# Treatment Of Poly- and Perfluoroalkyl Substances: Feasibility and Challenges

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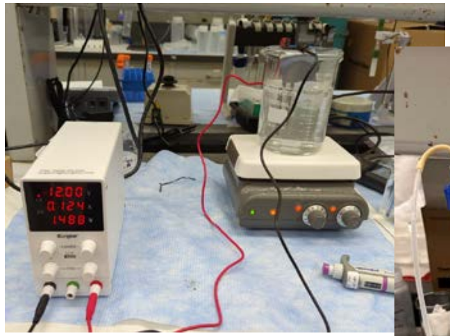
# Program to Address Contaminants of Emerging Concern

- 1,4-Dioxane, PFAS, PPCPs: Occurrence, fate and transport
- Develop and test treatment technologies
- Transformation of chemicals during water treatment
- Assess toxicity of chemicals and byproducts

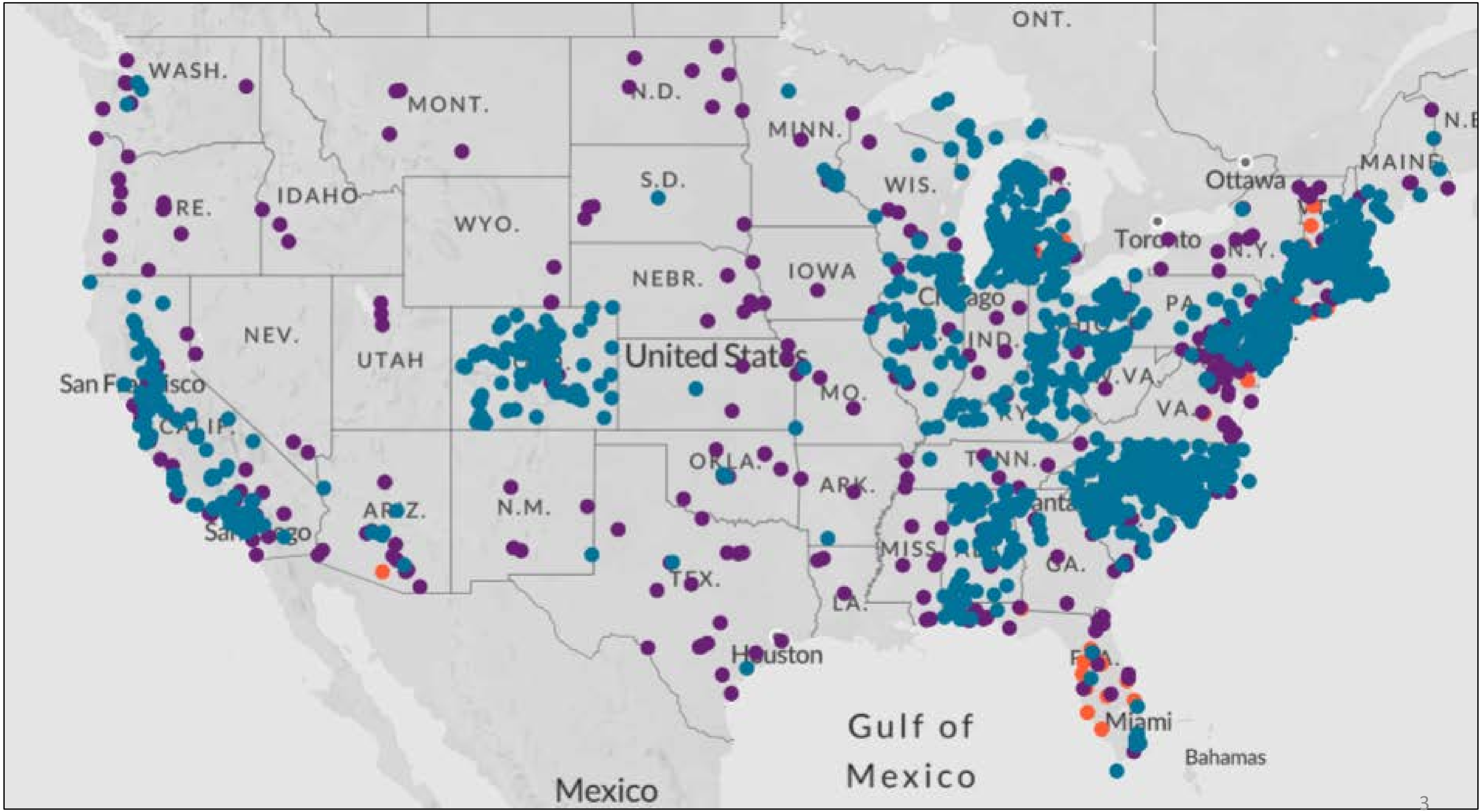

Mass spectrometry


Batch systems


Flow-through systems


Pilot systems

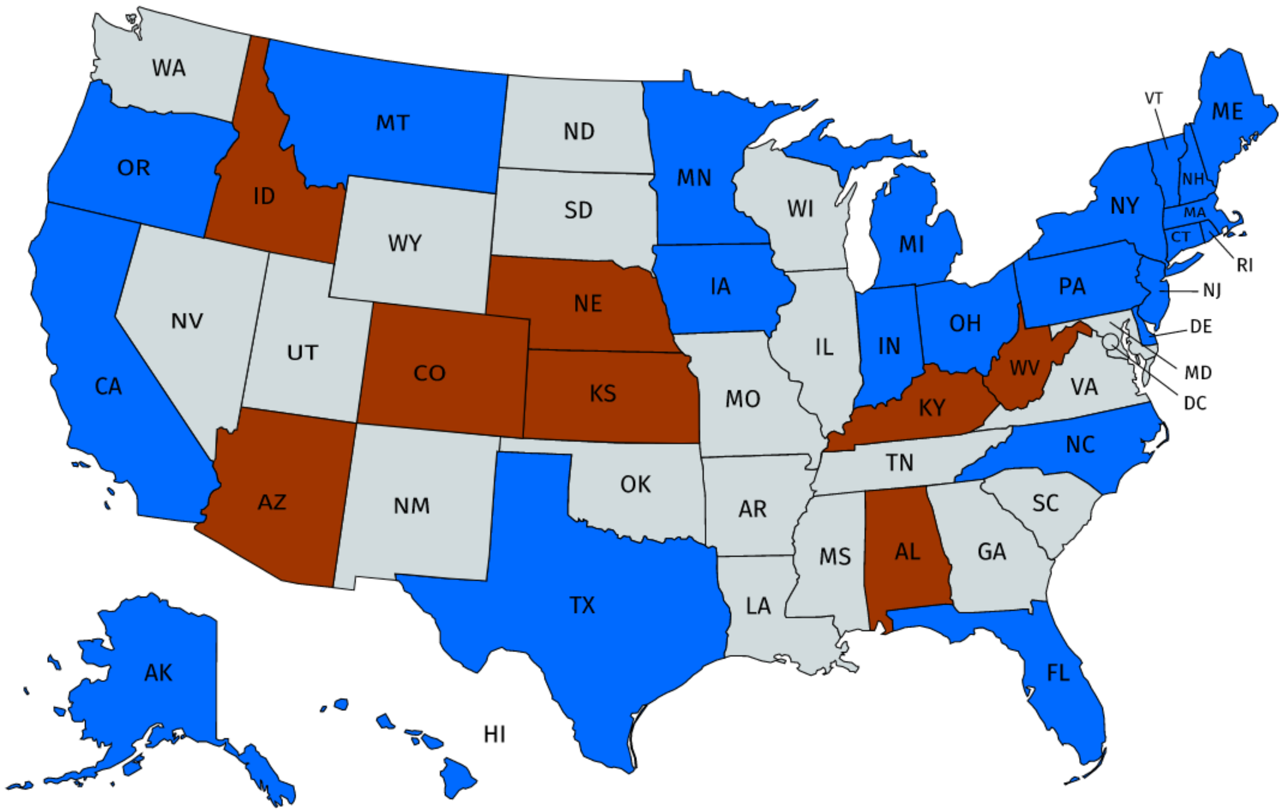
# Widespread PFAS Occurrence in U.S.




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

# U.S. PFAS water regulations

- New U.S. EPA health advisory level (non-enforceable and non-regulatory): 4 parts per quadrillion for PFOA (0.004 ppt) and 20 ppq for PFOS (0.020 ppt).
- Two other PFAS: GenX - 10 ppt; PFBS - 2,000 ppt



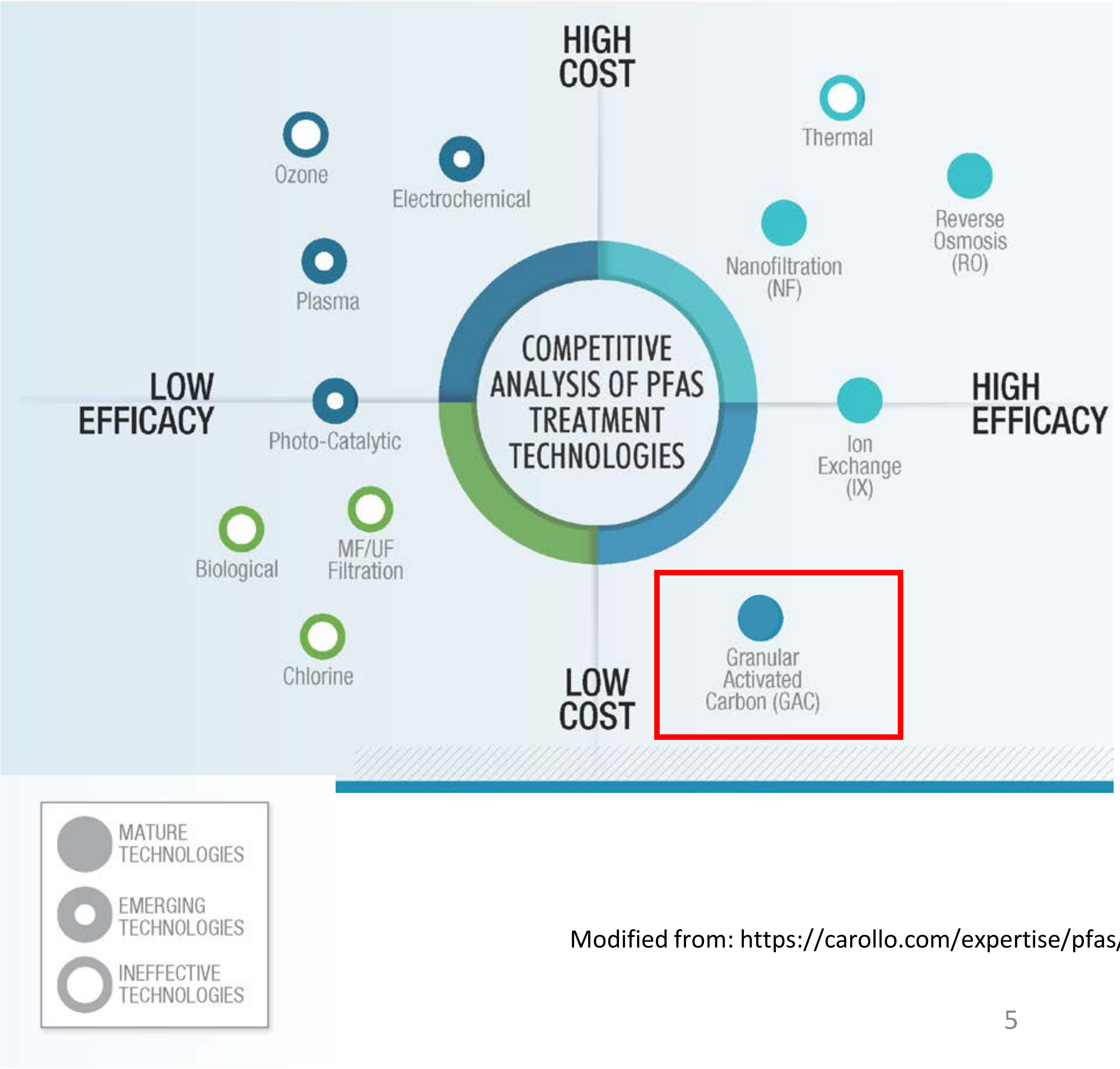

NYS: 10 ng/L of PFOA and PFOS
Other PFAS under consideration by NYS: PFNA, PFHpA, PFHxS, PFHxA, PFPeA, PFBA, and PFBS

Establish standards and guidance values for PFAS

Use old EPA health advisory (70 ppt)

# PFAS treatment technologies: a summary

| Treatment Type | Technology Category | Technology |
|---|---|---|
| Sequestration Technologies | Sorption | Activated Carbon |
| | | Anion Exchange Resin |
| | | Biochar |
| | | Zeolites/clay minerals |
| | Membrane Filtration | Reverse Osmosis |
| | | Nanofiltration |
| | Coagulation | Specialty Coagulants |
| Transformation or destruction technologies | Redox treatment | Electrochemical |
| | | Electron beam |
| | | Ozone |
| | | Plasma |
| | Other | Sonochemical |
| | | Thermal |
| | | Biological |




Modified from: https://carollo.com/expertise/pfas/

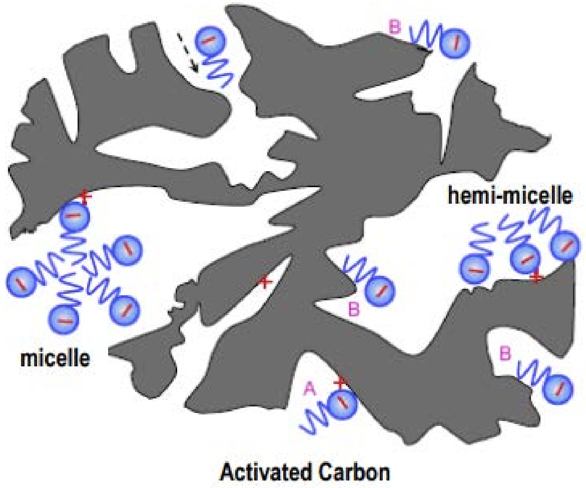
# 1. Granular Activated Carbon (GAC)

Most common approach for PFAS treatment

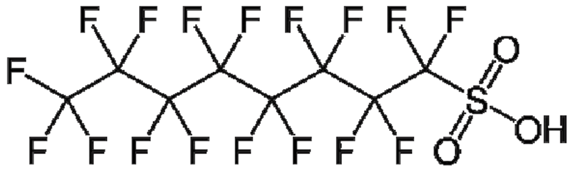
Sorption Mechanism:

- Hydrophobic interactions - dominant mechanism
- Long-chain PFAS with higher hydrophobicity show better removal compared to short-chain PFAS
- Electrostatic interactions – minor but important for short-chain PFAS


Granular mean particle diameter (1mm)
Powdered mean particle diameter (0.043 mm)



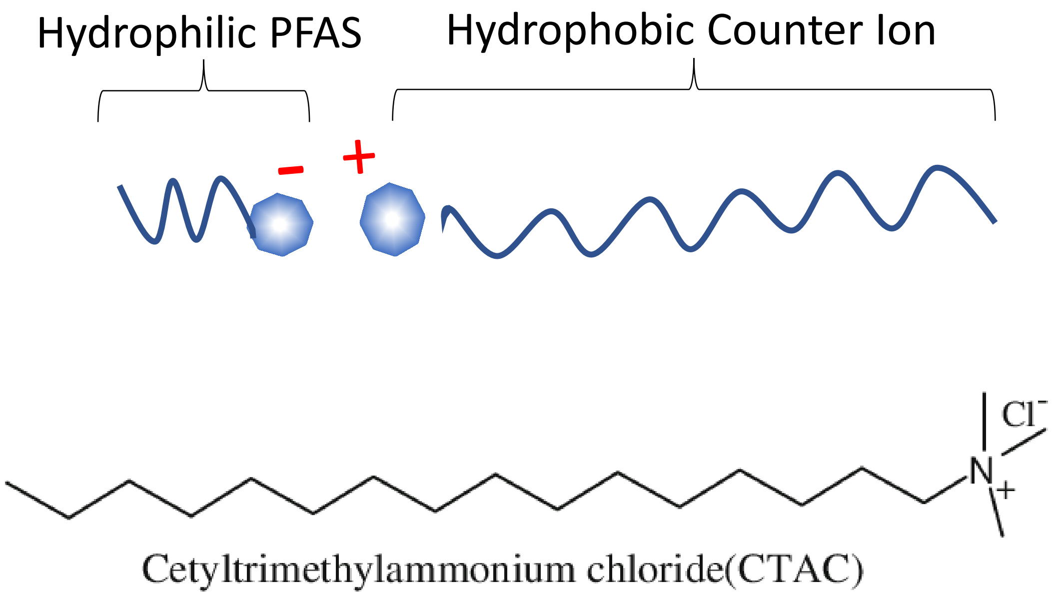

Yu et al, 2009



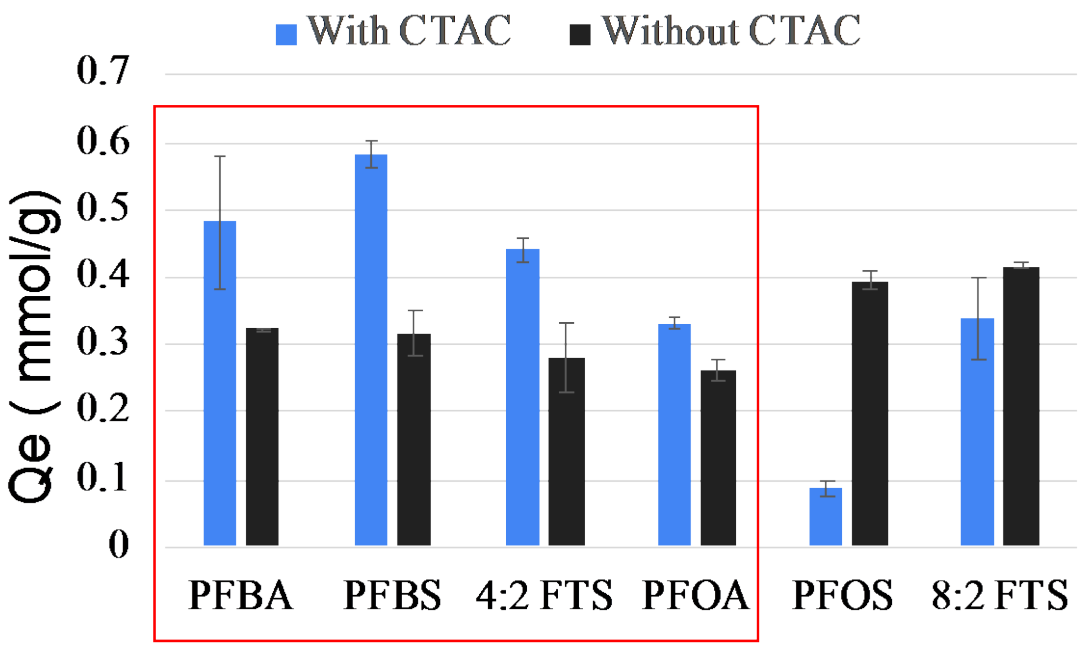
Perfluorooctanesulfonic acid (PFOS) (C8)

# How can we improve GAC performance for hydrophilic PFASs?

- Modify GAC surface – introduce more positive functional groups
- Hydrophobic ion pairing (HIB)

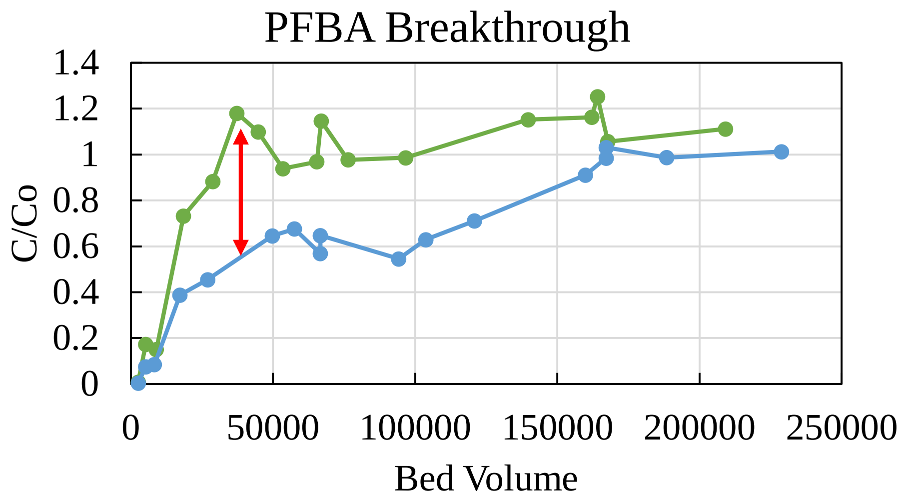



Batch Adsorption Experiments

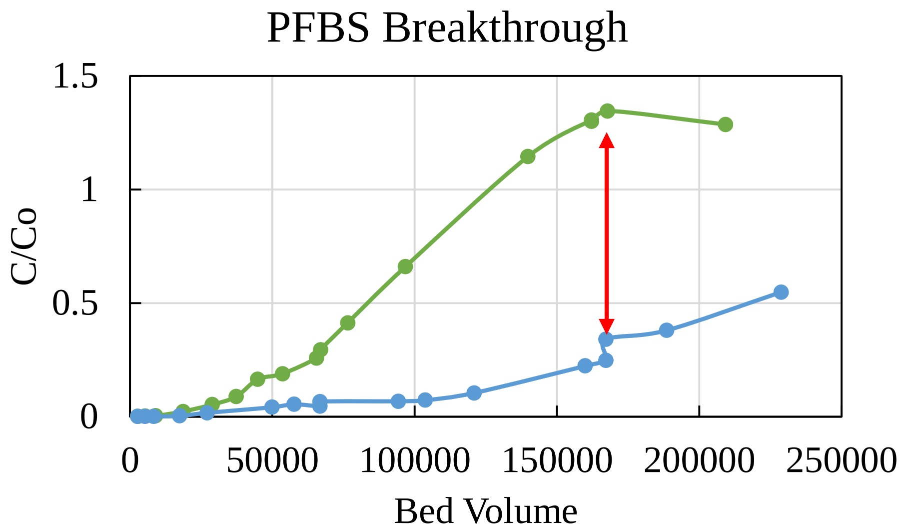


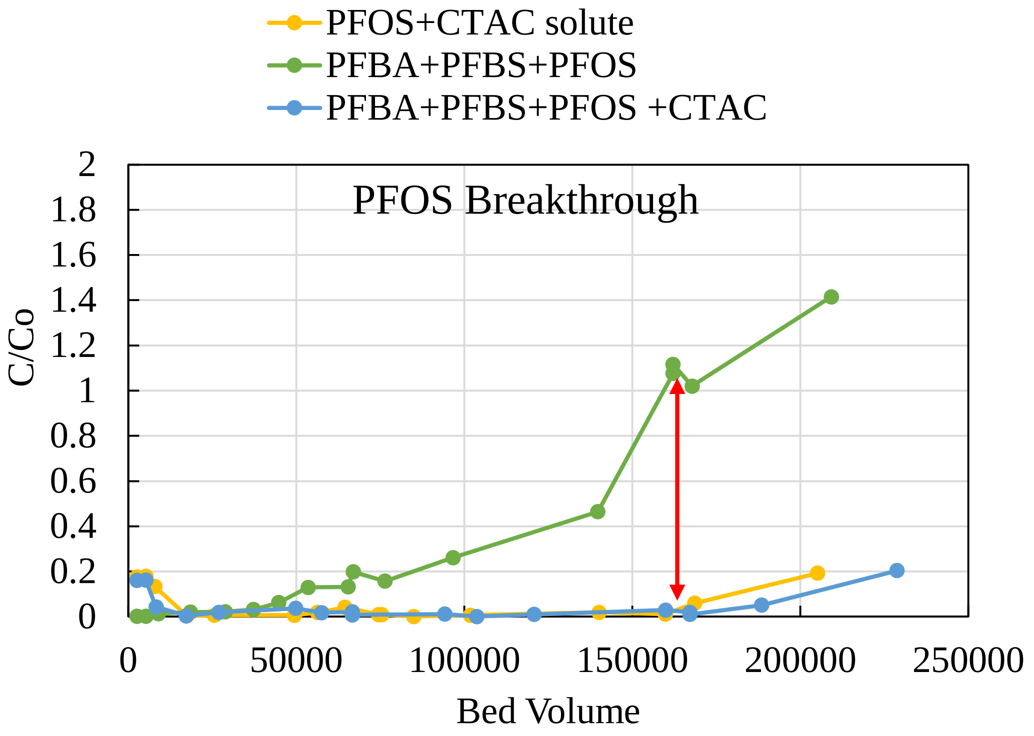

Zhang et al., *In Preparation*

# Rapid Small Scale Column Tests



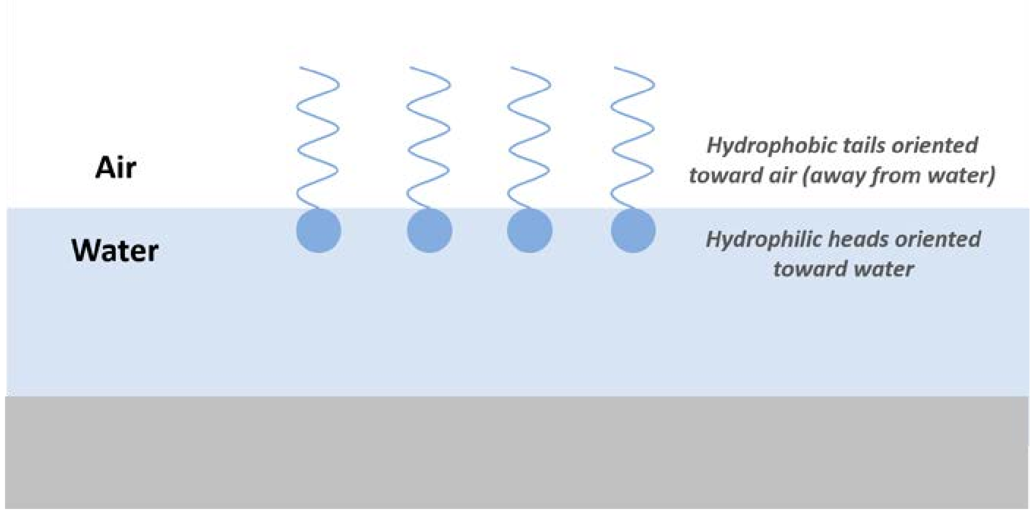

| Influent | PFBA-PFBS-PFOS | PFBA-PFBS-PFOS-CTAC |
|---|---|---|
| PFBA (ppb) | 5.67 | 6.06 |
| PFBS (ppb) | 6.36 | 6.44 |
| PFOS (ppb) | 4.43 | 4.79 |
| CTAC (ppm) | 0 | 1.5 |

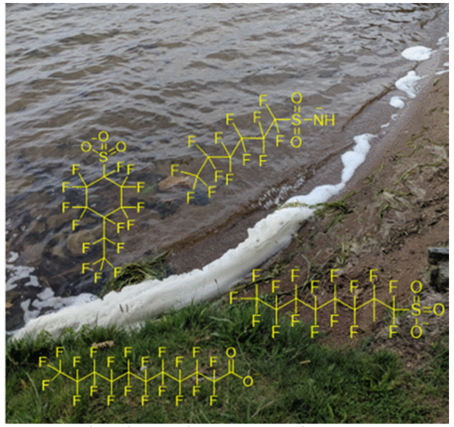


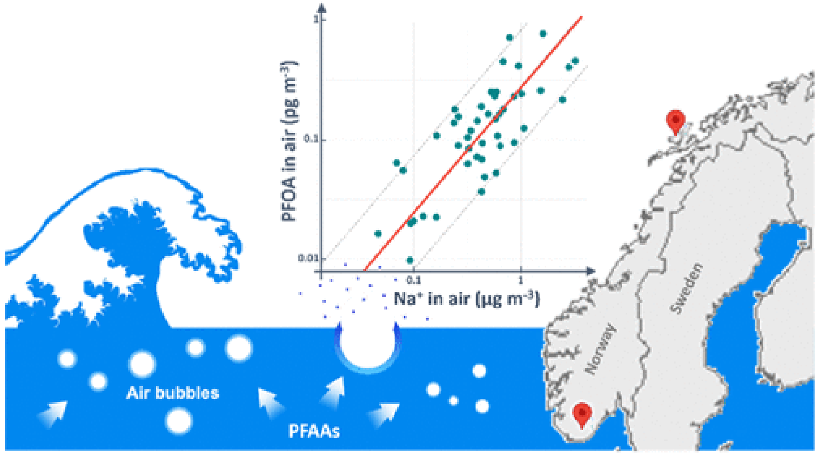

Zhang et al., *In Preparation*

# 2. Foam fractionation (air bubbling) to remove PFAS



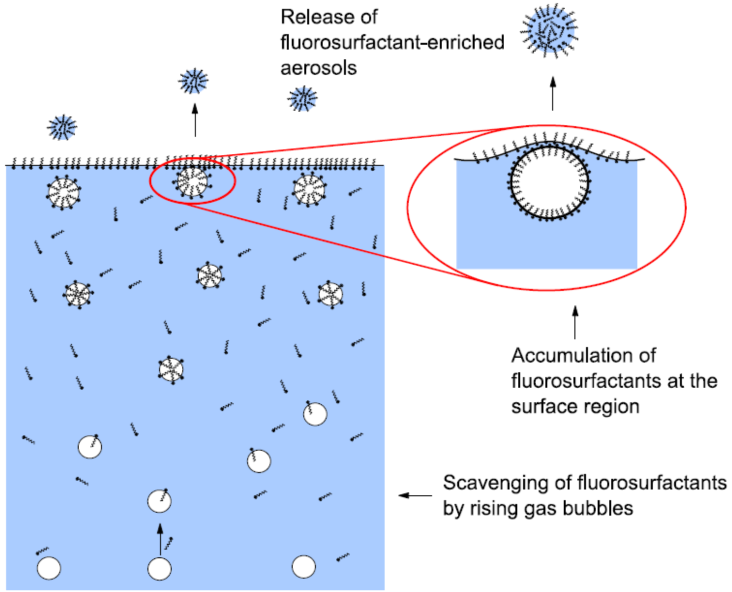



Schichtenberg et al., 2020



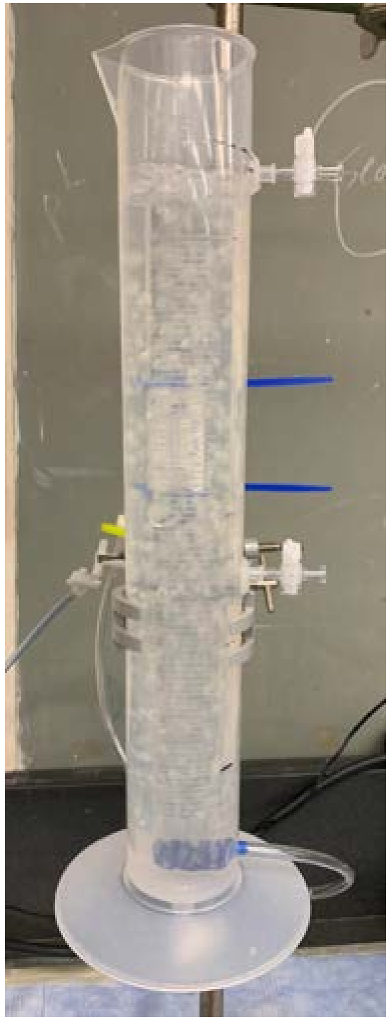

Sha et al., 2021

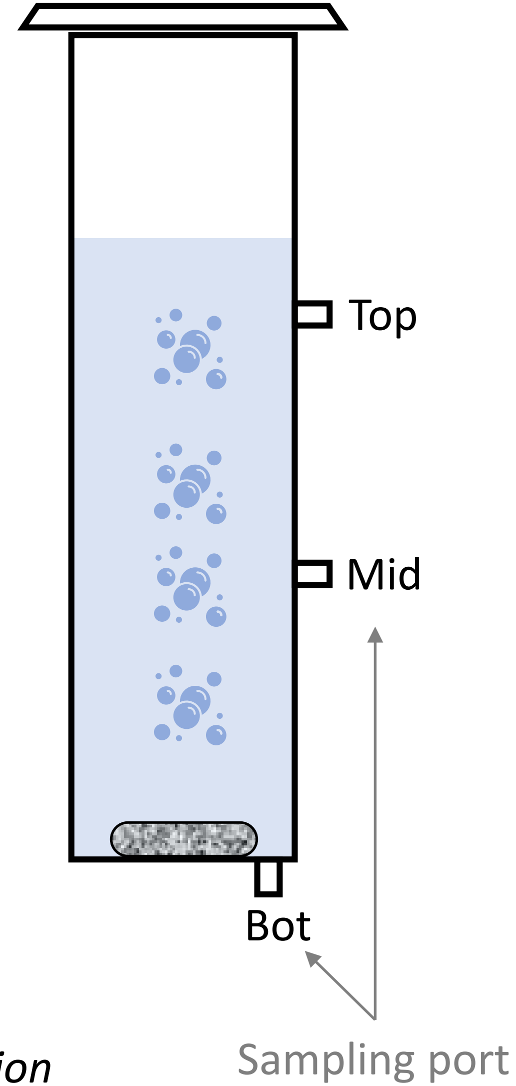
National Synchrotron Light Source II at BNL (Dr. Ben Ocko)

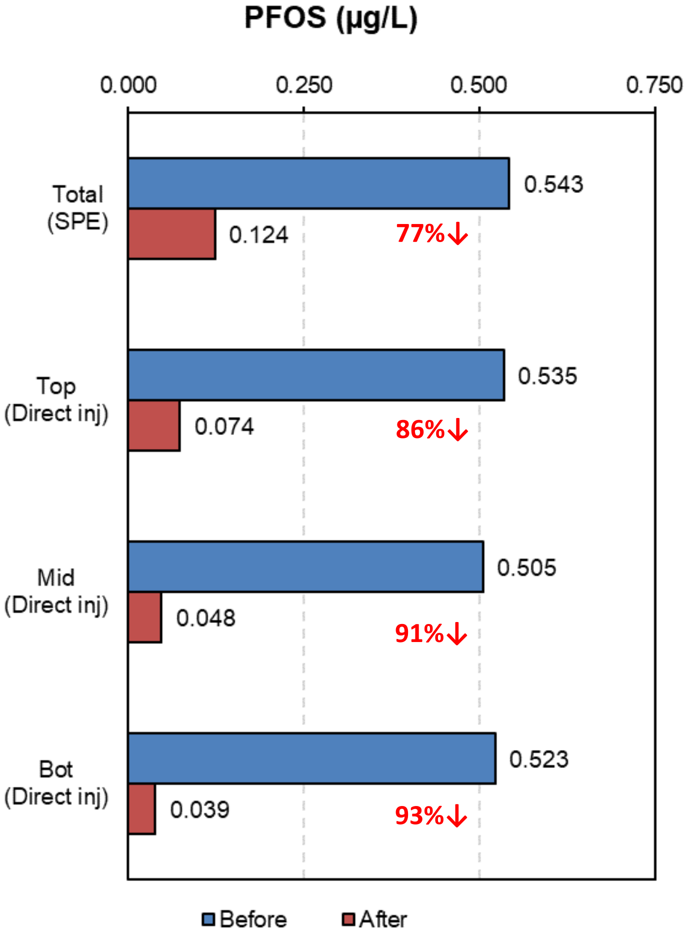


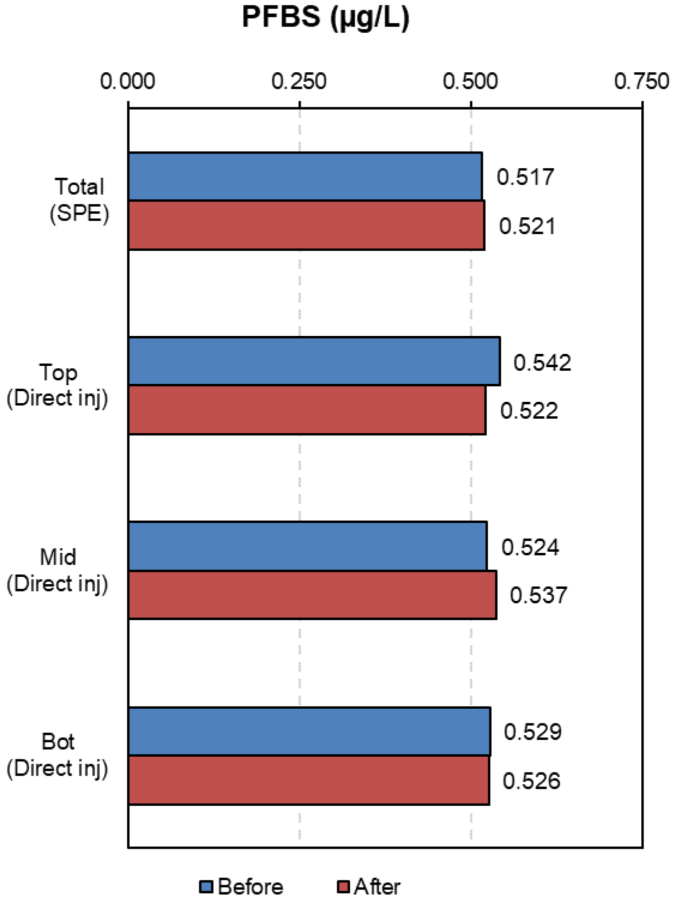

(Ebersbach et al., 2016)

# PFAS air-bubbling experiment



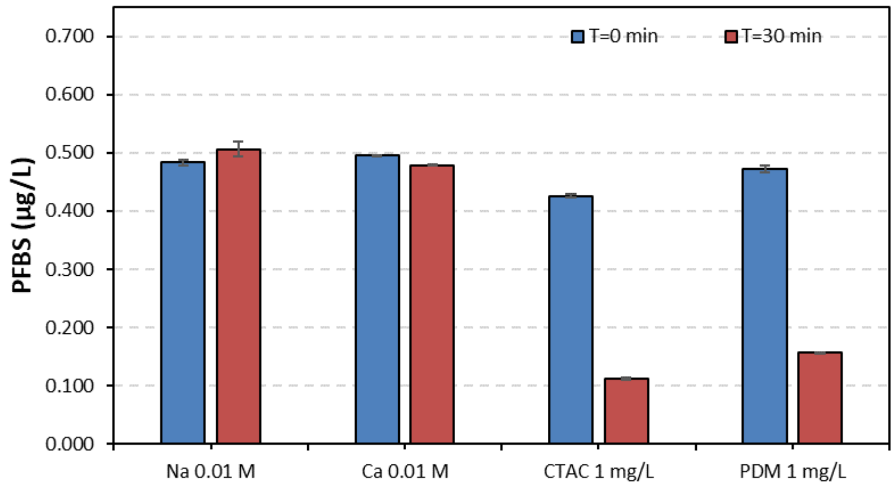


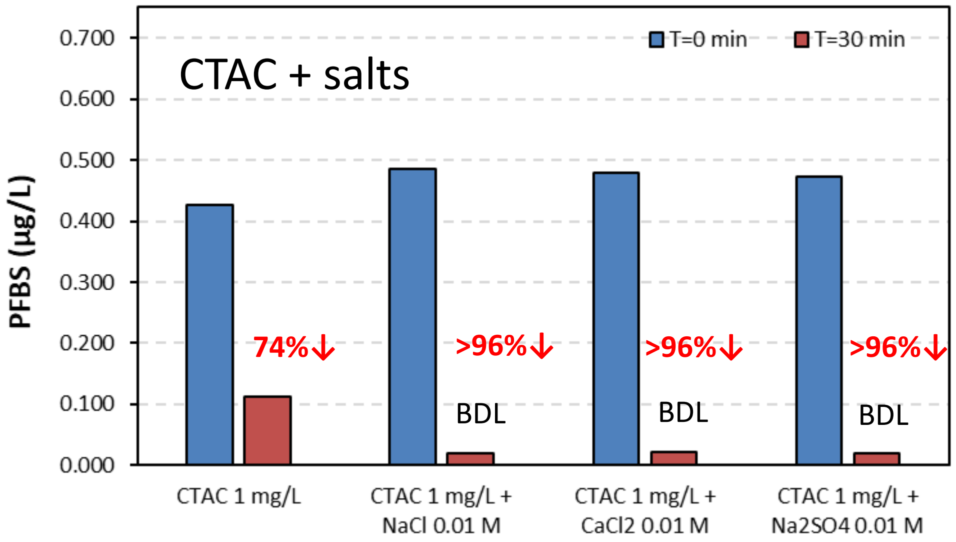




Lee et al., *In Preparation*

# Effect of cationic modifiers/additives



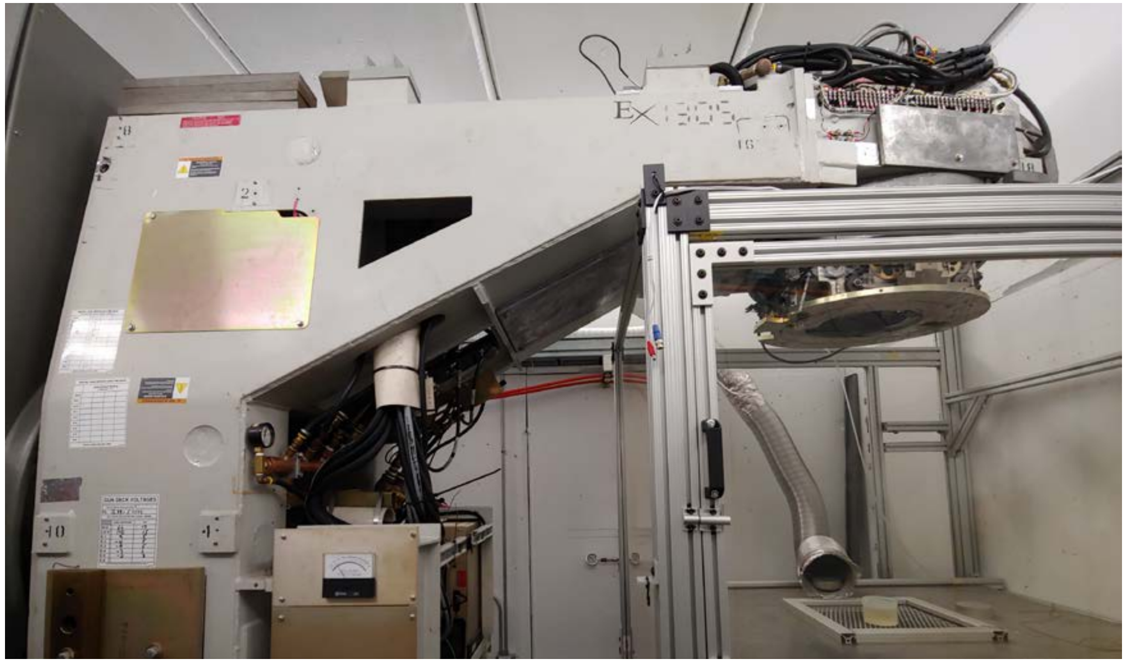

1 mg/L CTAC

1 mg/L CTAC + 0.01 M salt

Lee et al., *In Preparation*

# 3. Treatment of PFAS using e-beam

- E-beam : Advanced Oxidation/Reduction process
- Generates reactive species such as $H^+_{aq}$ , $e_{aq}^-$ and $OH^{\cdot}$ amongst others
- Collaboration with FermiLab to treat PFAS and 1,4-dioxane



Accelerator Applications Development and Demonstration (A2D2) at FermiLab

$$H_2O \rightsquigarrow H_2O^* \longrightarrow H + OH$$
$$H_2O \rightsquigarrow H_2O^+ + e^-$$

$e^- \longrightarrow e^-_{th} + n\,H_2O \longrightarrow e^-_{aq}$ (solvated electron)

$$H_2O^+ + H_2O \longrightarrow H_3O^+(H^+_{aq}) + OH$$
$$e^-_{aq} + OH \longrightarrow {}^-OH_{aq}$$
$$e^-_{aq} + H^+_{aq} \longrightarrow H$$

**Primary products of water radiolysis :**

$$H_2O \rightsquigarrow e^-_{aq}\,,\ H\,,\ OH\,,\ H_2\,,\ H_2O_2\,,\ H^+_{aq}\,,\ {}^-OH_{aq}$$
$$G_i = (2.7)\ (0.6)\ (2.8)\ (0.45)\ (0.72)\ (3.2)\ (0.5)$$

$$1\ kGy = 6.344 \times 10^{-4}\ mol.dm^{-3}\ (e^-_{aq} + H + OH)$$

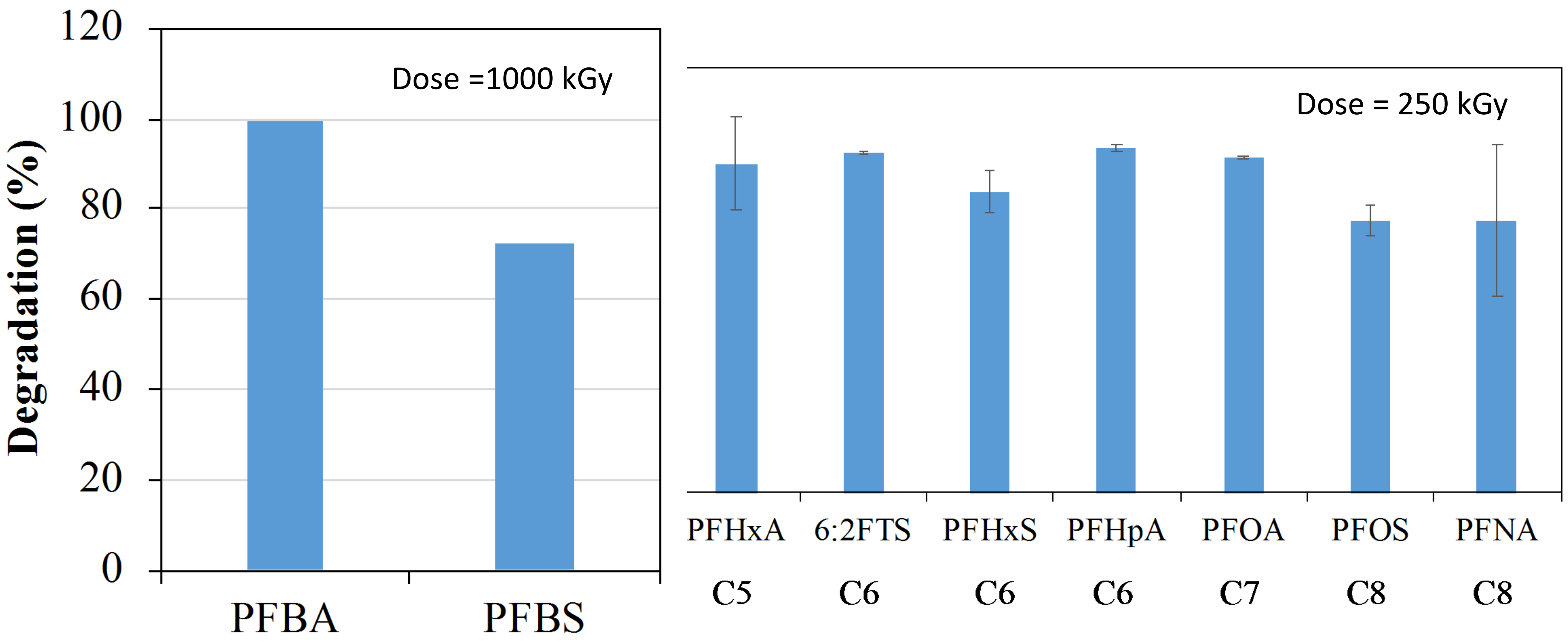
G-value = number of produced or decomposed Molecules per 100 eV absorbed energy

For conversion into SI-units multiply the G-values by 0.10364 to obtain G(x) in $\mu mol.J^{-1}$

Source : Getoff, 2002

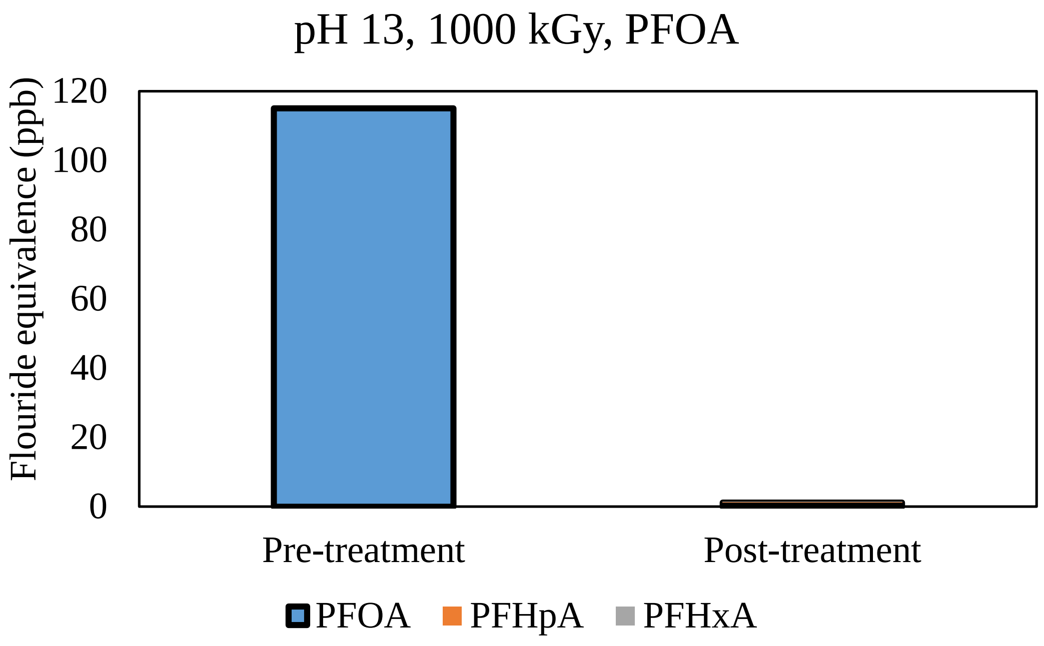
# Degradation of PFASs

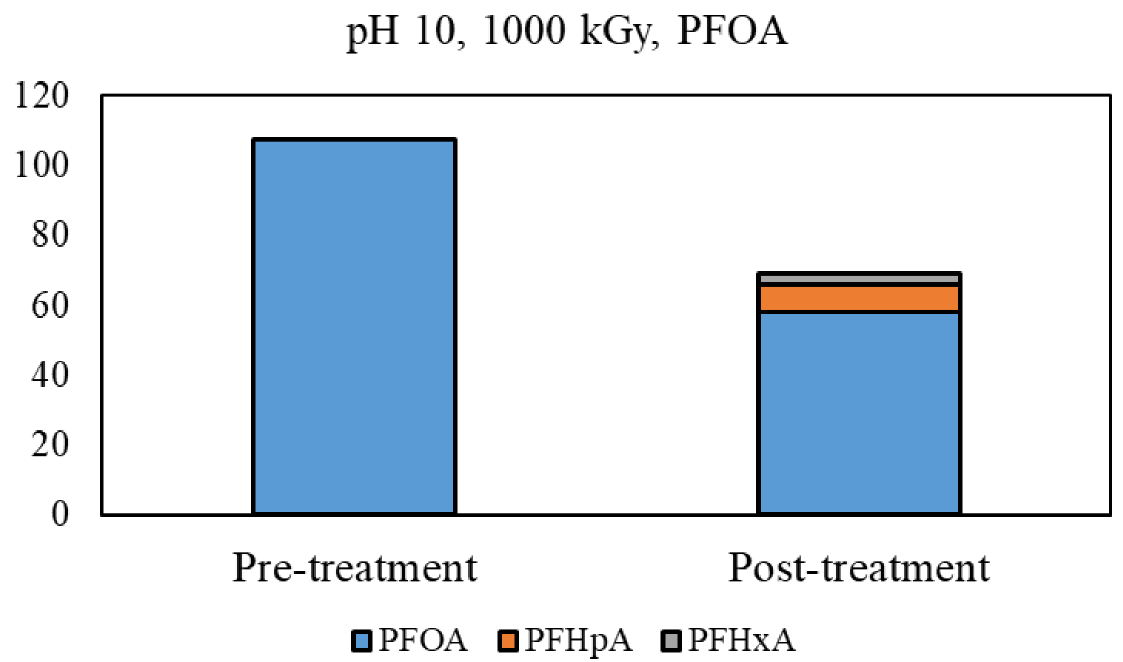
Alkaline (pH 13) and low dissolved oxygen (2 mg/L) at a dose of 250 kGy (1 kGy = 1 kJ/kg)




Londhe et al., *In Preparation.*

# Incomplete Mass balance – A Challenge



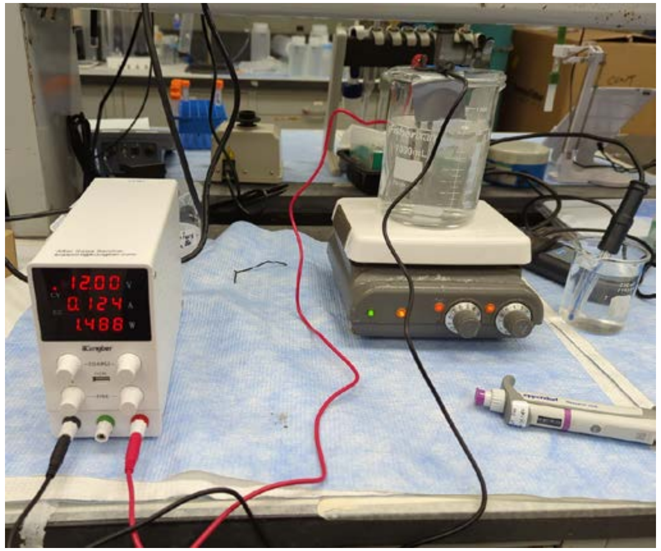



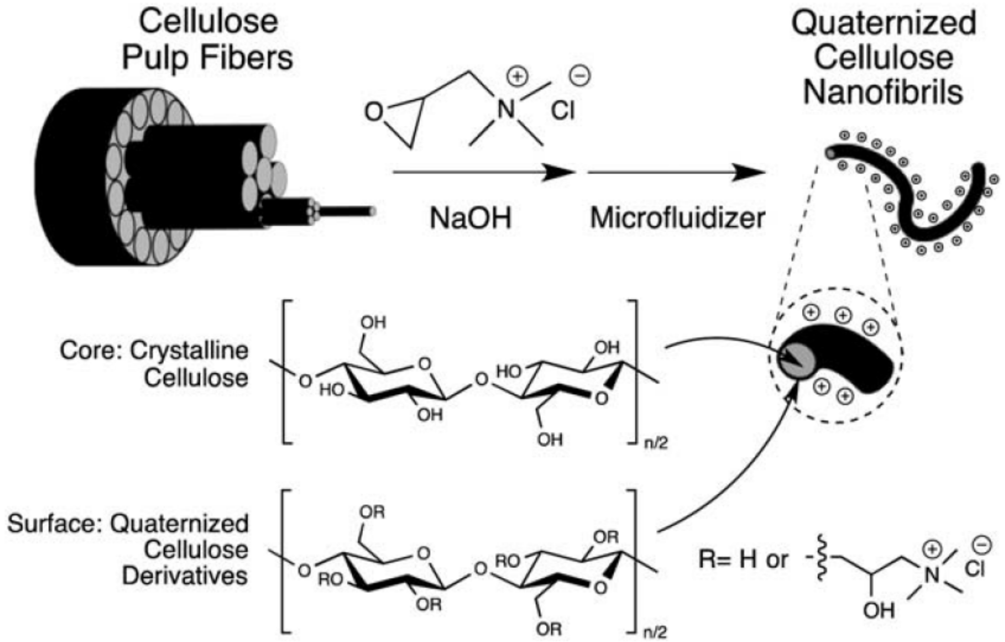

- No fluoride was detected
- TOP assay of treated samples did not reveal oxidizable transformation products
- Polyfluorinated compounds and/or volatiles
- Non target screening can provide more insight into degradation mechanism

Londhe et al., *In Preparation.*

# Ongoing Work and Next Steps

- Other technologies: electrochemical oxidation, ion exchange treatment, functionalized bio-adsorbents, enhanced coagulation
- Pilot testing: GAC, foam fractionation
- Mechanism of PFAS removal, degradation, and transformation products
- Toxicity of PFASs






Source: Duning Li, Dr. Ben Hsiao

# Take homes

- Sequestration approaches are effective in the treatment of most PFASs
- Sequestration approaches do not degrade PFAS
  - Concentrated PFAS waste stream is created
- Destructive approaches are in development stages and more research is needed
- Short-chain compounds are difficult to treat
- Critical challenge: inability to close the PFAS mass balance
  - Production of unknown transformation products
  - How toxic are these products?
- Treatment train combining sequestration and destructive approaches are needed to remove and destroy PFAS

# Acknowledgment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