

MANAGEMENT OF DBP FORMATION USING ENHANCED TREATMENT
TECHNOLOGIES & AN ARRAY OF PREDICTION TOOLS

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Management of DBP Formation Using Enhanced Treatment Technologies & an Array of
Prediction Tools

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This work is dedicated to my father, Mr. Purnachander
Rao Poleneni - without him I wouldn't be the person I am today.

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1. Introduction

Developing new technologies to help small scale utilities achieve compliance with increasingly stringent water quality regulations is vital for maintaining uniform health standards for all citizens, but given the financial, infrastructural and technical constraints these utilities face on a daily basis, it is just as important to develop simple, non-invasive and cost-effective ones that require minimal organizational and structural changes (Shih et al., 2006). Drinking water treatment process includes a series of unit processes that change the composition of water with an aim to decrease or eliminate biological, organic and inorganic contaminants while making it safer for human consumption (Hass, 1999). Disinfection is one such process primarily used to inactivate microorganisms that can cause significant harm to humans upon intake. Chlorine is predominantly used as a disinfectant in the United States, though known for its ease of usage and efficiency it does produce carcinogenic by-products known as disinfection by-products (DBPs) (Sadiq & Rodriguez, 2004). DBPs are regulated dissolved organic substances usually present in micro or nano grams per liter quantities in finished water. Dealing with such low concentrations of contaminants in terms of controlling their production while at treatment plant and in distribution system requires operational and treatment technology changes. Because the extent of DBP production depends on precursors present in raw water, the efficiency of unit processes in removing them during treatment and the amount of disinfectant available to react with precursors, their control strategy should include optimizing the process with respect to all the above factors (Gang, 2001).

1.1.Objective:

The goal of this research is to develop cost-effective and non-invasive technology that uses recycled materials from the treatment plant to address the issue of DBP formation by enhancing TOC removal efficiency of the treatment process and for the control of their formation in distribution systems, commonly used operational strategies versus different pipe materials is also investigated using predictive models such as Pipe Loop, Material Specific Simulated Distribution System Test (MS-SDS), Simulated Distribution System Test (SDS) and Pipe Section Reactor (PSR).

1.2.Scope:

Objective 1: Development of a non-invasive technology to decrease to enhance TOC removal efficiency of treatment plants.

Task 1: Identify effluent materials from drinking water unit processes that can be recycled to increase the efficiency of the treatment process with respect to TOC concentration.

Task 2: Design an experimental plan to test multiple ratios of recycled materials

Task 3: Analyze the data collected in terms of change in TOC, turbidity, aluminum, iron and pH concentrations

Objective 2: Compare DBP prediction models built using different pipe materials under commonly used operational strategies.

Task 1: Identify models available to predict DBPs, pipe materials commonly used in distribution systems and operational strategies used by treatment plants.

Task 2: Design and build the chosen models using pipe sections extracted from distribution systems

Task 3: Analyze the effect of materials and operational strategies on chlorine decay and TTHM formation kinetics in all the models.

Objective 3: Analyze the relationship between additional TOC removal and its effect on chlorine demand and TTHM formation potential of treated water.

Task 1: Design an experimental plan to test waters from multiple sources for TTHM formation potentials after being treated with recycled materials

Task 2: Analyze the data collected in terms of difference in chlorine demand and TTHM formation rate with additional TOC removal

2. Literature Review

2.1 Typical Drinking Water Treatment Process

Many fresh water aquifers and isolated surface waters usually have high quality water which can be directly pumped to meet any designated needs including human consumption, industrial use and irrigation (Vesilind & Peirce, 1982). However, that is not the case in many regions in this nation, especially in the regions with dense populations or the ones that are agriculture dominant. In these situations, varying degree of water treatment is used to make water from the available sources fit for human consumption. Because most cities across the US have only one water supply, water distributed can be used to meet wide variety of daily and seasonal needs such as human consumption, industrial use, irrigation, lawn maintenance, and domestic use. Though most of these needs can be easily met using low quality water, the water supplied through single distribution lines are aimed to meet the 'highest use' which, in most cases, is human consumption.

In addition to human activities and industrial processes, natural processes such as coming in contact with atmosphere, earth's surface and movement over the soil surface can add impurities to the water (Vesilind & Peirce, 1982). This kind of contamination can either make water unsightly and unaesthetic or have higher pathogen concentrations leading to serious complications. Whichever the situation, the water needs to be treated appropriately based on raw water characteristics.

A typical water treatment process (Figure 1) is designed to remove odors, taste, color and turbidity as well as bacteria and other contaminants. The treatment plant uses a sequence of coagulation, flocculation, sedimentation, filtration and disinfection unit processes to treat incoming raw water with an aim to decrease TOC and turbidity to a required level

(Wulff, 2011; U.S. Environmental Protection Agency (USEPA), 1998) and produce finished water with little to no taste and odor issues. In addition to these parameters the finished water is also expected to comply with rules such as Total Coliform Rule, Maximum Residual Disinfectant Level (MRDL) and Stage-II D/DBP Rule. Achieving a balance between TOC reduction and chlorination has been a great concern to both environmental officials and the utility managers since the late 1970s when research began to show a direct link between trihalomethane (THMs) formation and reaction between TOC and free chlorine (Rook, 1977).

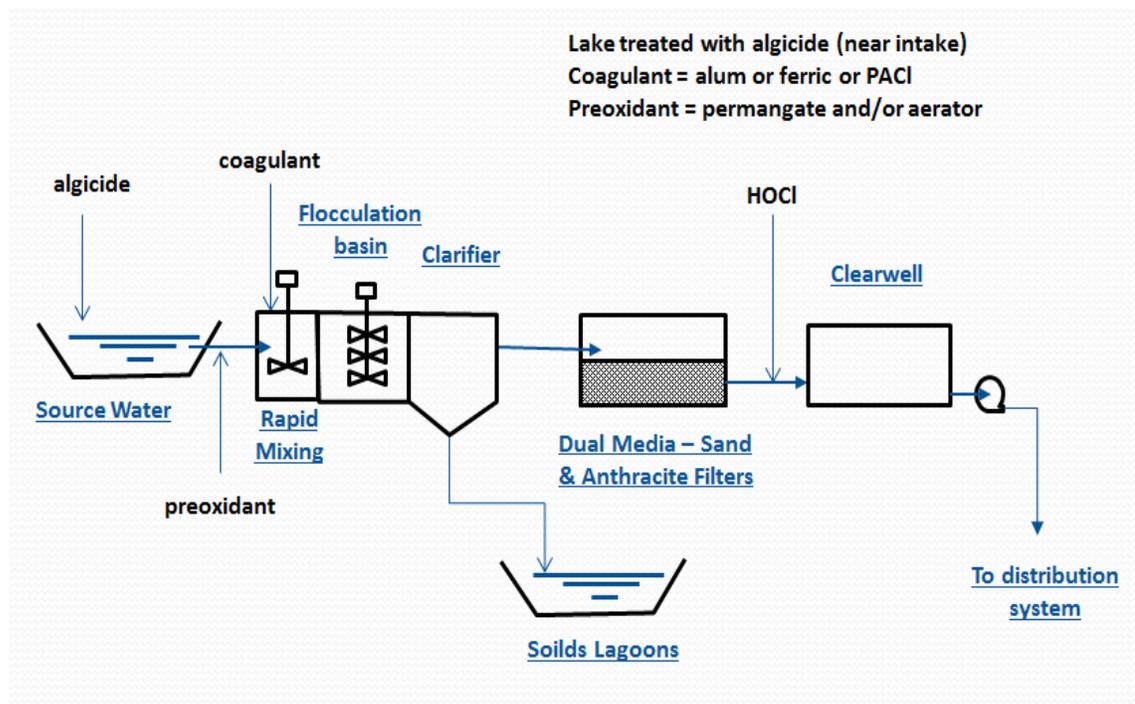


Figure 1: Typical drinking water treatment process

2.1.1 Coagulation and Types of Coagulants

Most raw surface waters and some ground water entering a treatment plant usually contain significant turbidity caused by tiny colloidal clay and silt particles (Vesilind & Peirce,

1982; Symons et al., 1975). These naturally occurring soil particles that are suspended in water are difficult to remove because of their small size and negative charges/natural electrostatic charge which keeps them moving continuously and prevent them from coming together to form bigger particles that are easy to remove (Vesilind & Peirce, 1982; Clark & Adams, 1993). Chemicals such as aluminum sulfate, also known as alum are used to first neutralize some of the charge on the particles and therefore making these tiny particles more electrically attractive to each other so they can coalesce and form large particles called flocs. A simple explanation of coagulation is available in the double-layer model as shown in Figure 2.

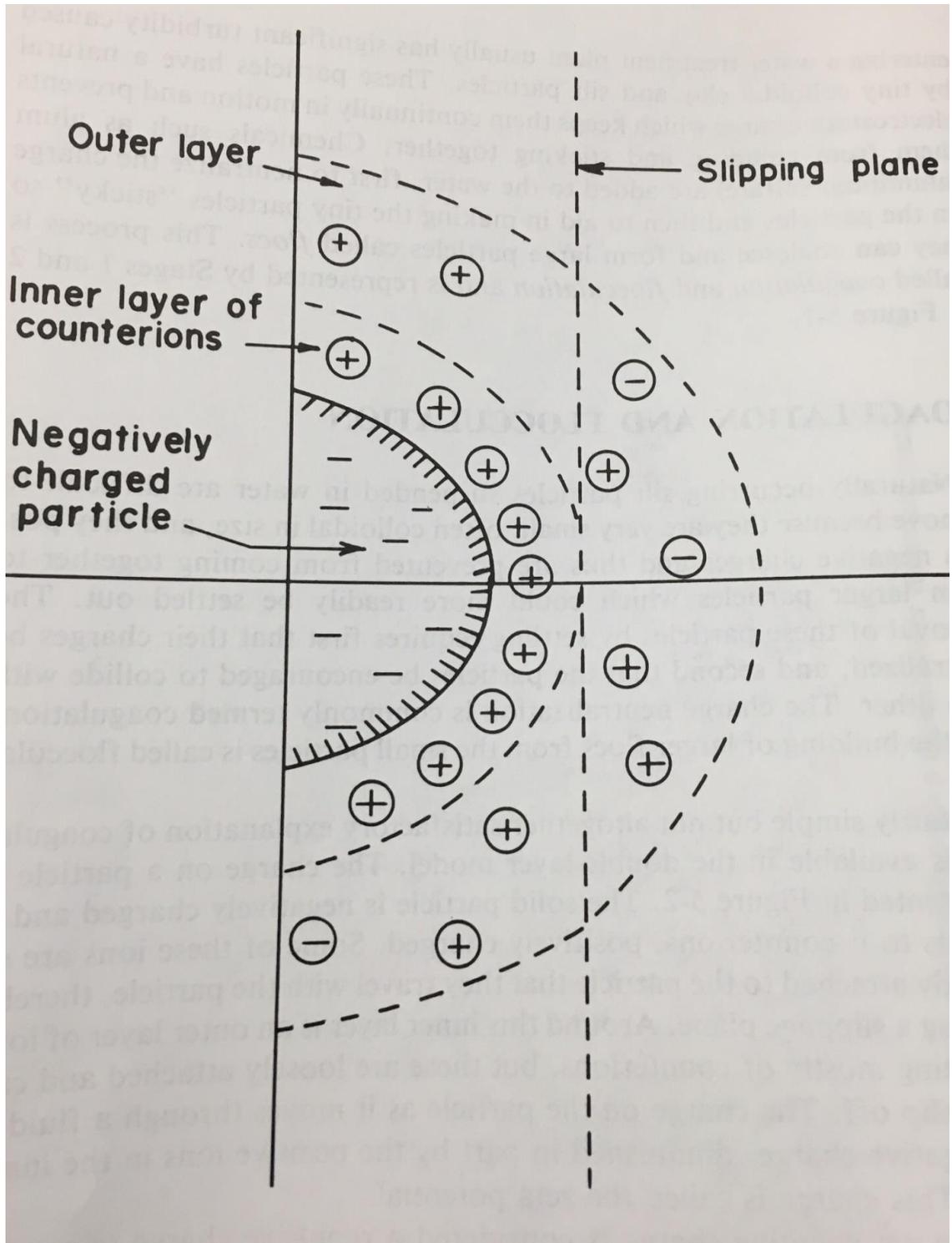


Figure 2: Charges on a suspended particle, as explained by Double-Layer theory
 (adapted from Vesilind & Peirce, 1982).

Chemicals that are used in coagulation process to neutralize the negative charge on particles are known as coagulants. Type and dose of coagulants used depends on the following (Vesilind & Peirce, 1982; Symons et al., 1975):

- Characteristics of the coagulant
- Characteristics of the particles to be removed
- Characteristics of the water

Jar tests are commonly used to determine what coagulant needs to be used and what's the optimum dose and pH. There are a variety of primary coagulants in the market, alum (aluminum sulfate) is one of the earliest and still most extensively used. Alum can be bought in liquid form with a concentration of 8.3% or in dry form with a concentration of 17% (Figure 3).

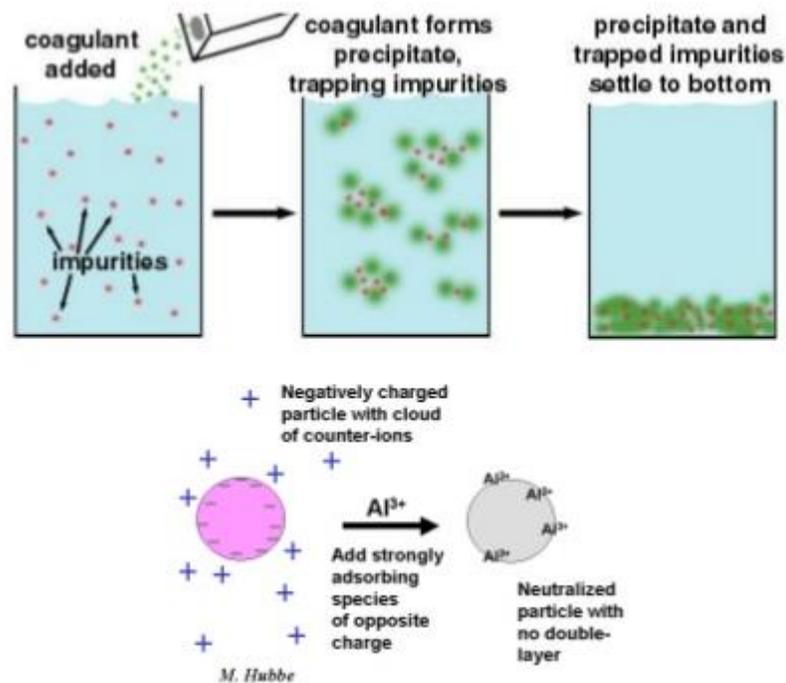


Figure 3: Coagulation Process (Hubbe, 2016)

Another coagulant that is used frequently is iron-based, either ferric sulfate or ferric chloride. Iron-based coagulants have some known advantages over aluminum-based namely they are efficient even at lower pH and the floc formed does not usually redissolve because it is heavier. The chemical reactions are shown in Figure 4:

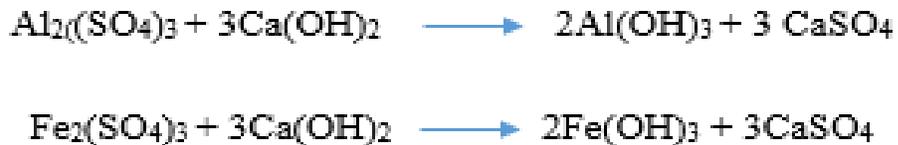


Figure 4: Chemical reactions in coagulation process

Some studies suggest that at pH levels ~ 5.0 for FeCl₃ and ~5.8 for AlCl₃, the highest removal of natural organic matter (NOM) was obtained, which is twice that without pH control (Ghernaout et al., 2014). In recent times, the concept of enhanced coagulation through coagulant optimization based on raw water characteristics is highly sought after. A product of such efforts is poly-aluminum chloride (PACl), which is known to enhance formation of magnesium hydroxide precipitate and remove NOM efficiently at a relatively lower pH range (Ghernaout et al., 2014).

2.1.1.1 Effective Coagulation and Thickness of Floc.

Thickness of the floc formed depends on both the effectiveness of the coagulants used and the type of colloidal particles present in the water being treated (Vesilind & Peirce, 1982; Symons et al., 1975). Coagulants such as aluminum sulfate and ferric chloride are used for coagulation and the floc that is formed settles out of solution while in the sedimentation basin before the water enters the filtration stage where the disinfectant is added. In most small-scale utilities around Missouri the floc that is formed may be too small or light in

weight for it to settle down and travels beyond the final clarification step into the filtration stage resulting in more frequent back wash cycles. This also allows for higher concentrations of TOC to react with chlorine forming higher concentrations of DBPs even before the finished water leaves the system. Factors such as detention time in primary and secondary basins, floc thickness, raw water quality and coagulant type and concentration used can dictate how efficient the treatment process is in removing TOC.

2.1.1.2 Treatment Efficiency: natural organic matter (NOM) Management

The study of natural organic matter (NOM) has become critically important as it significantly influences many aspects of water treatment, including the behavior of unit processes, the application of disinfectants, and the effectiveness of biological disinfection (Marhaba et al., 1998). NOM represents the raw organic material that plays a role in many of the regulatory challenges facing utilities. NOM contains precursors to disinfection byproducts (DBPs). Both, the proposed Disinfectant/disinfection by-product (D/DBP) Rule (USEPA, 1994a) and the Enhanced Surface Water Treatment Rule (ESWTR) (USEPA, 1994b) have provisions to limit the formation of DBPs by controlling reactivity and/or removal of NOM (Marhaba et. al., 1998).

NOM is very heterogeneous, in that it contains many classes of high molecular weight organic compounds. Humic substances constitute a major portion of the dissolved organic carbon (DOC) from surface waters (Liu, 2011; Rook, 1977; Krasner et al., 1989). They are complex mixtures of organic compounds with relatively unknown structures and chemical composition. Even the definition of humic substances is rather ambiguous and is frequently operationally defined according to the physical/chemical isolation procedure (Oliver & Lawrence, 1979; Marhaba et al., 1998)

Percentage removal of natural organic matter (NOM) dictates the efficiency of a drinking water treatment process (Oliver & Lawrence, 1979). More specifically NOM reduction may influence how effective disinfection using chlorine in terms of amount of disinfectant needed and the concentration of disinfection by-products (DBPs) formed as a result (Liu, 2011; Krasner et al, 1989; Rook, 1974). It is known that biologically refractory humic and fulvic acid fractions of NOM, generally of allochthonous origin, are the most reactive with chlorine (Rook, 1977). In the conventional water treatment processes, coagulation and slow filtration treatments have better efficiency to reduce the NOM in water, especially for the hydrophobic portion more than the hydrophilic one (Marhaba et. al., 1998).

Measurement and classification of NOM is a lengthy and complex process and is usually beyond the capabilities of drinking water treatment utilities irrespective of their size. Hence water quality parameters such as total organic carbon (TOC) and turbidity are commonly used by water utilities as a measure of treatment efficiency. TOC is also used to determine the amount of chlorine needed for disinfection. Small-scale utilities that can't afford to do TOC tests on a daily basis use turbidity, a simpler test as a representative of changing water quality throughout the treatment process. It is also widely believed that turbidity measurements can be used to make treatment process decisions as it is an acceptable surrogate for TOC changes in the system.

2.1.2 Significance of TOC Removal

Coagulation and disinfection are the main units in the drinking water treatment technology in both developing and industrialized countries (Hass, 1999; USEPA, 1999). Coagulation is expected to eliminate particles and colloids via reaction with a coagulant, like alum or ferric chloride, while disinfection is applied to inactivate pathogens by disinfectants like

aqueous chlorine (HOCl/OCl^-). During disinfection, chlorine can react with TOC in water and bromide in raw water to produce halogenated disinfection by-products (DBPs) (Freese & Nozaic, 2004; Sadiq & Rodriguez, 2004; Warton et al., 2006; USEPA, 1998). Many halogenated DBPs have been verified to possess potential genotoxicity and carcinogenicity to human beings (Clark & Sivaganesan, 1998; Vasconcelos et al., 1997; Clark et al., 1996; Teksoy et al., 2007; Bull, 1993). Therefore, improving removal efficiency of TOC through "enhanced coagulation", which is usually operated by decreasing pH to ~ 6 and/or increasing coagulant dosage (Bull, 1993), has received great attention from the environmental community (Mbonimpa, 2007). The United States Environmental Protection Agency (USEPA) specifies the required NOM removal in terms of total organic carbon (TOC) by enhanced coagulation under different TOC and alkalinity levels (Gang, 2001).

The complexion of chemical, biological, and physical reactions resulting in the formation of DBP's is extremely difficult to predict. This statement is especially true of small-scale water treatment plants, which are more likely to be resource-limited compared to more sophisticated research laboratories and high-MGD (million gallons per day) plants. These resource limitations include technical, managerial, and financial constraints (Shih et al., 2006). Furthermore, source water origin is also a controlling aspect influencing treatment plant demands and design considerations. Small-scale water treatment plants are more likely to employ surface water as a source, which can increase treatment requirements when compared to ground water sources (USEPA, 1999). Since DBP formation is based on the variables of chlorine decay, NOM/TOC, pH, and source water quality, both the

operational strategies and the source water location have the potential to affect and create issues with DBP formation (Boccelli et al., 2003).

Due to limitations, many small-scale water treatment plants have no method of directly measuring TOC concentration or TTHM formation. As a result, they often rely on correlating turbidity and chlorine residual measurements to TOC, TSS (total suspended solids), and TTHM concentrations. Due to a lack of information available to treatment plant operators, the following decision process may occur. When increased turbidity is detected during the treatment process, the plant operator may expect increased TOC concentrations to also be present. However, the original assumption of TOC increasing with turbidity is not always valid. Often times, high turbidity does not correspond to high TOC/TSS, and vice-versa (USACE, 2000; Wei et al., 1998). Therefore, the increased chlorine dosage, which has the potential to cause increased DBP formation, may not be a necessary action.

2.2. Disinfection By-Product (DBP) Formation Chemistry

Disinfection in potable water treatment may be defined as the reduction of pathogenic organisms to prevent waterborne diseases (Haas, 1999). Chlorination is one of the most widely used disinfection processes in water treatment plants. According to a survey conducted about disinfectant use in US systems in 1997, 90% of the systems use chlorine as primary disinfectant (Table 1) (Poleneni, 2013; USEPA, 1999). The reason being chlorination is one of the most common disinfectant processes due to chlorine being relatively easy to handle, cost-effective, simple to dose, measure, and control, having a reasonably prolonged residual, and having low capital installation costs (Calderon , 2000; Sadiq & Rodriguez , 2003; USEPA, 1998; Warton et al., 2006), it is cost effective, simple

to dose, measure and control, and it has a reasonably prolonged residual (USEPA, 1999; Freese & Nozaic, 2004; Sadiq & Rodriguez, 2004), which allows a system to maintain compliance for minimum disinfectant residual required in distribution system rule (USEPA, 1998; Clark & Sivaganesan, 1998; Vasconcelos et al., 1997; Clark et al., 1996). Though over the past decade number of utilities using chloramines as primary disinfectant has increased, chlorine still remains as the most preferred choice.

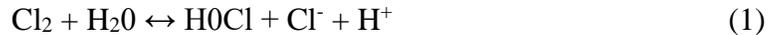
Table 1: Survey of disinfectant use in US systems 1997 (adapted from USEPA, 2001; Poleneni, 2013).

Type of Disinfectant	Number of systems
Chlorine dioxide	313
Ozone	30
Chlorine	22,307
Chloramines	135
Potassium permanganate	1,122

2.2.1 Chlorination Chemistry

The incorporation of disinfection techniques into drinking water treatment processes is one of the great public health accomplishments. Practices such as chlorination have proven cost-effective and tremendously proficient in controlling bacteria, virus, and other waterborne illness growth throughout the water distribution supply chain. Despite chlorination often occurring prior to treated water leaving the treatment facility, the responsibility of water utilities extends well beyond this point in time (Besner et al., 2001). As the water supply progresses through a distribution system towards the customer, chemical and physical reactions continue to take place and can cause significant changes in water quality (Singer et al., 2002; Boccelli et al., 2003; Clark, 2011).

Free chlorine is the most commonly used form of chlorine for disinfection. Its dissociation process into hypochlorite and then into hydrogen ions is described below (Equations 1 and 2) (Mbonimpa, 2007).



In regards to chlorination, the primary concerns are maintaining free chlorine residual throughout the system and managing the growth of disinfection by-products (DBPs). Chlorination can be a tricky process to master for any treatment plant, as both low and high disinfectant residuals in the distribution system pose risks. These risks include inadequate disinfecting properties, customers noting taste and odor irregularities, residual violations, and DBP violations (Ohar & Ostfeld, 2010; Haxton et al., 2011).

2.2.2 DBPs Classification

In 1974, chloroform, a product of the reaction of chlorine and naturally occurring organic matter, was identified in disinfected drinking water (Bellar et al., 1974; Rook, 1974; Symons, 1975; Symons et al., 1981). Since that time, a number of other chlorinated disinfection by-products (DBPs) have been identified, including other trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, haloketones, and haloaldehydes. All disinfectants are reactive, and the use of the other commonly used oxidants ozone,

chloramines, and chlorine dioxide result in additional organic and inorganic by-products (Poleneni, 2013).

More than 500 DBPs have been identified in tap water (Clark et al., 1996; Clark et al., 1994) and thousands more exist. To date, the identifiable DBPs cumulatively account for no more than 50% of the total organic halogen (TOX) in most chlorinated drinking waters, numerous halogenated DBPs formed from chlorine still remain unknown (Hua & Reckow, 2007; Hua & Reckow, 2007a; Zhang et al., 2000; Singer et al., 1995; Reckow & Singer, 1984). Most representative types of DBPs are categorized into three classes; Inorganic By-products, Organic Oxygenated By-products and Halogenated By-products. (Figure 5) (Mbonimpa, 2007). The list also includes DBPs and disinfectants left in water after the disinfectant demand is met known as disinfectant residuals.

Disinfectant Residuals	Halogenated Organic By-Products
Free chlorine	Trihalomethanes
Hypochlorous acid	Chloroform
Hypochlorite ion	Bromodichloromethane
Chloramines	Dibromochloromethane
Monochloramine	Bromoform
Chlorine dioxide	Haloacetic acids ^b
Inorganic By-Products	Monochloroacetic acid
Chlorate ion	Dichloroacetic acid
Chlorite ion	Trichloroacetic acid
Bromate ion	Monobromoacetic acid
Organic Oxygenated By-Products	Dibromoacetic acid
Aldehydes ^a	Haloacetonitriles
Formaldehyde (methanal)	Dichloroacetonitrile
Acetaldehyde (ethanal)	Bromochloroacetonitrile
Glyoxal (ethanedial)	Dibromoacetonitrile
Pyruvaldehyde (oxopropanal)	Trichloroacetonitrile
Other aliphatic aldehydes	Haloketones
Carboxylic acids	1,1-Dichloropropanone
Acetic acid	1,1,1-Trichloropropanone
Other aliphatic monocarboxylic acids	Chlorophenols
Oxalic (ethanedioic) acid	2-Chlorophenol
Ketoacids ^{a, b}	2,4-Dichlorophenol
Glyoxylic (oxoethanoic) acid	2,4,6-Trichlorophenol
Pyruvic (oxopropanoic) acid	Chloropicrin
Ketomalonic (oxopropanedioic) acid	Chloral hydrate
Assimilable organic carbon	Cyanogen chloride
	Organic chloramines
	MX (3-Chloro-4-(dichloromethyl)-
	5-hydroxy-2(5 <i>H</i>)-furanone)

Figure 5: Classification of DBPs (adapted from 12; Poleneni, 2013).

2.2.2.1 Regulated DBPs

Disinfection by-products (DBPs) have caused public health concerns since the discovery of chloroform as a chlorination by-product in drinking water in the early 1970s (Hua & Reckhow, 2007; Rook, 1974). Trihalomethanes (THMs) and Haloacetic Acid (HAAs) are two abundant classes of chlorinated DBPs that are currently regulated under Safe Drinking Water Act (SDWA) (USEPA, 1998; Hua & Reckhow, 2007). Some members of these two groups of DBPs are suspected human carcinogens (Hua & Reckhow, 2007; Singer 1994).

Table 2 lists names and chemical formulas of regulated DBPs under SDWA.

Table 2: Names and chemical formulas of regulated THMs and HAAs.

Compound Name	Abbreviation	Chemical Formula
Total Trihalomethanes	TTHM	----
Trihalomethane/Chloroform	TCM	CHCl ₃
Bromodichloromethane	BDCM	CHBrCl ₂
Dibromochloromethane	DBCM	CHBr ₂ Cl
Tribromomethane/Bromoform	TBM	CHBr ₃
Sum of 5 Haloacetic Acids	HAA5	----
Monochloroacetic Acid	MCAA	ClCH ₂ COOH
Dichloroacetic Acid	DCAA	Cl ₂ CHCOOH
Trichloroacetic Acid	TCAA	Cl ₃ CCOOH
Monobromoacetic Acid	MBAA	BrCH ₂ COOH
Dibromoacetic Acid	DBAA	Br ₂ CHCOOH

2.2.3 Exposure Implications

Though considerable amount of uncertainty exists about health effects of DBP exposure, over the past few decades studies have shown possible link between THM and HAA compounds and negative health effects (Table 3). It is an accepted fact that although we find disinfectant and disinfectant by-products in tap water, the elevated risk for cancer is only associated with DBPs but not the disinfectant that produces them (Dunnick & Melnick, 1993).

Table 3: Status of health Information for THMs and some HAAs (adapted from Mbonimpa, 2007; Clark & Boutin, 2001)

Contaminant		Cancer Classification
Chloroform		B2
Bromodichloromethane		B2
Dibromochloromethane		C
Bromoform		B2
Monochloroacetic acid		--
Dichloroacetic acid		B2
Trichloroacetic acid		C
Group	Classification	Definition
A	Human carcinogen	Sufficient evidence in epidemiologic studies to support casual association between exposure and cancer
B	Probable human carcinogen	Limited evidence in epidemiologic studies (Group B1) And /or sufficient evidence from animal studies (Group B2)
C	Possible human carcinogen	Limited evidence from animal studies and inadequate or no data in humans
D	Not classifiable	Inadequate or no human animal evidence of carcinogenicity
E	No evidence of human carcinogenicity	No evidence of carcinogenicity in at least two adequate animal tests in different species or in adequate epidemiologic and animal studies.

2.3. Regulatory Framework of Disinfectants and their By-products

Regulations dictate the way water treatment plants are operated on day to day basis and majority of the decisions they make in terms of process changes and distributions system modifications. They are also the main reason behind new treatment technology development in the market and research conducted by the educational institutions and

research labs. Therefore, it is justified to say that water industry is driven by regulatory policy.

2.3.1 History of DBP Regulations

Most political theories, like social construction of target populations, do not apply to environmental regulatory policies. Environmental policies usually are based on a specific goal to increase the general welfare of the people and, therefore, are not focused on any particular set of the population. Though the policy is written based on welfare, its implementation does take efficiency into consideration. History of environmental regulations in the United States of America has revealed a conflict between welfare and efficiency which still remains an issue of debate in the political community. Many analysts believe policies have a focal point that initiates mobilization in interest groups and influences agenda setting to a great extent (Bamgartner & Jones, 1993; Birkland, 1997; Cobb et al., 1976; Cobb & Elder, 1983; Kingdon, 1995; Light, 1982; Walker, 1977). This is true in the case of environmental regulations that are a result of an outburst or an accident, but most water quality regulations usually do not have a focal point (Poleneni, 2013). They often are considered to be problems that longer-term analysis of statistical evidence seeks to understand (Birkland, 1998). The harm from these problems is usually not concentrated in any particular geographic area or a particular community of interest (Bamgartner & Jones, 1993; Birkland, 1997; Birkland, 1998).

The Safe Drinking Water Act (SDWA) seems to have outbreaks of different microorganisms between 1974 and 1993 as its focal point. For example, the outbreak of E-Coli in Missouri that killed 4 people and made over 250 people sick lead to more focus on implementation of the SDWA. DBP regulations are enforced as part of Safe Drinking

Water Act (USEPA, 1998; Adams et al., 2005). Disinfection byproducts (DBPs) have been of great concern to both environmental officials and the public since the late 1970s when research began to show a direct link between the formation of trihalomethanes (THMs) and the reaction between free chlorine and natural organic matter (NOM) (Adams et al., 2005; Rook, 1977). Subsequent studies found that THMs were statistically linked to cancer in animals (Adams et al., 2005; Zavaleta et al., 1999). In the 1980s, first reports of adverse effects on human health of haloacetic acids, specifically dichloroacetic acid and trichloroacetic acid, were reported (USEPA, 1994; Adams et al., 2005). DBPs were part of the SDWA primary pollutant list and had been on the Contaminant Candidate List (CCL) for many years before they were regulated. The preference is given to the substances that are highly toxic and are known to be found in higher concentrations (Poleneni, 2013). With an elaborate investigation and expert advice from different departments of the government DBP regulations were enacted in 1998 as the Disinfectants and Disinfection By-products (D/DBP) Rule.

Though D/DBP rule took effect in 1998, the first national control placed on disinfectant byproducts was the establishment of a maximum contaminant level (MCL) of 100 µg/L for total trihalomethanes (TTHM) by the EPA in 1979 (USEPA, 1979). TTHM is defined as the sum of the concentrations of all four chlorine and bromine substituted trihalomethanes. Though the contemporary understanding of DBP formation was unclear, legislation was passed due to the intensity of the health effects associated with these by-products. On one hand the economic safety of the water industry is taken into consideration while on the other hand the non-economic values of the nation as a whole are given enough importance during policy making. The regulation took effect when the technology required to be in

compliance was not readily available. But the risk created a necessity and demand for such technology innovation (Poleneni, 2013). Ongoing research, assessing, and managing risk at every step of the way are the key points of this policy. The regulatory enforcement limit is set conservatively with highly vulnerable populations in mind.

2.3.2 Stage-1 Disinfectants and disinfection by-products Rule

Under the Stage 1 of the Rule, all water systems were required to comply with complex monitoring and reporting requirements as well as a 80 micrograms per liter ($\mu\text{g/L}$) maximum contaminant level (MCL) for total trihalomethanes (TTHM) and a 60 $\mu\text{g/L}$ MCL for five species of haloacetic acids (HAA5) (Adams et al., 2005; USEPA, 1999c; USEPA, 2001). The Stage 1 D/DBP Rule also required water treatment plants to remove certain amounts of total organic carbon (TOC), based on source water characteristics (USEPA, 1998; Wulff, 2011). Recognizing that HAAs and THMs can be and often are formed in slow reactions that will continue occurring beyond the time at which finished water exits the treatment facility, 25% of samples for these contaminants were required to be taken at locations of approximate maximum water residence time and the remaining 75% at “representative locations” in the distribution system (USEPA, 1998; Wulff, 2011).

2.3.3 Stage-2 Disinfectants and disinfection by-products Rule

While Stage 1 D/DBP rule proved to be successful in limiting the concentration of DBPs in drinking water, continuing research efforts have highlighted the need for further regulatory action. The MCL of 80 $\mu\text{g/L}$ MCL for TTHM and a 60 $\mu\text{g/L}$ MCL for HAA5 is considered appropriate, but the method of compliance needed some changes.

In Stage 1 D/DBP, a running annual average is required (RAA). This translates to concentrations of samples collected within the distribution system during one quarter are

averaged together as that quarter's sampling result (USEPA, 1998; Wulff, 2011). The quarter averaged are then averaged over four quarters to determine the compliance number of that year for comparisons with MCLs. This leads to usage of medium level concentration values produced as a result of averaging sites yielding both low and high concentration samples for compliance. To address this issue, the Stage 2 Rule changes the reporting and compliance methods such that the quarterly measurements for each location are reported separately throughout the year, with each four quarter average for those locations individually compared with the MCL to determine compliance. Using this calculation method, the locational running annual average (LRAA), it is no longer possible for utilities to be in compliance while one part of its distribution system is routinely above the established MCLs. Since different types and sizes of water systems have different capabilities and resources to use in response to new regulatory requirements, the Stage 2 D/DBP Rule has differing dates of implementation depending on system type (Table 4). The complete rule and its implications for drinking water utilities are described in the Federal Register (USEPA, 2006).

**Table 4: Stage 2 DBPR compliance schedule for wholesale and consecutive systems
(Adapted from USEPA, 2010)**

Population Served by the Largest System in the Combined Distribution System*	Date for Compliance with Stage 2 DBPR (subpart V) Monitoring Requirements
≥ 100,000 people	April 1, 2012
50,000 – 99,999 people	October 1, 2012
10,000 – 49,999 people	October 1, 2013
< 10,000 people	October 1, 2013 if no cryptosporidium monitoring is required under LT2ESWTR** OR October 1, 2014 if cryptosporidium monitoring is required under LT2ESWTR

*Combined distribution system consists of the distribution systems of wholesale systems and of the consecutive systems that receive some or all their finished water from those wholesale system(s), ** LT2ESWTR – Long Term 2 Enhanced Surface Water Treatment Rule.

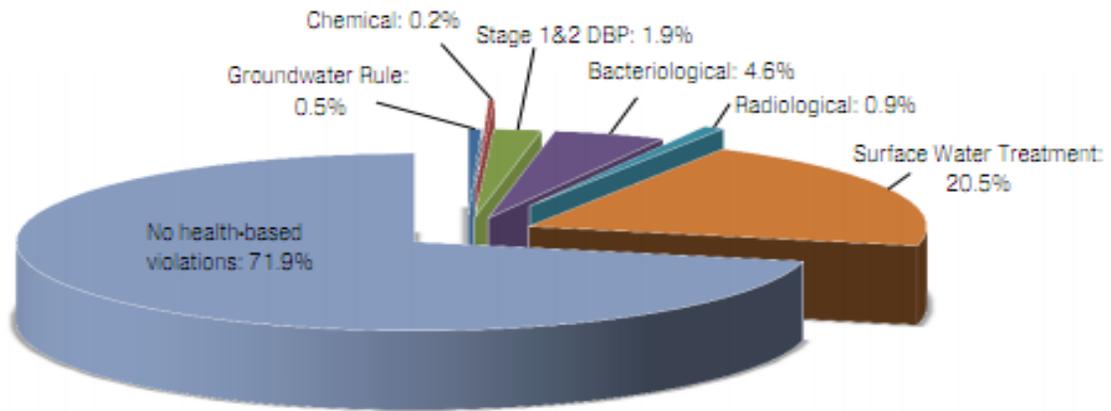
2.3.4 Statistics of Missouri Drinking Water Utilities

Missouri water system is divided into 5 regions (Table 5). 54 % of the total water systems use Missouri river and 28 % of them use ground water as their source water [51]. Unlike ground water considerable amount of water quality change can be observed in Missouri river over a span of a year which can be attributed to the seasonal changes in the adjoining watershed (Mbonimpa, 2007; Gang, 2001; Wulff, 2011).

Despite their best efforts many small-scale utilities in Missouri are having compliance issues with different regulations under SDWA and the most predominant ones being surface water treatment, Bacteriological and DBP regulations (Figure 6).

Table 5: Number of regulated systems by region and system type

Region	Number of Community systems	Number of Non-Transient Non-Community Systems	Number of Transient Non-Community Systems	Total Number of Systems
Kansas City Reg. Office (KCRO)	282	11	84	377
Northeast Reg. Office (NERO)	199	13	10	222
Southeast Reg. Office (SERO)	281	54	173	508
Southwest Reg. Office (SWRO)	508	127	735	1,370
St. Louis Reg. Office (SLRO)	200	36	84	320
Total Systems	1,470	241	1,086	2,797



There is overlap in that some systems violate more than one area.

Figure 6: Percent population of community water systems meeting health-based standards (MDNR, 2010)

2.4. Wall Effects and Operational Strategies: Impacts on Water Quality

Public utilities provide potable water for 90% of the United States (USEPA, 1999). Federal regulation of drinking water quality began in 1914 with the U.S. Public Health Service setting standards for the bacteriological quality of drinking water. Today, the number of regulations and their stringency increased dramatically based on vast scientific discoveries in the field and increasing health concerns. One area that has seen a considerable amount of focus is carcinogen control in finished water (Clark & Boutin, 2001). More than 500 DBPs have been identified in tap water (Clark et al., 1994; Clark et al., 1996) and thousands more exist. To date, the identifiable DBPs cumulatively account for no more than 50% of the total organic halogen (TOX) in most chlorinated drinking waters, numerous halogenated DBPs formed from chlorine still remain unknown (Hua & Reckow, 2007, 2007a; Zhang et al., 2000; Singer, 1995; Reckow & Singer, 1984). The Stage 1 Disinfection and disinfection by-products Rule (D/DBP1) (63 FR 69390-69476, December 16, 1998, Vol. 63, No. 241) and Stage 2 Disinfection and disinfection by-products Rule (D/DBP2) (71 FR 388, January 4, 2006, Vol. 71, No. 2) are the current regulations for the control of carcinogens in potable water throughout United States (USEPA, 1998). These regulations aim to reduce exposure to contaminants including total trihalomethanes, five haloacetic acids, bromate, chlorite, chlorine, chloramines, and chlorine dioxide (USEPA, 1998).

Pipe surfaces play a large part in the formation of DBPs occurring throughout the water treatment process (Digiano & Zhang, 2005). Even medium sized water utilities may have hundreds of miles of pipes constructed from various types of materials, ranging from newly lined pipes to unlined pipes that are more than 50 years old. Over time biofilms and

tubercles attached to pipe walls can result in significant loss disinfectant residual and, thereby adversely affect water quality (Besner et al., 2001). Many opportunities arise for water quality to change as it moves between the treatment plant and the customer (Singer et al., 2002; Boccelli et al., 2003; Clark, 2011).

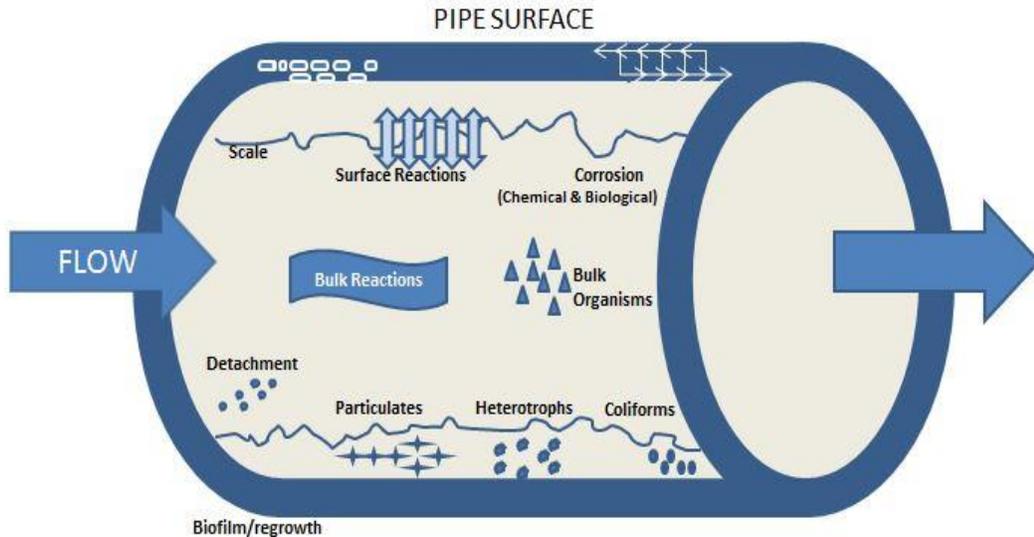


Figure 7: Water chemistry inside pipelines

Cross-connections, failures at the treatment barriers, and the transformations in bulk phase can all degrade water quality. Corrosion, leaching of the pipe material and biofilm formation and scour can occur at the pipe wall and are subject to change with changes in materials as well as with the operational strategies used (see Fig 7) (Clark, 2011).

In order to understand the change in water quality during distribution, we need to understand the effect of different materials in addition to effects of operational strategies (Sadiq & Rodriguez, 2004; Clark & Sivaganesan, 1998; Clark et al., 1996). The most

commonly used pipes today for water mains are ductile iron (DI), pre-stressed concrete, polyvinyl chloride (PVC), reinforced plastic, and steel (Brereton & Mavinic, 2002).

2.4.1 Prediction of DBPs in Distribution Systems

Finished water can undergo a variety of physical, chemical and biological changes during transportation through a distribution system. Understanding the sources of water quality degradation during distribution has become a priority of water producers because research has suggested that such degradation increases the rate of gastrointestinal illnesses (Besner et al., 2001; Payment et al., 1997; Payment et al., 1991). The analysis of changes in water quality in a full-scale distribution system can be difficult because it involves numerous parameters ranging from network structure and system operation to the physical and chemical characteristics of the water.

The dynamic nature of these parameters makes the analysis more complex. The distribution systems can be considered to behave like complex reactors and water quality degradation is caused by many factors (Grayman & Clark, 1993).

By-product concentrations vary both spatially and temporally within a distribution system. These variations are due to source water quality variability, variations in water treatment efficiency, and the dynamic nature of by-product formation during distribution. Twofold to fourfold difference in concentration may occur within a water distribution system, and the pattern of by-products from different sources can vary significantly over the course of a day as well as during a year (Clark & Sivaganesan, 1998; Clark & Adams, 1993).

2.4.1.1 Prediction Model Selection Process

Given that DBP formation is not a well understood science and is influenced by many factors that change over time, prediction of DBPs in dynamic natured distribution system

takes a good amount of effort on a utility's part. When trying to establish the cause of water quality degradation in terms of DBPs, utilities must consider structural, operational and water quality parameters. Because structural and operational data are not always directly available, water quality parameters are used to establish probable cause, often with little success (Besner et al., 2001).

There are many ways to predict DBPs in distribution systems and most of them use first order kinetic models which require a good estimate of initial concentrations and time. Different types of DBP formation models have been described in recent literature.

Models have been developed both from data generated in field studies or at laboratory scale. Some researchers have developed models to describe the formation of DBPs based on kinetics involved during chlorine reactions (Clark & Sivaganesan, 1998; Carrico & Singer, 2009; Haxton et al., 2011; Hallam et al., 2002; Jonkergouw et al., 2008; Clark et al., 1996; Clark, 1998). Other models are empirical and are based on multivariate regression equations that link a number of operational and water quality parameters with the concentrations of DBPs generated.

The process of predicting DBPs in distribution system involves selection of a prediction tool/method taking system specific conditions into consideration and evaluating the amount of data that is needed to be provided for the prediction model to give accurate estimates of concentrations of DBPs in different parts of distribution system.

2.4.1.2 Prediction Tools Available: their Features and Feasibility

There are many prediction models available that can be used to predict DBP formation in distribution systems using contact time and initial concentration data. These tools can be classified as Computer models, field-based techniques, Pilot-Scale models and Bench-

Scale models (Westbrook & Digiano, 2009). Each of these models comes with its own set of advantages and constraints. The amount of data needed to start and calibrate these models differs from one another for example water quality computer models such as EPANET, KY Pipe can be successful in predicting disinfectant residual and DBP concentrations if the rate models for disinfectant loss both in bulk water and at the pipe surface are known and rate constants are available (Westbrook & Digiano, 2009; USEPA, 2009) whereas, Bench-scale and Pilot scale models don't require kinetics data of the water. There are two most commonly used field-based techniques for prediction of DBPs and chlorine residual in distribution systems; Physical and Computer Hydraulic models and Prediction of chlorine residual based on batch reactor & distribution system data (Westbrook & Digiano, 2009; Mutoti et al., 2007). Measuring the chlorine residual loss between two points in distribution system and calculating loss due to bulk reaction using batch reactors in a laboratory (Westbrook & Digiano, 2009; Mutoti et al., 2007) is a straight forward process. The residence time in the pipe section is known by water velocity and pipe length. Subtracting this bulk contribution to decay from total loss and dividing by the residence time yield the contribution from surface reaction rate. Though it is one of the simplest ways of predicting DBPs, it has two drawbacks. First, it is hard to find a pipe section of uniform material and condition that is long enough to produce measurable amount of loss in residual but, without water demand along its length that prevent an estimate of residence time using pipe length and velocity. Second, is the need to assume a reaction order to allow calculation of surface rate constant because, such measurements effectively preclude testing for reaction kinetics (Westbrook & Digiano, 2009).

Hydraulic models are used to match disinfectant residuals throughout the distribution system by adjusting the rate constant for pipe surface reactions. This method has produced a correlation of surface reaction rate constant with Hazen -Williams's wall roughness coefficient (Vasconcelos et al., 1997; Westbrook & Digiano, 2009). This method comes handy when one aims to change the water quality entering the distribution and determine its effects on DBP formation over time without having it actually do it physically. Hydraulic models have been successful to some extent in predicting DBPs in distribution system but have two drawbacks. First, they lack a firm foundation in kinetic principles. For instance, both zero and first order rate models have been used to describe same data set. Second, the chemical and physical conditions in within distribution system are seldom constant (Westbrook & Digiano, 2009).

Pilot scale models have known to overcome uncertainties of field based models. Pilot scale such as pipe loops use long lengths of specific material and controlled feed conditions (Westbrook & Digiano, 2009; Mutoti et al., 2007). This method has been used by many researchers over last two decades to understand the decay and formation kinetics of contaminants in distribution systems. Though it has been successful with chlorinated systems, it couldn't produce measurable amount of chloramine decay with appropriate velocity in the system (Westbrook & Digiano, 2009; Mutoti et al., 2007) large pilot scale systems can produce long contact times, but they are relatively expensive.

Bench-scale models are hypothesized to overcome the limitations of both field based and pilot scale models (Westbrook & Digiano, 2009). There are different kinds of bench-scale models such as Pipe Section Reactor (PSR), Material-Specific Simulated Distribution System (MS-SDS). The one thing they have in common is that they are relatively

inexpensive and provide well-controlled pipe surface environment (Westbrook & Digiano, 2009). These models are built using sections of pipe from actual distribution under study and quality of water with respect to DBPs and chlorine residual is analyzed as function of either velocity or contact time (Westbrook & Digiano, 2009; APHA, 1998).

Temperature and chemical characteristics of water can be controlled easily in these models. Though they have been used with some success, validation of results over real distribution system takes good amount of calibration to account for complex hydraulics in place.

Each prediction model discussed above is known to have advantages and disadvantages of its own. The decision is to be made based on what needs to be analyzed and the resources available at hand.

2.4.2 Typical Operational Strategies Used

Water utilities use different operational strategies in order to overcome physical (infrastructure, source water quality, distribution system layout) and financial constraints it has to maintain consistent water quality throughout their distribution system and meet water demand of its customers. The selection of these strategies is mainly based on system-specific conditions and preferences of the utility operator. Many utilities use more than one strategy to ensure being in compliance even with seasonal changes in source water quality and water demand (Besner et al., 2001). With Stage-II DBP regulation compliance date being right around the corner, many small-scale utilities are adopting techniques to strike a balance between protection against microbial risks and the risks posed by harmful by-products (Clark & Sivaganesan, 1998; Clark et al., 1994; Carrico & Singer, 2009).

2.4.2.1 Normal Treatment Run

Normal treatment run is the most commonly used operational strategy where a water treatment plant treats the raw water for reduction/removal of inorganics like iron, organics like natural organic matter (NOM) using treatment processes that are based on type of source and quality of raw water (Reckhow & Singer, 1984; Wulff, 2011). Disinfection is an important part of water treatment process (Wulff, 2011; LeChevallier, 1999; Karim et al., 2003) and states like Missouri requires the primary disinfectant to be added before filtration. The detention time in the filtration basin is usually based on the required contact time with the primary disinfectant (USEPA, 1998).

After the process of filtration many systems allow the finished water to enter their distribution system but few introduce secondary disinfectant like ammonia before the water leaves the plant (Hua & Reckhow, 2007; Seidel et al., 2005). The amount of primary disinfectant added depends on the raw water quality and the expected water age in the distribution system (USEPA, 1998; Carrico & Singer, 2009). Striking a balance between chlorine residual and DBP concentrations gets tricky if the distribution system is too long or finished water quality is not good to start with (Ohar & Ostfeld, 2010). Figure 8 shows the chain of treatment processes involved in a normal run strategy. The process of maintaining appropriate water quality throughout the distribution system requires good amount of information about the distribution system and water chemistry that the plant is dealing with.

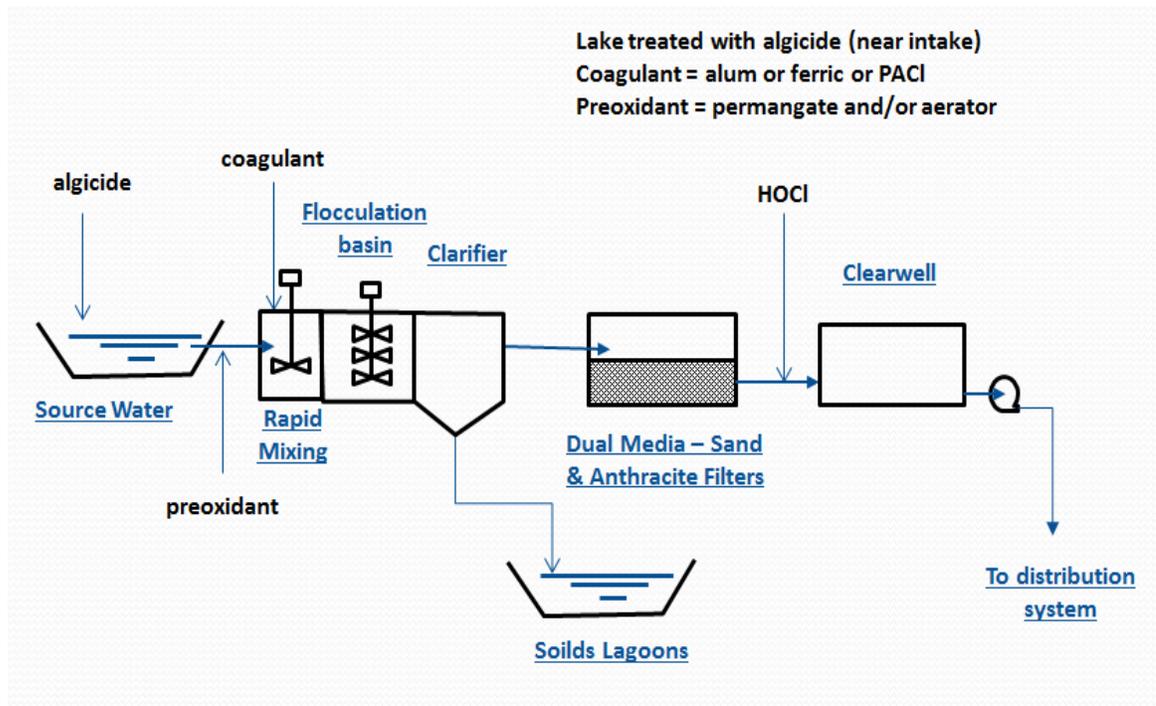


Figure 8: Typical drinking water treatment chain

2.4.2.2 High Chlorine Run

The quality of water supplied by a distribution network is usually assessed by evaluating if residual chlorine concentrations are maintained between lower and upper bounds, to ensure good disinfecting properties and avoid poor tasting water (Ohar & Ostfeld, 2010; Haxton et al., 2011). Since disinfectants decay over time either due to reactions with compounds contained within the bulk water (bulk decay) or due to reactions at the pipe wall (wall decay), the residual concentration may vary greatly from one location to another, and from one hour to the next (Hallam et al., 2002; Lee, 2004). Rules and regulations have been established under the Safe Drinking Water Act and its amendments of 1986 to ensure that disinfection protection be maintained in drinking water distribution systems (Vasconcelos et al., 1997; Clark et al., 1996; Shih, 2006; Clark et al., 2001). For example, the Surface Water Treatment Rule requires a minimum level of 0.2 mg/L of disinfectant

residual at the entrance to a distribution system. It also requires that a detectable chlorine residual level (or heterotrophic plate count of <500/mL) be maintained throughout the system (Vasconcelos et al., 1997; Clark et al., 1996; Clark et al., 2001).

Therefore the chlorine concentration entering the drinking water distribution system must be large enough to guarantee a sufficient residual throughout the distribution network. On the other hand, a large chlorine concentration may generate taste and odor complaints by consumers that are close to the source and consequently receive higher disinfectant concentrations (LeChevallier, 1999; Ohar & Ostfeld, 2010; Haxton et al., 2011; Lee, 2004; Besner et al., 2001) and the fact that the reaction rate of chlorine and organic matter to form DBPs is directly proportional to concentrations of either reactants poses health risks for this.

In a typical distribution system, the addition of chlorine is usually depended on the quality of the water being treated, the length of the distribution network and the chlorine demand of the system. In order to maintain required minimum residual in distribution system, utilities with long distribution networks or high chlorine demand add higher concentrations of chlorine at the point of injection (Jonkergouw et al., 2008). Typical range concentration of chlorine residual leaving the treatment plant is 0.75-3.0 mg/l, but in case of utilities adopting high chlorine strategy the concentration can go up to 5-6mg/l. This is the easiest but least preferable way to deal with residual issues and is often used by small scale utilities since the alternatives call for resources that usually are not at their disposal. Most high chlorine run systems face DBP concentration problems which indeed seem inevitable.

2.4.2.3 Chlorine Booster Run

In conventional disinfection (i.e., chlorine injection only at the water treatment plant), locations near the treatment plant have high chlorine concentrations while remote nodes often have low chlorine residuals (Ohar & Ostfeld, 2010; Kang & Lansey, 2010; Tryby et al., 1999). If a system has abnormally long distribution system or has a combination of consecutive systems attached to it, maintaining minimum residual throughout the distribution system by conventional process may require addition of very high concentrations of chlorine at the plant which can be over the Maximum residual disinfectant level (MDRL) (USEPA, 1998; Clark & Sivaganesan, 1998; Vasconcelos et al., 1997; Clark et al., 1996). To improve system-wide water quality, online booster disinfection may be coupled with treatment plant disinfection. Distributed disinfection is better than conventional disinfection for maintaining uniform chlorine concentrations throughout the system. Booster disinfection also helps to reduce: the total injection mass, the rate of reaction between chlorine & natural organic matter and subsequently the formation of DBPs while maintaining minimum chlorine residuals (Carrico & Singer, 2009; LeChevallier, 1999; Ohar & Ostfeld, 2010; Haxton et al., 2011; Kang & Lansey, 2010; Tryby et al., 1999).

3. Materials and Methods

3.1 General Description of Experimental Set-up

The experimental set-ups used for this research are built based on questions we are trying answer through this work. The following are the questions that this work intends to answer and brief description of the corresponding experimental set-up used.

Do we see a change in effluent TOC concentrations when treated with residual solids?

If yes, what is an optimal Coagulant/Residual ratio for utilities based on the coagulant they use and their source water quality? And does the additional TOC removal depend on the coagulant used and type of water?

Experimental set-up used consists of a series of jar tests conducted at the lab with the water being treated with three different most commonly used coagulants and their respective residual solids at multiple concentrations. The water for the jar tests was surface water brought from the Missouri River at Coopers Landing and ground water from Columbia Drinking Water Treatment plant. Detailed explanation of the design and the specifications is done in section 4.3.

Do we see a change in chlorine demand, chlorine decay and TTHM formation kinetics when the water is treated with residual solids? If yes, how does it correspond/compare with the change in TOC that was observed? Does the effect of residual solids treatment on water quality change with type of source water? If yes, how much and how do we quantify this change?

This part of the research is designed as a back-end process for effort presented in chapter 4 ‘Enhanced TOC Removal Using Drinking Water Treatment Plant Residual Solids’. Once the water brought from different sources is treated with residual solids, appropriate chlorine

dosage is added. Once the chlorine demand of the water is met, Simulated Distribution System (SDS) is performed on it under standard temperature and pressure conditions and samples are collected at 24-hour intervals for 4 days to capture the chlorine decay and DBP formation changes between multiple source waters, Coagulant/Residual ratios and coagulants used for treatment. Detailed explanation of design and specifications is done in section 6.3.

What kinds of water quality prediction models are available? How do they compare with each other in terms of efficiency and accuracy in predicting chlorine residual solids and TTHM formation in a distribution system? How do different distribution system pipes compare with each other under different operational strategies in terms of maintaining water quality for prolonged periods of time?

The experimental setups used for this research provide some basis for comparison and include a physical model of distribution system (Pipe Loop) which is a pilot-scale model of a distribution system, Material Specific-Simulated Distribution System (MS-SDS) which is a bench scale model built using pipe sections of different materials, Pipe Section Reactor (PSR) which is also a bench-scale model using ductile iron pipe sections from different actual distribution systems. Detailed explanation of design and specifications is done in section 3.3. Multiple operational strategies were used to answer the above asked questions namely, Normal Run, High chlorine Run and chlorine Booster Run. Detailed explanation of design and specifications is done in section 3.4.

3.1.1 Water Samples

Water from multiple treatment plants and process unit locations was used for this research.

Below is the tabular representation of the same (Table 6). Need to briefly explain what information is contained in the table.

Table 6: Sample collection matrix of the projects

Sample No.	Sample Location	Sample Type	Sample Volume	Experiment Used	Experiment Location	Collection Interval	Paper No.
1	Columbia Water Treatment Plant (CWTP)	Finished	200 gallons	Pipe Loop	Filtration building at CWTP	Twice a week for 10 months	2
2	CWTP	Finished	40 gallons	PSR	Filtration building at CWTP	Twice a week for 10 months	2
3	CWTP	Finished	5 gallons	MS-SDS	University Lab	Twice a week for 10 months	2
4	CWTP	Finished	1 gallon	SDS	University Lab	Twice a week for 10 months	2
5	CWTP	Raw	10 gallons	Jar tests	University Lab	Twice a week for 9 months	1
6	Missouri River @ Coopers Landing	Raw	10 gallons	Jar tests	University Lab	Twice a week for 9 months	1
7	Vandalia Water Treatment Plant	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3
8	Marceline Water Treatment Plant	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3
9	Odessa Water Treatment Plant	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3
10	CWTP	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3
11	Missouri River @ Coopers Landing	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3
12	Boonville Water Treatment Plant	Raw	10 gallons	Jar tests	University Lab	Once every 2 months for 8 months	3

3.1.2 Water Treatment Plants

For the purpose of this work, multiple water treatments plants across Missouri were contacted to participate voluntarily. Their selection process accounted for their location, source water type and quality, and the treatment train used.

3.1.2.1 Columbia Water Treatment Plant

Due to the ease of access, water from Columbia (Missouri) Water Treatment Plant (CWTP) was used for multiple projects over a 4-year time period. The CWTP serves approximately 100,000 customers and typically treats about 12 million gallons per day (MGD). The treatment facility uses ground water from 15 110ft deep wells, located in the McBaine Bottoms, which are strategically placed around the water treatment plant. The McBaine Bottoms formation is primarily a bed of sand and gravel beneath the bottom land bordering the Missouri River just southwest of the city of Columbia, Missouri. The treatment process includes aeration, lime softening, sedimentation, primary disinfection, filtration and secondary disinfection before final distribution. Treatment objectives include removal of iron and manganese by aeration followed by sedimentation of oxidized material along with turbidity, and removal of hardness using lime. Because of customer's average daily demands, the treatment plant needs to be operational 24 hours a day and 7 days a week.

3.1.2.2 Surface Water Sources

In order to evaluate the effect of treatment with residual solids on water from different source waters, raw water from Missouri river at Coopers landing and Boonville, Missouri drinking water treatment plant were collected over a period of 8 months. Boonville draws water from Missouri river about 30 miles west of Columbia.

3.1.2.3 Lake Water Sources

Lake water quality differs quite a bit in general and seasonally when compared to river and ground water systems. In order to capture the difference and to evaluate the efficiency of the proposed treatment process, water from Vandalia, Missouri and Marceline, Missouri was collected.

3.1.2.4 Ground Water Sources

Typically ground water has lower concentrations of natural organic matter in both dissolved and suspended states. Therefore, treatment train and compliance requirements as well as unit process efficiencies are different for this type of water. Water from CWTP and Odessa, Missouri was collected to capture these differences.

3.1.3 Other Sources of Data

In order to have a better knowledge both of the history of seasonal changes in raw water quality, effect of change in temperature on coagulation process, THM formation in the distribution system and of the operational strategy of the treatment plant, additional data collected by the treatment plant operators and historical data from a monitoring system was analyzed.

3.1.3.1 Standard Plant Operational Data

Data for water quality parameters such as free and total chlorine residual, pH, turbidity, hardness, iron and manganese concentrations within the facility and the distribution system was collected by plant personnel to satisfy regulatory monitoring requirements. This information is usually kept in daily and monthly log sheets at the facility and sensor data from the distribution system is stored in archives.

3.1.3.2 SCADA Historical Data

The federal regulatory agency requires a water treatment facility to have an online monitoring system in place to communicate to sensors placed in remote locations and to monitor and record data, which allows the operators to analyze trends over long periods of time. Most treatment facilities have had a Supervisory Control and Data Acquisition (SCADA) system in place for years. The change in water quality in terms of THM formation and chlorine decay at different locations in distribution system was verified as a result of changes in the treatment processes and operational strategy over time. Historical data collected and stored by SCADA since the early 1990's was analyzed.

3.1.4 Standard Solutions

3.1.4.1 TTHM Standard Solution

The THM standard solution was obtained from Supelco (Bellefonte, PA # 48140-U) as a concentration of 2000 µg/mL of each TTHM species in methanol. A representative certificate of analysis yielded values found in Table 7.

Table 7: THM standard concentrations, original solution

TTHM Species	Specified Concentration (µg/mL)	Analytical Concentration (µg/mL)
Chloroform	2000	1894
BDCM	2000	1946
DBCM	2000	1960
Bromoform	2000	2023

A Primary Dilution THM Standard (PDTS) with a concentration of 20 µg/mL of each THM species was prepared from this solution as needed, while using appropriate amounts of methanol. For a calibration curve, this PDTS solution was added to DI water to yield

desired concentrations (5, 10, 25, 50 and 100 ppb) to be analyzed prior to the analysis of a sample set.

3.2. Analytical Methods

3.2.1 Sample Collection

For each sampling event 2 duplicate samples were collected. Samples were analyzed for TTHM, pH, UV254, iron, aluminum and total organic carbon (TOC). Free & total chlorine residual of the water was tested on site using Hach chlorine Pocket Colorimeter™ II. Multiple 40-mL glass vials were used for the collection of water samples and it allowed for duplicate analysis of samples as needed for analytical quality control, as well as additional sample availability should errors occur during sample collection, preparation and/or instrumental analysis.

Sample vials were labeled with the sampling date, day of the scenario, time and location. Each glass vial used for THM sample collection was prepared by adding at least 100 mg/L ammonium chloride shortly before sampling to quench the reaction. Ammonium chloride is a dechlorinating agent that inhibits any further reactions with free chlorine by converting it to chloramines so that an accurate measurement from each sample location could be obtained.

After samples were collected from the treatment plant and pipe loop, they were transported back to a university laboratory by car and stored in a refrigerator at C until analyzed for TTHM (within 14 days of collection), as specified in the analytical methods section for each class of compounds.

3.2.2 UV₂₅₄

Standard Method 5910 B (APHA et al., 1998) was used to determine Absorbance of light at 254nm in the samples that were collected every time at every location. Samples were transferred to a 1-cm quartz cuvette using a syringe with a built-in 0.45- μ m filter prior to analysis. These samples were analyzed using a Varian Cary 50 Conc UV-Visible Spectrophotometer in the university's laboratory. To ensure accuracy the cuvette was cleaned multiple times using DI water prior to analysis and to ensure consistency between sets of results, the same instrument was used for measurements of all samples as part of this study.

3.2.3 Chlorine Residual

Free and total chlorine concentrations in the field as well as the lab were measured using appropriate DPD methods (Hach methods 8021 and 8167 (Hach, 1997), equivalent to Standard Method 4500-Cl G (APHA et al., 1998)) and a Hach pocket Colorimeter II (Cat # 5870000) designed for collecting on-site measurements. All on-site and most laboratory measurements were done using Hach pocket Colorimeter II and this method involves addition of a measured quantity of N, N-diethyl-p-phenylenediamine (DPD) to the sample which will then turn an intensity of pink proportional to the chlorine concentration immediately (free chlorine) or after 3 to 6 minutes (total chlorine); absorbance readings of this intensity are taken at 515nm. Total chlorine measurements involve the oxidation of iodide to iodine by combined chlorine in the sample. Both this iodine and free chlorine are then reactive with DPD. The kit has an effective range of LR-0.02 to 2.00 mg/L and HR-0.1 to 8.0 mg/L, which is typically adequate for concentrations experienced in the field such that dilutions are generally not required.

3.2.4 Total Organic Carbon

Combustion Infrared Method (Standard Method 5130B) was used to determine total organic carbon (TOC) using in the samples collected. The sample was acidified and purged to remove inorganic carbon. The sample was then injected into a high-temperature TOC analyzer. The samples were combusted at ~ 1350o C in an oxygen rich atmosphere. The carbon is converted to carbon dioxide and measured.

3.2.5 THM Species

The samples that were collected for TTHM analysis were analyzed with a Varian 3800 Gas Chromatograph (GC) equipped with a Saturn 2000 Mass Spectrometer (MS) for detection. An analysis method similar to that described by EPA method 524.2 (Munch, 1995) and Standard Method 6232 C [87] was used. Approximately 5 mL of 40-mL samples, which were collected in the field and brought back to the laboratory for analysis, was used for each analysis. Sample preparation methods and analysis conditions are described in Appendix A.

3.3 Experimental Set-up

3.3.1 Physical Model of Distribution System (Pipe Loop)

The physical model of a distribution system (Pipe Loop) was built in the filtration building of the City of Columbia water treatment facility as a means to understand changes in DBP formation kinetics under different operational conditions. It provided for manipulation of conditions like contact time and chlorine concentration and analyze the change in DBP formation over time without having to change anything in the actual distribution system. Surface conditions were close to a real system thereby increasing the accuracy and feasibility of conclusions/results presented.

3.3.1.1. Design

The pipe loop was designed based on contact time requirements, volume of water that could be used, point of extraction of finished (treated) water and the space availability in the filtration building. Provisions were made for sample collection, draining and to bypass the storage tank if and when needed (Figure 9). Design specifications of the loop can be seen in Table 8

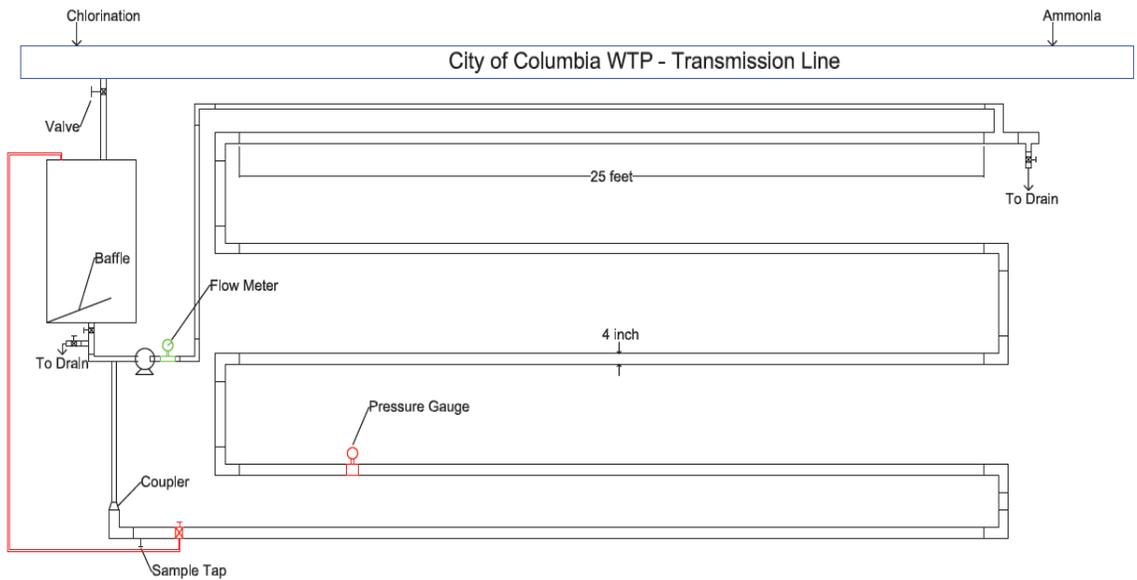


Figure 9: Physical model of distribution system (Pipe Loop) design (Poleneni, 2013)

Table 8: Design specifications of Pipe Loop

Parameter	Value
Location	Columbia Water Treatment Plant
Length of the pipe	135 ft
Type and Schedule of the pipe	PVC-40
Diameter of the pipe	4 "
Pressure	10 psi
Temperature	50 F
Storage tank volume	200 gallons
Type of the pump	Centrifugal
Capacity of the pump	40 gpm

3.3.1.2. Sampling Location and Description

Finished water after the filtration process was allowed to enter the storage tank in order to fill the Loop. Once the Loop was full, the water was re-circulated in the Loop until required amount of contact had been achieved. The quality of the water can be manipulated in the storage tank before it entered the Loop in order to run different operational scenarios.

Samples were collected at regular intervals via the sample tap at the end of the Loop. For the purpose of this study it was assumed that at any given point of time, the quality/age of water exiting the sample tap was approximately same as at any other location in the Loop. Samples were collected as a function of contact time in the Loop and usually in 24- hour intervals and collected samples were tested for pH, UV₂₅₄, Free and total chlorine residual and TTHMs (Table 9).

Table 9: Sampling matrix of Pipe Loop

Variable	Free chlorine residual	Total chlorine residual	TTHM	UV₂₅₄	TOC	pH
Interval	24 hour	24 hour	24 hour	24 hour	24 hour	24 hour
Entrance of Loop	Yes	Yes	Yes	Yes	Yes	Yes
End of Loop	Yes	Yes	Yes	Yes	Yes	Yes
No. of Samples	1	1	2	1	1	1
Sample Volume	40 mL	40 mL	40 mL	40 mL	40 mL	40 mL
Sampling Period	10 months	10 months	10 months	10 months	10 months	10 months

3.3.2 Material Specific Simulated Distribution System (MS-SDS)

Material Specific Simulated Distribution System (MS-SDS) and Simulated Distribution System (SDS) are most commonly used for determining the formation of biofilm inside

pipes over time but the test is flexible enough to be used for many other analytical purposes. MS-SDS test was conducted parallel to SDS test in accordance with Standard Method 5710C (APHA et al., 1998; Brereton & Mavinic, 2002; Chan et al., 2002), with an objective to determine the extent of influence of wall reactions in DBP formation kinetics. MS-SDS was set-up in the laboratory at the university using pipe sections from the City of Columbia water distribution system and from the Pipe Loop. SDS was conducted using an amber glass jar and both tests used finished water from the Columbia water treatment facility.

3.3.2.1. Design

MS-SDS was designed based on Standard Method 5710 C with appropriate provisions to accommodate heavy ductile iron (DI) pipe from the distribution system and a PVC pipe from the Pipe Loop (Figure 10). The design specifications are presented in Table 10.

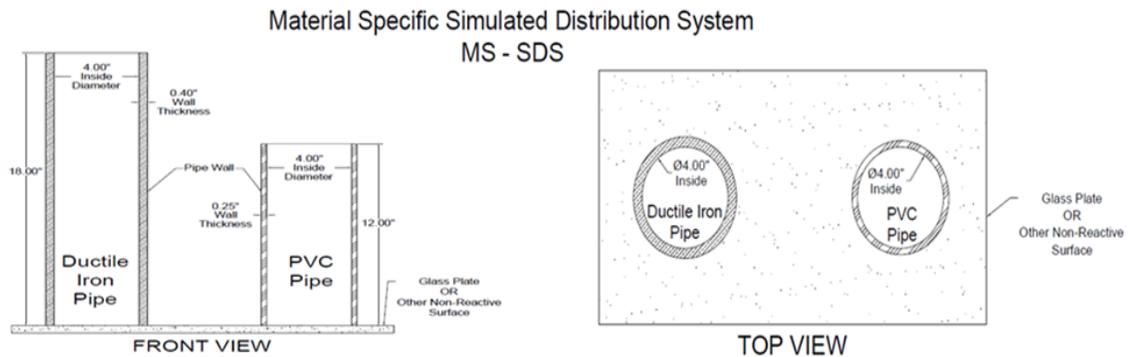


Figure 10: Material specific simulated distributed system (MS-SDS) design (Poleneni, 2013)

Table 10: Design specifications of MS-SDS

Parameter	Value
Location	University Laboratory
Material 1 & Source	DI pipe , Columbia Water Distribution System
Material 2 & Source	PVC pipe, Pipe Loop
Length and Diameter of DI pipe	18 " and 4"
Length and Diameter of PVC pipe	12" and 4"

3.3.2.2. Sampling Location & Description

Finished water was transported to the university laboratory and introduced into both the MS-SDS and the SDS simultaneously and the mouths were shut tight. The set-up was incubated for three days and samples were collected for TTHM and other analysis (Table 11). It was an open-ended set-up that gave an access to change the water quality if and when needed and samples were collected from the open end using a scooper or simply dipping the vial horizontally.

Table 11: Sampling matrix of MS-SDS

Variable	Free chlorine residual	Total chlorine residual	TTHM	UV₂₅₄	TOC	pH
Interval	24 hour	24 hour	24 hour	24 hour	24 hour	24 hour
Top of MS-SDS	Yes	Yes	Yes	Yes	Yes	Yes
No. of Samples	1	1	2	1	1	1
Sample Volume	40 mL	40 mL	40 mL	40 mL	40 mL	40 mL
Sampling Period	10 months	10 months	10 months	10 months	10 months	10 months

3.3.3 Pipe Section Reactor (PSR)

Pipe Section Reactors are a bench-scale model of the Pipe Loop with a provision of changing the type and size of the pipe under study for comparison purposes. It is smaller in size but provides same amount of data as the Loop.

3.3.3.1 Design

The PSR was designed using pipe sections from actual distribution systems (Francis AD & Weidong Z, 2005). The reactor set up was designed to allow for change in pipe length and material, collection of samples and addition of chemicals. Both ends of the PSR were

fitted with PVC 4" sections with one end running halfway through the DI section (Figure 11). This end was sealed inside the DI section and capped so that water can only pass through the perforations in the PVC section which ensures maximum wall surface contact. Design specifications of PSR are presented in Table 12.

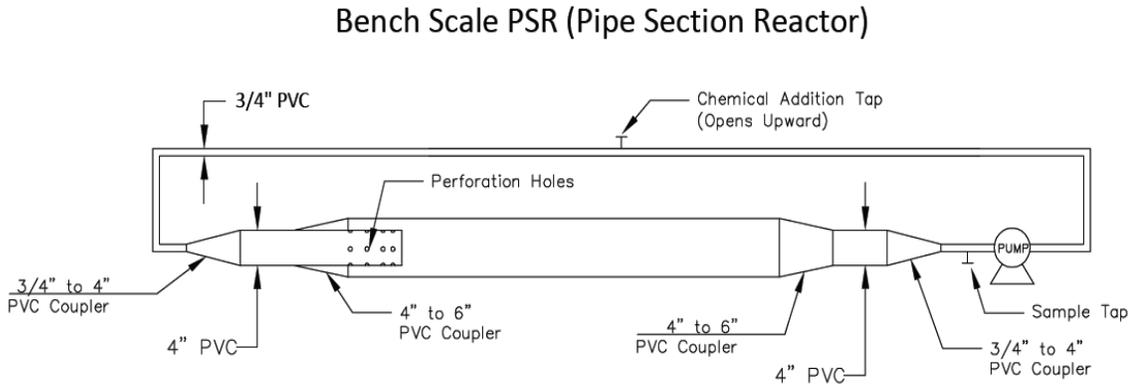


Figure 11: Pipe section reactor (PSR) design (Poleneni, 2013)

Table 12: Design specifications of PSR

Parameter	Value
Location	University Laboratory
Source of Pipe section 1	Columbia water distribution system
Source of Pipe section 2	Marshall water distribution system
Type, length and Diameter of the pipe sections	DI, 2.5 ft and 6"
Type and Capacity of the pump	Centrifugal & 40 gpm

3.3.3.2. Sampling Location and Description

Finished water from the Columbia water treatment facility was transported to the university laboratory and introduced into the PSR via a storage tank. The water was allowed to flow continuously in the PSR over 5 days using a pump (Table 13). The design is similar to the Pipe Loop but with a pipe section of 2.5ft and 6 in diameter made of ductile iron. This pipe section was collected from distributions system of Columbia and Marshall. The concept of

allowing finished water to run through the reactor for days and collecting samples every day is same as that of Pipe Loop. In both cases, it was assumed that at any given time, the quality of water in any section of the reactor was same as the sampling location.

Table 13: Sampling matrix of PSR

Variable	Free chlorine residual	Total chlorine residual	TTHM	UV₂₅₄	TOC	pH
Interval	24 hour	24 hour	24 hour	24 hour	24 hour	24 hour
Entrance of PSR	Yes	Yes	Yes	Yes	Yes	Yes
End of PSR	Yes	Yes	Yes	Yes	Yes	Yes
No. of Samples	1	1	2	1	1	1
Sample Volume	40 mL	40 mL	40 mL	40 mL	40 mL	40 mL
Sampling Period	10 months	10 months	10 months	10 months	10 months	10 months

3.3.4 Simulated Distribution System (SDS)

The standard Simulated Distribution System (SDS) procedure is explained in-detail as Standard Method 5710C. SDS was conducted using an amber glass jar. The data from SDS was used as an estimate for bulk flow reactions. For the Normal run strategy a simple standard SDS was conducted. The procedure is as follows: Finished water was collected from the Columbia water treatment plant before addition of ammonia and transported to the university lab. The pH of the water was maintained between 8.0 and 8.7, chlorine residual between 2.5 and 3.0 mg/L and a constant temperature of 25° C. The finished (treated) water had already had 0.2days of contact time with chlorine. This contact time leads to the formation of 40 µg/L of TTHM before the water was introduced into the SDS experimental set-up.

For High chlorine run on day 0 additional chlorine was added to increase the residual concentration from about 2.5 mg/L to about 6.4 mg/L which was consistent with the water entering the Loop. For chlorine Booster run on day 2, additional chlorine was added to SDS set-up to increase the residual concentration to be consistent with the increase in the Loop (Table 14).

SDS was also used to determine the impact of treatment using residuals on chlorine residual over 3 days. Simulated Distribution System (SDS) testing was completed by dosing one-liter samples with a constant concentration of free chlorine. To determine the initial chlorine dosage to be used for each sample, sodium hypochlorite was dosed into deionized water with a predetermined free chlorine concentration objective. Once the intended initial free chlorine concentration was reached in the deionized water-disinfectant solution, the concentration of sodium hypochlorite required to reach this concentration of free chlorine in solution was recorded. Deionized water was used for this process to provide an accurate basis of comparison between samples.

A total incubation period for samples of 72 hours was chosen as it closely represents the distribution time of many small-scale water utilities. The samples collected from the SDS testing will be tested for chlorine residual decay, formation of TTHM and chlorine demand of the water.

Table 14: Sampling matrix of SDS

Variable	Free chlorine Residual	Total chlorine Residual	TTHM	UV₂₅₄	TOC	pH
Interval	24 hour	24 hour	24 hour	24 hour	24 hour	24 hour
Top of SDS	Yes	Yes	Yes	Yes	Yes	Yes
No. of Samples	1	1	2	1	1	1
Sample Volume	40 mL	40 mL	40 mL	40 mL	40 mL	40 mL
Sampling Period	10 months	10 months	10 months	10 months	10 months	10 months

3.3.5 Jar Tests

This research was conducted using Jar testing to simulate drinking water treatment unit processes in the laboratory. Jar tests are a widely accepted and used method for understanding the effect of treatment process changes at lab scale (American Water Works Association (AWWA), 1992) and water treatment utilities are known to be able to replicate the results at plant scale. Standard Jar test allows for simulation of rapid mix during addition of chemicals, flocculation and sedimentation under constant temperature and pressure conditions.

The jar test method that was used involves addition of coagulant and residual together to all the jars simultaneously which is followed by 30 sec at 100 rpm to simulate rapid mix, 30 mins at 35 rpm to simulate flocculation and finally 20-30 mins at 0 rpm for settling/sedimentation. Samples were collected for water quality testing before and after the jar test from each of the jars. It should be noted that coagulant concentration was

maintained constant throughout the process with residual concentrations being the only variables making it easier to understand the effect of residuals on the treatment efficiency of the process.

3.4 Operational Strategies

3.4.1. Normal Run

Normal run was used as the control or baseline for comparing other strategies and is based on typical operation of a drinking water treatment process which models treated water with a measurable disinfectant residual entering the distribution system. Finished water from the City of Columbia water treatment plant (before addition of ammonia) is allowed to enter the Pipe Loop via Storage tank attached to it. Once the Loop was full, the valve was shut and the water was recirculated in the looped system for 7 days with water samples collected at daily intervals. Collected samples were tested for free and total chlorine residual, TOC, pH, UV254 and TTHM as a function of time over a period of 10 months. Similar procedure was followed with the PSR system.

The key points of the data generated are: 1) the TTHM concentration entering the Pipe Loop and PSR averaged 40 µg/L (half of MCL limit of 80). 2) the free chlorine residual of the water entering the Loop was on average 2.5 mg/L. 3) the pH during the run averaged 8.5 (considerably high for a chlorinated system).

3.4.2. High Chlorine Run

The Pipe Loop and PSR were operated in exactly same manner as in Normal run except the chlorine residual of the water entering the Loop averages 6.4 mg/L and 4 mg/L in the PSR (compared to 2.5 mg/L in Normal run). For this strategy, on day zero additional chlorine was added to the water to increase the residual concentration from 2.5 mg/L to 6.4

mg/L in the Loop and to 4 mg/L in the PSR. The water was then allowed to recirculate in the looped system for 7 days and water samples were collected at daily intervals. Collected samples were tested for free and total chlorine residual, TOC, pH, UV254 and TTHM.

The key points of the data generated are: 1) the TTHM concentration entering the Pipe Loop and PSR averaged 40 µg/L. 2) the free chlorine residual of the water entering the Loop was on average 6.4 mg/L and PSR was 4 mg/L. 3) the pH during the run averaged 8.5. 4) the increased residual concentrations are over the limit of maximum concentration allowable in the distribution system.

3.4.3. Chlorine Booster System Run

In order to simulate this strategy in Pipe Loop and PSR, finished water from Columbia water treatment plant (before addition of ammonia) was allowed to fill the Loop and PSR. The average concentration of chlorine residual in the water was estimated to be 2.4 mg/L, after 2 days of recirculation in the Loop and PSR, additional chlorine was introduced into the system and the water continues to recirculate for 2 more days before the Loop and PSR were drained and the strategy was run all over again. Water samples were collected at daily intervals as well as before and after boosting.

The key points of the data generated are: 1) the TTHM concentration entering the Pipe Loop and PSR averaged 40 µg/L. 2) the free chlorine residual of the water entering the Loop and PSR on day 0 was on average 2.5 mg/L. 3) on day 2, the residual was again increased to an average 2.5 mg/L. 4) the pH during the run averaged 8.5.

3.5 Data Formatting

3.5.1. Organization of the Data

All the experiments were run as function of time in order to maintain consistency in the format of the results from different experimental set-ups and to be able to compare the results with one another. Hence the data collected could be analyzed as change in concentration of each water quality parameter with change in operational conditions as function of time in days. Results for a particular parameter from different prediction tools under the same operational conditions were compared with each other in order to evaluate the difference in accuracy and efficiency of each prediction tool. This analysis not only provided with the best prediction tool option for each set of operational conditions, but also gave the best set of operational conditions to optimize the system for chlorine residual and DBP formation.

3.5.2. Statistical Methods

Results from all the experiments conducted were entered into Minitab to run statistical analysis. Analysis Of Variance (ANOVA) and hypothesis testing was used to analyze similarities in the results from different experimental set-ups under similar and different operational conditions. Multiple Regression analysis was used to analyze the relationship between each water quality parameter and their effect on DBP formation kinetics. The Paired t-test was used to compare results when two water quality parameters seem to be strongly dependent on each other like free chlorine concentration and TTHM formation. A 99% level of significance with alpha equal to 0.01 was expected from all the data collected, but anything equal to or over 90% was accepted to draw conclusions.

4. Enhanced TOC Removal Using Drinking Water Treatment Plant Residual solids

4.1 Abstract

Inefficient removal of total organic carbon (TOC) leads to the formation of carcinogenic disinfection by-products (DBPs) when a disinfectant is added. This study is performed in an effort to develop a simple, non-invasive and cost-effective technology that will effectively lower organic precursors by having water utilities reuse their treatment residual solids. Jar tests are used to simulate drinking water treatment processes with coagulants - aluminum sulfate (alum), poly-aluminum chloride (PACl) and ferric chloride and their residual solids. Ten Coagulant-to-Residual (C/R) ratios are tested with water from the Missouri River and alluvial ground waters. This treatment results in heavier floc formation and leads to improved sedimentation of organics and additional removal of aluminum and iron. An average of 21%, 28% and 33% additional TOC removal can be achieved with C/R ratios < 1 with alum, PACl and ferric chloride respectively. Data analysis proves that turbidity cannot solely be used as surrogate for TOC.

Keywords: Treatment Residual solids, Coagulation, Flocculation, TOC Removal, Turbidity.

4.2 Introduction

Percentage removal of natural organic matter (NOM) dictates the efficiency of a drinking water treatment process (Oliver & Lawrence, 1979). More specifically NOM reduction may influence how effective disinfection using chlorine in terms of amount of disinfectant needed and the concentration of disinfection by-products (DBPs) formed as a result (Liu, 2011; Krasner et al, 1989; Rook, 1974) It is known that biologically refractory humic and

fulvic acid fractions of NOM, generally of allochthonous origin, are the most reactive with chlorine (Rook, 1977). Measurement and classification of NOM is a lengthy and complex process and is usually beyond the capabilities of drinking water treatment utilities, irrespective of their size. Hence, water quality parameters such as total organic carbon (TOC) and turbidity are commonly used by water utilities as a measure of treatment efficiency. TOC is also used to determine the amount of chlorine needed for disinfection. Small-scale utilities that are unable to do TOC tests on a daily basis use turbidity, a simpler test as a representative of changing water quality throughout the treatment process. It is also widely believed that turbidity measurements can be used to make treatment process decisions as it is an acceptable surrogate for TOC changes in the system.

A typical drinking water treatment plant uses a sequence of coagulation, flocculation, sedimentation, filtration and disinfection unit processes to treat incoming raw water with an aim to decrease TOC and turbidity to a required limit (Wulff, 2011; U.S. Environmental Protection Agency (USEPA), 1998) and produce finished water with little to no taste and odor issues. In addition to these parameters the finished water is also expected to comply with rules such as Total Coliform Rule, Maximum Residual Disinfectant Level (MRDL) and Stage-II D/DBP Rule. Achieving a balance between TOC reduction and Chlorination has been a great concern to both environmental officials and the utility managers since the late 1970s when research began to show a direct link between trihalomethane (THMs) formation and reaction between TOC and free chlorine (Rook, 1977).

Coagulants such as aluminum sulfate and ferric chloride are used for coagulation and the floc that is formed as a result is allowed to settle down in a sedimentation basin before the water enters the filtration stage where the disinfectant is added. In most small-scale utilities

around Missouri the floc formed is usually too small or light in weight for it to settle down and travels beyond the final clarification step into the filtration stage resulting in more frequent back wash cycles. This also allows for higher concentrations of TOC to react with chlorine forming higher concentrations of DBPs even before the finished water leaves the system. Factors such as detention time in primary and secondary basins, floc thickness, raw water quality and coagulant type and concentration used can dictate how efficient the treatment process is in removing TOC. This study is performed as an effort to develop a simple, non-invasive and cost-effective technology that will effectively lower organic precursors/TOC while helping the water utilities to reuse their treatment residual solids, what would otherwise need to be disposed of. These residual solids are composed of mostly un-used coagulant, settled organic materials (suspended and dissolved) and impurities.

4.3 Methods

This research was conducted using Jar testing to simulate drinking water treatment unit processes in the laboratory. Jar tests are a widely accepted and used method for understanding the effect of treatment process changes at lab scale (American Water Works Association (AWWA), 1992) and water treatment utilities are known to be able to replicate the results at plant scale. Standard Jar test allows for simulation of rapid mix during addition of chemicals, flocculation and sedimentation under constant temperature and pressure conditions.

Raw water from the Missouri River and from alluvial ground water at McBaine bottoms in City of Columbia, Missouri (USA) was collected over a period of 1 year to capture water quality changes during fall, spring and summer seasons. Characteristics of incoming water are presented in Table 15.

Table 15. Characteristics of incoming water

Source	pH	TOC (mg/L)	turbidity (NTU)	aluminum (mg/L)	iron (mg/L)
River Water	(6.9 - 8.45)	(5.8 - 10.4)	(20.9 - 445)	*	*
Alluvial GW	(7.1 - 7.52)	(4.0 - 5.1)	(20 - 28)	0.07	5.34

*Testing not conducted

Aluminum sulfate (alum), poly-aluminum chloride (PACl) and ferric chloride (FeCl_3), the three most commonly used coagulants in water industry, and their respective residual solids (sludges) are used for jar testing. Coagulants and residual solids were collected from different treatment plants at the same time making them relatively fresh in nature. Nine Coagulant-to-Residual (C/R) ratios (4, 2, 1, 0.66, 0.5, 0.4, 0.33, 0.28 & 0.25) in addition to a control (coagulant with no residual solids) were tested with all three coagulants and both of the raw waters collected during every season.

The jar test method used involves addition of coagulant and residual solids together to all jars simultaneously, which is followed by 30 sec at 100 rpm to simulate rapid mix, 30 mins at 35 rpm to simulate flocculation and finally 20-30 mins at 0 rpm for settling/sedimentation. Samples were collected for water quality testing before and after the jar test from each jar. Noteworthy, the coagulant concentration was maintained constant throughout the process with residual solids concentrations being the only fluctuating variable making it easier to interpret the effect of residual solids on the treatment efficiency of the process.

pH, UV_{254} , TOC, turbidity, aluminum and iron tests were conducted on the source and effluent water from each jar test. Every jar test was repeated twice for redundancy and all

samples were collected in triplicates for each of the above water quality tests. UV₂₅₄ was measured using a Varian Cary 50 Conc. UV-Visible Spectrophotometer following Standard Method 5910 B (Standard Methods, 1998). TOC was measured using the combustion Infrared Method following Standard Method 5130 B (Standard Methods, 1998). A Hach DR5000 was used to measure aluminum and iron concentrations in the samples following Hach Method 8012 and 8008 (USEPA FerroVer) respectively (Hach, 1997). Turbidity was measured using Hach Method 8195 (Hach, 1997) and Hach Method 8196 was used to measure pH (Hach, 1997).

Percentage additional TOC removal for each C/R ratio tested was calculated as the percentage difference between the TOC concentration of effluent water using just the coagulant (no residual solids) and that of water treated with C/R ratios.

4.4 Results and Discussion

4.4.1 C/R Ratios and TOC Removal.

This analysis is intended to statistically explain the effect of each C/R ratio tested on water quality in terms of TOC removal. Data from jar tests using nine C/R ratios, alum, PACl and FeCl₃ as coagulants and their residual solids with Missouri River and alluvial ground water as incoming water is presented below. Though water from different seasons has been tested, similar results were obtained. Overall average of the results has been presented in this section. Statistical analysis is done in terms of percent additional TOC removal with respect to the control (coagulant with no residual solids).

Data from the jar tests with nine C/R ratios on Missouri River show that an additional reduction of TOC can be achieved with alum, PACl and FeCl₃ when the ratio is < 1.0

(Figure 12). This pattern can be clearly seen when the TOC concentration in effluent jars with $C/R < 1.0$ are compared against their respective controls (solid lines on the graph). This reduction can be attributed to the weight the residual solids added to the system, which allowed for heavier floc formation. Heavier floc leads to reduced carry-over, thus improving the sedimentation efficiency of the basins. When $C/R > 1.0$ (that is, when the concentration of residual solids is lower than that of the coagulant), the efficiency of the treatment process decreases. The TOC concentrations of the effluents with all 3 coagulants compared to their respective controls is higher by at least 26%. This implies that when residual solids concentration is less than the coagulant concentration, the amount of organics added into the system does not provide enough additional weight for this approach to make a difference. Therefore, instead of increased TOC removal, the system is underperforming, resulting in worse finished water quality with respect to their controls by at least 26 %.

When $C/R = 1.0$, the system is either working similar to the control or better, but not significantly better. The differences in quality of effluent from the jars in this case depend more on the type of coagulant used rather than the ratio with which it is treated.

Analysis of the data shows that a 3.5 – 23.1% additional TOC removal can be achieved with $C/R < 1$ for alum, a 10.5 – 24.6% for PACl and 1.0 – 44.7% for $FeCl_3$ relative to the control. Average percent additional TOC removal for alum, PACl and $FeCl_3$ are 17 %, 20% and 33% respectively for all C/R ratios < 1 . It can be concluded that when enough residual solids is added into the system with constant coagulant concentration ($[R] > [C]$), a considerable additional TOC decrease can be achieved resulting in better finished water quality.

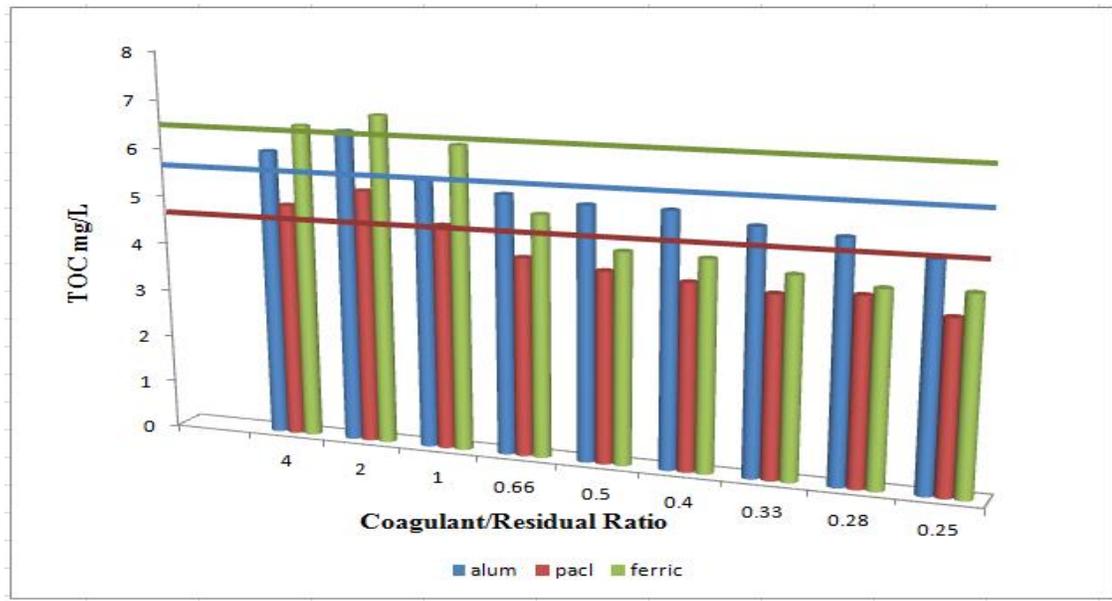


Figure 12. Surface water TOC removal using 9 C/R ratios

The optimum C/R ratio differs with each coagulant used and the raw water quality coming in; hence extensive jar tests need to be conducted before choosing a ratio that works best for a specific system.

From the initial nine C/R ratios tested, five best ratios for each coagulant were chosen and the jar tests were repeated with water collected from a different season. The best ratios for alum are 1, 0.5, 0.33, 0.28 & 0.25, for PACl are 1, 0.5, 0.33, 0.28 & 0.25 and for FeCl₃ are 0.66, 0.5, 0.33, 0.28 & 0.25. The following graph shows that the results from the jar tests with the six optimum ratios confirm the results from the earlier analysis (Figure 13). Even with change in incoming water quality the efficiency of treatment with residual solids did not change over 5% of originally tested water, though the optimum ratio for each coagulant can be different.

Analysis of the data shows that a 16.6 – 22.5% additional TOC removal can be achieved with the selected ratios for alum, a 27.2 – 36.2% for PACl and 9.5 – 24.4% for FeCl₃ relative to the control.

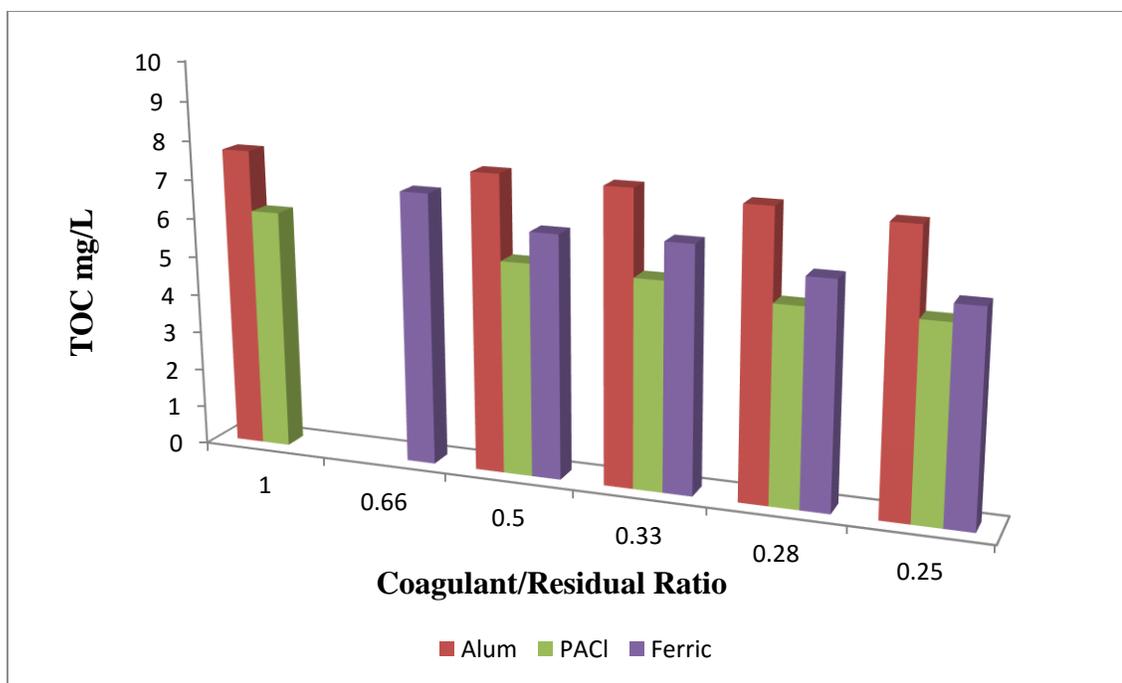


Figure 13. Surface water TOC removal using selected 5 C/R ratios

Average percent additional TOC removal for alum, PACl and $FeCl_3$ are 19.4%, 32% and 15.4% respectively for all selected ratios.

The quality of incoming ground water in terms of NOM species is considered to be different than that of a river (Chen et al, 2010). Typically, TOC and turbidity concentrations of ground water are lower than the surface water (Chen et al, 2010). In order to determine whether or not, treatment with residual solids will work with ground water, water from alluvial wells was collected and tested with the selected six C/R ratios using all three coagulants.

The data from the jar test shows that treatment with residual solids still was able to achieve additional TOC removal with respect to controls. Although the effect of each coagulant by itself on the water seems different than that on surface water and so are the ratios, the percentage difference in TOC removal is on average over 17 %. This can be clearly seen

in the graph when the effluent TOC concentrations are compared to solid lines which represent controls (Figure 14).

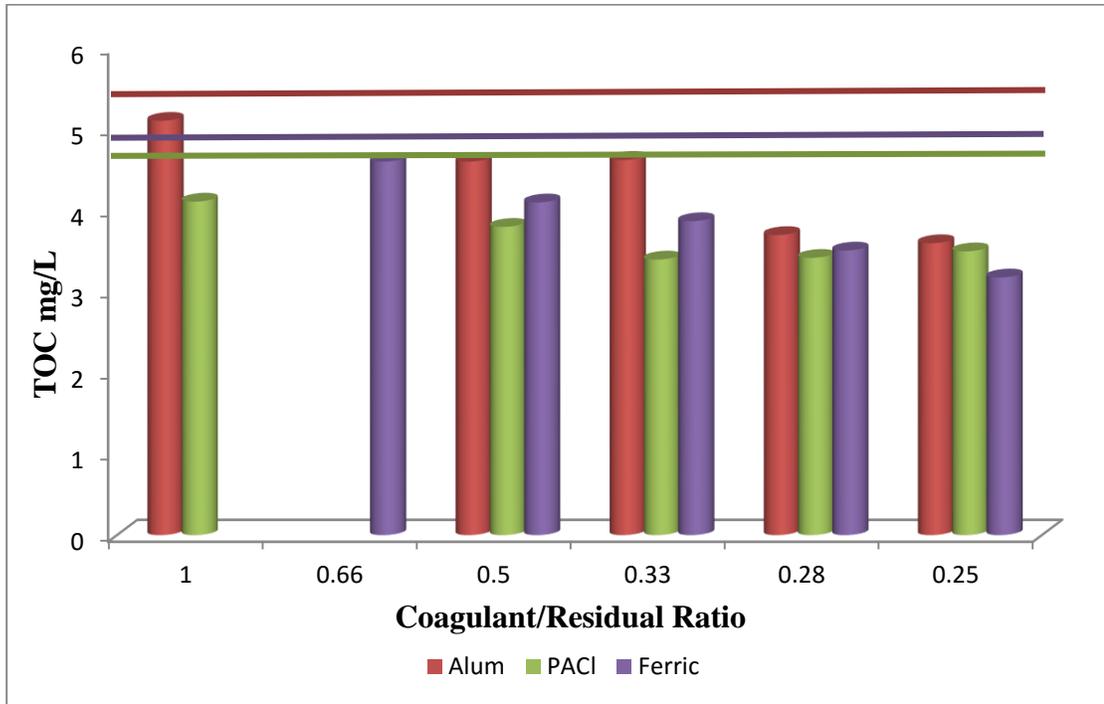


Figure 14: Ground water TOC removal using selected 5 C/R ratios

Analysis of the data shows that a 14.1 – 38.2% additional TOC removal can be achieved with the selected ratios for alum, a 21.2 – 32.1% for PACI and 6.3 – 42.6% for FeCl₃ relative to the control. Average percent additional TOC removal for alum, PACI and FeCl₃ are 25.4%, 28.5% and 24.6% respectively for all selected ratios.

For a ground water system, the best choice of coagulant can be different from that of surface water and therefore, so is the optimum C/R ratio of each coagulant. In determining the optimal ratio for a ground water system, additional jar testing with the water needs to be conducted. The result of this treatment on surface water is same as the ground water which is enhanced TOC reduction, but percentage reduction is not an exact match. This difference needs to be taken into consideration before making a treatment change decision.

4.4.2 C/R Ratios and aluminum Removal.

Aluminum concentrations of raw water differ depending on the source and so are the concentrations in effluent water depending on the treatment used. Using aluminum-based coagulants such as alum and PACl are known to increase the concentrations of aluminum in the effluent water, so this was an area of concern during this study (Clark et al., 1996). New treatment technologies that are aimed at improving water quality with respect to one contaminant or water quality parameter are sometimes known to degrade it with respect to another. Therefore, aluminum concentrations were tested before and after treating water with residual solids for all three coagulants used.

The concentration of aluminum in the raw ground water was measured to be 0.04 mg/L. As shown in the graph the residual aluminum in the water after being treated with alum, PACl and FeCl_3 is 1.45 mg/L, 1.26 mg/L and 0.07 mg/L respectively (Figure 15). Noteworthy, the residual aluminum in water treated with alum and PACl is higher than that treated by FeCl_3 as well or than in the raw water. This could be due to technician error, or an outlying circumstance.

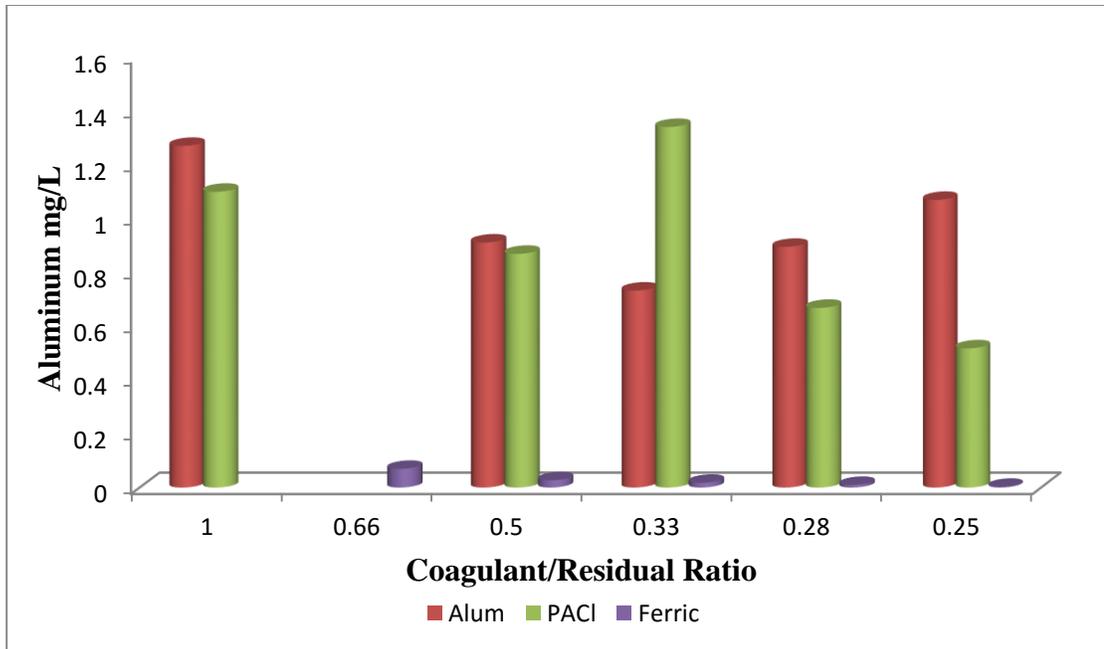


Figure 15: aluminum residual removal using selected 5 C/R ratios

Analysis of the data from jar tests shows that, contrary to our assumption, residuals might increase the aluminum concentrations in the effluent water, the treatment with residual is proven to decrease the aluminum residuals notably compared to the controls (solid lines). A 13.2 – 65.6% additional aluminum removal can be achieved with the selected ratios for alum and 13.6 – 83.1% for PACI relative to the control. Average percent additional aluminum removal for alum and PACI are 40.3%, and 37.7% respectively for all selected ratios. Aluminum residual in the control and in the treated water as in the case of FeCl_3 is not significant as the coagulant itself is not aluminum based. It can be concluded that addition of residuals not only improve the finished water quality with respect to TOC concentration, but also with respect to aluminum concentrations.

4.4.3 C/R Ratios and iron Removal.

Most drinking water utilities have to deal with iron concentrations in their source water on a day-to-day basis. Presence of iron ions in natural and treated waters is known to have

adverse effects on disinfection leading to increased formation of DBPs (Moncayo-Lasso, 2012; Liu et al, 2011; Henderson et al, 2001) With increasing drought conditions, changes in the land use, and decreasing dissolved oxygen concentrations in the water sources, iron concentrations in raw water is becoming a bigger problem (Neal et al., 2008). Aeration is typically used to precipitate iron from the raw water entering a treatment plant, but usage of iron-based coagulants to decrease TOC concentrations can sometimes have an adverse effect with respect to iron residual in finished water. The proposed treatment using residual solids raises concerns of increased iron concentrations in the effluent water as one of the coagulants used is FeCl_3 . Therefore, iron concentrations were tested before and after treating water with residual solids for all 3 coagulants used.

The concentration of iron in the raw water was measured to be 5.34 mg/L. The residual iron in the water after being treated with alum, PACl and FeCl_3 was 3.08 mg/L, 1.98 mg/L and 2.76 mg/L respectively (Figure 16).

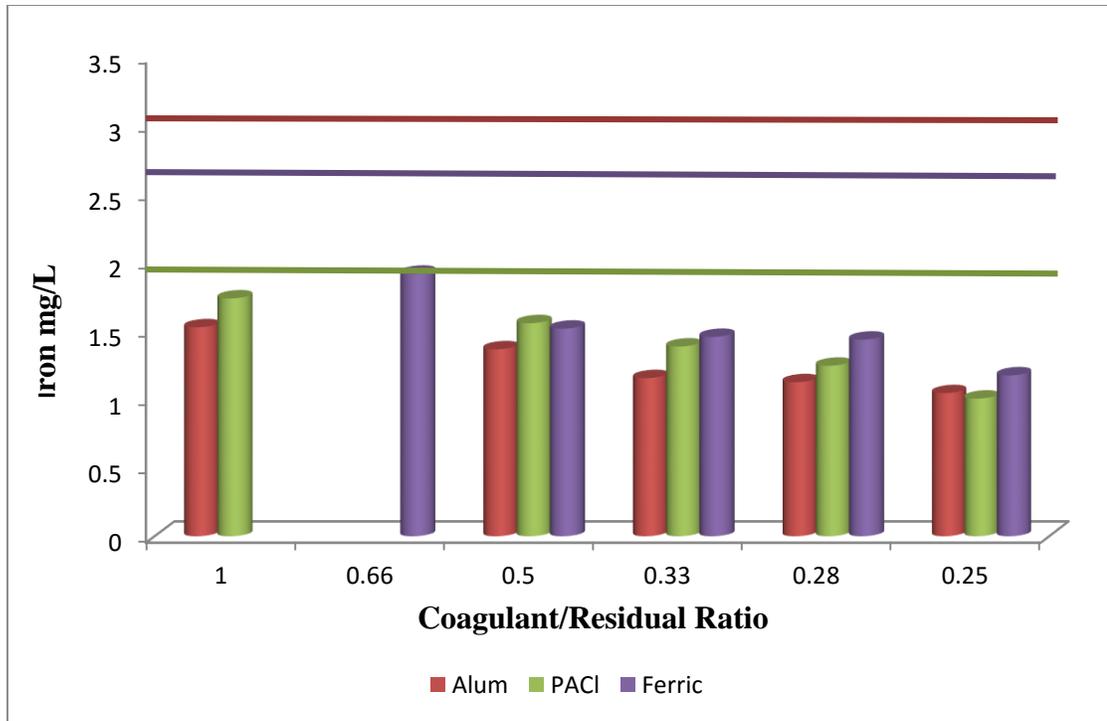


Figure 16: Iron residual removal using selected 5 C/R ratios

Analysis of the data from jar tests shows that, contrary to our assumption that residual solids might increase the iron concentrations in the effluent water, the treatment with residual solids is proven to decrease the iron residuals considerably compared to the controls (solid lines). A 67.2 – 98% additional iron removal can be achieved with the selected ratios for alum, a 12.91 – 64.9% for PACl and 35.9 – 80.2% for FeCl_3 relative to the control. Average percent additional iron removal for alum, PACl and FeCl_3 are 85%, 36.35% and 59.7% respectively for all selected ratios. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to iron concentrations.

4.4.4 Turbidity vs. TOC Concentrations.

Small scale utilities that unable to do TOC tests on a daily basis use turbidity, a simpler test as a representative of changing water quality throughout the treatment process (USEPA, 1983). It is also widely believed that turbidity measurements can be used to make treatment process decisions as it is an acceptable surrogate for water quality changes in the system (USEPA, 1999). Because this project is aimed at developing simple and non-invasive ways to decrease TOC concentrations and the fact that most small-scale utilities depend on turbidity rather than their TOC numbers while making treatment change decisions, an understanding as to how the proposed treatment with residual solids would affect the turbidity numbers of the effluent water allows for a broader and easier full-scale application of the technology. Therefore, turbidity was measured before and after treating water with residual solids for all three coagulants used for both surface and ground water.

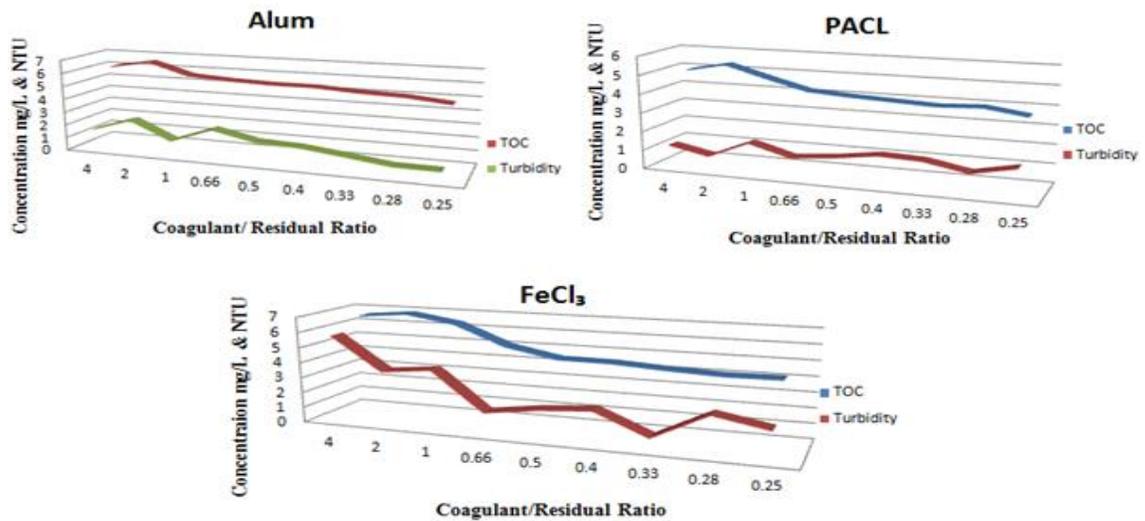


Figure 17: Turbidity vs. TOC removal using 9 C/R ratios, level of confidence (LOC)

95%.

Analysis of the data from the jar tests show that, TOC does not always increase when turbidity increases and vice-versa (Figure 17). This can be attributed to the fact that turbidity can only account for changes in suspended organic carbon, not the dissolved component which together adds up to TOC of the water. The range of turbidity values for alum, PACl and FeCl₃ treatments are 0.69 - 2.28, 0.8 - 1.69 and 0.74 - 5.73 mg/L respectively. The range of turbidity values for alum, PACl and FeCl₃ treatments are 4.6 - 6.5, 3.6 - 5.3 and 4.0 - 6.85 mg/L respectively. The graphical representation of the data above clearly shows that in many cases when turbidity value increases, a decrease in TOC occurs contrary to the popular belief. For all the three coagulants, two raw water types and most C/R ratios tested the change in magnitude and direction of TOC and turbidity is notably different, making it incorrect to use one as the surrogate for other while making important treatment decisions that could affect finished water quality This also explains why making a treatment process change based on turbidity numbers alone won't necessarily help utilities remain in compliance with DBP regulations every time.

4.4.5 pH Stability.

The drinking water treatment process is a pH based system. pH differences can be the result of coagulants added as part of the treatment and they are usually adjusted by addition of a base or an acid before disinfection (Wisconsin Department of Natural Resources (WIDNR), 2007). Different disinfectants work effectively at different pH ranges. For example, chlorine works well at lower pH (pH 6-7) when compared to chloramines (pH 7-8.5) (Yang, 2015; Monacayo-Lasso, 2012). Therefore, water utilities adjust their pH throughout the process to allow for different unit processes to work more efficiently. However, pH adjustment can sometimes be expensive or hard to achieve, and the expenses

of which could negate the benefit from this process. Different coagulant usage results in different pH in the effluent water and this raises the concern about dramatic pH changes as a result of proposed treatment with residual solids. Therefore, pH is measured before and after treating water with residuals for all three coagulants used for both surface and alluvial ground water and are compared against their respective controls (Figure 18).

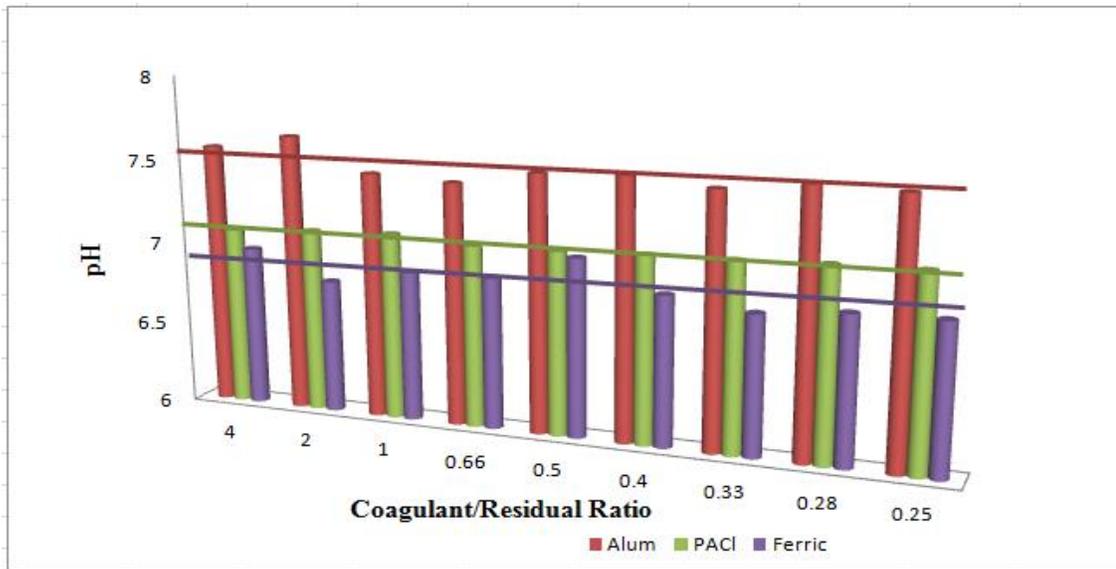


Figure 18: pH change due to treatment with residuals

Analysis of the data from jar tests shows that, contrary to our assumption that residuals might change the pH in the effluent water; the proposed treatment with residual is proven to cause no significant (± 0.2) changes in pH when compared to the controls (solid lines). Therefore, no additional efforts are required for pH adjustment as a result of addition of residual solids.

4.5 Conclusions

Enhanced TOC removal can be achieved when $C/R < 1$. The percent additional TOC removal for alum, PACl and $FeCl_3$ use in surface (river) water is 16.6 – 22.5%, 27.2 – 36.2% and 0.5 – 24.4%, respectively, and use in alluvial ground water is 14.1 – 38.2%,

21.2 – 32.1% and 6.3 – 42.6%, respectively. A slight increase in TOC is observed when $C/R > 1$. Enhanced aluminum and iron removal can also be achieved with this proposed treatment. The percent additional removal of aluminum residual for alum and PACl addition is 13.2 – 65.6% and 13.6 – 83.14%, respectively, whereas percent of additional iron residual removal for alum, PACl and $FeCl_3$ is 67.2 – 98%, 12.91 – 64.9% and 35.9 – 80.2%, respectively. It is shown here that turbidity should not be used as a surrogate for TOC when making decisions about changes in the treatment process in both surface and ground water systems. No significant changes in pH were observed as a result of the proposed treatment.

The percent additional TOC removal depends on the raw water quality and its changes, C/R ratios used, and type of coagulant needed. Finding a right match of coagulant and C/R ratio for a certain kind of raw water coming in requires rigorous jar testing and data analysis. Treatment using residual solids is proven to be a simple, non-invasive and cost-effective technology that will effectively lower TOC concentrations by having the water utilities reuse their treatment residual solids. The proposed treatment also has a potential to decrease the amount of coagulants needed for water treatment thereby reducing the cost of treatment process.

4.6 Acknowledgements

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5. Array of Prediction Tools for Understanding Extent of Wall Effects in DBP formation in Drinking Water Distribution Systems

5.1 Abstract:

Disinfection is a vital part of a drinking water treatment process and chlorine is the most widely used disinfectant in the world. Though known for its effectiveness, usage of chlorine does lead to the formation of carcinogens which are commonly called disinfection by-products (DBPs). The Stage-2 Disinfectant and disinfection by-product (D/DBP) regulations under Safe Drinking Water Act (SDWA) of United States force water utilities to be more concerned with their finished and distributed water quality.

Compliance requires a better understanding of reaction kinetics changes and wall effects with different materials used in the distribution system, which affect the formation of DBPs over time. To validate our results in full scale distribution system physical conditions, effect of different materials, wall effects, bulk reactions and water movement is analyzed using Simulated Distribution System (SDS) tests, Material Specific Simulated Distribution System (MS-SDS) tests Pipe Loop and Pipe Section Reactor (PSR); all built using materials from City of Columbia distribution system. PSR and MS-SDS are used to evaluate the change in water quality from typical operational conditions such as having a high chlorine dosage before entering the distribution system and using a chlorine booster system in the distribution system. These different processes contribute to different rates of DBP formation.

On an average, just the choice of pipe materials such as PVC and iron can account for as much as 36 % difference in TTHM formation and 60% difference in chlorine residual decay

over time irrespective of the prediction model and operational strategy used. Based on the data analysis, it can be concluded that, booster systems are optimal solutions for residual maintenance and TTHM control in all systems, more so in PVC. In case of iron pipe systems, the wall demand for chlorine dominates everything else leading to increased loss of residual and lower TTHMs formation over time irrespective of operational strategy in use. that in case of iron, PE is < 1 , leading us to conclude that in the iron pipe systems there is a net loss of TTHM yield due to non-TTHM forming chlorine demand imposed by the pipe environment, whereas in PVC pipe, PE is > 1 (Table 17). Therefore, in PVC systems there is an overall increase in TTHM formation as a result of pipe wall surface biofilm interaction with residual chlorine.

5.2 Introduction:

Public utilities provide potable water for 90% of the United States (USEPA, 1999). Federal regulation of drinking water quality began in 1914 with the U.S. Public Health Service setting standards for the bacteriological quality of drinking water. Today, the number of regulations and their stringency increased dramatically based on vast scientific discoveries in the field and increasing health concerns. One area that has seen a considerable amount of focus is carcinogen control in finished water (Clark & Boutin, 2001). More than 500 DBPs have been identified in tap water (Clark et al., 1994; Clark et al., 1996) and thousands more exist. To date, the identifiable DBPs cumulatively account for no more than 50% of the total organic halogen (TOX) in most chlorinated drinking waters, numerous halogenated DBPs formed from chlorine still remain unknown (Hua & Reckow, 2007, 2007a; Zhang et al., 2000; Singer, 1995; Reckow & Singer, 1984). The Stage 1 Disinfection and disinfection by-products Rule (D/DBP1) (63 FR 69390-69476, December

16, 1998, Vol. 63, No. 241) and Stage 2 Disinfection and disinfection by-products Rule (D/DBP2) (71 FR 388, January 4, 2006, Vol. 71, No. 2) are the current regulations for the control of carcinogens in potable water throughout United States (USEPA, 1998). These regulations aim to reduce exposure to contaminants including total trihalomethanes, five haloacetic acids, bromate, chlorite, chlorine, chloramines, and chlorine dioxide (USEPA, 1998).

Pipe surfaces play a large part in the formation of DBPs occurring throughout the water treatment process (Digiano & Zhang, 2005). Even medium sized water utilities may have hundreds of miles of pipes constructed from various types of materials, ranging from newly lined pipes to unlined pipes that are more than 50 years old. Over time biofilms and tubercles attached to pipe walls can result in significant loss disinfectant residual and, thereby adversely affect water quality (Besner et al., 2001) (Figure 19). Many opportunities arise for water quality to change as it moves between the treatment plant and the customer (Singer et al., 2002; Boccelli et al., 2003; Clark, 2011).

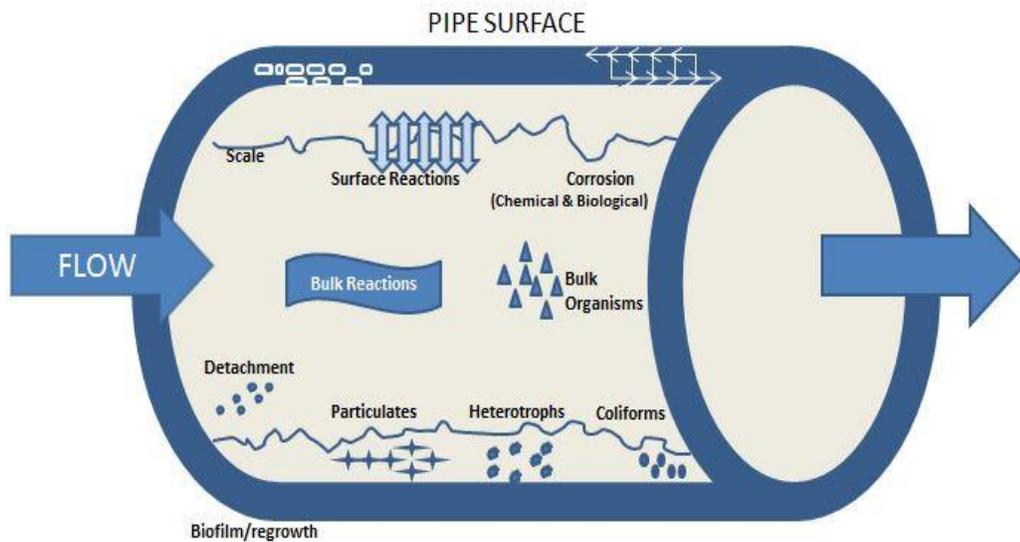


Figure 19: Water chemistry inside pipelines

Cross-connections, failures at the treatment barriers, and the transformations in bulk phase can all degrade water quality. Corrosion, leaching of the pipe material and biofilm formation and scour can occur at the pipe wall and are subject to change with changes in materials as well as with the operational strategies used (Clark, 2011).

In order to understand the change in water quality during distribution, we need to understand the effect of different materials in addition to effects of operational strategies (Sadiq & Rodriguez, 2004; Clark & Sivaganesan, 1998; Clark et al., 1996). The most commonly used pipes today for water mains are ductile iron (DI), pre-stressed concrete, polyvinyl chloride (PVC), reinforced plastic, and steel (Brereton & Mavinic, 2002). For the purpose of this research pipe sections made of PVC and DI were used. The selection is

justified by the fact that most of the treatment plants in Missouri and around US are either still using DI or upgraded to PVC in last decade (Gang, 2001).

The objective of this study is to evaluate the magnitude of effect of different pipe materials on chlorine decay rate and TTHM formation rate under commonly used operational strategies such as Normal Run (NR), High chlorine (HC) and Usage of chlorine boosters (BR) at constant pH and temperature. For this purpose, well-documented prediction methods such as Simulated Distribution System test (SDS), Material Specific Simulated Distribution System test (MS-SDS), Pipe Section Reactor (PSR) and Physical model of distribution system (Pipe Loop) were built using PVC and DI pipe sections from existing water distribution system.

5.3 Methods:

5.3.1 Materials:

Six-inch diameter and 4-inch diameter DI pipe with an estimated age over 40 years was extracted from the distribution system for PSR and MS-SDS processes respectively. Four-inch diameter PVC pipe with an age of 1 year was extracted from the Pipe Loop for this study (Figure 20). Finished water from the filters with about 40 $\mu\text{g/L}$ TTHMs and 2.5 mg/L chlorine residual was used as the source water for this work (Table 16).



Figure 20: Cross sectional view of PVC and iron pipe used

Table 16: Characteristics of Incoming water (FINISHED water)

TOC mg/L	TTHM µg/L	Cl₂ mg/L	pH
4.0	40.2	2.5	8.6

5.3.2 Design & Testing:

The physical model of a distribution system (Pipe Loop) was built in the filtration building of the City of Columbia water treatment facility as a means to understand changes in DBP formation kinetics under different operational conditions. It provided for manipulation of conditions like contact time and chlorine concentration and analyze the change in DBP formation over time without having to change anything in the actual distribution system. Surface conditions were close to a real system thereby increasing the accuracy and feasibility of conclusions/results presented (Figure 21A).

Material Specific Simulated Distribution System (MS-SDS) and Simulated Distribution System (SDS) are most commonly used for determining the formation of biofilm inside

pipes over time but the test is flexible enough to be used for many other analytical purposes. MS-SDS test was conducted parallel to SDS test in accordance with Standard Method 5710C (APHA et al, 1998; Brereton & Mavinic, 2002; Karen, 2002), with an objective to determine the extent of influence of wall reactions in DBP formation kinetics. MS-SDS was set-up in the laboratory at the university using pipe sections from the City of Columbia water distribution system and from the Pipe Loop. SDS was conducted using an amber glass jar and both tests used finished water from the Columbia water treatment facility (Figure 21B).

The Pipe Section Reactor (PSR) was designed using pipe sections from actual distribution systems (Francis & Weidong, 2005). The reactor set up was designed to allow for change in pipe length and material, collection of samples and addition of chemicals. Both ends of the PSR were fitted with PVC 4" sections with one end running halfway through the DI section. This end was sealed inside the DI section and capped so that water can only pass through the perforations in the PVC section which ensures maximum wall surface contact (Figure 21C)

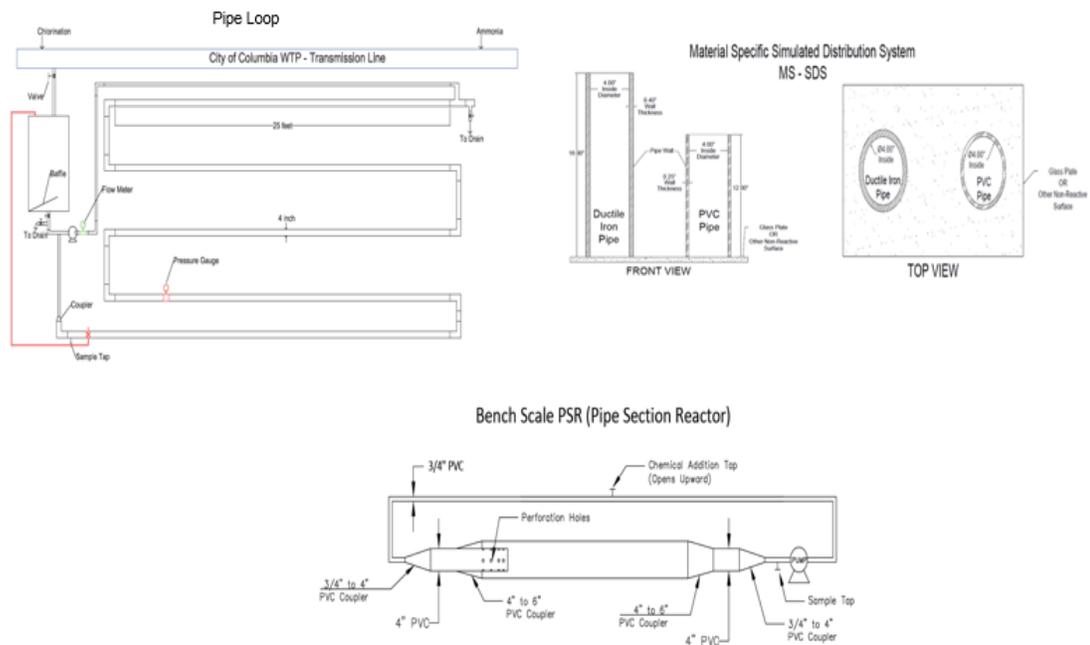


Figure 21: Prediction models design A) Pipe Loop design, B) MS-SDS design, C) PSR design

Normal run was used as the control or baseline for comparing other strategies and is based on typical operation of a drinking water treatment process which models treated water with a measurable disinfectant residual entering the distribution system. Finished water from the City of Columbia water treatment plant (before addition of ammonia) is allowed to enter the Pipe Loop via a Storage tank attached to it, the PSR via a stand pipe attached to it and for MS-SDS and SDS purposes water was transported back to lab. Once they are all full, the intake valve was shut for PSR and Loop and the water was recirculated/ remained in the systems for 4 days with water samples collected at daily intervals. Collected samples

were tested for free and total chlorine residual, TOC, pH, UV254 and TTHM as a function of time over a period of 10 months.

In case of High chlorine run, the Pipe Loop was operated in exactly same manner as in Normal run except the chlorine residual of the water entering the Loop, PSR, SDS and MS-SDS averages 6.4 mg/L (compared to 2.5 mg/L in Normal run). Many water utilities in order to maintain residual throughout the distribution system end up adding much higher concentration of chlorine which leads to finished water leaving the system with much higher residual. For this strategy, on day zero additional chlorine was added to the water to increase the residual concentration from 2.5 mg/L to 6.4 mg/L. The water was then allowed to recirculate/stay in the apparatus for 4 days and water samples were collected at daily intervals. Collected samples were tested for free and total chlorine residual, TOC, pH, UV254 and TTHM.

To simulate the Booster Run in Pipe Loop, PSR, SDS and MS-SDS finished water from Columbia water treatment plant (before addition of ammonia) was allowed fill them. The average concentration of chlorine residual in the water was 2.4 mg/L, after 2 days of recirculation in the apparatus, additional chlorine was introduced into the system and the water continues to recirculate/stay for 2 more days before the apparatus was drained and the strategy was repeated. Water samples were collected at daily intervals as well as before and after boosting.

All experiments were run as function of time in order to maintain consistency in the format of the results from different experimental set-ups and to compare results with one another. Hence the data collected could be analyzed as changes in concentration of each water quality parameter with change in operational conditions as a function of time in days.

Results for a particular parameter from different prediction tools under the same operational conditions were compared with each other to understand the difference in accuracy and efficiency of each prediction tool. This analysis is designed not only to provide the best prediction tool option for each set of operational conditions, but also to give the best set of operational conditions to optimize the system for chlorine residual and DBP formation.

For each sampling event four water samples were collected. Two were analyzed for TTHM and two for pH, UV254 and total organic carbon (TOC). Free & total chlorine residual of the water was tested on site using Hach chlorine Pocket Colorimeter™ II. Four 40-mL glass vials were used for the collection of water samples and it allowed for duplicate analysis of samples as needed for analytical quality control, as well as additional sample availability should errors occur during sample collection, preparation and/or instrumental analysis.

Sample vials were labeled with the sampling date, day of the scenario, time and location. Each glass vial used for THM sample collection was prepared by adding at least 60-100 µg/L ammonium chloride shortly before sampling to quench the reaction. Ammonium chloride is a dechlorinating agent that inhibits any further reactions with free chlorine by converting it to chloramines so that an accurate measurement from each sample location could be obtained.

After samples were collected from the treatment plant, pipe loop and PSR they were transported back to a university laboratory by car and stored in a refrigerator at 4 °C until analyzed for TTHM (within 14 days of collection), as specified in the analytical methods section for each class of compounds.

One of the four samples collected every time at every location was used to determine absorbance of light at 254nm following Standard Method 5910 B (APHA et al., 1998). Samples were transferred to a 1-cm quartz cuvette using a syringe with a built-in 0.45- μ m filter prior to analysis. These samples were analyzed using a Varian Cary 50 Conc. UV-Visible Spectrophotometer in the university's laboratory.

Free and total chlorine concentrations in the field as well as the lab were measured using appropriate DPD methods (Hach methods 8021 and 8167 (Hach, 1997), equivalent to Standard Method 4500-Cl G (APHA et al., 1998) and a Hach pocket Colorimeter II (Cat # 5870000) designed for collecting on-site measurements. All on-site and most laboratory measurements were done using Hach pocket Colorimeter II and this method involves addition of a measured quantity of N, N-diethyl-p-phenylenediamine (DPD) to the sample which will then turn an intensity of pink proportional to the chlorine concentration immediately (free chlorine) or after 3 to 6 minutes (total chlorine); absorbance readings of this intensity are taken at 515nm. Total chlorine measurements involve the oxidation of iodide to iodine by combined chlorine in the sample. Both this iodine and free chlorine are then reactive with DPD. The kit has an effective range of LR-0.02 to 2.00 mg/L and HR-0.1 to 8.0 mg/L, which is typically adequate for concentrations experienced in the field such that dilutions are generally not required.

One of the four samples collected every time at every location was used to determine total organic carbon (TOC) using Combustion Infrared Method (Standard Method 5130B). The sample was acidified and purged to remove inorganic carbon. The sample was then injected into a high-temperature TOC analyzer. The samples were combusted at $\sim 680^{\circ}$ C in an

oxygen rich atmosphere (achieve by using zero air). The carbon is converted to carbon dioxide and measured by an infrared detector.

The samples that were collected for TTHM analysis were analyzed with a Varian 3800 Gas Chromatograph (GC) equipped with a Saturn 2000 Mass Spectrometer (MS) for detection. An analysis method similar to that described by EPA method 524.2 (Munch, 1995) and Standard Method 6232 C (APHA et al., 1998) was used. Approximately 5 mL of 40-mL samples, which were collected in the field and brought back to the laboratory for analysis, was used for each analysis.

5.4 Results and Discussion:

5.4.1 PSR, Loop and SDS Data Analysis:

This analysis is intended to statistically explain the effect of each of the pipe materials and operational strategies on the chlorine decay rate and TTHMs formation rate. Chlorine residual change over time is considerably different between strategies as well as pipe materials (Figure 22) though all of them started with similar initial concentration, except HC run. The difference in residual concentration over time in each run across PSR and LOOP as compared to SDS gives us the effect of each material and its respective wall effects. This also differs based on the run, as can be seen in figure 4 HC run. PSR made out of DI material has the maximum decay rate throughout the runs with highest in HC run while SDS that accounts for only bulk reactions in the water has the lowest decay rate.

Water treatment plants aim to maintain at least 0.5mg/L of chlorine in their distribution system and based on the data for the NR, PVC and SDS are able to maintain the required residual whereas DI system runs out of compliance after Day 1. This explains why large

amount of chlorine is added at the treatment plants in order to maintain minimum required residual throughout distribution system when it is made of DI pipes. The data show that having boosters installed in the distribution system to boost chlorine after Day 1, would help all the systems (more so in Loop and SDS systems) to be under compliance while accounting for loss of chlorine due to bulk and wall reactions.

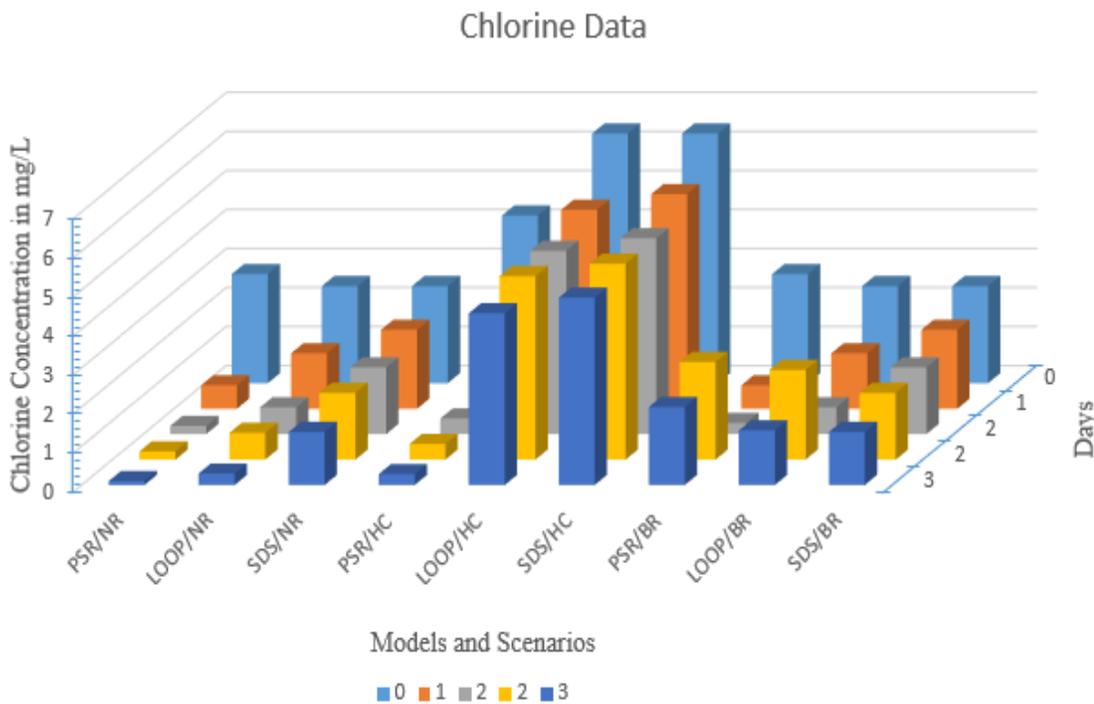


Figure 22: Chlorine concentrations in PSR, Loop and SDS under different operational strategies, LOC 95%.

It is frequently assumed that a majority of the chlorine lost in the distribution system is usually accounted for by the formation of DBPs and other compounds, while this might be true in systems made of PVC and glass where the wall demand of chlorine is minimal, it is far from the truth in DI systems. In DI systems, the wall demand of chlorine dominates to

such an extent that the higher rate of chlorine decay is accompanied by lower rate of TTHM formations throughout all the runs (Digiano & Zhang, 2005) (Figure 23).

In the HC run, it can be concluded that High Chlorine conditions tend to increase the rate of bulk reactions, which minimizes wall effects on chlorine decay. This can be partially explained by the concept of collision theory, which states that presence of higher concentration of one reactant particles in a solution has a potential to change/ influence the reaction path, thereby affecting the concentration and type of products formed (Hill, 1997). The High chlorine scenario is one situation in which ignoring the wall reaction coefficient during calibration of physical or computer models can be justified. However, as with most distribution systems, the operation tends to be more chlorine limited.

Data also proves that the booster systems with lower TTHM formation and chlorine decay rates is an optimal solution for both chlorine residual maintenance and TTHM control irrespective of pipe materials.

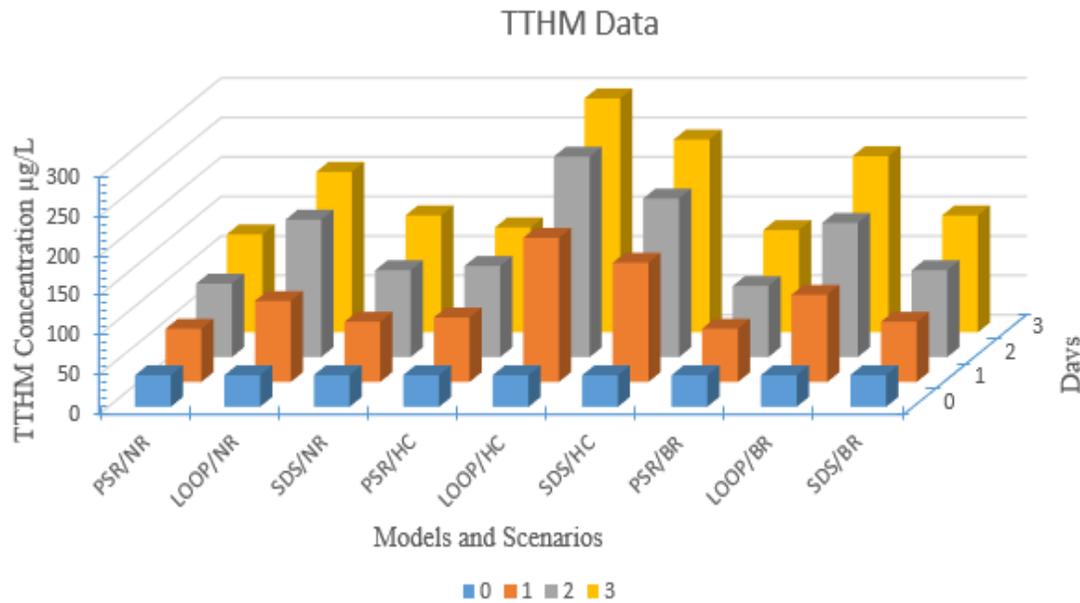


Figure 23: TTHM concentrations in PSR, Loop and SDS under different operational strategies, LOC 95%.

A considerable difference in TTHM concentration on day 1 is observed in all systems given the Day 0 is same throughout, this can be explained by the difference in chlorine residual remaining and the wall demand for it in each system. It is to be noted that the HC run though successful in maintaining required residual for longer times, a high concentration (over the maximum limit) of TTHMs formed starting Day 1 will push the water systems out of compliance. Meanwhile, the PSR systems that require higher concentrations of initial chlorine addition to maintain required residual might also end up out of compliance since initial reactions between high chlorine concentration and organics will produce TTHMs enough to counteract the benefit of higher wall demand of the pipes. In case of Loop (PVC) system addition of lower chlorine concentration initially and boosting the system later would help the system achieve compliance for residual and DBP regulations.

5.4.1.1 Normal Run vs. High Chlorine Run

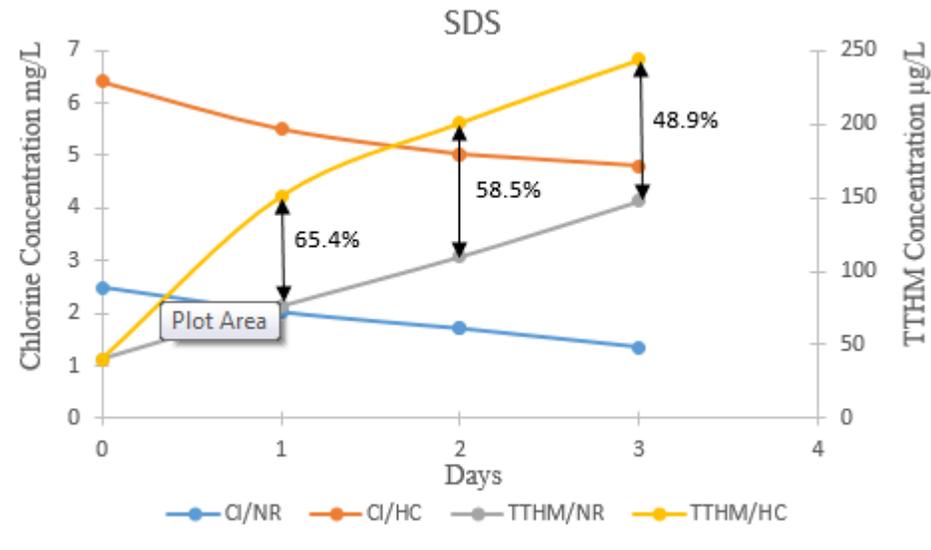


Figure 24: TTHM and chlorine residual concentrations NR vs. HC in SDS system

NR and HC are the most commonly used operational strategies by water utilities. In SDS the difference in the chlorine residual decay and TTHM formation is significant yet consistent (Figure 24). This can be attributed to only bulk reactions. In the absence of wall effects, the loss of chlorine residual and formation of TTHMs over time is known to be linear. The difference in TTHM concentration over time between NR and HC can solely be attributed to the higher reaction rates due to increased availability of free chlorine to the organics in treated water. It should be noted that in both runs, chlorine residual is maintained, but the system is out of compliance for TTHMs after Day1.

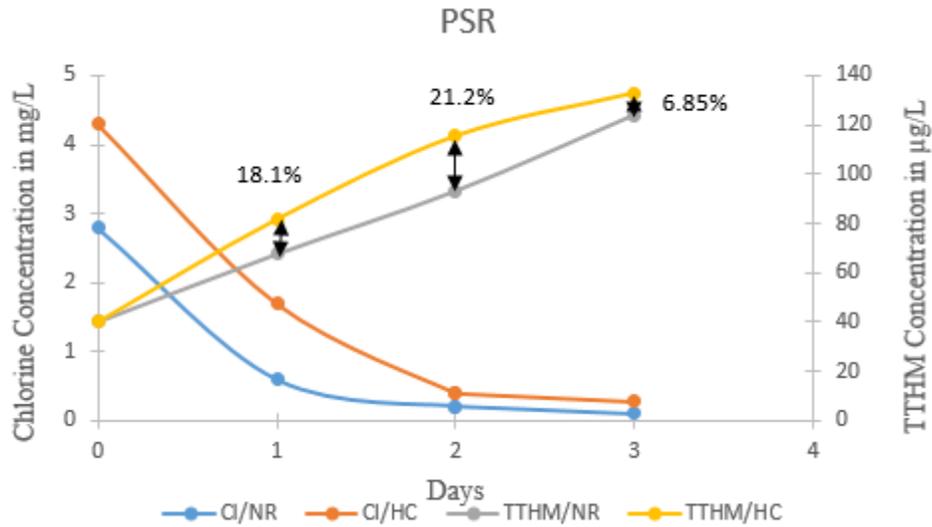


Figure 25: TTHM and chlorine residual concentrations NR vs. HC in PSR system

In PSR, a considerable amount of difference in chlorine residual can be seen on Day 0, which gradually reduces with time and by the end of Day 2 they are almost similar in both runs whereas in case of TTHMs, HC and NR started with same concentration and the difference on Day 1 and Day 2 is 18 % and 21% respectively (Figure 25). On day 3, the concentration of residual approaches zero in the difference in TTHM between drops by 14% which can be attributed to limited availability of residual for the formation. The impact of HC run is not as predominant in this system when compared to SDS and Loop, yet the system is out of compliance after Day 1.

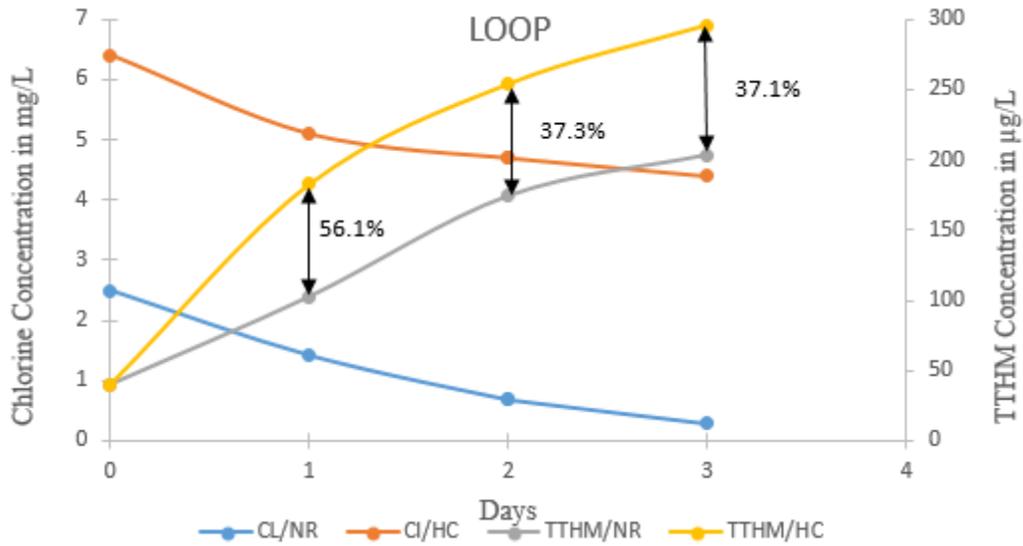


Figure 26: TTHM and chlorine residual concentrations NR vs. HC in Loop system

In the Loop system made of PVC pipe a considerable difference can be observed in both chlorine decay and TTHM formation rates which is similar to SDS and a lot different from PSR system. The effect of increased availability of chlorine can be attributed to all the difference in both rates, while the wall effect of PVC pipe explains the difference in rates between SDS and Loop systems in both runs. It can be concluded that HC run in the loop though allows for residual maintenance, it hinders TTHM control (Figure 26).

5.4.1.2 High Chlorine Run vs. Booster Run

Using boosters to help maintain residual in long distribution systems is a well-known and documented, yet less frequently used operational strategy. Especially in small scale water utilities with distribution systems lasting between 1-3 days, HC is preferred over boosters for various reasons that include the increased ease and control, minimal structural and operational changes associated with HC runs. The following analysis shows how these two runs affect chlorine and TTHMs in different systems.

In SDS systems, everything is attributed to bulk reactions in water and nothing to wall effects. The need for boosters arises when the residual gets under 0.5 mg/L before the distribution system end. In SDS system as the loss of residual due to wall effects is zero and bulk effects is minimal, thus eliminating a need for boosters to maintain the residual (Figure 27).

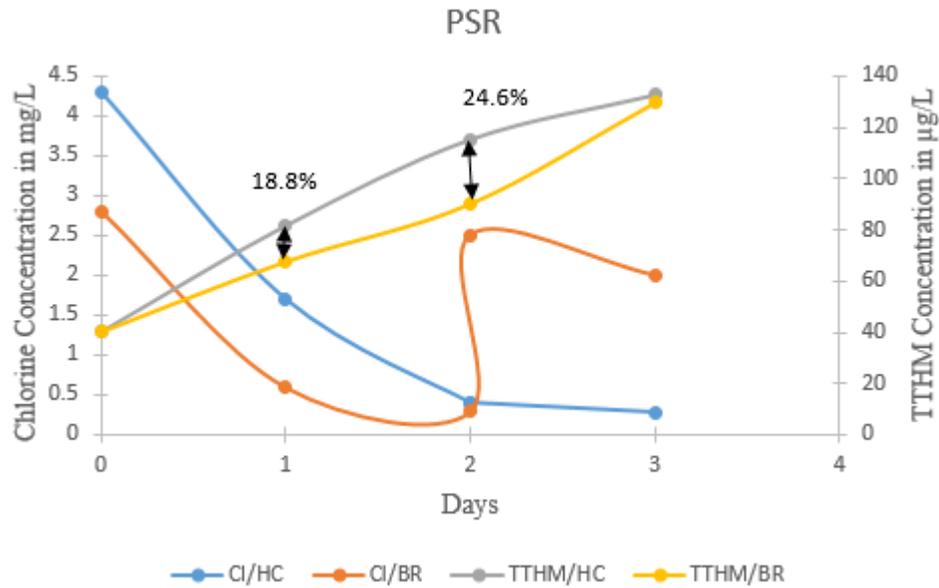


Figure 27: TTHM and chlorine residual concentrations HC vs. BR in PSR system

In PSR systems made of DI pipes, the need for boosters is evident. On Day 2, when the residual concentration is near 0.5 mg/L additional chlorine is added to the system instead of adding increased amount on Day 0 as seen in HC run. It can be observed using boosters did not just allow for residual maintenance, it led to decreased formation of TTHMs in the system helping with its compliance. A difference of 18% and 24 % can be seen in TTHM concentration between HC and BR on Day 1 and Day 2 respectively (see Fig. 16).

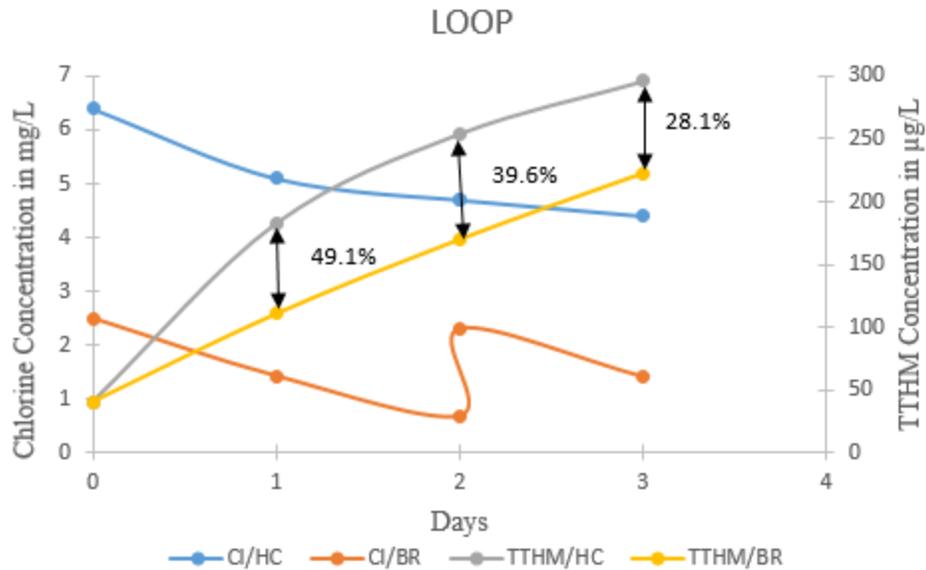


Figure 28: TTHM and chlorine residual concentrations HC vs. BR in Loop system

The merits of BR over HC can be seen clearly in the Loop system where both bulk and wall effects result in higher loss of residual and increased formation of TTHMs. On Day 2, when the residual in the system is under 0.5 mg/L, additional chlorine is added into the system. It can be noted that both runs lead to maintenance of residual for longer periods of time, while the TTHM concentration in HC run is 49%, 39% and 28% more than in BR run on Day 1, day 2 and Day 3 respectively (Figure 28). The difference in residual and TTHM between the loop system and PSR systems for both runs can be attributed to differences in chlorine demand in pipe materials.

5.4.2 MS-SDS Data and Analysis:

MS-SDS is used to better understand the extent of wall effects of different pipe materials on still /standing treated water over time when everything else is kept constant (Karen et al., 2002; Brereton et al., 1997; Brereton & Mavinic, 2002). This method was developed

by Brereton as a modification of standard SDS test that does not account for the biofilm formation on pipe surfaces and therefore, may not be adequate to evaluate the processes in distribution system (Brereton, 1998). When the two test are run simultaneously, it is possible to distinguish change in concentration of certain contaminant or chemical in water under the influence of two distinct environments: the bulk water and the pipe environment (Brereton & Mavinic, 1997). For the purpose of this project, MS-SDS was built using glass, iron and PVC materials and analysis was conducted to understand their effects on chlorine residual and TTHM concentrations over time.

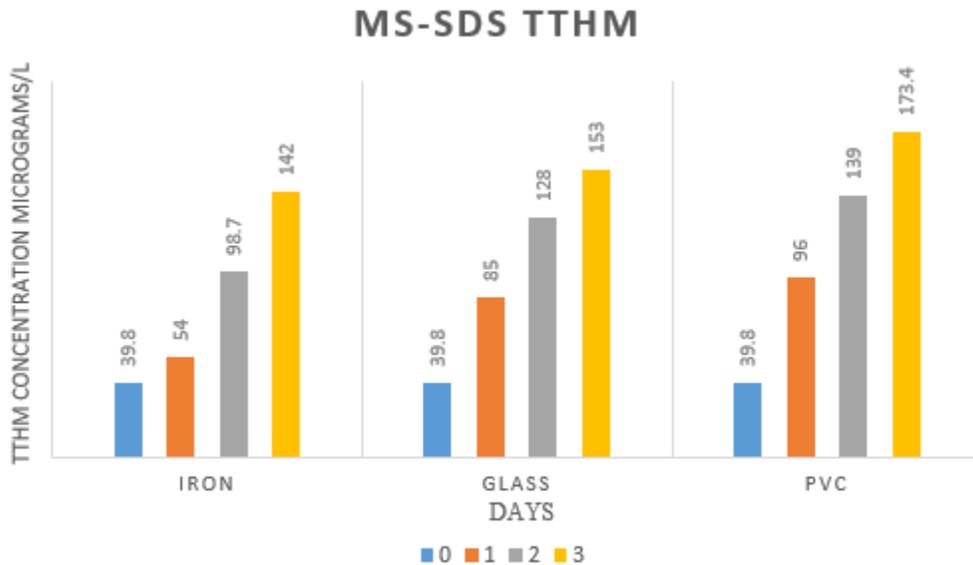


Figure 29: TTHM concentrations in MS-SDS system, LOC 99%.

The concentration of TTHMs is same in MS-SDS and SDS on day 0 while the difference in them on day 1, 2 and 3 can solely be attributed to the effect of material of pipe the water is stored in. It can be noted that lowest rate of TTHM formation can be seen in iron pipe and the highest in the PVC pipe (Figure 29). One might expect that system with least or zero wall effects like glass will have lowest TTHMs measured over time, while that's not

the case here as in the iron pipe wall effects dominate in a manner that don't necessarily lead to higher TTHM formation rates.

In case of chlorine residual, the glass pipe maintains residual longer and in higher concentrations over time as expected due to zero wall demand for chlorine. Between PVC and iron pipes, iron pipes have much higher wall demand for the chlorine leading to system with under 0.5 mg/L starting Day2 (Figure 30).

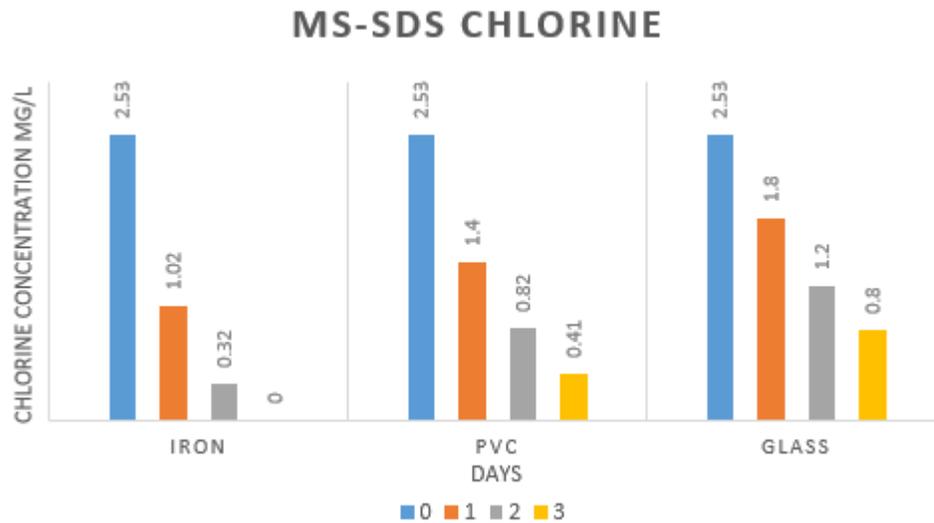


Figure 30: Chlorine concentrations in MS-SDS system, LOC 95%.

The effect of the pipe material (PE for pipe effect) is defined as TTHM formed during pipe incubation (MS-SDS) divided by TTHM formed during glass incubation (SDS).

$$\text{PE value} = \text{TTHM formed in MS-SDS} / \text{TTHM formed in SDS}$$

Pipe effect values greater than unity (>1.00) indicate an overall increase in TTHM formation as a result of pipe wall surface biofilm interaction with residual chlorine. Pipe effect values less than unity (<1.00) reveal a net loss of TTHM yield due to non-TTHM

forming chlorine demand imposed by the pipe environment (Ahmadi, 1981; Allen et al., 1980; Tuovinen et al., 1984; LeChevallier et al., 1987,1990).

Table 17: PE values of PVC and iron pipe in MS-SDS system

Material	0	1	2	3
Iron	1	0.63	0.77	0.92
PVC	1	1.1	1.08	1.13

Based on the data collected from the SDS and MS-SDS system over a long period of time, the above the Pipe Effect (PE) values are calculated. It can be seen that in the case of iron, PE is < 1 all 3 days the test was conducted, leading us to conclude that in the iron pipe systems there is a net loss of TTHM yield due to non-TTHM forming chlorine demand imposed by the pipe environment, whereas in PVC pipe, PE is > 1 the whole time (Table 17). Therefore, in PVC systems there is an overall increase in TTHM formation as a result of pipe wall surface biofilm interaction with residual chlorine.

5.5 Conclusions

The data analysis proves that wall effects due to different pipe materials lead to considerable differences in chlorine residual decay and TTHM formation over time. This difference will dictate whether or not an operational strategy is appropriate for the system at hand. On an average, just the choice of pipe materials such as PVC and iron can account for as much as 36 % difference in TTHM formation and 60% difference in chlorine residual decay over time irrespective of the prediction model and operational strategy used. Operators with limited resources will benefit vastly from just using MS-SDS with their

pipe and treated water to understand effect of a particular treatment change or operational change on distributed water.

Data proves that under normal operational conditions, it is easier to maintain residual in PVC pipe distribution systems when compared to iron pipe distribution systems meanwhile, the control of TTHM formation is much harder in PVC systems. Based on the data analysis, it can be concluded that, booster systems are optimal solutions for residual maintenance and TTHM control in all systems, more so in PVC. In case of iron pipe systems, the wall demand for chlorine dominates everything else leading to increased loss of residual and lower TTHMs formation over time irrespective of operational strategy in use. The data analysis also shows that assuming that wall effects are negligible while calibrating water quality models will lead to incorrect predictions of water quality parameter concentrations over time. Given that the results are only as good as the prediction model used and the model is only as good as the assumptions made, care needs to be taken while designing and using them for decisions making.

5.6 Acknowledgements

Funding for this project was provided by the Missouri Department of Natural Resources (MDNR). Analytical and technical support was provided by Missouri Water Resources Research Center (MWRRC).

6 DBP Formation Potential with Enhanced TOC Removal in Drinking Water Treatment Plants

6.1 Abstract

With the introduction of the Stage-II Disinfectant and disinfection by-product (D/DBP) regulations, water utility systems must be increasingly cognizant of water quality as it progresses through the supply system and ultimately reaches customers. Enhanced coagulation methods utilizing treatment residual solids is proven to cause a reduction in TOC as presented in paper 1. This study will focus on determining whether the addition of residual solids affects chlorine demand, chlorine residual, decay rates, and DBP formation. To simulate the DBP formation and chlorine decay kinetics in small-scale distribution systems, water treated with various coagulants and coagulant to residual solids ratios was tested in a jar-type simulated distribution system.

Coordination of enhanced TOC removal techniques (appropriate ratios based on site-specific conditions) can yield a decrease in chlorine demand while helping to prolong residual concentration in the distribution system.

Keywords: Chlorination, Chlorine Demand, Residuals, Total Organic Carbon, Trihalomethanes

6.2 Introduction

The incorporation of disinfection techniques into drinking water treatment processes is one of the great public health accomplishments. Practices such as chlorination have proven cost-effective and tremendously proficient in controlling bacteria, virus, and other waterborne illness growth throughout the water distribution supply chain. Chlorination is

one of the most common disinfectant processes due to chlorine being relatively easy to handle, cost-effective, simple to dose, measure, and control, having a reasonably prolonged residual, and having low capital installation costs (Calderon, 2000; Sadiq & Rodriguez, 2003; USEPA, 1998; Warton et al., 2006). Despite chlorination often occurring prior to treated water leaving the treatment facility, the responsibility of water utilities extends well beyond this point in time (Besner et al., 2001). As the water supply progresses through a distribution system towards the customer, chemical and physical reactions continue to take place and can cause significant changes in water quality (Singer et al., 2002; Boccelli et al., 2003; Clark, 2011).

Free chlorine is the most commonly used form of chlorine for disinfection. Its dissociation process into hypochlorite and then into hydrogen ions is described below (Equations 3 and 4) (Mbonimpa, 2007).



In regards to chlorination, the primary concerns are maintaining free chlorine residual throughout the system and managing the growth of disinfection by-products (DBPs). Chlorination can be a tricky process to master for any treatment plant, as both low and high disinfectant residuals in the distribution system pose risks. These risks include inadequate disinfecting properties, customers noting taste and odor irregularities, residual violations, and DBP violations (Ohar & Ostfeld, 2010; Haxton et al., 2011).

Hypochlorite and hypochlorous acid, when reacting with organic matter, have been proven to be the predominant chlorinating agents responsible for DBP formation (Vasconcelos et al., 1997; Gang, 2001). The prevailing type of disinfectant by-products that can form are trihalomethanes, which are included under Stage-II Disinfectants and Disinfectant By-Product (DBP) Rule (USEPA, 1998; Adams et al., 2005; Rook, 1977). ATSDR (2015) describes the process of natural organic matter (NOM) reacting with aqueous free chlorine which can cause the trihalomethanes known as chloroform, dibromochloromethane, chloromethane, and bromoform to form.

While trihalomethanes retained in the body may not generate negative consequences immediately, over time, these compounds can cause slowed brain activity, liver and kidney cancer, and heart disease, depending on the dosage (ATSDR, 2015). Due to the Stage-II DBP Rule, many small-scale water utilities must be pro-active in determining an adequate solution for controlling DBP formation. The relationship between chlorine consumption and TTHM formation is linear. Consequently, equation 5 states that TTHM formation increases as chlorine demand increases.

$$TTHM = Y(\textit{Chlorine Consumption}) + M \quad (5)$$

Where, Y = yield parameter (μg TTHM/mg chlorine consumed); TTHM = total trihalomethane formation ($\mu\text{g/L}$); M = intercept from linear regression analysis of experimental data (Clark & Sivaganesan, 1998; Boccelli et al., 2003).

The water samples used in this experiment are unique in that they contain various treatment residual solids to coagulant ratios in an effort to increase total organic carbon (TOC) removal efficiency during clarification. The additional pore space aids in adsorption of suspended particles which increases floc mass and TOC removal efficiency. This enhanced coagulation technique is capable of increasing TOC removal (Ciner & Ozer, 2013) as presented in paper 1. When a treatment process change is made such as this, it is imperative to understand any resulting ramifications on other treatment processes. These ramifications include effects on chlorine decay and DBP formation. Along with the residual solids and NOM concentration of samples differing greatly, the non-organic characteristics of samples will also differ greatly in each of the six source waters. These are the two major variables which complicate comparing chlorine demand between samples and cause the need for a carefully considered analysis method.

The traditional method of calculating chlorine consumption is the “APHA Method” where residual chlorine concentration is subtracted from initial chlorine dosage after some amount of time at a constant temperature and pH (Calderon, 2000). It is important to understand that chlorine reactivity will vary depending on dosage and chemical composition (e.g., DOC) differences between samples from the same water plant (Calderon, 2000). Therefore, since the samples in this experiment have a high variability of chlorine-consuming species, a variation of the aforementioned method will be used for analysis.

This chlorine demand analysis method is described by equation 6.

$$Demand_{Cl} = 100\% * (C_o - C_r)/C_o \quad (6)$$

Where, C_o = initial free chlorine (mg/L); C_r = residual free chlorine after 20 minutes (mg/L).

The most important aspect of this chlorine demand analysis method is that it allows for accurate comparison of samples with vastly different chemical, physical, and biological characteristics. Recycled residual solids to coagulant ratio, type of coagulant, and source water quality are the major factors in chlorine decay kinetics and DBP formation.

The complexion of chemical, biological, and physical reactions results in the formation of DBP's is extremely difficult to predict. This statement is especially true of small-scale water treatment plants, which are more likely to be resource-limited compared to more sophisticated research laboratories and high-MGD (million gallons per day) plants. These resource limitations include technical, managerial, and financial constraints (Shih et al., 2006). Furthermore, source water origin is also a controlling aspect in regards to treatment plant demands and design considerations. Small-scale water treatment plants are more likely to employ surface water as a source, which can increase treatment requirements when compared to ground water sources (USEPA, 1999). Since DBP formation is based on the variables of chlorine decay, NOM/TOC, pH, and source water quality, both the operational strategies and the source water location have the potential to affect and create issues with DBP formation (Boccelli et al., 2003).

Due to limitations, many small-scale water treatment plants have no method of directly measuring TOC concentration or TTHM formation. As a result, they often rely on correlating turbidity and chlorine residual measurements to TOC, TSS (total suspended solids), and TTHM concentrations. Due to a lack of information available to treatment plant operators, the following decision process may occur. When increased turbidity is

detected during the treatment process, the plant operator may expect increased TOC concentrations to also be present. However, the original assumption of TOC increasing with turbidity is not always valid. Often times, high turbidity does not correspond to high TOC/TSS, and vice-versa (USACE, 2000; Wei et al., 1998). Therefore, the increased chlorine dosage, which has the potential to cause increased DBP formation, may not be a necessary action.

Once analysis of chlorine demand is completed, conclusions will be made regarding their relationship to TOC, turbidity, residual solids-to-coagulant ratios, and source water location. This project will contain conclusions which could be beneficial to small-scale water treatment plants. TOC removal efficiency can be increased via enhanced coagulation, and if this poses no negative effects on chlorine demand, then it could be a viable strategy to meet DBP compliance.

6.3 METHODS

This research was conducted using water samples gathered from five different treatment plants. Two treatment plants use groundwater, while three use surface water (Table 18).

Table 18: Source water summary.

Source	Type of source	pH	turbidity NTU	aluminum Concentration mg/L	iron Concentration mg/L
Columbia	Ground water	6.9	43	1.7	2.7
Odessa	Ground Water	7.1	147	0.054	14.2
Vandalia	Lake water	7.4	7	0.019	0.14
Marceline	Lake water	6.3	31	0.049	1.27
Boonville	Surface water	8	159	.017	.72
Coopers Landing	Surface water	6.9	116	1.53	1.74

Vandalia which is in Audrain county and Marceline which is in Linn both fall under glacial plains category and have lake water with chlorophyll 22.4 and 31.4, total phosphorus 58 and 83 µg/l and total nitrogen of 905 and 1115 respectively (Jones et al., 2008). Free and total chlorine concentrations were measured in the laboratory using a Hach pocket Colorimeter II in accordance with Hach methods 8021 and 8167 (Hach, 1997). The method used requires addition of N-diethyl-p-phenylenediamine (DPD) which generates a pink coloring of the sample that correlates to chlorine concentration. The kit used has an effective low-range (LR) of 0.02 to 2.00 mg/L and a high-range (HR) of 0.1 to 8.0 mg/L. Sample vials were labeled with the sampling date, day of the scenario, time and location. Each glass vial used for THM sample collection was prepared by adding at least 100 mg/L ammonium chloride shortly before sampling to quench the reaction. Ammonium chloride is a dechlorinating agent that inhibits any further reactions with free chlorine by converting it to chloramines so that an accurate measurement from each sample location could be obtained. The samples that were collected for TTHM analysis were analyzed with a Varian

3800 Gas Chromatograph (GC) equipped with a Saturn 2000 Mass Spectrometer (MS) for detection. An analysis method similar to that described by EPA method 524.2 (Munch, 1995) and Standard Method 6232 C (APHA et al., 1998) was used.

Jar tests were conducted in which samples were given a constant coagulant dosing of 0.16 mg/L while the residual solids dosing was then based on specific coagulant to residual solids (C/R) ratios (Table 19). Aluminum sulfate (alum), ferric chloride (ferric), and poly-aluminum chloride (PACL) are the coagulants used during jar testing.

Table 19: Jar testing matrix for determining C/R ratios for treatment

Jar Test	Coagulant/Residual Ratio (C/R)	Coagulant Concentration mg/L	Treatment Residual Concentration in mg/L
Raw	0:0 (Raw)	0	0
Jar 1	1:0 (Control)	0.16	0
Jar 2	1:1	0.16	0.16
Jar 3	1:2	0.16	0.32
Jar 4	1:3	0.16	0.48
Jar 5	1:3.5	0.16	0.56
Jar 6	1:4	0.16	0.64

The following (Table 20) describes when residual chlorine and TTHMs concentration will be measured for each water sample relative to time of dosing. Free chlorine samples were taken in triplicates for redundancy during each sampling event.

Table 20: Sample collection and testing matrix.

Time Interval	Free chlorine Residual	TTHMs
20 min	3	-
24 hours	3	2
48 hours	3	2
72 hours	3	2

Simulated Distribution System (SDS) testing was completed by dosing one-liter samples with a constant concentration of free chlorine. To determine the initial chlorine dosage to be used for each sample, sodium hypochlorite was dosed into deionized water with a predetermined free chlorine concentration objective. Once the intended initial free chlorine concentration was reached in the deionized water-disinfectant solution, the concentration of sodium hypochlorite required to reach this concentration of free chlorine in solution was recorded. Deionized water was used for this process to provide an accurate basis of comparison between samples.

A total incubation period for samples of 72 hours was chosen as it closely represents the distribution time of many small-scale water utilities.

Significant difference are defined differently for different water quality parameters under study. For pH it is +/- 0.5 pH unit, for aluminum and iron concentration it is +/- 0.2 mg/L, for chlorine residual it is +/- 0.2 mg/L, for TOC it is +/- 0.1 mg/L and for TTHM it is +/- 20 µg/L. Due to the extended period in which research was conducted, the error in initial chlorine concentration is assumed to be ±10-15%. The main cause of error is the variation in chlorine standards used at various points in the study, as well as pipette and other various equipment errors.

6.4 Results and Discussion

Data analysis was performed to study the impact of proposed treatment on the following:

- pH
- aluminum and iron concentration
- chlorine demand of water
- chlorine residual over time
- TTHM concentration over time
- turbidity
- TOC
- Influence of source water
- Influence of coagulants
- Influence of coagulant to residual solids ratios used

6.4.1 pH Stability

The drinking water treatment process is a pH based system. pH differences can be the result of coagulants added as part of the treatment and they are usually adjusted by addition of a base or an acid before disinfection (Wisconsin Department of Natural Resources (WIDNR), 2007). Different disinfectants work effectively at different pH ranges. For example, chlorine works well at lower pH (pH 6-7) when compared to chloramines (pH 7-8.5) (Yang, 2015; Monacayo-Lasso, 2012). Therefore, water utilities adjust their pH throughout the process to allow for different unit processes to work more efficiently. However, pH adjustment can sometimes be expensive or hard to achieve, and the expenses of which could negate the benefit from this process. Different coagulant usage results in

different pH in the effluent water and this raises the concern about dramatic pH changes as a result of proposed treatment with residual solids. Therefore, pH is measured before and after treating water with residual solids for all three coagulants used for all water systems under study and are compared against their respective controls (Figure 31-35).

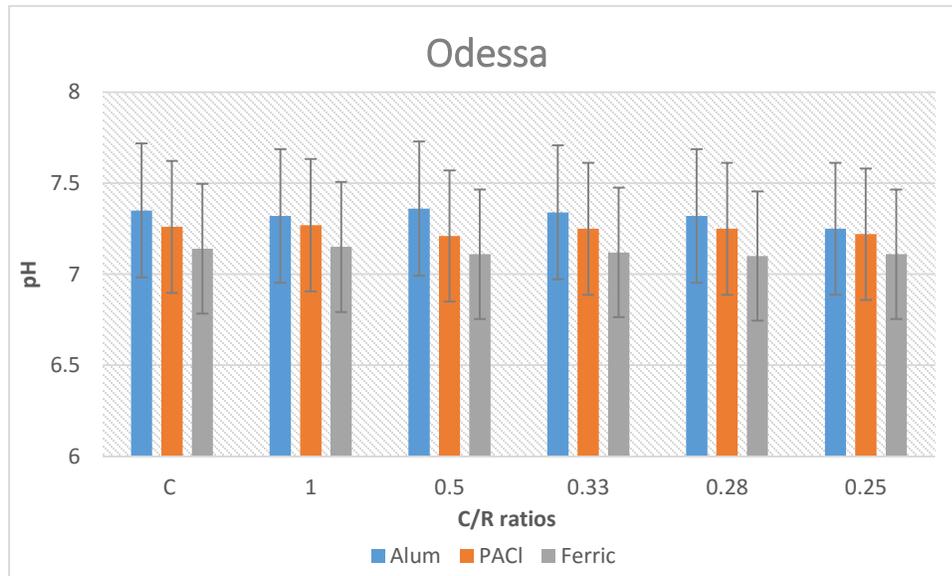


Figure 31: pH stability vs. C/R ratios treatment in Odessa, LOC 95%.

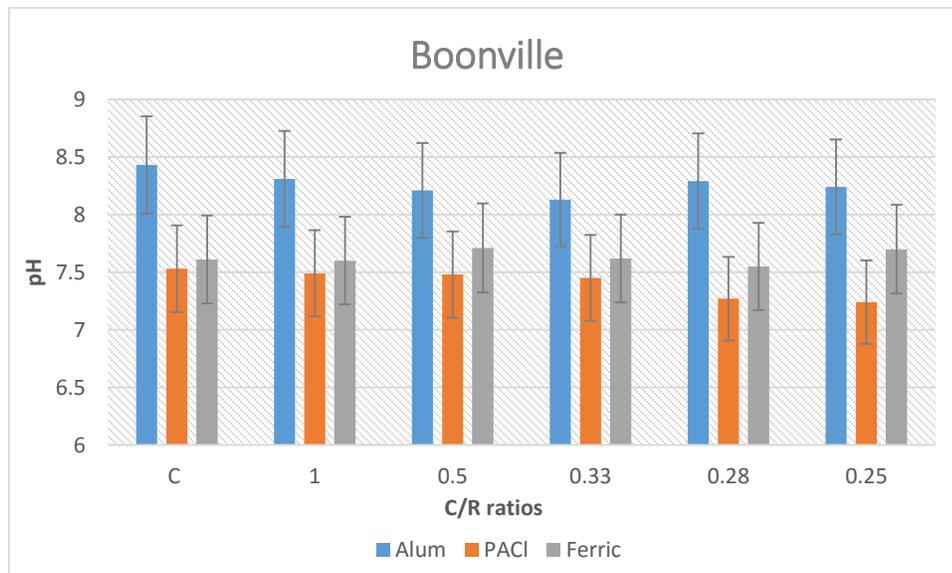


Figure 32: pH stability vs. C/R ratios treatment in Boonville, LOC 95%.

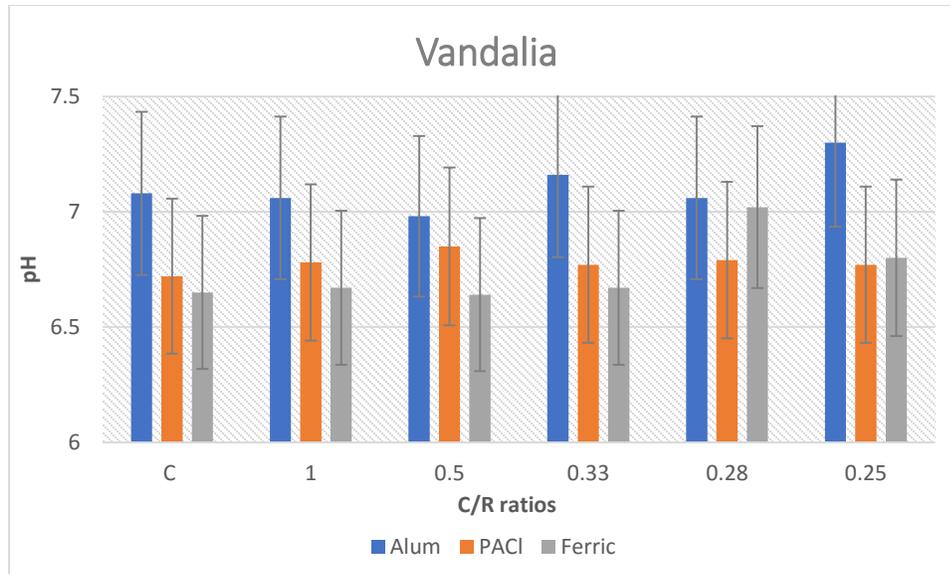


Figure 33: pH stability vs. C/R ratios treatment in Vandalia, LOC 99%.

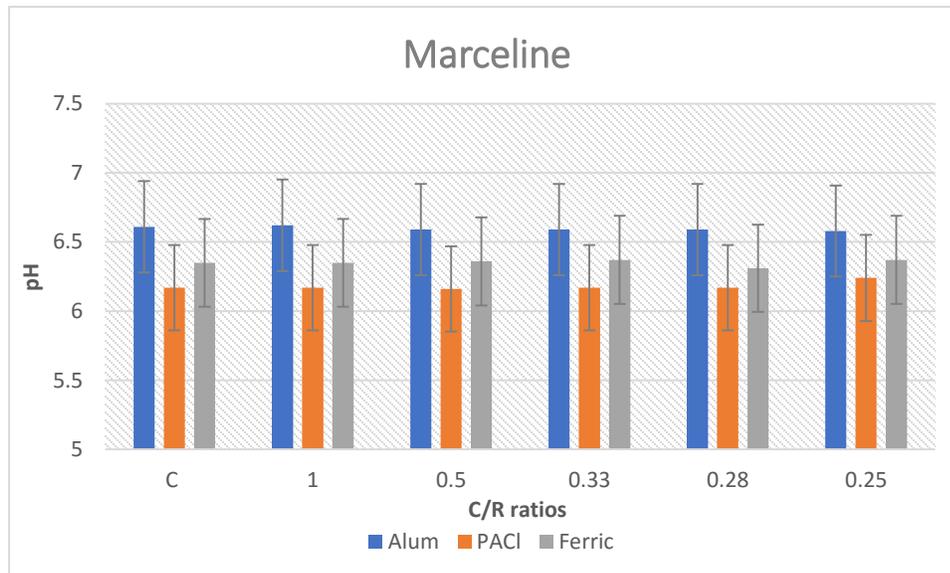


Figure 34: pH stability vs. C/R ratios treatment in Marceline, LOC 95%.

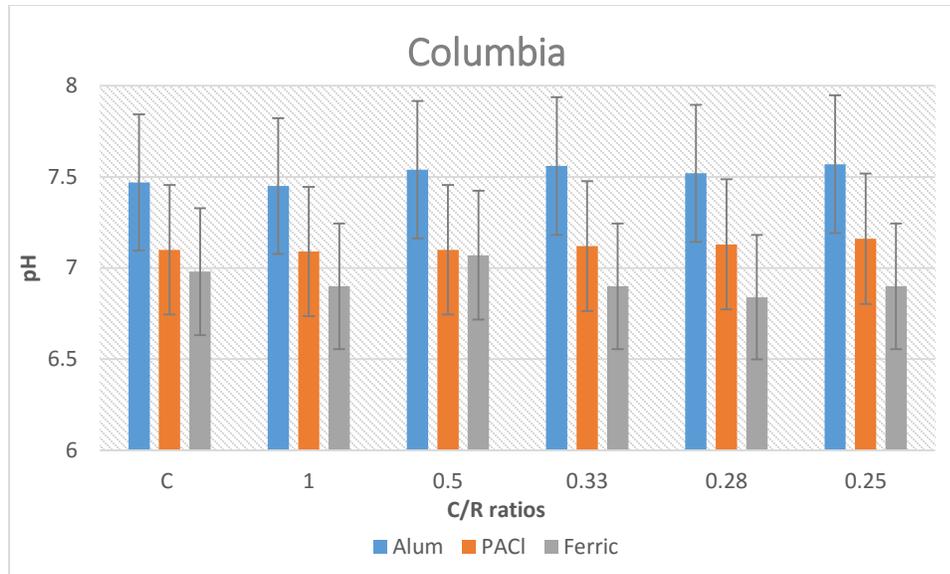


Figure 35: pH stability vs. C/R ratios treatment in Columbia, LOC 95%

Analysis of the data from jar tests shows that, contrary to our assumption that residual solids might change the pH in the effluent water; the proposed treatment with residual solids is proven to cause no significant (± 0.3) changes in pH when compared to the controls (C). Therefore, no additional efforts are required for pH adjustment as a result of addition of residual solids.

6.4.2 Aluminum concentration variations

Aluminum concentrations of raw water differ depending on the source and so are the concentrations in effluent water depending on the treatment used. Using aluminum-based coagulants such as alum and PACI are known to increase the concentrations of aluminum in the effluent water, so this was an area of concern during this study (Clark et al., 1996). New treatment technologies that are aimed at improving water quality with respect to one contaminant or water quality parameter are sometimes known to degrade it with respect to

another. Therefore, aluminum concentrations were tested before and after treating water with residual solids for all three coagulants used (Figure 36-40).

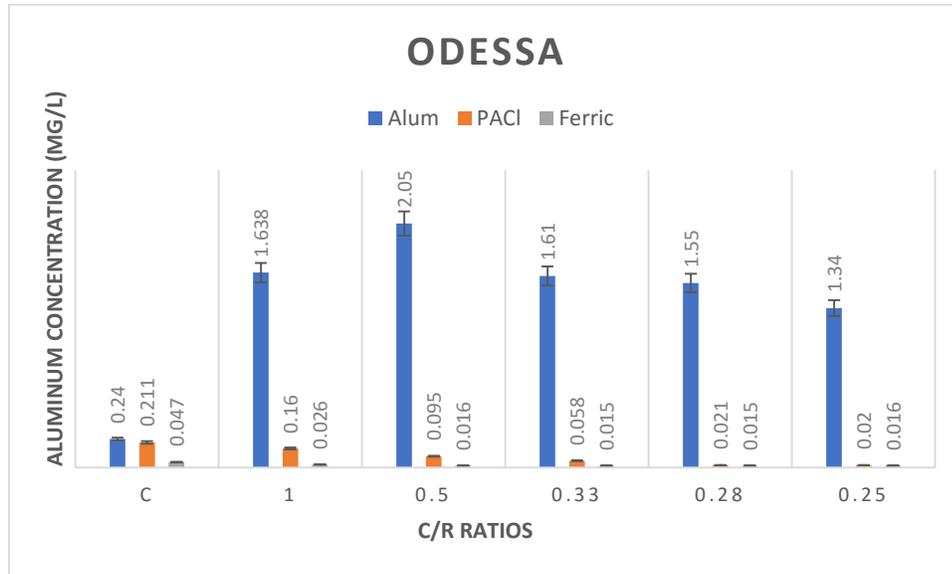


Figure 36: Aluminum concentration changes vs. C/R ratios treatment in Odessa, LOC 90%.

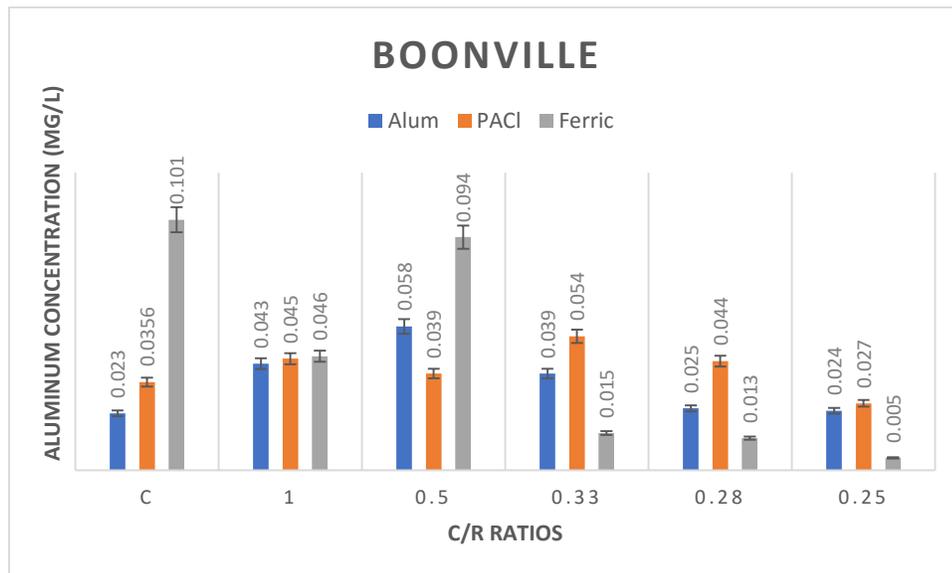


Figure 37: Aluminum concentration changes vs. C/R ratios treatment in Boonville, LOC 90%.

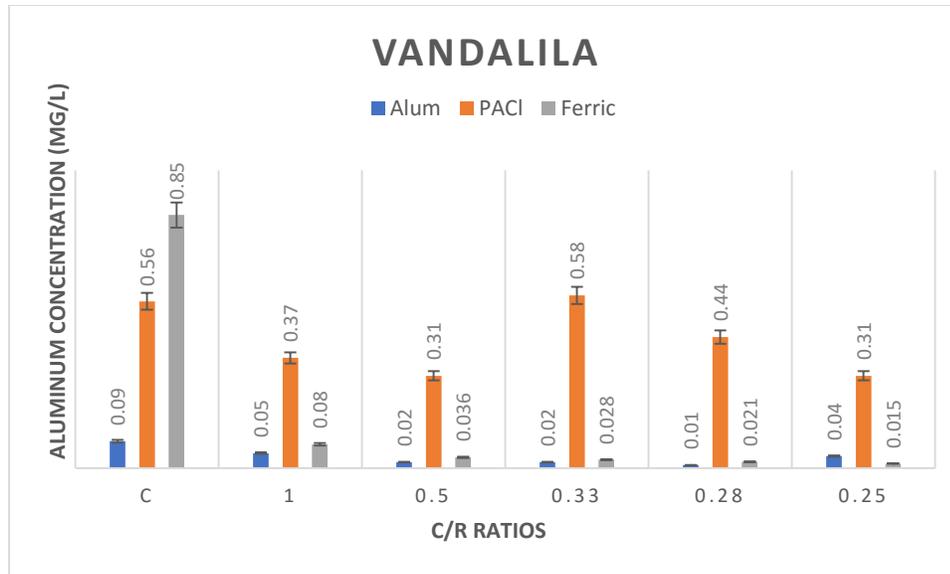


Figure 38: Aluminum concentration changes vs. C/R ratios treatment in Vandalia, LOC 90%.

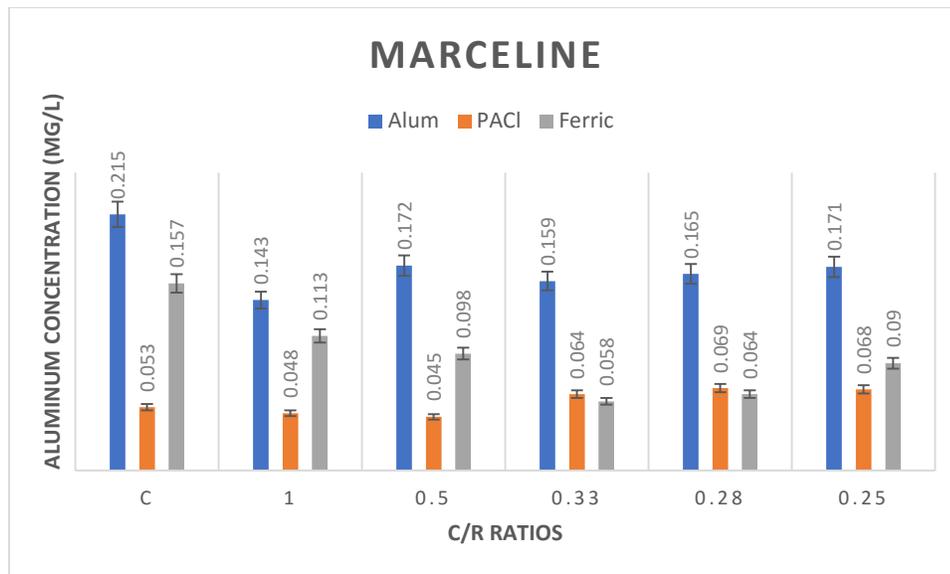


Figure 39: Aluminum concentration changes vs. C/R ratios treatment in Marceline, LOC 95%.

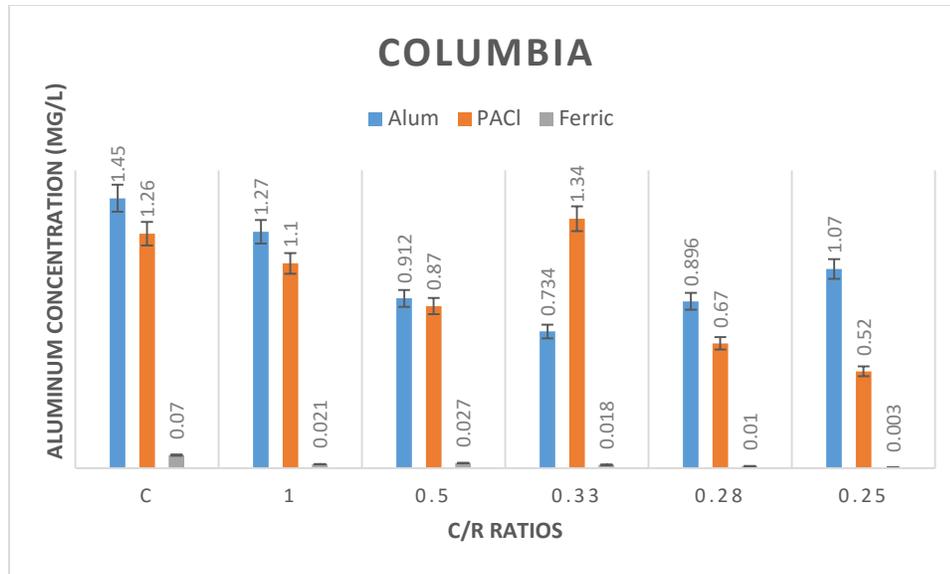


Figure 40: Aluminum concentration changes vs. C/R ratios treatment in Columbia, LOC 99%.

Noteworthy, the residual aluminum in water treated with alum and PACl is higher than that treated by FeCl_3 as well or than in the raw water. Analysis of the data from jar tests shows that, contrary to our assumption, residual solids might increase the aluminum concentrations in the effluent water, the treatment with residual solids is proven to decrease the aluminum residuals notably compared to the controls (solid lines). A (4 – 65) % additional aluminum removal can be achieved with the selected ratios for alum and (6–83) % for PACl relative to the control. Average percent additional aluminum removal for alum and PACl are 54%, and 42% respectively for all selected ratios. Aluminum residual in the control and in the treated water as in the case of FeCl_3 is not significant (+/- 10%) as the coagulant itself is not aluminum based. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to aluminum concentrations.

6.4.3 Iron concentrations variations

Most drinking water utilities have to deal with iron concentrations in their source water on a day-to-day basis. Presence of iron ions in natural and treated waters is known to have adverse effects on disinfection leading to increased formation of DBPs (Moncayo-Lasso, 2012; Liu et al, 2011; Henderson et al, 2001) With increasing drought conditions, changes in the land use, and decreasing dissolved oxygen concentrations in the water sources, iron concentrations in raw water is becoming a bigger problem (Neal et al, 2008). Aeration is typically used to precipitate iron from the raw water entering a treatment plant, but usage of iron-based coagulants to decrease TOC concentrations can sometimes have an adverse effect with respect to iron residual in finished water. The proposed treatment using residual solids raises concerns of increased iron concentrations in the effluent water as one of the coagulants used is FeCl_3 . Therefore, iron concentrations were tested before and after treating water with residual solids for all 3 coagulants used (Figures 41-45).

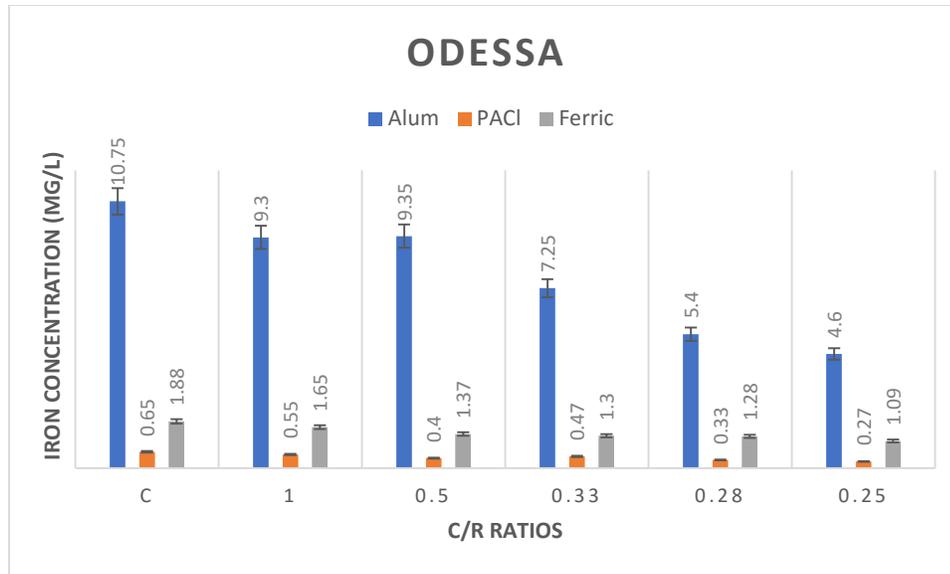


Figure 41: Iron concentration changes vs. C/R ratios treatment in Odessa, LOC 90%.

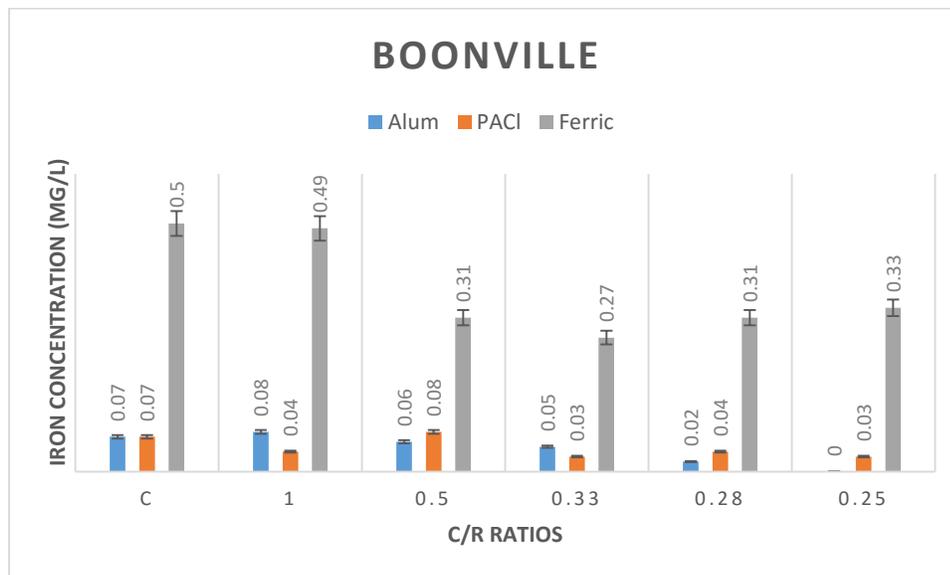


Figure 42: Iron concentration changes vs. C/R ratios treatment in Boonville, LOC 90%.

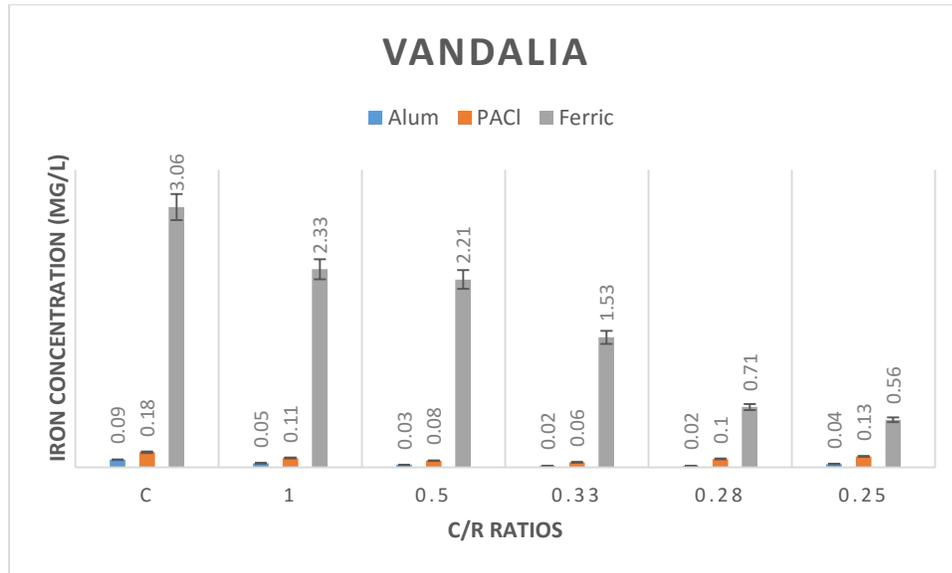


Figure 43: Iron concentration changes vs. C/R ratios treatment in Vandalia, LOC

90%.

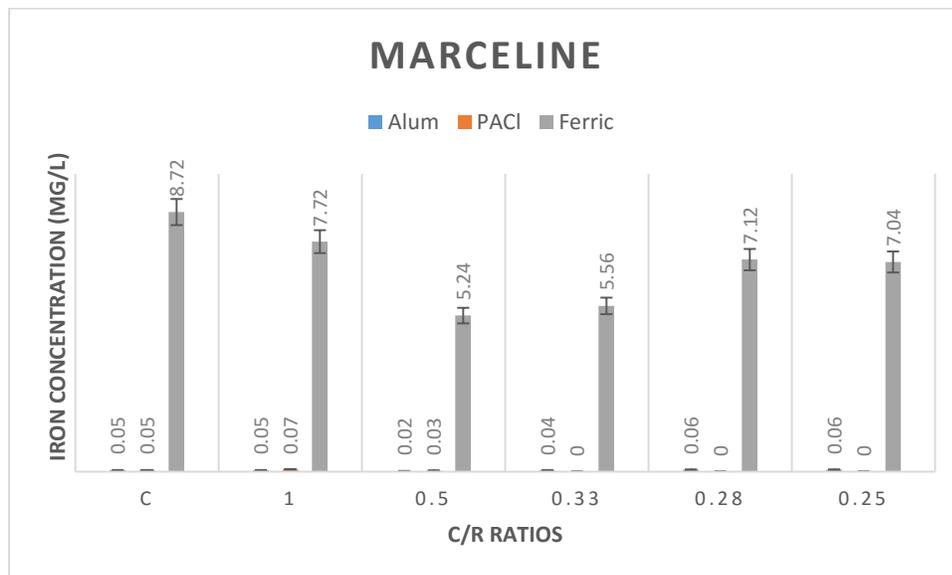


Figure 44: Iron concentration changes vs. C/R ratios treatment in Marceline, LOC

90%.

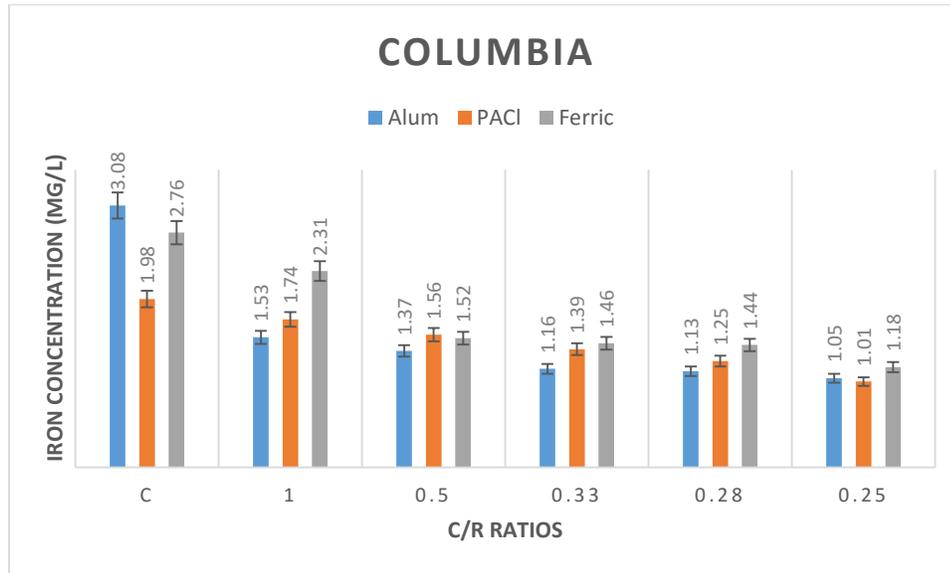


Figure 45: Iron concentration changes vs. C/R ratios treatment in Columbia, LOC

90%

Analysis of the data from jar tests shows that, contrary to our assumption that residual solids might increase the iron concentrations in the effluent water, the treatment with residual solids is proven to decrease the iron residuals considerably compared to the controls (solid lines). A 3 – 84% additional iron removal can be achieved with the selected ratios for alum, a 2 – 59% for PACl and 30 – 83% for FeCl₃ relative to the control. Average percent additional iron removal for alum, PACl and FeCl₃ are 63%, 39% and 68% respectively for all selected ratios. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to iron concentrations.

6.4.4 Chlorine demand vs. C/R ratios vs. Water sources

Chlorine demand (CD) calculations made on the water samples after jar test with different C/R ratios for each city show that there can only one best C/R ratio for each city and coagulant used that corresponds to the lowest chlorine demand value. Lower chlorine demands allows for the utility to use smaller amounts of chlorine and still have a chance to maintain residual in the distribution system over longer periods of time. Chlorine demand of water depends on the kinds of organics present in the water and their reactivity with chlorine. Therefore, it is justified to pick the C/R ratio that corresponds to lowest chlorine demand for each city and coagulant combination for further analysis in terms of chlorine residual, TOC and TTHM (Figures 46-50).

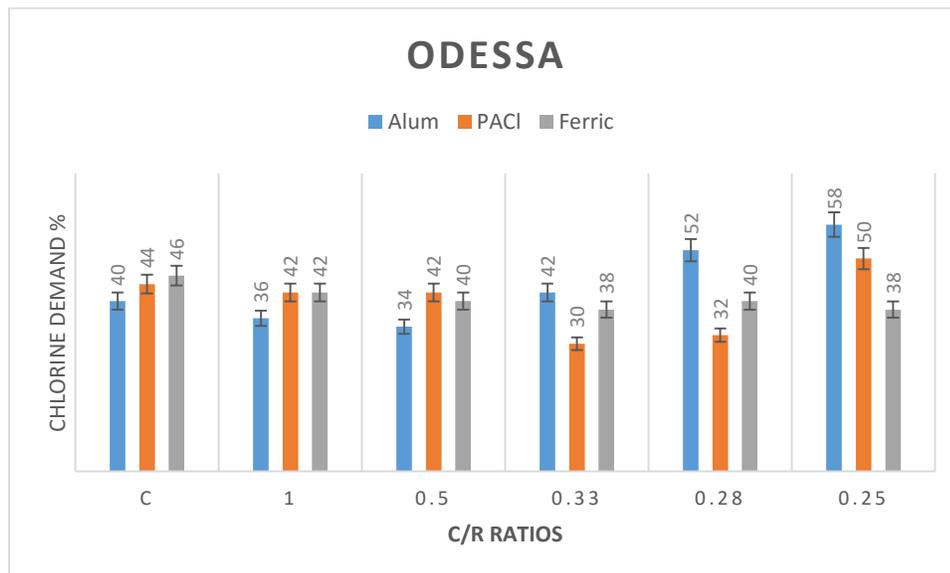


Figure 46: Chlorine Demand % vs. C/R ratios treatment in Odessa, LOC 99%.

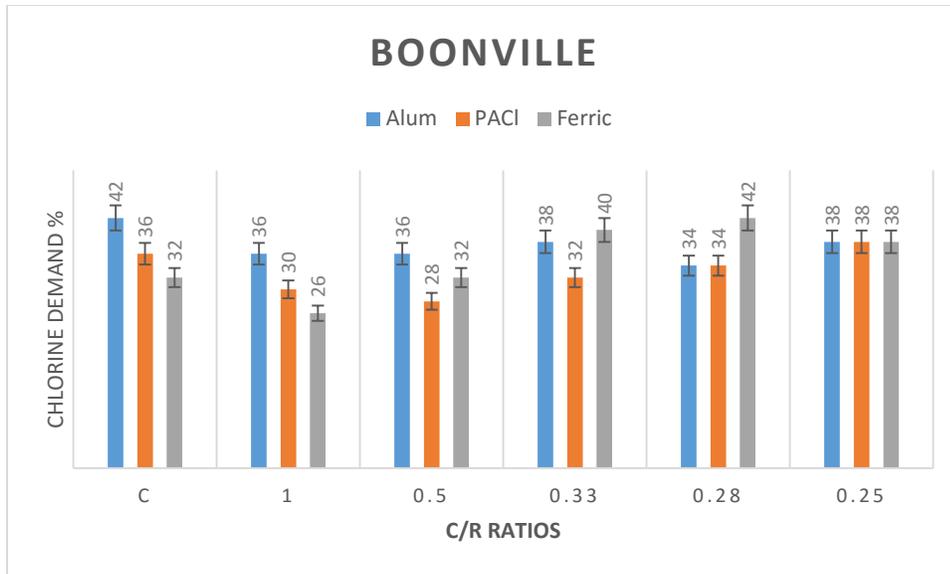


Figure 47: Chlorine Demand % vs. C/R ratios treatment in Boonville, LOC 99%.

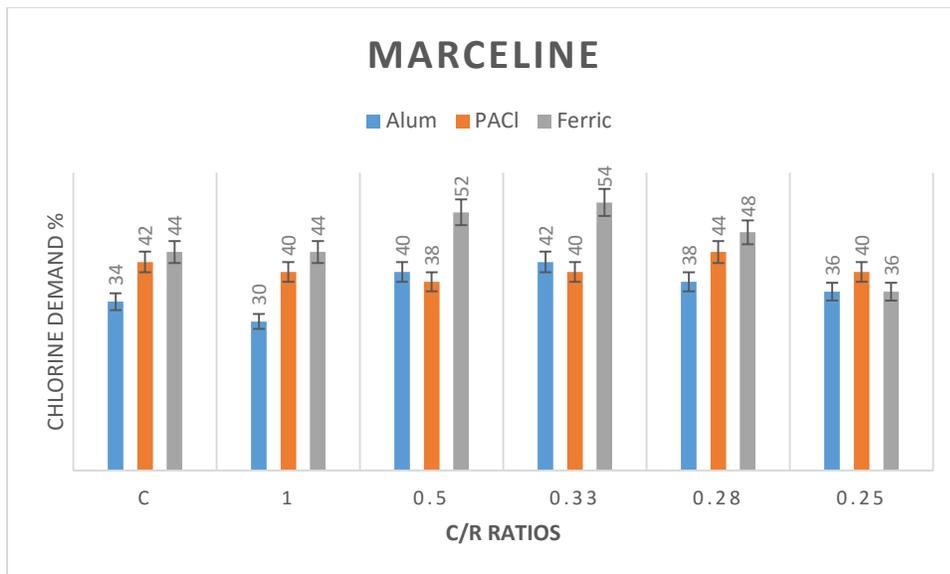


Figure 48: Chlorine Demand % vs. C/R ratios treatment in Marceline, LOC 99%.

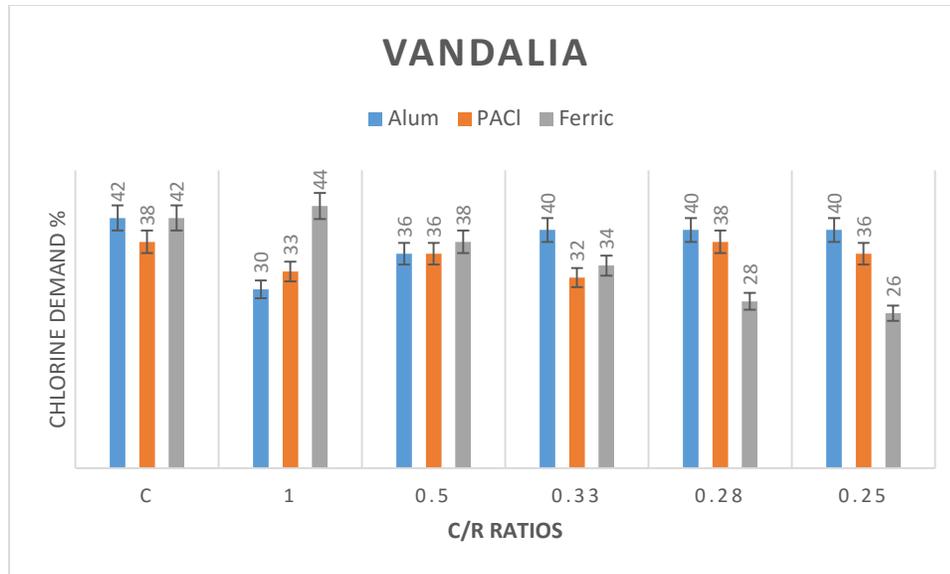


Figure 49: Chlorine Demand % vs. C/R ratios treatment in Vandalia, LOC 99%

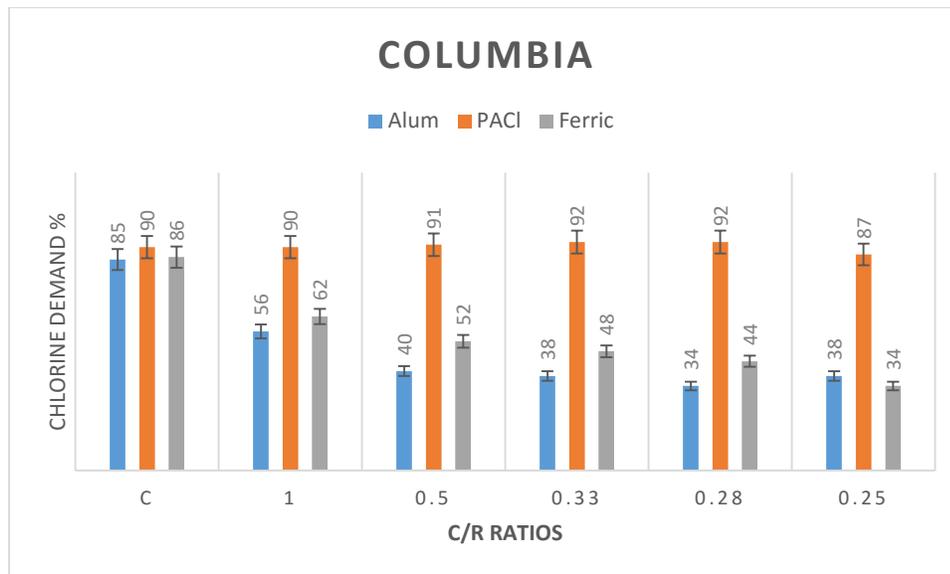


Figure 50: Chlorine Demand % vs. C/R ratios treatment in Odessa, LOC 99%

Noteworthy, the best C/R ratio corresponding to lowest CD is always lower than that of the control. This allows for adequate comparison of treatment effects on water quality using lowest CD of each city and coagulant combination (Table 21).

Table 21: Best CD values for all cities and coagulant combinations, LOC 99%.

Coagulant	Odessa	Boonville	Marceline	Vandalia	Columbia
alum	34	34	30	30	34
PACl	30	28	38	32	87
ferric	38	26	36	26	34

6.4.5 Chlorine residual decay over time vs. Best CD

Water utilities are expected to maintain chlorine residuals in distribution which can often be 2-3 days long. Each system works different with different coagulants and different C/R ratios. For example, it can be seen in Figure 51-53, that Marceline works well with ferric (~0.50 mg/L on day 3) in terms of chlorine residual maintenance over 3 days while it does not do good (<0.10 mg/L on day 3) with alum. On the other hand, Vandalia works really well (>1.0 mg/L on day 3) with alum and not so good (< 0.50 mg/L on day 3) with ferric. Evaluating which source water works well with what coagulant and C/R ratio is the key to improving water quality in terms of chlorine residual decay over time.

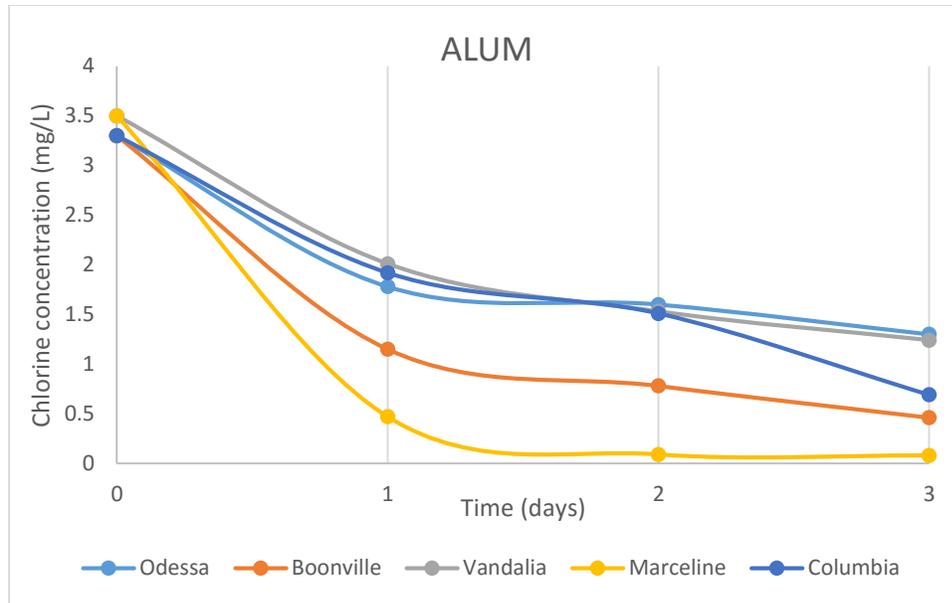


Figure 51: Chlorine residual decay over time at Best C/D % when systems are treated with alum, LOC 95%.

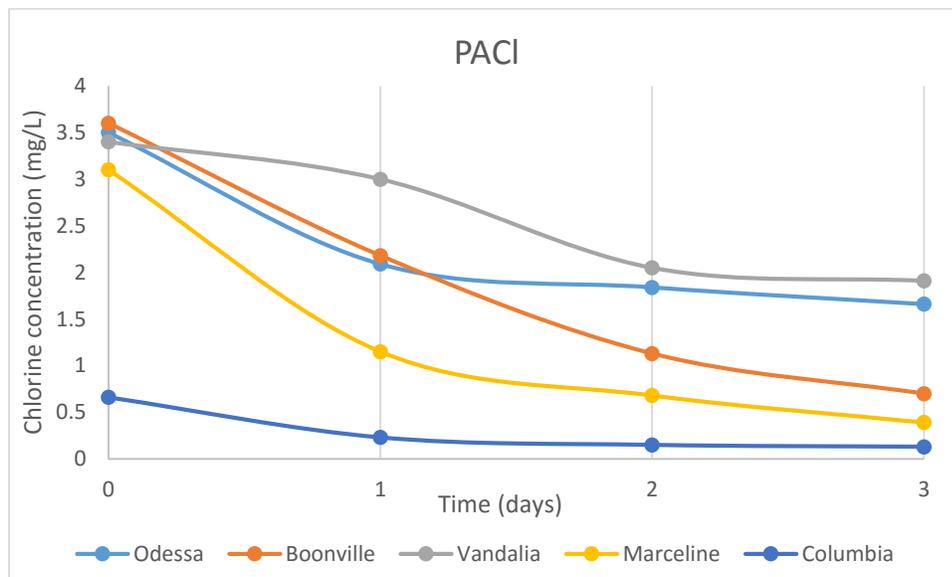


Figure 52: Chlorine residual decay over time at Best C/D % when systems are treated with PACI, LOC 95%.

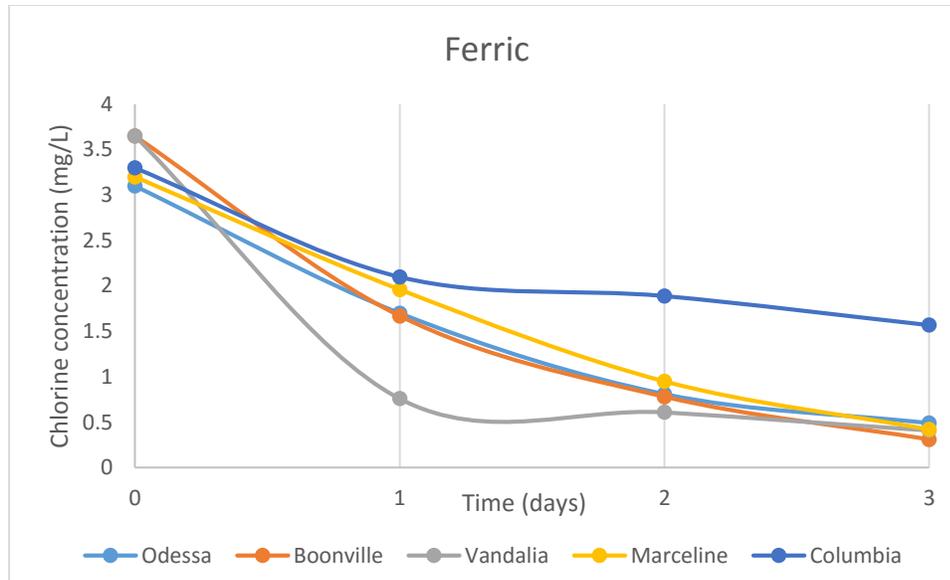


Figure 53: Chlorine residual decay over time at Best C/D % when systems are treated with ferric, LOC 95%.

Above data was analyzed for the best CD values and their corresponding C/R ratios for each city as shown in table 21. One needs to use the relationships between source water, CD value, residual over time and coagulants as shown in figures 51-53 before making any operational decisions to meet Minimum Residual Limit under Safe Drinking Water Act (SDWA).

6.4.6 TTHM formation over time and Chlorine decay over time vs. vs. best CD value and controls.

This analysis was done to interpolate the effect of treatment with residual solids (best CD values) on water quality in terms of TTHM formation and chlorine decay over time while comparing the data against controls (coagulant alone treatment). Three cities representing three different water sources were used for this analysis. Marceline represents lake water

system (Figure 54), Columbia represents ground water system (Figure 55) and Boonville represents surface water system (Figure 56).

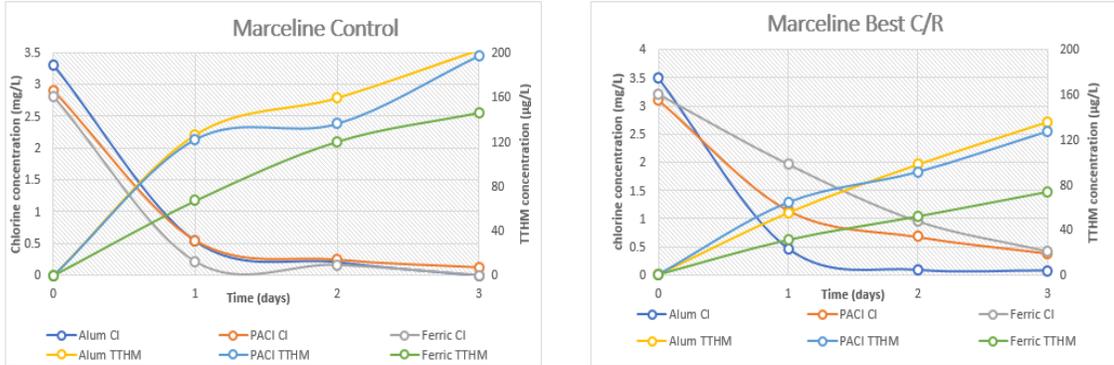


Figure 54: Chlorine residual decay and TTHM formation over time at Best C/D % and control in Marceline, LOC 90%.

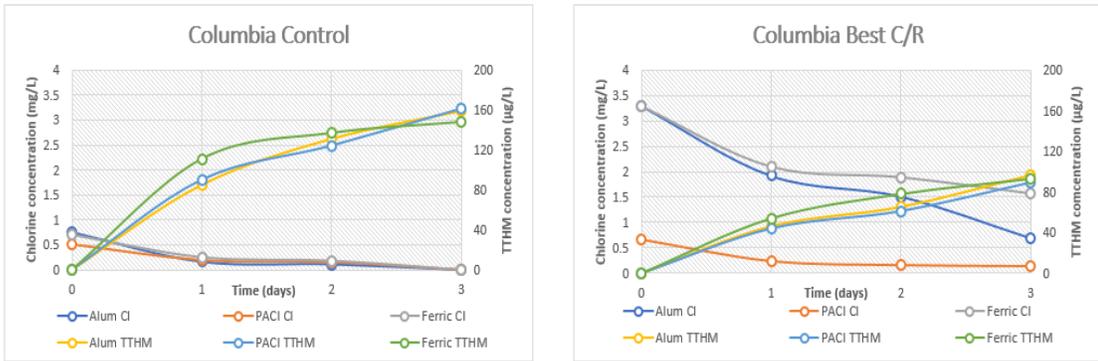


Figure 55: Chlorine residual decay and TTHM formation over time at Best C/D % and control in Columbia, LOC 90%.

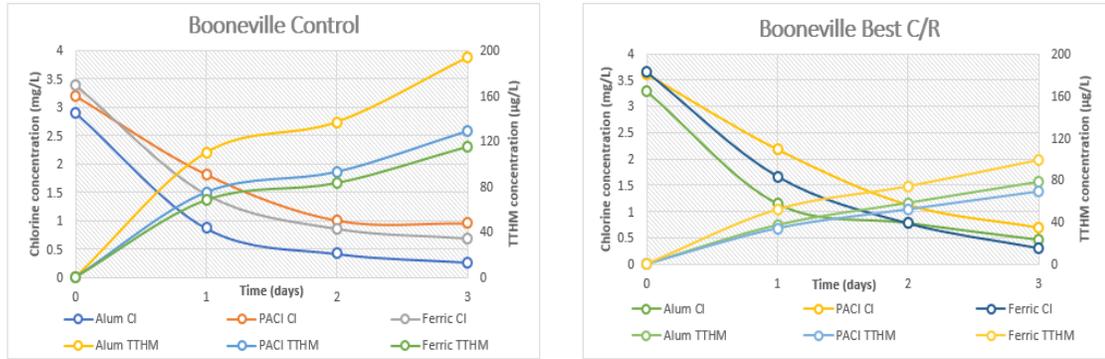


Figure 56: Chlorine residual decay and TTHM formation over time at Best C/D % and control in Boonville, LOC 90%.

Noteworthy, the TTHM formation over time is at least 35% higher on day 0, 39% higher on day 1 and 47% higher on day 3 in all systems when treated only with coagulants versus when treated with residual solids at best C/R ratios irrespective of what coagulant used. It can also be seen that higher (at least 42%) residual concentration can be maintained on day 3 in all water systems when treated with residual solids at best C/R ratios versus when treated with only coagulants. This confirms that treating water with residual solids at best C/R ratios with appropriate coagulant will allow the system to be under compliance for both residual and TTHM regulations with minimal efforts on a water utility's part.

6.4.7 TOC and turbidity vs. Best CD values and Best C/R ratios.

It is established in earlier analysis sections of this chapter that treating different source waters with their respective best C/R ratios (that correspond to lowest/best CD values) will allow for longer maintenance of chlorine residual and also be in compliance with TTHM regulations when compared to treating them with only coagulants. In this section effort is being made to evaluate the relation between TOC, turbidity and best C/R & CD values for three selected water systems. Many small-scale water utilities can't do TOC tests on their

water much less TTHM analysis to determine if an operational change made by them is resulting in expected water quality benefits. They solely rely on turbidity data to interpolate the effect of the operational changes made. As concluded in chapter 4, turbidity can't be used as a surrogate for TOC much less to evaluate impacts on chlorine residual and TTHM formation in the distribution system.

Table 22: Comparison between TOC, CD% and turbidity of three water systems under Best C/R and Control scenarios, LOC 90%.

Alum	Water Systems	Best C/R	CD % Best	CD % control	TOC (mg/L)	TOC Control (mg/L)	Turbidity (NTU)	Turbidity Control (NTU)
	Boonville	3.5	34	42	3.42	5	4.93	4.75
	Marceline	1	30	34	12.4	13.98	3	4
	Columbia	3.5	34	85	3.7	5.3	2.67	3.42
PACI								
	Boonville	2	28	36	3.1	4.8	3.95	3.01
	Marceline	2	38	42	7.74	14.9	3	3
	Columbia	4	87	90	3.5	4.7	2.66	1.47
Ferric								
	Boonville	14	26	32	2.64	3.21	4.02	5.04
	Marceline	4	36	44	3.04	6.7	15	30
	Columbia	4	34	86	3.18	4.9	2.99	3.11

Table 22 shows that TOC change corresponds to the improved water quality benefits from residual solids treatment for all three water systems whereas turbidity doesn't. For example, increase in turbidity doesn't lead to increase in TOC when treated with coagulants and vice versa when treated with residual solids at best C/R ratios. TOC, TTHM and chlorine residual follow the pattern of increasing and decreasing with each other and with

type of treatment (C/R ratios and coagulants) while turbidity doesn't irrespective of the coagulant used.

6.5 Conclusions

Analysis of the data from jar tests shows that, contrary to our assumption that residual solids might change the pH in the effluent water; the proposed treatment with residual solids is proven to cause no significant (± 0.3) changes in pH when compared to the controls (C). Therefore, no additional efforts are required for pH adjustment as a result of addition of residual solids. A (4 – 65) % additional aluminum removals can be achieved with the selected ratios for alum and (6–83) % for PACl relative to the control. Average percent additional aluminum removal for alum and PACl are 54%, and 42% respectively for all selected ratios. Aluminum residual in the control and in the treated water as in the case of FeCl_3 is not significant (± 0.2 mg/L) as the coagulant itself is not aluminum based. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to aluminum concentrations. A 3 – 84% additional iron removal can be achieved with the selected ratios for alum, a 2 – 59% for PACl and 30 – 83% for FeCl_3 relative to the control. Average percent additional iron removal for alum, PACl and FeCl_3 are 63%, 39% and 68% respectively for all selected ratios. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to iron concentrations.

It is justified to pick the C/R ratio that corresponds to lowest chlorine demand for each city and coagulant combination for analysis in terms of chlorine residual, TOC and TTHM. The best C/R ratio corresponding to lowest chlorine demand (CD) is always lower than

that of the control. Evaluating which source water works well with what coagulant and C/R ratio is the key to improving water quality in terms of chlorine residual decay over time. The TTHM formation over time is at least 35% higher on day 0, 39% higher on day 1 and 47% higher on day 3 in all systems when treated only with coagulants versus when treated with residual solids at best C/R ratios irrespective of what coagulant used. It can also be seen that higher (at least 42%) residual concentration can be maintained on day 3 in all water systems when treated with residual solids at best C/R ratios versus when treated with only coagulants. This confirms that treating water with residual solids at best C/R ratios with appropriate coagulant will allow the system to be under compliance for both residual and TTHM regulations with minimal efforts on a water utility's part.

Increase in turbidity doesn't always result in increase in TOC when treated with coagulants and vice versa when treated with residual solids at best C/R ratios. TOC, TTHM and chlorine residual follow the pattern of increasing and decreasing with each other and with type of treatment (C/R ratios and coagulants) while turbidity doesn't irrespective of the coagulant used.

6.6 Acknowledgments

Funding for this project was provided by the U.S. Environmental Protection Agency (EPA) through their Science to Achieve Results grant # 83517301 and the Missouri Department of Natural Resources (MDNR). Analytical and technical support was provided by Missouri Water Resource Research Center (MWRRC).

7.0 Conclusions

- Enhanced TOC removal can be achieved when $C/R < 1$.
- The percent additional TOC removal for alum, PACl and $FeCl_3$ use in surface (river) water is 16.6 – 22.5%, 27.2 – 36.2% and 0.5 – 24.4%, respectively, and use in alluvial ground water is 14.1 – 38.2%, 21.2 – 32.1% and 6.3 – 42.6%, respectively.
- A slight increase in TOC is observed when $C/R > 1$.
- Enhanced aluminum and iron removal can also be achieved with this proposed treatment. The percent additional removal of aluminum residual for alum and PACl addition is 13.2 – 65.6% and 13.6 – 83.14%, respectively, whereas percent of additional iron residual removal for alum, PACl and $FeCl_3$ is 67.2 – 98%, 12.91 – 64.9% and 35.9 – 80.2%, respectively.
- It is statistically shown here that turbidity can't be used as a surrogate for TOC when making decisions about changes in the treatment process in both surface and ground water systems.
- No significant changes in pH were observed as a result of the proposed treatment.
- The percent additional TOC removal depends on the raw water quality and its changes, C/R ratios used, and type of coagulant needed. Finding a right match of coagulant and C/R ratio for a certain kind of raw water coming in requires rigorous jar testing and data analysis.
- Treatment using residual solids is proven to be a simple, non-invasive and cost-effective technology that will effectively lower TOC concentrations by having the water utilities reuse their treatment residual solids.

- The proposed treatment also has a potential to decrease the amount of coagulants needed for water treatment thereby reducing the cost of treatment process.
- The data analysis proves that wall effects due to different pipe materials lead to considerable differences in chlorine residual decay and TTHM formation over time. This difference will dictate whether or not an operational strategy is appropriate for the system at hand.
- On an average, just the choice of pipe materials such as PVC and iron can account for as much as 36 % difference in TTHM formation and 60% difference in chlorine residual decay over time irrespective of the prediction model and operational strategy used.
- Operators with limited resources will benefit vastly from just using MS-SDS with their pipe and treated water to understand effect of a particular treatment change or operational change on distributed water.
- Data proves that under normal operational conditions, it is easier to maintain residual in PVC pipe distribution systems when compared to iron pipe distribution systems meanwhile, the control of TTHM formation is much harder in PVC systems.
- Based on the data analysis, it can be concluded that, booster systems are optimal solutions for residual maintenance and TTHM control in all systems, more so in PVC.
- In case of iron pipe systems, the wall demand for chlorine dominates everything else leading to increased loss of residual and lower TTHMs formation over time irrespective of operational strategy in use.

- The data analysis also shows that assuming that wall effects are negligible while calibrating water quality models will lead to incorrect predictions of water quality parameter concentrations over time.
- Given that the results are only as good as the prediction model used and the model is only as good as the assumptions made, care needs to be taken while designing and using them for decisions making.
- Analysis of the data from jar tests shows that, contrary to our assumption that residual solids might change the pH in the effluent water; the proposed treatment with residual solids is proven to cause no significant (± 0.3) changes in pH when compared to the controls (C). Therefore, no additional efforts are required for pH adjustment as a result of addition of residual solids.
- A (4 – 65) % additional aluminum removal can be achieved with the selected ratios for alum and (6–83) % for PACl relative to the control. Average percent additional aluminum removal for alum and PACl are 54%, and 42% respectively for all selected ratios. Aluminum residual in the control and in the treated water as in the case of FeCl_3 is not significant (± 0.2 mg/L) as the coagulant itself is not aluminum based. It can be concluded that addition of residual solids not only improve the finished water quality with respect to TOC concentration, but also with respect to aluminum concentrations.
- A 3 – 84% additional iron removal can be achieved with the selected ratios for alum, a 2 – 59% for PACl and 30 – 83% for FeCl_3 relative to the control. Average percent additional iron removal for alum, PACl and FeCl_3 are 63%, 39% and 68% respectively for all selected ratios. It can be concluded that addition of residual solids not only

improve the finished water quality with respect to TOC concentration, but also with respect to iron concentrations.

- It is justified to pick the C/R ratio that corresponds to lowest chlorine demand for each city and coagulant combination for analysis in terms of chlorine residual, TOC and TTHM.
- The best C/R ratio corresponding to lowest chlorine demand (CD) is always lower than that of the control. Evaluating which source water works well with what coagulant and C/R ratio is the key to improving water quality in terms of chlorine residual decay over time.
- The TTHM formation over time is at least 35% higher on day 0, 39% higher on day 1 and 47% higher on day 3 in all systems when treated only with coagulants versus when treated with residual solids at best C/R ratios irrespective of what coagulant used. It can also be seen that higher (at least 42%) residual concentration can be maintained on day 3 in all water systems when treated with residual solids at best C/R ratios versus when treated with only coagulants. This confirms that treating water with residual solids at best C/R ratios with appropriate coagulant will allow the system to be under compliance for both residual and TTHM regulations with minimal efforts on a water utility's part.
- Increase in turbidity doesn't always result in increase in TOC when treated with coagulants and vice versa when treated with residual solids at best C/R ratios. TOC, TTHM and chlorine residual follow the pattern of increasing and decreasing with each other and with type of treatment (C/R ratios and coagulants) while turbidity doesn't irrespective of the coagulant used.

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Appendices A: TTHM Analysis by Purge and Trap Chromatographic/Mass Spectrometric Method

Standard Method for the Examination of Water and Wastewater 6232C and US EPA Method 524.2

Sampling and storage

Ammonium chloride, a dechlorination reagent, is added to the sample vial to yield a concentration of 100 mg/L ammonium chloride in the finished sample. At sampling, the sample vial is filled to just overflowing, but without flushing out the ammonium chloride. No air bubbles should pass through the sample as the vial is filled or be trapped in the sample when the vial is sealed. Samples are stored at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

Apparatus

1. *Purge and trap system:* The purge and trap system consists of purging device, trap, and desorber; a Tekmar 3000 purge and trap concentrator is used in the laboratory.
2. *Gas chromatograph:* Varian 3800 gas chromatograph.
3. *Detector:* Varian Saturn GC/MS 2000.
4. *Sample vials:* 40 mL clear glass EPA vials, fitted with Teflon-lined septa and screw caps (Fisher 03-339-14A).
5. *Syringes:* 10 µL (Hamilton 80300), 25 µL (Hamilton 8040), 50 µL (Hamilton 80500), 100 µL (Hamilton 80600), 250 µL (Hamilton 80700), 500 µL (Hamilton 80800), 1000 µL (Hamilton 81130).

6. *Balance*: analytical, capable of weighting to 0.0001g.
7. *Autosampler vials for preparation of standards*: 2.0 mL autosampler vials with open screw top caps and Teflon-faced septa (Supelco 2-7078)

Reagents and standards

1. *Methanol (CH₃OH)*: High purity liquid demonstrated to be free of analytes (Fisher A457-4).
2. *THM Standard Solution (TSS)*: 2000 µg/mL of each THM species (CHCl₃, CHCl₂Br, CHClBr₂, CHBr₃) in methanol (Supelco 48140-U).
3. *Primary Dilution THM Standard (PDTS)*: 20 µg/mL THMs in methanol. Inject 10 µL 2000 µg/mL (TSS) and 990 µL methanol into a 2.0 mL autosampler vial.
4. *QC Check Standard*: Environmental Resources Associates 702
5. *Ammonium chloride*: granular (Fisher A649-3).
6. *Ammonium chloride solution*: 88.0 g/L. Dissolve 22.0 g ammonium chloride in 250 mL deionized ultra-filtered (DIUF) water.
7. *DIUF water*: 20 L pack (Fisher W2-20).

Preparation of standards

A minimum of five calibration standards is required. 40-mL sample vials are filled with DIUF water, 50 µL of 88 g/L ammonium chloride is injected, and vials are capped headspace-free. For a typical calibration curve over the range 0-100 µg/L for each THM species, 10 µL, 20 µL, 50 µL, 100 µL, and 200 µL of 20 µg/mL PDTS is injected into each

of the five sample vials to yield 5 µg/L, 10 µg/L, 25 µg/L, 50 µg/L, and 100 µg/L THM calibration standards, respectively; vials are then inverted slowly to mix.

Table A.1 Purge and Trap Method

Dry purge time: 0 minutes	Purge time: 11 minutes
Purge ready temperature: 35°C	Valve temperature: 150°C
Purge flow: 30-40 mL/min	Transfer line temperature: 170°C
Mount: 40°C	Desorb preheat: 220°C
Desorb: 2 minutes at 225°C	Bake: 10 minutes at 230°C

Table A.2 Ion Trap Parameters

Prescan ionization time: 100 microseconds	Target TIC: 18,000 counts
Background mass: 33m/z	RF dump value: 650 m/z

Table A.3 Segment breaks, turn factors are as follows

Segment	Mass Range	Ion Storage Level	Ion Time Factor
1	10 - 70	32 m/z	120%
2	71-78	32 m/z	70%
3	79-150	32 m/z	100%
4	151-650	32 m/z	70%

GC Method

A DB-5MS column (J&W Scientific) with an I.D. 0.25 mm and length of 60m is used; the carrier gas is helium flowing at 1mL/min at 35°C. Injector split ratio is 10. Column oven temperature and injector temperature are listed in following table.

Table A.4: Column Oven and Injector Temperatures

	Temp(°C)	Rate(°C/min)	Hold(min)	Total(m in)
Column oven temperature	35		2.00	2.00
	50	10.0	1.00	4.50
	200	20.0	6.00	18.00
Injector temperature	125		18	18

Table A.5: Typical Column Retention Times of THM Species

Compounds	Retention Time (min)
Chloroform	8.715
Bromodichloromethane	10.420
Dibromochloromethane	11.860
Bromoform	13.150

Calculations

Calibration standards are analyzed with each sample set, and values are recorded by the GC/MS software for use in determining the relationship between peak area and concentration. Calculations of concentrations based on the peak area are performed automatically by the software based on the calibration curve data set selected. A representative set of calibration curves is given in Figure A.1.

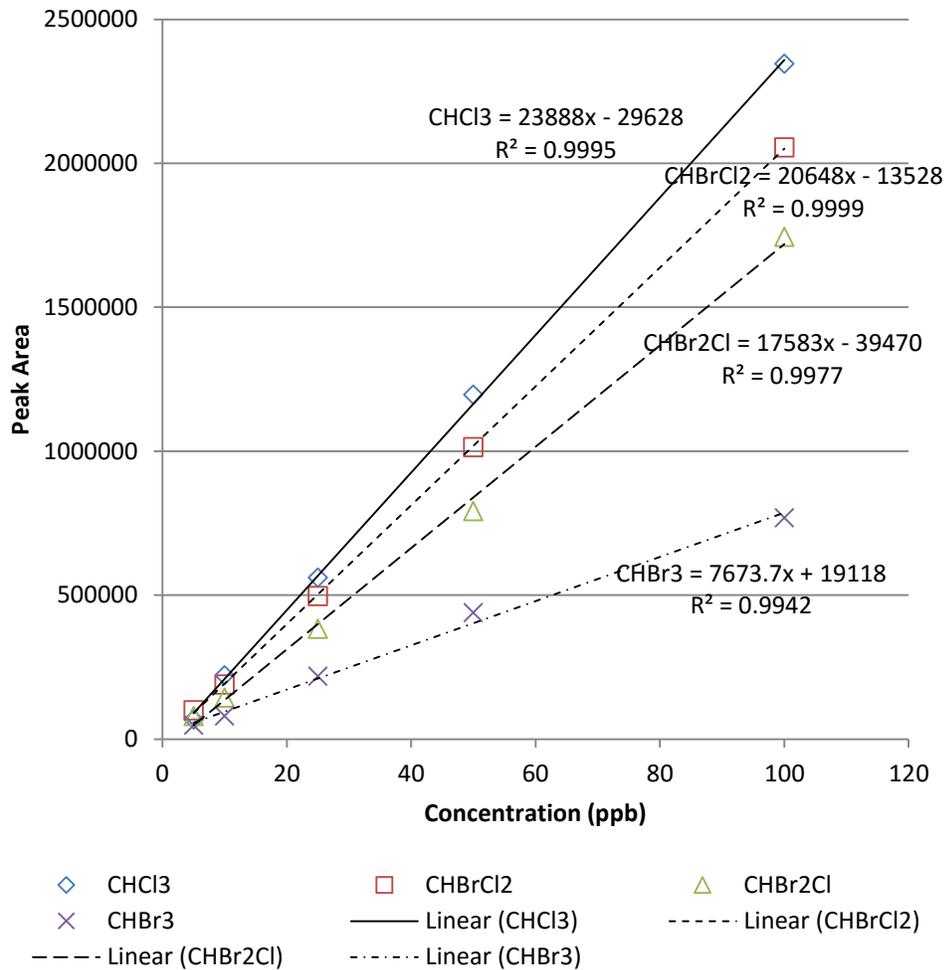


Figure A.1: Example Calibration Curves for TTHM Species

Quality Control

Use 50 µg/L standard as a reference standard. Analyze reference standard as though it was a sample. Results are compared with known concentration of the reference standard (50 µg/L); if the measured concentration falls within the range of 45 to 55 µg/L (± 10%), the result is acceptable.

The QC sample is prepared as directed, then prepared and analyzed as though it were a regular sample. Acceptable ranges for analytical results are given, and sample results are accepted if values fall within these ranges and other QC requirements discussed are also met.

VITA

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