Reduction of DBP Formation Potential in Drinking Water through Forced Alkaline Conditions and Aeration

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LIN LIU

Enos C. Inniss, Ph.D., Thesis Supervisor

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The undersigned, appointed by the dean of the Graduate School, have examined the Thesis entitled

Reduction of DBP Formation Potential in Drinking Water through Forced Alkaline Conditions and Aeration

presented by Lin Liu,

candidate for the degree of Master of Science

and

hereby certify that, in their opinion, it is worthy of acceptance.

Enos Inniss, Ph.D.

Kathleen Trauth, Ph.D.

Yuyi Lin, Ph.D.
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Chapter 1.0 Introduction

1.1 DBPs and its health concern

One of the most crucial treatment processes for the production of potable drinking water is disinfection. Typhoid and cholera were commonly spread epidemics in United States over one hundred years ago. The disinfection process was the major step in reducing these epidemics, with the primary disinfectant used in the United States being chlorine, more specifically hypochlorous acid (HOCl). Chlorine has been successfully used to disinfect drinking water for more than a century. According to the United States Environmental Protection Agency (USEPA) as chlorine inactivates microbial pathogens, it also reacts with naturally-occurring materials in water to form undesired byproducts (USEPA 1998).

Extensive research has been published on improving our understanding of disinfection by-products (DBPs) formation mechanism and health concerns (Plewa et al. 2004) since the 1976 discovery of DBPs from chlorination of drinking water. An increase in the intake of DBPs in drinking water is associated with an increase in cancer risk, especially bladder and colorectal cancer, which is generally associated with trihalomethanes (THMs), one class of byproducts among DBPs (Cantor 1997, Villanueva et al. 2007). To reduce DBP intake and ultimately to reduce cancer risk for consumers, while maintaining effective disinfection to control pathogens, the USEPA currently uses the DBP Stage 2 rule to regulate four THMs and five haloacetic acids (HAAs).
1.2 Current issues with small scale systems

The term “Small scale system” used here is referring to those systems serving fewer than 10,000 customers (USEPA 1999). As the USEPA moves from DBP Stage 1 rule to the more stringent DBP Stage 2 rule, small systems have particular difficulties in complying with federal and state water quality requirements. These difficulties include operational constraints, financial constraints, technical assistance constraints, infrastructure constraints and regulatory constraints (Shih et al. 2006).

1.3 Solution for small scale system

Due to the above constraints, small systems are having troubles meeting their permit requirements to stay in compliance and typically have violations caused by high DBP concentrations. The goal of this research is to investigate treatment options which may assist small systems with their current compliance issues, with emphasis on demonstrating performance of certain types of source waters and treatment processes. These options include chemical enhancements of the precipitative softening to reduce DBP precursor concentrations and aeration to strip off formed DBPs.

1.3.1 Coagulants and dosage

After several visits to drinking water treatment plants, researchers tested the current coagulation dosage in the laboratory, and researchers noticed that the amount of coagulant added in the process was not optimized for DBP precursor removal. Therefore, developing a procedure for optimizing the dosage was the first task in this project. Particular emphasis was placed on enhanced lime softening using alum and ferric coagulants of the raw water, and the performance
of these combinations were compared with the coagulation processes currently used in selected treatment plants.

1.3.2 Aeration

Using compliance numbers from the Missouri Department of Natural Resources (MDNR) Drinking Water Watch (DWW MO 3.2) database (http://www.dnr.mo.gov/DWW/), it was determined that several treatment plants were out of compliance with the DBP rule due to higher percentage of chloroform (CHCl₃), which is one of the regulated THM species. Chloroform has its unique physical characteristic, high volatility, which means that it prefers to be in air rather than in water. Due to this unique property, a consideration of how to supply air into the water system to reduce DBPs was the second project task.
Chapter 2.0 Literature Review

2.1 DBP formation mechanism

To reduce pathogenic organisms to prevent waterborne disease, disinfection is used in the drinking water treatment process (Haas 1999). Several techniques for disinfection are practiced, including the use of potassium permanganate, chlorine, ozone, and ultraviolet light. Among these disinfection techniques, chlorine has been the most commonly used disinfectant. Chlorine has been popular because it is a very effective disinfectant (high potency), it is relatively easy to handle, it is cost effective, it is simple to dose, measure and control, and it has a reasonably prolonged residual (Freese and Nozaic 2004, Sadiq and Rodriguez 2004, Warton et al. 2006).

2.1.1 Chlorine chemistry

In drinking water treatment, chlorine is normally added in the form of compressed gas under pressure (equation 1). Sometimes chlorine is introduced in the form of either sodium hypochlorite (equation 2) or solid calcium hypochlorite (equation 3). However, these three forms are chemically equivalent. All of the forms will reach chemical equilibrium rapidly. This equilibrium exists between dissolved molecular gas and the dissociation products of hypochlorite compounds (Haas 1999).

\[
\begin{align*}
\text{Gaseous chlorine: } Cl_2 + H_2O &= H^+ + Cl^- + HOCl \\ 
\text{Sodium hypochlorite: } NaOCl + H_2O &= H_2O + Na^+ + OCl^- \\ 
\text{Calcium hypochlorite: } Ca(OCl)_2 + 2H_2O &= Ca^+ + OH^- + 2 HOCl
\end{align*}
\]

Once HOCl is formed, it react with natural organic matter (NOM) (Singer 1994), DBPs are generated in this step.
\[ \text{HOCl} + \text{Br}^- + \text{NOM} = \text{THMs and other halogenated DBPs} \] (4)

2.1.2 Types of DBPs formed

Using advanced analytical technologies, 600-700 chlorinated by-products have now been identified (Itoh et al. 2011). Numerous DBPs formed from chlorine still remain unknown (Reckhow and Singer 1984, Hua and Reckhow 2008). DBPs can be categorized into three classes of most representative types; Inorganic By-Products, Organic Oxygenated By-Products and Halogenated By-Products (Figure 2.1) (Mbonimpa 2007).

The halogenated organic byproduct group discussed here are mainly THMs and HAAs. These two abundant classes of DBPs are currently regulated under the Safe Drinking Water Act (SDWA). Table 2.1 lists chemical formulas for these DBPs.
### Table 2.1 Names and Chemical Formulas of Regulated THMs and HAAs (Poleneni 2013)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Abbreviation</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Trihalomethanes</strong></td>
<td>TTHM</td>
<td>----</td>
</tr>
<tr>
<td>Trihalomethane/Chloroform</td>
<td>TCM</td>
<td>CHCl3</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>BDCM</td>
<td>CHBrCl2</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>DBCM</td>
<td>CHBr2Cl1</td>
</tr>
<tr>
<td>Tribromomethane/Bromoform</td>
<td>TBM</td>
<td>CHBr3</td>
</tr>
<tr>
<td><strong>Sum of 5 Haloacetic Acids</strong></td>
<td>HAA5</td>
<td>----</td>
</tr>
<tr>
<td>Monochloroacetic Acid</td>
<td>MCAA</td>
<td>C1CH2COOH</td>
</tr>
<tr>
<td>Dichloroacetic Acid</td>
<td>DCAA</td>
<td>Cl2CHCOOH</td>
</tr>
<tr>
<td>Trichloroacetic Acid</td>
<td>TCAA</td>
<td>C13CCOOH</td>
</tr>
<tr>
<td>Monobromoacetic Acid</td>
<td>MBAA</td>
<td>BrCH2COOH</td>
</tr>
<tr>
<td>Dibromoacetic Acid</td>
<td>DBAA</td>
<td>Br2CHCOOH</td>
</tr>
</tbody>
</table>
2.1.3 Factors that influence DBP formation

Source water quality characteristics are the primary reasons for DBP formation. The most important factors to influence DBP formation in water quality parameters include pH, water temperature, concentration of organic precursor materials, and condition under which the disinfectant is used, such as the contact time, disinfectant dose, and residual disinfectant concentration (Liang and Singer 2003).

2.1.3.1 pH and contact time effects

Hua 2008 showed that the formation of THMs, trihaloacetic acids (THAAs), dihaloacetic acids (DHAAs) and Unknown Total Organic Halogen (UTOX) is a function of pH and reaction time during chlorination (Figure 2.2). THAAs are the sum of trichloro-, bromodichloro-, dibromochloro-, and tribromoacetic acids whereas DHAAs include dichloro-, bromochloro-, and dibromoacetic acids (Hua and Reckhow 2008).

Figure 2.2 Effect of reaction time and pH on THM, THAA and DHAA (Hua and Reckhow 2008)
Hua found that with increasing pH and contact time THM concentration also increases. Hua noted that the THM concentration was 148, 246, and 420 µg/L for pH 5, 7, and 10, respectively, for a 72-hr contact time. For that contact time range, the THM concentration at pH 10 was almost three times that of the THM concentration at pH 5. Differently with THM, THAA formation at pH 10 did not increase significantly with time. At pH 5 and pH 7, there was a significant increase as contact time increase. For DHAA formation, pH and contact time was also a factor. DHAA formation was similar for both pH 5 and pH 7. Formation at pH 10 was substantially higher than the rest. At 3 pH levels, DHAA concentration increased rapidly within several hours and slowed to a steady rate. (Hua and Reckhow 2008)

2.1.3.2 Temperature

Chloroform formation in drinking water increased with increasing water temperature (Fig 2.3). Moreover, higher water temperatures yielded faster formation of chloroform. The similar patterns to chloroform were observed for both DCAA and TCAA (Fig 2.4). Furthermore, at higher temperatures (30 to 35 °C) the concentration of THMs and HAAs has a large increase in a very short time (e.g., 0.5h) (Zhang et al. 2013).
Figure 2.3 The concentration variation profiles of chloroform at various temperature (Zhang et al. 2013)

Figure 2.4 The concentration profiles of DCAA and TCAA at various temperatures (Zhang et al. 2013)
2.1.3.3 Chlorine dosage

Hua (2008) found that DBPs formation increases with increasing chlorine dosage. Hua noted that when a chlorine dose of 2 mg/L and above was applied, THMs and HAAs increased nearly linearly with increasing chlorine dose (Fig 2.5). At chlorine doses of 0.5 to 2 mg/L, THMs increased more than HAAs. Hua concluded that at higher chlorine dose, NOM reacts with chlorine for the formation of smaller, more halogenated end products such as THMs and HAAs.

![Figure 2.5 Chlorine dose effects on DBP formation (Hua and Reckhow 2008)](image)

2.1.4 Health Effects Associated with DBPs

Since chloroform has been identified as an animal carcinogen by a National Cancer Institute study in 1976, further study on the potential carcinogenicity of chloroform and other halogenated organic compound formed in water treatment had been prompted (Gerwe 2003). The table below list USEPA cancer classification and $10^{-6}$ cancer risk for select DBPs. In the table, B2 refers to probable human carcinogen, C refers to possible human carcinogen and ND stands for not determined.
More and more recent studies recognize a possible link between DBP exposure and reproductive risks such as low birth weight, birth defects, miscarriage, and stillbirth (Scharfenaker 2001). A Swedish report indicated that the risk for cardiac defects in infants increased with increasing THM concentration in the drinking water (Cedergren et al. 2002). As the concern of DBPs affecting human health increases, it drives the DBP regulation requiring treatment plants to mediate DBP formation.

### 2.2 DBP regulation

In 1974, USEPA was required by SDWA to regulate drinking water by creating the national interim primary drinking water regulations (NIPDWR). The first interim standard was then promulgated in 1979, and the standard addressing DBPs was set for total trihalomethanes (USEPA 2001). Since then, there have been other rules enacted to improve the drinking water quality.
2.2.1 Stage 1 D/DBP Rule

Compared to 1979 TTHM standard, which set the Maximum Contaminant Level (MCL) at 100 µg/L, the Stage 1 Disinfectants and Disinfection By-Product (D/DBP) rule updated and lowered the MCL for TTHMs to 80 µg/L and established a new MCL for HAA5 at 60 µg/L (USEPA 2001). HAAs and THMs can be and often are formed in a slow reaction, where the reaction will continue occurring even after the “finished” (treated) water leaves the water treatment plants. Therefore, in the stage 1 DBP rule, 25% of samples were required to be taken at the location in the distribution system that approximates the maximum water residence time, and the remaining 75% at “representative locations” in the distribution system (USEPA 2007).

2.2.2 Stage 2 D/DBP Rule

The stage 2 D/DBP rule was built upon the stage 1 D/DBP rule. Stage 2 DBP rule provides more stringent protection from DBPs across the entire distribution system, and Stage 2 DBP is focusing on reduction of DBP peaks. An initial distribution system evaluation (IDSE) must be conducted to identify compliance monitoring locations that represent high TTHM and HAA5 levels for the Stage 2 DBP rule. Stage 1 DBP Rule used the system-wide running annual average (RAA). Stage 2 DBP Rule changed the way sampling results are averaged to determine compliance. Stage 2 DBP Rule is using on a locational running annual average (LRAA) (see Fig 2.6) (USEPA 2007).
2.2.3 Benefits

According to USEPA, Stage 2 DBPR may reduce bladder cancer on an average of 103 to 541 cases per year. Under Stage 2 DBPR, the benefits for reduction in bladder cancer are measured as willingness to pay (WTP) for avoiding lymphoma and bronchitis. The WTP estimates for lymphoma range from $233 million to $3,536 million, annualized over 25 years using a 3 percent discount rate. USEPA also stated that there might be un-quantified health related benefits. The un-quantified benefits are the potential reduction in adverse reproductive and developmental effects associated with DBP exposure.

2.3 Possible treatment approaches

Depending on the facility, DBP reduction can be approached in multiple ways, such as biofiltration, membrane filtration, and UV disinfection. Among all of the treatment strategies, this
study is mainly focused on enhanced coagulation, which occurs at in the front of the treatment process (Figure 2.7). Typically in a drinking water facility, raw water is introduced in coagulation basin first, in this basin a coagulant is added to treat water and a rapid mixer will strongly mix coagulant and water, the water then flows into flocculation basin where slow mix is provided for flocs to form. The water is then sent to a clarifier for those flocs to settle out. After the clarifier water has to pass through a filter for removal of suspended solids which did not settle, and then water is disinfected. Ideally this process should remove DBP precursors before the precursors come in contact with chlorine in the later processes to form DBPs. Another approach in this study will be focusing on an aeration process, where DBP precursors have already been in contact with chlorine and DBPs have been formed. Aeration may occur in the end of the water treatment process, likely in the clearwell, and volatile DBPs can be stripped out.

2.4 Enhanced coagulation

Coagulation and flocculation steps historically were primarily designed for particle and turbidity removal. They are now important steps in the treatment of water for the removal of particles and
natural organic matter. In January 2006, the USEPA finalized the acceptance of enhanced coagulation as an accepted treatment process to meet the Stage 2 DBPR (Bratby 2006). The goals desired for enhanced coagulation experiments include easily enforced regulatory criteria with minimal state transactional costs and significant total organic carbon (TOC) reduction without the addition of unreasonable amounts of coagulants.

USEPA defines enhanced coagulation as the term used to define the process of obtaining improved removal of DBPs by conventional treatment. The traditional coagulation process is focusing on turbidity removal, however, the enhanced coagulation process focus on optimized removal of DBP organic precursors (DeWolfe 2003). The removal of organic precursor has been characterized by total organic carbon (TOC), dissolved organic carbon (DOC), and UV absorbance at 254 nm wavelength (UV254) (Rizzo et al. 2005).

2.4.1 Aluminum Sulfate (Alum)\((\text{Al}_2(\text{SO}_4)_3\cdot 14\text{H}_2\text{O})\)

Alum is the most widely used coagulant, and has been in use for water treatment for several centuries. The specific gravity of liquid alum at 4.2% Al varies from approximately 1.32 at 15 °C to 1.33 at 40 °C. The corresponding viscosity varies from approximately 0.011 N•s/m² at 40 °C to 0.028 N•s/m² at 15 °C. In general, storage temperature for liquid alum is above 10 °C (Brathy 2006).

Assuming that the reactions of alum in water proceed to the electroneutral precipitate, Al(OH)_3, the reaction with alkaline compounds (either calcium bicarbonate in Equation 6, soda ash in Equation 7, or lime in Equation 8) which are present in water are expected to be one of the following (Brathy 2006):
\[
\text{Al}_2(\text{SO}_4)_3*14\text{H}_2\text{O} + 6\text{Ca(HCO}_3)_2 = 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 6\text{CO}_2 + 14\text{H}_2\text{O} \quad (6)
\]
\[
\text{Al}_2(\text{SO}_4)_3*14\text{H}_2\text{O} + 3\text{Na}_2\text{CO}_3 = 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 6\text{CO}_2 + 14\text{H}_2\text{O} \quad (7)
\]
\[
\text{Al}_2(\text{SO}_4)_3*14\text{H}_2\text{O} + 3\text{Ca(OH)}_2 = 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 14\text{H}_2\text{O} \quad (8)
\]
Jar test results (Bose and Reckhow 2007) showed that as alum dose increases DOC concentration decreases, as Figure 2.8 shows. The better DOC removal was also observed at a lower pH of 5.5 at all alum dosage levels. Flocs generated from alum are more positive at pH 5.5 than at 7 (Mazet et al. 1990). It is expected that more positive flocs interact more completely with negative charge functional groups on NOM molecules at pH 5.5. Study have also found that NOM removal with alum is most complete at around pH 5.5 (Qin et al. 2006).

Figure 2.8 Alum dose and DOC removal. *pH at 5.5; □ pH at 7.0 (Bose and Reckhow 2007)

**2.4.2 Ferric Chloride (FeCl₃)**

The reaction between ferric chloride with alkalinity in water (either with calcium bicarbonate in Equation 9 or with lime in Equation 10) yields primarily in insoluble ferric hydroxide (Brathy 2006):

\[
2\text{FeCl}_3 + 3\text{Ca(HCO}_3)_2 = 2\text{Fe(OH)}_3 + 3\text{CaCl}_2 + 6\text{CO}_2 \quad (9)
\]
\[
2\text{FeCl}_3 + 3\text{Ca(OH)}_2 = 2\text{Fe(OH)}_3 + 3\text{CaCl}_2 \quad (10)
\]
The jar tests (Childress and Vrijenhoek 1999) showed a result of increases in TOC and UV reduction as they increased the dose of FeCl$_3$ (Fig 2.9). Because the optimal pH for NOM removal is around 5 for ferric chloride (Hall and Packham 1965), Childress (1999) lowered the pH to 5.5 to enhance the removal of TOC and UV254. Figure 2.9 shows the maximum removals of TOC and UV at pH 5.5 are 48 and 53%. At lower FeCl$_3$ doses (<8mg/L), the enhanced removal at pH 5.5 is attributed to formation of insoluble ferric-humate complexes (Cheng et al. 1995). At a dosage level greater than 16 mg/l, the NOM adsorption is increased which increased ferric hydroxide precipitates (Cheng et al. 1995).

![Figure 2.9 Ferric chloride dose on reduction of TOC and UV on Colorado River Water (CRW)](Childress and Vrijenhoek 1999)

### 2.4.3 Poly-aluminum chloride (PACl)

Researchers (Iriarte-Velasco et al. 2007) found that the optimum pH of PACl for his work is in the range of 6.0 to 7.0 units. The optimal dosage of PACl is about 40 mg/L. Any additional dosage does not result in any notable improvement of water quality. As the dose of PACl increased from 40 to 60 mg/L, UV and THMFP removal decreased from 69.3 to 64.7 percent, and 53.7 to 49.9 percent, respectively. This trend might due to colloid re-stabilization phenomena. From Alvarez-Uriarte’s results in 2007, the re-stabilization can occur when PACl is used.
2.5 Enhanced softening

Softening is the process primarily used by many facilities in the United States for removal of hardness from drinking water by precipitating calcium using lime (Ca(OH)\textsubscript{2}). During lime softening, calcium carbonate and magnesium hydroxide are precipitated, and it leads to a significant reduction of hardness in drinking water. After the first discovery of DBPs in the 1970s, many studies (Liao and Randtke 1985, Thompson et al. 1997) have demonstrated the potential for softening to be enhanced for removal of natural organic matter by co-precipitation with or adsorption onto the calcium and magnesium precipitates. This approach to improve NOM removal during the softening process substantially increases the amount of lime (in some other case with additional soda ash or MgCl\textsubscript{2}) added into the system.

Experiments (Liao and Randtke 1985) showed that instead of direct precipitation as a calcium fulvate the removal of fulvic acid occurs mainly by adsorption onto the precipitate surface. In the experiment, results suggested that only less than 2% of fulvic acid removal was by direct precipitation. In contrast, Randtke and co-workers (1982) found that up to 50% of peat fulvic acid removal was by direct precipitation under alkaline condition where pH is greater than 11 and in the presence of high soluble calcium concentrations. The degree of calcium fulvate precipitation increased with increasing pH and increasing soluble calcium. The degree of NOM adsorption onto CaCO\textsubscript{3} is affected by the presence of Ca\textsuperscript{2+}. Liao and Randtke (1985) found that at a higher pH (e.g. pH 8.9) the adsorption on to preformed calcite crystals was negligible. However, at a higher pH level (>10.8) the adsorption of up to 20% was observed as the Ca\textsuperscript{2+} concentration increased.
Many studies indicated that magnesium enhances NOM removal (Thompson et al, 1997; Liao and Randtke, 1985). Another study showed that Mg(OH)₂ had a greater adsorption capacity (Gerwe, 2003). Researchers demonstrated the formation of a mixed Mg-CaCO₃ precipitate in the pH range before Mg(OH)₂ precipitation suggest that magnesium precipitates may have an important role in NOM removal during softening.

During an enhanced softening process (illustrated by equations 11-14) (Davis, 2011), NOM removal is accomplished by some combination of adsorption onto the calcium and magnesium solids formed (calcium carbonate or magnesium hydroxide), and direct precipitation as a calcium or magnesium humate or fulvate (Liao and Randtke, 1985). The surface characteristics are more likely have significant impacts on the mechanism for and the degree of NOM removal that can be achieved (Russell et al, 2009).

\[
\begin{align*}
\text{CO}_2 + \text{Ca(OH)}_2 &= \text{CaCO}_3(s) + \text{H}_2\text{O} \\
\text{Ca}^2+ + 2\text{HCO}_3^- + \text{Ca(OH)}_2 &= 2\text{CaCO}_3(s) + 2\text{H}_2\text{O} \\
\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{Ca(OH)}_2 &= \text{MgCO}_3 + \text{CaCO}_3(s) + 2\text{H}_2\text{O} \\
\text{Mg}^{2+} + \text{CO}_3^{2-} + \text{Ca(OH)}_2 &= \text{Mg(OH)}_2(s) + \text{CaCO}_3(s)
\end{align*}
\]

2.5.1 Surface area

In the study (Russell et al, 2009), it was found that with a low lime dose, CaCO₃ precipitates formed exhibited the rhombohedral shape characteristic of calcite (Fig 2.8 A). On the other hand, there are more edges observed at a higher lime dosage (Fig 2.10 C). In the image C the clustered calcite crystals may be attributed to which un-dissolved lime serves as a “nucleus” for calcite growth to form the CaCO₃ precipitation. Research showed that with magnesium incorporated, the CaCO₃ morphology was more pronounced at the higher lime dose (Fig 2.10 C and D). With no Mg²⁺, the CaCO₃ particles in image C exhibit a rhombohedral shape. On the other side, in the
presence of Mg$^{2+}$, the particles became highly elongated. At the higher pH, the greater number of edges may have enhanced the capacity for magnesium incorporation into crystal structure, which results into a more pronounced effect on the morphology. The precipitates with high surface area was anticipated to correlate to a greater NOM adsorption affinity.

Figure 2.10 Effect of magnesium on CaCO3 morphology (Russell et al. 2009)

2.5.2 Surface Charge

Experiments to show zeta potential for each species were done for lime softening (Russell et al. 2009). The zeta potential results for precipitates formed in the Ca-only, Mg-only and Ca+Mg are shown in Figure 2.11. At a low lime does (lower pH) calcium carbonate precipitates exhibited a lightly positive zeta potential when there is only calcium presented in the experiment. The zeta
potential switched to a negative value when lime dose increased at the range of pH of 9.0 to 10.5, and as the lime dose kept increasing from 10.5 to 11.6, the zeta potential moved to a more positive value. The zeta potential of Mg(OH)$_2$ particles increased significantly as pH value increased. However, the most of the pH range Mg(OH)$_2$ particles showed a negative zeta potential. In the presence of magnesium, as softening pH increases, the surface charge zeta potential tends to have a very large positive charge compare to Ca-only and Mg-only experiments. These results of positive surface charge indicated favorable conditions for removing negatively charged organic matter during softening.

Coagulation happens at the front of a treatment process to reduce DBP precursors. The reaction happens before DBP precursors been contacted with chlorine to form DBP. Once the DBP precursors which was unsuccessful removed during the coagulation process or only partially removed at the front of a treatment process has been contact with chlorine, it produces DBPs in
the end of treatment process. Then this where one might introduce an aeration step into the
treatment train. Aeration can strip out some of the very volatile DBP compounds, such as
chloroform which in some of facility has been considered as a major contribution to THMs,
ultimately to DBPs.

2.6 DBP reduction by aeration

Four of regulated THM compounds, chloroform, bromodichloromethane (DBCM),
dibromochloromethane (DBCM) and bromoform, are relatively volatile, especially chloroform.
Due to the volatility of THMs, THMs can be easily removed by exposing THMs to air. These
volatile organic compounds (VOCs) tend to reach saturation equilibrium in air. When water with
THMs is exposed to air, the VOCs move freely from water to the air until equilibrium is
achieved or the air is saturated with the compound moving to the air phase. The state of
equilibrium for compounds removed from water by aeration is defined by Henry’s law (Equation
5) (Shambaugh and Posse 2010).

\[ H = \frac{A_{\text{air}}}{A_{\text{aq}}} \]  \hspace{1cm} (15)

Here, \( H \) is Henry Law’s constant and \( A \) is activity of the compound in equilibrium either in air or
water. The larger the Henry’s constant, the more freely the compound moves between two
phases, and the better the reduction of THMs. Table 2.2 provides Henry’s constant for each of
the regulated DBP compound (Sherant 2008).
Table 2.2 Physical and chemical properties of THMs and HAAs (Sherant 2008).

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight</th>
<th>Boiling Point (°C)</th>
<th>Experimental Henry's Law Constant (25°C)</th>
<th>Experimental Reference Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>119.4</td>
<td>61.1</td>
<td>$1.72 \times 10^1$</td>
<td>Hand et al. (1999)</td>
</tr>
<tr>
<td>BDCM</td>
<td>163.8</td>
<td>90</td>
<td>$9.04 \times 10^2$</td>
<td>Warner et al. (1987)</td>
</tr>
<tr>
<td>DBCM</td>
<td>208.3</td>
<td>120</td>
<td>$4.83 \times 10^2$</td>
<td>Hand et al. (1999)</td>
</tr>
<tr>
<td>BF</td>
<td>252.7</td>
<td>149.1</td>
<td>$2.19 \times 10^3$</td>
<td>Mutz &amp; Roberts (1987)</td>
</tr>
<tr>
<td>MCAA</td>
<td>94.5</td>
<td>189.3</td>
<td>$3.78 \times 10^7$</td>
<td>Bowden et al. (1998)</td>
</tr>
<tr>
<td>DCAA</td>
<td>128.9</td>
<td>194</td>
<td>$3.43 \times 10^7$</td>
<td>Bowden et al. (1998)</td>
</tr>
<tr>
<td>TCAA</td>
<td>163.4</td>
<td>196.5</td>
<td>$5.53 \times 10^7$</td>
<td>Bowden et al. (1998)</td>
</tr>
<tr>
<td>MBA</td>
<td>139.0</td>
<td>208</td>
<td>$2.67 \times 10^7$</td>
<td>Bowden et al. (1998)</td>
</tr>
<tr>
<td>DBAA</td>
<td>217.9</td>
<td>233</td>
<td>$1.81 \times 10^7$</td>
<td>Bowden et al. (1998)</td>
</tr>
</tbody>
</table>

Aeration is the process of bringing water and air into close contact in order to remove these harmful compounds from water. Aeration generally falls into two categories. One either introduces air to the water or water to the air. The water into air type is generally designed for small water droplet travel in air. The air into water type is designed for fine air bubble travelling from the bottom of water to top.

**2.6.1 Water into air types**

A cascade aerator (see Fig 2.12) consists of a series of stairs which allows water to fall from stair to stair driven by gravity. As water traveling from one stair layer to another there is a splash zone created, and at the splash zone, aeration is accomplished.
Spray aerators (see Fig 2.13) spray fine water droplet by nozzles. The fine water droplets and its surrounding air creates the air-water interface necessary for the contaminated to transfer from water to air.

Packed tower aerator: the contaminated raw water is supplied at the top of the aerator, and the air is introduced from the bottom. The packing material is placed in the middle of the aerator to increase the water-air contact surface area when water passes by.

2.6.2 Air into water type

Diffused aeration (see Fig 2.14) is one of the common aeration type falling into this catalog. A membrane is placed in the bottom, and air is supplied into the piping to the membrane, fine
bubble are created by the membrane, and the air bubble travels from the bottom to the top. As it travels in water, water-air interface is created to remove contaminants.

![Diagram of Diffuse Aerator](image)

Figure 2.14 Diffuse Aerator (USEPA 2015)

For both types of aeration, temperature plays a role in the efficiency of the system. Because Henry’s constants are temperature dependent, with increasing temperature, the THMs are more free to move between water and air (Shambaugh and Posse 2010). Sherant (2008) confirmed this temperature effect in her laboratory study. Sherant used a 250 gal cylinder tank, and used 200 gallons of tap water spiked with TTHM and HAA5 standards filled into the tank. The tank was aerated for 6 hours using air from an air hose. Sherant set the air flow at 0.03 m$^3$/min and aerated the water in three different temperatures increased from 14 °C, 17 °C to 21 °C. The results showed (see Fig 2.15) with higher temperature the greater the chloroform removal.
In the same experimental set up, Sherant tested how different air flow impacts the removal of THMs from water. Sherant set the temperature at 21 °C, and the air flow used at 0.03 m³/min, 0.09 m³/min and 0.14 m³/min. The results showed that at 0.14 m³/min have a chloroform removal of 93%, where 0.03 m³/min and 0.09 m³/min air flow have a removal of 57% and 75%.

For the water into air type, the water travel distance matters the VOCs reduction. Researchers (Wood et al. 1981) tested VOCs reduction by using spray head. One of the tests Wood did was comparison of distance effects on VOCs reduction. Wood used the same spray head spray water downward at a height of 8 feet compared spray upward at the height of 8 feet which is approximately a 24 feet of water travel distance. In each of these tests, the flow rate and energy input is set the same. The results showed that spray downward for a water travel distance of 8 feet reached a VOCs reduction of 77%. On the other hand, the spray upward which results in a
water travel distance of 24 feet had a reduction 99% on VOCs. It became apparent that the droplet travel distance was the controlling factor in the removal rate.

In the same study, Wood (1981) also tested the water droplet sizes affecting VOC removal. One of the tests Wood did was set the water pressure at the same and the same average droplet travel distance, the only major difference was in the droplet size. From all of the data, Wood concluded that it appears that in general a small droplet is desirable for VOCs reduction.

Chlorine residual concern was raised in aeration process. Although chlorine can be removed through the aeration process, the Henry’s Constant of chlorine is 0.104 which is less than chloroform 0.17. Henry’s constant comparison see Fig 2.16. When chlorine added into water, it undergoes a hydrolysis process to form hypochlorous acid and hydrochloric acid.

\[
\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}
\]  

(16)

Hypochlorous acid is a weak acid, and it further dissociates into the hypochlorite ion and the hydrogen ions.

\[
\text{HOCl} = \text{H}^+ + \text{OCl}^-
\]  

(17)

Both hypochlorous acid and hypochlorite have much lower Henry’s constants (4.52 \times 10^{-5} and 5.31 \times 10^{-18} respectively) compared to chlorine and chloroform. The mixture of HOCl and OCl\(^{-}\) in the water give the chlorine residual in the water a lower Henry’s law constant and keep the chlorine at equilibrium in the water without the tendency to move to the air (Shambaugh and Posse 2010).
In addition, Shambaugh (2010) showed a reduction of 0.3 mg/L in chlorine after aeration. However, Shambaugh and Posse thought that the reduction might due to a normal chlorine decay during 1.7 days of his pilot study. Later on, Shambaugh and Posse conducted a 2 day bulk chlorine decay rate test in non-aerated water. The initial chlorine decay samples collected indicated a chlorine decay of approximately 80% during 2 days. This decay rate in no-aerated water is greater than the chlorine reduction rate that Shambaugh observed in the pilot test during 1.7 days. Therefore, the aeration treatment did not result in significant chlorine decay in addition to that which would have occurred over the same detention time without aeration (Shambaugh and Posse 2010).

2.7 Research directions

As USEPA moves to more stringent stage 2 regulations, small drinking water systems tend to have problems meeting the requirement for carcinogen compounds, especially THMs which pulls many facilities out of compliance.
From the literature, there are ways to solve this issue. Methods, such as, enhanced lime softening and enhanced coagulation, are designed for the front process of a treatment plant to remove THM precursors through lowering available NOM for chlorine reacting with to form harmful THM. Methods such as aeration are designed for the end of treatment process, where harmful THMs have already formed. Aeration is designed to strip out those volatile THM compounds to lower the TTHM.

This research is focusing on how to solve the issues small facilities are facing. In this study, several coagulants will be tested for those waters by using literature suggested pH condition and dosage to compare with the method which the facilities are using currently. Some other facilities have issue of high chloroform in THMs. In this study, aeration is planned to strip out those chloroforms due to its physical condition-volatility.
Chapter 3.0 Material and Methods

3.1 Source raw water collection and storage

The raw water for coagulation tests was taken from three source water locations. These locations are all located in the northern part of Missouri (MO). The raw waters were directly taken from water treatment plants prior to any significant treatment. The only treatment was done for the raw water before sampling is algae control by adding CuSO₄. The raw water was surface water either from local lakes or from the Missouri river with an initial TOC varies from 5 mg/L to 14 mg/L and alkalinity of around 100 mg/L.

The “raw water” for aeration tests was taken from the Columbia, MO water treatment plant. The “raw water” here refers to finish water in the plant. The water was already treated with lime and disinfected with chlorine. The ideal raw water for aeration tests are those waters high in chloroform. Columbia “raw water” has a moderate chloroform level, so it is a good “worst case scenario” water for bench scale testing.

All the raw waters were stored in plastic carboys at 4°C till used. All the tests were performed within 1 week after raw water collection.

3.2 Materials

The reagents are used in testing are all analytical grade, except those otherwise specified. Lime used for the jar test was from one of the partner facilities which practices lime softening. Polyaluminum chloride (PACl) mixed with CuSO₄ was taken from another partner facility which practices traditional coagulation-flocculation for turbidity removal.
3.3 Analytical procedure

Jar testing (Phipps & Bird; http://www.phippsbird.com/procedure.html) ASTM D2035-08

Jar tests (Figure 3.1) used to simulate the coagulation-flocculation-sedimentation processes at the full-scale system and are conducted in 2 L square beakers at room temperature (20-25°C). For each jar, beakers were filled with 1L of raw water. Depending on the purpose of the jar tests, each jar received different types of chemicals or coagulants. To run the jar test, the rapid mix was set for 1 min at 100 rpm, flocculation for 30 min at 35 rpm, and settling for 30 min. At the end of setting, water samples were collected and analyzed for TOC, UV254, pH, and THMs concentration.

TOC (Total Organic Carbon) Analysis of Precursors
(Shimadzu TOC-V cpn) (EPA Method 415.3)

In order to evaluate the organic matter removed by the coagulation process, the water samples were analyzed by TOC analyzer (Figure 3.2). Both raw water and treated water were analyzed by TOC, so the amount of organics removed can be obtained. The TOC sample was prepared by adding 15 mL of treated water to TOC vials, and the vials were sealed with by Para-film.
To operate the TOC analyzer, the first step is connecting the analyzer with the computer. Turn on the gas, choose a method, and then fill up the sample information, and put all the samples in the sample plate. Once everything is ready, then click start. The TOC analyzer used for testing is shown below.

The sample inserted will be acidified with 2M HCl, and purged with zero air to ensure no inorganic carbon been analyzed in the later on process. After the pretreatment, the sample is sent to the furnace. Under high temperature, the sample is burned and presented in the form of CO₂ in furnace. A detector then measures CO2 to quantify the amount of carbon within the sample.

![Figure 3.2 Shimadzu TOC-Vcpn instrument with auto sampler used to measure NPOC UV254 (Varian Cary 50 Conc)(UV-Visible Light Spectrometer Analysis of Precursors; EPA Method 415.3)](image)

In order to understand how much aromatic matter was removed by coagulation process, the samples went through UV testing (Figure 3.3), because aromatic bonds absorb ultra violet light. Therefore, the absorbance of raw water and treated water was compared using UV to gain the information on the reduction rate of aromatic matter.
First step to operate the Cary 50 instrument is open the software “simple read”, click set up to adjust the wavelength to 254nm. Use DI water as a blank to zero the reading, then each sample was read by the instrument three times to get the mean value. All of the sample to test by UV must be filtered by a 45 micrometer filter to remove any particles which could affect the readings. The sample cuvettes used are silico-cuvettes. Within the instrument, a light at wavelength of 254nm was emitted from the light source, this light passed through the cuvette, with some amount of light being absorbed by the sample, and the rest of light go through the sample and reached to the detector. This absorbance is expressed as transmittance showing up in the computer monitor.

![Varian Cary 50 Conc UV-Visible Spectrometer used](image)

**pH Analysis**

At beginning and end of each test the pH values were measured for reference. Prior to using the Thermo Orion model 410 pH meter (Figure 3.4), a calibration solution was made by dissolving a
pack of standard powder into 50 ml of DI water. The pH electrode was then inserted into the solution to calibrate the pH meter. All the pH readings then were taken by pH meter.

Figure 3.4 Thermo Orion model 410 pH meter used for testing pH

**Colorimetry used for analysis of various water quality parameters (Hach Methods)**

**Description:**

- **Chlorine Residual Method 8021**

Chlorine is monitored with the aeration method. Concerns, such as that aeration would strip out chlorine leading to a less effective disinfection process, were raised. Monitoring chlorine would verify how chlorine changes with the aeration.
Titration used for analysis of testing Alkalinity

Description:

Alkalinity of a water is its acid-neutralizing capacity. As coagulant added into the system, alkalinity would be consumed. Following the USEPA Buret Titration Method (HACH 8221 Standard Method 2320B), Phenolphthalein indicator was added to 50ml of water sample. If the water turns to pink color, titrate the sample by 0.02 N H₂SO₄ to colorless which means the alkalinity is hydroxide alkalinity. Then add Bromcresol Green-Methyl Red indicator to water sample and titrate the sample by 0.02 N H₂SO₄ to light pink. If the water stays colorless after adding phenolphthalein, meaning that the alkalinity is bicarbonate alkalinity, Bromcresol Green-Methyl Red indicator is also required to be added to water sample, and titrated to light pink.
GC (Gas Chromatograph) Analysis of Disinfection By-Products

Compounds separated by the Varian 3800 GC column need to be detected. For total trihalomethane (TTHM) analysis (EPA Method 524.2), the detector used is a Saturn 2000 mass spectrometer (MS) (Figure 3.7). The auto sampler (Tekmar AquaTek 70 Vial Autosampler) takes samples from the sample tray, the samples are air stripped by N₂ gas to extract the volatile THM compounds in a purge and trap concentrator, and the THM compounds are then condensed in the same unit and sent to the GC. In the GC, the THM are trapped in the column, by heating the column the THM compound are released in a timed fashion and carried out to the MS for detection.
Diffused Aeration

The bench scale aeration test (Figure 3.8) was designed to address the high chloroform issue. A 4 Liter glass tank was used in this test. A fine bubble diffuser in the bottom of the tank produces air bubbles to assist with the transfer of chloroform from liquid to air. An air flow meter on the side monitored the rate of air flow. The airflow meter has a range of 0 to 5 L/min. The airflow used in the experiments were 1, 2 and 3 L/min; the duration for aeration were 10, 20 and 40 minutes. A compressed air motor provided air into the system.
3.4 Enhanced Coagulation

Four types of chemicals are used to treat the same water. The chemicals used can be seen in the table below. Different dosages of chemical are used for each jar in the jar test to find the optimal dosage. The treated water was filtered with 0.45 um filter, the TOC and UV254 tests were followed to indicate the best dosages for reduction of DBP precursors.

For PACl, the raw water pH was adjusted to pH 6.0 prior to the addition of PACl. The dosage for the control jar was 70 mg/L, and other jars were 50, 60, 80, 90 and 100 mg/L. The pH was adjusted to 6.5 prior to the addition of PACs. The control jar dosage was 11.6 mL, with the rest of jars at 7, 9, 15, 20 and 25 mL. Lime was added until the jars had a pH of 9.5, 10.0, 10.5, 11.0 and 11.5, respectively. FeCl₃ was added at dosages of 15, 20, 26, 32 and 38 mg/L, and the pH
was adjusted to 5.0 prior to adding FeCl₃. The pH was adjusted to 6.0 prior to the addition of alum, and the dosages was 62, 86, 111, 136 and 160 mg/L.

Table 3.1 Scheme for Coagulation Testing

<table>
<thead>
<tr>
<th>Jar #</th>
<th>PACl (mg/L)</th>
<th>Lime to pH</th>
<th>FeCl₃ (mg/L)</th>
<th>Alum (mg/L)</th>
<th>TOC (mg/L)</th>
<th>UV254 (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>week 1</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.1 Enhanced Softening at different pH

Six beakers constitutes one set of a jar test. The first beaker in every set was used as a control, which is mimics the coagulation process in our partner facility. The rest of the beakers was adjusted with lime to certain pH values. pH increments scale of 0.5 were used. For example, if the pH value starts at 9.0, the next beaker will have a pH of 9.5. The jars were then started with 1 min of rapid mix at 100 rpm, followed by 30 min of slow mix at 35 rpm. The beakers then settled for 30 min.

The expectation for enhanced softening is that the more lime that is added, the more precipitation that is generated in the jar test, the more NOM has been adsorbed in the surface of the precipitation, and the greater the reduction on TOC and UV254. With pH increment scale of 0.5, the reduction performance for each pH unit will be observed, and it is easier to obtain the pH value associated with the best reduction.
3.4.2 Enhanced Softening with additional chemicals

MgCl$_2$ and Na$_2$CO$_3$ were added to each beaker after it was dosed with lime to a specified pH, but the control beaker is not dosed with MgCl$_2$ or Na$_2$CO$_3$. The beakers then followed with rapid mix, slow mix and settling procedure as in section 3.4.1.

Additional chemicals assist the lime precipitation, As Na$_2$CO$_3$ introduced into water, it results in more CaCO$_3$ formation. On the same hand, as Mg$^{2+}$ introduced into the system, there will be additional precipitates of Mg(OH)$_2$ and more Mg-Ca precipitation. Therefore, at the same dosage of lime, with additional chemicals would expected to have a greater TOC and UV reduction.

3.4.3 Other coagulants

PACl, alum and FeCl$_3$ are also used to test the performance of coagulation. The jar setting is the same as section 3.4.1. For each of these three chemicals, different dosage are used to find the optimize dosage for coagulation.

3.5 Aeration

To achieve a good performance through aeration, several variables matter. The variables include, contact time, air flow rate, temperature, air bubble size. In a water treatment plant, the best place for aeration is a tower. To save energy, the sequence aeration should be implemented. Because some of the treatment facilities don’t have an aeration tower, the ideal place then became to clearwell. In this bench scale, the above concerns as well as chlorine residue concern were designed in the experiment accordingly.
3.5.1 Vary contact time

The glass chamber was filled with 3L of raw water ready for aeration. The airflow rate was set at 1 L/min. The test was performed for different time intervals of 10 min, 20 min, and 40 min (Table 3.2). At the end of each time period, three DBPs samples and chlorine samples were taken to compare with the DBP and chlorine readings for raw water.

3.5.2 Vary airflow rate

The glass chamber was filled with 3L of raw water ready for aeration. The contact time was set at 10 min. With the different air flows used in this case. The flow rates were 1L/min, 2L/min and 3L/min (Table 3.2). At the end of the each test, three DBPs samples and chlorine samples were taken to compare with the DBP and chlorine reading for raw water.

3.5.3 THMs 5 days formation

The water was collected on day 1, and left at room temperature for 2 days for DBP formation. On day three, the water was aerated for 10 min at an airflow rate of 1L/min (Table 3.3). The water was then stored at room temperature for future monitoring of DBP formation and chlorine residue.

3.5.4 Sequenced aeration

The water was collected on day 1, and then left at room temperature for 2 days for DBP formation. On day three, the water was aerated for 20 min at an airflow rate of 2L/min, with the same aeration repeated on day 4 and day 5.
Table 3.2 Aeration for very time and flow

<table>
<thead>
<tr>
<th>Aeration</th>
<th>Very Time (min)</th>
<th>Very Flow (L/min)</th>
<th>THMs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.3 Aeration for 5 days and sequent aeration

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>1L/min</td>
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<td>10 min</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>N/A</td>
<td></td>
<td>N/A</td>
</tr>
</tbody>
</table>

2L/min | 2L/min | 2L/min | 20 min | 20 min | 20 min
Chapter 4.0 Preliminary Study

4.1 Enhanced coagulation and softening

The raw waters for enhanced coagulation and softening tests were from the three partner facilities, which are the city A drinking water plant, the city B drinking water plant and city C drinking water plant. A preliminary study was conducted before any coagulation test to have a better understanding of each system. The study included treatment process understanding and water quality testing from each treatment process. The enhanced coagulation and softening experiments were performed on the raw water from each of the facilities.

4.1.1 System Process

Figure 4.1 is illustrates the treatment process of the City A drinking water treatment facility. The process starts at the intake structure (located on Lake Viking). The influent pump station then moves water and sodium permanganate to the mechanical treatment process. The old pre-sedimentation ponds are typically bypassed. The process units used are Neptune Microfloc Waterboy units (2) which include rapid mix followed by flocculation, sedimentation tank, and granular filtration at the start of which a coagulant (polyaluminum chloride, PACI) is added, followed by membrane filtration (Koch) units and granular activated carbon (GAC, 4) units, after which chlorine and polyphosphate are added, through a clearwell (285,000 gallon, baffled, 4-bay), and finally through the high service pumps to the standpipe and elevated storage tank in the distribution system.
Figure 4.2 is an illustration of the treatment process at the City B drinking water treatment facility. The process starts at the intake structure (located in the lake). The influent pump station then moves water and sodium permanganate to the mechanical treatment process. The process units used are rapid mix of the coagulant and a polymer followed by a flocculator-clarifier tank, a mixing basin (where pH adjustment may be performed) followed by chlorine dioxide addition, two (2) plain sedimentation tanks, four (4) granular filtration units, after which chlorine (HOCl) is added, through a clearwell (85,000 gallon), and finally through the high service pumps to the distribution system.
Figure 4.3 is an illustration of the treatment process of the City C drinking water treatment facility. The process starts at the intake structure (located in Lake Elizabeth). The influent pump station then moves water from the pre-sedimentation basin to the mechanical treatment process. Sodium permanganate is added before entering the process. The process units used include the first-stage rapid mix, flocculation, and sedimentation, where a coagulant (polyaluminum chloride sulfate, PACS) is added, at the start of the second-stage rapid mix, flocculation, and sedimentation process chlorine dioxide is added, and then caustic soda is added just before granular filtration for pH adjustment, after filtration both chlorine and polyphosphate are added. Contact time is achieved through a clearwell (112,540 gallon). The high service pumps either move the water to the either Grant City or to the Stanberry distribution systems.
4.1.2 Preliminary test results for coagulation

For each visit of the facility, water samples were taken at the end of each process unit including raw water to understand how each unit contributes to the overall performance. Each percent reduction is compared with raw water, and the equation is (raw - #)/raw *100.

Table 4.1 Preliminary test for the City A drinking water plant

<table>
<thead>
<tr>
<th>Samples</th>
<th>UV254 (1/cm)</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>0.1201</td>
<td>5.946</td>
</tr>
<tr>
<td>before settling tube</td>
<td>0.0639</td>
<td>5.087</td>
</tr>
<tr>
<td>after settling tube</td>
<td>0.0621</td>
<td>4.646</td>
</tr>
<tr>
<td>after media filter</td>
<td>0.0659</td>
<td>4.898</td>
</tr>
<tr>
<td>membrane filter</td>
<td>0.0575</td>
<td>4.707</td>
</tr>
<tr>
<td>after GAC</td>
<td>0.0630</td>
<td>4.776</td>
</tr>
<tr>
<td>Stand pip tank</td>
<td>0.0464</td>
<td>4.081</td>
</tr>
</tbody>
</table>
From above figure, it shows almost the majority of TOC and UV reduction happens at coagulation process, which PACl has been added in this process. The TOC and UV reduction in coagulation is 14% and 47% respectively. When water went through Granular Activated Carbon there were a significant reduction on both UV and TOC. However, the reduction amount in mg/L or 1/cm is still smaller than the reduction amount in coagulation process.

Table 4.2 Preliminary test for the City B drinking water plant

<table>
<thead>
<tr>
<th>Samples</th>
<th>UV254 (1/cm)</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>0.1817</td>
<td>9.227</td>
</tr>
<tr>
<td>Primary</td>
<td>0.1190</td>
<td>7.335</td>
</tr>
<tr>
<td>1st settling</td>
<td>0.0936</td>
<td>7.486</td>
</tr>
<tr>
<td>2nd settling</td>
<td>0.0927</td>
<td>7.846</td>
</tr>
<tr>
<td>Clearwell</td>
<td>0.0851</td>
<td>6.903</td>
</tr>
</tbody>
</table>
The water quality for the City B is very similar to the City A. The majority of reduction happens at the coagulation process, and then a significant reduction happens after filter.

Table 4.3 Preliminary test for the City C drinking water plant

<table>
<thead>
<tr>
<th>Samples</th>
<th>UV254 (1/cm)</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw</td>
<td>0.2051</td>
<td>11.230</td>
</tr>
<tr>
<td>raw + NaMnO₄</td>
<td>0.1424</td>
<td>10.370</td>
</tr>
<tr>
<td>1st mix</td>
<td>0.1480</td>
<td>10.080</td>
</tr>
<tr>
<td>2nd mix</td>
<td>0.0931</td>
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<td>top filter</td>
<td>0.0627</td>
<td>6.699</td>
</tr>
<tr>
<td>bottom filter</td>
<td>0.0624</td>
<td>6.885</td>
</tr>
</tbody>
</table>
4.2 Preliminary Study for aeration

Five years of compliance data of our partner facility was taken from the Missouri Department of Natural Resources (MoDNR) Drinking Water Watch database and is shown as figure 4.7. As is shown, almost all of the data are out of compliance; that is higher than 80 µg/L for TTHM. The highest point is 124 µg/L of THMs which occurred in July 2009.
When THMs were divided into species in a typical water (Figure 4.8), it is clear that for this facility, chloroform contributes on average of 80 percent through 5 years. If aeration is applied to this facility in an ideal condition, 80 percent of chloroform could be stripped out. The highest THMs for this facility is 124 mg/L, and removing 80% of the chloroform will result only 25 µg/L of THMs remaining (assuming no other compound than chloroform being stripped out) which is much lower than the MCL of 80 µg/L. Accounting for all volatile compounds, the water might produce a much lower value of THMs after aeration has been applied to this typical water.
Figure 4.8 Percentage of each THMs species
Chapter 5.0 Results and Discussion

5.1 Enhanced Coagulation/Softening

The raw water were collected from each partner facility, and jar tests performed on these raw waters and compared with a control following the same treatment method as each facility.

As Table 5.1 shows, compared with the control the best enhanced softening occurs at pH 11.5, where the reductions for TOC and UV are 32 and 62 percent, respectively, compared with the control. The best coagulation dosage for this raw water quality occurs at 26 mg/L FeCl$_3$ at pH 5 and 111 mg/L alum at pH 6, and the TOC reduction percentage are 43 and 26, respectively, for FeCl$_3$ and alum at the optimized level. The UV percent reductions at the same levels are 41 and 27 for FeCl$_3$ and alum respectively.
Table 5.1 Coagulation/Softening data for City A

<table>
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<tr>
<th>Jar #</th>
<th>Week 2</th>
<th>Week 3</th>
<th>Week 4</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>raw</td>
<td>control</td>
<td>raw</td>
</tr>
<tr>
<td></td>
<td>PACI mg/L</td>
<td>pH</td>
<td>Lime to pH</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>7.7</td>
<td>9.5</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>7.7</td>
<td>10.0</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
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<td>10.5</td>
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</table>

As table 5.2 below shows, the facility is not using the optimized dosage when water was treated by Polyaluminum chloride sulfate (PACS). The best treatment for UV reduction occurs at 7 mg/L which result in a 13% reduction compared to the control. The percentage might increase as the dosage decrease, but further tests might be needed to confirm this supposition. When PACS used, the best TOC reduction occurs at 9 mg/L compared with the control. As the future increase the PACS dosage, both TOC and UV reduction has dropped. When lime was used to treat the City C water, it showed a similar pattern; the higher the lime dosage the higher the reduction for both TOC and UV. The best dosage of FeCl₃ and alum for the City C water occurs at 32 mg/L.
and 111 mg/L, respectively. The reduction from FeCl₃ dosage compared to the control is 51% for TOC and 58% for UV. The reduction from alum at its optimized dosage is 45% for TOC and 58% for UV.

### Table 5.2 Coagulation/Softening data for the City C

<table>
<thead>
<tr>
<th>Jar #</th>
<th>PACS (mL)</th>
<th>pH</th>
<th>Lime to pH</th>
<th>FeCl₃ (mg/L)</th>
<th>Alum (mg/L)</th>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV254 (1/cm)</th>
<th>%TOC Redc</th>
<th>%UV Redc</th>
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</tbody>
</table>
The same method and dosage was used to treat The City B’s water. As dosage was increased a better reduction was shown. Similarly to the City C, the best dosage for FeCl₃ and alum occurred at 32 mg/L and 111 mg/L, respectively. The reduction from FeCl₃ dosage compared to control is 54% for TOC and 57% for UV. The reduction from alum at its optimized dosage is 32% for TOC and 32% for UV.

5.2 Aeration

Aeration is another approach to reduce THMs. THM compounds are relatively volatile, especially chloroform. Due to this unique characteristic of THMs, introducing air through the water is an option to reduce the THMs present in the water. This method is efficient when chloroform is the greatest contribute to the THMs in the water, the reason being that chloroform has a much higher Henry’s constant than other species, the more the chloroform THMs the better the reduction that aeration can achieve.

5.2.1 Test Results

All of the aeration bench scale tests were performed in the system shown as figure 5.1. A 4L glass chamber was filled with 3L of water. A small water pump supplied air into two diffuser sets in the bottom of the glass chamber. An air flow meter monitors the airflow rate of the system. Samples were taken periodically from the chamber for THM analysis.
5.2.1.1 Variable Contact Time

The raw water was collected from the Columbia, MO drinking water facility right after chlorine had been dosed into the treated water. The water was incubated in the laboratory for two days for DBP formation at room temperature. After day 2, the water was then poured into the glass chamber to the 3L mark and aerated for 10 minutes at an airflow rate of 1L/min. This test was repeated for 20 and 40 minutes, respectively (figure 5.2).

At time 0, the THM concentration was 110 µg/L; after 10 minutes of aeration, the THM level was down to 61 µg/L, with the reduction percentage off 44. After 20 minutes of aeration, the THM concentration was reduced to 44 µg/L, with the reduction percentage increased to 59. At a
time of 40 minutes, the reduction was even more enhanced, with the THM concentration down to 23 \( \mu g/L \), a 79\% reduction.

The concentration data fit a curve of \( Y = 0.0625x^2 - 4.555x + 105.9 \) with an \( R^2 \) value of 0.99. Where the X axis represents time and Y axis represents the concentration. For a given duration X with airflow of 1L/min, an expected concentration of Y might be calculated. The removal rate can be calculated by \( dy/dx = 0.125x - 4.5555 \). The negative number in the rate means a reduction of THM. When the time is at 36.44 minutes, the removal rate is 0, which means that at airflow of 1 L/min there is no significant THM remove after 36 minutes of aeration.

![TTHM reduction graph](image)

Figure 5.2 THMs Concentration and Percent Reduction as a function of Aeration time with an airflow rate of 1 L/min.

5.2.1.2 Vary Airflow

After 2 days of THM formation, 3L of water for each experiment were transferred into the glass chamber. The water was aerated for 10 minutes at a flow rate of 1 L/min. After 10 minutes, samples were collected for THM analysis. This experiment was repeated for air flow rates of 2 L/min and 3 L/min (figure 5.3).
The concentration data fits a curve of \( Y = 7.8125x^2 - 45.193x + 101.48 \) with an \( R^2 \) of 0.99, where the X axis represents airflow, and the Y axis represents the concentration. For airflow of x at duration of 10 minutes, a concentration of Y may be calculated. The removal rate can be calculated by \( \frac{dy}{dx} = 15.625x - 45.193 \). The negative number in the rate means a reduction of THM. When the airflow is at 2.89 L/min, the removal rate is 0, which means for 10 minutes aeration there is no significant THM remove at a higher airflow than 2.89 L/min.

The initial THMs concentration in figure 5.3 before aeration is 103 µg/L. After 10 minutes of aeration at an airflow of 1 L/min, the THM concentration is reduced to 61 µg/L which is a 41% reduction. The THMs concentration went down even further to 46 µg/L which is 55% of reduction after 10 minutes aeration at 2L/min. When the air flow was increased to 3L/min, the reduction reached 66%.
Chlorine residual was tested in this method to determine the extent to which the chlorine residual is lost as a result of aeration of chlorinated water. According to the data (Figure 5.4), the residual was decreased very little during aeration. The chlorine residual is 2.75 mg/L at the sampling point. After two days of the THM formation, the chlorine itself decayed to 1.44 mg/L. After 10 minutes of aeration at air flowrates of 1, 2, and 3 L/min, the chlorine residual were 1.40, 1.41, and 1.39 mg/L, respectively. From these experiments, aeration is not shown to accelerate loss of chlorine residual. The reason for chlorine having a small loss is that as soon as chlorine comes contact with water, it dissociates into HOCl and OCl-, both of which have very low Henry’s Constants. With a very low Henry’s constant, there will be a very small opportunity to aerate chlorine out of water.

![Figure 5.4 Chlorine residual when varies airflow](image)

### 5.2.1.3 THMs Formation Rate after Initial Aeration

The third experiment considered a five day water age, during which aeration occurred once at day 3. The duration of aeration was 20 minutes at airflow of 2 L/min. The first two days allowed
for THM formation under normal circumstances. After aeration on day 3, changes in THM concentrations (Figure 5.5) and chlorine residual (Figure 5.6) were monitored for both aerated and non-aerated water.

Figure 5.5 shows a significant THMs concentration decrease after aeration occurred on day three which is represented by square dots at the bottom. The concentration of THMs in aerated water then stayed at approximately 20 µg/L for the rest of the monitoring period. The top diamond shape dots represents the same raw water with no aeration taking place. During the first three days the THMs increased exponentially, then the THM concentration increase flattened out. The concentration of THMs exceeded the MCL (80 µg/L) after about 24 hours into the monitoring period. On the last day of monitoring, the THMs were over 100 µg/L without aeration.

![THMs VS Time](image)

Figure 5.5 The Effect of Aeration of Five days formation
Figure 5.6 shows the chlorine residual changes within the monitoring days. The diamonds represent chlorine residual for un-aerated water and the squares represent chlorine residual for aerated water. Due to chlorine decay the chlorine concentration decrease over the entire monitoring period. At the point of aeration, the chlorine residual have no difference in two water. At the end of monitoring point the chlorine difference is very little, and the concentration of chlorine is much higher than the current Treatment Rule which requires a minimum level of 0.2 mg/L of disinfectant residual at the entrance to a distribution system (Clark et al. 1996, Vasconcelos et al. 1997).

### 5.2.1.4 Sequential Aeration

The last experiment determined the effects of sequential aeration steps during a 5-day monitoring period. After two days of THMs formation, the water was aerated once each day for the remaining of the monitoring period. The air flow rate used was 1L/min for 10 minutes each time.
The un-aerated water was then compared with aerated water for both THMs (Figure 5.7) and chlorine residual (Figure 5.8).

In Figure 5.7, the square dots in the bottom represents aerated water and the diamond shape dots on the top represents un-aerated water. The un-aerated water follows the trend of the un-aerated water in five days formation test, in which the concentration increased from 36 to 101 µg/L throughout the days. The aerated water had a huge reduction after the first time of aeration, which THMs were reduced to about 22 µg/L from an initial concentration of 90 µg/L, a 75% reduction. Within the first period of aeration, the chloroform was reduced from 37.3 µg/L to 5.5 µg/L, which is an 85% reduction. Other THM species, such as BDCM, DBCM and bromoform, have a reduction of 76%, 60% and 45%, respectively, which is in the same trend as Henry`s Constant. Then for each time of aeration, there was a concentration drop. After the last period of aeration, the THMs concentration went down to 10 µg/L.
Figure 5.8 shows a chlorine residual trend very similar to the chlorine residual trend from the single aeration step experiment. There was no difference in chlorine residual after the first aeration step. However, a small divergence occurred between aerated water and un-aerated water after aeration session. All the monitoring points are much higher than the required chlorine residual level for distribution system.
Figure 5.8 The Effect of Aeration on days 2, 3, and 4 on Chlorine residual

Chlorine Limits in distribution system are 0.2 mg/L
Chapter 6.0 Conclusions

6.1 Test Summary

The experimental results indicate that enhanced lime softening at pH 11.5 can increase UV reduction 60 to 70% and can increase TOC reduction by 30% compared to the control set. For FeCl$_3$, the improvements compared to control set are 41 to 50% for UV and 43 to 54% for TOC reductions. PACl does not have significant percent reduction for either TOC or UV254; the improvement for both only at about 10%. When water was treated with alum, the percent reductions of UV are 29 to 60 and the percent reductions of TOC are 29 to 45 compared with the controls.

When chloroform is the more abundance component of THMs, aeration can be a very efficient way of removing THMs. The THM produced from raw water used yielded about 40% chloroform. When airflow was set at 1L/min, the THMs reduction was at least of 44% after 10 minutes aeration. Within this time frame, Chloroform, BDCM, DBCM and Bromoform concentration reduced by 52%, 45%, 35% and 22%, respectively, and the chloroform was reduced to 19.2ug/L from 40.3ug/L. For greater reductions in all THM species, the aeration time can be increased. When the aeration time was set at 10 minutes, the aeration achieved 66% reduction in THMs at an airflow of 3 L/min. For both 5 days aeration and sequent aeration, the THMs are about 12 µg/L in the end of monitoring period, while the un-aerated water had approximately 102 µg/L of THMs.
6.2 Suggestions and recommendation

The first part of this research was focused on understanding precursor reduction through optimization of chemical dosage with particular emphasis on studying enhanced softening (or higher pH conditions) for each type of raw water to resolve the DBP compliance issue for those facilities. The results of this study show that most of the facilities have a less efficient treatment process with coagulation by using current chemicals. For instance, if the City C drinking water plant used lime to increase the pH to 11.5, the facility would improve TOC and UV 32 and 70%, if 32 mg/L of FeCl$_3$ were used at pH 5.0, the TOC and UV reduction could be 51% and 58%. If 111 mg/L of alum were used at pH of 6.0, the TOC and UV reduction are 45% and 58%, respectively. For other facilities the enhanced coagulation testing showed a promise results in DOC and UV reduction as well. Facilities might consider switching to other coagulants for better performance, such as lime and FeCl$_3$.

From an operational perspective, when lime is chosen as the coagulant, a large pH raise is expected in the coagulant basin. Facility operators need to consider how to neutralize the pH upstream of the process after the settling basin. Options for decreasing the pH can be adding acid and supplying CO$_2$ into the system. When FeCl$_3$ and alum were chosen, the pH reduction is required prior to coagulation. Later on in the treatment process, the pH needs to be brought up by adding lime and NaOH.

The second part of this research was solely focused on aeration to reduce THMs already formed in the system. If facilities are predominately producing THMs over HAAs at 142 µg/L (The lowest percent reduction of 44% happened at 1 L/min airflow for 10 minutes, so to meet compliance of 80 µg/L, the highest initial concentration should be $x^*(1-0.44) = 80 \, \mu g/L$, which
yields 142 µg/L) or less of THMs, they would be suitable candidate for aeration for at least 10 minutes with an airflow of at least 1L/min. The study also tested the chlorine residual for the concerns of losing chlorine while aeration is taking place. The results showed there is not much chlorine lost by aeration. Because HOCl and OCl` have very small Henry`s Constants, it was predicted that there would not be much loss of chlorine residual due to aeration; the results here are consistent with the perdition. In conclusion, this study showed that the aeration method could reduce THMs as much as 80%, while the chlorine residual remains above the required level. Those facilities whose THMs are high in chloroform should consider this method in addition to efforts to reduce precursor concentrations.

6.3 Future work

6.3.1 Remaining Concerns

During the aeration experiments, the divergence of chlorine residual was not expected. The expectation was that chlorine residual for both aerated water and un-aerated water should not have a divergence. Another unexpected result is that the THM concentration for aerated water appeared to continue to decrease during the period after aeration. Because the aerated water still contain chlorine and NOMs in the water, they both should react to form more THMs. However, the THMs decreased in this case. The reasons might be each time of a sample was taken, there would be about 170 mL of water taken, and there would be more void spaces left in the chamber for volatile compounds to escape to the air. More tests are need in the future to discover the reasons for both phenomena.
6.3.2 Pilot/Field testing

Based on a conceptual design (Figure 6.1), a pilot-scale aeration column has been built (Figure 6.2). The intention of this column is for field testing to verify the aeration performance. Pilot-scale units are being proposed to test the effects of each of the aeration approaches mentioned previously. (The detailed dimensions of this unit see appendix A)
The column would be carried to each facility with high chloroform concentration in THMs. The column would be connected to the unit in the facility where chlorine has been added to water. The ideal location would be the end of a clear well or the end of a water tower, where the majority of chloroform has been formed (For general guidance procedures for testing please see Appendix B).
References


Gerwe, C. E. (2003). Natural organic matter (NOM) adsorption onto and coprecipitation with solids formed during softening, University of Texas at Austin. PhD.


Aeration [Internet]. [MECC] Mountain Empire Community College; [cited 2015 Jan 10]. Available from: http://water.me.vccs.edu/courses/env115/Lesson5_print.htm
Appendix A

The schematic of the diffused aeration pilot unit design is provided (Figure 6.1). The design of this system includes reservoirs for water entering and leaving the aeration unit. Water pumped from the source water tank would enter a 6 foot tall PVC pipe which would serve as the aeration unit. This pipe has a working volume of approximately 1.18 ft$^3$. An acrylic baffle measuring about 5.5 feet in length would be placed in the center of the PVC pipe. A 4 inch diameter bubble disk diffuser (provided by EDI, Environmental Dynamics International) would be located at 0 or 1 inches above the floor of the unit or as low as possible to increase the contact time. The floor would include a 6” PVC cap. A pump whose capacity should be at least 17952 Pa or 2.6 psi would be used to move the water through the unit. An air pump would deliver 1 to 5 ft$^3$/min of air into the water. Samples will be collected from the unit using a faucet and a collection of 40 mL TTHM vials for GC analysis.
Appendix B

When a facility has no water tower, this column would need to be connected to the front of a clearwell. Pump the water into the column. Flush the system each time by flowing water through the column, the duration of flushing must be at least of the column retention time which varies by facility (water flow rate varies). After flushing the column, set a few integrals of aeration time from 0 to clearwell retention time. Combine the aeration time with airflow rate to optimize the aeration. Outlet water discharged back to the clearwell or drainage. Samples are taken before the water being discharged by outlet.

When a facility have a water tower, the column is then connected to the end of the clearwell. Flush the column at least of its retention time. Close the outlet value and fill column with the water. Set airflow rate, aeration duration and times of aeration each day. The water should not be aerated after it stayed in the column longer than the retention time of the water tower. Samples are taken the bottom faucet.

Two sets samples have to be collected by the facility staff. The first set of samples are THMs samples, which has to be taken each aeration or each time integral for monitoring, and it needs to be stored in a 40mL vail with 88 mg/L of NH₄Cl preservatives. The vials MUST HAVE NO AIR. The sample need to stay in a refrigerator, and be sent to for a lab testing. The second set of samples are chlorine residual samples, which need to be tested at site after each aeration or each time integral for monitoring. It MUST BE TEST ON SITE each time due to chlorine decay.