FEASIBILITY OF BIOLOGICAL ION EXCHANGE IN REMOVAL OF ORGANIC CARBON FROM DRINKING WATER AT DIFFERENT TEMPERATURES

by

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis entitled:

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Abstract

Removing organic carbon (OC) from drinking water effectively while utilizing technologies that are both low cost and easy to operate poses challenges. Current available technologies are either very complex, expensive and/ or cannot achieve high removal efficiencies. Conventional biological filtration has long been used to remove OC from water however it has not done so effectively and therefore cannot be used as a standalone technology. Biological ion exchange (BIEX) is a new technology that promises to address the limitations of existing technologies. Initial studies have indicated that this technology is effective at reducing OC in water, further studies are needed to optimize the design parameters under a variety of environmental conditions. Previous studies on conventional (BAC) biofilters have indicated that empty bed contact time (EBCT) and operating temperature influences the efficacy of OC removal. The objective of the present study is to determine the EBCT needed in BIEX biofilters to effectively remove NOM at different temperatures. To determine the impact of EBCT on OC removal biofilters at three different EBCT (7.5, 15 and 30-minutes) and three different temperatures (4, 10 and 20°C) were operated for 150 days.

Results from the present research indicate that BIEX biofilters more effectively remove OC from water than BAC biofilters. BIEX biofilters remove 46.5-77.5% OC while BAC biofilters remove 4.6-31.3% OC depending on the experimental conditions (temperature and EBCT). Statistical analysis indicated that both temperature and EBCT significantly impact OC removal in both BIEX and BAC biofilters. The temperature activity coefficients were calculated to be 1.044 and 1.066 for BIEX and BAC biofilters respectively indicating that temperature has a greater impact on OC removal for BAC biofilters than for BIEX biofilters. The rate constant for removal of OC was calculated for both BIEX and BAC biofilters and ranged from 0.156 to 0.312

min^{-1} and 0.034 to 0.108 min^{-1} respectively. These results indicate that BIEX biofilters can also remove OC at a higher rate than BAC biofilters. To ensure adequate removal of OC at all temperatures that were tested (90% removal of OC) BIEX and BAC biofilters require an EBCT of 55-minutes and 90-minutes respectively.

Lay Summary

Drinking water is frequently taken from surface water sources. Surface water contains organic carbon (OC) that can discolour the water and form harmful by-products when water is chlorinated prior to being distributed to users. Existing technologies are either expensive or difficult to operate, posing challenges to municipalities, especially remote communities. Currently, biofilters such as biological activated carbon (BAC), are used to remove OC, BAC removes a small amount of OC and must be used with other technologies. Biological ion exchange (BIEX) is a new biofilter that is cheap and easy to operate. Performance of biofilters can be impacted by temperature and filtration time. The current study indicated the BIEX biofilters can remove a higher percentage of OC than BAC biofilters at both low (winter) and high (summer) temperatures. BIEX biofilters require a shorter filtration time than BAC biofilters to remove OC at low temperatures when OC removal is most difficult.

Preface

This dissertation is original, unpublished, independent work by the author, E. Mills.

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"Every step we take we are closer to the end"

Kevin Robb

1 Introduction

Across Canada fifty-six First Nations communities face long term boil water advisories (Indigenous Services Canada, 2019a). There are currently 45 short-term boil water advisories in First Nations communities south of the 60th parallel, excluding British Columbia and the Saskatoon Tribal Council jurisdictions (Indigenous Services Canada, 2019b). According to the Government of Canada in 2017 83% of boil water advisories were due to equipment and process related problems (Environment and Climate Change Canada, 2018). Regardless of the reasons behind the equipment and process related problems, making drinking water treatment systems simpler and cheaper to operate will help reduce the frequency of boil water advisories.

Many communities draw their drinking water from surface water sources; as of 2017 88% of Canadians received their water from surface sources (Statistics Canada, 2019). Surface water must be treated to remove contaminants such as turbidity, pathogens and natural organic matter (NOM). Although NOM has no known negative impacts on human health it is a notable contaminant of concern because it negatively impacts the aesthetic quality of the water, contributes to bacterial regrowth and the formation of disinfection by-products (DBPs) in distribution systems. NOM can cause the water to have an unpleasant colour, odour or taste making it undesirable for the end user to consume. Bacterial regrowth can occur in distribution systems when NOM is present, increasing the risk of microbial contamination. Disinfection can also lead to the formation of DBPs in waters with high levels of NOM; DBPs are regulated in many jurisdictions as some have been identified as possible carcinogens (Singer, 2006).

Many technologies exist to remove NOM from water. However, existing technologies are both complex and expensive, such as nanofiltration, or do not achieve high NOM removal

efficiencies, such as biological activated carbon (BAC). Biological ion exchange (BIEX) promises to overcome the limitations of existing NOM removal technologies by providing a simple, low cost and effective approach to NOM removal (Winter et al., 2018).

2 Literature Review

2.1 Natural Organic Matter Removal Technologies

There are many technologies that remove NOM from raw water. These include coagulation, nanofiltration, activated carbon, ion exchange and biofiltration.

The coagulation process is an effective method of reducing NOM. NOM is adsorbed to solids generated by adding a coagulant to the water and then removed from the water via sedimentation or filtration. The efficacy of coagulation varies based on water quality and coagulant type; in general, coagulation can achieve approximately 25% to 67% removal of NOM (Matilainen, Vepsäläinen, & Sillanpää, 2010). Coagulation systems are difficult and expensive to operate due to the complexity of the treatment process and the high chemical (coagulant) requirements. The cost of purchasing and transporting the required chemicals can be prohibitive, especially in rural areas. Further, this treatment process creates waste solids that must be collected and disposed of.

Nanofiltration (NF) utilizes membranes with a very small molecular weight cut-off (200-1000 Da) to filter out NOM (Winter, Barbeau, & Bérubé, 2017). NF provides up to 90% NOM removal (Orecki, Tomaszewska, Karakulski, & Morawski, 2004). However, NF treatment systems are typically complex. Pre-treatment, which often involves coagulation along with filtration, is required to minimize membrane fouling. Further, NF has relatively high energy requirements for permeation and chemical requirements for membrane cleaning.

Activated carbon can also remove high levels of NOM through adsorption (Jacangelo, DeMarco, Owen, & Randtke, 1995). Activated carbon does not require the use of chemicals

however; its removal capacity is exhausted over time. The exhausted activated carbon has to be shipped out for re-generation, or to be replaced, both of which are expensive.

Anionic ion exchange resins also have the ability to remove NOM from water. The ability of anionic exchange resins to remove NOM from water depends on the type of organic matter present, the physical properties of the filters and properties of the resin (Bolto, Dixon, Eldridge, King, & Linge, 2002). Like activated carbon, ion exchange resins are exhausted over time and must be regenerated in order for NOM removal to continue. Regeneration creates a waste stream that must be treated and disposed of, increasing the complexity and cost of treatment.

Biofiltration is capable of removing biodegradable organic matter and particles from water. The ability of biofilters to remove NOM from water depends on many factors such as media type, pre-ozonation dose, empty bed contact time (EBCT), water temperature and type of NOM present in the water being treated (Basu, Dhawan, & Black, 2016). Traditionally, these filters have been composed of sand, anthracite or granular activated carbon and NOM removal though these filters is low (Basu et al., 2016). However, recent studies have indicated that a greater percent of NOM removal can be achieved when using ion exchange resins as biofilter media (Winter, et al., 2018).

2.2 Variables Affecting Biofilter Performance

2.2.1 Effect of Temperature

For a water treatment system to successfully operate the technology must provide treatment at various temperatures. Especially in northern climates, where temperature fluctuates significantly, it is important that the system is able to effectively remove NOM at high summer

temperatures as well as at low winter temperatures. Limited research has investigated the effect of temperature on NOM removal using BIEX biofilters, however a significant amount of research has been conducted on the effect of operating temperature on NOM removal using conventional biofilters using sand, anthracite or activated carbon.

Past studies have not demonstrated a consistent impact of temperature on NOM removal through conventional biofilters. Several studies have indicated that low temperatures (less than 10°C) negatively impact removal. Welté and Montiel (1996) reported that at temperatures less than 9°C, biodegradation of NOM is limited in slow sand filters, while at 6°C, removal of NOM occurred only through adsorption. Studies by Seger and Rothman (1996), Moll, Summers, Fonseca and Matheis (1999) and Halle (2009) support these findings. Seger and Rothman (1996) reported that at temperatures greater than 15°C around 20% of NOM was removed; removal decreased to 5% at temperatures less than 3°C. Moll et al. (1999) reported that NOM removal decreased by 42% on average (different organic compounds were measured) when conventional biofilters were operated at 5°C than when the filter was operated at 20 and 35°C. Halle (2009) reported that conventional biofilters removed 11-14% NOM over the summer months and less than 5% over the winter months when water temperature was between 3 and 4°C.

Other studies have reported that there was no difference in NOM removal between studies carried out at high (21-24°C) or low temperatures (1-3°C). However, all studies that have reported no impact of temperature on NOM removal were performed utilizing a relatively long (greater than approximately 20 minutes) empty bed contact time (EBCT). Studies by Emelko Huck, Coffey and Smith (2006) (EBCT 17-36 minutes), Persson, Heinicke, Uhl, Hedberg and Hermansson (2006) (EBCT 31 minutes) and Van der Aa, Rietveld and Van Dijk (2011) (EBCT 40 minutes) all observed no impact of temperature on NOM removal. Studies by

Welté and Montiel (1996) as well as Seger and Rothman (1996) demonstrated that temperature impacted NOM removal at short EBCT.

Limited knowledge exists regarding the impact of temperature change on the microbial community in conventional biofilters. However, it is likely that NOM removal decreases at low temperatures due to a decrease in biological activity. Welté and Montiel (1996) reported that when temperatures dropped from 15 to 9°C NOM (measured as biodegradable dissolved organic carbon) removal decreased from 76 to 20%. They inferred that biological degradation was no longer occurring (Welté & Montiel, 1996). Moll et al. (1999) reported that conventional biofilters operated at higher temperatures have a higher mass of attached biomass and this increased biological growth likely contributed to higher NOM removal at higher temperatures. Halle (2009) concluded that microbial kinetics were only affected after several weeks at a new temperature after observing a lag between a temperature change and a change in NOM removal.

2.2.2 Effect of Media Type

Biofilters can be developed on various types of media such as sand, anthracite, activated carbon and ion exchange resins. Previous studies have demonstrated that biofilters of different media types remove different amounts of NOM. A study by Thiel et al. (2006) reported that granular activated carbon (BAC) conventional biofilters removed higher amounts of NOM than anthracite conventional biofilters at both high and low temperatures. Liu, Huck and Slawson (2001) observed that temperature had a greater impact on the removal of NOM through anthracite conventional biofilters than for BAC conventional biofilters. A study by Wang, Summers and Miltner (1995) also observed the difference in removal of NOM between BAC (29% dissolved organic carbon (DOC) removal), anthracite-sand (16% DOC removal) and sand (20% DOC removal) conventional biofilters. The same study noted that the BAC conventional

biofilters had developed at lot more biomass than the anthracite-sand or sand filters (Wang et al., 1995)

2.2.3 Effect of NOM Type

The effectiveness of NOM removal depends on the type of NOM present in the water. Pharand, Van Dyke, Anderson, Yohannes and Huck (2015) reported that certain organic compounds were more difficult to remove than others, especially at low temperatures. The removal of biopolymers and low molecular weight acids was significantly affected by the change in temperature. However, the removal of humics and low molecular weight neutrals, molecules with both low molecular weight and low ion density (Huber, Balz, Abert & Pronk, 2011), was not affected by temperature. These results are consistent with those observed by Liu et al. (2001) and Emelko et al. (2006) and indicate that temperature has no impact on the removal of organic compounds that are easily biodegradable. This conclusion is further supported by studies that utilize ozonation prior to treatment of water through a biofilter. Seger and Rothman (1996) reported that ozonation increased NOM removal at low temperatures more than at high temperatures. Ozonation likely increases the biodegradability of NOM.

2.2.4 Effect of EBCT and HLR

EBCT is commonly used as one of the main design parameters for biofilters (Basu et al., 2016). It can be estimated by Equation 1.

Equation 1: Definition of Empty Bed Contact Time

$$EBCT = \frac{A * l}{Q}$$

where A is the cross-sectional area, l is the length of the column and Q is flow rate through the column

EBCT is closely related to hydraulic loading rate (HLR) which also quantifies flow through biofilters. HLR can be estimated using Equation 2.

Equation 2: Definition of Hydraulic Loading Rate

$$HLR = \frac{Q}{A} = \frac{l}{EBCT}$$

where A is cross sectional area and Q is hydraulic flow rate

Several studies have reported that NOM removal is impacted by EBCT. Le Chevallier, Becker, Schorr and Lee (1992) reported that NOM removal increased by over 20% when the EBCT of a conventional biofilter was increased from 5 to 20 minutes. Le Chevallier et al. (1992) did not control temperature. However, several other studies have indicated the contrary; that NOM removal is not impacted by EBCT. Hozalski, Goel and Bouwer (1995) controlled temperature at 22.5°C and reported that NOM removal was between 16 and 30% regardless of EBCT (4, 10 and 20 minutes) and that what impacted NOM removal was NOM type. These findings were supported by Wert, Neemann, Rexing and Zegers (2008) where EBCT varied between 3.2 and 8.3 minutes. Wert et al. also reported that changes in HLR did not impact NOM removal. As discussed in section 2.2.1 the impact of EBCT on NOM removal is likely impacted by other process variables such as temperature. As previously mentioned, Hozalski et al. (1995) demonstrated that at high temperatures (22.5°C) EBCT did not impact NOM removal. However, in subsequent studies Hozalski, Bouwer and Goel (1999) observed that at lower temperatures a longer EBCT was needed to achieve the same degree of NOM removal.

While the effect of EBCT on NOM removal through conventional biofilters has been extensively studied, the effect of HLR on NOM removal is not well understood (Basu et al.,

2016). However, a study by Carlson and Amy (1998) indicated that HLR did not affect NOM removal through biofilters if the system was operating at steady sate.

2.3 Variables and Affecting Exchange Resins Performance

Limited experiments have investigated the impact of temperature, EBCT and NOM type on NOM removal using anionic exchange resins (IEX) and therefore the impact of these process variables on NOM removal using IEX is largely unknown. Humbert, Gallard, Suty and Croué (2005) reported that temperature only impacted removal of NOM at high temperatures (36°C) while there was no difference in NOM removal at lower temperatures (6, 16 and 26°C). If the contact time is increased to 15 minutes, temperature had no impact on NOM removal (Humbert et al., 2005). Existing studies indicate that temperature and contact time impact biofitlers and IEX in a similar manner; longer contact times reduce the impact of temperature (Humbert et al., 2015, section 2.2).

2.4 Knowledge Gap

Given that previous studies have indicated that temperature and EBCT impact NOM removal through conventional biofilters it is reasonable to hypothesize that these variables will also impact the performance of BIEX biofilters. However, this assumption needs to be confirmed. Currently, there have been very few studies on BIEX biofilters and none which investigate the impact of temperature and EBCT in a controlled environment.

Additionally, the mechanisms responsible for the removal of NOM in BIEX biofilters are unknown. Traditional biofilters rely of biological activity to remove NOM from water. However, considering the difference in removal mechanisms of NOM between conventional and

BIEX biofilters, it is likely that mechanisms in addition to biodegradation contribute to NOM removal in BIEX biofilters.

3 Proposed Research

3.1 Objective

The overall objective of the present study is to determine the EBCT needed in BIEX biofilters to effectively remove NOM at different operating temperatures. As discussed in section 2, EBCT is one of the most important process variables affecting the removal of NOM through biofilters and is one of the main design parameters. The intermediate objectives are as follows.

1. Benchmark the performance of BIEX and conventional (BAC) biofilters at different temperatures and EBCTs. BAC is used as a model conventional biofilter for comparison purposes.
2. Demonstrate if BIEX biofilters are more effective at NOM removal than conventional (BAC) biofilters.
3. Gain insight into the NOM removal mechanism in BIEX biofilters.

3.2 Outcomes

The results obtained from the present study will help to determine whether BIEX biofilters are a viable and more effective alternative to conventional biofilters for the removal of NOM at both high and low temperatures. Specifically, the present study aims to:

1. determine the EBCT to be used for the design of BIEX biofilters;
2. compare the performance of BIEX biofilters to conventional (BAC) biofilters; and
3. provide insight into the NOM removal mechanism for both BIEX and conventional (BAC) biofilters.

4 Materials and Methods

4.1 Experimental Set-up and Materials

4.1.1 Feed Water Preparation

The feed water for the BIEX and BAC biofilters consisted of a mixture of pond water and tap water. The pond water was collected from Jericho Pond in Vancouver, British Columbia. The location of Jericho Pond is displayed in Figure A-1 (Appendix A).

Pond water was collected from Jericho Pond monthly and then stored in a dark 4°C refrigerator until use. The dates that water was collected from Jericho Pond are listed in Table 1.

Table 1: Dates that water was collected from Jericho Pond and when it was first used as influent

Date Collected	Date Use Started	Experiment Day Number Use Started
Dec 13	Dec 15	9
Feb 5	Feb 6	62
March 13	March 30	103
April 23	April 28	142

Pond water was removed from storage as required and was vacuum filtered through VWR Glass Microfibre 691 filters with a pore size 1.5μm. After filtration the pond water was mixed with tap water to achieve a TOC concentration to approximately 5 mg/L prior to use. Note that the actual TOC of the feed water ranged from 3 to 6 mg/L as illustrated in Figure 3.

4.1.2 Biofiltration Apparatus

Three laboratory scale biofiltration apparatus were assembled. Two of the apparatus were placed in two separate temperature-controlled rooms, one at 4°C and one at 10°C. The third apparatus was placed in the laboratory at ambient temperature, which was approximately 20(±3)°C. During one period of the study, (Day 72-78) the ambient laboratory temperature dropped to 15°C. This was an isolated incident and did not appear to impact NOM removal. As

discussed in section 2.2.1, temperature only impacts NOM removal after several weeks at a new temperature (Halle, 2009). Each filtration apparatus had one influent tank, two BIEX and two BAC biofilter columns and a pump. The two BIEX and two BAC biofilter columns were operated in parallel (i.e. replicates of each experimental condition). A schematic and a picture of the apparatus are presented in Figure 1 and Figure 2 respectively. A summary of the 36 experimental conditions that were investigated with the three apparatus are presented in Table 3.

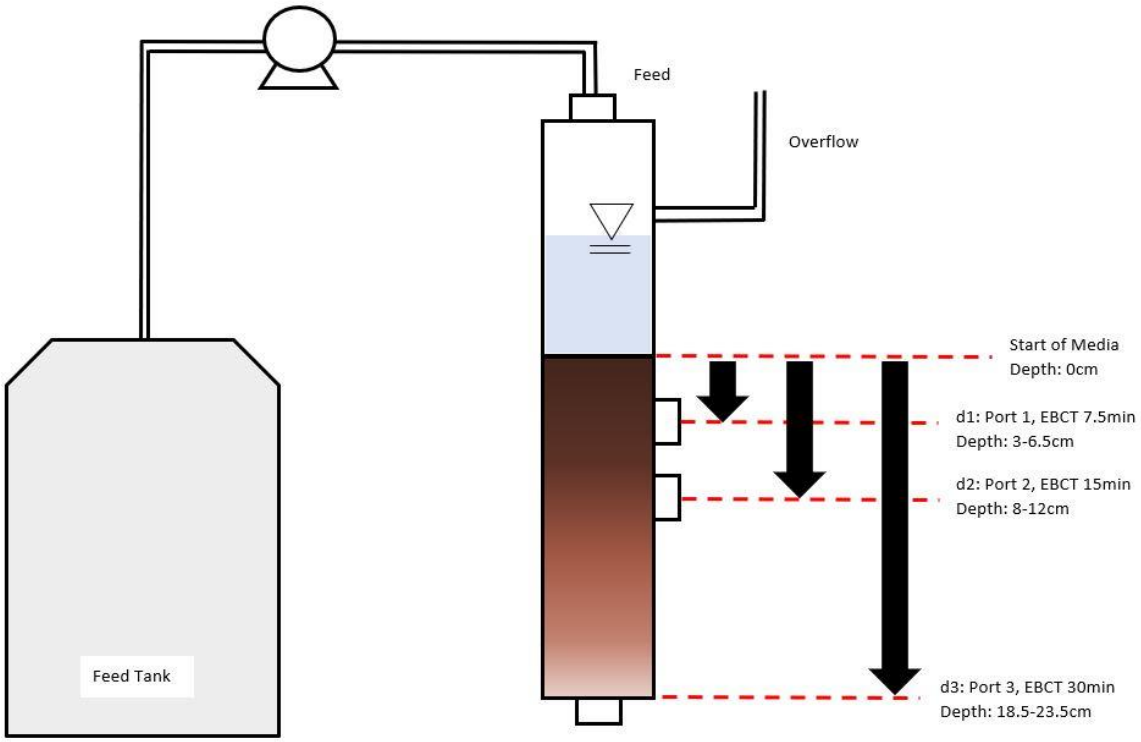


Figure 1: Illustration of biofilter apparatus;
In this figure a single biofilter is displayed. During the study each apparatus had four biofilters attached to the feed tank and pump in the manner displayed above;
The equivalent bed volumes for each EBCT is:
EBCT 7.5 min, 192BV/day; EBCT 15min, 96BV/day; EBCT 30min, 48BV/day

The biofilter columns had an internal diameter of 1.25cm (a cross-sectional area of 1.23cm^2) and a depth of approximately 20cm. The BIEX biofilter columns were filled with Purolite ® A860 while the BAC biofilter columns were filled with exhausted Picabiol ® GAC.

Each biofilter column had three ports to enable three different EBCT to be considered (7.5, 15 and 30 min or 192, 96 and 48 bed volumes (BV/ day respectively) simultaneously. The range of media depths associated with each port is listed in Table 2. A typical column is illustrated in Figure 1. The exact depths of the biofilter media for the different conditions investigated varied slightly are presented in Table B-1 (Appendix B).

Table 2: Design depth of port from the top of the media

	Depth from top of Media (cm)
Port 1, EBCT 7.5 minutes (192 BV/day), d1	3-6.5
Port 2, EBCT 15 minutes (96 BV/day), d2	8-12
Port 3, EBCT 30 minutes (48BV/day), d3	18.5-23.5

Feedwater was pumped from the feed tanks (5-gallon (19L) Pyrex Tank) through a multi-channel peristaltic pump at a rate of 0.82mL/min (HLR of 0.4m/h) to the top of the biofilters (the port labelled Feed in Figure 1). Details of the pumps used in each apparatus are presented in Table B-2 (Appendix B). Feedwater was replenished in the feed tanks once every two days. During normal operation the water flowed out of Port 3 and was collected in a filtrate tank (the valves at Ports 1 and 2 were closed).

The water flowed through the biofilter by gravity. The height of the water column above the biofilter changed as the headloss through the biofilter changed. When water reached a height of approximately 1m the biofilter was backwashed. To backwash the biofilter the flow was reversed by redirecting the feed through Port 3. The pump was operated at maximum flow to dislodge excess material from the surface of the media. The biofilters operated at 20°C were backwashed approximately every 6 to 8 weeks. The biofilters operated at 4 and 10°C never required backwash.

The components of the filtration apparatus operated at 20°C were covered in aluminum foil to minimize potential algal growth in the tank. The apparatus operated at 4 and 10°C were in dark rooms and therefore algal growth was not a concern. All system components were connected using soft tubing. The overflow tubes were connected using 1/4" tubing and all other system components were connected through 1/16" tubing. Tubing was replaced periodically to ensure that the potential biological growth in the system was minimized. The tubing utilized throughout the apparatus operating at 20°C was replaced approximately every 10 to 14 days. The tubing utilized throughout the apparatus operating at 10°C was replaced approximately every 8 weeks. No growth was observed on the tubing utilized in the apparatus operating at 4°C and therefore the tubing was not replaced. Tubing connectors were also cleaned with a wire to remove any biological growth when the tubing was replaced.

A picture of the apparatus is presented in Figure 2.

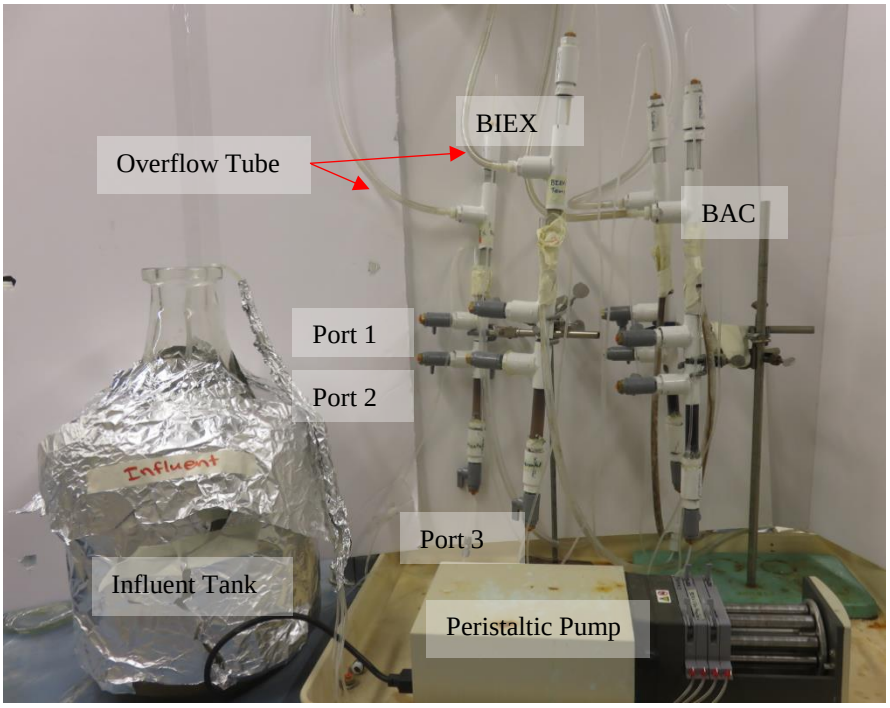


Figure 2: Photo of the experimental set-up at 20°C;
The apparatus operating at 4 and 10°C were designed and built in a similar manner

Table 3: Summary of all experimental conditions tested. E= EBCT, T= temperature, R= replicate; The equivalent bed volumes for each EBCT is:
EBCT 7.5 min, 192 BV/day; EBCT 15min, 96BV/day; EBCT 30min, 48BV/day

EBCT (min)	Temperature (°C)					
	4		10		20	
7.5	BIEX 3, E 7.5min, T 4°C, R1	BIEX 4, E 7.5min, T 4°C, R2	BIEX 5, E 7.5min, T 10°C, R1	BIEX 6, E 7.5min, T 10°C, R2	BIEX 1, E 7.5min, T 20°C, R1	BIEX 2, E 7.5min, T 20°C, R2
	BAC 3, E 7.5min, T 4°C, R1	BAC 4, E 7.5min, T 4°C, R2	BAC 5, E 7.5min, T 10°C, R1	BAC 6, E 7.5min, T 10°C, R2	BAC 1, E 7.5min, T 20°C, R1	BAC 2, E 7.5min, T 20°C, R2
15	BIEX 3, E 15min, T 4°C, R1	BIEX 4, E 15min, T 4°C, R2	BIEX 5, E 15min, T 10°C, R1	BIEX 6, E 15min, T 10°C, R2	BIEX 1, E 15min, T 20°C, R1	BIEX 2, E 15min, T 20°C, R2
	BAC 3, E 15min, T 4°C, R1	BAC 4, E 15min, T 4°C, R2	BAC 5, E 15min, T 10°C, R1	BAC 6, E 15min, T 10°C, R2	BAC 1, E 15min, T 20°C, R1	BAC 2, E 15min, T 20°C, R2
30	BIEX 3, E 30min, T 4°C, R1	BIEX 4, E 30min, T 4°C, R2	BIEX 5, E 30min, T 10°C, R1	BIEX 6, E 30min, T 10°C, R2	BIEX 1, E 30min, T 20°C, R1	BIEX 2, E 30min, T 20°C, R2
	BAC 3, E 30min, T 4°C, R1	BAC 4, E 30min, T 4°C, R2	BAC 5, E 30min, T 10°C, R1	BAC 6, E 30min, T 10°C, R2	BAC 1, E 30min, T 20°C, R1	BAC 2, E 30min, T 20°C, R2

4.1.3 Sampling Procedure

During the first two weeks following the start-up of the biofiltration apparatus, samples of filtrate were drawn from each port twice a week. During the remainder of the study samples of filtrate were drawn from each port once a week. 100mL of sample were collected during each sampling period. All ports were sampled on separate days.

When sampling from ports 1 and 2 valve 3 was closed and the filtrate tube was disconnected from port 3 and moved to the relevant port. The relevant valve was then opened and, following sampling, this valve was closed, the filtrate tubing was re-attached to port 3 and valve 3 was re-opened. Flow out of sampling ports 1 and 2 was carefully controlled to ensure sampling did not impact EBCT.

4.1.4 Hydraulic Retention Time Tests

The HRT of the BIEX and BAC biofilters were determined through hydraulic step tests. Sodium chloride was added to the feed tank after the experiment was concluded and the change in conductivity of the filtrate from different ports was monitored. 1.2g/L of sodium chloride was added to the influent tank in order to increase the conductivity of the feed water to 1980µS/cm. The biofilter filtrate was sampled continuously. Volumes were collected over a 2-minute period and each of these was diluted 15-fold; the conductivity was then measured.

The concentration of sodium chloride used is not expected to impact either the exchange capacity of the resin or the biological activity of the biofilter. Studies have reported that a concentration of approximately 100g/L NaCl is required for regeneration of IEX to occur (Winter et al., 2018). Other studies have reported that the removal of organic material through BAC biofilters is not affected by concentrations of salt under 4g/L (Mochidzuki & Takeuchi, 1999). Therefore, addition of sodium chloride to the system feed is not expected to affect either ion exchange or biodegradation.

Note that the HRT was only determined for the biofilters operated at 20°C.

4.1.5 Specific Ultraviolet Absorbance Tests

SUVA is a normalized measure of the aromatic carbon in the water. SUVA can be calculated using Equation 3.

Equation 3: SUVA Equation

$$SUVA = \frac{UV254}{DOC} * 100$$

4.2 Analytical Methods

4.2.1 Glassware

All glassware used during the sampling procedure was cleaned prior to use. Glassware was rinsed three times with de-ionized water and placed in an oven at 450°C for one hour.

4.2.2 Total Organic Carbon and Dissolved Organic Carbon Measurements

TOC and DOC measurements were made in accordance with Standard Methods 5310A. 40mL of sample water was placed into a clean, glass TOC vial. The vial was cleaned using the procedure outlined in section 4.2.1. The TC-IC (Total Carbon- Inorganic Carbon) analysis method was used to obtain the TOC measurement. All samples were analyzed using the TOC-L CPH/CPN total organic carbon analyzer from Shimadzu. The instrument was calibrated to provide accurate readings from 0 to 250 mg/L for TC and 0 to 50mg/L for IC. The standards used to calibrate TC analysis were: 0, 10, 25, 50 and 100mg/L and the standards used to calibrate IC analysis were 0, 1, 5, 10 and 20mg/L. The standards were prepared from a 1000mg/L stock potassium hydrogen phthalate solution that was stored at 4°C in the dark until use

DOC measurements were made in a similar manner to TOC measurements. Prior to being analyzed by the TOC analyzer all DOC samples were filtered through a 0.45µm filter paper (Supor ® 0.45µm 47mm PES Membrane Disk filters from Pall) using a filtration

apparatus. To ensure that no organics from the filter dissolved into the sample from the filter paper the filter was rinsed with 1L of de-ionized water prior to sample filtration. Once the DOC sample was filtered it was analyzed in the same manner as TOC samples.

A standard with a known concentration of TOC was analyzed at the start of every series of analysis as well as after every 20th analysis as a quality control step. On one occurrence (samples collected for days 147 and 148) the measured and expected concentration for the QC sample differed. All the data from the TOC analysis performed on that day were omitted from the data analysis.

For each sampling period one TOC and one DOC replicate for each experimental condition was analyzed. The low flow rate through the biofilters allowed for a relatively small volume of filtrate to be collected. That, along with the destructive nature of the TOC/DOC analysis meant that no replicates of either sample type were tested.

4.2.3 Ultraviolet Absorbance Measurement

All measurements were made in accordance with Standard Methods 5910B. Ultraviolet absorbance measurements were made with a wavelength of 254nm using a UV 300 UV-Visible Spectrometer. Prior to analysis in the UV spectrometer all samples were filtered through a 0.45µm vacuum filter (Supor ® 0.45µm 47mm PES Membrane Disk filters from Pall). As a quality control step, the instrument was calibrated to generate an absorbance of zero for a sample containing de-ionized water. The UVA of each sample was measured three times to ensure a consistent measurement was obtained.

4.3.4 Chloride and Sulphate Measurement

All measurements were made in accordance with Standard Methods 4110. Measurements of chloride and sulphate ions were made using the DIONEX ICS-1100. Prior to analysis all samples were filtered through 0.45μm filters (Millex ®-HV Sterile 33mm PVDF Syringe driven filter units). 5mL samples were placed into PolyVials from Thermo Scientific. Samples were stored at 4°C in the dark prior to analysis using a DIONEX ICS-1100. The DIONEX ICS-1100 utilized Dionex AS22 Eluent Concentrate as an eluent. 100mL of eluent was added to 900mL of deionized water and the solution was degassed for 30 minutes.

As a quality control step one blank and three standards were analyzed at the beginning of each series of measurements. Dionex Seven Anion Standard II from Thermo Scientific was used as a bulk standard. This bulk standard was diluted 100 times so that its concentration was similar to that of the concentration of chloride and sulphate expected in the samples tested. The chloride and sulphate of each sample was measured twice to ensure that a consistent measurement was obtained.

Due to the DIONEX ICS-1100 malfunctioning, results for a series of measurements collected on: February 20 (Day 76), March 7 (Day 91), March 21 (Day 104) were erroneous. The results from this series of measurements was not included in the analysis.

4.3.5 Conductivity Measurement

Conductivity measurements were made using an Oakton Conductivity Data Meter CON 400 series from Eutech Instruments and a CONSEN 91W 185/02 probe.

A standard (986 μS/cm, potassium chloride) was used to ensure that the measurements obtained from the conductivity meter were accurate. Conductivity test were run at ambient temperature (20°C).

4.4 Quality Assurance and Quality Control (QA/QC)

4.4.1 Analytical Methods

The QA/QC approaches relating to analytical methods are discussed in section 4.3

4.4.2 Data Analysis

TOC and DOC measurements of biofilter filtrate that were two standard deviations outside the mean for each experimental condition were eliminated according to standard practice (Berthouex, Brown, & CRC Press, 2002). Based on this approach 27 of 603 measurements made on BIEX biofilters were eliminated and 32 of 657 measurements made on BAC biofilters were eliminated. TOC and DOC data was averaged, as t-tests demonstrated there was no difference in effluent concentration between the two data sets.

For each sample of UV-254 three replicates were analyzed. If all measurements were similar the average was determined and used as the true measurement. If one measurement differed significantly from the other two measurements it was discarded and the other two were averaged. SUVA values for individual days and experimental conditions were calculated using Equation 3 and the respective UV-254 measurements and averaged TOC and DOC measurements. SUVA measurements that were two standard deviations outside the mean for each experimental condition were eliminated according to standard practice (Berthouex et al., 2002). Based on this approach 20 of 473 measurements made on BIEX biofilters and 20 of 499 measurements made on BAC biofilters were eliminated.

For each sample of chloride and sulphate two replicates were analyzed. These measurements were averaged before further analysis was performed.

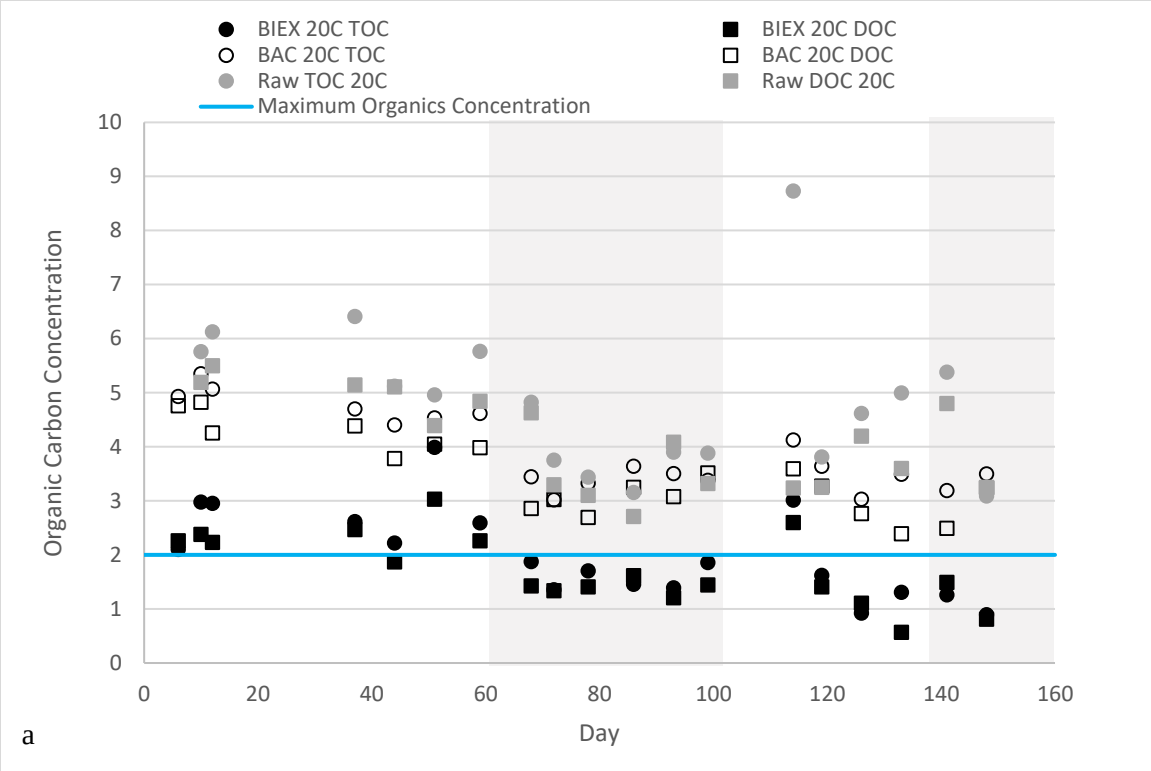
5 Results and Discussion

5.1 Natural Organic Matter Removal

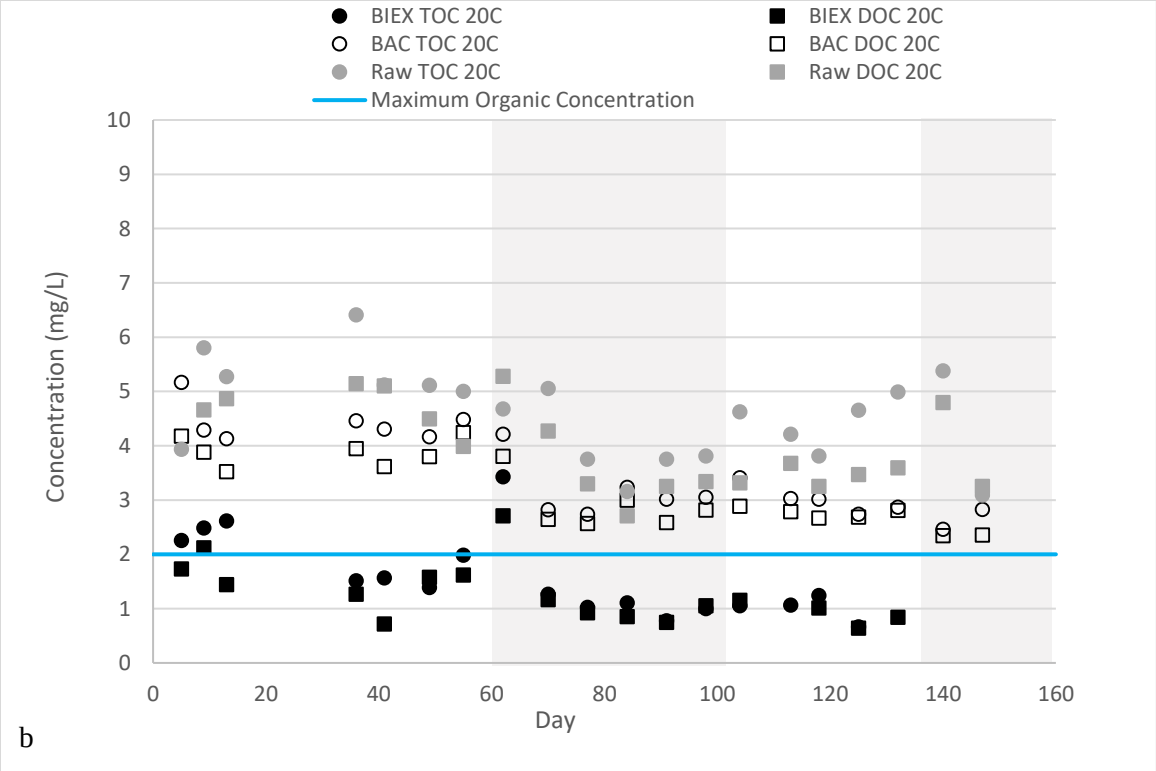
5.1.1 Effect of Temperature and Empty Bed Contact Time

Typical TOC and DOC concentrations for feed and filtrate streams from BIEX and BAC biofilters (at room temperature) are presented in Figure 3. Typical TOC and DOC concentrations for the systems operated at 4 and 10°C are presented in Appendix C.

Figure 3 illustrates that the concentration of TOC and DOC in the filtrate for BIEX biofilters were consistently lower than the target of 2mg/L (Amini et al., 2018). A target concentration of 2mg/L is used because it is the generally accepted concentration below which DBP formation is sufficiently low (Amini et al., 2018). On the other hand, the concentration in the filtrate for BAC biofilters was consistently greater than the target value.


BIEX 20C TOC
BAC 20C TOC
Raw TOC 20C
Maximum Organics Concentration
BIEX 20C DOC
BAC 20C DOC
Raw DOC 20C
Organic Carbon Concentration
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

a


BIEX TOC 20C
BAC TOC 20C
Raw TOC 20C
Maximum Organic Concentration
BIEX DOC 20C
BAC DOC 20C
Raw DOC 20C
Concentration (mg/L)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

b

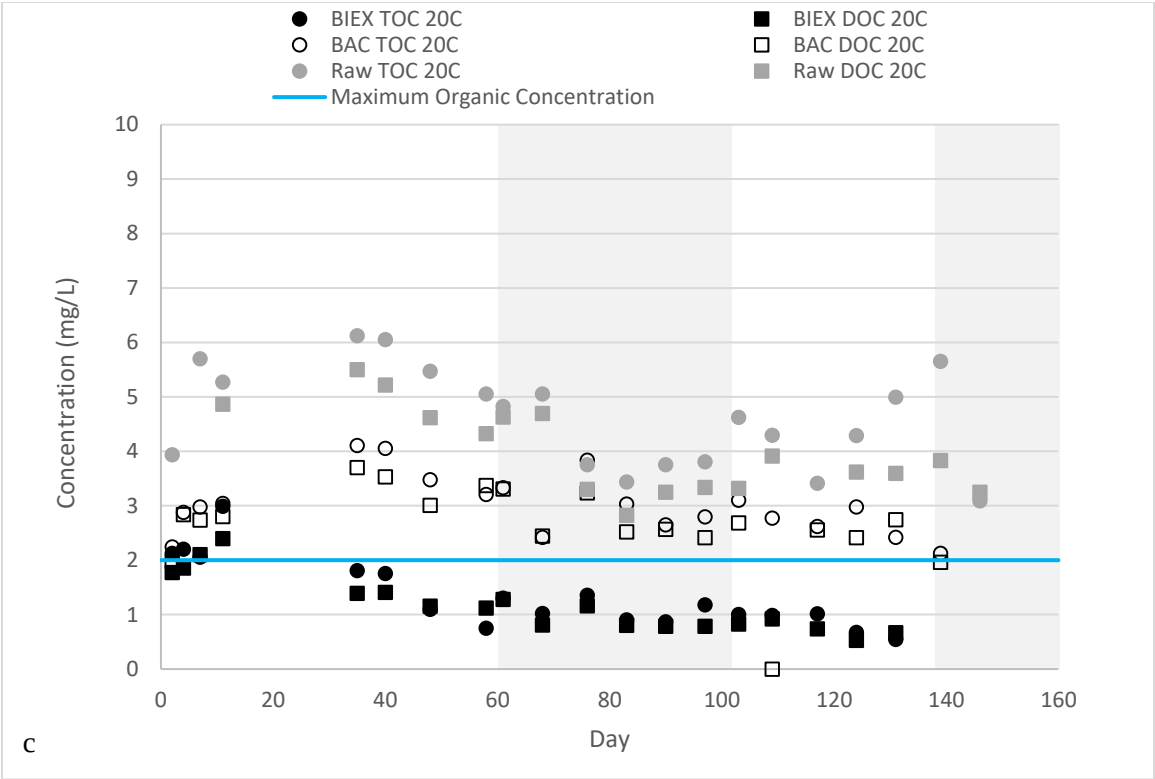


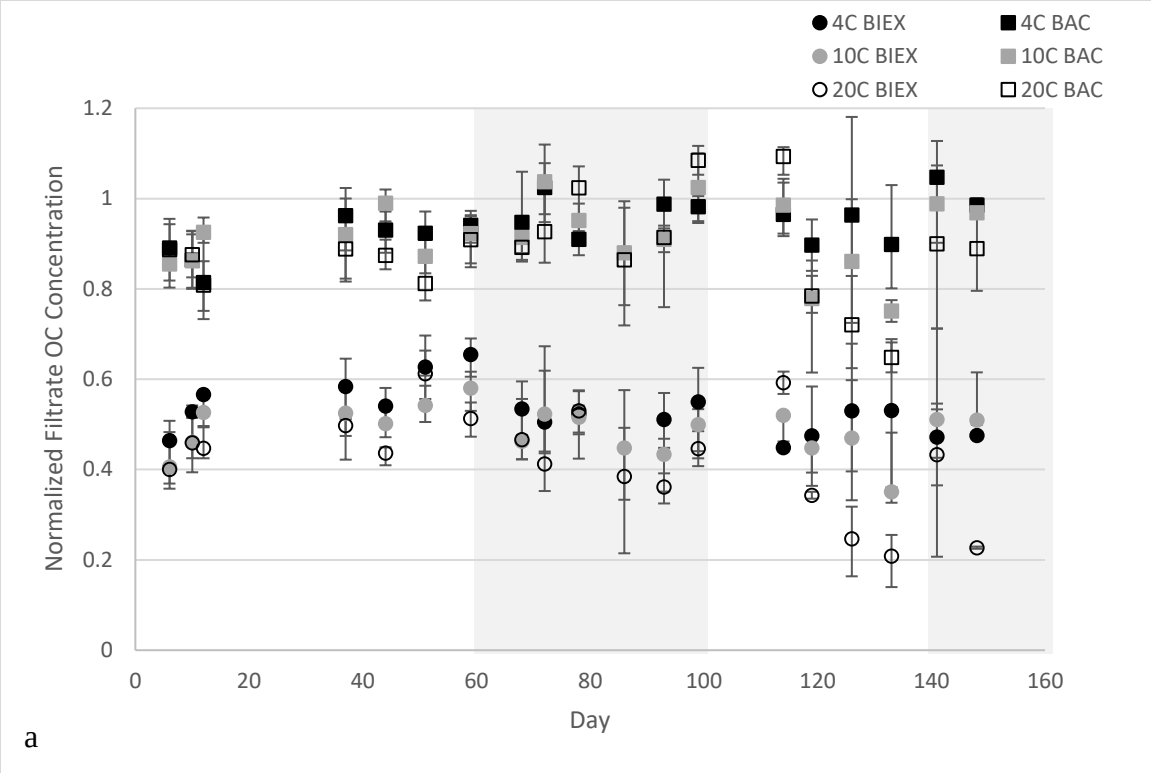
Figure 3: Typical TOC and DOC concentrations for feed and filtrate streams for BIEX and BAC biofilters at different EBCT;
a) EBCT 7.5-minutes (192BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond

As indicated in Figure 3 the concentration of TOC and DOC in the feed water changes throughout the experiment. To account for the changes in the feed water, the filtrate TOC and DOC concentrations were normalized with respect to those in the feed using Equation 4. Note that because the normalized TOC and DOC concentrations were statistically similar, they were averaged to obtain a singular organic carbon (OC) measurement. Normalized TOC and DOC measurements were not different based on a 95% confidence interval.

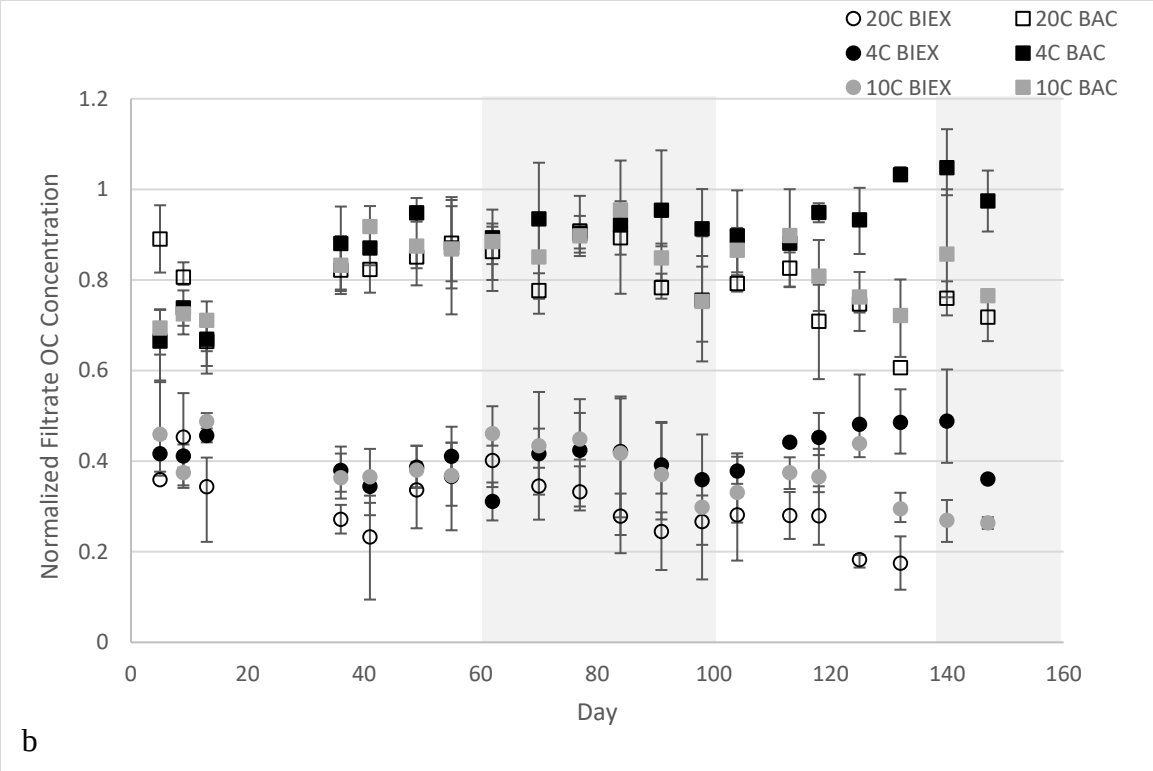
Equation 4: Normalized Effluent Concentration

$$C_N = \frac{C_E}{C_O}$$

where: C_O is the TOC or DOC concentration of the feed water in mg/L, C_E is the TOC or DOC concentration of the filtrate in mg/L, C_N is the normalized TOC or DOC concentration, all concentrations are for a given temperature and EBCT


4C BIEX
4C BAC
10C BIEX
10C BAC
20C BIEX
20C BAC
Normalized Filtrate OC Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
140
160

a


20C BIEX
20C BAC
4C BIEX
4C BAC
10C BIEX
10C BAC
Normalized Filtrate OC Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
140
160

b

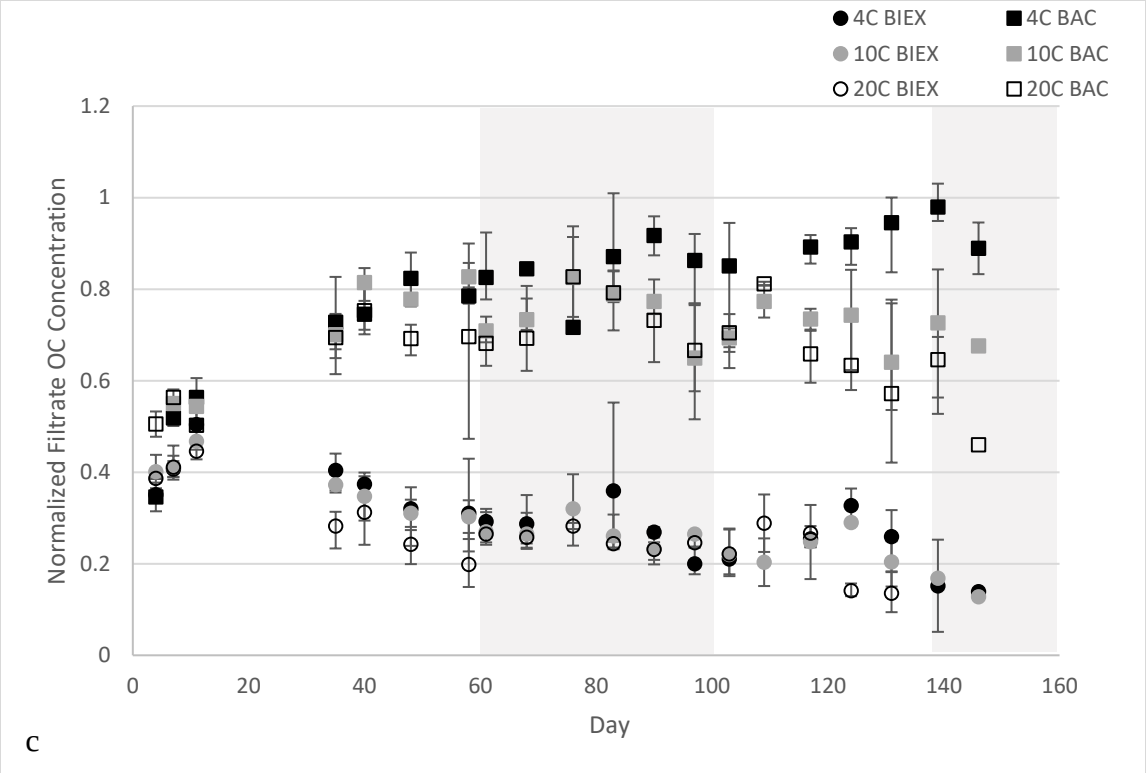
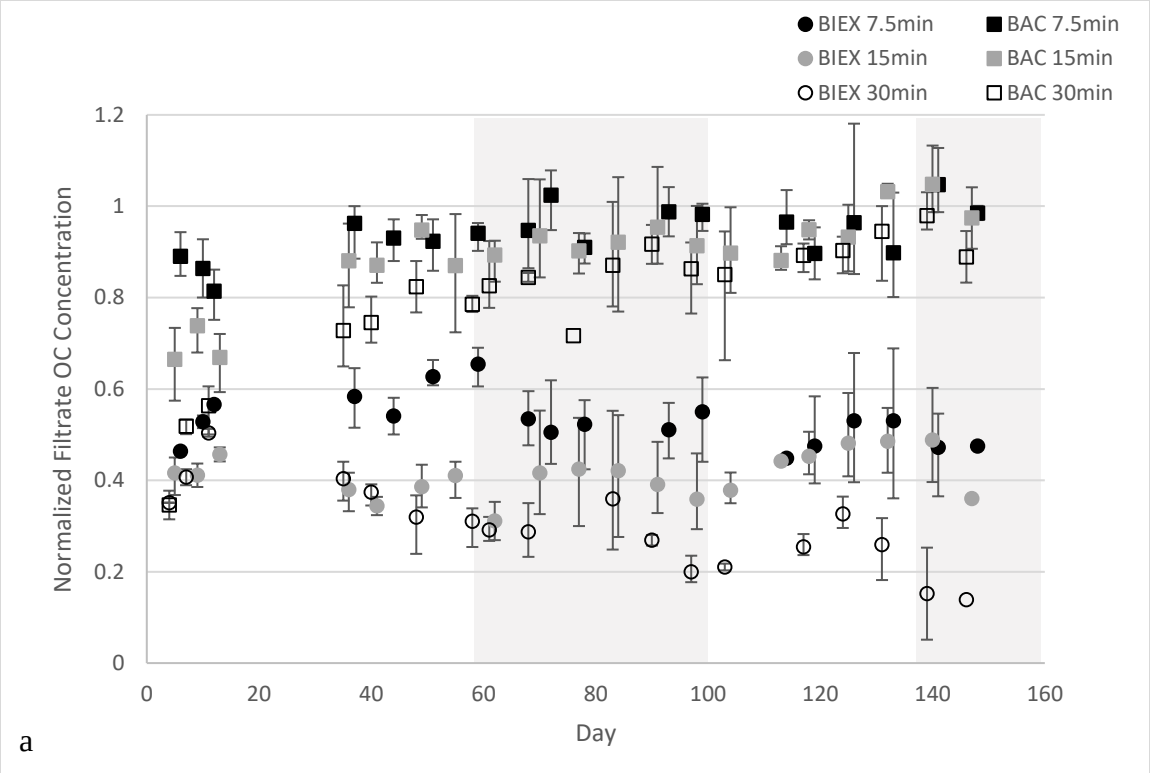
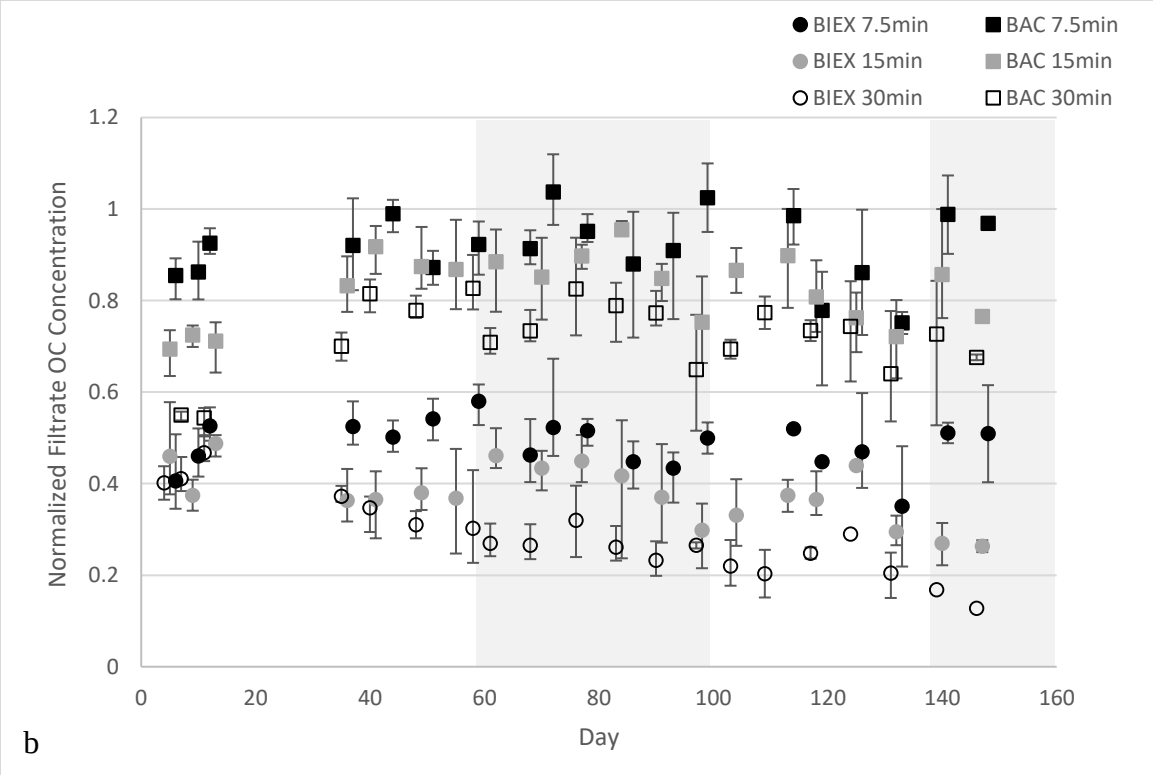


Figure 4: All normalized effluent concentration of OC from BIEX and BAC biofilters for different EBCT;
a) EBCT 7.5-minutes (192BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond; Data presented is an average from replicate biofilters (of both TOC and DOC measurements) and errors bars correspond to the minimum and maximum values from the replicate biofilters


BIEX 7.5min
BAC 7.5min
BIEX 15min
BAC 15min
BIEX 30min
BAC 30min
Normalized Filtrate OC Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
140
160

a


BIEX 7.5min
BAC 7.5min
BIEX 15min
BAC 15min
BIEX 30min
BAC 30min
Normalized Filtrate OC Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
140
160

b

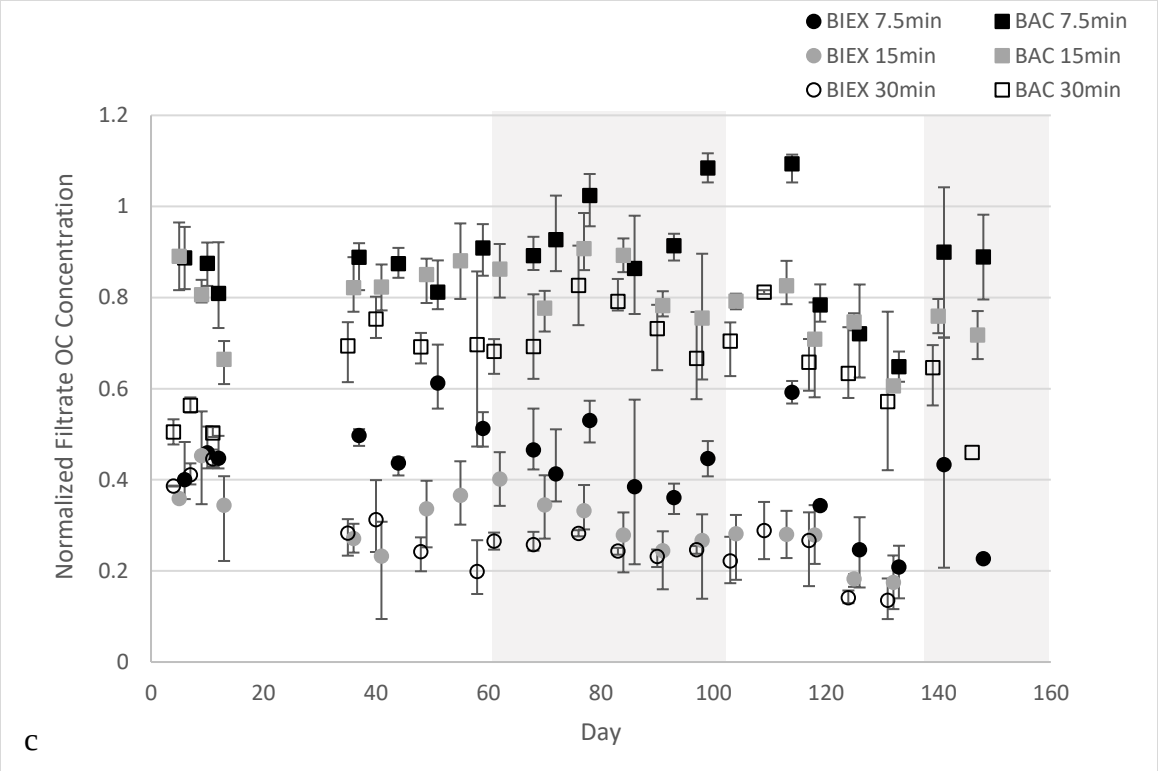


Figure 5: All normalized effluent concentration of OC from BIEX and BAC biofilters for different temperatures;
a) 4°C; b) 10°C; c) 20°C;
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond;
Data presented is an average from replicate biofilters (of both TOC and DOC measurements) and errors bars correspond to the minimum and maximum values from the replicate biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

Figure 4 and Figure 5 illustrate that OC removal varies initially however becomes relatively constant after several weeks of operation. Linear regressions were performed on all experimental conditions to determine if and when steady state was reached. Steady state was considered to have been reached when the slope of a linear regression model (fitted to the normalized OC concentration) was not significantly different from zero based on a 98% confidence interval. Of the 36 experimental conditions investigated (see Table 3 for experimental conditions), 27 were determined to have reached steady state between 40 to 60 days of operation. Details of the linear regressions are presented in Appendix D.

Most biofilters operated at shorter EBCT (7.5-minutes and 15-minutes) reached steady state after 40 days of operation (7680 and 3840BV respectively). Most biofilters operated at a longer EBCT (30-minutes) reached steady state after 60 days of operation (2880BV). Steady state was not reached for ten experimental conditions as their slopes were significantly different from zero. Note that although statistically different from zero, the slopes we nonetheless low, ranging from -2.40×10^{-3} and 2.2×10^{-3} mg/L/day. The results of the steady state test for all experimental conditions are listed in Table 4. Note that results for the experimental conditions that did not reach steady state were still included in the following data analysis (including the determination of percent removal). For conditions that did not reach steady state data collected after 40 days of operation for shorter EBCT (7.5-minutes and 15-minutes) and after 60 days of operation for longer EBCT (30-minutes) was used in the analysis.

Table 4: Results for the steady state test for all experimental conditions;
Experimental conditions that are not shaded reached steady state while experimental conditions that are shaded did not reach steady state;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

EBCT (min)	Temperature (°C)					
	4		10		20	
7.5	BIEX 3, E 7.5min, T 4°C, R1	BIEX 4, E 7.5min, T 4°C, R2	BIEX 5, E 7.5min, T 10°C, R1	BIEX 6, E 7.5min, T 10°C, R2	BIEX 1, E 7.5min, T 20°C, R1	BIEX 2, E 7.5min, T 20°C, R2
	BAC 3, E 7.5min, T 4°C, R1	BAC 4, E 7.5min, T 4°C, R2	BAC 5, E 7.5min, T 10°C, R1	BAC 6, E 7.5min, T 10°C, R2	BAC 1, E 7.5min, T 20°C, R1	BAC 2, E 7.5min, T 20°C, R2
15	BIEX 3, E 15min, T 4°C, R1	BIEX 4, E 15min, T 4°C, R2	BIEX 5, E 15min, T 10°C, R1	BIEX 6, E 15min, T 10°C, R2	BIEX 1, E 15min, T 20°C, R1	BIEX 2, E 15min, T 20°C, R2
	BAC 3, E 15min, T 4°C, R1	BAC 4, E 15min, T 4°C, R2	BAC 5, E 15min, T 10°C, R1	BAC 6, E 15min, T 10°C, R2	BAC 1, E 15min, T 20°C, R1	BAC 2, E 15min, T 20°C, R2
30	BIEX 3, E 30min, T 4°C, R1	BIEX 4, E 30min, T 4°C, R2	BIEX 5, E 30min, T 10°C, R1	BIEX 6, E 30min, T 10°C, R2	BIEX 1, E 30min, T 20°C, R1	BIEX 2, E 30min, T 20°C, R2
	BAC 3, E 30min, T 4°C, R1	BAC 4, E 30min, T 4°C, R2	BAC 5, E 30min, T 10°C, R1	BAC 6, E 30min, T 10°C, R2	BAC 1, E 30min, T 20°C, R1	BAC 2, E 30min, T 20°C, R2

The percent removal of OC at steady state for all experimental conditions investigated are presented in Figure 6 and Table 5. Removal of OC using a BIEX biofilter was greatest at 20°C with a 30-minute EBCT, (i.e. 77.5±0.9%) while it was lowest at 4°C with a 7.5-minute EBCT, (i.e. 46.5±1.3%). It should be noted that, previous studies conducted at UBC (i.e. feed water from a similar source) reported a lower removal of approximately 60% for DOC by BIEX biofilters at a 30-minute EBCT (Winter et al., 2018). However, results of the present study are similar to those reported by Amini et al. (2018). They reported a DOC removal of approximately

74% for water temperatures over 15°C and approximately 44% for water temperatures between 5 and 15°C at EBCTs between 10 and 15-minutes. Amini et al. (2018), also reported low DOC removal (< 30%) at temperatures of approximately 3°C.

The removal of OC using BAC biofilters ranged from 4.6±1.1% (4°C, EBCT 7.5-minutes) to 31.3±1.5% (20°C, EBCT 30-minutes). This variation in NOM removal through a conventional biofilter is consistent with what has been reported in literature (see section 2.2). Using a feed water similar to that used in the present study, Winter et al. (2018) reported that BAC biofilters removed approximately 15% of the DOC at 20°C and with a 30-minute EBCT, lower than the removal observed in the present study. Amini et al. (2018) observed low DOC removal (approximately 7%) regardless of water temperature.

The differences in removal of organic carbon between the present study and studies by others, Winter et al. (2018) and Amini et al. (2018), was likely related to the different feed water characteristics.

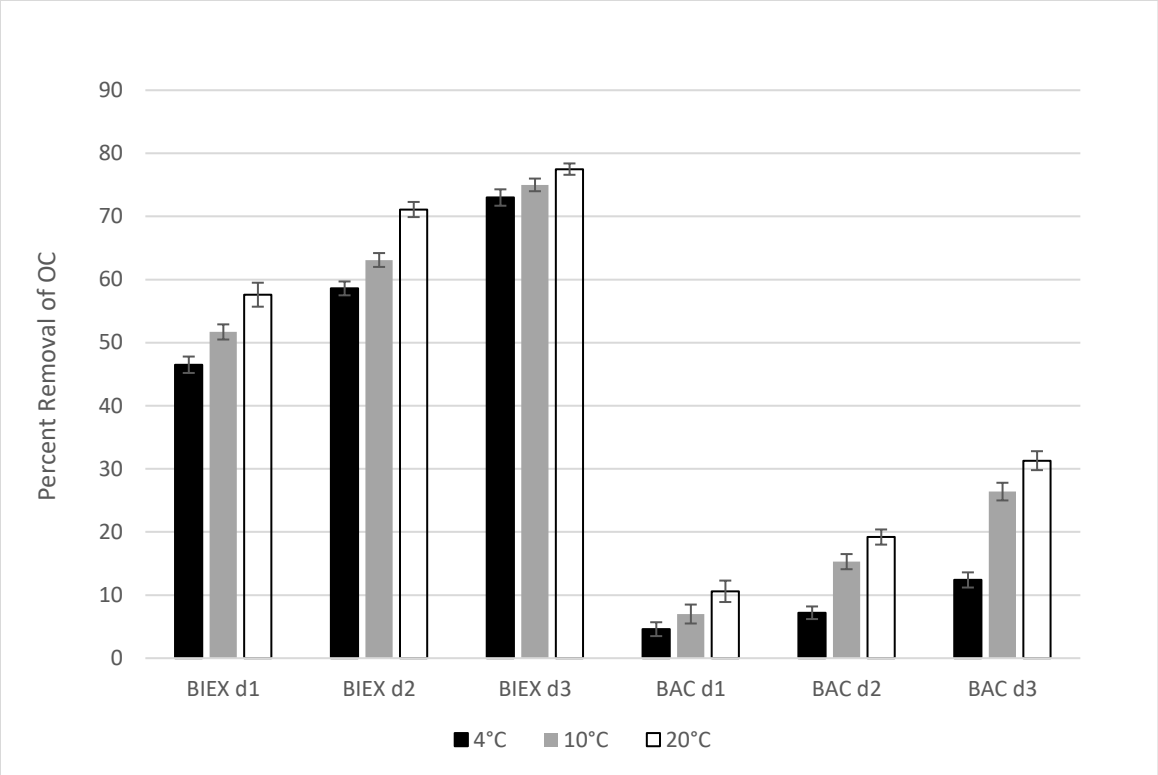


Figure 6: Percent removal of OC at steady state for both BIEC and BAC biofilters;
d1, d2 and d3 correspond to EBCTs of 7.5-minutes (192 BV/day), 15-minutes (96 BV/day) and 30-minutes (48 BV/day) respectively;
Data presented is the average percentage removal calculated from data points collected at steady state for a given experimental condition and error bars correspond to one standard error

Table 5: Average percentage removal through BIEX and BAC biofilters under different experimental conditions at steady state with a confidence interval of;
Data presented is the average percentage removal calculated from data points collected at steady state for a given experimental condition and error bars correspond to one standard error;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

	BIEX			**BAC**		
	EBCT 7.5min, d1	**EBCT 15min, d2**	**EBCT 30min, d3**	**EBCT 7.5min, d1**	**EBCT 15min, d2**	**EBCT 30min, d3**
4°C	46.5±1.3	58.6±1.1	73.0±1.3	4.6±1.1	7.2±1.0	12.4±1.2
10°C	51.7±1.2	63.1±1.1	75.0±1.0	7.9±1.5	15.3±1.2	26.4±1.4
20°C	57.6±1.9	71.1±1.2	77.5±0.9	10.6±1.7	19.2±1.2	31.3±1.5

For all temperatures and EBCT considered, the BIEX biofilters removed more OC than BAC biofilters. The detailed results of the statistical comparison are presented in Appendix E.

An ANOVA analysis was conducted to determine the impact of temperature and EBCT in BIEX and BAC biofilters. The detailed results of the analysis are presented in Appendix F and indicate that both temperature and EBCT significantly impacted OC removal for both the BIEX and BAC biofilters. The analysis also revealed significant interaction between the two variables with respect to OC removal for both the BIEX and BAC biofilters.

A visual summary of the results of the (ANOVA) analysis with respect to OC removal over the range of conditions investigated is presented in Figure 7 (BIEX biofilters) and Figure 8 (BAC biofilters). As illustrated in Figure 7 there was no significant impact of temperature on OC removal at long EBCT (30-minutes) for BIEX biofilters. At shorter EBCT (7.5 and 15-minutes), OC removal changed with temperature. For all temperatures, OC removal changed as EBCT changed. Figure 8 demonstrates that temperature impacts OC removal in BAC biofilters slightly differently than in BIEX biofilters and is not consistent with what has been reported in literature. Most previous studies have reported that lower temperatures had a greater impact on OC removal when EBCT was short (Persson et al., 2006; van der Aa et al., 2011). As illustrated in Figure 7 and Figure 8, OC removal differed with EBCT for all temperatures.

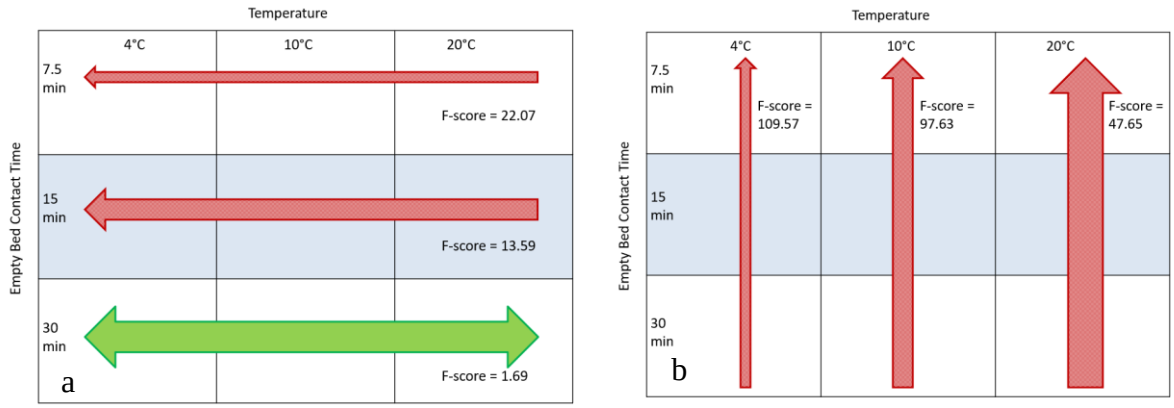


Figure 7: Summary of impact of temperature and EBCT on OC removal for BIEX biofilters;
a) Temperature b) EBCT;
Arrows illustrate expected trend with respect to impact of temperature or EBCT on OC removal;
Thickness of the arrow corresponds to extent of OC removal. The direction of the arrow indicates the impact of a given parameter (temperature or EBCT) on OC removal;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

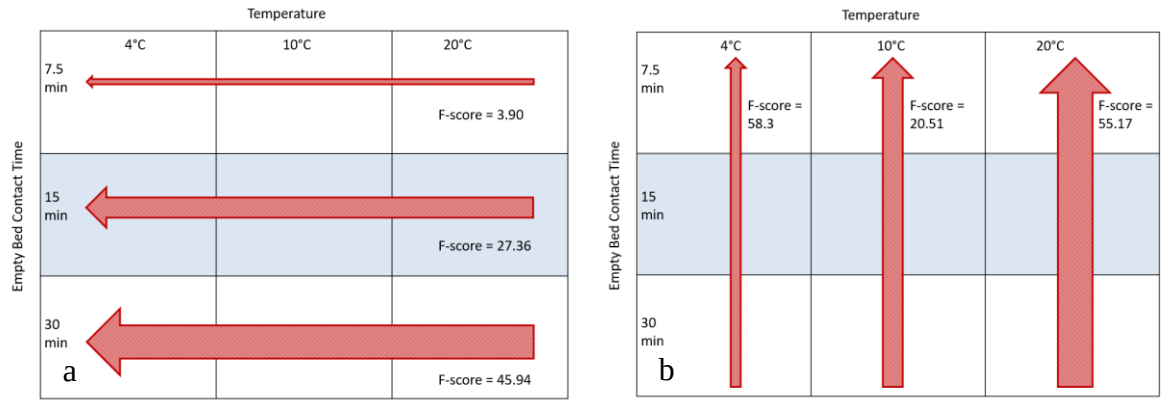


Figure 8: Summary of impact of temperature and EBCT on OC removal for BAC biofilters;
a) Temperature impact; b) EBCT impact;
Arrows illustrate expected trend with respect to impact of temperature or EBCT on OC removal;
Thickness of the arrow corresponds to extent of OC removal. The direction of the arrow indicates the impact of a given parameter (temperature or EBCT) on OC removal;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

It is generally accepted that OC removal in a biofilter can be approximated by a first-order model such as presented in Equation 5, where removal is a function of a rate constant (k) and a residence time (t) (Urfer, Huck, Booth, & Coffey, 1997). The rate constant associated with the removal of OC for both BAC and BIEX biofilters was estimated by fitting Equation 5 to the normalized OC concentrations.

Equation 5: Exponential decrease in organic carbon through a column

$$\frac{C}{C_o} = \frac{C_R}{C_o} + \frac{C_o - C_R}{C_o} e^{-kt}$$

where: C_R is the concentration of non-biodegradable NOM present in the water, C_o is the initial concentration of NOM in the water, k is the rate constant and t is the hydraulic residence time (HRT) in the biofilter.

The hydraulic residence time in the BIEX and BAC biofilters for the different EBCT was determined using tracer tests. The procedure for calculating the HRTs is presented in Appendix G. The HRTs, for each biofilter are listed in Table 6.

Table 6: HRT for BIEX and BAC biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

	BIEX	**BAC**
Port 1, EBCT 7.5min, d1	3.9	1.9
Port 2, EBCT 15min, d2	7.6	7.5
Port 3, EBCT 30min, d3	11.7	14.3

The value of C_R was determined through an iterative process that maximized the coefficient of regression (R^2) as presented in Appendix H. Equation 5 was transformed (i.e. linearized) as presented in Equation H-1 (Appendix H) so that a linear regression could be used to refine the estimate of C_R and estimate the rate constants at different temperatures for both BIEX and BAC biofilters. The details of the procedure used to estimate the rate constants that were determined are presented in Appendix H. The rate constants estimated for each temperature for both BIEX and BAC biofilters are listed in Table 7 and illustrated in Figure 9. The data used to calculate the error values associated with the estimated rate constants are presented in Appendix H.

Table 7: Rate constant values for BIEX and BAC biofilters at different temperatures the error corresponds to the standard error of the estimated parameter

	4°C	**10°C**	**20°C**
BIEX (min^{-1})	0.156±0.014	0.195±0.016	0.312±0.005
BAC (min^{-1})	0.034±0.005	0.055±0.005	0.108±0.008

The temperature activity coefficient (θ) was used to quantify the impact of the temperature on OC removal and was calculated using Equation 6. If temperature had no impact on OC removal the temperature activity coefficient would be expected to be one. A temperature activity coefficient greater than one indicates that temperature impacts OC removal.

Equation 6: Temperautre Activity Equation

$$k_T = k_{20}\theta^{(T-20)}$$

where: k_T is the rate constant associated with removal of OC at a given temperature, k_{20} is the rate constant associated with removal of OC at 20°C, θ is the temperature coefficient and T is the temperature in °C.

The temperature activity coefficient associated with the removal of OC was estimated by fitting Equation 6 to the estimated rate constants for BIEX and BAC biofilters as illustrated in Figure 9. Note that Equation 6 was transformed (i.e. linearized) as presented in Equation I-1 (Appendix I) so that a linear regression could be used to estimate the temperature activity coefficients for both BIEX and BAC biofilters. The temperature activity coefficients were estimated to be 1.044 (1.042-1.047) for BIEX biofilters and 1.066 (1.058-1.077) for BAC biofilters. The range reported in parenthesis corresponds to the standard error on the temperature activity coefficient. Note that, because of the nature of the transformation performed (Equation 6 to Equation I-1) the error range is not symmetrical about the estimated temperature activity coefficient. For both BIEX and BAC biofilters the temperature activity coefficient was >1, indicating that temperature impacted OC removal for both biofilters. The estimated temperature

activity coefficient for the BAC biofilters was greater than that for the BIEX biofilters indicating that temperature has a greater impact on OC removal in BAC biofilters than in BIEX biofilters.

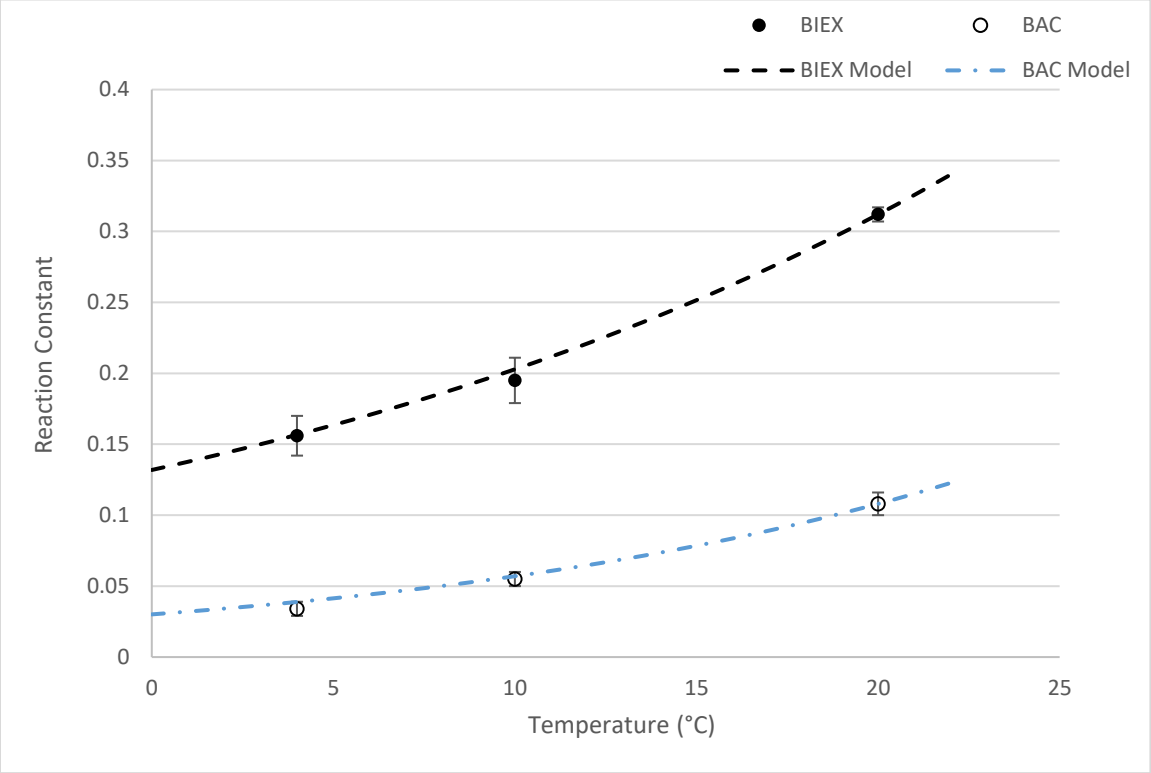


Figure 9: Effect of temperature on rate constants;
Estimated values of the rate constant at 20°C (k_{20}) and the temperature activity coefficient (θ) were used to create models for the change in the rate constant with temperature in both BIEX and BAC biofilters using Equation 6;
Error on the rate constant was determined using the method described in Appendix H

Figure 10 and Figure 11 illustrate the average removal of normalized OC as a function of HRT for all experimental conditions investigated. As illustrated in Figure 10 and Figure 11 the maximum removal of OC is achieved sooner (i.e. a shorter HRT is required) in BIEX biofilters than in BAC biofilters.

Figure 10 illustrates that OC removal is similar at longer HRTs (EBCTs) for BIEX biofilters while Figure 11 illustrates that OC removal is similar at shorter HRTs (EBCTs) for BAC biofilters. These results are consistent with those summarized in Figure 7 and Figure 8 for the ANOVA analysis. Unlike the ANOVA analysis these results from the regression analysis do

not suggest that the temperature does not impact OC removal in BIEX at high EBCT or in BAC at low EBCT. For BIEX biofilters, at long HRTs (EBCTs), most of the biodegradable OC has been removed and therefore OC removal does not appear to be impacted by temperature. Similarly, for BAC biofilters, at short HRTs (EBCTs), limited OC biodegradation has occurred and therefore OC removal does not appear to be impacted by temperature. However, because the temperature activity coefficient is greater than 0 for both BIEX and BAC biofilters temperature significantly impacts OC removal for both biofilters at different EBCT.

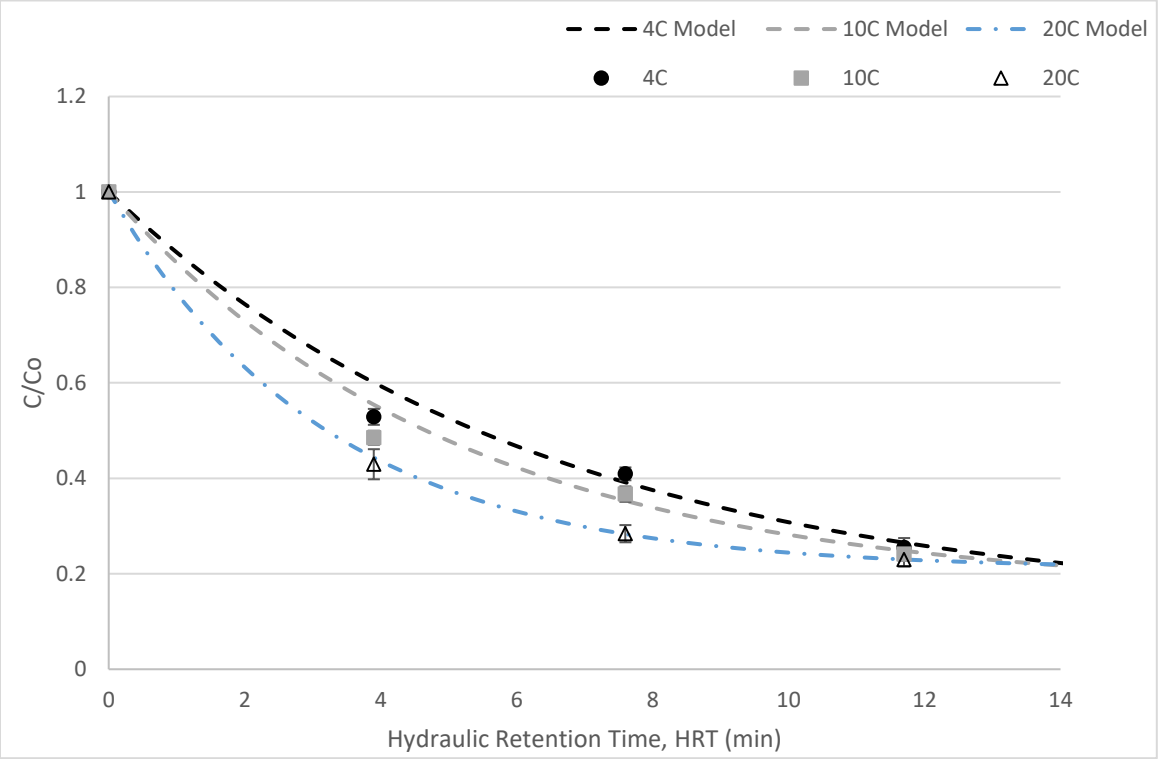


Figure 10: Reduction of OC for BIEX biofilters over time at different temperatures;
HRTs of 3.9, 7.6 and 11.7 minutes correspond to EBCTs of 7.5-minutes (192BV/day), 15-minutes (96BV/day) and 30-minutes (48BV/day) respectively;
The model for OC removal was determined using Equation 5 and the estimated rate constant (k) and C_R values;
Error bars on OC reduction represent one standard error

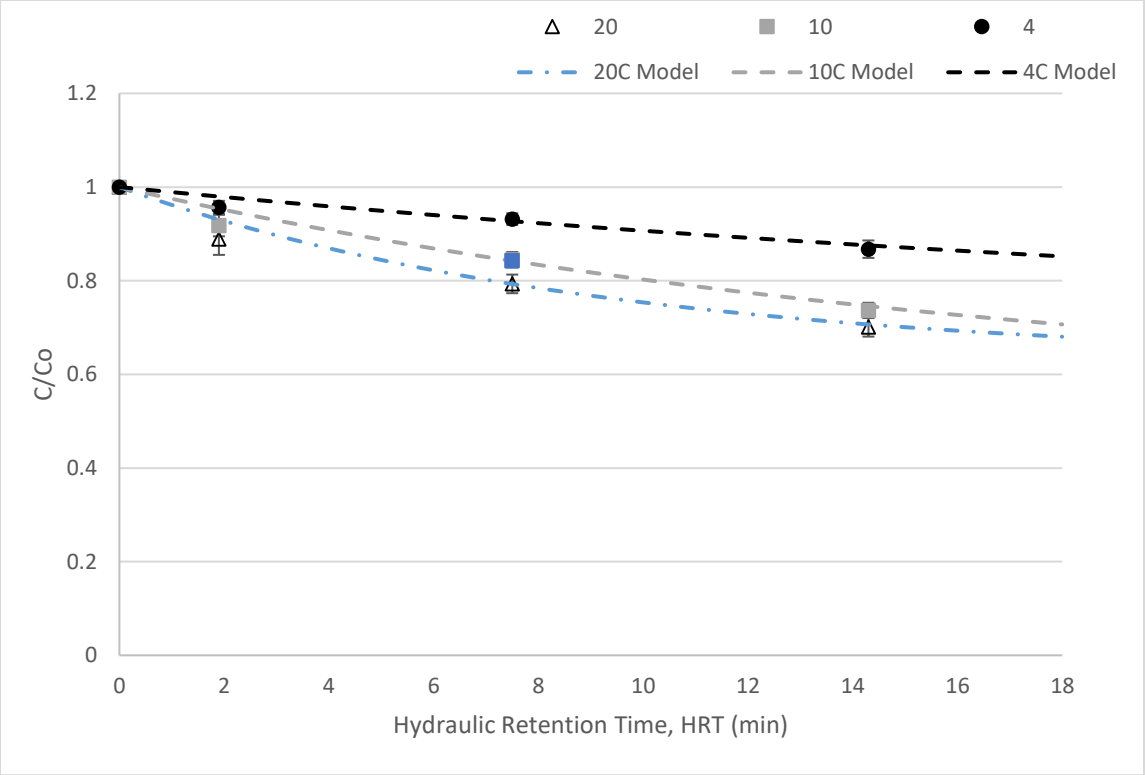


Figure 11: Reduction of OC for BAC biofilters over time at different temperatures;
HRTs of 1.9, 7.9 and 14.3 minutes correspond to EBCTs of 7.5-minutes (192BV/day), 15-minutes (96BV/day) and 30-minutes (48BV/day) respectively;
The model for OC removal was determined using Equation 5 and the estimated rate constant (k) and C_R values;
Error bars on OC reduction represent one standard error

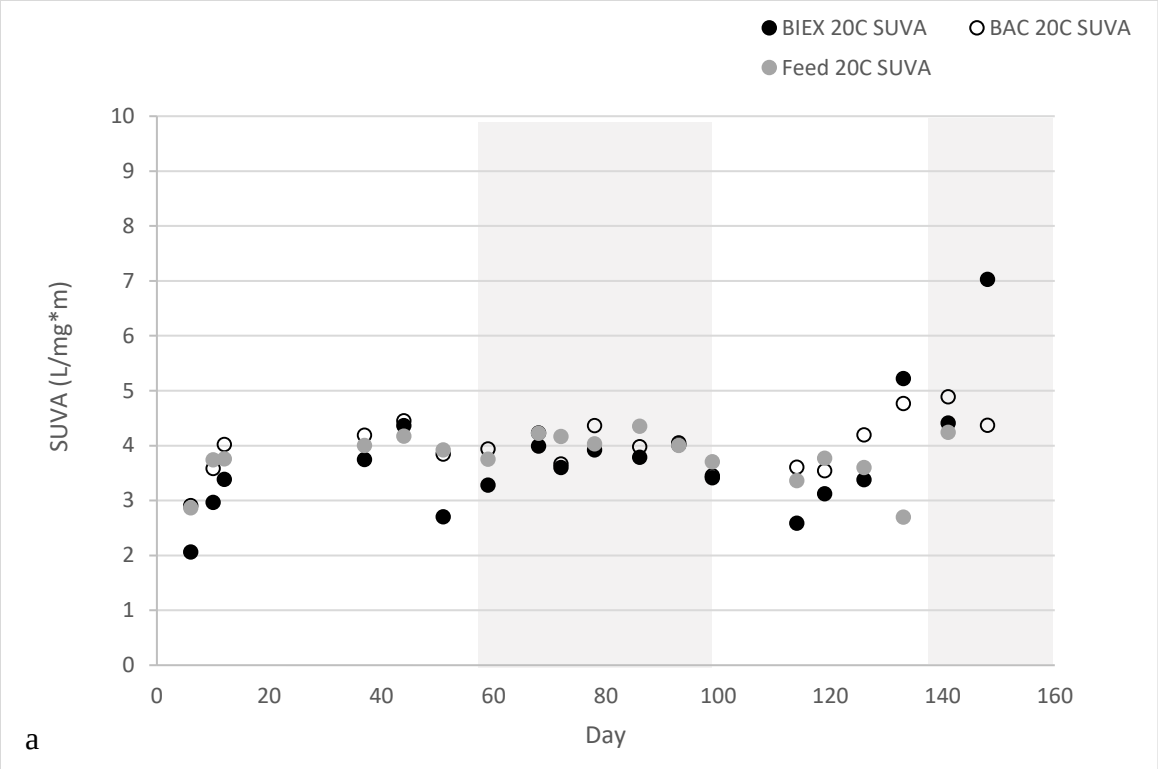
To gain further perspective on the impact of temperature on OC removal, the HRT (EBCT) required to remove 90% of biodegradable OC (C_o-C_R) was calculated, using Equation 5, the estimated rate constants and the estimated temperature activity coefficients. The calculated HRTs are listed in Table 8. 90% removal of biodegradable OC is achieved more rapidly in BEIX biofilters at all temperatures. BIEX biofilters require an HRT of approximately 30 minutes (equivalent to an EBCT of approximately 55 minutes, 26.2BV/day) to achieve a 90% reduction in OC at 4°C. BAC biofilters would require an HRT of approximately 45 minutes (equivalent to an EBCT of approximately 90 minutes, 16BV/day) to achieve the same extent of OC removal at the same temperature. It can be concluded that BIEX biofilters remove OC significantly faster and to a greater extent than BAC biofilters.

Table 8: HRT at which biofilters achieve 90% removal of OC

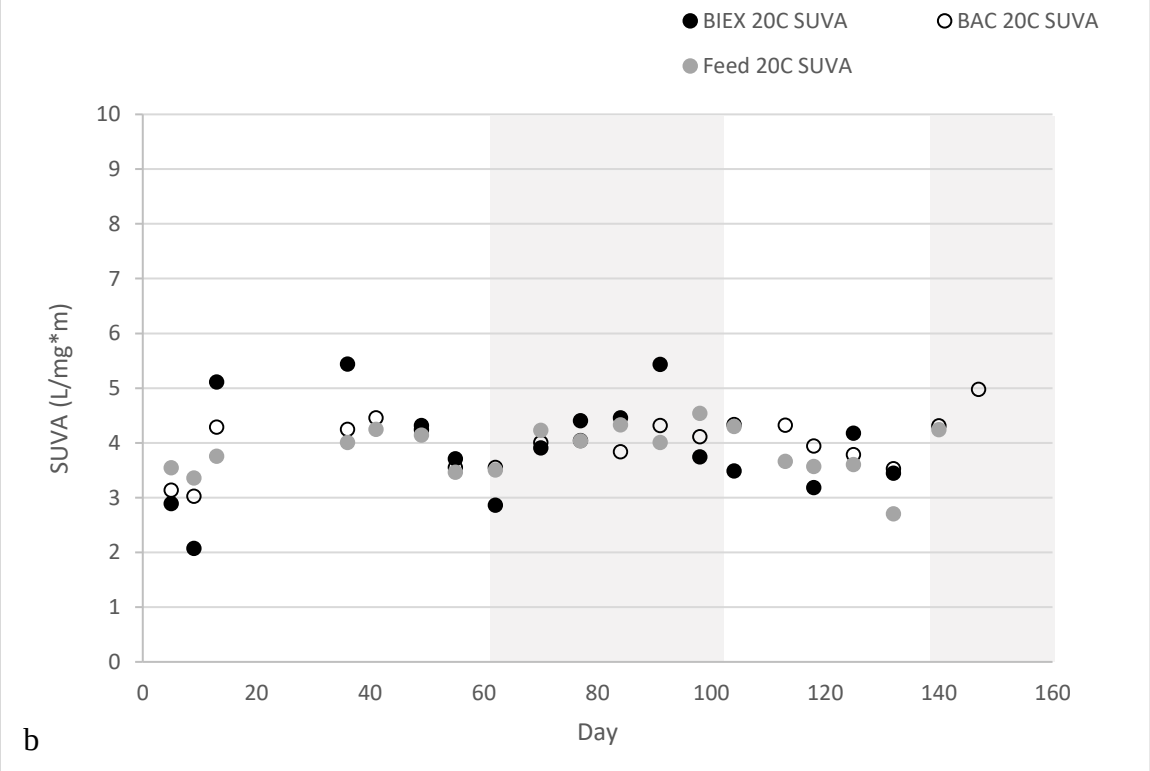
HRT (min)	**4°C**	**10°C**	**20°C**
BIEX	27.3	20.2	11.6
BAC	45.7	39.4	16.5

5.1.2 Specific Ultraviolet Absorbance Analysis

SUVA was calculated for all experimental conditions for both BIEX and BAC biofilters as well as the influent conditions. Typical SUVA values are presented in Figure 12. Typical SUVA measurements for the systems operated at 4 and 10°C are presented in Appendix J. Figure 12 illustrates that unlike OC measurements there is not a substantial change in SUVA between the feed and the filtrate.


BIEX 20C SUVA
BAC 20C SUVA
Feed 20C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

a


BIEX 20C SUVA
BAC 20C SUVA
Feed 20C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

b

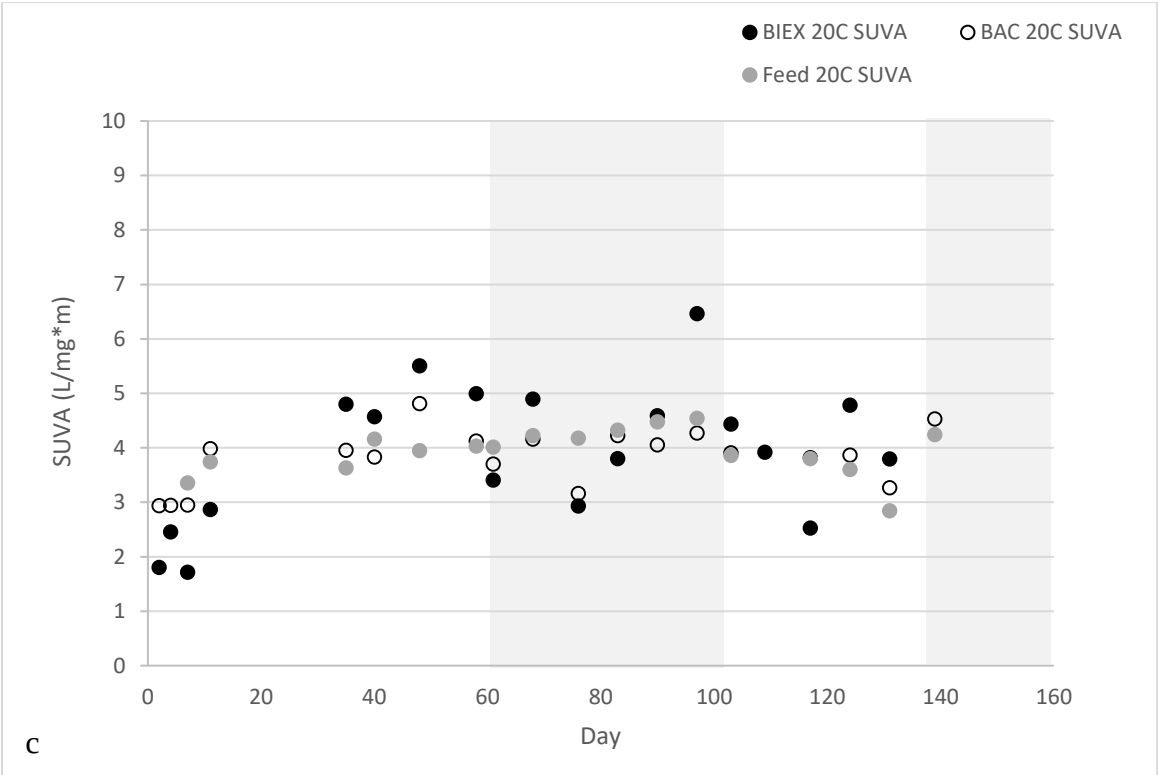


Figure 12: Typical SUVA values for feed and filtrate streams for BIEX and BAC biofilters at 20°C; a) EBCT 7.5-minutes (192BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond

As indicated in Figure 12, the SUVA of the feed water varied throughout the experiment. To account for the variation in the feed water, the filtrate SUVA values were normalized with respect to those in the feed using Equation 7.

Equation 7: Normalized SUVA Value

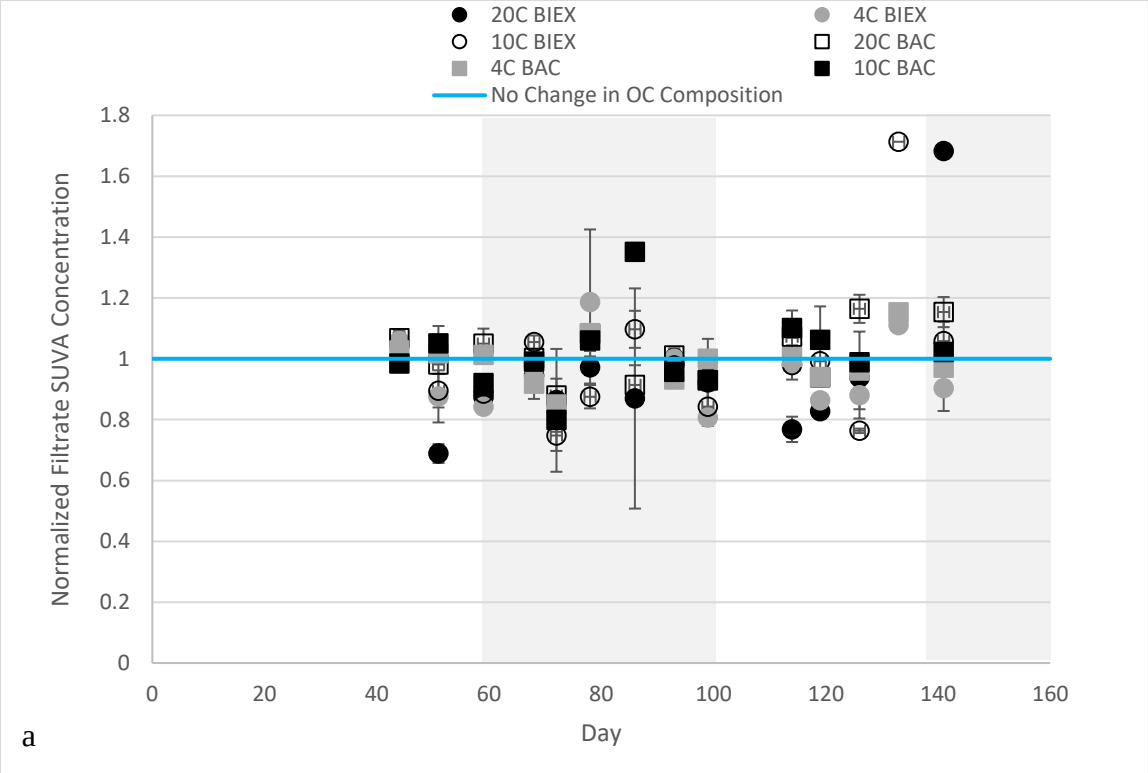
$$SUVA_{N_{T,EBCT}} = \frac{SUVA_{\mathrm{E}}}{SUVA_{\mathrm{O}}}$$

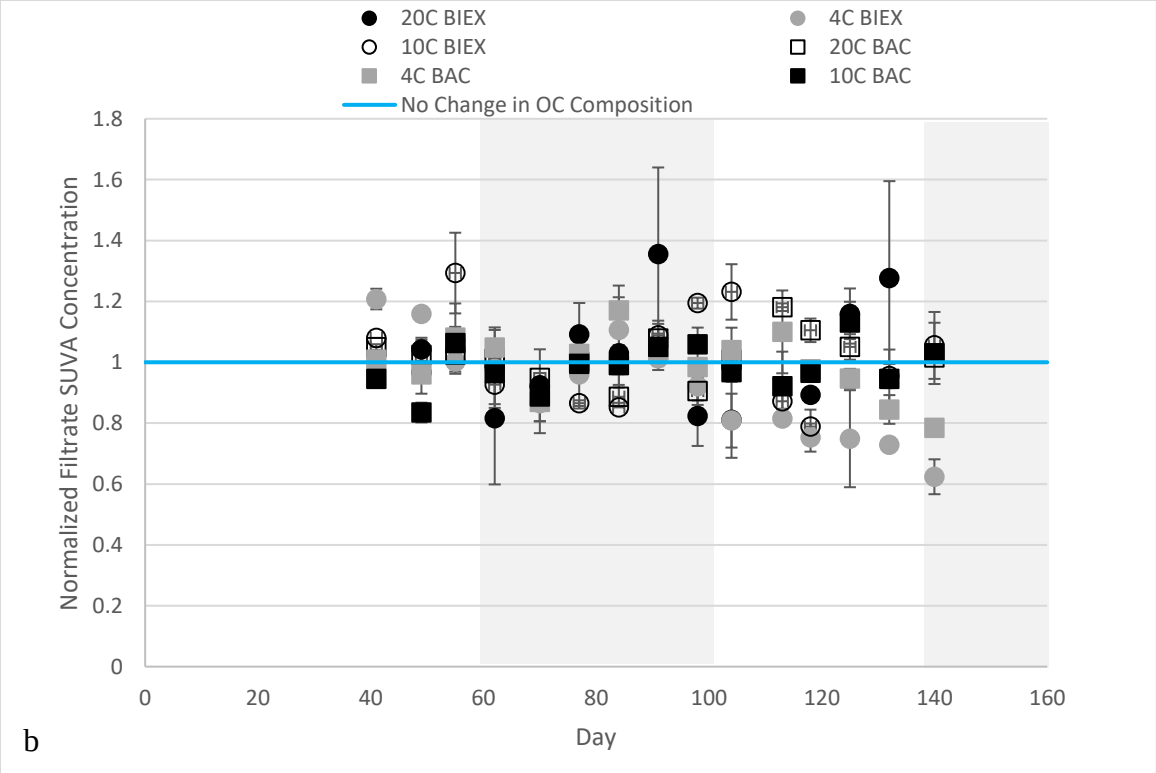
where: $SUVA_O$ is the SUVA value of the feed water in $cm^{-1}/(mg/L)$, $SUVA_E$ is the SUVA value of the filtrate $cm^{-1}/(mg/L)$, $SUVA_N$ is the normalized SUVA value, all SUVA values are for a given temperature and EBCT.

As illustrated in Figure 13 and Figure 14 the normalized SUVA remained relatively constant for all conditions investigated. Linear regressions were performed on all experimental conditions to determine if and when steady state was reached. Steady state was considered to have been reached when the slope of a linear regression model (fitted to the normalized OC concentration) was not significantly different from zero based on a 98% confidence interval. Of the 36 experimental conditions investigated (see Table 3 for experimental conditions), 34 were observed to have operated at steady state for the entirety of the experiment. Steady state was not reached for two experimental conditions, BIEX 1 at 20°C and an EBCT of 7.5 minutes and BAC 3 at 4°C and an EBCT of 15 minutes, as their slopes were significantly different from zero. Note that although statistically different from zero, the slopes were nonetheless low, BIEX 1 had a slope of 0.00487 L/mg*m/day and BAC 3 had a slope of -0.00148 L/mg*m/day. Results for the experimental conditions that did not reach steady were still included in the following data analysis. The details of the linear regression are presented in Appendix K.

The normalized SUVA values were used to quantify the change in the types of OC present in the water. Some types of OC, such as biopolymers, do not adsorb UV254 while other types of OC, such as humics, adsorb UV254. A normalized SUVA value of one indicates that the type of OC present in both the feed and filtrate were similar. A normalized SUVA value greater than one indicates that OC that does not adsorb UV254 is predominantly removed while a normalized SUVA value less than one indicates that OC that adsorbs UV254 is predominantly removed. The normalized SUVAs for BIEX biofilters were observed to be statistically different from one for three of the experimental conditions investigated: at 4 and 10°C with an EBCT 7.5-minutes and at 4°C at and EBCT of 7.5-minutes indicating that all types of OC are removed at the same rate. Results of the present study are different from those reported by Winter et al.

(2018) at high temperatures (20°C) and long EBCT (30-minutes). They observed that BIEX biofitlers predominantly remove organics that adsorb UV254. The normalized SUVA values for BAC biofilters were observed to be statistically similar to one for all of the experimental conditions investigated indicating all types of OC are removed at the same rate. These results are also different from those reported in previous studies. Studies by Zheng, Ernst and Jekel. (2010), Winter, Bérubé, Uhl and Barbeau (2013) and Winter et al. (2018) indicated that BAC biofilters predominantly remove organics that do not adsorb UV254 (e.g. biopolymers). The differences in the normalized SUVA values observed between the present study and studies by others (Zheng et al., 2010, Winter et al. 2013, and Winter et al. 2018) was likely related to the different feed water characteristics. The detailed results of the statistical analysis are presented in Appendix L.


20C BIEX
10C BIEX
4C BAC
No Change in OC Composition
4C BIEX
20C BAC
10C BAC
Normalized Filtrate SUVA Concentration
Day
a


20C BIEX
10C BIEX
4C BAC
No Change in OC Composition
4C BIEX
20C BAC
10C BAC
Normalized Filtrate SUVA Concentration
Day
b

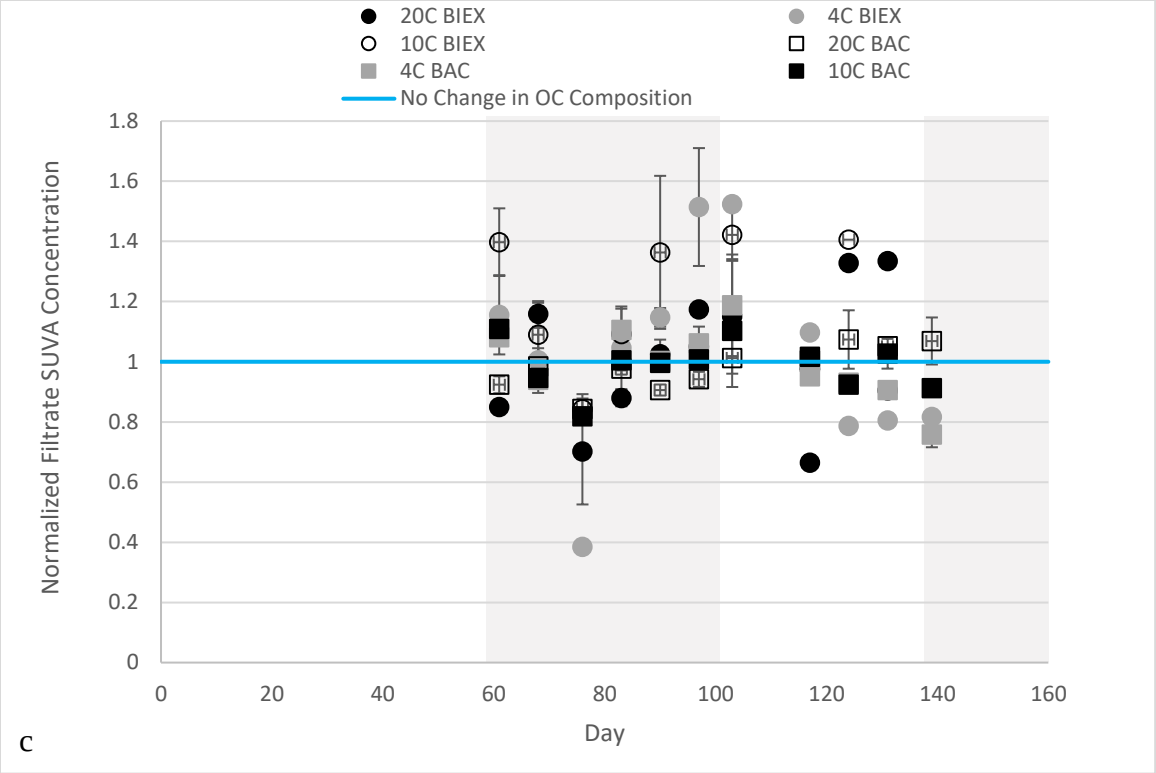
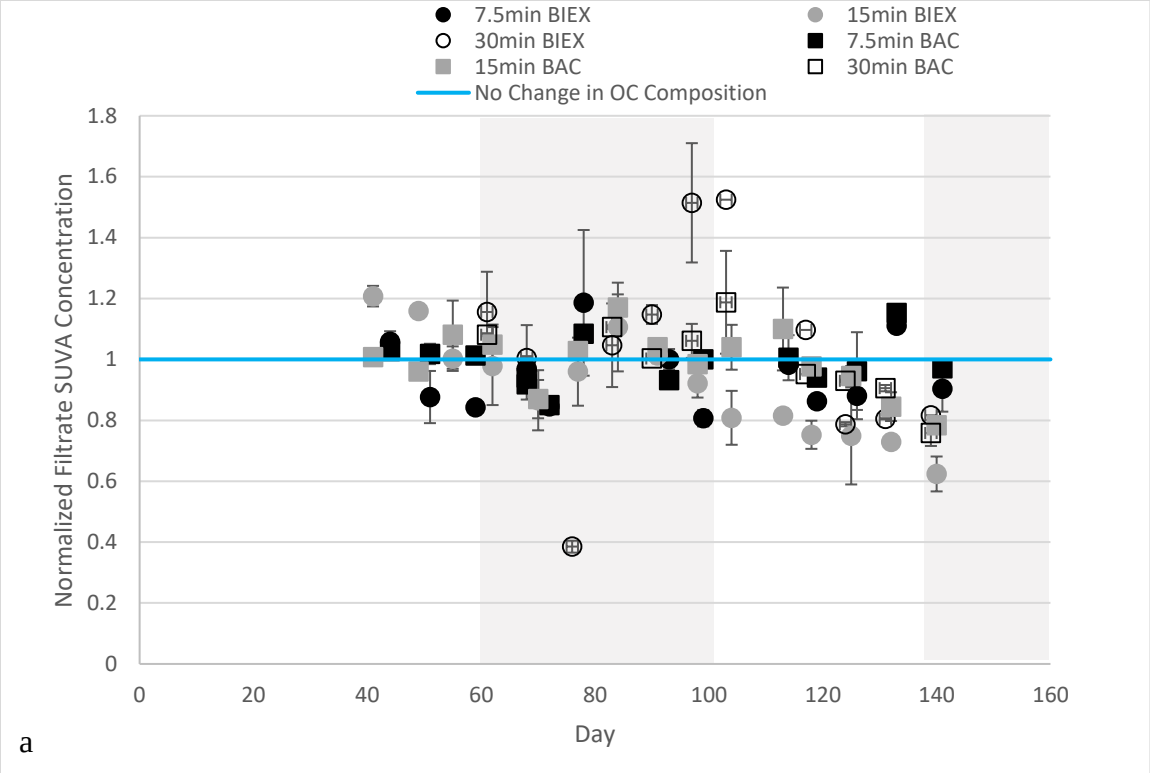
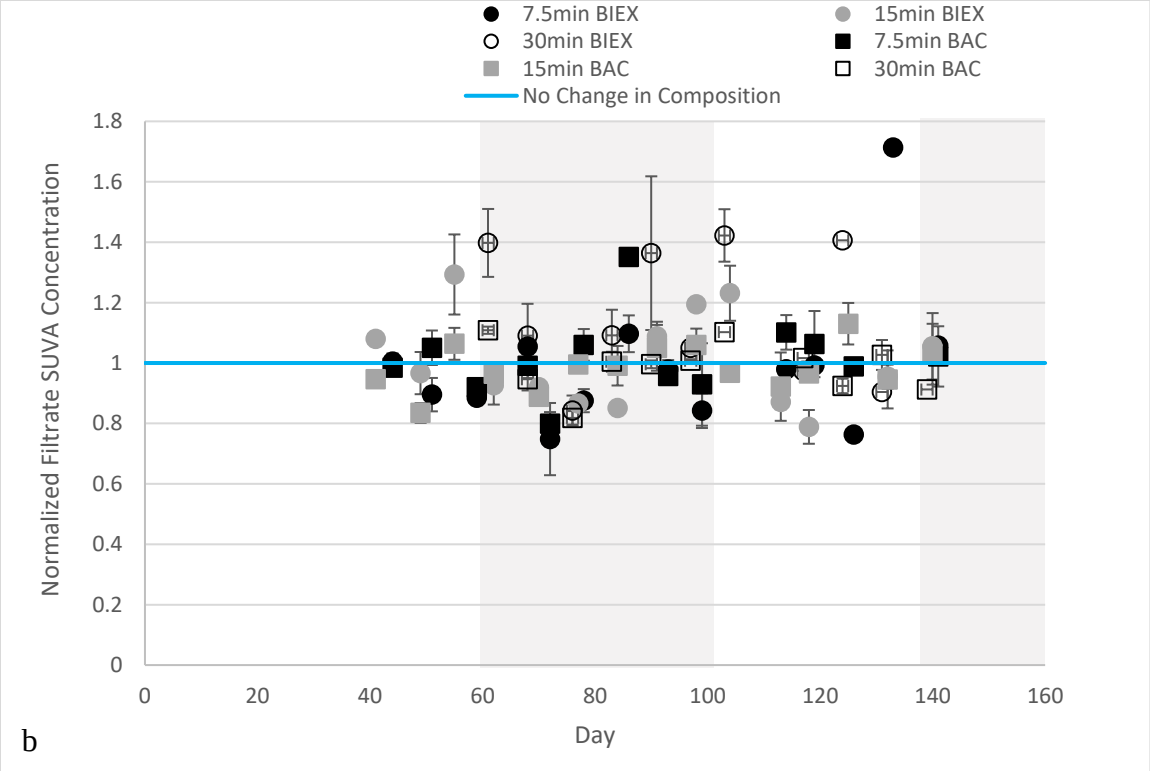


Figure 13: All normalized SUVA values for BIEX and BAC biofilters for different EBCT: a) EBCT 7.5-minutes (192BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond; Data presented is an average from replicate biofilters and error bars correspond to the minimum and maximum values from replicate biofilters


7.5min BIEX
15min BIEX
30min BIEX
7.5min BAC
15min BAC
30min BAC
No Change in OC Composition
Normalized Filtrate SUVA Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
20
40
60
80
100
120
140
160

a


7.5min BIEX
15min BIEX
30min BIEX
7.5min BAC
15min BAC
30min BAC
No Change in Composition
Normalized Filtrate SUVA Concentration
Day
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
20
40
60
80
100
120
140
160

b

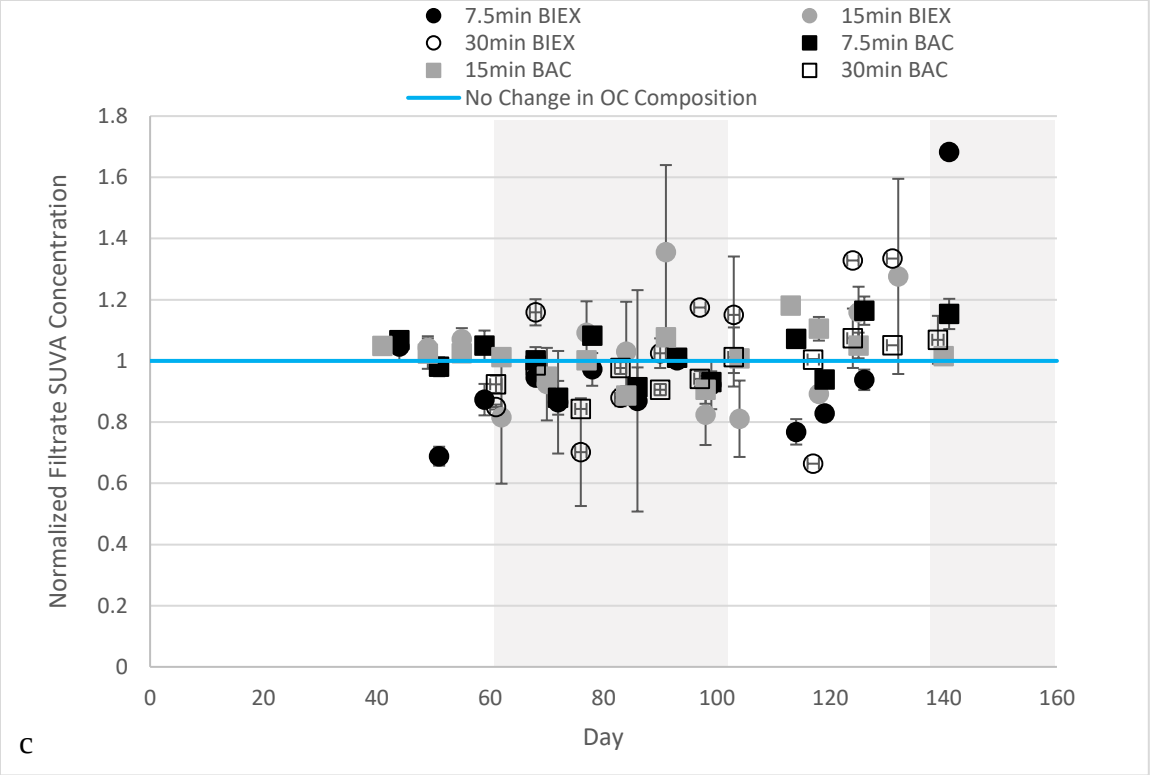


Figure 14: All normalized SUVA values for BIEX and BAC biofilters for different temperatures a) 4°C; b) 10°C; c) 20°C;
Shaded grey areas indicate a change in feed water based on when it was collected from Jericho Pond;
Data presented is an average from replicate biofilters and error bars correspond to the minimum and maximum values from replicate biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

A statistical analysis was conducted to determine the impact of temperature and EBCT on the type of OC removed. The analysis revealed that neither temperature nor EBCT impacted the normalized SUVA of either BIEX or BAC biofilters. The detailed results of the statistical analysis are presented in Appendix M. These results suggest that even if the extent to which NOM is removed differs with temperature and EBCT, as indicated in the previous section, the relative proportions of the different types of NOM is not impacted by either BIEX or BAC biofilters.

5.2 Removal Mechanism

5.2.1 Chloride Release and Sulphate Capture

The selected anionic exchange resin removes NOM through exchanging chloride ions with negatively charged organic molecules. This exchange process is not selective and ions other than NOM, such as sulphate, can also be removed. Once the exchange capacity of the resin (in the BIEX biofilter) has been exhausted, the removal of NOM through ion exchange is expected to stop. Similarly, once the resin capacity has been exhausted the removal of other ions, such as sulphate, is also expected to stop. The release of chloride ions and the uptake of sulphate ions were monitored to identify when the ion exchange capacity for the different conditions was exhausted.

The concentrations of chloride and sulphate in the feed water varied throughout the experiment. To account the changes in the feed water, the filtrate chloride and sulphate concentrations were normalized to those in the feed. Note that because the concentrations of chloride and sulphate ions in the feed were not consistently measured throughout the experiments those in the filtrate from BAC biofilters were used to normalize the chloride and sulphate ion concentrations. BAC biofitlers are not expected to significantly interact with chloride or sulphate ions and therefore the filtrate from the BAC biofitlers is a good surrogate for chloride and sulphate ions in the feed water.

The normalized chloride concentrations were similar for all temperatures investigated, and therefore the normalized chloride concentration for all temperatures measured on a given day at a given EBCT were averaged together to generate a single value. Temperature also did not impact normalized sulphate concentrations; these were also averaged.

As illustrated in Figure 15, for all conditions investigated, the normalized chloride concentration decreased to one within 70 to 100 days. This indicates that for the conditions investigated, the exchange capacity had been exhausted within 100 days. The data suggests that exhaustion occurred more rapidly at shorter EBCT.

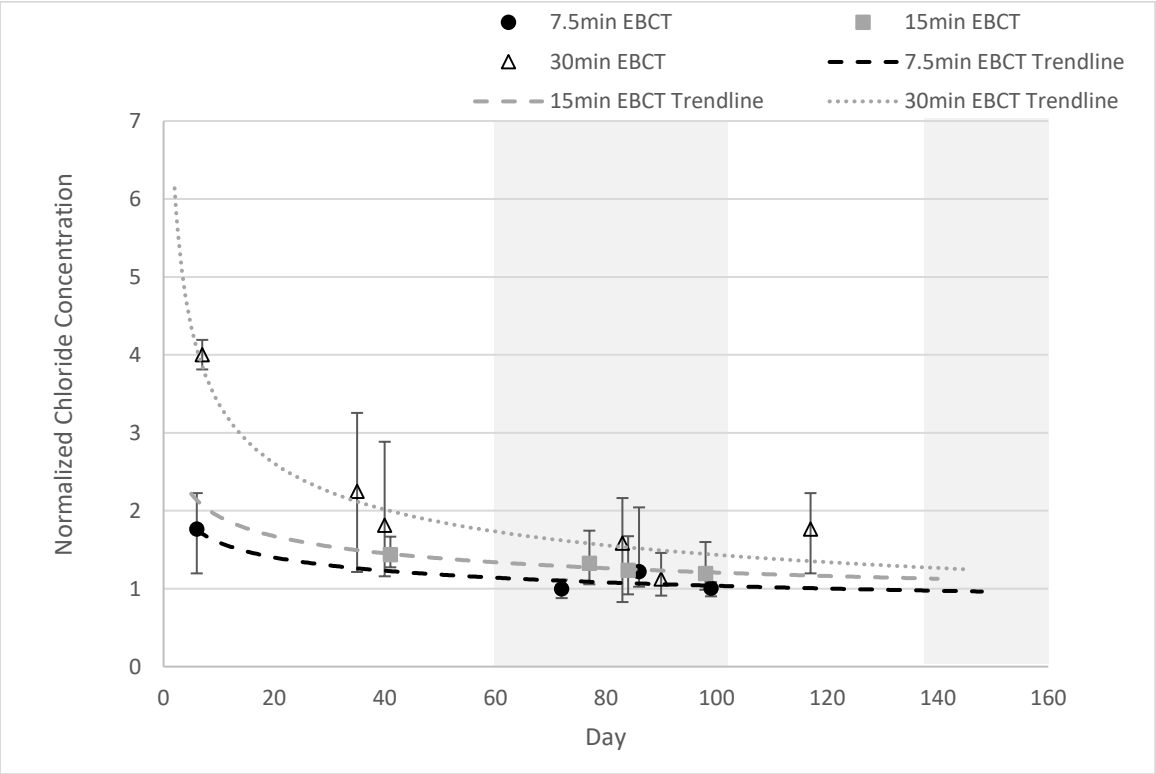


Figure 15: Normalized effluent chloride concentration at different EBCT;
There was no variation between normalized chloride concentration at different temperatures, data from different temperatures is averaged;
Error bars represent the maximum and minimum measured normalized chloride concentration;
Lines presented reflect the overall trend of the data at a given EBCT;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

The expected amount of chloride released can be estimated based on the reported ion exchange capacity of the resin, which is 0.68mEq/mL (Amini et al., 2018). The reported ion exchange capacity corresponds to a release of 0.76g of chloride (range of 0.70-0.84g based on range of media depth for different columns used), for an EBCT of 30 minutes. Based on a mass balance analysis, it was estimated that 0.93±0.36g of chloride, at an EBCT 30 minutes, was

released in the first 100 days (4800BV). The estimated amount of chloride is not statistically different from the theoretical amount of chloride that should be released. Unfortunately, there was insufficient data available to estimate the amount of chloride released for EBCTs of 7.5 and 15 minutes.

As previously discussed, ion exchange is not selective, and both sulphate and NOM can be removed. Sulphate tends to be preferentially removed over NOM by the resins (Fu & Symons, 1990) and therefore can be used as an indicator of whether the resin is exhausted or not. As illustrated in Figure 16 the normalized sulphate concentrations were very low for the first 40 days indicating that ion exchange occurred throughout this period of time. The normalized sulphate concentration increased to a value above one by day 70 for an EBCT of 7.5 minutes (13400BV), the normalized sulphate concentration increased to a value of approximately one for an EBCT of 15 minutes (6720BV) while the normalized sulphate concentration for an EBCT of 30 minutes remained low throughout the experiment (120 days or 5760BV).

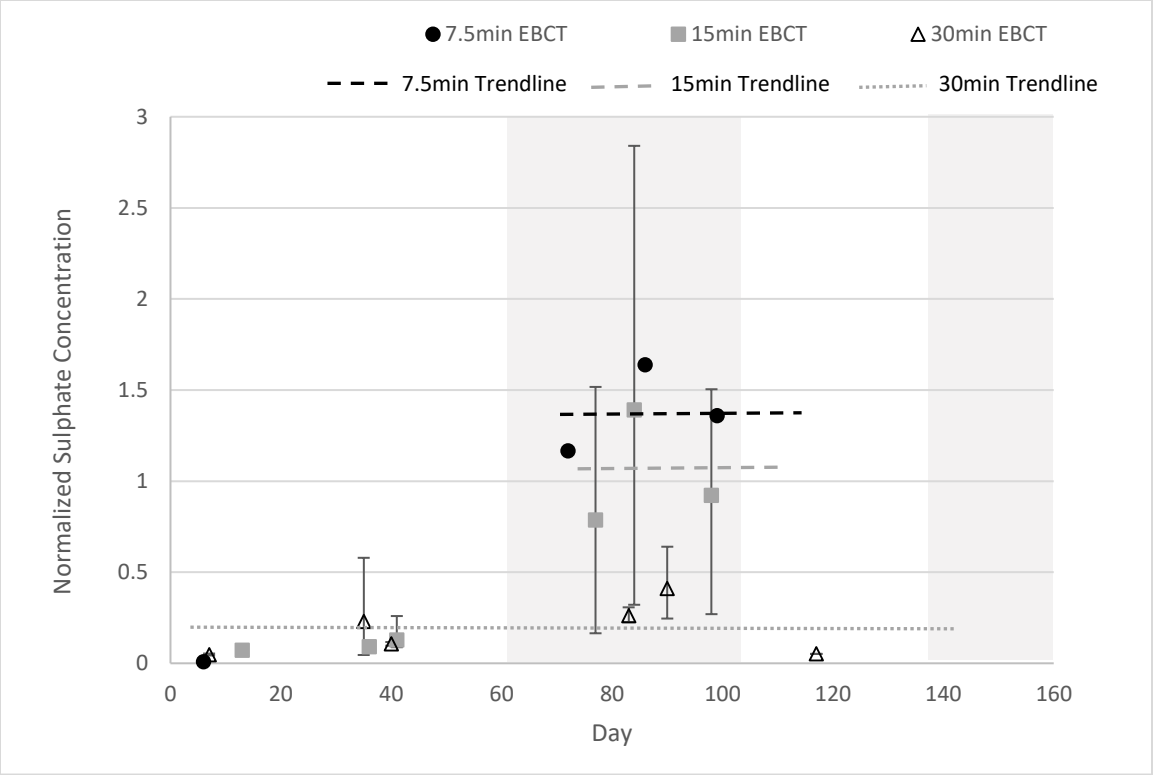


Figure 16: Normalized sulphate concentration at different EBCT;
There was no variation between normalized sulphate concentrations at different temperatures; data from all temperatures was averaged;
Error bars represent the maximum and minimum measured normalized chloride concentration;
Lines presented reflect the overall trend of the data at a given EBCT;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

The normalized sulphate concentration of approximately one after 70 days (6720 BV) for an EBCT of 15 minutes are consistent with the results for the release of chloride. These results indicated that the exchange capacity had been exhausted after 70 to 100 days (6720 to 9600BV). However, the normalized sulphate concentration greater than one for an EBCT of 7.5 minutes and the low normalized sulphate concentration for an EBCT of 30 minutes are not consistent with the results for the release of chloride. A normalized concentration of greater than one suggests that the sulphate that was previously removed was now being released; while a low normalized concentration suggests that the exchange capacity has not been exhausted.

Additional research beyond the scope of the current study is required to gain further insight into the removal mechanisms in BIEX biofilters.

The normalized chloride concentrations in the BIEX effluent suggests that the ion exchange capacity of the resin was consistently exhausted for all conditions investigated within the timeline of the study. For EBCT of 7.5 to 15 minutes, the normalized chloride concentration of one suggests that the exchange capacity was exhausted after approximately 70 days (i.e. 13400 and 6720 bed volumes for EBCT of .5 minutes to 15 minutes respectively), while for an EBCT of 30 minutes, the capacity was exhausted after approximately 100 days (i.e. 4800 bed volumes).

In contrast, the normalized sulphate concentration in the BIEX effluent suggests that the ion exchange capacity of the resin was not exhausted for all conditions investigated within the timeline of the study. For an EBCT of 30 minutes the normalized sulphate concentration remained low, suggesting that the exchange capacity was not exhausted. For an EBCT of 15 minutes the normalized sulphate concentration increased to one after approximately 70 days (i.e. 6720 bed volumes) suggesting that the ion exchange capacity was exhausted at this time. For an EBCT of 7.5 minutes, the normalized sulphate concentration increased to greater than one after approximately 70 days (i.e. 13400 bed volumes) not only indicating that the exchange capacity was exhausted, but that previously removed sulphate was now being released.

Note raw chloride and sulphate concentrations are presented in Appendix N.

5.2.2 Activation Energy

The activation energy is the energy that must be provided for a chemical reaction to occur. Activation energy can be used as an indicator of the pathway by which OC is removed.

The activation energy associated with the removal of OC was estimated by fitting Equation 8 to the estimated rate constants for BIEX and BAC biofilters that were estimated in section 5.1.1 and listed in Table 7. Equation 8 was transformed as presented in Equation O-1 in Appendix O so that a linear regression could be used to estimate the activation energy.

Equation 8: Arrhenius Equation

$$k = Ae^{\frac{-E_a}{RT}}$$

where: k is the rate constant that was calculated in section 5.1.1, E_a is the activation energy, R is the universal gas constant and T is the temperature in Kelvin and A is the pre-exponential factor

The estimated activation energy for BIEX and BAC biofilters are presented in Table 9. Data from a recent study (Amini et al., 2018) comparing IEX columns and BIEX and BAC biofilters at a pilot scale over an extended period of time under transient conditions where water temperature varied between 2 and 23°C is also presented in Table 9.

Table 9: Comparison of activation energy for various OC removal technologies in different studies; The confidence interval corresponds to the standard error on the estimated parameter

	IEX	**BIEX**	**BAC**
Present Study	-	29.5±2.2	48.6±5.4
Amini et al., 2018	20±5	30±4	30±8

The estimated activation energy for BIEX biofilters from both the present study and a recent study by Amini et al. (2018) are similar. The estimated activation for BAC biofilters from the present study is greater than that from Amini et al. (2018), however other studies have reported that BAC biofilters have activation energies between 40 and 45kJ/mol (Terry & Summers, 2018) and 54kJ/mol (Laurent, Prévost, Cigana, Niquette and Servais, 1991).

As presented in Table 9 the activation energy for BAC biofitlers is significantly higher than that of BIEX biofilters while the activation energy for IEX columns is significantly lower

than that of BIEX biofilters. This suggests that the mechanism of NOM removal in BIEX biofilters utilizes both ion exchange and biodegradation. As the activation energy of BIEX biofilters is closer to that of IEX columns it is hypothesized that the ion exchange mechanism of NOM removal dominates. However, further research is needed to confirm the NOM removal mechanism in BIEX biofilters and whether ion exchange is the dominant mechanism of removal.

6. Conclusion and Recommendations

6.1 Conclusion

6.1.1 Objective 1

The first objective of this work was to benchmark the performance of BIEX and conventional (BAC) biofilters at different temperatures and EBCTs. The major conclusions from Objective 1 are:

1. Organic carbon removal rate was greater for BIEX than BAC biofilters.
2. Temperature significantly impacts the removal of organic carbon using both BIEX and BAC biofilters. As temperature decreases so does the rate of organic carbon removal (i.e. temperature activity coefficient is greater than one).
3. Temperature had a larger impact on rate of removal of organic carbon in BAC than BIEX biofilters.
4. The negative impact of temperature on organic carbon removal rate can be compensated for by providing a longer retention time (i.e. EBCT) in the biofilters to enable effective organic carbon removal. To ensure effective (i.e. ≥ 90%) removal organic carbon over a wide range of temperature (4°C-20°C) the HRT for BIEX and BAC biofilters should be at least 30 minutes and 45 minutes respectively. This is equivalent to a 55-minute and 90-minute EBCT or 26.2 and 16BV/day respectively.
5. Temperature and EBCT have no impact on the type of organic carbon removed by BIEX and BAC biofilters.

6.1.2 Objective 2

The second objective of this work was to demonstrate that BIEX biofilters are more effective at NOM removal than BAC biofilters. The major conclusions from objective 2 are:

1. BIEX biofilters removed a more organic carbon than BAC biofilters at all temperatures (4, 10 and 20°C) and EBCT (7.5, 15 and 30-minutes or 192, 96 and 48 BV/day).
2. BIEX biofitlers remove 46.5-77.5% organic carbon while BAC biofilters remove 4.6-31.3% organic carbon depending on the experimental conditions (temperature and EBCT).

6.1.3 Objective 3

The third objective was to determine the removal mechanism for BIEX biofilters and compare it to that of BAC (conventional) biofilters.

Inconsistent results with respect to resin exhaustion were observed. Normalized chloride concentration suggest that the resin capacity was fully exhausted after approximately 70 to 100 days for all conditions investigated. Normalized sulphate concentrations suggest that the resin capacity was not fully exhausted even after 120 days (5760BV) of operation for an EBCT of 30 minutes.

6.2 Engineering Significance and Future Work

6.2.1 Engineering Significance

Objective 1: Organic carbon removal in BIEX biofitlers is negatively impacted at low temperatures when the EBCT is short. When designing BIEX biofitlers it is important to ensure that the EBCT is sufficient to remove the desired amount of organic carbon at the lowest expected operating temperatures.

Objective 2: This work demonstrated that BIEX biofilters remove organic carbon faster and to a greater extent under all experimental conditions than BAC biofilters. BIEX biofilters are a viable, better performing alternative to BAC biofilters.

Objective 3: Organic carbon removal in BIEX biofilters likely occurs through both ion exchange and biological activity.

6.2.2 Future Work

The mechanism of organic carbon removal for BIEX biofilters was not comprehensively investigated in this work and as such it was difficult to draw meaningful conclusions. Nonetheless, the activation energy suggests that BIEX and BAC biofilters remove organic carbon through different mechanisms and the BIEX biofitlers likely remove organic carbon through a combination of ion exchange and biological activity. More work is needed to identify the mechanisms (either biological or ion exchange) governing organic carbon removal by BIEX biofilters.

Past studies on BAC biofilters have indicated that type of organic carbon present in the feed impacts the amount of organic carbon that can be removed. Future work should aim to determine the impact of type of organic carbon present in the feed on removal. Changes in organic material may also impact the effect of temperature and EBCT on its removal and should also be investigated.

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Appendix A: Location of Feed Water Source

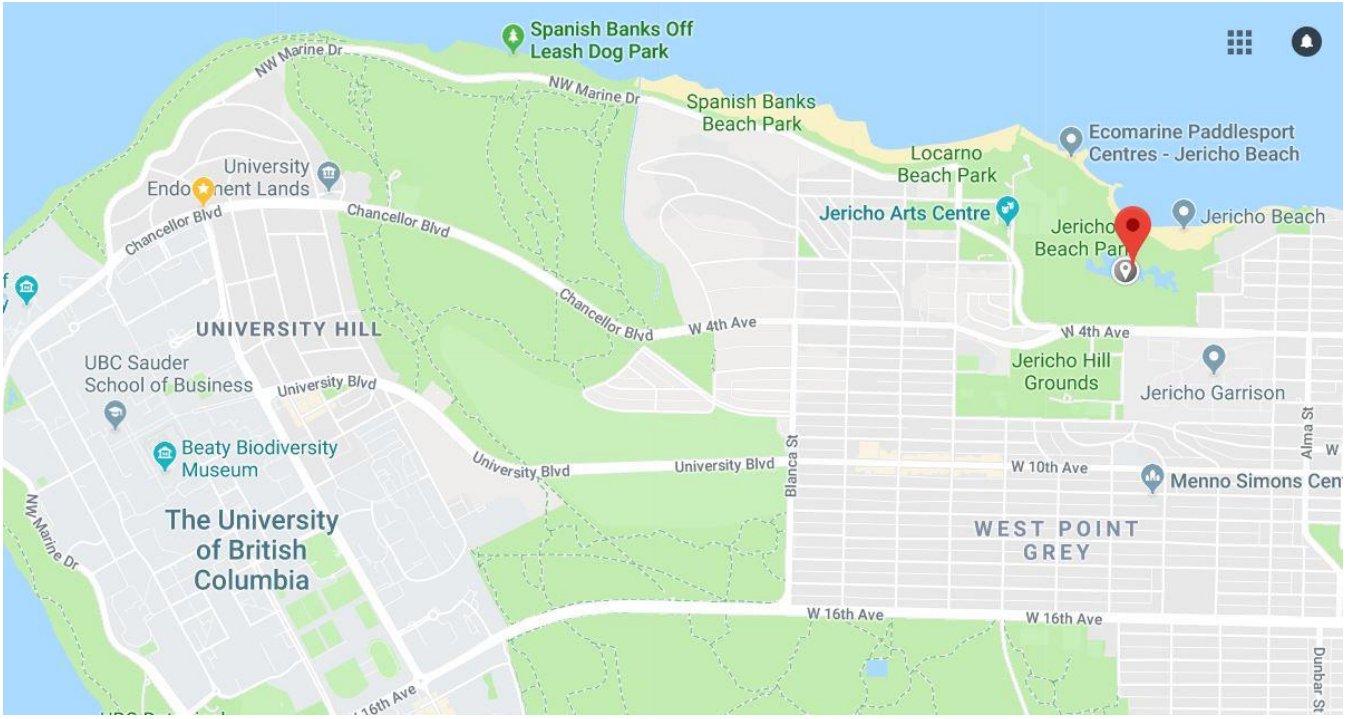


Figure A-1: Location of Jericho Pond in Vancouver, BC, Canada

Appendix B: Details of the Experimental Apparatus

Table B-1: Actual depth of ports by biofilter from top of media;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

	Depth from top of Media (cm)											
	4°C				10°C				20°C			
Name	BIEX 3	BIEX 4	BAC 3	BAC 4	BIEX 5	BIEX 6	BAC 5	BAC 6	BIEX 1	BIEX 2	BAC 1	BAC 2
Port 1, EBCT 7.5min	3.5	4.5	3	3	4	3.25	3.5	3.5	4.5	6.5	4	3.5
Port 2, EBCT 15min	9.75	10.5	9.5	9.5	10	9.5	8	10	10.5	12	10.5	9.5
Port 3, EBCT 30min	20.5	21	20	20	21	20	18.5	21	23.5	24	22.5	21

Table B-2: Type of pump and tubing used at each temperature

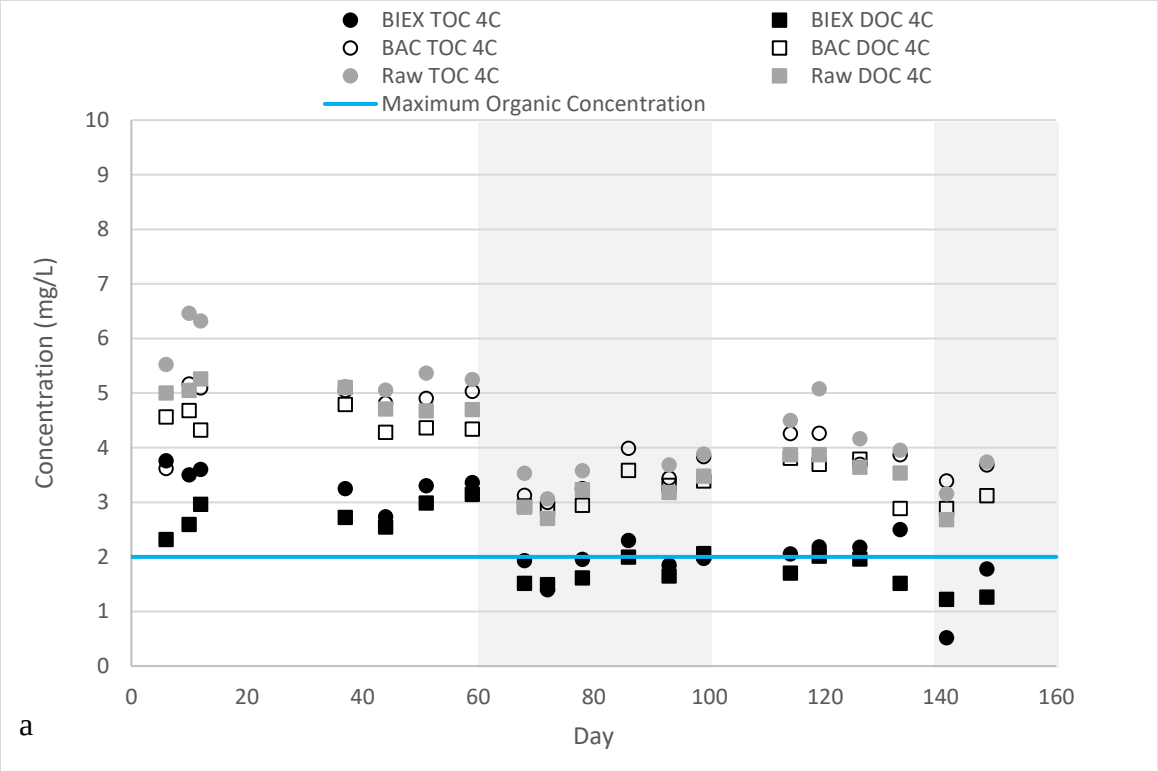
Apparatus	Pump utilized	Pump Tubing
Room (20°C) Temperature		Fisher Brand Manifold Pump Tubing, ID 1.14mm, Red-Length 16”
10°C	Cole- Palmer Masterflex ® L/S	Masterflex Microbore two-stop tube, silicone (platinum cured) 1.42mm ID
4°C	Cole- Palmer Masterflex ® L/S	Masterflex Microbore two-stop tube, silicone (platinum cured) 1.42mm ID

Each of the columns was constructed from the following material:

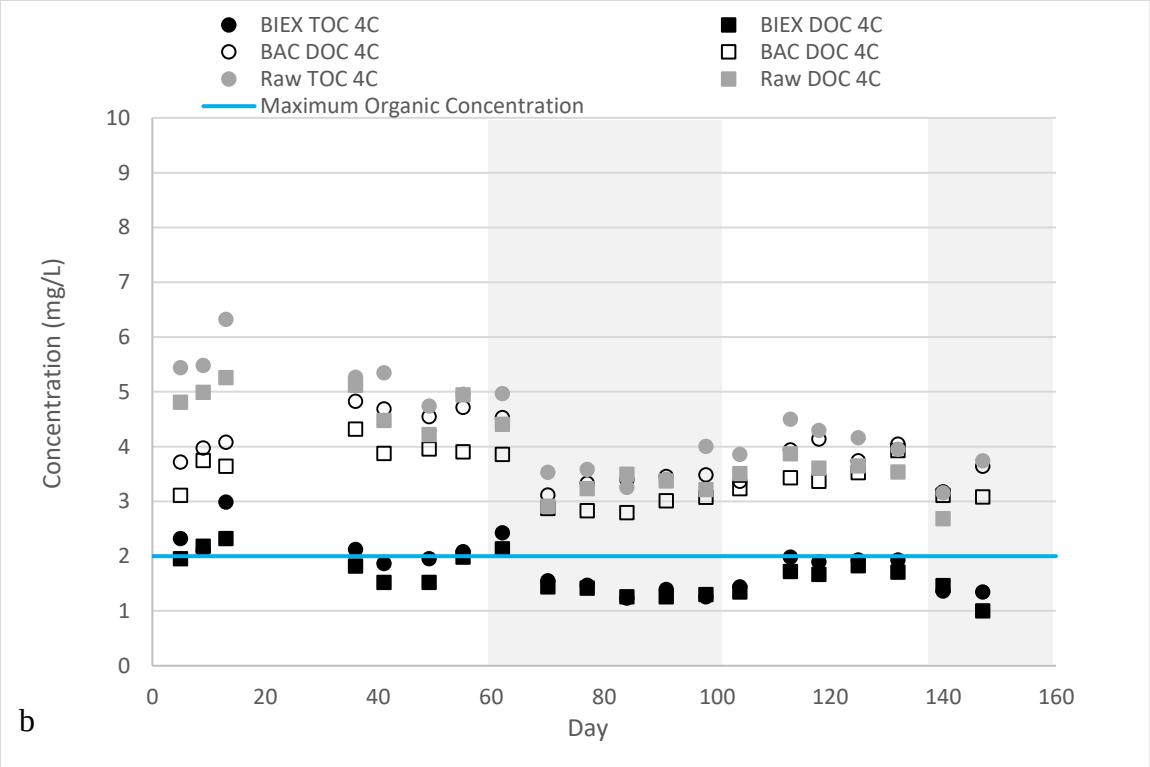
- 40 cm of 3/8” PVC Schedule 40 pipe
- 3x ¼” NPT Female x ¼” NPT Male on/off valve
- 3x 3/8” Socket Female x ½” Socket Female Reducing T
- 5x ½” Socket Male x ¼” NPT Female Reducer
- 4x push-to-connect tube fitting with universal thread 1/8” OD Tubing x ¼” pipe
- 2x ½” Female Socket Connector
- 1x plastic barbed tube fitting straight adaptor ¼” OD Tubing x ¼” NPT Male Connector
- 2x ½” Socket Male x 3/8” Socket Female Connector
- 1.5 m of ¼” OD Tubing
- 1/16” ID, 1/8” OD Masterkleer PVC Clear Tubing

Appendix C: Graphical Raw Data: OC Concentration

Raw TOC and DOC data was collected weekly from each port for both BIEX and BAC biofilters throughout the experiment. Due to limitations on TOC machine all measurements under 0.5mg/L were eliminated. The raw data was plotted in three figures one for each temperature. Each figure contains three graphs one for each EBCT.


BIEX TOC 4C
BAC TOC 4C
Raw TOC 4C
Maximum Organic Concentration
BIEX DOC 4C
BAC DOC 4C
Raw DOC 4C
Concentration (mg/L)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

a


BIEX TOC 4C
BAC DOC 4C
Raw TOC 4C
Maximum Organic Concentration
BIEX DOC 4C
BAC DOC 4C
Raw DOC 4C
Concentration (mg/L)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

b

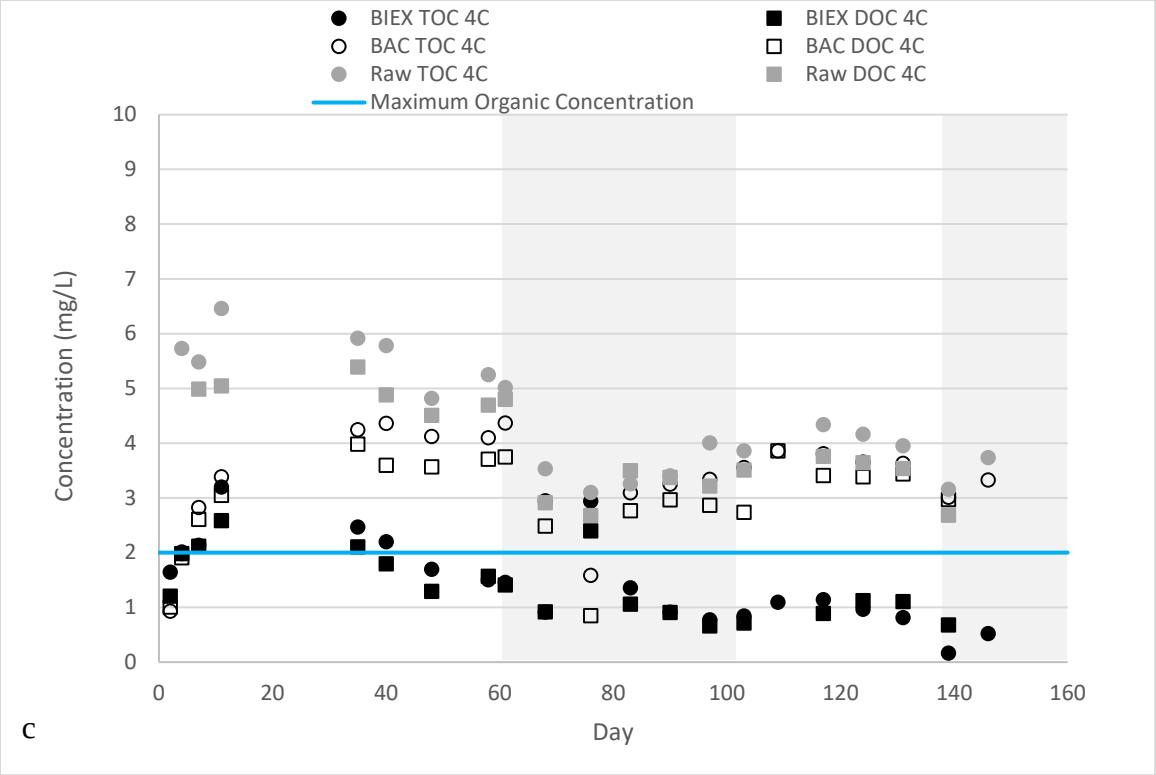
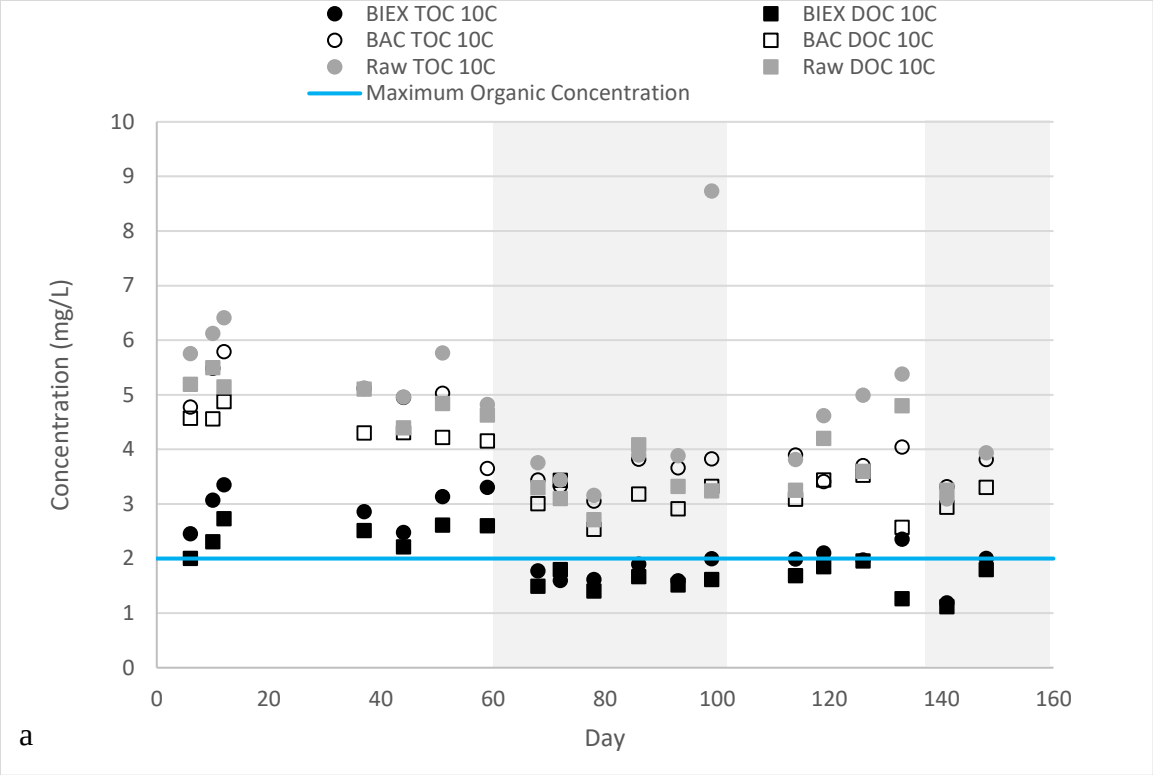
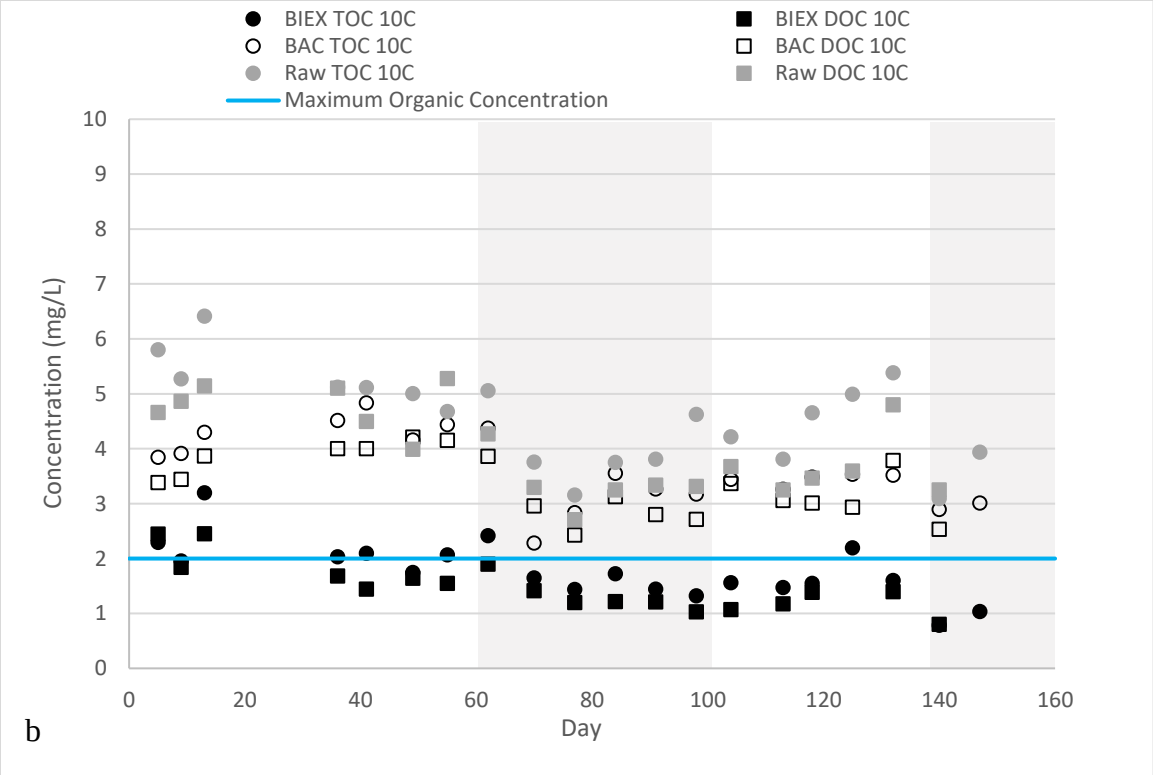


Figure C-1: Raw Data at 4°C, absolute removal of TOC and DOC for both BIEX and BAC biofilters; a) EBCT 7.5-minutes (192BV/day) b) EBCT 15-minutes (96BV/day) c) EBCT 30-minutes (48BV/day); Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond;
The blue indicates the target NOM concentration to minimize DBP formation;


BIEX TOC 10C
BAC TOC 10C
Raw TOC 10C
Maximum Organic Concentration
BIEX DOC 10C
BAC DOC 10C
Raw DOC 10C
Concentration (mg/L)
Day
a


BIEX TOC 10C
BAC TOC 10C
Raw TOC 10C
Maximum Organic Concentration
BIEX DOC 10C
BAC DOC 10C
Raw DOC 10C
Concentration (mg/L)
Day
b

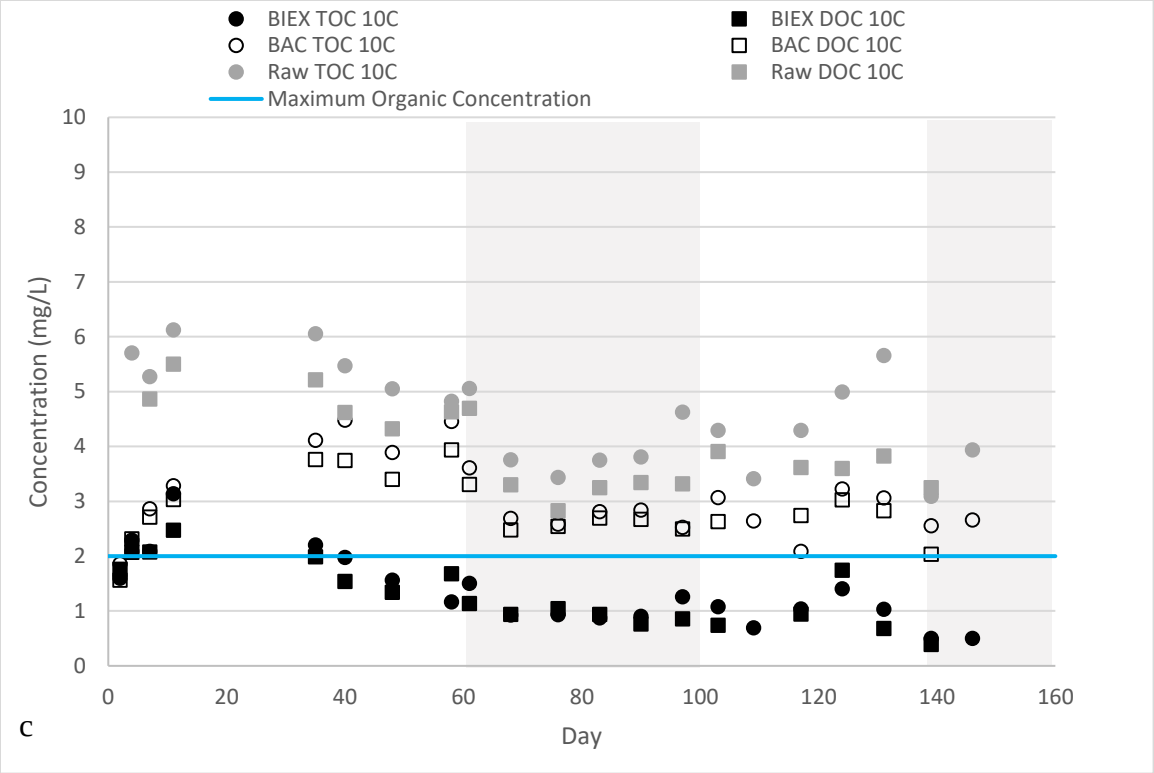


Figure C-2: Raw Data at 10°C, absolute removal of TOC and DOC for both BIEX and BAC biofilters; a) EBCT 7.5-minutes (192BV/day) b) EBCT 15-minutes (96BV/day) c) EBCT 30-minutes (48BV/day); Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond;
The blue indicates the target NOM concentration to minimize DBP formation

Appendix D: Determination of Steady State for OC Removal

The following tables display the major parameters calculated during the linear regression of the normalized filtrate data for both BIEX and BAC biofilters. The error on the slope of the linear regression was used to determine whether the slope was statistically different from 0. If it was not, steady state was considered to be achieved. A 98% confidence interval was used.

Table D-1: Linear regression of relative effluent concentration data to determine whether biofilter is at steady state for biofilters with and EBCT of 7.5-minutes (192BV/day)

Biofilter Name	BIEX 1	BIEX 2	BAC 1	BAC 2	BIEX 3	BIEX 4	BAC 3	BAC 4	BIEX 5	BIEX 6	BAC 5	BAC 6
Temperature	20°C	20°C	20°C	20°C	4°C	4°C	4°C	4°C	10°C	10°C	10°C	10°C
B_1	-2.23E-03	-2.23E-03	-1.04E-03	-7.30E-04	-7.93E-04	-1.42E-03	4.10E-04	5.24E-04	-9.30E-04	-3.39E-03	-1.12E-03	-5.02E-04
B_o	6.17E-01	6.54E-01	9.79E-01	9.67E-01	6.36E-01	6.42E-01	9.27E-01	8.99E-01	5.90E-01	7.58E-01	1.03E+00	9.60E-01
variance B_1	9.07E-03	8.97E-03	8.78E-03	8.78E-03	8.97E-03	8.79E-03	8.79E-03	9.06E-03	8.78E-03	1.04E-02	8.78E-03	8.78E-03
variance B_o	8.91E-01	8.85E-01	8.79E-01	8.79E-01	8.95E-01	8.89E-01	8.89E-01	9.04E-01	8.79E-01	9.57E-01	8.79E-01	8.79E-01
s	1.05E-01	1.02E-01	1.35E-01	1.21E-01	7.58E-02	6.14E-02	7.07E-02	4.44E-02	4.86E-02	1.53E-01	8.41E-02	9.85E-02
t -score 98%	2.718	2.718	2.681	2.681	2.764	2.718	2.718	2.821	2.681	2.821	2.681	2.681
Count	13	13	14	14	12	13	13	11	14	11	14	14
Error B_1 98%	2.58E-03	2.48E-03	3.17E-03	2.84E-03	1.88E-03	1.47E-03	1.69E-03	1.14E-03	1.14E-03	4.48E-03	1.98E-03	2.32E-03
max B_1 98%	3.49E-04	2.48E-04	2.13E-03	2.11E-03	1.09E-03	4.25E-05	2.10E-03	1.66E-03	2.15E-04	1.09E-03	8.57E-04	1.82E-03
min B_1 98%	-4.81E-03	-4.71E-03	-4.22E-03	-3.57E-03	-2.67E-03	-2.89E-03	-1.28E-03	-6.11E-04	-2.07E-03	-7.87E-03	-3.10E-03	-2.82E-03

Table D-2: Linear regression of relative effluent concentration data to determine whether biofilter is at steady state for biofilters with an EBCT of 15-minutes (96BV/day)

Biofilter Name	BIEX 1	BIEX 2	BAC 1	BAC 2	BIEX 3	BIEX 4	BAC 3	BAC 4	BIEX 5	BIEX 6	BAC 5	BAC 6
Temperature	20°C	20°C	20°C	20°C	4°C	4°C	4°C	4°C	10°C	10°C	10°C	10°C
B_1	-1.94E-03	-8.38E-04	-8.37E-04	-2.40E-03	2.20E-03	1.37E-03	8.35E-04	1.11E-03	-1.21E-03	-1.19E-03	-8.40E-04	-1.56E-03
B_o	4.21E-01	3.84E-01	8.82E-01	1.01E+00	2.43E-01	2.60E-01	8.67E-01	8.13E-01	4.97E-01	4.57E-01	9.14E-01	1.00E+00
variance B_1	9.47E-03	9.78E-03	8.11E-03	8.31E-03	6.95E-03	7.73E-03	7.73E-03	7.73E-03	7.98E-03	7.73E-03	7.73E-03	7.75E-03
variance B_o	8.67E-01	9.13E-01	7.86E-01	7.99E-01	6.91E-01	7.69E-01	7.69E-01	7.69E-01	7.78E-01	7.69E-01	7.69E-01	7.69E-01
s	6.32E-02	5.30E-02	4.35E-02	6.25E-02	9.08E-02	6.77E-02	4.37E-02	5.24E-02	6.96E-02	5.46E-02	5.48E-02	6.34E-02
t -score 98%	2.681	2.718	2.65	2.65	2.718	2.624	2.624	2.624	2.65	2.624	2.624	2.65
Count	14	13	15	15	13	16	16	16	15	16	16	15
Error B_1 98%	1.61E-03	1.41E-03	9.35E-04	1.38E-03	1.71E-03	1.37E-03	8.85E-04	1.06E-03	1.47E-03	1.11E-03	1.11E-03	1.30E-03
max B_1 98%	-3.31E-04	5.71E-04	9.80E-05	-1.02E-03	3.91E-03	2.74E-03	1.72E-03	2.17E-03	2.61E-04	-8.15E-05	2.72E-04	-2.58E-04
min B_1 98%	-3.54E-03	-2.25E-03	-1.77E-03	-3.77E-03	4.87E-04	-7.45E-06	-5.04E-05	4.73E-05	-2.68E-03	-2.30E-03	-1.95E-03	-2.86E-03

Table D-3: Linear regression of relative effluent concentration data to determine whether biofilter is at steady state for biofilters with an EBCT of 30-minutes (48BV/day)

Biofilter Name	BX 1	BX2	BAC 1	BAC 2	BX 3	BX 4	BAC 3	BAC 4	BX 5	BX 6	BAC 5	BAC 6
Temperature	20°C	20°C	20°C	20°C	4°C	4°C	4°C	4°C	10°C	10°C	10°C	10°C
B_1	-9.82E-04	-9.87E-04	-2.28E-03	7.98E-05	-5.44E-04	-1.15E-03	1.55E-03	1.39E-03	-1.30E-03	-1.64E-03	-7.73E-04	-1.49E-03
B_o	3.28E-01	3.09E-01	9.39E-01	6.63E-01	3.55E-01	3.57E-01	6.99E-01	7.54E-01	3.56E-01	4.14E-01	8.08E-01	8.96E-01
variance B_1	1.23E-02	1.26E-02	1.08E-02	1.11E-02	1.29E-02	9.92E-03	9.64E-03	1.06E-02	1.09E-02	9.61E-03	9.61E-03	9.61E-03
variance B_o	1.18E+00	1.23E+00	1.08E+00	1.13E+00	1.24E+00	1.05E+00	9.99E-01	1.15E+00	1.07E+00	1.00E+00	9.98E-01	1.00E+00
s	5.23E-02	6.13E-02	6.85E-02	7.16E-02	6.85E-02	5.03E-02	6.13E-02	3.77E-02	3.35E-02	4.13E-02	5.19E-02	6.60E-02
t -score 98%	2.821	2.821	2.681	2.764	2.998	2.764	2.681	2.821	2.764	2.681	2.681	2.681
Count	11	11	13	12	9	12	13	11	12	13	14	13
Error B_1 98%	1.81E-03	2.18E-03	1.98E-03	2.20E-03	2.66E-03	1.38E-03	1.58E-03	1.12E-03	1.01E-03	1.07E-03	1.34E-03	1.70E-03
max B_1 98%	8.32E-04	1.19E-03	-2.96E-04	2.28E-03	2.11E-03	2.28E-04	3.14E-03	2.52E-03	-2.89E-04	-5.73E-04	5.64E-04	2.06E-04
min B_1 98%	-2.80E-03	-3.16E-03	-4.26E-03	-2.12E-03	-3.20E-03	-2.53E-03	-3.13E-05	2.70E-04	-2.30E-03	-2.70E-03	-2.11E-03	-3.19E-03

Appendix E: Comparison of BIEX and BAC Performance

A paired t-test was used to determine whether BIEX biofilters removed significantly more OC than BAC biofilters. The test was two-tailed with a confidence interval of 95%

Table E-1: T-tests comparing the normalized OC by BIEX and BAC biofilters at steady state; The equivalent bed volumes for each EBCT is: EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

	EBCT, P1, 7.5 minutes			EBCT, P2, 15 minutes			EBCT, P3, 30 minutes		
	20°C	10°C	4°C	20°C	10°C	4°C	20°C	10°C	4°C
BIEX Average	0.42	0.48	0.53	0.29	0.37	0.41	0.23	0.24	0.26
BAC Average	0.89	0.92	0.96	0.81	0.85	0.93	0.69	0.73	0.88
BIEX Standard Deviation	0.14	0.08	0.09	0.08	0.08	0.08	0.06	0.06	0.08
BAC Standard Deviation	0.12	0.11	0.07	0.09	0.09	0.08	0.10	0.09	0.08
BIEX Count	50	49	50	44	58	55	37	38	35
BAC Count	53	53	49	47	58	60	45	44	40
Degrees of Freedom	98.6	96.8	95.0	89.0	112.7	111.8	73.6	72.8	71.5
T-Score	-18.60	-23.76	-25.61	-29.20	-30.07	-34.42	-25.19	-29.08	-33.42
Critical T-Score	1.98	1.98	1.99	1.99	1.98	1.98	1.99	1.99	1.99
Result	Reject Null	Reject Null	Reject Null	Reject Null	Reject Null	Reject Null	Reject Null	Reject Null	Reject Null

Appendix F: Determination of the Effect of Temperature and EBCT on Removal of OC

Two two-way ANOVA tests were conducted comparing the impact of temperature and EBCT on OC removal through both BIEX and BAC biofilters. Both BIEX and BAC biofilters were analysed separately but in the same manner. The critical F-scores were determined using 95% confidence interval.

Table F-1: Impact of temperature and EBCT on OC removal through BIEX biofilters

	Sum of Squares	Degrees of Freedom	Mean Square	F-Score	Critical F-Score	Result
Sum of Squares EBCT	3.46	2	1.73	227.38	3.02	Reject Null
Sum of Squares Temperature	0.70	2	0.35	45.70	3.02	Reject Null
Sum of Squares Within Groups	3.13	411	0.01			
Sum of Squares Both Factors	0.09	4	0.02	2.91	2.40	Reject Null
Total Sum of Squares	7.38	419				

Table F-2: Impact of temperature and EBCT on OC removal through BAC biofilters

	Sum of Squares	Degrees of Freedom	Mean Square	F-Score	Critical F-Score	Result
Sum of Squares EBCT	1.85	2	0.92	105.05	3.02	Reject Null
Sum of Squares Temperature	1.18	2	0.59	66.99	3.02	Reject Null
Sum of Squares Within Groups	3.90	444	0.01			
Sum of Squares Both Factors	0.23	4	0.06	6.55	2.40	Reject Null
Total Sum of Squares	7.15	452				

Twelve one-way ANOVA tests were conducted to determine the impact of temperature and each EBCT and the impact of EBCT at each temperature for both BIEX and BAC biofilters. Both BIEX and BAC biofilters were analysed separately but in the same manner. The critical F-scores were determined using 95% confidence interval.

Table F-3: Impact of temperature on OC removal through BIEX biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day;

EBCT	P1, 7.5 min	P2, 15 min	P3, 30 min
Total Sum of Squares	1.16	0.87	0.24
Sum of Squares Between Groups	0.42	0.21	0.01
Sum of Squares Within Groups	0.75	0.66	0.22
DOF Within	2	2	2
DOF Between	79	85	59
SSWG DFA	0.21	0.10	0.01
SSBG DFA	9.44E-03	7.72E-03	3.81E-03
Calculated F-Score	22.07	13.59	1.69
Critical F-Score	3.04	3.04	3.04
Result	Reject Null	Reject Null	Accept Null

Table F-4: Impact of EBCT on OC removal through BIEX biofilters;

Temperature	20C	10C	4C
Total Sum of Squares	1.13	1.37	1.35
Sum of Squares Between Groups	0.45	0.78	1.00
Sum of Squares Within Groups	0.68	0.59	0.35
DOF Within	2	2	2
DOF Between	146	148	77
SSWG DFA	0.22	0.39	0.50
SSBG DFA	4.68E-03	4.00E-03	4.56E-03
Calculated F-Score	47.65	97.63	109.57
Critical F-Score	3.04	3.04	3.04
Result	Reject Null	Reject Null	Reject Null

Table F-5: Impact of temperature on OC removal through BAC biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day

EBCT	P1, 7.5 min	P2, 15 min	P3, 30 min
Total Sum of Squares	0.82	0.65	0.84
Sum of Squares Between Groups	0.07	0.25	0.48
Sum of Squares Within Groups	0.75	0.40	0.36
DOF Within	2	2	2
DOF Between	83	88	68
SSWG DFA	0.04	0.13	0.24
SSBG DFA	9.05E-03	4.58E-03	5.28E-03
Calculated F-Score	3.90	27.36	45.94
Critical F-Score	3.10	3.10	3.10
Result	Reject Null	Reject Null	Reject Null

Table F-6: Impact of EBCT on OC removal through BAC biofilters;

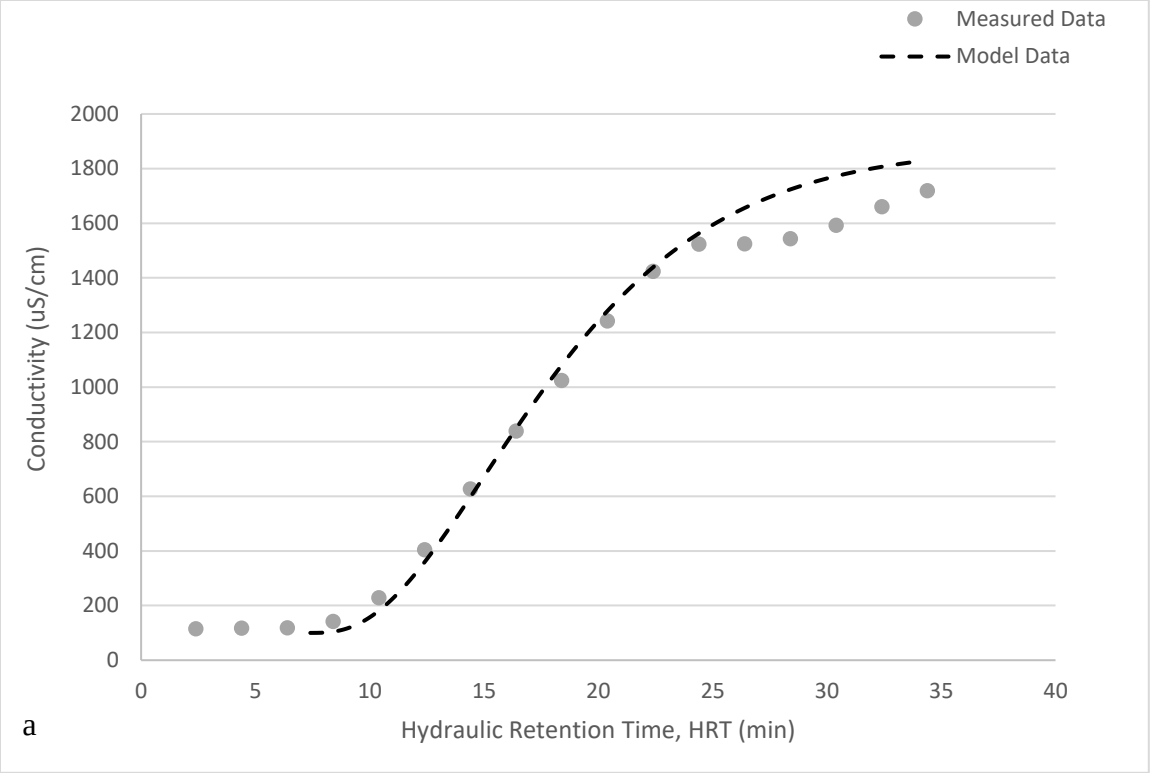
Temperature	20C	10C	4C
Total Sum of Squares	1.32	0.35	1.13
Sum of Squares Between Groups	0.55	0.07	0.67
Sum of Squares Within Groups	0.78	0.28	0.46
DOF Within	2	2	2
DOF Between	156	158	80
SSWG DFA	0.27	0.04	0.34
SSBG DFA	4.97E-03	1.76E-03	5.76E-03
Calculated F-Score	55.17	20.51	58.31
Critical F-Score	3.04	3.04	3.04
Result	Reject Null	Reject Null	Reject Null

Appendix G: Hydraulic Step Test Results

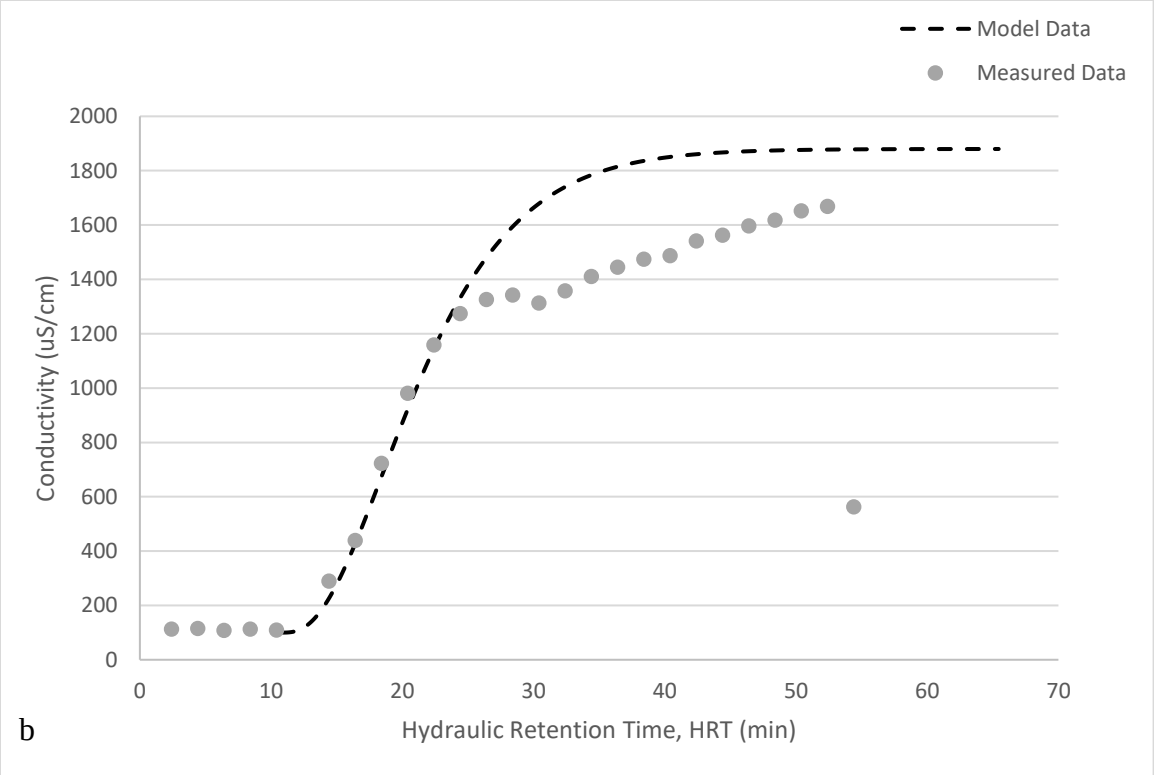
Flow through the biofilters was modelled as three CSTRs above the media and a PFR through the media using the data from the hydraulic step tests. All other BIEX biofilters are assumed to operate like BIEX 1 and 2 since they were designed, built and operated in a similar manner. The same assumption was made for BAC biofilters.

The data from the hydraulic step tests was collected and modelled. The water head on top of the resin bed was modelled as 3 CSTRs in series while the resin bed itself was modelled as a PFR. The CSTRs were sized based on the amount of head measured in the biofilter during each step test. The flow rate through the biofilter was assumed to be the design flow. These models were used to determine the HRT at each port for the three biofilters tested. The HRT of the PFR was determined by finding the minimum difference of squares between the model and measured values

It should be noted that the results from BIEX 2 Port 3 test were disregarded because a change in head in the biofilter for this experiment altered the flow rate impacting the measured HRT.


Measured Data
Model Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
Hydraulic Retention Time, HRT (min)

a


Model Data
Measured Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
Hydraulic Retention Time, HRT (min)

b

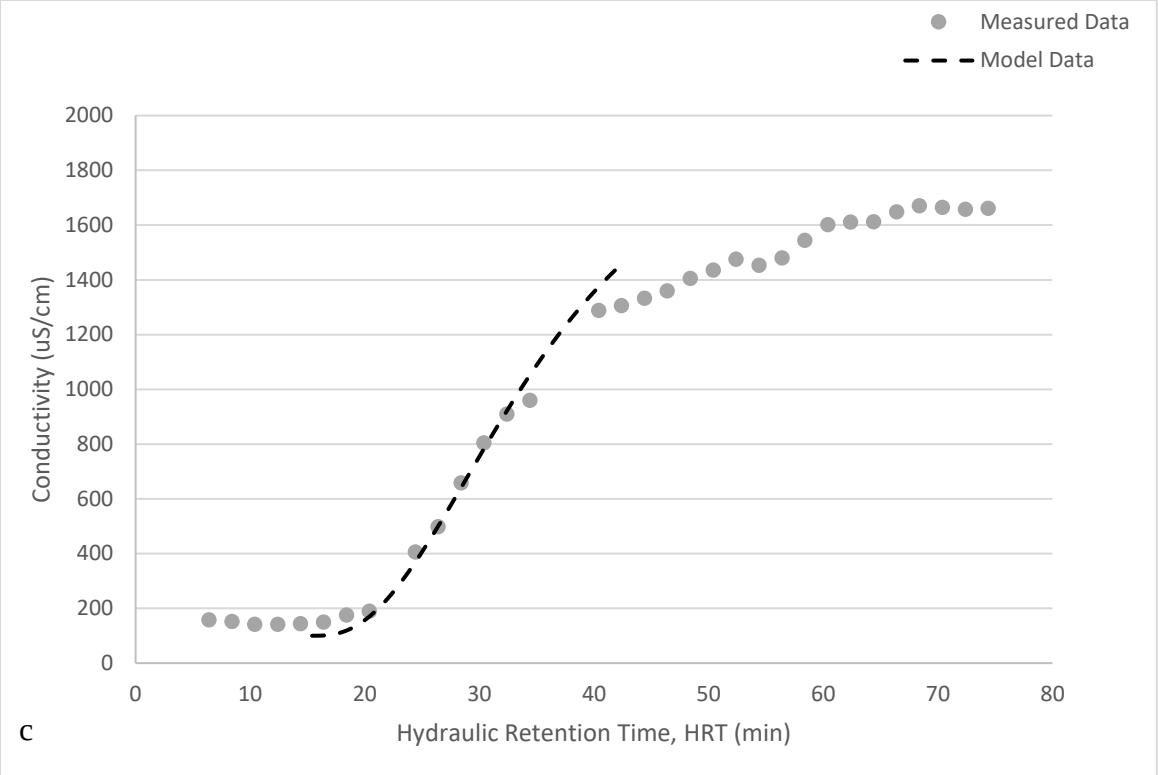
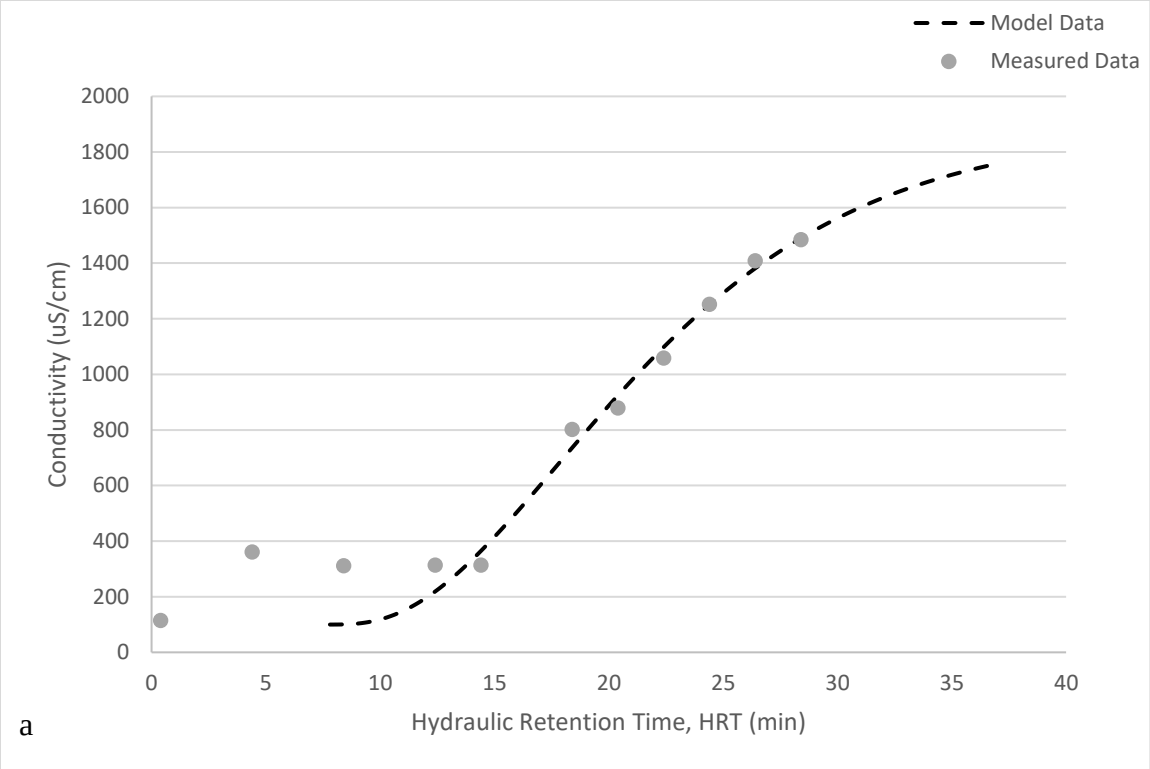
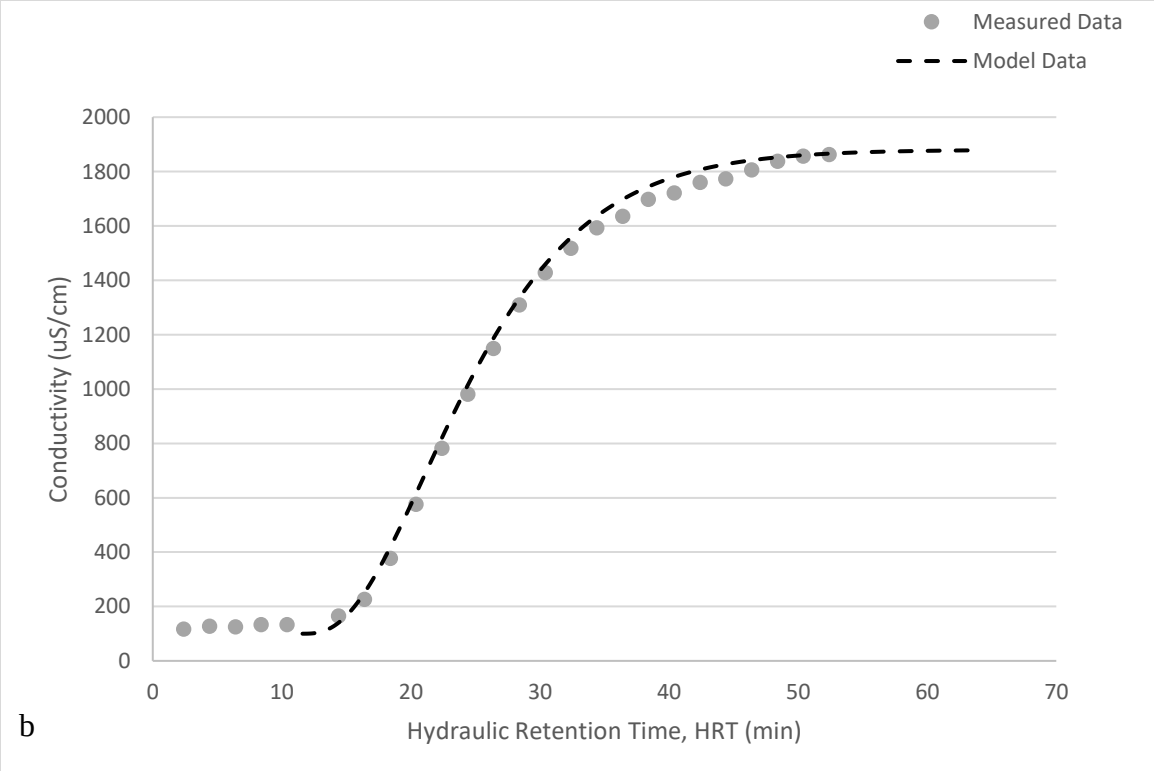


Figure G-1: Model of Flow through BIEX 1;
a) EBCT 7.5-minutes (192BV/day) b) EBCT 15-minutes (96BV/day) c) EBCT 30-minutes (48BV/day); The dashed line represents the theoretical model of flow through the biofilter and the dots represent the data measured in the laboratory


Model Data
Measured Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
Hydraulic Retention Time, HRT (min)

a


Measured Data
Model Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
Hydraulic Retention Time, HRT (min)

b

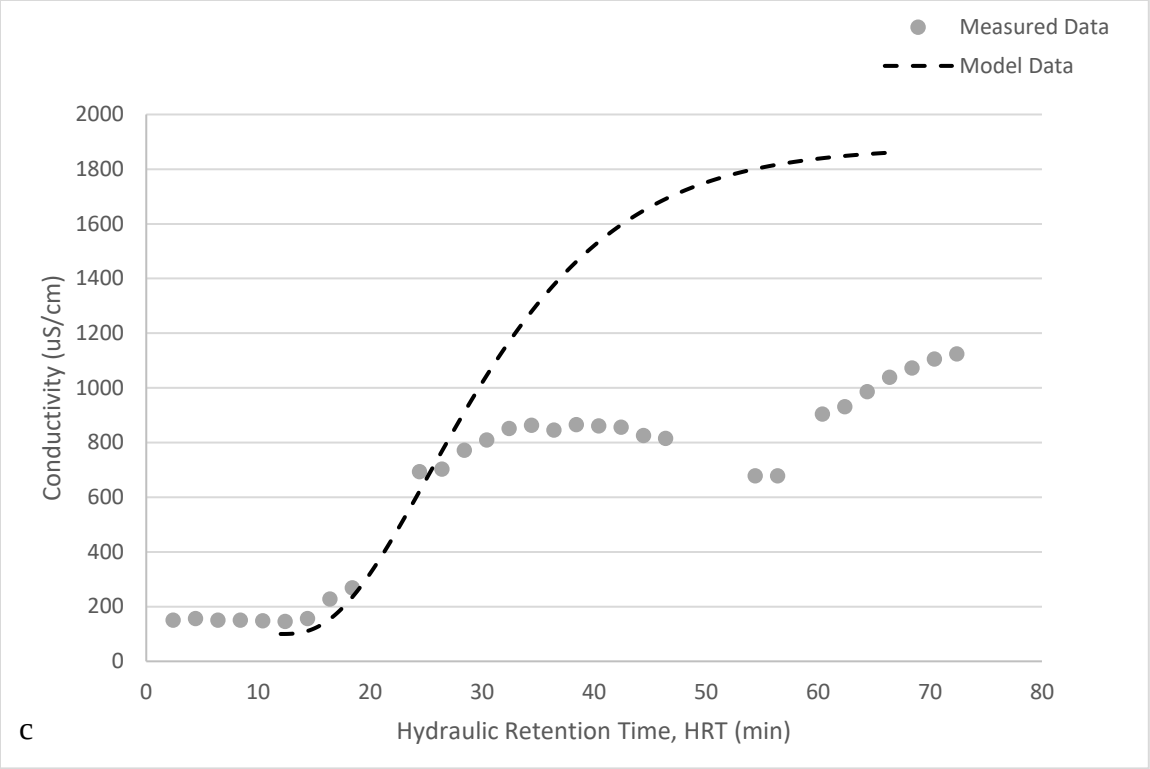
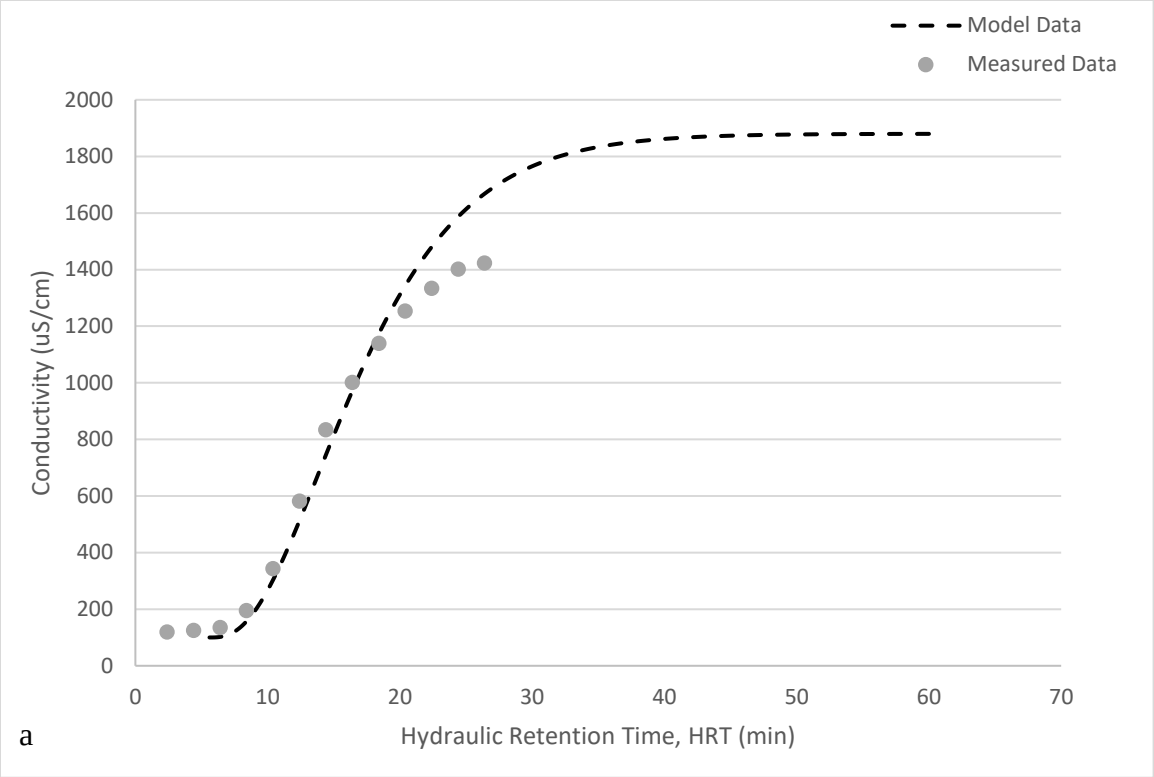
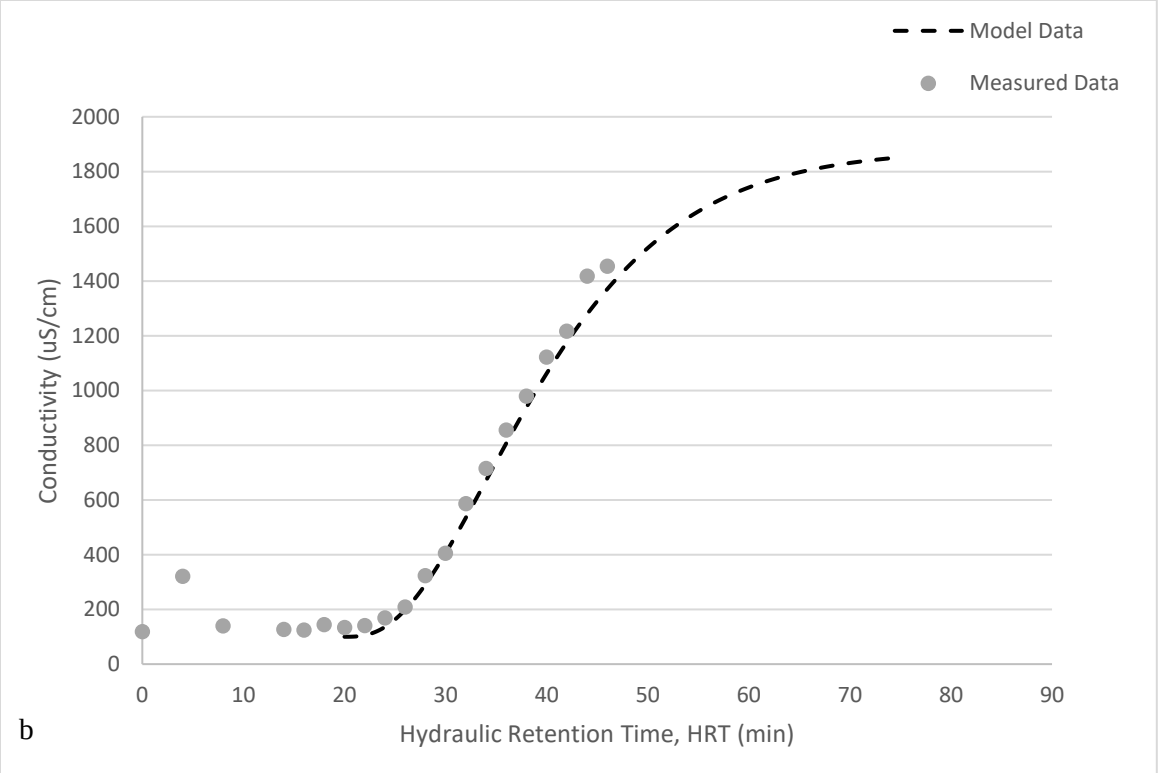


Figure G-2: Model of Flow through BIEX 2;
a) EBCT 7.5-minutes (192BV/day) b) EBCT 15-minutes (96BV/day) c) EBCT 30-minutes (48BV/day); The dashed line represents the theoretical model of flow through the biofilter and the dots represent the data measured in the laboratory


Model Data
Measured Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
Hydraulic Retention Time, HRT (min)

a


Model Data
Measured Data
Conductivity (uS/cm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
Hydraulic Retention Time, HRT (min)

b

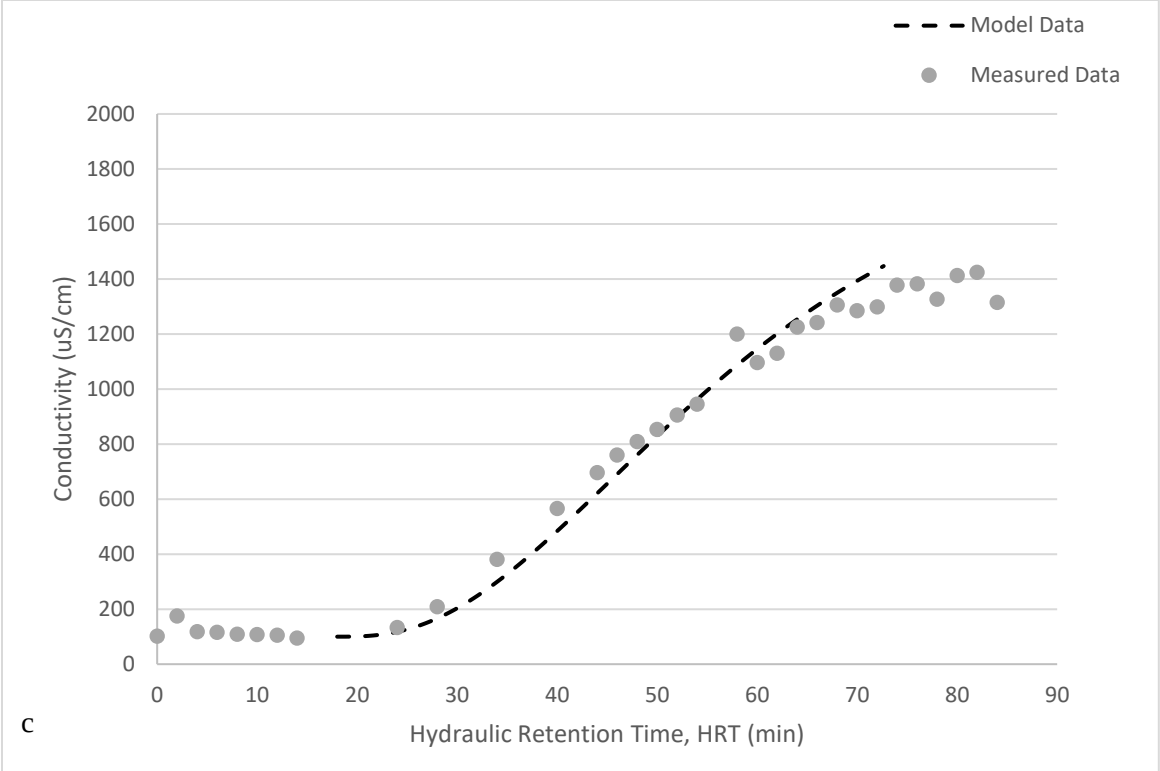


Figure G-3: Model of flow through BAC 1;
a) EBCT 7.5-minutes (192BV/day) b) EBCT 15-minutes (96BV/day) c) EBCT 30-minutes (48BV/day); The dashed line represents the theoretical model of flow through the biofilter and the dots represent the data measured in the laboratory

Table G-1: Calculated HRT for all tested biofilters;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day

	BIEX 1	BIEX 2	BAC 1
Port 1, EBCT 7.5min	3.7	4.1	1.9
Port 2, EBCT 15min	6.9	8.3	7.5
Port 3, EBCT 30min	11.7	8.3	14.3

The highlighted value in Table G-1 was eliminated. As can be seen in Figure G-2 the model for BIEX 2, Port 3 does not fit the data well. It is thought that head loss through the biofilter at this time was particularly high and affected the flow of water through the biofilter.

Appendix H: Determination of the Rate Constant

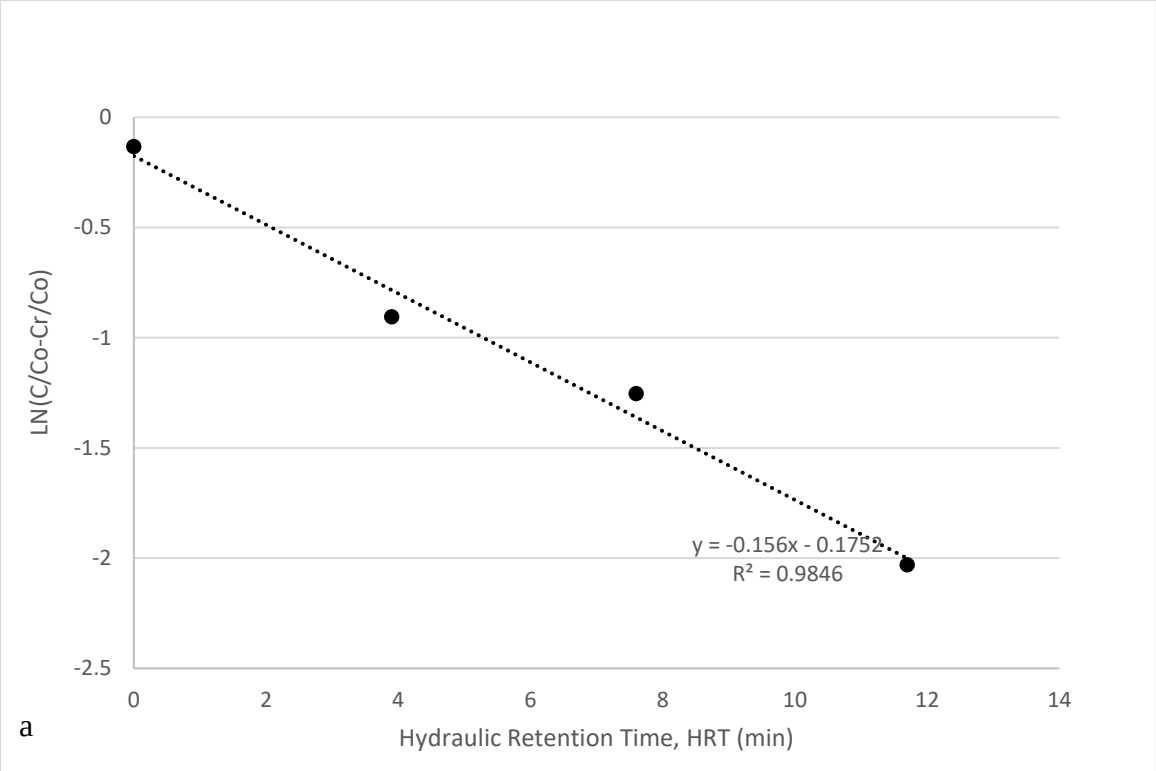
Equation 5 was linearized to Equation H-1 as discussed in Section 5.1.1. Equation H-1 was used as a linear model to determine the rate constant for OC removal at each temperature through both BIEX and BAC biofilters.

Equation H-1: Linearized exponential decrease in organic carbon through a biofilter

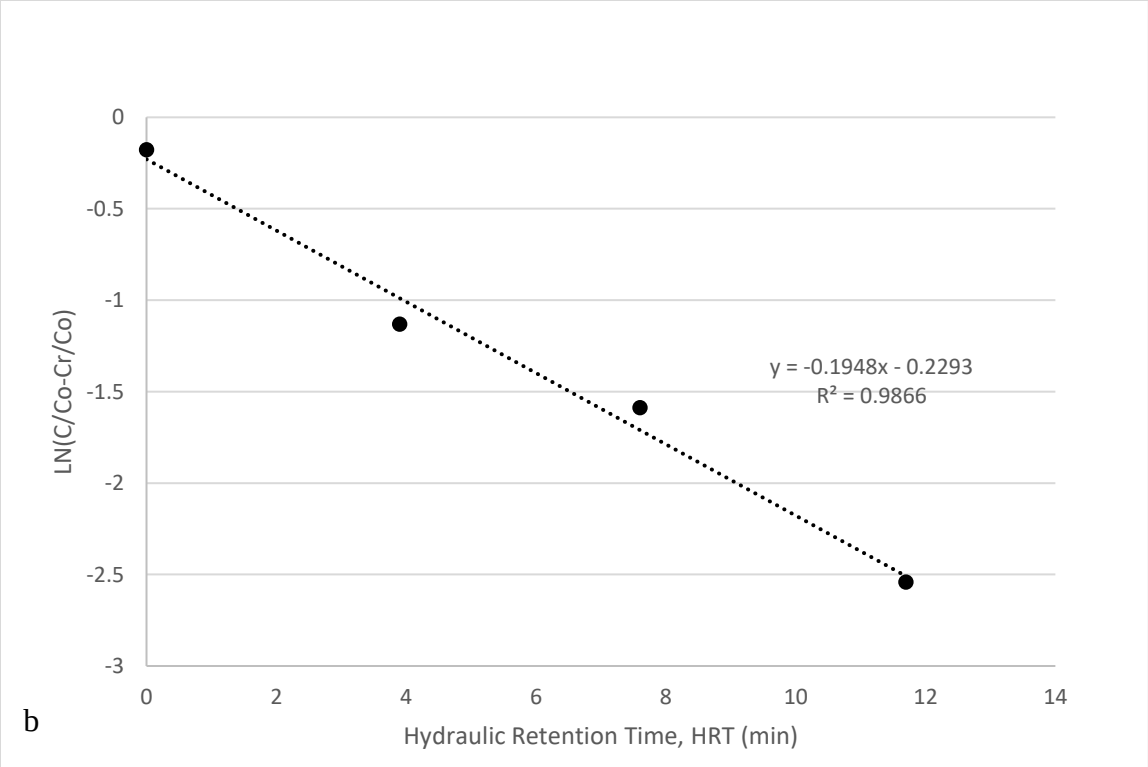
$$\ln\left(\frac{C - C_R}{C_o}\right) = -kt + \ln\left(\frac{C_o - C_R}{C_o}\right)$$

where: C is the OC concentration in the effluent at a given HRT (corresponding to a given EBCT), C_R is the estimated normalized concentration of non-biodegradable NOM in the water, C_O is the initial concentration of NOM in the water, t is the HRT and k is the rate constant associated with removal of OC

The y-value, $\ln\left(\frac{C-C_R}{C_o}\right)$, was determined for all experimental conditions through an iterative process. C/C_O was determined in Section 5.1.1 however, C_R/C_O was unknown and could not be easily calculated. Initially an estimate of C_R/C_O based on the C/C_O value at an EBCT of 30-minutes was used. The estimated y-value was then graphed with the HRT that corresponded to the EBCT for which the y-value was determined. Data was graphed according to temperature for both BIEX and BAC biofilters as illustrated in Figure H-1 (BIEX biofilters) and Figure H-2 (BAC biofilters). For each a graph a linear regression model was fit to the existing data. An estimate of C_R/C_O determined through performing iterative linear regressions to maximize the R^2 value. The rate constant for OC removal (at a specific temperature) was determined from the slope of the graph corresponding to the C_R/C_O value that gave the largest R^2 value.


0
-0.5
-1
-1.5
-2
-2.5
LN(C/Co-Cr/Co)
y = -0.156x - 0.1752
R² = 0.9846
0
2
4
6
8
10
12
14
Hydraulic Retention Time, HRT (min)

a


0
-0.5
-1
-1.5
-2
-2.5
-3
LN(C/Co-Cr/Co)
y = -0.1948x - 0.2293
R² = 0.9866
0
2
4
6
8
10
12
14
Hydraulic Retention Time, HRT (min)

b

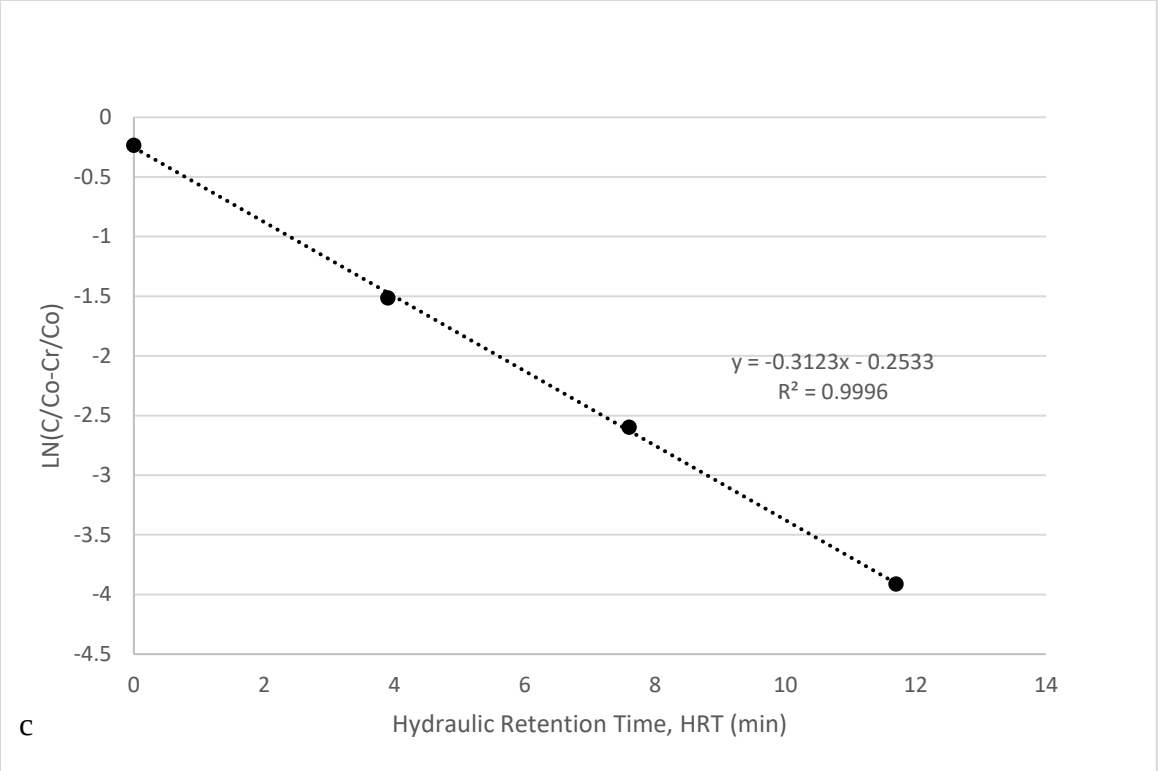
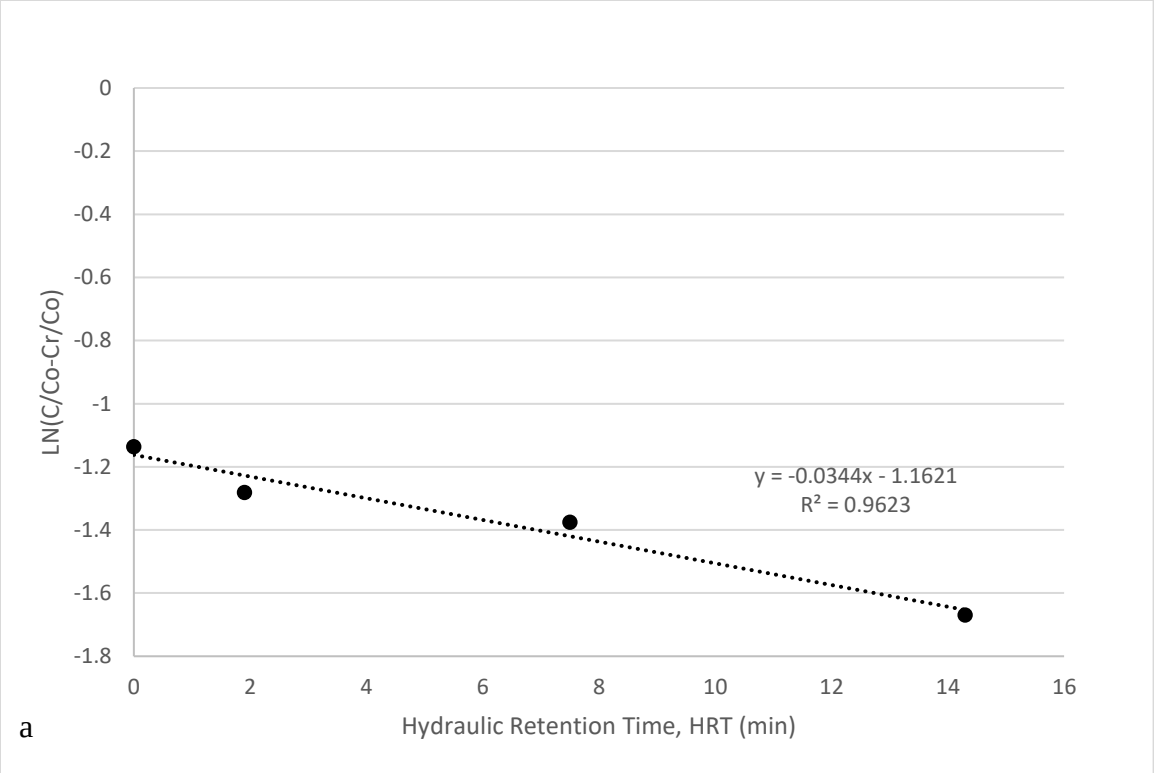
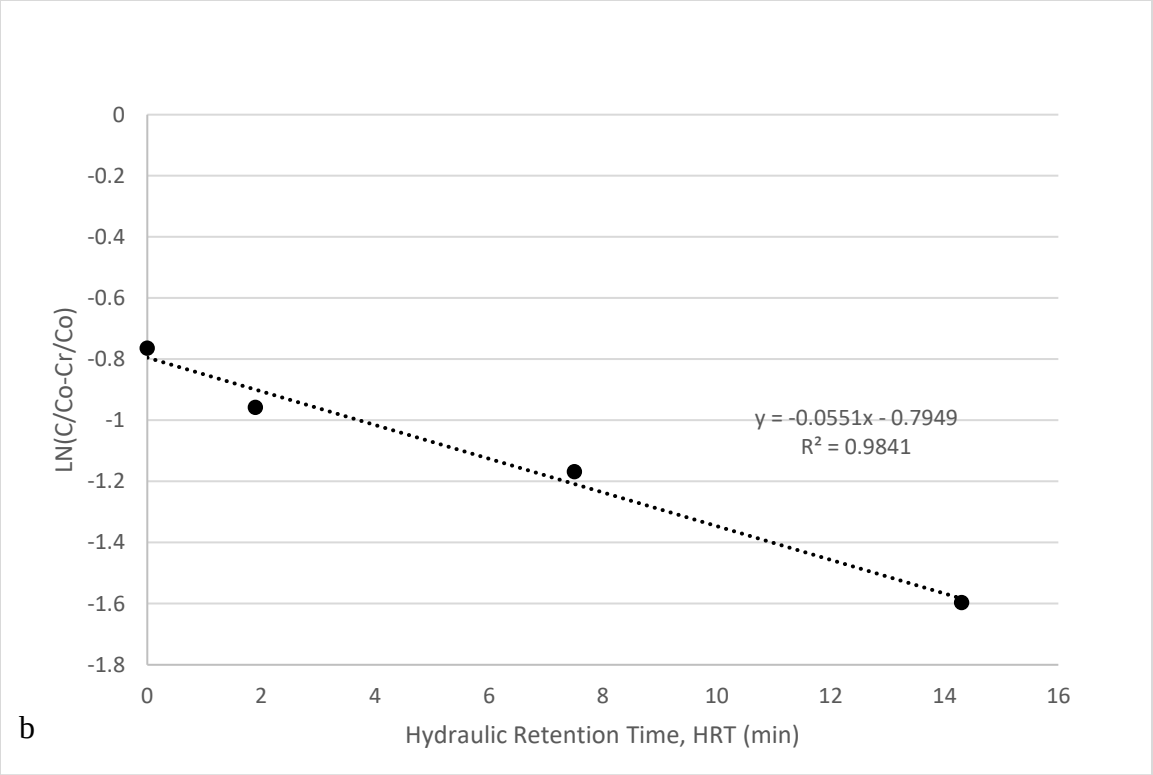


Figure H-1: Linear regression to determining rate constant (k) for BIEX biofitlers at different temperatures;
a) 4°C; b) 10°C; c) 20°C;
Data points on each graph represent the estimated normalized non-biodegradable OC fraction subtracted from the natural log of the average OC removal over steady state at a given temperature;
A linear regression fitted to the data along with the corresponding equation and R^2 value is also visible on each graph


0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
LN(C/Co-Cr/Co)
y = -0.0344x - 1.1621
R² = 0.9623
0
2
4
6
8
10
12
14
16
Hydraulic Retention Time, HRT (min)

a


0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
LN(C/Co-Cr/Co)
y = -0.0551x - 0.7949
R² = 0.9841
0
2
4
6
8
10
12
14
16
Hydraulic Retention Time, HRT (min)

b

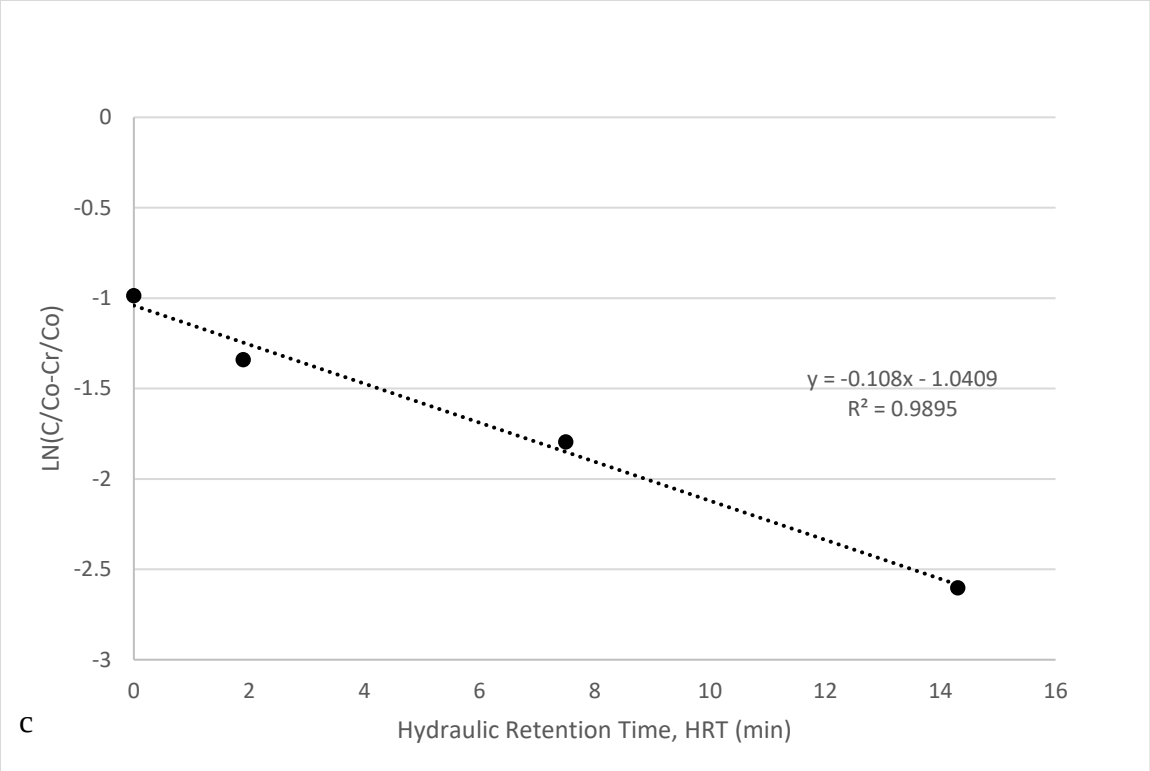


Figure H-2: Linear regression to determining reaction constant (k) for BAC biofilters at different temperatures;
a) 4°C; b) 10°C; c) 20°C;
Data points on each graph represent the estimated normalized non-biodegradable OC fraction subtracted from the natural log of the average OC removal over steady state at a given temperature;
A linear regression fitted to the data along with the corresponding equation and R^2 value is also visible on each graph

The error on the rate constant at each temperature for both BIEX and BAC biofilters was determined at one standard error. The details of how the error on the rate constant was determined are presented in Table H-1.

Table H-1: Linear regression on data from BIEX and BAC biofilters to determine the reaction constant, k and its error

	20°C	10°C	4°C
B_1	-0.312	-0.195	-0.156
B_o	-0.253	-0.229	-0.175
var B_1	0.115	0.115	0.115
var B_o	0.835	0.835	0.835
s	0.039	0.139	0.120
t	1	1	1
error B_1	0.005	0.016	0.014
k	0.312	0.195	0.156
k_{max}	0.317	0.211	0.170
k_{min}	0.308	0.179	0.142

	20°C	10°C	4°C
B_1	-0.108	-0.055	-0.034
B_o	-1.041	-0.795	-1.162
var B_1	0.090	0.090	0.090
var B_o	0.730	0.730	0.730
s	0.087	0.055	0.054
t	1	1	1
error B_1	0.008	0.005	0.005
k	0.108	0.055	0.034
k_{max}	0.116	0.060	0.039
k_{min}	0.100	0.050	0.030

Appendix I: Determination of the Temperature Activity Coefficient

Equation 6 was transformed to Equation I-1 as discussed in section 5.1.1. Equation I-1 was used as a linear model to determine the temperature activity coefficient for both BIEX and BAC biofilters.

Equation I-1: Linearized Temperature Activity Equation

$$\ln(k_t) = \ln(\theta)(T - 20) + \ln(k_{20})$$

where: k_T is the rate constant associated with the removal of OC at a given temperature, k_{20} is the rate constant associated with the removal of OC at 20°C, T is temperature and θ is the temperature activity coefficient associated with a given type of biofilter.

The rate constants determined, are displayed in Table 7 at each temperature and were graphed according to Equation I-1. A linear regression was fitted to the data and the slope was determined allowing for the temperature activity coefficient to be identified. Figure I-1 and Figure I-2 illustrate the experimental data transformed according to Equation I-1.

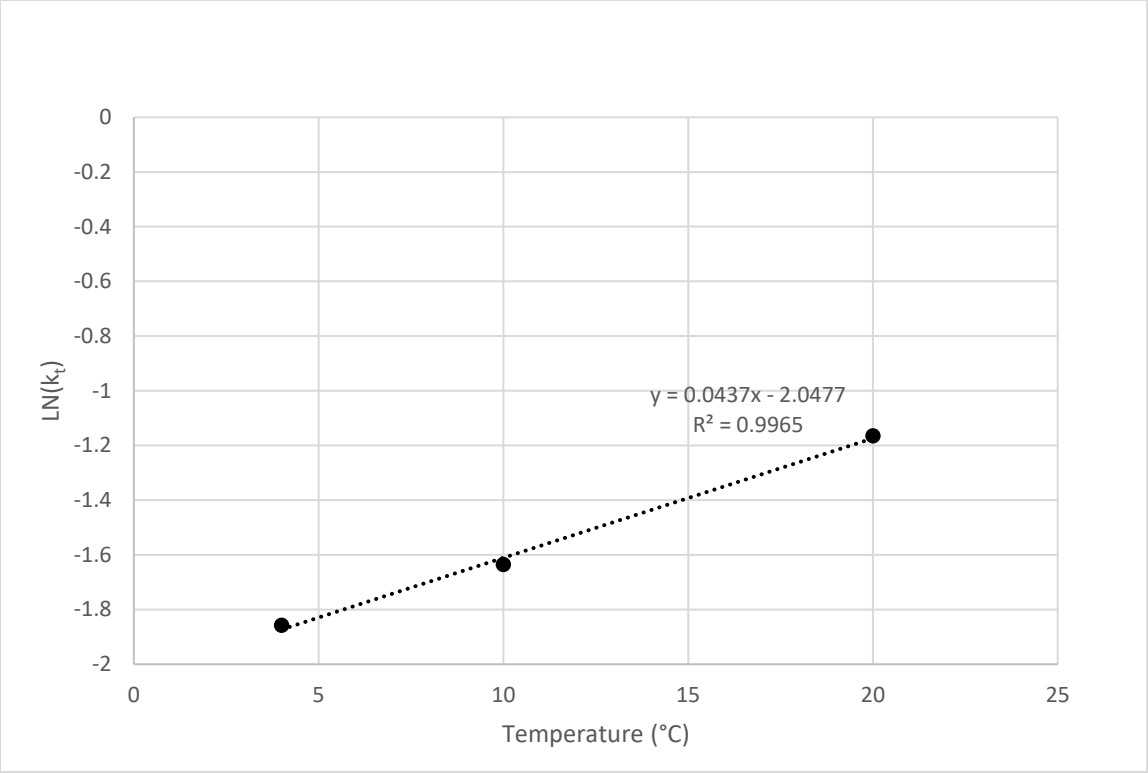


Figure I-1: Linear regression on BIEX reaction constants to determine temperature coefficient; Data points represent a transformation of the rate constants listed Table 7 according to Equation I-1; The line is a linear regression fitted to the data according to Equation I-1

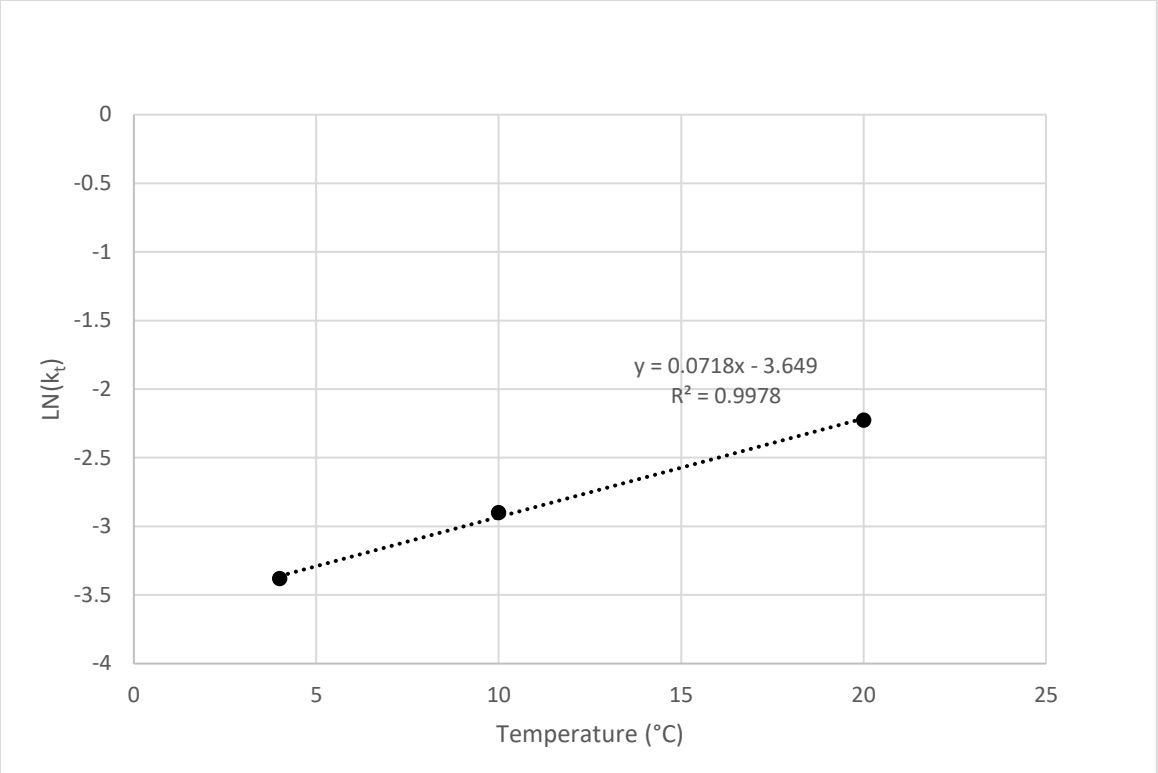


Figure I-2: Linear regression on BAC reaction constants to determine temperature coefficients; Data points represent a transformation of the rate constants listed Table 7 according to Equation I-1; The line is a linear regression fitted to the data according to Equation I-1

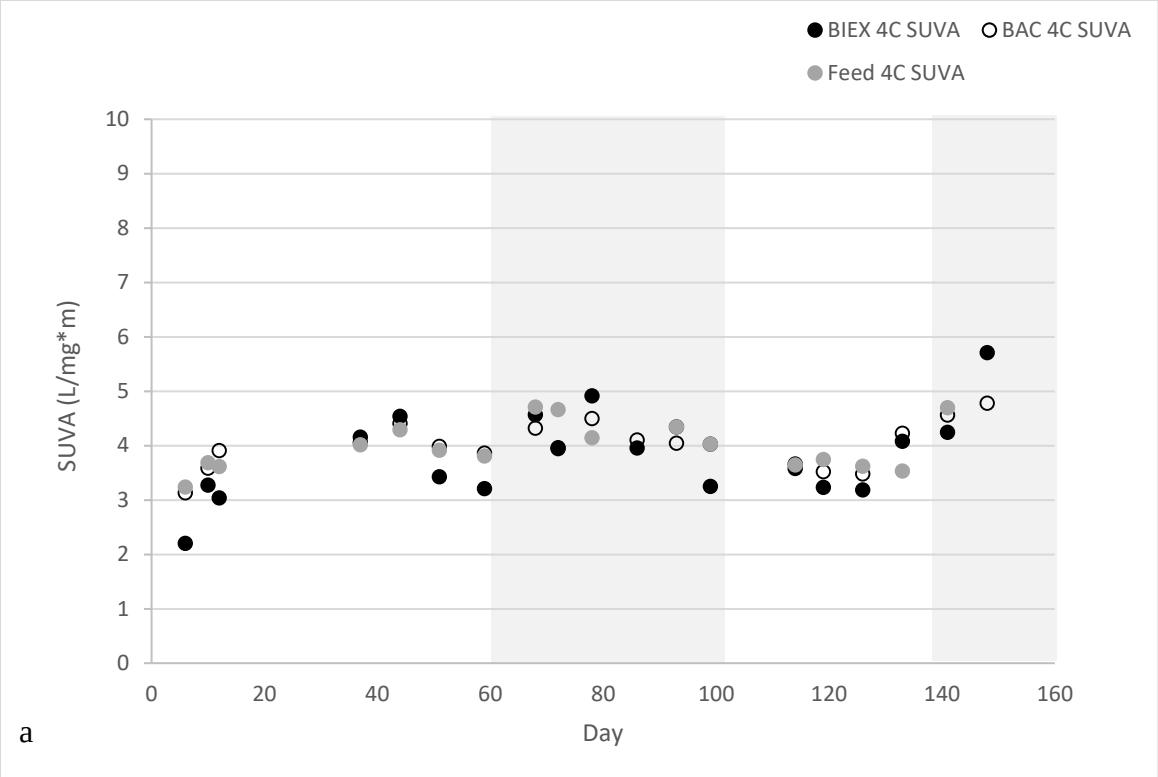
The error on the temperature activity coefficient was determined at one standard error. Due to the transformation from Equation 6 to Equation I-1 the error on the temperature activity coefficient is asymmetric. The details of how the error on the temperature activity coefficient were determined are listed in Table I-1.

Table I-1: Linear regression and error calculation to determine temperature coefficient for BIEX and BAC biofilters

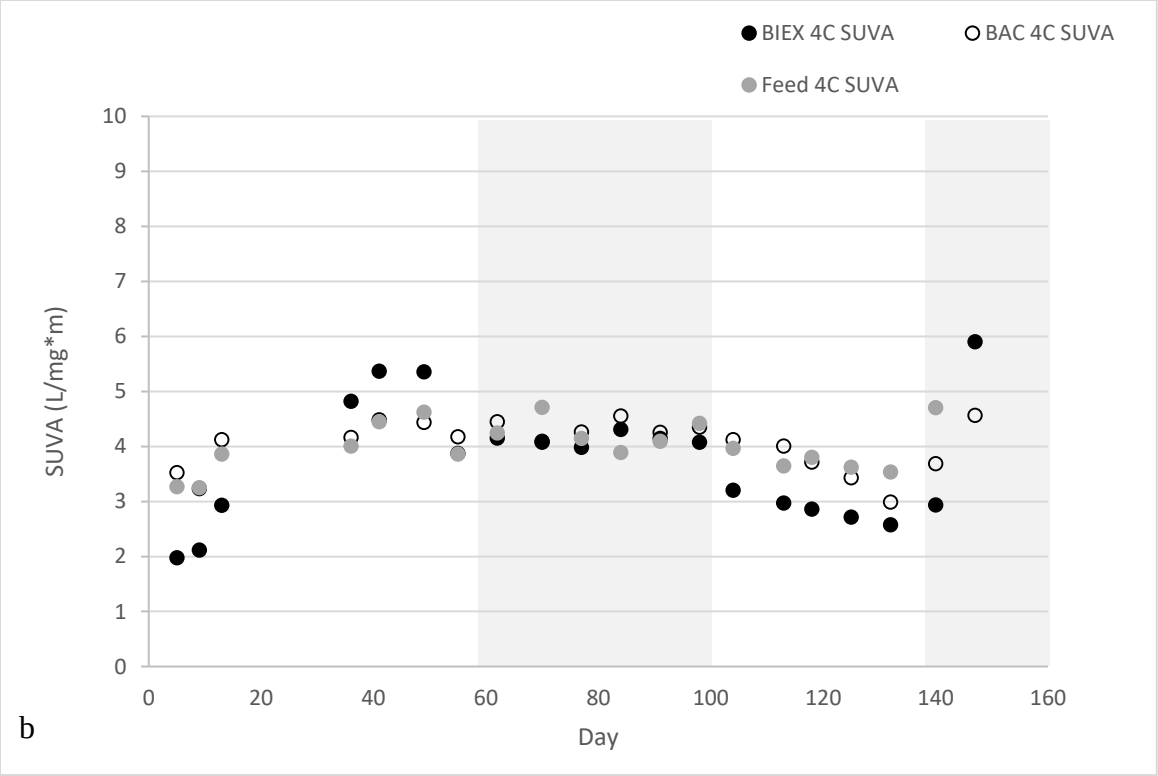
	BIEX	BAC
B_1	0.04	0.07
B_o	-2.05	-2.89
var B_1	0.09	0.09
var B_o	1.15	1.15
s	0.03	0.10
standard error	1	1
error B_1	0.00	0.01
Θ	1.04	1.07
Θ_{max}	1.05	1.08
Θ_{min}	1.04	1.06

Appendix J: Graphical Raw Data: SUVA Values

Raw UV254 data was collected weekly from each port for both BIEX and BAC biofilters throughout the experiment. The raw data was plotted in three figures one for each temperature. Each figure contains three graphs one for each EBCT.


BIEX 4C SUVA
BAC 4C SUVA
Feed 4C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

a


BIEX 4C SUVA
BAC 4C SUVA
Feed 4C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

b

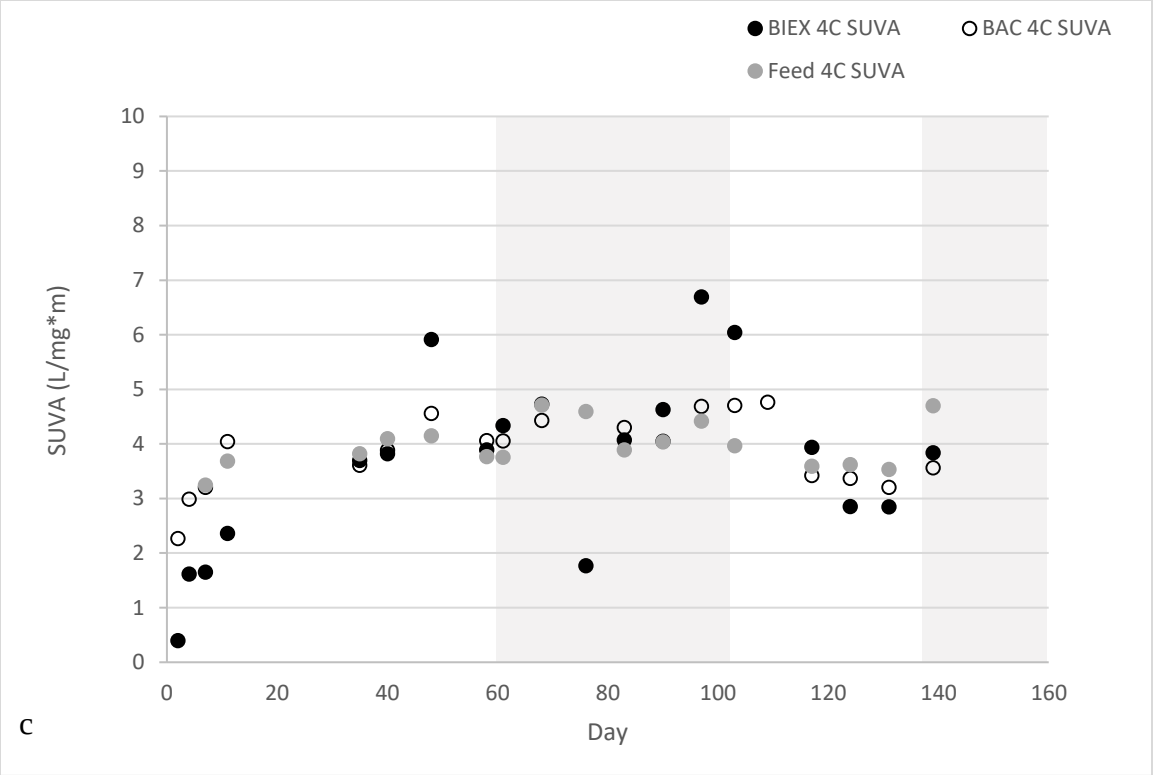
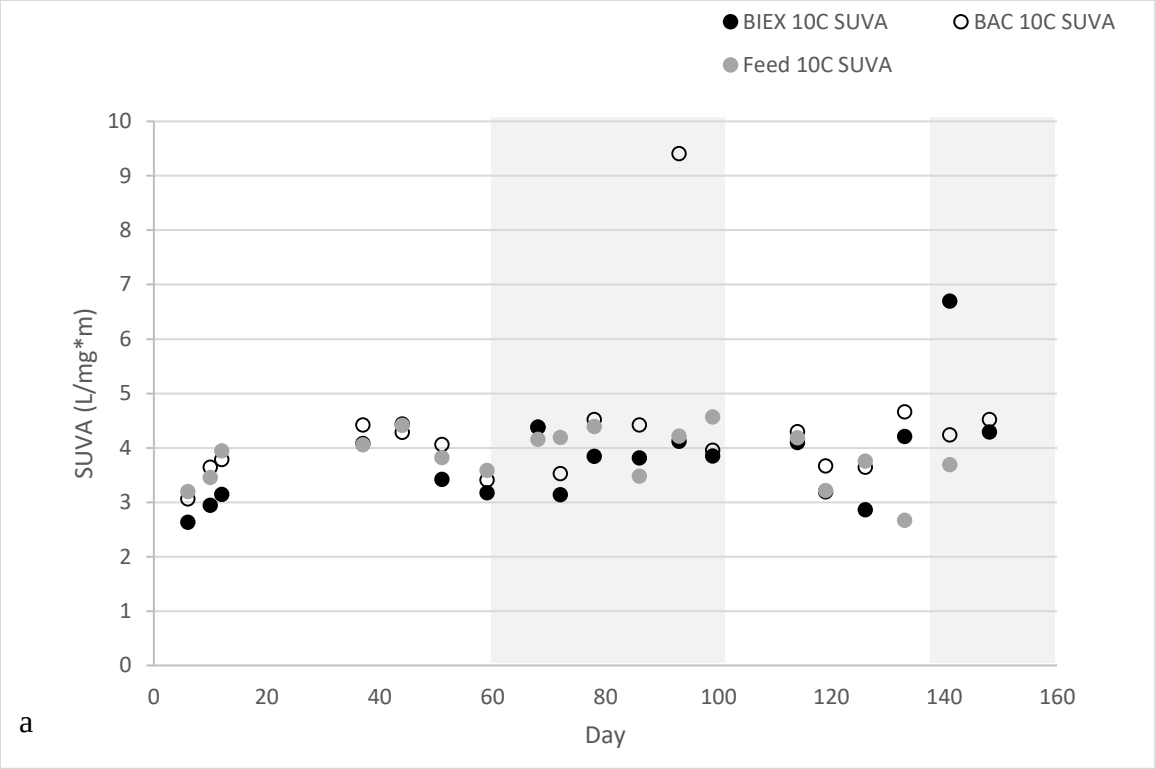
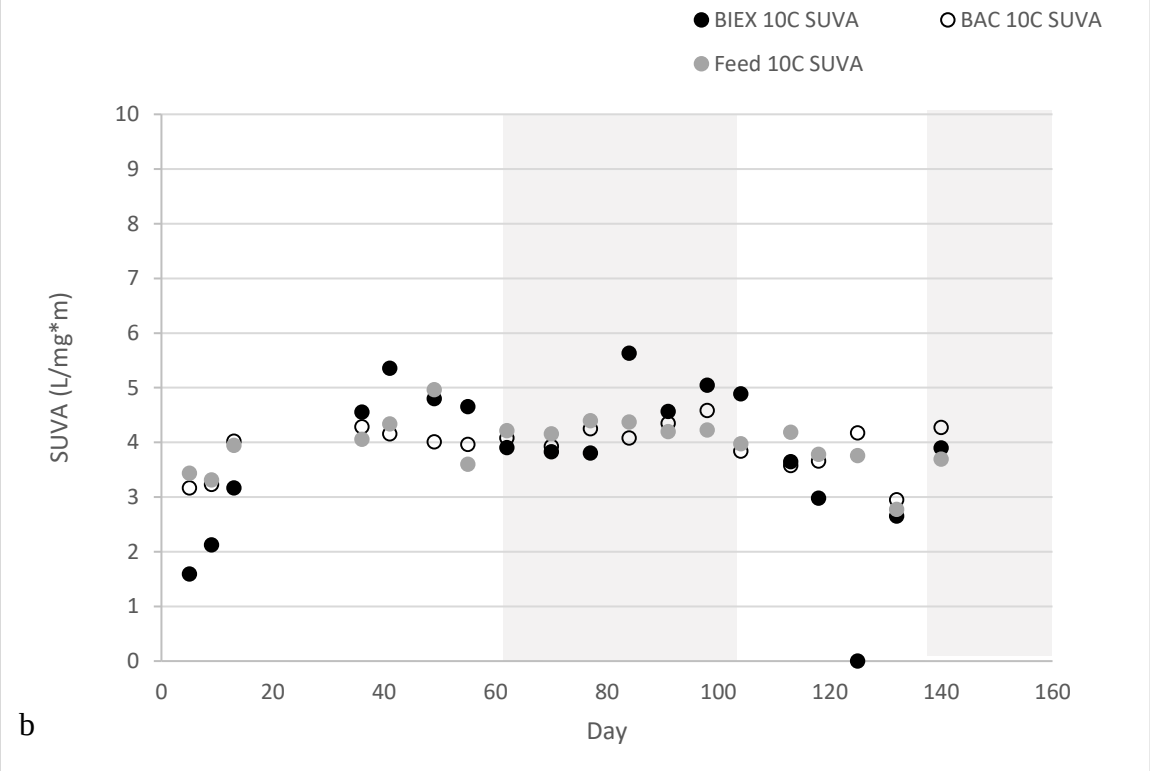


Figure J-1: Raw Data at 4°C, absolute SUVA values for both BIEX and BAC biofilters;
a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond


BIEX 10C SUVA
BAC 10C SUVA
Feed 10C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

a


BIEX 10C SUVA
BAC 10C SUVA
Feed 10C SUVA
SUVA (L/mg*m)
Day
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
80
100
120
140
160

b

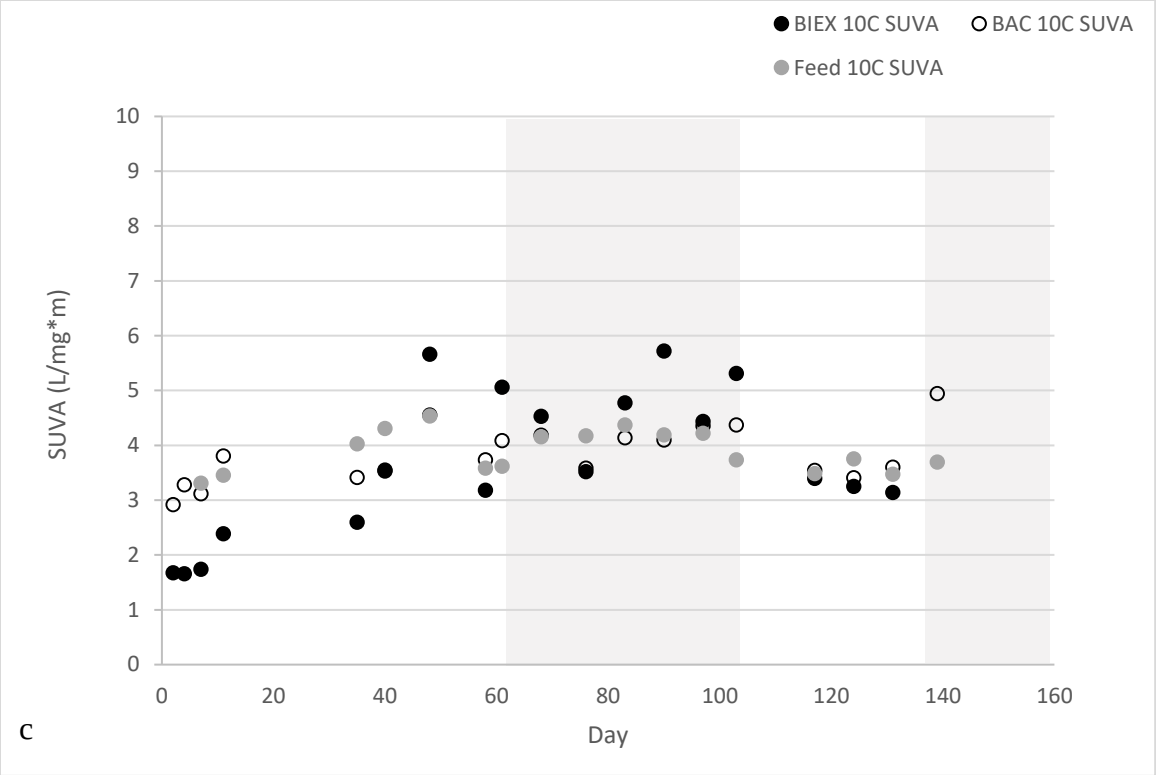


Figure J-2: Raw Data at 10°C, absolute SUVA values for both BIEX and BAC biofilters a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond

Appendix K: Determination of Steady State for SUVA values

The following tables display the major parameters calculated during the linear regression of the normalized SUVA filtrate data for both BIEX and BAC biofilters. The error on the slope of the linear regression was used to determine whether the slope was statistically different from 0. If it was not, steady state was considered to be achieved. A 98% confidence interval was used.

Table K-1: Linear regression of normalized SUVA data to determine whether a biofilter is at steady state for an EBCT of 7.5-minutes (192BV/day)

	BIEX 1	BIEX 2	BIEX 3	BIEX 4	BIEX 5	BIEX 6	BAC 1	BAC 2	BAC 3	BAC 4	BAC 5	BAC 6
Temperature	20°C	20°C	4°C	4°C	10°C	10°C	20°C	20°C	4°C	4°C	10°C	10°C
B_1	4.87E-03	-1.57E-03	1.08E-04	8.63E-04	5.63E-04	-1.15E-04	1.78E-03	2.09E-03	2.47E-04	2.40E-04	6.43E-04	4.21E-04
B_o	6.87E-01	9.41E-01	9.20E-01	8.54E-01	8.91E-01	9.09E-01	9.28E-01	9.09E-01	9.87E-01	9.94E-01	9.74E-01	9.98E-01
variance B_1	3.04E-06	1.39E-06	4.14E-07	7.38E-07	6.30E-07	8.24E-07	1.63E-06	1.21E-06	2.91E-07	3.95E-07	3.56E-07	6.82E-07
vairance B_o	2.06E-02	9.15E-03	2.87E-03	6.12E-03	4.44E-03	5.07E-03	1.17E-02	8.67E-03	2.12E-03	2.90E-03	2.51E-03	4.99E-03
s	1.74E-03	1.18E-03	6.44E-04	8.59E-04	7.94E-04	9.08E-04	1.28E-03	1.10E-03	5.39E-04	6.28E-04	5.97E-04	8.26E-04
t-score 98%	2.624	2.624	2.681	2.650	2.624	2.681	2.602	2.602	2.624	2.718	2.624	2.624
Count	16	16	14	15	16	14	17	17	16	13	16	16
Error B_1 98%	4.58E-03	3.10E-03	1.73E-03	2.28E-03	2.08E-03	2.43E-03	3.32E-03	2.86E-03	1.42E-03	1.71E-03	1.57E-03	2.17E-03
max B_1 98%	9.45E-03	1.53E-03	1.83E-03	3.14E-03	2.65E-03	2.32E-03	5.11E-03	4.95E-03	1.66E-03	1.95E-03	2.21E-03	2.59E-03
min B_1 98%	2.92E-04	-4.67E-03	-1.62E-03	-1.41E-03	-1.52E-03	-2.55E-03	-1.54E-03	-7.73E-04	-1.17E-03	-1.47E-03	-9.24E-04	-1.75E-03

Table K-2: Linear regression of normalized SUVA data to determine whether a biofilter is at steady state for an EBCT of 15-minutes (96BV/day)

	BIEX 1	BIEX 2	BIEX 3	BIEX 4	BIEX 5	BIEX 6	BAC 1	BAC 2	BAC 3	BAC 4	BAC 5	BAC 6
Temperature	20°C	20°C	4°C	4°C	10°C	10°C	20°C	20°C	4°C	4°C	10°C	10°C
B_1	-5.52E-04	1.39E-04	-3.99E-04	-2.98E-03	2.34E-04	2.68E-03	4.35E-04	3.74E-04	-1.48E-03	-1.17E-04	5.25E-04	4.69E-05
B_o	1.10E+00	9.91E-01	8.71E-01	1.19E+00	9.68E-01	7.84E-01	9.79E-01	1.00E+00	1.10E+00	1.05E+00	9.62E-01	9.81E-01
variance B_1	4.56E-06	3.69E-06	1.06E-06	1.74E-06	2.20E-06	2.03E-06	3.29E-07	3.17E-07	3.01E-07	4.51E-07	1.79E-07	3.03E-07
vairance B_o	2.79E-02	2.25E-02	7.49E-03	1.41E-02	1.45E-02	1.40E-02	2.37E-03	1.99E-03	2.17E-03	3.14E-03	1.33E-03	2.12E-03
s	2.13E-03	1.92E-03	1.03E-03	1.32E-03	1.48E-03	1.43E-03	5.73E-04	5.63E-04	5.49E-04	6.72E-04	4.23E-04	5.51E-04
t-score 98%	2.650	2.624	2.602	2.302	2.650	2.650	2.583	2.624	2.583	2.602	2.602	2.650
Count	15	16	17	17	15	15	18	16	18	17	17	15
Error B_1 98%	5.66E-03	5.04E-03	2.68E-03	3.03E-03	3.93E-03	3.78E-03	1.48E-03	1.48E-03	1.42E-03	1.75E-03	1.10E-03	1.46E-03
max B_1 98%	5.11E-03	5.18E-03	2.28E-03	4.97E-05	4.17E-03	6.46E-03	1.92E-03	1.85E-03	-6.59E-05	1.63E-03	1.63E-03	1.51E-03
min B_1 98%	-5.66E-03	-5.04E-03	-2.68E-03	-3.03E-03	-3.93E-03	-3.78E-03	-1.48E-03	-1.48E-03	-1.42E-03	-1.75E-03	-1.10E-03	-1.46E-03

Table K-3: Linear regression of normalized SUVA data to determine whether a biofilter is at steady state for an EBCT of 30-minutes (48BV/day)

	BIEX 1	BIEX 2	BIEX 3	BIEX 4	BIEX 5	BIEX 6	BAC 1	BAC 2	BAC 3	BAC 4	BAC 5	BAC 6
Temperature	20°C	20°C	4°C	4°C	10°C	10°C	20°C	20°C	4°C	4°C	10°C	10°C
B_1	1.20E-03	2.78E-03	1.66E-03	-4.57E-04	3.36E-03	4.28E-03	-8.94E-05	-3.02E-05	-8.46E-04	-1.10E-03	9.46E-04	-2.75E-05
B_o	9.05E-01	8.62E-01	8.00E-01	1.02E+00	7.97E-01	6.69E-01	9.91E-01	1.03E+00	1.07E+00	1.09E+00	9.39E-01	9.70E-01
variance B_1	3.76E-06	8.71E-06	4.62E-06	5.08E-06	9.26E-06	2.99E-06	5.79E-07	4.94E-07	7.17E-07	2.80E-07	5.35E-07	3.73E-07
vairance B_o	2.19E-02	4.44E-02	2.67E-02	4.21E-02	4.84E-02	1.88E-02	4.02E-03	3.59E-03	5.27E-03	2.10E-03	3.67E-03	2.56E-03
s	1.94E-03	2.95E-03	2.15E-03	2.25E-03	3.04E-03	1.73E-03	7.61E-04	7.03E-04	8.47E-04	5.29E-04	7.32E-04	6.10E-04
t-score 98%	2.681	2.718	2.718	2.681	2.681	2.650	2.650	2.650	2.624	2.650	2.624	2.650
Count	14	13	13	14	14	15	15	15	16	15	16	15
Error B_1 98%	5.20E-03	8.02E-03	5.84E-03	6.05E-03	8.16E-03	4.58E-03	2.02E-03	1.86E-03	2.22E-03	1.40E-03	1.92E-03	1.62E-03
max B_1 98%	6.40E-03	1.08E-02	7.50E-03	5.59E-03	1.15E-02	8.86E-03	1.93E-03	1.83E-03	1.38E-03	3.02E-04	2.87E-03	1.59E-03
min B_1 98%	-4.00E-03	-5.24E-03	-4.18E-03	-6.50E-03	-4.80E-03	-3.05E-04	-2.11E-03	-1.89E-03	-3.07E-03	-2.50E-03	-9.74E-04	-1.64E-03

Appendix L: Comparison of Normalized SUVA values for BIEX and BAC biofilters

A paired t-test was used to determine whether normalized SUVA values differed significantly between BIEX and BAC biofilters. The test was two-tailed with a confidence interval of 95%.

Table L-1: T-tests comparing the relative removal of different types of organic material, through normalized SUVA values, by BIEX and BAC biofilters at steady state;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192 BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day

	EBCT, P1, 7.5 minutes			EBCT, P2, 15 minutes			EBCT, P3, 30 minutes		
	20°C	10°C	4°C	20°C	10°C	4°C	20°C	10°C	4°C
BIEX Average	0.93	0.92	0.93	1.03	0.98	0.89	1.01	0.99	0.95
BAC Average	1.06	1.05	1.01	1.02	0.99	1.01	1.00	0.99	1.01
BIEX Standard Deviation	0.28	0.12	0.11	0.28	0.22	0.20	0.28	0.33	0.27
BAC Standard Deviation	0.20	0.18	0.09	0.09	0.10	0.11	0.12	0.10	0.12
BIEX Count	32	30	29	31	30	34	27	29	27
BAC Count	35	33	29	34	35	36	33	31	31
Degrees of Freedom	54.7	55.5	53.4	35.1	38.0	50.2	33.9	33.0	34.1
T-Score	-2.13	-3.50	-3.08	0.20	-0.18	-2.95	0.15	0.02	-1.02
Critical T-Score	1.99	1.99	1.99	1.95	1.95	1.98	1.95	1.95	1.98
Result	Reject Null	Reject Null	Reject Null	Accept Null	Accept Null	Reject Null	Accept Null	Accept Null	Accept Null

A t-test was used to determine whether the normalized SUVA value for BIEX and BAC biofilters varied from one. A normalized SUVA value of one indicates that there was no difference between the feed SUVA value and filtrate SUVA value and therefore different types of organic material are not removed preferentially through the biofilter. The test was two-tailed with a confidence interval of 95%.

Table L-2: T-tests comparing the relative removal of different types of organic material, through normalized SUVA values, to the feed of the BIEX biofilter;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192 BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day

	EBCT, P1, 7.5 minutes			EBCT, P2, 15 minutes			EBCT, P3, 30 minutes		
	20°C	10°C	4°C	20°C	10°C	4°C	20°C	10°C	4°C
Average	0.93	0.92	0.93	1.03	0.98	0.89	1.01	0.99	0.95
Standard Deviation	0.28	0.12	0.11	0.28	0.22	0.20	0.28	0.33	0.27
Count	32	30	29	31	30	34	27	29	27
T-Score	-1.32	-3.84	-3.54	0.60	-0.47	-3.01	0.25	-0.16	-0.97
Critical T-Score	2.04	2.05	2.05	2.04	2.05	2.04	2.06	2.05	2.06
Result	Accept Null	Reject Null	Reject Null	Accept Null	Accept Null	Reject Null	Accept Null	Accept Null	Accept Null

Table L-3: t-tests comparing the relative removal of different types of organic material, through normalized SUVA values, to the feed of the BAC biofilter;
The equivalent bed volumes for each EBCT is:
EBCT 7.5-minutes, 192 BV/day; EBCT 15-minutes, 96BV/day; EBCT 30-minutes, 48BV/day

	EBCT, P1, 7.5 minutes			EBCT, P2, 15 minutes			EBCT, P3, 30 minutes		
	20°C	10°C	4°C	20°C	10°C	4°C	20°C	10°C	4°C
Average	1.06	1.13	1.00	1.03	1.00	1.00	1.00	1.01	1.11
Standard Deviation	0.19	0.45	0.09	0.11	0.10	0.11	0.12	0.14	0.42
Count	36	36	31	37	37	38	34	32	33
T-Score	1.89	1.76	0.11	1.73	-0.31	0.17	-0.02	0.22	1.47
Critical T-Score	2.03	2.03	2.04	2.03	2.03	2.03	2.04	2.04	2.04
Result	Accept Null	Accept Null	Accept Null	Accept Null	Accept Null	Accept Null	Accept Null	Accept Null	Accept Null

Appendix M: Determination of Effect of Temperature and EBCT on Type of Organic Removed through Biofilter

Two two-way ANOVA tests were conducted comparing the impact of EBCT and temperature on normalized SUVA values. Both BIEX and BAC were analysed separately but in the same manner. The critical F-scores were determined using a confidence of 95% confidence interval.

Table M-1: Impact of temperature and EBCT on normalized SUVA values for BIEX biofilters

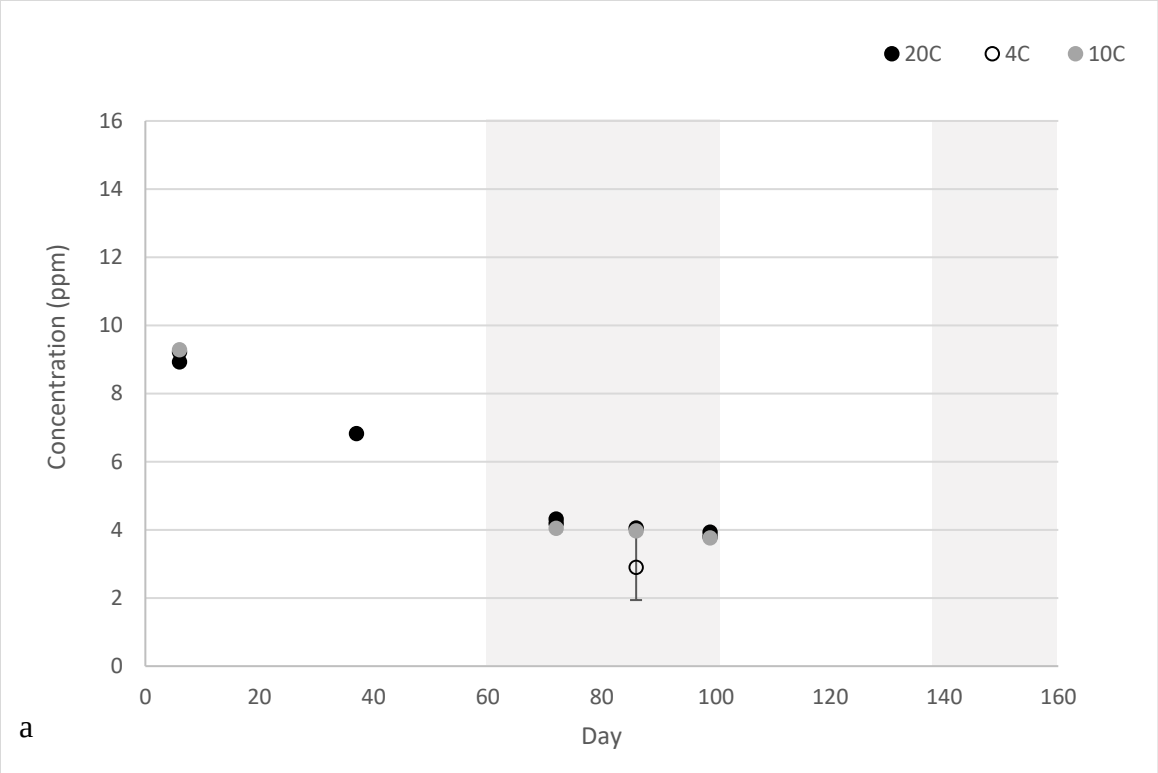
	Sum of Squares	Degrees of Freedom	Mean Square	F-Score	Critical F-Score	Result
Sum of Squares EBCT	0.16	2	0.08	1.30	3.04	Accept Null
Sum of Squares Temperature	0.22	2	0.11	1.86	3.04	Accept Null
Sum of Squares Within Groups	15.49	260	0.06			
Sum of Squares Both Factors	0.15	4	0.04	0.63	2.42	Accept Null
Total Sum of Squares	16.01	268				

Table M-2: Impact of temperature and EBCT on normalized SUVA values for BAC biofilters

	Sum of Squares	Degrees of Freedom	Mean Square	F-Score	Critical F-Score	Result
Sum of Squares EBCT	0.10	2	0.05	3.00	3.04	Accept Null
Sum of Squares Temperature	0.03	2	0.01	0.84	3.04	Accept Null
Sum of Squares Within Groups	4.75	288	0.02			
Sum of Squares Both Factors	0.04	4	0.01	0.54	2.42	Accept Null
Total Sum of Squares	4.91	296				

Appendix N: Chloride and Sulphate Raw Data

Raw chloride and sulphate data were collected intermittently from each port for both BIEX and BAC biofilters throughout the experiment. The raw data was plotted in three figures one for each temperature. Each figure contains three graphs one for each EBCT.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4C
10C
Concentration (ppm)
Day
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6
8
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100
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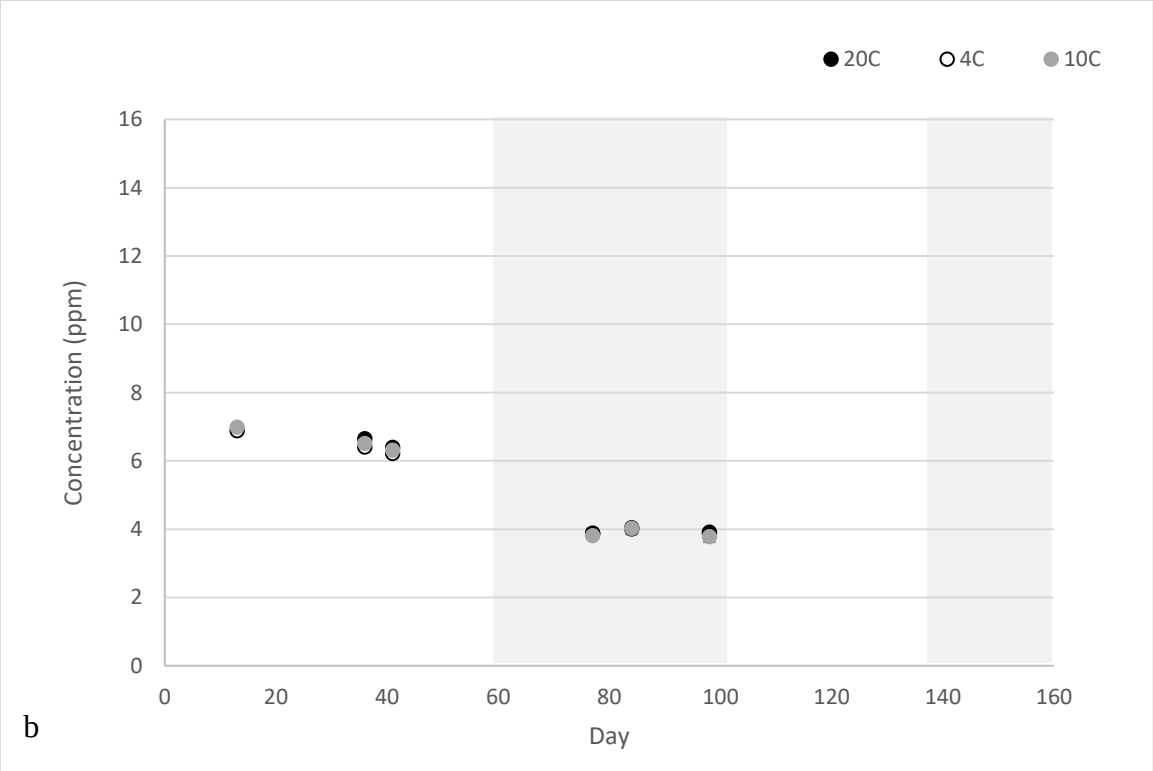
140
160

a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4C
10C
Concentration (ppm)
Day
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100
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160

b

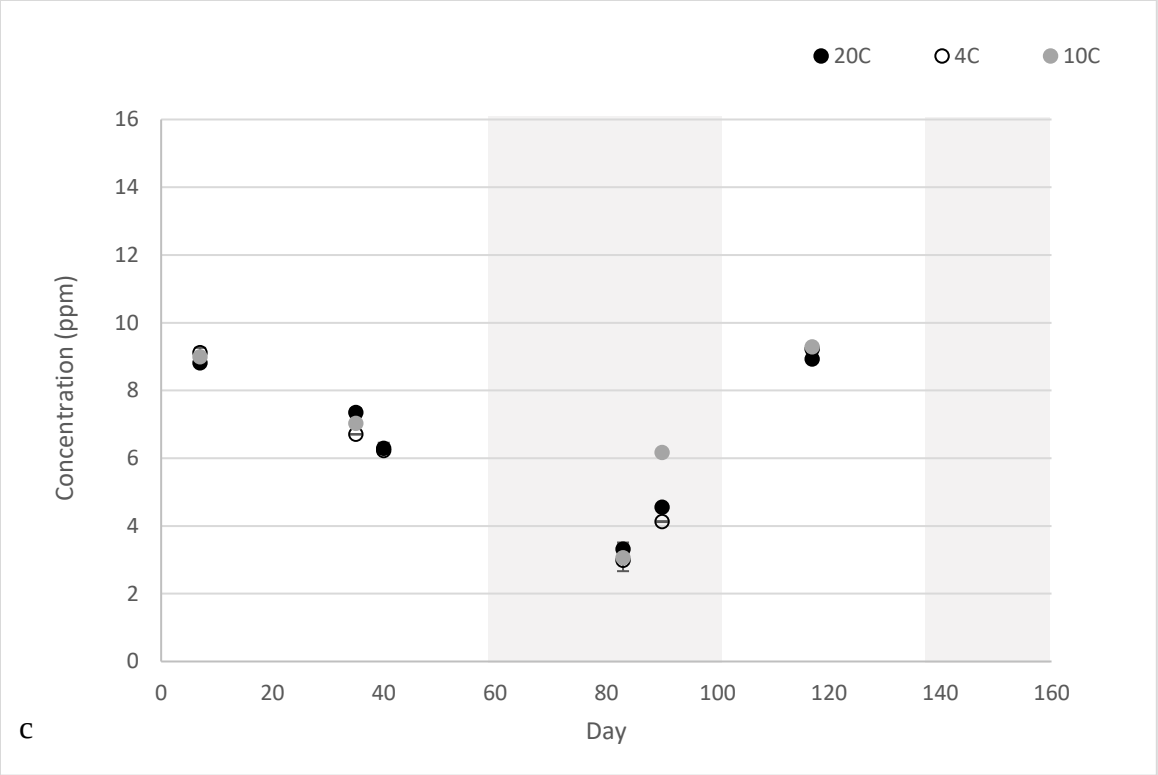
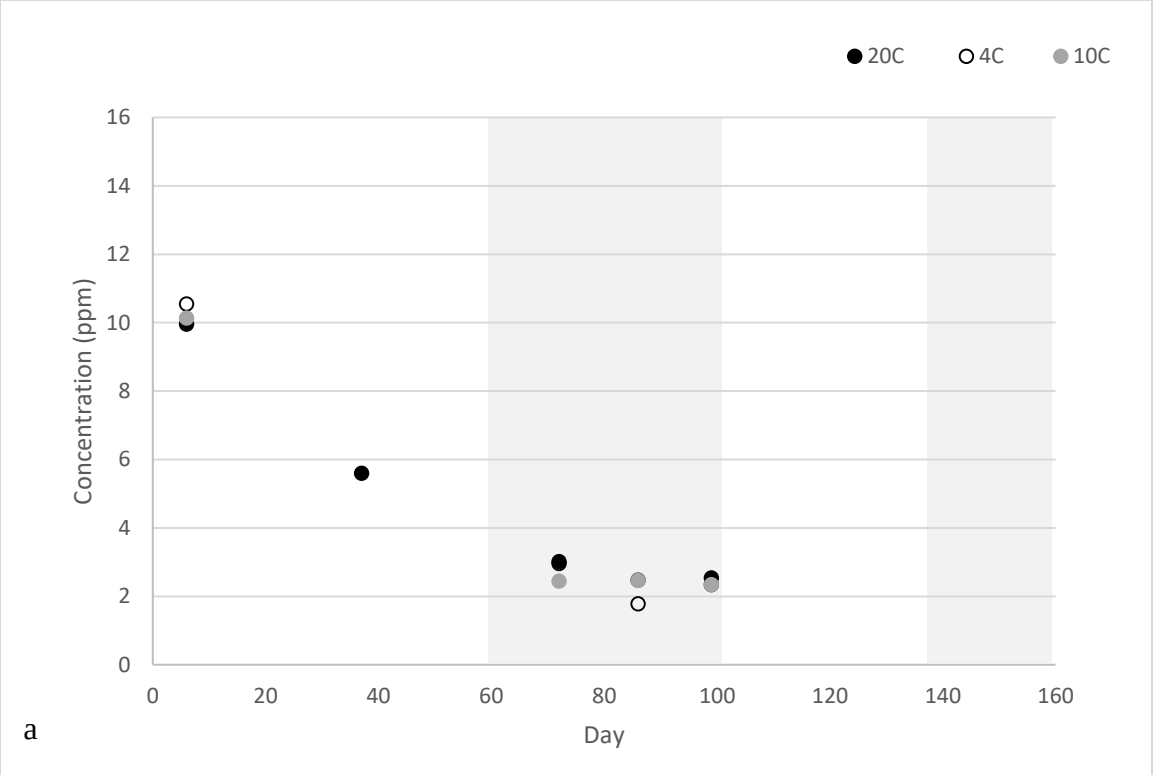


Figure N-1: Average chloride concentration in BAC biofilters at different EBCT;
a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond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Concentration (ppm)
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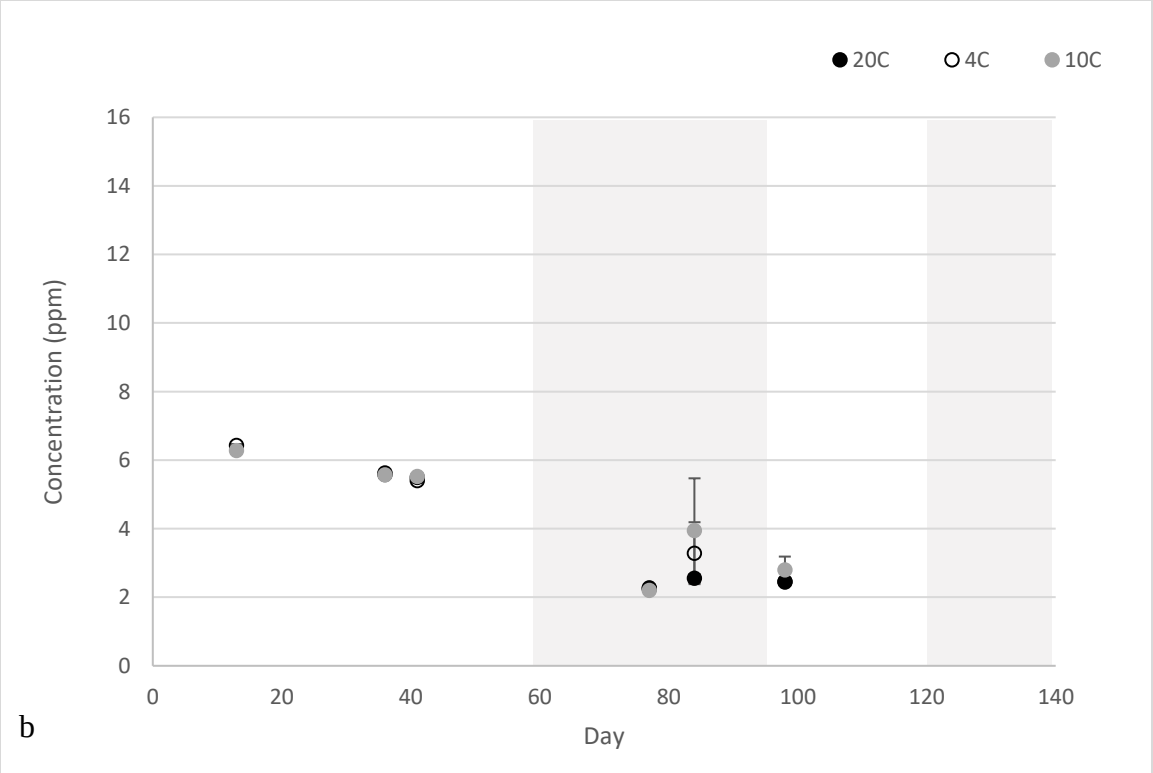
a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4C
10C
Concentration (ppm)
Day
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b

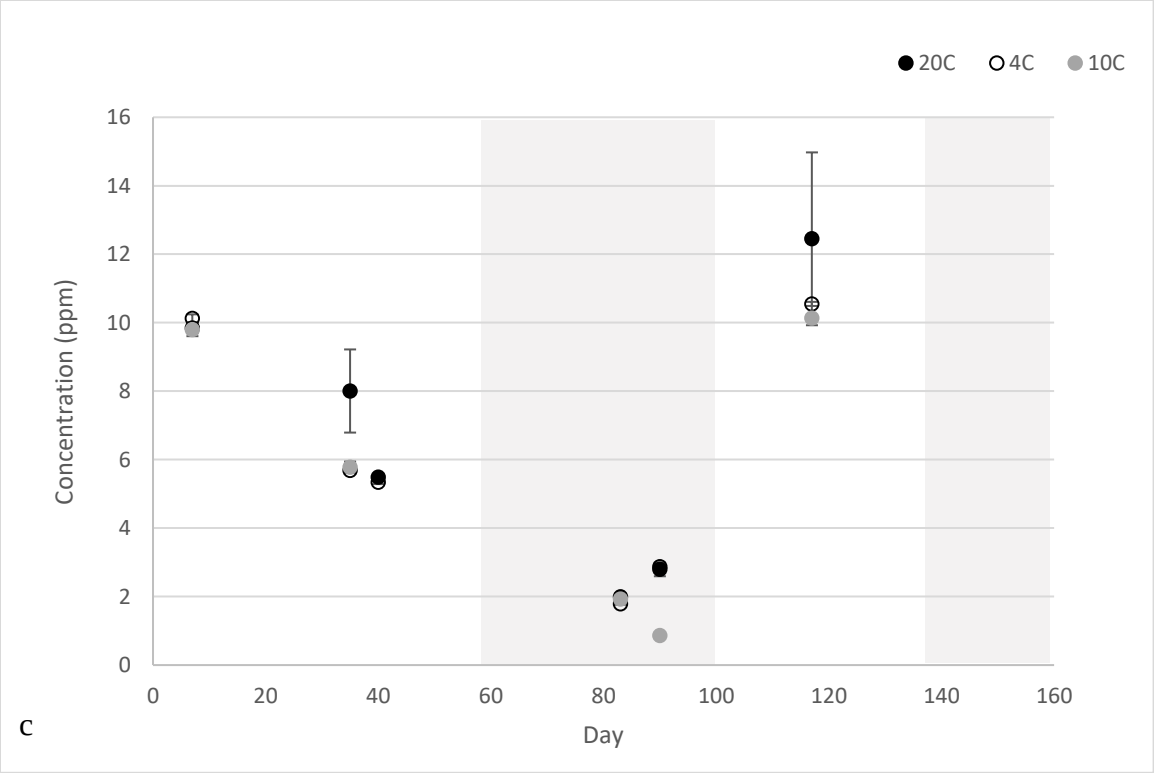
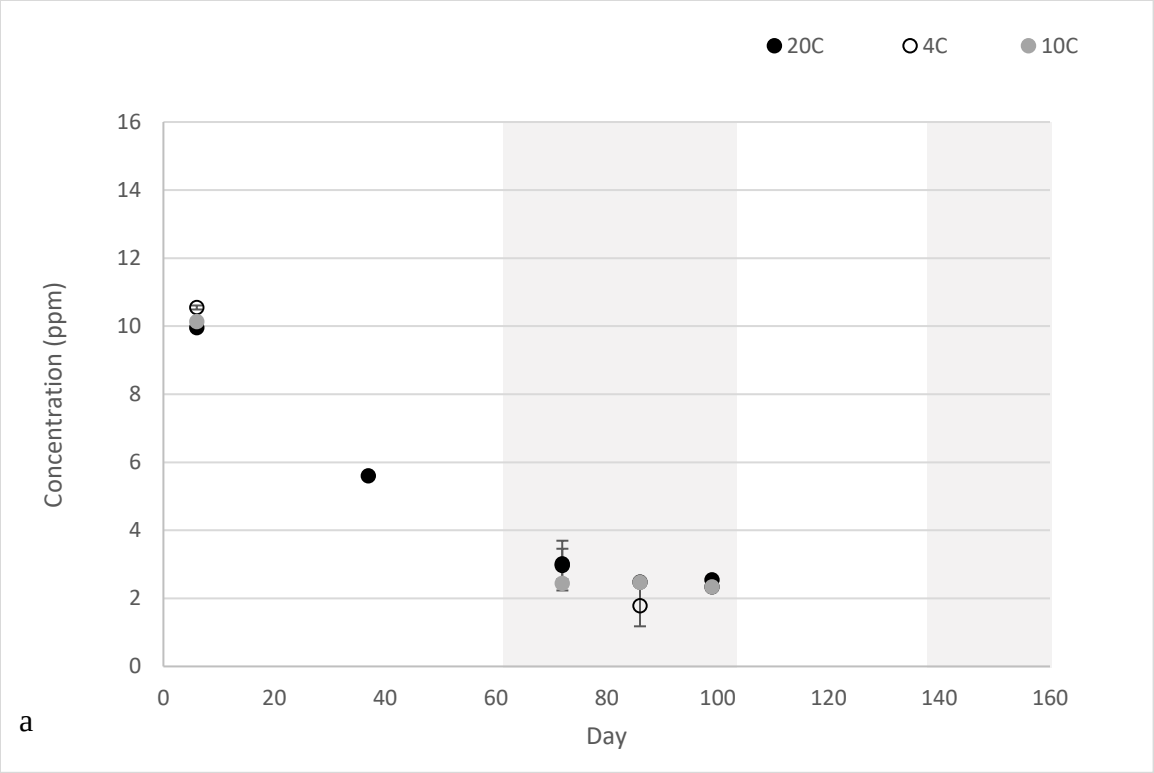


Figure N-2: Average chloride concentration in BIEX biofilters at different EBCT;
a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond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4C
10C
Concentration (ppm)
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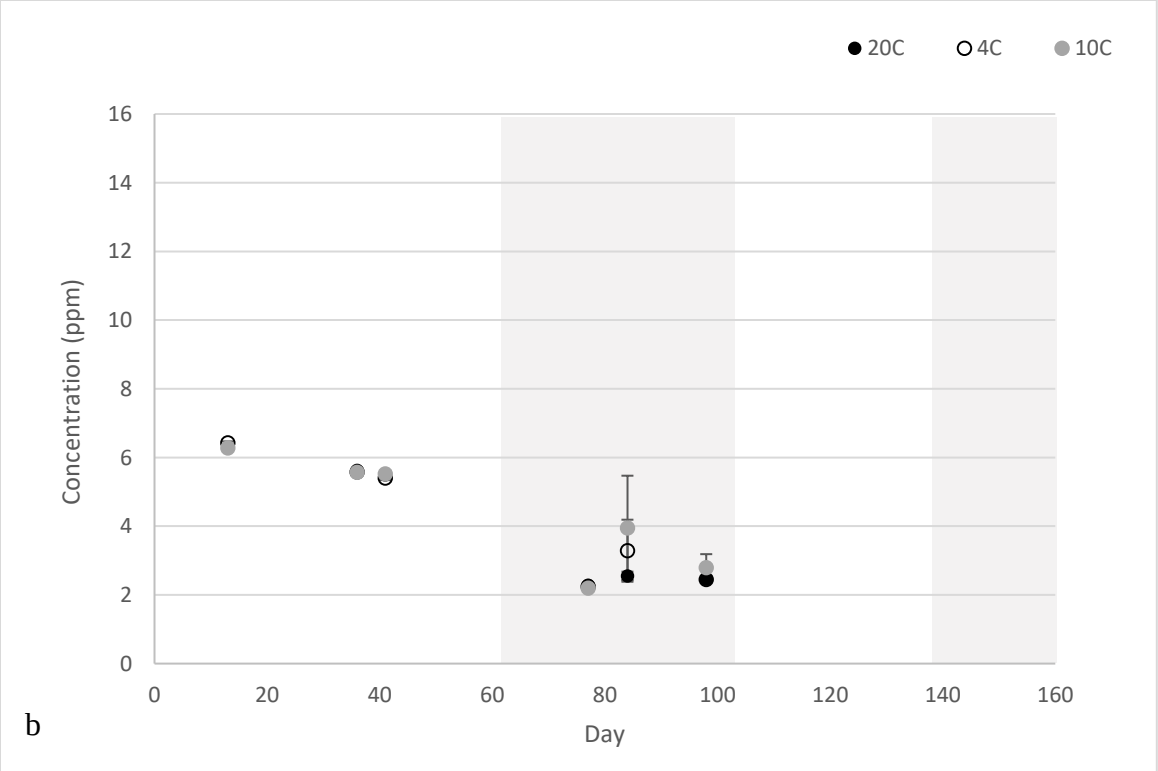
a


20C
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Concentration (ppm)
Day
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b

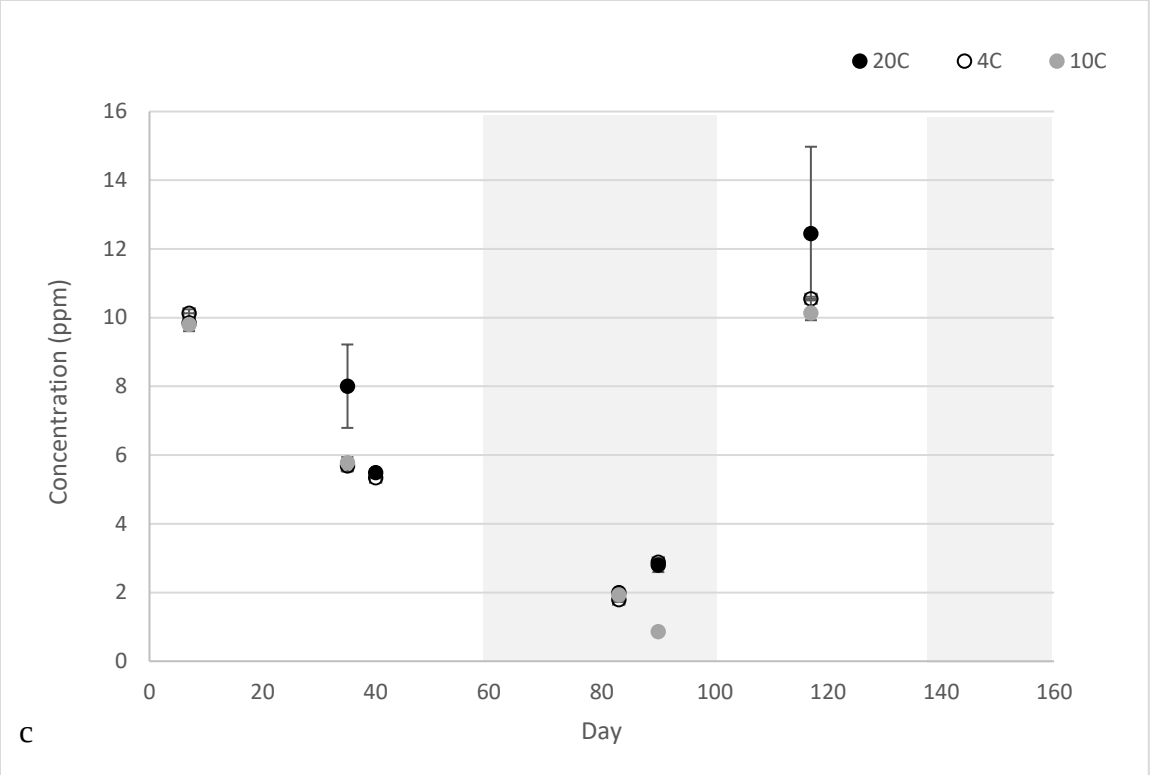
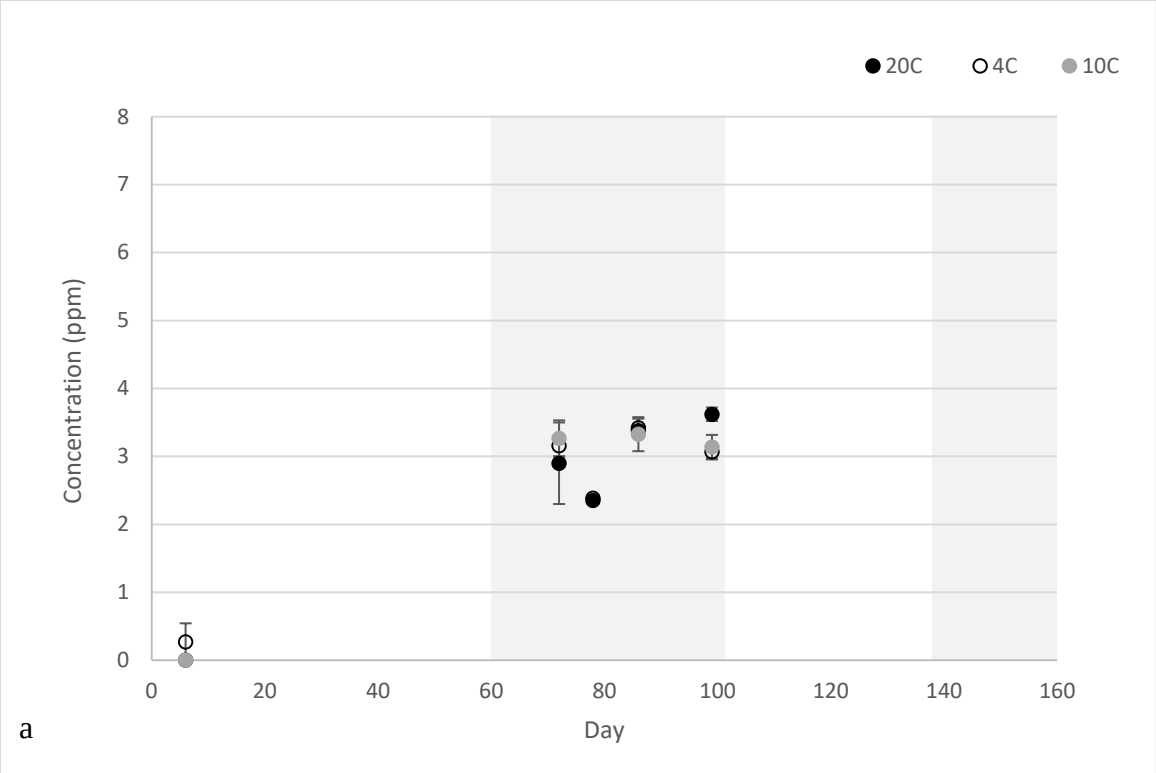


Figure N-3: Average sulphate concentration in BAC biofilters at different EBCT;
a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond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4C
10C
Concentration (ppm)
Day
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2
3
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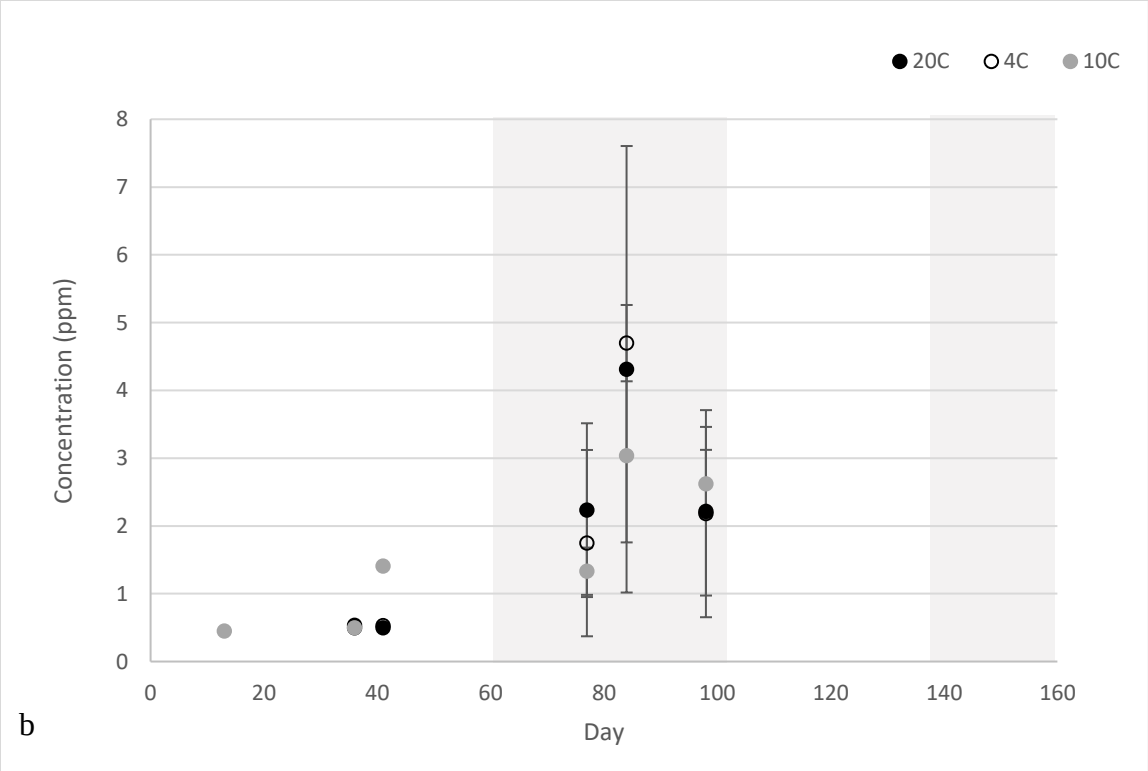
5
6
7
8
0
20
40
60
80
100
120
140
160

a


20C
4C
10C
Concentration (ppm)
Day
0
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0
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b

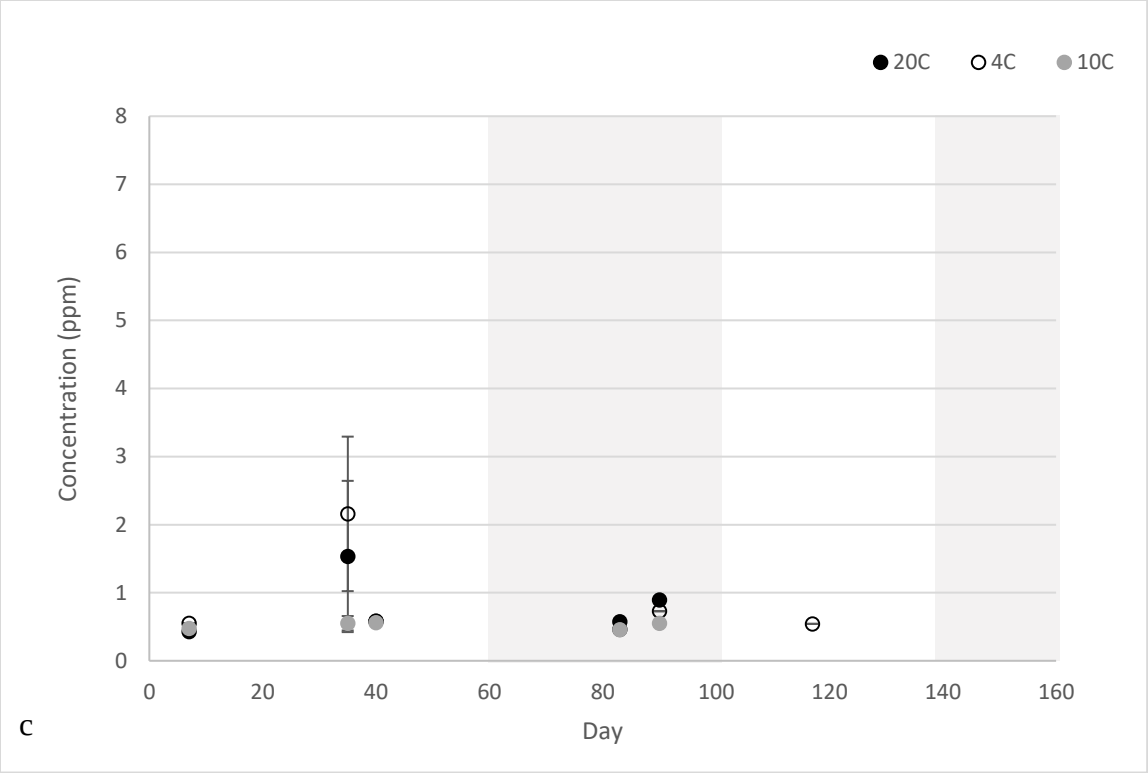

Figure N-4: Average sulphate concentration of BIEX biofilters at different EBCT;
a) EBCT 7.5-minutes (192 BV/day); b) EBCT 15-minutes (96BV/day); c) EBCT 30-minutes (48BV/day);
Shaded grey areas indicate a change in the raw water based on the time it was collected from Jericho Pond

Appendix O: Determination of Activation Energy

Equation 8 was transformed to O-1 as discussed in section 5.2.2. O-1 was used as a linear model to determine the activation energy for both BIEX and BAC biofilters.

Equation O-1: Linearized Arrhenius Equation

$$\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(A)$$

where: k is the rate constant that was calculated in section 5.1.1, E_a is the activation energy, R is the universal gas constant and T is the temperature in Kelvin and A is the pre-exponential factor

The rate constants determined, are displayed in Table 7 at each temperature and were graphed according to Equation O-1. A linear regression was fitted to the data and the slope was determined allowing for the activation energy to be identified. Figure O-1 and Figure O-2 illustrate the experimental data transformed according to Equation O-1.

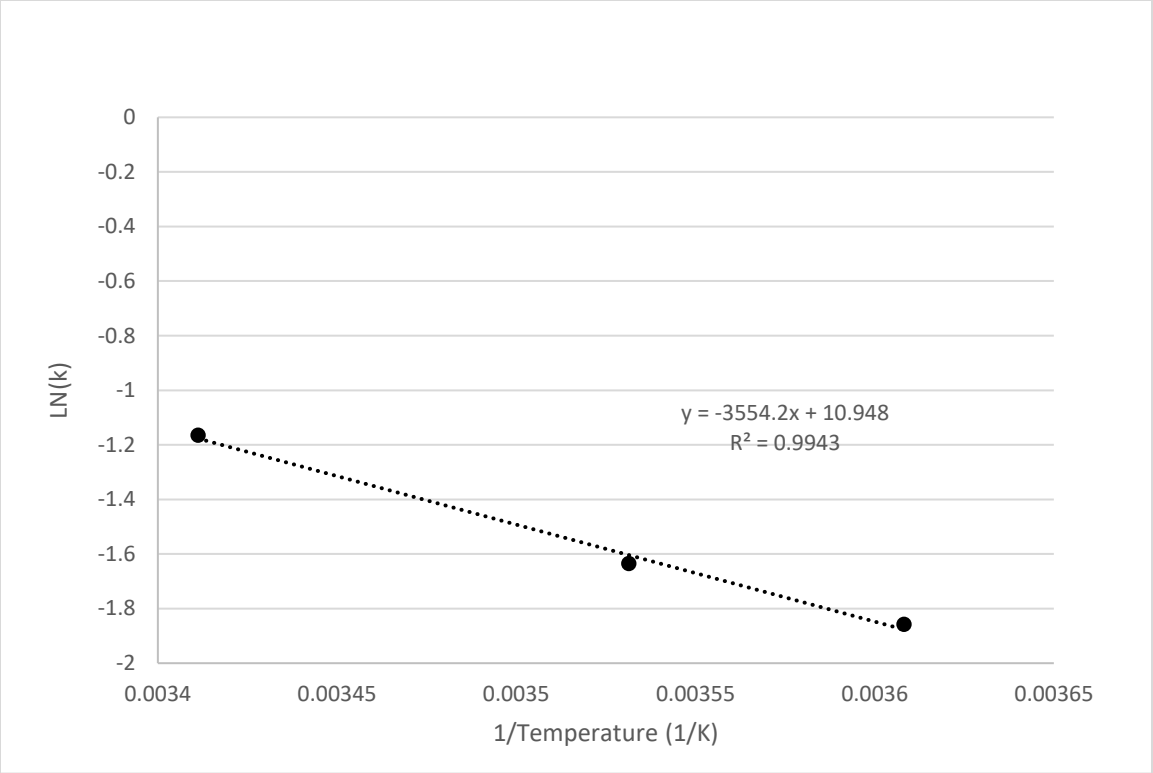

Figure O-1: Linear regression using reaction constants to determine activation energy for BIEX biofilters;
Data points represent a transformation of the rate constants listed Table 7 according to Equation O-1;
The line is a linear regression fitted to the data according to Equation O-1

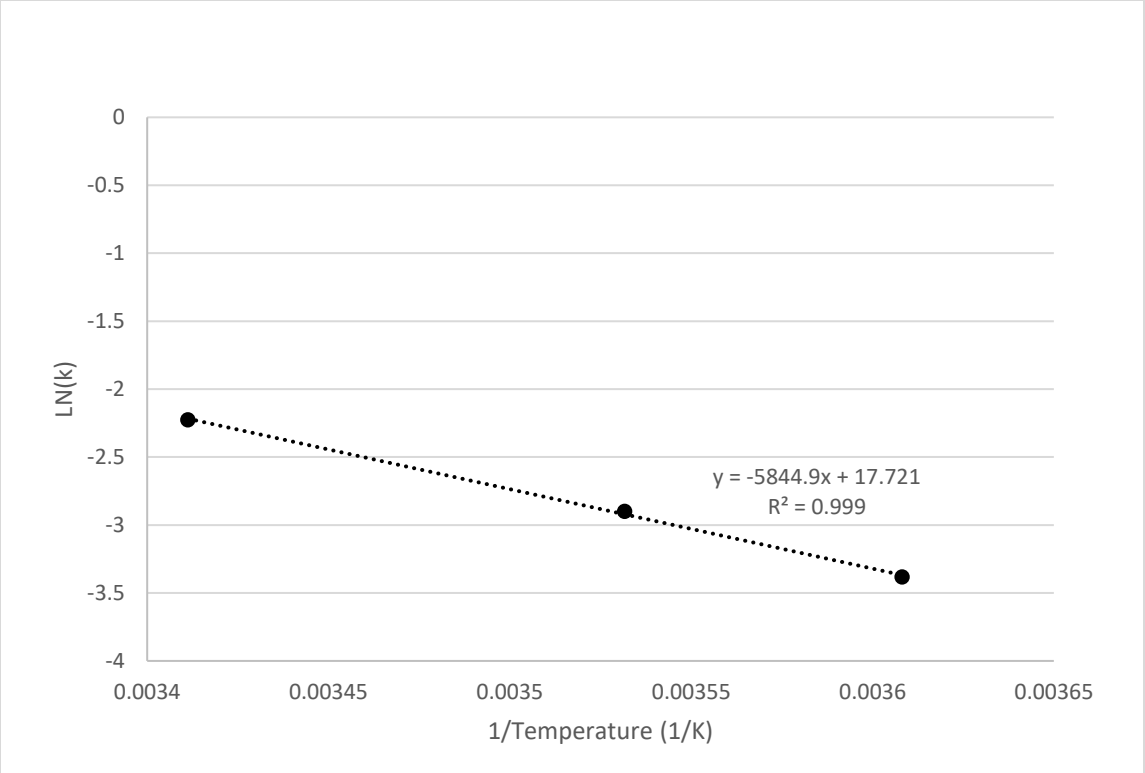

Figure O-2: Linear regression using reaction constants to determine activation energy for BAC biofilters;
Data points represent a transformation of the rate constants listed Table 7 according to Equation O-1;
The line is a linear regression fitted to the data according to Equation O-1

The error on the rate constant at each temperature for both BIEX and BAC biofilters was determined at one standard error. The details of how the error on the rate constant was determined are presented in Table O-1.

Table O-1: Linear regression and error calculations to determine activation energy for BIEX and BAC biofilters

	BIEX	BAC
B_1	-3554	-5335
B_o	10.9	16.6
var B_1	7124	7122
var B_o	0.6	25.1
s	0.038	0.090
standard error	1	1
error B_1	270	5354
E_a	29550	44354
$E_{a,max}$	29820	49708
$E_{a,min}$	29280	39001