

Part 1: Research Objectives

Chapter 1: Problem Statement

Chlorine (Cl_2) is the most common primary disinfectant used in potable water treatment in North America to eliminate pathogenic organisms and prevent infections from waterborne diseases (White, 1999). The application of chlorine disinfection is extremely important to the safety of the public; however, in 1974, Rook discovered the presence of halogenated disinfection by-products (DBPs), namely chlorinated and brominated compounds, such as trichloromethane (TCM) and tribromomethane (TBM), commonly referred to as chloroform (CHCl_3) and bromoform (CHBr_3) (Rook, 1974). Toxicological and epidemiological studies of these, and other halogenated DBPs, have been conducted since the late 1970's to establish the potential health concerns associated with the consumption of drinking water containing these compounds. Toxicological studies have shown that some halogenated compounds, such as THMs, have a negative impact on the health of laboratory animals, causing cancers of the liver, kidney and/or large intestine (Krasner, 2009). Epidemiological studies have concluded that there is a possible concern for the health of an unborn fetus in women who consume waters with chlorinated DBPs over a long period of time (Krasner, 2009; Reif *et al.*, 1996). As a result, the introduction of regulatory standards for some of the halogenated by-products, mainly THMs and haloacetic acids (HAAs), has been applied, or at least suggested, in most developed countries throughout the world. In 1979, the United States Environmental Protection Agency (USEPA) established a national regulation of 100 microgram per liter ($\mu\text{g l}^{-1}$) for Total THMs (TTHM), which was further reduced to 80 $\mu\text{g l}^{-1}$ in 1998 as a regulation in the Stage 1 Disinfectants and Disinfection By-products Rule (USEPA, 2010). In 1996, Health Canada followed the USEPA guideline of 100 $\mu\text{g l}^{-1}$ TTHMs (Health Canada, 1996) and in 2006 added an amendment to the regulation by introducing a guideline for bromodichloromethane (BDCM), however in 2009

Health Canada removed BDCM from the regulated halogenated DBPs (Health Canada, 2006). As a result of the introduction of regulatory standards on THMs, and other halogenated DBPs, numerous investigations into the formation of these compounds in water treatment have been conducted to better understand, control, and meet governmental guidelines.

The formation of halogenated DBPs is largely believed to be a reaction with natural organic matter (NOM), mainly humic substances, found heavily in surface water sources, such as lakes and rivers (Liang and Singer, 2003; Singer, 1999; Rook, 1974;). NOM composition in surface water is extremely complex containing both particulate organic matter (POM) and dissolved organic matter (DOM), which is often measured as dissolved organic carbon (DOC) (Leenheer and Croué, 2003). In the focus of water treatment, POM is largely ignored as it is easily removed during conventional water treatments such as coagulation and filtration (Chow *et al.* 2005). Therefore, DOM is the main focus of THM precursor studies as it is more difficult to remove and remains in the treated water to react with chlorine during chlorine disinfection. DOM is defined as the fraction of NOM that can pass through a 0.45 micrometer (μm) filter and is largely comprised of complex mixture of aromatic and aliphatic hydrocarbons varying degrees of attached amide, carboxyl, carbonyl, hydroxyl, ketone, and various other minor functional groups (Leenheer and Croué, 2003). Due to the complexity of DOM, methods to isolate smaller fractions of DOM have been conducted to better understand the compounds responsible for the formation of DBPs, such as THMs (Leenheer and Croué, 2003). The first standardized DOM fractionation procedure was developed by Leenheer in 1981 which separated DOM into six fractions based on hydrophobicity and acid/base functionality. The six fractions isolated by the Leenheer method are hydrophobic acid (HPOA), hydrophobic base (HPOB) hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPON) compounds using various ionic exchange resins (Leenheer, 1981). The Leenheer

method has been further refined by Aiken *et al.*, Marhaba *et al.*, and others to better separate DOM into the six fractions (Ratpukdi *et al.*, 2009; Marhaba *et al.*, 2003; Aiken *et al.*, 1992). To date, extensive investigations into the fractions of DOM that contain THM precursors have been conducted. The results from many studies suggest the HPOA fraction of NOM, largely comprised of humic material, contains the greatest potential to form DBPs due to the compounds having a high degree of aromaticity (Chow, 2005; Singer, 1999). However, a review paper on DOM fractionation and THM precursors by Chow *et al.* outlines several studies which contest that the hydrophilic fractions contain a greater potential to form THMs, while others conclude that THMs are formed in both the hydrophilic and hydrophobic fractions (Chow, 2005). As a result of the contradicting outcomes of these studies no fraction has been determined to contain all the THM precursors. The likely explanation for the contradicting results in NOM composition is that this is specific to location due to local environmental conditions such as pH, alkalinity, salinity, nutrients, and various hydrological cycles (Leenheer and Croué, 2003). In turn, an estimation of THM formation potential (THMFP) of a particular water body based on literature results is problematic. Therefore, to fully understand the potential for a particular body of water to form THMs it is necessary to conduct a THMFP study on that specific source.

The objective of this research is to determine the composition of DOM, measured as DOC, in two surface water sources in Manitoba, the Red River and Assiniboine River, using a modified Leenheer fractionation method developed by Ratpukdi *et al.* using solid phase extraction (SPE) (Ratpukdi *et al.* 2009). The isolated fractions from each source were evaluated for the THMFP in order to establish which fraction(s) have the greatest concentration of THM precursors. This study will further focus on the removal of DOC at two potable water treatment plants located in Manitoba, the Morris Water Treatment Plant (MWTP) and the Portage la Prairie Water Treatment Plant

(PPWTP). These two water treatment plants use the Red River and Assiniboine River, respectively, as their water sources. Evaluation of DOM removal at these two water treatment plants has provided insight as to which treatment processes in the MWTP and PPWTP are better suited at removing DOC and controlling the formation of THMs.

Part 2: Literature Review

Chapter 2: Natural Organic Matter

2.1 Composition of Natural Organic Matter in Aquatic Environments

Natural organic matter is a heterogeneous mixture of particulate and dissolved organic species. The major difference between the two is that particulate organic matter (POM) is retained on a 0.45 μ m filter while dissolved organic matter (DOM) is that fraction of the total NOM that passes through the filter paper (Chow, 2005; Leenheer and Croué, 2003). From the water treatment perspective POM is largely ignored as it is easily removed during conventional potable water treatment processes (Chow, 2005) such as coagulation, flocculation, and filtration and usually only comprises a small fraction (~10%) of the total organic matter found in natural raw waters (Leenheer and Croué, 2003). DOM, on the other hand, is far more difficult to remove during conventional treatments and therefore will be the focus of this section. DOM can be described as a “*complex mixture of aromatic and aliphatic hydrocarbons that have attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups*” (Leenheer and Croué, 2003). The molecular weight for DOM species can range from small molecules of 100-2000 Daltons to near macromolecule size of ~100,000 Daltons. The concentration of DOM in natural water sources can have a wide range with ground water having as little as 0.1 milligrams per liter (mg l⁻¹) to >50 mg l⁻¹ in a surface waters (Leenheer and Croué, 2003). The overall composition of DOM in natural waters is heavily

influenced by local environmental conditions such as pH, alkalinity, salinity, nutrients, temperature, water depth, turbidity, water flow rate, and many other factors (Chow, 2005). The large degree of environmental influences on the DOM composition in an aquatic environment will result in DOM character that is unique to that specific location.

Researchers have applied strategies to better study the bulk DOM sample of a water source by separating DOM into smaller, more unified fractions that will have similar properties and chemical interactions (Chow, 2005). However, due to the relatively high complexity of DOM, there is no method developed to completely separate DOM into defined fractions and overlap between fractions can occur during a separation method (Chow, 2005). The most common methods for separating DOM into smaller fractions with similar chemical characteristics apply the use of ionic and non-ionic exchange resins (Śweitlik, 2004). The most notable fractionation method that used ionic and non-ionic exchange resins to separate DOM was developed by Leenheer in 1981 (Leenheer, 1981). The Leenheer method used a combination of resins including an Amberlite XAD-8 resin, Bio-Rad AG-MP-50 cation-exchange resin, and a Duolite A-7 anion exchange resin. This method allowed Leenheer (1981) to separate a total organic matter sample in water into the following six fractions based on the hydrophobicity, either hydrophobic (HPO) or hydrophilic (HPI), and acid/base functionality: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPON) components. The HPO fractions are all retained on the XAD-8 resin while the HPI fractions are that which are not contained on the XAD-8 column. The HPI fractions are separated using the Bio-Rad AG-MP-50 column, which retains the HPIB, followed by the Duolite A-7 resin, retaining the HPIA fraction, while the HPIN fraction is that which does not adsorb to any of the three resins (Leenheer, 1981). The HPIN fraction is composed of short chain aliphatic amines, alcohols, ketones, aldehydes, and

esters; <C5 aliphatic amides; carbohydrates and polysaccharides. Short chain (<C5) aliphatic carboxylic acids, polyfunctional carboxylic acids, and hydroxyl acids make up the HPIA fraction, while amphoteric proteinaceous materials such as aliphatic amino acids, amino sugars, proteins and peptides comprise the HPIB fraction. The HPOB fraction is made up of 1- and 2- ring aromatic amines, except pyridine which is a HPIB. HPON compounds are a mix of hydrocarbons such as >C5 aliphatic alcohols, amides, esters, ketones and aldehydes, as well as long chain >C9 aliphatic carboxylic acids and amines. Carboxylic acids and amines with >3 rings are also HPON in nature (Śweitlik, 2004). The HPOA fraction contains humic substances, fulvic acids, C5-C9 aliphatic carboxylic acids, 1- and 2- ring aromatic carboxylic acids, and 1- and 2- ring phenols (Śweitlik, 2004). Humic material can take up nearly 50% of the total organic carbon in surface water sources, as well as terrestrial sediments (VanLoon and Duffy, 2010). Due to the reactive nature of humic matter, as well as the large portion of the total organic composition in aquatic environments, the HPOA fraction is often a major focus of DOM fractionation studies (Jung and Son, 2008; Chow, 2005; Singer, 1999). The formation of humic compounds in nature is poorly understood, however VanLoon and Duffy describe two theories on the formation of humic material (1) the degradative pathway and (2) the synthetic pathway (VanLoon and Duffy, 2010). The degradative pathway suggests that macromolecules, such as carbohydrates and proteins, are removed during microbial activity in the environment. However, biopolymers, such as lignin and cutin, are selectively transformed producing a high molar mass precursor to humin which further degrades, via oxidative reactions, to humic and fulvic acids. On the other hand, the synthetic pathway suggests that the biopolymers degrade to small molecules which repolymerize to form humic matter. The polymerization of these small molecules is achieved through an oxidative polymerization reaction of polyphenols, formed from microbial activities, and oxidative degradation products of lignin

(VanLoon and Duffy, 2010). VanLoon and Duffy suggest that both pathways are capable of explaining the formation of humic matter and that both may be contributing to the formation of humic materials and environmental factors may dictate the formation pathway (VanLoon and Duffy, 2010). The extreme complexity of NOM eliminates the possibility of separating each individual compound leaving bulk fractionation as the most appropriate method to study the chemical reactivity and properties of these compounds.

2.2 Brief History of NOM Fractionation Methods

Many fractionation methods are modifications of methods developed at the US Geological Survey by Leenheer (Leenheer, 1981; Leenheer and Huffman, 1979) and further more by Thurman and Malcolm (Malcolm, 1981), and Aiken *et al.* (1992). These methods utilized a series of ionic and non-ionic exchange resins, namely the XAD 8 resin developed by Rohm and Haas (Rohm and Haas, Philadelphia, Pennsylvania) to separate NOM into hydrophobic and hydrophilic fractions, which are further separated based on acid/base functionality (Leenheer, 1981). In 2003, Marhaba *et al.* developed a method based on the Leenheer model to evaluate the removal of NOM fractions in two water treatment plants (WTPs) that used the same intake source but different treatment methods. This model allowed for fractionation of NOM at smaller concentrations ($<5 \text{ mg l}^{-1}$) that could be used to evaluate DBP precursors (Marhaba *et al.*, 2003). The Marhaba method used three columns of DAX-8 resin, an AG-MP-50 cationic resin, and a WA 10 weak anionic resin. Marhaba *et al.* replaced the Duolite A7 anionic exchange resin with the WA 10 weak anion exchange resin to maintain the Leenheer concept of hydrophobic and hydrophilic NOM (Marhaba *et al.*, 2003). The change in anionic resins was due to bleeding contamination of the Duolite A7 column reported by Day *et al.* who replaced the Duolite A7 column with an AG-MP-1 column (Marhaba *et al.*, 2003), as well as in a quantitative investigation on NOM fractionation conducted by Malcolm and MacCarthy

who replaced the Duolite A7 with an XAD-4 anion exchange resin (Malcolm and MacCarthy, 1992). It has been noted by Aiken and others that the changes made to fractionation procedures may in fact alter the sample or cause contamination of other fractions making it difficult to compare results which use different methods (Chow *et al.*, 2005; Marhaba *et al.*, 2003; Aiken *et al.*, 1992). Often methods are modified to account for a specific objective in a study. Currently, there is no universal fractionation method for NOM that can be applied to all objectives and sample matrices (Marhaba *et al.*, 2003).

Modifications have been made to established methods, such as those by Leenheer, Aiken, and others, to investigate the NOM composition of natural waters, ground waters and wetlands (Aiken *et al.*, 1992), as well as the removal or effects of fractions by water and wastewater treatment processes (Śweitlik, 2004), and in the potential for fractions to form DBPs, such as trihalomethanes and haloacetic acids (Hwang *et al.*, 1999). A recent modification to NOM fractionation of raw and treated waters has been developed by Ratpukdi *et al.* which uses a series of prepackaged solid phase extraction (SPE) cartridges to separate NOM in the six common fractions based on hydrophobicity and acid/base character (Ratpukdi *et al.*, 2009). The fractionation procedure uses three nonpolar Bond Elute ENV cartridges (Varian Inc., Lake Forest, California), one Phenomenex Strata XC strong cation exchange cartridge, and one Phenomenex Strata X-AW weak anion exchange cartridge (Phenomenex, Torrance, California). The sorbent in the Bond Elute ENV cartridges is a modified polystyrene divinylbenzene polymer that is used in the extraction of polar compounds from aqueous solutions. The Strata XC sorbent is a benzene sulfonic acid that retains basic compounds while the Strata X-AW sorbent is a mixture of primary and secondary amines. Functional groups for the sorbents in the three SPE cartridges used in the Ratpukdi method can be found in Figure 1. The Ratpukdi method has several advantages over the earlier resin-based methods. The main advantage

is that the SPE cartridges are prepackaged and do not require long preparatory step for resin clean up. Secondly, the run times for the SPE method is significantly shorter (~12 hours) compared to resin fractionation methods which require roughly 24 hours to complete (Ratpukdi *et al.*, 2009). The development of more rapid and simple fractionation techniques should be explored in order to establish a standardized fractionation method for NOM. A standardized method will allow comparisons between results without having to account for differences due to procedural changes.

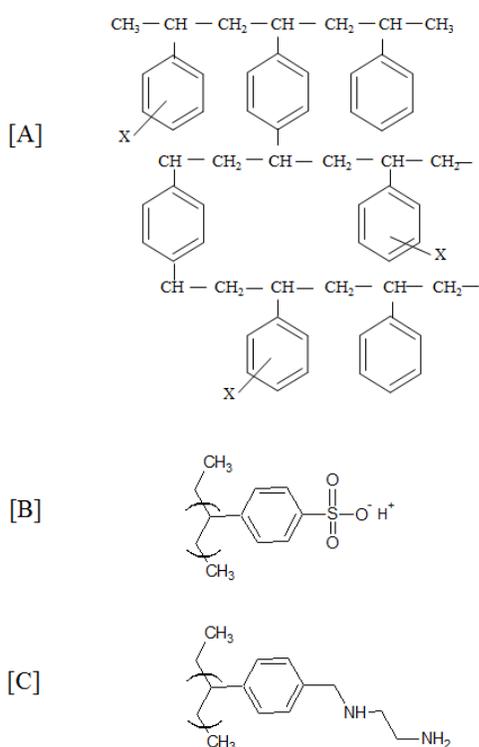


Figure 1: Chemical structures for SPE sorbents used in the Ratpukdi *et al.* NOM fractionation method. [A] Bond Elute ENV-styrene divinylbenzene polymer [B] Strata XC- benzene sulfonic acid [C] Strata X-AW- primary and secondary amines.

2.3 Natural Organic Matter in Potable Water Treatment

Currently, in Canada there is no federal guideline for natural organic matter, often measured as total organic carbon (TOC) or dissolved organic carbon (DOC), in potable drinking water (Health

Canada, 2010). However, water treatment plants (WTPs) remove NOM to meet aesthetic objectives such as color, taste, and odour, as well as to meet regulatory guidelines for halogenated disinfection by-products (Haarhoff *et al.* 2009, Leenheer and Croué, 2003, Singer, 1999). When treating surface water sources high in NOM, potable water treatment plants are faced with several challenges to meet both aesthetic and regulatory objectives. Treatment processes such as chemical coagulation and flocculation, sand and granular activated carbon (GAC) filtration, and more recently developed methods which use membrane filtration and reverse osmosis (RO) are all applied to remove NOM from raw waters. The following section will review major potable water treatment processes applied to reduce the concentration of NOM and control the formation of DBPs in drinking water.

2.3.1 Removal of NOM by Various Water Treatment Processes

2.3.2 Removal of NOM by Coagulation

Conventional chemical coagulation is a treatment technique which commonly uses aluminum (Al [III]), or iron (Fe[III]) based salts to remove turbidity, caused by clays and other inorganic materials, from raw waters (Yigit *et al.* 2009). When metal (Al and Fe) salts are added to water they dissociate forming their trivalent ions, Al^{3+} and Fe^{3+} , respectively. These ions further hydrolyse to form soluble complexes that have an increased positive charge, e.g. $\text{Al}_{13}(\text{OH})_{34}^{5+}$ (Sawyer *et al.*, 2003). The removal of NOM using aluminum or iron salts is achieved through charge neutralization of the largely negatively charged surface of NOM, due to hydroxyl and carboxylic acid functional groups, by the positively charged metal complexes (Matilainen *et al.*, 2010). The charge neutralization destabilizes the surface of NOM allowing smaller particles to coagulate and undergo flocculation (Sawyer *et al.*, 2003). There are several other mechanisms involved in the removal of NOM such as entrapment in the metal complexes, adsorption onto the surface of metals, or

complexation to form insoluble aggregates (Matilainen *et al.*, 2010). The ability of coagulants to remove NOM depends on several factors such as coagulant type, dose, pH and alkalinity of the raw water, temperature, and the chemical composition of NOM found in the water (Matilainen *et al.*, 2010). Therefore, it is important to understand the characteristics of the source water, as well as the coagulant, in order to establish the optimal conditions for the removal of NOM.

For removal of NOM through coagulation, pH and alkalinity of the source water during addition of the coagulant may have the greatest impact on the overall ability to remove NOM and are the major parameters optimized during enhanced coagulation (Matilainen *et al.*, 2010; Yu *et al.*, 2007). The optimal removal of NOM by a given coagulant occurs at a pH where the coagulant has the least solubility forming amorphous solid phase metal-hydroxide complexes (Pernitsky and Edzwald, 2006). For example, alum ($\text{Al}_2(\text{SO}_4)_3$), the most common aluminum-based coagulant, has the lowest solubility at a pH of around 6.0, while ferric salts, such as ferric chloride (FeCl_3) or ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), have an optimal pH range between 4.5 and 6, although the lowest solubility of ferric chloride occurs at about pH of 8.8 (Matilainen *et al.*, 2010; Pernitsky, 2011). The explanation for using ferric chloride at a pH lower than the coagulants minimum solubility is due to the weak positive charge of $\text{Fe}(\text{OH})_2^+$ species (Pernitsky and Edzwald, 2006). The reason for optimal removal at a pH lower than the minimum solubility is that at a lower pH ferric species have a greater positive charge, whereas NOM and other colloids have a less negative surface charge (Pernitsky, 2011). Alkalinity, along with pH, of the raw water will also affect the removal efficiency of chemical coagulants. Surface waters with high alkalinity will have a higher pH (Pernitsky, 2011). This decreases the efficiency of coagulants as more negatively charged species, e.g. $\text{Al}(\text{OH})_4^{1-}$, are formed (Pernitsky and Edzwald, 2006). Also, because alum and ferric salts are acidic they tend to consume large amounts of alkalinity requiring for increased doses of coagulant to reduce the pH and promote

favourable coagulation and flocculation (Pernitsky, 2011). This increase in chemical required to promote the removal of NOM will reflect on the yearly operating costs for the plant.

Polyaluminum coagulants, e.g. polyaluminum chloride (PACl) or polyaluminum sulphate (PAS), have shown promise to replace the classic alum and ferric salts. The production of these coagulants occurs through a controlled reaction with aluminum chloride (AlCl_3) and a base. Polyaluminum coagulants are therefore characterized by the degree of neutralization, or basicity. The resulting reactions with Al and OH during production to form a highly positively-charged tridecameric Al_{13} species, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Matilainen *et al.*, 2010; Pernitsky and Edzwald, 2006). The basicity of the coagulant reduces the consumption of alkalinity and promotes the abundance of polymeric and monomeric species. Also, the optimal pH for PACl has a wider range due to the Al_{13}^{7+} polymer being the major specie found from pH 5 to 7.5 (Pernitsky and Edzwald, 2006). This will allow for greater removal of NOM from typical surface waters that range in pH from 7.5 to 9.

Enhanced coagulation is a standard coagulation process that has been optimized for the removal of NOM to better control DBP formation, as opposed to reducing turbidity such as in conventional coagulation (Matilainen *et al.*, 2010; Freese *et al.* 2001). By means of optimization of the pH and coagulant adjustments, high levels of NOM can be removed thereby reducing the amount of organics in the water prior to chlorine disinfection (Matilainen *et al.*, 2010; Javis *et al.*, 2008; Edzwald and Tobiason, 1999). The USEPA has developed a two-step standard for enhanced coagulation in order to control DBP formation and meet the Stage 1 USEPA DPB Rules. These steps are applied to reduce NOM without the use of unreasonable amounts of coagulant and to be able to enforce the regulatory criteria with minimal costs to the state (USEPA, 1999). Step 1 requires that treatment plants remove a percentage of the total NOM concentration through coagulation which is

determined based on the alkalinity of the source water. This is because it is more difficult to reduce the pH of waters with higher alkalinity to the optimal pH for a given coagulant (USEPA, 1999). This criterion was established to allow for >90% of the treatment plants that use enhanced coagulation to meet the NOM removal limits. This would prevent the requirement of Step 2 which states that if a treatment plant is unable to meet the NOM removal requirements set in Step 1, bench scale jar testing must be conducted to establish optimal removal requirement for NOM. Once defined, the utility is allowed to meet that requirement using any combination of treatment methods (USEPA, 1999).

Although enhanced coagulation is a useful treatment process, Edzwald and Tobiason (1999) have pointed out several problems with the USEPA's approach to enhanced coagulation; (1) Step 2 does not allow for poly-aluminum coagulants or coagulant aids to be used, only Al and Fe salts. The authors point out that poly-aluminum coagulants may be more effective at neutral pH ranges than the Al and Fe salts. (2) The USEPA requires that total organic carbon be tested after settling to determine coagulant dose. Edzwald and Tobiason discuss several short-comings of this approach namely that DOC can make up >90% of the total organic carbon (TOC) and can impact coagulation rather than particulate organic carbon (POC). Selection of coagulant dose based on total rather than dissolved organic carbon may lead to overdosing which can increase costs and production of sludge. Edzwald and Tobiason suggest that DOC measurements be used over TOC when conducting jar tests (Edzwald and Tobiason, 1999). As a result, Edzwald and Tobiason suggest using "optimum coagulation" which they define as "*coagulation conditions of dosages and pH that achieve maximum particle and turbidity removal, maximum TOC and DBP precursor removal, and minimum coagulant dose*" (Edzwald and Tobiason, 1999). The authors believe that this approach to coagulation optimization would account for the short-comings of the USEPA approach.

2.3.3 Removal of NOM by Slow Sand Filtration and GAC Filtration

Slow sand filtration is a simple, inexpensive, and reliable technology for treating water for potable use making it an ideal treatment process for developing countries and rural communities (Moncayo-Lasso *et al.*, 2008; Logsdon *et al.*, 2002; Collins *et al.*, 1992). Although believed to be an older method of water treatment, new interest in slow sand filtration has increased due to its effectiveness at removing viruses, *Giardia* cysts, and *Cryptosporidium* oocysts (Collins *et al.*, 1992). The most notable example of the use of sand filtration to treat water and remove bacteria occurred in 1892 where two cities in Germany, Hamburg and Altona, suffered from a cholera outbreak due to contamination of the River Elbe, the water source for the two communities. Hamburg did not treat the water and only allowed for settling to take place, while Altona filtered the river water before use. As a result, nearly one-third of the population of Hamburg were infected with cholera causing more than 7500 deaths, while Altona had only 328 deaths (Logsdon *et al.*, 2002; Huisman and Wood, 1974). Although slow sand filtration has been successfully applied for the removal of turbidity and harmful bacteria, the removal of NOM by sand filtration in order to control the formation of DBPs has had limited success (Moncayo-Lasso *et al.*, 2008). A study on the removal of NOM by sand filters at three treatment plants by Collins *et al.* (1992) found that NOM removal ranged from 12-33% following sand filtration. Collins also established that hydrophilic components of NOM were less affected by sand filtration compared to hydrophobic compounds. In terms of controlling THM formation, Collins found that the formation of THMs was only reduced by 9-27% by sand filtration (Collins *et al.*, 1992). Therefore, the sole use of slow sand filtration for controlling the formation of DBPs is not recommended. Often, modifications to the slow sand filter, such as media depth or the addition of granular activated carbon or anionic exchange resins, or additional treatment processes,

such as preozonation, are applied along with sand filtration to better remove organics and control DBP formation.

The application of granular activated carbon to slow sand filters has been shown to improve the removal of organics and control the formation of DBPs (Logsdon *et al.*, 2002; Page *et al.*, 1997; Collins *et al.*, 1996). GAC amendments to slow sand filters have been shown to improve the removal of organics by as much as 65% over conventional slow sand filters (Collins *et al.*, 1996). The primary mechanism for the removal of NOM by activated carbon is adsorption in that the GAC (non-polar) has a relatively high attractive force for other non-polar materials, (i.e. more hydrophobic compounds). If the attractive forces of the GAC media are greater than the forces that are keeping the target removal species dissolved in water then the compound will adsorb to the carbon media (Michaud, 1988). On the other hand, compounds that are polar and highly soluble in water are more difficult to remove using GAC. There are several factors that can affect the adsorption of NOM to GAC such as, pore size and type of GAC media, pH, temperature, properties of the contaminant targeted for removal and flow rates (Dastgheib *et al.*, 2004; Michaud, 1988). Temperature of the water will affect NOM removal by GAC filtration. For example, at lower temperatures, organic compounds are less soluble in water and therefore adsorption to GAC media is increased (Michaud, 1998). Properties of the compounds targeted for removal, in this case NOM, can influence the degree of adsorption to GAC media. NOM carries a negative charge at pH values found in typical natural waters due to the presence of carboxylic groups; yet GAC media can have a positive, negative, or neutral surface charge which will affect the electrostatic interactions between NOM and GAC (Velten *et al.*, 2011; Weber, 2004). Pore size of the GAC media is believed to have the greatest effect on the removal of NOM from water. The pore size of GAC that has been reported to have the greatest capacity for NOM adsorption is the mesopores (2-50nm) and is negligible on activated

carbon with a pore size less than 1nm (Velten *et al.*, 2011). Large molecular weight (MW) organic compounds (>10,000 Daltons (Da)) adsorb less to GAC filters due to size exclusion effects, whereas medium MW compounds (500-4000 Da) would adsorb more readily. Large molecular weight compounds are more easily removed by other treatment processes such as coagulation and therefore GAC is tailored to remove medium and lower weight compounds. On the basis of pore size low molecular weight compounds (<500 Da) should be readily removed during GAC filtration. However low molecular weight compounds tend to be more hydrophilic which will influence the adsorption rate (Velten *et al.*, 2011; Dastgheib *et al.*, 2004).

Modifications have been made to GAC media to improve the uptake of NOM and control DBP formation. A study by Dastgheib *et al.* (2004) examined the effects of NOM adsorption onto GAC media with different physical and chemical parameters. The study looked at the NOM adsorption capacity of two common GAC media with different characteristics, F400 (Calgon Corp) and Macro (Westvaco Inc.) which underwent specific modifications: (1) heat treatment under helium or hydrogen flow, (2) oxidation with nitric acid, (3) nitridation under ammonia flow, and (4) iron impregnation. The results from the study found that heat treatment under helium and hydrogen had minimal effects, while oxidation with nitric acid showed a reduction in NOM uptake. This was due to the acidification of the carbon media forming a charged surface which repelled the negatively charged NOM. Ammonia treatment of the GAC media showed an improvement due to the increase in pore size resulting from an etching effect from the ammonia, as well as the addition of nitrogen groups increasing the basicity of the surface. Iron impregnated carbon had mixed results due to the oxidative addition of iron to the carbon causing the surface to exhibit acidic properties. This was resolved with ammonia treatment following iron impregnation to increase basicity and surface area. Therefore, enhanced GAC filtration, i.e. optimization of NOM uptake, should focus on (1) increasing

the basicity of the surface of the activated carbon and (2) increasing mesoporosity (Dastgheib *et al.*, 2004). A potential drawback for the use of activated carbon can be the release of coliform bacteria captured by the GAC media. There is research to suggest that the biological layer that forms on the surface of the activated carbon could provide an optimal environment for growth. Furthermore, the layer could protect the bacteria from disinfectants. If activated carbon particles break off the filter and are able to enter the distribution system, there is potential for transport of pathogenic bacteria (USEPA, 2002).

2.3.4 Removal of NOM by Membranes

A membrane can simply be defined as a thin film separating two phases that allows some physical or chemical components to pass more readily than others and are therefore termed *semi-permeable* (Judd, 2006; Mallevalle, 1996). Membranes operate by taking a feed stream (stream that requires separation) and passing it through the membrane producing two separate streams, the permeate stream and the retentate stream. The permeate stream contains materials or compounds that have effectively passed through the membrane while the retentate stream contains materials that were unable to pass the membrane barrier (Mallevalle, 1996). There are several advantages to the use of membranes to separate or purify solutions. First, membranes can operate at ambient temperatures and do not require phase change. This advantage is exemplified in desalination using membranes compared to distillation. Another advantage with using membranes in water treatment is that separation occurs without the accumulation of materials in the membrane itself. This allows membranes to run continuously without the need for an elution cycle; however, membrane cleaning is required. Lastly, separation does not require the use of chemicals, such as coagulants, in order to achieve separation. This reduces the costs associated with the purchase of chemicals, chemical handling and storage, and chemically generated sludge removal (Mallevalle, 1996). Furthermore,

membranes can shorten treatment trains by eliminating processes such as coagulation, flocculation and sedimentation (Meyn and Leiknes, 2010; Ates *et al.*, 2009). The use of membranes in the treatment of potable water has been applied since the 1980's and has become increasingly popular in the last decade due to improvements in performance and reduction in costs (Ates *et al.*, 2009; Guo *et al.*, 2009).

There are several types of membranes used in the treatment of potable water; the most common are, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis. The most notable differences between the membranes are either pore size, such as with MF and UF, or with mode of operation as found with RO membranes.

Reverse osmosis membrane technology was developed for desalination of seawater to combat the potential water shortage in California in the 1950's (Glater, 1999). RO membranes are currently being used to remove low molecular weight compounds and organics. RO works by applying pressure that exceeds the osmotic flow of water from areas of low solute concentration to areas of high solute concentration. Typically, pressures of 5 – 8 MPa are used in reverse osmosis operations (Aptel, 1996).

Nanofiltration is often regarded as membrane softening resulting from its application in the removal of multivalent ions such as magnesium and calcium. NF is not capable of removing monovalent ions; as a result lower osmotic backpressure is required compared to RO (0.5-1.5 MPa). NF has more recently been used in the removal of organics in water treatment (Aptel, 1996).

Microfiltration and ultrafiltration are referred to as clarification membranes since the primary application is to remove coarse material and macromolecules. The only major difference between MF and UF is in membrane pore size, with MF ranging from 10.0 μm to 0.1 μm while UF ranges

from 0.1 μm to 0.001 μm . Also UF membranes are able to remove viruses and bacteria and can be used for disinfection in water and wastewater treatment (Aptel, 1996).

In order to comply with increasingly stringent water quality guidelines, especially with regards to NOM removal and DBP formation, research into the removal of NOM using membrane technology has increased in the past decade. The applications of membrane filtration for the removal of NOM have been investigated in numerous studies to better understand the influence of membrane technology on controlling DBPs (Meyn and Leiknes, 2010; Ates *et al.*, 2009; Chang *et al.*, 2009; Guo *et al.*, 2009; Kabsch-Korbutowicz, 2008; Schäfer *et al.*, 2004; Schäfer *et al.*, 1998). Although the removal of NOM by NF membranes, as described in Schäfer *et al.* (2004), can have significant variation due to differences in source waters, there are some general trends observed for NOM rejection: (1) hydrophobic NOM fractions appear to be the most readily retained, (2) lower and neutral pH have relatively high NOM removal, and (3) ionic species may promote conformational changes in NOM fractions which could increase rejection (Schäfer *et al.*, 2004). However, membrane composition such as hydrophobicity, pore size, and surface charge can influence the rejection of NOM and NOM fractions (Schäfer *et al.*, 2004). A study by Ates *et al.* (2009), which evaluated the rejection of NOM by different membranes as well as at differing operational conditions, i.e. transmembrane pressure (TMP), found that pore size was not the only mechanism for removal. Ates *et al.* reported that the adsorption on to the membrane surface or particles in the cake layer may also be a mechanism for rejection. Furthermore, Ates *et al.* suggested that constriction of the pore size due to irreversible fouling may also increase the removal of NOM (Ates *et al.*, 2009). In the investigation of the effects of TMP on NOM removal, Ates *et al.* found that at higher TMPs, low molecular weight NOM compounds were more readily removed. Ates *et al.* suggested that when

operating at a higher TMP, the cake layer may be more compact increasing the rejection of smaller compounds that may pass through a less dense layer (Ates *et al.*, 2009).

The use of membranes in water treatment has one major drawback which results from fouling of the membranes over extended periods of use. During membrane operation, materials begin to accumulate near, on, or within the membrane surface resulting in the reduction of permeability (Wiesner, 1996). When the permeate flux drops due to a buildup of materials on the membrane, the system is shut down and cleaned through either hydraulic or chemical methods. The extent to which the pressure returns to normal is termed reversible fouling. Irreversible fouling occurs after the system is cleaned the flux nearly returns to normal showing the extent of reversible fouling. The flux that is not recovered is a result of irreversible fouling. There are two major mechanisms of fouling: (1) precipitative and (2) adsorption. Precipitative fouling occurs when the concentration of sparingly soluble salts in the concentration polarization layer near the surface of the membrane increases to a point where they can no longer stay in a dissolved form (Wiesner, 1996). The species most commonly associated with precipitative fouling are calcium, magnesium, iron, and other metals which precipitate out as either hydroxides, carbonates, or sulfates. Adsorptive fouling is largely due to the deposition of NOM to the surface or pores of the membrane. Several properties of organic matter can determine their tendency to foul membranes including their affinity for the membrane, molecular weight, functional groups, and conformation. The composition of the membrane itself may, in fact, promote adsorptive fouling. Polysulfone, cellulose acetate, and thin film composite membranes are, to some degree, negatively charged. The charged surface of the membrane can repel negatively charged functional groups (eg. COO^-) of humic acids (Wiesner, 1996).

The use of membrane technology for the removal of NOM and DBP precursors is increasing; consequently, numerous studies have been conducted to better understand and prevent fouling from

NOM. However, understanding the mechanisms involved in NOM fouling is especially challenging as it entails physical and chemical interactions between local NOM, the source water, and the membrane itself (Carroll *et al.*, 2000). Typically, many of the studies which evaluate the fouling of membranes by NOM employ fractionation studies to have a more clear idea which fraction, or fractions, impact the function of membranes and reduce expected lifetimes. However, there are conflicting results as to which NOM fraction has the greatest propensity to foul membranes. Carroll *et al.* (2000) investigated the rates of fouling of a polypropylene hollow-fiber membrane by NOM which was fractionated based on hydrophobicity and charge (see Figure 2).

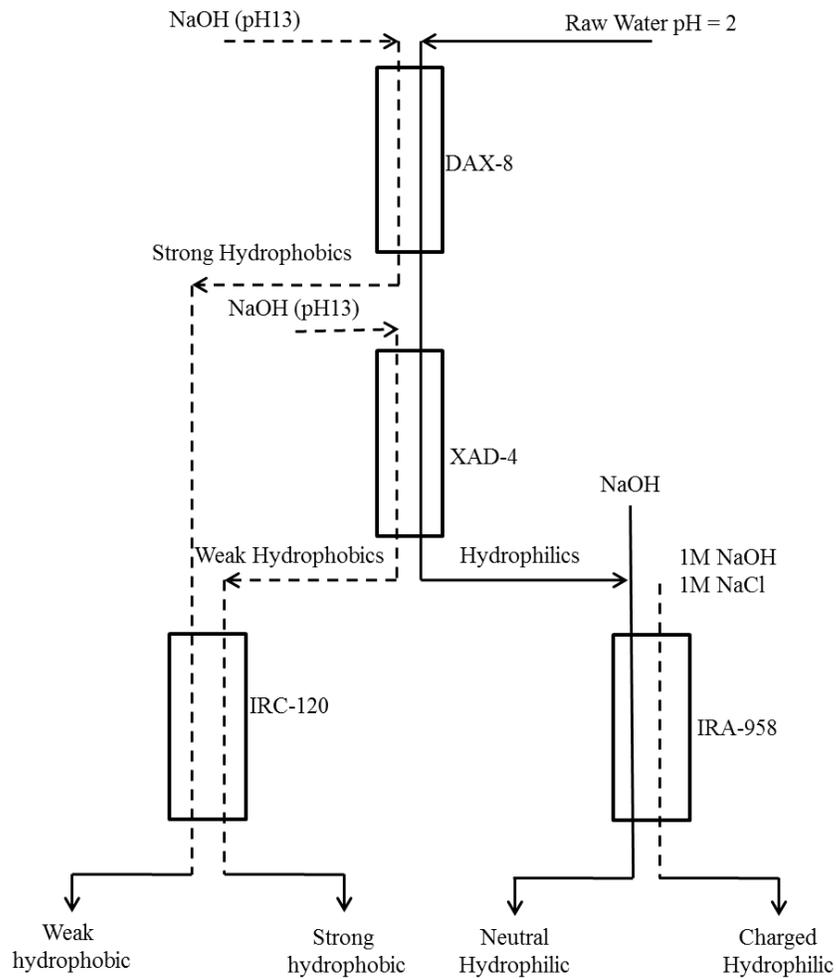


Figure 2: Fractionation method by Carroll *et al.* (2000). Figure adapted from Carroll *et al.*, 2000.

The Carroll *et al.* study found that the neutral hydrophilic fraction of NOM, collected from the Moorabool River, had the greatest rate of fouling compared to the hydrophobic and charged hydrophilic fractions (Carroll *et al.*, 2000). Linhua *et al.* (2001) evaluated the rate of fouling of two polyvinylidene fluoride (PVDF) membranes, one hydrophobic and the other modified to have a hydrophilic surface. The Linhua *et al.* study showed similar results of the Carroll *et al.* study with the hydrophilic neutral causing the greatest fouling of the fractions evaluated. It was suggested that the presence of high molecular weight compounds in this fraction was contributing to the decline in membrane flux. However, Linhua *et al.* found that hydrophobic acid compounds caused greater flux decline than the transphilic acids due to the large molecules found in the hydrophobic acid fraction along with the adsorption of hydrophobic compounds to the membrane surface, which also happened to be hydrophobic (Linhua *et al.*, 2001). Kwon *et al.* (2006) found similar results to the Carroll *et al.* and Linhua *et al.* studies with hydrophilic neutral having the greatest fouling potential for negatively charged membranes. The Fourier-Transform infrared spectroscopy (FTIR) results from the Kwon *et al.* study found that there was a significant reduction of carbonyl and aromatic character of NOM fouled membranes and an increase of *N*-acetyl groups, i.e.) carbonyl and amide groups, which are indicative of hydrophilic neutral compounds such as amino sugars and polysaccharides (Kwon *et al.*, 2006). Kweon and Lawler (2005) investigated the extent of fouling on ultrafiltration membranes by different polysaccharides. This study concluded that dextran had a different fouling profile compared to alginic acid. Dextran was found to rapidly reduce flux through the membrane but eventually maintained a stable flux, while alginic acid showed continuous flux decline during operation. Scanning electron microscope (SEM) analysis found that dextran formed a large single deposit attributed to organic deposition while alginic acid induced fibrils in extended coils. The shape of the coils suggested a high charge density and subsequent electro-static repulsion (Kweon and Lawler,

2005). Although the results from the Kweon and Lawler study do not fully explain the cause for different fouling from the two polysaccharides, they do provide further evidence that different organic compounds foul membranes in different manners, even within a similar group. On the other hand, several studies have suggested the hydrophobic NOM fraction contains the greatest potential to foul membranes. Nilson and DiGiano (1996) investigated the effects of hydrophobic and hydrophilic NOM fractions on the performance of a hydrophilic sulfonated polysulfone nanofiltration membrane. The Nilson and DiGiano study found that hydrophilic compounds did not reduce permeate flux compared to the hydrophobic compounds. This study also suggested that the hydrophilic fraction was poorly rejected by the NF membrane. Nilson and DiGiano further concluded, that in a water treatment scenario, the results suggest membrane filtration of source waters high in hydrophobic NOM would require more cleaning to maintain permeate flux however NOM rejection would be greater. The authors suggest that membranes similar to those used in the study could be used to control the formation of DBPs as the hydrophobic component of NOM generally has a high disinfection by-product formation potential (Nilson and DiGiano, 1996).

When analyzing membrane-NOM fouling studies, such as the ones described above, the results presented should be taken with caution. Most of the studies reviewed here use different membranes with varying characteristics, i.e.) pore size, membrane charge, membrane composition, and different water sources which can influence the results of the studies. For example, Nilson and DiGiano found that hydrophobic compounds caused a greater flux decline in a hydrophilic sulfonated polysulfone membrane while Carroll *et al.* found that hydrophilic compounds fouled the hydrophobic PVDF membrane more readily. Therefore, Nilson and DiGiano suggest that the results from their study should be used in comparison to membranes similar to the ones they tested (Nilson and DiGiano, 1996). Likewise, Kweon and Lawler only used two model polysaccharides in their study

which would suggest only a limited number of conclusions can be made due to a small range in sample set. Therefore, when comparing membrane fouling studies, evaluation of not only NOM characteristics in the source water but also of membrane composition and operating parameters should be conducted.

Chapter 3: Trihalomethanes

3.1 Formation of Trihalomethanes from NOM

The formation of chlorination disinfection by-products in natural waters from the reaction of hypochlorous acid with NOM was first discovered by Rook in 1974. Rook suggested that, “*the natural polyhydroxybenzene building blocks of the natural color of water molecules are responsible for the haloform reaction*”, which Rook believed was believed to largely be due to the humic fraction of NOM (Rook, 1974). The following year Rook provided further evidence that humic matter was the major precursor to halogenated DBP formation by investigating the formation of chloroform from model compounds of fulvic acid (Rook, 1977). Rook believed that hydroxylated aromatic rings with two free *meta* positioned OH-groups could be an available reaction site for haloform formation. Boyce and Hornig (1983) further examined the effects of pH and reactant concentrations on formation pathways of THM formation from dihydroxyaromatic compounds used to model humic acids. The results found that 1,2-dihydroxybenzenes formed appreciable amounts of chloroform and bromoform at neutral and alkaline pH, however the formation of THMs from 1,2- and 1,4-benzenediols only occurred at acidic pH (pH=4) (Boyce and Hornig, 1983). The decline in chloroform production at highly basic pH (pH 11-12) suggests that other mechanisms may be competing with the proposed haloform mechanism pathway. Boyce and Hornig suggest that the formation of intermediates haloform precursors may not occur as rapidly from the hypochlorite anion

(ClO⁻), the dominant form of chlorine at basic pH (pK_a = 7.5 at 25°C), compared to hypochlorous acid (HOCl) (Boyce and Hornig, 1983). Furthermore, the authors suggest that at acidic pH HOCl participates in electrophilic substitution and addition reactions, while at neutral and basic pH chloroform is produced via hydrolysis reactions (Boyce and Hornig, 1983). Boyce and Hornig provided a more extensive reaction pathway for the formation of chloroform from 1,3-dihydroxyaromatic structures showing possible intermediates.

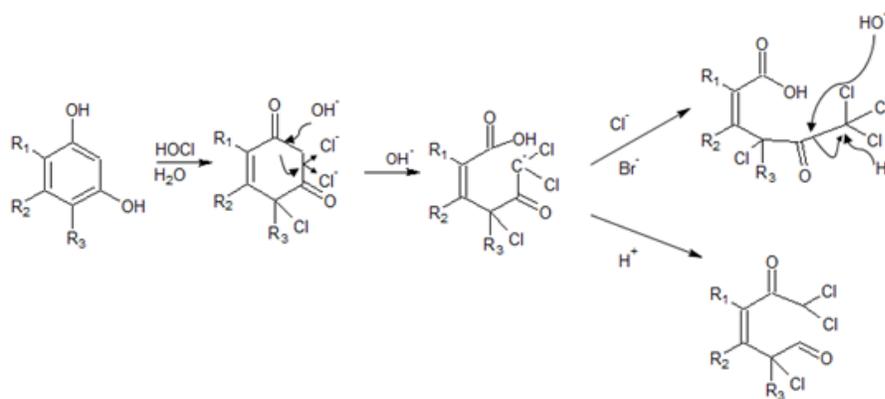


Figure 3: Proposed degradative pathway of fulvic acids and resorcinol (Adapted from Rook, 1977)

In 1990, Reckhow, along with Singer and Malcolm, analyzed ten different yet well characterized humic and fulvic acid samples from five water sources for their halogenated by-product formation potential. This group wanted to establish a relationship between halogenated by-product formation potentials and the fundamental properties of different humic sources. The ten samples of humic and fulvic acids ranged from 30-35% aromatic character for humic acids and from 14-17% for the fulvic acids. All samples were shown to have varying degrees of molecular size, acidic groups and specific UV absorbance at 254nm and 400nm (Reckhow *et al.*, 1990). The Reckhow, Singer and Malcolm study found that each sample formed significantly different concentrations of halogenated by-products for the same concentration of total organic carbon (10mg/L) of each humic and fulvic

acid sample. Furthermore, the results found that in all five sources the humic acid fraction formed greater concentrations of all halogenated by-products studied compared to the fulvic acid fraction from the same source. This group further reported that, in general, the activated, i.e.) ring containing an electron donating group, electron-rich aromatics have a greater propensity to react with chlorine and that humic matter rich in activated aromatic centers will react to a greater degree (Reckhow *et al.*, 1990). Reckhow *et al.* applied the relationships between chlorine consumption and % aromatic carbon, activated aromatic rings ($\mu\text{M}/\text{mg-C}$), and phenolic-OH ($\mu\text{eq}/\text{mg-C}$) to formulate an equation (Eq. 1) to represent the formation of total organic halides (TOX) from the amount of activated aromatic rings (Act Ar-R) (Reckhow *et al.*, 1990).

$$TOX^{corr} (\mu\text{g}/\text{mg C}) = 50 + 85[\text{Act Ar} - R] \quad \text{Eq.1}$$

This equation presented by Reckhow, Singer and Malcolm provided excellent agreement ($r^2=0.96$) for the fulvic acids however the relationship was different for humic acids. This group also established a relationship of THM formation potential based on the observation that ~20% of the incorporated chlorine, or TOX, formed chloroform. As a result the group suggested Eq. 2 could be used as an estimation of THMFP based on multiplying Eq.1 by 0.2.

$$THMFP (\mu\text{g}/\text{mg C}) = 10 + 17[\text{Act Ar} - R] \quad \text{Eq.2}$$

The work conducted by Reckhow, Singer and Malcolm put forward that the calculations suggest, but do not prove, that most of the chlorine consumption is due to the reaction with activated aromatic structures (Reckhow, Singer and Malcolm, 1990).

Chiadou *et al.* (1999) studied the formation of chloroform from a series of organic compounds ranging from straight chain aliphatic compounds, such as hexane, to ring and phenolic structures, for example benzene and resorcinol (Chiadou *et al.*, 1999). Chaidou *et al.* found that all

compounds used in the study formed chloroform in the parts per million (ppm) range with resorcinol and phloroglucinol forming the highest concentration of chloroform with 11ppm and 13ppm, respectively. Chaidou *et al.* determined that the formation of chloroform from substituted phenols was not affected by the numbers of chlorine or hydroxyl moieties, but by their position on the phenolic compound (Chaidou *et al.*, 1999). These results provided further evidence that the hydroxylated aromatic rings, such as those described by Rook, Boyce and Hornig, had the greatest potential to form THMs, mainly chloroform. However, the results from the Chaidou *et al.* study also suggested that other organic compounds were capable of forming significant amounts of chloroform.

As a result of the significant discovery by Rook and others much focus has been directed to establishing the link between the humic fraction of natural organic matter and the formation of DBPs, such as THMs. However, due to the complexity of NOM, researchers have employed NOM fractionation techniques to better understand the formation of these by-products from other fractions of natural organic matter.

One such study was conducted by Hwang *et al.* (1999) looked at the THMFP from samples of the Colorado River. This river is characterized as having low organic concentration with 50% non-humic DOC and low specific UV absorbance (Hwang *et al.*, 1999). Hwang *et al.* fractionated DOC samples from the Colorado River followed by chlorination to establish which fraction of the river contributes to the formation of halogenated DBPs. When comparing the yields for the total THMs formed from the DOC fractions, the hydrophilic acid and neutral fractions produced the highest concentrations of THMs. Hwang *et al.* also found that the nine haloacetic acids measured in the study formed greater concentrations from the hydrophilic acid and neutral fractions than the hydrophobic one. Furthermore, Hwang *et al.* reported that the hydrophilic neutrals, although did not yield high concentrations of THMs, formed a significant amount of HAAs. The conflicting results

(i.e. hydrophilic NOM forms greater concentrations of THMs) from the Hwang *et al.* study suggest that the removal of both the hydrophobic and hydrophilic fractions of NOM need to be addressed to prevent the formation of halogenated DBPs (Hwang *et al.*, 1999). Marhaba and Van (2000) found similar results to that of the Hwang *et al.* study when analysing the THMFP of NOM fractions collected from the Passaic River in New Jersey (Marhaba and Van, 2000). Like the Colorado River, the Passaic River was found to have a greater degree of hydrophilic content (~71%) than hydrophobic. The results for the THMFP for each fraction obtained from the Passaic River found that almost 70% of the total THMs formed was from the hydrophilic acid fraction, not the hydrophobic as prominently reported in literature. However, the Marhaba and Van results for HAA formation differed from the Hwang *et al.* study in that the hydrophobic fraction formed nearly 83% of the total HAA formation while the hydrophilic fractions formed more HAA in the Hwang *et al.* study (Marhaba and Van, 2000; Hwang *et al.*, 1999). Marhaba and Van suggested that even though all fractions formed THMs removal of the hydrophilic fraction of NOM from this source could manage the formation of THMs and meet current and future regulations (Marhaba and Van, 2000). However, targeting the removal of the hydrophilic fraction of NOM would not address the formation of HAAs. Marhaba and Van suggest targeting the removal of the hydrophobic neutral fraction of NOM from the Passaic River would prevent the formation of roughly 53% of the total HAAs (Marhaba and Van, 2000).

The contradictory results from the studies described above, as well as others not mentioned here, may be a result of several factors. First, the fractionation methods used by each group, although many based on the original Leenheer method, alter the fractionation procedure to meet the objectives of the study. For example, when comparing the results from two studies which report contradicting results, one must consider the fractionation procedure used to isolate NOM fractions. In a review

study of NOM fractionation and THM formation by Chow *et al.* (2005) several potential issues were stated when comparing fractionation studies. Chow *et al.* suggested because there is no standard method to isolate NOM fractions, alterations to the fractionation procedure, such as the use of alkaline agents compared to deionized water, may alter the reactivity of the isolated NOM to THM formation. Furthermore, Chow *et al.* mention that the separation of NOM by fractionation methods is not sharply defined, in that some NOM under certain conditions may pass through a resin in waters with low specific UV absorbance, while in waters with high UV absorbance the same compounds may adsorb. The use of different resins to isolate NOM may also affect the fractionation of NOM. For instance, the XAD-8 resin used by Leenheer in his original fractionation method has been discontinued and subsequently replaced by many groups with the Superlite DAX-8 resin (Carroll *et al.*, 2000; Marhaba *et al.*, 2000; Marhaba *et al.*, 2003). Although the resins both isolate the same fraction in relatively equal quantities, the composition of the fraction has been found to vary slightly (Chow *et al.*, 2005). Not only do the differences in fractionation procedures make it difficult to compare different NOM and THMFP studies, the constituents in the sample water and THMFP methods may also affect the results. Constituents such as bromine and organic nitrogen may affect the formation of brominated species and the formation of other DBPs (Chow *et al.*, 2005).

The differences in NOM fractionation results seen by many research studies suggest a need for a standard method for fractionating NOM or in isolating THM precursors. The presence of THMs in drinking water, along with the increasingly stringent regulatory standards for these compounds (i.e. USEPA suggests that allowable THM concentrations may be reduced from 0.080mg/L to 0.040mg/L (Marhaba and Van, 2000)) suggest there is a need to establish a standardized procedure for the fractionation and isolation of THM precursors and subsequent chlorination of the samples to determine the THMFP. The development of such a method would

allow for practical comparisons between studies on different water bodies. This would allow for better control and reduction of halogenated disinfection by-products, as a result of better understanding as to what compounds form by-products to a greater degree, as well as what treatment processes can be applied to remove the precursors from water prior to chlorine disinfection. Currently, there is no such method.

3.1.2 Relationship between THMs and Specific UV Absorbance

Specific UV₂₅₄ absorbance (SUVA) has been used as a good indicator for estimating the potential for raw surface waters to form THMs (Singer, 1999). This is because it is generally believed that there is a relation between the amount of aromaticity in the raw water, measured at 254 nm, and the reactivity towards THM formation. However, SUVA is an indication of aromatic content and there are conflicting beliefs as to its effectiveness to estimate THM formation. Chow *et al.* evaluated the THMFP and the relationship to DOC concentration and SUVA₂₅₄ for three organic carbon sources; soil, fecal and aquatic. Their results show that although the DOC concentration was linearly correlated with THMFP for all three samples, there was a difference seen with THMFP and UV₂₅₄ in regards to sample type. The aquatic and soil sample were found to have similar relationships to THM formation and DOC concentration, however the fecal sample did not follow the same trend. However, the aquatic and soil samples were similar in terms of THMFP and UV₂₅₄ even though were different in terms of formation potential and DOC concentrations. The authors suggest that this is evidence that SUVA is not always a good indicator of THMFP (Chow *et al.*, 2008).

In a United States Geological Survey (USGS) study that evaluated the relationship between THMFP, UV absorbance, DOC content and percent aromaticity of DOC in samples collected from the Delta, which refers to the Sacramento-San Joaquin Delta in California, and National Water

Quality Assessment (NAWQA) Program, data sets. The NAWQA was started in 1991 by the USGS to collect and interpret data on national surface and ground water in order to . The results from these two data sets found high linear correlations between DOC and UV absorbance less than 400nm between (Fram *et al.*, 1999). However, the two regressions were distinctly different with the Delta samples having a shallower slope. This indicated that DOC present in the Delta samples had DOC with a higher UV absorbance than the NAWQA samples. The authors suggest that this is consistent with the presence of organics derived from peat, which has a higher content of phenolic structures, found in the Delta samples (Fram, 1999). Furthermore, the regression for the THMFP and UV absorbance is again shallower for the Delta suggesting that although there is higher content of aromatic structures in the Delta samples, they are less reactive to chlorination (Fram, 1999). These results suggest caution should be taken when estimating the formation of THMs from specific UV₂₅₄ absorbance.

3.2 Health Concerns Associated With THMs

Regulatory standards for the presence of trihalomethanes in finished drinking water have been set by many governmental and water governing agencies. This section will review the current guidelines and regulations, as well as the future limits for these compounds. To provide an understanding of the limits set by governing bodies this section will first provide health concerns that were used in the determination of guideline limits.

3.2.1 Health Concerns Associated With Trihalomethane in Drinking Water

Since the discovery of chloroform and other halogenated by-products in the early 1970's, many studies on the health concerns with the presence of trihalomethanes in waters. Due to the high volatility of these compounds humans can uptake THMs via ingestion, inhalation, or dermal exposure

though activities such as swimming in a pool or bathing (Nieuwenhuijsen *et al.*, 2009). However, much of the research focus has been on exposures through ingestion of potable water disinfected with chlorine. Furthermore, significant research into the carcinogenic and reproductive effects from chloroform exposure has been conducted. In 2006, Health Canada stated that, “*studies conducted prior to 1993 that explored the associations between and adverse health outcomes often had limitations, particularly in the area of exposure management* (Health Canada, 2006)”. Since then improvements in the estimation of exposure of THMs to a person or population has been made, therefore this chapter will focus mainly on studies post-1993 regarding the health effects associated to THM exposure.

3.2.2 Carcinogenic Effects

In 1996, King and Marrett published a study looking at the relationship between chlorination by-products and bladder cancer (King and Marrett, 1996). Their study included estimating the exposure of chlorinated DBP, measured as THM concentration, for 696 cases of bladder cancer diagnosed from 1994-1996. The study used an exposure assessment which included an evaluation of exposure of a specific individual to THMs via ingestion of cold and hot water, as well as the use of bottled versus tap waters. The assessment also included determining confounding variables such as history of smoking and diet in order to evaluate individuals that may have had other causes to bladder cancers. Water treatment data over a 40 year period was used to estimate the exposure of a person to THMs. From this, King and Marrett concluded that long term exposure (>35 years) to THMs increased the risk of developing bladder cancer by 1.63 times compared to those exposed to THMs at the same concentration for less than 10 years. Furthermore, risk seemed to increase with increasing concentrations of THMs (i.e. risk was greater for individuals that consumed waters with THM concentrations of 50 µg/L compared to 25 µg/L) (King and Marrett, 1996). Villanueva *et al.* (2004)

reported similar results to that of King and Marrett in that exposure of chloroform increase the odds of getting bladder cancer, but only found this relationship in men (Villanueva *et al.*, 2004).

In 2002, Lévesque *et al.* published a paper that looked at the household exposure of chloroform through inhalation. This study examined the inhalation of chloroform during showering. The results found that after a 10 minute shower the chloroform concentration in the alveolar air (air that is exhaled from the lungs) was 6 times greater than basal levels. Additionally, it took over 30 minutes for basal levels of chloroform to return. A second objective of the Lévesque *et al.* study was to estimate the concentration of metabolites bound to the hepatic (liver) and renal (kidney) over a 24 hour period following inhalation exposure due to showering, as well as multiroute exposure scenarios (ingestion of water, indoor air and showering). The results estimated that about 0.01 µg/L of chloroform metabolites can be found on both the liver and the kidney. Multiroute exposures were estimated to increase the concentrations of metabolites on the liver and kidneys by 10 and 5 fold, respectively (Lévesque *et al.*, 2002). Although these chloroform levels are below those that have been shown to cause liver tumors the results suggest that exposures to chloroform other than liquid ingestion can occur. In 2005, Do *et al.* evaluated the risk of chlorination disinfection by-products and pancreatic cancer and determined there was no evidence supporting increased risk (Do *et al.* 2005).

Though there seems to be a relation between ingestion of chloroform and bladder cancer (King and Marrett, 1996; Villanueva *et al.*, 2004), there is limited evidence to suggest that exposure to chlorinated DBPs can be associated with other cancers such as liver, kidney, brain, lung, breast, and pancreatic (Nieuwenhuijsen *et al.*, 2009). As a result, the International Agency for Research on Cancer (IARC) has classified chloroform as a Group 2B carcinogen which is defined as possibly carcinogenic to humans based on limited evidence (WHO, 2008). Bromoform and dibromochloromethane have been classified by the IARC as Group 3, or not classifiable as to its

carcinogenicity to humans. Bromodichloromethane follows the same classification as chloroform, Group 2B, due to carcinogenic effects in mice and rats (WHO, 2008).

3.2.3 Reproductive Effects

Not only are the carcinogenic effects of THMs of concern, there have been many studies examining the impact on fetal and human development resulting from exposures to chloroform and other THMs. In 1992, Kramer *et al.* published the first study which evaluated the negative effects of THMs. The study mainly focused on chloroform due to previous studies which demonstrated negative fetal development in mice, on intrauterine development in humans. The study evaluated 151 towns; each town was supplied by a single water source (i.e. a single source from surface water or from ground water with a single aquifer). Chloroform was found to range from 0-350 µg/L with no chloroform detected in 45.7% of the municipalities, while 41.7% had concentrations of 1-9 µg/L and only 12.6% had concentrations exceeding 10 µg/L. The results from the Kramer *et al.* study found that risk associated with chloroform on intrauterine growth retardation increased 80% in sources that contained ≥ 10 µg/L chloroform, while intermediate chloroform levels showed a 30% increase. A study the following year that examined the relationship between drinking water quality and adverse pregnancy outcomes established that the outcomes for women who consumed chlorinated, rather than chloraminated, surface waters showed a 2.2-fold increase in stillbirths and a 1.5 fold increase in major malformations (Aschengrau *et al.*, 1993). In 1996, Reif *et al.* reviewed studies which focused on the consumption of chlorinated waters and adverse reproductive effects. Reif *et al.* suggest that the Kramer *et al.* and the Aschengrau *et al.* studies, as well as others, suffer from methodological problems that make it difficult to interpret the results. Reif *et al.* points out that each study used different methods of classification of exposure to THMs, such as measuring chloroform only as opposed to THMs or use of chlorine compared to chloramination. Reif *et al.*

conclude by suggesting a series of short term projects to strengthen previous studies and direct new ones (Reif *et al.*, 1996).

An important issue to consider regarding epidemiological studies that measure chloroform alone is that chloroform may not be a good surrogate to measure the risk to cancers and other health issues. The metabolism of DBP will vary and in turn the risks associated with exposure, therefore analysis of multiple chlorination DBPs, (i.e. HAAs), should be conducted to have a better judgement of risks associated with chlorine disinfection (Nieuwenhuijsen *et al.*, 2009). Water sources high in natural bromine or iodine can form brominated DBPs which are suspected of having greater toxicity than chlorinated ones (Richardson, 2005).

3.3 Current Regulatory Standards for Trihalomethanes

3.3.1 World Health Organization

The World Health Organization (WHO), in 1958, published its first document which specifically dealt with drinking water quality titled *International Standards for Drinking-water*. This document was later revised under the same title however none of these documents gave a guideline limit for individual or total trihalomethanes (WHO, 2004^A). In 1984, the WHO published the first edition of the *Guidelines for Drinking Water Quality* (GDWQ) which did not provide a guideline limit for total THMs but did provide a limit of 0.03 mg/L for chloroform due to chloroform being the most common by-product found in water supplies (WHO, 2004^B). In 1993, the second edition of the GDWQ again did not provide a guideline for total THMs, however did set limits for the following four: chloroform, bromoform, bromodichloromethane (BDCM) and dibromochloromethane (DBCM). Bromoform and DBCM had a guideline of 0.1mg/L, while BDCM and chloroform has

limits of 0.06mg/L and 0.2mg/L, respectively. For authorities wanting to enforce a total THM limit, the WHO suggests the following fractionation approach to determining the limit (WHO, 2004^B):

$$\frac{C_{chloroform}}{GV_{chloroform}} + \frac{C_{Bromoform}}{GV_{Bromoform}} + \frac{C_{BDCM}}{GV_{BDCM}} + \frac{C_{DBCM}}{GV_{DBCM}} = \leq 1 \quad \text{Eq.3}$$

In the recent release of the fourth edition of the *Guidelines for Drinking Water Quality*, the limits for individual THMs have remained the same, except for chloroform which was increased from 200µg/L to 300µg/L (WHO, 2011). The WHO provided a total daily intake (TDI) for three of the four THMs; chloroform (15µg/kg body weight), bromoform (17.9 µg/kg body weight), and DBCM (21.4 µg/kg body weight) (WHO, 2011). The guideline limits are derived using 75% of the TDI for chloroform, 20% from bromoform and DBCM, using a 60kg adult and consuming 2 liters of water per day (WHO, 2011). Although the WHO mentions routes of exposure other than water consumption, the WHO does not specify if those routes impacted the development of the current guideline. The reasoning provided by the WHO for the guideline limits of the four monitored THMs is largely based on the possible carcinogenic properties in the Group 2B compounds, (i.e. chloroform and BDCM), and the fact that bromoform and DBCM show carcinogenic properties in laboratory animals (WHO, 2011).

3.3.2 United States Environmental Protection Agency

In 1974, the United States Congress passes the *Safe Drinking Water Act* (SDWA) which authorise the USEPA to set national health based standards for drinking water. The original SDWA focused primarily on providing safe drinking water at the tap. However, later amendments to the act included regulations on source waters, operator training, and funding for water quality improvements. In 1979, the USEPA set a *Total Trihalomethane Rule* which set a maximum contaminant level (MCL) of 0.1 mg/L for the sum of all four THMs taken as a quarterly average (USEPA, 1998). In

1996, the USEPA set forth an *Information Collection Rule* (ICR) which was designed to monitor treatment information to better aid in designating future regulations regarding disinfectants and disinfection by-products. The ICR was used to establish the *Stage 1 Disinfectants and Disinfection By-product Rule* (Stage 1 D/DBPR), in 1998 (USEPA, 1998). The Stage 1 D/DBPR established new and updated existing MCLs for many chlorination by-products, such as THMs and HAAs, as well as maximum residual disinfectant levels for three chemical disinfectants, chlorine, chloramine, and chlorine dioxide (USEPA, 2001). Treatment systems servicing >10,000 people were required to comply with this new rule by January 1, 2002, while smaller systems were required to meet the new regulations by January 1, 2004. Table 3 outlines the maximum residual disinfectant level goals (MRDLG), maximum contaminant level goals (MCLG), and MCLs set in the Stage 1 D/DBPR (USEPA, 2001).

Table 1: USEPA Stage 1 Disinfectant and Disinfection By-product Rule guidelines for chlorine disinfectants and THMs (Table values found in USEPA, 2001).

Disinfectant Residual	Maximum Residual Disinfectant Limit (mg/L)	Compliance Based On
Chlorine	4 (as Cl ₂)	Annual Average
Chloramine	4 (as Cl ₂)	Annual Average
Chlorine Dioxide	0.8 (as ClO ₂)	Daily Samples
Disinfection By-Products	Maximum Contaminant Level (mg/L)	Compliance Based On
Total THMs	0.08	Annual Average
HAA5	0.06	Annual Average
Chlorite	1.0	Monthly Average
Bromate	0.01	Annual Average

On January 4, 2006 the USEPA finalized the Stage 2 DBPR, which was part of a series of rules referred to as the *Microbial-Disinfectants/Disinfection By-product Cluster* (M-DBP Cluster). This rule not only aimed to minimize health risks associated with microbial pathogens but also the risks associated with disinfectants and DBPs (USEPA, 2007). A few key additions to the Stage 2 rule include an Initial Distribution System Evaluation (IDSE) which requires the identification of monitoring locations for DBPs, mainly THMs and HAAs. Also, the use of locational running annual average is required for each of the established monitoring locations from the IDSE. This is a significant change to the Stage 1 rule which used a system wide running annual average which does not require that the average be met at each location. Stage 2 rules also require that systems which are found to exceed the guidelines for DBPs must conduct an operational evaluation in order to establish

problematic treatment processes (USEPA, 2007). The new MCL implemented in the Stage 2 DBPR are found in Table 3:

Table 2: Summary of the Stage 2 Disinfection By-products Rule maximum concentration level guidelines (Table values found in USEPA, 2007).

Contaminant	MCL Guideline (mg/L)
Bromodichloromethane	zero
Bromoform	zero
Bromate	zero
Chlorite	0.8
Chloroform	0.07
Dibromochloromethane	0.06
Dichloroacetic Acid	zero
Monochloroacetic Acid	0.07
Trichloroacetic Acid	0.02

The USEPA provide a number of quantified and non-quantified health benefits to the implementation of the Stage 2 DBPR, such as the reduction of an average of 103-541 cases of bladder cancer related to consumption of high DBPs. Furthermore, the potential reduction in adverse fetal and reproductive developmental effects would also be minimised by the Stage 2 DBPR (USEPA, 2007). As for non-health related issues, the USEPA estimates that consumers will feel more safe about drinking tap water and will avoid purchasing bottled water. Likewise, the Stage 2 DBPR will address issues such taste and odour associated with disinfectants which will further reduce the need for bottled water (USEPA, 2007).

Compliance of the Stage 2 DBPR will take place in April, 2012 for systems serving >100,000 people, while smaller systems must be in compliance with the new regulations before October, 2013 (USEPA, 2007).

3.3.3 Health Canada

Canada issued its first regulations for drinking water quality standards, published in 1968, entitled *Canadian Drinking Water Standards and Objectives*. In 1978, a more comprehensive document, the *Guidelines for Canadian Drinking Water Quality* (GCDWQ), was published that evaluated the 1968 standards, as well as emerging concerns. Although subsequent editions were published, the first guideline for THMs was not established until the 6th edition in 1996 (Health Canada, 1996). In this document, Health Canada and the Federal-Provincial subcommittee on Drinking Water set a guideline limit of 0.1mg/L for total THMs (Health Canada, 2006). This guideline was set as a running quarterly average and is based upon the fact that optimized treatment systems should be able to reduce THM precursors allowing for total THM concentrations to be below the guideline. Furthermore, the lifetime risk of cancer is low, or essentially negligible, for consumption of drinking waters below 0.1mg/L. The guideline of 0.1mg/L for total THMs is an interim maximum allowable concentration (IMAC) meaning that there is insufficient data to derive a MAC within reasonable certainty and therefore compounds that are designated interim are reviewed periodically to evaluate new toxicological information and address guideline changes if needed (Health Canada, 1996). In 2006, Health Canada published a technical document titled, *Trihalomethanes*, which specifically looked at the guidelines for total and individual THMs. For total THMs the limit set in the 6th edition of the GCDWQ remained, however a guideline for bromodichloromethane (<0.016mg/L) was introduced to account for scientific findings regarding the toxicity of this by-product (Health Canada, 2006). Further recommendations in the technical document were that samples be taken at the treatment plant as well as at a point in the distribution system suspected to have the highest THM formation potential, likely the end of the distribution line due to increase contact times between chlorine and organic matter (Health Canada, 2006). Health

Canada suggests that although the risks from THMs, including BDCM, are low measures should be taken to reduce the formation of THMs, and other DBPs, without compromising disinfection (Health Canada, 2006).

In the 6th Edition of the *Guidelines for Canadian Drinking Water Quality*, Health Canada states, “... *guidelines and recommendations listed are intended to apply to all drinking water supplies, public or private. However, they are not to be regarded to as legally enforceable standards less promulgated as such by an appropriate provincial, territorial, or federal agency* (Health Canada, 1996).” Therefore, each province can choose to follow the Canadian guidelines or establish a separate provincial guideline for water quality. Manitoban guidelines for drinking water quality are set by Manitoba Water Stewardship. In 2011, Manitoba Water Stewardship published the *Manitoba Water Quality Standards, Objectives, and Guidelines* which follows the GCDWQ limits for THMs of 0.1mg/L, based on a quarterly average (Manitoba Water Stewardship, 2011). This guideline was set to accordance to the studies regarding health concerns with DBPs reviewed by Health Canada, the USEPA and the WHO.

3.4 Chlorine dioxide as an alternative disinfectant

In 1967, the USEPA registered aqueous chlorine dioxide as a sanitizer and disinfectant. The major use for the product is in the bleaching process in the pulp and paper industry (USEPA, 2006). Although, chlorine dioxide disinfection is largely used throughout Europe its use in North America is still limited mainly due to the ease of use associated with traditional chlorine disinfection. The first reported use of chlorine dioxide as a water disinfectant was at the Niagara Falls, New York, in 1944 (Aieta and Berg, 1986). In the 1990’s the AWWA estimated that less than 10% of the 1300 treatment facilities reviewed in the study used chlorine dioxide, furthermore chlorine dioxide was

mainly used for taste and odour control, not disinfection (Hofmann, 2001; AWWA, 1978). The restrictions of THMs set forth by the USEPA and other regulatory agencies has made the use of chlorine dioxide as an alternative disinfectant in North America a more viable option due to the fact that chlorine dioxide does not form THMs (Aieta and Berg, 1986).

Chlorine dioxide has been shown to be an effective method for disinfection of *Giardia* and *Cryptosporidium*, as a peroxidation for the removal of iron and manganese, as well as taste and odour issues. Although chlorine dioxide does not form THMs, about 50-70% of the chlorine dioxide applied as a water disinfectant will be converted to chlorite, with the remaining 50-30% forming chloride (Aieta and Berg, 1986). The USEPA and Health Canada have set limits on chlorite concentration in finished waters of 1.0mg/L (Health Canada, 2010; USEPA, 1998). Therefore, the chlorine dose applied generally cannot exceed 1.4-2.0mg/L in order to comply with the regulatory guideline for the chlorite by-product (Hua and Reckhow, 2007). Similarly, chlorine dioxide has been found to form di-haloacetic acids (DHAAs) however, the concentrations formed are minor in comparison to traditional chlorination methods (Hua and Reckhow, 2007). This is due to the fact that chlorine dioxide does not chlorinate but reacts via oxidation-reactions. Conversely, chlorine reacts via oxidation reactions as well as electrophilic substitution reactions which results in chlorinated organic products, such as THMs (Gordon and Bubnis, 2000; Aieta and Berg, 1986).

Although chlorine dioxide has been shown not to produce THMs, there have been studies to evaluate the adverse health effects of water disinfection with chlorine dioxide. In 1981, Michael *et al.* published a study that looked at the hemolytic activity of chlorine dioxide (Michael, *et la.* 1981). Chlorite, a by-product of chlorine dioxide disinfection, oxidizes hemoglobin to methemoglobin in the human body (Michael, *et la.* 1981). Methemoglobin has a Fe (III) oxidation state rather than the normal Fe (II) of hemoglobin. This prevents methemoglobin from accepting oxygen, furthermore the

Fe (III) has a higher affinity for oxygen due to the chemical structure and therefore does not release oxygen to the body (Denshaw-Burke *et al.*, 2011). Although, Michael *et al.* did not find any significant adverse effects in health adults, the authors did not that one individual manifested a glucose-6-phosphate deficiency and had reduced red blood cell, hemoglobin and hematocrit declined during the study but increased 90 days after exposure stopped (Michael *et al.*, 1981). The authors could not establish if the direct cause was due to chlorine dioxide, they suggest that future studies be conducted to evaluate a direct relation to chlorine dioxide and individuals sensitive to this condition (Michael *et al.*, 1981). In 1996, Kanitz *et al.* evaluated the relationship between somatic parameters at birth and chlorine dioxide treated waters consumed by mothers during pregnancy. The study found a possible statistical relationship between the size of the body and cranial circumference of mothers that drank either chlorine dioxide or sodium hypochlorite compared to mothers that did not. Furthermore, Kanitz *et al.* stated that neonatal jaundice is twice as likely when consuming chlorine dioxide treated waters (Kanitz *et al.*, 1996). However, a USEPA review of chlorine dioxide cites a study that critically reviews the findings by Kanitz *et al.* in regards to lack of consideration to confounding variables and that interpretation of the results is limited (USEPA, 2000). The USEPA report on chlorine dioxide and chlorite further concluded the most of studies review found negative results for the carcinogenic effects of chlorine dioxide in humans or animals. Chlorite, on the other hand, is a Group D carcinogen which is defined as, “*not classifiable to human carcinogenicity due to inadequate data on humans and animals* (USEPA, 2000). Therefore, further studies as to the human health concerns related to chlorine dioxide, and its disinfection by-products, are warranted to establish any future guideline considerations.

Part 3: Experimental

Chapter 4: General Materials and Methods

4.1 Research Objectives

The objective of this study was to determine the NOM composition for two surface waters, the Red River and Assiniboine River, found in Manitoba. It is beneficial for potable water treatment to understand the composition of NOM in potable water sources in order to estimate and control the formation of disinfection by-product formation, such as THMs. Two potable water treatment plants that use the Red and Assiniboine Rivers, the Morris water treatment plant and Portage la Prairie water treatment plant, respectively, have been found to have THM concentrations that exceed the Manitoba guideline of 100 µg/L. Due to the reportedly high THM concentrations at these two plants, it is believed that both the Red and Assiniboine Rivers are high in hydrophobic acid compounds, which is believed to contain the greatest potential to form THMs. A second objective was to establish NOM fraction removal by the Morris and Portage la Prairie WTPs. Due to THM concentrations exceeding the guideline at both plants in the past, it was hypothesised that NOM was not being effectively removed during treatment leading to increased DBPs formed during chlorination. The final major objective was to determine the THM formation potential for NOM fractions collected from the Red and Assiniboine Rivers. As there are contradicting results in literature regarding which NOM fraction contains the greatest potential to form THMs, it is important to establish the potential of THM formation from local surface water sources. Results from this study could provide water treatment plants with a greater understanding of the cause for reportedly high THMs. Information gained from the results of the NOM fraction removal at the two plants would provide insight as to what processes are not removing NOM as expected which would provide

preliminary data for future optimization studies on treatment processes found to be ineffective at controlling NOM.

4.2 Water Treatment Plants Used in Study

4.2.1 Portage la Prairie Water Treatment Plant

The City of Portage la Prairie has a population of roughly 13,000 people and has been growing at a steady rate for the past several years due to the development of food processing industries and agriculture in the region. To meet the long term water demands of the growing community, along with the construction of a new potato processing facility in the area, the Potage la Prairie Water Treatment Plant (PPWTP) underwent several upgrades from 2000-2003. Upgrades to increase water production from 18 mega liters per day (ML/d) to 34ML/d were implemented in order to meet growing demands, as well as, improving and adding treatment processes to overcome challenges such as high turbidity, hardness, and organic matter, along with occasional increased algal growth often seen in the Assiniboine River. Turbidity levels at the PPWTP were found to exceed 1500 nephelometric turbidity units (NTU) and peaks of 6000 NTU have been recorded (Table 4). The high levels of DOC (15mg/L) found in the river resulted in THM levels that often exceeded the 0.100 mg/L guideline set by the Province of Manitoba.

Table 3: Water quality for the Assiniboine River and PPWTP for samples collected in May 1999. Guidelines presented here are according to the Canadian Drinking Water Quality Guidelines for 2001 (Table adapted from Anderson, 2003)

Parameters	Raw Water	Treated Water	Guideline
Hardness (mg/L CaCO ₃)	349	133	200*
Turbidity (NTU)	140	0.3	1
TOC (mg/L)	15	7	10**
Chloroform (mg/L)	0.0003	0.100	-
Bromoform (mg/L)	0.0010	0.001	-
BDCM (mg/L)	0.0002	0.021	-
DBCm (mg/L)	0.0002	0.031	-
Total THMs (mg/L)	0.0017	0.153	0.1

Note: * = Operational objective
 **= Aesthetic guideline

To improve the removal of turbidity, a John Meunier ACTIFLO[®] Ballasted Flocculation Clarification system was implemented as a preclarification step. Pilot studies found that raw waters with turbidity levels of 2500 NTU could be reduced to 3 NTU overcoming the occasional high spikes in turbidity seen in the Assiniboine River (Anderson, 2003 and 2004).

Along with the ACTIFLO[®] system, an additional clarifier and new chemical dosing systems were installed to increase plant flow. Improvements to the backwash system for the four dual media sand filters were made to increase plant performance and promote organics removal. Ozone was applied to softened and clarified water to promote biologically stable water, to minimize chlorine demand, reduce the formation of DBPs, and to improve taste and odor. In addition to sand filtration, granular activated carbon adsorption was introduced to further remove organics. Upgrades were made to the storage reservoirs to increase disinfectant contact time and plant capacity. Lastly, a state of the art control system replaced the original system in order to provide operators with complete control and monitoring of the system.

Although preliminary plant performance tests indicate that the new system improved the removal of turbidity and hardness, tests in 2007-2008 suggest the plant may not be effectively removing organics as THM levels were found to occasionally exceed guideline limits (Table 4).

Table 4: THM concentrations at the Portage la Prairie Water Treatment Plant from 2007-2008. Data supplied by the Portage la Prairie Water Treatment Plant.

Date	THM concentration (µg/L)				Total THM
	Chloroform	BDCM	DBCM	Bromoform	
January 9, 2007	20	16	12	<1	48
May 9, 2007	17	11	8	<1	36
August 23, 2007	79	30	13	1	123
December 11, 2007	42	23	6.7	0.3	72
January 7, 2008	57	26	8.9	0.6	92.5
April 22, 2008	50	<	9.5	<	59.5

*BDCM = Bromodichloromethane
 DBCM = Dibromochloromethane
 < = less than detection limits

4.2.2 Morris Water Treatment Plant

In 1998 the Morris Water Treatment Plant (MWTP) in Morris, Manitoba was constructed to deliver potable water to the rural municipalities (RM) of Morris, Roland, Stanley, Montcalm and Thompson. The original Morris plant was a cold lime/soda softening plant with a capacity of 32 L/s. However, from 2005-2007 the required daily production exceeded the plant's maximum output capacity by as much as 10 L/s. It was recommended that a plant upgrade would be required to meet the current demand (~50 L/s) as well as future demands for the distribution area. Improvements to the MWTP would also address the concerns with high disinfection by-products found in finished waters. The source water for the MWTP is the Red River which flows along agricultural areas which often experience flooding. This results in high NOM concentrations which often exceed 15 mg/L and turbidity levels as high as 455 NTU. The high levels of NOM in the source water react with chlorine during the disinfection process causing levels of DBP, mainly trihalomethanes (THMs), to exceed the maximum allowable concentration (MAC) set by the Manitoba government and Health

Canada. A proposal set forth to update the existing lime/soda plant to a modern integrated membrane facility. The new membrane facility would allow the MWTP to meet the higher demand of 45 L/s as well as to meet the MAC criteria for DBP (Anderson, 2009).

The proposed plant would be a dual membrane (microfiltration and nanofiltration) plant that was to be built onto the existing lime/soda plant. The new facility would be able to initially treat 66 L/s with the ability to expand to 100 L/s, easily meeting the current and future distribution needs. The membrane plant would also improve removal of organic matter prior to chlorination disinfection which would reduce the DBP levels to within Manitoba regulations.

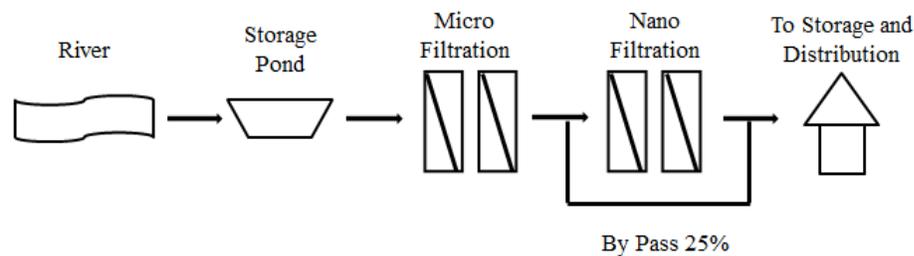


Figure 4: Proposed membrane process for Morris Water Treatment Plant

In April 2009 construction of the membrane addition to the Morris plant was initiated. This included the construction of a 1.3 million cubic meter storage pond that would be used as a pretreatment for the removal of organic and particulate material through gravity settling. The pond would draw water from the Red River and would be aerated to maintain homogeneity. The storage pond will allow the influent to remain relatively constant throughout the year and the plant would not experience flash peaks in turbidity and total organics due to periodic seasonal flooding.

The membrane system includes three Skid Mounted ARIA™ AP-6 micro filtration modules from the Pall Corporation, each with a maximum flow of 44 L/s or 132 L/s total. The micro filtration membranes are hollow fiber made from polyvinylidene fluoride (PVDF) with 0.1 µm pore size and functions from outside to inside. The microfiltration system will provide a thousand-fold reduction of *Giardia* and *Cryptosporidium* and effectively reduce turbidity levels to <0.1 NTU and total removal of suspended solids (Pall Corporation, 2008). The microfiltration membranes will be followed by 2 nanofiltration membrane skids. The nanofiltration membranes are Ultipreat High Flow polypropylene membranes effective at removing hardness by 75%, total organic carbon by 70% TDS to <500 ppm and color to <5 TCU. Each nanofiltration skid is capable of treating 25 L/s or 50 L/s total. Construction of the membrane facility allowed room for expansion of a third NF skid increasing total treatment through the NF system of 75 L/s.

The MF-NF system at Morris operates with a roughly 75% blend rate (see Figure 10) of MF treated water to NF treated water. Blending provides some hardness back to the treated water to achieve the recommended hardness of 80-100 mg/L CaCO₃ (Health Canada, 1996).

The Morris membrane system is complete with a fully automated Clean-In-Place (CIP) system for both the nano and micro filters. Cleaning includes both acidic and caustic washes roughly every 30 minutes or when permeate flow is reduced by 10-15% (Pall Corporation, 2008).

In November 2009, the MF-NF membrane train at Morris went online. The total cost of the membrane addition was roughly \$15,000,000 for all parts and labor including the construction of the offline settling pond.

4.3 Sample Collection

4.3.1 Sampling at the Portage la Prairie Water Treatment Plant and Assiniboine River

1 liter (L) water samples were collected from the Assiniboine River, via an intake in the plant, as well as throughout the water treatment plant three times during this study; November 8, 2010, January 20, 2011 and April 2, 2011. These three sampling dates represent river water conditions during fall (prior to snow fall), winter and spring. Figure 12 diagrams the sampling locations at the PPWTP. November 8th samples only tested the overall removal of DOC throughout the plant and general water quality tests. Samples were collected from before and after the GAC filter on January 20, 2011 to establish the DOC fraction removal efficiency of the filter. All samples collected at Portage la Prairie and the Assiniboine on April 2, 2011 were fractionated using SPE method (described below).

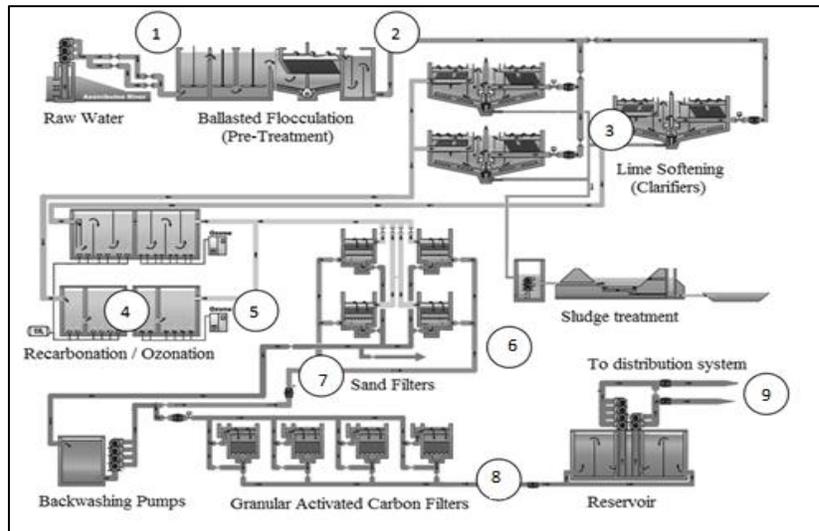


Figure 5: Sampling locations for Portage la Prairie water treatment plant. (1) Assiniboine River (2) after ACTIFLO ballasted flocculation (3) after lime softening (4) after recarbonation (5) after ozonation (6) after sand filtration (7) after sand filter reservoir (8) after GAC (9) Finished water

4.3.2 Sampling at the Morris Water Treatment Plant and Red River

1-4L water samples were collected at various times during the study from the Red River as well as from the retention pond, post micro filter, and post nano filter effluent, prior to blending. Samples were collected on August 11, 2010 to establish an estimate of the summer THM concentrations and formation potential from the Red River and treated MWTP effluent. THM concentration and THMFP analysis for this sample set was conducted by ALS laboratories (ALS Laboratories Winnipeg, Manitoba).

Samples collected from the Red River on September 25, 2010 were fractionated to establish the relative composition of the river DOC during late summer. On November 23, 2010 and February 28, 2011 samples were collected from the river, as well as the retention pond, post micro filter and post nano filter for a full fractionation study. Note that February sampling did not include the Red River due to ice cover.

All DOC measurements were made using *Standard Method 5310C* with a Tekmar Dohrmann Phoenix 8000 total organic carbon analyzer (Tekmar Dohrmann, Ohio) which was calibrated according to the instrument manual. All DOC measurements were made in triplicate. All samples collected during this study were filtered through 0.45µm nitro cellulose filter paper prior to analysis except for THM and THMFP analysis conducted by ALS laboratories.

4.4 General Water Quality Tests for Red River and Assiniboine River

Water quality testing was conducted on the November 8th, 2010 sampling of the Assiniboine River and PPWTP. Testing was conducted in part by Maryam Hooshire (Hooshire, 2010). Testing included turbidity, pH, UV₂₅₄, and dissolved organic carbon. General water quality testing was done on the Red River and at the MWTP on November 23, 2010 and February 28, 2011. November tests from the Red River and MWTP included pH, turbidity, dissolved organic carbon concentration,

UV₂₅₄, and specific UV absorbance (SUVA). February testing at the MWTP and Red River followed the same testing as November with the addition of alkalinity. November 8, 2010 water quality tests from the PPWTP and Assiniboine River included turbidity, UV₂₅₄, pH and dissolved organic carbon.

The pH was measured using a Fisher Scientific Accumet 50 pH (Fisher Scientific, New Jersey, USA) meter equipped with an Oakton pH probe. The pH meter was calibrated weekly using calibration standards. UV₂₅₄ was measured using an Ultrospec 2100 UV/Vis spectrophotometer (Biochrom, Cambridge, England). The Ultrospec 2100 was also used to measure the specific UV absorbance (SUVA) which was conducted at 254nm according to USEPA Method 425.3 (USEPA, 2005). Turbidity was measured using a HF Scientific Micro 100 Turbidimeter (HF Scientific, Fort Worth, Florida, USA) and true color was established from filtered samples using an Orbeco-Hellige Aqua Tester (Orbeco Analytics, New York, USA). Alkalinity was determined using titration method according to *Standard Methods 2320B*.

4.5 Dissolved Organic Matter Fractionation Method Using Solid Phase Extraction

Prior to fractionation all samples were filtered through 0.45µm nitrocellulose filter paper and were brought to room temperature. The fractionation method used in this study was developed by Ratpukdi *et al.* (2009). The method fractionates DOC into six fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral fractions and is as follows. The fractionation procedure uses three nonpolar Bond Elute ENV cartridges (Varian Inc, Lake Forest, California), one Phenomenex Strata XC strong cation exchange cartridge, and one Phenomenex Strata X-AW weak anion exchange cartridge (Phenomenex, Torrance, California). All SPE cartridges contained 1gram of sorbent (see Figure 1 for sorbent of each SPE cartridge). The fractionation procedure begins with

all cartridges being conditioned with 10mL of HPLC grade methanol, MeOH (Fisher Scientific, New Jersey, NY, USA). The Strata XC and X-AW cartridges were then conditioned with 10mL of 1.0M hydrochloric acid, HCl (Sigma Aldrich, St. Louis, MS, USA). All five cartridges are then rinsed with deionized water until the effluent DOC measured <0.100 mg/L. 1L of sample was adjusted to pH 7.0 using either concentrated sulfuric acid (H₂SO₄) (Fisher Scientific, New Jersey, NY, USA) or 1M sodium hydroxide (NaOH) (Sigma Aldrich, St. Louis, MS, USA) and was drawn through the first ENV cartridge labeled ENV-1. The fraction collected on the ENV-1 SPE cartridge is defined as the HPON fraction. The same sample water was then adjusted to pH of 10 using 1.0M NaOH and drawn through the second ENV cartridge (ENV-2). The fraction retained on this cartridge is the HPOB fraction. Next, the sample water was adjusted to pH of 2 with H₂SO₄ and drawn through the third ENV cartridge (ENV-3), capturing the HPOA fraction. Following the ENV-3 cartridge the sample water was drawn through the Strata XC cartridge without pH adjustment (pH=2). The HPIB fraction was retained on the Strata XC cartridge. Lastly, the sample water was adjusted to pH of 7 with NaOH and drawn through the Strata X-AW cartridge which captured the HPIA fraction. The fraction of organic matter that was not retained by any of the five cartridges is defined as the HPIN fraction. All samples were drawn through the SPE cartridges at 10-15 mmHg vacuum pressure. After the sample was drawn through each SPE cartridge a 40mL sample was collected to measure the DOC concentration. Elution of DOC fractions is as follows: HPON fraction contained on ENV-1 was extracted using 10mL of methanol. The methanol was subsequently removed from the DOC extract using roto-evaporation at 60°C. After removal of the methanol, the DOC collected in ENV-1 was dissolved in 10mL of deionized water. The HPOB fraction was eluted using 10mL of 0.1M HCl, while the HPOA, HPIB and HPIA fractions were eluted using 0.1M NaOH. Figure 13 outlines the Ratpukdi *et al.* method. All acid/base dilutions were made using deionized water.

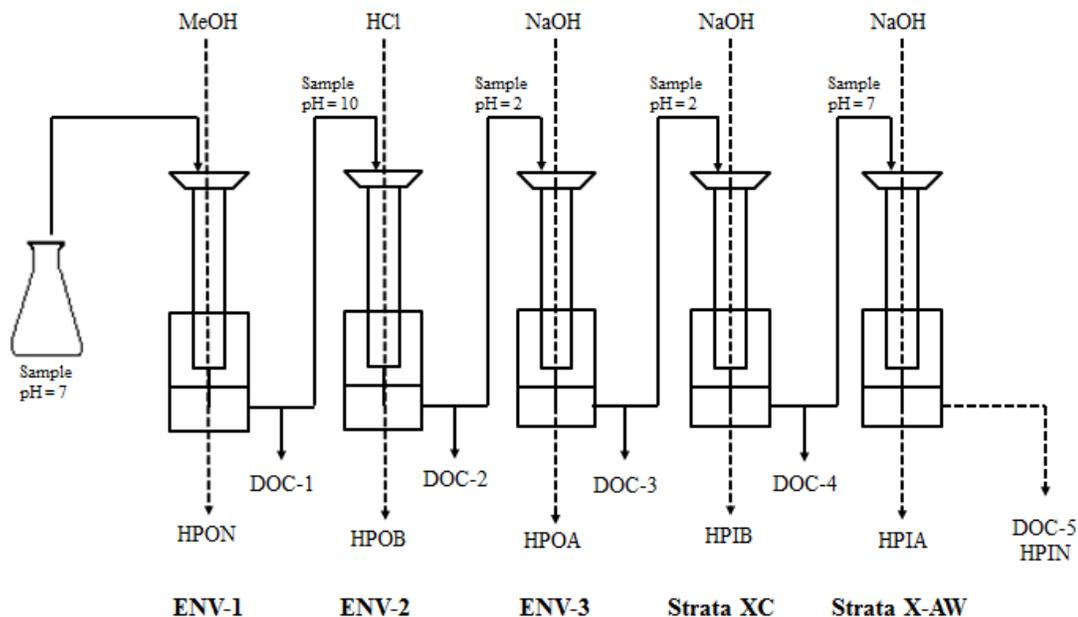


Figure 6: DOC SPE fractionation setup (Adapted from Ratpukdi *et al.*, 2009)

4.6 THM Formation Potential from Isolated DOC Fractions

Water samples, collected from the Red River on August 15, 2011 and the Assiniboine River on September 1, 2011, were fractionated and extracted using the procedure stated above. Raw water from each river, along with the extracted fractions, were collected in 45mL glass vials with tetrafluoroethylene (TFE) caps which was used as the reaction vials for the formation potential tests. The trihalomethane formation potential test was conducted as stated in *Standard Methods 5710B* for each of the six fractions, and raw river waters. An alteration to the 5710B procedure was that the chlorine demand for each fraction was not measured prior to chlorination due to minimal sample (~10mL). Therefore, 50mg/L sodium hypochlorite was used for 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.

4.7 THM Measurement

THM concentrations were measured as described in *Standard Methods 6232B Liquid-Liquid Extraction*. The extraction solvent used was HPLC grade pentane (Fisher Scientific, New Jersey, NY, USA). The following modification was made to the 6232B method: the method asks for 20mL sample be extracted using 2mL of extraction solvent. However, upon testing the remaining 20mL sample significant levels of THMs were found. This was modified by using 10mL of water sample and 10mL of pentane. The 10mL sample was extracted in 3 separate additions of pentane, (3mL, 3mL and 4mL) to ensure all THMs present in the water sample were extracted into the organic phase. The 2mL of the pentane sample was used for THM measurement using gas chromatography (GC).

Trihalomethane measurements were made using an Agilent 7890A GC System (Agilent Technologies, Santa Clara, California) equipped with a CombiPAL CTC Analytics auto sampler and used electron capture detection (ECD). The column used was an Agilent DB-5 column (Agilent Technologies, Santa Clara, California) with the following specifications and temperature program: 30 meters length; 0.32mm diameter; 0.24 μ m film. Temperature program: 35°C (4min), 10°C/min to 70°C (0min), 20 °C/min to 200°C (4min).

The concentrations of THMs were established using external calibration. All four THM standards were >99% pure (Sigma Aldrich, St. Louis, MS, USA). An internal standard, 1, 2-dibromopropane (Sigma Aldrich, St. Louis, MS, USA), was used as described in *Standard Methods 6232B*. The retention times used were established from standards for each separate trihalomethane. The following retention times were used: chloroform=3.93 minutes, bromodichloromethane=5.48 minutes, dibromochloromethane=7.47 minutes, 1,2-dibromopropane (IS)=8.70 minutes, and bromoform=9.21minutes. The external calibration graph for each individual THM were all found to have excellent linearity with the coefficient of determination (r^2) > 0.999 (see Appendix Figure 20).

4.8 THM Formation Potential Using Chlorine Dioxide

A sample of the Red River water collected from the University of Manitoba campus in September, 2011 was tested for the THMFP from chlorination with chlorine dioxide. Chlorine dioxide was generated using a bench top method which utilized the addition of a solution of a 0.295 millimole per liter (mmol/L) potassium persulfate (Sigma Aldrich, St. Louis, MS, USA) to a 3.5 mole per liter (mol/L) solution of sodium chlorate (Sigma Aldrich, St. Louis, MS, USA). The chlorine dioxide gas generated was dissolved in distilled water using a carrier gas of N₂. The working chlorine dioxide solution was standardized at 360 nm according to Beer-Lambert's Law using a molar absorptivity constant of 1225 (mol/L)⁻¹cm⁻¹ (Masschelein and Rice, 1979). THM formation potential of the Red River samples was tested using *Standard Methods 5710B* with 50mg/L chlorine dioxide as the chlorinating agent. THM measurements were conducted according to the procedure described in Section 3.5.

4.9 THMFP of Citric Acid (Technical Report)

Samples of >98% pure citric acid (Sigma Aldrich, St. Louis, MS, USA) were diluted in distilled water to concentrations of 0mg/L, 10mg/L, 20mg/L and 30mg/L. These samples were tested for THMFP (as described in Section 3.4) and chlorinated using 50mg/L sodium hypochlorite. After 7 days the samples were tested for THM concentration as described in Section 3.5.

Part 4: Results and Discussion

Chapter 5: General Water Quality Tests

5.1 Red River and Assiniboine River Water Quality

November 23rd, 2010 testing occurred prior to snow fall and was considered to represent late fall water. The February sampling was representative of winter water with ice cover. The samples collected on each date show small differences in all the parameters tested. For the fall water (November samples) pH, turbidity, dissolved organic carbon (DOC) and UV_{254} were found to exceed the February sampling results. However, the SUVA values were higher for the winter sampling, $SUVA=3.4 \text{ L mg}^{-1} \text{ M}^{-1}$, compared to the fall sampling which had a SUVA value of $2.9 \text{ L mg}^{-1} \text{ M}^{-1}$ (Table 6). Table 7 provides the expected composition of natural organic matter in relation to SUVA values. SUVA values ranging from 2-4 correspond with a mixture of hydrophobic and hydrophilic NOM. The results from here show a slightly higher aromatic content in the winter than the fall suggesting that THM formation may be greater in the winter. These results are inconsistent with a previous study that looked at the seasonal variation of DOC (Sharp *et al.*, 2006). The Sharp *et al.* study suggests that if the organic composition increases the majority of added organics will be hydrophobic in character (Sharp *et al.*, 2006). However, the samples collected in February, 2011 had a lower DOC concentration compared to the November, 2010 samples but a higher SUVA, suggesting a greater proportion of hydrophobic matter in the February samples compared to the November set.

Table 5: November 23rd, 2010 and February 28, 2011 water quality tests for the Red River. All testing was conducted at the University of Manitoba Environmental Laboratory.

Sample Date	Turbidity (NTU) Filtered	pH	DOC (mg/l)	UV ₂₅₄ (cm ⁻¹)	SUVA (Lmg ⁻¹ M ⁻¹)	Alkalinity (mg/LCaCO ₃)	True Color (TCU)
November 23, 2010	0.12	8.1	12.04	0.353	2.932	N/A	N/A
February 28, 2011	0.03	7.93	8.02	0.273	3.403	254	25

Table 6: Expected composition of natural organic matter in relation to SUVA values (Table adapted from Edzwald and Tobiason, 1999)

SUVA	Composition
<2	Mostly Non-humics Low hydrophobicity Low Molecular Weight
2-4	Mixture of aquatic humic matter and other NOM Mixture of hydrophobic and hydrophilic NOM
>4	Mostly aquatic humics High hydrophobicity High molecular weight

The water quality results for the Assiniboine River collected on November 8, 2011 are presented in Table 7. The results show a high DOC concentration of 16.1mg/L and a high turbidity of 166 NTU, although low in comparison to plant reports of the Assiniboine River which can spike to >1500NTU (Anderson, 2003). The high SUVA of 2.92 L mg⁻¹ M⁻¹ is representative of a water source with a mixture of hydrophobic and hydrophilic organic matter.

Table 7: November 8, 2010 water quality tests for the Assiniboine River. All testing was conducted at the University of Manitoba Environmental Laboratory. Testing was conducted by M. Hooshier in part of M.Sc. work (Hooshier, 2010).

Assiniboine River	pH	DOC (mg/L)	Turbidity (NTU)	UV ₂₅₄ (cm ⁻¹)	SUVA (L mg ⁻¹ M ⁻¹)
November 8, 2011	8.12	16.1	16.60	0.470	2.92

The relatively high SUVA values for the Red and Assiniboine Rivers is not surprising if the historical data of THMs found from each plant are considered. Concentrations of total THMs often exceeded the Manitoba guideline of 100µg/L (Table 4). However, caution should be taken when estimating the THMFP from UV₂₅₄, and further examination into the THMFP of the organic content of a water source, such as the Red and Assiniboine Rivers, is warranted.

Chapter 6: Identification of NOM Fractions Isolated from the Red and Assiniboine Rivers

6.1 Red River Dissolved Organic Carbon Composition

Samples collected from the Red River on September 25, 2010, November 23, 2010, February 28, 2011, and June 7, 2011 were fractionated using SPE into the six fractions described in Section 3.3 to evaluate the relative dissolved organic matter composition of the river during late summer, late fall, winter and mid-summer. Table 8 and Figure 7 show the dissolved organic matter composition for the four sampling dates.

The hydrophobic/hydrophilic composition of the Red River changed significantly throughout the study. The Red River has the most hydrophobic composition during the winter months with the November 23, 2010 and February 28, 2011 samples having a total of 57% and 52% hydrophobic character (hydrophobic = HPOA+HPOB+HPON). During the warmer months (September, 2010 and June, 2011) the Red River was found to have more hydrophilic character with 55% and 58%, respectively. The relative 50/50 composition of hydrophobic/hydrophilic character of the Red River is typical for surface waters (Chow *et al.*; 2005, Owen *et al.*, 1993).

The fractionation results for the four periods found significant variations in composition throughout the study. The HPON fraction for September and November were similar at 22% and 18% DOC, respectively, and during the February and June sampling had % DOC of 11.7% and

11.2%. The HPOB and HPIB fractions were found to have the lowest concentrations each, ranging from less than 2% to 6% during the study. The HPIA fraction was found to remain constant during the colder periods in late summer, late fall and winter of between 11% and 13%, however showed a significant reduction in mid-summer. During the late fall and winter sampling dates, the HPIN fraction was significantly lower, 25% and 16%, respectively, compared to the late summer and summer periods which were found to have 40% and 51% total DOC. It might be noted that the unusually low concentration of HPIA fraction and the slightly higher HPIN fraction found during the June 7, 2011 sample may be an indication of poor adsorption to the Strata X-AW cartridge.

Table 8: Dissolved organic matter fractions collected from the Red River over a 9 month sampling period from September, 2010 to June 2011.

Fraction	September 25, 2010		November 23, 2010		February 28, 2011		June 7, 2011	
	DOC (mg/L)	% DOC	DOC (mg/L)	% DOC	DOC (mg/L)	% DOC	DOC (mg/L)	% DOC
HPON	2.47	22	2.19	18.2	1.06	11.7	1.00	11.5
HPOB	0.21	<2	0.43	3.6	0.62	6.8	0.21	2.4
HPOA	2.47	22	4.33	35.9	2.98	33.1	2.35	27.1
HPIB	0.21	<2	0.67	5.5	0.56	6.2	0.46	5.3
HPIA	1.46	13	1.40	11.6	1.37	15.2	0.20	2.3
HPIN	4.49	40	3.02	25.1	1.44	16.0	4.44	51.4
Total	11.3	100	12.0	100	8.02	100.0	8.65	100.0

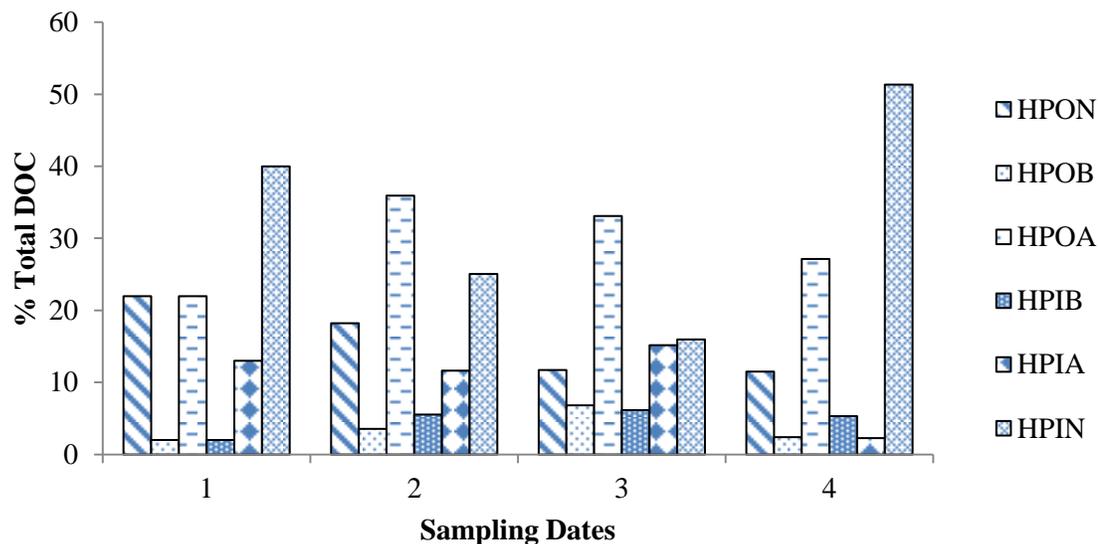


Figure 7: DOC fractions, in % total DOC, of the Red River for the four sampling periods: (1) September 25, 2010, (2) November 23, 2010, (3) February 28, 2011, and (4) June 7, 2011.

The high % HPOA fraction found in November and February, 36% and 33% total DOC, can be related with the relatively high SUVA results presented in Section 4.1. The HPOA fraction is said to contain largely humic matter and is characterized with having a large degree of aromaticity which will absorb in the UV range (Leenheer, 1981; Chow *et al.*, 2008). Aromatic carbons are also considered to be one of the most reactive moieties in relation to THM formation (Chow *et al.*, 2008). Although literature suggests that summer will have a greater HPOA content, due to influx of soil derived organics entering surface waters through rain runoff (Scott *et al.*, 2005; Sharp *et al.*, 2006), the results found to be higher in the winter months. One reason for a higher aromatic content in the Red River during cold months is that the Red River is known to be fast moving with a significant undercurrent. During the winter months scouring of the river bed may increase the amount of soil organics in the water contributing to a higher DOC content.

6.2 Assiniboine River Dissolved Organic Carbon Composition

The organic composition for the Assiniboine River was measured on April 2, 2011 and September 1, 2011 to estimate the organic composition during spring (April, 2011) and late summer (September, 2011). Samples were collected at the Portage la Prairie water treatment plant. The results for the Assiniboine River composition can be found in Table 9. The Assiniboine River, like the Red River, showed seasonal variations in organic matter composition. During the spring (April, 2011 sample) the composition was only 38% hydrophobic, while in the late summer the composition was nearly equal in hydrophobic/hydrophilic composition. The increase in hydrophobic fractions found in the late summer maybe due to the extensive flooding in the area. As mentioned above, rain and flooding events can increase the concentration of hydrophobic compounds in surface waters resulting from runoff. However, compared to the Red River, the Assiniboine River seems to follow a more conventional pattern with hydrophobic fractions increasing in the summer, compared to the Red River which found hydrophobic to be greater in the winter. The cause for the differences can be related to several factors such as environmental location, temperature of the water, pH, alkalinity, and other water parameters. However, the extreme flooding events in the south west part of Manitoba during the spring and summer of 2011 may have contributed to the increase in hydrophobics in the Assiniboine River. However, due to the fact that the Assiniboine River has never been studied for its organic matter composition, it is difficult to determine if the increase was a result of overland flooding in the area or if the increase in hydrophobic compounds is a naturally occurring event. Further analysis into the seasonal change in the Assiniboine River could establish if the increase in hydrophobics was a result of flooding.

The fractionation results found that there was little seasonal variation between the fractions except for the HPON and HPIA fractions which changed by roughly 50% between the two sampling

periods. The HPON fraction was found to increase from 5.8% to 10.8%, while the HPIA fraction was found to decrease from 15.3% to 7.9% between the two sampling periods. As with the Red River, the Assiniboine River has a considerable amount of HPOA and HPIN accounting for 70-75% of the total organic composition.

Due to the fact that only two sample sets were collected during this study (late spring and late summer) a more complete seasonal variation study of the organic composition of the Assiniboine River would allow for a more thorough evaluation of the seasonal variation of organic matter in the river. Furthermore, a more complete seasonal evaluation could provide evidence as to the contribution of flooding events in the area to the increase in hydrophobic matter in the river.

Table 9: Dissolved organic matter fractions of the Assiniboine River collected in April, 2011 and September, 2011.

Fraction	April 2, 2011		September 1, 2011	
	DOC (mg/L)	% DOC	DOC (mg/L)	% DOC
Raw Water	16.23	100	11.79	100
HPON	0.93	5.8	1.27	10.8
HPOB	0.20	1.2	0.09	0.7
HPOA	5.10	31.4	4.35	36.9
HPIB	0.80	4.9	0.38	3.2
HPIA	2.49	15.3	0.93	7.9
HPIN	6.71	41.3	4.67	39.6

Chapter 7: Removal of DOC Fractions by the Morris and Portage la Prairie WTPs

The objective of this portion of the study was to evaluate the natural organic matter fraction removal by the Morris and Portage la Prairie water treatment plants to determine which fractions were preferentially removed during the treatment processes and which fractions were unaffected.

7.1 Removal of DOC at the Morris Water Treatment Plant

To evaluate the removal of dissolved organic carbon fraction at the MWTP, samples were collected on November 23, 2010 and February 28, 2011 from the Red River, the retention pond, after the micro filter and after the nano filter (prior to blending). Note that the February samples did not include the Red River due to ice coverage. Table 10 shows the DOC removal results from the November sample set. The results found were unexpected showing an increase in DOC after the nano filter. According to the manufacturers of the membrane system at Morris, Pall Corporation, the nanofiltration membranes should reduce organic matter to $<0.5\text{mg/L}$. However, the results found during this sampling set showed an increase in DOC after the nano filter. The reason for the increase was unclear; however there are a few potential possibilities: (1) the sampling may have occurred prior to a cleaning event which could have been seen as a time where the membrane was not efficiently removing organics, or (2) the sampling could have occurred just after a cleaning period. The membranes are cleaned with an organic acid, citric acid, which, if not properly rinsed, could have contributed to the increase in DOC post nano filter. It should be noted that the plant manager, Mr. Jake Fehr, contacted this group just following the November 23, 2010 sampling with THM results from the plant that were higher than the previous THM results taken by the plant after the membranes were implemented at the plant (Fehr, 2010). The THM results collected by the MWTP in December, 2010 (results not shown here) were found to be between 70 and $84\mu\text{g/L}$. Although the THM results are below guideline limits in Manitoba, they were nearly double the THM results taken just following the membrane implementation (Fehr, 2010). It is difficult to determine if the increase in DOC after the nano filter during the November sampling period was the cause for the elevated THMs found by the MWTP in December, however it is believed to be a contributor considering the

THM results taken just following the start-up of the membrane system at Morris was well below 50µg/L (Fehr, 2010).

Table 10: Dissolved organic carbon removal from the Morris water treatment plant for samples collected on November 23, 2010 from the Red River and throughout the treatment plant

Sample Location	DOC (mg/L)	Standard Deviation
Raw	12.04	0.12
Pond	8.53	0.13
Post Micro	8.77	0.01
Post Nano	10.20	0.07

The DOC from the November sampling set taken from the Red River and throughout the MWTP was fractionated to establish which fractions were affected by the membranes. The results for DOC removal at the MWTP can be found in Tables 11 and 12, as well as Figures 8 and 9. The results show that there is an increase in HPOA following the micro filters and the nano filters were found to remove only a small amount (0.34mg/L DOC) of the HPOA fraction. It must be noted that due to the time needed to complete a fractionation experiment of a sample, only single fractionation analysis was conducted on all samples. Therefore, no significant statistical analysis could be used to evaluate the fractionation results from this study. However, in times where multiple fractionation experiments were able to be conducted on a single sample, as much as 5-10% difference between fractionation results was found. Therefore, changes in DOC fractions of <10% throughout this study cannot be seen as significant. The HPIA and HPIN fractions were found to increase following the nano filter by 10% and 16%, respectively. The increase in HPIA could have resulted from the use of citric acid as a cleaning agent for membranes, if samples were taken just following a cleaning cycle, however cleaning cycles were not evaluated during this study and therefore this can only be seen as a hypothetical possibility. All other fractions were found to be reduced by the nano filter. The major

fractions in the effluent following nano filtration are the HPIN and HPOA fractions. The HPOA fraction is largely believed to contain the greatest concentration of THM precursors which may have contributed to the increased THM concentration reported by the plant in December 2010 (Singer, 1999; Leenheer, 1981; Rook, 1977).

Table 11: DOC concentrations (mg/L DOC) at the Morris water treatment plant for samples collected on November 23, 2010.

Location	Concentration DOC (mg/L)						Total
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN	
Red River	2.19	0.43	4.33	0.67	1.40	3.02	12.04
Retention Pond	0.70	0.74	2.67	0.53	1.28	2.61	8.53
Post Micro	0.97	0.47	4.07	0.91	0.35	2.00	8.77
Post Nano	0.43	0.01	3.73	0.61	1.41	4.01	10.20

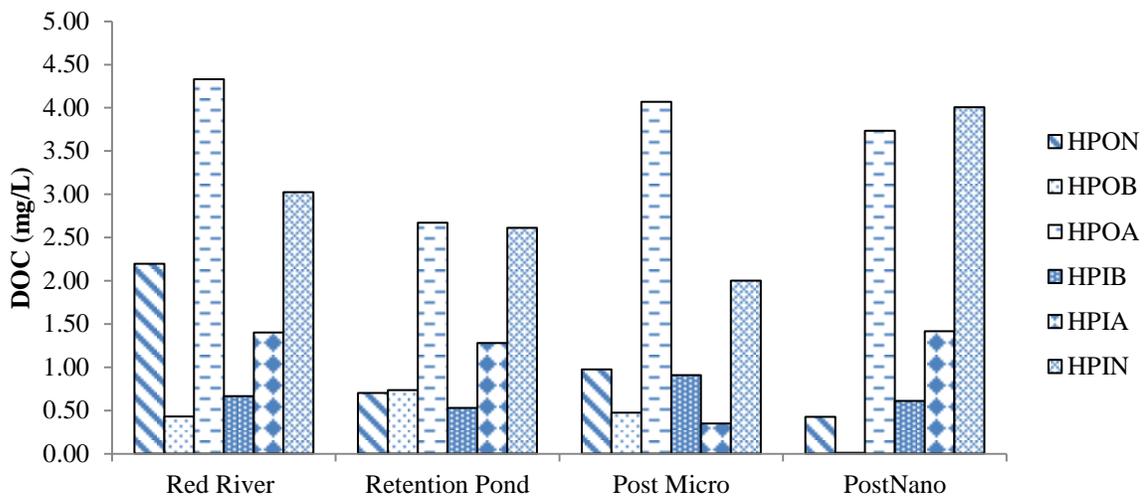


Figure 8: Concentrations of DOC fractions (mg/L) at the Morris water treatment plant for November 23, 2010 samples.

Table 12: DOC fraction removal (% DOC) at the Morris water treatment plant for samples collected on November 23, 2010

Location	Percent Total DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	18.22	3.58	35.94	5.53	11.63	25.09
Pond	8.24	8.62	31.30	6.19	15.01	30.64
Post Micro	11.10	5.39	46.39	10.34	3.98	22.80
Post Nano	4.17	0.11	36.60	5.97	13.87	39.28

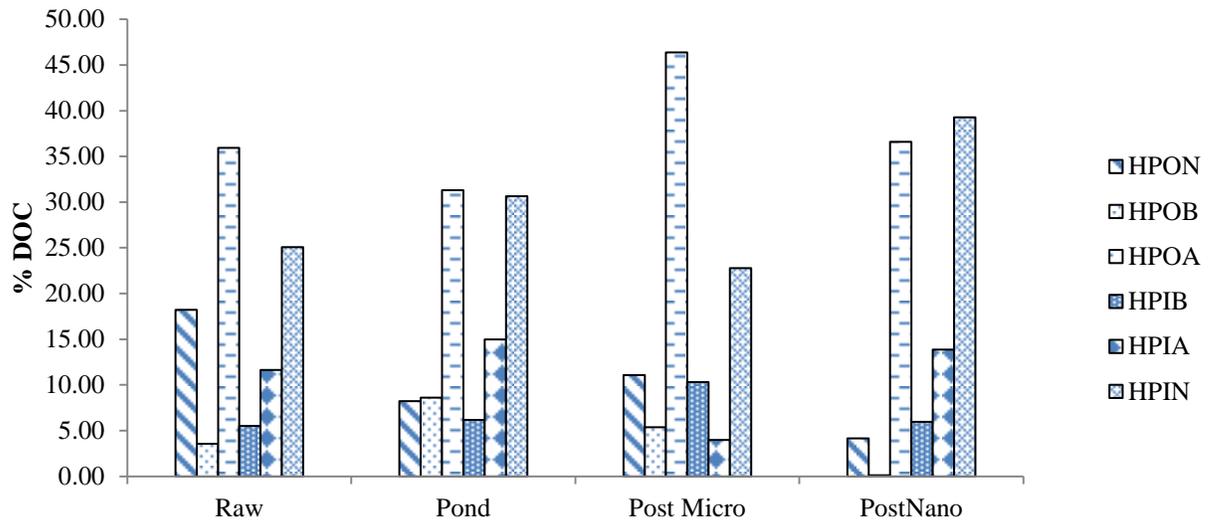


Figure 9: DOC fraction removal (% DOC) at the Morris water treatment plant for samples collected on November 23, 2010

The February, 2011 results for the removal of DOC fractions from the MWTP were more indicative of the removal of organics suggested by the manufacturers (Table 13). The removal of organics by the micro filter found that the HPIA fraction increased by roughly 50% following micro filtration and the HPON decreased by nearly 50%. The sample taken following the nano filter found that the total DOC was reduced to <0.5mg/L as described by the manufacturers. It should be noted that the sample taken post nano filter for this period could not be fractionated due to insufficient DOC in the sample. THMs were not reported by the MWTP to exceed 50µg/L during this sampling period showing the nano filter, when effectively removing organics, can control the formation of THMs. However, an important point to consider is that the nano filters had been fouled and were not operating to 100% efficiency at the time of sampling. The operators are in the process of trying new cleaning solutions to remove the foulants from the membrane (Fehr, 2011). Although, it is unclear as to the exact cause of fouling, organic fouling should be considered as a possibility. Organic fouling

of membranes has been the focus of several research studies although the exact mechanisms of NOM fouling are not fully understood as fouling can be affected by membrane composition, as well as NOM composition, concentration, polarity and size (Agenson and Urase, 2007; Kilduff and Belfort, 2002; Hong and Elimelech, 1997). However, humic fractions have been shown to have a role in fouling of nano filtration membranes (Hong and Elimelech, 1997). Although the propensity of organic fractions to foul nano membranes was not a focus of this study, the relative concentration of humic matter in the Red River would warrant further investigation as to the rate and cause of fouling at the MWTP. An important point in the evaluation of fouling and the removal of NOM at the Morris plant would be the fact there is no pretreatment process to remove NOM prior to membrane filtration. A simple coagulation process would reduce the organic load on the micro and nano filters and prevent situations where the nano filter is not removing DOC efficiently.

Table 13: Removal of DOC fractions (mg/L) at the Morris water treatment plant for February 28, 2011

Fraction	Pond DOC (mg/L)	Post Micro DOC (mg/L)	Post Nano DOC (mg/L)
HPON	1.06	0.53	0.419
HPOB	0.62	0.63	
HPOA	2.98	3.06	
HPIB	0.56	0.61	
HPIA	1.37	2.46	
HPIN	1.44	1.44	

7.2 Removal of DOC at the Portage la Prairie Water Treatment Plant

The removal of dissolved organic carbon fractions from the Portage la Prairie water treatment plant was investigated to establish the cause for THM concentrations which were found to occasionally exceed the Manitoba guideline limits. Three sample sets were taken from the Assiniboine River and Portage plant on November 8, 2010, January 20, 2011 and April 2, 2011. The

November sample set (Table 14) was tested for total DOC removal by the plant. Table 14 also provides changes in some general water quality parameters, such as pH, turbidity and UV absorbance, during treatment. Figure 10 shows the change in DOC during the treatment processes at the PPWTP. Nearly all treatment processes show a reduction in DOC with coagulation and clarification having the greatest reduction of approximately 8.5mg/L DOC. The only process where there was an increase in DOC occurred after the GAC filter, which was found to increase from 3.6mg/L to 6.7mg/L. This increase was not expected as GAC filtration was implemented at the Portage plant to reduce the organic concentration prior to chlorination disinfection (Anderson, 2003; Anderson, 2004). Therefore, the results presented here suggest that the GAC filter is not removing organic matter, and is in fact increasing the concentration of DOC.

Table 14: Changes in DOC, pH, Turbidity, UV₂₅₄ and SUVA for samples collected from the Assiniboine River and throughout the Portage la Prairie water treatment plant for samples collected November 23, 2010.

Sample Location	pH	DOC (mg/L)	Turbidity (NTU)	UV 254 (cm ⁻¹)	SUVA (L mg ⁻¹ M ⁻¹)
Assiniboine River	8.12	16.1	16.60	0.470	2.92
After ACTIFLO	7.97	13.6	8.30	0.437	3.21
After Clarifier	10.87	5.0	1.76	0.096	1.91
After Recarbonation	8.96	4.8	1.20	0.057	1.18
After Sand Filter	8.03	3.8	0.38	0.068	1.79
Sand Filter Reservoir	7.75	3.6	0.32	0.063	1.75
After GAC	7.53	6.7	0.40	0.067	1.00
Finished Water	7.28	1.5	0.36	0.041	2.73

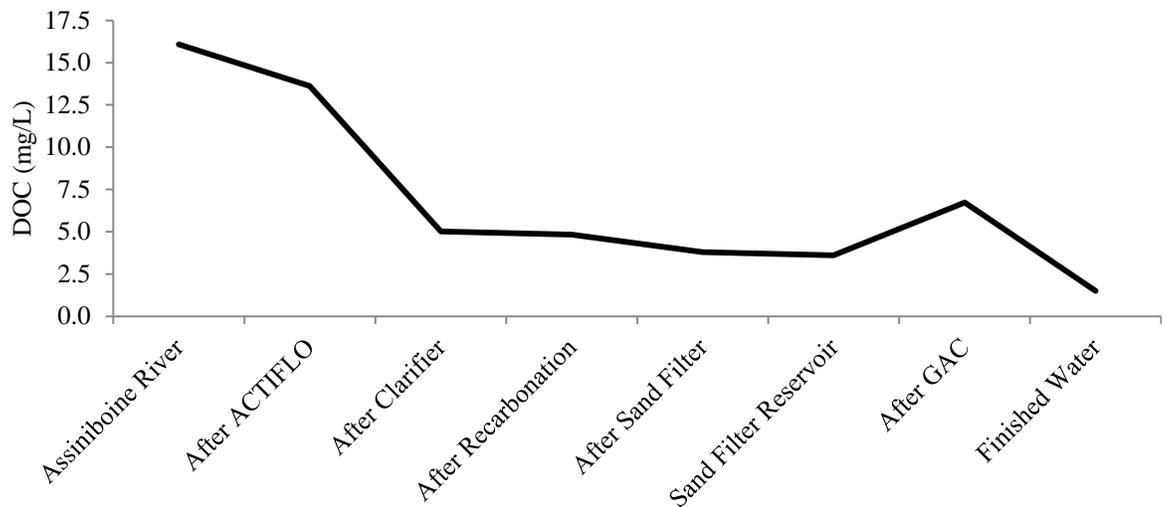


Figure 10: Changes in DOC during treatment at the Portage la Prairie water treatment plant for samples collected on November 23, 2010

To better understand the concentration of specific organic fractions found to increase after the GAC filter, fractionation of samples before and after the filter was conducted on samples collected on January 20, 2011. Table 15 shows the fractionation results of DOC samples collected in January, 2011 for samples taken before and after the GAC filter. The overall removal by the GAC filter for this sample was similar to the November, 2010 samples in that DOC increased following GAC filtration. The fractionation results show that there is a significant increase in HPIB and HPIA fractions after the GAC, while the HPON and HPOB fractions were found to decrease. The HPOA and HPIN fractions were found to have the highest concentrations after the GAC filter and were largely unaffected by the GAC media. Although the results do not conclude as to the cause for the increase in DOC following GAC filtration, it is suspected that the GAC media is over capacity and therefore releasing organics back into the water. The presence of microbial communities on the GAC, or interaction between the media and the NOM itself, may cause the changes in organic composition found after the GAC filter, however further analysis would be required to fully establish the cause.

Table 15: Fractionation results for DOC samples collected on January 20, 2011 from before and after the GAC filter at the Portage la Prairie water treatment plant.

Fraction	DOC concentration (mg/L)	
	Before GAC	After GAC
HPON	0.6 ± 0.1	0.1075
HPOB	0.288 ± 0.003	0.0441
HPOA	2.3 ± 0.1	2.4442
HPIB	0.2950 ± 0.0006	1.12 ± 0.01
HPIA	0.04 ± 0.05	0.32 ± 0.03
HPIN	3.7688 ± 0.0008	3.4585
Total	7.2674	7.5000

On April 2, 2011 samples were collected from the Assiniboine River and throughout the PPWTP to evaluate the effects of each treatment process on the removal of natural organic matter fractions (Table 16 and Figure 11). The results found were similar to those of the November, 2010 and January, 2011 samples which showed an increase in DOC following the GAC filter. The HPON and HPOB fractions, like the January, 2011 samples, were found to decrease after the GAC. The HPIN fraction was also found to decrease from 3.9 mg/L to 3.5 mg/L following GAC filtration. All other fractions were reduced by the GAC media. One difference found between the November, 2010 total DOC removal results and the April results is that there is an increase seen in DOC from post GAC to finished water. In the November, 2010 results the total DOC was found to be lower in the finished water than the post GAC sample while the April, 2011 results show an increase. Since there is no process following GAC filtration and the finished water, it is likely an error occurred in the DOC measurement of the finished water taken in November, 2011. Almost all fractions, except the HPIA and HPIB fractions, increased from the GAC filter to the finished water. The DOC in the finished water for the April, 2011 sample was found to be 9.1 mg/L and consisted of 32.5% HPOA and 55% HPIN fractions. The high concentration of organic matter in the finished water will likely cause the high THM concentrations reported by the Portage la Prairie plant; however the contribution

of THMs from each organic fraction would provide better insight as to the fraction containing the greatest numbers of THM precursors.

Table 16: Dissolved organic matter fractionation results for samples collected April 2, 2011 from the Assiniboine River and Portage la Prairie water treatment plant.

Fraction	DOC (mg/L)								
	Raw Assiniboine River	Post ACTIFLO	Post Lime Softening	Post Recarbonation	Post Ozonation	Post Sand Filter	Post Sand Filter reservoir	Post GAC	Finished
HPON	0.934	2.715	1.509	0.733	0.858	0.885	0.415	0.151	0.458
HPOB	0.201	0.960	0.082	0.125	0.238	0.056	0.147	0.000	0.366
HPOA	5.100	5.511	3.788	2.288	3.136	2.237	1.644	2.082	2.829
HPIB	0.797	0.792	0.539	0.249	0.020	0.594	0.255	0.555	0.303
HPIA	2.490	2.333	1.326	0.636	1.273	0.897	0.554	1.010	0.216
HPIN	6.710	5.220	3.839	2.979	4.004	3.191	3.922	3.483	4.976
Total	16.232	17.531	11.083	7.009	9.528	7.860	6.937	7.188	9.149

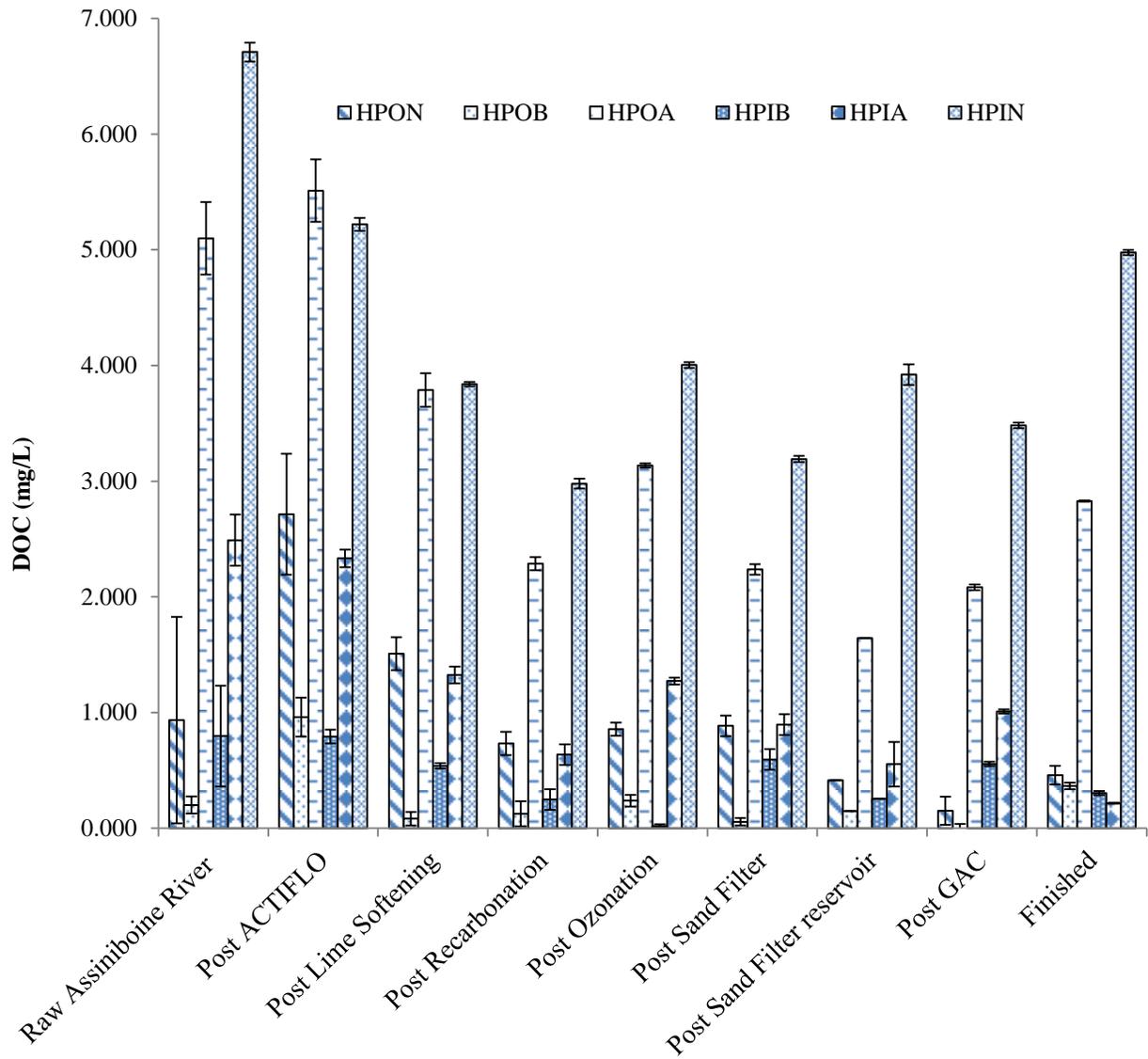


Figure 11: Dissolved organic matter fractionation results for samples collected April 2, 2011 from the Assiniboine River and Portage la Prairie water treatment plant.

Chapter 8: Trihalomethane Formation Potential of the Red and Assiniboine Rivers

Evaluation of the removal of DOC fractions by the Morris and Portage la Prairie water treatment plants provides insight as to which fractions remain in the treated water available for reaction with chlorine during disinfection. Although, it is largely believed that the HPOA fraction,

containing the humic matter, has the greatest potential to form THMs (Singer, 1999), there have been reports of other fractions having equal or greater potential to for THMs (Hwang *et al.*, 1999). The formation of THMs from specific organic fractions is likely dependant on several factors such as pH, alkalinity, concentration of organic matter, and concentration and type of chlorinating chemical. Furthermore, the distinct chemical characteristics of the DOC of a particular water body will be unique to that source and therefore it is difficult to predict the formation of THMs without testing the local organic matter for the THM formation potential (Chow, 2005). To better understand the formation of THMs at the Morris and Portage la Prairie water treatment plants, samples of raw Red River and Assiniboine River were collected and fractionated. Fractions collected from each river were then tested for the THM formation potential to establish which fractions were found to form higher concentrations of THMs.

8.1 THMFP of DOC Fractions Collected from the Red River

A sample of the Red River was collected from the University of Manitoba campus and fractionated using SPE. The fractions collected were then chlorinated, using sodium hypochlorite, to determine the THM formation potential after 7days following *Standard Methods 5710B*. After the 7day reaction time the samples were tested for THM. One note is that the THMFP test requires a baseline THM concentration test to be taken and the difference between the initial concentration and the concentration of THMs formed after 7 days is the THMFP. However, because initial concentrations of THMs could not be established due to minimal sample volume (~10 mL), an assumed initial concentration of total THMs = 0 µg/L was used. This assumption was based on a total THM concentration = 0 µg/L found in the raw Red River. It was assumed that if there are no THMs present in the raw river water, there would be no THMs present in the fractions of DOC collected following fractionation as there is no chlorination during the fractionation procedure. Prior

to THM testing, all samples were tested for free available chlorine to ensure there was free chlorine after the 7day reaction time. All samples were found to have >1.0 mg/L free chlorine which can be concluded that all THM formation reactions were driven to completion. Table 17 shows the results for the average concentration of DOC fractions collected from the Red River on August 15, 2011, along with the concentration of the four THMs measured following a 7day reaction period. The concentration of THMs was normalized to the concentration of DOC for that particular fraction for more appropriate comparison of micrograms THMs formed per milligram of DOC ($\mu\text{gTTHM}/\text{mg DOC}$). The results show that all fractions of DOC formed THMs to some degree. Chloroform was found to be the most abundant THM ranging from 73 $\mu\text{g}/\text{L}$ for the HPOA fraction to 988 $\mu\text{g}/\text{L}$ for the HPIB fraction. Bromoform was only found in one fraction, HPIN, with a concentration of 2.7 $\mu\text{g}/\text{L}$, which is likely due to low levels of bromine in the Red River ($\text{Br} < 0.1 \text{ mg}/\text{L}$ reported by ALS, 2010). DBCM and BDCM also formed significantly less than chloroform, which is likely the result of low bromine concentrations.

When comparing the THMs formed from the hydrophobic and hydrophilic fractions, the hydrophilic fractions (total THMs (TTHM) formed = 1426 $\mu\text{g}/\text{L}$ by taking the sum of HPIA, HPIB and HPIN) was significantly greater than the hydrophobic fraction (total THMs formed = 405 $\mu\text{g}/\text{L}$ by taking the sum of HPOA, HPOB and HPON). The results found here do not follow the expected formation of THMs described by Rook (1974), Singer (1999) and others which suggest the HPOA, or humic, fraction contains the greatest potential to form THMs due to high aromaticity and reactivity. The results presented here show that the HPOA fraction was the least reactive only forming an average of 76 $\mu\text{g}/\text{L}$ THMs for the THMFP test and a normalized THMFP of 23 $\text{TTHM}\mu\text{g}/\text{mg DOC}$. Furthermore, the results found that the base fractions (HPOB and HPIB) were the most reactive in forming THMs with normalized concentrations of 1002 $\mu\text{gTTHM}/\text{mg DOC}$ and 1372 $\mu\text{gTTHM}/\text{mg}$

DOC, respectively. Although, the HPOB and HPIB fractions were the most reactive in forming THMs, these fractions were found to have the lowest concentrations (<1.0 mg/L) in all fractionation tests on the Red River.

When evaluating the formation of THMs from the raw Red River and the fractions collected following fractionation, it was found that the sum of the THMs formed from the fractions exceeded the total THMs formed from the raw water. It is unclear why more THMs formed from the DOC fractions than the unfractionated raw Red River water. One hypothetical explanation could be that interactions between DOC fractions in the raw water could prevent chlorination reactions from occurring; however following fractionation chlorination reactions can readily take place.

Table 17: Trihalomethane formation of fractions collected on August 15, 2011 from the Red River at the University of Manitoba campus. Concentrations of THMs (μg) were normalized to the concentration of DOC (mg/) of that fraction of organic matter.

Fraction	Concentration (mg/L)	% DOC	Chloroform ($\mu\text{g/L}$)	Bromoform ($\mu\text{g/L}$)	Dibromochloromethane ($\mu\text{g/L}$)	Bromodichloromethane ($\mu\text{g/L}$)	THMFP ($\mu\text{g/L}$)	THM (μg) /DOC (mg)
Raw	9.8 \pm 0.5	100.0	249.0 \pm 90	MDL	3.0 \pm 0.1	31.3 \pm 5.2	283 \pm 98	29 \pm 11
HPON	1.3 \pm 0.2	13 \pm 2	165.0 \pm 56	MDL	1 \pm 1.4	13.4 \pm 4.3	179 \pm 50	147 \pm 60
HPOB	0.14 \pm 0.2	1.5 \pm 2	144 \pm 190	MDL	MDL	5.7 \pm 4.5	150 \pm 194	1002.1
HPOA	3.2 \pm .2	32.5 \pm 0.2	73.2 \pm 94	MDL	MDL	2.6 \pm 0.2	76 \pm 94	23 \pm 30
HPIB	0.56 \pm 0.4	6 \pm 4	988 \pm 1200	MDL	1.5 \pm 2.1	16.8 \pm 0.1	1007 \pm 1220	1372 \pm 1100
HPIA	0.55 \pm 0.1	5.6 \pm 0.8	160 \pm 120	MDL	2.4 \pm 0.6	21 \pm 11	183 \pm 131	349 \pm 273
HPIN	4.1 \pm 0.1	42 \pm 10	159 \pm 182	2.7 \pm 3.8	29 \pm 37	46 \pm 18	236 \pm 123	65 \pm 49

*MDL= Method detection limit (DL approximately 0.1 $\mu\text{g/L}$ according to *Standard Methods 6232B*)

8.2 THMFP of DOC Fractions Collected from the Assiniboine River

The THMFP of DOC fractions were collected from the Assiniboine River on September 1, 2011 from the intake at the Portage la Prairie water treatment plant. The fractions collected were then chlorinated, using sodium hypochlorite, to determine the THM formation potential after 7days. After the 7day reaction time the samples were tested for THM. As used in the THMFP of the Red

River, the Assiniboine River was assumed to have baseline concentration of total THMs = 0 µg/L based on 0 mg/L found in raw Assiniboine River water.

Table 18 shows the THMFP results for the dissolved organic matter fractions collected from the Assiniboine River. Similarly to the Red River, all fractions collected from the Assiniboine River formed THMs. Also, chloroform was the most abundant THM formed during this study and bromoform was not found to form in any fractions collected from the Assiniboine River. This is likely due to the low bromine concentration of the Assiniboine River.

When comparing the formation of THMs from the hydrophilic and hydrophobic fractions, the opposite result of the total THMs formed from the Red River was found for the Assiniboine River. The Assiniboine, unlike the Red River, found the THMFP for the hydrophobic fractions was 2827 µg/L, whereas the THMFP for the hydrophilic fractions were 534 µg/L. The HPOA fraction for the Assiniboine River was found to form the most THMs, largely chloroform, of 1995 µg/L. This follows literature which suggests that the HPOA fraction has the greatest potential to form THMs (Singer, 1999; Leenheer and Croué, 2003). However, when analyzing the normalized THMFP, a more even distribution of THMFP of the individual organic fractions is found. The normalized THM results for the Assiniboine River fractions show that the HPIB, as found in the Red River fraction, show significant potential to form THMs with a total of 472 µgTHM/mg DOC. However, the HPOB from the Assiniboine River did not show as significant of a normalized THM concentration as the HPOB collected from the Red River. Also, the HPON and HPIA fractions of the Assiniboine River formed greater normalized THM concentrations than the Red River.

The fractions that remain in the treated water at the Portage la Prairie water treatment plant largely consisted of HPOA and HPIN, accounting for >75% of the total organic composition (Table

16). The HPOA fraction consisted of approximately 20% of the total composition providing a significant number of THM precursors to the water which could react to form THMs that exceed the Manitoba guideline. However, the HPON, HPIB and HPIA fractions were found to produce a significant amount of THMs. Even though these fractions are found in small concentrations, their contribution to the total THMs formed should not be ignored. Therefore, it would be recommended for the Portage la Prairie plant to target removal of all fractions, with special focus given to removing the HPOA fraction. Although the HPOA fraction is shown to have similar reactivity as other fractions of the Assiniboine River, this fraction is a significant percent of the overall total DOC found in the Assiniboine River. A study should be conducted which focuses on optimizing the coagulation and softening processes to remove DOC, and more specifically the HPOA fraction, to prevent the formation of THMs above the Manitoba guideline.

Table 18: Trihalomethane formation of fractions collected on September 1, 2011 from the Assiniboine River taken from the Portage la Prairie water treatment plant. Concentrations of THMs (μg) were normalized to the concentration of DOC (mg) of that fraction of organic matter.

Fraction	DOC (mg/L)	% DOC	Chloroform ($\mu\text{g/L}$)	Bromoform ($\mu\text{g/L}$)	Dibromochloro methane ($\mu\text{g/L}$)	Bromodichlorom ethane ($\mu\text{g/L}$)	THMFP ($\mu\text{g/L}$)	THM (μg)/DOC (mg)
Raw	11.8 \pm 0.3	100.0	474.2 \pm 3.2	MDL	8.6 \pm 3	77. \pm 12	560 \pm 11	47.5 \pm 0.4
HPON	1.3 \pm 0.3	11.7 \pm 3.8	707 \pm 584	MDL	10 \pm 14	68 \pm 82	786 \pm 680	575 \pm 416
HPOB	0.1 \pm 0.1	0.9 \pm 1.2	20 \pm 12	MDL	3 \pm 4	4 \pm 1	28 \pm 17	112 \pm 159
HPOA	4.4 \pm 0.4	39.9 \pm 8.9	1995 \pm 1028	MDL	7 \pm 10	17 \pm 23	2019 \pm 1042	478 \pm 287
HPIB	0.4 \pm 0.2	3.6 \pm 1.9	120 \pm 91	MDL	3 \pm 1	20 \pm 12	142 \pm 104	472 \pm 472
HPIA	0.9 \pm 0.9	8.0 \pm 6.8	308 \pm 389	MDL	2.8 \pm 0.3	30 \pm 27	342 \pm 416	281 \pm 189
HPIN	4.7 \pm 0.3	42.4 \pm 2.2	33 \pm 20	MDL	4 \pm 2	13 \pm 6	50 \pm 27	11 \pm 5

*MDL= Method detection limit (DL approximately 0.1 $\mu\text{g/L}$ according to *Standard Methods 6232B*)

There are several drawbacks to the THMFP analysis of the Red and Assiniboine Rivers which must be noted when evaluating the results for THMFP: (1) the results are only representative of the THMFP of summer water, (2) 50mg/L of sodium hypochlorite was used for the chlorination of organic fractions. This is not representative of the conditions found in a typical water treatment plant which chlorinate around 2-6mg/L, (3) the pH of the solution was buffered to pH 7, however the pH

of the Red River reported by the Morris plant is around pH 8-8.5. There have been reports that THMs form in higher concentration at higher pH (Chowdhury *et al.* 2009). Therefore, to get a better understanding of the formation of THMs from the two rivers and the impact on water treatment plants that use the Red River or Assiniboine River as a source, experimental conditions should mirror that of the particular water treatment plant. Furthermore, the THMFP for the Red River and Assiniboine Rivers should be studied over a longer period of time to establish seasonal and temporal variations in formation potential. A final drawback for this study is that trials were conducted in duplicate making statistical analysis difficult. To provide more appropriate analysis of the formation potential, more trials should be conducted to have a statistically viable representation of the THMFP from the two rivers.

Chapter 9: Trihalomethane Formation Potential of the Red River Using Chlorine Dioxide

Chlorine dioxide has been an attractive alternative for controlling the formation of THMs in water treatment due to the fact that chlorine dioxide does not chlorinate organic matter (Aieta and Berg, 1986). However, to the best of this author's knowledge, there is no published study that tests the Red River for the chlorine dioxide-THM formation potential. Therefore, to provide further evidence of the effective use of controlling THM formation in local potable water systems, chlorine dioxide-THM formation potential of the Red River was tested. Three samples of Red River water were taken from the University of Manitoba campus on August 15, 2011. These samples were filtered and chlorinated with 50 mg/L chlorine dioxide generated and standardized in house (White, 1999). After a 7 day reaction time the samples were tested for THM concentration. Initial concentrations of THMs in the raw Red River were found to be below detection and therefore were assumed to be zero. The results show that for 2 of the 3 trials no THMs were formed, however for the 3rd trial 2.7 µg/L of chloroform was formed (Table 19). A similar result was found for a study

conducted by Hua and Reckhow which evaluated five water bodies including Shoal Lake, the water source for Winnipeg, Manitoba (Hua and Reckhow, 2007). In the Shoal Lake sample Hua and Reckhow noted a THM formation of <3 µg/L from chlorination using chlorine dioxide. Although a small amount of THMs were formed from the chlorination of Red River water, 2.7 µg/L is significantly smaller than the THMFP of the Red River collected on the same day and chlorinated with sodium hypochlorite which formed >280 µg/L total THMs (Tables 18 and 19).

Chlorine dioxide is not known to form considerable levels of THMs, however other by-products such as chlorite, chlorate, and di-haloacetic acids. Further investigation into the formation of these and other by-products of chlorine dioxide disinfection should be explored to establish if chlorine dioxide could be used as an alternative disinfectant in Manitoba.

Table 19: Red River chlorine dioxide trihalomethane formation potential results for samples collected on August 15, 2011 from the University of Manitoba campus.

Red River Sample	Chloroform (µg/L)	Bromoform (µg/L)	Dibromochloromethane (µg/L)	Bromodichloromethane (µg/L)	Total THMs (µg/L)
Trial 1	0	0	0	0	0
Trial 2	0	0	0	0	0
Trial 3	2.7	0	0	0	2.7

Part 5: Conclusions

The first objective of this study was to determine the natural organic matter composition, through solid phase extraction fractionation, of two surface water sources in Manitoba, the Red River and Assiniboine River, which are used as potable water sources. Both rivers showed seasonal variation in hydrophobic character. The composition of the Red River was found to be slightly more hydrophobic in warmer months and more hydrophilic in character in winter months. The Assiniboine River was found to have more hydrophilic components in the spring sampling period, while in the

summer the composition of the river was roughly equal in hydrophobic and hydrophilic character. The hydrophobic acid and hydrophilic neutral compounds were found to be the largest contributors in both rivers; however the Red River was also found to have significant concentration of hydrophobic neutral organic matter. The results from this study show that the composition of each river is unique even though the Assiniboine River is a tributary to the Red River. Furthermore, potable water treatment plants using these two water sources should test NOM removal strategies on that particular water, instead of taking a broader approach to treatment design implementation. Processes that are found to be successful in removing organics from one body of water may not effectively remove NOM from another source with different NOM composition.

The second goal of this study was to evaluate the removal of NOM and NOM fractions from two Manitoban potable water treatment plants, located in the towns of Morris and Portage la Prairie. The Portage la Prairie water treatment plant reduced all NOM fractions after coagulation and clarification; however the HPOA and all hydrophilic fractions increased after the GAC filter. This increase in DOC post GAC filter suggests that the GAC filter is not effectively removing organics from the water which is likely contributing to the increased THMs found at the plant.

The DOC removal at the Morris plant was found to significantly remove all DOC fractions using nano filtration, reducing concentrations of total DOC to <0.5mg/L. This reduction in DOC has allowed the Morris plant to control THM concentrations in the finished water, often with concentrations below detection limit. However, one sampling period (November, 2010) found the nano filter was not effectively removing DOC showing a slight increase after the nano filter. It is unclear as to the reason for the increase in DOC during this sampling period, therefore it is suggested that DOC removal monitoring be conducted to establish if the poor removal found in this period was related to any change in operational procedures.

The final major objective of this study was to evaluate the trihalomethane formation potential of the Red and Assiniboine River using sodium hypochlorite as the disinfectant. Even though the two rivers were found to have similar organic matter composition during the sampling period used for THMFP analysis, they showed significant differences in THMFP when using sodium hypochlorite as the chlorinating agent. The fractions containing the greatest concentrations of THM precursors in the Red River were the hydrophobic and hydrophilic base compounds, while the hydrophobic acid was found to form the least THMs per milligram DOC. On the other hand, the hydrophobic acid fraction collected from the Assiniboine River was found to form the highest THMs per milligram DOC, next to the hydrophobic neutral fraction. Lastly, nearly all fractions of DOC in the Assiniboine, except the HPIN fraction, formed similar concentrations of THMs per milligram DOC, while the Red River found significant deviation of THMFP between fractions. The results suggest that the Morris plant and Portage la Prairie plant need to approach organic matter removal in reduction of THMs differently. Morris should focus on removing hydrophobic and hydrophilic base compounds, while Portage la Prairie should focus on total removal with attention paid to the HPOA fraction in order to control THMs.

The chlorine dioxide THM formation potential for the Red River was also tested to evaluate the use of chlorine dioxide as an effective method for controlling THMs in Manitoba water. The results confirmed those found in literature indicating that chlorine dioxide is an effective method for controlling the formation of THMs. However, further investigation into the formation of other DBPs from the use of chlorine dioxide should be further evaluated on Manitoban surface water sources to prevent the contamination of potable water with harmful chlorinated by-products. Furthermore, research and development into more reliable methods or instruments for measuring free chlorine

dioxide and its subsequent by-products, chlorite and chlorate, is needed before chlorine dioxide is accepted as a potable water disinfectant in Canada.

Part 6: Recommendations and Future Work

From this study several recommendations can be made. First, an investigation into the seasonal variation of NOM, NOM fractions, and the THMFP of the Red and Assiniboine Rivers should be conducted. These tests should include a larger data set than conducted in this study to obtain more statistically reliable results. This study only captured seasonal “snap shots” of the composition of NOM in the two rivers. A larger sampling set conducted more frequently throughout the year could yield seasonal trends in the changes of organic fractions in the Red and Assiniboine Rivers. However, fractionation procedures are time consuming methods. Although the SPE method used in this study was significantly faster, roughly 12-16 hours, than the original Leenheer method, which could take upwards of 24 hours, it is difficult to replicate large data sets without a significant amount of equipment and time. However, the development of new, more rapid, fractionation methods in the future could allow researchers the ability to form large data sets of natural organic matter composition changes in a body of water. This could provide treatment plants with knowledge of how to adjust treatment processes in the plant to remove NOM fractions known, or suspected, to form disinfection by-products.

Recommendations can also be made to both the Morris and Portage la Prairie water treatment plants regarding removal of NOM and control of DBPs.

Although NOM removal by the nano filters at the Morris plant is excellent (NOM reduced to <0.5 mg/L) the plant should target removal of the hydrophobic and hydrophilic base fractions as these fractions were found to have the greatest THMFP.

Recommendations to the Portage la Prairie water treatment plant would be to optimize the treatment processes prior to the GAC filter, i.e.) the ACTIFLO system and the coagulation process, to reduce the load on the GAC filter and should be tailored to remove the HPOA fraction as it was found to form the greatest THMs. Also, an investigation into alternative forms of GAC media may provide a media capable of adsorbing greater concentrations of DOC and prevent the filter from reaching capacity.

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Part 8: Appendix

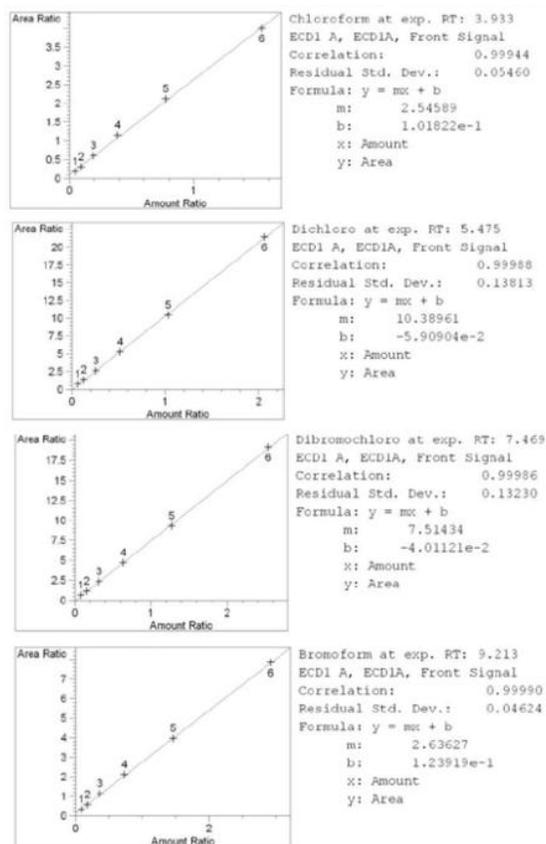


Figure 12: Standard calibration curves for four trihalomethane measured using gas an Agilent 7820A gas chromatography equipped with electron capture detection.

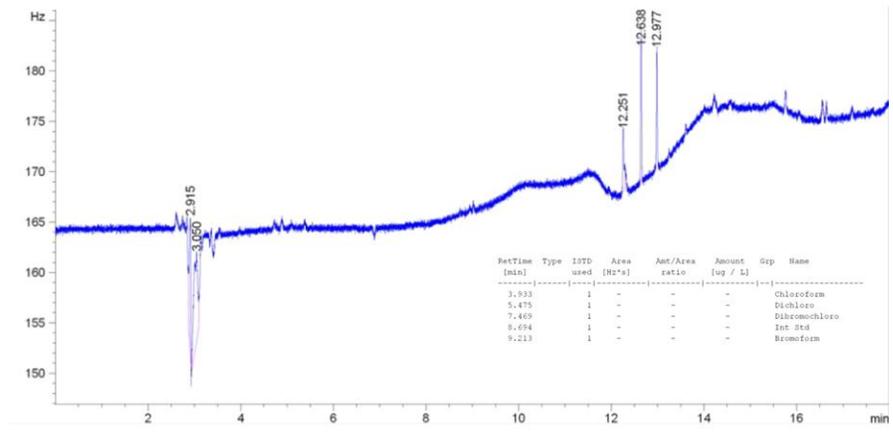


Figure 13: THM concentration for blank sample of Red River water collected August 15, 2011 using GC/ECD

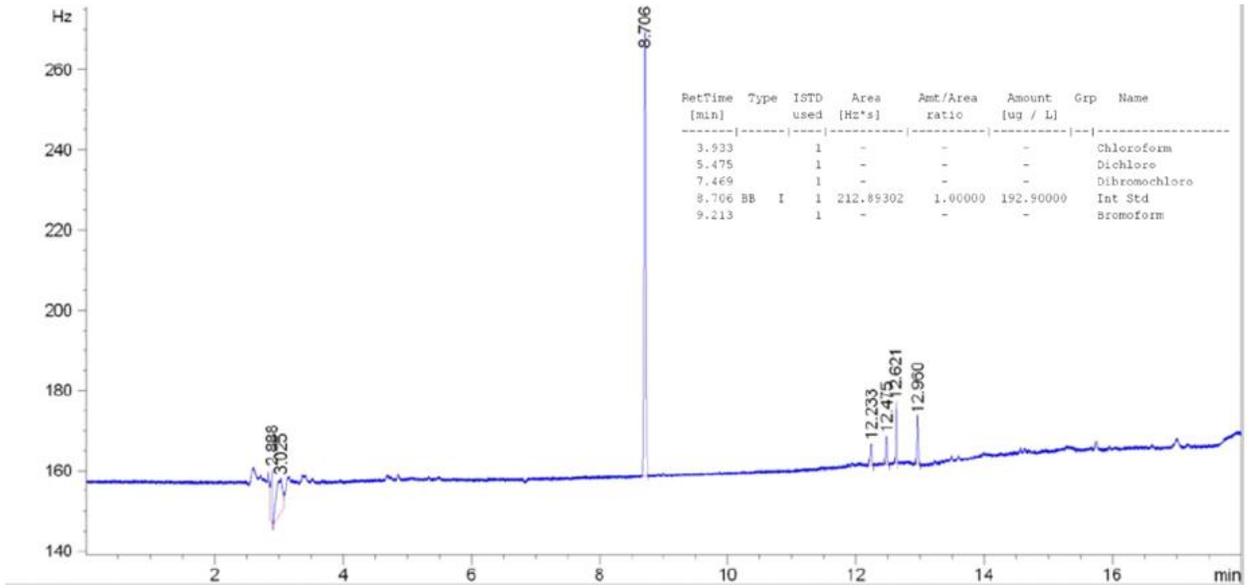


Figure 14: THM concentration for method blank sample of Red River water collected August 15, 2011 using GC/ECD

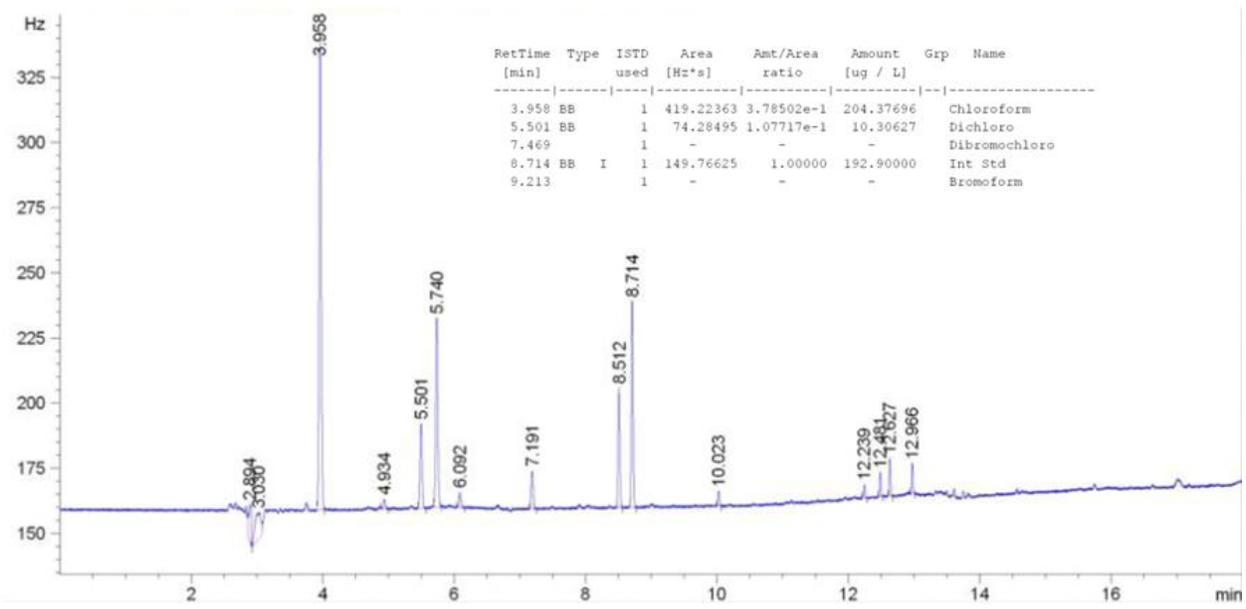


Figure 15: THM concentration for HPOB fraction sample of Red River water collected August 15, 2011 using GC/ECD

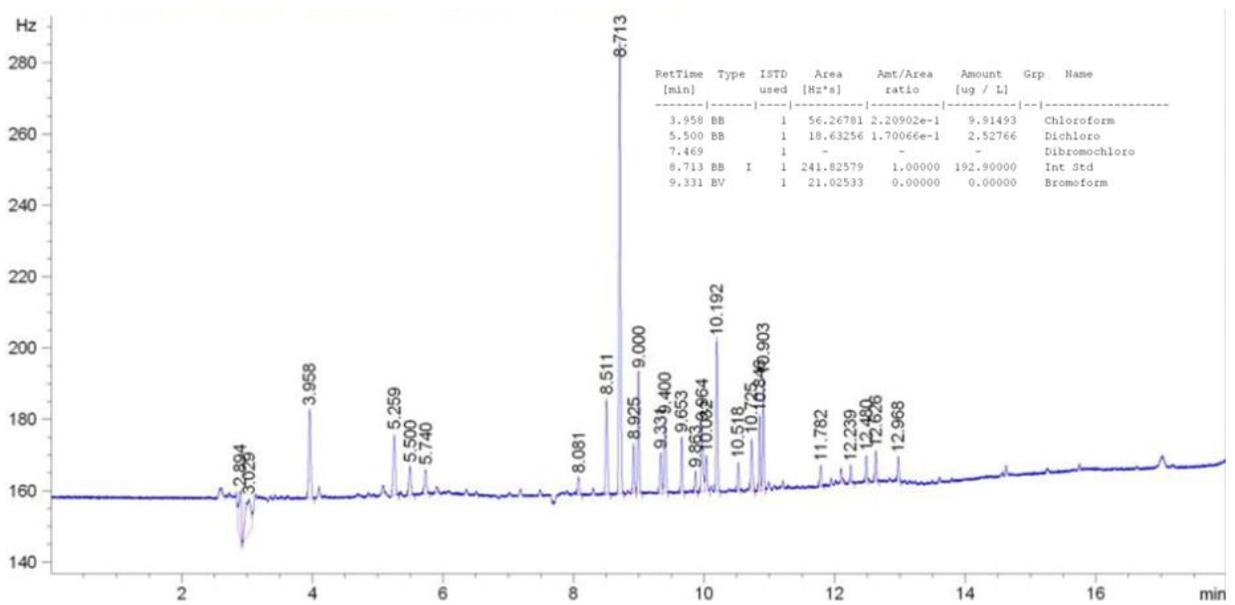


Figure 16: THM concentration for HPOB fraction sample of Red River water collected August 15, 2011 using GC/ECD

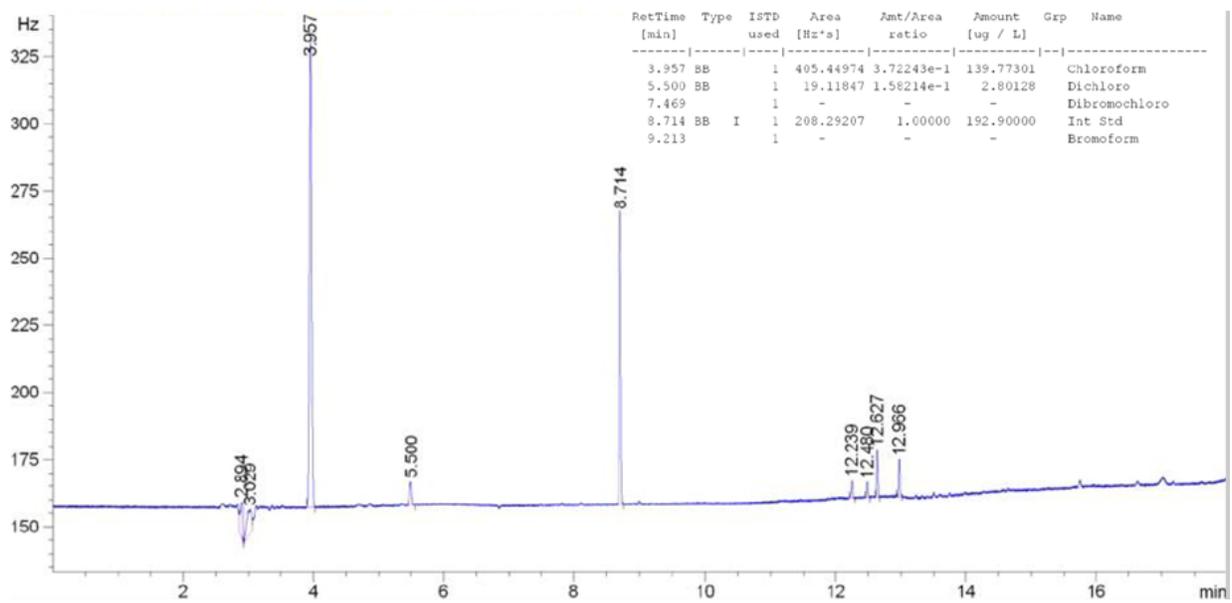


Figure 17: THM concentration for HPOA fraction sample of Red River water collected August 15, 2011 using GC/ECD

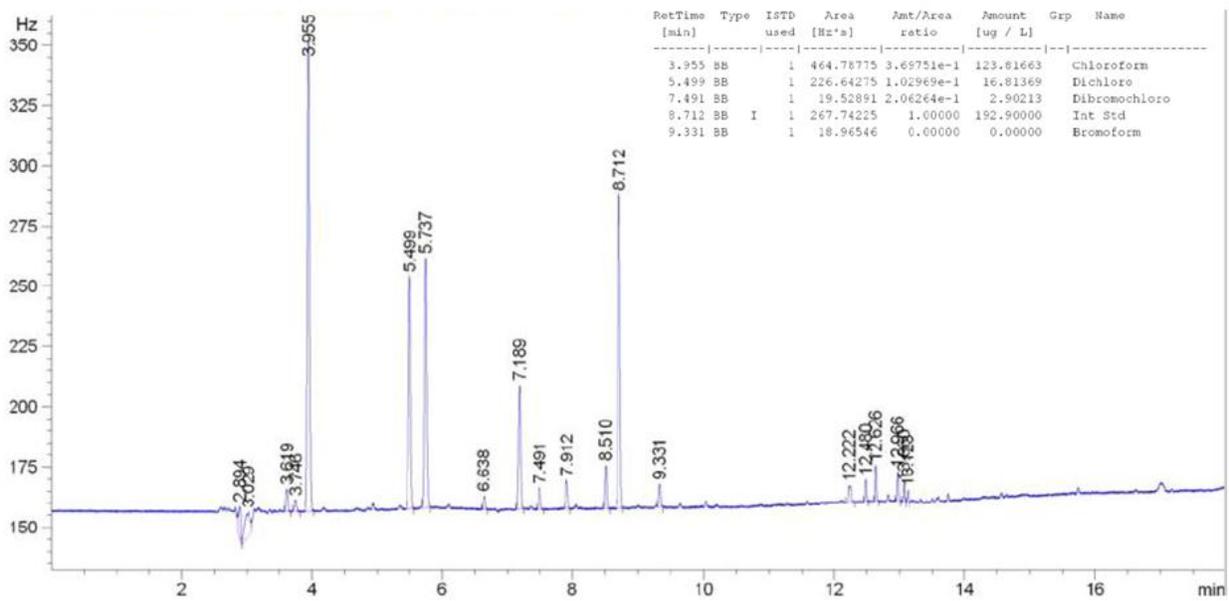


Figure18: THM concentration for HPIB fraction sample of Red River water collected August 15, 2011 using GC/ECD

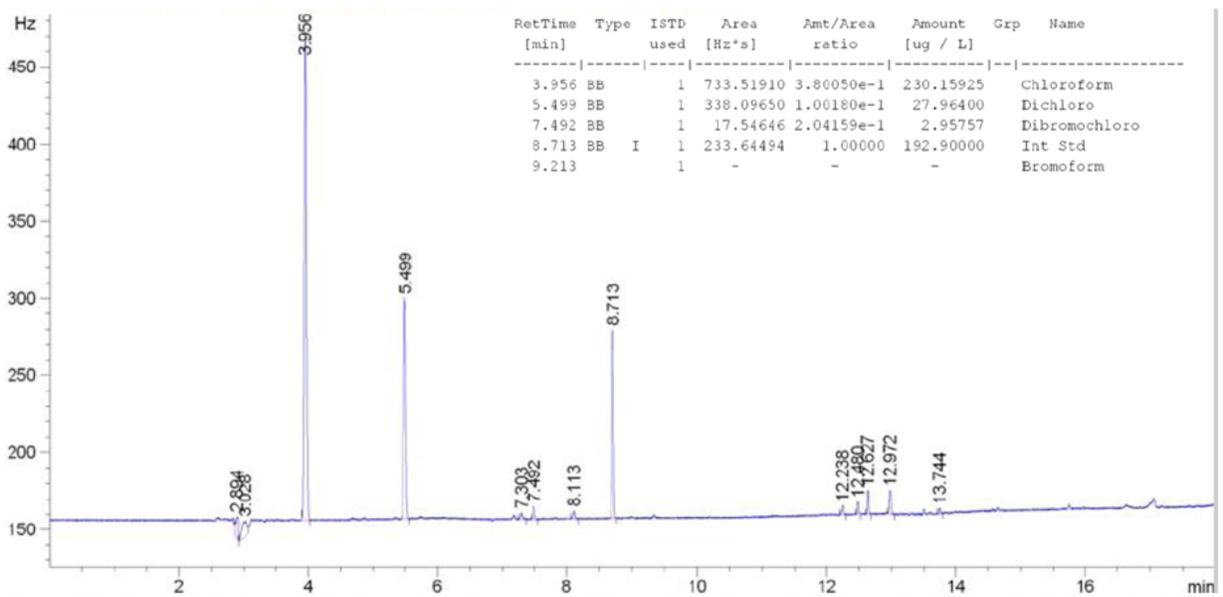


Figure 19: THM concentration for HPIA fraction sample of Red River water collected August 15, 2011 using GC/ECD

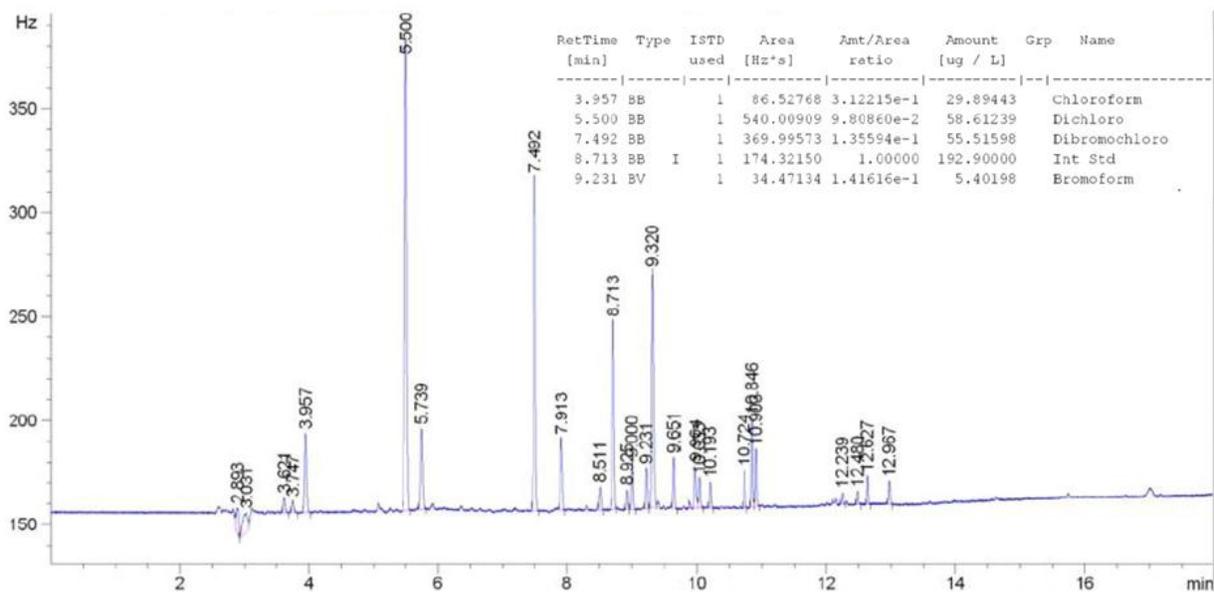


Figure 20: THM concentration for HPIN fraction sample of Red River water collected August 15, 2011 using GC/ECD

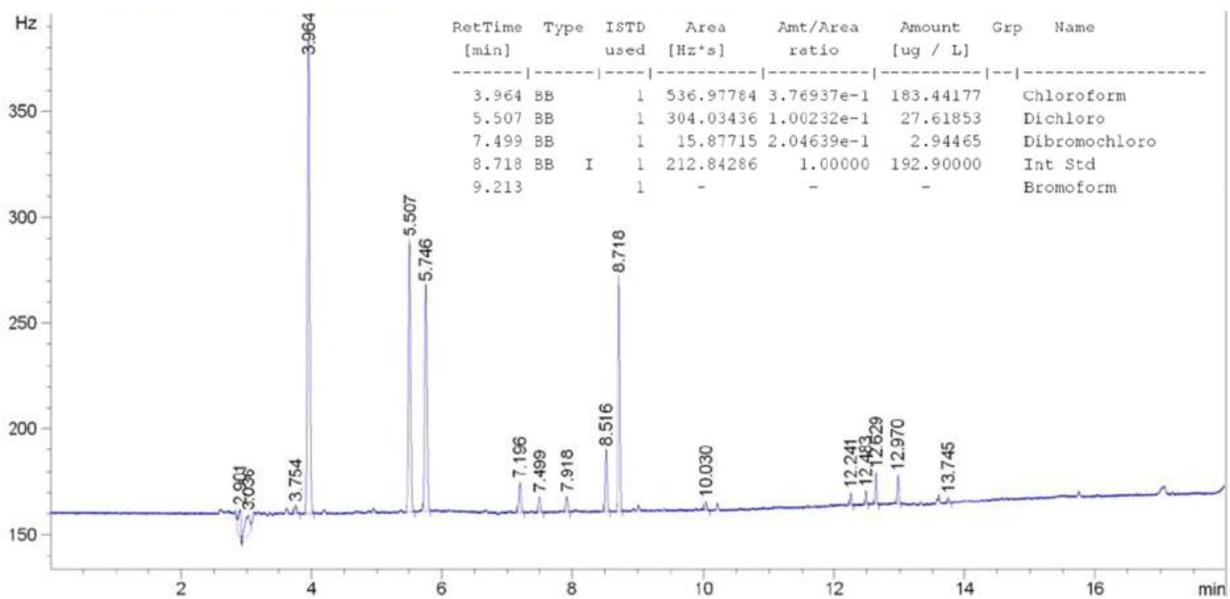


Figure 21: THM concentration for raw sample of Red River water collected August 15, 2011 using GC/ECD

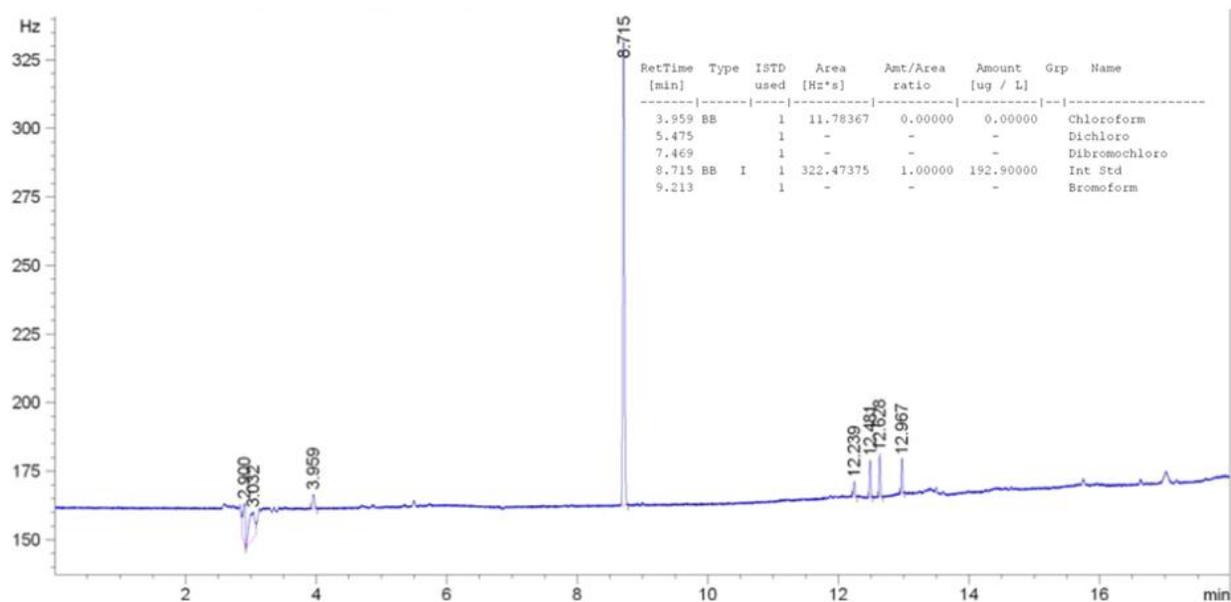


Figure 22: Trial 1-THM concentration from chlorination with chlorine dioxide for raw sample of Red River water collected August 15, 2011 using GC/ECD.

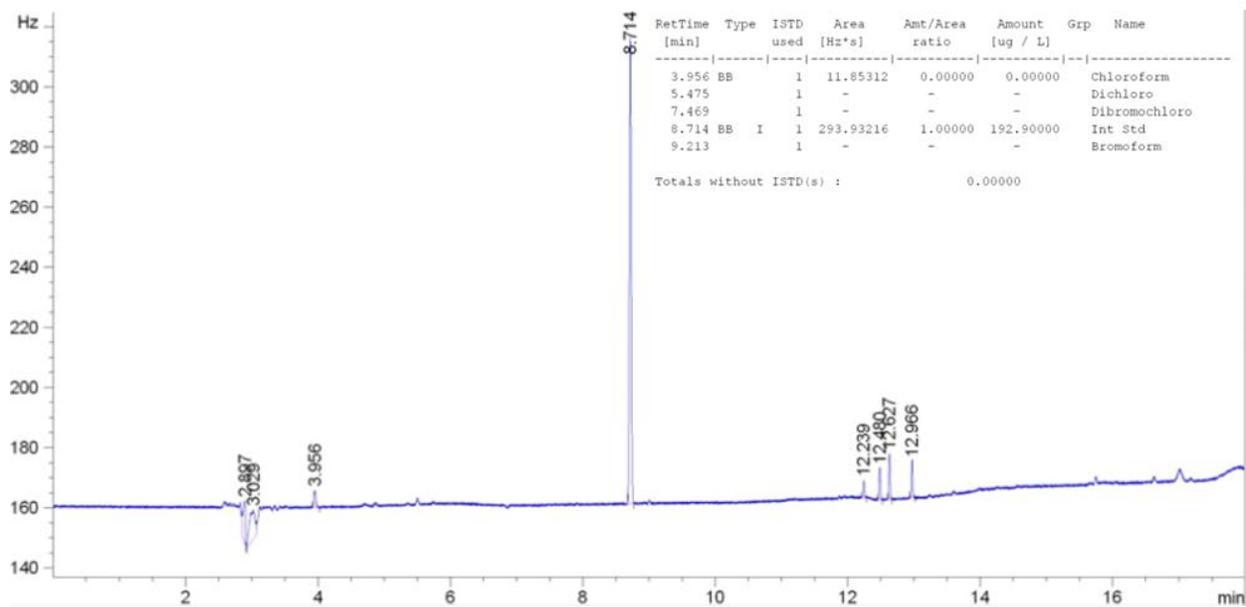


Figure 23: Trial 2-THM concentration from chlorination with chlorine dioxide for raw sample of Red River water collected August 15, 2011 using GC/ECD.

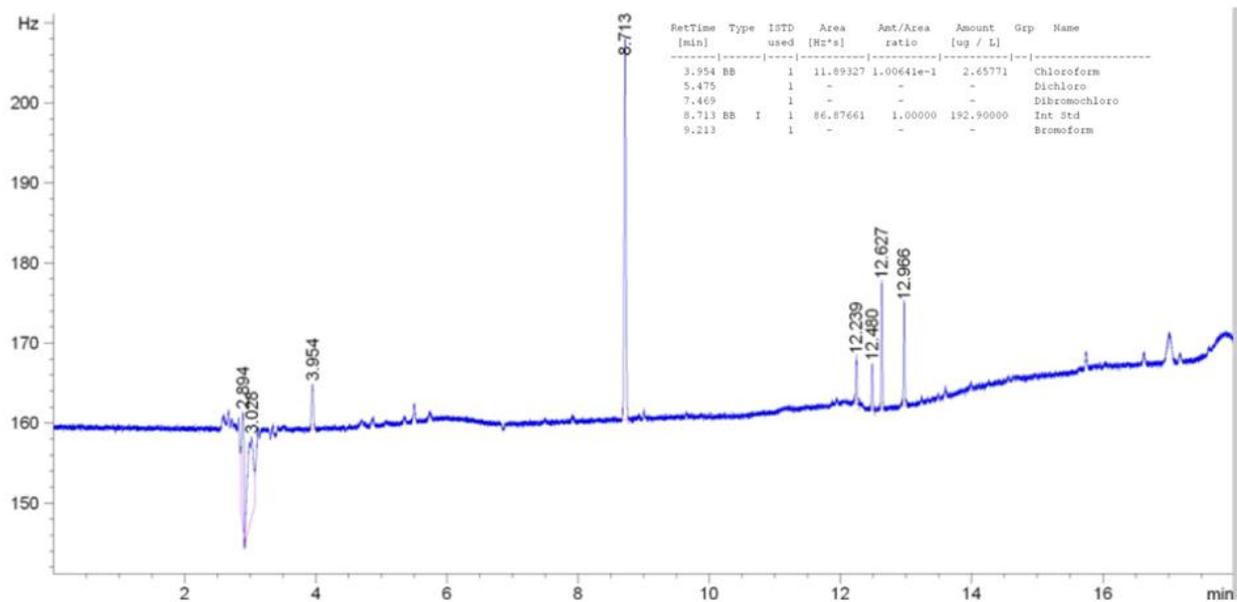


Figure 24: Trial 3-THM concentration from chlorination with chlorine dioxide for raw sample of Red River water collected August 15, 2011 using GC/ECD.

Part 9: Technical Report: Waterhen, Manitoba

MITACS ACCELARATE

Technical Report:

Identification of organic disinfection byproduct precursors at the Waterhen
Water Treatment Plant

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Abstract

The objective of this study was to determine the cause for extreme trihalomethane (THM) concentrations at the Waterhen water treatment plant located in Waterhen, Manitoba. The study was conducted over a six month period starting in May 2011. As dissolved organic carbon (DOC) is the main precursor to THM formation upon chlorination disinfection, DOC concentrations in raw source water (Waterhen River) and changes throughout the treatment plant were the major focus of this study. Water samples were collected on May 30th, 2011 for DOC and general water quality tests. As the THM concentrations at the Waterhen plant can reach as high as 1600ppb it was hypothesised that the incoming DOC would be extremely high, however the raw DOC concentration was only 9.6 mg/L. The DOC was reduced by chemical coagulation followed by sand filtration to 8.1 mg/L. However, the DOC concentration in the finished water taken from a tap in the plant was 25.9 mg/L. It was determined that the cause for the increase in DOC from the sand filter to the finished water was the addition of citric acid used to adjust the pH of the final water from >9 to about 8.5. To determine if the citric acid was contributing to the formation of THMs at the plant samples of citric acid ranging from 0-30 mg/L was tested for the THMFP. Samples were chlorinated with 50 mg/L of sodium hypochlorite and stored at 4°C for 7 days. The samples were tested for total THMs using gas chromatography with electron capture detection according to *Standard Methods 6232B*. The results found that the THMs formed largely consisted of chloroform with a concentration for the 20 mg/L citric acid sample (20 mg/L citric acid is the average addition of citric acid at the Waterhen plant) of >3000 ppb. It was determined from these results that the major cause for THM formation was the addition of citric acid to the water for pH adjustment. It was recommended that the use of citric acid to adjust pH be changed to an inorganic acid, hydrochloric acid, which is known not to form THMs. On about October 24, 2011 citric acid was discontinued at the Waterhen plant and the use of hydrochloric acid was implemented to reduce pH of the treated water. Samples were collected on

November 2, 2011 from the treated water at the plant and from the Waterhen Community Center located on the south east edge of town and tested for THM concentrations to determine if the use of HCl, instead of citric acid, reduced the overall formation of THMs. The results determined that a significant reduction in total THMs was observed (TTHM = 167 µg/L). Although the concentrations are significantly lower than during the use of citric acid, the total THMs still exceeds Manitoba guidelines. Therefore, it is recommended that further optimization of processes at the plant, such as coagulation and GAC filtration, be pursued to increase the removal of organics preventing the formation of THMs.

Introduction

Surface waters, such as lakes and rivers, often contain large concentrations of natural organic matter (NOM). Potable water treatment facilities in Manitoba often suffer from sources waters with high concentrations of natural organic matter (NOM). High NOM causes concern due to the formation of harmful disinfection by-products (DBPs), such as trihalomethanes (THMs), which form when chlorine reacts with NOM, during disinfection treatment (Singer, 1999). In Manitoba water chlorine demands often exceed 5 milligrams per liter (mg/L), resulting in residuals of 0.04-2.0 mg/L. If NOM is not removed prior to chlorination treatment the unreacted chlorine can react with the NOM and form THMs, and other halogenated by-products, which are potential carcinogens (Krasner, 2009). As a result, the province of Manitoba had adopted standards set by The Drinking Water Quality Act which requires all public potable water suppliers meet a quarterly average of <0.100 mg/L for total THMs (TTHMs) (Manitoba Water Stewardship, 2007; Health Canada, 2006). Therefore, water treatment facilities are faced with improving the removal of the organic matter from the raw water prior to chlorination in order to reduce the concentrations of THMs and other halogenated by-products. Small rural water treatment plants have the greatest difficulties in meeting the Manitoba requirements due to the fact that these plants are less advanced in terms of treatment processes compared to water treatment plants found in larger cities. Therefore, it is important to study these smaller water treatment plants in order to establish treatment processes that are inefficient at removing DOC and controlling the formation of THMs, while optimizing those processes found to improve the removal of THM precursors.

Waterhen Water Treatment Plant

The Waterhen Water Treatment Plant is located in the aboriginal community of Waterhen found in the Manitoba Interlake region. The source for this plant is the Waterhen River; water quality can be found in Table 1A. The Waterhen plant is a small facility with a flow of 3.2 L/s and is equipped with a package treatment plant (BCA Model ST&GAC-50 system). The treatment process at Waterhen can be found in Figure 1 and is as follows: raw water is treated using chemical coagulation (SternPAC) with polymer aid (LT22S). The water then enters a packaged treatment plant unit that utilizes flash mixing followed by flocculation and clarification. The water then undergoes dual media filtration (sand and anthracite) followed granular activated carbon (GAC) (FILTRASORB 400) filtration. The treated water is disinfected using sodium hypochlorite (NaOCl) and pH is reduced to ~8.0-8.5 using an average dose of 20mg/L citric acid. It must be noted that currently the GAC filter is not used at the plant due to the need for frequent cleaning and replacing of the media. A major concern for this plant is the THM concentrations which often reach extreme levels ranging from 700-2000 mg/L (Table 1A). It is believed that the high organics in the water during disinfection treatment is the source of the increased THMs at the plant.

Table 1A: Raw and treated water quality for Waterhen Water Treatment Plant and Waterhen River. Analysis was conducted in July, 2010 by ALS Laboratories

Parameter	Raw	Treated
Organic Carbon (mg/L)	10.6	26.3
pH	8.65	7.91
Alkalinity (mg/L CaCO ₃)	127	111
Hardness (mg/L CaCO ₃)	171	177
Turbidity (NTU)	0.67	0.18
True Color (TCU)	10	10
THM (ppb)	N/A	1650

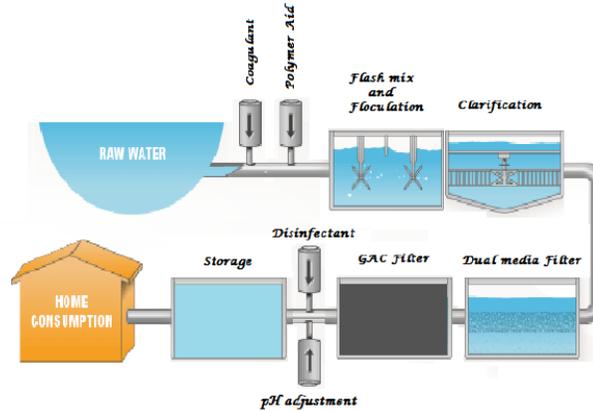


Figure 1A: Treatment process at the Waterhen Water Treatment Plant

Research Objectives

The objective of the following study was to determine the cause for extreme THM concentrations at the Waterhen water treatment plant located in Waterhen, Manitoba. The Manitoba guideline for total THMs is $100\mu\text{g/L}$; however concentrations at the Waterhen plant often range from 700ppb to greater than 1600ppb. It was suspected that the concentration of dissolved organic carbon (DOC) found in the raw source water, the Waterhen River, was high and likely contained greater numbers of disinfection byproduct precursors which was contributing to the increased formation of THMs. Although the Waterhen plant was equipped with a BCA Model ST>AC-50 System, capable of reducing incoming DOC, the overall formation of THMs indicate that the system is inefficient at removing organics prior to chlorination disinfection. This study looked at the concentrations of DOC in the source water, as well as the removal of DOC during the treatment process at the plant. General water quality tests at the Waterhen plant were also taken to establish the water quality during the study period.

Research Techniques

This research project initially was designed to determine the concentrations of DOC fractions largely believed to contain THM precursors. This involved the use of solid phase extraction (SPE) to fractionate the bulk DOC into six fractions based on hydrophobicity and acid/base functionality. Each fraction would then be evaluated for the THM formation potential (THMFP) providing evidence as to which fraction(s) have the greatest potential to form THMs and which fractions were removed from the treatment processes. However, upon the initial plant evaluation it was determined that the cause for THM formation at the plant was suspected to be from the addition of citric acid to the raw water to reduce the pH. The results from the plant evaluation caused some changes to the overall techniques stated in the proposal of this project. The focus turned from incoming DOC in the raw source water to the formation of THMs from citric acid. To determine the formation of THMs from citric acid the THMFP of citric acid was determined using *Standard Methods 5710B*. Samples of >99.8% citric acid with concentrations ranging from 0-30mg/L were used in the evaluation of the THMFP. Citric samples were chlorinated with 50mg/L sodium hypochlorite and were stored at 4°C for 7 days. After 7 days the THM concentration was determined using *Standard Methods 6232B*. General water quality tests were also conducted at the Waterhen plant and included pH, alkalinity, turbidity, UV₂₅₄, and SUVA. The alkalinity was determined using *Standard Methods 2320B*. UV₂₅₄ and SUVA were determined using US EPA Method 415.3.

Discussion and Recommendations

The objective of this study was to determine the cause for extreme trihalomethane (THM) concentrations at the Waterhen water treatment plant located in Waterhen, Manitoba. The study was conducted over a six month period starting in May 2011. As dissolved organic carbon (DOC) is the main precursor to THM formation upon chlorination disinfection, DOC concentrations in raw source

water (Waterhen River) and changes throughout the treatment plant were the major focus of this study. Water samples were collected on May 30th, 2011 for THMs, DOC and general water quality tests (Tables 2A and 3A).

The THM results from this sampling period were similar to those recorded by the plant for the last few years with a concentration of 765 ppb. According to the plant operator the free chlorine concentration exiting the plant ranges from 1.0-2.2mg/L. The Waterhen plant serves the town of Meadow Portage which is roughly 22km away. This high free chlorine concentration is used to ensure there is sufficient residual at the end of the distribution system. With the low flow rate and long distance it is believed that the time in the distribution system may be several days.

Table 2A: THM results for treated water collected from the bathroom tap at the Waterhen water treatment plant. Samples were collected on May 31st, 2011. Analysis was conducted at the University of Manitoba Environmental Laboratory.

THMs	Concentration (ppb)
Chloroform	723.38 ± 13.55
Bromoform	UND
Dibromochloromethane	9.78 ± 0.19
Bromodichloromethane	32.28 ± 0.23
Total	765.44 ± 13.36

UND= Undetectable

Table 3A: General water quality parameters for samples taken from the Waterhen River and throughout the Waterhen water treatment plant. Samples were collected on May 31st, 2011. Analysis was conducted at the University of Manitoba Environmental Laboratory.

Location	pH	Alkalinity (mg/L CaCO ₃)	DOC (mg/L)	UV254 (cm ⁻¹)	SUVA	Turbidity (NTU)
Waterhen River	8.51	140	9.60 ± 0.2	0.115	1.19807	0.43
After Coagulation	7.61	128	8.12 ± 0.01	0.08	0.98624	0.23
Top of Clarifier	7.60	128	8.15 ± 0.08	0.078	0.9575	0.21
After Sand Filtration	7.55	120	8.10 ± 0.07	0.074	0.9134	0.13
Treated	7.10	116	25.9 ± 0.7	0.183	0.70619	0.12

Initially, it was believed that the DOC concentration in the Waterhen River was high and that there was poor DOC removal by the BCA system at the plant. As suspected the DOC removal was inefficient at reducing the DOC as the coagulation and filtration processes only removed about 1.5mg/L DOC. However, the DOC concentration of the Waterhen River was not as high as expected (Table 1A) and was not believed to be the total cause for the extremely high THM concentrations (>1600ppb) found at the plant. Also, the increase in DOC from 8.1mg/L to 25.9mg/L found in the treated water was unexpected. It was determined that the increase was due to the addition of roughly 20mg/L of citric acid used to reduce the pH of the raw water. It was suspected that the citric acid was contributing to the formation of THMs however it was unclear to what degree. To determine the contribution of citric acid to the formation of THMs, the THMFP of samples of citric acid in deionized water were conducted. Concentrations ranging from 0-30mg/L of citric acid were chlorinated with 50mg/L sodium hypochlorite and allowed to react for 7 days at 4°C. The results (Figure 2A) confirmed suspicion that a significant degree of THM formation was a result of the addition of citric acid used to reduce pH. For the 20mg/L citric acid sample, which is the average addition of acid at the plant, produced greater than 3000µg/L total THMs. It must be noted that the results from this show the potential for THMs to form and can be looked at as a worst case scenario.

However, the extremely high concentrations found at the plant suggest there is a direct relation for the formation of THMs from the addition of citric acid.

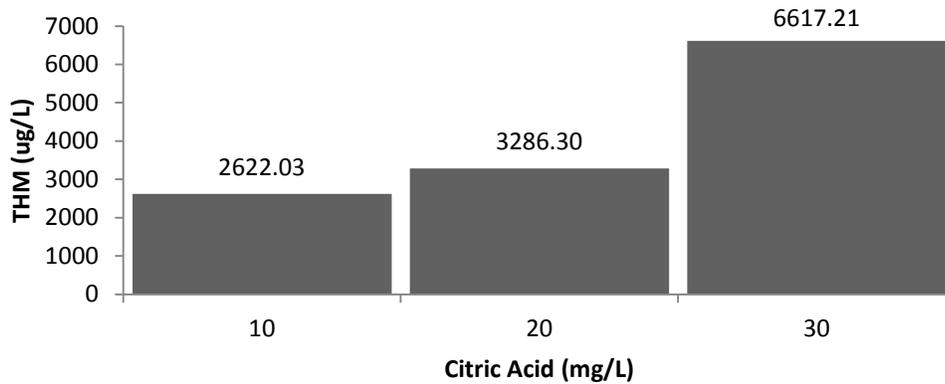


Figure 2A: THMFP of citric acid chlorinated with 50mg/L sodium hypochlorite

The location for the addition of the citric acid to the treated water to adjust pH is also problematic. The addition of the acid occurs in the effluent line directly following the GAC filter (Figure 3A). On the same line directly across from the addition of the acid is the addition of chlorine disinfection using sodium hypochlorite. This provides a situation that will increase mixing and contact which could lead to increased THM formation. This can be seen in the THM results found in Table 2A. The treated water was collected from the bathroom tap at the plant and would have the shortest chlorine contact time, yet $>700\mu\text{g/L}$ THMs were found. This suggests that there is a rapid formation of THMs for the reaction of citric acid with chlorine and that the locations of the inlets for chlorine and acid addition are providing a situation which increases THM formation.

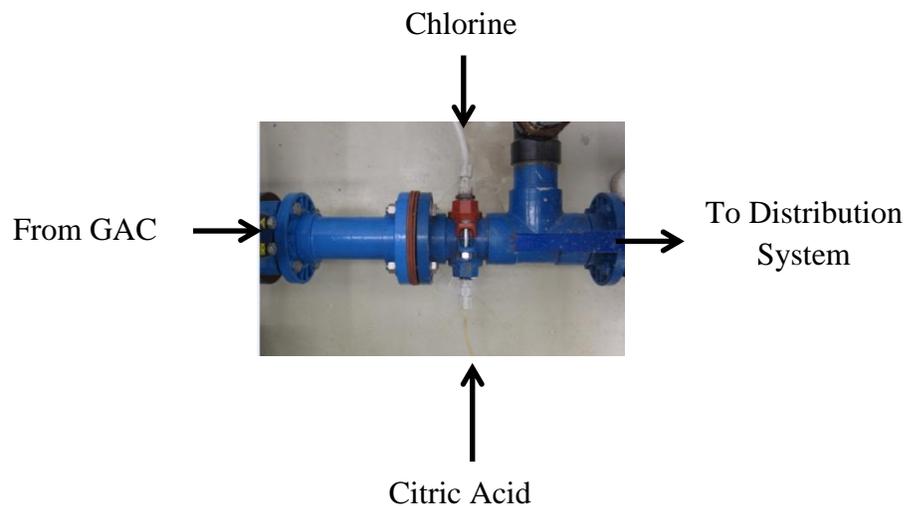


Figure 3A: Locations for the addition of chlorine disinfectant and citric acid at the Waterhen Water Treatment Plant

To reduce the formation of THMs at the Waterhen plant, it was recommended that the use of citric acid be replaced with an inorganic acid (hydrochloric acid, HCl) that is known to not react to form THMs. It was also recommended that the addition of HCl be moved from the backend, post GAC filter, to the front end prior to chemical coagulation. The reduction of pH prior to coagulation will promote flocculation and reduce organics preventing the formation of THMs.

On about October 24th, 2011 the Waterhen implemented the recommended changes of acid type and location of acid addition at the plant. Citric acid was replaced with hydrochloric acid to adjust the pH of the water. Currently, the Waterhen plant is adding roughly 0.8% HCl to the raw water to reduce the pH from >9 to roughly 7.5. The adjustment of pH requires only small amounts of HCl due to the low alkalinity of the water (Table 3A). Although the changes have only been in place for roughly 2 weeks, the operator at the plant has noticed an immediate reduction in amount of acid required to adjust pH and is expecting a decrease in the yearly cost for the chemical. Also, the location for the addition of the acid was changed from post GAC filter to the front end of the plant prior to coagulation. The addition of HCl prior to coagulation will improve the removal of organics

due to the pH of the water being closer to the optimum solubility of the chemical coagulant used at Waterhen, poly-aluminum chloride (PAC) (Figure 4A).

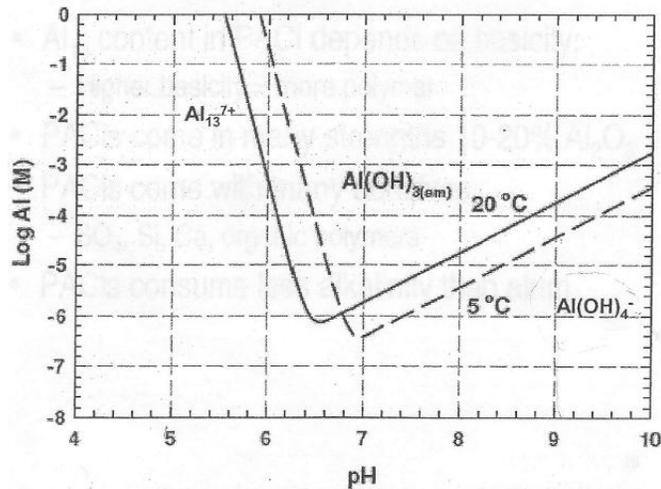


Figure 4A: Solubility of poly-aluminum chloride

The implementation of the changes at the Waterhen plant has made a significant impact on the water quality, especially the overall removal of organics and reduction of THMs. The removal of DOC prior to the relocation of the acid addition to the front end was poor with a total reduction of about 1.6mg/L DOC from coagulation. However, when the pH is adjusted prior to the addition of PAC, a slight improvement in the removal of DOC (2.3mg/L) was found (Table 4A).

Table 4A: Dissolved organic carbon removal at the Waterhen water treatment plat after the implementation of HCl for the adjustment of pH

Sample	DOC (mg/L)
Raw	7.85 ± 0.8
After Coagulation	5.57 ± 0.06
Top Sand Filtration	5.76 ± 0.17
After Sand Filtration	5.57 ± 0.05
Treated	5.72 ± 0.11

The overall focus of this study was to reduce the THM concentrations leaving the Waterhen plant. The use of HCl, over citric acid, removed a major precursor to the formation of THMs and, in turn, a significant reduction in the total THMs formed (Table 5A).

Table 5A: Total THM results for samples taken on November 2nd, 2011 from the Waterhen treatment plant (tap) and from the Waterhen Community Center located on the south east side of Waterhen

Location in Waterhen	THMs ($\mu\text{g/L}$)				Total THMs
	Chloroform	Bromoform	Dibromochloro methane	Bromodichloro methane	
Treatment Plant Tap	96.03 ± 0.14	UND	25.65 ± 0.07	45.24 ± 0.14	166.91 ± 0.07
Community Center	180.8 ± 5.6	UND	30.9 ± 1.8	61.4 ± 3.3	273.1 ± 10.8

UND = undetectable

Initial samples collected in May, 2011 found that the total THMs were $765\mu\text{g/L}$, significantly exceeding the allowable concentration of $100\mu\text{g/L}$. However, it was determined that a substantial portion of this concentration was formed due to the use of citric acid. After the use of citric acid was replaced with HCl a major decrease in the formation of THMs, mainly chloroform, was found. The total THMs found in the sample taken from the bathroom tap at the Waterhen plant was $167\mu\text{g/L}$ which accounted for a reduction of roughly $500\mu\text{g/L}$ total THMs from the samples taken from the tap in May, 2011. Samples taken from the Waterhen Community Center on November 2nd, 2011 found that the total THM concentration increase to $273\mu\text{g/L}$. This result suggests that THMs are still forming in the distribution system but that concentrations are still far less than those taken before the use of HCl. These results provide further evidence that the cause for extreme THM concentrations were a result of the use of citric acid to adjust pH.

Although the total THM concentration still exceeds the Manitoba guideline of $100\mu\text{g/L}$, the reduction of THMs from $>1600\mu\text{g/L}$ to $<200\mu\text{g/L}$ is a substantial improvement to the safety and quality of water in the community. However, recommendations can still be made to reduce the THM

concentration further. One suggestion would be to begin using the GAC filter at the plant. In times when the GAC filter was active at the Waterhen plant significant issues would occur, such as clogging of the media causing increase cleaning cycles and media replacement. As a result of the poor operation of the filter the operator decided to bypass the GAC filter. It can be hypothesised that the GAC filter was reaching capacity extremely quickly due to roughly 20mg/L of citric acid being added to adjust pH just prior to the filter. Once the GAC filter was discontinued the acid was added to the treated water just after the GAC filter (see Figure 3A). However, now that no citric acid is being added to the water it can be expected that the media should not reach capacity as quickly as when citric acid was applied. Another recommendation would be to reduce the pH from >9 to about 6.8-7.0 which is the pH of optimal solubility for PAC. This would increase the DOC removal efficiency by the coagulant and prevent the formation of THMs. However, the pH would need to be increased slightly to prevent corrosion of the pipes. A more costly recommendation would be to install nano-filtration (NF) membrane module in place of the GAC filter. The Waterhen plant has an issue with higher concentrations of brominated THMs (Table 2A and 5A) which are suspected to be more toxic than the chlorinated species. The likely cause for the increased concentrations of brominated species is the presence of bromine in the water source. A NF system would remove a significant amount of the bromine preventing the formation of brominated THMs. A NF membrane system would be a costly upgrade to the Waterhen plant, however there is sufficient space available in the plant to account for the addition of one NF module. NF membranes have significantly improved in the last decade and are far more robust. With the low incoming DOC at the Waterhen plant, along with the low flow rate, the likelihood of NF membranes to foul before the end of their expected life is low however an overall analysis of the system should be conducted to evaluate the use of a NF membrane system at the Waterhen plant.

Conclusions

The focus of this study was to determine the cause for extreme THM concentrations at the Waterhen plant. This six month study concluded that the major cause for the formation of THMs was the use of citric acid to adjust pH. It was recommended that an citric acid be replaced by an inorganic acid, hydrochloric acid, and that the location of the addition of acid occur prior to the addition of poly-aluminum chloride in order to improve the removal of organics by chemical coagulation. Upon implementation of the recommended changes a significant reduction (~500µg/L) was found. Also, a slight improvement of DOC removal was noticed which provided further control of THM formation. THM concentrations still exceed the Manitoba guideline of 100 µg/L however concentrations of ~200 µg/L is significantly move safe for consumption compared to >1600 µg/L. Additional recommendations, such as coagulation optimization or the use of NF membranes, could further reduce the DOC in the system preventing the formation of THMs, especially the brominated species.

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