UTILIZATION OF GRANULAR ACTIVATED CARBON MEDIA TO IMPROVE BIOFILTRATION FOR THE PURPOSE OF TASTE AND ODOR REMOVAL

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Title

Utilization of Granular Activated Carbon Media to Improve Biofiltration for the Purpose of Taste and Odor Removal

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

To determine the role biofiltration in organic removal and taste and odor compound removal within the Moorhead Water Treatment Plant, a comparative two-year pilot scale study was initiated to determine the feasibility of replacing anthracite with granular activated carbon (GAC). To determine the biomass associated with the pilot system and the different media types, ATP tests and qPCR measurements for the 16S rRNA bacteria gene were made over the course of the study to evaluate the potential impact of biomass for organics removal. The data suggests that the ATP method may have resulted in under estimation of amount of attached biomass on GACs due to their adsorptive properties and was not effective for biomass monitoring. In addition, ATP was unable to correlate with organics removal within the system during summer months. In addition, analysis was conducted to determine the impact of Empty Bed Contact Time (EBCT) on removal of geosmin.

ACKNOWLEDGEMENTS

I would like to acknowledge the support and guidance of Dr. Wei Lin, of the Civil and Environmental Engineering Department, and members of my thesis review committee. I would also like to acknowledge the staff and support of Moorhead Public Service to complete this work. Thank you to Marc Pritchard and Emily von Hagen who assisted in collection and processing of samples, along with preparation of data for this work. I would also like to acknowledge my mentors Troy Hall, Cliff McLain, William Schwandt and Dr. Anne Hinderliter. Lastly, I would like to acknowledge the support of friends, family, and God. Thank you to my wife and son for your support and encouragement to finish this work.

DEDICATION

This is dedicated to my wife Su, my son Alexander, my Parents, my coworkers, and my mentors.

I love you.

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LIST OF ABBREVIATIONS

ATP ..... Adenosine Tri-Phosphate

BAC..... Biological Activated Carbon

BOM..... Biodegradable Organic Matter

CT..... Concentration × Time

DNA ..... Deoxyribonucleic Acid

DOC ..... Dissolved Organic Carbon

D/DBP ..... Disinfectants/Disinfection By-products

EBCT..... Empty Bed Contact Time

ES..... Effective Size

ft^2..... Square feet

GAC ..... Granular Activated Carbon

gpm..... Gallons Per Minute

HRT..... Hydraulic Retention Time

MDH ..... Minnesota Department of Health

MIB 2-Methylisoborneol

MGD ..... million gallons per day

MPS..... Moorhead Public Service

MWTP..... Moorhead Water Treatment Plant

NOM ..... Natural Organic Matter

NTU..... Nephelometric Turbidity Units

OTC..... Odor Threshold Concentration

PFS ..... Pilot Filter Skid

PPB..... Parts Per Billion

PPM..... Parts Per Million

PPT ..... Parts Per Trillion

qPCR ..... quantitative Polymerase Chain Reaction

SCADA ..... Supervisory Control and Data Acquisition

SEM ..... Scanning Electron Microscope

SUVA ..... Specific Ultraviolet Absorbance

SWTR ..... Surface Water Treatment Rule

TOC ..... Total Organic Carbon

T&O ..... Taste and Odor

UC ..... Uniformity Coefficient

USEPA ..... United States Environmental Protection Agency

UV254 ..... Ultraviolet Absorbance at 254 nanometers

WTP ..... Water Treatment Plant

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CHAPTER 1. INTRODUCTION

The presence of Natural Organic Matter (NOM) in surface waters is a challenge for drinking water utilities to remove. If not removed in the treatment process, the presence of NOM can lead to the formation of disinfection by products and lead to distribution bacterial regrowth. One of the key components of NOM is BOM. Biofiltration plays and important role within surface water treatment plants to remove BOM. Despite the importance of biofiltration, the understanding of how biofiltration can impact BOM removal is lacking. Additionally, attempts to correlate biomass to biological removal of organic carbon have proven to be difficult in numerous research efforts. To characterize the removal of BOM as measured by Total Organic Carbon (TOC) within a pilot filtration system, and to determine if BOM removal correlates to biomass on filtration media a two-year study at the Moorhead Water Treatment Plant (MWTP) was undertaken.

The Moorhead Water Treatment Plant (MWTP) provides drinking water to approximately 46,900 customers in the cities of Moorhead, MN and Dilworth, MN. MWTP utilizes a lime-softening treatment process, followed by ozone disinfection, dual media filtration, and chloramination. The MWTP was constructed in 1995 and has a design capacity of 10 MGD. The MWTP utilizes both the Red River of the North, and the Buffalo and Moorhead Aquifers for source waters for treatment.

As part of ongoing capital improvements plan to replace the existing anthracite media at the MWTP, Moorhead Public Service (MPS) decided to conduct a pilot study to determine if granular activated carbon (GAC) would be a suitable replacement for anthracite as a filter medium. In addition, MPS wanted to determine if GAC would improve organic removal and offer additional benefit for taste and odor removal. MWTP has experienced taste and odor events during spring

runoff events and surmised that GAC could potentially offer additional taste and odor compound removal during those time periods.

To determine the effectiveness of GAC and to select a GAC product that would provide the best treatment results, MPS and the City of Fargo, ND collaboratively contracted with Wigen Water Technologies® to construct a Pilot Filter Skid (PFS) to mimic the existing MWTP filtration system. For reference, images of the PFS are found in Appendix A1-A5. To determine the effectiveness of the GAC media, and to satisfy requirements of MPS' primary compliance agency, the Minnesota Department of Health, MPS began a two year-long pilot study. The first year of the study of the study consisted primarily of tests and experiments to determine if the proposed GAC media types would meet requirements specified by the MDH, and to determine the most effective GAC and media configuration for the full-scale implementation of the GAC into the MWTP. During the second year of the study, a variety of additional research experiments to evaluate biomass, organic removal, and taste and odor compound removal were completed.

1.1. Goal and Objectives of Research

Following completion of the construction of the PFS, the study period for analysis began. The overall goal of the two-year study was to determine if biological activity is correlated with representative organic removal in the pilot filter skid (PFS) and to understand the biological diversity associated with filter media. In addition, evaluation of the PFS system included the following objectives:

1) Determine if ATP can be used as a biomass measurement to correlate biofilm growth to TOC removal in the PFS;
2) Determine quantity of biomass; speciation; and biodiversity through the filter depth of anthracite-sand filter and Norit BAC filter; and,

3) Determine the impact of EBCT on geosmin removal through the filter media bed. Results of the study are expected to provide additional information to aid in the operation of the MWTP and to understand how EBCT impacts geosmin removal.

1.2. Scope of Work

1.2.1. Task 1: MWTP Background and Literature Review

Significant attention within this thesis is paid to the MWTP within Chapter 2, to provide a background with respect to the basis of design for the PFS. A literature review spanning the past thirty years of relevant work in the field of biological filtration was conducted to gain understanding of the research to be conducted at the MWTP which can be found in Chapter 3. Specific attention within the literature review was also given to the operational parameters that influence the components of biological filtration. Finally, specific focus was directed toward TOC removal within the MWTP.

1.2.2. Task 2: Procurement and Operation of PFS

A five (5) column PFS was procured that allowed for a testing of a variety of conditions with respect to water quality and biological components of the media.

1.2.3. Task 3: Water Sampling and Analysis for the Assessment of Biomass and Organics Removal

Water and filter media samples were collected throughout the two-year pilot project. To determine characteristics associated with the biomass on filter media, Scanning Electron Microscopy (SEM), Adenosine Tri-Phosphate (ATP), and quantitative PCR (qPCR) measurements were utilized. To determine if biomass and organic removal are correlated, TOC measurements were taken in conjunction with ATP analysis. These methods all provide insight

into the biomass associated with filtration media of the PFS and are detailed in Chapter 4 of this thesis.

1.2.4. Task 4: Analysis of Data

During the two-year piloting study, data was analyzed to determine the effectiveness of GAC to remove geosmin with different EBCT, in addition to the determination of factors associated with biological growth. The results of this study are discussed in Chapter 5, with recommendations for future work indicated in Chapter 6.

CHAPTER 2. WATER TREATMENT PLANT

2.1. MWTP Background

The MWTP withdraws water from the Red River of the North (80%), Buffalo Aquifer (15%) and Moorhead Aquifer (5%) to provide approximately 46,900 customers treated water. The MWTP uses coagulation, softening, sedimentation, ozonation, filtration, and chloramination as treatment techniques to meet EPA criteria for the Surface Water Treatment Rule (SWTR). The MWTP, which has a design capacity of 10 MGD, has been in service since 1995. After the treatment process, water is stored in two finished water reservoirs and distributed to the system via a recently constructed (2015) High Service Pumping Station. The process flow diagram as shown in Figure 1 indicates the major treatment processes and chemical addition points within the MWTP.

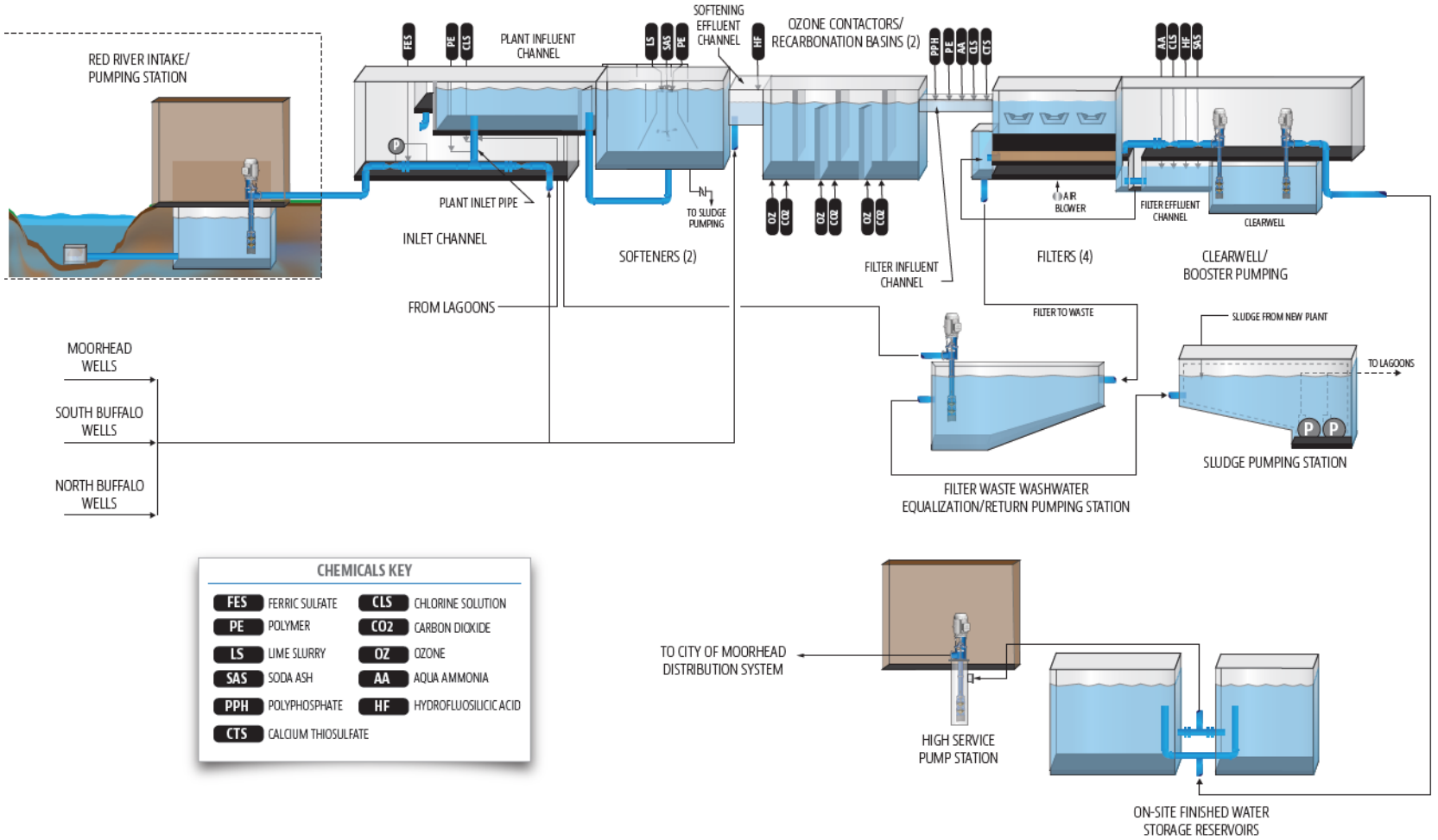

Figure 1: MWTP Process Flow Diagram (Advanced Engineering and Environmental Services 2018)

2.2. MWTP Unit Processes

2.2.1. Softening and Coagulation Unit Process

Before treatment with softening, water is drawn from both the Red River of the North and the Buffalo and Moorhead Aquifers and pumped to the MWTP. Water is then treated by lime and soda ash softening to remove carbonate and non-carbonate hardness from influent water. Coagulation, softening and sedimentation processes within the MWTP occur concomitantly within the Infilco Degremont® Accelator (Accelator) softening basins (Figure 2). The MWTP has two Accelator solids contact upflow clarifiers (White and Bench 1992), each of which has dimensions of 50 foot by 50 foot with a sidewall water depth of 18 feet. Softening is achieved through the addition of lime ($Ca(OH)_2$) and soda ash (Na_2CO_3). Lime is produced onsite by slaking quick lime (CaO) in water. The MWTP has two (2) lime slakers with capacity of 480 pounds per hour each. Coagulation in the Accelator is achieved through the addition of ferric sulfate and an anionic polymer. The cumulative impact of the addition of ferric sulfate and anionic polymer is to neutralize negative surface charges found on NOM and colloidal particles. Charge stabilization subsequently allows coagulated particles to form larger particles called floc, which can then be settled out in the Accelators. Water treated as a result of the soften process generally has a turbidity of 1-5 NTU and a pH of 10.6 to 11.5.

The MWTP is required to achieve a total 3 log Giardia removal and 4 log virus removals throughout the entirety of the treatment process. The MWTP is awarded 2.5-log Giardia and 2-log virus removal for the coagulation and sedimentation process. The remaining 0.5 log Giardia and 2 log virus removals are achieved at MWTP by ozonation.

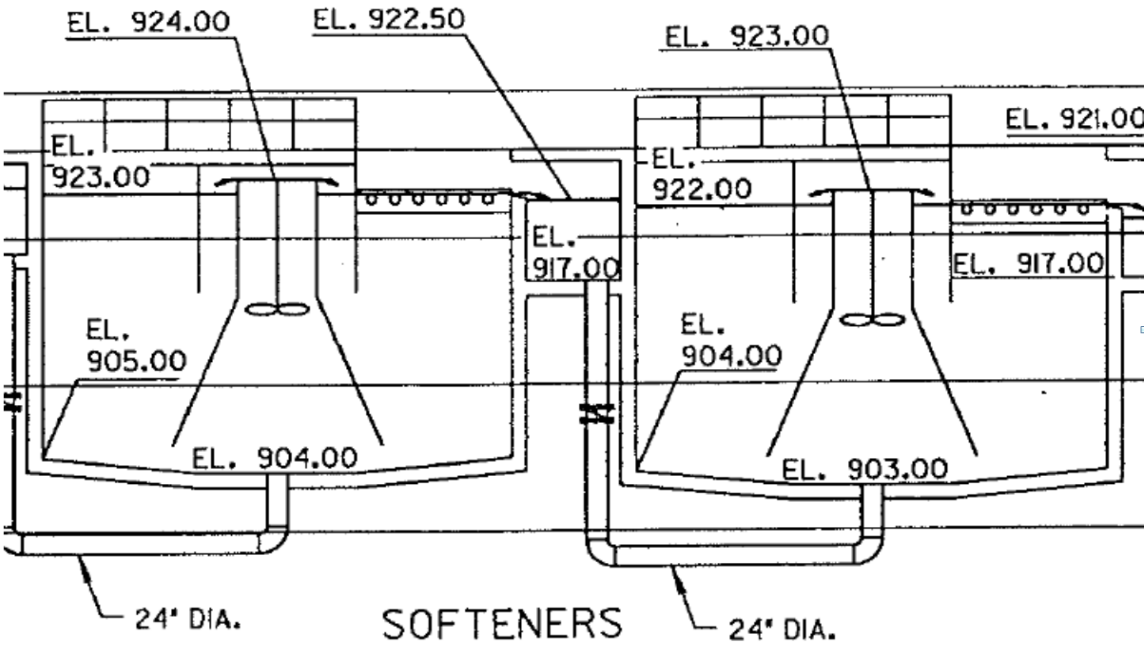

Figure 2: Accelator-Hydraulic Profile (White and Bench 1992)

2.2.2. Ozone Treatment Unit Process

Following the softening process, ozonation and recarbonation process are utilized to treat the water. Because ozonation is an upstream process to filtration, water quality changes in the ozonation system are critical to the design and operation of the MWTP media filters. In addition to achieving disinfection goals for giardia and virus, the ozonation system at the MWTP was also designed for taste and odor removal. Ozonation is also beneficial to the treatment process as it can breakdown conjugated organic compounds. Typically, ozone is applied in a dosage range of 3 PPM to 8 PPM to obtain residuals necessary to achieve 2 log virus and 0.5 log virus removal as required by the SWTR. The ozonation system has been extensively studied in previous research efforts (Storlie 2013; Young 2014).

The MWTP has two (2) horizontal ozone contactor units measuring 15 ft by 29 ft by 17 ft. Each ozone contactor is partitioned into three (3) sections, and each section is composed of two cells, as shown in Figure 3. Ozone (O_3) is applied to the water in Cells A, C, and E and sample

taps are located at the effluent of Cells B, D, and F to measure the ozone residual. Carbon dioxide can be added to Cells A, C, and E to lower water pH. Typically, no carbon dioxide is applied in cell A. In normal operation, carbon dioxide is applied concomitant with the application of ozone in cells C and D.

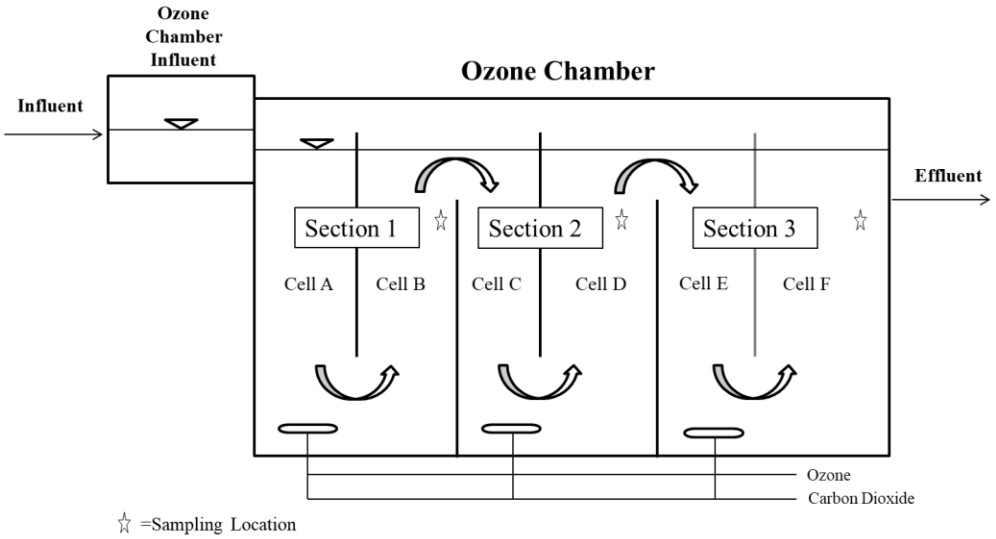

Figure 3: MWTP Ozone Chamber-Process Flow Diagram

Section 1 of the ozone contactors was designed for NOM oxidation and taste and odor control. Ozonation in this section is conducted at a pH of approximately 11, and oxidation of organic compounds in chamber 1 is primarily due to the presence of hydroxyl radical (OH•). At high pH, ozone is converted to hydroxyl radical, a much stronger and highly reactive oxidant with significantly shorter half-life in comparison to ozone. Hydroxyl radical reactions rapidly oxidize NOM, providing excellent removal of taste and odor compounds. Because very little ozone residual present in cell B, and the residual in cell B is not monitored, Section 1 is not considered in CT calculations.

After treatment in section 1, ozone and carbon dioxide are added in Sections 2 and 3 of the ozone contactors. Ozone is dosed in cells C and E, and residual monitoring for the determination of CT occurs within cells D and F. CT is defined by the USEPA as the concentration of the

disinfectant concentration at the effluent point of a chamber multiplied by the contact time (t_{10}) in that chamber. Carbon dioxide is usually applied to cell C and functions to recarbonate the water through the production of carbonic acid, which subsequently lowers the pH of the water from approximately 11.0 to approximately 9.3. Lowering the pH within the ozone contact chamber is necessary to obtain enough ozone residual, as ozone is more soluble at lower pH. In the MWTP, ozone residual is measured in real time and is utilized to calculate the CT of the treated water along with the hydraulic residence time in the contact chamber. The CT ratio (actual CT/required CT) is calculated in real time to ensure that adequate ozone is being fed and disinfection requirements are satisfied. After ozonation, calcium thiosulfate is added to quench the residual ozone to ensure that no residual ozone enters the filters.

Ozone is generated on site at MWTP using a pressure swing adsorption (PSA) system that produces approximately 95% pure oxygen using atmospheric air. After the oxygen purification is achieved, oxygen is piped to the ozone generator, which utilizes corona discharge to convert oxygen to ozone. `Corona discharge is achieved through the application of a high voltage alternating current applied to two adjacent conductive plates. When oxygen gas passes through the plates in the presence of electrical corona discharge, oxygen is converted to approximately 3 to 6 percent ozone gas as oxygen molecules are split into oxygen atoms which quickly react with O_2 to form O_3. The ozone/oxygen mixture and carbon dioxide are then applied to the water using fine bubble diffusors.

Specified CT values for the ozonation process are given by the US EPA as a function of temperature. CT values for 0.5-log Giadia and 2-log virus inactivation by ozonation are listed in Table 1. At MWTP, CT is calculated in real-time utilizing dissolved ozone monitoring in Cell D and Cell F within the ozone chamber by Equation 1. During operation of the MWTP, calculated

CT values for the treatment of water are kept above the amount specified in Table 1 and above the line shown in Figure 4. Because virus requires a higher CT than giardia, virus is the controlling factor for operation, and thus the line in Figure 4 is plotted for the virus requirements. The baffling factor of 0.7, which is assigned for mixing chambers of superior mixing, was assigned by MDH during the design of the MWTP.

$$Actual\ CT\ (\frac{mg}{L} \cdot\ min) = 0.7[C_2 \frac{V_2}{Q} + C_3 \frac{V_3}{Q}] \qquad \text{(Equation 1)}$$

Where:

C = ozone residual in effluent of sections 2/3 in mg/l

V = Volume of each section in gallons

Q = Flow rater through the ozone chambers, gpm

0.7 = Baffling factor

Table 1: EPA Listed Values for Ozonation CT Process of Giardia and Viruses

Temperature (°C)	1	5	10	15	20	25
0.5-log Giardia	0.48	0.32	0.23	0.16	0.12	0.08
2.0-log Viruses	0.9	0.6	0.5	0.3	0.25	0.15

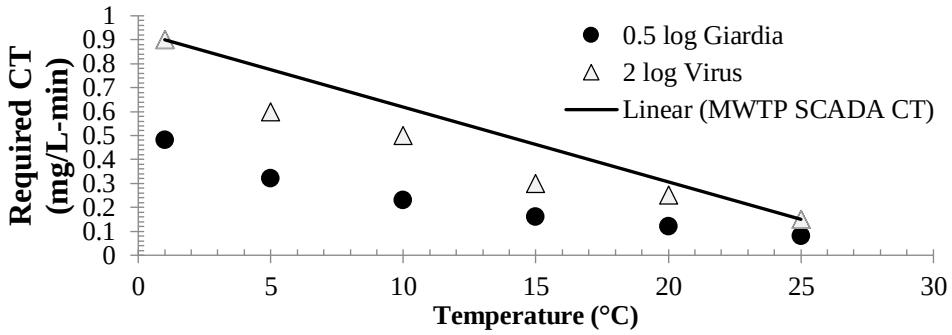

Figure 4: CT Values for Giardia and Virus at Various Temperatures Within the MWTP

2.2.3. Filtration Unit Process

Following ozonation, filtration is employed to remove particles from influent water. The MWTP utilizes four dual media filters, each measuring 13 feet wide by 26 feet in length providing

a total surface area of 1352ft^2 (338 ft^2 per filter). The design flow for each of the filters is 5.1 gpm/ ft^2 with all filters in service and 6.9 gpm/ ft^2 with one filter out of service (White and Bench 1992). The filters are composed of 24 inches of anthracite media on top of 12 inches of silica sand. The anthracite and sand media layers are supported by 5 inches of sand in a MONOFLOR (Infilco-Degremont) false bottom nozzle type underdrain system. Each filter at the MWTP has an influent valve, and an effluent valve controls the level of the water in each of the filters. The operation of the filters is currently conducted in a manner whereby the level of the water in the filter remains constant. As such, when flow to the MWTP increases, the filter effluent valve opens proportionally to the increase in flow.

The filters at the MWTP are backwashed with chlorinated backwash water at timed intervals, usually within the range of 80 to 96 hours. The frequency and timing of backwashes depends largely on influent water quality but can be impacted by the effectiveness of the softening process prior to the filtration system. The backwash sequence for the filters includes an air scour process, which is typically 5-7 minutes in duration, followed by a short rest period of 1-3 minutes. The air scour process is fed at a 3 standard cubic feet per minute/ft^2 rate and functions to break up any "mud balls' or compacted material located within the media. After the air scour process, chlorinated backwash water from the clearwell is fed at a rate of 4,800 gal/min to 5,300 gal/min through the filter which results in backwash velocity of (14.2 gal/ft^2 to 15.68 gal/ft^2) for a period of 7-8 minutes.

Backwash water from the filter washing process is collected via troughs and enters the waste-washwater basin, where flow is usually recycled to the beginning of the plant. Following the backwash sequence, filters are operated in filter-to-waste mode for a period of approximately 50 minutes, whereby the filtered water passed through the filter is collected in the waste-washwater

basin. After the filter to waste sequence passes, and filtered effluent water is below 0.10 NTU, the filter returns to service. Within the MWTP operation; only 10% of the total flow for the MWTP can be recycled water as part of SWTR requirements. The amount of chlorinated water used for backwashing is approximately 1 percent of all produced water from the MWTP.

The configuration of filter media has been used since the construction of the MWTP to remove suspended particles and meet the requirements of the SWTR. The media filters also are operated as biofilters to removal biodegradable organic matter generated in the ozonation process. Because the filters are operated in a biological manner, some TOC removal occurs during the treatment process. TOC removal as a result of biological filtration within the MWTP filters is further discussed in section 2.5.

2.3. Water Demand for MWTP

Following the chloramination process, finished water from the MWTP is pumped to the distribution system from the High Service Pumping Station. The High Service Pumping Station was constructed in 2015 with a capacity of 20 MGD at a head pressure of 50 PSI. With respect to historical system demands, the MWTP has produced an average of 4.5 MGD for the period of 2012-2019. During winter months, flow averages about 4.0 MGD, and rises to an average flow of just over 5.0 MGD during peak summer utilization as shown in Figure 5. When analyzing instantaneous flows for the MWTP (Figure 6), the maximum day flow for a period of 2012 to 2019 is 7.05 MGD. Peak flows for the MWTP most often occur during summer months, which usually occurs as a result of seasonal irrigation.

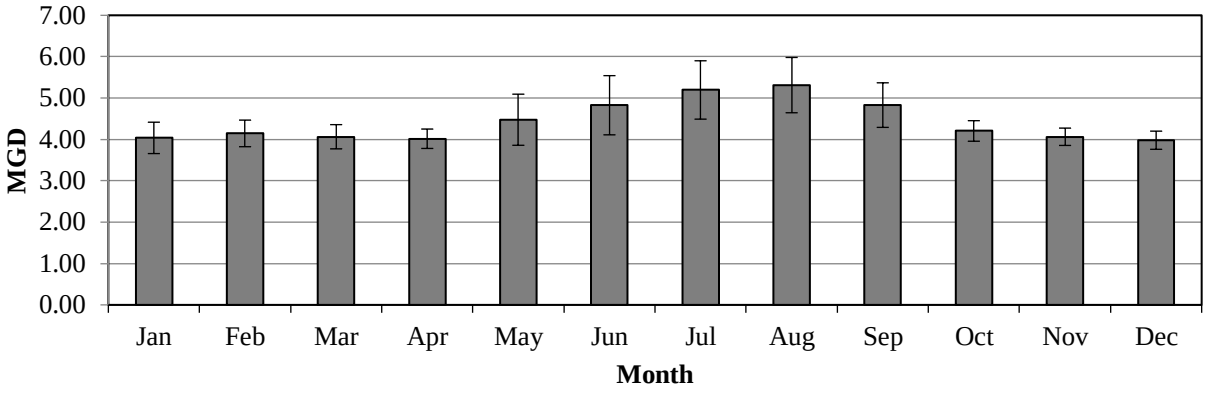

Figure 5: MWTP Average Daily Water Demands (2012-2019)

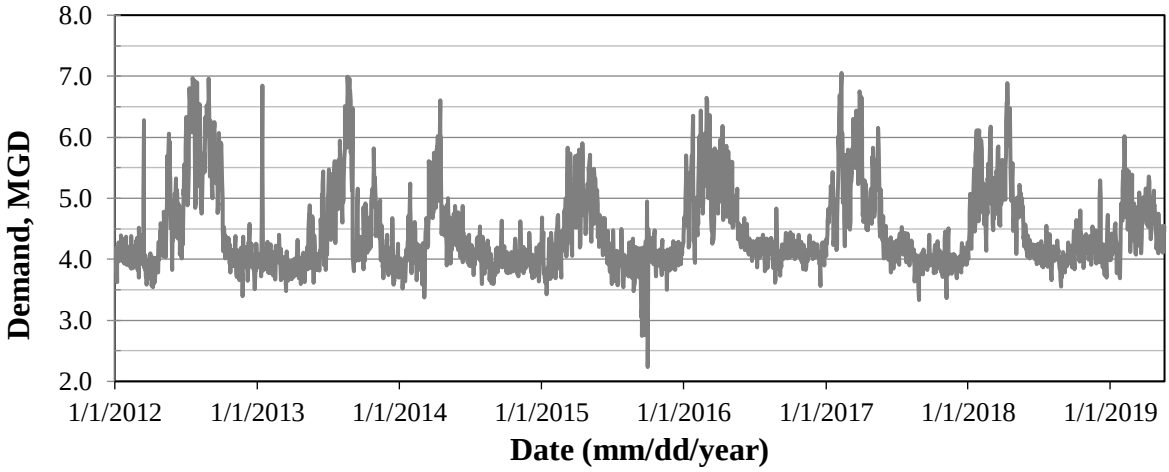

Figure 6: MWTP Average Daily Water Demands (2012-2019)

2.4. Source Water for MWTP

2.4.1. Red River as a Water Source for the Moorhead WTP

The Red River of the North is subject to a variety of variations in water quality due to upstream discharges and precipitation events. The Red River is fed mainly by Lake Traverse, and discharge to the Red River is controlled by the U.S Army Corps of Engineers at several locations including the White Rock Dam and Orwell Dam. The Red River supplies approximately 80% of the source water for MWTP. The Red River is also subject to variations in water quantity and quality due to upstream discharges and precipitation events. Due to the climate of the northern

region, the Red River is also subject to significant temperature variation over the course of the year as observed in Figure 7. The Red River average temperature from 2012 to 2019 is 52.2° F, with averages for the period of 2012 to 2019 approaching nearly 80° F in the month of July and can get as cold as 33° F in the winter (Figure 8).

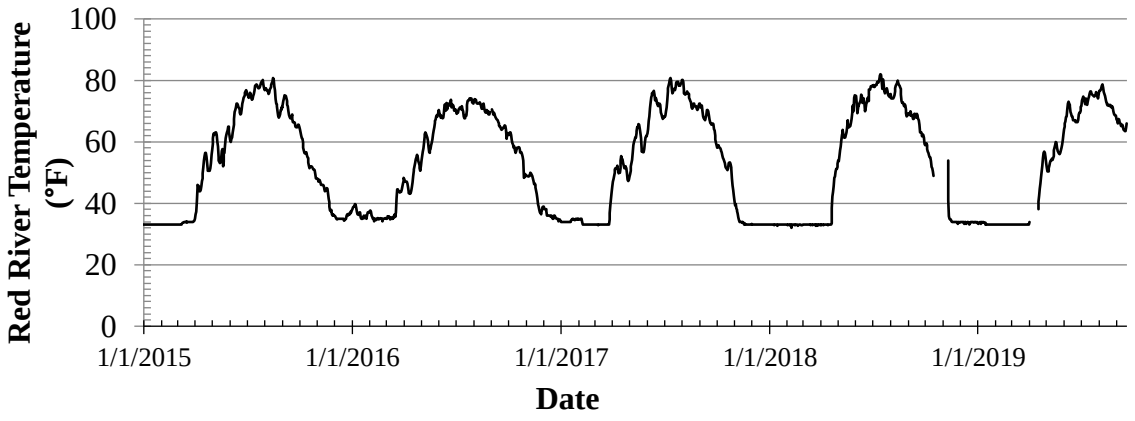

Figure 7: Red River Temperature from 2015 to 2019

The Red River water is subject to variability in several parameters, including NOM (organic carbon) and hardness. Often, during operation of the MWTP facility, groundwater is used to supplement Red River water during times in which water quality in the Red River is poor. Poor quality of Red River water for treatment at the MWTP is usually characterized as having high turbidity, increased concentrations of total hardness and increased concentrations of TOC. In addition, during spring runoff conditions, taste and odor compounds can complicate the treatment process as well.

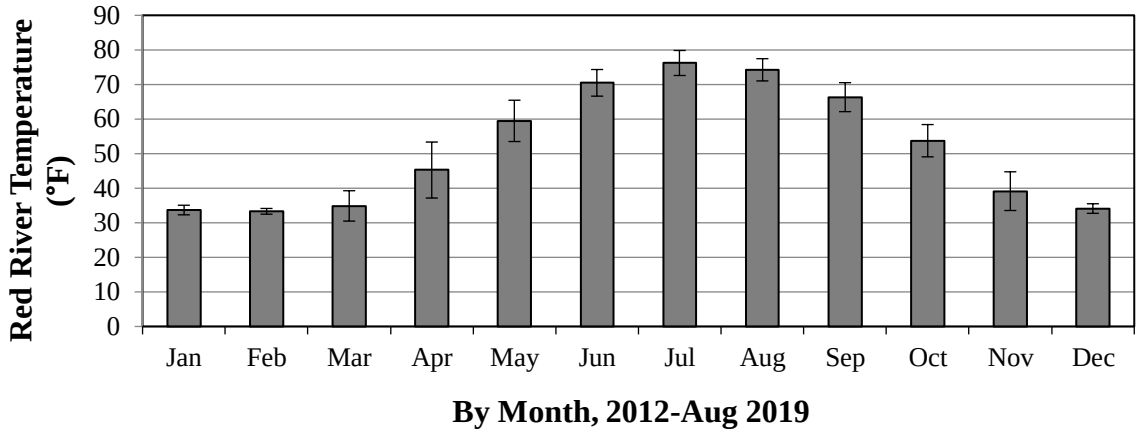

Figure 8: Temperature Averages for Red River of the North from 2012 to 2019

As a result of precipitation events and runoff occurring on the Red River, turbidity of the Red River to be highly variable during the summer months. As displayed in Figure 9, numerous turbidity events exceeding 500 NTU were observed during several occasions from 2012 to 2019.

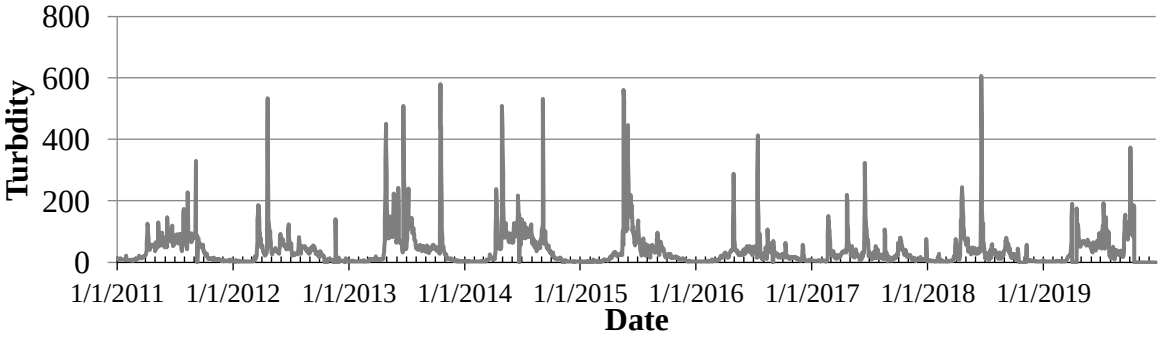

Figure 9: Turbidity Data for Red River of the North from 2012 to 2019

Red River spring runoff events experienced at the MWTP are typically characterized by cold water temperatures, high turbidity and influxes of NOM. Increases in turbidity can be a result of discharges from upstream sources, spring melt conditions, or precipitation events. Generally, turbidity in the Red River occurs either during sprint melt conditions, or when runoff is observed during summer months. During spring runoff conditions, flows in the Red River increase substantially due to the meltwater and flooding conditions. In addition to turbidity spikes as a result of runoff conditions, organic loading can also increase during runoff conditions observed during

precipitation events. In comparison to other surface waters, the Red River is characterized by high TOC, which typically is in the range of 8 to 10 mg/l (Figure 10).

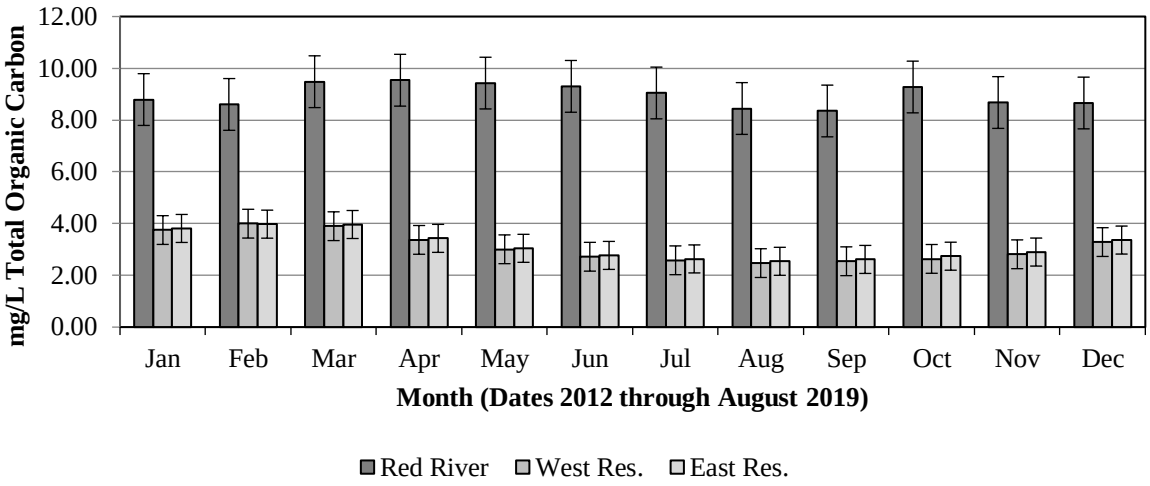

Figure 10: TOC Concentrations of both the Red River, and West and East Reservoirs

In Figure 10, higher TOC is typically observed during spring months, with generally less TOC during summer months. In addition, spikes of TOC have been associated with significant precipitation and runoff events. It is likely that the TOC spikes are associated with urban runoff. For example, in Figure 11, a significant increase of TOC in the Red River was observed as a result of fall precipitation event.

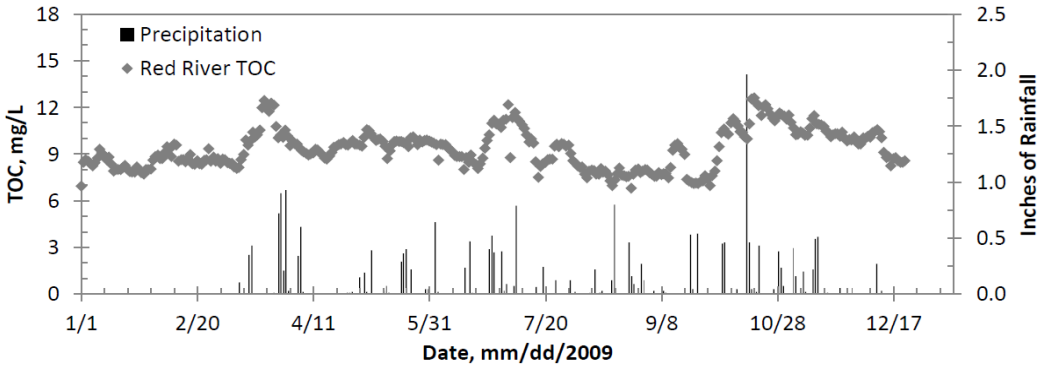

Figure 11: TOC Concentrations Plotted with Precipitation Events During 2009 (Porlock 2012)

Although operations staff typically increase the ozone dose during spring runoff events to compensate for increased organic load, MPS still has received taste and odor complaints during spring runoff scenarios.

Recently, the City of Fargo began monitoring geosmin on an ongoing basis. In 2019, geosmin was determined to be present during runoff events (Figure 12). For example, during the spring of 2019, Geosmin concentration spiked coincident with an increase of turbidity of the Red River (Figure 12). This increase of both geosmin concentrations and turbidity was due to the initiation of spring melt conditions and a significant increase in runoff. It is worth noting that the geosmin concentrations increase during the spring thaw conditions was slightly above the Odor Threshold Concentration (OTC.)

The absence of turbidity data from 4/1/2019 to 4/16/2019 in Figure 12 is because the Red River intake was shut off for a period while groundwater was used in lieu of Red River water at the MWTP due to degraded water quality conditions observed on the Red River. The increase in geosmin concentrations in the Red River during spring conditions suggest that the selection of geosmin as an indicator for the pilot study is appropriate.

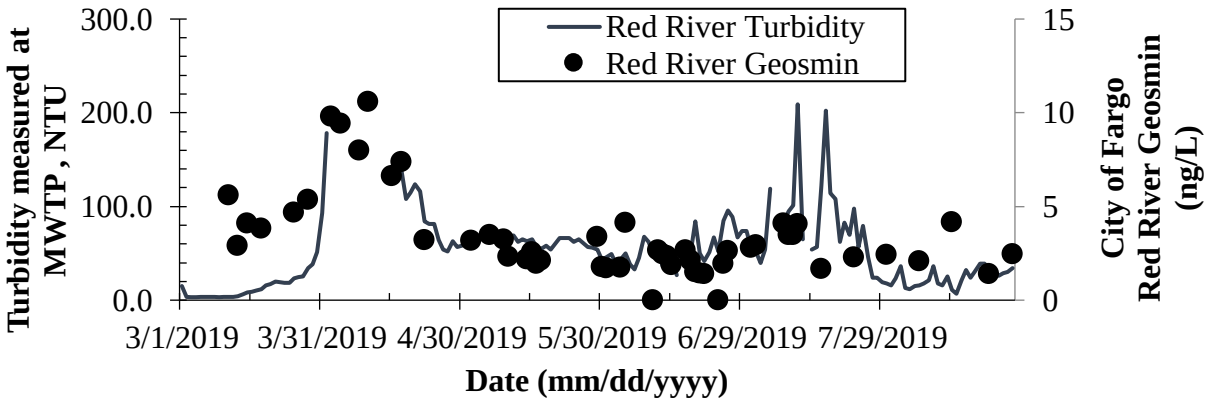

Figure 12: Geosmin Concentration Plotted with Red River Turbidity and Temperature Data (Geosmin Data courtesy of the City of Fargo WTP Laboratory)

In addition to influxes of turbidity, hardness values on the Red River fluctuate substantially. Generally, for the period of 2012-2019, average hardness concentrations were lowest in the fall, and increased during the winter and spring months (Figure 13). The variability in hardness concentrations increases the difficulty of water treatment as both non-carbonate and carbonate hardness concentrations can vary. This induces a condition that necessitates the alteration of both lime and soda ash dosages to ensure that the output hardness of the MWTP is around 100 PPM.

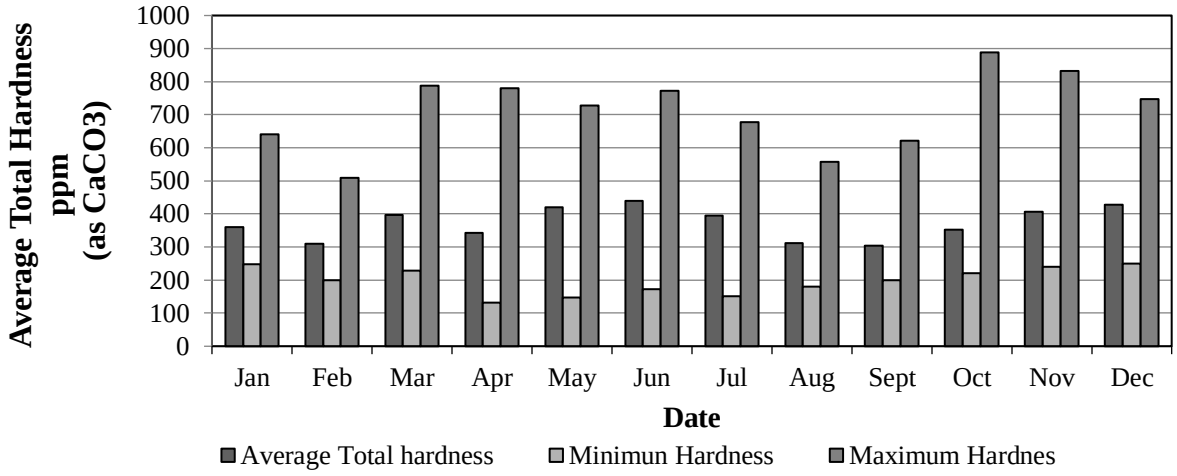

Figure 13: Average, Minimum and Maximum Total Hardness Concentrations on the Red River for 2012-2019

2.4.2. Groundwater as a Water Source for the MWTP

The MWTP uses both the Moorhead Aquifer and Buffalo Aquifers as water supply sources during either poor water quality events or contamination events on the Red River. In addition, because the Red River has periods in which little to no flow has been observed, the Aquifers are planned to be used during a drought situation. The water quality characteristics of the Moorhead and Buffalo Aquifers are listed in Table 2. The Buffalo Aquifer is a large aquifer containing approximately 270 billion gallons of water storage, of which only 120 billion of which can be physically withdrawn by wells (Wolf 1981). The Buffalo Aquifer is generally between 20 and 120 feet deep and is approximately 32 miles long. The water quality of the Buffalo Aquifer is generally

described as very hard water with hardness levels above 380 mg/L, as described in Table 2. The Moorhead Aquifer, that is located adjacent to the MWTP, is a much smaller confined aquifer and is approximately 180 to 260 feet deep. The water quality associated with the Moorhead Aquifer is good, with generally softer water characteristics of less than 200 mg/L of harness. Notably, the Moorhead Aquifer contains significantly higher bromide levels than the Buffalo aquifer (Storlie 2013), which requires that the utilization of the Moorhead Aquifer be curtailed during summer months as higher bromide levels generally are correlated with more pronounced production of an ozone DBP, bromate. (Storlie 2013)

Table 2: Water Quality Characteristics of Buffalo Aquifer

Aquifer	MPS Well Number	Unique Number	Capacity (MGD)	Hardness (mg/L)	Ammonia (mg/L)	TOC (mg/L)
North Buffalo	1	511085	1.53	516	0.37	1.62
	2	511086	1.21	516	0.32	1.59
South Buffalo	8	222049	1.15	464	0.66	1.75
	9	222050	1.43	396	0.94	2.00
	10	222051	2.74	396	0.25	N/A
Moorhead	6	241492	0.65	188	1.09	2.09
	6B	437645	0.79	188	n.a.	2.00

2.5. Organics Removal in the MWTP

The MWTP must monitor TOC removal and alkalinity in the softening process to meet requirements specified Stage 1 (D/DBP) Rule requirements specified by the USEPA (Table 3).

Table 3: Stage 1 D/DBP Rule Requirements Specified by the USEPA

Source Water TOC (mg/L)	Source Water Alkalinity, mg/L as CaCO3		
	0-60	>60-120	>120
>2.0 to 4.0	35.0%	25.0%	25.0%
>4.0 to 8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

The requirements set forth in the Stage 1 (D/DBP) ensure that the formation of disinfection by-products is minimized through the removal of TOC within the treatment process. The average alkalinity between 2013 and 2017 was 316 as $CaCO_3$, with the average TOC as 8.8 mg/L. As such,

the removal requirements for the MWTP fall within the range of 25% to 30%. To maintain compliance, the MWTP monitors TOC regularly throughout the MWTP process. The MWTP measures TOC at the following sampling points: Red River, water, aquifer water, softening basin effluent, ozone chamber effluent, combined filter effluent, clearwell and reservoirs. Sampling at the aforementioned locations for TOC allows for analysis for the removal of organics for each of the respective treatment processes.

As noted previously, one of the significant components of the treatment process at the MWTP is the removal of TOC. Most of the TOC present in both the plant influent water is removed within the softening process. The softening process removed an average of 5.2 mg/L for the period between 2013 and 2017, which corresponds to a removal percentage of 58%. (von Hagen 2019). Although the contribution to overall organics removal is much less than softening, ozonation functions to remove up to approximately 10 percent of the TOC present after softening. Organic removal within the ozone chamber is characterized by partial oxidation of long chain or aromatic conjugated organics into smaller aliphatic organic compounds. The organic molecules that are produced as a result of the ozonation process are described as assimilable organic carbon (AOC) and typically much more easily biodegradable, and as such, can often be removed in the filters.

An additional parameter that gives insight into the character of organics through the ozone chamber is UV absorbance at 254 nanometers (UV254). UV254 is a commonly used parameter within drinking water to measure organics as aromaticity and saturated double or triple bonds in organic molecules selectively absorb light at 254 nm. UV254 data within the MWTP is not routinely measured through the process, however, several studies have analyzed UV254 reduction within the ozone treatment process at the MWTP. In a study from August 2012 to January 2013, UV254 reduction of 54% was recorded in the ozonation chamber through the study period (Storlie

2013). The reduction in UV254 indicates that in addition to some removal of organics through the ozone chamber, double and triple bonds within long chain organic molecules are broken down through the ozone process. The breakdown of conjugated organics through the ozone chamber results in the formation of AOC, which can subsequently be removed in the filtration system by biomass.

TOC removal in the filtration system displays significant variability due to the changing temperature of incoming source water. For example, TOC removal percentages during a four-year period at the MWTP ranged from 1.7 mg/L (36%) to 0.19 mg/L (5.8%). TOC removal percentage for 2012 to 2017 is shown in Figure 14. TOC percentage removals for the entirety of the treatment process are given in Table 4. Noticeably, TOC removal percentages within the filtration system follow a seasonal variation, with markedly high TOC removal percentages in the summer, and very little TOC removal in the winter.

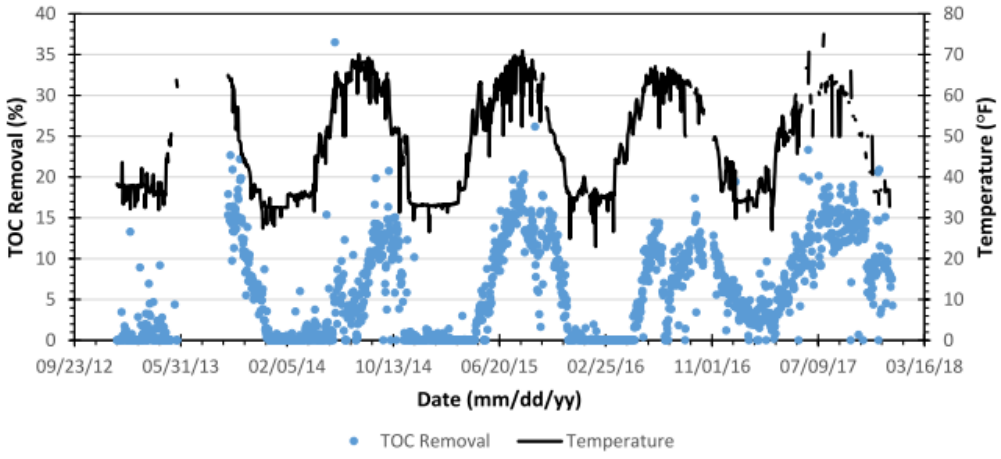

Figure 14: TOC Removal Percentages in the Filter System (von Hagen 2019)

From a period of 2012 to 2017, the total TOC removal reached its peak of 71 percent removal in July, with the lowest observed monthly TOC removal percentage occurring in February at 54% (Figure 15 and Table 4). TOC removal percentages increase in the summer up to 15 percent,

likely due to the additional removal achieved by biological filtration within the filter media (von Hagen 2019).

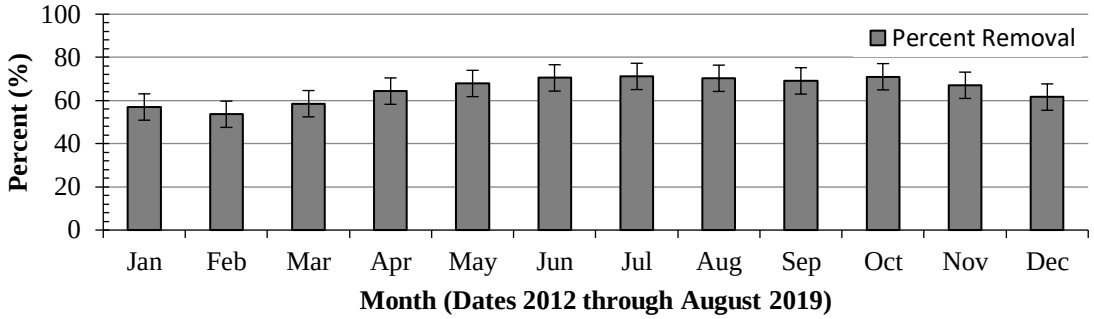

Figure 15: Total TOC Removal Within the MWTP

Table 4: TOC Removal Summary Within MWTP (Adapted from von Hagen 2019)

Treatment Process	Min TOC Removal		Average TOC Removal (mg/L)		Max TOC Removal	
	mg/L	%	mg/L	%	mg/L	%
Softening	2.2	29	5.2	58	11	90
Ozonation	0.0	0.0	0.19	5.3	2.1	47
Filtration	0.0	0.0	0.19	5.8	1.7	36

CHAPTER 3. LITERATURE REVIEW

Clean water that is free of odor, color, and particulates is an essential function of water treatment. One of the key steps in producing clear water is filtration. Filtration is an essential process in drinking water treatment and is usually preceded in water treatment by coagulation and sedimentation. Filtration is defined as the physical process by which suspended solids are removed from water and is usually the last barrier to the release of particles the distribution system (Betancourt and Rose 2004). The removal of suspended solids and microbes by filtration is often achieved by a variety of different media materials such as sand, diatomaceous earth, GAC media, or a combination of coarse anthracite coal covering finer sand (often denoted as dual media). The effectiveness of filtration is measured through the usage of turbidity, which measures the clarity of water. In order to achieve disinfection credit, turbidity of produced water must meet the requirements of the SWTR for surface water systems.

The mechanisms by which particles are removed from drinking water are complex and include: removal by straining through the pores in the filter bed; by adsorption of the particles to the filter grains; by sedimentation of particles while in the media pores; by coagulation while traveling through the pores; and by biological mechanisms. Filtration is regulated by the US EPA through the US SWTR. The SWTR requires the disinfection and filtration of influent water. The USEPA has allowed exceptions under the SWTR if watershed protection and water quality standards can be demonstrated.

The purpose of this chapter is to define the role of activated carbon and anthracite-sand play in the filtration process and the role of biomass that contribute to remove of organics and taste and odor compounds within filtration systems. In addition, determination of the role or biomass on filter performance, and the factors that impact biomass on filtration media will be explored.

3.1. History, Properties and Utilization of Activated Carbon

3.1.1. History of Activated Carbon Usage

The first uses of activated carbon trace back to Egyptians in 1550 B.C, where it was used to remove unpleasant odors or for intestinal ailments (Hassler 1963). Some of the first notable applications of activated carbon included it's use as a water treatment tool which was invented by Frederick Lipscombe (Lipscombe 1862) and in respirators as a protective tool to counteract a variety of gases (Stenhouse 1855). Applications of activated carbon were commercialized in the early 1900s and was utilized in gas masks in World War 1 to counteract the use of chlorine gas as a chemical warfare agent (Hassler 1963). Since its use in World War 1, the utilization of activated carbon in other markets developed, including the utilization of activated carbon for treatment of water supplies in the 1930s (Hassler 1963). Since that time, activated carbon has been frequently used in water treatment for removal of tastes and odors.

Often recognized for its unique ability to remove natural organic matter, utilization of activated carbon can specifically remove unwanted dissolved organic compounds, hydrocarbons, and taste and odor compounds. Adsorption by activated carbon is the entrapment of substances (adsorbate) on the carbon surface (adsorbent) (Chowdhury 2013). The effectiveness of activated carbon adsorption is largely dependent on well-developed pore structures, which enables activated carbon an extremely large surface area.

3.1.2. Properties of GAC and PAC

Activated carbons are typically produced from wood, coconut shells, peat, lignite, and other carbonaceous materials (Roy 1995). The selection of raw material, and the activation procedure applied, influences the pore structure and surface chemistry of the activated carbon (Chowdhury 2013). Typically, commercial activated carbon is a two-step production in which the

raw material is carbonized and activated (Chowdhury 2013). Activated carbon can be classified as granular activated carbon (GAC) and powder activated carbon (PAC). PAC particles are amount 100 times smaller than GAC particles. GAC particles are typically 0.6 to 3.0 mm in diameter, whereas PAC particles are 0.01 to 0.03 mm in diameter (Chowdhury 2013). GAC also has an apparent dry density ranging between 300 kg/m^3 to 650 kg/m^3, whereas PAC has a dry density of 200 kg/m^3 to 750 kg/m^3 (Chowdhury 2013). The UC is a numerical expression of the variety of particle sizes in a mixture and is defined as the ratio of the diameter at which 60 percent of the grains are smaller by weight to the effective size. The uniformity coefficient of GAC is quite large, typically about 1.9. Activated carbon has internal surface areas with a typical range of 400 to 1500 m^2/g and pore volumes in the range of 0.1 to 0.8 mL/g (Crittenden et al. 2012).

The surface area associated with activated carbon is critical to water treatment as it provides multiple adsorption locations on the activated carbon. In addition, the irregular surface provides a surface for bacterial attachment (Urfer et al. 1997). Activation during the manufacturing process produces a highly porous surface on the activated carbon that contains macropores and mesopores (greater than 2 nm), in addition to micropores which are less than 2 nm (Chowdhury 2013). Activated carbon pores exhibit a variety of different pore structures, which strongly influences the effectiveness of adsorption for desired contaminant removal.

Unlike GAC, PAC is often used on an infrequent basis to attenuate taste and odor and is typically used at the beginning of the plant. PAC is usually added to water treatment process as a slurry in the WTP. PAC application as a slurry enables it to remove compounds while the PAC mixture is suspended in water.

3.1.3. GAC Filter and Design Configurations

Three commonly used configurations of GAC filters include: filter caps, contactors, and biological filters, all of which can be associated with biological growth (Schindeman et al. 2012). When a GAC filter is used to support microbial growth and removal of organic contaminants it is commonly called as a BAC filter. Typically, GAC as a fixed biological filter or filter cap can be colonized by biological growth. These systems are usually preceded by an oxidation step such as ozone prior to filtration and do not typically carry any oxidant residual through the filter bed. A fixed bed utilizing GAC is described as 12-40 inches of GAC added onto an existing layer of sand such-that dual media filtration is achieved.

GAC in a filter cap configuration is an installation of GAC on top of an existing layer of an anthracite-sand filter. GAC filter caps are usually utilized in the top 6 inches of filter media where granular anthracite and dual media filtration are already in place. The main difference between GAC contactors and GAC utilized as filtration media is that media in contactors is typically replaced as sorption capacity is reached, whereas GAC filtration media is likely utilized in a BAC configuration long after adsorption capacity has been reached. (Schindeman et al. 2012).

3.2. Removal Mechanisms of Organics and Taste and Odor Compounds

3.2.1. Activated Carbon Adsorption Capacities

GAC adsorption is an accumulation of substance by either nonspecific interactions with the adsorbate of interest (physical adsorption) or site specific interaction where electrons are transferred between the adsorbate and adsorbent (chemical adsorption) (Chowdhury 2013). In contrast to anthracite-sand filters, GAC can remove compounds through adsorption. Most of the adsorption of compounds for drinking water occurs by non-specific interactions, which is described as physical adsorption.

The modeling of adsorption of compounds onto activated carbon has been accomplished using several different methods. The modeling approach to describe adsorbent attachment can vary depending on the adsorbent of interest, but generally uses a binding isotherm to describe the binding of adsorbents to activated carbon. The two most commonly used methods to model adsorption are the Freundlich isotherm and the Langmuir isotherm.

The equation for the Freundlich isotherm is $q_e = K_f C_e^{1/n}$ $(where\ n > 1)$, where q_e is the solid phase concentration at equilibrium, K_f and n are empirical constants, and C_e is the liquid phase concentration at equilibrium. Generally, for most compounds, it has been shown that the value of K_f is related to the total adsorbent capacity while n value is related to the strength of adsorption (Weber 1972).

Another commonly used model to define the binding capacity of adsorbates to the surface of adsorbent is the Langmuir model. The Langmuir isotherm describes that a saturated monolayer of solute molecules exists on the adsorbent surface, that the binding energy of adsorption is constant, and no migration of adsorbate occurs in the plane of the surface (Weber 1972). The Langmuir equation is $q_e = \frac{Q^o b\ C_e}{1+b\ C_e}$, where q_e is the equilibrium adsorbent phase concentration of adsorbate, Q^o the monolayer adsorption capacity, C_e is the equilibrium aqueous adsorbate concentration, and b is the constant for free adsorption energy.

The model used depends largely on the adsorbate characteristics and the nature of adsorption, however, the Freundlich isotherm has been more widely used to describe activated carbon binding characteristics organic compounds because the Langmuir isotherm describes binding on a monolayer and is a different phenomenon. In contrast, the Freundlich isotherm is a power function that describes binding of different sites on the GAC particle by a distribution of adsorption site energies.(Chowdhury 2013)

3.2.2. NOM Removal in GAC Filters

An important aspect of the GAC system is its ability to remove NOM. NOM is a complex mixture of organic compounds and varies with water source and seasonal changes. Typically, NOM is composed of humic substances which include humic acids (HA), fulvic acids (FA) and humins (Thurman 1985). Humic substances are high molecular weight poly-electrolytic large compounds that can be extracted with a strong base and are further separated by acid treatment. Humins are identified as the non-extractable plant residue portion of humic substances after acidification. Humic acid is the material that precipitates from the humins following acidification, and fulvic acid is the acidified portion of humins that remains in the acid extract. The components of the NOM can also be divided into hydrophobic and hydrophilic fractions (Matilainen et al. 2011). The hydrophobic organic matter is largely composed of high molecular weight (MW) organics which have low solubility in water and exhibit a high degree of aromaticity while hydrophilic organic matter is composed of lower molecular weight aliphatic compounds. These NOM characteristics, along with NOM concentration, vary between water sources and seasonally within a water source.

NOM concentrations are of concern to water utilities due to their respective Disinfection By-Product Formation Potential (DBPFP). During the chlorination process, NOM can react with chlorine, subsequently producing DBPs and lowering the available chlorine concentrations (Viessman et al. 2009). NOM adsorption by different types of GAC media is variable due to differences in GAC properties such as charge, type and number of surface groups (Summers and Roberts 1988). The matrix of the surface water also has a dramatic impact on the binding of the sorbent of interest adsorption by GAC (Newcombe 1999).

In water treatment, GAC filtration is typically employed after sedimentation, coagulation, and ozonation have occurred. After sedimentation and coagulation the remaining NOM is typically comprised of lower molecular weight compounds that can be removed by GAC through adsorption or biological mechanisms (Chowdhury 2013). Interestingly, ozonation of raw water leads to faster biodegradability of NOM as ozonated organic fractions are generally easier for biomass to metabolize. Generally, shorter conjugated aromatic compounds such as carboxylic acids are easier to biodegrade than large NOM aggregates present in natural sources water (Yavich et al. 2004). One of the important components of NOM is biodegradable organic matter (BOM). BOM is comprised of humic substances, amino acids, carbohydrates and the ozonated by-products (OBPs) aldehydes and ketoacids (Kaplan et al. 1980). The most common surrogate for BOM within water treatment plants are BDOC and AOC. For systems in which ozone is employed, AOC most likely represents the fraction of BOM within the system (Zhang and Huck 1996). Although AOC is a relatively small percentage of TOC within the system, the removal of AOC is important as it is desirable for WTPs to remove as much AOC as possible within the plant, such that excess AOC does not encourage bacterial regrowth within the water distribution network (van der Kooij et al. 1989).

3.2.3. BOM Removal in BAC Filters

Shortly after GAC is installed within a WTP, biomass begins to accumulate and colonize the filtration media. Concomitant to the colonization of the media, the GAC particles also adsorb organic compounds dissolved in the water (Velten et al. 2011). Traditionally, GAC has often been replaced after adsorption capacity has been reached, although BAC filters are recognized for their ability to remove BOM long after adsorption capacity of GAC media has been reached.

It has been well understood that GAC can support biological growth and proliferation (Klotz et al. 1976; Mathur et al. 2007). Long recognized for its ability to remove compounds after GAC adsorption has been exhausted, initially biological growth was a concern as pathogens were suspected to be associated with the growth (Klotz et al. 1976). After extensive study, the consensus within literature is that the respective ability of biomass to breakdown biological substrates before water enters the distribution system offers a significant treatment advantage because water produced from biofiltration contains less AOC, and therefore has a diminished capacity to encourage regrowth within the distribution system (Juhna and Melin 2006). In addition, because biofiltration precedes the final step of chlorination, the risk of propagation of disease causing organisms through biofiltration is low. (Brown et al. 2015)

Biological filtration has the unique ability to facilitate degradation of organic compounds long after the binding capacity of GAC becomes saturated (Fonseca et al. 2001; Huang and Chen 2004; Kasuga et al. 2007; Servais et al. 1994; Urfer et al. 1997; Velten et al. 2007, 2011). In addition, biological filtration associated with GAC has the ability to biodegrade previously adsorbed trace compounds, restoring the ability of GAC to continue to as trace compound sorbent (Xiaojian et al. 1991). GAC typically supports biofilm due to its macropores and irregular surface, shelter of microorganisms from shear fluid forces, and due to adsorptive properties that are able to shelter microorganisms from intermittent influxes of toxic compounds (Characklis 1973). BAC filters offer the ability to reduce concentrations of BDOC (Hozalski et al. 1995) and have been shown to reduce both chlorine demand and DBP precursors.

Although BAC filters are sufficiently colonized with bacteria, an interesting property of GAC is that GAC micropores appear to exclude growth in the GAC particle based on the size of bacteria. As the micropores of GAC are less than 2nm, bacteria which are often 200nm or larger,

cannot penetrate the micropore of the particle (Urfer et al. 1997). The degree of biological activity is dependent on type of GAC, hydraulic conditions, contact time, temperature, backwashing protocol, and others (Emelko et al. 2006; Kim et al. 2014; Moll et al. 1999; Urfer and Huck 2001; Velten et al. 2011; Zhu et al. 2010). Several studies have shown that GAC offers a better substrate for growth than non-absorbent media (Herzberg et al. 2005).

3.2.4. Taste and Odor Removal in BAC Filters

In addition to removal of NOM, attenuation of taste and odor is an important benefit of BAC utilization. Taste and odor events are a significant issue for water utilities to control, and between 5 to 10% of their respective budgets go toward the control of taste and odor compounds (Suffet et al. 1996). Compounds such as geosmin and MIB impart an earthy–musty odor to water are primarily responsible for seasonal taste and odor events for utilities with reported odor threshold concentrations (OTCs) ranging from 4 to 15 ng/L (Young et al. 1996). Geosmin and MIB are secondary metabolites of microorganisms (e.g., cyanobacteria, actinomycetes) (Zaitlin and Watson 2006) and occur seasonally in northern climates with concentrations peaking in the summer months. Microbial degradation of geosmin was first reported in the 1960s (Silvey and Roach 1964). In the Silvey and Roach (1964) study, gram-negative bacteria populations were noticed to increase after an algal bloom. Although geosmin was not specifically quantified in the study, woody and grassy odors were noticed after an algal bloom. Both gram-negative and gram-positive bacteria have been shown to degrade geosmin, however geosmin has been shown to be particularly difficult to degrade when it is the sole carbon source for bacteria (Saito et al. 1999). A number of different bacteria species have been identified to degrade geosmin including *Arthrobacter atrocyaneus*, *Arthrobacter globiformis*, *Chlorophenolicus strain N-1053*, and *Rhodocuccus maris* (Saadoun and Ei-Migdadi 1998)

One study showed that ethanol was required as a carbon source co-metabolite in addition to geosmin in order for metabolic breakdown of geosmin to occur (Saito et al. 1999). Although NOM concentrations are significantly higher than geosmin concentrations, BAC filters have been shown to be effective at removing geosmin well after adsorption capacity has been reached (Scharf et al. 2010). In the Scharf et al. 2010 study, the BAC was shown to remove geosmin influent concentrations in the pilot study to below the OTC of 10 ng/L, two years after the initiation of the study. The combined effect of biodegradation and continued adsorption have the cumulative impact of continued taste and odor compound removal although the individual contributions of both adsorption and biodegradation mechanisms are difficult to discriminate (Scharf et al. 2010).

3.3. Biomass and Filtration

3.3.1. The Impact of Backwashing to Biomass on BAC filters

Control of the backwashing process is also a critical component of managing the biomass associated with biofilters. Management of the backwashing process is critical as excess biomass can be associated with filter clogging and the development of headloss within the filter (Simpson 2008). Since backwashing is the primary means to control biomass within a BAC filter, optimization of the timing and sequence of backwashing of BAC filters is a critical control parameter. One study has shown that as much as 20 to 40% of biomass can be displaced during the backwash process in small pilot-scale studies (Bouwer and Hozalski 1998). Biomass associated with filter media is generally stable and is restored after backwashes. This stability was evident in a Seoul, Korea study, where research on the backwash process was conducted on a (coagulation/ozonation/GAC) WTP. It was observed that only minor losses of biomass was observed using 16S rRNA sequencing and that the relative biomass diversity was preserved after backwash (Kim et al. 2014).

Utilizing markedly different tools, an additional study conducted in the Choisy–le-Roi WTP in Paris, (an coagulation/sand filtration/ozonation/GAC plant) indicated that backwashing with water at a frequency of every 50 to 100 hours and air scour did not have a significant effect on the vertical stratification of biomass as measured by carbon-14 isotope (Servais et al. 1991). The authors in the Choisy-le-Roi study measured carbon-14 isotope for glucose before and after backwash and did not show significant changes in the vertical stratification of biomass, although only results for one filter were given. Like other biomass stratification studies, the Choisy-le-Roi study indicated that more biomass was located at the top of the filter, which remained the case after backwash.

Optimizing the duration and spacing of backwash times must be done to assess the abundance of biomass and its relative impact on BAC performance. In addition to the duration and spacing of backwashing, utilizing a disinfectant is an important control factor for filter operation. Although backwashing with chlorinated backwash has been associated with a reduction in biomass, the impact on filter performance has been less clear, with several studies indicating that backwashing with chlorinated backwash water does not significantly impact BOM removal. In a one study, chlorinated backwash reduced biomass and worsened BOM removal (Wang et al. 1995). In contrast, another study determined that utilization of chlorinated backwash water, and the time the filter media is exposed to chlorinated backwash water can reduce the total biomass of the filter (Urfer et al. 1997).

Although biomass reduction as a result of chlorinated backwash was observed in (Urfer et al. 1997), the removal of biodegradable compounds such as formaldehyde and AOC was not impacted. Another study found BOM removal was also not impacted by utilization of chloraminated backwash water (Liu et al. 2001). In a separate study using pilot filters in an ozone-

biofilter treatment system, reduction of backwashing frequency was found to increase biomass in the top of the biofilter, although this study was conducted on sand media (Fonseca et al. 2001). Sand exhibits significantly different less biomass attachment than GAC (Fox et al. 1990), therefore, the results from the sand study are difficult to compare to GAC studies.

Several other factors, including backwash duration and the utilization of air scour have been evaluated for the relative impact on biomass. One study did find that backwashing with and without air scour did not impact the biomass associated with BAC and anthracite filters (Emelko et al. 2006). The lack of impact as a result of air-scouring is likely due to the biodiversity of the filter bed and robust nature of the biomass to resist additional disturbance. To determine the relative impact of backwashing on filter performance, often, system specific evaluations must be completed.

3.3.2. Temperature Impact on BAC Filters

Temperature is also an important factor in the operation of BAC filters. Generally, as temperatures increase, mass transfer and the enzymatic reactions of bacteria are more rapid, allowing for faster metabolism of compounds (Fonseca et al. 2001). In addition, colder temperatures have been shown in some studies to support less biomass at the top of the filter (Emelko et al. 2006). The reduction in biomass as a result of colder temperatures has been associated with worsening performance, which was the case in Emelko et al. 2006, where colder temperatures decreased oxalate removal in GAC filters. Similarly, Moll et al. 1999 found that DOC removal was reduced by 15% during colder temperatures (around 5° C) in comparison to filters operated in a temperature range of 20-35° C.

Interestingly, several studies have noted the impact of temperature on removals, but not the total amount of biomass. Fonseca et al. 2001 noted that while biomass concentration was not

significantly impacted by temperature, the activity of the filters that were operated at 3°C was 70% lower than filters operated above 12°C. In addition, Persson et al. 2006 noted that the biomass activity of the filter was correlated with temperature. Generally, the consensus within the literature is that warmer temperatures typically are associated higher metabolic activities of biomass, and thus higher removals of BOM.

3.3.3. Impact of EBCT on BAC Filters

EBCT is a key design and operation parameter for BAC filters and can be controlled by design of the filter media depth tor decreasing the hydraulic loading rate. Several studies have evaluated the impact of EBCT on the performance of BAC filters with respect to removal of several compounds. Generally, higher EBCT has been shown to increase removal of BDOC and DOC (Urfer et al. 1997). One study observed that longer times led EBCT to decrease AOC in first order manner (Huck et al. 1994).

3.4. Methods of Assessment of Biomass Associated with Filtration Media

The assessment of biomass associated with filtration media has long been of interest due to the role of biomass in the removal of a variety of compounds. Although a desirable parameter for optimizing filter operation, quantification of biomass on filtration media has long been complicated by the challenging nature of the measurements and the difficulty in interpreting of analysis. In addition, the harvesting of biomass for analysis is often challenging

Commonly used methods include quantification of phospholipids, heterotrophic plate count, and enzyme assay, all of which are identified in Table 5. Each of the respective methods has advantages and disadvantages. MWTP staff have utilized heterotrophic plate count in the past for biological analysis to quantify biomass within the Moorhead water distribution system (Porlock

2012). However, the method is only able to culture a small percentage of viable cells present; therefore, the biomass associated with the sample is likely underrepresented.

In addition to the difficulty associated with the variety of methods associated with the assessment of biomass, harvesting biofilm in a consistent manner is also a challenge. Often, methods to obtain the biomass can be destructive in nature or can be difficult to reproduce. In some cases, sonication has been used to detach biomass from filter media (Magic-Knezev and van der Kooij 2004). Recently, for methods such as the ATP or qPCR cell lysis is often accomplished through enzymatic means to obtain the desired biological compound of interest.

Table 5: Biological Assessment Methods (Adapted from Pharand et al. 2014)

Biological Assessment Method	Parameter	Advantages	Disadvantages
Heterotrophic Plate Count	Colonies on Media	Simple, inexpensive	Small percentage colonies cultured
Chloroform fumigation–extraction	Organic carbon Released from Cells	Good sensitivity	Time consuming and complex
Oxygen Consumption	Aerobic Respiration	Good sensitivity	Biofilm sensitivity
Phospholipid Method	Phospholipids from Cell membranes	Good sensitivity	No live/dead differentiation
Enzyme Hydrolysis	ß-N-acetylhexosamini-dase activity	Rapid and Simple	Does not measure all types of cells

3.4.1. Previous Comparisons of BAC and Anthracite Filters for Biomass

A wide range of studies have been conducted to compare the biomass associated with BAC filters to biomass on anthracite as filter medium. Past research has not demonstrated which media definitively harbors more biomass. Some studies have found that GAC has higher biomass (Wang et al. 1995) , whereas other studies have found higher biomass for anthracite in warmer conditions (Emelko et al. 2006). Several studies have found comparable levels of biomass on both GAC and anthracite (Evans et al. 2013; Pharand et al. 2014).

3.4.2. Recent Utilization of ATP Method to Assess Biomass

Recently, the utilization of the ATP method has grown within the drinking water community for the assessment of biomass within filtration media. As ATP is the energy currency of cells, the utilization of ATP offers a direct method to determine live biomass within filtration media. In addition, the ATP method has the additional advantages of being a relatively simple technique with rapid results. For these reasons, ATP has been used in a variety of studies including (Evans et al. 2013) and (Jo and Brown 2012). Numerous studies on a variety of different types of water have been conducted worldwide (Pharand et al. 2014). One of the advantages of the ATP method over the phospholipid method is that the ATP method is selective for live biomass, as compared to both live and dead biomass for the phospholipid method. Heterotrophic Plate Count has been utilized by several authors to assess biomass of filtration media, however, as many authors have noted, HPC suffers from only being able to enumerate a small percent of total organisms present, as no microbiological growth media can support all of the bacteria types in water (Allen et al. 2004). As such, it is likely that the HPC method underestimates the total amount of biomass present in the sample.

Luminescent-based ATP methods, such as the one used in this study, consist of an initial cell lysis step. The cell lysis used for the breakdown of cell membranes can be physical, chemical or enzymatic in nature. Following cell lysis, a luciferin-luciferase complex is added to mixture, which reacts then reacts with ATP to form light. After light is formed, the intensity of produced light is measured using a luminometer (Hammes et al. 2010).

Although the ATP method has been used to compare the relative biomass from a variety of different utilities (Evans et al. 2013; Pharand et al. 2014), one of the drawbacks of the ATP method include the possibility of bias when comparing biomass on sorptive versus non-sorptive

filtration media. As one study noted, adsorption of compounds used for the ATP analysis should be considered when GAC (sorptive) media is compared to anthracite (non-sorptive) (Evans et al. 2013).

Biomass has also been assessed through the depth of the filter media using the ATP method to determine the distribution of biomass through the filter profile. For example, most GAC filters are 24 to 36 inches in depth. Biomass has typically been located near the top of the filter surface with most of the biomass located at or near the surface. As biomass has been assessed toward the bottom of the filter media profile, progressively less biomass has been observed (Pharand et al. 2014).

3.4.3. Biomass Community Analysis Using Molecular Techniques

In addition to ATP, recently, community analysis has recently been utilized to understand the microbial community associated with drinking water filter media. Community analysis is a relatively new tool that will allow for enhanced characterization and relative abundance of various types of bacteria within the biofilm. Up until now, community analysis in the drinking water field had typically used the 16S rRNA *Bacteria* gene. Typically, pyrosequencing has been used to determine the relative abundance of respective species on the filter media. One study found that *Proteobacteria, Bacterioidetes, Actinobacteria,* and *Nitrospira* were the most dominant species with *Proteobacteria* comprising nearly 74 percent of the operational taxonomic units present in the drinking water filtration media (Kim et al. 2014). In another study, *Proteobacteria* and *Planctomycetes* were the most abundant phyla in filter media (Zhang et al. 2018). Interestingly, community analysis has been used to show that operational treatment parameters such as EBCT and the presence of preozonation can significantly influence the microbiology of the system (Pinto et al. 2012). In addition, a study also determined that the type of source water utilized (either

surface or ground water) can have a significant influence on the type of bacteria found within the treatment plant (Assche et al. 2019). It has also been determined that the microbiological community found within the filtration system is largely responsible for dominant species found within the distribution system (Pinto et al. 2012).

3.4.4. Metabolic Activities within Filter Media Biofilm

Several metabolic processes are concurrently conducted by biomass associated with water filtration media. Some of the major metabolic processes include the degradation of carbohydrates, along with the process of nitrification. Nitrification occurs by the oxidation of ammonia to nitrite, which is subsequently oxidized to nitrate by nitrite oxidizing bacteria. Often, separate metabolic processes are complete by separate species of bacteria. For example, oxidation of ammonia typically occurs by ammonia oxidizing bacteria or ammonia oxidizing *Archaea*, while nitrate oxidizing Bacteria catalase the second step of conversion of nitrite to nitrate.

Several studies have detected organisms responsible for nitrification. For example, (Kasuga et al. 2010) identified that ammonia oxidizing bacteria and ammonia oxidizing archaea are present in a large scale ozonation-GAC facility. In addition, nitrate oxidizing bacteria *Nitrospira* have been detected in Pinto et al. 2012. The detection of nitrifying bacteria within biomass suggests that nitrification does occur within filter media. Nitrification is a concern as excessive nitrate can cause methemoglobinemia, or “blue baby syndrome” and is regulated by the USEPA with an MCL of 10 mg/L.

CHAPTER 4. MATERIALS AND METHODS

4.1. Pilot Filter Skid Design and Construction

The Pilot Filter Skid (PFS) utilized for this study was designed by Advanced Environmental and Engineering Services (AE2S of Fargo, ND) and fabricated by Wigen Water Technologies (Chaska, MN). The PFS contains five clear PVC columns that measured eight inches in outer diameter (7.942-inch inner-diameter) and with a height of 97.5 inches. Influent water for the PFS was from the ozone effluent chamber and included chemical additions of calcium thiosulfate and polyphosphate to ensure an adequate comparison to the full-scale filters (Figure 16). Ozone chamber effluent water has a pH of approximately 9.3. Each of the respective columns contained both media and water sampling ports at media depths of 8-, 14-, 26-, and 32-inches (Figure 17). An effluent water sampling port was also available (e.g., after full media depth).

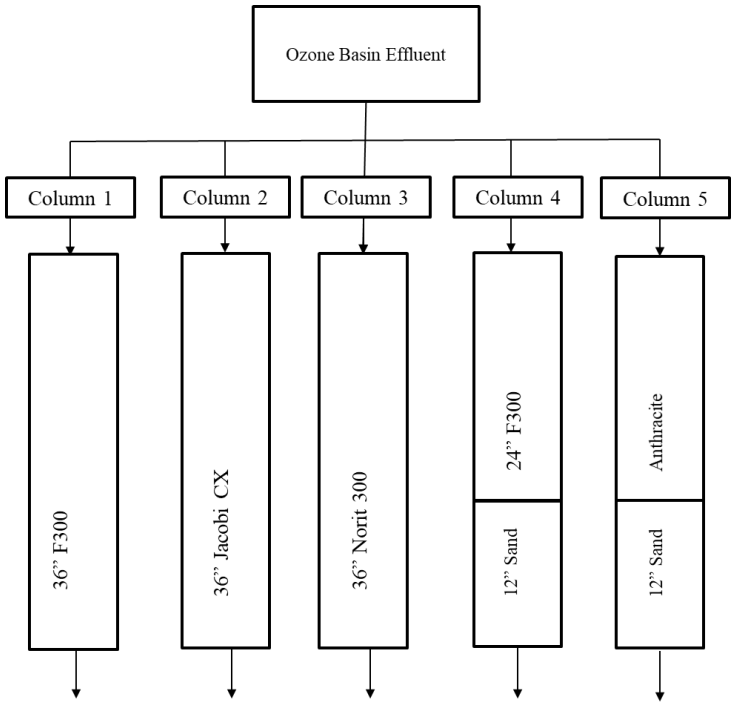

Figure 16: Diagram of Columns from PFS (Adapted from von Hagen 2019)

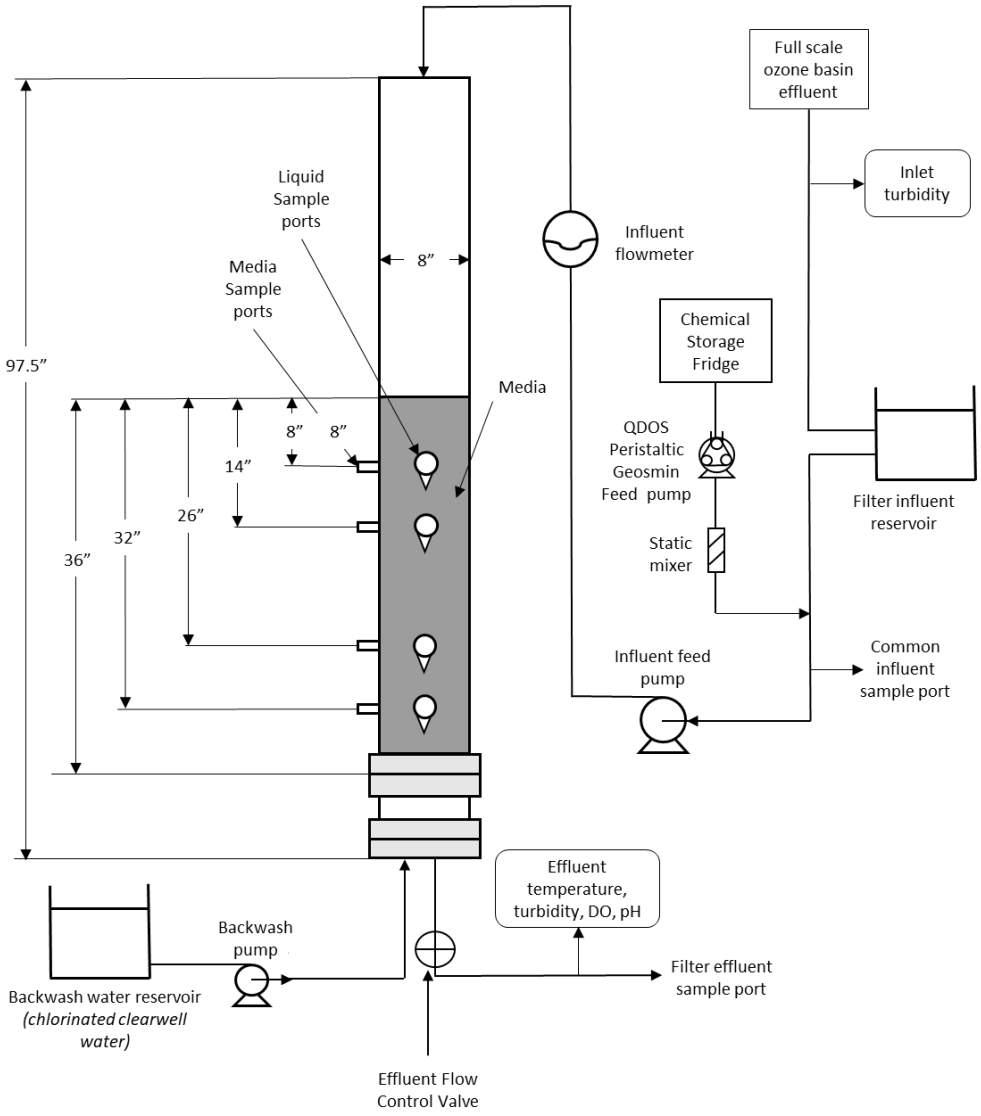

Figure 17: Diagram of Individual Column from PFS (Adapted from von Hagen 2019)

Column 1 was filled with 36 inches of F300 GAC. Column 2 contained 36 inches of Jacobi CX GAC. Column 3 was filled with 36 inches of Norit GAC 300. Column 4 contained 24 inches of F300 GAC and 12 inches of silica sand. Finally, column 5 served as the control column and was filled with 24 inches of anthracite and 12 inches of silica sand. A schematic diagram of the pilot filter skid is shown in Figure 17. Each of the columns contains an independent variable frequency drive pump, so that flow rate to each respective column can be independently controlled. In addition, the PFS has an independent backwash feed pump. Each of the feed pumps for the

individual columns on the PFS was Goulds® 0.5 HP pumps capable of 2 gpm output (at 10 psi). The feed water for the PFS was pumped from the ozone effluent chamber of the full-scale MWTP and stored in two 275-gallon polypropylene totes.

Each column contained a Rosemount® one-inch model 8705 magnetic flow meter that was utilized to measure flow for each of the respective filters. The PFS also contained an on-board air compressor, so that filter backwashes that include air-scour could be conducted on a regular basis. The PFS chlorinated backwash water supply came from the clearwell, the same source of backwash water for full scale, which was supplied by a 15 gpm Goulds® pump. The PFS also contained a 5.5 CFM Gardner® VDTE-10 air scour blower for use during the air scour sequence of the backwash cycle, which was fed by compressed air from a 6.5 CFM Castair® D212P50 air compressor. Backwash water was stored in a 275-gallon tote and manually filled as needed by operators. Backwashes were completed every three to four days, or as needed.

4.2. GAC Media Selection for the PFS

In the initial stages of design of the PFS, three different GAC media were used for the PFS to ascertain the impact of various characteristics of GAC to support biomass and removal of TOC and geosmin. Of the three selected, two were coal based (Calgon and Norit) and one was coconut shell based (Jacobi). Calgon Filtrasorb (F300) is a coal based reagglomerated carbon material that has been used by several surface water treatment facilities in the upper Midwest. Cabot® Norit 300 GAC (Norit 300) is very similar material to Calgon, however, it is different that Calgon because is a non-reagglomerated. In contrast to the Norit and Calgon Medias, Jacobi Aquasorb™ CX media was selected because it has significantly different surface morphology and pore structure. The Jacobi Aquasorb™ media has a great deal more micropore structure as a result of

the coconut-based material used to synthesize it. The specific data regarding each media type is listed in Table 6.

Table 6: GAC Specifications

Media Characteristic		Granular Activated Carbon Name		
		Calgon Filtrasorb® 300	Jacobi AquaSorb™ CX	Cabot Norit® GAC 300
Raw material		Bituminous coal	Coconut shell coal	Bituminous coal
Uniformity coefficient		2.1 (max)	<1.6	2.1 (max)
Effective size (mm)		0.8-1.0	1.0	0.8-1.0
Iodine number (mg/g)		900 (min)	1,100 (min)	900 (min)
Moisture by weight (%)		2 (max)	5 (max)	2 (max)
Particle size (US Mesh)	On 8 mesh (%)	15 (max)	<5	15 (max)
	Through 30 mesh (%)	4 (max)	<4	4 (max)

4.3. GAC Media Exhaustion

Prior to utilization within the PFS, media supplied was required to be exhausted so that no organic removal capacity would remain within the media. In addition, it was anticipated that exhaustion of the media would allow for establishment of biomass within the filter media matrix. To complete the exhaustion process, on February 13th, 2017, four 55-gallon barrels were filled with three types of GAC as well as anthracite coal and silica sand, as described in Table 7.

On February 14th, 2017, raw water began to flow continuously at a rate of approximately one to two gallons per minute entering from the bottom and exiting the top of each barrel. Raw water was applied until August 2nd, 2017, when the contents of each barrel were rinsed thoroughly with tap water to remove mud and other debris prior to being placed into the appropriate columns of the pilot filter.

Table 7: Contents of Media Conditioning Barrels

Barrel	Contents
A	2- 55-lb bags of Calgon Filtrasorb® 300 GAC
B	1 55-lb bag Jacobi AquaSorb™ CX GAC
C	1 55-lb bag Cabot Norit® GAC 300
D	2 ft^3 anthracite and 1 ft^3 sand from full scale filter

4.4. PFS Operational Procedures

The PFS study was carried out from mid -August 2017 to the end of August 2019. The use of a two-year study allowed for the establishment of mature biomass within the PFS system, as well as the opportunity to evaluate seasonal impacts on the filtration media. Daily checks on the PFS, as well as monthly calibrations for turbidimeters were performed to ensure accuracy of data.

4.4.1. PFS Hydraulic Loading Rate

The PFS study was carried out from mid-August 2017 to the end of August 2019. The use of a two-year study allowed for the establishment of mature biomass within the PFS system, as well as the opportunity to evaluate seasonal impacts on the filtration media. The loading rates for the PFS are listed in Table 8.

Table 8: Hydraulic Loading Rate and Flow Information for PFS over 2-year Study

Time Period	Start Date	End Date	Duration (weeks)	Filtration Rate (gpm)	EBCT (minutes)	HLR (gpm/ft^2)
1	08/02/2017	12/19/17	20	0.95	8.0	2.8
2	12/19/17	01/09/18	3	0.70	11.2	2.0
3	01/09/18	01/31/18	3	1.27	6.1	3.7
4	1/31/18	02/07/18	1	0.95	8.0	2.8
5	02/07/18	02/22/18	2	1.27	6.1	3.7
6	8/19/2019	7/22/2019	48	0	8.0	2.8
7	7/22/2019	7/29/2019	1	0.5	15	1.5
8	7/29/2019	8/5/2019	1	0.75	10	2.2
9	8/5/2019	8/12/2019	1	1.0	7.62	2.9
10	8/12/2019	8/19/2019	1	1.25	6.69	3.6
11	8/20/2019	8/26/2019	1	0.5	15	1.45

4.4.2. PFS Backwashing Procedure.

Backwashing was performed by operations staff within the MWTP and was conducted at intervals of approximately every five days. Backwashes were conducted and observed manually, to ensure that the backwash process adequately cleaned the filtration media. The backwash sequence for the PFS was intended to mimic the full scale MWTP backwash operation. As such, the backwash sequence commenced with an air scour of approximately three minutes, which was used to break up any "mud balls" or debris that had built up within the PFS columns. Following the air scour, chlorinated backwash water at a concentration of approximately 3.0 mg/L monochloramine was pumped through the media to obtain a bed expansion rate of approximately 50%. After the backwash water had been pumped through the column, the filter media settled before the filtering sequence commenced.

4.5. EBCT Test on Geosmin Removal

To determine the impact of EBCT on geosmin removal, a challenge test was conducted from July 23rd, 2019 to August 26th, 2019. A stock concentration of 10 mg/L geosmin was prepared in methanol and diluted to a working concentration of 1.3 mg/L in reagent grade water. Geosmin was purchased from a wholesale supplier and was supplied at 21.2 percent purity. The working geosmin solution was stored at 4°c throughout the duration of the experiment and pumped from an air-tight bag to ensure minimal degradation of the stock solution. The geosmin stock was pumped prior to a static mixer to ensure proper mixing during the experiment. Geosmin was added via a Watson Marlow Qdos peristaltic pump at a varying flow rates to feed obtain influent concentrations of approximately 204 ng/L to 331.2 ng/L (Table 9). The geosmin feed pump and column feed pumps were adjusted and allowed to equilibrate 24 hours prior to sampling. The influent flow rate to the respective columns was varied to determine the relative impact of EBCT

on geosmin removal performance for filter 3 and filter 5. The flows rates were adjusted for each respective column to alter the EBCT for each column and are listed in Table 9. In addition, the Qdos pump feeding geosmin was adjusted to ensure that the concentration of the influent geosmin remained constant. The temperature range during the study was from 68.14° F to 75.22° F with an average temperature of 73.06° F. Over the course of the study, geosmin samples were collected for the samples were collected from the filter influent sample port and effluent ports for column 3 and column 5.

Table 9: Experimental Conditions for Determination of EBCT Geosmin Removal Experiment

Time Period	EBCT (minutes)	Flow Rate Per Column (gpm)
July 22nd to July 29th	15	0.5
July 29th to August 5th	10	0.75
August 5th to August 12th	7.62	1.0
August 12th to August 19th	6.69	1.25
August 20th to August 26th	15	0.5

4.6. Water Quality Measurements

4.6.1. Online Water Quality Monitoring

Each column was outfitted with its own pH meter, and turbidimeter. In addition, the filter influent stream was also measured for pH meter and turbidity. The online pH meter for the skid were manufactured by Rosemount, Inc®. and were Rosemount® model 3900 general purpose pH/ORP sensors. The turbidimeters included with the FPS are manufactured by TB 500 Global Water® and have a functional measuring range of 0-1000 NTU. The turbidimeters utilized ultrasonic cleaning to achieve accurate online data. The TB-500 turbidity meter utilizes USEPA operating method 180.1, whereby a white light is utilized to measure the turbidity of the sample. Daily grab samples for column effluent turbidity were also taken and measured Hach 2100N according to USEPA Method 180.1. Although online turbidity was also collected as part of the study, it was found that utilization of the grab samples produced more reliable measurements.

4.6.2. Quality Control of Online Data

All the data generated by the PFS were transmitted to a Rockwell® Compactlogix 5370 and skid controls were achieved by utilization of a Panelview® Performance Plus 7 by Allen Bradley. Historical data generated by the skid was then transmitted to the SCADA system on an hourly basis and stored for future usage on the historical data server. To ensure the accuracy of turbidity throughout the study, verification of online data was performed on an ongoing basis. Verification of turbidity was accomplished utilizing benchtop turbidimeters to determine that the online turbidities were accurate. Online turbidimeters were calibrated on an as needed basis.

4.6.3. Organics Sample Analysis

Water samples from the filter effluent for the BAC and anthracite sand filter were collected on a weekly basis from the PFS and analyzed for UV254, DOC, and TOC. The purpose of the analysis was to compare the organic removal capabilities of the four BAC filters with the anthracite-sand filter. TOC samples were analyzed at the MWTP analytical laboratory. Calibration was performed at monthly intervals to ensure data integrity. DOC and UV254 measurements were also taken at weekly intervals. Organic analysis was completed utilizing USEPA method 415.3: Determination of Total Organic Carbon and Specific UV absorbance at 254 nm in Source Water and Drinking Water. TOC was analyzed utilizing an O-I Analytical® 1030D TOC analyzer. TOC samples were preserved with phosphoric acid and held at 4 ± 2° C for less than 28 days prior to analysis. UV analysis was performed utilizing a ThermoFisher® Scientific Orion Aquamate UV-VIS Spectrophotometer and one-centimeter pass through quartz cells.

4.6.4. Analytical Determination of Geosmin by GCMS

Water samples were collected free of headspace and analyzed within seven days of collection. Samples were collected in 40 milliliter amber vials and preserved with sodium omadine.

Geosmin concentrations were determined by a commercial lab (AEL Labs®, Tyler Texas), and were analyzed according to standard method 6040D using solid-phase micro-extraction (SPME) gas chromatography mass spectrometry (GC/MS). The method detection limit (MDL) of geosmin was 0.360 ng/L.

4.6.5. Online pH Measurement of PFS Water

The pH of PFS produced water was measured using five Rosemount® pH probes measuring the effluent of each of the individual columns. Standard method SM 4500-HB was utilized for analysis. The purpose of monitoring pH within the PFS was to ensure that the columns were operating properly.

4.7. Biomass Assessment

4.7.1. ATP Testing Plan

ATP was tested at 8 inches below the top of the media on all five columns to determine the relative biomass associated with each of the respective media types. Previous studies (Pharand et al. 2014) had indicated that the majority of biomass was located at within the upper portion of the filter bed. As such, media was collected in as sterile of means as possible and analyzed in the MPS laboratory.

4.7.2. ATP Test Protocol for PFS Media

Adenosine triphosphate (ATP) is the energy currency of cells and is prevalent in organisms ranging from humans to bacteria. ATP concentrations have been used to quantify biomass in several studies (Jo and Brown 2012; Pharand et al. 2014). For this study, approximately 3 grams of wet media were collected from 8-inch depth on the Pilot columns on an ongoing basis. ATP was measured in media collected from the respective columns utilizing the manufacturer (Luminultra) instructions and samples were run in triplicate. Briefly, 1 gram of wet media was

weighed and added to 5 milliliters of Ultralyse reagent. After a 5-minute incubation period, 1 milliliter of lysate was transferred to 9 milliliters of Ultralute reagent. After mixing the Ultralute reagent, a 100-microliter aliquot is withdrawn and mixed with 100 µL of Luminase. Samples were then measured for luminescence in a 12x55mm test tube after calibration of the Luminometer. Samples were run in triplicate and measured as relative light units (RLU) on the Luminometer. Media samples were saved and dried for a 24-hour period at 100°C. RLU values are reported as ng ATP/ cm3 GAC (dry weight).

4.7.3. SEM

Scanning electron microscope (SEM) analysis was conducted at the North Dakota State University (NDSU) core facility on virgin GAC media to observe the morphology associated with each media type, and to assess its potential impact on biofilm formation. SEM analysis was also carried out on media sampled at depths of 8- and 26-inches after a period of 10 months to observe and compare the biomass associated with each media type, and to evaluate the impacts of filter bed depth on biomass formation. Samples were also collected to determine the morphology and biomass associated with the sand layer in the respective columns. Samples were fixed in 2.5% glutaraldehyde in sodium phosphate buffer (Tousimis, Rockville MD) and stored at 4C. Samples were rinsed in buffer and water and then dehydrated using a graded alcohol series from 30% to 100% ethanol. The samples were critical-point dried using an Autosamdri-810 critical point drier (Tousimis, Rockville MD) with liquid carbon dioxide as the transitional fluid. Dried samples were attached to aluminum mounts with silver paint (SPI Supplies, West Chester PA) and sputter coated with a conductive layer of carbon (Cressington 208, Ted Pella Inc., Redding CA). Images were obtained using a JEOL JSM-6490LV scanning electron microscope operating at an accelerating voltage of 15 kV.

4.7.4. Microbial Community Analysis

For microbial analysis, two sets of data were collected. The first set of data was media collected from each of the respective columns at 8 inches of media depth on July 30th, 2019. The second set of samples were collected on August 26th, 2019. For the collection of the August 26th samples, approximately 4 grams of media was collected from each of the respective media depths for column 3 and column 5. Of the 4 grams collected, 3 grams was used for ATP analysis, and approximately 1 gram was sent to Luminultra commercial labs for qPCR analysis. For the Luminultra analysis, microbial DNA is extracted from each sample using Luminultra's GeneCount DNA Purification kit (HT). For the DNA purification, a GeneCount DNA purification kit was utilized. The DNA purification protocol was carried out by Luminultra. A brief description of the Genecount DNA purification kit protocol is provided. Samples were mixed with 1000 µL of Phenol: Chloroform: Isoamyl Alcohol (25:24:1) and centrifuged for 5 minutes. During centrifugation, the Inhibitor Removal reagent was prepared by combining 50 µL of Inhibitor Removal Reagent I and 200 µL of Inhibitor Removal Reagent II. After combining, 800 µL of Inhibitor Removal Reagent III was added and the mixture was vortexed.

After DNA samples were transferred, up to 1400 µL of the top aqueous phase was placed into respective tubes containing inhibitor removal mixture. The tubes containing the inhibitor removal mixture and supernatant were then mixed by inverting at least 10 times and incubated at room temperature for 10 minutes. The tubes are then centrifuged, and up to two millilitres of the supernatant was transferred to a new tube, and 3000 µL of binding buffer was added. After the binding buffer was added and mixed, samples were filtered using a vacuum manifold. DNA was then removed from the membrane using 100 µL of elution buffer. The eluted DNA was then processed for sequencing or qPCR.

Purified DNA then proceeds to qPCR analysis for total prokaryote or target-specific quantification using the GeneCount Q48 instrument®, and furthermore to 16S rRNA sequencing of the sample's microbial community (Illumina® MiSeq, 515F/806R primers). Sequencing data was finally processed using Mothur in conjunction with the silva taxonomic database. In order to provide taxonomic assignments and relative abundances of the microbial community members present within each sample. Real-time quantitative polymerase chain reaction (qPCR) was used to quantity the 16S rRNA for total bacterial biomass. Targeting the 16S rRNA gene allowed for phylogenetic analysis to be performed. The microbial analysis was conducted by Luminultra commercial labs. Data for the phyla analysis were normalized to 100% total population.

4.8. Data Analyses

4.8.1. Shannon Index Calculations

Biodiversity within a sample is an important measure to determine the adaptability and sustainability of the biota present to environmental changes. Although biodiversity is an important measure within numerous fields within biology, there is no university accepted methodology to measure it (Allen et al. 2009). Shannon index is a calculation that can determine the species richness and evenness of the species present within a sample and has been used in several studies to determine the relative diversity within a dataset (Shannon 1948; Wang et al. 2013). The index uses two components to determine both the "richness" and "evenness" within a dataset. The total number of species present within a sample is characterized as the "richness" of the data, whereas the distribution of the species is characterized as the "evenness" of the data. In this study, all the individual columns (1-5) and depth samples for columns 1 and 3 were characterized using the following Shannon index calculation

$$H' = -\sum_{i=1}^{R} p_i \ln p_i \qquad \text{(Equation 2)}$$

In Equation 2, p_i defined as the proportion of characters belonging to the *i*th type of letter in the string of interest. In population studies, the proportion of species *i*, relative to the total number of species p_i, which is then multiplied by the natural log of the proportion p_i. Each of the respective species' abundance was used to perform the calculation.

4.8.2. Statistical Analysis

Statistical analysis was completed on a variety of the data collected throughout the study. The student's t-test was used to determine statistical significance using the data analysis tool within Microsoft® excel. Statistical significance was computed using the student's t-test to determine if the null hypothesis was the same for both means of the respective data sets. The difference in means were not considered statically significant for values of $p>0.05$ and were considered significantly different if $p<0.05$. Data that is plotted within this thesis that contains error bars indicate one standard deviation.

CHAPTER 5. RESULTS AND DISCUSSION

Results of this study are discussed in this chapter. First, results of weekly collection of water samples is provided, followed by the biological assessment conducted during the pilot study. Finally, detail is given regarding a challenge test conducted to determine the impact of EBCT on geosmin removal.

5.1. Pilot Filter Skid Operation

The PFS was operated for a period of 8/15/2017 to 9/1/2019. The temperature difference between the average effluent temperatures of Filters 1-5 and the full-scale system measured in the PFS influent reservoir temperature was approximately 5.1° F (Table 10) and shown Figure 18.

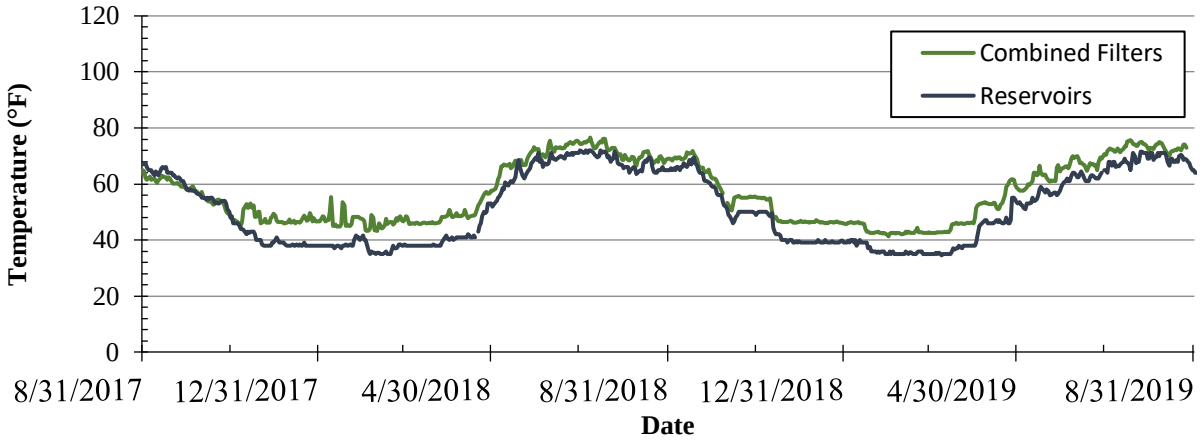

Figure 18: Temperatures of Reservoirs and Combined Filter PFS Effluent During the Study Period

Observed differences between the temperature of the reservoirs and the combined filters effluent was more significant in the winter as the minimum temperature observed for the pilot was 41.3 °F while the minimum observed temperatures for the reservoirs was 34.5°F (Table 10). The temperature difference in the study is noteworthy as the PFS did have a higher temperature than the reservoirs, which could potentially increase the amount of biomass growth in the PFS system in comparison to the full-scale system.

Table 10: Temperatures for the PFS in Comparison to Reservoir Temperatures

	Pilot Temperature (°F)	Reservoir (°F)	Difference (°F)
Average	57.1	52.0	5.1
Minimum	41.3	34.5	6.8
Maximum	76.7	72.0	4.7

5.1.1. Turbidity Data and Analysis

Turbidity for grab samples was recorded and analyzed for Filters 1-5 and the softening basin effluent. Softening basin grab samples were utilized for the analysis as the data was utilized as the data was more reliable than online turbidity data for the PFS. Effluent turbidity of all five of the filters was very similar, and Filters 2-5 averaged an effluent turbidity of 0.11 NTU, with Filter 1 averaging 0.12 NTU over the two-year PFS study. Daily grab samples were not collected for a period of 5/28/19 to 7/10/19, thus a gap in the data is present for that time period. Effluent turbidities for the course of the two-year study are presented in Figure 19 and summarized in Table 11.

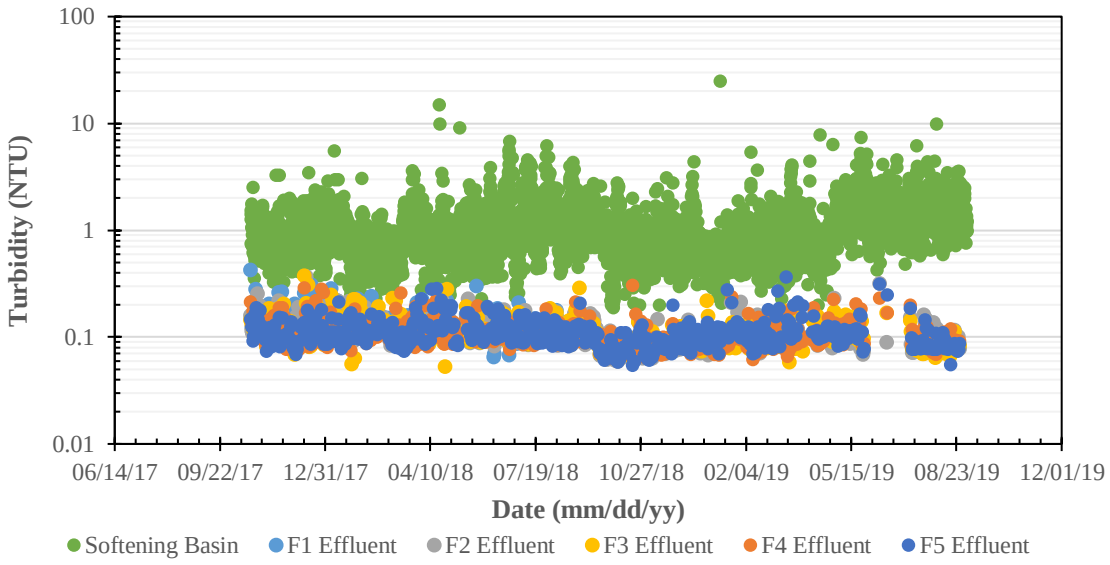

Figure 19: Filter Turbidities for FPS for All 5 Columns and Softening Basin Effluent

Table 11: Turbidity Minimum, Average, Maximum and Std. Dev. for Two-Year PFS Study

Filter Number	Minimum (NTU)	Average (NTU)	Maximum (NTU)	Std. Dev. (NTU)
1	0.06	0.12	0.42	0.04
2	0.059	0.11	0.37	0.04
3	0.053	0.11	0.38	0.04
4	0.062	0.11	0.31	0.03
5	0.055	0.11	0.37	0.04

Because Filter 3 was selected as the GAC media to replace anthracite within the MWTP, further analysis of the performance of Filter 3 was warranted. For the two-year study, there was no statistically significant difference between GAC and anthracite as filter medias in terms of effluent turbidity. In addition, the effluent turbidities were similar throughout the course of the study were very similar (Figure 20). Similar to the observations noted in (von Hagen 2019), it appears that the relatively larger GAC grain size can provide equivalent turbidity removal.

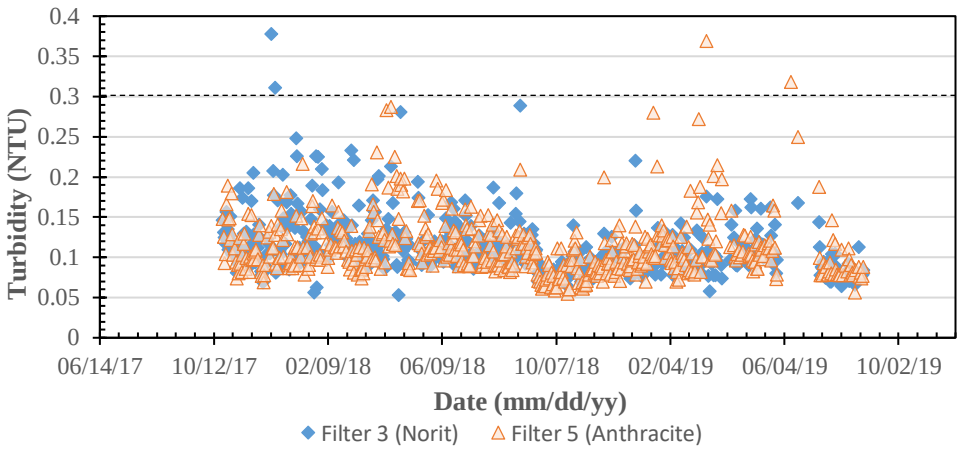

Figure 20: Filter Effluent Turbidities for Filter 3 and Filter 5

5.2. Organics Data and Analysis

The results for the analysis of TOC concentrations are presented in this section. In previous research (von Hagen 2019), it was determined that there was no significant difference between DOC and TOC results for organic analysis in this study. Therefore, the primary intent of analysis

for this study was to compare the TOC and UV254 removal for various filters, with specific attention on Filter 3 and Filter 5.

5.2.1. TOC Analysis in the PFS system

TOC measurements were recorded on the influent of the PFS and effluent of the PFS on a weekly basis. The influent values for TOC were between 5.7 ppm and 1.6 ppm, with an average TOC value for the two-year period at 3.4 ppm. The filter influent values spiked in the winter of 2018 at a value of 5.7 ppm, which is likely due to source water discharge events. The lowest influent TOC values were recorded in the fall of 2018, when the source water for the MWTP was switched to aquifer water for a Red River Transmission Line relocation construction event as shown in Figure 21. During year-one of the pilot study, it was determined that Filter 3 had a statistically significant higher removal of organics in comparison to Filter 5 (von Hagen 2019). In this study (two-year study), it was also determined that Filter 3 had a significantly higher removal percentage of organics at the 95% confidence level (p= 0.0094), compared to Filter 5. The difference in removal of TOC between filter 3 and filter 5 is shown in Figure 22.

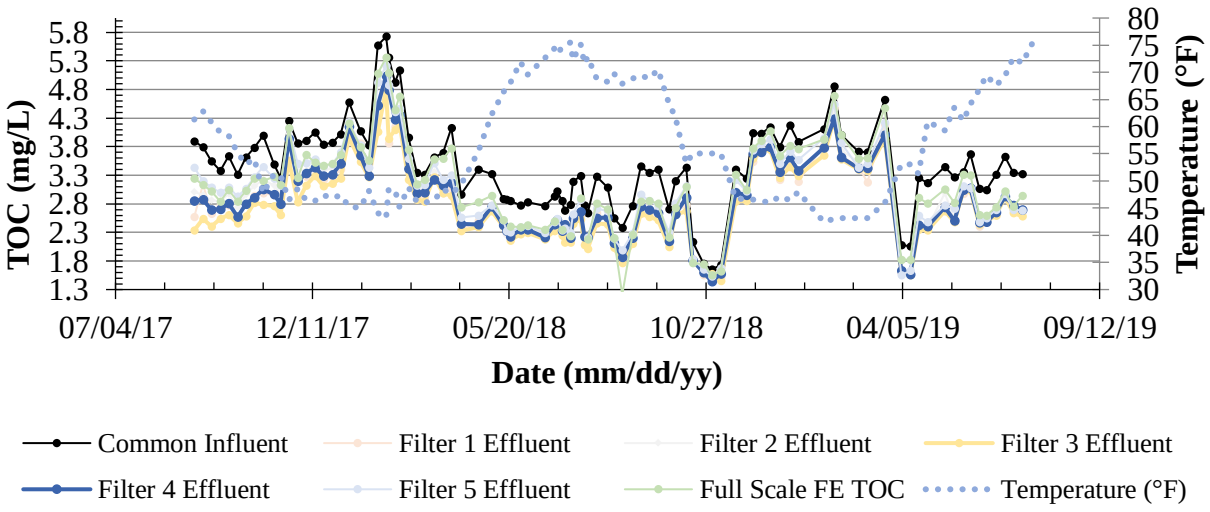

Figure 21: TOC Influent and Effluent Values for the PFS and Full Scale MWTP, Plotted with Temperature

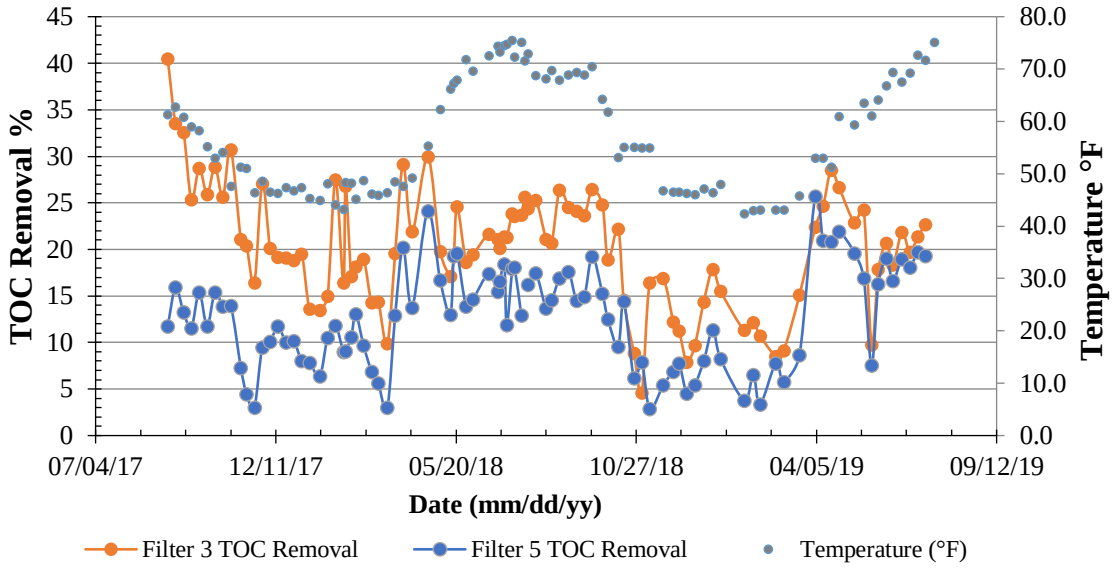

Figure 22: TOC Removal Percentage and Temperature in Filters 3 and 5

Over the course of the two-year study, organics removal percentage for Filter 3 was higher than Filter 5 with an average removal of 20.2 percent for Filter 3 compared with an average removal percentage of 12.7 percent for Filter 5 (Figure 23). For the two-year period, Filter 3 had a significantly ($p<0.05$) lower average effluent TOC concentration of 2.72 mg/L in comparison to an average effluent concentration of 3.00 mg/L for Filter 5 at the 95% confidence interval.

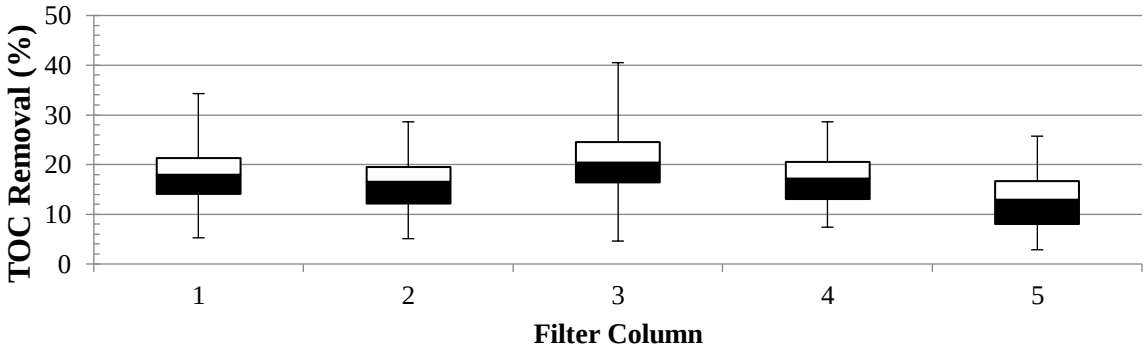

Figure 23: Box and Whisker Plot for TOC Removal for Columns 1-5 on PFS

5.2.2. UV Analysis in the PFS system

UV254 analysis was completed within the PFS two-year study to determine the degree of aromaticity within the organic matter of the influent and produced water of the filters. UV254

measurements followed the same general trend as TOC measurements, indicating that the organics within the PFS system have a high degree of aromatic character, as those are the respective species that absorb UV light (Figure 24).

UV254 values for Filter 3 and Filter 5 over the course of the two-year study averaged 0.019 cm^{-1} ±0.006 $cm^{-1}$and 0.021 cm^{-1} ±0.007 cm^{-1}, respectively, as shown in Table 12. The UV254 values for Filter 3 were significantly lower than Filter 5 at the 95% confidence level (p=0.024). UV254 values for the full-scale WTP were 0.025 cm^{-1}±0.008 cm^{-1}.

Table 12: UV 254 Values for Filters 3,5 and Full Scale

Filter Number	UV 254 cm^{-1}	Std. Dev. cm^{-1}
Filter 3	0.019	0.12
Filter 5	0.021	0.11
Full Scale WTP Filter Effluent	0.025	0.11

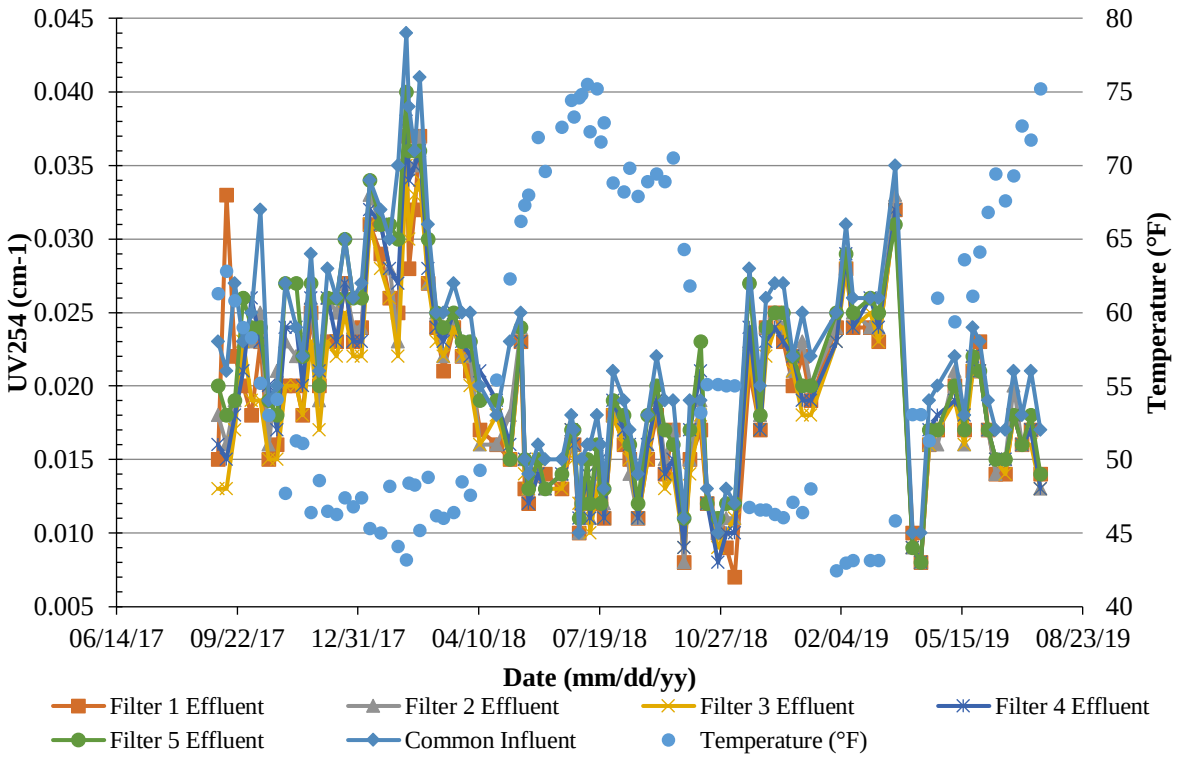

Figure 24: UV254 Values for PFS Influent and Effluent for Two-Year Pilot Study

5.2.3. Temperature Impact on UV254 and TOC Removal

Statistical analysis of effluent TOC concentration and UV254 was performed to determine the impact of temperature on organics removal. For the purpose of the statistical analysis, the period of 4/11/2018-11/01/2018 was defined as the "warm" period, whereas the time period from 11/8/2018-3/21/2019 was defined as the cold period. Temperatures in the warm period averaged 67°F with a range of 49.3°F to 75.5°F. The "cold" period had a range of 42.4°F to 55.0°F with an average temperature of 51.2°F.

The usage of the cold and warm time periods allowed comparison to the ATP biomass assessment. For the warm period, the effluent TOC was significantly lower for filter 3 (2.21 mg/L) than filter 5 (2.39) (Table 13). However, for the cold period, although Filter 3 had a lower concentration of TOC than filter 5 (3.31 vs. 3.51), respectively. The difference was not statistically significant (p=0.35). Statistical analysis of UV for the same periods produced the same conclusion, that effluent organics was significantly lower in filter 3 compared to filter 5 for the warm period, but not the cold period.

Table 13: Effluent TOC and UV254 Values for Filter 3 and Filter 5 for Varying Temperature Periods

Parameter	Statistic	Filter 3		Filter 5	
		Warm	**Cold**	**Warm**	**Cold**
TOC (ppm)	Average	2.21	3.31	2.39	3.53
TOC (ppm)	Std Dev	0.29	0.76	0.36	0.81
UV254 (abs)	Average	0.014	0.022	0.015	0.024
UV254 (abs)	Std Dev	0.003	0.005	0.003	0.005

Interestingly, TOC removal percentages during the summer were significantly higher for Filters 3 and 5. Filter 3 had a statistically significantly higher TOC removal percentage for summer compared to winter, 21.4% versus 12.6%, respectively. For Filter 5 the summer removal was

15.3% versus 6.4% for winter. The higher removal percentage for both Filter 3 and Filter 5 suggest that biomass plays an important role in TOC removal.

5.3. Biomass Assessment

5.3.1. ATP Analysis of Filter Media

ATP was used to determine if biomass correlated to organics removal and to determine seasonal variations of biomass on filter media for all filter media types. ATP was sampled on a bi-weekly monthly basis for most of the two-year study. During the initial phase of the study it appears as though the biomass decreases for the first several weeks until December of 2017, at which point biomass begins to increase for all the filters (Figure 25). It has been reported in the literature that biomass can take several weeks and even up to 6 months for biomass to establish (Magic-Knezev and van der Kooij 2004).

Average ATP values over the course of the two-year study was: F1: 232 ± 15 ng ATP/cm^3; F2: 304 ± 20 ng ATP/cm^3; F3: 215 ± 19 ng ATP/cm^3; F4: 247 ± 18 ng ATP/cm^3; and F5 393 ± 29 ng ATP/cm^3. Filter 5 had significantly higher ATP than all filters over the course of the two-year study which is displayed Figure 26. Filter 2 was the next highest average ATP concentration at 304 ± 20 ng ATP/cm^3 followed by Filter 4 at 247 ± 18 ng ATP/cm3, F1: 232 ± 15 ng ATP/cm3, and Filter 3 at F3: 215 ± 19 ng ATP/cm^3. During the study, significantly lower biomass was observed during the summer months in comparison to winter months for all columns (Table 14).

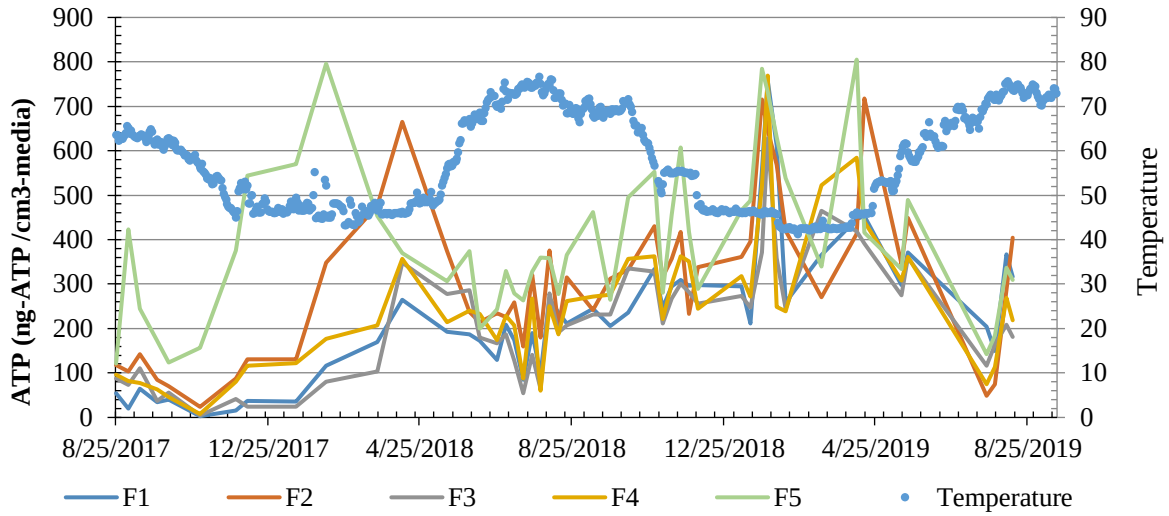

Figure 25: ATP for Various Media Types and Temperature for the Two-Year Pilot Study

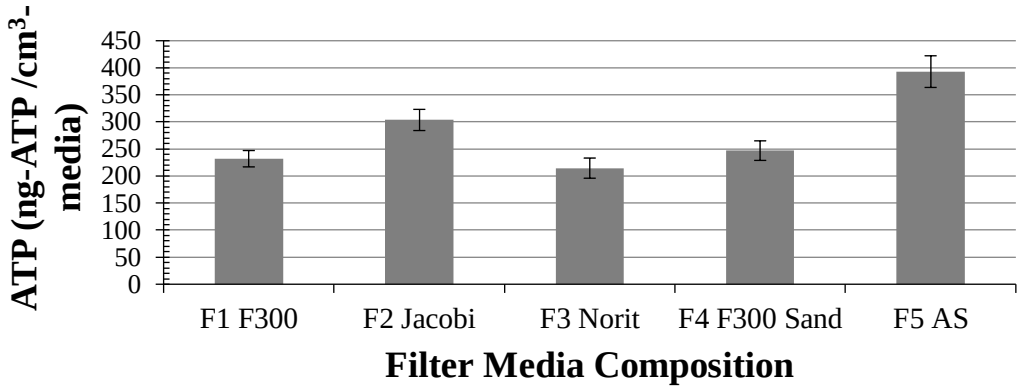

Figure 26: Total ATP ng-ATP/cm^3 for the PFS media over the Course of the Two-Year Study

Table 14: ATP Comparison Between Warm and Cold Temperatures

Filter	Mean Warm ATP ng/cm^3	Mean Cold ATP ng/cm^3	Significant Difference Between Cold and Warm?
1	202	375	Yes
2	299	420	Yes
3	214	326	Yes
4	237	364	Yes
5	343	502	Yes

Some of the advantages to the ATP method include the rapid nature of the analysis and the ability of the ATP method to determine changes in the biomass over time. One of the potential disadvantages of the ATP analysis and comparison between sorptive (GAC) and non-sorptive media is complicated by potential interference of sorption of the ATP reagents (Evans et al. 2013). Significant attention has been given toward the utilization of ATP as a possible method to determine if biomass quantity can be used to predict filter performance. Of the three BAC medias tested, Jacobi media had the highest ATP yearly concentration compared to the Norit 300 and Calgon 300 (Figure 26).

Regarding the lower ATP observed during summer months and the significantly higher ATP concentrations observed in the winter months, several authors have noted that metabolism slows during colder temperatures, and subsequently, reduced removal of DOC and other contaminants occurs. The reduction of removal has often been associated with reduced metabolism of the biomass associated with the filter media.

In a study conducted at the Moorhead Wastewater Plant, biomass decreased during summer months when warmer temperatures were observed in the influent of the Moorhead Wastewater Plant (Bjornberg 2009). A possible explanation is that because metabolism is typically faster in the summer the system potentially supports lower biomass; whereas slower metabolism may support higher biomass levels in winter months. The explanation of slower metabolism supporting higher biomass for the Moorhead Wastewater plant may help explain the higher ATP data during the winter of this study.

Because higher ATP was observed in anthracite as compared to BAC media, and this did not support the hypothesis that higher biomass would be associated with higher organic removal,

further investigation into the quantification of Biomass with SEM, Confocal microscopy, and qPCR was completed.

5.3.2. ATP and Correlation with Organics Removal

Significant effort within the drinking water research field have tried to correlate DOC removal with total biomass concentration (Moll et al. 1999; Pharand et al. 2014; Wang et al. 1995). Making the correlation between removal of DOC with biomass has proven difficult, as numerous operating conditions such as backwashing, temperature, and EBCT can have operational impacts to the biomass associated with the filter media. Effort was made within this study to correlate TOC removal to observed ATP, but no significant correlation could be found for comparison of ATP data to organics removed for anthracite from 4/11/2018 to 11/01/2018 (Figure 27). For the Norit GAC, there is slight upward trend for organics removal, although the correlation between ATP and organics removal is weak (Figure 28).

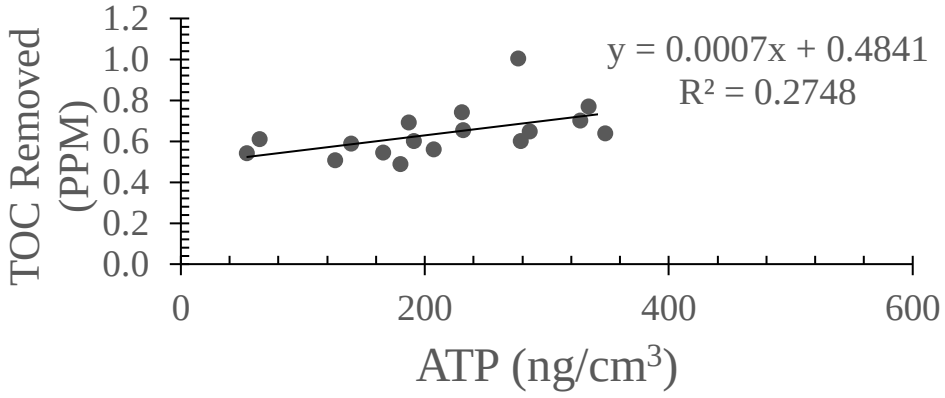

Figure 27: TOC Removed (PPM) vs ATP (ng/cm^3) for Norit Filter 3 for Period of 4/11/2018 to 10/30/2018

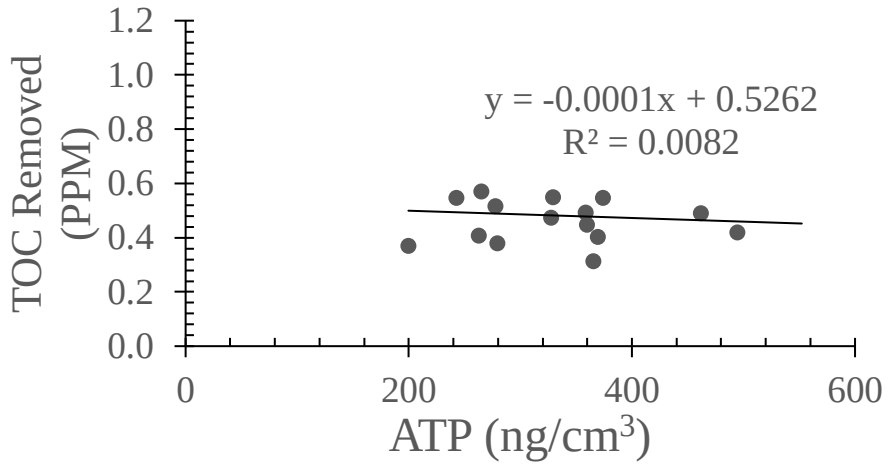

Figure 28: TOC Removed (PPM) vs ATP (ng/cm^3) for Filter 5 for Period of 4/11/2018 to 10/30/2018

5.3.3. SEM Analysis of Filter Media

SEM analysis of biofilm on GAC and anthracite samples was performed to understand the biomass abundance, surface coverage, and impact of surface morphology of the media on biofilm attachment. In addition, because initial ATP collected in study suggested that anthracite biomass concentrations were higher than that of BAC filters, SEM was used to test if more biomass was present on the anthracite in comparison to GAC. Images were collected of both the colonized and virgin media to understand how surface morphology impacts the attachment of biomass over the course of operation. Sample of uncolonized (virgin) media were collected and analyzed at 30 and 1500 magnification. As observed in the 30 magnification, the media particles for Jacobi and Anthracite appear to have a similar particle shape and smooth surface texture as shown in Figure 29. In comparison, media for the Norit 300 and Calgon F300 appear to have a rougher outer surface with greater variation in surface morphology (Figure 30).

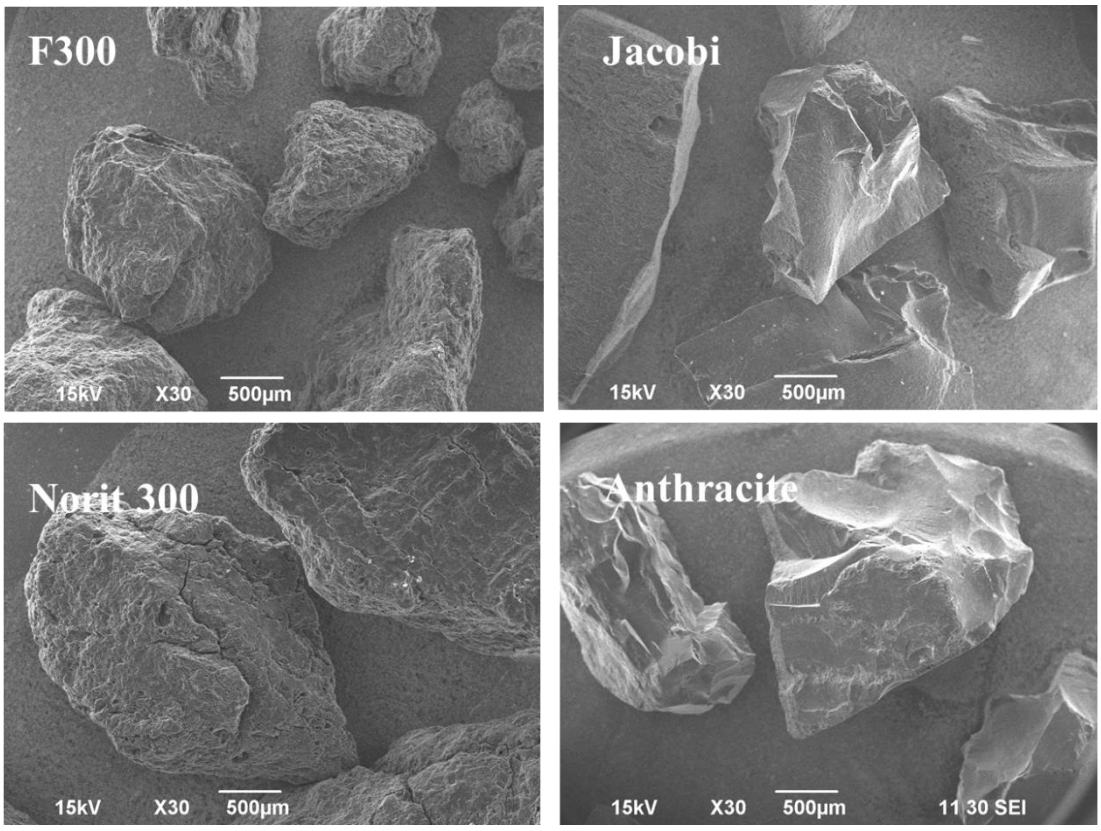

Figure 29: SEM Images of Virgin Pilot Filter Media at 30x

Virgin media was also analyzed at 1500 magnification to determine the respective microstructure of the media, and how the microstructure would potentially influence the attachment of biomass. The microstructure of both Calgon F300 and Norit 300 demonstrate unique surface morphology at the 1500 resolution. Interestingly, the Calgon F300 microstructure displays more heterogenous surface morphology in comparison to the Norit 300. One of the reasons for the more diverse surface morphology on the Calgon F300 in comparison to the Norit 300 is that the Calgon 300 was manufactured using reagglomeration, which combines previous crushed GAC particles using a binder. The Jacobi media has a unique microstructure due the relatively smooth exterior structure and the presence of channels. The presence of channels within the microstructure is likely due to the base material for the carbon, which is coconut shell. Channels have been observed in other SEM studies of coconut husk GAC filter material. (Li et al. 2011)

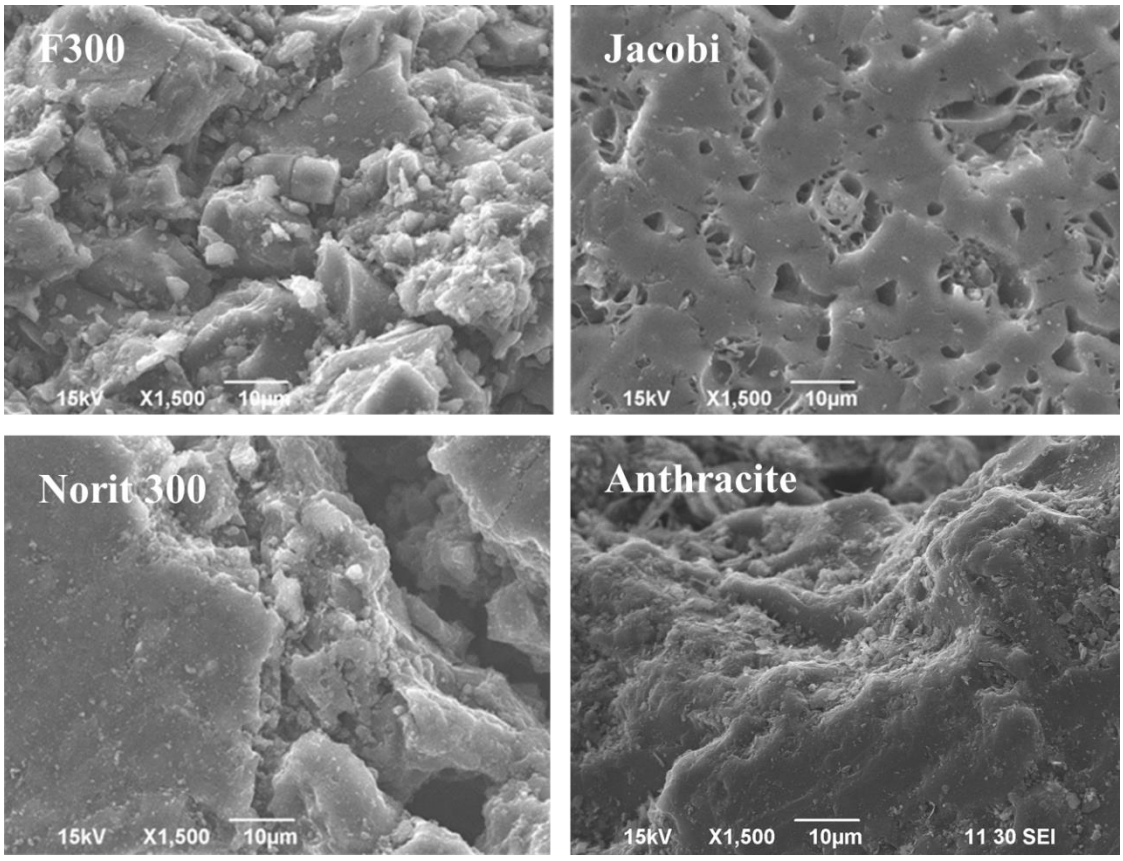

Figure 30: SEM Images of Virgin Pilot Filter Media at 1500x

After a period of 10 months of operation, samples were collected at 8-inch and 26-inch depths to determine the biomass coverage and appearance on the filter media. SEM was utilized also used to determine if ATP measurements were representative of the total amount of biomass present within the filtration media. At the 8-inch depth, F300 and Norit 300 appear to have significant biomass coverage, with what appear to be filamentous growth patterns on the surface of the Calgon F300 and the Norit 300 media. It appears the Jacobi media has somewhat sparse biofilm coverage at the 1500 magnification level. The anthracite media also appears to have biofilm coverage, with the appearance of less filamentous structures than the F300. Additional images of the anthracite and F300 media were taken using confocal imagery, which is shown in Appendix A6 and A7. It should be noted that debris and other material can complicate the analysis of how much biofilm is observed in the SEM analysis of the colonized samples. In addition,

because SEM is a destructive method, it is impossible to determine what biomass is viable. Because on a few sections of the media particle were viewed, the SEM analysis is dependent on only the areas of the particle viewed, which may not be representative of the entire particle.

However, it appears as though the F300 and Norit 300 BAC media had significantly more biomass coverage than that of Jacobi BAC or anthracite (Figure 31). In addition, the confocal data collected also indicated more biomass coverage on F300 in comparison to the anthracite media. Because ATP can be significantly bound by BAC media, it appears as though the biomass as measured by the ATP method for BAC media was significantly underrepresented.

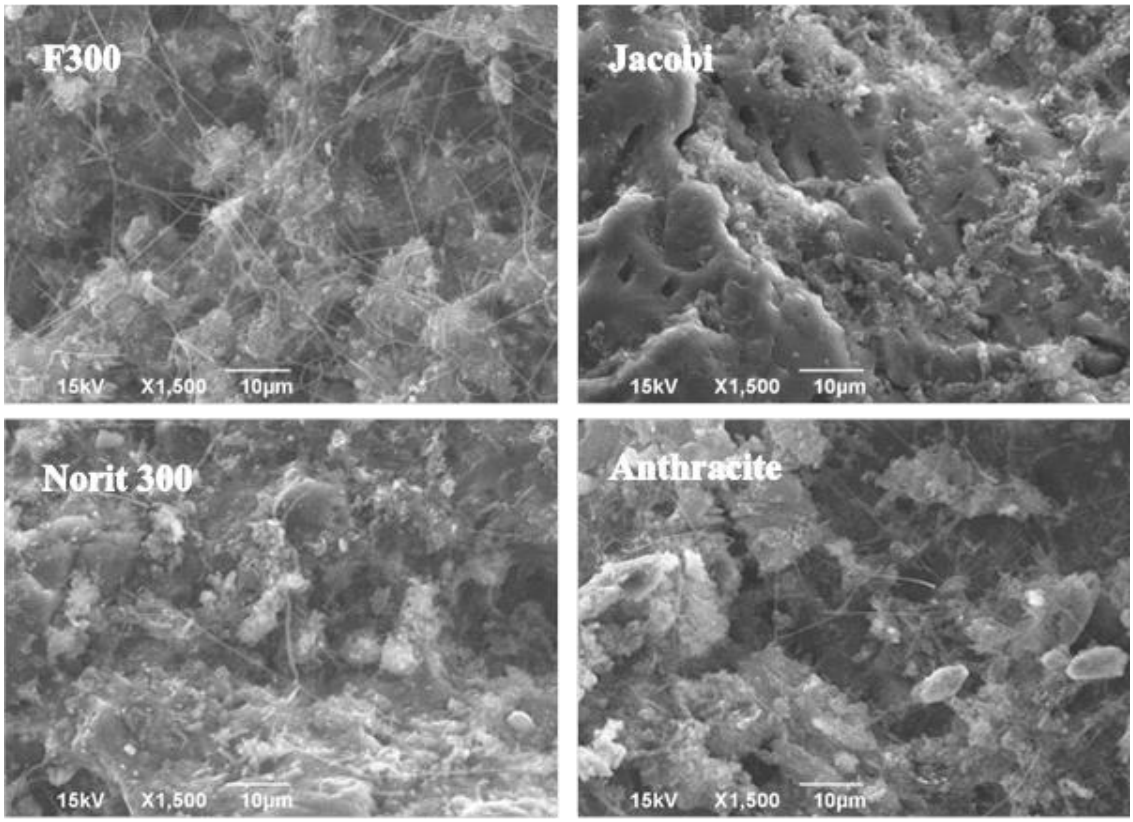

Figure 31: SEM Images of Colonized Pilot Filter Media Sampled at 8-inch Bed Depths at 1,500x Magnification

Although not visible in the coverage image observed in Figure 31, further images of the colonized Jacobi channels were taken to observe if biomass could penetrate the channels within the Jacobi media. To obtain the data, the sample was embedded in epoxy and polished with a cross-

sectional beam of argon to determine the depth of penetration of organisms within the channel. In Figure 32, a variety of different magnification levels were obtained on a channel within the media. As observed in Panel C and Panel D images, it appears as though biomass can penetrate approximately 50µm in diameter channels, the presence of biomass could be fibers or another biological material.

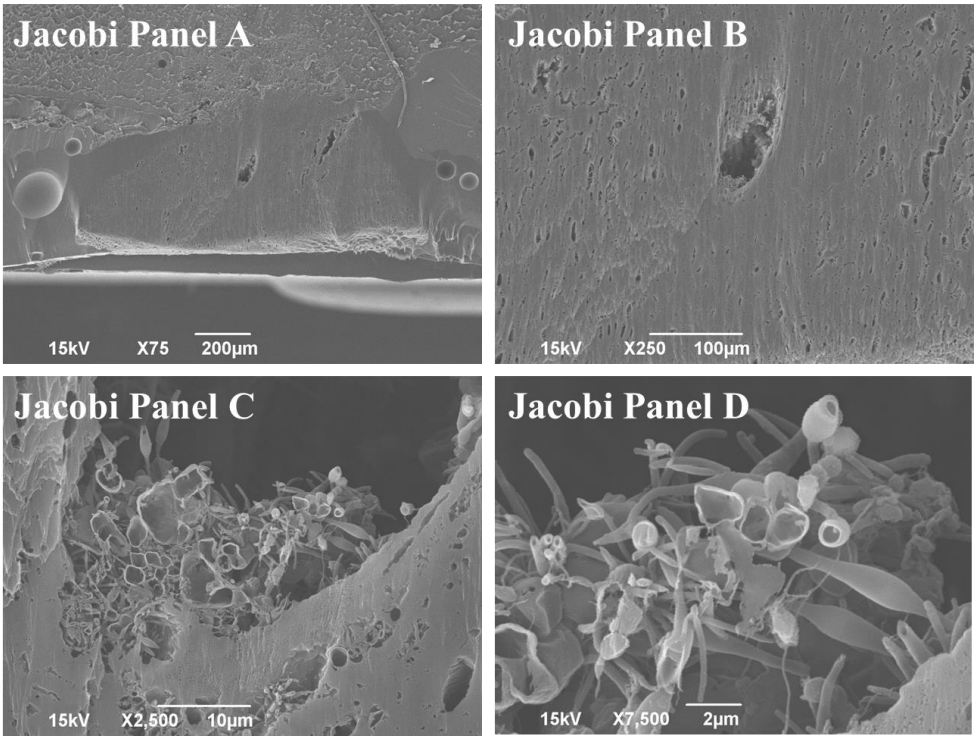

Figure 32: SEM Images of Channel Within Jacobi Media. Jacobi Panel A is 75x Magnification, Jacobi Panel B is 250x Magnification, Jacobi Panel C is 2500x Magnification, and Jacobi Panel D is 7500x Magnification

For the 26-inch depth samples, it appears as though significantly less biomass is present for all samples. Interestingly, the presence of filamentous biofilm is absent for the Calgon F300 and less coverage is present for the Norit 300 and Calgon 300. It also appears that less coverage is present for the Jacobi and anthracite media for the 26 inch depth (Figure 33).

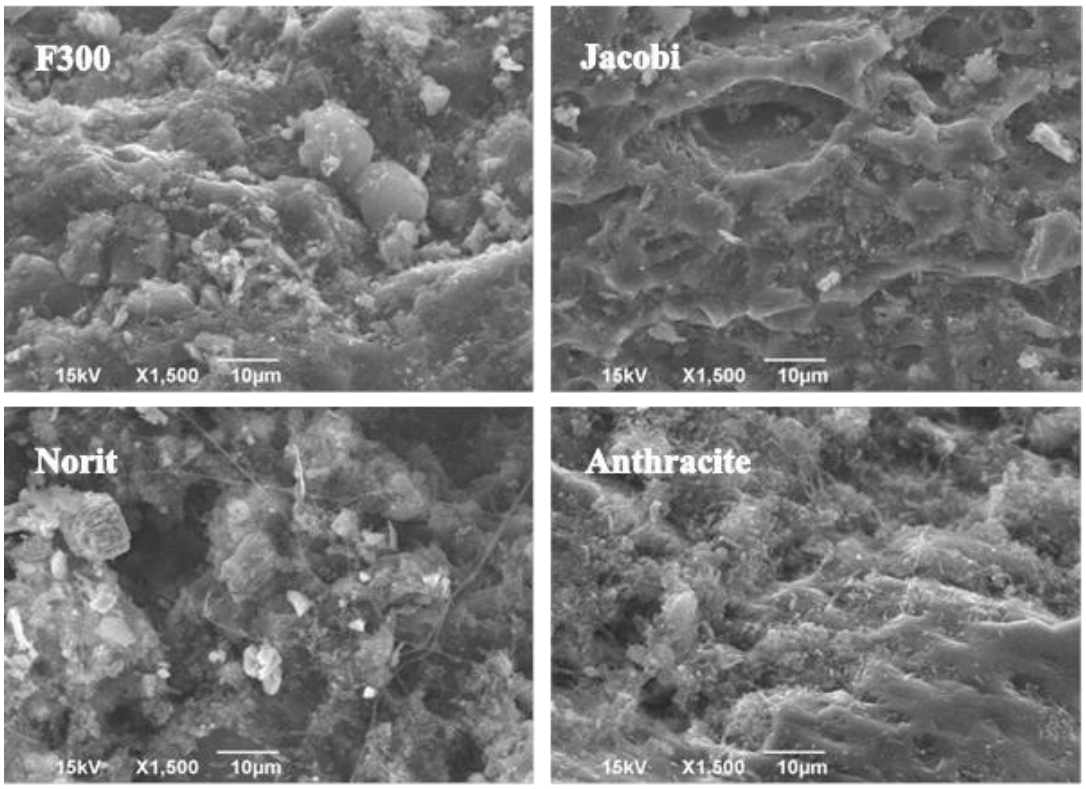

Figure 33: SEM Images of Colonized Pilot Filter Media Sampled at 26-inch Bed Depths at 1,500x Magnification

In addition to the GAC and anthracite media samples, a sand sample was also collected from the anthracite/sand filter. The sand sample appeared to have some biomass, but a significant amount of debris was also present (Figure 34). It appears some colonies are present on the sand sample. It should be noted for all the SEM samples that the biomass images are merely "a snapshot" of the biofilm on the particle and may not necessarily represent the biofilm coverage of the entirety of the particle.

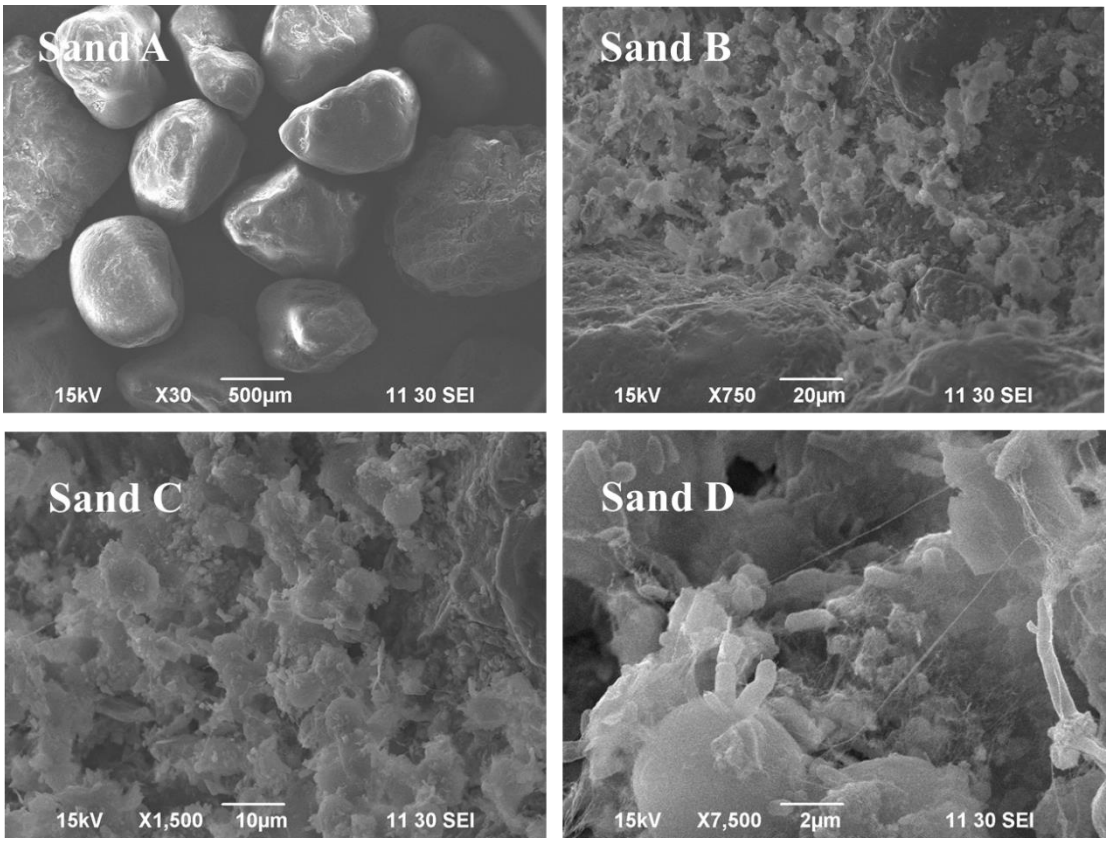

Figure 34: SEM Images of Colonized Sand at the Following Magnification Levels. Sand A 30x, Sand B 750x, Sand C 1500x, Sand D 7500x

5.3.4. qPCR Community Composition Analysis

Further investigation into the microbial community was investigated using qPCR was for high-throughput Illumina sequencing of PCR amplified 16S rRNA genes. A better understanding of the microbial community of each of the five columns, in addition to the changes of the microbial community associated with the depth of the filter profile was desired to determine if the community could have a relationship to filter performance. Using the community composition data, diversity of the community could be analyzed, so that a better understanding of how the filters respond to operational changes within the filtration system. In addition, real-time qPCR was utilized to quantify the 16S rRNA gene present within the biomass.

5.3.4.1. qPCR Community Composition Analysis for All Five Columns

Community qPCR composition sampling was conducted for all five columns on July 30, 2019. Results of these tests are shown in Figure 35, Figure 36, and Figure 37. The most dominant phylum in the analysis was *Proteobacteria* which made up 50.9 %, 54.6 %, 50.0 %, 24.7 % and 55.5 % of the community for Filters 1-5, which includes the Calgon F300 GAC, Jacobi, and Norit 300, Calgon 300-sand and anthracite-sand filters respectively. *Bacteroidetes* was the second highest at 14.07%, 16.27%, 15.87%, 18.75%, 18.9% for Calgon F300 GAC, Jacobi, and Norit 300 GAC filters, Calgon 300/sand and anthracite filters, respectively. It is not particularly surprising that Phylum *Proteobacteria* is the most dominant Phylum found within the PFS media, as it has been found to be the dominant phylum within drinking other water biofilters (Liao et al. 2013). Several studies have shown that subcategories of *Proteobacteria* (*Alpha-*, *Beta-*, and *Gamma-Proteobacteria*) can shift in abundance as a result of DOC and ammonia nitrogen within the influents of the sample (Liao et al. 2013). The second most common phyla present, *Bacteroidetes,* have been uniquely identified to function in the removal of high molecular weight organic compounds (Thomas et al. 2011). *Bacteroidetes* are also commonly found within the environment, often identified within the rhizosphere, as well as marine environments.

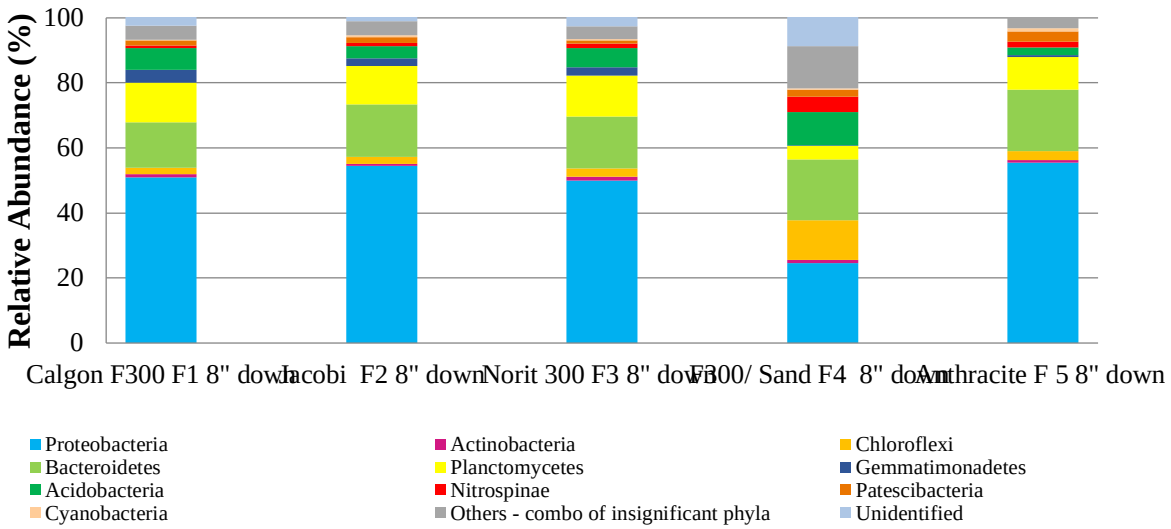

Figure 35: Phylum qPCR Data for All 5 Columns Sampled on 7.30.2019

5.3.4.2. qPCR Community Composition Analysis for Anthracite Depth Sample

Additional qPCR analysis was also conducted on Norit 300 (Filter 3) and Anthracite (Filter 5) media to determine the abundance of respective phyla in the depth of the media of the filter. The analysis collected samples for the depths of 8 inches, 14 inches, 26 inches and 32 inches from the top of the media surface for each of the respective columns. As depth from the top increased for the anthracite column, Proteobacteria decreased (48.45, 46.15, 45.55, 40.71). Interestingly, *Planctomycetes* was more prevalent in the filter depths as depth increased from the top of the media for the depths of 8 inches, 14 inches, 26 inches and 32 inches, planctomycetes went from 9.92%, 9.73%, 17.11%, 21.01%. *Plactomycetes* are a unique divergent phylum of bacteria that have a variety of unique properties such cell compartmentalization and the ability of certain species, such as anammox planctomycetes, to complete ammonia oxidation in anoxic environments. It should be noted that anammox was not found in the anthracite sample.

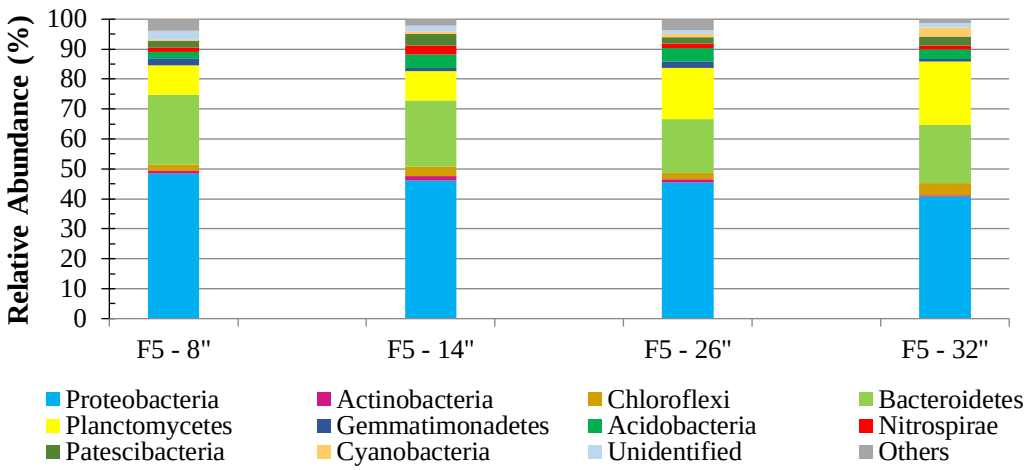

Figure 36: Anthracite-Sand qPCR Depth Profile

5.3.4.3. qPCR Community Composition Analysis for Norit BAC Filter Depth Sample

qPCR analysis was also conducted on the Norit BAC sample. As depth from the top increased for the anthracite-sand column, *Proteobacteria* increased (46.89, 50.73, 51.77, 61.18). The *Proteobacteria* showed an opposite trend to the anthracite-sand column, in which Proteobacteria decreased as depth in the column increased. Generally, *Proteobacteria* consist of a wide variety of organisms, some of which are responsible for nitrogen-fixation. The second most dominant phylum in the depth sample for the Norit BAC filter was *Bacteroidetes*, which decreased in the filter column as depth increased, (21.97,15.99, 14.38, 14.17). Interestingly, the decrease in *Bacteroidetes* could possibly due to the relative decrease of available BOM as the filter depth increases.

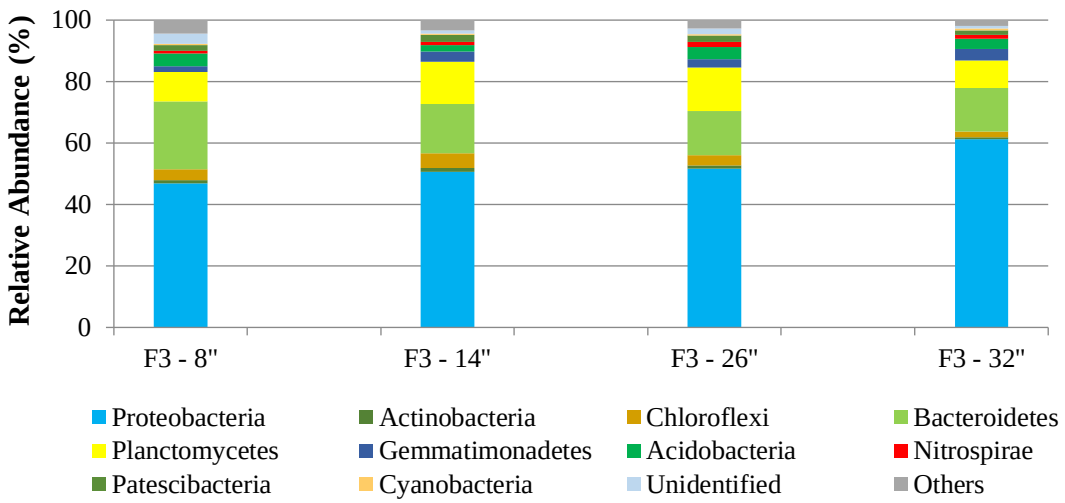

Figure 37: Norit 300 qPCR Depth Profile

5.3.5. Shannon Index of 5 PFS Columns

The Shannon index is a tool commonly used to measure biological diversity within a biological community. The qPCR data obtained from the depth samples and all 5 columns was compared to see if biological diversity changes within the depth of the profile of the filter. Within the Luminultra provided dataset, a total 468 genus level sequence-abundance data were given and utilized for analysis. For the five filters sampled, the number of genus level sequences identified within each of the columns was F1: 282; F2: 250; F3: 211; F4: 211; and F5: 197 (Table 15). For the five filters sampled, the values for Shannon Index f were as follows: F1: 4.81, F2: 4.73, F3: 4.61, F4: 4.43, F5: 4.54 as listed in Figure 38 and Table 15.

Table 15: Genus Level Sequences Detected and Shannon Index Values for Columns 1-5

Column	Genus Level Sequences Detected	Shannon Index value
1	282	4.81
2	250	4.73
3	211	4.63
4	211	4.43
5	197	4.51

Filters 1-5 all had very similar Shannon index values within a range of 4.43-4.81, while Filter 1 was noticeably higher at 4.81. It is unclear as to why the Shannon index value for Filter 4 was lower than other columns, as it would have been expected to have a comparable index value to Filter 1 as they were comprised of the same filter media. Samples completed for the depth study (Figure 39) were collected one month later (August 26th, 2019) and demonstrated values of 4.73 for Filter 3 and 4.90 for Filter 5 which were close to the values obtained in this study of 4.61 for Filter 3 and 4.5 for Filter 5 in the Samples taken on July 30th, 2019. The similar values for Shannon index for Filters 3 and 5 over a monthlong period suggest that the bacterial community is stable over a relatively static temperature range. In a similar study, significant variations of Shannon index were noted for a BAC as a result of seasonal variation, where higher values of the Shannon index were recorded for the BAC filter in the summer in comparison to winter. (Strait 2015).

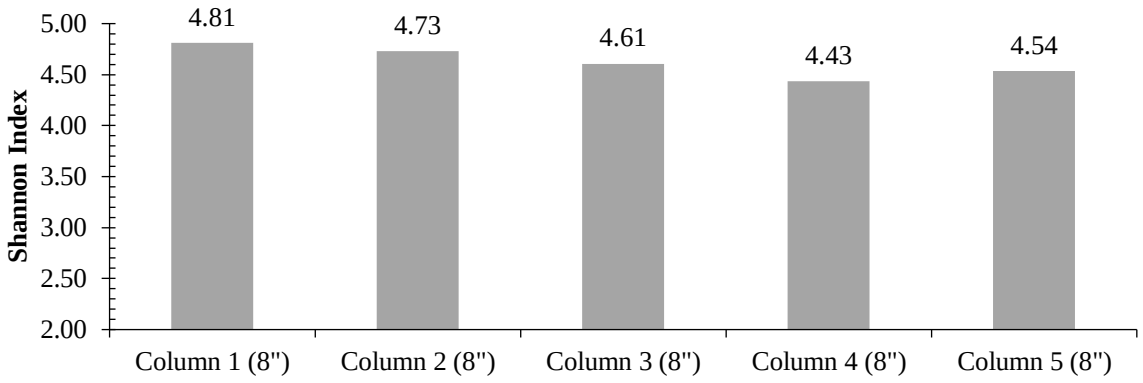

Figure 38: Shannon Index for All Five Columns Sampled at 8-inch Depth

The Shannon index values obtained from this study was comparable to other values for filter media. For example, a study in Minneapolis, MN obtained a Shannon index value of 3.5 for GAC filters and 4.5 for anthracite filters. (Strait 2015). The values observed within the MWTP for both the anthracite and BAC filter media for Shannon index are similar to values obtained for other studies testing GAC media, and significantly higher than samples for tap water (Revetta et al. 2010). The values obtained for the MWTP Shannon index indicate that the PFS biomass has a

substantial amount of diversity and suggests that the biomass should be capable of withstanding a variety of operational conditions. In contrast to several studies, ozone was utilized as pre-oxidant in this study. One of the additional factors that could lead to less diversity within the biomass of the filter media is the use of ozone prior to filtration within this study. In one study, ozone was used as a pre and post oxidant and the Shannon index was slightly less for the ozonated water than untreated influent (6.17 vs 7.06) (Liao et al. 2013). The use of ozone prior to filtration could have preselected the bacterial community that could exist within the filtration media by differentially inactivating microorganisms prior to filtration. The similarity in diversity between the columns profiles suggest that although the filter medias tested all have different morphology and adsorptive properties), that the diversity between columns is similar.

5.3.6. Shannon Index Filter 3 and Filter 5

Shannon index was also carried out on the depth profile of Filter 3 (Norit) and Filter 5 (Anthracite-sand). The Shannon index was calculated on 385 genus sequences provided within the Luminultra dataset which was the total amount of sequences detected in the analysis. For the depths of 8 inches, 14 inches, 26 inches and 32 inches on the anthracite-sand the number of genus level species identified through qPCR sequencing was 257 for 8 inch depth, 165 for 14 inch depth, 158 for 26 inch, and 137 for 32 inch depth (Table 16). For the depths of 8 inches, 14 inches, 26 inches and 32 inches on the Norit GAC the number of species identified through qPCR sequencing was 198 for the 8 inch depth, 158 for 14 inch depth, 210 for 26 inch, and 180 for 32 inch depth. Shannon Index values for F3 column were as follows: 4.73, 4.50, 4.65, 4.55 whereas the anthracite-sand column (F5) had values of 4.90, 4.54, 4.55, 4.27 (Figure 39).

Table 16: Genus Level Sequences Detected and Shannon Index Value for Depth Analysis

Depth	Anthracite-Sand Genus Level Sequences Detected	Anthracite-Sand Shannon Index value	Norit Genus Level Sequences Detected	Norit Genus Level Sequences Detected
8”	257	4.90	198	4.73
14”	165	4.54	158	4.50
26”	158	4.55	210	4.65
32”	137	4.27	180	4.55

One of the interesting findings from this study was the relative decrease of Shannon diversity as the depth from the top of the filter increases for the anthracite-sand (F5) column. Interestingly, for column F3, the diversity decreased from 8” to 14”, but then increased at the 26” level followed by a decrease to 4.55 at the 32” level. The minor decrease in diversity could be attributable to less phyla of bacteria being well suited to an environment at the lower depths of the filter column which may have less nutrients present. The interpretation of the significance of the decrease is limited by the lack of replicates within the dataset. Replicates were not completed on the qPCR dataset due to the expense associated with the analysis. Both the anthracite-sand and Norit BAC column supported similar levels of diversity at the top of the respective columns for each of the filter types.

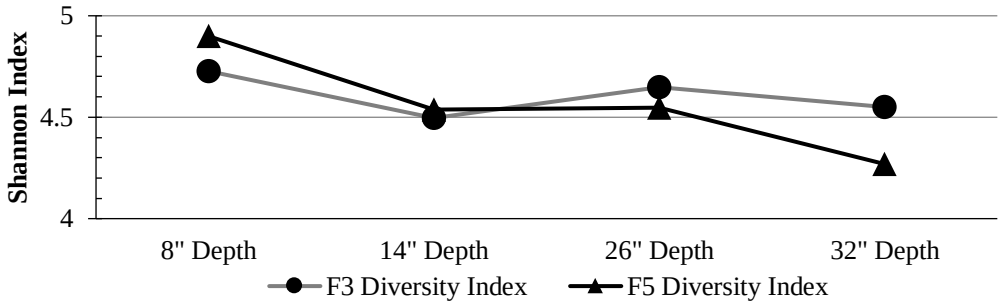

Figure 39: Shannon Index for Depth Samples for Norit (F3) and Anthracite-Sand (F5)

The author is not aware of any studies that have evaluated the diversity of the biomass as column depths increase for either anthracite or GAC.

5.3.7. ATP and qPCR Quantification Comparison

ATP and qPCR analysis for the 16S rRNA gene was also conducted on anthracite-sand and Norit 300 media to determine the total biomass in the depth of the media of the column. Samples were collected at depths of 8", 14", 26" and 32", and split for analysis by both ATP and qPCR analysis. It should be noted for the 26" and 32" depths for the anthracite-sand column were in the sand layer. The purpose of the experiment was to determine if biomass was at the top of the filer and to determine if biomass decreased as the depth from the top of the filter media increased. Both the ATP and qPCR suggest that the biomass in anthracite-sand column decreases in a linear manner (Figure 40). In similar studies, ATP has been measured through the profile of the filter column for other anthracite-sand columns and has been observed to decrease (Pharand et al. 2014).

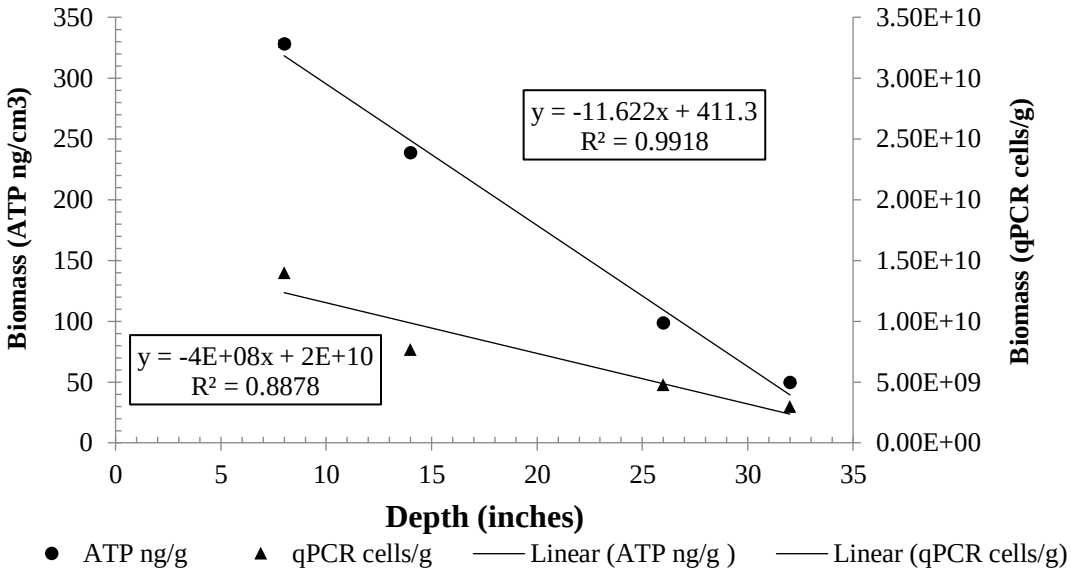

Figure 40: qPCR for 16S rRNA and ATP Comparison for Anthracite-Sand

For the analysis on the Norit media (Column 3), the ATP results showed a linear decrease with column depth, whereas no clear trend for the 16S rRNA was observed (Figure 41). The ATP

method showed relatively linear decreases for both the Anthracite-Sand and BAC filters, whereas the qPCR 16S rRNA showed a linear decrease for the ATP method, with no significant decrease observed for biomass with the qPCR method for column 3. Further investigation into the use of 16S rRNA as a surrogate for total biomass is warranted as the tool has yet to be used extensively with drinking water filtration media. A possibility for future research would be to continue the investigation of qPCR and if the qPCR method correlates to ATP for both sorptive and non-sorptive media.

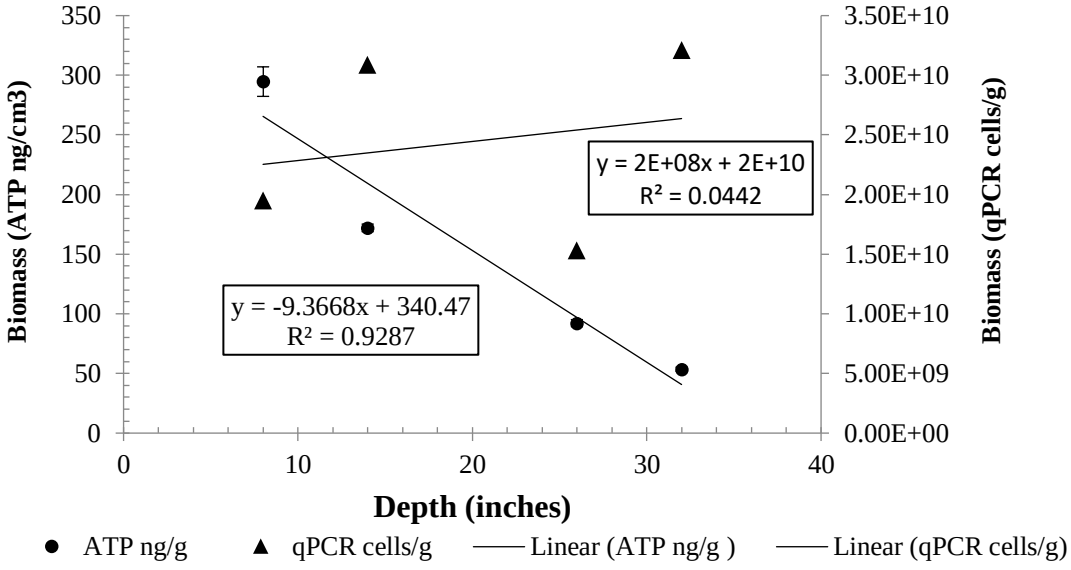

Figure 41: qPCR for 16S rRNA and ATP Comparison for Norit 300 (Filter 3)

5.4. Previous Research on Taste and Odor

In year-one of the PFS study, significant analysis was completed on the taste and odor compound removal in the PFS system. During the first year, three challenge tests were conducted during a variety of operational conditions and temperatures. The purpose of the challenge tests performed within year one off the study included the following three research objectives: determine if geosmin was more effectively removed by GAC in comparison to anthracite/sand; to determine whether adsorption or biodegradation is the mechanism of removal for GAC; and to

determine which GAC provided the highest removal. As noted in (von Hagen 2019), the most effective media for removal of Geosmin was Norit (Filter 3). The summary of removal percentages for the three challenge tests performed are listed in Table 17.

Table 17: Experimental Conditions of EBCT Challenge Test. Summary of Challenge Test Data (Adapted from von Hagen 2019)

Challenge Test Number	Temperature Range of Study	Filter 3[Gesomin] Effluent/ Removal Percentage	Filter 5 [Gesomin] Effluent / Removal Percentage
1	53.8 to 48.3°F	4.2 ng/L (98.3% removal)	192 ng/L (16.5% removal)
2	Below 50°F.	33.4 ng/L (82.2% removal)	150 ng/L (16.1% removal)
3	Above 68 F	11.4 ng/L (90.5% removal)	107 ng/L (6.3% removal)

Previous taste and odor testing had been completed by (von Hagen 2019) to show that geosmin was significantly removed by BAC filters. Of the BAC filters tested, Norit 300 (Filter 3) provided the highest removal percentage. The conclusion of the previous research was that colder temperatures may have reduced the intraparticle rate of adsorption, thus reducing the removal efficiency which is observed in Table 17. Over the course of the two-year study, Norit was determined to be the most effective BAC of the three BAC medias tested at removing geosmin, and was the media selected to be installed in the full scale MWTP installation (Table 17). Additional testing was desired to determine the impact of EBCT on geosmin removal.

5.5. EBCT Evaluation of Filter 3 (Norit) and Filter 5 (Anthracite)

EBCT is an important factor when designing GAC filters or GAC contactors, as such, evaluation of the impact of EBCT on taste and odor compounds was valuable because it can be used for the design of future WTP expansions, which is likely planned for the MWTP in the next 10 to 15 years. In addition, understanding the impact of EBCT can help optimize the existing operation of the MWTP. Because taste and odor events are likely transient events (usually several days up to two weeks), functionally, the MWTP could also alter flow rates into the plant, such-

that when taste and odor events occur, flows though the MWTP could accordingly be adjusted to lower flow rates which would result in higher EBCTs.

EBCT is an important factor for removal of compounds because longer EBCT times have been shown to increase removal percentage. For example, in one study a EBCT of 20 minutes was show to completely remove geosmin (Drikas et al. 2009). To study the impact of EBCT on geosmin removal efficiency rates, a challenge test was conducted over a between July 22nd and August 26th, 2019, during which the temperatures remained relatively constant with an average temperature over the period of 73°F, with a minimum of 68°F and a maximum of 75°F.

Table 18: Experimental Conditions of EBCT Challenge Test for Column 3.

Time Period	EBCT	Flow Rate Per Column (gpm)	Average Influent Geosmin Concentration (ng/L)	Average Removal Percentage	Average Removal Standard Deviation (%)
July 22nd to July 29th	15.3	0.5	204	98.4	0.31
July 29th to August 5th	10.2	0.75	294	96.5	1.01
August 5th to August 12th	6.1	1.0	280	87.6	1.17
August 12th to August 19th	4.4	1.25	331	72.7	2.68
August 20th to August 26th	15.3	0.5	309	91.9	1.65

The geosmin concentration throughout the course of the EBCT challenge test varied from 204 ng/L to 331 ng/L (Table 18). Due to the low concentration of geosmin pumped to the column, it was often difficult to maintain a consistent geosmin concentration for the column influent. Over the course of the monthlong EBCT trial, the anthracite-sand column achieved an average removal percentage of 4.59%, which agrees with previous challenge tests that indicated a removal in the 6% to 16% range. It should be expected that the anthracite-sand column exhibits very little removal of geosmin, as the anthracite is a non-sorptive media.

Because Norit 300 was selected for utilization within the MWTP, the EBCT analysis was conducted on only Column 3 and Column 5. For Column 3, as the EBCT increased, the corresponding removal percentage of geosmin decreased as EBCT increased through the study (Figure 42). Raw data for the trial is provided in Appendix Table 1A. Removal percentages for Geosmin are shown in Figure 43. Following completion of the lowest EBCT of 4.4, the flow rate was set to 0.5 and the EBCT was at 15. The removal percentage observed for the last trial of an EBCT of 15 did not fully recover the removal percentage demonstrated in the beginning of the study 98.4% vs 91.9%, respectively. One of the possible reasons that the percentage removal did not fully is the possibility of desorption from the column.

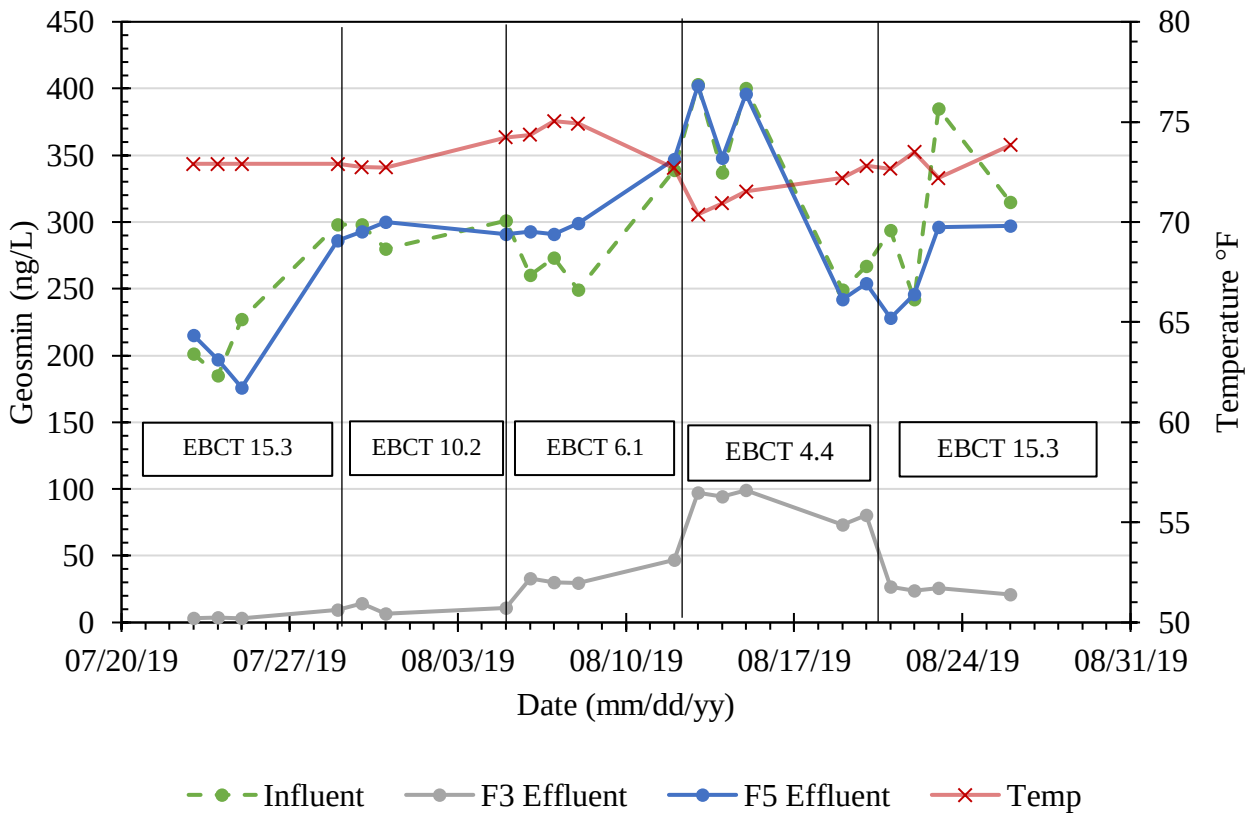

Figure 42: Geosmin Challenge Test with EBCT Variation

Geosmin samples were also taken at various depths to determine where most of the removal of geosmin occurs within Filter 3. For the EBCT values of 15.3, 10.2, and 6.1 percentage removal through the depth of the column at depths of 8",14", and 22", 26" and 36" were collected (Figure 43). As EBCT increases more removal is gained in the 8" and 14" depths for the Norit column (Figure 44). Very little removal takes place between the 26' and 36" depth, indicating that the use of 24" of Norit media within the WTP will likely provide adequate geosmin removal for most flow conditions.

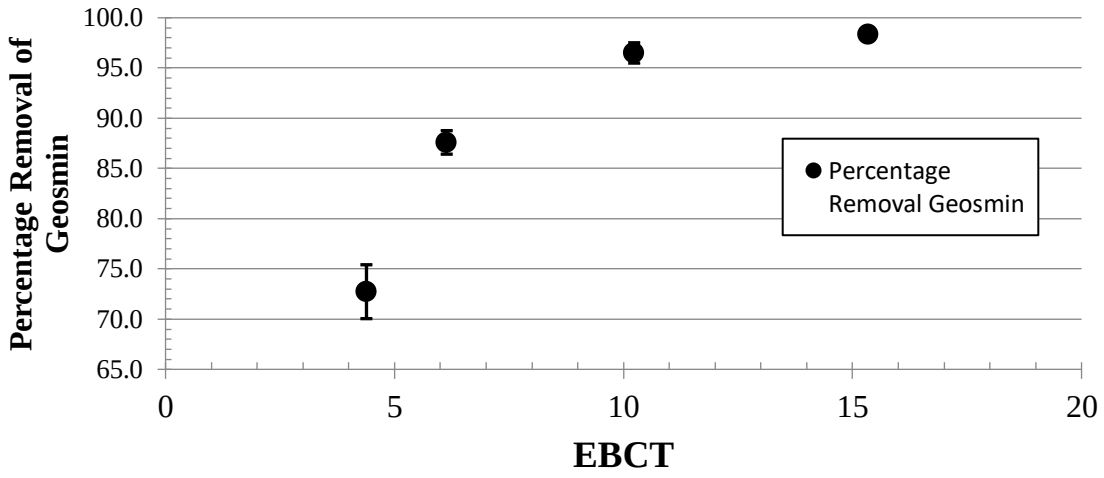

Figure 43: Geosmin Challenge Test with EBCT Variation for Column 3

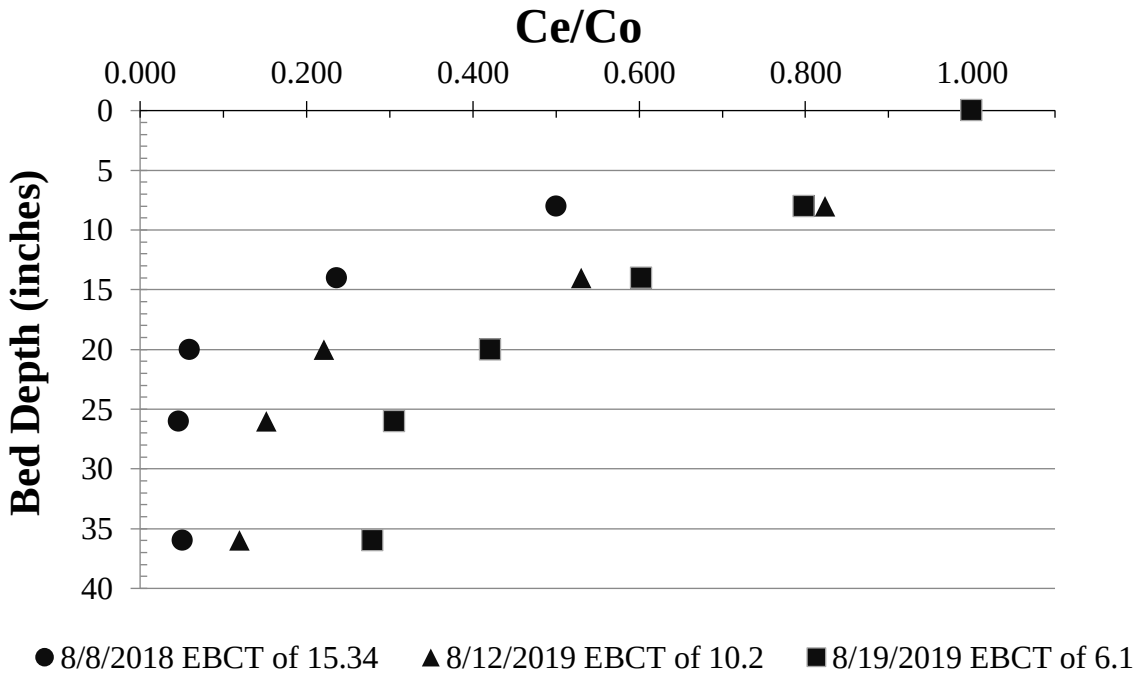

Figure 44: Geosmin Challenge Test with EBCT Variation

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The purpose of this study was to determine the biomass associated with several different types of filter media within a two-year PFS study at the MWTP and to determine if biomass could be correlated to organics removal with the PFS. In addition to the determination of biomass by ATP, qPCR, and SEM was also performed. To validate the results of year 1 of the PFS study, analysis of the effluent turbidity was also performed.

- Turbidity:
    - Turbidity was very similar for all five columns over the course of the two-year study, suggesting that the larger grain size associated with BAC media provides comparable performance to that of anthracite media, which has a much smaller grain size.
- Organics Removal:
    - Organics removal over the course of the two-year study was significantly higher for the Norit-300 BAC filter in comparison to the anthracite-sand filter as determined by TOC and UV removal.
    - Organics removal over the course of the two-year study was significantly higher in the summer compared to the winter for both the anthracite-sand column and the Norit BAC column.
- ATP Analysis of Biomass:
    - The highest ATP concentrations for the two-year study were on anthracite media, with a yearly average of F5 393 ± 29 ng ATP/cm^3. Although anthracite had significantly higher ATP than all filters over the course of the two-year study, SEM and confocal

analysis did not validate that more biomass was present on the anthracite media in comparison to the BAC media.

  - ATP measurements on BAC media was complicated by the adsorptive nature of GAC. Of the three BAC medias tested, Jacobi media had the highest ATP yearly concentration compared to the Norit 300 and Calgon 300, which had the lowest ATP measurements.
  - ATP analysis did not show strong correlation with organics removal for either Norit 300 or anthracite filters, suggesting that the ATP method may have significant limitations for determination of biomass on filtration media and may underrepresent the amount of biomass associated with the filtration media.

- SEM Analysis of BAC Media:
  - As observed in the SEM analysis, the media particles for Jacobi and Anthracite appear to have a similar particle shape and smooth surface texture, whereas the Norit 300 and Calgon F300 appear to have a rougher outer surface with greater variation in surface morphology.
  - After colonization of the filter media, Norit 300 and Calgon 300 appear to have more biomass than anthracite media as determined by SEM.
- Biomass and Organic Removal
  - Effort was made within this study to correlate TOC removal to observed ATP, but no significant correlation could be found for comparison of ATP data to organics removed for anthracite. For the Norit GAC, the correlation between ATP and organics removal is weak

- qPCR analysis of 16S rRNA and ATP Comparison
    - Both qPCR and ATP decreased in a linear fashion for the anthracite-sand column, but only ATP decreased in a linear fashion for the Norit BAC column. Further investigation into the correlation between qPCR and ATP is needed for sorptive media.
    - Shannon Index values for all the columns measured at 8-inch depth was similar. Diversity in the anthracite-sand column decreased as the depth increased, suggesting that decreased nutrient availability through the profile of the filter decreases biodiversity. Diversity for the Norit BAC column was similar throughout the depth of filter profile.
- Evaluation of EBCT for T/O Removal
    - During the EBCT challenge test, EBCT values were shown to significantly increase geosmin removal in the Norit BAC filter. EBCT showed only a small percentage of removal of geosmin in the anthracite-sand filter.

6.2. Recommendations for Future Work

At the writing of this document, the MWTP is currently installing Norit 300 as a replacement for the anthracite media that was installed as part of the original MWTP. As the new Norit GAC is installed, it would be beneficial to analyze how long it takes for biomass to be established in the full-scale MWTP. Once biomass is established within the new media, ATP testing on the top of the filtration media should continue until it has been determined that a baseline level of biomass is established.

One of the limitations of the study was that water that fed the PFS system warmed significantly as it was pumped into the PFS columns. The warming of water during winter conditions could potentially have enhanced biomass growth on PFS media when colder

temperatures are observed within the full-scale MWTP. When Norit is implemented in the full scale MWTP, care should be taken to monitor biomass within the full-scale system to see if biomass levels on the full-scale plant are the PFS system are comparable to what was observed within the PFS. More trials of 16S rRNA should be done on the full-scale implementation of GAC to see if 16S rRNA correlates to ATP. In addition, it would be beneficial to conduct biomass testing within the distribution system to determine if the biodiversity found within the pilot system matches the biodiversity found within the distribution system.

If the PFS can be utilized in the future, it would be useful to study the stratification of backwash to determine if biomass changes significantly before and after backwash. In addition, it would be useful to continue to study the continued removal of geosmin in the PFS. If possible, it would also be helpful to determine if the utilization of non-chloraminated water for backwash could be used to enhance the biomass. Further study is needed to determine the impact of non-chloraminated water for backwash changes the total amount and community composition of biomass.

Another possibility for future research would be to investigate if the Shannon index values change seasonally and if those seasonal changes correspond to values of ATP on the filter media. Some studies have indicated that the Shannon index for filter media changes seasonally.

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APPENDIX A. EBCT CHALLENGE TEST DATA

Date Sampled	Time Sampled	Sample Description	GSM (ng/L)
07/23/19	4:00 PM	Common Filter Influent	201
07/23/19	4:05 PM	Filter 3 Effluent	3.12
07/23/19	4:10 PM	Filter 5 Effluent	215
07/24/19	5:00 PM	Common Filter Influent	185
07/24/19	5:05 PM	Filter 3 Effluent	3.66
07/24/19	5:10 PM	Filter 5 Effluent	197
07/25/19	2:30 PM	Common Filter Influent	227
07/25/19	2:30 PM	Filter 3 Effluent	3.1
07/25/19	2:30 PM	Filter 5 Effluent	176
07/29/19	4:00 PM	Common Filter Influent	298
07/29/19	4:05 PM	Filter 3 Effluent	9.34
07/29/19	4:10 PM	Filter 5 Effluent	286
07/30/19	5:00 PM	Common Filter Influent	298
07/30/19	5:05 PM	Filter 3 Effluent	14.3
07/30/19	5:10 PM	Filter 5 Effluent	293
07/31/19	9:10 PM	Common Filter Influent	280
07/31/19	9:15 PM	Filter 3 Effluent	6.71
07/31/19	9:20 PM	Filter 5 Effluent	300
08/05/19	9:20 AM	Common Filter Influent	301
08/05/19	9:25 AM	Filter 3 Effluent	11
08/05/19	9:30 AM	Filter 5 Effluent	291
08/06/19	11:50 AM	Common Filter Influent	260
08/06/19	11:54 AM	Filter 3 Effluent	33
08/06/19	11:59 AM	Filter 5 Effluent	293
08/07/19	5:15 PM	Common Filter Influent	273
08/07/19	5:20 PM	Filter 3 Effluent	30.3
08/07/19	5:25 PM	Filter 5 Effluent	291
08/08/19	9:33 AM	Common Filter Influent	249
08/08/19	10:00 AM	Filter 3 Effluent	29.8
08/08/19	10:02 AM	Filter 5 Effluent	299
08/12/19	10:00 AM	Common Filter Influent	339
08/12/19	10:05 AM	Filter 3 Effluent	47
08/12/19	10:10 AM	Filter 5 Effluent	347
08/13/19	4:30 PM	Common Filter Influent	403
08/13/19	4:35 PM	Filter 3 Effluent	97.4
08/13/19	4:40 PM	Filter 5 Effluent	402
08/14/19	1:40 PM	Common Filter Influent	337
08/14/19	1:45 PM	Filter 3 Effluent	94.2
08/14/19	1:50 PM	Filter 5 Effluent	348

Date Sampled	Time Sampled	Sample Description	GSM (ng/L)
08/15/19	8:30 AM	Common Filter Influent	400
08/15/19	8:35 AM	Filter 3 Effluent	99
08/15/19	8:40 AM	Filter 5 Effluent	396
08/19/19	4:40 PM	Common Filter Influent	249
08/19/19	4:45 PM	Filter 3 Effluent	73.3
08/19/19	4:50 PM	Filter 5 Effluent	242
08/20/19	7:10 AM	Common Filter Influent	267
08/20/19	7:15 AM	Filter 3 Effluent	80.2
08/20/19	7:20 AM	Filter 5 Effluent	254
08/21/19	7:50 AM	Common Filter Influent	294
08/21/19	7:55 AM	Filter 3 Effluent	26.6
08/21/19	8:00 AM	Filter 5 Effluent	228
08/22/19	12:55 PM	Common Filter Influent	242
08/22/19	1:00 PM	Filter 3 Effluent	23.9
08/22/19	1:05 PM	Filter 5 Effluent	246
08/23/19	8:40 AM	Common Filter Influent	385
08/23/19	8:45 AM	Filter 3 Effluent	25.8
08/23/19	8:50 AM	Filter 5 Effluent	296
08/26/19	8:40 AM	Common Filter Influent	315
08/26/19	8:45 AM	Filter 3 Effluent	20.9
08/26/19	8:50 AM	Filter 5 Effluent	297

APPENDIX B. SUPPLEMENTARY FIGURES

Figure A1: Photograph of Filter Pilot Skid Located Within MWTP

Figure A2: Photograph of Sample Ports Within PFS System

Figure A3: Photograph of Sample Ports of Column Loaded with GAC Within PFS System

Figure A4: Photograph of Sample Feed Pump for PFS

Figure A5: Backwash Tank Used for Storing Chlorinated Backwash Supply Water

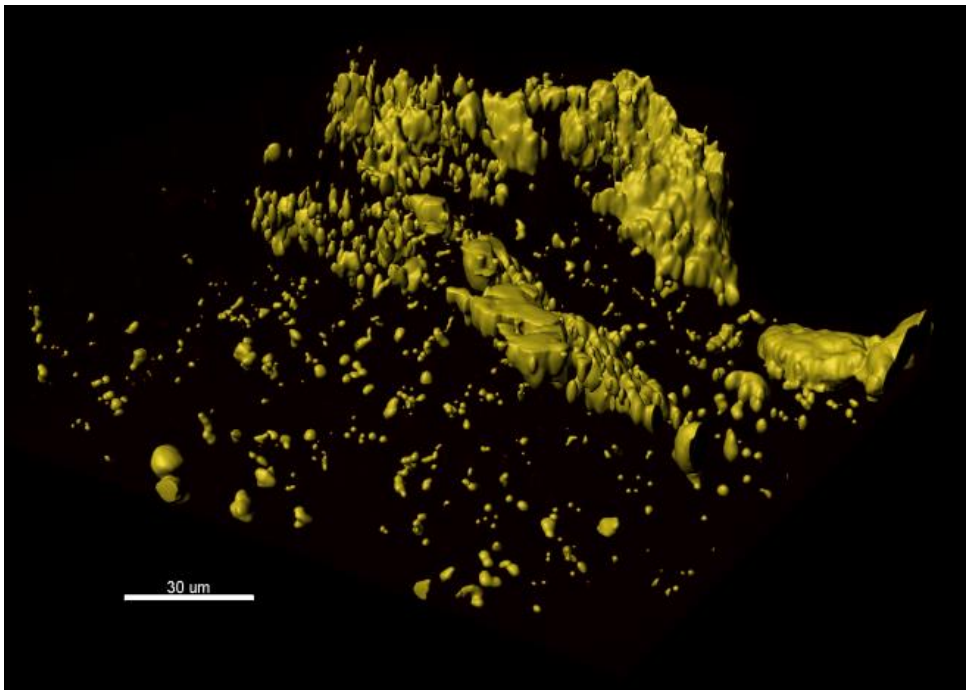

Figure A6: Confocal Analysis of Live Cells on Anthracite Media

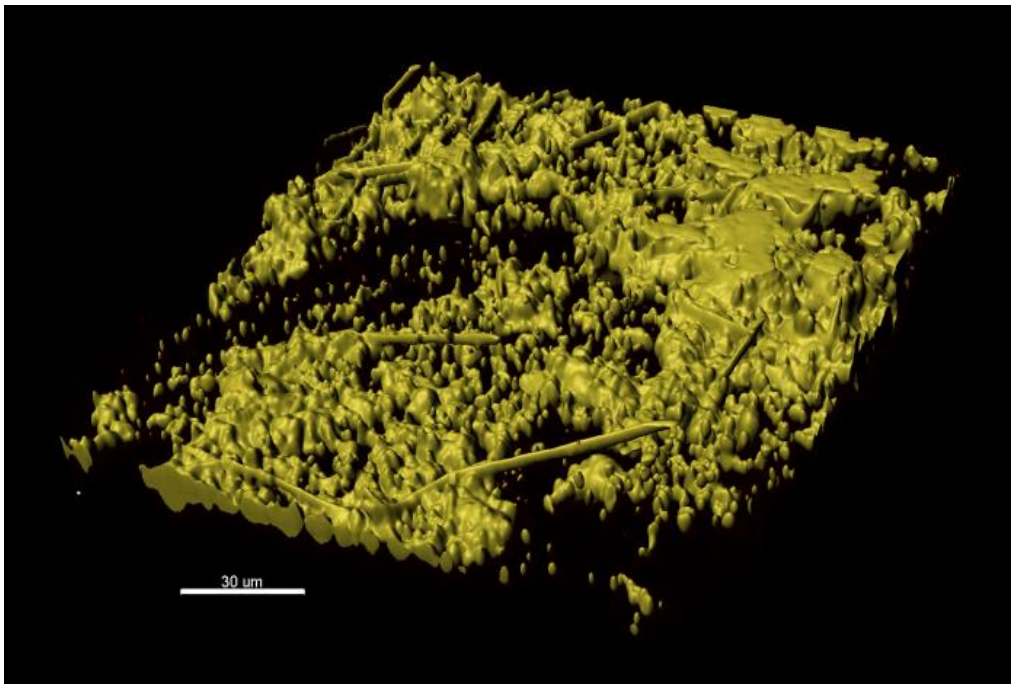

Figure A7: Confocal Analysis of Live Cells on GAC Media