Methods for Reduction of Trihalomethanes in the Rural Municipality of Macdonald Potable Water Supply System

By

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ABSTRACT

Monitoring data for potable water in the R.M. of Macdonald regional water system indicates elevated levels of chlorine disinfection by-products (DBPs), trihalomethanes (THMs). Dissolved Organic Carbon (DOC) and chlorine dose are the key precursors for the formation of THMs. Currently, the DOC is not removed efficiently at the Sanford water treatment plant, which supplies the R.M.'s potable water distribution system. The raw water DOC concentration incoming to the plant varied from 8.9mg/L to 31.8mg/L during this study. Sanford treated water effluent contained an average DOC of 6.5mg/L and the THM levels ranged from 86.6ppb to 175.7ppb.

One of the objectives of this study was to conduct jar tests to optimize Sanford's water treatment process to improve removal of DOC. Optimization of the coagulation process successfully reduced the DOC level in the plant effluent by 51% during the summer and 34% in the winter. The DOC reduction resulted in a THM reduction of 73.5ppb in the summer and 59.9ppb during the winter. Results showed that removal of 1mg/L of DOC eliminates 26.8ppb of THMs in summer and 11.9ppb during the winter.

Another goal of this project was to investigate the relationship between THMs and their precursors, which includes: water DOC, free chlorine residual, and the chlorine contact time. Water samples were strategically collected throughout the Sanford regional water distribution system; the samples were tested for DOC, UV254, SUVA, chlorine residual, and contact time. A linear relationship between THM formation and chlorine contact time (R^2 of 0.92) was found. This indicates that the content of THMs can be decreased by reducing the amount of time the water stays in the distribution system.

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1 INTRODUCTION

The La Salle River supplies water for the Sanford water treatment plant at the Rural Municipality of Macdonald. The Sanford plant was constructed in 1991 with three satellite reservoir stations at the villages of La Salle, Oak Bluff, and Starbuck with the support from the local government. Cochrane Engineering designed the key components of the regional water system.

Due to increasing local demand, the Sanford water treatment plant was expanded to provide approximately 150% more water in 1996. Currently, the Sanford water treatment plant provides water to six communities, as well as many farms and rural residences. At the Sanford plant, water is treated with alum coagulation, lime, and soda softening, sand filtration, and chlorine disinfection. Recently, UV disinfection was implemented to provide higher quality of drinking water. The R.M. of Macdonald water distribution system currently has five 315ML satellite reservoirs located at Brunkild, Starbuck, Oak Bluff, La Salle, and Domain.

Water in the R.M. of Macdonald often contains elevated concentrations of carcinogenic chlorine disinfection by-products – trihalomethanes (THM) (Table 1). Common THM in drinking water supplies include chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$), dichloroiodomethane ($CHCl_2I$), and bromochloroiodomethane (CHIBrCl). Epidemiological studies show that increased bladder, colon and rectal cancers, as well as possible acute and chronic effects (e.g. cardiac anomalies, still births, miscarriages, low birth weights and pre-term deliveries) are associated with water containing high levels of chlorine disinfection by-products (Cantor *et al.* 1998, Mills *et al.* 1998, King *et al.* 2000). In March 2007, *The Drinking Water Safety Act* was introduced and specifies that the level of THM should not exceed 100ppb in the province of Manitoba based on annual average of minimum quarterly samples (Manitoba Water Stewardship 2007). This standard is in place in most of the provinces in Canada.

Water of the La Salle River, like many other water sources in Manitoba, has a high and variable content of Natural Organic Matter (NOM). Concentrations of Natural Organic Matter can be estimated by the measurement of Dissolved Organic Carbon (DOC). DOC represents the dissolved portion of the Natural Organic Matter (NOM) in the water, which includes: humic acid; fulvic acid; and other non-humic substances. Composition and quantity of the organic matter depends on the seasonal variation of algal and bacterial growth (Goslan *et al.* 2002). DOC is believed to be the main precursor for the formation of chlorination disinfection by-products (DBPs), and trihalomethanes (THMs)(AWWA Research Foundation *et al.* 1995). Several studies indicated that the amount of THMs produced in treated waters is proportional to the concentration of DOC (Xie and Reckhow 1994, Singer 1999, Croue *et al.* 2000, Xie 2004).

1.1 Water Quality at R.M. of Macdonald

The quality of the raw water supplying R.M. of Macdonald is presented in Table 1. The DOC levels in La Salle River fluctuated seasonally; there was a much higher DOC concentration during the winter. Raw water DOC in March 2007 was recorded to be 31.8 mg/L (Cho 2007) which was significantly higher than the measurement taken in July, 2007 (8.9mg/L). Similarly, raw water DOC in March, 2008 was recorded to be 20.1mg/L, which was also higher than the measurement taken in July, 2008 (9.7mg/L). Within the last few years, the DOC concentration has been somewhat lower perhaps be due to the heavy amount of rainfall during the past few summers. The low water turbidity of 1.8NTU and true colour of 25TCU in July 2007 (compared to 17.70NTU and 62TCU in June 2005) could be an indication of dilution created by heavy rainfall. Furthermore, water quality could also be affected by the nearby runoff due to agricultural practices. For instance, the water in July, 2008 shows an increase in turbidity of 6.32NTU and true colour of 30TCU. The pH values of the raw water varied from 7.53 to 8.62.

The treated water DOC was recorded at 6.1mg/L (summer 2005) and 6.8mg/L (fall 2006). The 2008 to 2009 annual average DOC in treated water was 6.5mg/L (Epler 2009). The total THM concentrations measured at the plant ranged from 86.6ppb to 175.8ppb in 2005 to 2009 and were mostly above the Manitoba standard of 100ppb.

Table 1 Rural Municipality of Macdonald average raw and treated water quality in 2005 to 2009

RAW WATER					TREATED WATER					
Measurement Date	DOC (mg/L)	pH	True Colour (TCU)	Turbidity (NTU)	Measurement Date	DOC (mg/L)	pH	True Colour (TCU)	Turbidity (NTU)	THM (ppb)
Summer 2005 to 2008										
June 2005	24.0	8.1	62	17.70	June 2005	6.1	7.0	< 5	0.3	121.9
August 2006	16.0	8.6	14	4.50	August 2006	6.8	8.6	< 5	0.1	163.3
July 2007	8.9	8.0	25	1.80	August 2007	NA	NA	NA	NA	175.8
July 2008	9.7	8.0	30	6.32	NA	NA	NA	NA	NA	NA
Winter 2007 to 2009										
March 2007	31.8	8.1	30	2.05	NA	NA	NA	NA	NA	NA
March 2008	20.1	7.6	50	9.80	NA	NA	NA	NA	NA	NA
April 2009	17.0	7.5	40	4.20	April 2009	6.5	NA	NA	NA	86.6
Manitoba Guideline (2002) and Regulation (2007)										
Most Recent Requirement						NA	6.5 - 8.5	< 15	< 0.3	**< 100**

1.2 *Canadian Drinking Water Guidelines and Regulations*

Health Canada publishes the Guidelines for Canadian Drinking Water Quality and updates them on a regular basis (Health Canada 2008). Table 1 shows the Manitoba guidelines

(2002) and regulations (2007) for drinking water (Manitoba Water Stewardship 2002, 2007). Manitoba applies aesthetic objectives from the Guidelines for Canadian Drinking Water Quality as guidelines for drinking water systems such that the pH for drinking water should be of 6.5 to 8.5. Colour is suggested to be less than 15CTU and the standardized iron concentration is reported to be less than 0.3mg/L. Manitoba applies MACs and IMACs from the Guidelines for Canadian Drinking Water Quality as health-based standards. The regulations require that the turbidity is to be less than 0.3NTU for plants such as the Sanford Plant, that employ chemically assisted filtration. DBPs (e.g. THMs) must less than 100ppb respectively based on their annual quarterly average collected both at the plant and in the distribution system.

1.3 Water Treatment Process at Sanford Plant

Most of the existing water treatment plants in Manitoba, including Sanford, were designed before the introduction of a THM standard. Water treatment in Sanford was designed with a combined coagulation and lime softening process for space and construction saving (Figure 1). Chemical coagulation is used to reduce the turbidity, colour, and most importantly, DOC using the technique of charge destabilization of suspended particles. Water softening occurs after coagulation for reducing the water hardness by removing calcium and magnesium ions. However, DOC is not removed effectively when coagulation and softening take place in the same reactor at the same pH. This can be attributed to the high softening pH value of 10, which is significantly higher than the optimal pH for turbidity and DOC removal that ranges from 6 to 8 (Crittenden and Montgomery Watson 2005). As a result, the water DOC cannot be reduced at the Sanford water treatment plant to an acceptable level to ensure low THM level. The relatively high DOC in Sanford treated water results in high chlorine demand and THMs levels in the plant effluent (Table 1).

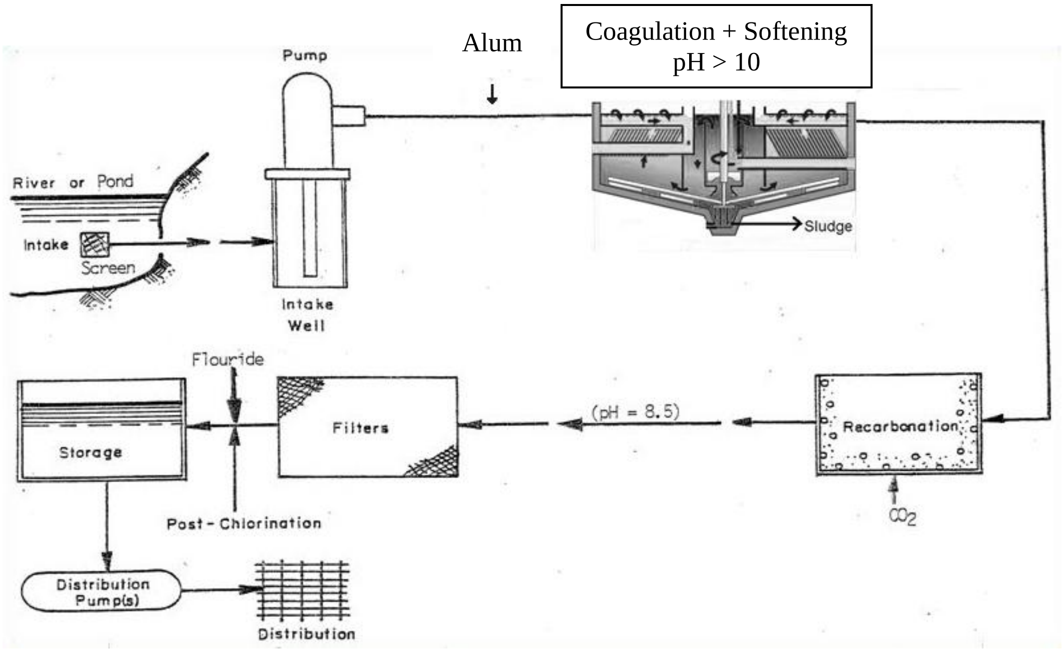


Figure 1Sanford water treatment plant diagram

Another drawback of combining coagulation with softening is the production of large amounts of lime sludge. Lime sludge has a pH above 10, which prohibits vegetation growth; therefore, it is not suitable to be used for land application. Currently, lime sludge is being land filled at Sanford. Also, the supernatant from the combined coagulation and softening reactor has relatively high loading of coagulation and softening solids. Consequently, the sand filters receive a high solids loading and require frequent backwashing, which requires significant amounts of energy and consumes water.

2 OBJECTIVES OF THIS RESEARCH

2.1 Improve Removal of DOC by Optimizing Coagulation and Softening

The Sanford water treatment plant combines water coagulation and softening in the same reactor, which operates at pH higher than 10 and does not favor DOC removal. The primary objective of this research is to improve the removal of DOC, the THM precursor, by enhancing coagulation and softening in separate optimized reactors. This configuration provides an optimal pH for removal of DOC in coagulation. It is believed that with lower water DOC, the formation of THMs in the plant effluent will be reduced.

2.2 Investigation of relationships between THMs and their precursors

The second objective of this research is to investigate the relationships between THM and their precursors, such as DOC, chlorine concentration, and the chlorine/water contact time. With these relationships, water quality parameters can be identified, which can be correlated to THM formation in the Sanford distribution system.

3 LITERATURE REVIEW

3.1 Surface Water Properties

Surface water usually contains inorganic particles such as: clay; silt; mineral oxides; and organic particulates (e.g. bacteria, algae, viruses, and other pollutants). The quality of water is usually described in terms of turbidity, colour, pH, alkalinity, hardness, and the concentration of organic matter.

3.1.1 Turbidity of Surface Water

Turbidity is a measure of the clarity of the surface water. Turbidity measurements require a light source that allows light to travel through the sample with a sensor in order to measure the scattered light. The scattered light is affected by the size, shape, refractive index, and the composition of the suspended particles of the water sample. The reading also depends on the intensity and the wavelength of the light source. Turbidity is expressed in Nephelometric Turbidiy Units (NTU) and it can be measured with a turbidimeter. An increase in turbidity may indicate that there is an increase in the concentration of water constituents (e.g. bacteria) (Crittenden *et al.* 2005). Turbidity of rivers can range from under 10NTU to 4000NTU depending on the storm events, runoff from agricultural irrigation, and water flow rate of the source. Generally, the regulatory standard for turbidity in treated potable water is 0.3 NTU (Crittenden *et al.* 2005). According to Manitoba Water Stewardship, water turbidity of treatment plant effluents with a chemically assisted filtration must be less then 0.3NTU for at least 95% of the time and it cannot exceed 1.0NTU at any time (Manitoba Water Stewardship 2007 (Manitoba Water Stewardship 2007). Plants using slow sand filtration must have turbidity less than 1.0NTU 99% of the time without exceeding 3.0NTU at any moment. Plants employing membrane filtration must have water turbidity measurements less than 0.1NTU at least 99% of the time without exceeding 0.3NTU. Many water treatment plants try to achieve a turbidity of less than 0.1 NTU, which is near the detection limit for many modern turbidimeters.

3.1.2 The pH of Surface Water

The pH of surface water plays an important role in the water treatment process because it influences the dosages and the effectiveness of chemical coagulation and softening techniques. Acidic water increases the chance of metal corrosion in pipelines and water treatment equipment. The surface water pH can be measured using pH meters. Manitoba Water Stewardship suggests the pH for drinking water should be between 6.5 to 8.5 (Manitoba Water Stewardship 2002).

3.1.3 Alkalinity of Surface Water

Alkalinity is a measure of the concentration of mostly carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in water, as well as the hydroxyl (OH^-) ion concentration in some instances. Other substances, such as phosphates and carboxylates, also contribute to the total alkalinity. Generally, alkalinity indicates the buffering power of water and it neutralizes acid and resists changes in pH. Alkalinity is expressed in terms of mg/L as $CaCO_3$ (or mg $CaCO_3$/L), which can be measured and calculated through titration with a strong acid. Usually diluted sulfuric acid (0.02N H_2SO_4) is used to titrate against water until a pH of 4.5 is achieved (APHA *et al.* 2005). All the carbonate ions and bicarbonate ions are consumed by acid base neutralization at this pH. Most of the carbonates are destroyed at a pH of 8.3 (Davis and Cornwell 1998). In environmental engineering, alkaline water has a pH greater than 7.

3.1.4 Water Corrosion Potential

Alkalinity and pH are important parameter to determine Langelier Saturation Index (LSI) which indicates the corrosion potential of water. The corrosively of water increases when LSI becomes negative. Equation 1 shows that alkalinity increases the LSI (AWWA *et al*. 1999):

$$\boldsymbol{LSI = pH + \log\left[\frac{\mathrm{K}_2'}{\mathrm{K}_s'}\right] + \log[Ca^{2+}] + \log[HCO_3^-]} \qquad \text{(Eq. 1)}$$

K_2' is the second dissociation constant of carbonic acid and Ks' is the solubility product of calcium carbonate.

3.1.5 Hardness of Surface Water

Water hardness is typically caused by the excessive amount of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in water. Although calcium and magnesium are essential substances to maintain human health, excessive amounts of calcium and magnesium can reduce the strength and solubility of detergents while leaving large amounts of scales along the pipelines in the distribution system. Hardness also creates scum in bathtubs and scales on hot water heaters. The scales are a solid form of mixed calcium and soap (Davis and Cornwell 1998):

$$Ca^{2+} + (Soap)^- \Leftrightarrow Ca(Soap)_2(s) \qquad \text{(Eq. 2)}$$

3.1.6 Particles in the Surface Water

Particle size in surface water generally ranges from 0.001 to 100µm; meanwhile, suspended particles are larger than 1um (Crittenden *et al.* 2005). Colloids represent the suspended matter that range from 0.001µm to 1µm (Crittenden *et al.* 2005). These substances exist in between dissolved and non-dissolved states (e.g. clay particles, organic matter, bacteria, and viruses) and other components contribute to colour and turbidity of water. Colloids cannot be removed by gravitational sedimentation because they are small and very stable due to their negative surface charge. Although most of the large suspended particles can be removed through conventional filtration, colloids smaller than 0.45µm such as DOC cannot be removed by filtration. Also, DOC content varies seasonally due to bacterial and algae growth along with the different compositions of organic content (Croue *et al.* 2000, Chow *et al.* 2005). From this, water treatment plants must adjust coagulant dosages in order to effectively remove DOC.

3.1.7 Surface Charge of Particles in Water

The surface charge of suspended particles is usually negative. Accordingly, a thin layer of positively charged cations tightly surround the particle surface via electrostatic and adsorption forces (Crittenden *et al.* 2005). Beyond this cation layer, the net negative electric field from the particle continues to attract cations from the bulk solution. Due to this negative electric field, an ionic cloud is formed around the particle, which is a diffused layer consisting of cations and anions. The tight cation layer and the diffused layer neutralize the overall charge between the particle and the water; these two layers form the electrical double layer (EDL). Within the EDL, the concentration of cations is high near the particle surface and it decreases further away from the surface until the electric potential neutralizes the bulk solution. EDL is mainly responsible for particle suspension stability.

3.1.8 Particle Interactions in Water

When two suspended particles contact each other, their EDLs also overlap with each other. The interaction and mixing between these two EDLs destroys the neutralized charge balance between the particles and the bulk solution. This interaction also re-establishes the initial negative electric potential of both particles. As a result, a repulsive potential energy is created between the two particles due to their recreated negative electric potential. This repulsive energy substantially increases as the distance between the two particles decreases. This repulsive force depends on the characteristics of the solution and the surface charge of the particles (Crittenden *et al.* 2005).

Attractive forces such as van der Waals forces come into play when two colloidal particles contact with each other. These attractive forces increase when the two particles become closer to each other. However, the particles cannot naturally combine together since the attractive forces cannot overcome the repulsive forces. This is due to the repulsive electrostatic forces and the EDL; they extend further into the solution than the van der Waals forces (Crittenden *et al.* 2005). Particles cannot get close enough for attractive forces to overcome the energy barrier created by the repulsive forces. As a result, colloid particles usually remain suspended in the surface water.

The repulsive forces greatly depend on the thickness of the EDL. The thickness of the double layer decreases as the ionic strength of the solution increases (Crittenden *et al.* 2005). The EDL becomes more condensed due to the excessive amount of ions in the solution. Temperature also affects the thickness of the double layer such that the double layer thickness increases with higher temperature. Equation 3 shows the relationship between the double layer and the following parameters (Crittenden *et al.* 2005).

$$\boldsymbol{\kappa^{-1} = 10^{10}\left[\frac{(2)(1000)e^2 N_A I}{\varepsilon\varepsilon_0 kT}\right]} \qquad \text{(Eq. 3)}$$

κ^{-1} = double layer thickness, Å

e^2 = electron charge, 1.60219 x 10^{-19} C

N_A = Avagadro's number, 6.02205 x 10^{23}

I = ionic strength, $1/2\sum Z^2M$, mole/L

Z = magnitude of positive or negative charge on ion

M = molar concentration of cationic or anionic species, mole/L

ε = permittivity relative to a vacuum (ε for water is 78.54)

ε_0 = permittivity in a vacuum, 8.854188 x 10^{-12} $C^2/J\cdot m$

k = Boltzmann constant, 1.38066 x 10^{-23} J/K

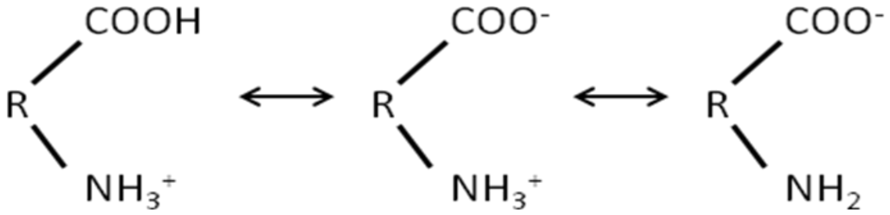
T = absolute temperature, K (°C + 273)

The thickness of the EDL also depends on the concentration of cations in the solution, which can be controlled by chemical coagulation. Positively charged ions are added into the solution to reduce the thickness of the EDL and its repulsive force. The energy barrier for particles to combine together is reduced during flocculation and the combined particles can be removed through sedimentation by gravity or by filtration.

3.1.9 DOC

Dissolved organic matter particles smaller than 0.01µm are within the colloidal range (Crittenden *et al.* 2005). Humic substances, which are mostly responsible for THM formation, are usually the major component of DOC in surface water (AWWA and Letterman 1999). These substances usually come from leaching of humus-rich soils and the decomposition of vegetation. Humic substances in surface water can by distinguished into two principal components: humic acid (HA) and fulvic acid (FA). Generally, HA has a higher molecular weight (up to 200,000g/mole) than FA (up to 1,000g/mole). FA is more soluble than HA over a wide range of pH (Crittenden *et al.* 2005). Furthermore, humic acid has a higher potential to form THM than fulvic acid due to its high aromatic content (Nikolaou and Lekkas 2001)

The surface charge of DOC directly affects the DOC removal in coagulation. DOC, specifically humic acid, often contains functional groups such as the carboxyl group (COO^-) and the amino group (NH_3^+) on their surface. These functional groups release protons and produce negatively charged surfaces at pH levels greater than 5 (Crittenden *et al.* 2005). The surface charge of DOC depends on the concentration of protons (H^+) of the surface water (AWWA and Letterman 1999). As shown in Equation 4 below, the reaction shifts to the right and the negative surface charge of the DOC increases with an increase in water pH.



(Eq. 4)

Research shows that DOC with high humic content can be removed effectively by coagulation with alum and polymer at pH of 5.5 due to their functional groups (Krasner and Amy 1995, Vrijenhoek *et al.* 1998, Carriere *et al.* 2009). It is also believed that DOC with high molecular weight and low solubility, such as humic acid, can be significantly reduced by coagulation with alum and ferric chloride at pH of 5 to 6 (Duan *et al.* 2002, Kaleta and Elektorowicz 2009).

3.2 Water Treatment Processes

Water treatment plants typically utilize several processes to produce water that meets the quality that complies with regulatory standards. The conventional treatment process include: coagulation; softening; sedimentation; filtration; and disinfection. Different water treatment configurations are employed in different cities and countries in order to reduce colour, turbidity, hardness, DOC, and THMs, and pathogens including bacteria, Giardia and Cryptosporidium to satisfy regulatory guidelines. Guidelines (Health Canada 2008) and legislations (Manitoba Water Stewardship 2007) are established such that water is of high quality and safe enough to drink.

3.2.1 Chemical Coagulation

Coagulation is usually the first step in the water treatment process, which combines small colloidal and suspended particles into larger flocs; finally, they are removed by sedimentation and filtration. Coagulation involves chemical addition in order to achieve flocculation by destabilizing the surface charge of the colloids. The effectiveness of coagulation and sedimentation processes directly impacts downstream filtration and disinfection. Successful removal of suspended matters reduces membrane and filter fouling. Additionally, removal of DOC reduces the formation of disinfection by-products such as trihalomethanes (THMs) in chlorine disinfection.

3.2.2 Chemical Reactions in Coagulation

Chemical reactions occurring during coagulation greatly depend on the type of coagulant. Commercial aluminum sulfate (alum) in hydrated form has a chemical formula of

$Al_2(SO_4)_3{\cdot}14H_2O$, which is often used in coagulation. According to Equation 5, alum hydrolyzes in the presence of alkalinity (Crittenden *et al.* 2005):

$$Al_2(SO_4)_3{\cdot}14H_2O + 6HCO_3^- \Leftrightarrow 2Al(OH)_3(s)\downarrow + 3SO_4^{2-} + 14H_2O + 6CO_2 \qquad \text{(Eq. 5)}$$

In contrast, alum hydrolizes according to Equation 6 in the absence of alkalinity (Davis and Cornwell 1998):

$$Al_2(SO_4)_3{\cdot}14H_2O \Leftrightarrow 2Al(OH)_3(s)\downarrow + 3H_2SO_4 + 8H_2O \qquad \text{(Eq. 6)}$$

Hydrated ferric chloride ($FeCl_3{\cdot}6H_2O$) can be also used in coagulation. Ferric chloride ($FeCl_3$) follows Equation 7 in the presence of alkalinity (Crittenden *et al.* 2005):

$$FeCl_3{\cdot}6H_2O + 3HCO_3^- \Leftrightarrow Fe(OH)_3(s)\downarrow + 3Cl^- + 3CO_2 + 6H_2O \qquad \text{(Eq. 7)}$$

Ferric chloride follows Equation 8 in the absence of alkalinity (Davis and Cornwell 1998):

$$FeCl_3 + 3H_2O \Leftrightarrow Fe(OH)_3(s)\downarrow + 3HCl \qquad \text{(Eq. 8)}$$

Hydrated ferric sulfate ($Fe_2(SO_4)_3{\cdot}9H_2O$) is also used for coagulation. It follows Equation 9 in the presence of alkalinity (Crittenden *et al.* 2005):

$$Fe_2(SO_4)_3{\cdot}9H_2O + 6HCO_3^- \Leftrightarrow 2Fe(OH)_3(s)\downarrow + 3SO_4^{2-} + 6CO_2 + 9H_2O \qquad \text{(Eq. 9)}$$

In summary, each mole of trivalent metal ion reacts with 3 moles of water to produce 1 mole of hydroxide and 3 moles of hydrogen ions (Crittenden *et al.* 2005):

$$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3(s)\downarrow + 3H^+ \qquad \text{(Eq. 10)}$$

$$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3(s)\downarrow + 3H^+ \qquad \text{(Eq. 11)}$$

$Al(OH)_3$ and $Fe(OH)_3$ precipitates adsorb and trap the suspended solids while DOC forms particle aggregates (i.e. flocs). The precipitate of alum and ferric sulfate can be calculated using equations 4 and 8 respectively. One gram of alum produces 0.26g of insoluble $Al(OH)_3$, while one gram of ferric chloride produces 0.5g of $Fe(OH)_3$.

3.2.3 Coagulation Jar Tests

Surface water quality changes seasonally; therefore, the coagulant dosage must be determined through experimentation. The jar test is a pilot scale experiment that effectively simulates coagulation and softening in order to determine the required chemical dosage. Usually the jar test consists of rapid mixing followed by slow mixing, which is supposed to simulate flocculation. Several beakers and jars are filled with equal amounts of surface water and each beaker is treated with a different chemical dosage. Samples are then allowed to settle and the supernatant is then analyzed to see if it meets the required chemical dosage. The jar testing procedure is further explained in detail in the experimental methods section.

3.2.4 Factors Affecting Coagulation

Coagulation depends on many factors that include: water pH; alkalinity; temperature; and coagulants.

3.2.4.1 The Solubility of Coagulants

Alkalinity is the water buffering capacity that can affect the chemical reaction of coagulants. In the absence of alkalinity, Equations 6 and Equation 8 show that H_2SO_4 or HCl are formed in the coagulant hydrolysis step, which reduces the water pH (Crittenden *et al.* 2005). The pH level directly affects the DOC removal in coagulation because coagulants become more insoluble at optimal pH; hence, increasing sweep floc formation and promoting DOC removal. Generally, ferric coagulants are more insoluble at a wider pH range than alum. The optimal pH for alum is at 5.5 to 7.7 and it has a minimum solubility at pH of 6.2. In comparison, the optimal pH for ferric salt is 5 to 8.5 and it has a minimum solubility at a pH of 8 (Crittenden *et al.* 2005). Coagulants become soluble outside their optimal pH range. Soluble alum species include Al^{+3}, $Al(OH)_4^-$, $Al(OH)^{+2}$, and $Al(OH)_2^+$ and soluble ferric species include Fe^{+3}, $Fe(OH)_4^-$, $FeOH^{+2}$, and $Fe(OH)_2^+$. These species can directly by-pass coagulation; thus, reducing the DOC removal efficiency.

Alufer shares the chemical properties of alum and ferric sulfate; therefore, factors affecting alum and ferric coagulants will also affect alufer S25. The optimal pH range for alufer S25 is around 5.0 to 7.0 (Kemira Water Solutions, Inc., Quebec, Canada). According to equations 4 and 8, one gram of alufer S25 produces 0.195g of $Al(OH)_3$ and 0.125g of $Fe(OH)_3$, with a total of 0.32g of precipitate. Each gram of alufer precipitate contains 0.61g of $Al(OH)_3$ and 0.39g of $Fe(OH)_3$.

The temperature of water affects the solubility of ions (Crittenden *et al.* 2005, AWWA 1999). Flocs formed in cold water are weaker than those at room temperature. This is because the chemical reaction is slower in cold temperatures. Research has shown that flocs formed with aluminum polymer in cold water are smaller and lighter (Braul, 2001). The impact on coagulation by temperature may also be due to changes in viscosity of the water and the hydrolysis rate of metal ions (Hurst *et al.* 2004). Hurst found that temperature significantly impacted turbidity removal (2003). He also found that the required coagulant dosage increases at 5℃ when compared to 15℃. Also, both alum and ferric coagulants have a short hydrolysis at room temperature, which may increase at low temperature. It is expected that less DOC is removed at cold temperature due to the poor formation of flocs. However, several researchers found no impact on DOC removal in cold water compare to room temperature (Knocke *et al.* 1986, Randtke 1988, Hanson and Cleasby 1990). This may be achieved by gentle mixing, which allows contact between coagulants and colloids without breaking the flocs apart. The temperature in Manitoba during the winter is usually below 0℃, which may impact the performance of coagulation due to the low temperature of water. The Sanford water treatment plant stores surface water in an inlet reservoir. Water temperature in the coagulation process is about 25℃ in the summer and 10℃ in the winter.

3.2.5 Chemical Softening

Softening removes water hardness by removing the dissolved calcium and magnesium ions from water. Water acidity (i.e. CO_2) is first removed by lime ($Ca(OH)_2$), which increases the pH to a value greater than 10. Calcium and magnesium precipitate at high pH values in the form of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). The required lime and soda (Na_2CO_3) dosages are calculated using water pH, alkalinity, calcium hardness, and magnesium hardness.

3.2.6 Chemical Reactions in Softening

During softening, several chemical reactions occur; some of them happen simultaneously. First, CO_2 in water is removed as calcium carbonate ($CaCO_3$) by adding lime (Davis and Cornwell 1998):

$$CO_2 + Ca(OH)_2 \Leftrightarrow CaCO_3(s)\downarrow + H_2O \qquad \text{(Eq. 12)}$$

Afterwards, the calcium and magnesium hardness are removed differently by the addition and the removal of alkalinity. In the presence of alkalinity, calcium ions precipitate with lime as shown below (Davis and Cornwell 1998):

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \Leftrightarrow 2CaCO_3(s)\downarrow + 2H_2O \qquad \text{(Eq. 13)}$$

In the presence of alkalinity, magnesium ions precipitate with lime as demonstrated below (Davis and Cornwell 1998):

$$Mg^{2+} + 2HCO_3^- + Ca(OH)_2 \Leftrightarrow MgCO_3 + CaCO_3(s)\downarrow + 2H_2O \qquad \text{(Eq. 14)}$$

$$Mg^{2+} + CO_3^{2-} + Ca(OH)_2 \Leftrightarrow Mg(OH)_2(s)\downarrow + CaCO_3(s)\downarrow \qquad \text{(Eq. 15)}$$

In the absence of alkalinity, soda ash is added as a source of alkalinity. Calcium ions precipitate with soda ash as follows (Davis and Cornwell 1998):

$$Ca^{2+} + Na_2CO_3 \Leftrightarrow CaCO_3(s)\downarrow + 2Na^+ \qquad \text{(Eq. 16)}$$

Finally, magnesium ions precipitate with lime in the absence of alkalinity (Davis and Cornwell 1998):

$$Mg^{2+} + Ca(OH)_2 \Leftrightarrow Mg(OH)_2(s)\downarrow + Ca^{2+} \qquad \text{(Eq. 17)}$$

3.2.7 Sedimentation

Sedimentation is the oldest and most common form of the solid/liquid separation process in water and wastewater treatment (Crittenden *et al.* 2005). Sedimentation often follows coagulation and softening in a typical water treatment plant in order to remove heavy particles. It removes flocs from coagulation and softening before filtration to reduce filter fouling. Usually, mineral particles have a density of 2000 to 3000 kg/m^3; hence, they tend to settle quickly. Organic matter has a much lower density that ranges from 1010 to 1100 kg/m^3; thus, it requires a longer time to settle (Crittenden *et al.* 2005). The design of the solid/liquid separation apparatus is based on the surface overflow velocity and the minimum settling velocity that is required for particles to be separated in the process. Dissolved air floatation (DAF) can effectively remove small and light particles, however, at a higher operation cost.

3.2.8 Filtration

Filtration removes particulate matter from water prior to disinfection using sand, activated carbon, or membrane filtration. Pressure drives water and small materials through the filter; meanwhile, larger materials are rejected or are trapped inside the filter. The sand filter removes most of the large suspended particles. Sometimes sand filter media is combined with activated carbon in order to improve the effluent quality.

Membrane filtration provides high effluent quality with various options. For instance, the microfiltration (MF) membrane removes suspended particles and reverse osmosis (RO) removes all the organic matter and most of the dissolved ions in water. The maintenance cost of RO membranes can be significant as they reject most of the water pollutants, which tends to foul the membrane.

3.2.9 Disinfection

Disinfection is usually the last process in water treatment plants. During this procedure, pathogenic microorganisms are inactivated in drinking water (AWWA and Letterman 1999). Coagulation, sedimentation, and filtration remove certain amounts of bacteria and viruses. However, disinfection is essential to the removal of the remaining bacteria for safe drinking water. Chlorine, chlorine dioxide, ozone, and UV light are common disinfectants; some of which have been applied since the 18th century (AWWA *et al*. 1999). These disinfectants kill or inactivate pathogens through different mechanisms. For instance, UV inactivates most of the pathogens immediately at the plant while chlorine disinfection continues inactivating microbes within the distribution system. Chlorine is the most popular disinfectant; however, it produces THMs that also need to be controlled. Regulation for disinfection of surface water sources in Manitoba requires immediate reduction or inactivation of 99.9% of Cryptosporidium oocysts, 99.9% of Giardia lamblia cysts, and 99.99% of viruses (Manitoba Water Stewardship 2007).

3.2.9.1 Disinfection with Chlorine

Chlorine gas (Cl_2) and sodium hypochlorite solution (NaOCl) are common methods of chlorine disinfection. Small plants may utilize calcium hypochlorite powder as disinfectant. Chlorine forms hydrochloric acid and hypochlorous acid when dissolved in water (Crittenden *et al.* 2005):

$$Cl_2(g) + H_2O \rightarrow HCl + HOCl \qquad \text{(Eq. 18)}$$

Hydrochloric acid immediately dissociated into hydrogen and chloride ions, which reduces the water pH:

$$HCl \rightarrow H^+ + Cl^- \qquad \text{(Eq. 19)}$$

Hypochlorous acid is a weak acid, which distributes itself in the forms of HOCl and OCl^- :

$$HOCl \Leftrightarrow H^+ + OCl^- \qquad \text{(Eq. 20)}$$

Generally, hypochlorous acid has a greater disinfection power than hypochlorite ion due to its fast disinfection kinetics. Free chlorine, which includes HOCl and OCl^-, is mainly responsible for water disinfection.

In practice, ammonia (NH_3) is often present in surface water and it influences the chlorine reactions. Chlorine combines with ammonia and forms combined chlorine in the form of: monochloramine (NH_2Cl); dichloramine ($NHCl_2$); and trichloramine (NCl_3). Ammonia must be combined with chlorine before a desired free chlorine residual concentration can be achieved for disinfection. The amount of required chlorine to completely combine with ammonia and other constituents is called the chlorine demand. The chlorine demand can usually be determined by the chlorination breakpoint such that ammonia is completely removed. Free chlorine residuals increase proportionally with chlorine addition beyond the breakpoint.

Manitoba regulation for chlorine disinfection requires a minimum contact time, time during chlorination, of 20 minutes. The free chlorine residual must be above 0.5mg/L immediately after chlorination and 0.1mg/L throughout the distribution system (Manitoba Water Stewardship 2007).

3.3 Trihalomethanes (THMs)

Since Rock reported the formation of chloroform in chlorination of water with organic matter in 1976 (Rook 1976), the impact of chlorination still remains an intensive research subject. THMs are one of the main disinfection by-products in chlorine disinfection. Three hydrogen atoms on the methane molecule (CH_4) are substituted with three halogen atoms such as fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). Common THMs in drinking water include chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$), dichloroiodomethane ($CHCl_2I$), and bromochloroiodomethane ($CHIBrCl$).

Regulations and rules were first created by the United States Environmental Protection Agency (U.S. EPA) in 1979 due to the negative health effects of chloroform reported by the National Cancer Institute (NCI) in 1976 (Crittenden *et al.* 2005). U.S. EPA specifically wanted to reduce the chronic exposure by controlling the total concentration of chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) to levels below 100ppb in drinking water. Currently, the U.S. EPA has a regulation for THMs at 80ppb (U.S. EPA 2006). The THM measurement rules require a minimum of four monitoring locations in the distribution system. Three of these monitoring locations must be located at the average hydraulic travel time of the system leaving one monitoring location at the end of the distribution line. The THM rules also require that the water treatment plant utilizes chemical coagulation and clarification to remove the THM precursor, DOC. Manitoba established THM regulations of 100ppb for potable water on 28th of February 2007. Measurements are based on an annual average of quarterly samples taken at the water treatment plant and at the point in the distribution system with the highest THM formation potential. These points generally represent the areas in the distribution system with the longest disinfectant retention time, which are typically at the far end of the distribution system. (Manitoba Water Stewardship 2007, Health Canada 2009).

3.3.1 Measurement of THMs Concentrations

Water treatment plants have to monitor THM in the distributed water to meet the regulatory standard. The most accurate and standard THM measurement method utilizes gas chromatography with mass spectrometry (GC/MS) (APHA *et al.* 2005), which is costly and requires professional technicians for operation and maintenance. Most Canadian water systems cannot afford GC/MS nor the staff required; therefore, send water samples to accredited water testing laboratories for THM analysis. Alternatively, THM measurements using a spectrophotometer with the total trihalomethanes reagent kit, such as the total THMs reagent set with THM Plus Methods 10132 by HACH Company (Loveland, USA).

THMs are quite volatile and easily vaporize when exposed to air. Vaporized THMs can enter the human body through inhalation and are still carcinogenic. Research shows that 28% of THMs, including $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, vaporize at 25℃ within a four hour period (Batterman *et al.* 2000). Furthermore, 16.5% of THMs vaporize at 4℃ within a two hour period. Therefore, it is necessary to preserve THM samples at low temperature (about 0℃) without any contact with air.

3.3.2 Factors Affecting THM Formation

It is difficult to monitor THM formation by isolating individual chemical reactions in chlorine disinfection. However, it is believed that natural organic matter and chlorine content are the primary factors affecting THM formation (AWWA Research Foundation *et al.* 1995).

DOC, in general, has different potentials for forming THM (Croue *et al.* 2000, Chow *et al.* 2005). Research has shown that aromatic organic matter has high chemical reactivity with respect to THM formation (Norwood *et al.* 1987, Westerhoff *et al.* 2004). Ultraviolet and Visible (UV) water absorbance at 254nm are often used as a surrogate measurement for the concentration of this aromatic organic matter, which is based on the measurement of the unsaturated carbon double bonds (Dobbs *et al.* 1972, Traina *et al.* 1990, Goel *et al.* 1995). Since the early 1980's, UV absorption has been used to measure the concentration of humic substances in Europe and North America (Braul *et al.* 2001). Specific Ultraviolet and Visible Absorbance

(SUVA) at 254nm is the normalized UV absorbance at 254nm with respect to DOC content (Equation 21) (AWWA *et al.* 1999). SUVA is believed to be related to the formation of THMs (Korshin *et al.* 1999, Chow *et al.* 2005).

$$SUVA = \frac{UV@254nm}{DOC} \text{ x } 100 \qquad \text{(Eq. 21)}$$

Aromatic compounds are more likely to be removed by coagulation and precipitative softening due to their high chemical reactivity. Previous studies have demonstrated that 50 to 80% of DOC can be removed by coagulation in water, which contains high humic acid with SUVA between 3 to 5 L/mg C.m^{-1} (AWWA *et al.* 1999). UV absorbance at 254nm tends to decrease faster than the total water DOC during the removal of DOC in coagulation. As a result, coagulated water usually has a lower SUVA value than raw water.

The relationship between SUVA and THM formation may not be straight forward. Prior investigations have demonstrated that seasonal variations of THM formation is related to the water source characteristics and seasonal changes (Uyak *et al.* 2008). The reactivity of the organic matter with respect to THM formation varies throughout the year. Generally, organic matter has the lowest reactivity in the winter and it usually increases during the spring with a maximum level achieved in the fall. This may due to the difference in temperature and the composition of DOC. Trihalomethane Formation Potential - THMFP is the total THM concentration analyzed seven days contact time with chlorine.

3.3.2.1 Chlorine Dose, Residual and Contact Time for THM Formation

THM formation also depends on the concentration of the free chlorine residual and the contact time. Chlorine is initially added at the water treatment plant for water disinfection. The chlorine dosage at the plant depends on the water chlorine demand. This demand can be quite significant for systems that are not removing DOC, iron, manganese, or other compounds that can be oxidized by chlorine.

Many rural water distribution networks are extensively long and chlorine has to be re-introduced into the system either at the middle points of the distribution system or at satellite reservoirs in order to maintain the required chlorine residual for disinfection. This additional dosage of chlorine at the network reservoirs is sometimes difficult to estimate. The contact time of the water and chlorine depends on the location within the distribution network. The endpoint locations typically have the longest contact time.

3.4 Control of THMs

THM formation can be controlled by minimizing the reaction of chlorine with organic carbon or by introducing alternative disinfectants rather than chlorine, which do not form THMs.

3.4.1 Removal of Disinfection By-product Precursor, DOC

Generally, DOC cannot be removed through sedimentation by gravity due to its small size and stable negative surface charge. It can be removed by enhanced coagulation and softening, which occurs in most water treatment plants.

3.4.2 Enhanced Coagulation for DOC Removal

The removal of disinfection by-product precursors, such as DOC, is improved in enhanced coagulation through pH control. Enhanced coagulation with ferric sulfate removes an additional 32% of DOC over conventional coagulation when the pH level is controlled between 6 to 8 (Volk *et al.* 2000). Trivalent charged coagulants, such as aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), or ferric sulfate ($Fe_2(SO_4)_3$), are added to neutralize the negative surface charge of the colloids. DOC can be removed together with flocs by gravitational sedimentation or filtration; thereby reducing the availability of DOC to react with chlorine. The required coagulant dosage for removal of DOC is usually ten times more than the DOC concentration of the raw water (Crittenden *et al.* 2005).

3.4.3 Coagulants Typically Used for Enhanced DOC Removal

The concentration of NOM, expressed as DOC, controls the required dosage of the coagulant. High NOM generally requires high coagulant dosage. Alum and ferric coagulants have an average NOM removal efficiency of 70% and 80% respectively (Crittenden *et al.* 2005). Alufer by Kemira Water Solutions, Inc. (Quebec, Canada) is a mixture of alum and ferric solution, which has been used in the treatment of drinking water. It provides improved NOM removal over alum even though it does not leave elevated iron and aluminum concentrations in the treated water. Also, it does not significantly reduce the alkalinity, which is essential for water corrosivity control and water softening. Alufer is available in different ferric to alum ratios (S25 contains 25% ferric and 75% alum; S50 contains 50% ferric and 50% alum).

3.4.4 Suggested pH for DOC Removal

It is believed that the interaction between organic matter, such as humic acid, and coagulants greatly determine the coagulant dosages (O'Melia *et al.* 1999). Organic matter has a negative surface charge at a pH above 5 because carboxyl groups in humic substances release protons as pH increases. As a result, the required coagulant dosage for DOC removal increases with increase of pH. Although NOM can be removed effectively at pH values at 5 to 5.5 with ferric coagulants, the corrosion rate accelerates at pH values below 6 (Crittenden *et al.* 2005). At optimal pH of 5.5, alum has an average NOM removal efficiency of 70% and ferric sulfate, at optimum pH of 5, has an average NOM removal efficiency of 80% (Crittenden *et al.* 2005).

3.4.5 Enhanced Softening for DOC Removal

Some removal of DOC can also be achieved in enhanced softening. Enhanced softening is a treatment process that removes DOC through precipitative softening. Calcium and magnesium precipitate in the form of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$) with part of the DOC adsorbed mainly on the precipitate surface (Roalson *et al.* 2003).

Previous studies have shown that the removal of NOM with calcium carbonate precipitation alone is often limited (Black and Christman 1961, Randtke *et al.* 1982, Semmens and Staples 1986, Randtke 1988). On the other hand, magnesium hydroxide aids NOM precipitation during lime-soda softening (Leentvaar and Rebhun 1982, Liao and Randtke 1985). Bob (2003) showed that NOM removal increases with sludge recycling, which introduces lime sludge back to the softening tank. This is because the $Mg(OH)_2$ particles in the sludge provide surface area to adsorb organic matter. Additionally, the recycling sludge has nucleation sites that promote co-precipitation of $Mg(OH)_2$-NOM complexes. Raw water containing a high magnesium concentration significantly increases DOC removal in softening. Bob (2003) also suggested that DOC removal reaches 43% with 7.5mg/L of $MgCl_2$ and 457mg/L recycle sludge. However, the performance of recycling sludge may decrease at low DOC concentration after coagulation since most of the reactive humic substances are removed. Also, the modification cost of the sludge recycling system could be a disadvantage for sludge recycling.

The amount of lime and soda addition in enhanced softening is often higher than in conventional softening. The common problem with enhanced softening is the high chemical cost and the large amount of waste sludge produced after softening (Thompson *et al.* 1997). This creates difficulties on sludge treatment for water treatment plants.

3.5 Alternative Techniques for The Removal of DOC

Recently, alternatives such as floating media filter coupled with microfiltration have been investigated to remove over 80% of water DOC (Chiemchaisri *et al.* 2008). However, DOC and particle accumulation on membrane surfaces are responsible for membrane fouling and an increase in the transmembrane pressure. This results in an increase in the operation cost and a decrease in the permeate flux. Periodical cleaning with air scouring and water flushing is required every 8 to 24 hours. Also, granular activated carbon (GAC) reduces the THM formation potential up to 85%, such that each gram of GAC reduces 5mg of DOC (Iriarte-Velasco *et al.* 2008). GAC must be replaced or regenerated on a regular basis to remove the accumulated DOC; therefore, increasing the operational cost for water treatment plants.

3.6 Alternative Disinfectants for THMs Control

Alternative disinfectants such as chlorine dioxide, chloramines, and ozone can substitute for chlorine in water disinfection. These disinfectants are believed to produce less THMs or none but may produce other disinfection byproducts of concern or have other operational drawbacks. Chlorine dioxide (ClO_2) disinfection is more pH dependent than chlorine. It is a more powerful disinfectant than chlorine and it produces less THMs (AWWA *et al*. 1999). Inorganic by-products of chlorine dioxide are chloride, chlorate, and chlorite. Chlorite and chlorate are associated with health and drinking water guidelines and standards have been established for these byproducts.

Chloramination combines chlorine with ammonia to produce chloramine (NH_2Cl), which inactivates bacteria and forms less THMs and HAAs than chlorine; however, it forms N-nitrosodimethylamine (NDMA) and other disinfection byproducts (AWWA *et al*. 1999, Crittenden *et al.* 2005). However, it is a much weaker disinfectant that requires long contact time. Regulatory guidelines in Manitoba require a minimum of 1.0mg/L monochloramine residual after chloramination and 0.3mg/L throughout the distribution system (Manitoba Water Stewardship 2007).

Ozone can also inactivate bacteria; however, it is not very stable and has a short lifetime in the distribution system. Additionally, ozone may also produce bromate (BrO_3^-) and other disinfection by products.

3.6.1 Membrane Filtration for Control of THMs

Recently, membrane filtration has been particularly tested for THM removal in chlorinated water. Research indicates that Nanofiltration (NF) membranes produce a maximum

THM rejection of above 90% and 80% for 80ppb and 200ppb feed concentration respectively (Uyak, 2008). However, the removal rate slightly decreases with higher transmembrane pressure. NF membranes significantly reduce chloroform, bromodichloromethane, and dibromochloromethane by 81%, 84%, and 93% respectively at low feed concentration (50 and 60ppb) (Uyak *et al.* 2008). Uyak explains brominated THMs have higher removal efficiency due to their high molecular weight. Membrane filtration of THM must occur after chlorination. However, this requires further research before application.

Other new methods for THM and DOC removal utilizing high energy photocatalysis, have been tested (Gerrity *et al.* 2009). These methods usually have high energy requirements.

4 EXPERIMENTAL METHODS

4.1 Optimization of the DOC Removal at the Sanford Plant

The Sanford water treatment plant performs coagulation and softening together in one reactor at the same pH, which is above 10. This pH is necessary for water softening but it is not favorable for DOC removal. Currently, Sanford water treatment plant is applying about 50mg/L of alum with undeterminable lime and soda dosage. Figure 2 shows the experimental design for enhanced coagulation and softening in two separate, optimized reactors that was tested in this study. This new setup provides an optimal pH range of 6 to 8 for DOC coagulation; subsequently, water pH is increased above a value of about 10 during softening. The pH is adjusted by adding sulfuric acid (H_2SO_4) to approximately 8 prior to filtration and chlorination.

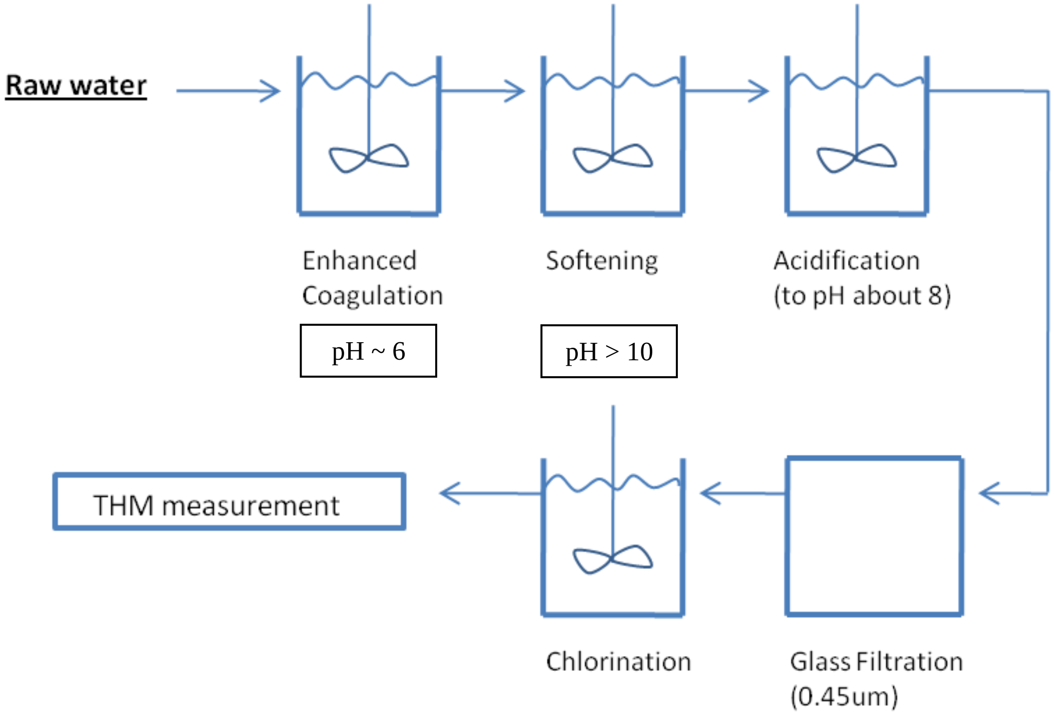


Figure 2 Bench scale experimental design

4.1.1 Raw Water Sampling

The raw water was collected from the Sanford water treatment plant during the summers and winters of 2007 through 2009. Both summer and winter water samples were taken to account for seasonal DOC variation. The raw water is transported from the inlet reservoir to the plant by gravity. Occasionally, the reservoir water level was too low for sample collection. In this case, the raw water was collected from a raw water storage pond located behind the water treatment plant. The water samples were then immediately delivered to the University of Manitoba Environmental Laboratory after collection. Raw water was stored in the fridge at temperature of 2 - 4℃ to minimize the chemical reactions and biological activities.

4.1.2 Water Quality Analysis

Water was removed from the fridge 24 hours prior to chemical coagulation so that the water could reach room temperature (approximately 21℃ in the summer and 17℃ in the winter). Alkalinity, pH, turbidity, true colour, and DOC were measured in the Environmental Laboratory of the University of Manitoba following standard methods (APHA *et al.* 2005). Water pH was measured directly with pH meter by OAKTON Instruments (Vernon Hills, USA). Turbidity was measured with a turbidimeter Micro 100 by HF Scientific, Inc. (Fort Myers, USA). Water was filtered through 0.45µm glass filter to remove large particles for true colour measurement using a Hellige Aqua Tester by Orbeco-Hellige Inc. (Sarasota, USA). DOC was measured with the Phoenix 8000 DOC analyzer by Tekmar Dohrmann (Mason, USA). DOC samples were filtered with 0.45um glass filters to remove any suspended solids, which could create interference for the DOC analyzer. All the above equipment was appropriately calibrated to minimize systematic error.

4.1.3 Jar Test Setup

Coagulation and the softening jar test were performed in the Environmental Engineering Laboratory at the University of Manitoba (Figure 3). Raw water was placed in 1L glass beakers under the PB-700^{TM} Standard JarTester by Phipps & Bird (Richmond, USA) with the speed of stirrer initiated at 100rpm. A range of chemical dosages were added into raw water. Water was rapidly mixed at 100rpm for 20 seconds and then flocculated at 30rpm for 30 minutes according to the standard jar testing procedure. Water was settled for 30 minutes after flocculation as flocs settled at the bottom of the jars by gravity and the qualities of the supernatant were measured.

Figure 3 Jar testing apparatus used in this study

4.1.4 Enhanced Coagulation Experiments

Eight sets of coagulation jar tests were performed at the Environmental Lab on July 31st, 2007, March 31st, 2008, August 26th, 2008, and April 28th, 2009. Several trials were performed before each set of successful coagulation. Aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), and alufer S25 (mixture of 25% ferric sulfate and 75% aluminum sulfate) were tested for their effectiveness on DOC removal. Figure 4 shows the experimental procedure for double stage coagulation using alum and ferric chloride with the same hydraulic retention time. Supernatant was analyzed for water pH, alkalinity, turbidity, colour, and DOC. Optimum coagulation dosages were determined based on the quality of the supernatant. The coagulated water was subsequently softened with lime and soda ash.

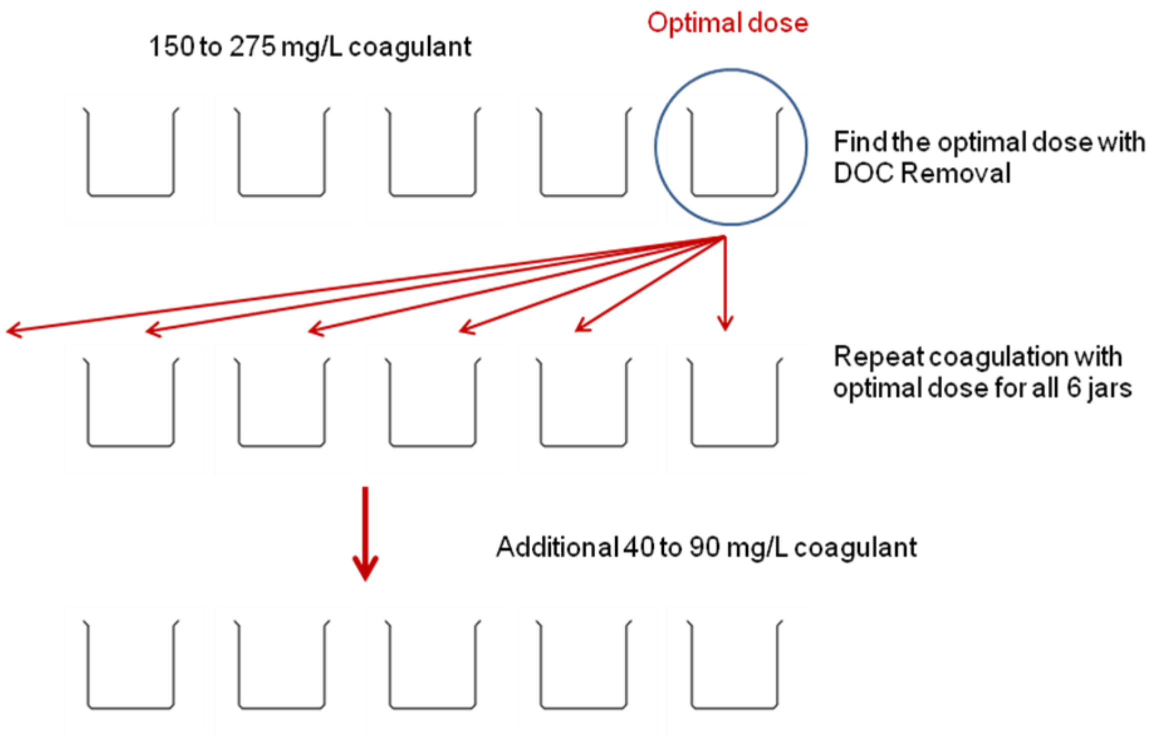


Figure 4 Double stages coagulation procedure

4.1.5 Softening Experiments

Three sets of lime softening were performed on August 2nd, 2007, August 27th, 2008 and April 30th, 2009 on the optimally coagulated water. Required lime ($Ca(OH)_2$) and soda (Na_2CO_3) dosages were calculated (Appendix A) and added to the coagulated and settled water. Both coagulation and softening were performed with an identical mixing time. Softened water was settled for 30 minutes, which allowed lime sludge settlement by gravity. The supernatant was analyzed for pH, DOC, hardness, alkalinity, colour, and turbidity. Optimal lime and soda dosages were determined based on the quality of the supernatant. The softened water was subsequently chlorinated with sodium hypochlorite.

4.2 Chlorination and Water THMs Content Determinations

4.2.1 Determination of Water Chlorine Demand (winter 2007)

Determination of water chlorine demand was performed on filtered water samples collected directly from Sanford on November 16th 2007. DOC of the treated water was 5.9mg/L. Chlorine residuals were detected using N,N-Diethyl-p-phenylene-diamine oxalate (DPD) according to Standard Method 4500 (APHA *et al*. 2005). A spectrophotometer Ultrospec 2100 Pro by Biochrom Ltd. (Cambridge, United Kingdom) was used to measure absorbance and the wavelength was set at 522 nm.

Figure 5 shows the relationship between the applied chlorine dose and the residual. The breakpoint at 5mg/L of chlorine is similar to the same average chlorine dose applied at Sanford (5mg/L). It is expected that with improved DOC removal, the chlorine demand will be less than 5 mg/L; hence, less THMs will be formed.

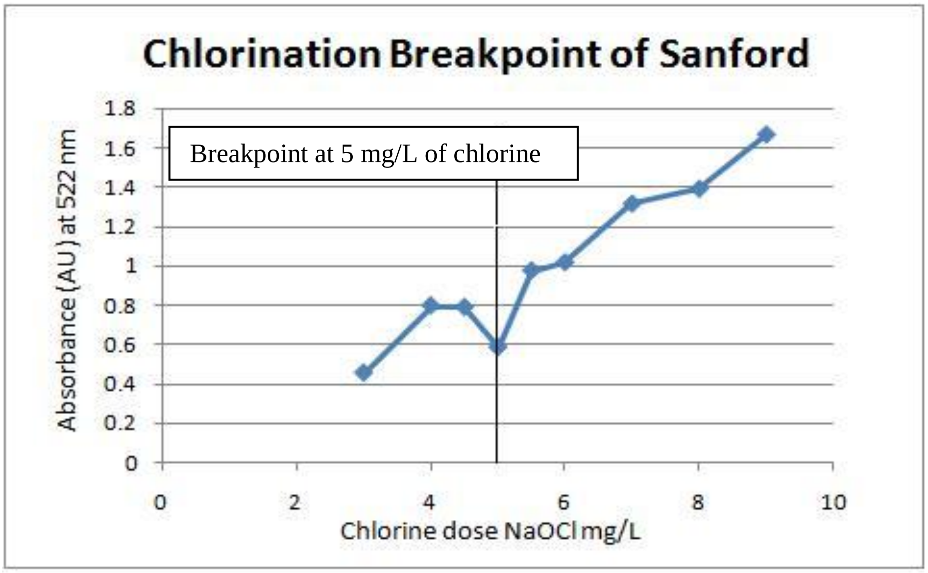


Figure 5 Breakpoint of preliminary chlorination on Sanford water sample

4.2.2 Chlorination Experiments

The laboratory coagulated and softened water was chlorinated with commercial bleach, which contained 7.45% sodium hypochlorite (NaOCl) as a chlorine source. Two sets of chlorination were performed on August 29th, 2008 and May 1st, 2009. The pH of the softened water was reduced to about 8 with the addition of 1N of sulfuric acid (H_2SO_4). Although the determined chlorine demand was about 5 mg/L, a higher dosage of 8mg/L of chlorine was added using the calculation from Standard Methods 5710 (APHA *et al*. 2005).

$$\boldsymbol{Chlorine\ Dose = Chlorine\ solution\ concentration * V_D} \qquad \text{(Eq. 22)}$$

$$\boldsymbol{V_D = \frac{Chlorine\ Demand + 3}{5}\ \mathbf{X}\ \frac{Sample\ Volume(mL)}{1000}} \qquad \text{(Eq. 23)}$$

The standard methods suggest that a higher chlorine dosage drives the reaction of organic carbon with chlorine sooner to completion (APHA *et al*. 2005). The high chlorine dosage ensures enough free chlorine residual for disinfection. It also prevents free chlorine residual from being the limiting factor for THM formation. Manitoba Water Stewardship requires a minimum contact time of 20 minutes for chlorine disinfection. However, water samples were allowed to react with chlorine for 1 hour so that the THM concentrations are close to the TTHFM.

Preserved THM samples were delivered to the ALS Laboratory Group (Winnipeg, Manitoba, Canada) for measurement. Chlorinated samples were collected without headspace or bubbles in 40 ml glass vials with preservative, sodium thiosulphate, which removes chlorine residual to prevent further formation of THM during delivery. Alternative THM measurements were tested using the Spectrophotometer Ultrospec 2100 Pro and the total trihalomethanes reagent set (THM Plus Methods 10132 by HACH Company (Loveland, USA). The THM reagent set contained four types of reagents that were added to the sample as described in the THM Plus Methods. Absorbance was recorded at a wavelength of 515nm and THM was reported as ppb of chloroform with the use of a calibration curve.

4.3 Investigation of Relationships between THM, DOC, chlorine dose and contact time

Samples were analyzed for DOC, UV254, chlorine residual, contact time, and THM throughout the R.M. Macdonald water supply system on November 6th, 2008, February 6th, 2009, and April 9th, 2009.

4.3.1 Sample Locations

Plant effluent samples were collected from the tap water, post chlorine disinfection, in Sanford water treatment plant as well as from the distribution system (Figure 6). Samples were collected in several locations distributed throughout the Sanford regional distribution system.

Sampling locations were strategically selected with a starting point located at the Sanford water treatment plant, ten middle points located at the five satellite reservoirs, and five end points from local residences at the ends of the distribution system. The starting point samples were collected directly from the plant treated effluent after chlorine disinfection. Mid-point samples were collected at two locations: before re-chlorination and after re-chlorination. Both were collected from the five satellite reservoirs that were evenly distributed around the Sanford water treatment plant at Brunkild, Starbuck, Oak Bluff, La Salle, and Domain. The pre re-chlorination samples were collected at the reservoir inlets whereas the post re-chlorination samples were collected at the reservoir outlets. End points samples were collected at the ends of the distribution system of each reservoir. All samples were kept in range of 0 - 4℃ before sample analysis.

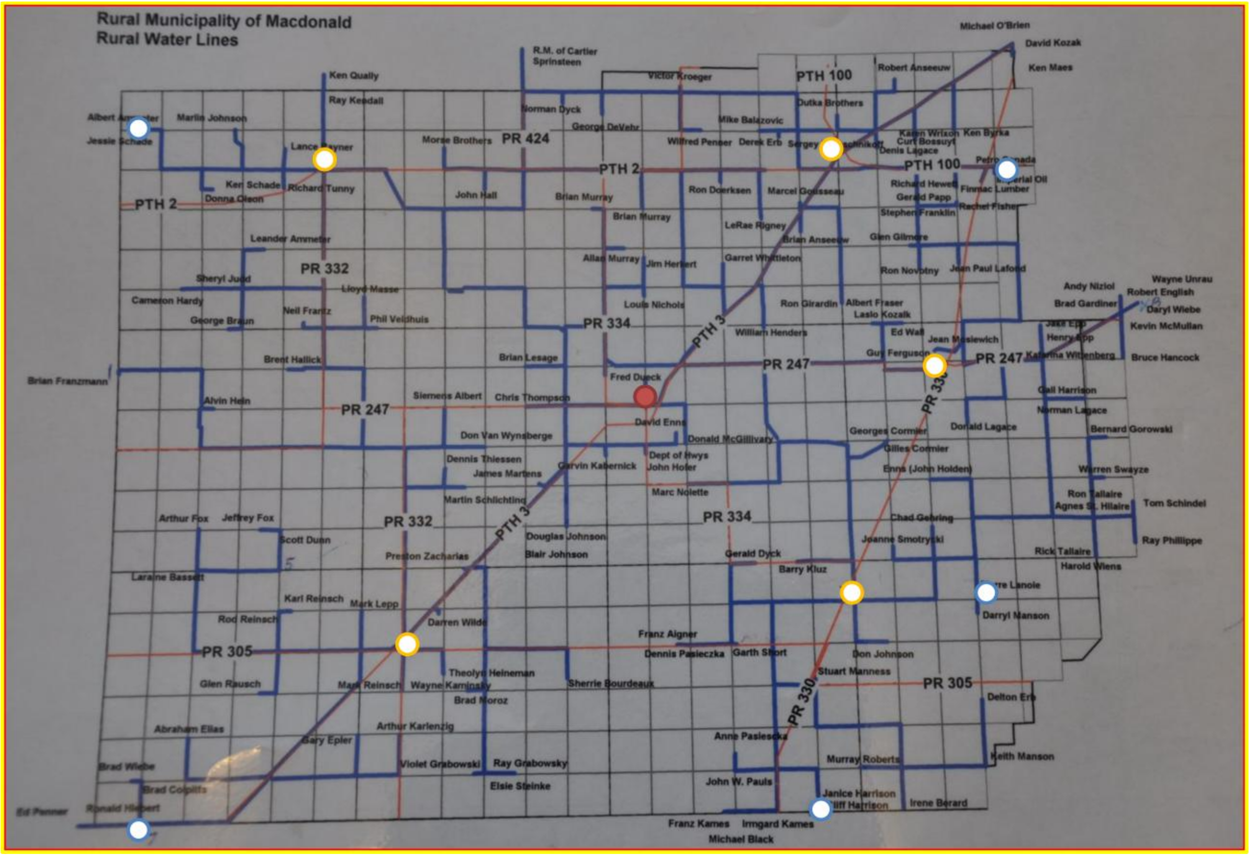


Figure 6 Sanford distribution system water sampling locations (red - plant; yellow - reservoirs; blue-endpoints)

4.3.2 Sample Collection and Analysis

All samples were collected in 500mL glass bottles sealed with parafilm and stored at the Environmental Laboratory at a temperature range between 2 to 4°C prior to sample analysis.

The samples for the THM analyses were preserved with sodium thiosulphate in 40ml glass vials near 0°C and they were then delivered to ALS Laboratory Group (Winnipeg, MB) on the date of sample collection. Each set of THM samples consisted of three glass vials containing identical water samples. A total of sixteen sets of THM samples were collected from the distribution system with forty-eight glass vials delivered to ALS Laboratory Group for THM measurement on November 6th, 2008, February 6th, 2009, and April 9th, 2009.

Both free and total chlorine residual were measured on-site with the standard DPD indicator and measurement kit. DOC was measured using the DOC analyzer in the Environmental Laboratory. UV absorbance was measured using the UV/Visible spectrophotometer Ultrospec 2100 Pro at wavelength 254nm with a 10cm quartz cuvette (APHA *et al.* 2005).

4.3.3 Estimation of Water Chlorine Contact Time

WaterCAD, a water flow simulation software program by Bentley Systems Incorporated (Exton, USA), was used to estimate water travel time and chlorine contact time in the Sanford regional water distribution system. Contact time within the system was estimated based on pipeline diameters and the head loss of the existing distribution system. Unfortunately, WaterCAD only provided contact time up to the midpoint reservoirs. Water storage time at reservoirs entirely depended on regional water consumption. Contact time beyond re-chlorination was estimated assuming that the storage time was 18 hours and transportation time for reaching the distribution endpoints was 15 hours. These estimations were based on information provided by the manager of the Sanford plant.

4.3.4 Limits of Detection

Laboratory water analysis equipments have a different limit of detection (LOD), which is the lowest quantity of substance that can be detected. Turbidimeter Micro 100 has a LOD of 0.01NTU. Hellige Aqua Tester has a LOD of 2.5CTU. Phoenix 8000 DOC analyzer has a LOD of 0.002mg/L and a detection accuracy of 0.1mg/L due to the impurity of compressed gas and solution. Ultrospec 2100 Pro has a LOD of 0.001 Absorbance Unit (AU). Photometer YSI 9100 has a LOD of 0.01 AU.

5 EXPERIMENTAL RESULTS AND DISCUSSIONS

5.1 Improve Removal of DOC by Enhanced Coagulation and Softening

5.1.1 Enhanced Coagulation with Ferric Chloride (summer 2007)

Enhanced coagulation was first performed with ferric chloride ($FeCl_3$) on July 31st, 2007. Table 2 shows the results of ferric chloride with an applied dosage that ranged from 75 mg/L to 200 mg/L; this was also performed at room temperature (21℃). The high dosage of ferric chloride reduced the pH value to below 6. After adding 175mg/L of ferric chloride, the pH of the water decreased from 8.07 to 5.85.

Table 2 Coagulation with Ferric Chloride (July 31st, 2007)

Jar	$FeCl_3$ Dose (mg/L)	pH	Turbidity (NTU)	True Colour (TCU)	Alkalinity (as $CaCO_3$) (mg/L)	DOC (mg/L)	Fe^{3+} (mg/L)
1	75	7.10	0.67	10.0	94	3.5	0.00
2	100	6.80	0.29	10.0	80	2.7	0.00
3	125	6.55	0.15	10.0	56	2.1	0.01
4	150	6.20	0.15	7.5	42	1.5	0.03
5	175	5.85	0.12	7.5	24	1.1	0.01
6	200	6.00	0.21	7.5	20	1.4	0.00

Ferric chloride coagulation removed DOC from 8.9mg/L to a minimum of 1.1mg/L at a dosage of 175mg/L. The results indicate that the optimum ferric chloride dosage was between 150mg/L to 175mg/L (Figure 7). The true colour was reduced from 25TCU to 7.5TCU and the turbidity was reduced from 1.80NTU to 0.12NTU prior to filtration. The dissolved iron concentration of 0.01mg/L was recorded at 175mg/L $FeCl_3$ determined using a photometer YSI 9100 by YSI Inc. (Yellow Spring, USA), which was well below the aesthetic objective of 0.3mg/L (Health Canada 2008).

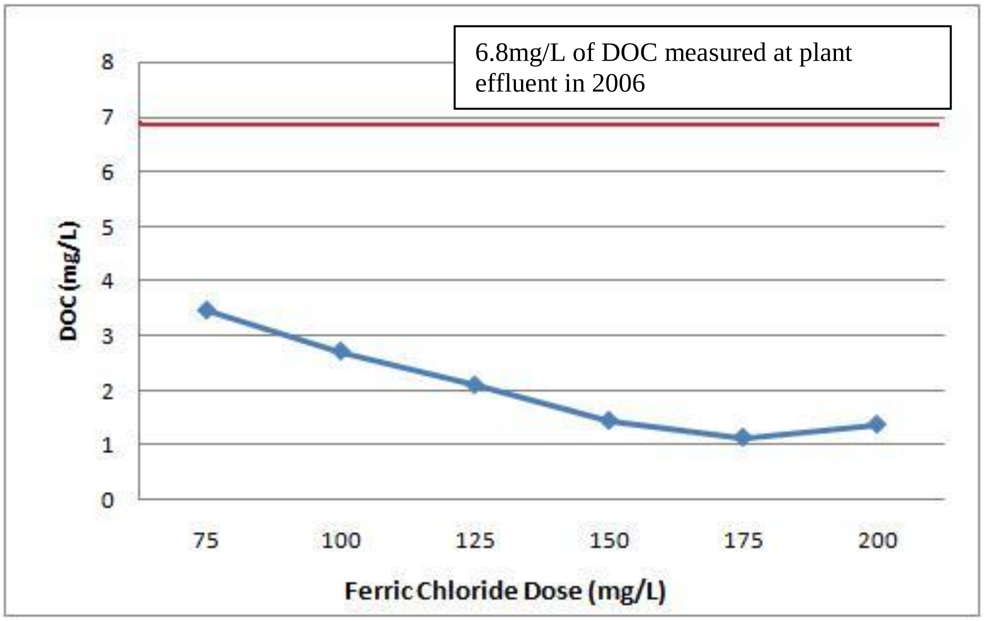


Figure 7 DOC removal performance of single step ferric chloride coagulation (July 31st, 2007)

Although ferric chloride produced high DOC removal, alkalinity was recorded lower than 100mg $CaCO_3$/L with a minimum of 20mg $CaCO_3$/L (Figure 8). Low alkalinity water could be corrosive and requires a high soda demand in the softening process. Consequently, alternative coagulants such as alum and a mixture of alum and ferric chloride were tested in winter 2008.

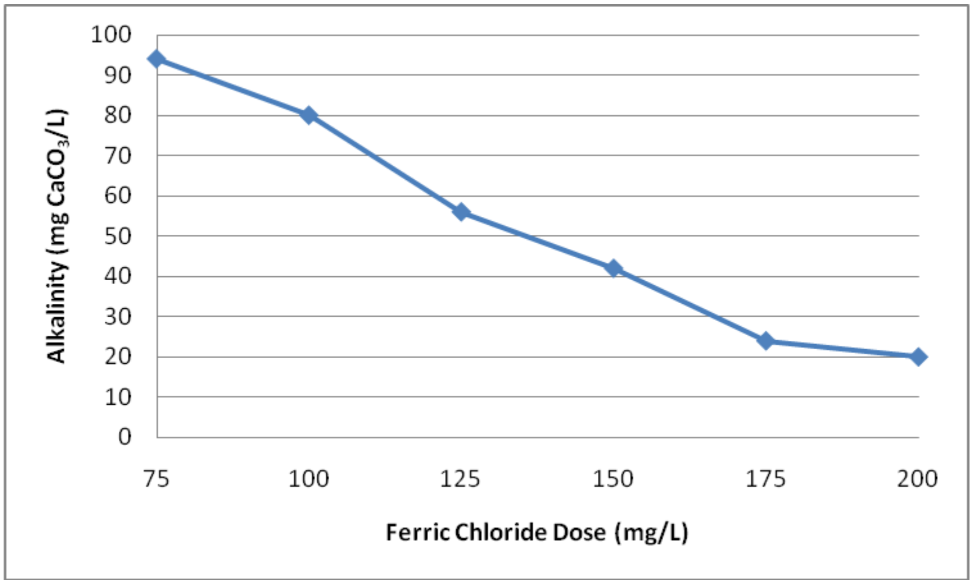


Figure 8 Alkalinity of single step ferric chloride coagulation (July 31st, 2007)

5.1.2 Enhanced Coagulation with Alum, Ferric and Mixture of the Coagulants (winter 2008)

Enhanced coagulation was performed with single and double stages of alum and ferric chloride as well as a mixture of alum and ferric coagulants on March 31st, 2008. Raw water contained DOC of 20.1mg/L with a true colour of 50TCU, turbidity of 9.80NTU, and an alkalinity of 313mg $CaCO_3$/L. The DOC concentration was significantly higher than July, 2007, which was 8.9mg/L. As a result, coagulation required higher dosages for water in the winter due to the higher DOC level. Winter water was collected at the inlet reservoir because of the ice formation on the surface of the pond water. Collected water DOC was recorded at 14.0mg/L before coagulation.

5.1.2.1 Coagulation with alum and ferric chloride

Single stage coagulation with a single coagulant

Coagulation with alum and ferric were tested at a dosage range between 150mg/L to 275mg/L on March 31st, 2009 (Table A1 and A2 in appendix). Table 3 summarizes the optimal dosage for DOC removal of coagulants and their different combinations. Figure 9 shows the DOC removal ability of each coagulant. Results show that water DOC was reduced in all tests. Single stage ferric coagulation reduced DOC more than alum. The optimum coagulant dose was 275 mg/L for both alum and ferric. With this dosage, the DOC reduced from 14.0mg/L to 7.9mg/L in alum coagulation and to 4.6mg/L with ferric coagulation.

Two stage coagulation with a single coagulant

Double stage coagulations with alum and ferric chloride were performed on March 31st, 2008. Water was first coagulated with 275mg/L of alum and ferric chloride. Coagulated water was settled for 30 minutes after adding the first dosage; the supernatant was transferred into clean beakers for second stage coagulation (Figure 4). Secondary doses varied from 40mg/L to 90mg/L (Tables A3 and A4). Results confirmed that ferric chloride removed DOC more efficiently than alum. Two stages of ferric coagulation lowered water DOC from 14.0mg/L to 3.2mg/L (355mg/L total ferric dose). Two stages of coagulation with alum was only able to reduce DOC to 6.9mg/L (365mg/L total alum dose). Both single and double stage ferric reduced alkalinity to undesirable levels below 100mg $CaCO_3$/L. Overall, the two stages of coagulation achieved more DOC removal than single stage coagulation.

Table 3 Removal of DOC by various coagulants (March 31st, 2008)

Coagulation Configuration	Coagulants Dose (mg/L)	DOC (mg/L)	Turbidity (NTU)	Alkalinity (mg $CaCo_3$/L)	pH
Alum	275 Alum	7.9	1.06	250	6.4
2 stages alum	275 + 90 Alum	6.9	0.07	164	7.1
Ferric	275 Ferric	4.6	0.60	85	5.9
2 stages ferric	275 + 80 Ferric	3.2	0.89	20	5.8
Mixture of alum and ferric	275 Alum + 60 Ferric	6.4	1.02	150	6.6

Two stage coagulation with mixture of coagulants

The mixture of alum and ferric chloride coagulation was performed in two stages. Water was coagulated with 275mg/L of alum followed by lower doses of 10 to 60mg/L of ferric to prevent alkalinity and a pH drop. DOC was reduced to 6.4mg/L with 275mg/L of alum and 60mg/L of ferric chloride. Coagulation with the mixture of alum and ferric chloride removed DOC better than the two stage alum coagulation; however, it was not as effective as ferric chloride coagulation alone (Table 3)

Figure 10 shows the turbidity of coagulated water. Turbidity was significantly reduced by all coagulants. Two stages of alum coagulation showed the best turbidity removal, which reduced the turbidity from 9.80NTU to 0.07NTU with 365mg/L of alum. The mixed coagulation of alum and ferric chloride ranked in between the alum and the ferric chloride, which had a turbidity of 0.43NTU.

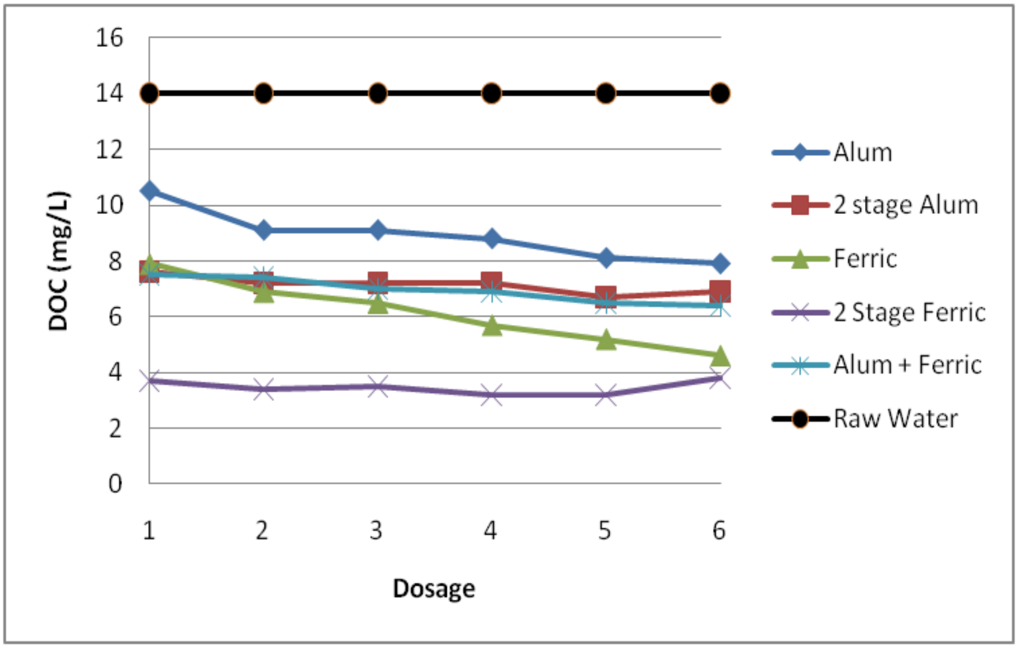


Figure 9 Removal of DOC by various coagulants (March 31st, 2008)

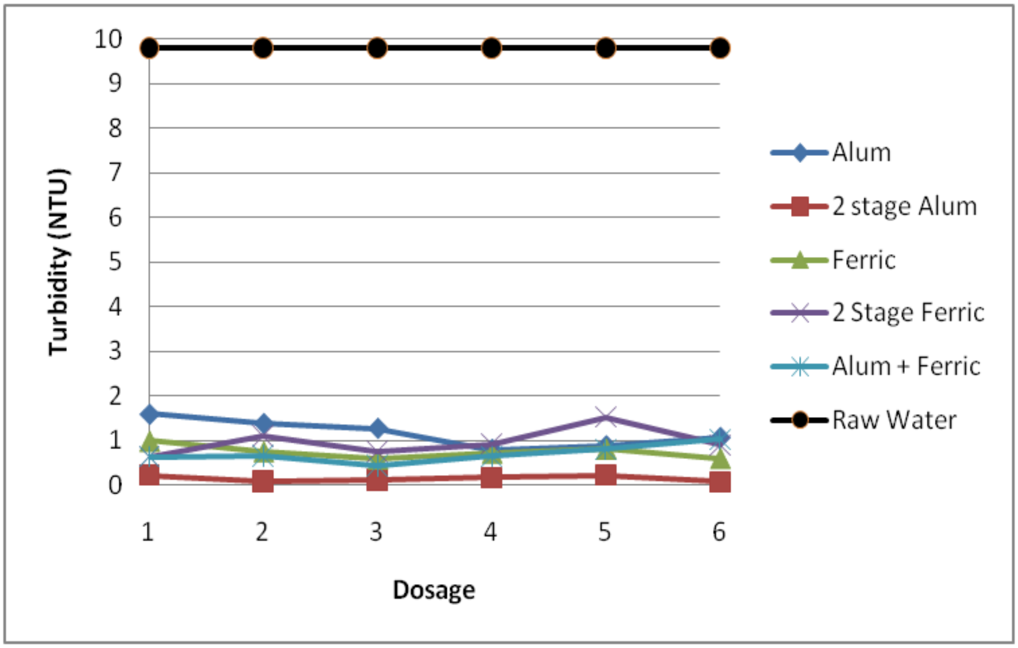


Figure 10 Removal of turbidity by various coagulants (March 31st, 2008)

Effects of various coagulants on water alkalinity and pH

Although ferric coagulation removed DOC and turbidity well, the water pH reduced significantly from 7.6 to 5.8 in two stage ferric coagulation. Figure 11 shows the impact on water pH by various coagulants. Water pH reached a minimum of 5.5 with 365mg/L of ferric chloride (Table A 4). Even one stage ferric coagulation decreased the pH to 5.72 with 275mg/L of ferric chloride (Table A 2). On the other hand, pH of mixed alum and ferric varied between 6.6 and 7.0 (Table A 5).

Figure 12 shows that alkalinity was also reduced significantly with ferric chloride. Single stage ferric reduced the alkalinity from 313mg $CaCO_3$/L to 85mg $CaCO_3$/L and two stage ferric coagulation further decreased the alkalinity to 6mg $CaCO_3$/L. Ferric chloride reduced alkalinity to an unacceptable level, which would lead to water corrosivity and an increase in the soda dosage. On the contrary, the mixture of alum and ferric chloride produced moderate impact on alkalinity of 150mg $CaCO_3$/L with 275mg/L alum and 60mg/L ferric chloride.

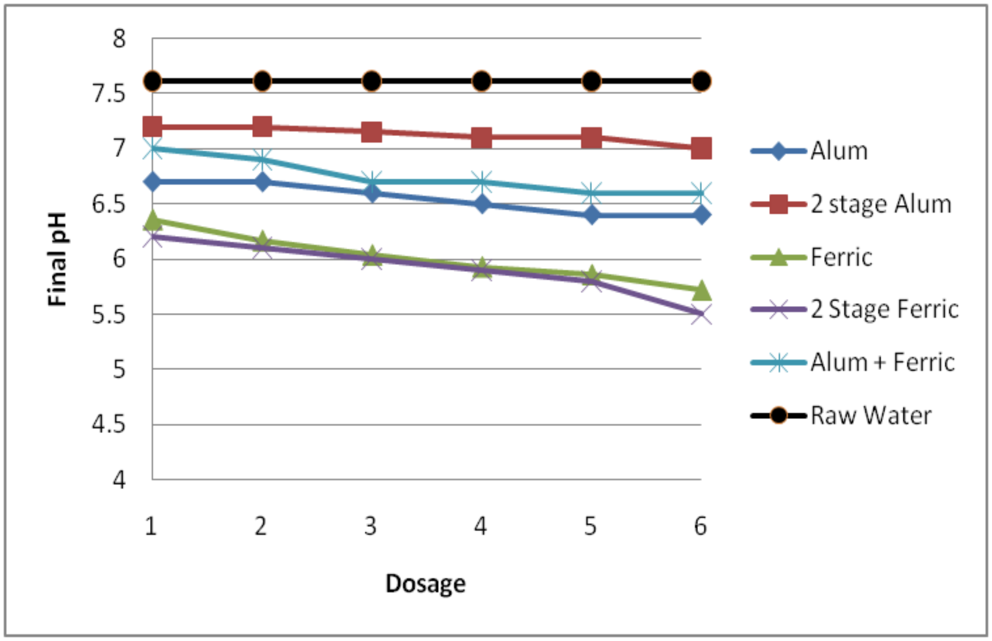


Figure 11 The pH of coagulated water with various coagulants (March 31st, 2008)

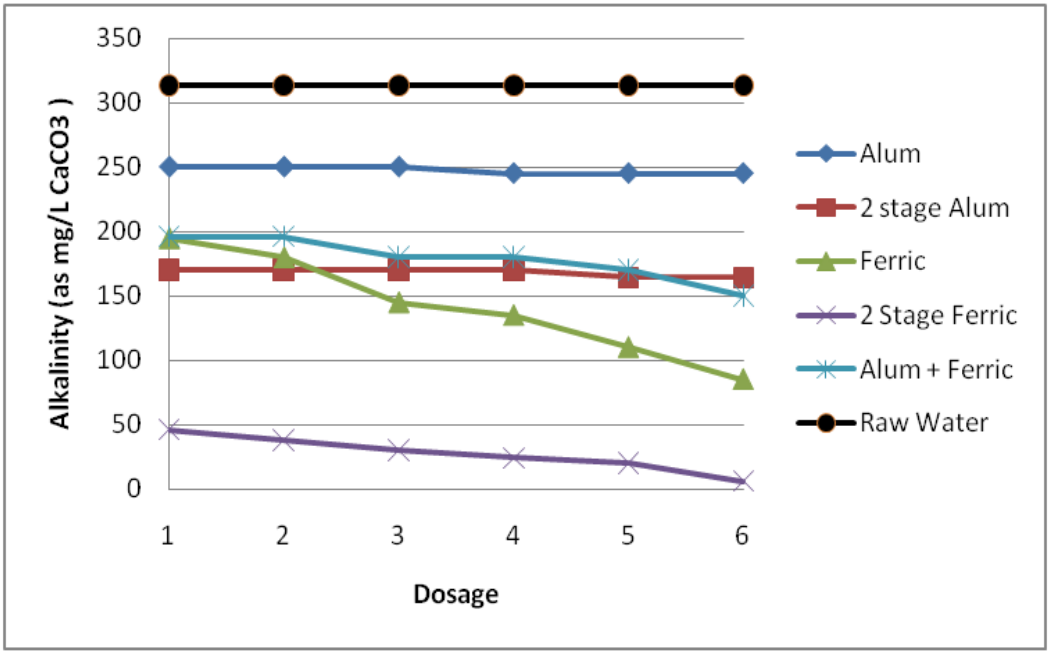


Figure 12 Alkalinity of coagulated water with various coagulants (March 31st, 2008)

This part of the study indicated that although ferric chloride removes DOC effectively, it significantly reduces pH and alkalinity of the water to undesired levels. For this reason, the mixture of alum and ferric is recommended for coagulation of Sanford water.

5.1.3 Enhanced Coagulation with Alufer S25 (summer 2008)

Enhanced coagulation tests were performed with alufer S25 (a mixture with 25% alum and 75% ferric sulfate) on August 26th, 2008. The coagulant dosages ranged from 100mg/L to 200mg/L (Table 4). DOC was reduced from 9.7mg/L to a minimum of 4.0mg/L with 200mg/L of alufer S25. Results indicated that the optimized alufer dosage was 175mg/L with DOC of 4.2mg/L, which was lower than the plant effluent of 6.5mg/L. We considered 175mg/L as the optimal dosage because alkalinity dropped to less than 100 mg $CaCO_3$/L with higher alufer dosage.

5.1.4 Evaluation of Sludge Production of Alufer S25

Separating coagulation sludge prior to softening could reduce the volume of high pH lime sludge. Coagulation sludge production was estimated by the sludge index, the volume ratio of sludge to water, after 30 minutes of settling. Alufer S25 produced 25.0 to 67.5ml of sludge/L of water with the actual sludge volume expected to be less after sludge dewatering. This indicated that alufer did not produce a large volume of sludge while removing most of the suspended solids and DOC.

Sludge produced at 175mg/L alufer had pH of 6.2, which was more environmentally friendly in comparison to the current Sanford sludge, which has a pH greater than 10. Figure 13 shows the improvement on DOC removal by alufer S25 relative to the current Sanford effluent. With much better quality water flowing onto the filters, filter solid loading may be reduced, which can significantly reduce filter backwash.

Table 4 Enhanced coagulation with alufer S25 (August 26th, 2008)

Jar	Alufer S25 (mg/L)	pH	Turbidity (NTU)	Alkalinity (as mg/L $CaCO_3$)	DOC (mg/L)	Sludge Index (ml sludge/ L water)
1	100	6.6	0.56	130	5.7	25.0
2	125	6.4	0.37	122	5.0	32.5
3	150	6.3	0.55	108	4.6	50.0
4	175	6.2	0.67	105	4.2	57.5
5	200	6.1	0.52	93	4.0	67.5

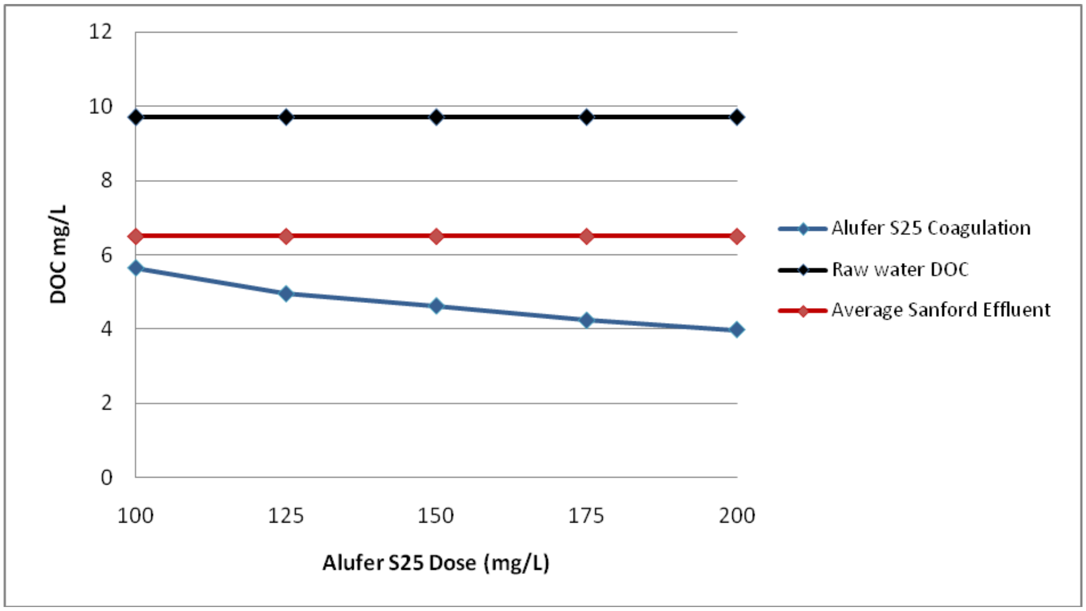


Figure 13 DOC removal performance of alufer S25 coagulation (summer 2008)

5.1.5 Enhanced Coagulation with alufer S25 (winter 2009)

Enhanced coagulation tests were performed with alufer S25 on April 28th, 2009. The dosages ranged from 250mg/L to 550mg/L (Table 5). The coagulation dosage in winter was higher than the one in the summer. This is due to the high winter DOC of 17.0mg/L whereas the summer DOC was 9.7mg/L. Table 5 shows that the DOC was reduced to a minimum of 5.8mg/L at 500mg/L of alufer. Figure 14 shows slight improvement over Sanford at 450mg/L to 550mg/L of alufer. However, alkalinity was lower than 100mg $CaCO_3$/L at 500mg/L of alufer. Due to the impact on alkalinity, the optimal alufer dosage was chosen to be 450mg/L, which produced water with a 6.2mg/L DOC and an alkalinity of 100mg $CaCO_3$/L. The water pH was recorded to be 6.1. Figure 14 shows the comparison of coagulated water quality and the current Sanford plant effluent. Although the coagulation in the winter did not reduce DOC as well as in the summer, the final DOC concentration was expected to be further decreased by softening.

Table 5 Enhanced coagulation with alufer S25 (April 28th, 2009)

Jar	Alufer (mg/L)	pH	Turbidity (NTU)	Alkalinity (as $CaCO_3$ mg/L)	DOC (mg/L)
1	250	6.3	0.86	196	9.3
2	350	6.2	0.53	160	7.4
3	400	6.2	0.66	144	6.5
4	450	6.1	0.75	100	6.2
5	500	5.8	0.45	84	5.8
6	550	5.5	0.43	76	6.0

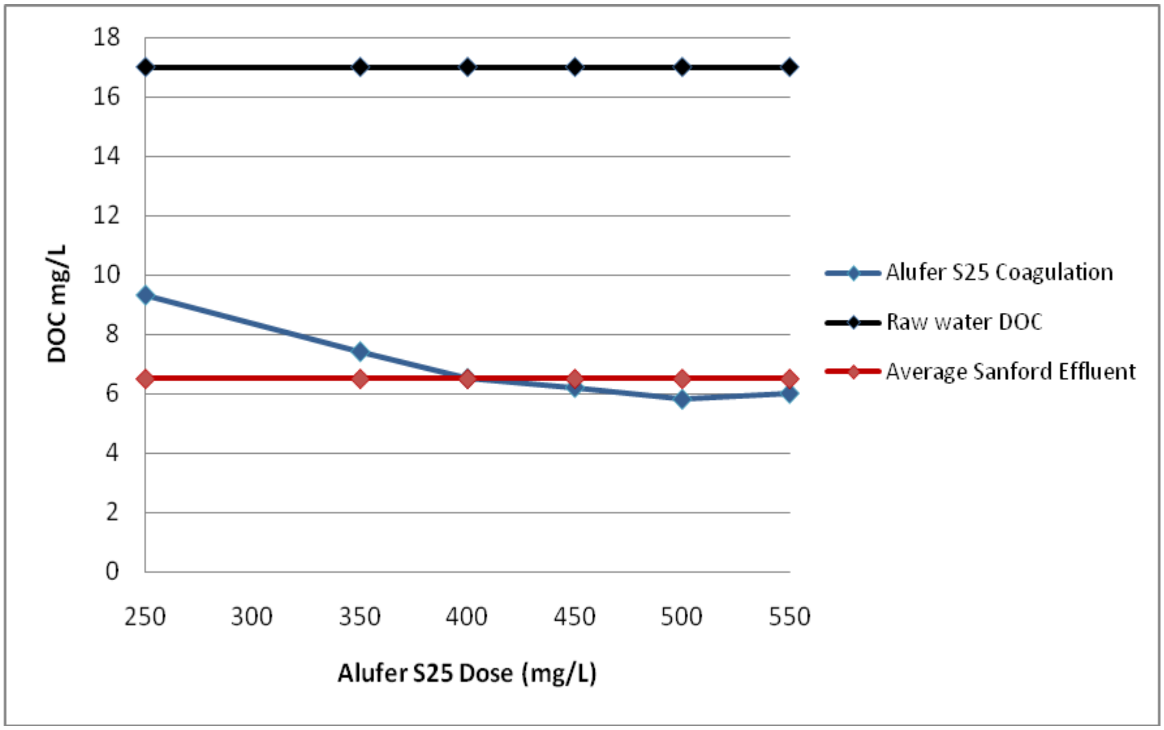


Figure 14 DOC removal performance of alufer S25 coagulation (winter 2009)

5.1.6 Lime Softening on Coagulated Water (summer 2007)

Water coagulated with an optimal dosage of 175mg/L ferric chloride, which was subsequently softened with lime and soda ash, was obtained directly from the plant. Table 6 shows the quality of water softened with 350 -500 mg $CaCO_3$/L of lime (assuming 80% purity) and 200 -350 mg $CaCO_3$/L of soda (assuming 100% purity). Lime and soda were added separately and water hardness was measured after lime addition for a better understanding of softening. Figure 15 shows the water hardness after lime addition and Figure 16 shows the water hardness after soda addition. The total hardness increased because of the increase in calcium concentration due to lime ($Ca(OH)_2$) addition in the absence of alkalinity. Total hardness was successfully reduced after soda addition to a minimum of 80mg $CaCO_3$/L with 500mg $CaCO_3$/L of lime and 350mg $CaCO_3$/L of soda. The DOC concentration increased from 1.1mg/L to 2.6mg/L; this may be attributed to the impurity of the lime. Iron may have precipitated during softening as its concentration was reduced to non-detectable levels.

Table 6 Softening results after 175 mg/L ferric chloride (August 2nd, 2007)

Pre - filtration									Post - filtration	
Jar	Lime $Ca(OH)_2$ (mg/L $CaCO_3$) 80% purity	Pre Soda Addition		Soda Na_2CO_3 (mg/L $CaCO_3$) 100% purity	Post Soda Addition		Turbidity (NTU)	True Colour (TCU)	DOC (mg/L)	Fe^{3+} after filtration (mg/L)
		Total Hardness (mg/L $CaCO_3$)	Calcium Hardness (mg/L $CaCO_3$)		Total Hardness (mg/L $CaCO_3$)	Calcium Hardness (mg/L $CaCO_3$)				
1	350	245	150	200	200	90	0.23	7.5	1.6	0.00
2	400	270	160	250	180	80	0.40	7.5	2.3	0.00
3	450	340	220	300	100	60	0.29	5.0	2.1	0.00
4	500	400	180	350	80	60	0.10	5.0	2.6	0.00

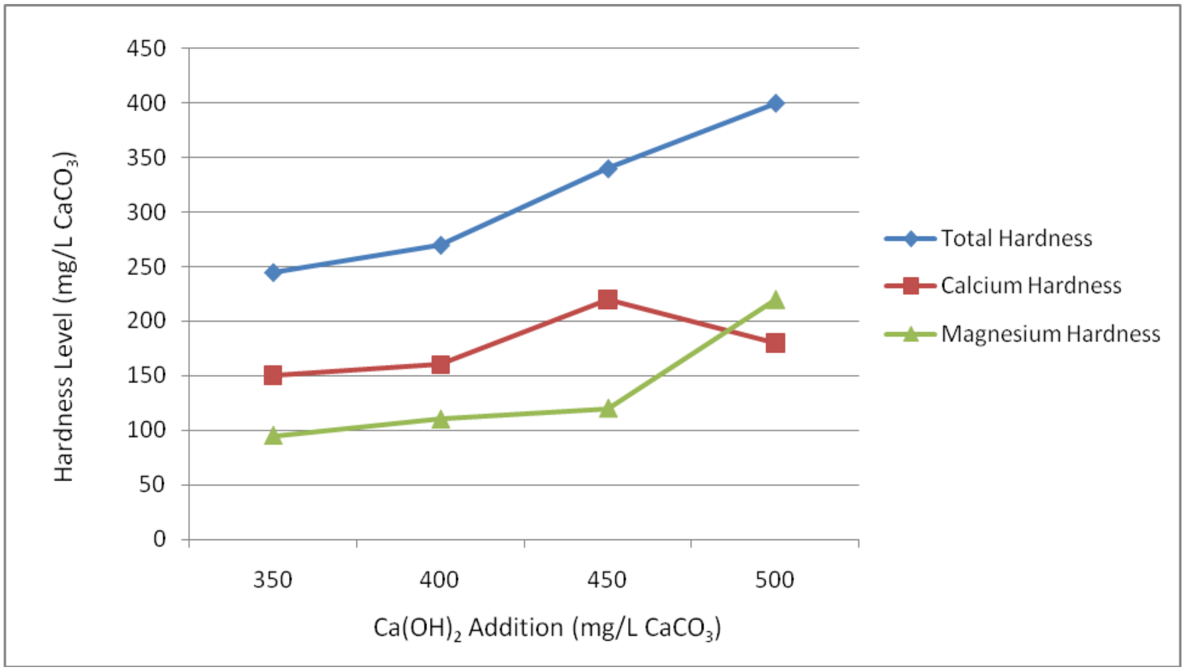


Figure 15 Total hardness after lime addition (winter 2008)

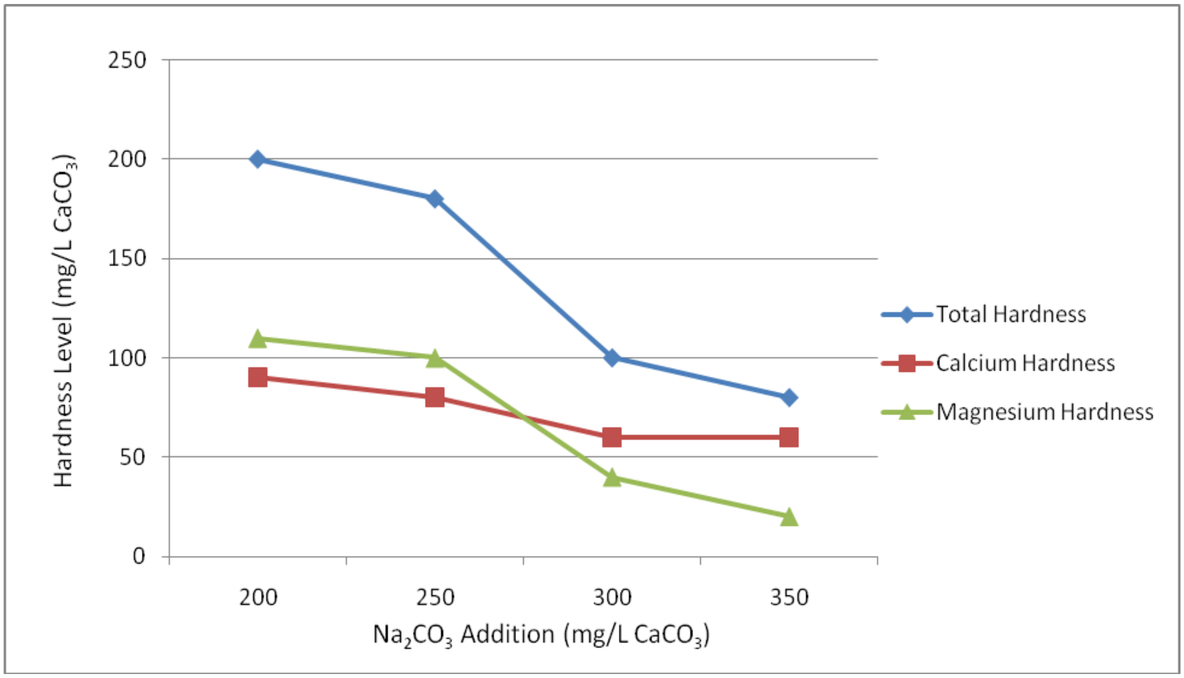


Figure 16 Total hardness after soda ash addition (winter 2008)

5.1.7 Lime Softening on Coagulated Water (summer 2008)

Lime softening was performed on settled water that was coagulated with 175mg/L of alufer S25. The lime dosage ranged from 300 to 550mg $CaCO_3$/L while the soda dosage ranged from 150 to 300mg of $CaCO_3$/L (Table 7). Results showed that 350mg $CaCO_3$/L of lime and 200mg $CaCO_3$/L soda further reduced DOC from 4.2mg/L (175mg/L of alufer S25) to 3.3mg/L. Total hardness decreased to 88mg of $CaCO_3$/L and turbidity was recorded to be 0.18NTU. The pH was observed to be 10.7 and the alkalinity was recorded to be 150mg $CaCO_3$/L prior to filtration. Increasing the lime and soda dosage reduced the total hardness to a minimum of 32mg $CaCO_3$/L without significantly decreasing the DOC concentration.

Table 7 Softening results after 175mg/L Alufer S25 (August 27th, 2008)

Pre - filtration								Post-filtration
Jar	$Ca(OH)_2$ (mg/L $CaCO_3$) 80% purity	$NaCO_3$ (mg/L $CaCO_3$)	Total Hardness (mg/L $CaCO_3$)	Calcium Hardness (mg/L $CaCO_3$)	Turbidity (NTU)	pH	Alkalinity (as $CaCO_3$) (mg/L)	DOC (mg/L)
1	300	150	132	117	0.18	10.5	160	3.5
2	350	200	88	77	0.14	10.7	150	3.3
3	400	250	48	61	0.18	10.9	157	3.3
4	450	300	32	56	0.26	11.2	177	3.3
5	550	150	168	120	0.29	10.8	200	3.2

5.1.8 Lime Softening on Coagulated Water (winter 2009)

Lime softening was performed on coagulated water with 450mg/L of alufer S25. Lime dosages from 600 to 750mg $CaCO_3$/L and soda dosages from 300 to 350mg $CaCO_3$/L (Table 8) are required due to the high water hardness of 428mg $CaCO_3$/L. The data shows that at 750mg $CaCO_3$/L of lime and 350mg $CaCO_3$/L soda, this further decreased the DOC from 6.2mg/L (450mg/L of alufer S25) to 4.3mg/L. Water hardness was measured to be 100mg $CaCO_3$/L, and the turbidity post-filtration was recorded to be 0.12.NTU. Also, the pH was recorded to be 11.1 and the alkalinity was observed to be 148mg $CaCO_3$/L after softening.

Table 8 Softening results after 450mg/L Alufer S25 (April 30th, 2009)

Pre - filtration						Post-filtration	
Jar	$Ca(OH)_2$ (mg/L $CaCO_3$) 80% purity	$NaCO_3$ (mg/L $CaCO_3$)	Total Hardness (mg/L $CaCO_3$)	pH	Alkalinity (as $CaCO_3$) (mg/L)	Turbidity (NTU)	DOC (mg/L)
1	600	300	300	10.9	268	0.18	5.6
2	650	350	280	11.5	272	0.15	5.4
3	700	300	48	10.6	148	0.22	5.0
4	750	350	100	11.1	148	0.12	4.3

5.1.9 Post Chlorination THM concentration (summer 2008)

Coagulated (175mg/L alufer) and softened (350mg $CaCO_3$/L of lime and 200mg $CaCO_3$/L soda) water was filtered through a 0.45um glass filter and the pH dropped to value about 8 with 1N H_2SO_4. Approximately 8mg/L of chlorine was added into the filtered water and 1 hour of contact time was allowed. The total THMs concentration of the optimally coagulated and softened water in this study was 65.0ppb (Table 9). This is significantly lower than the 2005 to 2007 summer average plant effluent THM, which was 153.5ppb.

THMs were also measured using the spectrophotometer Ultrospec 2100 Pro with the total THM reagent set and THM Plus Methods 10132 from Hach. Figure 17 shows the calibration curve of absorbance versus THMs concentration with a R^2 of 0.98. The total THMs concentration was measured with the Hach kits; it was determined to be 58.5ppb, which is 10% less than the ALS results (GC/MS method). Nonetheless, GC/MS is considered to be more accurate when measuring THMs. Therefore, all of the samples for THM analysis were sent to the ALS laboratory.

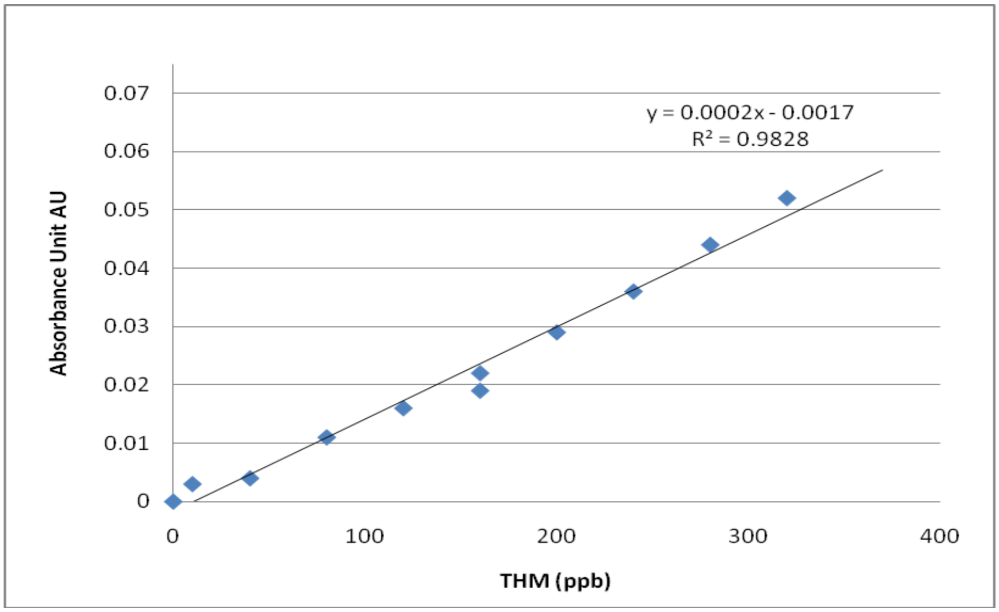


Figure 17 THM calibration curve with Hach Micro 100 and THM plus Methods 10132

Table 9 Results of bench scale coagulation and softening tests for summer 2008 (ALS Group)

Dissolved Organic Carbon (mg/L)		
Season	Laboratory	Plant
	Summer 2008	2008 Annual Average
Raw water	9.8	9.8
Coagulated/filtered water	4.3 (alufer S25)	6.5
Softened water	3.2	
Post Chlorination THM		
Chlorine Dose (mg/L)	Total THM Laboratory (ppb)	Average Plant THM Summer 2005 to 2007 (ppb)
8mg/L (Summer 2008)	65.0	153.5

Figure 18 summarizes the 2008 summer results from enhanced coagulation and softening. The results suggest that the DOC level was reduced by 51% due to optimized coagulation and softening (175.0mg/L alufer S25 followed by 350mg/L lime and 200mg/L soda ash). The lower DOC resulted in THM concentration reductions up to 58%. The data indicates that removal of 1mg/L of DOC eliminated 26.8ppb of THM.

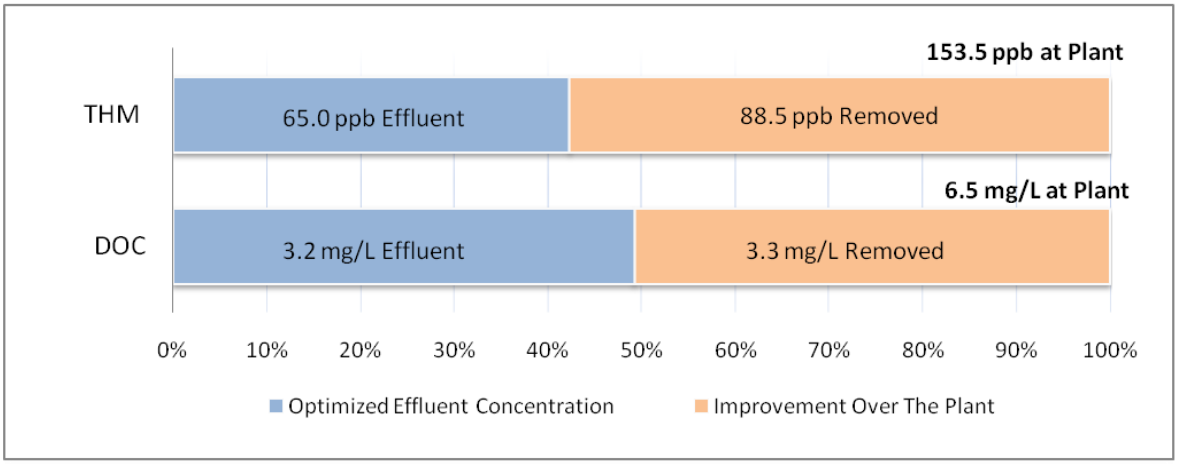


Figure 18 Summer 2008 DOC and THM removal with optimized coagulation and softening

5.1.10 Water THM concentration (winter 2009)

Effluent total THMs concentration of the coagulated (450mg/L alufer) and softened ($750mg\ CaCO_3/L$ of lime and $350mg\ CaCO_3/L$ soda) winter water was 59.9ppb as reported by the ALS Group (Table 10); this was lower than the plant effluent THM of 86.6ppb.

Table 10 Results of bench scale coagulation and softening tests for winter 2008 (ALS Group)

Dissolved Organic Carbon (mg/L)		
Season	Laboratory	Plant Annual Average
	Winter 2009	2005 to 2009
Raw water	17.0	8.9 – 31.8
Coagulated/filtered water	6.2 (alufer S25)	6.5 (2008 – 2009)
Softened water	4.3	
THM		
Chlorine Dose (mg/L)	Total THM Laboratory (ppb)	Total THM Plant (April 2009) (ppb)
8mg/L (Winter 2009)	59.9	86.6

Figure 19 summarizes the results of the winter during 2009. The results suggest that the DOC level was reduced by 34% in winter (450.0mg/L alufer S25 followed by 750mg/L lime and 350mg/L soda ash). The lower DOC resulted in THM concentration reductions up to 31%. The data shows that removal of 1mg/L of DOC eliminated 11.9ppb of THM. Results from this part of the study confirmed that both DOC and THM were significantly reduced by optimized coagulation and softening.

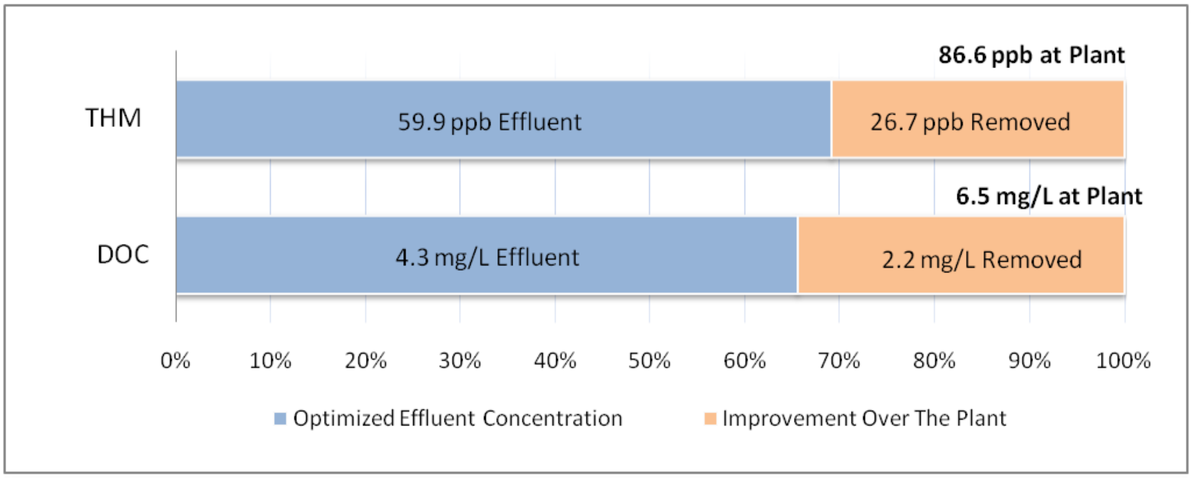


Figure 19 Winter 2009 DOC and THM removal with optimized coagulation and softening

5.1.11 Experimental Results Discussion

It is difficult to compare the removal of DOC to literature results due to the differences in water sources and types of coagulants used. Also the application of Alufer, a mixture of alum and ferric coagulant, is relatively new in the water treatment practice. Nevertheless, the results of this study show that the removal of 51% of DOC in the summer through alufer coagulation is better than Volk's result of 32% with ferric chloride (Volk *et al.* 2000). The 31% removal of DOC in winter is similar to Volk's result. Note however that the coagulant dosage is higher in this study due to the larger DOC content of the water.

Results show that more THMs can be reduced through the removal of DOC in the summer (26.8ppb) than in the winter (11.9ppb). This may be a result of the higher humic content in the summer water due to soil leaching and the decomposition of vegetation. Humic substances, which are mostly responsible for THM formation, were also efficiently removed by enhanced coagulation.

Table 11 shows that the laboratory treated water contents were all below the aesthetic objectives and the maximum acceptable concentrations. The total THMs were 65ppb suggesting that the water may comply with provincial requirements for running average annual THM level below 100ppb. Turbidity (0.14NTU) was also well below the maximum acceptable level of 0.3NTU.

Table 11 Comparison on laboratory treated water to Canadian Drinking Water Guideline 2002

Variables	Aesthetic Objective	Maximum Acceptable Concentration	Sanford Plant Effluent (August 2006)	Laboratory Treated Water
Iron	0.3mg/L	-	0.08mg/L	0.03mg/L (with ferric chloride)
Colour	< 15TCU	-	<5CTU	7.5TCU
Turbidity	< 5NTU	< 0.3NTU (for chemically assisted filtration)	0.1NTU	0.12 – 0.14NTU
pH	6.5 - 8.5	-	8.6	~ 8
DOC	-	-	6.8	3.2 – 4.3mg/L
Bromodichloromethane	-	-	65ppb	4.5 – 12.5ppb
Total THMs	-	100ppb	163.3ppb	59.9 – 65.0ppb

5.2 Relationship between THM and other water quality parameters

5.2.1 Sanford Plant Effluent

In April 2009, the THM concentration of the plant effluent was 86.6ppb. The chlorine dose at the plant is about 5 mg/L. Table 12 shows that the plant effluent free chlorine residual averaged at 1.50mg/L with DOC of 9.45mg/L.

5.2.2 Water Distribution Network

5.2.2.1 Distribution network midpoints water samples– before re-chlorination

Samples from mid-points of the distribution network before re-chlorination had a free chlorine residual of 0.02mg/L to 0.47mg/L, which was much lower than the plant effluent (Table 12). Both Brunkild and Starbuck were below the required free chlorine concentration of 0.1mg/L. Also, the THM concentration increased from 86.6ppb at the plant to a range of 106.0 to 133.4ppb. This indicates that additional THMs were formed as chlorine had more time to react with DOC.

Table 12 shows that the contact time for water transported from the plant to the reservoirs ranged from 10 to 22 hours. The DOC concentrations were expected to slightly decrease due to additional THM formation during transportation. Instead, the DOC concentrations of the mid-points before re-chlorination ranged from 8.22 - 10.23mg/L. The slight increase of DOC concentration might due to bacterial growth inside the pipelines since some of the pipelines were more than 20 years old.

5.2.2.2 Distribution network midpoints water samples – after re-chlorination

Samples analyzed from mid-points after re-chlorination showed an increase of free chlorine residual that ranged from 0.85 to 1.32mg/L. This was due to the chlorine addition inside the reservoirs. The THM concentrations also increased to a range of 140.0 to 210.0ppb. This was due to additional chlorine dosages and contact times in the reservoirs. Both the pre- and post-rechlorination water had a THM concentration above 100ppb. If the annual average of the THM concentration was measured, it would likely be greater than the Manitoba standard of 100ppb. Another observation on the distribution line was that even the plant effluent THM was lower than 100ppb; consequently, residents would still suffer from high THM concentration in their drinking water. This was because the THM concentrations continued to increase within the distribution system.

5.2.2.3 Distribution network endpoint water samples

Samples analyzed from the end points had a range of 0.07 to 0.50mg/L free chlorine residual that were lower than the mid points of 0.85 to 1.32mg/L due to the consumption within the system. The THM concentrations ranged from 95.0 - 197.0ppb in April, 2009. THM concentrations at the Brunkild, La Salle, and Domain end-points increased as expected. This may due to the additional DOC due to bacteria growth and contact time in the pipeline; however, THM levels decreased at Starbuck and Oak Bluff. This was possibly due to the depletion of free chlorine residual and the volatility of THM within the distribution system. Results showed that the individual THM concentrations throughout the distribution system were above the Manitoba THM standard except the Oak Bluff end point, which was 95ppb. However, running annual averages for THMs are required to determine compliance with the standard.

Table 12 shows that the contact time did affect THM formation. THM concentrations continued to increase as contact time increased. THM concentrations continued to increase for Brunkild, La Salle, and Domain after re-chlorination and reached maximum levels of 189.0ppb, 188.0ppb, and 197.0ppb, respectively at these end points. The results showed that both the chlorine dosage and contact time increased the formation of THM, with two exceptions: Starbuck and Oak Bluff. Both the Starbuck and Oak Bluff pipelines might have leakage, which would reduce the chlorine contact time and may cause THM volatilization.

Table 12 Water quality of Sanford distribution system (measured at the University of Manitoba and by ALS)

<table>
<tr><th colspan="6">Sanford Plant Effluent (April 2009)</th></tr>
<tr><th>Sampling Locations</th><th>Free Chlorine Residual (mg/L)</th><th>Total Chlorine (mg/L)</th><th>DOC (mg/L)</th><th>THM (ppb)</th><th>Contact Time (h)</th></tr>
<tr><td>Sanford Plant Effluent</td><td>1.50</td><td>2.10</td><td>9.45</td><td>86.6</td><td>1.00</td></tr>
<tr><th colspan="6">Middle Points Before Re-chlorination (February 2009)</th></tr>
<tr><th>Sampling Locations</th><th>Free Chlorine Residual (mg/L)</th><th>Total Chlorine (mg/L)</th><th>DOC (mg/L)</th><th>THM (ppb)</th><th>Contact Time (h)</th></tr>
<tr><td>Brunkild Reservoir Inlet</td><td>0.03</td><td>0.26</td><td>8.22</td><td>123.5</td><td>16.47</td></tr>
<tr><td>Starbuck Reservoir Inlet</td><td>0.02</td><td>0.60</td><td>10.23</td><td>133.4</td><td>21.76</td></tr>
<tr><td>Oak Bluff Reservoir Inlet</td><td>0.16</td><td>0.71</td><td>9.00</td><td>108.1</td><td>10.49</td></tr>
<tr><td>La Salle Reservoir Inlet</td><td>0.47</td><td>0.88</td><td>9.33</td><td>106.0</td><td>11.78</td></tr>
<tr><td>Domain Reservoir Inlet</td><td>0.11</td><td>0.69</td><td>9.58</td><td>106.1</td><td>14.87</td></tr>
<tr><th colspan="6">Middle Points After Re-chlorination (November 2008)</th></tr>
<tr><th>Sampling Locations</th><th>Free Chlorine Residual (mg/L)</th><th>Total Chlorine (mg/L)</th><th>DOC (mg/L)</th><th>THM (ppb)</th><th>Contact Time (h)</th></tr>
<tr><td>Brunkild Reservoir Outlet</td><td>1.32</td><td>1.94</td><td>8.46</td><td>160.0</td><td>34.47</td></tr>
<tr><td>Starbuck Reservoir Outlet</td><td>0.85</td><td>1.09</td><td>9.79</td><td>210.0</td><td>39.76</td></tr>
<tr><td>Oak Bluff Reservoir Outlet</td><td>1.04</td><td>1.50</td><td>9.38</td><td>140.0</td><td>28.49</td></tr>
<tr><td>La Salle Reservoir Outlet</td><td>0.96</td><td>1.67</td><td>9.51</td><td>160.0</td><td>29.78</td></tr>
<tr><td>Domain Reservoir Outlet</td><td>0.90</td><td>1.64</td><td>9.50</td><td>180.0</td><td>32.87</td></tr>
<tr><th colspan="6">End Points (April 2009)</th></tr>
<tr><th>Sampling Locations</th><th>Free Chlorine Residual (mg/L)</th><th>Total Chlorine (mg/L)</th><th>DOC (mg/L)</th><th>THM (ppb)</th><th>Contact Time (h)</th></tr>
<tr><td>Brunkild Residence</td><td>0.17</td><td>0.81</td><td>9.01</td><td>189.0</td><td>49.47</td></tr>
<tr><td>Starbuck Residence</td><td>0.07</td><td>0.46</td><td>9.24</td><td>195.0</td><td>54.76</td></tr>
<tr><td>Oak Bluff Residence</td><td>0.48</td><td>0.99</td><td>9.17</td><td>95.0</td><td>43.49</td></tr>
<tr><td>Lasalle Residence</td><td>0.13</td><td>0.42</td><td>9.19</td><td>188.0</td><td>44.78</td></tr>
<tr><td>Domain Residence</td><td>0.50</td><td>0.99</td><td>7.22</td><td>197.0</td><td>47.87</td></tr>
</table>

5.2.3 Correlation of THM concentration with SUVA and Chlorine Contact Time

No clear trend between the UV 254nm absorbance and SUVA in R.M. of Macdonlad supply system was observed. Further investigation is required to understand the unusual DOC and UV values at the Domain end-point.

It is currently believed that THM formation occurs due to the presence of DOC and SUVA in water. However, Figure 20 and Figure 21 show weak correlation between DOC, SUVA, and THM in the Sanford distribution system (excluding the Domain end-point due to its exceptionally high SUVA value). This indicated that THM formation might not depend on SUVA alone. Chlorine dosage and contact time might also play major roles in THM formation. It was difficult to determine the relationship between chlorine dosage and THM formation because the re-chlorination dosage at each reservoir fluctuated depending on the local water consumption. Nevertheless, a linear relationship (excluding the Starbuck and Oak Bluff end-points due to the suspected leakage) between THM formation and chlorine contact time with correlation factor, R^2, of 0.92 was observed (Figure 22). Results also showed that THM concentrations increased with water SUVA; however, no specific relationship could be determined between these two parameters.

Table 13 Analyzed UV and SUVA in Sanford distribution system

Starting Point (Winter 2008)

Sampling Locations	UV absorbance @254(AU)	SUVA (L/mg $C.m^{-1}$)	THM (ppb)
Sanford Water Treatment Plant	0.104	1.102	86.6

Middle Points Pre Re-chlorination (February 2009)

Sampling Locations	UV absorbance @254 (AU)	SUVA	THM (ppb)
Brunkild Reservoir Inlet	0.095	1.153	123.5
Starbuck Reservoir Inlet	0.129	1.263	133.4
Oak Bluff Reservoir Inlet	0.100	1.108	108.1
La Salle Reservoir Inlet	0.109	1.166	106.0
Domain Reservoir Inlet	0.113	1.182	106.1

Middle Points Post Re-chlorination (November 2008)

Sampling Locations	UV absorbance @254 (AU)	SUVA (L/mg $C.m^{-1}$)	THM (ppb)
Brunkild Reservoir Outlet	0.087	1.033	160.0
Starbuck Reservoir Outlet	0.115	1.174	210.0
Oak Bluff Reservoir Outlet	0.105	1.117	140.0
La Salle Reservoir Outlet	0.113	1.188	160.0
Domain Reservoir Outlet	0.111	1.167	180.0

End Points (2008 Annual Average)

Sampling Locations	UV absorbance @254 (AU)	SUVA (L/mg $C.m^{-1}$)	THM (ppb)
Brunkild Residence	0.095	1.054	189.0
Starbuck Residence	0.097	1.050	195.0
Oak Bluff Residence	0.099	1.080	95.0
La Salle Residence	0.100	1.088	188.0
Domain Residence	0.137	1.898	197.0

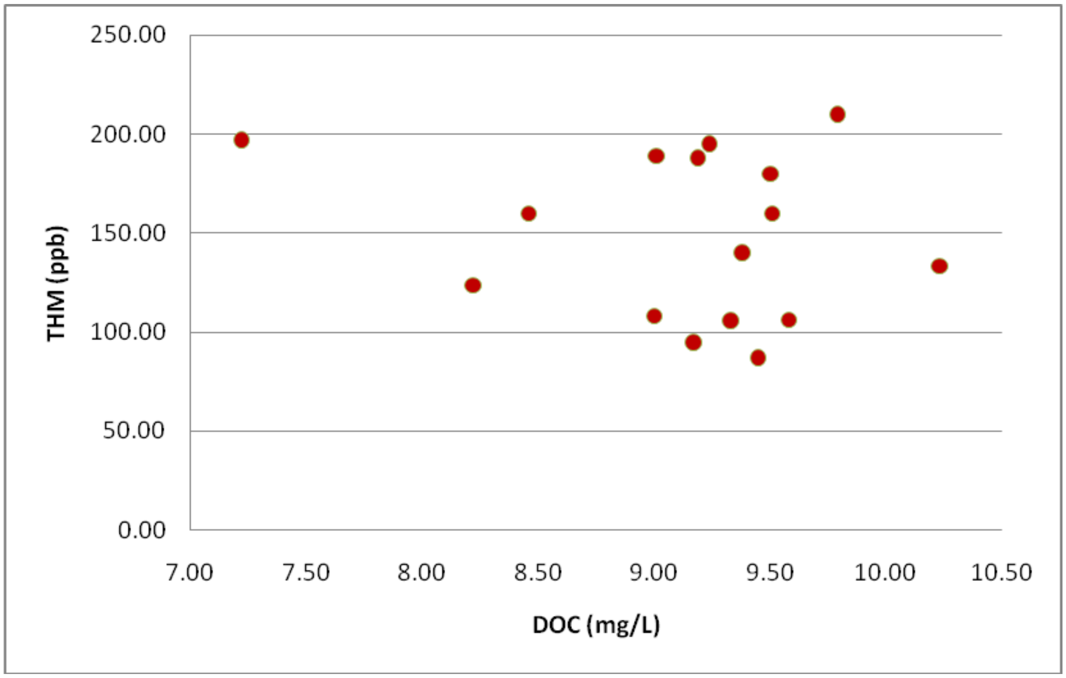


Figure 20 THM and DOC correlation

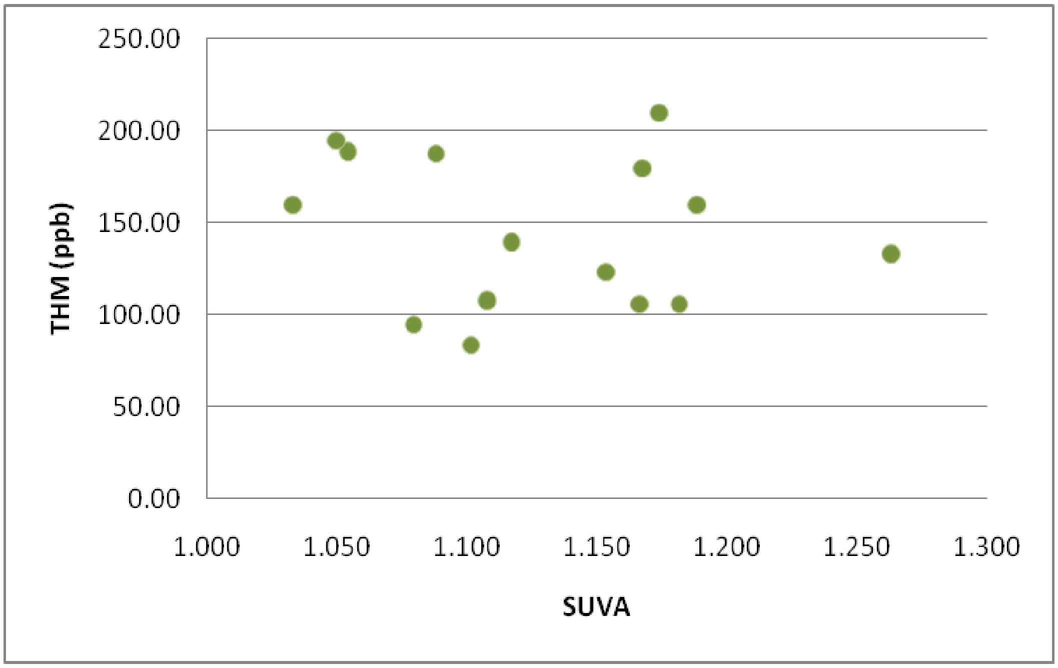


Figure 21 THM and SUVA correlation

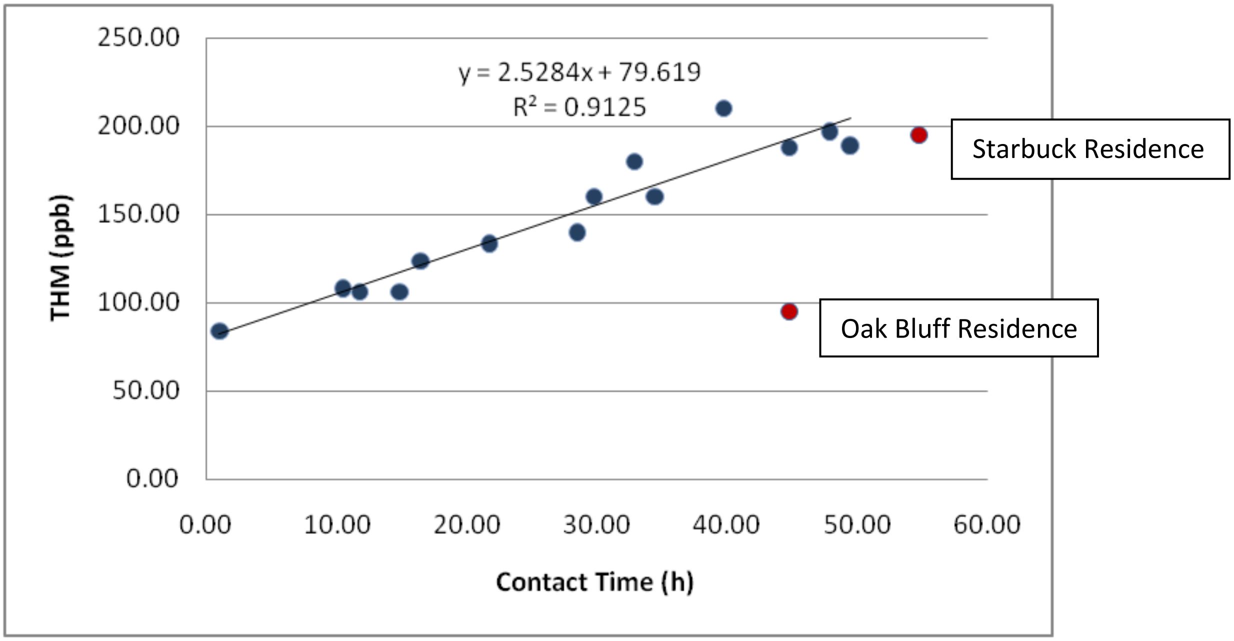


Figure 22 Correlation between THM and chlorine contact time

6 CONCLUSION

Monitoring in the R.M. of Macdonald regional water system indicates elevated THM levels. The province of Manitoba in 2007 introduced a standard of 100ppb for THMs based on a running annual average of minimum quarterly samples. The R.M. has the following options to reduce the THMs in their potable water:

1. An increasing trend of total THMs concentration with water DOC was observed in this study; therefore, the THM can be reduced by improving the removal of DOC at the water treatment plant. Coagulation with alufer S25 and lime/soda softening successfully optimized the removal of DOC by an additional 51% in the summer and 34% in the winter. Due to the lower DOC, the THM concentration in the finished water was reduced by 58% in summer and by 31% in winter. Results indicate that removal of 1mg/L of DOC eliminated 26.8ppb of THMs during the summer and 11.9ppb of THMs during the winter.

2. The THM concentration continued to increase in the of the distribution system with samples reaching levels higher than 200ppb. The results of this study suggest a linear increase in THM with an increase of chlorine contact time. This suggests that reducing the water travel time in the distribution system may be another possible method to lower THMs concentration.

7 RECOMMENDATIONS

7.1 Suggestion for Removal of DOC

Separating coagulation and softening processes would require construction of an additional tank. Figure 23 suggests a design plan for the Sanford water treatment plant with enhanced coagulation and softening; however, this is associated with a significant cost. THMs can also be controlled using monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3), all of which inactivate bacteria while forming less THMs compared to chlorine.

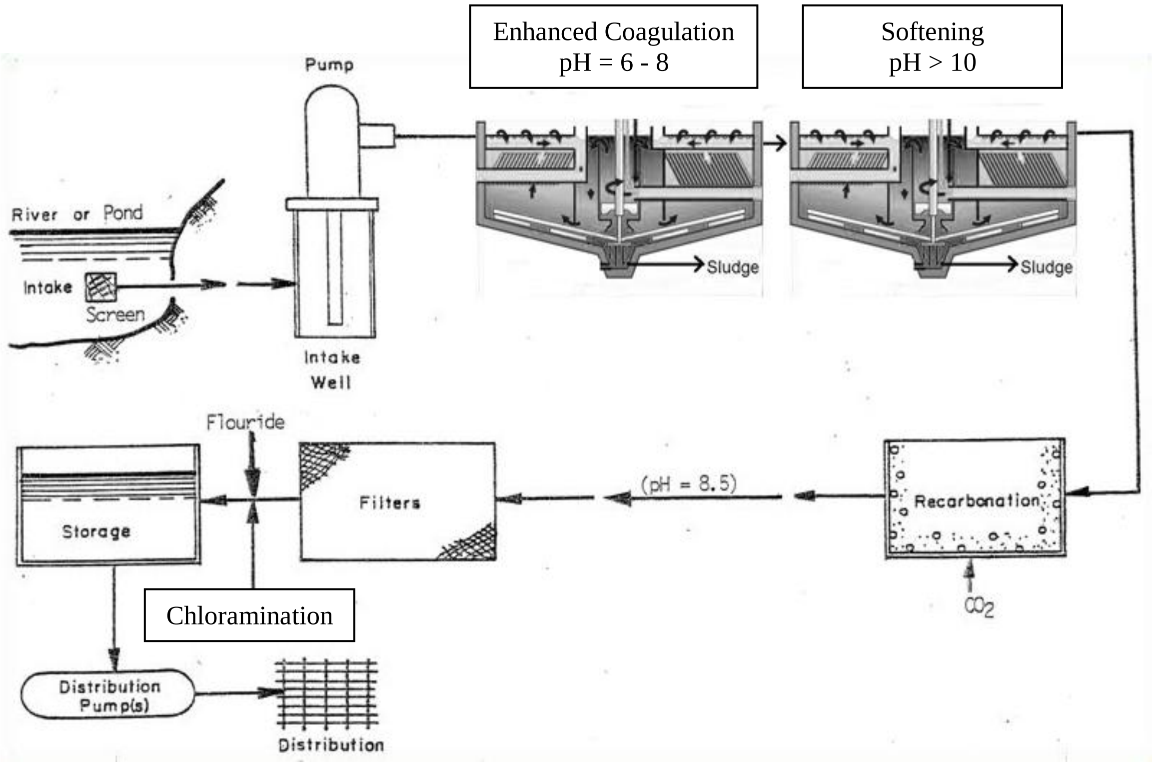


Figure 23 Suggested design for Sanford plant with enhanced coagulation and softening

The lime/soda softening process can be replaced by membrane softening. If Sanford implements NF or RO membrane filtration for softening, enhanced coagulation can be performed as a filtration pre-treatment in the current lime softening reactor (Figure 24). Construction costs for an additional reactor can be eliminated. Considering the high water DOC, membrane fouling may be a limiting factor in this scenario and may need to be researched further in detail.

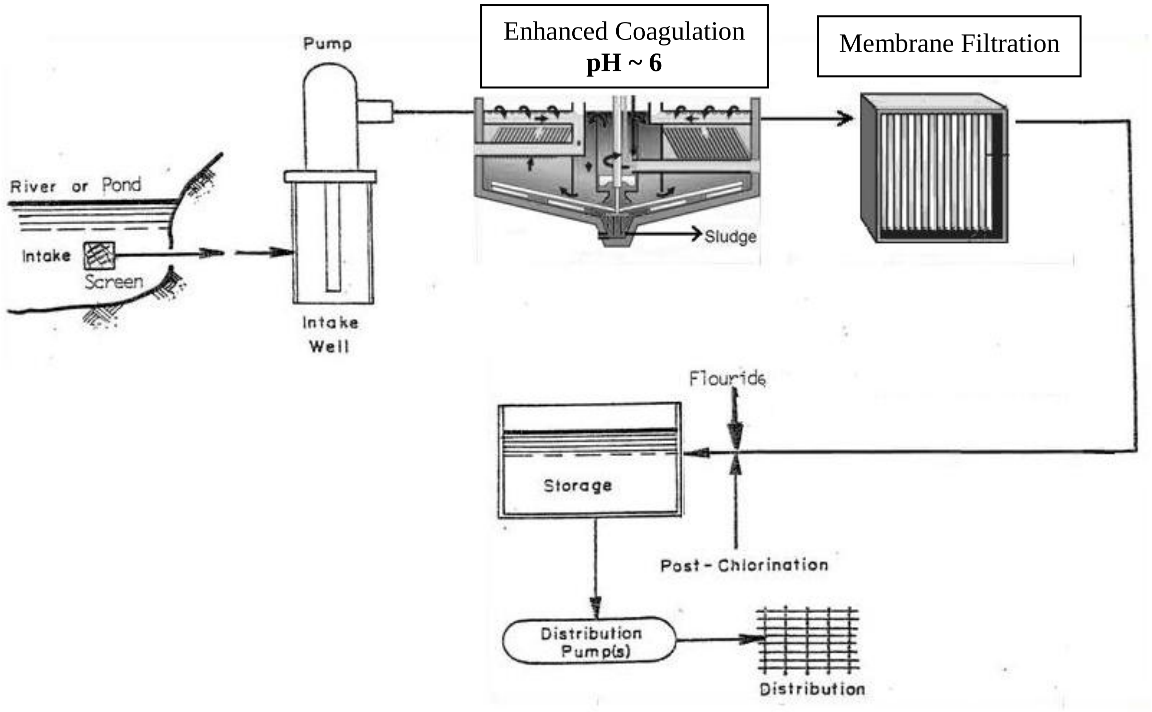


Figure 24 Suggested water treatment design utilizing membrane filtration

7.2 Membrane Water Softening

Application of alternative softening methods such as membrane softening can eliminate lime sludge production. Membrane softening removes calcium and magnesium ions that are responsible for water hardness through filtration with high quality effluent. For instance, nano-filtration (NF) and reverse osmosis (RO) membranes capture dissolved ions (Ca^{2+} and Mg^{2+}), suspended particles, bacteria, and viruses (AWWA, 1996).

Membrane fouling is one of the major concerns in membrane filtration. Membrane fouling increases the membrane resistance and transmembrane pressure, which reduces the permeate flux across the membrane. Higher pressure is required to maintain the desired permeate flux; thus, the operational cost will be greatly increased. Serious membrane fouling can lead to membrane failure, which requires membrane replacement. Species rejected by the membrane form a cake layer on the surface of the membrane. The size of the species depends on the membrane pore size and the accumulated cake layer. Most of the rejected particles are larger than the membrane pore size. Materials from the feed water that attach on the membrane surface reduce the permeate flux; these materials are referred to as foulants (AWWA, 1996). Most of the foulants are small particles but are larger than the pore size of the membrane. This is because the shear force created by the turbulence lifts up and carries away large particles near the membrane surface (AWWA, 1996). As a result, fouling is mostly created by small particles deposited along the membrane surface. Dissolved Organic Carbon is believed to be the major cause of membrane fouling (Crittenden *et al.* 2005)

Cleaning processes, such as hydraulic back flush, are usually performed periodically with a time separation to allow a decrease in membrane fouling. Sometimes chemical agents are added to help wash away the foulants from the membrane surface. However, even with the cleaning process, the membrane performance will still decrease over time. This is because certain foulants will still attach onto the membrane surface. These remaining foulants create an irreversible permeate flux loss. Membrane cleaning recovers up to a certain amount of permeate flux loss until membrane replacement is required.

Combining coagulation with membrane filtration may increase permeate flux by reducing membrane fouling and operation cost. The flocs rejected by the membrane will form a cake layer on the membrane surface with a smaller resistance; this is due to the increase in the cake porosity. Also, large flocs can be easily washed away by back flush. Therefore, coagulation reduces the transmembrane pressure while retaining the permeate flux.

7.3 Estimation of Solids Production

Experimental observation suggests that coagulation prior to softening reduces the lime sludge production. Sludge produced by coagulation is more environmentally friendly because of its relatively natural pH. Coagulation also produces more sludge than softening as most of the colloids are removed as coagulation sludge. According to Equations 5 and 9, 175mg/L of alufer S25 produces 56mg/L of precipitate in the summer and 450mg/L of alufer S25 produces 144mg/L of precipitate in the winter. The calculated summer and winter daily precipitate production rates of alufer are 123.2kg/day and 158.4kg/day respectively. Currently, the Sanford plant is applying approximately 50mg/L of alum throughout the year (Epler 2009). This gives an estimated daily precipitate production of 28.6kg/day in the summer and 14.3kg/day in the winter. However, coagulation sludge includes both the precipitate and the removed colloids. Therefore, the total amount of coagulation sludge must be physically measured after dewatering.

It is difficult to calculate the amount of softening sludge at Sanford due to the complication in measuring the applied lime and soda dose. It is also difficult to compare coagulation sludge with softening sludge using the sludge index because softening sludge is hard to settle. Dry mass measurement would be a better expression of true sludge production. Sludge containing high aluminum content is not suggested for land application because it prohibits vegetation growth. Disposing of sludge to a landfill is a possible option when free land is available. However, sludge quality, sludge utilization, and the impact of solid loading on filtration should be studied intensively in the future.

7.4 Reducing Contact Time in Distribution System

Although DOC can be significantly reduced through enhanced coagulation, the THM concentration may still exceed the regulation of 100ppb due to its long contact time in the distribution system. THM formation could be reduced by performing statistical analysis on the seasonal local water demand. It is believed that the water demand in Sanford is higher in the summer than in the winter due to the water consumption of nearby farms. Sanford could adjust the water supply seasonally according to this water demand in order to reduce the contact time in satellite reservoirs. As a result, THM formation would be reduced due to the shorter contact time.

7.5 Improving THM Measurement in The Distribution System

ALS Group only performed one measurement on each delivered sample, which does not allow for a standard deviation calculation in the THM concentration. It would have been very expensive to measure multiple samples in the distribution system to get a standard deviation. Currently, the environmental engineering laboratory performs gas chromatography which still requires a mass spectrometer for accurate THM measurement. There, it is more convenient to duplicate THM measurement and get a standard deviation. Moreover, it would be more cost efficient to measure multiple THM concentrations at the distribution system with GC/MS.

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APPENDIX A

Table A 1 Alum Coagulation Experimental Results (March 31st, 2008)

Jar	Alum Dose (mg/L)	pH	Turbidity (NTU)	Alkalinity (as CaCo3 mg/L)	DOC (mg/L)
1	150	6.7	1.59	250	10.5
2	175	6.7	1.38	250	9.1
3	200	6.6	1.27	250	9.1
4	225	6.5	0.79	250	8.8
5	250	6.4	0.87	250	8.1
6	275	6.4	1.06	250	7.9

Table A 2 Single Stage Ferric Chloride Coagulation Experimental Results (March 31st, 2008)

Jar	Ferric chloride (mg/L)	pH	Turbidity (NTU)	Alkalinity (as CaCo3 mg/L)	DOC (mg/L)
1	150	6.4	0.99	195	7.9
2	175	6.2	0.75	180	6.9
3	200	6.0	0.58	145	6.5
4	225	5.9	0.72	135	5.7
5	250	5.9	0.81	110	5.2
6	275	5.7	0.60	85	4.6

Table A 3 Double Stages Alum Enhanced Coagulation Experimental Results (March 31st, 2008)

Jar	Pre-coagulated Alum (mg/L)	Alum (mg/L)	pH	Turbidity (NTU)	Alkalinity (as CaCo3 mg/L)	DOC (mg/L)
1	275	40	7.2	0.22	170	7.6
2	275	50	7.2	0.08	170	7.2
3	275	60	7.2	0.12	170	7.2
4	275	70	7.1	0.16	170	7.2
5	275	80	7.1	0.22	164	6.7
6	275	90	7.0	0.07	164	6.9

Table A 4 Double Stages Ferric Chloride Enhanced Coagulation Experimental Results (March 31st, 2008)

Jar	Pre-coagulated Ferric (mg/L)	Ferric chloride (mg/L)	pH	Turbidity (NTU)	Alkalinity (as CaCo3 mg/L)	DOC (mg/L)

1	275	40	6.2	0.63	46	3.7
2	275	50	6.1	1.10	38	3.4
3	275	60	6.0	0.74	30	3.5
4	275	70	5.9	0.92	24	3.2
5	275	80	5.8	1.52	20	3.2
6	275	90	5.5	0.89	6	3.8

Table A 5 Double Stages Alum Plus Ferric Coagulation Experimental Results (March 31st, 2008)

Jar	Pre-coagulated Alum (mg/L)	Ferric chloride (mg/L)	pH	Turbidity (NTU)	Alkalinity (as CaCo3 mg/L)	DOC (mg/L)
1	275	150	7	0.63	196	7.5
2	275	175	6.9	0.66	196	7.4
3	275	200	6.7	0.43	180	7
4	275	225	6.7	0.64	180	6.9
5	275	250	6.6	0.8	170	6.5
6	275	275	6.6	1.02	150	6.4

Softening Dose Calculation

Evaluation of dissolved CO_2 in mg/L $CaCO_3$

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

$$k_A = \frac{(H^+)\ (HCO_3{}^-)}{(H_2CO_3)}$$

$$(H_2CO_3) = (CO_2)$$

$$pH = -\log (H^+) \quad \rightarrow \quad (H^+) = 10^{-pH}$$

$$(HCO_3{}^-) = (HCO_3{}^- mg/L\ CaCO_3)\ \frac{1EQ}{50{,}000\ mg\ CaCO_3}$$

$$(CO_2) = \frac{(H^+)\,(HCO_3{}^-)}{k_A}$$

$$(CO_2 mg/L\ CaCO_3) = \frac{(CO_2)\ \mathrm{x}\ \left(44.01\,\frac{\mathrm{g}}{\mathrm{mol}}\right)\mathrm{x}\ (\frac{1000\mathrm{mg}}{\mathrm{g}})}{\frac{22{,}000mg}{EQ}}\ \ \mathrm{x}\ \ 50{,}000\ \frac{mg}{EQ}\ CaCO_3$$

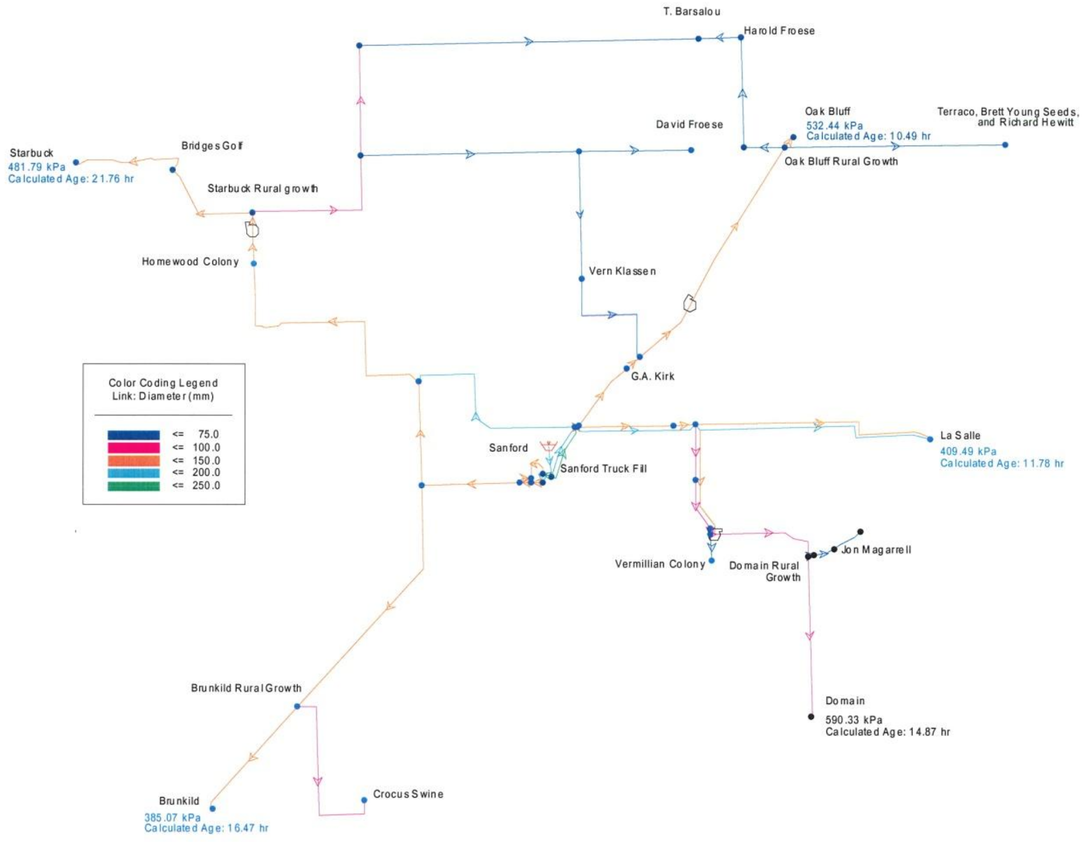
Coagulated water quality:
pH after coagulation: 6.85
Total Hardness : 226 mg/L $CaCO_3$
Calcium Hardness: 161.8 mg/L
Alkalinity = 96.667mg/L $CaCO_3$

Table A 6 Softening dose sample calculation for summer 2008

	Amount to be removed	Lime $Ca(OH)_2$ (mg/L $CaCO_3$)	Soda $NaCO_3$ (mg/L $CaCO_3$)
CO_2	61.63	68.98	0
Calcium (carbonate hardness)	96.66	96.66	0
Magnesium (carbonate hardness)	0.00	0	0
Calcium (non-carbonate hardness)	65.13	0	65.13
Magnesium (non-carbonate hardness)	64.20	64.20	64.20
Total Dosage		**222.50**	**129.33**

WaterCAD Simulation for Sanford Distribution System

Scenario: Actual Peak Day Current



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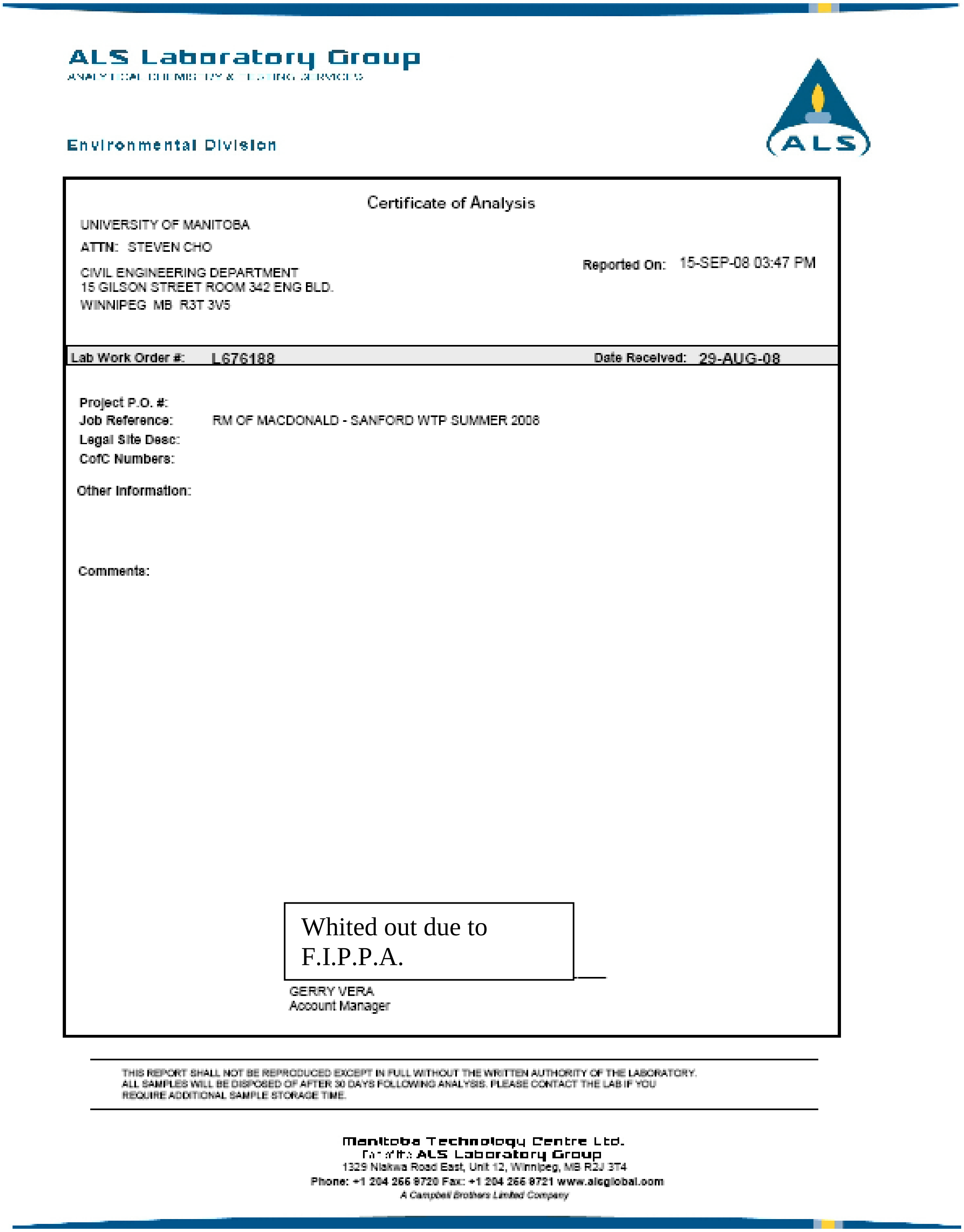
04/29/09 10:45:04 AM © Haestad Methods, Inc. 37 Brookside Road Waterbury, CT 06708 USA +1-203-755-1666 Page 1 of 1

APPENDIX B

ALS Report 1 Laboratory treated water THM concentration (August 29th, 2008)



ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

Environmental Division

Certificate of Analysis

UNIVERSITY OF MANITOBA
ATTN: STEVEN CHO
CIVIL ENGINEERING DEPARTMENT
15 GILSON STREET ROOM 342 ENG BLD.
WINNIPEG MB R3T 3V5

Reported On: 15-SEP-08 03:47 PM

Lab Work Order #: L676188

Date Received: 29-AUG-08

Project P.O. #:
Job Reference: RM OF MACDONALD - SANFORD WTP SUMMER 2008
Legal Site Desc:
CofC Numbers:

Other Information:

Comments:

Whited out due to F.I.P.P.A.

GERRY VERA
Account Manager

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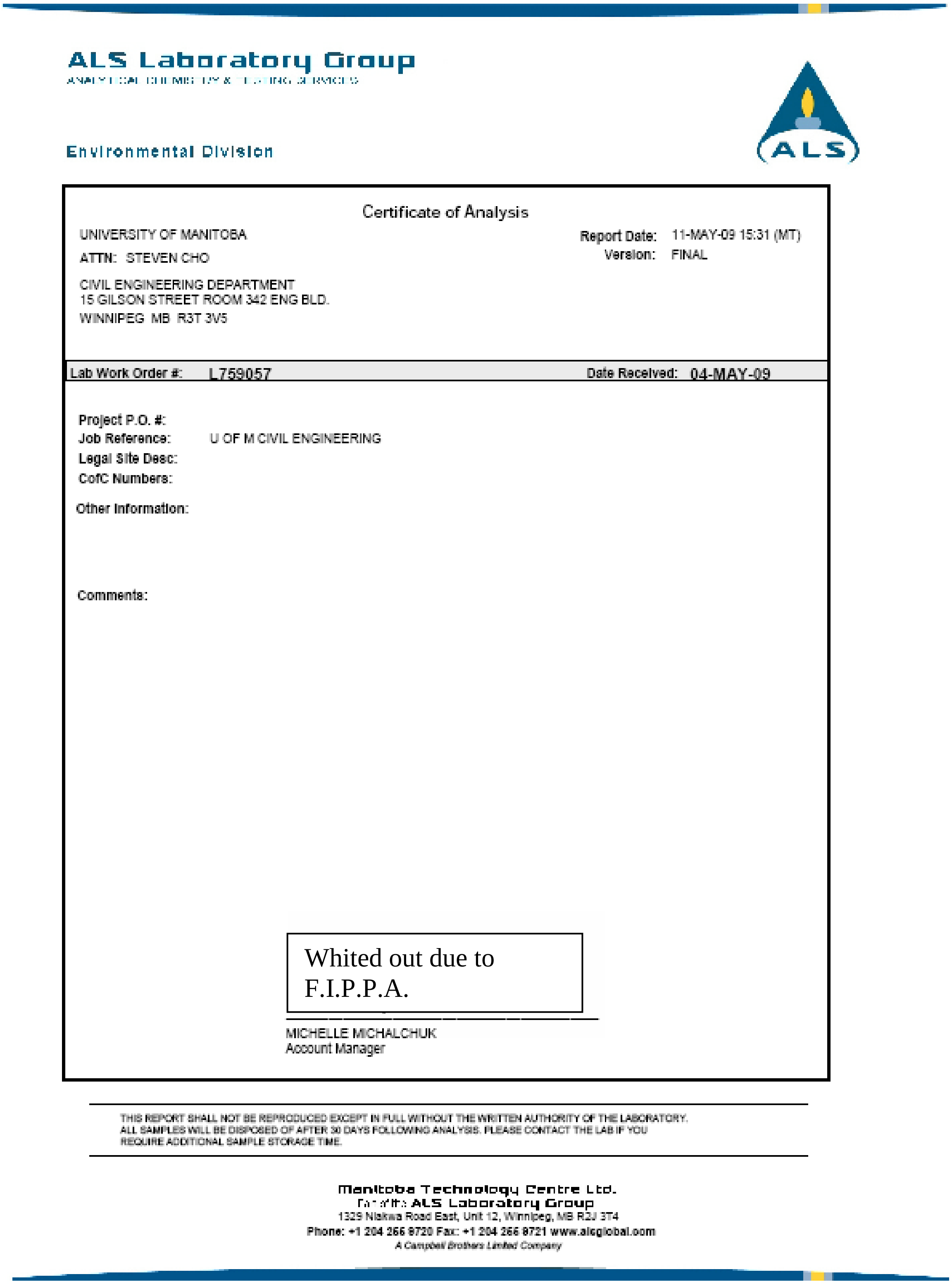
ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L676188-2	WATER AFTER CHLORINATION, ENHANCED COAGULATION & SOFTENING							
Sampled By:	CLIENT on 29-AUG-08							
Matrix:	WATER - TREATED							
THM preserved								
Bromodichloromethane	0.0045		0.0002	mg/L		11-SEP-08	GEV	R722577
Bromoform	<0.0001		0.0001	mg/L		11-SEP-08	GEV	R722577
Chloroform	0.060	DLM	0.0005	mg/L		11-SEP-08	GEV	R722577
Chlorodibromomethane	0.0008		0.0002	mg/L		11-SEP-08	GEV	R722577
THMs	0.065		0.001	mg/L		11-SEP-08	GEV	R722577

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS Report 2 Laboratory treated water THM concentration (May 4th, 2009)



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UNIVERSITY OF MANITOBA
ATTN: STEVEN CHO
CIVIL ENGINEERING DEPARTMENT
15 GILSON STREET ROOM 342 ENG BLD.
WINNIPEG MB R3T 3V5

Report Date: 11-MAY-09 15:31 (MT)
Version: FINAL

Lab Work Order #: L759057
Date Received: 04-MAY-09

Project P.O. #:
Job Reference: U OF M CIVIL ENGINEERING
Legal Site Desc:
CofC Numbers:

Other Information:

Comments:

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MICHELLE MICHALCHUK
Account Manager

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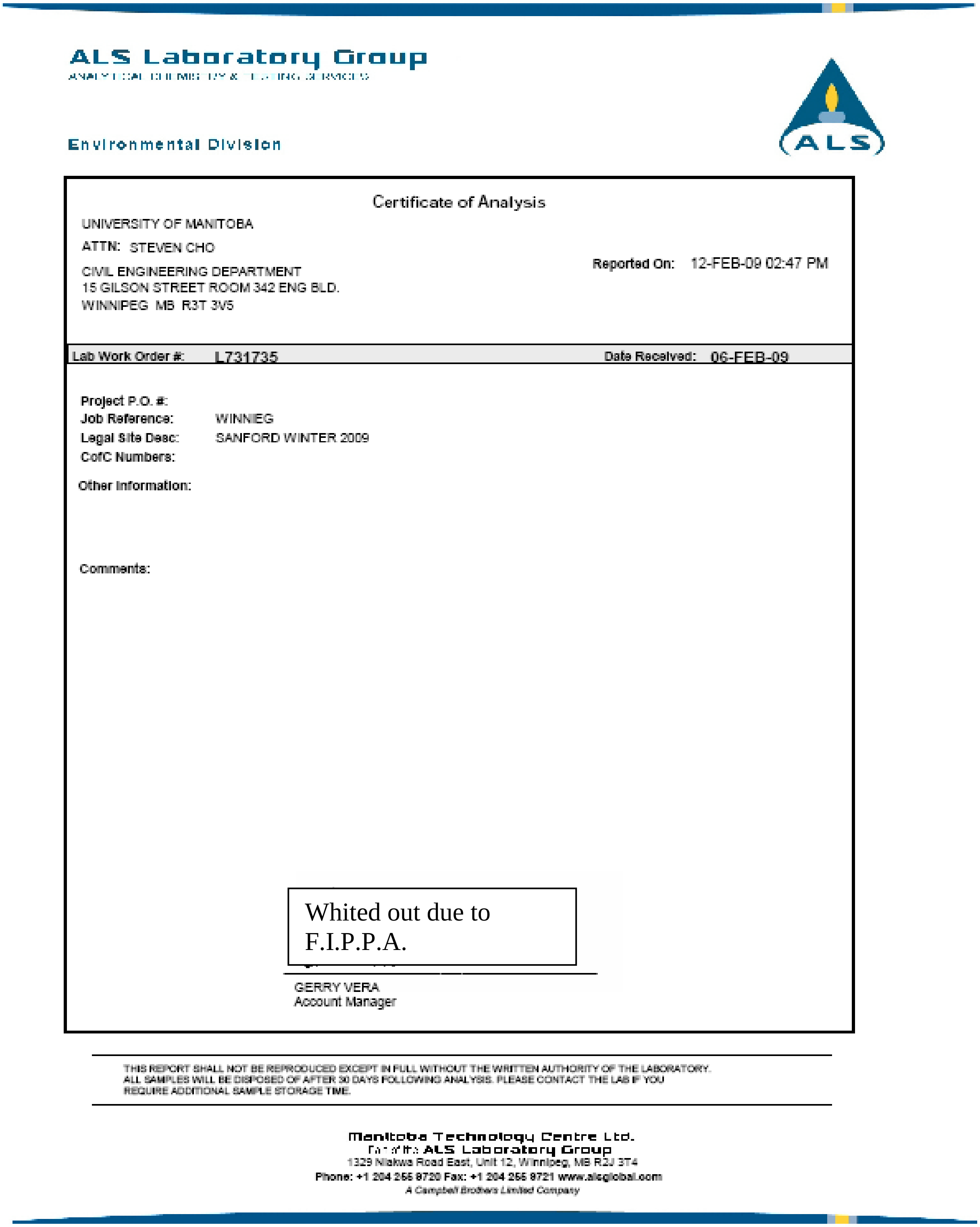
ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters		Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L759057-1	SANFORD THM SPRING 2009 (FROM CIVIL LAB)								
Sampled By:	CLIENT on 04-MAY-09								
Matrix:	WMT								
THMPreserved									
Bromodichloromethane		0.0125		0.00050	mg/L		09-MAY-09	MDM	R825763
Bromoform		<0.00050		0.00050	mg/L		09-MAY-09	MDM	R825763
Chloroform		0.0453		0.00050	mg/L		09-MAY-09	MDM	R825763
Chlorodibromomethane		0.00211		0.00050	mg/L		09-MAY-09	MDM	R825763
THMs		0.0599		0.0020	mg/L		09-MAY-09	MDM	R825763

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS Report 3 Pre re-chlorinated reservoirs water THM concentration (February 6th, 2009)



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UNIVERSITY OF MANITOBA
ATTN: STEVEN CHO
CIVIL ENGINEERING DEPARTMENT
15 GILSON STREET ROOM 342 ENG BLD.
WINNIPEG MB R3T 3V5

Reported On: 12-FEB-09 02:47 PM

Lab Work Order #: L731735 **Date Received:** 06-FEB-09

Project P.O. #:
Job Reference: WINNIEG
Legal Site Desc: SANFORD WINTER 2009
CofC Numbers:

Other Information:

Comments:

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F.I.P.P.A.

GERRY VERA
Account Manager

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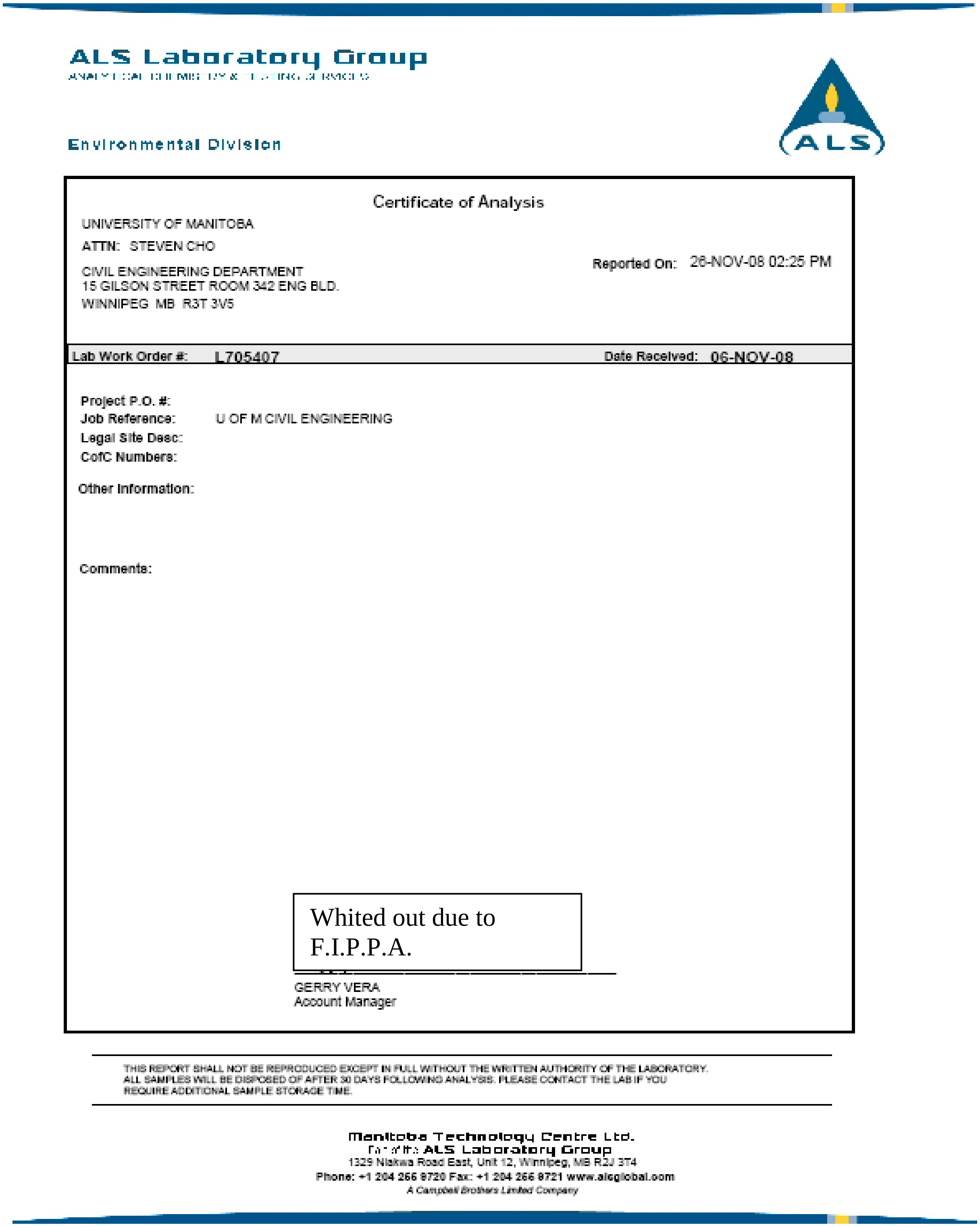
ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L731735-1 #1- BRUNKILD - RESERVOIR - IN Sampled By: CLIENT on 06-FEB-09 Matrix: MUNICIPAL TREATED - WATER								
THM preserved								
Bromodichloromethane	0.025		0.0005	mg/L		11-FEB-09	MDM	R787872
Bromoform	<0.0005		0.0005	mg/L		11-FEB-09	MDM	R787872
Chloroform	0.13		0.0005	mg/L		11-FEB-09	MDM	R787872
Chlorodibromomethane	0.0038		0.0005	mg/L		11-FEB-09	MDM	R787872
THMs	0.16		0.002	mg/L		11-FEB-09	MDM	R787872
L731735-2 #2- STARBUCK RESERVOIR - IN Sampled By: CLIENT on 06-FEB-09 Matrix: MUNICIPAL TREATED - WATER								
THM preserved								
Bromodichloromethane	0.027		0.0005	mg/L		11-FEB-09	MDM	R787872
Bromoform	<0.0005		0.0005	mg/L		11-FEB-09	MDM	R787872
Chloroform	0.18		0.0005	mg/L		11-FEB-09	MDM	R787872
Chlorodibromomethane	0.0025		0.0005	mg/L		11-FEB-09	MDM	R787872
THMs	0.21		0.002	mg/L		11-FEB-09	MDM	R787872
L731735-3 #3- OAK BLUFF RESERVOIR - IN Sampled By: CLIENT on 06-FEB-09 Matrix: MUNICIPAL TREATED - WATER								
THM preserved								
Bromodichloromethane	0.019		0.0005	mg/L		11-FEB-09	MDM	R787872
Bromoform	<0.0005		0.0005	mg/L		11-FEB-09	MDM	R787872
Chloroform	0.12		0.0005	mg/L		11-FEB-09	MDM	R787872
Chlorodibromomethane	0.0024		0.0005	mg/L		11-FEB-09	MDM	R787872
THMs	0.14		0.002	mg/L		11-FEB-09	MDM	R787872
L731735-4 #4- LA SALLE - RESERVOIR - IN Sampled By: CLIENT on 06-FEB-09 Matrix: MUNICIPAL TREATED - WATER								
THM preserved								
Bromodichloromethane	0.022		0.0005	mg/L		11-FEB-09	MDM	R787872
Bromoform	<0.0005		0.0005	mg/L		11-FEB-09	MDM	R787872
Chloroform	0.14		0.0005	mg/L		11-FEB-09	MDM	R787872
Chlorodibromomethane	0.0025		0.0005	mg/L		11-FEB-09	MDM	R787872
THMs	0.16		0.002	mg/L		11-FEB-09	MDM	R787872
L731735-5 #5- DOMAIN RESERVOIR - IN Sampled By: CLIENT on 06-FEB-09 Matrix: MUNICIPAL TREATED - WATER								
THM preserved								
Bromodichloromethane	0.023		0.0005	mg/L		11-FEB-09	MDM	R787872
Bromoform	<0.0005		0.0005	mg/L		11-FEB-09	MDM	R787872
Chloroform	0.15		0.0005	mg/L		11-FEB-09	MDM	R787872
Chlorodibromomethane	0.0025		0.0005	mg/L		11-FEB-09	MDM	R787872
THMs	0.18		0.002	mg/L		11-FEB-09	MDM	R787872

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS Report 4 Post re-chlorinated reservoirs water THM concentration (November 6th, 2008)



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ATTN: STEVEN CHO
CIVIL ENGINEERING DEPARTMENT
15 GILSON STREET ROOM 342 ENG BLD.
WINNIPEG MB R3T 3V5

Reported On: 26-NOV-08 02:25 PM

Lab Work Order #: L705407

Date Received: 06-NOV-08

Project P.O. #:
Job Reference: U OF M CIVIL ENGINEERING
Legal Site Desc:
CofC Numbers:

Other Information:

Comments:

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Account Manager

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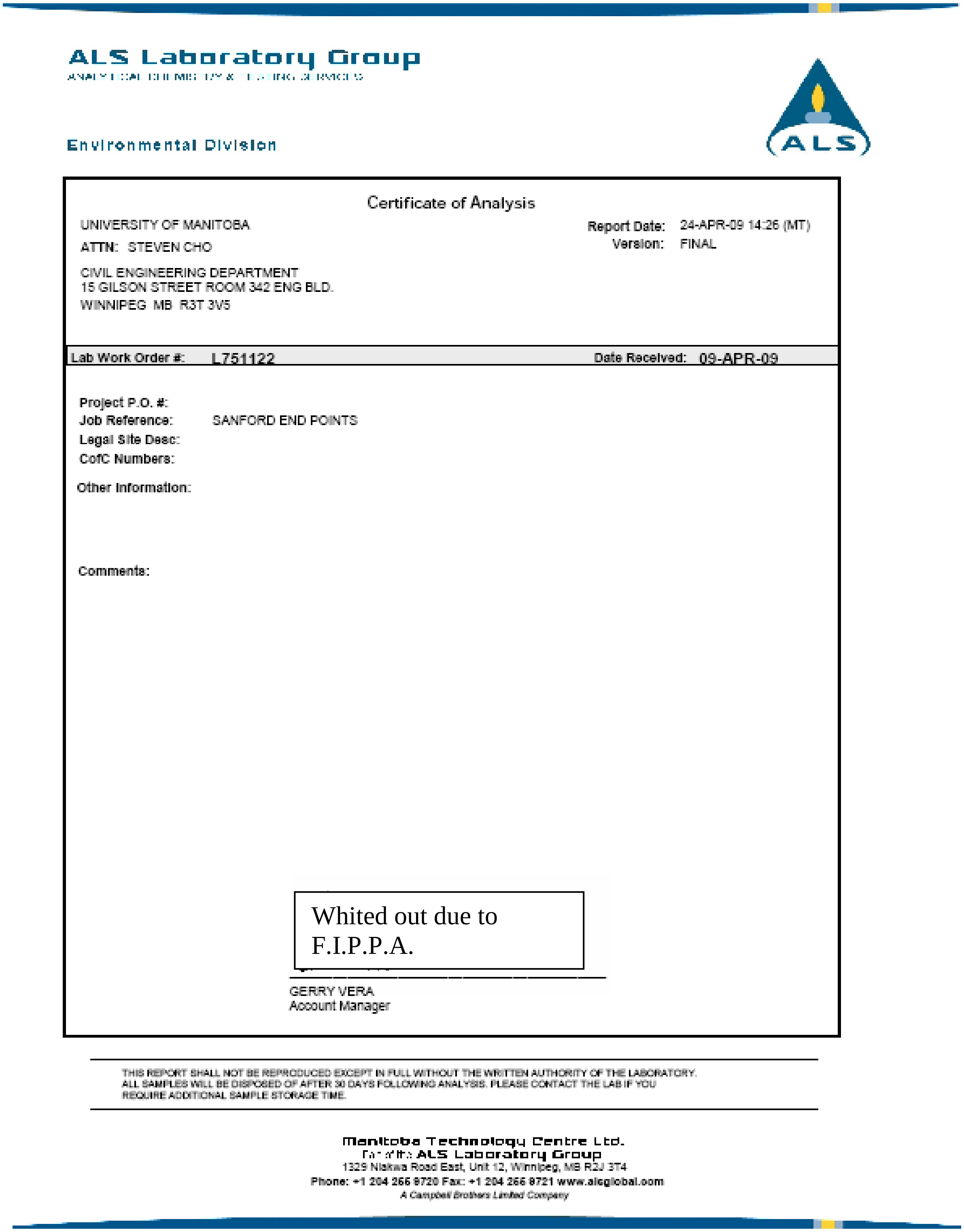
Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L705407-1 1. BRUNKID RESERVOIR RECHLORINATED								
Sampled By: CLIENT on 06-NOV-08								
Matrix: water								
THM preserved								
Bromodichloromethane	0.021		0.0005	mg/L		24-NOV-08	MDM	R759769
Bromoform	<0.0005		0. 0005	mg/L		24-NOV-08	MDM	R759769
Chloroform	0.10		0.0005	mg/L		24-NOV-08	MDM	R759769
Chlorodibromomethane	0.0025		0.0005	mg/L		24-NOV-08	MDM	R759769
THMs	0.12		0.002	mg/L		24-NOV-08	MDM	R759769
L705407-2 2 STARBUCK RESERVOIR RECHLORINATED								
Sampled By: CLIENT on 06-NOV-08								
Matrix: water								
THM preserved								
Bromodichloromethane	0.021		0.0005	mg/L		24-NOV-08	MDM	R759769
Bromoform	<0.0005		0. 0005	mg/L		24-NOV-08	MDM	R759769
Chloroform	0.11		0.0005	mg/L		24-NOV-08	MDM	R759769
Chlorodibromomethane	0.0024		0.0005	mg/L		24-NOV-08	MDM	R759769
THMs	0.13		0.002	mg/L		24-NOV-08	MDM	R759769
L705407-3 3. OAK BLUFF RESERVOIR RECHLORINATED								
Sampled By: CLIENT on 06-NOV-08								
Matrix: water								
THM preserved								
Bromodichloromethane	0.019		0.0005	mg/L		24-NOV-08	MDM	R759769
Bromoform	<0.0005		0. 0005	mg/L		24-NOV-08	MDM	R759769
Chloroform	0.087		0.0005	mg/L		24-NOV-08	MDM	R759769
Chlorodibromomethane	0.0021		0.0005	mg/L		24-NOV-08	MDM	R759769
THMs	0.11		0.002	mg/L		24-NOV-08	MDM	R759769
L705407-4 4. LA SALLE RESERVOIR RECHLORINATED								
Sampled By: CLIENT on 06-NOV-08								
Matrix: water								
THM preserved								
Bromodichloromethane	0.018		0.0005	mg/L		24-NOV-08	MDM	R759769
Bromoform	<0.0005		0. 0005	mg/L		24-NOV-08	MDM	R759769
Chloroform	0.086		0.0005	mg/L		24-NOV-08	MDM	R759769
Chlorodibromomethane	0.086		0.0005	mg/L		24-NOV-08	MDM	R759769
THMs	0.11		0.002	mg/L		24-NOV-08	MDM	R759769
L705407-5 5 DOMAIN RESERVOIR RECHLORINATED								
Sampled By: CLIENT on 06-NOV-08								
Matrix: water								
THM preserved								
Bromodichloromethane	0.018		0.0005	mg/L		25-NOV-08	MDM	R759769
Bromoform	<0.0005		0. 0005	mg/L		25-NOV-08	MDM	R759769
Chloroform	0.086		0.0005	mg/L		25-NOV-08	MDM	R759769
Chlorodibromomethane	0.0020		0.0005	mg/L		25-NOV-08	MDM	R759769
THMs	0.11		0.002	mg/L		25-NOV-08	MDM	R759769

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS Report 5 Sanford plant and distribution endpoints THM report (April 9th, 2009)



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Environmental Division

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UNIVERSITY OF MANITOBA
ATTN: STEVEN CHO

CIVIL ENGINEERING DEPARTMENT
15 GILSON STREET ROOM 342 ENG BLD.
WINNIPEG MB R3T 3V5

Report Date: 24-APR-09 14:26 (MT)
Version: FINAL

Lab Work Order #: L751122 **Date Received:** 09-APR-09

Project P.O. #:
Job Reference: SANFORD END POINTS
Legal Site Desc:
CofC Numbers:

Other Information:

Comments:

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GERRY VERA
Account Manager

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ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L751122-1 BRUNKILD END POINT Sampled By: CLIENT on 08-APR-09 Matrix: MUNICIPAL TREATED WATER								
THM preserved								
Bromodichloromethane	0.0327		0.00050	mg/L		15-APR-09	MDM	R813512
Bromoform	<0.00050		0.00050	mg/L		15-APR-09	MDM	R813512
Chloroform	0.153		0.00050	mg/L		15-APR-09	MDM	R813512
Chlorodibromomethane	0.00330		0.00050	mg/L		15-APR-09	MDM	R813512
THMs	0.189		0.0020	mg/L		15-APR-09	MDM	R813512
L751122-2 STARBUCK END POINT Sampled By: CLIENT on 08-APR-09 Matrix: MUNICIPAL TREATED WATER								
THM preserved								
Bromodichloromethane	0.0335		0.00050	mg/L		15-APR-09	MDM	R813512
Bromoform	<0.00050		0.00050	mg/L		15-APR-09	MDM	R813512
Chloroform	0.158		0.00050	mg/L		15-APR-09	MDM	R813512
Chlorodibromomethane	0.00325		0.00050	mg/L		15-APR-09	MDM	R813512
THMs	0.195		0.0020	mg/L		15-APR-09	MDM	R813512
L751122-3 OAK BLUFF END POINT Sampled By: CLIENT on 08-APR-09 Matrix: MUNICIPAL TREATED WATER								
Trihalomethanes								
Chloroform	86.1		0.50	ug/L		23-APR-09	SK	R816365
Bromodichloromethane	17.4		0.50	ug/L		23-APR-09	SK	R816365
Dibromochloromethane	1.90		0.50	ug/L		23-APR-09	SK	R816365
Bromoform	<0.50		0.50	ug/L		23-APR-09	SK	R816365
Total THMs	105		2.0	ug/L		23-APR-09	SK	R816365
1,2-Dichloroethane d4Surr:	95		50-150	%		23-APR-09	SK	R816365
L751122-4 LA SALLE END POINT Sampled By: CLIENT on 08-APR-09 Matrix: MUNICIPAL TREATED WATER								
THM preserved								
Bromodichloromethane	0.0342		0.00050	mg/L		15-APR-09	MDM	R813512
Bromoform	<0.00050		0.00050	mg/L		15-APR-09	MDM	R813512
Chloroform	0.151		0.00050	mg/L		15-APR-09	MDM	R813512
Chlorodibromomethane	0.00326		0.00050	mg/L		15-APR-09	MDM	R813512
THMs	0.188		0.0020	mg/L		15-APR-09	MDM	R813512
L751122-5 DOMAIN END POINT Sampled By: CLIENT on 08-APR-09 Matrix: MUNICIPAL TREATED WATER								
THM preserved								
Bromodichloromethane	0.0338		0.00050	mg/L		15-APR-09	MDM	R813512
Bromoform	<0.00050		0.00050	mg/L		15-APR-09	MDM	R813512
Chloroform	0.160		0.00050	mg/L		15-APR-09	MDM	R813512
Chlorodibromomethane	0.00272		0.00050	mg/L		15-APR-09	MDM	R813512
THMs	0.197		0.0020	mg/L		15-APR-09	MDM	R813512

ALS LABORATORY GROUP ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	By	Batch
L751122-6 SANFORT WATER PLANT EFFLUENT								
Sampled By: CLIENT on 08-APR-09								
Matrix: MUNICIPAL TREATED WATER								
THM preserved								
Bromodichloromethane	0.0177		0.00050	mg/L		15-APR-09	MDM	R813512
Bromoform	<0.00050		0.00050	mg/L		15-APR-09	MDM	R813512
Chloroform	0.0665		0.00050	mg/L		15-APR-09	MDM	R813512
Chlorodibromomethane	0.00238		0.00050	mg/L		15-APR-09	MDM	R813512
THMs	0.0866		0.0020	mg/L		15-APR-09	MDM	R813512

* Refer to Referenced Information for Qualifiers (if any) and Methodology.