



# Analyzing PFAS Concentrations Along the Blackstone River Watershed

A Major Qualifying Project Report  
submitted to the faculty of  
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WORCESTER POLYTECHNIC INSTITUTE

## **Abstract**

PFAS are a pervasive class of chemicals that can have detrimental impacts to human health. In order to understand how different concentrations of PFAS affect a watershed, it's important to consider major point sources such as wastewater treatment plants. In this study we analyzed multiple samples taken from different locations under the influence of various potential PFAS sources in the Blackstone River Watershed. Analysis of the samples was conducted using solid phase extraction and HPLC. From these results we estimated the amount of PFAS load coming from different sources and how PFAS concentrations change in a river system.

## **Acknowledgements**

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We would also like to thank Professors Andrew Teixeira, Geoffrey Tompsett, and any student researchers working with them for running our samples on the HPLC/MS and spending the time optimizing those results on a new piece of equipment.

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## **PE Licensure Statement**

A professional engineering (PE) license is an honor and sign of credibility in the engineering profession. It signifies that you are a qualified and trusted engineer capable of making ethical and high-quality engineering designs. There are four main steps to becoming a PE: earning a 4-year degree from an accredited institution, completing the fundamentals of engineering exam, gaining four years of engineering experience under the supervision of a professional engineer, and completing the Principles and Practices of Engineering Exam.

Having a PE license means that an engineer is held to a higher standard of ethics. The National Society of Profession Engineers Code of Ethics is an important aspect of receiving a licence as it outlines rules of practice and profession obligations that engineers have to their clients, the public, and the environment. A breach of ethics could result in the loss of an engineer's PE licence.

A PE licence is a necessary step toward career development if an engineer wants to take on positions of more authority, leadership, or independence. A PE license is required to sign off on engineered drawings, own a private firm, or do independent consulting. Having a licence provides great opportunity, pay, and flexibility to an engineer.



## **Design Statement**

The Accreditation Board for Engineering and Technology (ABET) has set requirements for students to graduate with a Baccalaureate program in engineering, including a major engineering design that incorporates the engineering standards based on the knowledge and skills the students acquired through their previous coursework.

Worcester Polytechnic Institute (WPI) completes the capstone design in part through the Major Qualifying Project (MQP). This MQP demonstrates the hypothetical design a GAC adsorption system to treat 8 common PFAS substances in the near downstream Upper Blackstone location. The tower was designed to treat the concentrations found in that location in the 2020 Mass DEP PFAS in Surface Waters study and to match the amount of water that Worcester supplied for Milbury in 2022, the town directly downstream.

The designed system includes a PFD and equipment summary for the system including the pump to get the water from the river to the top of the tower, the two-tower series, necessary controls, and configuration of valves based on which tower is lead or lag. All the thermodynamic, sizing, and utility specifications can be found in section 4.3 of this report.

## Executive Summary

Per and Polyfluoroalkyl substances (PFAS) are an emerging class of organic chemicals known for their resistance to degradation and bioaccumulation in the environment. They have been linked with various health human issues but many of the regulations around PFAS are recent. PFAS can enter WWTPs from household consumer products, industries like fluoropolymer manufacturing and electroplating, and landfill leachate. Most WWTPs do not have a process to treat PFAS and have been shown to increase total PFAS concentration, resulting in WWTP effluent being identified as one of the major point sources for PFAS in the environment. Few studies have been done on PFAS concentrations in the Blackstone River watershed which found increases of 21-27 ppt  $\Sigma$ PFAS between upstream and downstream of a WWTP effluent. Fish in the area have also had tissue concentrations ranging from 6-40 ng/g PFAS.

The goal of this project was to quantify PFAS in the Blackstone Watershed from the effluent of multiple wastewater treatment facilities to assess their impact on the watershed. This was achieved by determining which wastewater treatment facilities to focus on and how far upstream and downstream from these facilities we would sample. From there, we collected samples from these areas and analyzed the samples using high-performance liquid chromatography (HPLC), allowing us to determine if there are or what types of PFAS the samples may contain.

Based on the accessibility of the locations and their location along the watershed, three wastewater treatment facilities were identified: Upper Blackstone, Upton, and Woonsocket. These locations were chosen as a result of online research and onsite inspections. Using the protocols and recommendations from EPA Methods 1633 and 533, samples were taken both

upstream and downstream from each site and an additional sample was taken from Institute Pond, which is the start of the watershed. Samples were extracted following EPA Method 537.1. This method consisted of passing the 250-milliliter sample through an SPE cartridge containing polystyrene divinylbenzene, which are then eluted with methanol, dried using a Rapid Vap with nitrogen, and were made into a 1-milliliter volume with a 96:4% (vol/vol) methanol: water solution combined with an internal standard. After samples were extracted, they were analyzed through the HPLC. Our data, along with data collected by others, indicates significant PFAS presence in the watershed.

# 1.0 Introduction

Per and Polyfluoroalkyl substances (PFAS) are a class of chemicals known as forever chemicals due to their resistance to degradation and bioaccumulation in the environment and living organisms. They have been linked with various health concerns such as reproductive issues and multiple types of cancer. It is well understood that these chemicals can enter the environment through wastewater treatment discharge to surface water since most treatment plants do not have processes meant to address PFAS and some WWTP processes can transform precursor chemicals into more problematic PFAS. Other common sources of PFAS in the environment include firefighting facilities, fluoropolymer manufacturing, and electroplating industry.

The goal of this study was to quantify PFAS concentrations upstream and downstream of WWTPs and compare that to past data that has been collected in the area. Single direct samples were taken from seven sites and extracted using a solid phase extraction procedure adapted from EPA method 537.1 and sent for analysis using the HPLC/MS in Goddard. Additionally, a hypothetical GAC contactor design is included to treat water at the downstream Upper Blackstone location.

We were able to successfully develop a procedure for sampling and extraction to work in the WPI water laboratory, but we were only able to get quantitative results for PFOA. These results did show that larger WWTPs are a source of PFAS in the environment especially in Woonsocket where regulations are less stringent.

## 2.0 Background

### 2.1 What is PFAS?

PFAS (per- and polyfluoroalkyl substances) are a group of man-made compounds that have been used for a variety of purposes starting in the 1940s (EPA, 2022). Of the 15,000 compounds that are known, the most common compounds studied are perfluorooctanoic acid, perfluorooctane sulfonic acid, perfluorohexane sulfonic acid, and perfluorononanoic acid (PFOA, PFOS, PFHxS, and PFNA, respectively). These compounds are commonly found in products such as non-stick cookware, some fire-fighting foams, personal care products, and products that are oil, grease, and water-repellent (Lenka et al., 2021). During production and use, these chemicals can migrate through soil, water, air. In the environment, they persist for a long period of time as PFAS does not break down (known as “forever chemicals” by the EPA) (2022). While the United States has attempted to phase out the use of some PFAS compounds, PFAS are still in wide use. Since these chemicals are widely used across a multitude of different applications, buildup of these compounds in the environment and humans has had a substantial increase over the years, especially with new PFAS compounds being produced (EPA, 2022).

### 2.2 Sources and Exposure Pathways

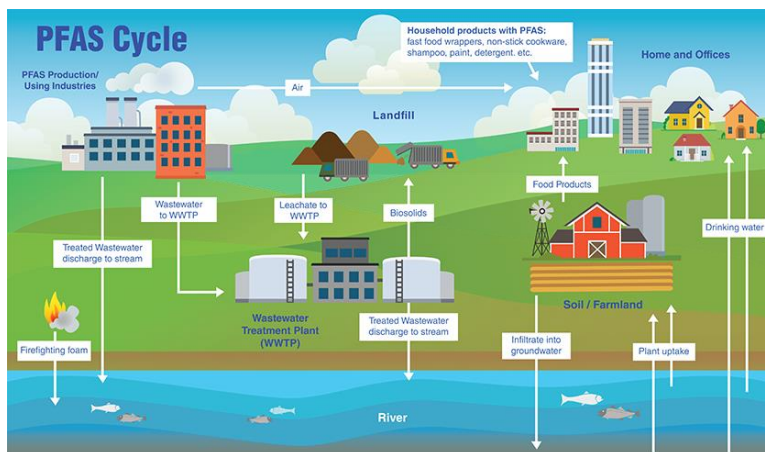


Figure 1. PFAS Cycle (New Jersey Department of Environmental Protection, 2023)

### ***2.2.1 Domestic Sources***

There are a variety of everyday products that can result in PFAS release into the environment through domestic and municipal wastewater or landfill leachate. PFAS are used as anti-grease or waterproofing agents, and are commonly found in nonstick cookware, food packaging, outdoor clothing, cosmetics, shampoos, and stain removers (Andrews, 2021, O’Conner, 2022). One study testing fast food packaging around the U.S. found total fluorine above a detection limit of 16 nmol F/cm<sup>3</sup> in 33% of food contact paper tested positive tests in 56% of dessert/bread, 57% of Tex-Mex, and 36% of sandwich/burger packaging (Schaidler et al., 2017). In a study done on water and stain-resistant soft goods like outdoor apparel, bedding, and tablecloths sold in the U.S., 72% of items tested positive for PFAS across all 10 retailers (Schreder & Goldberg, 2022). In a study covering a range of U.S. cosmetic products, PFAS was found in a range of 147-10,500 ng/L and a 1,354 ng/L average of the Σ53 PFAS tested (Whitehead et al., 2021). In an international study of cosmetics and personal care products all 38 products sampled had at least 1ng/g of total PFAS with an average of 100 ng/g including 4 PCPs with no listed fluorinated ingredients (Harris et al., 2022). All these products can contribute to domestic PFAS load in wastewater through human waste, grey water, or landfill leachate.

### ***2.2.2 Industrial Sources***

Common industries responsible for PFAS release into WWTPs and the environment are fluoropolymer manufacturing, electroplating, electronic industries, aerospace, manufacture of metal products, textile, oil and gas, and wood industries (O’Conner, 2022). A study focusing on the Cape Fear River in North Carolina found that an average of 3.4 kg of PFAS passed into marine systems each day during the 2-year sampling period stemming from a wastewater treatment plant and a PFAS manufacturing factory (Pétre et al., 2022). A China-based study

testing electroplating industrial WWTPs found total PFAS concentrations as high as  $2100 \pm 130$  ng/L in the influents and  $4200 \pm 270$  ng/L in the effluents with PFOS making up 62% of the samples. The same study found lesser, yet still concerning concentrations from a textile manufacturing WWTP of  $590 \pm 39$  ng/L in the influents and  $520 \pm 30$  ng/L in the effluents (Liu et al., 2022). Another study based in China found an average concentration of 780ng/L of a sum of 11 PFAS in the wastewater of different workplaces in an electroplating facility (Jiawei et al., 2019).

### ***2.2.3 Other Sources***

Other sources such as agricultural runoff and firefighting foams can also act as sources for PFAS in the environment that often don't go through WWTFs. Many farms use biosolids from WWTFs as economic and environmental alternatives to other fertilizers, but those biosolids are often contaminated with toxic chemicals including PFAS, which can be stored in the soil for extended periods (Jha et al., 2021). Some studies have suggested that shorter-chain PFAS will build up in the soil during spring and summer and then release into the environment over fall and winter (O'Conner, 2022). A study done in the Midwest U.S. found soil using biosolids had total PFAS concentrations of 22.9 ng/g dry weight with 71% being long-chain PFAS (Caniglia et al., 2022).

Firefighting foams from airports or firefighting facilities can also be a large source of PFAS in surface waters. A study looking at a civilian airport found runoff concentrations of PFAS 57 and 18 ng/L at two sites directly downstream. The same study found a concentration downstream of a firefighting training facility of 360 ng/L composed of short-chain due to being easier to travel through the soil (Dauchy et al., 2017). Another study done recently after training found  $1.2 \times 10^8$  ng/L in direct drainage and  $5.3 \times 10^6$  ng/L in the WWTP after other dilution.

Total concentrations of quantified PFAS in the runoff water network around the facility ranged from  $2.9 \times 10^7$  to  $1.0 \times 10^3$  ng/L (Dauchy et al., 2019).

#### **2.2.4 Exposure Pathways**

The most common ways for humans to be exposed to PFAS via surface waters are by drinking contaminated water and eating fish or other seafood from contaminated water bodies. The Blackstone River remains one of the top 5 polluted rivers in the U.S, which has led to communities not drawing any drinking water from it or the Seekonk River which it feeds into (National Parks Service, 2023). Although, the Blackstone River, Seekonk River, and further downstream the Narragansett Bay are major areas for recreational and consumer fishing which is an area of concern since PFAS concentration in human blood has been positively associated with seafood contamination in the U.S. (Christensen et al., 2017). A study measuring PFAS concentration in seafood in the U.S. Northeast detected PFAS in half of fish samples and one-fourth of seafood samples with concentrations between 0.5 and 1.3 mg/g (Ruffle et al., 2020).

### **2.3 PFAS Health Effects**

While research regarding the effects of PFAS on human health are still ongoing, there are current studies that determine that the risk of health effects depends on exposure dose, frequency, and duration, the individual's existing health, and access to health benefits (safe water, healthcare, etc.). PFAS is linked to reproductive issues, prostate, kidney, and testicular cancer, reducing the immune system's response to vaccines (antibody response), developmental effects in children, changes in liver enzymes, and increased levels of cholesterol (Sunderland et al., 2019). Below are the specific compounds related to each known health effect:

1. Reproductive Effects (pregnancy-induced hypertension and high blood pressure) - PFOA and PFOS (Yang et al., 2022)
2. Cancer (prostate, kidney, and testicular) - PFOA (Barry et al., 2013, Vieira et al., 2013)



3. Immune System (lower antibody response) - PFOA, PFOS, PFHxS, PFDA (Dong et al., 2013, Grandjean et al., 2012)
4. Developmental Effects (birth weight) - PFOA, PFOS (Chen et al., 2012, Wang et al., 2016)
5. Changes in Liver Enzymes – PFOA, PFOS, PFHxS (Darrow et al., 2016, Fan et al., 2014)
6. Cholesterol levels – PFOA, PFOS, PFNA, PFDA (Frisbee et al., 2010, Nelson et al., 2010)

In addition to the known compounds and their effects on human health, certain individuals may be predisposed to PFAS exposure based on their place of residency, occupation, or the amount of water they consume especially in pregnant women (Gao et al., 2021). Furthermore, children may be at a higher risk of exposure due to their water and food intake. They are also more at risk since young children tend to put items into their mouths, leading to exposure through carpets, toys, and other items (Lee et al., 2021). There is current research to determine the effects of PFAS in breast milk since PFAS in the mother's bloodstream could cause health effect for children (Zheng et al., 2021). Unfortunately, the uncertainty of these chemicals complicates solidifying what health effects are associated with PFAS. Since there are thousands of compounds with varying toxicity levels that can be exposed at any stage of life, it is difficult to pare down the direct causes. In addition, new compounds and uses for PFAS changes daily making it more challenging for researchers to track and identify how PFAS will affect human health over time (ASTDR 2024).

## **2.4 Current Regulations and TMDLs**

The Environmental Protection Agency (EPA) has made significant progress to address and regulate PFAS in the environment. While these rules and regulations do not directly remove

PFAS from the environment, they do attempt to detect these compounds, prevent further contamination, and protect human health and the environment.

#### ***2.4.1 EPA Regulations and Proposals***

One of the main strategies the EPA has used to address PFAS is to propose regulations to prevent further contamination, as well as to provide a base line for state governments to propose their own regulations on PFAS. The majority of their regulations consist of proposals that aim to bring awareness to these chemicals. Specifically, one of the proposals is to designate two of the PFAS compounds, PFOA and PFOS, as hazardous substances under the Superfund Act or the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Blackman, 2022). This will require companies to immediately report release of these compounds into the environment if they meet or exceed the reportable quantity. Currently, the EPA is reviewing public comments on this proposal. The EPA has also developed risk management practices for PFAS under the Toxic Substances Control Act (TSCA). In January 2024, the agency finalized a significant new use rule that will prevent manufacturers from using discontinued PFAS compounds from being used without EPA review of the “significant new use”. In addition, the agency has requested certain regulations and reporting requirements that align with the Emergency Planning and Community Right-to-Know Act (EPA Press Office, 2024).

On April 10<sup>th</sup>, 2024, EPA released the final National Primary Drinking Water Regulation (NPDWR) for 6 of the most well understood PFAS compounds. This regulation included enforceable Maximum Contaminant Levels (MCL) levels and health based, unenforceable Maximum Contaminant Level Goal (MCLG), for each compound. These regulations are also paired with substantial funding for PFAS treatment in public water systems. This rule would require water systems to monitor for the next three years, at the end of which they will be

required to publicly report levels of these three PFAS and have until 2029 to address contamination if found (EPA, 2024).

**Table 1.** MCLGs, and MCLs for select PFAS compounds that qualify for the EPA’s final National Primary Drinking Water Regulation.

<b>Compound</b>	<b>Proposed MCLG</b>	<b>Proposed MCL (enforceable levels)</b>
PFOA	Zero	4.0 ppt
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

Despite this new drinking water regulation, the EPA has minimal regulations regarding effluent limits of PFAS and primarily focuses on new proposals to measure PFAS. Specifically, the EPA has drafts, such as the EPA Method 1633 and 1621, that focuses on measuring PFAS in the environment. In particular, Method 1633 focuses on measuring PFAS in wastewater, surface water, groundwater, biosolids, etc., and Method 1621 focuses on measuring the presences of carbon-fluorine BOD in wastewater.

#### ***2.4.2 Massachusetts Regulations***

In addition to federal regulations, most states develop stricter regulations regarding PFAS compared to EPA standards. Specifically, Massachusetts is one of sixteen states that has developed regulations to reduce the amount of PFAS that is released into the environment. On October 2, 2022, the Massachusetts Department of Environmental Protection established their drinking water standard for six PFAS compounds; PFOS, PFOA, PFHxS, PFNA, PFHpA, and PFDA. According to the standard, the Massachusetts Maximum Contaminant Level (MMCL)

cannot exceed 20 parts per trillion (ppt or 20 nanograms per liter) in community and non-transient non-community systems (Mass DEP, 2020). Massachusetts also has set regulations on reporting PFAS concentrations in soil, groundwater, or surface water (shown in Table #) as well as providing guidance on PFAS sampling and analysis for potentially contaminated sites (Mass DEP, 2023b). Regulations are continuing to be proposed as new compounds emerge and the abundance of PFAS in the environment increases.

**Table 2.** Reportable Quantities and Reportable Concentrations for PFAS in Massachusetts

	RQ (lbs)	RCGW-1 (ng/L)	RCGW-2 (mg/L)	RCS-1 (mg/kg)	RCS-2 (mg/kg)
$\sum$ 6 PFAS (listed below)	-	20	-	-	-
PFDA	1	See $\sum$ 6 PFAS	40	3E-04	0.4
PFHpA	1	See $\sum$ 6 PFAS	40	5E-04	0.4
PFHxS	1	See $\sum$ 6 PFAS	0.5	3E-04	0.4
PFNA	1	See $\sum$ 6 PFAS	40	3.2E-04	0.4
PFOS	1	See $\sum$ 6 PFAS	0.5	2E-03	0.4
PFOA	1	See $\sum$ 6 PFAS	40	7.2E-04	0.4

## 2.5 PFAS in WWTPs

Many studies have been conducted comparing concentrations of PFAS both upstream and downstream of WWTP effluent, and facility influent and effluent. Sample concentrations are shown to be proportional to raw inlet temperature, meaning PFAS loads are often larger in the summer than other seasons (Thompson, 2022). Common treatment processes done in WWTPs are shown to be ineffective for treating PFAS. Studies consistently show that select PFAS species are greater in the effluent stream than influent because common precursor compounds in wastewater can be transformed into PFAS during biological treatment under both anaerobic and aerobic conditions. PFHxA, PFPeA, and N-MeFOSAA concentrations were significantly higher in effluent than their respective influent samples regardless of time of year (Tavasoli, 2021).

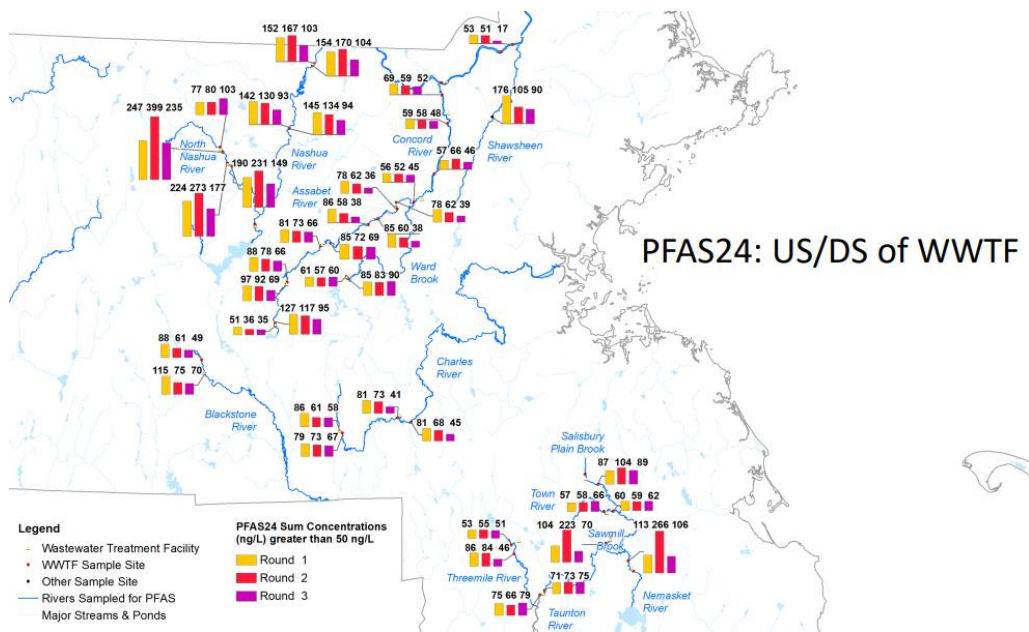
Following the banning of longer chain PFAS, such as PFOA and PFOS, the concentration of those compounds has been decreasing by an average of  $-14 \pm 3 \text{ ng L}^{-1} \text{ year}^{-1}$  and  $-18 \pm 6 \text{ ng L}^{-1} \text{ year}^{-1}$ , respectively (Thompson, 2022). However, they remain one of the most detected compounds in analysis of PFAS because of their accumulation throughout the water cycle and environment. It has also been speculated that specific shorter-chain PFAS compounds are harder to detect with analytical instrumentation like HPLC (O’Conner, 2022). A New Jersey based study showed longer-chain PFAS such as PFOA, PFOS, PFNA, PFDA, PFUnDA, and PFHpA account for more than 87% of total PFAS measured, while other identified PFAS were less than 10% (Tavasoli, 2021). A study in Michigan covering 10 WWTPs had effluent concentrations from 50 to 1114 ng/L total PFAS with widely varying compositions with the largest facility discharging an estimated 128 kg/yr into surface waters (Helmer et al., 2022).

Studies that examine differences in PFAS concentrations upstream and downstream of WWTPs often find significant increases. A study done in Pittsburgh found increases from upstream to downstream ranging from 11.6-34.9 ppt across the three WWTPs (Launtz, 2024). A broader midwestern study covering 14 WWTPs found upstream and mixing zones average concentrations of 37.7 and 71.4 ng/L, respectively (Caniglia et al., 2022).

## **2.6 PFAS in the Blackstone River Watershed**

There are a few publicly released studies covering PFAS contamination in the watershed. A 2020 Mass DEP study showed PFAS concentrations upstream and downstream of 48 WWTPs in Massachusetts including Upper Blackstone for three rounds of testing. For the main PFAS 6 analytes the concentrations were shown to decrease from upstream to downstream in the first two rounds and only increased from 17 to 19 ng/L in the third round. For an expanded 24 analytes all rounds had an increase from upstream to downstream ranging from 21-27 ng/L with the highest concentration measured being 115 ng/L at the downstream in round 1 (Savoie & Argue, 2022).

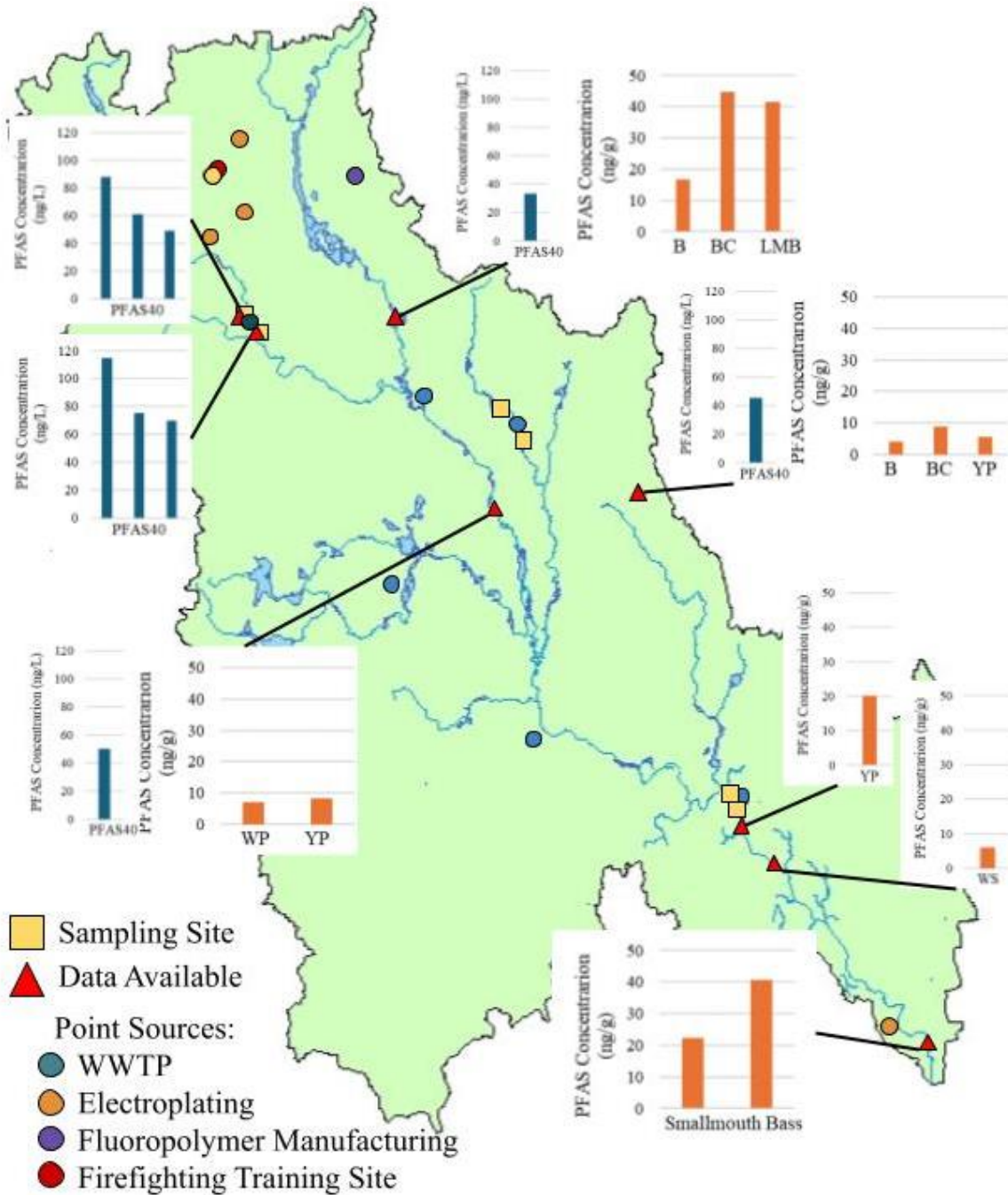
The findings of that report for other Massachusetts Rivers are shown below in Figure 2. For most treatment plants the downstream PFAS24 concentrations were only slightly greater than upstream, but Westborough, Marlborough East, Blackstone, E. Finchburg, MCI Bridgewater, Middleborough, and Brockton has significant and consistent increases between upstream and downstream (Savoie & Argue, 2022). Another Mass DEP study done in 2022 focusing on more rural areas found PFAS in all sites tested even with no known source.



**Figure 2.** PFAS 24 Concentrations Upstream and Downstream of WWTPs (Savoie & Argue, 2022)

Rhode Island Department of Environmental Management has only one study on record for PFAS in non-drinking surface waters and it's a 2009 study on fish tissue which found 20-40 ng/g of 6 PFAS compounds in fish caught downstream of a WWTPs (U.S. Geological Survey (2009). From the Mass DEP study that compared fish tissue and aqueous samples from the same site calculated BAFs for the fish species studied which with log BAFs for yellow perch ranging between 2.5-3.5 for most PFAS compounds and species (MassDEP, 2023). As of 2024 RIDEM

is required to take samples of WWTP effluent to monitor PFAS twice a year, but that data is not available to the public yet (RIDEM, 2023). Figure 3 shows a summary of the findings across fish tissue and surface water samples from the Blackstone watershed.



**Figure 3.** Map of Blackstone Watershed showing PFAS data for surface water (blue) and fish tissue (orange) compared to the sites selected for this study and potential PFAS sources

## **2.7 Treatment Options**

### ***2.7.1 GAC Adsorption***

The use of adsorption to treat PFAS is common due to the low cost, ease of operation, and low energy required. The process is well understood as it has been used for water treatment for decades (Xiao et al., 2017). Due to its high surface area, running contaminated water through a tower of granular activated carbon (GAC) has been shown to effectively treat long chain PFAS, however, it has been shown to be less effective for shorter-chain PFAS treating as little as 40% (O’Conner, 2022). GAC has a reported adsorption capacity of 71.6–290 mg/g and 41.3–120 mg/g for PFOS and PFOA respectively with equilibrium times ranging from 24-240 hours (Zhang et al., 2019). Treatment system design often require bench scale tests due to thermodynamic data varying based on concentration and composition (Brown & LeBlanc, 2022, Burkhardt et al., 2022). Systems are typically designed to be backflushed to prevent clogging and the GAC can be remediated through heat treatment (Crone et al., 2019).

### ***2.7.2 Ion Exchange***

The use of an ion exchange resin has been shown to be a highly effective treatment method for PFAS and PFAS that have strong anionic or cationic functional groups, though the absorbent is more expensive than most GACs (O’Conner, 2022). Ion exchange resin has been shown to treat over 90% of PFAS both short-chain and long-chain (Dixit et al., 2020). Equilibrium time has been reported between 6-168 hours due to their higher adsorption capacity and faster kinetics (Crone et al., 2019). Compared to GAC, IX has been shown to have higher absorptive capacity for long chain PFAS like PFOA and PFOS and as well as ionic short chain PFAS but lower capacity for short chain PFCAs (Murry et al., 2021).



## **Chapter 3: Methods**

To determine the concentrations of PFAS in the watershed, first determined the wastewater treatment facilities to sample from and how far upstream and downstream from these facilities we will sample. After locations were determined, we collected samples from these sites. PFAS was then extracted from the samples using SPE cartridges and eluted into methanol and vapourised until dry. To analyze the samples in an HPLC/MS, a curve of external standard was prepared, and 1 mL of methanol water mixture and 5  $\mu$ L of an internal standard was added to each sample. Samples were analyzed by the research team in Goddard Hall

### **3.1 Site Selection**

Sampling sites were selected based on their accessibility and location along the Blackstone River. We started by identifying all the WWTPs along the Blackstone River and used Google Maps to identify which facilities had public access or walkways around the river and the Mass DEP records to find the upstream and mixing point coordinates they used for similar tests. We identified five possible WWTPS based on this research: Upper Blackstone, Grafton, Uxbridge, Upton, and Woonsocket. We then surveyed the areas on foot to identify the effluent outlet and confirm sampling locations were safe and easily accessible for our purposes. We determined there was no safe downstream location for us to get a sample from Grafton on the side of the river with the public nature reserve and the river was also inaccessible in Uxbridge so both of those sites were eliminated. We then added Insitute Pond as a location as it feeds into the river, is downstream of a firefighting training facility, and is accessible to our study.

### **3.2 Sampling Procedure**

After determining the specific locations where sampling would occur, we determined how to safely sample these areas while avoiding cross-contamination from PFAS. Before

sampling, we ensured that samples were obtained safely by following safety protocols that aligned with the EPA's method of sampling for PFAS. Specifically, we followed protocols and recommendations from the EPA Method 1633 and EPA Method 533. We used the method to identify equipment required for sampling and ways to avoid cross-contamination. When possible, we avoided products, specifically sampling equipment and attire, that contain PFAS. For our purposes, Additionally, we ensured that our safety protocols aligned with the EPA Safety Manual. To ensure there is no cross-contamination with PFAS, we used polypropylene (PPCO) bottles and nitrile gloves, since both items do not contain high levels of PFAS. We wore closed toed shoes and long pants as a safety precaution. In the cases where we did need to enter the river, we ensured the boots we were using did not contain PFAS from the company website. To ensure our safety, we wore personal flotation devices while sampling.

We identified the date of November 24<sup>th</sup>, 2024, to take samples based on our availability and weather conditions. We took PFDs, boots, waders, nitrile gloves, 500 mL and 250mL polypropylene bottles, a cooler, and ice. For sampling, we followed the guidelines listed under the EPA Method 1633 and 533. At each site one team member first put on PFDs and boots when necessary then gloves. They then grabbed 1 500 mL or 2 250 mL bottles, positioned themselves at an accessible point at the edge of or in the river. Each bottle was rinsed using the river water three times by holding the bottle upstream of the person sampling and pouring it out downstream. A sample was then taken at a depth of 3-6 inches from the surface and sealed. During this process the other team member would make a label with our names, the location, date, time, and other information necessary for storage in the WPI water laboratory. These labels were then added to each bottle. Samples were put into a cooler with ice 5-10 minutes after retrieval. After all samples were collected, they were stored in a refrigerator in water laboratory.

### 3.3 Extraction Procedure

First, the 6-mL SDVB SPE cartridges were conditioned by passing 15 mL of methanol and 18 mL of reagent water dropwise through the cartridge under vacuum, ensuring the cartridge did not go dry. In the cases where it did dry out, the conditioning process was repeated. After the cartridge was conditioned the transfer tube was moved to the sample bottles. Samples were watched closely while passing through the cartridge to ensure it did not go dry and the vacuum and relative elevation of the bottle were adjusted as necessary. After the entire sample had gone through the cartridge, each sample bottle was rinsed with 7.5 mL of reagent water that was then also passed through the cartridge. The rinsing process was repeated once more for each sample bottle.

The vacuum was then adjusted to 10-15 in Hg. And air was drawn through the cartridge for five minutes. After this, the vacuum was released, and a plastic storage vial was placed underneath the cartridge. The vacuum was turned back on, and each sample bottle was rinsed with 4 mL of methanol. The methanol was then drawn through the cartridge in a dropwise fashion. The 4 mL methanol rinsing process was repeated once more for each bottle. After all the methanol passed through, the vacuum was released, and the vials were sealed and stored in the lab refrigerator until all samples had been extracted.

The extract was concentrated to dryness under a stream of nitrogen using a Rapid Vap set to 60-65°C and no agitation. Extract remained in the machine until dry which took between 4-6 hours. During this time a 10 mL 94:6 volume % methanol: water solution was prepared using 9.4 mL of methanol measured in a graduated cylinder and 600 µL of water measured in a 1000 µL micropipette. 1 mL of this mixture was then added to each extract vial and moved into a 2mL HPLC vial using a 1000 µL micropipette.

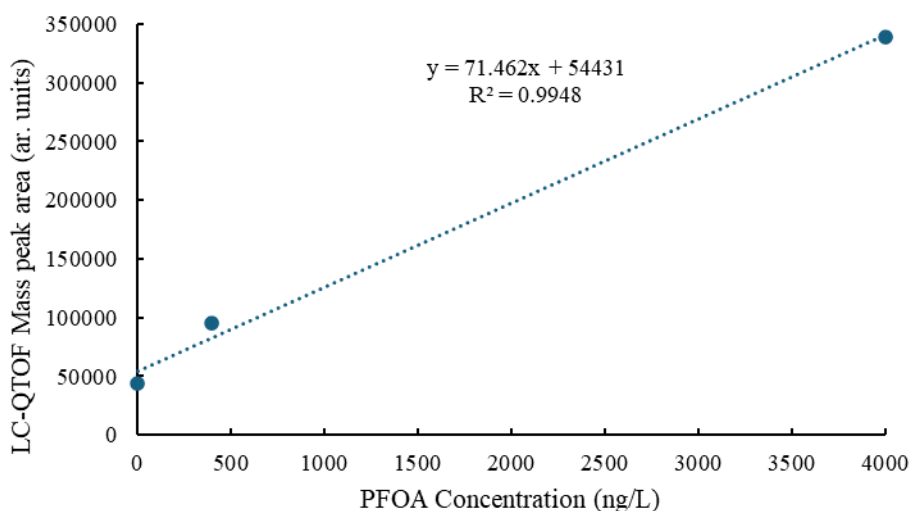
A set of external standards was prepared using a 1,000 µg/L Wellington Laboratories PFC-CVS-C standard. To create a standard set of 4,000, 400, 40, and 4 ng/L series of serial dilutions with methanol were made. The first was 2 mL of methanol and 8 µL of the standard. The subsequent ones were all 9 mL of methanol and 1 mL of the previous standard measured with a 10 mL graduated cylinder and a 1,000 µL micro pipette respectively. Additionally, 5 µL of a 2,000 ng/mL Wellington Laboratories MPFAC-C-IS was added to each sample extract.

All vials of external standard and samples were then delivered to Prof. Geoffery Tompsett in Goddard Hall to be run and analyzed in the HPLC/MS. The institute pond sample was excluded from the extraction procedure due to constraints relating to the extraction procedure and timeline of the HPLC analysis.

# 4.0 Results and Discussion

## 4.1 HPLC/MS Results

As of the time of this report, we have only received analysis for PFOA. Of our external standards we were able to establish a quality calibration curve from the 4000, 40, and 4 ng/L samples with the linear model having an R<sup>2</sup> value of 0.9948 as seen in Figure 4.

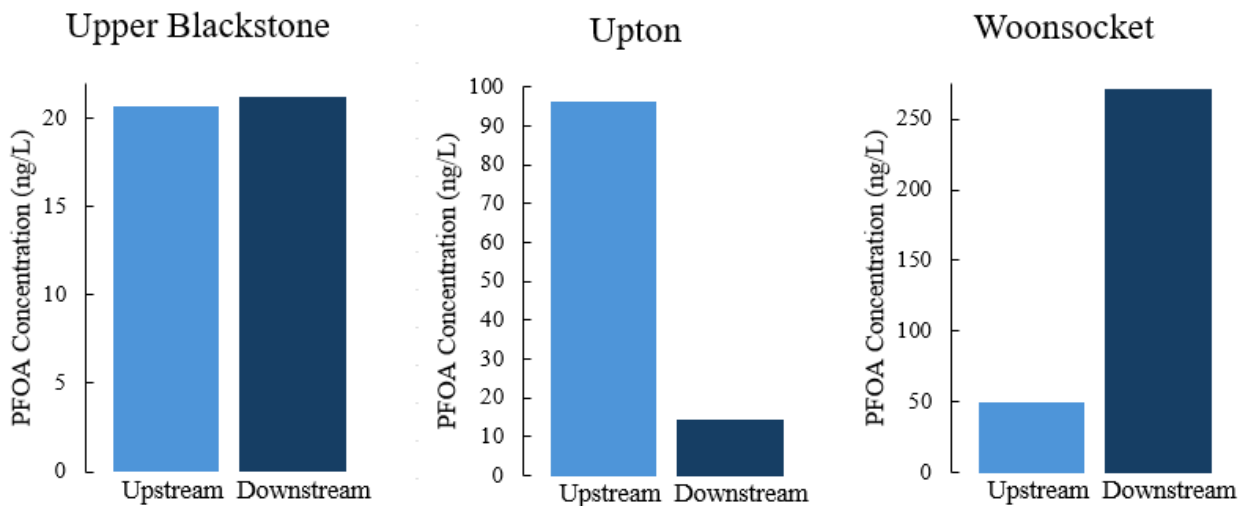


**Figure 4.** PFOA Calibration Curve

Using this calibration curve, we were able to determine the PFOA concentration in each of our extracts. We determined the sample concentration using the following equation, which assumes all our samples were exactly 500 mL and that all the PFOA in the sample was both extracted and eluted which decreases the accuracy of our results. The PFOA concentrations for each sample are shown in Figure 5.

$$C_{sample} = \frac{C_{extract} \cdot V_{extract}}{V_{sample}} = \frac{C_{extract} \cdot 1 \text{ mL}}{500 \text{ mL}}$$

The upstream and downstream concentrations of PFOA for Upper Blackstone WWTP were within 1 ppt. It is therefore inconclusive on whether the WWTP is a significant source of PFAS into the river. It could also be reasonable that the effluent discharge and the river had not fully mixed where we sampled downstream since we sampled on the opposite side of the where the effluent discharge is. The upstream concentration was greater than the downstream concentration for the samples around Upton WWTP. One possible explanation for this is a difference in streamflow between the two sites. While we did not measure streamflow while sampling there was a substantial qualitative distance in the streamflow of the upstream location which was barely moving and had a smaller cross-sectional area and the downstream location which was larger and had moved faster. We also expected to see the smallest concentrations around this site because it is almost entirely domestic and has a design flowrate of only about 100,000 gallons per day compared to the 45 and 9.3 MGD from Upper Blackstone and Woonsocket respectively (Antonellis, n.d., RIDEM, 2017, Upper Blackstone Clean Water, n.d.). The high upstream concentration could also be a result of other influent sources that were out of the scope of this project (i.e., runoff).



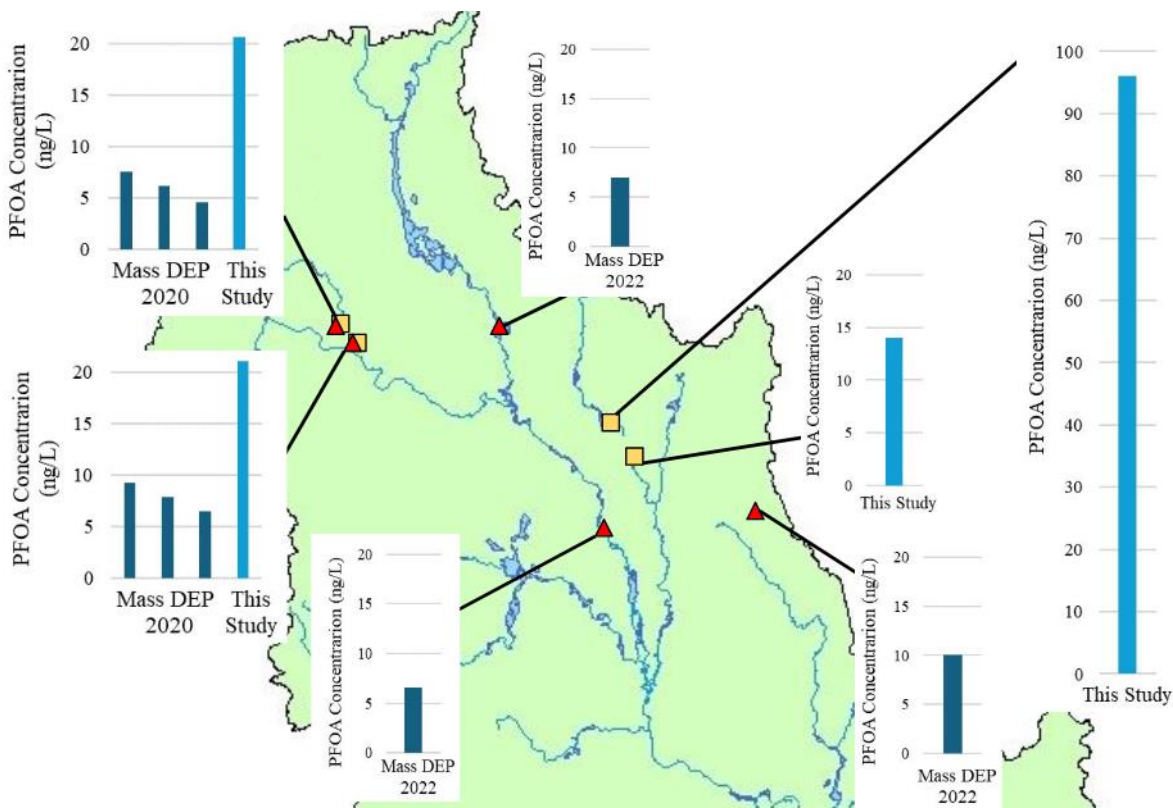
**Figure 5.** PFOA results of 6 sites from HPLC Analysis

There was a major increase in PFOA concentrations from upstream to downstream at Woonsocket WWTP which is concerning for the city and the environment downstream. Even though the downstream concentration may not reflect the true concentration of PFAS based on our calibration and volume of sample we ran through, we can say that the Woonsocket location may be a potential source of PFAS.

## **4.2 PFOA Comparison to Watershed Data**

To better understand our results in the context of previous works, we compared them to the PFOA values from the previous two Mass DEP studies done on surface water as seen in Figure 6. For Upper Blackstone, we can compare our results directly with the study done in 2020. From that study, we can see an upstream-to-downstream difference of about 1-2 ng/L is typical between these sites. However, our concentration is 2-3 times higher than some of the PFOA values found four years previously which could be a sign of a concerning increase in PFOA concentration over time. This is especially interesting because the sample from this study was taken in November while the ones in the 2020 study were taken from August thru October, meaning if there had been no change after four years, we would have expected the value to be lower.

Comparing the Upton data to the data for other nearby streams and lakes further suggests that the experimental value for upstream may be the result of some sort of contamination or experimental error. The value of 96 ng/L PFOA far surpasses the scale of all other PFOA concentrations in previous studies in Massachusetts.



**Figure 6.** Comparison of PFOA Data from previous studies by location

### 4.3 GAC Adsorber Design

First, the PFAS compounds and concentrations the column would be designed to were determined. We used the data collected from the 2020 Mass DEP study on PFAS in surface waters from USGS site 01109660. Any compounds that had concentrations below the detection limit were omitted. PFAS compounds that were not included in the study that was used for thermodynamic data were also not included in the design. Most of the excluded compounds had relatively small concentrations (<5 ng/L) that would not significantly impact the overall design but the exclusion of PFBA and PFPeA impacted the accuracy of this design as they had concentrations of 7.58-15.7 and 14.3-33.3 ng/L respectively. It is well understood that a design like this would not be implemented without lab and bench tests with specific site water to



determine isotherms. Design concentrations were selected from the largest concentration between the three sampling rounds in the study. A summary of thermodynamic data and concentration used can be found in Table 3 below.

A  $q_e$  value for each compound and carbon type was found using the following equation:

$$q_e = K \cdot \left( \frac{C_i \left( \frac{ng}{L} \right)}{1000 \left( \frac{ng}{\mu L} \right)} \right)^{\frac{1}{n}}$$

The  $q_e$  for each compound were combined to get an overall  $q_e$  value for each carbon type. F400 had an overall value of 2.79 and F300 had a value of 2.40. With this information, we determined the column would use the Calgon F400 activated carbon; the data sheet for this product can be found in Appendix B.

**Table 3.** Freundlich Parameters by GAC from Burkhardt et al. (2022) and average concentration from Savoie& Argue (2022) for 7 PFAS compounds

Carbon Type Freundlich Parameters	Calgon F400		Calgon F300		concentration (ng/L)
	K	1/n	K	1/n	
PFBS	7.8	0.64	1.36	0.35	4.16
PFDA	15.1	0.82	3.85	0.62	0.756
PFHpA	3.77	0.56	0.83	0.31	4.46
PFHxA	6.61	0.57	3.22	0.41	35.3
PFHxS	1.7	0.31	4.03	0.51	2.55
PFNA	3.77	0.56	0.83	0.31	1.88
PFOA	9.08	0.67	6.08	0.61	9.26
PFOS	15	0.65	4.04	0.4	5.95

We used a bed life design approach to determine the maximum volume ration of water treated to GAC using the equation below where  $C_i$  is the sum of concentrations across all compounds.

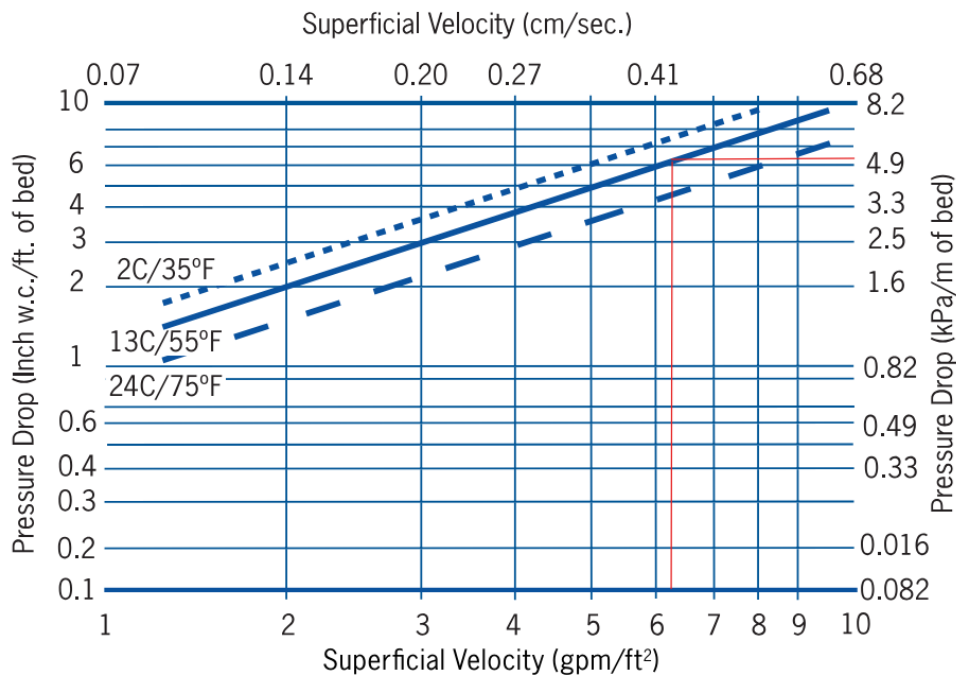
$$\frac{V_{fluid}}{V_{GAC}} = \frac{q_e \cdot \rho_{GAC}}{C_i} = \frac{2.79 \frac{\mu g}{g} \cdot 0.54 \frac{g}{cm^3} \cdot \frac{1000 cm^3}{1 L}}{0.06432 \frac{\mu g}{L}} = 23100$$

The design flowrate for the columns is 109.4 million gallons/year or 47.27 m<sup>3</sup>/h

in attempt to address the water deficit the downstream town of Milbury has experienced in the past few years (Sterns, 2024). Using the heuristic that the linear velocity through a GAC column is 10-20 m/h a column diameter could range from 2.45 to 1.73 m. Assuming a whole number diameter would be ideal for equipment ordering the value of 2.0 m was chosen, resulting in a linear velocity of 15.05 m/h.

The height was determined using heuristic that for low concentration treatment empty bed contact time should be at least 15 minutes. From this a packing height of 3.76 m was determined using the set flowrate and the fluid to GAC volume ratio. To accommodate the backwashing needs of the column an expansion percentage of 30% was determined using a chart and backwashing guide in the F400 data sheet. Meaning the tower height would need to be at least 4.89 m or 5 m for ease of equipment ordering.

A pressure drop of 18.8 kPa was found using the Carbon data sheet in Figure 7 below and assuming an 18°C operating temperature and the 15.05 m/h linear velocity.



**Figure 7.** The Calgon Filtrasorb 400 pressure drop chart annotated with the system values.

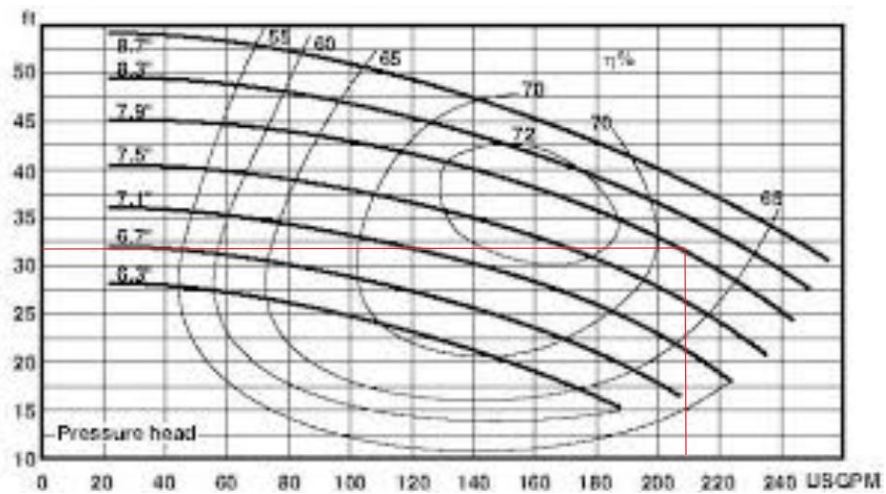
The design pressure for the pump to get the water into the column was determined based on the Bernoulli equation in form below where  $\Delta h_v$  and  $h_f$  are considered negligible.

$$\Delta h_p + \Delta h_v + \Delta h_z = h_s - h_f$$

Assuming  $\Delta h_z$  is equal to double tower height and  $\Delta h_p$  is equal to double the head drop in a column the head supplied from the pump would need to be 10.004 for a two-column series as shown here:

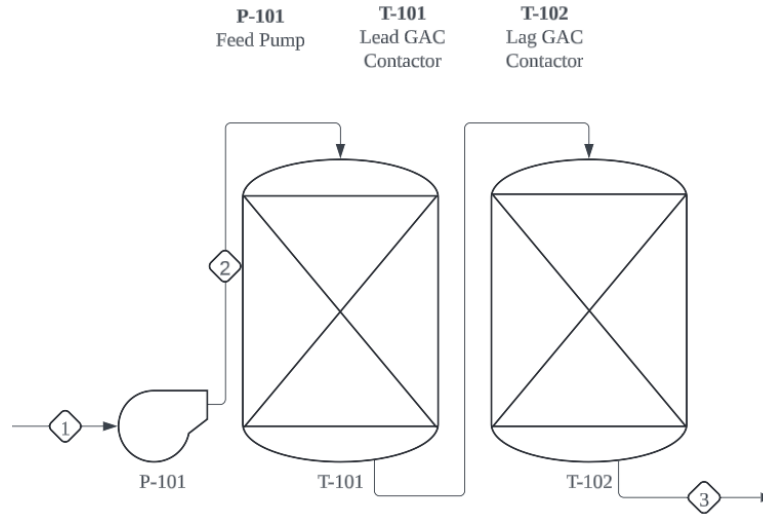
$$\frac{2 \cdot 18.8 \text{ kPa}}{998.57 \frac{\text{kg}}{\text{m}^3} \cdot 9.81 \frac{\text{m}}{\text{s}^2}} + 10 \text{ m} = 10.004$$

A typical pump performance curve from MG Newell was used to determine an efficiency of 68% as shown in Figure 8. Power requirements for the pump were calculated to be 1.28 kW in hydraulic power and 1.90 kW in actual power.



**Figure 8.** Pump performance chart annotated with the system specifications.

A process flow diagram, stream table, and equipment summary are included below. A diagram showing the necessary valving and piping configurations for the towers to switch order is also included. All equipment materials are assumed to be carbon steel or fiberglass due to affordability and lack of major corrosives.



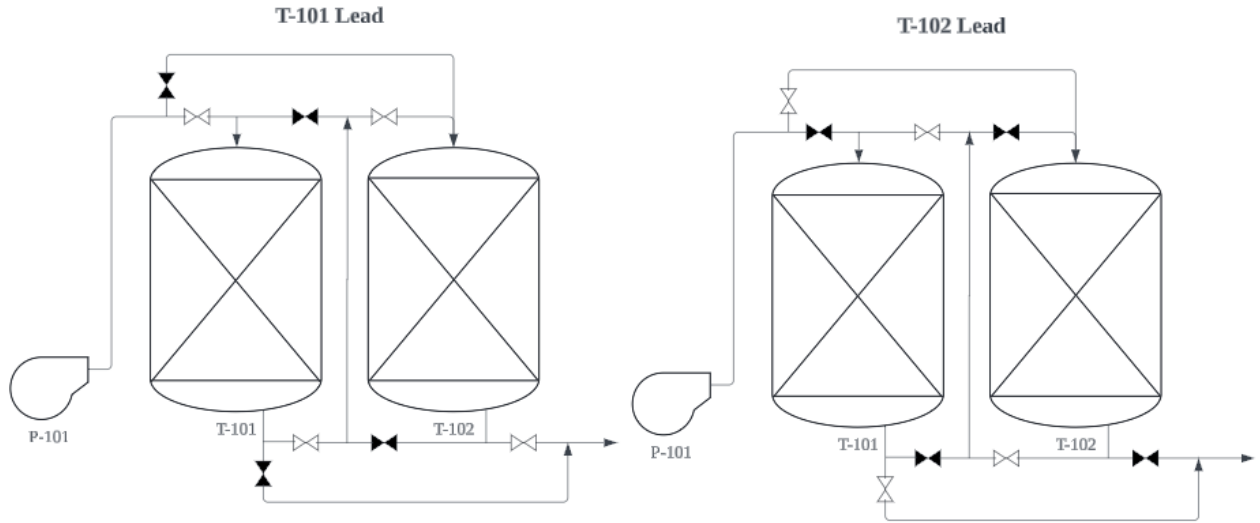
**Figure 9.** Process flow diagram for the GAC adsorption system

**Table 4.** Adsorber design stream table

Stream	1	2	3
Temperature (C)	18	18	18
Pressure (kPa)	101.3	111.3	101.3
Mass flowrate (kg/hr)	0.0473	0.0473	0.0473
ΣPFAS Concentration (µg/L)	0.0643	0.0643	0

**Table 5.** Adsorber design equipment summary

<b>P-101</b>	<b>T-101</b>	<b>T-102</b>
Centrifugal	Fiberglass	Fiberglass
Carbon Steel	Packing height = 3.76 m	Packing height = 3.76 m
Actual power = 1.90 kW	Column height = 5 m	Column height = 5 m
Efficiency = 68%	Diameter = 2 m	Diameter = 2 m



**Figure 10.** The open (white) and closed (black) valve scheme for each lead/lag configuration.

## **5.0 Conclusion and Recommendations**

This research shows that WWTPs can be a significant source of PFAS in the environment, especially in areas that are less monitored and regulated. Massachusetts's regulatory work of restricting the new manufacturing of PFOA and PFOS and being one of the first states to set strict PFAS regulations in drinking water is correlated to low and insignificant increases in PFOA concentrations upstream and downstream of large domestic and industrial WWTPs as compared to the extreme increases seen in Rhode Island which has just recently set up monitoring procedures and has been known to be less strict in their regulations. This study also suggests that for the same location in the river, PFOA concentrations have increased in the last four years despite regulatory action.

### **5.1 Recommended Avenues for Further Research**

If future MQP groups were interested in continuing this research, there are a few recommendations we have for further research efforts. First, we would recommend taking multiple samples starting early in the fall and continuing throughout the first semester to compare PFAS levels across a season, this would be especially helpful if the sampling conditions lined up well with those in the Mass DEP 2020 surface water study.

We would also recommend trying to survey the east side of the Blackstone near Grafton WWTP to find a safe site for sampling as it is larger than Upton, and the flowrates are more even while remaining a site that has mostly domestic sources. Another possible additional site to sample would be Pawtucket WWTP as having another Rhode Island facility, the Bucklin Point WWTP in East Providence, to compare with would strengthen the conclusion that the state's PFAS regulations and policy impact differences in upstream and downstream concentrations.

Though, that would expand the area of interest outside of the Blackstone River Watershed and into the receiving Seekonk River.

We would also suggest adding a method for determining river flow into the sampling procedure so that more precise calculations of the PFAS load could be made. We would also recommend creating a series of PFAS mixtures with higher known concentrations and performing the same extraction and HPLC procedure with only 250-mL of sample to validate the results and perform specific error calculations. This way, the machine will be able to detect higher levels of PFAS that were not expected. We would also recommend a greater research effort go into optimizing HPLC conditions for PFAS and analysis to allow the team greater control over the fate of their HPLC results.

## **5.2 Future of PFAS Implications**

Despite our data quality issues, MassDEP's data does show that WWTPs are a significant source of PFAS and as the data evolves, it is important to consider the effect surface water PFAS concentrations will have on the surrounding environment and human health. While there are no current regulations for PFAS in surface water, MassDEP continues to monitor the levels of PFAS in the effluent of WWTPs (MassDEP). If these concentrations continue to increase or remain steady throughout the watershed, environmental agencies may resort to implementing PFAS removal technologies in WWTPs to further reduce the concentrations into receiving waterbodies. It is unclear how these levels will have on human health, but close monitoring should be advised to ensure the safety of individuals around the watershed, especially those who use well water. However, with the new EPA Drinking Water Regulation that was just announced on April 10<sup>th</sup>, 2024, regarding the nationwide legally enforceable limits (for PFOA it is 4ppt), we

will start to see new regulations pertaining to surface water levels and even wastewater treatment levels as well (EPA 2024).



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# Appendices

## Appendix A: Sampling Locations

Upstream Location of Upper Blackstone (42°12'54.9"N 71°47'03.9"W)





**Downstream Location of Upper Blackstone (42°12'10.4"N 71°46'40.6"W)**





**Upstream Location of Upton (42°10'01.3"N 71°37'38.5"W)**





**Downstream Location of Upton (42°09'27.3"N 71°37'20.3"W)**



**Upstream Location of Woonsocket (42°00'09.8"N 71°29'53.7"W)**





**Downstream Location of Woonsocket (41°59'49.1"N 71°29'38.8"W)**



## Appendix B: GAC Data Sheet

# FILTRASORB® 400

Granular Activated Carbon

### Applications



FILTRASORB 400 activated carbon can be used in a variety of liquid phase applications for the removal of dissolved organic compounds. FILTRASORB 400 has been successfully applied for over 40 years in applications such as drinking and process water purification, wastewater treatment, and food, pharmaceutical, and industrial purification.

### Description

FILTRASORB 400 is a granular activated carbon for the removal of dissolved organic compounds from water and wastewater as well as industrial and food processing streams. These contaminants include taste and odor compounds, organic color, total organic carbon (TOC), industrial organic compounds such as TCE and PCE, and PFAS.

This activated carbon is made from select grades of bituminous coal through a process known as reagglomeration to produce a high activity, durable, granular product capable of withstanding the abrasion associated with repeated backwashing, hydraulic transport, and reactivation for reuse. Activation is carefully controlled to produce a significant volume of both low and high energy pores for effective adsorption of a broad range of high and low molecular weight organic contaminants.

FILTRASORB 400 is formulated to comply with all the applicable provisions of the AWWA Standard for Granular Activated Carbon (B604) and Food Chemicals Codex. This product may also be certified to the requirements of NSF/ANSI 61 for use in municipal water treatment facilities. Only products bearing the NSF Mark are certified to the NSF/ANSI 61 - Drinking Water System Components - Health Effects standard. Certified Products will bear the NSF Mark on packaging or documentation shipped with the product.

### Features / Benefits

- Produced from a pulverized blend of high quality bituminous coals resulting in a consistent, high quality product.
- Carbon granules are uniformly activated through the whole granule, not just the outside, resulting in excellent adsorption properties and constant adsorption kinetics.
- The reagglomerated structure ensures proper wetting while also eliminating floating material.
- High mechanical strength relative to other raw materials, thereby reducing the generation of fines during backwashing and hydraulic transport.
- Carbon bed segregation is retained after repeated backwashing, ensuring the adsorption profile remains unchanged and therefore maximizing the bed life.
- Reagglomerated with a high abrasion resistance, which provides excellent reactivation performance.
- High density carbon resulting in a greater adsorption capacity per unit volume.

### Specifications<sup>1</sup>

### FILTRASORB 400

Iodine Number, mg/g	1000 (min)
Moisture by Weight	2% (max)
Effective Size	0.55–0.75 mm
Uniformity Coefficient	1.9 (max)
Abrasion Number	75 (min)
Screen Size by Weight, US Sieve Series	
On 12 mesh	5% (max)
Through 40 mesh	4% (max)

<sup>1</sup>Calgon Carbon test method

### Typical Properties\*

### FILTRASORB 400

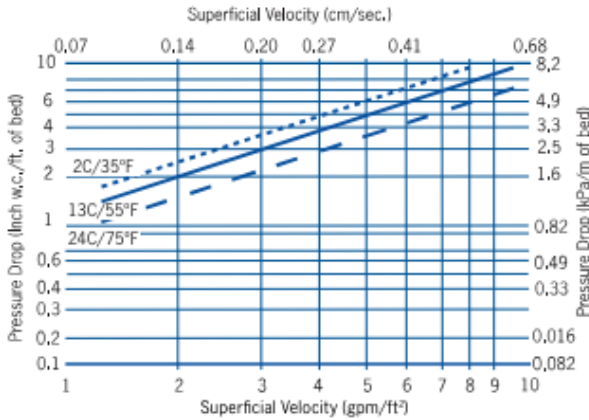
Apparent Density (tamped)	0.54 g/cc
Water Extractables	<1%
Non-Wettable	<1%

\*For general information only, not to be used as purchase specifications.



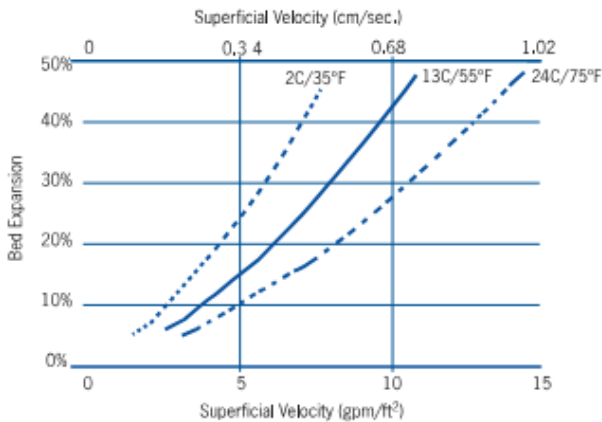
### Typical Pressure Drop

Based on a backwashed and segregated bed



### Typical Bed Expansion During Backwash

Based on a backwashed and segregated bed



### Conditioning and Backwashing

Backwashing and conditioning fresh GAC before placing into operation is critical to GAC performance. The reasons for backwashing before placing fresh media online are to: (1) size segregate the media so subsequent backwashing will return the media to the same relative position in the bed, (2) remove any remaining air from the bed, and (3) remove media fines which can lead to excessive pressure drop and flow restriction. In addition, proper backwashing is a crucial step to collecting the most representative and meaningful post-start up data on compounds of interest, such as metals listed in the NSF/ANSI 61 standard.

Below are the recommended steps for proper conditioning and backwashing of GAC based on Filtrasorb 400 GAC being backwashed at 55°F:

1. Fully submerge GAC bed in clean, contaminant free water for at least 16 hours (overnight)
2. Open backwash inlet and begin up-flow at 3 gpm/ft<sup>2</sup> for 2 minutes
3. Increase flow to 5 gpm/ft<sup>2</sup> and maintain for 2 minutes
4. Increase flow to 7 gpm/ft<sup>2</sup> and maintain for 2 minutes
5. Increase flow to 8.5 gpm/ft<sup>2</sup> and maintain for 30 minutes\*
6. Decrease flow to 7 gpm/ft<sup>2</sup> and maintain for 2 minutes
7. Decrease flow to 5 gpm/ft<sup>2</sup> and maintain for 2 minutes
8. Decrease flow to 3 gpm/ft<sup>2</sup> and maintain for 2 minutes
9. Close backwash inlet and stop flow

\*Duration representative of initial backwash conditions. Required duration during operational backwashes can be shorter but will vary by utility, solids load, and GAC throughput. Contact Calgon Carbon for more information"

### Design Considerations

FILTRASORB 400 activated carbon is typically applied in down-flow packed-bed operations using either pressure or gravity systems. Design considerations for a treatment system is based on the user's operating conditions, the treatment objectives desired, and the chemical nature of the compound(s) being adsorbed.