Understanding and enhancing PFAS phytoremediation mechanisms using hemp plants

R01ES032712

Progress in Research
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Team Members

Principal Investigators

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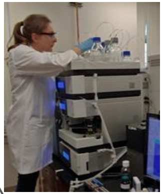
Christy Haynes Nanomaterials, nanotoxicity, analytical methods

Jason C. White, Phyto-remediation, nanotechnology

Collaborators

Georgia Charkoftaki, LC-MS, PFAS detection

Nubia Zuverza-Mena, Phyto-remediation, nanotechnology



Sara Nason, LC-MS, PFAS detection, phyto-remediation

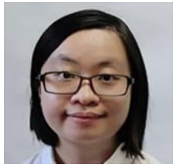
Predrag Petrovic, Computational modeling

Trainees

Sara Thomas, LC-MS, PFAS detection

Riley Lewis Carbon dot synthesis and characterization

James Licato, PFAS analytics, MS



Cheng-Hsin Huang Porous silica synthesis and characterization

Phil Zuccaro, PFAS

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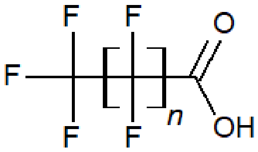
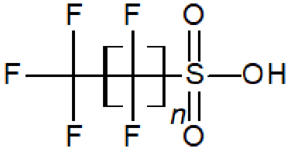
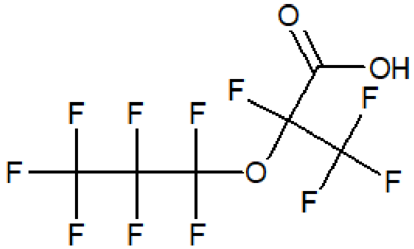
PFAS: Per- and Polyfluoroalkyl Substances

- Molecules that contain carbon-fluorine chains
  - Over 10,000 listed on US EPA website
  - “Forever chemicals” that don’t degrade
- In use since the 1940s
- Used in many consumer products
- Widely spread environmental contaminants







Project Beginnings

- The burn house and parking lot located at the former Loring Air Force Base in northern Maine were used for firefighting drills and testing
- The land now belongs to the Aroostook Band of the Micmac Nation, an indigenous people
- Community members reached out to CAES for help with a hemp phytoremediation project focused on cleaning up PFAS

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Field Team at Loring Air Force Base

Analytical Methods

- LC-HRMS based analysis of soil and plant tissue
- Targeted list of ~30 PFAS
- Non-targeted analysis with FluoroMatch and Compound Discoverer
  - Found over 90 suspected PFAS in Loring soil
  - Aided in development of FluoroMatch software updates

- Methods also used in additional projects - like this one
- Always interested in additional collaborations!

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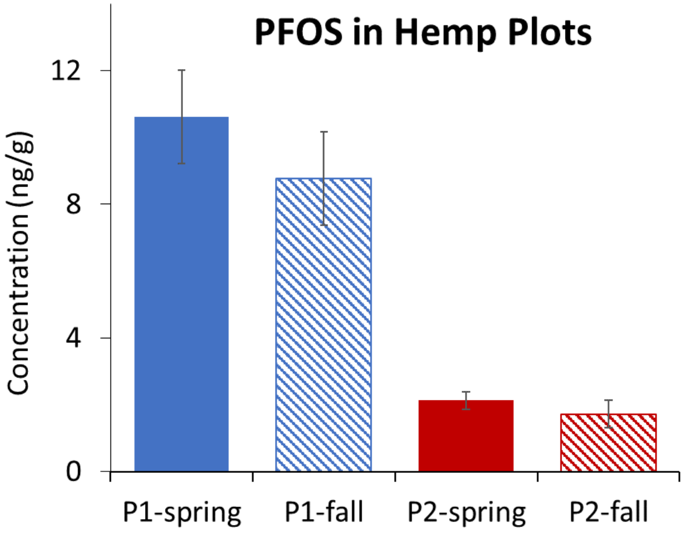
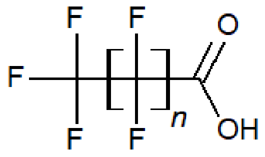
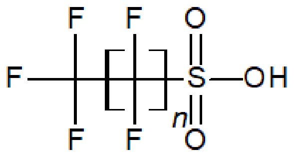
Preliminary Data



Compound	Bioconcentration Factor
PFBA (n=2)	4
PFPeA (n=3)	5
PFBS (n=3)	10
PFHxS (n=5)	7
PFOS (n=7)	0.13





- Statistically significant decreases in soil PFOS in both hemp growth plots
- Lower bioconcentration for longer chain PFAS

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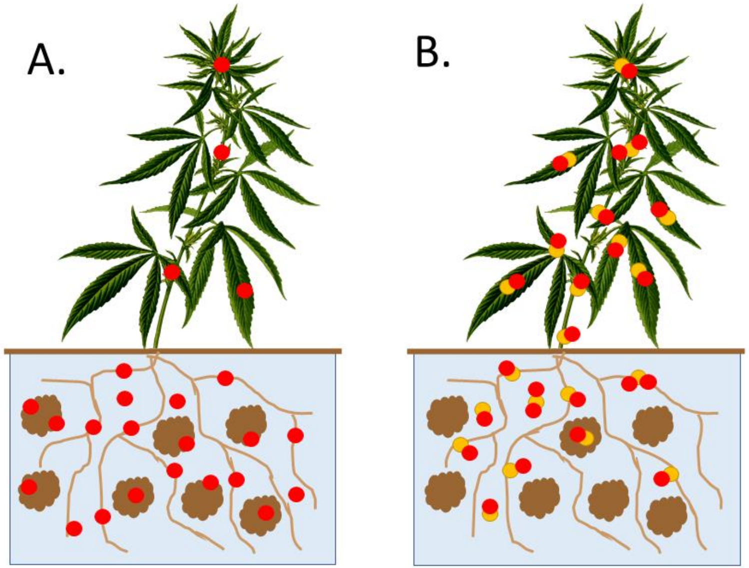
Overarching goal: use novel materials to make phytoremediation a viable solution for removing a wide range of PFAS from soil

Specific Aim 1: *Synthesize novel nanomaterials (NNMs) designed to sorb PFAS and translocate through plants*

- **Haynes Group**, University of Minnesota - nanomaterial synthesis/characterization, analytical method development

Specific Aim 2: *Determine capacity of NNMs to promote PFAS uptake into plants and retain PFAS in soils.*

- **CAES team** - plant growth, PFAS measurement, soil column studies
- **Vasiliou Group**, Yale University - imaging studies and computational modeling



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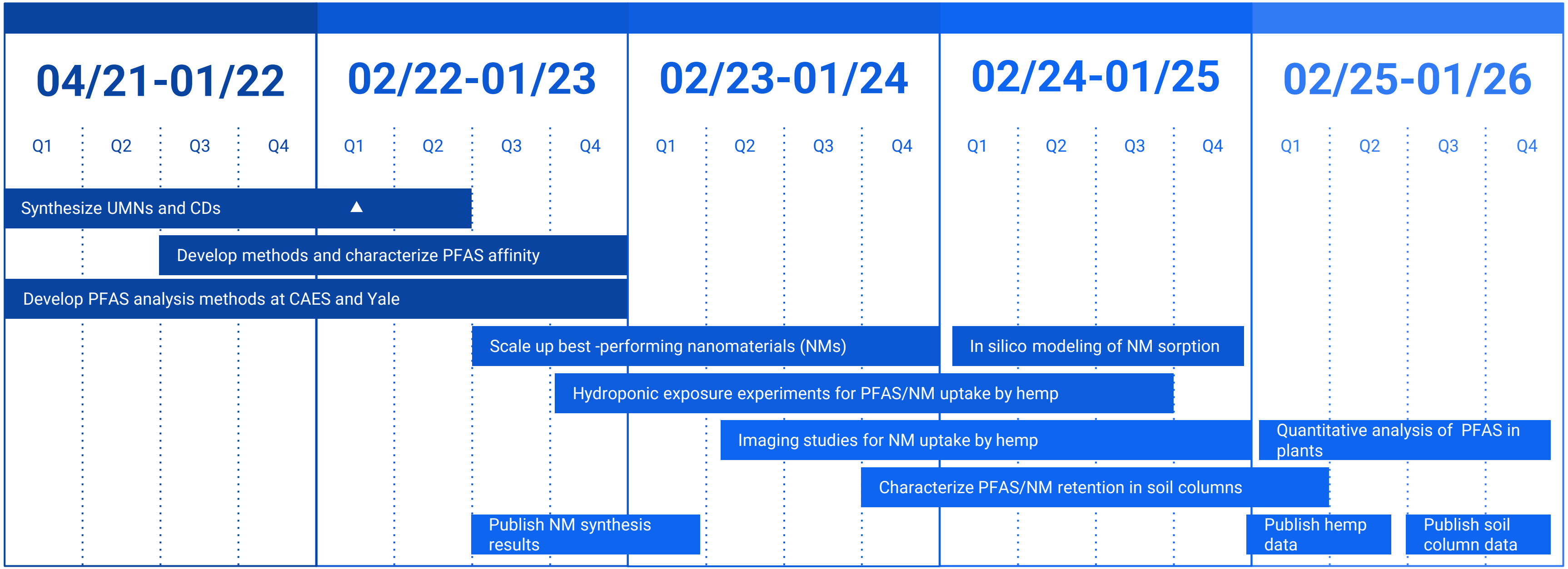
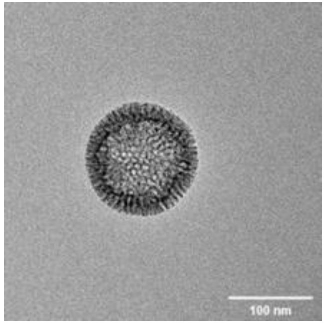
Overall Project Timeline

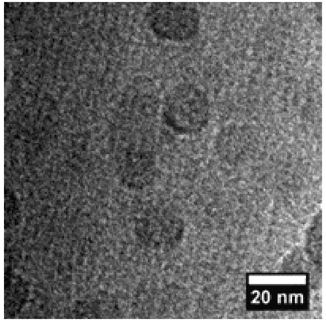


Overall Plan for Aim 1

Ultraporous Mesostructured Silica Nanoparticles (UMNs):

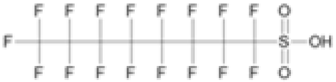


Carbon Dots (CD):

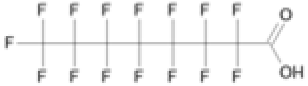


+

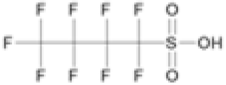
PFOS



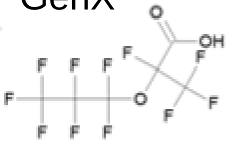
PFOA



PFBS



GenX



→

Characterize PFAS affinity for UMNs with varied:

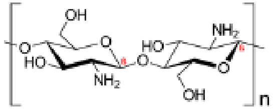
- Hydrophobicity
- Surface charge

Characterize PFAS affinity for CDs with varied:

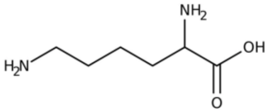
- Amine content
- Surface charge

Specific Aim 1: Carbon dots

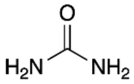
Carbon dot synthesis: microwave-assisted hydrothermal synthesis with amine rich precursors



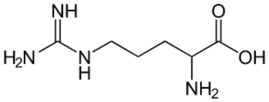
Chitosan



L-Lysine

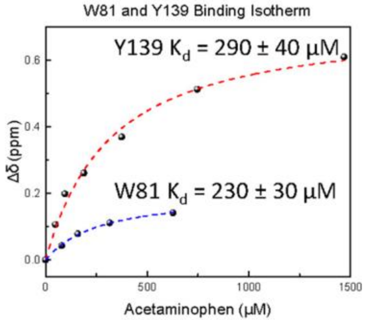


Urea



Arginine

Characterization and sorption assessment:
Zeta potential, dynamic light scattering (DLS), and ^{19}F NMR

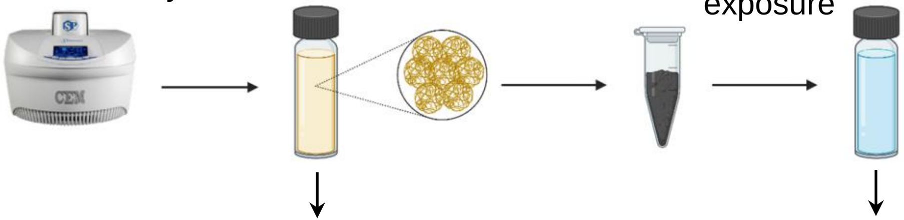


Experimental setup:

Synthesis

Purification

PFAS exposure



Zeta potential, DLS

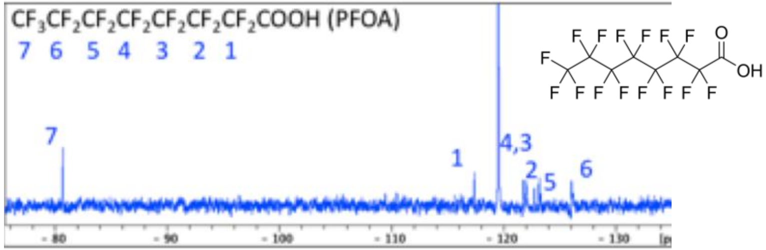
^{19}F NMR, Zeta potential, DLS

Why ^{19}F NMR?

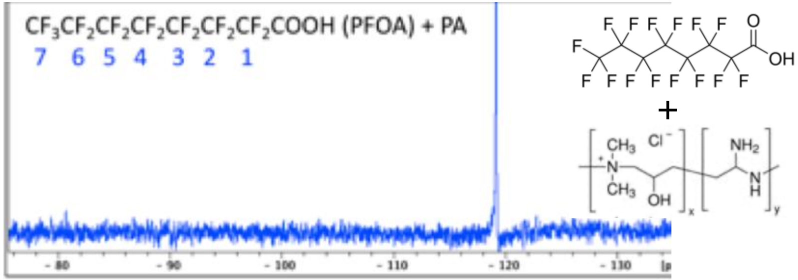
Goal: determine most effective carbon dots at PFAS sorption

- Only detects fluorine
    - Assess CD/PFAS solution directly
- No sample processing (filter, column, etc)
- Gives insight into local environment of fluorine atoms
    - Changes in peak intensity and location
- Quantify interactions between PFAS and CDs to compare effectiveness

Perfluorooctanoic acid



Perfluorooctanoic acid + sorbent polymer



Using ^{19}F NMR to assess PFAS sorption

Chitosan, lysine, malic acid	
Zeta potential	+22 mV
Avg. size	80 nm

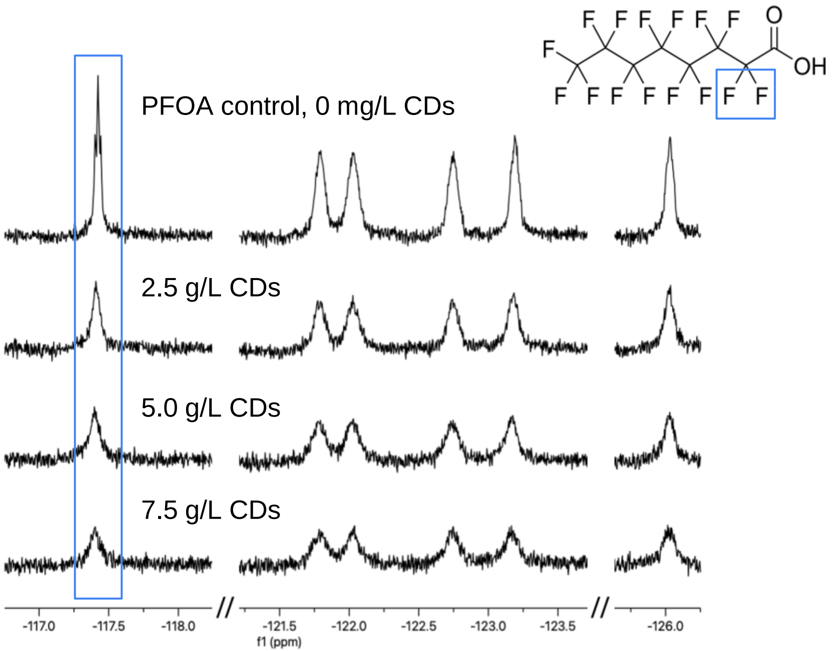


Fig 1. ^{19}F NMR of PFOA with increasing carbon dot concentrations

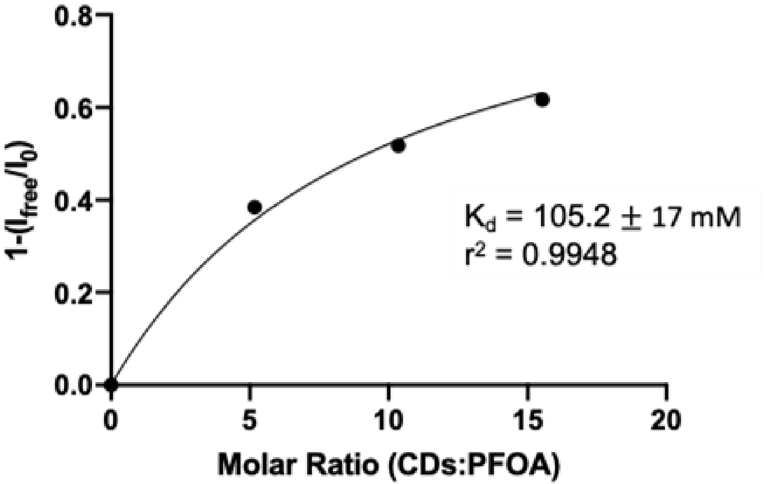


Fig 2. CD/PFOA binding curve from peak intensity changes ^{19}F NMR

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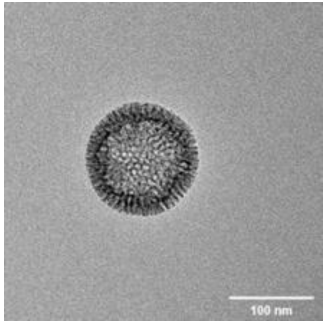
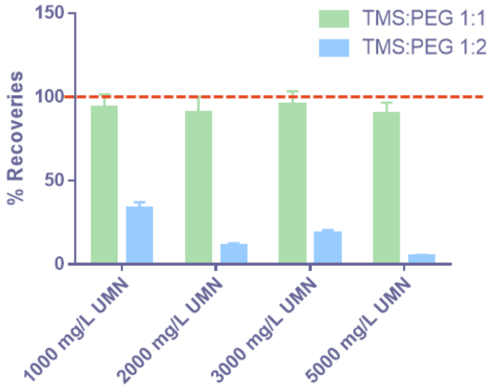
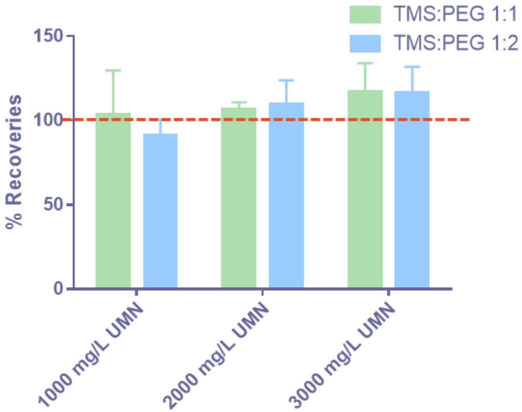
Specific Aim 1: Ultraporous Mesostructured Silica

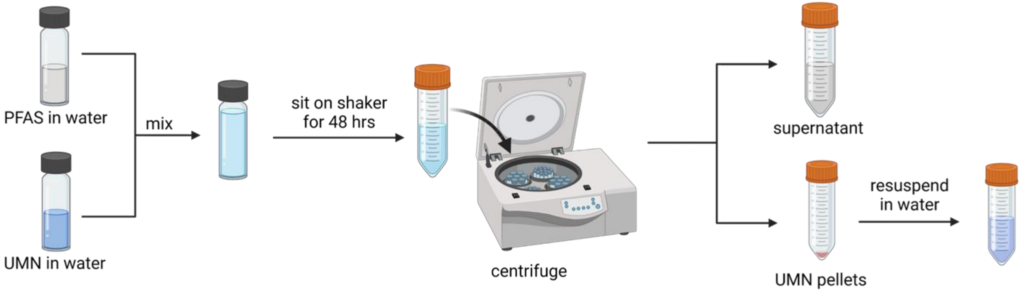


Initial PFOA exposure data:



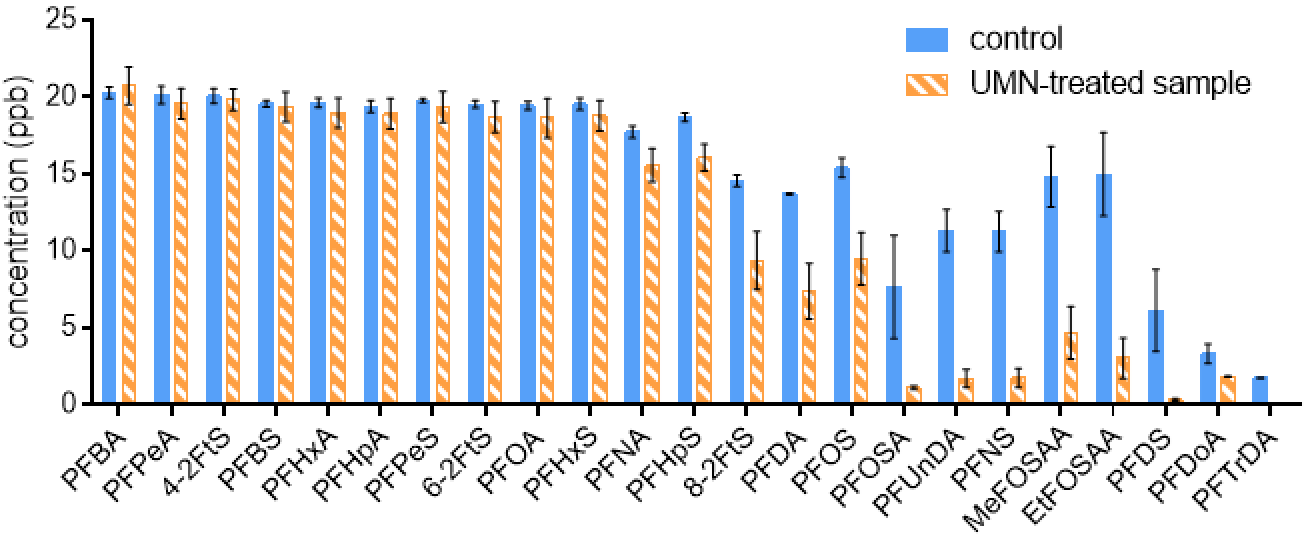
Initial GenX exposure data:





% recovery < 100%: UMNs taking up PFAS

CAES Preliminary Analysis of UMN/PFAS Sorption



The best early candidate silica nanoparticle has significant affinity for hydrophobic PFAS based on LC-HRMS analysis at CAES.

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