CONTROLLING DISINFECTION BY-PRODUCT FORMATION WITH GAC ADSORPTION AND POTENTIAL ROLE FOR UV-LEDS WITH CHLORINE

by

Xuedongzi Jiang

Submitted in partial fulfillment of the requirements
for the degree of Master of Applied Science

at

Dalhousie University
Halifax, Nova Scotia
November 2023

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The J. Douglas Kline Water Supply Plant (JDKWSP) is one of the main drinking water facilities in Halifax, Nova Scotia. The treatment process of JDKWSP is characterized by direct anthracite-sand filtration and chlorine disinfection. Natural organic matter (NOM) as one of the components impacting water quality has increased in Pockwock Lake, the water source of JDKWSP. Increasing NOM has required higher alum doses and higher chlorine demand, which shortens filtration efficiency and tends to produce more disinfection by-products (DBPs) in drinking water. The Centre for Water Resources Studies (CWRS) operates a pilot plant at JDKWSP for optimizing the treatment processes, where sedimentation was added followed by three parallel filters, the first being anthracite sand to mimic the full-scale facility. This study looked at using Granular Activated Carbon (GAC) applied in two of the pilot-scale filters for increasing the NOM removal rate and minimizing DBP formation. Specifically, the full-scale filtered water and pilot-scale filtered waters that were filtered by these three filters were analyzed for exploring the effect of sedimentation and GAC adsorption on NOM removal and DBP formation.

Ultraviolet light emitting diode (UV LED) disinfection was also investigated as a potential full-scale disinfection technology and was compared to current plant conditions using chlorine. DBP formation potential of THMs and HAAs was measured for UV exposed, chlorine exposed, and UV + chlorine exposed to understand the impact that UV disinfection has on mitigating DBP formation. UV Fluences of 20, 40, and 80 mJ /cm^2 were used to characterize the optimal conditions for the Pockwock Lake water matrix.

This study identified that GAC filters were able to remove DBP precursor material and reduce DBP formation. Sedimentation did not help to remove NOM and lower DBP formation potential, but it can improve filtration efficiency and increase filter run times. Additionally, the UV fluences and the sequence of UV LED and chlorine did not significantly impact the formation of trihalomethanes (THMs) and haloacetic acids (HAAs).

LIST OF ABBREVIATIONS AND SYMBOLS USED

JDKWSP – J. Douglas Kline Water Supply Plant

FSP – Full-Scale Plant

AC – Activated carbon

GAC – Granular Activated Carbon

PAC – Powdered activated carbon

T&O – Taste and odor

DBP – Disinfection by-product

FAC – Free available chlorine

DWT – Drinking water treatment

ANC – Acid neutralization capacity

DNA – Deoxyribonucleic acid

RNA – Ribonucleic acid

ES – Effective size

EBCT – Empty bed contact time

BV – Bed volumes

UF – Ultrafiltration

NF – Nanofiltration

Ant-Sand – Anthracite-Sand

GAC-Ant-Sand (GAC-Cap) – GAC-Anthracite-Sand

UV_{254} – The ultraviolet absorbance of water at a UV wavelength of 254 nanometers (nm)

AOPs – Advanced Oxidation Processes

RCS – Reactive chlorine species

Cl-DBP – Chlorinated disinfection DBP

DBPFP – Disinfection By-product Formation Potential

UV-Vis Abs – UV-visible absorbance

EEM – Excitation-emission matrix

FEEM – Fluorescence excitation-emission matrices

Ex – Excitation spectra

Em – Emission spectra

PCA – Principal component analysis

FRI – Fluorescence regional integration

HAA – Haloacetic acid

THAA – Total haloacetic acid

MCA (CH_2ClCO_2H) – Monochloroacetic Acid

MBA (CH_2BrCO_2H) – Monobromoacetic Acid

BrAA – Bromoacetic acid

ClAA – Chloroacetic acid

$Br_2AA/DBA/Br_2CHCO_2H$ – Dibromoacetic acid

$Cl_2AA/DCA/CHCl_2CO_2H$ – Dichloroacetic acid

Br_3AA – Tribromoacetic acid

$Cl_3AA/TCA/CCl_3CO_2H$ – Trichloroacetic acid

BrClAA – Bromochloroacetic acid

$BrCl_2AA$ – Bromodichloroacetic acid

Br_2ClAA – Chlorodibromoacetic acid

THM – Trihalomethane

TTHM – Total trihalomethane

$CHCl_3$ – Chloroform

$CHCl_2Br$ – Bromodichloromethane

$CHBr_2Cl$ – Chlorodibromomethane

$CHBr_3$ – Bromoform

NDMA – N-Nitroso dimethylamine

NOM – Natural organic matter

TOC – Total organic carbon

DOC – Dissolved organic carbon

Alum – Aluminum sulfate

$KMnO_4$ – Potassium permanganate

UFC – Uniform formation condition

SDS – Simulated distribution system

FP – Formation potential

DOM – Dissolved organic matter

POM – Particulate organic matter

COM – Colloidal organic matter

AOM – Algal organic matter

UV LED – Ultraviolet light emitting diode

LP – Low pressure

MP – Medium pressure

Cl_2 – Chlorine

USEPA – U.S. Environmental Protection Agency

MAC – Maximum acceptable concentration

SUVA – Specific ultraviolet absorbance

H_2SO_4 – Sulfuric acid

NaOH – Sodium hydroxide

Na_2SO_4 – Sodium sulfate

MTBE – Methyl tert butyl ether

g/L – Gram per liter

mg/L – Milligram per liter

µg/L – Microgram per liter

cm – centimeter

mm – millimeter

µm – micrometer

mL/min – milliliter per minute

V – Volt

nA – Nanoampere

µs – Microsecond

NTU – Nephelometric Turbidity Unit

CDWQG – Canadian drinking water quality guidelines

ECD – Electron capture detector

NDIR – Non-dispersive infrared detector

GC – Gas Chromatograph

HPLC – High-performance liquid chromatography

pCBA – Para-chlorobenzoic acid

ACKNOWLEDGEMENTS

First and foremost, I would like to give my sincerest gratitude to my research supervisor Dr. Graham Gagnon for giving me guidance, support, inspiration, and encouragement throughout my graduate studies. I would also like to thank him for giving me the opportunity to present my research at various conferences.

I would also like to thank Dr. Adam Donaldson and Dr. Margaret Walsh for joining my supervisory committee and for reviewing my thesis.

To my awesome colleagues at the Centre for Water Resources Studies (CWRS), including Lindsay Anderson, Sean MacIsaac, Jessica Bennett, Paul Bjorndahl, Benjemin Trueman and all the other peers, thank you for your unwavering support and invaluable help. I wish to express a special appreciation to Heather Daurie for her helpfulness and laboratory expertise. Her patience and technical support have contributed to the success of my research.

I would also like to acknowledge the financial support from the Natural Science and Engineering Research Council (NSERC) /Halifax Water Industrial Research Chair (IRC) program and its partners.

Last but not least, I would like to extend my deepest gratitude to my parents and my boyfriend for their love and encouragement in these past two years. Thanks to my parents for their lifelong support and unwavering presence since my birth. To my boyfriend, thank you for your remote companionship and thoughtful care.

CHAPTER 1 Introduction

1.1 Research rationale

There are many different components that impact water quality, one of them being natural organic matter (NOM). NOM is generated by the degradation of plant and animal matter in freshwater or the surrounding ecosystem (Alomar et al., 2023), which is a group of extremely varied compounds, whose composition is governed by climate, temperature, and many other factors (Bhatnagar & Sillanpää, 2017; Fabris et al., 2008). It is challenging to measure the exact amount of NOM directly given the complexity and variety of compounds that may be present in a given water sample. Instead, total organic matter (TOC), dissolved organic matter (DOC), and UV-visible (UV-Vis) absorbance are the parameters used to characterize NOM in water (Barceló, 2012). Climate change, temperature, and human activities impact algal activity and NOM levels in freshwater (Delpla et al., 2009). In recent decades, increasing amounts of total NOM have been observed worldwide, and locally in most areas of Atlantic Canada(Anderson et al., 2017; Eikebrokk et al., 2004).

Coagulation & flocculation is a conventional process used for removing particulate and colloidal substances from water. In this process, the hydrophobic NOM is removed while the dissolved portion, dissolved organic matter (DOM), remains in the water, and can later interact with the disinfection stage of the drinking water process (Matilainen et al., 2011). In the disinfection stage, one of the most predominant and efficient types of disinfectant is chlorine, which is measured as free available chlorine (FAC) (Mazhar et al., 2020). Chlorine can efficiently inactivate most bacteria and pathogens to lower the transmission

of waterborne diseases, while reacting with DOM to generate disinfectant byproducts (DBPs) (Ang et al., 2015; Chaukura et al., 2020). DBPs are the main drawback of chlorine disinfection, since they are mutagenic, cytotoxic, genotoxic, and carcinogenic (H. Chen et al., 2019; Omar et al., 2023). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two main types of DBPs (Health Canada, 2014). Due to the health concern, many countries have developed a regulated concentration limit for THMs and HAAs in drinking water. Health Canada regulates the maximum acceptable concentration (MAC) of 100 μg/L for THMs and 80 μg/L for HAAs (Health Canada, 2014).

With increasing NOM in source water, there are more DBPs formed during chlorine disinfection. Some studies have indicated that NOM can be considered the main component of DBP precursors in drinking water (Hua & Reckhow, 2007). Thus, the optimization of NOM removal and disinfection processes has been brought to the forefront. Several methods can be used to remove NOMs, such as Granular Activated Carbon (GAC), membrane filtration, and ion exchange (Levchuk et al., 2018; Yuan et al., 2022; Zazouli & Kalankesh, 2017). GAC for drinking water treatment is featured with cost-effectiveness and a small environmental footprint (Kim & Kang, 2008). In this study, GAC was used as a filter media to remove NOM. As well, ultraviolet light-emitting diodes (UV LEDs) have become one of the emerging disinfection options in water treatment plants (Dotson et al., 2012; Hull et al., 2019). UV LEDs can be combined with other disinfectants (e.g., chlorine) to enhance disinfection efficiency and lower DBP formation. Some studies have observed the combination of UV and chlorine to be more efficient in disinfection than applying only UV or chlorine disinfection (Shang et al., 2007; Zyara et al., 2016).

1.2 Research Objectives

With increasing NOM in Pockwock Lake, in Halifax, GAC filtration and UV LEDs disinfection were selected to evaluate for ability to reduce DBP formation at J. Douglas Kline Water Supply Plant (JDKWSP). The main objectives of this research are described below:

1) Evaluate the impact of implementing GAC filtration on DBP formation at the pilot-scale plant.
2) Explore the effect of UV LEDs disinfection, chlorination, and their combination on DBP formation for the JDK treated water matrix.

To achieve the above objectives, the experiments were designed and conducted in three parts:

- Conduct the uniform formation condition (UFC) test to compare the DBP formation for different pilot-scale filters.
- Radiate filtered waters with different UV fluences to observe the impact of different UV doses on DBP formation.
- Perform the combined disinfection with UV LEDs and chlorine in different sequences on filtered waters.
- Determine the effect of UV LEDs/chlorine sequence on DBP formation.

1.3 Organization of Thesis

This thesis consists of five chapters. Chapter 2 provides a literature review on relevant topics including NOM, DBP, GAC, UV LEDs, and UFC test. In Chapter 3, experiment materials and methods used throughout this study are presented. Chapter 4 is comprised of two parts where the first part describes the performance of different filters at the pilot-scale plant on NOM removal. The other part shows the effect of UV LED disinfection and chlorination on DBP formation under different conditions. Chapter 5 summarizes the conclusions of this research and states the recommendations for future research.

CHAPTER 2 Literature Review

This chapter outlines the source of DBP formation, the technologies for reducing DBP precursors, the emerging UV LED technologies in the drinking water disinfection process, and the measurement of DBP formation potential.

Chlorine as one of the most common disinfection technologies in drinking water treatment (DWT) is characterized by high disinfection efficiency (Xu et al., 2023). The formation of chlorinated DBPs is considered the main disadvantage of chlorine disinfection (Omar et al., 2023). While, the occurrence of DBPs is not only contributed by the disinfection agents (especially chlorine) but also led by water quality (Gilca et al., 2020). The formation of DBPs will be introduced in this chapter. Activated carbon (AC) is capable of adsorbing organic matter from water and is also outlined in this chapter as a treatment method for removing DBP precursors from drinking water. This chapter also details the UV LED technologies, an emerging disinfection method, which is derived from conventional UV disinfection with high disinfection efficiency.

2.1 Natural organic matter

NOM is a complex mixture of organic compounds, which is mainly derived from biological degradation, such as decaying plant material, microbial activity, and terrestrial vegetation, and may also be caused by human activities (Sillanpää et al., 2018). NOM commonly presents in all natural water bodies, especially surface waters, as a result of the interactions between the hydrologic cycle and the biosphere and geosphere (Bhatnagar & Sillanpää,

2017). Figure 1 demonstrates the main NOM sources of the surface water bodies. Dissolved organic carbon (DOC) shown in this figure is defined as the portion of organic carbon that can pass through a filter with 0.45 micrometer (μm) of pore size (Zsolnay, 2003), which is one of the most commonly-used parameters to quantify NOM, which has been found relevant to the lake recovery in previous studies (Monteith et al., 2007).

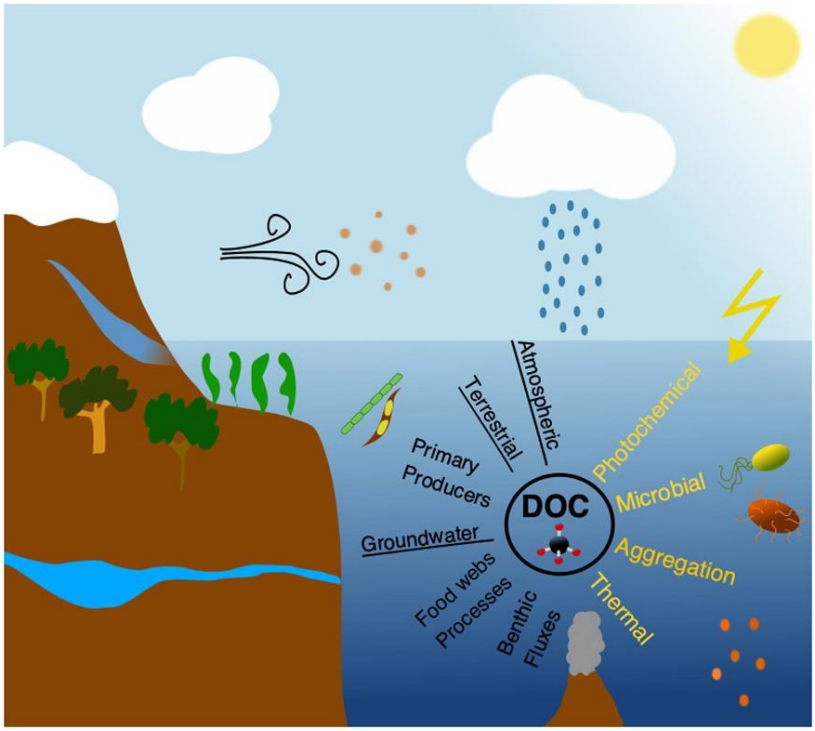

Figure 1. A simplified view of the DOC sources of natural water bodies (Lønborg et al., 2020).

NOM consists of a wide variety of compounds with various physical and chemical characteristics. NOM is commonly classified into three groups of organic matter: dissolved organic matter (DOM), particulate organic matter (POM), and colloidal organic matter (COM) (Newcombe & Dixon, 2006). NOM consists of both hydrophilic and hydrophobic components (Matilainen et al., 2011). Characterized by a high percentage of aliphatic

carbon and nitrogenous compounds, hydrophilic NOM has a strong affinity for water. Humic acids (HAs), proteins, amino acids, and carbohydrates all contribute to hydrophilic NOM (Matilainen et al., 2011). Many studies have shown the presence of HAs in natural water bodies is related to the precursors of disinfection by-products (DBPs) and contributes to their formation in the chlorination process of drinking water treatment (Ang et al., 2015a; Rizzo et al., 2008). Hydrophobic NOM tends to be more insoluble and can exhibit characteristics of organic compounds that repel water. It is worth noting that the composition and concentration of NOM can greatly vary depending on the climate, geology, human activity, and other factors (Fabris et al., 2008).

NOM can contribute to color, odor, and taste issues in drinking water sources and can also increase the demand for coagulants and disinfectants, which can have an adverse effect on drinking water processes (Jacangelo et al., 1995; Yan et al., 2008). Reductions in harmful aerosols over the last few decades have resulted in reductions in acid rain events at national and regional scales, which results in surface waters recovering from acidification since the 1980s (Driscoll et al., 1998; Shannon, 1999; Skjelkvåle et al., 1998). Lake recovery usually comes with increasing acid neutralization capacity (ANC) and alkalinity, and has been demonstrated as a leading cause of NOM increases (Anderson et al., 2017). Increasing NOM in source water represents increasing DBP formation potential in disinfection treatment. Several conventional and advanced treatment techniques have been applied in drinking water treatment processes to remove NOM and improve drinking water treatment efficiency.

1) Coagulation & flocculation: this is one of the most conventional treatment methods no matter in drinking water or wastewater treatment, which can remove most of NOM except the hydrophilic, low molecular weight fractions of NOM (Jacangelo et al., 1995; Matilainen et al., 2010).

2) Activated carbon adsorption: adsorption by activated carbon is a prevailing treatment method for removing dissolved organic matter from water. Especially for removing DBP and its precursors, GAC is considered an optimal technology (Jacangelo et al., 1995).

3) Membrane filtration: depending on the membrane pore size and membrane types, the contaminants removed by membrane processes are different. Microfiltration, Ultrafiltration (UF), and Nanofiltration (NF) are three membrane filtration processes helping water treatment and purification at water plants (AWWA Membrane Technology Research Committee, 1998). NF has been found suitable for removing hardness and color, which is also capable of reducing organic compounds and DBP precursors, but with fouling concerns (Ang et al., 2015; Fu et al., 1994)

4) Advanced Oxidation Processes (AOPs): AOPs involve the application of ultraviolet (UV) radiation and powerful oxidants, including ozone, hydrogen peroxide, chlorine, etc. to generate reactive radicals for degrading organic matter in water (Miklos et al., 2018). The combination of UV and chlorine (UV & Cl) has been developed as one of the emerging technologies of AOPs. During UV & Cl AOP process, chlorine is radiated by UV to produce hydroxyl radicals, and chlorine atom

radicals, and furtherly generate secondary reactive chlorine species (RCS) as well. Radicals can degrade organic compounds efficiently and reduce DBP formation in the disinfection stage (Yeom et al., 2021).

2.2 Disinfection by-product (DBP)

2.2.1 DBP Formation Mechanisms

There are several commonly used disinfectants (chlorine, ozone, chlorine dioxide, and chloramines) applied in drinking water treatment. Chlorine is one of the most widely used disinfectants in water treatment, which is featured with outstanding oxidizing potential, cost-effectiveness, residual protection, easy application, and many other advantages. Chlorine residual can protect water against recontamination from microorganisms in the distribution system (Gopal et al., 2007). However, it is inevitable for chlorination to generate DBP by reacting with disinfection precursors in water, which has been the main concern of chlorine disinfection (Grünwald et al., 2002; Singer, 1994). Disinfection precursors consist of many substances, including NOM (e.g. humic and fulvic acids), algal organic matter (AOM) (Goslan et al., 2017; Stevens et al., 1976), anthropogenic contaminants (e.g. pharmaceuticals, pesticides, detergents, etc.), free bromine, iodine, and nitrogen existing in the source water (Alexandrou et al., 2018). With varying water quality and DWT conditions (disinfectant dosage, temperature, pH, and contact time), DBPs are formed as extremely complex compounds, which are genotoxic, cytotoxic, and developmentally toxic (Li & Mitch, 2018).

2.2.2 Regulated DBPs

Over 600 types of DBP have been found in studies, while only a very small portion of them has been quantified in drinking waters, such as trihalomethanes (THMs), haloacetic acids (HAAs), organic halides (Krasner et al., 2006; Lavonen et al., 2013). Chlorinated disinfection DBP (Cl-DBP) is the most common group of DBPs. Brominated and iodinated DBPs can also form when present in source waters (Sharma et al., 2017). Many studies have reported DBPs can be harmful to community health and even causes cancer and other health concerns (Boorman, 1999; Chen et al., 2019; Hrudey, 2009). For public safety and health, many developed countries have set corresponding regulations to limit DBPs' noxious effects (Alver et al., 2018). However, there are still some lesser-known and unregulated DBPs, which may have very complex forms and low concentrations (Y. Li et al., 2015).

2.2.2.1 Trihalomethanes (THMs)

THMs are halogen-substituted single-carbon compounds, which can be formed by chlorine, bromine, fluorine, and iodine. While chlorinated THMs are the most common types (Adin et al., 1991; Brown et al., 2011). Some studies have found a relationship between THM formation and hydrophobic fraction (Kim & Yu, 2005; Yee et al., 2009). Thus, humic acids are considered the main fraction of NOM-generating THMs during disinfection treatment (Kim & Yu, 2005). Currently, four THMs are regulated in most of drinking water guidelines. Their names and chemical formulas are listed in Table 1. All of the regulated

DBPs are harmful to the liver, kidneys, and colon (Health Canada, 2014). Moreover, chloroform is considered a possible carcinogen (Health Canada, 2014).

Table 1. Names and chemical formulas of regulated THMs (Health Canada, 2014)

Disinfection By-products (DBPs)		***Chemical Formula***
Trihalomethanes (THMs)	Chloroform	$CHCl_3$
	Bromodichloromethane	$CHCl_2Br$
	chlorodibromomethane	$CHBr_2Cl$
	Bromoform	$CHBr_3$

In disinfected drinking water, THMs account for the majority of total DBPs, which also were the first group of synthetic compounds defined as the by-product of chlorination (Boorman, 1999; J. He et al., 2020; Marais et al., 2019). The maximum acceptable concentration (MAC) of THMs is regulated by Health Canada as 100 μg/L (Health Canada, 2014). The United States Environmental Protection Agency (USEPA) sets a more stringent limit for DBPs, with a maximum contaminant level (MCL) of 80 μg/L for THMs (US EPA, 2015).

2.2.2.2 Haloacetic acids (HAAs)

There are five regulated HAAs listed below according to the Guidelines for Canadian Drinking Water Quality (Health Canada, 2014). Those HAAs are DBPs of the disinfection process with chlorine. They are considered harmful to human health and potentially lead to cancers (Health Canada, 2014). The maximum acceptable concentration (MAC) of HAAs is regulated by Health Canada as 80 μg/L (Health Canada, 2014). A more stringent

limit for HAAs has been set by USEPA, with a maximum contaminant level (MCL) of 60 μg/L (US EPA, 2015). Different from THMs, the formation potential HAAs have been found to rely more on the hydrophilic part of NOM, which is relatively difficult to be removed from water (Kim & Yu, 2005).

Table 2. Names and chemical formulas of regulated HAAs (Health Canada, 2014)

Disinfection By-products (DBPs)		***Chemical Formula***
Haloacetic Acids (HAAs)	Monochloroacetic Acid (MCA)	CH_2ClCO_2H
	Dichloroacetic Acid (DCA)	$CHCl_2CO_2H$
	Trichloroacetic Acid (TCA)	CCl_3CO_2H
	Monobromoacetic Acid (MBA)	CH_2BrCO_2H
	Dibromoacetic Acid (DBA)	Br_2CHCO_2H

2.2.2.3 Other Regulated DBPs

1) Bromate is regulated by Health Canada with 0.01 mg/L of MAC, which is not as common as THMs and HAAs. Bromate is usually from the contaminated hypochlorite solution or generated by ozone as a DBP (Health Canada, 2014).
2) Chlorate and chlorite are two types of DBP in drinking water treatment with chlorine dioxide as a disinfectant. According to the Guidelines for Canadian Drinking Water Quality, both have the same MAC of 1 mg/L. They can be controlled by respecting the chlorine dioxide dose below 1.2 mg/L (Health Canada, 2014).
3) Formaldehyde is the DBP of ozone disinfection. As the only type of regulated DBP without a guideline value, formaldehyde usually exists below the health-threatening level in drinking water (Health Canada, 2014).

4) N-Nitroso dimethylamine (NDMA) is stringently regulated in Canada, which can be the DBP of disinfection with chlorine or chloramines in drinking water. It is a probable carcinogen of liver cancer. The MAC of NDMA is 0.04 μg/L (Health Canada, 2014).

2.2.3 Surrogate parameters of DBP formation

Previous studies have found many surrogate parameters of DBP formation, such as total organic carbon (TOC), DOC, UV_{254}, specific ultraviolet absorbance (SUVA), and fluorescence spectroscopy(Chow et al., 2007; Edzwald et al., 1985; Singer & Chang, 1989).

1) TOC & DOC

   TOC has been studied as an indicator of THM formation potentials (Singer & Chang, 1989). All colloidal, particulate, and dissolved NOM are counted as TOC. DOC as the dissolved portion of TOC is measured after passing through a 0.45 micrometer (μm) membrane filter, which has been found more accurate to indicate the DBP formation potential of waters (Najm et al., 2000). Because DBP formation is mainly contributed by the hydrophilic part of TOC, which is what DOC representing (Karanfil et al., 2002).

2) UV_{254}

   UV_{254} is defined as the ultraviolet absorbance of water at a UV wavelength of 254 nanometers (nm) (White et al., 2003). The incident UV light at 254 nm was emitted to pass through water samples, in which organic matters with high aromaticity (like

humic acids) can absorb part of the light. It has been proved to be an excellent parameter for predicting THM formation by Edzwald et al.

3) SUVA

SUVA cannot be measured directly, which is determined by the DOC concentration (mg/L) and UV_{254} of water samples (Archer & Singer, 2006). The equation of SUVA is shown below. SUVA represents the average ability of DOC in water samples to absorb UV light of 254 nm, which is widely used for predicting DBP formation potential in water (Weishaar et al., 2003). Higher SUVA represents the water has more DBP precursors and has the potential to produce more DBP (Harrington et al., 1996; Reckhow et al., 1990).

$$SUVA\ \left(\frac{L}{mg \cdot m}\right) = \frac{UV_{254}\ (cm^{-1})}{DOC\ (\frac{mg}{L})} \times\ 100\ (\frac{cm}{m}) \qquad \text{(Equation 1)}$$

4) Fluorescence of organic matters

Fluorescence spectroscopy has been developed as a prevalent method for characterizing and quantifying NOM in water (Wassink et al., 2011). Those fluorescent NOM consist of humic acids, fulvic acids, and proteins. Previous studies have found humic-like substances take the dominant portion of fluorescent NOM, which is relevant to DBP formation in the disinfection process (Coble, 1996). There are various techniques of fluorescence spectroscopy, including emission scan with fixed excitation wavelengths, synchronous scan with a constant offset wavelength, and excitation-emission matrix (EEM) (Chen et al., 2003; Senesi et al., 1991).

EEM has been widely used for water to measure the organic compounds' absorbance of incident light and the fluoresce with the light at different wavelengths (Bridgeman et al., 2011). In fluorescence excitation-emission matrices (FEEM),

excitation and emission lights combine UV light and visible light, with a wavelength range of 200 nm ~ 600 nm (Trueman et al., 2016). In Figure 2.2, there is a typical three-dimensional (3-D) scan of EEM, which is a collection of complex DOM fluorescence signals occurring under successively increasing wavelength of excitation (Ex) and emission spectra (Em) (Duarte & Duarte, 2020; Fellman et al., 2010; Rho & Stuart, 1978). The specific wavelength of Em and Ex is associated with like compounds, such as humic substances, fulvic materials, or proteins (W. Chen et al., 2003). And the Z axis shows the intensity of the fluorescence signals. With a wide range of wavelengths, FEEM produces a large volume of data for each sample. Hence, information extraction from FEEM data is important. There are several methods developed for analyzing EEM spectra, such as principal component analysis (PCA), fluorescence regional integration (FRI), and so on (W. Chen et al., 2003; Fernández-Pascual et al., 2023; Murphy et al., 2013).

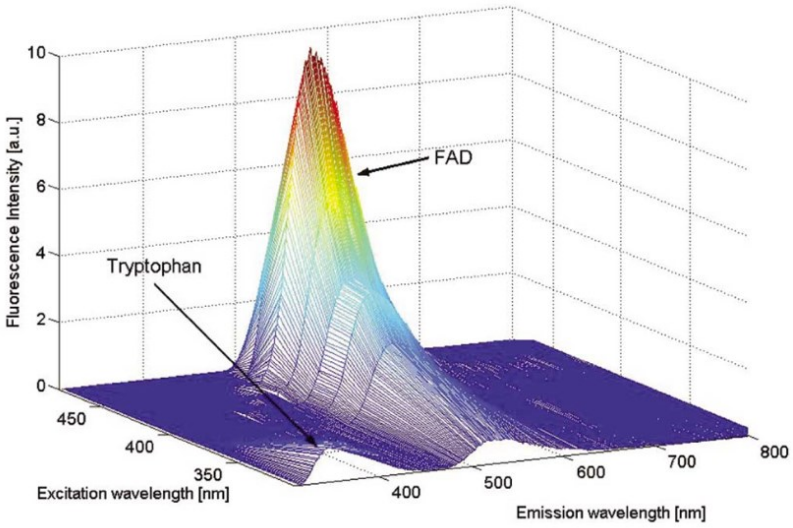

Figure 2. A Typical 3-D scan of EEM (Tunnell et al., 2003).

Some studies divide the fluorescent area into five regions by the excitation-emission wavelength boundaries as below. The five regions are defined as protein I, protein II, fulvic acid-like, soluble microbial by-product-like, and humic acid-like (W. Chen et al., 2003). Humic substances are a main source of DBP precursors during drinking water treatment, which consists of humic and fulvic acid (Nikolaou et al., 2004). The integrated EEM peaks of humic and fulvic acid-like can be used to describe the DBP formation potential of water samples.

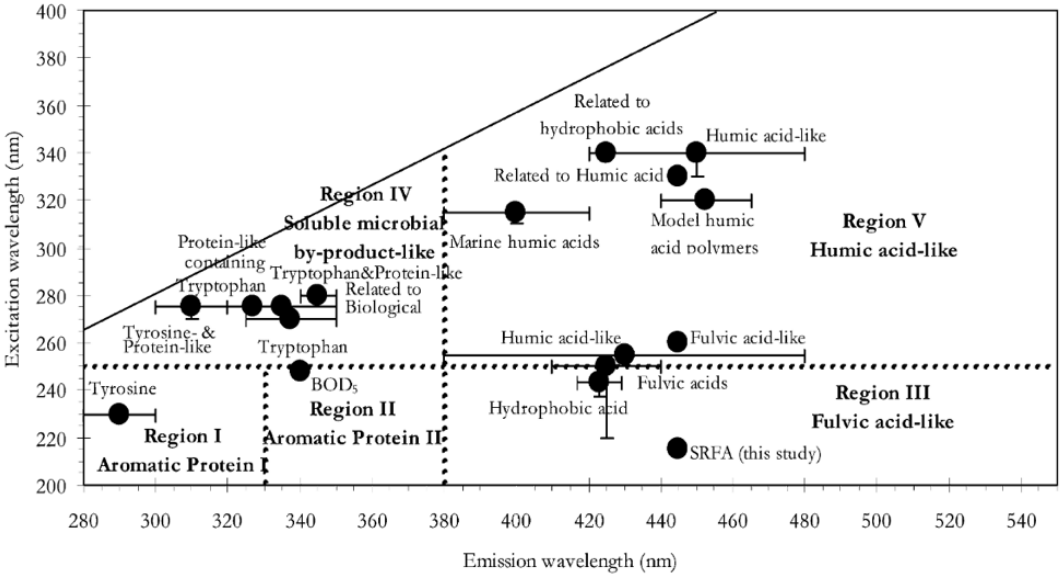

Figure 3. The E_x-E_m wavelength boundaries of five EEM regions (W. Chen et al., 2003).

2.3 Granular Activated Carbon (GAC)

Activated carbon (AC) can be manufactured from many natural carbonaceous materials, such as plants, coal, nutshell, and so on (Arena et al., 2016; Chowdhury, 2013). It is applied extensively in drinking water treatment for adsorbing dissolved organic matter, removing

taste and odor (T&O) compounds, removing heavy metals, and many other contaminants (Hoslett et al., 2018; Sun et al., 2018). Activated carbon is commonly used in either powdered form or granular form, which is defined by the activated carbon particle size. Powdered activated carbon (PAC) has a typical particle diameter of less than 0.1. Small PAC particle size refers to a large contact surface, high adsorption efficiency, and short equilibrium time. Thus, PAC can be added to the water treatment stream and kept suspended for adsorption mm (Cook et al., 2001). By contrast, GAC is defined with an average particle size ranging from 0.5 to 5 mm, which is preferred in filtration processes (Karanfil, 2006). Notably, despite PAC and GAC having different particle size, their adsorption properties should be the same, but the adsorption kinetics is different (Cook et al., 2001).

GAC is a prevalent adsorbent in drinking water treatment processes, which is usually situated downstream of coagulation & flocculation or clarification process and combined with sand filtration for removing dissolved organic matters/ DBP precursors (Golea et al., 2020; Liao et al., 2020). With increasing NOM in natural water bodies and concerns about harmful DBPs, GAC has been considered as one of the methods to decrease DBP formation by many water utilities. Although GAC has been found to be good at removing dissolved organic compounds several decades ago, the relation between adsorption capacity and its physicochemical properties still needs to be studied for improving GAC adsorption efficiency and DBP precursors removal rate. In 2005, Rodriguez et al. found the surface area of GAC particles in a specific pore width range and the tannin adsorption can describe the GAC's potential capability of adsorbing DBP precursors. Furthermore, the useful pore

size range of GAC has been found from 1 nm to 50 nm, which can be referenced by water utilities (Dastgheib et al., 2004; Velten et al., 2011). GAC is also characterized by the finite adsorption capacity, which needs to be replaced or thermally regenerated when it is exhausted (Dong et al., 2014).

2.4 Ultraviolet (UV) and UV Light-Emitting Diodes (UV LEDs) Disinfection

UV radiation naturally exists in sunlight with shorter wavelengths than visible light (400~700 nm). The corresponding wavelength ranges of UV light and visible light are demonstrated in Figure 4.

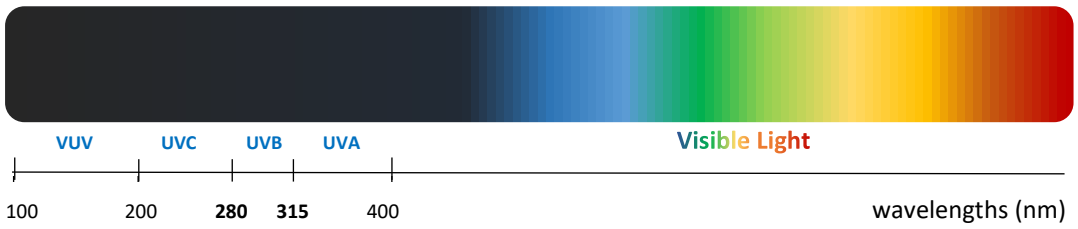

Figure 4. Ultraviolet and visible spectrum.

According to the wavelength ranges, UV light is divided into three parts: UV-A, UV-B, and UV-C, which are featured with wavelength ranges of 315~400 nm, 280~315 nm, and 200~280 nm respectively. With the shortest wavelength, UV-C radiation is commonly applied in water treatment for disinfection purposes due to its germicidal properties (Parrotta & Bekdash, 1998). A shorter wavelength refers to a higher energy level. UV-C light can penetrate microorganisms' cells, disrupting the replication of their genetic materials (deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)), and inactivating

them eventually (Dotson et al., 2012). UV disinfection as a non-chemical disinfection treatment has been used to kill bacteria and pathogens since the early 1900s, which can provide high disinfection efficiency without forming DBPs (Parrotta & Bekdash, 1998; Pontius, 1991).

2.4.1 Traditional UV Lamps

Mercury vapor UV lamps are used commercially for disinfection processes. UV light is generated by striking a voltaic arc through the mercury vapor within the lamp, where the electric current excites the mercury molecules to emit UV light and generates lots of heat at the same time (Parrotta & Bekdash, 1998). Conventionally, low-pressure (LP) and medium-pressure (MP) mercury vapor UV lamps are two types of lamps used to emit UV-C light for municipal drinking water treatment. LP UV lamps monochromatically emit UV light at a wavelength of 253.7 nm (Parrotta & Bekdash, 1998). Figure 5 is a bench-scale LP UV system in the lab. MP UV lamps are polychromatic, radiating UV light across a broad spectrum from 200 nm to beyond the UV light range (> 400 nm) (Dotson et al., 2012; Shah et al., 2011). Although LP UV lamps can emit an extremely high percentage of germicidal UV light, it is only available in low energy outputs (below 200W). Oppositely, MP UV lamps work with high energy outputs and emit more intense UV light, which means fewer MP UV lamps are required than LP UV lamps to generate the same intensity of UV light (Jeyanayagam & Cotton, 2002). With more attention given to the environment and energy saving, the disadvantages of traditional mercury vapor UV lamps have been becoming noticeable, such as toxic mercury content, high energy consumption, limited lifespan, environmental concerns, and so on.

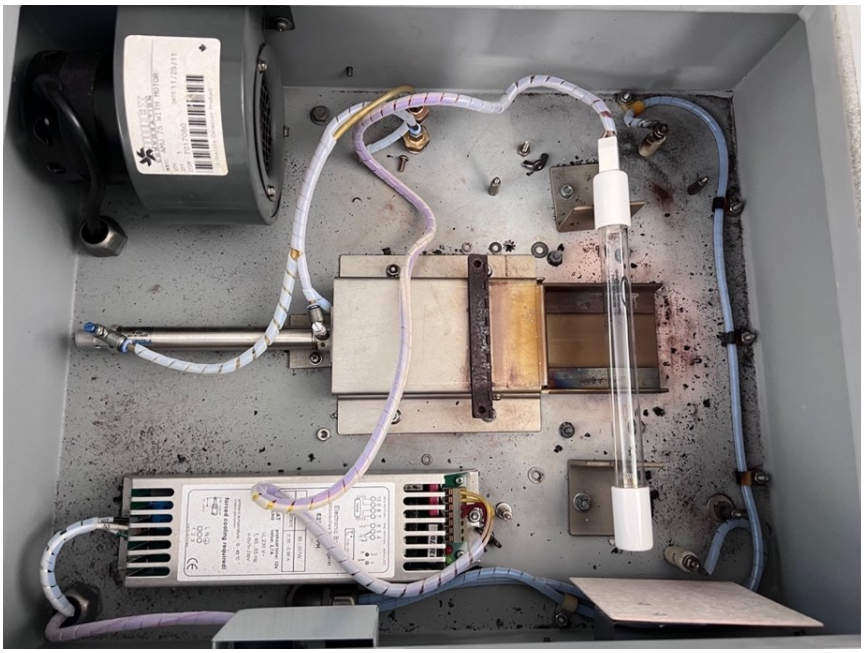

Figure 5. A bench-scale low-pressure (LP) mercury UV lamp system in CWRS lab.

2.4.2 UV LEDs

In recent decades, UV-LED has become one of the most representative emerging UV technologies for drinking water treatment. There is no mercury in UV-LED lamps, where aluminum gallium nitride and aluminum nitride are used to emit UV light (Oto et al., 2010). UV-LEDs are characterized as hazard free, having a smaller footprint, higher disinfection efficiencies, zero temperature influence, no advanced lamp decay, lower energy consumption, and fewer maintenance needs (Kheyrandish et al., 2018; Oguma et al., 2013). Moreover, UV-LEDs have adjustable wavelengths, which can be adjusted for different bacteria and pathogens to improve disinfection efficiency. Figure 6 presents the size comparison of a traditional MP UV lamp and a UV-LED beam. In this study, the UV-LED

PearlBeam collimated beam is from an AquiSense, which has three options of wavelength (265 nm, 280 nm, and 365 nm). Each wavelength is controlled by a switch, which can be chosen individually or combined with other wavelengths. However, as an emerging technology, UV-LEDs are still being developed to overcome their drawbacks and waiting for sound production regulation (Oguma et al., 2013). Some previous studies have found the combination of UV irradiation and chlorine can achieve better disinfection efficiency than the individual application of any one of them (Lee & Shin, 2011). For protecting chlorine from being degraded by UV irradiation, drinking water treatment plants often radiate water with UV first and chlorinate radiated water after (Zyara et al., 2016). While the effect of different sequences of UV and chlorine on DBP formation needs to be studied.

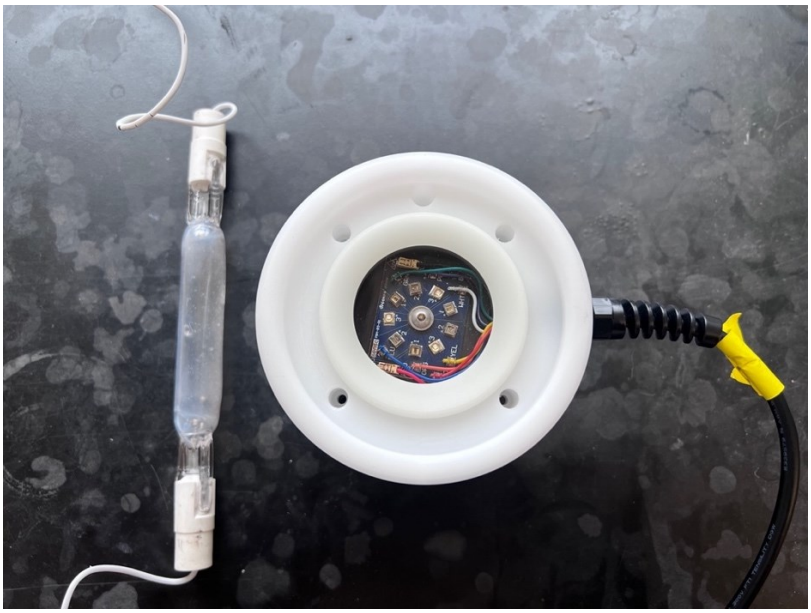

Figure 6. A traditional medium-pressure UV lamp and a collimated beam unit (265/280/365 nm) from AquiSense Technologies in CWRS lab.

2.5 Uniform Formation Condition (UFC) Test

For comparing the concentration of DBP that is potentially formed during & after chlorination treatment and evaluating different water treatment processes/technologies, there are several methods designed to determine the formation potential of DBP in waters, which include the formation potential (FP) test, the simulated distribution system (SDS) test, and the uniform formation condition (UFC) test. As the previous section shows, the formation of DBP is sensitive to chlorine dosage, temperature, pH, and contact time (Albanakis et al., 2021; Summers et al., 1996). Thus, each DBP formation potential method has its own unique test conditions, which are listed in the following table.

Table 3. DBP formation conditions of three DBP formation potential (FP) tests.

	Chlorine dose	**Temperature**	**pH**	**Incubation**
FP Test	Chlorine residual of 3~5 mg/L	25 ± 2 ˚C	7.0 ± 0.2	7 days
SDS Test	Site-specific (SS)	SS	SS	SS
UFC Test	Chlorine residual of 1 ± 0.4 mg/L	20 ± 1 ˚C	8.0 ± 0.2	24 ± 1 hours

As Table 3 demonstrates, the FP test provides the highest chlorine dosage and longest incubation time, which aims at maximizing DBP formation by overdosing with chlorine and extending contact time. Under the FP test, the highest potential concentration of DBP in different waters is determined and compared with each other. However, the conditions in FP tests are worse than the common treatment conditions at water plants, and the result is much higher than the DBP formed practically at plants. Therefore, the FP tests cannot

be used to predict DBP formation at water plants (Minear & Amy, 1995; Symons et al., 1993).

It is well known that DBP formation not only occurs at the plant but also in the distribution system with chlorine residual. For determining DBP formation after a specific distribution system, the SDS test is conducted under a series of customized conditions, which depend on the practical conditions at the plant and distribution system. This test has been performed and found to well simulate DBP formation in distribution systems since 1978 (Koch et al., 1991; Summers et al., 1996). However, the SDS test is not suitable for comparing DBP formation from site to site. The specific conditions at different plants result in the various conditions of SDS tests, which is an ineluctable limitation of SDS and also the reason why the conditions for SDS tests are not listed in the above table. Moreover, temperature change gives another limitation to this test. At the plant with temperatures varying greatly from season to season, the SDS test cannot be used to evaluate the DBP potential formation accurately throughout the year.

After these limited DBP formation potential tests, the UFC test was developed with clear and constant conditions. The values of these four conditions were based on the average conditions in the US distribution system (Summers et al., 1996). The UFC test allows the direct comparison of DBP formation among different waters and helps optimize water treatment processes for decreasing DBP formation. In this study, UFC tests were conducted to evaluate the effect of different filters and disinfection methods on the subsequent DBP formation.

Chapter 3 Materials and Methods

This chapter outlines materials, bench-scale equipment, experimental set-up, and analytical, and data analysis methods that are used throughout this study. Some basic parameters of source water are introduced briefly in the first section of this chapter. Besides, the treatment processes of JDK full-scale and pilot-scale plants will be described in the chapter as well.

3.1 Water Source and Water Characteristics

Pockwock Lake Watershed is a surface water area protected under the Nova Scotia Environment Act., which supplies raw water to J. Douglas Kline Water Supply Plant (JDKWSP) in Upper Hammonds Plains, Nova Scotia, Canada. The lake water is characterized as low pH ($pH < 6$), low alkalinity (< 5 mg as $CaCO_3$ / L), low turbidity (< 0.5 NTU), low nutrient content, and moderate NOM (Knowles et al., 2012; Stoddart & Gagnon, 2015). In recent years, increasing NOM and color have been observed in Pockwock Lake (Anderson et al., 2017). With the seasons and the temperature of the atmosphere changing, a seasonal temperature variation occurs in Pockwock Lake. Usually, the top and bottom of this lake's temperature occur in August and January (Stoddart & Gagnon, 2015). Aiming at studying the impact of UV LED and chlorine disinfection on the DBP formation under all conditions of temperature, the post-filter waters from full-scale and pilot-scale JDKWSP were collected biweekly for 6 months (from August 2022 to January 2023).

3.1.1 J.D. Kline Water Supply Plant Overview

JDKWSP is a direct filtration drinking water treatment plant in Halifax, which is operated by Halifax Water to meet the water demands of the greater urban core of Halifax, Bedford, Sackville, Fall River, Waverly, and Timberlea. The treatment process of JDKWSP consists of pre-screening, pre-oxidation coagulation, hydraulic flocculation, direct dual media (2-feet anthracite and 1-foot sand) filtration, and chlorine disinfection. Raw water is pre-oxidated with 0.15 mg/L of potassium permanganate ($KMnO_4$) at a pH range of 9.6 ~10 (lime is used for adjusting pH). Pre-chlorination is performed seasonally to control the biomass from seasonal algal bloom. Aluminum sulfate is used as the primary coagulant with an average dosage of around 20 mg/L Al_2SO_4. During coagulation, the pH of water is adjusted by adding CO_2 to achieve 6.2. Cationic polymer (FLOPAM, SNF Canada) is added subsequently for enhancing coagulation & flocculation performance and reducing floc time. The dosage of flocculant is 0.05 mg/L for the winter season and ranges between 0.015 to 0.03 mg/L for other seasons. There is a tapered three-stage basin for the flocculation stage, where flocculation takes a time ranging from 30 to 45 mins. As a direct filtration water treatment plant, there is no clarification stage after flocculation. Water with flocs flows onto eight dual-media anthracite (2 feet, effective size (ES) = 0.9 mm) and sand (1 foot, ES = 0.45 mm) filters. After filtration, filtered water needs to be chlorinated before the distribution system. The chlorine dosage at JDKWSP is not constant, which is being adjusted as the concentration of organic matter in filtered water for ensuring around 1 mg/L of chlorine residual in distribution systems.

3.1.2 Pilot Plant Overview

The JDKWSP is equipped with a research pilot plant, which consists of two identical and parallel adaption trains. One is named as Full-Scale Plant (FSP) Train, which is used as a control to mimic the JDK full-scale treatment, where the sedimentation process is bypassed and the coagulated water from the last flocculation tank goes directly to an anthracite-sand (Ant-Sand) filter. The other train is named Adaptation Train, which is operated with a sedimentation tank for improving filter hydraulic performance. In the Adaptation Train, there are three parallel filters in the filtration process. One is an anthracite-sand filter, which is the same as the filter at the full-scale plant. The other two contain GAC filter media for a higher NOM removal rate.

In this study, all filtered water samples were from the Adaptation Train, aiming at assessing the DBP precursors removal rate of different filters. Figure 7 demonstrates the process schematic of the second treatment trains at the JDKWSP pilot plant. Raw water comes from Pockwock Lake feeding each treatment train at an average flow rate of 10 L/min. Different from the JDKWSP full-scale plant, a sedimentation tank was added before filtration for extending filter run times. This sedimentation tank is a 330 L basin with 30 adjustable plates with a settling area of 0.1 m^2. Besides, there are three different filter columns operated in this treatment train. The first filter (labeled as Ant-Sand) consists of 2 feet of anthracite (ES = 0.9 mm) and 1 foot of silica sand (ES = 0.52 mm). The second filter (labeled as GAC-Ant-Sand or GAC-Cap) contains 2 feet of anthracite (ES = 0.9 mm), 1 foot of silica sand (ES = 0.52 mm) and is capped with 1 foot of GAC (ES = 0.8 ~ 1.0 mm). The third filter (labeled as GAC-Sand) contains 2 feet of GAC (ES = 0.8 ~ 1.0 mm)

and 1 foot of silica sand (ES = 0.52 mm). The first filter (F210) is the same as the filter employed at the full-scale plant. The Ant-Sand and GAC-Sand filters have 12 min of total empty bed contact time (EBCT), while the GAC-Ant-Sand filter has 16 min of EBCT. Before this study, the GAC-Ant-Sand filter has been operated for approximately 26,700-bed volumes (BV) (based on a GAC EBCT = 4 min), while the GAC-Sand filter was operated for approximately 11,800 BV based on a GAC EBCT = 8 min), which represented approximately 74 and 65 operational days, respectively. Water evenly passes through each filter at a flow rate of 2.4 L/min and is collected right after the filters.

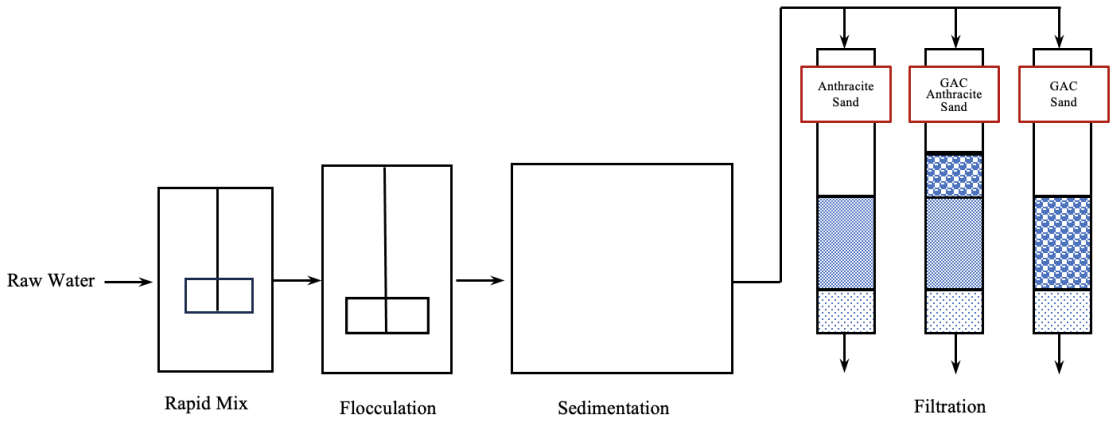

Figure 7. The schematic of the JDKWSP pilot plant treatment process.

3.2 Bench-Scale Methods

Filtered waters collected from the JDK full-scale and pilot-scale plants were analyzed for pH, TOC, UV_{254}, and FEEM. All those analytical methods will be described in the following sections of this chapter. Before disinfection treatment, the UFC test was conducted to determine the chlorine dose for each filtered water. By following the UFC, all filtered waters were buffered with 2 mL/L of pH 8 borate buffer and adjusted to pH 8 ±

0.2 with 1N sodium hydroxide (NaOH) or 1N sulfuric acid (H_2SO_4) if necessary. Buffered waters were chlorinated with a series of chlorine dosages and incubated for 24 ± 1h under 20 ± 1 ˚C to determine the chlorine dose that can provide a chlorine residual of 1 ± 0.4 mg/L after 24-hour incubation period.

Filtered waters were exposed to designed UV fluence. A collimated beam unit (PearlLab Beam™ 265/280/365, AquiSense Technologies) with 280 nm of UV wavelength was applied for all UV-LED experiments in this study. Before disinfection treatment, a spectroradiometer (OCEAN OPTICS USB 2000) was placed under the UV beam with 2.1 centimeters (cm) to the UV LEDs for detecting UV light intensity. Based on the UV light intensity and the desired fluences, a method described by Bolton and Linden was used to calculate the corresponding UV exposure time (Bolton & Linden, 2003). The experiment setup is shown in Figure 3.2. A crystallizing dish (VWR International) carrying 52 mL of water sample with a spinner was placed under the center of the UV beam. The distance between the water surface and the bottom of the UV beam was 2.1cm.

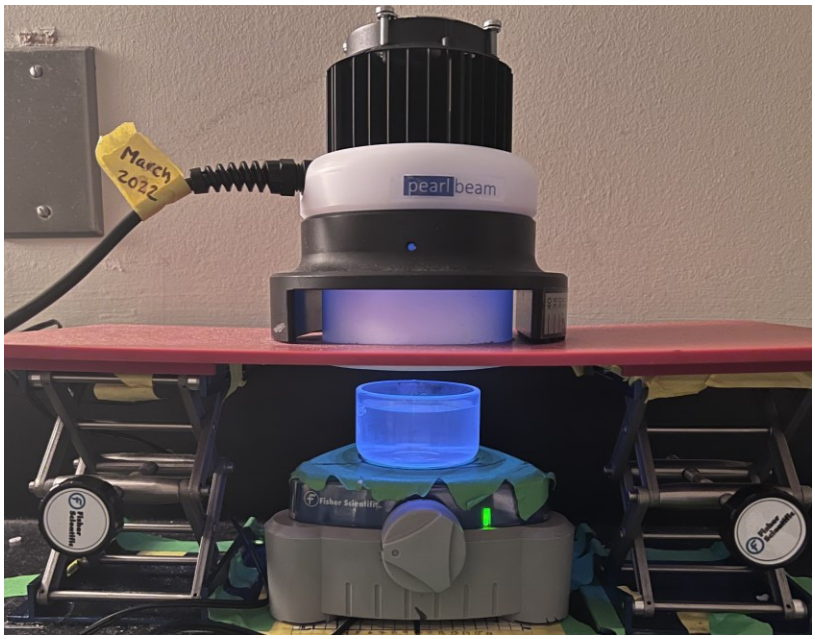

Figure 8. Experimental set-up with a collimated beam from AquiSense Technologies.

UV and chlorine disinfection were compared in this study along with the sequencing of combined disinfection treatment strategies. Figure 9 shows the disinfection experimental setup, including chlorination only, UV radiation only, and the UV LED/chlorine combined disinfection treatment. Figure 9 (c) demonstrates water was dosed with chlorine and followed by being radiated by UV light at 280 nm of wavelength. Conversely, Figure 9 (d) shows water was irradiated by UV light at 280 nm and chlorinated later. All disinfected water was collected headspace-free in the 130mL chlorine demand-free amber bottles and incubated for 24 ± 1h. After incubation, a portion of water was used for measuring DBP concentration, and the remaining part was tested for free chlorine residual and FEEM.

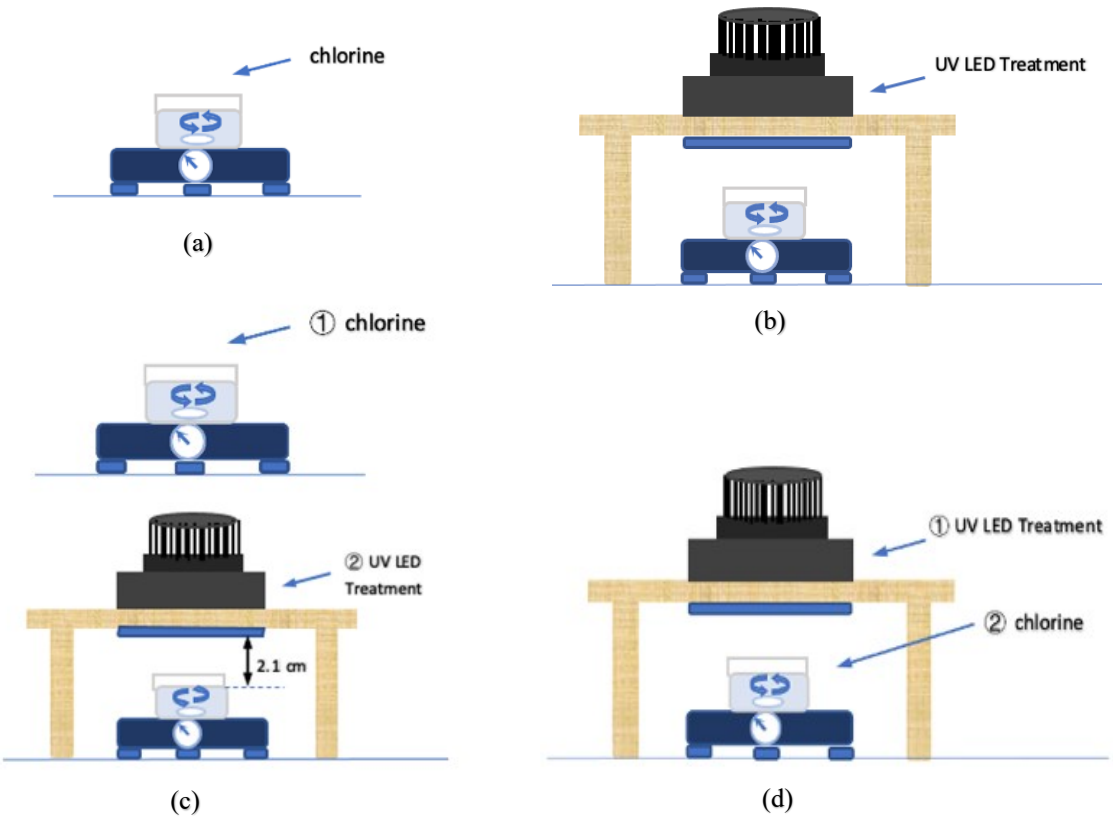

Figure 9. Schematic of UV/chlorine disinfection treatment. (a) Chlorination only (Cl); (b) UV radiation only (UV); (c) Chlorine first, UV radiation after (ClUV); (d) UV radiation first, chlorine after (UVCl).

Filtered waters were planned to be collected biweekly from August 2022 to January 2023. While waters were just collected nine times throughout this period, because of some maintenance issues at JDK pilot-scale plant. In this study, there were three UV fluences used in disinfection treatment, 20, 40, and 80 mJ/cm^2. With four types of filtered waters (full-scale, Ant-Sand, GAC-Ant-Sand, and GAC-Sand filtered waters), three UV fluences, and different sequences of UV radiation and chlorination, there were ten disinfection conditions for each filtered water evaluated in this study.

3.3 Analytical Methods

All laboratory procedures applied in this study were operated in accordance with *Standard Methods for the Examination of Water and Wastewater* (Trujillo, 2017). The analytical parameters measured throughout this research include pH, TOC, UV_{254}, free chlorine, FEEM, THMFP, and HAAFP.

3.3.1 General Water Quality Parameters (pH)

In this study, the de-ionized (DI) water from a Milli-Q purification system (Reference A+, Millipore) with 0.22μm of filter pore size was used for preparing all chemical stock solutions and cleaning experimental apparatus. pH was measured by using an Orion Star A111 pH meter (Thermo Scientific Company). pH meter was calibrated with pH standard solutions (pH at 4.00, 7.00, and 10.00) before measurement.

3.3.2 Organic Matters

3.3.2.1 TOC measurement

For measuring TOC, water samples were collected headspace-free in 40mL glass vials and preserved with 4 drops of phosphoric acid (pH < 2) under 4˚C for analysis. DOC is defined as the organic carbon in water which has been filtered by a 0.45μm filter paper. In this study, all water samples were post-filter water, which means TOC and DOC were pretty similar. TOC/DOC of water samples was analyzed in a TOC-V CPH analyzer which is equipped with a Shimadzu ASI0-V autosampler and a catalytically aided combustion

oxidation non-dispersive infrared detector (NDIR). This detector has a detection limit of 0.08 mg/L, which means the detectable concentration of TOC is above 0.08 mg/L.

3.3.2.2 UV_{254} measurement

In terms of measuring UV_{254}, a UV-VIS Spectrophotometer (HACH, UV-VIS Spectrophotometer DR6000) was used to collect UV absorbance at a wavelength of 254nm for each water sample. Before running a sample set, the instrument was zeroed with a 1cm path-length quartz glass flow-through cuvette filled with Milli-Q water. Milli-Q water also was used to rinse the cuvette three times before it was rinsed by a water sample. After the cuvette was rinsed with a water sample three times, it was filled with the sample and placed in the UV-VIS Spectrophotometer for the UV_{254} measurement.

3.3.2.3 FEEM

All FEEM scans were collected with a Horiba's Aqualog Spectrophotometer and a 1cm path length quartz glass flow through the cuvette. Before running a sample set, a FEEM scan of the ramen sample or blank sample was collected by using the purified Milli-Q water. Same with the UV_{254} measurement, the cuvette was rinsed with Milli-Q water and the sample three times prior to running each sample. Then the cuvette filled with water sample was processed with an integration time of 1 second, an excitation wavelength range of 240 nm ~ 600 nm with 3 nm of increments, and an emission wavelength range of 213.65 nm ~ 620.46 nm with 3.15 nm of increments. The FEEM scan was normalized by the ramen sample/blank sample before being exported as an Excel file (CSV) for data analysis.

FEEM was applied in this study to monitor the intensity of fluorophores related to humic acids, fulvic acids, proteins, and microbial materials. This measurement will show the effect of GAC filtration on NOM/DBP precursors removal by demonstrating the difference of organic components in studied filtered waters. The following table lists the excitation and emission wavelength ranges used to define the fluorescent regions of the components of NOM. Fluorescence regional integration (FRI) was the method used to integrate the fluorescence signal for qualifying and quantifying the designated regions (Chen et al., 2003).

Table 4. Excitation and emission wavelength ranges of five regions (W. Chen et al., 2003).

Region	Characteristics	Excitation wavelength range (nm)	Emission wavelength range (nm)
Region I	Aromatic Protein I	200 ~ 250	200 ~ 330
Region II	Aromatic Protein II	200 ~ 250	330 ~ 380
Region III	Fulvic acid-like materials	200 ~ 250	380 ~ 550
Region IV	Soluble microbial materials	250 ~ 340	200 ~ 380
Region V	Humic acid-like materials	250 ~ 400	380 ~ 550

3.3.3 Free Chlorine Measurement

In this study, free chlorine measurement was not only applied to the chemical solution but also to incubated water samples, which was conducted on a DR6000 HACH Spectrophotometer. On this spectrophotometer, the F&T chlorine method was selected with the upper limit of 2 mg/L. Samples containing free chlorine of above 2 mg/L need to be diluted. Milli-Q water was used to zero the method. A DBP-free chlorine reagent

(PERMACHEM REAGENTS from HACH) was used in every single free chlorine measurement, which contains disodium EDTA, sodium phosphate dibasic, and salt of N, N-Diethyl-p-phenylenediamine (-). 10 mL of water sample was mixed with a bag of reagent powder in the glass cell by shaking and let it sit for three minutes before measurement.

3.3.4 Uniform Formation Potential (UFC) Test

The UFC test provides a constant and representative condition for chlorinated DBP formation. Under UFC, the selected chlorination conditions include pH 8 ± 0.2, incubation temperature = 24 ± 1˚C, incubation time = 24 ± 1h, and 24h free chlorine residual = 1.0 ± 0.4 mg/L (Summers et al., 1996).

In the UFC test, the glassware used for incubation needed to be chlorine demand-free. 130 mL amber bottles with PTFE-faced caps were used for incubation, which was soaked in a diluted sodium hypochlorite solution with a free chlorine concentration of around 20 mg/L for at least 24 h and rinsed three times with Milli-Q water. Then amber bottles were placed in the Thermo Scientific Isotemp Oven at 105˚C for at least 24h. PTFE-faced caps were air dry under room temperature.

Before the disinfection procedure, pH 6.7 borate buffer, pH 8 borate buffer, and pH 8 buffered sodium hypochlorite solution were prepared. According to Method 5710 in *Standard Methods for the Examination of Water and Wastewater 22nd edition*, the pH 8 borate buffer was made by filling a 250 mL volumetric flask with 15.46 g boric acid, 2.6 g

sodium hydroxide, and Milli-Q water. The pH 6.7 borate buffer was prepared also with 15.46 g boric acid and Milli-Q water in a 250 mL volumetric flask but just needed 1.1 g sodium hydroxide. In terms of yielding a pH 8 sodium hypochlorite-buffer solution, 5 mL of 5.65~6% sodium hypochlorite solution was diluted with DI water in a 100 mL volumetric flask and transferred into a 500 mL beaker for adjusting the pH to 8 with pH 6.7 borate buffer. Eventually, the concentration of free chlorine in this solution was around 3000 mg/L. All those chemical solutions were labeled and stored at 4 ˚C for up to 3 weeks.

Before performing this test, the filtered waters were buffered with 2 mL/L of pH 8 borate buffer and adjusted to pH 8 ± 0.2 with 1N sodium hydroxide or 1N sulphuric acid if necessary. Three chlorine dosages were applied to each water sample for determining the optimal chlorine dosage. The series of chlorine dosages were calculated with the TOC of the water. Considering inorganic demand, Summers et al. recommended the chlorine and TOC ratios (Cl_2 : TOC) of 1.2:1, 1.8:1, and 2.5:1. Three amber bottles were assigned to each water sample and were three-quarters full with the buffered water. pH 8 sodium hypochlorite buffer solution was dosed and mixed evenly with water samples by shaking. Amber bottles were filled headspace-free with buffered water and capped for 24 ± 1h incubation time in the dark. After incubation, the free chlorine residual in each amber bottle was measured by DR5000 HACH Spectrophotometer. And the chlorine dosage that can yield a 24-h chlorine residual of 1.0 ± 0.4 mg/L was selected for the following UV LED/chlorine disinfection experiment.

23-mL glass vials that were used to carry disinfection by-product samples were washed and placed in the oven at 105˚C for 24 hours. In terms of THM sample collection, a drop of 50 g/L ammonium chloride solution, 2 drops of 8 g/L sodium thiosulfate solution, and 3 drops of 0.1N hydrochloric acid were added into each pre-cleaned glass vial, and THM samples were collected headspace-free in those glass vials. HAA samples were preserved headspace-free in 23-mL baked glass vials with one drop of 50 g/L ammonium chloride solution.

3.3.5 DBP Analysis

3.3.5.1 THM extraction and analysis

THM samples were extracted as Trihalomethanes and Chlorinated Organic Solvents: Liquid-Liquid Extraction Gas Chromatographic Method (Bridgewater et al., 2017). 23-mL glass vials that were used to carry DBP samples were washed and placed in the oven at 105˚C for 24 hours. Water samples of THM analysis were collected headspace-free in those 23 mL glass vials with a drop of 50 g/L ammonium chloride solution, 2 drops of 8 g/L sodium thiosulfate solution, and 3 drops of 0.1N hydrochloric acid. Before DBP analysis, a series of THM standard samples were prepared for calibration. A 23 mL pre-cleaned glass vial was used to transfer 23 mL of Milli-Q water to 40 mL baked amber vials. Place a cap with a Teflon line septa on each vial. Amber vials were spiked with a certain volume of THM Working Calibration Solution (20,000 μg/L) as standard volumes shown in the following tables. According to the concentration range, there were two sets of THM calibration standards.

Table 5. The concentration of THM standards for low calibration range (Bridgewater et al., 2017).

	Working THM Calibration Solution (20000 g/L)						
Standard	1	2	3	4	5	6	7
Spiked Volume (uL)	0	5	10	20	30	40	50
Chloroform (µg/L)	0.00	4.35	8.70	17.39	26.09	34.78	43.48
Dichlorobromomethane (µg/L)	0.00	4.35	8.70	17.39	26.09	34.78	43.48
Chlorodibromomethane (µg/L)	0.00	4.35	8.70	17.39	26.09	34.78	43.48
Bromoform (µg/L)	0.00	4.35	8.70	17.39	26.09	34.78	43.48

Table 6. The concentration of THM standards for high calibration range (Bridgewater et al., 2017).

	Working THM Calibration Solution (20000 g/L)						
Standard	1	2	3	4	5	6	7
Spiked Volume (uL)	0	20	40	60	80	110	150
Chloroform (µg/L)	0.00	17.39	34.78	52.17	69.57	95.65	130.43
Dichlorobromomethane (µg/L)	0.00	17.39	34.78	52.17	69.57	95.65	130.43
Chlorodibromomethane (µg/L)	0.00	17.39	34.78	52.17	69.57	95.65	130.43
Bromoform (µg/L)	0.00	17.39	34.78	52.17	69.57	95.65	130.43

Amber vials with THM standards were spiked with 50 uL of Working THM Internal Standard (9.66 mg/L) before extraction. Afterward, a teaspoon of anhydrous sodium sulfate (Granular/Certified ACS, Thermo Fisher Scientific) and 4 mL of pentane (HPLC grade, Fisher Chemical) were added to each vial. With the cap on, amber vials were placed in a vial tray, shaken for two minutes, and sat for 10 minutes. After layers in amber vials were

separated, a 1000 uL pipette was used to remove 800 uL of the aliquot of extract from each sample and transfer it to a 2 mL autosampler vial for Gas Chromatograph analysis.

In terms of water samples, water samples were removed from the fridge and equilibrated to room temperature before being transferred to 40 mL amber extraction vials. Besides, every set of water samples was set up with one blank, one low-range quality control sample, one low-range, and one high-range external quality control sample. The same extraction process of calibration standards was used to extract water samples, blank samples, and water quality control samples. Aliquots of extract were placed in 2 mL autosampler vials.

As USEPA Method 551.1, THM concentration was analyzed by a Thermo Scientific Trace 1310 Gas Chromatograph equipped with an AI/AS 1310 Autosampler (Hodgeson & Munch, 1990). There were four THMs measured by this method, which include Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Chlorodibromomethane ($CHBr_2Cl$), and Bromoform ($CHBr_3$). At an injector temperature of 220°C along with a 15% of split ratio and a split flow of 18 mL/min, 1 uL of THM extract was injected on the Gas Chromatograph by a Thermo Scientific Split/Splitless Inert 4 mm gooseneck liner containing glass wool. Ultra-high purity helium (99.999%) was used as a carrier gas in a Thermo Scientific TG-5SILMS 30m x 0.25 mm x 0.25 μm column. The oven temperature started at 35°C, which was held for 3.00 minutes, then rose to 80°C at a rate of 60.0 °C/minute with no hold. At a rate of 1.0°C/minute, the temperature was then increased to 85°C with no hold and climbed again at a final ramp of 125.0°C/minute to 180°C with no hold. The final runtime is 9.510 minutes for each sample. THM samples were run at a

constant flow rate of 1.2 mL/min. THMs were detected by an electron capture detector (ECD) at a temperature of 320°C, pulse amplitude of 50 V, pulse width of 1.0 us, and a reference current of 0.5 nA. The data collection rate is set at 10 Hz.

3.3.5.2 HAA extraction and analysis

HAA samples were extracted as Disinfection By-products: Haloacetic Acids and Trichlorophenol Micro Liquid-Liquid Extraction Gas Chromatographic Method (Bridgewater et al., 2017). The same glass vials for THM sample collection were used for collecting HAA samples as well. HAA samples were preserved headspace-free in 23-mL baked glass vials with one drop of 50 g/L ammonium chloride solution. The calibration curve needs to be plotted for every set of HAA analyses. For preparing standards, a 23 mL glass vial was used to transfer 23 mL of Milli-Q water to 40 mL baked amber vials. Place a cap with a Teflon line septa on each vial. Each standard was spiked with a certain volume of HAA Working Calibration Stock (20,000 μg/L) as Table 7 shown. Different from THM analysis, there were seven standards, one blank, and one quality control sample in HAA analysis.

Table 7. Concentration of HAA calibration standards (Bridgewater et al., 2017).

	HAA Working Calibration Standard Stock (20000µg/L)						
Standard	1	2	3	4	5	6	7
Spike Volume (uL)	5	10	15	25	40	60	70
Chloroacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Bromoacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Dichloroacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Trichloroacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Bromochloroacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Dibromoacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Bromodichloroacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Chlorodibromoacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870
Tribromoacetic acid (µg/L)	4.348	8.696	13.043	21.739	34.783	52.174	60.870

Amber vials with HAA standards were spiked with 50 uL of 3,5-Dichlorobenzoic Acid Working Internal Standard (16000µg/L) before extraction. Afterward, 2 drops of sodium sulfite solution (100 g/L), 1 mL of concentrated sulfuric acid (H_2SO_4), a teaspoon of anhydrous sodium sulfate (Na_2SO_4) (Granular/Certified ACS, Thermo Fisher Scientific), and 4 mL of methyl tert butyl ether (MTBE) (HPLC grade, Fisher Chemical) were added to each vial. With the cap on, amber vials were placed in a vial tray, shaken for two minutes, and sat for 10 minutes. After layers in amber vials were separated, a 1000 uL pipette was used to remove 800 uL of the aliquot of extract from each sample and transfer it to a 2 mL autosampler vial. Different from THM extraction, 100 uL of diazomethane was added to each sample and all standards, blanks, and quality control samples.

All water samples were removed from the fridge and equilibrated to room temperature before being transferred to 40 mL amber extraction vials. The same extraction process of calibration standards was used to extract water samples. Aliquots of extract were placed in 2 mL autosampler vials and spiked with 100 uL of diazomethane.

HAA analysis was conducted as USEPA Method 552, by which nine HAAs were measured, including Bromoacetic Acid (BrAA), Chloroacetic Acid (ClAA), Dibromoacetic Acid (Br_2AA), Dichloroacetic Acid (Cl_2AA), Tribromoacetic Acid (Br_3AA), Trichloroacetic Acid (Cl_3AA), Bromochloroacetic Acid (BrClAA), Bromodichloroacetic Acid ($BrCl_2AA$) and Chlorodibromoacetic Acid (Br_2ClAA) (Hodgeson et al., 1995). The same gas chromatograph and autosampler used in THM analysis were performed for the gas chromatographic analyses of HAAs, using the same gooseneck liner at an injector temperature of 220°C with an 8% of split ratio and a split flow of 10 mL/min. With the same column and carrier gas used in THM analysis, a volume of 1 uL HAA extract was injected into the GC. The oven temperature started at 40 ˚C and was held for 1 minute then ramped to 70.0°C at a rate of 2.00°C/min with no hold. The temperature was increased again at a rate of 60.00°C/min until reaching 120.0˚C and held for 3 minutes, then ramped to 180˚C at a rate of 35°C/min and then immediately climbed to 200.0˚C at a final ramp of 20.0°C/min with a 1-minute hold. The total runtime was 23.548 minutes for each sample. At a constant flow of 1.2mL/min, samples finally were analyzed by an electron capture detector (ECD) at a temperature of 300°C, with the same pulse amplitude, pulse width, and a reference current used in THM analysis. The data collection rate is set at 10 Hz as well.

3.4 Statistical Methods

The data were compared by paired t-test and ANOVA (single factor) in Microsoft Excel. The significance level (Alpha) was usually set to 0.5 for comparing two sets of data. For multiple comparisons, the Bonferroni correction was applied with the Bonferroni corrected alpha. The Bonferroni corrected alpha is defined by dividing the significance level by the number of tests (Dunn, 1961).

Chapter 4 Impact of Different Filters and UV LED Disinfection Combining with Chlorine on DBP Formation

4.1 Evaluation of GAC Filtration for the Removal of DBP Precursors / NOM

This chapter provides analysis of the DBP formation potential of different filtered waters to evaluate the effect of sedimentation and GAC adsorption on DBP formation. Apart from comparing DBP concentration directly, previous studies have found many parameters are surrogated with NOM and DBP formation, such as DOC, TOC, UV_{254}, and SUVA (Chow et al., 2007; Edzwald et al., 1985; Singer & Chang, 1989). A selection of those surrogate parameters will be used for the assessment of GAC filtration for removing NOM/DBP precursors in this section.

4.1.1 DBP in different filtered waters

Figure 10 shows the formation potential of total THM (TTHM) and total HAA (THAA) in the studied filtered waters. Although DBP formation is sensitive to contact time, environment temperature, pH, and chlorine dosage, all those factors were controlled as the UFC's requirements (incubation time = 24 ± 1 hour, incubation temperature = 24 ± 1˚C, pH = 8 ± 0.2, and 24-hour free chlorine residual = 1.0 ± 0.4 mg/L). Thus, the DBP results of those studied waters are comparable.

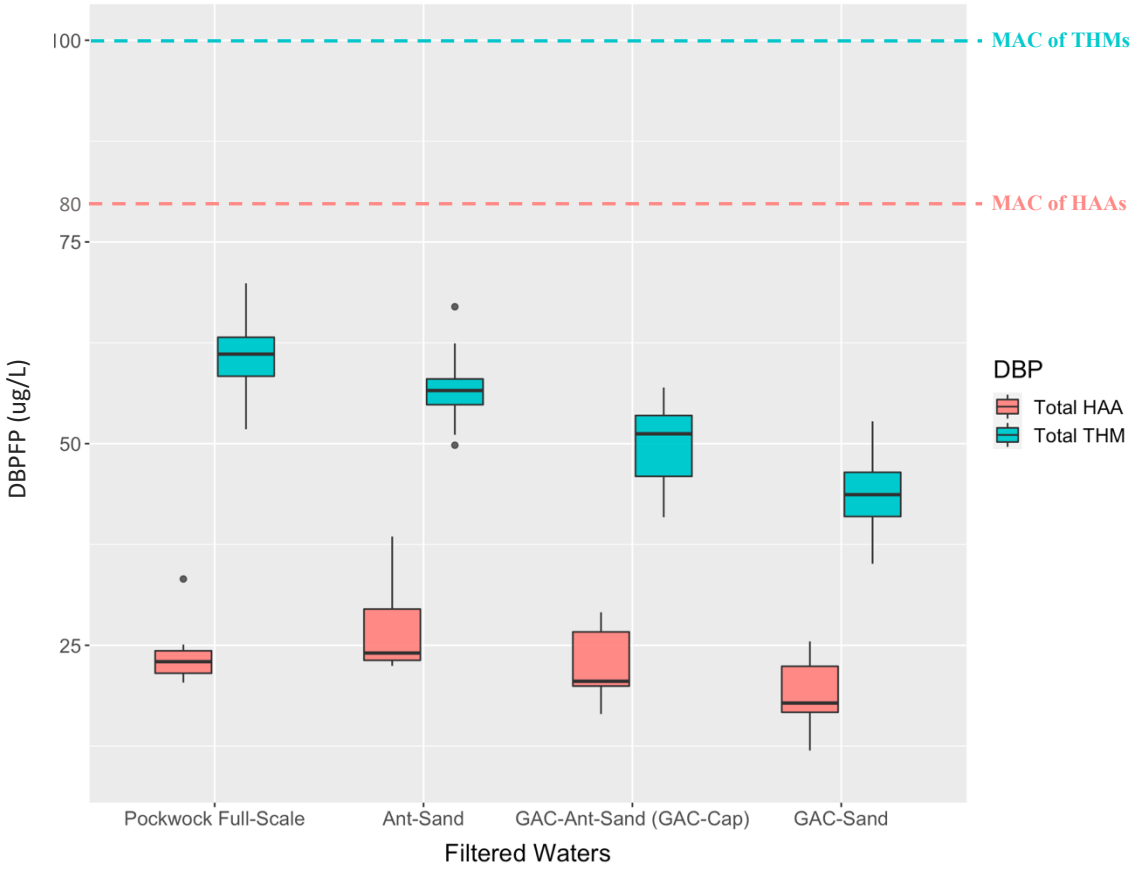

Figure 10. DBP formation potential in different filtered waters.

As shown in Figure 10, the TTHM level was always higher than THAA levels in filtered waters. The TTHM and THAA in all studied waters are under the MAC of 100 µg/L and 80 µg/L, respectively. The MAC is just the upper limit that Health Canada regulates for chemical substances. The lesser DBP generated in drinking water is better for public health. In the pilot plant, a sedimentation tank was added before the filters. Compared to the DBP levels in full-scale filtered water, the Ant-Sand filtered water did not show a statistically lower DBP concentration, no matter on TTHM or THAA. This result identifies the sedimentation process does not have an influence on removing DBP precursors and

reducing DBP formation, also shows this pilot-scale plant is good representation of the full-scale plant.

For the pilot-scale filtered waters, the DBPFP concentrations were markedly different from each other. The average total DBPFP in GAC-Ant-Sand filtered water was at 72.7 mg/L, which contained approximately 13% less total DBPFP than the Ant-Sand filtered water. In terms of the comparison of THMFP and HAAFP between these two filtered waters, the GAC-Ant-Sand filter around 12% less TTHM and 16% less THAA, respectively. Furthermore, the difference in DBP between Ant-Sand filtered waters and GAC-Sand filtered waters were significant as well. The GAC-Sand filtered water produced much less TTHM and THAA, at 44.11 mg/L and 18.52 mg/L, respectively. Compared to the DBPFP levels in Ant-Sand filtered water, the reduction rates of total DBPFP, THMFP, and HAAFP in GAC-Sand filtered water were about 25%, 23%, and 31%, respectively. The statistically significant difference in DBP concentrations in these pilot-scale filtered waters indicates GAC plays an important role in reducing DBP formation, and the thickness of GAC media in the filter impacts the reduction rate of DBP formation as well.

According to the operation record of these GAC filters, the GAC in GAC-Ant-Sand and GAC-Sand filters was nearly exhausted during this study. Thus, the effect of GAC adsorption on DBP reduction was assumed to be limited. Once the adsorption sites are full, GAC can remove NOM/DBP precursors through biodegradation. Some reduction of DBP formation might be caused by the GAC biofiltration, of which the evidence will be presented by FEEM data later.

4.1.2 Surrogate parameters of NOM/DBP formation

4.1.2.1 TOC in different filtered waters

Figure 11 demonstrates the TOC concentration in the studied filtered waters. Experiments of this research were conducted from summer to winter, TOC of source water fluctuated seasonally in the range of 2.7 mg/L to 3.7 mg/L, resulting in the variance of TOC in filtered waters. The full-scale filtered water and the Ant-Sand filtered water from the pilot plant were observed to have a similar TOC with an average TOC of 1.7 mg/L. The similar TOC level in these two filtered waters accords with the DBP formation data. This is also comparable to other studies that have demonstrated that sedimentation alone does not provide significant improvements in NOM removal and the pilot-scale plant is an excellent model of full-scale treatment system. For example, Abkar et al. (2019) found implementing a sedimentation stage did not enhance NOM removal but decreased the head loss accumulation rate of the filter and extended filter run times. During the coagulation & flocculation process, NOM with a high molecular weight and negative charge density is coagulated and flocculated to form big flocs, so that they can be removed in subsequent sedimentation or filtration (Wang et al., 2021). Flocs settle to the bottom of the sedimentation tank by gravity and the remaining part of NOM in water becomes the precursors of DBP. Thus, sedimentation cannot help removing NOM/DBP precursors, but extend filter run times.

Many studies have shown evidence of GAC can be implemented for TOC removal, especially for some low molecular weight organic compounds that are difficult to be

removed by coagulation & flocculation (Matilainen et al., 2002; Velten et al., 2011). With the comparison between different filters, a statistically significant difference (p-value = 2.396 E-05) was observed among three pilot-scale filtered waters in Figure 11. The GAC-Ant-Sand filtered water showed a 10% higher TOC removal rate compared to the Ant-Sand filter. GAC-Sand filter with two feet of GAC provided the highest TOC removal rate among all studied filters. The TOC in GAC-Sand filtered water was 80% of TOC in Ant-Sand filtered water and 50% of TOC in raw water.

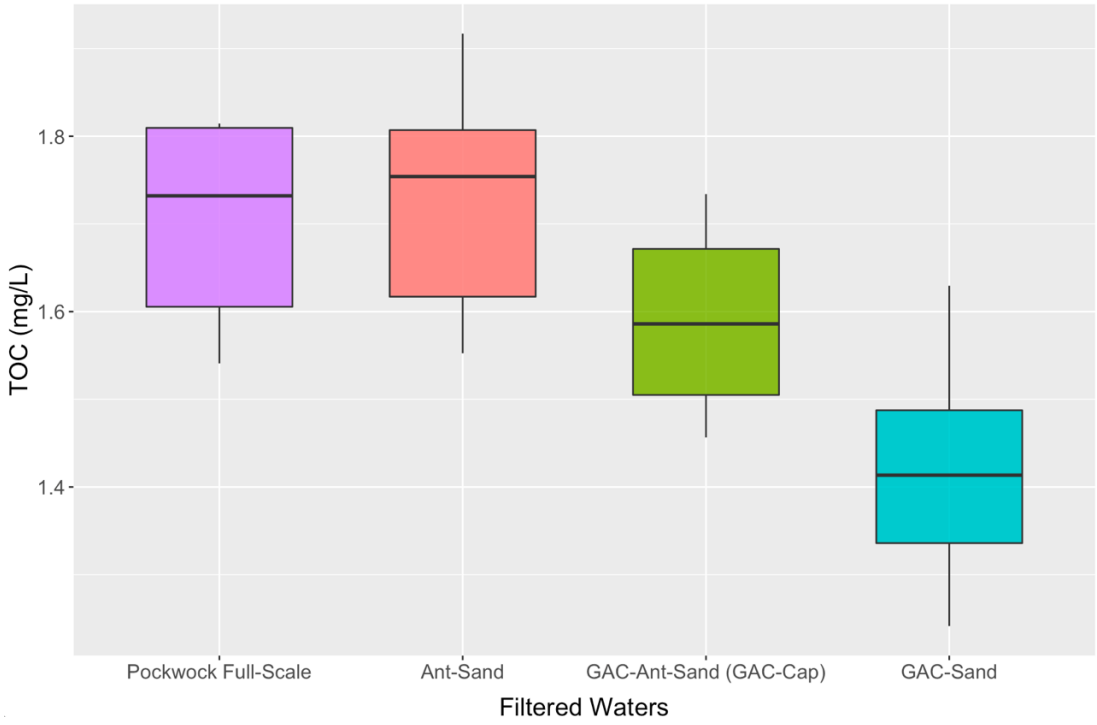

Figure 11. TOC concentration in different filtered waters.

Usually, the NOM removal rate of GAC implementation is higher than 20%, which is impacted by the GAC properties (such as bed volumes (BV), surface area, material, etc.) and water quality (Kaarela et al., 2021; Marais et al., 2018). Previous studies have found

the efficiency of GAC for removing organic compounds will decrease with GAC operational days and BV (J. Kim & Kang, 2008; National Research Council (US) Safe Drinking Water Committee, 1980). Before this study, the GAC-Ant-Sand filter and the GAC-Sand were operated for 74 and 65 operational days, respectively. Figure 12 illustrates the BV of these two GAC filters. The capability and efficiency of GAC adsorption declined with increasing BV. Throughout this study, the exhaustion percentage of the GAC-Ant-Sand filter increased from 90% to 100%, which showed that the GAC-Ant-Sand filter was able to remove 10% of NOM or less. For the GAC-Sand filter, the exhaustion percentage increased from 75% to over 90%. Compared to the theoretical adsorption capability of these two GAC filters, they were showing a higher TOC removal rate, which means GAC adsorption and possible biodegradation contributed to NOM/DBP precursors removal in this study.

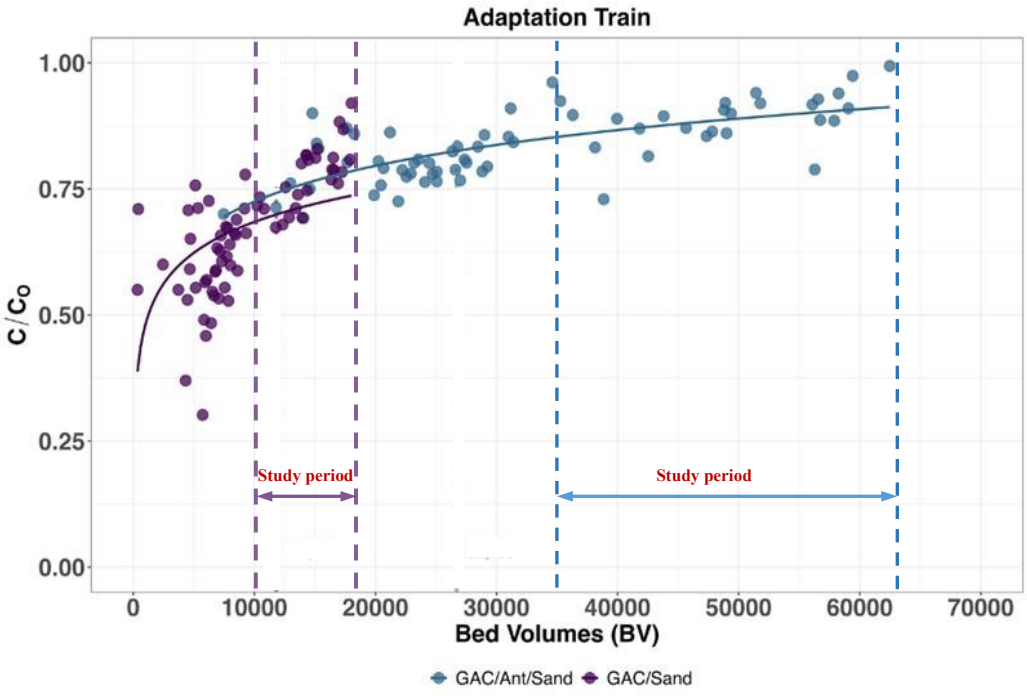

Figure 12. Bed volumes of GAC-Ant-Sand and GAC-Sand filters at JDK pilot plant (Anderson et al., 2023).

4.1.2.2 UV_{254} in different filtered waters

Figure 13 demonstrates the UV_{254} in all studied waters. The UV_{254} of full-scale filtered water and Ant-Sand filtered water were similar with an approximate average at 0.033 cm^{-1}, indicating sedimentation does not influence UV_{254} removal. GAC-Ant-Sand filtered water and GAC-Sand filtered water had an averaged UV_{254} of 0.028 and 0.023 cm^{-1}, respectively. The significant difference among pilot-scale filtered waters showed the ability of GAC to remove NOM. Overall, the difference in UV_{254} among studied filtered waters illustrated the same results that DBP and TOC data showed previously.

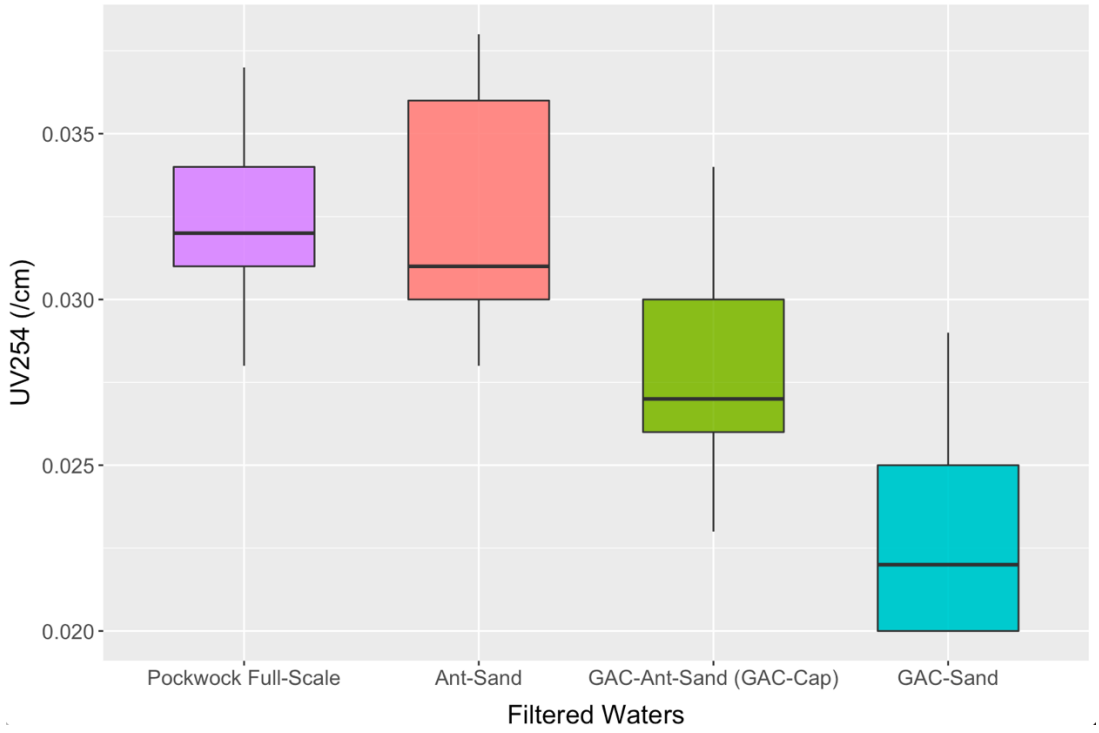

Figure 13. UV_{254} of studied filtered waters from JDKWSP.

4.1.2.3 SUVA in different filtered waters

Figure 14 presents the SUVA of all studied filtered waters. The mean SUVA in full-scale filtered water and Ant-Sand filtered water were not significantly different (p-value = 0.315), which represents the sedimentation process does not reduce DBP formation potential, same as the previous section showing. Among three pilot-scale filtered waters, a difference was observed in Figure 14. After paired t-test, the Ant-Sand and GAC-Sand filtered waters had significant differences in SUVA ($p = 0.032 < 0.05$). But the difference of SUVA ($p = 0.087 > 0.05$) between Ant-Sand and GAC-Ant-Sand filtered waters was not statistically significant. This part of SUVA suggested the similarity of DBP formation potential in Ant-Sand and GAC-Ant-Sand filtered waters, which did not accord with DBP formation data.

Theoretically, all surrogate parameters should show the same results. While a portion of SUVA data was not correlated with DBP formation in this case. The exhaustion of GAC filters might be the reason. Both GAC filters were mostly exhausted, especially the GAC-Ant-Sand filter, just able to contribute 10% or less NOM removal rate. The low adsorption capacity of GAC caused the similarity of SUVA between Ant-Sand and GAC-Ant-Sand filtered waters. Apart from this, SUVA of all three pilot-scale filtered waters remained under 2 L/mg·m. Some studies have reported SUVA has a limited correlation with DOC in water samples with low SUVA (< 2 L/mg·m) and low humic acid (Ates et al., 2007; Weishaar et al., 2003). Although SUVA was found not correlated with regulated THM and HAA formation in this study, it still could be correlated with other unknown DBPs. In 2015,

Hua et al. investigated SUVA could be a good indicator to identify the formation potential of unknown DBPs.

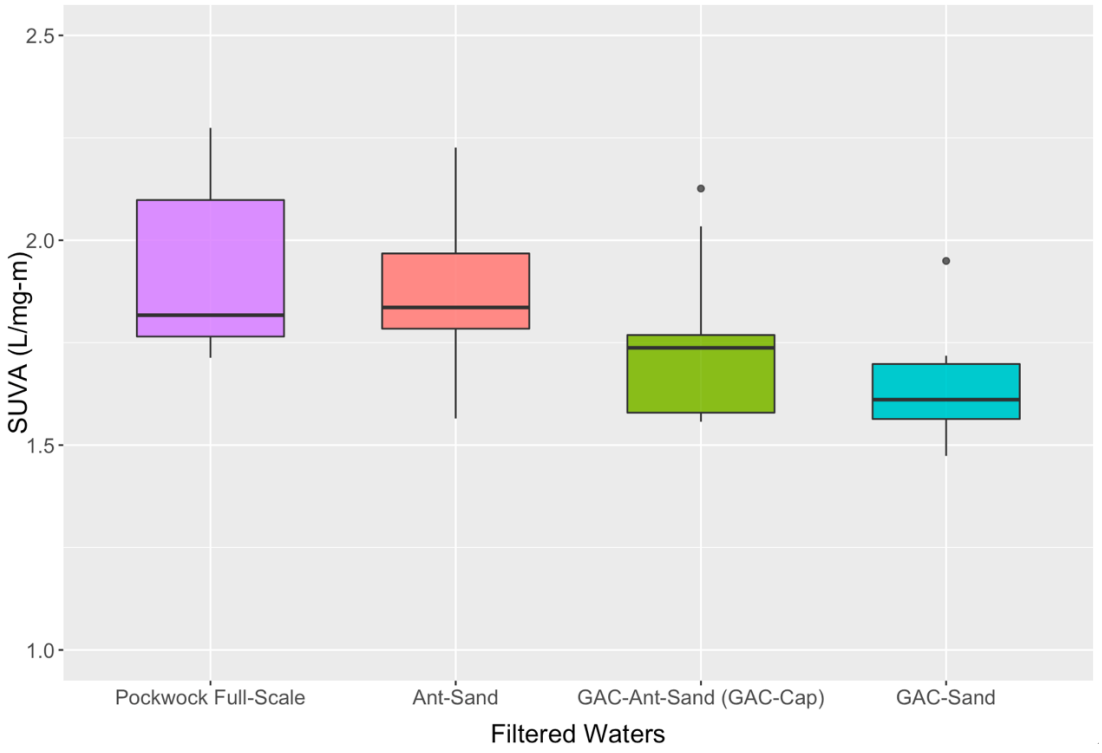

Figure 14. SUVA of studied filtered waters.

Overall, TOC and UV_{254} showed well correlation with DBPFP result. SUVA was not a good predictor of DBP formation in this study. And all these three surrogate parameters only broadly described the change of NOM instead of presenting the difference occurring in the components of NOM. The following section will use FEEM to monitor the effect of GAC filtration on the components of NOM.

4.1.3 FEEM of different filtered waters

Figure 15 demonstrates the FRI volume of these fluorescent regions in studied filtered waters. Both the humic acid-like and the fulvic acid-like materials are humic substances, which are considered the precursors of DBP (Marhaba & Kochar, 1999). The FRI volume of fulvic acid-like materials in all studied filtered waters stayed low and was pretty similar to each other. Thus, the difference in DBP formation potential among studied filtered waters just depended on the difference of humic acid-like materials. As this graph shows, humic acid accounted for the major portion of fluorescent organic compounds in all studied waters. And compared to the rest of the regions, the humic acid-like component was most amenable to be removed by GAC filtration, which has been also observed in other research ((Peleato et al., 2016). The FRI volume of humic acid-like materials decreased with the implementation of GAC. Compared with the Ant-Sand filtered water, the FRI volume of humic acid-like materials in GAC-Sand was significantly lower. The median of humic acid-like materials in GAC-Sand filtered water was approximately 50% of that in Ant-Sand filtered water. While the difference in humic acid-like materials between Ant-Sand and GAC-Ant-Sand filtered waters were not statistically significant ($p = 0.228 > 0.05$), which could be the result of GAC exhaustion. The great error bars of humic acid-like materials could be because the FEEM has such high resolution that it is capturing changes in NOM character (seasonal or other kinds) that could cause variability in the measurement that might not be captured by other metrics. Based on the FRI volume of humic substances in pilot-scale filtered waters, the effect of GAC filtration on DBP precursors removal was still

observed in GAC-Sand filtered water. DBP formation was predicted to decline with the implementation of more GAC in the filtration process.

In terms of other regions, there was no significant difference among all filtered waters on aromatic proteins. While the difference in soluble microbial materials among pilot-scale filtered waters was noticeable. The FRI volume of microbial materials decreased with the implementation of GAC, which illustrated GAC filtration also removed a certain part of soluble microbial products from water. Microbial materials in water are a mixture of carbohydrates, which are consumable for microorganisms that grow on the GAC surface and are removed by biofiltration (Korotta-Gamage & Sathasivan, 2017; Peleato et al., 2016). Microorganisms exist in source water, which goes onto the filter with coagulated water, grow on the surface of GAC, and produce microbial communities eventually (Weber, Jr. et al., 1978). These microbial communities form the biofilm which contributes to removing biodegradable compounds from water (Servais et al., 1992). This is also the reason why GAC filters were able to provide a higher TOC removal rate than GAC adsorption capability. Some researchers have found that biofilm causes the biodegradation of NOM and contributes to NOM removal during GAC filtration, which also extends the lifetime of GAC filters (Velten et al., 2011).

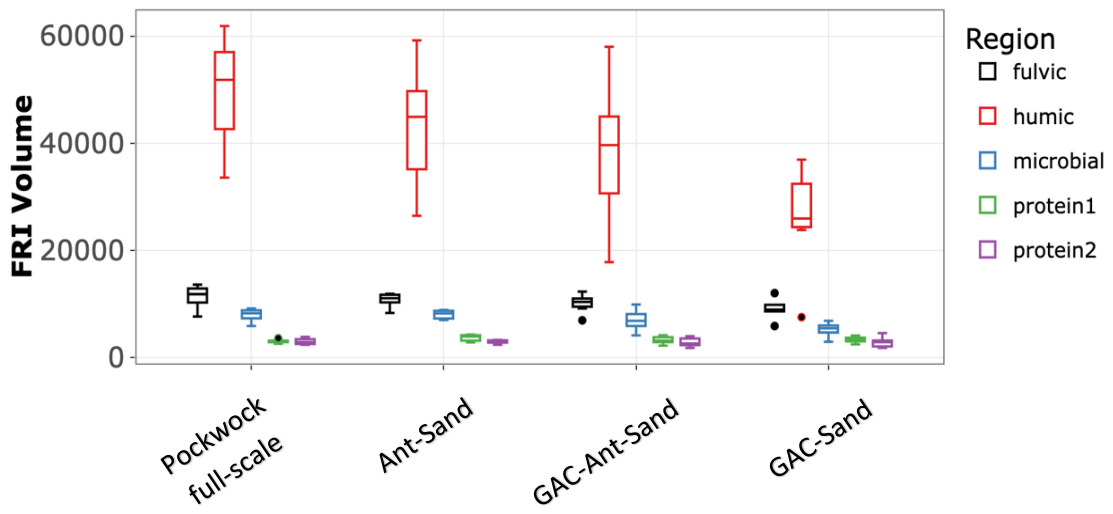

Figure 15. FRI volume of five EEM regions in studied filtered waters.

4.2 Exploration of The Impact of The Sequence of UV LED and Chlorine Disinfection on DBP Formation

The following box plots describe the concentration of DBP formed under different disinfection conditions in studied filtered water. The total DBP in this study represents the sum of THAA and TTHM. There are seven disinfection treatments in each plot made of three UV fluences (20, 40, and 80 mJ/cm^2), different sequences of UV radiation and chlorination (UVCl and ClUV), and a control (Cl). The impact of these disinfection conditions on the DBP formation is shown below.

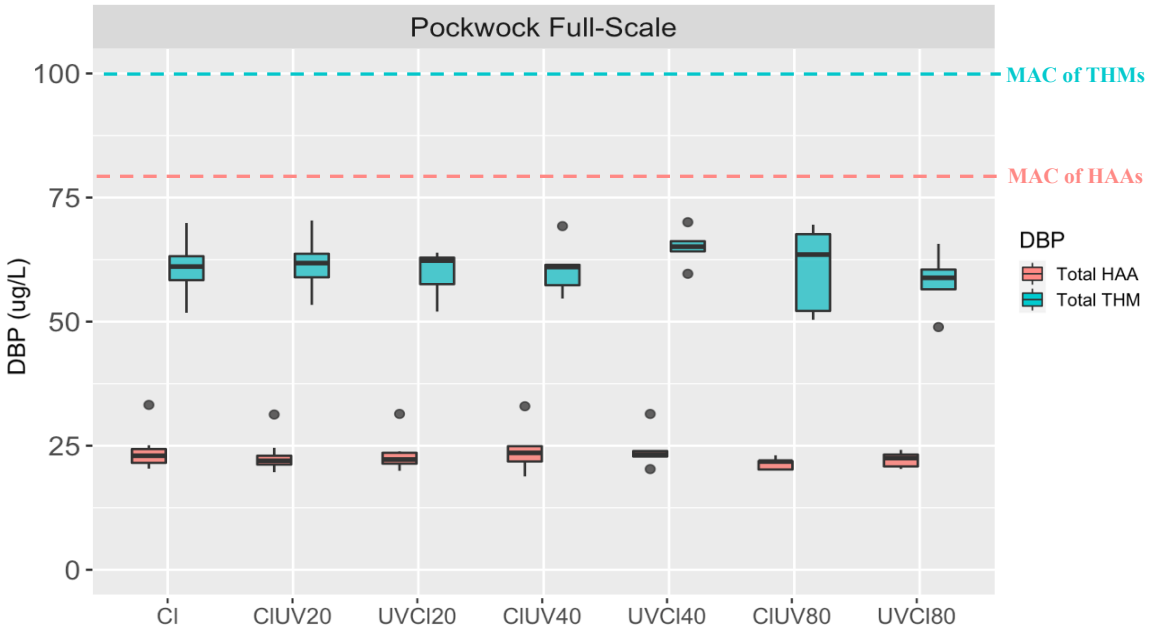

Figure 16. DBP formation under different disinfection treatment conditions in Pockwock full-scale filtered water.

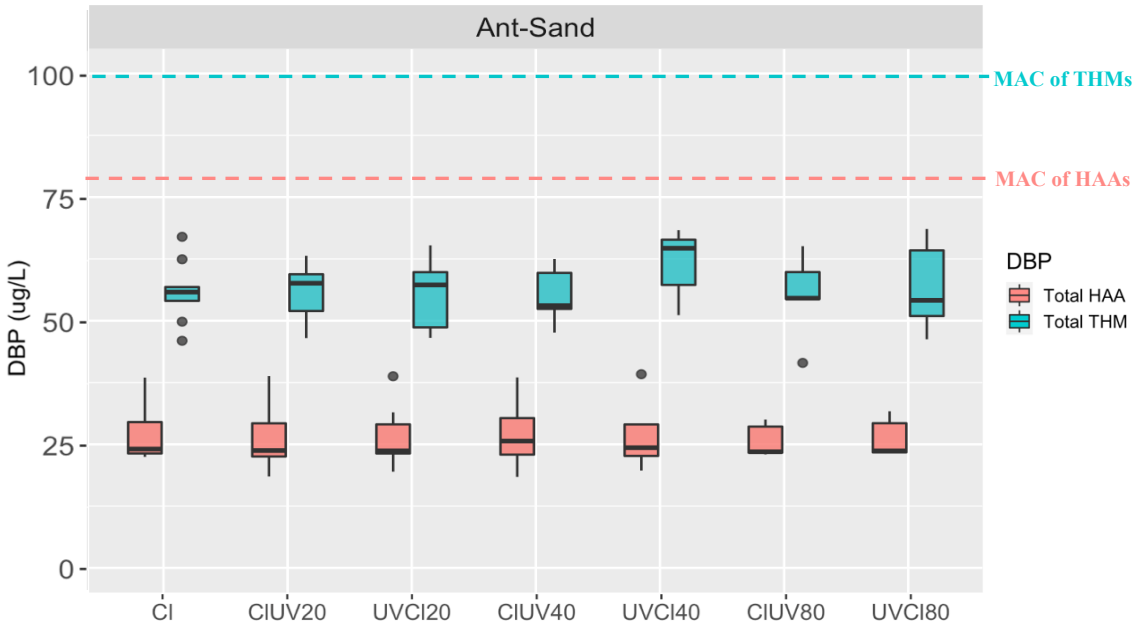

Figure 17. DBP formation under different disinfection treatment conditions in Ant-Sand filtered water.

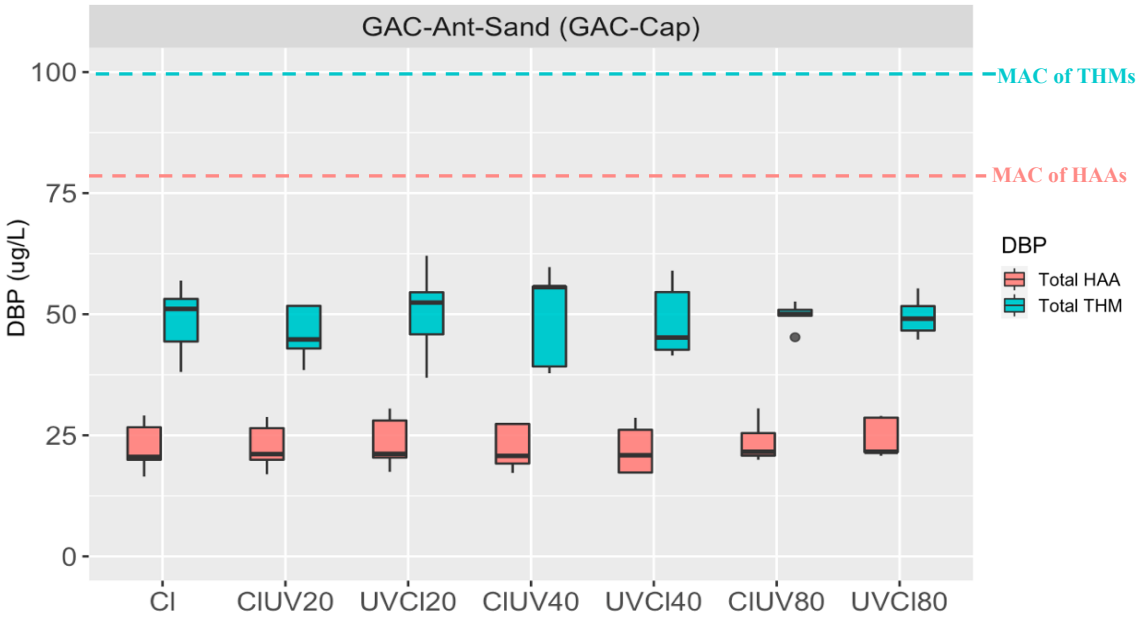

Figure 18. DBP formation under different disinfection treatment conditions in GAC-Ant-Sand filtered water.

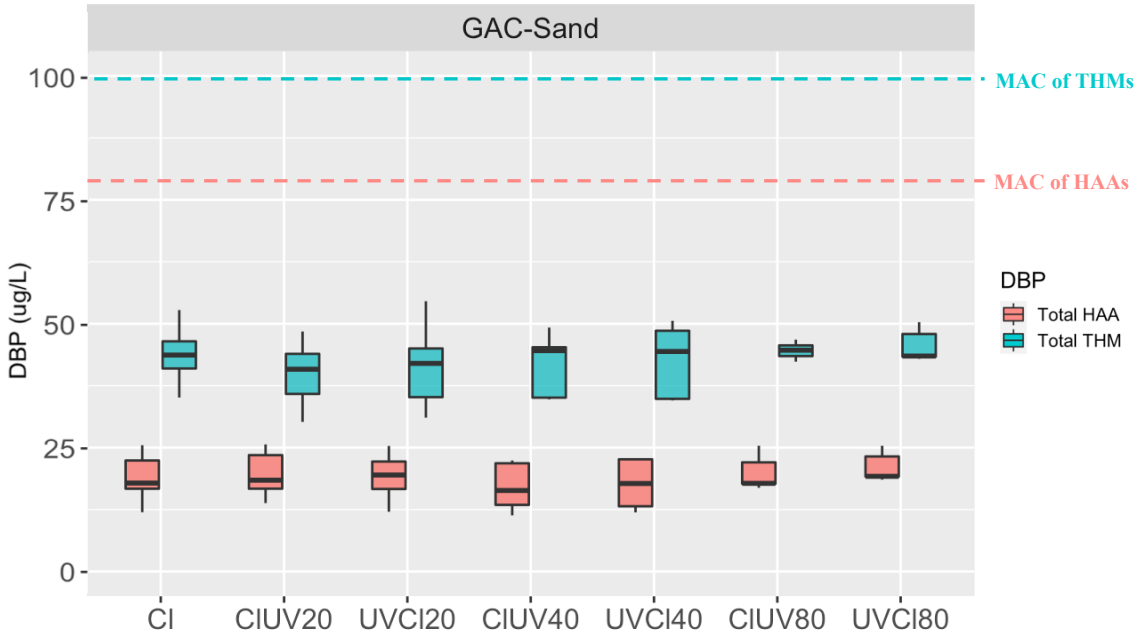

Figure 19. DBP formation under different disinfection treatment conditions in GAC-Sand filtered water.

The overall results of this study found that the combination of UV LED and chlorine did not significantly impact DBP formation in all studied waters. In the first three filtered waters, the THAA levels stayed consistent under different disinfection conditions. In the GAC-Sand filtered water, some minor difference in THAA levels was observed. Besides, there was no significant difference in TTHM among all studied filtered waters. While in Ant-Sand and GAC-Sand filtered waters, water chlorinated first produced relatively lesser THMs than being radiated by UV LED first. For more details about the impact of the sequence of UV LED and chlorine and UV doses on DBP formation, GAC-Sand filtered water can be taken as an example. Figure 20 presents the DBP formation in GAC-Sand filtered water.

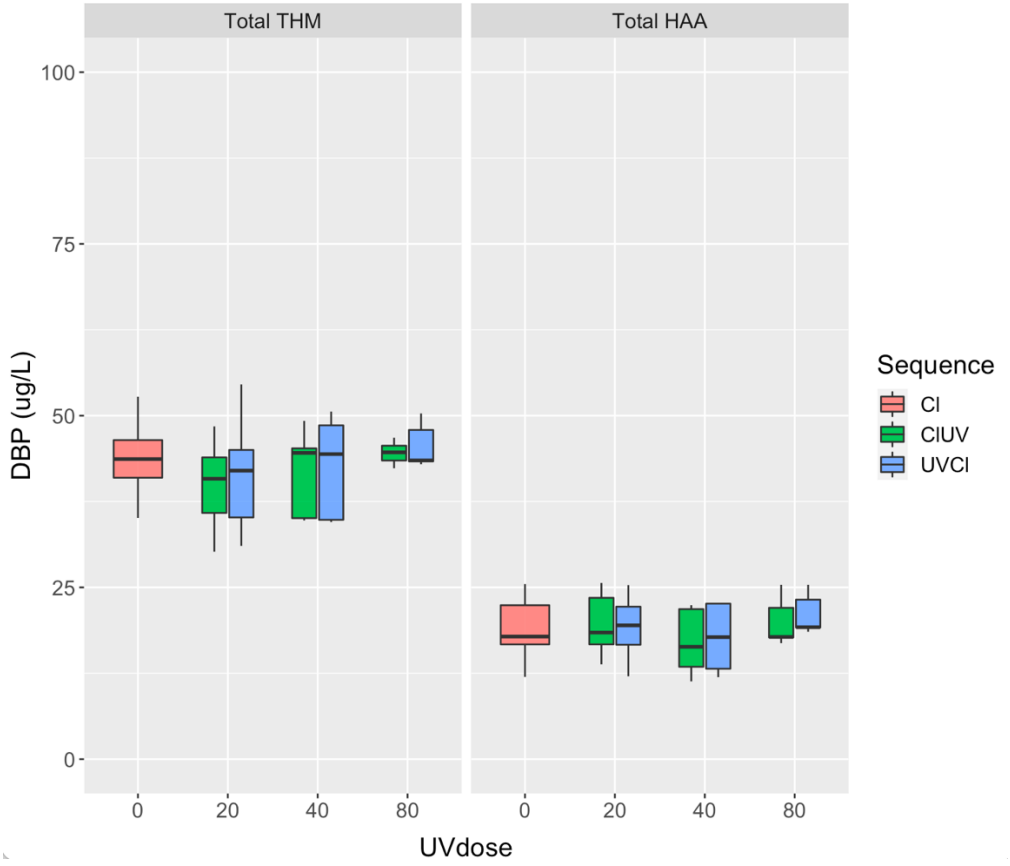

Figure 20. DBP formation under different disinfection treatment conditions in GAC-Sand filtered water.

Figure 20 illustrates more details about the effect of UV fluences on DBP formation, including the formation of TTHM, and THAA. As the plot shows, no matter in terms of TTHM or THAA, under the same UV & chlorine sequence, there was no significant difference among different UV doses. Table 8 lists the p-values of paired T-tests, which clearly shows all the p-values of the listed comparisons are above 0.05. Thus, the UV fluence employed in this study did not significantly impact DBP formation.

Table 8. P-values of paired T-test between different UV doses with the same UV/Cl sequence.

p-values of Paired T-test (Alpha = 0.05)				
	UVCl20/UVCl40	UVCl20/UVCl80	ClUV20/ClUV40	ClUV20/ClUV80
TTHM	0.50	0.16	0.16	0.50
THAA	0.74	0.96	0.76	0.10

For further exploring the effect of the sequence of UV & chlorine, the boxes representing different sequences but under the same UV dose in Figure 20 can be paired. With the exception of the paired THAA data under UVCl20 / ClUV20, other pairs showed the box of ClUV has a higher upper quartile than UVCl. A series of paired T-tests was conducted for those paired data and the corresponding p-values are listed in Table 9 as below.

Table 9. P-values of paired T-test between different UV & chlorine sequences.

p-values of Paired T-test (Alpha = 0.05)			
	UVCl20/ClUV20	UVCl40/ClUV40	UVCl80/ClUV80
TTHM	0.91	0.12	0.039
THAA	0.96	0.33	0.23

Overall, among studied filtered waters, different UV fluences (20, 40, and 80 mJ/cm^2), had little influence on TTHM and THAA formation. Within the studied UV dose range (< 80 mJ/cm^2), the sequence of UV LED and chlorination did not significantly impact TTHM and THAA formation. While this result only clarified the impact of UV doses and UV & chlorine sequences on regulated THM and HAA in drinking water disinfection treatment. Their impact on unknown DBPs needs to be explored further.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

This study used different filtered waters from JDKWSP to investigate the performance of GAC filtration on removing NOM and reducing DBPFP in drinking water. The UFC test was conducted for comparing the DBPFP in studied filtered waters, which indicated that sedimentation in the pilot plant had little effect on the DBP formation reduction and the implementation of GAC significantly decreased the DBP formation potential of filtered water.

A comparative evaluation of some surrogate parameters (TOC, UV_{254}, and SUVA) of NOM and DBPFP showed that TOC and UV_{254} were good indicators of DBP precursors in this case. Compared to the TOC of Ant-Sand filtered water, GAC-Ant-Sand and GAC-Sand filters contributed 10% and 20% of TOC removal, respectively. GAC medias employed in the GAC-Ant-Sand and GAC-Sand filters were mostly exhausted, which theoretically were only able to remove around 5% and 17.5% average by adsorption. The extra TOC removal proportion could be the result of biodegradation. Biodegradation occurring in GAC filtration has been observed and studied by many researchers, which happens since active biofilm forms onto the GAC surface and extends the service life of GAC to some extent (Babi et al., 2007; Gibert et al., 2013; Yuan et al., 2022). The UV_{254} accorded well with TOC and DBP formation potential in all studied filtered waters.

Different from TOC and UV_{254}, SUVA did not demonstrate a significant difference between Ant-Sand and GAC-Ant-Sand filtered waters, which identified SUVA as not a good predictor of DBP formation in this study. One of the reasons could be that SUVA is a parameter strongly correlated with aromaticity, which is not associated well with NOM/DBP formation in water with low aromaticity and SUVA (Ates et al., 2007; Weishaar et al., 2003). The other reason could be the exhaustion of GAC. Exhausted GAC had a low capacity to adsorb NOM/DBP precursors, which caused the similarity of SUVA between some studied waters.

To investigate the change of organic components after GAC filtration, fluorescence spectroscopy was used in this study. Unsurprisingly, humic acid-like materials accounted for the largest proportion of FRI volume in all studied filtered waters, and it decreased with the implementation of GAC. The FRI volume of the humic acid-like region in GAC-Sand filtered water was significantly lower than that in the Ant-Sand filtered water. Same as SUVA showing, the difference in humic acid-like FRI volume between Ant-Sand and GAC-Ant-Sand filtered waters was not statistically significant, which proved the exhaustion of GAC in the GAC-Ant-Sand filter. Apart from the GAC exhaustion, the great error bars of humic acid materials might be the other reason cause the insignificant difference. The FEEM is featured with high resolution, which can capture changes in NOM character that could cause variability in the measurement (Peleato et al., 2016). The other component impacted by GAC filtration was microbial materials, which decreased with GAC implementation as well. The rest of the three components (fulvic acid-like materials,

protein I, and protein II) were not significantly removed by GAC filtration in all studied waters.

In the subsequent disinfection experiments, the sequences of UV LED disinfection and chlorination were found to have little impact on regulated THM and HAA formation, which accords with the results that Y. Chen et al. reported in 2022. While in terms of the inactivation of microorganisms, some studies have found irradiating water with UV before chlorination can enhance disinfection efficiency during disinfection treatment (L. Liu et al., 2019). Thus, for designing the practical UV/Cl disinfection treatment process, WTPs do not need to concern different UV/Cl sequences might impact DBP formation, but the disinfection efficiency. The combination of UV and chlorine also has been investigated as an AOP technology in water treatment. Different from disinfection condition, UV/Cl AOP is characterized by high UV and chlorine dose, in which the sequence of UV and chlorine significantly impact DBP formation, especially for THM formation (Cerreta et al., 2020; W.-L. Wang et al., 2017).

5.2 Recommendations

Based on the results of this study, some recommendations will be provided for further research in this section.

(1) Some recent studies have found that UV radiation can react with chlorine in water to generate radicals, which play an important role in organic matter degradation (S. He et al., 2023; H. Liu et al., 2020). Para-chlorobenzoic acid (pCBA) has been used recently as a

hydroxyl radical probe and can be detected by high-performance liquid chromatography (HPLC) (Peng et al., 2022; Pi et al., 2005). The results in this study did not show significant differences among different UV/chlorine disinfection treatments on DBP formation. Thus, pCBA can be used as a hydroxyl radicals' probe to monitor radicals that are generated under different UV/chlorine disinfection treatments.

(2) The same experiments can be conducted with higher UV fluences for determining the effect of combining higher UV LED dose disinfection and chlorination on DBP formation.

(3) Apart from DBP formation, disinfection efficiency is also an aspect to evaluate a disinfection treatment process. Although the UV dose (below 80 mJ/cm^2) and the sequence of UV LED and chlorine did not impact DBP formation, it might have influence on inactivating pathogens and bacteria. Thus, the disinfection performance of disinfection conditions with different UV doses and UV/Cl sequences can be monitored for comparison.

(4) In this research, only total THMs and HAAs were monitored and considered as total DBPs. However, there are over 600 kinds of DBPs have been found in previous studies (Krasner et al., 2006; Lavonen et al., 2013). The remaining of DBPs might be sensitive with different UV LED disinfection dose and the UV/Cl sequence. Thus, detecting more types of DBP will help to accurately determine if the UV disinfection dose and UV/Cl sequence impact the formation of all types of DBP or not.

References

Abkar, L., Stoddart, A. K., & Gagnon, G. A. (2019). Sedimentation: Hydraulic improvement of drinking water biofiltration. AWWA Water Science, 1(5), e1160. https://doi.org/10.1002/aws2.1160

Adin, A., Katzhendler, J., Alkaslassy, D., & Rav-Acha, Ch. (1991). Trihalomethane formation in chlorinated drinking water: A kinetic model. Water Research, 25(7), 797–805. https://doi.org/10.1016/0043-1354(91)90159-N

Albanakis, C., Tsanana, E., & Fragkaki, A. G. (2021). Modeling and prediction of trihalomethanes in the drinking water treatment plant of Thessaloniki, Greece. Journal of Water Process Engineering, 43, 102252. https://doi.org/10.1016/j.jwpe.2021.102252

Alexandrou, L., Meehan, B. J., & Jones, O. A. H. (2018). Regulated and emerging disinfection by-products in recycled waters. Science of The Total Environment, 637–638, 1607–1616. https://doi.org/10.1016/j.scitotenv.2018.04.391

Alomar, T., Qiblawey, H., Almomani, F., Al-Raoush, R. I., Han, D. S., & Ahmad, N. M. (2023). Recent advances on humic acid removal from wastewater using adsorption process. Journal of Water Process Engineering, 53, 103679. https://doi.org/10.1016/j.jwpe.2023.103679

Alver, A., Baştürk, E., & Kılıç, A. (2018). Disinfection By-Products Formation Potential Along the Melendiz River, Turkey; Associated Water Quality Parameters and Non-Linear Prediction Model. International Journal of Environmental Research, 12(6), 909–919. https://doi.org/10.1007/s41742-018-0145-4

Anderson, L. E., Krkošek, W. H., Stoddart, A. K., Trueman, B. F., & Gagnon, G. A. (2017). Lake Recovery Through Reduced Sulfate Deposition: A New Paradigm for Drinking Water Treatment. Environmental Science & Technology, 51(3), 1414–1422. https://doi.org/10.1021/acs.est.6b04889

Ang, W. L., Mohammad, A. W., Teow, Y. H., Benamor, A., & Hilal, N. (2015a). Hybrid chitosan/FeCl3 coagulation–membrane processes: Performance evaluation and membrane fouling study in removing natural organic matter. Separation and Purification Technology, 152, 23–31. https://doi.org/10.1016/j.seppur.2015.07.053

Ang, W. L., Mohammad, A. W., Teow, Y. H., Benamor, A., & Hilal, N. (2015b). Hybrid chitosan/FeCl3 coagulation–membrane processes: Performance evaluation and membrane fouling study in removing natural organic matter. Separation and Purification Technology, 152, 23–31. https://doi.org/10.1016/j.seppur.2015.07.053

Archer, A. D., & Singer, P. C. (2006). An evaluation of the relationship between SUVA and NOM coagulation using the ICR database. Journal AWWA, 98(7), 110–123. https://doi.org/10.1002/j.1551-8833.2006.tb07715.x

Arena, N., Lee, J., & Clift, R. (2016). Life Cycle Assessment of activated carbon production from coconut shells. Journal of Cleaner Production, 125, 68–77. https://doi.org/10.1016/j.jclepro.2016.03.073

Ates, N., Kitis, M., & Yetis, U. (2007). Formation of chlorination by-products in waters with low SUVA—correlations with SUVA and differential UV spectroscopy. Water Research, 41(18), 4139–4148. https://doi.org/10.1016/j.watres.2007.05.042

AWWA Membrane Technology Research Committee. (1998). Committee Report: Membrane processes. Journal AWWA, 90(6), 91–105. https://doi.org/10.1002/j.1551-8833.1998.tb08457.x

Babi, K. G., Koumenides, K. M., Nikolaou, A. D., Makri, C. A., Tzoumerkas, F. K., & Lekkas, T. D. (2007). Pilot study of the removal of THMs, HAAs and DOC from drinking water by GAC adsorption. Desalination, 210(1), 215–224. https://doi.org/10.1016/j.desal.2006.05.046

Barceló, D. (Ed.). (2012). Emerging Organic Contaminants and Human Health (Vol. 20). Springer. https://doi.org/10.1007/978-3-642-28132-7

Bhatnagar, A., & Sillanpää, M. (2017). Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review. Chemosphere, 166, 497–510. https://doi.org/10.1016/j.chemosphere.2016.09.098

Bolton, J. R., & Linden, K. G. (2003). Standardization of Methods for Fluence (UV Dose) Determination in Bench-Scale UV Experiments. Journal of Environmental Engineering, 129(3), 209–215. https://doi.org/10.1061/(ASCE)0733-9372(2003)129:3(209)

Boorman, G. A. (1999). Drinking water disinfection byproducts: Review and approach to toxicity evaluation. Environmental Health Perspectives, 107(suppl 1), 207–217. https://doi.org/10.1289/ehp.99107s1207

Bridgeman, J., Bieroza, M., & Baker, A. (2011). The application of fluorescence spectroscopy to organic matter characterisation in drinking water treatment. Reviews in Environmental Science and Bio/Technology, 10(3), 277–290. https://doi.org/10.1007/s11157-011-9243-x

Bridgewater, L. L., Baird, R. B., Eaton, A. D., Rice, E. W., American Public Health Association, American Water Works Association, & Water Environment Federation (Eds.). (2017). Standard methods for the examination of water and wastewater (23rd edition). American Public Health Association.

Brown, D., Bridgeman, J., & West, J. R. (2011). Predicting chlorine decay and THM formation in water supply systems. Reviews in Environmental Science and Bio/Technology, 10(1), 79–99. https://doi.org/10.1007/s11157-011-9229-8

Cerreta, G., Roccamante, M. A., Plaza-Bolaños, P., Oller, I., Aguera, A., Malato, S., & Rizzo, L. (2020). Advanced treatment of urban wastewater by UV-C/free chlorine process: Micro-pollutants removal and effect of UV-C radiation on trihalomethanes formation. Water Research, 169, 115220. https://doi.org/10.1016/j.watres.2019.115220

Chaukura, N., Marais, S. S., Moyo, W., Mbali, N., Thakalekoala, L. C., Ingwani, T., Mamba, B. B., Jarvis, P., & Nkambule, T. T. I. (2020). Contemporary issues on the occurrence and removal of disinfection byproducts in drinking water—A review. Journal of Environmental Chemical Engineering, 8(2), 103659. https://doi.org/10.1016/j.jece.2020.103659

Chen, H., Lin, T., Chen, W., Tao, H., & Xu, H. (2019). Removal of disinfection byproduct precursors and reduction in additive toxicity of chlorinated and chloraminated waters by ozonation and up-flow biological activated carbon process. Chemosphere, 216, 624–632. https://doi.org/10.1016/j.chemosphere.2018.10.052

Chen, W., Westerhoff, P., Leenheer, J. A., & Booksh, K. (2003). Fluorescence Excitation−Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. Environmental Science & Technology, 37(24), 5701–5710. https://doi.org/10.1021/es034354c

Chen, Y., Jafari, I., Zhong, Y., Chee, M. J., & Hu, J. (2022). Degradation of organics and formation of DBPs in the combined LED-UV and chlorine processes: Effects of water matrix and fluorescence analysis. Science of The Total Environment, 846, 157454. https://doi.org/10.1016/j.scitotenv.2022.157454

Chow, A. T., Dahlgren, R. A., & Harrison, J. A. (2007). Watershed Sources of Disinfection Byproduct Precursors in the Sacramento and San Joaquin Rivers, California. Environmental Science & Technology, 41(22), 7645–7652. https://doi.org/10.1021/es070621t

Chowdhury, Z. K. (2013). Activated Carbon: Solutions for Improving Water Quality. American Water Works Association.

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry, 51(4), 325–346. https://doi.org/10.1016/0304-4203(95)00062-3

Cook, D., Newcombe, G., & Sztajnbok, P. (2001). The application of powdered activated carbon for mib and geosmin removal: Predicting pac doses in four raw waters. Water Research, 35(5), 1325–1333. https://doi.org/10.1016/S0043-1354(00)00363-8

Dastgheib, S. A., Karanfil, T., & Cheng, W. (2004). Tailoring activated carbons for enhanced removal of natural organic matter from natural waters. Carbon, 42(3), 547–557. https://doi.org/10.1016/j.carbon.2003.12.062

Delpla, I., Jung, A.-V., Baures, E., Clement, M., & Thomas, O. (2009). Impacts of climate change on surface water quality in relation to drinking water production. Environment International, 35(8), 1225–1233. https://doi.org/10.1016/j.envint.2009.07.001

Dong, L., Liu, W., Jiang, R., & Wang, Z. (2014). Physicochemical and porosity characteristics of thermally regenerated activated carbon polluted with biological activated carbon process. Bioresource Technology, 171, 260–264. https://doi.org/10.1016/j.biortech.2014.08.067

Dotson, A. D., Rodriguez, C. E., & Linden, K. G. (2012). UV disinfection implementation status in US water treatment plants. Journal (American Water Works Association), 104(5), E318–E324.

Driscoll, C. T., Likens, G. E., & Church, M. R. (1998). Recovery of Surface Waters in the Northeastern U.S. from Decreases in Atmospheric Deposition of Sulfur. Water, Air, and Soil Pollution, 105(1), 319–329. https://doi.org/10.1023/A:1005008315977

Duarte, R. M. B. O., & Duarte, A. C. (2020). Multidimensional analytical techniques in environmental research: Evolution of concepts. In Multidimensional Analytical Techniques in Environmental Research (pp. 1–26). Elsevier. https://doi.org/10.1016/B978-0-12-818896-5.00001-6

Dunn, O. J. (1961). Multiple Comparisons among Means. Journal of the American Statistical Association, 56(293), 52–64. https://doi.org/10.1080/01621459.1961.10482090

Edzwald, J. K., Becker, W. C., & Wattier, K. L. (1985). Surrogate Parameters for Monitoring Organic Matter and THM Precursors. Journal AWWA, 77(4), 122–132. https://doi.org/10.1002/j.1551-8833.1985.tb05521.x

Eikebrokk, B., Vogt, R. D., & Liltved, H. (2004). NOM increase in Northern European source waters: Discussion of possible causes and impacts on coagulation/contact filtration processes. Water Science & Technology: Water Supply, 4(4), 47–54.

Fabris, R., Chow, C. W. K., Drikas, M., & Eikebrokk, B. (2008). Comparison of NOM character in selected Australian and Norwegian drinking waters. Water Research, 42(15), 4188–4196. https://doi.org/10.1016/j.watres.2008.06.023

Fellman, J. B., Hood, E., & Spencer, R. G. M. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. Limnology and Oceanography, 55(6), 2452–2462. https://doi.org/10.4319/lo.2010.55.6.2452

Fernández-Pascual, E., Droz, B., O'Dwyer, J., O'Driscoll, C., Goslan, E. H., Harrison, S., & Weatherill, J. (2023). Fluorescent Dissolved Organic Matter Components as Surrogates for Disinfection Byproduct Formation in Drinking Water: A Critical Review. ACS ES&T Water, acsestwater.2c00583. https://doi.org/10.1021/acsestwater.2c00583

F. Trueman, B., A. MacIsaac, S., K. Stoddart, A., & A. Gagnon, G. (2016). Prediction of disinfection by-product formation in drinking water via fluorescence spectroscopy. Environmental Science: Water Research & Technology, 2(2), 383–389. https://doi.org/10.1039/C5EW00285K

Fu, P., Ruiz, H., Thompson, K., & Spangenberg, C. (1994). Selecting membranes for removing NOM and DBP precursors. Journal AWWA, 86(12), 55–72. https://doi.org/10.1002/j.1551-8833.1994.tb06286.x

Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M., & Pons, M. (2013). Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production. Water Research, 47(8), 2821–2829. https://doi.org/10.1016/j.watres.2013.02.028

Gilca, A. F., Teodosiu, C., Fiore, S., & Musteret, C. P. (2020). Emerging disinfection byproducts: A review on their occurrence and control in drinking water treatment processes. Chemosphere, 259, 127476. https://doi.org/10.1016/j.chemosphere.2020.127476

Golea, D. M., Jarvis, P., Jefferson, B., Moore, G., Sutherland, S., Parsons, S. A., & Judd, S. J. (2020). Influence of granular activated carbon media properties on natural organic matter and disinfection by-product precursor removal from drinking water. Water Research, 174, 115613. https://doi.org/10.1016/j.watres.2020.115613

Gopal, K., Tripathy, S. S., Bersillon, J. L., & Dubey, S. P. (2007). Chlorination byproducts, their toxicodynamics and removal from drinking water. Journal of Hazardous Materials, 140(1–2), 1–6. https://doi.org/10.1016/j.jhazmat.2006.10.063

Goslan, E. H., Seigle, C., Purcell, D., Henderson, R., Parsons, S. A., Jefferson, B., & Judd, S. J. (2017). Carbonaceous and nitrogenous disinfection by-product formation from algal organic matter. Chemosphere, 170, 1–9. https://doi.org/10.1016/j.chemosphere.2016.11.148

Grünwald, A., Šťastný, B., Slavíčková, K., & Slavíček, M. (2002). Formation of Haloforms during Chlorination of Natural Waters. Acta Polytechnica, 42(2), Article 2. https://doi.org/10.14311/334

Harrington, G. W., Bruchet, A., Rybacki, D., & Singer, P. C. (1996). Characterization of Natural Organic Matter and Its Reactivity with Chlorine. In Water Disinfection and Natural Organic Matter (Vol. 649, pp. 138–158). American Chemical Society. https://doi.org/10.1021/bk-1996-0649.ch010

He, J., Wang, F., Zhao, T., Liu, S., & Chu, W. (2020). Characterization of dissolved organic matter derived from atmospheric dry deposition and its DBP formation. Water Research, 171, 115368. https://doi.org/10.1016/j.watres.2019.115368

He, S., Ling, L., Wu, Y., Yang, S., Hua, Z., Tang, K., Wang, M., Zhu, M., & Fang, J. (2023). Roles of Activated Carbon in UV/Chlorine/Activated Carbon–TiO 2 Process for Micropollutant Abatement and DBP Control. Environmental Science & Technology, acs.est.3c01989. https://doi.org/10.1021/acs.est.3c01989

Health Canada. (2014, October 22). Guidelines for Canadian Drinking Water Quality—Summary Tables [Guidance]. Summary of the Guidelines for Canadian Drinking Water Quality. https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/water-quality/guidelines-canadian-drinking-water-quality-summary-table.html

Hodgeson, J. W., Collins, J., Barth, R. E., Munch, D. J., Munch, J. W., & Pawlecki, A. M. (1995). DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION.

Hodgeson, J. W., & Munch, D. J. (1990). DETERMINATION OF CHLORINATION DISINFECTION BYPRODUCTS, CHLORINATED SOLVENTS, AND HALOGENATED PESTICIDES/HERBICIDES IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION.

Hoslett, J., Massara, T. M., Malamis, S., Ahmad, D., van den Boogaert, I., Katsou, E., Ahmad, B., Ghazal, H., Simons, S., Wrobel, L., & Jouhara, H. (2018). Surface water filtration using granular media and membranes: A review. Science of The Total Environment, 639, 1268–1282. https://doi.org/10.1016/j.scitotenv.2018.05.247

Hrudey, S. E. (2009). Chlorination disinfection by-products, public health risk tradeoffs and me. Water Research, 43(8), 2057–2092. https://doi.org/10.1016/j.watres.2009.02.011

Hua, G., & Reckhow, D. A. (2007). Characterization of Disinfection Byproduct Precursors Based on Hydrophobicity and Molecular Size. Environmental Science & Technology, 41(9), 3309–3315. https://doi.org/10.1021/es062178c

Hua, G., Reckhow, D. A., & Abusallout, I. (2015). Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. Chemosphere, 130, 82–89. https://doi.org/10.1016/j.chemosphere.2015.03.039

Hull, N. M., Herold, W. H., & Linden, K. G. (2019). UV LED water disinfection: Validation and small system demonstration study. AWWA Water Science, 1(4), e1148. https://doi.org/10.1002/aws2.1148

Jacangelo, J. G., DeMarco, J., Owen, D. M., & Randtke, S. J. (1995). Selected processes for removing NOM: On overview. Journal (American Water Works Association), 87(1), 64–77.

Jeyanayagam, S., & Cotton, C. (2002). Practical considerations in the use of UV light for drinking water disinfection. 373Megabytes.

Kaarela, O., Koppanen, M., Kesti, T., Kettunen, R., Palmroth, M., & Rintala, J. (2021). Natural organic matter removal in a full-scale drinking water treatment plant using ClO2 oxidation: Performance of two virgin granular activated carbons. Journal of Water Process Engineering, 41, 102001. https://doi.org/10.1016/j.jwpe.2021.102001

Karanfil, T. (2006). Chapter 7 Activated carbon adsorption in drinking water treatment. In T. J. Bandosz (Ed.), Interface Science and Technology (Vol. 7, pp. 345–373). Elsevier. https://doi.org/10.1016/S1573-4285(06)80016-5

Karanfil, T., Schlautman, M. A., & Erdogan, I. (2002). Survey of DOC and UV measurement practices with implications for SUVA determination. Journal AWWA, 94(12), 68–80. https://doi.org/10.1002/j.1551-8833.2002.tb10250.x

Kheyrandish, A., Taghipour, F., & Mohseni, M. (2018). UV-LED radiation modeling and its applications in UV dose determination for water treatment. Journal of Photochemistry and Photobiology A: Chemistry, 352, 113–121. https://doi.org/10.1016/j.jphotochem.2017.10.047

Kim, H.-C., & Yu, M.-J. (2005a). Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Research, 39(19), 4779–4789. https://doi.org/10.1016/j.watres.2005.09.021

Kim, H.-C., & Yu, M.-J. (2005b). Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Research, 39(19), 4779–4789. https://doi.org/10.1016/j.watres.2005.09.021

Kim, J., & Kang, B. (2008). DBPs removal in GAC filter-adsorber. Water Research, 42(1–2), 145–152. https://doi.org/10.1016/j.watres.2007.07.040

Kitis, M., Karanfil, T., Kilduff, J. E., & Wigton, A. (2001). The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance. Water Science and Technology, 43(2), 9–16. https://doi.org/10.2166/wst.2001.0067

Knowles, A. D., MacKay, J., & Gagnon, G. A. (2012). Pairing a pilot plant to a direct filtration water treatment plant. Canadian Journal of Civil Engineering, 39(6), 689–700. https://doi.org/10.1139/l2012-060

Koch, B., Krasner, S. W., Sclimenti, M. J., & Schimpff, W. K. (1991). Predicting the Formation of DBPs by the Simulated Distribution System. Journal (American Water Works Association), 83(10), 62–70.

Korotta-Gamage, S. M., & Sathasivan, A. (2017). A review: Potential and challenges of biologically activated carbon to remove natural organic matter in drinking water purification process. Chemosphere, 167, 120–138. https://doi.org/10.1016/j.chemosphere.2016.09.097

Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Sclimenti, M. J., Onstad, G. D., & Thruston, A. D. (2006). Occurrence of a New Generation of Disinfection Byproducts. Environmental Science & Technology, 40(23), 7175–7185. https://doi.org/10.1021/es060353j

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-Kopplin, P., & Köhler, S. J. (2013). Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts. Environmental Science & Technology, 47(5), 2264–2271. https://doi.org/10.1021/es304669p

Lee, J.-K., & Shin, G.-A. (2011). Inactivation of human adenovirus by sequential disinfection with an alternative UV technology and free chlorine. Journal of Water and Health, 9(1), 53–58. https://doi.org/10.2166/wh.2010.044

Levchuk, I., Rueda Márquez, J. J., & Sillanpää, M. (2018). Removal of natural organic matter (NOM) from water by ion exchange – A review. Chemosphere, 192, 90–104. https://doi.org/10.1016/j.chemosphere.2017.10.101

Li, C.-W., Korshin, G. V., & Benjamin, M. M. (1998). Monitoring DBP formation with differential UV spectroscopy. Journal AWWA, 90(8), 88–100. https://doi.org/10.1002/j.1551-8833.1998.tb08488.x

Li, X.-F., & Mitch, W. A. (2018). Drinking Water Disinfection Byproducts (DBPs) and Human Health Effects: Multidisciplinary Challenges and Opportunities. Environmental Science & Technology, 52(4), 1681–1689. https://doi.org/10.1021/acs.est.7b05440

Li, Y., Shen, W., Fu, S., Yang, H., Yu, G., & Wang, Y. (2015). Inhibition of bromate formation during drinking water treatment by adapting ozonation to electro-peroxone process. Chemical Engineering Journal, 264, 322–328. https://doi.org/10.1016/j.cej.2014.11.120

Liao, X. B., Cheng, Y. S., Liu, Z. H., Shen, L. L., Zhao, L., Chen, C., Li, F., & Zhang, X. J. (2020). Performance of BAC for DBPs precursors' removal for one year with micro-polluted lake water in East-China. Environmental Technology, 41(27), 3554–3561. https://doi.org/10.1080/09593330.2019.1615132

Liu, H., Zhang, B., Li, Y., Fang, Q., Hou, Z., Tian, S., & Gu, J. (2020). Effect of Radical Species and Operating Parameters on the Degradation of Sulfapyridine Using a UV/Chlorine System. Industrial & Engineering Chemistry Research, 59(4), 1505–1516. https://doi.org/10.1021/acs.iecr.9b06228

Liu, L., Xing, X., Hu, C., Wang, H., & Lyu, L. (2019). Effect of sequential UV/free chlorine disinfection on opportunistic pathogens and microbial community structure in simulated drinking water distribution systems. Chemosphere, 219, 971–980. https://doi.org/10.1016/j.chemosphere.2018.12.067

Lønborg, C., Carreira, C., Jickells, T., & Álvarez-Salgado, X. A. (2020). Impacts of Global Change on Ocean Dissolved Organic Carbon (DOC) Cycling. Frontiers in Marine Science. https://doi.org/10.3389/fmars.2020.00466

Marais, S. S., Ncube, E. J., Msagati, T. A. M., Mamba, B. B., & Nkambule, T. T. I. (2018). Comparison of natural organic matter removal by ultrafiltration, granular activated carbon filtration and full scale conventional water treatment. Journal of Environmental Chemical Engineering, 6(5), 6282–6289. https://doi.org/10.1016/j.jece.2018.10.002

Marais, S. S., Ncube, E. J., Msagati, T. A. M., Mamba, B. B., & Nkambule, T. T. I. (2019). Assessment of trihalomethane (THM) precursors using specific ultraviolet absorbance (SUVA) and molecular size distribution (MSD). Journal of Water Process Engineering, 27, 143–151. https://doi.org/10.1016/j.jwpe.2018.11.019

Marhaba, T. F., & Kochar, I. H. (1999). Rapid prediction of disinfection by-product formation potential by fluorescence. Environmental Engineering and Policy, 2(1), 29–36. https://doi.org/10.1007/BF03500904

Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A., & Sillanpää, M. (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere, 83(11), 1431–1442. https://doi.org/10.1016/j.chemosphere.2011.01.018

Matilainen, A., Lindqvist, N., Korhonen, S., & Tuhkanen, T. (2002). Removal of NOM in the different stages of the water treatment process. Environment International, 28(6), 457–465. https://doi.org/10.1016/S0160-4120(02)00071-5

Matilainen, A., Vepsäläinen, M., & Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment: A review. Advances in Colloid and Interface Science, 159(2), 189–197. https://doi.org/10.1016/j.cis.2010.06.007

Mazhar, M. A., Khan, N. A., Ahmed, S., Khan, A. H., Hussain, A., Rahisuddin, Changani, F., Yousefi, M., Ahmadi, S., & Vambol, V. (2020). Chlorination disinfection by-products in municipal drinking water – A review. Journal of Cleaner Production, 273, 123159. https://doi.org/10.1016/j.jclepro.2020.123159

Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. Water Research, 139, 118–131. https://doi.org/10.1016/j.watres.2018.03.042

Minear, R. A., & Amy, G. (1995). Disinfection By-Products in Water TreatmentThe Chemistry of Their Formation and Control. CRC Press.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., & Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature, 450(7169), Article 7169. https://doi.org/10.1038/nature06316

Murphy, K. R., Stedmon, C. A., Graeber, D., & Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. PARAFAC. Analytical Methods, 5(23), 6557–6566. https://doi.org/10.1039/C3AY41160E

Najm, I., Marcinko, J., & Oppenheimer, J. (2000). Evaluating TOC analytical results. Journal AWWA, 92(8), 84–92. https://doi.org/10.1002/j.1551-8833.2000.tb08995.x

National Research Council (US) Safe Drinking Water Committee. (1980). Drinking Water and Health: Volume 2. National Academies Press (US). http://www.ncbi.nlm.nih.gov/books/NBK234592/

Newcombe, G., & Dixon, D. (2006). Interface Science in Drinking Water Treatment: Theory and Applications. Academic Press.

Nikolaou, A. D., Golfinopoulos, S. K., Lekkas, T. D., & Kostopoulou, M. N. (2004). DBP Levels in Chlorinated Drinking Water: Effect of Humic Substances. Environmental Monitoring and Assessment, 93(1–3), 301–319. https://doi.org/10.1023/B:EMAS.0000016798.53163.43

Oguma, K., Kita, R., Sakai, H., Murakami, M., & Takizawa, S. (2013). Application of UV light emitting diodes to batch and flow-through water disinfection systems. Desalination, 328, 24–30. https://doi.org/10.1016/j.desal.2013.08.014

Omar, B., Zalouk, R., EL-Gammal, M., & Soliman, S. (2023). Controlling Disinfection by-Products via Enhanced Coagulation: A Case Study, El-Nobarya Drinking Water Treatment Plant, Egypt. Scientific Journal for Damietta Faculty of Science, 0(0), 0–0. https://doi.org/10.21608/sjdfs.2023.200127.1093

Oto, T., Banal, R. G., Kataoka, K., Funato, M., & Kawakami, Y. (2010). 100 mW deep-ultraviolet emission from aluminium-nitride-based quantum wells pumped by an electron beam. Nature Photonics, 4(11), Article 11. https://doi.org/10.1038/nphoton.2010.220

Parrotta, M. J., & Bekdash, F. (1998). UV disinfection of small ground water supplies. Journal AWWA, 90(2), 71–81. https://doi.org/10.1002/j.1551-8833.1998.tb08379.x

Peleato, N. M., McKie, M., Taylor-Edmonds, L., Andrews, S. A., Legge, R. L., & Andrews, R. C. (2016). Fluorescence spectroscopy for monitoring reduction of natural organic matter and halogenated furanone precursors by biofiltration. Chemosphere, 153, 155–161. https://doi.org/10.1016/j.chemosphere.2016.03.018

Peng, T., Xu, C., Yang, L., Yang, B., Cai, W.-W., Gu, F., & Ying, G.-G. (2022). Kinetics and Mechanism of Degradation of Reactive Radical-Mediated Probe Compounds by the UV/Chlorine Process: Theoretical Calculation and Experimental Verification. ACS Omega, 7(6), 5053–5063. https://doi.org/10.1021/acsomega.1c06001

Pi, Y., Schumacher, J., & Jekel, M. (2005). The Use of para-Chlorobenzoic Acid (pCBA) as an Ozone/Hydroxyl Radical Probe Compound. Ozone: Science & Engineering, 27(6), 431–436. https://doi.org/10.1080/01919510500349309

Pontius, F. W. (1991). Disinfectant–Disinfection By-product Rule Update. Journal AWWA, 83(12), 24–115. https://doi.org/10.1002/j.1551-8833.1991.tb07257.x

Reckhow, D. A., Singer, P. C., & Malcolm, R. L. (1990). Chlorination of humic materials: Byproduct formation and chemical interpretations. Environmental Science & Technology, 24(11), 1655–1664. https://doi.org/10.1021/es00081a005

Rho, J. H., & Stuart, J. L. (1978). Automated three-dimensional plotter for fluorescence measurements. Analytical Chemistry, 50(4), 620–625. https://doi.org/10.1021/ac50026a020

Rizzo, L., Di Gennaro, A., Gallo, M., & Belgiorno, V. (2008). Coagulation/chlorination of surface water: A comparison between chitosan and metal salts. Separation and Purification Technology, 62(1), 79–85. https://doi.org/10.1016/j.seppur.2007.12.020

Rougé, V., von Gunten, U., & Allard, S. (2020). Efficiency of pre-oxidation of natural organic matter for the mitigation of disinfection byproducts: Electron donating capacity and UV absorbance as surrogate parameters. Water Research, 187, 116418. https://doi.org/10.1016/j.watres.2020.116418

Senesi, N., Miano, T. M., Provenzano, M. R., & Brunetti, G. (1991). CHARACTERIZATION, DIFFERENTIATION, AND CLASSIFICATION OF HUMIC SUBSTANCES BY FLUORESCENCE SPECTROSCOPY. Soil Science, 152(4), 259.

Servais, P., Billen, G., Bouillot, P., & Benezet, M. (1992). A pilot study of biological GAC filtration in drinking-water treatment. Journal of Water Supply: Research and Technology - AQUA, 41, 163–168.

Shah, A. D., Dotson, A. D., Linden, K. G., & Mitch, W. A. (2011). Impact of UV Disinfection Combined with Chlorination/Chloramination on the Formation of Halonitromethanes and Haloacetonitriles in Drinking Water. Environmental Science & Technology, 45(8), 3657–3664. https://doi.org/10.1021/es104240v

Shang, C., Cheung, L.-M., & Liu, W. (2007). MS2 Coliphage Inactivation with UV Irradiation and Free Chlorine/Monochloramine. Environmental Engineering Science, 24(9), 1321–1332. https://doi.org/10.1089/ees.2006.0261

Shannon, J. D. (1999). Regional trends in wet deposition of sulfate in the United States and SO2 emissions from 1980 through 1995. Atmospheric Environment, 33(5), 807–816. https://doi.org/10.1016/S1352-2310(98)00143-5

Sharma, V. K., Yang, X., Cizmas, L., McDonald, T. J., Luque, R., Sayes, C. M., Yuan, B., & Dionysiou, D. D. (2017). Impact of metal ions, metal oxides, and nanoparticles on the formation of disinfection byproducts during chlorination. Chemical Engineering Journal, 317, 777–792. https://doi.org/10.1016/j.cej.2017.02.071

Sillanpää, M., Ncibi, M. C., & Matilainen, A. (2018). Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. Journal of Environmental Management, 208, 56–76. https://doi.org/10.1016/j.jenvman.2017.12.009

Singer, P. C. (1994). Control of Disinfection By-Products in Drinking Water. Journal of Environmental Engineering, 120(4), 727–744. https://doi.org/10.1061/(ASCE)0733-9372(1994)120:4(727)

Singer, P. C., & Chang, S. D. (1989). Correlations Between Trihalomethanes And Total Organic Halides Formed During Water Treatment. Journal AWWA, 81(8), 61–65. https://doi.org/10.1002/j.1551-8833.1989.tb03260.x

Skjelkvåle, B. L., Wright, R. F., & Henriksen, A. (1998). Norwegian lakes show widespread recovery from acidification; results from national surveys of lakewater chemistry 1986-1997. Hydrology and Earth System Sciences, 2(4), 555–562. https://doi.org/10.5194/hess-2-555-1998

Stevens, A. A., Slocum, C. J., Seeger, D. R., & Robeck, G. G. (1976). Chlorination of Organics in Drinking Water. Journal AWWA, 68(11), 615–620. https://doi.org/10.1002/j.1551-8833.1976.tb02506.x

Stoddart, A. K., & Gagnon, G. A. (2015). Full-Scale Prechlorine Removal: Impact on Filter Performance and Water Quality. Journal AWWA, 107(12), E638–E647. https://doi.org/10.5942/jawwa.2015.107.0180

Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G., & Owen, D. (1996). Assessing DBP yield: Uniform formation conditions. Journal AWWA, 88(6), 80–93. https://doi.org/10.1002/j.1551-8833.1996.tb06573.x

Sun, Y., Angelotti, B., Brooks, M., Dowbiggin, B., Evans, P. J., Devins, B., & Wang, Z.-W. (2018). A pilot-scale investigation of disinfection by-product precursors and trace organic removal mechanisms in ozone-biologically activated carbon treatment for potable reuse. Chemosphere, 210, 539–549. https://doi.org/10.1016/j.chemosphere.2018.06.162

Symons, J. M., Krasner, S. W., Simms, L. A., & Sclimenti, M. (1993). Measurement of THM and Precursor Concentrations Revisited: The Effect of Bromide Ion. Journal AWWA, 85(1), 51–62. https://doi.org/10.1002/j.1551-8833.1993.tb05921.x

Trujillo, A. F. O. (2017). Standard Methods for the Examination of Water and Wastewater 23RD Edition. https://www.academia.edu/42904639/Standard_Methods_for_the_Examination_of_Water_and_Wastewater_23RD_Edition

Tunnell, J. W., Desjardins, A. E., Galindo, L., Georgakoudi, I., McGee, S. A., Mirkovic, J., Mueller, M. G., Nazemi, J., Nguyen, F. T., Wax, A., Zhang, Q., Dasari, R. R., & Feld, M. S. (2003). Instrumentation for Multi-modal Spectroscopic Diagnosis of Epithelial Dysplasia. Technology in Cancer Research & Treatment, 2(6), 505–514. https://doi.org/10.1177/153303460300200603

US EPA, O. (2015, October 13). Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules [Other Policies and Guidance]. https://www.epa.gov/dwreginfo/stage-1-and-stage-2-disinfectants-and-disinfection-byproducts-rules

Velten, S., Knappe, D. R. U., Traber, J., Kaiser, H.-P., Von Gunten, U., Boller, M., & Meylan, S. (2011). Characterization of natural organic matter adsorption in granular activated carbon adsorbers. Water Research, 45(13), 3951–3959. https://doi.org/10.1016/j.watres.2011.04.047

Wang, P., Ding, S., Xiao, R., An, G., Fang, C., & Chu, W. (2021). Enhanced coagulation for mitigation of disinfection by-product precursors: A review. Advances in Colloid and Interface Science, 296, 102518. https://doi.org/10.10116/j.cis.2021.102518

Wang, W.-L., Zhang, X., Wu, Q.-Y., Du, Y., & Hu, H.-Y. (2017). Degradation of natural organic matter by UV/chlorine oxidation: Molecular decomposition, formation of oxidation byproducts and cytotoxicity. Water Research, 124, 251–258. https://doi.org/10.1016/j.watres.2017.07.029

Wassink, J. K., Andrews, R. C., Peiris, R. H., & Legge, R. L. (2011). Evaluation of fluorescence excitation-emission and LC-OCD as methods of detecting removal of NOM and DBP precursors by enhanced coagulation. Water Science & Technology: Water Supply, 11(5), 621–630. https://doi.org/10.2166/ws.2011.101

Weber, Jr., W., Pirbazari, M., & Melson, G. (1978). Biological growth on activated carbon: An investigation by scanning electron microscopy. Environmental Science & Technology, 12(7), 817–819. https://doi.org/10.1021/es60143a005

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science and Technology, 37(20), 4702–4708. Scopus. https://doi.org/10.1021/es030360x

White, D. M., Garland, D. S., Narr, J., & Woolard, C. R. (2003). Natural organic matter and DBP formation potential in Alaskan water supplies. Water Research, 37(4), 939–947. https://doi.org/10.1016/S0043-1354(02)00425-6

Xu, J., Guo, Y., Yang, Q., Bai, X., Lu, R., Liu, M., Kuang, Z., Zhang, L., & Li, J. (2023). Enhanced cyanogen chloride formation after UV/PS and UV/H2O2 pre-oxidation and chlorination in natural river water. Journal of Environmental Sciences, 126, 48–57. https://doi.org/10.1016/j.jes.2022.03.049

Yan, M., Wang, D., Yu, J., Ni, J., Edwards, M., & Qu, J. (2008). Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation. Chemosphere, 71(9), 1665–1673. https://doi.org/10.1016/j.chemosphere.2008.01.019

Yee, L. F., Abdullah, P., Abdullah, A., Ishak, B., & Abidin, K. N. Z. (2009). HYDROPHOBICITY CHARACTERISTICS OF NATURAL ORGANIC MATTER AND THE FORMATION OF THM. 13(1).

Yeom, Y., Han, J., Zhang, X., Shang, C., Zhang, T., Li, X., Duan, X., & Dionysiou, D. D. (2021). A review on the degradation efficiency, DBP formation, and toxicity variation in the UV/chlorine treatment of micropollutants. Chemical Engineering Journal, 424, 130053. https://doi.org/10.1016/j.cej.2021.130053

Yuan, J., Passeport, E., & Hofmann, R. (2022). Understanding adsorption and biodegradation in granular activated carbon for drinking water treatment: A critical review. Water Research, 210, 118026. https://doi.org/10.1016/j.watres.2021.118026

Zazouli, M. A., & Kalankesh, L. R. (2017). Removal of precursors and disinfection by-products (DBPs) by membrane filtration from water; a review. Journal of Environmental Health Science and Engineering, 15(1), 25. https://doi.org/10.1186/s40201-017-0285-z

Zsolnay, Á. (2003). Dissolved organic matter: Artefacts, definitions, and functions. Geoderma, 113(3), 187–209. https://doi.org/10.1016/S0016-7061(02)00361-0

Zyara, A. M., Torvinen, E., Veijalainen, A.-M., & Heinonen-Tanski, H. (2016). The Effect of UV and Combined Chlorine/UV Treatment on Coliphages in Drinking Water Disinfection. Water (20734441), 8(4), 130. https://doi.org/10.3390/w8040130

APPENDIX: R Code for Blox plots

```
# DBP in different waters script

library(tidyverse)
library(readxl)
library(ggplot2)

dbp <- read_excel("TOC.xlsx", sheet='Sheet4') %>% group_by(Name)

dbp %>%
 ggplot(aes(x=fct_relevel(Name, "Pockwock Full-Scale", after = 0L),
            y= Value,
            fill=DBP,
            cex.axis = 2)) +
 geom_boxplot(alpha=0.8,width=0.6) +
 ylim(10,100) +
 theme(text=element_text(size=15))+  theme(axis.title.x = element_text (vjust = -1))+
 theme(axis.title.y = element_text (vjust = 1))+
 scale_fill_brewer(palette = "BuPu") +
 labs(y="DBP (mg/L)", x="Filtered Waters")
```

```
# TOC script

library(tidyverse)
library(readxl)
library(ggplot2)

df <- read_excel("TOC.xlsx", sheet='Sheet1') %>% group_by(Name)
```

```
df %>%
 ggplot(aes(x=fct_relevel(Name, "Pockwock Full-Scale", after = 0L),
            y=TOC,
            fill=Name,
            cex.axis = 2)) +
 geom_boxplot(alpha=0.8,width=0.6) +
 theme(text=element_text(size=15))+ #change font size of all text
 theme(axis.title.x = element_text (vjust = -1))+
 theme(axis.title.y = element_text (vjust = 1))+
 theme(legend.position = "none") +
 scale_fill_brewer(palette = "BuPu") +
 labs(y="TOC (mg/L)", x="Filtered Waters") # alter the labels on the axis
```

```
# SUVA script

library(tidyverse)
library(readxl)
library(ggplot2)

suva <- read_excel("SUVA.xlsx", sheet='SUVA') %>% group_by(Name)

suva_mean <- summarise(df, mean(SUVA))
suva_sd <- summarise(df, sd(SUVA))

suva %>%
 ggplot(aes(x=fct_relevel(Name, "Pockwock Full-Scale", after = 0L),
            y=SUVA,
            fill=Name,
            cex.axis = 2)) +
 geom_boxplot(alpha=0.8,width=0.6) +
 ylim(1,2.5) +
```

```
 theme(text=element_text(size=15))+
 theme(axis.title.x = element_text (vjust = -1))+
 theme(axis.title.y = element_text (vjust = -1))+
 theme(legend.position = "none") +
 scale_fill_brewer(palette = "BuPu") +
 labs(y="SUVA (L/mg-m)", x="Filtered Waters")
```

```
# UV254 script

library(tidyverse)
library(readxl)
library(ggplot2)

uv <- read_excel("SUVA.xlsx", sheet='UV254') %>% group_by(Name)

uv %>%
 ggplot(aes(x=fct_relevel(Name, "Pockwock Full-Scale", after = 0L),
            y=UV254,
            fill=Name,
            cex.axis = 2)) +
 geom_boxplot(alpha=0.8,width=0.6) +
 #ylim(1,2.5) +
 theme(text=element_text(size=15))+ #change font size of all text
 theme(axis.title.x = element_text (vjust = -1))+
 theme(axis.title.y = element_text (vjust = 1.5))+
 theme(legend.position = "none") +
 scale_fill_brewer(palette = "BuPu") +
 labs(y="UV254 (/cm)", x="Filtered Waters") # alter the labels on the axis
```

```
# Different Sequences_DBP script

library(tidyverse)
library(readxl)
library(ggplot2)

dbp <- read_excel("Sequence_DBP.xlsx", sheet='Sheet1') %>%
  group_by(Waters)

dbp$UVdose <- as.factor(dbp$UVdose)

dbp %>% mutate(Treatment=factor(Treatment, levels=c("Cl", "ClUV20", "UVCl20", "Cl
UV40", "UVCl40", "ClUV80", "UVCl80"))) %>%
       mutate(Waters=factor(Waters, levels=c("Pockwock Full-Scale", "Ant-Sand", "GAC-
Ant-Sand (GAC-Cap)", "GAC-Sand"))) %>%
  ggplot(aes(x=Treatment,
             y= Value,
             fill=DBP)) +
  geom_boxplot(alpha=0.8,width=0.6) +
  theme(text=element_text(size=15))+ #change font size of all text
  facet_wrap(~Waters, ncol=2)+
  scale_fill_brewer(palette = "BuPu") +
  labs(y="DBP (mg/L)") # alter the labels on the axis

dbp %>% filter(Waters =="GAC-Sand") %>% mutate(Treatment=factor(Treatment, level
s=c("Cl", "ClUV20", "UVCl20", "ClUV40", "UVCl40", "ClUV80", "UVCl80"))) %>%
mutate(DBP=factor(DBP, levels=c("Total DBP", "Total THM", "Total HAA"))) %>%
  ggplot(aes(x=UVdose,
             y= Value,
             fill=Sequence)) +
  geom_boxplot(alpha=0.8,width=0.6) +
```

```
theme(text=element_text(size=15))+ #change font size of all text
theme(axis.title.x = element_text (vjust = -1))+
theme(axis.title.y = element_text (vjust = 1))+
facet_wrap(~DBP, ncol=3)+
scale_fill_brewer(palette = "BuPu") +
labs(y="DBP (mg/L)") # alter the labels on the axis
```