



UNIVERSITY
OF MANITOBA



**REMOVAL OF TRIHALOMETHANES PRECURSORS FROM SURFACE
WATERS TYPICAL FOR CANADIAN PRAIRIE AND SHIELD**

by

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ABSTRACT

Many Canadian water treatment plants supplied by surface waters of the Canadian Prairie and Shield have elevated concentrations of trihalomethanes (THMs), which exceed the provincial standards. These water sources are characterized by elevated levels of dissolved organic carbon (DOC) and varying levels of calcium hardness, which causes a challenge for the removal of THMs precursors.

The objective of this study was to investigate the effect of two treatment methods: chemical coagulation and pre-ozonation-coagulation on the removal of DOC as the main THMs precursor. Surface waters typical for the Canadian Prairie and Canadian Shield were used in the experiments which includes Assiniboine River, Red River, and Rainy River. The effects of different experimental conditions such as coagulant dose, coagulant type, and solution pH as well as ozone dosage on THMs removal were investigated. The structural and chemical characteristics of natural organic matter and isolated humic substances, before and after the reaction with ozone, were studied using spectroscopic techniques.

The results illustrated that the quality of source water (DOC characteristics, concentration of water DOC and Calcium) has a significant impact on THMs reduction by chemical coagulation and ozonation. Coagulation results showed that reduction of total DOC does not guarantee THMFP reduction and chemical coagulation should be optimized to remove the hydrophobic acid fraction which forms most THMs. The removal of DOC by aluminum-based coagulants was affected more by the concentration of polymeric and colloidal aluminum speciation. This finding is especially important for plants supplied by high alkalinity waters where pH adjustment is a serious challenge.

The effect of pre-ozonation on coagulation varies depending on the concentration of calcium, which has the ability to form complexes with DOC compounds promoting their removal in coagulation. For the surface water with high levels of organic carbon and calcium hardness, ozonation prior to coagulation was beneficial in terms of DOC reduction. However, it showed the opposite effect on water with high levels of DOC accompanied with low level of calcium hardness. Spectroscopic results showed that ozonation of NOM and humic substances cause a significant reduction of aromatic and highly conjugated compounds (constituting primarily the hydrophobic acid fraction).

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CO-AUTHORSHIP

The journal articles written from the present work are listed below:

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M. Sadrnourmohamadi conducted all the experiments, analyzed the data and wrote the manuscript for this paper. This work was supervised by B. Gorczyca. Various drafts of the paper were reviewed by M. Sasdrnourmohamadi, C. D. Goss and B. Gorczyca.

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LIST OF SYMBOLS

μg	Micrograms
$\mu\text{g THM/mg DOC}$	Specific THMFP
λ_{em}	Emission Wavelength
λ_{ex}	Excitation Wavelength
$\Delta\lambda$	Offset Value
AC	Activated Carbon
ACH	Aluminum Chlorohydrate
AHSs	Aquatic Humic Substance(s)
Al_a	Aluminum Monomeric Species
Al_b	Aluminum Medium Polymeric Species
Al_c	Aluminum Large Polymeric Species and/or Solid-phase $\text{Al}(\text{OH})_3$
Alum	Aluminum Sulfate
AOC	Assimilable Organic Carbon
BAC	Biological Activated Carbon
BDNOM	Biodegradable natural organic matter
BDCM	Bromodichloromethane
CHCl_2Br	Bromodichloromethane
CHBr_3	Bromoform
cm	Centimeter
CHCl_3	Chloroform
d	Day
CHClBr_2	Dibromochloromethane
DBPR	Disinfectant/Disinfection By product Rule
Da	Daltons
kDa	Kilo Daltons
DBCM	Dichlorobromomethane
DBP(s)	Disinfection By Product(s)
DOC	Dissolved Organic Carbon

DOM	Dissolved Organic Matter
EEM	Excitation- Emission Matrix
ESF	Emission Scan Fluorescence
Ex	Excitation
E253/E203	UV absorbance ratio at 253 and 203 nm
E465/E665	UV absorbance ratio at 465 and 665nm
FA(s)	Fulvic Acid(s)
FTIR	Fourier Transform Infrared Spectroscopy
FTIR- ATR	Fourier Transform Infrared Coupled to Attenuated Total Reflectance
GAC	Granular Activated Carbon
GCDWQ	Guidelines for Canadian Drinking Water Quality
GC- ECD	Gas Chromatography Electron Capture Detection
GDWQ	Guidelines for Drinking Water Quality
HA(s)	Humic Acid(s)
HAA(s)	Haloacetic Acid(s)
HCl	Hydrochloric Acid
HPI	Hydrophilic
HPIA	Hydrophilic Acid
HPIB	Hydrophilic Base
HPIN	Hydrophilic Neutral
HPO	Hydrophobic
HPOA	Hydrophobic Acid
HPOB	Hydrophobic Base
HPON	Hydrophobic Neutral
HS	Humic Substance
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
IR	Infrared
MCLs	Maximum total contaminant levels
MF	Microfiltration

MW	Molecular Weighth
MWCO	Molecular Weigth cut-off
NaOH	Sodium Hydroxide
NF	Nanofiltration
OH [•]	Hydroxyl Radical
PAC	Powdered Activated Carbon
PACl	Polyaluminum Chloride
POM	Particulate Organic Matter
ppb	Parts per Billion
ppm	Parts per Million
PPWTP	Portage la Prairie Water Treatment Plant
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
s	Second
SPE	Solid Phase Extraction
SSF	Synchronous Scanning Fluorescence
SUVA	Specific Ultraviolet Absorbance at 254 nanometers
SRNOM	Suwannee River Natural Organic Matter
SRFA	Suwannee River Fulvic Acid
SRHA	Suwannee River Humic Acid
TBM	Tribromomethane
TCM	Trichloromethane
TCU	True Color Unit
THM(s)	Trihalomethane(s)
THMFP	Trihalomethane Formation Potential
TTHMs	Total Trihalomethane(s)
TMP	Trans-membrane Pressure
TOC	Total Organic Carbon
TOX	Total Organic Halide
TTHM	Total Trihalomethane

UF	Ultrafiltration
USA	United States of America
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV _{abs}	Ultraviolet Absorbance
UV ₂₅₄	Ultraviolet Absorbance at 254 nanometers
UV ₂₈₀	Ultraviolet Absorbance at 280 nanometers
UV/Vis	Ultraviolet/Visible Absorbance
WHO	World Health Organization
WTP(s)	Water Treatment Plant(s)

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CHAPTER 1: INTRODUCTION

1.1. BACKGROUND

Natural organic matter is a complex mixture of naturally occurring compounds found in both surface and ground waters containing both dissolved organic matter (DOM), generally measured as dissolved organic carbon (DOC), and particulate organic matter (POM) (Leenheer and Croué 2003). They result from the chemical, microbiological, and photochemical reactions that occur during the degradation of vegetable organic matter (both allochthonous and autochthonous source) (Matileinen et al. 2010; Rodríguez et al. 2014). DOC is generally a complex mixture of humic and non-humic organic compounds with varying chemical properties (Leenheer and Croué 2003). Humic substances are composed of humic acids (HAs) and fulvic acids (FAs) which account for 40-80% of the DOC in surface waters (Thurman 1985). The characteristics and diversity of organic components of DOC may vary from site to site and seasonally due to weather events and seasonal variations such as rainfall, snowmelt runoff, floods or droughts (Matilainen et. al. 2010). In this research project, the term DOC will be analogous to DOM.

Generally, POM can be easily removed with conventional pre-treatment methods. Thus, DOC is the main concern of research in potable water treatment. DOC is the cause of aesthetic issues in water, impacting its color, taste, and odor. Additionally, it can promote bacterial regrowth in treatment units and water distribution systems (Leenheer and Croué 2003; Kim and Yu 2005). It can also have a deteriorative effect on treatment processes such as contributing to membrane fouling, and the pore blocking and exhaustion of activated carbon filters (Amy 1994). Most importantly, DOC and mainly humic substances serve as the main precursor for the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Reckhow et al. 1990; Leenheer and Croué 2003). These by-products are formed when chlorine

is used as a disinfectant and reacts with DOC present in water. The US Environment Protection Agency (USEPA 1998) classifies them as human carcinogens. USEPA has established the maximum total contaminant levels (MCLs) of $80 \mu\text{gL}^{-1}$ for Total THMs as the main DBPs (USEPA 2010).

Chemical coagulation is one of the most widely used and cost effective methods applied in many treatment plants for DOC removal. However, it is not always possible to reduce the water DOC to sufficiently low concentrations to prevent the formation of THMs using coagulation alone (Crozes et al. 1995). High coagulant dosages are required for organic rich waters which results in excessive sludge production (Chiang et al. 2002). In addition, pH adjustment is required to optimize the removal of DOC by coagulation. This is quite costly for waters with very high alkalinity and large buffering capacity, which is typical of Canadian Prairie surface waters.

Ozone has been widely used in the water treatment industry as a disinfectant. It is also used for the removal of color, taste, odor, and turbidity as well as oxidation of inorganic species, a result of its superior oxidation potential. Some water treatment systems have taken advantage of the benefits of ozonation to improve coagulation (referred to as coagulating effect of ozone and ozone induced particle destabilization), and its ability to control trihalomethane formation. The reported effects of ozonation by different researchers are ambiguous and range from being beneficial to detrimental depending on the reported raw water quality (Bose 1994). Therefore, the effect of ozonation alone and as a coagulation aid on DOC removal from any source water and its DBPs formation potential needs to be evaluated for each specific water source. It is also important to understand the mechanism and the factors that play role in ozone oxidation and ozone induced coagulation relative to characteristics of the water source.

1.2. PROBLEM STATEMENT

Manitoba, Canada has a large abundance of surface waters (>110,000 lakes) that are readily used as potable water sources. Many of these surface waters are high in dissolved organic carbon, sometimes exceeding 20 mg L⁻¹. Furthermore, Manitoba has a large geographic region which has surface waters that vary significantly in terms of water quality parameters such as pH, alkalinity, and hardness which can all impact the removal of DOC during treatment. Moreover, DOC removal from these waters is a critical task; particularly during spring time when the concentration of organic carbon is increased by snowmelt runoff into water bodies (Sadrnourmohamadi et al. 2013). In Manitoba 70% of potable water treatment plants using surface water sources are reported to not be in compliance with THMs regulations set by the Province (Manitoba Water Stewardship 2011). Therefore, water treatment facilities are aiming to improve DOC removal from the raw water before chlorination in order to reduce total THMs to meet current provincial guidelines.

1.3. THE OBJECTIVE OF THIS RESEARCH

The overall objective of this research was to improve DOC removal and consequent THMs reduction from Canadian Prairie and Canadian Shield surface waters, containing varying water qualities. The coagulation and pre-ozonation-coagulation treatments were evaluated to achieve this goal by examining the removal of organic compounds, and understanding the mechanisms that are at play in their removal

The detailed objectives of this research study are:

- To evaluate the impact of different chemical coagulation conditions such as coagulant type, pH, and coagulant dose on the reduction of DOC and trihalomethane formation potential (THMFP) for each source water.

- To investigate the mechanism of DOC removal by aluminum-based coagulation.
- To study the effects of ozone on DOC and different fractions of DOC for each specific source water.
- To evaluate the effect of ozonation on the total THMFP of the water samples.
- To investigate the effect of ozone as an aid to coagulation treatment.
- To investigate the effect of certain water characteristics (e.g. calcium hardness) on the effectiveness of ozone-induced coagulation.
- To study the effect of ozone on the functional and structural properties of humic and fulvic acids by means of analysis using different physical and spectroscopic techniques.

The Detailed objectives of research, results and discussions will be provided in the following chapters.

1.4. THESIS PLAN

This thesis is written in an article-integrated format (Sandwich thesis) as specified by Faculty of Graduate Studies at the University of Manitoba.

The layout of this thesis is as follows:

Chapter 2:

Chapter 2 provides a literature review of dissolved organic carbon in drinking water. The literature review presents general information about DOC, composition and characterization of this term, its effect in drinking water treatment, the urgency in its removal from drinking water sources and the different treatment methods applied for its removal.

Chapter 3:

In this chapter the removal of dissolved organic carbon and its fractions by chemical coagulation were studied. Natural water collected from the Red River (Manitoba, Canada) containing high

levels of DOC and hardness were used in this study. Four coagulants (aluminum sulphate, ferric sulphate, ferric chloride, and titanium sulphate) were tested under different coagulation conditions.

Chapter 4:

This chapter is devoted to investigating the mechanism of DOC removal from the Assiniboine River water - characterized by its high alkalinity, hardness, and DOC. Three aluminum based coagulants (alum, polyaluminum chloride, and aluminum chlorohydrate) were used to remove DOC. The focus of this chapter was to discern the role of different aluminum species (Al_a , Al_b and Al_c) in terms of DOC removal. Removal of organic compounds was quantified by measurement of DOC, DOC fractions, and UV_{254} .

Chapter 5:

This chapter investigates the effect of ozone as a stand-alone and as a coagulation aid on the removal of dissolved organic carbon from the Assiniboine River (Manitoba, Canada) characterized as having high levels of DOC and calcium hardness. Effectiveness of ozone treatment was evaluated by measurement of DOC, DOC fractions, UV_{254} , and trihalomethane formation potential. Additionally, zeta potential and dissolved calcium concentration were measured to discern the mechanism of ozone reactions.

Chapter 6:

This chapter is devoted to examining the effect of ozone as a stand-alone, and as a coagulating aid for the removal of dissolved organic carbon from Rainy River source water characterized as having high levels of DOC accompanied with low level of calcium hardness. Three aluminum based coagulants (alum, polyaluminum chloride, and aluminum chlorohydrate) were tested to compare their efficiency. Effectiveness of each treatment process: ozonation, coagulation and

pre-ozonation-coagulation was evaluated by measurement of DOC, UV₂₅₄, DOC fractions, and trihalomethane formation potential.

Chapter 7:

In this chapter the structural and chemical characteristics of natural organic matter (NOM) and isolated humic substances: humic acid and fulvic acid were examined before and after reaction with ozone. This was examined using fourier transform infrared spectroscopy (FTIR-ATR), UV/Vis spectroscopy, and synchronous scanning fluorescence (SSF) measurements. Three natural aquatic organic substances standards were obtained by the International Humic Substance Society (IHSS) and studied in this work. These included: Suwannee River Natural organic matter (SRNOM), Suwannee River Humic Acid (SRHA), and Suwannee River Fulvic Acid (SRFA).

The effectiveness of ozonation was evaluated by monitoring removal of DOC, UV₂₅₄, SUVA, and total trihalomethane formation potential. The results were linked to the performance of the ozonation process in reducing THM formation potential of waters with high levels of THM precursors.

Chapter 8:

This chapter aims to provide the general conclusion of this thesis and to summarize recommendations for future studies.

CHAPTER 2: LITERATURE REVIEW

2.1. NATURAL ORGANIC MATTER

Natural organic matter is a complex mixture of naturally occurring compounds that can be found in all surface waters, and to a lesser extent in ground waters. The interactions between the geosphere, the biosphere and the hydrological cycle result in water sources containing NOM (Matilainen et al. 2010). NOM is an extremely complex mixture of organic compounds with varying functional and structural characteristics (Lamsal et al. 2011). They result from the photochemical, chemical, and microbiological reactions that occur during the degradation of vegetable organic matter in water (Matileinen 2007; Rodríguez et al. 2014) .

NOM in surface water is a heterogeneous mixture of dissolved organic matter (DOM) and particulate organic matter (POM). DOM is generally measured in terms of dissolved organic carbon (DOC) and includes more than 90% of natural organic matter in surface waters while particulate organic matter compromises around 10% of the organic carbon pool (Leenheer and Croué, 2003). Due to size effects, conventional pre-treatment steps such as sedimentation can easily remove POM; therefore, DOC is the main concern in NOM research from a drinking water treatment perspective (Chow et al. 2005; Goss 2011).

2.2. DISSOLVED ORGANIC CARBON

DOC is the soluble portion of NOM that can pass through a 0.45-micrometer (μm) filter (Thurman 1985). It is a complex mixture of aromatic and aliphatic hydrocarbons with various functional groups such as carboxyl, carbonyl, hydroxyl, ketones, and amides (Leenheer and Croué 2003). The concentration and composition of organic components of DOC varies from site to site and is subjected to seasonal changes due to weather events such as rainfall, snowmelt

runoff, floods or droughts (Murray and Parsons 2004; Matilainen et. al. 2010). DOC concentration has been reported to range from 0.1-1 mgL⁻¹ in ground water and seawater sources, to >30 mgL⁻¹ in river water sources (Leenheer and Croué 2003; Goss 2011). There is a general agreement that the molecular weight (MW) of DOC species range from 100-2000 Daltons (Da) to greater than ~100,000 Da for macromolecules.

2.2.1. Composition of Dissolved Organic Carbon

Generally, DOC composition depends on origin and degradation rate of its source materials (Lankest et al. 2008; Baghoth 2012). For instance, organic compounds derived from aquatic algae are found to contain a lower percent aromatic carbon, and phenolic content, and contain appreciably high levels of nitrogen. Alternatively, terrestrial-derived sources are reported to have low nitrogen content and high levels of phenolic and aromatic content (Fabris et al. 2008).

DOC usually consists of two major classes: humic and non-humic organic substances (Thurman and Malcolm 1981; Ratpukdi et al. 2008; Liying et al. 2009). Humic substances (HS) are described as an undefined diverse group of organic compounds formed during the degradation of animal and plant tissues and/or synthesis of the products by chemical and biological processes (Corin 1996; Yu et al. 2005). The composition of humic substances are site specific and is strongly influenced by the local environment by factors such as pH, water alkalinity, and temperature (Chow et al. 2005).

The humic substances are generally less soluble, of higher molecular size, yellow to brown-black in colour, poor in nitrogen and contain greater aromatic moieties than the non-humic fraction. They form the major fraction of DOC representing 40–80% of the DOC in many surface waters (Zhao et al. 2006). On the contrary, the non-humic fraction contains high concentrations of

nitrogenous organic compounds such as amino acids, proteins, carbohydrates, and lipids (Garcia 2011).

Humic substances consist of humic acids (HA), insoluble at pH less than 2; and fulvic acids (FA) which are soluble at all pHs (Thurman 1985; Freese et al. 2001; Kerc et al. 2003a). Humic acids are characterized as being highly aromatic containing unsaturated and sp^2 hybridized carbon bonds. It also can be described as a heterogeneous poly-functional polymer due to its polymeric network that can entrap volatile organic compounds (Kerc et al. 2003b). Fulvic acids comprise the predominant fraction of humic substances, which are lower in molecular weight and aromatic content than humic acids (Amy et al. 1986; Van Benschoten et al. 1990; Matilainen et al. 2011). Figure 2.1 shows a hypothetical molecular structure of humic and fulvic acids (adapted from Stevenson 1982).

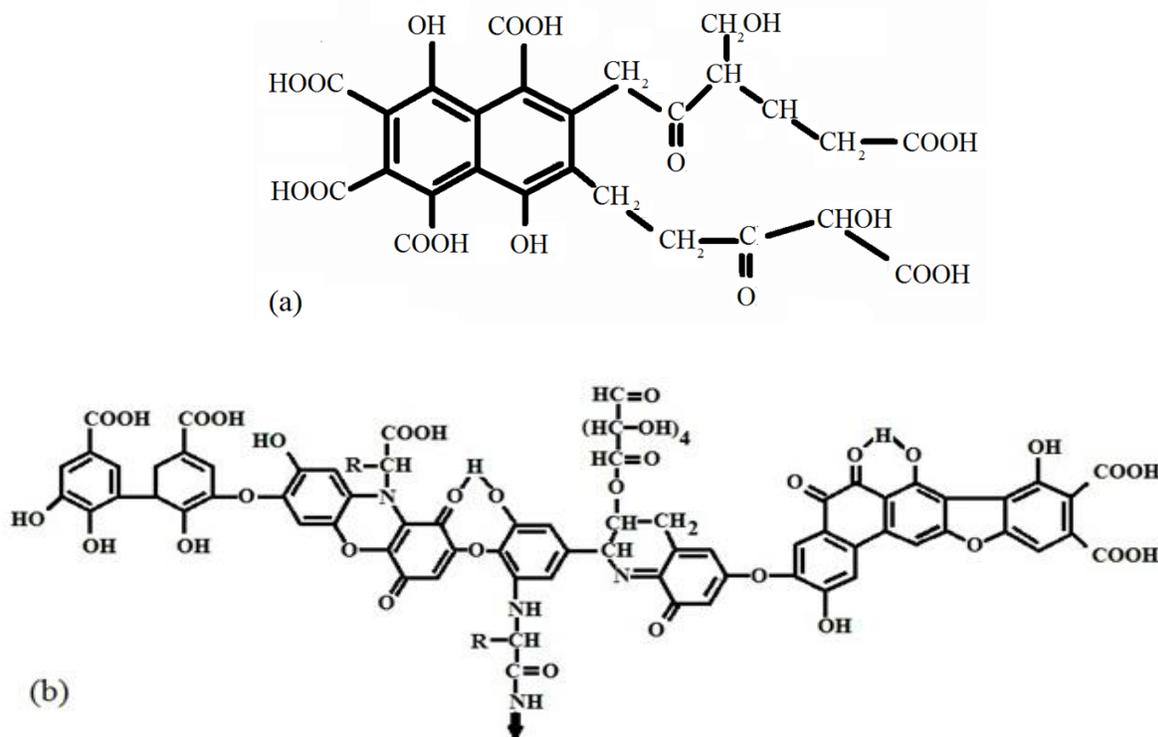


Figure 2.1: Hypothetical molecular structure of (a) fulvic acid and (b) humic acid (adapted from Stevenson 1982).

2.2.2. Dissolved Organic Carbon as an Environmental Concern

DOC can cause several problems in drinking water. It is a source of aesthetic problems in water, impacting color, taste, and odor. In addition it can promote bacterial regrowth in the treatment units and water distribution systems (Leenheer and Croué 2003; Kim and Yu, 2005; Xue et al. 2015). Most importantly, DOC and mainly humic substances have been reported as the major contributor to the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Reckhow et al. 1990; Leenheer and Croué 2003; Chow et al. 2005). Chlorination as the last step in conventional water treatment is a necessary process to reduce the potential risks of waterborne diseases. DBPs are formed when DOC present in water reacts with chlorine (Rook 1974; Sadiq et al. 2004).

Several toxicological and epidemiological studies have reported potential health effects of consumption of drinking water containing DBPs. As reported by Krasner (2009) toxicological studies have indicated that THMs show adverse health effects on laboratory animals. These by-products cause cancer of the kidney, large intestine, and liver and cause adverse reproductive or developmental effects (Goss 2011).

Epidemiological studies have shown a cancer risk of colon, bladder, and rectal cancer for long term consumers of chlorinated surface waters (Krasner 2009). Moreover, some of the epidemiological studies have indicated a relation between possible concern of abortion or undeveloped fetus and consumption of waters with chlorinated DBPs (Reif et al.1996; Krasner 2009).

Due to these negative health effects, US Environment Protection Agency (USEPA) has established the maximum total contaminant levels (MCLs) of $100 \mu\text{gL}^{-1}$ for Total THMs (TTHM) in 1979. It was later updated to $80 \mu\text{gL}^{-1}$ in 1998 as a regulation in the Stage 1

disinfectants and disinfection by-products rule (USEPA 2001). Stage 2 of the disinfection by-product rule is expected to reduce the MCLs for THMs and HAAs to $40 \mu\text{g l}^{-1}$ and $30 \mu\text{g l}^{-1}$, respectively (Grunwald et al. 2002). In 1996, Health Canada has set the MCLs of $100 \mu\text{gL}^{-1}$ for THMs by following the USEPA guideline (Health Canada 1996). Each province of Canada can either establish a separate provincial regulation for water quality or follow the Canadian guidelines. In 2011, Manitoba Water Stewardship has set a provincial THMs guideline of $100 \mu\text{gL}^{-1}$ (Manitoba Water Stewardship 2011).

Trihalomethanes formation

Trihalomethanes are known as the first discovered disinfection by-products. These substances are formed during reaction between DOC and chlorine disinfectant. THMs as the main DBPs, with higher concentration compared to HAAs, consist of four compounds: chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3). The United States Environmental Protection Agency has reported CHCl_3 , CHCl_2Br and CHBr_3 as class B₂ carcinogens (human carcinogen) and CHClBr_2 as a class C carcinogen (probable human carcinogen) (Malika et al. 2008; Liu et al. 2011). The occurrence of THMs depends upon many water quality parameters (e.g., temperature, pH, concentration and composition of DOC, bromide concentration, and alkalinity) and treatment conditions (e.g. DOC concentration prior to disinfection, chlorine dosage, chlorine contact time). Generally, increased parameters along with higher chlorine dosages can lead to greater THM formation (USEPA 1999; Grunwald et al. 2002; Sadiq and Rodriguez 2004). THMs formation increases with increasing pH where it can have the reverse effect for HAA formation. (Sadiq and Rodriguez 2004). During the winter season especially when surface waters are protected by ice cover, THMs concentrations tend to be lower due to lower water temperatures and lower levels of DOC (Sadiq and Rodriguez 2004).

It has been reported that not only the concentration of DOC but also the composition may impact THM formation (Bell et al. 2012). The humic fraction of DOC has been reported to contribute the highest THM formation potential due to the fraction having a greater degree of aromaticity (Reckhow et al. 1990; Singer 1999; Leenheer and Croue 2003; Chow et al. 2005).

Based on the harmful health effects of THMs and the strict regulations that accompany it, the control of these by-products is the most pressing concern for water treatment operators in recent years. The most effective strategy in the control of THM formation is limiting the presence of precursor species prior to disinfection with chlorine. Many Canadian Prairie and Canadian Shield water treatment plants (WTPs) that use surface water sources are not in compliance with THMs regulations. This is more critical for the province of Manitoba where almost 70% of potable (Sadrnourmohamadi et al. 2013, Sadrnourmohamadi and Gorczyca 2015a, 2015b). Therefore WTPs are motivated to improve the removal of DOC and reactive precursors to meet current THMs guidelines.

2.3. CHARACTERIZATION of AQUATIC ORGANIC CARBON

The quantification and characterization of aquatic organic carbon is necessary in drinking water treatment due to the problematic effects already described. Due to their complex chemical structure, no direct and unique analytical method has been reported to determine both the type and amount of aquatic organic carbon present in the water (Wang and Hsieh 2001). Some general methods are widely used to represent it quantitatively and qualitatively such as measurement in terms of total and dissolved carbon (TOC and DOC), ultraviolet absorbance at 254 nm (UV_{254}), and specific UV absorbance (SUVA). Color measurement can also indicate the presence of aquatic organic carbon since it can impact water color by its brownish yellow tint. There are many spectroscopic, chromatographic, and fractionation methods that have been

utilized by researchers to provide alternative information about the composition and chemical structure of NOM (Karanfil et al. 2001; Chowdhury 2005; Matilainen et al. 2011).

2.3.1. Total Organic Carbon/Dissolved Organic Carbon

TOC in surface water is the sum of two major components: dissolved organic carbon and particulate organic carbon (Leenheer and Croué, 2003). DOC is defined as the soluble portion of organic carbon that can pass through a 0.45 micrometer (μm) filter (Thurman 1985). TOC is used as a surrogate parameter to represent the aquatic organic carbon concentration (Wang and Hsieh 2001). In TOC-analysis, the instrument goes through a series of oxidation steps in order to convert all organic carbon into CO_2 . The resulting CO_2 is measured mostly by infrared (IR) spectroscopy to provide information on total organic carbon (Matilainen et al. 2011).

2.3.2. Ultraviolet Absorbance

Ultraviolet (UV) absorbance at 254 nm (UV_{254}) is commonly used to characterize the structure of aquatic organic carbon in water (Wang and Hsieh 2001). Generally, higher aromaticity results in higher UV_{254} absorbance (Wang and Hsieh 2001). The measurement of UV_{254} absorbance has also been used to provide a gross characterization of organic carbon concentrations in water samples along with DOC measurement. This wavelength has been chosen for aromatic structure due to several reasons: (i) the absorbance of aromatic aquatic organic carbon can be measured sensitively and reliably at this wavelength, (ii) inorganic compounds present in natural waters can have minimal or negligible interferences at this wavelength, and (iii) some researchers have reported correlations between UV_{254} and DOC for water samples (Edzwald et al. 1985; Karanfil et al. 2003).

2.3.3. Specific Ultraviolet Absorbance

Specific UV absorbance (SUVA) is defined as the DOC-normalized absorbance at UV₂₅₄

(Matilainen et al. 2010).

$$SUVA = 100 \times \left\{ \frac{[UV\ 254\ (1/cm)]}{DOC\left(\frac{mg}{L}\right)} \right\} \quad [\text{Eq.2.1}]$$

SUVA as a single parameter including both DOC and UV₂₅₄ absorbance which can provide more information about the nature of aquatic organic carbon (Chowdhury 2005). Higher SUVA values suggest that NOM sources are highly aromatic in nature (Edzwald and Tobiason 1999; Chowdhury 2005). There are some conflicting literature regarding the correlation between SUVA values and THM formation potential. Some studies have reported cases with good correlation between SUVA values and THMs formation potential (Singer 1999). Other studies, on the contrary, have not confirmed this relationship (Wei et al. 2008; Jung and Son 2008).

Table 2.1 shows the relation between SUVA values and expected composition of natural organic matter provided by Edzwald and Tobiason (1999). A SUVA value greater or equal to 4 mg⁻¹.m⁻¹.L indicates that NOM composition has a high content of hydrophobic compounds while a SUVA less than 2 suggests mainly hydrophilic materials. A SUVA value ranging from 2-4 mg⁻¹.m⁻¹.L indicates the water is a mixture of hydrophilic and hydrophobic NOM (Edzwald and Tobiason 1999).

Table 2.1: Relation between SUVA values and expected composition of natural organic matter (Edzwald and Toiason 1999)

SUVA (mg ⁻¹ .m ⁻¹ .L)	Composition
≈ 4 or greater	High molecular weight High hydrophobicity Mostly aquatic humics
2-4	Mixture of hydrophilic and Hydrophobic NOM
<2	Low Molecular Weight Low hydrophobicity Mostly Non-humics

2.3.4. Fractionation

DOC fractionation is necessary in order to further characterize the reactivity of NOM. Due to the complex and heterogeneous nature, no unique fractionation method has been developed yet. Some commonly used fractionation methods such as resin fractionation and membrane filtration have been reported to characterize NOM by isolating the more highly reactive fraction of NOM that contributes more to THM formation (Chow et al. 2005; Matilainen et al. 2011). Membrane filtration separates based on physical size while resin fractionation separates based on chemical structure and functional group characteristics (Chow et al. 2005).

2.3.4.1. Resin fractionation

Resin fractionation is a common method to characterize NOM by dividing the whole mixture into two sub-fractions: hydrophilic and hydrophobic fractions. Generally, hydrophobic fractions of NOM consist of humic substances that mainly contain aromatic, carboxyl, carbonyl, and aliphatic units. The hydrophilic fraction of NOM mainly consists of carbohydrates, amino acids, amino sugars, and proteins. There is a general agreement that hydrophobic species are of large MW organic compounds (5000-10000 and >10,000 Da) while hydrophilic are of low MW (<1000 Da) (Swietlik et al. 2004; Matilainen et al. 2006).

This method was initially introduced by Leenheer (Leenheer and Huffman 1979; Leenheer 1981). The Leenheer method isolates DOC into six fractions based on hydrophobicity/hydrophilicity and acid/base functionality. The fractions isolated include: hydrophobic acids (HPOA), hydrophobic bases (HPOB), hydrophobic neutrals (HPON), hydrophilic acids (HPIA), hydrophilic bases (HPIB), and hydrophilic neutrals (HPON) (Figure 2.2).

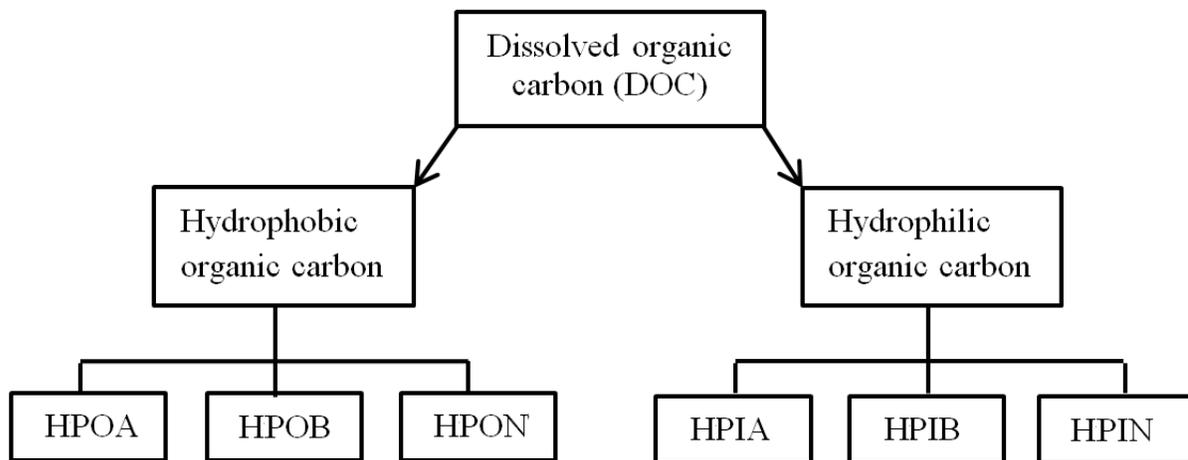


Figure 2.2: DOC classification diagram (source Leenheer and Croue 2003).

The method uses three separate columns containing a Duolite A-7 anion exchange resin, AG-MP-50 cation-exchange resin, and an Amberlite XAD-8 resin. The XAD-8 column retains all three hydrophobic (HPO) fractions including HPOB, HPOA, and HPON. After passing a water sample through the XAD-8 column, HPOB is the first fraction eluted by hydrochloric acid. By adjusting the pH of same water sample to 2 and passing the sample through the column HPOA is retained and can be eluted by sodium hydroxide. Hydrophobic neutral is the last hydrophobic fraction extracted using methanol. HPIB is the fraction retained on AG-MP-50 while Duolite A-7 resin retains the HPIA fraction. The fraction that cannot be retained by any of the three resins is HPIN (Leenheer 1981; Ratpukdi et al. 2009; Goss 2013).

The HPOA fraction is made up of humic and fulvic acids, 1- and 2- ring phenols, 1- and 2- ring aromatic carboxylic acids and C5-C9 aliphatic carboxylic acids whereas HPOB fraction contains 1- and 2- ring aromatic amines (Śweitlik et al. 2004). HPON fraction is reported to be a mix of long chain aliphatic carboxylic acids, ketones, esters, aldehydes, amides, and amines (Leenheer 1981; Marhaba et al. 2000; Śweitlik et al. 2004). Polyfunctional carboxylic acids, and hydroxy acids, and short chain (<C5) aliphatic carboxylic acids comprise the HPIA fraction whereas

amphoteric proteinaceous materials containing aliphatic amino acids, amino sugars, peptides, and proteins make up the HPIB fraction (Śweitlik et al. 2004). HPIN fraction is reported to be composed of polysaccharides and short chain alcohols, aliphatic amines ketones, aldehydes, and esters (Leenheer 1981; Marhaba et al. 2000; Śweitlik et al. 2004). Table 2.2 shows the general chemical groups and composition of each DOC fraction reported by Leenheer et al. (1981), Leenheer and Noyes (1984), and Tipping (2002) in detail.

During the past decade, researchers have made several modifications to the original method developed by Leenheer (Croue' et al. 2000; Leenheer et al. 2000; Marhaba et al. 2003; Chow et al. 2004). Ratpukdi et al. (2009) has reported one of the recent modifications for DOC fractionation in natural water as well as in treated water. This method uses pre-packed solid phase extraction (SPE) sorbent to fractionate DOC into six fractions based on acid/base character and hydrophobicity/hydrophilicity similar to the classic resin fractionation method developed by Leenheer (1981). The properties of the sorbents for the three SPE cartridges used in the Ratpukdi method are listed in Table 2.3 (Ratpukdi et al 2009).

In this method three Bond Elute ENV cartridges (Varian Inc., Lake Forest California), one Strata X-AW cartridge, and one Strata XC cartridge (Phenomenex, Torrance, California), all containing 1g of sorbent are used to separate DOC into the six fractions isolated: HPIA, HPIB, HPIN, HPOA, HPOB, and HPON. This SPE method significantly reduces the need for long resin preparation time and need for specialized equipment which make this an attractive alternative to classic resin separation methods.

Table 2.2: Natural organic Matter Fractions and Chemical Groups, Baesd on Leenheer and Noyes (1984), Leenheer et al. (1981)

Fraction	Chemical groups
Hydrophobic	
Acids	humic and fulvic acids, Humic-bound carbohydrates, aromatic carboxylic acid
Bases	aromatic amines except pyridine, Proteins
Neutrals	aliphatic ketones, esters, aldehydes, amides, high MW carboxylic acid
Hydrophilic	
Acids	Hydroxy acids, short chain (<C5) aliphatic carboxylic acids
Bases	Aliphatic amino acids, pyrimidines, amino sugars
Neutrals	Polysaccharides; short chain alcohols, ketones, and aldehydes

Table 2.3: Properties of the SPE sorbents (Ratpukdi et al. 2009)

Sorbent	Category	Functional group
Bond Elute ENV (Varian, Inc.)	Nonpolar	Styrene divinyl Benzene
Strata X-C (Phenomenex)	Cation exchanger	Benzene sulfonic Acid
Strata X-AW (Phenomenex)	Anion exchanger	Primary and secondary amines

2.3.4.2. Membrane filtration

Membrane filtration has been reported as a physical fractionation method that can separate DOC of different molecular weight ranges. Filters with different molecular weight cut-off (MWCO) levels are used in this method. MWCO is defined as the mass of molecular weight which can be 90% retained by this membrane. This value is generally expressed in standard daltons or kilo dalton units. Membrane filters are available in various MWCO levels (e.g. 3kDa, 10 kDa, 30 kDa and 100 kDa) (Kuchler and Miekeley 1994; Matilainen 2011). In addition to molecular weight,

the shape and the charge of the molecules also play a role in this fractionation method (Assemi et al. 2004). Each separated fraction can be further characterized by other methods such as DOC analysis or UV₂₅₄ (Gjessing 1970; Amy et al. 1987). A common problem associated with this method is that the membrane pores are prone to blockage and consequently the permeability decreases. This can be due to adhesion or deposition of macromolecules on the membrane surface (Amy et al. 1987).

2.3.5. Spectroscopic Methods

Several spectroscopic methods have been used to provide deep insight into structural and functional properties of aquatic organic carbon. Among them, fluorescence spectroscopy, UV/Vis absorbance, and FTIR are the commonly used spectroscopic methods for DOC characterization (Peuravuori et al. 2002; Chen et al. 2003; Chouparova et al. 2004; Kim and Yu. 2005; Kanokkantapong et al. 2006; Yanan Xing 2010). These methods have been applied due to their time efficiency and ease of usability (Schnitzer and Khan 1972; Chen et al. 2002; Rodríguez and Núñez 2011).

2.3.5.1. Ultraviolet and visible spectroscopy (UV/VIS)

UV/Vis absorbance has been applied as one of the spectroscopic methods used to estimate the structural and composition of bulk DOC in natural waters. Generally, DOC compounds can absorb light over a wide range of wavelength from ultraviolet (UV) to visible (Vis) whereas inorganic chemicals don't show significant light absorption at $\lambda > 230$ nm (Korshin et al. 1997; Wang 2001). However, UV spectroscopic methods are more popular than visible since UV light is more readily absorbed by organic compounds (Xing 2010).

The absorption of both ultraviolet and visible light is attributed to the aromatic organic compounds and especially chromophores present in DOC, primarily the humic fraction

(Schnitzer and Khan 1972; Chin et al. 1994; Croue et al. 2000). Chromospheres are functional groups containing the electrons that can be promoted by absorbing UV/Vis light (Korshin et al. 1997). As a result, the energy and intensity of absorbed light can be used to infer structural information about the DOC molecules (Croue et al. 2000).

The UV/visible spectrum of DOC is typically broad and nearly featureless increasing with decreasing wavelength. Several ratios of UV/visible absorbance such as E_{465}/E_{665} and E_{253}/E_{203} have been defined for characterization of organic compounds in DOC (Wang et al. 1990; Xing 2010). E_{465}/E_{665} is related to the molecular size and degree of aromaticity and is used for the characterization of humic substances (Schnitzer and Khan 1972; Senesi et al. 1989). Kim and Yu (2005) also used the UV absorbance ratio at 253 and 203 nm (E_{253}/E_{203}) to indicate the functional distribution of DOC between the phenolic fraction and carboxylic fractions. A greater E_{253}/E_{203} ratio means a larger phenolic content and an increased potential for formation of DBPs (Kim and Yu 2005).

2.3.5.2. Fluorescence spectroscopy

Fluorescence spectroscopy has been widely applied in drinking water sciences to study the structural and functional characteristics of organic compounds such as humic substances. Compared to absorbance spectroscopy where the amount of light is absorbed at a specific wavelength, fluorescence spectroscopy measures the light that is re-emitted by a given wavelength (Coble et al. 1990, 1993; Cammack 2003). In this method irradiation at a certain wavelength excites molecules, called fluorophores. They later release the energy in the form of emitted light at a specific higher wavelength. As a result, the energy and intensity of emitted light can be used to provide structural information about the DOC molecules (Golsan 2003;

Carstea 2012). The concentration of fluorophores can be correlated with concentration and provide the means of a qualitative assessment.

Figure 2.3 shows the general principle of Fluorescence spectroscopy in a simplified Jablonski diagram (Lakowicz 2006). Fluorescence occurs when an electron in ground state (S_0) is excited by the adsorption of light. Following that, it is transferred to a higher energy level (S_1 or S_2 electronic states). Due to vibrational relaxation and/or internal conversion, excited electrons lose some of their energy and transfer from an upper excited state (S_2) to a lower one (S_1). Finally the electrons return to the ground state (S_0) and light is emitted in the form of fluorescence (Valeur 2001; Lakowicz 2006; Carstea 2012). As shown in the Jablonski diagram (figure 2.3) emission occurs at lower energies (greater wavelengths) compared to excitation which occurs due to the energy lost during vibrational relaxation and/or internal conversion. This effect is called a Stokes shift (Lakowicz 2006).

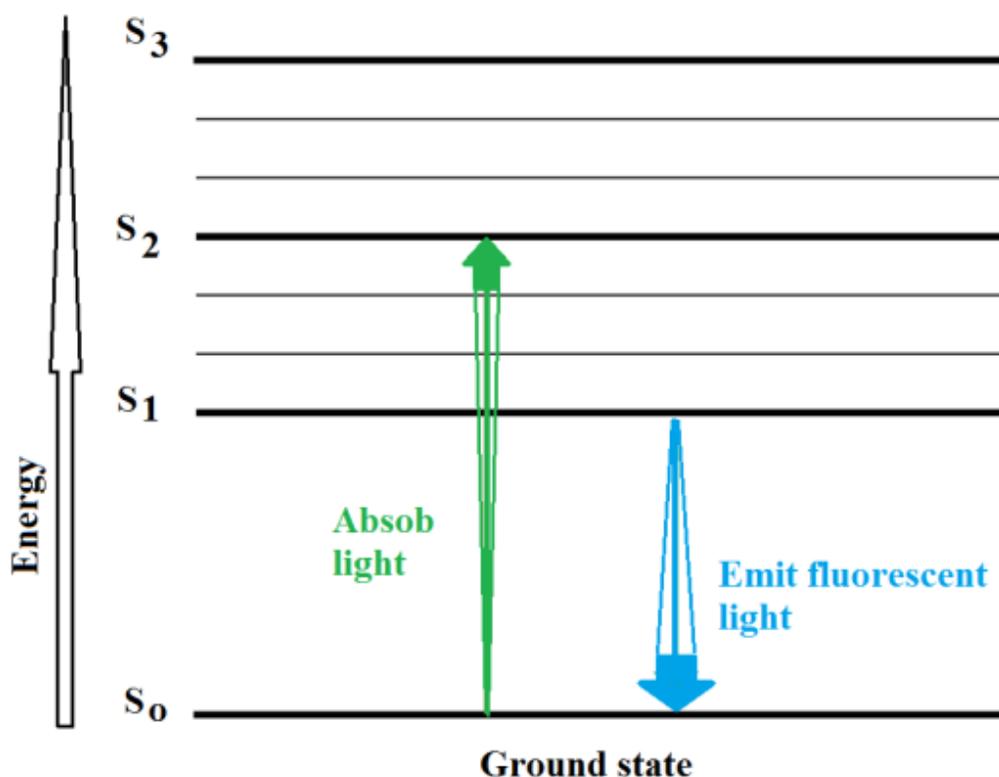


Figure 2.3: A simplified Jablonski diagram (showing the absorption and fluorescence process).

The intensity, position, and shift of fluorescence peaks can be related to structural information of DOC such as functional groups (electron-donating/withdrawing groups) and aromaticity (Chen et al. 2003; Zhang et al. 2008; Rodríguez et al. 2014a). There are several fluorescence techniques used such as emission scan fluorescence (ESF), Synchronous scanning fluorescence (SSF), and excitation- emission matrix (EEM) (Carstea 2012; Rodríguez et al. 2014a, and b). In emission scan fluorescence, the emitted light will be analyzed as a function of its wavelength at a fixed excitation wavelength. A Synchronous-scan excitation spectrum is collected when both the excitation and emission wavelength are scanned but the difference between them (offset), $\Delta\lambda=\lambda_{em}-\lambda_{ex}$, is kept constant (Carstea 2012; Chen et al. 2003). SSF presents several advantages over conventional ESF such as additional structural and chemical information of DOC, better sensitivity, and improved peak resolution (Chen et al. 2002; 2003). It can also reduce peak overlapping; therefore identifying each fluorescent in a specific spectral range (Rodríguez et al. 2014a, and b).

EEM a technique in which emission spectra is obtained over a series of excitation wavelengths is the most complete technique. It can identify single fluorescent compounds and/or complex mixtures of fluorescent components (Coble 1996; Chen et al 2003, Rodríguez et al. 2014a). This technique has some advantageous such as sensitivity and minimal sample preparation (Miano et al. 1988). However, due to the complex structures of DOC in natural surface waters and the way the different fluorophore emission bands overlap, the identification of fluorophores in DOC can become difficult and challenging (Chen et al. 2003; Swietlik and Sikorska 2004).

2.3.5.3. Fourier transform infrared (FTIR)

Fourier transform Infrared (FTIR) has been used as a non-invasive method for the structural and functional groups identification of DOC compounds (Stevenson and Goh 1971). The method

identifies specific functional groups that can absorb/ transmit infrared (IR) light at specific wavelengths. This results in an absorbance/transmission spectrum which acts as a unique fingerprint for each compound (Matilainen et al. 2011). In DOC molecules due to complex structure, not all of the functional groups but only the strongest bands attributed to certain functional groups can be identified (Croue et al. 2000). Several researchers have applied FTIR to characterize DOC collected from several stages of a water treatment process and its fractions. Kanokkantapong et al. (2006) have applied FTIR and resin fractionation to identify organic compounds associated with the formation of haloacetic acids. Kim and Yu (2005) have used FTIR to characterize the hydrophobic fraction of DOC in source and treated waters at a conventional water treatment plant. Ma (2004) has applied FTIR spectroscopy to show the effect of ozone on the humic acid fraction and to relate the effects of ozone on the reduction of DBPs. There are some problems associated with this technique especially in complex and aqueous samples. Sometimes samples require pre-treatment to give good quality spectrums. In some cases DOC needs to be concentrated to simulate levels which are normally present in natural waters (Matilainen et al.2011). Moreover the water present in aqueous samples interfere with the FTIR spectrum since hydrogen bonds between hydroxyl groups present in aqueous sample can mask the absorption spectra of dissolved organic components .

Pressed-pellet method (KBR method) is one way to remove the water interferences which allows FTIR measurements to be done on a pellet containing dried sample and KBR. There are some challenges associated with this method - most importantly - sample preparation, and sample destruction during mixing with KBR (Minor et al. 2014). To avoid these problems fourier transform infrared spectroscopy coupled to attenuated total reflectance (FTIR-ATR) has been applied for DOC samples. In this technique infrared beam is directed at a highly refractive index

crystal. The sample is pressed against this dense crystal and beam is penetrated through that at a certain angle and bounces multiple times internally and then exits to the detector (Tejedor-Tejedor and Anderson 1986). Figure 2.4 shows a schematic representative of the FTIR-ATR method.

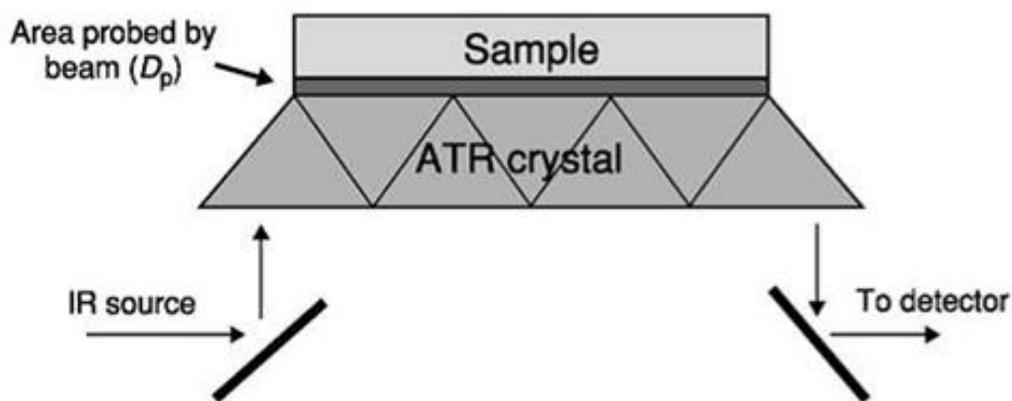


Figure 2.4: Schematic representative of FTIR-ATR method.

FTIR-ATR method has been applied by several researchers to investigate the functional groups and structure of organic compounds in DOC and humic substances (Song et al. 2004; Kim et al. 2006; Duarte et al. 2007; Lin et al. 2012).

2.4. NATURAL ORGANIC MATTER IN DRINKING WATER TREATMENT

Generally, NOM has significant effects on drinking water quality as well as the performance of water treatment processes such as coagulation, membrane filtration, oxidation, and activated carbon adsorption. This leads to operational problems and increased cost to water treatment (Chowdhury 2005). Some of the ways where NOM can affect drinking water quality and the performance of water treatment process are summarized below:

1. NOM causes aesthetic problems for drinking water.
2. NOM contributes to the fouling of membranes, reducing flux which results in increased frequency of membrane cleaning and backwashing.
3. NOM increases the exhaustion and usage rate of activation carbon.
4. NOM increases the dosage of oxidants, coagulants, and disinfectants needed for drinking water treatment
5. Biodegradable NOM in water distribution system can serve as a substrate for bacterial growth when a sufficient disinfectant residual is not maintained in the distribution system.
6. Some NOM fractions may promote corrosion in the distribution system.
7. If NOM is not sufficiently removed, it acts as the precursors for disinfection by-products formation (Reckhow et al. 1990; Leenheer and Croué 2003; Chow et al. 2005).

The concentration of NOM - and more specifically, DOC - has to be minimized before disinfection either by controlling the source of precursors or at treatment. Surface water reservoirs are readily used as potable water sources in rural areas of the Canadian Prairies and Canadian Shields. These surface water reservoirs often have poor water quality due to high concentration of NOM (Xing 2010). Currently there are no guidelines for total organic carbon or dissolved organic carbon. However, water treatment facilities need to improve the removal of DOC from the raw water prior to chlorination in order to reduce the concentrations of THMs to meet current provincial guidelines.

2.5. WATER TREATMENT FOR NOM REMOVAL

2.5.1. Coagulation Process

Coagulation is one of the most widely used and cost effective methods applied in many water treatment plants. In this method, metal salts, most commonly ferric-based and aluminum-based salts, are used as coagulants for the reduction of DOC, turbidity, color, and pathogens (Amirtharajah and Omelia 1990; Zouboulis et al 2007; Zouboulis et al. 2008).

Upon adding to water, the metal salts are dissociated to form positively charged ions such as Al^{3+} and Fe^{3+} . These ions are further hydrolyzed and form highly positively charged soluble complexes (Duan et. al. 2003). Several mechanisms have been reported for NOM removal during coagulation. The main mechanisms are charge neutralization/precipitation and adsorption of NOM on metal hydroxides. The first mechanism involves charge neutralization of negatively charged organic matter by positively charged coagulant species. This may lead to the formation of neutral compounds, which will precipitate and consequently be removed if present in excess of their solubilities. The second mechanism involves the adsorption of NOM on metal (aluminum/ferric) hydroxide flocs by surface complexation or partitioning, and the subsequent removal of these flocs (Ezdwald 1993; Jarvis et. al. 2004; Yigit et. al. 2009). Other mechanisms involved in NOM removal during coagulation are: NOM-metal species complexation resulting in insoluble aggregates formation and also NOM entrapment in metal complexes (Matilainen et al. 2010). Figure 2.5 shows the possible NOM removal mechanisms during coagulation. The composition and nature of NOM, the water characteristics such as temperature, ionic strength, and pH, and operating conditions of the coagulation process determines which mechanisms are responsible for NOM removal.

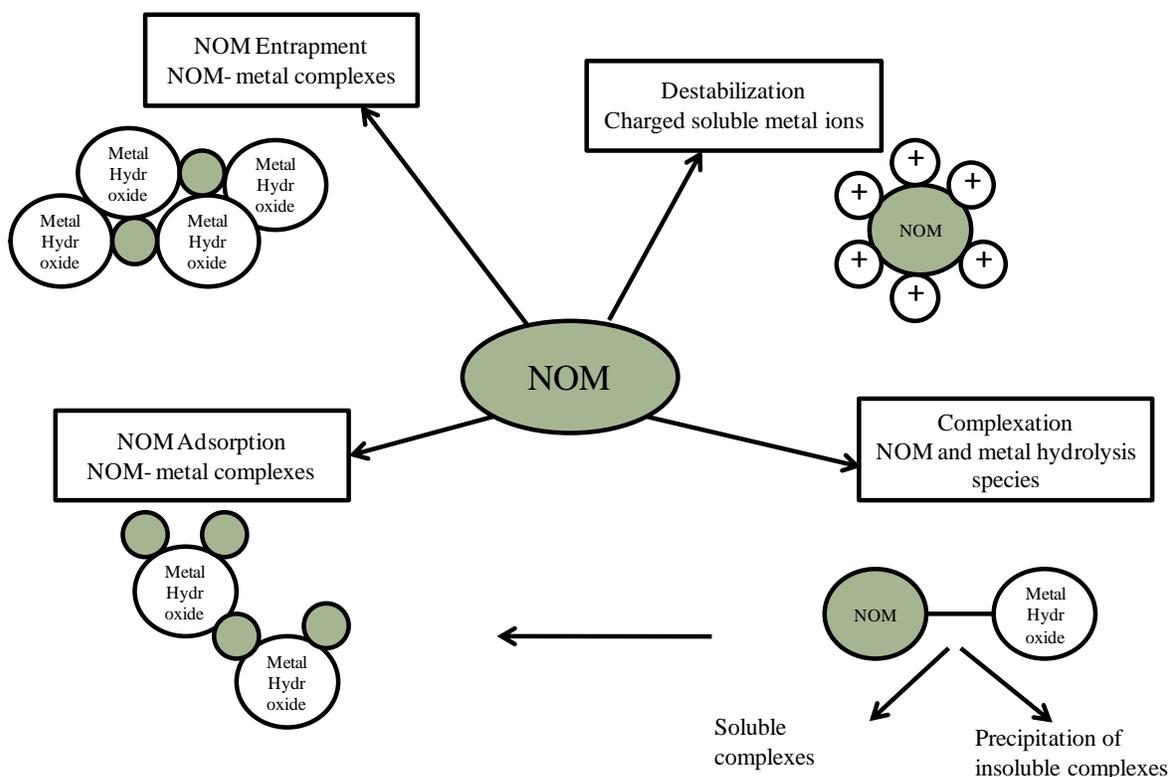


Figure 2.5: Possible NOM removal mechanism during coagulation (Adopted from Jarvis et al. 2004).

There are two different coagulation strategies used in the water industry: conventional coagulation and enhanced coagulation. Conventional coagulation is generally defined by the conditions that lead to optimal turbidity removal, whereas enhanced coagulation is defined as the optimized condition of coagulation pH and dosage that results in maximum removal of DOC as precursors to DBPs formation and minimal residual coagulant concentration (Edzwald and Tobiasson 1999). To determine optimal conditions for coagulation (dose and pH) bench scale runs using standard jar tests have to be done first (Freese et al. 2001; Yigit et al. 2009).

Among the different coagulants used in drinking water treatment industry, aluminum based coagulants especially aluminum sulphate (alum), $Al_2(SO_4)_3$, are reported to be capable of treating water with widely varying chemical parameters (Van Benschoten et al. 1990a). However, there is an unclaimed hypothesis regarding the relation between the usage of alum in

the water treatment process and alzheimer's disease (Haarhoff and Cleasby 1988). On the contrary, ferric-based coagulants have been shown to lead to higher removal rates of NOM specifically at low temperatures ($< 3^{\circ}\text{C}$) (Haarhoff and Cleasby 1988). Compared to alum, ferric coagulants are considered less desirable. They are more acidic and effective over narrower pH ranges, and add colour to water resulting in a non-optimal treatment condition (MacPhee et al. 1994). According to literature, selection of an appropriate coagulant to maximize NOM removal for a given source water depends on many water characteristics (DOC composition, DOC concentration, alkalinity, pH, and temperature), and coagulation conditions (coagulant type and coagulant dose) (Edzwald and Tobiason 1999; Pernitsky 2001; Duan et al. 2003; Hu et al. 2006; Matilinen et al. 2010). Our recent study showed that maximizing the total DOC removal could not assure the lowest THM formation (Sadrnourmohamadi et al. 2013). Coagulants that effectively remove fractions of DOC which contain most THM precursors successfully lower total trihalomethanes after disinfection. Therefore, to establish the optimal coagulation conditions to reduce the levels of THMs precursors, the characteristics of the source water, as well as the coagulant need to be studied for each specific water source (Matilainen et al. 2005; Zouboulis et al 2008).

2.5.1.1. Aluminum based coagulants

Aluminum based coagulants are one of the most widely applied coagulants in Canadian drinking water treatment plants due to their effectiveness and low costs (Niquette et al. 2004; Liu et al. 2009, Sadrnourmohamadi and Gorczyca 2015b). Recently, some types of pre-polymerized coagulants, with the general formula of $(\text{Al}_n(\text{OH})_m\text{Cl}_{(3n-m)})$, such as polyaluminum chlorides (PACl) ($n=2, m=3$) and aluminum chlorohydrate (ACH) ($n=2, m=5$) have been applied for water treatment (Duan and Gregory 2003; Pernitsky and Edzwald 2006). Compared to conventional

alum, these coagulants have been proved to produce stronger flocs, lower sludge volume, and have higher charge neutralization capacity and rapid aggregation rate. They also have been proved to be more effective in DOC removal within a broader range of pH (Chen et al. 2006). Polymeric aluminum coagulants have been shown to perform better than traditional Al coagulants in removal of turbidity, total organic carbon, and UV_{254} under certain conditions (Duan and Gregory 2003; Hu et al. 2006; Sadrnourmohamadi and Gorczyca 2015b). However, there have been some reports indicating that for some water sources alum shows greater removal of DOC than with polymeric aluminum coagulants (Van Benschoten and Edzwald 1990; Chen et al. 2006). Numerous researchers have discussed the effect of pH on DOC and UV_{254} removal by aluminum-based coagulants. This effect can be discussed in two aspects: the effect on the charge of DOC compounds functional groups and the effect on the distribution of aluminum species. Firstly, the decrease of pH causes the functional groups such as carboxylic and phenolic groups to become less negatively charged due to protonation, requiring less coagulant to achieve neutralization (Chen et al. 2006; Shi et al. 2007). Secondly, the water pH also affects the distribution of aluminum species in coagulants (Yan et al. 2008).

2.5.1.2. Coagulant hydrolysis species.

The performance of aluminum-based coagulants for DOC and UV_{254} removal has been recognized to depend largely on raw water quality and Al speciation during coagulation (Yan et al. 2007; Shi et al. 2007; Wu et al. 2009; Yang et al. 2010). To study the distribution of Al hydrolysis species different chemical and instrumental methods such as Al-Ferron complexation timed spectroscopy and ^{27}Al NMR have been applied (Zhou et al. 2006). Parker and Bertsch (1992) showed that ferron method is an inexpensive and simple alternative compared to ^{27}Al -NMR analyses. It also is capable of quantification of aluminum species at 10-100 times lower

concentrations compared to NMR. In ferron assay method, the species are characterized as hydrolyzed Al monomeric species (Al_a), medium polymeric species (Al_b), and large polymeric species and/or solid-phase $Al(OH)_3$ (Al_c) based on the kinetic difference of the complexation reactions with ferron (Duan and Gregory 2003; Yan et al. 2007; Lie et al. 2009). Parker and Bertsch (1992) confirmed that the Al_b species measured with ferron corresponds with Al_{13} measured with ^{27}Al -NMR in freshly prepared solutions. Higher concentrations of Al_{13} are claimed to improve coagulation properties of polyaluminum coagulant due to having nano- sized diameter, structure stability, and high charge neutralization capacity (Chen et al. 2006; Pernitsky and Edzwald 2006; Zouboulis and Tzoupanos 2010; Gebbie 2011).

Polyaluminum coagulants can be produced by the reaction of aluminum salts with base under controlled conditions in commercial scale. These coagulants are characterized by their degree of neutralization (B) or basicity (Pernitsky and Edzwald 2006)

$$B = \frac{[OH^-]}{[Al_T]} \quad [\text{Eq. 2.2}]$$

$$\text{Basicity} = \left(\frac{B}{3}\right) \times 100 \% \quad [\text{Eq. 2.3}]$$

A range of zero to three corresponding to a basicity of 0 to 100% is reported for B value. For commercial polyaluminum coagulants basicity is reported to be in the range of 15% to 85%. The basicity also affects the relative prevalence of polymeric and monomeric species as well as the consumption of alkalinity by the coagulant (Pernitsky and Edzwald 2006; Sadrnourmohamadi and Gorczyca 2015b). In general higher basicity (up to 2.5) results in a greater fraction of polymeric species, lower consumption of alkalinity and hence, lower pH depression (Bottero et al. 1981; Gebbie 2011). According to literature (Chen et al. 2006; Yan et al. 2007) the traditional coagulants and pre-polymerized ones with low basicity undergo significant hydrolysis after

dosing resulting in changes in aluminum speciation. Coagulants with high neutralization ratios contain more stable hydrolysis species which has lower effect on water pH and alkalinity.

2.5.2. Activated Carbon

Activated carbon (AC) has been widely used in water treatment to control organic compounds, taste, odour, color, and more recently to remove DOC. It also has the ability of removing the toxicity from drinking water (Bolto et al. 2004).

The removal of DOC by activated carbon strongly depends on its adsorption capacity occurring in 3 steps: (i) the organic compounds need to be transferred from the bulk solution to the surface of the carbon by passing through a film of solvent that surrounds the AC. This process is referred to as film diffusion; (ii) these organic molecules must then be transferred to an adsorption site within the pore of the AC. This is known as pore diffusion; and (iii) the adsorbed molecule must become attached to the surface of the sorbent which is called adsorption process. The physical and chemical characteristics of AC such as pore size distribution, AC surface area, and AC surface chemistry are important factors affecting the adsorption process (Valten et al 2001). Moreover the characteristics of DOC as the adsorbate such as solubility, size distribution, charge distribution, degree of hydrophilicity and/or hydrophobicity, influence the DOC adsorption onto activated carbon (Newcombe 1999). Furthermore some other factors including solution temperature, pH, hardness, and ionic strength play important role here (Dastgheib et al. 2004). It has been reported by Newcombe (1999) that pH reduction results in higher adsorption due to the negative charge reduction of DOC. Also by increasing the temperature organic compounds become highly soluble in water which consequently results in higher level of DOC adsorption to AC (Goss 2011). DOC species compete with other compounds to get to the adsorption sites of activated carbon. When DOC is adsorbed by AC it blocks some of the adsorption sites thus

limiting adsorption of other micro-organic pollutants (Newcombe et al. 2002). Due to higher concentration of these organic compounds in natural waters compared to the other pollutants this method is very effective in DOC removal (Karanfil et al. 1999). Adsorption capacity of AC for DOC removal is determined by two parameters: the size exclusion and the electrostatic interactions, the former determines the availability of a pore for adsorption and the latter determines the attractive interaction between the carbon surface and the DOC molecules (Dastgheib et al. 2004). From size exclusion perspective, the size distribution of AC pores and DOC mixture needs to be compatible (Lee et al. 1981; Dastgheib et al. 2004). Due to size effect, large molecular weight organic compounds (>10,000 Da) such as humic acid don't readily adsorb to AC while intermediate molecular weight organic compounds (500-5000 Da) can be absorbed easily (Zhao et al 2006; Velten et al. 2011). Organic compounds with low molecular weight (<500 Da) have greater ability to access AC surfaces due to their size effect and are expected to be removed easily. However, these organic compounds are reported to be more soluble and hydrophilic and less absorbable. Therefore despite their smaller size they don't exhibit high adsorption (Karanfil et al. 1999). From electrostatic interaction perspective DOC is known to be negatively charged mixture at ambient pH values in natural waters. Electrostatic attraction is expected between these negatively charged species and positively charged group present on the surface of AC leading to higher extent of adsorption (Dastgheib et al. 2004; Velten et al. 2011). However this adsorption will continue to a certain acidity level of DOC. By increasing the acidity beyond that level, the electrostatic adsorption forces begin to compete against the DOC solubility which will result in lower adsorption (Newcombe 1999). AC can be used into two forms in water treatment process: powdered activated carbon (PAC) and granular activated carbon (GAC). PAC is usually added in powdered form at different points in the water

treatment system while GAC is used as a filtration step, packed into a column. Moreover biological activated carbon (BAC) process is applied in water treatment industry where ozonation is combined with GAC (Chow 2010). GAC is widely employed when there is odor and taste problem while PAC is less expensive and is more effective when the incoming water quality changes in time (Chow 2010). BAC is normally used to control the concentration of assimilable organic carbon (AOC) which can cause the bacterial regrowth in distribution systems (Bose 1994). As already discussed, DOC removal by AC significantly depends on some factors such as carbon type, carbon properties, DOC composition, and DOC concentration. Therefore it is important to understand the interaction between DOC and AC and the adsorptive capacity of activated carbon under controlled conditions (Matsui et al. 2002).

2.5.3. Membrane Filtration

Membrane filtration as a new and advanced technique is widely applied in drinking water industry to enhance the treated water quality (Shengji et al. 2008). Compared to conventional treatment technologies such as coagulation, clarification and softening, membrane technology has several benefits such as less need to chemicals addition and less sludge production. It is also competitive with conventional treatment methods when water of high quality is desired (Laine et al. 1991; Nakatsuka et al. 1996). Membranes are used to remove particles, colloids, inorganic and organic species from raw water. They are also effective in removing DOC. Moreover they have been reported to show high efficiency at retaining micro-organisms, resulting in effluents with high microbiological quality (Gomez et al. 2006). However, membrane filtration cannot be classified as sterile and they should not be relied on as the sole disinfection process (Bourgeois et al. 2001). Recently membrane filtration has been reported particularly for THMs precursors' removal with nanofilters showing effective THMFP reduction up to 80-90% (Uyak et al 2008).

In membrane process pressure as a driving force is applied to separate undissolved species from solution; Depending on the membrane pore size there are four types of pressure-driven membrane processes described as microfiltration (MF) ($> 0.1 \mu\text{m}$), ultrafiltration (UF)($0.1\text{-}0.001 \mu\text{m}$), nanofiltration (NF) and reverse osmosis (RO) ($<0.001 \mu\text{m}$) (Bose 1994). Ultrafiltration is used to remove larger MW NOM but is limited by its range of molecular weight cut-off (MWCO) in effectively removing a significant fraction of lower MW organic matter. Nanofiltration membranes, which have a lower MWCO, is one of promising option in water treatment plants and could be effectively used for removal of NOM fractions which cannot be retained by ultrafiltration (Frimmel et al. 2006; Baghoth 2012). Nanofilters reject a wide range of materials with different chemical properties and molecular weight cut-off compared to reverse osmosis membrane. Moreover they require less pressure (energy) than osmosis membrane and are able to produce good water quality; therefore nanofilters are mostly used in drinking water treatment nowadays (Lee et al. 2005). In the application of membrane technology membrane fouling is known as one of the main problems (Laine et al. 2003). Fouling is phenomena where available substance in raw water such as colloidal and soluble natural organic matter, inorganic particles, bacteria and viruses can either plug the membrane pores or accumulate on the membrane surface (Nakatsuka et al. 1996). Membrane fouling results in permeate decline which needs more frequent backwashing, higher energy consumption and higher chemical consumption as the membrane cleaning agents. It consequently increases the cost of production of drinking water (Lee et al. 2005; Bing-zhi et al. 2007). Some parameters are important in membrane fouling such as operation condition (temperature, pressure), feed solution quality, nature of foulants, interaction of raw water and membrane, and membrane roughness (Nakatsuka et al. 1996).

There are physical and chemical ways to reduce membrane fouling. Physical methods include back washing, high cross flow velocity and scouring with air bubbles (Nakatsuka et al. 1996). Physical cleaning is not effective in long term operation because of some irreversible fouling. Chemical cleaning also cannot be used in wide range because of the effect of chemical reagents on membrane life and high amount chemical agent usage. It has been reported that the application of coagulation, activated carbon adsorption, and ozonation before membrane can be effective in fouling reduction (Fang et al. 2005).

2.5.4. Ozonation

2.5.4.1. Ozone chemistry

Ozone is a selective, colorless, and pungent smelling gas, with high oxidation potential of 2.07 volts (Carey 2006; Tootchi 2009).

As shown in Figure 2.6 ozone molecule has an extreme resonance structure. Its molecular configuration is the reason of its high reactivity in aqueous solution.

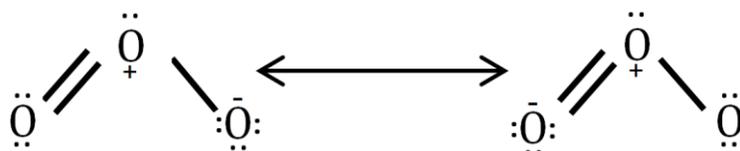


Figure 2.6: Electric configuration of molecular ozone (Adapted from Langlais et al. 1991).

Ozone structure shows that it can act as a dipole, as an electrophilic and nucleophilic agent (Gardoni et al. 2012). Generally three types of reactions can be evidenced in ozone interaction with NOM:

(i) Cyclo addition (Criegee mechanism): because of ozone dipolar structure, it can react with unsaturated bond by 1-3 dipolar cyclic reaction to form cyclic structure. Then water reacts with carbon-carbon bond which further decomposes into carbonyl compounds (ketones or aldehydes).

(ii) Electrophilic attack by ozone: This type of reaction occurs mostly at high electron density sites of aromatic compounds which results in the opening of aromatic rings and results in the formation of compounds with carboxyl and carbonyl groups.

(iii) Nucleophilic attack by ozone: This type of reaction happens on NOM molecules with electron deficient sites, particularly on carbons carrying electron-withdrawing groups. This mechanism is not very common and hence not widely reported (Bose 1994).

Aqueous ozone is unstable and under certain conditions it dissociates rapidly to produce the OH° radical, an even stronger oxidant (Elovitz and von Gunten 1999; Brookman 2007). There are two general mechanisms through which ozone can react with various compounds (M) in an aqueous solution: direct reaction that involves molecular ozone, and indirect (radical-type) reaction involving hydroxyl radicals (OH°) that are generated when ozone decomposes in water (Hoigne and Bader 1976; Esplugas 2002, Staehelin and Hoigne 1985). These two basic reactions of ozone in water are illustrated in Figure 2.7.

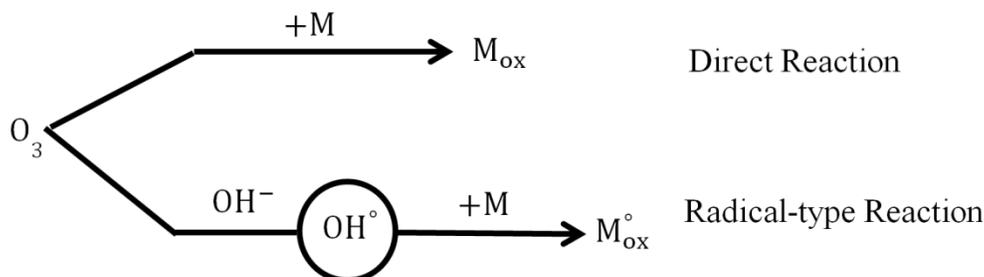


Figure 2.7: Two basic reactions of ozone in water.

The direct reaction has high selectivity but is slow compared to the indirect reaction which is quick but low selective (Hoigne and Bader 1983).

During ozonation various compounds present in water such as organic, and inorganic species are oxidized by direct reaction, or radical type reaction or combination of both of them. The reaction pathway depends on several parameters such as presence of some scavenger chemicals (carbonate, bicarbonate) in water and water pH (Von Gunten 2003). Carbonate and bicarbonate which are available in considerable amount in natural waters can react with hydroxyl radical and produce radicals with lower oxidation potential (equation 2.4 and 2.5). These chemical species behave as free radical scavengers shifting the pathway to direct ozone oxidation (Crittenden et al. 1999; Von Gunten 2003; Chu and Ching 2003).



Moreover, at the condition of high pH levels indirect hydroxyl reactions predominate while direct ozone reactions prevail at low pH values since the OH^\bullet formation rate decreases at acidic condition (Chang and Singer 1991). The decomposition of ozone is a result of a chain reaction initiated by hydroxyl radical, and free radicals produced by reactions may be involved as chain carriers (Hoigne and Bader 1976). The overall ozone decomposition mechanism pattern is shown in Figure 2.8.

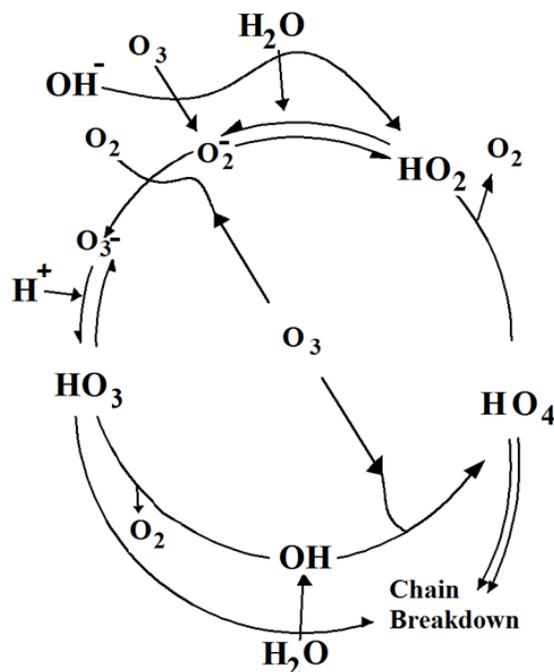


Figure 2.8: Reaction diagram for ozone decomposition (from Staehelin and Hoigne 1985).

2.5.4.2. Ozone in drinking water

The application of ozone in drinking water treatment has been widespread; due to its high oxidation potential (Le Pauloue and Langlais 1999). Molecular Ozone is a strong oxidant; by dissociating in water, it can produce hydroxyl radicals, even stronger oxidants (Brookman 2010). Ozone has been used for removal of organic species, turbidity, color, taste and odor. It also has been applied for partial natural organic matter degradation and microorganisms inactivation (Von Gunten 2003; Camel & Bermond 1998; Hoigne 1998; Sarathy 2006, Bose et al.2007). Ozonation has been reported as an effective way to remove disinfection by-products precursors present in drinking water sources (Hu et al. 1999; Galapate et al. 2001). Ozone can convert NOM from higher molecular weight organic compounds to lower molecular weight by-products. These by-products are less reactive with chlorines and results in reduction of formation of THMs and HAAs upon subsequent chlorination (Amy et. al. 1991; Kerc et al. 2003a; Akcay et al. 2008). However, studies have demonstrated that in some cases, ozonation can have a deteriorative effect

(Toor and Mohseni 2007; Chowdhury et al. 2008). This is because, the NOM has a complex structure, and the effect of ozone on NOM from different sources cannot be directly compared. Ozone application can also change the solution pH. In ozonation of natural waters containing both bicarbonate and TOC, the direction and magnitude of the pH change can be determined by the balance between acid producing and acid consuming reactions. Depending on solution composition and ozonation practice, ozonation can either increase or decrease pH (Edwards and Benjamin 1991). It was reported that solutions containing relatively high ratios of TOC to bicarbonate would be expected to be acidified during ozonation, whereas the pH of solutions containing low ratios of TOC to bicarbonate would be expected to increase (Edwards and Benjamin 1991). Despite beneficial effects of disinfection and oxidation, disadvantages of ozone may include the increased formation of bromate and brominated by-products. This is a critical issue especially for bromide-containing waters (Tobiason et al 1995). Ozonation also increase the biodegradability of NOM due to cleavage of aromatic rings (Von Gunten 2003). The biodegradable natural organic matter (BDNOM) promotes bacterial regrowth in the treatment units and water distribution systems, therefore biologically active filters such as BAC and GAC are suggested to be applied after ozone in order to remove these compounds from treated water (Leenheer and Croué 2003; Kim and Yu, 2005; Kasprzyk-Hordern 2006). Ozone doses used for reduction of THMs precursors in drinking water treatment is reported to be in the range of 0.5-1 mg Ozone/mg DOC approximately (Amy et. al. 1991). It has been reported that this dose of ozone results in partial oxidation of organic carbon, alternating the nature of DOC, rather than total mineralization and oxidation (Chang and singer 1991, Yan et al. 2007). Therefore if ozone is combined with treatment processes such as coagulation, filtration, and GAC, it can result in further removal of DOC (Uyguner et. al. 2007b, Amy et. al. 1991).

2.5.4.3. Ozone as coagulation aid

Beside the widespread use of ozone such as disinfectant, other beneficial effects such as aiding coagulation and filtration have also been observed. The reports on the effects of ozone as a coagulation aid are complex and unpredictable. Some studies have reported cases in which ozone enhanced DOC removal by subsequent coagulation in lower coagulant dosage and effectively reduced THM formation (Farvardin and Collins 1989; Camel and Bermond 1998; Chiang et al. 2002; Singer et al. 2003; Li et al. 2008). Other studies, on the contrary, pointed out that pre-ozonation could not reduce the dosage of coagulant (Reckhow and Singer 1984; Tobiason 1995; Becker and O'Melia 1996). The conflicting reports of the ozone effect on coagulation can be explained by a number of simultaneous mechanisms taking place during this treatment process. Some of these mechanisms have positive effects, while others may have negative effects on subsequent coagulation treatment. Ozone-enhanced coagulation can be optimised by understanding these mechanisms (Currie et al. 2003). When ozone is used as a pre-oxidant in water treatment, it assists in the destabilization and aggregation of particles by several hypothesized mechanisms, which have been proposed by Reckhow et al. (1986):

1. Ozone can increase the concentration of oxygenated functional groups, such as carboxylic acid, leading to interaction and complexation with coagulant cations or naturally available cations, such as calcium. These effects result in promoted coagulation and flocculation in ozonated waters.
2. Ozone may reduce stabilizing organic coatings on particles, causing desorption of organics and reducing repulsive forces between the particles.
3. Ozone can polymerize meta-stable organics, leading to particle aggregation via bridging reactions.

4. Ozone can rupture organo-metal complexes, causing in-situ production of coagulants.

The ozone dose, coagulation conditions (coagulant type and dose), and raw water characteristics (DOC type and concentration, hardness, and alkalinity), as the important variables, determine the effect of ozone on coagulation (Bose and Reckhow 2007; Yan et al. 2007).

2.5.4.4. The role of calcium hardness in ozone enhanced coagulation

Calcium is a key parameter in ozone-induced coagulation. It has been reported that ozonation, prior to coagulation, benefits waters with moderate to high levels of calcium hardness. Moreover, ozone-induced particle destabilization and aggregation occurs only in the presence of significant concentrations of calcium (Dowbiggin and Singer 1989; Chang and Singer 1991; Chandrakanth and Amy 1996). Chandrakanth (1994) reported ozone enhanced coagulation only when the raw waters had calcium hardness concentration higher than $100 \text{ mgL}^{-1} \text{ CaCO}_3$. Chang and Singer (1991) investigated the raw water characteristics that would promote ozone-induced coagulation. The study showed that optimal ozone-induced particle destabilization can occur in waters with calcium hardness-to-total organic carbon ratios $>25 \text{ mg CaCO}_3/\text{mg DOC}$. Calcium has a high tendency to form strong complexes with functional groups containing oxygen. Ozonation of water organic compounds can produce oxygen-rich compounds, such as carboxylic groups, leading to increased complexation of calcium with both aqueous NOM and particle-sorbed NOM (Edwards and Benjamin 1992a; Chandrakanth and Amy 1998; Rodríguez et al. 2012b). Also, calcium can neutralize the organic particle anionic surface charge which can lead to a reduction in particle stability through surface charge reduction (Edwards and Benjamin 1992b; Chandrakanth and Amy 1996). This mechanism is important when source water has a high level of calcium hardness (Dowbiggin and Singer 1989).

**CHAPTER 3: REMOVAL OF DOC AND ITS FRACTIONS FROM CANADIAN
PRARIES SURFACE WATER CONTAINING HIGH LEVELS OF DOC AND
HARDNESS**

ABSTRACT

In this paper removal of Dissolved Organic Carbon and its fractions by chemical coagulation was studied. Raw water was collected from the Red River (Manitoba, Canada). This source water has a DOC ranging from 8 mg L^{-1} to 12 mg L^{-1} and total hardness of about $400 \text{ mg L}^{-1} \text{ CaCO}_3$, which represents a typical surface water quality of the Canadian Prairie. Four coagulants were tested at different pH levels: alum, ferric sulphate, ferric chloride and titanium sulphate. Coagulation effectiveness was evaluated by removal of DOC, DOC fractions, specific UV absorbance, and trihalomethane formation potential of the coagulated water. The water DOC was separated into six fractions based on hydrophobicity and acid base functionality: hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base, and hydrophilic neutral. Results showed that ferric sulfate had the highest total DOC removal of 66% while ferric chloride had the lowest DOC reduction of 54%. Although the THMFP found to be lowered significantly with all four coagulants the ferric chloride showed the greatest THMFP reduction. Fractionation results found the significant reduction in HPOA fraction for all coagulants with 91% for ferric chloride as the highest removal value. Poor removal of hydrophilic fractions was found for all coagulants. The result of this study showed that total DOC reduction cannot guarantee THMFP reduction and coagulation should be optimized to remove DOC fractions which form most THMs.

3.1. INTRODUCTION

High dissolved organic carbon (DOC) in potable water sources is of concern due to the formation of harmful chlorine disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), following chlorine disinfection (Rook 1974; Singer 1999). Potable water sources in Manitoba (Canada) often contain concentrations of DOC exceeding 20 mg L⁻¹. As a result of high DOC concentrations approximately 70% of the potable water treatment plants (WTPs) in Manitoba using surface water sources are not in compliance with THMs regulations set by the Province (Manitoba Water Stewardship 2011). Therefore, water treatment facilities are faced with improving the removal of DOC from the raw water prior to chlorination in order to reduce the concentrations of THMs to meet current provincial guidelines. A recent study of the THMs formation potential (THMFP) on two Manitoban rivers showed that THMFP of these rivers can be 10 times higher than those reported in literature (Goss and Goeczyca 2012). This study focused on Trihalomethanes because the Province regulates only these chlorine disinfection by-products (Manitoba Water Stewardship 2011). HAAs are not currently regulated in the Province of Manitoba (Canada).

UV₂₅₄ absorbance has been used as an indicator for estimating the potential of raw surface waters to form THMs, but there are conflicting beliefs regarding its effectiveness in estimating THM formation. The major limitation of using specific UV absorbance (SUVA) to predict DBPs formation in drinking water treatment is probably the involvement of non-reactive components in DOC. Indeed, not all organic carbon having absorbance at 254nm reacts with chlorine to form THMs (Weishaar et al. 2003). Chow et al. (2008) suggested that the correlation between UVA₂₅₄ and DOC concentration is source dependent and each carbon source showed a distinctly different linear regression. Poor correlations between SUVA and specific trihalomethane formation

potential (STHMFP) have been occasionally reported and the reliability of using SUVA to predict trihalomethane formation has been questioned (Fram et al. 1999; Chow et al. 2008). Cho et al. (2010) have shown that SUVA does not correlate successfully with water DOC for one of the tributaries to the Red River. In addition, some studies have questioned the reliability of using SUVA to predict reactivity of DOC in natural waters (Weishaar et al. 2003). Iriarte-Velasco et al. (2007) showed that coagulation optimization based on DOC and UV_{254} removal does not ensure optimum results for THMs precursors removal. One possible source is formation of UV absorbing moieties during coagulation which interfere UV measurements.

It has been strongly believed that the hydrophobic acid (HPOA) fraction of DOC, which contains mainly humic matter, has the greatest potential to form THMs (Reckhow et al. 1990; Singer 1999; Leenheer & Croué 2003; Chow et al. 2005). However, it has been recently reported that the hydrophilic (HPI) fractions from the Red River had greater potential to form THMs compared to the hydrophobic (HPO) (HPOA+HPOB+HPON) fractions (Goss and Gorczyca 2012). It has been reported that the hydrophilic fractions are far less amendable to be removed with conventional coagulation and is believed to be a major component of DOC found in finished waters coagulated using metal salts (Sharp et al. 2006). Therefore, in this study special focus will be given to reduction of the HPO and HPI fractions.

Objectives

The objective of this study was to evaluate the removal of DOC fractions from the Red River water (Manitoba, Canada) by chemical coagulation. The Red River water represents a typical surface water quality of the Canadian Prairie. Its DOC can vary from 8 mg L^{-1} to 12 mg L^{-1} . The pH averages about 8 and hardness can range from a low of 232 mg L^{-1} to a high of 411 mg L^{-1} (Goss 2011). The results show that the Red River has high alkalinity, pH, and DOC, suggesting

that this water has characteristics that make DOC removal by coagulation difficult. Typically, better removal of DOC is achieved at lower pH, furthermore the high alkalinity of the Red River makes pH reduction prior to coagulation more difficult and costly (Okour et al. 2009).

The four coagulants used in this study were ferric sulfate, ferric chloride, aluminum sulfate and titanium sulfate. The first three coagulants were tested because they are commonly used in water treatment plants due to their effectiveness, accessibility and low price (Baghvand et al. 2010; DeWolfe et al. 2003). Titanium sulfate was tested because it has been shown to have better removal of the humic fraction of DOC compared to aluminum and iron based coagulants. In addition it has been reported that titanium salts as new coagulants are economical in terms of sludge reduction (Okour et al. 2009). It has been reported that the performance of a particular coagulant is dependent upon the specific characteristics of the NOM and the test conditions (Volk et al. 2000). Therefore, in this study special focus will be given to reduction of the HPO and HPI DOC fractions. Different coagulant types, doses, and pH were evaluated to establish the optimal conditions for the removal of these fractions from the water to better control the formation of THMs.

3.2. MATERIALS AND METHODS

3.2.1. Sample Collection from the Red River

One hundred litres of the Red River water were collected on May 12, 2011 via an inlet within the Morris Water Treatment Plant which is located approximately 50 kilometers south of Winnipeg, Manitoba. The Red River water is stored in a 1.3 million cubic meter settling pond prior to entering the WTP. All water samples were filtered through 0.45 micron nitrocellulose filter paper which represents the dissolved fraction of natural organic matter. Water samples were stored at 4°C until analysis where the samples were allowed to reach room temperature.

3.2.2. Analytical Methods

DOC concentrations were determined using a total organic carbon analyser (Phoenix 8000, Tekmar Dohrmann, USA) after filtration through a 0.45 micron nitrocellulose filter paper. The UV absorbance at 254 nm (UV_{254}) was measured using a UV/visible spectrophotometer Ultraspec 2100 pro, (GBC Scientific Equipment, Australia) with a 1 cm quartz cell. Specific UV absorbance (SUVA) was calculated as UV_{254} normalized for DOC. Turbidity was measured using a HF Scientific Micro 100 Turbidimeter (HF Scientific, Fort Worth, Florida, USA). The pH of the samples was measured using a Fisher Scientific Accumet 50 pH meter (Fisher Scientific, New Jersey, USA). Alkalinity was determined as $mg\ L^{-1}\ CaCO_3$ by titration of sample water with 0.02 N sulphuric acid titrated to pH 4.48 according to *Standard Methods 2320B* (APHA 2012). All measurements were repeated at least three times to assure the reproducibility of experimental results.

3.2.3. DOC Fractionation

The method of DOC fractionation used in this study was developed by Ratpukdi et al. (2009) using solid phase extraction (SPE) compared to the classic resin fractionation methods developed by Leenheer (1981). This SPE method significantly reduces the need for long resin preparation time and need for specialized equipment making this an attractive alternative to classic resin separation methods (Ratpukdi et al 2009). The SPE fractionation procedure used three Bond Elute ENV cartridges (Varian Inc., Lake Forest California), one Phenomenex Strata XC cartridge, and one Phenomenex Strata X-AW cartridge (Phenomenex, Torrance, California). The fractionation method separates DOC into the six fractions isolated using the Leenheer method: hydrophilic acid (HPIA), hydrophilic base (HPIB), hydrophilic neutral (HPIN), hydrophobic acid

(HPOA), hydrophobic base (HPOB) and hydrophobic neutral (HPON). The full procedure for this method can be found in Ratpukdi et al. (2009).

3.2.4. Coagulation Jar Tests

The jar tests were performed using a conventional method in six paddle PB-700TM standard jar tester by Phipps & Bird (Richmond, USA). One litre of water was placed in each jar. A measured amount of coagulant was pipetted into the test water to give a desired coagulant concentration while stirring rapidly at 120 rpm for 1 minute, followed by a slow mix at 40 rpm for 30 minutes. The samples were then allowed to settle for 30 minutes. Aluminum sulfate, ferric sulfate, ferric chloride and titanium sulphate stock solution (10,000 mg L⁻¹ as Al for aluminum sulfate) were prepared in Milli-Q (Millipore, France) water. Coagulants doses were in the range of 20 mg L⁻¹ to 120 mg L⁻¹ based on the coagulant to DOC ratio of about 10:1(Garcia 2005). The surface water we used in this study has pH above 8 as well as significant alkalinity and related carbonate hardness. Most of the water treatment plants supplied by the Red River utilize lime/soda softening process, where water pH is increased to 11. Reduction of water pH to below 6 prior to softening would require significant increase of amount of lime required for softening. This would significantly increase the operational cost of the water plants (Pembina Valley Water Co-op 2012). Therefore, the coagulation tests were conducted at pH of 6, 7, and 8. Most DOC compounds are reported to be negatively charged in this pH range and can be destabilized by metal salts as coagulants through charge neutralization (Crittenden et al. 2005).

The pH was adjusted with 0.1 M sodium hydroxide solution (NaOH) and 0.1 M hydrochloric acid (HCl). Sodium hydroxide and hydrochloric acid were analytical grade chemicals (Sigma-Aldrich Company Ltd, UK). Residual aluminum and iron concentration analysis were performed

by Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES, Agilent Technologies, USA) with acidification using 5% HCl.

3.2.5. Trihalomethane Formation Potential

Raw and coagulated water samples were collected in 45mL glass vials. THMs formation potential (THMFP) measurements were conducted according to *Standard Methods 5710B* (APHA 2012). Chlorine demand for each fraction was not measured prior to chlorination due to small sample volume (~10 mL). 50 mg L⁻¹ sodium hypochlorite was added to each sample to ensure there was a sufficient amount of chlorine available to react with organics. All samples were buffered to pH=7 using a phosphate buffer. Sample vials were sealed with TFE caps and were kept in the dark at 4°C for 7days. THM concentrations were determined with liquid-liquid extraction method according to *Standard Methods 6232B* (APHA 2012). THMs concentration was determined using an Agilent 7890A GC System (AgilentTechnologies, Santa Clara, California) equipped with a CombiPAL CTC Analytics auto sampler and used electron capture detection.

3.3. RESULTS AND DISCUSSION

3.3.1. General Water Quality

General water quality tests were taken for samples collected from the Red River on May 12, 2011 (Table 3.1). The DOC composition of the Red River can be found in Table 3.2. The composition of the Red River was similar to that reported earlier by Goss and Gorczyca (2012) which found that the composition of the Red River was more hydrophilic (63%) than hydrophobic (37%).

Table 3.1: General water quality of the Red River. Samples were taken on May 12, 2011

Parameter	Unit	Value
pH	pH unit	8.6
Turbidity	NTU	0.5
Alkalinity	mg L ⁻¹ CaCO ₃	220
UV ₂₅₄	cm ⁻¹	0.23
DOC	mg L ⁻¹	11.78
SUVA	m ⁻¹ mg L ⁻¹	2.36

Table 3.2: The DOC composition of the Red River. Samples were collected on May 12, 2012 and fractionated on May 14, 2011.

Fraction	Concentration (mg L ⁻¹)	DOC %
Hydrophobic neutral (HPON)	1.42	12.05
Hydrophobic base (HPOB)	0.16	1.36
Hydrophobic acid (HPOA)	2.74	23.26
Hydrophilic base (HPIB)	1.32	11.21
Hydrophilic acid (HPIA)	0.93	7.89
Hydrophilic neutral (HPIN)	5.21	44.23
Total	11.78	100

3.3.2. DOC removal by Coagulation

The results show that for all coagulants DOC removal efficiency increases with the increase of coagulant dosage (Figure 3.1). Ferric chloride and titanium sulfate had the greatest removal of DOC at pH 7, while aluminum sulfate and ferric sulfate had optimal removal at pH 6. All four coagulants achieve the highest DOC removal at the dose of 120 mg L⁻¹. However, most of this removal was achieved with the coagulant doses of 100 mg L⁻¹. The additional DOC removal at coagulant doses higher than 100 mgL⁻¹ was found statistically to be insignificant at a significance

level (α) of 0.05 (Montgomery 2001). At a pH of 6 ferric sulfate and aluminum sulfate was found to have the greatest removal of DOC showing a total reduction of 66% and 62% respectively. Ferric chloride and titanium sulfate had the lower DOC reduction of 54% and 58%. Therefore, ferric sulfate would be the coagulant that achieved the highest DOC removal.

SUVA data (not shown here) showed that coagulation with ferric sulfate at the highest dosage and pH 6 caused 45% reduction in the SUVA values. The reduction is 27% for aluminum sulfate at the same pH and dosage. The SUVA reduction is 32% and 52% for ferric chloride and titanium sulphate coagulated samples at pH of 7, respectively. It should be mentioned that recent studies have questioned the reliability of using SUVA to predict reactivity of DOC in natural waters.

Residual metal concentration measurement of all coagulated samples showed that values were below the Canadian Drinking Water Guidelines (Health Canada 2010).

3.3.3. Removal of Red River DOC fractions using optimized coagulation

Coagulated water using the optimized dose and pH conditions for the four coagulants was fractionated to determine the removal of specific DOC fractions. Ferric sulfate showed the greatest overall reduction of DOC with the final DOC concentration in coagulated water of 3.9 mg L⁻¹ (66% reduction), whereas ferric chloride was only able to reduce the DOC to 5.4 mg L⁻¹ (54% reduction). All coagulants were found to have poor removal of the HPIN fraction with 58-65% of the total DOC remaining following coagulation being composed of the HPIN fraction (Tables 3.3 & 3.4). On the other hand, all coagulants were able to reduce the HPOA fraction significantly representing only 2-9% of the remaining DOC. Titanium sulfate was able to reduce the HPO fraction to 1.15 mg L⁻¹ while ferric chloride only reduced the HPO fraction to 1.78 mg L⁻¹. Titanium sulfate has been reported by Okour et al. (2009) to be able to reduce the SUVA

value, suggesting the removal of DOC aromatic compounds believed to be the main THMs precursors. However, ferric chloride and ferric sulfate showed superior removal of the DOC and its HPOA fraction, believed to contain the highly reactive humic fraction, compared with titanium sulfate.

3.3.4. Reduction of THMFP using coagulation

THMFP of the water coagulated at the optimum conditions was determined for all four coagulants. The raw Red River water had a THMFP of $327.7 \mu\text{g L}^{-1}$ and a specific THMFP of $27.8 \mu\text{gTHM/mgDOC}$ (Table 3.5). All four coagulants significantly reduced the THMFP with aluminum sulfate and ferric chloride showing the greatest reduction in THMFP to $42.8 \mu\text{g L}^{-1}$ and $45.2 \mu\text{g L}^{-1}$, respectively. Ferric sulfate and titanium sulfate showed the least reduction in THMFP of $52.8 \mu\text{g L}^{-1}$ and $87.9 \mu\text{g L}^{-1}$, respectively. Titanium sulfate had more effect on removing HPO compared to HPI fractions, which is in agreement with the earlier study (Okour et al. 2009). However, titanium sulfate showed the poorest removal of the HPI fractions, reported by Goss and Gorczyca (2012) to be more reactive in the Red River. The lowest removal of HPOA and poor removal of HPI fraction may be the cause of the high specific THMFP for this coagulant. On the other hand, the ferric chloride also showed poor removal of the HPI fraction, but the highest removal of the HPOA fractions, and this coagulant showed the lowest coagulated water specific THMFP of all coagulants tested. Of the four coagulants tested, ferric chloride and aluminum sulfate showed the greatest reduction in THMFP and specific THMFP; however ferric sulfate and titanium sulfate showed the greater reduction in total DOC. Although ferric sulfate showed the highest removal of bulk DOC, it did not change the concentration of HPOA and HPI

fraction as effectively as other coagulants do. These results suggest that coagulation should be optimized for the removal of target DOC fractions forming THMs rather than the total DOC.

3.4.CONCLUSION

Effectiveness of removal of DOC using four coagulants at different pH was investigated.

Canadian Prairie water containing high levels of DOC and hardness was used in the experiments.

The following conclusions can be made from this study:

- 120 mg L⁻¹ of ferric sulfate with pH 6 was found to achieve the highest DOC removal (66%).
- Ferric chloride showed the highest removal (91%) of HPOA DOC fraction.
- Ferric chloride had the THMFP reduction from 327.7 µg L⁻¹ to 42.8 µg L⁻¹.
- The isolation of DOC fractionation and their removal using optimized coagulation showed that HPOA fraction can be removed effectively whereas HPI fractions had the poorest removal.

These results suggest that reduction of total DOC cannot guarantee THMFP reduction and chemical coagulation should be optimized to remove fractions of DOC which form THMs.

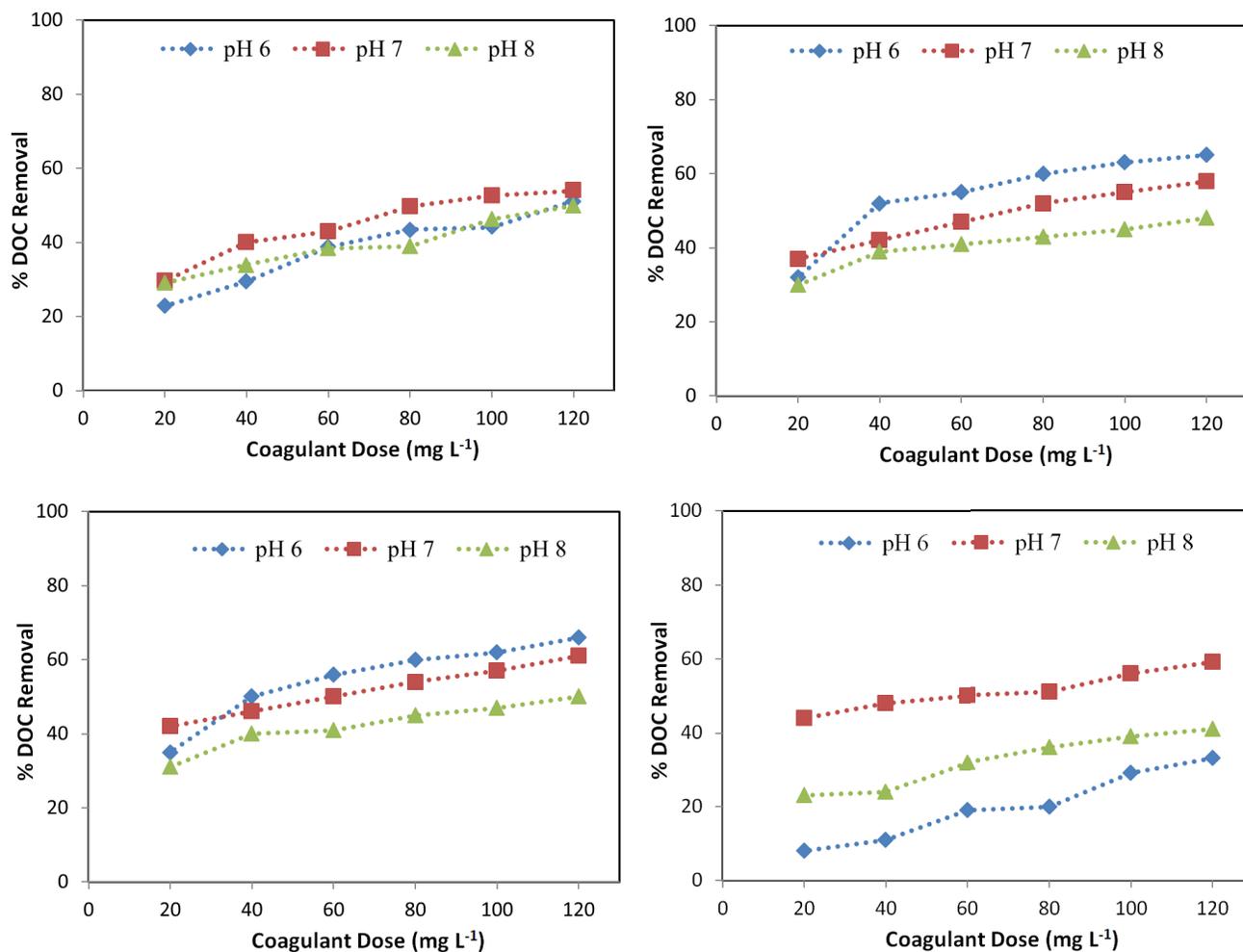


Figure 3.1: Removal of Red River DOC for (A): ferric chloride, (B): aluminum sulfate (C): ferric sulphate and (D): titanium sulfate at varying pH and coagulant dose.

Table 3.3: DOC fractions (shown as % DOC remaining), following coagulation using optimal conditions for total DOC removal.

Sample	% DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	12.05	1.36	23.26	11.21	7.89	44.23
Ferric chloride	27.03	3.89	2.04	6.11	2.78	58.15
Aluminum sulfate	12.50	6.25	7.08	8.54	1.25	64.38
Ferric sulfate	27.41	0.51	5.58	3.04	10.91	52.54
Titanium sulfate	10.53	4.34	8.9	7.02	4.13	65.08

Table 3.4: DOC fractions remaining in solution following coagulation

Sample	HPON	HPOB	HPOA	HPIB (mg L ⁻¹)	HPIA	HPIN	Total
Raw	1.42	0.16	2.74	1.32	0.93	5.21	11.78
Ferric chloride	1.46	0.21	0.11	0.33	0.15	3.14	5.40
Aluminum sulfate	0.60	0.30	0.34	0.41	0.06	3.09	4.80
Ferric sulfate	1.08	0.02	0.22	0.12	0.43	2.07	3.94
Titanium sulfate	0.51	0.21	0.43	0.34	0.20	3.15	4.84

Table 3.5: THMFP and specific THMFP for raw and coagulated water

Sample	DOC (mg L ⁻¹)	Chloroform	Bromoform	DBCM* (µg L ⁻¹)	BDCM*	THMFP	Specific THMFP (µgTHM/ mgDOC)
Raw	11.78±0.13	290± 40	ND	3.5±0.12	34.2±2.23	327.7±11	27.8
Ferric chloride	5.43±0.11	33.3±4.10	ND	2.2±0.051	9.7±1.42	45.2±2.3	8.3
Aluminum sulfate	4.47±0.10	28.5±1.22	ND	3.0±0.06	11.3±2.03	42.8±3.11	9.6
Ferric sulfate	3.94±0.17	39.5±2.1	ND	2.5±0.10	10.9±2.2	52.8±5.23	13.4
Titanium sulfate	4.84±0.01	70.6±3.2	ND	2.5±0.13	14.8±4.3	87.9±10.1	18.2

*BDCM- Bromodichloromethane

DBCM- Dibromochloromethane

**CHAPTER 4: REMOVAL OF DOC FROM HIGH DOC AND HARDNESS WATER BY
CHEMICAL COAGULATION-RELATIVE IMPORTANCE OF MONOMERIC,
POLYMERIC, AND COLLOIDAL ALUMINUM SPECIES**

ABSTRACT

This study investigates the mechanism of Dissolved Organic Carbon (DOC) removal from water with high alkalinity and DOC, typical in the Canadian Prairie, by three aluminum based coagulants: aluminum sulphate (alum), polyaluminum chloride (PACl), and aluminum chlorohydrate (ACH). Our focus is to discern the role of aluminum species: Al_a , Al_b and Al_c to explain the performance of these coagulants in the removal of DOC. Removal of organic compounds is quantified by measurement of DOC, DOC fractions and UV_{254} .

Results show that coagulation with alum at pH of 6.0 achieves highest DOC removal attributed to the highest content of in situ formed polymeric species (Al_b). At pH adjusted to 7 and 8 ACH shows the highest content of Al_b and consequently better removal of DOC compared to alum and PACl. When no pH adjustment is applied, coagulation with ACH achieves the highest DOC and UV removal, because of the highest concentration of Al_b and Al_c species in the solution.

Trihalomethane Formation Potential (THMFP) of the water after the application of coagulation has also been studied. Water coagulated with alum shows the lowest trihalomethane formation potential ($94.7 \mu\text{g L}^{-1}$) in comparison to the raw water ($202.4 \mu\text{g L}^{-1}$) followed by ACH and PACl. This can be related to the coagulant effectiveness in reduction of hydrophobic acid (HPOA) as the main precursor for THMs formation.

4.1. INTRODUCTION

Coagulation is one of the most widely used and cost effective methods applied in many treatment plants for the reduction of DOC and THMs (Edzwald 1993). The effect of coagulation on the removal of DOC from water depends on several factors: DOC concentration, coagulant type and dosage, pH, water alkalinity, and the chemical composition of source water (Edzwald and Tobiason 1999; Matilainen and Silanpaa 2010). Our recent study showed that maximizing the total DOC removal could not assure the lowest THMs formation (Sadrnourmohamadi et al. 2013). Coagulants that effectively remove fractions of DOC, containing most precursors of THMs, and not necessarily the total DOC, successfully lower water total trihalomethane formation potential.

Aluminum based coagulants are one of the most widely applied coagulants in Canadian drinking water treatment plants due to its effectiveness and low cost (Niquette et al. 2004; Zouboulis et al. 2008; Liu et al. 2009). Recently some types of pre-polymerized coagulants such as polyaluminum chlorides (PACl) and aluminum chlorohydrate (ACH) have been applied for water treatment (Vanbenschoten and Edzwald 1990; Duan and Gregory 2003; Pernitsky and Edzwald 2006). Compared to conventional alum, these coagulants have been proved to produce stronger flocs, lower sludge volume, and have higher charge neutralization capacity and rapid aggregation rate (Chen et al. 2006; Zouboulis and Tzoupanos 2010). These polymeric aluminum coagulants also have been shown to perform better than traditional Al coagulants in removal of turbidity, total organic carbon, and UV_{254} under some conditions (Duan and Gregory 2003; Hu et al. 2006; Yan et al. 2007). However, there have been some reports, indicating that for some water sources alum shows greater removal of DOC than polymeric aluminum coagulants (Vanbenschoten and Edzwald 1990; Chen et al. 2006).

It has been recognized that the performance of aluminum-based coagulants for DOC and UV₂₅₄ removal depends largely on raw water quality and Al speciation during coagulation (Yan et al. 2007; Shi et al. 2007; Wu et al. 2009; Yang et al. 2010).

Objectives

The purpose of this study was to examine the removal of DOC and UV₂₅₄ by three aluminum-based coagulants: Al₂(SO₄)₃, PACl and ACH with various basicity values. The raw water used in the experiments had high levels of alkalinity, pH, and DOC. The pH adjustment for this type of water requires a large volume of acid. Therefore, the system owners looked into coagulation conditions that may not require pH adjustment. Coagulation effectiveness was evaluated by removal of DOC, UV₂₅₄, DOC fractions, and THMFP of the coagulated water.

The mechanism of DOC removal by chemical coagulation was studied as follows: (1) investigation of the distribution of Al coagulant hydrolysis species at different pH condition; (2) comparison of effectiveness of different coagulants in terms of DOC and UV₂₅₄ removal; (3) investigation of the relationship between aluminum hydrolysis species and DOC and UV₂₅₄; removal efficiency and (4) investigation of the removal of specific DOC fractions and THMFP for coagulated water at the optimized dose and pH conditions.

4.2. MATERIALS AND METHODS

4.2.1. Water Source

The water used in this study was collected from the Assiniboine River in western Canada in May 2013. The raw water was taken from the Portage La Prairie water treatment plant, approximately 70 kilometers (45 miles) west of Winnipeg. This surface water source is high in DOC (13.8 mg L⁻¹), hardness (349 mg L⁻¹ CaCO₃), and alkalinity (330 mg L⁻¹ CaCO₃) and pH of 7.8.

Portage La Prairie water treatment plant is a conventional lime/soda softening plant with chemical coagulation as the first step in the treatment process (Figure 4.1).

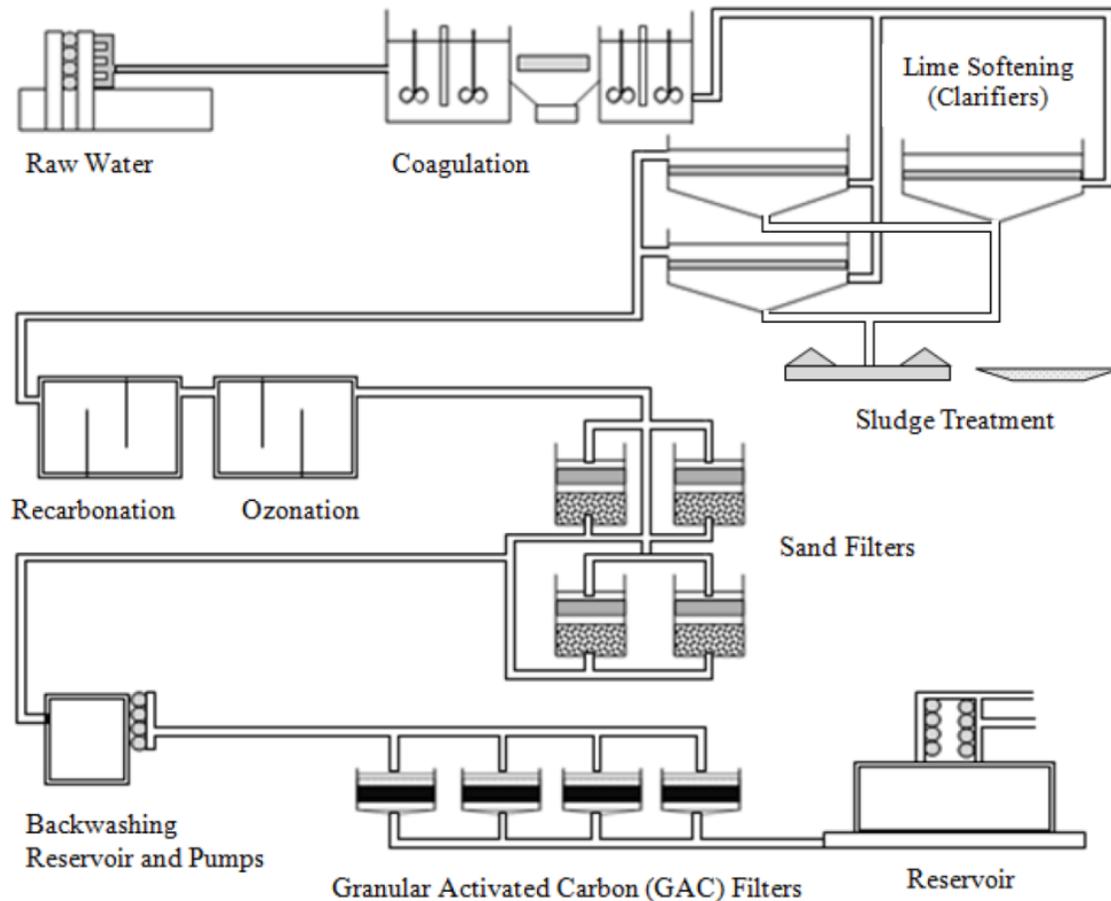


Figure 4.1: Portage water treatment plant schematic diagram.

Decreasing water pH in coagulation, for effective DOC removal, is not desired as subsequent treatment step, lime soda softening requires high level of pH. Coagulants that effectively remove DOC from the water without pH adjustment are therefore most desirable in this situation.

4.2.2. Coagulation Jar Tests

Three commercial aluminum-based coagulants with different basicity value obtained from ClearTech Industrial Ltd, Canada were used in this study: aluminum sulphate (alum) with

basicity value of 0, poly-aluminum chloride (ClearPAC 180, denoted as PACl here) with basicity value of 43%, and aluminum chlorohydrate (CTI 4900, denoted as ACH here) with basicity value of 83%. The properties of coagulants used are summarized in Table 4.1. Coagulant doses were in the range of $2 \text{ mg L}^{-1} \text{ Al}$ to $10 \text{ mg L}^{-1} \text{ Al}$ based on the previous experience with the similar water quality (Sadrnourmohamadi et al. 2013).

Coagulation experiments were carried out at room temperature using a conventional method in six paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA).

The pH of the working solutions was adjusted to certain values with analytical grade 0.1 M sodium hydroxide solution (NaOH) and 0.1 M hydrochloric acid (HCl) before the addition of coagulants. A measured amount of coagulant was pipetted into the working solution to give a certain Al concentration under rapid stirring. One litre of raw water was stirred rapidly at 120 rpm for 1 minute followed by slow mix at 40 rpm for 30 minutes. The samples were then allowed to settle for 30 minutes.

4.2.3. Aluminum Speciation Method

The Al species distribution in initial-commercially available coagulants was measured by timed spectrophotometric procedure involving reactions of Al with ferron (Smith 1971).

The procedure applied in this study is a modified method of Parker and Bertsch (1992) developed by Zhou et al. (2006). Al species in coagulants were divided into three types: monomeric species (Al_a) (reacting with ferron within 1 min), medium polymeric Al species (Al_b) (reacting with Ferron from one to 120 min), and large polymeric species or solid-phase $\text{Al}(\text{OH})_3$ (Al_c) (reacting with ferron after 120 min and non-reacting with ferron). Al_c was obtained by subtracting Al_a and Al_b from Al_T (Liu et al. 2009 and Chen et al. 2006).

From the results shown in Table 4.1, it can be seen that $\text{Al}_2(\text{SO}_4)_3$ can be considered to have almost completely monomeric Al speciation, and PACl and ACH can be considered as the mixture of various Al species.

Table 4.1: The speciation distribution and pH value of coagulants.

Coagulant	B	pH	$\text{Al}_a(\%)$	$\text{Al}_b(\%)$	$\text{Al}_c(\%)$
Alum	0	2.1	93.4	6.6	0
PACl	1.3	2.8	44.3	39	16.7
ACH	2.5	4.0	5.3	70	24.7

Note: Al_a (monomers), Al_b (oligomers and polymers) and Al_c (colloidal hydroxides).

4.2.3.1. Effect of pH on aluminum species Distributions in the coagulation process

The performance of the coagulant is determined by the species present at the time during the coagulation process rather than those in the original solution. To examine the effect of coagulation pH on aluminum speciation, synthetic water containing 5×10^{-4} mol/L NaHCO_3 and NaNO_3 in deionized water was prepared for control coagulation experiments (Hu et al. 2006 and Wang et al. 2004). NaOH or HCl solution was added to the deionized water to adjust pH. The coagulants were added to and stirred at 120 rpm for 2 min. The final solution contained 2×10^{-4} mol Al/L which is the common dosage in actual coagulation practice. The solution was analyzed for aluminum hydrolysis species subsequently by ferron assay. The speciation of Al species may be different in the raw river water, than that in deionized water as the natural water contains many dissolved chemical species that may significantly affect Al species distributions. However, the various chemical species present in the raw water can also affect the ferron method. Deionized water is used to provide baseline species distributions data during the coagulation

process and highlight differences in Al species distributions among the three different coagulants (Hu et al. 2006).

4.2.4. Analytical Methods

The details of Analytical methods and SPE fractionation used in this study are reported in chapter 3. THMs formation potential (THMFP) measurements were conducted according to *Standard Methods 5710B* (APHA 2012) as stated in our previous paper (Sadrnourmohamadi et al. 2013). 50 mg L⁻¹ sodium hypochlorite was added to each sample to ensure there was a sufficient amount of chlorine available to react with organics. All samples were buffered to pH=7 using a phosphate buffer. Sample vials were sealed with TFE caps and were kept in the dark at 4°C for 7days. THMs concentrations were determined with liquid-liquid extraction method according to *Standard Methods 6232B* (APHA 2012). THMs concentration was determined using an Agilent 7890A GC System (Agilent Technologies, Santa Clara, California) equipped with a CombiPAL CTC Analytics auto sampler and used electron capture detection. Residual aluminum concentration analysis was performed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Agilent Technologies, USA) according to *Standard Methods 3120B* (APHA 2012).

4.3. RESULTS AND DISCUSSIONS

4.3.1. General Water Quality

General water quality tests were done on samples collected from the Assiniboine River (May 12, 2013) (Table 4.2). The SUVA value for Assiniboine River water is 3.40 m⁻¹mg⁻¹ L which indicates a high level of aromatic substance and hydrophobic components (HPO) in this source water (Kueseng et al. 2011). The result of fractionation done in May 2013 confirmed the high

level of HPO components with up to 50% of the organic matter being associated with the hydrophobic acid fractions. This result is consistent with the view that the high DOC waters tend to be more hydrophobic in character (Sharp et al. 2006).

The DOC composition of the Assiniboine River is shown in Table 4.3. The results of these tests show that during spring the Assiniboine River was dominated by the HPOA fraction (50%) and the composition was more hydrophobic (71%) than hydrophilic (29%).

The results confirm earlier findings that, in river water, humic and hydrophobic components are the major portion of DOC at about 50-65% whereas non-humic and hydrophilic ones exist at about 35-55% (Kueseng et al. 2011). The hydrophobic fraction of surface water can also be elevated due to snowmelt and spring runoff (Sharp et al, 2006).

Table 4.2: General water quality of the Assiniboine River. Samples were taken on May 12, 2013

Parameter	Unit	Value
pH	pH unit	7.80
Turbidity	NTU	3.50
Alkalinity	mg L ⁻¹ CaCO ₃	330
Hardness	mg L ⁻¹ CaCO ₃	349
UV ₂₅₄	cm ⁻¹	0.470
DOC	mg L ⁻¹	13.8
SUVA	m ⁻¹ mg ⁻¹ L	3.40

Table 4.3: The DOC composition of the Assiniboine River water (May 2013).

Fraction	Concentration (mg L⁻¹)	DOC %
Hydrophobic neutral (HPON)	2.71±0.03	19.6
Hydrophobic base (HPOB)	0.18±0.01	1.30
Hydrophobic acid (HPOA)	6.91±0.07	50.1
Hydrophilic base (HPIB)	0.46±0.01	3.33
Hydrophilic acid (HPIA)	0.89±0.02	6.45
Hydrophilic neutral (HPIN)	2.65±0.04	19.2
Total	13.8±0.03	100

4.3.2. Effect of pH on Water Coagulation

4.3.2.1. Effect of pH on Coagulants Hydrolysis Species Concentration

The Al species distribution of the three coagulants during coagulation under various pH values (6, 7, and 8) was examined by ferron assay and results are shown in Figure 4.2. Results show that Al species distribution changes with pH. Figure 4.2 shows that the Al species distributions of aluminum sulfate during coagulation process were greatly changed compared to the initial species distributions (Table 4.1). The concentration of monomeric species Al_a in this coagulant increases with an increase in pH, with the proportion of the species changing from 3% at pH 6, to 16% at pH 7 and 23% at pH 8. The concentration of polymeric species Al_b follows the opposite trend, with the proportion changing from 70% at pH 6, to 62% at pH 7 and 55% at pH 8. The distribution of colloidal species Al_c in this solution follows the trend reported for Al_b, but the scale of decrease is smaller. Therefore, alum solution at pH 6 contains mostly polymeric and colloidal hydrolysis species and least monomeric species.

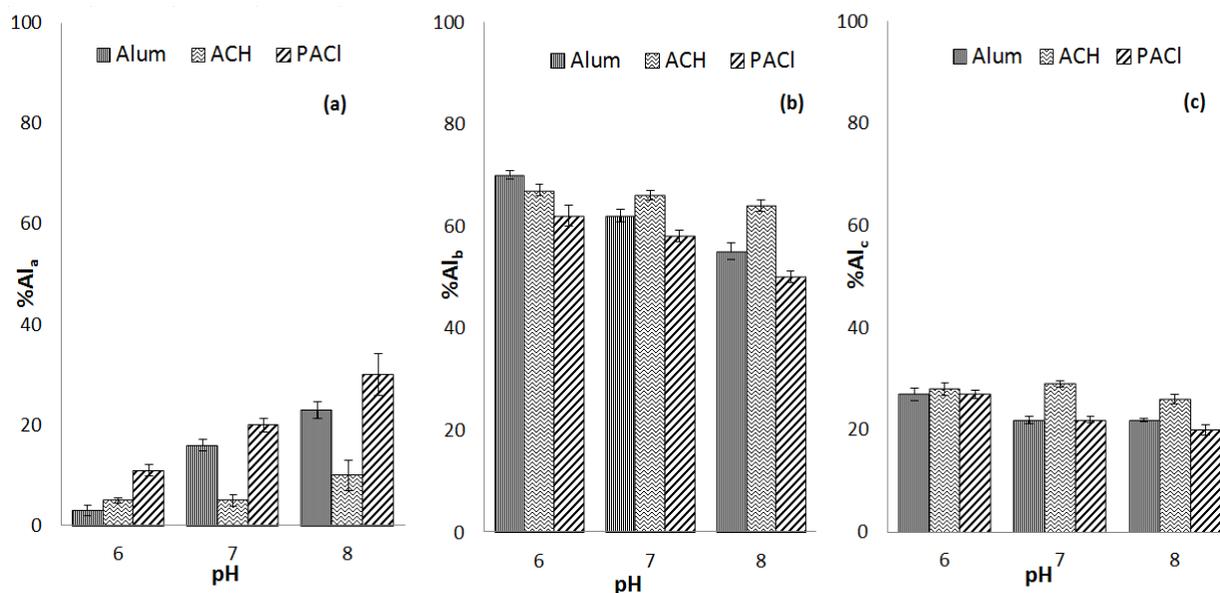


Figure 4.2: Al speciation characterization after dosing the Al coagulants under various pH conditions at dosage of 2×10^{-4} mol Al/L: (a) Al_a, (b) Al_b, (c) Al_c.

Similar trends of the change in Al_a, Al_b, and Al_c species with pH can also be observed for PACl and ACH. For PACl, at pH of 6 the concentration of Al_a decreases to 11% with large yield of Al_b to 62% compared to the proportion of species in PACl prior to dosing (Table 4.1). The observed changes in the speciation of ACH throughout the investigated pH ranges were the smallest for all the coagulants studied, specifically the concentration of Al_b stays relatively stable.

The results above confirm that the Al_a, the most unstable species in the all studied coagulants hydrolyze upon dosing and transform into Al_b and then Al_c, depending on the reaction pH (Yan et al. 2007 and Yang et al. 2010). This effect is especially pronounced for alum.

4.3.2.2. Effect of coagulant dose and pH on DOC removal

To gain more insight into the role of different aluminum species in the removal of DOC from the Assiniboine river water, coagulation tests were performed at different doses and pHs. DOC removal at three different pHs by coagulation with alum, ACH, and PACl is shown in Figure 4.3. As shown in Figure 4.3 the DOC removal efficiency increases with the increase of coagulant

dosage and the decrease in pH for all coagulants. All three coagulants achieve the highest DOC removal at the dose of $10 \text{ mg L}^{-1}\text{Al}$ and pH of 6. However, most of this removal was achieved with the coagulant doses of about $6 \text{ mg L}^{-1}\text{Al}$. Coagulant doses higher than $6 \text{ mg L}^{-1}\text{Al}$ show minimal improvement of DOC removal. At a pH of 6, alum achieves 71% DOC removal at the dose of $10 \text{ mg L}^{-1}\text{Al}$ followed by ACH and PACl showing 68% and 54% removal respectively. At pH of 7 and 8 maximum DOC removal is achieved by ACH (60% and 38%) followed by alum (54% and 32%) respectively. PACl shows the lowest DOC removal of 42% and 20% at pH 7 and 8 respectively. DOC removal is most efficient at pH 6.0 for alum; our experiments with the synthetic water showed that at that pH alum has the highest content of in situ formed Al_b . As pH increases to 7, DOC removal efficiency for this coagulant decreases together with its Al_b content. At pH 7, ACH shows maximum concentration of Al_b and the best DOC removal of all the coagulants studied.

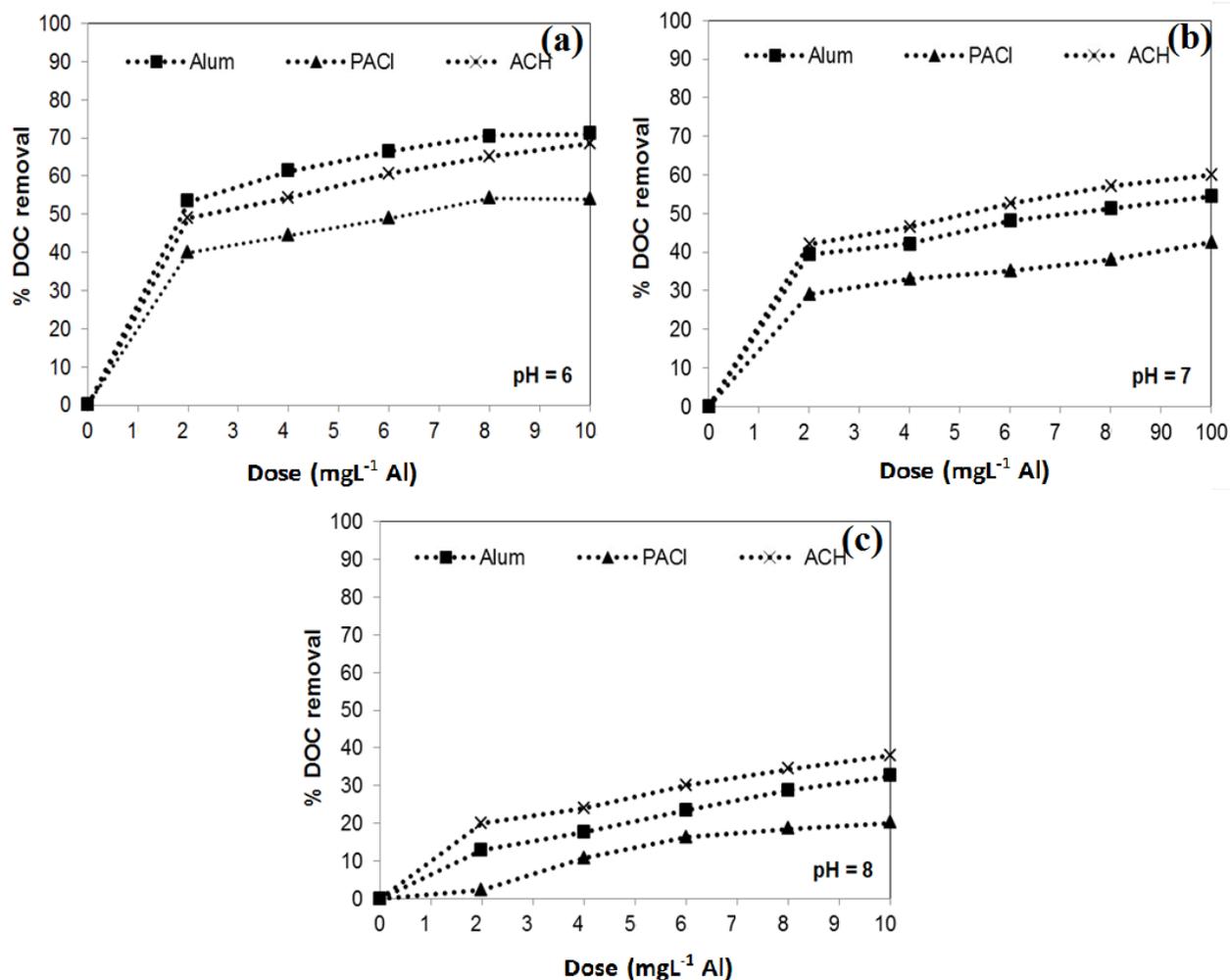


Figure 4.3: Removal of Assiniboine River DOC with alum, PACl, and ACH at varying pH and coagulant dose.

4.3.2.3. Effect of Coagulant Dose and pH on UV₂₅₄ Removal

The results of UV₂₅₄ removal with pH variation by three coagulants at different doses are shown in Figure 4.4. Results show that UV₂₅₄ removal increases with an increase in coagulant dosage and decrease of pH, similar to the trend in DOC removal, but the trends seem to be more linear. At pH 6, alum at dose of 10 mg L⁻¹Al shows the maximum UV₂₅₄ removal (62%) followed by ACH and PACl showing 54% and 42% UV₂₅₄ reduction respectively. At pH adjusted to 7 and 8 the trend of UV₂₅₄ removal is similar to DOC removal with maximum UV₂₅₄ removal of 46%

and 41% for ACH, and 41% and 38% for alum. Here PACl shows the lowest effectiveness by 24% and 20% of UV₂₅₄ removal at pH 7 and 8 respectively. These results support the previous findings indicating that the effects of pH on removal of UV₂₅₄ and DOC can be related to the changes in the concentrations of Al hydrolysis species. The removal of UV₂₅₄ is closely related to the content of Al_b and Al_c (Yan et al. 2007, Yang et al. 2010 and Yang et al. 2011). At pH 6, alum has the highest concentration of Al_b while the content of Al_c is almost the same for all three coagulants. This can explain the superior removal of UV₂₅₄ by alum at pH 6. Upon increasing the pH to 7, the concentration of Al_b and Al_c in alum decreases, while in ACH the same increase in pH causes an increase in the concentration of these species. That increase in Al_b and Al_c concentration results in the increased UV₂₅₄ removal by ACH. Our results, therefore, confirm the earlier findings that at acidic pHs, more Al_b is produced in coagulation with low basicity aluminum-based coagulants which results in efficient removal of UV₂₅₄. When the pH is increased to the basic region, coagulants with high basicity value remove UV₂₅₄ more efficiently due to the high content of preformed and stable Al_b (Yan et al. 2008).

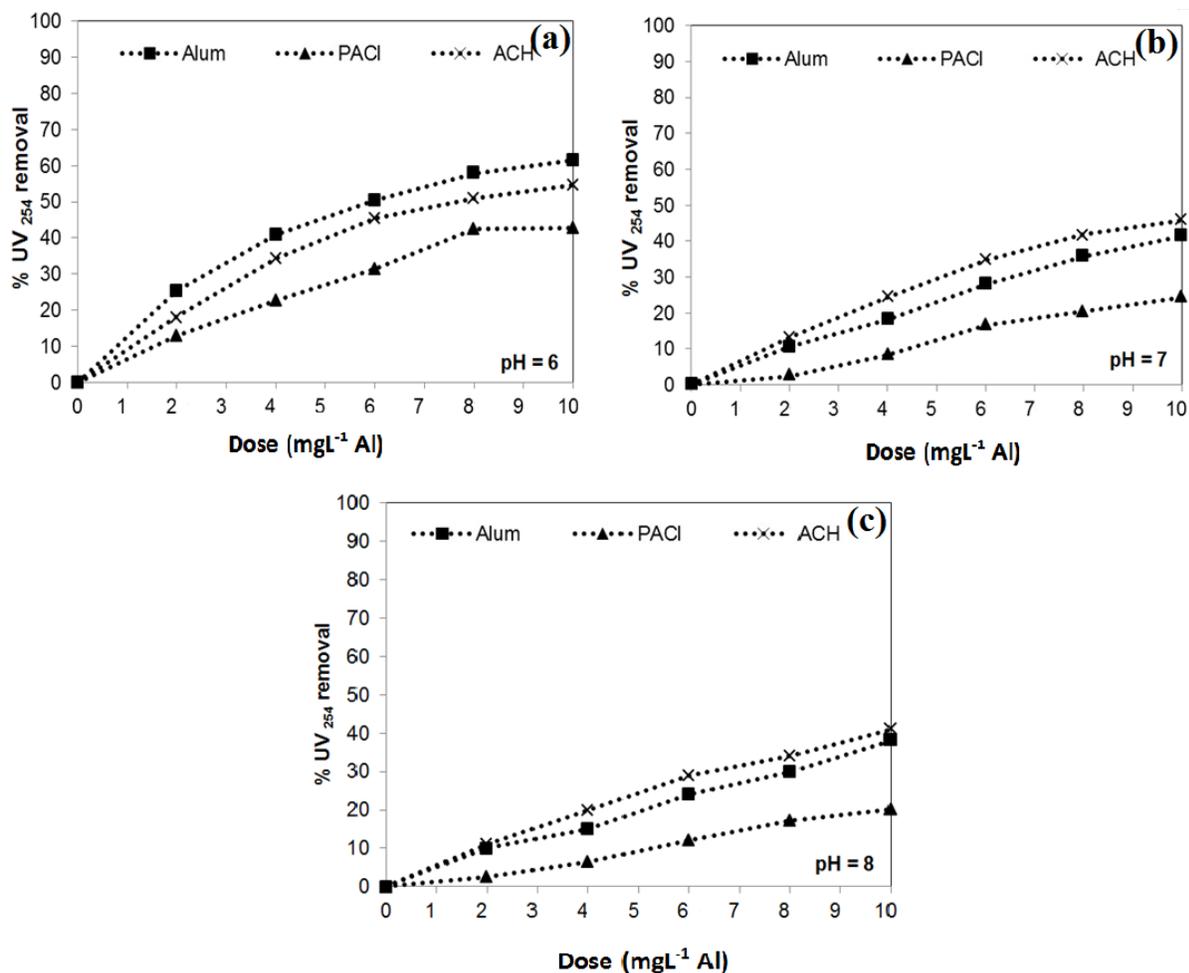


Figure 4.4: Removal of Assiniboine River UV₂₅₄ for with alum, PACI, and ACH at varying pH and coagulant dose.

4.3.2.4. Coagulation Efficiency With no pH Control

The raw water used in this set of studies is the same as that used during coagulation under controlled pH condition (Table 4.2). Figure 4.5 shows the change in pH and removal of DOC and UV₂₅₄ at different coagulant dosages. Figure 4.5 (a) shows that the depression of solution pH due to coagulant addition follows the order of alum>PACI>ACH and correlates with the basicity ratios for these coagulants. The difference in pH depression between PACI and ACH appears to be non-significant, as expected. Also it can be seen that the coagulated water pH is above 7.0 for

all three coagulants and has not achieved the optimum value for DOC removal of pH 6 (Yan et al. 2007 and Edwards et al. 1985).

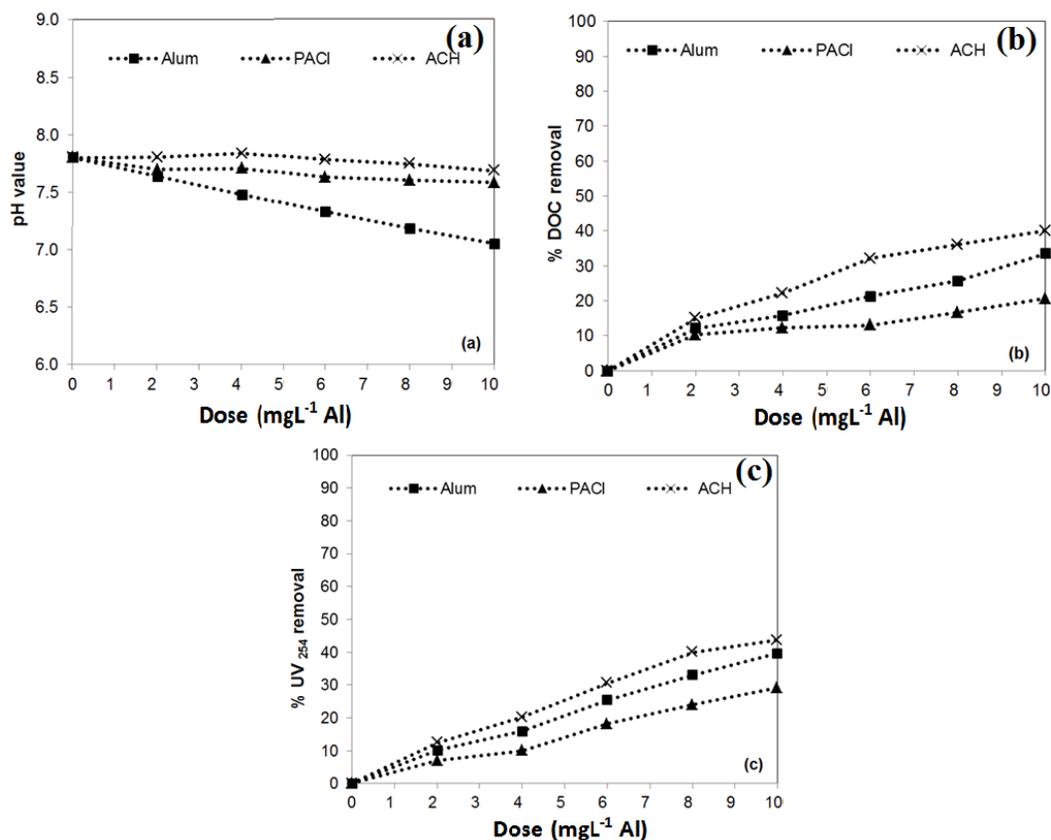


Figure 4.5: Effect of coagulant dosage on: (a): pH, (b): DOC and (c): UV₂₅₄, No pH adjustment (Raw water pH 7.8).

Figure 4.5 (b) shows DOC removal by different coagulants. The DOC removal was in the order of ACH > alum > PACl. UV₂₅₄ removal shows similar trend as in DOC removal, with ACH showing the most efficient removal followed by alum and PACl (Figure 4.5 c).

The above results confirm the mechanisms of DOC and UV₂₅₄ removal are related to aluminum species formed during the coagulation discussed earlier in this paper.

The standards of aluminum concentration in Canadian drinking water issued by Health Canada prescribe that the aluminum concentration in drinking water must be lower than 0.1 mg L⁻¹ (Health Canada 2012). The measurement of residual aluminum concentration of all filtered coagulated

samples showed that values were below the Canadian Drinking Water Guidelines of 0.1 mg L^{-1} (Health Canada 2012).

4.3.3. DOC fractions Removed and Remaining after Coagulation

The DOC of raw water and water coagulated with all three coagulants ($10 \text{ mg L}^{-1} \text{ Al}$) at pH of 6 was fractionated to investigate the removal of specific DOC fractions. From Figure 4.6 it can be seen that alum removed hydrophobic and high molecular weight humic fractions better than ACH and PACl. HPO removal by alum coagulation is 84% while the removal of HPI fractions is only 39% only. The respective HPO and HPI removal efficiencies are 81% and 38% using ACH and 70% and 14% using PACl. These results are in agreement with previous findings that showed efficient removal of HPO through coagulation (Sadroumohamadi et al. 2013 and 2014). All coagulants were found to have high removal of the hydrophobic acid (HPOA) fraction with the highest removal by alum (84%) followed by ACH (79%) and PACl (64%). These results are consistent with some research showing that coagulants with preformed Al species are less effective than conventional alum at the removal of DOC with large molecular size and hydrophobic properties (Shi et al. 2007, Omelia et al. 1999 and Rizzo et al. 2005). Hydrophobic fractions of DOC have been shown to be removed by large hydrolyzed Al species, such as Al_b and Al_c rather than monomeric Al_a species (Yan et al. 2004). Referring to Figure 4.2 which shows Al species distribution, it can be seen that at pH of 6, alum has a high content of in situ formed Al_b and Al_c compared to ACH and PACl. This study supports the previous literature showing that HPO fractions are more amenable to be removed by coagulation while HPI ones are less treatable by this treatment process (Chen et al. 2006 and Singer 1999). Therefore HPI fractions constitute the main part of the post-coagulation DOC and determine the behaviour of remaining DOC on the subsequent treatment steps in Portage La Prairie water treatment plant

such as ozonation, sand filtration, activated carbon and chlorine disinfection. Although HPI fractions constitute the main part of the post-coagulation DOC, HPO fractions are also present to some extent. Ozonation of this stream converts a portion of the remaining HPO fractions into HPI ones and results in higher concentration of HPI DOC fractions. The coagulated water is rich in HPI fraction rather than HPO ones this stream can be easily biodegraded by sand filters (Baghoth 2012).

Table 4.4: DOC fractions (shown as % DOC remaining), following coagulation using optimal conditions for total DOC removal

Sample	% DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	19.6	1.30	50.1	3.33	6.45	19.2
Alum	9.25	2.75	27.2	5.25	9.50	46.0
ACH	6.24	3.93	32.8	7.62	9.70	39.7
PACl	4.40	2.35	39.1	9.73	15.2	29.2

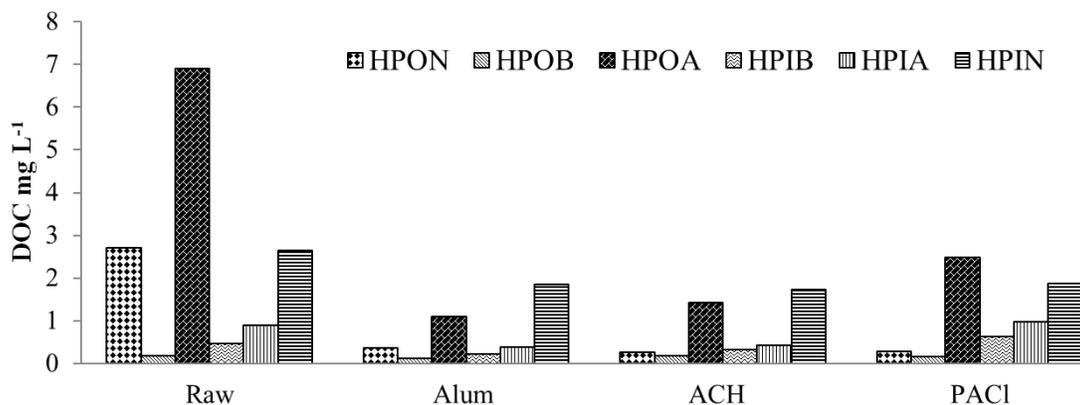


Figure 4.6: DOC fractions remaining in solution following coagulation.

Hydrophilic fractions mainly low molecular weight and biodegradable fractions, have been reported to be more amenable to be adsorbed onto activated carbon than high molecular weight

hydrophobic ones. DOC after coagulation is high in these fractions since HPO ones have already been removed by coagulation. Therefore, if activated carbon is located after coagulation these highly biodegradable fractions can be adsorbed and removed therefore total DOC is decreased (Xing 2010). The following section also presents the behaviour of the coagulated water in chlorination.

4.3.4. THMFP for Three Aluminum Based Coagulants

THMFP of the raw and coagulated water at the optimum conditions for all three coagulants was determined. The raw Assiniboine River water had a THMFP of $202.4 \mu\text{g L}^{-1}$ (Table 4.5). Alum showed the highest reduction in THMFP to 94.7 (which is below the Canadian guideline of $100 \mu\text{g L}^{-1}$) followed by ACH and PACl.

Of the coagulants tested, alum showed the greatest reduction in THMFP and total DOC followed by ACH. This is because alum effectively removed the HPOA fraction which is reported to have the greatest potential to form THMs (Singer 1999, Chow et al. 2005, Leenheer et al. 2003 and Sadrnourmohamadi et al. 2012). PACl showed the lowest reduction of THMFP which can be due to lowest reduction of the HPOA fractions (Figure 4.6). The results indicate that the removal of DOC as THMs precursors in nature water depends not only on coagulant dosage and pH of source water, but also on the coagulant speciation. Different DOC fractions react differently with different coagulants. pH and dosage control as well as coagulation speciation optimization can yield cost effective and optimum THMs precursors removal.

Table 4.5: THMFP for raw and coagulated water

Sample	DOC	Chloroform	Bromoform ^a	DBCM ^b	BDCM ^c	THMFP
Unit	(mg L ⁻¹)	(µg L ⁻¹)				(µg L ⁻¹)
Raw	13.8±0.03	180±2.2	ND	2.4±0.12	20.0±0.09	202.4±3.1
Alum	4.00±0.02	74.1±1.6	ND	16.9±0.2	3.7±0.02	94.7±2.2
PACl	6.37±0.05	99.2±0.9	ND	19.0±0.2	3.5±0.01	121.7±1.12
ACH	4.33±0.01	90.6±1.01	ND	17.5±0.4	4.1±0.04	112.2±2.21

^aNot determined^bBromodichloromethane^cDibromochloromethane

4.4. CONCLUSION

Surface water sources in Manitoba, Canada, have high concentration of dissolved organic carbon sometimes exceeding 20 mg L⁻¹, accompanied by high pH, hardness and alkalinity. DOC contains precursors to harmful disinfection by-product-trihalomethanes. In the Province of Manitoba, Canada, about 70% of the potable water treatment plants using surface water sources are not in compliance with THMs regulations set by the Province. This study was conducted in a water treatment system that is not in compliance with the THMs provincial standard. Effective removal of DOC from this high pH and alkalinity water creates a significant chemical cost for the operations. This is because the optimization of conventional coagulation requires water pH to be lowered and subsequent water softening and chlorination will require the pH to be increased. Therefore, those coagulants that effectively remove DOC from the water without pH adjustment are the most desirable in this situation. In this study, we investigated the removal of DOC from this water source by three aluminum based coagulants: alum, ACH and PACl. Our focus was to

discern the role of aluminum hydrolysis species in removal of DOC. The main conclusions are as follows:

1. Alum coagulant at pH 6.0 had the highest content of in situ formed polymeric species (Al_b). This resulted in the highest DOC removal (71%). Therefore, higher concentrations of polymeric coagulant hydrolysis species (Al_b) in the coagulant may indicate better DOC removal at pH of 6.

However, the water supply system studied in this paper is supplied by raw water with high pH and alkalinity, and the pH reduction from 8 to 6 is costly and not applicable due to significant addition of chemicals to the drinking water under treatment. Although pH correction to 6 can be beneficial for some of subsequent treatment steps such as ozonation and activated carbon, low pH of coagulated water presents challenge for subsequent lime softening, where high pH is desired. Therefore, alum coagulation at adjusted pH of 6 may not be recommended.

2. ACH at pH 7 had the highest concentration of polymeric coagulant (Al_b) and colloidal and particulate hydrolysis species (Al_c). At this pH the removal of DOC and UV_{254} was maximized. Therefore, both polymeric and colloidal/particulate hydrolysis species play a major role in lowering UV_{254} .
3. ACH at pH 7 and 8 (natural raw water pH) achieved the highest DOC and UV_{254} removal (40% and 44% respectively), from natural water. Therefore, both polymeric and colloidal/particulate hydrolysis species play an important role in removal of DOC in coagulation of the studied water with no pH adjustment. ACH coagulant is recommended for systems where pH adjustment represents a challenge.

4. The fractions of DOC removed by the coagulants were determined to study the effects of residual (post-coagulation) DOC on subsequent treatment processes. All three coagulants removed hydrophobic DOC fractions better than hydrophilic ones. Fractionation results showed that alum has the highest removal (84%) of hydrophobic acid (HPOA) fraction.

Water coagulated with alum had the lowest THMFP of $94.72\mu\text{g L}^{-1}$ followed by ACH and PACl.

The low THMFP can be related to the reduction of HPOA fraction of DOC in alum coagulation.

**CHAPTER 5: EFFECTS OF OZONE AS A STAND-ALONE AND COAGULATION-AID
TREATMENT ON THE REDUCTION OF TRIHALOMETHANES PRECURSORS
FROM HIGH DOC AND HARDNESS WATER**

ABSTRACT

This study investigates the effect of ozone as a stand-alone and coagulation aid on the removal of dissolved organic carbon (DOC) from the water with a high level of DOC (13.8 mgL^{-1}) and calcium hardness (270 mgL^{-1}) CaCO_3 .

Natural water collected from the Assiniboine River (Manitoba, Canada) was used in this study.

Effectiveness of ozone treatment was evaluated by measurement of DOC, DOC fractions, UV_{254} , and trihalomethane formation potential (THMFP). Additionally, zeta potential and dissolved calcium concentration were measured to discern the mechanism of ozone reactions.

Results indicated that $0.8 \text{ mg O}_3/\text{mg DOC}$ ozone stand-alone can cause up to 86% UV_{254} reduction and up to 27% DOC reduction. DOC fractionation results showed that ozone can change the composition of DOC in the water samples, converting the hydrophobic fractions into hydrophilic ones and resulting in the reduction of THMFP. Also, ozone caused a decrease in particle stability and dissolved calcium concentration. These simultaneous ozonation effects caused improved water flocculation and enhanced removal of DOC. This resulted in reduction of the coagulant dosage when ozone doses higher than $0.2 \text{ mg O}_3/\text{mg DOC}$ were applied prior to coagulation with ferric sulfate. Also, pre-ozonation-coagulation process achieved preferential THMFP removal for all of the ozone doses tested ($0-0.8 \text{ mg O}_3/\text{mg DOC}$), leading to a lower specific THMFP in pre-ozonated-coagulated waters than in the corresponding ozonated waters

5.1. INTRODUCTION

Strict guidelines for disinfection by products (DBPs), such as trihalomethanes (THMs) have caused water treatment plants (WTPs) to improve the removal of natural organic matter (NOM). NOM is typically measured as dissolved organic carbon (DOC). Removal of DOC is a critical issue, especially for the Province of Manitoba (Canada), where surface waters are characterized as having high DOC that sometimes exceeds 20 mg L^{-1} . It has been reported that almost 70% of Manitoba potable water treatment plants that use surface water sources are not in compliance with THMs regulations set by the Province (Sadrnourmohamadi et al. 2013). The authors studied composition of DOC of two major rivers in Southern Manitoba earlier. The studied waters were found to be rich in the hydrophobic acid (HPOA) fraction; this fraction of DOC contains mainly humic substances (Goss and Gorczyca 2012; Sadrnourmohamadi et al. 2013). The humic substances have been reported to have the greatest potential to form THMs (Reckhow et al. 1990; Chow et al. 2005). Thus, removal of the humic fraction is the key to reducing the level of chlorine disinfection by products in the treated water (Chiang et al. 2002; Sadrnourmohamadi et al. 2013). The removal of THMs precursor from water can be achieved by different physical and chemical methods, such as chemical coagulation, activated carbon adsorption, ion exchange, advanced oxidation, and biological degradation. Chemical coagulation is the most commonly used of all these processes. However, sometimes, it is not possible to reduce the water DOC to sufficiently low concentrations to prevent the formation of THMs by coagulation alone (Crozes et al. 1995; Chiang et al. 2002). Also, adjustment of pH is required to optimize the removal of DOC by coagulation; this is quite costly for waters with very high alkalinity and pH, which are typical of the Canadian Prairie surface water.

5.1.1. Ozone Application in Drinking Water Treatment

The application of ozone in drinking water treatment has been widespread, due to its high oxidation potential (Le Pauloue and Langlais 1999). Molecular O₃ is a strong oxidant; when it dissociates in water ozone can produce hydroxyl radicals, even stronger oxidants (Brookman 2010). Ozonation has been reported as an effective way to remove disinfection by-products precursors that are present in drinking water sources (Hu et al. 1999; Galapate et al. 2001). However, studies have demonstrated that in some cases, ozonation can have a deteriorative effect (Toor and Mohseni 2007; Chowdhury et al. 2008). Therefore, the effect of ozonation on the characteristics of source water and its DBPs formation potential needs to be evaluated for each specific water source. This is because, the NOM has a complex structure, and the effect of ozone on NOM from different sources cannot be directly compared.

5.1.2. Effects of Ozone on Chemical Coagulation Process

The reports on the effects of ozone as a coagulation aid are complex and unpredictable. Some studies have reported cases in which ozone enhanced DOC removal by subsequent coagulation and effectively reduced THMs formation (Farvardin and Collins 1989; Camel and Bermond 1998; Chiang et al. 2002). Other studies, on the contrary, pointed out that pre-ozonation could not reduce the dosage of coagulant (Reckhow and Singer 1984; Becker and O'Melia 1996).

The conflicting reports of the ozone effect on coagulation can be explained by a number of simultaneous mechanisms taking place during this treatment process. Some of these mechanisms have positive effects, while others may have negative effects on subsequent coagulation treatment. Ozone-enhanced coagulation can be optimised by understanding these mechanisms (Currie et al. 2003).

The ozone dose, coagulation conditions (coagulant type and dose), and raw water characteristics (DOC type and concentration, hardness, and alkalinity), as the important variables, determine the effect of ozone on coagulation (Bose and Reckhow 2007; Yan et al. 2007).

5.1.3. The Role of Calcium Hardness in Ozone Enhanced Coagulation

Calcium hardness is reported as a key parameter when ozone is applied prior to coagulation. It has been reported that ozonation, prior to coagulation, benefits waters with moderate to high levels of calcium hardness. (Chang and Singer 1991; Chandrakanth and Amy 1996). Chang and Singer (1991) have shown that ozone-induced coagulation can occur in waters with calcium hardness-to-total organic carbon (TOC) ratios >25 mg CaCO_3 /mg DOC. Calcium has a high tendency to form strong complexes with functional groups containing oxygen. Ozonation of water organic compounds can produce oxygen-rich compounds, such as carboxylic groups, leading to increased complexation of calcium with both aqueous NOM and particle-sorbed NOM (Edwards and Benjamin 1992a; Chandrakanth and Amy 1998; Rodríguez et al. 2012b). Also, calcium can neutralize the organic particle anionic surface charge which can lead to a reduction in particle stability through surface charge reduction (Edwards and Benjamin 1992b; Chandrakanth and Amy 1996). This mechanism is important when source water has a high level of calcium hardness (Dowbiggin and Singer 1989).

The contribution of this work is in reporting the effects of ozone on the reduction of THMs precursors by coagulation, from unique source water. Manitoba surface water has very high DOC accompanied by high calcium hardness. This source of water is an ideal candidate for the study on how water quality can affect the role of ozone in the chemical coagulation process.

Objectives

This work presents the effect of ozone as a stand-alone and a coagulation aid in the removal of dissolved organic carbon (as THMs precursors) from the water with a high level of DOC and calcium hardness.

The objectives of this study are:

- To study the effects of ozone on DOC and different fractions of DOC in this specific source water.
- To evaluate the effect of ozonation on the total THMs Formation Potential of the water samples.
- To investigate the effect of calcium concentration in the ozone-induced coagulation.
- To investigate the effect of ozone as an aid to ferric sulfate coagulation, targeting the reduction of DOC and THMFP. We selected ferric sulfate as a coagulant because his coagulant showed the highest DOC removal in the source water used in this study (Sadrnoumohamadi et al. 2013).

5.2. MATERIALS AND METHODS

5.2.1. Water Sources

Raw water studied in this experiment was collected from the Assiniboine River at Portage la Prairie Water Treatment Plant (PPWTP), located approximately 70 kilometers (45 miles) west of Winnipeg, Manitoba. The Assiniboine River water has high levels of alkalinity, hardness, and DOC. The water has also a relatively high pH of 8 (Table 5.1).

5.2.2 Experimental Setup

Semi-batch ozonation experiments (continuous gas admission and static liquid volume) were conducted in the laboratory. Ozone was produced by a laboratory ozone generator (Model OZO

1VTTL, Ozomax Ind., Canada), employing the corona discharge method with dehumidified atmospheric air as the feed gas to generate ozone. A spherical stone diffuser was used to disperse the air enriched with ozone directly into a 2 L sample at the bottom of the reactor. The ozone reactor was made of plexiglass with an inner diameter of 6 cm and a height of 75 cm.

All materials used in the reactor were ozone-resistant. The scheme of the experimental ozonation setup is shown in Figure 5.1. All experiments were conducted at a constant flow rate of 0.23 liter per minute (L/min), and ozone dosage was adjusted by changing the ozonation time.

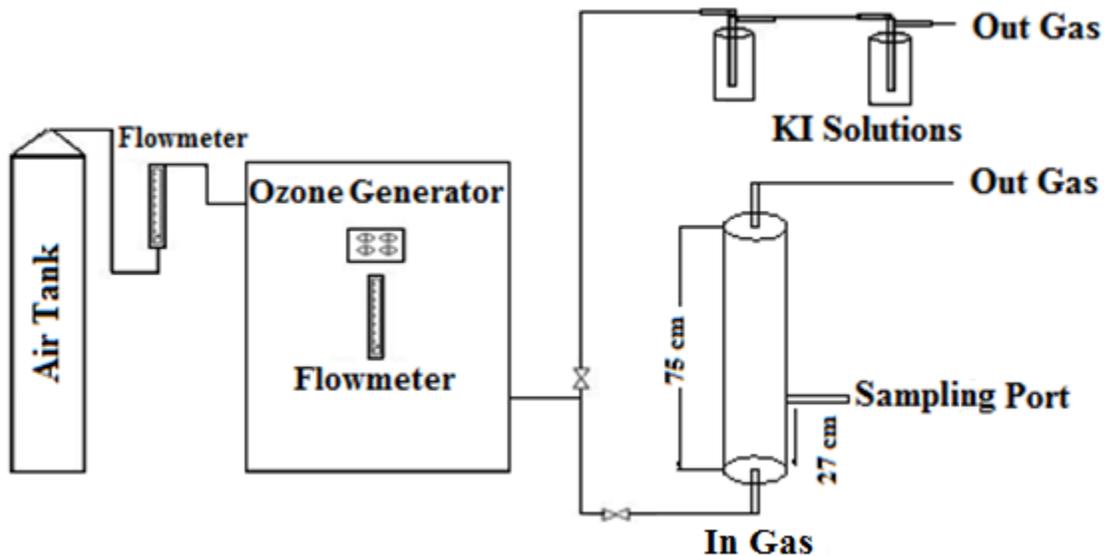


Figure 5.1: Schematic diagram of ozonation set-up.

Ozone output from the generator and ozone concentration in the reactor off-gas were determined by the iodometric method (APHA 2012), while the indigo method was used for ozone measurement in the aqueous phase (Bader and Hoigne 1981). Nitrogen gas was bubbled into the water sample after each ozonation run for at least 10 minutes to purge the unreacted ozone gas.

Throughout this article, ozone dose refers to the transferred ozone dose (difference of the mass of applied ozone and the mass of ozone in the off-gas), which in this study ranged from 0- 0.8 mg Ozone/mg DOC. These ozone dosages were selected since the applied ozone doses less than 1

mg Ozone/mg DOC has been reported to be the most effective on the coagulation effect (Grasso and Weber 1988; Amy et al. 1991).

5.2.3. Experimental Procedure

Two sets of experiments were conducted:

Part I - Effect of ozone stand-alone;

To observe the effects of ozone stand-alone on the studied water, the raw water was ozonated with 6 different doses: 0, 0.10, 0.20, 0.40, 0.60, and 0.80 mg Ozone/mg DOC.

Part II - Effects of ozonation on chemical coagulation process;

To study the effects of ozone on coagulation, the raw water was ozonated (0.2, 0.6, and 0.8 mg Ozone/mg DOC) and subsequently coagulated with ferric sulfate.

Coagulation experiments were carried out at room temperature by using a conventional method in six-paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA). The dose of ferric sulfate coagulant was in the range of 20 mg L⁻¹ to 100 mg L⁻¹, based on our previous experience (Sadrnourmohamadi et al. 2013).

One litre of raw water was placed in each jar. A measured amount of coagulant was pipetted into the test water to give a desired coagulant concentration. pH was adjusted to a desired value with analytical grade 0.1 M sodium hydroxide solution (NaOH) and 0.1 M hydrochloric acid (HCl) .

The rapid mix was at 120 rpm for 1 minute followed by slow mix at 40 rpm for 30 minutes. The samples were then allowed to settle for 30 minutes.

5.2.4. Analytical Methods

The ozonation effectiveness was evaluated by measurements of DOC, DOC fractions, UV absorbance (UV₂₅₄), and trihalomethane formation potential. Details of these measurements have

been described in previous chapters. The zeta potential and dissolved calcium concentration were measured as well, to discern the mechanism of ozone reactions.

The method of DOC fractionation used in this study was developed by Ratpukdi et al. (2009) using solid phase extraction (SPE) described in previous chapters. This SPE method significantly reduces the need for long resin preparation time and specialized equipment making this method an attractive alternative to classic resin separation methods.

THMs formation potential measurements were conducted according to *Standard Methods 5710B* (APHA 2012); Details of this procedure have been described elsewhere (Sadrnourmohamadi et al. 2013; Goss and Gorczyca 2012). 50 mg L⁻¹ sodium hypochlorite was added to each filtered sample to ensure that there was a sufficient amount of chlorine available to react with the organics. All samples were buffered to pH=7 by using a phosphate buffer. Sample vials were sealed with TFE caps and were kept in the dark at 4°C for 7 days. After 7 days all samples were found to have >1.0 mg/L (3-5 mg/L) free chlorine which shows that all THM formation reactions were driven to completion. An alteration to the *5710B* procedure was the chlorinated water incubation temperature. In this study chlorinated water samples were incubated at 4°C to simulate the water temperature in distribution systems, representative for the Canadian cold region. THMs concentrations were determined with a liquid-liquid extraction method according to *Standard Methods 6232B* (APHA 2012). The zeta potential measurement was performed by zeta-Meter system 4.0 (Staunton, Virginia, USA). The general accuracy of the zeta meter was determined using standard solutions (Malvern Instruments, UK). Analysis of water-dissolved calcium concentration was conducted on filtered (0.45 µm) sample by using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Agilent Technologies, USA). All

measurements were repeated at least three times to assure the reproducibility of experimental results.

5.3. RESULTS AND DISCUSSION

5.3.1. General Water Quality

General raw water quality is shown in Table 5.1. The Assiniboine River water has a high level of DOC, hardness, and alkalinity. The SUVA value of $3.40 \text{ m}^{-1}\text{mg}^{-1} \text{ L}$ indicates that the water is more hydrophobic in character (Edzwald and Tobiason 1999). The DOC fractionation results of the Assiniboine River are shown in Table 5.2. For many different surface waters the organic carbon has been reported to have primarily hydrophobic character (Leenheer and Huffman 1976; Chow et al. 2005). For Assiniboine River water, the fractionation results showed that more than 70% of DOC is due to hydrophobic fractions, and up to 50% of the organic carbon is associated with the hydrophobic acid fraction. This result is consistent with the view that the waters with high DOC tend to be more hydrophobic in character (Sharp et al. 2006). Hydrophobic base fraction had the lowest concentration in this source water, which is consistent with other studies reporting the low concentration of hydrophobic base in many natural waters (Leenheer 1981; Swietlik et al. 2004).

Table 5.1: General raw water quality characteristics (samples collected on May, 2013)

Sample	DOC (mgL^{-1})	UV_{254} (cm^{-1})	SUVA ($\text{m}^{-1}\text{mg}^{-1}\text{L}$)	pH	Alkalinity ($\text{mgL}^{-1}\text{CaCO}_3$)	Total Hardness ($\text{mgL}^{-1}\text{CaCO}_3$)	Calcium ($\text{mgL}^{-1} \text{CaCO}_3$)
Assiniboine River Water	13.8	0.470	3.40	7.9	330	349	270

Table 5.2: The DOC composition of the Assiniboine River water sample

Fraction	Concentration (mgL ⁻¹)	DOC %
Hydrophobic neutral (HPON)	2.71±0.03	19.6
Hydrophobicbase (HPOB)	0.18±0.01	1.30
Hydrophobic acid (HPOA)	6.91±0.07	50.1
Hydrophilic base (HPIB)	0.46±0.01	3.33
Hydrophilicacid (HPIA)	0.89±0.02	6.45
Hydrophilicneutral (HPIN)	2.65±0.04	19.2
Total	13.8±0.03	100

5.3.2. Effect of Ozone on Aquatic Organic Carbon of Assiniboine River Water

5.3.2.1. Results part I - effect of ozone stand-alone

5.3.2.1.1. DOC and UV₂₅₄.

Figure 5.2 shows the impact of ozonation on the source water quality. Results showed that increased ozone dose improves DOC removal and UV₂₅₄ reduction.

At the dose of 0.8 mg Ozone/mg DOC, up to 27% of DOC was removed. At the lower ozone doses, lower DOC removals were obtained (i.e., 4% and 8% at 0.2 and 0.6 mg Ozone/mg DOC, respectively). The higher DOC removal at the higher ozone dose can be explained as follows; an increase in the ozone dosage provides more available ozone molecules and hydroxyl radical, which results in an increase in organic carbon removal (Ratpukdi et al. 2010).

UV₂₅₄ is commonly used as an indicator of a relative amount of unsaturated and/or aromatic carbon of DOC. For all ozone doses, a decrease of UV₂₅₄ was observed, indicating the oxidation

of unsaturated and/or aromatic carbon molecules, which is in accordance with previously reported results (Gilbert 1988, Camel and Bermond 1998; Swietlik et al. 2004).

Figure 5.2 shows that the UV_{254} reduction was higher compared to the DOC removal. This suggests incomplete mineralization of organic molecules degraded from unsaturated and/or aromatic organics (Chang and Singer 1991; Ratpukdi et al. 2010). DOC removal by ozonation depends on the studied water characteristics such as DOC concentration and composition; therefore cannot be compared for different water sources. However the values obtained in this study can be compared with some published literatures showing DOC reduction ranged from 5%-25% under typical ozone dose of 0.4-1 mg Ozone/ mg DOC (Tuhkanen et al 1994, Molnar et al. 2012). Pryor et al. (2002) have reported up to 25% TOC reduction at lower applied ozone doses of 0.3 to 0.5 mg Ozone / mg DOC. Also Can and Gurol (2003) and Mao et al. (2014) have reported DOC reduction up to 20% achieved by ozonation in conventional treatment plants with ozone doses of 2-.5 mg/L. Joo et al. (2002) has reported 16% TOC removal obtained at ozone range of 1-2 mg/L. Galapate et al. (2001) has achieved DOC removal ranging from 10-16%. Therefore, our reported DOC removals compare well with other published works.

5.3.2.1.2. Effects of ozone on water DOC fractions

The effect of ozone on DOC fractions, known as a precursor of THMs is important for the control of these disinfection byproducts. The DOC of raw and ozonated water at three different doses (0.2, 0.6, and 0.8 mg Ozone/mg DOC) was fractionated to investigate the effect of ozone on specific DOC fractions (Table 5.3). Ozone changes the water DOC characteristics to more hydrophilic (Figure 5.3). When the ozone dose is increased, the concentration of hydrophobic fractions of DOC decreases, while the concentration of hydrophilic fractions, especially HPIN, increases. Also, ozone was found to be especially effective in removing (or transforming) the

HPOA fraction with only 15% of this fraction remaining, following ozonation. These findings are in agreement with previous reports (Chang et al. 2002).

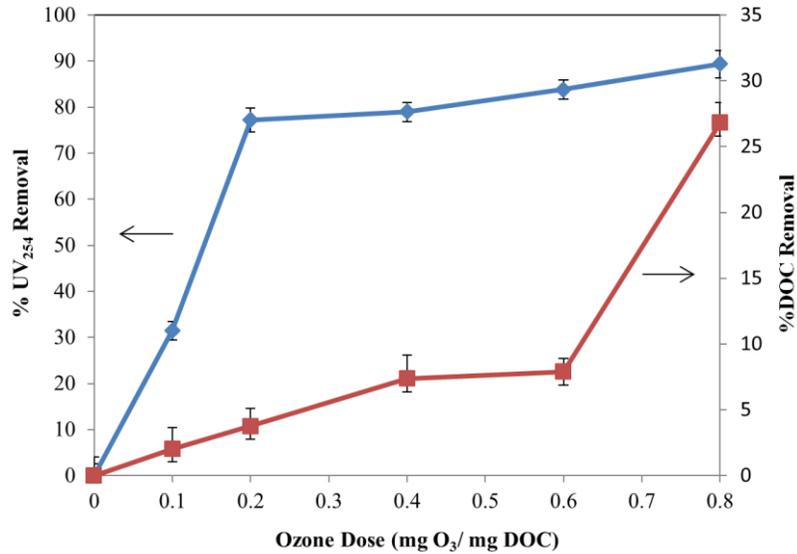


Figure 5.2: Parameters of Assiniboine River water under different dose of ozone.

Table 5.3: DOC fractions (shown as % DOC remaining), following ozone application

Sample	% DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	19.64	1.3	50.07	3.33	6.45	19.21
0.2 mg Ozone/mg DOC	2.44	2.41	21.50	17.11	11.43	45.11
0.6 mg Ozone /mg DOC	2.58	2.36	15.97	9.2	7.57	62.32
0.8 mg Ozone /mg DOC	2.01	2.2	10.5	11.1	12.02	62.17

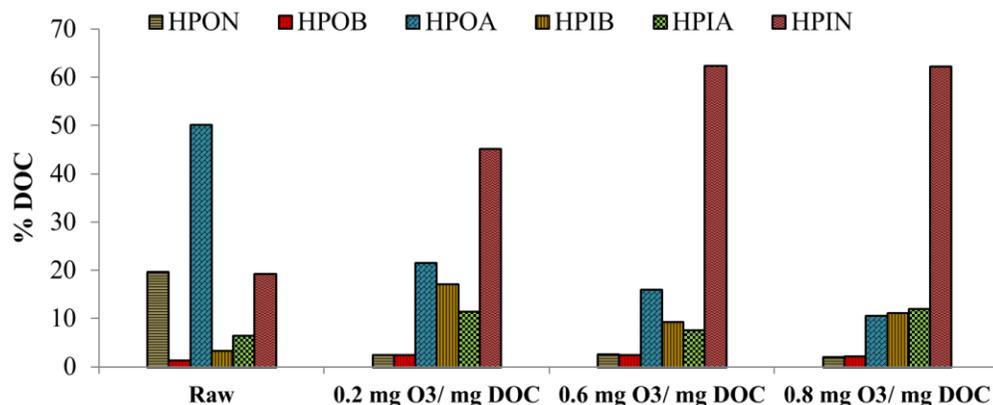


Figure 5.3: DOC fractions remaining in solution following ozone application.

5.3.2.1.3. Effects of ozone on the trihalomethane formation potential

The effects of ozone on THMFP are shown in Table 5.4. Generally, as the dose of ozone increased, the value of THMFP decreased. The raw water of the Assiniboine River had a THMFP of $202 \mu\text{g L}^{-1}$ and a specific THMFP of $14.63 \mu\text{g THM/mg DOC}$ (Table 5.4). These results are lower than the THMFP reported for this water source earlier (Goss and Gorczyca, 2012). In the related article by Goss and Gorczyca (2012), THMFP and specific THMFP values for Assiniboine River raw water (collected in September 2011), is reported to be $560 \mu\text{g/L}$ and $47.5 \mu\text{g THM/mg DOC}$ respectively. The main reason for lower value of THMFP and specific THMFP obtained in this study is the seasonal variation in the concentration of HPO fractions especially HPOA fraction of DOC.

The concentration of hydrophobic fractions for Assiniboine River water during the spring (April) was shown to be lower than late summer (September) (Goss 2011). This seasonal change can be due to naturally occurring events or the flooding happens in the south west part of Manitoba. Rain and flooding events can increase the concentration of hydrophobic compounds especially HPOA in surface waters resulting from runoff. These results are consistent with literature

reporting greater HPOA content in summer time, due to influx of soil derived organics entering surface waters through rain runoff (Scott et al. 2001; Sharp et al. 2006).

Table 5.4: THMFP for Assiniboine raw and ozonated water samples

Sample	DOC	Chloroform	Bromoform ^a	DBCM ^c	BDCM ^b	THMFP	Specific THMFP
Unit	(mg L ⁻¹)	(µg L ⁻¹)					µg THM/mg DOC
Raw	13.8±0.03	179.6±2.31	ND	2.5±0.12	19.9±1.23	202±2.09	14.63
0.2 mg Ozone/mg DOC	13.28±0.12	173.7±1.09	ND	2.6±0.17	15.4±1.09	191.7±1.11	14.43
0.6 mg Ozone/mg DOC	12.71±0.09	148.9±2.94	ND	ND	8.2±1.01	157.1±4.04	12.36
0.8 mg Ozone/mg DOC	10.10±0.16	101.3±4.01	ND	ND	4.3±0.90	105.6±3.08	10.45

^aNot determined

^bBDCM-Bromodichloromethane

^cDBCM- Dibromochloromethane

Ozonation decreased THMFP up to 48% which is higher than reduction of DOC (27%). Several researchers have found that the ozone application (0.1 – 1 mg Ozone/mg DOC) could reduce THMFP by 10-64% (Galapate et al. 2001; Chang et al. 2002; Chin 2003; Singer et al 2003; Ma 2004; Chin and Berube 2005, Rodríguez et al. 2012a, Rodríguez et al. 2012b). Therefore, our THMFP reductions are within the reported values.

These results, however, are in agreement with previous studies showing that the transformation of dissolved organic carbon during ozonation results in a higher reduction in trihalomethane formation potential relative to the reduction of dissolved organic carbon (Amy et al. 1986; Amy

et al. 1991; Galapate et al. 2001). The hydrophobic (HPO) fractions are the main contributors to the formation of THMs (Chow et al. 2005; Sadrnourmohamadi 2013). Therefore, their conversation to hydrophilic fractions can be the reason for lower THMFP.

5.3.2.2. Ozone effect on particle stability and dissolved calcium concentration

Figure 5.4 depicts the effect of ozone on particle stability and dissolved calcium concentration of water samples. The y-axes on the left and right side show the variations of zeta potential and dissolved calcium concentration as functions of ozone dose, respectively. The error bar indicates the standard deviation of experimental error. Zeta potential of raw water was -32.42 mV, and it increased (less negative) to approximately -6.9 mV when the water was ozonated with 0.8 mg Ozone/mg DOC.

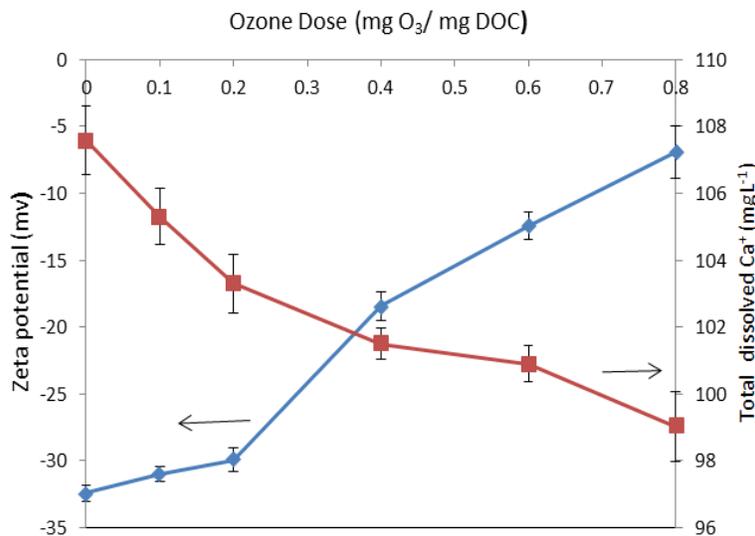


Figure 5.4: Zeta-potential and calcium concentration following ozone application.

For the ozone dose up to 0.2 mg Ozone /mg DOC, the rate of the increase in zeta potential was low, but at the higher ozone doses, the zeta potential showed a sharp increase.

Less negative zeta potential at the increasing ozone dosage implies reduction of the water particles' stability and increased coagulation ability. These data are consistent with previous findings (Chedal 1982). Figure 5.4 demonstrates that ozonation decreased the dissolved calcium concentration in the water samples. Calcium plays an important role in complexation with both aqueous NOM and particle-sorbed NOM and results in the overall removal of DOC. These results confirm the previous findings that a part of organic carbon removal in water sources with high concentration of NOM and calcium can occur by direct precipitation of NOM-calcium complex; this is caused by the increase in the concentration of oxygenated and complexing functional groups, especially the carboxylic acid upon ozone application (Jekel 1994; Chandrakanth and Amy 1996; Chandrakanth et al. 1996; Huang and Wu 2008). To discuss whether there is a correlation between dissolved calcium concentration and zeta potential, statistical analysis consisting of 18 data points was performed by using SPSS. Figure 5.5 supports the correlation with the R^2 value of 0.908.

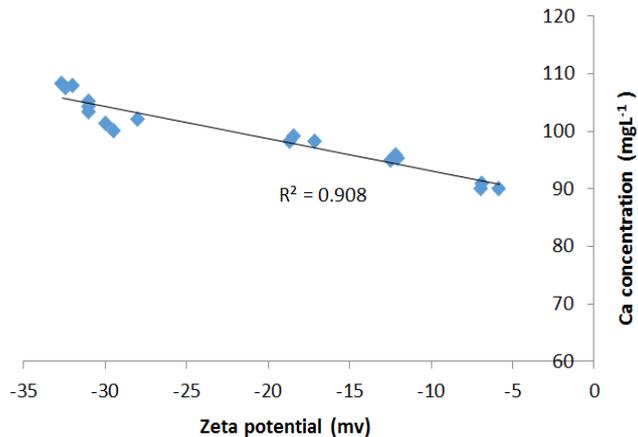


Figure 5.5: Correlation of dissolved calcium concentration and zeta potential.

5.3.2.3. Part II - effects of ozonation on chemical coagulation process

5.3.2.3.1. DOC removal

The effects of pre-ozonation on the removal of the studied water DOC by coagulation with ferric sulphate are shown in Figure 5.6. Three ozone doses (0.2, 0.6, and 0.8 mg Ozone/mg DOC) and three pH (6, 7, and 8) were applied during ozonation. The results showed that DOC removal by coagulation was enhanced by ozonation. The positive effect of pre-ozonation is more pronounced at the higher ozone dose. Application of ozone allowed for significant DOC removals at lower coagulant dosages (Figure 5.6). These data are in agreement with previous findings showing that at low coagulant dose, the performance of the coagulation by itself is relatively poor (Saunier et al. 1983). The largest incremental DOC removal was achieved at the dose of 20 mgL^{-1} regardless of the ozone dose. However statistical analysis of experimental data showed that the DOC removals at dosages 40 and 60 were higher than that at 20 mgL^{-1} . Only the differences in the DOC removals at coagulant doses higher than 60 mgL^{-1} were insignificant. Figure 5.6 shows that pre-ozonation enhanced removal of DOC by coagulation at the ozone doses of 0.6 and 0.8 mg Ozone/mg DOC for this water. Ozone dose of 0.2 mg Ozone/ mg DOC did not show a considerable effect on DOC removal. As shown in Figure 5.6, pH was found to have a substantial effect on DOC removal by ozonation. The highest removals of DOC were obtained by coagulation preceded by ozone at pH 6 (25%, 44%, and 60% of DOC removal at 0.2, 0.6, and 0.8 mg Ozone/mg DOC, respectively). When the pH is increased to 7 and 8, DOC removal decreased for all ozone doses. The results confirm the earlier findings reporting a similar observation that DOC removal rate in coagulation of similar waters, also ozone assisted increased as pH decreased (Ratpukdi et al. 2010, Sadrnourmohamadi et al. 2013). Higher pH results in more OH^- and that accelerates the decomposition of ozone to OH° and consequently decreases the direct reaction between the ozone and the dissolved compounds. The positive

effect of low applied ozone dose (0.2-0.8 mg ozone/mg TOC) on coagulation in waters with high concentration of calcium hardness has been reported earlier. (Farvardin and Collins 1989).

ANOVA results, at a significance level (α) of 0.05, indicated that the overall DOC removal differences are insignificant after coagulant dosage equals to 60 mg/ L. Therefore, authors assumed no significant change in DOC removal with coagulant dosages higher than 60 mg/L.

Therefore, 60 mg/L is assumed to be the optimum dose of the coagulant and is used for subsequent THMFP testing.

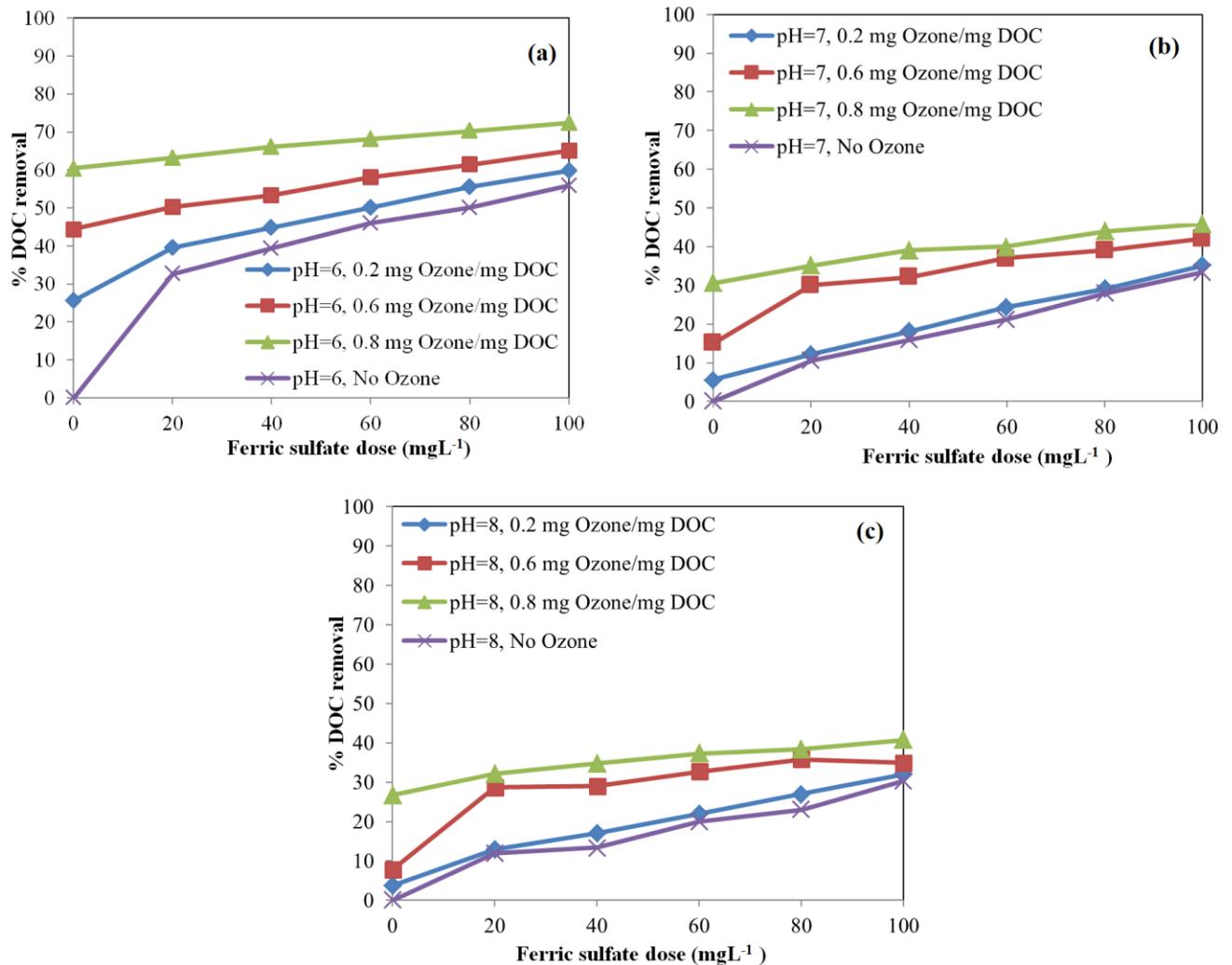


Figure 5.6: Removal of Assiniboine River DOC at varying pH and coagulant doses (a, b, and c).

5.3.2.3.2. Effects of combined pre-ozonation-coagulation on the trihalomethane formation potential (THMFP)

The effect of pre-ozonation, followed by coagulation on the reduction of THMFP for the Assiniboine River water, is shown in Table 5.5. THMFP of the water coagulated at the condition of pH of 6 and coagulant dose of 60 mgL^{-1} was determined for non-ozonated and ozonated samples. This dose of coagulant was used because of insignificant differences in the DOC removals at coagulant doses higher than 60 mgL^{-1} .

Table 5.5: Effects of preozonation-coagulation on THMFP removal;

Sample	DOC	Chloroform	Bromoform ^a	DBCM ^c	BDCM ^b	THMFP	Specific THMFP
Unit	(mg L^{-1})	($\mu\text{g L}^{-1}$)					$\mu\text{g THM/mg DOC}$
0 mg Ozone/mg DOC	11.04±0.06	138.2±2.2	ND	ND	2.6±0.09	140.8±2.08	12.57
0.2 mg Ozone/mg DOC	10.76±0.12	124.9±1.15	ND	ND	2.5±0.02	127.4±4.12	11.84
0.6 mg Ozone/mg DOC	9.28±0.09	103.4±3.51	ND	ND	2.4±0.01	105.8±2.02	11.40
0.8 mg Ozone/mg DOC	8.64±0.10	87.4±2.09	ND	ND	2.4±0.01	89.8±1.09	10.34

^aNot determined

^bBDCM-Bromodichloromethane

^cDBCM- Dibromochloromethane

The results show that THMFP removal was achieved by the pre-ozonation-coagulation process for all of the ozone doses tested. As shown in Table 5.5, the coagulated water sample had a THMFP of $140.8 \mu\text{g L}^{-1}$ and a specific THMFP of $12.57 \mu\text{g THM/mg DOC}$. An increase in ozone dose resulted in an increase in THMFP reduction. Comparing these results with Table 5.4, it can

be concluded that pre-ozonation, followed by coagulation, results in more THMFP reduction rather than ozonation alone. Figure 5.7 shows the specific THMFP ($\mu\text{g THM}/\text{mg DOC}$) as a function of the ozone dose for both ozonated and pre-ozonated coagulated water samples. Since the THMFP of water samples always depends on DOC concentration, the reactivity of forming THMFP is reported in terms of specific THMFP ($\mu\text{g THMFP}/\text{mg DOC}$) (Galapate et al. 2001). The results show that specific THMFP in pre-ozonated-coagulated waters is lower than that in the corresponding ozonated waters for all of the ozone doses tested (0–0.8 mg Ozone/mg DOC).

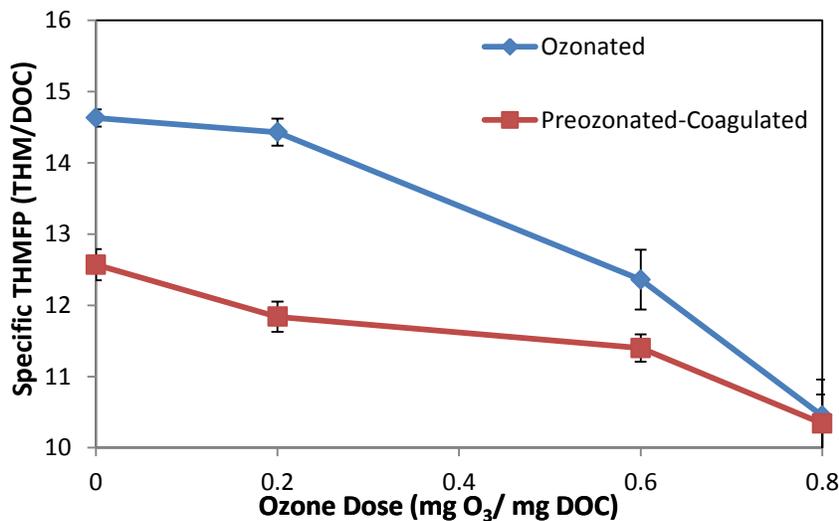


Figure 5.7: Effects of ozonation and preozonation-coagulation on specific THMFP (THMFP/DOC) reduction, coagulant dose = 60 mgL⁻¹.

5.4. CONCLUSION

The effect of ozonation stand-alone and as coagulation aid for the removal of THMs precursors is site-specific and strongly dependent on raw water characteristics. In this study, the effect of ozone on water with unique characteristics, such as high level of DOC (13.8 mgL^{-1}) and calcium hardness (270 mgL^{-1}) CaCO_3 was studied. The following conclusions can be made from this study:

1. Ozonation of water rich in DOC and calcium hardness was able to lower DOC up to 27% and UV₂₅₄ up to 86%.
2. Transformation of DOC due to ozonation resulted in THMFP reduction up to 47%. Our earlier study indicated that HPOA fraction of DOC formed most THMs in this water source. HPOA fraction in this source water was lowered to only 15% of this fraction remaining, following ozonation under ambient pH conditions.
3. Ozonation prior to coagulation enhanced DOC removal at ozone doses of 0.6 and 0.8 mg Ozone/mg DOC. The low ozone dose of 0.2 mg Ozone/mg DOC didn't show a considerable effect on DOC removal. The highest removals of DOC were obtained by coagulation preceded by ozonation at pH of 6; such pH reduction is not economical for water with high alkalinity as the one used in this study.
4. This enhanced removal of DOC can be attributed to ozone-induced particle destabilization and DOC complexation by calcium, specifically: (a) transformation of hydrophobic DOC fraction to hydrophilic fractions with less particle adsorption affinity, resulting in lower particle surface charge, and (b) an increase in calcium complexation with NOM constituents.
5. Pre-ozonation-coagulation also decreased THMFP, showing a higher THMFP reduction for higher ozone doses. Specific THMFP in pre-ozonated-coagulated water samples was lower than that in the corresponding ozonated waters for all of the ozone doses tested.

The effect of ozone on coagulation may vary according to the raw water characteristics.

Therefore, it needs to be evaluated for each specific water source.

It can be concluded from this study that for Canadian prairie surface water, which has a high level of organic carbon, calcium hardness and alkalinity, ozonation prior to coagulation, is

beneficial in terms of coagulant dose reduction and reduction of THMFP. The effect of ozone on the structural and chemical characteristics of natural organic typical for the Canadian Prairie in the absence of calcium hardness is currently being studied in this research group.

CHAPTER 6: EFFECTS OF OZONE AS COAGULATION-AID TREATMENT ON THE REDUCTION OF TRIHALOMETHANES PRECURSORS FROM WATER WITH HIGH DOC AND LOW CALCIUM HARDNESS

ABSTRACT

This study investigates the effect of ozone as a stand-alone and a coagulating aid on the removal of dissolved organic carbon (DOC) from a water source with high level of DOC (16.11 mgL^{-1}) accompanied by low level of calcium hardness ($44 \text{ mgL}^{-1} \text{ CaCO}_3$) (focusing on the influence of calcium hardness). Two types of water were used in this study: a natural water from Rainy River, as a Canadian Shield surface water, and a synthetic water prepared using Suwanee River Humic Acid (HA) standard.

Three aluminum based coagulants: alum, PACl, and ACH were also tested to compare their efficiencies. The effectiveness of each treatment process: ozonation, coagulation and pre-ozonation-coagulation was evaluated by measurement of DOC, UV_{254} , DOC fractions, and trihalomethane formation potential (THMFP).

Results showed that for the natural water from Rainy River ozone stand-alone at the dose of 0.8 mg Ozone/mg DOC is capable of reducing DOC, UV_{254} , and specific THMFP up to 31%, 90%, and 36% respectively. When ozone was applied prior to coagulation it did not enhance DOC removal by subsequent coagulation; however it resulted in reduction of specific THMFP.

The negative effect of pre-ozonation on DOC removal by further coagulation decreased with increasing ozone dosage and was less significant when the coagulant dosage decreased.

The adverse effect of ozone on DOC removal by subsequent coagulation in this study was related to low concentration of calcium hardness in the Canadian Shield water used as source water compared to the water from the Canadian Prairie reported in authors' recent study where

high level of calcium hardness showed a beneficial effect on DOC removal by further coagulation. This statement was confirmed by the results of pre-ozonation-coagulation of synthetic water containing different level of Ca.

The Rainy River coagulation results showed that the highest removal of DOC (69%) was achieved by the water coagulation with alum. Here the reduction of concentration of THMFP in the water treated by coagulation alone follows the following order: alum > ACH > PACl. The superior reduction of THMFP by coagulation with alum is attributed to the highest reduction of hydrophobic acid (HPOA) -the main THMs precursor- by this coagulant.

6.1. INTRODUCTION

Water treatment plants supplied by surface waters in the Canadian Prairies and the Canadian Shield, suffer from high concentrations of chlorine disinfection by-products, THMs. This is due to high concentration of dissolved organic carbon (DOC) in the raw water. The concentration of DOC for these water sources can vary from 8 to 25 mg L⁻¹; the level of calcium hardness for these waters varies significantly from 60 to 350 mg L⁻¹ CaCO₃ (Sadrnourmohemadi and Gorczyca 2015a, 2015b).

Chemical coagulation has been applied widely for DOC removal in drinking water treatments (Zouboulis et al. 2007). However, the effect of this process on the removal of DOC from water depends on several factors such as DOC concentration, DOC chemical composition, coagulant type, coagulant dosage, pH, and water alkalinity (Matilainen and Sillanpää 2010).

Also for waters with high concentration of organic compounds high coagulant dosages required for removal of DOC results in excessive sludge production (Crozes et al. 1995). Also, alkalinity and pH control required to optimize the removal of DOC by coagulation is very costly for waters with such high DOC concentration (Sadrnourmohamadi and Gorczyca 2015b). Several

researchers have investigated the effect of ozone as a stand-alone and a coagulation aid on the reduction of DOC and THMs (Camel and Bermond 1998; Chiang et al. 2002; Singer et al. 2003). However, the benefits of these methods have been reported to be site specific and dependent on the water quality characteristic (Camel and Bermond 1998; Chiang et al. 2002).

The effect of ozonation, as one of the pre-oxidation techniques, on coagulation process is complicated and unpredictable (Hai-long et al. 2006). Some studies pointed out the deteriorative effect of pre-ozonation on subsequent coagulation in terms of reduction of DOC and THMs (Reckhow and Singer 1984; Becker and O'Melia 1996). Others have reported cases in which the application of ozone before coagulation offered potential benefits related to improved DOC removal, and reduced coagulant dosages (Farvardin and Collins 1989; Camel and Bermond 1998; Galapate et al. 2001; Ma 2004; Sadrnourmohamadi and Gorczyca 2015a).

The coagulation type, coagulation pH, ozone dose, and raw water characteristics (DOC and calcium hardness concentration) are important variables that can determine the effect of ozone on coagulation (Bose and Reckhow 2007; Yan et al. 2007; Sadrnourmohamadi and Gorczyca 2015a). Therefore, the effect of ozone (stand-alone as well as coagulant aid) needs to be evaluated for each specific water source. Calcium hardness has been reported as a key factor in determining the effect of pre-ozonation on coagulation (Dowbiggin and Singer 1989; Chandrakanth and Amy 1996). The mechanism of how calcium is involved in effect of ozonation on coagulation is described in literature (Edwards and Benjamin 1992a, b; Chandrakanth and Amy 1996; Chandrakanth and Amy 1998, Sadrnourmohamadi and Gorczyca 2015a). The authors have already reported the effects of ozone stand alone and as a coagulation aid on the reduction of DOC and THMFP from the Prairie water with a high level of DOC and calcium hardness (Sadrnourmohamadi and Gorczyca 2015a). For that particular water source, the

ozonation prior to coagulation enhanced the reduction of DOC and THMFP at ozone doses of 0.6 and 0.8 mg Ozone/mg DOC. The enhanced removal of DOC was attributed to ozone-induced particle destabilization and DOC complexation by calcium, specifically: (a) transformation of hydrophobic DOC fraction to hydrophilic fractions with less particle adsorption affinity, resulting in lower particle surface charge, and (b) an increase in calcium complexation with NOM constituents.

Objectives

To further investigate the mechanism of ozone reactions identified in the earlier study, this work presents the effect of ozone on the Canadian Shield water with a high level of DOC and low calcium hardness. The Rainy River water, supplying the Town of Rainy River (Ontario, Canada) was used in this study. The River raw water is characterized by high DOC (16.11 mgL^{-1}) and low calcium hardness ($44 \text{ mgL}^{-1} \text{CaCO}_3$). To further evaluate the role of calcium in pre-ozonation-coagulation, synthetic water containing different levels of calcium, but the same level of DOC, were tested. This study evaluates the effect of pre-ozonation on the removal of dissolved organic carbon (containing THMs precursors) by further coagulation. The focus of this study is on the effect of calcium hardness. Additionally ozonation stand alone and aluminum-base coagulation were also conducted to compare their efficiencies.

The specific objectives of this study are:

- To compare the performance of aluminum based coagulants :Alum, ACH, and PACl in terms of reduction of DOC, DOC fractions, and UV_{254} from Rainy River water, characterized by high DOC (16.11 mgL^{-1}) and low calcium hardness ($44 \text{ mgL}^{-1} \text{CaCO}_3$)
- To evaluate the effects of these coagulants on the THMs formation potential of the Rainy River water samples.

- To study the effects of ozonation on DOC and the total THMs formation potential of the Rainy River water samples.
- To investigate the effect of ozone as an aid on above mentioned three aluminum based coagulants targeting the reduction of DOC and total THMFP. Pre-polymerized aluminum based coagulants were selected due to low alkalinity of Rainy River water used as source water in this study. For low alkalinity waters these coagulants cannot consume all of the available alkalinity depressing the pH to values too low for effective treatment.
- To investigate the effect of calcium hardness on DOC removal by pre-ozonation-coagulation using synthetic water.
- To compare the effect of ozone stand alone and as a coagulation aid on THMs precursors' reduction for Canadian Shield and Canadian Prairie natural waters with different calcium hardness concentration

6.2. MATERIALS AND METHODS

6.2.1. Water sources

Two types of water have been used in this study: (1) a natural water collected from the Rainy River Water Treatment Plant intake, which is located on the Canadian Shield in the Town of Rainy River, Ontario (Canada). This water is a high DOC water with low calcium hardness (Table 6.1). (2) a synthetic water prepared using Suwanee River Humic Acid (HA) standard diluted to approximately 16 mgL^{-1} with pH adjusted to 6.5, a similar DOC and pH to those detected in Rainy River Water. Synthetic water containing different levels of calcium were tested to further investigate the effect of calcium in pre-ozonation-coagulation

6.2.2. Coagulation experiments

The coagulation experiments were conducted using a conventional method in six paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA) at room temperature.

Three commercial aluminum-based coagulants obtained from ClearTech Industrial Ltd, Canada were used in this study: aluminum sulphate (alum) with basicity value of 0; poly-aluminum chloride (ClearPAC 180, denoted as PACl) with basicity value of 43%; and aluminum chlorohydrate (CTI 4900, denoted as ACH) with basicity value of 83%. One litre of water was placed in each jar. A measured amount of coagulant was pipetted into the test water to give a desired coagulant concentration while stirring rapidly at 120 rpm for 1 minute, followed by a slow mix at 40 rpm for 30 minutes. The samples were then allowed to settle for 30 minutes.

Coagulant doses were in the range of $1 \text{ mgL}^{-1}\text{Al}$ to $10 \text{ mgL}^{-1}\text{Al}$ based on the previous experience with the similar water quality (Sadrnourmohamadi and Gorczyca 2015b).

6.2.3. Ozonation Experiments

Ozonation was conducted on a semi-batch basis by bubbling the desired amount of ozone through the 2L water sample. The detail of ozonation test is described in previous chapter.

6.2.4. Analytical Methods

The details of Analytical methods used in this study are reported in chapter 3. All measurements were repeated at least three times to assure the reproducibility of experimental results.

6.2.5. Trihalomethane Formation Potential

THMs formation potential measurements were conducted according to *Standard Methods 5710B* (APHA 2012); Details of this procedure have been described in previous chapters.

6.2.6. DOC Fractionation

DOC fractions were characterized using solid phase extraction (SPE) developed by Ratpukdi et al. (2009). The full fractionation procedure can be found in previous chapters.

6.3. RESULTS AND DISCUSSION

6.3.1. General water quality

Table 6.1 shows the general water quality of the Rainy River samples. The general water quality of Assiniboine River water is also included for comparison. Rainy River water source has a high level of DOC (16.11 mgL^{-1}) accompanied by low levels of calcium hardness ($44 \text{ mgL}^{-1}\text{CaCO}_3$) compared to Assiniboine River water which has high level of DOC (13.8mgL^{-1}) and calcium hardness ($270 \text{ mgL}^{-1}\text{CaCO}_3$) respectively. The SUVA value higher than $3 \text{ m}^{-1}\text{mg}^{-1} \text{ L}$ for both Rainy River and Assiniboine River raw waters is representative of a water source more hydrophobic in character (Edzwald and Tobiason 1999). The fractionation results of the Rainy River water are shown in Table 6.2. The results showed that more than 55% of DOC is due to hydrophobic fractions, and up to 49% of the organic matter is associated with the hydrophobic acid fraction. The HPOA fraction (the DOC fraction forming most THMs) in the Rainy River water is very similar to that reported for Assiniboine River in authors earlier paper (Sadrnourmohamadi and Gorczyca 2015b).

Table 6.1: General Rainy River and Assiniboine River raw water quality characteristics

Sample	DOC (mgL^{-1})	UV ₂₅₄ (cm^{-1})	SUVA ($\text{m}^{-1}\text{mg}^{-1}\text{L}$)	pH	Alkalinity ($\text{mgL}^{-1}\text{CaCO}_3$)	Total Hardness ($\text{mgL}^{-1}\text{CaCO}_3$)	Calcium ($\text{mgL}^{-1} \text{CaCO}_3$)
Rainy River Water	16.11	0.612	3.23	6.5	26	65	44
Assiniboine River Water	13.8	0.470	3.40	7.9	330	349	270

Table 6.2: The DOC composition of the Rainy River water sample

Fraction	Concentration (mgL ⁻¹)	DOC %
Hydrophobic neutral (HPON)	0.43±0.02	2.68
Hydrophobic base (HPOB)	0.57±0.06	3.54
Hydrophobic acid (HPOA)	7.94±0.15	49.3
Hydrophilic base (HPIB)	0.92±0.04	5.73
Hydrophilic acid (HPIA)	0.12±0.01	0.75
Hydrophilic neutral (HPIN)	6.12±0.14	38
Total	16.11±0.20	100

Results also showed the lowest concentration of hydrophobic base fraction in this source water, which is consistent with previous reports showing that many natural surface waters are low in concentration of hydrophobic base (Leenheer 1981; Swietlik et al. 2004).

6.3.2. Water Coagulation Experiments

6.3.2.1. DOC and UV₂₅₄ and pH

The effects of coagulation conditions (coagulant type and dose) on Rainy River water samples pH, DOC, and UV₂₅₄ was investigated and the results are shown in Figure 6.1. Figure 6.1 (a) shows that the depression of solution pH, due to coagulant addition, follows the order of alum>PACl>ACH; this correlates with the basicity ratios for these coagulants. The difference in pH depression between PACl and ACH appears to be non-significant, as expected.

Figure 6.1 (b) shows the DOC removal by different coagulants. Considering the DOC removal effectiveness, the coagulants can be ranked in the following order alum > ACH > PACl. These results are consistent with the authors' recent study (Sadrnourmohamadi and Gorczyca 2015b)

where the mechanisms of DOC removal by aluminum based coagulants is shown to be related to aluminum species formed during the coagulation. In that study, alum at pH 6, showed the highest content of in situ formed coagulant polymeric species (Al_b). The removal of DOC has been found closely related to the content of Al_b (Yang et al. 2010, 2011; Sadrnourmohamadi and Gorczyca 2015b). For all coagulants the DOC removal increased with higher coagulant dosage. All three coagulants achieved the highest DOC removal at the dose of $10 \text{ mgL}^{-1}Al$. However, most of this removal was achieved with the coagulant doses of about $7 \text{ mgL}^{-1}Al$. The additional DOC removal at coagulant doses greater than $7 \text{ mgL}^{-1}Al$ was found statistically insignificant at a significance level (α) of 0.05 (Montgomery 2001). At this coagulant dose ($7 \text{ mgL}^{-1}Al$) alum showed the greatest reduction of DOC with the final DOC concentration in coagulated water of 5.5 mgL^{-1} (66% reduction), whereas PACl was only able to reduce the DOC to 8.5 mgL^{-1} (47% reduction). Literature has shown that the performance of each coagulant depends on water characteristics and applied test conditions (Uyak and Toroz 2007). Author's previous study conducted on Assiniboine River (the Canadian Prairie water) showed the similar results where alum achieved the highest DOC reduction (71%) followed by ACH (68%) and, PACl (54%) at pH 6 (Sadrnourmohamdi and Gorczyca 2015b). UV_{254} removal shows similar trend as DOC removal does, with alum showing the most efficient removal followed by ACH and PACl (Figure 6.1c).

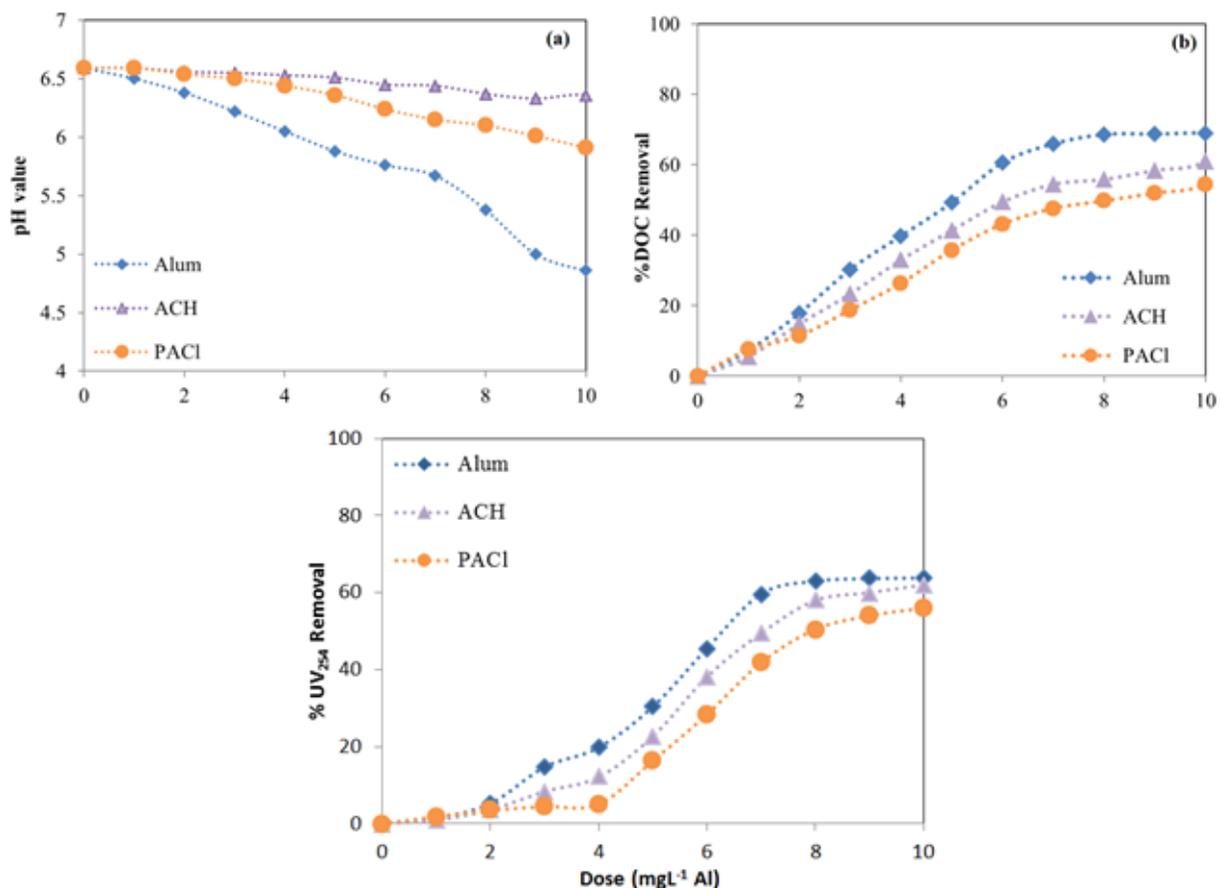


Figure 6.1: Effect of coagulant type and dosage on pH (a), DOC (b) and UV₂₅₄ (c), (Rainy River Raw water pH 6.5).

6.3.2.2.DOC fractions

The DOC of coagulated Rainy River water samples at coagulant dose of 7 mgL⁻¹ Al was fractionated to determine the removal of specific DOC fractions (Table 6.4). This dose of coagulant was used because of insignificant differences in the DOC removals at coagulant doses higher than 7 mgL⁻¹ Al (Table 6.3).

All the coagulants were found to reduce HPO fractions significantly. Table 6.3 shows that alum had the highest removal of HPO fractions (85%); the HPOA fraction has been reported to be most reactive in formation of THMs. Alternatively, the coagulants used were not able to remove HPIN fraction with 52-55% of these fractions remained following coagulation (Figure 6.2).

Table 6.3: DOC fractions (shown as % DOC remaining), following coagulation at coagulant dose of $7 \text{ mgL}^{-1} \text{ Al}$

Sample	% DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	2.68	3.54	49.3	5.73	0.75	38.0
Alum	1.84	2.93	20.5	9.53	10.1	55.1
ACH	2.01	3.29	25.3	7.20	8.10	54.1
PACl	2.08	3.41	27.5	4.51	10.2	52.3

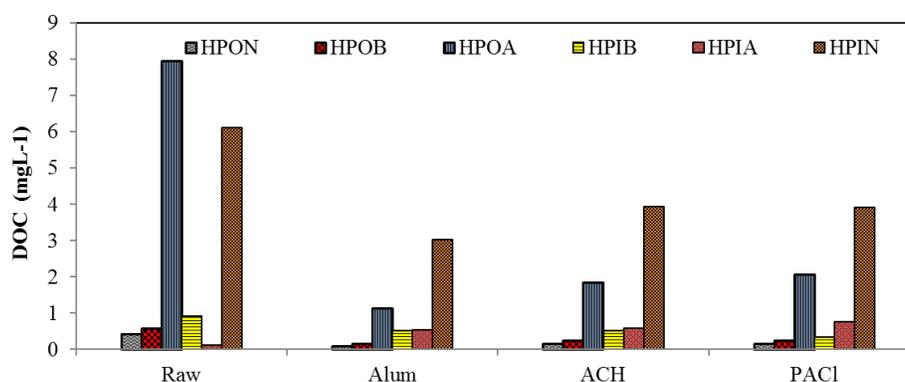


Figure 6.2: DOC fractions remaining in solution following coagulation at coagulant dose of $7 \text{ mgL}^{-1} \text{ Al}$.

6.3.2.3. THMFP

THMFP results for raw and coagulated water samples at $7 \text{ mgL}^{-1} \text{ Al}$ coagulants doses are shown in Table 6.4. The raw water of Rainy River had a THMFP of $308.4 \mu\text{g L}^{-1}$ (Table 6.4). All three coagulants significantly reduced the THMFP. For this source water alum and PACl showed the greatest and the least reduction in THMFP to $113.1 \mu\text{g L}^{-1}$ and $137 \mu\text{g L}^{-1}$ respectively.

At similar coagulant dose alum outperformed ACH and ACH in terms of reduction of THMFP and total DOC. This is because of effective removal of HPOA fraction by alum which is reported to have the greatest potential to form THMs (Chow et al. 2005; Sadrnourmohamadi and Gorczyca 2015b).

Table 6.4: THMFP for Rainy River raw and coagulated water samples (at coagulant dose of 7 mgL⁻¹ Al)

Sample	DOC	CHCl ₃	CHBr ₃	CHClBr ₂	CHCl ₂ Br	THMFP
Unit	(mg L ⁻¹)	(µg L ⁻¹)				(µg L ⁻¹)
Raw	16.11±0.2	304.9±2.05	ND	ND	3.5±0.2	308.4±2.7
Alum	5.5±0.12	110.6±1.31	ND	ND	2.5±0.3	113.1±1.11
PACl	8.5±0.17	134.2±3.12	ND	ND	2.8±0.07	137±2.01
ACH	7.3±0.07	130.3±1.01	ND	ND	2.4±0.11	132.7±2.31

6.3.3. Effect of The Ozonation Treatment

6.3.3.1. DOC and UV₂₅₄ removal

The effect of ozone on the Rainy River water quality is shown in Figure 6.3. Figure 6.3 shows increased DOC removal and UV₂₅₄ reduction at increased ozone doses. Ozone dose of 0.8 mg Ozone/mg DOC achieved the highest reduction of DOC (31%) and UV₂₅₄ (90%) respectively. These removals are very similar to those reported for high DOC and high Calcium hardness water of Assiniboine River (DOC reduction of 27% and UV₂₅₄ reduction of 86% respectively) (Sandnourmohamadi and Gorczyca 2015a) and are within the range of the published data (Tuhkanen et al 1994; Molnar et al. 2012). The pH value of 6.5 in this study can also result in higher DOC removal (Ratpukdi et al. 2010). pH reduction results in less OH⁻ which hinders the decomposition of ozone to OH• and consequently increase the direct reaction between the ozone and the dissolved compounds.

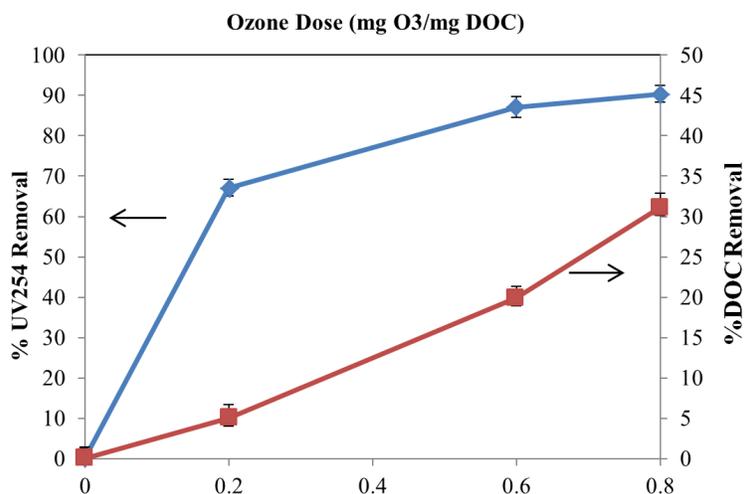


Figure 6.3: Parameters of Rainy River water under different dose of ozone (Raw water pH 6.5).

The higher DOC removal at the higher ozone dose can be explained as follows; an increase in the ozone dosage provides more available ozone molecules and hydroxyl radical, which results in higher reduction of organic carbon (Ratpukdi et al. 2010). Generally UV₂₅₄ indicates the relative amount of unsaturated and/or aromatic carbon of DOC. For all ozone doses, a decrease of UV₂₅₄ was observed, indicating the oxidation of unsaturated and/or aromatic carbon molecules, which is in accordance with previously reported results (Gilbert 1988; Camel and Bermond 1998; Swietlik et al. 2004). Higher UV₂₅₄ reduction compared to DOC removal, shown in Figure 4-3, suggests incomplete mineralization of organic molecules degraded from unsaturated and/or aromatic organics (Chang and Singer 1991; Ratpukdi et al. 2010).

6.3.3.2. THMFP

THMFP of ozonated water samples at four applied ozone doses was determined (Table 6.5). Generally, as the dose of ozone increased, the value of THMFP decreased. The raw water of Rainy River had a THMFP of 308.4 $\mu\text{g L}^{-1}$ and a specific THMFP of 19.14 $\mu\text{g THM/ mg DOC}$. These results are within the range of those reported for high DOC and high Calcium hardness water of Assiniboine River (THMFP of 202 $\mu\text{g L}^{-1}$ and specific THMFP of 14.63 $\mu\text{g THM/ mg}$

DOC respectively). Ozonation resulted in a significant decrease in THMFP down to $135.8 \mu\text{g L}^{-1}$ and specific THMFP of 12.23 at the ozone dose of 0.8 mg Ozone/mg DOC (Table 6.5). Author's previous paper showed that ozone can change the water DOC from hydrophobic to more hydrophilic in the Assiniboine River, which is Canadian Prairie surface water source (Sadrnourmohamadi and Gorczyca 2015a). The hydrophobic fractions are the main contributors to the formation of THMs. Therefore, their conversation to hydrophilic fractions can be the reason for lower THMFP (Chow et al. 2005; Sadrnourmohamadi et al. 2013). The percent decrease in THMFP at the highest dose of ozone (56%) was higher compared to DOC (31%). These results are in agreement with previous studies showing that the transformation of dissolved organic carbon during ozonation results in a higher reduction in trihalomethane formation potential relative to dissolved organic carbon (Amy et al. 1991; Galapate et al. 2001; Sadrnourmohamadi and Gorczyca 2015a).

Table 6.5: THMFP for Rainy River raw and ozonated water samples

Sample	DOC	CHCl_3	CHBr_3	CHClBr_2	CHCl_2Br	THMFP	Specific THMFP
Unit	(mg L^{-1})	($\mu\text{g L}^{-1}$)				($\mu\text{g L}^{-1}$)	$\mu\text{g THM}/\text{mg DOC}$
Raw	16.11 ± 0.5	304.9 ± 3.2	ND	ND	3.5 ± 0.4	308.4 ± 2.7	19.14 ± 0.41
0.2 mg Ozone/mg DOC	15.3 ± 0.31	238.3 ± 2.8	ND	ND	2.3 ± 0.1	240.6 ± 2.1	15.72 ± 0.18
0.6 mg Ozone/mg DOC	12.9 ± 0.2	185.6 ± 4.11	ND	ND	1.7 ± 0.3	187.3 ± 1.6	14.51 ± 0.6
0.8 mg Ozone/mg DOC	11.1 ± 0.4	135.8 ± 4.3	ND	ND	ND	135.8 ± 3.4	12.23 ± 0.2

6.3.4. Effect of Ozonation on Chemical Coagulation Process

6.3.4.1. DOC removal

The effects of pre-ozonation on the removal of the Rainy River water DOC by further coagulation processes are shown in Figure 6.4. Three ozone doses (0.2, 0.6, and 0.8 mg Ozone/mg DOC) were applied during ozonation followed by 3 aluminum based coagulation. Results showed that pre-ozonation did not enhance DOC reduction by coagulations for this water source. Alum coagulation at the dose of 6 mgL⁻¹Al achieved 61% of DOC removal when no ozone was applied. It decreased to 54% when 0.8 mg Ozone/mg DOC ozone was applied before coagulation. The negative effect of pre-ozonation decreased with increasing ozone dosage; this unfavorable effect is less significant when the coagulant dosage is decreased. This adverse effect of ozone on DOC removal by subsequent coagulation could be related to low concentration of calcium hardness in this specific water source which is supported by others previous findings (Rodríguez et al. 2012; Sadrnourmohamadi and Gorczyca, 2015a).

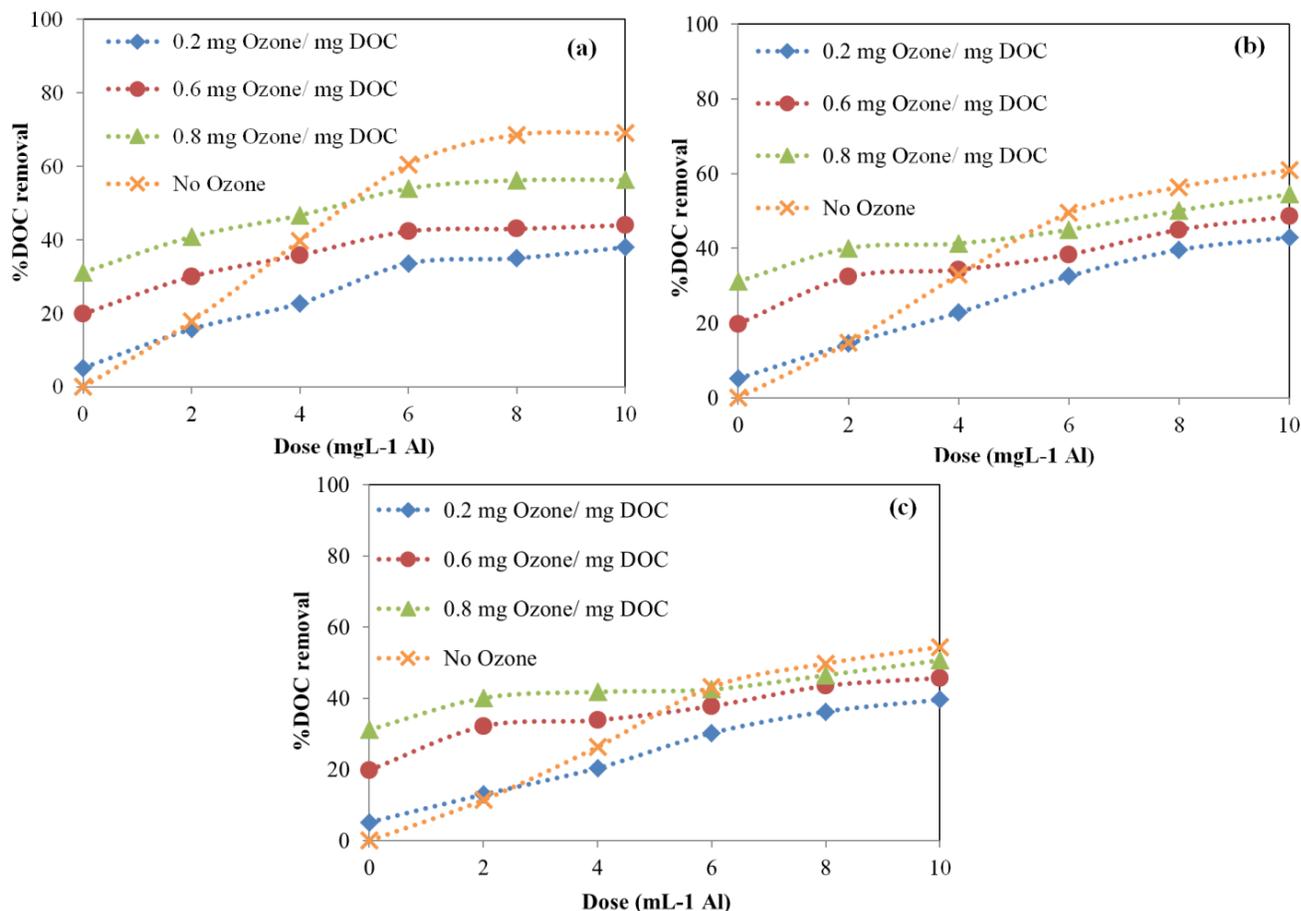


Figure 6.4: Removal of Rainy River DOC at varying ozone and coagulant doses, (a): alum, (b): ACH, (c): PACl.

6.3.4.2. Total trihalomethane formation potential

The effect of pre-ozonation-coagulation on the reduction of THMFP for the Rainy River water samples is shown in Table 6.6. THMFP of pre-ozonated water samples at three different ozone doses followed by coagulations at coagulants dose of 6 mgL⁻¹Al was determined for all three coagulants (Table 6.6). This dose of coagulant was selected as optimal because of insignificant differences in the DOC removals at coagulant doses higher than 6 mgL⁻¹ Al (Figure 6.4). The results show that pre-ozonation followed by coagulation can reduce THMFP for all ozone doses. An increase in ozone dose resulted in an increase in THMFP reduction with ACH showing the

highest reduction of specific THMFP. As shown in Table 6.5, Rainy River raw water sample had a THMFP of $308.4 \mu\text{g L}^{-1}$ and a specific THMFP of $19.14 \mu\text{g THM/ mg DOC}$. Comparing these results with Table 6.5, it can be concluded that pre-ozonation-coagulation at ozone dose of 0.6 and 0.8 mg Ozone/mg DOC, result in more THMFP reduction rather than ozonation alone. When pre-ozonation at 0.6 and 0.8 mg Ozone/mg DOC ozone dose is applied prior to coagulation, the highest reduction in specific THMFP is achieved by ACH (46%, 70%) followed by PACl (42%, 66%) and alum (41%, 60%) respectively (Table 6.6). At these specific ozone doses, ozonation alone can reduce specific THMFP by 24% and 36% respectively.

To further confirm the role of calcium in pre-ozonation-coagulation, more experiments using synthetic water containing different levels of calcium, but the same level of DOC were conducted. Synthetic water containing HA with a concentration of 16 mg L^{-1} and different Ca concentration (0, 40, 140, and $240 \text{ mg L}^{-1} \text{ CaCO}_3$) were pre-ozonated and further coagulated by alum (Figure 6.5). Results showed the beneficial effect of calcium in coagulation of pre-ozonated water samples. Non-ozonated HA sample without Ca achieved 60% of DOC removal whereas this number decreased by applying pre-ozonation. This trend changes for water samples containing Ca with concentration of 140 and $240 \text{ mg L}^{-1} \text{ CaCO}_3$ where preozonation increases the DOC removal by further alum coagulation (Figure 6.5). Results also showed that for non-ozonated samples increased concentration of Ca improved the DOC removal by coagulation alone. Calcium can enhance the HA coagulation by forming the HA- coagulant species bridging which results in improved DOC removal (Duan et al. 2012).

Table 6.6. Effects of preozonation-coagulation on THMFP removal; Coagulants dose = 6 mgL⁻¹Al

Sample	DOC	CHCl ₃	CHBr ₃	CHClBr ₂	CHCl ₂ Br	THMFP	Specific THMFP
Unit	(mg L ⁻¹)	(µg L ⁻¹)				(µg L ⁻¹)	µg THM/ mg DOC
<u>Alum</u>							
0.2 mg Ozone/mg DOC	10.70±0.3	187.4±2	ND	ND	7.4±0.12	194.8±3.2	18.20±1.4
0.6 mg Ozone/mg DOC	9.28±0.4	102.5±4	ND	ND	2.4±0.09	104.9±4.4	11.30±1.1
0.8 mg Ozone/mg DOC	7.40±0.11	54.9±2.1	ND	ND	2.2±0.06	57.1±2.11	7.71±0.09
<u>ACH</u>							
0.2 mg Ozone/mg DOC	10.86±0.3	155.2±5.2	ND	ND	2.8±0.1	158±2.09	14.54±1.03
0.6 mg Ozone/mg DOC	9.93±0.2	100±1.1	ND	ND	2.5±0.1	102.5±1.11	10.32±0.82
0.8 mg Ozone/mg DOC	8.87±0.2	48.2±2.01	ND	ND	1.95±0.09	50.15±2.07	5.65±1.01
<u>PACl</u>							
0.2 mg Ozone/mg DOC	11.23±0.09	206.1±4.3	ND	ND	3.2±0.08	209.3±4.3	18.63±2.1
0.6 mg Ozone/mg DOC	10.02±0.11	108.6±2.1	ND	ND	2.6±0.1	111.2±2.2	11.09±1.04
0.8 mg Ozone/mg DOC	9.18±0.1	57.5±3.6	ND	ND	2.1±0.2	59.6±4	6.49±1.13

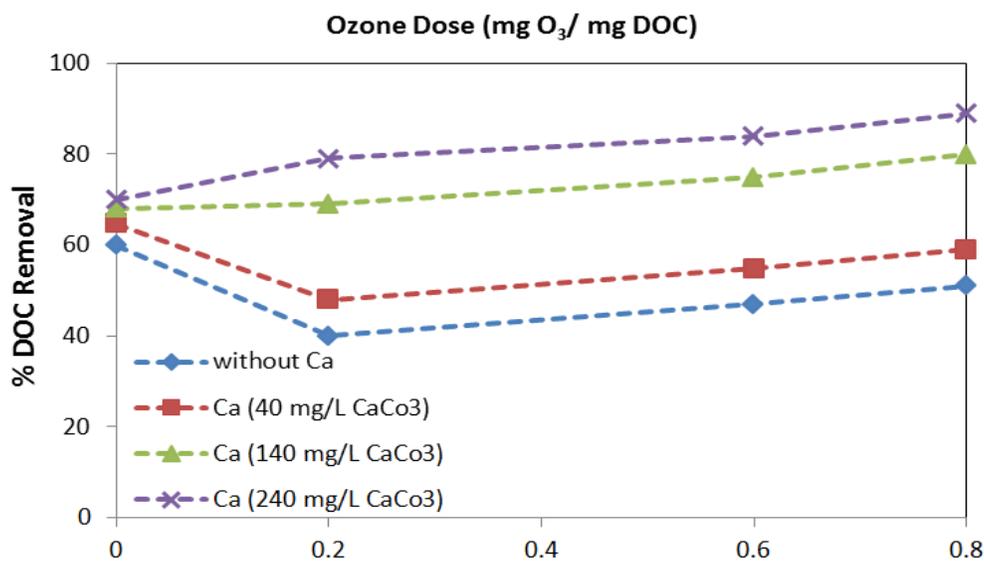


Figure 6.5: Effect of calcium on pre-ozonation-coagulation, initial condition (HA concentration: 16 mgL^{-1} , coagulation: alum, coagulant dose: $6 \text{ mgL}^{-1}\text{Al}$, coagulation pH: 6.5).

6.3.5. Ozone enhanced coagulation comparison for two Canadian Shield and Canadian Prairie natural waters with different calcium hardness concentration

Calcium has been reported as a key parameter in ozone-enhanced coagulation. It has been reported that ozonation, prior to coagulation, benefits waters with moderate to high levels of calcium hardness. Chandrakanth (1994) reported ozone enhanced coagulation cases only when the raw waters had calcium hardness concentration higher than $100 \text{ mgL}^{-1} \text{CaCO}_3$. The transformation of hydrophobic DOC fraction to hydrophilic fractions upon ozonation results in reduction of THMFP regardless of level of calcium hardness in source water (Chow et al. 2005; Sadrnourmohamadi 2013). However these hydrophilic fractions can be complexed with the aid of calcium ion and incorporated into a coagulation floc resulting in overall DOC reduction. This was the case in our earlier study, where ozone application on water with high level of DOC and calcium hardness showed that ozonation improved both the DOC removal and THMFP reduction by subsequent coagulation. The enhanced removal of DOC in our previous study was attributed

to complexation of calcium with both aqueous NOM and particle-sorbed NOM upon ozonation (Edwards and Benjamin 1992a; Rodríguez et al. 2012). On the contrary, the Canadian Shield water (Rainy River water) used in this study has a low level of calcium hardness (44 mgL⁻¹ CaCO₃); therefore the beneficial effect of calcium hardness is negligible compared to the water from the Canadian Prairie studied earlier (Sadrnourmohamadi and Gorczyca, 2015a). These results confirm that calcium hardness is a key factor involved in preozonation-coagulation process.

6.4. CONCLUSION

The results of this study along with our previous work confirm that the effect of pre-ozonation on the efficiency of coagulation process aimed at reducing DOC strongly depends on the characteristics of the raw water and it needs to be evaluated for each specific water source. In this study, authors specifically focused on the effect of water calcium hardness concentration on preozonation-coagulation in terms of removal of THMs precursors.

The following conclusions can be made from this study:

1. When coagulation was applied alone alum (10 mgL⁻¹ Al) achieves the highest removal of DOC (69%) and UV₂₅₄ (84%) respectively. Most of this removal (66% and 83%) was achieved with the coagulant doses of 7 mgL⁻¹Al.
2. All three coagulants removed hydrophobic DOC fractions better than hydrophilic ones. Fractionation results showed that alum has the greatest removal (85%) of HPOA fraction of DOC.
3. Coagulation with alum showed the greatest reduction in THMFP from 308.4 µg L⁻¹ to 113.1 µg L⁻¹ followed by ACH and PACl. This can be related to the reduction of HPOA which confirms our earlier results (Chapter 5).

4. Ozone stand-alone at the dose of 0.8 mg Ozone/mg DOC was capable of reducing DOC, UV₂₅₄, and specific THMFP up to 31%, 90%, and 36% respectively.
5. Ozonation prior to coagulation did not enhance DOC removal by subsequent coagulation; however it resulted in reduction of specific THMFP.
6. The negative effect of pre-ozonation on DOC removal by further coagulation decreased with increasing ozone dosage and was less significant when the coagulant dosage decreased.
7. The adverse effect of ozone on DOC removal by subsequent coagulation is related to low concentration of calcium hardness in this water source. This statement was confirmed by the results of pre-ozonation-coagulation of synthetic water containing different level of Ca. Calcium can be complexed with both aqueous NOM and particle-sorbed NOM upon ozonation and enhance removal of DOC as reported in our previous study.

It can be concluded that for this specific high DOC and low calcium water, application of ozone prior to coagulation is beneficial in terms of reduction of specific THMFP but not in terms of reduction of DOC. While our previous study on water with high levels of DOC and calcium hardness showed the opposite effect. This difference can be attributed to a significant role of calcium concentration in the removal of DOC by coagulation.

These results are especially useful for water treatment systems with high DOC, and significantly different alkalinity and calcium hardness levels in their raw waters.

CHAPTER 7: OZONATION OF NATURAL ORGANIC MATTER AND AQUATIC HUMIC SUBSTANCES: THE EFFECT OF OZONE ON THE STRUCTURAL TRANSFORMATION AND SUBSEQUENT TRIHALOMETHANES FORMATION POTENTIAL

ABSTRACT

The structural and chemical characteristics of natural organic matter (NOM) and its isolated humic fractions: humic acid (HA) and fulvic acid (FA) were studied by means of fourier transform infrared coupled to attenuated total reflectance (FTIR-ATR), UV/Vis, and synchronous scanning fluorescence (SSF) before and after the reaction with ozone.

The effectiveness of ozonation was evaluated by removal of dissolved organic carbon (DOC), and UV₂₅₄ absorbance. The results were linked to the effect of the ozonation on total trihalomethane formation potential (TTHMFP) reduction for water samples with high levels of trihalomethanes (THMs) precursors. Results showed that ozonation at the dose of 1 mg Ozone/mg DOC was capable of reducing DOC, UV₂₅₄, and THMFP up to 42%, 95%, and 89% for HA water sample –the main THMs precursor-respectively. The study of UV/Vis, FTIR-ATR, and SSF reveals consistent trends showing that ozone can change the composition of DOC in the water samples, causing a significant reduction in aromaticity. The reduction of UV₂₅₄ for each ozonated sample also affirms that the ozone mainly targets aromatic moieties of organic carbon molecules. FTIR-ATR results showed that the reduction of unsaturated functional groups such as aromatic rings and C=C bonds in water samples are the major reaction mechanism in ozone application. SSF results also revealed that ozonation decrease the fluorescence intensity of the maximum peak as well as the whole spectra. Ozonation reduced concentration of aromatic and

highly conjugated compounds in the water. This is the main reason why ozonation is effective in reduction of water THMFP, as they contain the main THMs precursors.

7.1. INTRODUCTION

Natural organic matter is a complex and heterogeneous mixture of organic compounds with varying functional and structural characteristics (Lamsal et al 2011). This poorly defined ubiquitous mixture varies in terms of its organic carbon character and concentration with both season and source (Owen et al. 1993). DOC, the poorly defined complex and heterogeneous mixture of organic compounds with varying functional and structural characteristics is separated into two major classes: humic and non-humic organic substances which vary in chemical properties. Humic substances (HS) are defined as a diverse group of organic materials formed during the degradation of plant and animal tissues (Yu et al. 2005). The composition of this group is site specific and strongly influenced by the local environment, by factors such as water temperature, alkalinity, and pH (Chow et al. 2005). HS form the major fraction of dissolved organic carbon in surface water, representing 40-80% and sometimes up to 90% of DOC (Thurman 1985; Zhao et al. 2006). Our recent study of the DOC in two major rivers in southern Manitoba, Red River and Assiniboine River has found them to be rich in aquatic humic substances (Sadrnourmohamadi et al. 2013; Sadrnourmohamadi and Gorczyca 2015a, 2015b). Aquatic humic substances (AHS) consist of humic acids (HA), insoluble at pH less than 2, and fulvic acids (FA) soluble at all pHs (Thurman 1985; Zhao et al. 2006; Rodriguez and Nunez 2011). Humic acids are characterized as having an aromatic structure with unsaturated carbon bonds. It can be described as a heterogeneous polyfunctional polymer due to its polymeric network that can entrap volatile organic compounds (Kerc et al. 2003b). Fulvic acids comprise the dominant fraction of humic substances with lower molecular weight and lower level of

aromaticity than humic acids (Amy et al. 1986; Matilainen et al. 2011). Recently most attention has been paid to the removal of HS (fulvic and humic acids) fraction of DOC acting as the main precursor towards THMs formation (Kerc et al. 2003a; Zhao et al. 2006).

Ozonation has been reported to be an effective treatment to reduce THMs precursors that are present in drinking water sources even without a significant decrease in total organic carbon content. In these cases ozone transforms high molecular weight organic compounds into smaller ones, which are resistant to reaction with chlorine as a disinfectant (Camel and Bermond 1998; Chiang et al. 2002). However, some studies have demonstrated some cases where ozonation had a deteriorative effect on THMs reduction (Toor and Mohseni 2007; Chowdhury et al. 2008). Therefore DOC composition and distribution in natural waters determines the efficiency of ozone for the reduction of THMs precursors (Camel and Bermond 1998). A lot of complex and complicated reactions are involved in ozone application on natural waters especially those with a high level of DOC, and calcium hardness which is common in the Canadian Prairies. Moreover, the heterogeneous and complex structure of DOC makes treatment by ozonation extremely challenging. Fundamental studies covering the effect of different variables such as ozone dose and type of DOC under controlled laboratory conditions are needed. The transformation in chemical behaviour and structural characteristics of NOM post ozonation at varying ozone doses needs to be further investigated, as it will lead to a better understanding on how ozone affects DOC concentration and THMs formation.

Objectives

The effect of ozone on the structural composition of THMs precursors depends on several parameters such as DOC composition and ozone dosage. This study investigated the effect of

ozone on THMs precursors: NOM, humic acid, and fulvic acid at pH of natural waters. The results were also linked to the change in the formation potential of THMs upon ozone reaction.

The effect of ozone on the functional and structural properties of each source of organic compounds will be assessed by different physical (DOC, UV₂₅₄ measurement) and spectroscopic techniques (FTIR-ATR, UV/Vis, and fluorescence spectroscopy). Humic species are found to be dominant fractions of DOC in two Manitoba surface waters. It has been reported that almost 50-70% of Manitoba potable water treatment plants that use these surface water sources are not in compliance with THMs regulations set by provincial regulators. Therefore the results of this study would be beneficial for local drinking water treatment industry in order to meet the provincial regulation.

7.2. MATERIALS AND METHODS

7.2.1. Water Sources

Synthetic water samples prepared in the laboratory were used in this study. Three different commercial organic compounds including Suwannee River Natural organic matter (SRNOM), Suwannee River Humic Acid (SRHA), and Suwannee River Fulvic Acid (SRFA) standards provided by the International Humic Substance Society (IHSS) (St. Paul, Minnesota, USA) were used to simulate three different types of organic compounds. These standards, considered as the reference material, were selected because of the extensive studies that have been done on them (Averett et al. 1994; Leenheer et al. 1995; Ratpukdi et al. 2009). The results of this work can be compared with those found in the literature and with future studies. Synthetic water was prepared by dissolving NOM, HA, and FA standards in deionized water and diluting to approximately 15 mgL⁻¹ with pH adjusted to 7.0, typical DOC and pH range of the source water used for Manitoba water treatment plants. The solution was stirred overnight and then filtered through 0.45 micron

nitrocellulose filter paper to remove any residual, non-dissolved NOM. In this study conducting experiments with simulated water rather than natural water is preferred to avoid a lot of complex and complicated reactions involving ozone and other natural water particulate such as clay, and organic and inorganic compounds. It can provide capability of extending the obtained results to various real water treatment conditions.

7.2.2. Ozonation Tests

Ozonation was conducted on a semi-batch basis by bubbling the desired amount of ozone through the 2L water sample. The details of ozonation test is described in previous chapters.

7.2.3. Analytical Methods

The details of Analytical methods used in this study are reported in chapter 3.

7.2.4. THMs Formation Potential (THMFP)

THMs formation potential measurements were conducted according to *Standard Methods 5710B* (APHA 2012); Details of this procedure have been described in previous chapters

7.2.5. Spectroscopic Analysis

7.2.5.1. UV/Vis spectra

UV/Vis spectra of water samples were recorded on a UV/visible spectrophotometer Ultrospec 2100 pro, (GBC Scientific Equipment, Australia) using 1 cm cuvettes in the wavelength range 190 to 800 nm.

7.2.5.2. FTIR-ATR spectroscopy

All FTIR-ATR spectra were recorded on the freeze-dried samples using a Bruker Alpha FT-IR spectrometer, equipped with ALPHA's Platinum ATR, single reflection diamond ATR module, in the 4000-500 cm^{-1} region.

7.2.5.3. Fluorescence

Fluorescence spectra in synchronous scan mode were obtained by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technology). Synchronous scan excitation spectra are acquired by recording the fluorescence intensity while simultaneously scanning over both the emission (λ_{em}) and excitation (λ_{ex}) wavelength keeping a constant optimized wavelength difference (offset): $\Delta\lambda = \lambda_{\text{em}} - \lambda_{\text{ex}}$ (Chen et al. 2003; Rodriguez et al. 2014a). Synchronous excitation spectra can improve peak resolution and reduce the overlapping interferences. It also can identify the effect of ozone on structural signatures such as intensity, position, and shift of fluorescence peak for each sample (Uyguner and Bekbolet 2005 a, 2005b; Zhang et al. 2008). Synchronous scan spectra were recorded in the excitation wavelength range of a 360–650 nm using the bandwidth of $\Delta\lambda = 44$ nm between the excitation and emission monochromators. Although most studies on HS synchronous fluorescence have used $\Delta\lambda = 18$ –20 nm, some researchers have reported the offset value of 44 nm as the powerful tool for DOC characterization before and after the oxidation with chlorine dioxide and ozone (Swietlik and Sikorska 2004; Zhang et al. 2008). In this study both the excitation and emission slits of the instrument were set at 10 nm band width and a 600 nm/min scan speed.

7.3. RESULTS AND DISCUSSION

7.3.1. Effect of Ozone on Water Characteristics

7.3.1.1. DOC and UV₂₅₄,

Figure 7.1 shows the effect of ozonation on the removal efficiencies of DOC and UV₂₅₄, for all water samples. Generally increased ozone dosage resulted in increased reduction of DOC and UV₂₅₄ values for all water samples. However HA water samples show the highest reduction of these parameters compared to NOM and FA samples. For this sample 1 mg ozone/mg DOC ozone resulted in 42% reduction of DOC and 96% reduction in UV₂₅₄ respectively. Generally more available ozone molecules and hydroxyl radicals are produced as ozone dosage increases, leading to an increase in organic carbon removal (Ratpukdi et al. 2010). Chang et al. (2002) have investigated the effect of ozone on HA removal at different ozone doses. They have reported 47% DOC reduction at an ozone dosage of 1.5 mg Ozone/ mg DOC. Tuhkanen et al. (1994) and Molnar et al. (2012) have shown DOC reduction ranged from 5%-25% under typical ozone doses of 0.4-1 mg Ozone/ mg DOC. Pryor et al. (2002) have also reported up to 25% DOC reduction at lower applied ozone doses of 0.3 to 0.5 mg Ozone / mg DOC. Water samples used in these studies were natural waters, however our reported DOC removal values still can be compared with these published works.

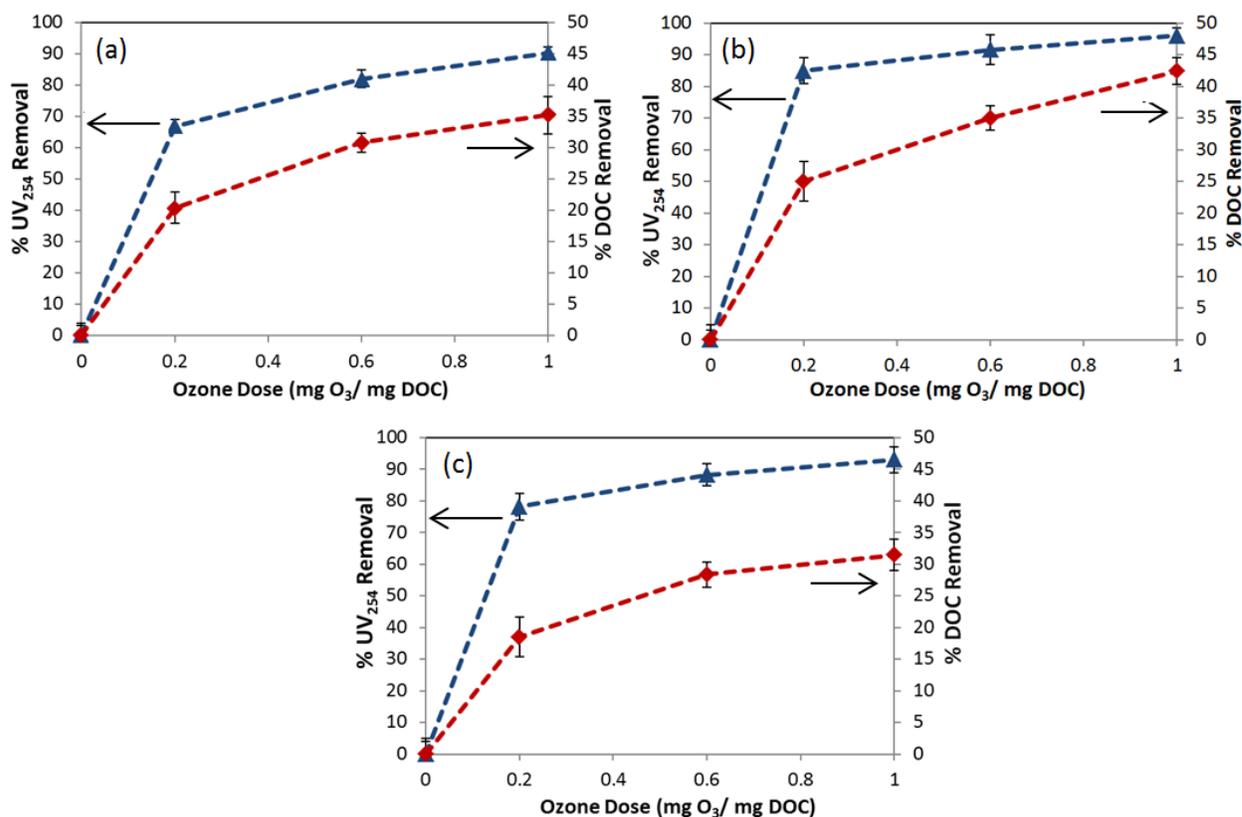


Figure 7.1: Water quality parameters for samples under different doses of ozone, (a) NOM, (b) HA, and (c) FA.

UV₂₅₄ is the parameter indicating the unsaturated and/or aromatic carbon content of water samples. (Edzwald and Tobiason 1999). For all the water samples studied, UV₂₅₄ values decreased significantly after ozone application regardless of ozone dose. This can be due to oxidation of unsaturated and/or aromatic carbon molecules, which is in accordance with previously reported results (Gilbert 1988, Camel and Bermond 1998; Swietlik et al. 2004; Sadrnourmohamadi and Gorczyca 2015a). Figure 7.1 shows a higher reduction in UV₂₅₄ values compared to DOC. This indicates the oxidation of a large portion of conjugated species by ozone even with low DOC reduction. (Chang and Singer 1991; Chang et al. 2002; Ratpukdi et al. 2010). This is indicative of a targeting of aromatic, conjugated species rather than aliphatic groups.

7.3.1.2. THMs formation potential

Table 7.1 indicates the results of total trihalomethane formation potential (TTHMFP) for different water samples pre- and post ozonated. In Table 7.1 it is clear that chloroform (CH_3Cl) is the major detected species of THMs since NaOCl was used for chlorination. No brominated species was detected since the simulated water samples did not contain bromide. Results indicate that prior to ozonation HA yielded a higher TTHMFP followed by NOM and FA standards. Upon ozonation this value is reduced significantly with the highest reduction (89%) observed for HA water samples (Table 7.1). A lower ozone dose accomplished a relatively significant reduction of TTHMFP; however, by increasing the ozone dose a relatively small incremental reduction was achieved. This indicates that ozone can eliminate a large portion of the precursor that promotes THMs formation quickly while it has a lesser effect on other portions of the precursors under this study's conditions (Amy et al. 1986). As shown in Figure 7.1 ozone can oxidize/ decompose aromatic, UV absorbing moieties of NOM resulting in a higher reduction of trihalomethane formation potential relative to dissolved organic carbon which is consistent with previous studies (Amy et al. 1986; Amy et al. 1991; Galapate et al. 2001). Improved reduction of THMFP at higher ozone doses is related to increased reduction of the humic substances as the main precursor of THMs (Rodriguez and Nunez 2011). Humic substances are reported to show high aromaticity and consequently, high UV absorbance (Amy et al. 1986). As reported, UV_{254} removal can be related to TTHMFP (Uyak and Toroz 2007). Figure 7.2 shows a plot of UV_{254} removal against TTHMFP data from this study. A good correlation of $R^2=0.82$ was achieved between UV_{254} removal and TTHMFP reduction.

Table 7.1: TTHMFP for different water samples pre- and post ozonation

Organic compound type	Ozone dose (mg O ₃ / mg DOC)	CH ₃ Cl (µg L ⁻¹)	CHBrCl ₂ (µg L ⁻¹)	CHBr ₂ Cl (µg L ⁻¹)	CHBr ₃ (µg L ⁻¹)	TTHMFP (µg L ⁻¹)
NOM	0	95.5±0.3	ND	ND	ND	95.5±0.3
	0.2	51.6±0.2	ND	ND	ND	51.6±0.2
	0.6	40.7±0.3	ND	ND	ND	40.7±0.3
	1.0	27.7±0.1	ND	ND	ND	27.7±0.1
HA	0	134.0±1.3	ND	ND	ND	134.0±1.3
	0.2	35.3±2.0	ND	ND	ND	35.3±2.0
	0.6	25.0±0.2	ND	ND	ND	25.0±0.2
	1.0	14.6±0.9	ND	ND	ND	14.6±0.9
FA	0	89.4±2.3	ND	ND	ND	89.4±2.3
	0.2	51.6±1.0	ND	ND	ND	51.6±1.0
	0.6	22.5±0.13	ND	ND	ND	22.5±0.13
	1.0	18.1±0.7	ND	ND	ND	18.1±0.7

7.3.2. Spectroscopy Characterization

7.3.2.1. UV-Visible spectroscopic analysis

Figure 7.3 shows the UV-Vis spectra of each water sample before and after a series of ozone applications. All non-ozonated samples show quite similar UV-vis absorption spectra with a featureless decrease in absorption intensity with increasing wavelength which is in accordance with previously reported results (Wang and Hsieh 2001; Imai et al. 2009). UV_{abs} at wavelengths < 275 nm is much greater than those at longer wavelengths. Due to the complex structure of organic compounds in each water sample, UV spectra did not exhibit many distinct features. However in the case of non-ozonated samples, a shoulder in the wavelength range of 260-290 nm, indicates the occurrence of π - π^* electron transitions for polycyclic aromatic hydrocarbons, benzoic acids, and phenolic substances (Fukushima and Tatsumi 2001). It can also be related to general unsaturated and aromatic compounds, with the conjugation structure (Chin et al. 1994; Purmalis et al. 2013). Moreover, UV_{280} provides important clues regarding the extent of humification, degree of aromaticity, and possible estimations of molecular weight (Chin et al. 1994; Fukushima et al. 2001). Fig 7.3b shows that non-ozonated HA has the highest UV_{280} absorbance values compared to those of NOM and FA. This behaviour is expected since HA contains a relatively high amount of aromatic and functional groups and UV absorbing moieties. The difference decreases at increased wavelength (Chen et al. 2002).

UV_{abs} spectra of ozonated water samples showed that UV absorbance decreased with increasing ozone dosage. The shoulder in the range of 260-290 nm for the raw water samples disappeared as a result of the ozone application. Also, the absorptivity at 280 nm decreased with increasing ozone dose. It is expected since ozone can remove or oxidize the moieties responsible for UV absorbance in this wavelength range (Rositano et al. 2001). Ozonation is found to target NOM at all wavelengths with a drastic decrease at the shorter wavelengths which is in agreement with

previous works (Rositano et al. 2001; Ho et al. 2013). The absorptivity of ozonated water samples approaches zero in visible range (400-700 nm).

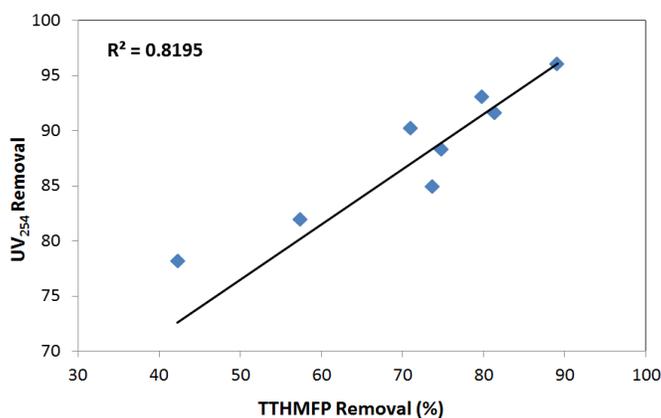


Figure 7.2: Removal of UV₂₅₄ against TTHMFP for three ozonated water samples.

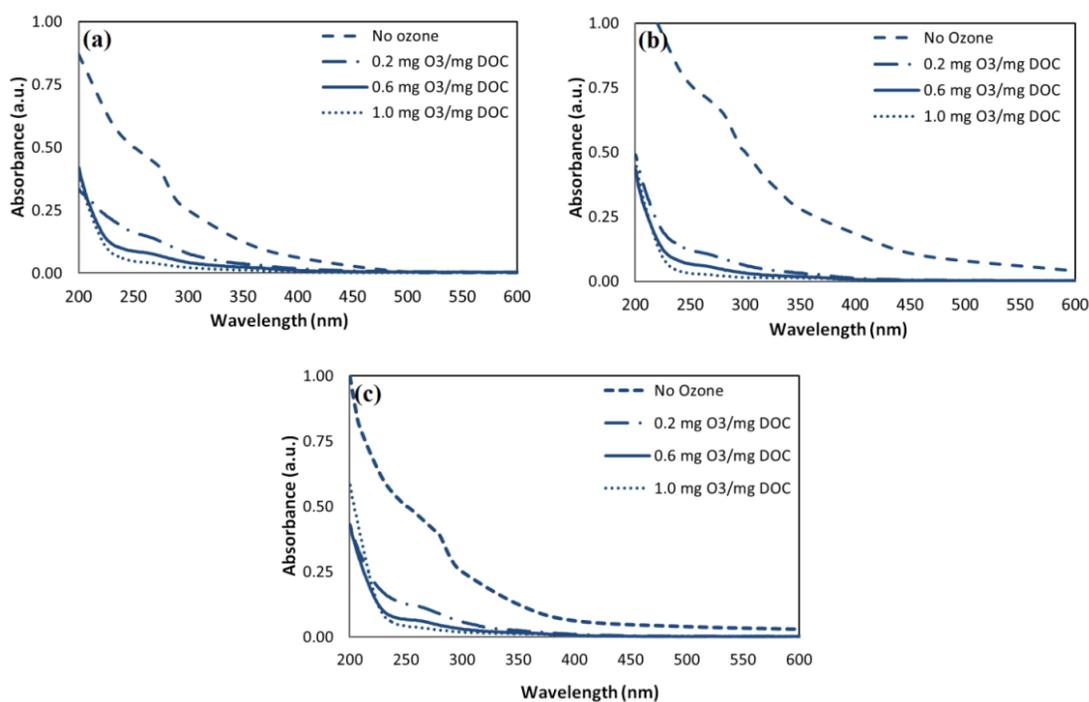


Figure 7.3: UV-Visible spectra of Suwannee River (a) NOM, (b) HA, and (c) FA, before and after ozonation (pH = 7 and total organic carbon concentration = 15 mgL⁻¹).

7.3.2.2. Fluorescence spectroscopic analysis

The effect of ozonation on NOM, HA, and FA samples was also studied by synchronous scan spectra recorded at $\Delta\lambda= 44$. Figure 7.4. shows the spectra of non-ozonated samples as well as ozonated samples at 0.2, 0.6, and 1 mg Ozone/ mg DOC doses. The three non-ozonated samples showed a well-defined maximum peak at $\lambda= 380-400$ nm and a shoulder-like small peak at $\lambda= 260$. These results are consistent with previous studies (Senesi et al. 1989; Rordiguez et al. 2014 a, 2014b).The non-ozonated HA sample exhibited a fluorescence peak with half intensity compared to the FA sample which is in agreement with the higher molecular weight of HA. Intensity of the fluorescence peak is affected by the molecular structure of NOM and decreases with increasing molecular weight of analysed organic matter fractions (Chen et al. 2003; Swietlik and Sikorska 2004; Rodriguez et al. 2014a). Although the HA is known to be rich in aromatic character, its low fluorescence intensity can also be related to HA internal/ or intramolecular bonding, and reabsorption of emitted radiation by other absorption centers of humic macromolecules (Miano et al. 1988; Senesi 1990; Chen et al. 2003). Moreover the peak of maximum intensity of HA occurred at a higher excitation wavelength compared to FA which is consistent with literature. According to Rodriguez et al. (2014 a, 2014b) the maximum peaks located at higher wavelengths are indicative of aromatic and/or conjugated unsaturated systems, characteristics that fit well with humic acids. Peaks of maximum intensity at lower wavelength are related to a low degree of aromatic and conjugated chromophores, in agreement with the typical characteristics of the fulvic acids. Some additional small sub peaks also can be seen for HA at Excitation λ of 270-290 nm and for FA samples at Ex of 270-290 nm respectively. These peaks are indicative of the polydispersive structure of humic substances (Rodriguez et al. 2014a). Upon ozonation, the fluorescence intensity of the maximum peak as well as the whole spectra decreased for all water samples. This can be attributed to a lower degree of aromaticity, and

lower level of conjugation (Uyguner and Bekbolet 2005a; Zhang et al. 2008; Rodriguez et al. 2014a).

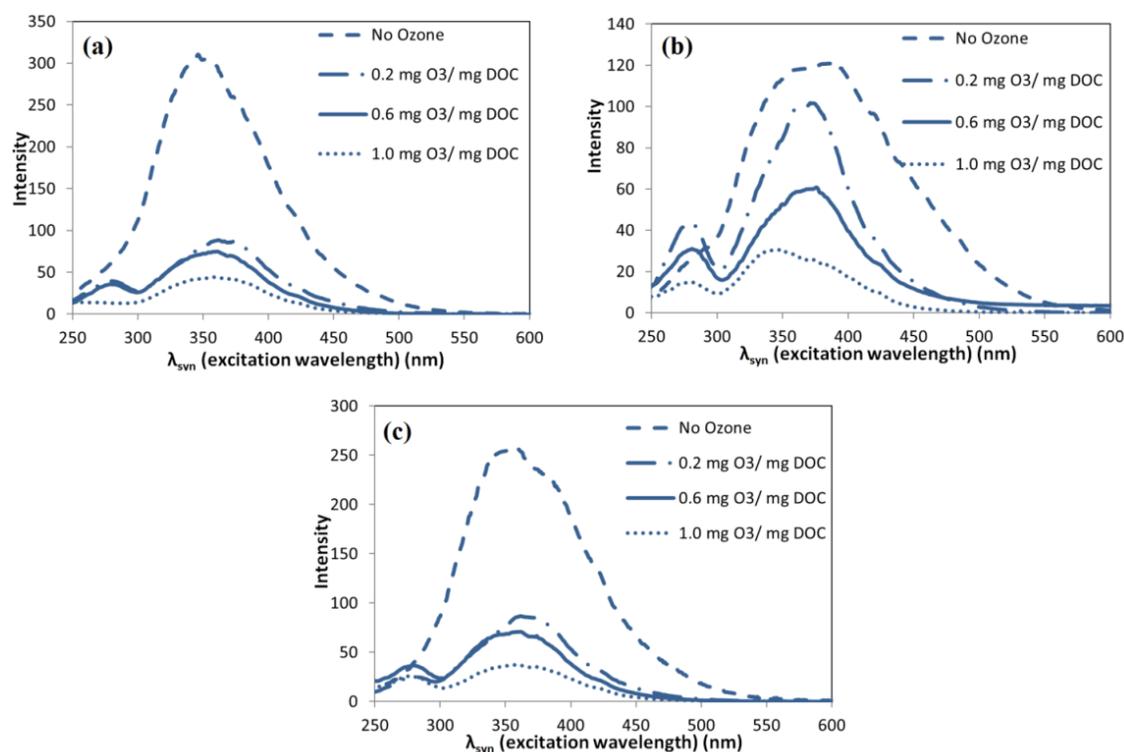


Figure 7.4: Synchronous fluorescence spectra of Suwannee River, (a): NOM, (b): HA, and (c): FA (pH = 7 and total organic carbon concentration = 15 mgL⁻¹).

A protein-like peak at shorter wavelength of 260 nm with low intensity increased when 0.2 mg Ozone/ mg DOC ozone dosage is applied. According to literature this peak can be attributed to aromatic amino acids (Coble 1996; Zhang et al. 2008; Rodriguez et al. 2014a). By increasing the ozone dose the intensity of this peak decreased significantly even below the non-ozonated sample due to the extensive structural degradation of the humic macromolecule at high ozone dosages (Rodriguez et al. 2014b). The results obtained in this study are similar to those achieved by Zhang et al. (2008) (ozone dose = 1 mg Ozone/mg TOC and synchronous spectra recorded at $\Delta\lambda = 66$ nm). He reported an increase in the fluorescence of the protein-like peak but a decrease in the fluorescence of the maximum peak of the spectrum for both fulvic and humic acids

extracted from river water samples. The disappearance of these characteristic peaks which is accompanied by a reduction in DOC, UV_{254} , and TTHMFP can be attributed to the destruction of aromatic moieties (Uyguner and Bekbolet 2005 a, 2005 b).

7.3.2.3. FTIR-ATR spectroscopic analysis

The FTIR-ATR spectra of HS and FA samples obtained before and after ozonation are shown in Figure 7.5. The change in functional groups after ozone application can be the main reason for THMs reduction (Chang et al. 2002). All the spectra for the two non-ozonated humic substances (HA, and FA) were similar. The absorption bands of all samples were interpreted based on the literature (Senesi et al. 1989; Silverstein and Webster 1998).

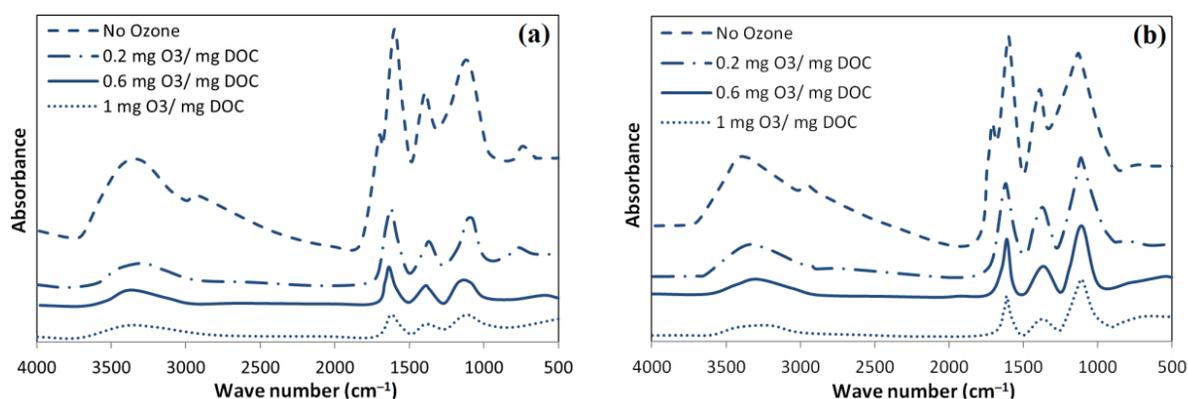


Figure 7.5: FTIR-ATR spectra of Suwannee River, (a): HA, and (b): FA (pH = 7 and total organic carbon concentration = 15 mgL^{-1}).

A broad peak at the $3700\text{-}3200 \text{ cm}^{-1}$ region is generally assigned to O-H groups and the shoulder present in the $3000\text{-}2800 \text{ cm}^{-1}$ region can be attributed to aliphatic CH, CH₂, CH₃ stretching. The peak in the range of $1720\text{-}1700$ is indicative of carbonyl groups (C=O stretching mainly due to carboxylic acids, and C=O including ketones). The peak at 1637 cm^{-1} is a typical peak of an aromatic C=C vibration and C=O conjugated with the aromatic ring. The peak at $1380\text{-}1400 \text{ cm}^{-1}$ is assigned to C-H deformation of aliphatic and CH₃ groups. In addition a peak in the range of

1150 cm^{-1} is indicative of C-O stretching and O-H deformation of COOH (Li et al. 2008). The C-O stretching of alcoholic compounds, esters, ethers, and phenols is shown at 1066 cm^{-1} . Also aromatic C-H bending can be observed at 850 cm^{-1} . Carboxylic character (O-H band at 3400-3300 cm^{-1} and a C=O band at 1730-1700 cm^{-1}) was found for all samples. O-H peak (3700-3200 cm^{-1}) is more intense for HA samples than for FA which is consistent with literature (Senesi et al. 1989). HA shows relatively higher absorption intensity at $\sim 1620 \text{ cm}^{-1}$ and 2920 cm^{-1} . These results suggest that the un-treated HA sample is rich in aromatic compounds and aliphatic CH_2/CH_3 groups than FA sample which is consistent with UV/Vis spectroscopy analysis. After 0.2 mg Ozone/ mg DOC ozonation, the peak area of O-H band decreases. Further increase in ozone dosage results in removal of this peak and a shoulder in 2900 cm^{-1} (attributed to C-H functional groups). A reduction is also observed for aromatic C=C vibration and C=O conjugated attached to an aromatic ring (1600 cm^{-1}). Moreover in HA samples the absorbance of aromatic C-H bending (850 cm^{-1}) was reduced. In summary FTIR results indicate that although after ozonation O-H, C-H, and CO/OH peaks are still present, the strength of aromatic C=C and C=O conjugated with aromatic rings (1600 cm^{-1}), and O-H (3200 cm^{-1}) peaks decrease remarkably. The degradation of these functional groups which is more significant for HA samples similar to UV/Vis spectra data (Fig 7.3) accounts for the TTHMFP reduction by ozonation. These data are consistent with previous reports (Chang et al. 2002; Kanokkantapong et al. 2006).

7.4. CONCLUSION

In this study the composition and chemical characteristics of NOM and isolated humic substances: HA and FA (provided by the International Humic Substance Society) before and after the ozone application were studied by means of fourier transform infrared spectroscopy coupled to attenuated total reflectance, UV/Vis, and synchronous scanning fluorescence

measurements. The main objective of this study was to show the effect of ozone oxidation on the structural and chemical composition of three types of aquatic organic standards. The results also were linked to the effect of the ozonation process in reducing THMs formation potential of water samples with high levels of THMs precursors. The following conclusions can be made from this study:

1. Ozonation at the dose of 1 mg Ozone/mg DOC was capable of reducing DOC, UV₂₅₄, and THMFP up to 42%, 95%, and 89% for HA water sample –the main THMs precursor – respectively.
2. The study of UV/Vis, FTIR-ATR, and SSF reveals consistent trends showing that ozone can change the composition of DOC in the water samples, causing a significant reduction in aromaticity. The reduction of UV₂₅₄ for each ozonated sample also affirms that the ozone mainly targets aromatic moieties of organic carbon molecules.
3. FTIR-ATR results showed that the reduction of unsaturated functional groups such as aromatic rings and C=C bonds in water samples are the major reaction mechanism in ozone application.
4. SSF results also revealed that ozonation decrease the fluorescence intensity of the maximum peak as well as the whole spectra. Ozonation reduced concentration of aromatic and highly conjugated compounds in the water. This is the main reason why ozonation is effective in reduction of water THMFP, as they contain the main THMs precursors.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1. RESEARCH OVERVIEW

This thesis investigated the effects of two treatment methods: chemical coagulation and pre-ozonation-coagulation on the removal of THMs precursors from three examples of surface waters typical for the Canadian Prairie and Canadian Shield. Natural waters collected from the Assiniboine River, Red River (Canadian Prairie), and Rainy River (Canadian Shield) were used in this study. All of the tested waters have extremely high DOC, varying from 8 mg/L to 20 mg/L accompanied sometimes by a very high alkalinity and hardness. We are not aware of any other studies using natural, potable surface water sources with such extreme water quality parameters. The effect of different experimental conditions such as coagulant dose, coagulant type, and solution pH as well as ozone dosage on the THMs removal from three different water resources was investigated. The effectiveness of each treatment method was evaluated by measurement of DOC, DOC fractions, UV_{254} , and trihalomethane formation potential (THMFP). Moreover, the mechanism of THMs reduction by each treatment was discerned.

The structural and chemical characteristics of natural organic matter and isolated humic substances, before and after the reaction with ozone, were studied by spectroscopic techniques. For this purpose synthetic water samples containing Suwannee River standards were tested under controlled laboratory conditions. However, the results of the study conducted on the synthetic water confirmed our observations and conclusions related to the effects of ozone on the natural waters.

8.2. SUMMARY AND CONCLUSION

The highlights of the conclusion are as follows:

8.2.1. Removal of THMs precursors by chemical coagulation

1. Results showed that reduction of total DOC cannot guarantee THMFP reduction and chemical coagulation should be optimized to remove fractions of DOC which form most THMs.

The results of DOC removal from Red River water by coagulation showed that Ferric sulfate at coagulation pH of 6 was found to achieve the highest DOC removal compared to other coagulants. However, Ferric chloride showed the highest removal of HPOA fraction of DOC and consequently resulted in the highest THMFP reduction. Fractionation results of coagulated water samples at the optimum condition showed that HPOA fraction can be removed effectively by coagulation regardless of coagulant type whereas HPI fractions had the poorest removal.

2. The removal of DOC by aluminum based coagulants is determined by coagulant species distribution.

The results of DOC removal from Assiniboine River water by aluminum based coagulants showed that both polymeric (Al_b) and colloidal/particulate (Al_c) hydrolysis species of aluminum during the coagulation play an important role in removal of DOC and UV_{254} . At pH of 6, alum had the highest content of in situ formed Al_b species which resulted in the highest DOC and UV_{254} removal. However, at pH of 7 and 8, ACH achieved the highest removal of DOC and UV_{254} for this specific water source. This was due to the highest concentration of Al_b and Al_c species in ACH at those specific pH levels. Although alum at pH of 6 showed the highest removal of DOC and UV_{254} , for this specific water source ACH coagulant is recommended since pH adjustment is costly and represents serious challenges for this high alkalinity water. Fractionation results of coagulated water samples at the optimum condition showed the higher removal of hydrophobic DOC fractions rather than hydrophilic ones. Among them, alum showed the highest removal of hydrophobic acid fraction and lowest THMFP respectively.

The results of DOC removal from Rainy River, high DOC and low alkalinity water by aluminum based coagulants showed that alum achieved the highest removal of DOC (69%) and UV₂₅₄ (84%) respectively with no pH adjustment. This is because alum addition in low alkalinity water causes reduction of pH, providing optimum conditions for removal of DOC. Alum coagulation of this water also resulted in the highest removal (85%) of HPOA fraction of DOC and the greatest reduction in THMFP from 308.4 µg L⁻¹ to 113.1 µg L⁻¹.

8.2.2. Removal of THMs precursors by Ozonation

1. Ozonation changes the composition of DOC and effectively reduces the THMs formation.

Ozonation stands-alone resulted in removal of DOC up to 27%-31% and UV₂₅₄ up to 86%-90% for high DOC and calcium hardness Assiniboine River water, and high DOC and low calcium hardness Rainy River water respectively.

2. Calcium concentration determines the DOC removal when ozone is applied prior to coagulation process. However in terms of THMs reduction coagulation with pre-zonation is effective regardless of calcium concentration.

Results showed that raw water characteristics specifically concentration of calcium hardness plays an important role here. For Assiniboine River water, ozonation prior to coagulation enhanced DOC removal at ozone doses of 0.6 and 0.8 mg Ozone/mg DOC. This was attributed to ozone-induced particle destabilization and DOC complexation by calcium, more specifically, the transformation of hydrophobic DOC fraction to hydrophilic fractions with less particle adsorption affinity, resulted in lower particle surface charge, and an increase in calcium complexation with NOM constituents. For this water source, pre-ozonation-coagulation decreased THMFP, showing a higher THMFP reduction for higher ozone doses. Specific THMFP in pre-ozonated-coagulated water samples was found to be lower than that in the

corresponding ozonated waters for all of the ozone doses tested. On the contrary, for Rainy River water, ozonation prior to coagulation did not enhance DOC removal by subsequent coagulation; however it resulted in reduction of specific THMFP. The negative effect of pre-ozonation on DOC removal by further coagulation decreased with increasing ozone dosage and was less significant when the coagulant dosage decreased. This adverse effect was related to low concentration of calcium hardness in this water source. This conclusion was confirmed by the results of pre-ozonation-coagulation of synthetic water containing different level of Ca. Calcium was complexed with both aqueous NOM and particle-sorbed NOM upon ozonation and so the mechanism of enhanced DOC removal by pre-ozonation-coagulation process was confirmed.

8.2.3. Conclusion for Spectroscopic Studies

The spectroscopic characterization of natural organic matter and aquatic humic substances before and after reacting with ozone showed that ozone can change the composition of DOC in the water samples, causing a significant reduction in aromaticity. Ozone mainly targeted aromatic moieties of organic carbon molecules and the reduction of unsaturated functional groups such as aromatic rings and C=C bonds in water samples were the major reaction mechanism in ozone application. Ozonation decreased the fluorescence intensity of the maximum peak as well as the whole spectra attributed to the destruction of aromatic structure in humic substances resulting in a lower degree of aromaticity, and lower level of conjugation.

Ozonation reduced concentration of aromatic and highly conjugated compounds (constituting primarily HPOA fraction) in the water. This is the main reason why ozonation is effective in reduction of water THMFP, as our research showed that HPOA fraction contains most THM precursors.

8.3. ENGINEERING SIGNIFICANCE

This research was aimed at resolving the high concentrations of THMs issues in some of Canadian Prairie and Canadian Shield treated water. Long term data analyses of Portage La Prairie, Rainy River, and Morris water treatment plants showed the currently applied treatment methods, including coagulation and ozonation, cannot provide treated water in compliance with THMs regulations. This can be due to the exceptional source water quality and the treatment methods not optimized for water of such particular quality.

It has been reported that in Manitoba almost 70% of potable water treatment plants that use surface water sources are not in compliance with THMs regulations set by the Province. The main objective of this research was the removal of THMs precursors by chemical coagulation, and pre-ozonation-coagulation. These treatment techniques are commonly applied in many water plants. Therefore, the findings of this thesis, in terms of the mechanism of THMs precursor reduction by each treatment method will be important for water treatment plants that currently experience difficulty in meeting THMs regulation.

Attempts had been undertaken to investigate the mechanism of DOC and THMFP reduction by ozonation and chemical coagulation. The novelty of this thesis is in discerning such mechanisms in treatment of waters with extreme quality in terms of high DOC and varying level of calcium hardness.

8.4. RECOMMENDATIONS FOR FUTURE WORK

1. The experimental results of this research points to the key role of calcium hardness in ozone-induced coagulation. More laboratory experiments with both synthetic and real water are needed to estimate the influence of different level of calcium concentration.
2. The performance of ozonation is reported to decrease in the presence of inorganic scavengers such as carbonate and bicarbonate. It is worthwhile to better study the effect

of these scavengers on the ozonation treatment performance. The study can be conducted for ozone stand-alone as well as its combination with subsequent coagulation.

3. One of the concerns of using ozone in drinking water treatment plant is the creation of ozonation by-products. This is a critical issue especially for bromide-containing waters. Although these classes of DBPs are not regulated, there is concern of health risks for each of them. Therefore, more research is required to understand the health risk associated by these classes of DBPs. Also, monitoring the concentration of these DBPs would be of interest.
4. The use of on-line data measurement systems such as ozone analyzer, thermometer, and pH probe, would allow for continuous monitoring of key parameters and better kinetic studies. Modifying the reactor configuration and changing the ozone dosage will provide more information.
5. Some fractions of DOC, particularly HPOA fraction, is shown to be the main contributor to formation of THMs. More laboratory experiments are needed to see the effects of ozone alone or combined with coagulation on these fractions and consequently on the level of THMs.
6. Effectiveness of the removal of DOC and THMFP in ozonation prior to activated carbon adsorption should be investigated. Such ozone application is currently used at the Portage la Prairie water treatment plant, which is supplied by the Assiniboine River. The system is ineffective in terms of removal of DOC and reduction of THMFP.
7. Ozone increases the DOC biodegradability, which promotes the bacterial regrowth in the treatment units and water distribution systems. This may be a serious issue for water

containing high concentration of carbon source, i.e. DOC. Investigation of bacterial growth following ozonation in such waters should be undertaken.

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APPENDIX A
OZONATION OF SUWANEE RIVER HUMIC ACID, KINETIC STUDY

OZONATION

The degradation of humic substances such as humic acid (HA) by ozone in aqueous solution are described by two general mechanisms: direct ozone reaction and indirect reaction involving hydroxyl radicals (OH°) (Hoigne and Bader 1983; Benitez et al. 2003). Thus, the kinetic of ozonation of HA with respect to HA concentration can be represented by Eq (A.1) (Bekbolet et al. 1998; Gonenc and Bekbolet 2001):

$$-\frac{d[HA]}{dt} = k_{OH}[OH^\circ][HA] + k_O[O_3][HA] \quad \text{[Eq. A.1]}$$

Where $[OH^\circ]$ is the concentration of hydroxyl radical, $[HA]$ is the concentration of HA, $[O_3]$ is the concentration of ozone, and k_{OH} and k_O are the rate constants of the reaction between HA and hydroxyl radicals and ozone, respectively.

Eq (A.1) can be rearranged to Eq. (A.2):

$$-\frac{d[HA]}{dt} = (k_{OH}[OH^\circ] + k_O[O_3])[HA] \quad \text{[Eq. A.2]}$$

The concentration of hydroxyl radical and ozone can be assumed to be constant since the ozone was offered in excess (Beltran et al. 1988; Chu and Ma 1999). Therefore Eq (A. 2) can be rearranged to a pseudo-first-order equation, Eq (A.3)

$$-\frac{d[HA]}{dt} = k[HA] \quad \text{[Eq. A.3]}$$

Where k is the pseudo first-order rate constant for ozonation process (Yurteri and Gurol 1988).

$$k = k_O[O_3] + k_{OH}[OH^\circ]$$

By integrating both sides of Eq. (A.3) using the boundary conditions (1) and (2) Eq. (A.4) will be obtained.

$$\text{B.C.1. } [HA] = [HA]_0 \text{ at } t=0$$

$$\text{B.C.2. } [HA] = [HA] \text{ at } t=t$$

$$\ln \frac{[HA]}{[HA]_0} = -kt \quad [\text{Eq. A.4}]$$

The reaction rate constant, k can be determined as a slope of straight line by plotting $\ln [HA]/[HA]_0$ versus time.

The kinetic study of SRHA degradation by ozone is presented below:

Ozonation experiments were carried out at room temperature. The initial concentration and pH of solution were 7 and 15 mgL⁻¹ respectively. Figure A.1 shows the change in DOC concentration (in the forms as DOC/DOC₀) of SRHA as a function of reaction time.

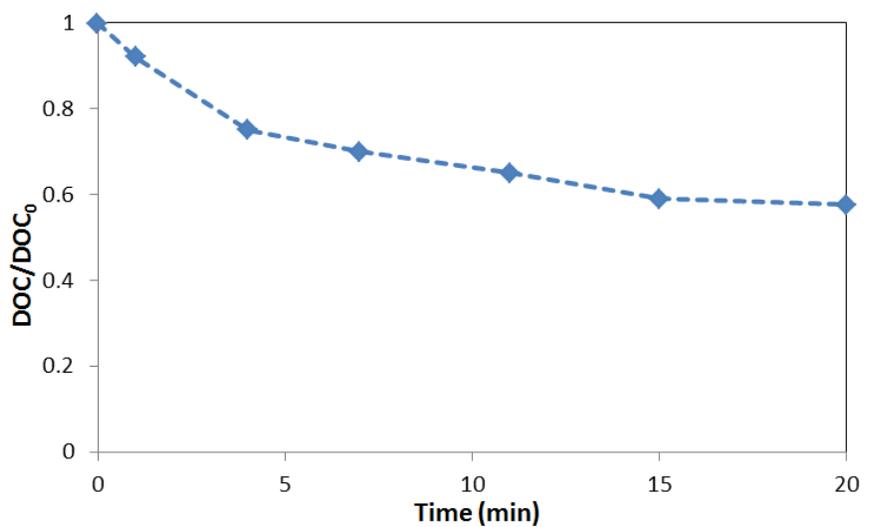


Figure A.1: DOC removal by ozonation, Suwannee River HA (Initial concentration= 15 mgL⁻¹, pH 7, ozone flow rate: 0.23 liter per minute).

Results showed that increased ozone dosage resulted in increased DOC degradation. After 20 minutes, 42% of the Suwannee River HA was removed. The reaction rate constant of SRHA ozonation is determined as a slope of straight line by plotting $\ln \text{DOC}/\text{DOC}_0$ versus time (Figure A.2).

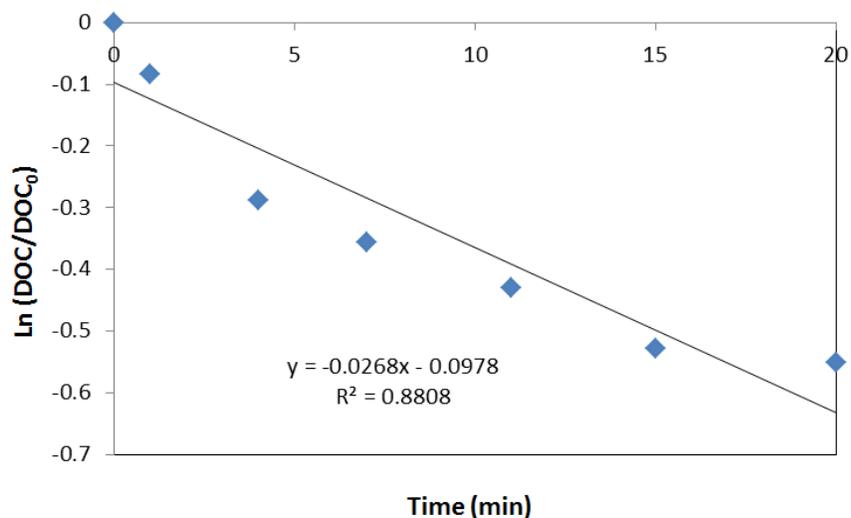


Figure A.2: Determination of rate constant for pseudo-first-order reaction of ozone and Suwannee river HA (Initial concentration= 15 mgL⁻¹, pH 7, ozone flow rate: 0.23 liter per minute).

The pseudo first-order kinetic model of HA ozonation is shown in Figure A.2 where the correlation coefficient, R^2 , is shown to be 0.8808. This indicates that this model can describe the experimental data of SRHA degradation with ozone. As shown in Fig A.2, the pseudo-first-order rate constant (k) is calculated to be 0.026 (min⁻¹) based on DOC parameter. The rate constant calculated here is in the same range as those reported in other previous studies (Kerc et al. 2003; Miao et al. 2008)

**APPENDIX B
RAW DATA**

Raw Data for Chapter 3

Table B1: Raw data for DOC removal, coagulation of Red River

pH-Coagulant dosage(aluminum sulfate)	Average DOC	STD	% Removal
6-120	4.12	0.26	62.0543
6-100	4.36	0.07	55.9422
6-80	4.71	0.05	54.3293
6-60	5.30	0.03	44.9066
6-40	5.65	0.04	34.0407
6-20	8.01	0.05	39.9830
7-120	4.95	0.07	51.5280
7-100	5.30	0.03	48.47198
7-80	5.65	0.04	46.1799
7-60	6.24	0.02	42.9541
7-40	6.83	0.09	39.1341
7-20	7.42	0.03	37.35144
8-120	6.13	0.08	49.8302
8-100	6.48	0.06	46.3497
8-80	6.71	0.09	43.7181
8-60	6.95	0.06	38.7945
8-40	7.19	0.06	38.5398
8-20	8.25	0.11	35.9083
pH-Coagulant dosage(Ferric sulfate)	Average DOC	STD	% Removal
6-120	4.01	0.12	66.0441
6-100	4.48	0.03	62.3089
6-80	4.71	0.09	59.9320
6-60	5.18	0.13	56.28183
6-40	5.89	0.23	50.4244
6-20	7.66	0.08	34.8047
7-120	4.59	0.089	61.5449
7-100	5.07	0.19	57.4702
7-80	5.42	0.062	54.4991
7-60	5.89	0.054	50.6791
7-40	6.36	0.17	46.1799
7-20	6.83	0.12	41.7657
8-120	5.89	0.09	49.9151
8-100	6.24	0.12	47.6230
8-80	6.48	0.067	45.0764
8-60	6.95	0.21	41.1714
8-40	7.07	0.1	32.0882

8-20	8.13	0.23	29.2020
pH-Coagulant dosage(Titanium sulfate)	Average DOC	STD	% Removal
6-120	7.89	0.11	33.7861
6-100	8.36	0.27	29.7114
6-80	9.42	0.056	20.6282
6-60	9.54	0.091	19.6095
6-40	10.48	0.23	11.7148
6-20	10.84	0.51	8.1426
7-120	4.83	0.081	58.9134
7-100	5.18	0.21	56.7912
7-80	5.77	0.067	51.8676
7-60	5.89	0.14	50.8489
7-40	6.13	0.18	48.6418
7-20	6.60	0.51	44.6520
8-120	6.95	0.17	41.2564
8-100	7.19	0.023	38.9643
8-80	7.54	0.031	36.3328
8-60	8.01	0.091	32.6825
8-40	8.95	0.26	23.8540
8-20	9.07	0.11	23.0051

pH-Coagulant dosage(Ferric Chloride)	Average DOC	STD	% Removal
6-120	5.76	0.18929	51.1036
6-100	6.58	0.18972	44.1426
6-80	6.66	0.21227	43.4635
6-60	7.21	0.11547	38.7097
6-40	8.32	0.39004	29.3718
6-20	9.09	0.21107	22.8353
7-120	5.42	0.22486	53.9049
7-100	5.57	0.21892	52.7165
7-80	5.93	0.20831	49.6604
7-60	6.71	0.1714	42.9542
7-40	7.07	0.29585	39.9830
7-20	8.29	0.24296	29.6265
8-120	5.91	0.31247	49.8302
8-100	6.33	0.28086	46.2649
8-80	7.20	0.09405	38.8795
8-60	7.26	0.4957	38.3701
8-40	7.78	0.2311	33.9559
8-20	8.36	0.1025	29.0323

Table B2: UV @ 254 nm of Coagulated Water Samples

Ferric Chloride	UV ₂₅₄		Average
6-120	0.122	0.116	0.119
6-100	0.147	0.153	0.15
6-80	0.252	0.286	0.269
6-60	0.113	0.115	0.114
6-40	0.157	0.153	0.155
6-20	0.239	0.234	0.2365
7-120	0.103	0.1	0.1015
7-100	0.116	0.117	0.1165
7-80	0.143	0.146	0.1445
7-60	0.2	0.168	0.184
7-40	0.338	0.346	0.342
7-20	0.363	0.322	0.3425
8-120	0.097	0.11	0.1035
8-100	0.129	0.13	0.1295
8-80	0.151	0.147	0.149
8-60	0.146	0.147	0.1465
8-40	0.203	0.185	0.194
8-20	0.424	0.45	0.437

Alum	UV ₂₅₄		Average
6-120	0.071	0.071	0.071
6-100	0.11	0.11	0.11
6-80	0.118	0.119	0.1185
6-60	0.12	0.114	0.117
6-40	0.192	0.193	0.1925
6-20	0.199	0.208	0.2035
7-120	0.116	0.11	0.113
7-100	0.138	0.137	0.1375
7-80	0.138	0.145	0.1415
7-60	0.214	0.228	0.221
7-40	0.315	0.327	0.321
7-20	0.194	0.206	0.2
8-120	0.159	0.163	0.161
8-100	0.176	0.177	0.1765
8-80	0.155	0.157	0.156
8-60	0.162	0.162	0.162
8-40	0.177	0.178	0.1775

8-20	0.202	0.203	0.2025
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Ferric Sulphate	UV ₂₅₄		Average
6-120	0.19	0.187	0.1885
6-100	0.196	0.194	0.195
6-80	0.21	0.207	0.2085
6-60	0.221	0.226	0.2235
6-40	0.255	0.242	0.2485
6-20	0.268	0.27	0.269
7-120	0.13	0.133	0.1315
7-100	0.14	0.147	0.1435
7-80	0.15	0.152	0.151
7-60	0.166	0.165	0.1655
7-40	0.202	0.208	0.205
7-20	0.215	0.217	0.216
8-120	0.151	0.152	0.1515
8-100	0.168	0.169	0.1685
8-80	0.191	0.196	0.1935
8-60	0.201	0.202	0.2015
8-40	0.261	0.283	0.272
8-20	0.371	0.372	0.3715

Table B3: ICP data

Ferric Chloride	Ca (ppm)	Fe (ppm)	Mg (ppm)	Na (ppm)	Vol (ML)	Ca (mg)	Fe (mg)	Mg(mg)	Na(mg)
pH:6, Coagulant: 20mg/L	75.57	<0.1	43.8	37.73	50	3.7785	-	2.19	1.8865
pH:6, Coagulant: 40mg/L	77.3	<0.1	44.41	38.48	50	3.865	-	2.2205	1.924
pH:6 Coagulant: 60mg/L	80.47	<0.1	46.83	40.56	50	4.0235	-	2.3415	2.028
pH:6, Coagulant: 80mg/L	73.84	<0.1	42.55	36.18	50	3.692	-	2.1275	1.809
pH:6, Coagulant: 100mg/L	77.15	<0.1	44.74	38.66	50	3.8575	-	2.237	1.933
pH:6 Coagulant: 120mg/L	79.69	<0.1	45.48	40.48	50	3.9845	-	2.274	2.024
pH:7 Coagulant: 20mg/L	72.3	0.23	40.94	35.6	50	3.615	-	2.047	1.78
pH:7 Coagulant: 40mg/L	83.36	<0.1	48.82	42.68	50	4.168	-	2.441	2.134
pH:7 Coagulant: 60mg/L	74.32	<0.1	43.01	36.96	50	3.716	-	2.1505	1.848
pH:7 Coagulant: 80mg/L	75.86	<0.1	44.29	38.2	50	3.793	-	2.2145	1.91
pH:7 Coagulant: 100mg/L	77.62	<0.1	45.87	39.43	50	3.881	-	2.2935	1.9715
pH:7 Coagulant: 120mg/L	81.86	<0.1	47.66	42.38	50	4.093	-	2.383	2.119
pH:8 Coagulant: 20mg/L	83.19	<0.1	48.65	44.15	50	4.1595	-	2.4325	2.2075
pH:8 Coagulant: 40mg/L	70.83	<0.1	41.22	41	50	3.5415	-	2.061	2.05
pH:8 Coagulant: 60mg/L	79.56	<0.1	46.75	57.42	50	3.978	-	2.3375	2.871
pH:8 Coagulant: 80mg/L	69.9	<0.1	40.4	55.52	50	3.495	-	2.02	2.776
pH:8 Coagulant: 100mg/L	76.45	<0.1	45.32	72.98	50	3.8225	-	2.266	3.649
pH:8 Coagulant: 120mg/L	70.17	<0.1	40.2	69.25	50	3.5085	-	2.01	3.4625
Raw Water	82.24	<0.1	47.45	41.93	50	4.112	-	2.3725	2.0965

Alum	Ca (ppm)	Al (ppm)	Mg (ppm)	Na (ppm)	Vol (ML)	Ca (mg)	Al (mg)	Mg(mg)	Na(mg)
pH:6, Coagulant: 20mg/L	71.32	0.63	40.43	34.85	50	3.566	0.0315	2.0215	1.7425
pH:6, Coagulant: 40mg/L	71.29	0.22	40.81	34.63	50	3.5645	0.011	2.0405	1.7315
pH:6 Coagulant: 60mg/L	70.85	<0.1	40.36	45.36	50	3.5425	#VALUE!	2.018	2.268
pH:6, Coagulant: 80mg/L	71.39	0.23	40.51	34.71	50	3.5695	0.0115	2.0255	1.7355
pH:6, Coagulant: 100mg/L	70.65	0.13	40.13	34.08	50	3.5325	0.0065	2.0065	1.704
pH:6 Coagulant: 120mg/L	71.34	<0.1	40.54	35.3	50	3.567	#VALUE!	2.027	1.765
pH:7 Coagulant: 20mg/L	71.75	0.14	40.61	34.5	50	3.5875	0.007	2.0305	1.725
pH:7 Coagulant: 40mg/L	72.75	<0.1	40.86	35.07	50	3.6375	#VALUE!	2.043	1.7535
pH:7 Coagulant: 60mg/L	71.96	<0.1	40.45	43.23	50	3.598	#VALUE!	2.0225	2.1615
pH:7 Coagulant:	71.68	<0.1	40.72	43.36	50	3.584	#VALUE!	2.036	2.168

80mg/L									
pH:7 Coagulant: 100mg/L	71.37	<0.1	40.2	42.28	50	3.5685	#VALUE!	2.01	2.114
pH:7 Coagulant: 120mg/L	70.35	<0.1	40.01	70.07	50	3.5175	#VALUE!	2.0005	3.5035
pH:8 Coagulant: 20mg/L	71.38	0.14	39.81	43.04	50	3.569	0.007	1.9905	2.152
pH:8 Coagulant: 40mg/L	71.56	<0.1	40.23	35.71	50	3.578	#VALUE!	2.0115	1.7855
pH:8 Coagulant: 60mg/L	70.51	<0.1	39.79	40.17	50	3.5255	#VALUE!	1.9895	2.0085
pH:8 Coagulant: 80mg/L	70.13	<0.1	39.45	46.03	50	3.5065	#VALUE!	1.9725	2.3015
pH:8 Coagulant: 100mg/L	68.59	0.15	38.88	59.74	50	3.4295	0.0075	1.944	2.987
pH:8 Coagulant: 120mg/L	68.43	0.15	38.81	61.86	50	3.4215	0.0075	1.9405	3.093

Ferric sulphate	Ca (ppm)	Fe (ppm)	Mg (ppm)	Na (ppm)	Vol (MI)	Ca (mg)	Fe (mg)	Mg(mg)	Na(mg)
pH:6, Coagulant: 20mg/L	68.31	0.22	38.72	34.16	50	3.4155	0.011	1.936	1.708
pH:6, Coagulant: 40mg/L	67.96	0.21	39.21	33.65	50	3.398	0.0105	1.9605	1.6825
pH:6 Coagulant: 60mg/L	68.77	<0.1	39.4	34.1	50	3.4385	#VALUE!	1.97	1.705
pH:6, Coagulant: 80mg/L	70.2	<0.1	39.89	35.06	50	3.51	#VALUE!	1.9945	1.753
pH:6, Coagulant: 100mg/L	69.63	<0.1	40.39	34.51	50	3.4815	#VALUE!	2.0195	1.7255
pH:6 Coagulant: 120mg/L	69.76	<0.1	39.65	34.65	50	3.488	#VALUE!	1.9825	1.7325
pH:7 Coagulant: 20mg/L	70.01	<0.1	39.99	35.39	50	3.5005	#VALUE!	1.9995	1.7695
pH:7 Coagulant: 40mg/L	70.27	<0.1	39.93	35.54	50	3.5135	#VALUE!	1.9965	1.777
pH:7 Coagulant: 60mg/L	68.32	<0.1	39.29	34.19	50	3.416	#VALUE!	1.9645	1.7095
pH:7 Coagulant: 80mg/L	69.07	<0.1	39.15	34.92	50	3.4535	#VALUE!	1.9575	1.746
pH:7 Coagulant: 100mg/L	68.78	<0.1	39.26	34.74	50	3.439	#VALUE!	1.963	1.737
pH:7 Coagulant: 120mg/L	68.48	<0.1	38.8	34.4	50	3.424	#VALUE!	1.94	1.72
pH:8 Coagulant: 20mg/L	68.16	<0.1	38.75	33.8	50	3.408	#VALUE!	1.9375	1.69
pH:8 Coagulant: 40mg/L	68.62	<0.1	39.21	40.39	50	3.431	#VALUE!	1.9605	2.0195
pH:8 Coagulant: 60mg/L	70.08	<0.1	39.41	45.53	50	3.504	#VALUE!	1.9705	2.2765
pH:8 Coagulant: 80mg/L	61.54	<0.1	36.05	46.65	50	3.077	#VALUE!	1.8025	2.3325
pH:8 Coagulant: 100mg/L	60.81	<0.1	35.08	49.08	50	3.0405	#VALUE!	1.754	2.454
pH:8 Coagulant: 120mg/L	57.38	<0.1	31.64	47.51	50	2.869	#VALUE!	1.582	2.3755
Raw Water	82.24	<0.1	47.45	41.93	50	4.112	#VALUE!	2.3725	2.0965

B1: Fractionation Data

The fraction retained on the ENV-1 SPE cartridge is defined as the HPON fraction while HPOB is the fraction retained on ENV-2 SPE. HPOA fraction is captured by ENV-3 SPE whereas the

HPIB fraction is retained on the Strata XC cartridge. Finally Strata X-AW cartridge can capture the HPIA fraction and the fraction that cannot be collected by any of the five cartridges is defined as the HPIN fraction.

Therefore DOC of each fraction can be found by equation

$$\text{DOC}_{\text{HPON}} = \text{DOC}_{\text{raw}} - \text{DOC}_{\text{ENV1}}$$

$$\text{DOC}_{\text{HPOB}} = \text{DOC}_{\text{ENV1}} - \text{DOC}_{\text{ENV2}}$$

$$\text{DOC}_{\text{HPOA}} = \text{DOC}_{\text{ENV2}} - \text{DOC}_{\text{ENV3}}$$

$$\text{DOC}_{\text{HPIB}} = \text{DOC}_{\text{ENV3}} - \text{DOC}_{\text{XC}}$$

$$\text{DOC}_{\text{HPIA}} = \text{DOC}_{\text{XC}} - \text{DOC}_{\text{X-AW}}$$

$$\text{DOC}_{\text{HPIN}} = \text{DOC}_{\text{X-AW}}$$

Table B4: Fractionation Data

Raw water	Average DOC	STD	Ferric sulfate	Average DOC	STD
raw	11.78	0.1324	raw	3.94	0.1702
ENV-1	10.36	0.1034	ENV-1	2.86	0.0412
ENV-2	10.2	0.0961	ENV-2	2.84	0.0623
ENV-3	7.46	0.0623	ENV-3	2.62	0.0276
Strata X-C	6.14	0.0934	Strata X-C	2.5	0.0241
Strata X-AW	5.21	0.0512	Strata X-AW	2.07	0.0643
Fraction	Concentration (mg/L)	Fraction %	Fraction	Concentration (mg/L)	Fraction %
HPON	1.4200	12.05	HPON	1.08	27.4111675
HPOB	0.1600	1.36	HPOB	0.02	0.50761421
HPOA	2.7400	23.26	HPOA	0.22	5.58375635
HPIB	1.3200	11.21	HPIB	0.12	3.04568528
HPIA	0.9300	7.89	HPIA	0.43	10.9137056
HPIN	5.2100	44.23	HPIN	2.07	52.5380711

Alum	Average DOC	STD	Ferric chloride	Average DOC	STD
raw	4.8	0.1005	raw	5.4	0.1143
ENV-1	4.2	0.0512	ENV-1	3.94	0.0321
ENV-2	3.9	0.0121	ENV-2	3.73	0.0156
ENV-3	3.56	0.0165	ENV-3	3.62	0.0121
Strata X-C	3.15	0.0090	Strata X-C	3.29	0.1323
Strata X-AW	3.09	0.0134	Strata X-AW	3.14	0.0103
Fraction	Concentration (mg/L)	Fraction %	Fraction	Concentration (mg/L)	Fraction %
HPON	0.6000	12.50	HPON	1.4600	27.04
HPOB	0.3000	6.25	HPOB	0.2100	3.89
HPOA	0.3400	7.08	HPOA	0.1100	2.04
HPIB	0.4100	8.54	HPIB	0.3300	6.11
HPIA	0.0600	1.25	HPIA	0.1500	2.78
HPIN	3.0900	64.38	HPIN	3.1400	58.15

Titanium sulfate	Average DOC	STD
raw	4.84	0.0152
ENV-1	4.3300	0.1412
ENV-2	4.1200	0.0225
ENV-3	3.6900	0.0167
Strata X-C	3.3500	0.1589
Strata X-AW	3.1500	0.0102
Fraction	Concentration (mg/L)	Fraction %
HPON	0.5100	10.54
HPOB	0.2100	4.34
HPOA	0.4300	8.88
HPIB	0.3400	7.02
HPIA	0.2000	4.13
HPIN	3.1500	65.08

Table B5: ANOVA test results for coagulation treatment, Red River water

Coagulant	Analyzed coagulant dosages (mgL ⁻¹)	F	P-Value	F _{cr}	Effect
Fe-chloride	80 and 100	11.32253	0.0281	7.7086	Significant
	100 and 120	0.4895	0.5226	7.7086	Insignificant
Ti-sulfate	80 and 100	28.8	0.0058	7.7086	Significant
	100 and 120	6.2608	0.0666	7.7086	Insignificant
Fe-sulfate	80 and 100	30.625	0.0052	7.7086	Significant
	100 and 120	6.0204	0.0701	7.7086	Insignificant
Al-sulfate	80 and 100	66.1606	0.00124	7.7086	Significant
	100 and 120	3.4361	0.1374	7.7086	Insignificant

* If P-Value < 0.05 and $F > F_{cr}$; the additional DOC removal at coagulant doses higher than 100 mgL⁻¹ is statistically significant or else insignificant.

Raw Data for Chapter 5

Table B6: Fractionation data

Raw water

Sample	Average DOC (mg/L)	Standard Deviation
Raw	13.80	0.030
ENV-1	11.09	0.01
ENV-2	10.91	0.07
ENV-3	4.00	0.01
Strata X-C	3.54	0.02
Strata X-AW	2.65	0.04
Fraction	Concentration (mg/L)	Fraction %
HPON	2.71	19.64
HPOB	0.18	1.30
HPOA	6.91	50.07
HPIB	0.46	3.33
HPIA	0.89	6.45
HPIN	2.65	19.21
Total HPO	9.80	71.01
Total HPI	4.00	28.99

Ozonated water: 0.2

Sample	Average DOC (mg/L)	Standard Deviation
Raw	13.2400	0.1270
ENV-1	12.9169	0.1034
ENV-2	12.5979	0.0510
ENV-3	9.7513	0.0920
Strata X-C	7.4859	0.1560
Strata X-AW	5.9726	0.1034
Fraction	Concentration (mg/L)	Fraction %
HPON	0.3231	2.44
HPOB	0.3191	2.41
HPOA	2.8466	21.50
HPIB	2.2654	17.11
HPIA	1.5133	11.43
HPIN	5.9726	45.11
Total HPO	3.4887	26.35
Total HPI	9.7513	73.65

Ozonated water: 0.6

Sample	DOC concentration (mg/L)	Standard Deviation
Raw	12.6900	0.0960
ENV-1	12.3626	0.0671
ENV-2	12.0631	0.0231
ENV-3	10.0365	0.1371
Strata X-C	8.8690	0.0165
Strata X-AW	7.9084	0.0521
Fraction	Concentration (mg/L)	Fraction %
HPON	0.3274	2.58
HPOB	0.2995	2.36
HPOA	2.0266	15.97
HPIB	1.1675	9.20
HPIA	0.9606	7.57
HPIN	7.9084	62.32
Total HPO	2.6535	20.91

Ozonated water: 0.8

Sample	DOC concentration (mg/L)	Standard Deviation
Raw	10.0700	0.1602
ENV-1	9.8676	0.0241
ENV-2	9.6461	0.0312
ENV-3	8.5887	0.1570
Strata X-C	7.4709	0.1621
Strata X-AW	6.2605	0.0920
Fraction	Concentration (mg/L)	Fraction %
HPON	0.2024	2.01
HPOB	0.2215	2.20
HPOA	1.0574	10.50
HPIB	1.1178	11.10
HPIA	1.2104	12.02
HPIN	6.2605	62.17
Total HPO	1.4813	14.71
Total HPI	8.5887	85.29

Table B7: SPSS Results (Correlation of dissolved calcium concentration and zeta potential)

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
y	Ca concentration	107.6	108	108.4	105.3	104.3	103.3	101.3	100	102	99.02	98.2	98.1	95	95.3	95.9	91	90	90.02
x	ozone dose	0	0	0	0.1	0.1	0.1	0.2	0.2	0.2	0.4	0.4	0.4	0.6	0.6	0.6	0.8	0.8	0.8
	x (bar)	0.35		y(bar)	99.59667														
	x,y	0	0	0	10.53	10.43	10.33	20.26	20	20.4	39.608	39.28	39.24	57	57.18	57.54	72.8	72	72.016
	sigma(x,y)	598.614																	
	x2	0	0	0	0.01	0.01	0.01	0.04	0.04	0.04	0.16	0.16	0.16	0.36	0.36	0.36	0.64	0.64	0.64
	sigma (x2)	3.63																	
	b	158.291895	a2	44.1945															
		63.4054965	63.8055	64.2055	45.27631	44.27631	43.27631	25.44712	24.14712	26.14712	-8.49126	-9.31126	-9.41126	-44.1696	-43.8696	-43.2696	-79.828	-80.828	-80.808
		4020.2699	4071.141	4122.346	2049.944	1960.391	1872.839	647.5538	583.0833	683.6718	72.10152	86.69959	88.57184	1950.957	1924.545	1872.262	6372.513	6533.169	6529.936
		45441.9836																	
	S2	2840.12398	S	33.29281															
	(x-XBAR)2	0.1225	0.1225	0.1225	0.0625	0.0625	0.0625	0.0225	0.0225	0.0225	0.0025	0.0025	0.0025	0.0625	0.0625	0.0625	0.2025	0.2025	0.2025
	sum	1.425		1.193734															
	T	3.54566304																	
	zeta potential	-32.42	-32	-32.66	-31.02	-31	-31.01	-29.94	-29.5	-28	-18.44	-17.2	-18.66	-12.46	-12	-12.22	-6.9	-7	-5.8

Table B8: DOC removal raw data, Assiniboine River, coagulation alone and with pre-ozonation

mean																			
PH=6, PRE-OZ, 0.2 mg Ozone/mg DOC																			
Coagulant dose (mg/L)	0	10.39	10.25	10.17	10.27														
		20	40	60	80	100													
DOC (mg/L)		8.11, 8.55	7.38, 7.83	6.71, 7.06	5.93, 6.35	5.37, 5.72													
average	10.27	8.33	7.61	6.89	6.14	5.54													
St. Dev		0.31	0.316	0.247	0.295	0.246													
% DOC removal	25.58	39.64	44.86	50.07	55.51	59.86													
					mean	St, Dev													
PH=6, PRE-OZ, 0.6 mg Ozone/mg DOC																			
Coagulant dose (mg/L)	0	7.52	7.83	7.67	0.215														
		20	40	60	80	100													
DOC (mg/L)		6.76, 6.96	6.37, 6.53	5.67, 5.90	5.22, 5.44	4.71, 4.94													
average	7.67	6.86	6.45	5.78	5.33	4.82													
St. Dev		0.135	0.115	0.162	0.157	0.162													
% DOC removal	44.42	50.29	53.26	58.12	61.38	65.07													
					mean	St. Dev													
PH=6, PRE-OZ, 0.8 mg Ozone/mg DOC																			
Coagulant dose (mg/L)	0	5.21	5.55	5.63	5.46	0.224													
		20	40	60	80	100													
DOC (mg/L)		5.00, 5.14	4.57, 4.80	4.31, 4.46	4.05, 4.17	3.72, 3.87													
average	5.46	5.07	4.69	4.39	4.11	3.8													
St. Dev		0.101	0.161	0.109	0.087	0.106													
% DOC removal	60.43	63.26	66.01	68.19	70.22	72.46													
pH=6 coagulation																			

DOC (mg/L)		5.70, 5.75	4.52, 4.78	3.32, 3.29	4.10, 4.27	2.51, 2.51
average		5.72	4.65	3.3	4.19	2.51
St.Dev		0.038	0.19	0.02	0.122	0.004
% DOC removal	0	58.64	66.38	76.14	69.70	81.85

No pH adj, PRE-OZ, 0.2 mg Ozone/mg DOC	Coagulant dose (mg/L)					
	0	20	40	60	80	100
DOC (mg/L)		12.06, 11.93	11.56, 11.30	10.92, 10.78	10.31, 10.24	10.15, 10.09
average		11.99	11.43	10.85	10.27	10.12
St.Dev		0.089	0.184	0.102	0.047	0.038
DOC removal	0.5	3.78	7.93	12.22	16.52	17.63
No pH adj, PRE-OZ, 0.6 mg Ozone/mg DOC	0	20	40	60	80	100
DOC (mg/L)		8.96, 8.82	8.92, 8.92	8.45, 8.37	8.10, 7.94	10.19, 10.10
average		8.92	8.88	8.41	8.02	10.14
St.Dev		0.1	0.0006	0.057	0.116	0.069
DOC removal	7.87	28.64	28.96	32.72	35.84	35
No pH adj, PRE-OZ, 0.8 mg Ozone/mg DOC	0	20	40	60	80	100
DOC (mg/L)		8.63, 8.59	8.39, 8.16	7.98, 7.94	7.89, 7.74	7.58, 7.48
average		8.61	8.28	7.96	7.82	7.53
St.Dev		0.026	0.163	0.029	0.108	0.07
DOC removal	26.77	32.20	34.80	37.32	38.43	40.71
No pH adj. coagulation						
	0	20	40	60	80	100
DOC (mg/L)		11.90, 11.89	11.70, 11.52	10.83, 10.74	10.40, 10.27	8.95, 8.77
average		11.89	11.61	10.78	10.33	8.86
St.Dev		0.005	0.123	0.06	0.09	0.13
DOC removal	0	11.93	14.00	20.15	23.48	34.37
	0	11.93	13.41	20	23	30.37

Raw Data for Chapter 6

Table B9: Coagulation alone:

Alum

Coagulant Dose (mg/L)	Volume of Coagulant (ml)	pH	DOC	Percent Removal DOC	UV ₂₅₄	%UV Removal
0		6.59	18.29	0.00	0.612	0
1	1	6.50	16.96	7.29	0.603	1.47
2	2	6.38	15.04	17.81	0.58	5.22
3	3	6.22	12.76	30.27	0.52	14.7
4	4	6.05	11.02	39.78	0.49	19.77
5	5	5.88	9.28	49.26	0.42	31.37
6	6	5.76	7.21	60.58	0.27	55.55
7	7	5.67	6.23	65.97	0.12	79.69
8	8	5.38	5.74	68.64	0.1	83
9	9	5.00	5.71	68.76	0.1	83.66
10	10	4.86	5.67	69.01	0.099	83.82

ACH

Coagulant Dose (mg/L)	Volume of Coagulant (ml)	pH	DOC	Percent Removal DOC	UV ₂₅₄	%UV Removal
0		6.59		0		0
1	1	6.59	16.91	7.539177157	0.603	0.9
2	2	6.54	16.19	11.4598991	0.59	3.59
3	3	6.50	14.85	18.80230226	0.561	8.33
4	4	6.44	13.46	26.36990232	0.538	12.09
5	5	6.36	11.14	39.0612787	0.461	24.67
6	6	6.24	9.68	47.02679953	0.378	38.18
7	7	6.15	8.58	53.08197277	0.26	57.47
8	8	6.10	7.58	58.54135807	0.232	62
9	9	6.01	6.58	64.0073025	0.208	66
10	10	5.91	5.83	68.11222677	0.831	70.02

PACl

Coagulant Dose (mg/L)	Volume of Coagulant (ml)	pH	DOC	Percent Removal DOC	UV ₂₅₄	%UV Removal
0		6.59		0.00		0
1	1	6.59	17.28	5.49	0.601	1.79
2	2	6.56	15.59	14.81	0.591	3.43
3	3	6.55	14.03	23.29	0.585	4.41
4	4	6.53	12.26	32.99	0.582	5.01
5	5	6.51	10.73	41.37	0.512	16.33
6	6	6.45	9.25	49.45	0.438	28.41
7	7	6.44	8.33	54.46	0.374	38.86
8	8	6.37	7.17	60.79	0.352	42.48
9	9	6.33	6.61	63.87	0.318	48
10	10	6.36	5.13	71.96	0.293	52.06

Table B10: ANOVA test results for coagulation treatment

Coagulant	Coagulant dose (mg L ⁻¹ Al)	F	P-Value	F _{cr}	Effect
Alum	6 and 7	61.9345	0.0002	5.9873	Significant
	7 and 8	3.7051	0.1025	5.9873	Insignificant
ACH	6 and 7	111.6484	4.23e-5	5.9873	Significant
	7 and 8	4.6032	0.0755	5.9873	Insignificant
PACl	6 and 7	49.6083	0.0004	5.9873	Significant
	7 and 8	5.5028	0.0573	5.9873	Insignificant

Table B11:DOC fractions following coagulation at coagulant dose of 7 mgL⁻¹ Al

Sample	DOC concentration (mg/L)	Standard Deviation
Raw	16.11	0.20
ENV-1	15.6785	0.36
ENV-2	15.1077	0.15
ENV-3	7.6652	0.04
Strata X-C	6.7424	0.13
Strata X-AW	6.6221	0.14
Fraction	Concentration (mg/L)	Fraction %
HPON	0.4315	2.68
HPOB	0.5708	3.54
HPOA	7.4425	46.20
HPIB	0.9228	5.73
HPIA	0.1203	0.75
HPIN	6.6221	41.11
Total HPO	8.4448	52.42
Total HPI	7.6652	47.58

Alum		
Sample	DOC concentration (mg/L)	Standard Deviation
Raw	5.5	0.12
ENV-1	5.3988	0.09
ENV-2	5.2377	0.04
ENV-3	4.1102	0.23
Strata X-C	3.5860	0.11
Strata X-AW	3.0305	0.15
Fraction	Concentration (mg/L)	Fraction %
HPON	0.1012	1.84
HPOB	0.1612	2.93
HPOA	1.1275	20.50
HPIB	0.5242	9.53
HPIA	0.5555	10.10
HPIN	3.0305	55.10
Total HPO	1.3899	25.27
Total HPI	4.1102	74.73

ACH			PAC1		
Sample	DOC concentration (mg/L)	Standard Deviation	Sample	DOC concentration (mg/L)	Standard Deviation
Raw	7.3	0.07	Raw	8.5	0.17
ENV-1	7.1533	0.04	ENV-1	8.3232	0.03
ENV-2	6.9131	0.06	ENV-2	8.0334	0.02
ENV-3	5.0662	0.12	ENV-3	5.6959	0.21
Strata X-C	4.5406	0.09	Strata X-C	5.3125	0.08
Strata X-AW	3.9493	0.12	Strata X-AW	4.4455	0.11
Fraction	Concentration (mg/L)	Fraction %	Fraction	Concentration (mg/L)	Fraction %
HPON	0.1467	2.01	HPON	0.1768	2.08
HPOB	0.2402	3.29	HPOB	0.2899	3.41
HPOA	1.8469	25.30	HPOA	2.3375	27.50
HPIB	0.5256	7.20	HPIB	0.3834	4.51
HPIA	0.5913	8.10	HPIA	0.8670	10.20
HPIN	3.9493	54.10	HPIN	4.4455	52.30
Total HPO	2.2338	30.60	Total HPO	2.8042	32.99
Total HPI	5.0662	69.40	Total HPI	5.6959	67.01

Raw Data for Chapter 7

UV/Vis Raw data

Table B12: Sample: NOM

NOM- Raw		NOM- 0.2		NOM- 0.6		NOM- 1.0	
wavelength (nm)	Abs. (a.u.)						
600	0.0076	600	0.0046	600	0.0042	600	0.0027
599.5	0.0074	599.5	0.0047	599.5	0.0041	599.5	0.0024
599	0.0076	599	0.0046	599	0.0041	599	0.0023
598.5	0.0078	598.5	0.0046	598.5	0.0041	598.5	0.0024
598	0.0076	598	0.0047	598	0.0041	598	0.0024
597.5	0.0074	597.5	0.0044	597.5	0.004	597.5	0.0023
597	0.0074	597	0.0045	597	0.004	597	0.0024
596.5	0.0077	596.5	0.0047	596.5	0.0039	596.5	0.0025
596	0.0079	596	0.0046	596	0.004	596	0.0025
595.5	0.0079	595.5	0.0046	595.5	0.0042	595.5	0.0026
595	0.0078	595	0.0048	595	0.0043	595	0.0026
594.5	0.0078	594.5	0.0048	594.5	0.0042	594.5	0.0024
594	0.0077	594	0.0046	594	0.0042	594	0.0024
593.5	0.0076	593.5	0.0045	593.5	0.0042	593.5	0.0023
593	0.0078	593	0.0045	593	0.0042	593	0.0022
592.5	0.0079	592.5	0.0046	592.5	0.0042	592.5	0.0023
592	0.0078	592	0.0047	592	0.0044	592	0.0024
591.5	0.0079	591.5	0.0048	591.5	0.0043	591.5	0.0023
591	0.0079	591	0.0047	591	0.0043	591	0.0022
590.5	0.008	590.5	0.0045	590.5	0.0041	590.5	0.0023
590	0.008	590	0.0045	590	0.004	590	0.0022
589.5	0.0079	589.5	0.0046	589.5	0.004	589.5	0.0023
589	0.0078	589	0.0044	589	0.004	589	0.0023
588.5	0.0077	588.5	0.0045	588.5	0.0041	588.5	0.0024
588	0.0078	588	0.0047	588	0.0041	588	0.0025
587.5	0.0079	587.5	0.0049	587.5	0.0042	587.5	0.0023
587	0.0079	587	0.0049	587	0.0043	587	0.0023
586.5	0.0079	586.5	0.0047	586.5	0.0042	586.5	0.0024
586	0.0078	586	0.0046	586	0.0041	586	0.0024
585.5	0.0078	585.5	0.0046	585.5	0.004	585.5	0.0023
585	0.008	585	0.0046	585	0.0039	585	0.0021
584.5	0.0079	584.5	0.0045	584.5	0.0039	584.5	0.002

584	0.0078	584	0.0045	584	0.004	584	0.0021
583.5	0.0081	583.5	0.0045	583.5	0.0041	583.5	0.0022
583	0.0083	583	0.0045	583	0.004	583	0.0023
582.5	0.0083	582.5	0.0045	582.5	0.004	582.5	0.0022
582	0.0082	582	0.0047	582	0.004	582	0.0022
581.5	0.008	581.5	0.0048	581.5	0.0041	581.5	0.0022
581	0.0079	581	0.0049	581	0.0042	581	0.0023
580.5	0.008	580.5	0.0049	580.5	0.0042	580.5	0.0023
580	0.0083	580	0.0049	580	0.0041	580	0.0022
579.5	0.0085	579.5	0.0047	579.5	0.0041	579.5	0.0023
579	0.0084	579	0.0046	579	0.0042	579	0.0022
578.5	0.0081	578.5	0.0045	578.5	0.0043	578.5	0.002
578	0.0079	578	0.0045	578	0.004	578	0.002
577.5	0.008	577.5	0.0046	577.5	0.0038	577.5	0.0021
577	0.0082	577	0.0049	577	0.004	577	0.0022
576.5	0.0084	576.5	0.0049	576.5	0.0043	576.5	0.0024
576	0.0085	576	0.0049	576	0.0044	576	0.0025
575.5	0.0088	575.5	0.0049	575.5	0.0042	575.5	0.0023
575	0.0088	575	0.005	575	0.0041	575	0.0022
574.5	0.0085	574.5	0.0048	574.5	0.0042	574.5	0.0024
574	0.0086	574	0.0047	574	0.0043	574	0.0025
573.5	0.0087	573.5	0.0048	573.5	0.0045	573.5	0.0024
573	0.0087	573	0.0048	573	0.0045	573	0.0024
572.5	0.0087	572.5	0.0049	572.5	0.0042	572.5	0.0026
572	0.0088	572	0.005	572	0.0043	572	0.0026
571.5	0.009	571.5	0.0049	571.5	0.0043	571.5	0.0026
571	0.0091	571	0.0048	571	0.0043	571	0.0025
570.5	0.009	570.5	0.0045	570.5	0.0043	570.5	0.0024
570	0.009	570	0.0047	570	0.0043	570	0.0023
569.5	0.009	569.5	0.0049	569.5	0.0044	569.5	0.0023
569	0.009	569	0.0049	569	0.0042	569	0.0022
568.5	0.0089	568.5	0.0047	568.5	0.0041	568.5	0.0022
568	0.009	568	0.0047	568	0.0043	568	0.0023
567.5	0.0091	567.5	0.0048	567.5	0.0043	567.5	0.0021
567	0.0091	567	0.0049	567	0.0042	567	0.002
566.5	0.009	566.5	0.0047	566.5	0.004	566.5	0.0022
566	0.0089	566	0.0045	566	0.0041	566	0.0021
565.5	0.009	565.5	0.0047	565.5	0.0043	565.5	0.0022
565	0.0092	565	0.0047	565	0.0043	565	0.0023
564.5	0.0091	564.5	0.0049	564.5	0.0042	564.5	0.0023
564	0.0091	564	0.0048	564	0.0044	564	0.0023

563.5	0.0092	563.5	0.0049	563.5	0.0044	563.5	0.0023
563	0.0093	563	0.0051	563	0.0042	563	0.0023
562.5	0.0093	562.5	0.005	562.5	0.0042	562.5	0.0022
562	0.0094	562	0.0049	562	0.0042	562	0.0021
561.5	0.0094	561.5	0.0048	561.5	0.0042	561.5	0.002
561	0.0093	561	0.0048	561	0.0042	561	0.0021
560.5	0.0093	560.5	0.005	560.5	0.0041	560.5	0.0023
560	0.0094	560	0.0049	560	0.0042	560	0.0022
559.5	0.0095	559.5	0.0048	559.5	0.0042	559.5	0.002
559	0.0095	559	0.0048	559	0.0042	559	0.0021
558.5	0.0093	558.5	0.0049	558.5	0.0042	558.5	0.0023
558	0.0094	558	0.0049	558	0.0043	558	0.0023
557.5	0.0096	557.5	0.0048	557.5	0.0043	557.5	0.0022
557	0.0096	557	0.0048	557	0.0042	557	0.0022
556.5	0.0095	556.5	0.0049	556.5	0.0043	556.5	0.0021
556	0.0095	556	0.005	556	0.0043	556	0.0019
555.5	0.0098	555.5	0.005	555.5	0.0043	555.5	0.002
555	0.0098	555	0.0049	555	0.0045	555	0.0021
554.5	0.0098	554.5	0.005	554.5	0.0044	554.5	0.002
554	0.0096	554	0.005	554	0.004	554	0.0021
553.5	0.0096	553.5	0.0049	553.5	0.004	553.5	0.0021
553	0.0099	553	0.0049	553	0.0042	553	0.002
552.5	0.01	552.5	0.005	552.5	0.0043	552.5	0.002
552	0.01	552	0.005	552	0.0043	552	0.0021
551.5	0.0101	551.5	0.0052	551.5	0.0044	551.5	0.0021
551	0.0101	551	0.0052	551	0.0046	551	0.002
550.5	0.0101	550.5	0.0051	550.5	0.0046	550.5	0.0021
550	0.0103	550	0.0052	550	0.0045	550	0.002
549.5	0.0103	549.5	0.0051	549.5	0.0045	549.5	0.002
549	0.0101	549	0.0051	549	0.0044	549	0.0021
548.5	0.0101	548.5	0.0051	548.5	0.0044	548.5	0.0021
548	0.0103	548	0.0051	548	0.0045	548	0.0022
547.5	0.0101	547.5	0.0052	547.5	0.0045	547.5	0.0021
547	0.0103	547	0.0051	547	0.0044	547	0.0022
546.5	0.0105	546.5	0.0052	546.5	0.0044	546.5	0.0022
546	0.0104	546	0.0054	546	0.0044	546	0.0024
545.5	0.0105	545.5	0.0054	545.5	0.0045	545.5	0.0025
545	0.0107	545	0.0053	545	0.0046	545	0.0025
544.5	0.0108	544.5	0.0054	544.5	0.0046	544.5	0.0025
544	0.0108	544	0.0055	544	0.0047	544	0.0023
543.5	0.0108	543.5	0.0056	543.5	0.0047	543.5	0.0023

543	0.0109	543	0.0054	543	0.0047	543	0.0023
542.5	0.0109	542.5	0.0052	542.5	0.0045	542.5	0.0022
542	0.0109	542	0.0053	542	0.0045	542	0.0022
541.5	0.0111	541.5	0.0053	541.5	0.0046	541.5	0.0022
541	0.0109	541	0.0053	541	0.0046	541	0.0023
540.5	0.0108	540.5	0.0052	540.5	0.0047	540.5	0.0024
540	0.0107	540	0.0053	540	0.0045	540	0.0022
539.5	0.0109	539.5	0.0054	539.5	0.0043	539.5	0.002
539	0.0108	539	0.0053	539	0.0045	539	0.0019
538.5	0.0108	538.5	0.0053	538.5	0.0047	538.5	0.002
538	0.0111	538	0.0052	538	0.0046	538	0.0021
537.5	0.0112	537.5	0.0054	537.5	0.0045	537.5	0.0021
537	0.0113	537	0.0057	537	0.0047	537	0.0023
536.5	0.0111	536.5	0.0055	536.5	0.0044	536.5	0.002
536	0.0111	536	0.0055	536	0.0045	536	0.0018
535.5	0.0112	535.5	0.0056	535.5	0.0046	535.5	0.0021
535	0.0111	535	0.0055	535	0.0044	535	0.0021
534.5	0.0114	534.5	0.0054	534.5	0.0043	534.5	0.002
534	0.0114	534	0.0053	534	0.0043	534	0.0019
533.5	0.0113	533.5	0.0056	533.5	0.0044	533.5	0.0019
533	0.0114	533	0.0057	533	0.0046	533	0.002
532.5	0.0116	532.5	0.0056	532.5	0.0047	532.5	0.0021
532	0.0116	532	0.0055	532	0.0047	532	0.0021
531.5	0.0116	531.5	0.0054	531.5	0.0046	531.5	0.0022
531	0.0116	531	0.0056	531	0.0044	531	0.0022
530.5	0.0116	530.5	0.0054	530.5	0.0043	530.5	0.0022
530	0.0115	530	0.0056	530	0.0045	530	0.0022
529.5	0.0117	529.5	0.0056	529.5	0.0045	529.5	0.002
529	0.0119	529	0.0054	529	0.0043	529	0.002
528.5	0.0117	528.5	0.0055	528.5	0.0044	528.5	0.002
528	0.0118	528	0.0055	528	0.0045	528	0.0022
527.5	0.012	527.5	0.0056	527.5	0.0045	527.5	0.0022
527	0.012	527	0.0057	527	0.0045	527	0.0022
526.5	0.012	526.5	0.0058	526.5	0.0047	526.5	0.0023
526	0.0121	526	0.006	526	0.0048	526	0.0022
525.5	0.0122	525.5	0.0059	525.5	0.0049	525.5	0.0022
525	0.0124	525	0.0059	525	0.0051	525	0.0021
524.5	0.0125	524.5	0.0058	524.5	0.0049	524.5	0.0022
524	0.0123	524	0.0058	524	0.0048	524	0.0023
523.5	0.0126	523.5	0.0058	523.5	0.0048	523.5	0.0022
523	0.0127	523	0.0057	523	0.0048	523	0.0024

522.5	0.0128	522.5	0.0058	522.5	0.0049	522.5	0.0024
522	0.0128	522	0.0058	522	0.005	522	0.0025
521.5	0.0128	521.5	0.006	521.5	0.0051	521.5	0.0025
521	0.0132	521	0.006	521	0.005	521	0.0024
520.5	0.0131	520.5	0.0059	520.5	0.0051	520.5	0.0024
520	0.013	520	0.006	520	0.0051	520	0.0023
519.5	0.0131	519.5	0.006	519.5	0.005	519.5	0.0024
519	0.0133	519	0.006	519	0.0048	519	0.0021
518.5	0.0131	518.5	0.0061	518.5	0.0046	518.5	0.0021
518	0.013	518	0.0061	518	0.0049	518	0.0023
517.5	0.0134	517.5	0.0061	517.5	0.0049	517.5	0.0025
517	0.0135	517	0.006	517	0.0049	517	0.0025
516.5	0.0134	516.5	0.0061	516.5	0.0049	516.5	0.0023
516	0.0132	516	0.0059	516	0.0048	516	0.0023
515.5	0.0132	515.5	0.0059	515.5	0.0046	515.5	0.0021
515	0.0132	515	0.006	515	0.0045	515	0.0021
514.5	0.0132	514.5	0.0059	514.5	0.0047	514.5	0.0021
514	0.0133	514	0.006	514	0.0047	514	0.002
513.5	0.0134	513.5	0.0061	513.5	0.0048	513.5	0.0021
513	0.0136	513	0.0063	513	0.0049	513	0.0019
512.5	0.0136	512.5	0.0061	512.5	0.0047	512.5	0.002
512	0.0136	512	0.0061	512	0.0047	512	0.0021
511.5	0.0138	511.5	0.0063	511.5	0.0049	511.5	0.0021
511	0.0139	511	0.0062	511	0.0051	511	0.0023
510.5	0.014	510.5	0.0063	510.5	0.0049	510.5	0.0022
510	0.0141	510	0.0063	510	0.0049	510	0.0022
509.5	0.0142	509.5	0.0064	509.5	0.005	509.5	0.0021
509	0.014	509	0.0062	509	0.0048	509	0.0022
508.5	0.0141	508.5	0.0063	508.5	0.0051	508.5	0.0023
508	0.0142	508	0.0065	508	0.005	508	0.0023
507.5	0.0144	507.5	0.0064	507.5	0.005	507.5	0.0025
507	0.0146	507	0.0062	507	0.005	507	0.0023
506.5	0.0144	506.5	0.0062	506.5	0.0048	506.5	0.0022
506	0.0144	506	0.0063	506	0.005	506	0.0019
505.5	0.0144	505.5	0.0061	505.5	0.0049	505.5	0.002
505	0.0145	505	0.0062	505	0.005	505	0.002
504.5	0.0146	504.5	0.0062	504.5	0.0049	504.5	0.0019
504	0.0145	504	0.0063	504	0.0049	504	0.002
503.5	0.0147	503.5	0.0062	503.5	0.005	503.5	0.0021
503	0.0149	503	0.0061	503	0.0049	503	0.0023
502.5	0.0151	502.5	0.0065	502.5	0.0052	502.5	0.0022

502	0.0151	502	0.0063	502	0.0052	502	0.0021
501.5	0.0153	501.5	0.0063	501.5	0.0052	501.5	0.0022
501	0.0154	501	0.0064	501	0.0052	501	0.0021
500.5	0.0154	500.5	0.0064	500.5	0.0052	500.5	0.0023
500	0.0154	500	0.0065	500	0.0052	500	0.0021
499.5	0.0155	499.5	0.0064	499.5	0.0051	499.5	0.0021
499	0.0155	499	0.0064	499	0.0052	499	0.0023
498.5	0.0156	498.5	0.0066	498.5	0.0052	498.5	0.0023
498	0.0157	498	0.0066	498	0.0052	498	0.0023
497.5	0.0157	497.5	0.0067	497.5	0.0052	497.5	0.0024
497	0.016	497	0.0066	497	0.0053	497	0.0024
496.5	0.016	496.5	0.0067	496.5	0.0053	496.5	0.0025
496	0.0161	496	0.0069	496	0.0055	496	0.0024
495.5	0.0161	495.5	0.0068	495.5	0.0054	495.5	0.0022
495	0.0163	495	0.0069	495	0.0052	495	0.0024
494.5	0.0165	494.5	0.0068	494.5	0.0052	494.5	0.0023
494	0.0163	494	0.0067	494	0.005	494	0.0023
493.5	0.0166	493.5	0.0065	493.5	0.0053	493.5	0.0023
493	0.0164	493	0.0065	493	0.0053	493	0.0024
492.5	0.0165	492.5	0.0069	492.5	0.0053	492.5	0.0023
492	0.0165	492	0.007	492	0.0055	492	0.0022
491.5	0.0168	491.5	0.0072	491.5	0.0052	491.5	0.0026
491	0.017	491	0.0069	491	0.0055	491	0.0023
490.5	0.0172	490.5	0.007	490.5	0.0053	490.5	0.0024
490	0.0175	490	0.007	490	0.0054	490	0.0023
489.5	0.0171	489.5	0.0069	489.5	0.0055	489.5	0.0023
489	0.0172	489	0.007	489	0.0052	489	0.0024
488.5	0.0171	488.5	0.0068	488.5	0.0055	488.5	0.0023
488	0.0174	488	0.0071	488	0.0054	488	0.0024
487.5	0.0177	487.5	0.0072	487.5	0.0055	487.5	0.0023
487	0.0177	487	0.0075	487	0.0054	487	0.0027
486.5	0.0179	486.5	0.0074	486.5	0.0055	486.5	0.0024
486	0.0178	486	0.0072	486	0.0055	486	0.0023
485.5	0.018	485.5	0.0074	485.5	0.0052	485.5	0.0023
485	0.0178	485	0.0074	485	0.0054	485	0.0023
484.5	0.0181	484.5	0.0073	484.5	0.0055	484.5	0.0027
484	0.0182	484	0.0072	484	0.0056	484	0.0025
483.5	0.0183	483.5	0.0073	483.5	0.0055	483.5	0.0023
483	0.0184	483	0.0073	483	0.0055	483	0.0023
482.5	0.0181	482.5	0.007	482.5	0.0057	482.5	0.0022
482	0.0182	482	0.0071	482	0.0055	482	0.0024

481.5	0.0183	481.5	0.0072	481.5	0.0055	481.5	0.0025
481	0.0185	481	0.0073	481	0.0057	481	0.0025
480.5	0.0189	480.5	0.0073	480.5	0.0057	480.5	0.0024
480	0.0192	480	0.0075	480	0.0056	480	0.0021
479.5	0.0192	479.5	0.0077	479.5	0.0056	479.5	0.0023
479	0.0192	479	0.0077	479	0.0056	479	0.0023
478.5	0.0194	478.5	0.0077	478.5	0.0057	478.5	0.0023
478	0.0193	478	0.0076	478	0.0056	478	0.0026
477.5	0.0193	477.5	0.0074	477.5	0.0056	477.5	0.0024
477	0.0194	477	0.0072	477	0.0056	477	0.0022
476.5	0.0195	476.5	0.0075	476.5	0.0054	476.5	0.0023
476	0.0197	476	0.0077	476	0.0056	476	0.0023
475.5	0.0201	475.5	0.0077	475.5	0.0056	475.5	0.0024
475	0.0203	475	0.0079	475	0.0056	475	0.0022
474.5	0.0202	474.5	0.0079	474.5	0.0058	474.5	0.0022
474	0.0204	474	0.0079	474	0.0057	474	0.0023
473.5	0.0206	473.5	0.0079	473.5	0.0056	473.5	0.0023
473	0.0204	473	0.0078	473	0.0055	473	0.0023
472.5	0.0204	472.5	0.008	472.5	0.0055	472.5	0.0023
472	0.0206	472	0.008	472	0.0057	472	0.0024
471.5	0.0208	471.5	0.0081	471.5	0.0057	471.5	0.0023
471	0.0209	471	0.008	471	0.0055	471	0.0021
470.5	0.0212	470.5	0.0078	470.5	0.0057	470.5	0.0023
470	0.0212	470	0.008	470	0.0058	470	0.0026
469.5	0.0214	469.5	0.008	469.5	0.0058	469.5	0.0024
469	0.0215	469	0.0081	469	0.0059	469	0.0022
468.5	0.0216	468.5	0.0081	468.5	0.0059	468.5	0.0023
468	0.0217	468	0.0082	468	0.006	468	0.0024
467.5	0.0219	467.5	0.0083	467.5	0.006	467.5	0.0024
467	0.022	467	0.0083	467	0.0059	467	0.0024
466.5	0.0221	466.5	0.0082	466.5	0.0059	466.5	0.0024
466	0.0223	466	0.0083	466	0.006	466	0.0025
465.5	0.0223	465.5	0.0083	465.5	0.006	465.5	0.0024
465	0.0224	465	0.0083	465	0.0059	465	0.0022
464.5	0.0227	464.5	0.0083	464.5	0.0059	464.5	0.0022
464	0.0228	464	0.0083	464	0.0057	464	0.0022
463.5	0.0229	463.5	0.0083	463.5	0.0058	463.5	0.0021
463	0.0231	463	0.0081	463	0.0057	463	0.002
462.5	0.0233	462.5	0.0082	462.5	0.0057	462.5	0.002
462	0.0234	462	0.0083	462	0.0058	462	0.0022
461.5	0.0235	461.5	0.0083	461.5	0.0059	461.5	0.0022

461	0.0235	461	0.0085	461	0.006	461	0.0023
460.5	0.0237	460.5	0.0085	460.5	0.0058	460.5	0.0022
460	0.0239	460	0.0085	460	0.006	460	0.0021
459.5	0.024	459.5	0.0088	459.5	0.0061	459.5	0.0022
459	0.0241	459	0.0088	459	0.006	459	0.0021
458.5	0.0242	458.5	0.0088	458.5	0.006	458.5	0.0022
458	0.0245	458	0.0089	458	0.0061	458	0.0024
457.5	0.0248	457.5	0.009	457.5	0.0061	457.5	0.0024
457	0.0252	457	0.009	457	0.0062	457	0.0025
456.5	0.0253	456.5	0.0089	456.5	0.0065	456.5	0.0027
456	0.0252	456	0.0088	456	0.0065	456	0.0027
455.5	0.0252	455.5	0.0091	455.5	0.0066	455.5	0.0026
455	0.0255	455	0.0094	455	0.0065	455	0.0026
454.5	0.026	454.5	0.0093	454.5	0.0064	454.5	0.0025
454	0.0261	454	0.0094	454	0.0065	454	0.0026
453.5	0.0263	453.5	0.0096	453.5	0.0067	453.5	0.0027
453	0.0266	453	0.0097	453	0.0067	453	0.0027
452.5	0.0269	452.5	0.0096	452.5	0.0066	452.5	0.0027
452	0.0267	452	0.0095	452	0.0067	452	0.0026
451.5	0.0267	451.5	0.0094	451.5	0.0068	451.5	0.0025
451	0.027	451	0.0096	451	0.0068	451	0.0025
450.5	0.0273	450.5	0.0097	450.5	0.0066	450.5	0.0027
450	0.0274	450	0.0092	450	0.0064	450	0.0026
449.5	0.0274	449.5	0.0092	449.5	0.0065	449.5	0.0026
449	0.0276	449	0.0095	449	0.0063	449	0.0023
448.5	0.0279	448.5	0.0096	448.5	0.0065	448.5	0.0023
448	0.0284	448	0.0098	448	0.0067	448	0.0027
447.5	0.0287	447.5	0.0098	447.5	0.0066	447.5	0.0027
447	0.029	447	0.01	447	0.0066	447	0.0026
446.5	0.0293	446.5	0.0103	446.5	0.0069	446.5	0.0026
446	0.0294	446	0.0103	446	0.007	446	0.0028
445.5	0.0296	445.5	0.01	445.5	0.007	445.5	0.0027
445	0.0298	445	0.01	445	0.0071	445	0.0028
444.5	0.0298	444.5	0.0103	444.5	0.0067	444.5	0.0029
444	0.0302	444	0.0102	444	0.0068	444	0.0028
443.5	0.0305	443.5	0.0103	443.5	0.007	443.5	0.0028
443	0.0307	443	0.0107	443	0.0072	443	0.0029
442.5	0.0307	442.5	0.0108	442.5	0.0072	442.5	0.0028
442	0.0311	442	0.0108	442	0.0071	442	0.0026
441.5	0.0314	441.5	0.0106	441.5	0.0073	441.5	0.0029
441	0.0313	441	0.0106	441	0.0072	441	0.0027

440.5	0.0315	440.5	0.0105	440.5	0.0073	440.5	0.0028
440	0.0315	440	0.011	440	0.0071	440	0.0029
439.5	0.0317	439.5	0.0113	439.5	0.0072	439.5	0.0031
439	0.0323	439	0.0113	439	0.0072	439	0.0028
438.5	0.0328	438.5	0.0113	438.5	0.0074	438.5	0.0026
438	0.0331	438	0.0114	438	0.0077	438	0.0029
437.5	0.0336	437.5	0.0115	437.5	0.0076	437.5	0.0031
437	0.0337	437	0.0114	437	0.0076	437	0.0034
436.5	0.0338	436.5	0.0117	436.5	0.0076	436.5	0.0035
436	0.0341	436	0.0116	436	0.0078	436	0.0033
435.5	0.0342	435.5	0.0117	435.5	0.008	435.5	0.003
435	0.0345	435	0.0119	435	0.0079	435	0.0028
434.5	0.0351	434.5	0.0116	434.5	0.0078	434.5	0.0031
434	0.0352	434	0.0119	434	0.0074	434	0.0032
433.5	0.0354	433.5	0.0119	433.5	0.0076	433.5	0.0031
433	0.0355	433	0.0119	433	0.0077	433	0.0032
432.5	0.0357	432.5	0.012	432.5	0.0077	432.5	0.0033
432	0.036	432	0.012	432	0.0078	432	0.0033
431.5	0.0365	431.5	0.0123	431.5	0.0079	431.5	0.0033
431	0.0367	431	0.0124	431	0.0082	431	0.0033
430.5	0.037	430.5	0.0127	430.5	0.0083	430.5	0.0036
430	0.0372	430	0.0128	430	0.0082	430	0.0034
429.5	0.0371	429.5	0.0125	429.5	0.008	429.5	0.0033
429	0.0376	429	0.0122	429	0.0078	429	0.0034
428.5	0.0383	428.5	0.0121	428.5	0.0079	428.5	0.0032
428	0.0384	428	0.0125	428	0.0082	428	0.0029
427.5	0.0386	427.5	0.0125	427.5	0.0084	427.5	0.0029
427	0.0388	427	0.0124	427	0.0081	427	0.003
426.5	0.0389	426.5	0.0125	426.5	0.0083	426.5	0.0033
426	0.0392	426	0.013	426	0.0083	426	0.0034
425.5	0.0395	425.5	0.0131	425.5	0.0083	425.5	0.0034
425	0.0397	425	0.0131	425	0.0083	425	0.0035
424.5	0.0401	424.5	0.0133	424.5	0.0082	424.5	0.0035
424	0.0402	424	0.0132	424	0.0085	424	0.0034
423.5	0.0403	423.5	0.013	423.5	0.0086	423.5	0.003
423	0.0407	423	0.0128	423	0.0085	423	0.0029
422.5	0.0409	422.5	0.0131	422.5	0.0085	422.5	0.0031
422	0.0412	422	0.0135	422	0.0084	422	0.0032
421.5	0.042	421.5	0.0135	421.5	0.0083	421.5	0.0034
421	0.0421	421	0.0132	421	0.0086	421	0.0033
420.5	0.0421	420.5	0.0134	420.5	0.0087	420.5	0.0031

420	0.0424	420	0.0135	420	0.0086	420	0.0029
419.5	0.0432	419.5	0.0132	419.5	0.0086	419.5	0.0031
419	0.0433	419	0.0133	419	0.0083	419	0.0035
418.5	0.0434	418.5	0.0138	418.5	0.0081	418.5	0.0035
418	0.0439	418	0.0141	418	0.0085	418	0.0034
417.5	0.0443	417.5	0.014	417.5	0.0087	417.5	0.0032
417	0.0445	417	0.0141	417	0.0084	417	0.003
416.5	0.045	416.5	0.0144	416.5	0.0085	416.5	0.0033
416	0.0454	416	0.0143	416	0.0085	416	0.0036
415.5	0.0459	415.5	0.0145	415.5	0.0088	415.5	0.0033
415	0.0467	415	0.015	415	0.0095	415	0.0035
414.5	0.0471	414.5	0.0148	414.5	0.0092	414.5	0.004
414	0.0474	414	0.0149	414	0.0092	414	0.0037
413.5	0.048	413.5	0.0153	413.5	0.0095	413.5	0.0038
413	0.0481	413	0.0154	413	0.0094	413	0.004
412.5	0.0481	412.5	0.0155	412.5	0.0095	412.5	0.0041
412	0.0486	412	0.0155	412	0.0096	412	0.004
411.5	0.049	411.5	0.0152	411.5	0.0094	411.5	0.0036
411	0.0491	411	0.015	411	0.0094	411	0.0036
410.5	0.0497	410.5	0.0154	410.5	0.0096	410.5	0.0039
410	0.0503	410	0.0159	410	0.0098	410	0.0042
409.5	0.0508	409.5	0.0159	409.5	0.0099	409.5	0.0044
409	0.0513	409	0.016	409	0.0101	409	0.0044
408.5	0.0514	408.5	0.0163	408.5	0.0101	408.5	0.004
408	0.0517	408	0.0163	408	0.0099	408	0.0038
407.5	0.0519	407.5	0.0162	407.5	0.01	407.5	0.0036
407	0.0523	407	0.0161	407	0.0102	407	0.0038
406.5	0.0534	406.5	0.0167	406.5	0.0103	406.5	0.0041
406	0.0537	406	0.017	406	0.0106	406	0.0041
405.5	0.0538	405.5	0.0168	405.5	0.0108	405.5	0.004
405	0.0548	405	0.0169	405	0.0106	405	0.004
404.5	0.0553	404.5	0.0169	404.5	0.0105	404.5	0.0044
404	0.0556	404	0.0171	404	0.0107	404	0.0046
403.5	0.0558	403.5	0.0172	403.5	0.0104	403.5	0.0044
403	0.0558	403	0.0171	403	0.0104	403	0.0045
402.5	0.0565	402.5	0.0171	402.5	0.0106	402.5	0.0047
402	0.0571	402	0.0174	402	0.0108	402	0.0045
401.5	0.0575	401.5	0.0178	401.5	0.011	401.5	0.0043
401	0.058	401	0.0179	401	0.0112	401	0.0044
400.5	0.0585	400.5	0.018	400.5	0.0114	400.5	0.0048
400	0.059	400	0.0181	400	0.0115	400	0.0048

399.5	0.0593	399.5	0.0181	399.5	0.0115	399.5	0.0044
399	0.0597	399	0.0178	399	0.0111	399	0.0045
398.5	0.0605	398.5	0.0179	398.5	0.0112	398.5	0.0047
398	0.061	398	0.0184	398	0.0115	398	0.0046
397.5	0.0613	397.5	0.0189	397.5	0.0116	397.5	0.0046
397	0.0616	397	0.0192	397	0.0115	397	0.0048
396.5	0.0624	396.5	0.0191	396.5	0.0116	396.5	0.0048
396	0.0631	396	0.0193	396	0.0115	396	0.0051
395.5	0.0634	395.5	0.0195	395.5	0.0117	395.5	0.005
395	0.0639	395	0.0195	395	0.0123	395	0.0049
394.5	0.0645	394.5	0.02	394.5	0.0124	394.5	0.0054
394	0.065	394	0.0203	394	0.0128	394	0.0058
393.5	0.0656	393.5	0.0204	393.5	0.0129	393.5	0.0058
393	0.0664	393	0.0203	393	0.0127	393	0.0058
392.5	0.0671	392.5	0.0203	392.5	0.0129	392.5	0.0059
392	0.0678	392	0.0205	392	0.0132	392	0.0058
391.5	0.0685	391.5	0.0204	391.5	0.0128	391.5	0.0058
391	0.0685	391	0.0205	391	0.0126	391	0.0057
390.5	0.069	390.5	0.0207	390.5	0.0131	390.5	0.0057
390	0.07	390	0.0206	390	0.013	390	0.0057
389.5	0.0703	389.5	0.0211	389.5	0.013	389.5	0.0058
389	0.0708	389	0.0214	389	0.0132	389	0.0063
388.5	0.0716	388.5	0.0215	388.5	0.0135	388.5	0.0065
388	0.072	388	0.0221	388	0.0138	388	0.0066
387.5	0.0727	387.5	0.022	387.5	0.014	387.5	0.0066
387	0.0731	387	0.0218	387	0.0139	387	0.0065
386.5	0.0731	386.5	0.0219	386.5	0.0134	386.5	0.0066
386	0.074	386	0.0222	386	0.0135	386	0.0066
385.5	0.0747	385.5	0.0223	385.5	0.0137	385.5	0.0065
385	0.0753	385	0.0226	385	0.0138	385	0.007
384.5	0.0759	384.5	0.0227	384.5	0.0137	384.5	0.0069
384	0.0767	384	0.0234	384	0.014	384	0.0066
383.5	0.0772	383.5	0.0237	383.5	0.0144	383.5	0.0067
383	0.0779	383	0.0235	383	0.0149	383	0.0072
382.5	0.0789	382.5	0.0239	382.5	0.015	382.5	0.0077
382	0.0791	382	0.0241	382	0.015	382	0.0073
381.5	0.0796	381.5	0.0245	381.5	0.015	381.5	0.0073
381	0.0802	381	0.0246	381	0.015	381	0.0075
380.5	0.0811	380.5	0.0251	380.5	0.0162	380.5	0.0075
380	0.0822	380	0.0253	380	0.017	380	0.0079
379.5	0.0831	379.5	0.0254	379.5	0.0166	379.5	0.0085

379	0.0836	379	0.0255	379	0.0163	379	0.0083
378.5	0.0836	378.5	0.0256	378.5	0.0168	378.5	0.0081
378	0.0837	378	0.0253	378	0.0168	378	0.0082
377.5	0.0847	377.5	0.0255	377.5	0.0169	377.5	0.0084
377	0.0864	377	0.0255	377	0.0171	377	0.0087
376.5	0.0871	376.5	0.0255	376.5	0.0169	376.5	0.0081
376	0.0877	376	0.0264	376	0.0171	376	0.0082
375.5	0.0883	375.5	0.0264	375.5	0.0173	375.5	0.0087
375	0.0897	375	0.0269	375	0.0182	375	0.0093
374.5	0.0908	374.5	0.0272	374.5	0.0186	374.5	0.0094
374	0.091	374	0.0279	374	0.0183	374	0.0093
373.5	0.0918	373.5	0.0284	373.5	0.0181	373.5	0.0095
373	0.0921	373	0.0286	373	0.0184	373	0.0093
372.5	0.0928	372.5	0.029	372.5	0.019	372.5	0.0098
372	0.0933	372	0.0285	372	0.019	372	0.0099
371.5	0.0947	371.5	0.0288	371.5	0.0195	371.5	0.01
371	0.0956	371	0.0288	371	0.0187	371	0.0101
370.5	0.0955	370.5	0.0292	370.5	0.0187	370.5	0.0103
370	0.0964	370	0.0289	370	0.0196	370	0.0099
369.5	0.0972	369.5	0.0294	369.5	0.0201	369.5	0.0103
369	0.0983	369	0.0302	369	0.0201	369	0.0104
368.5	0.099	368.5	0.0303	368.5	0.0196	368.5	0.0099
368	0.1001	368	0.0307	368	0.0208	368	0.0105
367.5	0.1006	367.5	0.0308	367.5	0.0215	367.5	0.0109
367	0.1015	367	0.0311	367	0.0217	367	0.0108
366.5	0.1024	366.5	0.0314	366.5	0.0211	366.5	0.0105
366	0.1036	366	0.0321	366	0.0211	366	0.0118
365.5	0.1057	365.5	0.032	365.5	0.0215	365.5	0.0122
365	0.1058	365	0.0319	365	0.0221	365	0.0114
364.5	0.1065	364.5	0.0324	364.5	0.0222	364.5	0.0112
364	0.1072	364	0.0324	364	0.0213	364	0.0111
363.5	0.1076	363.5	0.032	363.5	0.0217	363.5	0.0116
363	0.1083	363	0.0327	363	0.0223	363	0.0119
362.5	0.1091	362.5	0.0332	362.5	0.0219	362.5	0.0106
362	0.1102	362	0.0332	362	0.022	362	0.0109
361.5	0.1116	361.5	0.0338	361.5	0.0225	361.5	0.0125
361	0.1124	361	0.0343	361	0.022	361	0.0129
360.5	0.112	360.5	0.0328	360.5	0.0211	360.5	0.0111
360	0.1133	360	0.0321	360	0.0218	360	0.0105
359.5	0.1142	359.5	0.0328	359.5	0.0227	359.5	0.0114
359	0.1141	359	0.0322	359	0.022	359	0.0107

358.5	0.1162	358.5	0.0329	358.5	0.0213	358.5	0.0107
358	0.1169	358	0.0338	358	0.0212	358	0.0116
357.5	0.1173	357.5	0.034	357.5	0.0219	357.5	0.0118
357	0.1193	357	0.0339	357	0.0224	357	0.0114
356.5	0.1208	356.5	0.0346	356.5	0.0234	356.5	0.0115
356	0.1215	356	0.0357	356	0.0234	356	0.0117
355.5	0.1229	355.5	0.0359	355.5	0.023	355.5	0.0117
355	0.1241	355	0.0359	355	0.0232	355	0.0118
354.5	0.1242	354.5	0.0352	354.5	0.0233	354.5	0.0123
354	0.1254	354	0.035	354	0.0226	354	0.0128
353.5	0.1264	353.5	0.0353	353.5	0.0223	353.5	0.0128
353	0.1269	353	0.0357	353	0.0238	353	0.0127
352.5	0.1287	352.5	0.0365	352.5	0.024	352.5	0.0127
352	0.1304	352	0.0368	352	0.0237	352	0.0134
351.5	0.1312	351.5	0.0374	351.5	0.0247	351.5	0.014
351	0.1316	351	0.038	351	0.025	351	0.013
350.5	0.1335	350.5	0.0382	350.5	0.0246	350.5	0.0125
350	0.1351	350	0.0383	350	0.0249	350	0.0126
349.5	0.1356	349.5	0.0382	349.5	0.0251	349.5	0.0128
349	0.1366	349	0.0383	349	0.0247	349	0.0132
348.5	0.1368	348.5	0.0385	348.5	0.0247	348.5	0.0133
348	0.1379	348	0.0383	348	0.0248	348	0.0133
347.5	0.1394	347.5	0.0385	347.5	0.0251	347.5	0.0127
347	0.1406	347	0.0387	347	0.0245	347	0.0125
346.5	0.1421	346.5	0.0391	346.5	0.0237	346.5	0.0123
346	0.143	346	0.0394	346	0.0238	346	0.013
345.5	0.1437	345.5	0.0388	345.5	0.0239	345.5	0.0139
345	0.1451	345	0.0383	345	0.0245	345	0.0135
344.5	0.146	344.5	0.0392	344.5	0.0249	344.5	0.0134
344	0.1463	344	0.0405	344	0.0244	344	0.0138
343.5	0.1484	343.5	0.0406	343.5	0.0248	343.5	0.0137
343	0.1506	343	0.0405	343	0.0256	343	0.0141
342.5	0.1517	342.5	0.0404	342.5	0.0256	342.5	0.0146
342	0.152	342	0.0404	342	0.0262	342	0.0141
341.5	0.153	341.5	0.041	341.5	0.0269	341.5	0.0139
341	0.1544	341	0.042	341	0.0268	341	0.0136
340.5	0.1548	340.5	0.0421	340.5	0.027	340.5	0.014
340	0.1559	340	0.042	340	0.0269	340	0.0149
339.5	0.1575	339.5	0.0425	339.5	0.0267	339.5	0.0148
339	0.1584	339	0.0432	339	0.0267	339	0.0147
338.5	0.1592	338.5	0.0433	338.5	0.026	338.5	0.0145

338	0.1605	338	0.0427	338	0.0262	338	0.0142
337.5	0.1618	337.5	0.043	337.5	0.027	337.5	0.0139
337	0.1629	337	0.044	337	0.0268	337	0.0134
336.5	0.1637	336.5	0.0436	336.5	0.0266	336.5	0.0139
336	0.1645	336	0.0435	336	0.0271	336	0.0143
335.5	0.1659	335.5	0.0443	335.5	0.0276	335.5	0.0146
335	0.1669	335	0.0444	335	0.0272	335	0.014
334.5	0.1679	334.5	0.0449	334.5	0.027	334.5	0.0139
334	0.1699	334	0.0458	334	0.0272	334	0.0148
333.5	0.1718	333.5	0.0462	333.5	0.0278	333.5	0.0152
333	0.1729	333	0.047	333	0.0287	333	0.0157
332.5	0.1735	332.5	0.0477	332.5	0.0287	332.5	0.0161
332	0.175	332	0.0475	332	0.029	332	0.0158
331.5	0.1761	331.5	0.0474	331.5	0.0292	331.5	0.0154
331	0.1771	331	0.0476	331	0.0291	331	0.0151
330.5	0.1782	330.5	0.0477	330.5	0.0287	330.5	0.0156
330	0.1788	330	0.0475	330	0.0288	330	0.0152
329.5	0.1805	329.5	0.0479	329.5	0.0298	329.5	0.0147
329	0.1822	329	0.049	329	0.03	329	0.0155
328.5	0.1842	328.5	0.0499	328.5	0.0299	328.5	0.0155
328	0.1855	328	0.0503	328	0.0301	328	0.0162
327.5	0.1866	327.5	0.0502	327.5	0.0299	327.5	0.0164
327	0.1882	327	0.0506	327	0.03	327	0.0162
326.5	0.1897	326.5	0.0511	326.5	0.0303	326.5	0.0165
326	0.1911	326	0.0518	326	0.0308	326	0.0165
325.5	0.1918	325.5	0.0518	325.5	0.0311	325.5	0.0161
325	0.1924	325	0.0517	325	0.0314	325	0.016
324.5	0.1938	324.5	0.0526	324.5	0.0312	324.5	0.016
324	0.1949	324	0.052	324	0.0303	324	0.0156
323.5	0.1959	323.5	0.0526	323.5	0.0305	323.5	0.0157
323	0.1979	323	0.0539	323	0.0315	323	0.0163
322.5	0.1995	322.5	0.0541	322.5	0.0319	322.5	0.0168
322	0.2004	322	0.0542	322	0.0324	322	0.0174
321.5	0.202	321.5	0.0544	321.5	0.0324	321.5	0.0173
321	0.2031	321	0.0553	321	0.0323	321	0.017
320.5	0.2041	320.5	0.0557	320.5	0.0329	320.5	0.0174
320	0.2059	320	0.0561	320	0.0326	320	0.0172
319.5	0.2073	319.5	0.0563	319.5	0.0327	319.5	0.0171
319	0.2084	319	0.0563	319	0.0328	319	0.0173
318.5	0.2093	318.5	0.0572	318.5	0.0323	318.5	0.0174
318	0.2107	318	0.0576	318	0.0325	318	0.0176

317.5	0.2128	317.5	0.0583	317.5	0.0333	317.5	0.0178
317	0.2152	317	0.0589	317	0.034	317	0.0175
316.5	0.2162	316.5	0.0582	316.5	0.034	316.5	0.0173
316	0.2164	316	0.0575	316	0.0333	316	0.017
315.5	0.2175	315.5	0.058	315.5	0.0334	315.5	0.0168
315	0.2193	315	0.0598	315	0.0344	315	0.0175
314.5	0.2215	314.5	0.0611	314.5	0.0353	314.5	0.018
314	0.2238	314	0.0621	314	0.0361	314	0.0189
313.5	0.2258	313.5	0.0624	313.5	0.0364	313.5	0.0194
313	0.2276	313	0.0624	313	0.0361	313	0.019
312.5	0.229	312.5	0.0626	312.5	0.0357	312.5	0.0187
312	0.2297	312	0.0631	312	0.0358	312	0.019
311.5	0.2313	311.5	0.0643	311.5	0.0362	311.5	0.0197
311	0.2332	311	0.0652	311	0.037	311	0.0199
310.5	0.2348	310.5	0.0659	310.5	0.0372	310.5	0.0202
310	0.2364	310	0.0661	310	0.0363	310	0.0196
309.5	0.2381	309.5	0.0663	309.5	0.0361	309.5	0.0194
309	0.2393	309	0.0669	309	0.0367	309	0.02
308.5	0.2416	308.5	0.0674	308.5	0.0375	308.5	0.0199
308	0.2435	308	0.0679	308	0.0386	308	0.0202
307.5	0.2451	307.5	0.0681	307.5	0.0395	307.5	0.0203
307	0.2469	307	0.0688	307	0.039	307	0.0203
306.5	0.2475	306.5	0.0702	306.5	0.0385	306.5	0.0209
306	0.2494	306	0.0713	306	0.0387	306	0.021
305.5	0.2515	305.5	0.0713	305.5	0.0389	305.5	0.0212
305	0.2536	305	0.0717	305	0.0393	305	0.0211
304.5	0.2557	304.5	0.0729	304.5	0.0404	304.5	0.0212
304	0.2567	304	0.073	304	0.0408	304	0.0217
303.5	0.2578	303.5	0.0724	303.5	0.0402	303.5	0.0214
303	0.2591	303	0.0723	303	0.0402	303	0.0208
302.5	0.2608	302.5	0.0735	302.5	0.0404	302.5	0.0213
302	0.2626	302	0.075	302	0.0405	302	0.0217
301.5	0.265	301.5	0.0755	301.5	0.0407	301.5	0.0218
301	0.2672	301	0.0766	301	0.0411	301	0.0221
300.5	0.2688	300.5	0.0774	300.5	0.042	300.5	0.0219
300	0.271	300	0.0779	300	0.0429	300	0.0221
299.5	0.2726	299.5	0.0789	299.5	0.0432	299.5	0.0229
299	0.2742	299	0.0796	299	0.0432	299	0.0235
298.5	0.2765	298.5	0.0803	298.5	0.0435	298.5	0.0234
298	0.278	298	0.0815	298	0.0441	298	0.0234
297.5	0.2793	297.5	0.0821	297.5	0.0444	297.5	0.0239

297	0.2819	297	0.0829	297	0.0445	297	0.0236
296.5	0.284	296.5	0.084	296.5	0.0452	296.5	0.0238
296	0.2858	296	0.0847	296	0.0462	296	0.0245
295.5	0.2877	295.5	0.0859	295.5	0.0472	295.5	0.0246
295	0.2896	295	0.0873	295	0.0474	295	0.0248
294.5	0.2919	294.5	0.0877	294.5	0.0475	294.5	0.0246
294	0.2936	294	0.0881	294	0.0477	294	0.0246
293.5	0.2953	293.5	0.0889	293.5	0.048	293.5	0.0253
293	0.2976	293	0.0896	293	0.0488	293	0.0259
292.5	0.3004	292.5	0.0905	292.5	0.049	292.5	0.0261
292	0.3022	292	0.0913	292	0.0491	292	0.0263
291.5	0.3041	291.5	0.0919	291.5	0.0498	291.5	0.0266
291	0.3058	291	0.0925	291	0.0506	291	0.0266
290.5	0.3078	290.5	0.0938	290.5	0.0513	290.5	0.0268
290	0.3107	290	0.0953	290	0.0515	290	0.0271
289.5	0.3125	289.5	0.0964	289.5	0.0513	289.5	0.0273
289	0.3143	289	0.0972	289	0.0524	289	0.0278
288.5	0.3167	288.5	0.0981	288.5	0.0535	288.5	0.0281
288	0.3197	288	0.0993	288	0.0536	288	0.0286
287.5	0.3217	287.5	0.1001	287.5	0.0538	287.5	0.029
287	0.3234	287	0.1013	287	0.0546	287	0.0291
286.5	0.3257	286.5	0.1023	286.5	0.0559	286.5	0.0294
286	0.3275	286	0.1027	286	0.0568	286	0.0294
285.5	0.3297	285.5	0.1038	285.5	0.0568	285.5	0.0294
285	0.332	285	0.1054	285	0.0566	285	0.0298
284.5	0.3342	284.5	0.1067	284.5	0.0576	284.5	0.0304
284	0.3364	284	0.1078	284	0.0583	284	0.0307
283.5	0.3389	283.5	0.1089	283.5	0.0583	283.5	0.0305
283	0.341	283	0.1096	283	0.0585	283	0.0305
282.5	0.343	282.5	0.1103	282.5	0.0586	282.5	0.0309
282	0.3452	282	0.1108	282	0.059	282	0.0309
281.5	0.3472	281.5	0.1113	281.5	0.0601	281.5	0.0311
281	0.3491	281	0.1124	281	0.0615	281	0.0318
280.5	0.3517	280.5	0.1142	280.5	0.0621	280.5	0.0324
280	0.3547	280	0.1156	280	0.0628	280	0.0328
279.5	0.3577	279.5	0.1164	279.5	0.0633	279.5	0.0332
279	0.36	279	0.1179	279	0.0639	279	0.0338
278.5	0.3617	278.5	0.1189	278.5	0.0646	278.5	0.0338
278	0.3643	278	0.1194	278	0.0646	278	0.0337
277.5	0.3664	277.5	0.1202	277.5	0.0649	277.5	0.0339
277	0.368	277	0.1213	277	0.0656	277	0.0342

276.5	0.3705	276.5	0.1224	276.5	0.0659	276.5	0.0348
276	0.3734	276	0.1235	276	0.0664	276	0.0354
275.5	0.3764	275.5	0.1246	275.5	0.0676	275.5	0.0357
275	0.3791	275	0.1258	275	0.0686	275	0.0357
274.5	0.3814	274.5	0.1268	274.5	0.0692	274.5	0.0356
274	0.3835	274	0.1276	274	0.0697	274	0.036
273.5	0.3858	273.5	0.1286	273.5	0.0698	273.5	0.0367
273	0.3882	273	0.1293	273	0.0701	273	0.0372
272.5	0.391	272.5	0.1306	272.5	0.071	272.5	0.0371
272	0.3936	272	0.1317	272	0.0716	272	0.0374
271.5	0.3959	271.5	0.1328	271.5	0.0723	271.5	0.038
271	0.3989	271	0.1337	271	0.073	271	0.0382
270.5	0.4015	270.5	0.1346	270.5	0.0734	270.5	0.0387
270	0.4037	270	0.1358	270	0.0739	270	0.0393
269.5	0.4061	269.5	0.1367	269.5	0.0747	269.5	0.0392
269	0.4091	269	0.1375	269	0.0757	269	0.0396
268.5	0.411	268.5	0.1385	268.5	0.0756	268.5	0.0406
268	0.4134	268	0.1393	268	0.0757	268	0.041
267.5	0.4168	267.5	0.1401	267.5	0.0765	267.5	0.0405
267	0.4188	267	0.1406	267	0.0773	267	0.0404
266.5	0.4207	266.5	0.1412	266.5	0.0777	266.5	0.0407
266	0.4228	266	0.1419	266	0.0779	266	0.0409
265.5	0.4251	265.5	0.1424	265.5	0.0779	265.5	0.041
265	0.4275	265	0.1429	265	0.0785	265	0.0409
264.5	0.429	264.5	0.1435	264.5	0.0793	264.5	0.0414
264	0.4315	264	0.1448	264	0.0795	264	0.0421
263.5	0.434	263.5	0.1456	263.5	0.0801	263.5	0.0422
263	0.4361	263	0.1463	263	0.0806	263	0.0427
262.5	0.4384	262.5	0.1471	262.5	0.0808	262.5	0.0426
262	0.4409	262	0.1476	262	0.0811	262	0.0431
261.5	0.4438	261.5	0.1481	261.5	0.0814	261.5	0.0437
261	0.4455	261	0.1486	261	0.0818	261	0.0438
260.5	0.4469	260.5	0.149	260.5	0.082	260.5	0.0439
260	0.4487	260	0.1498	260	0.0823	260	0.0437
259.5	0.4513	259.5	0.1504	259.5	0.0827	259.5	0.0439
259	0.4537	259	0.151	259	0.0832	259	0.044
258.5	0.4558	258.5	0.1518	258.5	0.0837	258.5	0.0445
258	0.4581	258	0.1526	258	0.0843	258	0.045
257.5	0.4599	257.5	0.1532	257.5	0.0837	257.5	0.045
257	0.4615	257	0.1537	257	0.0834	257	0.0446
256.5	0.4632	256.5	0.1541	256.5	0.0837	256.5	0.0444

256	0.4653	256	0.154	256	0.0837	256	0.0449
255.5	0.4676	255.5	0.1547	255.5	0.084	255.5	0.0453
255	0.4699	255	0.156	255	0.0844	255	0.0458
254.5	0.4727	254.5	0.1568	254.5	0.0852	254.5	0.0459
254	0.4745	254	0.1573	254	0.0857	254	0.0462
253.5	0.4761	253.5	0.1576	253.5	0.0855	253.5	0.0464
253	0.4782	253	0.1585	253	0.0859	253	0.0468
252.5	0.4803	252.5	0.1591	252.5	0.0867	252.5	0.0473
252	0.483	252	0.1595	252	0.0867	252	0.0474
251.5	0.485	251.5	0.1609	251.5	0.0871	251.5	0.0471
251	0.4873	251	0.1615	251	0.0874	251	0.0473
250.5	0.4899	250.5	0.162	250.5	0.0872	250.5	0.0479
250	0.492	250	0.1627	250	0.0879	250	0.0486
249.5	0.4943	249.5	0.1644	249.5	0.088	249.5	0.049
249	0.4968	249	0.1659	249	0.0882	249	0.0498
248.5	0.4998	248.5	0.1665	248.5	0.0891	248.5	0.0504
248	0.5031	248	0.1676	248	0.09	248	0.0503
247.5	0.5052	247.5	0.1683	247.5	0.0901	247.5	0.0506
247	0.5068	247	0.169	247	0.09	247	0.0511
246.5	0.5097	246.5	0.1689	246.5	0.0901	246.5	0.0519
246	0.5125	246	0.1696	246	0.0904	246	0.0516
245.5	0.5143	245.5	0.1709	245.5	0.0907	245.5	0.052
245	0.5175	245	0.1717	245	0.0911	245	0.0529
244.5	0.5214	244.5	0.1729	244.5	0.0922	244.5	0.0535
244	0.5244	244	0.1743	244	0.0929	244	0.0546
243.5	0.5275	243.5	0.1763	243.5	0.0934	243.5	0.0551
243	0.5313	243	0.1776	243	0.0937	243	0.0558
242.5	0.5343	242.5	0.1784	242.5	0.0944	242.5	0.0566
242	0.5366	242	0.18	242	0.0955	242	0.0565
241.5	0.5393	241.5	0.181	241.5	0.0963	241.5	0.057
241	0.5432	241	0.1824	241	0.0969	241	0.0585
240.5	0.5472	240.5	0.1836	240.5	0.0979	240.5	0.0591
240	0.551	240	0.1848	240	0.0986	240	0.0598
239.5	0.5543	239.5	0.1863	239.5	0.0991	239.5	0.0613
239	0.5571	239	0.1874	239	0.1	239	0.062
238.5	0.561	238.5	0.1887	238.5	0.1002	238.5	0.062
238	0.5655	238	0.1903	238	0.1009	238	0.0634
237.5	0.5691	237.5	0.1921	237.5	0.1025	237.5	0.064
237	0.5738	237	0.1936	237	0.1033	237	0.0646
236.5	0.5779	236.5	0.1953	236.5	0.103	236.5	0.0659
236	0.582	236	0.1969	236	0.1044	236	0.067

235.5	0.5871	235.5	0.1977	235.5	0.1056	235.5	0.0677
235	0.5919	235	0.1998	235	0.105	235	0.0682
234.5	0.5978	234.5	0.2009	234.5	0.1059	234.5	0.0693
234	0.6037	234	0.2025	234	0.107	234	0.0699
233.5	0.6102	233.5	0.2044	233.5	0.1084	233.5	0.0715
233	0.6148	233	0.2043	233	0.1095	233	0.0723
232.5	0.6198	232.5	0.2055	232.5	0.1103	232.5	0.0729
232	0.6272	232	0.2077	232	0.1115	232	0.0747
231.5	0.6344	231.5	0.2088	231.5	0.1141	231.5	0.0766
231	0.6405	231	0.2107	231	0.1154	231	0.0779
230.5	0.6448	230.5	0.2132	230.5	0.1162	230.5	0.0795
230	0.6514	230	0.2145	230	0.1174	230	0.0819
229.5	0.657	229.5	0.2155	229.5	0.1186	229.5	0.0839
229	0.6626	229	0.2171	229	0.1222	229	0.0855
228.5	0.6698	228.5	0.2188	228.5	0.1236	228.5	0.0866
228	0.6751	228	0.2202	228	0.1245	228	0.0884
227.5	0.6814	227.5	0.2225	227.5	0.1266	227.5	0.0907
227	0.686	227	0.2234	227	0.129	227	0.0937
226.5	0.6906	226.5	0.2243	226.5	0.1302	226.5	0.0959
226	0.6978	226	0.2253	226	0.1321	226	0.0988
225.5	0.7044	225.5	0.2268	225.5	0.1357	225.5	0.1016
225	0.709	225	0.2303	225	0.1378	225	0.1044
224.5	0.7134	224.5	0.2307	224.5	0.1409	224.5	0.1067
224	0.7203	224	0.2325	224	0.1431	224	0.1097
223.5	0.7253	223.5	0.236	223.5	0.1459	223.5	0.1138
223	0.7306	223	0.2374	223	0.1506	223	0.1167
222.5	0.7358	222.5	0.2388	222.5	0.1534	222.5	0.1213
222	0.7396	222	0.2399	222	0.156	222	0.1249
221.5	0.7449	221.5	0.2417	221.5	0.1599	221.5	0.1279
221	0.748	221	0.2435	221	0.1636	221	0.1323
220.5	0.7528	220.5	0.2455	220.5	0.167	220.5	0.1375
220	0.7579	220	0.248	220	0.1722	220	0.142
219.5	0.7632	219.5	0.2512	219.5	0.1772	219.5	0.1461
219	0.7682	219	0.2536	219	0.1814	219	0.1517
218.5	0.7688	218.5	0.254	218.5	0.1852	218.5	0.157
218	0.7742	218	0.256	218	0.1884	218	0.162
217.5	0.7801	217.5	0.2554	217.5	0.1943	217.5	0.1653
217	0.7813	217	0.2578	217	0.1979	217	0.1694
216.5	0.785	216.5	0.262	216.5	0.2015	216.5	0.1758
216	0.7908	216	0.2622	216	0.2083	216	0.181
215.5	0.7958	215.5	0.2641	215.5	0.2128	215.5	0.187

215	0.7993	215	0.266	215	0.2179	215	0.1903
214.5	0.8032	214.5	0.2696	214.5	0.2215	214.5	0.1953
214	0.8072	214	0.2723	214	0.2253	214	0.2022
213.5	0.8116	213.5	0.2749	213.5	0.233	213.5	0.2081
213	0.816	213	0.2789	213	0.2384	213	0.214
212.5	0.8201	212.5	0.2816	212.5	0.2431	212.5	0.2199
212	0.822	212	0.2838	212	0.2479	212	0.2277
211.5	0.8237	211.5	0.2821	211.5	0.2534	211.5	0.2327
211	0.8277	211	0.2822	211	0.2605	211	0.238
210.5	0.8299	210.5	0.2838	210.5	0.2666	210.5	0.2437
210	0.8367	210	0.2888	210	0.2727	210	0.2499
209.5	0.8415	209.5	0.293	209.5	0.2764	209.5	0.2572
209	0.8408	209	0.294	209	0.2812	209	0.2622
208.5	0.84	208.5	0.2948	208.5	0.2863	208.5	0.2674
208	0.8372	208	0.2937	208	0.2921	208	0.2737
207.5	0.8447	207.5	0.2974	207.5	0.2998	207.5	0.2834
207	0.8534	207	0.302	207	0.3074	207	0.2917
206.5	0.8542	206.5	0.3062	206.5	0.3154	206.5	0.2984
206	0.8575	206	0.3097	206	0.3201	206	0.3077
205.5	0.8615	205.5	0.3087	205.5	0.33	205.5	0.3127
205	0.8593	205	0.3142	205	0.3389	205	0.3194
204.5	0.8577	204.5	0.3165	204.5	0.3446	204.5	0.3305
204	0.8603	204	0.3153	204	0.3539	204	0.3355
203.5	0.8681	203.5	0.3157	203.5	0.3614	203.5	0.3451
203	0.8667	203	0.3201	203	0.3705	203	0.3573
202.5	0.8618	202.5	0.3224	202.5	0.3753	202.5	0.3644
202	0.8743	202	0.323	202	0.3843	202	0.3677
201.5	0.8774	201.5	0.3249	201.5	0.3946	201.5	0.3759
201	0.8765	201	0.3268	201	0.405	201	0.3879
200.5	0.8881	200.5	0.334	200.5	0.4176	200.5	0.4041
200	0.8951	200	0.3355	200	0.4206	200	0.4172

Table B13: Water quality parameters for samples under different doses of ozone, (a) NOM, (b) HA, and (c) FA.

Organic Compound Type	O ₃ Dose (mg Ozone/ mg DOC)	DOC (mgL ⁻¹)	%DOC Removal	%UV ₂₅₄	SUVA
NOM	0	15±2.0	0	0	3.16±0.21
	0.2	11.94±2.5	20.4	66.85	1.18±0.09
	0.6	10.38±1.5	30.8	81.94	0.82±0.03
	1	9.72±3.0	35.2	90.26	0.47±0.02
HA	0	15±2.3	0	0	5.5±0.32
	0.2	11.25±3.1	25	84.94	1.02±0.05
	0.6	9.75±1.9	35	91.57	0.73±0.03
	1	8.64±2.1	42.4	96	0.51±0.02
FA	0	15±2.5	0	0	4.6±0.72
	0.2	12.22±3.1	18.5	78.13	1.23±0.11
	0.6	10.74±2.0	28.36	88.25	0.75±0.08
	1	10.28±2.5	31.44	93.02	0.45±0.04

Table B14: Ozonation efficiency (Calculation for HA sample)

DOC	Ozonation time (min)	inlet(mg)	outlet(mg)	In-Out(mg)	Applied ozone dose (mgO ₃ /mg DOC)	Applied ozone dose(mg O ₃ /L)	Solubility(mg Liquid/mg Gas)	Equilibrium ozone concentration in liquid	Ozone Residual
15	0	0		0	0.000	0	0.4695	0.000	0
13.8	1	1.7	0.9	0.8	0.053	0.4	0.4695	0.376	0.003
11.25	4	6.8	3.7	3.1	0.207	1.55	0.4695	1.455	0.008
10.5	7	11.9	5.2	6.7	0.447	3.35	0.4695	3.146	0.01
9.75	11	18.7	9.7	9	0.600	4.5	0.4695	4.226	0.018
8.85	15	25.5	13.6	11.9	0.793	5.95	0.4695	5.587	0.033
8.64	20	34	18.9	15.1	1.007	7.55	0.4695	7.089	0.4