Development of Passive PFAS Samplers for Detection in Natural Waters

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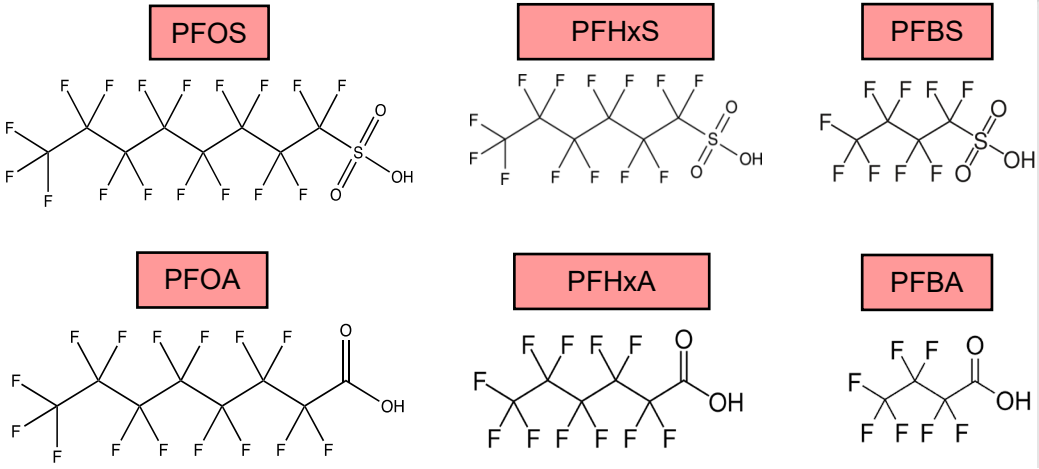
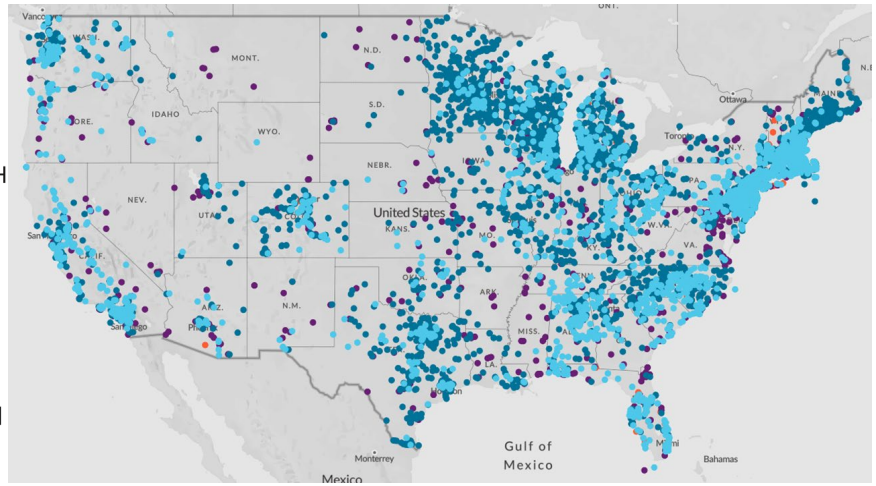
What are PFAS Compounds?

Per- and Poly Fluoroalkyl substances (PFAS), aka forever **chemicals**, are man-made substances with applications in firefighting foams and non-stick cookware

- Longer chain PFAS are more **hydrophobic**, and generally easier to adsorb relative to their short chain counterparts.
- Long chain PFAS are **bio-accumulative** and are linked to **developmental issues in children and other negative health impacts (high cholesterol, cancer, immunodeficiency).**



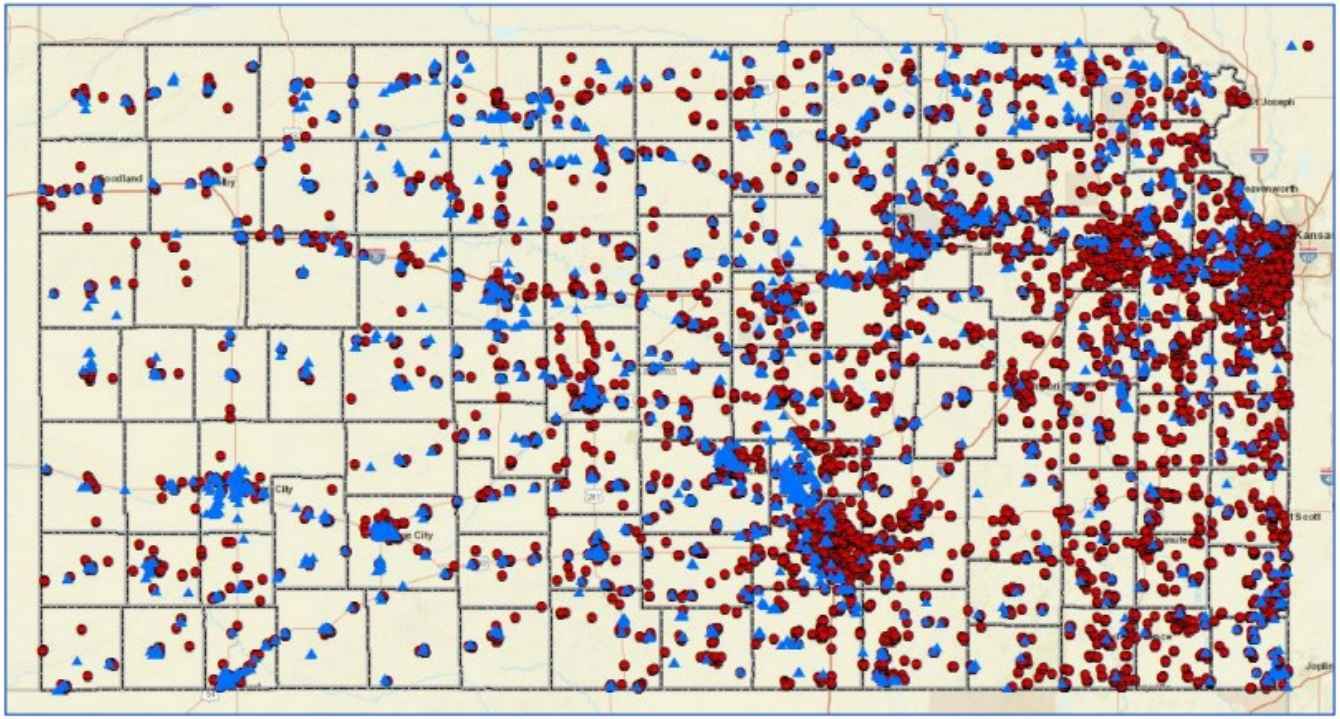
Examples of Long-, Medium-, and Short-Chain PFAS



PFAS Contamination in the U.S. (August, 2024) ewg.org

PFAS in Kansas

Location of Potential PFAS Sites in Relation to PWS Sources



Blue Triangle = Public Water Supply Red Circle = Potential PFAS Site

National Primary Drinking Water Regulation

Compound	Final MCLG	Final MCL (enforceable levels)
PFOA	Zero	4.0 parts per trillion (ppt) (also expressed as ng/L)
PFOS	Zero	4.0 ppt
PFHxS	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
HFPO-DA (commonly known as GenX Chemicals)	10 ppt	10 ppt
Mixtures containing two or more of PFHxS, PFNA, HFPO-DA, and PFBS	1 (unitless) Hazard Index	1 (unitless) Hazard Index

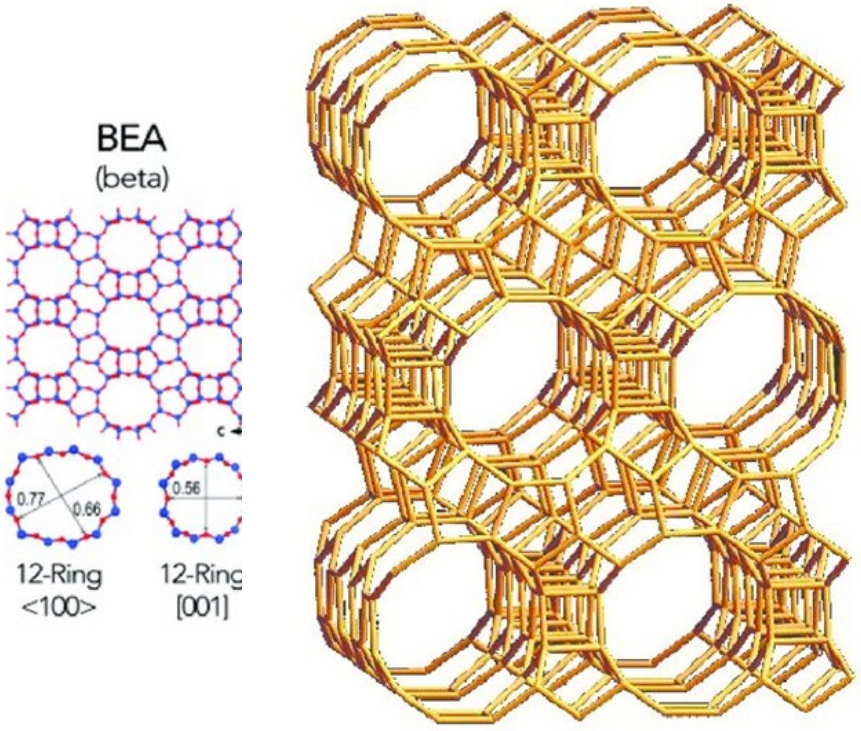
- PWS have until 2027 initial monitoring
- PWS have until 2029 for solutions if above MCL

Development of a Zeolite-Based Passive Sampler for PFAS Detection

Zeolites- hydrous, aluminosilicate, porous crystalline materials, both naturally occurring and synthesized

$M_{x/n}(AlO_2)_x(SiO_2)_y*zH_2O$

Beta zeolite structures have shown potential for effective PFAS adsorption and desorption

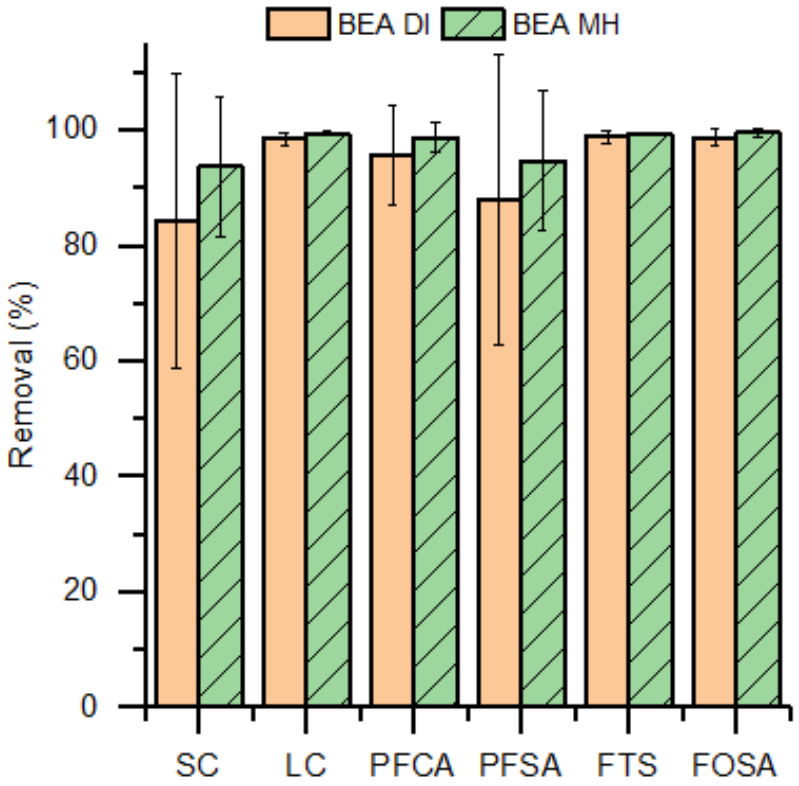


Beta zeolite structures in 2D (Hong et al. 2023) and along the 100 axis (Albayati and Doyle, 2014)

Beta zeolite performance for broad PFAS removal

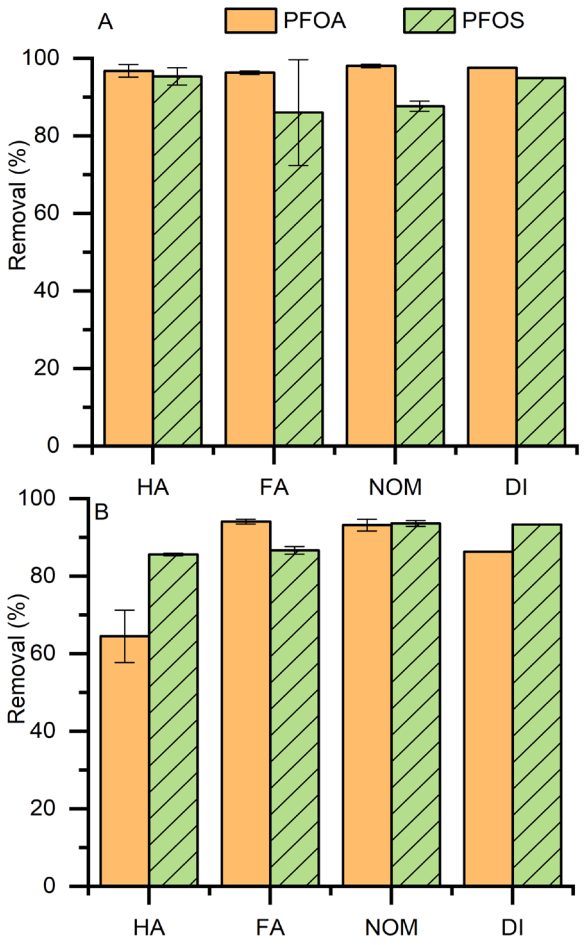
Screening tests of 24 PFAS compounds in the ppm range with 1 g/L beta zeolite in DI and EPA Moderately Hard water

>90% removal for all compounds except PFBA (9%), PFBS (26%), PFPeA (55%) and PFPeS (84%)



SC is ≤ 7 carbon (CA) or ≤ 6 carbon (SA)

Performance in with Natural Water Constituents



PFAS sorption to beta zeolite tested with a variety of inorganic and organic compounds typical of natural water systems

Increase in effectiveness in synthetic fresh-water matrices

Minimal impact of organic matter (humic acid, fulvic acid, NOM) on PFAS sorption at 10 mg C/L

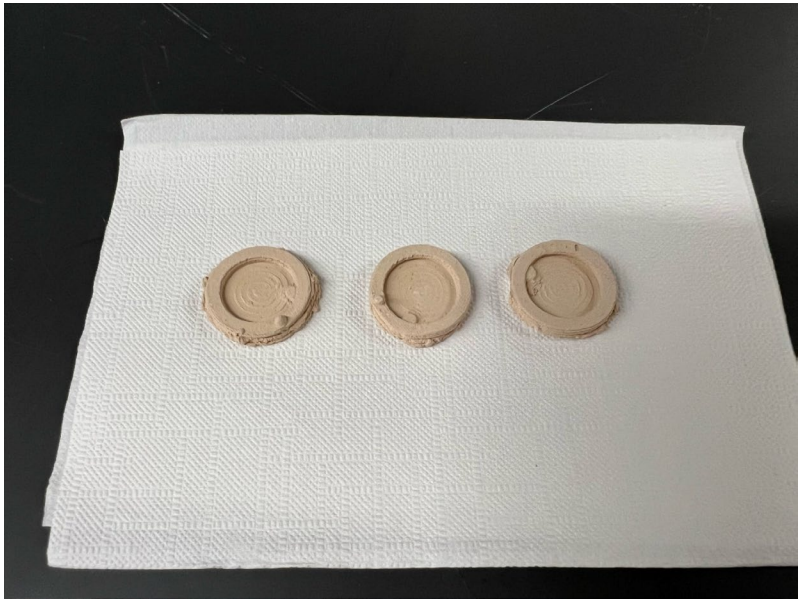
Desorption Studies: Can we recover PFAS from the zeolite after sampling?

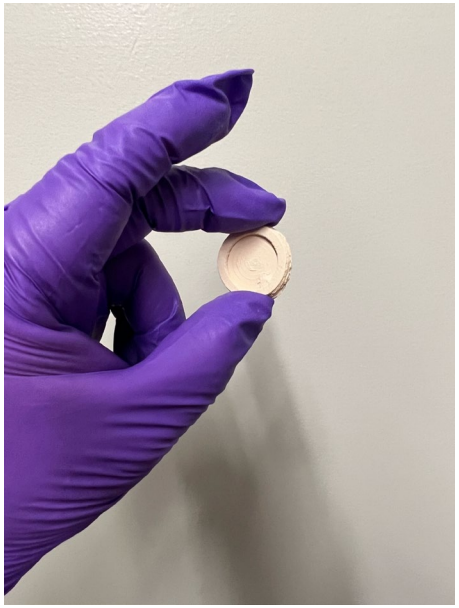
- Desorption experiments with a variety of solvents after PFAS sorption to zeolite at 100 ppm initial concentration
- Methanol provides most of the desorption work, primarily through hydrophobic interactions
- Base solutions provide additional electrostatic interactions with adsorbed compounds
- Overall, a mixture of methanol and water with 2% NH4OH had best recovery

Solvent	Average Recovery
Water 49%, MeOH 49%, NH4OH 2%	114%
MeOH 94.375%, Water 4%, NH4OH 1%, Citric acid 0.625%	112%
NH4OH 2%, MeOH 98%	111%
Water 29%, MeOH 69%, NH4OH 2%	108%
Hot Methanol	93%
Hot Ethanol	91%
Water 30%, MeOH 69%, NaCl 1%	84%
EtOH 50%, Water 50%	72%
Water 49%, MeOH 49%, 1% NaCl	69%
MeOH 50%, Water 50%	69%
Methanol 95%, Isopropanol 4%, Water 1%	66%
Methanol	55%
Ethanol	47%
NH4OH 2%, Water 98%	28%
Octanol	28%

Passive Sampler Development

Zeolite powders embedded into kaolinite support material to create 3-D printed sampling disks at USACE Engineering Research & Design Center

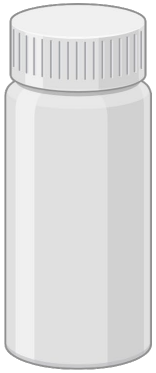




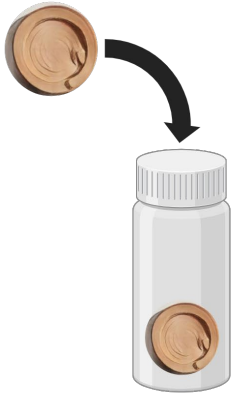
Zeolite embedded into 3-D printed clay monoliths

3-D Print Monolith Testing

1) Create Stock Solutions of PFAS in Nalgene Bottles

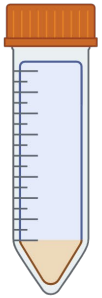


2) Put Pucks into PFAS solutions

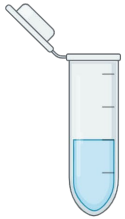


3) Remove pucks and crush using Mortar and Pestle

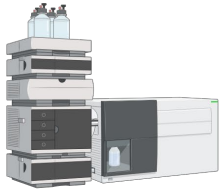
4) Add 50% HPLC, 50% Methanol and 1% Ammonium Hydroxide for desorption



5) Transfer desorbed liquid to 2mL vials to centrifuge

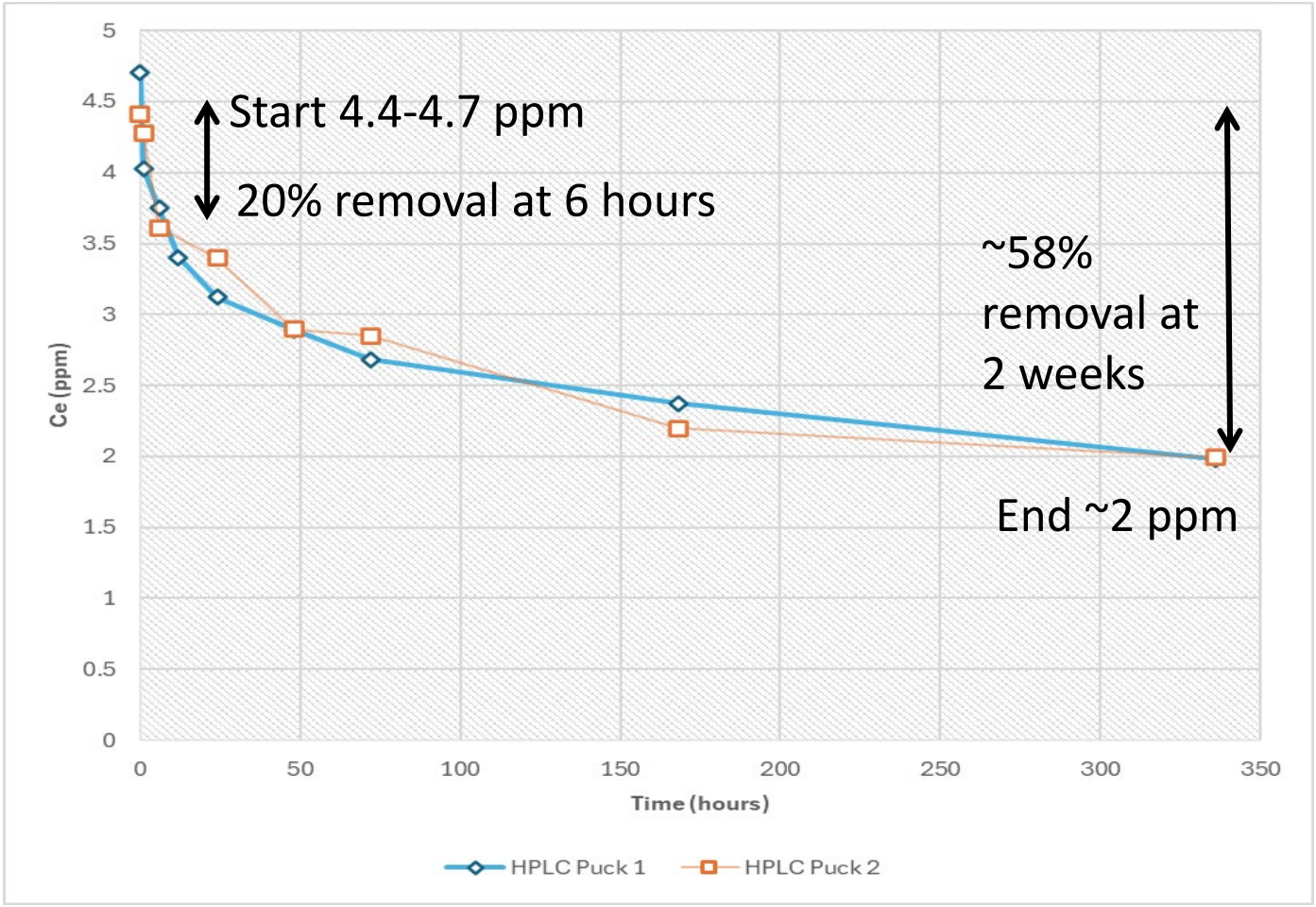


6) After centrifuging, transfer to LC vial with 1mL solution + methanol and IS

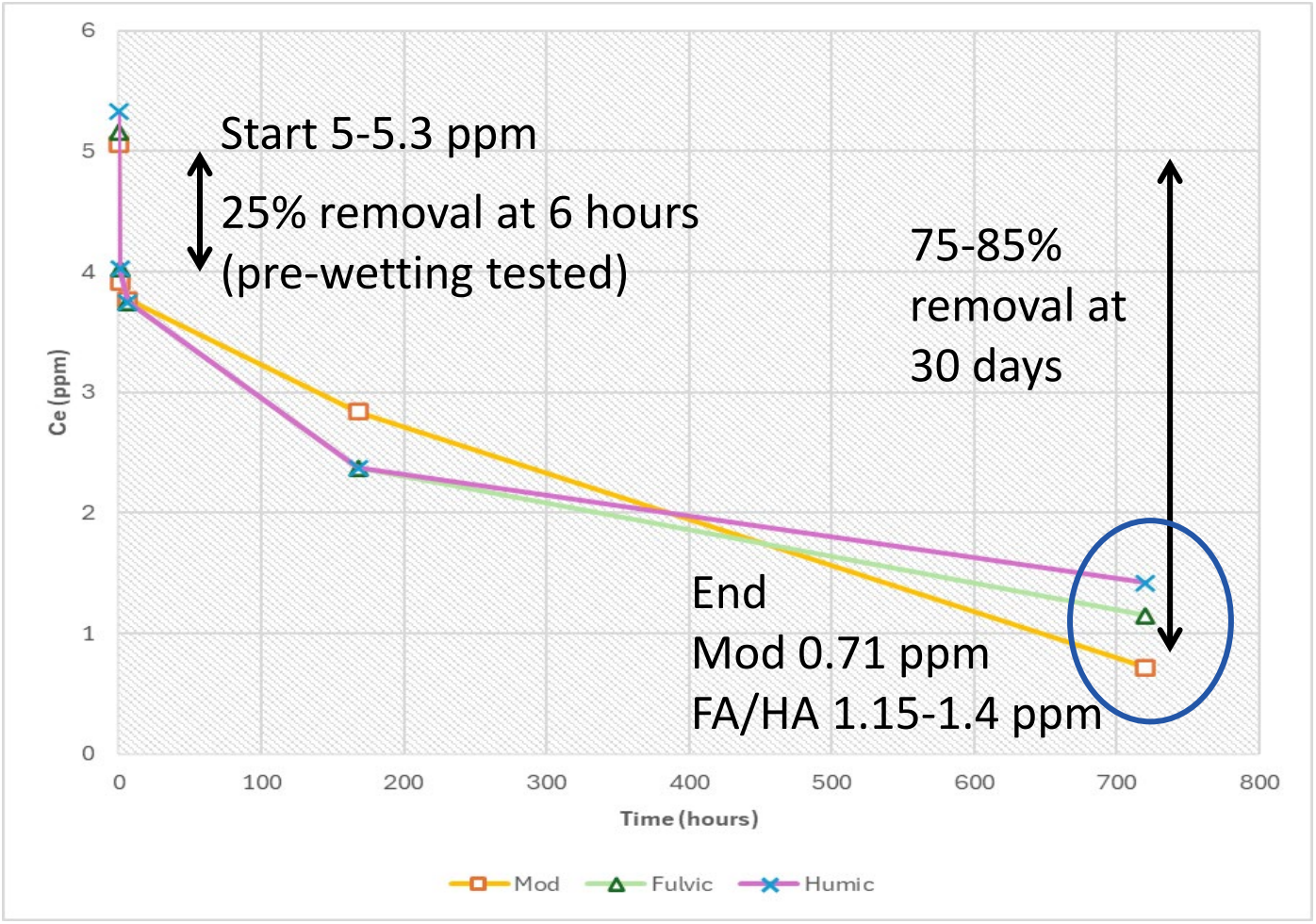


7) PFAS Analysis with Triple Quadrupole

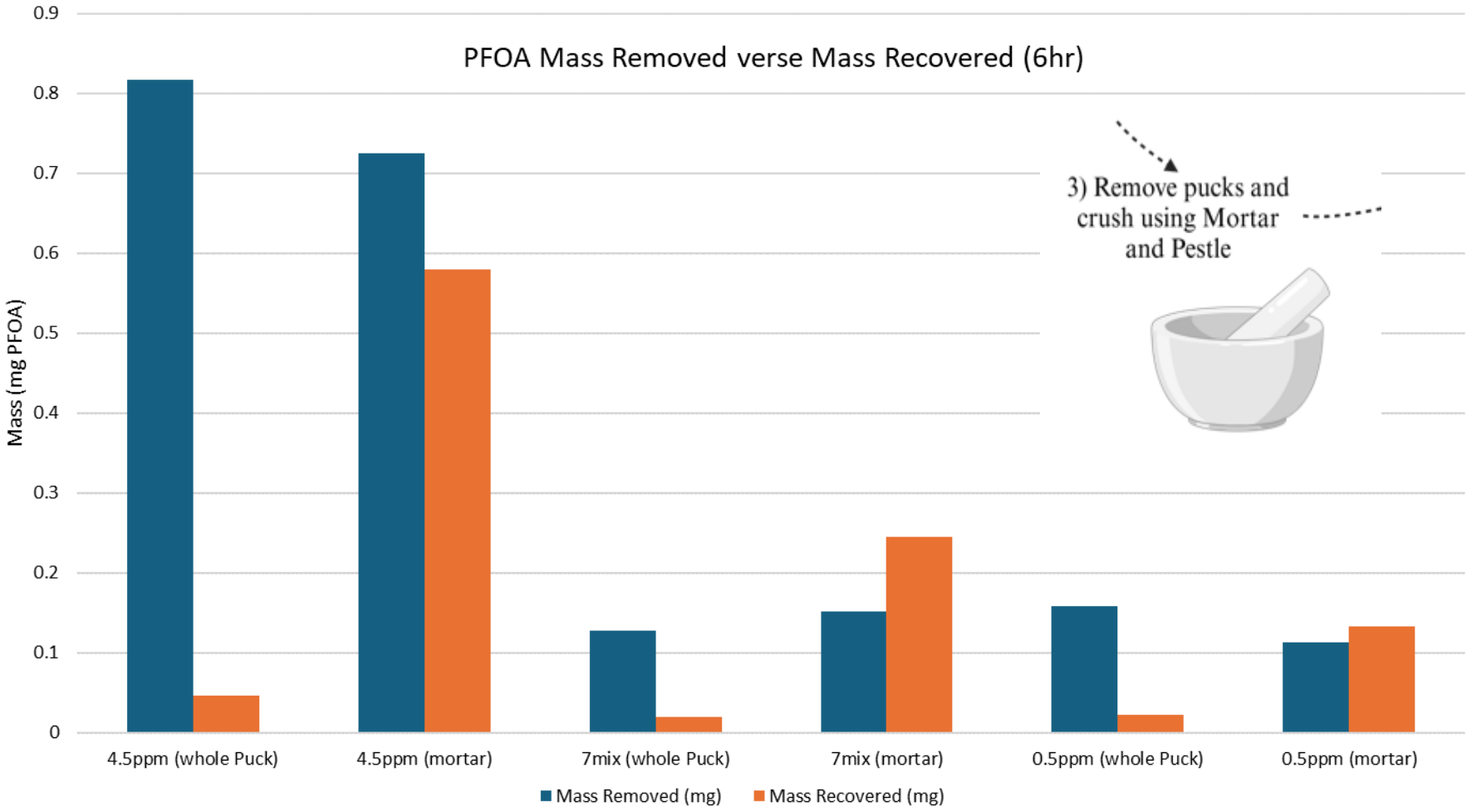
PFOA Removal HPLC Water



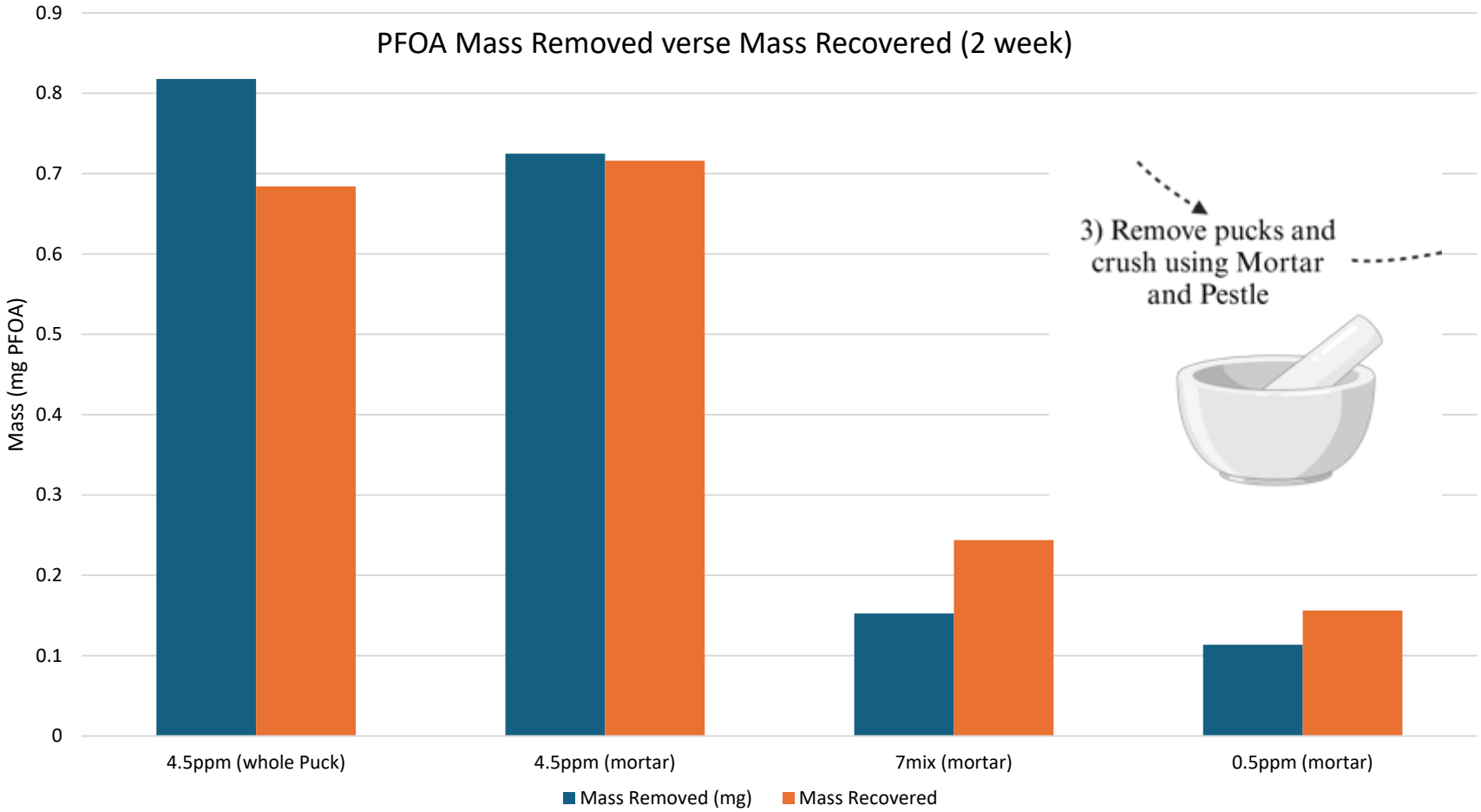
PFOA Removal Interferents



Short Term Desorption vs Removal

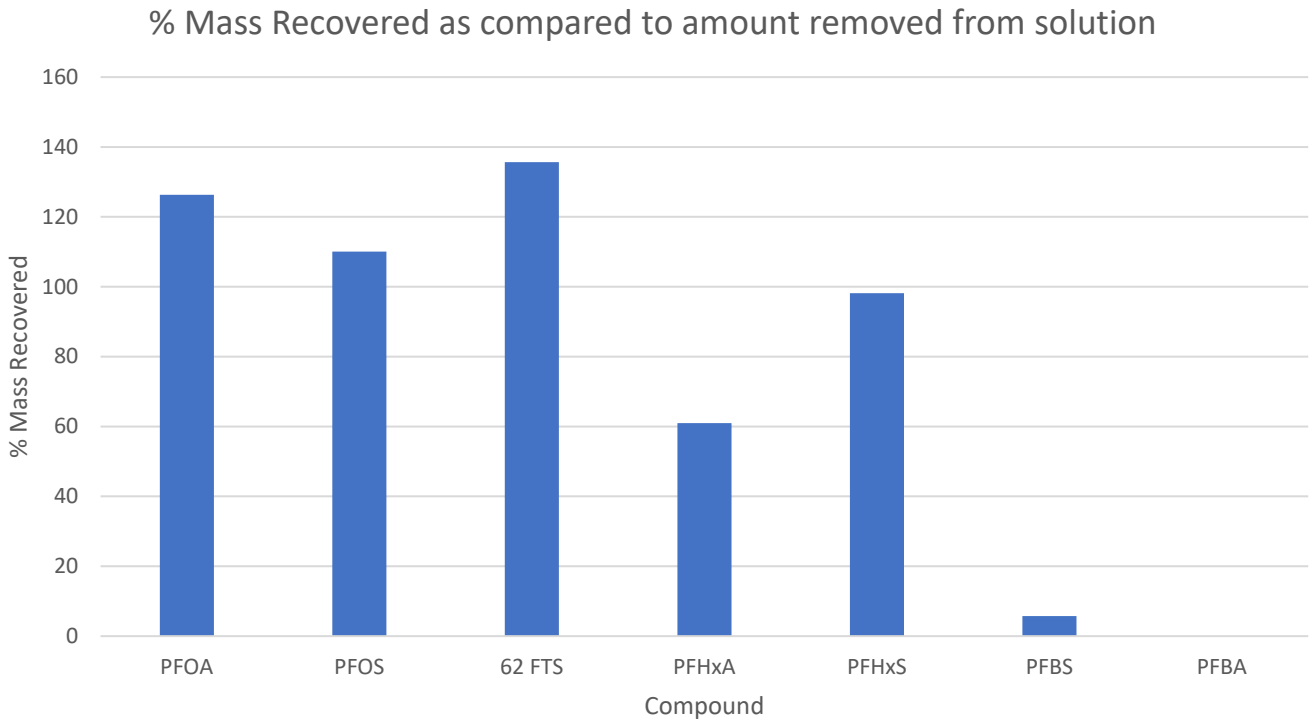


Long Term Desorption vs Removal



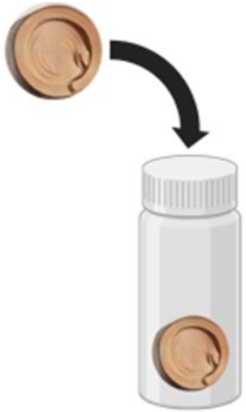
7 PFAS Desorption vs Removal

3) Remove pucks and crush using Mortar and Pestle



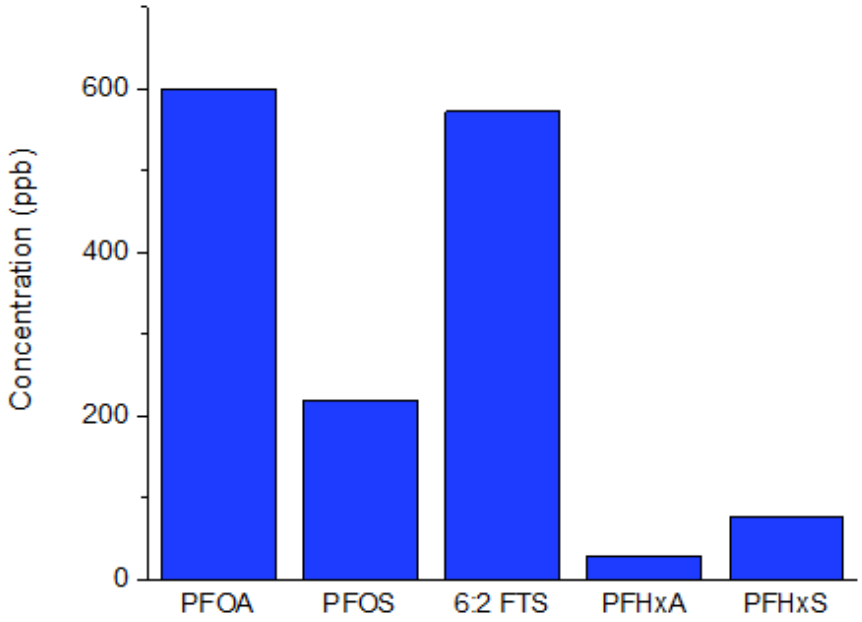
Puck with mix of 7 PFAS conc. 0.2-1.3 ppm start

PFAS concentration for better analysis



Multiple PFAS compounds adsorbed from lab water at 1-2 ppb initial concentration, followed by desorption from crushed disks

Measured concentrations in desorbing solution



Concentration factors of 15- 500x

Next Steps

- Ongoing testing at ppt level
- Characterize and optimize performance
- Field testing in groundwater / surface water sources

Acknowledgements

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U.S. Army Medical Center of Excellence

Questions?

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