Removal of DOC and its fractions from surface waters of the Canadian Prairie containing high levels of DOC and hardness
Mehrnaz Sadrnourmohamadi, Charles D. Goss and Beata Gorczyca

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

Key words | dissolved organic carbon, DOC fractionation, trihalomethane precursors, trihalomethanes

INTRODUCTION
High dissolved organic carbon (DOC) in potable water sources is of concern due to the formation of harmful chlorine disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), following chlorine disinfection (Rook 1974; Singer 1999). Potable water sources in Manitoba (Canada) often contain concentrations of DOC exceeding 20 mg L\(^{-1}\). As a result of high DOC concentrations approximately 70% of the potable water treatment plants (WTPs) in Manitoba using surface water sources are not in compliance with THM regulations set by the Province (Manitoba Water Stewardship 2011). Therefore, water treatment facilities are faced with improving the removal of DOC from the raw water prior to chlorination in order to reduce the concentrations of THMs to meet current provincial guidelines. A recent study of the THM formation potential (THMFP) on two Manitoban rivers showed that THMFP of these rivers can be 10 times higher than those reported in literature (Goss & Goeczyca 2013). This study focused on THMs because the Province regulates only these chloride DBPs (Manitoba Water Stewardship 2011). HAAs are not currently regulated in the Province of Manitoba (Canada).

UV\(_{254}\) absorbance has been used as an indicator for estimating the potential of raw surface waters to form THMs, but there are conflicting beliefs regarding its effectiveness in estimating THM formation. The major limitation of
using specific UV absorbance (SUVA\textsubscript{254}) to predict DBP formation in drinking water treatment is probably the involvement of non-reactive components in DOC. Indeed, not all organic carbon having absorbance at 254 nm reacts with chlorine to form THM (Weishaar et al. 2003).

Chow et al. (2008) suggested that the correlation between UVA\textsubscript{254} and DOC concentration is source dependent and each carbon source showed a distinctly different linear regression. Poor correlations between SUVA\textsubscript{254} and specific trihalomethane formation potential (STHMF) have been occasionally reported and the reliability of using SUVA\textsubscript{254} to predict THM formation has been questioned (Fram et al. 1999; Chow et al. 2008). Our group was not able to successfully correlate UVA\textsubscript{254} with water DOC for one of the tributaries to the Red River (Cho et al. 2010). In addition, some recent studies have questioned the reliability of using SUVA\textsubscript{254} to predict reactivity of DOC in natural waters (Weishaar et al. 2003). Iriarte-Velasco et al. (2007) showed that coagulation optimization based on DOC and UV\textsubscript{254} removal does not ensure optimum results for THMs precursors removal. One possible source is formation of UV absorbing moieties during coagulation which interfere with UV measurements.

It has been strongly believed that the hydrophobic acid (HPOA) fraction of DOC, which contains mainly humic matter, has the greatest potential to form THMs (Reckhow et al. 1990; Singer 1999; Leenheer & Croué 2005; Chow et al. 2005). However, it has been recently reported that the hydrophilic (HPI) fractions from the Red River had greater potential to form THMs compared with the hydrophobic (HPO) (HPOA + HPOB + HPON) (Goss & Gorczyca 2013). It has been reported that the HPI fractions are far less amenable to removal with conventional coagulation and are believed to be a major component of DOC found in finished waters coagulated using metal salts (Sharp et al. 2006). Therefore, in this study special focus will be given to reduction of the HPO and HPI fractions.

**OBJECTIVES**

The objective of this study was to evaluate the removal of DOC fractions from the Red River water (Manitoba, Canada) by chemical coagulation. The Red River water represents a typical surface water quality of the Canadian Prairie. Its DOC can vary from 8 to 12 mg L\textsuperscript{-1}. The pH averages about 8 and hardness can range from a low of 232 mg L\textsuperscript{-1} to a high of 411 mg L\textsuperscript{-1} (Goss 2013). The results show that the Red River has high alkalinity, pH, and DOC, suggesting that this water has characteristics that make removal of DOC by coagulation difficult. Typically, better removal of DOC is achieved at lower pH, furthermore the high alkalinity of the Red River makes pH reduction prior to coagulation more difficult and costly (Okour et al. 2009).

The four coagulants used in this study were ferric sulfate, ferric chloride, aluminum sulfate and titanium sulfate. The first three coagulants were tested because they are commonly used in WTPs due to their effectiveness, accessibility and low price (DeWolfe et al. 2003; Baghvand et al. 2010). Titanium sulfate was tested because it has been shown to have better removal of the humic fraction of DOC compared with aluminum and iron based coagulants. In addition it has been reported that titanium salts as new coagulants are economical in terms of sludge reduction (Okour et al. 2009).

It has been reported that the performance of a particular coagulant is dependent upon the specific characteristics of the natural organic matter (NOM) and the test conditions (Volk et al. 2000). Therefore, in this study special focus will be given to reduction of the HPO and HPI DOC fractions. Different coagulant types, doses, and pH were evaluated to establish the optimal conditions for the removal of these fractions from the water to better control the formation of THMs.

**METHODS**

**Sample collection from the Red River**

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

The pH of the samples was measured using a Fisher Scientific Accumet 50 pH meter (Fisher Scientific, New Jersey, USA). Alkalinity was determined as mg L\(^{-1}\) CaCO\(_3\) by titration of sample water with 0.02 N sulfuric acid titrated to pH 4.48 according to *Standard Methods 2320B* (APHA 2012). DOC concentrations were determined using a total organic carbon analyser (Phoenix 8000, Tekmar Dohrmann, USA). Turbidity was measured using a HF Scientific Micro 100 Turbidimeter (HF Scientific, Fort Worth, Florida, USA). The UV absorbance at 254 nm (UV\(_{254}\)) was measured using a UV/visible spectrophotometer (Ultraspec 2100 pro, GBC Scientific Equipment, Australia) with a 1 cm quartz cell. SUVA was measured as the DOC normalized absorbance at UV\(_{254}\).

DOC fractionation

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

Coagulation jar tests

The jar tests were performed using a conventional method in a six paddle PB-700™ standard jar tester by Phipps & Bird (Richmond, USA). On May 12 and 13, 2011 1 L samples of raw water were coagulated; the rapid mix was at 120 rpm for 1 min followed by a slow mix at 40 rpm for 50 min. The samples were then allowed to settle for 30 min. Aluminum sulfate, ferric sulfate, ferric chloride and titanium sulfate stock solution (10,000 mg L\(^{-1}\) as Al for aluminum sulfate) were prepared in Milli-Q (Millipore, France) water. Sodium hydroxide and hydrochloric acid were analytical grade chemicals (Sigma-Aldrich Company Ltd, UK). Coagulants doses were in the range of 20–120 mg L\(^{-1}\) based on the coagulant to DOC ratio of about 10:1 (Garcia 2005).

The surface water we used in this study has a pH above 8 as well as significant alkalinity and related carbonate hardness. Most of the WTPs supplied by the Red River utilize a lime/soda softening process, where water pH is increased to 11. Reduction of water pH to below 6 prior to softening would require a significant increase in the amount of lime required for softening. This would significantly increase the operational cost of the water plants (Pembina Valley Water Treatment Co-operative 2012). Therefore, the coagulation tests were conducted at pH values of 6, 7, and 8. Most DOC compounds are reported to be negatively charged in this pH range and can be destabilized by metal salts as coagulants through charge neutralization (Crittenden *et al.* 2005).

The pH was adjusted with 0.1 M sodium hydroxide solution (NaOH) and 0.1 M hydrochloric acid (HCl). Residual aluminum and iron concentration analyses were performed by an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES, Agilent Technologies, USA) with acidification using 5% HCl.

Trihalomethane formation potential

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

## RESULTS AND DISCUSSION

### General water quality

General water quality tests were taken for samples collected from the Red River on May 12, 2011 (Table 1).

The DOC composition of the Red River can be found in Table 2. The composition of the Red River was similar to that reported earlier by Goss & Gorczyca (2013) which found that the composition of the Red River was more HPI (63%) than HPO (37%).

### Optimization of coagulants for removal of DOC

The results found that for all coagulants the greatest reduction of DOC occurred at the highest coagulant dose (Figure 1). Ferric chloride and titanium sulfate had the greatest removal of DOC at pH 7, while aluminum sulfate and ferric sulfate had optimal removal at pH 6. Ferric sulfate was found to have the greatest removal of DOC showing a total reduction of 66%, while ferric chloride had the lowest reduction of 54% total DOC. Therefore, ferric sulfate would be the optimal coagulant for total DOC removal.

SUVA measurements showed that coagulation with ferric sulfate at the highest dosage and pH 6 caused 45% reduction in the SUVA values. The reduction is 27% for aluminum sulfate at the same pH and dosage. The SUVA reduction is 32 and 52% for ferric chloride and titanium sulfate coagulated samples, respectively. It was noted earlier that recent studies have questioned the reliability of using SUVA to predict reactivity of DOC in natural waters.

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

### Removal of Red River DOC fractions using optimized coagulation

Coagulated water using the optimized dose and pH conditions for the four coagulants was fractionated to determine the removal of specific DOC fractions. Ferric sulfate showed the greatest overall reduction of DOC with the final DOC concentration in coagulated water of 3.9 mg L$^{-1}$ (66% reduction), whereas ferric chloride was only able to reduce the DOC to 5.4 mg L$^{-1}$ (54% reduction).

All coagulants were found to have poor removal of the HPIN fraction with 58–65% of the total DOC remaining following coagulation being composed of the HPIN fraction (Tables 3 and 4). On the other hand, all coagulants were able to reduce the HPO fraction significantly, representing only 2–9% of the remaining DOC. Titanium sulfate was able to reduce the HPO fraction to 1.15 mg L$^{-1}$ while ferric chloride only reduced the HPO fraction to 1.78 mg L$^{-1}$. Titanium sulfate has been reported by Okour et al. (2009) to be able to reduce the SUVA value, suggesting the removal of DOC aromatic compounds believed to be the main THMs precursors. However, ferric chloride and ferric sulfate showed superior removal of the DOC and its HPOA

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The DOC composition of the Red River. Samples were collected on May 12, 2011 and fractionated on May 14, 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td>Concentration (mg L$^{-1}$)</td>
</tr>
<tr>
<td>Hydrophobic neutral (HPON)</td>
<td>1.42</td>
</tr>
<tr>
<td>Hydrophobic base (HPOB)</td>
<td>0.16</td>
</tr>
<tr>
<td>Hydrophobic acid (HPOA)</td>
<td>2.74</td>
</tr>
<tr>
<td>Hydrophilic base (HPIB)</td>
<td>1.32</td>
</tr>
<tr>
<td>Hydrophilic acid (HPIA)</td>
<td>0.93</td>
</tr>
<tr>
<td>Hydrophilic neutral (HPIN)</td>
<td>5.21</td>
</tr>
<tr>
<td>Total</td>
<td>11.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 1</th>
<th>General water quality of the Red River. Samples were taken on May 12, 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Unit</td>
</tr>
<tr>
<td>pH</td>
<td>pH unit</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg L$^{-1}$ CaCO$_3$</td>
</tr>
<tr>
<td>UV$_{254}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>DOC</td>
<td>mg L$^{-1}$</td>
</tr>
<tr>
<td>SUVA</td>
<td>m$^{-1}$ mg L$^{-1}$</td>
</tr>
</tbody>
</table>
fraction, believed to contain the highly reactive humic fraction, compared with titanium sulfate.

**Reduction of THMFP using coagulation**

THMFP of the water coagulated at the optimum conditions was determined for all four coagulants. The raw Red River water had a THMFP of 327.7 μg L⁻¹ and a specific THMFP of 27.8 μgTHM/mgDOC (Table 5). All four coagulants significantly reduced the THMFP with aluminum sulfate and ferric chloride showing the greatest reduction in THMFP to 42.8 and 45.2 μg L⁻¹, respectively. Ferric sulfate and titanium sulfate showed the least reduction in THMFP of 52.8 and 87.9 μg L⁻¹, respectively. Titanium

<table>
<thead>
<tr>
<th>Sample</th>
<th>HPON</th>
<th>HPOB</th>
<th>HPOA</th>
<th>HIPB</th>
<th>HIPA</th>
<th>HPIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>12.05</td>
<td>1.36</td>
<td>23.26</td>
<td>11.21</td>
<td>7.89</td>
<td>44.23</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>27.03</td>
<td>3.89</td>
<td>2.04</td>
<td>6.11</td>
<td>2.78</td>
<td>58.15</td>
</tr>
<tr>
<td>Aluminum sulfate</td>
<td>12.50</td>
<td>6.25</td>
<td>7.08</td>
<td>8.54</td>
<td>1.25</td>
<td>64.38</td>
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<tr>
<td>Ferric sulfate</td>
<td>27.41</td>
<td>0.51</td>
<td>5.58</td>
<td>3.04</td>
<td>10.91</td>
<td>52.54</td>
</tr>
<tr>
<td>Titanium sulfate</td>
<td>10.53</td>
<td>4.34</td>
<td>8.9</td>
<td>7.02</td>
<td>4.13</td>
<td>65.08</td>
</tr>
</tbody>
</table>

Table 3 | DOC fractions (shown as % DOC remaining) following coagulation using optimal conditions for total DOC removal
sulfate had more effect in removing HPO compared with HPI fractions, which is in agreement with the earlier study (Okour et al. 2009). However, titanium sulfate showed the poorest removal of the HPI fractions, reported by Goss & Gorczyca (2015) to be more reactive in the Red River. The lowest removal of HPOA and poor removal of HPI fractions may be the cause of the high specific THMFP for this coagulant.

On the other hand, the ferric chloride also showed poor removal of the HPI fraction, but the highest removal of the HPOA fraction, and this coagulant showed the lowest coagulated water specific THMFP of all coagulants tested. Of the four coagulants tested, ferric chloride and aluminum sulfate showed greatest reduction in THMFP and specific THMFP; however ferric sulfate and titanium sulfate showed the greater reduction in total DOC. Ferric sulfate showed the highest removal of DOC but it didn’t remove the HPOA and HPI fractions as effectively as other coagulants.

These results suggest that coagulation should be optimized for the removal of target DOC fractions forming THMs rather than the total DOC.

TABLE 5 | THMFP and specific THMFP for raw and coagulated water

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC (mg L⁻¹)</th>
<th>Chloroform (μg L⁻¹)</th>
<th>Bromoform</th>
<th>DBCM</th>
<th>BDCM</th>
<th>THMFP</th>
<th>Specific THMFP (μg THM/mg DOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>11.78</td>
<td>290</td>
<td>0</td>
<td>3.5</td>
<td>34.2</td>
<td>327.7</td>
<td>27.8</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>5.43</td>
<td>33.3</td>
<td>0</td>
<td>2.2</td>
<td>9.7</td>
<td>45.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Aluminum sulfate</td>
<td>4.47</td>
<td>28.5</td>
<td>0</td>
<td>3.0</td>
<td>11.3</td>
<td>42.8</td>
<td>9.6</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>3.94</td>
<td>39.5</td>
<td>0</td>
<td>2.5</td>
<td>10.9</td>
<td>52.8</td>
<td>13.4</td>
</tr>
<tr>
<td>Titanium sulfate</td>
<td>4.84</td>
<td>70.6</td>
<td>0</td>
<td>2.5</td>
<td>14.8</td>
<td>87.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

*BDCM – Bromodichloromethane. DBCM – Dibromochloromethane.

- Ferric chloride showed the highest removal (91%) of the HPOA DOC fraction.
- Ferric chloride had the highest THMFP reduction, from 327.7 to 42.8 μg L⁻¹.
- The isolation of DOC fractions and their removal using optimized coagulation showed that the HPOA fraction can be removed effectively whereas HPI fractions had the poorest removal.
- These results suggest that reduction of total DOC cannot guarantee THMFP reduction and chemical coagulation should be optimized to remove fractions of DOC which form THMs.

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