# Distribution of Per- and Polyfluorinated Alkyl Substances (PFAS) in Wastewater Treatment Plants


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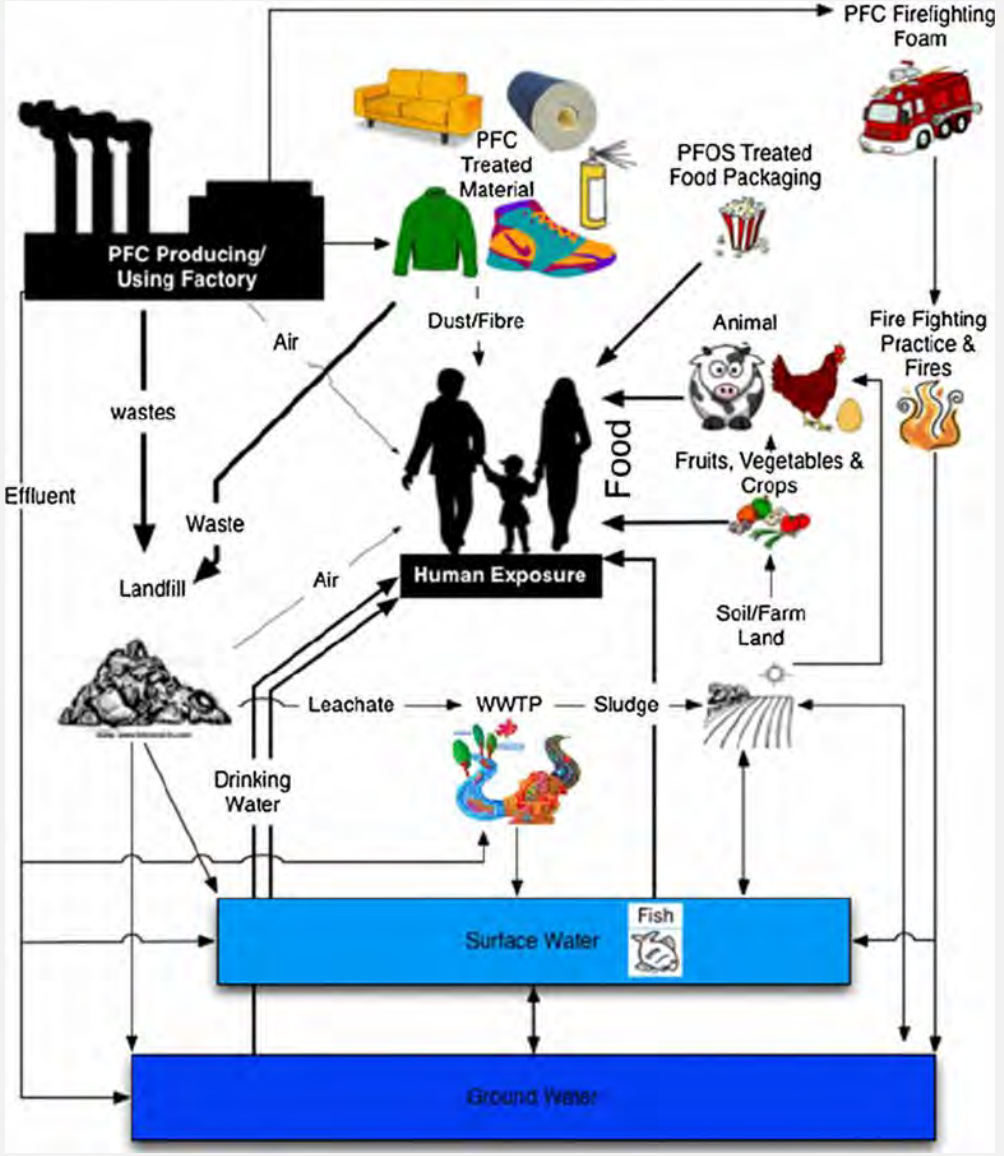
# Outline

- PFAS Background
- Research Plan
- Sampling Procedure
- Preliminary Results

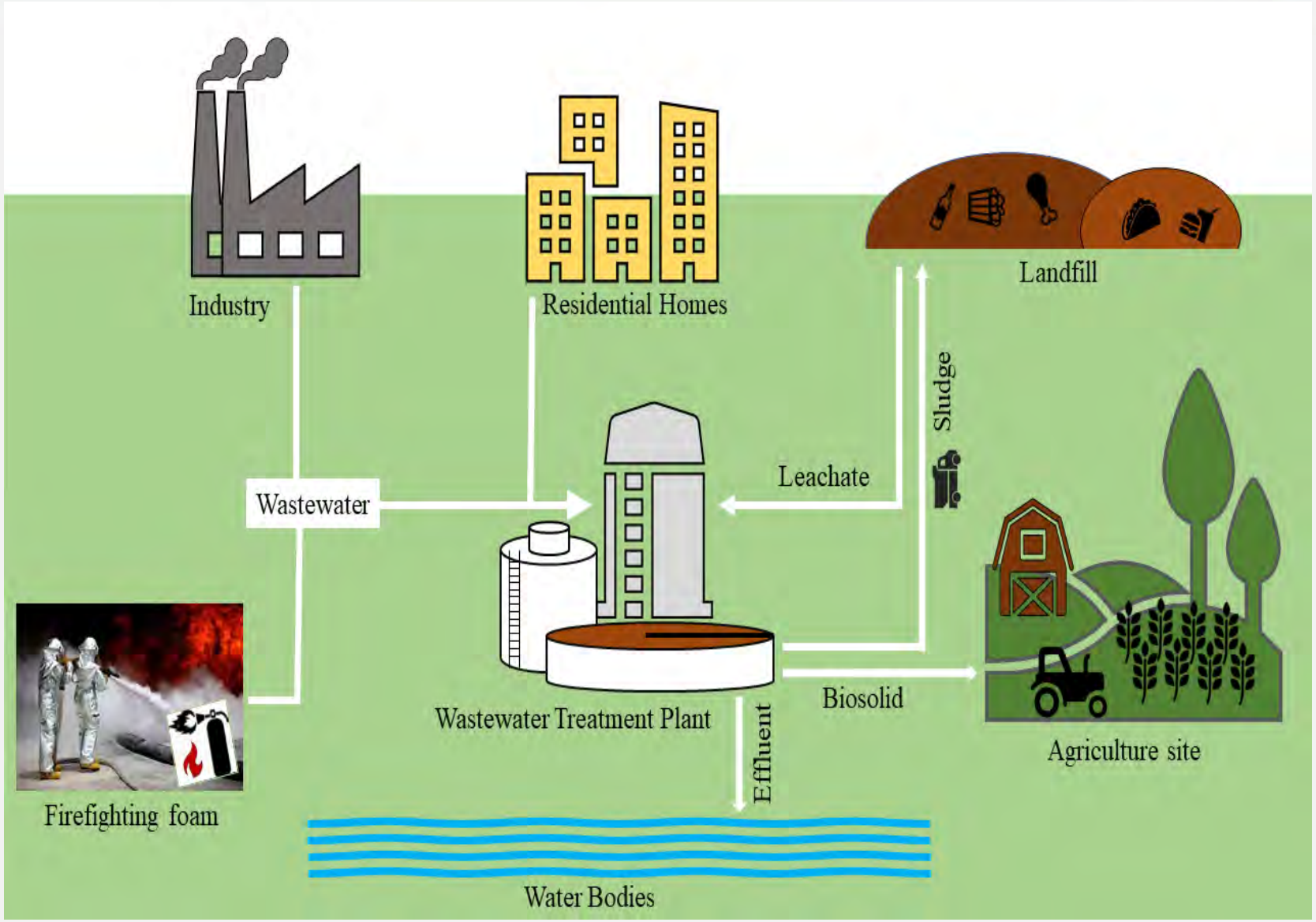
# Why PFAS?

- Persistent and bioaccumulative
- Thermally and chemically stable
- Adverse human health impact

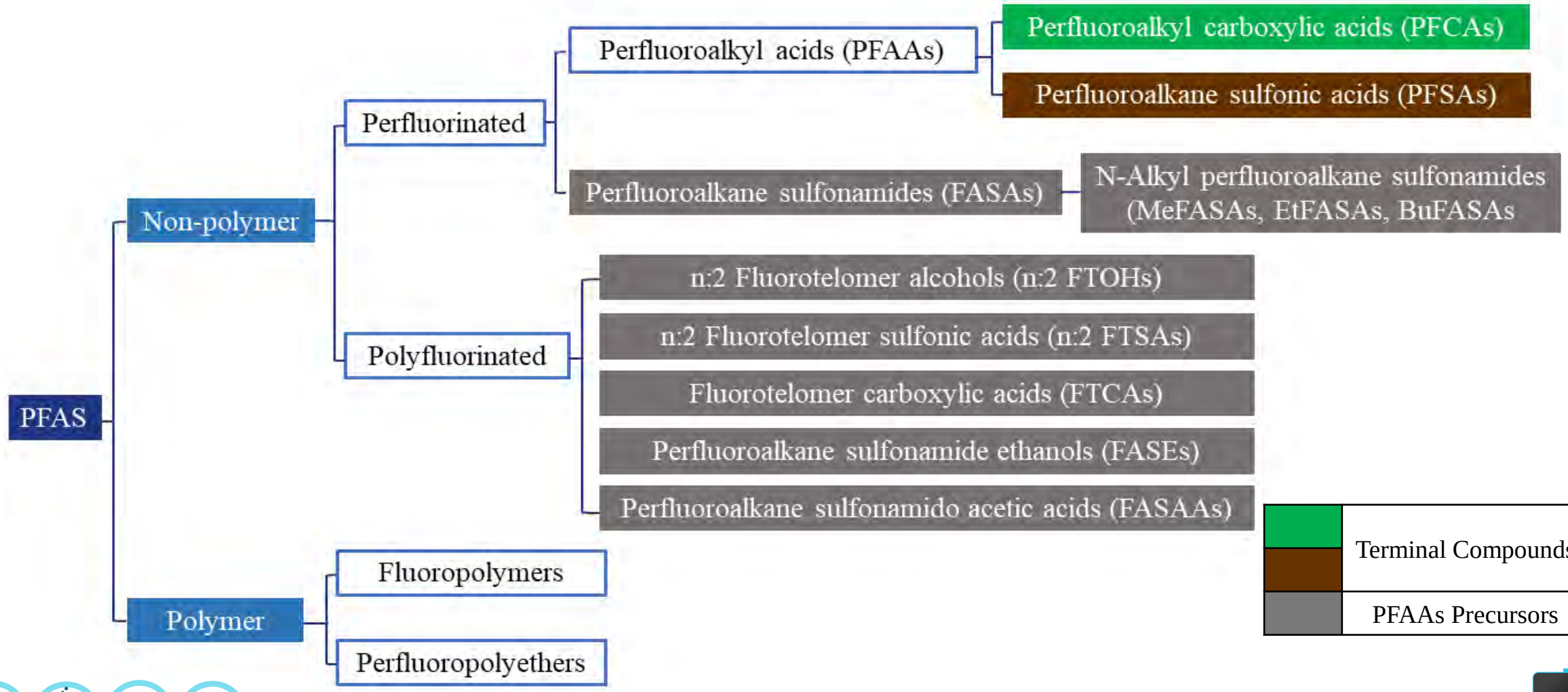



(Source:Oliaei,2013)

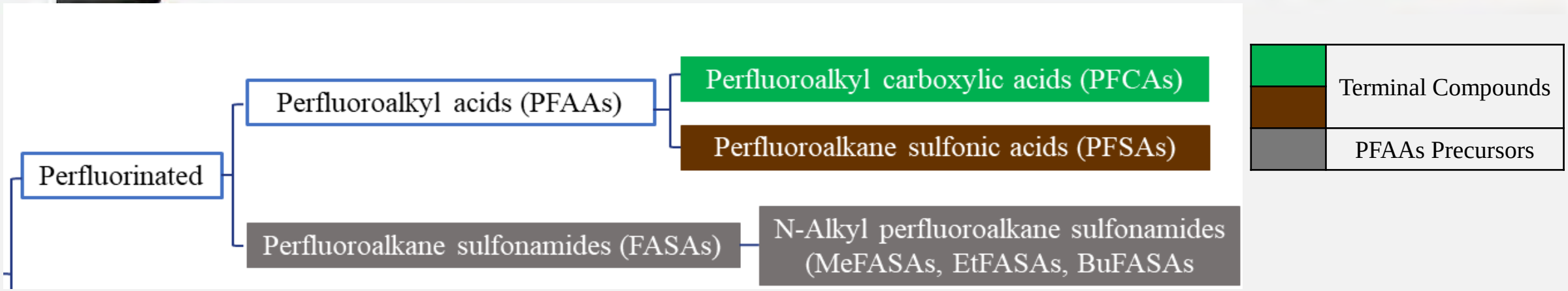
# Why WWTP?


Industry
Residential Homes
Landfill
Sludge
Wastewater
Leachate
Wastewater Treatment Plant
Biosolid
Agriculture site
Effluent
Firefighting foam
Water Bodies

# PFAS Family

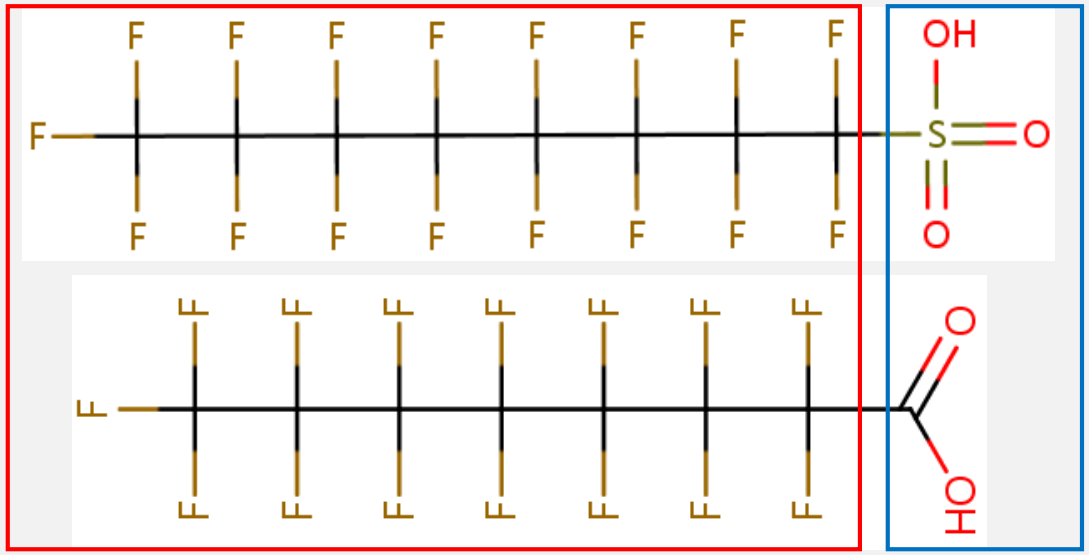

PFAS
Non-polymer
Perfluorinated
Perfluoroalkyl acids (PFAAs)
Perfluoroalkyl carboxylic acids (PFCAs)
Perfluoroalkane sulfonic acids (PFSAs)
Perfluoroalkane sulfonamides (FASAs)
N-Alkyl perfluoroalkane sulfonamides (MeFASAs, EtFASAs, BuFASAs
Polyfluorinated
n:2 Fluorotelomer alcohols (n:2 FTOHs)
n:2 Fluorotelomer sulfonic acids (n:2 FTSAs)
Fluorotelomer carboxylic acids (FTCAs)
Perfluoroalkane sulfonamide ethanols (FASEs)
Perfluoroalkane sulfonamido acetic acids (FASAAs)
Polymer
Fluoropolymers
Perfluoropolyethers
Terminal Compounds
PFAAs Precursors

# PFAS Family




PFOS

- Fully fluorinated
- Hydrophobic
- Different C-F length




PFOA

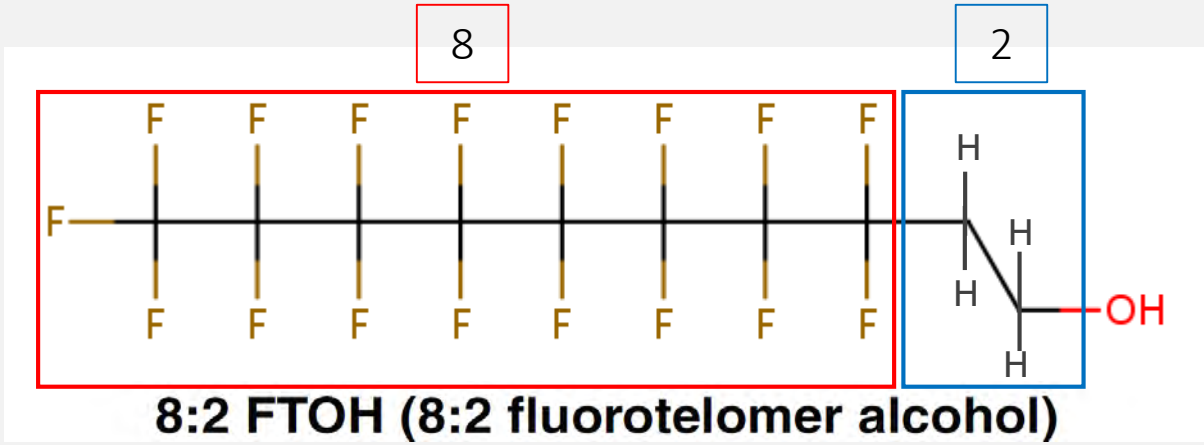
- Functional group (carboxylic or sulfonic acids)
- Hydrophilic
- Degradable function

# PFAS Family

- Polyfluorinated
  - n:2 Fluorotelomer alcohols (n:2 FTOHs)
  - n:2 Fluorotelomer sulfonic acids (n:2 FTSAs)
  - Fluorotelomer carboxylic acids (FTCAs)
  - Perfluoroalkane sulfonamide ethanols (FASEs)
  - Perfluoroalkane sulfonamido acetic acids (FASAAs)

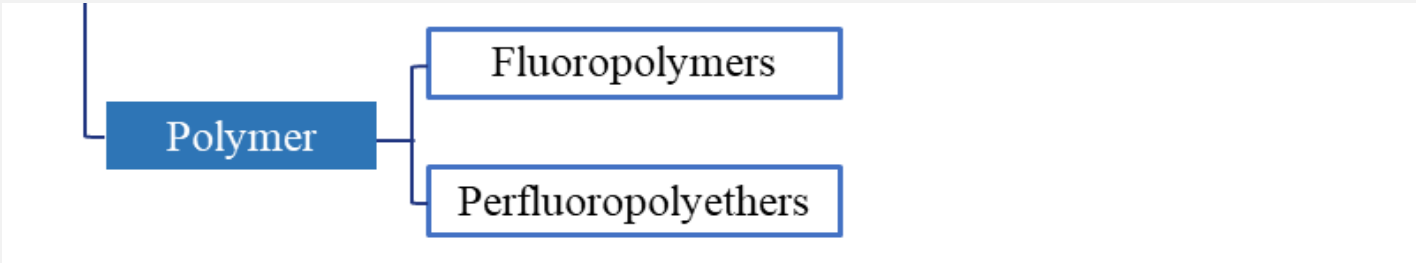
| | |
|---|---|
| | Terminal Compounds |
| | PFAAs Precursors |

- Partially fluorinated
- Non-fluorine atoms (O,H) attached to at least one carbon atom

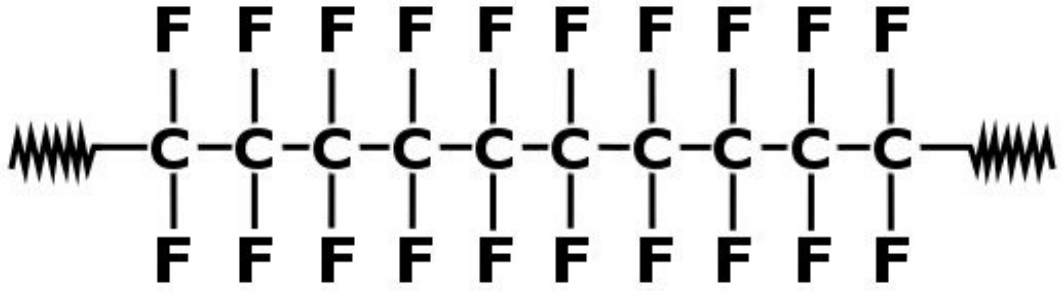



8:2 FTOH (8:2 fluorotelomer alcohol)

# PFAS Family




- Large molecules formed by combining many identical smaller molecules in a repeating pattern
- have/not functional group
- Potential PFAAs precursors
- Hydrophobic



polytetrafluorethylene (PTFE)

# PFAS Family

12 ng/L

11 ng/L

**18 Terminal End Products & Intermediate Metabolites**

18 ng/L

15 ng/L

| ANALYTE<br>Perfluoroalkylcarboxylic Acids (PFCAS) | ACRONYM |
|---|---|
| Perfluorobutanoic acid | PFBA |
| Perfluoropentanoic acid | PFPeA |
| Perfluorohexanoic acid | PFHxA |
| Perfluoroheptanoic acid | PFHpA |
| Perfluorooctanoic acid * | PFOA |
| Perfluorononanoic acid * | PFNA |
| Perfluorodecanoic acid | PFDA |
| Perfluoroundecanoic acid | PFUnA |
| Perfluorododecanoic acid | PFDoA |
| Perfluorotridecanoic acid | PFTrDA |
| Perfluorotetradecanoic acid | PFTA |
| **Perfluoroalkylsulfonic Acids (PFASs)** | |
| Perfluorobutanesulfonic acid | PFBS |
| Perfluoropentanesulfonic acid | PFPeS |
| Perfluorohexanesulfonic acid * | PFHxS |
| Perfluoroheptanesulfonic acid | PFHpS |
| Perfluorooctanesulfonic acid * | PFOS |
| Perfluorononanesulfonic acid | PFNS |
| Perfluorodecanesulfonic acid | PFDS |

## 6 Precursors

| Perfluorooctanesulfonamides (FOSAs) | |
|---|---|
| Perfluorooctanesulfonamide | FOSA |
| **Telomer Sulfonates** | |
| 1H,1H,2H,2H-perfluorohexane sulfonate (4:2) | 4:2FTS |
| 1H,1H,2H,2H-perfluorooctane sulfonate (6:2) | 6:2FTS |
| 1H,1H,2H,2H-perfluorodecane sulfonate (8:2) | 8:2FTS |
| **Perfluorooctanesulfonamidoacetic Acids** | |
| N-methyl perfluorooctanesulfonamidoacetic acid | NMeFOSAA |
| N-ethyl perfluorooctanesulfonamidoacetic acid | NEtFOSAA |

* Proposed Drinking Water Limits-NHDES

# PFAS Knowledge and Gaps

| What We 'Know' | Current Gaps |
| --- | --- |
| 1. PFAS are toxic to both human and animals (e.g. PFOA and PFOS: elevated cholesterol, obesity in human and reproductive effect on animals) | • Effect of other PFAS constituents<br>• Lack of toxicity values for many PFAS compounds |
| 2. Drinking water PFAS concentrations limits (e.g. PFOA, PFOS, PFNA, PFHxS) | • Other PFAS constituents limits<br>• Different environmental matrices |
| 3. PFAS removal in drinking water plants (e.g. GAC, Membrane filtration, Ion Exchange, Plasma) | • Mechanism not well understood<br>• incomplete degradation<br>• Waste brine management |
| 4. PFAS biotransformation and their precursors degradation during biological treatment in WWTFs (e.g. AS, OD) | • PFAS fate during secondary treatment<br>• Lack of PFAS precursors knowledge |
| 5. WWTFs as a main source of PFAS distribution to water bodies | • PFAS fate after discharging to water bodies from effluent of WWTFs |

# Research Goal

1. What **portion** of PFAS are being **detected** within local WWTFs?

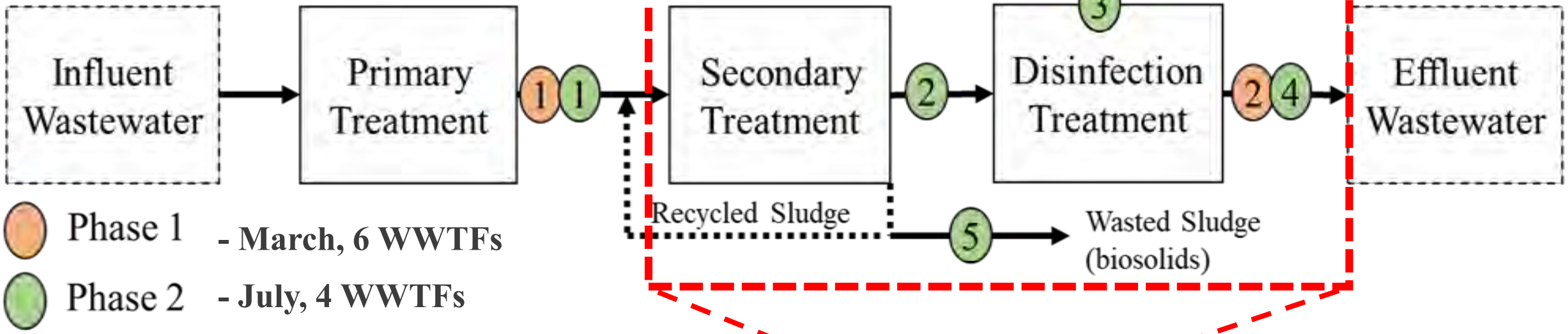
2. How does **WWTF design** and operation influence **PFAS diversity and removal efficiency?**

3. Are PFAS concentrations influenced by **seasonal variation**?

4. What is the **distribution of PFAS** in receiving **water bodies** (Great Bay Estuary) versus the PFAS in the WWTFs?

# Methods & Sampling Plan

Surface water Locations




Phase 1 - **March, 6 WWTFs**

Phase 2 - **July, 4 WWTFs**

Commercial Lab:

Alpha Analytical Lab

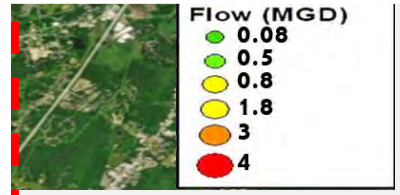
**WWTF Treatment Operations:**

Secondary Treatment Options:

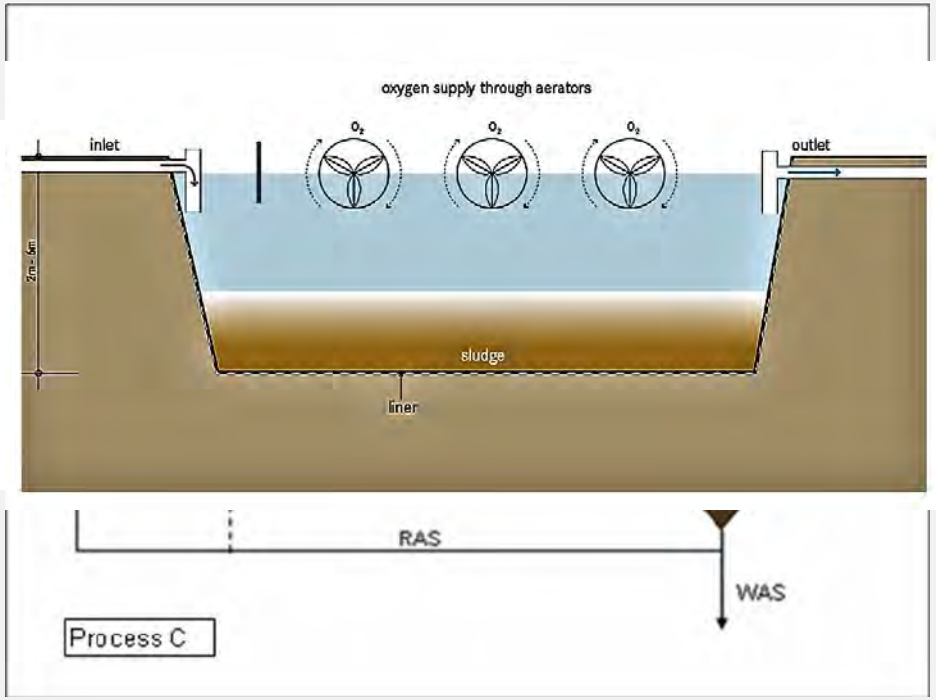
1. Aerated Lagoons (**AL**)
2. Activated Sludge (**AS**)
3. 4-Stage Bardenpho (**Bar4**)
4. Oxidation Ditch (**OD**)

Disinfection Options:

1. Chlorination -Dechlorination (**CD**)
2. Ultraviolet Light (**UV**)

# Methods & Sampling Plan




| Phase 1 – March | Phase 2 – July |
|---|---|
| WWTF # 1 → OD + CD | WWTF # 1 → OD + CD |
| WWTF # 2 → AL + CD ⟶ | WWTF # 2 → Bar4 + CD(1) |
| WWTF # 3 → Bar4 + CD(2) | WWTF # 3 → Bar4 + CD(2) |
| WWTF # 4 → Bar4 + CD(3) | WWTF # 4 → Bar4 + CD(3) |
| WWTF # 5 → AS + UV(1) | |
| WWTF # 6 →AS + UV(2) | |

# PFAS Detection

| WWTF# | | | 1 | | | | 2 | | | | 3 | | | | 4 | | | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment | | | OD+CD | | | | AL+CD | | Bard+CD(1) | | Bard+CD(2) | | | | Bard+CD(3) | | | | AS+UV(1) | | AS+UV(2) | |
| | | | Influent | | Effluent | | Influent | | Effluent | | Influent | | Effluent | | Influent | | Effluent | | March | | March | |
| Analysis | Group | Compound | March | July | March | July | March | July | March | July | March | July | March | July | March | July | March | July | Inf | Effl | Inf | Eff |
| 24 PFAS | PFCA(11) | PFBA | | | | | | | | | | | | | | | | | | | | |
| | | PFPeA | | | | | | | | | | | | | | | | | | | | |
| | | PFHxA | | | | | | | | | | | | | | | | | | | | |
| | | PFHpA | | | | | | | | | | | | | | | | | | | | |
| | | PFOA | | | | | | | | | | | | | | | | | | | | |
| | | PFNA | | | | | | | | | | | | | | | | | | | | |
| | | PFDA | | | | | | | | | | | | | | | | | | | | |
| | | PFUnA | | | | | | | | | | | | | | | | | | | | |
| | | PFDoA | | | | | | | | | | | | | | | | | | | | |
| | | PFTrDA | | | | | | | | | | | | | | | | | | | | |
| | | PFTA | | | | | | | | | | | | | | | | | | | | |
| | PFSA(7) | PFBS | | | | | | | | | | | | | | | | | | | | |
| | | PFHxS | | | | | | | | | | | | | | | | | | | | |
| | | PFOS | | | | | | | | | | | | | | | | | | | | |
| | | PFDS | | | | | | | | | | | | | | | | | | | | |
| | | PFPeS | | | | | | | | | | | | | | | | | | | | |
| | | PFHpS | | | | | | | | | | | | | | | | | | | | |
| | | PFNS | | | | | | | | | | | | | | | | | | | | |
| | PRECURSOR(6) | 6:2FTS | | | | | | | | | | | | | | | | | | | | |
| | | 8:2FTS | | | | | | | | | | | | | | | | | | | | |
| | | NMeFOSAA | | | | | | | | | | | | | | | | | | | | |
| | | NEtFOSAA | | | | | | | | | | | | | | | | | | | | |
| | | 4:2FTS | | | | | | | | | | | | | | | | | | | | |
| | | FOSA | | | | | | | | | | | | | | | | | | | | |

| | |
|---|---|
| | Non-Detect |
| | Detected |
| | In > Eff |
| | In < Eff |

- Consistently, **8PFCAs**, **4PFSAs**, and **4 Precursors** detected.
- Generally, PFCAs concentrations increased in all WWTFs in both seasons
- More PFCAs detected than PFSA and precursors

# PFAS Detection

| WWTF# | | | 1 | | | | 2 | | | | 3 | | | | 4 | | | | 5 | | 6 | | Surface water Samples | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment | | | OD+CD | | | | AL+CD | | Bard+CD(1) | | Bard+CD(2) | | | | Bard+CD(3) | | | | AS+UV(1) | | AS+UV(2) | | | | | | |
| Analysis | Group | Compound | Influent | | Effluent | | Influent | | Effluent | | Influent | | Effluent | | Influent | | Effluent | | March | | March | | Hilton Park (July) | Mill Pond (Aug.) | Adams Point (Aug.) | Great Bay (Aug.) | Squam -scott (Aug.) |
| | | | March | July | March | July | March | July | March | July | March | July | March | July | March | July | March | July | Inf | Effl | Inf | Eff | | | | | |
| 24 PFAS | PFCA(11) | PFBA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFPeA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFHxA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFHpA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFOA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFNA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFDA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFUnA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFDoA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFTrDA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFTA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | PFSA(7) | PFBS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFHxS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFOS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFDS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFPeS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFHpS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | PFNS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | PRECURSOR(6) | 6:2FTS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | 8:2FTS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | NMeFOSAA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | NEtFOSAA | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | 4:2FTS | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | FOSA | | | | | | | | | | | | | | | | | | | | | | | | | |

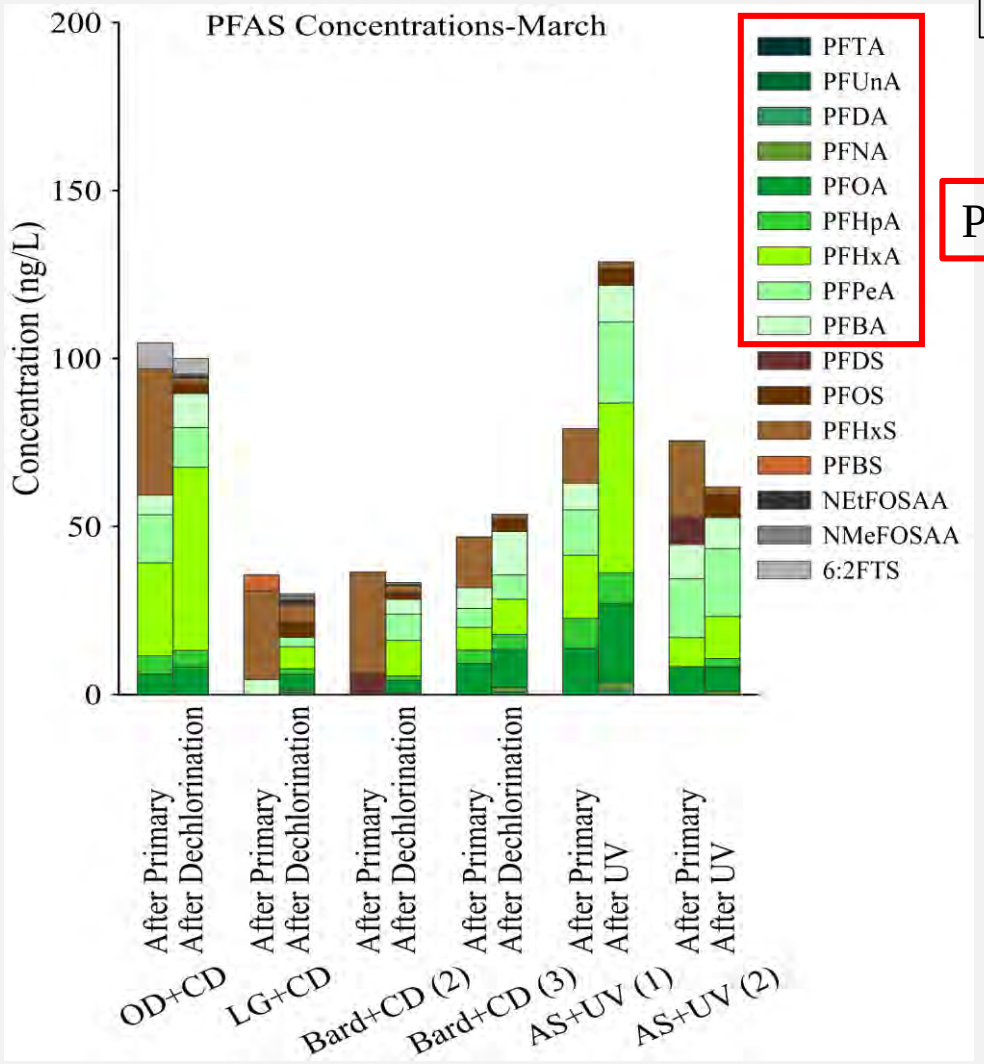
| | |
|---|---|
| | Non-Detect |
| | Detected |
| | In > Eff |
| | In < Eff |

- **5 PFCAs** and **2 PFSAs** were detected in Great Bay.
- **Same** constituents detected in **surface water and WWTP**.

# PFAS Distribution

**Avg Water Temp: 45˚F**

- PFCAs were dominant detected compounds.
- No consistent trend in PFAS concentrations in effluent of all WWTPs in March.



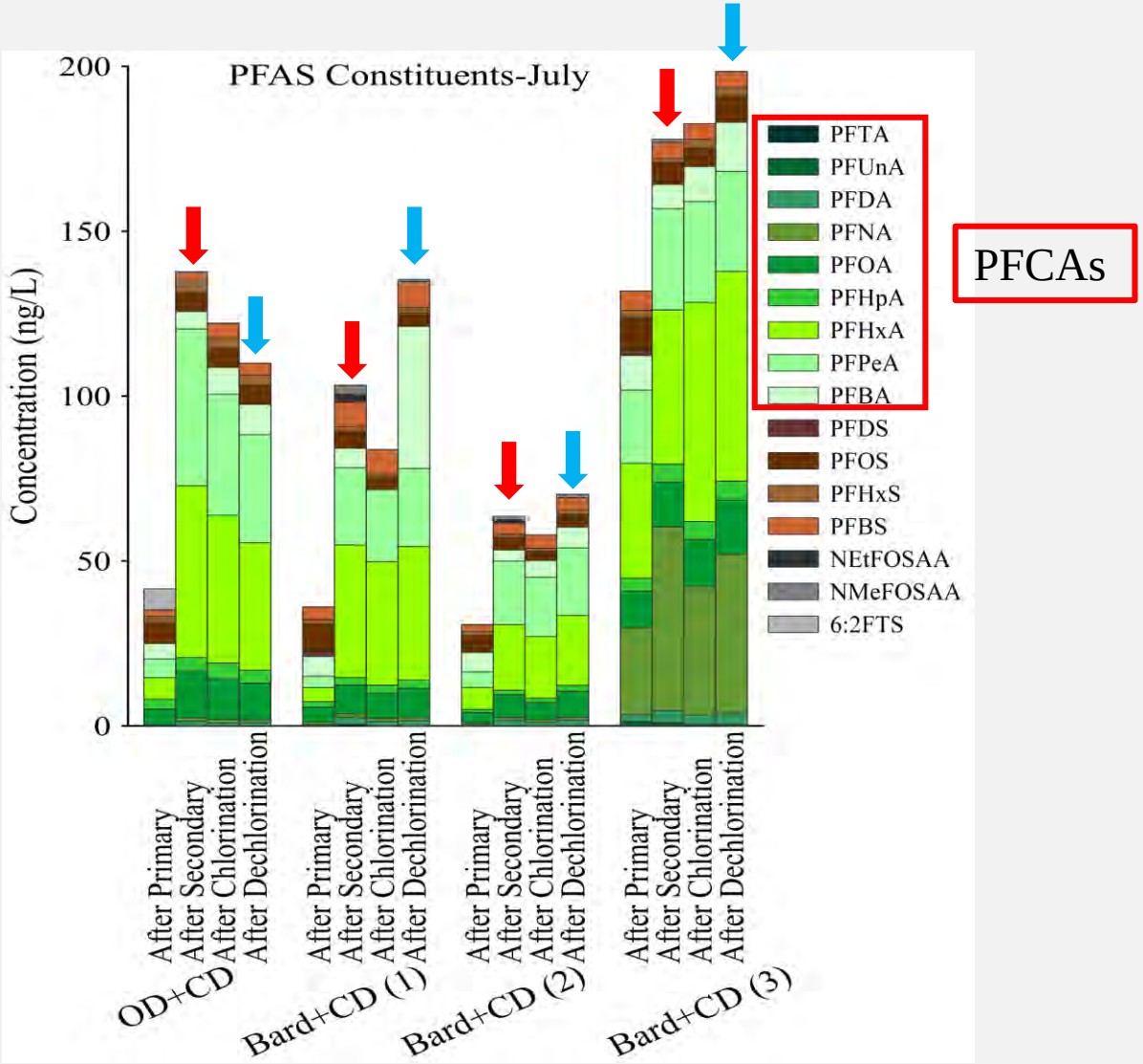
# PFAS Distribution

**Avg Water Temp: 71˚F**

- PFAS concentrations **increased** after secondary treatment, it may due to **higher Temperature** in July.
- **PFCAs** were dominant detected compounds.

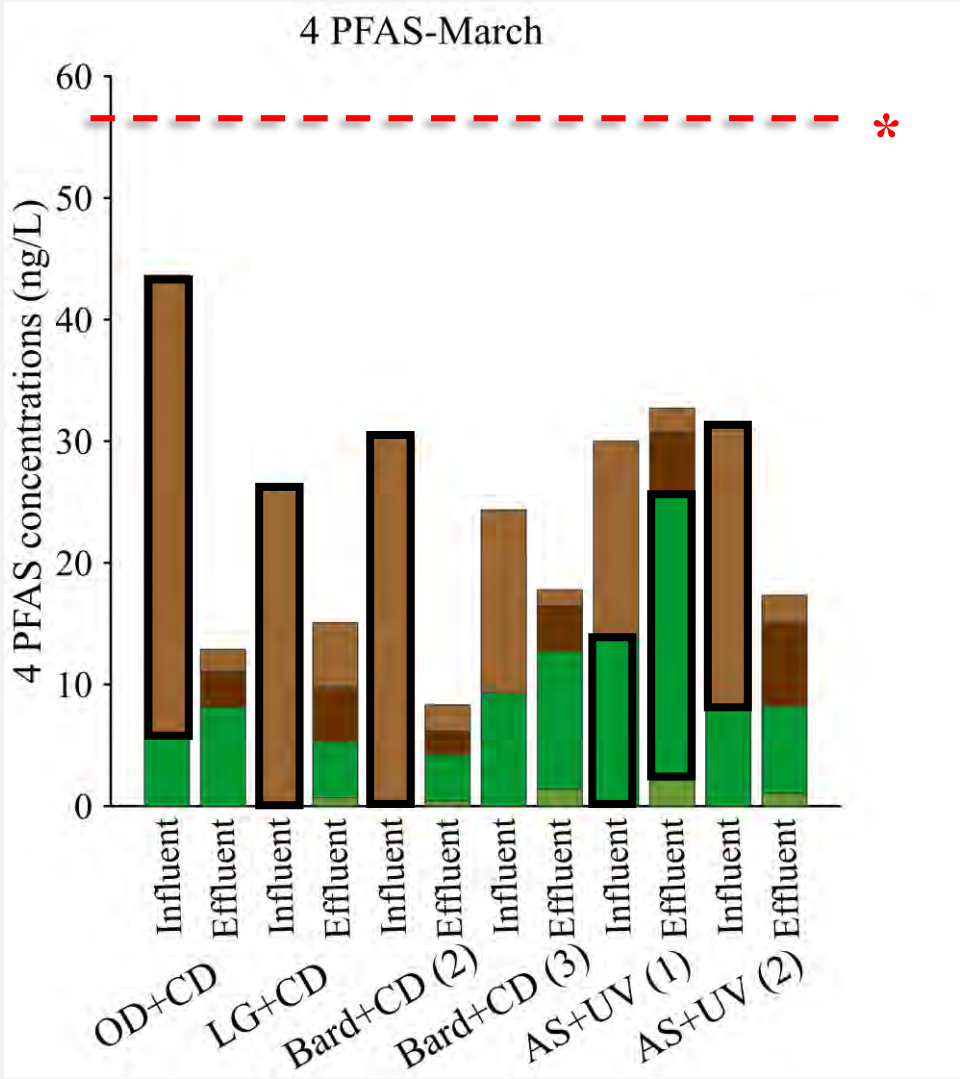
Caveats:

1. Analytical method (only 6 precursors measured)
2. Different matrix issue (different detection limits in influent and effluent)
3. Sampling method (A grab sample)



# PFAS Distribution

- The sum of the **4 PFAS** concentrations were **lower** than proposed Maximum concentration limits(MCL) regulated by **NHDES** for influent and effluent of all WWTFs

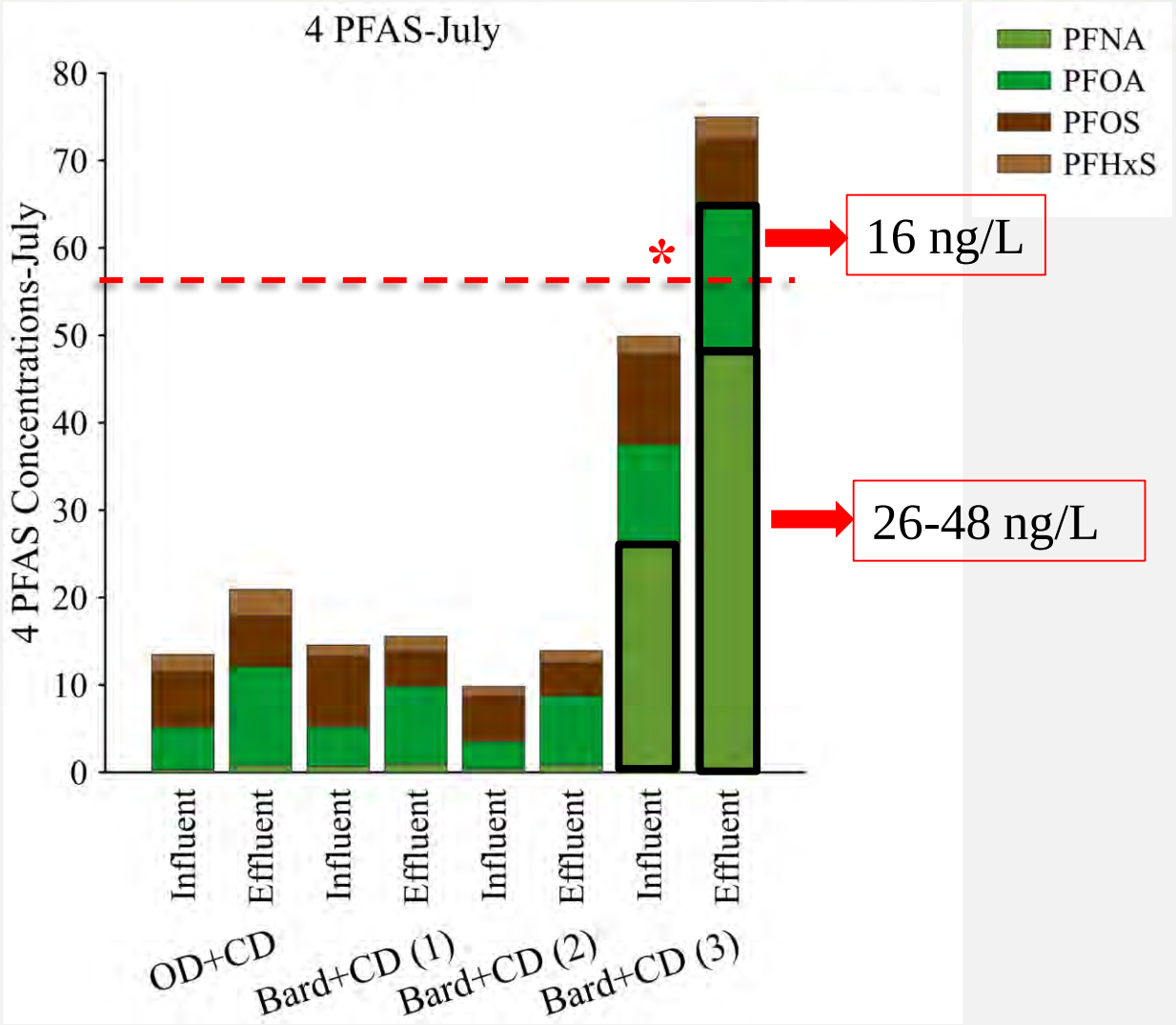



*** Σ of Four PFAS Proposed MCL=56 ng/L**

# PFAS Distribution

- The sum of **4 PFAS** concentrations were **lower** than proposed Maximum concentration limits(MCL) regulated by **NHDES** for influent and effluent of three WWTFs

- **PFNA** (MCL:11 ng/L), **PFOA** (MCL:12ng/L) were detected **higher** in effluent of **Bard+CD (3)**



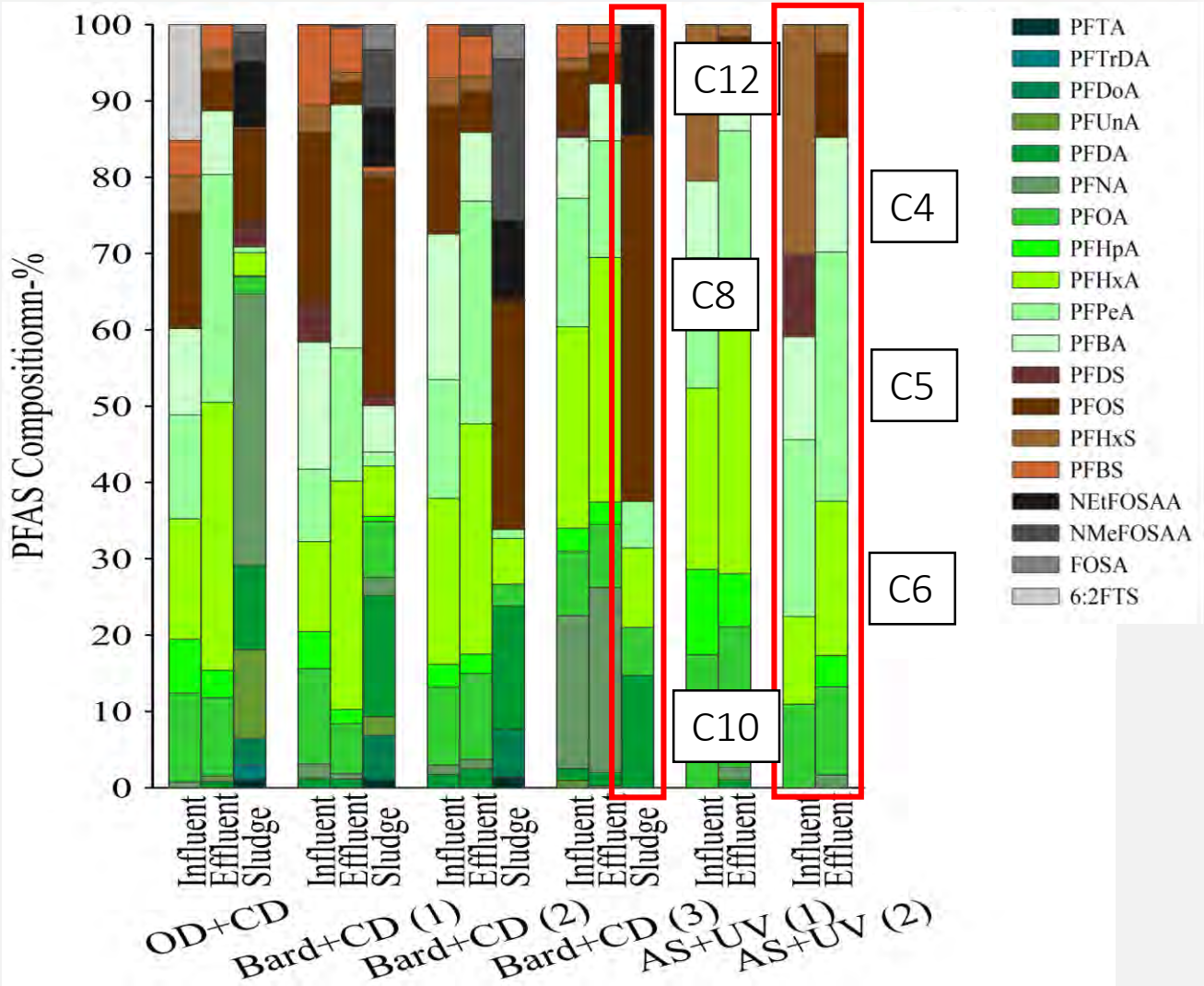

*** Σ of Four PFAS Proposed MCL=56 ng/L**

# PFAS Fate

- **18 constituents** were detected in Sludge and **11 constituents** are detected in Effluent.

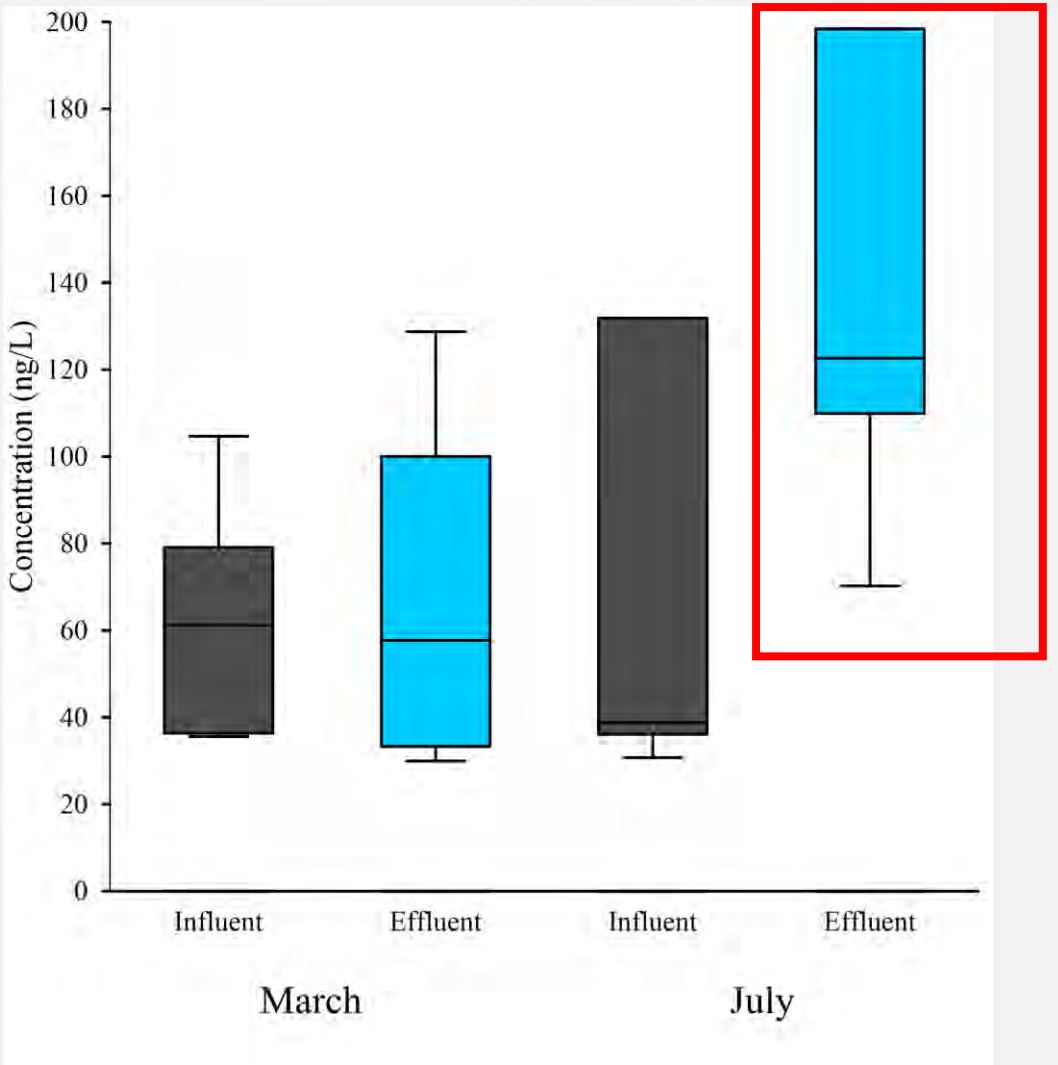
- The contribution of **Long-chain** compounds were detected more in **sludge** due to higher **hydrophobicity**

- The contribution of **short-chain** compounds were detected more in **aqueous** phase, due to their **hydrophilicity**



# PFAS Seasonal Variation

- Total concentration of PFAS **increased** in effluent of the summer samples.
- The total influent concentration of PFAS **were not significantly different** between the two seasons.



# Main Result

1. What portion of PFAS are being detected within local WWTFs?

- **8PFCAs**, **4PFSAs**, and **4 Precursors** were detected

2. How does WWTF design influence PFAS diversity and removal efficiency?

- **None of the designs** seems to **efficiently remove PFAS** (4-18% removal)

3. Are PFAS concentrations influenced by seasonal variation?

- The effluent concentration of **second season increased**

4. What is the distribution of PFAS in receiving water bodies (Great Bay Estuary)?

- **5 PFCAs** and **2 PFSAs** were detected

# Thank you