Impact of Operational and Design Parameters on Natural Organic Matter Removal and its Correlation with NDMA Precursor Removal or Formation during Biofiltration in Drinking Water Treatment

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This work was part of project #4669 by the Water Research Foundation (WRF) entitled "Biological Filtration: NDMA Control or Source of Precursors", funded by WRF, as well as by the Natural Sciences and Engineering Research Council of Canada (NSERC) through the NSERC Chair in Water Treatment at the University of Waterloo, and its partners.

Data analysis and interpretation of all the natural organic matter (NOM) characterization data for all the bench-, pilot-, and full-scale experiments were conducted by the author. The author contributed to the design, and then installed, operated, collected samples, analyzed and interpreted all the data for the entire bench-scale experiment at Facility B. Writing and analysis of the dataset and all relevant interpretation presented in this thesis were also conducted by the author.

The work presented in this thesis also included valuable contributions of different individuals. Ashley Evans, Sarah Page and Jason Carter from Arcadis, and Caroline Russell from Carollo were leading the entire WRF project (project #4669) including coordinating the full-scale sampling, and pilot-scale experiments. The University of Waterloo (UW) team (Drs. Peter Huck, Michele Van Dyke, and Sigrid Peldszus) took the lead on NOM characterisation for the entire project and guided/supported the author in her research. The UW team also designed and coordinated the pilot-scale experiments at Facility Q and contributed scientifically to the overall WRF project. The University of Minnesota (Ben Ma and Dr. Raymond Hozalski) constructed the bench-scale columns used at Facilities I and L, and with utility support installed, operated, sampled, and analyzed the samples from the bench-scale experiment at Facility I. The participating utilities and their staff members provided information about the full-scale treatment processes, and they installed, operated and sampled the bench-scale tests at Facilities L and the pilot-scale tests at Facilities C and Q. Also, all the participating utilities measured Adenosine Triphosphate (ATP) and general water quality parameters, except for Facility B where these parameters were measured by the author. All samples for N-nitrosodimethylamine (NDMA) and NDMA Uniform Formation Condition (UFC) analyses for all the bench-, pilot-, and full-scale experiments were shipped to and analyzed by Stanford University (Zhong Zhang and Dr. William Mitch). The microbial analysis for all the bench-, pilot-, and full-scale experiments was done by the University of Minnesota (Ben Ma and Dr. Raymond Hozalski) although these results were not used in this thesis.

Several individuals in our research group and other students at the University of Waterloo also provided valuable contributions. Lin Shen performed all the liquid chromatography-organic carbon detector (LC-OCD) sample analysis for all the bench-, pilot-, and full-scale experiments and provided the raw data files used by the author in further analysis. Jesse Skwaruk performed the total organic carbon (TOC) sample analysis for all bench-scale samples from Facility B and provided the raw data files used in further analysis. Several undergraduate research assistants including Thomas Uhlenbruck, Benjamin Moir, and Daniel Chisholm provided valuable technical help in the lab and with operating the bench-scale experiments at Facility B. These tasks included helping with the installation of the experiment, cleaning glassware, sampling and analysing some parameters (such as turbidity, ammonia, nitrite, and nitrate), and shipping samples for NDMA and microbial analysis to Stanford University and the University of Minnesota, respectively.

Some figures in this thesis are adapted from figures in the WRF project #4669 report: "Biological Filtration: NDMA Control or Source of Precursors ". WRF granted the author permission to reprint and print adaptions in this thesis only of the following figures in the WRF project #4669: Figures 2-7, 8-14, 8-15, 8-16, 8-17, 8-22, 8-23, 8-24, 8-25, 8-26, 8-27, 8-28, and 8-30. These figures in the WRF project report were originally generated, designed, and plotted by the author with help from Dr. Sigrid Peldszus. Although the author of this thesis is not a co-author of the WRF project #4669 report (Evans et al., forthcoming), the authors contribution to the WRF project is mentioned on page 3 in the WRF report. Only the principle investigators and co-investigators (including co-supervisor Dr. Peter Huck) are co-authors of the WRF report.

Abstract

NOM is a complex mixture of organic compounds that are present in all natural waters and is mainly originating from plant and aquatic organism degradation products. Therefore, the specific composition of NOM is site-specific. Removing NOM during drinking water treatment is very beneficial, since NOM not only causes aesthetic problems, such as taste, odour, and colour problems, but also impacts other treatment processes. NOM, for examples, causes increased coagulant and disinfectant demands; contributes to corrosion and bacterial regrowth throughout the distribution system; transports metals and hydrophobic chemicals; and interferes in adsorption processes of other contaminants. However, one of the most important points for removing NOM is that NOM fractions have been identified as being precursors to potentially carcinogenic disinfection by-products (DBPs).

The goal of this research was to identify the impact of different operational, design, and water quality parameters on the characteristics and removal of NOM fractions during bench-scale and pilot-scale biofilter columns at different drinking water treatment plants (DWTPs). Parameters investigated in bench-scale biofilter columns at three different facilities (Facilities B, I, and L) include: water sources, media acclimated/operated in different water sources, and pre-ozonation. During these bench-scale experiments, three different biofilter media (from Facilities B, I, and L media) were tested simultaneously at each of the three facilities. Also, two different pilot-scale experiments were carried out, one at Facility C, which investigated the following parameters: media type, backwash type, and ammonia addition. The other pilot-scale experiment was at Facility Q, which investigated the following parameters: full-scale treatment processes prior to biofiltration, media type, backwash type, and backwash frequency. At both the pilot-scale facilities, the biofilter profiles and kinetics of the NOM fraction removals for the different parameters were also investigated. Lastly, the NOM fraction removals from both the bench-scale and pilot-scale experiments were correlated to the NDMA precursor removals or formations.

The NOM fractions in this research were characterized by using two relatively new NOM characterization techniques: LC-OCD and fluorescence excitation emission matrix (FEEM). LC-OCD separates NOM into five different fractions based on molecular weight size, and these fractions are: biopolymers (BP), humics (HS), building blocks (BB), low molecular weight (LMW)

acids/humics, and LMW neutrals. FEEM detects molecules that contain fluorophores and it can therefore identify three different fractions: humic acids (HA), fulvic acids (FA), and protein-like materials. Furthermore, the NDMA concentrations in this research was analysed using a measuring technique called uniform formation condition (UFC). UFC mimics average chloramination conditions used at DWTPs across North America.

The bench-scale experiments at Facilities B, I, and L showed that when all the different media acclimated/operated in different water sources were fed the same water source they behaved very similarly in terms of NOM fraction removal and water sources therefore matters. However, when the same media was fed the water sources from each of these facilities, then there were barely any similarities and the media acclimated/operated in different water sources therefore barely had any influence. Also, the pre-ozonation at Facility B improved the NOM fraction removals when combined with the bench-scale biofiltration columns. The pilot-scale experiments at Facilities C and Q showed that powdered activated carbon (PAC) drastically removed various NOM fractions, it, for example, successfully removed more than 83% of BP. Also, granular activated carbon (GAC) media was the media type that had the best removals of various NOM fractions at both pilot-scale facilities. At facility C, the chloraminated backwashed columns had higher removals of DOC (4.3 percentage points higher), BP (20 percentage points higher), LMW acids/humics (3.9 percentage points higher), and LMW neutrals (11 percentage points higher) than the GAC control columns. However, at Facility Q there were no noticeable differences between backwash types or backwash frequencies on the NOM removals, due to low removals at most sampling events. These low removals made it difficult to assess conclusively the influence from these parameters on NOM fraction removals. At Facility C, only DOC, BP, and HS relatively fitted the kinetics models, and the best data fit was for BP. At Facility Q, BP during phase 1 and DOC for only one column during phase 2 poorly fitted the kinetics models. However, there were no clear trends regarding which reaction order fitted each fraction removal the best. The reason is that the change in the coefficients of determination (R^2 coefficients) only marginally changed from 0^{th} to 2^{nd} order model. Also, these poor fits between NOM fraction removals and kinetics models is due to, for example, only 4-5 data points for each profile and only low removals across the biofilters. For the NDMA UFC, pre-ozonation at facility B also substantially reduced NDMA UFC, and pre-ozonation combined with biofiltration had the lowest NDMA UFC concentrations. Softening also substantially increased NDMA UFC at the full-scale treatment process at Facility Q. Last, there was a statistically

significant correlation between higher protein-like materials intensities as measured by FEEM in the biofilter influents and higher NDMA UFC concentrations in the biofilter influents. The same was also observed for the biofilter effluents.

This research provides greater insight into NOM fraction removals, biofiltration performance, and the correlation between NOM and NDMA UFC. Although the results might be site-specific, these results indicated that to optimize the NOM fraction removals at a DWTP PAC, pre-ozonation, and GAC media in the biofilters should be employed. Also, to minimize NDMA precursor formation during drinking water treatment, pre-ozonation prior to the biofilters should be employed, but softening should be avoided. These findings provide insight to municipalities, consultants, and staff members at DWTPs on some operational and design parameters that should be taken into consideration when designing or upgrading a DWTP.

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List of Acronyms

α: significance level

AMPB/N: Amphiphilic bases/neutrals

AOC: Assimilable organic carbon

ATP: Adenosine Triphosphate

BB: Building blocks

BP: Biopolymers

BOM: Biodegradable organic matter

CCL4: Fourth drinking water contaminant candidate list

DBPs: Disinfection by-products

Df: Degree of freedom

DMA: Dimethylacetamide

DO: Dissolved oxygen

DOC: Dissolved organic carbon

DOM: Dissolved organic matter

DON: Dissolved organic nitrogen

DPA: Dipropylamine

DWTPs: Drinking water treatment plants

EBCT: Empty bed contact time

FA: Fulvic acids

FEEM: Fluorescence excitation emission matrix

FP: Formation potential

GAC: Granular activated carbon

HA: Humic acids

HPIA/N: Hydrophilic acids/neutrals

HPIB: Hydrophilic bases

HPOA: Hydrophobic acids

HP-SEC: High performance size exclusion chromatography

HS: Humic substances

IOM: Intercellular organic matter

LC-OCD: Liquid chromatography-organic carbon detection

LMW: Low molecular weight

MDL: Methods detection limits

Mn: Average molecular weight

N/C: Nitrogen to carbon

NDMA: N-nitrosodimethylamine

NOM: Natural organic matter

NSERC: Natural Sciences and Engineering Research Council of Canada

OND: Organic nitrogen detection

PAC: Powdered activated carbon

SDS: Simulated distribution system

SEC: Size exclusion chromatography

SMPs: Soluble microbial products

SPE/GC/MS: Solid-phase extraction/gas chromatography/mass spectrometry

SUVA: specific ultraviolet absorbance

TOC: Total organic carbon

UDMH: Unsymmetrical dialkylhydrazine

UFC: Uniform formation condition

USEPA: US Environmental Protection Agency

UV: Ultraviolet

UVD: Ultraviolet light detection

UV_{254}: Absorbance of ultraviolet light at a wavelength of 254nm

WRF: Water Research Foundation

WTPs: Water Treatment Plants

WWTPs: Waster Water Treatment Plants

X*: Dimensionless contact time

Chapter 1
Introduction

1.1 Problem Statement

Natural organic matter (NOM) is a mixture of thousands of different organic compounds, which is present in all water bodies. NOM predominantly consists of carbon, oxygen, nitrogen and hydrogen atoms. However, the composition and properties of NOM are site specific and are therefore significantly impacted by the water source at a specific location (Fabris et al., 2008; Thurman, 1985). NOM can cause lots of problems in our drinking waters; NOM, for example, has been linked to aesthetic problems, such as taste, odour and colour problems; forms carcinogenic or potentially carcinogenic disinfection by-products (DBPs); contributes to corrosion and bacterial regrowth throughout the distribution system; leads to higher coagulant demands; transports metals and hydrophobic chemicals; and interferes in adsorption processes of other contaminants (Jacangelo et al., 1995). If higher levels of NOM are present in the raw water it may therefore be necessary to optimize the NOM removal during drinking water treatment, and one drinking water treatment step that removes NOM is biofiltration.

Biofiltration is a filter process with a filter media that becomes biologically active due to attachment of bacteria to the surface of the media, which form a bacterial biofilm. Some commonly used media types include granular activated carbon (GAC), anthracite, expanded ceramics, plastics, sand, and gravel (Basu et al., 2016; Simpson, 2008). Biofiltration is becoming more popular at water treatment plants (WTPs) due to its ability to biodegrade organics (e.g. NOM) and inorganic constituents, low in maintenance, and simple to operate (Bablon et al., 1988; Basu et al., 2016). Therefore, optimizing biofilter performance will improve the NOM fraction removals (Moll et al., 1999). It is therefore important to understand how the following conditions and variables influence biofiltration performance: source water, media acclimated/operated to these water sources, full-scale pre-treatment processes prior to biofiltration, media type (GAC vs. anthracite), backwash type (chloraminated vs. non-chloraminated water), backwash frequency, and ammonia levels. This can provide a better insight into optimizing biofiltration performance and NOM fraction removals, which will improve the drinking water quality. Although much research has been conducted in this area, limited information is available on the effect of these factors on the

removal of different NOM fractions, as characterized by Liquid chromatography-organic carbon detection (LC-OCD) and Fluorescence excitation emission matrix (FEEM), techniques which are used in this research.

How severely the problems caused by NOM impact a certain treatment plant depends both on the concentration and composition of NOM in the water (Baghoth et al., 2011). Due to this and the complexity of NOM, it is therefore desirable to characterize NOM in drinking water using various analytical techniques. This can provide a greater understanding of NOM removal during drinking water treatment. Some traditional NOM characterization techniques include measuring ultraviolet light at a wavelength of 254 nm (UV_{254}) and total organic carbon (TOC), but these techniques can only characterize bulk NOM and they do not characterize different NOM fractions. Therefore, more in-depth analytical techniques are required, such as LC-OCD and FEEM. These two analytical techniques are relatively new methods and they are becoming more popular due to their ability to characterize multiple NOM fractions in a water sample, their high sensitivity, their low sample preparation time, and in the case of FEEM their low operational costs. LC-OCD separates the NOM in a sample by size into five fractions: biopolymers (BP) (e.g. polysaccharides, proteins, and amino sugars), humic substances (HS) (e.g. HA and FA), building blocks (BB) (breakdown products of HS), low molecular weight (LMW) acids/humics (e.g. aliphatic compounds and small breakdown products of HS), and LMW neutrals (e.g. alcohols, aldehydes, ketones, sugars, and amino acids) (Huber et al., 2011). FEEM detects molecules that contain fluorophores, and it is therefore capable of identifying three different fractions: humic acids (HA), fulvic acids (FA), and protein-like materials (e.g. containing tryptophan) (Baghoth et al., 2011; Bieroza et al., 2009; Matilainen et al., 2011). However, as mentioned above there is only limited information, from LC-OCD and FEEM, on the characteristics of NOM removal from the previously mentioned conditions and variables during biofiltration.

As mentioned above, portions of the NOM can form potentially carcinogenic DBPs, and one of these DBPs is N-nitrosodimethylamine (NDMA) (Chang et al., 2013; Chen and Valentine, 2007; Chuang et al., 2013; Kristiana et al., 2013; Richardson and Ternes, 2014, 2002). NDMA is, for example, of particular interest since it is the most detected nitrosamine, and it is also inconclusive how NDMA and/or its precursors are getting removed/formed during biofiltration (Barzi, 2008; Chuang and Mitch, 2017; Farré et al., 2011a; Krasner et al., 2012a, 2015; Liu et al., 2017; Sgroi et

al., 2018). Some research showed a decrease in NDMA during biofiltration (Barzi, 2008; Chuang and Mitch, 2017; Farré et al., 2011; Krasner et al., 2012) while other research showed an increase (Krasner et al., 2015; Liu et al., 2017). The main NDMA formation mechanism proposed is a reaction between disinfectants (for example, chloramine) and secondary amine precursors (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Mitch et al., 2003; Najm and Trussell, 2001; Schreiber and Mitch, 2006a). Also, US Environmental Protection Agency (USEPA) placed NDMA on the fourth drinking water contaminant candidate list (CCL4), due to NDMA's health risks, and they are considering to regulate NDMA in the future (USEPA, 2016). Unfortunately, all current research in correlating NDMA formation with NOM characterization, from LC-OCD and FEEM, are inconclusive, and it is therefore desirable having a better understanding on how NDMA formation correlates with NOM removal during biofiltration (Bridgeman et al., 2011; Fu et al., 2017; Kristiana et al., 2017; Yang et al., 2015). This can ultimately provide a better insight into control strategies for NDMA, which would allow water facilities to minimize the NDMA formation during drinking water treatment.

1.2 Objectives

The major goals of this research were to identify the impact of operational and design parameters on characteristics and removal of NOM fractions during biofiltration in drinking water treatment plants. Parameters investigated include: water sources, media types, media acclimated/operated in different water sources, and operating conditions. To reach these goals, sub-objectives were identified and are summarized as follows:

1. Identify the importance of different water sources and media acclimated/operated to these sources on NOM fraction removal by conducting bench-scale biofilter experiments located at three different water treatment plants.
2. Investigate the impact of the following operational conditions and design variables on NOM fraction removal in pilot-scale biofilter experiments: media type (GAC vs. anthracite), backwash type (chloraminated vs. non-chloraminated water), and backwash frequency.
3. Explore how the following full-scale pre-treatment processes prior to biofiltration influence NOM fraction removals: pre-ozonation, PAC, lime softening, and $FeCl_3$ coagulation (with vs. without polyDADMAC).

4. Determine how ammonia influences the NOM fraction removal during pilot-scale biofilter experiments.
5. Characterize kinetics of NOM fraction removals for different operating conditions and design variables in pilot-scale biofilter experiments.
6. Correlate NOM fraction removals with NDMA precursor formations or removals in bench-scale and pilot-scale biofilter experiments.

The first and third sub-objectives were addressed through experiments at three different water treatment plants, from May 2018 to June 2018, where biofilter media from the same three plants were tested at each of the facilities. Facility B therefore tested media from Facilities B, I and L, Facility I tested media from Facilities B, I and L, and Facility L tested media from Facilities B, I, and L. The only condition that differed between these bench-scale tests was therefore the water source. Also, pre-ozonation was only investigated at one of these facilities.

The second, third, fourth, and fifth sub-objectives were investigated at two different drinking water treatment plants in North America. Each location had multiple pilot-scale biofilter columns that contained different biofilter media, and influents and effluents from these columns were sampled frequently. Water samples were taken less frequently at different biofilter depths in each column to characterize the kinetics of NOM fraction removal. Also, the following full-scale pre-treatment processes prior to biofiltration were also investigated at one of the facilities: PAC, lime softening, and coagulation with $FeCl_3$ (with vs. without polyDADMAC).

The sixth sub-objective compared the NOM fraction removal from sub-objectives one to five with the corresponding NDMA precursor data to elucidate whether removal of NOM fractions correlates with the formation or decline of NDMA precursors during biofiltration.

1.3 Thesis Structure

This thesis consists of six chapters, including an introduction (Chapter 1), literature review (Chapter 2), three results chapters (Chapters 3, 4, and 5), and conclusions and recommendations (Chapter 6). Each of the three results chapters (Chapters 3, 4, and 5) are written as separate journal articles, a paper-format thesis, and they therefore each include a method section, a results and discussions section, and a conclusion.

Chapter 1 includes the research statement, research objectives, and the structure of this thesis.

Chapter 2 includes a literature review to provide an overview of published material relevant to this work, which include the current understanding of NOM, NOM removal by biofiltration, NOM characterization techniques, and NDMA. Also, at the end of this chapter, the research gaps and needs identified through the literature review are presented.

Chapter 3 is a detailed study of the influence of source water, media acclimated/operated to different source waters, and pre-ozonation on NOM fraction removals during bench-scale biofilter columns, where three different water sources and biofilter media from those sources were tested.

Chapter 4 is a detailed study on the impacts of different operational conditions, biofilter design variables, and water quality parameters on NOM fraction removals during pilot-scale biofiltration. These conditions, variables, and parameters include full-scale pre-treatment processes prior to biofiltration, media type, backwash type, backwash frequency, and ammonia addition. This chapter also presents the kinetics of NOM fraction removals for these conditions, variables and parameters.

Chapter 5 includes the NDMA precursor data from the experiments in Chapters 3 and 4, which are used to investigate the correlation between NOM fraction removals and NDMA precursor formation or removal.

Chapter 6 presents the major conclusions from Chapters 3, 4, and 5 and suggests recommendations for future work.

Chapter 2
Literature Review

2.1 Natural Organic Matter

NOM is a mixture of organic compounds that are present in natural waters such as surface water and groundwater and the specific composition of NOM is site-specific (Thurman, 1985). Since there are many different organic compounds with different chemical properties, they are usually divided into different fractions with similar chemical properties. These fractions, determined by Thurman (1985) was HS, hydrophilic acids, carboxylic acids, amino acids, carbohydrates, and hydrocarbons (Fabris et al., 2008; Thurman, 1985).

NOM is the main cause of aesthetic problems, such as colour, odour, and taste problems in drinking water, and can also contribute to elevated DBPs levels. DWTPs are therefore focused on removing the NOM fraction if it is too high, which is, for example, being reduced through biofiltration (Baghoth et al., 2011). Some well researched treatment options for the removal of NOM include coagulation/flocculation, adsorption, oxidation, and membrane filtration (Kristiana et al., 2013; Zhang et al., 2015). However, more research is needed in how biofiltration reduces NOM, and on NOM characteristics analyzed by LC-OCD and FEEM. Due to lack of research, the current understanding of the influence of biofiltration on NOM removal will therefore be discussed in this literature review.

Besides causing aesthetic problems, several studies also proved that NOM with oxidants, such as chlorine and chloramine, in drinking water generates potentially carcinogenic DBPs. One of these DBPs is NDMA, which will be discussed in details later (Chang et al., 2013; Chen and Valentine, 2007; Chuang et al., 2013; Kristiana et al., 2013; Richardson and Ternes, 2014, 2002). Usually between 1% to 5% by weight of NOM consists of organic nitrogen, which potentially is a fraction of NOM that can contain NDMA precursors (Lee and Westerhoff, 2006). Furthermore, numerous researchers studied the composition of dissolved organic nitrogen (DON) in NOM in both wastewater and surface water to establish a link between NOM and NDMA formation (Chang et al., 2013; Chen and Valentine, 2007; Chuang et al., 2013; Kristiana et al., 2013). Studies suggested that the most important DON for NDMA formation are hydrophobic acids (HPOA), hydrophilic

acids/neutrals (HPIA/N), hydrophilic bases (HPIB) and amphiphilic bases/neutrals (AMPB/N) fractions (Chang et al., 2013; Chen and Valentine, 2007). During chloramination the highest NDMA formation occurred from AMPB/N and under NDMA formation potential (FP) conditions 734.2 ng NDMA/mg-C was formed (Chang et al., 2013). However, when taking into consideration the formation efficiency and the water composition then another study indicated that the dominant source for NDMA formation in the NOM fraction is the hydrophobic acid fraction, but the hydrophilic fractions tend to produce more NDMA (Chen and Valentine, 2007). Together, these studies suggest that the DON fraction in NOM is an important NDMA precursor. However, there has also only been little research conducted in linking NOM characteristics, from LC-OCD and FEEM, with NDMA formation, and this will also be discussed later in this literature review.

2.2 NOM Removal by Biofiltration

Biofiltration, also known as biological filtration, is a filter process where a granular filter media becomes biologically active due to attachment of bacteria to the surface of the media, which form a bacterial biofilm. Some commonly used media types include GAC, anthracite, expanded ceramics, plastics, sand, and gravel (Basu et al., 2016; Simpson, 2008). Many DWTPs are either already using or are considering implementing biofiltration to meet water quality goals, which include removals of organics, taste, colour, and odour compounds, ammonia, DBP precursors, and chlorine demand. Biofiltration is therefore becoming more popular due to their ability to biodegrade organic and inorganic constituents, and it is also low in maintenance, simple to operate, and their ability to remove fine particulate (Bablon et al., 1988; Basu et al., 2016; Huck et al., 2013). Also, biofiltration can provide some removals of contaminants, such as pharmaceuticals and endocrine disruptors (Chu et al., 2012; Huck and Sozanski, 2008; Huck et al., 2013).

Since biofiltration removes a portion of the NOM, one of the best ways to optimize the NOM removal through biofiltration is therefore by optimizing the biofilter performance (Moll et al., 1999). Factors influencing biofiltration performance include pH, temperature, nutrient supplementation, influent water's quality, pre-oxidation, filter media, empty bed contact time (EBCT), and backwashing (Moll et al., 1999; Urfer et al., 1997). This section will therefore describe the current understanding of these operational parameters influence on biofiltration performance, their correlation with NDMA formation, and NOM removal throughout a biofilter depth.

2.2.1 Influence of Operational Parameters on Biofiltration Performance

Several studies have been completed in optimizing biofiltration performance through operational parameters and some of these parameters will be discussed below. However, only little research has been conducted in how these parameters influences the NOM characteristics of the drinking water and how these links to NDMA formation.

2.2.1.1 pH

Water with a pH below 6 or above 8 might negatively influence the microbial activity, and pH adjustment prior to biofiltration might therefore be necessary (Evans et al., 2010). Therefore, this study suggests that biofiltration performance is optimal at pH between 6 and 8 but it is not normally feasible to adjust pH to improve biofiltration performance (Evans et al., 2010).

2.2.1.2 Temperature

Temperature significantly influences the removal efficiency of biofiltration, and several studies reported a decrease in removal efficiency with decreasing temperature (Huck et al., 2013; Liu et al., 2001; Moll et al., 1999; Zhang and Huck, 1996). These reductions can possibly be ascribed to changes in the microbial community over prolonged periods of time, decreased biological activity, and kinetics (Huck et al., 2013; Moll et al., 1999; Zhang and Huck, 1996). Zhang (1996) introduced a dimensionless contact time (X*), which is used to quantify biofiltration performance, and X* include the effect of temperature, actual contact time, the reactor specific surface area, biodegradable organic matter (BOM) diffusivity, biofilm density, and biodegradation kinetic parameters to calculate the biofiltration performance. Another research suggests that for keeping an optimal biofiltration performance a temperature above 15 ℃ should be achieved (Moll et al., 1999).. Even though temperature has a significant impact on biofiltration performance, the temperature of the influent water to the biofilters cannot be controlled (Huck et al., 2013). Collectively, these studies suggest that decreasing water temperature decreases the biofiltration performance, but the temperature cannot be controlled.

2.2.1.3 Nutrient Supplementation

Research suggest that to ensure a balanced growth of the biomass on the filter media a proper carbon, nitrogen, phosphorus ratio (C:N:P) must be obtained (Basu et al., 2016). If the ratio is less than 100:10:1, then the microbial community might be nutrient limited although cycling of nutrients within the biofilm must be considered. Since phosphorus is typically the limiting factor, phosphorus supplements might therefore be necessary to increase the biofiltration performance.

2.2.1.4 Source Water

The influent water to the biofilters impacts biofiltration performance; and the water quality in the influent water varies greatly depending on the substrate concentration in the water source and the upstream pre-treatments prior to the biofilter (Huck et al., 2013; Volk and Lechevallier, 2002). Research has found that X* demonstrated that the amount of substrate removed during biofiltration is proportional to the substrate concentration in the influent water (Huck et al., 2013; Zhang and Huck, 1996), because kinetics are effectively first-order. These substrates consist of BOM, which promotes bacterial growth by serving as an energy source for the bacterial biofilm. The substrates available for growth of the biofilm is determined by the concentration and composition of the BOM fraction in the influent water (Huck et al., 2013; Volk and Lechevallier, 2002). These studies therefore suggest that the substrate concentration in the influent water influences the biofilter performance, but this is site-specific and cannot be controlled.

2.2.1.5 Pre-oxidation

Pre-oxidation can either increase or decrease biofiltration performance; and some commonly used pre-oxidation treatment steps include ozonation, free chlorine, and chloramine. A review from 2008 observed that dissolved organic matters (DOM) is transformed into compounds with a higher biodegradability during oxidation, which then can be removed more easily by biofiltration (Huck and Sozanski, 2008). However, if the pre-oxidation is with chlorine or chloramines, it might reduce the biomass growth and therefore negatively affect the microbial activity (Huck and Sozanski, 2008). Other studies indicated that ozonation prior to biofiltration impacts BOM concentration by increasing the biodegradable fractions of NOM and therefore increases the biofiltration performance (Huck et al., 2013; Volk and Lechevallier, 2002). These studies therefore suggest that

pre-oxidation steps, such as ozonation can increase biofiltration performance, while chlorine and chloramines might decrease biofiltration performance.

2.2.1.6 Filter Media

Researchers have tested different filter media to improve biofiltration performance, such as GAC, anthracite, sand, and dual-media filter (Barzi, 2008; Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001). GAC and anthracite remove total organic carbon (TOC) and BOM with the same efficiency at 20 – 25 ℃. However, at lower temperature, 1 – 10 ℃, GAC removes TOC and assimilable organic carbon (AOC) much more efficiently than anthracite (Emelko et al., 2006; Liu et al., 2001). Furthermore, a study found that GAC removes TOC better than sand or dual-media filter (LeChevallier et al., 1992). Moreover, bacterial biofilm attaches better to GAC due to the larger surface areas. Bacteria do not have access to the small pores, which are responsible for adsorption, however may be able to access the entrances to some of the larger external pores. There is some indication that the bacteria on the GAC may be able to consume the compounds attached to the adsorptions sites of GAC, which re-activate these adsorption sites and increase the removal of organics (LeChevallier et al., 1992; Volk and Lechevallier, 2002; Zhu et al., 2010), however this has not been widely demonstrated to be a significant contributor to process performance. Besides the media type, the media size also influences biofiltration performance. As introduced earlier, the dimensionless contact time (X*), which is used to calculate biofiltration performance, also include the media size (Huck and Sozanski, 2008; Huck et al., 2013; Zhang and Huck, 1996). X* shows that even though parameters such as media type and flow rate, stay the same, X* can still differ (Huck and Sozanski, 2008; Huck et al., 2013; Zhang and Huck, 1996). Huck and Sozanski (2008) showed that using a coarser media lead to a reduction in X*, while all other factors, such as flow rate, remained the same. All of these studies indicate that GAC filter media can have better biofiltration performance than, for example, anthracite, and the size of the media also influence biofiltration performance.

2.2.1.7 Empty Bed Contact Time

Studies proved that the performance of biofiltration is linked to EBCT, but EBCT varies depending on the operating conditions, but is usually between 5 and 20 minutes (Liu et al., 2017). One study reported an increase in the reduction of TOC from 29% to 51.2% when EBCT was increased from

5 to 20 minutes (LeChevallier et al., 1992). In contrast, another study found little change in reduction of TOC when EBCT was increased from 4 to 20 minutes (Hozalski et al., 1995). Furthermore, another study indicated that 50% of 40 full-scale drinking water treatment plants have an EBCT of 5 to 10 minutes, and when considering cost and maintenance this should be the target EBCT for optimal biofilter performance (Liu et al., 2017). The evidence presented here suggests that an optimal biofiltration performance might be kept by reaching an EBCT target of minimum 5 minutes.

2.2.1.8 Backwashing

Backwashing influences biofiltration performance, but it is dependant on backwash frequency, backwash type, and backwash duration. Backwashing is performed to avoid filter clogging and to keep an optimal biofiltration performance. Furthermore, there are different backwashing methods used at drinking water treatment plants and these are: oxidant-free water, and oxidant spiked water (e.g. chloraminated) (Emelko et al., 2006; Rasheed et al., 1998; Urfer et al., 1997; Zhu et al., 2010). However, if backwashing is being performed with free chlorine or chloraminated water, the backwash might reduce the biomass, since detachment and removal of biomass from the filter media occur along with removal of accumulated particles (Basu et al., 2016; Rasheed et al., 1998). Studies indicated that using air scour during backwash did not significantly increase biofilter performance (Emelko et al., 2006; Rasheed et al., 1998). Rasheed (1998) also showed that backwashing biofilters with chlorinated water reduced the microbial counts in the biofilter media and is detrimental to biofiltration performance. However, this study also pointed out that the last point should be confirmed by further research (Rasheed et al., 1998). Another study found that backwashing has to remove 60% or more of the biomass to have an impact of the biofiltration performance (Hozalski and Bouwer, 2001). Therefore, backwashing is not expected to have a quantifiable effect of biofiltration performance, but it depends on the specific biofilter how backwash frequency, duration, and backwash type influence the performance of the biofilter.

2.2.1.9 Operational Parameters Influence on NDMA during Biofiltration

Some studies indicated that when pH is high during chloramination and ozonation prior to biofiltration, the NDMA formation increases and keeping a pH below 8 helps both the biofiltration performance and decreases the NDMA formation potential (McCurry et al., 2017; Padhye et al.,

2011; Schreiber and Mitch, 2006a; Yang et al., 2009). Another study found that increasing water temperature led to increased NDMA formation during chloramination (Chang et al., 2011). These studies therefore indicate pH below 8 and low water temperatures can decrease the NDMA formation during chloramination and biofiltration.

Backwashing also influences NDMA formation potential development during biofiltration but it is also dependant on the backwash frequency, backwash type, and backwash duration. If backwashing is being performed with chloraminated water, the backwash might promote NDMA formation on subsequent chloramination. A study indicated that backwashing improved the biofilters removal of nitrosamines (Liao et al., 2015a). This study indicated a significant increase in removal performance, from 65% to 85%, of nitrosamine FP immediately after backwashing (Liao et al., 2015a). However, the removal of nitrosamine precursors decreased over time after backwashing, which is probably due to recovery of the microbial community. This study therefore indicates that a frequent backwash might decrease NDMA formation, but the frequency, duration, and backwash type depend on the specific biofilter used and the specific location.

2.2.2 NOM Removal as a Function of Biofilter Depth

As previously mentioned, biofiltration can remove NOM fractions, but there has only been one study conducted in biofiltration profiling of NOM removal by biofilter depth using LC-OCD and FEEM. This study created a biofiltration profile of NOM removal and measured the NOM characteristics, by LC-OCD and FEEM, at different depths in a drinking water pilot-scale biofilter, which was fed with water from the Grand River (Chen et al., 2016). This study sampled water over a two-month period and the results showed an increasing removal efficiency of BP and protein-like materials with increasing biofilter depth, and the removal efficiencies were >70% and >20%, respectively. However, this study only showed low removal of HS, BB, LMW fractions, HA, and FA of maximum 13%. Furthermore, this study also showed that DOC decreased with increasing media depth, as would be expected; the biofilter decreased DOC by 15% at 23 min EBCT. Lastly, the researchers stated that the biodegradability of the NOM components will differ depending on the source water characteristic and the biofilter (Chen et al., 2016). This also correlates to X*, which showed, because the kinetics are effectively first order, the percentage substrate removal in the biofilters would be independent of the substrate concentration in the influent water (Huck et

al., 2013; Zhang and Huck, 1996). More research in biofiltration profiling of NOM removal by biofilter depth is therefore needed.

2.3 NOM Characterization Techniques

There are many different analytical techniques to check the water quality and to perform a characterization of NOM, such as TOC, DOC, UV254, specific UV-absorbance (SUVA), LC-OCD, and FEEM. Each technique possesses some advantages and disadvantages, for example, LC-OCD divides NOM into different fractions whereas all the other techniques only characterize the bulk parameter. This section will describe the following two analytical techniques used to characterize NOM in this thesis: LC-OCD and FEEM.

2.3.1 LC-OCD

LC-OCD is a high performance size exclusion chromatography (HP-SEC) and was developed by Huber and Frimmel (Huber and Frimmel, 1991). LC-OCD is used to characterize NOM. Moreover, it is becoming a more popular HP-SEC measuring technique due to its high sensitivity and low sample preparation time. Additionally, LC-OCD separates NOM into molecular weight size fractions by eluting larger molecules first and smaller molecules last. These fractions are BP; HS; BB; LMW acids/humics; and LMW neutrals (Huber et al., 2011). An example of a typical LC-OCD chromatogram, which illustrates the signals for the various fractions, can be seen in Figure 2.1 below. In addition to an organic carbon detector, LC-OCD also comprises an organic nitrogen detector (OND), and an ultraviolet light detector (UVD) (Huber et al., 2011).

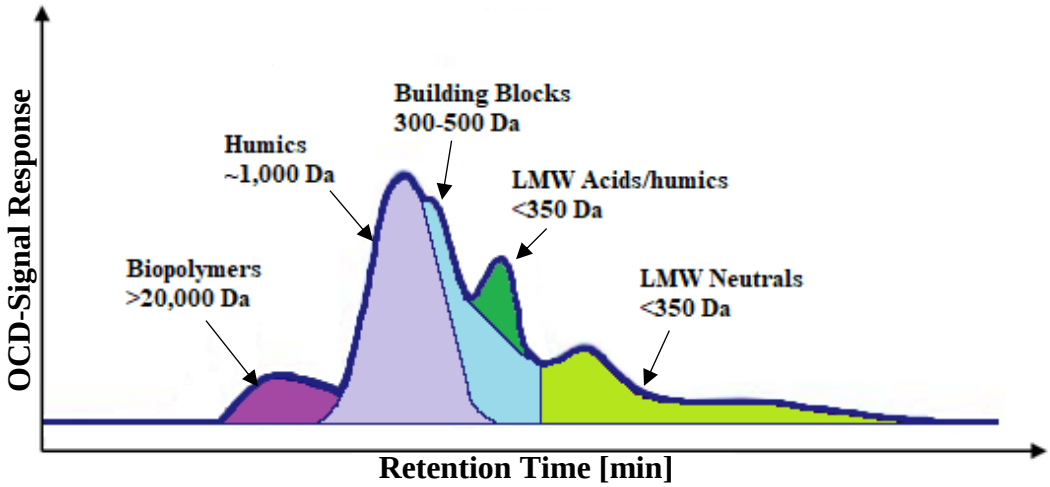


Figure 2.1. LC-OCD chromatogram integration boundaries for different LC-OCD fractions.

BP is the first peak on the chromatogram, in Figure 2.1, and this fraction has the highest molecular weight (>20kDa). Furthermore, the BP fraction is hydrophilic and consists of polysaccharide, polypeptides, proteins, and amino sugars, which almost all contain nitrogen compounds. Moreover, this fraction usually does not respond to UVD, which means that it does not contain any unsaturated structures (Huber et al., 2011). The second fraction, and the most dominant peak in OCD, is HS, which consist of HA and FA. HA are usually larger and elute faster than FA, and FA are usually smaller and hold a higher content of phenolic and carboxylic acids. Furthermore, FA usually show a high signal in OND, due to the nitrogen content, and UVD, due to the concentration of aromatic and unsaturated compounds in the FA fraction (Huber et al., 2011). The average molecular weight for this fraction is approximately 1 kDa (Velten et al., 2011a). The third fraction is BB, which elutes as a shoulder to the HS. This fraction consists of breakdown products from HS and it usually shows some UVD signal (Huber et al., 2011). The fourth fraction is LMW acids/humics, which is an aliphatic fraction. The last fraction is LMW neutrals and this fraction consists of hydrophilic and amphiphilic compounds, such as alcohols, aldehydes, ketones, sugars, and amino acids (Huber et al., 2011).

As previously mentioned, only a little research has been conducted in linking NOM characteristics from LC-OCD with NDMA formation. One study reported no correlation between NDMA and DOC from LC-OCD, but a reasonable correlation between NDMA formation and DON (Kristiana et al., 2017). However, another study found that NDMA FP is highly correlated to DON from LC-OCD, especially the DON fractions in BB and LMW fractions. This study also suggested that most of the NDMA precursors come from DON fractions with a molecular weight less than 500 g/mol (Qi et al., 2014). It is therefore inconclusive whether NOM characteristics from LC-OCD can be linked to NDMA formation and more research needs to be conducted.

2.3.2 FEEM

FEEM is also frequently used for characterization of NOM in water samples, since it is highly sensitive and inexpensive to use (Baghoth et al., 2011; Bieroza et al., 2009; Matilainen et al., 2011). In this method, excitation of electrons occurs when electrons absorb energy to reach a higher energy level, for example, by a photon. Afterwards, fluorescence occurs when the electron loses its energy by emitting light and returns to its ground state. The structure of the compound that absorbs light is called chromophores and when it emits light it is called fluorophores. Also, the

wavelengths where excitation and emission occur are specific for each functional group in the water sample (Hudson et al., 2007). Therefore, during FEEM analysis a 3-dimensional contour plot gets created, where the intensities are measured at different excitation and emission values. Usually in drinking water samples, the excitation values measured are between 250-380 nm and the emission values measure are between 300-600 nm. Peaks that can be observed on FEEM contour plots are: HA, FA, and protein-like material (tyrosine and tryptophan) (Baghoth et al., 2011; Bieroza et al., 2009; Hudson et al., 2007; Matilainen et al., 2011). Besides these peaks, the contour plots usually also contain light scattering regions. One of these scattering regions is Raman scattering, which is due to the light scattering properties of the O-H covalent bonds in water. Raman scattering is usually at excitation wavelengths between 260-350 nm and emission wavelengths between 280-400 nm. Another light scattering region is first and second order Rayleigh-Tyndall scattering, which is due to excitation energy reflected off the cuvette walls(Hudson et al., 2007).

Although there are many different techniques to analyse FEEM contour plots, peak picking is the technique that will be used in this thesis, due to its popularity and simplicity (Chen, 2016; Matilainen et al., 2011; Sierra et al., 2005). In this study the intensity for HA is measured at Ex/Em = 270 nm/460nm, the intensity for FA is measured at Ex/Em = 320nm/415nm, and intensity for protein-like materials is measured at Ex/Em = 280/330 nm (Chen, 2016; Matilainen et al., 2011; Sierra et al., 2005).

As stated earlier, there has only been little research conducted in linking NOM characteristics from FEEM with NDMA formation. However, several studies found no relationship between NDMA formation and NOM characteristics from FEEM (Bridgeman et al., 2011; Chen and Valentine, 2007; Ma et al., 2016a). On the other hand, other studies suggested a correlation between FEEM and NDMA formation (Fu et al., 2017; Hua et al., 2007; Sgroi et al., 2016; Wang et al., 2017; Yang et al., 2015). One of these studies reported a moderate relationship between protein-like materials measured from FEEM and NDMA FP (Fu et al., 2017). A second study also reported a significant correlation between a protein-like material, tryptophan-like components, from FEEM with NDMA FP (Yang et al., 2015). This correlation can be attributed to the composition of tryptophan-like components since they are rich in nitrogen and usually contain dialkylamine, which is a NDMA precursor (Yang et al., 2015). A third study found that waters with a peak at

around Ex/Em = 290-310nm/330-350nm were related to high NDMA FPs, and that FEEM could be a suitable parameter for monitoring NDMA FP (Hua et al., 2007). Lastly, another study reported that removal of the FA fraction in FEEM leads to decreases in NDMA FP and that removal of protein-like material in FEEM leads to increases in NDMA FP (Wang et al., 2017). It seems that some NOM characteristics from FEEM can be linked with NDMA formation but more research would be beneficial.

2.4 NDMA

This section will describe the current understanding of measuring techniques for NDMA, NDMA formation, NDMA precursors, and removal of NDMA and NDMA precursors.

2.4.1 Methods to Assess NDMA Formation Potential

The three mostly used methods to assess NDMA are: FP, realistic simulated distribution system (SDS) and UFC. The most commonly used technique to quantify NDMA is the FP test, which maximizes NDMA formation by applying a much higher monochloramine dose than used in drinking water treatment, which is 140 mg/L monochloramine for 10 days (Mitch and Sedlak, 2004). SDS and UFC tests were developed to gain information about NDMA formation under more realistic conditions (Koch et al., 1991; Shah et al., 2012). The SDS test mimics actual site-specific plant conditions and distribution systems to match the observed NDMA formation in a corresponding distribution system (Koch et al., 1991). Alternatively, UFC test mimics chloramination conditions at water treatment plants, where pH is first changed to pH 8 and then a sufficient chlorine dosage is applied during the UFC test to leave approximately 2.5 mg/L as chlorine after 3 min. Furthermore, ammonium chloride is added to reach a Cl_2:N ratio of 4.75:1 and then the sample is left in the dark for 3 days at 25 ℃ to react (Shah et al., 2012). Therefore, FP test maximises the NDMA formation while SDS and UFC tests show NDMA formation under more realistic conditions.

2.4.2 NDMA Formation

In this section the different NDMA formation pathways related to drinking water treatment and the influence nitrifying biofilters has on NDMA formation will be described. These mechanisms are: NDMA formation during chloramination and ozonation.

2.4.2.1 NDMA Formation during Chloramination

It has been proposed that the main NDMA formation mechanism is a reaction between chloramine and secondary amine precursors (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Mitch et al., 2003; Najm and Trussell, 2001; Schreiber and Mitch, 2006a). This reaction includes a nucleophilic substitution reaction between dichloramines and nitrogen precursors containing a N,N-dimethylamino group, which produce chlorinated unsymmetrical dialkylhydrazine (UDMH-Cl) intermediates, which through oxidation will form NDMA (Schreiber and Mitch, 2006a).

As previously mentioned, researchers have also indicated that during chloramination when the pH or temperature are increasing, the NDMA formation increases too (Chang et al., 2011; McCurry et al., 2017; Schreiber and Mitch, 2006a). A study suggests that when pH is increasing, the NDMA formation is increasing due to a higher amount of amines in their active unprotonated form (Schreiber and Mitch, 2006a). Another study found that during prolonged periods of low pH, monochloramines (NH_2Cl) is getting converted to dichloramines ($NHCl_2$). Then, when pH increases again, the NDMA precursors are converted to their more neutral forms, which then react with the higher amount of dichloramines resulting in a higher NDMA formation than when there was no pH change (McCurry et al., 2017). Besides from increased NDMA formation with pH, studies also reported that NDMA formation is increased with increasing water temperatures (Chang et al., 2011; Krasner et al., 2012b). Overall, these studies suggest that water quality parameters influence NDMA formation during chloramination.

Other recent studies reported that tertiary and quaternary amines can also serve as precursors. These amines are an important functional group in, for example, amine-based cationic polymers used during water treatment (e.g. polyDADMAC and polyamines), and pharmaceuticals (Le Roux et al., 2012a; Najm and Trussell, 2001; Selbes et al., 2013; Shen and Andrews, 2011, 2013; Zeng et al., 2016a). These amines are degraded to secondary amines, when exposed to chlorine or chloramines, which then form NDMA. A study indicated wide ranges, from 0.02% to 83.9%, of NDMA yield from tertiary amines and the yield depends both on the structure of the tertiary amines, and on the stability and electron distribution of the leaving group (Selbes et al., 2013). This study also indicated that some tertiary amines can form NDMA directly, if one of the alkyl substituents in the tertiary amine contained an aromatic group in the β-position to the nitrogen, for example, a benzyl functional group. Furthermore, this study also indicated that aliphatic and

aromatic tertiary amines with electron withdrawing groups mostly reacted with monochloramine to form NDMA while compounds with electron donating groups mostly reacted with dichloramines (Selbes et al., 2013). Together, these studies indicate that tertiary and quaternary amines can also be NDMA precursors, but they are not as potent NDMA precursors as secondary amines.

Other studies also found that NDMA formation increased when bromide was present in the water, since bromochloramine will be formed, which then forms a UDMH-Br intermediate (Le Roux et al., 2012b, 2012b; Luh and Mariñas, 2012). Overall, these studies report that this increase is significant at pH around 8 to 9, and this pH range is within the normal-high pH range for water during water treatment processes (Luh and Mariñas, 2012).

2.4.2.2 NDMA Formation during Ozonation

The NDMA formation during ozonation is significantly lower compared to the NDMA formation during chloramination (Yang et al., 2009). Researchers have proposed two possible NDMA formation mechanism during ozonation when pH is either neutral or alkaline. The first possible pathway is a reaction between secondary amines and hydroxylamines (NH_2OH), which is an oxidation by-product of ammonia and amines. This reaction forms an UDMH intermediate, which is then converted to NDMA. The second possible pathway is where dinitrogen tetroxide (N_2O_4) acts as a nitrosating reagent (Padhye et al., 2011; Yang et al., 2009). In addition, these studies also reported that the NDMA yield is increasing with increasing pH during ozonation, however the yield is generally low (0.02%) (Padhye et al., 2011; Yang et al., 2009). Nevertheless, if ammonia and bromide are present, the NDMA yield is significantly increased due to the UDMH-Br intermediate (Sgroi et al., 2014). Collectively, these studies indicate that NDMA is also getting formed through ozonation, but the NDMA formation is significantly lower than during chloramination. However, water quality parameters and the presence of bromide also increase NDMA formation during ozonation.

Other studies also suggested that tertiary and quaternary polymers containing an N,N-dimethylamino group (e.g. polyDADMAC) can form NDMA during ozonation. However, the NDMA yield is less than 0.01% (Oya et al., 2008; Padhye et al., 2011; Sgroi et al., 2014). On the contrary, some studies found that N,N-dimethylamino compounds containing either hydrazine,

hydrazide, 1,1,5,5-tetramethylcarbohydrazide, carbazide or sulfamide as a functional group had high NDMA formation yields between 10% to 140% during ozonation. However, NDMA was only formed from a sulfamide if bromide was present (Gunten et al., 2010; Kosaka et al., 2009, 2014; Lim et al., 2016; Schmidt and Brauch, 2008; Trogolo et al., 2015). Taken together, these studies indicate that tertiary and quaternary amines also serve as NDMA precursors during ozonation, but the NDMA yield is in general low.

2.4.2.3 Nitrifying Bacteria Influence on NDMA Formation

Some studies suggested that nitrifying bacteria might have a negative impact on NDMA formation (Krasner et al., 2015; Liu et al., 2017). There have been 3 studies in the last 10 years that are particularly relevant to nitrifying bacteria impact on NDMA formation. A study found that heterotrophic bacteria sloughed off soluble microbial products (SMPs), which formed 134 ng/L of NDMA FP and 36 ng NDMA/mg TOC (Krasner et al., 2008). However, when this experiment was repeated, no significant NDMA levels were observed from SMPs and there was only a low NDMA concentration on 1.6 ng NDMA/mg TOC, which was ascribed to precursors from heterotrophic bacteria (Krasner et al., 2015). This might be caused by the significant difference in the ammonia levels in the media in the two studies. In the first study the ammonia concentration was 3.6 mg N/L and during the second study it was only 0.78 mg N/L. The last study reported an increase in NDMA formation, under SDS conditions, in several full-scale chloraminated drinking water distribution systems. The researchers suggest that the nitrifying biofilms in the distribution system are responsible for the NDMA formation upon chloramination (Zeng and Mitch, 2016). The evidence presented here suggests that NDMA formation may correlate with nitrifying bacteria.

2.4.3 NDMA Precursors

This section describes the NDMA precursors sources from source waters; polymers, such as polyDADMAC; and microorganisms and biomass.

2.4.3.1 NDMA Precursors in Source Water

There are many nitrogenous compounds that are NDMA precursors, for example, pharmaceuticals, personal care products, amine-based polymers, herbicides, fungicides, pesticides, chelating agents,

and numerous unidentified compounds (Sgroi et al., 2018). Since there are several different types of NDMA precursors it is difficult to identify all of them, and only a few specific compounds have been related to substantial NDMA formation, such as anti-yellowing agents (Kosaka et al., 2009, 2014) or the fungicide tolylfluanide (Schmidt and Brauch, 2008). Aside from these cases, researchers have been unsuccessful in identifying precursors accounting for a significant portion of the NDMA formation.

However, several studies recognized that the source for the majority of the precursors within a watershed are introduced through the source waters (Aydin et al., 2012; Bei et al., 2016; Zeng and Mitch, 2015; Zeng et al., 2016b). A recent study indicated that the dominant source of NDMA precursors in surface water is wastewater discharge and their chloramine- and ozone-reactive precursors (Zeng et al., 2016b). The NDMA precursors in wastewater are site-specific and can, for instance, come from industrial discharges, such as anti-yellowing agents (Kosaka et al., 2009, 2014) or domestic wastewater. NDMA precursors from domestic wastewater are harder to control and consist of two fractions: greywater and blackwater. Greywater includes shower, kitchen, laundry, and sink water and personal care products (e.g. shampoos, detergents, etc.); and blackwater includes urine and feces (Kemper et al., 2010; Zeng and Mitch, 2015). The most significant source for NDMA precursors in the domestic wastewater fraction is laundry waters followed by shower water (both are greywater), and urine (blackwater) (Zeng and Mitch, 2015). However, studies indicated that waste water treatment plants (WWTPs) performing nutrient removal significantly reduced the nitrogen content and the NDMA precursors in their discharge (Gerrity et al., 2015; Mamo et al., 2016; Sgroi et al., 2016; Zeng et al., 2016b). Overall, these studies therefore suggest that source water, specially when contaminated with wastewater, contribute with the most NDMA precursors.

Other studies also indicated that algal blooms and agricultural or storm water runoff contain NDMA precursors, but these fractions are only important if they represent a major part of the water supply (Bei et al., 2016; Zeng et al., 2016b). However, natural processes in the environment are capable of decreasing the amount of NDMA precursors with an estimated half-life of 1.5 to 7 days (Schreiber and Mitch, 2006b; Woods and Dickenson, 2016). Research have indicated that maximizing the time water spends in the environment before it enters the plant might decrease the amount of NDMA precursors in the source water, for example, by large reservoirs and

impoundments on rivers (Schreiber and Mitch, 2006b; Woods and Dickenson, 2016). However, these reservoirs and impoundments can cause other problems, such as algal blooms.

2.4.3.2 NDMA Precursors from Polymers

As mentioned earlier, amine-based cationic polymers, such as polyDADMAC, are used as a coagulant or flocculant during drinking water treatment, and studies indicated that they form NDMA when free chlorine, chloramine or ozone is present (Mitch and Sedlak, 2004; Padhye et al., 2011; Park et al., 2009a, 2009b, 2015; Sgroi et al., 2014, 2016). A study found that polyDADMAC, under FP conditions, formed 31 ng NDMA/mg polymer active ingredient, and the polymer with the highest NDMA formation was Mannich with a formation of 114 μg NDMA/mg polymer active ingredient (Park et al., 2009b). Mannich still showed the highest NDMA yield upon ozonation with a yield on 0.011%, whereas the yield for polyDADMAC was 0.003% (Padhye et al., 2011; Sgroi et al., 2014). Researchers suggested the quaternary ammonium ring in polyDADMAC is degraded to dimethylacetamide (DMA) during either chloramination or ozonation, which is a NDMA precursor (Padhye et al., 2011; Park et al., 2009a, 2009b; Sgroi et al., 2014). Collectively, these studies indicate that amine-based cationic polymers form NDMA, but the NDMA yield is low.

Researchers proposed to modify the structure of, for example, polyDADMAC to inhibit NDMA formation during chloramination. Some studies suggested no NDMA formation from these modified polymers (Zeng et al., 2014, 2016a). Their approaches for modifying the structures involved three steps: first, treating the polymers with methyl iodide (MeI) to convert polymer bound tertiary amine groups to quaternary ammonium groups, which are less reactive with chloramine. Second, synthesizing polymers with the quaternary ammonium groups with dipropylamine (DPA) substituents, and last, using the modified polymers (Zeng et al., 2014, 2016a). Taken together, these studies indicate that using modified polymers prevent them from being NDMA precursors while still working as coagulants and flocculants.

2.4.3.3 Microorganisms and Biomass as NDMA Precursors

Some studies suggested that microorganisms, SMPs, and biomass might serve as NDMA precursors (Dickenson et al., 2017; Krasner et al., 2015; Liu et al., 2017). However, a study found

no significant NDMA formation either from several pure cultures of microorganisms or from lysed cells of either pure gram-negative or gram-positive bacterial cultures (Mitch and Sedlak, 2004). Also, this study indicated that no cellular constituents serve as NDMA precursors not even under NDMA FP conditions (Mitch and Sedlak, 2004). A compound must contain a dimethylamine group as its functional group to serve as an NDMA precursor, which is not the case for most biomolecules (Shah et al., 2012). However, albumin, N-acetylglucosamine, and phosphatidylcholine are biomolecule materials and they contain dimethylamine groups, but they did not form any significant levels of NDMA during the experiments (Mitch and Sedlak, 2004). Another study sampled raw eutrophic waters that contain both algal and bacterial cells during severe algal blooms; the average NDMA concentration was 9 ng/L under NDMA UFC conditions (Dickenson et al., 2017). The research cited indicates that, under the conditions studied, microorganisms and bacterial cells did not serve as NDMA precursors. This does not completely exclude the possibility that microorganisms or microbial material may contribute to NDMA formation, including the possibility that nitrifying biofilms can promote NDMA formation.

2.4.4 Removal of NDMA and NDMA Precursors

This section describes how different drinking water treatment process steps remove NDMA and NDMA precursors. This section describes the process steps: coagulation and lime softening; oxidation; adsorption to activated carbon; biofiltration; membrane filtrations such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis; and UV treatment. A summary of the removal efficiencies for NDMA and NDMA precursors can be seen in Table 2.1.

2.4.4.1 Removal by Coagulation and Lime softening

Since NDMA and its precursors also naturally appears in source waters, several studies studied how pre-treatment steps such as coagulation and lime softening influence NDMA and its precursors concentration. Studies reported that both coagulation and lime softening are ineffective at removing NDMA and its precursors (Beita-Sandí et al., 2016; Farré et al., 2011a; Krasner et al., 2012a; Mitch et al., 2009). Studies found that coagulation can remove less than 10% of NDMA and less then 10 to 30% of NDMA precursors and is therefore considered ineffective (Beita-Sandí et al., 2016; Farré et al., 2011a; Krasner et al., 2012a). In some cases, amine-based cationic polymers are used as coagulants, which as mentioned previously, increases the concentration of

NDMA (Krasner et al., 2012a). Furthermore, lime softening has also been proven to be ineffective at removing NDMA (Mitch et al., 2009). Some studies even suggested that lime addition can increase NDMA formation after chloramination due to the increase in pH (Krasner et al., 2012a; McCurry et al., 2017; Sgroi et al., 2015). Overall, these studies therefore indicate that coagulation and lime softening are ineffective at removing NDMA and they might even increase NDMA formation.

2.4.4.2 Removal by Oxidation

Oxidation processes are ineffective at removing NDMA, in fact some studies even found that several oxidants are responsible for NDMA formation (Lee et al., 2007a; Mitch et al., 2003). However, other studies suggested a significant reduction of both NDMA and its precursors when pre-oxidation with strong oxidants, such as ozone and free chlorine, was applied prior to chloramination (Chen and Valentine, 2008; Lee et al., 2007b, 2008; McCurry et al., 2015; Pisarenko et al., 2012; Shah et al., 2012; Wang et al., 2015; Yang et al., 2013). These studies also indicated that the most effective oxidant at reducing NDMA and its precursors was ozone. Nevertheless, other cases reported increase in NDMA FP after pre-oxidation and chloramination (Farré et al., 2012; Lee et al., 2007b; McCurry et al., 2015; Radjenovic et al., 2012; Selbes et al., 2014; Shah et al., 2012; Shen and Andrews, 2013; Zhao et al., 2008). Together, these studies suggest that it is inconclusive whether oxidation causes increases or decreases in NDMA and it is precursors.

2.4.4.3 Removal by Adsorption to Activated Carbon

Studies indicated that activated carbon is ineffective at removing NDMA (Fleming et al., 1996; Ho et al., 2011). However, other studies found that NDMA precursors were efficiently removed during adsorption in activated carbon media (Dai et al., 2009; He and Cheng, 2016; Zhu et al., 2001). A recent study reported that the impacts on NDMA FP is dependent on the water source and that PAC has a removal efficiency of 50 to 82% of NDMA FP in water impacted by wastewater. However, the removal efficiency was reduced to 10 to 30% in surface water (Beita-Sandí et al., 2016). The efficiency of NDMA removal depends on the pore size, surface areas, pH and chemistry of the sorbent materials (Beita-Sandí et al., 2016; Dai et al., 2009; He and Cheng, 2016; Zhu et al., 2001). When PAC is used after coagulation/flocculation in drinking water

treatment processes, the NDMA FP is further reduced by 20% with a PAC dose of 7-10 mg/L (Beita-Sandí et al., 2016). Another study also found reduction in NDMA FP of 37, 59, and 91% with a PAC dose of 3, 8, and 75 mg/L, respectively (Hanigan et al., 2012). Also, a full-scale study reported that GAC efficiently reduced NDMA FP with a removal efficiency of 54 to 84% in surface water, but the efficiency depended on the GAC bed life (Hanigan et al., 2012). A more recent study also suggested reduction in NDMA precursors by a pilot-scale GAC filter under SDS conditions (Chuang and Mitch, 2017). However, no studies reported complete removal of NDMA and its precursors from adsorption to activated carbon, which indicate that some precursors are strongly adsorbed onto the activated carbon, but other precursors are not (Beita-Sandí et al., 2016; Hanigan et al., 2012). Collectively, these studies suggest that adsorption to activated carbon is ineffective at removing NDMA, but it can decrease the NDMA precursor concentration by 10-91%.

2.4.4.4 Removal by Biofiltration

Several studies reported that biofiltration combined with pre-ozonation effectively can decrease NDMA formation (Barzi, 2008; Chuang and Mitch, 2017; Farré et al., 2011b; Krasner et al., 2012a; Liao et al., 2014, 2015b; Mitch et al., 2009; Selbes et al., 2016, 2017). One of these studies indicated that biofiltration combined with pre-ozonation removes NDMA formation and that the removal efficiency ranges from 2 to 87%, with a median of 52% at four different full-scale drinking water treatment plants (Krasner et al., 2012a). Furthermore, a pilot-scale study found a removal efficiency from biofiltration combined with pre-ozonation in NDMA FP from 60% to more than 90% in the NDMA precursors originating from wastewater (Hanigan et al., 2012). Also, another pilot-scale study suggested an average removal efficiency from biofiltration combined with pre-ozonation in NDMA under SDS conditions of 60% in wastewater impacted rivers (Barzi, 2008). Nevertheless, a more recent study indicated that ozonation decreased NDMA formation by 72% in one municipal wastewater discharge, but ozonation did not influence NDMA formation in the other municipal wastewater discharge. However, the NDMA formation in the first wastewater discharge, after pre-ozonation and biofiltration, was decreased by 86% and the other wastewater discharge decreased the NDMA formation by 38% (Chuang and Mitch, 2017). Taken together, these studies suggest that biofiltration combined with pre-ozonation decreases the NDMA formation potential, but that the efficiency of the biofilter depends on source water and the biofilter system.

In contrast to biofiltration combined with pre-ozonation, other studies using biofiltration combined with both pre-ozonation and pre-chloramination, sometimes reported an increase in NDMA formation and sometimes a decrease (Krasner et al., 2015; Liu et al., 2017). Some studies found an increase in nitrosamine after pre-ozonation combined with biofiltration, and they indicated that this might be due to sloughing off biomass and the release of both SMPs and intercellular organic matter (IOM) (Krasner et al., 2015; Liu et al., 2017). During 9 out of 15 full-scale sampling events, across 5 different drinking water treatment plants, the NDMA formation increased, during 4 sampling events the NDMA formation decreased, and at 2 sampling events the NDMA formation did not change (Krasner et al., 2015). Furthermore, this study had a removal efficiency ranging from -270% to 70%, and even at some of the utilities the results differed from each other during the different sampling events. The researchers ascribed the increase in NDMA FP to biomass that sloughed off from the biofilter and release of SMPs. Moreover, a subsequent survey with 23 samples confirmed the increase in NDMA FP in the biofilter effluent (Liu et al., 2017). 5 of these 23 samples showed little to no change, in 5 samples the NDMA FP decreased, and in 13 samples the NDMA FP increased after biofiltration and the NDMA precursor removal efficiency ranged from -344% to 38% (Liu et al., 2017). Collectively, these studies indicate that there are either an increase or decrease in NDMA formation after biofiltration, pre-ozonation, and chloramination. These studies also suggest that the increase in NDMA precursors after biofiltration might depend on location. These inconsistencies suggest that more research needs to be conducted by running bench, pilot, or full-scale experiments at various locations simultaneously under the exact same conditions for consistency. Furthermore, it is still unknown if biomass, SMPs or IOM can be considered NDMA precursors.

Researchers disagree whether, even without pre-ozonation, biofiltration increases or decreases the NDMA concentration (Liu et al., 2017; Pramanik et al., 2015). One study found high removal efficiency of NDMA precursors through biofiltration without pre-ozonation when plastic, sand, or GAC filter media was used (Pramanik et al., 2015). Furthermore, this study also suggested complete removal of NDMA precursors under NDMA FP conditions from 125 ng/L to 0 ng/L, when GAC filter media was used. However, another pilot-scale study indicated an increase in NDMA precursors in 93% of the sampling events after biofiltration under SDS conditions, and the highest increase in NDMA precursors was 90 ng/L (Liu et al., 2017). Also, in 80% of the samples in this study anthracite increased the concentration of NDMA precursors more than GAC (Liu et

al., 2017). Additionally, this study also showed that increasing EBCT from 3.1 to 6.2 minutes increased the concentration of NDMA precursors. Alternatively, the full-scale study reported an increase in NDMA precursors after biofiltration in just 78% of the samples, and the highest increase in NDMA precursors, under SDS conditions, was only 25 ng/L. Researchers indicated that the increase might be due to sloughing off SMPs, microorganisms or nitrifying bacteria. Overall, these studies suggest that there is either an increase or decrease in NDMA formation after biofiltration without pre-ozonation.

To sum up, all of the above-mentioned studies are therefore inconclusive how biofiltration impacts NDMA formation, since studies either reported a decrease, increase or no change at all in NDMA after biofiltration (Barzi, 2008; Chuang and Mitch, 2017; Krasner et al., 2012a, 2015; Liao et al., 2014, 2015b; Liu et al., 2017; Mitch et al., 2009; Selbes et al., 2016, 2017). More research is therefore needed to determine whether biofiltration can remove NDMA or its precursors.

2.4.4.5 Removal by Membrane Filtration

NDMA is, in general, not removed by microfiltration or ultrafiltration, and only partially removed by nanofiltration and reverse osmosis membranes. Neither microfiltration nor ultrafiltration can remove NDMA (Fujioka et al., 2012a, 2013a, 2013b; Plumlee et al., 2008; Sgroi et al., 2015). However, other studies reported that nanofiltration and reverse osmosis membranes can remove NDMA and the removal efficiency ranges from negligible to 54% (Fujioka et al., 2012b, 2012a, 2013c, 2013a, 2013b; Mitch and Sedlak, 2004; Plumlee et al., 2008; Sgroi et al., 2015). A laboratory-scale experiment indicated that nanofiltration rejected 8% of NDMA and four reverse osmosis membranes at low pressure, used at water reclamation, rejected 37 to 52% of NDMA (Fujioka et al., 2013a). Several full-scale studies for reverse osmosis found a lower rejection of NDMA in full-scale than at laboratory-scale and the overall NDMA rejection ranges from 4 to 54% (Fujioka et al., 2012a, 2013b; Plumlee et al., 2008; Sgroi et al., 2015). Taken together, these studies suggest that microfiltration and ultrafiltration are ineffective at removing NDMA, but nanofiltration can remove 8% and reverse osmosis can remove 4-54%.

Even though membrane filtration, in general, does not remove NDMA, several studies indicated that membrane filtration effectively removed NDMA precursors. Some studies indicated a reduction in NDMA precursors, expressed as formation potential, of up to 10% for microfiltration

and ultrafiltration (Fujioka et al., 2012a; Mitch and Sedlak, 2004). Furthermore, both laboratory- and full-scale tests suggested a reduction in NDMA FP of more than 98% for reverse osmosis membranes (Farré et al., 2011b; Krauss et al., 2010; Mitch and Sedlak, 2004). Also, a recent study in nanofiltration indicated a removal of NDMA precursors of 57 to 83% (Ersan et al., 2016). The evidence presented here suggests that microfiltration and ultrafiltration remove up to 10% of NDMA precursors, nanofiltration removes 57 to 83%, and reverse osmosis removes more than 98% of NDMA precursors.

Other studies indicated that different operational parameters, such as membrane permeate flux; the pH, ionic strength, and temperature of the water; and membrane fouling, influence the rejection of NDMA and its precursors in nanofiltration and reverse osmosis. One study found that a decrease in the pH of the source water from 9 to 3 resulted in a decrease in the rejection of NDMA both for nanofiltration and reverse osmosis (Fujioka et al., 2012b). This study also reported that a change in ionic strength from 26 to 260 mM in the source water resulted in a decrease in the rejection of NDMA from 52 to 34%. Additionally, an increase in temperature of the source water also resulted in a decrease in the rejection of NDMA, for example, the NDMA rejection dropped from 49 to 25% when the temperature increased from 20 to 30 ℃ (Fujioka et al., 2012b). In contrast, the rejection of NDMA increased when membrane fouling occurred and when permeate flux increased (Fujioka et al., 2012b, 2012a, 2013c, 2017). Overall, these studies indicate that a higher decrease in NDMA can be obtained when pH is high, ionic strength and temperature are low. Furthermore, increasing membrane fouling and permeate flux also resulted in higher decrease in NDMA formation.

2.4.4.6 Removal by UV Treatment

The most commonly used and effective treatment process to remove NDMA is UV treatment, (Afzal et al., 2016; Sharpless and Linden, 2003; Stefan and Bolton, 2002). However, to accomplish more than 90% reduction in NDMA, a UV fluence of ~1000 mJ/cm^2 is essential, which is a considerably higher dosage than required for disinfection and therefore much more energy intensive and expensive (Sharpless and Linden, 2003). UV irradiation is only partly effective at reducing NDMA precursors. Furthermore, studies suggested a removal of NDMA precursors of only up to 80% after UV treatment (McCurry et al., 2015; Sgroi et al., 2015; Shah et al., 2012).

Together, these studies indicate that UV treatment is the most effective method to remove NDMA, but it is very energy intensive, and UV treatment can only partly remove NDMA precursors.

2.4.4.7 Summary Table

Table 2.1 below summarises the removal efficiency of NDMA and NDMA precursors for each of the treatment processes mentioned above.

Table 2.1. NDMA and NDMA precursors removal by different water treatment processes

Process	NDMA removal (%)	NDMA precursors removal (%)
Coagulation	<10	<10-30
Lime softening	Ineffective	Ineffective
Oxidation	Some show increase in NDMA other show decrease	Some show increase in NDMA precursors other show decrease
Pre-oxidation prior to chloramination	Some show increase in NDMA other show decrease	Some show increase in NDMA precursors other show decrease
Adsorption to activated carbons	Ineffective	10-91
Biofiltration	Inconclusive	Inconclusive
Microfiltration	Ineffective	<10
Ultrafiltration	Ineffective	<10
Nanofiltration	8	57-83
Reverse osmosis	4-54	>98
UV treatment	>90	<0-80

2.5 Knowledge Gaps and Research Needs

The review of the literature reveals several research gaps, and they will be presented in this section.

2.5.1 Biofiltration Impacts on NOM removal

As mentioned earlier, not enough research has been conducted in how different operational parameters influence NOM removal during biofiltration. Also, all studies conducted until today are impossible to compare to each other because they were not run under the same conditions. Therefore, more research is needed to determine how these operational conditions influences NOM removal during biofiltration. Conditions that might influence biofiltration of NDMA include source water quality, operational parameters, media types, and nitrifying biofilm on the biofilter media. To research how these conditions influence NOM removal during biofiltration, some bench- and pilot-scale experiments should be conducted at various locations simultaneously under

the exact same conditions for consistency. During these experiments, only one condition should be changed at a time, or else a factorial design should be conducted, which will allow the results to be compared to each other. The impacts from the above mentioned conditions on NOM removal during biofiltration provide insight into control strategies for NOM, which would allow water facilities to optimize their drinking water quality.

2.5.2 Biofiltration Profile and Kinetics of NOM Removal by Biofilter Depth

A study in biofiltration profiling and kinetics of NOM removal has been conducted by Chen et al. (2016), and this study focused on removal behaviours and kinetics for different NOM fractions throughout the media depth. However, additional research would be beneficial on how different operational parameters influence the biofiltration profile of NOM removal and their kinetics. These parameters include media type (GAC vs. anthracite), backwash type (chloraminated vs. non-chloraminated water), backwash frequency, and ammonia addition. Knowing how these parameters influence the biofiltration profile and its kinetics of NOM removal will optimize biofiltration performance, contribute a better insight into control strategies for NOM, and it will also expand the usage of biofiltration as a treatment alternative for water facilities. Also, by implementing biofilters in water facilities and optimizing biofiltration performance, consumers will have higher quality drinking water.

2.5.3 Linking NOM Characterization from LC-OCD and FEEM with NDMA Formation

As previously mentioned, DOC is a potential NDMA precursor, but whether the NOM characteristics, from LC-OCD and FEEM, can be linked with NDMA formation were only investigated by a few studies. Therefore, more research needs to be conducted to investigate whether a linkage between NOM characteristics, from LC-OCD and FEEM, and NDMA formation can be established. NDMA is difficult, time consuming, and expensive to monitor, and some NOM characteristics are easier and faster to measure. Some water facilities are already running different NOM characterization techniques. NOM characterizations, from LC-OCD and FEEM, could be a better monitoring technique to quantify the NDMA formation and water quality. This would also provide better insight into control strategies for NDMA, which would allow water facilities to

minimize the NDMA formation in, for example, our drinking water. This could therefore decrease our exposure to NDMA and reduce our risk for cancer.

2.6 Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for their use by the authors or funding agencies.

Chapter 3
Influence of Pre-ozonation, Source Water, and Media Acclimated/Operated in Different Water Sources on NOM Fraction Removals in Bench-scale Biofilters

3.1 Introduction

NOM is a mixture of organic compounds that are present in all water bodies. The composition and properties of NOM are site specific and are therefore significantly impacted by the water source at a specific location (Thurman, 1985). The conditions in the specific water source that impact NOM include water quality, and discharge into the water upstream of the water intake. Furthermore, NOM can cause aesthetic problems in drinking water including taste and odour problems but the severity of the problem depends on the concentration and composition of the NOM in the water (Baghoth et al., 2011). Another problem that NOM can cause in drinking water is the formation of potential carcinogenic DBPs, and one of these DBPs is NDMA, which can be formed when NOM reacts with disinfectants (Chang et al., 2013; Chen and Valentine, 2007; Chuang et al., 2013; Crittenden et al., 2012; Kristiana et al., 2013; Lee and Westerhoff, 2006; Richardson and Ternes, 2014). NOM in drinking water might also contribute to corrosion and bacterial regrowth throughout the distribution system; lead to higher coagulant demands; transport metals and hydrophobic chemicals; and interfere in adsorption processes of other contaminants (Jacangelo et al., 1995).

It is therefore desirable to reduce elevated concentrations of NOM in drinking water, and one of the treatment steps for removing NOM in drinking water is biofiltration. Other treatment steps that remove NOM include coagulation/flocculation, adsorption, oxidation, and membrane filtration (Kristiana et al., 2013; Zhang et al., 2015). Biofiltration is a filter process with a biologically active filter media due to a bacterial biofilm attached on the surface of the media. Some commonly used media types include GAC, anthracite, expanded ceramics, plastics, sand, and gravel (Basu et al., 2016; Simpson, 2008). Biofiltration is gaining popularity due to its ability to biodegrade organic and inorganic constituents, low maintenance, simple to operate, and their ability to remove fine particulate (Bablon et al., 1988; Basu et al., 2016). Since the composition of NOM is significantly

impacted by the water source, the water source therefore potentially influences the removal of NOM during biofiltration. Also, the water source will influence the biofilm on the biofilter media, and media acclimated/operated in different water sources therefore also potentially influence the removal of NOM during biofiltration.

There are multiple analytical techniques to characterize the NOM fractions in water samples. Two of these analytical techniques are LC-OCD and FEEM. Some advantages of LC-OCD and FEEM are their ability to characterize multiple NOM fractions in a water sample, their high sensitivity, their low sampling preparation time, and their low operational costs. These techniques are therefore becoming more frequently used NOM characterization tools in analyzing drinking water samples. LC-OCD and FEEM are based on different physical principles and they can therefore combined help describe compositional and physicochemical properties of various NOM components. Therefore, this study will use these two analytical techniques to measure the water quality and to characterize NOM.

LC-OCD is becoming a more popular analytical technique that provides information on the organic carbon and organic nitrogen content, and UV properties of various NOM fractions. Furthermore, LC-OCD separates the sample by size and the NOM is therefore separated into five fractions: BP (e.g. polysaccharides, proteins, and amino sugars), HS (e.g. HA and FA), BB (breakdown products of HS), LMW acids/humics (e.g. aliphatic compounds), and LMW neutrals (e.g. alcohols, aldehydes, ketones, sugars, and amino acids) (Huber et al., 2011). These fractions are of particular interest since these fractions can act to differing degrees as precursors to DBPs (Wassink et al., 2011). Also, studies have shown that BP can contribute to hydraulically reversible and irreversible fouling of low pressure membranes (Hallé et al., 2009; Peldszus et al., 2012; Tian et al., 2013), and LMW acids/humics can contribute to biofouling of certain membranes (Huck and Sozanski, 2008). However, LC-OCD has a relatively long signal acquisition time, making it unsuitable for online application (Peiris et al., 2008). Also, LC-OCD requires filtration of the samples prior to measurement and it is therefore not suitable for measuring colloidal/particulate matter.

FEEM is also becoming a more popular analytical technique due to its many attractive advantages. FEEM detects molecules in the NOM fraction that contain fluorophores and is therefore capable of characterizing intrinsically fluorescent NOM groups. It is therefore capable of identifying three different fractions: HA, FA, and protein-like materials (e.g. tyrosine and tryptophan). These groups

are quantified in this study by applying peak picking (Baghoth et al., 2011; Bieroza et al., 2009; Hudson et al., 2007; Matilainen et al., 2011). These fractions are also of particular interest since HA and FA are components in HS, as measured by LC-OCD, which potentially can act as precursors to DBPs (Wassink et al., 2011). Also, protein-like materials (from FEEM) are a component in BP, as measured by LC-OCD, which potentially can contribute to low pressure membrane fouling (Hallé et al., 2009; Peldszus et al., 2012; Tian et al., 2013).

The main objectives of this study were to assess the impacts of pre-ozonation, water sources, and media acclimated/operated in different water sources on NOM removal through bench-scale biofilter columns. To investigate how these parameters impact the NOM removal during biofiltration, bench-scale biofilter tests were executed simultaneously at three different WTPs with biofilter media from these three plants. Because only one of these facilities is using pre-ozonation, this study therefore also investigated how pre-ozonation influences NOM removal during biofiltration. The three different biofilter media were tested at each of the three plants simultaneously under the exact same conditions. The only condition that differed between these bench-scale tests was the water source. Overall, the insights gained from this study may be of assistance to conclude whether the change in NOM removal during biofiltration is due to the water source or the biofilter media.

3.2 Material and Methods

An experiment using bench-scale columns was conducted, which is described in Table 3.1. This test ran for six consecutive weeks (from 09.05 2018 to 18.06 2018) simultaneously at three different locations: Facilities B, I, and L. Each location tested the same three biofilter media, which were collected at the three locations mentioned above. The author contributed to the design, and then installed, operated, collected samples, analyzed and interpreted all the data for the entire bench-scale experiment at Facility B. The University of Minnesota (Ben Ma and Dr. Raymond Hozalski) constructed the bench-scale columns used at Facilities I and L, and they also installed, operated, sampled, and analyzed the samples from the bench-scale experiment at Facility I. The staff members at Facilities I and L helped by providing information about their full-scale treatment processes, and with the installation, operation and sampling of the bench-scale tests at Facilities I and L. All the NOM characterization samples were shipped to the University of Waterloo, where Lin Shen performed all the LC-OCD sample analysis and the author performed all the FEEM

sample analysis. All the samples for NDMA UFC determination were shipped to and analyzed by Stanford University (Zhong Zhang and Dr. Bill Mitch). The interpretation, writing and analysis of all the data presented in this chapter were conducted by the author.

Two days prior to the tests started, the plant operators at each location collected approximately 10L of biofilter media from the top 15 cm of the full-scale biofilters. The media samples were collected mid-cycle, 24 hours after backwash, transferred into a sterile plastic bucket, and transported back to the laboratories. In the laboratory, the media were stirred gently and transferred into 1L sterile plastic bottles. Approximately, 2L of each media was shipped to each of the three locations, Facilities B, I, and L, on ice with overnight shipment. The rest of the biofilter media were stored in a 4℃ fridge for two days. Once the media from the other locations arrived, the media were also stored in a 4℃ fridge until the tests started. Just before the tests started, the media were taken out of the fridge, stirred gently and added directly to each column. Each test location included six columns, three sets of duplicate columns, all fed the same water as the full-scale biofilters. However, the bench-scale column test at Facility B included two additional columns, one extra set of duplicate columns, which were fed with pre-ozonated water. The column IDs, media source, and influent water can be seen in Table 3.2.

Table 3.1. Overview of media source, influent water, and schedule for the bench-scale test

Location	Bench-scale biofilter influent water	Media sources	Dates
Facility B	Facility B full-scale pre-ozonated water, and post-ozonated biofilter influent water	Same media sources at all test locations, (i.e. from Facilities B, I, and L)	09.05.18 - 18.06.18
Facility I	Facility I full-scale biofilter influent water		
Facility L	Facility L full-scale biofilter influent water		

Table 3.2. Overview of column ID, and media source for the bench-scale column test

Column ID	Media source
1A	Facility B
1B	Facility B
2A	Facility I
2B	Facility I
3A	Facility L
3B	Facility L
4A*	Facility B
4B*	Facility B

** These columns were only located at Facility B.*

3.2.1 Setup at Facility B

The bench-scale column test at Facility B was run by the University of Waterloo, and the schematics for this location can be seen in Figure 3.1. The columns used for this setup were gravity fed glass columns (5 cm inner diameter and 65 cm length) with a stainless steel metal filter mesh, a PVC cap at the bottom, and an open top. All tubing used for the entire setup were 1/4 inch PTFE tubing. The operational parameters are shown in Table 3.3.

Table 3.3. Operational parameters for bench-scale experiments

Operational parameter	Unit	Value
Effluent flow per column	L/day	60.5
Media depth	cm	25.4
EBCT	min	12
Hydraulic loading	m/h	1.3

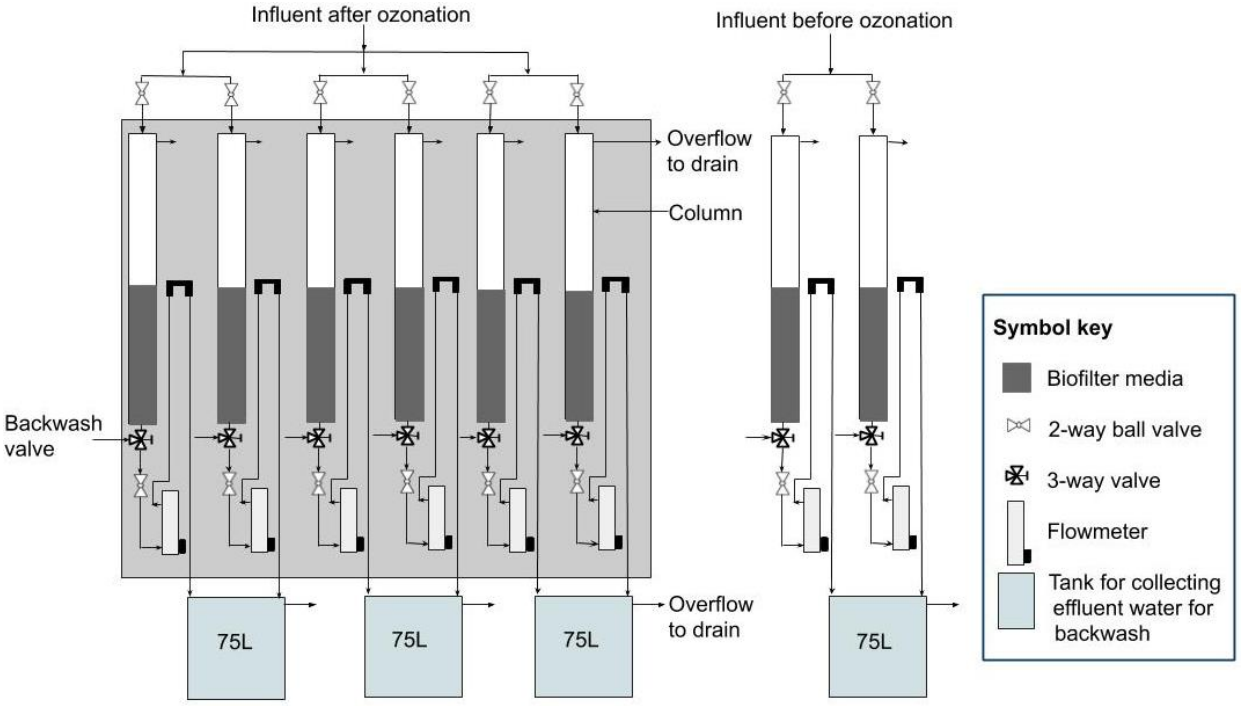


Figure 3.1. Schematics for bench-scale experiments at Facility B
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Samples were collected weekly or twice per week. Table 3.4 shows the analytical parameters measured, including sample location and time. After sampling, all parameters were analyzed at the University of Waterloo aside from NDMA UFC and qPCR which were shipped to Stanford University and the University of Minnesota, respectively.

Table 3.4. Analytical parameters, sample location, and time at Facility B

Analytical parameters	Sample location	Sampling time
pH	Influents	09.05 2018 14.05 2018 21.05 2018 04.06 2018 18.06 2018
Temperature, DO, turbidity, TOC, UV254, ammonia, nitrite, nitrate	Influents and effluents from each column	
LC-OCD	Influents and effluents from each column	14.05 2018 21.05 2018 04.06 2018 18.06 2018
FEEM	Influents and effluents from each column	14.05 2018 18.06 2018
NDMA UFC	Influents and effluents from 1A, 1B, 2A, 3A, 4A	09.05 2018
	Influents and effluents from 1A, 2A, 2B, 3A, 4A	14.05 2018
	Influents and effluents from 1A, 2A, 3A, 3B, 4A	21.05 2018
	Influents and effluents from 1A, 2A, 3A, 4A, 4B	04.06 2018
	Influents and effluents from 1A, 1B, 2A, 3A, 4A	18.06 2018
ATP and qPCR	Media for each column	07.05 2018 18.06 2018

Backwash was only conducted when the head loss got too high. In this experiment, it was necessary to backwash the columns every 2 to 3 days. When backwashing was performed, water from effluent tanks was fed to the columns in an upward motion at around 1.5 L/min to reach a filter bed expansion of approximately 30-50%. Each backwash was performed until the backwash water did not show any discoloration or particles, which usually took approximately 10 minutes. During backwashing, peristaltic pumps with Norprene tubing were used.

3.2.2 Setup at Facilities I and L

The bench-scale column tests at Facilities I and L were both run by the plant operators at the WTPs and the setup at these plants was identical, see Figure 3.2. The columns used at both plants were provided by the University of Minnesota, made of polycarbonate, and had an inner diameter of 5 cm, and a length of 30 cm. These tests were also run under the same operational parameters as at Facility B (Table 3.3). However, the columns at Facility B were gravity fed whereas the columns at the other facilities were pressurized and fed with water in a down-flow mode. All tubing used was ¼ inch stainless steel tubing aside from the tubing for the peristaltic pumps, which was Norprene tubing.

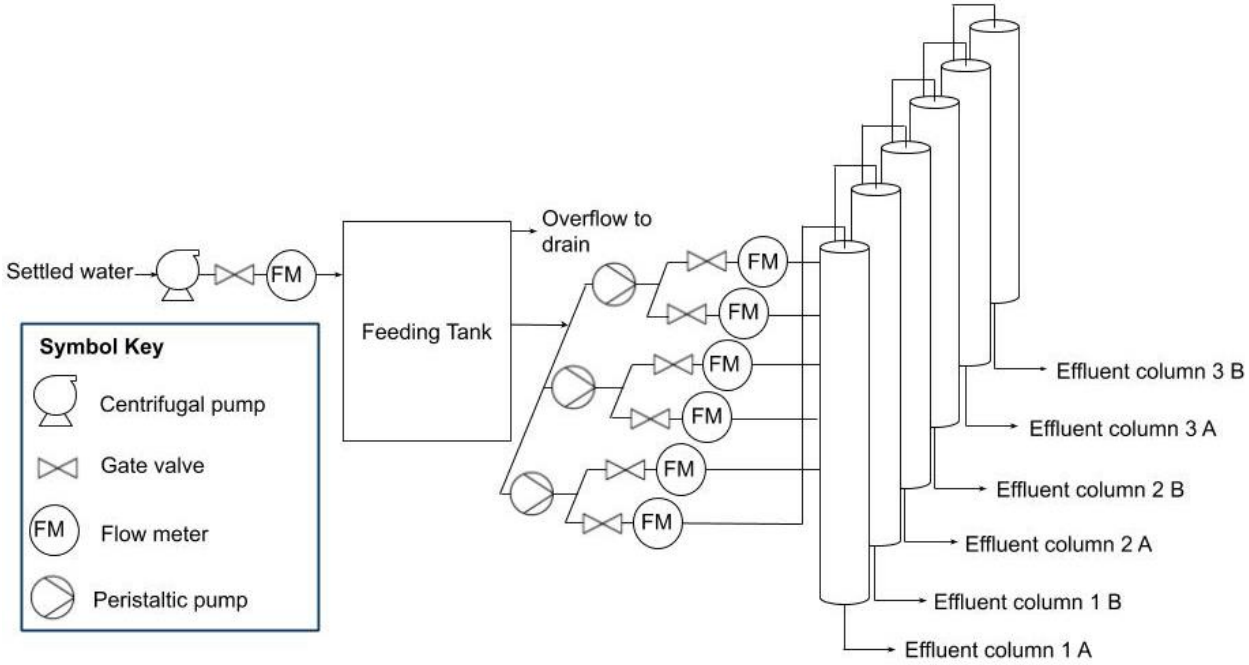


Figure 3.2. Schematics for bench-scale experiments at Facilities I and L

Samples were collected on weekly or twice per week; the analytical parameters measured in this experiment, including sample location and date, can be seen in Table 3.5. After sampling, all parameters were analyzed by the treatment plant operators aside from LC-OCD and FEEM which were analyzed at the University of Waterloo; NDMA UFC, at Stanford University; and qPCR at the University of Minnesota.

Table 3.5. Analytical parameters, sample location, and time at Facilities I and L

Analytical parameters	Sample location	Sample time
pH	Influent	09.05 2018 14.05 2018 21.05 2018 04.06 2018 18.06 2018
Temperature, DO, turbidity, TOC, UV254, ammonia, nitrite, nitrate	Same sampling locations as NDMA UFC	
LC-OCD	Influent and effluents from each column	14.05 2018 21.05 2018 04.06 2018 18.06 2018
FEEM	Influent and effluents from each column	14.05 2018 18.06 2018
NDMA UFC	Influent and effluents from 1A, 1B, 2A, 3A	09.05 2018
	Influent and effluents from 1A, 2A, 2B, 3A	14.05 2018
	Influent and effluents from 1A, 2A, 3A, 3B	21.05 2018
	Influent and effluents from 1A, 1B, 2A, 3A	04.06 2018

	Influent and effluents from 1A, 2A, 2B, 3A	18.06 2018
ATP and qPCR	Media for each column	07.05 2018 18.06 2018

3.2.3 Analytical Parameters

All the parameters were determined in the laboratory at each test location. Temperature was determined directly on-site immediately after sampling by using a thermometer and following Standard Methods: 2550 B. DO was also measured directly on-site immediately after sampling using a DO pen (model # 850045 from Sper Scientific, Scottsdale, AZ) and following Standard Methods: 4500-O G Membrane Electrode Method. pH was measured on Orion model 420A pH meter (Thermo Scientific, Waltham, MA) following Standard Methods: 4500-H^+ B Electrometric Method. Turbidity was measured on Hach 2100Q (Hach, London, ON) and following Standard Methods: 2130 B Nephelometric Method. UV254 was measured on filtered samples only, using a Cary 100 UV-Vis Spectrophotometer (Agilent Technologies, Santa Clara, CA), and following Standard Methods: 5910 B Ultraviolet Absorption Method. Ammonia, nitrite and nitrate were measured on Hach DR1900 (Hach, London, ON) and by following the standard methods: Hach 8155 and Standard Methods: 4500-NH_3 for ammonia; Hach 8507 and Standard Methods: 4500-NO_2^- for nitrite; and Hach 8171 and Standard Methods: 4500-NO_3^- E Cadmium Reduction Method for nitrate. However, data for NDMA UFC was obtained from Stanford University; qPCR from the University of Minnesota; and LC-OCD and FEEM from the University of Waterloo.

3.2.3.1 LC-OCD

Liquid chromatography organic carbon detection–organic nitrogen detection-ultraviolet light detection (LC-OCD-OND-UVD) (DOC-Labor Dr. Huber, Karlsruhe, Germany) was conducted at the University of Waterloo. LC-OCD-OND-UVD was performed on filtered samples, which were each filtered through a 25 mm sterile syringe filter with 0.45 μm Supor membrane (Pall Life Sciences, Washington, NY). After filtration, the samples were stored at 4℃ until analysis, which usually occurred within 72 hours of sampling. LC-OCD was equipped with a size exclusion column (TSK HW-50S, 3000 theoretical plates from Tosoh Bioscience, Tokyo, Japan). The mobile phase in the column was 28 mmol/L phosphate buffer at 1mL/min with a resin separation range of 0.1 to 18 kDa. The eluted sample passed through the three detectors, mentioned above, which determined the content of organic carbon, organic nitrogen, and the UV absorbance at 254 nm.

OCD was measured on the sample after it was oxidized to CO_2 in a Gräentzel thin film reactor; and OND was measured on a side stream prior to the Gräentzel thin film reactor where the organic nitrogen was converted to NO_3 (Huber et al., 2011). The chromatograms generated by this LC-OCD-OND-UVD were integrated using the customized ChromCALC Software (DOC-Labor Dr. Huber, Karlsruhe, Germany).

3.2.3.2 FEEM

FEEM was conducted at the University of Waterloo, and it was performed on filtered samples, which were filtered through the same type of syringe filters as LC-OCD, and then stored at 4℃ until analysis. The analysis usually occurred within 48 hours of sampling on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, Santa Clara, CA) in quartz cuvette. The split widths for the emission wavelengths was set to 1 nm, and ranged from 300 to 600 nm. The split widths for the excitation wavelengths was set to 10 nm, and ranged from 250-380 nm. The Raman scattering regions were removed by subtracting the FEEM spectra for MilliQ water from the samples. Peak picking was used to categorize the three FEEM fractions: HA, FA, and protein-like materials (Chen, 2016; Matilainen et al., 2011; Sierra et al., 2005). The intensities for these fractions were measured at Ex/Em = 270 nm/460nm for HA, Ex/Em = 320nm/415nm for FA, and Ex/Em = 280/330 nm for protein-like materials (Chen, 2016).

3.2.3.3 NDMA UFC

NDMA UFC was performed at Stanford University. NDMA UFC measures the NDMA formation in water samples by mimicking the chloramination conditions at the water treatment plants. NDMA UFC was performed on each 500 mL water sample where pH was increased to 8.0 with borate buffer. Increasing pH to 8 prior to chloramination is a typical practice at DWTPs in the U.S. After the pH increase, sufficient chlorine was added so approximately 2.5 mg/L was present as chlorine after 3 minutes. Then, 0.53 mg/L of ammonium chloride was added to reach a Cl_2:N ratio of 4.75:1, which with the chlorine formed chloramines. Subsequently, the water samples were stored in the dark for 3 days at room temperature to react. After the 3 days, the chloraminated samples were quenched with 33 mg/L ascorbic acid (Shah et al., 2012). The NDMA UFC levels were then measured in a modified Solid-phase extraction/gas chromatography/mass spectrometry (SPE/GC/MS) by employing USEPA method 521, which can capture 8 nitrosamines: NDMA, N-

nitrosomethylethylamine, N-nitrosopiperidine, N-nitrosodiethylamine, N-nitrosodipropylamine, N-nitrosodibutylamine, N-nitrosopyrrolidine, and N-nitrosomorpholine (Zeng and Mitch, 2016).

3.2.3.4 ATP

ATP was performed in the laboratory at each test location, and each location measured ATP on the unwashed media using a Turner BioSystems Modulus Luminometer model # 9200-102 (LuminUltra, Baltimore, MD) following ASTM Standard Method: D4012. First, water was pipetted off the media sample, then 1 g of media was added to 5 mL Ultralyse 7 reagent, mixed well together, and incubated for 5 minutes. After 5 minutes of incubation time, 1 mL from the Ultralyse 7 reagent was added to 9 mL Ultralute reagent. Immediately after, 100 µL of this Ultralute reagent was added into a clear sterile microfuge tube containing 100 µL Luminase reagent. This microfuge tube was swirled gently 5 times and the RLU value was measured within 1 minute. During each analytical event, a standard was measured, which was done by mixing 100 µL of Ultracheck 1 (ATP standard, 1 ng ATP/mL) with 100 µL of Luminase reagent in a clear sterile microfuge tube. Afterwards, this sample was swirled gently 5 times, and the RLU value was measured within 1 minute. Furthermore, the dry-weight of the media was also measured, by drying 1 g of wet media in a 110℃ oven for at least 48 hours, or until the media was completely dry. All this information was used to calculate the total ATP by using the following equation provided by the supplier:

$$Total\ ATP\ \left(\frac{ng}{cm^3}\right) = \frac{RLU(sample)}{RLU(Standard)} \cdot \frac{50{,}000(\rho g\ ATP)}{dried\ sample\ weight\ (g)} \cdot \frac{density\ (\frac{g}{cm^3})}{1000(\frac{\rho g}{ng})}$$

3.2.3.5 TOC

TOC was conducted at the University of Waterloo on unfiltered water samples and analyzed within 48 hours of sampling. After sampling, the water samples were stored at 4℃ until analysis. However, if the samples could not be analyzed within 48 hours, then the samples were preserved by adding phosphoric acid until the samples reached pH 2. The preserved samples were then stored at 4℃ until analysis, which had to occur within 28 days. TOC was measured on GE Sievers TOC M9 instrument (SUEZ Water Technologies & Solutions, Trevose, PA) by following Standard Methods: 5310 C Persulfate-UV or Heated-Persulfate Oxidation Method. Each sample was

measured 5 times, and then an average of these measurements was calculated and used as the TOC value.

3.3 Results and Discussions

3.3.1 Water Quality of Bench-scale Biofilter Feed

At each facility, the bench-scale columns were located at the full-scale plants and they were fed with the same water as the full-scale biofilters.

3.3.1.1 Raw Water Sources and Treatment Processes Prior to Biofiltration at Full-scale Plants

The raw water source at Facility B is from a river in Southern Canada. The full-scale treatment steps at Facility B prior to the biofilters include the conventional treatment steps: coagulation, flocculation, and sedimentation, and ozonation. The coagulant used at Facility B is Polyaluminium Chloride (Stern PAC) and the polymer used is Cationic Magnafloc (LT22S). The raw water source at Facility I is from a river in Northern USA. The full-scale treatment steps prior to the biofilters include the conventional treatment steps: coagulation, flocculation, and sedimentation, and lime softening and recarbonation. The coagulant used at Facility I is Aluminium Sulfate. The raw water source at Facility L is from a reservoir in Western USA. The full-scale treatment steps prior to the biofilters only include the conventional treatment steps: coagulation, flocculation, and sedimentation. The coagulant used at Facility L is Alum and Ferric Chloride and the polymer used is Cationic PolyDADMAC (C-308P). Overall, all test locations use an aluminium coagulant, which makes it possible to compare the test locations. Also, the main differences between these facilities are that Facility B has ozonation and Facility I has lime softening and recarbonation prior to the biofilters, which might influence the NOM composition in the influent to the biofilters.

3.3.1.2 Water Quality of Biofilter Influents

Table 3.6 shows that the bench-scale influent water quality at all facilities was fairly constant throughout the experiments, except for temperature, dissolved oxygen (DO), and UV254. The temperature increased at Facility B from 15.5 °C to 23.6 °C, from 9 °C to 22 °C at Facility I, and from 10.3 °C to 13.1 °C at Facility L. This is due to increasing ambient temperatures when

transitioning from spring to summer (Table A.2, Table A.3, and Table A.4 in Appendix A, respectively). DO varied at each Facility but there was no clear trend when it increased or decreased. UV254 was rather constant at Facilities I and L, but the UV254 values were much higher both for the pre- and post-ozone influents at Facility B during week 6. It is not known what caused this high increase in the UV254 values, but the TOC values were also increased during week 6 (Table A.1 and Table A.2 in Appendix A). The pH in the influents at Facilities B, I, and L were near neutral and only ranged from 7.7 to 8.0 at Facility B, 7.8 to 8.1 at Facility I, and 6.7 to 7.0 at Facility (Table A.2, Table A.3, and Table A.4 in Appendix A, respectively). The turbidity in the influents at Facilities I and L were very low, but the turbidity in the pre- and post-ozone influents at Facility B were higher and varied more (Table 3.6). However, these turbidity values are in the usual range for water going on to filters. Facility L was the only test location that added chlorine prior to the biofilters, and the chlorine level was relatively low (Table 3.6). The total ammonia and nitrite were low in all the influents at Facilities B, I and L, except for total ammonia at Facility L (Table 3.6). The nitrate was only measured at Facilities B and I, and the nitrate concentration was higher, although still moderate, in the influents at Facility B, but very low at Facility I (Table 3.6). The TOC was only measured at Facility B and the concentrations were very similar in the pre- and post-ozone influents. Overall, Facility B post-ozone influents, in general, had the highest concentrations for the measured water quality parameters, and Facility L, in general, had the lowest water quality concentrations. Also, the pre-ozone and post-ozone influents at Facility B had very similar water quality concentrations except for DO, nitrite, and UV254.

Table 3.6 Influent water quality at Facilities B, I and L

	Units	Facility B pre-ozone	Facility B post-ozone	Facility I	Facility L
pH		7.8 ± 0.2	7.7 ± 0.1	7.9 ± 0.2	6.8 ± 0.2
Temperature	**°C**	19.2 ± 4.0	19.0 ± 4.6	16.1 ± 7.1	12.6 ± 2.5
DO	**mg/L**	8.9 ± 1.4	15.8 ± 4.3	9.8 ± 3.0	9.3 ± 1.7
Turbidity	**NTU**	1.2 ± 0.44	1.4 ± 0.55	0.34 ± 0.22	0.24 ± 0.06
Total Chlorine	**mg/L**	N/A	N/A	N/A	0.39 ± 0.13
Total ammonia	**mg/L**	0.02 ± 0.02	0.03 ± 0.03	0.029 ± 0.026	0.11 ± 0.06
Nitrite	**mg/L**	0.012 ± 0.005	0.005 ± 0.002	0.012 ± 0.003	0.005±0.000
Nitrate	**mg/L**	3.1 ± 1.2	2.7 ± 0.6	0.48 ± 0.11	N/A
TOC	**mg/L**	4.34 ± 0.35	4.25 ± 0.6	N/A	N/A
UV254	**cm^{-1}**	0.0313±0.0582	0.0201±0.0400	0.0584±0.0041	0.027±0.003

The dataset shows the average concentrations and the ranges over the duration of the experiment for each water quality parameter. N/A indicate that the data is not available.

3.3.1.3 NOM Characterization of Biofilter Influents

Figure 3.3 a. shows the concentrations for DOC and HS and Figure 3.3 b. for BP, BB, LMW acids/humics, and LMW neutrals for in the biofilter influents at Facilities B, I, and L. These fractions are of particular interest since, for instance, HS can contribute to formation of DBPs (Wassink et al., 2011), BP can contribute to hydraulically reversible and irreversible fouling of low pressure membranes (Hallé et al., 2009; Peldszus et al., 2012; Tian et al., 2013), and LMW acids/humics can contribute to biofouling of certain membranes (Huck and Sozanski, 2008). The concentrations for DOC and HS for Facilities B and I were similar but the concentrations were lower at Facility L. The concentration for HS was higher than the concentrations for all the other fractions, which was expected The BP observed was much lower at Facility I and they were very similar at Facilities B and L, and these trends for BP were different than the trends in HS. However, BB varied a lot at all the facilities, and the concentration was approximately double the concentration of BP. LMW acids/humics also differed a lot between the facilities, and the concentration was similar to BP. Furthermore, the LMW neutrals was approximately 400 µg carbon/L at each facility. In general, the different LC-OCD fractions were relatively constant throughout the experiment, which is indicated by the low ranges of the error bars. However, during week 6 at Facility I the concentration for both BB and LMW acids/humics were doubled, while the LMW neutrals concentration was much lower, which is also indicated by the higher ranges of the error bars. Furthermore, during week 2 at Facility L the concentrations for DOC, BB, LMW acids/humics, and LMW neutrals were also higher. This is also reflected by the higher ranges of the error bars, and it is not known what caused these high concentrations. Moreover, the pre-ozone and post-ozone influents at Facility B were very similar, but post-ozone influent had lower BB and higher LMW acids/humics, which is consistent with other studies from DWTPs that also investigated ozonation (Croft, 2012; Pharand, 2014). Ozonation can transform BB into the more oxidized and polar LMW acids/humics. Other studies also report that ozone oxidizes NOM fractions and creates lower molecular weight by-products with higher biodegradability, which contribute substantially to AOC and BOM (Hammes et al., 2006; Ramseier et al., 2011; Volk and Lechevallier, 2002; Volk et al., 1993).

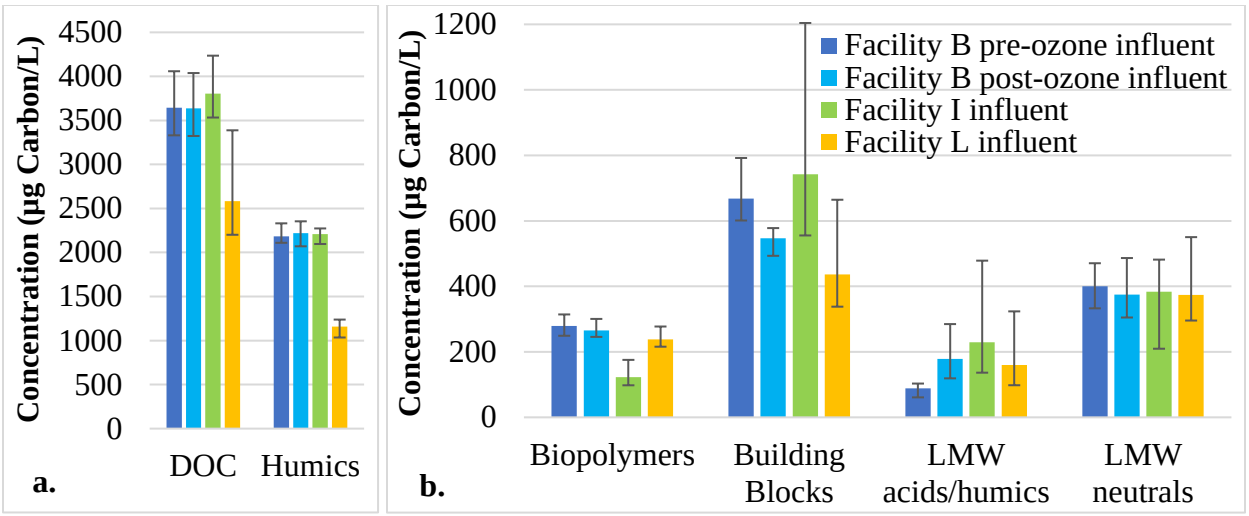


Figure 3.3 NOM characterization of biofilter influents at Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for a. DOC and HS, b. BP, BB, LMW acids/humics, and LMW neutrals. Error bars indicate maximum and minimum values.
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Table 3.7 shows that the majority of the DOC at all facilities consisted of HS (49 to 62%), which is the case for most natural water that typically consist of 40 to 60% HS (Thurman, 1985). All the other fractions were only present in much lower concentrations. For all the other fractions, the DOC in the pre-ozone influent at Facility B consisted mostly of BB, then LMW neutrals, BP, and the lowest concentration was LMW acids/humics. The post-ozone influent at Facility B was very similar to the pre-ozone influent, except for a lower concentration of BB and higher concentration of LMW acids/humics, which is consistent with Figure 3.3 and other studies (Croft, 2012; Pharand, 2014). After humic substances the DOC in the influent at Facility I consisted mostly of BB, then LMW neutrals, LMW acids/humics and a low concentration of BP. The HS composition in the influent at Facility L was lower than at the facilities, and the composition of the other fractions were therefore much higher. The highest was BB, then LMW neutrals, BP, and LMW acids/humics.

Table 3.7 NOM composition as a percentage of DOC in average influents at Facilities B (pre- and post-ozone), I, and L.

	Facility B Pre-ozone	Facility B Post-ozone	Facility I	Facility L
BP	7.7	7.4	3.3	10
HS	60	62	60	49
BB	19	15	20	19
LMW acids/humics	2.4	5.0	6.2	6.8
LMW neutrals	11	11	10	16

Figure 3.4 shows that the nitrogen in HS and BP in the influents at Facilities B, I, and L were differing from each other. Facility B had the highest nitrogen in HS followed by Facility I. The nitrogen in BP was very similar for Facilities B and L, but the nitrogen for Facility I was below the detection limit of 10 µg nitrogen/L. Furthermore, the nitrogen in both HS and BP for the pre- and post-ozone influents at Facility B were fairly similar to each other.

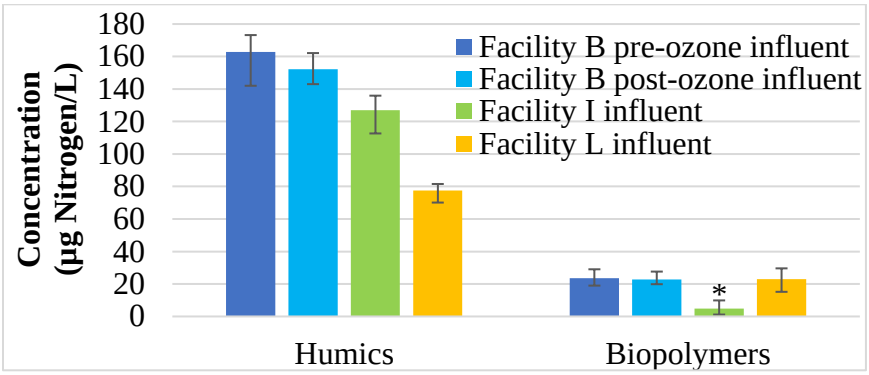


Figure 3.4 NOM characterization of biofilter influents at Facilities B, I and L analyzed by LC-OND. Reporting average nitrogen concentrations in HS and BP. Error bars indicate maximum and minimum values, and * indicate that values are below methods detection limits.
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Table 3.8 shows that the nitrogen to carbon (N/C) ratios in the influents for all the facilities for both HS and BP were between 6% and 10% by weight. Also, the N/C ratios for both HS and BP in the influents at all facilities were very similar to each other, except for the N/C ratio for BP in the influent at Facility I, which could not be calculated since the nitrogen in BP was below methods detection limits. Other studies have also reported similar N/C ratios in drinking water (Chang et al., 2013; Lee and Westerhoff, 2006; Lee et al., 2006).

Table 3.8 N/C ratios of average HS and BP in influents at Facilities B, I, and L.

	Facility B pre-ozone	Facility B post-ozone	Facility I	Facility L
HS	0.07	0.07	0.06	0.07
BP	0.09	0.09	<MDL	0.10

<MDL indicate that the data is below methods detection limits.

Figure 3.5 shows a humics diagram, developed by Huber et al. (2011), which compares the NOM characteristics for the influents at Facilities B, I and L. This humics diagrams illustrates the characteristics of HS in the influents by plotting the aromaticity against the average molecular weight of the HS fraction. The aromaticity is calculated as the ratio of the UV absorbance obtained

from the UVD to the organic carbon concentration. The average molecular weight is calculated from the retention time in LC-OCD of the humics peak. Figure 3.5 shows that the HS characteristics for the influent at each facility were very consistent throughout the experiment since they are clustered together by location. The HS in the Facility B pre-ozone influent water had a considerably higher aromaticity and average molecular weight than the other facilities and even higher than the post-ozone influent water at Facility B. This indicates, that ozonation changed the structure of the molecules to less aromatic and somewhat lower molecular weight, which is also consistent with Figure 3.3 and other studies (Hammes et al., 2006; Ramseier et al., 2011; Volk and Lechevallier, 2002; Volk et al., 1993). These studies showed that ozone oxidizes NOM fractions and creates lower molecular weight by-products with higher biodegradability. Even after ozonation, the HS in the post-ozone influent water at Facility B still had a marginally higher aromaticity and somewhat higher molecular weight than Facilities I and L. Also, the HS in the influents at Facilities I and L had similar molecular weight, but the HS in the influent at Facility I had a somewhat higher aromaticity. The HS in the influent at Facilities B post-ozone, I, and L had low aromaticity and average molecular weight, which is distinctive for FA of autochthonous (aquagenic) origin (Huber et al., 2011).

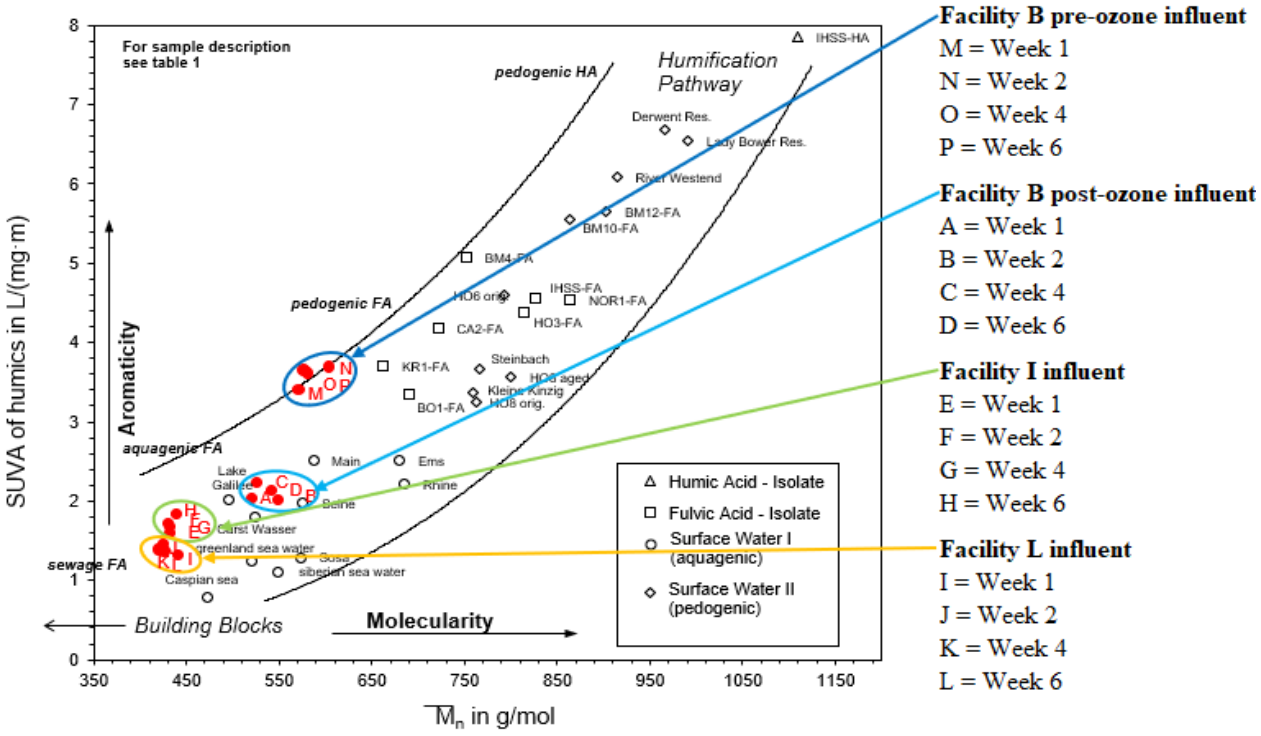


Figure 3.5 HS characteristics of biofilter influents at Facilities B (pre- and post ozone), I and L. M_n: Average molecular weight of HS.

Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Figure 3.6 shows the intensities for the FEEM fractions: HA, FA, and protein-like materials in the influent waters at the three facilities. The pre-ozone influent at Facility B had much higher values for all three FEEM fractions than post-ozone water. Ozonation drastically decreased the fluorescence signals, and previous studies showed that this decrease is because ozonation changes the structure of the molecules (Baghoth et al., 2011; Croft, 2012). This decrease is also consistent with the findings in the LC-OCD fractions. When not taking Facility B pre-ozone influent into account, the influent at Facility I always had the highest and the influent at Facility L always had the lowest intensities for all the FEEM fractions. The post-ozone influent at Facility B had similar levels as Facility I for HA and as Facility L for protein-like materials. The high protein like materials in the influent at Facility I differs from Figure 3.3 and Table 3.7, which indicated that the nitrogen in BP in the influent at Facility I was below methods detection limits. Also, HA and FA in the influent at Facility I also differ from Figure 3.3 and Table 3.7, which showed a similar HS concentration in the influents at Facilities B and I.This is probably due to the differences in the methodology for FEEM and LC-OCD. FEEM measures the fluorescence signals for any protein-like materials no matter the size, whereas the larger BP molecules for LC-OCD are separated by size.

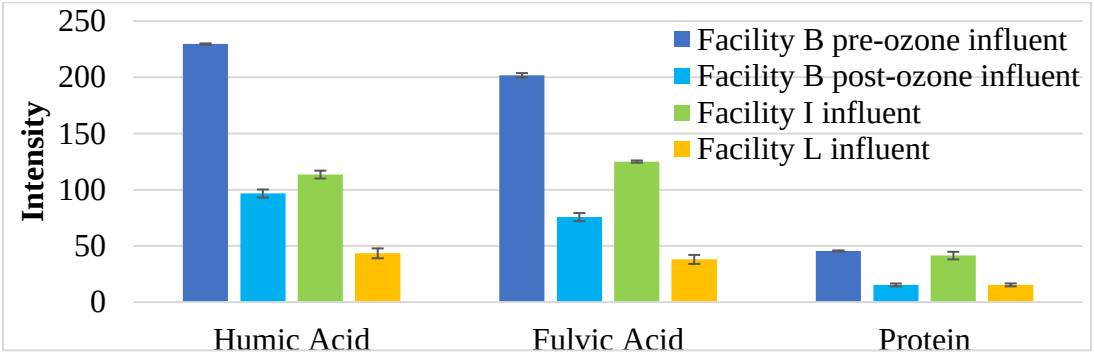


Figure 3.6 NOM characterization of biofilter influents at Facilities B, I and L analyzed by FEEM. Reporting average intensities. Error bars indicate maximum and minimum values.
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Overall, the pre- and post-ozone influents at Facility B had very similar LC-OCD fractions, but the HS in the pre-ozone influent had much higher aromaticity and higher average molecular weight. Furthermore, the post-ozone influent had lower BB and higher LMW acids/humics concentrations, and much lower intensities for all the FEEM fractions. In general, the influent at

Facility L had the lowest LC-OCD concentrations, the lowest aromaticity and average molecular weight, and the lowest FEEM intensities. The influent at Facility I, in general, had the highest LC-OCD concentrations (except for BP) and highest intensities in all the FEEM fractions. However, the post-ozone influent at Facility B had the highest nitrogen in the LC-OCD fractions and higher aromaticity and average molecular weight in HS than Facilities I and L.

3.3.1.4 ATP

ATP was measured to quantify the total active biomass on the surface of the biofilter media, which identifies whether the biofilter media is biologically active (Magic-Knezev and van der Kooij, 2004; Pharand, 2014; Velten et al., 2011b). At Facility B, the pre-ozone columns with Facility B media had the lowest ATP at the end of the experiment (Table 3.9). This is also consistent with previous research, which showed that the availability of carbon for microbial growth are greater in post-ozonated biofilters which leads to increased biological activity (Magic-Knezev and van der Kooij, 2004; Urfer et al., 1997). The ATP for the Facility B media fed post-ozone water also decreased at all the different test locations. However, the decrease was much less than the columns fed pre-ozone influent water from Facility B (Table 3.9). The ATP for Facility I media also substantially decreased at the two test locations for which data are available. However, the ATP for Facility L media substantially increased when fed Facility B influent water and did not change when fed Facility I influent water. Unfortunately, the ATP values were not measured prior to the experiment at Facility L. However, the highest ATP values after the experiment for Facilities B and I media were found at Facility L. The chlorine addition at Facility L has therefore not affected the biological activity of the biofilter columns located at Facility L. Also, the highest decreases in ATP through the experiment occurred in the columns fed Facility I influent water. Overall, all the ATP values in all the columns were still above 100 ng/cm^3, except for Facility L media tested at Facilities I and L. Some studies reported a range of 100-10,000 ng ATP/cm^3 for active biofilter media for different full-scale biofilters (ElHadidy, 2016; Evans et al., 2013; Pharand, 2014). This indicates that all the columns were biologically active except for the columns with Facility L media at Facilities I and L which only could be considered marginally biologically active. However, although it was not measured, it is expected that the biofilter media will evolve during the course of the experiment when it was fed a different water source than the one it had been acclimated. It

is therefore difficult to make a statement whether the changes in ATP is caused by these changes of the biofilter media.

Table 3.9 ATP values (ng/cm^3) for the bench-scale biofilters at Facilities B, I, and L

		Facility B		Facility I		Facility L	
Column	**Media source**	**Start**	**End**	**Start**	**End**	**Start**	**End**
4A	**Facility B receiving pre-ozone influents**	364	156	Not applicable			
4B			159				
1A	**Facility B receiving post-ozone influents**	364	196	223	176	N/A	303
1B			224	195	141	N/A	267
2A	**Facility I**	562	248	386	166	N/A	419
2B			262	384	166	N/A	438
3A	**Facility L**	60	170	57	67	N/A	72
3B			194	56	71	N/A	82

Columns 4A and 4B were only located at Facility B, and data at Facilities I and L are therefore not applicable. At Facility B, ATP was measured on the media prior to loading the columns. However, at Facility I, the media was first divided, then ATP was measured for each column individually prior to loading the columns. N/A indicates that the data is not available.

3.3.2 Impacts of Water Sources on NOM Removal during Biofiltration

The objectives of this section are to investigate how different water sources and ozonation influence removal of various NOM fractions during biofiltration through bench-scale biofilter columns. As noted previously, the columns were located at the full-scale plants and fed the same water as the full-scale biofilters at each test location.

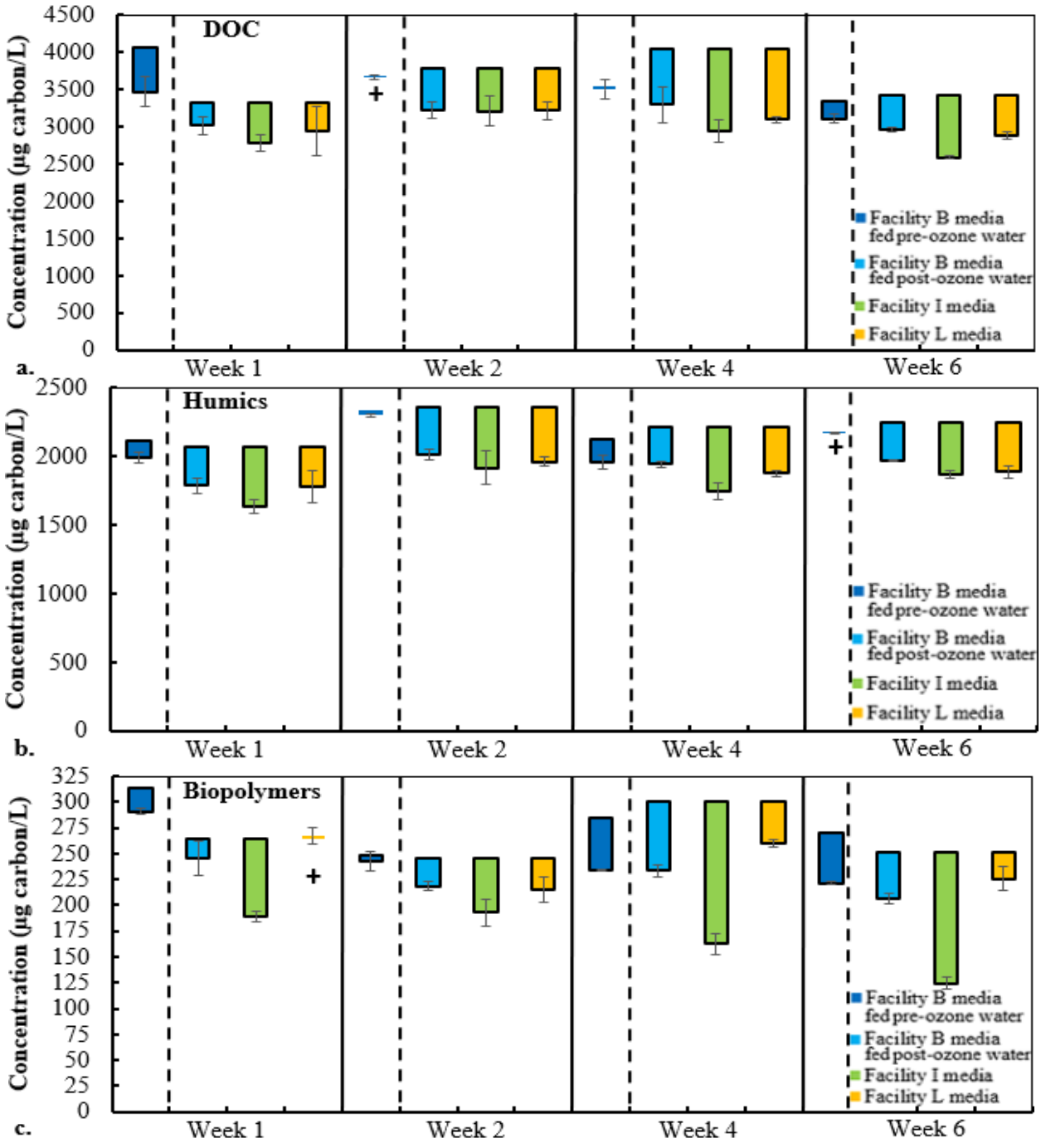
3.3.2.1 NOM Removals at Facility B

All bench-scale columns at Facility B received either pre- or post-ozone water from the full-scale plant, and it was only the media in the different bench-scale columns that differed. Figure 3.7 shows the change across the biofilters for each week for all the different LC-OCD fractions. In most cases, the top value of each bar is the influent concentration, and the bottom value is the effluent concentration for each biofilter column. However, a plus sign located near a bar indicates an increase in the NOM fraction across the biofilter column. In this case, the top value is therefore the effluent concentration for the biofilter column and the bottom value is the influent concentration. Figure 3.7 a. shows that DOC in the influents was rather constant throughout the experiment, ranging from 3330 to 4069 µg carbon/L. There were fairly similar removals of DOC for all media each week, but the Facility I media had slightly higher removals some weeks. Since

all the biofilters removed DOC each week, this indicates that all the biofilter columns were biologically active, which is consistent with the ATP values in Table 3.9. Figure 3.7 b. shows that HS in the influents also was rather constant throughout the experiment, ranging from 2070 to 2354 µg carbon/L. Also, the HS removal was low but fairly similar for all media each week but the Facility I media had slightly higher removals some weeks. This low removal is not always the case, since no change of HS during biofiltration is rather common too. The BP concentration in the influents fluctuated a bit more than for HS and DOC (Figure 3.7 c.). The removals were also more variable over the duration of the experiment and there was a higher removal during weeks 4 and 6. Also, the Facility I media had higher removals each week and Facilities B and L media were fairly similar. Figure 3.7 d. shows negligible change and no clear trends in BB for all the media each week. Figure 3.7 e. shows high fluctuations in the LMW acids/humics concentration in the influent throughout the experiment, ranging from 61 to 285 µg carbon/L. The removals were fairly similar through the different media, but there were high variations throughout the experiment, and the highest removals were during weeks 4 and 6. Figure 3.7 f. shows that the LMW neutrals concentration in the influents fluctuates a bit more on a percentage basis than, for example, HS and DOC. There were fairly similar removals of LMW neutrals for all media each week, but the Facility I media had slightly higher removals some weeks. Also, there was a higher removal during weeks 4 and 6. Figure 3.8 a. and b. show that the nitrogen in both HS and BP in the influents were rather constant throughout the experiment. Also, there were fairly similar removals of the nitrogen in HS and BP for all media each week, but the Facility I media had slightly higher removals some weeks. It could be hypothesized that the higher removals in Facility I media columns could be related to the higher ATP values in these columns, which indicate a higher biological activity, although the presence of nitrifying organisms, which was not measured, could play a role. Overall, all the media tend to behave very similarly when fed the influent water at Facility B. However, for some fractions, the columns with Facility I media had a slightly higher removal each week, and the columns with Facilities B and L media had the most similar removal trends.

The removals of the different LC-OCD fractions in the columns with Facility B media fed pre-ozone and post-ozone influent water, respectively, were not similar. In general, the columns fed pre-ozone water had slightly lower removals of DOC, HS, BP, and LMW neutrals. Also, the columns fed pre-ozone water, in general, had higher removals of BB and high increases of LMW acids/humics. However, there were no clear trends for nitrogen in both HS and BP. Also, the

columns fed post-ozone water also had higher ATP values, indicating that these columns had a higher biological activity. This higher biological activity is likely attributable to the higher concentration of more biodegradable compounds in the influent water, which allows the bacteria on the biofilm to grow more. This is also consistent with another study, which indicated high removals in NOM fraction removals at a DWTPs treating water from the Grand River through pre-ozonation and biofiltration, which was similar to Facility B (Croft, 2012). That study reported removals of 0-15% HS, 0-37% BP, 10% BB, 84% LMW acids/humics, and 17% LMW neutrals during combined ozonation and biofiltration. Another study showed similar high removals at a DWTPs treating water from the Grand River, also through both pre-ozonation and biofiltration. This ozonation and biofiltration on average removed 12% DOC, 6% HS, 31% BP, 10% BB, 31% LMW acids/humics, and 14% LMW neutrals (Pharand, 2014; Pharand et al., 2015). A third study reported that pre-ozonation and biofiltration, from a full-scale WTPs treating organic-rich water from Germany, removed 35% DOC, 25% BB, and 50% LMW neutrals (Vasyukova et al., 2013). Another study, which also included ozonation and biofiltration, showed that a DWTPs also treating water from the Grand River removed 15% DOC, 13% HS, 70% BP (Chen et al., 2016). These studies therefore show that pre-ozonation and biofiltration together has high removals of various LC-OCD fractions, specially BP and LMW compounds, which is consistent with the results presented in Figure 3.7.


DOC
Concentration (µg carbon/L)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Week 1
Week 2
Week 4
Week 6
Facility B media fed pre-ozone water
Facility B media fed post-ozone water
Facility I media
Facility L media
a.
Humics
Concentration (µg carbon/L)
2500
2000
1500
1000
500
0
Week 1
Week 2
Week 4
Week 6
Facility B media fed pre-ozone water
Facility B media fed post-ozone water
Facility I media
Facility L media
b.
Biopolymers
Concentration (µg carbon/L)
325
300
275
250
225
200
175
150
125
100
75
50
25
0
Week 1
Week 2
Week 4
Week 6
Facility B media fed pre-ozone water
Facility B media fed post-ozone water
Facility I media
Facility L media
c.

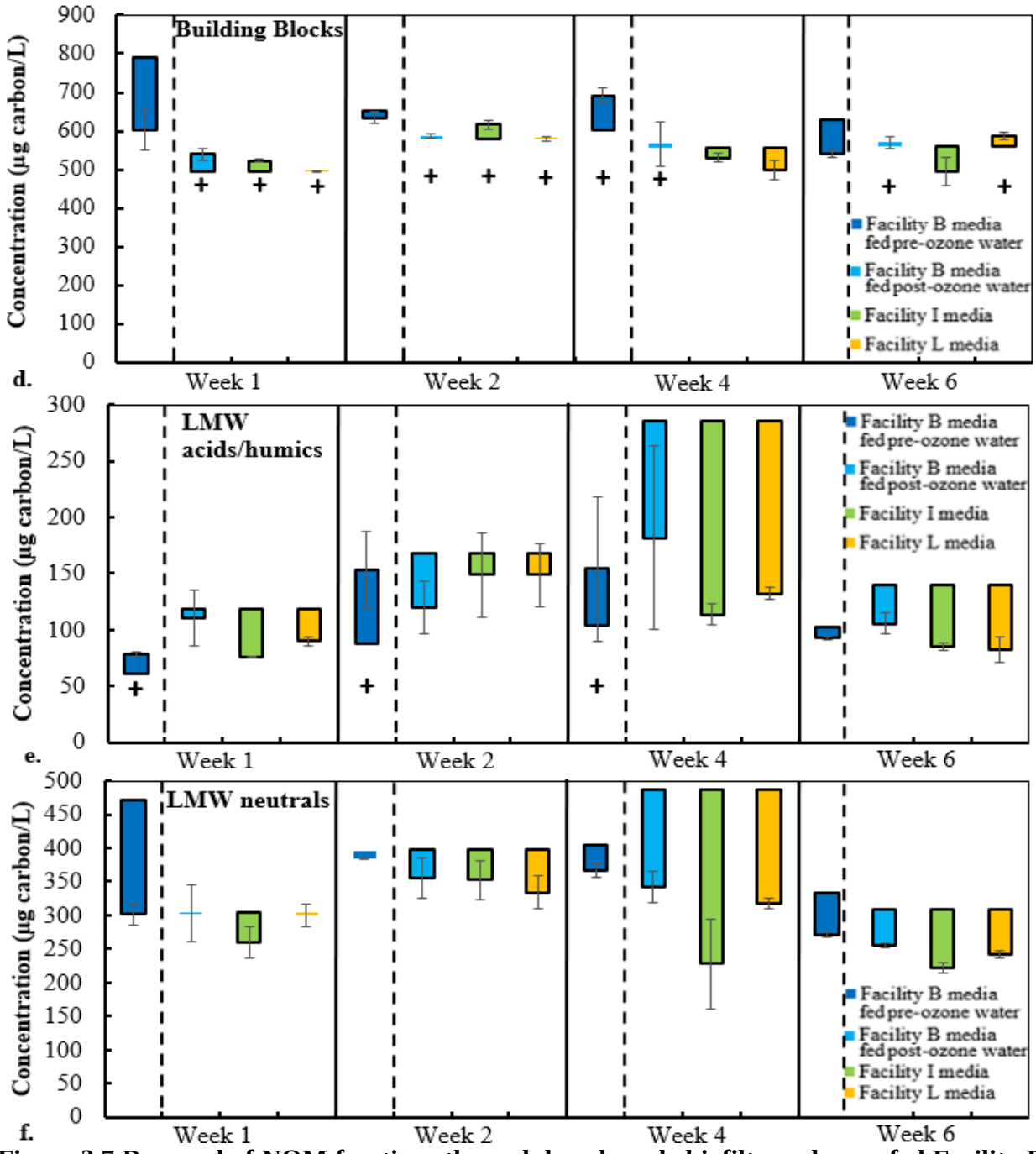


Figure 3.7 Removal of NOM fractions through bench-scale biofilter columns fed Facility B water with Facilities B, I and L media analyzed by LC-OCD. Facilities I and L media were fed with Facility B post-ozone water. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. HS, c. BP, d. BB, e. LMW acids/humics, and f. LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. Dark blue bars left of dashed lines are fed pre-ozone water and all others are fed post-ozone water.

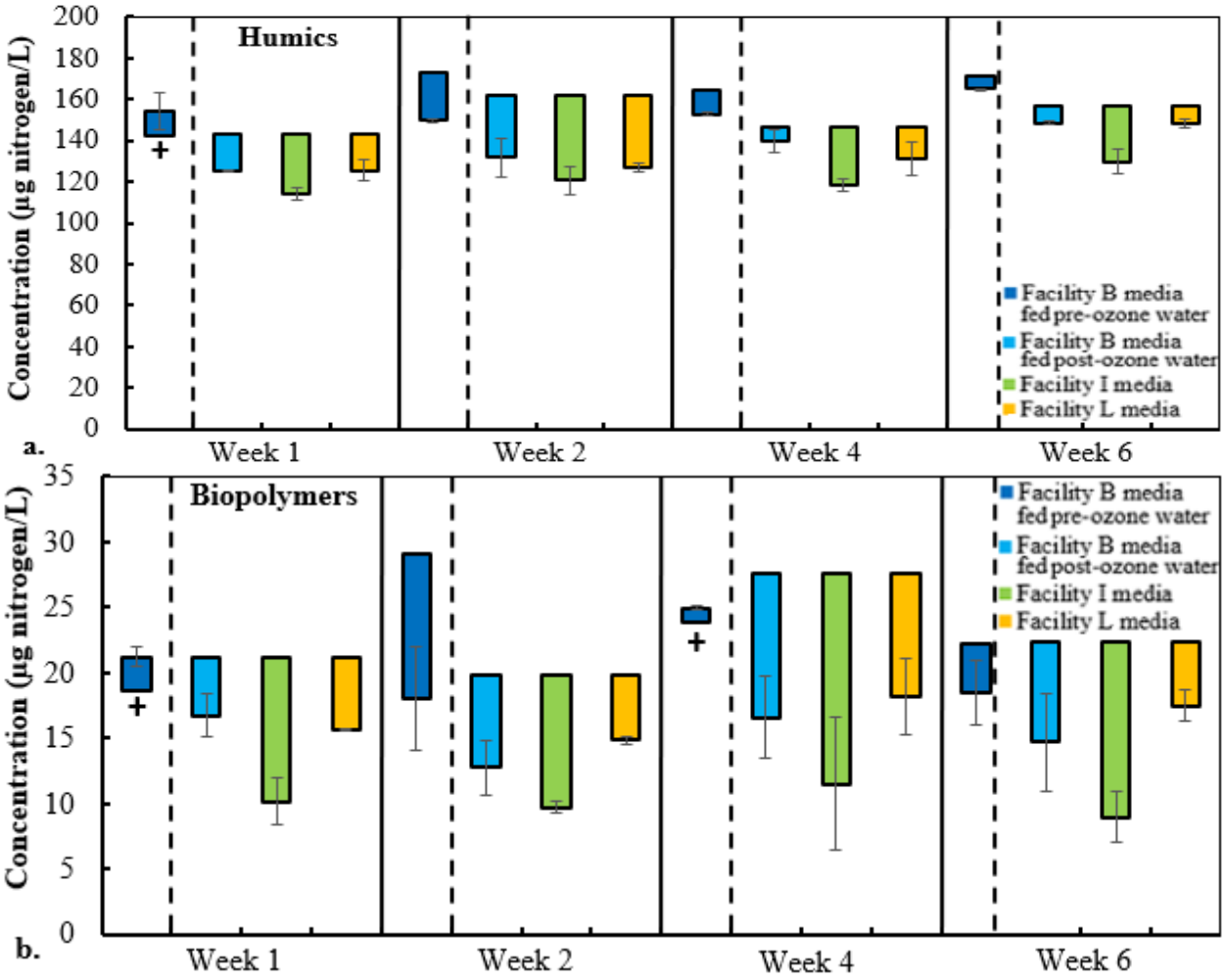


Figure 3.8 Removal of NOM fractions through bench-scale biofilter columns fed Facility B water with Facilities B, I and L media analyzed by LC-OND. Facilities I and L media were fed with Facility B post-ozone water. Reporting average nitrogen concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. Dark blue bars left of dashed lines are fed pre-ozone water and all others are fed post-ozone water.

Figure 3.9 shows that the HS characteristics were very consistent throughout the experiment for the pre- and post-ozone influents at Facility B since they were clustered together by water source. The HS characteristics for the pre-ozone influent at Facility B had considerably higher aromaticity and slightly higher average molecular weight, which confirms that ozonation changed the structure of the molecules. Moreover, biofiltration did not considerably change the HS characteristics since all the influents and effluents also were clustered together for each water source.

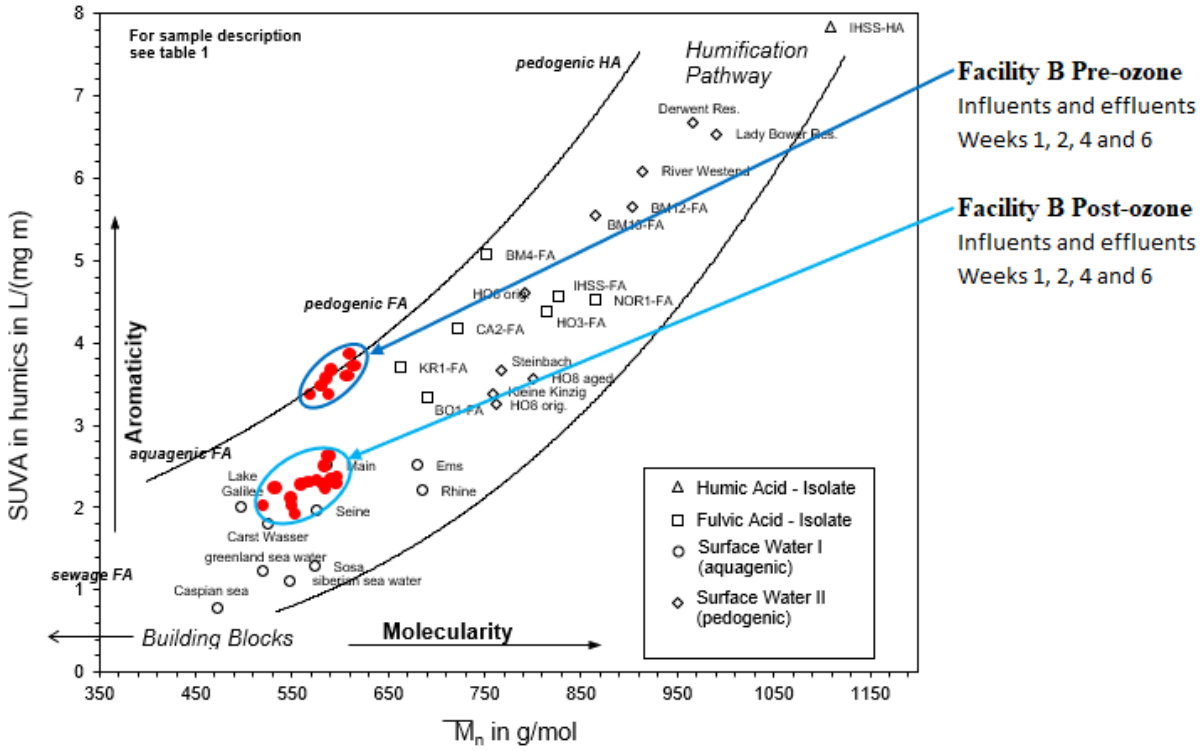


Figure 3.9 HS characteristics of biofilter influents and effluents at Facility B (pre- and post-ozone influents). Mn: Average molecular weight of HS.

Figure 3.10 a. and b. show that the HA and FA intensities in the biofilter influents were essentially unchanged at the beginning and end of the experiment (Weeks 1 and 6). There were also fairly similar removals of HA and FA for all the media in each week. However, Facility L media had slightly higher removals some weeks, and Facility I media had increasing FA intensities. The trends for HA and FA reductions are not similar to the removal trends for HS in LC-OCD. For example, Facility I media had slightly higher removals of HS some weeks, which was not the case for either HA or FA. Figure 3.10 c. shows very constant protein-like materials intensities at the beginning and end of the experiment in all the biofilter influents. Also, there were only low changes of the protein-like materials, and there was an increase in reduction from week 1 to week 6. Overall, the reductions for all FEEM fractions for all the media were very similar to each other both weeks.

The reductions of the different FEEM fractions in the columns with Facility B media fed pre- and post-ozone influent water were not similar. The influents and the reductions across the biofilters for all FEEM fractions were much higher in the columns fed pre-ozone water. However, ozonation substantially reduced the intensities for all the FEEM fractions and this would have contributed to lower overall removal when ozonation and biofiltration were combined. This was not similar to

the removal trends for HS in LC-OCD, because the columns fed post-ozone water had higher removals of HS than the columns fed pre-ozone water. This is consistent with another study, which also showed significant reductions of all FEEM fractions during ozonation, and lowest intensities when ozonation and biofiltration were combined (Baghoth et al., 2011). That study also found that the reason for the drastic decreases in the fluorescence signals during ozonation is a change in the structure of the molecules, which is caused by ozonation.

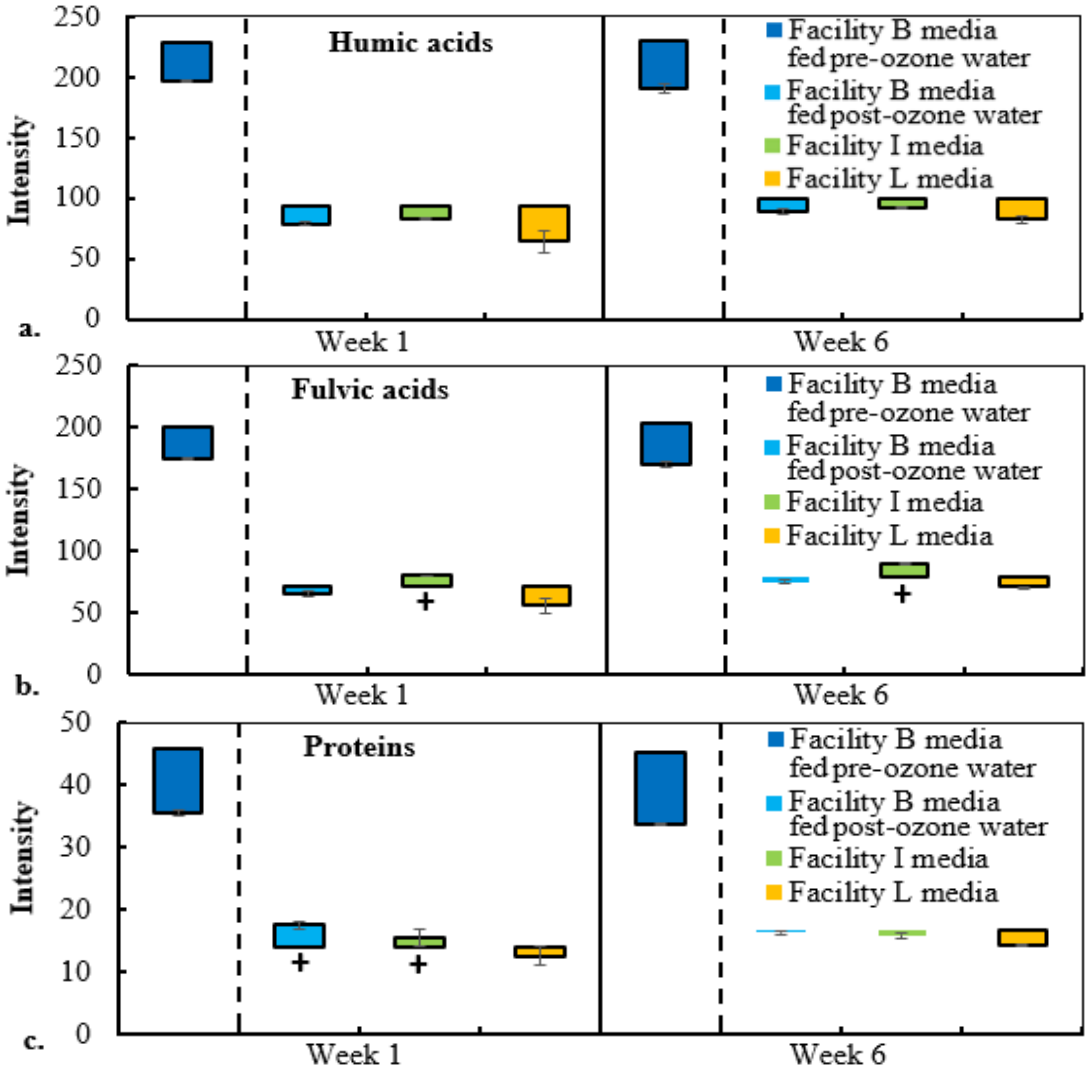


Figure 3.10 Removal of NOM fractions through bench-scale biofilter columns fed Facility B water with Facilities B, I and L media analyzed by FEEM. Facilities I and L media were fed with Facility B post-ozone water. Reporting average intensities for the duplicate columns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. Dark blue bars left of dashed lines are fed pre-ozone water and all others are fed post-ozone water.

Overall, all the media behaved similarly, and the removal trends of LC-OCD-OND and FEEM fractions were also very similar when fed the influent water at Facility B. However, sometimes there were slightly higher removals with Facility I media. Also, all the ATP values at Facility B for all media after the experiment were very similar to each other, which indicate that all the biofilters had very similar biological activity. These findings indicate that the media had negligible effect on the removal of various NOM fractions during biofiltration and that the water source might influence these removals.

Furthermore, ozonation converted BB to LMW acids/humics and substantially reduced the intensities for of all the FEEM fractions. Therefore, confirming earlier results by others, ozonation changed the structure of the molecules in the solution to create lower molecular weight by-products with higher biodegradability. Also, these changes in the structure of the molecules happening during ozonation also drastically reduced the fluorescence signals. Moreover, since ozonation changes the structure of the molecules to more biodegradable molecules, ozonation improves the removals of various NOM fractions during biofiltration. Therefore, the concentration of all LC-OCD-OND and FEEM fractions, in general, were much lower when ozonation and biofiltration were combined. For example, the columns with Facility B media fed with post-ozone water had a higher removal of DOC, HS, BP, and LMW acids/humics than the columns fed with pre-ozone water. These findings are also consistent with previous studies (Chen et al., 2016; Pharand et al., 2015). Also, the ATP values were lower in the columns fed pre-ozone water after the experiment, which confirms that these columns had a lower biological activity. This is undoubtedly due to the lower availability of biodegradable compounds. Therefore, these results indicate that ozonation prior to the biofilters at this facility improved the removal of the NOM fractions and the biofilter performance, which was also reported by other studies, as mentioned earlier (Baghoth et al., 2011; Croft, 2012; Rittmann et al., 2002; Vasyukova et al., 2013).

3.3.2.2 NOM Removals at Facility I

All bench scale columns at Facility I received the same water as the full-scale biofilter columns at the plant, and it was only the media in the different bench-scale columns that differed. Some of the results in this section are shown in the appendix. Figure 3.11 a. shows that DOC increased for all the media each week except for Facility I media week 1 and Facility L media week 6. Only the columns with Facility I media showed extremely high increases and variations in DOC during

weeks 2, 4, and 6. Figure A.1 b. and c. in Appendix A also show the same high increases and variations in LMW acids/humics and LMW neutrals only for the columns with Facility I media during weeks 2, 4, and 6. These increases only occurred in the columns with Facility I media for DOC, LMW acids/humics, and LMW neutrals during weeks 2, 4, and 6. Also, during weeks 2 and 4, it was only the duplicate column A that showed these increases, but it was the duplicate column B that showed these increases during week 6. The initial idea was that the extreme increases were caused by contamination in the sampling vial. However, the duplicate sampling vial for week 2 showed the same increases. Afterwards, the second idea was that the increases were caused by contamination in the sampling port. However, when the high increases re-occurred during weeks 4 and 6, the increases cannot be caused by contamination in the sampling ports. Another thought is that the biofilters are sloughing off compounds in the LMW region, because the DOC concentrations through all the biofilter columns were increasing each week. Due to the high increases in DOC, LMW acids/humics, and LMW neutrals, these fractions at Facility I will not be discussed any further. Figure 3.11 b. shows that HS in the influents was very constant throughout the experiment. However, initially all biofilters showed a slight removal of HS, which decreased over the duration of the experiment. By week 6, HS actually increased slightly after biofiltration for all the media. Figure 3.11 c. shows that BP in the influents was very constant throughout the experiment except for week 6 where in influent concentration was almost doubled. There were fairly similar removals of BP for all the media each week, but the removals increased over the duration of the experiment. Also, Facility I media had a slightly higher removals some weeks. Figure A.1 a. in Appendix A shows no clear trends for BB. It could be hypothesized that the biofilm on biofilter I media was better acclimated/operated to reduce NOM fractions in facility I feed water than in facility B or L feed water. Also, the higher removals in the columns with Facility I media could be related to the higher ATP values in these columns, which indicate a higher biological activity. Overall, all the media tend to behave fairly similarly when fed the influent water from Facility I. However, there were no clear trends for these biofilters, due to the extreme increases, high variations, and variating removal trends for each fraction.

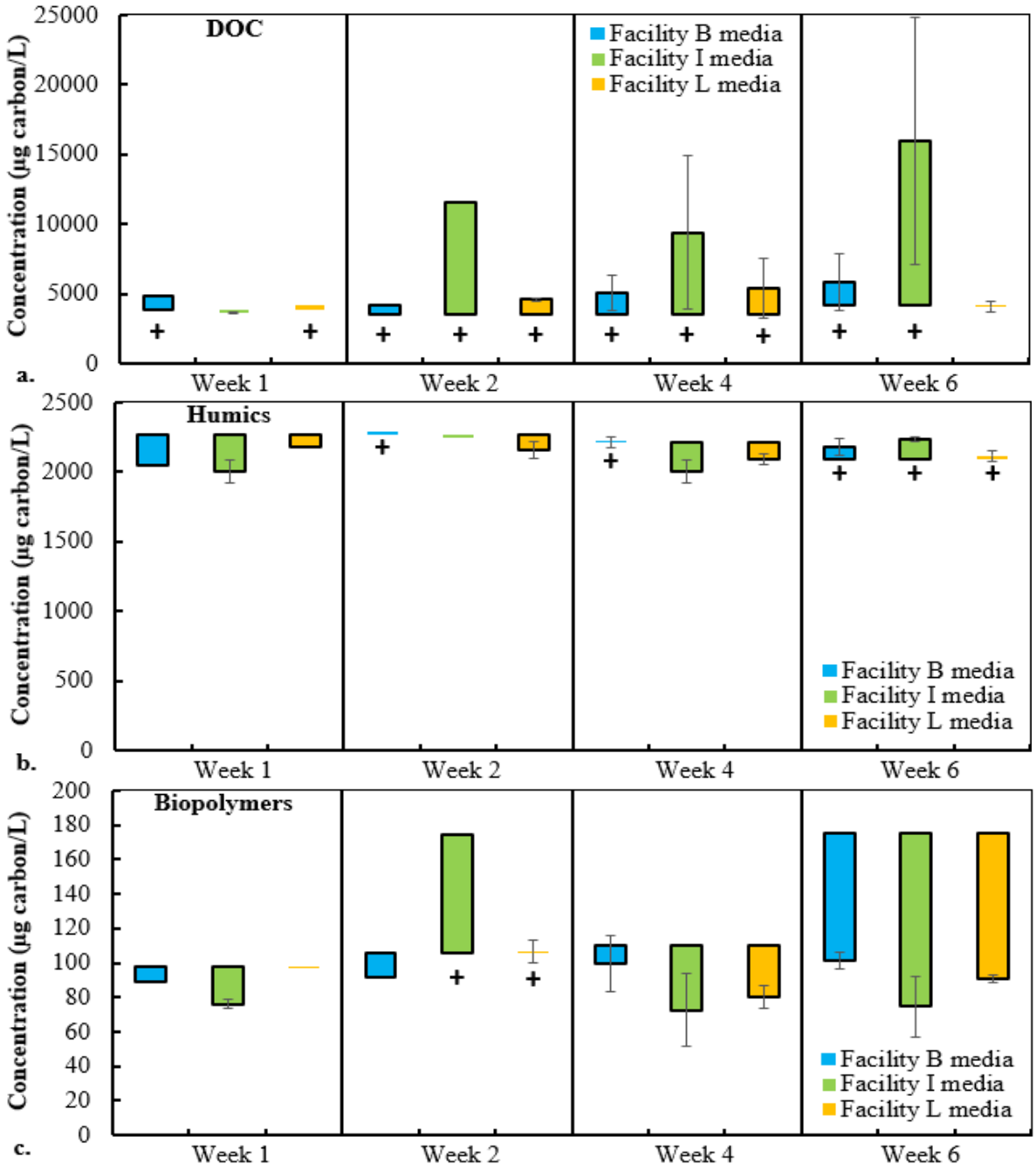


Figure 3.11 Removal of NOM fractions through bench-scale biofilter columns fed Facility I water with Facilities B, I and L media analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. HS, and c. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Figure 3.12 a. shows that the nitrogen in HS in the influents was very constant throughout the experiment, but there were no other clear trends. However, the nitrogen in the BP in both the

influents and effluents for all the media were below the methods detection limits and results are therefore not shown in this thesis. Overall, the trends for the nitrogen in HS in the influent at Facility I were not similar to the carbon in HS in the influent at Facility I.

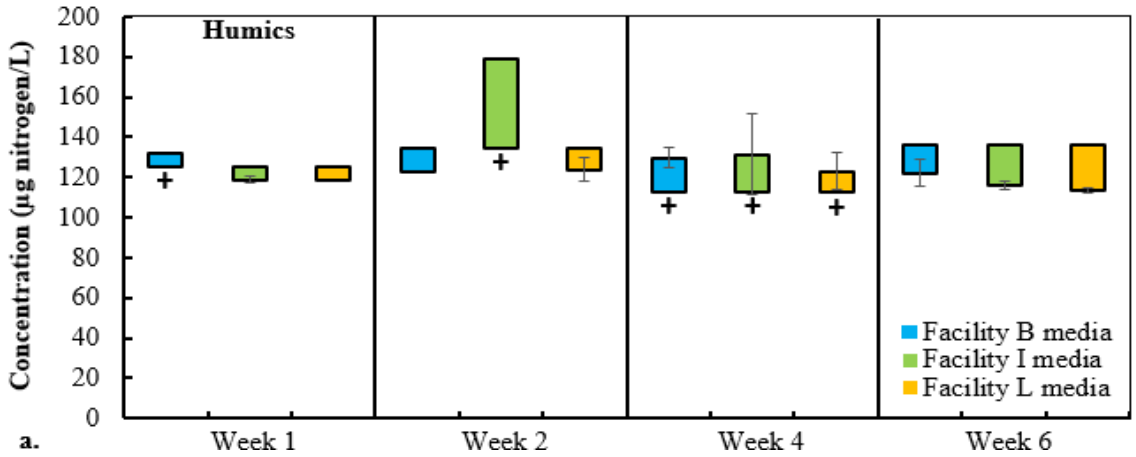


Figure 3.12 Removal of humics fraction through bench-scale biofilter columns fed Facility I water with Facilities B, I and L media analyzed by LC-OND. Reporting average nitrogen concentrations for the duplicate columns for HS. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

The intensities for the FEEM fractions in the influent at Facility I were not impacted by the contaminations observed in the DOC, LMW acids/humics, and LMW neutrals. The biofilters located at Facility I reduced several FEEM fractions (Figure 3.13). Figure 3.13 a. shows that HA in the influents was essentially the same at the beginning and end of the experiment. However, there was only a slight reduction of HA in week 1 for all the media, and this reduction increased in week 6 except for the biofilter with media from Facility I. Figure 3.13 b. also shows that FA in the influents was very similar in Weeks 1 and 6. However, there were only low reductions of FA in week 1 for all the media, and the reductions were much higher during week 6 except for the biofilter with media from Facility I, which showed a high increase in FA. The trends for HA and FA reductions are not similar to the removal trends for HS in LC-OCD. For example, there was a decreasing removal trend of HS over the duration of the experiment, whereas there were increasing removal trends of HA and FA from week 1 to week 6. Figure 3.13 c. also shows that protein-like materials in the influents were very constant throughout the experiment. However, the reductions of protein-like materials were low during week 1 and much higher during week 6. Both the protein-

like materials and BP from LC-OCD increased during biofiltration with all the different media. Otherwise, there were no similar trends between protein-like materials and BP.

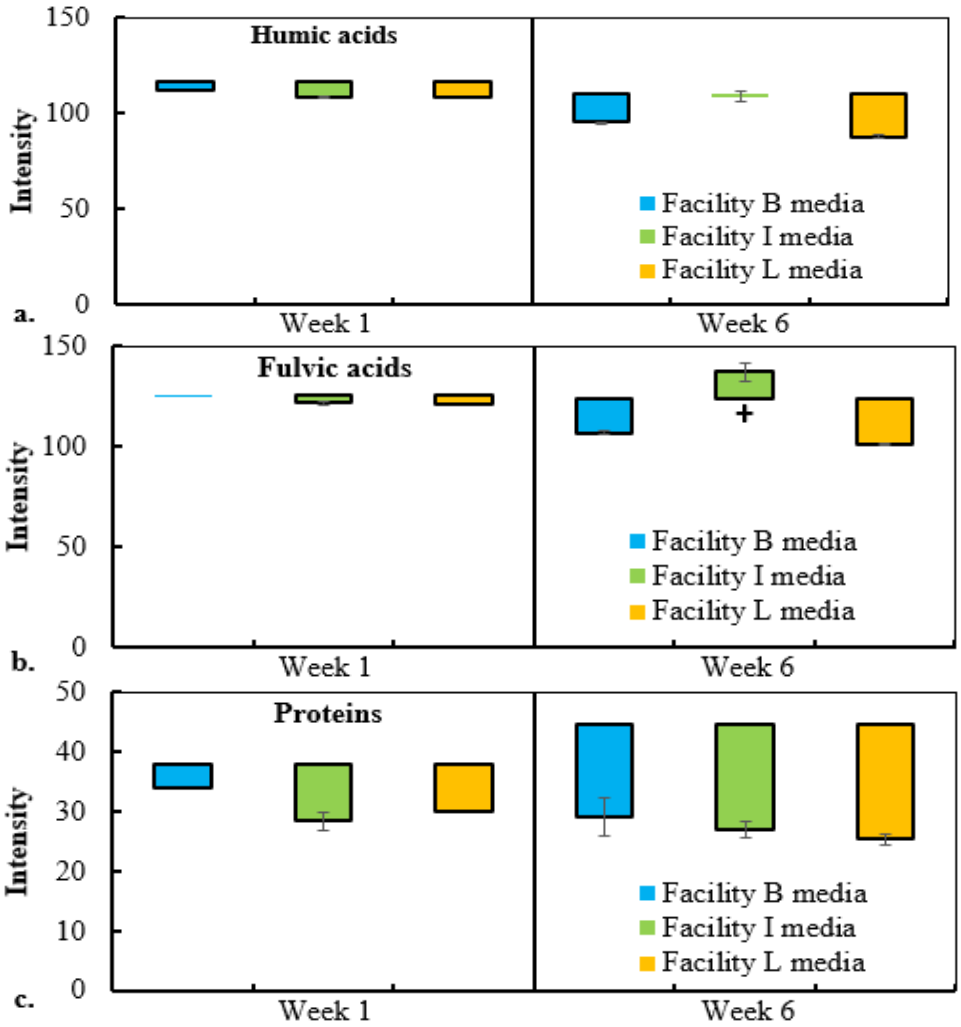


Figure 3.13 Removal of NOM fractions through bench-scale biofilter columns fed Facility I water with Facilities B, I and L media analyzed by FEEM. Reporting average intensities for the duplicate columns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

3.3.2.3 NOM Removals at Facility L

All bench scale columns at Facility L received the same water as the full-scale biofilter columns at the plant, and it was only the media in the different bench-scale columns that differed. Some of the results in this section are shown in the appendix. Figure 3.14 a. shows that DOC in the influents was rather constant throughout the experiment, except for week 2. DOC removals were very

similar among the biofilters but differed somewhat from week to week with week 2 having the highest DOC removals (41.3%), and week 6 having the lowest DOC removals (from 5.6% increase to 6.8% removal).The removal of DOC throughout the experiment indicate that all the biofilters were biologically active, which is also consistent with the ATP values in Table 3.9. Figure 3.14 b. and c. also show that HS and BP in the influents were very constant throughout the experiment. There were fairly similar removals of HS and BP for all media each week, but the removals varied from low increases to some removals for all the media. Also, the columns with Facility I media had slightly higher removals some weeks for both HS and BP. There were no clear trends for BB (Figure A.2 a. in Appendix A), and BB will therefore not be discussed. Figure A.2 b. and c. in Appendix A also show that LMW acids/humics and LMW neutrals in the influents were very constant throughout the experiment, except for week 2. The LMW acids/humics and LMW neutrals removals were very similar among the biofilters but differed somewhat from week to week with week 2 having the highest removals (75.5% and 50.1%, respectively). Also, LMW acids/humics had the lowest removals during week 6 (0-18%), and LMW neutrals had the lowest removals during week 1 (2.2-7.7%). It could be hypothesized that the higher removals in Facility I media columns could be related to the higher ATP values in these columns, which indicate a higher biological activity. Overall, there were no clear trends for the biofilter columns fed Facility I influent water due to the extreme increases, high variations, and variating removal trends for each fraction. Overall, all the media tended to behave very similarly when fed the influent water from Facility L.

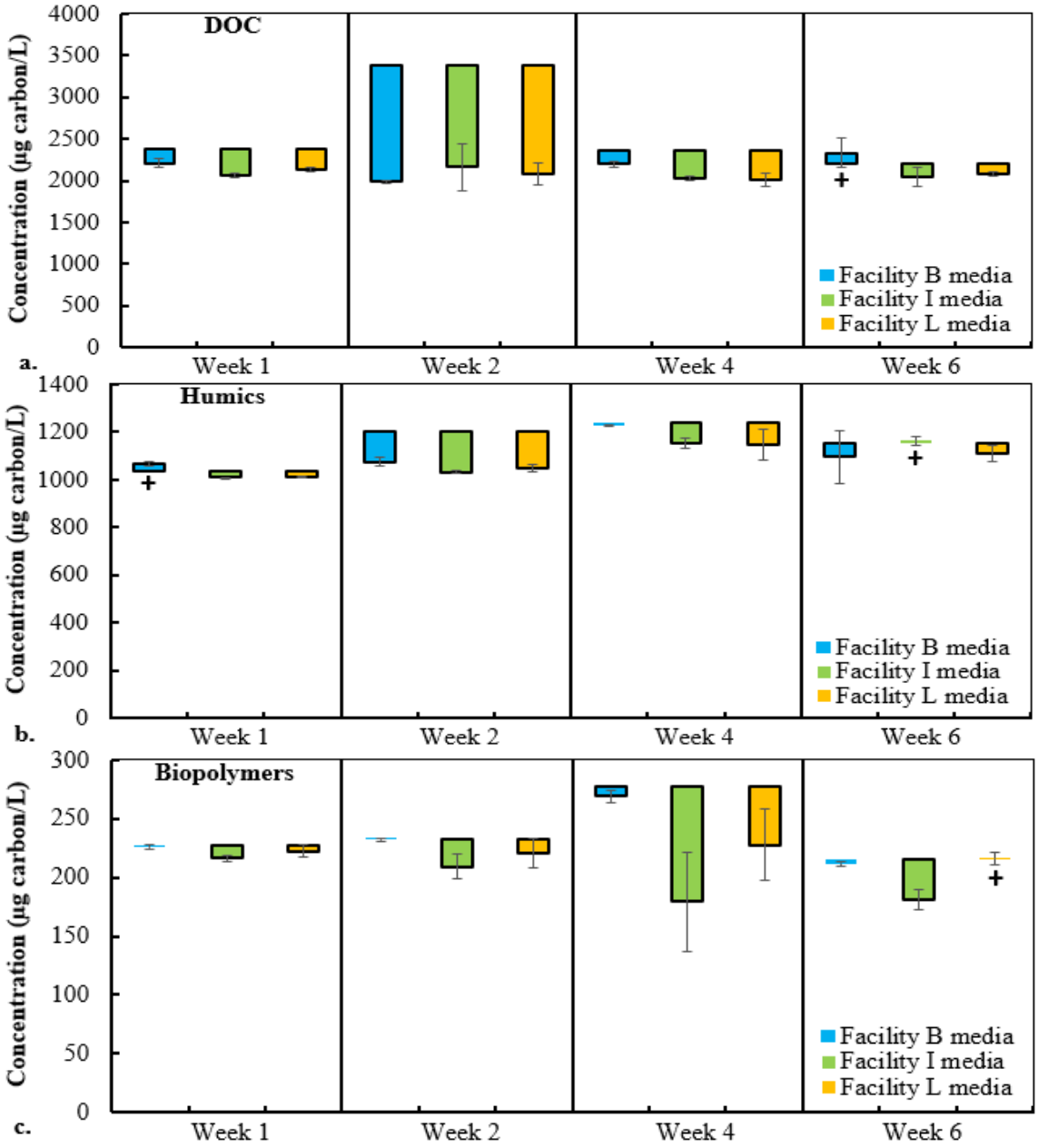


Figure 3.14 Removal of NOM fractions through bench-scale biofilter columns fed Facility L water with Facilities B, I and L media analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. HS, and c. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Figure A.3 a. in Appendix A shows that the nitrogen in HS in the influents was very constant throughout the experiment. Removals of this nitrogen fraction were very similar among the biofilters but differed somewhat from week to week, with a slight increase in week 1, which decreased over the duration of the experiment. Figure A.3 b. in Appendix A shows that the nitrogen

in BP in the influents fluctuated a bit more than for the nitrogen in HS. Also, removals of the nitrogen in BP in the influents were fairly similar among the biofilters but differed somewhat from week to week. There were high removals of this nitrogen fraction in week 1, which increased over the duration of the experiment to a slight increase in week 6. These removal trends in the nitrogen fractions of HS and BP in the influents were not similar to the trends in the carbon fractions. However, there were some similarities in the HS fractions, for example, the change across the biofilters for the HS fractions were equally low. Moreover, there were no decreasing removal trend over the duration of the experiment for the carbon fraction, which was the case for the nitrogen fraction.

Figure A.4 a. in Appendix A shows that HA in the influents was rather constant throughout the experiment. The biofilters with Facilities B and L media had higher reductions than the biofilters with Facility I media, and the reductions were slightly higher in week 6 compared to week 1. Figure A.4 b. in Appendix A shows that the trends for FA were very similar to the HA results in all aspects. However, the trends for HA and FA were not similar to the removal trends for HS in LC-OCD. Figure A.4 c. in Appendix A shows that protein-like materials in the influents was rather constant throughout the experiment. However, the biofilters with Facilities I and L media had higher reductions than the biofilters with Facility B media, and the reductions were slightly higher in week 6 compared to week 1. Also, the trends in protein-like materials were not similar to the removal trends of BP in LC-OCD. Overall, all the media tend to behave rather similarly when fed the influent water from Facility L.

3.3.2.4 Comparison of NOM Removals at the Different Facilities

Overall, all the media, when fed the same influent water, behaved similarly, and the removal trends of LC-OCD-OND and FEEM fractions were also very similar. All NOM fractions in the influents at each test location were rather constant throughout the experiment, but Facility L had lower influent concentrations and Facility I had the highest influent concentrations for all NOM fractions. In general, there were higher removals of all LC-OCD-OND fractions at Facility B all weeks. Also, there were higher reductions of HA and FA at Facility L and higher reductions of protein-like materials at Facility I all weeks. However, Facility I media had slightly higher removals of some LC-OCD-OND fractions at all test locations. This is also consistent with ATP, since Facility I media, in general, had higher ATP values throughout the experiment. This indicates a higher

biological activity in the columns with Facility I media. Also, all test locations had low HS removals, and an increased removal of BP over the duration of the experiment. There were also increased reductions of FEEM fractions for all media at all test locations from week 1 to week 6, except for HA and FA with Facility B media. In general, Facility L media had slightly higher reductions of some FEEM fractions some weeks at all test locations. Also, Facilities B and L media tend to behave very similarly at each test location. Moreover, Facility I media tend to either have increases or much lower reductions of all FEEM fractions at each test location than Facilities B and L media. For most LC-OCD-OND and FEEM fractions, Facilities B and L media behaved most similar at each test location all weeks. However, there were some differences in removals between the different test locations. There were some extremely high increases at Facility I, which only occurred at Facility I with Facility I media. These increases were only noticed in DOC, LMW acids/humics, and LMW neutrals. Also, the cause of these increases is unknown, the only potential reason for these increases might be the media sloughing off compounds in the LMW area. Also, all the media fed with Facility I water increased DOC all weeks, whereas all the media fed with Facilities B and L water removed DOC all weeks. Taken together, this section therefore showed similar trends in NOM removal and biofilter performance when different media were fed the same water source. This indicates that water source matters, and that the concentration of the NOM fractions upstream of the biofilters impact NOM fraction removals and biofilter performance.

3.3.3 Impacts of Media Acclimated/Operated in Different Water Sources on NOM Removal during Biofiltration

The objective of this section is to investigate how media acclimated/operated in different water sources influence removal of various NOM fractions during biofiltration through bench-scale biofilter columns. The plots in this section are similar to plots in the last section. Also, the data in this section is the same data as presented previously, but has been replotted to look at the data from a different point of view. Therefore, in this section, each media acclimated/operated in different water sources is plotted in separate figures, and the only difference is the water source that is feeding the biofilter columns. Also, all the columns were located at the full-scale plants and fed the same water as the full-scale biofilters at each test location. Only the HS, BP, and FEEM fractions will be discussed in this section, and some of the results are shown in the appendix.

3.3.3.1 NOM Removals with Facility B Media

All bench-scale columns in this section were loaded with media from Facility B and all were fed the same water as the full-scale biofilters. Figure 3.15 a. shows that there were higher removals of HS when biofilter media from Facility B was fed with Facility B water, and HS removals were much lower when filter B media was fed with facility I or L water. This behaviour was consistent from week 1 through to week 6. BP removals followed the same trend as observed for HS removals (Figure 3.15 b.). It could be hypothesized that the biofilm on biofilter B media was better acclimated/operated to reduce NOM fractions in facility B feed water than in facility I or L feed water. Or, it could be that the NOM in these two fractions in Facility B water was more biodegradable. Another potential reason for the higher removals in the columns fed Facility B water might be the full-scale pre-ozonation treatment step prior to biofiltration, which converts the NOM fractions into smaller more biodegradable compounds. A potential reason for low reductions in the columns fed facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. Also, the lowest ATP values at the end of the experiment were found in the columns fed with Facility I water, which might be a potential reason for the low removals in these columns fed with Facility I water. Overall, there were barely any similarities in the removals of the LC-OCD fractions when Facility B media were fed different water sources.

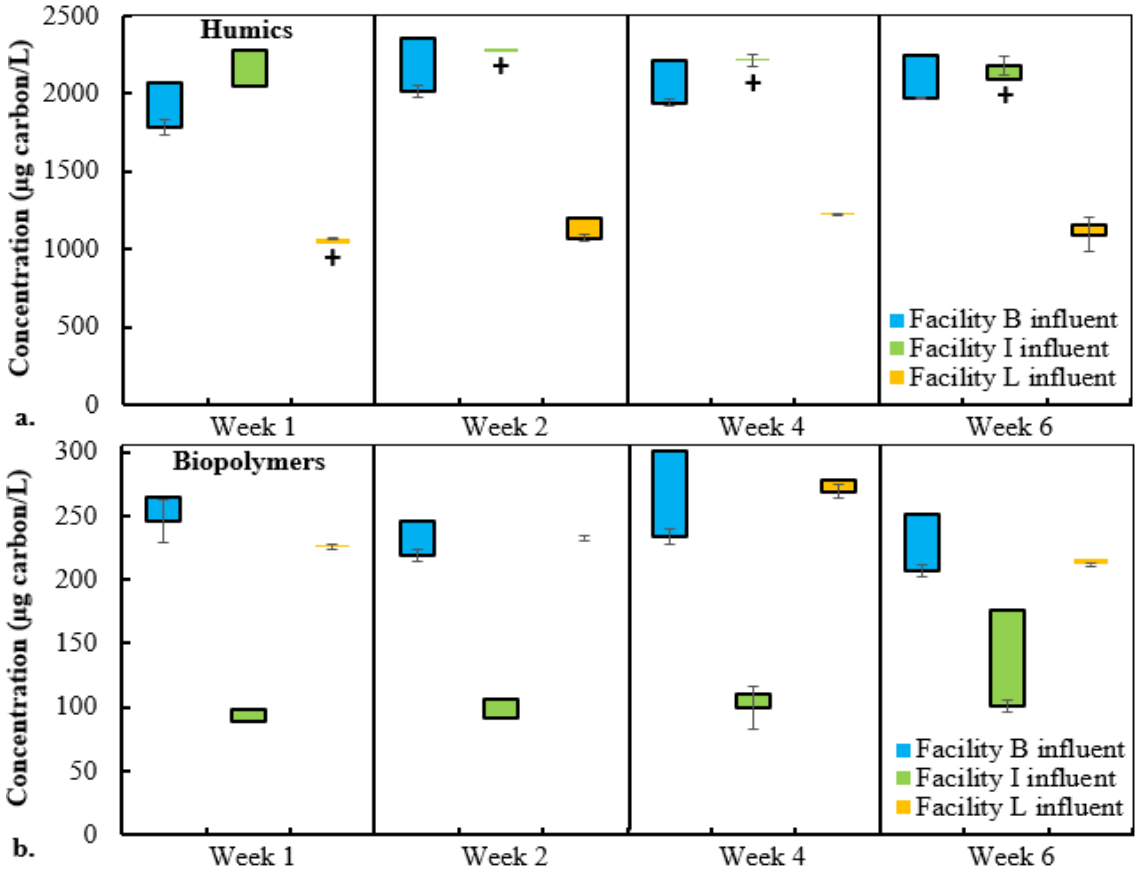


Figure 3.15 Removal of NOM fractions through bench-scale biofilter columns with Facility B media, fed water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Figure 3.16 a. shows that the removals of nitrogen in HS followed the same trends as observed for the carbon in HS with Facility B media. Figure 3.16 b. shows that the nitrogen in BP for the columns fed Facility I water was constantly below methods detection limits. Also, there were higher removals of nitrogen in BP when biofilter media from Facility B was fed with Facility B water for all weeks except for week 1. This nitrogen in BP did therefore not follow the same trends as the carbon in BP. Taken together, similar to the LC-OCD fractions, there were barely any similarities in the removals of the LC-OND fractions when Facility B media were fed different water sources.

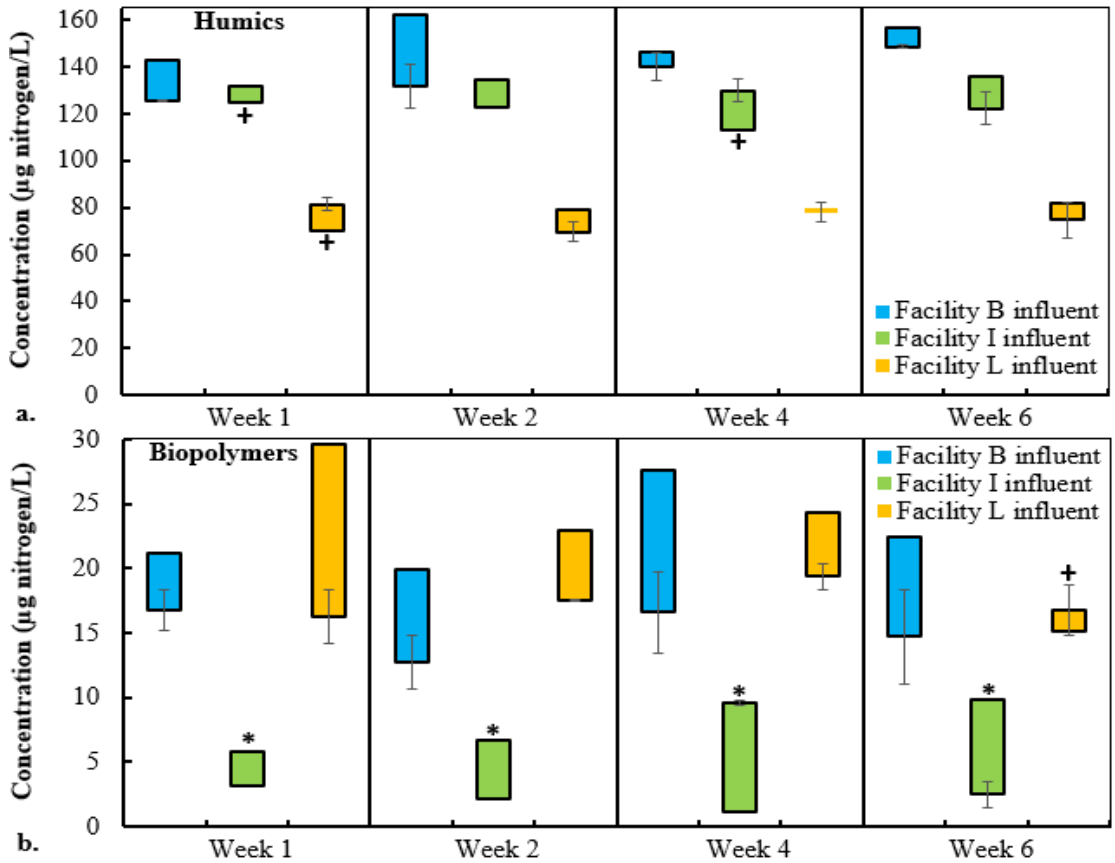


Figure 3.16 Removal of Nitrogen in NOM fractions through bench-scale biofilter columns with Facility B media, fed water from Facilities B, I and L analyzed by LC-OND. Reporting average nitrogen concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. * indicate that values are below methods detection limits.

Figure A.6 a. in Appendix A shows that there were higher reductions of HA when biofilter media from Facility B was fed with Facility I water, and HA reductions were lower when filter B media was fed with facility L water. This behaviour was consistent both in weeks 1 and 6. Figure A.6 b. in Appendix A shows no clear trends for FA. Figure A.6 c. in Appendix A shows that there were higher reductions of protein-like materials when biofilter media from Facility B was fed with Facility I water. However, the protein-like materials in the columns fed with Facilities B and L water increased during week 1, and all the water sources had an increase in the reductions from week 1 to week 6. A potential reason for low reductions in facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. However, there are no explanations for the trends in the columns fed with Facilities B and I water. Also, the trends in all the FEEM fractions were not similar to the trends

in the LC-OCD fractions. Collectively, similar to LC-OCD-OND fractions, there were barely any similarities in the reductions of the FEEM fractions when Facility B media were fed different water sources.

3.3.3.2 NOM Removals with Facility I Media

All bench-scale columns in this section were loaded with media from Facility I. Figure 3.17 a. shows that there were higher removals of HS when biofilter media from Facility I was fed with Facility B water, and HS removals were much lower when filter I media was fed with facility I or L water. This behaviour was consistent from week 1 through to week 6. BP removals followed the same trend as observed for HS removals (Figure 3.17 b.). These were the same trends as the columns with Facility B media. One reason for the low reductions in the columns fed Facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. A potential reason for the higher removals in the columns fed Facility B water might be the full-scale pre-ozonation treatment step prior to biofiltration, which converts some material in the NOM fractions into smaller more biodegradable compounds. Another potential reason for the higher removals in the columns fed Facility B water might be the higher ATP values in these columns (Table 3.9). The higher ATP values indicate a higher biological activity, which might cause the higher removals. Even though the columns fed with Facility I water had a longer time to acclimate, the ATP values for these columns were substantially lower than the columns fed with Facilities B and L water. This might be a potential reason for the lower removals in the columns fed with Facility I water. Taken together, these figures indicate that there were barely any similarities in the removals of the LC-OCD fractions when Facility I media were fed different water sources. This was similar to the columns with Facility B media.

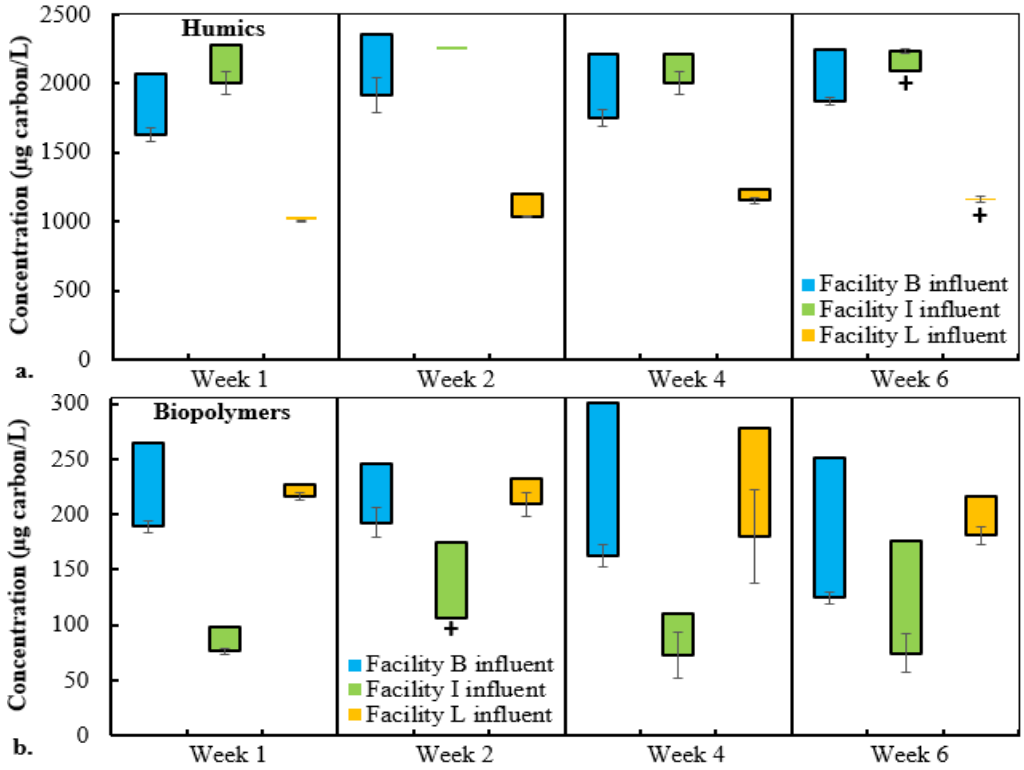


Figure 3.17 Removal of NOM fractions through bench-scale biofilter columns with Facility I media, fed with water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Figure A.8 a. in Appendix A shows that the removals of nitrogen in HS followed exactly the same trends as observed for the carbon in HS with Facility B media. Figure A.8 b. in Appendix A shows that the nitrogen in BP in the influents and effluents for the columns fed Facility I water and the effluents for the columns fed Facility B water were below method detection limits. Otherwise, there were no clear trends for this fraction. Collectively, similar to the LC-OCD fractions, there were barely any similarities in the removals for the LC-OND fractions when Facility I media were fed different water sources.

Figure A.9 a. in Appendix A shows that there were only very low reductions of HA in all the columns, and there were no other trends. Figure A.9 b. in Appendix A shows an increase in FA when fed all the different water sources both weeks except for week 1 when fed with Facility I water. Otherwise, there were fairly similar increases of FA for the different water sources. Figure A.9 c. in Appendix A shows that there were higher reductions of protein-like materials when

biofilter media from Facility I was fed with Facility I water, and HA reductions were lower when filter I media was fed with facilities B and L water. This behaviour was consistent both in weeks 1 and 6. It could be hypothesized that the biofilm on biofilter I media was better acclimated to reduce NOM fractions in facility I feed water than in facility I or L feed water. Also, a potential reason for the low FEEM reductions in facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. Also, the trends in all the FEEM fractions were not similar to the trends in the LC-OCD fractions. Overall, similar to LC-OCD-OND fractions, there were barely any similarities in the reductions of the FEEM fractions when Facility I media were fed different water sources. However, all the biofilters had higher reduction of protein-like materials and very low reductions or even increases of HA and FA, which is consistent with a previous study performed at a DWTP treating water from the Grand River (Chen et al., 2016). That study showed high reductions of protein-like materials (>20%) and low reductions for HA (<13%) and FA (<8%).

3.3.3.3 NOM Removals with Facility L Media

All bench-scale columns discussed in this section were loaded with media from Facility L. Figure 3.18 a. shows that the removals of HS followed exactly the same trends as observed for the columns with Facilities B and I media (Figure 3.15 and Figure 3.17). However, the BP removals in the columns with Facility L media were quite different from the columns with Facilities B and I media. Figure 3.18 b. shows that the BP removals were much more varied, with low removals initially and increasing removal from week 1 through to week 6. This might be due to the lower initial biological activity in the columns with Facility L media, as indicated by low ATP values. A potential reason for the higher removals in the columns fed Facility B water might be the full-scale pre-ozonation treatment step prior to biofiltration, which converts the NOM fractions into smaller more biodegradable compounds. Anther potential reason for the higher removals in the columns fed Facility B water might be the much higher ATP values at the end of the experiment in these columns. This indicate that these columns had a much higher biological activity, which might be the reason for the higher removals in these columns. A potential reason for the low removals in the columns fed with Facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. Overall, there

were barely any similarities in the removals of the LC-OCD fractions when Facility L media were fed different water sources.

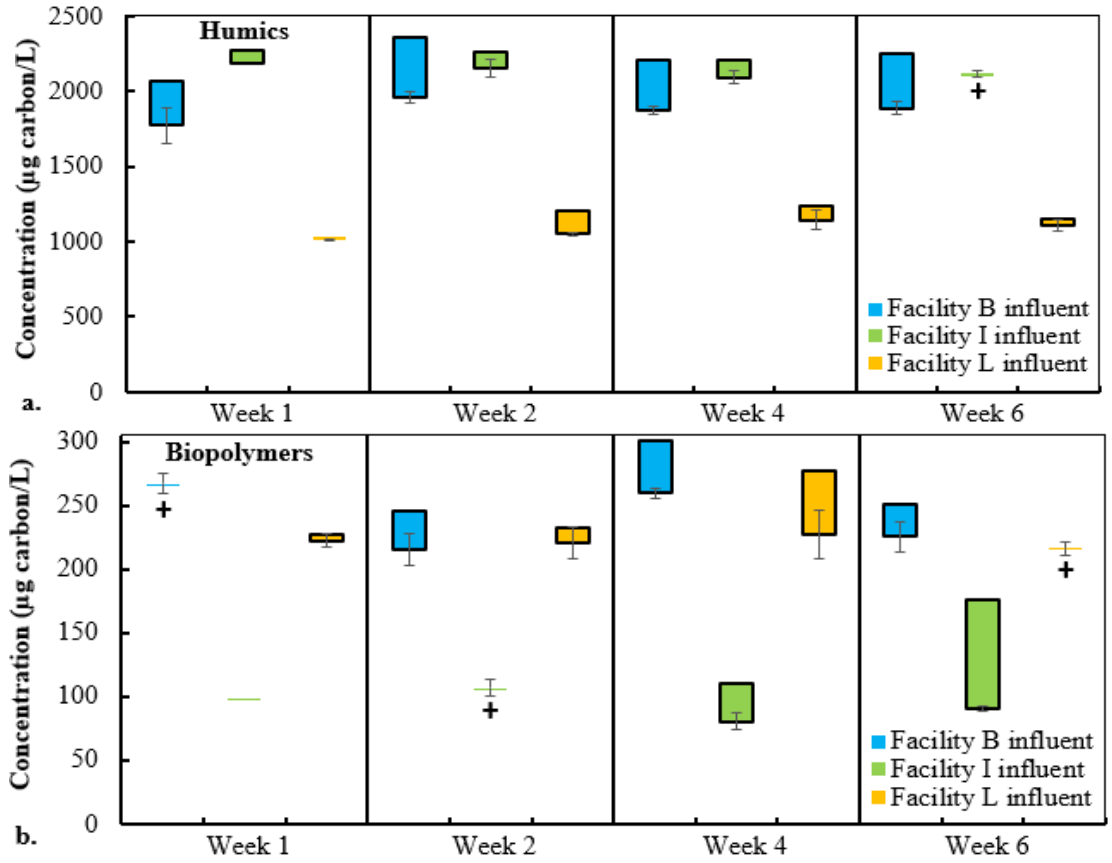


Figure 3.18 Removal of NOM fractions through bench-scale biofilter columns with Facility L media, fed water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Figure A.11 a. in Appendix A shows that the removals of nitrogen in HS followed the same trends as observed for the carbon in HS with Facility L media. Figure A.11 b. in Appendix A shows that the nitrogen in BP for the columns fed Facility I water was constantly below method detection limits. Also, there were higher removals of this fraction in the columns with Facility L media fed with Facility L water during weeks 1 and 2, but during weeks 4 and 6 the highest removals were in the columns fed with Facility B water. Collectively, similar to the LC-OCD fractions, there were barely any similarities in the removals for the LC-OND fractions when Facility L media were fed different water sources.

Figure A.12 a. and b. in Appendix A show that there were higher reductions of HA and FA when columns with Facility L media were fed with Facility B water during week 1, but during week 6 the highest reductions were in the columns fed with Facility I water. Also, the columns fed with Facility B water had higher reductions in week 1, but the columns fed with Facilities I and L water had higher reductions in week 6. Figure A.12 c. in Appendix A shows that there were higher reductions of protein-like materials when columns with Facility L media was fed with Facility I water. Also, the reductions of protein-like materials increased from week 1 to week 6. A potential reason for low reductions in the columns fed facility L water may be its lower water temperature and the presence of low levels of chlorine residual, both of which did not apply to facility B and I water. Also, the increasing reduction trends, over the duration of the experiment, might be due to the increase in biological activity, as indicated by the increase in the ATP values for facility L media. Also, the trends in all the FEEM fractions were not similar to the trends in the LC-OCD fractions. Overall, similar to the LC-OCD-OND fractions, there were barely any similarities in the reductions of the FEEM fractions when Facility L media were fed different water sources.

3.3.3.4 Similarities in NOM Removals with the Different Media

Overall, there were barely any similarities in any of the NOM fractions when a media was fed different water sources. The columns fed with Facility B water, in general, had higher removals of both the HS and BP LC-OCD fractions all weeks. All the nitrogen in BP were below methods detection limits at Facility I. Otherwise, the only similarity for the LC-OND fractions was that all the columns fed with Facility B water had higher removals of HS. For the FEEM fractions HA and FA, there was a decreased reduction from week 1 to week 6 in the columns with Facilities B and I media but an increased reduction in the columns with Facility L media. However, all the media had an increased reduction of protein-like materials from week 1 to week 6 at all the test locations. Taken together, there were barely any similarities in either the LC-OCD-OND or FEEM fractions when the three media were fed different water sources. This is consistent with previously mentioned studies (Croft, 2012; Pharand, 2014; Vasyukova et al., 2013), which indicated high variations in NOM fraction removals when biofilters were located at different DWTPs and therefore fed different water sources. However, they did not know if these variations were due to the water source or if it was the media that were acclimated/operated in different water sources. The results in this chapter confirm that the water source influences the NOM fraction removals

and biofilter performance and that these three media acclimated/operated in different water sources barely had any influence on the NOM removal or biofilter performance.

3.4 Conclusions

Removing NOM during drinking water treatment processes improves not only the aesthetic problems (taste, colour, and odour problems) but can also minimize potentially harmful carcinogenic DBPs. At three different facilities (Facilities B, I, and L) three different biofilter media (Facilities B, I, and L media) were investigated simultaneously in duplicate bench-scale biofilter columns to determined how pre-ozonation, water sources, and different media acclimated/operated in different water sources affect NOM removal during biofiltration.

The following conclusions can be made:

- Pre-ozonation improved the NOM removal and biofilter performance at Facility B, because ozone oxidizes NOM fractions and creates lower molecular weight by-products with higher biodegradability, which are more easily removed during biofiltration.
- Ozonation substantially reduced the intensities for of all the FEEM fractions. The reason for the drastic decreases in the fluorescence signals during ozonation is that ozonation changes the structure of the molecules by destroying the fluorophores.
- Water source influences the NOM removal and biofilter performance and water source therefore matters. The reason is that biofilters containing media acclimated/operated in different water sources behaved very similarly when fed the same water source during this bench-scale experiment.
- Media acclimated/operated in different water sources barely influenced the NOM removal and biofilter performance at a given location. The reason is that when a biofilter media were fed different water sources it behaved very differently at each water source. Also, it would be expected that, during the six-week experimental period, biofilms acclimated/operated in other water sources would gradually adapt to the water being used in the experiment.

3.5 Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for their use by the authors or funding agencies.

Chapter 4
Influence of Operational Conditions, Design Variables, and Water Quality Parameter on NOM Fraction Removals and Kinetics in Pilot-scale Biofilters

4.1 Introduction

Biofiltration is a filter process with a biologically active filter media due to a bacterial biofilm attached on the surface of the media. Some commonly used media types include GAC, anthracite, sand, and gravel, and some less commonly used media types include expanded ceramics and plastics (Basu et al., 2016; Simpson, 2008). Biofiltration is becoming more popular at WTPs due to its ability to biodegrade NOM and inorganic constituents, low in maintenance, and simple to operate (Bablon et al., 1988; Basu et al., 2016). Some other treatment steps that remove NOM include coagulation/flocculation, adsorption, oxidation, and membrane filtration (Kristiana et al., 2013; Zhang et al., 2015).

One of the best ways to optimize the biofilter performance is by changing operational conditions and design variables (Moll et al., 1999). However, only one study has been conducted on the removal of NOM fractions as measured by LC-OCD and FEEM and the corresponding kinetics. The latter was determined by profiling NOM fractions over the entire depth of a pilot-scale biofilter (Chen et al., 2016). This study only focused on removal behaviours and kinetics of NOM fractions for one pilot-scale biofilter and they did not investigate varying operational conditions and design variables. Various studies have been conducted on how media type or different backwash conditions influence NOM removal during biofiltration. Some studies have shown that the GAC media has a higher NOM removal than, for example, anthracite media (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010). Other studies reported that besides the media type, media size can also influence the biofiltration performance (Huck and Sozanski, 2008; Huck et al., 2013; Zhang and Huck, 1996). Another study showed that chloraminated backwash reduced microbial counts in the biofilter media (Rasheed et al., 1998). However, other studies showed that backwash oxidants are not expected to have a quantifiable effect on biofiltration performance, but it depends on the specific biofilter (Emelko et

al., 2006; Hozalski and Bouwer, 2001). Emelko et al. (2006) investigated the influence from different backwash types (chloraminated water, nonchloraminated water, and air scour) on the biofilters biomass, and there were no statistical differences. Hozalski and Bouwer (2001) investigated the influence from different backwash types (chloraminated water, nonchloraminated water, and air scour) and backwash frequency (daily or every second day) on removals of biofilter biomass. This study showed that there was little or no biomass removals from different backwash types (chloraminated water, nonchloraminated water, and air scour), and backwashing had to remove 60% or more of the biomass to impact the biofiltration performance. Also, these studies showed that backwash frequency is not expected to have a quantifiable effect on biofiltration performance. However, these studies only looked at DOC and TOC except for Chen (2016), which used LC-OCD and FEEM to characterise NOM fractions. Therefore, more research is needed on how different backwash conditions and how different media types influence the LC-OCD and FEEM fraction removals and their kinetics.

NOM is difficult to characterize due to the complex mixture of organic compounds with varying properties, molecular sizes, and functional groups (Thurman, 1985). Furthermore, some traditional NOM characterization techniques include UV254, SUVA, and TOC. Other analytical techniques, such as LC-OCD and FEEM, characterize multiple fractions in a water sample, and these techniques are therefore becoming more accepted NOM characterization tools in analysing water samples, and these two analytical techniques are therefore used in this research.

Chapter 3 already showed the influence of pre-ozonation, water source, and media acclimated/operated in different water sources on NOM removal during biofiltration. This chapter will therefore investigate how different operational conditions and design variables influence NOM removal and its kinetics during pilot-scale biofiltration. These conditions and variables include other full-scale pre-treatment processes prior to biofiltration (PAC, lime softening, and recarbonation), media type (GAC vs. anthracite), backwash type (chloraminated vs. non-chloraminated water), backwash frequency (daily vs. twice weekly), and ammonia addition to biofilter feed. It is important to have a better understanding of how different conditions and variables influence NOM removal and its kinetics to generate control strategies for NOM.

The main objectives of the research described in this chapter were to investigate how the above mentioned conditions and variables influenced the overall NOM removal, the removal of

individual fractions, and their kinetics throughout pilot-scale biofilter columns. To achieve these objectives pilot-scale biofilter tests were run in two locations, and each pilot-scale test included multiple biofilter columns run simultaneously, and only one condition was tested at a time. During the tests, water samples were collected from the biofilter influents and effluents, and sometimes from different biofilter depths as well. Samples were analysed on LC-OCD and FEEM to determine the NOM characteristics and to calculate biofilter kinetics of NOM removal for each biofilter column at each condition. The work presented in this thesis was done as part of a larger WRF project (project #4669), and the conditions tested were primarily related to the WRF objectives, which centered around NDMA precursor formation or removal (Evans et al., forthcoming). Therefore, the designs of these pilot-scale experiments were limited and tailored to the WRF objectives. Overall, the insights gained from this study will be of assistance to optimize biofiltration performance and improve NOM removal throughout biofilters. This could potentially expand the usage of biofiltration during drinking water treatment and improve biofiltration performance.

4.2 Material and Methods

Two different pilot-scale tests were conducted, one at Facility C and another at Facility Q, and these tests are described below. The participating utilities and their staff members provided information about the full-scale treatment processes, and installed, operated and sampled the pilot-scale biofilters during tests at Facilities C and Q. All samples for NOM characterization were shipped to the University of Waterloo, where Lin Shen performed the LC-OCD sample analysis while the author performed all the FEEM sample analysis. Evaluation and interpretation of all LC-OCD chromatograms was performed by the author. All samples for the NDMA UFC tests were shipped to and analyzed by Stanford University (Zhong Zhang and Dr. Bill Mitch). They provided the NDMA UFC data to the author. The interpretation, writing and analysis of all the data presented in this chapter were conducted by the author.

4.2.1 Pilot-scale Tests at Facility C

There were three 20.3 cm diameter pressurized biofilter columns used in these tests, as described in Table 4.1. All the columns were dual media filters with 20.3 cm of sand in the bottom of each filter. The GAC media was approximately 7 years old, so the majority of the adsorption capacity

has been exhausted, and the anthracite was approximately 15 years old. Each column was fed with water from the full scale WTP, which had been through the following pre-treatment steps: coagulation with alum, flocculation, sedimentation, and pre-ozonation. The influent water flow to the biofilters was 3.4 L/min, which resulted in an EBCT of approximately 10 min. Furthermore, these columns were backwashed approximately every 48 hours with non-chloraminated water with air scour (3-5 scfm/sf) for 1.6 minutes followed by water at 37.9 L/min for 4 minutes and then 11.6 L/min for 1 minute.

Table 4.1. Overview of pilot-scale biofilters' media type and depth, and sampling ports for pilot-scale tests at Facility C.

Filter number	Media type and depth	Sampling ports
1	GAC – 105.4 cm Sand – 20.3 cm	Port 3: 21.6 cm Port 5: 57.2 cm Effluent: 105.4 cm
2	GAC – 106.7 cm Sand – 20.3 cm	Port 3: 17.8 cm Port 5: 71.1 cm Effluent: 106.7 cm
3	Anthracite – 101.6 cm Sand – 20.3 cm	Port 3: 17.8 cm Port 5: 71.1 cm Effluent 101.6 cm

Two rounds of pilot-scale tests were conducted at Facility C; the first round was run from August 2nd to August 15th 2017, and the second round was run from September 15th to September 25th 2017. Before the two rounds of experiments, the columns had an acclimation period, which started on June 1st 2017 (approximately 2 months before the first round of experiment). During this acclimation period, the columns were run under the same conditions as described above. During the first round of tests, 1±0.05 mg-N/L of ammonia was added to the feed water for columns 2 and 3, and no chemicals were added to column 1, since it served as a control column. The second round of tests evaluated the impact of chloraminated backwash on NDMA formation. Therefore, column 1 was still backwash with non-chloraminated water, since column 1 still served as a control column, and columns 2 and 3 were backwashed with chloraminated water with a chloramine residual of approximately 3.5-4 mg/L.

Table 4.2 shows the analytical parameters measured in this experiment, including sampling location and time. Water quality samples were collected weekly from June 1st 2017 to December 18th 2017. After sampling, all parameters were analyzed at Facility C aside from LC-OCD/FEEM

and NDMA which were shipped for analysis to the University of Waterloo and Stanford University, respectively.

Table 4.2 Analytical parameters, sampling location, and time for Facility C phases 1 and 2.

Analytical parameters	Sample location	Sample time
pH, temperature, DO, turbidity, total chlorine, total ammonia, nitrite, nitrate, TOC, DOC, UV254	Influents	Weekly from 01.06 2017 to 18.12 2017
LC-OCD, FEEM, NDMA UFC	Influents and effluents	17.07 2017 15.08 2017 25.09 2017
	Sampling ports 1 and 2	15.08 2017 25.09 2017

4.2.2 Pilot-scale Tests at Facility Q

For the pilot tests at Facility Q, eight biofilter columns, with a diameter on 10.16 cm, were used, and these columns are described in Table 4.3 including filter number, media type, and the depths of each sampling port. All the columns were dual media filters with 10.2 cm pea gravel and 25.4 cm of sand in the bottom of each filter. New media were placed in the columns in July 2015, so the media was approximately 2 years old when the experiments took place. Also, the columns had been in operation ever since and they were therefore fully acclimated when the experiment took place. Each column was fed with water from the full-scale WTP, which had been through the following pre-treatment steps prior to biofiltration: PAC, lime softening, recarbonation, ferric chloride coagulation, flocculation, and sedimentation. The influent water flow to the biofilters were 7.6 L/min and the columns therefore had an EBCT of 9.4 minutes. During the recarbonation step, the water was adjusted to a pH at around 8.5 to 8.8 with hydrochloric acid. The filters were backwashed with either chloraminated water (3.7 mg/L chloramine) or nonchloraminated water for approximately 5 minutes with an air scour at 36.8 L/min to reach a filter bed expansion of 30%. Regular backwashes were usually performed every Monday and Thursday or if the head loss got too high.

Table 4.3. Overview of pilot-scale biofilters' media type and depth, and sampling ports for pilot-scale tests at Facility Q.

Filter number	Media type and depth	Sampling ports
1	GAC – 50.8 cm Sand – 25.4 cm Pea gravel – 10.2 cm	Port 1: 13.3 cm Port 2: 28.6 cm Port 3: 43.8 cm
2		Port 1: 14.3 cm Port 2: 29.2 cm Port 3: 44.5 cm
3		Port 1: 12.7 cm Port 2: 27.9 cm Port 3: 43.2 cm
4	Anthracite – 50.8 cm Sand – 25.4 cm Pea gravel – 10.2 cm	Port 1: 9.5 cm Port 2: 24.1 cm Port 3: 39.2 cm
5		Port 1: 12.1 cm Port 2: 27.0 cm Port 3: 42.5 cm
6		Port 1: 8.6 cm Port 2: 23.2 cm Port 3: 38.7 cm
7	GAC – 50.8 cm Sand – 25.4 cm Pea gravel – 10.2 cm	Port 1: 7.62 cm Port 2: 22.9 cm Port 3: 38.1 cm
8		Port 1: 6.0 cm Port 2: 21.0 cm Port 3: 36.2 cm

Two phases of pilot-scale tests were conducted at Facility Q; the first phase was run from March 26th 2018 to April 30th 2018, and the second phase was run from July 17th 2018 to August 13th 2018. The operational parameters can be seen in Table 4.4. During the first phase, the columns were either backwashed using chloraminated water or nonchloraminated water and they were all backwashed regularly (every Monday and Thursday as full-scale biofilters). During the second phase of tests, the backwash frequency for some columns was increased from regular backwash frequency, the same frequency as phase 1 (twice weekly), to a frequent backwash (daily backwash), and these columns were: 1, 2, 4, 5, and 7. Furthermore, during phase 2, all columns were still backwashed using the same backwash types as in phase 1. These operational parameters can be seen in Table 4.4.

Table 4.4. Operational parameters for phases 1 and 2 for pilot-scale tests at Facility Q. None = Nonchloraminated, Regular = backwashed twice weekly, and frequent = backwashed daily.

Columns	Media type	Phase 1		Phase 2	
		Backwash water	Backwash frequency	Backwash water	Backwash frequency
1	GAC	Chloraminated	Regular	Chloraminated	Frequent
2					
3					Regular
7		None		None	Frequent
8					Regular
6	Anthracite	Chloraminated		Chloraminated	Regular
4		None		None	Frequent

Table 4.5 shows the analytical parameters measured in this experiment, including sampling location and time. After sampling, all parameters were analyzed at Facility Q aside from LC-OCD/FEEM, and NDMA UFC which were shipped to the University of Waterloo and Stanford University, respectively. At the end of phase 1 (April 30th 2018), influents were sampled for LC-OCD and FEEM, each sampling port, and effluents for columns 1-2, and 4-8. Column 3 was not sampled during phase 1 since it was identical to columns 1 and 2 and it would therefore have been a triplicate. At the end of phase 2 (August 13th 2018), LC-OCD and FEEM were sampled for influents, each sampling port, and effluents for columns 1-4, and 6-8. Column 5 was supposed to be sampled during phase 2, but an error occurred during backwash and all the media were lost in the column prior to this phase. Unfortunately, there was not enough time to add new media and get it acclimated and column 5 was therefore excluded from phase 2.

Table 4.5 Analytical parameters, sampling location, and time for Facility Q phases 1 and 2.

Analytical parameters	Sampling location	Sampling time
pH, temperature, DO, turbidity, total chlorine, total ammonia, nitrite, nitrate, TOC, DOC, UV254	Influents	Mondays and Fridays from 02.04 to 13.08 2018
LC-OCD, FEEM, NDMA UFC	Influents and effluents	02.04 2018 09.04 2018 16.04 2018 23.04 2018 30.04 2018 02.07 2018 17.07 2018 24.07 2018 07.08 2018

		13.08 2018
	Sampling ports 1, 2, and 3	30.04 2018 13.08 2018
	Full-scale treatment processes upstream of biofilters	09.04 2018 24.07 2018
ATP	Media for each column	15.03 2018 14.08 2018

4.2.3 Analytical Parameters

All the instruments and methods used for analysis during these tests were identical to those described in chapter 3. Also, these parameters were determined in the laboratory at each Facility except for LC-OCD/FEEM and NDMA UFC which were shipped for analysis to the University of Waterloo and Stanford University, respectively.

4.2.4 Kinetic Analysis of NOM Removals during Biofiltration

To analyse the kinetics of the NOM removals during biofiltration, zero-, first- and second-order kinetics models were applied to the biofilter profiles of the various NOM fractions for samples obtained on 15.08 and 25.09 2017 at Facility C, and on 30.04 and 13.08 2018 at Facility Q. The linearized forms of equations for first- and second-order kinetics were used, and all of the equations are summarized as follows:

Zero order kinetics: $[A] = -kt + [A]_0$

First order kinetics: $ln[A] = -kt + ln[A]_0$

Second order kinetics: $1/[A] = kt + 1/[A]_0$

Where $[A]$ is the concentration or intensity of the component, k is the reaction rate constant, and t is the time.

The kinetics order was calculated for various LC-OCD and FEEM fractions, and the best-fit reaction order(s) and the corresponding rate constants were determined.

4.3 Results and Discussions

4.3.1 Water Quality of Pilot-scale Biofilter Feed

4.3.1.1 Raw Water Sources and Treatment Processes Prior to Biofiltration at Full-scale Plants

The pilot-scale columns were located at the full-scale plants (Facilities C and Q) and the pilot-scale columns were therefore fed with the same water as the full-scale biofilters. The influent water to Facility C was from a nearby lake in Southern USA, and the full-scale treatment steps prior to the biofilters include the conventional treatment steps: coagulation, flocculation, sedimentation, and pre-ozonation. The coagulant used at Facility C is Aluminium Sulfate and the polymer used is Cationic PolyDADMAC (C-308P). Furthermore, the full-scale biofilters were typically backwashed with non-chloraminated filtered water. The influent water at Facility Q was from a nearby river in Northern USA, and the full-scale treatment steps prior to the biofilters consist of PAC, lime softening, recarbonation, coagulation, flocculation, and sedimentation. During recarbonation, the pH was adjusted to 8.5 to 8.8 with hydrochloric acid, and the coagulant Ferric Chloride was added at approximately 2.0 mg/L. If there was an increase in organics (usually during spring and summer) then the polymer polyDADMAC (AquaHawk 101) may be added during coagulation to enhance the organic removals. The full-scale biofilters were typically backwashed with non-chloraminated water.

4.3.1.2 Water Quality of Biofilter Influents

Table 4.6 shows that the influent water quality at both facilities was fairly constant throughout the experiments, except for the influent at Facility Q from June 1st to August 10th 2018 where local storm events might have impacted the influent water quality. The tests at Facility C were conducted during the summer and therefore under warm water conditions, with a minimum influent water temperature of 19.1°C. However, Facility Q phase 1 was conducted during spring, which was during cold water conditions with a minimum of 4°C, and phase 2 was conducted during summer, which was during warm water conditions with a maximum of 28°C. The pH in the influent at Facility C was near neutral and only ranging from 7.3 to 7.7 and it was therefore very constant. However, the pH was much higher in the biofilter influent at Facility Q, which was due to upstream lime softening and recarbonation, and the pH was very similar during the two phases. Furthermore, DO was higher in the influent at Facility C, which was due to upstream ozonation. The DO in the influent at Facility Q was lowest during the summer (phase 2). Also, turbidity was very low in the

influent at Facility C, but at Facility Q the turbidity was at least a factor of 10 higher and varied a lot. A potential reason for the low turbidity in the influent at Facility C and high turbidity in the influent at Facility Q is that the water source at Facility C is from a reservoir whereas it is from a river at Facility Q. Also, at Facility Q the turbidity was 19% higher in the influent in phase 2 than during phase 1, and this differs from another study, which showed that the turbidity was usually lowest during the summer in various raw water sources (Croft, 2012). However, as previously mentioned, there were local storm events during phase 2, which might have impacted the turbidity. The total chlorine at both facilities were very low and close to the detection limits. Total ammonia, nitrite, and nitrate were also low in the influents at both facilities. However, total ammonia and nitrate were higher in the influent at Facility Q phase 1, which is consistent with a previous study of another river water that showed that total nitrogen (ammonia, nitrite, and nitrate) usually was higher during winter and spring (Pharand, 2014). The increased nitrogen concentrations in surface water during spring might be due to surface runoff, and at cold temperature the nitrogen is usually washed into the rivers rather than taken up by plants due to reduced plant growth (Pharand, 2014). The TOC and DOC showed that almost all organics were present as dissolved organics in the influents at both facilities and it was lowest at Facility C and highest at Facility Q phase 2. This differs from a previous study, which showed that both TOC and DOC usually were lower during the summer than the spring at various raw water sources (Croft, 2012). Also, UV254 was lowest in the influents at Facility Q phase 1 and highest at Facility Q phase 2, which also differs from the previous study that showed that UV254 usually were lower during the summer than the spring at various raw water sources (Croft, 2012). SUVA indicates how large a portion of the organics present in the water are aromatic, and aromatic organics can potentially form more DBPs. Therefore, a high SUVA indicates there is a higher potential for the formation of DBPs. Table 4.6 shows that the SUVA in Facility Q influent was more than double the value of the Facility C influent, meaning that the risks for forming DBPs are potentially higher at Facility Q. Overall, the influent at Facility C had the lowest concentrations for all parameters. Also, the influents at Facility Q phases 1 and 2 were fairly similar, but phase 1 had higher DO, total ammonia, and nitrate concentrations, and lower temperature, turbidity, TOC, DOC, UV254, and SUVA values.

Table 4.6 Average influent water quality at Facility C and Facility Q Phases 1 (spring) and 2 (summer).

	Units	Facility C	Facility Q Phase 1	Facility Q Phase 2
pH		7.4 ± 0.3	9.0 ± 0.7	8.9 ± 1.0
Temperature	**°C**	25.3 ± 9.6	16 ± 12	25 ± 5
DO	**mg/L**	11.4 ± 2.1	9.2 ± 4.2	7.8 ± 0.4
Turbidity	**NTU**	0.47 ± 0.56	5.7 ± 8.3	6.8 ± 4.2
Total Chlorine	**mg/L**	0.02 ± 0.05	0.02 ± 0.08	<0.02
Total ammonia	**mg-N/L**	0.05 ± 0.09	0.10 ± 0.19	0.02 ± 0.01
Nitrite	**mg-N/L**	0.002±0.002	0.02 ± 0.02	<0.015
Nitrate	**mg-N/L**	0.35 ± 0.12	0.82 ± 0.58	0.55 ± 0.33
TOC	**mg-C/L**	3.46 ± 0.81	4.2 ± 1.8	5.5 ± 1.8
DOC	**mg-C/L**	3.42 ± 0.61	4.2 ± 1.7	5.5 ± 1.8
UV254	**cm^{-1}**	0.028±0.010	0.07 ± 0.05	0.12 ± 0.05
SUVA	**L/mg·m**	0.82 ± 0.18	1.67 ± 0.87	2.18 ± 0.29

This dataset shows the average concentrations and the ranges over the duration of the experiment for each water quality parameter.

4.3.1.3 NOM Characterization of Biofilter Influents

Figure 4.1 a. shows the concentrations for DOC and HS and Figure 4.1 b. for BP, BB, LMW acids/humics, and LMW neutrals for the biofilter influents at Facilities C and Q. These fractions are of interest since, for example, HS can contribute to formation of DBPs (Wassink et al., 2011), BP can contribute to hydraulically reversible fouling of low pressure membranes (Hallé et al., 2009; Peldszus et al., 2012; Tian et al., 2013), and LMW acids/humics can contribute to biofouling of certain membranes (Huck and Sozanski, 2008). Figure 4.1 shows that the biofilter influent at Facility C, in general, had the lowest concentrations in all LC-OCD fractions except for LMW neutrals, where Facility Q phase 2 had the lowest concentration. The LMW neutrals in the influents at Facility C were high and had a high variation due to an unusually high LMW neutrals concentration on August 15th 2017. It is unknown why the LMW neutrals concentration was high on this day. In general, the variability of DOC and all other fractions for the influent at Facility C was less than at Facility Q, which might be because of the influent at Facility C is from a reservoir and it was only sampled over a shorter period of time (during summer only). The influents at Facility Q phases 1 and 2 also had high variations, especially for DOC and HS, which are also indicated by the error bars in Figure 4.1. These variations were caused by high fluctuations in the source water over time, and both DOC and HS were particularly high on July 2nd and August 7th 2018, which can also be seen in Figure 4.14. As mentioned earlier, from June 1st to August 10th

2018 there were local storm events that might have impacted the influent water quality. The concentration for HS was higher than the concentrations for all the other fractions, which was expected. Furthermore, influents at Facility Q phases 1 and 2 were, in general, fairly similar, and any differences may be caused by seasonal changes since phase 1 was during spring and phase 2 was during summer.

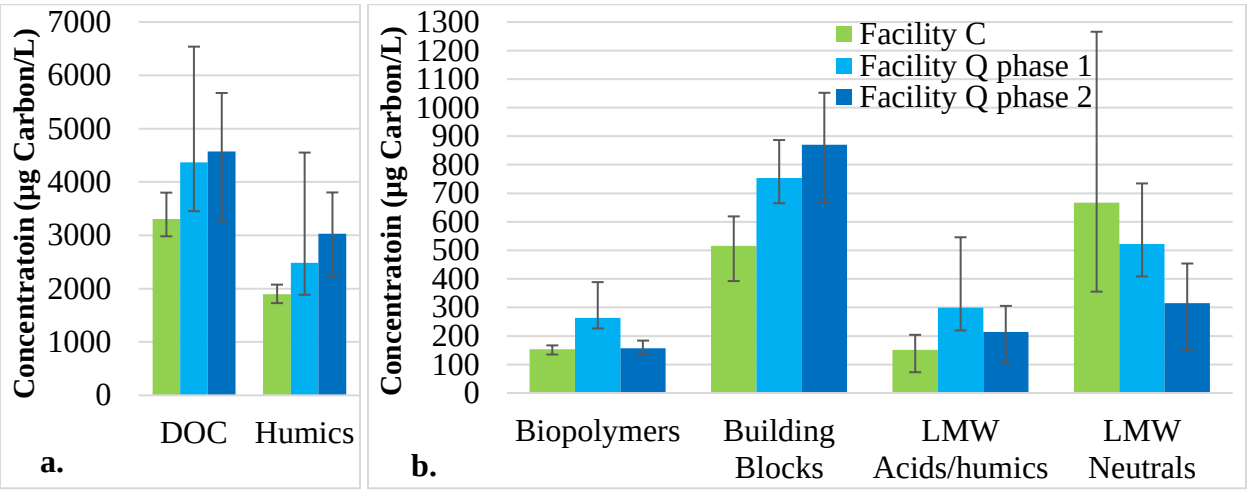


Figure 4.1 NOM characterization of biofilter influents at Facilities C and Q analyzed by LC-OCD, reporting average organic carbon concentrations in a. DOC and HS, b. BP, BB, LMW acids/humics, and LMW neutrals. Error bars indicate maximum and minimum values for n=3 at Facility C, n=6 for Facility Q phase 1, and n=4 at Facility Q phase 2.
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Table 3.7 shows that the majority of the DOC at both facilities consisted of HS (56-66%), which is the case for most natural waters that typically consist of 40 to 60% HS (Thurman, 1985). The influents at Facility C had a much higher LMW neutrals concentration and slightly lower HS, BB, and LMW acids/humics concentrations than the influents at Facility Q. The influent at Facility Q phase 2 had the highest HS and BB, and the lowest BP and LMW neutrals compositions. The composition of the DOC changed from spring to summer.

Table 4.7 NOM composition as a percent of DOC of average influents at Facilities C and Q.

	Facility C	Facility Q Phase 1	Facility Q Phase 2
BP	4.6	6.1	3.4
HS	56	57	66
BB	15	17	19
LMW acids/humics	4.5	6.9	4.7
LMW neutrals	20	12	6.9

Figure 4.2 shows that the HS and BP nitrogen concentrations in the influents at both Facilities C and Q were fairly similar to each other. However, the HS nitrogen concentration was slightly higher in the influent at Facility Q phase 2. The BP nitrogen concentration was below the detection limits of 10 µg Nitrogen/L in the influents at Facility C and Facility Q phase 2.

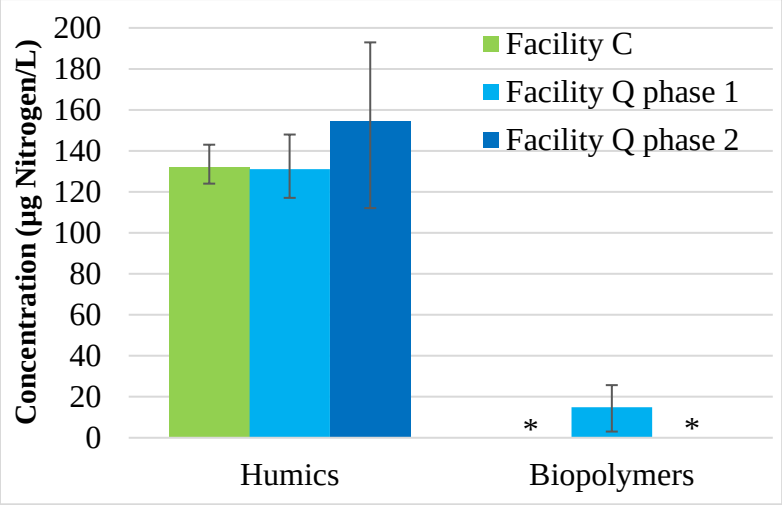

Figure 4.2 NOM characterization of biofilter influents at Facilities C and Q analyzed by LC-OND, reporting average organic nitrogen concentrations in HS and BP. Error bars indicate maximum and minimum values for n=3 at Facility C, n=6 for Facility Q phase 1, and n=4 at Facility Q phase 2. * indicate that BP was detected but values were below the method detection limit of 10 µg nitrogen/L.
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Table 4.8 shows that the N/C ratios for Facilities C and Q for both HS and BP were between 5% to 7% by weight. This table also indicates that the N/C ratios for both HS and BP at both facilities were very similar to each other. Also, other studies have reported similar N/C ratios in drinking water (Lee et al., 2006 a; b; Chang et al., 2013).

Table 4.8 N/C ratios of average HS and BP in influents at Facilities C and Q.

	Facility C	Facility Q Phase 1	Facility Q Phase 2
HS	0.07	0.06	0.05
BP	0.06	<MDL	0.05

<MDL indicate that the data is below methods detection limits.

Figure 4.3 shows that the HS characteristics were very consistent for the different influents since they were clustered together by location. The influents at Facility C had the lowest aromaticity and low average molecular weight. Facility C had ozonation prior to the biofilters, which was similar to Facility B in Chapter 3, which might have influenced the HS characteristics. The influent at

Facility Q phase 1 had similar low average molecular weight as the influent at Facility C but a higher aromaticity. Also, both the aromaticity and average molecular weight for the influents increased at Facility Q from phase 1 to phase 2. This might be due to a seasonal shift in composition from spring to summer, and it is consistent with Figure 4.1, Figure 4.2, and Table 3.7. Furthermore, all the influents had low aromaticity and average molecular weight, which is distinctive for FA of autochthonous (aquagenic) origin (Huber et al., 2011). However, the influent at Facility Q phase 2 was on the border of being allochthonous (pedogenic) FA (Huber et al., 2011).

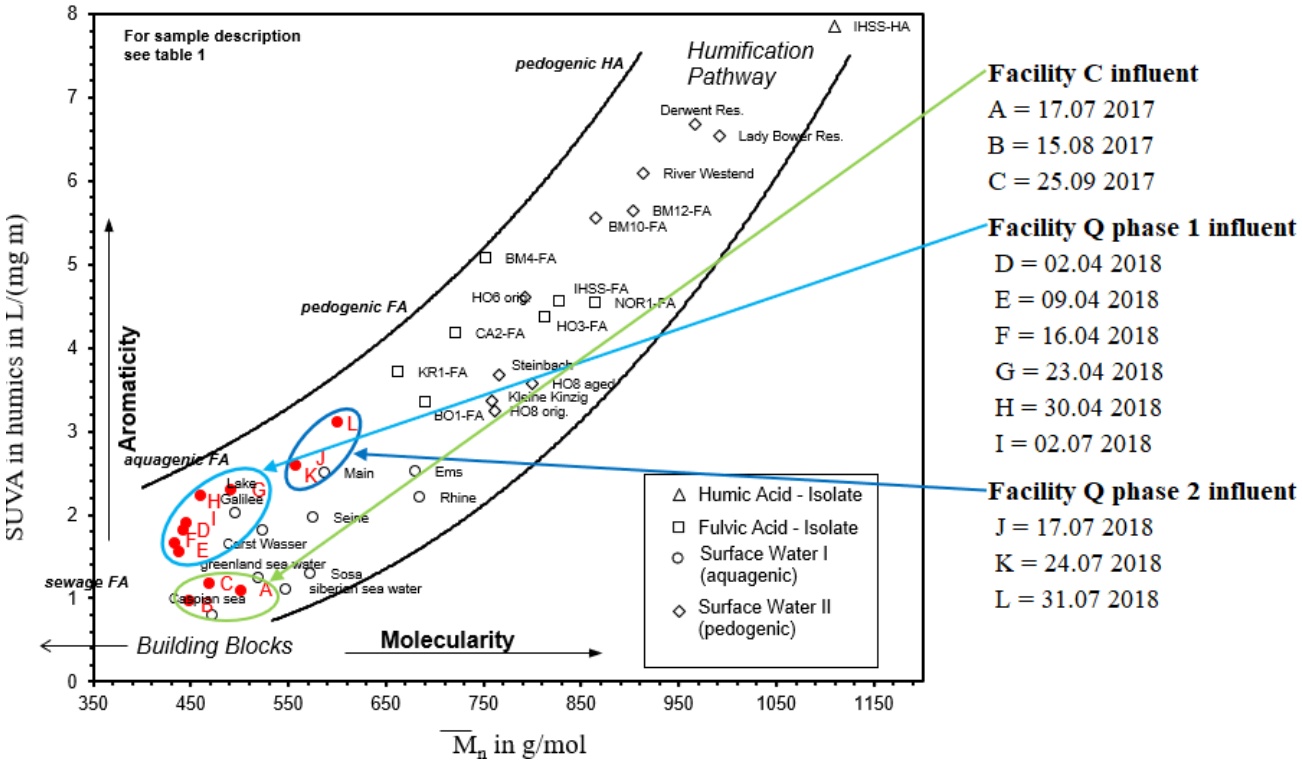

Figure 4.3 HS characteristics of biofilter influents at Facilities C and Q.
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Figure 4.4 shows the intensities for the FEEM fractions HA, FA, and protein-like materials in the influents at Facilities C and Q. The influent at Facility C had very low intensities for all three fractions, and they were very constant throughout the experiment. The ozonation at Facility C was probably a major contributing factor to the drastically decreased the fluorescence signals, which is consistent with the findings above (Figure 4.1, Figure 4.2, and Figure 4.3), in chapter 3, and other studies (Baghoth et al., 2011; Croft, 2012). Ozonation changes the structure of the molecules, which caused the significant decrease in the fluorescence signals. The intensities for HA and FA in the influents at Facility Q varied a lot during the different weeks (indicated by the error bars),

and the average intensities were much lower in the influent during phase 1. The higher intensities in the influents during phase 2 might be due to seasonal change. Also, this seasonal trend for HA and FA as measured by FEEM is consistent with a change in HS character as measured by LC-OCD and shown in Figure 4.3. However, the protein-like materials in the influents at Facility Q phases 1 and 2 were very similar to each other and higher than the influents at Facility C.

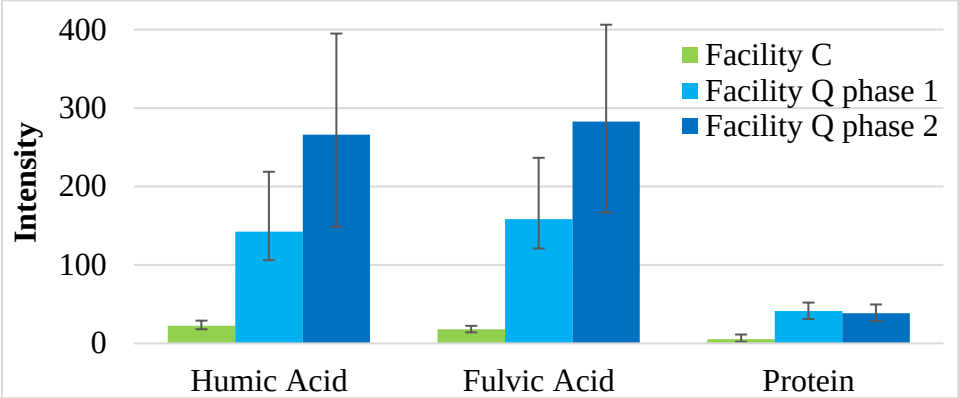

Figure 4.4 NOM characterization of biofilter influents at Facilities C and Q analyzed by FEEM, reporting average intensities for HA, FA, and protein-like materials. Error bars indicate maximum and minimum values.
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4.3.2 Biological activity of biofilter media as indicated by ATP

ATP was measured at the start and end of the experiment, and it was measured to quantify the total active biomass on the surface of the biofilter media, which identifies whether the biofilter media is biologically active (Magic-Knezev and van der Kooij, 2004; Pharand, 2014; Velten et al., 2011a). Unfortunately, ATP was not measured at Facility C, and ATP is therefore only available for Facility Q. Some studies have reported a range of 100-10,000 ng ATP/cm^3 for active biofilter media for different full-scale biofilters (ElHadidy, 2016; Evans et al., 2013; Pharand, 2014). Since almost all columns had an ATP value just above 100 ng/cm^3 (except for column 6 at the beginning and columns 1 and 2 at the end of these experiments), these columns were therefore only marginally biologically active. Table 4.9 shows that except for column 3 all GAC columns had higher ATP values at the start of the experiment, than at the end of the experiment. However, the ATP values for the anthracite columns increased. The GAC columns backwashed with chloraminated water had the lowest ATP value at the end of the experiment. This seems to indicate that chloraminated backwash water reduced the active biomass in the biofilters, which is consistent

with other research (Rasheed et al., 1998). However, another study found that backwashing had to remove 60% or more of the biomass to have an impact of the biofiltration performance (Hozalski and Bouwer, 2001).

Table 4.9 ATP values for pilot-scale biofilters at Facility Q. None = Nonchloraminated.

Columns	Media Type	Backwash water	15.03.2018 ng/cm^3	14.08.2018 ng/cm^3
1	GAC	Chloraminated	142	88
2			142	78
3			127	135
7		None	246	168
8			307	229
6	Anthracite	Chloraminated	56	152
4		None	111	143

4.3.3 Impact of Full-scale Treatment Steps Prior to Biofiltration on NOM Removal

As stated in chapter 3, pre-ozonation improved the NOM removal and biofiltration performance. Therefore, this section will determine how the upstream full-scale treatment at Facility Q influenced NOM fraction removals during biofiltration. The results discussed in this section are from April 9th, and the July 24th sampling results were very similar to these results and are shown in the Appendix (Figures B.1, B.2, and B.3). Figure 4.5, Figure 4.6, and Figure 4.7 show that the majority of various LC-OCD and LC-OND fractions were removed during PAC application. These fractions were DOC, HS, BP, BB, and only small amounts of LMW neutrals. PAC, for example, removed more than 50% of DOC, and HS and more than 83% of BP. PAC also reduced FEEM fractions substantially, it for example, reduced HA and FA by more than 50%. These results between LC-OCD-OND and FEEM are therefore consistent with each other. However, the rest of the treatment processes showed no removals, except for $FeCl_3$ coagulation with and without polyDADMAC which increased LMW neutrals (Figure 4.5 b.), and $FeCl_3$ coagulation only without polyDADMAC increased protein-like materials (Figure 4.7). Overall, PAC application successfully removed high amounts of various NOM fractions at Facility Q, for example, more than 83% of BP, which is consistent with previous studies (Löwenberg and Wintgens, 2017; Löwenberg et al., 2014; Seo et al., 2004; Tomaszewska and Mozia, 2002).

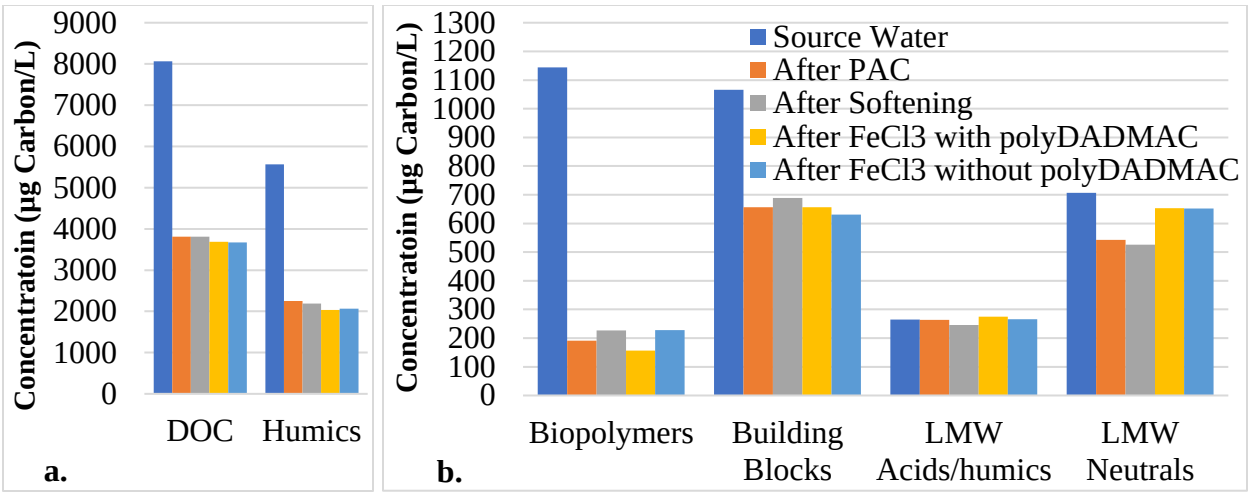

Figure 4.5 NOM characterization through the full-scale treatment processes prior to biofiltration at Facility Q on April 9, 2018 analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC and HS, b. BP, BB, LMW acids/humics, and LMW neutrals.
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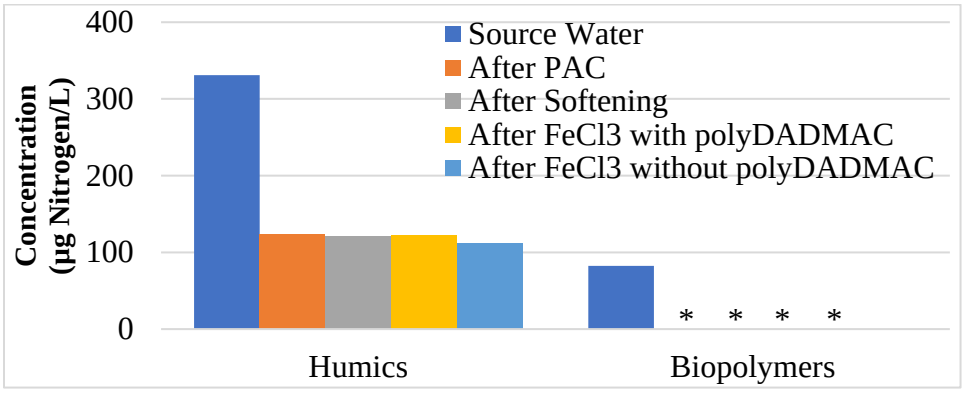

Figure 4.6 NOM characterization through the full-scale treatment processes prior to biofiltration at Facility Q on April 9, 2018 analyzed by LC-OND. Reporting organic nitrogen concentrations in HS and BP. * indicates that values are below the methods detection limit of 10 µg nitrogen/L.
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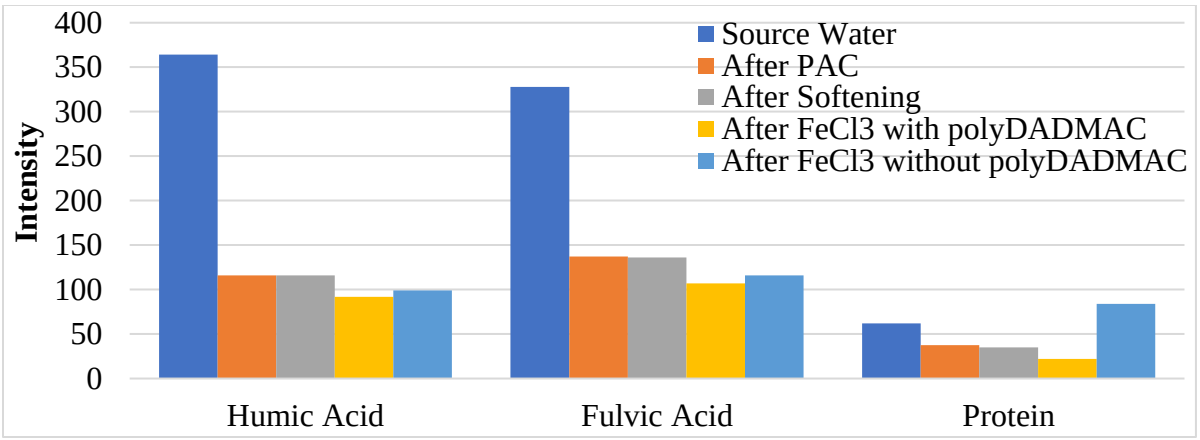

Figure 4.7 NOM characterization through the full-scale treatment process prior to biofiltration at Facility Q on April 9, 2018 analyzed by FEEM. Reporting average intensities for HA, FA, and protein-like materials.
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4.3.4 Impact of Ammonia Addition and Chloraminated Backwash on NOM Removal during Biofiltration at Facility C

The objectives of this section are to investigate how ammonia addition and chloraminated backwash influence removal of various NOM fractions during biofiltration at Facility C through some pilot-scale biofilter columns. The test conditions were chosen as part of the WRF project #4669, where changes in NDMA formation during biofiltration were investigated, which limited the design of these experiments (Evans et al., forthcoming). The columns were fed the same water as the full-scale biofilters at Facility C.

4.3.4.1 NOM Removals over Time at Facility C

The biofilters located at Facility C removed several LC-OCD fractions (Figure 4.8). Figure 4.8 a. and b. show that the DOC and HS concentrations in the biofilter influent at Facility C were relatively constant throughout the experiment. There were fairly similar removals of DOC and HS in all columns each week even during ammonia addition and chloraminated backwash. However, the GAC columns had a slightly higher removal of both DOC and HS (DOC: 24-34%, and HS: 26-36%) than the anthracite columns (DOC: 18-21%, and HS: 21-27%). Figure 4.8 c. shows that the BP concentration was fairly constant in the influent throughout the experiment. Also, the BP removal was fairly similar in all the columns each week except for the GAC column backwashed in chloraminated water, which had the highest removal. Figure 4.8 d. shows that the BB

concentration in the influent was very constant, but there were only low removals of BB. The August 15th sampling for LMW acids/humics and LMW neutrals in the influent was different from the other two sampling dates (Figure 4.8 e. and f.). The LMW acids/humics removal was very similar in all the columns each week, but there was only negligible/no removal of LMW neutrals each week. Figure 4.9 shows that the HS nitrogen concentrations in the influent were very constant throughout the experiment, and all the columns had fairly similar removals each week. The GAC columns removed 13-26% and the anthracite column removed 16-23%. However, the HS nitrogen removals were somewhat lower than the HS carbon removals, and unlike for HS carbon removals there did not seem to be a difference between HS nitrogen removals on GAC and anthracite media. However, the BP nitrogen concentrations were below the detection limit of 10 µg nitrogen/L and are therefore not shown. For all the FEEM fractions, all the intensities were quite low, which might be the reason that no clear trends were seen for these data (Figure B.4). The reason for the low FEEM intensities is that Facility C has pre-ozonation prior to the biofilters, which has drastically decreased the fluorescence signals. As mentioned in Chapter 3, previous studies showed that this decrease is because ozonation changes the structure of the molecules (Baghoth et al., 2011; Croft, 2012). Furthermore, the trends in the FEEM fractions were not similar to the trends in HS and BP in LC-OCD. Overall, all the columns, both the GAC and anthracite columns, removed DOC, HS, BP, and LMW acids/humics. The GAC columns had 6.6-13 percentage points higher removals of DOC, 5.5-8.3 percentage points higher of HS, and 1.8-19 percentage points higher of BP than the anthracite column. This was regardless of the ammonia addition and chloraminated backwash.

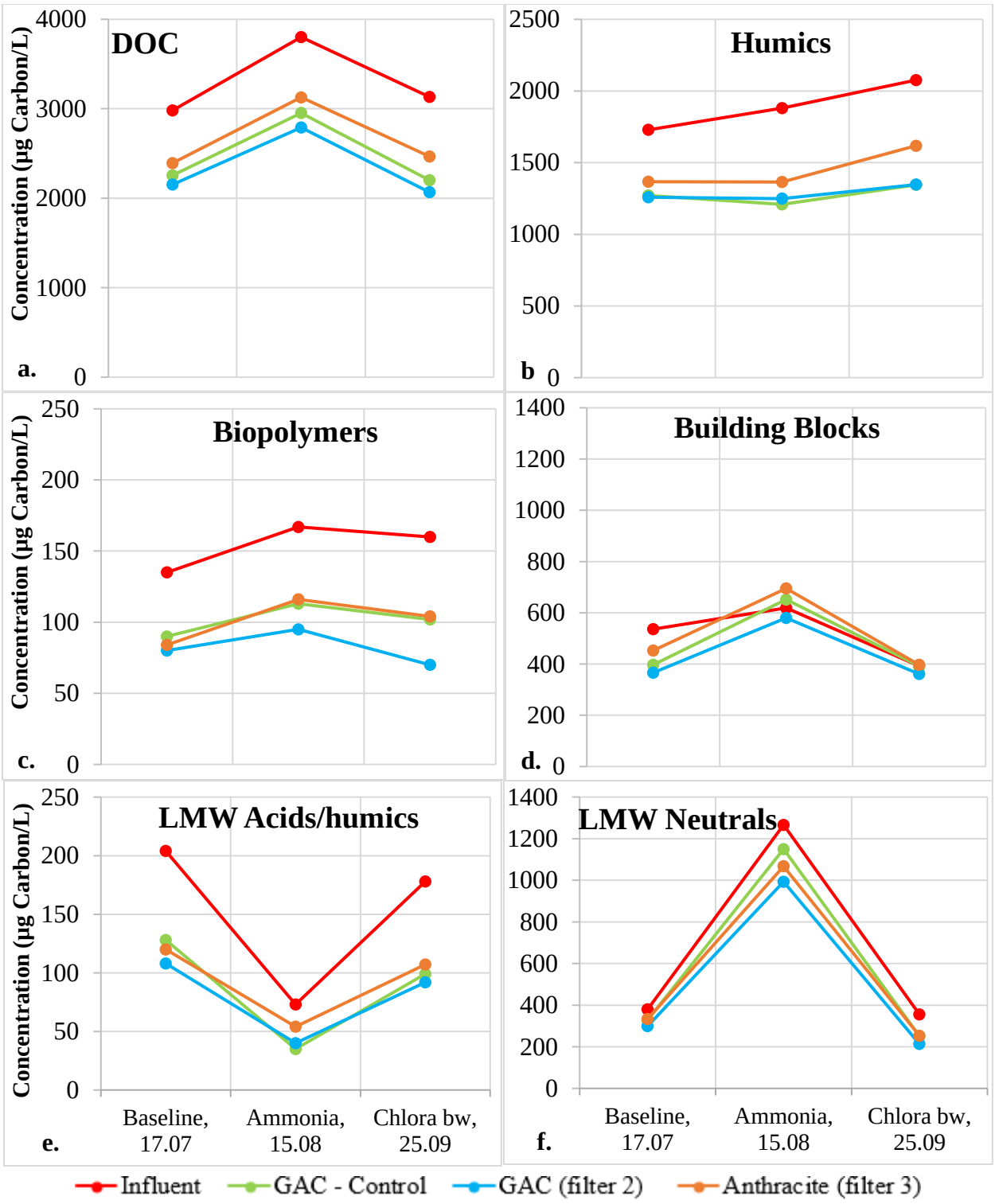


Figure 4.8 NOM characterization of biofilter influents and effluents at Facility C at baseline condition, during ammonia additions (filters 2 and 3), and during chloraminated backwash (filters 2 and 3) in 2017 analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC, b. HS, c. BP, d. BB, e. LMW acids/humics, and f. LMW Neutrals. Chlora = Chloraminated, bw = backwash, LMW = Low molecular weight.

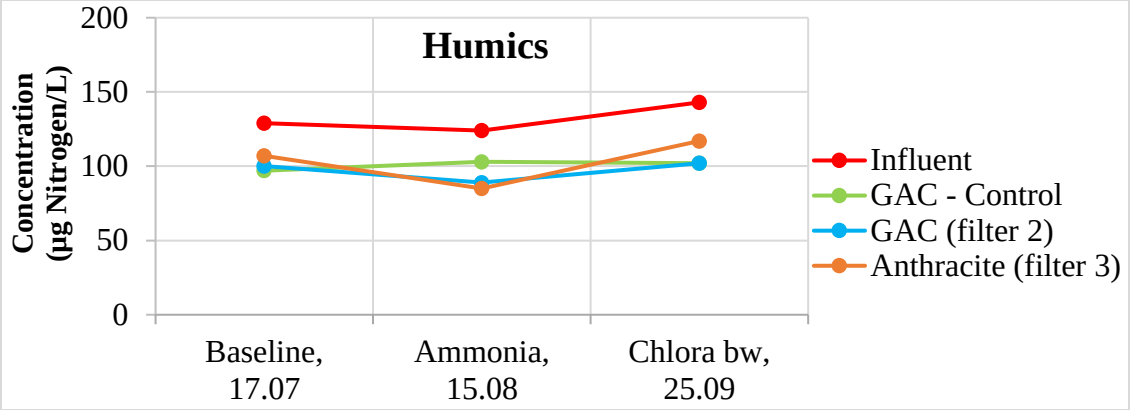


Figure 4.9 NOM characterization of biofilter influents and effluents at Facility C at baseline condition, during ammonia additions (filters 2 and 3), and during chloraminated backwash (filters 2 and 3) in 2017 analyzed by LC-OND. Reporting organic nitrogen concentration in HS. Chlora = Chloraminated, bw = backwash.

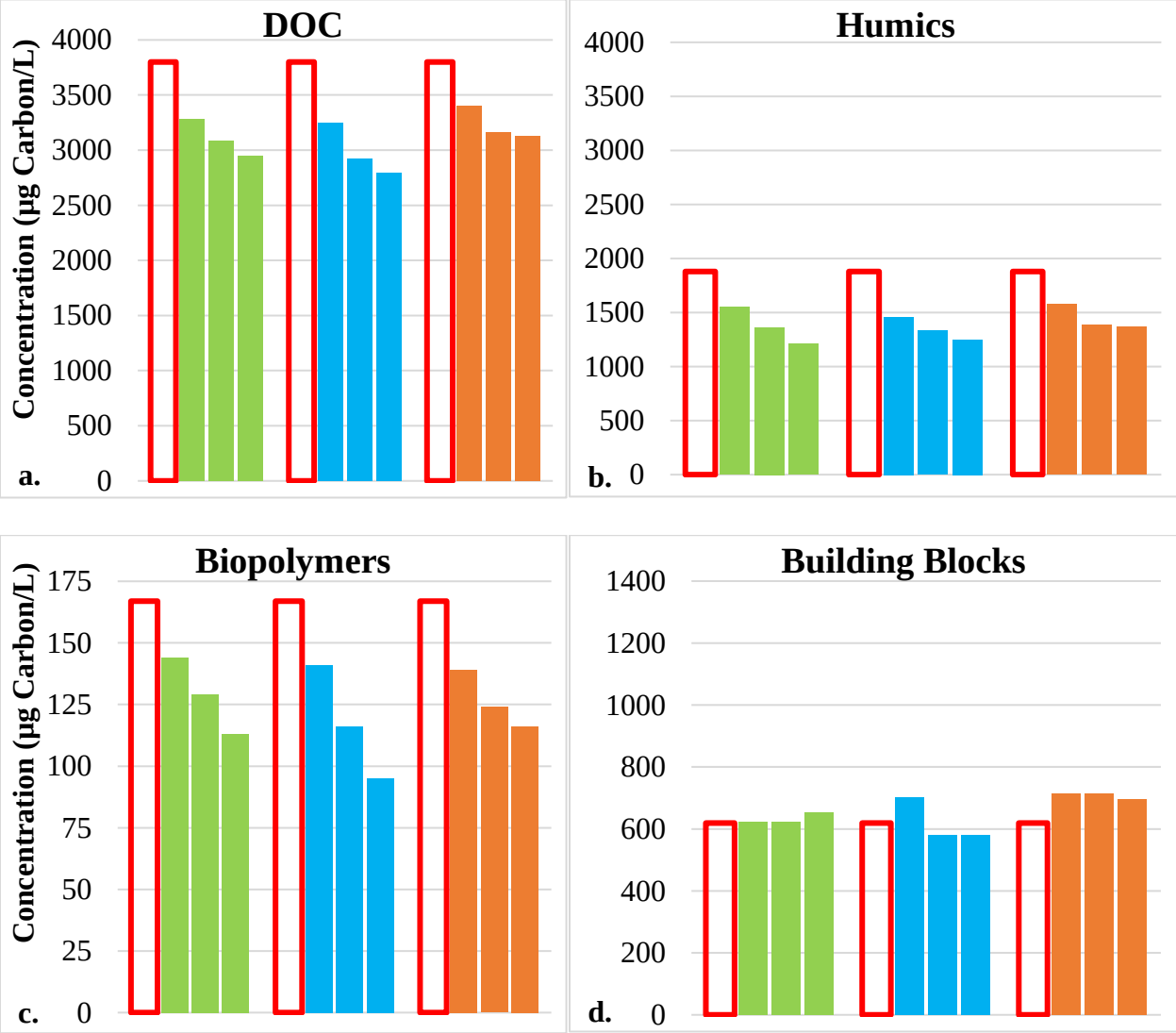
4.3.4.2 NOM Biofiltration Profiles at Facility C

NOM was measured at different depths throughout the pilot-scale columns once during ammonia addition (15.08 2017) and once during the chloraminated backwash condition (25.09 2017) to obtain biofilter profiles, which were used to establish removal kinetics.

4.3.4.2.1 NOM Biofiltration Profiles during Ammonia Addition

As expected, removals were observed to increase with increasing biofilter depth for all LC-OCD-OND fractions except for BB, which only showed negligible removal (Figure 4.10 and Figure 4.11). Overall removals were calculated by subtracting the effluent from the influent. Figure 4.10 f. shows only low removals of LMW neutrals, but the GAC biofilter with ammonia addition had a slightly higher removal (5.8 percentage points higher removal) than the anthracite columns. Similarly, the GAC columns had higher removals of DOC (4.6-8.9 percentage points higher), HS (6.1-8.3 percentage points higher), BP (1.8-13 percentage points higher), and LMW acids/humics (19-26 percentage points higher) than the anthracite column. Moreover, the GAC columns with ammonia addition had a marginally higher removal of DOC (4.3 percentage points higher), BP (11 percentage points higher), and LMW neutrals (12 percentage points higher) than the GAC control column. However, Figure 4.11 shows that there were only a slightly higher removals of the HS nitrogen concentration in the anthracite column, which differed from all the LC-OCD fractions. Unfortunately, the BP nitrogen concentrations were below the detection limit and are therefore not shown. The intensities for all the FEEM fractions were very low, which made it difficult to draw

any conclusion (Figure B.5). As mentioned above, a reason for these low intensities is the pre-ozonation prior to the biofilters at Facility C, which drastically decreased the fluorescence signals, which is consistent with other studies (Baghoth et al., 2011; Croft, 2012). Furthermore, the trends in FEEM were not similar to the trends in the LC-OCD-OND fractions and there were no reductions in either HA, FA, or protein-like materials through any of the filters (Figure B.5). Overall, the GAC biofilters generally removed a bit more of the LC-OCD-OND fractions than the anthracite columns. This is consistent with previous studies, which reported a better biofiltration performance with GAC media than anthracite (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010), but these studies did not use LC-OCD. These studies used other analytical techniques and, for example, measured TOC, AOC, and BOM instead.



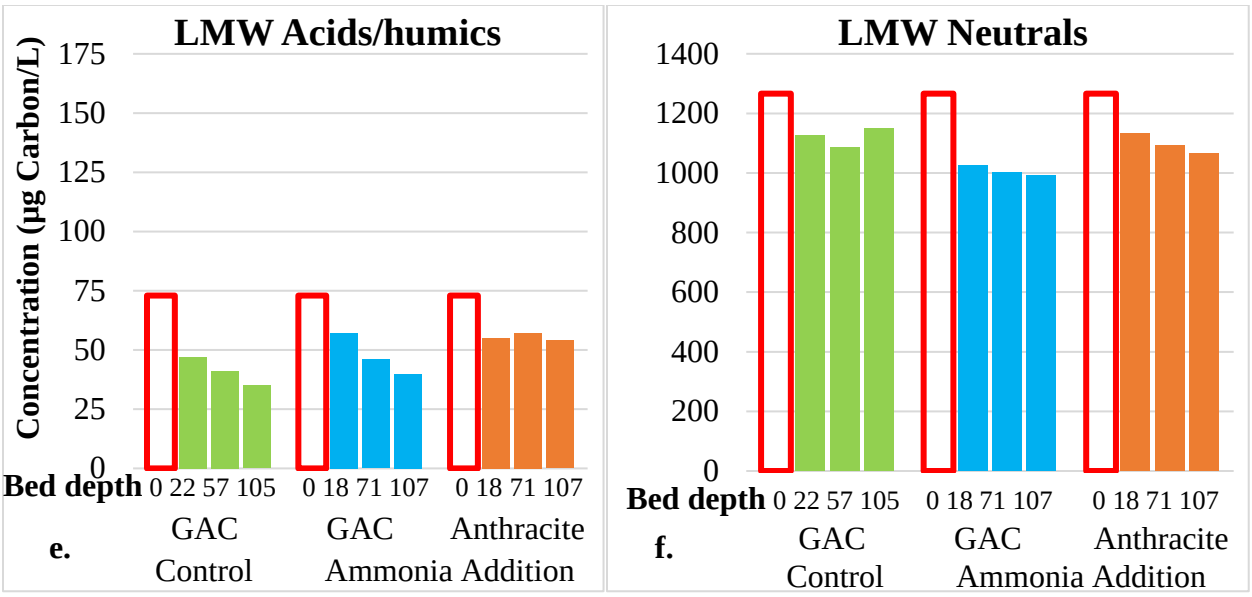


Figure 4.10 NOM biofilter profiles at Facility C on August 15th 2017 for the control column (no ammonia addition), and the other two columns tested with ammonia addition analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC, b. HS, c. BP, d. BB, e. LMW acids/humics, and f. LMW Neutrals. Bed depth is given in cm.

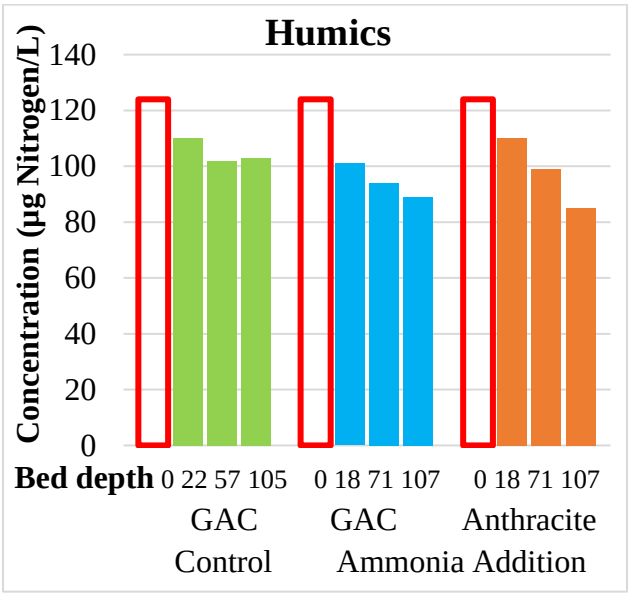


Figure 4.11 NOM biofilter profiles at Facility C on August 15th 2017 for the control column(no ammonia addition), and the other two columns tested with ammonia addition analyzed by LC-OND. Reporting organic nitrogen concentration in HS. Bed depth is given in cm.

4.3.4.2.2 NOM Biofiltration Profiles during Chloraminated Backwash

Unfortunately, during the chloraminated backwash sampling event at Facility C there was a contamination in sampling port 2 (71 cm depth) in the GAC biofilter (filter 2), and these data

points were therefore removed from all the profiles. The three biofilters at Facility C backwashed in chloraminated water showed decreasing concentrations/increasing removals with increasing filter depth of all LC-OCD and LC-OND fractions except for BB (Figure 4.12, 4.13, and B.6). Overall removals were calculated by subtracting the effluent from the influent. Both GAC columns had much higher removal of DOC (8.5-13 percentage points higher), HS (13 percentage points higher), BP (1.3-21 percentage points higher), LMW acids/humics (4.5-8.4 percentage points higher), and LMW neutrals (0.6-11.8 percentage points higher) than the anthracite column. Also, the GAC column backwashed with chloraminated water had a substantially higher removal of BP (20 percentage points higher) and only a slightly higher removal of DOC (4.3 percentage points higher), LMW acids/humics (3.9 percentage points higher), and LMW neutrals (11 percentage points higher) than the GAC control columns (Figure 4.12 a. and c., and Figure B.6 b. and c.). Figure 4.13 also shows that GAC columns had much higher removal of the HS nitrogen fraction (11 percentage points higher) than the anthracite column, which was similar the results for the HS carbon fraction. The BP nitrogen concentration was below the detection limits and therefore not shown in this thesis. Unfortunately, there were only negligible changes in HA, and FA from FEEM across all the columns at Facility C, which might be due to the low signal intensities (Figure B.7 a. and b., respectively). Moreover, there were only low removals of protein-like materials in all the columns (Figure B.7 b.). Overall, the GAC biofilters had somewhat higher removals than the anthracite biofilter during the chloraminated backwash phase. This is consistent with both the biofiltration profiles during ammonia addition, and previous studies that reported a better removal of TOC and DOC during biofiltration with GAC media than anthracite (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010). Also, the GAC biofilter backwashed in chloraminated water had slightly better removals of DOC, BP, LMW acids/humics, and LMW neutrals. However, this contradicts previous studies, which indicated that chloramination might reduce the biomass on the biofilter media, which might decrease biofiltration performance (Basu et al., 2016; Rasheed et al., 1998).

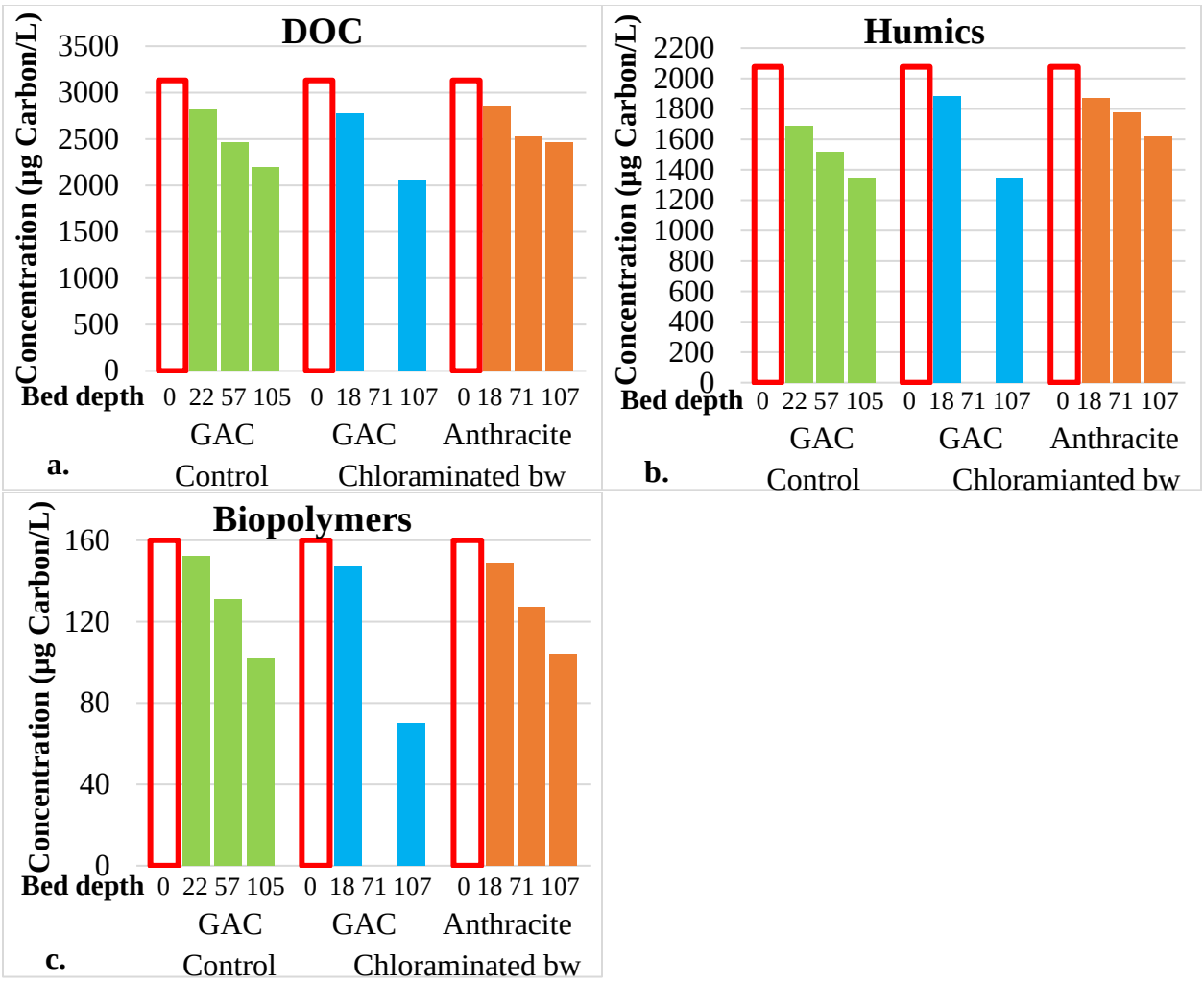


Figure 4.12 NOM biofilter profiles at Facility C on September 25th 2017 for the control column (nonchloraminated backwash), and the other two columns tested with chloraminated backwash analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC, b. HS, and c. BP. Bed depth is given in cm.

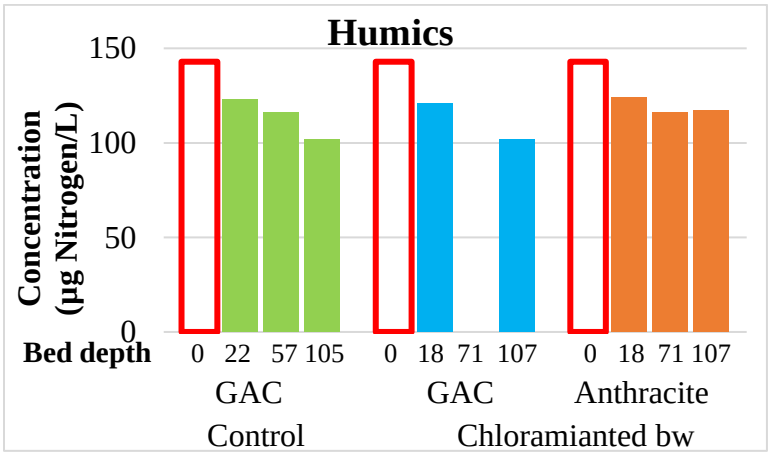


Figure 4.13 NOM biofilter profile at Facility C on September 25th 2017 for the control column (nonchloraminated backwash), and the other two columns tested with chloraminated

backwash analyzed by LC-OND. Reporting organic nitrogen concentration in HS. Bed depth is given in cm.

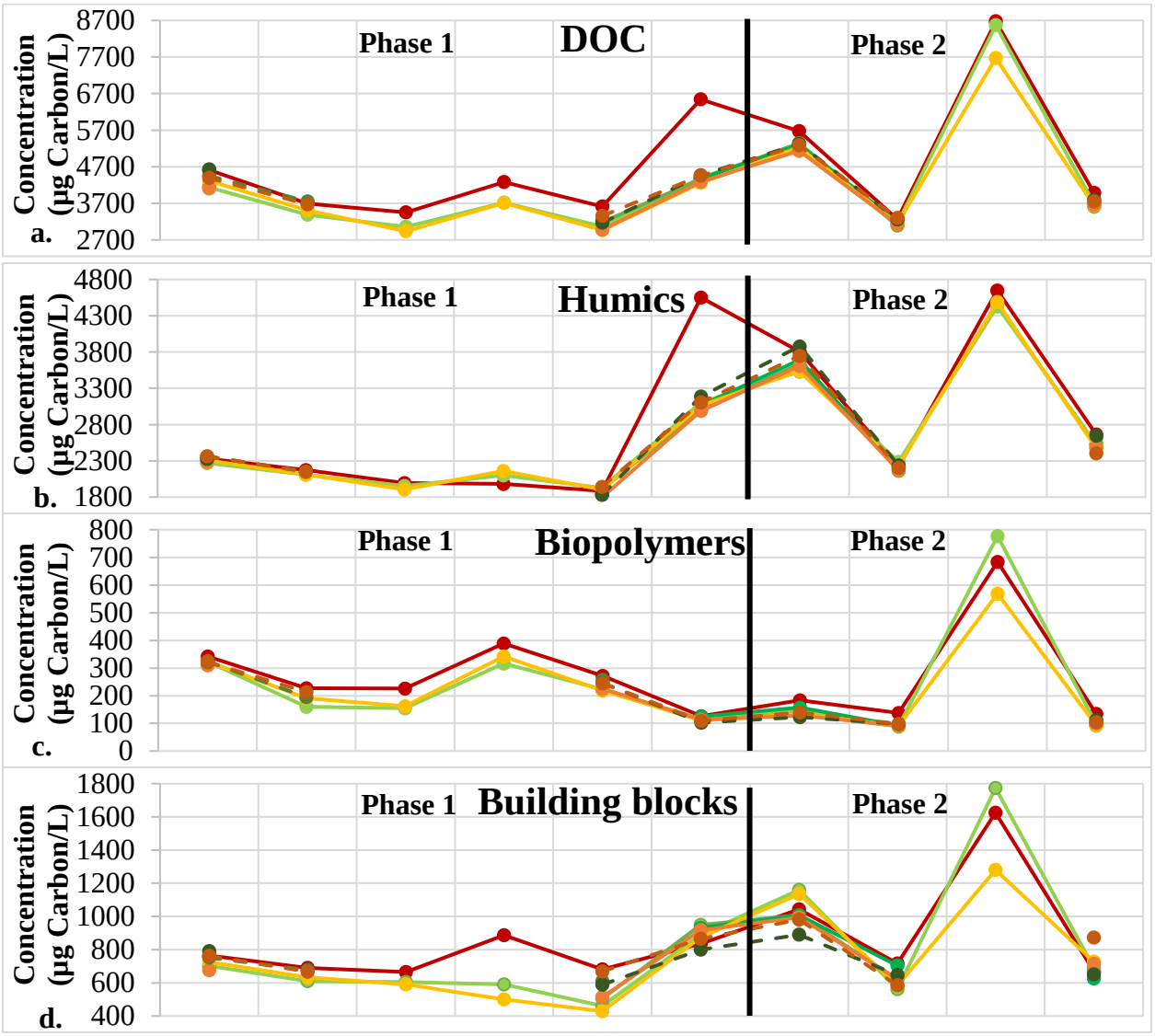
4.3.5 Impacts of Media Type, Backwash Type, and Backwash Frequency on NOM Removal during Biofiltration at Facility Q

The objectives of this section are to investigate how backwash type, media type, and backwash frequency influence removal of various NOM fractions during biofiltration by using data obtained from pilot-scale biofilter columns at Facility Q. These parameters were chosen as part of the WRF project #4669, where changes in NDMA formation during biofiltration were investigated, which limited the design of these experiments (Evans et al., forthcoming). The pilot columns were fed the same water as the full-scale biofilters at Facility Q. During phase 1, which was during spring 2018, the pilot columns were either backwashed in chloraminated water or nonchloraminated water. During phase 2, which was during summer 2018, the columns were backwashed with the same water as in phase 1. However, the backwash frequently for some columns changed from regular backwash frequency (twice weekly) to frequent backwash (daily).

4.3.5.1 NOM Removals over Time at Facility Q

Overall the biofilters located at Facility Q only had low or negligible removals of the various LC-OCD and LC-OND fractions (Figure 4.14 and 4.15). Figure 4.14 a. shows that there were only low removals of DOC during phase 1 (15% removal on average) and negligible removals during phase 2 (5.7% removal on average). The fractions that contributed to the DOC removals were BP, LMW acids/humics and LMW neutrals. Figure 4.14 b. only shows removal of HS on July 2nd. It is not possible to see any differences between the different filters for BP, BB, LMW acid/humics, LMW neutrals, HS nitrogen, and BP nitrogen since the removals for these fractions were low (Figure 4.14Figure 4.14 c. to f., and Figure B.8). Altogether, there were only low removals for certain NOM fractions during phase 1, and the removals were negligible for most fractions during phase 2, which was during the summer. A potential reason for these low removals at Facility Q, compared to Facility C, is that Facility Q does not have upstream ozonation. Ozonation breaks the NOM fractions into smaller fractions, which have been reported to be more biodegradable (Baghoth et al., 2011; Croft, 2012; Hammes et al., 2006; Huck, 1990; Huck and Sozanski, 2008; Ramseier et al., 2011; Rittmann et al., 2002; Vasyukova et al., 2013; Volk and Lechevallier, 2002; Volk et al., 1993). Studies have found that ozonation combined with biofiltration increases biofiltration

performance (Baghoth et al., 2011; Chen et al., 2016; Croft, 2012; Pharand et al., 2015; Rittmann et al., 2002; Vasyukova et al., 2013) However, the removals during phase 2 were unexpectedly low for summer results. A potential hypothesis could be changes in biodegradability of the NOM in the raw water. Overall the low removals in the different filters make it hard to discern whether media type, backwash type, or backwash frequency influenced biofiltration performance at Facility Q.



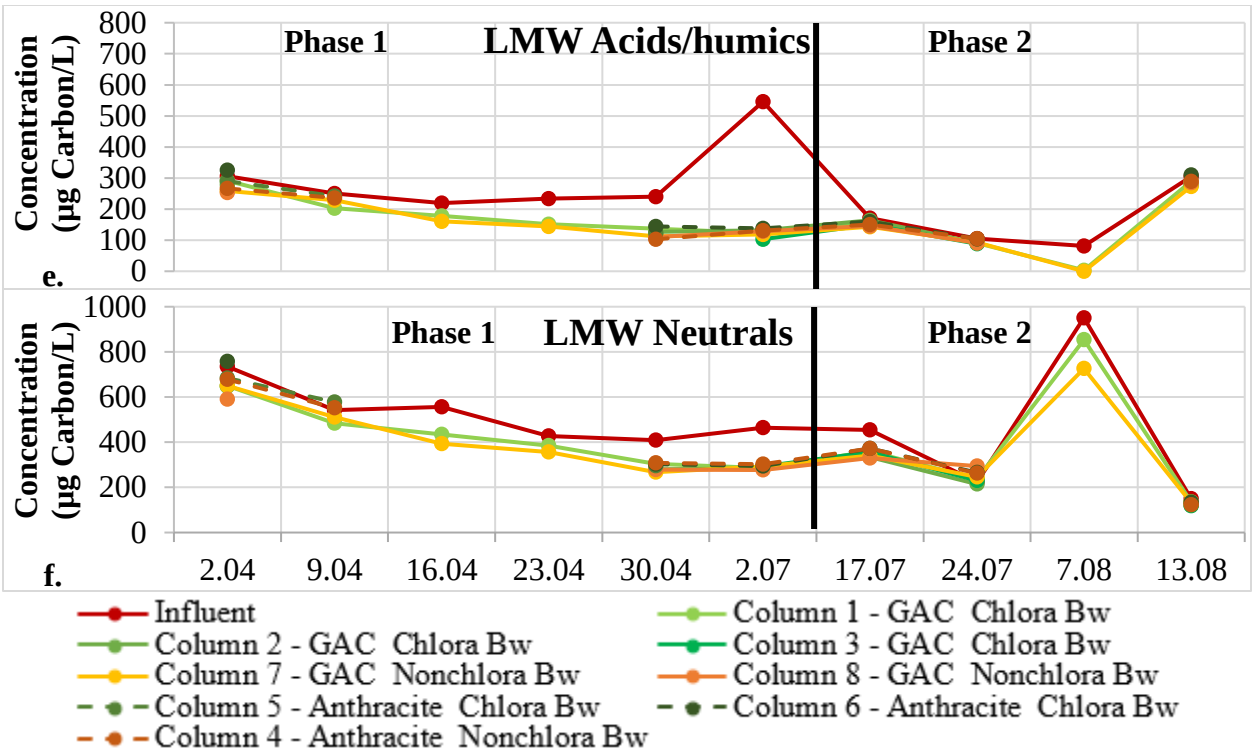


Figure 4.14 NOM characterization of biofilter influent and effluents at Facility Q in 2018 analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC, b. HS, c. BP, d. BB, e. LMW acids/humics, and f. LMW Neutrals. All columns were backwashed twice per week during phases 1 and 2, but during phase 2 columns 1, 2, 4, and 7 were backwashed daily. Chlora = Chloraminated, and Bw = Backwash.

Figure 4.15 plotted the DOC and BP concentrations in the biofilter influent and effluents at Facility Q as a bar chart to better ascertain whether there were differences between the different filter columns. Only sampling events where all columns were sampled are plotted in Figure 4.15. which confirms the very low removals of DOC at Facility Q during phase 1 and even lower removals during phase 2. The average removals during phase 1 were 6.5%, 13%, and 33% (on 02.04, 30.04, and 02.07 in 2018, respectively), and the average removals during phase 2 were 6.9%, 2.7%, and 7.3% (17.07, 24.07, and 13.08 in 2018, respectively). Figure 4.15 also plotted the BP concentrations in the biofilter influent and effluents at Facility Q. This figure confirms the very low removals of BP at Facility Q during phase 1 and phase 2. Figure 4.15 shows that the GAC biofilters seemed to have a slightly better removal performance of DOC and BP than the anthracite biofilters for some sampling dates. However, there were no noticeable differences in removal performance of DOC or BP from either backwash type or backwash frequency since the removals were very low. The low removals make it hard to notice a difference from the parameters tested on the removals.

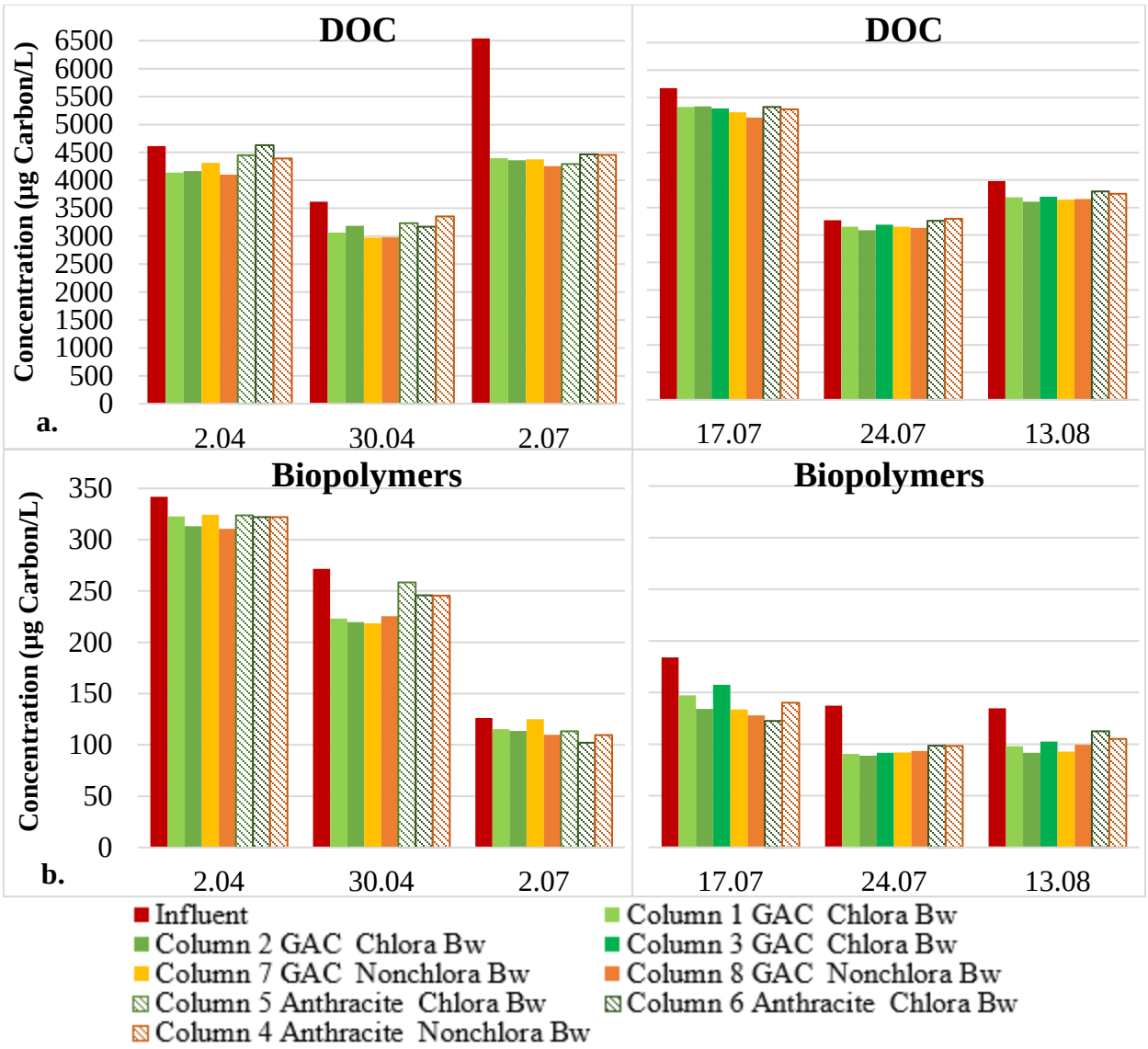
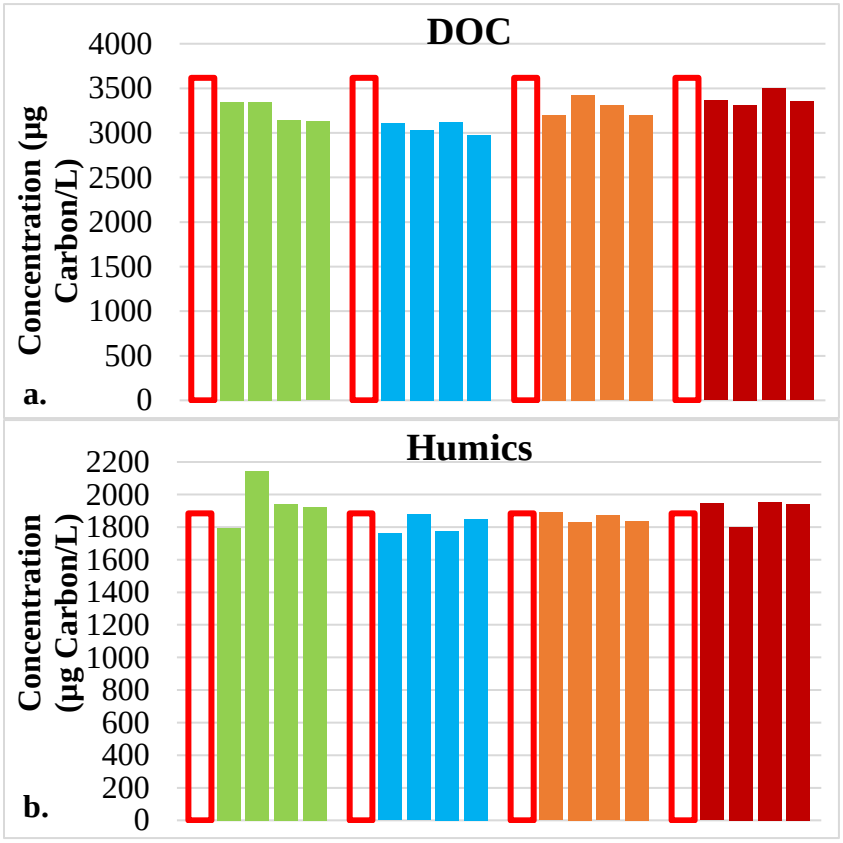


Figure 4.15 NOM characterization of biofilter influent and effluents at Facility Q in 2018 analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC, and b. BP only for days where all columns were sampled. All columns were backwashed regularly (twice per week) during phases 1 and 2, but during phase 2 columns 1, 2, 4, and 7 were backwashed daily. Chlora = Chloraminated, and Bw = Backwash.

4.3.5.2 NOM Biofiltration Profiles at Facility Q

During phase 1, biofilter profiles were measured at Facility Q on April 30th 2018, and only profiles for 4 biofilters were performed. Only 4 profiles were performed due to limitations in workload and instrumentation, and the duplicate columns were therefore not measured. However, these biofilters generally had relatively low removals of the various LC-OCD fractions (Figure 4.16 and Figure B.9), and the overall removals were calculated by subtracting the effluent from the influent. Figure

4.16 a., and c. show that the GAC biofilters had slightly increasing removals of DOC and BP throughout the biofilters. Also, the GAC biofilters had a higher removal of DOC (2-10 percentage points higher) and BP (9-11 percentage points higher) than the anthracite columns. Figure 4.16 b. and Figure B.10 a. show no removal of either the HS carbon or HS nitrogen in any of the biofilters. Figure B.9 a. b. and c. only show higher removals in the GAC biofilters for BB, LMW acids/humics, and LMW neutrals than in the anthracite biofilters. The removals in the GAC biofilters were 17-29 percentage points higher for BB, 1-9 percentage points higher for LMW acids/humics, and 2-9 percentage points higher for LMW neutrals than in the anthracite columns. Figure B.10 b. only shows a low increase in all the biofilters in the BP nitrogen concentration. Taken together, the GAC biofilters had a higher removal than the anthracite columns for DOC, BP BB, and LMW neutrals. Other studies also showed better removal of TOC and DOC during biofiltration with GAC media (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010). However, there were no noticeable differences between the different backwash types on removals of LC-OCD-OND fractions.



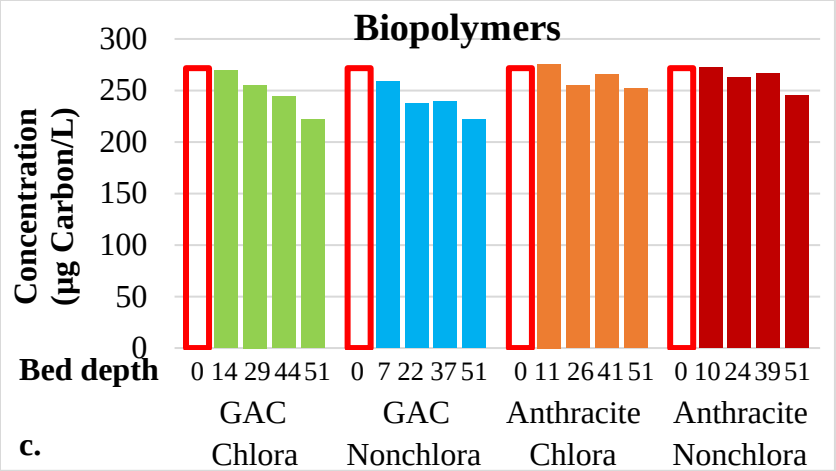


Figure 4.16 NOM biofilter profiles at Facility Q phase 1 on April 30th 2018 analyzed by LC-OCD, reporting organic carbon concentrations in a. DOC, b. HS, and c. BP. All columns had regular backwash frequency (twice per week), and bed depth is given in cm. Chlora = Chloraminated, nonchlora = nonchloraminated.

During phase 2 biofilter profiles were measured at Facility Q on August 13th, 2018, and profiles for 7 biofilters were performed, one profile for each condition. During phase 2 there were more conditions than in phase 1 since this phase also tested backwash frequency. However, these biofilters had generally very low removals of all LC-OCD-OND fractions (Figure 4.17, Figure 4.18, and Figure B.11), and the overall removals were calculated by subtracting the effluent from the influent. Figure 4.17 a. shows that there were very low removals of DOC in all the biofilters. Figure 4.17 c. shows that all the biofilters had an increasing removal of BP with increasing biofilter depth and the GAC biofilters had a slightly higher BP removal (2-15 percentage points higher) than the anthracite biofilters. Figure 4.17 b, Figure 4.18, and Figure B.11 a. b. and c. show low/negligible removal of HS carbon, HS nitrogen, BB, LMW acids/humics, and LMW neutrals and no clear trends for these fractions. Overall, the removals for the biofilter profiles from phase 2 were generally lower than for phase 1. The GAC biofilters only had slightly better removal of BP than the anthracite biofilters, which was similar to other studies (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010). However, as mentioned above, these studies only looked at TOC and DOC removals. Also, there were no noticeable differences between the different backwash types or backwash frequency on removals of LC-OCD-OND fractions, which was due to the very low/negligible removals.

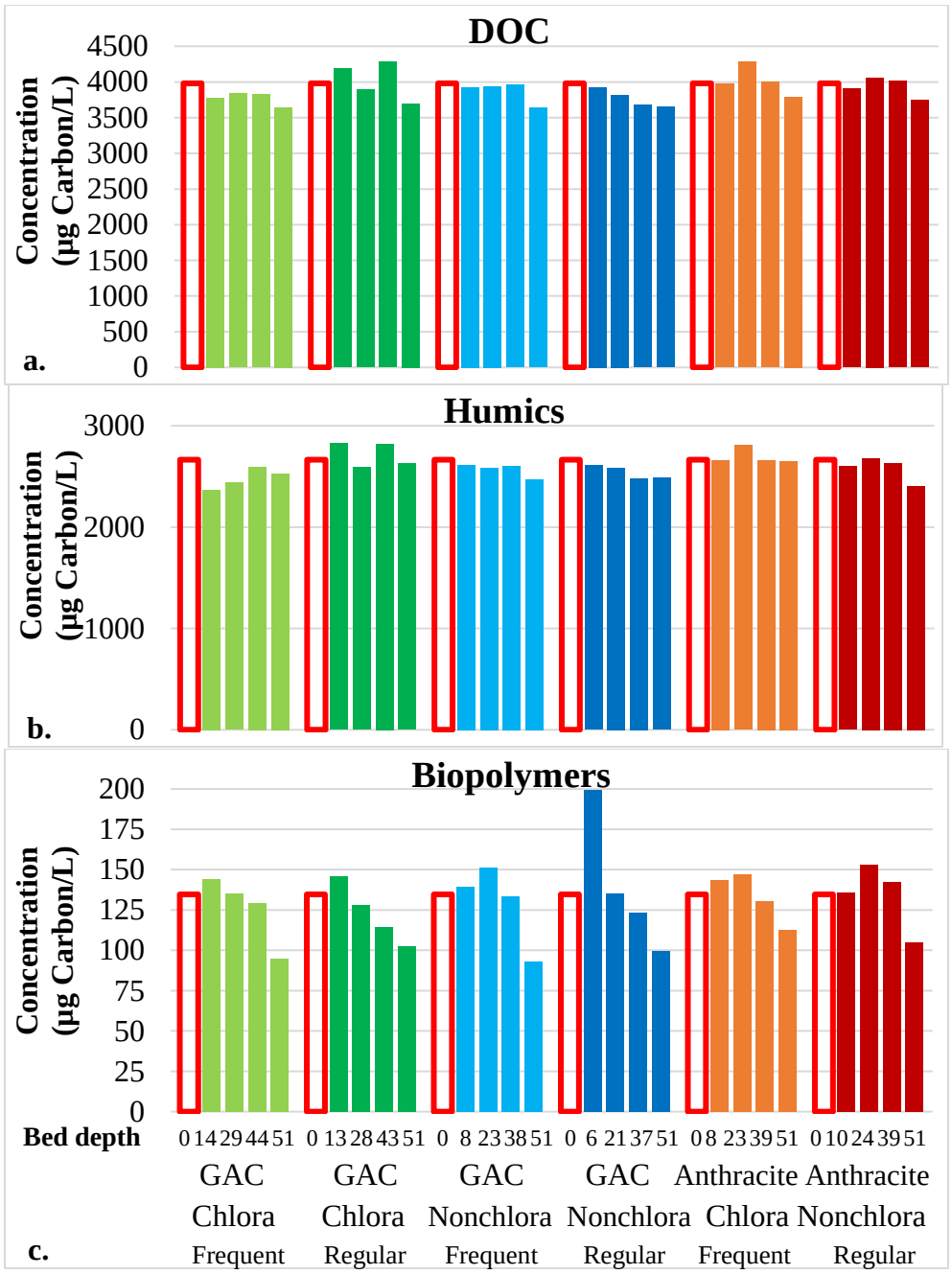


Figure 4.17 NOM biofilter profiles at Facility Q phase 2 on August 13th 2018 analyzed by LC-OCD, reporting organic carbon concentrations in a. DOC, b. HS, and c. BP. Bed depth is given in cm. Chlora = Chloraminated, nonchlora = nonchloraminated, frequent = frequent backwash frequency (daily), and regular = regular backwash frequency (twice per week).

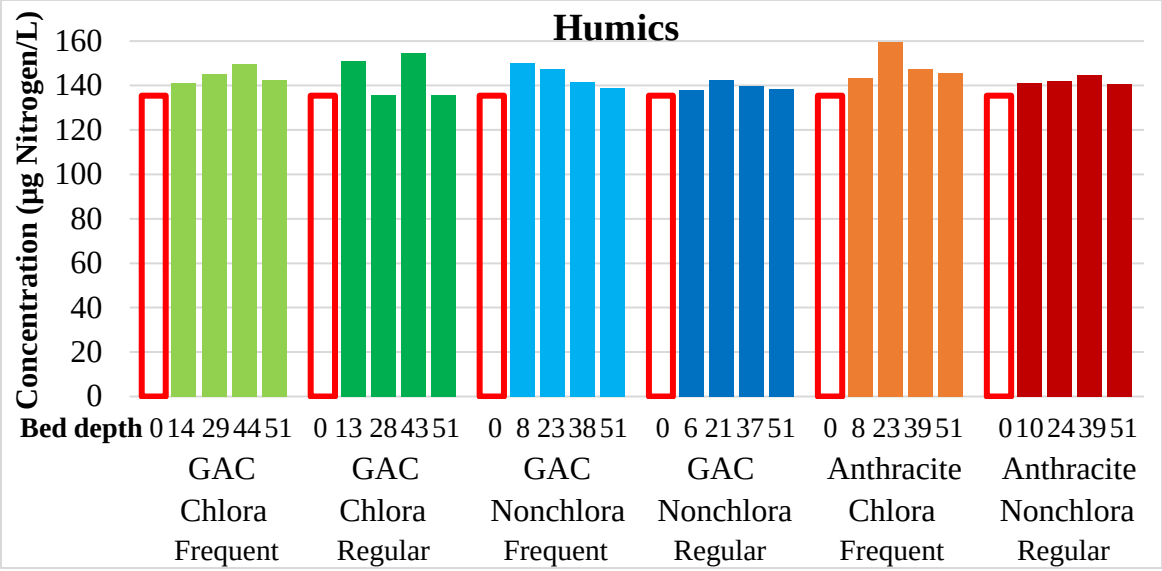


Figure 4.18 NOM biofilter profiles at Facility Q phase 2 on August 13th 2018 analyzed by LC-OND, reporting organic carbon concentration in HS. Bed depth is given in cm. Chlora = Chloraminated, nonchlora = nonchloraminated, frequent = frequent backwash frequency (daily), and regular = regular backwash frequency (twice per week).

4.3.6 Kinetics for NOM Fraction Removals

Kinetic analysis was only performed on fractions for which a removal was observed over the depth of the biofilter.

4.3.6.1 Kinetics for NOM Fraction Removals at Facility C

At Facility C, a noticeable removal with increasing filter depth was only observed for DOC, BP carbon, HS carbon, HS nitrogen and LMW acids/humics. Therefore, kinetics analysis was only performed for these fractions and the rate constants and corresponding R^2 values were calculated for these fractions (Table 4.10 for August 15th and September 25th 2017). The NOM fraction that best fit a reaction order during both ammonia addition and chloraminated backwash test was BP, however the difference between the R^2 values for some other fractions was not large. However, there were only 4 data points for each profile, and there were no clear trends regarding which reaction order fitted each fraction removal the best. The reason is that the change in the coefficients of determination (R^2 coefficients) only marginally increasing or the changes were negligible from 0th to 2nd order model (Table 4.10). However, the first order reaction rate constants were calculated since this is the reaction rate order that is to be expected in a biofilter, and to be able to compare these results with another study (Chen, 2016). This is the only study investigating the

kinetics of LC OCD fractions on biofilters, and Chen (2016) only calculated the first order reaction rate constants. The first order reaction rate constants for BP were calculated from the first order kinetic models, which are shown in Figure B.12. These constants for BP were 0.037 min-1, 0.053 min-1, and 0.033 min-1 for GAC control column, GAC column with ammonia addition, and anthracite column, respectively (Table B.1), which gives an average reaction rate constant of 0.041 min-1. For chloraminated backwash, the 1st order reaction rate constants for BP were 0.046 min-1, 0.085 min-1, and 0.041 min-1 for GAC control column, GAC column with chloraminated backwash, and anthracite column, respectively (Table B.2), which gives an average reaction rate constant of 0.057 min-1. The reaction rate constants were a bit higher during the chloraminated backwash test than during the ammonia addition. Also, the GAC columns had a somewhat higher reaction rate than the anthracite columns, and the GAC column with either ammonia addition or chloraminated backwash had the highest reaction rate. Another study, which calculated the kinetics for pilot-scale biofilters from a DWTP at the Grand River, showed no distinguishable kinetic models for either HS, BB, LMW acids/humics nor LMW neutrals (Chen, 2016). However, that study showed that the best-fit model for the BP was 1st order kinetics (Chen, 2016). Chen (2016) showed that the average 1st order reaction rate constant for the BP was 0.062 min-1. This fell well in the range for the 1st order BP rate constants estimated in this thesis; however, it should be noted that both investigations reported site-specific rate constants, rather than determining intrinsic rate constants. Overall, there were limitations, which made it difficult to fit the reaction order models to the NOM removals and draw a conclusion. These limitations were, for example, that there were only 4 data points per biofilter profile, and the kinetics were only measured and calculated once for each profile. However, for the 1st order reaction rates for BP, there were some slight differences, for example, that the GAC columns had higher reaction rate constants than anthracite, and the GAC columns with ammonia addition and chloraminated backwash had the highest reaction rate constants. These results are consistent with previous findings (see Figure 4.10, Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14).

Table 4.10 Summary of R^2 coefficients of zero-, first-, and second-order kinetic models for NOM fractions measured over the depth of the biofilters at Facility C during ammonia addition on August 15th 2017, and the chloraminated backwash test on September 25th 2017. A = acids/humics and N = neutrals.

Ammonia addition	Control			GAC			Anthracite		
	0	1	2	0	1	2	0	1	2
DOC	0.78	0.81	0.84	0.84	0.87	0.90	0.82	0.84	0.85
BP - OCD	0.93	0.96	0.98	0.96	0.98	0.98	0.86	0.89	0.92
HS - OCD	0.88	0.92	0.95	0.75	0.79	0.83	0.82	0.85	0.87
HS - OND	0.67	0.68	0.69	0.76	0.79	0.82	0.95	0.96	0.95
LMW A - OCD	0.73	0.81	0.88	0.89	0.94	0.97	0.48	0.48	0.48

Chloraminated backwash	Control			GAC			Anthracite		
	0	1	2	0	1	2	0	1	2
DOC	0.96	0.97	0.99	0.97	0.98	0.99	0.93	0.94	0.95
BP - OCD	1.00	0.99	0.97	1.00	1.00	0.99	0.98	0.97	0.95
HS - OCD	0.86	0.90	0.94	0.99	1.00	1.00	0.90	0.91	0.92
HS - OND	0.90	0.93	0.95	0.84	0.88	0.91	0.70	0.71	0.73
LMW A - OCD	0.96	0.99	1.00	0.85	0.91	0.95	0.82	0.87	0.91
LMW N - OCD	0.96	0.97	0.97	0.83	0.88	0.92	0.78	0.80	0.81

4.3.6.2 Kinetics for NOM Fraction Removals at Facility Q

At Facility Q, there were only very low removals or negligible removals for all fractions both during phases 1 and 2. Noticeable increasing removals with increasing bed depth were only observed for DOC and BP carbon. Therefore, kinetics analysis was only performed for these parameters, and their rate constants and corresponding R^2 values were calculated (Tables B.4, B.7, B.8, and Table 4.11 for April 30th and August 13th 2018). It was only during phase 1 that a NOM fraction best fitted a reaction order, which was BP. However, DOC for GAC chloraminated backwashed columns during phase 1 and for GAC nonchloraminated regular backwashed columns during phase 2 also fitted a reaction order. Otherwise, there were only poor fits between the data and the reaction orders. A reason for these poor fits was, for example, that there only were 5 data points for each profile. There were no clear trends regarding which reaction order fitted each fraction removal the best, which was the same at Facility C. The reason is that the change in the R^2 coefficients barely changed from 0th to 2nd order models (Table 4.11). Similar to Facility C, only the 1st order reaction rate constants were calculated since this was the rate to be expected and

to be able to compare them with Facility C and the other study (Chen, 2016). The reaction rate constants for BP were calculated from the first order kinetic models, and the models for BP during phase 1 are shown in Figure B.13. These 1st order reaction rate constants for BP during phase 1 were 0.020 min^{-1}, 0.019 min^{-1}, 0.020 min^{-1}, and 0.009 min^{-1} for GAC chloraminated columns, GAC nonchloraminated columns, anthracite chloraminated columns, and anthracite nonchloraminated columns, respectively (Table B.4). These values were much lower than at Facility C and the previously mentioned study, which reported a 1st order reaction rate constant of 0.062 min^{-1} (Chen, 2016). Overall, there were no noticeable differences in reaction rate constants for BP between the GAC and anthracite columns or any of the backwashing regimes.

Table 4.11 Summary of R^2 coefficients of zero-, first-, and second-order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 1 on April 30th 2018, and phase 2 on August 13th 2018. Chlora = Chloraminated, Nonchlora = Nonchloraminated, and bw = backwash.

Phase 1	GAC Chlora			GAC Nonchlora			Anthracite Chlora			Anthracite Nonchlora		
	0	1	2	0	1	2	0	1	2	0	1	2
DOC	0.91	0.92	0.92	0.50	0.51	0.52	0.37	0.36	0.35	0.18	0.18	0.17
BP-OCD	0.87	0.86	0.84	0.90	0.91	0.92	0.92	0.92	0.92	0.70	0.69	0.68

Phase 2	GAC Chlora Frequent bw			GAC Chlora Regular bw			GAC Nonchlora Frequent bw			GAC Nonchlora Regular bw		
	0	1	2	0	1	2	0	1	2	0	1	2
DOC	0.59	0.59	0.59	0.06	0.07	0.08	0.53	0.53	0.53	0.96	0.96	0.96
BP-OCD	0.51	0.49	0.48	0.57	0.83	0.56	0.44	0.46	0.48	0.51	0.59	0.66

Phase 2	Anthracite Chlora Frequent bw			Anthracite Nonchlora Regular bw		
	0	1	2	0	1	2
DOC	0.11	0.12	0.13	0.20	0.21	0.21
BP-OCD	0.50	0.51	0.52	0.21	0.24	0.27

4.3.7 Synthesis

The main difference between Facility C and Facility Q, was that Facility C had pre-ozonation prior to the biofilters, whereas Facility Q did not. As shown in Chapter 3, pre-ozonation changes the NOM fractions to smaller fractions, which have been reported to be more biodegradable, and it also lowers FEEM intensities, which is consistent with previous studies (Baghoth et al., 2011;

Croft, 2012; Hammes et al., 2006; Huck, 1990; Huck and Sozanski, 2008; Ramseier et al., 2011; Rittmann et al., 2002; Vasyukova et al., 2013; Volk and Lechevallier, 2002; Volk et al., 1993). The full-scale sampling at Facility Q showed that PAC substantially reduced the NOM fractions, which was consistent with previous studies (Löwenberg and Wintgens, 2017; Löwenberg et al., 2014; Seo et al., 2004; Tomaszewska and Mozia, 2002), but lime softening did not impact the removals of NOM fractions (Figure 4.5, Figure 4.6, and Figure 4.7). Also, the biofilter influent at Facility C had much lower concentrations of all LC-OCD fractions, except for LMW neutrals than Facility Q (Figure 4.1 and Figure 4.2). At Facility Q, the influent concentrations of all fractions were usually higher during the summer (phase 2) than spring (phase 1) except for BP, LMW acids/humics, and LMW neutrals. Furthermore, the biofilters at Facility C had much higher removals of all fractions than the biofilters at Facility Q. The lowest removals occurred in the biofilters at Facility Q phase 2 during the summer, which is unusual (Pharand, 2014). A potential reason for the higher removals at Facility C might be the upstream ozonation prior to biofiltration at Facility C, which breaks NOM fraction into lower molecular weight molecules with higher biodegradability (Baghoth et al., 2011; Croft, 2012; Hammes et al., 2006; Huck, 1990; Huck and Sozanski, 2008; Ramseier et al., 2011; Rittmann et al., 2002; Vasyukova et al., 2013; Volk and Lechevallier, 2002; Volk et al., 1993). Furthermore, at Facility C, the GAC biofilters had higher removals of all LC-OCD-OND fractions than the anthracite columns. Also, at Facility Q the GAC biofilters only had higher removals of DOC, BP, BB, LMW acids/humics, and LMW neutrals than the anthracite columns during phase 1, but this did not apply to all sampling dates. Furthermore, the GAC biofilters at Facility Q only had higher removals of BP than anthracite biofilters during phase 2. Therefore, the GAC biofilters at both locations had a better biofiltration performance than anthracite, which is consistent with earlier studies (Emelko et al., 2006; LeChevallier et al., 1992; Liu et al., 2001; Volk and Lechevallier, 2002; Zhu et al., 2010). However, these studies only showed a better removal of TOC and DOC during biofiltration with GAC media than anthracite. Furthermore, at Facility C, the chloraminated backwashed column had the highest removals of DOC, BP, LMW acids/humics, and LMW neutrals. However, at Facility Q there were no noticeable differences between the different backwash types or backwash frequency and the removals of LC-OCD-OND fractions, though removals were very low or negligible and conclusions can therefore not be drawn how these parameters affected the removals and biofiltration performance at Facility Q. For the kinetics, there were limitations, which made it

difficult to fit the reaction order models to the NOM removals and draw conclusions at both facilities. These limitations were, for example, that there were only 4-5 data points per biofilter profile, and the kinetics were only measured and calculated once for each profile. Also, there were only very low removals at Facility Q, which made it very difficult to notice any clear trends. For Facility C, the NOM fraction that best fitted a reaction order during both ammonia addition and chloraminated backwash test was BP. For BP at Facility C, the GAC columns had higher reaction rate constants than anthracite, and the GAC columns with ammonia addition and chloraminated backwash had the highest reaction rate constants. For Facility Q, it was only during phase 1 that a NOM fraction best fitted a reaction order, which was BP. However, DOC in the GAC nonchloraminated regular backwashed column during phase 2 also fitted a reaction order. However, there were no noticeable differences in reaction rate constants for BP between the GAC and anthracite columns or any of the backwashing regimes.

4.4 Conclusions

Removing NOM during drinking water treatment processes improves both aesthetic problems and might minimize the occurrence of potentially harmful carcinogenic DBPs. At Facility C, two different media types (GAC vs. anthracite), backwash type (chloraminated vs. nonchloraminated), and ammonia addition were investigated; and at Facility Q, full-scale upstream processes, two different media types (GAC vs. anthracite), backwash type (chloraminated vs. nonchloraminated), and backwash frequency (daily vs. twice weekly) were investigated in pilot-scale biofilter columns to determine how they affect removal of NOM fractions.

The following conclusions can be made for the source water and pre-treatments:

- The biofilter influent at Facility C had much lower concentrations of all LC-OCD-OND and FEEM fractions, except for LMW neutrals than Facility Q. A potential reason might be that the influent at Facility C comes from a reservoir.
- The variability of all LC-OCD fractions for the influent at Facility C was less than at Facility Q, which might be because the influent at Facility C is from a reservoir and it was only sampled over a shorter period of time (during summer only). Also, Facility Q was sampled over a longer period of time (during spring and summer), and there were local

storm events occurring frequently at Facility Q, which might have impacted the influent concentrations too.

- The biofilters at Facility C had much higher removals of all fractions than the biofilters at Facility Q. The lowest removals occurred in the biofilters at Facility Q phase 2 during the summer, which is unusual. The higher removals at Facility C might be caused by the upstream ozonation prior to biofiltration at Facility C.
- PAC, was the only full-scale treatment process that was extremely effective at removing several NOM fractions during drinking water treatment at Facility Q. PAC, for example, removed more than 83% of BP.

The following conclusions can be made for the pilot study at Facility C regarding the studied parameters:

- Biofilters with GAC media had higher removals of the NOM fractions: DOC, HS, BP, LMW acids/humics, and LMW neutrals than anthracite media and it improved biofiltration performance. These removals were 4.6-13%, 6.1-13%, 1.3-21%, 4.5-26%, and 0.6-12% higher than in the anthracite columns, respectively.
- Ammonia addition to the biofilter feed did not have any significant effect on NOM fraction removals in the biofilters at Facility C.
- The chloraminated backwashed GAC columns had higher removals of DOC (4.3 percentage points higher), BP (20 percentage points higher), LMW acids/humics (3.9 percentage points higher), and LMW neutrals (11 percentage points higher) than the GAC control columns.

The following conclusions can be made for the columns at Facility Q regarding the studied parameters:

- GAC media had a marginally better removal of DOC, BP, BB, LMW acids/humics, and LMW neutrals than the anthracite media for some sampling dates. However, there were very low removals at each sampling event, and the removals differed between the different sampling dates. Therefore, the trends could potentially change between different sampling events.

- There were no noticeable differences between the different backwash types or backwash frequencies on the NOM fraction removals. However, the influence from these parameters on NOM fraction removals was difficult to assess conclusively due to the very low removals at most sampling events.

The following conclusions can be made for the kinetics:

- At Facility C, increasing removals with increasing bed depth were observed for DOC, BP carbon, HS carbon, HS nitrogen, and LMW acids/humics. The kinetics was therefore only calculated for these fractions, and BP had the best data fit.
- At Facility Q, increasing removals with increasing bed depth were only observed for DOC and BP carbon during phase 1, and these removals were a lot less succinct than for Facility C. The kinetics was therefore only calculated for these fractions, and BP had the best data fit.
- There were no clear trends regarding which reaction order fitted each fraction removal the best. The 1^{st} order reaction rate constants were calculated since this is the reaction rate order that is expected for biofiltration, and to be able to compare them with the only other study performed on kinetics of the removal of LC OCD fractions for biofilters. That study also only calculated 1^{st} order reaction rate constants (Chen, 2016).
- At Facility C, the average 1^{st} order reaction rate constant for BP was 0.057 min^{-1}, which fell well in the range for the 1^{st} order BP rate constants estimated by Chen (2016) although in both cases these are site-specific rather than intrinsic rate constants. Also, the GAC columns had higher reaction rate constants than anthracite, and the GAC columns with ammonia addition and chloraminated backwash had the highest reaction rate constants.
- For Facility Q, the average 1^{st} order reaction rate constant for BP was 0.0017 min^{-1}, which was much lower than at Facility C and Chen (2016). Furthermore, there were no noticeable differences in reaction rate constants for BP between the GAC and anthracite columns or any of the backwashing regimes.
- There were limitations, which made it difficult to fit the reaction order models to the NOM removals and draw conclusions at both facilities. These limitations were, for example, that there were only 4-5 data points per biofilter profile, and the kinetics were only measured

and calculated once for each profile. Also, there were only very low removals at Facility Q, which made it very difficult to notice any clear trends.

There were the following limitations for the above findings:

- The work presented in this thesis was part of a larger WRF project (project #4669), where changes in NDMA formation during biofiltration were investigated, which limited opportunity to tailor design and operational factors of investigated biofilters.
- Facility C only had three biofilters and there were therefore no duplicates. Furthermore, there were only one sampling event per condition.
- The low removals at Facility Q made it difficult to draw any meaningful conclusion.

4.5 Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for their use by the authors or funding agencies.

Chapter 5
Correlation between NDMA Precursors Removal or Formation and NOM Fraction Removals during Biofiltration

5.1 Introduction

NDMA is the most detected nitrosamine and it is therefore also the most studied of the nitrosamines (Sgroi et al., 2018). However, NDMA only represents around 10% by weight of the total nitrosamines in water samples (Dai and Mitch, 2013). Furthermore, NDMA is a highly water-soluble semi volatile organic chemical (USEPA, 2017), which can also been found in wastewater, food, consumer products, and air (Choi and Valentine, 2002; Morran et al., 2011; Najm and Trussell, 2001; USEPA, 2017). Additionally, NDMA has been recognized as carcinogenic with a 10^{-6} life time cancer risk at 0.7 ng NDMA/L in drinking water (IARC, 1978). Due to NDMA's health risks, USEPA placed NDMA on CCL4. NDMA is therefore not regulated by USEPA at the moment, but it is being considered for regulation in the future (USEPA, 2016). However, NDMA is regulated nation-wide in Canada at 40 ng/L (Health Canada, 2011) and the province of Ontario in Canada regulates NDMA in drinking water at 9 ng/L (Government of Ontario, 2018).

It is therefore desirable to eliminate or minimize NDMA formation during drinking water treatment. NDMA is formed from NDMA precursors, and the main NDMA formation mechanism is a reaction between chloramine and secondary amine precursors. Some well researched treatment processes during bench- and full-scale experiments, which showed significant removal of NDMA, include UV treatment, reverse osmosis and nanofiltration (Afzal et al., 2016; Fujioka et al., 2012b, 2012a, 2013c, 2013a, 2013b; Mitch and Sedlak, 2004; Plumlee et al., 2008; Sgroi et al., 2015; Sharpless and Linden, 2003; Stefan and Bolton, 2002). However, studies show inconsistent results on how other full-scale treatment processes influence NDMA concentrations during drinking water treatment. These treatment processes include pre-ozonation, lime softening, ferric chloride coagulation with or without polyDADMAC and biofiltration. Some studies reported formation of NDMA during pre-oxidation processes, such as pre-ozonation (Lee et al., 2007b; Mitch et al., 2003), whereas other studies suggested significant reductions of NDMA during ozonation (Lee et al., 2007b, 2008; McCurry et al., 2015; Pisarenko et al., 2012; Shah et al., 2012; Wang et al., 2015; Yang et al., 2013). For lime softening, one study proved it to be ineffective at removing NDMA

(Mitch et al., 2009), while other studies suggested that lime softening might increase NDMA (Krasner et al., 2012a; McCurry et al., 2017; Sgroi et al., 2015). Also, some studies found coagulation ineffective at removing NDMA (Beita-Sandí et al., 2016; Farré et al., 2011b; Krasner et al., 2012a), while other studies indicated that polyDADMAC during coagulation might contribute to NDMA formation (Mitch and Sedlak, 2004; Padhye et al., 2011; Park et al., 2009a, 2009b; Sgroi et al., 2014, 2016). The pathways and reactions leading to NDMA are therefore very complex. Also, all the studies found different results depending on the specific case, which makes it difficult to make a general statement about NDMA and NDMA precursor formation and removal.

Current research that has been conducted on whether biofiltration can remove NDMA and its precursors is also inconclusive since studies showed either an increase or decrease in NDMA formation after biofiltration (Barzi, 2008; Chuang and Mitch, 2017; Krasner et al., 2012a, 2015; Liao et al., 2014, 2015b; Liu et al., 2017; Mitch et al., 2009; Selbes et al., 2016, 2017). Since many DWTPs are already using or are considering implementing biofiltration, it is therefore important to determine some strategies for controlling NDMA and its precursors during biofiltration. Moreover, operational parameters influence biofiltration performance, but research to-date is inconclusive how these operational parameters influence NDMA formations during biofiltration.

A portion of the NOM may serve as NDMA precursors, but studies to-date have given varied results (Chen and Valentine, 2007; Richardson and Ternes, 2014). However, there is only limited published data linking NOM fractions with NDMA formation. Also, there was even less data that has been published using the NOM characterization techniques LC-OCD and FEEM for the correlation and these studies were inconclusive. One study reported no correlation between NDMA formation and DOC from LC-OCD after chloramination, but a reasonable correlation between NDMA formation and DON (Kristiana et al., 2017). Another study reported high correlation between NDMA FP and DON from LC-OCD in natural water and wastewater sources (Qi et al., 2014). Several studies reported no relationship between NDMA formation and FEEM signals during full-scale drinking water treatment (Bridgeman et al., 2011; Chen and Valentine, 2007; Ma et al., 2016b). On the other hand, other studies suggested a qualitative relationship between NDMA formation and FEEM signals from, for example, water sources (Hua et al., 2007), DWTP influents and effluents (Yang et al., 2015), and ozonation (Sgroi et al., 2016). Also other studies showed a

correlation between NDMA precursors and FEEM signals from, for example, pilot-scale biofiltration (Fu et al., 2017) and biologically treated wastewater (Wang et al., 2017). It is therefore desirable to have a better understanding on how NDMA formation correlates with NOM removal during biofiltration, and using LC-OCD and FEEM to characterize the NOM fraction facilitates investigating this correlation.

Chapter 3 already established the impact of pre-ozonation, water source, and media acclimated/operated in different water sources on NOM removals with bench-scale biofilters columns. Also, Chapter 4 established the impact of different operational conditions, design variables, and water quality parameters on NOM fraction removals with pilot-scale biofilters.

The main objectives for portion of the research described in this chapter were to investigate how some of the parameters tested in Chapters 3 and 4 impacted NDMA UFC removal or formation during biofiltration. Only NDMA UFC data from investigation of certain parameters were chosen to be presented in this Chapter. The criteria for choosing these specific cases were to show some few interesting examples of NDMA UFC concentrations with interesting removal patterns, and only cases where considerable amount of NDMA UFC were detected. The chosen parameters include media acclimated/operated in different water sources when fed Facility B water (Chapter 3), and full-scale treatment processes prior to biofiltration (pre-ozonation, PAC, lime softening, and ferric chloride coagulation with or without polyDADMAC) (Chapters 3 and 4). Furthermore, this chapter also investigated how reductions or increases in these NDMA UFCs correlated to the NOM fraction removals. To investigate how these parameters impacted the NDMA formation, some bench-scale and pilot-scale biofilter tests were executed, as discussed in Chapters 3 and 4. Afterwards, the NOM data from these experiments, presented in Chapters 3 and 4, were correlated to the corresponding NDMA UFC data measured by others in the WRF project (Evans et al., forthcoming). These data include all relevant data from the bench-scale experiments at Facilities B, I, and L, and all relevant data from the pilot-scale experiments at Facilities C and Q. Overall, the insights gained from this study may be of assistance to determine how these parameters impact NDMA UFC concentrations during biofiltration, and to determine whether NDMA UFC can be linked with specific NOM fractions.

5.2 Materials and Methods

5.2.1 Bench-scale and Pilot-scale Tests

The experimental setups including operational and analytical parameters, sampling times, and locations for the bench-scale tests at Facilities B, I, and L were discussed in Chapter 3, and the pilot-scale tests at Facilities C and Q were discussed in Chapter 4. As mentioned in the previous chapters, the author contributed to the design, and then installed, operated, collected samples, analyzed and interpreted all the data for the entire bench-scale experiment at Facility B. The University of Minnesota (Ben Ma and Dr. Raymond Hozalski) constructed the bench-scale columns used at Facilities I and L, and they also installed, operated, sampled, and analyzed the samples from the bench-scale experiment at Facility I. The participating utilities and their staff members provided information about their full-scale treatment processes, and helped with the installation, operation and sampling of the bench-scale tests at Facilities I and L and the pilot-scale tests at Facilities C and Q. The participating utilities also fully operated the pilot-scale tests at Facilities C and Q. All samples for NDMA analysis for all the bench-, pilot-, and full-scale experiments were shipped to and analyzed by Stanford University (Zhong Zhang and Dr. Bill Mitch). The interpretation, writing and analysis of all the data presented in this chapter were conducted by the author.

5.2.2 Analytical Parameters

All the parameters were determined in the laboratory at each Facility except for LC-OCD/FEEM and NDMA UFC which were shipped for analysis to the University of Waterloo and Stanford University, respectively. All the instruments and standard methods used for analysis during these tests were identical to those described in chapters 3 and 4.

5.2.3 Correlation Analysis

To analyse the correlation between NDMA UFC and NOM concentrations, the correlation coefficients were calculated. The correlation coefficient tells how strongly two data sets are related to each other, and these were calculated using the CORREL function in Excel. One of these data sets was the NDMA UFC concentrations and the other data set was each of the NOM fractions. The data were measured at the bench-scale experiments at Facilities B, I, and L and the pilot-scale experiments at Facilities C and Q. However, the correlation only includes NDMA UFC data where

there were corresponding NOM data. All the NDMA UFC data were done by others as part of the WRF project #4669 (Evans et al., forthcoming). The correlations for these data sets were calculated for: NDMA UFC influents and NOM in influents; NDMA UFC in effluents and NOM in effluents; changes in NDMA UFC across the biofilters and changes in NOM across the biofilters; changes in NDMA UFC across the biofilters and NOM in influents; and NDMA UFC in effluents and NOM in influents. The correlation coefficient will be between -1 and +1, where -1 indicates a perfect negative correlation, which means that one data set increases while the other decreases. A coefficient of +1 indicates a perfect positive correlation, which means that both data sets are increasing/decreasing simultaneously. The closer the correlation coefficient is to either +1 or -1 the stronger the two data sets correlate to each other.

5.3 Results and Discussion

5.3.1 NDMA Precursor Removal or Formation during Biofiltration and Comparison to NOM Fraction Removals

The objectives of this section were to investigate how pre-ozonation and media acclimated/operated in different water sources (from Chapter 3, conducted from May 9th 2018 to June 18th 2018), and how some full-scale treatment steps prior to biofiltration (from Chapter 4, conducted on April 9th 2018) influence NDMA UFC concentrations. Furthermore, these NDMA UFC formation or removal trends were compared to the corresponding NOM fraction removals discussed in Chapters 3 and 4. The columns were located at the full-scale plants (Facilities B and Q) and fed the same water as the full-scale biofilters at each test location.

5.3.1.1 Impact of Prior Ozonation and Media Acclimated/Operated in Different Water Sources on NDMA Formation during Biofiltration and Comparison to NOM Fractions Reduction

This sections shows the influence of pre-ozonation and media acclimated/operated in different water sources on NDMA UFC formation or removal in the bench-scale columns at Facility B, and the comparison of these to the removals of NOM fractions.

Figure 5.1 shows that the NDMA UFC concentrations for the ozonated influent water ranged from 8 to 14 ng/L. Also, there were only almost negligible changes through the biofilter columns

receiving ozonated water usually less than 2 ng/L. Taken together, the three different biofilter media behaved very similarly when fed the same ozonated water source from Facility B. The NDMA UFC concentrations for the non-ozonated influent water ranged from 49-69 ng/L. Therefore, ozonation at Facility B decreased NDMA UFC by 41-58 ng/L, and the non-ozonated columns substantially decreased NDMA UFC by up to 29 ng/L. However, there were high variations for the effluents between the duplicate non-ozonated columns. Pre-ozonation substantially reduced NDMA UFC concentrations, which is consistent with at least some previous studies that indicated a significant reduction of both NDMA and its precursors with strong oxidants, such as ozonation (Chen and Valentine, 2008; Lee et al., 2007b, 2008; McCurry et al., 2015; Pisarenko et al., 2012; Shah et al., 2012; Wang et al., 2015; Yang et al., 2013). Although the NDMA UFC concentrations were substantially lower after ozonation and biofiltration combined, the reason for this was the greatly reduced NDMA UFC concentrations in the influent to the Facility B media biofilters fed with ozone aided water. Even though the other biofilters fed with ozonated water sometimes exhibited very low increases in NDMA UFC concentrations, the overall NDMA UFC concentrations were still much lower when pre-ozonation and biofiltration were combined. This is also consistent with other studies, which reported that biofiltration combined with pre-ozonation effectively decreased NDMA formation (Barzi, 2008; Chuang and Mitch, 2017; Farré et al., 2011b; Krasner et al., 2012a; Liao et al., 2014, 2015b; Mitch et al., 2009; Selbes et al., 2016, 2017).

The NOM fraction removals for these bench-scale columns were presented in Chapter 3 (Figures 3.7, 3.8, and 3.10), and showed that all the different media behaved very similarly when fed the water from Facility B. Also, prior ozonation combined with biofiltration at Facility B improved the biofilter performance, and the removal of the following NOM fractions: DOC, HS, BP, LMW neutrals, HA, FA, and protein-like materials. Overall, similar to the NOM fraction removals, all the different media behaved very similarly regarding NDMA UFC removals or formation when fed ozonated water from Facility B. Furthermore, ozonation combined with biofiltration at Facility B also improved the removal of the NDMA UFC.

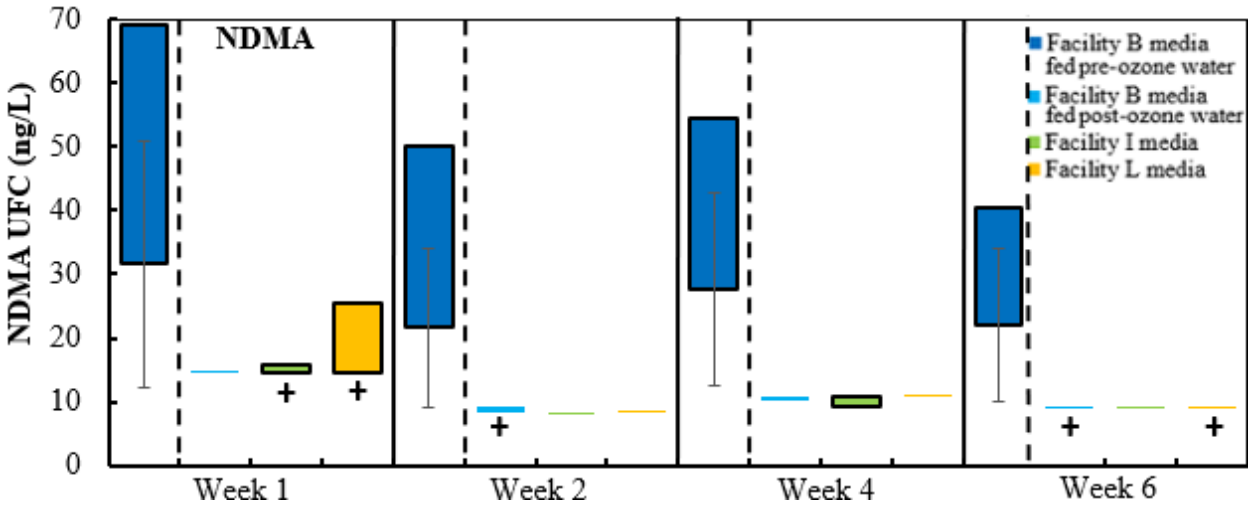


Figure 5.1 Removal of NDMA UFC through bench-scale biofilter columns fed with Facility B water with Facilities B, I and L media. Facilities I and L media were fed with Facility B post-ozone water. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. Dark blue bars left of dashed lines are fed pre-ozone water and all others are fed post-ozone water.

5.3.1.2 Impact of Upstream Full-scale Treatment Steps on NDMA Precursor Removal or Formation during Biofiltration and Comparison to NOM Fraction Removals

This section shows the NDMA UFC concentrations for the following full-scale treatment processes: PAC, lime softening, and ferric chloride coagulation with or without polyDADMAC. These were the full-scale treatment process steps prior to the biofilters at Facility Q. Figure 5.2 shows only a large increase in NDMA UFC concentrations after lime softening, and smaller increases after coagulation with ferric chloride both with and without polyDADMAC. Overall, softening drastically increases NDMA precursors at Facility Q, which is consistent with previous research, which suggested that lime addition can increase NDMA formation due to the increase in pH (Krasner et al., 2012; McCurry et al., 2017; Sgroi et al., 2015). Coagulation with or without polyDADMAC more modestly increased NDMA UFC concentrations, which is consistent with previous research (Krasner et al., 2012a). Also, polyDADMAC had a negligible effect on NDMA UFC formation, which differs from previous literature that reported that polyDADMAC is a potential NDMA precursor (Mitch and Sedlak, 2004; Padhye et al., 2011; Park et al., 2009a, 2009b; Sgroi et al., 2014, 2016). Researchers suggested the quaternary ammonium ring in polyDADMAC

is degraded to DMA, which is an NDMA precursor, during either chloramination or ozonation. However, these studies only indicated very low yield of NDMA from polyDADMAC of maximum 0.003% (Padhye et al., 2011; Sgroi et al., 2014). Therefore, this might explain the negligible effect of polyDADMAC on NDMA UFC formation in this thesis. The NOM fraction removals for these upstream treatment processes were presented in Chapter 4 (Figures 4.5, 4.6, and 4.7) and showed that only PAC substantially decreased the NOM fractions concentrations. Thus, the NDMA UFC formations were not similar to the NOM fraction removals.

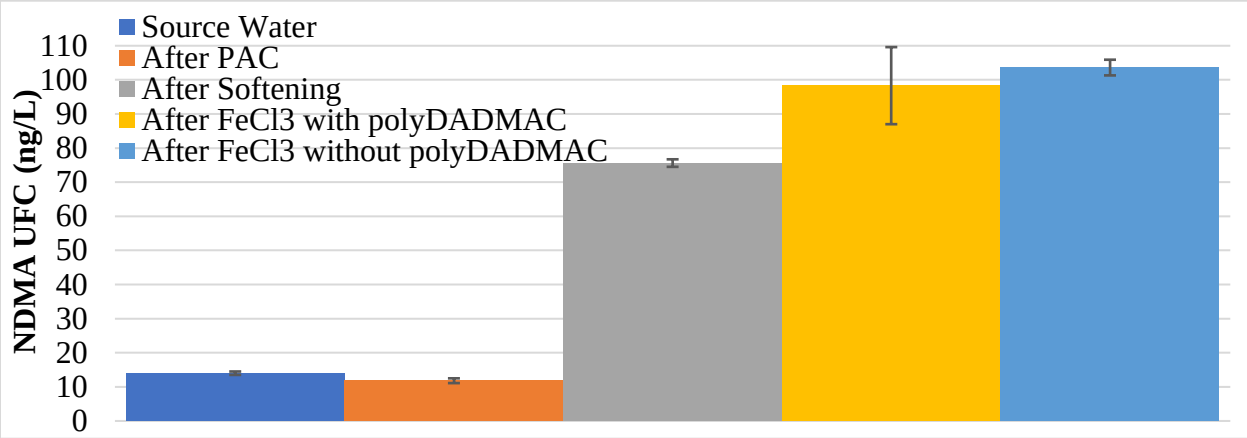


Figure 5.2 NDMA UFC concentrations through the full-scale treatment processes prior to biofiltration at Facility Q on April 9, 2018. Error bars indicate maximum and minimum values in the duplicate sampling.

5.3.2 Correlations between NDMA Precursor Removal or Formation and NOM Fraction Removals

Correlation analyses were done to determine whether the NDMA precursor formation or removal correlated to the NOM fraction removals, measured by LC-OCD and FEEM. NDMA UFC and NOM were measured during the bench-scale and pilot-scale experiments. However, there were no correlations between changes in NDMA UFC across the biofilters and either changes in NOM fractions across the biofilters or NOM fractions in influents (Figure C.1 and Figure C.2, respectively). Also, there were no correlations between NDMA UFC in effluents and NOM fractions in influents (Figure C.3). There were only weak correlations between NDMA UFC in influents and NOM fractions in influents, and NDMA UFC in effluents and NOM fractions in effluents. The best correlation was between protein-like materials as measured by FEEM in biofilter influents and NDMA UFC in biofilter influents, which had a correlation coefficient of 0.65 (n=27), which can be seen in Figure 5.3. The Pearson's critical value for this correlation (with

a degree of freedom (df) of 25, at the significance level (α) 0.01) is 0.49. Since the correlation coefficient of 0.65 is higher than Pearson's critical value of 0.49, the correlation between protein-like materials and NDMA UFC in biofilter influents is therefore statistically significant (Figure 5.3). This figure shows that the data can roughly be divided into two groups. The first group had low NDMA UFC concentrations and protein-like materials intensities and included data from Facilities B and C, which had pre-ozonation, and Facility L, which did not have pre-ozonation but had upstream oxidation through permanganate and chlorine instead. The second group had higher NDMA UFC concentrations and protein-like materials intensities and included the non-ozonated influents at Facility B, and the softened influents at Facility I and Q. Taken together, this correlation highlights the importance of upstream processes prior to biofiltration on NDMA UFC and NOM fractions concentrations.

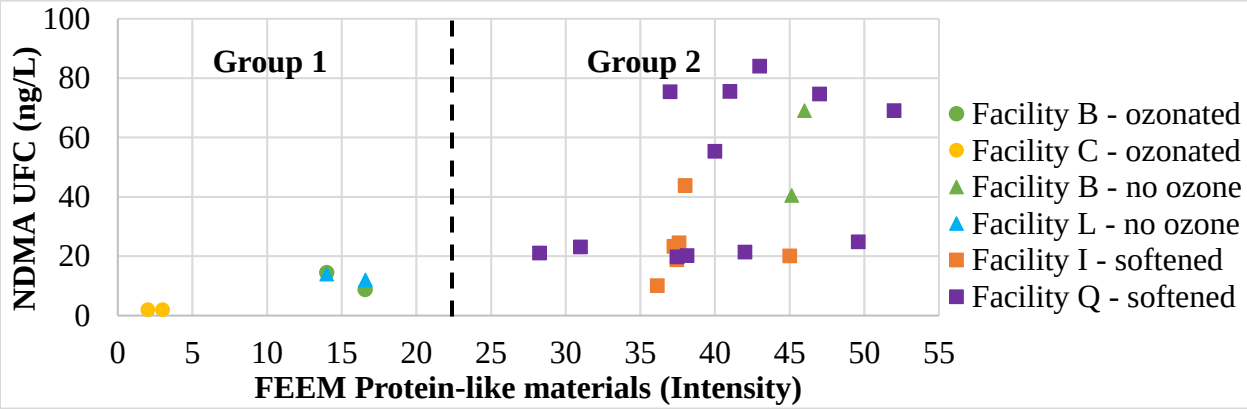


Figure 5.3 Relationship between FEEM Protein-like materials intensities in influents and NDMA Precursor concentrations in influents for all bench- and pilot-scale experiments. Ozonated, no ozone, and softened refers to upstream processes prior to biofiltration.
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Also, there were also correlations between NDMA UFC in biofilter effluents and concentrations of NOM fractions in these effluents. The best correlation was between protein-like materials in FEEM and NDMA UFC in effluents, which had a correlation coefficient of 0.63 (n=87), and this correlation can be seen in Figure 5.4. The Pearson's critical value for this correlation (at df=85, and α= 0.01) is 0.28. Since the correlation coefficient of 0.63 is higher than Pearson's critical value of 0.28, the correlation between protein-like materials and NDMA UFC in biofilter effluents is therefore statistically significant (Figure 5.4). This figure also shows that the data roughly can be divided into two groups, the same two groups as in Figure 5.3. Overall, this figure also highlights the importance of upstream processes prior to biofiltration on NDMA precursor concentrations

and NOM fraction removals. Most of the higher NDMA UFC concentrations and FEEM signals are from lime softening at Facility Q. Therefore, lime softening and the water source at Facility Q might be potential reasons for high NDMA UFC and FEEM values.

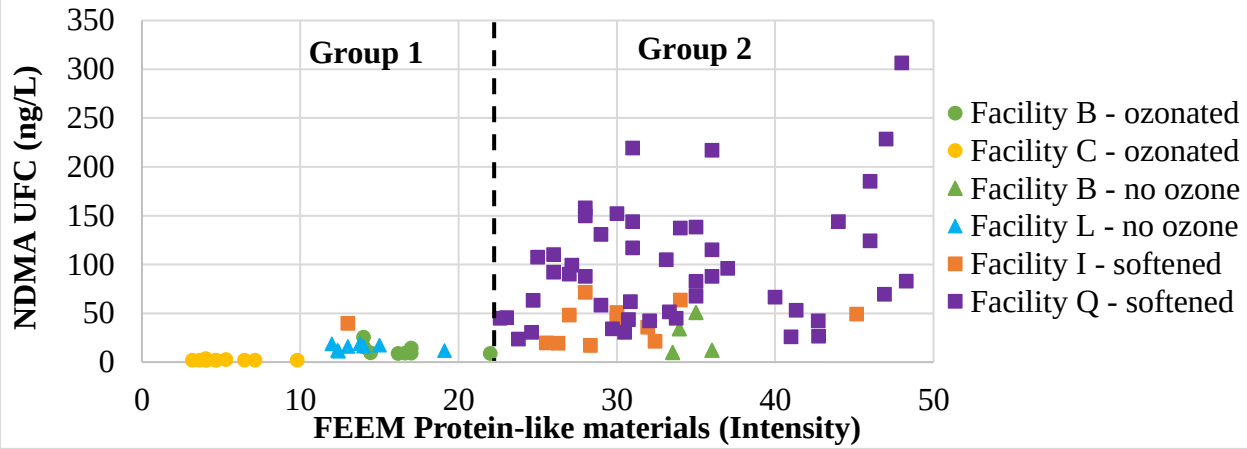


Figure 5.4 Relationship between FEEM Protein-like materials intensities in effluents and NDMA Precursor concentrations in effluents for all bench- and pilot-scale experiments. Ozonated, no ozone, and softened refers to upstream processes prior to biofiltration.
Source: Adapted from Evans et al., forthcoming. Reprinted with permission. © The Water Research Foundation.

Overall, there were only strong correlations between protein-like materials and NDMA UFC on 0.65 (n=27) for the influents and 0.63 (n=87) for the effluents. Protein-like materials include amino acids, which contain secondary amino acids that have nitrogenous content. This is also consistent with previous studies, which showed that NDMA was only detected after chloramination of certain nitrogenous NOM isolates (Dotson et al., 2009). Other studies also showed that the main NDMA formation mechanism is a reaction between chloramine and secondary amine precursors (Choi and Valentine, 2002; Lee et al., 2007c; Mitch and Sedlak, 2002; Mitch et al., 2003; Najm and Trussell, 2001; Schreiber and Mitch, 2006a). Furthermore, another study found that NDMA precursors increased with increasing nitrogen content in DOC (Lee et al., 2007b). All of these findings might be the reason for the correlations between protein-like materials in influents and NDMA UFC in influents, and protein-like materials in effluents and NDMA UFC in effluents (Figure 5.3 and Figure 5.4). The correlation for the influents was 0.65, for the effluents it was 0.63. However, the correlation for the changes in protein-like materials and NDMA UFC across the biofilters was only 0.07 and did not correlate (Figure C.1). A potential reason might be that the FEEM signals were very low and it was therefore difficult to detect any change across the biofilters and correlate these low signals to NDMA UFC. Also, there might be other NDMA precursor formation trends

involved that is not reflected in the FEEM signals. Also, it should be taking into consideration that the results presented in this thesis were only based on a few facilities with limited numbers of samples for some facility. In some cases, operational conditions changes as well. Furthermore, the NDMA UFC concentrations varied a lot at each facility and precursors were both removed and formed during biofiltration. These factors might have contributed to the fact that the correlations found were not even stronger. Therefore, further studies are needed to better understand if proteins are transformed during biofiltration to NDMA precursors and how upstream processes affect this relationship.

5.4 Conclusions

As mentioned earlier, since NDMA is a potential harmful DBP, it is therefore crucial to remove or even minimize NDMA formation during drinking water treatment. The removal or formation of NDMA UFC during biofiltration were therefore investigated and correlated to the NOM fraction removals findings at the bench-scale and pilot-scale experiments from Chapters 3 and 4.

The following conclusions can be made:

- The different media showed similar trends in NDMA UFC concentrations when fed the same influent water from Facility B, which is consistent with all the NOM fraction removal trends in Chapter 3.
- Pre-ozonation substantially reduced NDMA precursor concentrations (as measured by UFC) in the biofilter influent at Facility B, which also is consistent with the NOM fraction removals in Chapter 3.
- In the biofilters fed with ozonated water the change in NDMA UFC across the biofilters were usually less than 2 ng/L, whereas there were high decreases (up to 29 ng/L) in NDMA UFC in the biofilter receiving non-ozonated water.
- Ozonation and biofiltration combined had the lowest NDMA UFC concentrations. This is also consistent with the removals of the following NOM fractions in Chapter 3: DOC, HS, BP, LMW neutrals, HA, FA, and protein-like materials.
- Softening drastically increased the NDMA UFC concentration following the full-scale treatment process at Facility Q.

- Coagulation with ferric chloride addition showed small increases in NDMA UFC concentrations during the full-scale treatment process at Facility Q.
- PolyDADMAC had negligible effect on NDMA UFC formation during the full-scale treatment process at Facility Q.
- Higher protein-like materials intensities in FEEM in the biofilter influents and effluents might be related to higher NDMA UFC concentrations in the biofilter influents and effluents. The reason is that the correlation for both their influents and effluents values were statistically significant and therefore strongly correlated to each other.

5.5 Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for their use by the authors or funding agencies.

Chapter 6
Conclusions and Recommendations

The major conclusions of this thesis were presented at the end of Chapters 3, 4, and 5, and only some of the main conclusions are summarized in this chapter. The implications and recommendations for future work are also described in this chapter.

6.1 Summary of Conclusions

The bench-scale biofilter experiments at Facilities B, I, and L, presented in Chapter 3, were run simultaneously and each location tested three different biofilter media (from Facilities B, I, and L media) with their water source. During this bench-scale experiment, the impacts of pre-ozonation, water sources, and media acclimated/operated in different water sources on NOM removal through bench-scale biofilter columns were investigated. From this bench-scale experiment, the following conclusions can be made:

1. Pre-ozonation improved the NOM removal and biofiltration performance at Facility B, because ozone oxidizes NOM fractions and creates lower molecular weight by-products with higher biodegradability, which are easier removed during biofiltration.

2. Water source influences the NOM removal and biofiltration performance, and water sources therefore matters. The reason for this statement is that biofilters containing media acclimated/operated in different water sources behaved very similarly when fed the same water source during this bench-scale experiment.

3. Media acclimated/operated in different water sources barely influenced the NOM removal and biofiltration performance at a given location. It was observed that a biofilter media behaved very different when fed different water sources. Also, it would be expected that, during the six-week experimental period, biofilms acclimated/operated in other water sources would gradually adapt to the water being used in the experiment.

In Chapter 4, some pilot-scale experiments at Facilities C and Q were presented. The pilot-scale experiment at Facility C investigated how media type (GAC vs. anthracite), ammonia addition,

and chloraminated backwash influence NOM fraction removals through pilot-scale biofilters. The pilot-scale experiment at Facility Q investigated how some full-scale upstream treatment processes prior to biofiltration, media type (GAC vs. anthracite), backwash oxidants (chloraminated vs. non-chloraminated), and backwash frequency (daily vs. twice weekly) influence NOM fraction removals. Furthermore, the kinetics from biofilter profiles from these investigations were calculated. The following conclusions from these pilot-scale experiments can be made:

1. Among the upstream full-scale treatment process, PAC was extremely effective at removing several NOM fractions during drinking water treatment at Facility Q. PAC, for example, removed more than 83% of BP.

2. Biofilters with GAC media had higher removals of the NOM fractions: DOC, HS, BP, LMW acids/humics, and LMW neutrals at Facility C and of the NOM fractions: DOC, BP, BB, LMW acids/humics, and LMW neutrals at Facility Q than anthracite media, and improved biofiltration performance.

3. Chloraminated backwashed GAC columns had higher removals of DOC (4.3 percentage points higher), BP (20 percentage points higher), LMW acids/humics (3.9 percentage points higher), and LMW neutrals (11.2 percentage points higher) than the GAC control columns at Facility C.

4. There were no noticeable differences between the different backwash types or backwash frequencies on the NOM fraction removals at Facility Q. However, the influence from these parameters on NOM fraction removals was difficult to assess conclusively due to the very low removals at most sampling events.

5. The NOM fraction that had the best fit to a reaction order was BP at both Facilities C and Q. However, there were no clear trends regarding which reaction order fitted each fraction removal the best. The 1^{st} order reaction rate constants were calculated since this is the reaction rate order that is expected for biofiltration, and to be able to compare them with the only other study performed on kinetics of LC-OCD fractions for biofilters. This study also only calculated 1^{st} order reaction rate constants (Chen, 2016).

6. At Facility C, the average 1^{st} order reaction rate constant for BP was 0.057 min^{-1}, which fell well in the range for the 1^{st} order BP rate constants estimated by Chen (2016). Also,

the GAC columns had higher reaction rate constants than anthracite, and the GAC columns with ammonia addition and chloraminated backwash had the highest reaction rate constants. These rate constants, and those discussed below, are site-specific rather than intrinsic rate constants.

7. For Facility Q, the average 1st order reaction rate constant for BP was 0.0017 min^{-1}, which was much lower than at Facility C and Chen (2016). Furthermore, there were no noticeable differences in reaction rate constants for BP between the GAC and anthracite columns or any of the backwashing regimes.

8. The work presented in this thesis was part of a larger WRF project (project #4669), where changes in NDMA formation during biofiltration were investigated, which limited the opportunity to tailor design and operational factors of investigated biofilters. These limitations, for example, included only three biofilters at Facility C, and therefore no duplicate columns; only one sampling event per condition at Facility C; only 4-5 data points per biofilter profile at Facilities C and Q; and the kinetics were only measured and calculated once for each profile.

In Chapter 5, only the NDMA UFC concentrations from the bench-scale columns at Facility B, and from the full-scale upstream treatment processes prior to the biofilters at Facility Q were presented and compared to the NOM fraction removals, presented in Chapters 3 and 4. Furthermore, the correlation between all NOM fraction removals and NDMA UFC removals or formations were also investigated and presented in Chapter 5. From the analysis of these data, the following conclusions can be made:

1. The different media acclimated/operated in different water sources showed similar trends in NDMA UFC concentrations when fed the same influent water from Facility B, which is consistent with NOM fraction removal trends in Chapter 3.

2. Pre-ozonation substantially reduced NDMA UFC concentrations in the bench-scale biofilter influents at Facility B.

3. Ozonation and biofiltration combined had the lowest NDMA UFC concentrations. This is also consistent with the removals of the following NOM fractions in Chapter 3: DOC, HS, BP, LMW neutrals, HA, FA, and protein-like materials.

4. For the full-scale upstream treatment processes at Facility Q, lime softening substantially increased and coagulation with ferric chloride only marginally increased the NDMA UFC concentrations during these processes.

5. Higher protein-like materials intensities in FEEM in the biofilter influents and effluents might be related to higher NDMA UFC concentrations in both the influents and effluents. The reason is that the correlation for both their influents and effluents between protein-like materials and NDMA UFC were statistically significant.

6.2 Implications and Recommendations

Based on the conclusions from this research, the following implications and recommendations for future work are as summarized:

1. Water sources clearly impacted NOM fraction removals at various locations in this and other studies. Although there has been some investigation of how specific parameters in the water source for example phosphorus and nitrogen-containing nutrients influence biofiltration performance in terms of DOC removal, more comprehensive research should be performed examining a range of water quality parameters in different water source and how they influence biofiltration performance and NOM fraction removals. For example, water sources to be considered could include lake water vs. river water, upstream treatment processes at DWTP, and upstream discharges into the water sources such as wastewater, and agricultural activities.

2. Backwash type i.e. chloraminated vs. non-chloraminated backwash only had a small impact on NOM fraction removals in this research. However, it differed between this study and other studies which backwash oxidant had the best performance. Therefore, more comprehensive research should be performed to determine how backwash type influences biofiltration performance and NOM fraction removals during biofiltration. For example,

by running the experiments for a longer period of time, and running it at different facilities simultaneously with biofilters showing good NOM removals under residual free conditions.

3. In this study it could not conclusively be established whether backwash frequency showed negligible influence on NOM fraction removals mainly due to the overall low removals observed in the studied biofilters. However, previous studies indicated that the backwash frequency might influence biofiltration performance. Therefore, more comprehensive research is needed to investigate if backwash frequency influences biofiltration performance and NOM fraction removals. For example, by running tests at various facilities, and for longer periods of time with biofilters which show good NOM fraction removals.

4. The kinetics analysis in the pilot-scale study unfortunately showed no clear trends. Therefore, to achieve a more definitive conclusion regarding the kinetics of the various NOM fraction removals during biofiltration, a more comprehensive and thorough investigation should be conducted. For example, implementing more sampling ports along the media depth, run multiple identical columns simultaneously, and do several sampling events for each condition. Prerequisite are sufficiently high removals of NOM fractions in the studied biofilters.

5. The NDMA UFC concentrations and protein-like materials intensities as measured by FEEM showed statistically significant correlations in the influents and in the effluents in this study. Further research should be performed to ascertain these trends. This further investigation might provide a better insight into NDMA precursor transformation and formation trends, and control strategies for NDMA at DWTPs.

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Appendix A

Additional Data for Bench-Scale experiment at Facilities B, I, and L

Table A.1 Influent water quality at Facility B, Pre-ozone Columns

	Units	Week 0	Week 1	Week 2	Week 4	Week 6
pH		7.9	7.8	8.0	7.7	7.7
Temperature	**°C**	16.0	16.1	17.5	23.0	23.2
DO	**mg/L**	9.8	9.6	9.7	7.5	8.1
Turbidity	**NTU**	0.91	0.92	1.5	1.6	0.88
Total ammonia	**mg/L as N**	0.02	0.020	<0.01	0.04	0.02
Nitrite	**mg/L as N**	0.014	0.013	0.009	0.017	0.007
Nitrate	**mg/L as N**	2.4	3.1	4.3	2.5	3.3
TOC	**mg/L**	4.08	4.09	4.45	4.37	4.69
UV254	**cm^{-1}**	0.0168	0.0160	0.0191	0.0153	0.0895

Table A.2 Influent water quality at Facility B, Post-ozone Columns

	Units	Week 0	Week 1	Week 2	Week 4	Week 6
pH		7.7	7.7	7.7	7.8	7.7
Temperature	**°C**	15.5	15.7	17.0	23.3	23.6
DO	**mg/L**	18.0	15.9	19.4	11.5	14.2
Turbidity	**NTU**	1.3	1.8	1.9	0.81	0.99
Total ammonia	**mg/L as N**	0.04	0.04	0.02	0.06	0.01
Nitrite	**mg/L as N**	0.005	0.005	0.006	0.007	0.004
Nitrate	**mg/L as N**	3.3	2.9	2.7	2.5	2.1
TOC	**mg/L**	3.76	4.28	4.22	4.12	4.85
UV254	**cm^{-1}**	0.0101	0.0141	0.0091	0.0072	0.0601

Table A.3 Influent water quality at Facility I

	Units	Week 0	Week 1	Week 2	Week 4	Week 6
pH		8.0	7.8	8.1	N/A	7.8
Temperature	**°C**	9.0	12.0	16.5	21.0	22.0
DO	**mg/L**	11.9	12.0	10.9	7.6	6.8
Turbidity	**NTU**	0.54	0.34	0.12	N/A	0.34
Total ammonia	**mg/L as N**	0.013	0.032	0.052	0.047	0.003
Nitrite	**mg/L as N**	0.009	0.010	N/A	0.014	0.013
Nitrate	**mg/L as N**	0.56	0.50	0.52	0.43	0.37
DOC	**mg/L**	N/A	3.57	3.35	3.17	3.65
UV254	**cm^{-1}**	N/A	0.0568	0.0548	0.0625	0.0594

N/A indicate that the data is not available.

Table A.4 Influent water quality at Facility L

	Units	Week 0	Week 1	Week 2	Week 4	Week 6
pH		6.8	6.7	7.0	6.8	6.8
Temperature	**°C**	12.2	15.1	10.3	13.1	12.5
DO	**mg/L**	8.9	8.9	11.0	8.7	9.0
Turbidity	**NTU**	0.18	0.25	0.20	0.28	0.28
Total Chlorine	**mg/L**	0.29	0.32	0.35	0.45	0.52
Total ammonia	**mg/L as N**	0.06	0.05	0.12	0.14	0.17
Nitrite	**mg/L as N**	N/A	N/A	0.005	<0.005	0.005
UV254	**cm^{-1}**	0.024	0.026	0.027	0.030	0.028

N/A indicate that the data is not available.

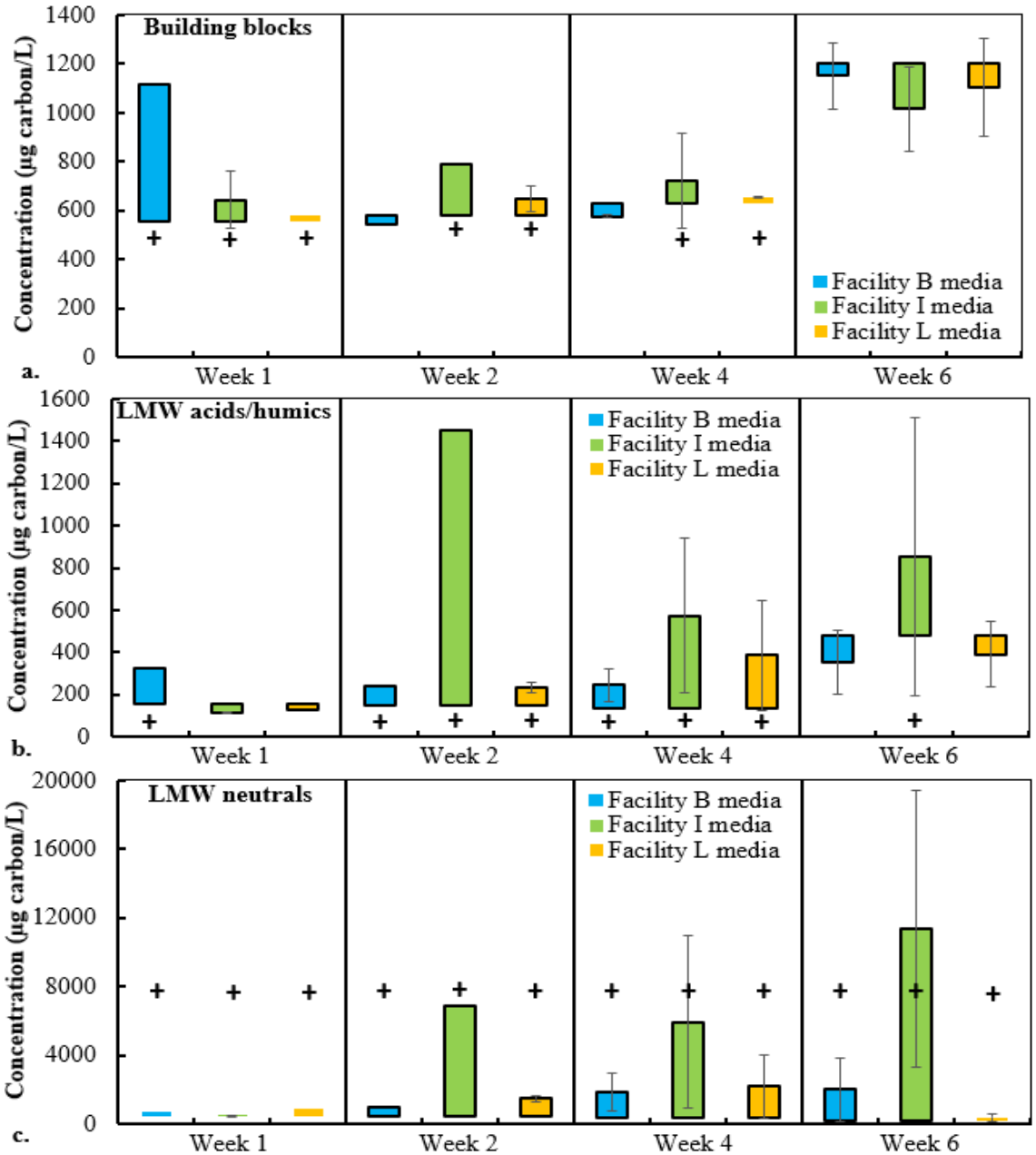

Figure A.1 Removal of NOM fractions through bench-scale biofilter columns fed Facility I water with Facilities B, I and L media analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. BB, b. LMW acids/humics, and c. LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

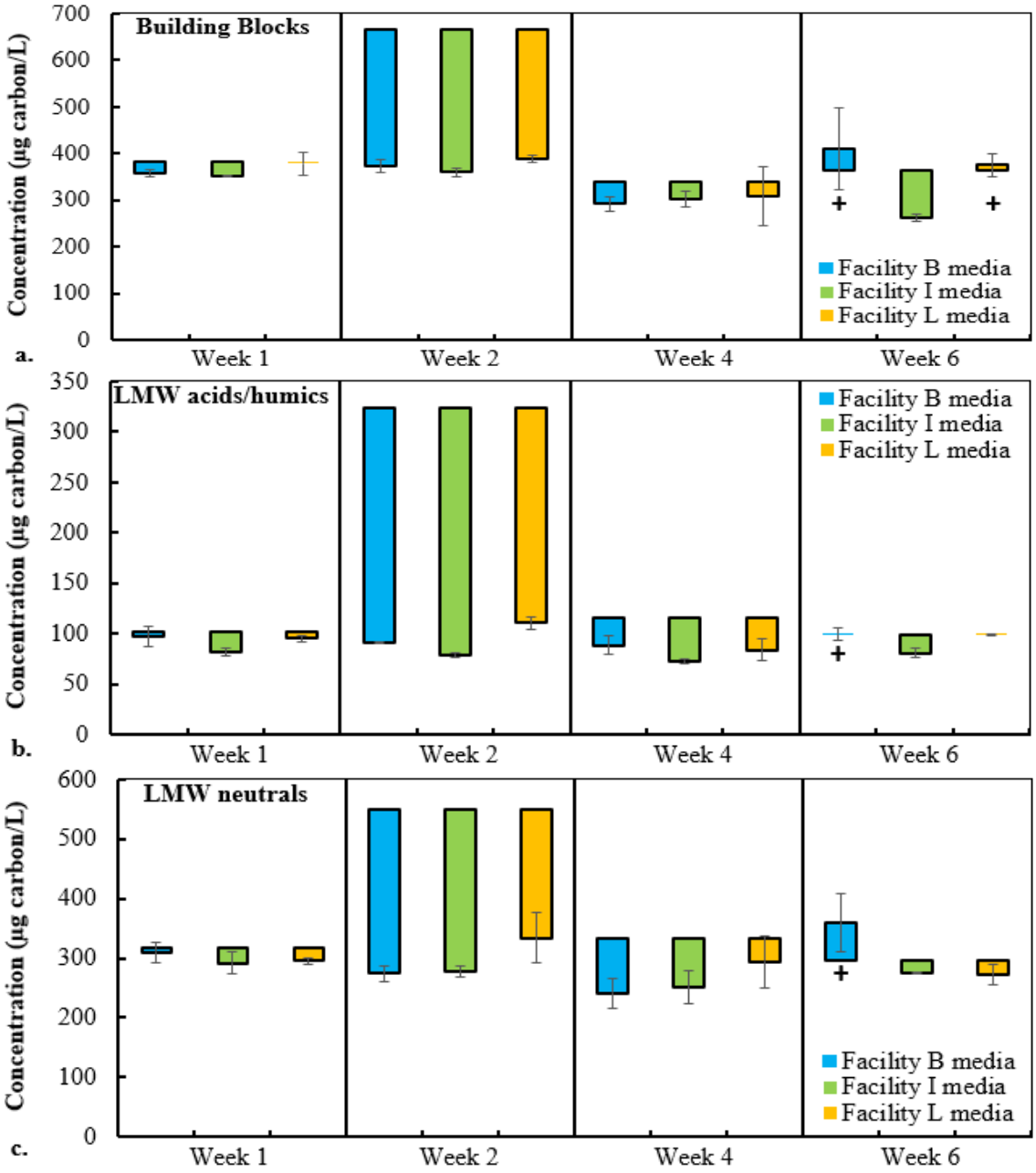

Figure A.2 Removal of NOM fractions through bench-scale biofilter columns fed Facility L water with Facilities B, I and L media analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. BB, b. LMW acids/humics, and c. LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

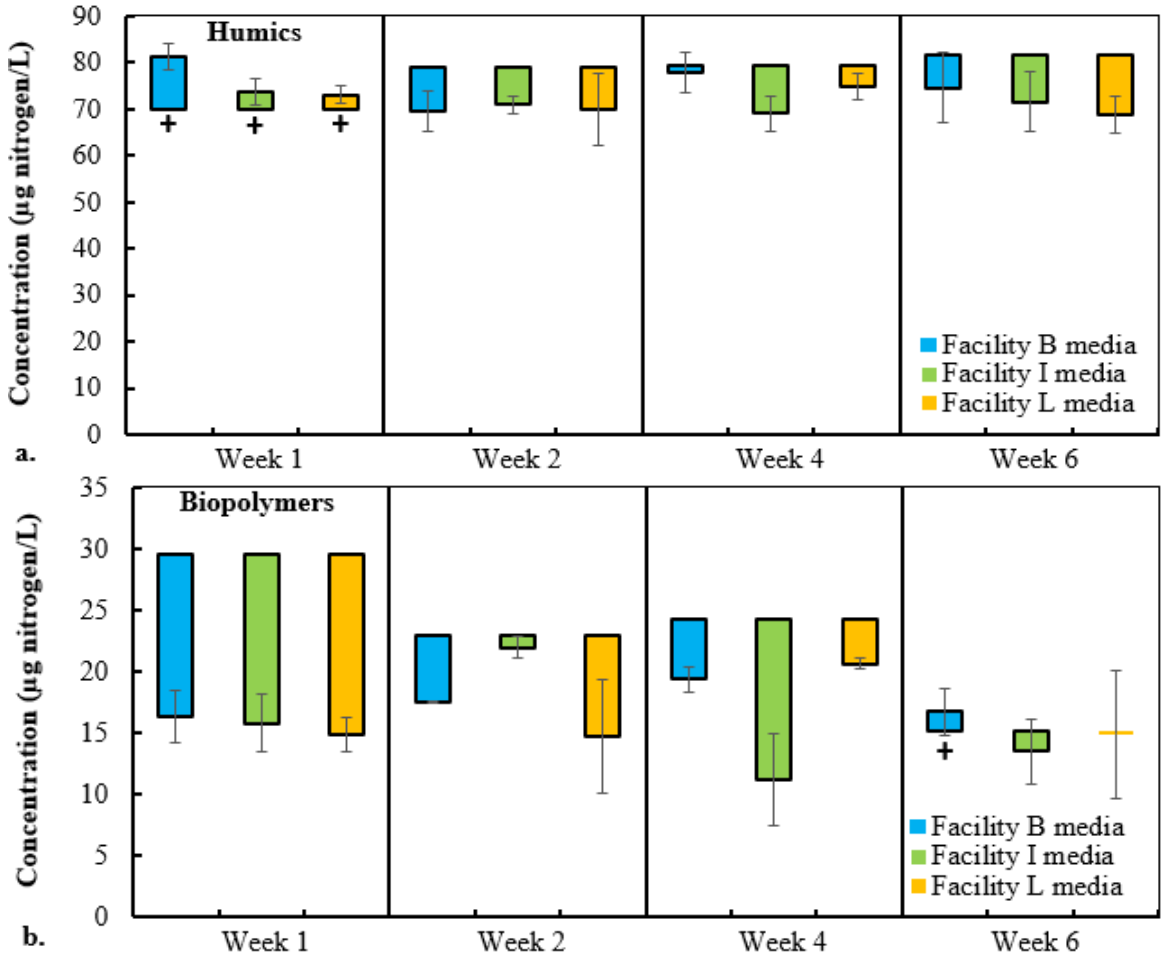

Figure A.3 Removal of NOM fractions through bench-scale biofilter columns fed Facility L water with Facilities B, I and L media analyzed by LC-OND. Reporting average nitrogen concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

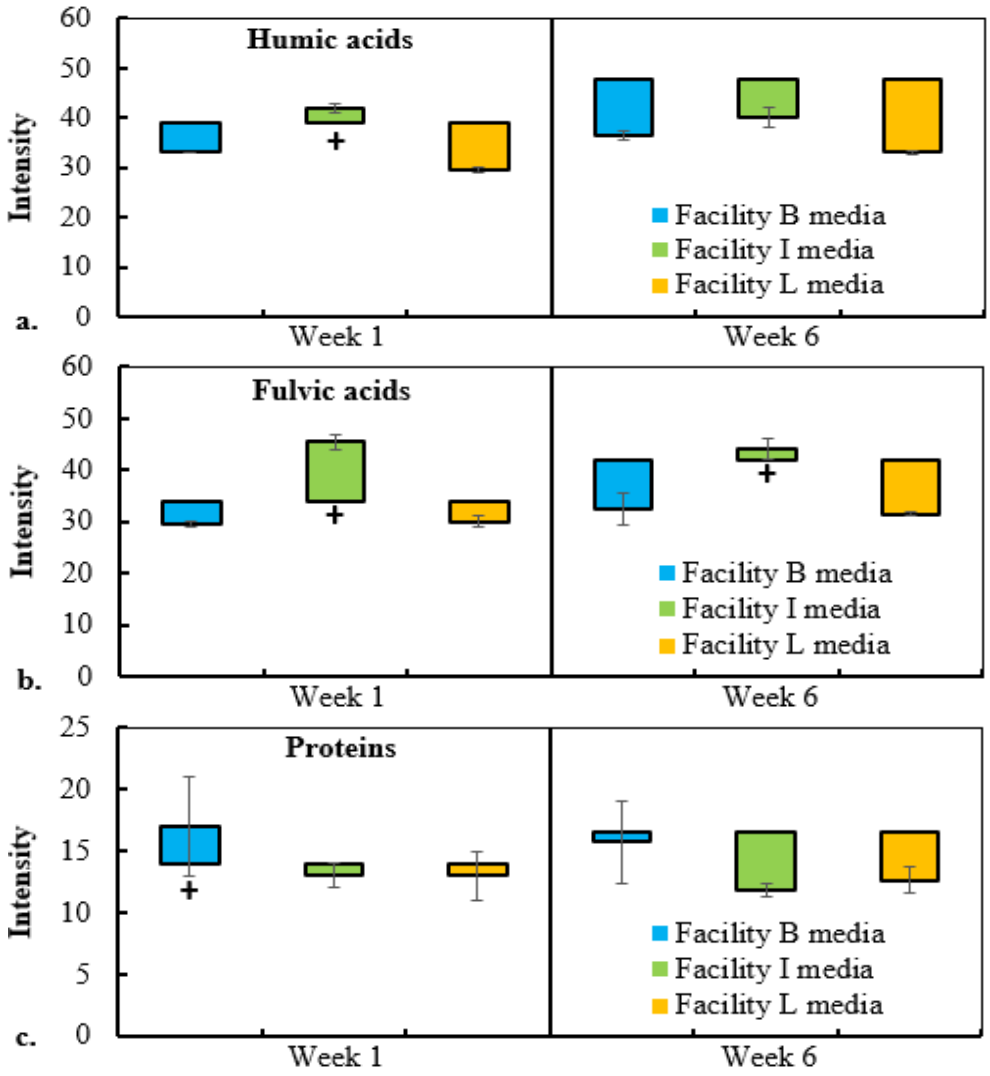

Figure A.4 Removal of NOM fractions through bench-scale biofilter columns fed Facility L water with Facilities B, I and L media analyzed by FEEM. Reporting average intensities for the duplicate colmns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

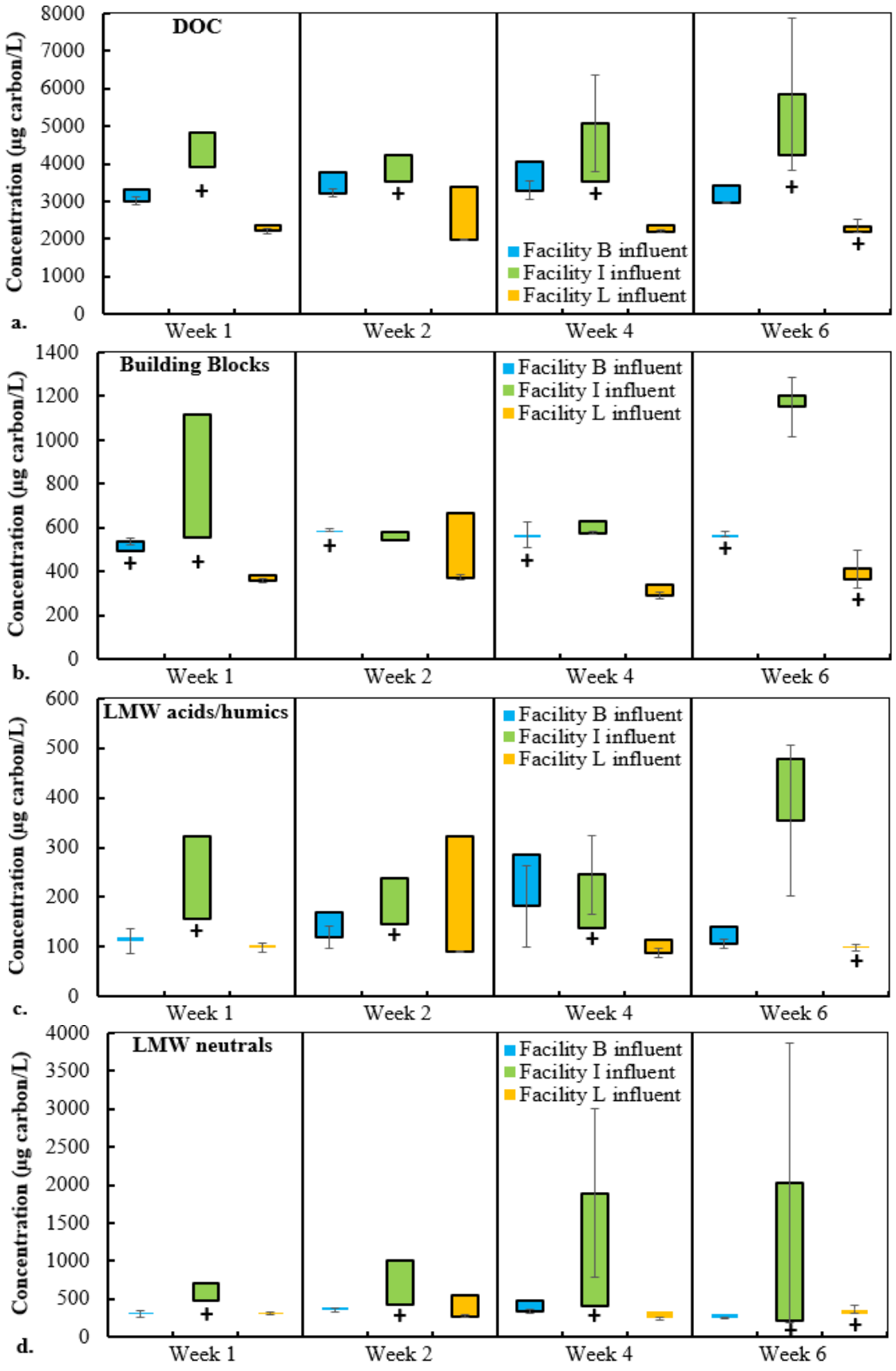
DOC
Concentration (µg carbon/L)
8000
7000
6000
5000
4000
3000
2000
1000
0
a.
Week 1
Week 2
Week 4
Week 6
Facility B influent
Facility I influent
Facility L influent
Building Blocks
1400
1200
1000
800
600
400
200
0
b.
LMW acids/humics
600
500
400
300
200
100
0
c.
LMW neutrals
4000
3500
3000
2500
2000
1500
1000
500
0
d.

Figure A.5 Removal of NOM fractions through bench-scale biofilter columns with Facility B media, fed water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. BB, c. LMW acids/humics, and d. LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

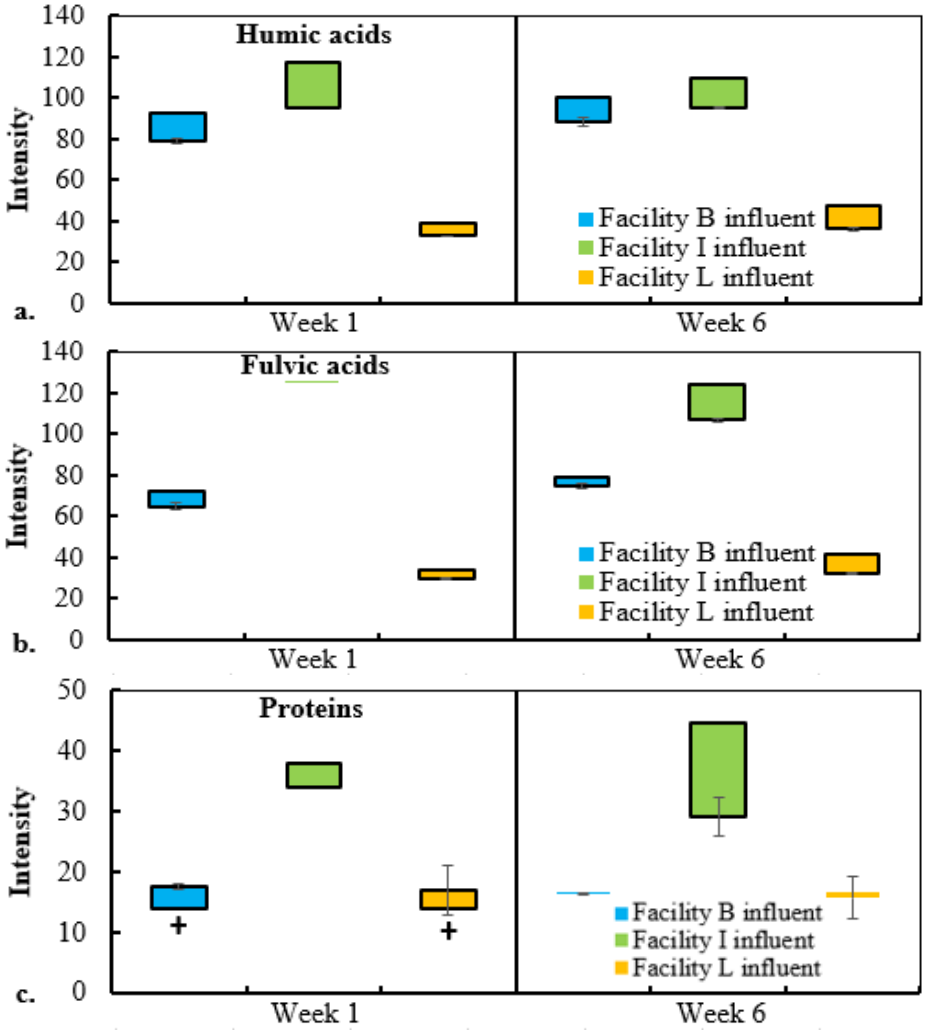

Figure A.6 Removal of NOM fractions through bench-scale biofilter columns with Facility B media, fed water from Facilities B, I and L analyzed by FEEM. Reporting average intensities for the duplicate columns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

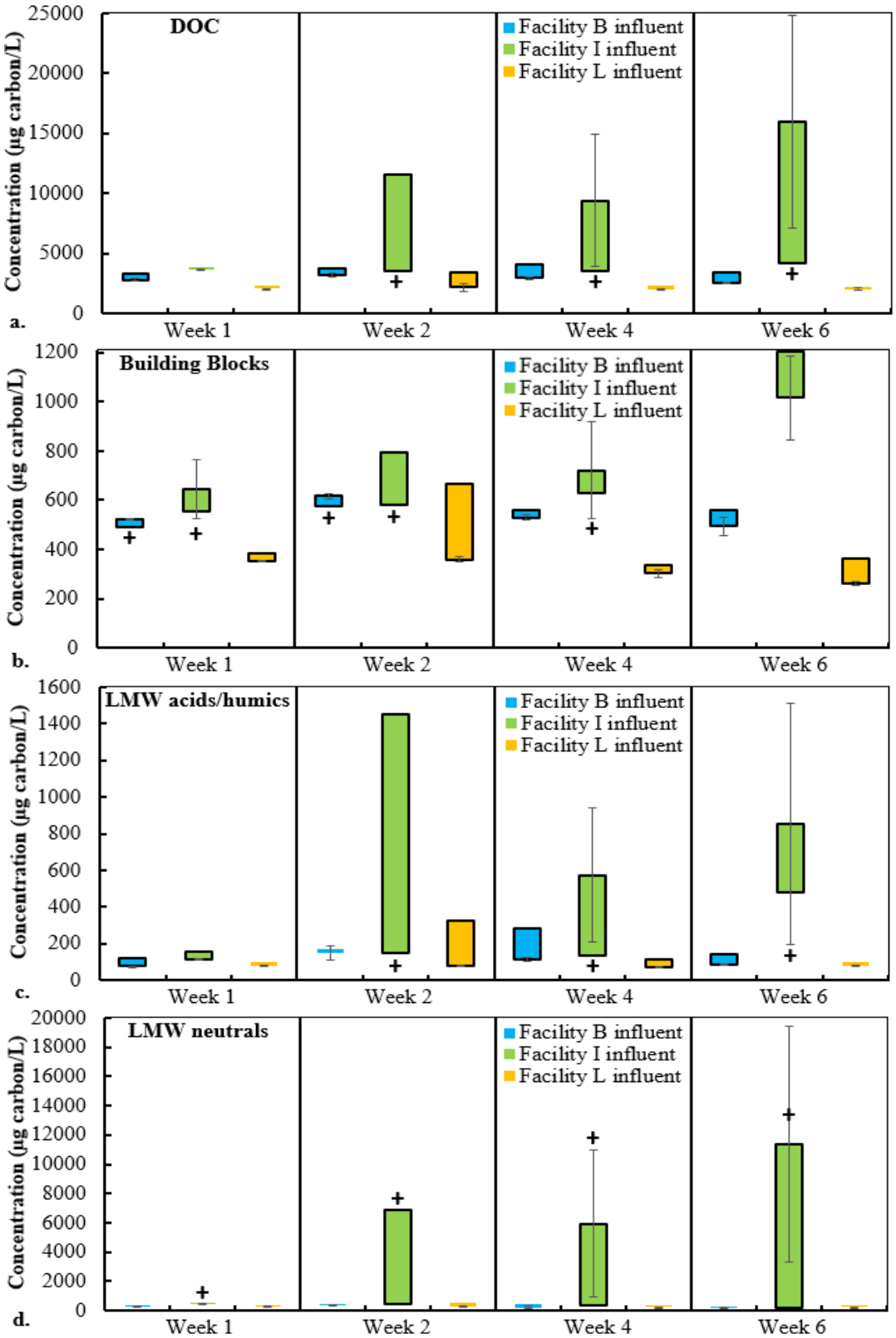

Figure A.7 Removal of NOM fractions through bench-scale biofilter columns with Facility I media, fed water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. BB, c. LMW acids/humics, and d.

LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

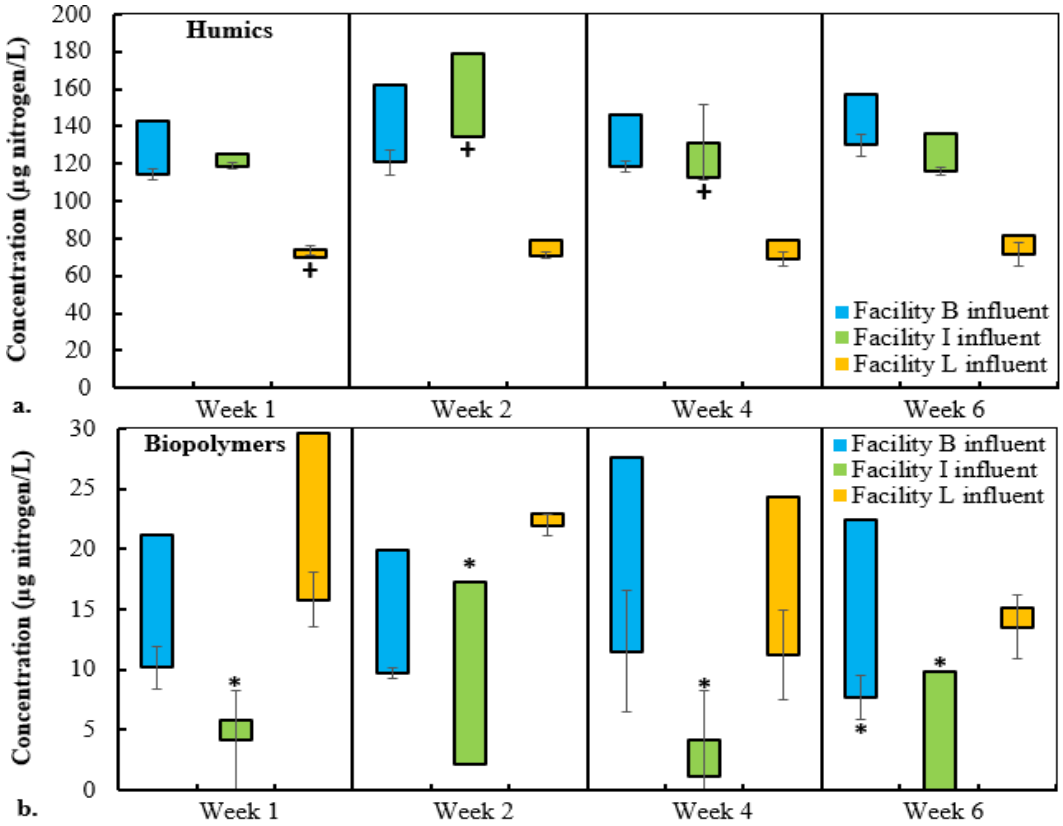

Figure A.8 Removal of NOM fractions through bench-scale biofilter columns with Facility I media, fed water from Facilities B, I and L analyzed by LC-OND. Reporting average nitrogen concentrations for the duplicate columns for a. HS, and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. * indicate that values are below methods detection limits.

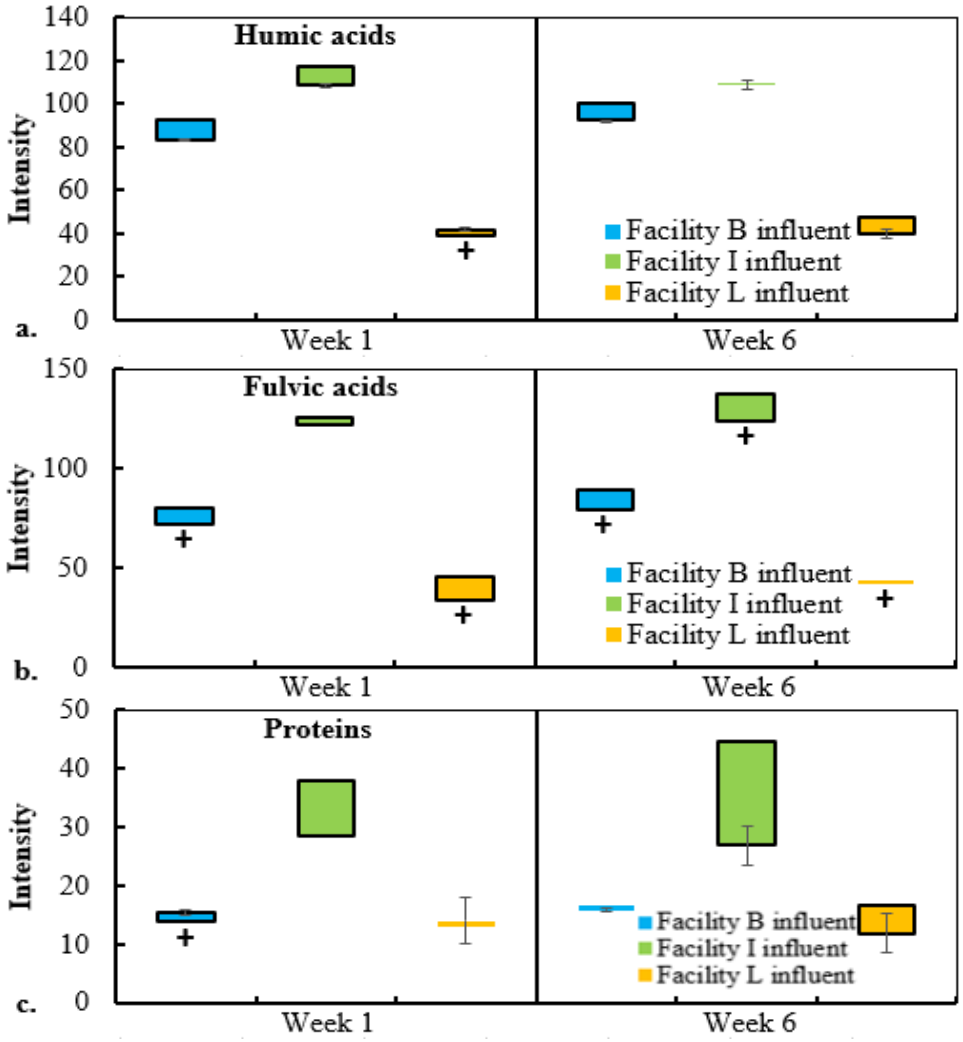

Figure A.9 Removal of NOM fractions through bench-scale biofilter columns with Facility I media, fed water from Facilities B, I and L analyzed by FEEM. Reporting average intensities for the duplicate columns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

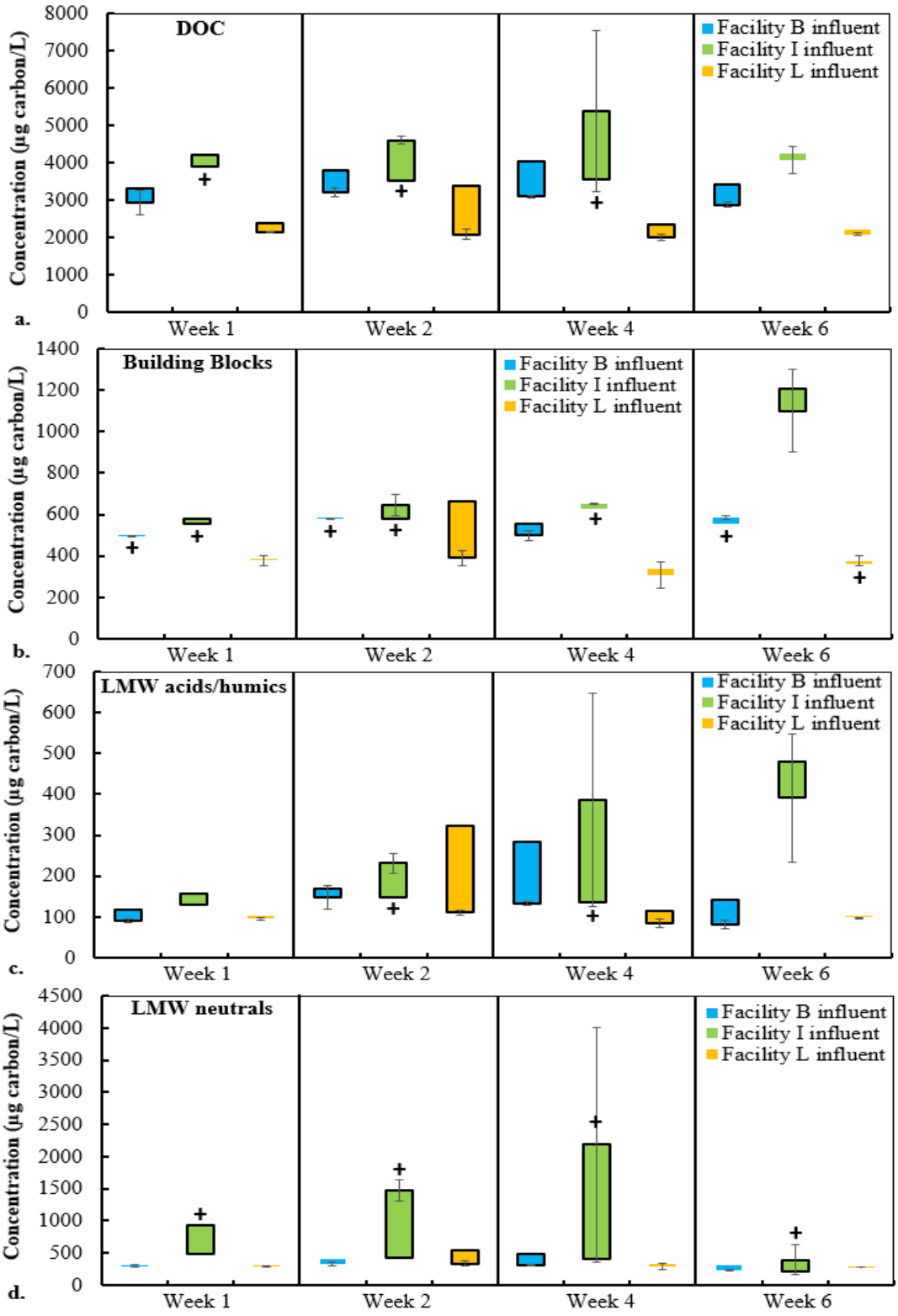

Figure A.10 Removal of NOM fractions through bench-scale biofilter columns with Facility L media, fed water from Facilities B, I and L analyzed by LC-OCD. Reporting average carbon concentrations for the duplicate columns for a. DOC, b. BB, c. LMW acids/humics, and d. LMW Neutrals. + indicate an increase across the biofilter, meaning that the top value

is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

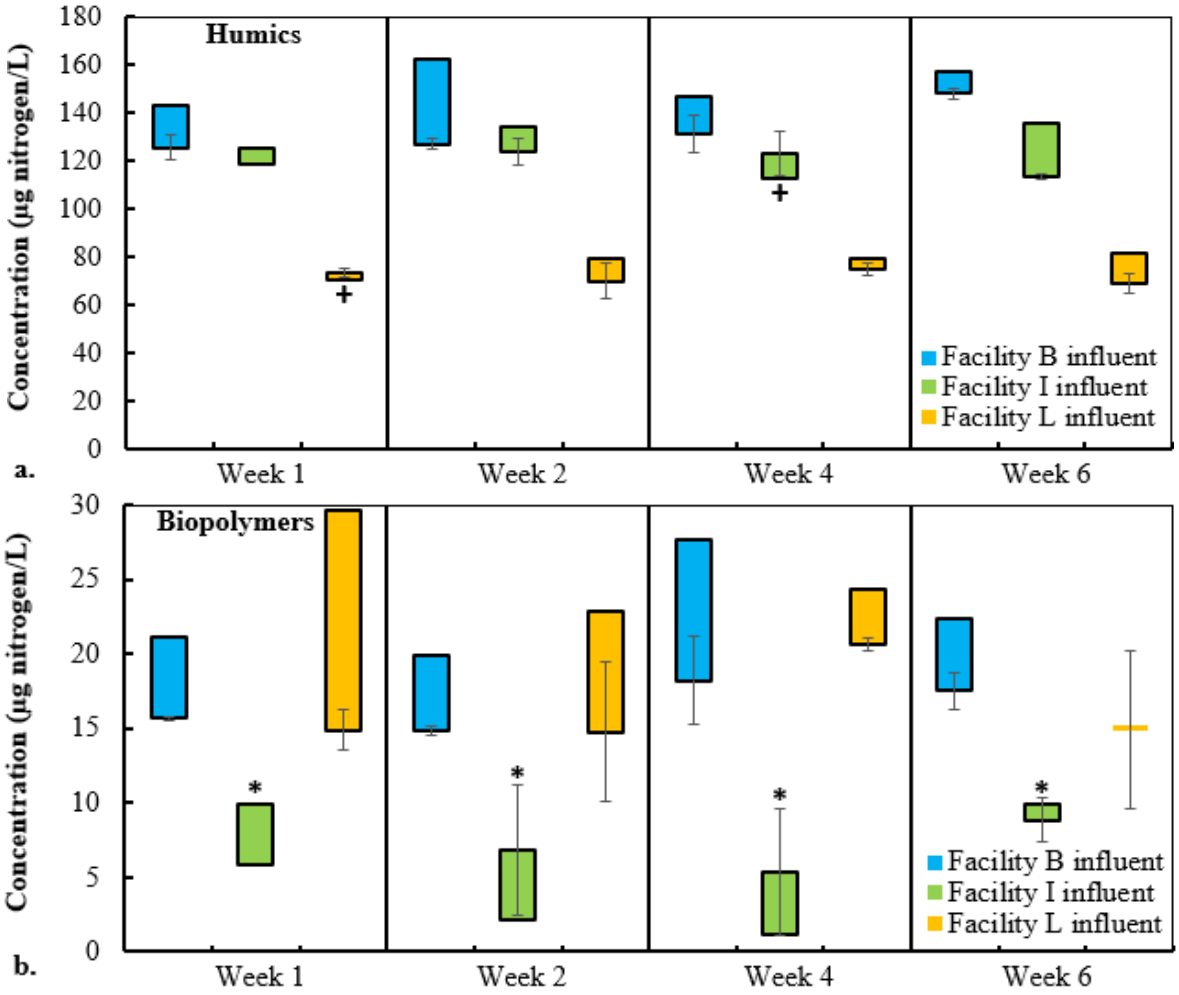

Figure A.11 Removal of NOM fractions through bench-scale biofilter columns with Facility L media, fed water from Facilities B, I and L analyzed by LC-OND. Reporting average nitrogen concentrations for the duplicate columns for a. HS and b. BP. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns. * indicate that values are below methods detection limits.

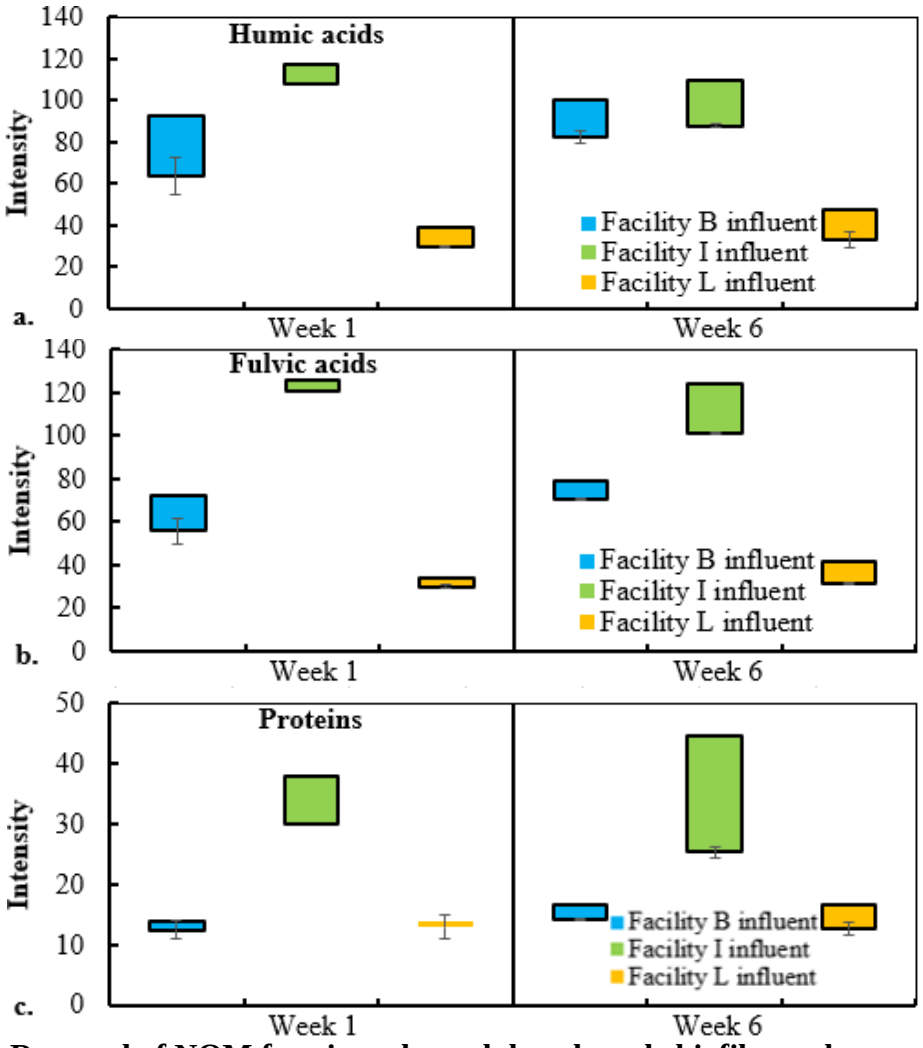

Figure A.12 Removal of NOM fractions through bench-scale biofilter columns with Facility L media, fed water from Facilities B, I and L analyzed by FEEM. Reporting average intensities for the duplicate columns for a. HA, b. FA, and c. protein-like materials. + indicate an increase across the biofilter, meaning that the top value is the effluent and the bottom value of the bar is the influent. All other bars without + indicate a decrease across the biofilter. Error bars indicate maximum and minimum values in the effluents for the duplicate columns.

Appendix B

Additional LC-OCD and FEEM Data for Chapters 4

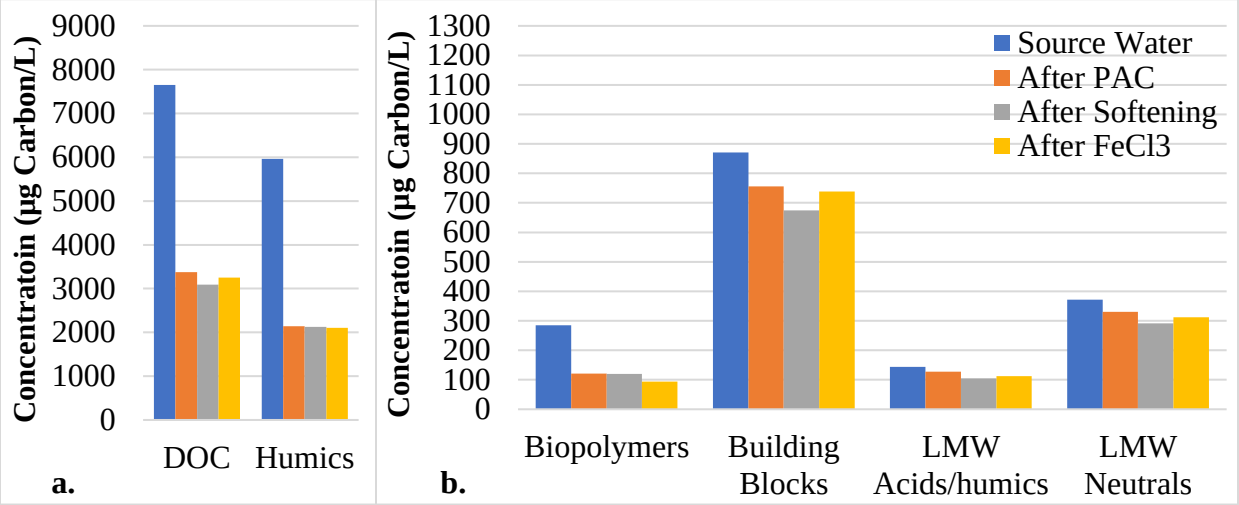

Figure B.1 NOM characterization through the full-scale treatment processes prior to biofiltration at Facility Q on July 24 2018 analyzed by LC-OCD. Reporting organic carbon concentrations in a. DOC and HS, b. BP, BB, LMW acids/humics, and LMW neutrals.

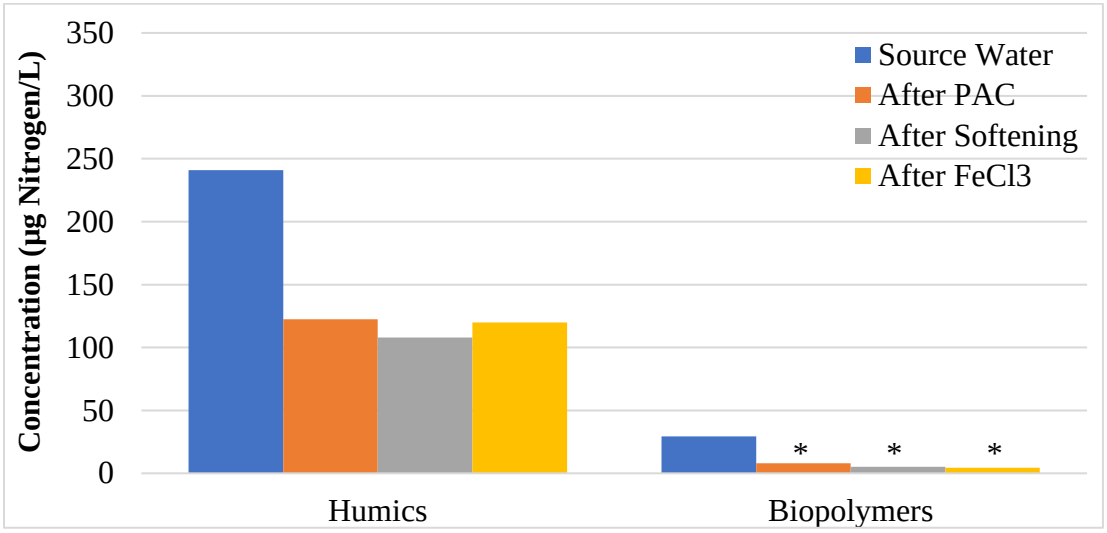

Figure B.2 NOM characterization through the full-scale treatment processes prior to biofiltration at Facility Q on July 24 2018 analyzed by LC-OND. Reporting organic nitrogen concentrations in HS and BP. * indicate that values are below methods detection limits.

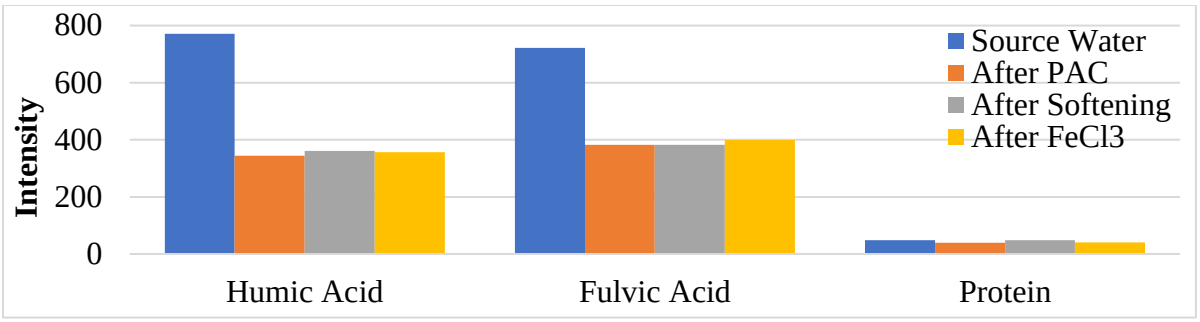

Figure B.3 NOM characterization through the full-scale treatment processes prior to biofiltration at Facility Q on July 24 2018 analyzed by FEEM. Reporting intensities in HA, FA, and Protein-like materials.

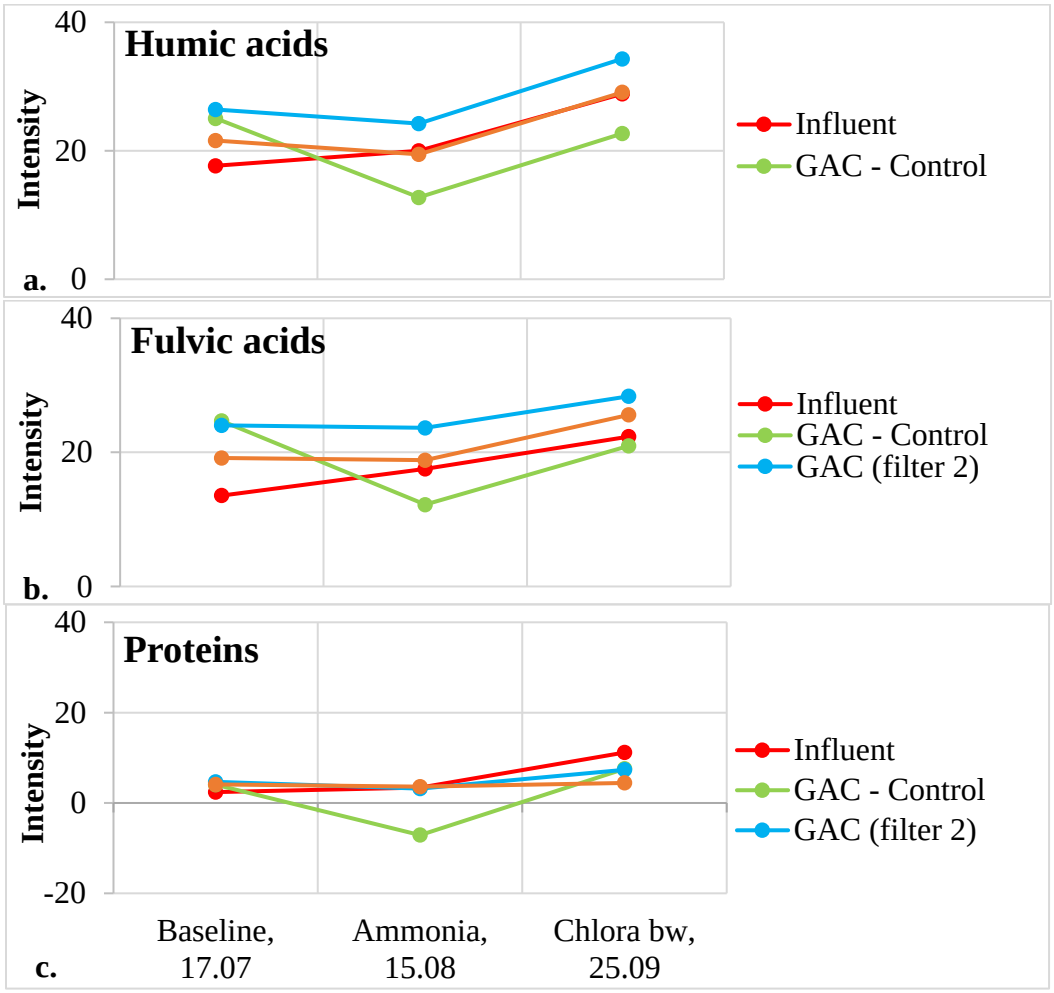

Figure B.4 NOM characterization of biofilter influents and effluents at Facility C at baseline condition, during ammonia additions (filters 2 and 3), and during chloraminated backwash (filters 2 and 3) in 2017 analyzed by FEEM. Reporting intensities for a. HA, b. FA, and c. protein-like materials. Chlora = Chloraminated, bw = backwash.

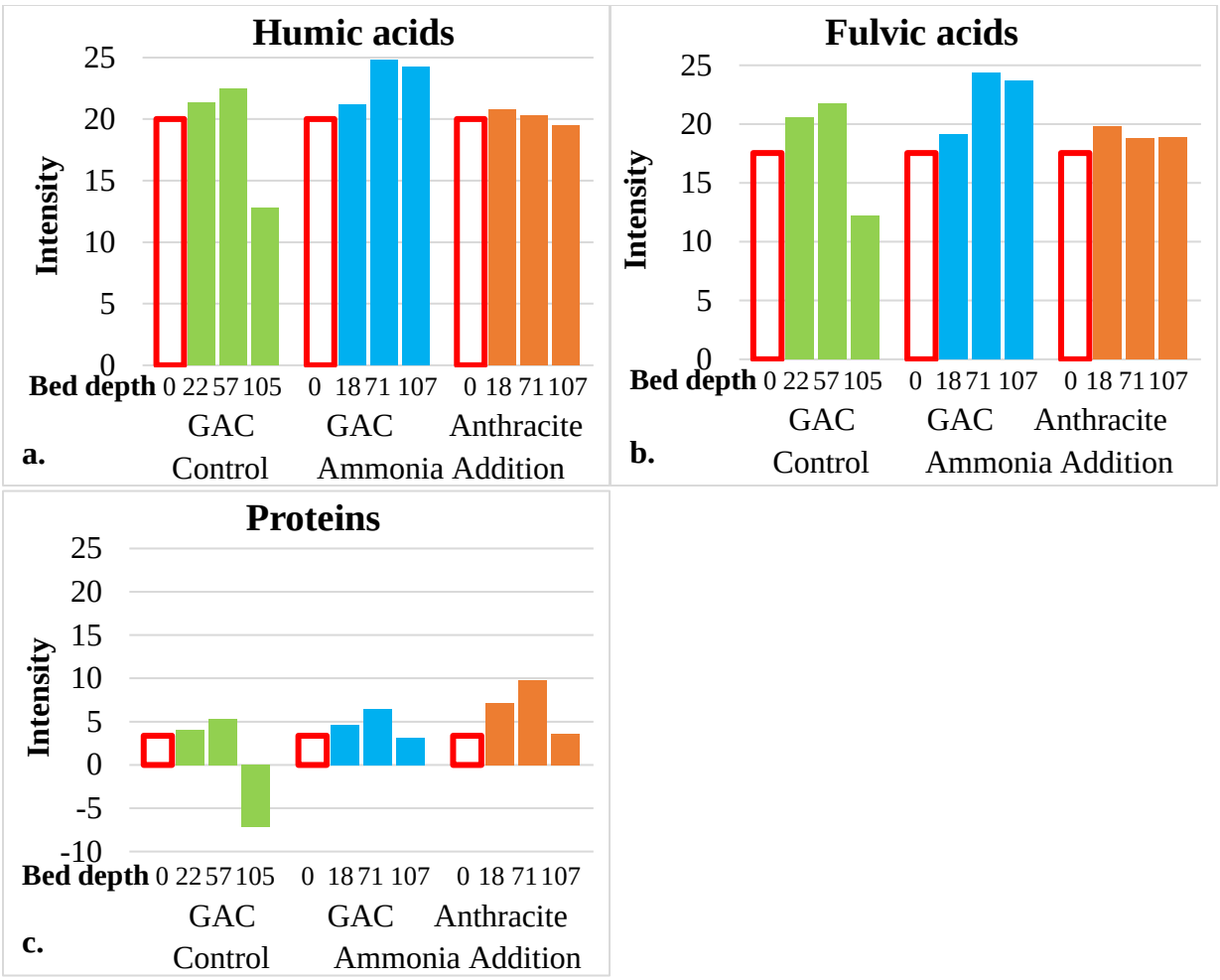

Figure B.5 NOM biofilter profile at Facility C on August 15th 2017 for the control column (no ammonia addition), and the other two columns tested with ammonia addition analyzed by FEEM. Reporting intensities for a. HA, b. FA, and c. protein-like materials. Bed depth is given in cm.

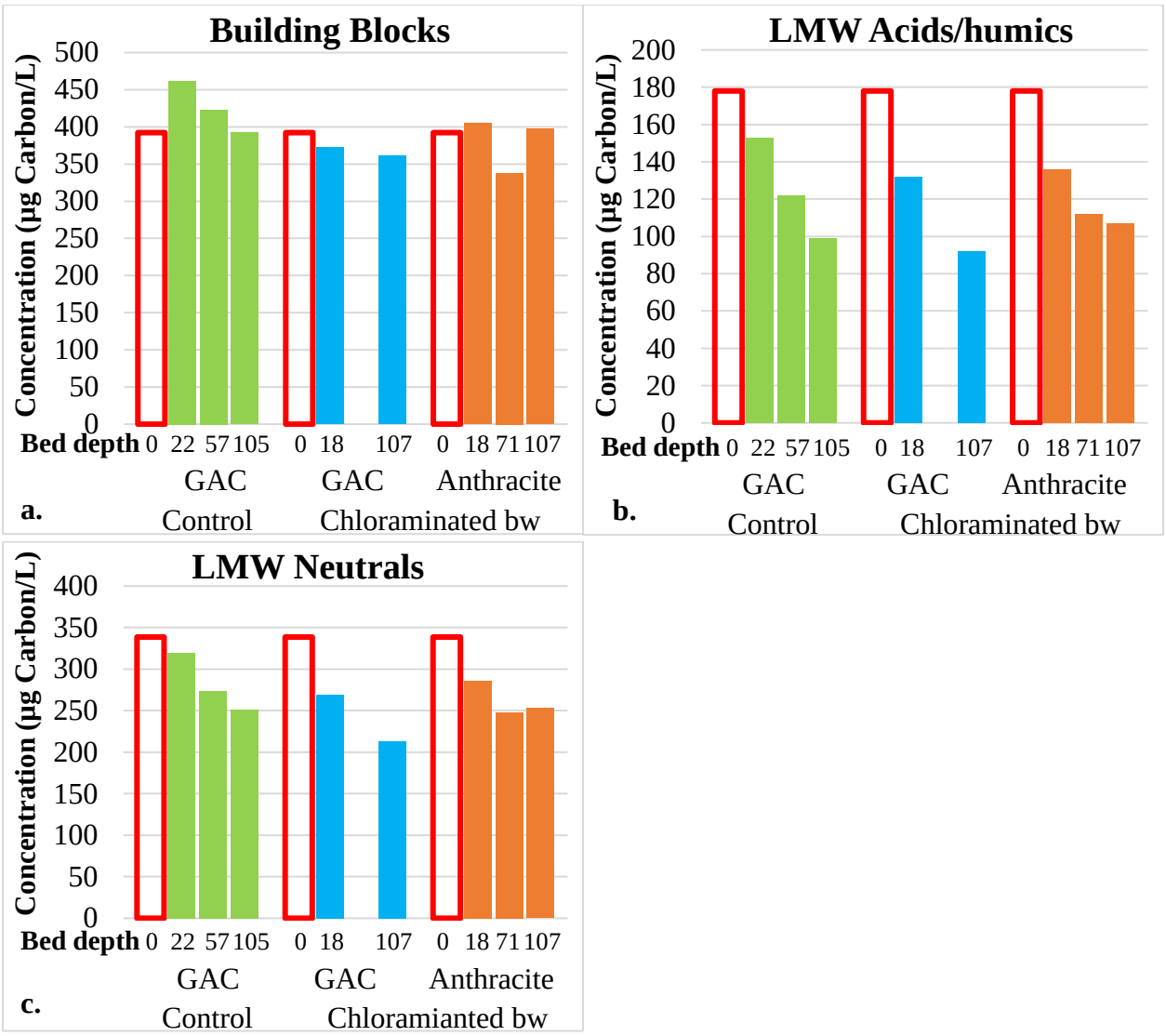

Figure B.6 NOM biofilter profile at Facility C on September 25th 2017 for the control column (nonchloraminated backwash), and the other two columns tested with chloraminated backwash analyzed by LC-OCD. Reporting organic carbon concentrations in a. BB, b. LMW acids/humics, and c. LMW Neutrals. Bed depth is given in cm.

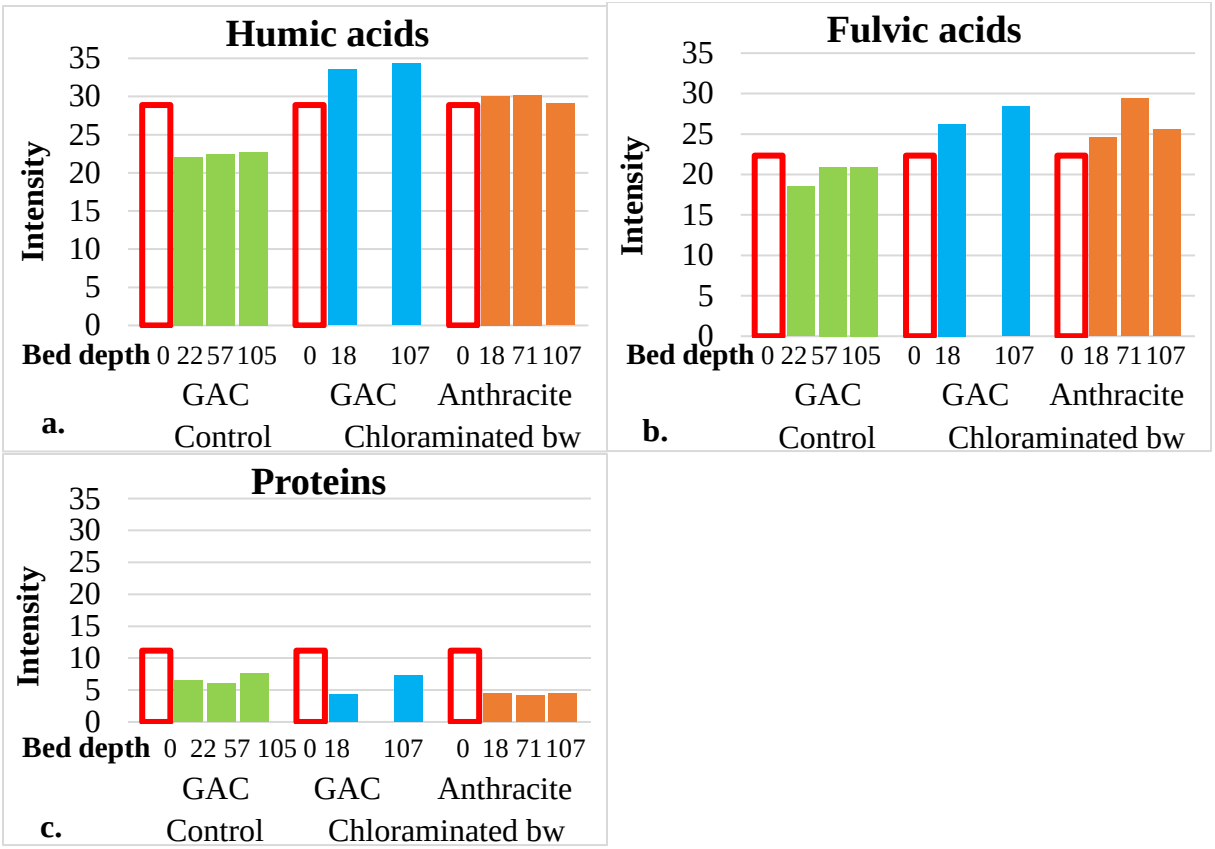

Figure B.7 NOM biofilter profile at Facility C on September 25th 2017 for the control column (nonchloraminated backwash), and the other two columns tested with chloraminated backwash analyzed by FEEM. Reporting intensities for a. HA, b. FA, and c. protein-like materials. Bed depth is given in cm.

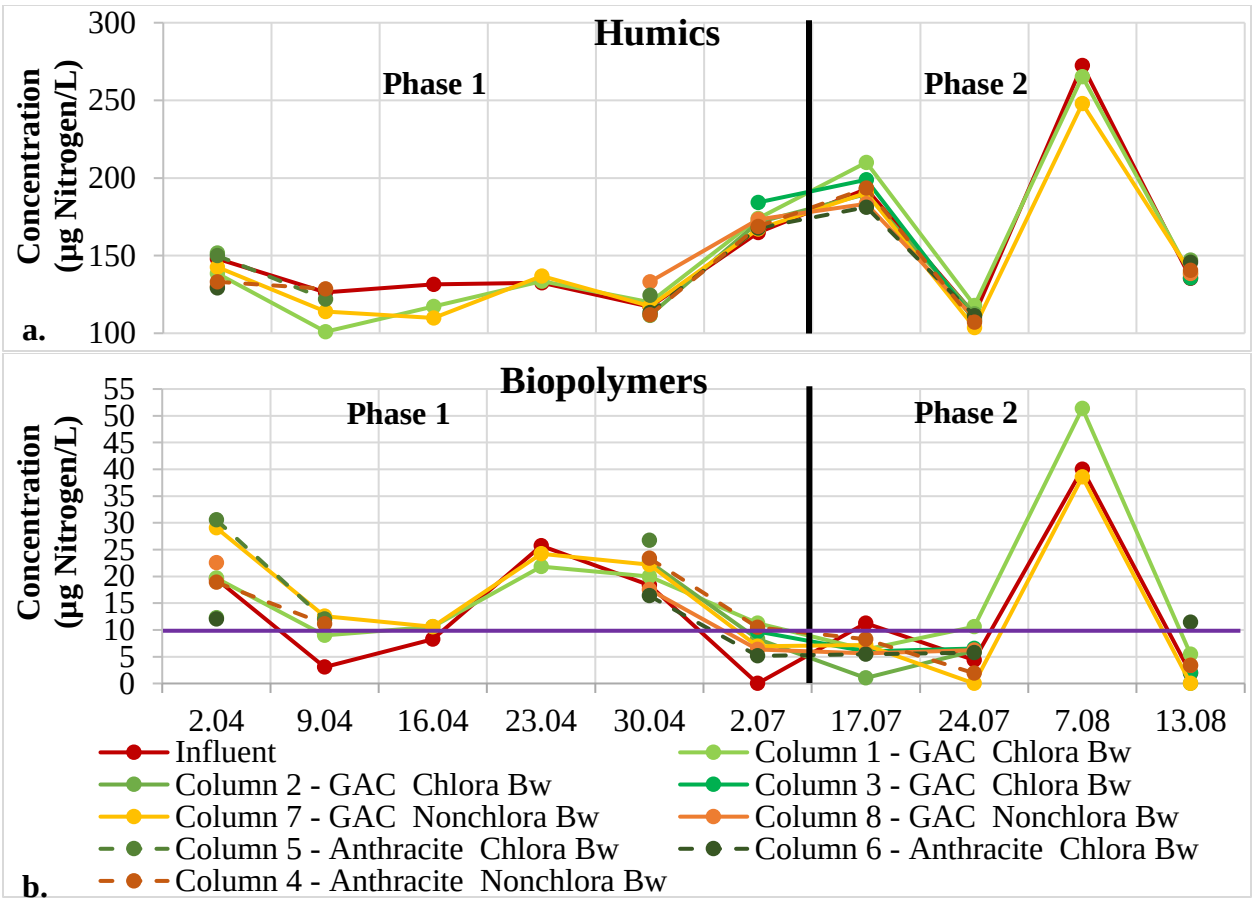

Figure B.8 NOM characterization of biofilter influent and effluents at Facility Q in 2018 analyzed by LC-OND. Reporting organic nitrogen concentration in a. HS, and b. BP. All columns were backwashed twice per week during phases 1 and 2, but during phase 2 columns 1, 2, 4, and 7 were backwashed daily. Chlora = Chloraminated, and Bw = Backwash. All datapoints below the horizontal purple line are below the methods detection limits.

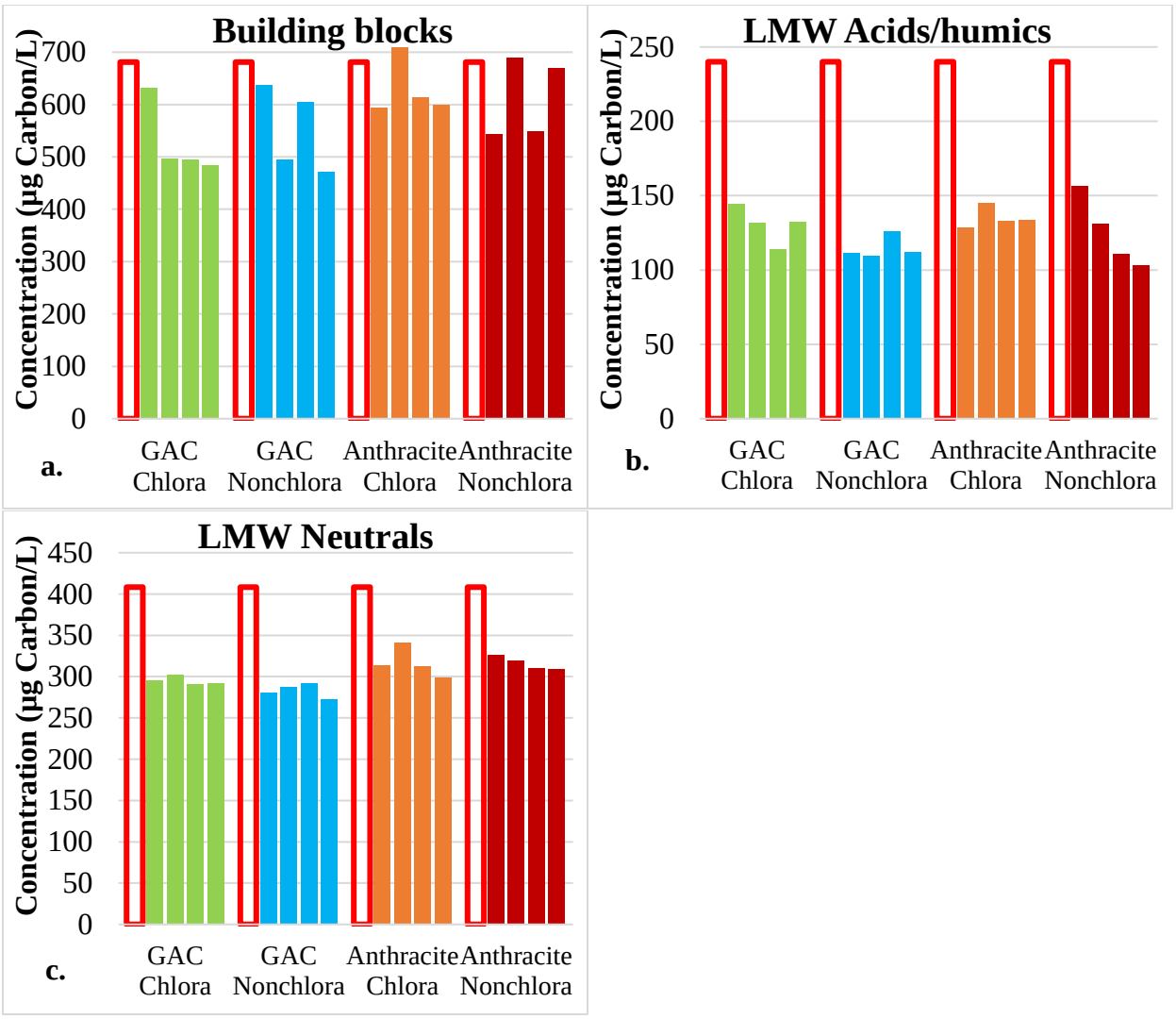

Figure B.9 NOM biofilter profiles at Facility Q phase 1 on April 30th 2018 analyzed by LC-OCD, reporting organic carbon concentrations in a. BB, b. LMW acids/humics, and c. LMW Neutrals. All columns had regular backwash frequency (twice per week). Chlora = Chloraminated, nonchlora = nonchloraminated.

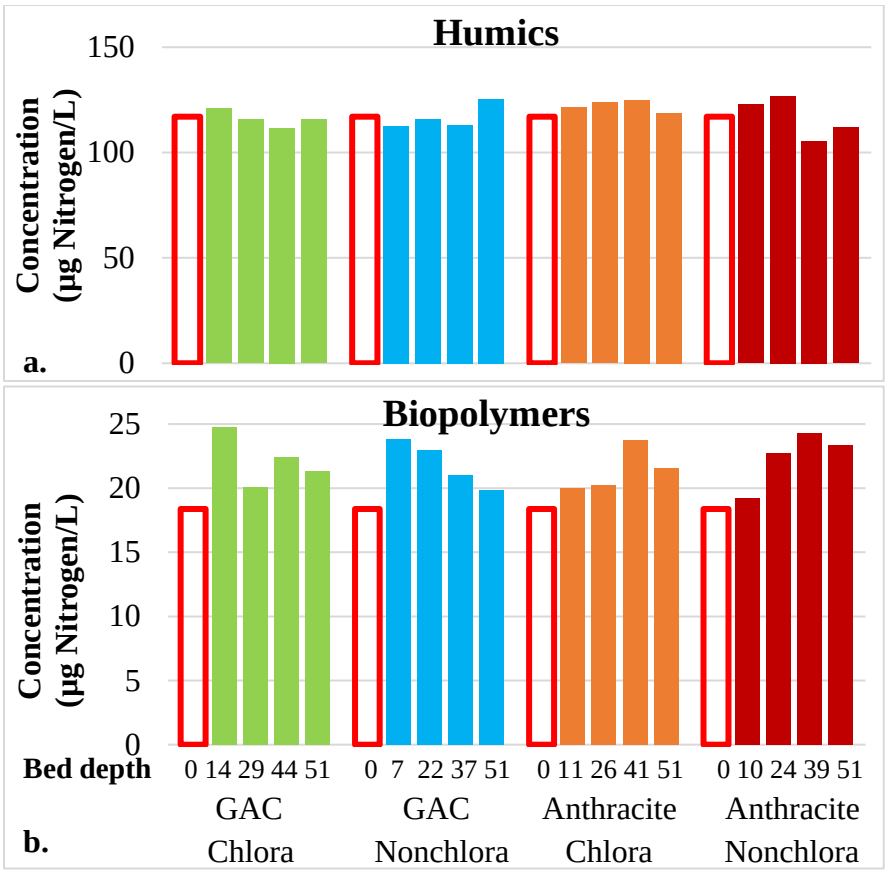

Figure B.10 NOM biofilter profiles at Facility Q phase 1 on April 30th 2018 analyzed by LC-OND, reporting organic nitrogen concentrations in a. HS, and b. BP. All columns had regular backwash frequency (twice per week), and bed depth is given in cm. Chlora = Chloraminated, nonchlora = nonchloraminated.

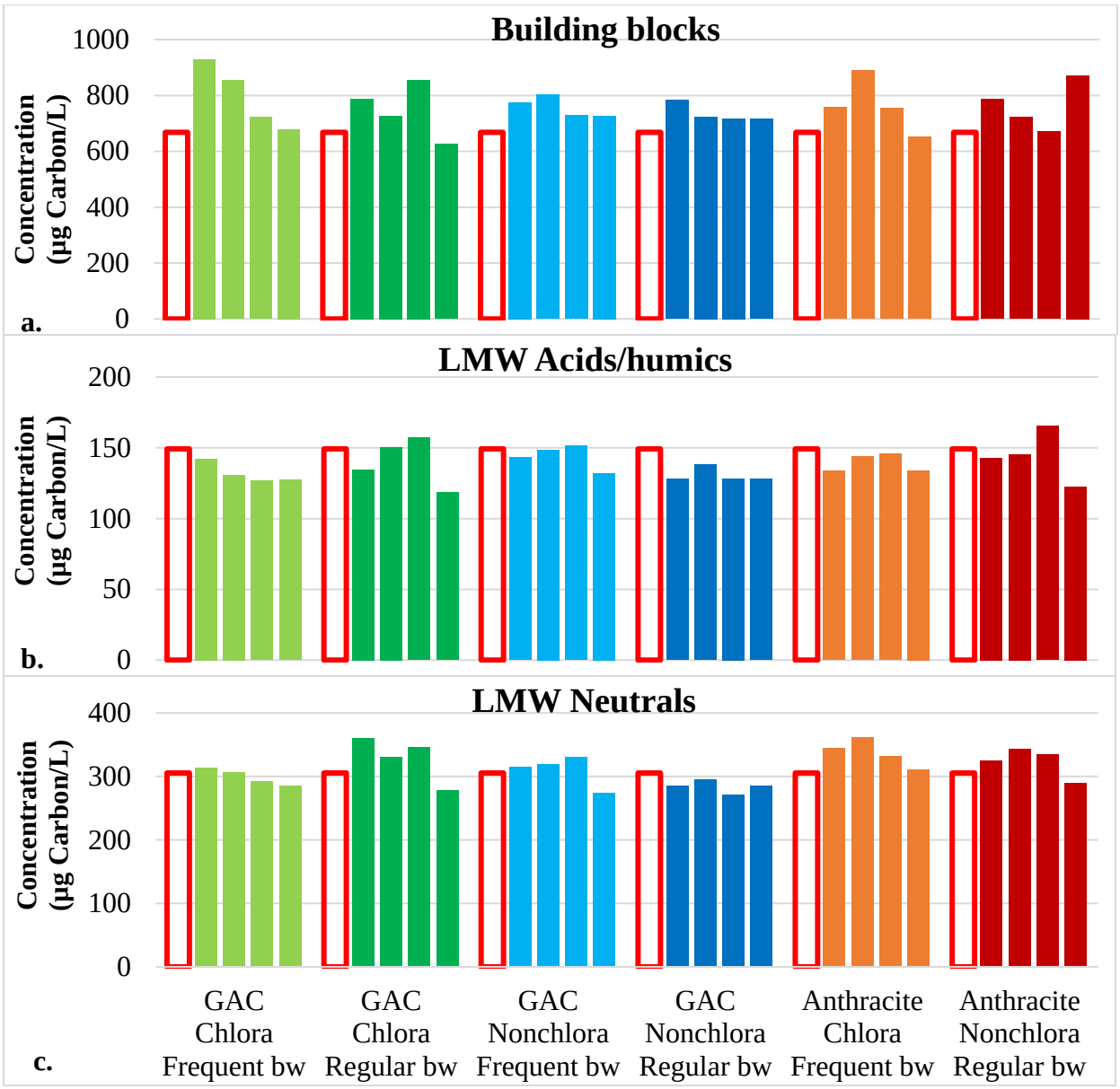

Figure B.11 NOM biofilter profiles at Facility Q phase 2 on August 13th 2018 analyzed by LC-OCD, reporting organic carbon concentrations in a. BB, b. LMW acids/humics, and c. LMW Neutrals. Bed depth is given in cm. Chlora = Chloraminated, nonchlora = nonchloraminated, bw = backwash.

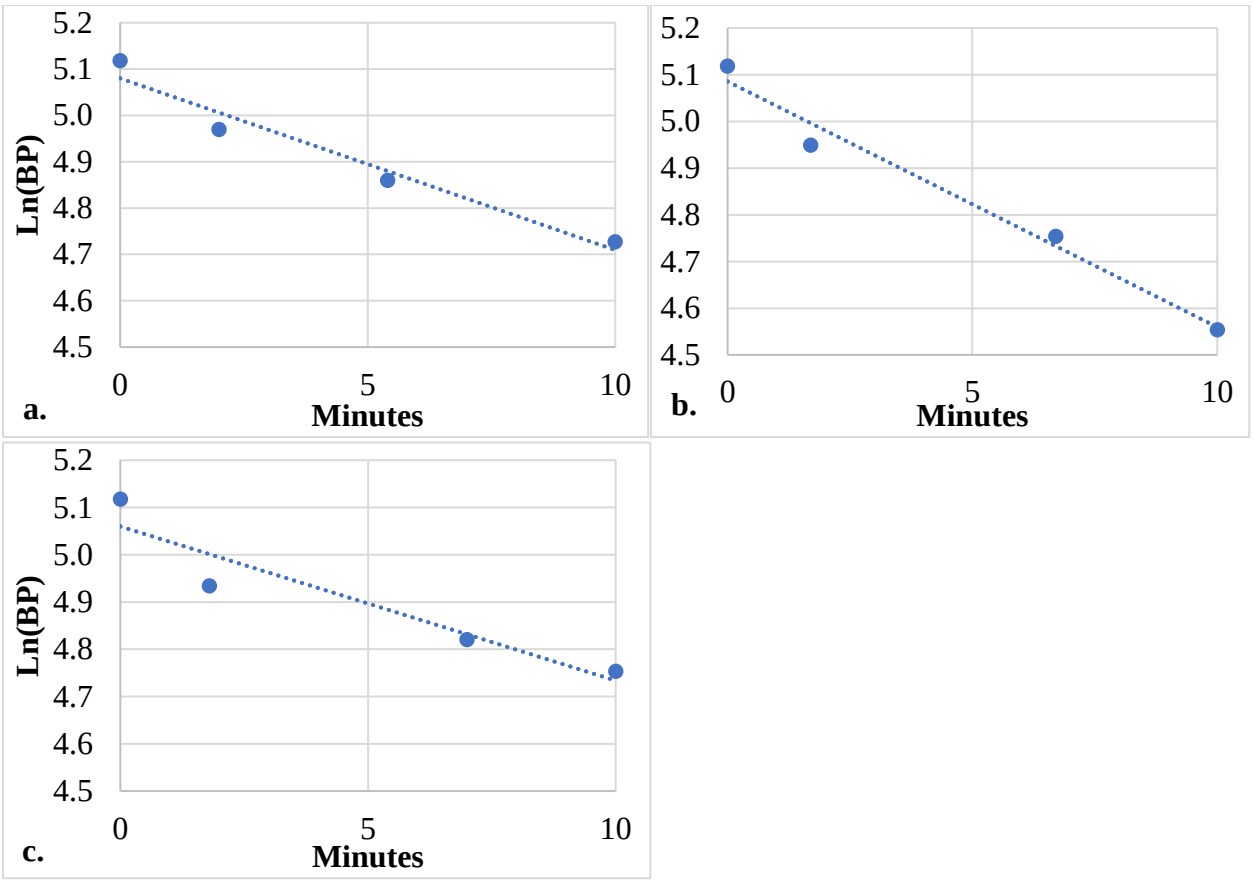

Figure B.12 1st order kinetic models for BP measured over the depth of the biofilters at Facility C during ammonia addition on August 15th 2017. A. is the control column (no ammonia addition), b. is the GAC column, and c. is the anthracite column.

Table B.1 Summary of reaction rate constants of zero- (m/min), first- (min^{-1}), and second- (1/(m·min)) order kinetic models for NOM fractions measured over the depth of the biofilters at Facility C during ammonia addition on August 15th 2017. A = acids/humics.

	Control			GAC			Anthracite		
	0	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**
DOC	75	0.023	7.0E-06	90	0.028	9.0E-06	61	0.018	5.0E-06
BP - OCD	5.1	0.037	3.0E-04	6.7	0.053	4.0E-04	4.5	0.033	2.0E-04
HS - OCD	62	0.041	3.0E-05	53	0.035	2.0E-05	47	0.030	2.0E-05
HS - OND	1.9	0.017	2.0E-04	2.9	0.028	3.0E-04	3.5	0.034	3.0E-04
LMW A - OCD	3.3	0.065	0.0013	3.0	0.055	0.0011	1.3	0.021	3.0E-04

Table B.2 Summary of reaction rate constants of zero- (m/min), first- (min^{-1}), and second- (1/(m·min)) order kinetic models for NOM fractions measured over the depth of the biofilters at Facility C during chloraminated backwash on September 25th 2017. A = acids/humics, and N = neutrals.

	Control			GAC			Anthracite		
	0	1	2	0	1	2	0	1	2
DOC	90	0.035	1.0E-05	99	0.040	2.0E-05	64	0.023	9.0E-06
BP - OCD	5.9	0.046	4.0E-04	9.1	0.085	8.0E-04	5.3	0.041	3.0E-04
HS - OCD	66	0.040	2.0E-05	70	0.042	3.0E-05	39	0.022	1.0E-05
HS - OND	3.7	0.031	3.0E-04	3.5	0.030	3.0E-04	2.3	0.018	1.0E-04
LMW A - OCD	7.8	0.058	5.0E-04	7.4	0.059	5.0E-04	6.4	0.047	4.0E-04
LMW N - OCD	9.0	0.031	1.0E-04	11	0.041	2.0E-04	8.0	0.028	1.0E-04

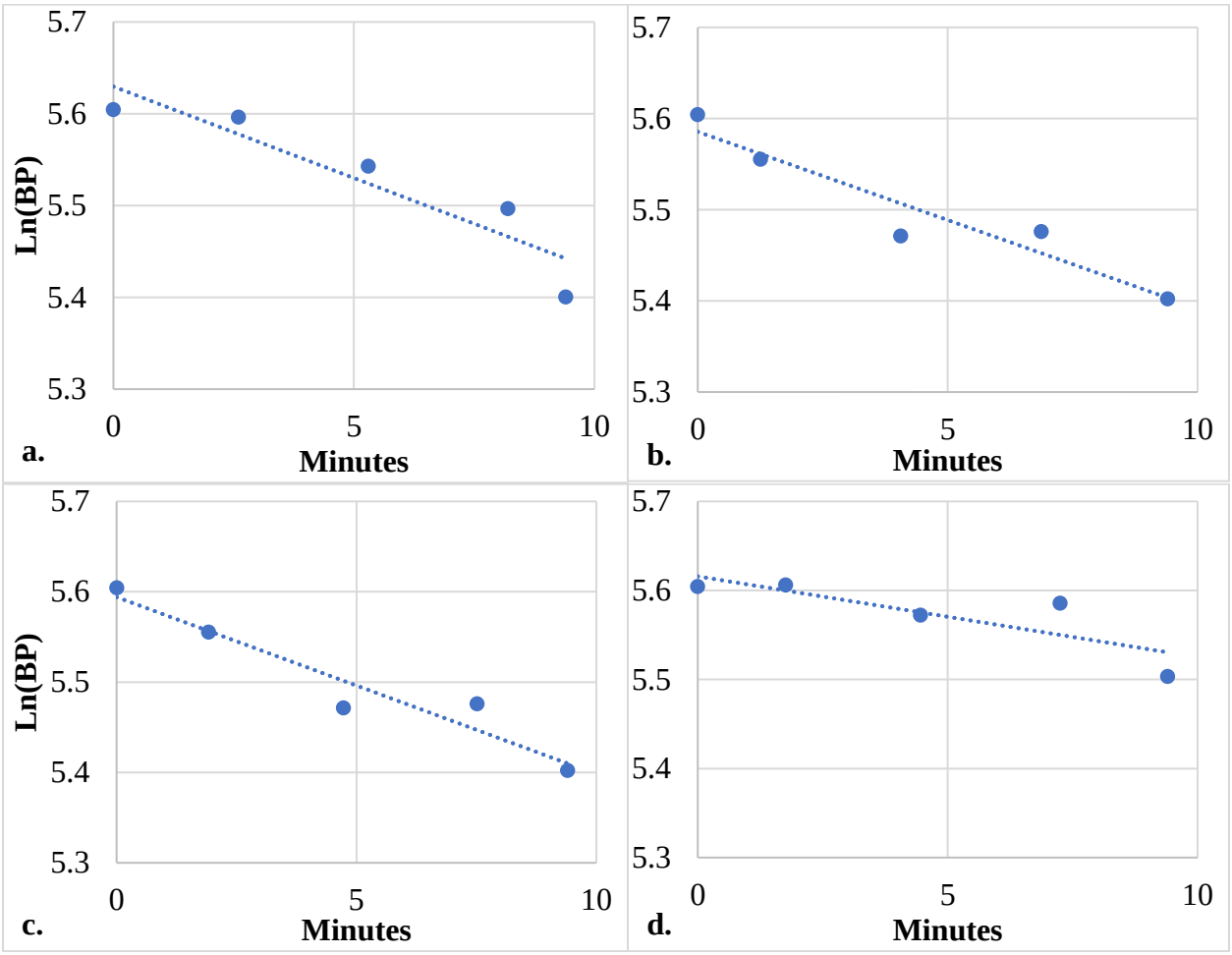

Figure B.13 1st order kinetic models for BP measured over the depth of the biofilters at Facility Q during phase 1 on April 30th 2018. A. is the GAC chloraminated column, b. is the GAC nonchloraminated column, c. is the anthracite chloraminated column, and d. is the anthracite nonchloraminated column.

Table B.3 Summary of R^2 coefficients of zero-, first-, and second-order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 1 on April 30th 2018. Chlora = chloraminated, A = acids/humics, and N = neutrals.

	GAC Chlora			GAC Nonchlora			Anthracite Chlora			Anthracite Nonchlora		
	0	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**
DOC	0.91	0.92	0.92	0.50	0.51	0.52	0.37	0.36	0.35	0.18	0.18	0.17
BP-OCD	0.87	0.86	0.84	0.90	0.91	0.92	0.92	0.92	0.92	0.70	0.69	0.68
HS-OCD	0.14	0.14	0.15	0.01	0.00	0.00	0.45	0.45	0.45	0.09	0.09	0.09
HS-OND	0.39	0.39	0.39	0.33	0.33	0.32	0.13	0.13	0.13	0.31	0.32	0.32
LMW A - OCD	0.67	0.70	0.72	0.35	0.33	0.30	0.44	0.43	0.42	0.80	0.88	0.95
LMW N - OCD	0.58	0.59	0.60	0.42	0.42	0.43	0.58	0.59	0.60	0.61	0.63	0.66

Table B.4 Summary of reaction rate constants of zero- (m/min), first- (min^{-1}), and second- (1/(m·min)) order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 1 on April 30th 2018. Chlora = chloraminated, A = acids/humics, and N = neutrals.

	GAC Chlora			GAC Nonchlora			Anthracite Chlora			Anthracite Nonchlora		
	0	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**
DOC	49	0.02	4.0E-06	46	0.01	4.0E-06	28	0.01	2.0E-06	14	0.00	1.0E-06
BP-OCD	5.0	0.02	8.0E-05	4.8	0.02	8.0E-05	4.8	0.02	8.0E-05	2.4	0.01	4.0E-05
HS-OCD	-5.4	0.00	-2.0E-06	1.1	0.00	3.0E-07	4.6	0.00	1.0E-06	-5.1	0.00	-1.0E-06
HS-OND	0.5	0.01	4.0E-05	-0.8	-0.01	-5.0E-05	-0.3	0.00	-2.0E-05	1.2	0.01	9.0E-05
LMW A - OCD	11	0.06	4.0E-04	8.5	0.05	3.0E-04	8.2	0.05	2.0E-04	13	0.08	6.0E-04
LMW N - OCD	10	0.03	8.0E-05	9.4	0.03	8.0E-05	8.7	0.03	7.0E-05	8.5	0.02	7.0E-05

Table B.5 Summary of R^2 coefficients of zero-, first-, and second-order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 2 on August 13th 2018. Chlora = chloraminated, bw = backwash, A = acids/humics, and N = neutrals.

	GAC Chlora Frequent bw			GAC Chlora Regular bw			GAC Nonchlora Frequent bw			GAC Nonchlora Regular bw		
	0	1	2	0	1	2	0	1	2	0	1	2
DOC	0.59	0.59	0.59	0.06	0.07	0.08	0.53	0.53	0.53	0.96	0.96	0.96
BP-OCD	0.51	0.49	0.48	0.57	0.83	0.56	0.44	0.46	0.48	0.51	0.59	0.66
HS-OCD	0.00	0.00	0.00	0.01	0.01	0.01	0.73	0.73	0.73	0.90	0.90	0.90
HS-OND	0.57	0.58	0.58	0.01	0.01	0.01	0.02	0.01	0.01	0.15	0.16	0.16
LMW A - OCD	0.93	0.93	0.94	0.09	0.11	0.13	0.25	0.27	0.28	0.39	0.39	0.38
LMW N - OCD	0.68	0.68	0.69	0.08	0.09	0.10	0.13	0.15	0.17	0.38	0.38	0.37

Table B.6 Summary of R^2 coefficients of zero-, first-, and second-order kinetics models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 2 on August 13th 2018. Chlora = chloraminated, bw = backwash, A = acids/humics, and N = neutrals.

	Anthracite Chlora Frequent bw			Anthracite Nonchlora Regular bw		
	0	1	2	0	1	2
DOC	0.11	0.12	0.13	0.20	0.21	0.21
BP - OCD	0.50	0.51	0.52	0.21	0.24	0.27
HS - OCD	0.01	0.01	0.01	0.46	0.46	0.46
HS - OND	0.17	0.19	0.20	0.42	0.42	0.42
LMW A - OCD	0.13	0.12	0.12	0.77	0.11	0.14
LMW N - OCD	0.01	0.01	0.01	0.01	0.00	0.00

Table B.7 Summary of reaction rate constants of zero- (m/min), first- (min^{-1}), and second- (1/(m·min)) order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 2 on August 13th 2018. Chlora = chloraminated, bw = backwash, A = acids/humics, and N = neutrals.

	GAC Chlora Frequent bw			GAC Chlora Regular bw			GAC Nonchlora Frequent bw			GAC Nonchlora Regular bw		
	0	1	2	0	1	2	0	1	2	0	1	2
DOC	24	0.01	2.0E-06	15	0.00	1.0E-06	26	0.01	2.0E-06	37	0.01	3.0E-06
BP-OCD	2.5	0.03	3.0E-04	3.8	0.05	3.0E-04	3.8	0.03	3.0E-04	6.8	0.05	4.0E-04
BP-OND	0.1	-0.01	-0.01	0.3	0.04	0.01	0.2	0.09	0.05	0.3	0.00	-0.01
HS-OCD	1.7	0.00	1.0E-07	2.1	0.00	3.0E-07	16	0.01	2.0E-06	19	0.01	3.0E-06
HS-OND	-1.0	-0.01	-5.0E-05	-0.3	0.00	-1.0E-05	0.2	0.00	8.0E-06	-0.3	0.00	-1.0E-05
LMW A - OCD	2.5	0.02	1.0E-04	1.2	0.01	8.0E-05	1.0	0.01	5.0E-05	1.5	0.01	8.0E-05
LMW N - OCD	2.5	0.01	3.0E-05	2.4	0.01	3.0E-05	2.1	0.01	3.0E-05	2.1	0.01	2.0E-05

Table B.8 Summary of reaction rate constants of zero- (m/min), first- (min^{-1}), and second- (1/(m·min)) order kinetic models for NOM fractions measured over the depth of the biofilters at Facility Q during phase 2 on August 13th 2018. Chlora = chloraminated, bw = backwash, A = acids/humics, and N = neutrals.

	Anthracite Chlora Frequent bw			Anthracite Nonchlora Regular bw		
	0	1	2	0	1	2
DOC	15.4	0.004	1.00E-06	14.2	0.004	1.00E-06
BP - OCD	2.48	0.020	2.00E-04	2.13	0.002	2.00E-04
HS - OCD	1.60	0.001	2.00E-07	19.6	0.008	3.00E-06
HS - OND	-0.93	-0.007	-5.00E-05	-0.56	-0.004	-3.00E-05
LMW A - OCD	0.65	0.005	3.00E-05	1.11	0.009	7.00E-05
LMW N - OCD	0.53	0.002	4.00E-06	0.41	0.001	3.00E-06

Appendix C

Additional Data for Correlation between NDMA UFC and NOM Fractions

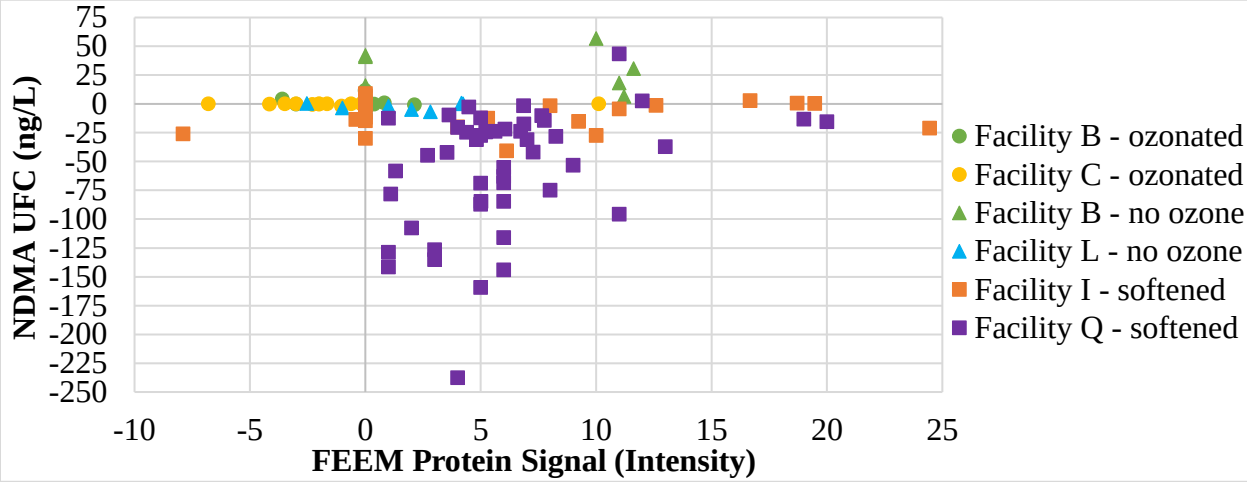

Figure C.1 Relationship between changes in FEEM Protein-like materials intensities across the biofilters and changes in NDMA Precursor concentrations across the biofilters for all bench- and pilot-scale experiments. Ozonated, no ozone, and softened refers to upstream processes prior to biofiltration.

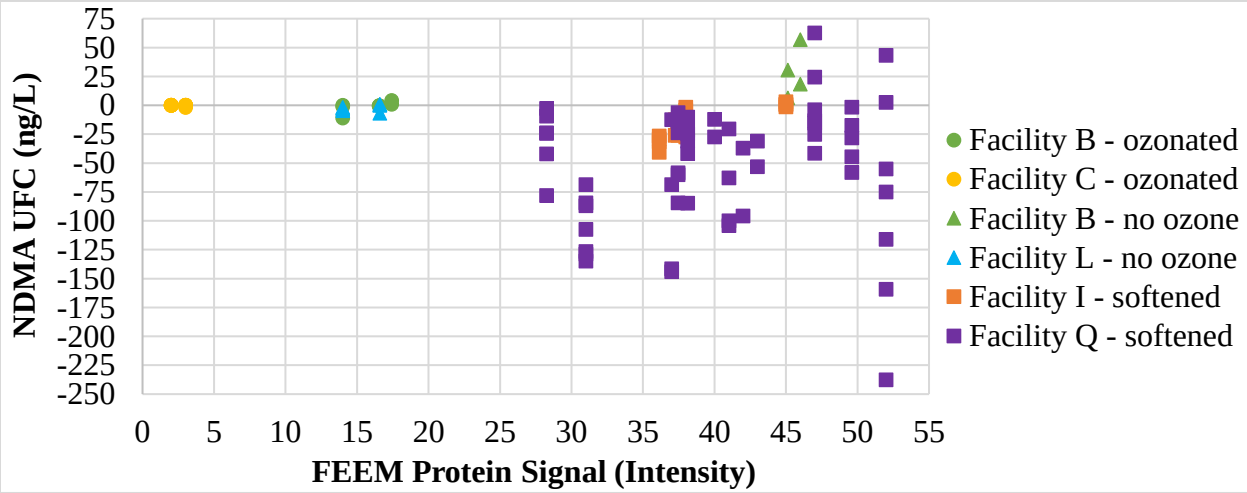

Figure C.2 Relationship between FEEM Protein-like materials intensities in biofilter influents and changes in NDMA Precursor concentrations across the biofilters for all bench- and pilot-scale experiments. Ozonated, no ozone, and softened refers to upstream processes prior to biofiltration.

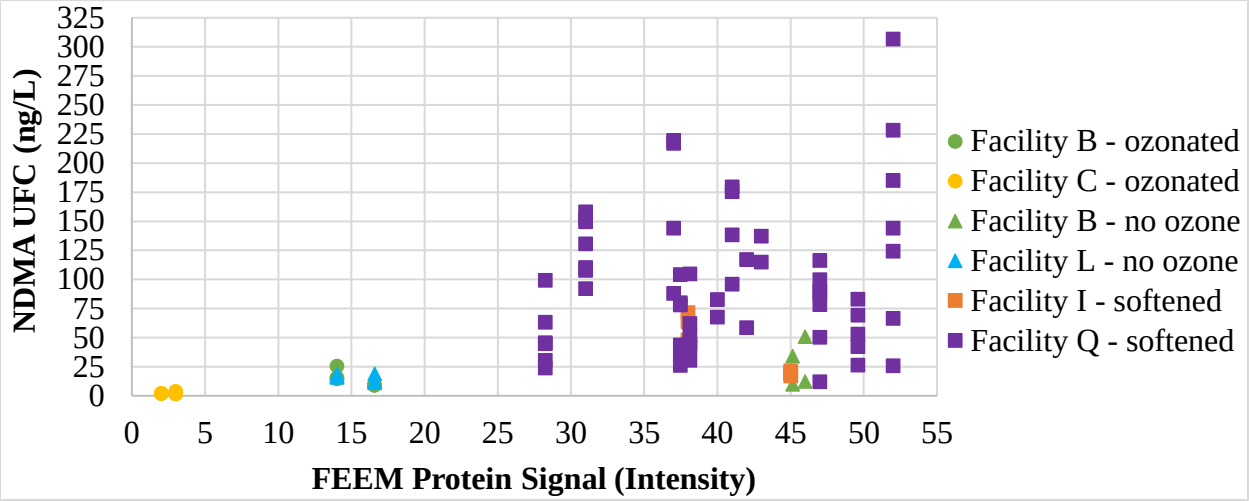

Figure C.3 Relationship between FEEM Protein-like materials intensities in biofilter influents and NDMA Precursor concentrations in the biofilter effluents for all bench- and pilot-scale experiments. Ozonated, no ozone, and softened refers to upstream processes prior to biofiltration.