponds with the findings by IDEM, indicating high sensitivity to long-chain PFAS.

- PFAS were detected in some coastal areas using PIGE, especially around the Deep River watershed and Grand Calumet River watershed (more industrial watersheds).

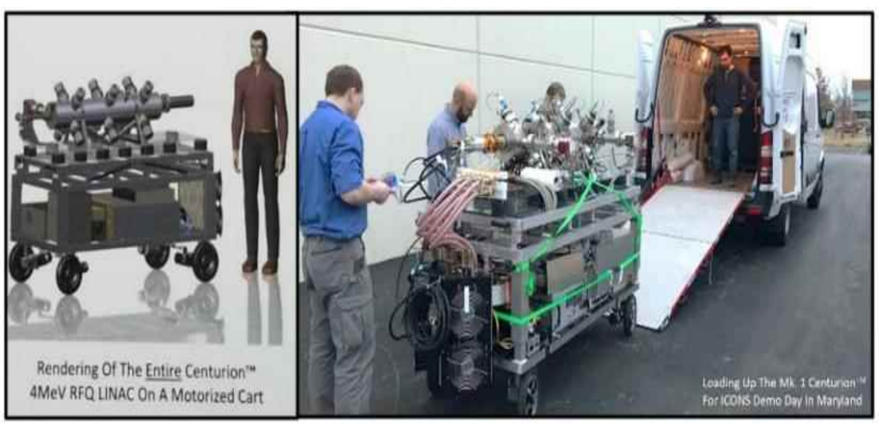
- PIGE can rapidly screen PFAS in actual drinking water samples.
  - PFAS trends from PIGE and LC-MS/MS are comparable.
  - PIGE often captures and detects additional AOF compared to targeted PFAS analysis by LC-MS/MS.

Future Directions

UNIVERSITY OF NOTRE DAME

Forever Analytical Solutions (FAS)

- Offer rapid screening for AOF (PFAS)
- Select specific samples for targeted PFAS analysis
- Scale up the sample volume for lower LoDs
- Explore testing other sample types
- “Portable PIGE” facility – real time analyses



starfire industries

Acknowledgments

Advisor: Dr. Graham Peaslee

Peaslee Group Members: Alyssa Wicks, Dr. Heather Whitehead, Gunnar Brown, Anthony Miller, Dan Baudendistel, Aiden Flynn, Esmee Belzer

Dr. Daniele Miranda, Alison Zachritz, Dr. Gary Lamberti

Dr. Matthew Sisk

IDEA Center, UND: Benjamin Sheyko, Hunter MacMillan, Tim Joyce

Funding by: Water Research Foundation, DoD SERDP, Indiana Department of Natural Resources, US EPA – SBIR, University of Notre Dame, Forever Analytical Services, Inc.

UND Mass Spectrometry & Proteomics Facility and Dr. Bill Boggess

UND Materials Characterization Facility

CEST Center for Environmental Science and Technology

UNIVERSITY OF NOTRE DAME College of Science

Thank you!

Graham Peaslee: gpeaslee@nd.edu

Yukun Jin: yjin8@nd.edu