

# NHDES Residuals Management Section –PFAS Impacts on Wastewater and Sludge / Biosolids

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**Wastewater Engineering Bureau; NHDES**



# Outline

- **Who is RMS?**
- **Up and Coming NPDES / SQC PFAS monitoring requirements**
- **Sludge Management Laws and Rules**
- **Establishing an SAP for PFAS sampling**
- **Equipment Decontamination**
- **Wastewater Collection System Sampling results**
- **Biosolids sampling results**
- **The future for wastewater and sludge management –developing treatment and destruction technologies**

# NHDES Residuals Management Section

- Water Division ↪
  - Wastewater Engineering Bureau ↪
    - Residuals Management Section

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Effluent Characteristic Parameter	Discharge Limitation <sup>13</sup>			Monitoring Requirement <sup>1,2</sup>	
	Average Monthly	Average Weekly	Maximum Daily	Measurement Frequency	Sample Type <sup>3</sup>
Fecal Coliform Bacteria <sup>8</sup> Class SA, Shellfishing Waters	14 organisms/ 100 mL	---	28 organisms/100 mL	1/Week	Grab
Fecal Coliform Bacteria <sup>8</sup> Class SB, Shellfishing Waters	88 organisms/ 100 mL	---	260 organisms/100 mL	1/Week	Grab
Total Residual Chlorine <sup>9</sup>	Limit mg/L	---	Limit mg/L	5/Week	Grab
Total Recoverable Metals <sup>10</sup>	Limit mg/L	---	Limit mg/L	2/Month	Composite
Total Phosphorus <sup>10</sup> Class B waters only	Limit mg/L	---	---	2/Month	Composite
Ammonia Nitrogen <sup>10</sup> (specify season)	Limit mg/L	---	Limit mg/L	2/Month	Composite
Total Nitrogen <sup>11</sup>	Report mg/L Report lb/day	---	---	Varies <sup>11</sup>	Composite
Total Kjeldahl Nitrogen <sup>11</sup>	Report mg/L	---	---	Varies <sup>11</sup>	Composite
Nitrate + Nitrite <sup>11</sup>	Report mg/L	---	---	Varies <sup>11</sup>	Composite
Perfluorohexanesulfonic acid (PFHxS) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluoroheptanoic acid (PFHpA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorononanoic acid (PFNA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorooctanesulfonic acid (PFOS) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorooctanoic acid (PFOA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorodecanoic acid (PFDA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Other <sup>10,13</sup>	Limit	---	Limit	Varies	Composite
<b>Whole Effluent Toxicity (WET) Testing<sup>14,15</sup></b>					
Dilution Factor (DF) $\geq 1$ and $< 20$	---	---	Chronic (C-NOEC) $\geq$ 100% / DF and Acute (LC <sub>50</sub> ) $\geq 100\%$	4/Year	Composite
Dilution Factor $\geq 20$ and $< 50$	---	---	Acute (LC <sub>50</sub> ) $\geq 100\%$	4/Year	Composite






Influent Characteristic	Reporting Requirements			Monitoring Requirements <sup>1,2,3</sup>	
	Average Monthly	Average Weekly	Maximum Daily	Measurement Frequency	Sample Type <sup>4</sup>
BOD <sub>5</sub> (or CBOD <sub>5</sub> <sup>6</sup> )	Report mg/L	---	---	2/Month	Composite
TSS	Report mg/L	---	---	2/Month	Composite
Perfluorohexanesulfonic acid (PFHxS) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluoroheptanoic acid (PFHpA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorononanoic acid (PFNA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorooctanesulfonic acid (PFOS) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorooctanoic acid (PFOA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite
Perfluorodecanoic acid (PFDA) <sup>12</sup>	---	---	Report ng/L	2/Year <sup>12</sup>	Composite

Sludge Characteristic	Reporting Requirements			Monitoring Requirements <sup>1,2,3</sup>	
	Average Monthly	Average Weekly	Maximum Daily	Measurement Frequency	Sample Type <sup>4</sup>
Perfluorohexanesulfonic acid (PFHxS) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>
Perfluoroheptanoic acid (PFHpA) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>
Perfluorononanoic acid (PFNA) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>
Perfluorooctanesulfonic acid (PFOS) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>
Perfluorooctanoic acid (PFOA) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>
Perfluorodecanoic acid (PFDA) <sup>20</sup>	---	---	Report ng/g	Varies <sup>20</sup>	Grab/Composite <sup>21</sup>

Beginning the first full calendar quarter following 6 months after EPA has notified the Permittee that a multi-lab validated method for wastewater is available, the Permittee shall commence annual sampling of the following types of industrial discharges into the POTW:

- Commercial Car Washes
- Platers/Metal Finishers
- Paper and Packaging Manufacturers
- Tanneries and Leather/Fabric/Carpet Treaters
- Manufacturers of Parts with Polytetrafluoroethylene (PTFE) or teflon type coatings (i.e. bearings)
- Landfill Leachate
- Centralized Waste Treaters
- Contaminated Sites
- Fire Fighting Training Facilities
- Airports
- Any Other Known or Expected Sources of PFAS

 For dischargers in Massachusetts, sampling shall be for the following PFAS chemicals:



	<p><u>Method 8327: PFAS Using External Standard Calibration and MRM LC/MS/MS (2019)</u></p>	<p>Direct injection method for non-drinking water aqueous (groundwater, surface water, and wastewater) samples. Validated for 24 analytes.</p>
<p><b>•Non-Potable Water and Other Environmental Media</b>  EPA develops methods for aqueous and solid (e.g., soil, biosolids, sediment) samples primarily through the Clean Water Act (CWA) and methods for solid waste (SW-846) under the Resource Conservation and Recovery Act (RCRA).</p> <p><b><u>•CWA analytical methods</u></b></p> <p><b><u>•Solid waste methods for RCRA</u></b></p>	<p><b><u>Draft Method 1633</u></b></p>	<p><b><u>Draft, single-laboratory validated, direct injection EPA method for 40 PFAS in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue.</u></b></p> <p><b><u>Note: EPA and the Department of Defense are collaborating on the development of this method. A multi-laboratory validation study will be conducted by DoD, in collaboration with EPA.</u></b></p>

<p><b>Ambient Air</b>EPA is considering both sampling and analysis methods, targeted and non-targeted for PFAS ambient air measurements. Applications will include fenceline monitoring for fugitive emissions, deposition, and receptor exposure.</p>	Ambient/Near-Source <i>(coming soon)</i>	Field deployable Time of Flight/Chemical Ionization Mass Spectrometer for real time detection and measurement.
	Semivolatile PFAS <i>(coming soon)</i>	A performance-based method guide by EPA TO-13a.
	Volatile PFAS <i>(coming soon)</i>	Uses SUMMA canisters and sorbent traps for GC/MS targeted and non-targeted analysis.
<p><u><b>Total</b></u> <u><b>These types of methods aim to quantify large groups of PFAS in environmental samples.</b></u></p>	<p><u><b>Total Organic Fluorine (TOF)</b></u> <u><i>(coming soon)</i></u></p>	<p><u>EPA is developing a potential rapid screening tool to identify total PFAS presence and absence. This eventual standard operating procedure will be used to quantify TOF.</u> <u>Note: EPA is working to develop this method in 2021.</u></p>
	<p><u><b>Total Organic Precursors (TOP)</b></u> <u><i>(coming soon)</i></u></p>	<p><u>EPA is considering the development of a method, based on existing protocols, to identify PFAS precursors that may transform to more persistent PFAS.</u> <u>Note: TOP methods are commercially available. EPA will consider the need for a thorough multi-laboratory validation study in 2021.</u></p>

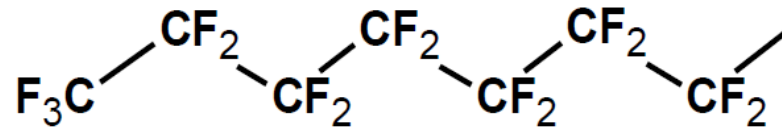


# NEIWPCC / NEBRA PFAS Sampling Guidance

*NEBRA Guidance:*

## Sampling and Analysis of PFAS in Biosolids and Associated Media v. 2.0

June 2017 (v. 1.0), updated January 2018 (v. 2.0).



### Acknowledgements

This guidance was written and produced by Michael Rainey, M.S. (Northwood, NH) with review and editing by members of the NEBRA PFAS Advisory Group and staff. Special thanks to New England Interstate Water Pollution Control Commission (Lowell, MA) for reliance on their biosolids sampling guide and to Professor Linda S. Lee, Ph.D., Purdue University (West Lafayette, IN).

# What is a sampling plan and why is it necessary?

- Sampling program vs. sampling plan
- “Sampling plan is a blueprint for how a sampling program will be executed.”
- First step in implementing a sampling program
- Ensures representative samples and data
- Ensures the goals of the sampling program are meet





# Need for Guidance

## Developed to assist Operators:

- “How-To” guide to producing comprehensive sampling plans
- Educate operators about biosolids sampling, analysis, and QA/QC
- Help operators be better consumers of lab services
- Help operators comply with biosolids management rules



## Will assist Regulators:

- Better confidence in the data submitted to demonstrate compliance

# Guidance Goals & Objectives

- Must be useable and useful for operators
- Worksheets with fill-in-the-blanks, for producing a comprehensive sampling plan
- Appended resources to provide examples and compliance information
- Linkage between worksheet and text to provide quick reference while developing the plan





## EQUIPMENT CHECKLIST – Biosolids / Residuals / Solids

1

1) Sample handling and collection

- a. Nitrile gloves
- b. Stainless steel bucket
- c. 500 mL Polypropylene or HDPE container
- d. Stainless steel trowel

2) Transporting and preservation

- a. Sample containers 15 ml graduated polypropylene tubes
- b. Sample cooler with ice

3) Sample ID and Documentation

- a. Markers and pens
- b. Sample container labels
- c. Custody seals
- d. Chain of custody/sample submittal form
- e. Field notebook/ sample log/field data sheet

4) Cleaning equipment

- a. Disposable towels
- b. Soap
- c. Scrub brush
- d. Tap water
- e. Deionized water
- f. Methanol
- g. Plastic wrap

5) Ensure that all equipment, supplies, and other materials assembled for sampling, including clothing worn by sampling staff, will not contaminate samples with PFAS extraneous to the residuals being sampled. See Appendix D-4 for materials that may contain PFAS and that should be avoided.

Category	Prohibited Items	Allowed Items
Pumps and Tubing	Teflon® and other fluoropolymer containing materials, pipe thread seal tape	High-density polyethylene (HDPE), low density polyethylene (LDPE), or silicone tubing, peristaltic pump or stainless steel submersible pump
Decontamination	Decon 90	Alconox® or Liquinox®, potable water followed by deionized rinse.
Sample Storage and Preservation	LDPE or glass bottles, PTFE-or Teflon®-lined caps, chemical ice packs, aluminum foil	Laboratory-provided sample container <i>preferred</i> ; or, HDPE or polypropylene bottles, regular ice sealed in plastic (polyethylene) bags to prevent melt water contaminating samples, thin HDPE sheeting
Field Documentation	Waterproof/treated paper or field books, plastic clipboards, non-Sharpie® markers, Post-It® and other adhesive paper products	Plain Paper, <i>metal</i> clipboard, Sharpies® (allowable per EPA, but other markers are not), pens
Clothing	New or unwashed clothing, clothing or boots made of or with Gore-Tex™ or other synthetic water resistant and/or stain resistant materials, coated Tyvek® material, anything washed with fabric softeners.	Well-laundered synthetic or 100% cotton material, previously laundered clothing (preferably previously washed greater than six times) <i>without</i> the use of fabric softeners . Steel-toed or other boots made with polyurethane and/or polyvinyl chloride (PVC). <i>Uncoated</i> Tyvek.
Personal Care Products (for day of sample collection)	Cosmetics, moisturizers, hand cream, some sunscreens, insect repellants, and other related products, dental floss and plaque removers	Suncscreens: Alba Organics Natural Yes to Cucumbers Aubrey Organics Jason Natural Sun Block Kiss My Face Insect Repellents: Jason Natural Quit Bugging Me Repel Lemon Eucalyptus Herbal Armor California Baby Natural Bug Spray BabyGanics Sunscreen and Insect Repellents: Avon Skin So Soft Bug Guard-SPF 30
Food and Beverage	Pre-packaged food, fast food wrappers or containers, aluminum foil, non-stick cookware & containers	Bottled water or hydration drinks.

## Recommendations for Working With Labs on PFAS Analysis

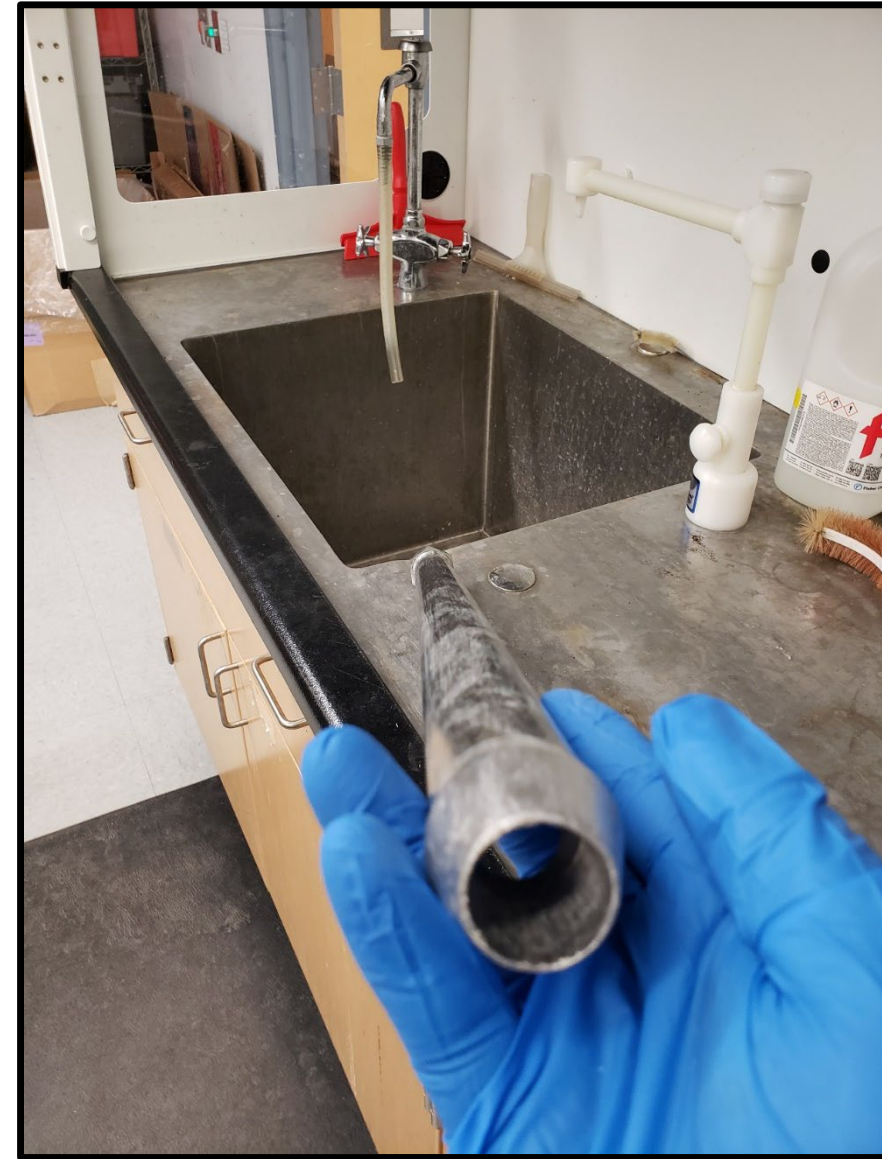
**MAKE SURE YOU KNOW WHAT TEST METHOD THE LAB IS USING TO ANALYZE YOUR SAMPLE**

### Before sampling and contracting with a lab:

- Learn what method the lab uses and discuss quality control with them.
- Ask for details on the lab's standard operating procedure (SOP) for their PFAS method and quality control (QC) procedures
- Discuss with the lab what compounds of PFAS they measure and report
- Obtain the CAS numbers for the compounds analyzed and be sure they match your sampling and analysis plan and any regulatory or screening standards
- Be sure to get their recommendations on sampling protocols, containers to use, sample sizes, field and other blanks, sample storage and shipping, and schedules



**Some labs have specific protocols that differ from other labs**





# **Sample equipment cleaning & sampling**

- **Rinse equipment with warm tap water to remove most solids.**
- **Using a brush and PFAS free lab detergent to scrub the equipment to remove all residues**
- **After scrubbing, rinse the equipment three times with tap water (make sure all detergent is removed).**
- **The tap water rinse should be followed by rinsing three times with PFAS free deionized water.**
- **To store, buckets, beakers and other containers can be inverted in a clean, dry location.**
- **Just prior to sampling, rinse the sample equipment three times in PFAS free deionized water. Take equipment blank rinsate samples to check if your cleaning process is preventing cross contamination.**















# Average Annual NH Sludge, Septage, and Leachate

- NH Biosolids Recycled to Land Application : **>40,000 wet tons**
- NH Sludge that was disposed at a landfill : **>50,000 wet tons**
- NH Sludge that was incinerated : **>17,500 wet tons**
- Over **>100,000,000 gallons** of septage is managed in NH annually
- 6 Operating lined landfills in NH : **~100,000,000 gallons** of leachate
  - ~80,000,000 gallons** managed at WWTFs within state
  - ~20,000,000 gallons** managed at WWTFs out of state



*\*2018 reporting values \*Sludge managed to lagoon systems not accounted for \*\*NH WWTF ONLY, no paper mill or drinking water treatment sludge accounted for*









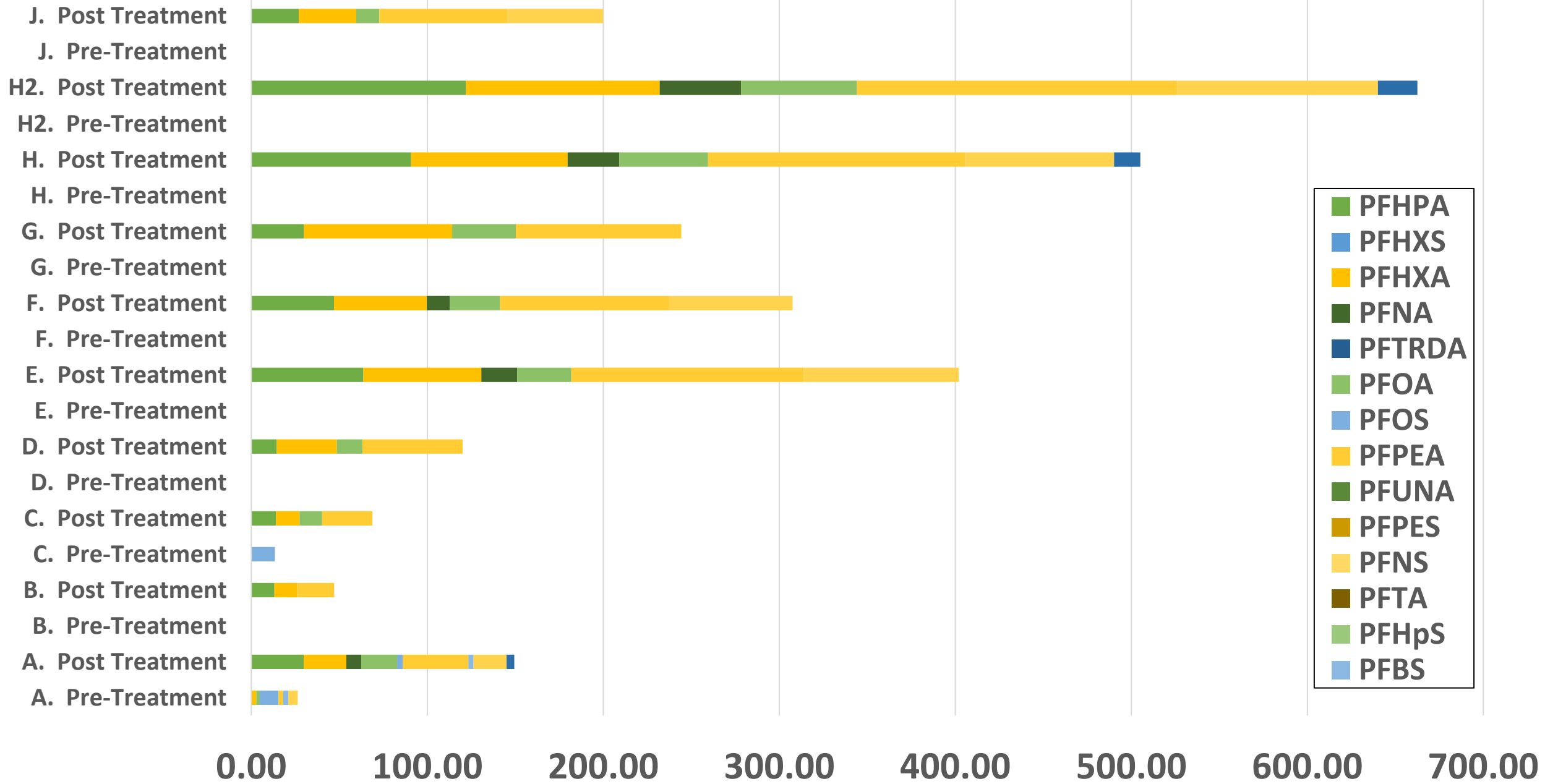




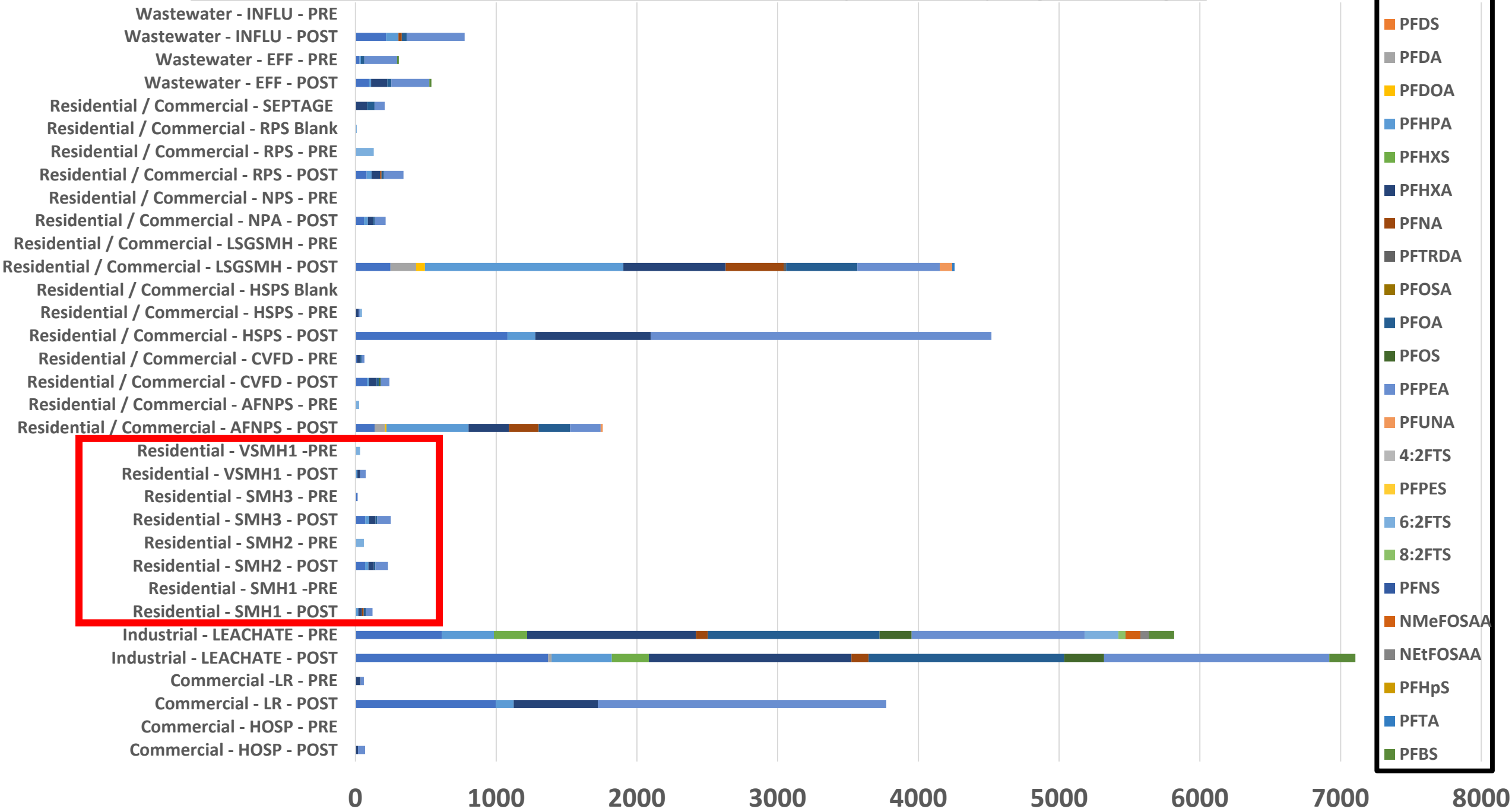




## WWTF Residential Community Collection System PFAS TOPA (ng/l)



Residential / Commercial / Industrial Collection System Sampling TOPA (ng/l)



## Per- and Polyfluoroalkyl Substances in Toilet Paper and the Impact on Wastewater Systems

Jake T. Thompson, Boting Chen, John A. Bowden, and Timothy G. Townsend\*



Cite This: <https://doi.org/10.1021/acs.estlett.3c00094>



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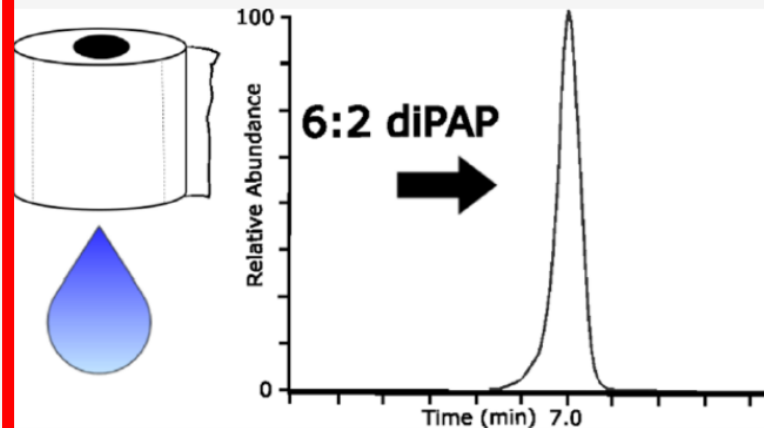
Article Recommendations



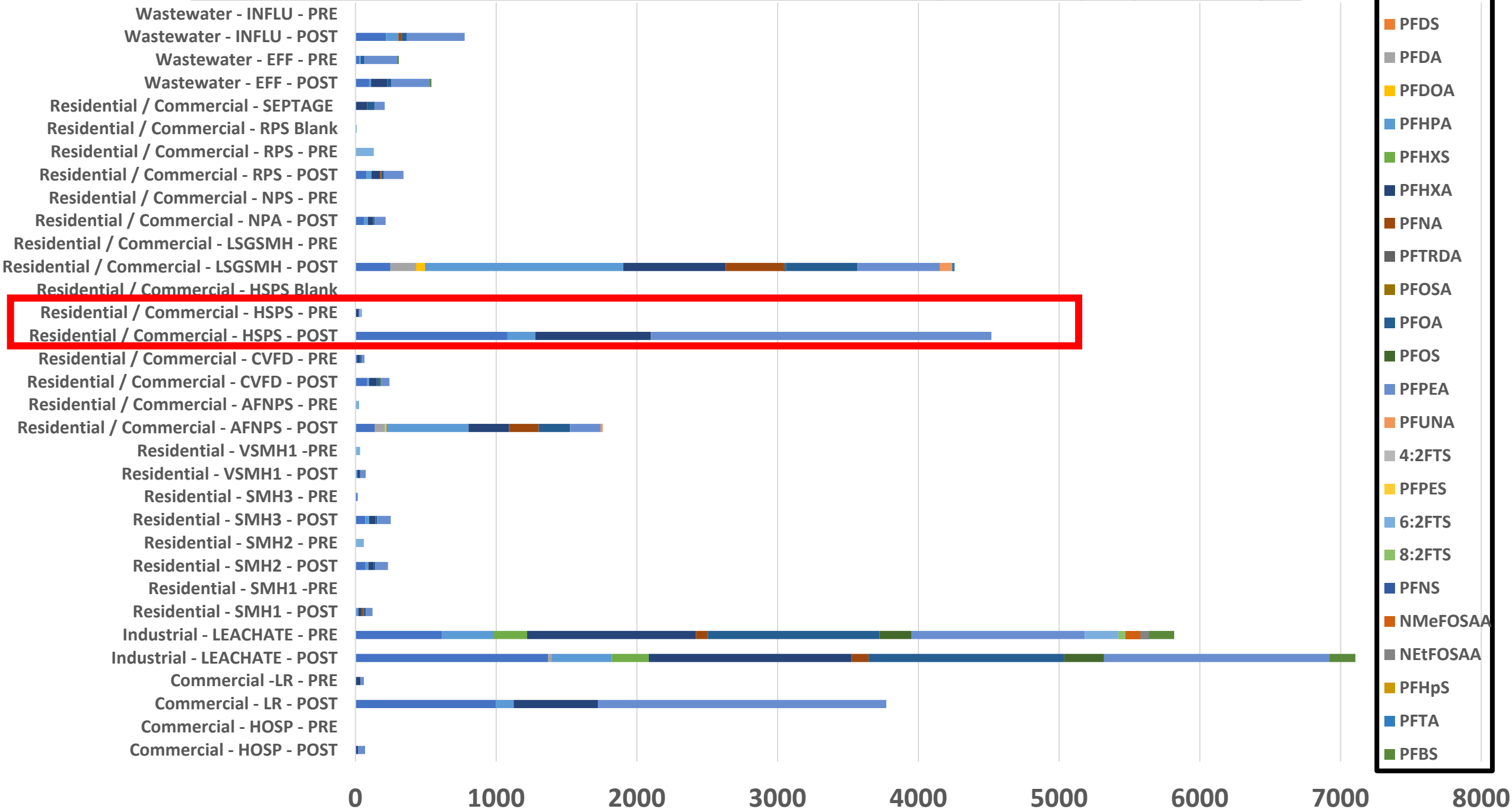
Supporting Information

**ABSTRACT:** Here, we evaluate a perhaps unexpected contributor of per- and polyfluoroalkyl substances (PFAS) to our wastewater, an input anticipated at every wastewater treatment facility—toilet paper. In this study, both toilet paper and wastewater sludge were characterized to explore the magnitude of the potential PFAS loading into wastewater systems from toilet paper. In both toilet paper and wastewater sludge, 6:2 fluorotelomer phosphate diester (6:2 diPAP) was the most prevalent PFAS detected, and toilet paper usage was estimated to contribute from 6.4 to 80  $\mu\text{g}$ /person-year of 6:2 diPAP to wastewater–water systems. Our results suggest that toilet paper should be considered as a potentially major source of PFAS entering wastewater treatment systems.

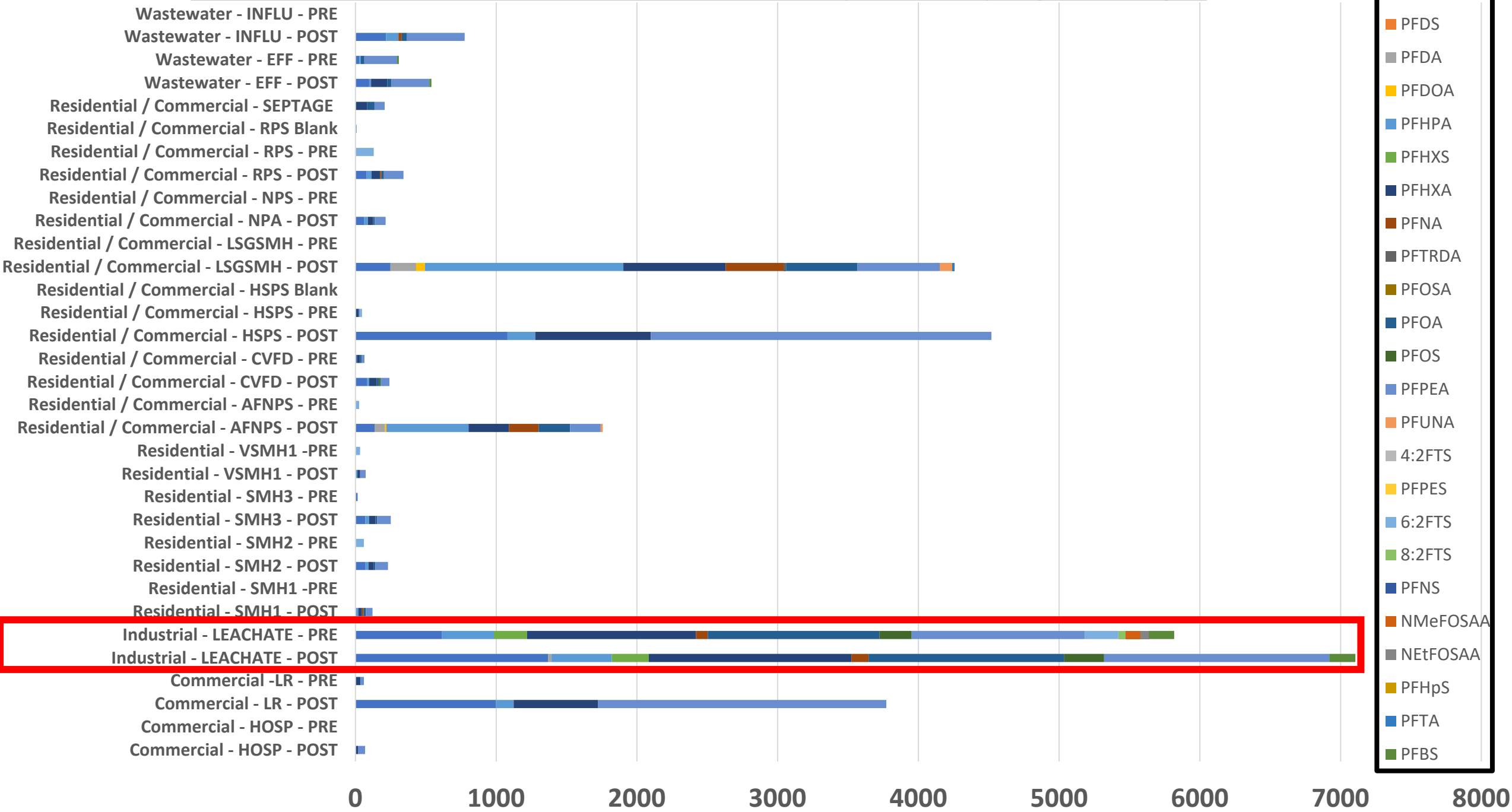
**KEYWORDS:** 6:2 diPAP, biosolids, wastewater sludge, PFCA precursor, PFAS, paper



WWTF Residential / Commercial / Industrial Collection System Sampling TOPA (ng/l)

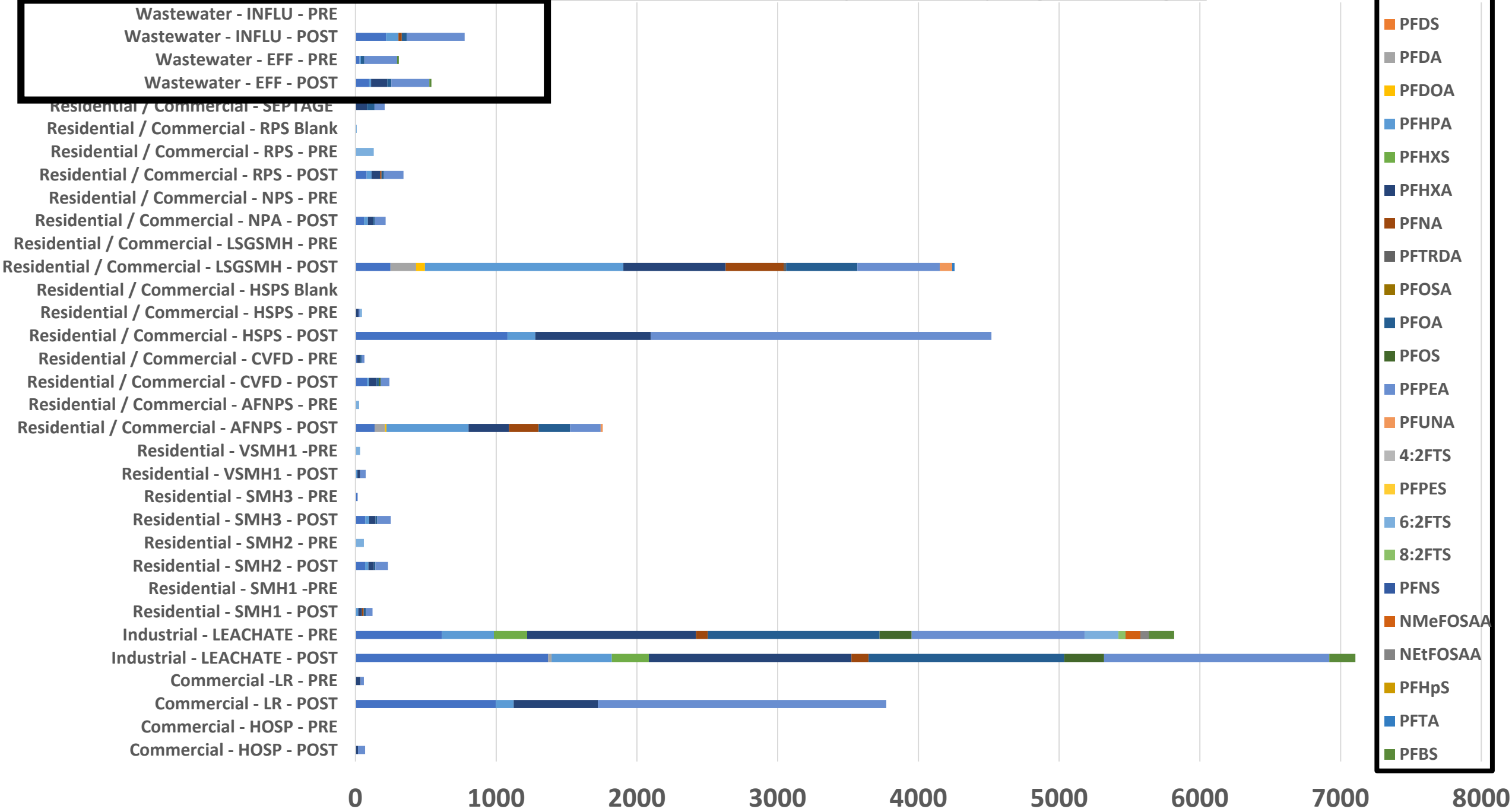


Residential / Commercial / Industrial Collection System Sampling TOPA (ng/l)





Residential / Commercial / Industrial Collection System Sampling TOPA (ng/l)



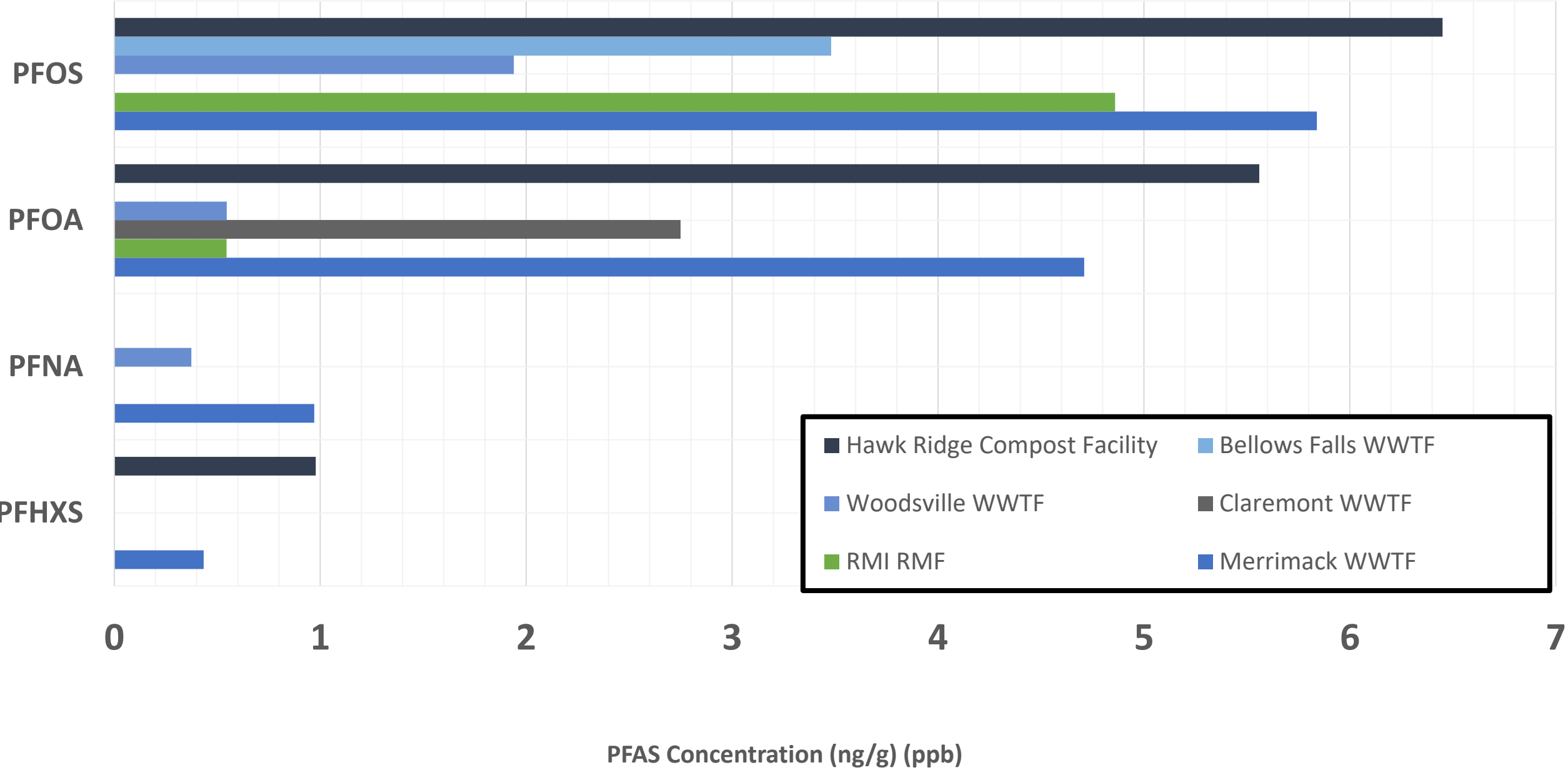
# Sludge Quality Certification

**Beneficial Use is the utilization of the nutrients and organic matter from the biosolids for the agronomic need as long as it does not pose a significant threat to human health or environment. Beneficial use applies to agricultural, forest, and land reclamation management practices**

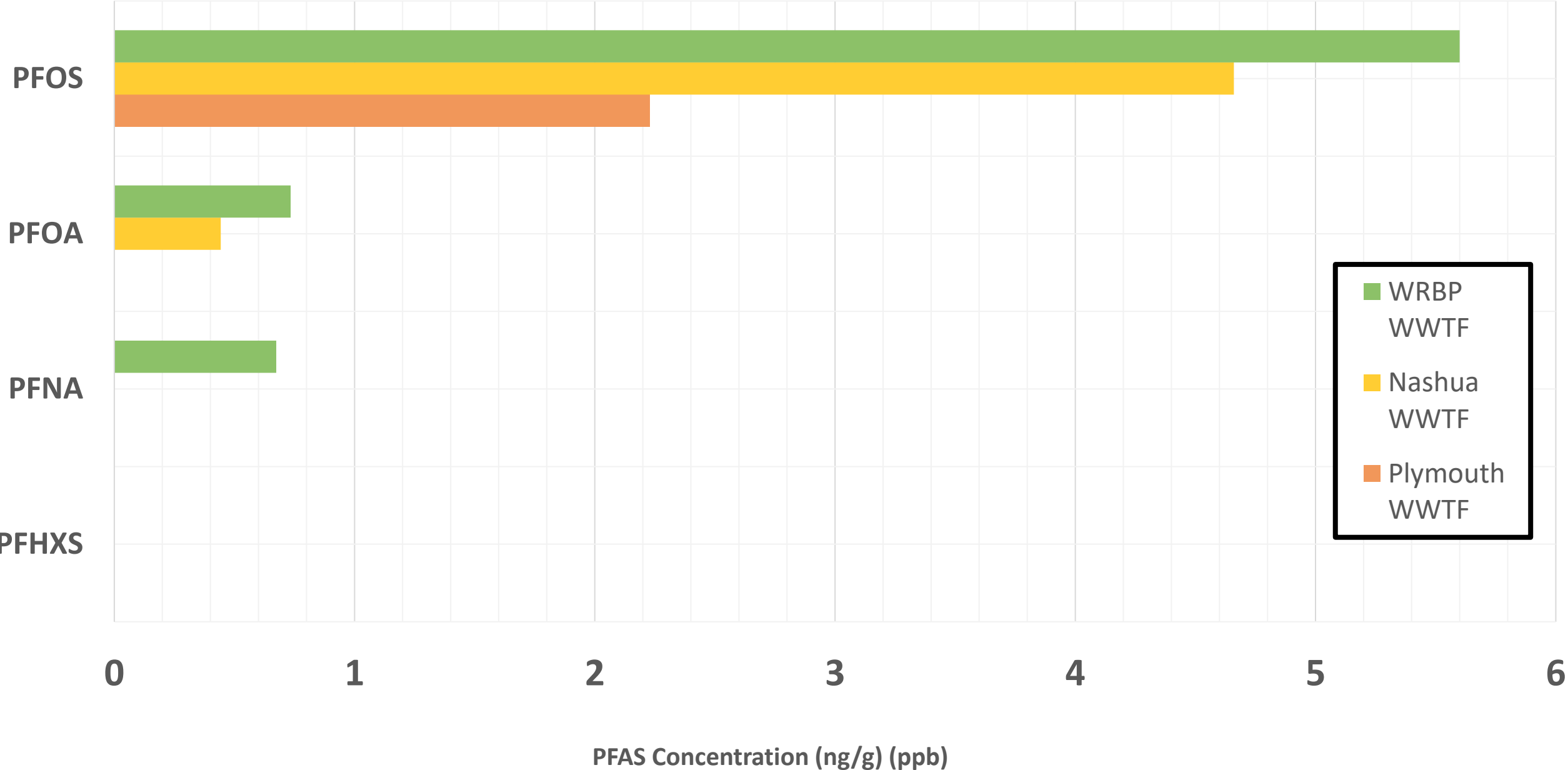
- Bulk biosolids must obtain an SQC to be distributed in NH
- Annual soil test determine crops nutrient demand supplied from biosolids (UNH BMP)
- Class B land application must obtain a site permit through RMS – many items covered in application process
- Concentration limits and screening standards set for VOC, SVOC, PCB's, Dioxin, & Metals – **168 analytes + PFAS**



# 2022 NHDES RMS SQC Class A Biosolids PFAS Investigation Data

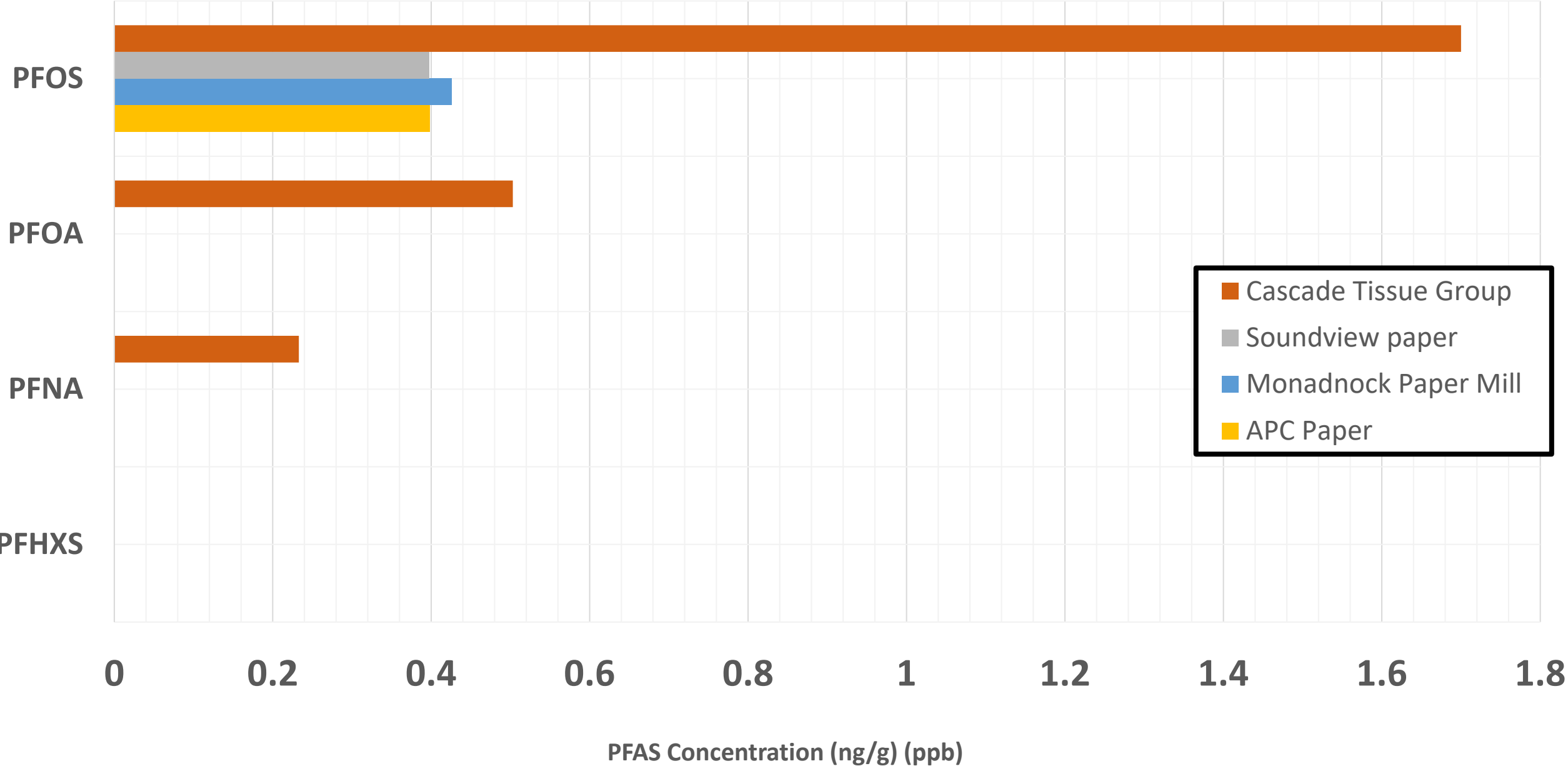


# 2022 NHDES RMS SQC Class B Biosolids PFAS Investigation Data

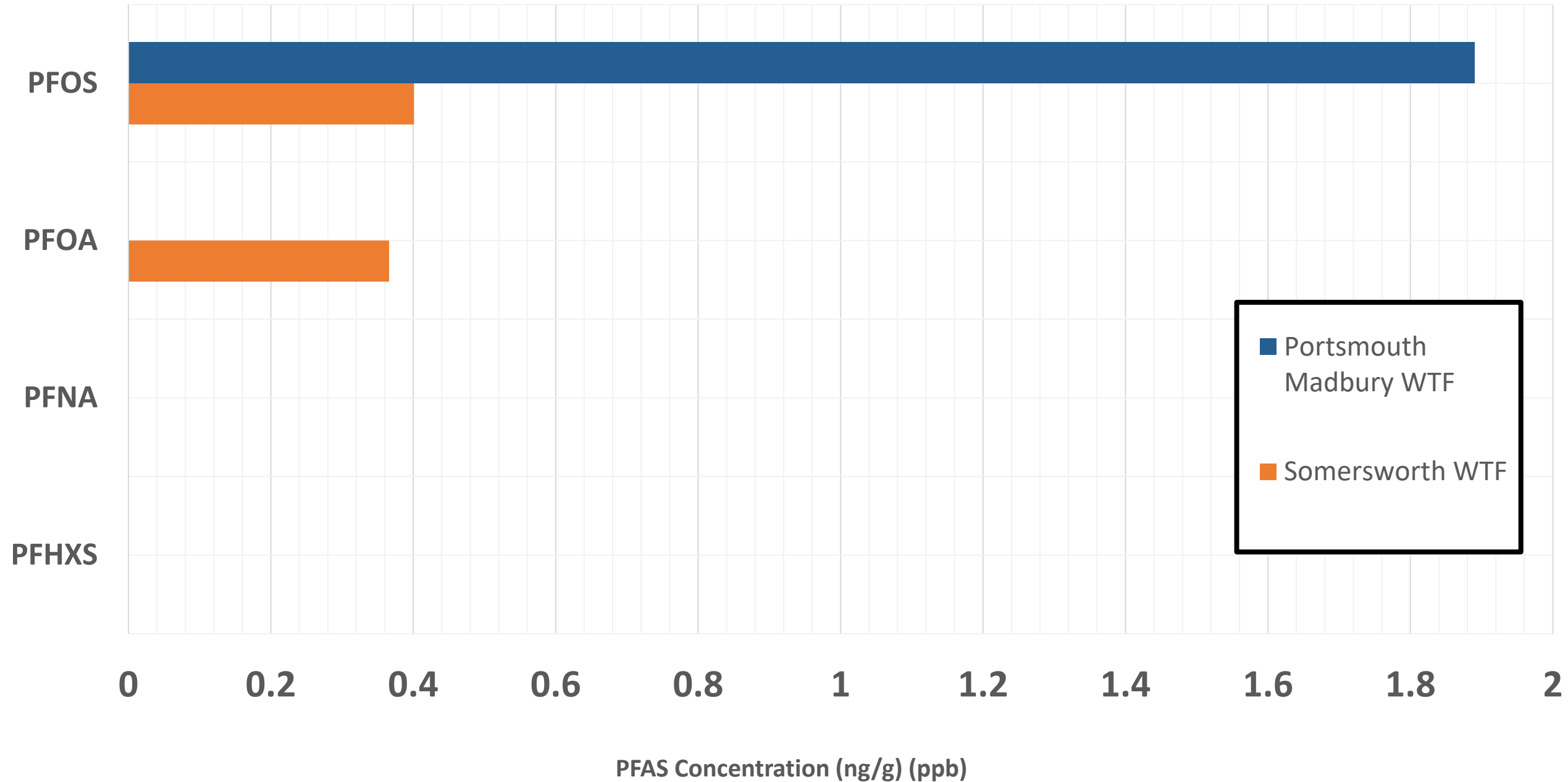




# 2022 NHDES RMS SQC Short Paper Fiber PFAS Investigation Data



## 2022 NHDES RMS SQC Drinking Water Treatment Residuals PFAS Investigation Data

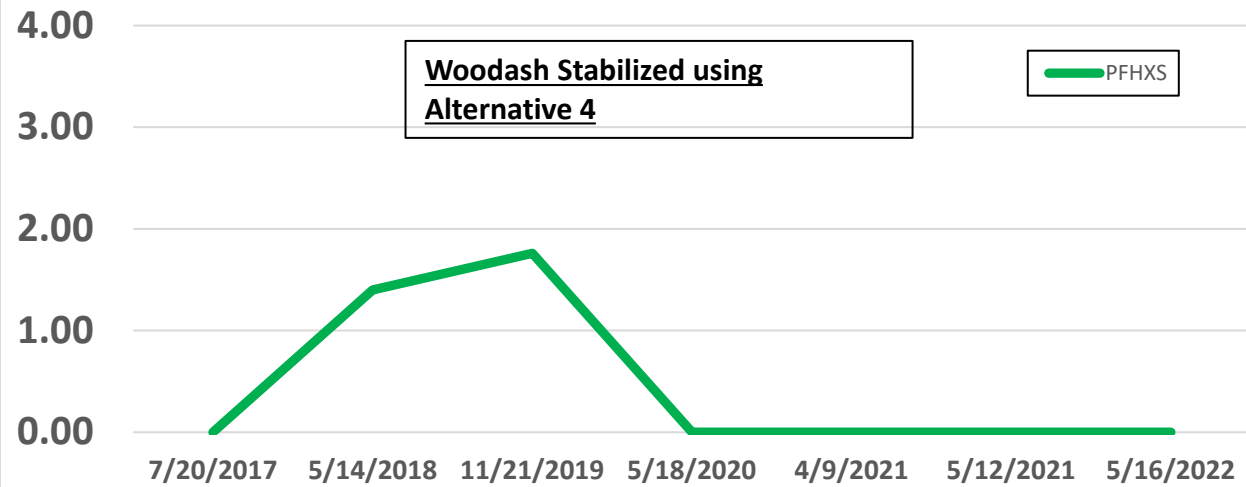




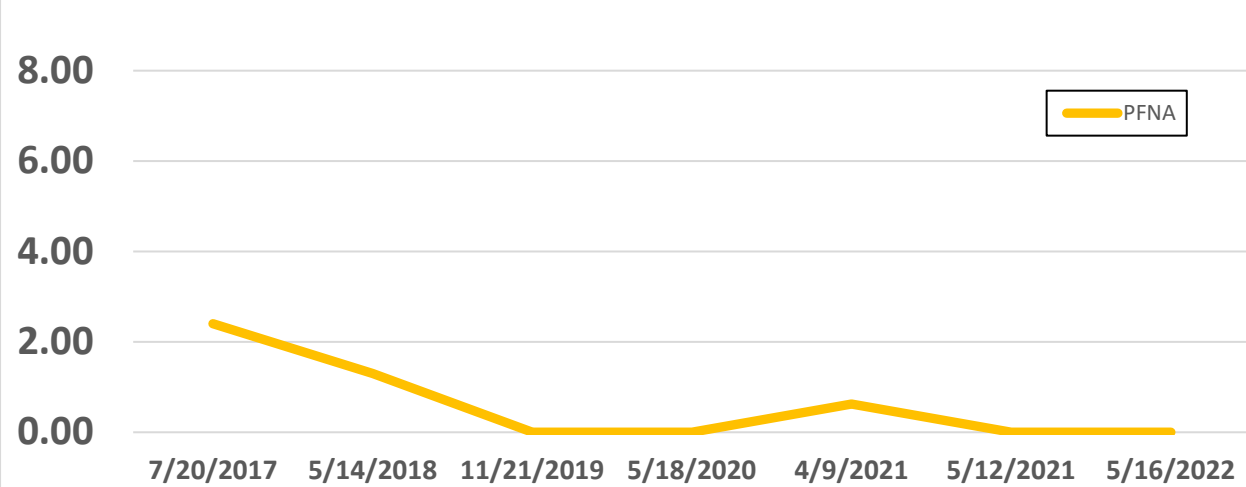




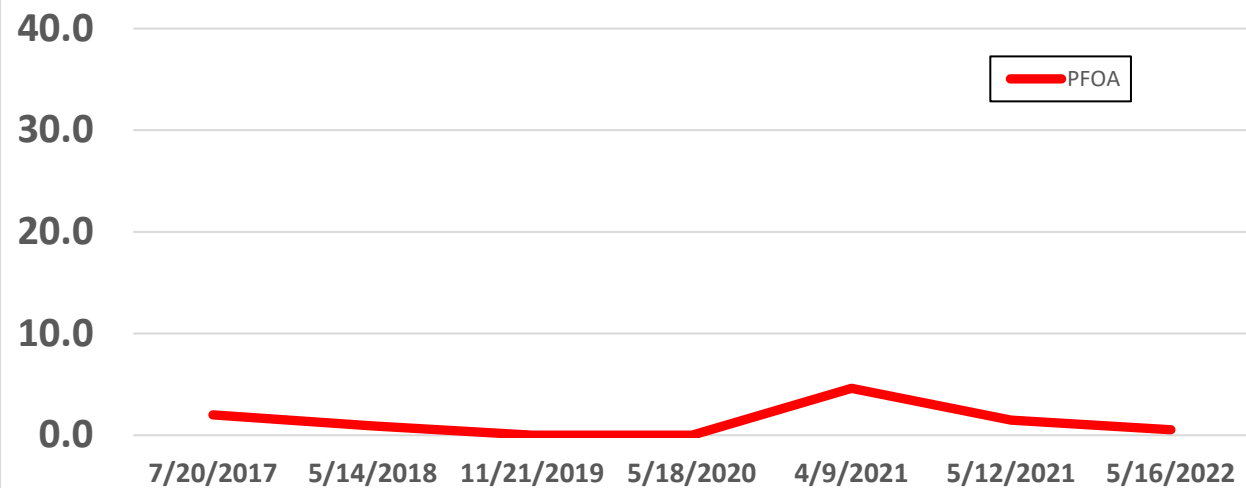
RMI - RMF (SQC13002) PFAS Concentrations (NH4)  
(ng/g) 2017 - present



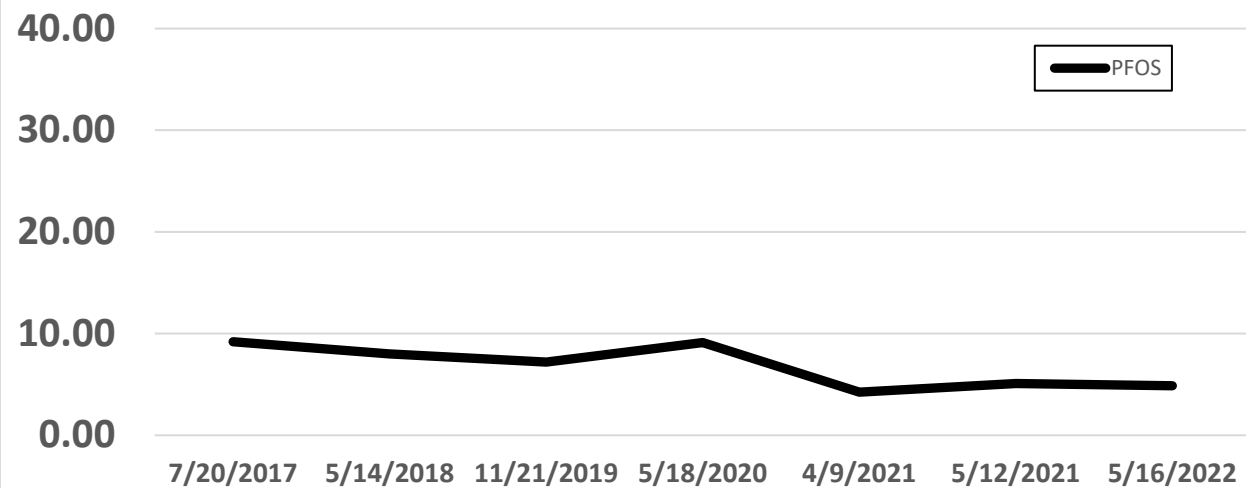
RMI - RMF (SQC13002) PFAS Concentrations (NH4)  
(ng/g) 2017 - present



RMI - RMF (SQC13002) PFAS Concentrations (NH4)  
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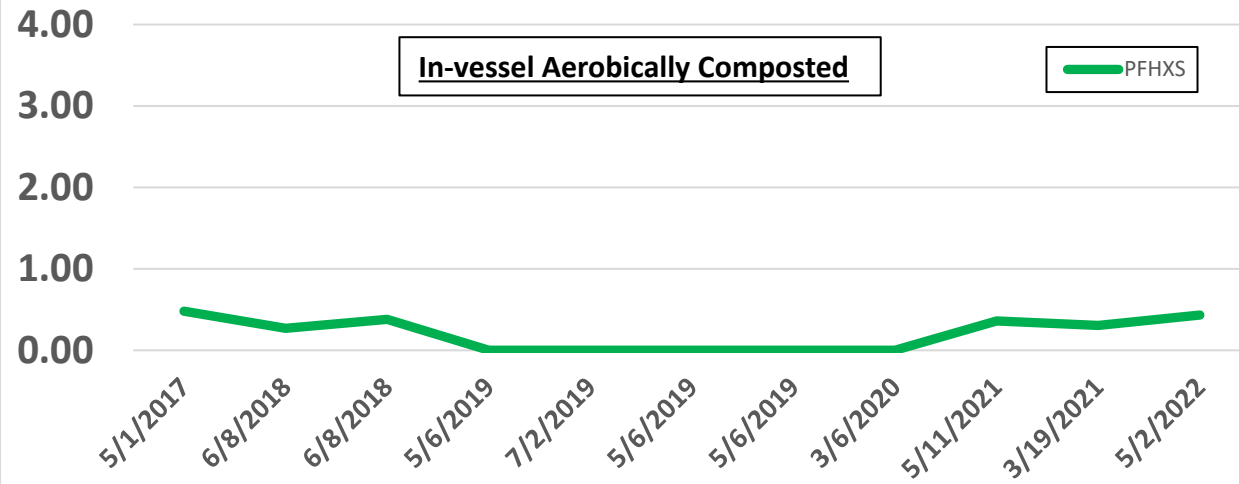


RMI - RMF (SQC13002) PFAS Concentrations (NH4)  
(ng/g) 2017 - present

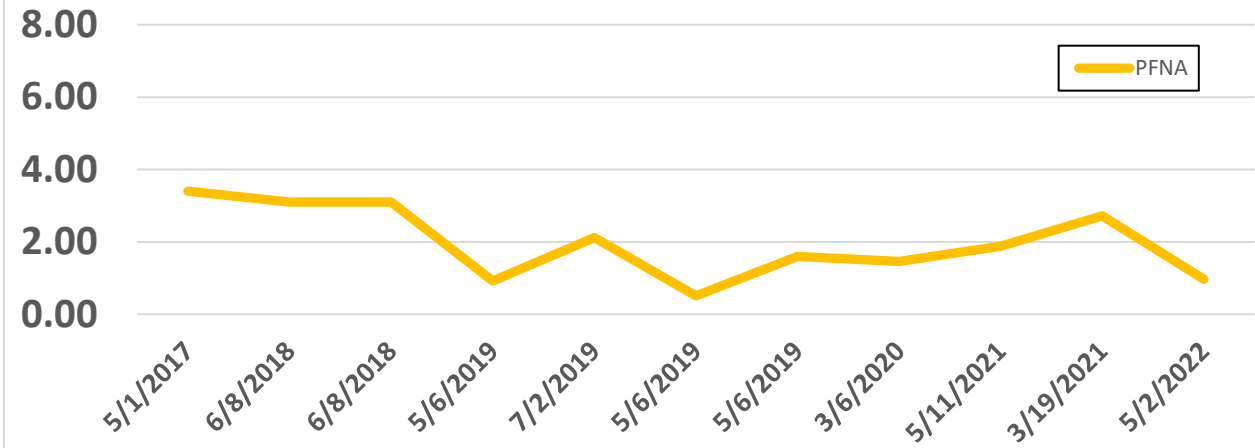




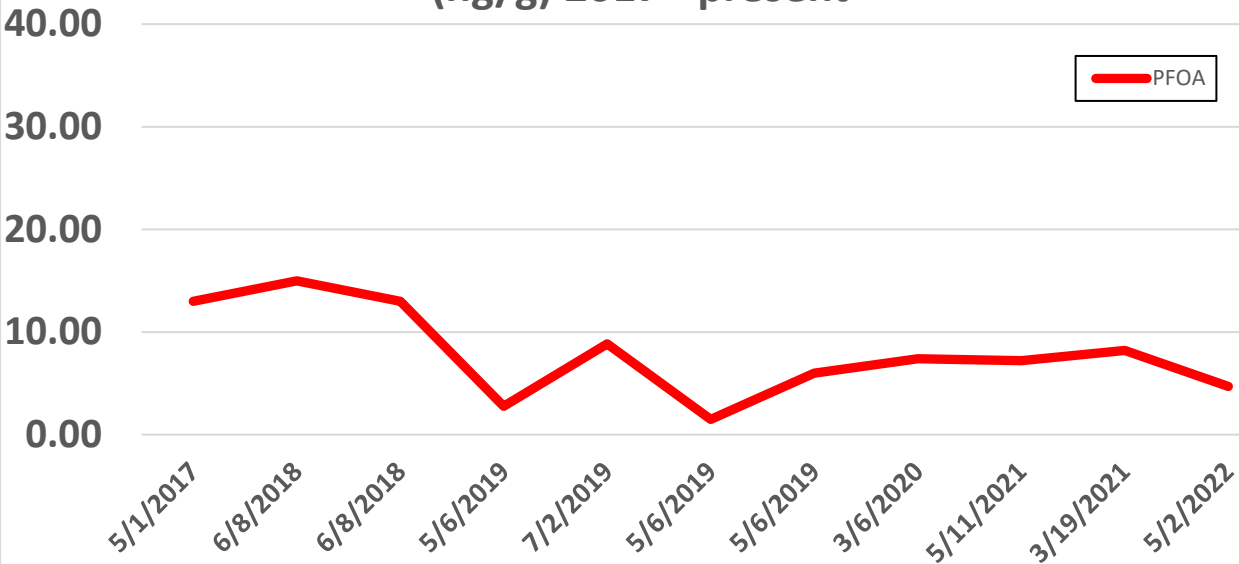
Merrimack WWTF (SQC9901) PFAS Concentrations  
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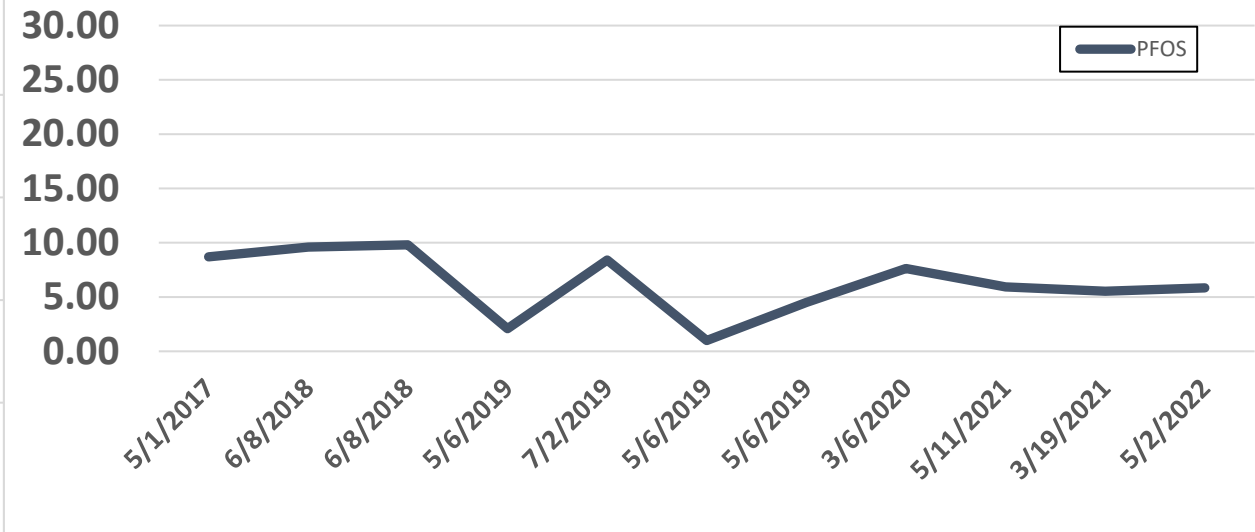
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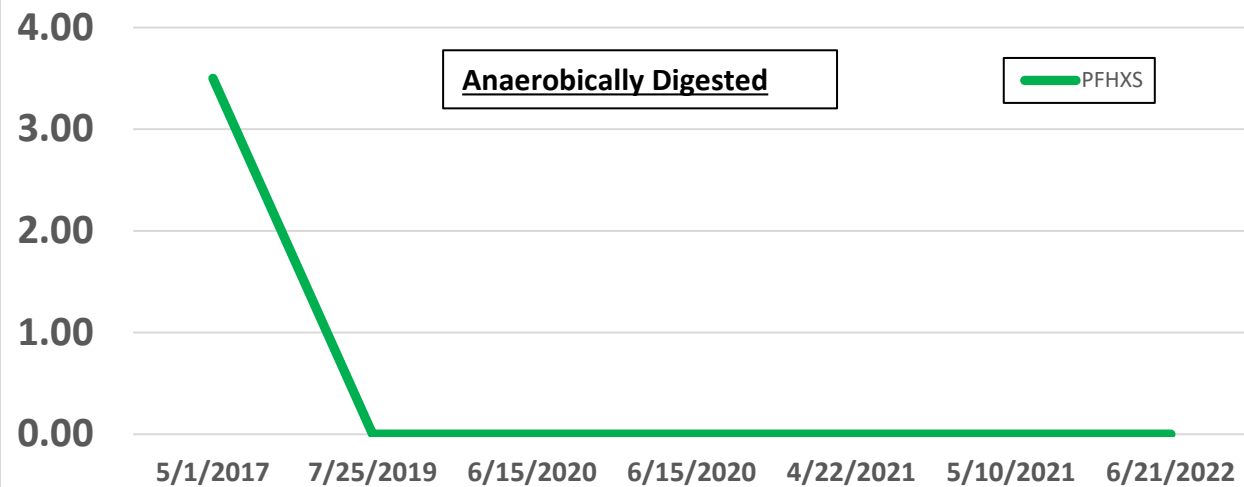
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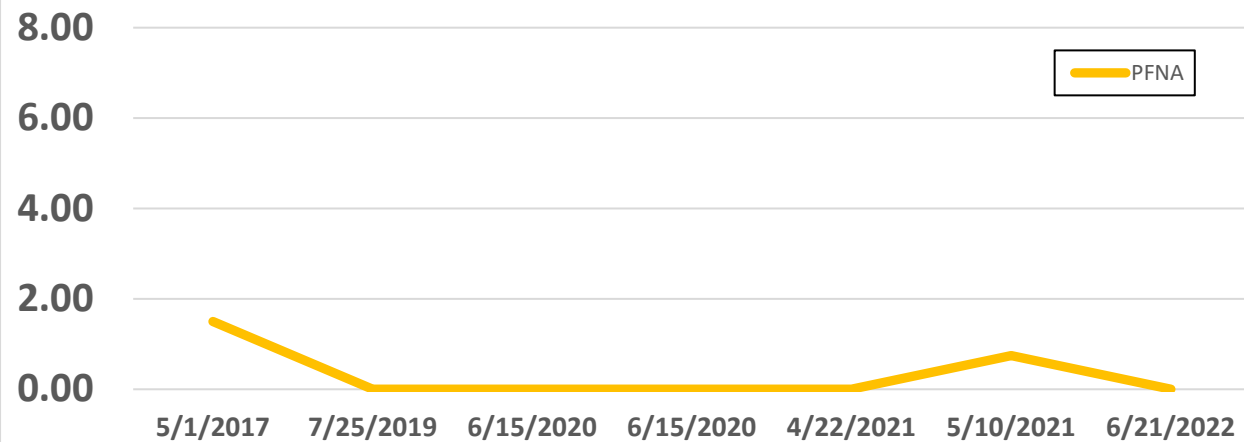
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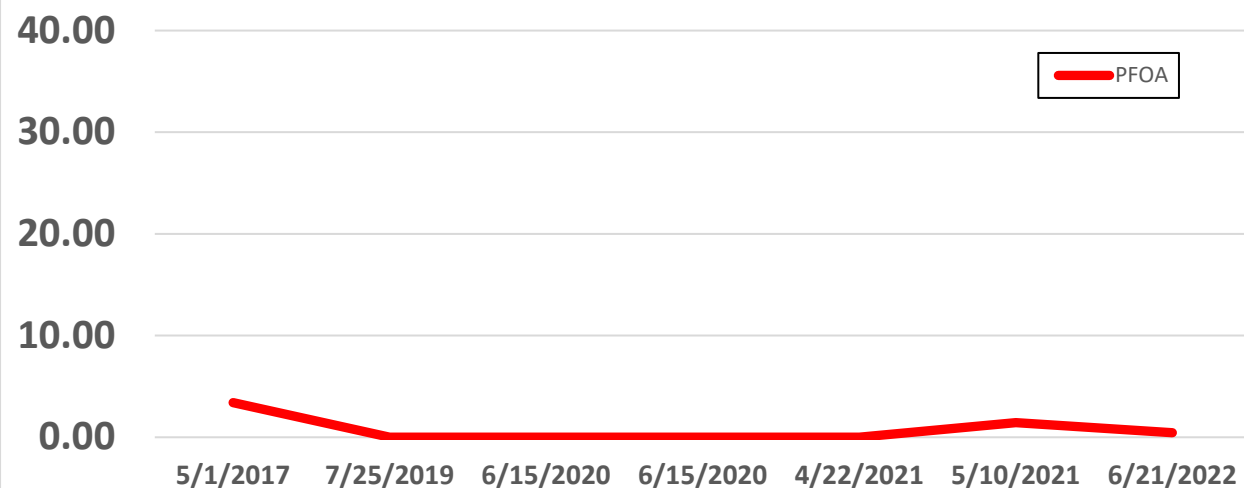
Nashua WWTF (SQC9908) PFAS Concentrations  
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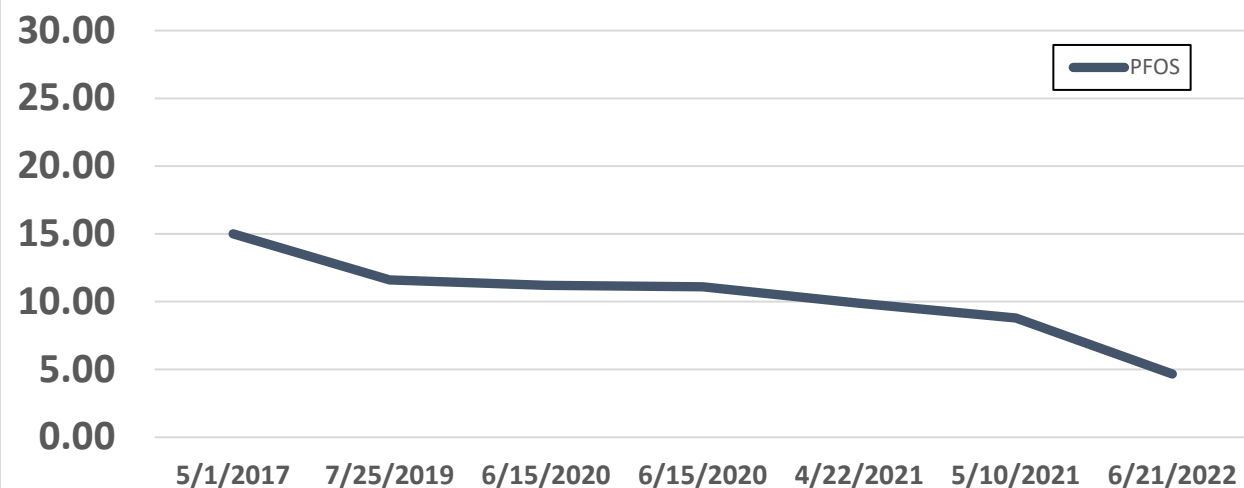
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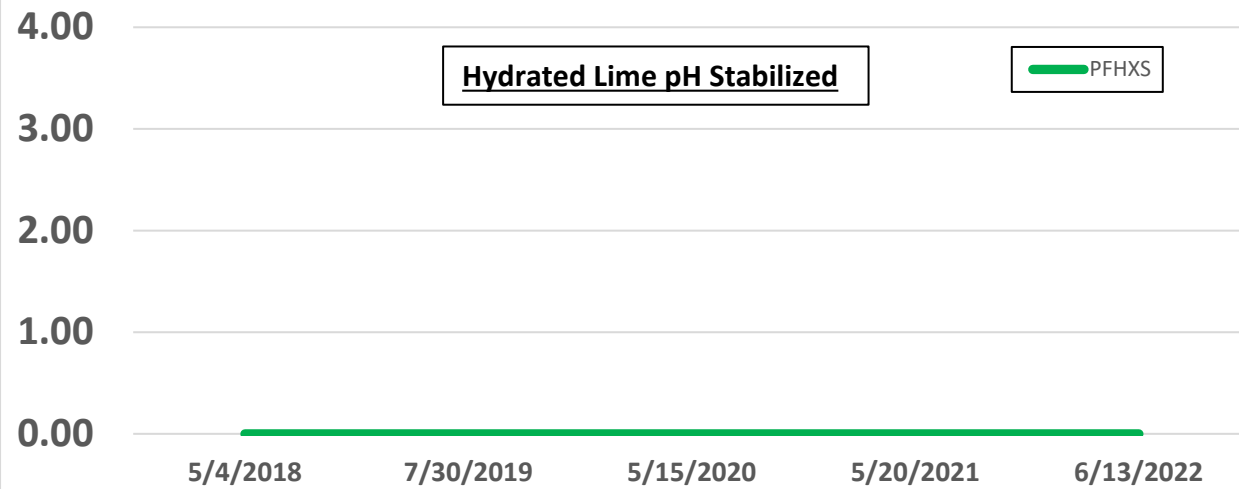
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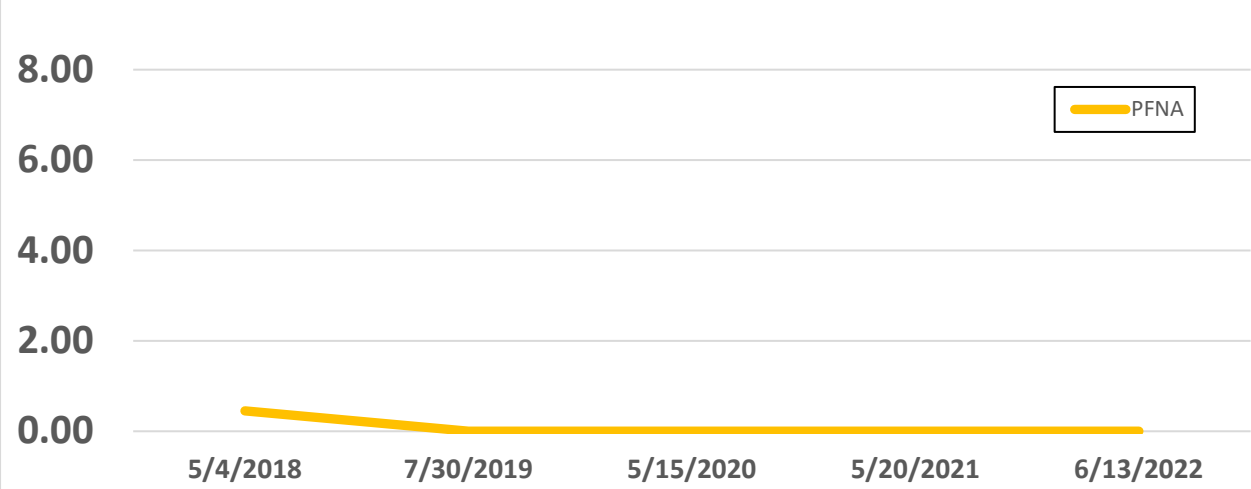
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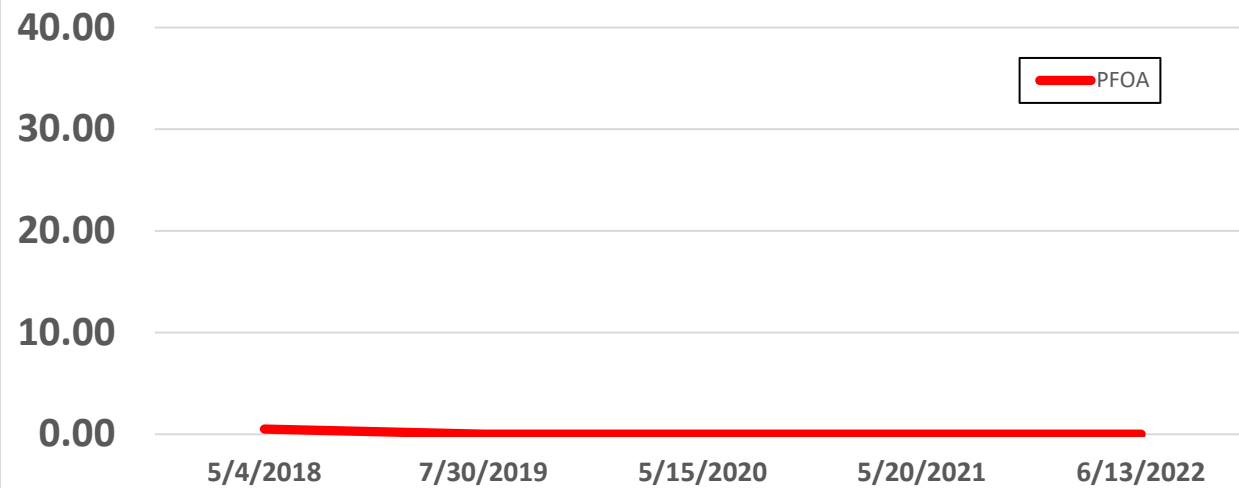
Plymouth WWTF (SQC9906) PFAS Concentrations  
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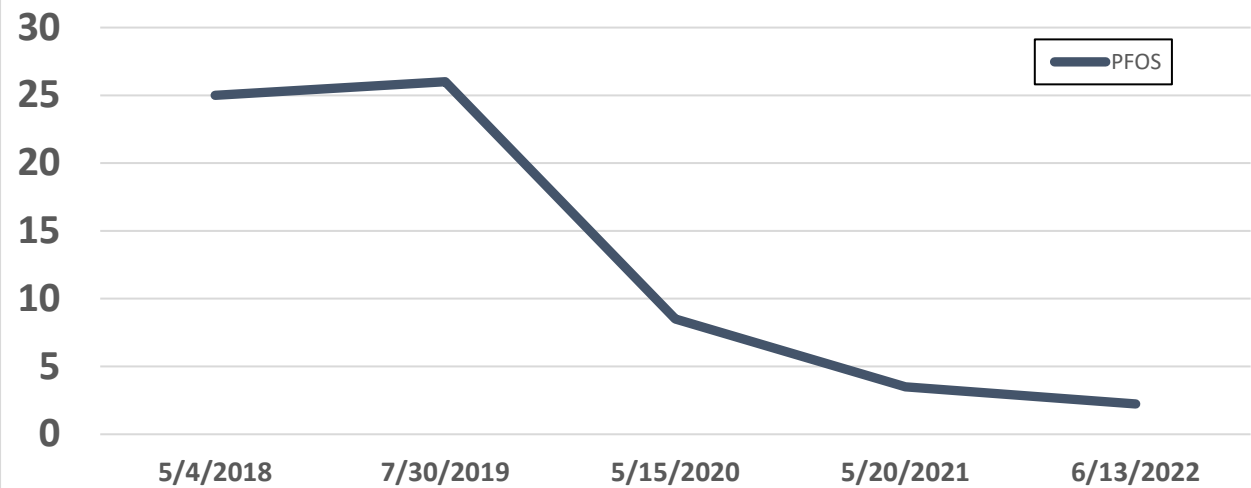
Plymouth WWTF (SQC9906) PFAS Concentrations  
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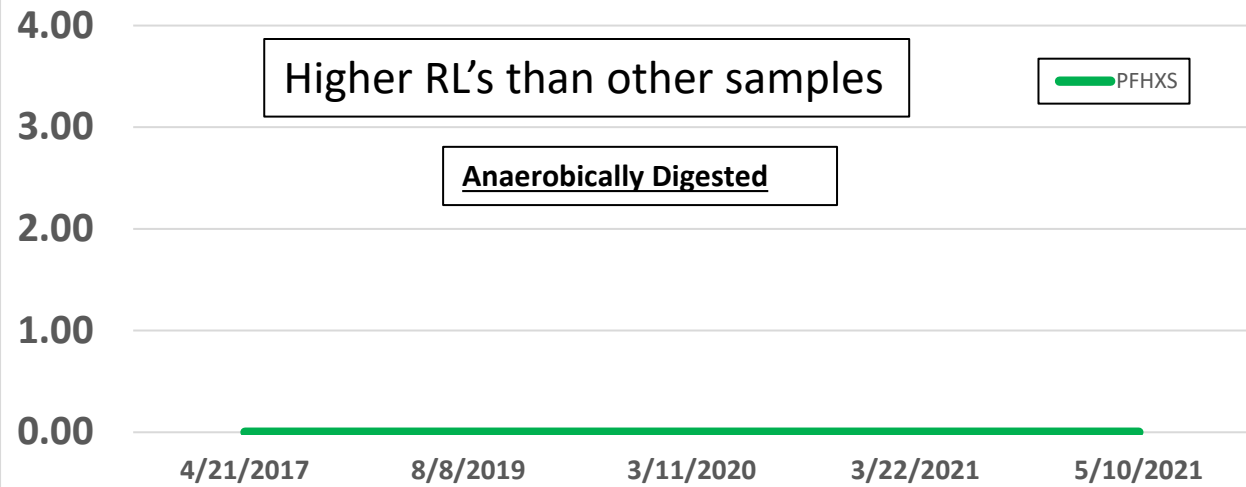
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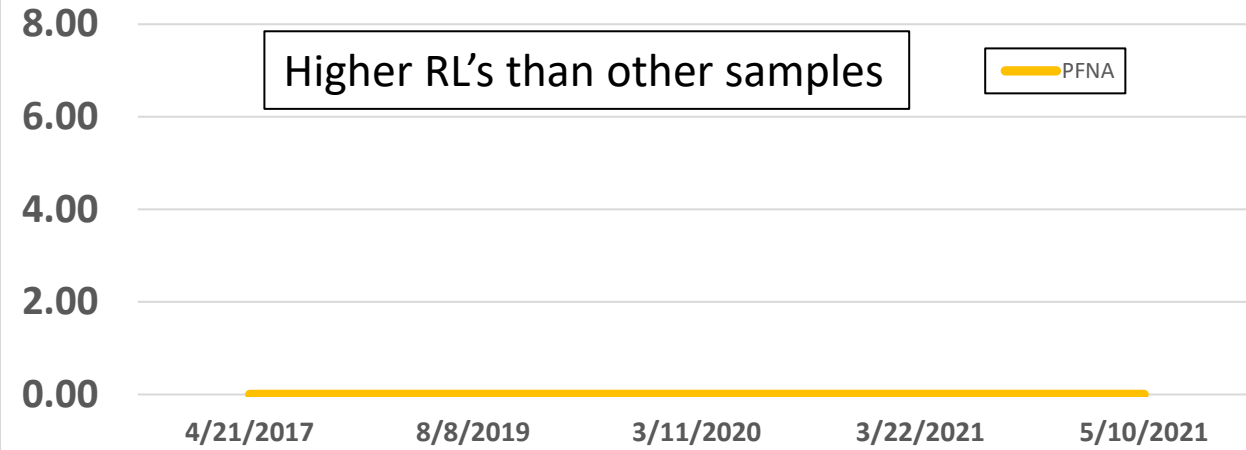
Plymouth WWTF (SQC9906) PFAS Concentrations  
(ng/g) 2018 - present



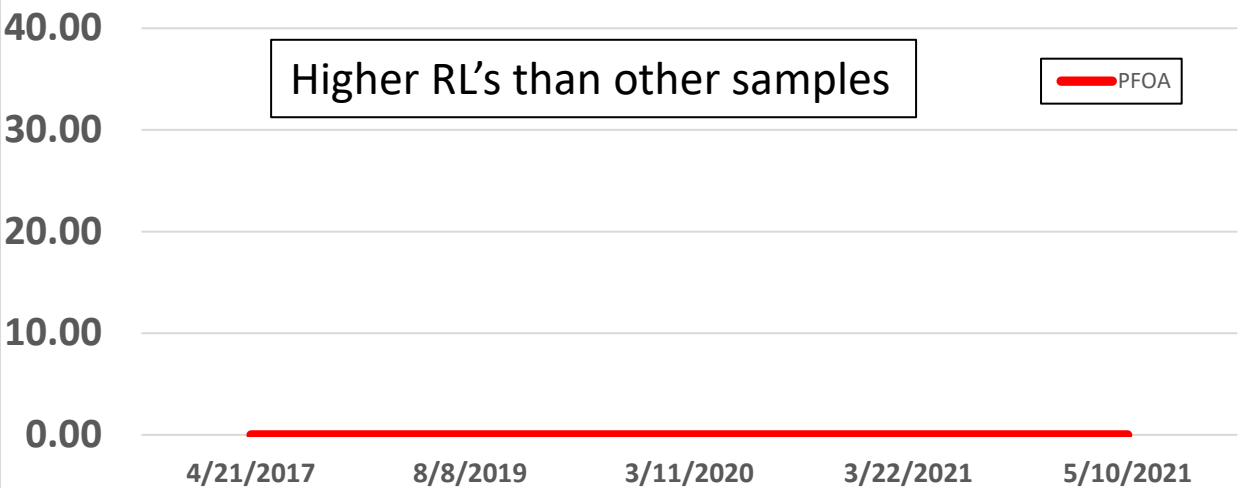
Winnepesaukee River Basin Program WWTF  
(SQC9706) PFAS Concentrations (ng/g)



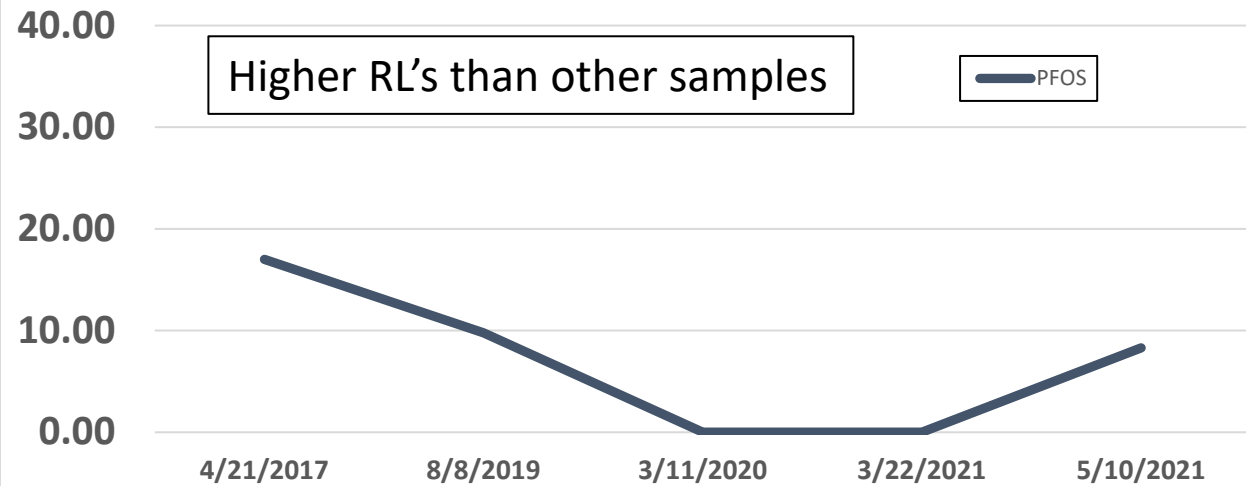
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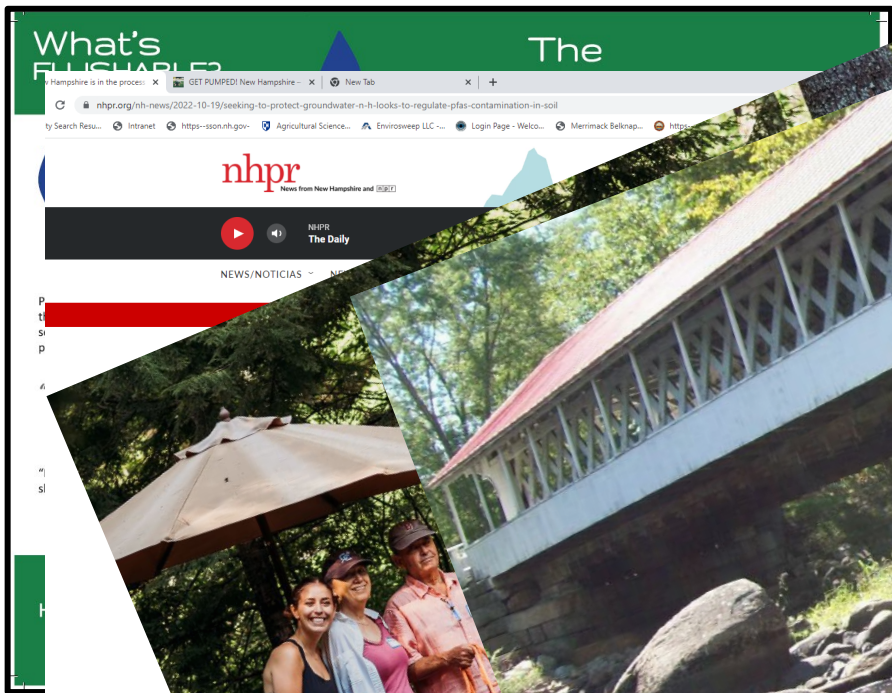


Winnepesaukee River Basin Program WWTF  
(SQC9706) PFAS Concentrations (ng/g)





# Education Outreach



## Wastewater Operator and Septage Hauler PFAS\* Guidance

\*PFAS stands for "Per- and polyfluoroalkyl substances" and is a group of manmade chemicals considered 'contaminants of emerging concern (CECs)'

Drafted by:  
The Northeast Biosolids Improvement Program

- Including...
- The importance of keeping PFAS out of biosolids
  - What is and isn't Domestic Septage?
  - What WWTF professionals do
  - Contaminants?



# Liquid Media Treatment Technologies

- **Supercritical Water Oxidation (SCWO)**

- Water above a temperature of 705F and a pressure of 3,210 psi is considered “supercritical,” which is a special state of water where certain chemical oxidation processes are accelerated.

- **Electrochemical Advanced Oxidation**

- Electrochemical advanced oxidation process (EAOP) is a water treatment technology that uses electrical currents passed through a solution to oxidize pollutants.

- **Foam Fractionation (FF)**

- Foam fractionation is a relatively new PFAS removal technology and has been used successfully for treating drinking water, wastewater, and leachate contaminated with PFAS.

- **Adsorption with Alternative Media**

- One area of development for removing PFAS from complex liquids such as leachate is the use of alternative adsorption media or resin that has an affinity for attaching and holding PFAS molecules. Examples of such alternative media include:

- *Coated Sands*
- *Zeolites and Clay Minerals*
- *Fluoro-Sorb*
- *Cyclodextrine*



# Liquid Media Treatment Technologies

- **UV Oxidation with Iodine and Sulfite Addition**

- adding iodine to a water treatment reactor that uses ultraviolet (UV) light, and sulfite destroys up to 90 percent of carbon-fluorine atoms in PFAS chemicals in just a few hours

- **Activated Persulfate**

- a strong and relatively stable oxidant, can be activated to generate free radicals to achieve a higher oxidative potential under conditions of heat, light or chemical activation (by a base or metal).

- **Catalyzed Hydrogen Peroxide (CHP)**

- It involves reaction of hydrogen peroxide with a catalyst to predominately generate hydroxyl radicals that have been demonstrated to degrade specific PFAS.

- **Sonichemical Oxidation**

- is a physio-chemical treatment that splits molecules by applying ultrasonic wave energy.

- **Electrocoagulation**

- Process involves destabilization and aggregation of contaminant particles in solution to create a floc of pollutant(s) that can be collected for Reducing PFAS in Leachate from State-Owned Landfills Sevee & Maher Engineers, Inc. and Crawford Engineers 6-13 January 2023 further treatment and/or disposal.





# The Future for contaminated sludge?



<https://www.renewableenergy-magazine.com/biomass/aries-clean-energy-receives-permits-for-worlda-20190716>



<https://rmirecycles.com/shincci-usa/>



<https://www.bioforcetech.com/>



<https://modernpumpingtoday.com/clean-energy-from-landfill-diversion-plus-the-bonus-of-biochar/>

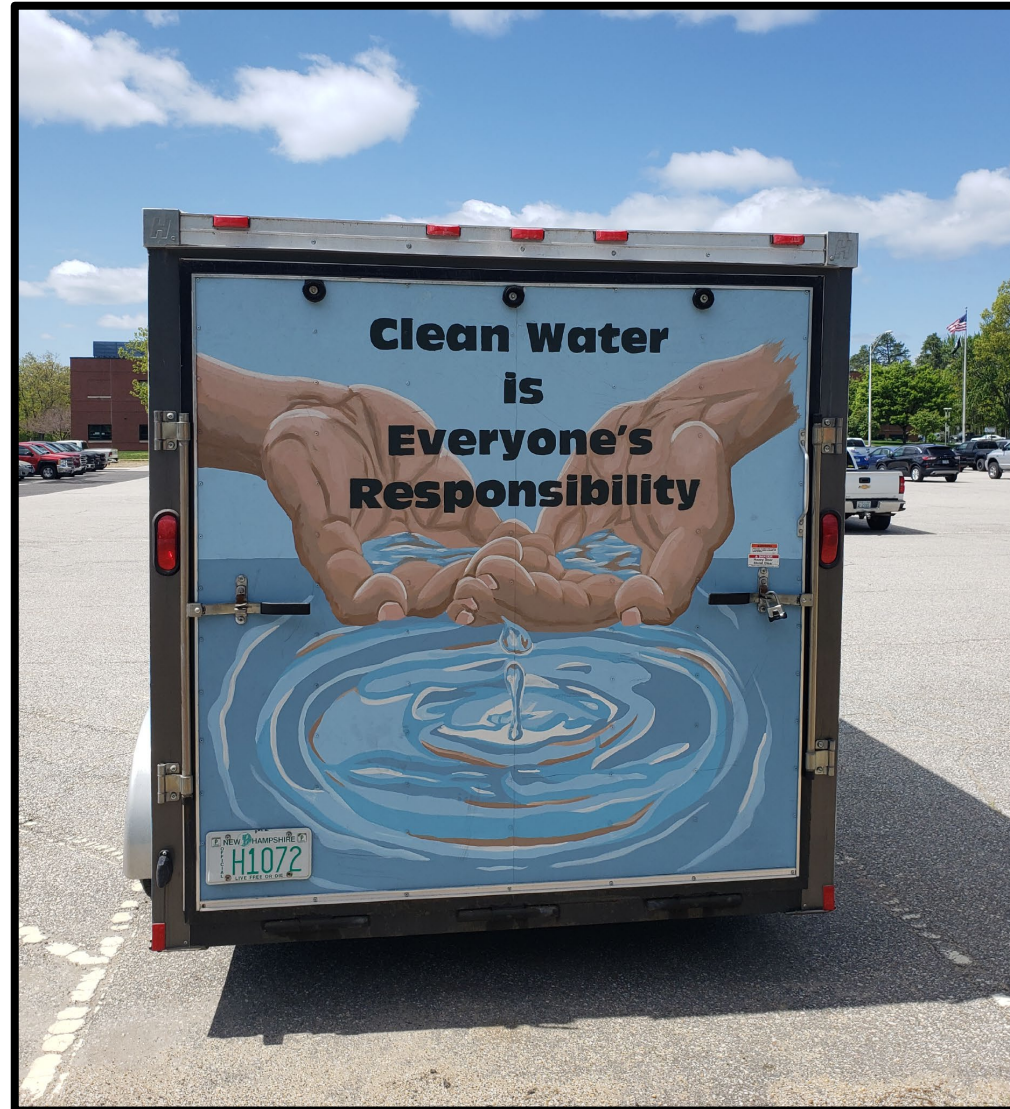
# The Future for contaminated sludge?



<https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.ec21.com%2Fproduct-details%2FElectrocoagulation-Water-Treatment-System--4324338.html&psig=AOvVaw13ecRf3aV4hqpGGOzuKemW&ust=1684603362541000&source=images&cd=vfe&ved=0CA8QjhxqFwoTCOjj-93ygf8CFQAAAAAdAAAAABAA>



Thank You !



Any  
Questions?



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