Removing Forever Chemicals (PFAS) From North Carolina Waters

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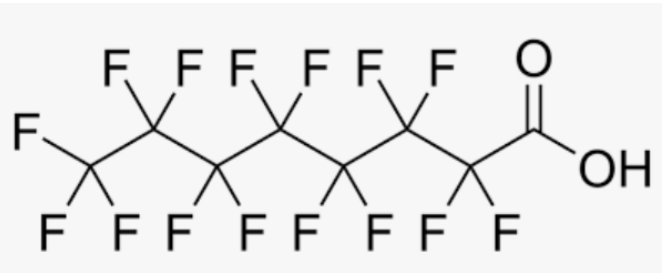
COI disclosure: Prof. Coronell and Prof. Leibfarth have a financial interest in Sorbenta, Inc. which could potentially benefit from the outcomes of this research

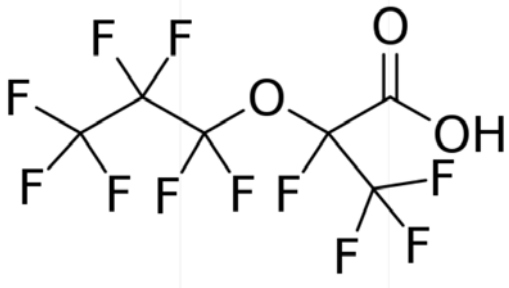
Part I: The Problem, The Challenges, and Our Efforts to Address Them

What are per- and polyfluorinated alkyl substances (PFAS)?

- Also known as "forever chemicals"
- Large class of man-made chemical with fluorinated backbones (since 1930s)
- Thousands of PFAS in use today

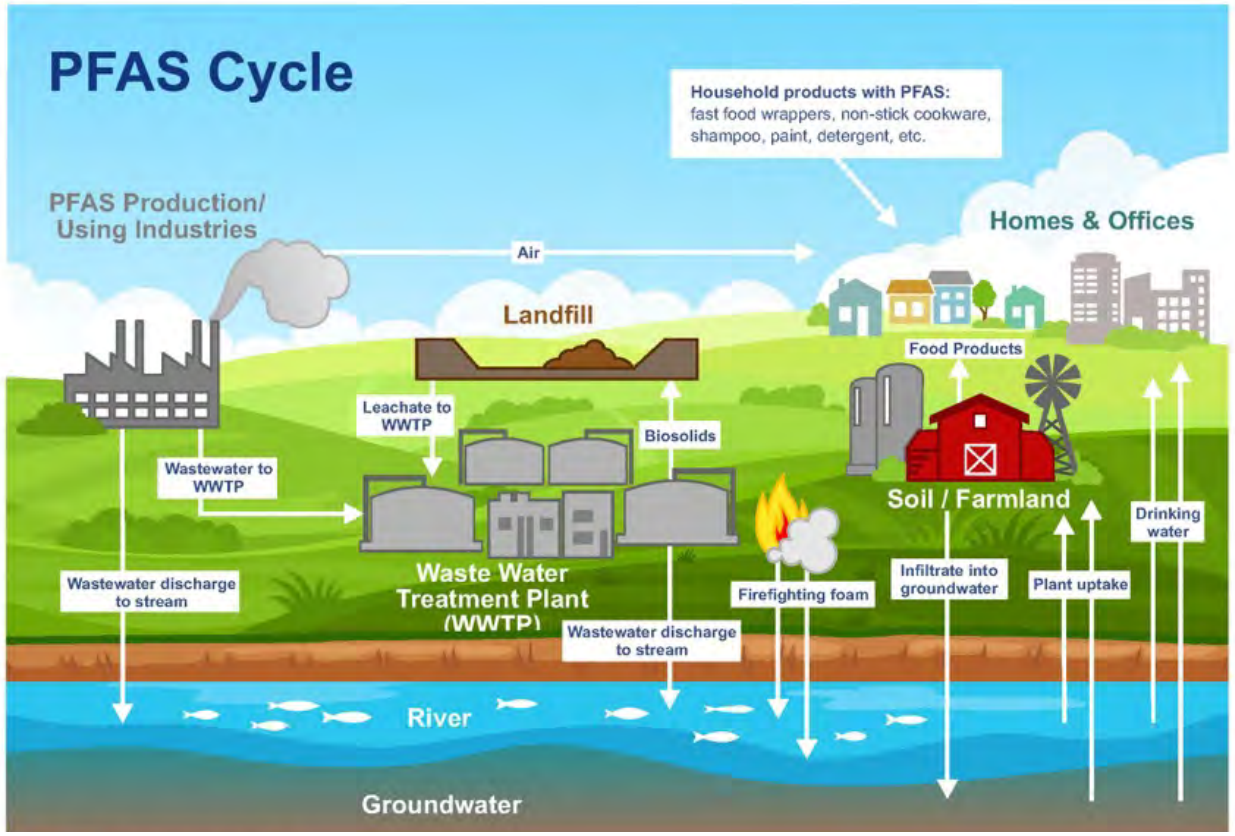


PFOA

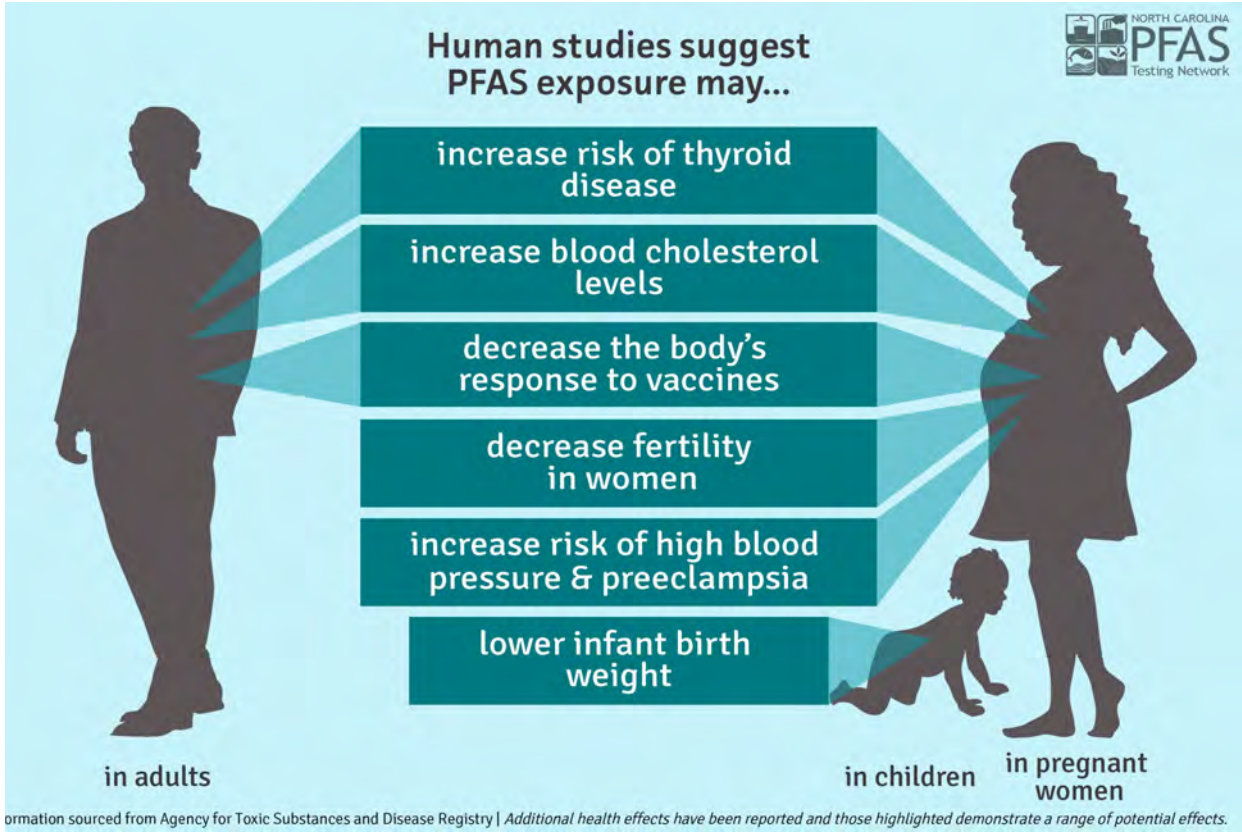


GenX

PFAS Are Pervasive, Persistent, Bioaccumulative, and Toxic



https://www.dep.pa.gov/pfas



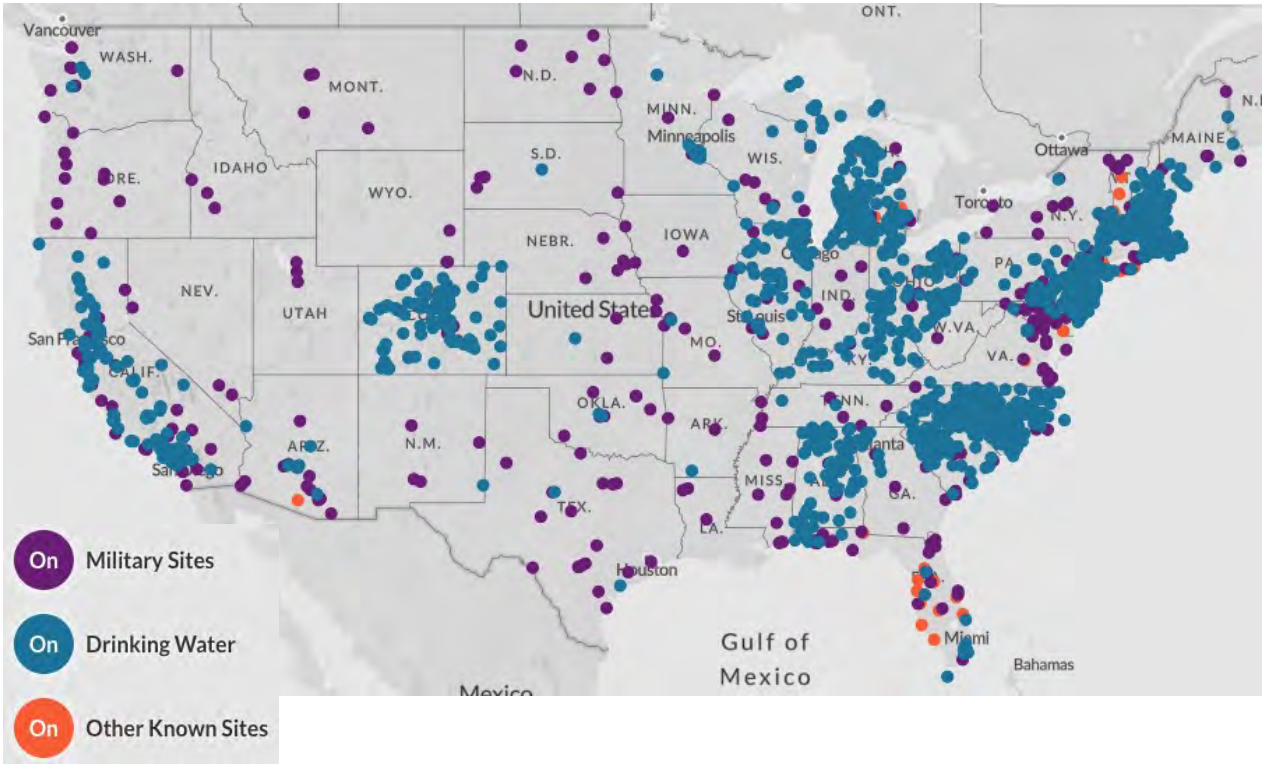
https://ncpfastnetwork.com/printed-materials/

PFAS Are Pervasive, Persistent, Bioaccumulative, and Toxic

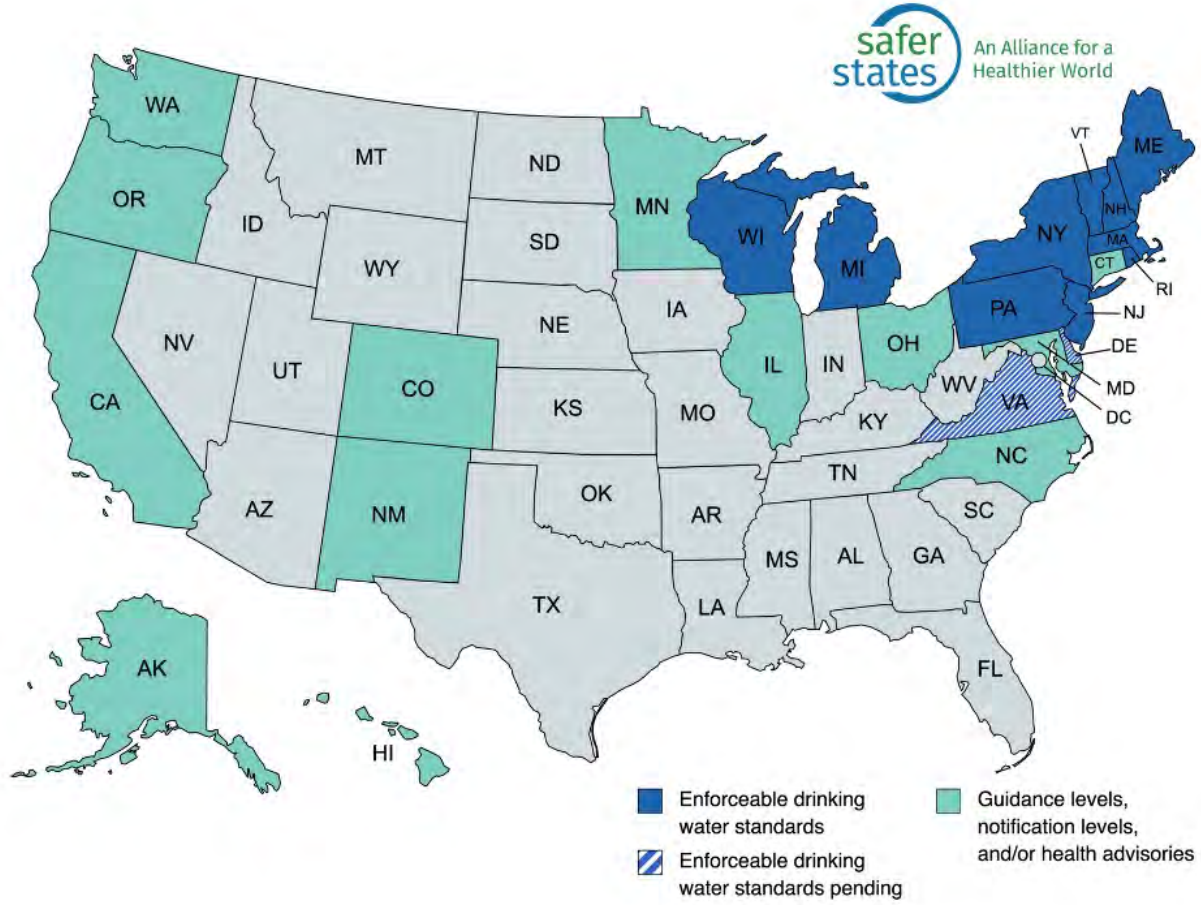
"Every level of government […] needs to exercise increased and sustained leadership **to accelerate progress to clean up PFAS contamination, prevent new contamination**, and make game-changing breakthroughs in the scientific understanding of PFAS. "

PFAS Strategic Roadmap
US Environmental Protection Agency

There Is a Need For Effective Technologies That Remove PFAS From Water



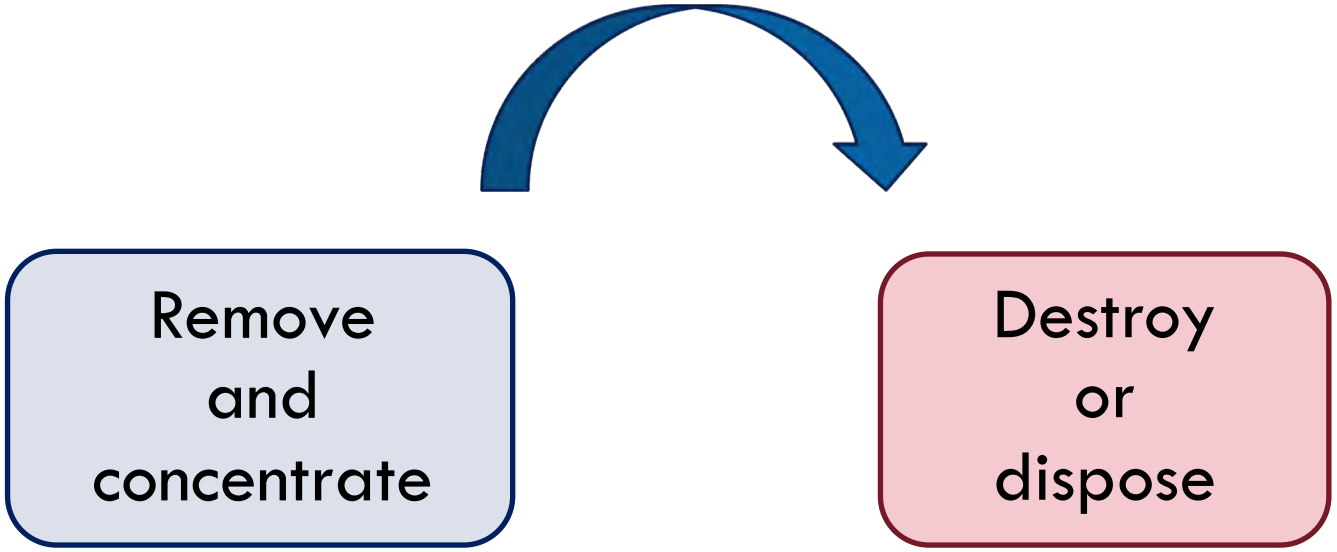
https://www.ewg.org/interactive-maps/pfas_contamination/map/



Federal (EPA) Regulations for 6 PFAS are imminent (Spring 2024)

https://www.saferstates.org/priorities/pfas/

Control of PFAS in Contaminated Waters



Technology Options For PFAS Removal and Concentration

RO Membranes

Sorbents

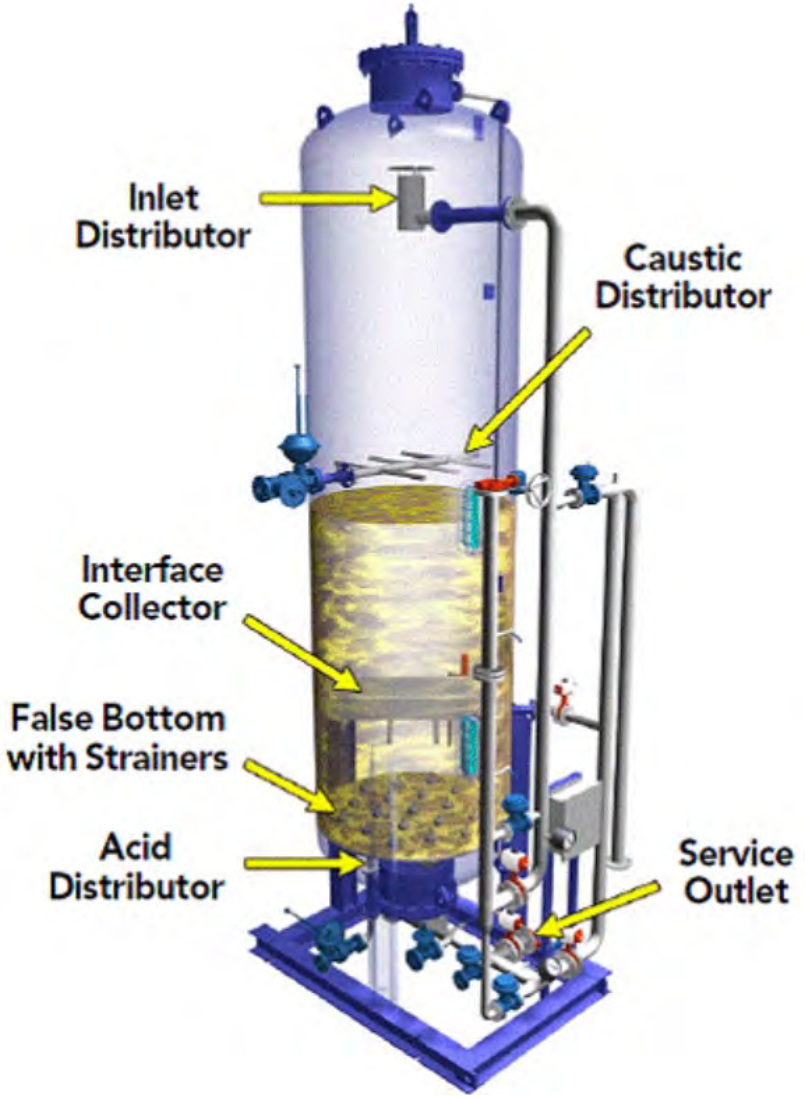
Activated Carbon (AC)

Anion Exchange Resins (AERs)

Novel Sorbents

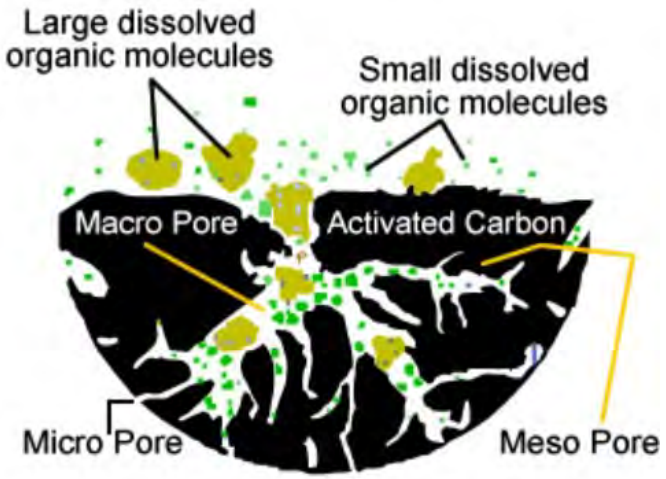
Activated Carbon (AC) And Ion Exchange Resins (IERs)

https://www.ovivowater.com/en/product/ion-exchange/

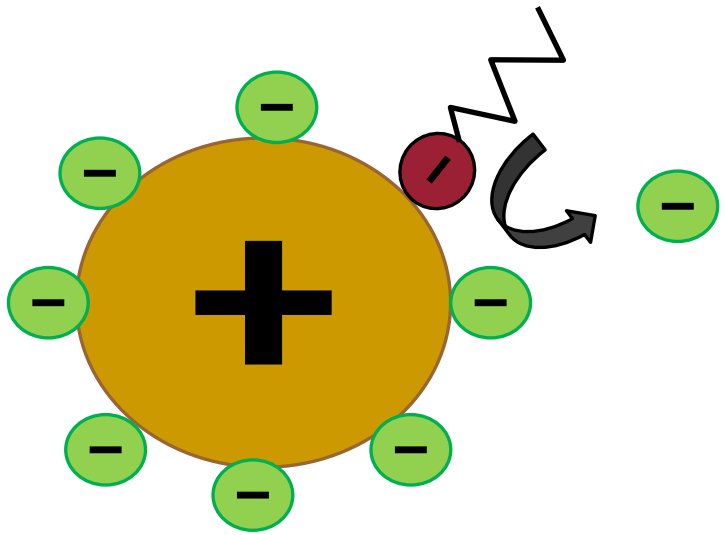


https://www.membranechemicals.com/

Activated Carbon (AC) And Ion Exchange Resins (IERs)



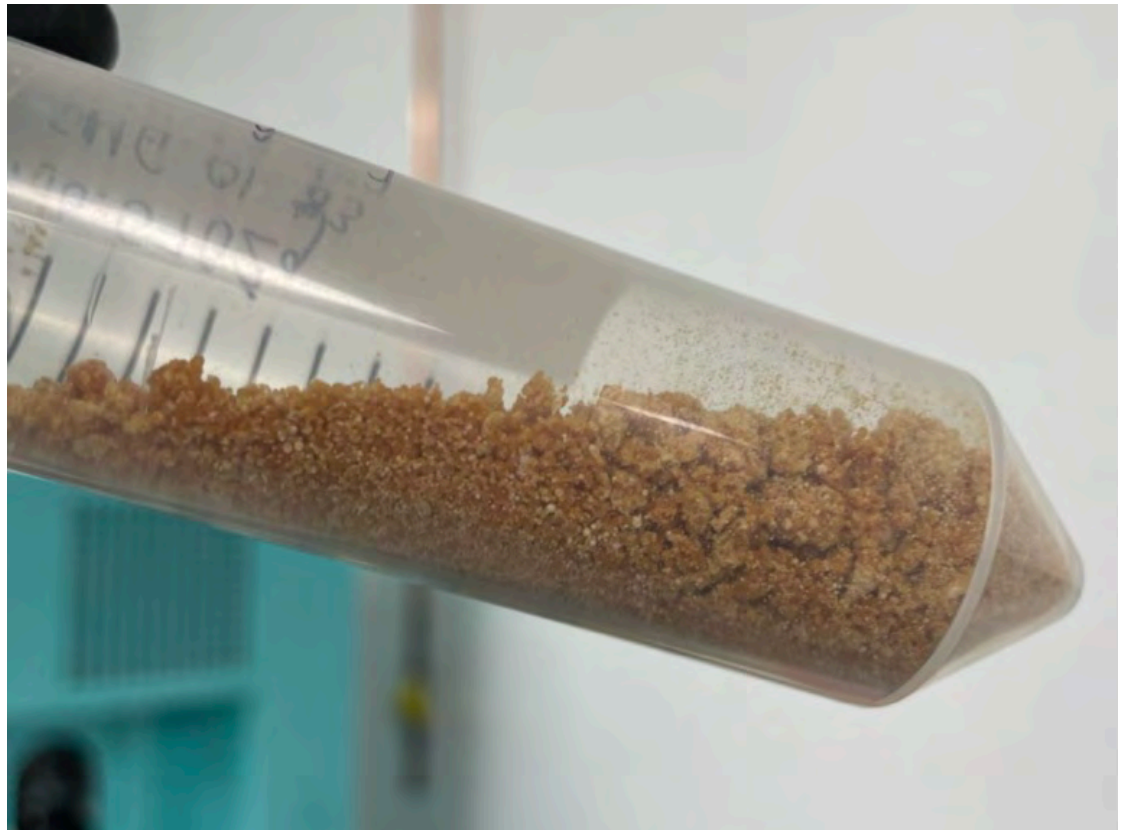
www.sushrutchemicals.com



- Strengths:
  - Effective for removal of long-chain PFAS
  - Trusted technologies
  - Multipurpose (AC)

- Weaknesses:
  - Insufficient selectivity
  - Not effective for short-chain PFAS
  - Single-use sorbents

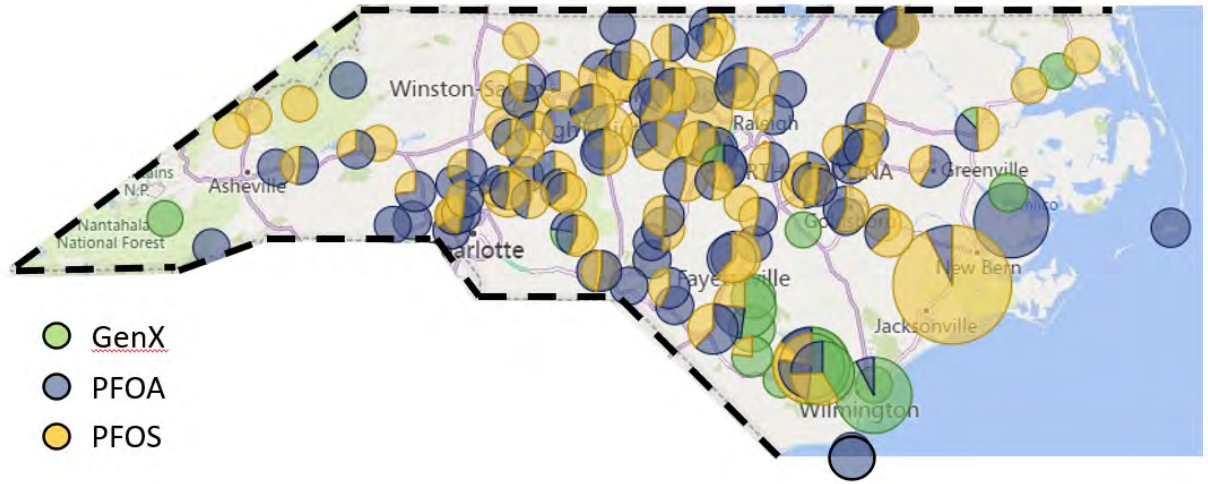
A Drop-In Novel Sorbent Solution With Differentiated Performance



- High capacity: more PFAS removed per mass of sorbent
- High selectivity: designed for PFAS affinity over background contaminants
- Broad efficacy: effective at removing long- and short-chain PFAS
- Regenerable: enables reuse and advantaged total cost of ownership

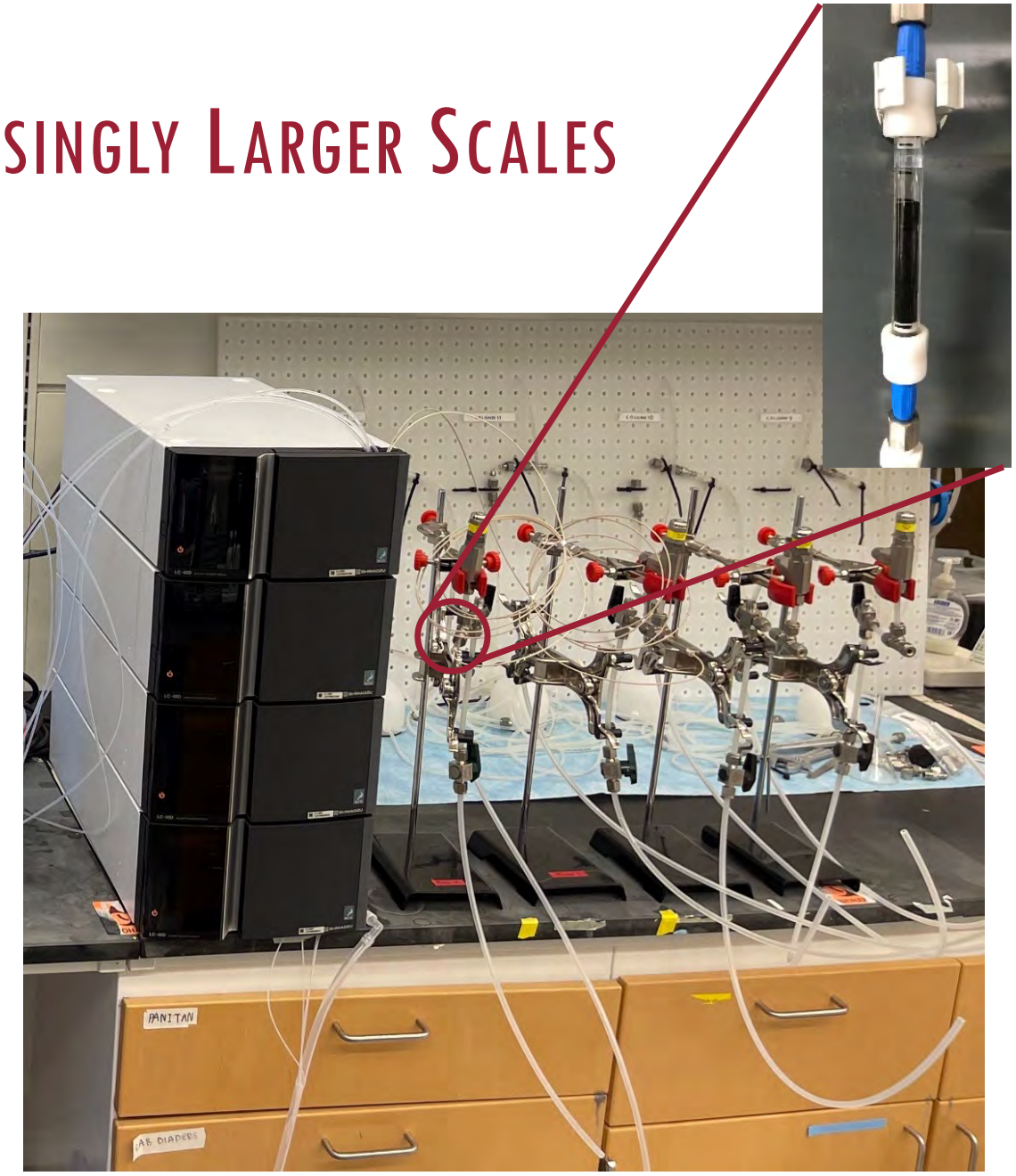
NC PURE

- **NC Pure** is developing and evaluating novel sorbents at sequentially larger scales, up to pilot scale
- This includes upscaling manufacturing and performance testing of novel sorbents alongside benchmark commercial sorbents



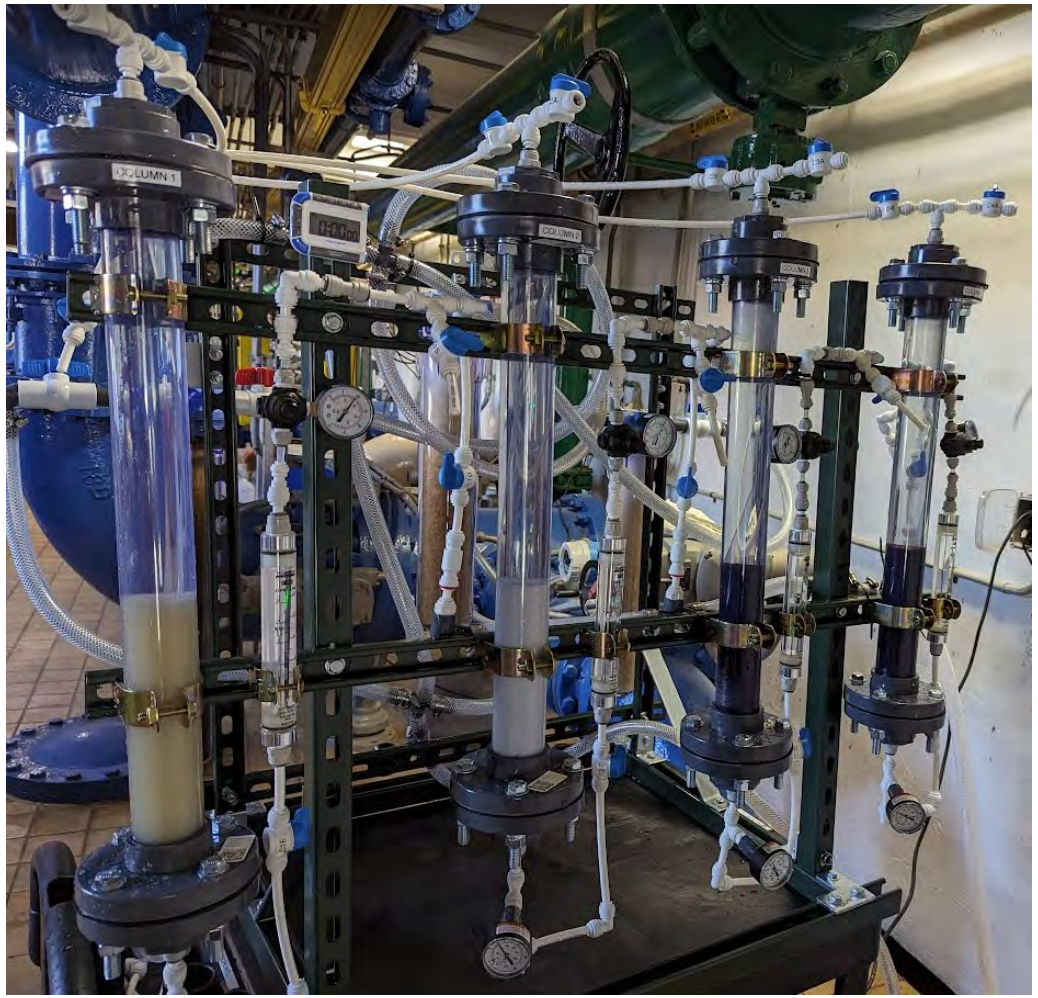
Performance Evaluation at Increasingly Larger Scales

Screening in Batch Tests

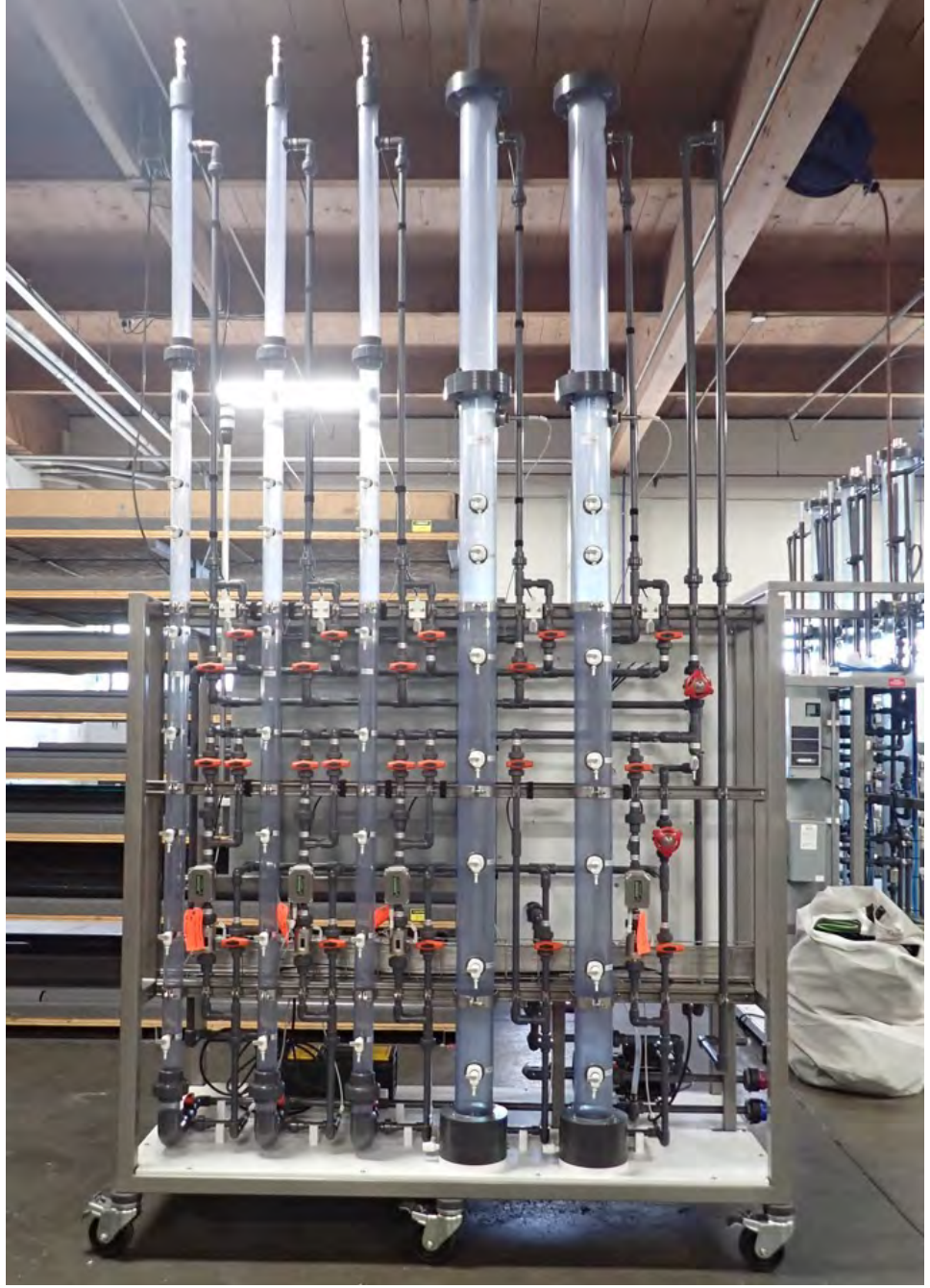


Screening in RSSCTs

Performance Evaluation at Increasingly Larger Scales



Accelerated Pilots



Full Pilots

Manufacturing and Analytical Facilities

Reactors of various scales for suspension polymerization resin manufacturing

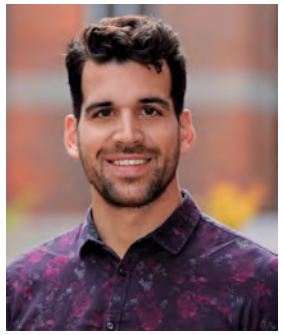
UHPLC-MS for measuring PFAS at low ng/L concentrations

Establishing Partnerships

Utility Region	Surface Water	Groundwater	Wastewater
Lower Cape Fear	✓ (RSSCT, Pilot)	✓ (RSSCT, Pilot)	
Piedmont Triad	✓ (RSSCT)		✓ (RSSCT, Pilot)
Piedmont Triad	✓ (RSSCT)		
Triangle	✓ (RSSCT, Acc. Pilot)		✓ (RSSCT)

NC Pure Project Team

- Interdisciplinary team of chemists, water engineers, and chemical engineers
- 14 team members working on project full or part time

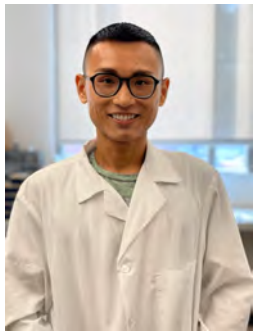


Prof. Frank Leibfarth
Co-Project Leader

Prof. Orlando Coronell
Co-Project Leader

Dr. Irene Manning
Lead Research Chemist

Dr. Alexander Gorzalski
Engineering Consultant



Dr. Nick Chew
Water Process Engineer

Sontia Gaither
Synthetic Chemist

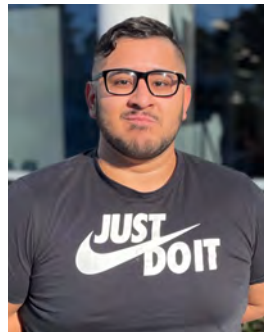
Jenna DeMartino
Analytical Chemist

Emily Watts
Chemical Engineer

Abigail Sveen
Water Process Scientist

Graham Parker
Graduate Student

Cynthia Corley
Lab Manager



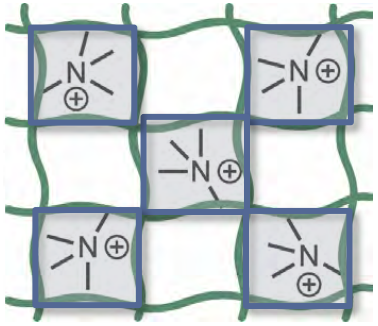
Elias Arroyo
Research Scientist

Part II: Novel Sorbents R&D At UNC

Ionic Fluorogel resins for PFAS remediation

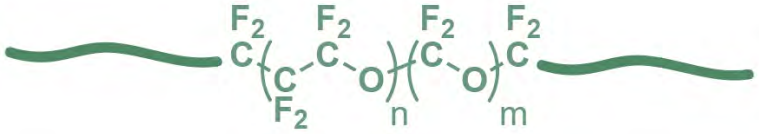
Challenge: Remove short chain PFAS in the presence of 1,000 to 100,000 times the concentration of natural organic contaminants

Hypothesis: Develop resins that are more selective for PFAS compared to organic contaminants



Ionic Fluorogel (IF)

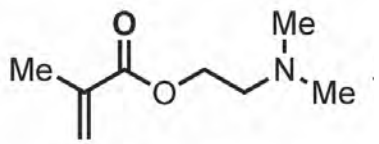
Fluorophilicity



Partially Fluorinated Polymers

- Amorphous oligomers with high fluorine density
- Synthesized without PFAS surfactants

Ion Exchange

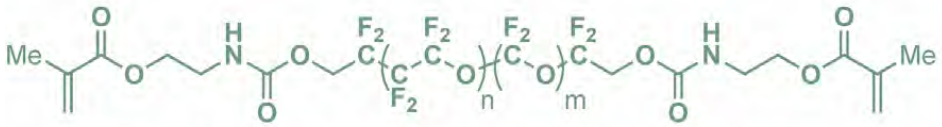


- State-of-the-art resin technology
- Exchange of anion PFAS with a cationic resin
- Limited success for short-chain PFAS

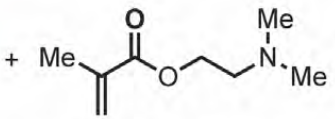
Synthesis of Ionic Fluorogels

Dr. Irene Manning

Dr. Elango Kumarasamy

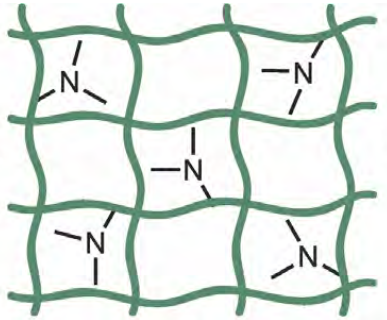


Fluorolink® MD700: M_n = 1800 g/mol



DMAEMA

X = 0 – 60 wt %



IF-X

- *Commercially available*
- *Surfactant-free production from tetrafluoroethylene*

ACS *Cent. Sci.* **2020**, *6*, 487–792.

Synthesis of Ionic Fluorogels

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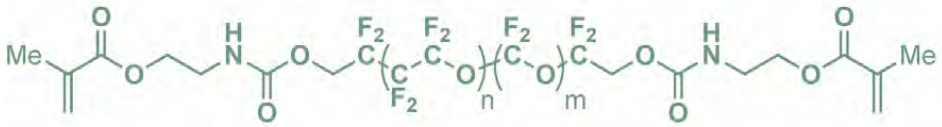

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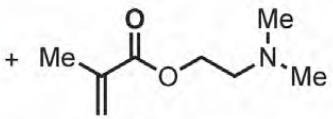

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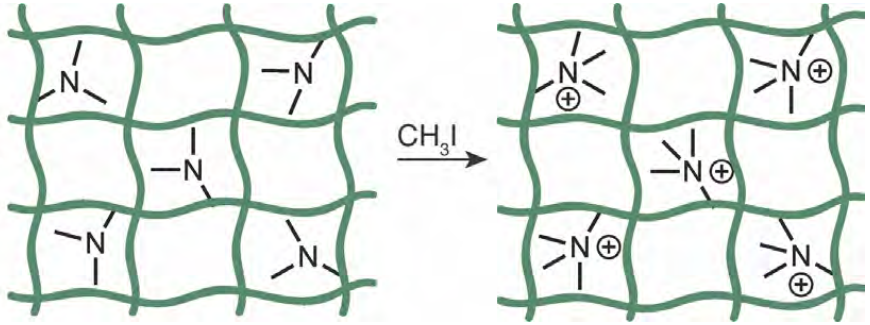


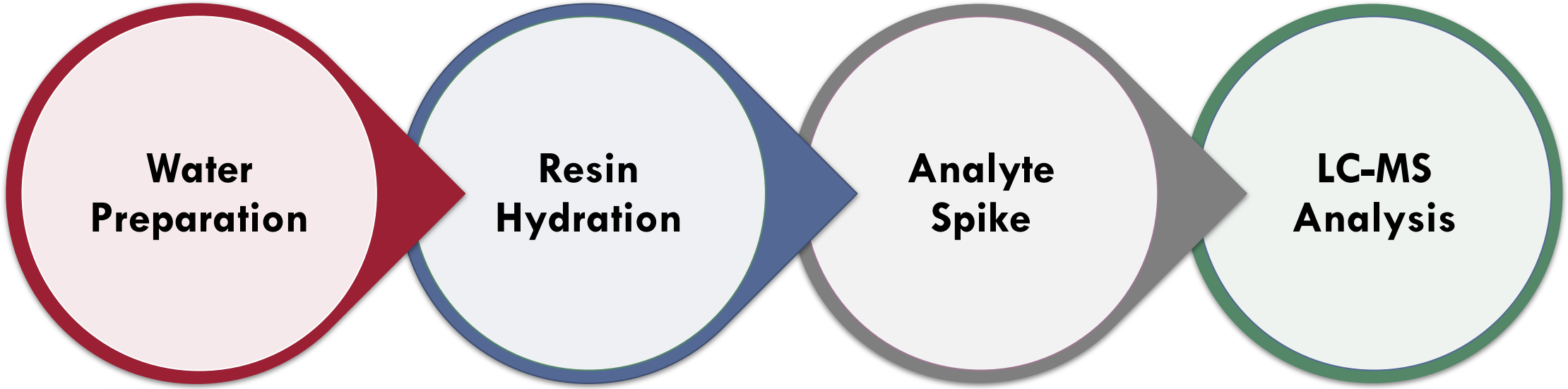
IF-X **IF-X+**

- *Commercially available*
- *Surfactant-free production from tetrafluoroethylene*

- *Systematic material library synthesized with varying ratios of fluorous and ionic interactions*
- *Mild reaction conditions*
- *Multi-gram scale*

ACS Cent. Sci. **2020**, 6, 487–792.

Experimental setup: Batch Equilibrium Sorption



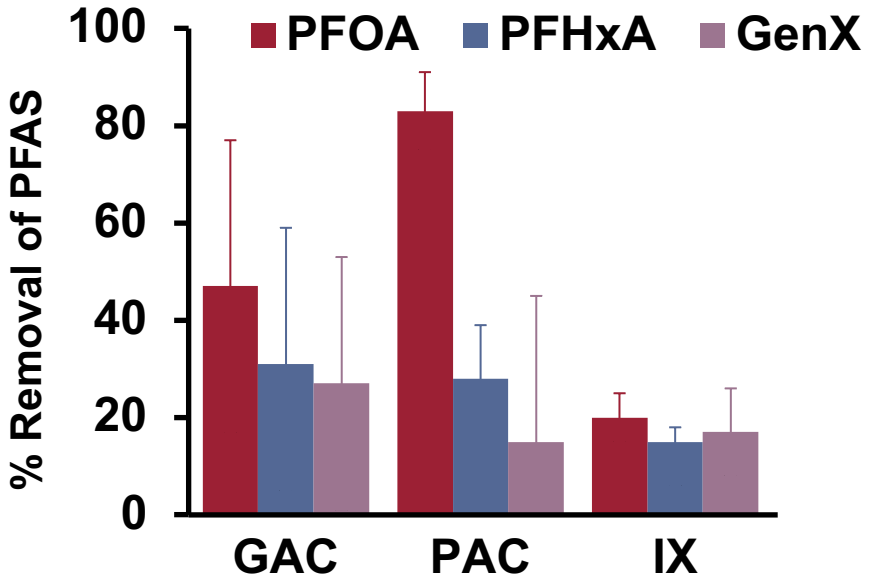
- Nanopure water
- 200 mg/L NaCl
- 20 mg/L Humic Acid
- Stir 18 hours

- 10 mg/L **IF**
- Stir 3 hours

- 1 µg/L PFOA
- 1 µg/L PFHxA
- 1 µg/L GenX
- Stir 21 hours

- Aliquot 8 mL
- Filter (0.2 µm cellulose acetate)
- LC-MS Analysis

Ionic Fluorogels demonstrate higher affinity for PFAS



[Resin] = 10 mg/L	$[PFAS]_0$ = 1 µg/L
GAC: Filtrasorb 400	[NaCl] = 200 mg/L
PAC: Picahydro MP23	[Humic Acid] = 20 mg/L
IX: PFA 694E	pH = 6.4

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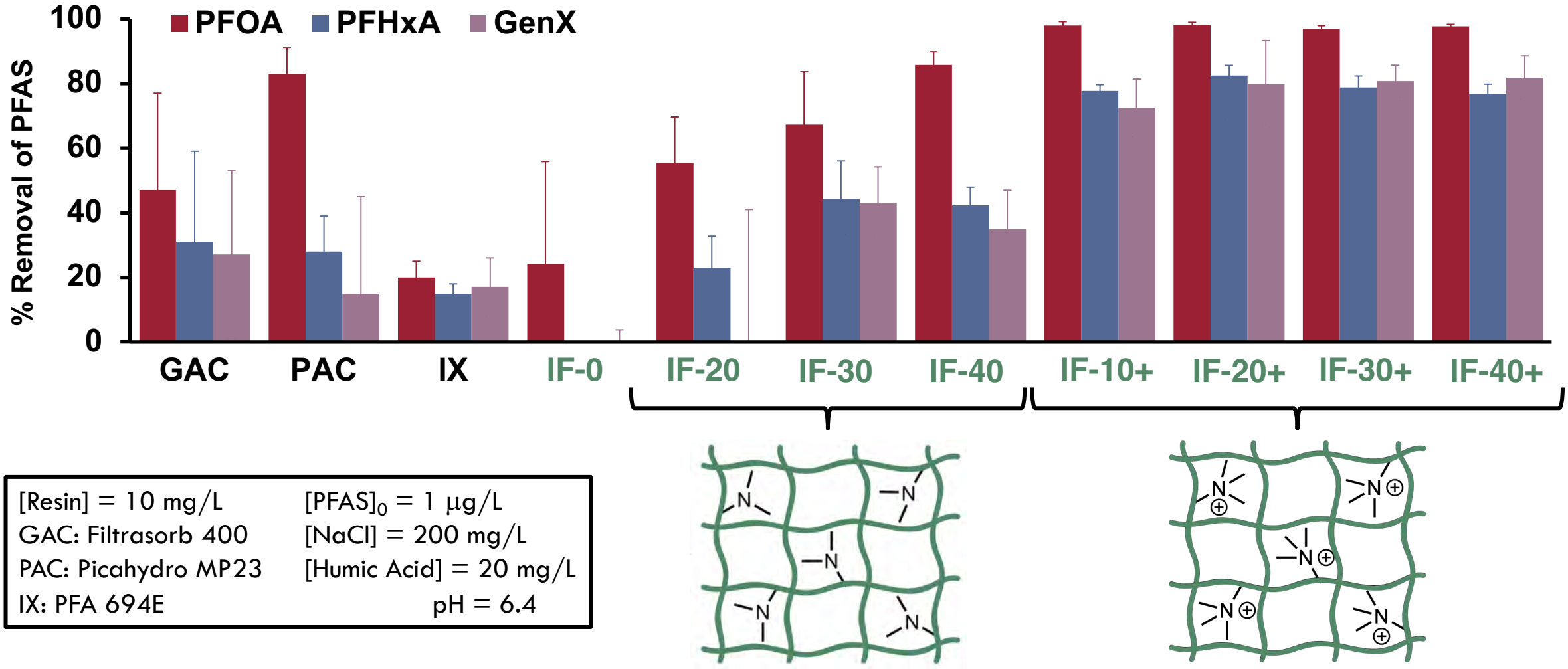

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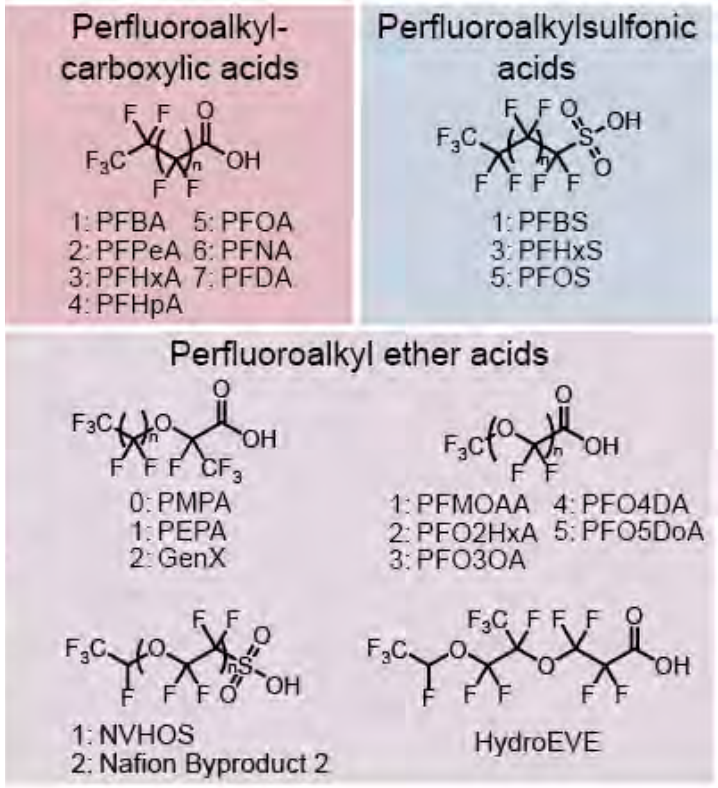
Diverse Analytes for Effective Remediation



Dr. Kelsey Miller

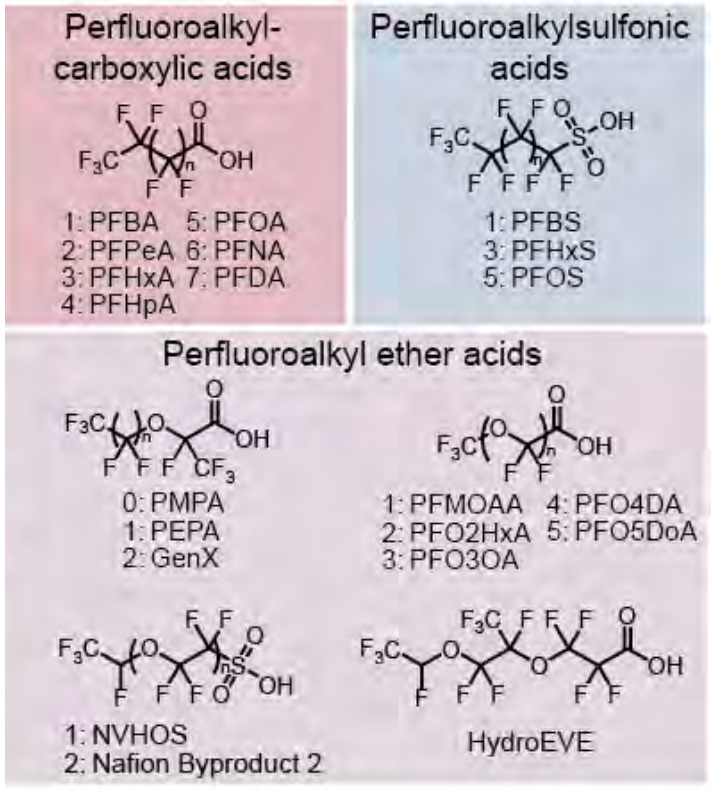
Dr. Mark Strynar

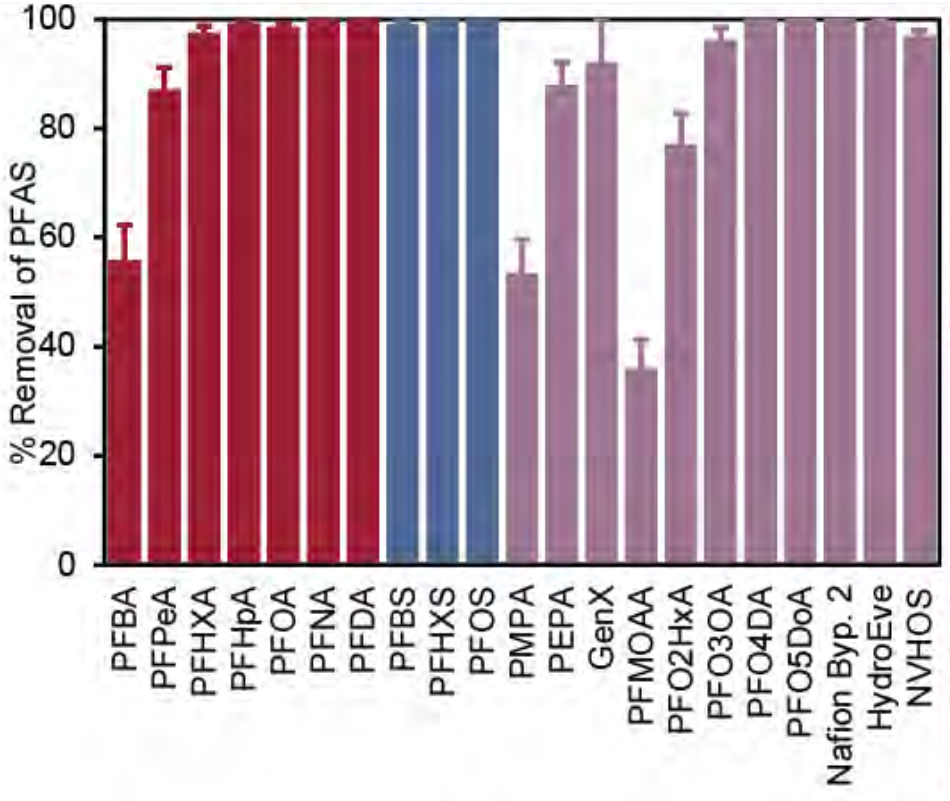
[Resin] = 100 mg/L; $[PFAS]_0$ = 1 μg/L
IF.2-1: Settled water, Chapel Hill, NC. Experiment conducted 09/2021

With Dr. Mark Strynar and Dr. Kelsey Miller

Diverse Analytes for Effective Remediation

Selectivity is driven by fluorophilic backbone, whereas ion exchange component enables tight binding





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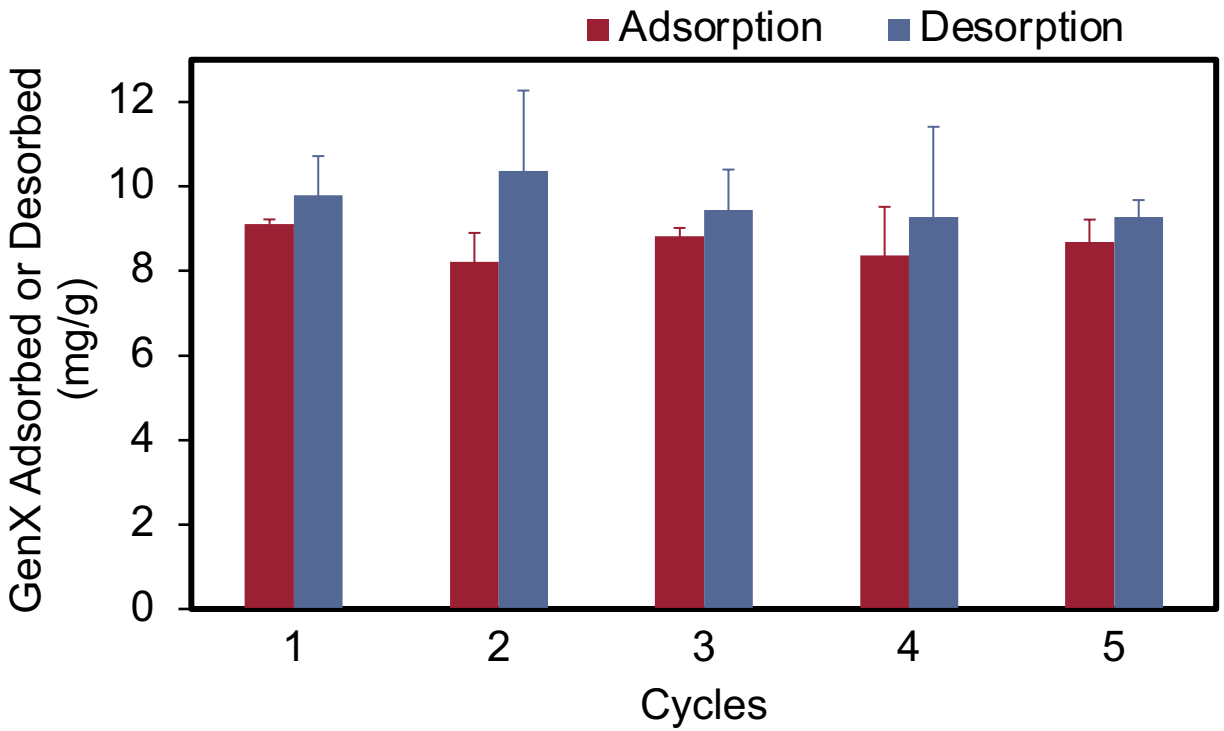
With Dr. Mark Strynar and Dr. Kelsey Miller

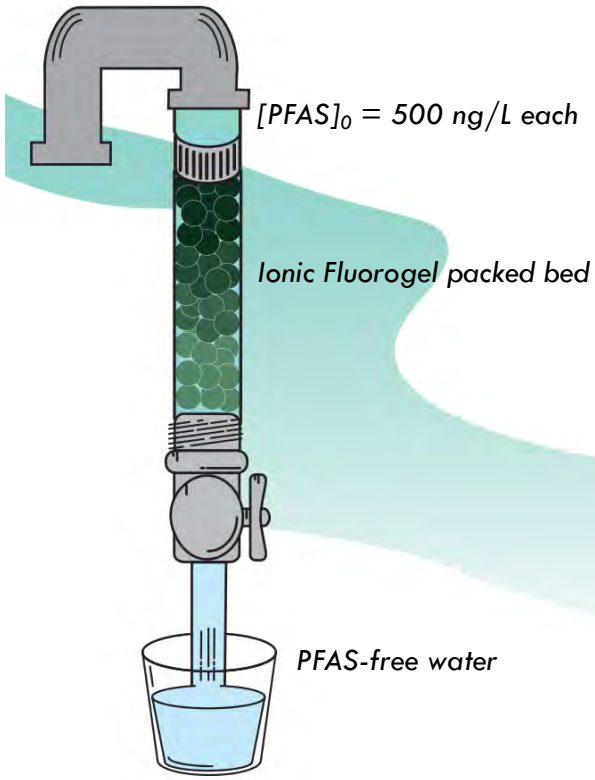
Regeneration Studies Enables Re-use of Resins

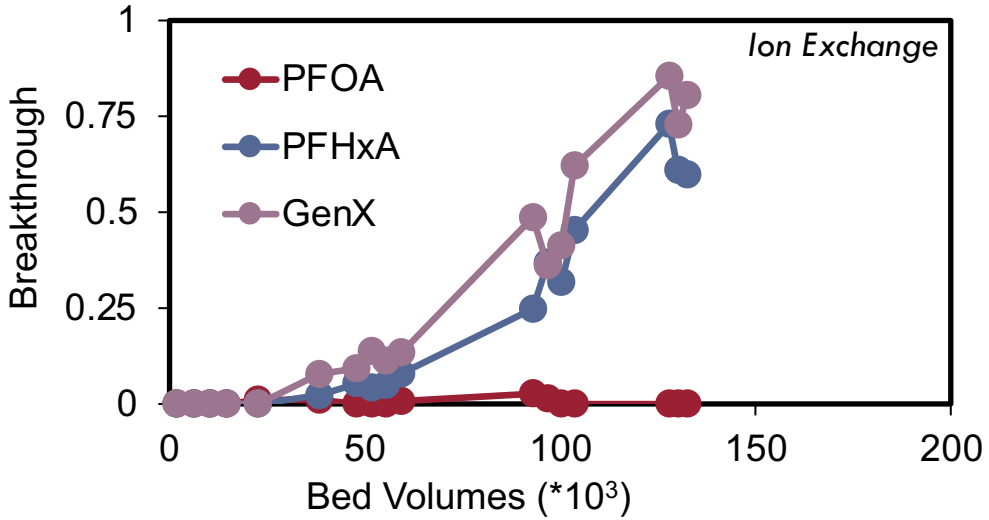


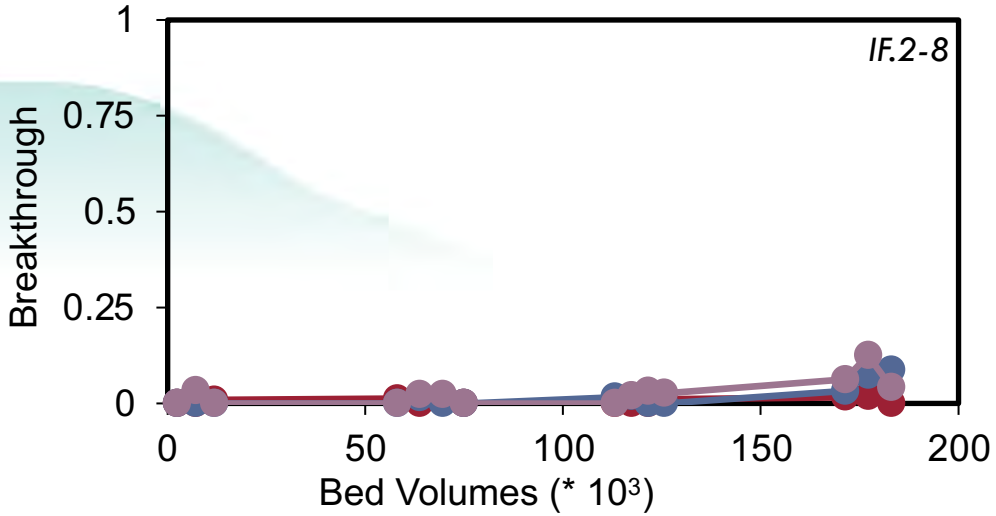
Methanolic ammonium acetate solution effectively regenerates IF-20+.

Kumarasamy, E.;* **Manning, I. M.**;* Collins, L. B.; Coronell, O.; Leibfarth, F. A. *Cent. Sci.* **2020**, *6* (4), 487–792.

Mini-Rapid Small Scale Column Tests Assess IF performance







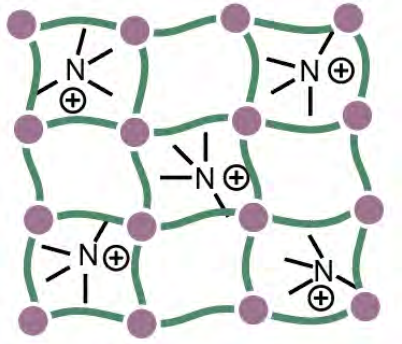
Bed volume: volume of the packed bed (resin + void space)

Breakthrough: ratio of PFAS in effluent to influent

No breakthrough of PFAS was observed for the Ionic Fluorogel over >180,000 bed volumes.

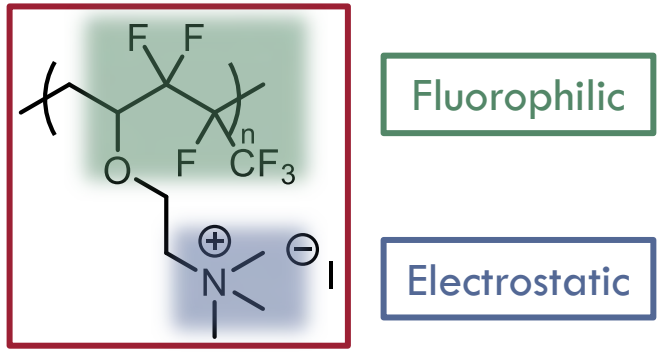
Rethinking Ionic Fluorogels: Beyond PFPEs

PFPE IFs: efficient but expensive



- ✓ Demonstration of fundamental design principles: fluorophilicity & ion exchange
- ✓ Selective for a variety of PFAS over other organic matter
- ✓ Able to be regenerated and reused
- ✓ **High-performing in column tests**
- ✓ **Hydrolytically stable**
- X Expensive, not scalable

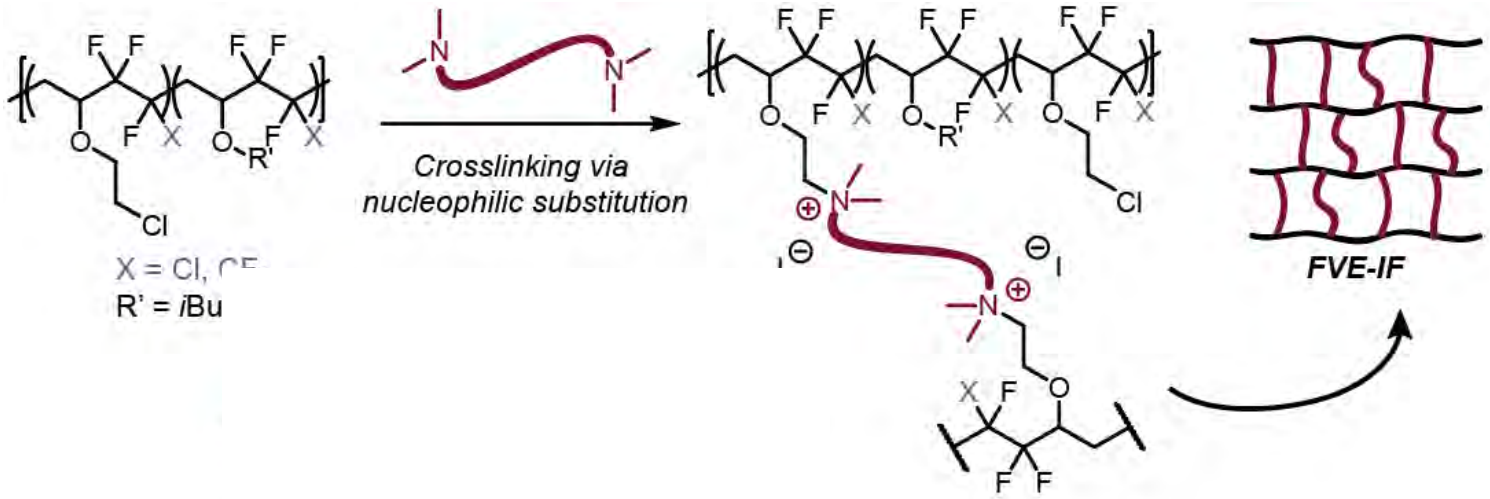
Fluoroolefin-Vinyl Ether copolymers (FVEs)

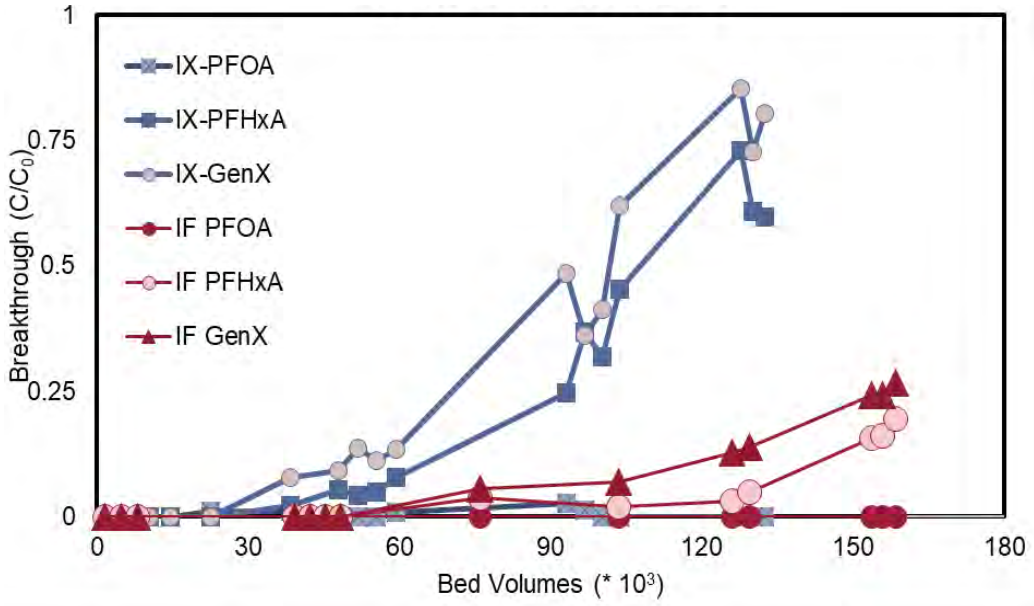


Améduri et al. *Macromolecules* **2009**, *42* (20), 7689–7700.

- ✓ Tunable chemical structure
- ✓ Limited hydrolytic degradation
- ✓ Inexpensive feedstocks

FVE-IFs are synthesized through crosslinking with multiamines





Roadblock: EPA requires additional reporting & review for new polymers containing fluorine

Science that Directly Impacts North Carolina

Senator Michael Lee
District 6; New Hanover

collaboratory
science. policy. solutions.

NC PURE

Hypothesis-Driven Rationale Improves Performance

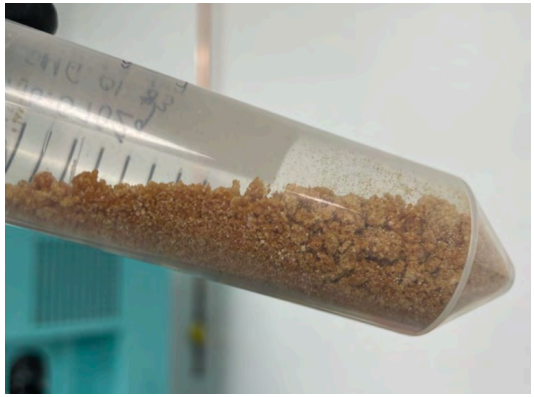
Generation I:

Perfluoropolyether-based Ionic Fluorogels

High-performing at the bench scale

Regenerable, broad-spectrum PFAS removal performance

Challenging to scale up due to environmental, cost, & supply chain concerns



Generation II:

Fluoroolefin-vinyl ether- based Ionic Fluorogels

Accessible starting materials at competitive price point

Bench-scale column testing revealed lower performance under realistic conditions

Scale-up beyond 50-gram scale proved challenging

Generation III:

Functionalized Novel Sorbents

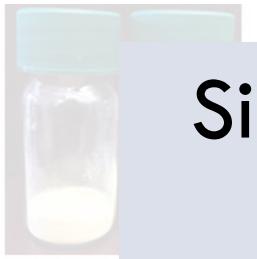
Accessible starting materials at competitive price point

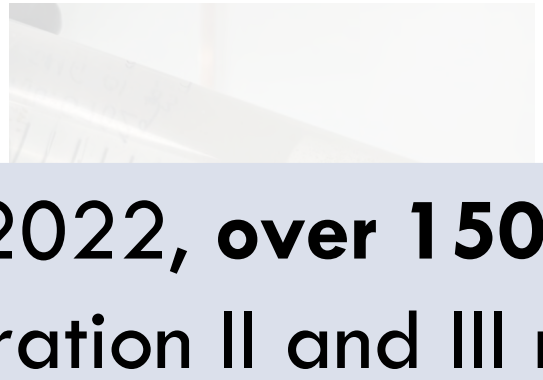
Modular synthetic platform enables quick iteration & scale-up

High-performing in real waters

Non-fluorinated backbone

Hypothesis-Driven Rationale Improves Performance





Since August 2022, **over 150 formulations** of Generation II and III materials have been synthesized and evaluated by NC Pure.

Gener

perfluoropolyet
Fluor

High-performing at the bench scale

Regenerable, broad-spectrum PFAS removal performance

Challenging to scale up to pilot scale due to environmental, cost, & supply chain concerns

Accessible starting materials at competitive price point

Bench-scale column testing revealed lower performance under realistic conditions

Scale-up beyond 50-gram scale proved challenging

on III:

ovel Sorbents

Accessible starting materials at competitive price point

Modular synthetic platform enables quick iteration & scale-up

High-performing in real waters

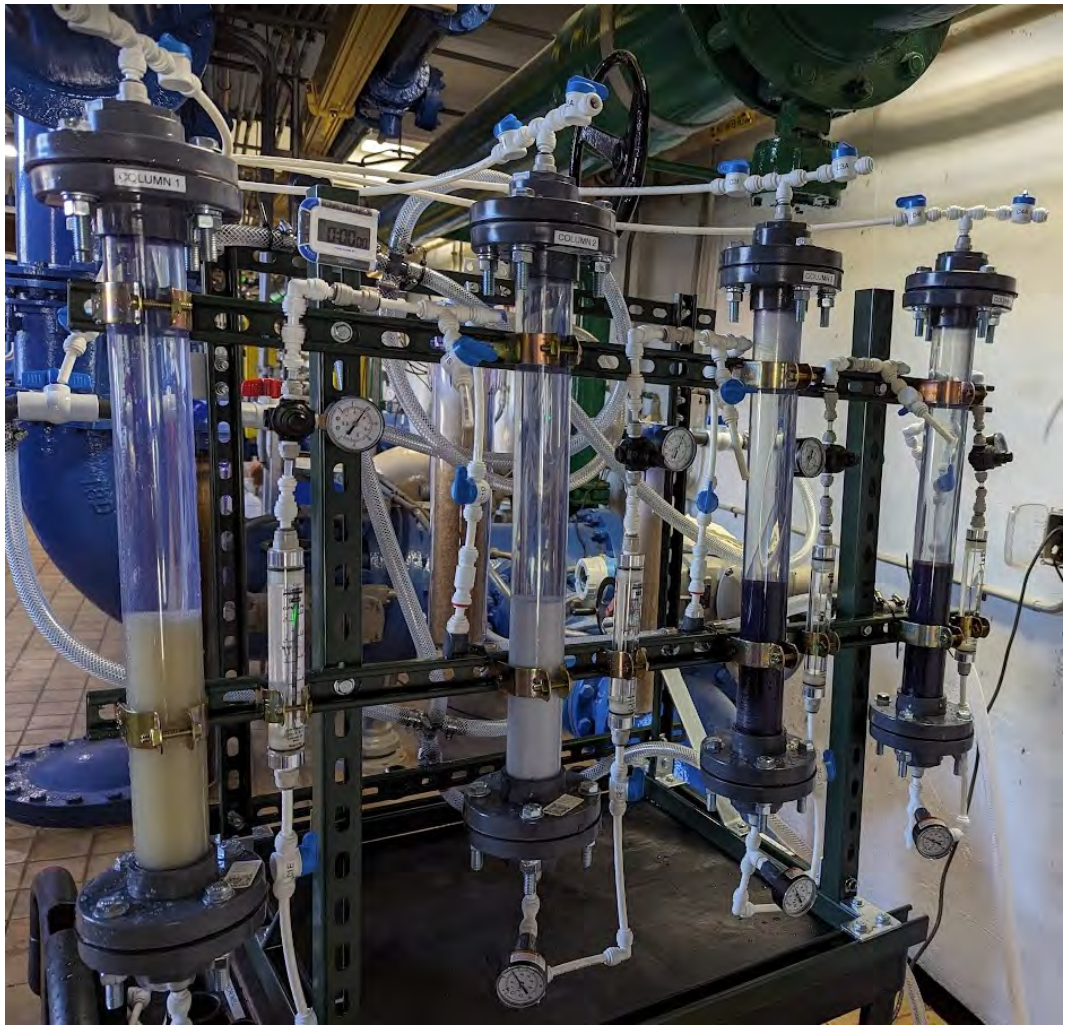
Non-fluorinated backbone

Pilot-Scale Manufacturing of Novel Sorbents

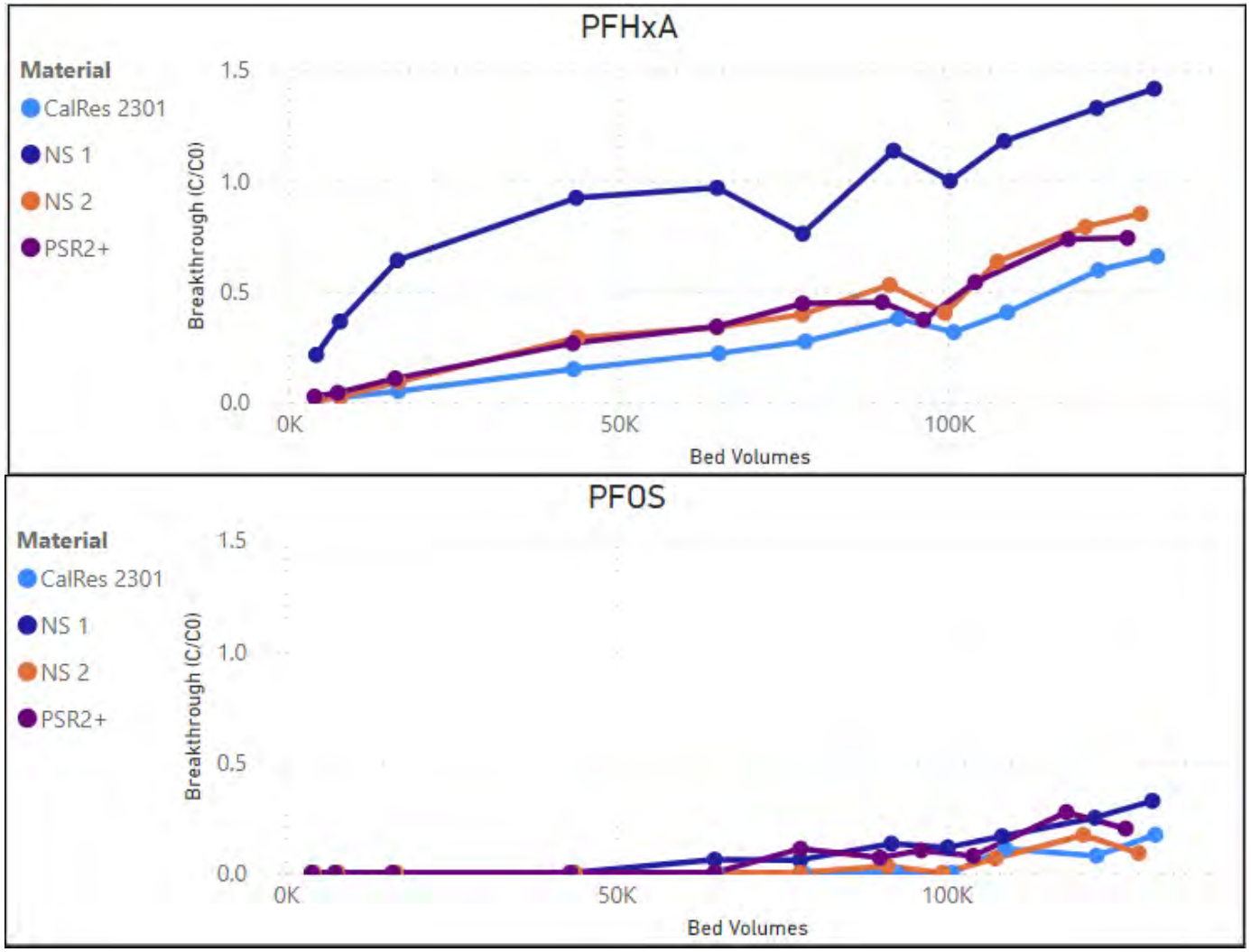
- Three novel sorbents have been identified as highest-performing and will be used for full-scale pilot studies
- Scale-up of manufacturing from 1.0 L to 10.0 L to 30.0 L enables production of multi-kilogram quantities of proprietary resins
- NC Pure is providing resources for technology development, de-risking, and generating data to inform NC Utilities

"Accelerated" Pilot Provided first Large-Scale Evaluation

- Constructed a pilot to conduct preliminary testing of full-size novel sorbent beads
- Columns were filled with 1/6 of the typical media depth to allow PFAS breakthrough to be observed in ~1/6 of the time of a regular pilot
- Served as a trial run for pilot operation and a training opportunity for NC Pure staff



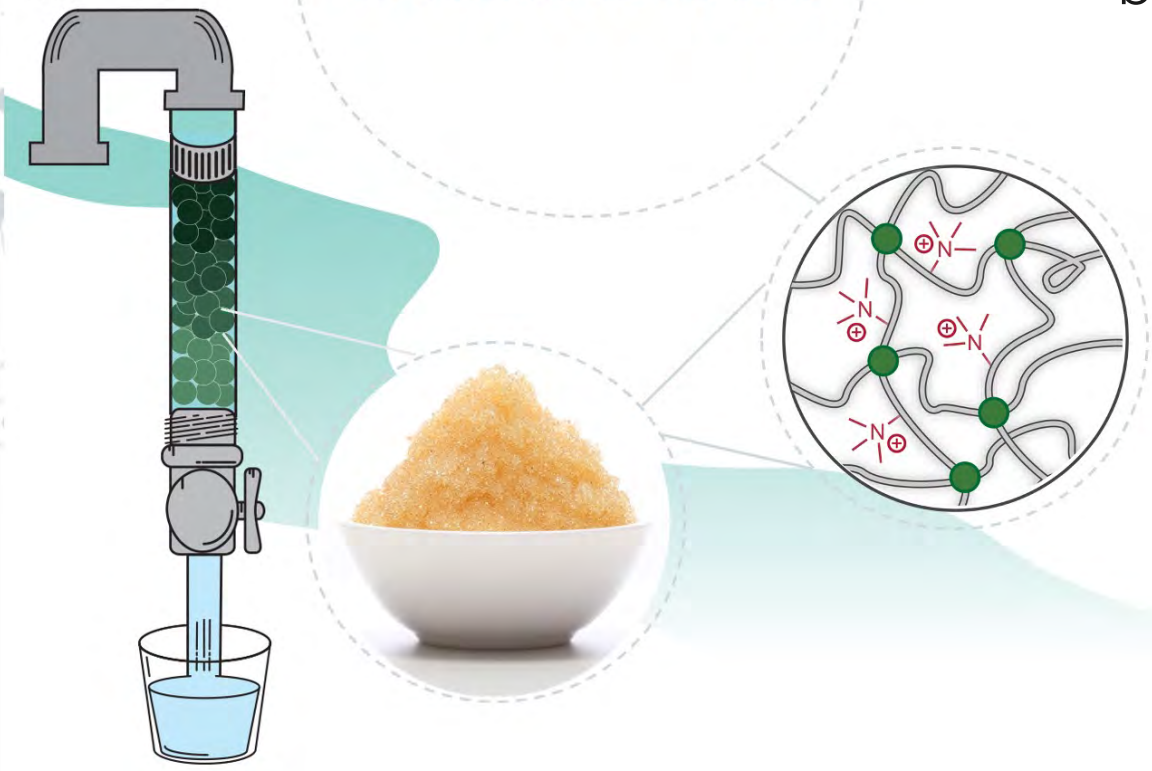
"Accelerated" Pilot Provides Initial Performance Data



- Non-fluorinated novel sorbents were able to achieve similar performance to commercial resins
- Tested regeneration using commonly-available solvents and salts – preliminary data indicates recovery of capacity after regeneration

Sorbenta®: Removing forever chemicals from our waters

Sorbenta



Our vision: manufacture and supply the world's best sorbents for PFAS concentration

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Co-Founder & Commercial Director

30-year chemical industry executive with a background spanning industrial operations, commercial development and scaling materials technologies.

Frank Leibfarth
Co-Founder

Orlando Coronell
Co-Founder

Acknowledgements

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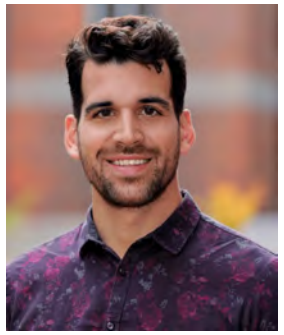
- Dr. Mark Strynar & Dr. Kelsey Miller at the US EPA
- NC Collaboratory for funding



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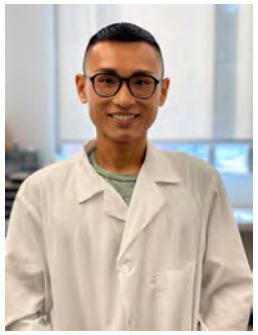

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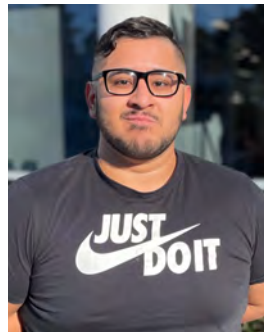

Elias Arroyo
Research Scientist

Acknowledgements

collaboratory
science. policy. solutions.

North Carolina Collaboratory

North Carolina General Assembly

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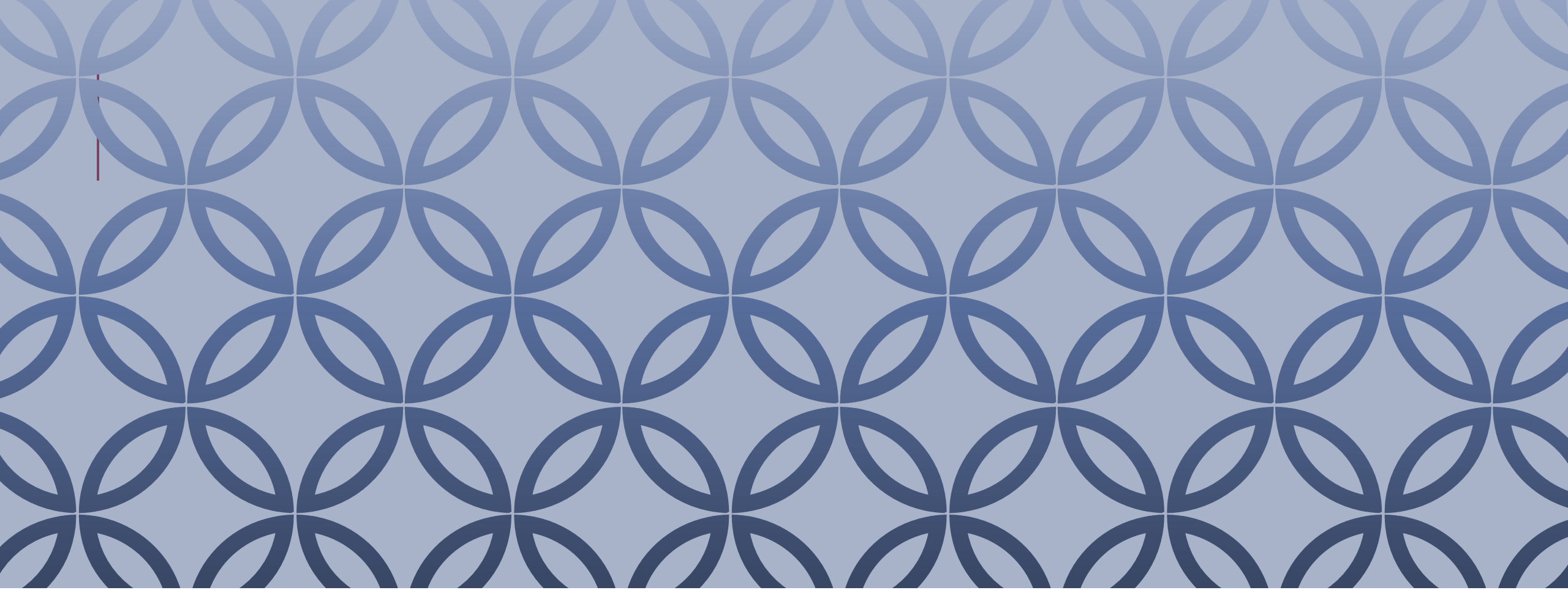

Thank You!