PFAS Research at UNH:
Characterizing Point Sources and their Receiving Water Bodies

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*Now at Seacoast School Tech.

Special Thanks:
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NH Sea Grant: Steve Jones and Great Bay National Estuarine Research Reserve: Cory Riley, Chris Peters
NHDES, Especially Ray Gordon, Tracy Wood, Brandon Kernen for helpful feedback on our analysis

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Research
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Graduate School
STAF Fellowship
Ellie

Engineered Removal of PFAS, Fate in Environment

• Some proven (GAC) and promising (resin) technologies for PFAS removal in drinking water

• Huge knowledge gaps in other sub-disciplines of environmental engineering:
  - Wastewater and their residuals (a.k.a sludge or biosolids)
  - Point and non-point source fate in aquatic environments
  - Fate in sediments, food-chain

• We do know: microorganisms can transforming some PFAS precursors to known and unknown daughter products. But when, where, how, and what?
Interest at UNH: WWTFs, Fate in Environment

**PFAS Wastewater Cycle**

Major PFAS sources to WWTFs:
- **Industrial users:** Landfills, Septic haulers
- **Commercial users:** Metal finishers, Paper manufacturers, Fabric/leather treaters
- **Contaminated sites:** Firefighting foams

**Air Emissions**

**Industrial Developers**

**Residential Development**

Effluent Discharge

NPDES Permit

PFAS Unregulated

Air Emissions

**Water Body**

**Sediment, Aquatic Biota**

**PFAS Wastewater Cycle**

Major PFAS sources to WWTFs:
- **Industrial users:** Landfills, Septic haulers
- **Commercial users:** Metal finishers, Paper manufacturers, Fabric/leather treaters
- **Contaminated sites:** Firefighting foams

**Shadowed WWTF Process**

**Influent Wastewater**

**Primary Treatment**

**Secondary Treatment**

**Disinfection Treatment**

**Effluent Wastewater**

**WWTF Treatment Operations:**
- **Secondary Treatment Options:**
  1. Aerated Lagoons (AL)
  2. Activated Sludge (AS)
  3. 4-Stage Bardenpho (Bar4)
  4. Oxidation Ditch (OD)
- **Disinfection Options:**
  1. Chlorination/Dechlorination (CD)
  2. Ultraviolet Light (UV)

WWTF were not designed for PFAS removal

Some WWTF processes may enhance PFAS breakdown, generating more mobile, toxic products
Unknown/unanticipated reactions occurring in WWTF

Fan et al, (Jan 2020) Chemical Engineering Journal

Research Goals

1) Characterize sources and sinks of PFAS in engineered facilities (WWTFs)
2) Evaluate how WWTF processes influence PFAS distribution
3) Investigate the fate of PFAS after discharge
Research Goals

1) Characterize sources and sinks of PFAS in engineered facilities (WWTFs)
2) Evaluate how WWTF processes influence PFAS distribution
3) Investigate the fate of PFAS after discharge

Sampling Approach

Six WWTF locations and
And FIVE locations in the Great Bay

Hilton Park
Mill Pond
Squamscott Point
Great Bay
Adams Point

Total:
28 WWTF Aqueous Samples
4 WWTF Sludge Samples
5 Surface Water Samples
Sampling and Analysis - We Are Applying Two Approaches

Method 1: Perfluorinated Alkyl Acids by Isotope Dilution
Alpha Lab: EPA 537 Rev 1.15
“Standard” Analysis - 24 PFAS Constituents

- **Sampling**
  - PFAS Free Clothing and Sampling Materials
  - Blanks w/Each Event

- **Extraction**
  - Internal Standard Added
  - Solid Phase Extraction (SPE)
  - Methanol Elution

- **Analysis**
  - HPLC/MS-MS

Method 2: Perfluorinated Alkyl Acids by Isotope Dilution with Total Oxidizable Precursor (TOP) Assay Analysis*
“TOP” Analysis - 18 PFAS Constituents

- **Sampling**
  - PFAS Free Clothing and Sampling Materials
  - Blanks w/Each Event

- **Extraction**
  - Internal Standard Added
  - Solid Phase Extraction (SPE)
  - Methanol Elution

- **Clean-Up**
  - Conversion of precursors to PFAAs
  - Can Detect with HPLC/MS-MS

- **Analysis**
  - HPLC/MS-MS

*Houtz & Sedlak, 2012, ES&T
Janda et al, 2019
Which Compounds Do We Measure?

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Acronym</th>
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<td>Perfluorobutanoic acid</td>
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<td>PFOA</td>
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<td>Perfluorodecanesulfonic acid</td>
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"Standard" Analysis - 24 PFAS Constituents

18 Intermediate Metabolites and Terminal End Products

6 Precursors

* 17 PFAS measured by NHDES

"TOP" Assay - 18 PFAS Constituents

TOP Only Measures Intermediate Metabolites and Terminal End Products

TOP Assay Converts these and other unknown precursors to PFAAs

<table>
<thead>
<tr>
<th>Analyte</th>
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<tr>
<td>Perfluoroctylsulfonamide</td>
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Which Compounds are Consistently Detected in Samples?

### Presence/Absence in Influent & Effluent

<table>
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<tr>
<th>Treatment</th>
<th>PFCA</th>
<th>PFSA</th>
<th>Precursor</th>
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<td>WWTP #6</td>
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**Consistently Detected:**
- 8 PFCA As
- 4 PFSA As
- 3 Precursors

**PFCA Concentrations Increased from Influent to Effluent**

**More PFCA As detected than PFSA As and Precursors**
### Presence/Absence in Influent & Effluent (UNH/NHDES)

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How does Influent/Effluent Data Compare with that Collected by NHDES?
• ΣPFAS appear to increase after wastewater treatment
  But this is likely due to WWTF matrix issues, detection limits not actual mass increases.

• Great Bay concentrations considerably lower than effluent

UNH ΣPFAS data in line with NHDES data

-Similar story for 4 PFAS compounds regulated with new MCL/AGQS
How are PFAS entering WWTFs distributed in effluent and sludge?

PFAS composition in effluent (left) differs from sludge (right)

- More PFAS detected in sludge (n=18) than effluent (n=11)
- Long-chain PFAS predominant in sludge; short-chain PFAS predominant in effluent (hydrophobicity)
- PFOS and other C8 PFAS are predominant in sludge
- More precursors found in sludge (more easily detected at higher concentrations?)
Do Great Bay Concentrations Compare to Other Surface Waters?

“Bulk” Great Bay Concentrations Consistent with Non-Contaminated NH Surface waters
Are PFAS Constituents in Receiving Water Bodies Consistent with WWTF Discharges?

More PFAS detected in effluent than Great Bay. PFAS concentrations higher in effluent than Great Bay.
Preliminary Findings

- Large PFAS fraction accumulating in sludge
- Sludge contains precursors and longer chain (hydrophobic) compounds
- Effluent contains shorter chain (hydrophilic) compounds
- Many PFAS in WWTF effluent detected in Great Bay, lower concentrations
- We will be looking more closely at connection to WWTF operational parameters

Concluding Thoughts

1) Research challenging due to
   - Chemical complexity
   - Matrix issues (sludge, freshwater/marine system)
   - Cost of analysis vs access to specialized equipment
   - Analysis potentially misses thousands of PFAS

2) Limited baseline data
   - Monitoring necessary to get a handle on distribution, fate
   - What about other sources (e.g., septage)?

3) Little is known about these compounds in the environment
   - Biosolids on farms into groundwater, surface water
   - Accumulation in sediments
   - Assimilation in biota

4) UNH students are very interested in topic
   - CEE 520: Environmental Pollution to CEE 896: Bioremediation
   - Honors thesis student
Thank You
Questions