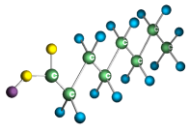
# Per- and polyfluoroalkyl substances (PFAS) in Lake Michigan fish

Daniele Miranda, Ph.D.



**PIs:** Gary Lamberti and Graham Peaslee
**Postdoctorate:** Daniele Miranda
**PhD students:** Alison Zachritz and Heather Whitehead
**Lab technician:** Sarah Klepinger

USGS science for a changing world

Sea Grant ILLINOIS-INDIANA

# Acknowledgments


ASSISTANCE

- Undergraduates: Peter Martin, Griffin Yates, Corbin Hite, Kristin Schaars, Juan Flores, Therese Reisch, Sam Bosio, Jack Boyle
- Lab Manager: Sarah Klepinger
- Center for Environmental Science and Technology: Mike Brueseke, Dana Biasatti



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# PFAS TEAM

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## PIs

Gary Lamberti

Department of Biological Sciences

Graham Peaslee

Department of Physics and Astronomy

## PhD candidates

Alison Zachritz

Heather Whitehead

## Postdoc

Daniele Miranda

## Lab manager

Sarah Klepinger

## Alumni

Whitney Conard

# PFAS TEAM - Undergrads

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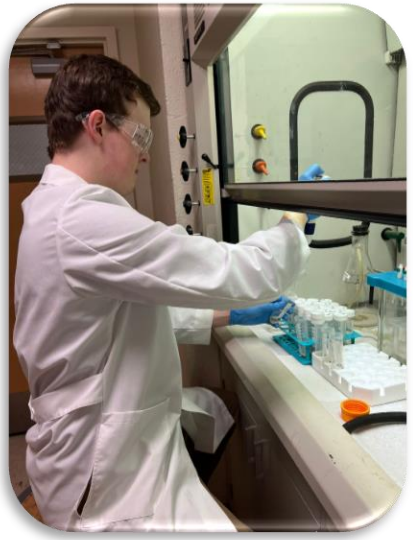
Juan Flores

Kristin Schaars



Peter Martin

Therese Reisch

Kaitlin Mohlenkamp

Josh von Werder

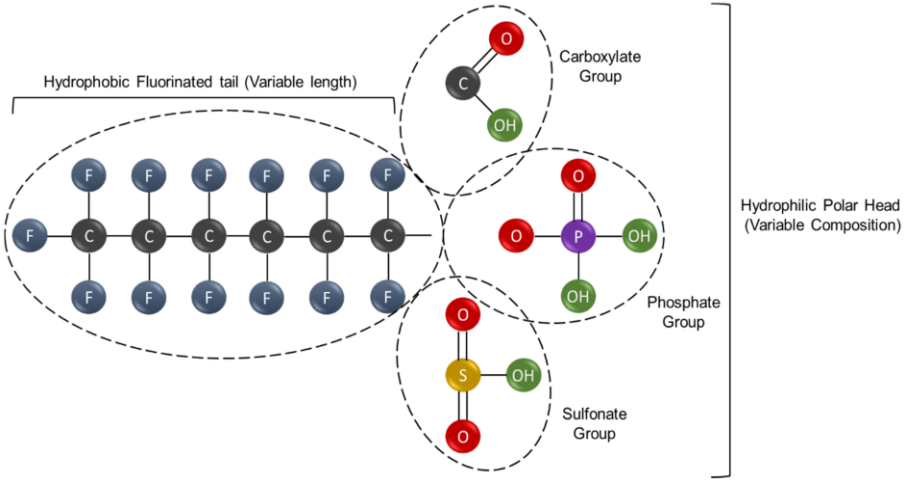
# Background

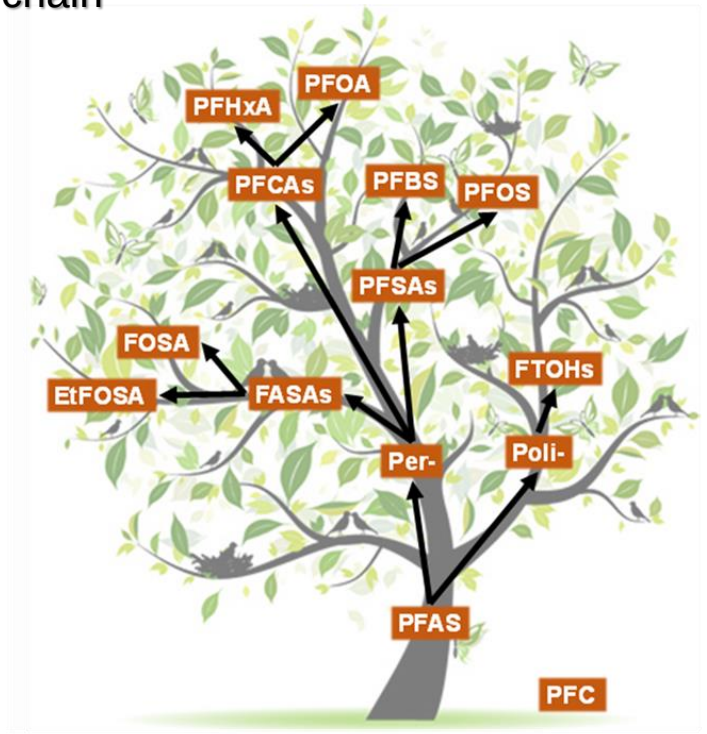
C-F bond

## Per- and polyfluoroalkyl substances

Carbon chain

Family of **manmade compounds** characterized by strong C-F bond




Adapted from ATSDR

Highly resistant to biotic and abiotic degradation

**More than 12,000 compounds identified (EPA, 2022)**

# Background

C-F bond

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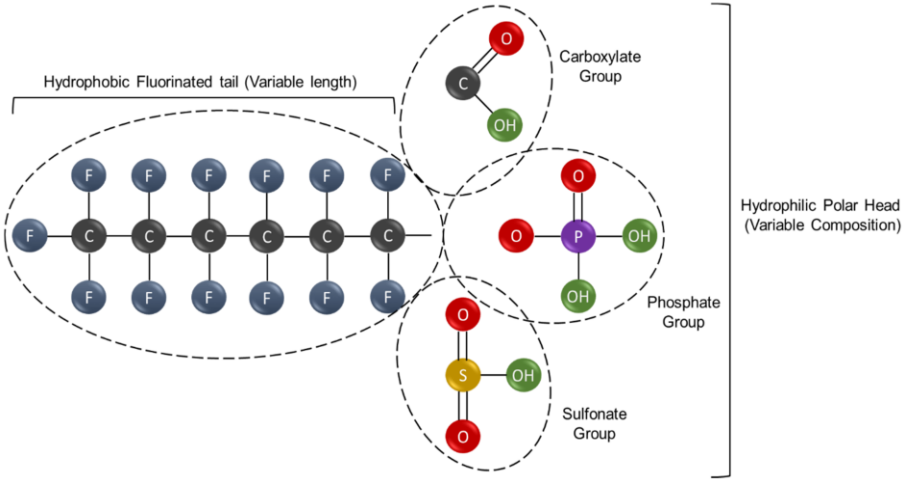


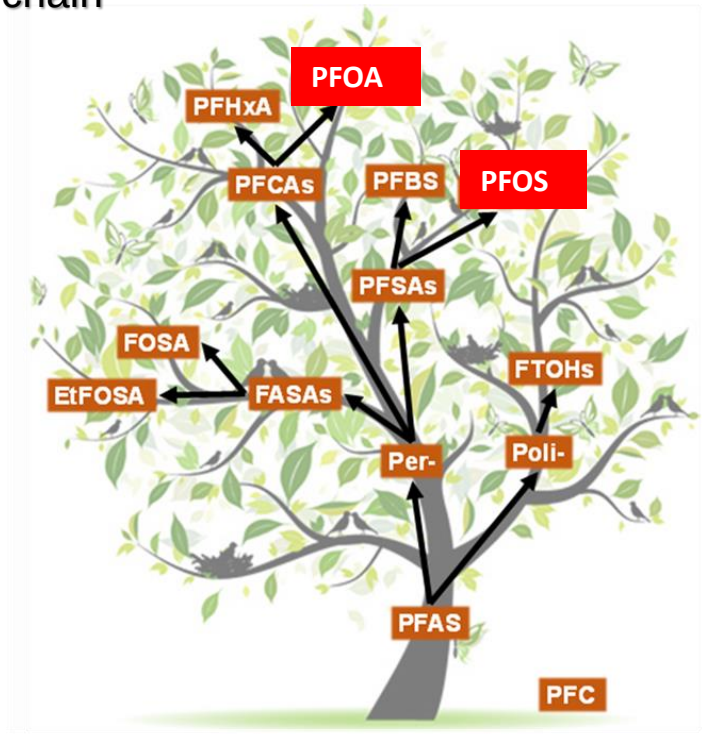


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# PFAS: Chemicals of concern that can be found in many industrial and everyday products

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Environmental Science & Technology Letters

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Letter

## Fluorinated Compounds in North American Cosmetics

Heather D. Whitehead, Marta Venier, Yan Wu, Emi Eastman, Shannon Urbanik, Miriam L. Diamond, Anna Shalin, Heather Schwartz-Narbonne, Thomas A. Bruton, Arlene Blum, Zhanyun Wang, Megan Green, Meghanne Tighe, John T. Wilkinson, Sean McGuinness, and Graham F. Peaslee*


pca.state.mn.us/waste/pfas-101

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ENVIRONMENTAL Science & Technology

pubs.acs.org/est

Article

## Per- and Polyfluoroalkyl Substances in North American School Uniforms

Chunjie Xia, Miriam L. Diamond, Graham F. Peaslee, Hui Peng, Arlene Blum, Zhanyun Wang, Anna Shalin, Heather D. Whitehead, Megan Green, Heather Schwartz-Narbonne, Diwen Yang, and Marta Venier*

Cite This: *Environ. Sci. Technol.* 2022, 56, 13845–13857 Read Online


pca.state.mn.us/waste/pfas-101

# Why do we care?

**Fish exposure to PFAS was related to:**

- Malformations and locomotor impairment in fish larvae
- Decrease in fish larval body length
- Morphological abnormalities and behavioral alterations
- Potential induction of differences in sex ratio

(Du *et al.*, 2009; Kielsen et al., 2016; Jantzen *et al.*, 2016; Liu *et al.*, 2015)

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**In humans:**

Low birth weight

Increased risk of kidney and testicular cancer, thyroid dysfunction, endocrine disruption and immunotoxicity.

(Du *et al.*, 2009; Kielsen et al., 2016; Jantzen *et al.*, 2016; Liu *et al.*, 2015)

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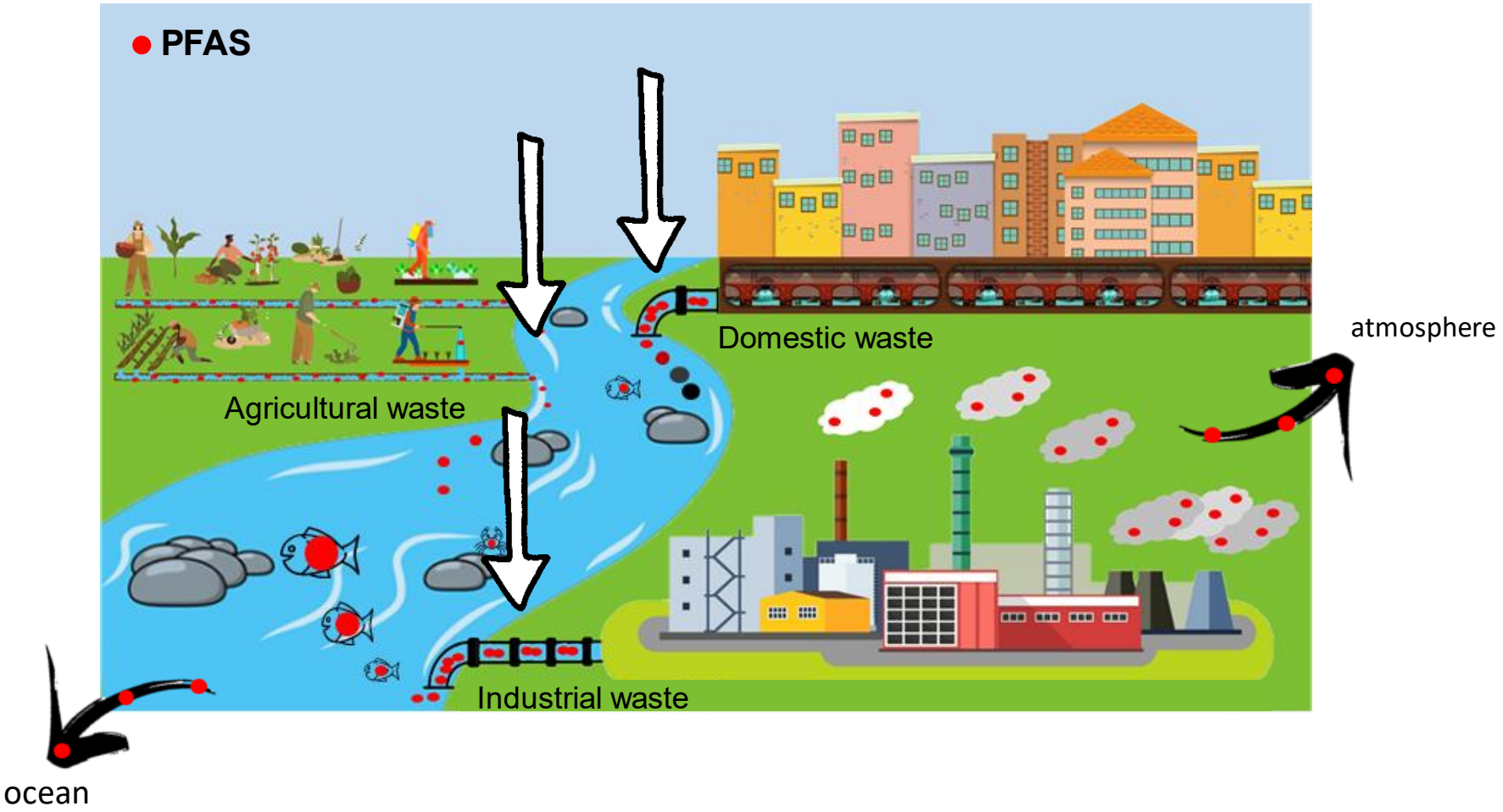
**PFAS** are known for their high persistence, toxicity, **rapid spread in water bodies**, and potential for bioaccumulation



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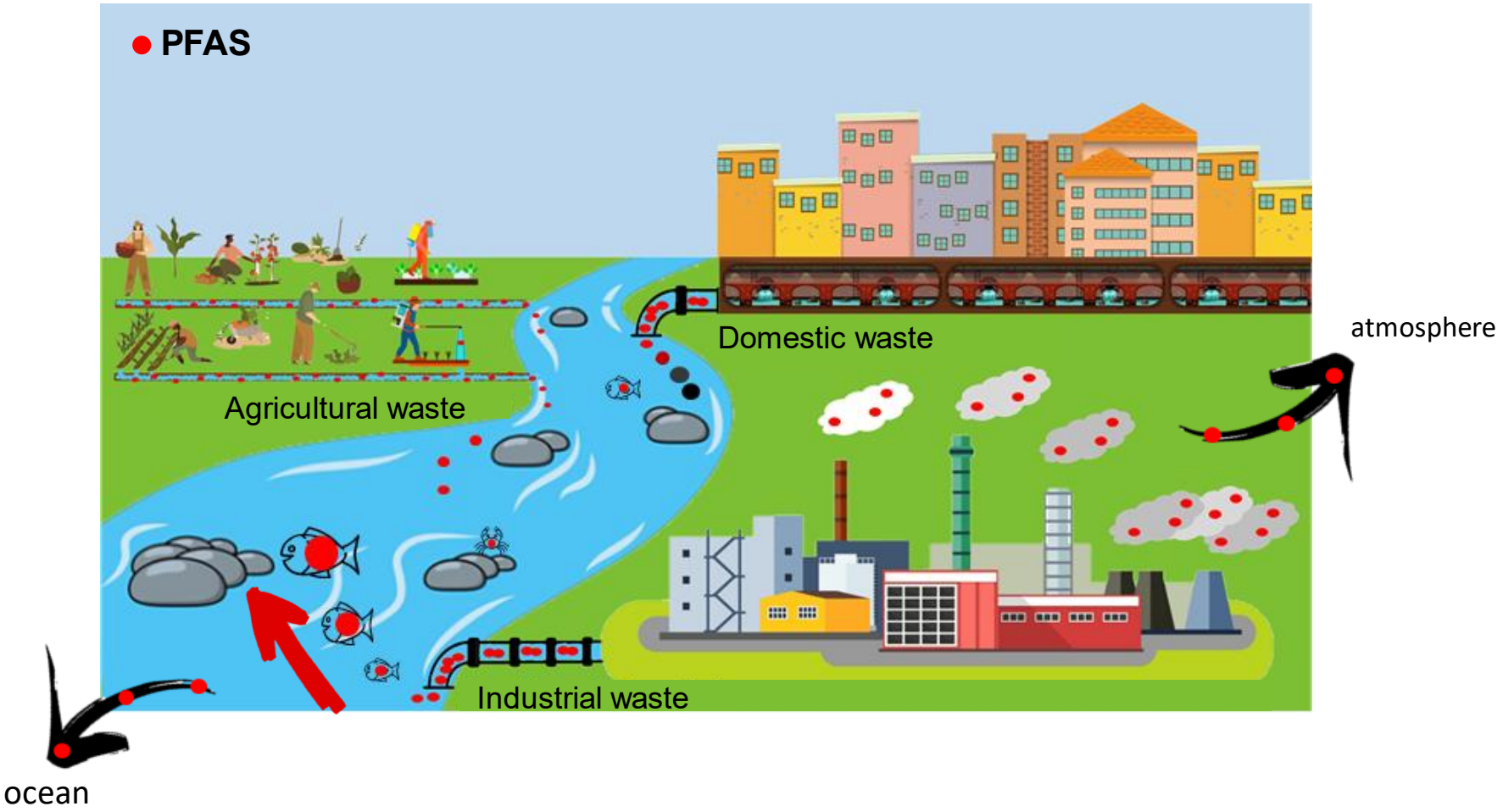


# Great Lakes Ecological Importance

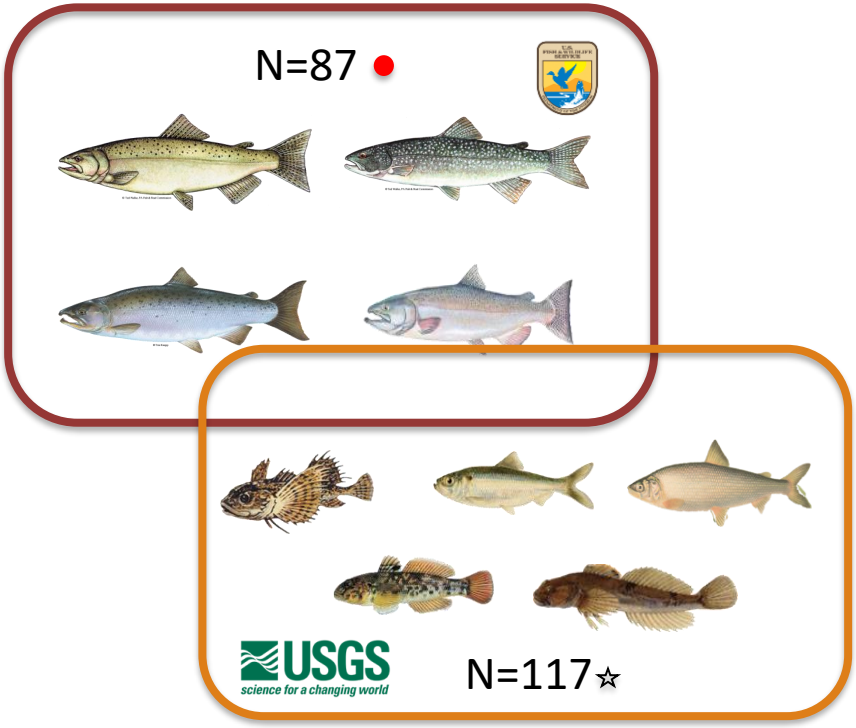
- 20% of world's surface freshwater
- Numerous ecosystem services
- Drinking water for 40 million people (EGLE 2019)
- Commercial and recreational fishery
- Economic driver for region

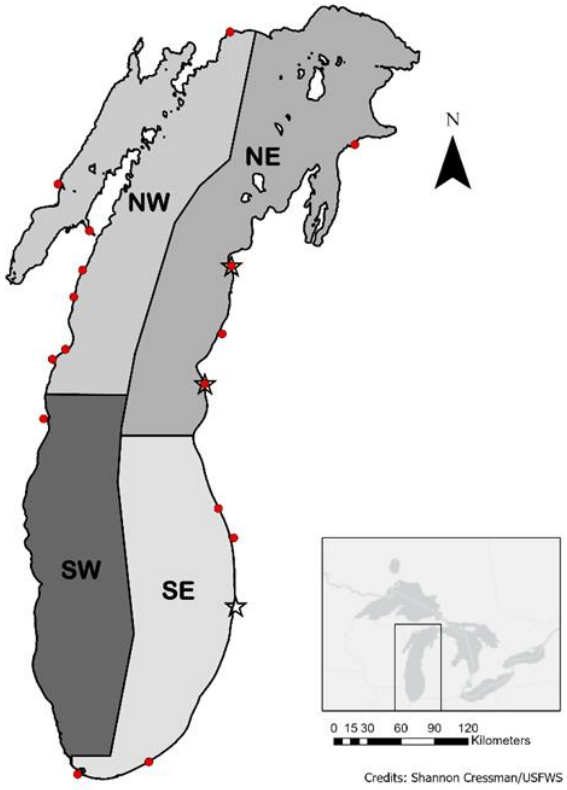
# Great Lakes Fishery

- ~$7B annual industry (GLFC)
- ~20M meals per year from commercial harvest alone (plus recreational)
- Indigenous importance and tribal fishing rights


Figure sourced from GLFC

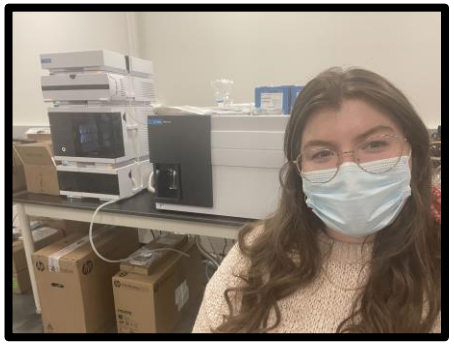
**Main goal:** In this study, **21 PFAS** were measured in **prey and predator fish** from Lake Michigan to understand how these compounds move through the **food web**.

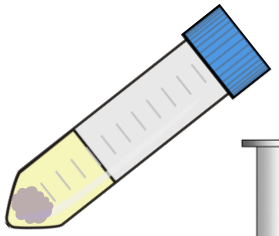



Miranda et al. (in prep)

# Methods: LC-MS/MS Analysis





0.5 g sample
(freeze-dried,
homogenized)

10 ppb ISTD

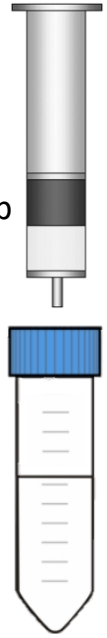
5 mL MeOH

**21 PFAS**: $C_4$-$C_{18}$ PFCA & $C_4$-$C_{12}$ PFSA


Sonication
30 minutes

Centrifugation
3.5 minutes
4500 rpm

ENVI-carb
Clean-up



Miranda et al. (in prep)

# Results

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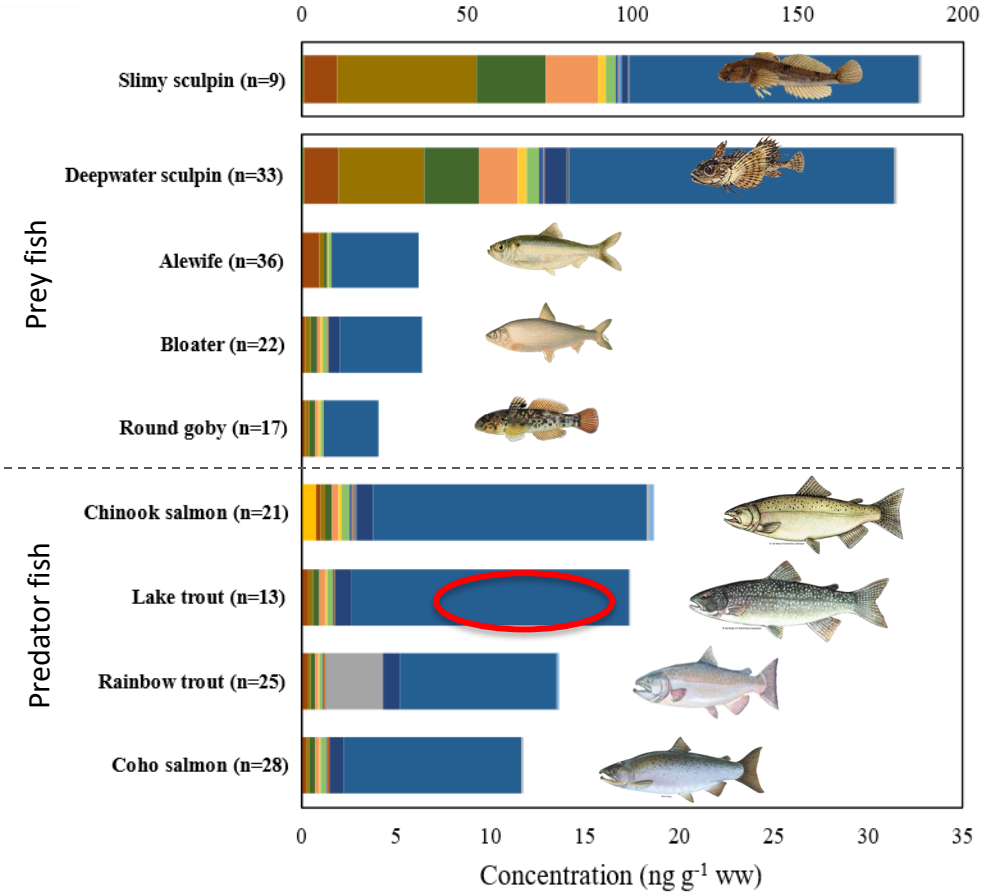
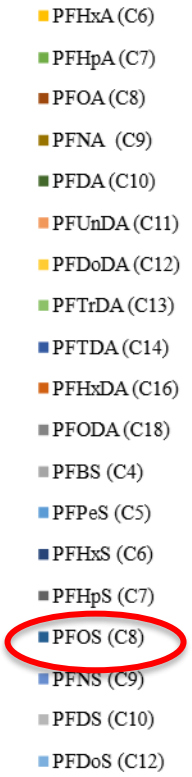
## PFAS were observed in all fish samples regardless of species




PFBA (C4)
PFPeA (C5)

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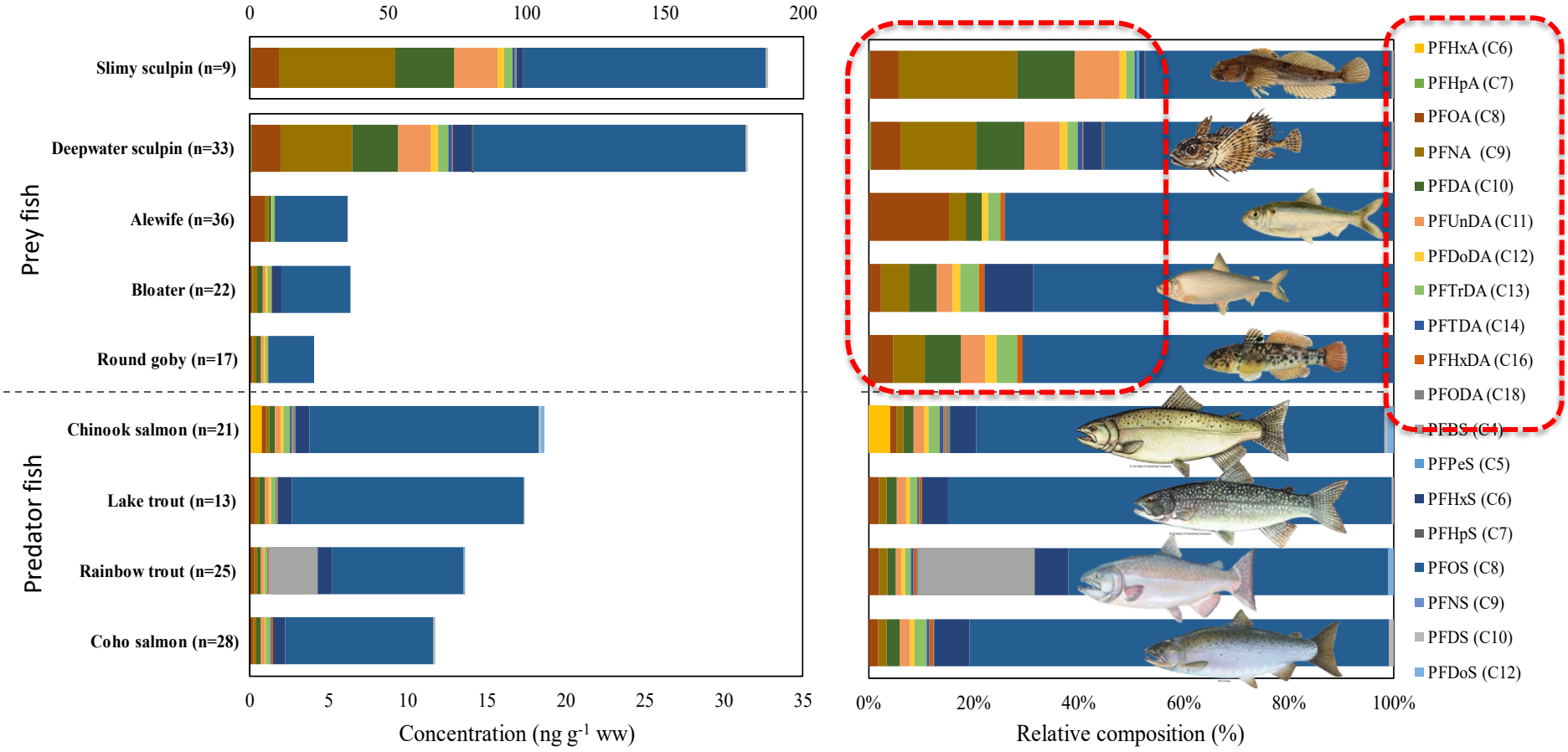


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# PFAS in Lake Michigan Fish - Take Home Points

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- PFAS were detected in all fish samples at varying concentrations
- PFOS was the most frequently detected compound (98% of samples)
- Generally, predator fish have higher concentrations of PFAS than prey fish, indicating potential for biomagnification of specific compounds
  - Interestingly, Slimy Sculpin and Deepwater Sculpin have higher PFAS concentrations than those in predator fish
- Proportion of PFCAs were higher in prey fish than in predator fish

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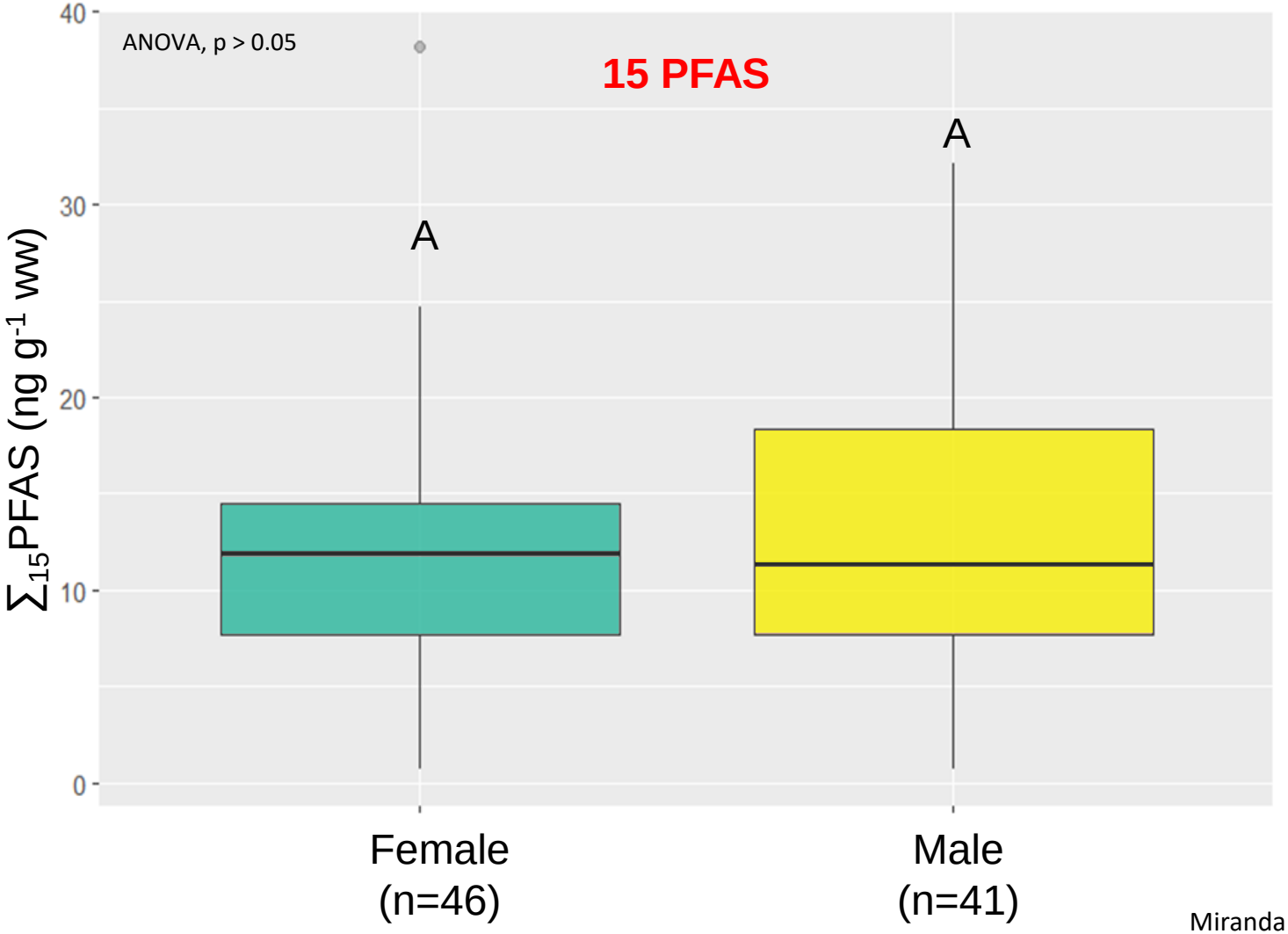
# PFAS in muscle of Males vs. Females (Salmonids)

PFAS concentrations **did not differ** between males and females for non-sexually mature salmonids

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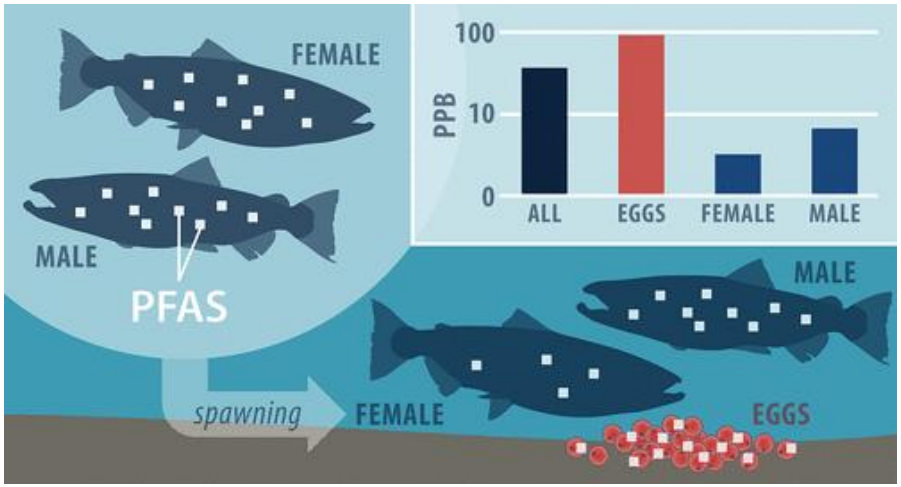
# Maternal offloading observed in salmonids




ENVIRONMENTAL Science & Technology LETTERS
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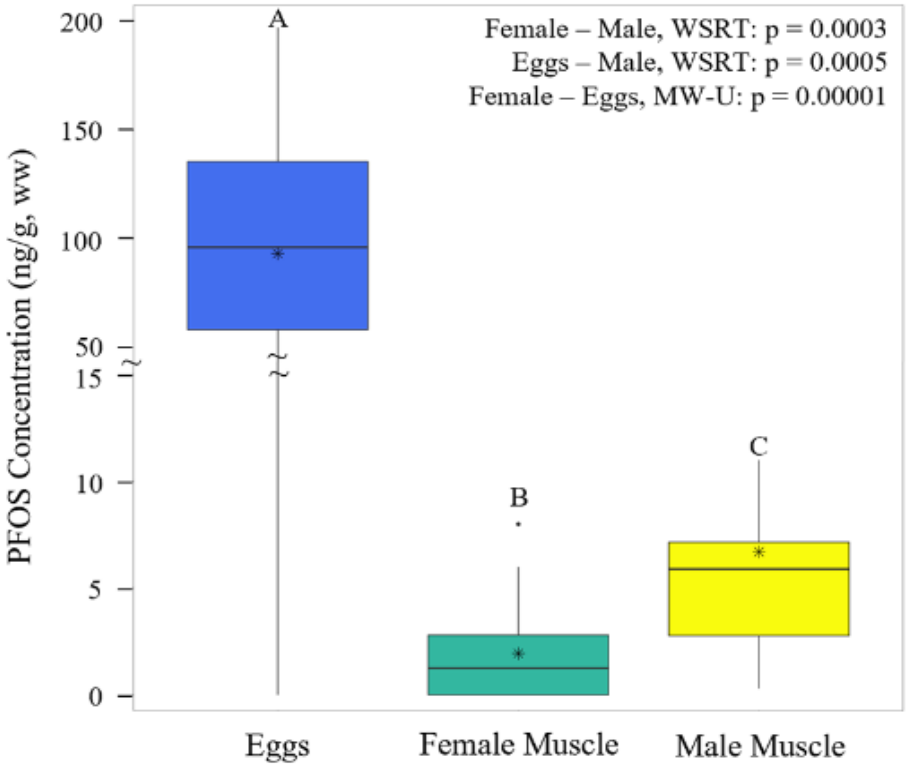
Letter

**Maternal Offloading of Per- and Polyfluoroalkyl Substances to Eggs by Lake Michigan Salmonids**

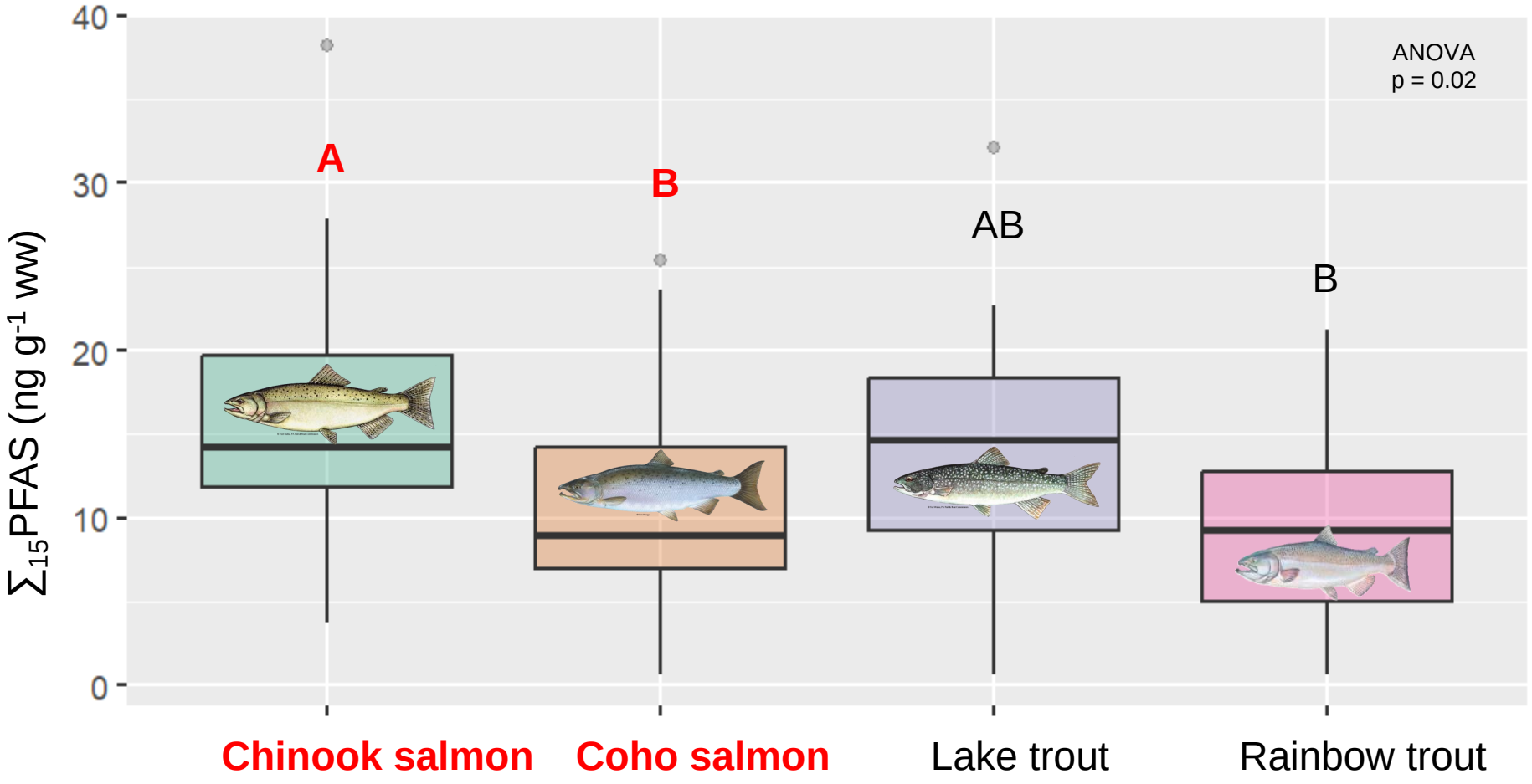
Whitney M. Conard,* Heather D. Whitehead, Keegan J. Harris, Gary A. Lamberti, Graham F. Peaslee, and Amy A. Rand

Cite This: *Environ. Sci. Technol. Lett.* 2022, 9, 937–942 Read Online

Sexually mature salmonids show difference **in PFOS accumulation**



# PFAS in different fish species

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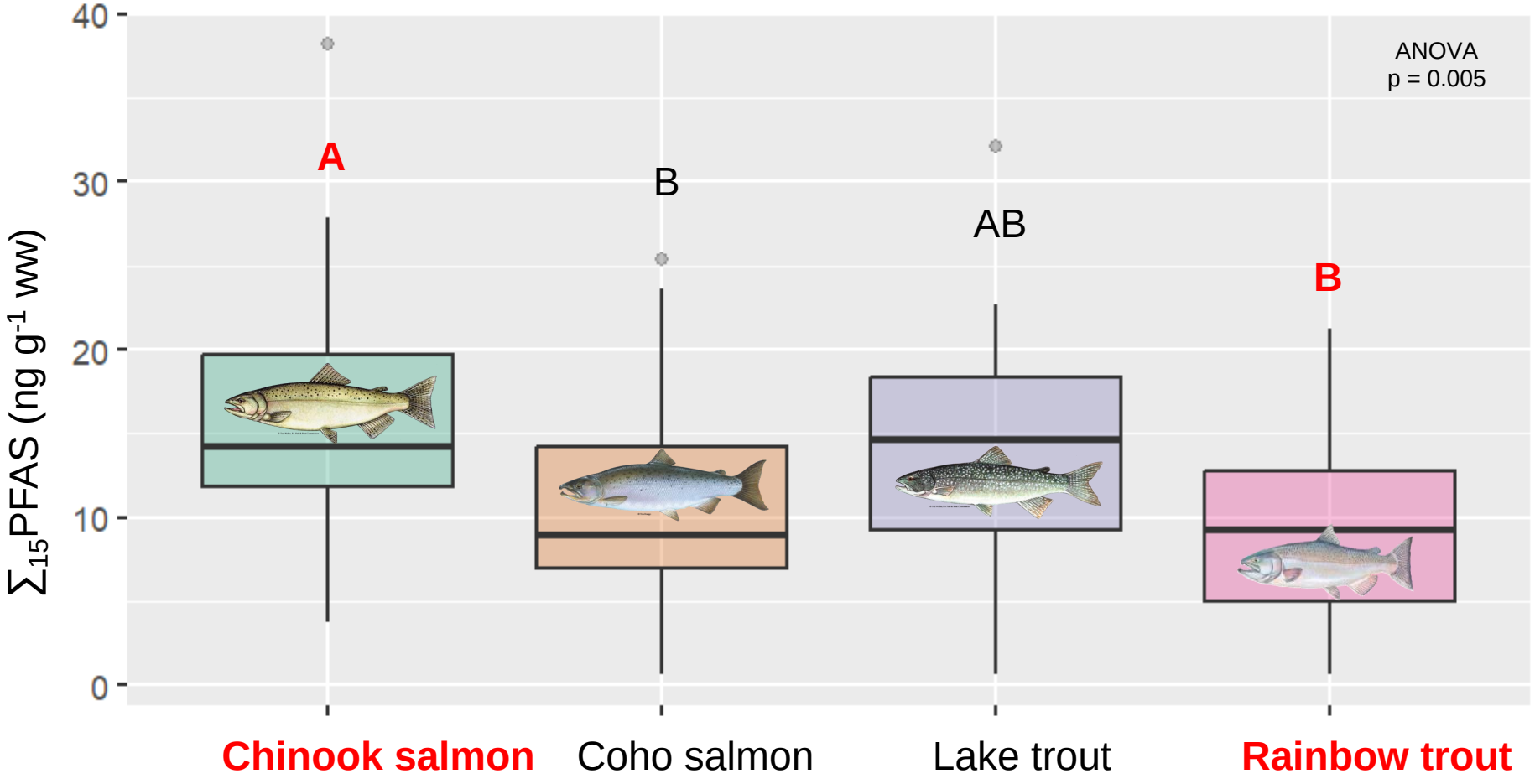
# PFAS in different fish species

PFOS, PFDA, PFDODA, and PFTrDA concentrations were **different** between some fish species

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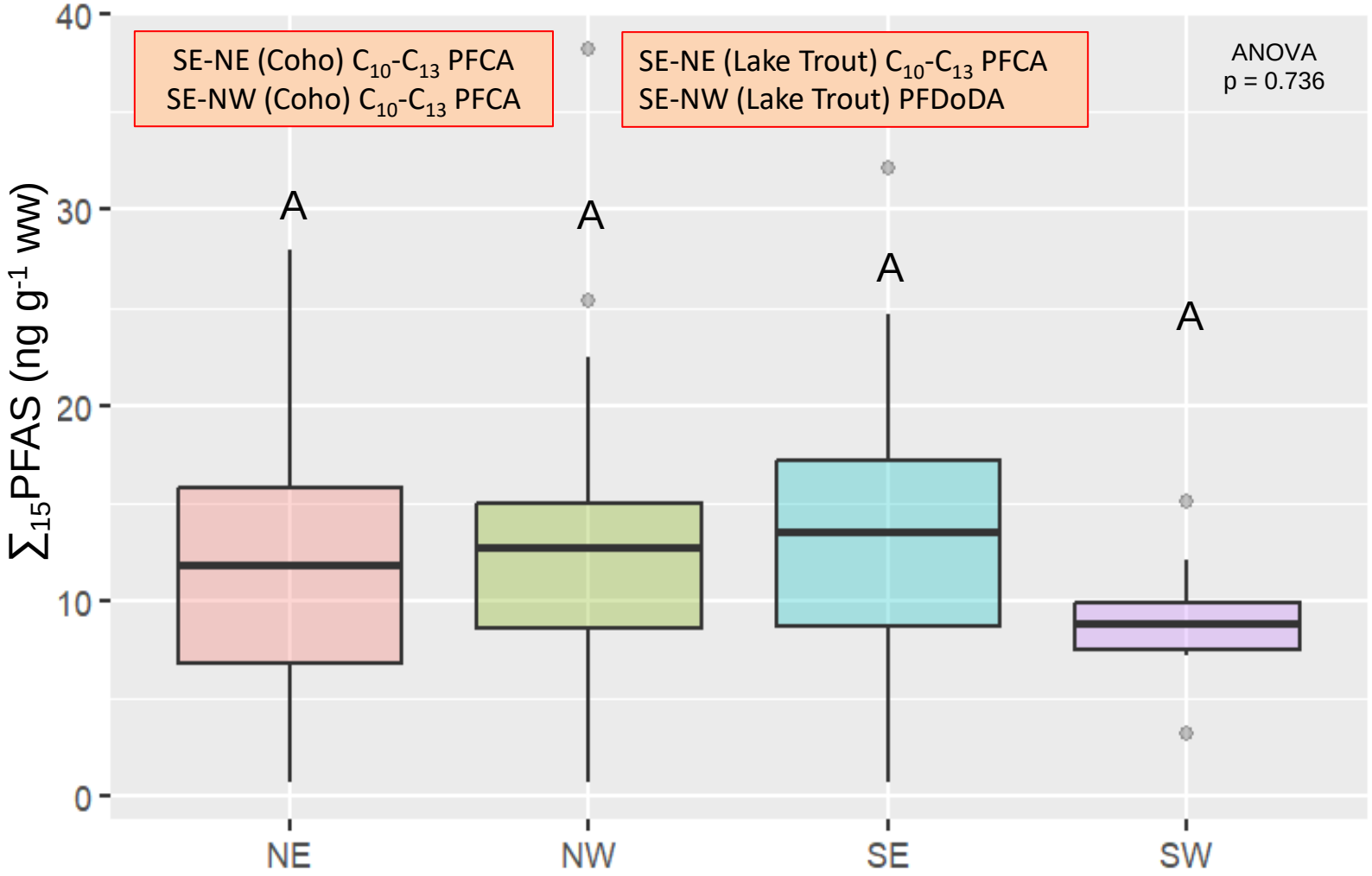
# PFAS in different Lake Michigan quadrants (all species)


PFAS sum was similar across Lake Michigan quadrants, but different for individual compounds in coho and lake trout




(small sample size)

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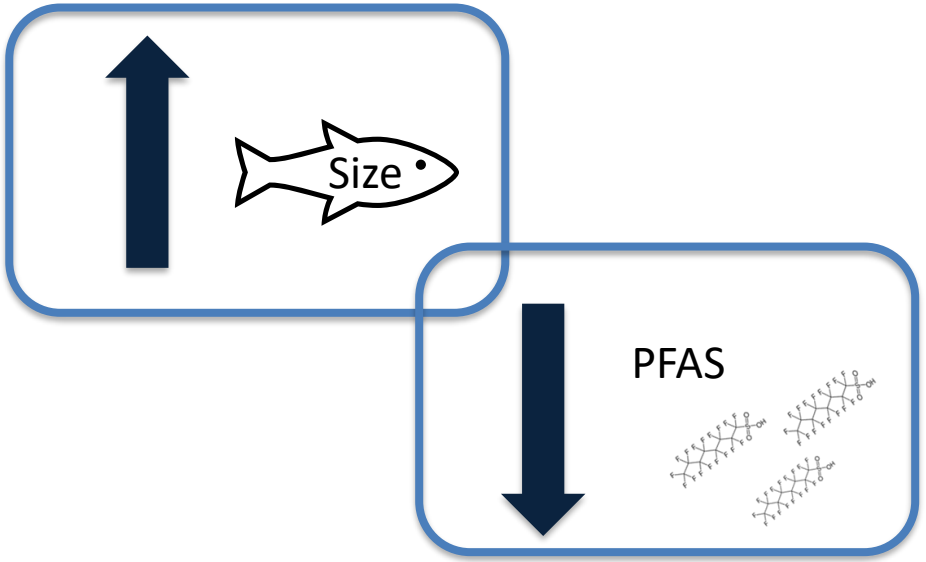
# PFAS x size - salmonids

PFAS decreased with increasing salmonid fish size

- All species: PFTrDA concentrations declined with increasing size
- Chinook
  - PFUnDA & PFDoDA
- Coho
  - PFUnDA & PFDA
- Lake trout
  - PFNA, PFUnDA and PFDoDA

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# Patterns Across Traits –Take Home Points

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- Concentrations of PFAS did not differ between sexes of salmonids caught in Lake Michigan
- Spawning salmon in tributaries showed a significant difference in PFAS concentrations between sexes, especially in PFOS
- Spawning females showed evidence of ‘offloading’ of PFOS to eggs
- PFAS concentrations were higher in Chinook Salmon than in Coho Salmon or Rainbow (Steelhead) Trout
- Specific PFAS compounds differed in concentration in the SE and NE quadrants for Coho and Lake Trout
- Specific PFAS compounds declined with increasing size in salmonids

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# Biomagnification Factors (**BMFs**)

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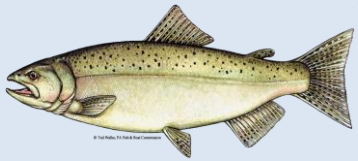
**PFOS**

$$BMF = \frac{Concentration\ in\ Predator}{Concentration\ in\ Prey}$$



Chinook salmon

Coho salmon

Lake trout

Rainbow trout

3.15

3.32

2.04

5.05

2.15

3.27

3.19

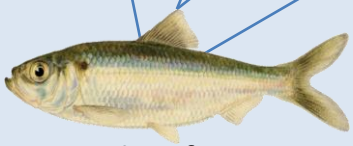
3.36

5.12

1.80

1.89

2.88



Alewife

Bloater

Round Goby

**Potential predator-prey relationships**

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# Biomagnification Factors (**BMF**s)

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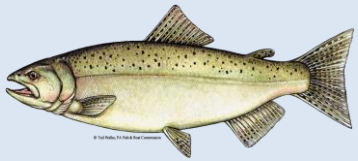
**PFOS**

$$BMF = \frac{Concentration\ in\ Predator}{Concentration\ in\ Prey}$$



Chinook salmon

Coho salmon

Lake trout

Rainbow trout

| Predator/Prey | PFOS | PFOA | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA |
|---|---|---|---|---|---|---|---|
| Chinook :alewife | **3.15** | 0.25 | **1.15** | **1.94** | 0.90 | **2.15** | **2.67** |
| Chinook : bloater | **3.32** | **1.51** | 0.68 | **1.06** | **1.88** | **1.94** | **1.77** |
| Chinook : round goby | **5.05** | **1.26** | 0.92 | **1.26** | **1.93** | **2.03** | **2.49** |
| Coho : alewife | **2.04** | 0.23 | **0.98** | **1.54** | 0.57 | **1.32** | **1.81** |
| Coho : bloater | **2.15** | **1.38** | 0.58 | 0.84 | **1.17** | **1.19** | **1.20** |
| Coho : round goby | **3.27** | **1.15** | 0.78 | 1.00 | **1.21** | **1.25** | **1.69** |
| Lake trout : alewife | **3.19** | 0.37 | **1.30** | **1.80** | 0.79 | **1.38** | **1.73** |
| Lake trout : bloater | **3.36** | **2.23** | 0.78 | 0.98 | **1.64** | **1.24** | **1.15** |
| Lake trout : round goby | **5.12** | **1.86** | **1.04** | **1.17** | **1.69** | **1.30** | **1.61** |
| Rainbow trout : alewife | **1.80** | 0.29 | **1.08** | **1.27** | 0.36 | **1.06** | 0.98 |
| Rainbow trout : bloater | **1.89** | **1.76** | 0.64 | 0.70 | 0.74 | 0.95 | 0.65 |
| Rainbow trout : round goby | **2.88** | **1.47** | 0.86 | 0.83 | 0.77 | 1.00 | 0.92 |

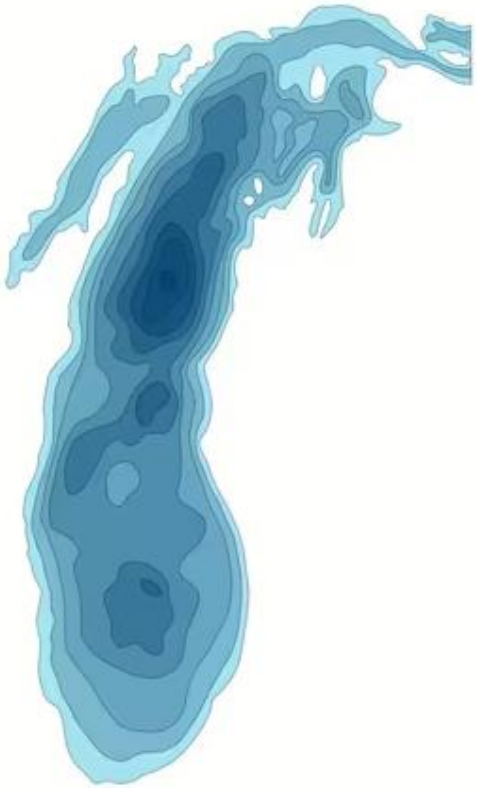
Alewife

Bloater

Round Goby

Miranda et al. (in prep)

# Summary



- PFAS were found in **all Lake Michigan fish** but display a lower burden when compared to other Great Lakes.
- PFAS composition and concentration were more similar in predator fish than among prey fish.
- PFAS in salmonids was observed across Lake Michigan independent of location, whereas compound profile accumulation varied depending on fish species and individual compounds.
- **PFOS** was the **dominant compound** in fish from Lake Michigan, even 20 years after its phase-out. PFOS also biomagnifies in these fish.

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# Current & Future Directions

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- Evaluation of PFAS in native fish species from Lake Michigan (GLFT)
- Investigation of PFAS distribution across different fish tissues (GLFT)
- Lake Michigan tributaries as storage and delivery areas for PFAS (USGS)
- Comparison of findings to evolving human health guidelines (USGS/IISG)
- Occurrence of PFAS in Water and Sediment from the Indiana Coastal Zone (IDNR/LMCP)

UND SWEL Stream & Wetland Ecology Lab

www.swel.nd.edu

# Acknowledgments


ASSISTANCE

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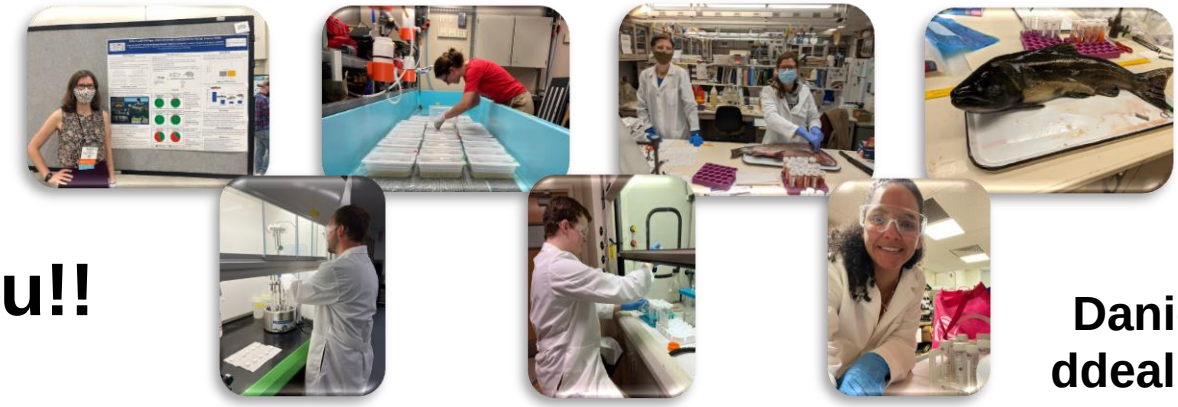

**Thank you!!**


**Daniele Miranda**
**ddealmei@nd.edu**