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Impacts of Ozone Dose and Empty Bed Contact Time on Total Organic Carbon Removal Through Ozone-Biological Activated Carbon Treatment

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IMPACTS OF OZONE DOSE AND EMPTY BED CONTACT TIME ON TOTAL ORGANIC CARBON REMOVAL THROUGH OZONE-BIOLOGICAL ACTIVATED CARBON TREATMENT

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ABSTRACT

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In the face of climate change, pollution, and population growth, water scarcity has become a global threat. Many populations have witnessed their drinking water sources dwindle to an unsustainable level. These severe conditions have sparked interest in potable reuse as an increasingly viable alternative to typical 'pristine' drinking water sources. Currently, the California Division of Drinking Water (DDW) provides the most stringent requirements for reuse water quality. The best way to meet these standards is through the use of full advanced treatment (FAT), which consists of reverse osmosis (RO) and an advanced oxidation process (AOP). Alternative treatment trains composed of ozone and biological activated carbon (BAC) have been employed in several locations throughout the world, but these systems have not yet been optimized and are unable to compete with RO-based treatment trains on the basis of total organic carbon (TOC) removal. The purpose of this study was to identify the relationship between ozone dose and empty bed contact time based on TOC removal through ozone-BAC treatment. By evaluating the effects of these two operational parameters on biofilter performance, improved TOC removal may be achieved or more suitable operating conditions identified.

A 0.6 liter-per-minute (LPM) pilot-scale ozone-biofiltration reactor was constructed and operated over a 16-month period. During the start-up phase, the biofiltration columns received non-ozonated membrane bioreactor (MBR) filtrate, but the bulk organic matter proved to be too recalcitrant to promote development of the microbial community. Upon ozonation, increases in adenosine triphosphate (ATP) concentration (up to 10^5-10^6 pg ATP/g media) were observed within the biofilm, thereby suggesting significant microbial growth on the BAC.

When coupled with biofiltration, the results showed that the highest ozone to TOC ratio tested (O_3/TOC = 1.12) achieved greater TOC removal than the two lower doses (O_3/TOC = 0.35 and 0.62), presumably due to differences in the transformation of bulk organic matter. Biofiltration kinetics also proved to be more rapid than expected. At an O_3/TOC ratio of 1.12, the optimum empty bed contact time (EBCT) was 10 minutes, which resulted in a 25% TOC reduction and an effluent TOC concentration of 5.0 mg/L. To further reduce effluent TOC concentrations from ozone-BAC systems, additional treatment in the form of ion exchange or granular activated carbon (GAC) columns could be viable options. A logarithmic relationship between the optimum EBCT and ozone dose appeared to exist but further investigation is warranted to validate the relationship.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 INTRODUCTION

There is a growing interest in potable reuse due to increased demand on natural water resources and the deleterious effects of climate change. Potable reuse, which has been successfully practiced around the world (Gerrity et al., 2014a), refers to the process of treating wastewater for drinking water purposes. For example, the Orange County Water District's (OCWD) Groundwater Replenishment System has been augmenting the county's drinking water supply with high quality reuse water for years (Orange County Water District [OCWD], 2013). With the recent increase in the number of potable reuse facilities throughout the U.S., the lack of a consistent regulatory framework has become a significant concern. No singular set of standards has been adopted at the federal level so it is up to the individual states to establish their own public health and treatment criteria. The California Division of Drinking Water (DDW) has established the strictest set of guidelines and is currently regarded as the 'gold standard' for potable reuse. Specifically, agencies must employ "full advanced treatment" (FAT) prior to direct injection of the treated water into any aquifer in California. FAT consists of reverse osmosis (RO) paired with an advanced oxidation process. While RO is highly effective at removing most contaminants (trace organic contaminants, pathogens, dissolved solids, organic carbon, etc.) from water, it is also energy intensive, expensive, and produces a concentrated brine stream that is difficult to manage (Gerrity et al, 2014a).

Due to the limitations associated with RO-based treatment trains, it is necessary for more sustainable alternatives to be considered. The synergistic relationship between ozonation and biological activated carbon (BAC) is a promising alternative to RO-based treatment trains. BAC typically consists of a fixed-bed column filled with exhausted

carbon, which serves as a vehicle for biofilm growth. This bacterial community converts a portion of the effluent organic matter (EfOM), including some trace organic contaminants (TOrCs), to carbon dioxide via cellular respiration, thereby completely removing them from the effluent. This differs from RO, which simply separates the contaminants from the water and concentrates them in a brine stream. Ozonation precedes the biofilter for the purpose of decomposing large organic compounds into more bioavailable forms. This provides the bacteria with a more abundant and bioamenable carbon source, thereby facilitating TOrC removal through secondary substrate utilization or cometabolism.

There are significant cost savings associated with ozone-BAC treatment versus FAT. When considering a 10 million gallon per day (MGD) reuse facility, ozone-BAC offers up to 27% savings in capital costs and 45% savings in operation and maintenance (O&M) costs in comparison to FAT (Gerrity et al., 2014a). Ozone-BAC treatment can compete with FAT in regards to TOrC mitigation, pathogen reduction, and other water quality parameters, but ozone-BAC struggles with respect to the removal of total organic carbon (TOC) and total dissolved solids (TDS). Although these parameters are typically more relevant to aesthetics rather than public health, the California DDW limits the amount of wastewater-derived TOC in groundwater recharge applications to 0.5 mg/L. It has yet to be demonstrated that ozone-BAC alone can achieve this TOC threshold so significant quantities of diluent would be required—effectively precluding ozone-BAC from direct potable reuse applications. However, identifying and utilizing the relationship between ozone dose and empty-bed contact time—two key operational parameters in ozone-BAC systems—may make this TOC threshold more attainable.

The objective of this study is to identify the necessary operational conditions needed for ozone-BAC treatment trains to compete with FAT on the basis of TOC reduction. The hypothesis is that by coupling greater effluent organic matter transformation via increased ozone doses with longer empty bed contact times, ozone biological activated carbon systems can achieve better TOC removal and possibly approach the 0.5-mg/L threshold for TOC set by the DDW.

CHAPTER 2 LITERATURE REVIEW

2.1 Biofiltration

Biofiltration, in the context of water treatment, is the use of attached growth on media for the treatment of water. The granular media acts as a filter to remove particulates from the water, while the biofilm biodegrades organic contaminants present. Biofiltration is very common in water treatment and has been employed in treatment facilities for an extensive amount of time (Ko, Lee, and Nam, 2007; Nugroho, Reungoat, and Keller, 2010). Biofiltration has proven to be highly successful in removing dissolved organic carbon (DOC) (Wang and Lee, 1997), pharmaceuticals (Gaterell and Lester, 2000), pesticides (Martin-Gullon and Font, 2001), and disinfection byproduct (DBP) precursors (Simpson, 2008). Biofiltration is often preceded by ozonation to help improve treatment efficacy.

Biofilters can be found in a packed-bed or fluidized-bed configuration. Dual- or single-media filters are the most common. Typically, dual media filters include a GAC/sand or anthracite/sand configuration. A generic single-media biofilter design is provided in Figure 1.

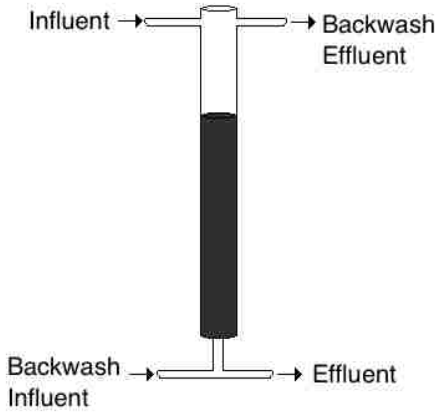

Figure 1. Generic biofilter schematic

2.1.1 Sand and Anthracite

Sand and anthracite are both non-adsorptive media. Sand possesses a smooth surface texture with a uniform grain size of about 0.2 mm (Page, Wakelin, van Leeuwen, and Dillon, 2006). Sand biofilters are operated either with very slow filtration rates of about 0.1 m/h or rapid filtration rates in full-scale applications. They are characterized by the formation of a schmutzdecke, or a thin biofilm formed on the top of the filter. This biofilm is the primary mechanism for removing organic matter from the water.

Anthracite is a variety of coal containing the highest carbon content. It is similar to sand in that it is highly uniform with a smooth surface. The media is typically larger than sand. Anthracite is often found in a dual-media configuration with sand filtration following anthracite filtration. Like sand, anthracite relies solely on biodegradation for organic contaminant removal.

2.1.2 Granular Activated Carbon

Granular activated carbon (GAC) is a carbon-based media used in water and wastewater treatment. A carbon source (coal, peat, etc.) is heated in the absence of oxygen, thus increasing the carbon content and activating the media (TSC Water Treatment and Engineering Group, 2010). GAC has a large surface area, which is used as adsorption sites for natural organic matter (NOM), disinfection byproducts (DBP) and other contaminants. Adsorption is the primary mechanism for contaminant removal with regards to GAC, but filtration also takes place. GAC is very effective at cleaning water but has special maintenance requirements that make it less desirable. The media must be regenerated periodically to reactivate the media, or the media must be replaced. This can

be costly and cumbersome. For this reason, many plants opt to use biological activated carbon (BAC) instead of GAC filters.

2.1.3 Biological Activated Carbon

2.1.3.1 Contaminant Removal Mechanisms

Biological activated carbon is GAC that has been exhausted of its adsorptive capability but with a biofilm developed on the media. This changes the principal mechanism of contaminant removal from adsorption to biodegradation. The biological community metabolizes assimilable organic carbon (AOC), and particulates are filtered out of the water simultaneously. It is also possible for bio-regeneration to take place. This is when adsorption sites are made available due to biological consumption of the contaminants occupying these areas (Seredynska-Sobecka, Tomaszewska, Janus, and Morawski, 2006).

2.1.3.2 Biofilm Stabilization

When starting a biofilter using fresh GAC, it is necessary to first deplete the adsorptive capacity of the media. The time needed for this to occur varies considerably depending on the type of GAC media used (Carlson, Heffernan, Ziesemer, and Snyder, 1994). The next phase requires the colonization and stabilization of a microbial community on the media. There are two things to consider when trying to reach steady-state conditions: steady-state biofilm formation and steady-state biological removal of organic matter (Juhna and Melin, 2006).

Reaching steady-state removal of organic matter generally requires less time than that of biofilm formation, but it depends greatly on the individual compound's physical and chemical properties. For instance, a study performed by Griffini et al (1999) found

that formaldehyde and acetaldehyde were removed after just 42 days compared with 64 days for ketoacids. In another study, pseudo steady-state for four ozone byproducts was discovered to be 20-40 days (Liu et al., 2001).

Biofilm steady-state achievement is dependent on several factors, including water quality, season, climate, hydraulic loading rate, etc. Ko et al. (2007) found that seven months were required to establish a steady-state biofilm whereas four to five months were necessary for Wang et al (1995). The reason steady-state removal of contaminants can be achieved prior to steady-state growth of the biomass is because the biomass activity does not necessarily relate to the amount of biomass (Juhna and Melin, 2006). This was discovered by Liu, Huck, and Slawson (2001) who witnessed a less significant effect on removal efficiency with temporal changes. This was attributed to the less active biomass, located deeper in the filter, compensating for the lower biodegradation rates in cold water conditions.

2.1.3.3 Maintenance

The longer a BAC filter is allowed to run, the larger the biological community will become, and the void spaces will become clogged with particulates. This can negatively impact the biofilter performance by increasing headloss, lowering effluent water quality, and incurring shorter filter runs (TSC Water Treatment and Engineering Group, 2010). To counter these effects, BAC filters must be regularly backwashed in order to maintain acceptable performance. Typically, a headloss or effluent turbidity threshold is designated and these parameters are monitored. When the threshold is reached, backwashing takes place.

Backwashing requires backfilling the biofilter with clean water and fluidizing the media. In the literature, bed expansion varies between 20 and 45% and the duration ranged from 6-12 minutes. The flow rate used will depend on the type of media and the shearing velocity. If the flow rate is too high, it can cause a significant portion of the biofilm to detach from the media. Air scour is sometimes employed to improve media fluidization. Air scour is usually performed at the beginning of the backwashing procedure. The addition of air scour reduces the filter-to-waste period but also increases the amount of biomass lost during backwashing (Emelko et al., 2006). Chlorinated water may be used during backwashing but at concentrations >1 mg/L have shown a negative effect in bulk organic matter (BOM) removal in the biofilters (Urfer, 1998).

After backwashing is performed, the effluent water quality will be compromised until stabilization occurs. In the study performed by Ko et al. (2007), turbidity breakthrough was recovered ten minutes after backwashing at all empty bed contact times (EBCTs), and dissolved organic carbon removal stabilization occurred 40 minutes after backwashing. During this stabilization period, the effluent water must be returned to the head of the plant for treatment but resumes normal operation afterwards.

Because BAC does not require regeneration, the same media can be in service for years. The only need for replacement occurs after attrition due to backwashing. Some media can be lost during backwashing; additional media may need to be installed periodically.

2.1.3.4 Performance

Trace organic contaminants (TOrCs) are anthropogenic organic compounds and are typically found at trace levels in water and wastewater (Reungoat et al., 2012). BAC

has been shown to successfully remove a wide range of TOrCs. In one study, 14 different TOrCs were investigated, and all but two compounds were removed to below their detection limits (Nugroho et al., 2010). Even compounds that are typically refractory in wastewater treatment plants (WWTPs) can experience substantial removal in BAC filters (Reungoat, Escher, Macova, and Keller, 2011). TOrC removals experienced in BAC filters are generally upwards of 90% for most compounds (Reungoat et al., 2012).

DBPs are those products formed between the interaction of oxidants (e.g., ozone or chlorine) and organic substances. Some have unknown toxicity and health effects while others (such as chloroform) are known to pose health risks to humans and aquatic life. The removal of DBPs has been investigated, and the results have been generally positive. Removals of aldehydes have been proven to exceed 90% (Wobma, Pernitsky, Bellamy, Kjartanson, and Sears, 2000). BAC filters have demonstrated >80% and 75% reductions in ketoacids and carboxylic acids, respectively. Haloacetic acids (HAA) are readily removed through BAC filtration, while trihalomethane (THM) reduction is negligible (Wobma et al., 2000).

Total organic carbon is a bulk organic parameter. TOC removal is somewhat site-specific, but typically does not exceed 50% removal through BAC filtration with preozonation. TOC reductions of 13-23%, 33%, and 29-51% were reported by Emelko et al. (2006), Kong, Zhang, and Wang (2006) and Ko et al.(2007), respectively. Dissolved organic carbon removal is substantial at 20-50% (Reungoat et al., 2012), as well as chemical oxygen demand (COD) at 56% (Kong et al., 2006). All of these cases studied

the efficiency of biofiltration following ozonation. Little data is available on BAC treatment of water alone.

BAC filters have consistently produced effluent turbidities <0.1 NTU (Wobma et al., 2000; Emelko et al., 2006). UV absorbance removal at 254 nm (UV_{254}) is limited. Biofiltration also increases the biostability of water by reducing the amount of bioamenable compounds present (Bonnet, Welte, and Montiel, 1992; Malley, Eighmy, Collins, Royce, and Morgan, 1993), which is particularly important for mitigating biofilm growth in distribution systems.

2.1.3.5 Factors Affecting Performance

2.1.3.5.1 Empty Bed Contact Time/Hydraulic Loading Rate

Empty bed contact time is the time required for water to pass through the biofilter. This is dictated by the flow rate through the column and the size of the column. EBCT and hydraulic loading rate (HLR) are inversely related, which means that high HLRs result in low EBCTs and vice versa. Hydraulic loading rate is the flow rate over the cross-sectional area of the filter media. The optimal EBCT is site-specific given the unique wastewater characteristics and biofilter biomass concentration (Urfer, Huck, Booth, and Coffey, 1997), however some trends exist between EBCT and contaminant removal. Reungoat et al. (2012) found that increasing EBCT is positively correlated with DOC, TOrC, and non-specific toxicity removal due to longer contact times that allow bacteria to degrade more organic matter. However, a lack of a direct linear relationship between EBCT and the various contaminant groups does not ensure significant additional removal given a longer EBCT. This nonlinearity is thought to be the result of different degradation rates of individual organic compounds that make up these bulk parameters.

Also, the extent at which NOM is removed, while increasing with increasing EBCT, showed significant variability among studies (Digiano, Singer, Parameswar, and LeCourt, 2001).

Biological growth in a biofilter can be inhibited by low HLRs, but high HLRs can limit organic matter removal due to insufficient contact times with the microbial community (Zhang et al., 2010). In a study performed by Ko et al. (2007), high HLRs (above 12 m/h) were found to restrict bacterial growth as well. HLR also dictates the structure of the biological community within a biofilter.

2.1.3.5.2 Water Quality

Water quality is site-specific and varies considerably depending on the water treatment application, pretreatment performed, and climate conditions. Temperature impacts the rate of biodegradation of contaminants. Generally, at higher temperatures, greater BOM removal is observed (Coffey, 1995; Fonseca, 1999). Temperature also influences the biomass stratification in the biofilter; in cold-water conditions, less biomass is observed at the top of biofilters as compared with warm water conditions (Emelko, 2006). Due to this, contaminant removal occurs throughout the column in lower temperatures but occurs mostly at the top of the filter in higher temperatures (Liu et al., 2001).

The type of organic matter present can significantly impact the performance of a biofilter. Not all organic compounds are easily biodegraded; some compounds may require an impractical amount of time for biodegradation to take place. If the DOC present in the water is recalcitrant, less removal will be achieved under normal operating conditions.

2.1.3.5.3 Media Characteristics

The filter media must be suitable for the application. The type of water being processed and the filter configuration are important factors in filter media performance. Media surface texture must be suitable to host microbial growth. Rough textures are better for biofilm attachment than smooth surfaces (United States Environmental Protection Agency [USEPA], 1999). Also, irregular media shape helps reduce shearing and sloughing of the biofilm. Larger surface area provides more space for microbial attachment.

GAC exhibits all of these properties, which makes it better suited for water treatment than sand or anthracite (Page et al, 2006). Generally, higher concentrations of biomass are found in BAC filters compared with anthracite filters (Huck et al., 2011). A larger biological community combined with some adsorption capability allows BAC filters to outperform anthracite and sand filters with regards to organic carbon removal (Zhang et al, 2010). BAC is more effective at removing DBP's than anthracite (Wobma et al., 2000), as well as increasing the biostability of water (Kong et al, 2006). Liu et al (2001) found anthracite to exhibit increased sensitivity to chlorine addition to backwash water and cold conditions.

2.2 Ozonation

Ozone is a gas composed of three oxygen atoms (O_3). It is highly unstable and reactive, as well as corrosive and toxic in some applications. It is only slightly water-soluble (chlorine is 12 times as soluble in water than ozone), but ozone is a powerful oxidant. With regards to water treatment, it is the second strongest oxidant next to the hydroxyl radical (EPA, 1999).

Given the unstable nature of ozone, it must be produced on-site (Erikkson, 2005). Ozone production generally requires the combining of an oxygen molecule and an oxygen atom (EPA, 1999), which is most commonly achieved through corona discharge. This reaction is endothermic, meaning it requires energy input to occur, and makes ozone production somewhat energy intensive.

2.2.1 Performance

Ozone has been utilized in wastewater treatment since the 1970s (Robson and Rice, 1991) and in water treatment since 1893 (EPA, 1999). It is most commonly used for disinfection and for the oxidation of iron, manganese, and taste and odor compounds.

2.2.1.1 Disinfection

Ozone, being a powerful oxidant, makes it ideal for inactivating bacteria, protozoa, and viruses. Bacterial inactivation is achieved through bacterial membrane damage, enzymatic activity disruption, or destruction of nuclear matter within the cell (EPA, 1999). Virus inactivation occurs through damaging of the viral capsid sites. Ozone destabalizes the protein capsid, thereby releasing the RNA (Kim, Gentile, and Sproul, 1980) or DNA (Sproul, 1982).

In a study performed by Wuhrmann and Meyrath (1995), a 4-log reduction of *E. coli* was observed at an ozone concentration of 9 ug/L and a contact time of one minute. Similar results were found for other types of bacteria. Even the most resistant forms of bacteria (sporular) are easily inactivated at low ozone doses (Bablon et al, 1991).

Compared with vegetative bacteria and viruses, protozoan cysts are much more resistant to ozone inactivation. For example, *Naegleria* cysts are highly resistant requiring a Ct of 4.23 mg-min/L to achieve 99% inactivation (Wickramanayake, Rubin,

and Sproul, 1984). Ct is a product of the ozone concentration and the ozone contact time with the water. It is used to demonstrate the level of disinfection achieved in a system; higher Ct's are necessary for more ozone resistant microorganisms. The more common protozoans, *Cryptosporidium* oocysts and *Giardia* cysts, have been extensively researched and shown to be inactivated by ozone. *Giardia lamblia* Ct values for ozone inactivation are shown in Table 1. It was reported that *Cryptosporidium* oocysts are significantly more resistant to ozone inactivation (10 times more), than *Giardia* cysts (Owens, 1994). In a study conducted by Finch, Black, and Gyurak (1994), *C. parvum* experienced 2-log inactivation with a Ct of 3.9 mg-min/L, at 22°C. At a temperature of 7°C, the Ct necessary for the same level of inactivation jumped to 9.0 mg-min/L.

It has been reported that viruses are less resistant than the sporular form of *Mycobacteria* (Bablon et al, 1991), and phages are the most sensitive to inactivation. In a pilot plant study performed by Keller, Morin, and Schaffernoth (1974), 5-log removal of coxsackie virus was achieved at an ozone concentration of 1.45 mg/L and batch testing yielded 2-log removal of polio virus 2 with an ozone residual of 0.8 mg/L. Virus inactivation CT values at various temperatures are provided in Table 1.

Table 1 Ozone Ct values for *Giardia lamblia* and virus inactivation
Giardia lamblia and virus Ct values were determined at a pH of 7 and 7.2, respectively. It was determined that pH had little effect on ozone disinfection and that these Ct values apply to pHs of 6.0-9.0 (Environmental Protection Agency [EPA], 1991)

Species	Log Inactivation	Temperature		
		5°C	10°C	15°C
Giardia lamblia	2	1.3	0.95	0.63
	3	1.9	1.43	0.95
Virus	2	0.6	0.5	0.3
	3	0.9	0.8	0.5

2.2.1.2 Oxidation of Inorganic and Organic Compounds

Ozone is used to remove the inorganic compounds iron and manganese from water through precipitation. Ozone has also been shown to reduce concentrations of geosmin up to 50% and MIB 2 up to 72%, at an ozone dose of 2 mg/L (Peter, 2008). Ozone is highly effective at oxidizing organic matter into lower molecular weight compounds. Oxidation can occur one of two ways: through a direct reaction with ozone or through an indirect reaction with hydroxyl radicals (•OH) (Reungoat et al., 2012). Hydroxyl radicals are formed through the reaction between ozone and electron-rich moieties, such as amines and phenols. Organic compounds possess unique rate constants for ozone reactivity. Those with large rate constants ($>10^4\ M^{-1}s^{-1}$) are highly reactive with ozone and are largely oxidized via the direct reaction with ozone. These compounds (diclofenac, naproxen, etc.) are easily removed by ozone independent of ozone dose (Reungoat et al., 2012). Those compounds with rate constants $<10^2\ M^{-1}s^{-1}$, are almost exclusively oxidized through the indirect reaction (Hollender et al., 2009). This is due to the fact that ozone is selective while •OH are non-selective.

Reungoat et al. (2012) found that less than 10% of DOC was removed during ozonation. This indicates that mineralization of organic compounds is minimal, while the formation of transformation products is prevalent. Lehtola, Miettinen, Vartiainen, Myllykangas, and Martikainen (2001) also noted that COD and TOC are not effectively reduced by ozone but that the biodegradability of the TOC was enhanced. Nugroho et al. (2010) witnessed between 14 and 97% removal of TOrC parent compounds. TOrC removal is strongly dependent on the individual compound and its ozone and •OH rate constants.

2.2.1.3 UV Reduction, Estrogenicity, and Non-Specific Toxicity

Ozone can significantly reduce the UV_{254} absorbance of water. A 45% reduction in UV_{254} was reported by Kong et al. (2006). This decrease in UV_{254} can be attributed mostly to the fraction of compounds for which aromaticity and unsaturated bonds are broken during ozonation. Estrogenic activity in wastewater is easily removed (87%) by ozone, and non-specific toxicity is generally reduced (Reungoat et al., 2012). This implies that the transformation byproducts are, overall, less toxic than the parent compounds.

2.2.2 Factors Affecting Performance

Higher temperatures reduce ozone solubility and stability in water (EPA, 1999). This will negatively affect the ozone dose in the water and could potentially inhibit the oxidation of organic matter. The disinfection capability of ozone was found to be relatively independent of temperature (Kinman, 1975).

Ozone decomposition rate increases with increasing pH (Langlais, Reckhow, and Brink, 1991). Conflicting reports concerning pH impact on microbial inactivation have surfaced. Farooq et al. (1977) found that pH shows little impact on microbial inactivation, while another study, performed by Harakeh and Butler (1984), documented a decrease in ozone inactivation of poliovirus 1, at alkaline pH. Higher pH increases hydroxyl radical formation, which would likely enhance NOM oxidation.

2.2.3 System Components

2.2.3.1 Oxygen Feed Gas

Either pure oxygen or an oxygen-rich gas must be supplied to produce ozone. Pure oxygen fed systems, using either liquid oxygen (LOX) or generated oxygen, will

yield the highest ozone concentrations (8-14%). LOX, however, must be purchased and stored on-site, which makes it expensive and raises safety concerns (EPA, 1999).

Air feed systems pull in ambient air and remove unwanted compounds, like nitrate and hydrocarbons, to produce an oxygen-rich gas. The concentration of oxygen in air feed systems is generally between 80-95%. These types of systems require additional equipment to prepare the air for ozone generation and typically yield ozone concentrations between 3-5%.

2.2.3.2 Ozone Generator

There are multiple ways in which ozone can be produced but the most common method is through corona discharge. This method requires two electrodes separated by a dielectric and discharge gap. Oxygen is passed between the electrodes as a voltage is applied to them. This voltage causes electrons to flow across the discharge gap, ultimately decomposing the oxygen molecules. This leads to the formation of ozone. About 85% of electrical energy input into an ozone generator is lost as heat (Rice, 1996). Also, the presence of heat negatively effects ozone production so cooling is required for maximum efficiency.

2.2.3.3 Ozone Injection and Contactors

There are three main mechanisms for introducing ozone into water: bubble diffuser, venturi injector, or turbine mixer. Bubble diffusers are popular because of their high transfer efficiency (85-95%) and ease of operation (EPA, 1999). They employ a porous material that allows the passage of ozone while simultaneously producing many small bubbles. A disadvantage to this type of injection is maintenance of the diffusers. The ozone may be introduced concurrently or countercurrent to the flow through ozone

contactors. Ozone contactors are simply basins that the ozonated water passes through to allow sufficient time for ozone transfer into the water.

A venturi injector utilizes the negative pressure generated in a venturi section, which 'pulls' ozone into the water (EPA, 1999). The water is then passed through contactors, usually in a plug-flow configuration. This set-up is advantageous because it is low maintenance while maintaining high transfer efficiency.

Turbine mixers mechanically mix the ozone into the water. They provide upwards of 90% transfer efficiency but are powered by a motor; this makes turbine mixers energy intensive (EPA, 1999). Also, maintenance required for the turbine and motor are higher than that needed for the diffuser and venturi.

2.2.3.4 Off-gas Destruction

Since 100% transfer efficiency does not occur in the contactors, there is excess ozone that collects at the top of the basins. This ozone is highly concentrated and is usually above the fatal concentration (EPA, 1999). The off-gas must be collected and directed to a destruct unit, which uses thermal, catalytic, or thermal/catalytic conversion of ozone to oxygen.

2.2.4 Advantages

Peroxide addition is often used in conjunction with ozone to assist in the formation of hydroxyl radicals. It has been shown, however, that with sufficient contact time, the •OH exposure achieved through ozonation is equivalent to that of the combination of ozone and peroxide (Pocostales, Sein, Knolle, von Sonntag, and Schmidt, 2010). Therefore, peroxide addition may not be necessary in many instances. Additionally, ozone has also been shown to provide similar disinfection as UV/H_2O_2 but

at significantly reduced costs (Rosenfeldt, Linden, Canonica, and von Gunten, 2006). This may not hold true for drinking water treatment due to the lower concentration of NOM present for ozone decomposition.

2.2.5 Limitations

2.2.5.1 Formation of Ozone Disinfection Byproducts

Ozonation leads to the formation of organic and inorganic DBPs; the most common inorganic DBP of concern is bromate, which is regulated at 10 μg/L by the U.S. EPA. At an ozone dose of 7 mg/L, bromate formation exceeded 10 μg/L in one tertiary treated wastewater effluent (Gerrity et al., 2011), and bromate concentrations of up to 60 μg/L have been reported (Krasner, Sclimenti, and Coffey, 1993). With respect to organics, not all DBPs are necessarily harmful, and none are currently regulated (Wobma et al., 2000). However, it is speculated that some organic ozone DBPs may soon be regulated. Some common groups include aldehydes, peroxides, and organic acids (Digiano et al., 2001; Erikkson et al., 2005). Formation concentration of aldehydes has been observed to range from 5 to 300 μg/L, depending on such factors as ozone dose and TOC concentration (Krasner, 1989; LeLaucher, Singer, and Charles, 1991).

The formation of N-Nitroso-dimethylamine (NDMA) is of concern to municipalities interested in utilizing ozone for treatment (Gerrity et al., 2014b) because it is a potential carcinogen. Although it is not yet regulated at the federal level, the California DDW has established a notification level of 10 ng/L (Gerrity et al., 2014b). In the study by Gerrity et al., (2014b), all but one of the nine full-scale treatment facilities monitored for ozone-induced NDMA formation, experienced higher NDMA concentrations following ozonation. At one particular site ozone-induced NDMA

formations of 14 ng/L and 7.7 ng/L (for two sampling events) were witnessed. Although NDMA formation mechanisms are largely unknown, it is speculated that ozone dose, water matrix complexity, and biological pre-treatment are all contributing factors to the extent of NDMA formation during ozonation (Gerrity et al., 2014b).

2.2.5.2 Biological Regrowth

Due to the increase in biodegradable organic matter (e.g., the organic ozone DBPs), the biostability of the water is impaired. This leads to potential regrowth of unwanted microorganisms (Emelko, Huck, Coffey, and Smith, 2006), however this can be mitigated through the use of biofiltration.

2.3 Combined Ozone and Biological Filtration

As was stated before, ozone transforms the organic matter present in water into a more bioamenable form. This means that the concentration of BDOC is increased through the transformation of bulk organic matter, and the dissolved oxygen (DO) concentration also increases through the decomposition of ozone. This provides ideal conditions for bacterial growth in filters. Refractory compounds that were once not easily removed, can then be removed through the combination of oxidation and biodegradation. When preceded by ozone, slow sand filters can achieve an additional 35% TOC reduction (Rachwal, 1988). Klevens, Collins, Negm, and Farrar (1996) reported a 9% increase in TOC removal and a 20% increase in BDOC removal with the addition of 0.5 mg/L ozone prior to BAC filtration. The level of treatment achieved is dependent on the water quality (e.g., the composition of the organic matter), ozone dose, and EBCT. If a high percentage of bulk organic matter is already assimilable prior to ozonation then little improvement will be noticed. Similarly, if the bulk organic matter is

highly recalcitrant and a small ozone dose is applied, the outcome will likely be the same. However, for organic matter that is susceptible to ozone-induced transformation, the increase in biodegradable fractions and subsequent removal with biofiltration can be significant.

BAC is also effective at removing ozone byproduct toxicity and improving biostability of the water (Emelko et al., 2006). BAC filters are capable of removing estrogenicity to below detection limits (Gerrity et al., 2011), and non-specific toxicity removal up to 54% has been observed when ozone is combined with biofiltration (Reungoat et al., 2012).

CHAPTER 3 METHODOLOGY

3.1 Pilot-Scale Reactor

3.1.1 Construction and Operation

A 0.6 liter-per-minute (lpm) pilot-scale reactor was constructed at a water recycling facility in the Las Vegas metropolitan area. It consisted of 12 ozone contactors and five BAC columns, which were used to treat full-scale membrane bioreactor (MBR) filtrate. The flow rate through the system was measured with an in-line flow meter. The addition of sodium chloride for a tracer study was achieved through a sample injection port followed by a static mixer. Ambient air, oxygen, or ozone were introduced through a Venturi injector downstream of the static mixer.

Concentrated oxygen was achieved with a portable medical system equipped with molecular sieves (AirSep, Denver, CO). The oxygen was generated at a flow rate of between 0.5 and 2 lpm and a pressure of 20 psig throughout the study. After passing through an air filter to remove particulates, the oxygen traveled to a Magnum-600 air dryer (Ozone Solutions Inc., Hull, Iowa) to remove any moisture from the oxygen prior to reaching the Nano dielectric ozone generator (Absolute Ozone, Edmonton, AB, Canada). The output from the ozone generator traveled either through a bypass line to a catalytic destruct unit or to the Venturi where the ozone was injected into the process flow. The bypass line was controlled by a standard gas flow meter. In addition to check valves, the feed gas line was equipped with a water trap that prevented water from entering the feed gas tubing and backing up into the generator, as well as a pressure gauge to monitor feed gas pressure entering the Venturi.

The ozonated water then traveled to the 12 ozone contactors connected in series (four were one inch in diameter and eight were two inches in diameter); some samples were collected from sample ports located at the bottom of the contactors. Ozone off-gas was collected in Teflon tubing at the top of each contactor and was sent to a catalytic destruct unit. The ozone off-gas line was also protected by a water trap that prevented water from reaching the catalytic destruct unit. The pilot reactor was equipped with an ozone analyzer from IN USA (Norwood, MA) for measuring ozone concentrations in the feed gas and off gas. The difference in ozone concentration between the feed gas and off gas was coupled with the reading from the mass flow controller to determine the transferred ozone dose. A sample conditioner (IN USA) equipped with a vacuum pump was also installed upstream of the ozone analyzer to remove any moisture from the feed gas and off gas and to control the flow to the analyzer. In later phases of the project, ozone doses were estimated by measuring differential UV_{254} absorbance after ozonation and then estimating the ozone to total organic carbon (O_3/TOC) ratio based on established correlations in the literature (Gerrity et al., 2012) and a site-specific correlation (Section 4.4.2).

The effluent from the final ozone contactor fed five parallel, one inch diameter biofilter columns: three filled with 1.2-mm diameter exhausted granular activated carbon (GAC) (Filtrasorb 300, Calgon Carbon, Pittsburgh, PA) provided by the Upper Occoquan Service Authority (Fairfax County, VA), one filled 0.95-mm diameter exhausted GAC (Norit 820, Cabot Corporation, Alpharetta, GA) from the F. Wayne Hill Water Resources Center (Gwinnett County, GA), and one filled with proprietary denitrifying biocatalyst. The column-to-media diameter ratios were approximately 21:1 and 27:1 for the 1.2-mm

BAC and 0.95-mm BAC, respectively. The biocatalyst was manufactured as a porous polyvinyl alcohol (PVA) bead containing denitrifying microorganisms. The biocatalyst has historically been used in suspended growth (i.e., activated sludge) systems so this will be the first evaluation of the biocatalyst in a packed-bed configuration. A separate control BAC column received non-ozonated pilot influent (i.e., MBR filtrate) to allow for the evaluation of organic matter removal with and without the synergistic effects of ozonation. An experimental BAC column, the biocatalyst column, and the control BAC column were all operated at the same EBCT during long-term operation to allow for direct comparisons of treatment efficacy. BAC sample ports were located at the bottom of each column, and the flow rates (and EBCTs) were controlled by independent needle valves. Activated carbon samples were also collected periodically from dedicated sample ports to evaluate the development of the microbial community. The microbial community in the BAC columns will be discussed in Section 3.3.3.

Figure 2 illustrates the layout of the pilot-scale reactor, and corresponding photos of the ozone contactors and BAC columns are provided in Figures 3A and 3B, respectively. The pink asterisks mark the biofilter effluent sampling locations, the white "X's" represent the lower media sampling locations at a 17.5-inch filter media depth, and the blue "X's" signify the upper media sampling locations at a depth of 5.5 inches. The green circles denote the non-filtered samples, the influent and effluent sample locations. The influent sample port was located prior to ozone injection into the water stream and the effluent sample location was located after the ozone contactors. The effluent samples received only ozonated water. The BC column did not have any media sample locations;

the samples had to be collected by backfilling the column with water and expanding the media to the top where it could be collected.

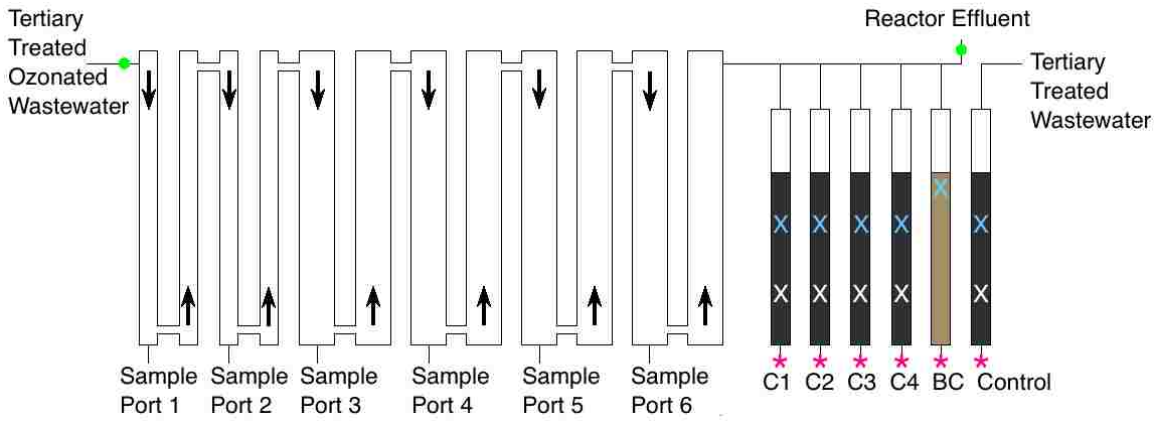

Figure 2. Schematic of pilot-scale reactor.
During the initial long-term operation of the pilot, C1-C4 and the Control were filled with 1.2-mm diameter BAC. During later phases of the project, C3 was switched to the 0.95-mm diameter BAC to evaluate potential hydraulic effects of grain diameter in relation to column diameter. The column containing the biocatalyst is denoted as BC.

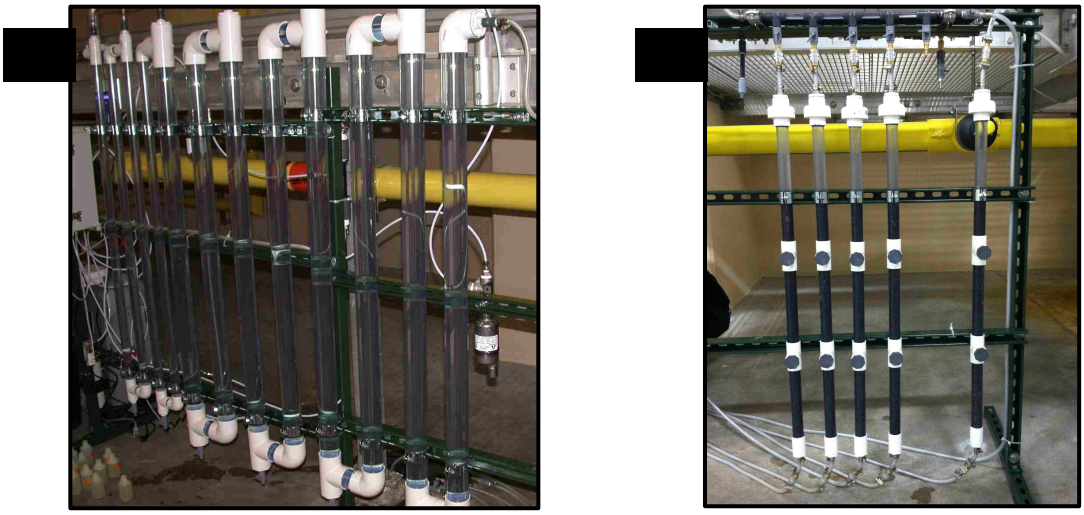

Figure 3. **Photos of the (A) ozone contactors and (B) BAC columns**
In photo (B) the biocatalyst is not shown.

3.1.2 Wastewater Treatment Facility Overview

The pilot-scale reactor was located at a full-scale water recycling facility with a design capacity of 8 MGD (currently operating at 4.2 MGD). The plant effluent is Category B reclaimed water that is used for irrigation. The facility uses course bar screens, grit removal, fine screens (2 mm), activated sludge (with biological nutrient removal and an 8-10 day solids retention time (SRT)), and membranes (0.04 μm) for wastewater treatment. Liquid chlorine disinfection is employed at concentrations of 2.5-3 mg/L. Provided below is a schematic of the treatment train in addition to the location of the pilot reactor within the treatment process.

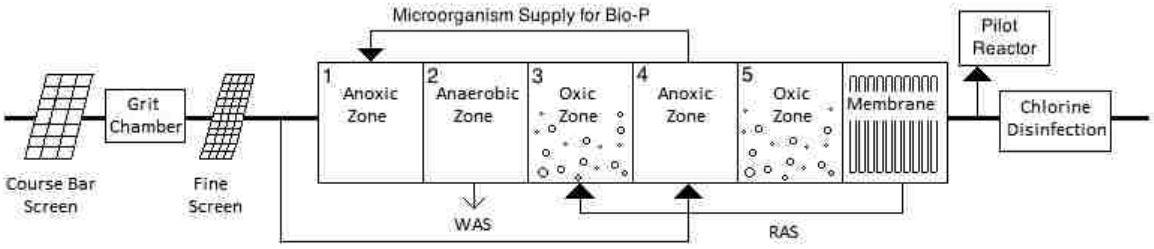

Figure 4. Full-scale reclamation facility treatment train
Membrane bioreactor (MBR) effluent was supplied to the pilot reactor. The average MBR effluent salinity concentration was 1.1 parts per thousand (ppt), the average temperature was 26 °C, the average pH was 6.9 and average dissolved oxygen concentration was 3.3 mg/L.

Bioreactor tank 1 is used to remove oxygen from the activated sludge. Phosphorus is released in tank 2 and luxury phosphorus uptake and nitrification occur in tank 3. Tank 4 is used for denitrification. Additional nitrification and phosphorus uptake take place in tank 5.

3.1.3 Backwashing

Backwashing of the pilot-scale biofilter columns was performed based on performance observations. When accumulation in the filters was too high, the flow rate

would drop significantly. This was used as an indication for backwashing to be performed. This method was chosen (as opposed to regular time intervals) because of the variability of the influent water quality and flow rate, which would impact the filter run time.

The biofilter effluent tubing was detachable making it possible for the backwash tubing to be attached at the bottom of the filter. The top of the filter was also detachable. Membrane bioreactor effluent was used as the backwash water and was pumped through the bottom of the filters using a MasterFlex peristaltic pump (Cole Palmer, USA). Backwashing flow rates varied between each filter and over time. A bed expansion of 34% was targeted and the flow rate adjusted accordingly. A 34% bed expansion was chosen because it was within typical values found in literature. Backwash duration was ten minutes. No air scour or chlorination was used.

3.1.4 Start-up

Initially, five columns were filled with the 1.2-mm exhausted GAC media (which was received previously exhausted in a full-scale treatment facility) and fed membrane bioreactor effluent without ozonation (C1, C2, C3, C4, and control). The total organic carbon was monitored for indications of microbial growth. Because the membrane component of the MBR eliminates nearly all bacteria from the filtrate, an external source of bacteria was required for the BAC columns. To supplement the bacteria already attached to the carbon prior to start-up, the columns were seeded with secondary treated wastewater effluent for 24 hours each.

Initially, the goal was to develop the microbial community without the use of ozone. This would allow for the identification of a TOC removal baseline from which

the synergistic impacts of ozone could be quantified. However, the MBR filtrate proved to be overly recalcitrant, and the bacteria were not being provided with a suitable carbon source. Potential solutions included seeding the reactors with an alternative carbon source, such as acetate or methanol, or implementing ozonation to transform the recalcitrant EfOM into a more bioavailable supply. Continuous ozonation was identified as the preferred alternative. Four months after startup, the ozone system was initiated to enhance biological growth in the filters.

A proprietary biocatalyst was provided as an alternative biofilter media for this study. The biocatalyst media has high concentrations of denitrifying bacteria that are trapped inside. It is made of a porous material, which allows the passage of water to allow contaminant contact with the entrapped bacteria. The biocatalyst was installed two months after ozone startup but did not receive ozonated water until three months after installation. Simultaneously, the control column feed water was switched from ozonated to non-ozonated MBR filtrate. The control was initially being fed ozonated water to promote biological growth. The empty bed contact times were adjusted to and held at 5, 10, 10, 15, 10, 10 minutes for C1, C2, C3, C4, Control, and BC, respectively for a three month period. During this time, the impact of EBCT on TOC removal was monitored. The media in C3 was replaced with the 0.95-mm Norit 820 GAC seven months after ozone initiation. This was done to examine the effects of media size in comparison with column size to determine whether hydraulic inefficiencies (e.g., wall effects and short circuiting) might compromise the validity of the results.

After examining the impact of EBCT on reactor performance, all columns were maintained at an EBCT of ten minutes in preparation of the kinetics tests discussed in section 3.2.2.

3.2 Sampling Methodology

In order to more accurately represent the change in water quality throughout the contactors, the same plug of water sampled at the influent was sampled at other sample ports (to the extent possible). This was achieved by determining the amount of time it would take the plug to reach other areas of the reactor and using those as sampling intervals. Sampling times were dependent on the influent flow rate and EBCTs in the filters.

3.2.1 Start-Up, Acclimation, and Long-Term Operation

For the first eight months of operation, TOC and UV_{254} samples were collected roughly once a week. The sampling frequency increased to every other day for the next three months, when possible. This was done to monitor the different treatment efficiencies of the filters being run at various EBCTs. Nitrate, ammonia, phosphate, and nitrite samples were collected once a week between 6/21/14 and 8/28/14 to document the biocatalyst performance against the BAC media.

3.2.2 Kinetics Tests

Three kinetics tests were performed, each at a different ozone dose. The ozone dose was held constant while the EBCT of the filters was changed. After adjustments to the EBCT were made, a time equivalent to three hydraulic retention times was allowed

prior to sampling. This was done to allow sufficient time for stabilization. The range of HLR employed during the kinetics tests was between 0.51 and 119 cm/min.

The first kinetics test was performed at an ozone to total organic carbon ratio (O_3/TOC) of 0.35. The EBCTs were increased step-wise from 1.75 minutes to 10 minutes. Ten sample events were performed during this test. The second kinetics test utilized an O_3/TOC ratio of 1.12. The EBCTs were varied between 2-30 minutes; the order of the EBCTs was random to determine if any systematic error occurs from increasing the EBCT step-wise. For the third test, an O_3/TOC of 0.62 was applied. Again, 10 sampling events were performed at EBCTs between 2 and 14 minutes.

3.2.3 Evaluation of Reactor Hydraulics

Step input tracer studies can be performed to characterize the hydraulics of a system. In these studies, a conservative chemical that will not react or be biodegraded, such as a salt, is added continuously at a sufficiently high concentration to allow it to be distinguished from the background concentration of the process water. The feed of the tracer is then stopped after a certain amount of time. In the pilot-scale reactor, a tracer can be added at the injection port located at the upstream end of the system. The concentration of the tracer or another indicator parameter, such as UV absorbance for organic chemicals or electrical conductivity for salts, is then measured at specific points within the reactor and at a sufficient frequency to capture the initial appearance, sustained concentration, and disappearance of the tracer. After analyzing the data, the actual hydraulic retention time (HRT) of the system can be determined and compared against the theoretical HRT (determined based on reactor dimensions and flow rate). The comparison of the experimental versus the theoretical HRT indicates whether there is

excessive short-circuiting or lags within the reactor, which can adversely impact treatment efficacy. The following equations were used to determine the actual HRT (t) and theoretical HRT (τ):

$$F(t) = {}^{C}/_{C_0} \quad (1)$$

$$t = \Sigma \bar{t} \Delta F(t) \quad (2)$$

$$\tau = {}^{V}/_{Q} \quad (3)$$

where, F(t) is the cumulative exit age distribution (i.e., the normalized conductivity); C and C_0 are the measured sample conductivity and initial tracer conductivity, respectively; $\bar{t}$ is the average time of two consecutive sample collections; V is the reactor volume; and Q is the reactor flow rate.

For this study, sodium chloride was used as the conservative tracer, and the concentration of the tracer was determined by electrical conductivity. The target concentration of the tracer was twice the background conductivity of the process water. The tracer was added at 0.8 L/min using a peristaltic pump for a period of time equal to four times the theoretical HRT. Samples were collected and measured for conductivity at intervals dictated by the step input duration. The process was repeated for each ozone contactor sample port and for the overall system.

3.2.4 Ozone Demand Decay Testing

An ozone demand decay study was performed on the source water using the indigo trisulfonate colorimetric method for dissolved ozone. Potassium indigo trisulfonate is dark blue in color but will quickly decolorize in the presence of ozone as

the chemical is oxidized. A spectrophotometer is used to determine the absorbance of the indigo trisulfonate solution at 600 nm, which is directly related to the strength of the blue color. The extent of decolorization, or bleaching, during ozonation is directly correlated with the dissolved ozone concentration. Using this method, the dissolved ozone concentration can be determined at various points within the reactor or in a batch configuration to evaluate the interaction of ozone, bulk organic matter, and target contaminants. This will allow for the characterization of the decay of ozone over time, which is matrix specific. This demand decay process can be used to calculate the total ozone 'Ct', or ozone exposure, which is a common metric used to estimate pathogen inactivation.

For this study, a preliminary ozone demand decay test was performed in a batch configuration. Five gallons of source water were collected and ozonated at the following O_3/TOC ratios: 0.25, 0.5, 1.0, and 1.5. Then, 10 mL of potassium indigo trisulfonate test solution were added to several 100 mL volumetric flasks that had been previously weighed. The ozonated source water was added to a single flask at specified time steps (every 30 seconds for the first two minutes, every minute for the next eight minutes, and then every two minutes thereafter). A sufficient sample volume was added to each flask to invoke a noticeable color change due to the combined effects of oxidation and/or dilution. The flasks, which now contained indigo trisulfonate plus sample, were weighed to determine the mass of sample added, which was later converted to volume. The absorbance of each sample was then measured with a spectrophotometer and the absorbance of each sample was converted to a dissolved ozone concentration using equation 4:

$$O_3(mg/L)=\frac{V_{blank+indigo} \times Absorbance_{blank} - V_{sample+indigo} \times Absorbance_{sample}}{f \times V_{sample} \times b} \quad (4)$$

where, f represents the proportionality constant (0.42) and b is the cell path length (1 cm) (Rakness, Wert, Elovitz. and Mahoney, 2010). The data was then used to calculate the ozone residual over time using Equation 5 and the ozone exposure using Equation 6.

$$O_3 \text{ residual} = \left({}^{O_3}/_{TOC} * TOC - IOD\right) * e^{-kt} \quad (5)$$

$$Ct = \frac{{}^{O_3}/_{TOC} * TOC - IOD}{k} * \left(1 - e^{-kt}\right) \quad (6)$$

Where Ct is the ozone exposure, TOC is the source water TOC concentration, IOD is the instantaneous ozone demand, k is the ozone decay rate constant and t is time (Gerrity et al, 2014a).

3.3 Analytical Methods

3.3.1 EfOM Characterization with UV Absorbance and Fluorescence

When light of a certain wavelength is passed through a sample, some of the molecules in the sample absorb the light. When photons are absorbed, the absorbing molecule is promoted to an electronically excited state, meaning that the outer electrons transition to a higher energy level. Only a fraction of the incident photons are absorbed by molecules in the solution and the remaining fraction passes through the solution. Using a spectrophotometer, the intensity of the transmitted radiation (I) is compared with that of the incident radiation (I_0), which yields the absorbance or transmittance of the sample (Horiba Scientific, 2012). Wavelength-specific absorbance—typically at 254

nm—is often used as an indicator of water quality. Evaluating absorbance across the UV spectrum also provides a means of characterizing the organic matter in a sample.

Fluorescence can also be used to assess water quality and characterize organic matter. When the excited electrons eventually relax to their ground state, they release energy in the form of light (i.e., fluorescence). The intensity of the emitted light, which is characterized by a longer wavelength (i.e., less energy) than the incident light, is measured by a spectrofluorometer. These excitation-emission couples can be evaluated across a broad spectrum to generate an excitation emission matrix (EEM), or fluorescence 'fingerprint', for a water sample.

For this study, UV absorbance (or transmittance) and fluorescence were determined with a Horiba Aqualog spectrofluorometer (Edison, NJ). Samples were collected from the pilot reactor, brought to room temperature and filtered using a 0.7-μm GF/F Whatman syringe filter (GE Healthcare Life Sciences, Piscataway, NJ). Analysis settings used are provided in Table 2. Data were processed using Matlab (MathWorks, Natick, MA) to generate contour plots of fluorescence emission and intensity (in arbitrary units) and identify critical fluorescence peaks and regional intensities. The standard operating procedure used for UV_{254} and fluorescence determination is provided in the Appendix.

Table 2 Raman and sample settings for fluorescence analysis.
The Raman settings are used to calculate the peak Raman area for a blank sample, which is then used to standardize the fluorescence intensities of experimental samples. That allows for direct comparisons between samples analyzed by different analysts, instruments, labs, etc. The sample settings are used to perform the 3D EEM analysis of samples.

Parameter	Raman	Sample
Integration Period	3 s	3 s
Excitation Wavelength Range	350 nm	240-470 nm
Emission Wavelength Range	380-410 nm	280-570 nm

A Matlab code was used for the evaluation of the fluorescence and UV absorbance as a way to characterize the composition of the samples. The EEMs were divided into three regions. Region I is representative of soluble microbial products, region II is associated with fulvic acids, and region III is indicative of humic acids present (Gerrity et al., 2011). An EEM showcasing the three regions can be seen below.

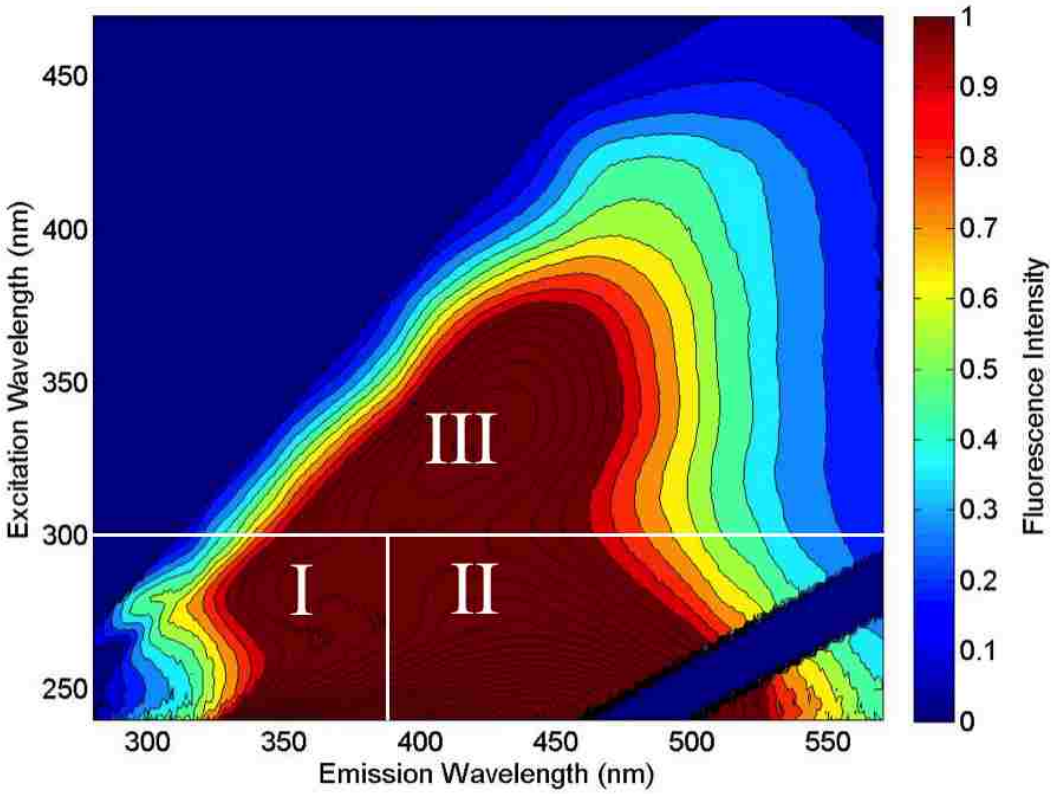

Figure 5. Fluorescence fractioning for the characterization of EfOM
Region I is representative of soluble microbial products, region II is representative of fulvic acids, and region III represents humic acids.

Using the area under the excitation-emission curve, in each region, and the associated fluorescence intensity, the fluorescence in each region is computed (Zhou, 2013). Fluorescence and concentration are directly related meaning that the higher the fluorescence the higher the concentration of that region. The fluorescence index (FI)

gives insight into the source of the organic matter. Higher FI values are associated with wastewater due to the presence of microbially-derived organic matter whereas lower FI values are indicative of terrestrially-derived organic matter (Gerrity et al., 2011). The FI compares the fluorescence at emission wavelengths of 450 nm and 500 nm while maintaining an excitation wavelength of 370 nm.

3.3.2 EfOM Quantification based on Total Organic Carbon

A Shimadzu TOC V-csn (Kyoto, Japan) was used for TOC analysis. This instrument measures total organic carbon using the non-purgeable organic carbon (NPOC) method. Acid is added to the sample to decrease the pH and convert inorganic carbon (i.e., carbonate species) to CO_2, and then the sample is purged with hydrocarbon-free compressed air to eliminate the CO_2. The sample is then sent to a combustion chamber where the remaining organic carbon is converted to CO_2 via combustion catalytic oxidation at 680°C. At this point, the CO_2 is sent to a non-dispersive infrared detector and analyzed, and the signals are correlated to TOC concentration.

A stock solution using 0.53 g of potassium hydrogen phthalate (KHP) and 250 mL of de-ionized water was used to produce a 1000 mg/L TOC stock solution. The stock solution was replaced every two months. Standard solutions of 0, 4, 8, 12, 16, and 20 mg/L TOC were prepared using 0, 200, 400, 600, 800, and 1000 uL of stock solution in 50 mL volumetric flasks. These were prepared fresh for each sampling event.

For this study, all glassware were cleaned according to the guidelines provided in Standard Method 5310B. The samples were collected in amber vials (with no headspace), capped with Teflon lined lids and kept cool prior to analysis. After the samples were acidified using 5N HCl to reduce the pH to less than 2, the samples were

covered with parafilm to reduce contamination potential, loaded in the autosampler, and analyzed according to the method parameters provided in Table 3.

Table 3. NPOC analysis parameter settings for both sample analysis and calibration curve determination

Injection Volume	80 µL
Number of Injections	3/7
Standard Deviation Max	0.100
CV Max	3.00%
Number of washes	2
Auto Dilution	1
Sparge Time	1:30 min
Acid Addition	0

3.3.3 Evaluation of Biological Activity based on ATP

Adenosine triphosphate (ATP) is a compound used by living organisms to store and transfer energy. When ATP reacts with the Luciferase enzyme, light is produced. This light can be measured with a luminometer to determine the concentration of ATP in the sample. The concentration of ATP can be used as an indicator of the presence of bacteria or the degree of biological activity in a system.

A deposit and surface analysis ATP test kit (Hach, Loveland, CO) was used to quantify the biological activity of the biofilm on the biofilter media according to ASTM D4012. This method measures both the intracellular ATP found inside living bacteria as well as ATP dispersed in the sample from decayed biomass.

For ATP analysis, media samples were extracted from the dedicated sample ports on the biofilter columns using sterile scoopulas and stored in sterile sample containers. Control BAC that had been stored in the refrigerator upon receipt from the Upper

Occoquan Service Authority was also collected to compare with the BAC from the pilot-scale reactor. One gram of dry media was added to individual test tubes containing 5 mL of LuminUltra UltraLyse 7 and the tubes were capped. The tubes were inverted several times for mixing and allowed to sit for five minutes to ensure that the ATP was extracted from the lysed bacteria. A 1 one mL volume of the resulting liquid (no solids) was transferred to another tube containing 9 mL of LuminUltra UltraLute (for dilution). Prior to analyzing the samples, an ATP standard calibration was performed by adding 100 uL of LuminUltra Ultracheck1 and Luminase to a test tube and analyzing using a PhotonMaster Luminometer (LuminUltra Technologies Ltd, New Brunswick, CA). This is done to monitor the luciferase enzyme activity in the Luminase. 100 µL of the new solution were transferred to another tube containing 100 µL of Luminase. The final sample tube was placed in the luminometer for analysis within 30 seconds.

3.3.4 Nutrient Quantification

For nitrate determination, method 8039 (Cadmium Reduction Method) using the Hach NitraVer 5 powder pillow test was utilized. This method measures high range nitrate between 0.3 and 30 mg/L NO_3-N. Nitrite was measured using Method 8507 (Diazotization Method) using Hach NitraVer 3 powder pillows for low range nitrite concentrations (0.002-0.3 mg/L NO_2-N). Method 10023 (Salicylate Method) for low range ammonia analysis (0.02-2.5 mg/L NH_3-N) was used. All of these compounds were measured using a DR5000 spectrophotometer (Hach Corp., USA). For phosphorus determination, Method 8048 (Ascorbic Acid) was used with Hach PhosVer 3 powder pillows. Phosphorus was measured using a DR 900 multiparameter handheld colorimeter (Hach Corp., USA).

3.3.5 Nitrite Evaluation of the BAC Media

To determine if any nitrite was adsorbed to the media and leaching into water in the BAC columns, an analysis was performed on the 1.2 mm BAC. Six samples total were evaluated, three crushed samples and three uncrushed samples. A pestle and mortar were used to manually crush the media to very fine particles. A 45 mL test tube was filled with 5.02g of media and filled to the 45 mL mark with distilled water. The samples were allowed to soak for one hour to allow for full saturation of the media and leaching of any nitrite into the water. The samples were then placed in a Sorvall Legend RT centrifuge (Thermo Fisher Scientific Inc., USA) for six minutes at 2500 rpm. The supernatant was passed through a 0.7 μm filter and analyzed for nitrite according to the method described in Section 3.3.4.

3.3.6 Total Coliform and *E. coli* Quantification

Standard Method 9223, using IDEXX Colilert-18, was used for total coliform and *E. coli* determination in the pilot-reactor samples. This method uses defined substrate technology nutrient indicators ortho-nitrophenyl- β -D-galactopyranoside (ONPH) and 4-methylumbelliferyl-β-D-glucuronide (MUG). The β-galactosidase enzyme found in coliform bacteria metabolizes ONPG, producing a yellow color. *E. coli*, on the other hand, uses the β-glucidonerase enzyme to metabolize MUG and fluoresce under long-wave ultraviolet light at 366 nm (IDEXX Laboratories, 2015).

For sample analysis, 100 mL of sample was collected in a sterilized, transparent, non-fluorescing IDEXX container containing sodium thiosulfate to quench any residual oxidant present. The samples were collected in triplicate for statistical analysis purposes. The samples were capped and shaken until the sodium thiosulfate dissolved completely.

They were then kept cool until the next step could be performed. A Colilert-18 reagent was added to each of the samples and shaken until all nutrients were dissolved. Samples were then transferred to an IDEXX Quanti-Tray/2000 and sealed in an IDEXX Quanti-Tray sealer. The sealed samples were allowed to incubate at 35°C for 18 hours. After incubation, the small and large wells that experienced a color change (yellow) were counted and quantified using the most probably number (MPN) table. Also, samples were inspected for fluorescence, which indicates the presence of *E. coli*.

3.3.7 Dissolved Oxygen Quantification

A YSI 85 dissolved oxygen meter (YSI Inc., USA) was used to measure pH, temperature, salinity, and DO in the samples. The instrument was calibrated based on temperature and altitude prior to sample collection. Samples were collected in a graduated cylinder and the electrode placed in the sample and swirled. Time was allowed for the temperature to stabilize before taking measurements. The measurements were provided instantly and the probe rinsed with DI water prior to collecting the next sample.

3.4 Operational Issues

The pressure buildup in the off gas tubing created an air pocket at the top of ozone contactor 11, which caused the water level to drop and reduced overall contact time. This did not have a significant impact on operation, but it required an adjustment to the hydraulic residence time in the reactor. Also, the change in water level changed pressures inside the system, which ultimately impacted the flow rates through the filters. Careful monitoring of ozone contactor 11 was necessary for normal operation to take place.

Some issues arose during backwashing as well. During backwashing, the carbon would stick together and rise as a single plug, which reduces the efficacy of the backwash cycle. Gentle tapping with a rubber mallet was implemented during backwashing to facilitate dispersion of the carbon. Air scour would be implemented in large-scale ozone-BAC applications to achieve the same result.

The biocatalyst presented issues during backwashing; the media would not fluidize. This could be attributed to the weight of the media or the material properties. The media was very light and a flow rate of approximately 56 mL/min (the lowest setting on the pump) would result in full bed expansion of the media but was too low for fluidization to take place. Also, the media is made of a soft material and would stick together forming a thick "cake." For this reason, the BC column was never effectively backwashed throughout the study. Also, the media began to compact after about five months of operation, which drastically inhibited flow through the column. It was difficult, and sometimes impossible, to achieve the desired flow rates. After initial signs of compaction, the BC column was backfilled with water and expanded and the media would slowly compact over time. However, after an extended period of time the media would compact instantly after expanding and nothing could be done to mitigate this phenomenon.

Issues with unwanted biofilm growth in various system components occurred. The BAC columns are equipped with mesh screens at the top and bottom to prevent loss of BAC through the effluent line during normal operation and through the influent line during backwashing. Microbial growth and accumulation of biopolymers was observed on the mesh screens, which reduced flow through the columns. More frequent

backwashing and cleaning of the mesh screens were implemented to mitigate this problem. There was significant growth observed in the static mixer and ozone contactors as well.

Several unavoidable issues also resulted in project delays. The full-scale ultraviolet (UV) disinfection reactors at the treatment facility periodically required maintenance, which resulted in the shutdown of feed water to the pilot-scale ozone-BAC reactor on several occasions. Because a continuous supply of water and EfOM is required for the development of the microbial communities in the BAC columns, this resulted in project delays. The feed line to the pilot-scale reactor was relocated to allow for a continuous supply of water.

One of the major hurdles encountered involved measuring the ozone concentration. The system was designed so that the ozone concentration could be evaluated in the feed gas and off-gas, using an ozone analyzer. Valves were in-place to select which gas stream would be directed to the analyzer. Initially, very low ozone concentrations were recorded and the analyzer readings were unstable; they would spike up and drop continuously over an extended period of time. Sometimes, the off-gas concentration would read higher than the feed gas, which is impossible. Many different valve and tubing configurations were tested but the results were inconsistent and did not correspond well with the UV_{254} data. Since the ozone concentration readings were not reliable, another method of determining ozone dose was necessary. This lead to the use of UV_{254} removal as an indication of the ozone dose.

The gas pressure of the ozone entering the venturi injector was also of concern. The oxygen concentrator was intended to supply 20 psig but the pressure gauge was

indicating less than 4 psi. It was speculated that major headloss across the mass flow controller was occurring so this component was removed from the system. The pressure remained largely the same but because the ozone dose could not be monitored through the ozone analyzer, the flow control was unnecessary and remained offline for the study. These were the main issues encountered over the course of the experiment but none of these significantly hindered the results of the research.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Hydraulic Characterization

The overall system tracer curve can be seen in Figure 6. This shape reveals that the system performs similar to an ideal plug-flow reactor. Theoretically, the slope of the curve as the tracer reaches the sample port should approach infinity, and the slope of the curve as the tracer leaves the sample port should approach negative infinity. The actual HRT can also be determined based on the time required for the tracer to initially arrive at the sample port or the time for the tracer to return to the background concentration after the tracer feed is shut off. A comparison of the actual HRTs (t) and the theoretical HRTs (τ) are provided in Table 4. The methodology for determining these values is provided in Section 3.2.3. Except for the first sample port (possibly due to error in measuring reactor volume through the influent tubing and Venturi injector), the values are very similar, thereby indicating a valid reactor design with minimal short-circuiting. The value t/τ would ideally be 1.0 (making the HRT and theoretical HRT equal to one another). The closer this value is to one, the more ideally the reactor performs. Again, with the exception of sample port 1, the rest of the system performs fairly well.

As mentioned in section 3.2.4, these values will assist in determining the ozone exposure, or Ct, values for each ozone contactor. Given that a peristaltic pump was used for the tracer study, a higher flow rate was necessary to provide a relatively steady feed of the sodium chloride tracer. For this reason, 0.8 L/min was used, which increased the overall flow rate of the pilot to 1.8 L/min. Typically, the tracer flow rate should be significantly lower than the flow rate of the system so as to have little impact on the operation of the reactor. At the time of the tracer study, the system had a flow rate of

about 1 L/min during normal operation, meaning that the flow rate nearly doubled with the addition of the tracer. Since this scenario did not accurately reflect standard operational conditions, the hydraulic retention times determined during the tracer study are not exactly representative of the hydraulic retention times during normal operation. However, the fact that the tracer study confirmed the similarity between the actual and theoretical hydraulic retention times increased confidence in ozone Ct values (i.e., the product of dissolved ozone concentration and contact time) that were based on flow rate and the dimensions of the reactor. However, some studies report lower hydraulic efficiencies at lower system flow rates, presumably due to an increase in dead space, so this limitation was considered when determining Ct values.

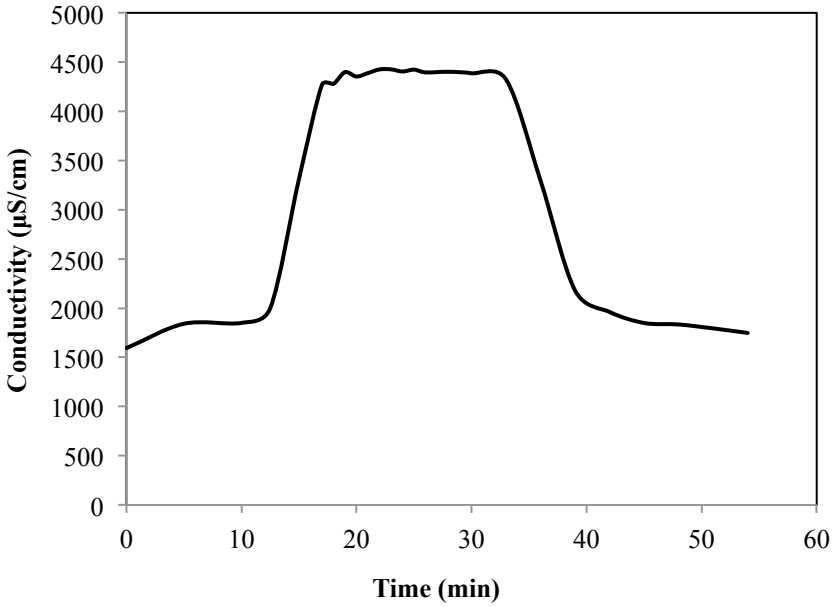

Figure 6. Overall system tracer curve.
This curve reflects the hydraulic movement of the tracer (NaCl) through the reactor. The shape indicates that the system performs close to ideal.

Table 4. Actual (t) and theoretical (τ) HRTs at various locations in the system.
Q = 1.8 LPM. The t/τ would be 1.0 for an ideal plug flow reactor.

Location	t (min)	τ (min)	t/τ
Sample Port 1	0.48	0.30	1.60
Sample Port 2	1.19	0.90	1.32
Sample Port 3	2.19	2.40	0.91
Sample Port 4	4.01	4.80	0.84
Sample Port 5	6.66	7.10	0.94
Sample Port 6	9.67	9.50	1.02
System	10.19	10.60	0.96

4.2 Ozone Demand and Decay Evaluation

Ozone demand decay curves were generated for O_3/TOC ratios of 0.5, 1.0, and 1.5 (Figure 7). It was not possible to generate a demand decay curve for the O_3/TOC ratio of 0.25 because the instantaneous ozone demand (i.e., the demand at 30 seconds) exceeded the transferred ozone dose.

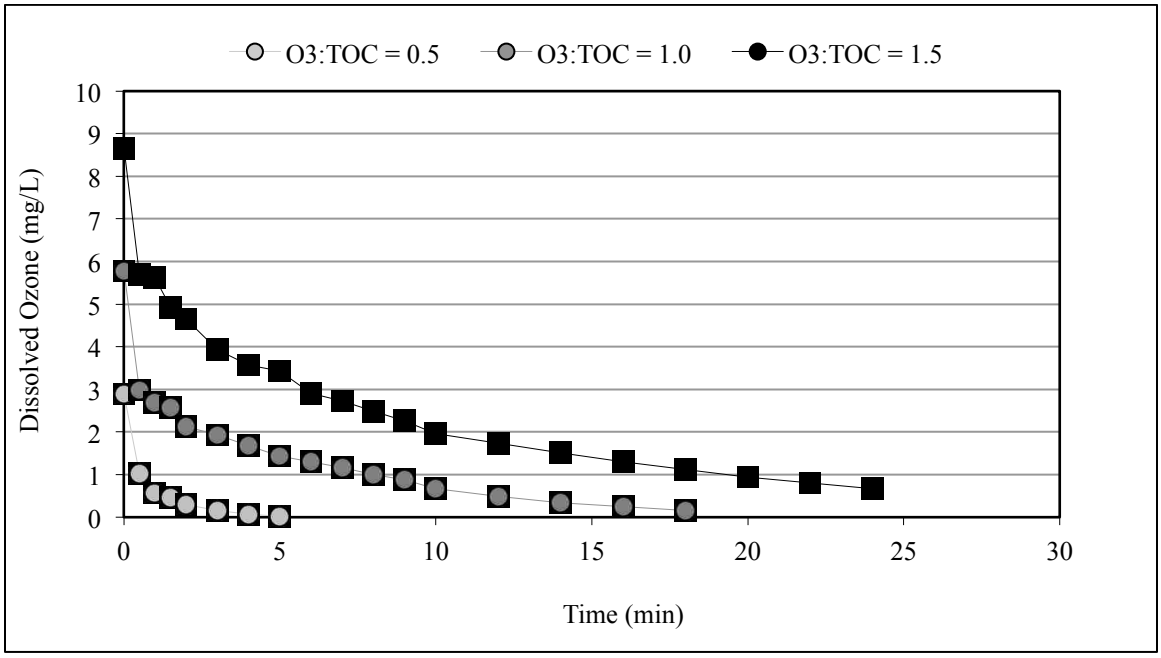

Figure 7. Ozone Demand Decay Curves for the MBR Filtrate as a Function of O_3/TOC Ratio
The decay witnessed by the ozone is due to natural ozone decay in pure water and ozone demand from the source water matrix.

The curves indicate the rate at which the ozone decays in this particular water source. This gives insight into the composition of the water (i.e., pH, the presence of bulk organic matter, and the reactivity of the bulk organic matter). The extended period of time necessary for complete ozone decay in the presence of 9.5 mg/L of TOC indicates that the bulk organic matter is highly recalcitrant. This is further supported when comparing the pseudo first-order ozone decay rate constants from the study (obtained from performing regressions on the decay curves) versus literature values for similar water matrices (Table 5).

Table 5. Ozone decay regression and rate constants at different ozone dosing conditions
The ozone decay rate constants observed in the study were much lower than the literature values, indicating the presence of ozone oxidation resistant compounds in the source water.

O_3/TOC	Regression	R^2	Study Rate Constant (min^{-1})	Literature Rate Constant[a] (min^{-1})
0.5	y = 1.8912e-0.887x	0.978	0.887	1.17-3.78
1	y = 3.5648e-0.168x	0.976	0.168	0.51-0.83
1.5	y = 5.6763e-0.093x	0.971	0.093	0.15-0.59

[a]Gamage, Gerrity, Pisarenko, Wert, and Snyder (2013); four secondary treated wastewater effluents

It is important to note that ozone decay naturally occurs in "pure water" due primarily to its reaction with OH^- ions (Staehelin & Hoigné, 1982). The presence of organic matter should increase the ozone rate of decay because of the additional reaction pathways available. According to Staehelin & Hoigné (1982), the rate of decay of ozone in pure water at a pH of 7 is 1.05×10^{-3} min^{-1}. Compared with the values in Table 5, this value is significantly smaller. This indicates that the decomposition of ozone that occurred during the demand/decay test is representative of the reaction between ozone and the source water matrix and not due to natural decomposition alone.

Using the exponential equations derived for each of the ozone doses along with the HRTs determined in the tracer study, the Ct values at the various ozone contactor sample points were computed and tabulated in Table 6. As can be seen, the ozone residual concentration decreases with increasing contact time while the ozone exposure increases with additional contact time.

Table 6. Ozone exposure through the pilot reactor
The ozone exposure was determined using the hydraulic data collected from the tracer study and the ozone demand/decay data. The ozone residual decreases with increasing contact time while the ozone exposure increases.

Location	t (min)	O_3/TOC=0.5		O_3/TOC=1.0		O_3/TOC=1.5	
		Residual O_3(mg/L)	Ct (mg-min/L)	Residual O_3(mg/L)	Ct (mg-min/L)	Residual O_3(mg/L)	Ct (mg-min/L)
Port 1	0.48	1.41	0.84	3.29	1.58	5.43	2.61
Port 2	1.19	0.76	1.59	2.92	3.47	5.08	6.05
Port 3	2.19	0.32	2.09	2.47	5.40	4.63	10.14
Port 4	4.01	0.06	2.38	1.82	7.29	3.91	15.68
Port 5	6.66	0.01	2.44	1.16	7.76	3.06	20.35
Port 6	9.67	0.00	2.45	0.70	6.79	2.31	22.33
System	10.19	0.00	2.45	0.64	6.56	2.20	22.42

4.3 Biofilter Startup and Long Term Operation

The first step in starting up the biofilters was developing a biological community on the media. Initially, non-ozonated membrane bioreactor (MBR) effluent was continuously run through the columns to promote biological growth on the media and to establish a TOC removal baseline. Figure 8 provides a graphical representation of the average collective TOC removal achieved by the BAC filters during the startup period. Excluding experimental variability, the TOC was not significantly removed from the water, which indicates a lack of microbial activity.

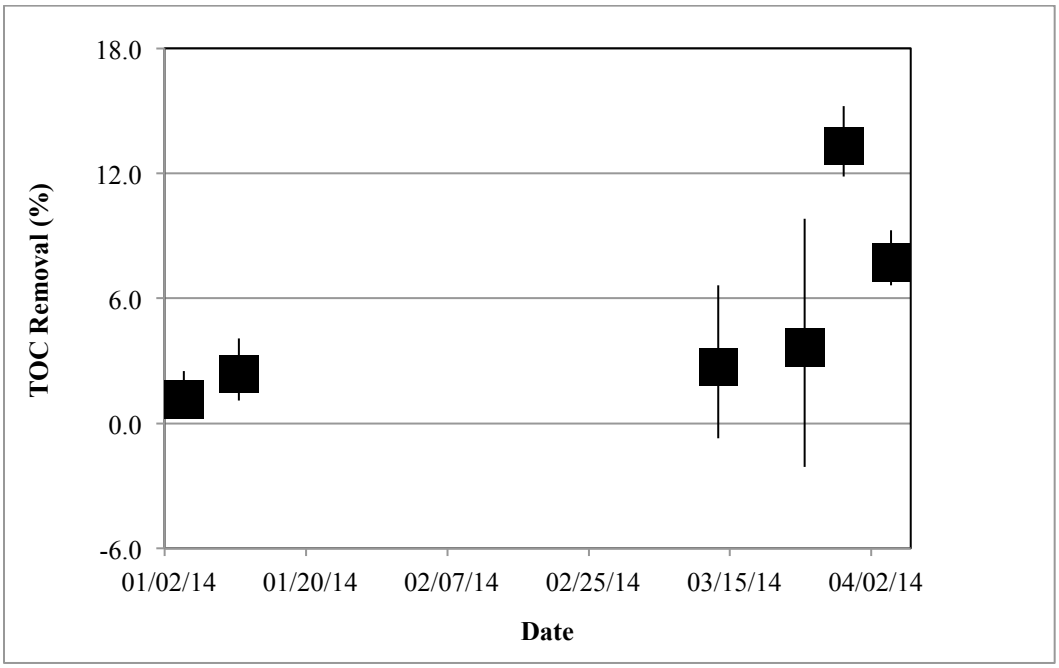

Figure 8. TOC removal during bioreactor startup (preozonation).
An average TOC removal of C1, C2, C3, C4, and the control column was plotted along with the standard deviations to showcase the limited TOC removal achieved across all columns.

TOC concentrations alone were insufficient to fully characterize the development of the microbial community; therefore, ATP samples were collected and analyzed for C1, C3, and the control. The 'control' column was designated to receive non-ozonated effluent for the duration of the project, but during this initial start-up phase, all columns were receiving non-ozonated effluent. Additional exhausted GAC that had been stored upon arrival was also tested for ATP as a secondary control. The results from the preliminary ATP analysis (prior to startup of the ozone generator) are tabulated in Table 7. There was a 10-fold increase in ATP compared to the original sample, but in comparison to typical values from the literature, it was apparent that the microbial community was grossly underdeveloped at the time the samples were collected. This could potentially explain the limited TOC removal observed during the start-up phase.

Table 7. Summary of the ATP analysis of the BAC compared against historical ATP data
The ATP concentration found on the BAC used in the study was significantly less than typical literature values. This indicates the gross underdevelopment of the biological community in the biofilters.

Media Sample	Sample Source	ATP (pg ATP/g media)	Reference
Stored BAC	N/A	$6.3x10^1$	Current Study
Column 1	Bottom of Contactor	$6.6x10^2$	Current Study
Column 3	Bottom of Contactor	$2.3x10^2$	Current Study
Control	Bottom of Contactor	$2.9x10^2$	Current Study
Literature	75-day old GAC	$1.8x10^6$	(Velten et al., 2007)
Literature	90-day old GAC	$8.0x10^5$-$1.8x10^6$	(Velten et al., 2011)
Literature	30 GAC filters from 9 WWTPs	$1.4x10^4$-$2.5x10^5$	(Magic-Knezev & van der Kooij, 2004)

Bacteria consume organic compounds as an energy and carbon source for cell synthesis. With a sufficient microbial community and a supply of biodegradable organic matter, the TOC concentrations in the BAC effluent would be lower than that of the influent water. Since there is typically 7 mg/L of TOC in the source water, this should provide sufficient substrate for biological growth. However, the lack of TOC removal implies that the effluent organic matter (EfOM) in the MBR filtrate is recalcitrant and cannot be easily biodegraded by microorganisms. Due to this fact, the ozone generator was started to increase the concentration of biodegradable organic matter being fed to the filters. This would, theoretically, improve biological growth as well as treatment efficacy.

Figure 9 depicts the change in TOC removal after bringing the ozone generator online. Immediately after startup of the ozone generator, TOC removal did not drastically change because ozonation is insufficient to induce significant mineralization (i.e., conversion of organic carbon to CO_2). However, the increase in biodegradable

organic carbon due to ozone-induced transformation of the bulk organic matter aided in the development of the microbial community, which is indicated by the gradual increase in TOC removal through the BAC columns over time. The period over which steady-state removal of TOC was achieved in the BAC filters is delineated in the figure. An initial decrease in TOC removal can likely be attributed to shocking the bacteria. Any drastic change in source water characteristics will impact the microbial community. Once the initial shock was overcome, a gradual increase in performance can be observed. Although steady-state removal of TOC was achieved relatively quickly, reaching steady-state for biofilm growth generally takes much longer. For this reason, the biofilters were operated and monitored long-term.

The biocatalyst media was not installed until two months after initiating ozonation; therefore, there is no data prior to that time for this filter. It is important to note that the control column, was receiving ozonated effluent for the first five months after starting up the ozone generator to promote bacterial growth. Once stabilized, it was relocated and was receiving only non-ozonated MBR filtrate for the duration of the project. The BC (biocatalyst) column began receiving ozonated MBR filtrate five months after ozone startup, to begin the acclimatization process. After installation of the BC column, a 26% increase in TOC concentration was observed through the column. Given that the media held denitrifying bacteria when installed, it is possible that byproducts of the microbial activity produced during shipping and storage were released into the water upon installation. This would drastically increase the TOC of the BC effluent water until these constituents were removed. After the initial increase in TOC, TOC removal through this column gradually increases over time.

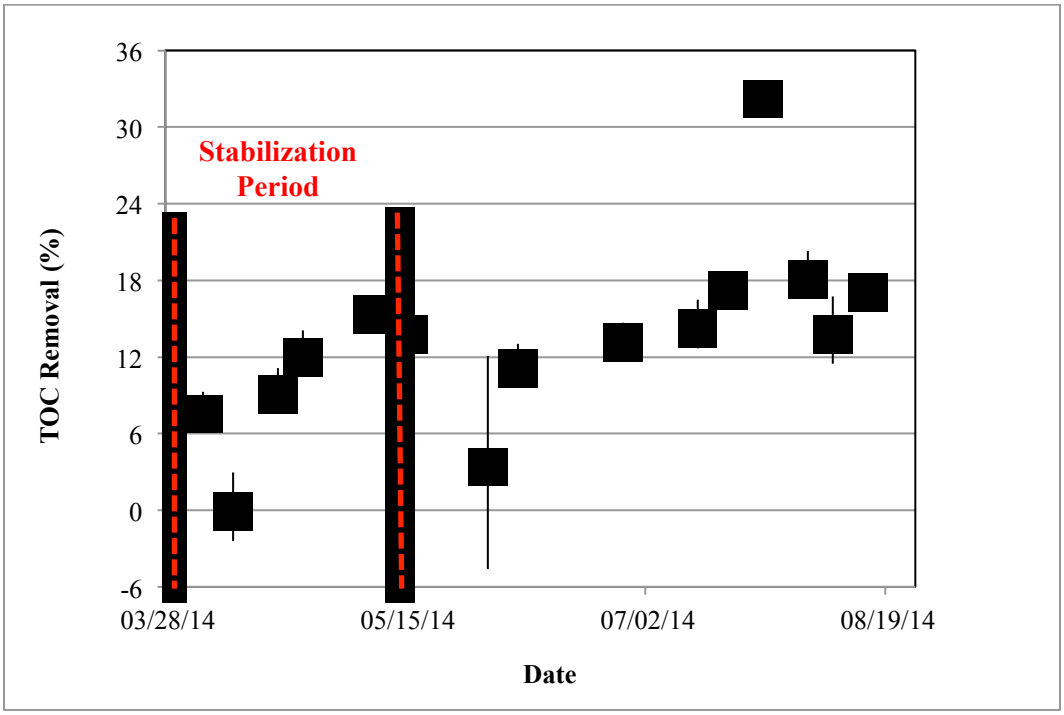

Figure 9. Summary of TOC removal through the BAC after startup of the ozone generator. The average collective TOC removal through all BAC columns is provided with the corresponding standard deviations. The abnormally low removal experienced in May and high removal achieved in July can likely be attributed to operational issues of the reactor. On those days, the water rose into the off-gas tubing and prevented flow through the columns. This likely impacted biofilter performance.

The UV absorbance at 254 nm (i.e., UV_{254}) reported in absorbance units (AU) and total fluorescence (reported in arbitrary fluorescence units (AFU)) for the samples collected for the first eight months of operation are illustrated graphically in Figures 10 and 11. All BAC columns performed similarly with regards to UV_{254} and fluorescence removal; therefore, the collective average UV_{254} and fluorescence values exhibited by the BAC columns are depicted rather than individual performance data. Although the values fluctuate over time, there is a general trend that can be observed. All of the sample locations exhibited UV_{254} absorbances of approximately 0.15 AU and total fluorescence values of approximately 49,000 AFU—consistent with the influent water quality—until 4/4/14. Up to this point, the BAC columns were not achieving any removal because of the lack of microbial activity (i.e., insufficient microbial development). After initiation

of the ozone generator, significant decreases in both UV_{254} absorbance (~40%) and fluorescence (~80%) were observed, thereby illustrating EfOM transformation (primarily attributable to ozone oxidation). As discussed earlier, the TOC concentration did not change as a result of ozonation alone, but the composition of the EfOM changed as more complex organic matter was converted into smaller, more bioamenable fragments.

The arrows, in Figures 10 and 11, mark the changes in UV_{254} and fluorescence witnessed in the BAC and BC columns due to the change in their feed waters. Once the BAC and BC columns were fed ozonated water, both parameters dropped drastically. The instantaneous removal of UV_{254} and fluorescence after ozone addition indicates that ozone is the primary contributor to UV_{254} and fluorescence reduction, which was expected based on the literature.

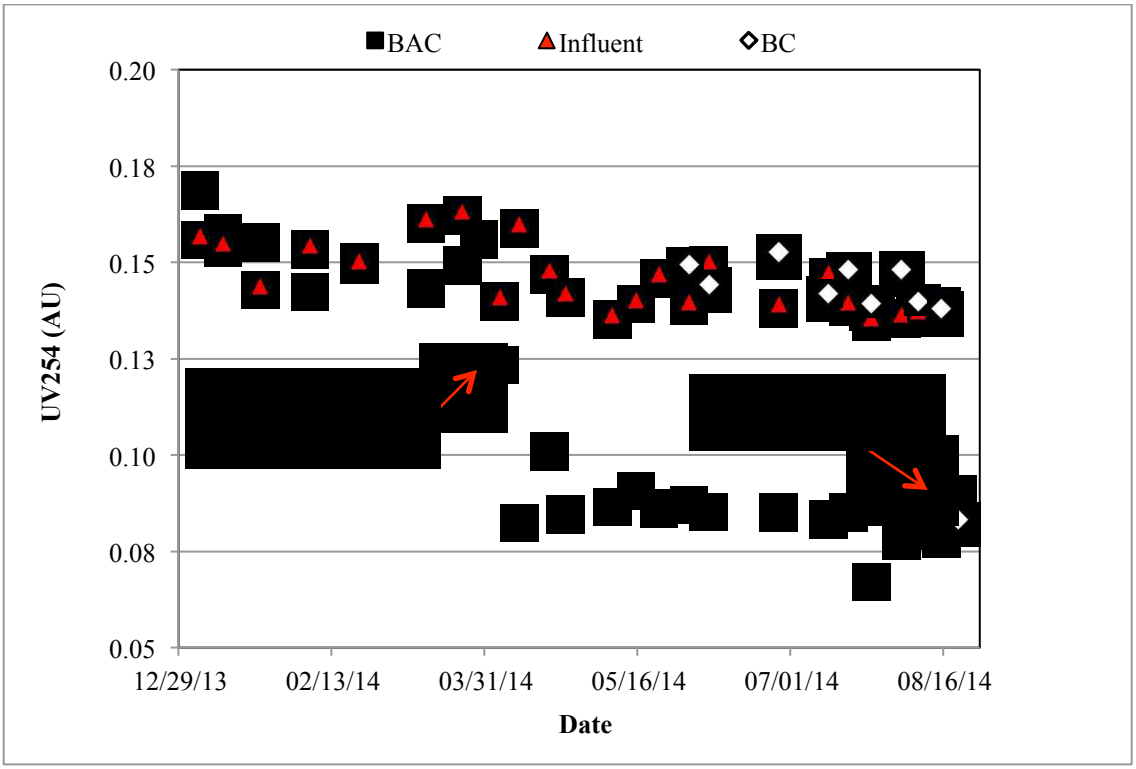

Figure 10. Historical UV_{254} absorbance data from the pilot-scale ozone-biofiltration system.
The figure depicts pre- and post-ozonation performance of the biofilters. Immediately after introducing ozone to the system, a significant reduction in UV_{254} is witnessed.

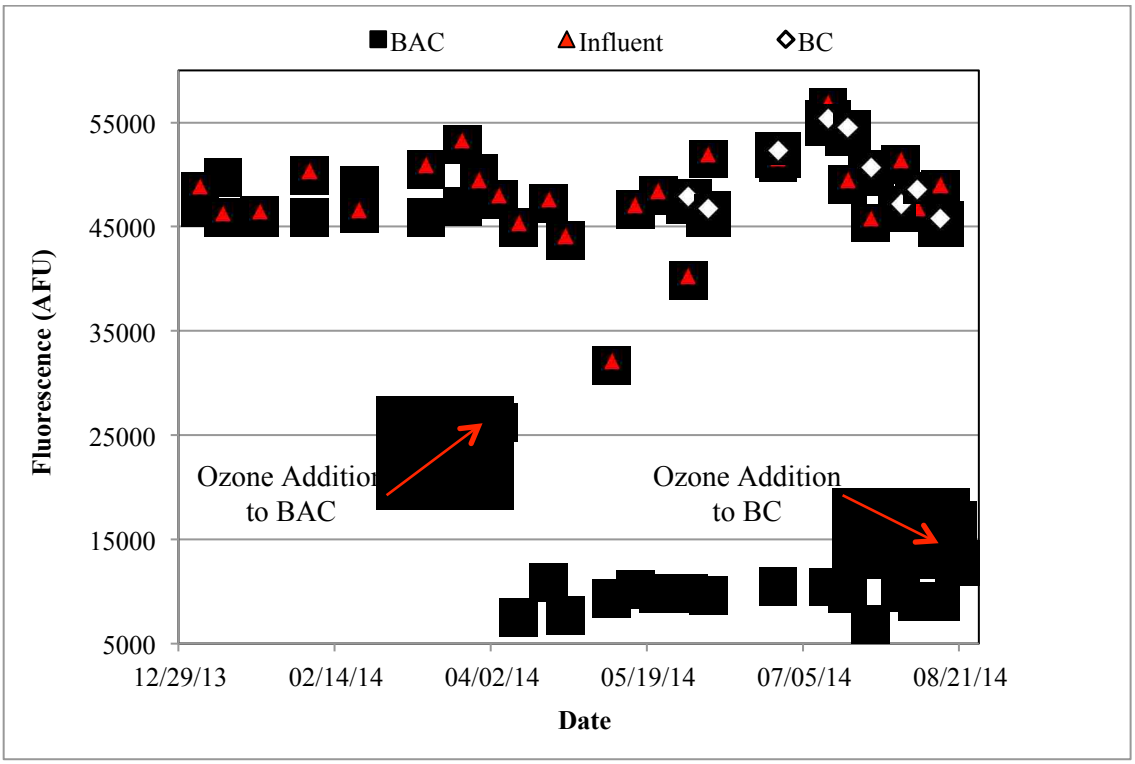

Figure 11. Historical fluorescence data for the pilot-scale ozone-biofiltraton system.
The figure depicts pre- and post-ozonation performance of the biofilters. Immediately after introducing ozone to the system, a significant reduction in fluorescence is witnessed.

The fluorescence values give insight into the extent of organic matter transformation taking place but tells little of the type of transformation occurring (i.e., organic fractions being targeted). Looking at an excitation emission matrix (EEM) allows one to evaluate the type of changes occurring during ozonation. As was stated in Section 3.3.1, various regions of the graph represent different types of organic matter. Two EEMs are provided in Figure 12. The samples were collected on two different days but little variation in fluorescence intensity or overall shape can be seen. This indicates that the influent water quality is relatively stable with regards to fluorescing compounds.

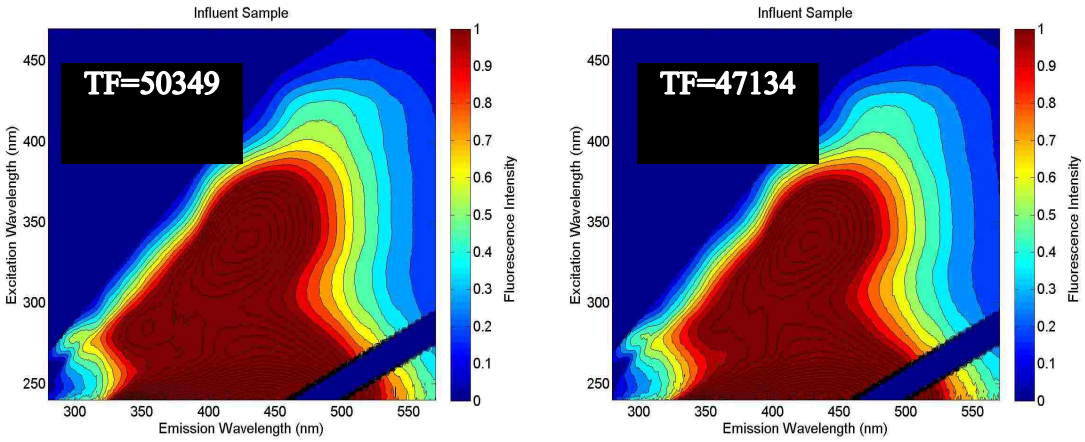

Figure 12. EEM comparison of two different influent samples
The EEM on the left is from the influent sample collected on 2/21/14 and the right EEM is from the 5/22/14 sampling event. TF is total fluorescence in units AFU. The similar EEM and total fluorescence demonstrate that the influent water quality, regarding fluorescence, is relatively stable.

To better understand how ozone transforms the composition of the water, EEMs of the pilot effluent and BAC effluent water before and after ozonation are provided in Figures 13 and 14. The samples collected on 2/21/14 (left side) were plotted on a fluorescence intensity scale of 1.0 whereas the 5/22/14 (right side) samples use a scale of 0.5 intensity. This was done to enhance the detail in each region for observational purposes. Samples collected on 2/21/14 were prior to ozone initiation and samples collected on 5/22/14 were post-ozonation.

It can be seen from the graphs that there is a significant reduction in fluorescence of the water after ozonation, and only a slight improvement is achieved through biofiltration. This agrees with the literature that states that ozone is the primary mechanism for removing fluorescence. Table 8 contains the proportion of fluorescence occurring within the three designated regions (Section 3.3.1) for each of the samples. There is a radical reduction of all three constituents after ozonation and a slight reduction after biofiltration. The fluorescence index (FI) is associated with the identity of the

water; a high FI is synonymous with microbially-derived organic matter (related to wastewater), and a low FI is associated with terrestrially-derived organic matter (natural waters). As the FI is lowered, the wastewater deviates from its wastewater identity. In Table 8, this change is witnessed by the reduction of FI from 1.81 to 1.39 after ozonation.

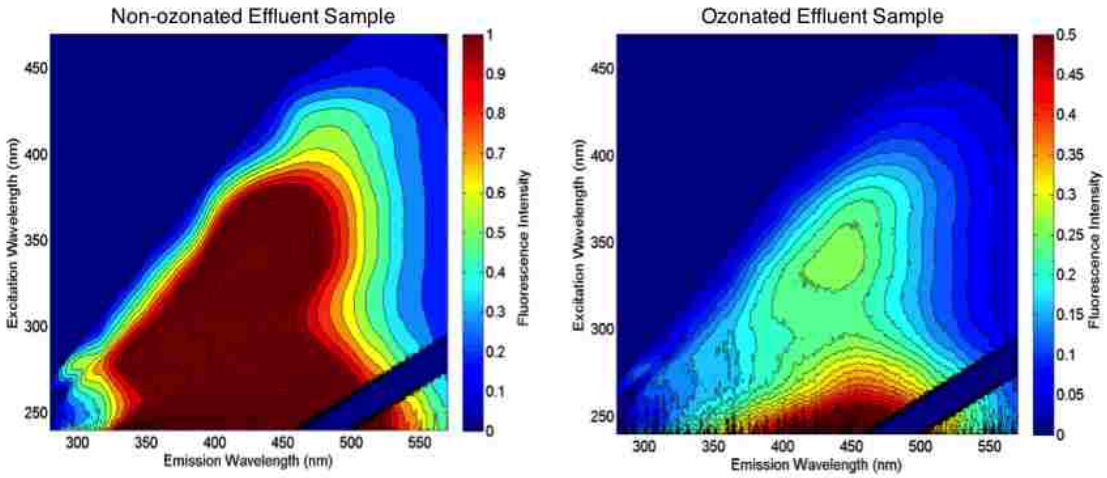

Figure 13. Pre-(left) and post-ozonation (right) comparison of fluorescence removal in effluent samples
The overall fluorescence of the sample was drastically reduced upon ozonation.

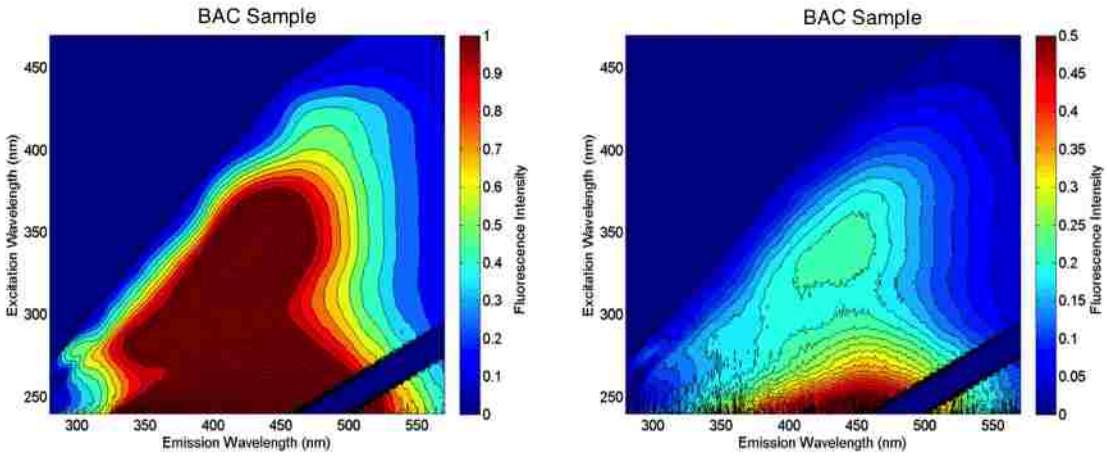

Figure 14. Pre-(left) and post-ozonation (right) comparison of fluorescence removal in BAC samples
The overall fluorescence of the sample was drastically reduced upon ozonation with little additional fluorescence removal achieved through biofiltration.

Table 8. EfOM characterization and ozone treatment efficacy

2/21/14 (Pre-ozonation)						
Sample	SMP (AFU)	Fulvic Acids (AFU)	Humic Acids (AFU)	TF (AFU)	TF Removal (%)	FI
Inf	16,708	22,804	10,837	50,349	N/A	1.79
Non-ozonated Eff	16,717	23,177	11,084	50,978	-1	1.79
BAC	15,939	22,288	10,676	48,903	3	1.79
5/22/14 (Post-ozonation)						
Sample	SMP (AFU)	Fulvic Acids (AFU)	Humic Acids (AFU)	TF (AFU)	TF Removal (%)	FI
Inf	15,292	21,731	10,111	47,134	N/A	1.81
Ozonated Eff	3,063	5,326	2,127	10,516	78	1.39
Ozone/BAC	2,965	4,891	1,871	9,728	79	1.37

All of the data, combined, confirmed that the ozone was effective in improving the biodegradability of the organic matter present in the water and that a biological community had developed on the media.

Nutrient removal was monitored over a two-month period after ozonation of the BAC columns C1-C4 and the control but prior to ozonation of the biocatalyst column. This was mainly evaluated to determine if the biocatalyst was performing the way it was designed to (denitrification). In theory, the presence of dissolved oxygen should inhibit denitrification. Ammonia, nitrate, nitrite, and phosphate were monitored. Due to the robust nitrification occurring in the full-scale bioreactor, ammonia concentrations were negligible. No phosphate removal was witnessed through the BAC or BC columns. Large variations in influent phosphate concentrations were experienced and subsequently the data collected was inconsistent. The collective average nitrate and nitrite concentrations through the BAC columns were plotted against the concentrations present

in the influent and BC effluent. One interesting point is the lower concentrations of nitrate and nitrite through BC (as seen in Figures 15 and 16). The nitrate data for the BAC columns is inconclusive due to its sporadic nature but it is evident that BC consistently achieved lower nitrite concentrations than the BAC columns and the influent water concentration. Although only small reductions, this information suggests that denitrification was taking place to some extent. This may have been more pronounced with dirtier source water. The average dissolved oxygen (DO) concentration in the influent water was 3.3 mg/L, however it is possible that anoxic conditions developed in the lower depths of the BC column, which would promote denitrification. The level of DO supplied to the BAC columns was significantly higher than that of BC given the use of ozone; this is likely the reason for the lack of nitrate removal observed in the BAC columns.

Influent nutrient concentrations were low because of the nutrient removal performed in the full-scale MBR of the treatment facility. All of the BAC columns performed poorly for nitrate, nitrite and phosphorus removal and actually contributed more nutrients to the water than was originally present. Nitrite concentrations were consistently higher after BAC filtration, as seen in Figure 16. The 1.2 mm BAC media was evaluated to determine if nitrite leaching was occurring and contributing to the higher nitrite concentrations in the BAC effluent. Since the media was previously exhausted in a full-scale treatment facility, it was possible that the media contained adsorbed nitrite. The average nitrite concentrations obtained from the uncrushed and crushed media were 0.001±0.004 mg-N/L and 0.007±0.004 mg-N/L, respectively. These concentrations are extremely low and indicate that the higher nitrite concentrations

observed were not due to leaching from the media. It is unclear what caused these increases but some type of EfOM transformation is evident. One possible explanation is the presence of micro-communities within the larger biofilter community. Although high influent dissolved oxygen concentrations were supplied to the BAC filters, it is possible that small portions of the filter developed anoxic conditions thereby supporting the conversion of nitrate to nitrite. Although no significant nitrate removal was observed, the low levels of nitrite witnessed would not require substantial nitrate transformation. Once the nitrite was formed, it is possible that an inadequate supply of available carbon source limited nitrite conversion to nitrogen. A study by Liu, Zhang, and Wang (2006), documented high levels of denitrification intermediates, such as nitrite, in the BAC filter effluent due to low concentrations of electron donors. Other sources also cite an inadequate supply of organic matter as the reason for residual nitrite in BAC filters (Sison, Hanaki, and Matsuo, 1995; Sison, Hanaki, and Matsuo, 1996).

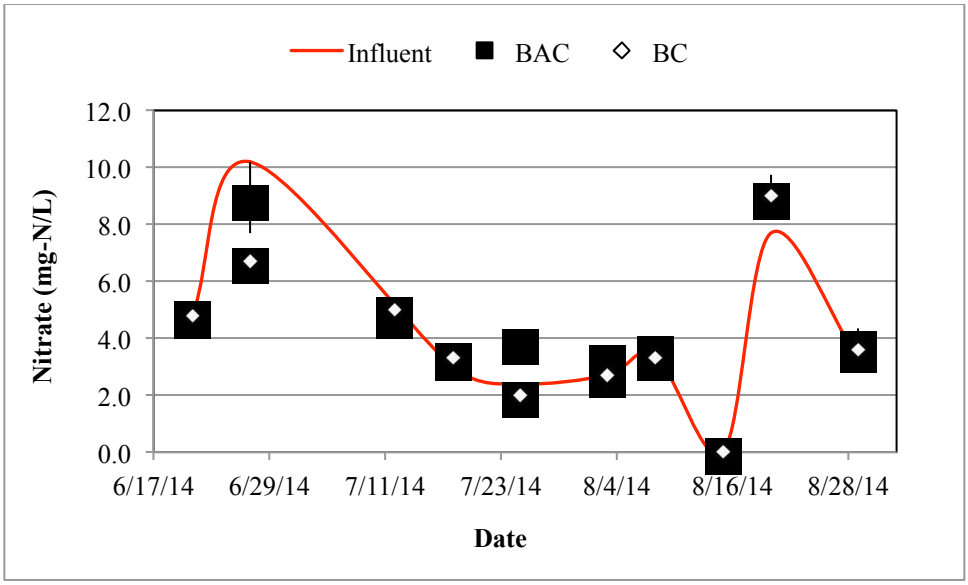

Figure 15. Nitrate concentrations exhibited by the BAC and BC columns.
The collective average concentrations of the BAC columns and corresponding standard deviations were used to demonstrate nitrate removal through the columns.

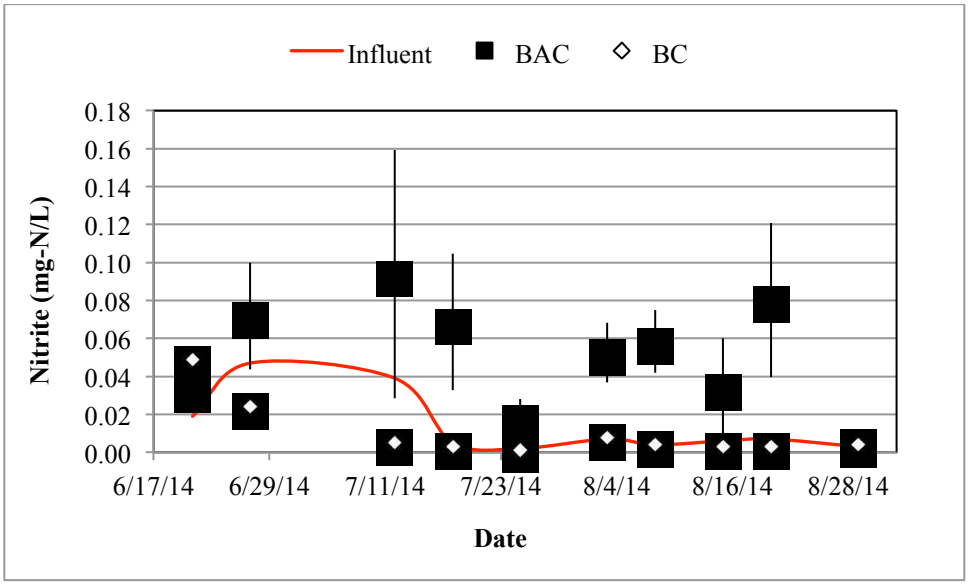

Figure 16. Nitrite concentrations observed in the BAC and BC column effluents. The collective average nitrite concentrations exiting the BAC filters are depicted. The standard deviations are large, showcasing the variability in performance. However, despite this variability, in almost all instances the BAC effluent concentrations were higher than the influent nitrite concentration.

In addition to the reduction in TOC, ATP was again analyzed in order to characterize the biological growth in the reactors after initiation of the ozone generator. The results are provided in Table 9. These ATP concentrations indicate significant microbial growth in the filters in comparison to the initial testing (Table 7) and more closely resemble concentrations found in the literature (10^4-10^6 pg ATP/g media; Table 7). Recall that the control had initially been receiving ozonated effluent to promote biological growth, but started receiving non-ozonated effluent during the long-term testing phase. Therefore, the microbial community on the control media was likely similar to that of the other columns but then decreased by nearly an order of magnitude once it started receiving the recalcitrant food source again. However, it is interesting to note that despite receiving recalcitrant organic matter most of the microbial community in the control column remained intact throughout the study.

Table 9. ATP Concentrations after ozonation
The ATP concentrations post-ozonation were greatly improved from concentrations prior to ozonation as seen from the concentration for column 1 during initial testing.

Media Sample	Sample Location	ATP (pg ATP/g media)
Unused BAC	Initial Testing	$6.3x10^{1}$
Column 1	Initial Testing	$6.6x10^{2}$
Column 1	Bottom	$3.4x10^{5}$
Column 2	Bottom	$2.0x10^{5}$
Column 3	Bottom	$3.0x10^{5}$
Column 4	Bottom	$1.4x10^{5}$
Control	Bottom	$5.8x10^{4}$
Biocatalyst	Top	$2.0x10^{6}$
Unused BC	N/A	$3.1x10^{5}$

After establishing a healthy biological community, the next goal of the research was to study the effect of EBCT on biofilter performance. For this purpose, the EBCT of the columns was adjusted to 5, 10, 10, 15, 10, 10 minutes for C1, C2, C3, C4, control, and BC, respectively. A positive correlation between EBCT and TOC removal was expected. The TOC removal of each biofilter at the adjusted EBCTs is provided in Figure 17.

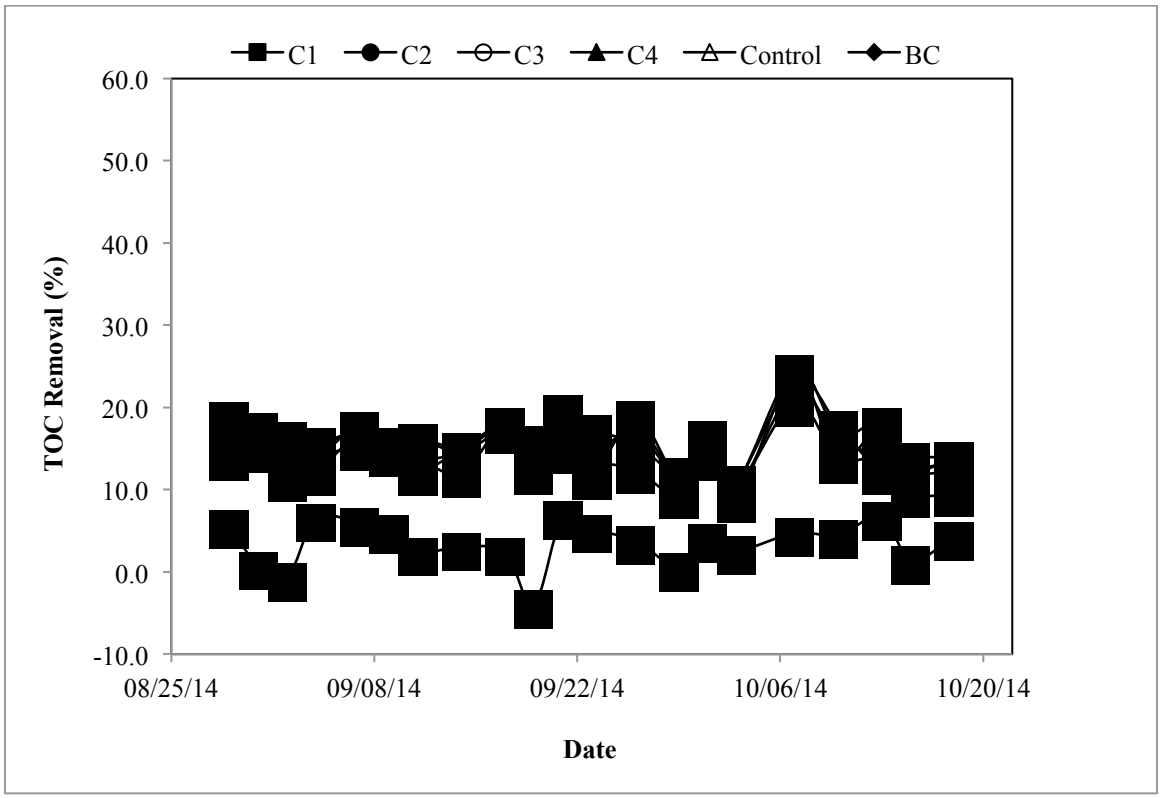

Figure 17. TOC removal at various EBCTs
The filters were operated at EBCTs of 5, 10, 10, 15, 10, 10 minutes for C1, C2, C3, C4, Control, and BC, respectively. No significant difference in TOC removal was observed between the various contact times.

From the graph, it is apparent that EBCT had little effect on the performance of the biofilters. This was not expected and does not coincide with the results of previous studies. A possible reason for this was the media size. If the diameter of the media is too large for the diameter of the column, the water may not flow evenly across the column but flow down the sides (i.e., hydraulic inefficiency due to wall effects). This would prevent adequate contact with the biofilm and thus reduce treatment efficiency. To test this theory, C3 was replaced with a smaller media of 0.95-mm 11 months after startup. Prior to changing the media in C3, the dissolved oxygen was measured (along with pH, temperature, and salinity) to characterize the oxic conditions within the filters. Due to the addition of ozone, the water at all points of the system was supersaturated with dissolved

oxygen, which can be seen in Table 10. Pre- and post-backwash conditions were evaluated to determine if backwashing had any impact on biofilter performance.

Table 10. Dissolved oxygen concentrations at various points in the system
All of the biofilters were operated under aerobic conditions based on the column effluent DO concentrations. An increase in DO concentration was witnessed in four of the six biofilters after backwashing was performed. This suggests that backwashing may negatively affect biological activity in the filters.

Pre-Backwash									
Parameter	Inf	Sample Port 6	C1	C2	C3	C4	Control	BC	Eff
Salinity (ppt)	0.9	0.8	0.8	0.8	0.8	0.8	1.1	0.8	1.0
Temperature	25.0	21.9	20.5	20.3	20.4	20.1	20.9	19.9	22.0
pH	6.8	7.37	7.27	7.28	7.24	7.20	6.92	7.20	7.25
DO (ppm)	3.5	17.7	18.5	20+	19.4	17.9	2.8	14.3	20+
Post-Backwash									
Parameter	Inf	Sample Port 6	C1	C2	C3	C4	Control	BC	Eff[a]
Salinity (ppt)	0.9	0.8	0.8	0.8	0.8	0.8	0.9	0.8	N/A
Temperature	25.3	20.7	20.5	20.1	19.8	20.1	21.5	19.3	N/A
pH	6.9	7.41	7.28	7.34	7.35	7.40	7.12	7.36	N/A
DO (ppm)	2.5	17.1	18.1	19.1	20+	20+	5.1	20+	N/A

[a]The flow rate through the effluent tubing was too low to measure these parameters

An increase in DO following backwashing would suggest a possible loss of biofilm and an inability of the smaller microbial population to degrade organic matter and consume oxygen at the pre-backwash rate. Four of the six columns experienced an increase in DO after backwashing, but it cannot be stated with certainty that this is a result of backwashing. This process was repeated for another backwashing event, but all DO measurements were above the range of the instrument (i.e., >20 mg/L), aside from the influent and control, making it impossible to make any conclusions about the effects of backwashing on the biofilm.

An unforeseen event required a shutdown of the pilot reactor for ten days (11/12/14-11/22/14). During this time, stagnant water filled the columns. This would likely significantly impact the biofilters; therefore, the TOC was monitored closely until the biofilm stabilized. Figure 18 highlights the variability in TOC removal following the shutdown; TOC removal began to stabilize around 12/17/14. After normal operation was resumed, all filters were set to an EBCT of ten minutes.

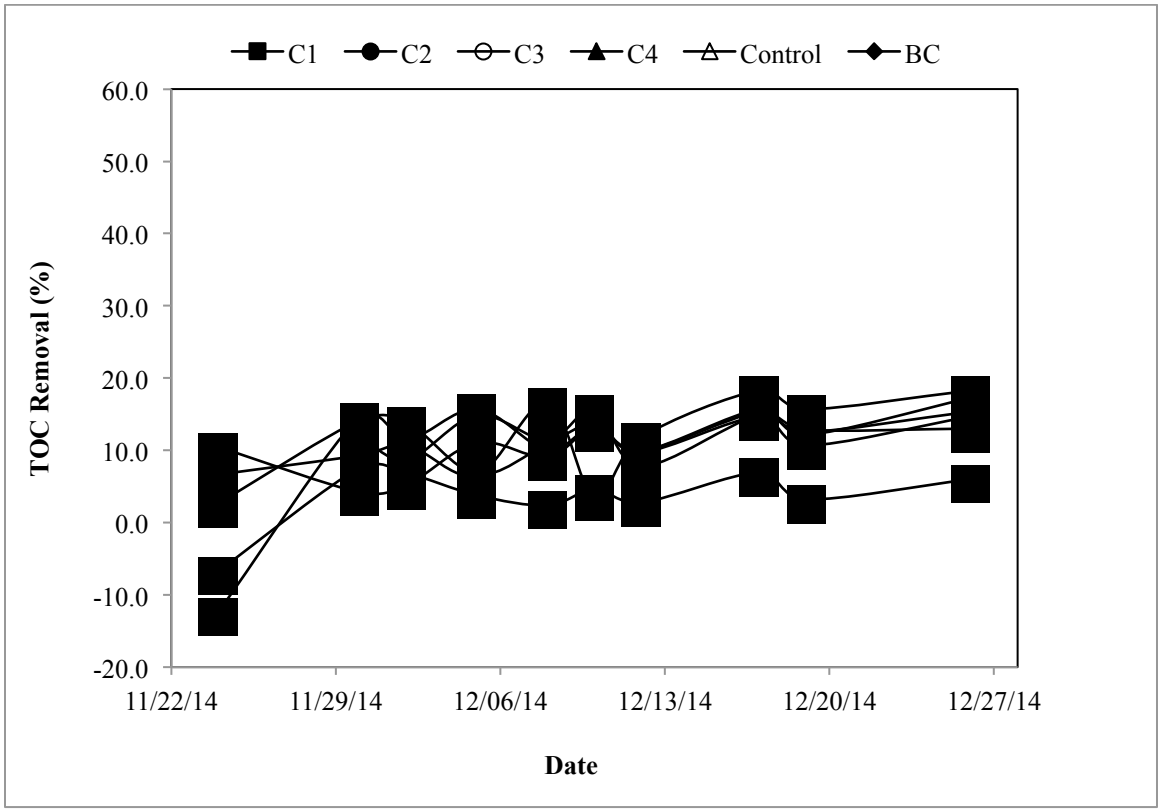

Figure 18. TOC removal after 10-day shutdown of the pilot reactor

4.4 Kinetics Testing

4.4.1 Ozone Generator Optimization

After observing no significant difference in TOC removal with varying EBCT during long-term operation, the system was re-evaluated to determine the cause of the

unexpected results. One potential explanation is that the ozone dose was too low to generate a sufficient quantity of biodegradable organic matter to sustain biological activity for EBCTs greater than 5-10 minutes. In other words, the bioavailable TOC was being consumed quicker than expected. Furthermore, it was assumed that once the biofilm was stabilized, changing the EBCT would have little impact on bulk biological activity. As with longer solids retention times in secondary biological treatment, longer EBCTs may have subtle effects on the composition of the microbial community, but this was not discernable with the bulk parameters tested in this study. To study these theories, a kinetics test with shorter EBCTs was performed.

Before the kinetics test could be executed, it was crucial to improve ozone generation efficiency and increase the ozone dose in the water. To do this, a desiccant type air dryer (Ozone Solutions, Hull, IA) was installed between the air filter and the ozone generator. The effect of this unit on the performance of the ozone generator and filters was examined. Figure 19 and Figure 20 highlight the UV_{254} and TOC removal, respectively, at different ozone flow rates with and without the air dryer. The ozone flow rate was controlled by the oxygen concentrator flow rate; the mass flow controller was removed to improve headloss through the ozone system. The data indicate that lower oxygen flow rates and lower moisture contents increase the efficiency of ozone generation. Again, it is also interesting to note the difference, particularly for the effluent sample, in differential UV_{254} absorbance versus TOC. Ozone is effective in transforming bulk organic matter (i.e., differential UV_{254} absorbance; Figure 10), but post-ozone biofiltration is necessary to achieve significant reductions in TOC (Figure 9).

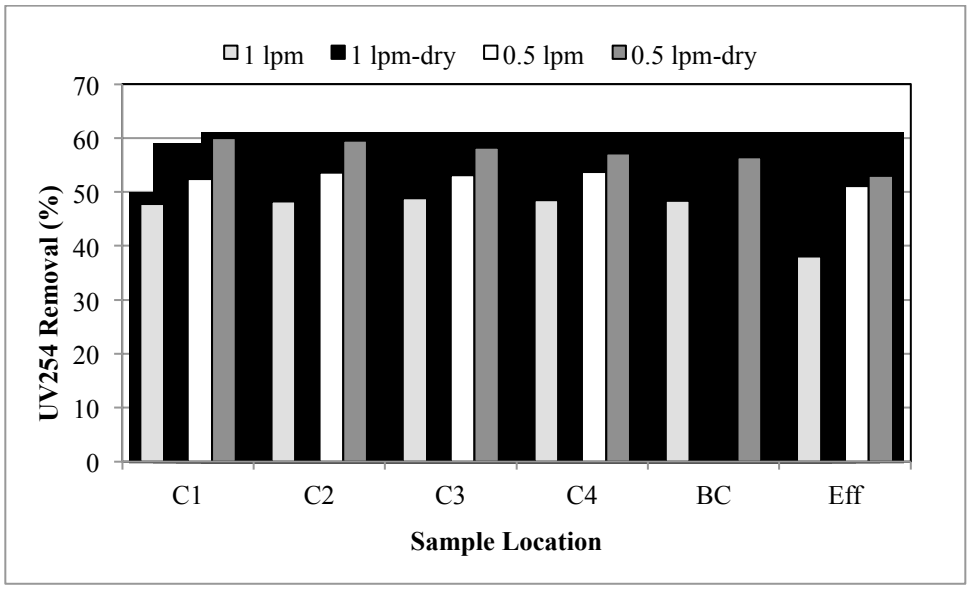

Figure 19. Air dryer performance on UV_{254} reduction.
The BC column was experiencing operational issues during the 1 lpm-dry and 0.5 lpm sampling events and samples could not be collected at those times.

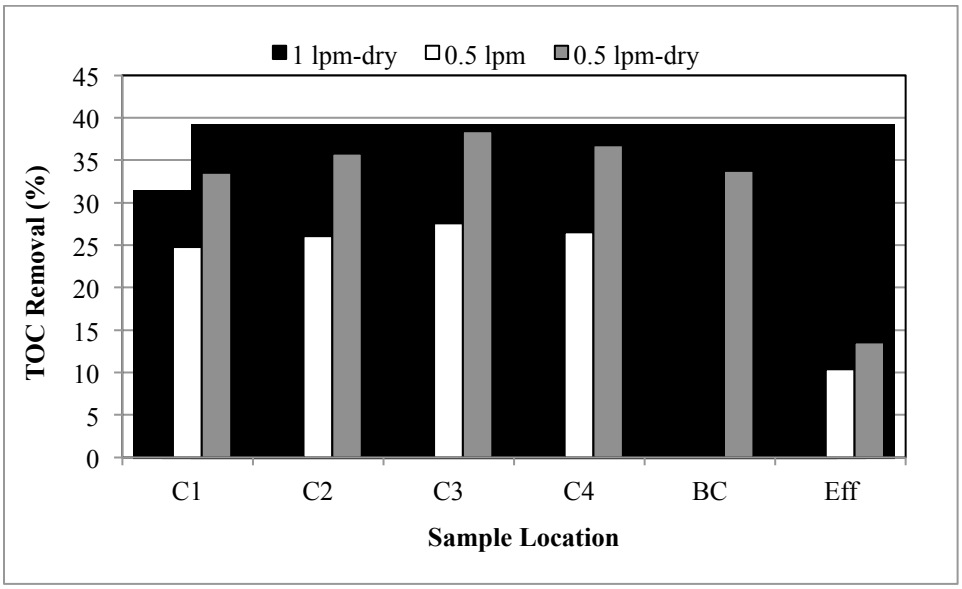

Figure 20. Air dryer performance on TOC removal.
The BC column was experiencing operational issues during the 1 lpm-dry and 0.5 lpm sampling events and samples could not be collected at those times. The TOC data for the 1 lpm sampling event was highly irregular and not included in the figure.

4.4.2 UV_{254} and O_3/TOC Correlation

Based on data obtained from the ozone demand/decay test, a correlation between UV_{254} and ozone dose was developed (Figure 21), consistent with similar correlations

presented in the literature (Gerrity et al., 2012). The data fits nicely in a logarithmic function. This function was used to estimate the ozone dose for the kinetics testing.

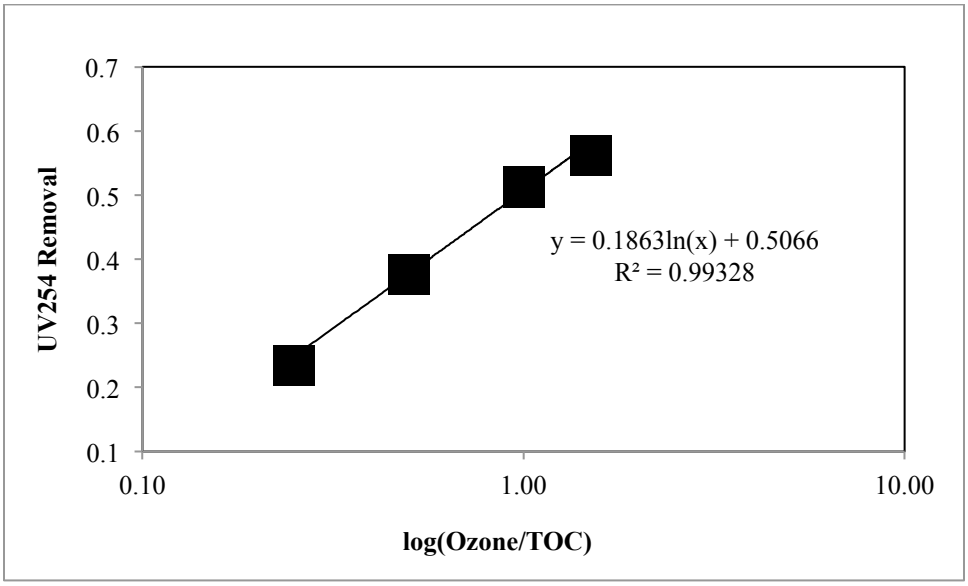

Figure 21. Characterization of the relationship between O_3/TOC and UV_{254} removal.
Data from the demand/decay was used to determine the relationship.

4.4.3 Kinetics Test Results

Three kinetics tests were performed for this study. Each one was targeting a different ozone flow rate and thus a different O_3/TOC. During the long-term operation, an average of 30% removal of UV_{254} (O_3/TOC of 0.35) was achieved at an oxygen (and ozone) flow rate of 2 lpm without the air dryer. This setting was used for the first test. The second test targeted the highest achievable UV_{254} removal, which was about 50% (O_3/TOC of 1.12). This corresponded to an oxygen (and ozone) flow rate of 0.5 lpm with the addition of the air dryer. Despite the lower gas flow rate, the ozone dose was actually higher due to more efficient ozone generation (i.e., a significantly higher ozone concentration in the gas phase). Lastly, kinetics test 3 utilized an oxygen (and ozone)

flow rate of 4 lpm to achieve an average UV_{254} reduction of 40% (O_3/TOC of 0.62) with the air dryer installed. The target sampling EBCTs, UV_{254} reduction, and estimated O_3/TOC are provided in Table 11. It should be noted that the only samples collected during the kinetics tests were influent, C2, C3, control, and effluent. C1 and C4 were redundant given that they contained the same media as C2. Due to severe compaction of the polyvinyl alcohol biobeads experienced with the BC, the flow rate was extremely low and could not be adjusted to flow rates necessary for the tests.

Table 11. Kinetics tests sampling comparison
Ozone doses estimated based on the UV_{254} and O_3/TOC correlation derived from the ozone demand/decay data. UV_{254} removal is based on ozonation alone and does not include removal through biofiltration.

EBCT (min)	Ozone UV_{254} Removal (%)	O_3/ TOC	EBCT (min)	Ozone UV_{254} Removal (%)	O_3/ TOC	EBCT (min)	Ozone UV_{254} Removal (%)	O_3/ TOC
Kinetics Test 1			Kinetics Test 2			Kinetics Test 3		
1.75	32.3	0.37	2	50.4	0.99	2	37.0	0.48
2.5	23.3	0.23	4	53.7	1.18	4	42.8	0.66
3	25.0	0.25	6	53.8	1.18	5	40.6	0.58
4	27.3	0.29	8	52.7	1.12	6	43.0	0.66
5	39.9	0.56	10	53.0	1.14	7	41.6	0.61
6	39.6	0.55	12	54.6	1.24	8	41.9	0.63
7	34.8	0.43	14	51.8	1.06	9	42.8	0.66
8	30.5	0.34	18	54.0	1.19	10	42.1	0.63
9	32.2	0.37	24	51.1	1.02	12	43.4	0.68
10	25.5	0.26	30	52.3	1.09	14	40.9	0.59
Avg.	31.0	0.35	Avg.	52.7	1.12	Avg.	41.6	0.62

The effect of the changing ozone dose can be seen in Figure 22. As the ozone dose increases, the fluorescence decreases. Humic substances are considerably reduced with an O3/TOC of 0.35, which is consistent with the observed reductions in fluorescence presented earlier in Table 8. The transition from O_3/TOC of 0.35 and 0.62

shows the largest reduction in SMP. From ozone doses 0.62 to 1.12, fulvic acids are significantly reduced. As the ozone dose increases, the water improves in all areas except for the fluorescence index (Table 12). This result was not expected and no explanation can be provided given the data that was collected.

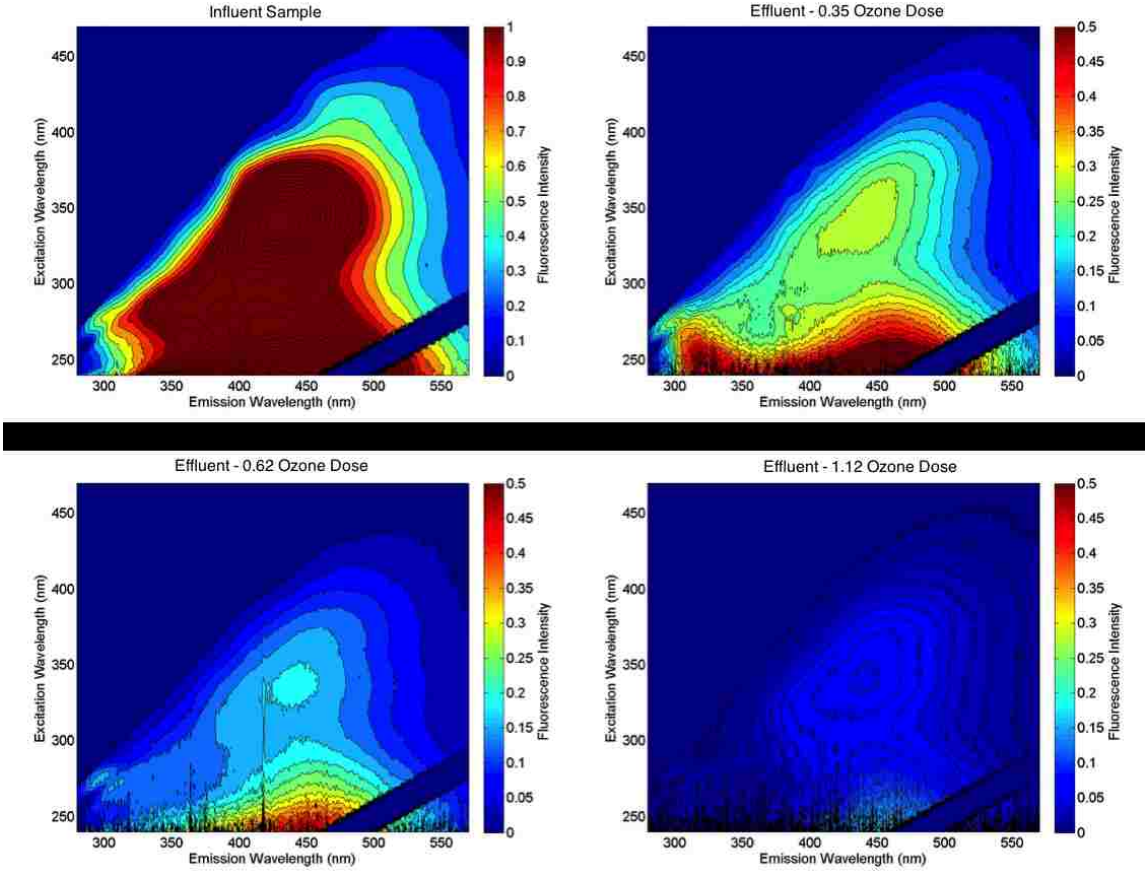

Figure 22. EEM comparison of 3 ozone doses
The changes in the fluorescence intensity of the EEM are indicative of the level of organic matter transformation through ozone oxidation. As the ozone dose increases, the more recalcitrant compounds become oxidized and the number of fluorescing compounds is reduced.

Table 12. EfOM characterization at different ozone doses
Increasing the ozone dose resulted in the removal of additional fluorescing compounds.

Sample	O_3/TOC	SMP	Fulvic Acids	Humic Acids	TF	TF Removal (%)	FI
Eff	0.35	5,214	6,200	2,437	13851	70	1.37
Eff	0.62	2,517	3,930	1,453	7900	86	1.41
Eff	1.12	576	1,381	615	2572	93	1.46

The results of kinetics test one (O_3/TOC=0.35) are provided in Figure 23. A positive correlation can be seen between TOC removal and EBCT up to around six minutes of contact time. After six minutes, little improvement is yielded with increasing contact time.

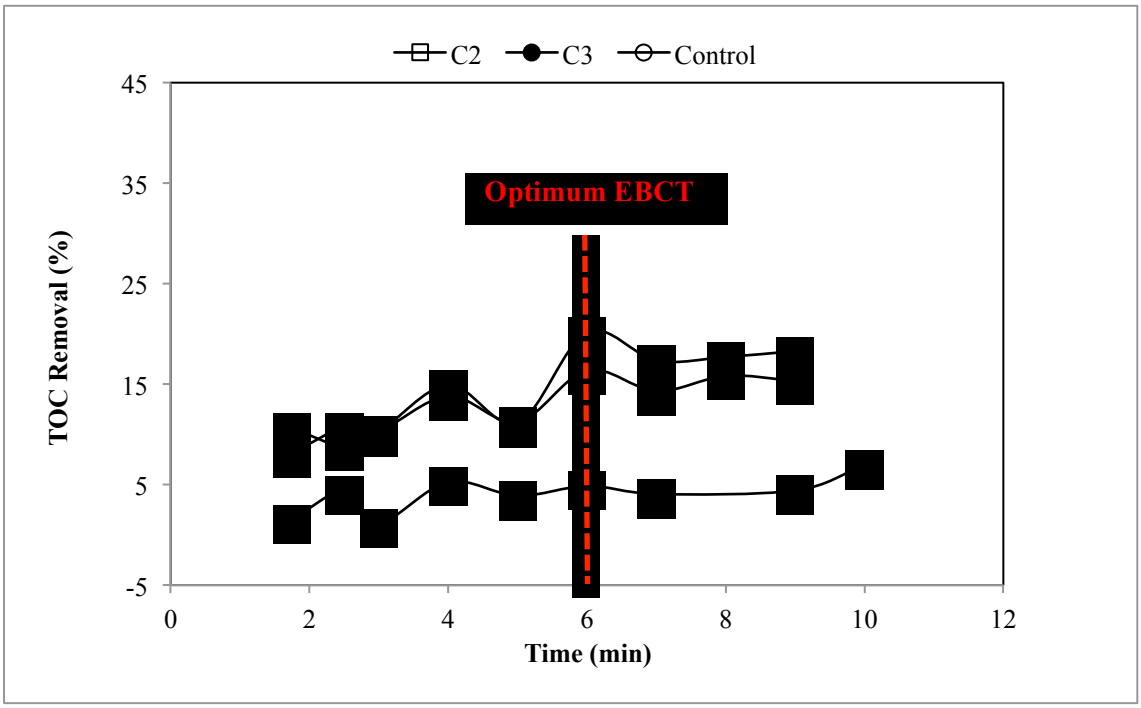

Figure 23. Kinetics test one (O_3/TOC=0.35) results for TOC removal at various EBCTs

Kinetics test two was performed at an O_3/TOC of 1.12. The same trend observed in the first kinetics test also applies to test two. However, the additional ozone improved TOC removal through the columns as indicated by Figure 24. Also, the contact time after which the TOC removal stabilizes increased to ten minutes compared with six minutes during test one.

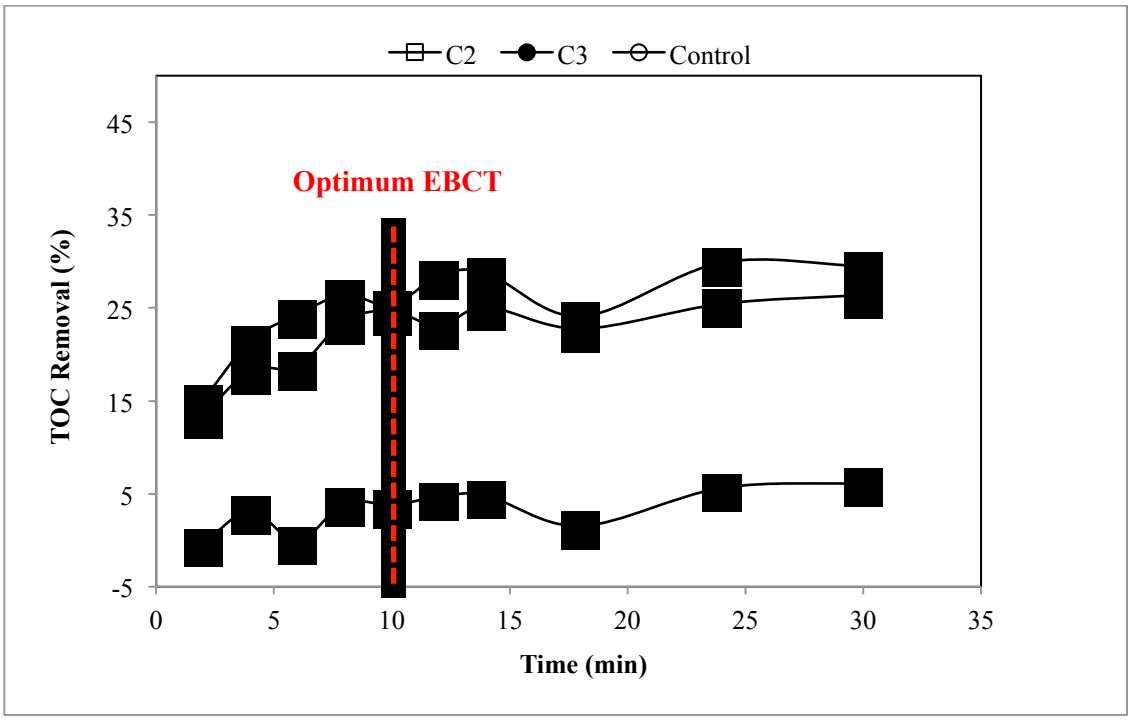

Figure 24. Kinetics test two (O_3/TOC=1.12) results for TOC removal at various EBCTs

The final kinetics test was executed using an intermediate O_3/TOC of 0.62. Again, the results are similar to the previous kinetics tests, as seen in Figure 25. As expected, based on tests 1 and 2, the TOC removal stabilized at an intermediate contact time of nine minutes.

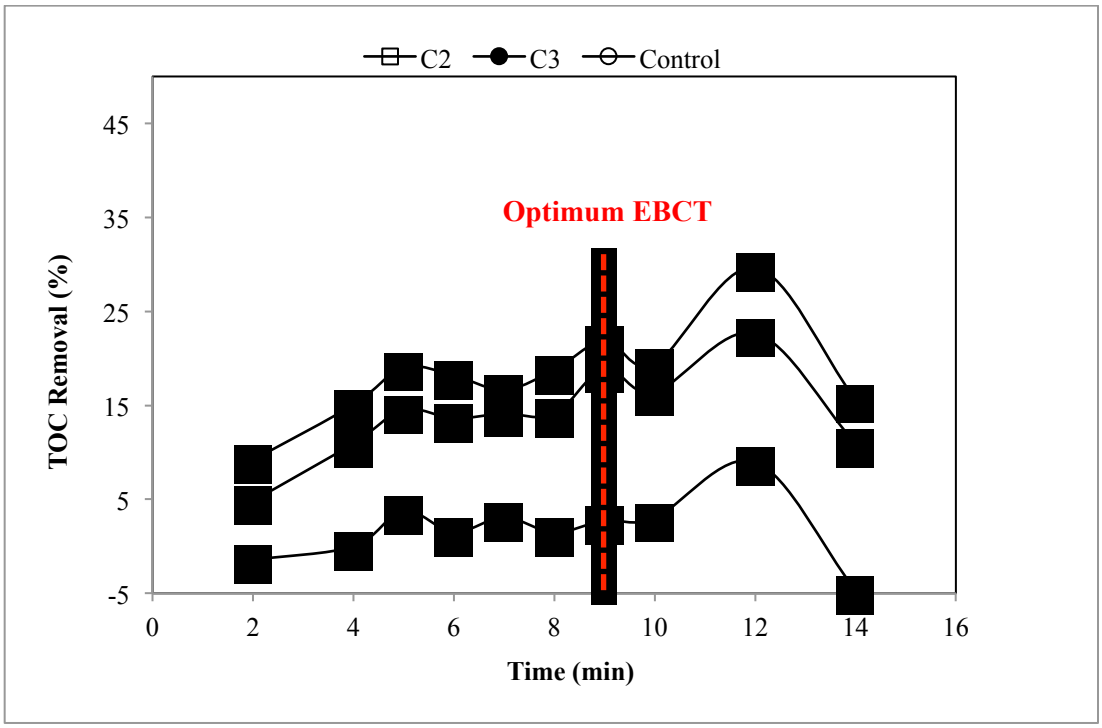

Figure 25. Kinetics test three (O_3/TOC=0.62) results for TOC removal at various EBCTs

It can be seen that the higher the ozone dose, the greater TOC removal was achieved. This was to be expected. Kinetics test 2, which had the highest ozone dose (O_3/TOC=1.12), provided the best treatment for both biofilters evaluated.

Each kinetics test was examined individually to determine the optimum EBCT at the specific ozone dose. These points were chosen through graphical observation of the point of diminishing return. This means, the optimum EBCT is the time after which little improvement in treatment efficacy is observed. Providing additional contact time with little treatment enhancement would have negative consequences to the utility; longer retention times equates to less water being treated or greater structural footprints and higher costs per unit of water treated. These results are tabulated in Table 13.

Table 13. Comparison of optimum conditions and treatment efficacy

O_3/TOC	Optimum EBCT	TOC Removal (1.2-mm Media)	TOC Removal (0.95-mm Media)	Minimum TOC Achieved
	minutes	%	%	mg/L
0.35	6	16	20	6.4
0.62	9	19	22	5.7
1.12	10	25	25	5.0

If higher ozone doses were used, it is possible that the minimum TOC values would be significantly reduced (i.e., more extensive transformation of bulk organic matter and greater removal of TOC after biodegradation). Unfortunately, due to constraints with the ozone generator, this was the highest achievable ozone dose. Based on Table 13, it appears that a relationship exists between ozone dose and optimum EBCT; therefore, the two parameters were graphed against one another and analyzed. The relationship between ozone dose and EBCT can be viewed in Figure 26. A logarithmic function appears to capture the relationship well, but additional data are warranted to further validate the relationship.

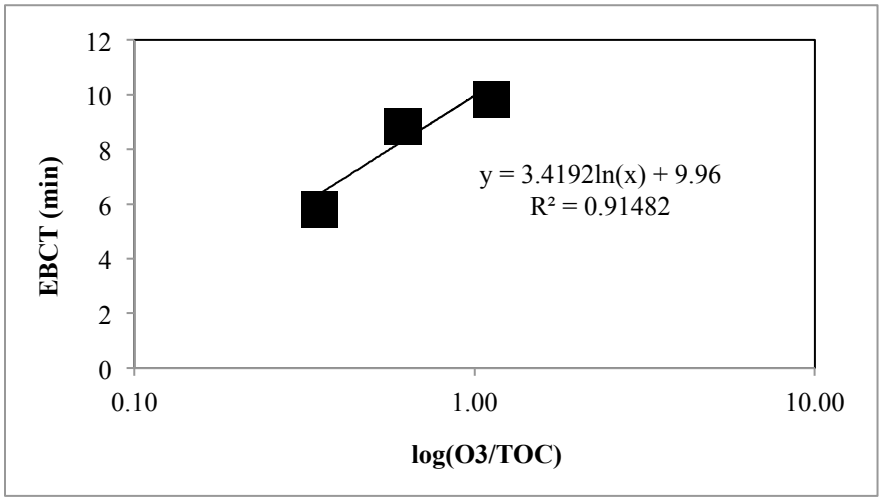

Figure 26. Relationship between ozone dose and optimum EBCT

Additionally, it is evident from the kinetics tests that C3 outperformed C2 at every ozone dose. There are two potential explanations for this observation: the smaller media provides more surface area for biological growth or the smaller media is better suited for the column size and enhances the hydraulics of the filter. To evaluate these theories, ATP samples were collected at the conclusion of the final kinetics test. Media samples were collected from two locations in C2 and C3. Based on literature, a higher concentration of ATP should be found towards the top of the column. This was true for this study as well. Both columns 2 and 3 exhibited significantly higher ATP concentrations at the top of the filter (Table 14).

Historical ATP data from this study was included to illustrate the increase in concentration in each of the columns. This may be attributed to the higher ozone doses used for the kinetics tests, which has been shown to improve biological growth. The concentration at the bottom of the filter was lower for the smaller media. Looking at the large concentration at the top of C3, this could be attributed to the depletion of available substrate for microorganisms located further down the column. Another interesting point is the significantly higher ATP concentration found in C3 versus C2 on 3/24/15. This difference in microbial growth could be the reason for the enhanced TOC removal achieved by C3. Although additional biological growth likely contributed to the additional treatment witnessed in C3, it cannot be stated explicitly because the potential impact of hydraulics was not directly evaluated.

It was also observed that the biocatalyst had significantly higher ATP concentrations but there was no appreciable improvement in biofilter performance. The same level of treatment was achieved with C2, which had much less ATP than BC.

Moreover, better treatment was witnessed in C3, which also exhibited a lower ATP concentration. This further proves that higher biomass concentrations do not always equate to more biological activity as measured by TOC removal, which has been stated in previous publications (Pharand, van Dyke, Anderson, and Huck, 2014).

Table 14. ATP concentration at various points in the filters
ATP concentrations increased from the previous sampling event likely due to the increased ozone dose and BOM concentrations. The 0.95 mm BAC exhibited a higher concentration than the 1.2 mm BAC, which may be due to a larger collective surface area of the smaller media.

Sample	tATP at Top of Column (pg ATP/g media)		tATP at Bottom of Column (pg ATP/g media)	
	9/10/14	3/24/15	9/10/14	3/24/15
C2	N/A	$6.3x10^5$	$2.0x10^5$	$3.1x10^5$
C3	N/A	$9.1x10^5$	N/A	$2.2x10^5$
Control	N/A	N/A	$5.8x10^4$	$2.0x10^5$
BC	$2.0x10^6$	$2.3x10^6$	N/A	N/A

4.4.4 Total Coliform and *E. coli* Evaluation

One of the concerns associated with biofiltration is the reintroduction of bacteria into the water. This is why it is necessary to monitor the presence of total coliform and *E. coli*; considering that the water might ultimately be used for potable applications, *E. coli* are also relevant in terms of compliance with U.S. EPA regulations. Samples were collected for the influent, effluent, C2, and the control column. The results are provided in Table 15. There was a small amount of total coliforms present in the influent water. Theoretically, there should be no coliform bacteria present in the influent water because it is MBR filtrate, and the pore size of the membrane is smaller than the size of bacteria. Instead, the presence of coliform bacteria may be attributable to growth in the system

tubing connecting the MBR sample port to the pilot reactor as well as growth within the reactor components. In fact, noticeable growth was observed in the static mixer located just ahead of the influent sample port. Once ozonated, all of the coliforms in the water were inactivated. This is evident based on the effluent values. Also, no coliforms were present in C2 effluent. The control column had the highest number of coliform bacteria, even higher than the influent. This means that some of the biofilm waas detaching from the media and entering the water. This could potentially be problematic in full-scale operations and would warrant a final disinfection process downstream of the biofilters. It is interesting that despite having a higher ATP concentration than the control, C2 effluent contains no coliform bacteria. It seems that the addition of ozone aids in, not only biofilm growth, but also biofilm attachment to the media or the selection of bacterial species other than coliform bacteria. All samples tested negative for *E. coli*.

Table 15. Total coliform most probable number (MPN/100 mL)
The total coliform concentration increased through the control column, which suggests detachment of the biofilm into the water. Ozone was effective at inactivating coliform bacteria resulting in zero coliform bacteria found in the effluent water sample.

Sample	Total Coliform (MPN/100 mL)			
	1	2	3	Average
Influent	8.5	3.1	6.3	6.0±2.7
C2	0.0	0.0	0.0	0.0
Control	13.4	14.5	8.6	12.2±3.1
Effluent	0.0	0.0	0.0	0.0

4.5 FAT and Ozone/BAC Cost Comparison

While treatment objectives are always the highest priority, associated treatment costs and environmental impacts are also very important. It is well known that FAT treatment is both energy intensive and expensive but to put it into perspective, a study by

Gerrity et al. (2014a) compared energy requirements and capitol and operation and maintenance (O&M) costs of a 10 MGD FAT treatment versus a 10 MGD O_3-BAC-microfiltration (MF)-UV treatment. The FAT system evaluated consisted of MF-RO-UV/H_2O_2. The O_3-BAC-MF-UV system can potentially achieve nearly 4 GWh of energy savings and capital and O&M cost savings of $25 million and $2.2 million, respectively. One caveat is that O_3-BAC-MF-UV systems cannot significantly remove TDS and additional treatment would be necessary for TDS management thus potentially undermining the cost benefits to this type of system.

CHAPTER 5 CONCLUSIONS

This study evaluated the performance of an ozone-biofiltration pilot reactor using BAC and a proprietary biocatalyst as the filter media. Biological growth was monitored based on TOC removal and ATP concentrations. Once a stable biological community was established, achieving improved TOC removal was attempted by assessing the relationship between ozone dose and EBCT. Based on the results of the study, several conclusions can be made regarding ozone-biofilter system performance and suitable operational conditions.

5.1 Findings Confirming Previous Work

- After monitoring dissolved oxygen concentrations prior to and after backwashing, an increase in dissolved oxygen was observed in the effluent from several columns post-backwash. This may indicate that backwashing disrupts the microbial community (e.g., by promoting biofilm detachment) and decreases their ability to consume biodegradable organic matter (and dissolved oxygen). Because of the potential water quality implications, such operational upsets warrant further investigation in future studies.
- It was found that oxygen feed rates and moisture content of the oxygen feed adversely impact ozone generator performance and ozone dosing. Lower moisture content and lower oxygen flow rates increase ozone concentrations in the feed gas.
- Based on the fluorescence of the treated water, it was found that humic substances were the most prevalent at all sample locations. Up to 92% of the humic substances were transformed through ozonation, with an additional 2% reduction

provided through biofiltration. In addition, there was minimal reduction in TOC during ozonation but a substantial reduction in TOC during biofiltration. Therefore, fluorescence and TOC are complementary bulk organic parameters for evaluating the performance of ozone-BAC treatment trains.

- A logarithmic relationship was identified between UV_{254} removal and O_3/TOC, which allows for estimation of ozone dosing based on changes in UV_{254} absorbance.
- Higher ozone doses yielded better TOC, UV_{254}, and fluorescence removal through biofiltration, as expected based on literature.
- ATP concentrations were higher at the top of the filters as compared with the bottom of the filters. The small media provided more surface area for biological growth, which explains the higher ATP concentration found on the small media. This may also explain the better treatment efficacy achieved with the small media, although improved hydraulic performance may also contribute.
- The biocatalyst housed the highest concentration of ATP (upwards of 50% more ATP) but did not yield additional removal of contaminants. This suggests that higher biofilm concentration does not necessarily correlate to better treatment in all applications, which is in agreement with literature findings.

5.2 Significant Findings

- The BAC filters were inadequate in removing NO_3-N, NO_2-N, and PO_4-P from the water and actually contributed to higher nutrient concentrations. The biocatalyst exhibited an average of 2.2% removal of NO_3-N and 12.8% removal

of NO_2-N. This indicates that despite the presence of DO in the reactor influent, the media was able to perform some denitrification.

- No *E. coli* was found at any point in the system, but total coliform were discovered in the influent and control effluent. The control exhibited higher total coliform numbers than the influent suggesting that the biofilm was detaching from the media and entering the water. The ozonated column, however, did not contribute any coliform bacteria despite the higher ATP concentration present. This suggests that ozonation may impact biological attachment to the media or it may select for different species of bacteria due to the change in biodegradable organic matter.
- One of the major objectives of the study was to identify a relationship between ozone dose and empty bed contact time based on TOC removal. Based on the kinetics tests performed, optimum EBCTs for various ozone doses were identified. The optimum EBCT for O_3/TOC of 0.35, 0.62, and 1.12 were found to be 6, 9, and 10 minutes, respectively. When plotting optimum EBCT versus O_3/TOC, a logarithmic relationship appeared to exist between the two parameters. Based on this relationship it appears that relatively low EBCTs are necessary for TOC removal; however, additional testing is warranted to validate the relationship.
- Another key finding derived from the kinetics tests was the resilience in bulk biological activity to changes in the EBCT based on TOC removal after a stable biological community is developed. A time interval equivalent to three HRTs was sufficient for biological activity stabilization in the biofilters.

- The highest ozone dose of 1.12 O_3/TOC was the optimum ozone dose used in this study. At this ozone dose, reductions of up to 95% of fluorophores associated with SMPs, 92% of fluorophores associated with fulvic acids, and 92% of fluorophores associated with humic substances were achieved. At the optimum ozone dose and EBCT, the minimum TOC concentration attained was 5.0 mg/L. It is assumed that higher ozone doses would achieve even better water quality, but the data suggests that there is a point of diminishing return for ozone dosing as well.
- Despite optimization, O_3/BAC systems alone are insufficient to meet the stringent DDW TOC requirement of 0.5 mg/L. If higher ozone doses were used, this goal may have been more attainable, but the data suggests the TOC removal would plateau far before reaching a 0.5 mg/L effluent TOC concentration. Also, considering that the source water was MBR filtrate, it might also be interesting to study differences between MBR filtrate and conventional secondary effluent to determine whether one is more recalcitrant.
- Possible strategies to comply with existing potable reuse regulations include: increasing the percentage of diluent water or adding additional treatment steps. The 0.5 mg/L target applies to 100% recycled water. If diluent water is added, this target value will increase accordingly. Some additional treatment options include adding a supplementary GAC column or employing ion exchange. Humbert, Gallard, Suty, and Croue (2005) demonstrated 80% DOC removal with a 30-minute contact time using strong anion exchange resins. Two GAC columns operated at 13 minute EBCTs achieved 65% TOC removal and over 70% DOC

removal (Gibert et al., 2013). However, it is important to note that not all states have such stringent regulations on effluent TOC concentrations. Therefore, the applicability of ozone-BAC facilities may vary by location. It is important to note that ozone-BAC is unable to reduce total dissolved solids (TDS) concentrations, which are typically high in wastewater. Therefore, additional treatment for TDS may also be needed in potable reuse applications.

5.3 Future Work

There is much potential in ozone-BAC systems, but additional research must be conducted that could not be performed given the limitations of this study. The apparent logarithmic relationship that exists between O_3/TOC and EBCT was not fully established. Higher ozone doses must be explored and larger data sets gathered to better understand the relationship that may exist. Also of interest would be examining this relationship based on various water matrices and media type. If different water qualities yield similar results, correlations could be made and utilized by water utilities at any location. This would save time and money on ozone dosing and biofilter performance experiments.

Another possible avenue for research would be to analyze the effect of ozonated water on biofilm attachment to media and biological community makeup. Events taking place within the biofilter are largely unknown and must be evaluated to better understand how to optimize this type of water treatment.

Based on the performance of the biocatalyst in removing TOC as well as nitrite and nitrate, it would be worth investigating different column configurations and operational conditions to enhance the performance of this media. For instance, an upflow biofilter (i.e., a fluidized bed) may be more suited for the biocatalyst since it was not

designed for packed-bed applications. Also, this would alleviate the issue of compaction and caking. The presence of dissolved oxygen likely inhibited denitrification; operating the biocatalyst column in series with a BAC filter or using nitrogen gas for sparging may help alleviate this problem.

It is unclear what possible health effects are associated with TOC; therefore, the 0.5 mg/L threshold may not be necessary to maintain public safety in potable reuse applications. Further examination of this bulk parameter is needed.

APPENDIX

FLUORESCENCE STANDARD OPERATING PROCEDURE

Samples should be at room temperature, filtered (0.7 μm), and analyzed within 48 hours

1. Turn on computer and Aqualog instrument
2. Allow Aqualog to warm up for 15 minutes
3. Open Aqualog software
4. Raman measurement (perform 3 separate times each time the Aqualog is turned on)
    a. Fill sample cell with nanopure water and place into holder
    b. Click **H2O** button to initialize instrument and open 'Aqualog Main Experiment Menu'
    c. Click **Spectra**
    d. Click **Emission 2D**
    e. Load archived experimental settings file or create new protocol
        i. Use a consistent filing system so that you can recall old settings
    f. Verify settings:
        i. Change Data Identifier (used to identify sample in workgroup)
        ii. Integration = 3 s
        iii. Accumulations = 1
        iv. Excitation Wavelength Park = 350 nm
        v. Emission Wavelength Increment = 0.82 nm (2 pixel)
        vi. CCD Gain = Medium
        vii. Blank/Sample Setup = Sample Only
    g. Click **Run**
    h. **(Only on first run of workgroup)** Choose directory to save project file
        i. Use a consistent filing system so that you can recall old files
        ii. Only run 5-10 samples per project file (workgroup) to limit file size
    i. Click **Emission Sample Data** tab
        i. Click **File → Export → ASCII** and save file as a **.txt file** with tab separator
    j. Open Excel and then open the exported file and save as an Excel Workbook
5. Sample Measurement
    a. Fill one sample cell with nanopure water (to be used for blank)
    b. Fill second sample cell with sample to be analyzed
    c. Click **H2O** button to initialize instrument and open 'Aqualog Main Experiment Menu'
    d. Click **3D**
    e. Click **EEM 3D CCD + Absorbance**
    f. Load archived experimental settings file or create new protocol
        i. Use a consistent filing system so that you can recall old settings

g. Verify settings:
    i. Change Data Identifier (used to identify sample in workgroup)
    ii. Integration = 3 s
    iii. Excitation Range: High = 470 nm, Low = 240, Increment = 1 nm
    iv. Emission Wavelength Increment = 0.82 nm (2 pixel)
    v. CCD Gain = Medium
    vi. Blank/Sample Setup = Sample and Blank
        1. Collect blank on first run or load archived blank from that day
h. Click **Run**
i. **(Only on first run of workgroup)** Choose directory to save project file
    i. Use a consistent filing system so that you can recall old files
    ii. Only run 5-10 samples per project file (workgroup) to limit file size
j. Click **Abs Spectrum Sample** tab
    i. Click **File → Export → ASCII** and save file as a **.txt file** with tab separator
k. Click **Sample – Blank** tab
    i. Click **File → Export → ASCII** and save file as a **.txt file** with tab separator
l. Click **Sample – Blank Waterfall Plot** tab
    i. Click **Inner Filter Effect** button (next to H_2O)
m. Click **Processed Data: IFE** tab
    i. Click **File → Export → ASCII** and save file as a **.txt file** with tab separator
n. Click **Processed Graph: IFE** tab
    i. Click **Rayleigh Masking** button (next to IFE)
    ii. "Mask 1st Order Rayleigh" should be checked
    iii. "Mask 2nd Order Rayleigh" should be checked
    iv. "SUM of slit widths (in bandpass)" should be 10
o. Click **Processed Data: IFE_RM** tab
    i. Click **File → Export → ASCII** and save file as a **.txt file** with tab separator
p. Save all files in a permanent folder named according to sample description

6. Process the data with MATLAB
    a. Open Excel and then open the **Processed Data: IFE_RM** file and save as an Excel Workbook
    b. Open the **Abs Spectrum Sample** file and save as an Excel Workbook
    c. Move a copy of the following files to your "working" folder for MATLAB analysis
        i. The 3 **Raman** Excel files
        ii. The **Processed Data: IFE_RM** Excel file
        iii. The **Abs Spectrum Sample** Excel file
        iv. Verify that your "working" folder also contains the **ABS and FRI** Excel files
    d. Open the appropriate MATLAB code (Aqualog.m)

e. Verify that the MATLAB home screen is linked to your working folder.
f. Verify that all directories in the MATLAB code (purple text) are valid.
g. Run the program.
h. Move all processed data to permanent folder.
i. Only move a copy of the **FRI** and **ABS** Excel files to your permanent folder. These files must remain in your working folder for future processing.

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