OPTIMIZATION OF CHEMICAL DOSING IN WATER TREATMENT FOR ENHANCED COAGULATION/SOFTENING AS IT PERTAINS TO DBP REMOVAL

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by

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

OPTIMIZATION OF CHEMICAL DOSING IN WATER TREATMENT FOR ENHANCED COAGULATION/SOFTENING AS IT PERTAINS TO DBP REMOVAL

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a candidate for the degree of master of science in civil and environmental engineering,

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

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Abstract

Treatment facilities out of compliance with EPA regulations are often not using optimal chemical treatment. Determination of the most effective chemical type, combination and concentration can aid in reduction of disinfection by-product precursors. The effects of optimal chemical treatment using enhanced coagulation and enhanced softening was tested on three surface waters (two reservoirs and one lake sources), and one ground water (alluvial wells). Results indicated enhanced coagulation was more effective at removing DBP precursors from waters with higher initial UV-254 absorbance values and lower alkalinities while enhanced softening was more effective for waters with lower initial UV-254 absorbance values and higher alkalinities. In a number of cases, ferric salts outperformed aluminum salts at reducing the DBP formation potential.

Redox potential measurements were added to the list of analyses to determine trends and the feasibility of using this parameter as an additional indicator of process efficiency. Redox potential indicates a transfer of electrons similar to the transfer of H^+ *indicated by pH. It is expected that* E_h *will trend as the inverse of pH when explicit oxidation or reduction reactions are not taking place. However, this research presents that under constant pH conditions, the* E_h *readings seem to indicate the destabilization and stabilization processes expected during the coagulation step in drinking water treatment. Comparison of the* E_h *readings from the start of various treatment stages to the end provides some indication of the effectiveness the enhanced coagulation or enhanced softening process has on the removal of organic precursors for disinfection by-products.*

Chapter 1: Historical Efforts to Reduce Disinfection By-Products through Enhanced Treatments

1.1 Introduction

Many communities have had problems with disinfection by-products (DBPs) in their water. DBPs result from organics present in the water reacting with the disinfectant, which is used to reduce the occurrence of waterborne disease (USEPA, 2007). Since some DBPs are regulated by the United States Environmental Protection Agency (US EPA), this research considers how optimized chemical treatments, such as enhanced coagulation and enhanced softening, may be used as a strategy for controlling the production of these disinfection by-products. The U.S. EPA assigns standards for pollutant discharges for each source water classification. In drinking water, the regulated DBPs include four trihalomethane species (THMs), five haloacetic acid species (HAAs), bromate and chlorite (Bratby, 2006).

1.1.1 Hypothesis

The goal of the overall research project is to demonstrate how selection of an enhanced softening treatment strategy at softening plants and an enhanced coagulation treatment strategy at turbidity removal plants can effectively reduce dissolved organic carbon (DOC), UV-254, TTHM, and HAA5 concentrations, and, therefore, allow select water treatment facilities to regain and remain in compliance with EPA regulations.

Optimization in these experiments involves varying the coagulants to find the coagulant type and dosage with the highest disinfection by-product precursor reduction under various pH and redox conditions. Enhanced coagulation typically increases coagulant dosage thus lowering pH for organics removal, such as those considered THM precursors, in addition to the more conventional particulate matter removal. With higher coagulant doses, more metal is available for floc formation. Lower pH values affect the metal complexes formed and reduce the charge density of humic and fulvic acids, making them more hydrophobic and absorbable (Vrijenhoek, et al., 1998). In contrast, with enhanced softening, the coagulant is added along with lime and the pH greatly increases. The enhanced softening experiments are based on the premise that natural organic matter (NOM) may be reduced in the water column by adsorption onto calcium precipitates (Bob and Walker, 2001).

1.1.2 Objectives

1. Using conventional jar testing experiments, develop a protocol for determination of the optimal combinations and type of chemicals needed for general precursor reduction based on measured source water quality, with primary focus on the more common chemicals used in drinking water treatment: ferric chloride, liquid alum and lime.
2. Develop trends for coagulant performance indicators.

3. Determine specific optimal enhanced treatment strategies for three Missouri drinking water treatment facilities using solitary and consecutive treatments as a case study of the protocol developed in objective 1.

1.1.3 Scope

Objective 1 – Protocol for using jar test setup to optimize DBP reduction strategy

- Task 1: Develop an experimental design for enhanced coagulation and enhanced softening tests following a random block design.
- Task 2: Experiment with coagulant dose as a variable to determine general trends of effects on water quality/chemistry.
- Task 3: Experiment with pH as a variable to determine responses of coagulant types.

Objective 2 – Performance Indicator Trends

- Task 1: Observe ORP (redox) profiles as an indication of reaction conditions throughout select jar testing sequences.
- Task 2: Develop a correlation of how ORP trends compare to observed water quality parameters used to characterize precursor removal performance.

Objective 3 – Specific Treatment Strategies for Select Missouri Communities

- Task1: Conduct jar tests using the water and chemicals currently used by each of the treatment facilities to determine the effects of each chemical individually as compared to combinations of the these chemicals used in the current practice.

- Task 2: Consider and test chemical combinations that are suspected to improve on the baseline DBP reduction performance observed during task 1.
- Task 3: Optimize the chemical types and dosages found during task 2 based on constraints presented by full scale operation of these selected treatment facilities.

1.2 Regulations Relating to Research Project

1.2.1 Stage 1 Disinfectants and Disinfection By-Product Rule (DDBPR)

The Stage 1 DDBPR applies to public water systems that are community water systems (CWSs) and nontransient noncommunity water systems (NTNCWs) that treat their water with a chemical disinfectant for either primary or residual treatment (AWWA, 2010). Increasing the disinfection dose will reduce waterborne pathogens, but it will increase the DBP risk. However, low doses of disinfectant will result in reduced DBP risk but will increase microbial risk. Thus, concurrent treatment is required to minimize both microbial and DPB risk (USEPA, 2009). Table 1.1 lists maximum contaminant level goals (MCLGs), which are not regulated, but are monitored during research. Table 1.2 lists maximum contaminant levels (MCLs), which are regulated, and experimental results must be significantly below these levels to be considered a realistic option for the drinking water facilities.

Table 1.1 MCLGs for the Stage 1 DDBPR (USEPA, 1998)

Disinfection By-Product	*MCLG (mg/L*
Bromoform	0
Chloroform	0
Bromodichloromethane	0
Dibromochloromethane	0.06
Dichloroacetic acid	0
Trichloroacetic acid	0.3
Bromate	0
Chlorite	0.8

Table 1.2 MCLs for the Stage 1 DDBPR (USEPA, 1998)

Disinfection By-products	MCL (mg/L)
Total Trihalomethanes (TTHMs)*	0.080
Haloacetic Acids (HAA5)*	0.060
Bromate*	0.010
Chlorite	1.0

** Compliance is based on a running annual average, computed quarterly*

Compliance is defined on the basis of a running annual average (RAA) of quarterly averages of all samples. For clarification, this means that four (4) sample locations may be averaged together at each quarterly sampling event and then the last four (4) quarter's averages are averaged together to yield the RAA. In total 16 samples are averaged together to produce this number. At least 25% of samples must be at locations representing maximum residence time and the remaining samples must represent average residence time and the entire distribution system, accounting for number of people served, different sources of water, and different treatment methods (USEPA, 2001).

1.2.2 Total Trihalomethane Rule

In November 1979, EPA set an interim MCL for total trihalomethanes (TTHM) of 0.10 milligrams per liter (mg/L) as an annual average. About the time of the development of the Stage 2 DDBPR (~2005), the annual average for TTHM was revised to 0.080 mg/L. The value for each sample is the sum of the measured concentrations of chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (USEPA, 1998).

1.2.3 Stage 2 Disinfectants and Disinfection By-Product Rule

The Stage 2 DDBP rule was put into effect in 2006 and builds upon earlier rules that addressed disinfection by-products to improve drinking water quality and provide public health protection. This rule tightened compliance monitoring requirements for trihalomethanes (TTHMs) and haloacetic acids (HAAs) (USEPA, 2007).

Under the Stage 2 DDBP rule, systems must conduct an assessment of their distribution systems, known as an Initial Distribution System Evaluation (IDSE), to identify the locations with the higher DBP concentrations in their system. These locations are then be used as the sampling sites for Stage 2 DDBP rule compliance monitoring. Compliance with the maximum contaminant levels for TTHMs and HAA5s are calculated for each monitoring location (American Water Works Association, 2010). This new compliance requirement is based on a locational running annual average (LRAA) in which compliance is based on the 4 quarterly samples taken at that location, rather than being averaged with 3 other locations in the system.

In addition, the Stage 2 DDBP rule requires each system to establish if they have exceeded an operational evaluation level identified using compliance monitoring results. This evaluation provides an early warning of possible future MCL violations. A facility that exceeds an operational evaluation level is required to review their operational practices and submit a report to their state that identifies actions that may be taken to mitigate future high DBP levels, particularly those that may jeopardize their compliance with the DBP MCLs (EPA 2009).

1.3 Disinfection By-Products Formation and Concern

Chlorine has traditionally been used to disinfect drinking water because it is very effective at inactivating microorganisms/pathogens that may be present in the water. However, it is also very reactive with natural compounds which may also be present, both organic and inorganic. Disinfection by-products (DBPs) form when disinfectants used to treat drinking water, such as chlorine, react with organic compounds in the water which are usually naturally occurring (USEPA, 1999). The formation of DBPs depends primarily on source water quality characteristics and on the location in the treatment process where disinfectants are added. In general, fewer DBPs will be formed if disinfectants are added later in the process (Liang and Singer, 2003). Major factors affecting the production of DBPs include the concentration and characteristics of natural organic matter (NOM), the type and concentration of disinfectants, contact time, pH, temperature, and the concentration of bromide ion. Among them, the concentration and characteristics of NOM are considered to have the most significant influence on the generation of DBPs (Jung and Son, 2008).

Concentration and characteristics of organic and inorganic matter depend on the source water quality. Groundwater quality is influenced by the quality of its source based primarily on soil and geologic conditions. Significant quantities of organic matter are typically not found in groundwater, however, inorganic constituents, such as iron or calcium, move easily through the soil due to weathering and leaching of rocks, soil and sediments (Qasim, et al., 2000). Surface waters are more affected by changes in weather, temperature and watershed impacts than ground water (Viessman, et al., 2009). Surface water also contains more organic compounds which originate from decaying plants and animal matter and from agricultural runoffs. Table 1.3 lists typical concentrations of common constituents based on source water. As a result of these differences, namely in total organic carbon (TOC), hardness, and turbidity, the method for treating surface water tends to differ from the treatment of groundwater. Surface waters are typically treated with coagulation, flocculation, sedimentation and granular filtration whereas ground waters are typically treated by softening and filtration.

Table 1.3 Typical Concentrations of Constituents Based on Source Water
(Qasim, et al., 2000)

Constituent	Surface Water	Ground Water
Coliform, MPN/100 mL	2,000	100
TOC, mg/L	3	0.5
Hardness, mg/L as $CaCO_3$	90	120
Alkalinity, mg/L as $CaCO_3$	100	150
pH	7.5	7.5
TDS, mg/L	150	250
Turbidity, NTU	10	<0.5

MPN = most probable number; TOC = total organic carbon; TDS = total dissolved solids

If free chlorine residual exists, THM formation will continue after the addition of chlorine. In the presence of bromides, brominated THMs are formed preferentially and chloroform concentrations decrease proportionally (Aizawa, et al., 1989). The ratio of chlorine to organic matter is an important factor in determining which by-products are formed. For example, at low chlorine dose rates, phenol is converted to taste-producing chlorophenols, whereas at higher dosages these are converted to tasteless chlorinated quinines (Gray, 1994).

The presence of halogens other than chlorine is important. Bromide, in particular, is oxidized by chlorine to form hypobromous acid (Eqn. 1), which then results in brominated analogues of the chlorinated by-products. The reaction of natural organic matter with hypobromous acid results in the formation of bromoform (Eqn 2) (Gray, 1994).

$$Br^- + HOCl \rightarrow HOBr + Cl^- \qquad \text{(Eqn 1)}$$

$$HOBr + NOM \rightarrow CHBr_3 \qquad \text{(Eqn 2)}$$

Other disinfection techniques, such as ozone and chloramination, can decrease the formation of the regulated by-products. However, monochloramine is best used as a secondary disinfectant because it needs an increased contact time compared to chlorine, and ozone is pH and temperature dependant and also may not remain in the water long enough for proper disinfection of certain microorganisms of concern (USEPA, 2003).

1.3.1 Natural Organic Matter

Natural organic matter (NOM) is the major component of organic precursors for disinfection by-products in chlorinated or chloraminated drinking waters. Aquatic NOM is an intricate combination of heterogeneous organic compounds varying in size, structure, and functionality from source to source. The five main chemical groups of NOM are humic substances, carboxylic acids, carbohydrates, amino acids, and proteins (Bond, *et al.*, 2009). In general, raw water contains organic matter of different characteristics depending upon geological conditions and the surrounding watershed. Surface water typically contains more organic constituents than ground water. As seen in Table 1.4, of the organic matter found in each of these sources, streams and rivers contain the highest amount of fulvic acid and humic acid, therefore the largest amount of hydrophobic organic matter. Conversely, ground water contains the highest amount of hydrophilic acids.

Table 1.4 Organic Matter Classification for Natural Waters
(Therman, 1986)

% Dissolved Organic Matter	0	25	50	75
Ground Water	FA	IC	H	HyA
Lakes	FA	IC	H	HyA
Streams/Rivers	FA	IC	H	HyA

FA = fulvic acid, IC = identifiable compounds: carboxylic acids, amino acids, carbohydrates, hydrocarbons, H = humic acids, HyA = hydrophilic acids

The organic matter gives taste, odor, and color in water and increases coagulant and disinfectant demand in the water treatment process. Organic matter also consumes residual chlorine in the distribution system and contributes to microbial regrowth by providing heterotrophic bacteria with carbon sources. Above all, natural organic matter existing in raw water reacts with chlorine or other disinfectants, and then generates halogenated disinfection by-products which are known to have adverse health effects (Jung and Son, 2008).

It is thought that humic substances, which tend to be aromatic and hydrophobic, contain the bulk of DBP precursors (Bond, et al., 2009). Aromatic compounds with electron donating groups, such as -OH, -OR, -NH2, -R, are more reactive and therefore react with chlorine more readily than aromatics with electron-withdrawing groups, such as -NO2, -COOH. –COOR, -X (Choudhry and Hutzinger, 1982). Knowledge of DBP formation as a function of precursor hydrophobicity or size may help drinking water utilities optimize treatment systems to remove the portions of NOM associated with high DBP yields (Hua and Reckhow, 2007).

Hydrophobic NOM primarily consists of humic acid (Figure 1-1) and fulvic acid and is rich in aromatic carbon, phenolic structures, and conjugated double bonds, while hydrophilic NOM is a mixture of organic compounds that can be simple organic acids, such as volatile fatty acids (Figure 1-2), or complex polyelectrolytic acids that contain many hydroxyl and carboxyl functional groups (Jug, 1997). Either the hypochlorous or the hypobromous acid attacks these structures and breaks down portions to produce the simpler trihalomethane (Figure 1-3) or haloacetic acid structures.

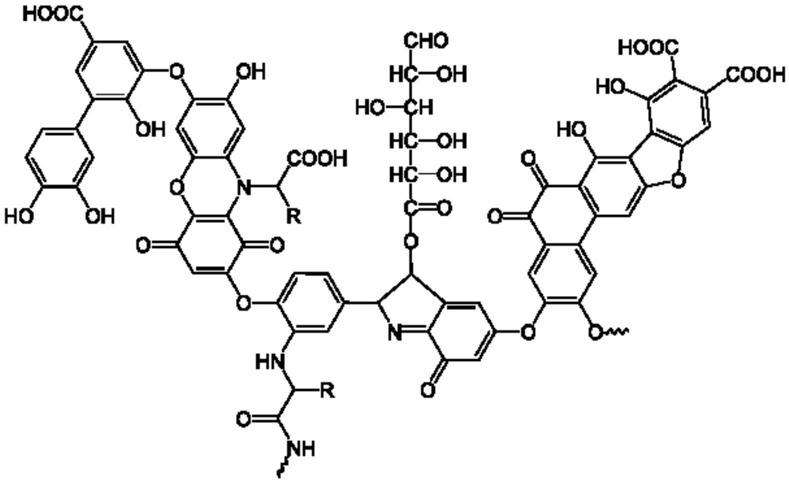

Figure 1-1 Humic Acid (Yikrazuul, 2009)

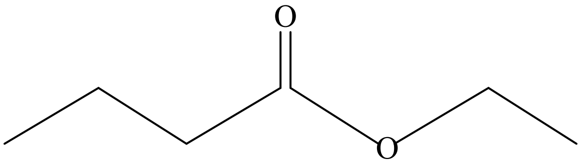

Figure 1-2 Ethyl Butyrate (fatty acid)

In general, hydrophobic NOM is found to be a more important source of precursors for trihalomethanes, haloacetic acids and total organic halogen than the corresponding hydrophilic NOM. However, hydrophilic NOM also contributes substantially to the formation of DBPs, especially for waters with low humic content (Hua and Reckhow, 2007).

A study by Jung and Son (2008) about formation potentials of DBPs for hydrophobic and hydrophilic fractions of NOM found that hydrophobic fractions showed a much higher THM formation potential. In addition, of the hydrophobic fractions, the THM formation potential of humic acids was higher than the formation potential of fulvic acids. The hydrophobic fraction also yielded twice as much THMs as the hydrophilic fractions (Jung and Son, 2008). Goel et al. (1995) reported that as the unsaturated bonds, like the carbon double bond in water, and the content of aromatic substances increase, the UV-254 values also increase, and that these substances show high reactivity with oxidizing agents like ozone and chlorine (Jung and Son, 2008).

1.3.2 Trihalomethanes

Trihalomethanes (THMs) are simple, single carbon compounds which have the general formula CHX_3, where X may be any halogen atom. Halogen atoms, found in group 17 of a IUPAC style periodic table, include chlorine (Cl), bromine (Br), fluorine (F), iodine (I) and are all volatile, colorless, easily dissolved in water and considered to be possible carcinogens (Porteous, 2000). The four regulated forms of THMs include chloroform (trichloromethane, $CHCl_3$), dibromochloromethane ($CHClBr_2$), bromodichloromethane ($CHCl_2Br$), and bromoform ($CHBr_3$) and are shown graphically in Figure 1-3.

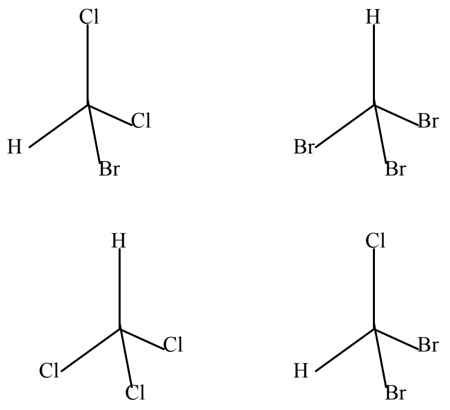

Figure 1-3: Regulated THM Chemical Compounds:

bromodichloromethane (top left), bromoform (top right), chloroform (bottom left), and dibromochloromethane (bottom right)

Equation 3 shows how chlorine added to water dissociates into hypochlorous acid. Hypochlorous acid then reacts with bromide and natural organic matter to form halogenated DBPs (Equation 4). These by-products formed are undesirable in the water because they are suspected carcinogens. Trihalomethanes (THMs) are the most common by-product measured.

$$Cl_2 + H_20 \longrightarrow HOCl + Cl^- + H^+ \tag{Eqn 3}$$

$$HOCl + Br^- + NOM \longrightarrow \text{Halogenated DBPs} \tag{Eqn 4}$$

The maximum allowable annual average level of THMs is 80 parts per billion. Several strategies are available to reduce THMs. One strategy is to remove them after they have formed. However, instead of trying to remove the problem after being formed, reducing the source is more ideal. Reducing disinfectant by-product precursors, such as natural organic matter (NOM), will reduce DBPs formed with disinfection (Faust and Aly, 1983).

1.3.3 Haloacetic Acids

Haloacetic Acids (HAAs) are colorless, have a low volatility, dissolve easily in water, and are fairly stable. They are formed when a halogen atom takes place of hydrogen atom in acetic acid. There are nine species of HAAs (HAA_9), of which five species are currently regulated (HAA_5) (USEPA, 1999). The five regulated HAAs (Figure 1-4) are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The nine species of HAAs include the five regulated HAAs along with bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). The Stage 2 Disinfectants and Disinfection Byproduct Rule set the maximum contaminant level for haloacetic acids (HAAs) to 60 parts per billion.

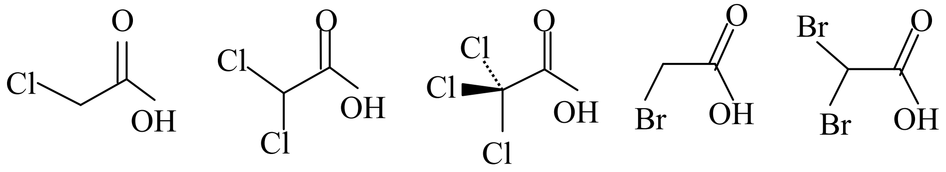

Figure 1-4: Regulated HAA Chemical Compounds

monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)

HAAs typically form when chlorine reacts with NOM, such as humic acids, found in raw water supplies. Other major sources of HAAs in the environment come from chemical and pharmaceutical manufacturing processes such as the bleaching of wood pulp by paper mills, the disinfection of municipal wastewater upstream of the water treatment plant, and cooling water (Jurenka, 2009).

1.4 Coagulation and Flocculation

Coagulation is defined as the addition of chemicals and mixing such that particles and some dissolved contaminants are aggregated into larger particles that can be removed by solids removal processes, such as clarification and filtration (DeWolfe, et al., 2003). Traditional coagulation has the primary purpose of removing suspended materials and organic matter with minimal sludge production in order to decrease turbidity (Ballard and MacKay, 2005).

Coagulation is a water treatment process that adds a substance, typically a metal, to a solution. The most common coagulants include ferric sulfate ($(Fe_2(SO_4)_3)\cdot 8H_2O$), ferrous sulfate ($FeSO_4\cdot 7H_2O$), ferric chloride ($FeCl_3$), aluminum sulfate, also known as alum, ($Al_2(SO_4)_3\cdot 14H_2O$), aluminum chloride ($AlCl_3\cdot 6H_2O$), and sodium aluminate ($NaAlO_2$) (Bratby 2006). Alum is most commonly used in drinking water whereas the iron compounds (both ferric and ferrous forms) are mostly used in treating waste waters. However, ferric chloride has been increasing in its application in drinking water. For alum, the stoichiometric coagulation reaction is seen in Eqn. 4:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(HCO_3)_2 = 2Al(OH)_{3(s)} + 3CaSO_4 + 6CO_{2(g)} + 18H_2O \qquad \text{(Eqn 4)}$$

For iron coagulation, the stoichiometric coagulation reaction is seen in Eqn. 5:

$$2FeCl_3 + 3Ca(HCO_3)_2 = 2Fe(OH)_{3(s)} + 3CaCl_2 + 6CO_{2(g)} \qquad \text{(Eqn. 5)}$$

In these reactions, calcium bicarbonate represents natural or added alkalinity which is needed in order to generate the precipitate as one of the products (Faust and Aly, 1983). As a result, these reactions consume alkalinity in addition to lowering the pH, thus creating water that is considered unstable if sufficient alkalinity is not present in the system.

The goal of coagulation is to change the oxidation state, and therefore change the chemical properties, to remove unwanted negatively charged colloids. Colloids typically have a diameter less than 10 μm which causes their sedimentation in water by gravity to be less than 10^{-2} cm/sec and therefore remain suspended (Faust and Aly, 1983). Coagulation masks the charge repulsion between these suspended particles so that they group together and form larger, heavier particles which are easier to remove from a solution than small particles. Typical coagulation is intended to reduce the turbidity (improve clarity) of the water. In short, coagulation is the addition of chemicals to water to destroy or reduce repulsive forces and induce particle agglomeration. Destabilization reduces the energy barrier between repulsive forces, providing conditions in which Van der Waals or other adhesive forces can dominate (Bratby 2006). In general, coagulation tends to remove more hydrophobic NOM compounds than hydrophilic NOM compounds (Hua and Reckhow, 2007).

In natural waters, colloids predominantly carry a negative charge due to a variety of functional groups on the surface of the particle (Faust and Aly, 1983). Chemicals used in coagulation are positively charged and act as neutralizing agents when interacting with the negative charges on NOM (Bolto, et al., 1999). Naturally occurring organics can be removed through coagulation by charge neutralization of the colloidal NOM, precipitation as humates or fulvates, and coprecipitation by adsorption on the metal hydroxide. Precipitation of NOM is the formation of an aluminum or iron humate or fulvate with a lower solubility product, therefore causing its precipitation into a solid form. In coprecipitation, the soluble organic material is adsorbed onto the metal hydroxide. Coagulation causes destabilization by either reducing the energy barrier so van der Waals forces (or other adhesive forces) can dominate or by double layer compression by reducing the surface potential as a result of changes in the surface chemistry (bridging or entrapment) (Gregory, 2007). Bonds involved in adsorption of NOM can include Van der Waals interactions, hydrogen bonding, hydrophobic bonding, ionic bonds or dipole interactions (Crozes, et al., 1995).

Following coagulation, flocculation is the physical process of promoting particle contact to facilitate the agglomeration to larger floc which can then settle by gravity. In a typical water treatment facility (illustrated by Figure 1-6), these processes are accomplished using two different tanks in series. The first tank is a rapid mix tank, with velocity gradients preferred in the range of 3000 to 5000 s^{-1}, to which the coagulant dose is added so that the particles become destabilized. The second tank is the flocculation tank, which is a slow mix tank, with velocity gradients preferred in the range of 20 to 80 s^{-1} for solids and color removal coagulation or 130 to 300 s^{-1} for softening, to promote particle collision and aggregation (Alley, 2000; Davis and Cornwell, 2007). Poor mixing can lead to the inefficient use of chemicals, with some portions of the suspension being under-dosed and other portions being over-dosed. An illustration of coagulation, flocculation and settling can be seen in Figure 1-5.

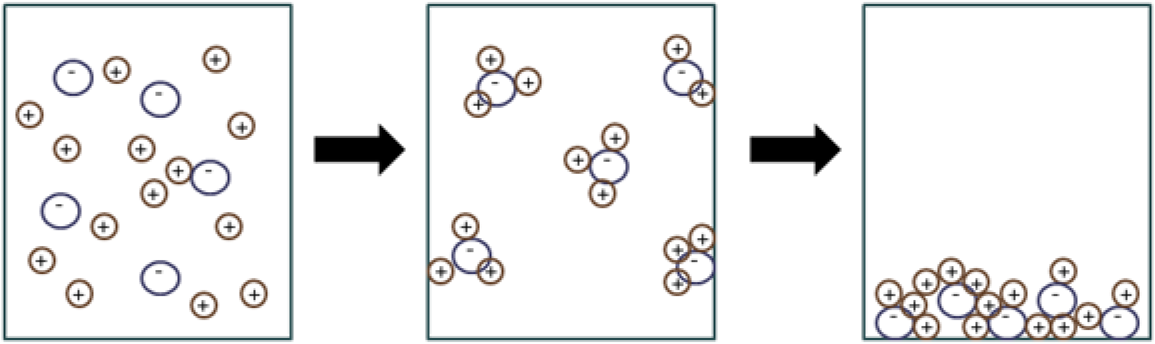

Figure 1-5: Coagulation (ion dispersion), Flocculation (floc formation), and Settling (flocs settle by gravity)

1.4.1 Water Treatment Facilities and Coagulation

Theoretical water treatment begins with the source water being pumped through a screen where larger debris, such as sticks and leaves, are removed. Next, water enters the coagulation/flocculation stage. Coagulation typically occurs for 30 – 60 seconds when the coagulant is added and chemical destabilization occurs. Water then goes into the flocculation basin for approximately 20 - 30 minutes where agglomeration of the metal and organic matter occurs. From flocculation, the water is sent to the sedimentation basin.

Solids (floc) formed during coagulation and flocculation settle out in the sedimentation basin. Solids are sent through thickening and dewatering and then sent to be disposed. After sedimentation, the water is sent through filtration where fine suspended particles and unsettled floc are removed. The water is then disinfected and sent to storage where it is finally sent through the distribution system. Figure 1- 6 demonstrates the theoretical layout for a theoretical water treatment facility. At a number of the lime softening treatment facilities, the separate rapid mix, slower mix, and sedimentation tanks are replaced by a single flocculator-clarifier unit. These process units are more typically known as solids contactors and require an established sludge blanket for efficient operation.

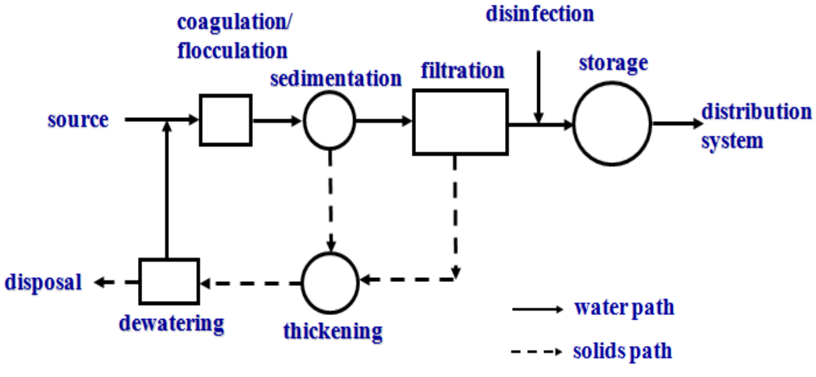

Figure 1-6: Theoretical Water Treatment Process

The most common coagulants used in drinking water treatment are liquid alum and ferric chloride. Table 1.5 lists alternative inorganic coagulants as well as their advantages and disadvantages.

Table 1.5 Advantages and Disadvantages of Coagulants

(US Army Corp of Engineers, 2001)

Name	**Advantages**	**Disadvantages**
Aluminum Sulfate (Alum) $Al2(SO_4)_3.18H_2O$	Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to water; effective over a limited pH range.
Sodium Aluminate $Na_2Al_2O_4$	Effective in hard waters; small dos-ages usually needed	Often used with alum; high cost; ineffective in soft waters
Polyaluminum Chloride (PAC) $Al_{13}(OH)_{20}(SO_4)_2.Cl_{15}$	In some applications, floc formed is more dense and faster settling than alum	Not commonly used; little full scale data compared to other aluminum derivatives
Ferric Sulfate $Fe_2(SO_4)_3$	Effective between pH 4–6 and 8.8–9.2	Adds dissolved solids (salts) to water; usually need to add alkalinity
Ferric Chloride $FeCl_3.6H_2O$	Effective between pH 4 and 11	Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum
Ferrous Sulfate $FeSO_4.7H_2O$	Not as pH sensitive as lime	Adds dissolved solids (salts) to water; usually need to add alkalinity
Lime $Ca(OH)_2$	Commonly used; very effective; may not add salts to effluent	Very pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality

1.4.2 Enhanced Coagulation

In January 2006, the US EPA finalized the acceptance of enhanced coagulation as an accepted treatment process to meet the Stage 2 Disinfectants and Disinfection By-Products Rule (Bratby, 2006). For enhanced coagulation experiments, goals desired include:

- Significant total organic carbon (TOC) reduction without the addition of unreasonable amounts of coagulant.
- Regulatory criteria which can be easily enforced with minimal state transactional costs.

The EPA defines enhanced coagulation as the term used to define the process of obtaining improved removal of DBPs by conventional treatment. However, the goals of enhanced coagulation differ from conventional coagulation due to its focus on optimized removal of DBP organic precursors rather than traditionally focusing on clarification or filter effluent turbidity (DeWolfe, et al., 2003).

In order to achieve more efficient TOC removal, enhanced coagulation utilizes changes in pH and coagulant dose. In order to change the traditional coagulation process to meet the requirements of the Stage 2 DDBP rule, enhanced coagulation can (DeWolfe, et al., 2003):

- Lower raw water pH with acids to enhance DBP precursor removal with the existing coagulant.
- Increase the dose of the existing coagulant to consume alkalinity and lower pH.
- Change to a coagulant that is more effective in DBP precursor removal under different conditions, such as lower pH or temperature.
- Use of polymers or filter aids to enhanced DBP precursor removal.
- Modify rapid mix or flocculation process to optimize coagulant efficiency.
- Change other pretreatment chemicals, such as the addition of ozone, to modify dissolved DBP precursor characteristics for improved removal through coagulation.

1.4.3 Enhanced Softening

Enhanced softening is defined by the U.S. EPA as the modification of chemical dosages for the increased removal of DBP precursors during the softening process (Thompson, et al., 1997). If the lime dose is simply raised during the softening treatment, it subsequently results in greater chemical costs and the increased production of sludge. Enhanced softening therefore involves lime addition for water softening along with the addition of a coagulant. High doses of lime (200 mg/L) may not be effective enough alone for the removal of DBP precursors due to electrostatic repulsion from the high negative charge density of humic substances and the negatively-charged calcium carbonate crystalline surface. Adding a cationic coagulant (e.g. ferric chloride or liquid alum), can alter the surface character of calcium carbonate precipitates for increased removal of NOM by adsorption (Yan, et al., 2008).

The ideal water source candidate for enhanced softening includes water treatment facilities which use surface waters or shallow wells, since these sources contain higher amounts of organic matter. NOM removal in lime softening is thought to occur through adsorption onto the surface of calcium (or magnesium) precipitates or coprecipitation in which NOM is incorporated into the crystal structure of the precipitate. NOM removal by $CaCO_3$ is thought to occur early in the precipitation process, when the $CaCO_3$ lattice structure is amorphous and the surface area is high. Within a few minutes, $CaCO_3$ solidifies into a negatively charged precipitate with a dense, crystalline structure and low surface area, which make it a poor adsorbent for negative charged NOM (Roalson, et al., 2003). On the other hand, magnesium hydroxide precipitates are positively-charged with an amorphous structure and larger surface area. It has been found that a small increase in magnesium precipitation results in a significant NOM removal, however, the precipitation of magnesium hydroxide requires high pH conditions (Yan, et al., 2008).

1.4.4 Enhanced Coagulation/Softening Applications Dictated by the U.S. EPA

While deciding on new treatment methods depending on research results, it is important to consider enhanced coagulation or enhanced softening can involve process adjustments and can be accompanied by side effects. Some side effects will aid the treatment process while others may be damaging. These impacts include the effect of enhanced coagulation/enhanced softening on the following:

- Inorganic constituents levels (manganese, aluminum, sulfate, chloride, and sodium)
- Corrosion control
- Disinfection
- Particle and pathogen removal
- Residuals (handling, treatment, disposal)
- Operation and maintenance
- Recycle streams

Public water utilities must implement enhanced coagulation or enhanced softening to achieve percent TOC removal levels specified if (EPA 1999):

- the source water is surface water or ground water under the direct influence of surface water (Subpart H systems); and
- The utility uses conventional treatment (i.e., flocculation, coagulation or precipitative softening, sedimentation, and filtration).

Some types of treatment trains and ground water systems are excluded from the enhanced coagulation/enhanced softening requirements because: (1) their source waters are generally expected to be of a higher quality and have lower TOC levels than waters treated by conventional water treatment plants; and (2) the treatment trains are not typically configured to allow significant TOC removal (i.e., they lack sedimentation basins to settle out TOC) (EPA 1999).

The TOC removal criteria presented in Table 1.6 were selected so that 90 percent of plants operating with enhanced coagulation or enhanced softening will be able to meet the TOC removal percentages. Setting the removal criteria this way is expected to result in: (1) smaller transactional costs to the State because fewer evaluations of Step 2 experimental data will be required; and (2) reasonable increases in coagulant doses at affected plants (EPA 1999).

Table 1.6 Required Removal of TOC by Enhanced Coagulation For Plants Using Conventional Treatment: Step 1 Removal Percentages [a, b]

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO3)		
	0 to 60	**>60 to 120**	**>120**[c]
>2.0 - 4.0	35.0%	25.0%	15.0%
>4.0 - 8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

a. Enhanced coagulation and enhanced softening plants meeting at least one of the six alternative compliance criteria in Section 2.4 are not required to meet the removal percentages in this table.
b. Softening plants meeting one of the two alternative compliance criteria for softening in Section 2.4 are not required to meet the removal percentages in this table.
c. Plants practicing precipitative softening must meet the TOC removal requirements in this column.

Plants that cannot meet the removal requirements in Table 1.6 are required to conduct jar or bench scale testing under the Step 2 procedure to establish an alternative TOC removal requirement. The purpose of the jar tests is to establish an alternative TOC removal requirement, not to determine full-scale operating conditions. Once an alternative removal requirement is defined by bench- or pilot-scale testing and approved by the State, the utility is free to achieve that removal in the full-scale plant with any combination of coagulant, coagulant aid, filter aid, and acid addition. Plants may wish to perform further jar and pilot testing before implementing full-scale changes (EPA 1999). While running research projects, it is important to follow the target pH and alkalinity values. Coagulant must be added in 10 mg/L increments until the target pH shown in Table 1.7 is achieved.

Table 1.7 Target pH Under Step 2 Requirements

Alkalinity (mg/L as CaCO3)	Target pH
0 – 60	5.5
>60 – 120	6.3
>120 – 240	7.0
>240	7.5

A plant can establish compliance with the enhanced coagulation or enhanced softening TOC removal requirement if any one of the following six alternative compliance criteria is met:

1. Source water TOC < 2.0 mg/L.

2. Treated water TOC < 2.0 mg/L.

3. Raw water specific ultraviolet absorption (SUVA) is ≤ 2.0 L/mg-m.

4. Treated Water SUVA ≤ 2.0 L/mg-m.

5. Raw Water TOC < 4.0 mg/L; Raw Water Alkalinity >60 mg/L (as CaCO3); TTHM <40 μg/L; HAA5 <30 μg/L: since it is more difficult to remove

appreciable amounts of TOC from waters with higher alkalinity and lower TOC levels.

6. TTHM <40 µg/L and HAA5 <30 µg/L with only chlorine for disinfection.

Softening plants may demonstrate compliance if they meet any of the six alternative compliance criteria listed above or one of the two alternative compliance criteria listed below:

1. Softening that results in lowering the treated water alkalinity to less than 60 mg/L (as CaCO3).

2. Softening that results in removing at least 10 mg/L of magnesium hardness (as CaCO3).

1.5 The influence of pH on chemical choice

The distribution and speciation of HAAs and THMs strongly depend on the chlorination pH and the Br/TOC or Br/Cl_2 ratio (Liang and Singer, 2003). Aluminum or iron based coagulants function with different solubility and coordination chemistries depending on operating conditions. For example, higher coagulant doses provide more metal for floc formation. Lower pH values affect the metal complexes formed and reduce the charge density of humic and fulvic acids, making them more hydrophobic and absorbable (Bratby, 2006). High pH favors the formation of known by-products over unknown DBPs. The adjustment of pH also tends to affect the hydrophobic and high molecular weight fractions more than hydrophilic and low molecular weight fractions (Hua and Reckhow, 2007). An increase in pH typically results in an increase of THM formation but a decrease of total organic halide (TOX) and HAA formation (Kalscheur, et al., 2006).

The coagulation pH affects the inorganic coagulating species and the level of dissociation of the fulvic and humic acids. At a lower pH, the concentration of organic protonation increases. As a result, the coagulant demand is reduced. In addition, the increased organic protonation causes the coagulating species to become more positively charged (Crozes, et al., 1995). Consequently, adsorption becomes more favorable causing the required coagulant dosage to decrease. A low pH condition also causes the mechanisms or charge neutralization and coprecipitation by adsorption to become enhanced. The precipitation of humate or fulvate forms may be reduced, or the precipitation of organic acids can still take place but with less active sites for humates and fulvates formation (Crozes, et al., 1995).

The addition of coagulants that contain Al(III) or Fe(III) salts result in the formation of $Al(OH)_3(s)$ or $Fe(OH)_3(s)$, which are positively charged at a pH less than 8.5. With a decrease in pH, the positive charge increases. The optimal pH of coagulants using Al(III) is limited to a pH above 5, but coagulants with Fe(III) can be used at much lower pH values due to a lower solubility of $Fe(OH)_3(s)$ (DeWolfe, et al., 2003). Due to the lower solubility, ferric based coagulants can be used over a much greater range of pH values without worrying about dissolved metal concentrations in the finished water (Pernitsky, 2003).

Alkalinity is a general indication of water's buffering capacity and is related to pH, therefore the higher the alkalinity, the higher the pH of the water. Since metal coagulants are acidic, both ferric and alum consume alkalinity as they form floc which causes the water's pH to drop. High alkalinity waters may require a higher dosage of coagulant to decrease the pH to favor coagulation (Pernitsky, 2003). For low alkalinity water, the addition of a coagulant may consume all the alkalinity, therefore decreasing the pH too low for effective treatment. Since metal coagulants work by reacting with the water's alkalinity, caustic soda (sodium hydroxide) or soda ash (sodium carbonate) is sometimes added for enough alkalinity to be present (Pizzi, 2002).

During enhanced softening with an increased pH, both $CaCO_3$and $Mg(OH)_2$ are positively charged at higher lime ($Ca(OH)_2$) and NaOH doses, therefore yielding a greater affinity for adsorbing negatively charged organic molecules (Russell, et al., 2009).

1.6 Chemical choice as influenced by the amount of natural organic matter (NOM) in your source water

Natural organic materials (NOM) are present to various degrees in all water supplies. It is a major component of total organic carbon (TOC) concentration and has been identified as the principal precursor in the formation of HAAs and THMs (Liang and Singer, 2003). Halogenated DBP formation decreases with the activated, or electron rich, aromatic content of NOM (Reckhow, et al., 1990). The effectiveness of removing NOM varies with the nature of the NOM, such as its molecular weight, charge density, and polarity, and with properties of the raw water such as turbidity and hardness (Bolto, et al., 2002). The effectiveness of a given coagulant to remove NOM varies depending upon the active charge density, floc surface area available for adsorption, and the nature of the bonds between the organics and the metal hydroxide flocs (Crozes, et al., 1995).

Typically, coagulation removes humic and high molecular weight organic matter better than it removes non humic and low molecular weight organic matter. In addition, aromatic materials are removed more effectively by coagulation than other NOM fractions. In addition, hydrophobic organic molecules are preferentially removed over their hydrophilic counterparts (Stanley, 2000).

1.7 Appropriate Modifications for DBP Precursor Reduction

In order to be effective, the EPA recommends first investigating what minor changes can be made to a treatment facility's operation with the existing coagulant before changing the primary coagulant. These minor changes include lowering or raising coagulant pH, increasing coagulant concentration, changing the feed system or mixing regimes, or altering pretreatment chemicals (DeWolfe, et al., 2003).

In a study by DeWolfe, et al (2003), pre-neutralized coagulants, such as aluminum chlorohydrate (ACH) or polyaluminum chloride (PACl) have been shown most effective for spring water with very low TOC and moderate alkalinity. ACH, alum, and PACl were most effective for charge-neutralization for water from a surface reservoir with moderate

TOC, low SUVA, and low alkalinity. Alum and ferric chloride has been shown to work best for river water that was high in TOC and SUVA with low alkalinity.

1.8 Oxidation-Reduction Potential

Oxidation-reduction potential has been used for many years in facilities that process wastewater generated by metal finishing plants, but only recently has it become prominent in municipal wastewater treatment plants. Important oxidation-reduction (redox) reactions in wastewater treatment systems include nitrification, denitrification, biological phosphorus removal, and the removal of carbonaceous biochemical oxygen demand (cBOD). ORP readings are instantaneous and easy to perform, and like all sampling measurements taken by operators, they are snapshots in time that can indicate process efficiency and identify treatment problems before they affect effluent quality. By monitoring the ORP of wastewater, an operator can determine what biological reaction is occurring and if operational conditions should be changed to promote or prevent that reaction. Figure 1-7 indicates redox potential ranges for wastewater treatment processes. These values give a general idea of reactions which occur at various redox ranges (W. Stumm, 1996).

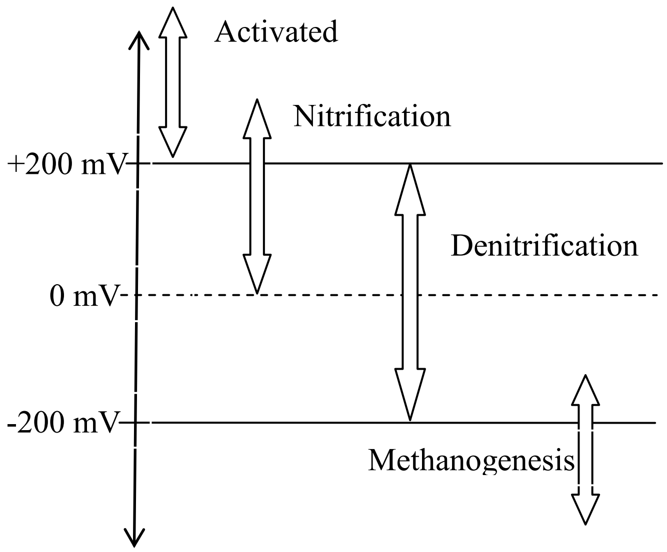

Figure 1-7: Redox potential ranges (mV) for typical wastewater processes

(Modified from Stumm and Morgan 1996 and Byl and Williams 2000)

Though this technology has demonstrated efficiency for wastewater treatment, redox potential has been minimally explored for drinking water treatment. Its ease of use for determining biological reactions in wastewater could be emulated if a strategy could be established for determining enhanced chemical reactions occurring in drinking water treatment (Gerardi, 2007).

Oxidation-reduction reactions, or “redox” reactions, are an essential part of water treatment. Compounds containing carbon, sulfur, nitrogen, oxygen and metals with more than one oxidation state, such as chromium, iron and manganese, encounter processes which change the oxidation state and substantially alter their chemical property. Oxidation-reduction reactions are represented by balanced chemical equations containing two “half” reactions. The first half is the oxidation state which is where the substance loses or donates and electron. The second half is the reduction state which is when the substance gains or accepts electrons (Alley, 2000).

An environment that accepts electrons from a normal hydrogen electrode is a half cell that is defined as having a positive redox potential; any system donating electrons to the hydrogen electrode is defined as having a negative redox potential. E_h is measured in millivolts (mV). A high positive E_h indicates a more oxidative environment where the constituents have a greater affinity for electrons. A low negative E_h indicates a strong reducing environment, such as free metals (Garrels and Christ, 1990). Measurement of redox potential, or E_h, provides a tool for monitoring changes in the system. Because redox potential indicates a transfer of electrons similar to the transfer of H^+ indicated by pH, in most cases one expects that the E_h will trend as the inverse of pH. However, because the coagulation step in drinking water treatment involves destabilization and stabilization processes, changes in E_h may also track these changes when the pH remains constant. Therefore the E_h condition may provide some indications of how effective the coagulation process will be with respect to removal of organic precursors for disinfection by-products (Evangelou, 1998).

Oxidation reduction potential (ORP) is a measure of a water system’s capacity to either release or gain electrons in chemical reactions. Oxidation is the addition of oxygen, removal of hydrogen or removal of electrons whereas reduction is the removal of oxygen, addition of hydrogen or addition of electrons. Water containing the salts of metals, such as Fe^{2+} or Fe^{3+}, and strong oxidizing and reducing agents, such as chlorine and sulfide ion, are ideal candidates for the determination of ORP. Thus, ORP can sometimes be utilized to track the metallic pollution of ground or surface water, or to determine the chlorine content of wastewater effluent.

More contaminants in the water may result in less dissolved oxygen because microorganisms are consuming both the organics and the oxygen and tend to result in lower ORP levels. The higher the ORP level, the more oxidative the conditions, which gives water the ability to destroy foreign contaminants such as microbes or transform carbon based contaminants. The electrode has two components: a measuring half cell comprised of platinum metal immersed in the solution in which the redox reaction is taking place, and a reference half cell (sealed gel-filled Ag/AgCl) to which the platinum half cell is referenced. The measuring platinum electrode serves as an electron donor or electron acceptor depending upon the test solution and the reference electrode is used to supply a constant stable output for comparison. The ORP electrode measures the redox potential, the difference in the voltage generated by the platinum measuring electrode and the voltage produced by the reference electrode in the range of -450 to +1100 mV (Center for Microcomputer Applications, 2004). Lower, or more negative, ORP values indicate reducing conditions whereas higher, or more positive, ORP values indicate oxidative conditions.

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Chapter 2: Enhanced Coagulation and Enhanced Softening Response to DBP Precursor Reduction

Abstract

The United States Environmental Protection Agency (EPA) defines enhanced coagulation as the process of improving the removal of disinfection by-product (DBP) precursors in a conventional water treatment plant and enhanced softening as the improved removal of DBP precursors by precipitative softening. The effects of enhanced coagulation and enhanced softening on two surface waters receiving water from reservoirs, one surface water receiving water from a lake, and one ground water receiving water from alluvial wells is presented. DBP precursor reduction was determined through UV-254 and dissolved organic carbon (DOC) analysis. Results indicated enhanced coagulation was more effective removing DBP precursors from waters with higher initial UV-254 absorbance values and enhanced softening was more effective for waters with lower initial UV-254 absorbance values.

2.1 Introduction

The research project was created as a response to four drinking water treatment facilities in Missouri whose potential for DBP limit violation was high. The overall goal was to determine if enhanced coagulation and/or enhanced softening were feasible methods in their treatment process to result in reduction of DBP precursors and ultimately decrease a potential violation of EPA regulations. Meeting disinfection by-product and total trihalomethane regulations are the main focus along with following TOC monitoring, enhanced coagulation and enhanced softening guidelines, and testing protocols advised by the EPA.

In order to determine DBP precursor reduction, UV-254 and DOC were measured. UV-254 indicates the aromatic organic content by measuring how much UV light is absorbed by the sample at a wavelength of 254 nm (Glover and Hauger, 2008). Some organic compounds commonly found in water, such as lignin, tannin, humic substances, and various aromatic compounds, strongly absorb ultraviolet (UV) radiation (Alley 2000). Lower adsorption values are an indication of lower concentrations of each of these compounds. Unlike UV-254, which measures the aromatic character of humic and fulvic acids by the amount of light at 254 nm wavelength is absorbed by the sample, DOC measures organic content in a sample by removing the inorganic carbon portion first and then measuring the leftover carbon (Alley, 2000).

Traditionally, coagulation with hydrolyzing metal coagulants, such as ferric chloride and alum, followed by sedimentation and granular filtration has been used to remove suspended particles. Enhanced coagulation uses higher dosages of metal salt coagulant, adjusts the pH of the source water, or both to remove NOM in addition to suspended particles (Vrijenhoek, et al., 1998). In order to achieve more efficient DOC removal, enhanced coagulation utilizes changes in pH and coagulant dose.

Enhanced softening is defined as the modification of chemical dosages for the increased removal of DBP precursors during the softening process (Thompson, et al., 1997). Enhanced softening therefore involves lime addition for water softening along with the addition of a coagulant.

Jar testing is used to simulate full-scale plant operations and model typical treatment plant conditions. These jar tests imitated the rapid mix, flocculation, and settling steps of a treatment process in order to determine the effectiveness of enhanced coagulation and enhanced softening on various source waters.

2.2 Materials and Methods

This section explains the materials used in the experiments and analytical procedures used in the enhanced coagulation and enhanced softening jar tests. The treatment studies were conducted on four Missouri waters to quantify the removal of natural organic matter by primarily measuring the reduction of dissolved organic carbon (DOC) and UV-254 and verified by the corresponding differences in disinfection by-product (DBP) concentration results.

2.2.1 Natural Water Collection and Storage

Water samples were collected from four small-to-medium drinking water supplies in Missouri which serve populations from 2,000 to 110,000 persons. The sites selected included lakes, rivers and relatively shallow community water supply wells (at approximately 130 feet below grade). Twenty liters of water (in 20 L carboys) was collected from each type of water source between April – May 2010. All carboys were pre-cleaned with MU Distilled water (DW) and within 24 hours, the collected water was returned and refrigerated in the dark at 10°C.

2.2.2 Reagents

A 35% Ferric Chloride ($FeCl_3$) stock solution and a 48% Liquid Alum ($Al_2(SO_4)_3 \cdot 14(H_2O)$) solution (both from Hawkins, Inc.) were used in the enhanced coagulation and enhanced softening experiments. Lime used in the enhanced softening experiments was 12% CaO by weight (generated by a lime slaker at the City of Columbia Water Treatment Facility). A detailed supplies list can be found in Appendix A.

2.2.3 Jar Testing

Experiments are run following a modified version of the standard jar test procedure (ASTM Standard D2035 (ASTM International, 2008)). Six 2-liter capacity square beakers (Bker^2, WU-99520-50, Cole-Parmer) are filled with 1 L of raw water from the treatment facility and dosed with prescribed concentrations of coagulant and/or lime

(Figure 2-1). Jars are then placed on the jar testing apparatus (Phipps and Bird PB-700 Jar Tester) and mixed for 60 seconds at 100 rpm to disperse ions then for 30 minutes at 35 rpm to form flocs. The stirrers are then turned off and the solids are allowed to settle for 30 minutes. Turbidity, UV-254, and dissolved organic carbon (DOC) are tested for each sample in addition to initial and final pH.

Figure 2-1: Jar Tester Apparatus

Raw water samples without chemical addition follow the same procedure and serve as a control or baseline sample to which the treated water samples may be compared. Table 2.1 lists the chemicals and chemical dosages which are used in the enhanced coagulation and enhanced softening jar tests. Dosages of coagulant used for these four facilities ranged from 30 – 150 mg/L, therefore coagulant dosages were chosen to closely imitate these values. From previous jar tests, 100 mg/L is theoretically an ideal coagulant dose, and was therefore used in the enhanced softening tests also along with lime. Lime dosages were chosen in order to have a wide range of pH values from 8 – 11.5 in order to determine if pH affects reduction of DBP precursors.

Table 2.1 Jar Testing Chemical Use Matrix

Chemical	Dosage (mg/L)	Analysis
Ferric Chloride	50 100 150	pH, turbidity, dissolved organic carbon (DOC), UV-254
Liquid Alum	50 100 150	pH, turbidity, dissolved organic carbon (DOC), UV-254
Ferric Chloride + Lime	100 + 60 100 + 180 100 + 300	pH, turbidity, dissolved organic carbon (DOC), UV-254
Liquid Alum + Lime	100 + 60 100 + 180 100 + 300	pH, turbidity, dissolved organic carbon (DOC), UV-254

2.2.4 UV-254

To measure UV-254 absorbance to indicate aromatic organic content, Standard Methods 5910 B was followed. Treated water samples from each of the jars are filtered through a 0.45 µm glass fiber filter disk (FisherBrand 09-719-2E), poured into a 1 cm quartz cell (Fischer Scientific #14385902C), and then run on a 50 UV-Visible Spectrophotometer (Cary 50) at 254 nm.

2.2.5 DOC Analysis

To quantify the amount of natural organic matter in a water source, dissolved organic carbon (DOC) analysis is performed. DOC analysis was performed following Standard Methods 5310 B: high temperature combustion method (APHA, et al., 1998). DOC analysis was performed on a Shimadzu TOC-Vcpn instrument with an ASI-V autosampler.

2.2.6 Turbidity

Turbidity consists of suspended particles in the water that may hinder disinfection by shielding microbes, some of them perhaps pathogens, from the disinfectant (Hauser, 2000). The federal limits are 0.5 NTU in 95% of samples tested reported as a monthly average. Reportable readings are taken at the entrance to the water distribution system and may never exceed 5 NTU (Hauser, 2000). However, it is important to note that low turbidity values do not necessarily mean decreased DOC. Though suspended particles are removed, soluble organics may still be present in the water. Standard Method 2130B (APHA, et al., 1998) was followed to measure turbidity using a Hach 2100P turbidimeter.

2.3 Influent Water Characteristics

Water samples from the four Missouri communities came from both surface and ground water. Surface water 1 (SW1) and surface water 2 (SW2) are both lakes/impoundments receiving runoff from the surrounding watershed, surface water 3 (SW3) is indirectly a river because the treatment facility pumps water from the river and stores it in reservoirs before treatment, and the fourth water source is an alluvial aquifer (AGW). As seen in Table 2-2, the facilities ranged in turbidity, UV-254, dissolved organic carbon (DOC) and alkalinity.

Table 2.2 Water qualities and sources of water samples

Source Water	pH	Turbidity (NTU)	UV-254 (abs/cm)	DOC (mg/L)	Alkalinity (mg/L)
Surface Water 1	8.03 ±0.2	11.4 ±5.6	0.199 ±0.08	6.23 ±0.2	62
Surface Water 2	7.7 ±0.1	17.8 ±2.4	0.262 ±0.005	6.25 ±0.9	46
Surface Water 3 (River to Reservoir)	8.23 ±0.2	3.3 ±1.2	0.076 ±0.005	4.12 ±0.3	168.3 ±3.5
Alluvial Groundwater	7.73 ±0.05	29.1 ±5.2	0.047 ±0.006	2.64 ±0.2	252

Typically, coagulation removes humic and high molecular weight organic matter better than it removes non humic and low molecular weight organic matter. In addition, aromatic materials are removed more effectively by coagulation than other NOM fractions. In addition, hydrophobic organic molecules are preferentially removed over their hydrophilic counterparts (Stanley, 2000).

Hydrophobic NOM primarily consists of humic acid and fulvic acid and is rich in aromatic carbon, phenolic structures, and conjugated double bonds, while hydrophilic NOM contains more aliphatic carbon and nitrogenous compounds. Since UV-254 detects the amount of aromatic organic compounds, it can be seen in Table 2.2 that SW1 and SW2 have higher concentrations of aromatic organic compounds in their influent water than either the river or the alluvial aquifer. These four waters were chosen because the treatment facilities using them are a turbidity removal process for SW1 and SW2 versus the lime softening process used by SW3 and AGW treatment facilities.

2.4 Results

Once the jar tests were complete, the final ranges of pH values were measured. In addition, the percent removal for UV-254 and dissolved organic carbon (DOC) was determined by the difference between the initial water quality and the final water quality divided by the initial water quality times 100%. These results can be seen in Table 2.3 (pH), Table 2.4 (UV-254) and Table 2.5 (DOC). Below each table are details about what chemical combinations were used in each jar.

Table 2.3: Final pH for Enhanced Coagulation/Softening Experiments

	Final pH											
	$FeCl_3$ only			**$FeCl_3$ + Lime**			**Alum only**			**Alum + Lime**		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
SW1	7.1	6.5	5.0	9.3	11.2	11.5	7.8	7.3	6.8	9.5	11.3	11.5
SW2	6.9	5.8	3.5	9.4	11.1	11.5	7.7	6.6	6.9	9.8	11.2	11.5
SW3	7.4	7.1	6.8	8.3	10.0	11.0	7.9	7.6	7.2	8.4	9.9	11.2
AGW	7.3	7.2	7.0	8.0	8.6	10.2	7.6	7.4	7.2	8.1	8.9	10.2

1 – 50 mg/L $FeCl_3$; **2** – 100 mg/L $FeCl_3$; **3** – 150 mg/L $FeCl_3$; **4** – 100 mg/L $FeCl_3$ + 60 mg/L CaO; **5** – 100 mg/L $FeCl_3$ + 180 mg/L CaO; **6** – 100 mg/L $FeCl_3$ + 300 mg/L CaO; **7** – 50 mg/L Alum; **8** – 100 mg/L Alum; **9** – 150 mg/L Alum; **10** – 100 mg/L Alum + 60 mg/L CaO; **11** – 100 mg/L Alum + 180 mg/L CaO; **12** – 100 mg/L Alum + 300 mg/L CaO

Table 2.4: Reduction of UV-254 for enhanced coagulation/softening experiments

	% Reduction UV-254											
	$FeCl_3$ only			**$FeCl_3$ + Lime**			**Alum only**			**Alum + Lime**		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
SW1	17.3	***81.3***	75.9	51.4	79.2	81.3	33.9	75.1	79.2	12.6	65.6	67.6
SW2	59.0	***90.7***	87.0	6.27	77.6	81.7	60.3	75.5	78.3	46.5	71.2	73.2
SW3	25.9	36.0	49.7	23.2	32.8	***58.9***	16.1	32.1	41.4	19.2	41.6	41.7
AGW	25.3	39.8	45.8	25.9	27.0	***58.2***	7.1	19.8	24.9	3.9	11.2	51.4

1 – 50 mg/L $FeCl_3$; **2** – 100 mg/L $FeCl_3$; **3** – 150 mg/L $FeCl_3$; **4** – 100 mg/L $FeCl_3$ + 60 mg/L CaO; **5** – 100 mg/L $FeCl_3$ + 180 mg/L CaO; **6** – 100 mg/L $FeCl_3$ + 300 mg/L CaO; **7** – 50 mg/L Alum; **8** – 100 mg/L Alum; **9** – 150 mg/L Alum; **10** – 100 mg/L Alum + 60 mg/L CaO; **11** – 100 mg/L Alum + 180 mg/L CaO; **12** – 100 mg/L Alum + 300 mg/L CaO

Table 2.5: Reduction of DOC for enhanced coagulation/softening experiments

	% Reduction DOC											
	$FeCl_3$ only			**$FeCl_3$ + Lime**			**Alum only**			**Alum + Lime**		
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
SW1	25.8	***58.8***	48.2	26.7	54.4	58.5	16.6	45.5	50.3	8.3	36.8	41.8
SW2	44.5	***66.2***	57.0	41.4	58.9	54.9	26.6	43.5	42.2	31.5	47.8	42.4
SW3	13.9	24.5	35.3	21.1	***44.4***	29.6	18.9	28.7	28.3	11.4	2.2	32.4
AGW	16.9	16.9	24.4	11.9	11.3	***31.3***	-6.0	-1.2	15.7	-8.1	-2.1	26.1

1 – 50 mg/L $FeCl_3$; **2** – 100 mg/L $FeCl_3$; **3** – 150 mg/L $FeCl_3$; **4** – 100 mg/L $FeCl_3$ + 60 mg/L CaO; **5** – 100 mg/L $FeCl_3$ + 180 mg/L CaO; **6** – 100 mg/L $FeCl_3$ + 300 mg/L CaO; **7** – 50 mg/L Alum; **8** – 100 mg/L Alum; **9** – 150 mg/L Alum; **10** – 100 mg/L Alum + 60 mg/L CaO; **11** – 100 mg/L Alum + 180 mg/L CaO; **12** – 100 mg/L Alum + 300 mg/L CaO

Reduction of UV-254 (Figure 2-2) and reduction of DOC (Figure 2-3) are important indicators for reduction of DBP precursors. UV-254 reduction indicates the aromatic organic matter reduced by the treatment techniques. Since aromatic organic matter is a large contributor in the formation of THMs, lower UV-254 values will likely indicate a lower potential for formation of disinfection by-products. Dissolved organic carbon reduction is also an indicator of how much organic carbon is reduced in the water and therefore decreases reactions with chlorine to form DBPs.

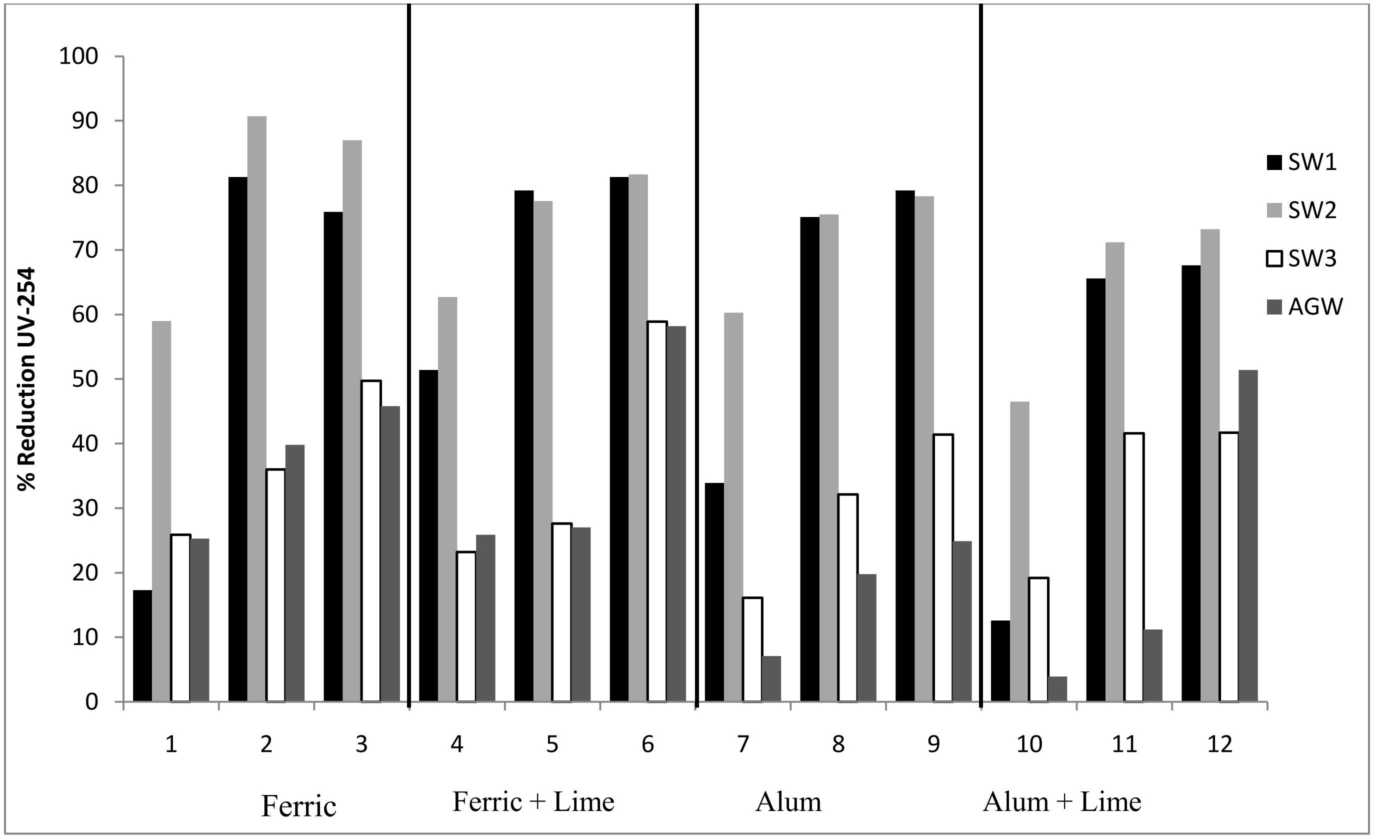

Figure 2-2: Percent Reduction UV-254 for Enhanced Coagulation/Softening

1 – 50 mg/L FeCl$_3$; **2** – 100 mg/L FeCl$_3$; **3** – 150 mg/L FeCl$_3$; **4** – 100 mg/L FeCl$_3$ + 60 mg/L CaO; **5** – 100 mg/L FeCl$_3$ + 180 mg/L CaO; **6** – 100 mg/L FeCl$_3$ + 300 mg/L CaO **7** – 50 mg/L Alum; **8** – 100 mg/L Alum; **9** – 150 mg/L Alum; **10** – 100 mg/L Alum + 60 mg/L CaO; **11** – 100 mg/L Alum + 180 mg/L CaO; **12** – 100 mg/L Alum + 300 mg/L CaO

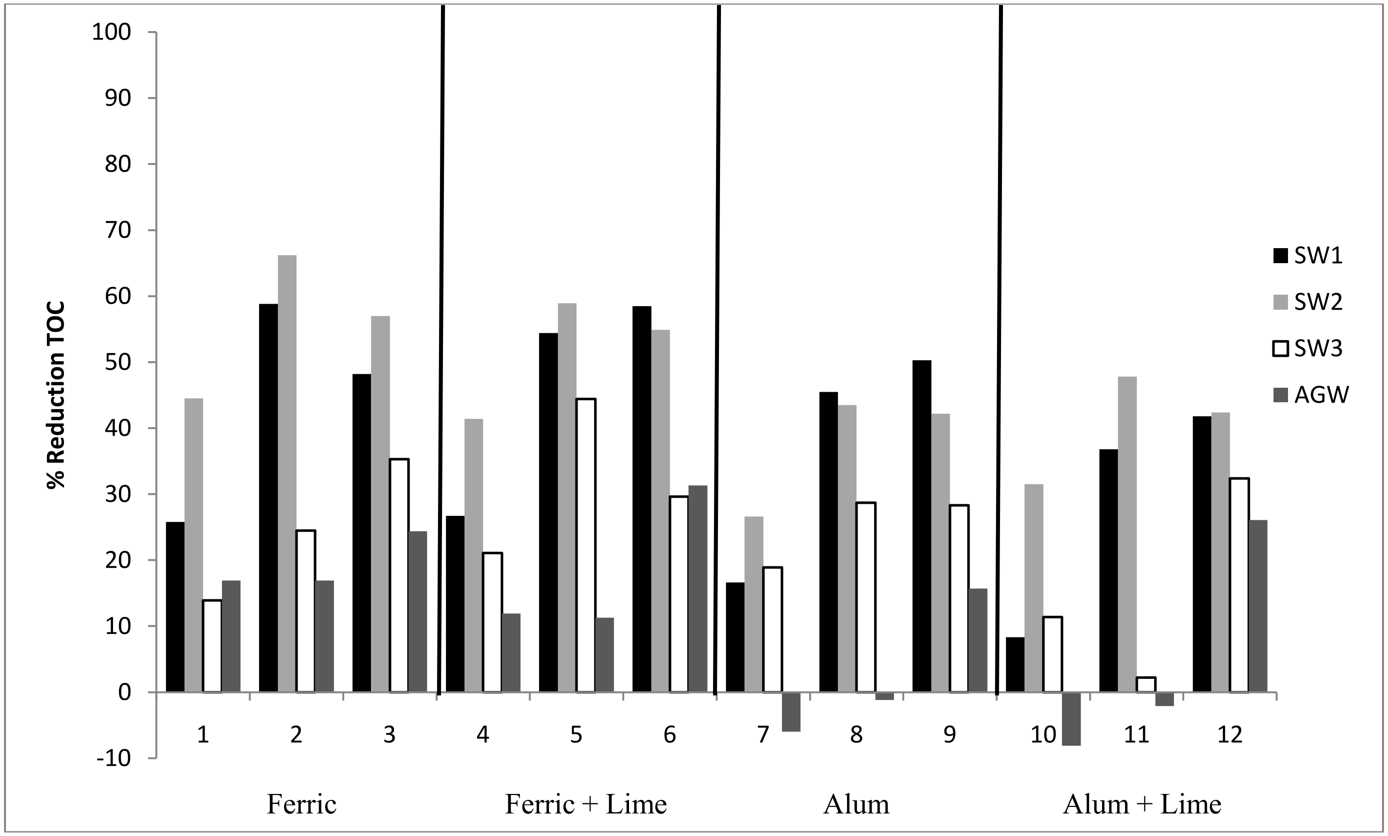

Figure 2-3: Percent Reduction DOC for Enhanced Coagulation/Softening

1 – 50 mg/L $FeCl_3$; **2** – 100 mg/L $FeCl_3$; **3** – 150 mg/L $FeCl_3$; **4** – 100 mg/L $FeCl_3$ + 60 mg/L CaO; **5** – 100 mg/L $FeCl_3$ + 180 mg/L CaO; **6** – 100 mg/L $FeCl_3$ + 300 mg/L CaO **7** – 50 mg/L Alum; **8** – 100 mg/L Alum; **9** – 150 mg/L Alum; **10** – 100 mg/L Alum + 60 mg/L CaO; **11** – 100 mg/L Alum + 180 mg/L CaO; **12** – 100 mg/L Alum + 300 mg/L CaO

Figures 2-2 and 2-3 also show SW1 and SW2 had much greater removal percentages than AGW and SW3. These results are due to the higher aromatic organic compounds present in SW1 and SW2's influent water which is more amenable to removal by coagulation. As the coagulant dosage increased, the removal efficiency for all the facilities increased. SW3 and AGW showed an increased removal with enhanced softening (6) since their source waters contain lower UV-254 absorbance values (less aromatics detected) and therefore organics are easier to remove by adsorption onto the lime precipitates.

Overall, ferric chloride showed a higher percent reduction in UV-254 and DOC than liquid alum. Little is still known about the difference in effectiveness of various coagulants based upon source water characteristics. However, the increased removal by ferric chloride compared to liquid alum could be due to the larger surface area and positive charges from the ferric hydroxide polymer formed when ferric chloride dissolves in water. The hydrophobic hydroxide readily absorbs onto the organic anionic particle surface causing charge neutralization and precipitation of the iron cations and organic anions. Iron has a strong tendency to form insoluble complexes with ligands, especially polar molecules with oxygen-containing functional groups such as hydroxyl or carboxyl (Dominguez, et al., 2005).

Percent reduction in UV-254 is a better indicator of aromatic organic reduction, which is of greater concern since hydrophobic NOM (containing aromatic and phenol groups) is the largest contributor to DBP formation. However, there is a direct correlation between DOC reduction and UV-254 reduction (Figure 2-4), though UV-254 shows higher removal rates than DOC. A slope of one (1) would indicate the reduction of DOC is proportionate to the reduction of UV-254. Therefore, a slope of less than one favors greater UV-254 percent removals when compared to DOC percent removal. Since UV-254 indicates the aromatic organic fraction of DOC, UV-254 is a better indicator of NOM reduction.

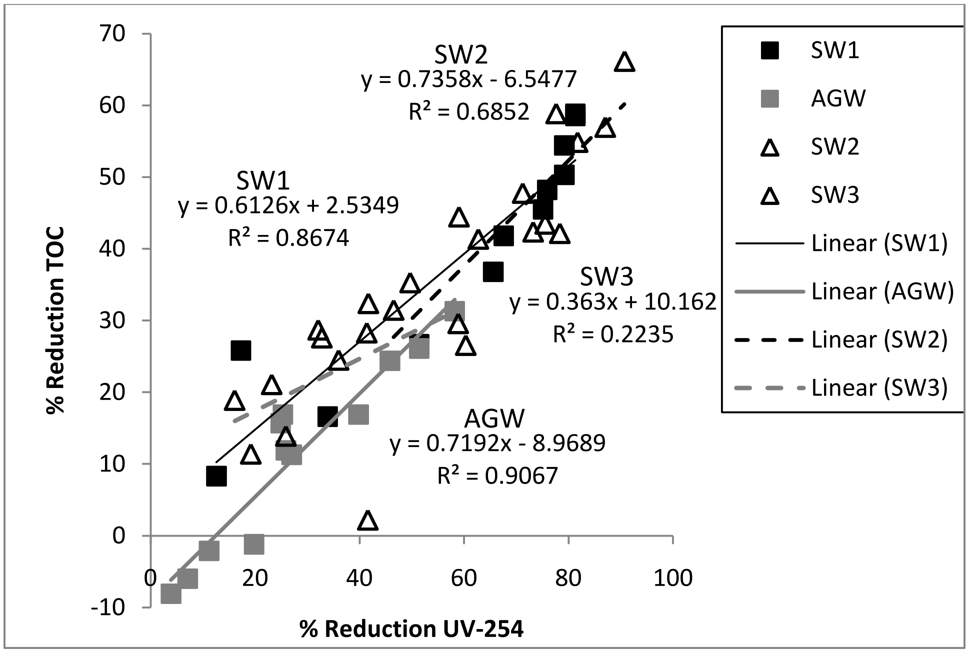

Figure 2-4: Percent Reduction DOC versus Percent Reduction UV-254

2.5 Conclusion

The greatest UV-254 and DOC removal was seen when using 100 mg/L ferric chloride for both SW1 and SW2. Increasing the dosage of ferric chloride to 150 mg/L caused an overdose of coagulant causing charge reversal and colloid restabilization therefore reduced the efficiency of precursor removal. For AGW and SW3, 100 mg/L ferric chloride along with 300 mg/L lime showed the greatest UV-254 and DOC removal percentage, with the exception of 100 mg/L ferric chloride with 180 mg/L lime for SW3's greatest DOC removal.

These experiments demonstrated the effectiveness of enhanced coagulation and enhanced softening on four Missouri waters. As seen by the results, ferric chloride showed a greater precursor removal than liquid alum. Precipitation of NOM is the formation of an aluminum or iron humate or fulvate with a lower solubility product, therefore causing its precipitation into a solid form (Crozes, et al., 1995). These higher removal efficiency of ferric chloride compared to liquid alum could be due to the lower solubility of $Fe(OH)_3(s)$ and therefore an increased precipitation of NOM (DeWolfe, et al., 2003).

The percent reduction of UV-254 and DOC was much greater for SW1 and SW2 due to the higher raw water UV-254 absorbance values. It can be seen by the results that waters with higher concentrations of detectable aromatics are more easily removed by coagulation. The results also indicated that lime added in addition to a coagulant showed the greatest reduction for UV-254 and DOC in waters with lower raw water UV-254 values since waters with less aromatic organics are more amenable for precursor removal by adsorption.

As seen by these experiments, general guidelines can be established for the effectiveness of enhanced treatments on a facility. Organics in the source water with a higher UV-254 absorbance value, indicating sufficient concentrations of aromatic organics, is easier to be removed by higher concentrations of coagulant. Organics in source water with lower UV-254 absorbance values respond better to lime softening and high dosages of coagulant.

2.6 References

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Chapter 3 Use of Oxidation-Reduction Potentials During Enhanced Coagulation/Softening In Four Missouri Communities

Abstract:

Oxidation reduction potential (ORP) has demonstrated efficiency for wastewater treatment, where the treatment process is dominated by microorganism-mediated oxidation and reduction reactions. Familiarity with water environmental conditions (indicated in part by ORP measurements) allows facility designers and operators to anticipate operating conditions more suited for enhanced process function. Therefore measurement of ORP, or E_h*, provides a tool for monitoring and/or making changes in the system but has been minimally explored for drinking water treatment. Since redox potential indicates a transfer of electrons similar to the transfer of* H^+ *indicated by pH, in general, it is expected that the* E_h *will trend as the inverse of pH when explicit oxidation or reduction reactions are not taking place. However, this research presents that under constant pH conditions the* E_h *readings seem to indicate the destabilization and stabilization processes expected during the coagulation step in drinking water treatment. Comparison of the* E_h *readings at the start of various treatment stages to the end provides some indication of the effectiveness the enhanced coagulation or enhanced softening process on the removal of organic precursors for disinfection by-products.*

3.1 Introduction

The goal of the overall research project was to determine if oxidation-reduction (redox) potential, or E_h, could be used as an indicator of process efficiency and DBP precursor removal during enhanced coagulation and enhanced softening. These experiments include testing of two coagulations, ferric chloride and liquid alum, in addition to combining the coagulants with lime in order to find the combination with the most favorable DOC and UV-254 reduction under various pH and redox conditions. The observation of the oxidation-reduction potential in this research is to determine if the environmental condition of the water prior to chemical treatment can be correlated to the success of efforts to lower the amount of dissolved organic carbon (DOC) from four cities in Missouri.

Oxidation-reduction potential has been shown to have significant applications in municipal wastewater treatment plants due to its instantaneous readings. Readings can indicate process efficiency and identify treatment problems before they affect effluent quality. Though this technology has demonstrated efficiency for wastewater treatment, redox potential has been minimally explored for drinking water treatment. Its ease of use for indicating the influence of biological reactions in wastewater could be imitated if a strategy could be established for determining the effectiveness of enhanced chemical reactions occurring in drinking water treatment (Gerardi, 2007).

An environment that accepts electrons from a normal hydrogen electrode is a half cell that is defined as having a positive E_h and indicates a more oxidative environment where the constituents have a greater affinity for electrons. Any system donating electrons to the hydrogen electrode is defined as having a negative E_h and indicates a strong reducing environment, such as free metals (Garrels and Christ, 1990). E_h is measured in millivolts (mV). Measurement of redox potential, or E_h, provides a tool for monitoring changes in the system. Because redox potential indicates a transfer of electrons similar to the transfer of H^+ indicated by pH, in most cases one expects that the E_h will trend as the inverse of pH. However, because the coagulation step in drinking water treatment involves destabilization and stabilization processes, changes in E_h may also track these changes when the pH remains constant. Therefore the E_h condition may provide some indications of how effective the coagulation process will be with respect to removal of organic precursors for disinfection by-products (Evangelou, 1998).

Enhanced coagulation optimizes coagulant dosage and pH to include organics removal, such as removal of THM precursors, in addition to particulate matter removal. With increased addition of coagulant, the pH of the water typically decreases (DeWolfe, et al., 2003). However, with enhanced softening, the coagulant is added along with lime and the pH greatly increases (Thompson, et al., 1997). The enhanced softening experiments are to test whether the amount of natural organic matter (NOM) may be lowered in the water column by adsorption onto calcium precipitates and the response of redox potential to these reactions (Bob and Walker, 2001).

When alum (Eqn. 1) and ferric chloride (Eqn. 2) are added to water with natural bicarbonate alkalinity, the following reactions occur:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(HCO_3)_2 = 2Al(OH)_{3(s)} + 3CaSO_4 + 6CO_{2(g)} + 18H_2O \quad \text{(Eqn. 1)}$$

$$2FeCl_3 + 3Ca(HCO_3)_2 = 2Fe(OH)_{3(s)} + 3CaCl_2 + 6CO_{2(g)} \quad \text{(Eqn. 2)}$$

The aluminum and iron cations undergo hydration reactions to form the insoluble metal hydroxides $Al(OH)_3$ and $Fe(OH)_3$, respectively (Gabelich, et al., 2002).

3.2 Materials and Methods

This section explains the materials used in the experiments and analytical procedures used in the enhanced coagulation and enhanced softening oxidation-reduction potential profiling jar tests. The treatment studies were conducted on four Missouri waters to quantify the removal of natural organic matter by measuring the reduction of both dissolved organic carbon (DOC) and UV-254.

3.2.1 Natural Water Collection and Storage

Water samples were collected from four small-to-medium drinking water supplies in Missouri which serve populations from 2,000 to 110,000 persons. The various source waters are lakes, rivers and deep wells. Twenty liters of water (20 L carboys) were collected from each treatment facility. Water samples were collected from April – May 2010. All carboys were pre-cleaned with MU Distilled water (DW) before collection and, within 24 hours, the collected water was returned and refrigerated in the dark at 10°C.

3.2.2 Reagents

A 35% Ferric Chloride ($FeCl_3$) stock solution and a 48% Liquid Alum ($Al_2(SO_4)_3 \cdot 14(H_2O)$) solution (both from Hawkins, Inc.) were used in the enhanced coagulation and enhanced softening experiments. Lime used in the enhanced softening experiments was 12% CaO by weight (generated by a lime slaker at the City of Columbia Water Treatment Facility). A detailed supplies list can be found in Appendix B.

3.2.3 Jar Testing

Experiments are run following a modified version of the standard jar test procedure (ASTM Standard D2035 (ASTM International, 2008)). Six 2-liter capacity square beakers (Bker^2, WU-99520-50, Cole-Parmer) are filled with 1 L of raw water from the selected source water and dosed with prescribed concentrations of coagulant and/or lime. From previous experiments, a coagulant dose of 100 mg/L was chosen since it was effective at reducing DBP precursors. The lime concentration of 300 mg/L was chosen to get a pH value of approximately 11 in order to test the effectiveness of a significant increase in pH. After dosing, the initial pH is measured and the ORP electrode is placed in the jar (Figure 3-1).

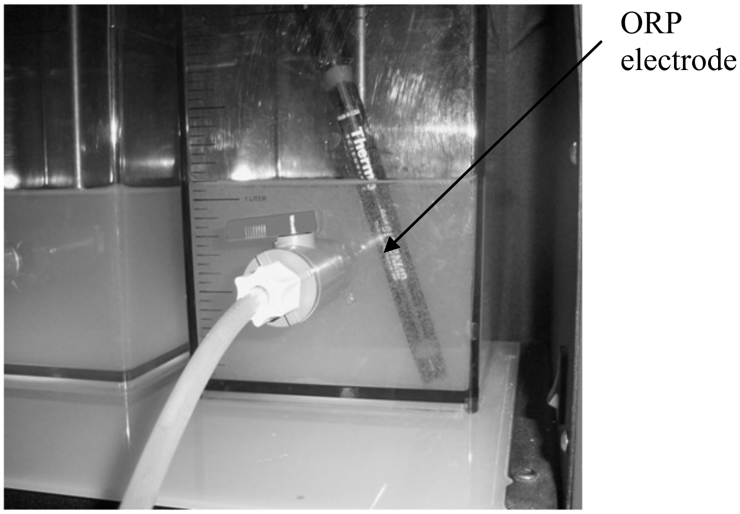


Figure 3-1 Jar Test with ORP Probe

Jars are then placed on the jar testing apparatus (Phipps and Bird, PB-700 Jar Tester) and mixed for 60 seconds at 100 rpm to disperse ions then 30 minutes at 35 rpm to form flocs. The stirrers are then turned off and the solids are allowed to settle for 30 minutes. Turbidity, pH, UV-254, and dissolved organic carbon (DOC) of filtered, settled water are tested for each sample and ORP verses time is transcribed and plotted.

Table 3.1 lists the chemicals and chemical dosages which were used in the redox potential profiling jar tests.

Table 3.1: Jar Testing Chemical Use Matrix

Chemical	Dosage (mg/L)	Analysis
Ferric Chloride	100	pH, turbidity, DOC, UV-254, ORP
Liquid Alum	100	pH, turbidity, DOC, UV-254, ORP
Ferric Chloride + Lime	100 + 300	pH, turbidity, DOC, UV-254, ORP
Liquid Alum + Lime	100 + 300	pH, turbidity, DOC, UV-254, ORP

3.2.4 UV-254

UV-254 absorbance measurements indicate aromatic organic content (Standard Methods 5910 B (APHA, et al., 1998)). Treated water samples from each of the jars are filtered through a 0.45 μm glass fiber filter disk (FisherBrand 09-719-2E), poured into a 1 cm quartz cell (Fischer Scientific #14385902C), and then run on a 50 UV-Visible Spectrophotometer (Cary 50) at 254 nm.

3.2.5 DOC Analysis

To quantify the amount of natural organic matter in a water source, dissolved organic carbon (DOC) analysis is performed (Standard Methods 5310 B: high temperature combustion method; (APHA, et al., 1998)). DOC analysis was performed on a Shimadzu TOC-Vcpn instrument with an ASI-V autosampler.

3.2.6 Turbidity

Turbidity consists of suspended particles in the water that may hinder disinfection by shielding microbes, some of them perhaps pathogens, from the disinfectant (Hauser, 2000). The federal limits are 0.5 NTU in 95% of samples tested reported as a monthly average. Reportable readings are taken at the entrance to the water distribution system and may never exceed 5 NTU (Hauser, 2000). However, it is important to note that low turbidity values do not necessarily mean decreased DOC. Though suspended particles are removed, soluble organics may still be present in the water. Standard Method 2130B (APHA, et al., 1998) was followed to measure turbidity using a Hach 2100P turbidimeter.

3.2.7 Oxidation Reduction Potential (ORP)

ORP, also referred to as redox potential or E_h, is a measure of environmental conditions. An Orion 5-star meter ORP probe with an Ag/AgCl reference electrode was used for oxidation-reduction potential measurements. Standard Method 2580 (APHA, et al., 1998) was followed for ORP procedures. In addition, the meter was set to record redox values every 30 seconds in order to develop an ORP profile for each chemical combination and facility by graphing E_h versus time.

3.3 Influent Water Characteristics

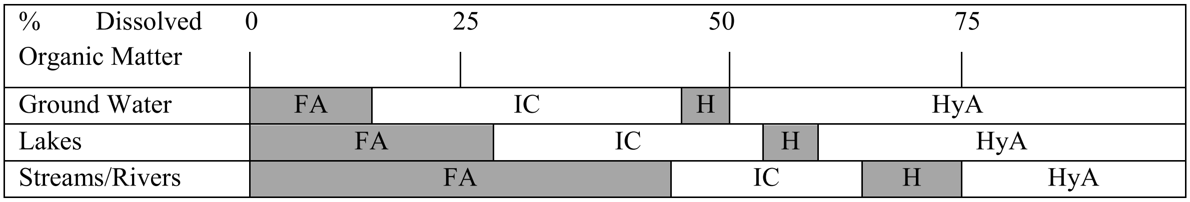
Water samples from the four Missouri communities came from both surface and ground water. Surface water 1 (SW1) and surface water 2 (SW2) are both lakes/impoundments receiving runoff from the surrounding watershed, surface water 3 (SW3) is indirectly a river because the treatment facility pumps water from the river and stores it in reservoirs before treatment, and the fourth water source is an alluvial aquifer (AGW). As seen in Table 3.2, the water qualities ranged in their turbidity, UV-254, dissolved organic carbon (DOC) and alkalinity.

Table 3.2: Initial water qualities of the various water sources used

	pH	Turbidity (NTU)	UV-254 (abs/cm)	DOC (mg/L)	Alkalinity (mg/L)	ORP (mV)
SW1	7.9 ± 0.3	15.0 ± 3.6	0.256 ±0.06	6.31 ± 0.2	62	186.6 ± 24.7
SW2	7.7 ± 0.2	19.2 ± 0.9	0.263 ± 0.01	6.81 ± 0.8	46	216.6 ± 20.5
SW3	8.4 ± 0.1	3.2 ± 1.4	0.073	4.27 ± 0.1	167	179.4 ± 24.8
AGW	7.7	24.7 ± 1.8	0.052 ± 0.001	2.71 ± 0.2	252	208.9 ± 19.3

In natural waters, six major groups of organic compounds exist: humic substances (humic and fulvic acids), hydrophilic acids, carboxylic acids, amino acids, carbohydrates, and hydrocarbons (Therman, 1986). Figure 3.3 shows their abundance in ground water, lakes, and rivers.

Table 3.3: Organic Matter Classification for Natural Waters (Therman, 1986)



FA = fulvic acid, IC = identifiable compounds: carboxylic acids, amino acids, carbohydrates, hydrocarbons, H = humic acids, HyA = hydrophilic acids

Typically, coagulation removes humic and high molecular weight organic matter better than it removes non humic and low molecular weight organic matter. In addition, aromatic materials are removed more effectively by coagulation than other NOM fractions. In addition, hydrophobic organic molecules are preferentially removed over their hydrophilic counterparts (Stanley, 2000).

Hydrophobic NOM primarily consists of humic acid and fulvic acid and is rich in aromatic carbon, phenolic structures, and conjugated double bonds, while hydrophilic

NOM contains more aliphatic carbon and nitrogenous compounds. Since UV-254 detects the amount of aromatic organic compounds, it can be seen in Table 3-2 that SW1 and SW2 have higher UV-254 absorbance values in their source water, and thus a higher concentration of detectable aromatic organics than SW3 and AGW. Since hydrophobic NOM is rich in aromatics, it can be concluded SW1 and SW2 have a higher hydrophobic fraction of NOM.

3.4 Results and Discussion

ORP profiles are important to show the trend of redox potential throughout the entire jar test process instead of one instant in the entire process. The coagulant dosage for both ferric chloride and liquid alum remained constant at 100 mg/L for each jar. High lime concentration (300 mg/L) was used to show a significant increase of the pH and increase the amount of lime for NOM adsorption onto the calcium precipitates. Table 3.4 shows the water quality results after jar tests for the four facilities treated using 100 mg/L liquid alum.

Table 3.4: 100 mg/L Liquid Alum ORP Profile Jar Test Results

	pH	Turbidity (NTU)	UV-254 (abs/cm)	% Reduction	DOC (mg/L)	% Reduction	Initial E_h (mV)	Final E_h (mV)
SW1	6.8	2.3	0.072	76.2	3.49	45.0	184	282
SW2	6.6	1.6	0.063	75.5	2.56	62.8	148	270
SW3	7.6	0.88	0.041	41.7	2.95	32.0	186	212
AGW	7.4	11.8	0.042	19.8	2.57	-1.2	192	166

As seen by Table 3.4, SW2 showed the greatest percent reduction of dissolved organic carbon (DOC) whereas SW1 showed the greatest percent reduction for UV-254 followed closely by SW2. These two waters have a much higher influent values for DOC and UV-254 than SW3 and AGW, and therefore is more amenable to removal by coagulation. SW1 and SW2 also showed higher final E_h values. The AGW was the only water which had a greater final UV-254 than the initial value. It is also the only water whose final E_h value is lower than the initial E_h value. Figure 3-2 shows the ORP profiles during the various stages of the jar test (coagulation = rapid mix; flocculation = slow mix; settling = no mix) for each of these facilities using 100 mg/L liquid alum as the coagulant.

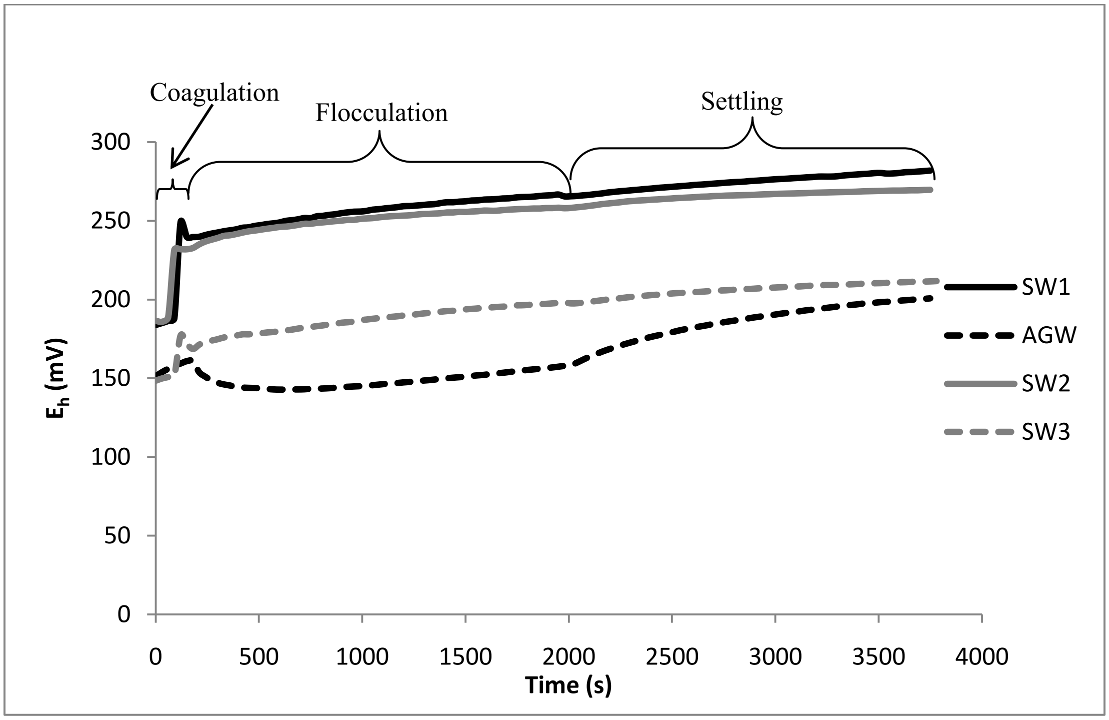


Figure 3-2: ORP profile for 100 mg/L Liquid Alum

The redox potential profiles for liquid alum showed a slight increase in redox potential with time. Additionally the slight jump in potential during coagulation is likely an indication of destabilization and then restabilization during the coagulation process (Bache and Gregory, 2007). Table 3.5 shows the results for jar tests for the four facilities using 100 mg/L liquid alum in addition to 300 mg/L lime.

Table 3.5: 100 mg/L Liquid Alum and 300 mg/L Lime ORP Profile Jar Test Results

	pH	Turbidity (NTU)	UV-254 (abs/cm)	% Reduction	DOC (mg/L)	% Reduction	Initial E_h (mV)	Final E_h (mV)
SW1	11.6	3.9	0.062	63.1	4.8	25.8	191	8
SW2	11.2	21.2	0.041	41.7	2.95	32	226	-5
SW3	10.6	2.8	0.025	51.4	1.88	26.1	207	21
AGW	11.5	2.0	0.068	74.6	3.72	49.3	193	26

As seen by Table 3.5, AGW showed the greatest percent reduction for DOC and UV-254. Since the AGW has a lower initial UV-254, there is less likely less aromatic organic carbon therefore the NOM is more easily removed by adsorption, or lime softening. AGW also had the most positive final E_h value of the four waters. Figure 3-3 shows the ORP profile for 100 mg/L liquid alum added with 300 mg/L lime.

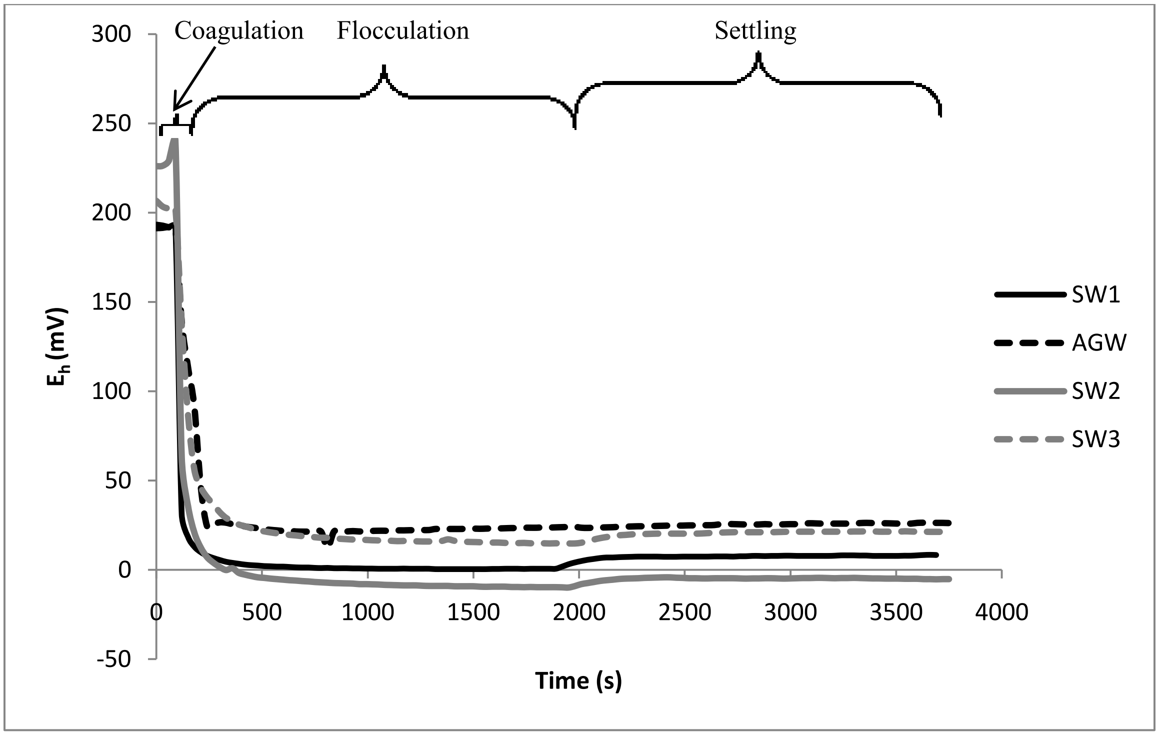


Figure 3-3: ORP profile for 100 mg/L Liquid Alum + 300 mg/L Lime

Figure 3-3 shows how the addition of lime causes the redox potential to greatly decrease. As suggested in the introduction, the addition of alum alone should cause a decrease in pH corresponding with an increase in E_h. Similarly, with the addition of lime, pH should increase and conversely, E_h should decrease. However, in addition to simply tracking with pH, E_h also provides some indications of slight changes in the environment as chemistry takes place.

Table 3.6 shows the results for jar tests for the four facilities using 100 mg/L ferric chloride.

Table 3.6: 100 mg/L Ferric Chloride ORP Profile Jar Test Results

	pH	Turbidity (NTU)	UV-254 (abs/cm)	% Reduction	DOC (mg/L)	% Reduction	Initial E_h (mV)	Final E_h (mV)
SW1	6.7	1.0	0.052	83.0	3.38	47	156	130
SW2	5.8	0.4	0.024	90.7	1.93	66.2	232	257
SW3	7	0.8	0.046	38.9	3.36	19.3	173	168
AGW	7.2	1.3	0.031	39.8	2.39	16.9	228	158

Similar to tests using liquid alum, ferric chloride worked best with SW1 and SW2. These results showed even greater percent reduction than with liquid alum. Again, these results are likely due to the higher UV-254 in the source water where the aromatic NOM is easier to remove by coagulation. Figure 3-4 illustrates the ORP profiles for the facilities when using 100 mg/L ferric chloride.

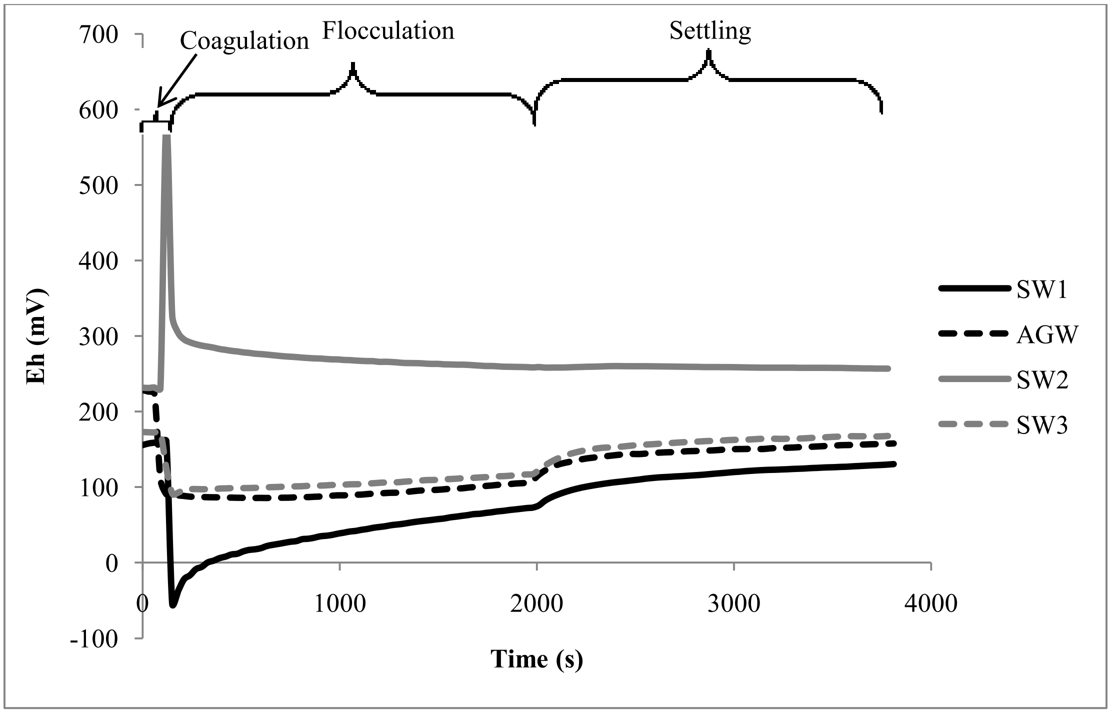


Figure 3-4: ORP profile for 100 mg/L Ferric Chloride

When using ferric chloride as the coagulant, the redox potential greatly decreased during coagulation except for SW2. SW2 had a low initial alkalinity (46 mg/L) which could have resulted in too much consumption of alkalinity with the addition of ferric chloride, causing a different response in the reaction. The four facilities then show similar results during flocculation and settling. Unlike with the addition of alum, the final E_h is lower than the initial E_h of the water. There is also a difference in the ORP profile even though the final pH values are similar.

Table 3.7 shows the results for jar testing for the four facilities using 100 mg/L ferric chloride along with 300 mg/L lime.

Table 3.7: 100 mg/L Ferric Chloride and 300 mg/L Lime ORP Profile Jar Test Results

	pH	Turbidity (NTU)	UV-254 (abs/cm)	% Reduction	DOC (mg/L)	% Reduction	Initial E_h (mV)	Final E_h (mV)
SW1	11.6	8.1	0.047	81.4	2.72	55.4	216	-12
SW2	11.5	1.6	0.048	82.1	2.58	64.8	222	-8
SW3	11	1.4	0.031	58.9	2.93	29.6	189	12
AGW	10.2	9.0	0.022	58.2	1.98	31.3	222	60

Though AGW is not the facility with the highest reduction, as seen when using liquid alum with lime, it does still show similar percent reduction in DOC and UV-254. The higher removal values for SW1 and SW2 compared to removal values in Table 3.5 indicate the higher efficiency for removal with ferric chloride compared to liquid alum when used with lime. This can be caused by ferric chloride's ability to be effective over a wider range of pH values than liquid alum (DeWolfe, et al., 2003). Figure 3-5 shows the ORP profile for 100 mg/L ferric chloride added with 300 mg/L lime.

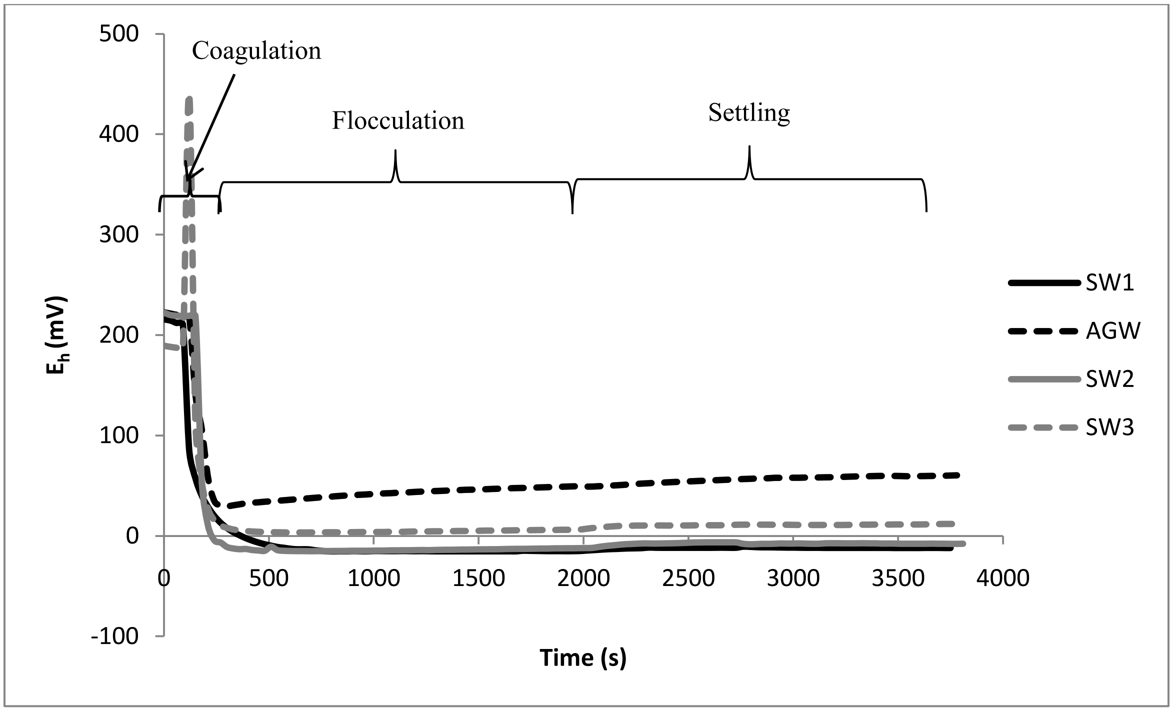


Figure 3-5: ORP profile for 100 mg/L Ferric Chloride + 300 mg/L Lime

Figure 3-5 shows similar redox trends to liquid alum and lime, showing lime has the predominant effect on E_h due to its much stronger effects on pH than the coagulant.

The redox potential trends showed an inverse relationship with E_h and pH. As seen in Figure 3-6, as the pH increased, the redox potential decreased. This is feasible since low pH favors an increase in H^+, allowing for more oxidative reactions, and high pH favors OH^-, allowing for more reductive reactions.

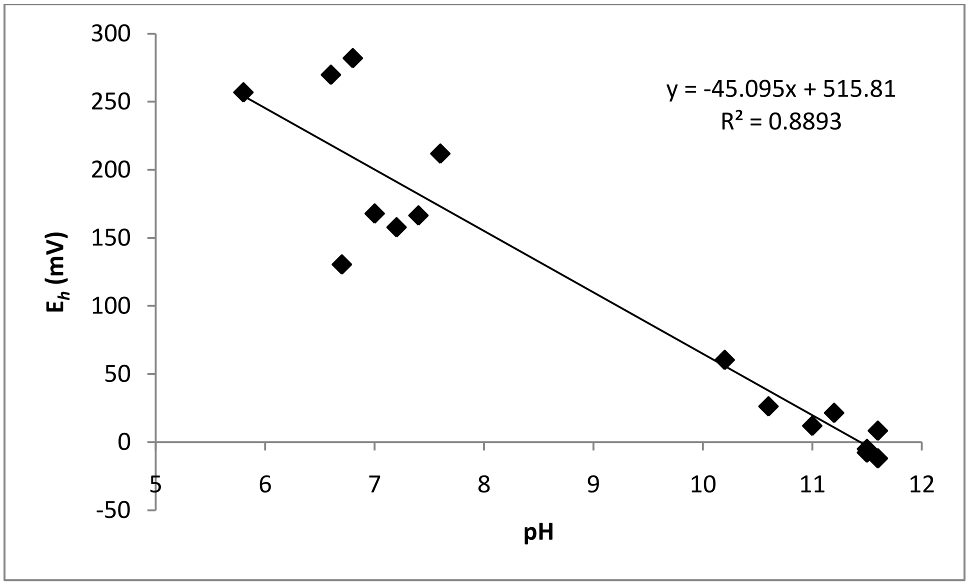


Figure 3-6: Relationship between final ORP and pH values for jar tests

Though final pH values confirm correlation between E_h and pH, the values in between indicate changes that are not pH dependant. In addition, the correlation seems to hold better during the softening process than during the coagulation process. High lime dosages can prevail over the reactions caused by coagulation destabilization.

3.5 Conclusion

Redox potential had a different response to alum than ferric chloride. When using alum, redox potential increased slightly during coagulation and the beginning of flocculation, whereas redox potential dropped rapidly when using ferric chloride as the coagulant. Both coagulants then steadily increased throughout flocculation and settling. The redox potential dropped a little below 150 mV with the addition of alum and below 50 mV for ferric chloride, even though the initial E_h values for all four waters were reasonably consistent throughout testing. Nevertheless, with the addition of lime, the redox potential showed similar redox results when using either ferric chloride or alum.

Experiments showed different types of coagulants will give different results depending on the source water and pH of the solution. Coagulant without the addition of lime was much more effective for reduction of DOC and UV-254 values for waters with higher UV-254 absorbance values for its influent water. Liquid alum was less efficient than ferric chloride for percent reduction of DOC and UV-254, particularly when used with lime due to reduction of efficiency for alum at higher pH values.

Most organics in raw water are negatively charged at typical pH values and will attract positively charged materials, such as metal coagulants. When the surface charge is neutralized with the introduction of coagulants, particle interactions are dominated by van der Waals forces, allowing rapid coagulation. It is probable that the destabilization caused by the introduction of the coagulant is indicated by the jump in redox potential during coagulation (Bache and Gregory, 2007). During flocculation, metal hydroxides form, causing the redox potential to increase near the initial value.

Liquid alum has a much smaller surface area for negative particle attraction than ferric chloride which could explain the less drastic redox change with the addition of alum. Ferric more readily absorbs onto the organic anionic particle surface causing charge neutralization and precipitation of the iron cations and organic anions (Dominguez, et al., 2005).

When ionic strength becomes sufficiently greater than the nonionic particles in the water, the destabilization energy barrier can be reduced to zero. This reaction is similar to the experiments using lime. The addition of lime along with the coagulant causes a considerable amount of ions to be dispersed into the water, causing the energy barrier to be reduced to zero and therefore keep the redox conditions also around zero (Bache and Gregory, 2007).

Reactions involving electrons and protons are pH-and Eh-dependent; therefore, chemical reactions in aqueous media often can be characterized by pH and Eh together with the activity of dissolved chemical species. Like pH, Eh represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction (APHA, et al., 1998).

Even though measurement of redox potential in aqueous solutions is moderately straightforward, many factors limit its analysis, such as effects of solution temperature and pH, irreversible reactions, slow electrode kinetics, non-equilibrium, presence of multiple redox couples, electrode poisoning, small exchange currents and inert redox couples (Garrels and Christ, 1990).

3.6 References

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Chapter 4: Optimizing Chemical Dosages for Reduction of DBPs in Smaller Communities

Abstract

Three Missouri drinking water treatment facilities, whose finished water trihalomethane (THM) and haloacetic acid (HAA) levels approach or exceed drinking water standards, were chosen for determination of optimal chemical treatment which will allow them to be in compliance with regulations. Optimal treatment was determined by reductions in precursors, indicated by UV-254 and dissolved organic carbon (DOC) analysis, as well as in formation potential of trihalomethane (THMFP) and haloacetic acid (HAAFP) . Due to the small size of the communities, preferred treatment solutions need to be easy and inexpensive to implement. After the effects of each chemical and chemical dosage currently being used at the treatment facility was determined, optimal dosages and alternative chemical substitutions were tested to determine the most efficient chemical combination for reduction of disinfection by-product precursors. As expected, waters with higher alkalinities were best served by enhanced softening, while waters with lower alkalinities were more amenable to enhanced coagulation. In a number of cases, ferric salts outperformed aluminum salts at reducing the DBP formation potential.

4.1 Introduction

In the United States, more than 94 percent of the nation's 156,000 public water systems serve fewer than 3,300 persons. These systems are classified as small by the United States Environmental Protection Agency (EPA) and face unique financial and operational challenges in supplying drinking water that meets EPA standards. Small water systems do not have the large customer base needed to provide the necessary financial assistance and cannot develop or access the technical, managerial and financial resources needed to comply with the increasing number of EPA regulations and rising customer expectations (USEPA, 2008).

Small drinking water systems need for assistance was recognized under the Safe Drinking Water Act. New federal regulations will greatly affect smaller communities. Since most of these communities are without the resources to respond, the Missouri Technology Assistance Center was funded in order to use their expertise to assess current drinking water technologies and establish nationally recognized test sites. The Center is in a position to help many small Missouri industries to develop and assess their current technologies (MoTAC, 2009).

Three drinking water treatment facilities from smaller communities in Missouri were selected for determination of optimal chemical dosing for reducing the amount of DBPs formed in the distribution systems based on their sequence of treatment and source water characteristics. These systems have finished water trihalomethane (THM) and haloacetic acid (HAA) levels in excess of forthcoming drinking water standards. If current treatment is not improved, many of the smaller systems will be out of compliance in the near future, and deliver water containing unhealthful levels of DBPs (MoTAC, 2009).

Treatment solutions should be simple and inexpensive to implement. Treatments, such as membrane and ozonation systems, are fairly expensive and complex alternatives for these smaller communities. For these three communities, the following objectives were followed:

- Determine the optimal coagulant doses for natural organic matter (NOM) removal by enhanced coagulation.
- Compare the efficiency of single and sequential treatment of enhanced coagulation.
- Investigate correlations between surrogate NOM parameters, such as UV-254 and dissolved organic carbon (DOC).
- Monitor the reduction of DBP precursors.

The treatment facility information needed to verify compliance results from quarterly testing is found in Table 4.1.

Table 4.1: Treatment facility descriptions

Water System ID	Water Plant (County)	Water source	Population served
MO2010538	Monroe City (Monroe)	Reservoir off South J	2,700
MO2010796	Trenton (Grundy)	Thompson River	6,216
MO2010497	Marceline (Linn)	New Lake	2,325

The testing for each facility was broken into two phases. The first phase was to profile the amount of disinfection by-products (DBPs) produced throughout the water treatment plant and in the distribution system, and specifically to determine which portions of the process provide the best opportunities for modifications that might provide further removal of DBP precursors. This includes performing disinfection by-product (DBP) and disinfection by-product formation potential (DBPFP) analyses and other related chemical analyses of samples.

The second phase identifies and tests potential options for the facility owner to use to achieve compliance with federal DBP limits. These analyses include, but are not limited to jar testing of higher and/or lower dosages of the chemicals currently being used in the treatment process, of alternate sequences of chemical dosing, and of alternate chemicals not currently being used. Chemical choices are limited to those commonly used by surface water treatment plants in northern Missouri. The source water DBP formation potential and precursor numbers determined during selected months of the year for each facility can be seen in Table 4.2. Phase 2 was the focus of these experiments.

Table 4.2: Measured influent water characteristics

Month	TTHMFP (µg/L)	HAA5FP (µg/L)	DOC (mg/L)	UV-254 (abs/cm)
		Monroe City		
May	694	344	7.3	0.773
June	402	287	8.0	0.333
August	421	275	7.4	*0.218*
Range	*401– 694*	*275 – 344*	*7.3 – 8.0*	*0.218 – 0.773*
		Trenton		
May	337	155	4.2	0.079
July	194	125	4.5	0.093
August	160	132	4.4	0.080
Range	*160 - 337*	*155 – 125*	*4.2 – 4.5*	*0.079 – 0.093*
		Marceline		
March	538	241	6.5	0.330
June	867	272	9.2	0.324
Range	*538 - 867*	*241 – 272*	*6.5 – 9.2*	*0.324 – 0.330*

4.2 Materials and Methods

This section explains the materials and the analytical procedures associated with the jar tests used to optimize chemical dosing. The treatment studies were conducted on three selected Missouri waters to quantify the removal of natural organic matter (precursors for DBP production) by first measuring the reduction of dissolved organic carbon (DOC) and UV-254 and then by measuring with haloacetic acid formation potential (HAA5 FP) and total trihalomethane formation potential (TTHM FP) values.

4.2.1 Natural Water Collection and Storage

Water samples were collected from three smaller drinking water supplies in Missouri which serve populations from 2,000 to 6,500 persons. The communities selected all received their water from surface water sources. Twenty liters of water (in 20 L carboys) were collected from each type of water source between December 2009 and May 2010. All carboys were pre-cleaned with MU Distilled water (DW) and within 24 hours, the collected water was returned and refrigerated in the dark at 10°C.

4.2.2 Reagents

The chemical reagents and concentrations used in these experiments are based upon the concurrent chemicals used at each facility at the time of sampling. These included ferric and aluminum coagulants, cationic polymers, activated carbon, soda ash (sodium carbonate), lime, baking soda (sodium bicarbonate), and magnesium hydroxide. A detailed supplies list can be found in Appendix C.

4.2.3 Jar Testing

Experiments are run following a modified version of the standard jar test procedure (ASTM Standard D2035 (ASTM International, 2008)). Six 2-liter capacity square beakers (Bker^2, WU-99520-50, Cole-Parmer) are filled with 1 L of raw water from the treatment facility and dosed with prescribed concentrations of chemicals. Jars are then placed on the jar testing apparatus (Phipps and Bird PB-700 Jar Tester) and first mixed for 60 seconds at 100 rpm to disperse ions, then mixed for 30 minutes at 35 rpm to form flocs. The stirrers are then turned off and the solids are allowed to settle for 30 minutes. Turbidity, UV-254, and dissolved organic carbon (DOC) are tested for each sample in addition to initial and final pH.

These waters were then analyzed to determine the 24-hour chlorine demand. The determined demand plus approximately 1 mg/L excess chlorine was add to each water so that total trihalomethane formation potential (TTHM FP), and haloacetic acid formation potential (HAA5 FP) could be found following the uniform formation conditions procedure (Summers, et al., 1996). Raw water samples without chemical additions followed the same procedure as the other jars at the time of testing and serve as a control or baseline sample to which the treated water samples may be compared.

4.2.4 UV-254

UV-254 absorbance measurements indicate aromatic organic content (Standard Methods 5910 B). Treated water samples from each of the jars are filtered through a 0.45 μm glass fiber filter disk (FisherBrand 09-719-2E), poured into a 1 cm quartz cell (Fischer Scientific #14385902C), and then run on a 50 UV-Visible Spectrophotometer (Cary 50) at 254 nm.

4.2.5 DOC Analysis

To quantify the amount of natural organic matter in a water source, dissolved organic carbon (DOC) analysis is performed (Standard Methods 5310 B: high temperature combustion method (APHA, et al., 1998)). DOC analysis was performed on a Shimadzu TOC-Vcpn instrument with an ASI-V autosampler.

4.2.6 Turbidity

Turbidity consists of suspended particles in the water that may hinder disinfection by shielding microbes, some of them perhaps pathogens, from the disinfectant (Hauser, 2000). The federal limits are 0.5 NTU in 95% of samples tested reported as a monthly average. Reportable readings are taken at the entrance to the water distribution system and may never exceed 5 NTU (Hauser, 2000). However, it is important to note that low turbidity values do not necessarily mean decreased DOC. Though suspended particles are removed, soluble organics may still be present in the water. Standard Method 2130B (APHA, et al., 1998) was followed to measure turbidity using a Hach 2100P turbidimeter.

4.2.7 Alkalinity

Alkalinity was performed following Standard Method 2320 B (APHA, et al., 1998).

4.2.8 THM analysis

THM formation potential concentrations were determined by a gas chromatograph (Varian, Model 3800)/ mass spectrometer (GC/MS) (Varian, Saturn 3800) equipped with a Tekmar 300 purge and trap concentrator following the uniform formation conditions procedure (Summers, et al., 1996).

4.2.9 HAA5 analysis

The formation potential concentrations of the five (5) regulated species of HAAs were determined by using a liquid/liquid extraction derivation GC method following the uniform formation conditions procedure (Summers, et al., 1996).

4.2.10 Chemical Choices

Optimal chemical treatment is the goal for efficient removal of DBP precursors. In order to meet this goal, a standard protocol was followed for each facility (Table 4.3)

Table 4.3 Chemical Optimization Procedure

Procedure	**Purpose**
Test current chemicals individually	Determine which chemical(s) are dominant for DBP precursor removal
Test current chemicals in various combinations	Determine which combinations achieve greatest DBP precursor removal
Test various chemical dosages	Determine what dosage is optimal for chemicals showing greatest removal
Test alternatives for each chemical	Determine if an alternative chemical can achieve greater results
Test various chemical dosages for alternative chemicals	Determine most advantageous dosage for alternatives to verify best results
Test most favorable chemicals in combination	Determine optimal chemicals and combination for greatest DBP precursor removal

4.3 City of Monroe

4.3.1 Process Description

Monroe City has an average flowrate of 0.25 MGD and serves a population of approximately 2,700. The process starts at the Reservoir (off of Route J), with South Lake as a backup water source. The influent pump station pumps the water to the mechanical treatment process. The types of chemicals used along with the location where they are added and their intended use are listed in Table 4.4.

Table 4.4: Current Chemical Type, Process Location and Reason for Use

Chemical	Process Location	Purpose
Potassium Permanganate ($KMnO_4$)	Pump station	Manganese removal
Alum ($Al_2 (SO_4)_3 \cdot 18H_2O$)	Rapid mix	Decrease turbidity; organics removal
Polymer (HyperIon 1090; 23% Al_2O_3)	Rapid mix	Flocculant aid
Soda Ash (Na_2CO_3)	Rapid mix	Increase alkalinity
Activated Carbon (WPH)	Rapid mix	Organics removal; taste, odor, and color removal
Chlorine	Before filters and in clearwell	Disinfectant
Fluoride (F^-)	Clearwell	Tooth decay prevention

Figure 4-1 illustrates the current treatment process for Monroe City. Potassium permanganate ($KMnO_4$) is added at the pump station. The process then continues to the mechanical process which includes a rapid mix tank, where alum, a polymer, soda ash, and activated carbon are added, solids contactor basins (2), which include a vacuum chamber and pulsator tanks, flocculator basins (2) followed by sedimentation basins (2), the latter has soda ash added to it, filters (4), before which chlorine is added, and then finally clearwells (2), to which both chlorine and fluoride are added directly. The distribution system sample locations include the two towers (one whose capacity is 250,000 gallons and the other is 500,000 gallons), Pottersfield (the IDSE compliance location), and Quinn’s Farm Supply.

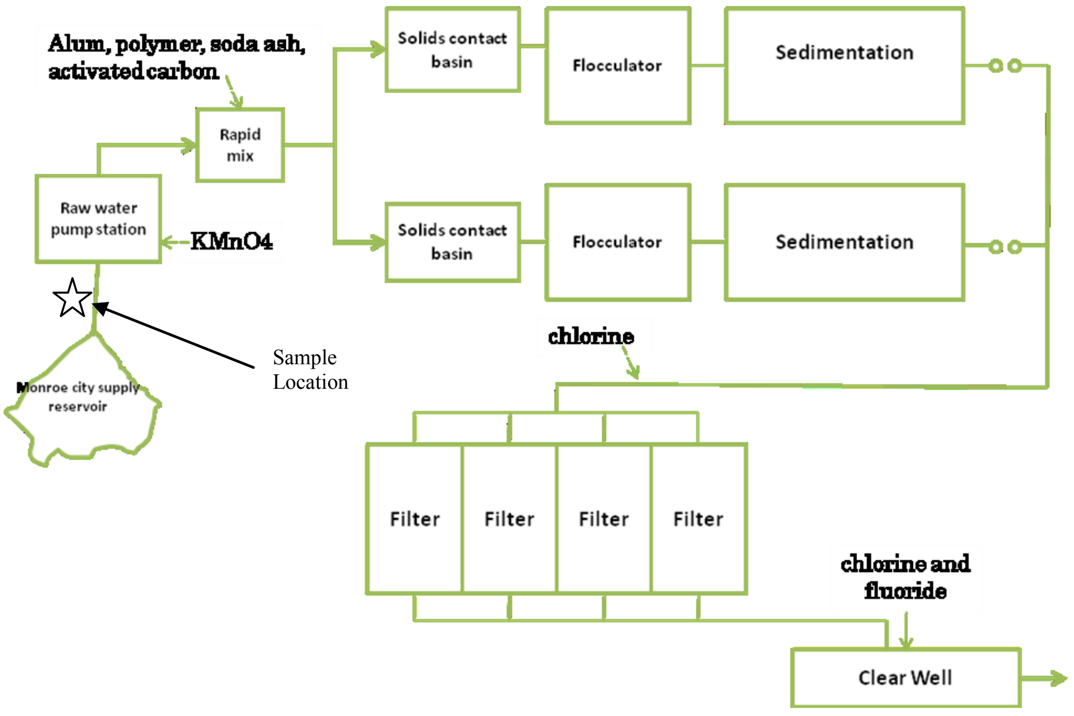

Figure 4-1 Monroe City Water Treatment Process

4.3.2 Phase I Water Sampling

Disinfection by-product (DBP) and disinfection by-product formation potential (DBPFP) analyses and other related chemical analyses of samples from nine (9) locations in the Monroe City water treatment plant and four (4) locations in the water distribution system that match the locations being used for DNR sampling. Late summer concentrations were expected to be higher than those found in earlier water samples partly because of the increase in temperature, which should increase the rate of DBP formation. The late August samples were the only samples measured out of compliance.

In order to determine the effects of each process unit on reducing the potential concentrations of disinfection by-products, formation potential (FP) tests were conducted on samples taken from each process unit. Formation potential is designed to determine the maximum of DBPs that could potentially form in the distribution system. The average TTHM and HAA5 samples (Figure 4-2) were taken at select locations in the treatment process to determine the locations of concern. DBPFP concentrations are extremely high in the reservoirs (400 - 700 μg/L for TTHMFP; 240 -350 μg/L for HAA5FP), suggesting that the use of the solids contactor dramatically reduces DBP concentrations.

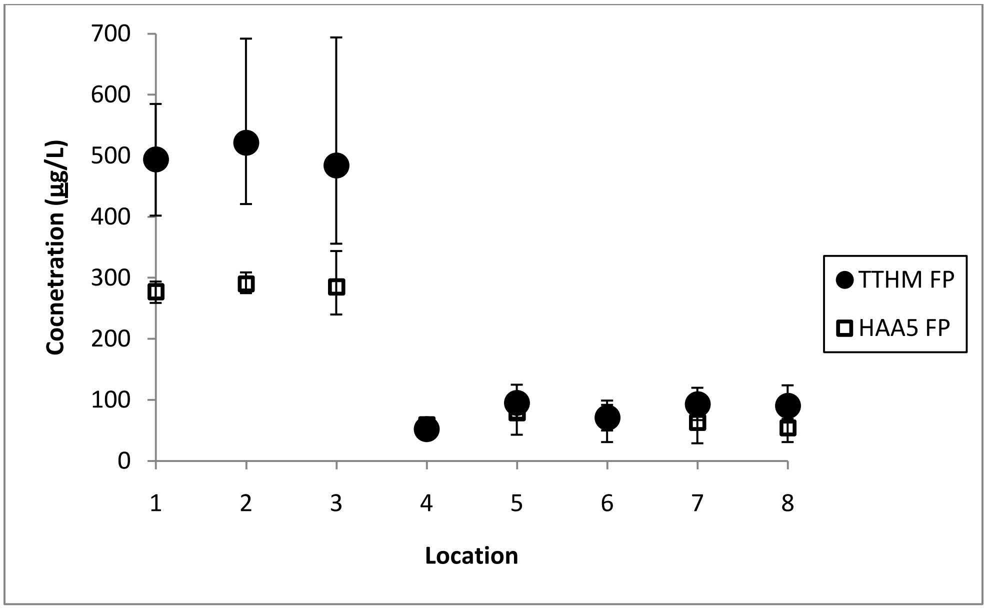

Figure 4-2 TTHM (MCL = 80 µg/L) and HAA5 (MCL = 60 µg/L) FP concentrations in Monroe City system

(**Locations: 1**- South lake surface, **2**- Reservoir Lake (Route J), **3**- Raw water (adding KMnO4), **4**- Solids contact effluent, **5**- Flocculation basin effluent, **6**- Sedimentation basin effluent before chlorination, **7**- Filter effluent before chlorine l, **8**- Finish water

4.3.3 Phase II Testing

For Monroe City, 58 different jar test combinations were run. The chemical choices were based off of their current chemical usage and alternatives to the current chemicals. *Liquid alum* is current used at the facility (29 mg/L) as a coagulant for turbidity and organics removal. Current concentration, lower concentration (14.5 mg/L) and higher concentration (48 mg/L) were tested to verify the most favorable dosage for DBP reduction. In addition, enhanced chemical dosages (50, 100, 150 mg/L) were also tested. *Ferric chloride* was tested as a coagulant alternative to determine if it was more effective than alum. Both were varied in dosage to determine optimal yield. Concentrations tested followed a similar pattern as for liquid alum.

Sodium carbonate (or soda ash) is currently used at the facility (77.5 mg/L) as a stabilizer to raise the water's alkalinity. *Magnesium hydroxide* and *sodium bicarbonate* were used as alternative chemicals to determine the most efficient stabilizer. A typical dosage (17 mg/L) for a drinking water treatment facility was tested.

A *polymer* (HyperIon 1090; 3.4 mg/L) is currently used as a coagulant aid for greater organics removal. It was tested to determine if it was efficient in the process at various doses (2, 3.4, 6, 8 mg/L).

Lime was used as an alternative chemical to determine the effectiveness of an increased pH in the treatment system. Dosages (60, 180, 300 mg/L) were chosen in order to achieve incremental pH values from 8 – 11.

Carbon was tested to determine the efficiency in the treatment process and if it could be improved at different dosages.

A summary of the various chemical combinations were used to determine which would be the most effective can be seen in Table 4.5 and the various combinations for test sets can be seen in Table 4.6.

Table 4.5 Chemical Choices and Concentrations for Monroe City Jar Testing

Chemical	Current Concentration (mg/L)	Concentration (mg/L)	Purpose
Liquid Alum ($Al_2(SO_4)_3 \cdot 18H_2O$)	29	14.5, 29, 43.5, 50, 100, 150	Determine current use effectiveness, enhanced coagulation/enhanced softening
Ferric Chloride ($FeCl_3$)	0	8, 16, 24, 50, 100, 150	Alum comparison, enhanced coagulation/enhanced softening
Soda Ash (sodium carbonate (Na_2CO_3))	77.5	77.5	Determine current use effectiveness
Magnesium Hydroxide ($Mg(OH)_2$)	0	17	Stabilizer comparison with baking soda
Baking Soda (Sodium bicarbonate ($NaHCO_3$))	0	17	Stabilizer comparison with $Mg(OH)_2$
Polymer (23% Hyperion 1090)	3.4	2, 3.4, 6, 8	Determine current use effectiveness
Lime	0	60, 180, 300	Enhanced softening comparison
Carbon (WPH)	48	24, 48	Determine current use effectiveness

Table 4.6 Chemical Combinations for Monroe City Test Sets

Test Set	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Alum	▨				▨	▨	▨				▨	▨		▨					▨		▨	
Ferric															▨	▨				▨		▨
Na_2CO_3		▨			▨			▨	▨		▨		▨	▨								
$Mg(OH)_2$																	▨					
$NaHCO_3$																		▨				
Polymer			▨			▨		▨		▨		▨	▨	▨							▨	▨
Lime																			▨	▨		
Carbon				▨			▨		▨	▨	▨	▨	▨	▨		▨						

The water used for jar testing was obtained from the raw water just before the addition of permanganate (designated as Site 3 in the Phase 1 sampling scheme). This site was selected in order to optimize the chemical choices in the rapid mix, flocculation and settling stage. Table 4.7 lists the average raw water quality for the tests. During the winter months the formation potential for the DBPs was much higher than was observed in late spring.

Table 4.7 Monroe City Average Raw Water Quality (December 2009 – April 2010)

Sampling Time	pH	Turbidity (NTU)	UV-254 (abs/cm)	DOC (mg/L)	TTHMFP (µg/L)	HAA5FP (µg/L)
Winter Average	8.3	15	0.36	9.1	612	287
Late Spring Average	7.7	17	0.26	6.4	287	181
Average	7.9	16.5	0.30	7.31	416.9	223.7
Std. Dev.	0.32	2.94	0.07	1.62	178.0	59.1

The first round of tests demonstrated the efficiency of each chemical used in the process separately and in different combinations. The TTHM and HAA5 FP results (Figure 4-3) indicated none of the combinations gave results where the HAAs were in compliance

(<60 μg/L) and only three (3) of the tests gave results where TTHMs were under EPA requirements (<80 μg/L).

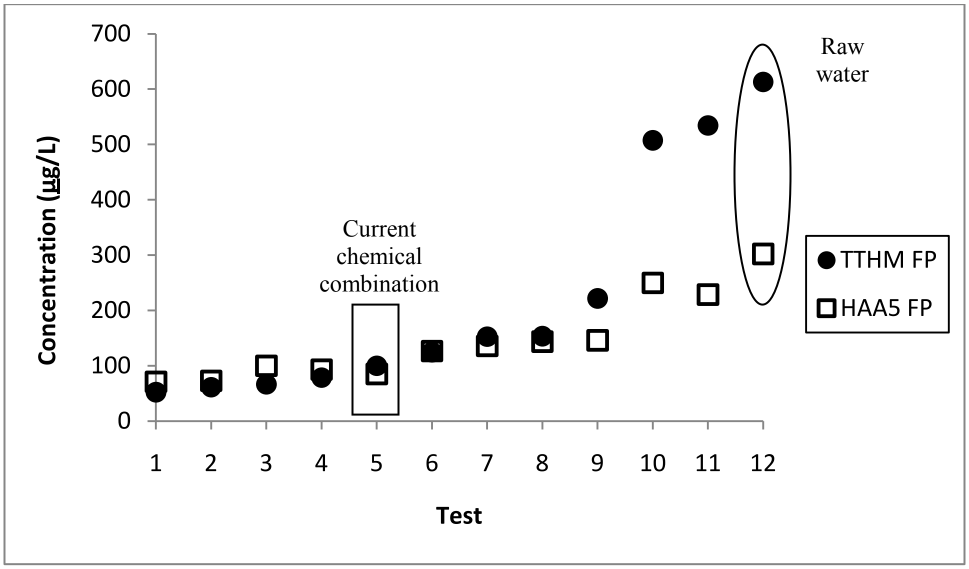

Figure 4-3 Current treatment combination jar tests for Monroe City

1 - 29 Al/47.5 C; **2** - 29 Al/3.4 poly/47.5 C; **3** – 29 Al; **4** – 29 Al/3.4poly; **5** – 29Al/77.5 soda ash / 3.4 polymer /47.5 C; **6** – 29Al/77.5soda ash /3.4 poly; **7** – 29Al/77.5soda ash; **8** – 3.4poly; **9** – 3.4 poly/47.5C; **10** – 47.5C; **11** – 77.5 soda ash/47.5C; **12** – raw water

From the results, liquid alum and carbon gave the best results for TTHM and HAA5 formation potential. However, since only tests 1 -4 gave TTHM FP concentrations below 80 μg/L and the remaining tests TTHM FP results were higher than the standard in addition to all combinations having numbers above compliance standards for HAA5s (HAA5 MCL = 60 μg/L), further testing was performed in order to determine chemical optimization in the rapid mix process.

The procedures performed for additional jar tests were as follows:

- Determine optimal dosage for liquid alum and carbon combination.

- Determine effectiveness of varying liquid alum dosages.
- Determine effectiveness of ferric chloride as coagulant in place of liquid alum.
- Test effectiveness of enhance coagulation with ferric chloride and liquid alum
- Test effectiveness of enhanced softening with ferric chloride, liquid alum and lime.
- Compare baking soda (sodium bicarbonate) and magnesium hydroxide for water stability (replacement of alkalinity and adjustment of pH toward neutral)

In addition to TTHM FP and HAA5 FP, UV-254 and dissolved organic carbon (DOC) can be useful indicators for DBP formation. As seen by the testing, the higher the percent reduction of UV-254 and DOC, the lower the TTHM FP (Figure 4-4) and HAA FP (Figure 4-5).

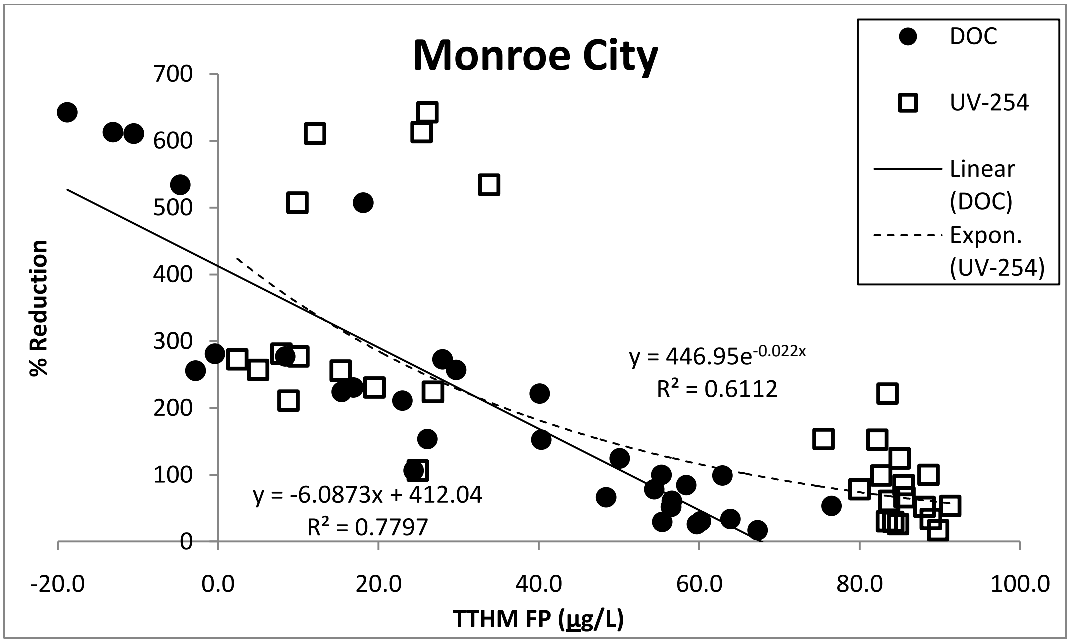

Figure 4-4 Trends for % Reduction DOC and UV-254 versus TTHM FP

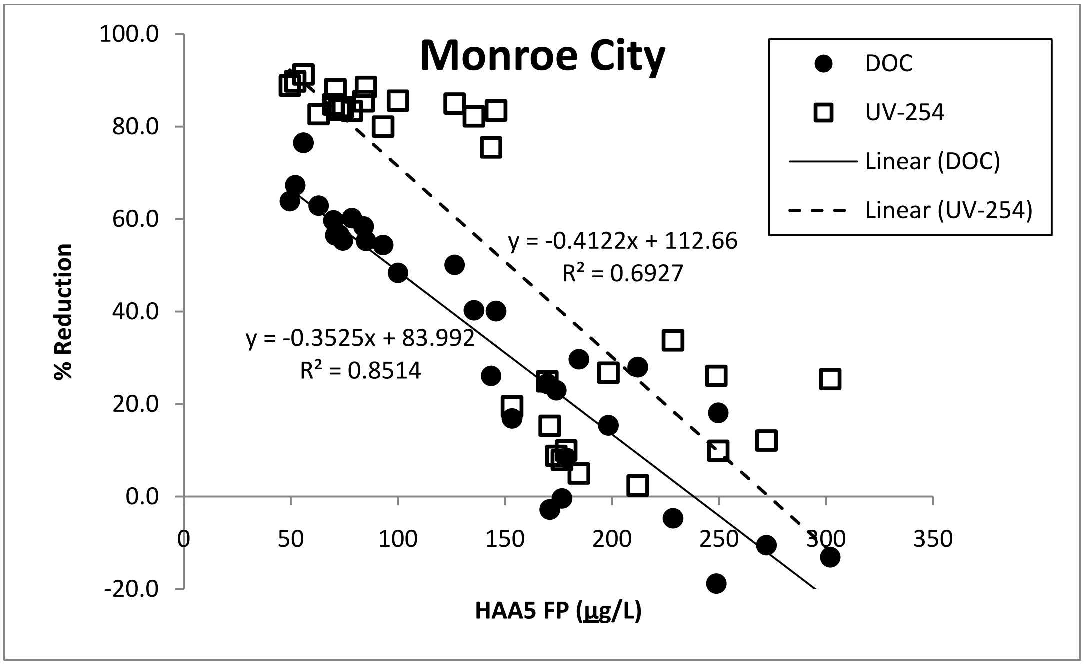

Figure 4-5 Trends for % Reduction DOC and UV-254 versus HAA5 FP

After trying various chemical combinations from Table 4-4, the top seven (7) combinations with the highest percent reduction DOC and UV-254 (Figure 4-6) in addition to the lowest TTHM FP and HAA5 FP (Figure 4-7) were chosen for recommendations.

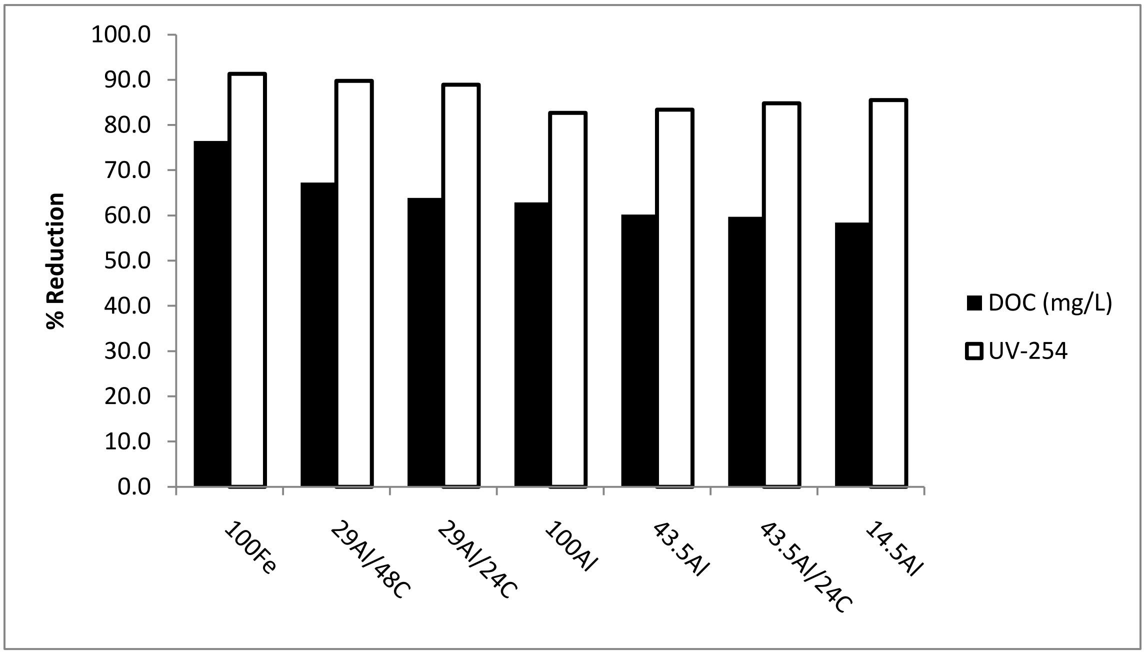

Figure 4-6 Monroe City: Top Combinations for Highest DOC and/or UV-254 Reduction

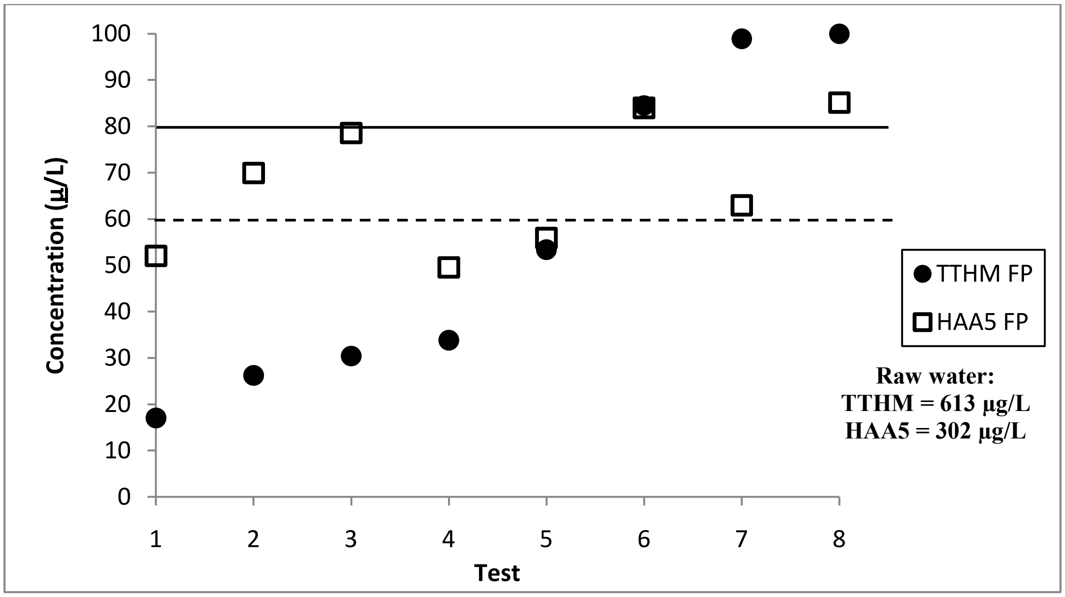

Figure 4-7 Monroe City: Top Combinations for Lowest TTHM FP and HAA5 FP Values

1 – 29Al/48C; **2** – 43.5Al/24C; **3** – 43.5Al; **4** – 29Al/24C; **5** – 100Fe; **6** 14.5Al; **7** – 100Al; **8** – Current treatment (TTHM MCL = 80 µg/L/ HAA5 MCL = 60 µg/L)

Overall, the top combinations for Monroe City included smaller dosages of liquid alum along with carbon and higher dosages of ferric chloride for enhanced coagulation.

4.4 City of Trenton

4.4.1 Process Description

The city of Trenton serves a population of approximately 6,200 people in Grundy County. The process starts at an intake structure from the Thompson River that sends water to two reservoirs. The chemicals used in the water treatment process along with their location of addition and their purpose are in Table 4.8.

Table 4.8 Current Chemical Type, Process Location, and Intended Use for Trenton

Chemical	Process Location	Purpose
Copper Sulfate ($CuSO_4$)	Reservoir	Minimize algae growth
Sodium aluminate ($NaAlO_2$)	Upflow clarifier	Turbidity removal; organics removal
Lime ($Ca(OH)_2$)	Upflow clarifier	Softening: Magnesium and calcium removal
Chlorine (Cl^-)	3rd contact basin and after filters	Disinfection

Figure 4-8 is an illustration of the treatment process. The influent pump station pumps the water to the mechanical treatment process. Copper Sulfate ($CuSO_4$) is sometimes added to the reservoir water to minimize algae growth. The process units used in the mechanical process include upflow clarifier basins (2), where sodium aluminate and lime are added, a basin for recarbonation, a 3rd contact basin (rapid mix followed by wood baffles, a flocculation area, and then sedimentation), where chlorine is added, filters (3), after which chlorine is added again, and then finally a clearwell. The distribution system sample locations include the Princeton Tower and the Iowa Tower, City Hall, and Hutchinson's House.

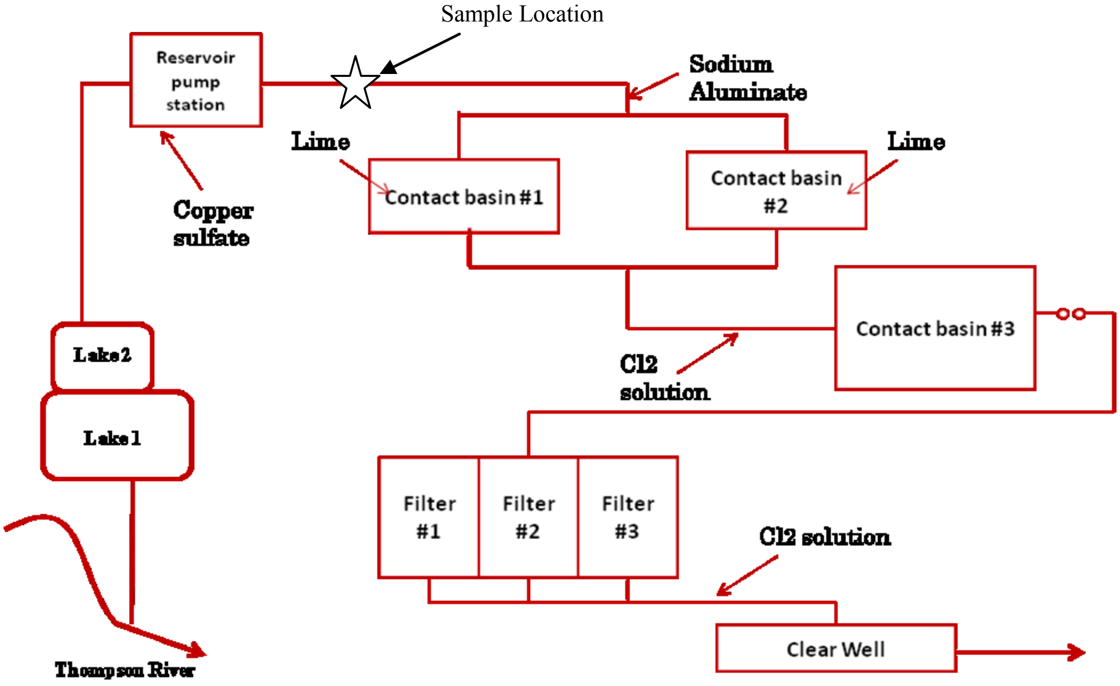

Figure 4-8 Trenton Water Treatment Process

4.4.2 Phase I Sampling

Averaged water quality samples from late May, early July, and late August are compared in Figure 4-9. Late summer concentrations were expected to be higher than those found in earlier water samples due to the increase in temperature, which could increase the rate of DBP formation. There were also some difficulties encountered when collecting samples from the clearwell itself that may have had some influence on the results from those samples.

The TTHM samples exceed the MCL quickly and continue to increase through the system. However, HAA5 concentrations remain below the MCL for most of the system (Figure 4-9).

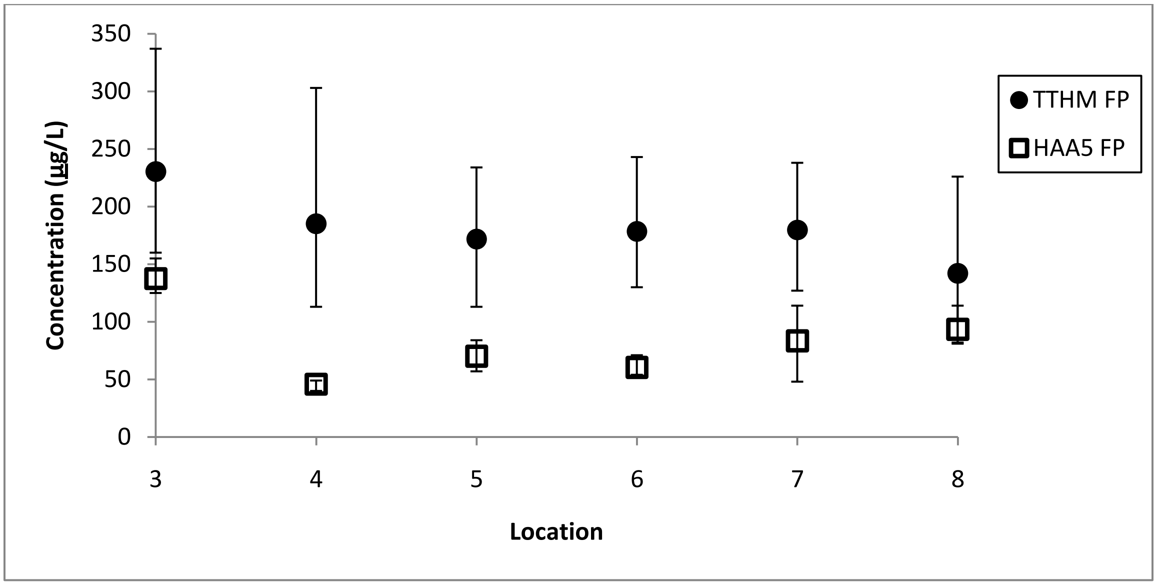

Figure 4-9 TTHM (MCL = 80 µg/L) and HAA5 (MCL = 60 µg/L) FP concentrations in Trenton system

(**Locations: 3** - Raw water entering splitter box, **4**- Contact Basin No2 effluent, **5**- Contact Basin No3 effluent, **6**- Filter effluent before chlorination, **7**- Entering clearwell, **8**- Exiting clearwell,

In order to determine the effects of each process unit on reducing the potential concentrations of disinfection by-products, formation potential (FP) tests were conducted on samples taken from each process unit. Formation potential is designed to determine the maximum of DBPs that could potentially form in the distribution system from each water sample taken.

In the reservoirs, before the mechanical treatment plant, DBPFP concentrations are high (230 - 360 µg/L TTHMFP and 140 - 200 µg/L HAA5FP). This data suggests that although the addition of lime and coagulant reduces some DBP precursors, the reduction is not enough to get the concentrations below the regulated limit. After basin #3, the FP stays steady due to no other treatment that would reduce the DBP concentrations. These numbers at the end of the process are comparable to the concentrations measured in the distribution system.

4.4.3 Phase II Testing

For Trenton, 31 different jar test combinations were run. Various chemical combinations were used to determine which would be the most effective. These chemicals were chosen in order to optimize the enhanced softening currently occurring at the treatment facility.

Sodium aluminate (8 mg/L) is used as a coagulant for turbidity and organics removal. It was tested to determine its current effectiveness in the treatment process. *Ferric chloride* and *liquid alum* were tested as alternative coagulants. Sodium aluminate is typically only used in small concentrations, so ferric chloride and liquid alum were tested at slightly higher doses (50 mg/L). In addition, enhanced treatment was tested using 100, 150, and 200 mg/L of coagulant.

Lime is used to remove hardness in the water and was tested at its current concentration (130 mg/L) to determine effectiveness for hardness removal and also organics removal. Lower (60 mg/L) and higher dosages (180, 300 mg/L) were tested to determine the optimal pH and lime dosage.

Carbon was tested to determine if it was efficient in the treatment process for DBP precursor reduction. A small dosage (9 mg/L) was tested due to system limitations. A summary of chemical usage can be seen in Table 4.9 in addition to the chemical combinations used in each test set in Table 4.10.

Table 4.9 Chemical choices and concentrations for Trenton jar testing

Chemical	**Current Concentration (mg/L)**	**Concentration (mg/L)**	**Purpose**
Sodium aluminate ($NaAlO_2$)	8	8	Determine effectiveness of current use
Ferric Chloride ($FeCl_3$)	0	50, 100, 150, 200	Coagulant comparison; enhanced coagulation and enhanced softening
Liquid Alum ($Al_2(SO_4)_3 \cdot 8H_2O$)	0	50, 100, 150, 200	Coagulant comparison; enhanced coagulation and enhanced softening
Lime ($Ca(OH)_2$)	130	60, 130, 180, 300	Determine effectiveness of current use; enhanced softening
Carbon	0	9	Determine if carbon is effective at DBP precursor removal in the system

Table 4.10 Chemical Combinations Used for Each Trenton Test Set

Test Set	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$NaAlO_3$	■			■	■	■								
Alum							■		■		■		■	
Ferric								■		■		■		■
Lime		■		■		■			■	■			■	■
Carbon			■		■	■					■	■	■	■

As seen in Table 4.11, sodium aluminate is used typically in only small dosages (US Army Corp of Engineers, 2001). Ferric chloride and alum, which are more commonly used in higher doses, were chosen as alternative chemicals.

Table 4.11 Chosen Experimental Coagulants and Advantages/Disadvantages
(US Army Corp of Engineers, 2001)

Name	Advantages	Disadvantages
Aluminum Sulfate (Alum) $Al_2(SO_4)_3.18H_2O$	Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to water; effective over a limited pH range.
Sodium Aluminate $Na_2Al_2O_4$	Effective in hard waters; small dosages usually needed	Often used with alum; high cost; ineffective in soft waters
Ferric Chloride $FeCl_3.6H_2O$	Effective between pH 4 and 11	Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum
Lime $Ca(OH)_2$	Commonly used; very effective; may not add salts to effluent	Very pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality

The water used for jar testing was obtained from Site #3, raw water before entering the splitter box. This site was selected in order to optimize chemical choice in the upflow clarifier basin. Table 4.12 lists the raw water quality for the tests.

Table 4.12: Trenton Raw Water Quality

	pH	Turbidity (NTU)	UV-254 (abs/cm)	DOC (mg/L)	TTHM FP (μg/L)	HAA5 FP (μg/L)
19-Jan-09	8.3	31.6	0.061	4.39	126	60
22-Apr-10	8.3	4.4	0.075	4.17	112	86
28-Apr-10	8.4	2.0	0.071	4.37		
12-May-10	8.0	3.5	0.082	3.82		
Average	8.25	10.4	0.072	4.18	118.8	72.76
Std. Dev.	0.17	14.2	0.010	0.26	10.11	18.04

The lower UV-254 values indicate less aromatic organic matter in Trenton's raw water. However, the high TTHM FP and HAA5 FP concentrations signify there is still a high amount of natural organic matter in the water that likely contains very little amounts of aromatic organic carbon. The first round of tests demonstrated the efficiency of each chemical used in the process separately and in different combinations. In addition to the current chemicals, carbon was also tested separately and in combination. The TTHM and HAA5 FP results (Figure 4-10) indicated none of the combinations gave results where the TTHMs were in compliance (<80 µg/L) and only three (3) of the tests gave results where HAAs were under EPA requirements (<60 µg/L).

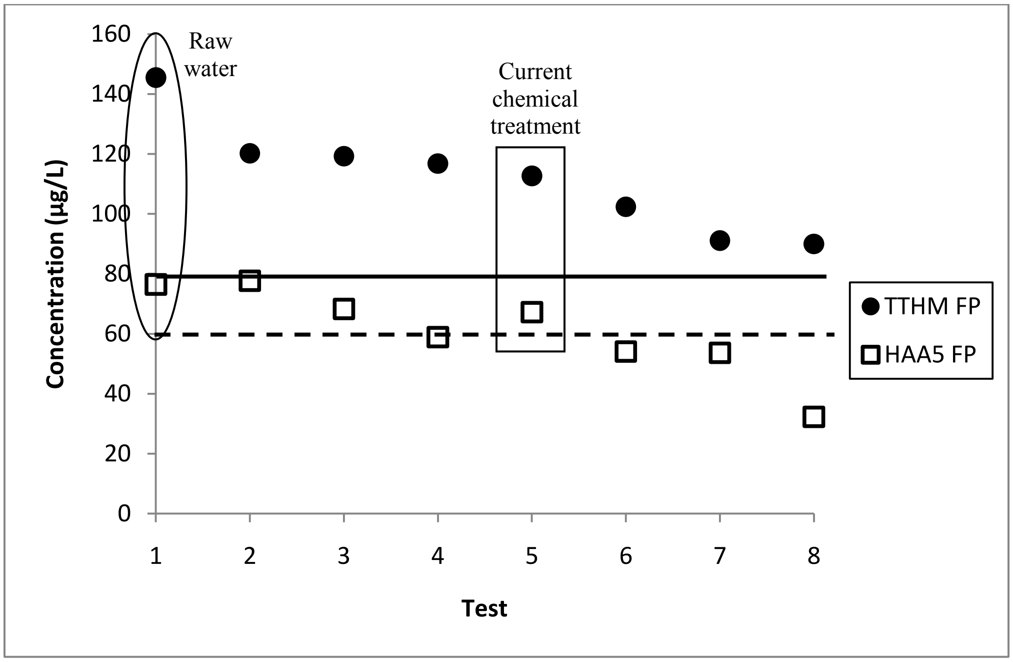

Figure 4-10 Current Treatment Combination Trenton Jar Tests

(TTHM MCL = 80 µg/L/ HAA5 MCL = 60 µg/L)
1 – Raw; **2** – 8NaAlO3; **3** – 130lime; **4** – 9C; **5** – 8 NaAlO3/130Lime; **6** – 8 NaAlO3/9C; **7** – 130 lime/ 9C; **8** – 8 NaAlO3/130 Lime/ 9C

For the initial jar tests, the chemical combination of 8 mg/L sodium aluminate with 130 mg/L lime and 9 mg/L carbon had the lowest HAA5FP concentration, but the TTHMFP concentration was still above the limit of 80 µg/L. Further testing was performed in order to optimize the chemicals used in the upflow clarifier in order to reduce DBP precursors and for TTHM and HAA5 concentrations to be in compliance.

In order to still be a softening facility, enhanced softening was the concentration for chemical optimization. Since sodium aluminate did not show positive results at the recommended lower dosages, liquid alum and ferric chloride were tried as coagulants in higher doses.

For the additional jar tests, the following approach was taken:

- Determine optimal dose of ferric chloride
- Determine optimal dose of liquid alum
- Determine effectiveness of enhanced softening (ferric/lime or alum/lime)
- Determine if carbon aids in organics removal

In addition to TTHM FP and HAA5 FP, UV-254 and dissolved organic carbon (DOC) can be useful indicators for DBP formation. As seen by the testing, the higher the percent reduction of UV-254 and DOC, the lower the TTHM FP (Figure 4-11) and HAA FP (Figure 4-12)

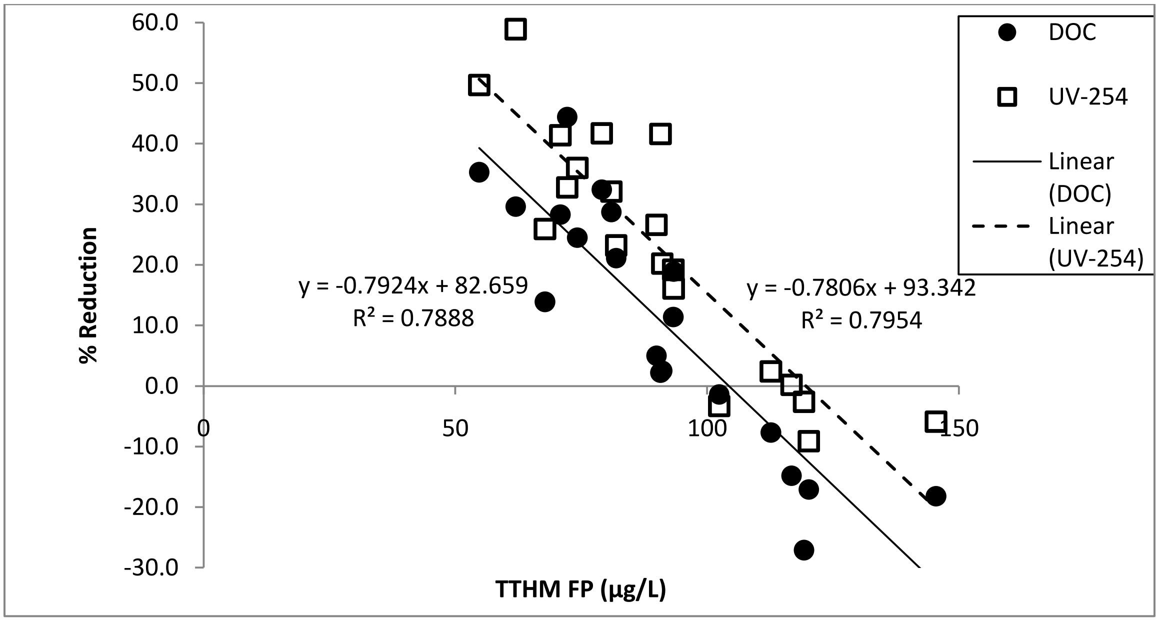

Figure 4-11 Trenton: Trends for % Reduction DOC and UV-254 versus TTHM FP

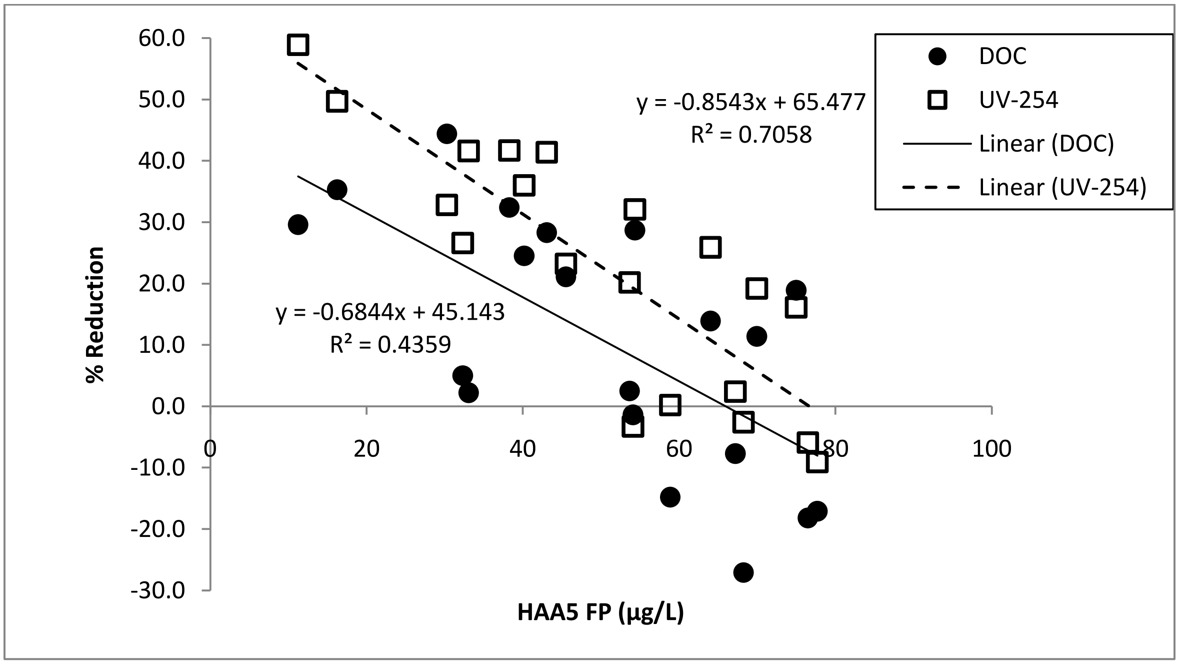

Figure 4-12 Trenton: Trends for % Reduction DOC and UV-254 versus HAA5 FP

After trying various chemical combinations from Table 4.8, the top eight (8) combinations with the highest percent reduction DOC and UV-254 (Figure 4-13) in addition to the lowest TTHM FP and HAA5 FP (Figure 4-14) were chosen for recommendations.

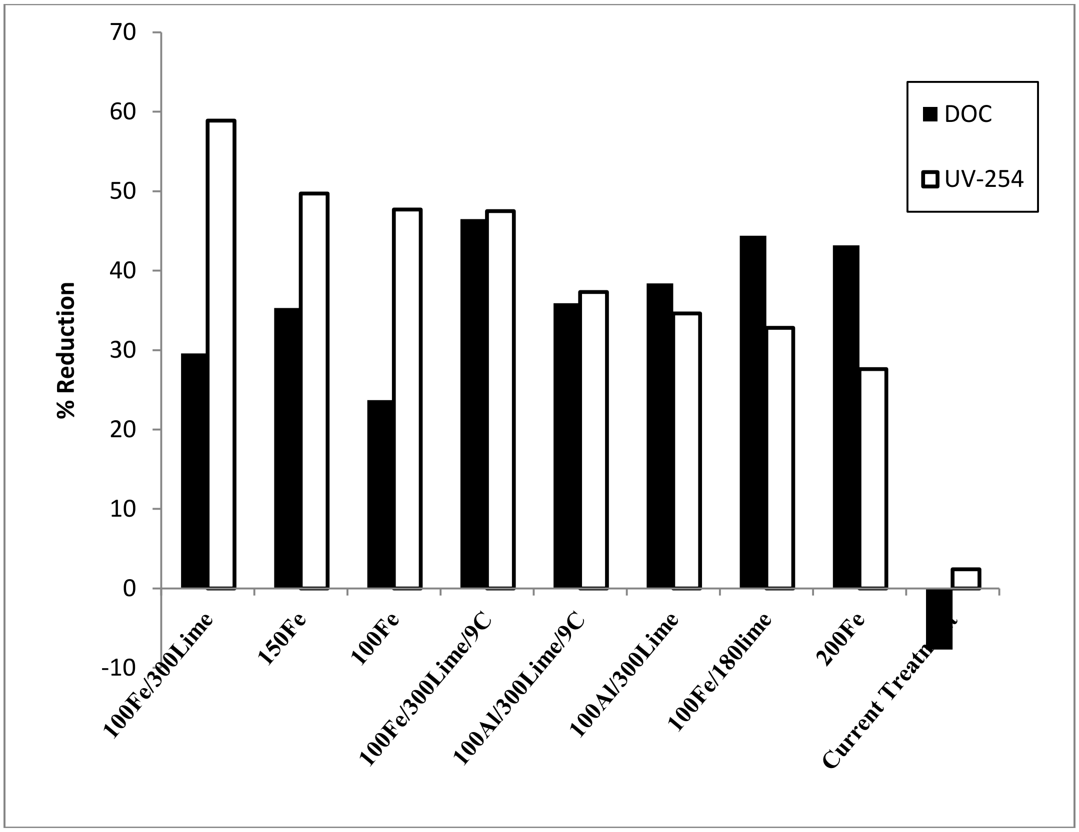

Figure 4-13 Trenton: Top Combinations for Highest DOC and UV-254 Reduction

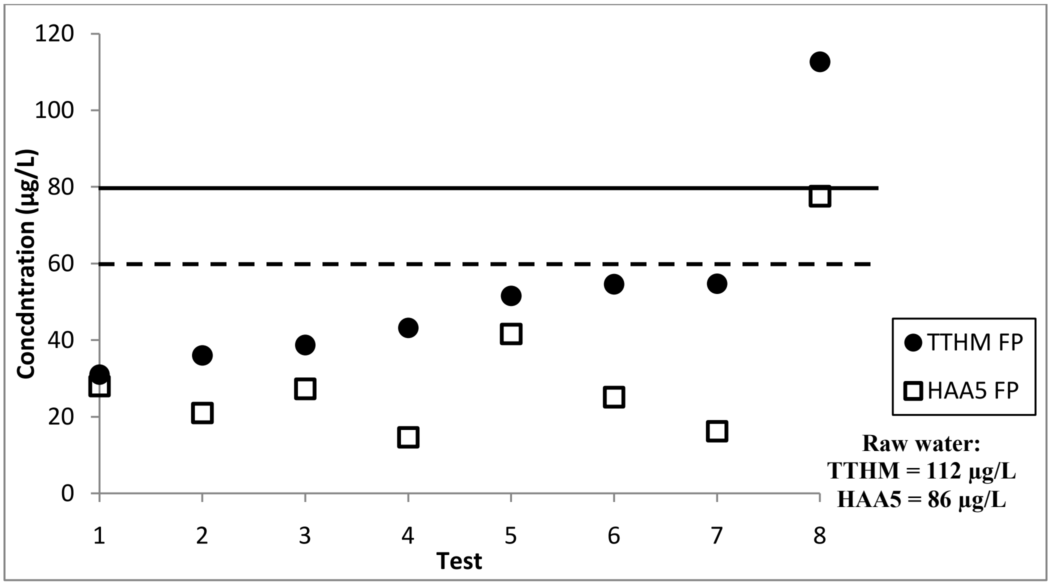

Figure 4-14 Trenton: Top Combinations for Lowest TTHM and HAA5 FP Values

1 – 200Fe; **2** - 100Al/300 lime/9C **3** – 100Fe/300lime **4** – 100Fe/300 lime/9C; **5** – 100Fe; **6** – 100Al/300lime; **7** – 150Al ; **8** – Current chemical combination

According to results, enhanced softening is the best treatment option for Trenton. Increased dosages of ferric chloride or alum along with lime show the greatest precursor reduction. Carbon also is shown to be effective when added in the enhanced softening process.

4.5 City of Marceline

The City of Marceline is located in the north central of Missouri with an approximate population of 2,300. The current Marceline Water Treatment Plant (MWTP) was upgraded for the operation in 2001. Water sources are from three different sources: Mussel Fork River, the Old Reservoir, and the New Reservoir located in an approximate 2400-acre watershed. Marceline has concerns about violating the US EPA regulations on the disinfection by-products trihalomethanes (THMs) and haloacetic acids (HAA5s).

4.5.1 Process Description

The water flow for the city of Marceline is by gravity throughout treatment process. The process units are described in Appendix E, which includes chemical usage. A summary of chemicals, dosing location and chemical use can be seen in Table 4.13.

Table 4.13: Chemical Usage at Marceline Drinking Water Treatment Facility

Chemical	**Process Location**	**Purpose**
Potassium permanganate ($KMnO_4$)	Influent pump station	Manganese removal
Carbon (20 – 30 mg/L AquaNuChar)	Carbon contact basin	Organics, odor, color, taste removal
150 mg/L Alum + acid (coagulant)	Primary rapid mix	Turbidity reduction/ Organics removal
$NaHCO_3$	Primary rapid mix	Raise alkalinity
Caustic soda (NaOH) (250lb@50%)	Secondary rapid mix	Softening
Lime ($Ca(OH)_2$)	Secondary rapid mix	Softening (magnesium and calcium removal)
Aluminum chlorohydrate	Secondary rapid mix	Help flocculate lime
Chlorine dioxide (~0.6ppm)	Secondary rapid mix	Oxidizer/disinfectant
AC 100 & Robin120	Filters	Filter aid
Chlorine (1.5 – 2.6 mg/L)	Clearwell	Disinfection

Figure 4-15 is an illustration of the treatment process for the City of Marceline. The process starts at the intake structure located in New Lake. Potassium permanganate ($KMnO_4$) is added to the water inside of the influent pump station and then pumped to the mechanical treatment process. The process units used are induced draft aerator, carbon contact basin (rapid mix followed by wood baffles), where carbon is added, primary stage (rapid mix, flocculation, and settling), where alum + acid and $NaHCO_3$ are added, secondary stage (rapid mix, flocculation, and settling), were caustic soda + lime + aluminum chlorohydrate + chlorine dioxide are all added, filters (4), before which AC

100 and Robin 120 are added, and then finally a clearwell, where additional chlorine is added before entering the distribution system.

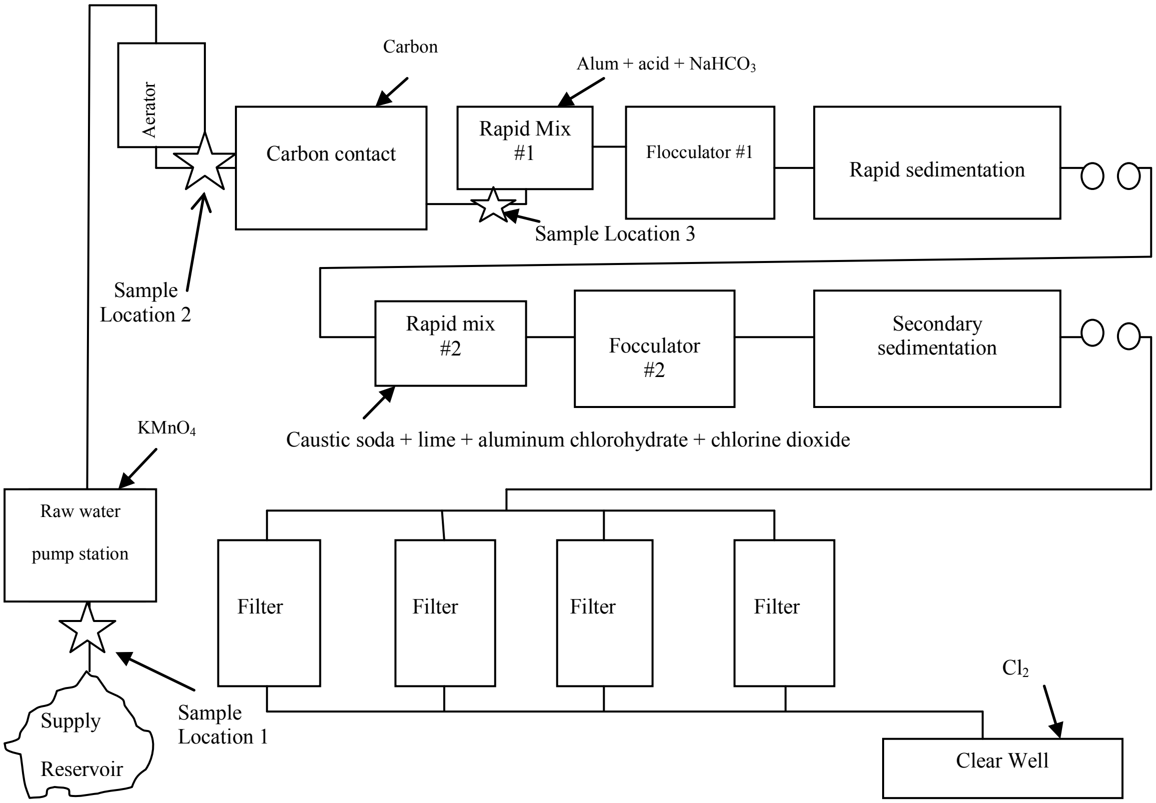

Figure 4-15: City of Marceline Water Treatment Plant Layout

4.5.2 Phase I Water Sampling

Water samples were collected from the twelve (8) locations in the Marceline water treatment plant. Figures 4-16 shows the average THM and HAA FP throughout the Marceline WTP.

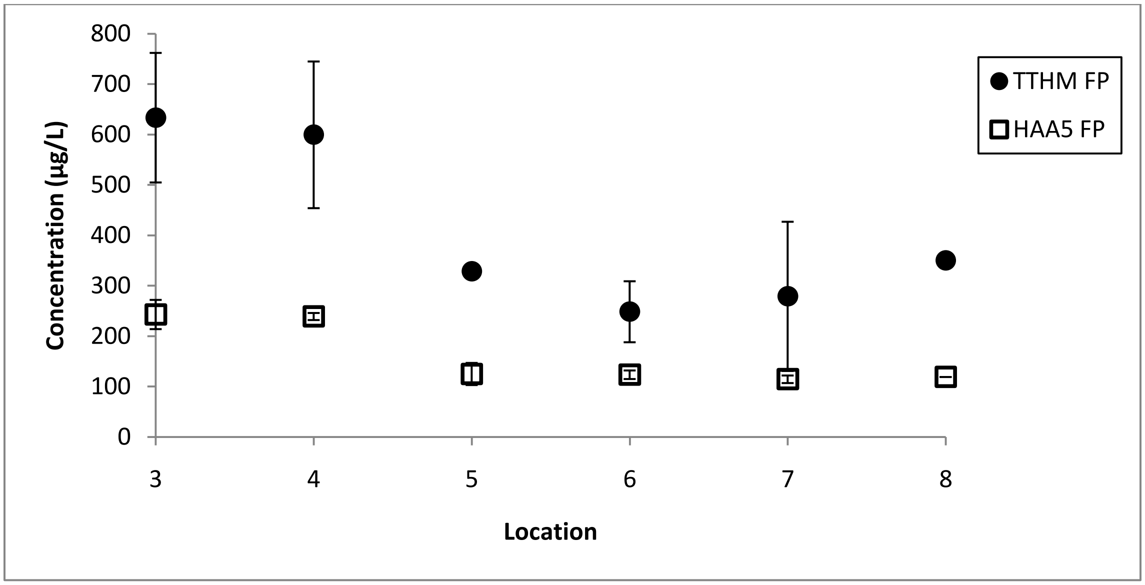

Figure 4-16 Average TTHM (MCL = 80 µg/L) and HAA5 (MCL = 60 µg/L) FP in the Marceline Treatment System

3-Influent water plant, **4**-Aerator effluent, **5**-Entry Floc contact basin, **6**-Primary Clarifier effluent, **7**-Secondary clarifier effluent, **8**-Tap water of plant water

Site 3 was very high (505 µg/L to 762 µg/L) suggesting that the addition of permanganate helps with the removal of manganese, but does little to reduce the formation potential of DBPs. The analysis of the water quality in WTP showed that the DBP formation potential could be decreased by treatment methods such as aeration, carbon adsorption, coagulation and flocculation, and chemical oxidation. The carbon adsorption removed about 40% of the DBPs FP. However, 40% removal efficiency was not enough to meet the requirement. The other treatment method removal efficiency is not as good as expected for DBP precursor removal. Specifically, coagulation was <10% removal and chemical oxidation with chlorine dioxide was <10% removal. These areas were considered for improving the removal efficiency of DBP precursors.

4.5.3 Phase II Testing

An initial 30 tests were run at Marceline drinking water plant July and August 2009. *Alum + acid* (60 mg/L) was tested to determine the efficiency in the current treatment process as a coagulant for turbidity and organics removal. *Ferric chloride* and *liquid alum* were tested as alternative coagulants.

Polymers (Robin 120 and AC 100) were tested for efficiency as coagulant aids.

Lime (100 mg/L) was tested to determine if the treatment process could efficiently reduce organic matter by adsorption by increasing the pH. *Soda ash* was tested as an alternative chemical to lime using the same dosage.

Magnesium hydroxide was tested to determine its effectiveness as a stabilizer. *Baking soda* (sodium bicarbonate) was tested as an alternative stabilize.

AquaNuChar carbon was tested to determine its current effectiveness for NOM removal by adsorption. *WPH carbon* was tested as an alternative carbon to see if it was more efficient at the same or lower dosages.

Table 4.14 lists a summary of the chemicals, concentrations and reasons for testing in the first round of jar tests.

Table 4.14 Chemical choices and concentrations for first round of Marceline jar testing

Chemical	Concentration (mg/L)	Purpose
Alum + acid	60	Determine effectiveness in current treatment
Ferric chloride ($FeCl_3$)	30, 80	Alternative coagulant
Liquid alum ($Al_2 (SO_4)_3 \cdot 18H_2O$)	20, 30, 40, 50, 60, 70, 80, 90, 100, 110	Test effectiveness in current treatment without acid
Polymer (Robin 120)	4, 4.5	Determine if polymer will aid in coagulation process
AC 100	5.6, 10, 15	Determine effectiveness in current treatment
Lime ($Ca(OH)_2$)	100	Determine effectiveness of enhanced softening
Soda Ash (Na_2CO_3)	100	Alternative to lime
$Mg(OH)_2$	7.3, 8	Determine effectiveness in current treatment
Baking Soda ($NaHCO_3$)	7.3	Alternative to $Mg(OH)_2$
AquaNuChar Carbon	30	Determine effectiveness of carbon in process
WPH Carbon	10, 23, 35	Alternative to carbon

After the first round of tests, only two of the tests showed results for TTHM FPs less than the regulatory limit of 80 μg/L and seven of the tests showed results for HAA5s less than the regulatory limit of 60 μg/L. The top seven results can be seen in Figure 4-17.

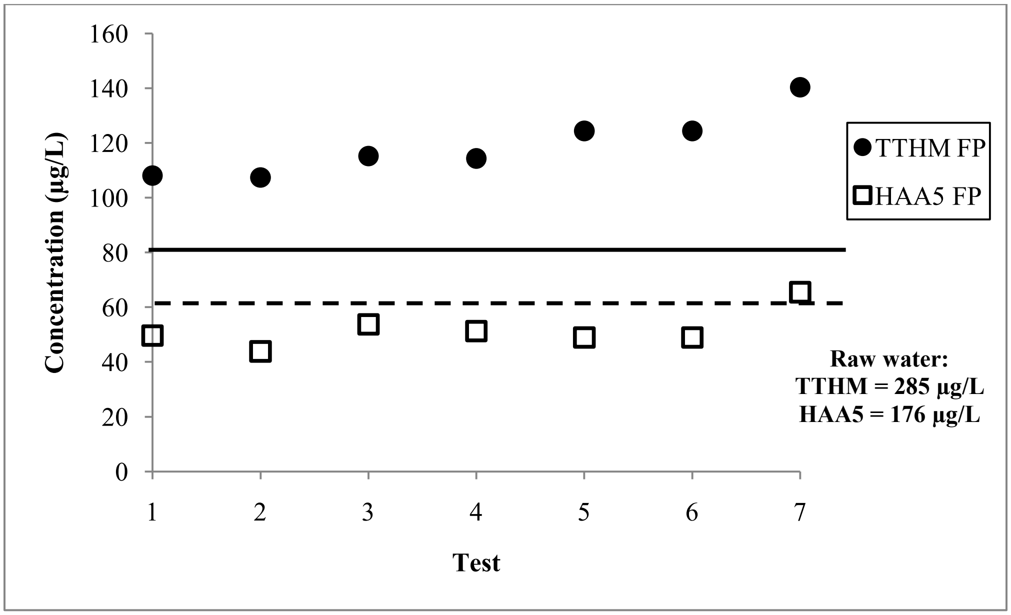

Figure 4-17 Marceline: Top Combinations for Lowest TTHM and HAA5 FP Values

(TTHM MCL = 80 µg/L/ HAA5 MCL = 60 µg/L)
1 – 4.5 poly/ 5.6 AC 100/100 soda ash; **2** – 4.5poly/5.6 AC 100/ 100 lime; **3** – 5.6 AC 100/ 100 soda ash; **4** – 5.6 AC 100/ 100 lime; **5** – 5.6 AC 100; **6** – 30 ferric; **7** – 80 ferric + 8 $Mg(OH)_2$

* Test 1 – 5: water from after primary mixing; Test 6 -7: water from after carbon

Even though all of the results had low enough values for HAA5FP, all of the tests from after the primary mix still had too high of TTHMFP values. This indicated that the current treatment in the primary rapid mix process (alum + acid + baking soda) is not sufficient enough to be in compliance with EPA standards. When adding ferric chloride to water obtained from after carbon addition, the TTHMFPs and HAA5FPs were lower than the standards, therefore future testing focused on using ferric chloride as the main chemical addition.

For Marceline's second round of testing, 54 different jar testing combinations were run. Various chemical combinations were used to determine which would be the most effective and can be seen in Table 4.15.

Table 4.15 Chemical choices and concentrations for second round of Marceline jar testing

Chemical	Concentration	Purpose
Ferric chloride ($FeCl_3$)	50, 100, 144, 150	Coagulant comparison; enhanced coagulation and enhanced softening
Liquid Alum ($Al_2(SO_4)_3 \cdot 18H_2O$)	50, 100, 150	Coagulant comparison; enhanced coagulation and enhanced softening
Lime ($Ca(OH)_2$)	60, 180, 240, 300, 420, 600	Determine effectiveness of enhanced softening
Magnesium hydroxide ($Mg(OH)_2$)	17, 34	Compare to baking soda as stabilizer
Baking soda ($NaHCO_3$)	17, 34	Compare to $Mg(OH)_2$ as stabilizer
WPH Carbon	15, 20, 30	Determine effectiveness as current treatment

Water used in testing came from raw water (site #3), after the aerator, and after carbon contact basin. Each of these locations would be feasible for the addition of coagulants and the other chosen chemicals. Raw water quality used for the tests can be seen in Table 4.16.

Table 4.16 Marceline Raw Water Quality

	pH	Turbidity (NTU)	UV-254 (abs/cm)	DOC (mg/L)	TTHMFP (µg/L)	HAA5FP (µg/L)	Location
11-Nov-09	8.3	3.98	0.103	6.28			Site #3
29-Nov-09	8.0	10.2	0.168	6.47			Site #3
25-Mar-10	7.1	17.7	0.302	6.34	285	176	Site #3
21-Apr-10	7.3	32	0.175	4.33			After Carbon
18-May-10	7.9	15.7	0.262	6.09			After Aerator
20-May-10	8.2	14.4	0.251	6.10			After Aerator
25-May-10	8.2	5.97	0.253	6.04			After Aerator
Average	7.86	14.28	0.216	5.95	285	176	
St. Dev.	0.47	9.31	0.069	0.73			

Due to permanganate residual, chlorine demand was not able to be determined for a majority of the tests, therefore TTHM and HAA5 formation potential could not be determined. Figure 4-18 shows the first set of tests where chlorine demand could be determined.

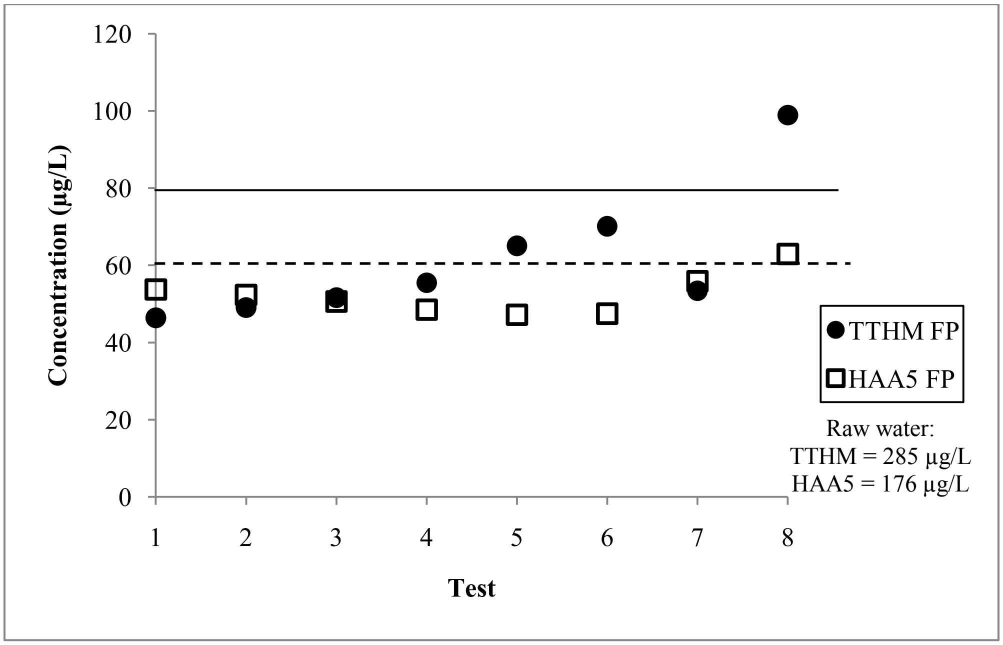

Figure 4-18 TTHMFP and HAA5FP results for first set of Marceline tests

1 – 144Fe/34 baking soda; 2 – 144Fe/17 baking soda; 3 – 144Fe/ 9baking soda; 4 – 100 Fe; 5 – 144Fe/ 34 $Mg(OH)_2$; 6 – 144Fe/17 $Mg(OH)_2$; 7 – 144Fe/9 $Mg(OH)_2$; 8 – 100 Al

All of the tests where ferric chloride was the coagulant showed TTHMFP and HAA5FP values below regulatory requirements, whereas the test with liquid alum were still too high. After trying various chemical combinations, as seen in Table 4.16, the top seven tests were chosen for recommendations based on the highest percent reduction of UV-254 and total organic carbon. These results can be seen in Figure 4-19.

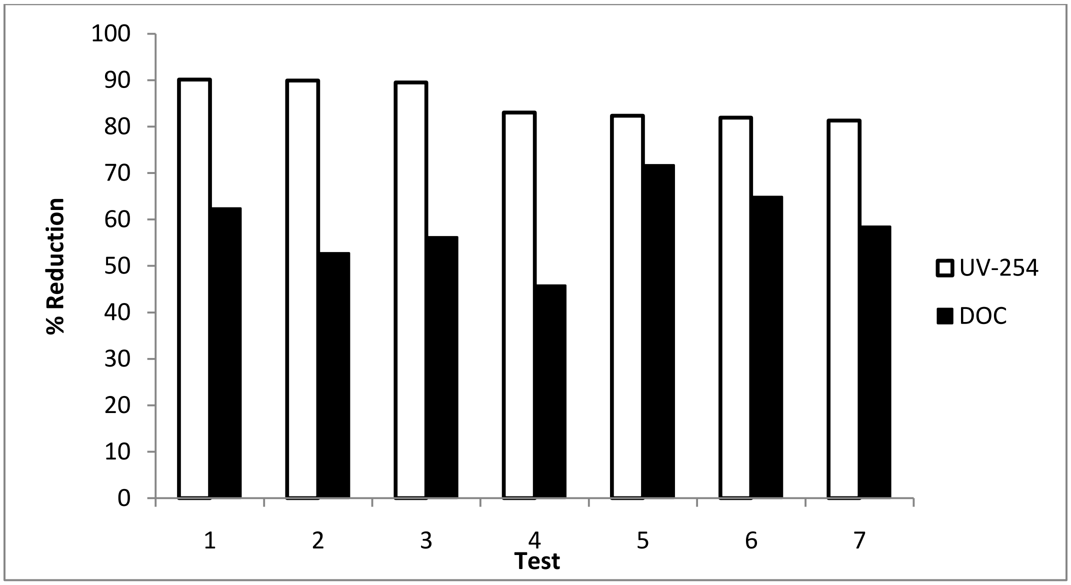

Figure 4-19 Marceline: Top Combinations for Highest DOC and/or UV-254 Reduction

1 – 100Fe; 2 – 100Fe/17 $Mg(OH)_2$ second mix; 3 – 100Fe/17 baking soda second mix; 4 – 100Al; 5 - 150Fe; 6 – 125Fe; 7 – 100Fe/300 lime

The last test ran for the City of Marceline was to determine if a change in treatment sequence could make a difference on DBP precursor reduction. Three tests were run where the order of addition for carbon and ferric chloride was changed. A first mix was run with rapid mix (1 min @ 100 rpm) and flocculation (20 min @ 35 rpm) and a second mix was run with rapid mix (1 min @ 100 rpm), flocculation (30 min @ 35 rpm) and settling (30 min). The tests were (Table 4.17):

1. Add ferric chloride during first mix and carbon during second mix.
2. Add carbon during first mix and ferric chloride during second mix.
3. Add carbon and ferric chloride during first mix and no chemical addition during second mix.

Table 4.17 Chemical addition matrix for Marceline's sequence test

	Jar	Ferric Chloride (mg/L)	AquaNuChar Carbon (mg/L)
First Addition:	1	100	0
	2	0	30
	3	100	30
Second Addition	1	0	30
	2	100	0
	3	0	0

Using UV-254 and dissolved organic carbon (DOC) as indicators for DBP precursor reduction, it can be seen by Table 4.18 that the addition of ferric chloride in the first mix yields better results for DBP reduction.

Table 4.18 Results from the Marceline sequence test

Jar	pH	Turbidity (NTU)	Alkalinity (mg/L)	UV-254 (abs/cm)	DOC (mg/L)
1	7.2	3.84	15	0.140	3.17
2	7.2	3.42	41	0.236	4.65
3	6.9	0.36	22	0.140	3.13

Due to Marceline's higher UV-254 values in the raw water, it can be assumed there is a high amount of aromatic organics present in the water. Since coagulation more easily removes aromatic organic matter, allowing two mixing cycles with the ferric chloride in the system will allow greater removal. Carbon is not as effective or as necessary to be used for two mixing cycles.

4.6 Conclusions and Recommendations

Based off the testing in the previous sections, some basic suggestions for each facility follow.

4.6.1 Monroe City

As seen by the results in Figure 4-10 and Figure 4-11, jars 1, 2 and 3 were the only tests to yield results that are in compliance for both TTHM and HAA5. Table 4.19 lists the recommendations, as well as the advantages and disadvantages associated with implementation of these recommendations.

Table 4.19 Recommendations from Monroe City Jar Tests

Recommendation	Advantage	Disadvantage
Increase coagulant dose (~ 100 mg/L) and switch to ferric chloride	Increased removal of DBP precursors; In compliance for TTHM FP and HAA5 FP	Increased sludge due to increase in ferric concentration; potential for increase in TTHM FP and HAA5 FP in warmer months (and therefore out of compliance)
Continue to use liquid alum and carbon	No change in chemicals; Increased removal of DBP precursors; In compliance for TTHM FP and HAA5 FP	As seen in Phase I, the water treatment plant shows out of compliance samples in warmer months using these chemicals

Testing performed in Phase I showed the current chemical usage caused TTHMFP concentrations in August to exceed the EPA limit of 80 μg/L. Due to the drastic reduction of TTHMFPs and HAA5FPs in the rapid mix basin, focus for chemical optimization was directed toward coagulation and carbon addition.

The first round of tests allowed a closer look at each chemical and chemical combination for the current treatment process in the rapid mix tank. These tests indicated none of the individual chemicals gave the TTHMFP and HAA5FP reduction necessary to be in compliance. When current chemicals were used in combination, 29 mg/L alum and 47.5 mg/L carbon (current dosages) gave TTHM FP and HAA5FP concentrations under compliance levels. These results suggest the current chemical usage has potential to be optimized by further testing of liquid alum and carbon concentration modification and prospective substitutions for the stabilizing agent that adds alkalinity back to the water and changing the type or concentration of polymer. Overall, if increased coagulant dosage is feasible for the facility, enhanced coagulation with ferric chloride worked the best for the treatment facility for DBP precursor reduction. Ferric chloride can continue to be tested for optimal dosage along with carbon and/or polymer.

4.6.2 Trenton

As seen by Figure 4-21, all of the top combinations had TTHM FP and HAA5 FP values less than needed to be in compliance. Higher amount of coagulant dosing (100 – 150 mg/L) showed more optimal results than lower dosing (50 mg/L) indicated enhanced coagulation is a better option. This could be due to the lower influent UV-254 absorbance values where organics are more difficult to remove by coagulation than in waters containing higher UV-254 values and therefore contain more aromatic organic matter. In addition to coagulants, enhanced softening with high concentrations of coagulant and lime also gives positive results for TTHM FP and HAA5 FP to be in compliance. Again, due to the lower UV-254 absorbance values and therefore less aromatic organic content in the source water, lime plays an effective role for organics removal by adsorption (Uyak, et al., 2007). Recommendations can be seen in Table 4.20.

Table 4.20 Recommendations from Trenton Jar Testing

Recommendation	Advantage	Disadvantage
Switch to ferric chloride as coagulant at increased dosage	Higher organic removal; TTHM FP and HAA5 FP below compliance level	Increased coagulant concentration and sludge
Increase lime dosage	Increased area for NOM adsorption	Increased pH; increased sludge

Testing performed in Phase I indicated the current chemicals added in the upflow clarifier were not sufficient for meeting TTHM FP and HAA5 FP requirements. Ferric chloride and liquid alum were tested in place of using sodium aluminate – a coagulant recommended for use only in small concentration. These results showed much higher DBP precursor reduction and lower TTHM FP and HAA5 FP concentrations, particularly in higher dosages. In addition, precursor removal was increased when using ferric chloride versus liquid alum. Lastly, increased concentrations of lime also showed better results for controlling DBP formation. Carbon did not seem to aid significantly in reducing TTHMFP and HAA5FP values.

4.6.3 Marceline

Based on all the tests performed on water from the city of Marceline, it is apparent ferric chloride works best as the coagulant of choice. Enhanced softening, when using lime and ferric chloride, also showed potential for reduction of DBP precursors. There was no significant difference between using baking soda ($NaHCO_3$) and $Mg(OH)_2$ as a stabilizer. Lastly, AWP carbon did not reduce DBP precursors as efficiently as needed. A summary of recommendations can be seen in Table 4.21

Table 4.21 Recommendations from Marceline Jar Testing

Recommendation	Advantage
Change from alum + acid to ferric chloride	TTHMFP and HAA5FP results are under regulatory concentrations
Continue to test different types of carbon	Determine a more efficient carbon for organics removal

Overall, the first round of testing indicated the current treatment process was not performing efficient enough to reduce TTHMFP and HAA5FP concentrations sufficiently. However, with the switch from alum + acid to ferric chloride, the TTHMFP and HAA5FP values were low enough to be in compliance. Further testing of carbon and polymer along with stabilization techniques could aid in additional reduction of DBP precursors.

4.7 References

[1] APHA, American Water Works Association, and Water Environment Federation (1998). *Standard Methods for Examination of Water & Wastewater, 20th Edition*, American Health Association, Baltimore, Maryland.

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[6] US Army Corp of Engineers (2001). "Engineering and Design - Precipitation/Coagulation/Flocculation." D. o. t. Army, ed.Washington, DC, 101.

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Chapter 5 Conclusions and Future Research Considerations

5.1 Summary of Research Effort

The goal of the overall research projects were to determine the effectiveness of enhanced treatments, such as enhanced coagulation and enhanced softening, at reducing disinfection by-product precursors. Optimization of chemical treatments is necessary in order to run a treatment facility efficiently and remain in compliance with EPA standards. Source water characteristics are an extremely important factor in determining the most favorable treatment combinations.

5.2 Conclusions/Key Points

Enhanced Coagulation and Enhanced Softening:

- The effectiveness of enhanced coagulation and enhanced softening is dependent upon source water characteristics
    - Water with higher initial UV-254 absorbance values, therefore contains higher detectable concentrations of aromatic (hydrophobic) organic matter, respond better to DBP precursor reduction when treated using enhanced coagulation.
    - Water with lower UV-254 absorbance values in their source water tends to respond better to DBP precursor reduction when treated using enhanced softening.

- Increased dosages of coagulant (~100 mg/L) showed optimal results when compared to traditional coagulant dosages (~30 mg/L).
    - Underdosing of coagulant did not provide enough positive metal ions to react with the negatively charged organic ions.
    - Overdosing of coagulant showed negative results for DBP precursor reduction due to charge reversal and colloid restabilization.
- DBP precursor reduction was effected by pH.
    - When the addition of lower dosages of lime increased the pH to around 8 – 9, DBP precursor reduction was not as efficient as increased pH values (from 10 – 11).
        - Low pH causes coagulation to be driven by charge reduction from an increased positive charge due to species formed at lower pH (Bratby, 2006).
            - Increased risk of overdosing
        - At a higher pH, there are larger Al or Fe species, up to polymers, but less charge per Al or Fe and coagulation driven by adsorption, bridging and sweep floc (Bache, 2007).
    - Increase in pH by lime causes more adsorption of NOM onto the surface of calcium precipitates or incorporation of NOM into the crystal structure of the precipitate by coprecipitation.

Use of Redox Potential

- Final E_h values follow the inverse trend of pH
    - Redox potential indicates the transfer H^+ occurring during change of pH.
- Redox potential can change throughout the coagulant process even during constant pH.
    - The destabilization and restabilization process which occurs during coagulation when the metal coagulant disperses and then forms a solid metal hydroxide can be seen in E_h values when tracked throughout the entire reaction process.
    - It is not clear if this response provides some indications of how effective the coagulation process will be with respect to removal of DBP precursors but it does give insight into the reactions occurring during coagulation.

Optimization of Chemical Treatment in Small Communities

- Simple and cost effective changes in chemical treatments, such as altering chemical dosage or using alternative chemicals, can have a significant impact on DBP precursor reduction.
- Determining the effectiveness of current chemicals used in the treatment process, both separately and in combination, is the first step in determining which chemicals need to be altered.

- Enhanced treatment, particularly with ferric chloride, indicated positive results for all three communities.

5.3 Recommendations/Future work

Enhanced coagulation and enhanced softening seem to be affected by source water characteristics. A more detailed look into the fractionation of natural organic matter contained in the source water is needed to quantify which process works best based on the organic characteristics. Smaller increments of coagulant and lime should also be tested in order to determine the optimal dosages of each chemical for DBP precursor reduction.

Redox potential has very interesting trends based on the coagulant or other chemicals, such as lime, used for treatment. A more thorough look at different chemical doses and source water characteristics may give more insight into the redox changes which take place even when the pH remains constant.

The research involving optimizing chemical treatments on smaller communities is still on-going. A sizeable amount of tests must be performed in order to effectively determine which treatment strategy will work best for each individual facility.

5.4 References

[1] Bache, D. H., and Gregory, R. (2007). *Flocs in Water Treatment*, IWA Publishing, London.

[2] Bratby, J. (2006). *Coagulation and Flocculation in Water and Wastewater Treatment*, IWA Publishing, Seattle.

Appendix A: Required Equipment and Chemicals for Enhanced Coagulation/Softening Experiments

The following equipment and chemicals are required to perform the enhanced coagulation/softening experiments:

- Phipps and Bird jar test apparatus with 2 L square beakers
- pH meter calibration buffer solutions, pH = 4.0, pH = 7.0, pH = 10.0
- Lime stock solution
- 35% ferric chloride stock solution made such that 1 mL = 10 mg/L
- 48% alum stock solution made such that 1 mL = 10 mg/L
- Vacuum filter and 0.45 µm glass fiber filter
- Sample bottles for DOC and UV-254 analysis
- Turbidity meter, bottles and calibration samples
- Pipettes, beakers, and graduate cylinders
- Carbon filtered distilled water
- 20 L carboys

Appendix B: Required Equipment and Chemicals for Redox Potential Experiments

The following equipment and chemicals are required to perform the redox potential experiments:

- Phipps and Bird jar test apparatus with 2 L square beakers
- pH meter calibration buffer solutions, pH = 4.0, pH = 7.0, pH = 10.0
- pH meter
- Lime stock solution (12% CaO)
- 35% ferric chloride stock solution made such that 1 mL = 10 mg/L
- 48% alum stock solution made such that 1 mL = 10 mg/L
- Vacuum filter and 0.45 µm glass fiber filter
- Sample bottles for TOC and UV-254 analysis
- Turbidity meter, bottles and calibration samples
- Pipettes, beakers, and graduate cylinders
- Carbon filtered distilled water
- 20 L carboys
- Orion 5 star meter, ORP probe and calibration standards

Appendix C: Required Equipment and Chemicals for Facility Optimization Experiments

The following equipment and chemicals are required to perform the enhanced coagulation/softening experiments:

- Phipps and Bird jar test apparatus with 2 L square beakers
- pH meter calibration buffer solutions, pH = 4.0, pH = 7.0, pH = 10.0
- Lime stock solution
- 35% ferric chloride stock solution made such that 1 mL = 10 mg/L
- 48% alum stock solution made such that 1 mL = 10 mg/L
- Vacuum filter and 0.45 µm glass fiber filter
- Sample bottles for DOC and UV-254 analysis
- Turbidity meter, bottles and calibration samples
- Pipettes, beakers, and graduate cylinders
- Carbon filtered distilled water
- 20 L carboys
- 1 L and 125 mL amber bottles
- NaClO free chlorine stock solution, pH 8 borate buffer, NH_4Cl, and free chlorine powder pillows for chlorine demand
- Assorted sizes of vials
- 0.02 M Sulfuric acid, Phenolphthalein, Bromcresol green indicator solution and Sodium thiosulfate for alkalinity testing

Appendix D: Water Quality Analysis Methods

UV-254 Analysis (for DBP precursor measurement)

UV-254 analysis was conducted using CARY 50 CONC UV-Visible Spectrophotometer with a 1-cm quartz cell. UV-254 was measured at the wavelength of 254 nm. Duplicate analyses were performed on each sample and the average was reported. If the difference between the two values was greater than 0.001/cm, a third analysis was performed and the averages of all three values were reported.

TOC/DOC Analysis (for DBP precursor measurement)

Total Organic Carbon (TOC) concentrations in water samples were determined on a Shimadzu TOC-V_{CPN} analyzer. Water samples were filtered using a 0.45-μm glass fiber filter (Whatman GF/F) before Dissolved Organic Carbon (DOC) concentrations were measured.

THM Analysis

Trihalomethane (THM) concentrations were determined by a gas chromatograph (Varian, Model 3800)/mass spectrometer (Varian, Saturn 3800) (GC/MS) equipped with a Tekmar 300 purge and trap concentrator (similar to Standard Method for the Examination of Water and Wastewater 6200 B and US EPA Method 524.1).

HAA Analysis

Haloacetic acid (HAA) concentrations were determined by using a liquid/liquid extraction, derivation GC method (similar to Standard Method for the Examination of Water and Wastewater 6521 and US EPA Method 552.2). The sample is extracted with methyl tertiary-butyl ether (MTBE) at an acid pH to extract the non-dissociated acidic compounds. A salting agent (sodium sulfate) is added to increase extraction efficiency.

The extracted compounds are methylated with methanol and sulfuric acid solution to produce methyl ester derivatives that can be separated chromatographically.

Chlorine Residual

Chlorine concentration was measured by DPD powder pillows photometric method (EPA approved HACH 8021) using HACH DR/2500 spectrophotometer. Samples were transferred into the 10 mL spectrophotometer cell and mixed with free chlorine powder pillow, and the absorbance of the solution was measured by the HACH spectrophotometer. This method is able to measure chlorine concentration up to 2.0 mg/L.

Sample Chlorination and chlorine demand

A 24-hour chlorine demand study was performed (sample buffered at pH 8.0 and incubated in the dark at 20 °C) using a series of three chlorine dosages based on the Cl_2:TOC ratios of 1.2:1, 1.8:1, and 2.5:1. From the results of these tests, the 24 hr chlorine dose for chlorine demand was selected in order to yield a chlorine residual of 1.0 ± 0.4 mg/L.

Before dosing, samples were buffered to pH 8.0 ± 0.2 with approximately 2 mL/L borate buffer [1.0 M boric and 0.26 M sodium hydroxide in Millipore water]. A concentrated sodium hypochlorite dosing solution (1 to 5 g/L) was added to obtain the desired disinfectant dose.

<u>THM, HAA Formation Potential Test</u>

After three days chlorine incubation, 40 mL of the sample was transferred to the extraction vial for HAAs analysis. The remaining sample was also transferred to 40 mL vials for THM measurement (making sure no air bubbles passed through the sample during the vial filling operation, or were trapped in the sample when the bottle was sealed). Before sampling, 50 μL of 88.0 g/L ammonium chloride was added to all extraction vials and 40 mL vials to quench the free chlorine. DBPs (THMs & HAAs) concentrations were measured using purge and trap GC/MS method and GC extraction derivative methods.

Appendix E: Process Stages/Unit Descriptions for City of Marceline

1) **Intake structure (located in reservoir)**
   - A gate valve allows for openings at different levels. Inlet level is typically at 4 ft below water surface.
2) **Influent Pump Station**
   - 6 lbs/day $KMnO_4$ added at the inlet to the raw water pumps is used to oxidize organics and to precipitate Mn (from 0.6 in raw water to 0.019 in finished water).
   - Flow of $KMnO_4$ depends on raw water pump flow (these run about 5 to 6 hrs/day).
   - The City plans on putting variable frequency drives (VFD) on pumps to better allow control of flow through the plant.
3) **Induced draft aerator**
   - For removal of VOCs and some metals in solution
4) **Carbon contact basin (rapid mix followed by wood baffles)**
   - Detention time of 20 min @ 1500 gpm.
   - Dosage: 20 to 30 mg/L carbon added.
5) **Primary stage (rapid mix, flocculation, and settling)**
   - Rapid mix for 30 s; turbidity ~0.27 NTU – add coagulant (alum (160 mg/L) + acid) and $NaHCO_3$ (to raise alkalinity).
   - Flocculation basin (vertical paddles) for ~ 45 min.
   - Rectangular clarifier (covered with precast concrete): 14 ft swd (L:W ~ 3:1 to 4:1), chain in flight to move sludge to screw pump drawoff.
6) **Secondary Stage (rapid mix, flocculation, and settling)**
   - Rapid mix for 30 s; turbidity ~1.99 NTU – add caustic soda (250 lb@50%) + lime + aluminum chlorohydrate (to help floc lime) + chlorine dioxide (~0.6 ppm).
   - Flocculation basin (vertical paddles) for ~ 45 min.
   - Rectangular clarifier (covered with precast concrete): 14 ft swd (L:W ~ 3:1 to 4:1), chain in flight to move sludge to screw pump drawoff.
7) **Filters (4)**
   - 500 gpm each; 10 ft depth; dual media: Anthracite and sand
   - Weir sets flow – free fall discharge
   - Water backwash only – 2 backwash cycles; Backwash water goes to a backwash basin and then to a creek
   - Control valves on both inlet and discharge sides – helps with plant startup to avoid turbidity spikes
   - AC 100 and Robin 120 added as a filter aid

8) **Clearwell**
    - 180 min (meets Ct); Baffled; Chlorine added (1.5 to 2.6 mg/L)

9) **Distribution system**
    - High Service Pumps – runs longer than raw water pumps to reduce clearwell level and fill towers.
    - South Tower (closest to the plant; fed directly from high service pumps; bottom in, bottom out).
    - North Tower (1968; closer to old reservoir; bottom in, bottom out).
    - Produce 450,000 to 600,000 gpd (1/2 sold to water district #3 – 2200 to 2400 service connections, 1200 to 1400 miles of 6" or smaller pipe; Dan Downy is water district operator).
    - Finished water DOC about 3.4 mg/L.