REDUCING TRIHALOMETHANE CONCENTRATIONS BY USING CHLORAMINES AS A DISINFECTANT

by

Elizabeth Anne Farren

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Dr. Jeanine D. Plummer, Major Advisor

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Dr. Frederick L. Hart, Head of Department

Abstract

Disinfectants such as chlorine are used in drinking water treatment to protect the public health from pathogenic microorganisms. However, disinfectants also react with humic material present in raw water sources and produce by-products, such as trihalomethanes. Total trihalomethanes (TTHMs) include four compounds: chloroform, bromodichloromethane, dibromochloromethane and bromoform. TTHMs are carcinogenic and have been found to cause adverse pregnancy outcomes. Therefore, the United States Environmental Protection Agency (U.S. EPA) has set the maximum contaminant limit for TTHMs at 80 μg/L. Additional regulations require reliable drinking water disinfection for resistant pathogens and treatment plants must simultaneously control TTHMs and achieve proper disinfection.

Research has shown that THM formation depends on several factors. THM concentrations increase with increasing residence time, increased temperature and increased pH. The disinfectant type and concentration is also significant: THM concentrations can be minimized by using lower disinfectant doses or alternative disinfectants to chlorine such as chloramines. Chloramines are formed by the addition of both chlorine and ammonia.

The Worcester Water Filtration Plant in Holden, MA currently uses both ozone and chlorine for primary disinfection. Chlorine is also used for secondary disinfection. This study analyzed the effect of using chloramines versus free chlorine on TTHM production at the plant. Water samples were collected from the plant, dosed with chlorine/chloramines and stored for their designated residence times. The residual chlorine was then quenched with sodium thiosulfate and the samples were analyzed for

TTHM concentration using a GC-MS. Experiments were conducted in December of 2001, April of 2002 and February of 2003, and examined varying residence times, pH conditions, temperatures, chlorine to nitrogen ratios and free chlorine reaction periods.

The study found that as the pH increased the TTHMs increased. For the free chlorine samples, as residence time increased, the TTHMs increased. For the chloramination samples it was found that most of the TTHMs were formed in the first six hour reaction period with free chlorine before ammonia was added. Therefore, reducing this free chlorine contact period to 0 or 3 hours would reduce THM formation further. Chlorine to nitrogen ratios between 3:1 and 7:1 were all effective at reducing THM concentrations. Using chloramination at a 3:1 ratio (with a 6 hour free chlorine time) reduced THM formation by approximately 38% for a 54 hour residence time compared to using free chlorine.

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1.0 Introduction

Water treatment began in the United States in the early 20th century. At this time, treatment typically consisted of chlorination and sand filtration. Disinfection with chlorine helped to reduce waterborne diseases significantly by inactivating harmful microorganisms and was one of the biggest advancements in disease control in the United States. Free chlorine is the most commonly used disinfectant for drinking water treatment systems. Although water disinfection is very important to the health of the public, the disinfectant itself reacts with humic substances in the water to create harmful disinfection by–products (DBPs). The production of DBPs was not discovered until the 1970's when samples were tested for the presence of certain halogenated compounds. The results of these tests found that nearly all of the United States drinking waters contained DBPs.

Different disinfectants produce varying types of and amounts of DBPs. For instance, ozone can produce bromate, formaldehyde, halopropanones, and chloral hydrates. The concentration of DBPs formed by ozonation depends on the raw water characteristics. DBPs resulting from ozone disinfection are often not a problem with regard to regulations because the U.S. EPA has not set limits on many of these types of DBPs. Free chlorine, on the other hand, produces DBPs such as trihalomethanes (TTHMs) and haloacetic acids (HAAs). The concentration of DBPs formed with free chlorine depends on the raw water content but generally free chlorine produces the largest quantities of DBPs when compared to other disinfectants.

Numerous studies have been conducted in the past three decades on the harmful effects of DBPs in drinking water supplies. Results have shown that DBPs are

carcinogenic and can cause adverse pregnancy outcomes. Therefore, the U.S. EPA has regulated the allowable concentrations of certain DBPs in finished drinking water. The first regulations were promulgated in 1979 and set a maximum contaminant limit (MCL) of 100 μg/L for TTHMs in a drinking water. TTHMs were the only known DBPs at that time, so they were the only compounds regulated. In the 1980's, HAAs and other potentially harmful DBPs were also found to be present in drinking waters.

For most of the last decade the U.S. EPA has been discussing enacting stricter regulations. In 1998, the U.S. EPA promulgated the Stage I Disinfectants and Disinfection By-Product (Stage I D/DBP) Rule. This rule set a new MCL for TTHMs at 80 μg/L, a MCL for HAA_5 at 60 μg/L, and limited chlorite and bromate concentrations at 1,000 μg/L, and 10 μg/L, respectively. The Stage II D/DBP Rule, which may have stricter limits than the Stage I Rule, is expected in 2003. In addition to these new stringent DBP regulations, the U.S. EPA has also proposed regulations requiring water treatment systems to provide stronger disinfection to their drinking water supply. Simultaneous compliance with both the DBP regulations and disinfection regulations is challenging for many water treatment systems.

The Worcester Water Filtration Plant in Holden, MA was completed in 1997. The plant uses pre – ozonation, coagulation, flocculation, filtration and chlorination to treat their drinking water. Disinfection with ozone in this treatment plant does not produce significant concentrations of DBPs. The largest concentrations of DBPs in the Worcester treatment facility are formed from chlorination. Since the plane came on-line, both DBP and disinfection regulations have been met, but new strict regulations may make it difficult for the treatment plant to comply with both requirements. The U.S. EPA

has suggested several options for reducing DBPs, one of which is using an alternative disinfectant other than free chlorine. Chloramines have been shown to produce lower concentrations of DBPs than free chlorine, and could be implemented at the treatment plant by adding ammonia with the existing disinfectant, chlorine.

The purpose of this research was to determine the effect of chloramination versus free chlorine on trihalomethane production using the Worcester Water Filtration Plant's water supply. Several variables were tested in the experiments to find the optimal chloramination conditions for reducing DBP formation. pH was varied from 6 and 10 and residence times were varied between 3 hours and 54 hours. The free chlorine period prior to ammonia addition was also varied: six hour, three hour and zero hour times were used. Lastly, chlorine to ammonia ratios between 2:1 and 7:1 were evaluated.

The next chapter of this report contains information about disinfection alternatives, background about disinfection by-products and factors affecting trihalomethane formation. Additional topics covered include health effects of DBPs, U.S. regulations, ways to decrease disinfection by-products and a description of the Worcester Water Filtration Plant. The third chapter explains the procedures for all of the experiments that were performed for this study. The fourth chapter presents the results from the experiments and the final chapter discusses the importance and significance of the results as well as recommendations for future work.

2.0 Literature Review

Water treatment is an evolving technology. Before the 1900s, drinking water in the United States was not regularly disinfected. It was not widely understood that water could transport diseases, and diseases like typhoid and cholera were once very common. In the early 20th century, disinfection of water supplies began in several U.S. cities. A recent report confirms that disinfection of water has made a significant improvement in human health during the last century (Calderon, 2000). Water disinfection, among other sanitation techniques, has almost eradicated many waterborne diseases in the U.S.

When the United States government regulated water treatment in 1979 with the National Primary Drinking Water Regulations (U.S. EPA, 1979), drinking water was only required to be disinfected once. This process was called primary disinfection. As water treatment technology improved, it became evident that secondary disinfection was required to provide safe drinking water for the general public. Secondary disinfection was intended to keep the water microbiologically safe as it traveled through the distribution pipes by providing a disinfectant residual to the water supply.

It was not until the 1970s that scientists discovered that by-products were created while disinfecting water. Also at this time period, the negative effects of disinfection by-products (DBPs) were first discovered. The U.S. EPA responded to these findings by setting limits for the allowable concentrations of DBPs in drinking water. Water treatment plants today have to balance providing adequate disinfection with meeting allowable concentration limits of DBPs.

The rest of this chapter provides a background of disinfectants and disinfection by-products. Different types of disinfection as well as the history of DBPs are explained.

Regulations regarding DBPs and disinfection and a description of the Worcester Water Filtration Plant are provided. The factors that affect DBP formation are described in detail. The health risks associated with TTHMs and ways to control DBPs are discussed.

2.1 Types of Disinfectants

The following sections provide historical background and chemical information for several disinfectants used in the U.S. Chlorine, chloramines, chlorine dioxide, ozone and ultraviolet disinfection are discussed.

2.1.1 Chlorine Disinfection

In 1881, a German named Koch showed the role bacteria play in waterborne diseases. Koch demonstrated that minute quantities of chlorine could inactivate harmful waterborne pathogens. The introduction of chlorination resulted in significant decreases in worldwide waterborne diseases, such as typhoid (Haas and Aturaliye, 1999). The use of chlorination for the disinfection of drinking water first occurred in the United States in Louisville, Kentucky in 1896. The first time a continuous supply of chlorine was used as a disinfectant for drinking water was in 1902, in Middlekerke, Belgium. In 1905, chlorination was used in London, England to disinfect the drinking water supply. The first continuous practice of chlorination in drinking water in the U.S. began in 1908 and was used on the Boonton Reservoir, the water supply for Jersey City, New Jersey. By World War II, disinfection with chlorine had become a treatment that was standard worldwide (Jacangelo and Trussell, 2002).

When chlorine reacts with water it forms hypochlorous acid (reaction 1). The hypochlorous acid can then undergo acid-base reactions to form hypochlorite ion

(reaction 2). The distribution of chlorine into HOCl and OCl^- is pH dependent. HOCl is a stronger disinfectant than OCl^-, and therefore a lower pH is preferred for disinfection with chlorine. The chlorine (HOCl or OCl^-) attacks bacterial cells and the protein coat of viruses, effectively killing both bacteria and viruses. Chlorination, while highly effective at inactivating pathogens, produces several potentially harmful by-products.

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \qquad \textbf{Reaction 1}$$

$$HOCl \Leftrightarrow OCl^- + H^+ \qquad \textbf{Reaction 2}$$

2.1.2 Chloramine Disinfection

Chloramines are an alternative disinfectant to chlorine. Chloramination does not cause the taste and odor problems often experienced when disinfecting with chlorine. The main disadvantage to chloramination is that it requires a very large CT (concentration * time) value to provide effective disinfection. A water treatment plant in Denver, Colorado was the first in the United States to use chloramination in 1908 (although it did not provide continuous use of chloramination). The first continuous use of chloramination in the United States occurred at the Greenville, Tennessee water treatment plant in 1926. Disinfection by chloramines was used often between 1929 and 1939; however, during World War II there was a lack of ammonia so treatment plants stopped disinfecting with chloramines.

In the first half of the 20th century, chloramines were used to prevent unpleasant tastes and odors when disinfecting. By the mid 1930s, chloramines were discovered to be more stable that free chlorine in the distribution system. As a result of this discovery, chloramines were often used to limit bacterial regrowth. Chloramines have grown in

popularity since the 1980s because chloramines do not produce as high concentrations of DBPs as free chlorine.

Chloramination involves the addition of chlorine and ammonia to the water source. When chlorine reacts with ammonia, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) are formed. Reactions 3, 4 and 5 show how these chemicals are formed.

$$NH_4^+ + HOCl \Leftrightarrow NH_2Cl + H_2O + H^+ \qquad \textbf{Reaction 3}$$

$$NH_2Cl + HOCl \Leftrightarrow NHCl_2 + H_2O \qquad \textbf{Reaction 4}$$

$$NHCl_2 + HOCl \Leftrightarrow NCl_3 + H_2O \qquad \textbf{Reaction 5}$$

Monochloramine is the best chemical for disinfecting water because unpleasant taste and odors can arise when dichloramines or trichloramines are formed. A chlorine to ammonia ratio of 3:1 to 5:1 is commonly used to limit the amount of dichloramines and trichloramines formed and promote the formation of monochloramines. In addition, these ratios limit nitrification and biofilm growth, which can occur when higher levels of ammonia are used (American Water Works Association, 1999).

Chloramines are not strong disinfectants compared to free chlorine. In order to meet the Surface Water Treatment Rule (SWTR) regulations for primary disinfection of such organisms as *Giardia* and viruses, extremely long detention times or high chloramine concentrations would be needed. However, since chloramines are capable of producing a stable disinfectant residual, chloramination is a possible secondary disinfectant to control bacterial growth in distribution systems.

2.1.3 Chlorine Dioxide Disinfection

Chlorine dioxide was first used as a water disinfectant in the United States in 1944, at the Niagara Falls, New York water treatment plant. A survey of United States water treatment facilities in 1977 showed that 84 water treatment plants used chlorine dioxide. As of 1977, 495 water treatment plants in Europe used chlorine dioxide in some part of their treatment processes, most often as a disinfectant residual for the distribution system (American Water Works Association, 1999). The main disadvantages of using chlorine dioxide as a water disinfectant compared to chlorine are higher operating costs, health risks caused by residual oxidants and the creation of harmful by-products.

Although not commonly used in the United States, chlorine dioxide is effective at inactivating waterborne pathogens. Chlorine dioxide does not react with organic material in water supplies to form trihalomethanes; however, some halogenated by-products are created when chlorine dioxide is used as a disinfectant (Haas and Aturaliye, 1999). Another disadvantage of chlorine dioxide is that it is a very unstable chemical and it rapidly dissociates into chlorite and chlorate. High concentrations of chlorite and chlorate can cause an increase in methemoglobanemia (Korn and Graubard, 2002).

2.1.4 Ozone Disinfection

Ozone is created when oxygen (O_2) is separated by an energy source into oxygen atoms. The oxygen atoms collide with each other to form a more stable configuration (O_2), which later forms ozone (O_3) gas. Ozone is a very strong purifier when used for primary disinfection in water and wastewater treatment plants. Because ozone gas does not have a stable chemical residual, it is not used as a secondary disinfectant (U.S. EPA, 1999a).

Ozone gas was first used in Europe in 1893. Ozone treatment for drinking water is still more common in Europe than in the United States. Recent changes in the cost of ozone equipment have led more communities in the United States to use ozone disinfection in their drinking water treatment plants. In addition, ozone is becoming more widely used today because very few, if any, TTHMs and HAAs are formed from this disinfectant.

When ozone reacts with water, free radicals such as HO_2 and $HO^{\cdot}$ are formed (reactions 6-9). These free radicals are thought to be the active chemicals in the disinfection of the pathogens. The free radicals disintegrate the cell wall of bacteria and act as a strong virucide also.

$$O_3 + H_2O \Leftrightarrow HO_3^+ + {}^{\bullet}OH^- \qquad \textbf{Reaction 6}$$

$$HO_3^+ + {}^{\bullet}OH^- \Leftrightarrow 2HO_2 \qquad \textbf{Reaction 7}$$

$$O_3 + HO_2 \Leftrightarrow HO^{\bullet} + 2O_2 \qquad \textbf{Reaction 8}$$

$$HO^{\bullet} + HO_2 \Leftrightarrow H_2O + O_2 \qquad \textbf{Reaction 9}$$

Ozone is more effective at inactivating organisms than chlorine. The other advantages to using ozone treatment include taste and odor control, oxidation of humic organic substances in water, and the destabilization of particles. There have been concerns about the safety of ozone with regard to DBP formation (other than TTHMs and HAAs). Bromate and formaldehyde can be formed in water after ozone disinfection, if the water has a high bromide ion concentration. Halopropanones and chloral hydrates are some other DBPs that are formed from disinfection with ozone. All of these DBPs are toxic.

2.1.5 Ultraviolet Disinfection

Ultraviolet light was first discovered in 1835 and was first used as a wastewater disinfectant in 1901 in Europe. At that time, ultraviolet light was unpredictable and difficult to control, so chlorine became the disinfectant of choice. Ultraviolet disinfection is the transmission of electromagnetic energy from a mercury arc lamp. As UV radiation enters the cell wall of a microorganism, the UV light damages the deoxyribonucleic acid (DNA) or ribonucleic acid (RNA), thus preventing the organism from reproducing. Pathogens are successfully killed at wavelengths ranging from 245 to 285 nm. Either low-pressure (254 nm) or medium-pressure (180 – 1,370 nm) mercury arc lamps, set at low or high intensities, can be used as the source of UV radiation (U.S. EPA, 1999b).

UV disinfection is very effective at inactivating pathogens at low dosages (U. S. EPA, 1999b). Very small concentrations of DBPs are formed when UV disinfection is used. However, high concentrations of turbidity and certain minerals can decrease the effectiveness of UV (U.S. EPA, 1999b). In addition, this type of disinfection does not produce a disinfectant residual; therefore it can only be used as a primary disinfectant. A secondary disinfectant, such as chlorine gas, in combination with UV radiation has to be used when treating drinking water with UV disinfection.

2.2 Disinfection By-products

Disinfection by-products (DBPs) are defined as the class of chemicals that are formed when disinfectants react with the organic compounds in water. Some of these compounds are carcinogens and some are suspected of causing acute health effects. As explained earlier, the addition of some type of disinfectant is a required step in creating a microbiologically safe drinking water. DBPs are chemical compounds produced as an

undesirable result of water disinfection and oxidation. The chemical compounds of most serious concern contain chlorine and bromine atoms. These compounds have been shown to be carcinogenic, mutagenic or hepatotoxic, and have caused negative reproductive or developmental effects in animal studies.

2.2.1 History of Disinfection By-products

In 1974, public awareness about DBPs was increased by several events. First *Consumer Reports* published three articles concerning organic contaminants in drinking water (Harris and Breecher, 1974). Second, there were several studies conducted by the Environmental Defense Fund (EDF) and the U.S. EPA showing the dangerous health effects of organic contaminants (The States-Item, 1974; Page *et al.,* 1974; Page *et al.,* 1976; U.S. EPA, 1975). Lastly, a national news program special was aired on CBS on December 5, 1974, called *Caution, drinking water may be dangerous to your health*. This television special reached a much wider audience in the United States than the published articles and studies (American Water Works Association, 1999).

The problem of organic contaminants in drinking water was perceived as a crisis by the American public. The Safe Drinking Water Act (SDWA) of 1974 mandated that all levels of government, local to federal, work together to resolve this issue. The SDWA required the creation of primary drinking water regulations designed to provide safe drinking water for the public. The SDWA was the first regulation to pertain to all consumer water systems in the United States and included both chemical and biological contaminants (Pontius and Clark, 1999). On November 8, 1974, the U.S. EPA announced that it would conduct a nationwide survey, called the National Organics Reconnaissance Survey (NORS), to find the concentrations and possible effects of certain

organic chemicals in drinking water. On December 18, 1974, the U.S. EPA named 80 cities to be involved in the NORS. These cities had a wide range of drinking water quality, and were chosen to ensure that the survey was comprehensive.

Symons *et al.* (1975) wrote a paper summarizing the findings of the National Organics Reconnaissance Survey (NORS). The survey concluded that total trihalomethanes (TTHMs) were present in finished waters due to chlorination practices. All the samples tested in the NORS contained detectable levels of chloroform. Ground water sources had a lower average TTHM concentration than surface waters. The survey noted higher average TTHM concentrations in locations where raw-water chlorination was practiced. Higher levels of TTHMs were also found when surface water was the source water and more than 400 μg/L free chlorine residual was present. When powdered activated carbon (PAC) was used, the average TTHM concentration was lower than when PAC was not used. The survey also showed that higher TTHMs were found at higher pH levels. The results of NORS showed that TTHMs were the most prevalent organic compounds in drinking water and that chloroform was one of the more common THMs. Other compounds that were found were 1,2-dichloroethane, carbon tetrachloride and nonvolatile total organic carbon. As a result of this survey, the U.S. EPA set regulations for controlling THMs in drinking water systems (Pontius and Clark, 1999).

2.2.2 Trihalomethanes

Trihalomethanes are organohalogen compounds; they are named as derivatives of the compound methane. Trihalomethanes are formed when three of the four hydrogen atoms attached to the carbon atom in the methane compound are replaced with atoms of chlorine, bromine and/or iodine. Trihalomethanes are formed when chlorine has a

chemical reaction with the organic material that is already present in the water supply. Trihalomethanes (THMs) include chloroform ($CHCl_3$), dibromochloromethane ($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$), and bromoform ($CHBr_3$). Chloroform is the THM most commonly found in drinking water and is usually present in the highest concentration (Vogt and Regli, 1981).

The existence of disinfection by-products, such as chloroform and other trihalomethane compounds, in chlorinated drinking water supplies was first discovered in 1974 (Rook, 1974). Almost all of the DBP studies in the 1970's were concerned with THMs. Since THMs were identified and studied long before other types of DBPs, the first DBP regulations, enacted on November 29, 1979, only set limits for TTHMs.

2.2.3 Haloacetic Acids

Haloacetic acids (HAAs) are disinfection by-products which were first detected in chlorinated drinking waters by Christman *et al.* (1983), nine years after trihalomethanes were discovered. Haloacetic acids (HAA) include nine different compounds (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, bromochloroacetic acid, dibromochloroacetic acid and dichlorobromoacetic acid). Currently, only monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid (referred to as HAA_5) are regulated. HAAs are the second most common group of DBPs and are very soluble in water. When using a chlorine disinfectant, dichloroacetic and trichloroacetic acids are the most common HAAs. If a water source has high bromide content, bromodichloroacetic acid and bromochloroacetic acid can be found at high levels.

2.2.4 Other Disinfection By-products

The first regulations to limit disinfection by-products were only concerned with TTHMs. More recent regulations (the Stage I D/DBP rule and the Stage II D/DBP rule; see sections 2.5.1 and 2.5.2) set limits for both TTHMs and HAA_5. New disinfection by-products are constantly being discovered. Table 1 lists some of the DBPs that have recently been identified and some brief information about them.

Table 1: Other disinfection by-products

Group	Disc.	Health effects	Compounds	Comments
Haloacetalde-hyde	1987	Limited; possible carcinogen	Chloro-, di- and tri-monohydrate.	Affects blood cells; causes mutations
Formaldehyde	1990	Conflicting data; possibly causes mutations	Formaldehyde	Ozone by-product
Haloacetonitriles	1987	Carcinogenic; mutagenic; causes weight loss	Chloro-, dichloro-, trichloro-, bromochloro-, and dibromochloro-	Chlorine by-product
Cyanogen chloride	1991	Acutely toxic	Cyanogen chloride	Chloramines by-product; has been used to create tear gas and fumigant gases
Chlorophenols	1987	Reduced growth rate; effects the liver's ability to detoxify	Mono-, di-, and tri-	Produced in industrial as biocides, dyestuffs, pesticides and herbicides
Haloketones	1991	Limited information	Hex-, tetra-, tri-, di-, and monochloroprop anoes	Minor constituents; chemical intermediates in industry

2.3 Factors Affecting the Formation of DBPs

There are several factors affecting the formation potential of DBPs. Previous research studies have shown that the major variables that affect DBP formation are: residence time, temperature, pH, disinfectant type and concentration, total organic carbon concentration and chlorine to nitrogen levels (for chloramination).

2.3.1 Type of Disinfectant

Each different type of disinfectant has both advantages and disadvantages in drinking water treatment. Free chlorine is very effective at inactivating pathogens but it produces some of the highest concentrations of DBPs. Chloramination is a weaker disinfectant compared to free chlorine but very few DBPs are formed when water treatment plants use chloramination. Ozone is an effective disinfectant and doesn't produce many DBPs of concern but ozone is not capable of providing a residual through the distribution system. Ultraviolet light has been shown to be effective at inactivating pathogens and it doesn't produce any DBPs that are yet regulated by the U.S. EPA but like ozone it does not produce a residual.

Regarding chloramination, the best Cl_2:N ratio for minimizing DBP formation depends on raw water quality. The type and concentration of humic substances present in the raw water source are the most important parameters that dictate which Cl_2:N ratio is the best. In a study examining chloramine disinfection, Diehl *et al.* (2000) found higher TTHM levels when disinfecting with chloramines at a Cl_2: N ratio of 7:1. They also found that as the Cl_2: N ratio decreased the HAAs decreased. The experiment showed that a Cl_2: N ratio of 3:1 was ideal for controlling DBP formation, but this ratio might not

be suitable for controlling bacterial regrowth. Additional information comparing DBP production from chlorine and chloramines is provided in section 2.6.2.

2.3.2 Disinfectant Concentration

Scientists have been studying how the disinfectant concentration affects DBP formation. The studies have shown that as the disinfectant concentration increases, DBP formation also increases. For example, Singer *et al.* (1995) conducted a study in North Carolina on eight conventional water treatment plants that practiced chlorine disinfection. The treatment plant that used the largest chlorine dose had average TTHM and HAA_9 levels of 52 μg/L and 80 μg/L, respectively. The plant which used the smallest chlorine dose had mean TTHM and HAA_9 levels of 19 μg/L and 39 μg/L, respectively.

2.3.3 Residence Time

Several research studies have been conducted to examine how residence time affects DBP formation. The studies have shown that as residence time increases, the concentration of TTHMs increases and the concentration of HAAs decreases.

Chen and Weisel (1998) conducted experiments examining the concentrations of DBPs in a conventional treatment plant that used chlorine to disinfect the water supply. Over 100 samples were collected in four groups, each group representing an increasing residence time from the point of disinfection. The average concentrations for TTHMs at days zero, one, two and three or more were 25±14 μg/L, 30±16 μg/L, 29±15 μg/L, and 30±14 μg/L, respectively. The average levels for HAA_5 at days zero, one, two and three or more were 24±6 μg/L, 23±7 μg/L, 21±8 μg/L, and 14±6 μg/L, respectively. These findings showed that as residence time increases, TTHMs increase (up to day one) and

HAAs decrease. Similar results were found by LeBel *et al.* (1997), who performed an experiment on a conventional water treatment system that used chlorine for its primary and secondary disinfectant. Four sampling points were used at an increasing distance from the treatment plant. At the first, second, third, and fourth points, TTHM levels were analyzed and the results were 24.8 μg/L, 37.5 μg/L, 48.4 μg/L, and 61.4 μg/L, respectively. HAA_5 concentrations were also determined at the four sites and the results were 31.2 μg/L, 34.4 μg/L, 33.1 μg/L, and 8.8 μg/L, respectively. The results showed that TTHM levels increased and HAA_5 levels decreased as the distance from the treatment plant increased.

2.3.4 Temperature

Many studies have been conducted to evaluate how temperature affects the rate of DBP formation and the concentration of DBPs that are formed. Some studies have shown that as the temperature increases, the concentration of TTHMs also increases. However, the results are not conclusive because conflicting results have been found from different research studies.

Nieminski *et al.* (1993) examined TTHM and HAA concentrations (during all four seasons) in 14 conventional water treatment plants which disinfect with chlorine. In this study, the mean TTHM levels for summer, fall, winter, and spring were 32.1 μg/L, 28.7 μg/L, 17.6 μg/L, and 16.5 μg/L, respectively. This study showed that the highest TTHM concentrations were found in the summer and fall seasons, and the lowest TTHM concentrations were present in the winter and spring. Chen and Weisel (1998) collected 144 water samples from the Elizabethtown, N.J. water system, which uses chlorine disinfection and conventional treatment, between November 1991 and October 1993.

The samples were collected in all seasons. As the water exited the treatment plant, the TTHM level in the winter was 14±4 μg/L, and the TTHM level in the summer was 33±13 μg/L. The HAA concentrations in the winter and summer were 24±6 μg/L and 26±8 μg/L, respectively. Chen and Weisel's research showed that TTHM levels increased significantly in the summer and the HAA levels remained the same throughout the year. An addition study was conduct by Doijlido *et al.* (1999), on water disinfected with chlorine and treated by conventional treatment. The smallest concentrations of HAAs were formed in January, February, and March (total HAA concentration of less than 13 μg/L). The highest concentrations of HAAs occurred in May and June, when the levels reached 120 μg/L. The results of Dojilido *et al.* are in contradiction with the results of the Chen and Weisel study. Therefore, the impact of temperature on HAA levels is unclear.

2.3.5 pH

Several studies have been done to analyze concentrations of DBPs and how they relate to pH levels of the water supply. The studies have shown that as the pH increases, the concentration of TTHMs also increases. HAA concentrations were not as dependent on pH.

Diehl *et al.* (2000) conducted a series of experiments to determine the effect of pH on DBP formation in water supplies treated with chloramines. TTHMs were measured at pH conditions of 6, 8 and 10 and the results were 161 μg/L, 259 μg/L, and 295 μg/L, respectively. HAAs were also examined at these pH conditions and the concentrations were 74.5 μg/L, 74.3 μg/L, and 55.5 μg/L, respectively. These results lead Diehl *et al.* (2000) to state that as pH increases, TTHM levels increase and HAA

levels decrease. Nieminski *et al.* (1993) evaluated 35 water treatment systems in Utah which used chlorine disinfection. TTHMs and HAAs were first analyzed at a pH of 5.5 and the results were 39.9 μg/L and 35.3 μg/L, respectively. TTHM and HAA levels were again tested at a pH of 8.46 and the results were 49.8 μg/L (TTHMs) and 14.6 μg/L (HAAs). The findings support the conclusion that higher pH conditions cause HAA concentrations to decrease and TTHM concentrations to increase.

2.3.6 Total Organic Carbon Concentrations

Several researchers have studied the impact of total organic carbon concentration on DBP formation. These experiments have found that as the total organic carbon level increased, the DBP formation also increased. Two studies which looked at the total organic carbon levels with respect to TTHMs and HAAs are discussed in the following paragraph.

Singer *et al.* (1995) conducted a study on eight North Carolina water supply systems. At a TOC concentration of 5.4 mg/L, an average of 82 μg/L of TTHMs was produced and an average of 106 μg/L of HAA_9 was formed. At a TOC level of 2.4 mg/L, a mean of 39 μg/L of TTHMs were created and a mean of 36 μg/L of HAA_9 were produced. These results showed that as TOC concentrations increased so did TTHM and HAA_9 levels. Dojilido *et al.* (1999) also found HAA formation was dependent on the organic matter present in the sample: higher concentrations of HAAs were formed at higher TOC concentrations.

2.3.7 Bromide Concentrations

Recent studies have been completed which examined the relationship between bromide concentration in a drinking water supply and DBP formation. These studies have shown that as the concentration of bromide is increased, the concentration of TTHMs and HAAs also increases. When there are high bromide concentrations in a raw water source and chlorine is added to the water supply, more brominated THMs will be formed because there is more bromide present in the water source for the organics to react with. In typical raw water supplies when chlorine is added, chloroform is the major compound of TTHMs found in the water supply.

Diehl *et al.* (2000) performed experiments on three different water sources and tested the effect of bromide levels on DBP formation. Results showed that as the bromide concentration increased, the TTHM concentration also increased. For example, at one treatment plant using chloramines at a Cl_2: N ratio of 5:1 and pH of 6, the TTHM concentration without bromide addition was 14.8 μg/L and with bromide addition was 40.2 μg/L. Pourmoghaddas *et al.* (1993) also conducted experiments to study the relationship of bromide concentrations to HAA formation in drinking water. The study used ultra pure water with humic acid added. The study included differing residence time and pH values to give a better representation of a true water source. Pourmoghaddas *et al.* (1993) found the highest HAA values were observed when the largest amount of bromide was added to the water. For monobromoacetic acid (MBAA), the highest concentration (15 μg/L) of this HAA was observed when 4.5 mg/L of bromide was added. When no bromide was added, almost no MBAA was found.

2.4 Health Risks

The first DBP to be identified was chloroform. At the time chloroform was found to be present in water supplies, chloroform was also a known carcinogen. Since the early 1970s, many additional DBPs have been discovered, and the effects on humans and animals have been studied. Many DBPs are known carcinogens, and some could possibly have adverse affects on pregnancy.

2.4.1 Animal Studies

Animal studies have shown the effect of DBPs on pregnancy outcomes. Table 2 is a summary of some of the results found by researchers examining the effect of TTHMs on animals. When the highest doses of chloroform were administered to the animals, either orally or by inhalation, all of the studies showed some type of embryotoxic or fetotoxic effect. Such effects included reduced fetal size and weight, and retarded skeletal ossifications. Specifically, Murray *et al.* (1979) saw an increase in cleft palates at higher doses of chloroform. Several additional studies (Whillhite, 1981; Whillhite *et al.*, 1981; and Doherty *et al.,* 1983) performed in the early 1980s with pregnant hamsters showed an increase in malformations in the offspring when acetonitrile, acrylonitrile, propionitrile, and succinonitrile were present in the drinking water supply. Lastly, George *et al.* (1985) found that reduced birth weight and reduced weight gain were more prevalent when haloacetonitriles were administered to pregnant rats compared to rats that did not ingest DBPs. When dichloroacetonitrile and trichloroacetonitrile were given to pregnant rats, an increase in neonatal mortality was observed.

Table 2: Chloroform developmental studies

Species	Dose (s)	Gestational days administered	Route of administration	Results	Reference
Rat	30, 100, 300 mg/L	6-15 (7 hr/day)	Inhalation	Embryotoxic, Fetotoxic, Teratogenic	Schwetz *et al.* (1974)
Rat	20, 50, 126 mg/kg/day	6-15	Oral	Fetotoxic	Thompson *et al.* (1974)
Rat	100, 200, 400 mg/kg	6-15	Oral	Fetotoxic	Ruddick *et al.* (1983)
Mouse	100 mg/L	1-7, 6-15, 8-15 (7 hr/day)	Inhalation	Embryotoxic, Fetotoxic, Teratogenic	Murray *et al.* (1979)
Rabbit	20, 35, 50 mg/kg/day	6-18	Oral	Fetotoxic	Thompson *et al.* (1974)

2.4.2 Human Studies

Several studies have shown the association between chlorination by-products and cancer in humans, especially bladder cancer. Morris *et al.* (1992) used a statistical method to compile the results of many studies conducted between 1966 and 1991 to evaluate the effects of chlorination by-products. Morris *et al.* (1992) found the studies supported a strong association between bladder cancer and exposure to disinfection by-products in drinking water. Morris *et al.* (1992) further indicated a fairly strong relationship between rectal cancer and chlorination by-products.

Reif *et al.* (1996) wrote a technical review about four epidemiologic studies of DBPs and health risks. The review summarized and critiqued four studies: 1) an Iowa study testing the relationship between chloroform and adverse pregnancy outcomes

(Kramer *et al.,* 1992), 2) a larger study in New Jersey testing TTHMs and birth defects (Bove *et al.,* 1992), 3) a Massachusetts study testing the association between chlorination, chloramination and birth defects (Aschengrau *et al.,* 1993), and 4) a North Carolina study comparing TTHM levels and adverse pregnancy outcomes (Savitz *et al.,* 1995). In the Kramer *et al.* (1992) study, an increased risk of intrauterine growth retardation (IUGR) was associated with chloroform levels greater than 10 μg/L. Bove *et al.* (1992) observed that pregnant women exposed to TTHM concentrations greater than 100 μg/L had babies with low birth weights and babies that were small for their gestational age. The Bove *et al.* (1992) research also showed an increase in central nervous system defects, neural tube defects, oral cleft defects, cardiac anomalies, and major cardiac defects when the mother was exposed to TTHM levels greater than 80 μg/L. In the Aschengrau *et al.* (1993) study, an increased risk of stillbirths was observed when the mother drank chlorinated water as opposed to chloraminated water. Aschengrau *et al.* (1993) concluded chlorination was associated with an increased risk for major malformation, such as respiratory and urinary tract defects. In the Savitz *et al.* (1995) study, an association was found between high TTHM concentrations and (1) an increased risk of miscarriage and (2) a low birth weight. Reif *et al.* (1996) believed that although these previous studies showed a strong correlation between adverse pregnancy outcomes and exposure to TTHMs, they did not prove that there is a true relationship. More research was required to understand the relationship between TTHMs and adverse birth outcomes.

Further studies on the relation between TTHM concentrations and adverse birth outcomes have been conducted in Canada. Dodds *et al.* (1999) constructed a database of 50,755 women who had delivered babies from 1988 to 1995 in Nova Scotia, Canada.

The database included a thorough case history of each woman. TTHM levels were obtained from the Nova Scotia Department of the Environment. The findings showed an association between stillbirths and TTHM concentrations. However, the study did not find an association between TTHM concentrations and the following adverse birth outcomes: low birth weight, fetal growth restrictions, gestational age outcomes, risk of neural tube defects, risk of cardiac defects, or risk of oral cleft defects. Magnus *et al.* (1999) created a national network of Norwegian births and Norwegian water characteristics. This allowed a relationship to be formed between chlorination and humic content in water and the occurrence of birth defects. The study included 181,361 births between 1993 and 1995. The study found birth defects were more prevalent in municipalities where chlorination occurred.

Gallagher *et al.* (1998) conducted a study to determine if drinking water had adverse birth outcomes on pregnant women during the third trimester. There were 1,244 test subjects in the study born between 1990 and 1993 in Denver, Colorado. Water samples were collected from the women's taps during the third term of their pregnancies and analyzed for TTHM concentrations. The study found an association between pregnant women, in their third trimester, being exposed to high trihalomethane levels and a risk of term low-birth weight deliveries. The study further concluded that an increase in risk of growth retardation with respect to higher trihalomethane levels could be expected.

2.5 Regulations

In the early 1970s, DBPs were first discovered to have harmful health effects to animals and humans. On November 29, 1979, the first legislation to limit the

concentration of TTHMs in drinking waters was passed (U.S. EPA, 1979). This rule set a TTHM limit of 100 μg/l.

2.5.1 Stage I D/DBP Rule

The Stage I Disinfectants and Disinfection By–Product (D/DBP) Rule was promulgated by the U.S. EPA on December 16, 1998 (U.S. EPA, 1998). The Stage I D/DBP Rule addresses four main provisions: (1) lower TTHM limits; (2) contaminant limit for HAAs which had not yet been regulated; (3) maximum residual levels for four disinfectants; and (4) required removals of TOC based on source water quality. The rule affects all community water systems (CWSs) and nontransient-noncommunity water systems (NTNCWSs) that use a chemical disinfectant for any type of water treatment.

The Stage I D/DBP Rule established maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for TTHMs, HAA_5, chlorite and bromate (see Table 3). The MCL for TTHMs was set at 80 μg/L and the MCL for HAA_5 was set at 60 μg/L. Chlorite and bromate MCLs were set at 1,000 μg/L, and 10 μg/L, respectively. The MCLs for TTHM and HAA_5 compliance are based on a running annual arithmetic average that is formulated every quarter. The number of test sites in the distribution system is dependent on the size of community which the treatment plant is serving. The bromate MCL is only for systems that use ozone as part of their treatment and the chlorite MCL is only for systems that use chlorine dioxide to disinfect their water supply. Bromate is required to be measured monthly and chlorite is required to be tested daily. The Stage 1 D/DBP Rule set maximum residual disinfectant level goals (MRDLGs), and maximum residual disinfectant levels (MRDLs) for chlorine, chloramines and chlorine dioxide (see Table 4).

Table 3: MCLs for disinfection by-products (Source: U.S. EPA, 1998)

Disinfection By-products	MCL (mg/L)
Total trihalomethanes	0.080
Haloacetic acids	0.60
Chlorite	1.0
Bromate	0.010

Table 4: MRDLs and MRDLGs for disinfectants (Source: U.S. EPA, 1998)

Disinfectant Residual	MRDL (mg/L)	MRDLG (mg/L)
Chlorine-as free Cl_2	4.0	4.0
Chloramines-as total Cl_2	4.0	4.0
Chlorine dioxide-as ClO_2	0.8	0.8

The Stage I D/DBP Rule also required removal of a percentage of organic matter in water as measured by total organic carbon (TOC). TOC has been known to react with disinfectants to produce DBPs. The amount of TOC required to be removed from a water source depends upon the TOC of the source water, as show in Table 5. The removal of TOC is accomplished through enhanced coagulation or enhanced softening. Enhanced coagulation is the addition of sufficient coagulants to improve the removal percentage of DBP precursors through the use of conventional filtration. Enhanced softening is the improved removal of DBP precursors by rapid softening.

Table 5: Required removal of TOC by enhanced coagulation and enhanced softening (Source: U.S. EPA, 1998)

Source water TOC (mg/L)	Source water Alkalinity as $CaCO_3$		
	0-60 mg/L	*>60-120 mg/L*	*>120 mg/L*
>2-4	35%	25%	15%
>4-8	45%	35%	25%
>8	50%	40%	30%

Water treatment systems can apply for an exception to enhanced coagulation or enhanced softening if they meet one of the following requirements:

1. The source water TOC is less than 2 mg/L
2. The treated water TOC is less than 2 mg/L
3. The source water TOC is less than 4 mg/L, the source water alkalinity is greater than 60 mg/L as $CaCO_3$ and the DBP levels for TTHMs are less than 40 μg/L and for HAA_5 are less than 30 μg/L
4. Chlorine is the only disinfectant used and the DBP levels for TTHM are less than 40 μg/L and HAA_5 are less than 30 μg/L
5. The source water specific ultraviolet absorbance (SUVA) prior to any treatment is less than 2.0 L/mg·m
6. The treated SUVA is less than 2.0 L/mg·m

The best available technologies for meeting the MRDLs for chlorine residual, chloramines residual, chlorine dioxide, and the MCL for chlorite entail the control of treatment methods to decrease the concentration of disinfectant needed. The best available technologies for minimizing TTHM and HAA_5 concentrations when chlorine is used as the disinfectant involve enhanced coagulation, enhanced softening, or using granular activated carbon. The ability of the ozonation method to lower the production of bromate is described as the best available technology for minimizing bromate concentrations (U.S. EPA, 1998).

2.5.2 Stage II D/DBP Rule

The SDWA amendments of 1996 required the promulgation of the Stage II D/DBP Rule. It is expected that the U.S. EPA will promulgate the Stage II D/DBP Rule in 2003. The most significant problems the U.S. EPA is facing with the Stage II D/DBP Rule development is the evaluation of information and research to determine the extent to which should the Stage I D/DBP Rule should be changed.

The Stage II D/DBP Rule and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) will be publicized at the same time. The first rule will address DBP and disinfectant issues, while the later will address microbial safety of drinking water supplies. The Stage II D/DBP Rule will affect all CWSs and NTNCWs that add a disinfectant to their water supply. It is anticipated that the Stage II D/DBP Rule will decrease DBP peaks in a distribution system (Pontius, 2001a).

The Stage II D/DBP Rule is expected to keep the same MCLs for TTHMs, HAA_5, chlorite and bromate. However, the MCLs for TTHMs and HAA_5 at each monitoring location are expected to be regulated by a Location Running Annual Average (LRAA). The Stage II D/DBP Rule is also supposed to focus on concerns about the risks between safely decontaminating a water source from pathogens and successfully reducing DBP concentrations (HDR Engineering Inc, 2001). All water treatment systems will have to complete an Initial Distribution System Evaluation (IDSE) to determine where DBP concentrations peak in the distribution system. The IDSE monitoring study will take place over a one year period under a schedule that is based on the source water type and the size of the treatment system. The sampling points should be chosen to reflect the differences in the concentrations of TTHMs and HAA_5 with respect to time and location in the distribution system. The results of the IDSE will help to locate the monitoring points used for the LRAA for the calculation of TTHM and HAA_5 concentration levels. After the IDSE study is conducted, the treatment system will monitor their water supply for DBPs. The time, location and number of sites to be sampled are shown in Table 6.

Table 6: Description of sampling times and location proposed by the Stage II D/DBP Rule (Source: U.S. EPA, 2001)

Description of treatment system	Time between sampling	Types of samples
Surface water; serving more than 10,000	90 days	4 sampling sites through the distribution systems
Surface water; serving from 500-9,999	90 days	Samples at the highest TTHM point and the highest HAA_5 point in the distribution system
Surface water; serving fewer than 500	Once per year	Samples at the highest TTHM point and the highest HAA_5 point in the distribution system
Ground water; serving more than 10,000	90 days	Samples at the highest TTHM point and the highest HAA_5 point in the distribution system
Ground water; serving from 500-9,999	Once per year	Samples at the highest TTHM point and the highest HAA_5 point in the distribution system
Ground water; serving fewer than 500	Once per year	Samples at the highest TTHM point and the highest HAA_5 point in the distribution system

2.5.3 Other Regulations

The Safe Drinking Water Act (SDWA) amendments were formed based on recent findings of potentially harmful contaminants in water supplies. The Surface Water Treatment Rule of 1989 requires that all U.S. treatment plants that use surface water filter and/or disinfect their water supply to protect the health of the public. The 1996 SDWA amendments require the U.S. EPA to create a final Enhanced Surface Water Treatment Rule (ESWTR), a Stage I D/DBP Rule and a Stage II D/DBP Rule.

The U.S. EPA developed the ESWTR limits to be effective enough to inactivate microorganisms while at the same time reducing the potential health risks associated with disinfection by-products. The Interim Enhanced Surface Water Treatment Rule

(IESWTR) was promulgated on December 16, 1998 (U.S. EPA 1998). The IESWTR strengthens the requirements of the SWTR that was passed in 1989. The IESWTR affects municipal water systems using surface water or ground water under the direct influence of surface water that serve at least 10,000 people. The IESWTR was designed to improve public health by reducing microbial contaminants, especially *Cryptosporidium*, by establishing a Maximum Contaminant Limit Goal (MCLG) at zero and requiring that municipal water systems that use filtration in their treatment process remove 99% of *Cryptosporidium* from their water supply. Municipal water systems that don't filter their water must create a watershed control plan/program. The IESWTR also created stricter regulations on turbidity. The maximum turbidity readings from conventional and direct filtration treatment plants were set at 0.3 Nephelometric Turbidity Units (NTU) in at least 95% of their effluent samples taken each month. The IESWTR also requires that the turbidity must not go above 1 NTU. The IESWTR made all states perform sanitary surveys of municipal water systems that use surface water or ground water under the direct influence of surface water, no matter the size of the treatment facility. Municipal water systems had to meet the IESWTR by January 1, 2002.

The Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR) was promulgated on January 14, 2002 (U.S. EPA, 2002). The LT1ESWTR was intended to provide more protection against *Cryptosporidium* in drinking water. The difference between the IESWTR and the LT1ESWTR is that the LT1ESWTR affects municipal water systems that use surface water or ground water under the direct influence of surface water, regardless of the size of the treatment plant. The LT1ESWTR also regulates

turbidity for municipal water systems that use different types of filters. Municipal water systems have to meet the requirements of the LT1ESWTR by January 14, 2005.

The Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) is not finalized yet but it is expected to be based on the IESWTR and the LT1ESWTR. The LT2ESWTR is expected to provide control over DBPs and microbial contaminants (i.e. *Cryptosporidium*). The LT2ESWTR will affect all community and non – community water systems that use surface water or ground water under the direct influence of surface water. The LT2ESWTR was supposed to be promulgated in May of 2002; but setbacks have delayed finalization until the middle of 2004.

2.6 Disinfection By-product Control

The U.S. EPA realized that Public Water Systems (PWSs) could have difficulties when attempting to meet both DBP limits and disinfection regulations. The regulations developed for disinfection and DBP control are of equal importance and both regulations must be met simultaneously. In the past 20 years, the U.S. EPA and members of the scientific community have conducted research and developed methods to address these issues. There are three basic methods for controlling DBPs in a water system: 1) reduce the DBP formation by lowering the organic precursor concentration at the point of disinfection, 2) reduce DBP formation by decreasing the disinfectant dose, altering the type of disinfectant or optimizing the disinfection environment, and 3) remove the DBPs after they have formed.

2.6.1 Removal of DBPs Precursor Material

Improved or modified coagulation can decrease the amount of humic and fulvic matter in natural waters. Using modified coagulation to lower the concentration of DBPs formed in a water supply has some important advantages compared to most other treatment techniques: 1) very little investment is required for a treatment plant to include improved coagulation, 2) modified coagulation requires a minute increase in operating costs, and 3) improved coagulation is a well understood and reliable treatment process. Symons (1976) conducted a study on the Ohio River that showed it was possible to achieve up 60% removal of TOC using coagulation-sedimentation-filtration with alum. Improving coagulation and altering the point of chlorine addition to after a significant portion of the TOC has been removed can produce an effluent water supply with lower trihalomethane levels. Modified coagulation has also been shown to be successful at reducing the concentrations of trichloroacetic acid, dichloroacetic acid and dibromochloroacetic acid, as well as TTHMs (Reckhow and Singer, 1990).

2.6.2 Altering Disinfection Conditions

The use of disinfectants other than chlorine is another way to control the concentration of halogenated by-products. Clark *et al.* (1994) examined two major disinfection alternatives (ozone and chloramines) with regard to DBP formation potentials in Jefferson Parish, Louisiana. In this study, the researchers found that when chlorine was applied to the water supply, 45 μg/L of dichloroacetic acid (DCAA) was formed. When ozone was used as a disinfectant in the water supply, 32 μg/L of DCAA was produced. When monochloramine was used as a disinfectant in the water system, 8 μg/L of DCAA was formed.

Norman *et al.* (1980) conducted a study that examined the production of TTHMs when chloramines were used instead of chlorine as a disinfectant. The study examined the Huron treatment plant in Huron, South Dakota and found that when chlorine disinfection was used, an average of 154 μg/L of TTHMs was produced. When chloramine disinfection was used at the same plant, 37 μg/L of TTHMs were formed. Nissinen *et al.* (2002) performed a study to quantify DBPs in Finnish water systems. This study found that chlorinated waters with conventional treatment created an average of 108 μg/L of HAA_6 and 26 μg/L of TTHMs. When the same water supply was treated with conventional treatment and chloramines, an average of 20 μg/L of HAA_6 and 2.1 μg/L of TTHMs were formed. Norton and LeChevallier (1997) examined two treatment plants, one in Muncie, Indiana and the other in Hopewell, Virginia, that recently switched their secondary disinfectant from chlorine to chloramines. While using chlorine, TTHM levels at the Indiana plant averaged 76 μg/L and while using chloramines the TTHM level averaged 63 μg/L. At this plant, HAA_5 averaged 88 μg/L when chlorine was used as a secondary disinfectant and 51 μg/L when chloramines were used as a secondary disinfectant. Similar reductions in both TTHM levels and HAA_5 were seen at the Virginia plant. Simpson and Hayes (1998) study chlorinated and chloraminated water supplies in Australia. Their study found that when chlorine was used as a secondary disinfectant, average values for TTHM levels were 189 μg/L and when chloramines were used as a secondary disinfection, average values of TTHMs were 6 μg/L.

Another study that examined using alternative disinfection conditions on a water supply was completed by Trussell and Umphres (1978) in Contra Costa County, Texas. The water treatment plant adjusted the pH of the water supply from 9.0 to 7.0. TTHM

measurements were taken before and after the adjustment. When the pH was decreased to 7.0, the TTHM concentration decreased by 50%. These results indicated that maintaining a low pH during disinfection could reduce THM problems, and the pH can be raised once a free chlorine residual is no longer present. Diehl *et al.* (2000) conducted a study of the Lake Huron water treatment system, which used chloramines for disinfection. The pH in this experiment was adjusted from 8.0 to 6.0. At a pH of 8.0, the TTHM levels averaged 346 μg/L and the HAA levels averaged 295 μg/L. At a pH of 6.0, the TTHM levels averaged 244 μg/L and the HAA levels averaged 282 μg/L.

2.6.3 Removal of DBPs After Formation

Several methods are available to remove trihalomethanes from waters after formation. These methods include: 1) oxidation; 2) aeration; and 3) adsorption.

2.6.3.1 Oxidation

The possibility of removing trihalomethanes by oxidation, using either ozone or chlorine dioxide as the oxidant, has been investigated in prior research. Glaze *et al.* (1980) studied the use of ozone in combination with ultraviolet radiation as a treatment process for removing THMs from drinking water. Table 7 summarizes the results obtained for the destruction of chloroform and bromodichloromethane using a laboratory–scale, sparged, stirred–tank, semi–batch, photochemical reactor. The first order reaction rates are expressed in terms of half–life. Ozone alone had little or no influence on the two trihalomethanes tested while ultraviolet radiation alone (photolysis) destroyed chloroform and bromodichloromethane slowly. Combined treatment by ozone and UV was much more effective, lowering the concentration of these trihalomethanes to one–half of their initial values in 3.3 to 6.3 minutes for the laboratory prepared water and

Table 7: Half Lives (in minutes) for Chloroform and Bromodichloromethane (Ozone dose rates = 0.775 mg/L min; UV intensity = 0.20 Watts/L)

Compound	Water type	Purging	Ozonolysis	Photolysis	Ozone/UV
$CHCl_3$	Lab prepared	462	No decline	139	3.25
	Lake	729	22,400	753	86.6
$CHBrCl_2$	Lab prepared	495	No decline	61.9	6.3
	Lake	2660	No decline	116	53.3

53.3 to 86.6 minutes in the lake water. Therefore, the combination of ozone and UV showed the fastest oxidation of the THMs tested.

2.6.3.2 Aeration

Rook (1976) studied the removal of chloroform in a 4 m high cascading countercurrent aerator filled with crosswise arranged racks of plastic tubing. The results of this study showed that there was a 50% removal of chloroform at an air–to–water ratio of 3.2 to 1. Houel *et al.* (1979) studied the removal of chloroform spiked into water by air stripping using a countercurrent tower having a cross section of 60 x 45 cm and a packing depth of 4 m. The air supply was carefully monitored and capable of delivering a maximum of approximately 35 m^3/min. Flow rates as high as 27 m^3/day were tested. Two packing materials were used: Type A, egg crate style; and type B, a proprietary product. Table 8 shows the results of this study. At very high air–to–water ratios, chloroform was very effectively removed. Aeration is a feasible approach for trihalomethane removal, with the difficulty of removal increasing with molecular weight from chloroform to bromoform.

Table 8: Tower Aeration for the Removal of Chloroform from Chloroform - spiked Water (source: Houel *et al.* (1979))

	Run Number					
Variable	1	2	3	4	5	6
Packing Type	A	A	A	B	B	B
Calculated air-to-water ratio (V/V)	6100:1	7700:1	9400:1	1800:1	2500:1	2600:1
Initial $CHCl_3$ Concentration (µg/L)	843	843	843	536	638	536
Final $CHCl_3$ Concentration (µg/L)	<0.1	<0.2	<0.1	13.2	1.6	<0.2
Percent $CHCl_3$ removal	>99.98	>99.97	>99.98	97.5	99.8	>99.96

2.6.3.3 Granular Activated Carbon Adsorption

Granular activated carbon (GAC) adsorption systems used in drinking water treatment typically use stationary beds with the liquid flowing through the absorbent (GAC) . Under these conditions, absorbed material first accumulates at the top of the bed and then through the bed depth. The maximum amount of a contaminant that can be adsorbed on activated carbon occurs when the adsorbed material is in equilibrium with the concentration of the contaminant in solution surrounding the absorbent.

The U.S. EPA's Drinking Water Research Division (Symons *et al.*, 1981) conducted a studied in which glass columns of 3.7 cm in diameter, filled with different depths and types of GAC, were exposed to Cincinnati, OH tap water at differing velocities and empty bed contact times (EBCTs). The goal of this study was to determine the ability of GAC to remove chloroform and two other trihalomethanes. The chloroform concentration was lowered by 90% or more for three weeks, at which point the effluent

chloroform concentration steadily grew until it was equivalent with the influent concentration at the tenth week. The trihalomethanes containing bromine were more effectively adsorbed by the GAC. It was hypothesized that the trihalomethanes containing bromine were better removed because there was a lower concentration of them in the water supply and they were better absorbed onto the GAC.

2.6.3.4 Advantages and Disadvantages of Trihalomethane Removal

Removal of trihalomethanes has the advantage of allowing treatment plants to continue with their current disinfection practices. Chlorination could continue to be used as a disinfection process, and the trihalomethanes could be removed by adding an additional treatment process. One disadvantage of this type of treatment is that the objective is to remove trihalomethanes after they have formed. Other DBPs may not be removed by the treatment process, only the specific one that the process is designed for. Another disadvantage is the fact that chlorine is an oxidant; therefore the possibility of producing oxidation by-products during chlorination still exists. The biggest disadvantage to trihalomethane removal after they have been formed is the problem that it is not cost effective.

2.7 Worcester Water Filtration Plant

Prior to 1997, the Worcester water supply came from ground water that was disinfected and then sent to the public for consumption. There are several reasons why Worcester began to consider building a new water treatment facility in 1984: 1) the watershed was faced with urbanization, 2) the infrastructure was old and was beginning to weaken and 3) more stringent water quality regulations were being proposed. The Surface Water Treatment Rule (SWTR) of 1989 required that all surface water supplies

must use filtration to treat drinking water. The existing plant did not have the capacity to meet the city's demand for water using ground water, so the city decided to use surface water sources in addition to the ground water wells. The city began its plan to protect, preserve and expand its supply of potable water by constructing a filtration plant.

The new treatment plant was designed to service 200,000 people and treat 50 millions gallon per day (MGD) of water. After pilot testing many methods, the following treatment train was decided upon: preozonation, coagulation, flocculation, filtration, and chlorination (see Figure 1). The new treatment plant opened in 1997 and met all state and federal requirements.

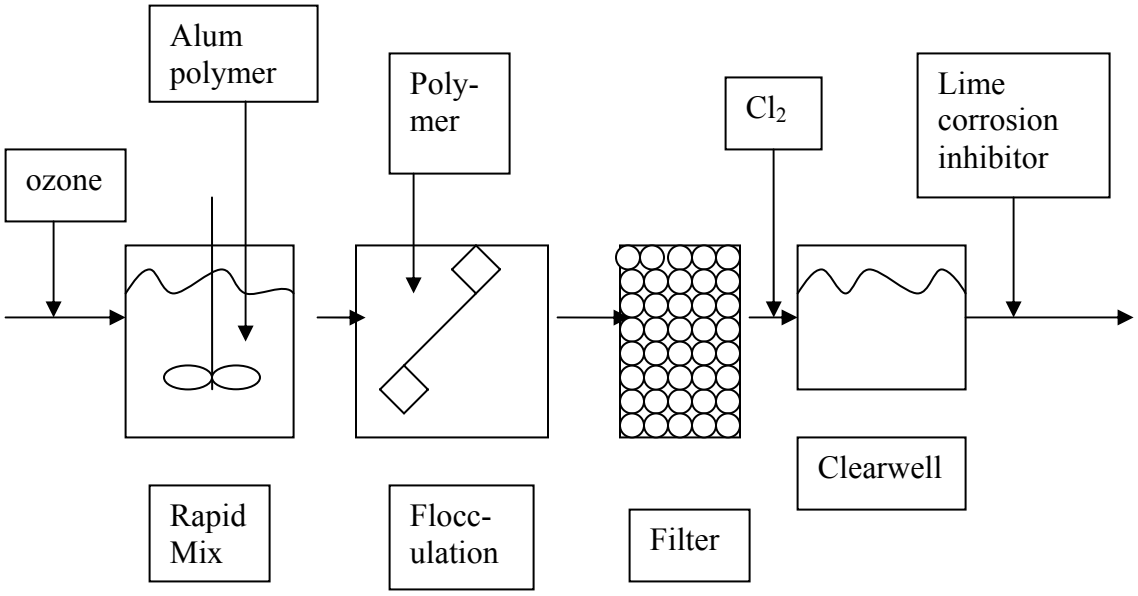

Figure 1: Worcester Water Filtration Plant treatment train.

The Worcester Water Filtration Plant treats approximately 8.8 billion gallons of water per year. The plant obtains its water from both reservoirs and local wells. The majority of the water, 7.4 billion gallons per year, comes from ten separate reservoirs located in Leicester, Paxton, Holden, Rutland, and Princeton. The rest of the city's water is taken from the two wells, one located in Worcester and the other in Shrewsbury.

The Worcester Water Filtration Plant uses ozone as a primary disinfectant. Four ozone generators create the ozone gas on site. The next treatment step is coagulation and rapid mixing. Rapid mixing is performed in two-stages, using vertical shaft turbine mixers. Aluminum sulfate (alum) and a cationic polymer are coagulant chemicals that are added during the rapid mix process. The third step in Worcester's water treatment system is flocculation. Flocculation involves three stages each with a detention time of 15 minutes, that use vertical-shaft, axial-flow flocculators. A nonionic polymer is added during the flocculation step to make the filtration step run more effectively. The fourth step in the treatment train is direct filtration through eight filters. The filters are designed to have a filtration rate of eight gallons per minute per square foot. The filters are composed of 60 inches of anthracite coal over 12 inches of sand. Following filtration, a chlorine disinfectant is added to the water supply. Chlorine is a both a primary and a secondary disinfectant in the treatment plant. The plant receives CT credit for the contact time of chlorine with the water from the point of application through the clearwells (two 2.75 million gallon storage tanks). After the clearwells, the pH is adjusted with lime and an orthophosphate corrosion inhibitor is added.

2.7.1 Disinfection By-products in Worcester

Trihalomethanes and haloacetic acids are measured in Worcester by collecting and analyzing eight water samples taken each quarter at specified sites in the distribution system. Compliance with the regulated MCLs is calculated by a running average of samples collected over four quarters. Since the treatment plant opened in 1997, the concentration of TTHMs in the water has been reduced by 30% compared to the levels when a disinfected ground water with no additional treatment was used. Table 9 shows TTHM and HAA concentrations in the distribution system in 1999.

Table 9: DBP levels for Worcester in 1999 (Source: City of Worcester 2001 Water Quality Report)

Contaminant	Annual running average (µg/L)	Range of levels detected for all samples (µg/L)	Maximum contaminant level (MCL) (µg/L)
Total Trihalomethanes	46.1	11 - 88	80
Haloacetic Acids	20.7	ND - 48.9	60

The plant currently meets the MCLs for TTHMs or HAAs; however future regulations as well as changes to source water quality may create problems with meeting DBP rules with using free chlorine for disinfection. Since the stricter regulations may require a change in disinfection, this research was conducted to examine chloramination as an alternative to the disinfection system that the Worcester Water Filtration Plant has in place today.

3.0 Methodology

The goal of this research was to find the optimum conditions for chloramination at the Worcester Water Filtration Plant in order to reduce trihalomethane formation. This chapter explains the experimental plan and how each experiment was conducted. This chapter also explains the analytical procedures that were used in the experiments.

3.1 Experimental Plan

This first section of the methodology provides a brief description of the current disinfection practices at the Worcester Water Filtration Plant and explains how chloramines could be used instead. Then the variables tested in the experiments and the experimental procedures are discussed.

3.1.1 Current Treatment

The Worcester Water Filtration Plant uses a combination of ozone treatment and free chlorine to disinfect their water source. The treatment train includes ozonation, rapid mixing, flocculation, filtration, and chlorination. The Worcester Water Filtration Plant receives part of their CT credit from ozonation and part of their CT credit from chlorination.

Numerous research studies (as shown in sections 2.3.1 and 2.6.2) have shown that using ammonia with chlorine produces fewer DBPs compared to using free chlorine to disinfectant drinking water. Although the treatment plant receives CT credit when it disinfects with chlorine, switching to chloramines would help reduce DBP levels and therefore a change in the disinfection practices may be warranted. The filtration plant has

two clearwells approximately 3500 ft from the treatment plant. If ammonia is added after the clearwells, the plant will still receive the same CT credit for chlorine. However, if ammonia is added before the clearwells, a change in the ozonation process may be needed to meet disinfection regulations.

The Worcester Water Filtration Plant operates two clearwells that can store 5.5 million gallons of water at the maximum elevation. Normally the clearwells hold between 4.5 and 5.0 million gallons of water (average of 4.75 million gallons). Running from the treatment plant to the clearwells are two pipes, each with a radius of 2 feet. The pipes are 3500 feet long each. The treatment plant has an average flow of 21.4 million gallons per day. To calculate the residence time it takes for the water to travel from the filtration plant to the clearwells, the following equations were used:

$$\text{Residence Time} = \frac{\text{Volume}}{\text{Flow}}$$

$$\text{Volume} = 4.75\ \text{MG} + (\pi \times (2\text{ft})^2 \times 3500\text{ft}) \times 2$$

$$\text{Volume} = 4.75\ \text{MG} + 87{,}965\ \text{ft}^3 \times 7.48\ {}^{\text{gal}}\!/_{\text{ft}^3} \times {}^{\text{MG}}\!/_{10^6\ \text{gal}} = 5.41\ \text{MG}$$

$$\text{Residence Time} = \frac{5.41\ \text{MG}}{21.4\ \text{MGD}} = 0.25\ \text{days} = 6\ \text{hours}$$

The residence time it takes for the water to travel from the filtration plant through the pipes and the clearwells is 0.25 days or 6 hours. Therefore, in order to preserve the current treatment practice of obtaining CT credit through the clearwells, ammonia would need to be added six hours after the addition of free chlorine.

3.1.2 Experimental Variables

As DBP production depends on many disinfection parameters, the experiments were designed to test several variables including pH, residence time and chloramination conditions. Table 10 shows the variables that were tested in the experiments and provides a brief description of why those variables were chosen. pH values were tested between 6 and 10, because previous research has shown that trihalomethane production is minimized at lower pH conditions. The pH of the water at the filtration plant as it leaves the filters but before chlorination was 7.5. This pH, as well as a higher pH and a lower pH condition, were tested. Researchers have shown that contact time with a disinfectant in the distribution system can cause THMs to increase, so residence times were tested. Residence times from 3 hours to 54 hours were chosen because these times were representative of distribution system residence times at locations used for regulatory testing. For chloramination, chlorine to nitrogen ratios of 2:1 to 7:1 were used because previous research has shown that these ratios have reduced THM formation compared to free chlorine.

Table 10: Experimental variables

Variable	Range of Variables	Comments
pH	6 to 10	Based upon previous research
Time (hours)	0 to 54	Shows peak values of TTHMs
Chlorine to Nitrogen Ratio	0 to 7:1	Compare THM formation from free chlorine and chloramines
Time of Ammonia Addition (hours) after chlorine addition	0 to 6	Decreasing the time before ammonia addition decreases the time free chlorine is permitted to react with the water

In the first two sets of experiments, ammonia was added six hours after the addition of chlorine. These experiments provided data on THM formation if the treatment plant wished to continue free chlorination through the clearwells. In the last set of experiments, ammonia was added simultaneously with or three hours after the addition of chlorine to determine if additional THM reductions could be achieved by changing the free chlorine contact time at the plant.

3.1.3 Experimental Procedure

Water was obtained from the Worcester Water Filtration Plant at the point in the treatment train after filtration but before chlorination and brought to Worcester Polytechnic Institute's (WPI) Environmental Engineering laboratory. The water was separated into three samples and the pH was adjusted for each sample using 0.1 N sodium hydroxide or 0.1 N hydrochloric acid. The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured.

Chlorination and/or chloramination was conducted in chlorine demand free 300 mL BOD bottles. The BOD bottles were filled 2/3 full with the sample water and then chlorine was added to all bottles. The chlorine concentration in use at the treatment plant was used. Ammonia was added only if the free chlorine contact time was zero hours. The BOD bottles were then filled the rest of the way and capped headspace free. The samples were then stored in the dark at the temperature of the water at the plant at the time of the experiment.

Six hours after chlorine addition (or 3 hours for the last set of experiments), one BOD bottle was taken out of incubator and was used to determine the free chlorine residual. Duplicate 40 mL samples were also taken from this BOD bottle, quenched with

sodium thiosulfate and stored in sulfuric acid washed 40 mL vials at 4°C. These duplicate samples were later used to determine the TTHMs formed during the free chlorine reaction time. The ammonia concentration to be added for chloramination was then determined based on the free chlorine residual and the chlorine to nitrogen ratio. The corresponding ammonia dosage was added the appropriate BOD bottles (see section 3.2.3) and they were placed back in the incubator.

After the appropriate reaction period, BOD bottles were removed from the incubator for analysis and preservation. Duplicate samples of each BOD bottle were quenched with $Na_2S_2O_3$ and stored in acid washed 40 mL vials for TTHM analysis. The quenched samples were stored for up to two weeks in the dark at 4º C in the refrigerator. In addition, free and total chlorine residual and the pH of each sample was measured.

3.2 Analytical Methods

This section provides detailed methods used in the experiments and discusses how total trihalomethanes were analyzed.

3.2.1 Glassware

For each sample, one chlorine demand free BOD bottles was required. The BOD bottles were soaked in a 100 mg/L chlorine bath for a minimum of one hour and rinsed five times with Epure water immediately before use.

For each sample, two 40 mL vials were used for quenching and storing the duplicate samples prior to trihalomethane analysis. The 40 mL vials were placed in a 20% sulfuric acid bath for one hour. The vials were then rinsed with Epure water and

placed in the oven to dry at 105 ºC for one hour. The vials were cooled in an organic free area. The vials were capped and stored until they were used.

For each set of data, four 40 mL vials were used to determine the total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations of the water sample. The four 40 mL vials were acid washed in a 20% sulfuric acid bath for one hour. The vials were cleaned in the same manner as the vials used for THM analysis.

3.2.2 Chlorine Calibration Curve and Chlorine Residual

A chlorine calibration curve was created to provide a relationship between chlorine concentration and absorbance measured using a spectrophotometer. The chlorine calibration curve was produced using both the Ferrous Titration Method (4500-Cl F) and DPD colorimetric Method (4500-Cl G) (APHA *et al.*, 1998). Chlorine residuals were then determined by measuring absorbance and calculating concentration from the calibration curve.

3.2.2.1 Chlorine Calibration Curve

The chlorine calibration curve was produced using a Cary 50 Scan (Varian Australia Pty Ltd., Mulgrave, Victoria, Australia) set to a wavelength of 515 nm. Fifteen volumetric flasks and fifteen Erlenmeyer flasks were taken out of the 100 mg/L chlorine bath (where they had been soaking for at least one hour) and rinsed five times each with Epure water. The flasks were split into three groups of five flasks each for free chlorine, monochloramine, and dichloramine measurements. Each volumetric flask was filled with 100 mL of Epure water and labeled one through five. For the free chlorine group, each Erlenmeyer flask received 5 mL of DPD buffer solution followed by 5 mL of DPD indicator solution. For the monochloramine group, each Erlenmeyer flask received one

small crystal of KI (potassium iodide), 5 mL of DPD buffer, and 5 mL of DPD indicator solution. For the dichloramine group, each Erlenmeyer flask received one gram of KI, 5 mL of DPD buffer and 5 mL of DPD indicator solution.

For the free chlorine group, a 10 µL syringe was used to transfer approximately 1 µL (exact volume recorded) of chlorine stock to the first volumetric flask. The contents of the volumetric flask were then poured into the corresponding Erlenmeyer flask that already contained the DPD buffer and indicator solutions. The contents of the Erlenmeyer flask would then turn pink, with the presence of chlorine. A small sample from the Erlenmeyer flask was poured into a spectrophotometer cell and the cell was placed in the spectrophotometer to obtain an absorbance reading.

Right after finding the absorbance, the contents of the cell were poured back into the Erlenmeyer flask. A magnetic stir bar was placed in the Erlenmeyer flask and it was placed on a magnetic stir plate. The sample was titrated with Ferrous Ammonium Sulfate (FAS) solution until the contents of the Erlenmeyer flask became clear. The volume of FAS used was recorded. The chlorine concentration in the original chlorine stock was calculated using the following equation:

$$100 \times \frac{FAS(mL)}{volume\ of\ \ chlorine\ stock(\mu L)} = Chlorine\ concentration\left(\frac{mg}{mL}\right)$$

The concentration of chlorine in the volumetric flask was also determined based on the volume transferred to the volumetric flask.

This technique was repeated for the five free chlorine volumetric flasks. Flasks 2-5 received increasing larger volumes of the chlorine stock solution (up to approximately 5 µg/L). The entire process was then repeated for the monochloramine and dichloramine flasks. Using a spreadsheet, three different calibration curves were created, by plotting

the chlorine concentration in the volumetric flasks on the vertical axis and the absorbance values found on the horizontal axis. Trendlines were found for each calibration curve, as well as the correlation factor (R^2) for each trendline. The calibration curves were then used to determine chlorine residual concentrations from the BOD bottle.

3.2.2.2 Chlorine Residual Measurements

Free chlorine, monochloramine and dichloramine residual concentrations were measured in the BOD bottles at the time that samples were preserved for THM analysis. The procedure used was an adaptation of Standard Method #4500 – Cl G (APHA *et al.*, 1998).

The Cary 50 Scan (Varian Australia Pty Ltd., Mulgrave, Victoria, Australia) was set to a wavelength of 515 nm. For each sample, three test tubes were taken out of the 100 mg/L chlorine bath (after soaking in the bath for at least one hour) and rinsed five times with Epure water. For the free chlorine residual measurement, 0.5 mL of DPD buffer solution, 0.5 mL of DPD indicator solution and 10 mL of the sample were added to a test tube. For the monochloramine and dichloramine residual measurements, 1 small crystal and 0.1 g of KI were also added to the test tubes, respectively. For the free chlorine and monochloramine residual measurements, the test tube contents were poured immediately into a spectrophotometer cell and the absorbance value was measured. For the dichloramine residual measurement, a two minute reaction period was allowed before the absorbance reading. The concentration of free chlorine, monochloramine or dichloramine was calculated from the equation of the corresponding chlorine calibration curve.

3.2.2.1 DPD Buffer and Indicator Solutions

The DPD buffer and indicator solutions were both used to create chlorine calibration curves and measure chlorine residuals. The buffer solution was prepared according to Standard Method #4500 Cl F (APHA *et al.*, 1998) by dissolving 24 grams of anhydrous Na_2HPO_4 and 46 grams of anhydrous KH_2PO_4 in Epure water. This solution was then mixed with 100 mL Epure water, to which 800 mg of disodium ethylenediamine tetraacetate dihydrate (EDTA) was added. This mixture was diluted to one L with Epure water. The DPD buffer solution was stored at 4˚C and had a shelf life of three months.

The DPD indicator solution was purchased from a supplier (DPD Solution APHA, LabChem Incorporated, Pittsburgh, PA). The DPD indicator solution was stored at 4˚C and was used for two months.

3.2.2.2 Ferrous Ammonium Sulfate

Ferrous Ammonium Sulfate (FAS) was used to titrate samples to form chlorine calibration curves and determine the concentration of chlorine in the stock solution. The solution was prepared according to Standard Method #4500 Cl F (APHA *et al.*, 1998). FAS was prepared by dissolving 1.106 grams $Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$ in Epure water that already had 1 mL of 1 + 3 H_2SO_4, to a total volume of one liter. The FAS mixture was stored at 4˚C and had a shelf life of one month.

3.2.3 Ammonia Dosing

The average chlorine dosage that was used by the Worcester Water Filtration Plant was 2.6 mg/L for the first set of experiments, 2.2 mg/L for the second set of experiments and 2.75 mg/L for the third set of experiments. The ammonia dosage was calculated from chlorine to nitrogen ratios using the chlorine residual found at the time of

ammonia dosing. Chlorine to nitrogen ratios of 2:1, 3:1, 4:1, 5:1 and 7:1 were used in this research. The chlorine to nitrogen ratios are mass ratios of chlorine to ammonia-N. For the 2:1 ratio (when the ammonia was added at time = 0 and the chlorine dosed at 2.6 mg/L), 1.3 mg/L of ammonia was added using $(NH_4)_2SO_4$, therefore 12.27 mg/L of $(NH_4)_2SO_4$ was needed as shown in the calculation below:

$$1.3\ mg/L\ NH_3 - N \times \frac{132.14\ (NH_4)_2 SO_4}{14\ g\ NH_3 - N} = 12.27\ mg/L$$

A 5 g/L concentration of the stock $(NH_4)_2SO_4$ was made. To determine the volume of stock $(NH_4)_2SO_4$ required for each BOD bottle, a mass balance equation was used. For example for the 12.27 mg/L ammonia dose in a 300 mL bottle, 0.736 mL (or 736 µL) of stock was need:

$$C_{Stock} V_{Stock} = C_{BOD\ bottle} V_{BOD\ bottle}$$

$$5000 \frac{mg}{L} \times V_{Stock} = 12.27 \frac{mg}{L} \times 300\ mL$$

$$V_{Stock} = 736\ \mu L$$

3.2.4 Quenching Solution

A quenching solution of sodium thiosulfate ($Na_2S_2O_3$) was made to preserve the samples after they had been disinfected. EPA method 624 was followed. This method states that 3 mg of sodium thiosulfate per 40 mL will quench 5 mg/L of chlorine. The sodium thiosulfate stock was prepared at a concentration of 6 g/L. 40 mL vials were used to store the samples after they had reacted in the BOD for the designated residence times. Therefore the quantity of sodium thiosulfate to add to each vial was calculated based upon the volume of 40 mL and found to be 0.5 mL:

$$Volume_{Stock} \times Concentration_{Stock} = Volume_{Vial} \times Concentration_{Vial}$$

$$6000\frac{mg}{L} \times Volume_{Stock} = \frac{3\ mg}{40\ mL} \times 40\ mL$$

$$V_{Stock} = 0.5\ mL$$

3.2.5 Total Organic Carbon and Dissolved Organic Carbon

The total and dissolved organic carbon concentrations were measured with a Shimadzu TOC-5000A Analyzer (Shimadzu Corporation: Process and Environmental Instrumentation Division, Nakagyou-Ku, Kyoto, Japan). Prior to use, the TOC/DOC vials were washed in a 20% sulfuric acid bath, rinsed with Epure water and dried in an oven set to 105ºC. For TOC analysis, a 20 mL sample was collected and acidified with 100 µL of 6N HCl. The TOC vials could be stored for up to two weeks at 4ºC before they were analyzed. For DOC measurement, the samples were filtered through a Whatman GF/C glass fiber filter with a 1.2 µm retention (Whatman International Ltd., Maidstorne, England) prior to acidification with 6N HCl. A calibration curve was created consisting of TOC standards (5, 2, and 0 mg/L) made from Potassium Hydrogen Phthalate (KHP). The TOC and DOC samples were then measured and compared to the calibration curve. The instrument was run in NPOC mode with the sparge turned on for three minutes. The gas used throughout the analysis was "Ultra Zero" grade air.

3.2.6 pH Measurement

The pH of the water taken from the Worcester Water Filtration Plant was measured and adjusted prior to the addition of chlorine with an Orion 420A pH meter (Orion Research Incorporated, Beverly, MA). At the time that each sample was quenched, the pH was measured again using the Orion 420A pH meter. The pH meter

was calibrated, before each time that it was used, with buffers of pH 4.01, 7.00 and 10.01. To measure the pH of a sample, the pH probe was inserted into the sample. When the Orion 420A pH meter had beeped (pH had equalized) the value displayed on the screen was recorded as the pH of the sample. Epure water was used to rinse off the pH probe before and after each usage. The procedure for measuring pH is an adaptation of Standard Methods #4500 - H^+B (APHA *et al.*, 1998).

3.2.6 Total Trihalomethane Analysis

The standard procedure for TTHM analysis used at the Worcester Water Filtration Plant was used to determine THM concentrations in this research. This procedure is a modification of EPA method 524.2 for Purgeable Organic Compounds in Drinking Water.

All analyses were performed on an HP 5890 series II gas chromatograph interfaced with an HP mass spectrometer (MSD 5972) at the water treatment plant in Holden, MA. The samples were purged on a HP Purge and Trap system that desorbed the sample components directly onto a narrow bore capillary column. Other equipment/apparatus that were needed are as follows:

- Helium gas (set at 40 psi)
- 40 mL sample bottles with Teflon caps
- 104ºC oven
- heated distilled deionzed water
- heated 1000 mL beaker
- 80 mL beaker
- 5 mL gastight #1005 Purge & Trap syringe/injector
- 10 µL syringe
- Internal standards with Bromofluorobenze (BFB)
- TTHM standard

The helium gas was turned on. A one liter beaker was heated in the 104ºC oven while the samples were being prepared. The one liter beaker was removed from the oven, filled with organic free distilled deionized water and returned to the oven. Before any samples were purged, the system had to be "baked out" to minimize any contamination that might be introduced into the system while it lay idle. The trap baked for ten minutes at 270˚C before it cooled down; at that time it was ready to be used.

Using the gastight syringe, 5 mL of hot water was pulled from the 1000 mL beaker into the syringe 3 to 5 times. A small portion of the sample was poured into a freshly cleaned 80 mL beaker, swirled around to cover all sides of the beaker, and then was disposed. About 20 mL of the sample was poured into the pre-rinsed 80 mL beaker. 2 ½ mL of the sample was pulled into the gastight syringe and ejected. This step was repeated two times. More than 5 mL of the sample was pulled into the gastight syringe. The extra sample was dispelled from the syringe until exactly 5 mL remained. This was done to help eliminate/reduce air bubbles present in the syringe. The gastight syringe was pulled back ½ mL, which created a vacuum in the syringe.

The internal standard with BFB and DCB was prepared with 0.25 mL of Fluorobenzene (at 2000 ppb), 0.25 mL 4-Bromofluorobenze (at 2000 ppb), 0.25 mL 1-2 Dichlorobenzene (at 2000 ppb) and 50 mL deionized water. The purpose of the internal standard was to give the GC a baseline to use to identify the THMs. The 10 µL syringe was rinsed five times with the internal standard. More than 5 µL of the internal standard was pulled into the 10 µL syringe with no air bubbles. The extra internal standard was dispelled until exactly 5 µL was left. The 10 µL syringe was injected all the way into the opened gastight syringe, dispensing the internal standard. The gastight syringe valve was

closed and the gastight syringe inverted several times to mix the internal standard with the sample. The ½ mL of air from the gastight syringe was dispelled. The valve on the HP purge and trap machine was opened. The gastight syringe was turned to the open position and the sample was injected into the purge and trap machine. The valve of the purge and trap machine was turned off and the gastight syringe was pulled away.

The GC-MS was controlled by software. The software allowed the user to input a unique data file name for each sample. The GC-MS has an injector temperature of 120 ˚C. The oven temperature ramping program started at 40˚C, and then the temperature ramped up at a rate of 8˚C/minute until it reached a final temperature of 180˚C. The ramping program for the pressure of the GC-MS increased at 12 psi/minute until it reached 12 psi. A 624 fused silica capillary column was used for the TTHM analyses. A description of the column used can be found in Table 11. Identification of THM compounds in each sample was based on mass spectroscopy while concentrations were determined by comparison of GC response to prepared calibration curves. Analysis was performed automatically by the GC-MS software.

Table 11: GC-MS column details

HP part number	**19091V – 402**
Length	30 m
Diameter	0.25 mm
Film thickness	1 μm
Initial flow	0.7 mL/minute
Average velocity	37 cm/s
Gas	He
Vacuum compensation	on

4.0 Results

The goal of this research was to determine the effect of chloramination versus free chlorine on the formation of trihalomethanes at the Worcester Water Filtration Plant. This chapter shows the data obtained from this study. After researching DBP formation, it was found that several conditions affect the level of TTHMs. This study examined differing temperatures, pH values, residence times and chlorine to nitrogen ratios on THM formation. The experiments tested pH values ranging from approximately 6 to 10, residence times from 3 hours to 54 hours, and chlorine to nitrogen ratios ranging from no nitrogen to a mass ratio of 7:1. The experiments were conducted in December of 2001, April of 2002, and February of 2003. The water temperatures at the treatment plant at these three times were used; therefore the impact of temperature and season could be evaluated. Trihalomethanes were measured by a gas chromatograph in duplicate. Tabulated results can be found in Appendix A.

4.1 December 2001

In December of 2001, the first set of experiments began. Water samples were obtained from the Worcester Water Filtration Plant after filtration but prior to chlorination. The water temperature was 7°C. The total organic carbon concentration was 2.97 mg/L and the dissolved organic carbon concentration was 2.72 mg/L. The water was chlorinated in Worcester Polytechnic Institute Environmental Engineering laboratory at 2.6 mg/L (the chlorine dose used at the filtration plant) and allowed to react for six hours. The chlorine was allowed to react for six hours because that is the average residence time of the water from the point of chlorination in the treatment plant through

the clearwells (refer to section 3.1.1). The plant receives CT credit from this six hour period of disinfection with chlorine. After the water had been chlorinated for six hours, ammonia was added to the samples that were designed to use chloramination as their secondary disinfectant. The amount of ammonia added varied between chlorine to nitrogen ratios of 2:1 and 7:1. Residence times of 6, 18, 30 and 54 hours were tested. In addition, pH was varied from 6.4 to 9.5 for samples with a 30 hour residence time. The samples were preserved in duplicate at their respective residence times by quenching with sodium thiosulfate, and trihalomethane concentrations were measured within two weeks. Average results for each condition are presented in this section.

Figure 2 shows the trihalomethane formation for various pH conditions at a residence time of 30 hours and a chlorine to nitrogen ratio of 3:1. As discussed above, this time period includes 6 hours of free chlorine and 24 hours of chloramination. At pH 6.8, the chloroform concentration was 12.8 μg/L, the bromodichloromethane concentration was 2.9 μg/L and the dibromochloromethane concentration was 0.2 μg/L. Chloroform was the most prevalent trihalomethane formed: its concentration was approximately 4 times greater than bromodichloromethane. In addition, as the pH of the water sample increased, the trihalomethane levels also increased. The TTHM concentration at pH 6.5 was 10.6 μg/L, while the TTHM concentration at pH 9.2 was 41.1 μg/L. This represents a 290% increase in the TTHM concentration for a 2.7 unit increase in pH. Results for free chlorine and the chloramination ratio of 5:1 showed the same trends: chloroform was the predominant THM and TTHM formation increased with increasing pH (see Appendix A). The relationship between pH and TTHM production has been shown repeatedly in previous research. For example, Diehl *et al.* (2000)

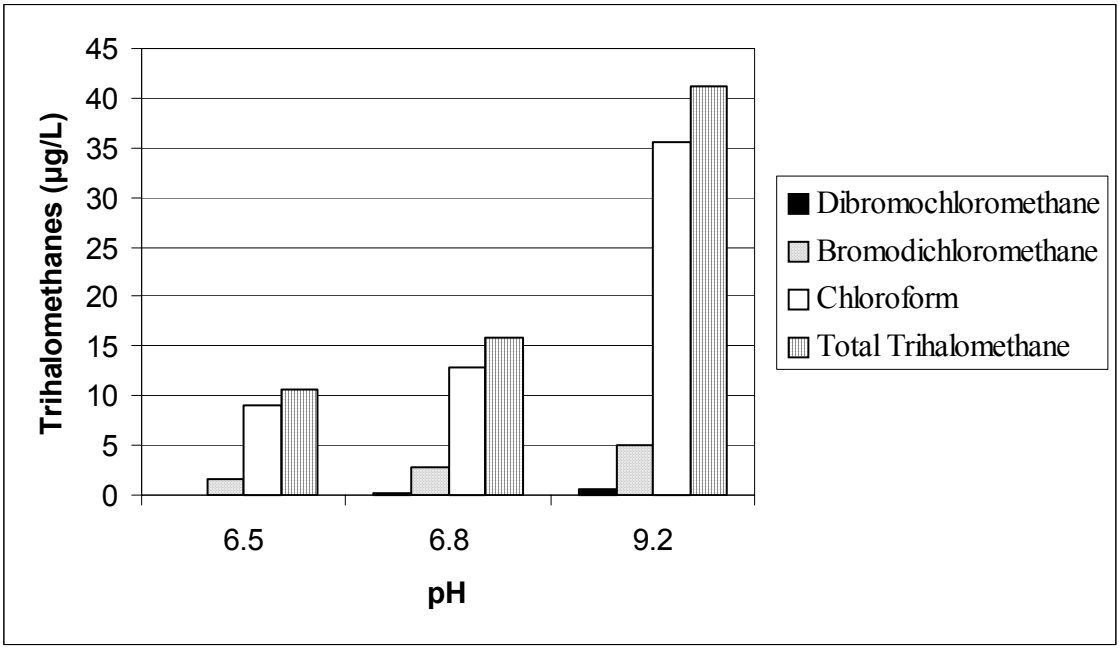

Figure 2: Dec. 2001- THM distribution for various pH conditions at t=30 hours and a chlorine to ammonia ratio of 3:1.

measured TTHM concentrations at pH values of 6, 8 and 10. They found that as pH increased, TTHM concentrations also increased.

The second combination of data examined in this experiment showed trihalomethane levels with respect to residence time at a pH of approximately 7.0 and a chlorine to nitrogen ratio of 3:1. The first six hour reaction period was with free chlorine. This data is shown in Figure 3. Total trihalomethane levels were greatest at the 30 hr residence time. The graph also shows that most of the trihalomethanes were formed in the first six hours. The total trihalomethane concentration after 6, 18, and 30 hours was 14.1 µg/L, 14.0 µg/L and 15.9 µg/L, respectively. There was no increase from 6 hours to 18 hours and a 13.6% increase in THM concentration from 18 hours to 30 hours. Similar results were found when using free chlorine and chlorine to nitrogen ratios of 2:1, 5:1 and

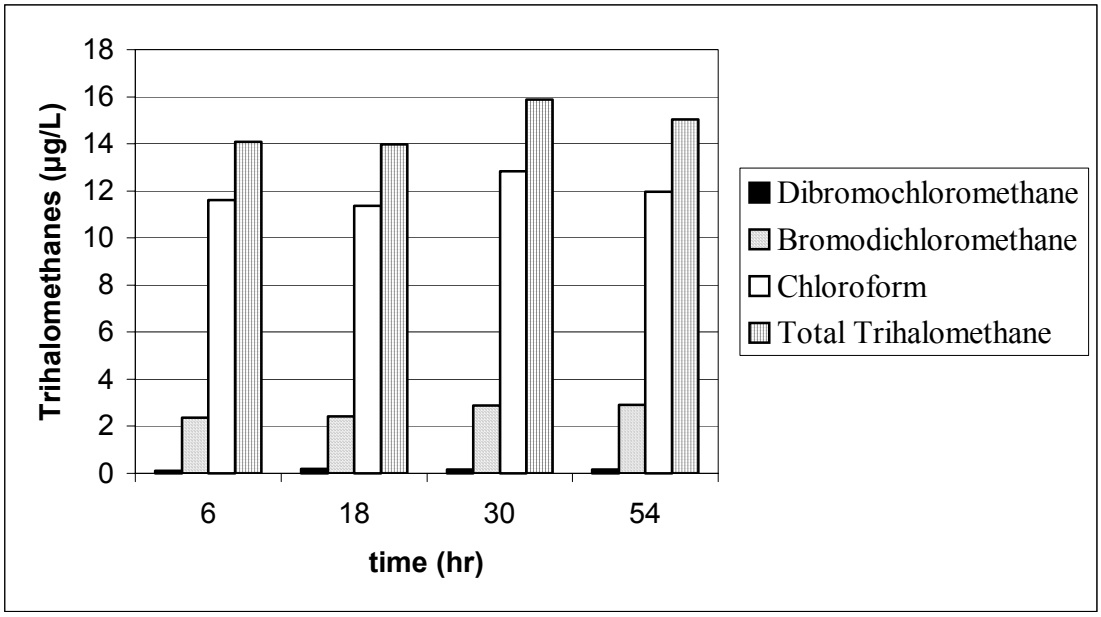

Figure 3: Dec. 2001-THM distribution versus time at pH 7.0±0.3 and a chlorine to ammonia ratio of 3:1.

7:1. Most TTHM formation occurred in the first six hours with only minor changes in concentrations from 6 to 54 hours.

The third combination of data obtained from the experiments run in December of 2001 was a relation between total trihalomethane levels and chlorine to nitrogen ratios. Again, a six hour free chlorine period proceeded chloramination. These experimental results for a 30 hour residence time are shown in Figure 4. The concentration of TTHMs at chloramination ratios of 2:1, 3:1, 5:1, and 7:1 were 16.1 µg/L, 15.9 µg/L, 18.3 µg/L and 17.8 µg/L, respectively. The two lowest ratios resulted in similar TTHM formation; however there was an increase of 15.1% from the ratio 3:1 to the ratio 5:1. Although there were differences in total THM concentrations for the 4 chlorine to ammonia ratios, there was only a 2.4 µg/L difference between the lowest and highest concentrations. Therefore, all four chloramination ratios were comparable. When using free chlorine at a

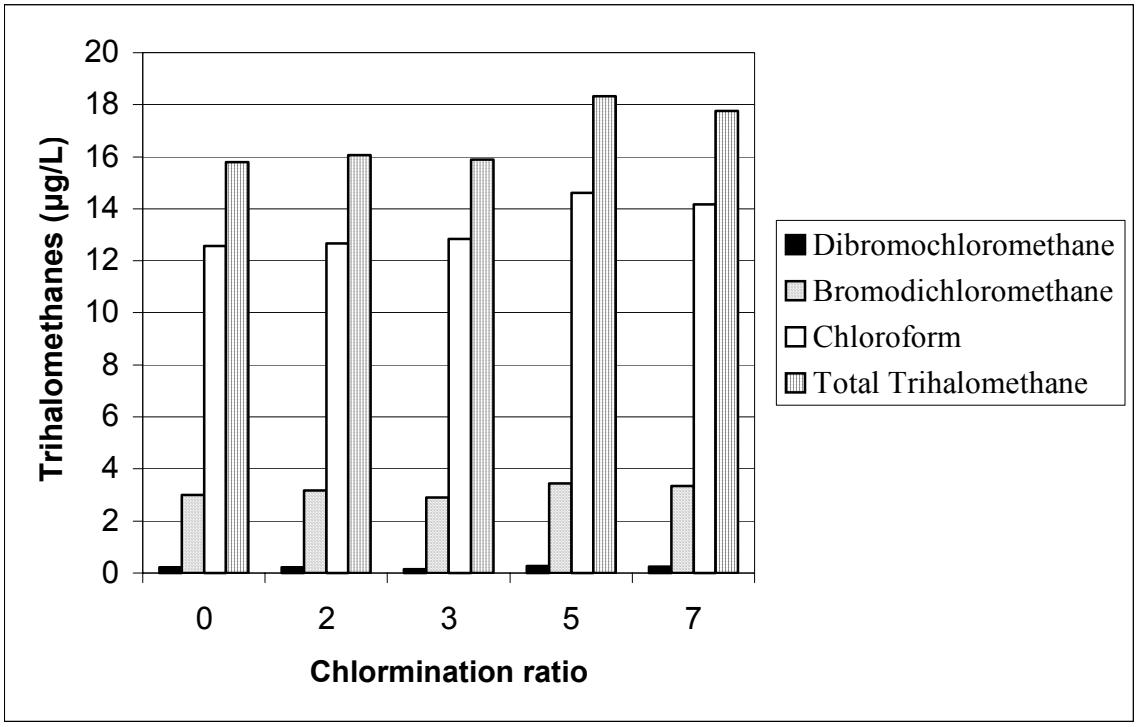

Figure 4: Dec. 2001-THM distribution versus chlorine to ammonia ratios at t=30 hours and a pH of 7.2±0.4.

residence time of 30 hours, the trihalomethane concentrations were similar to the TTHM concentrations of the samples that used chloramines as a disinfectant.

Table 12 shows TTHM concentrations (in µg/L) with respect to free chlorine versus chloramination and residence times. In the first six hours at a pH of approximately 7.0, 14.1 µg/L of TTHMs was formed for all samples as all samples had a free chlorine reaction time of six hours. For the sample with only free chlorine, the TTHM concentration continued to rise with time, reaching 23.9 µg/L after 54 hours. Using nitrogen in combination with chlorine had a positive effect on lowering the concentration of TTHMs compared to free chlorine. At a residence time of 54 hours, the trihalomethane concentrations for chloramines were 8.4 – 9.7 µg/L lower than the TTHM

Table 12: Dec. 2001 - concentrations of TTHMs (in µg/L) at varying residence times and varying chlorine to nitrogen ratios, at pH 7.2±0.5

	6 hours	6+12=18 hours	6+24=30 hours	6+48=54 hours
Free Chlorine	14.1	17.5	15.8	23.9
Ratio 2:1	14.1	20.9	16.1	15.5
Ratio 3:1	14.1	14.0	15.9	15.0
Ratio 5:1	14.1	14.0	18.3	14.4
Ratio 7:1	14.1	16.0	17.8	14.2

concentrations of the samples using free chlorine. These reductions represent a 35 to 41% decrease in TTHM formation when chloramines were used instead of free chlorine.

4.2 April 2002

In April of 2002, a second set of experiments was conducted that had an identical experimental plan as the December 2001 experiments. All chloramination samples had a free chlorine reaction period of six hours prior to the addition of ammonia. The second set of experiments was completed to determine the effects of temperature and season on TTHM concentrations. However, the water temperature did not change significantly between December (7°C) and April (9°C). The chlorine dose however did change from 2.6 mg/L in December to 2.2 mg/L in April. The total organic carbon concentration was not measured in April of 2002.

Figure 5 shows the trihalomethane distribution versus pH at a time of 30 hours and a chlorine to nitrogen ratio of 3:1. At a pH of 6.8, the chloroform,

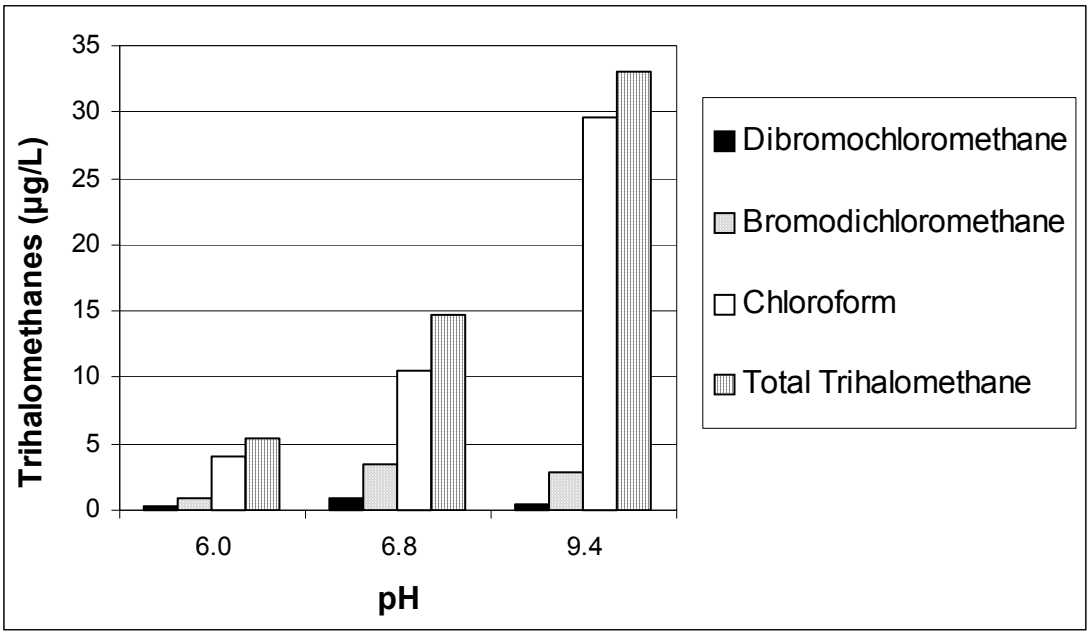

Figure 5: April 2002-THM distribution versus pH at t=30 hours and a chlorine to ammonia ratio of 3:1.

bromodichloromethane and dibromochloromethane concentrations were 10.4 µg/L, 3.5 µg/L and 0.8 µg/L, respectively. The chloroform concentration was nearly 3 times as large as the bromodichloromethane concentration. The TTHM concentration at pH values of 6.8 and 9.4 were 14.7 µg/L and 33.0 µg/L, respectively. There was a 124% increase in TTHM concentration as the pH increased from 6.8 to 9.4. These results show that as the pH increased, the level of trihalomethanes found in the samples also increased. Similar trends were observed in the data for free chlorine and chlorine to nitrogen ratios of 2:1, 5:1 and 7:1. These results were also shown in the December 2001 set of experiments.

The data from April 2002 was also examined to evaluate the trihalomethane distribution versus time at a pH of approximately 7.1 and with a chlorine to nitrogen ratio of 3:1. The results are shown in Figure 6. The majority of trihalomethanes were formed

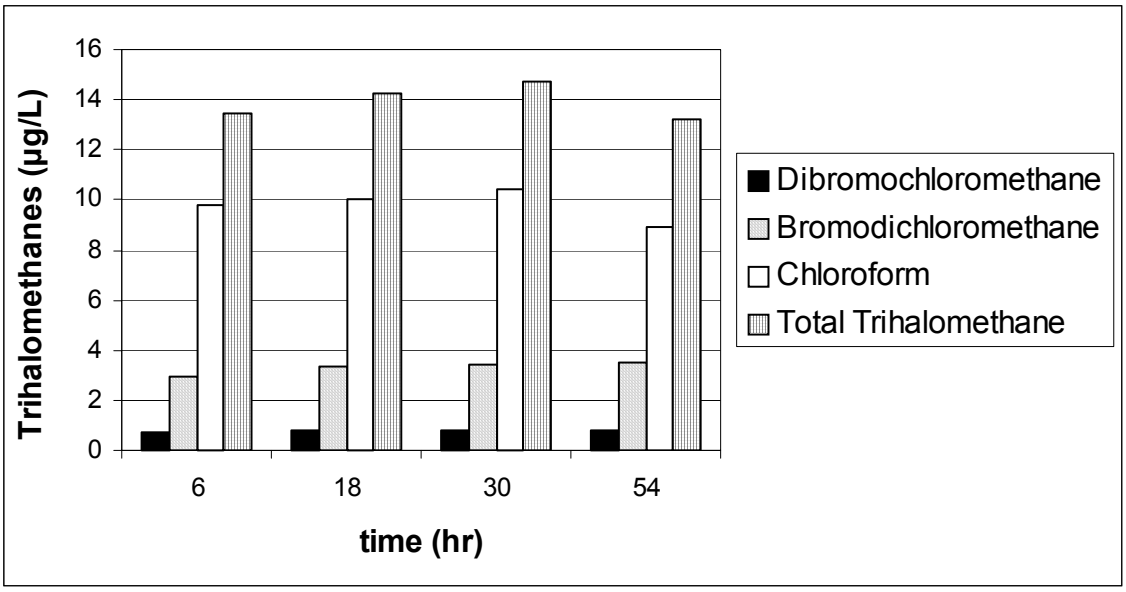

Figure 6: April 2002-THM distribution versus time at pH of 7.1±0.4 and a chlorine to ammonia ratio of 3:1.

in the first six hours. At residence times of 6, 18 and 30 hours, the TTHMs were 13.5 µg/L, 14.3 µg/L and 14.7 µg/L, respectively. This was an increase in TTHMs of 6% from 6 to 18 hours and 9% from 6 to 30 hours. The results also showed that the peak trihalomethane concentration occurred at a residence time of 30 hours. When analyzing data for a chlorine to nitrogen ratio of 7:1, the peak concentration was also observed at 30 hours. However, TTHMs were highest at the 54 hour residence times for free chlorine and chlorine to nitrogen ratios of 2:1 and 5:1.

The data from April of 2002 was analyzed to determine trihalomethane distribution for the different chloramination ratios. These results for a 30 hour residence time are shown in Figure 7. For the four chloramination samples, the total trihalomethanes formed ranged from 11.9 to 16.7 µg/L. Although a definitive trend between THM concentration and chlorine to ammonia ratios was not apparent, all

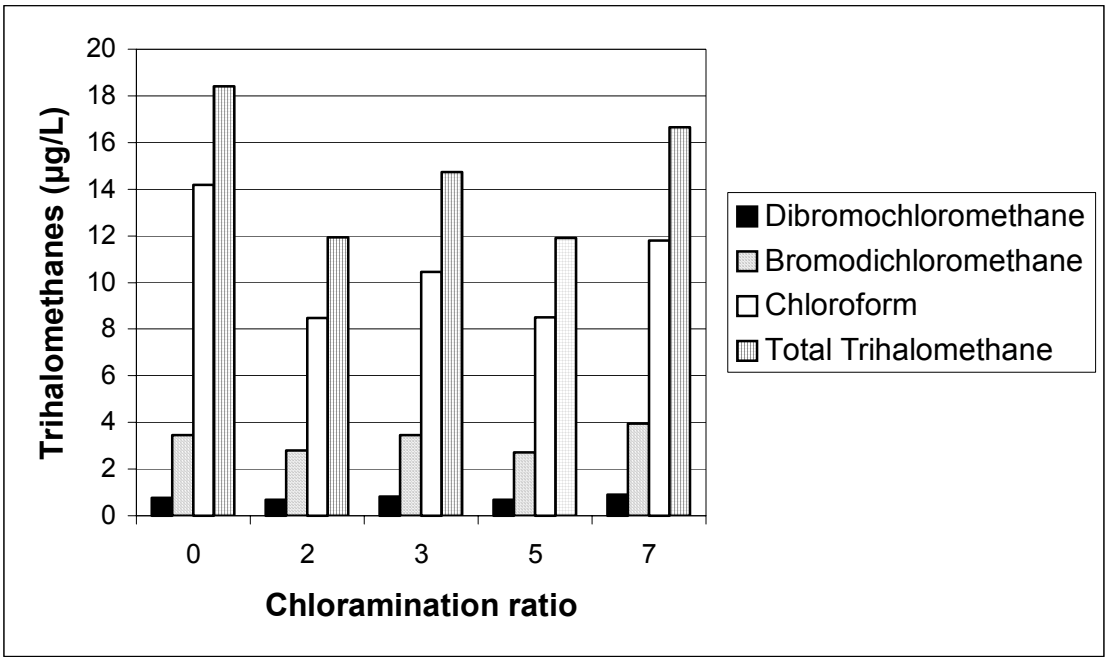

Figure 7: April 2002-THM distribution versus chlorine to ammonia ratio at t=30 hours and a pH of 7.1±0.3.

chloramination samples had lower TTHM concentrations than the free chlorine sample (18.4 µg/L).

Table 13 shows TTHM concentrations with respect to residence times and the chlorine to nitrogen ratios. In the first six hours of the experiment (free chlorine contact time), 13.5 µg/L of TTHMs were formed. Adding ammonia after six hours resulted in lower concentrations of TTHMs compared to the free chlorine samples. At a residence time of 54 hours for free chlorine the TTHM concentration was 21.6 µg/L compared to 13.2 – 14.6 µg/L for the chloraminated samples. This represents a 32% - 39% decrease in TTHMs when using chloramines.

Table 13: April 2002 - concentrations of TTHMs (in µg/L) at varying residence times and varying chlorine to nitrogen ratios, at pH 7.2±0.5.

	6 hours	6+12=18 hours	6+24=30 hours	6+48=54 hours
Free Chlorine	13.5	16.7	18.4	21.6
Ratio 2:1	13.5	13.3	11.9	13.3
Ratio 3:1	13.5	14.3	14.7	13.2
Ratio 5:1	13.5	14.9	11.9	13.7
Ratio 7:1	13.5	14.7	16.7	14.6

4.3 Comparison of December 2001 Results and April 2002

Figures 8 and 9 show that similar results were obtained from the December 2001 and the April 2002 sets of data. Figure 8 is a comparison of the total trihalomethane concentration versus pH for the chloramination samples from these two data sets. At a given pH, relatively the same concentration of total trihalomethanes was observed in both experiments. This figure also further validates the conclusion that as pH increased, the total trihalomethane concentration also increased. THM formation ranged from a low of 5.4 µg/L at pH 6.0 to a high of 41.1 µg/L at pH 9.4.

Figure 9 is a graph of total trihalomethane concentrations formed over time for various chlorine to ammonia ratios and includes data from both December 2001 and April 2002. For free chlorine, the concentration of TTHMs continued to increase with time and resulted in the highest concentration of TTHMs. All of the chloramination ratios produced fewer TTHMs than either of the free chlorine samples at a 54 hour residence time. Figure 9 shows that the samples that used chloramines at a ratio

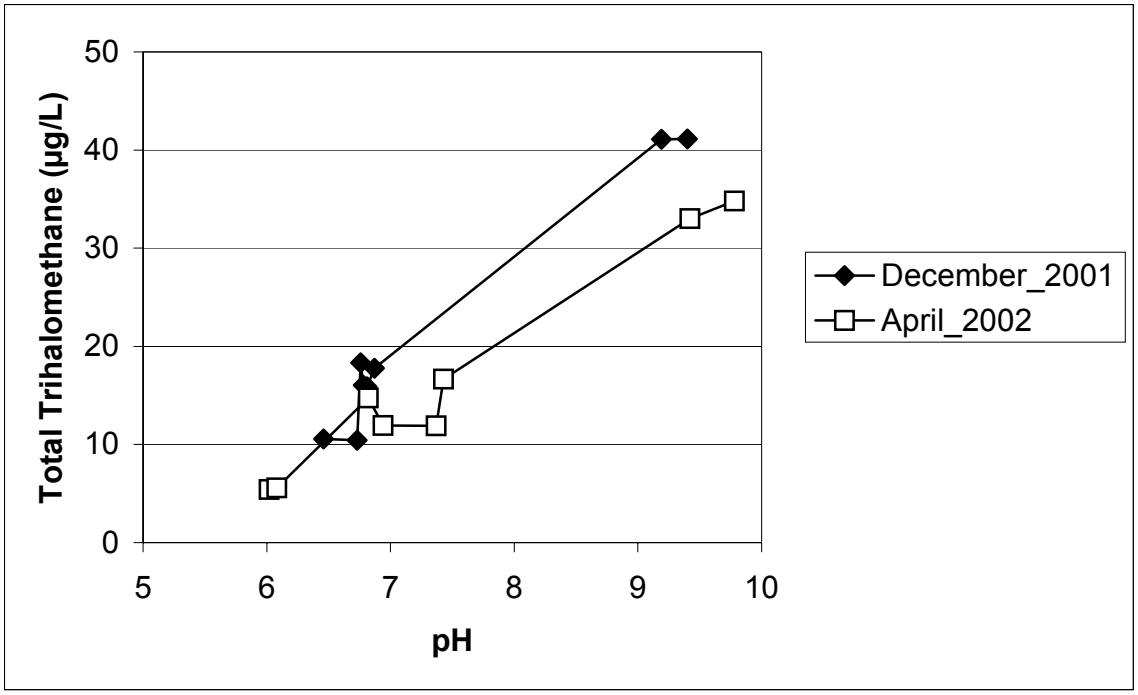

Figure 8: THMs versus pH for Dec. 2001 and April 2002 chloramination samples at t= 30 hours.

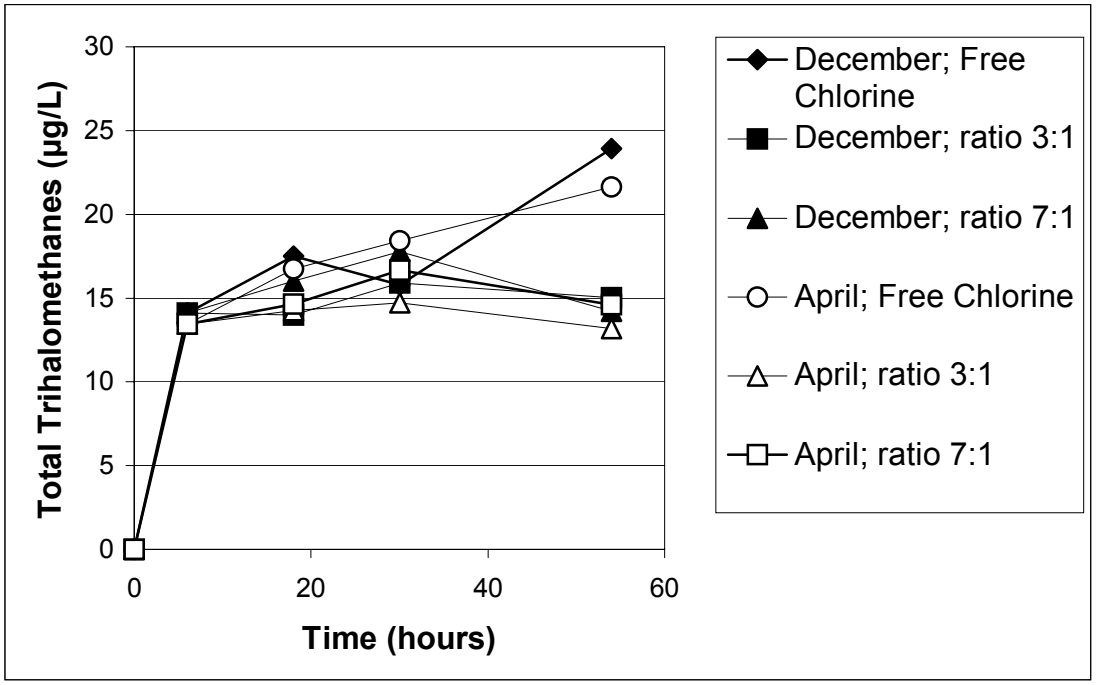

Figure 9: THMs versus time at a pH of 7.2±0.5.

of 3:1 or 7:1 had peak TTHM concentrations at a residence time of 30 hours. The peak TTHM concentration for the free chlorine samples ranged from 21.6 µg/L to 23.9 µg/L. The samples using chloramines had a peak TTHM concentration that varied between 14.7 µg/L to 17.8 µg/L.

4.4 February 2003

When designing the experiments to be conducted in February of 2003, the results of the prior two sets of data were examined. The two goals of the February 2003 experiments were to optimize the chlorine to nitrogen ratio to find the ratio that would produce the lowest trihalomethane levels and to shorten the free chlorine time period of the samples. Chlorine to nitrogen ratios of 3:1, 4:1 and 5:1 were tested to obtain more information in this range. In the first two sets of samples, the free chlorine period was six hours. The third set of experiments was designed to test the effects of shortening the free chlorine period to zero hours or three hours. The temperature of the water used in the February samples was 5°C and the chlorine dose was 2.75 mg/L. The total organic carbon concentration was 3.2 mg/L and the dissolved organic carbon concentration was 3.04 mg/L.

During the time period that the samples were being analyzed on GC-MS, the internal standards that needed to be injected with the samples began to degrade. The Worcester Water Filtration Plant laboratory manager adjusted the instrument manually; however the impact of this problem on the results is unknown. Duplicate results were not always consistent; therefore each individual measurement is plotted on the graphs in this section.

Figure 10 presents the trihalomethane concentrations versus time at a chlorine to nitrogen ratio of 3:1 and Figure 11 shows the same data for a chlorine to nitrogen ratio of 5:1. The data in both figures shows that using free chlorine produced the highest TTHM concentrations after 6 hours and using no free chlorine contact time, the smallest concentrations were formed. Figures 10 and 11 also show that the concentration of TTHMs generally increased with time; however, most THM formation occurred in the first 6 – 12 hours. Similar results were found for the chlorine to nitrogen ratio of 4:1. These trends were shown before in the previous sets of data.

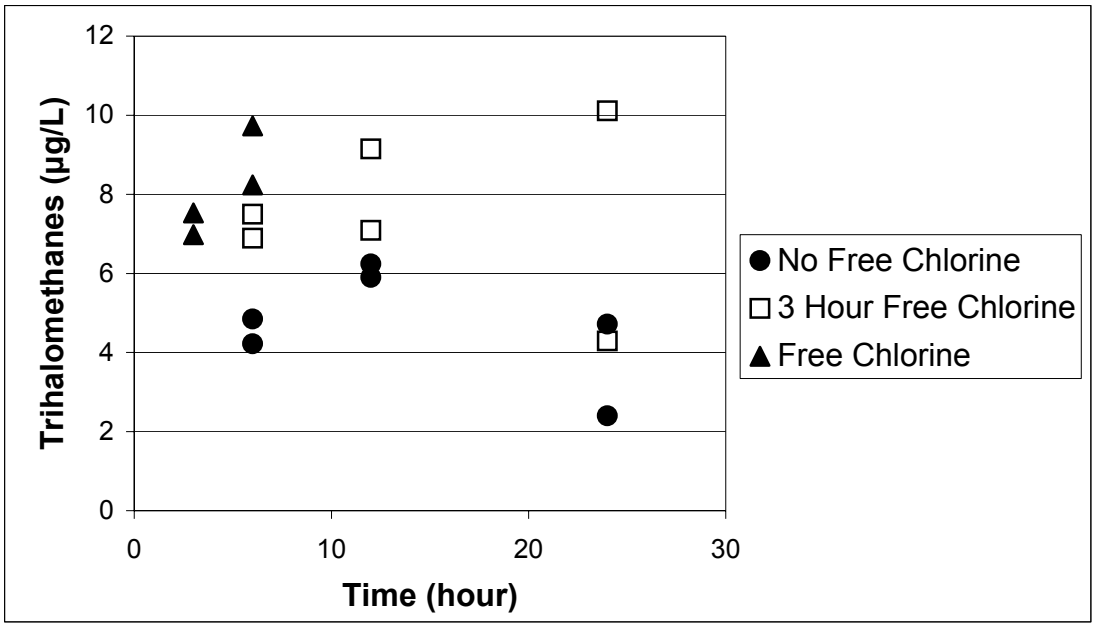

Figure 10: Feb. 2003-TTHMs versus time for a chlorine to ammonia ratio of 3:1 and a pH of 7.3 ±0.3.

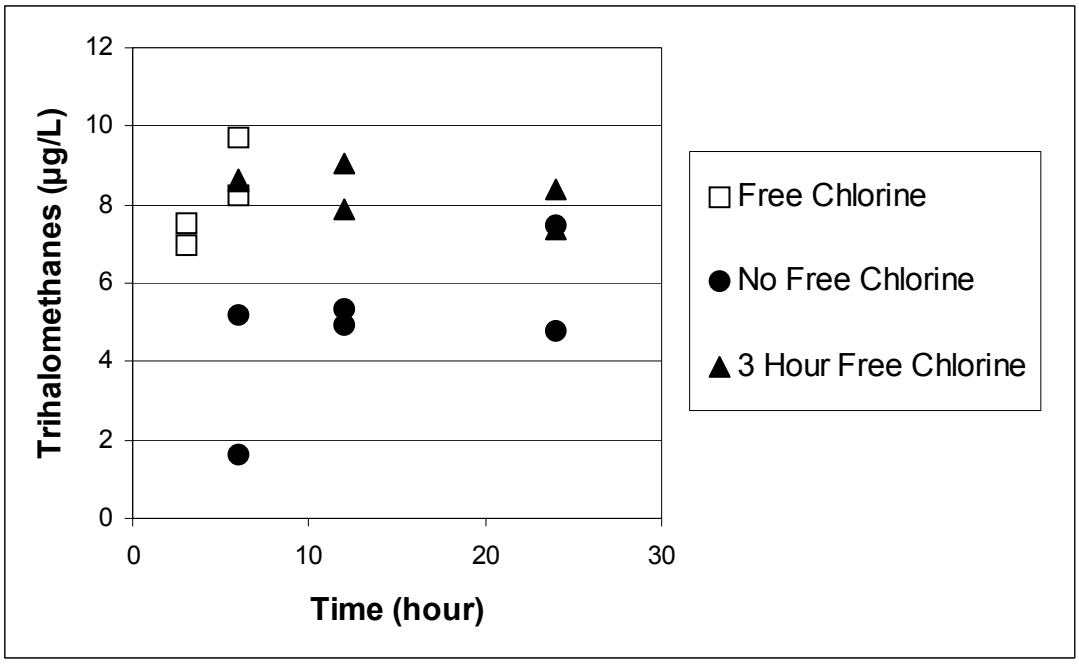

Figure 11: Feb. 2003-TTHMs versus time for a chlorine to ammonia ratio of 5:1 and a pH of 7.3 ±0.3.

The February 2003 data set was also analyzed to evaluate the relationship between trihalomethane distribution and chlorine to nitrogen ratios at a residence time of 24 hours using 3 hours of free chlorine (see Figure 12). All three ratios gave similar concentrations of TTHMs, ranging from 6.8 µg/L to 7.9 µg/L.

In Figures 10 and 11, the maximum concentration of total trihalomethanes for free chlorine at a residence time of 6 hours was 9.7 µg/L. From the December 2001 and the April 2002 sets of data, TTHM concentrations for these same conditions were 14.1 µg/L and 13.5 µg/L, respectively. Although test conditions were the same, there was a 31% decrease in THM formation between the February 2003 data and the December 2001 data, and a 28% decrease between the February 2003 data and the April 2002 data. This

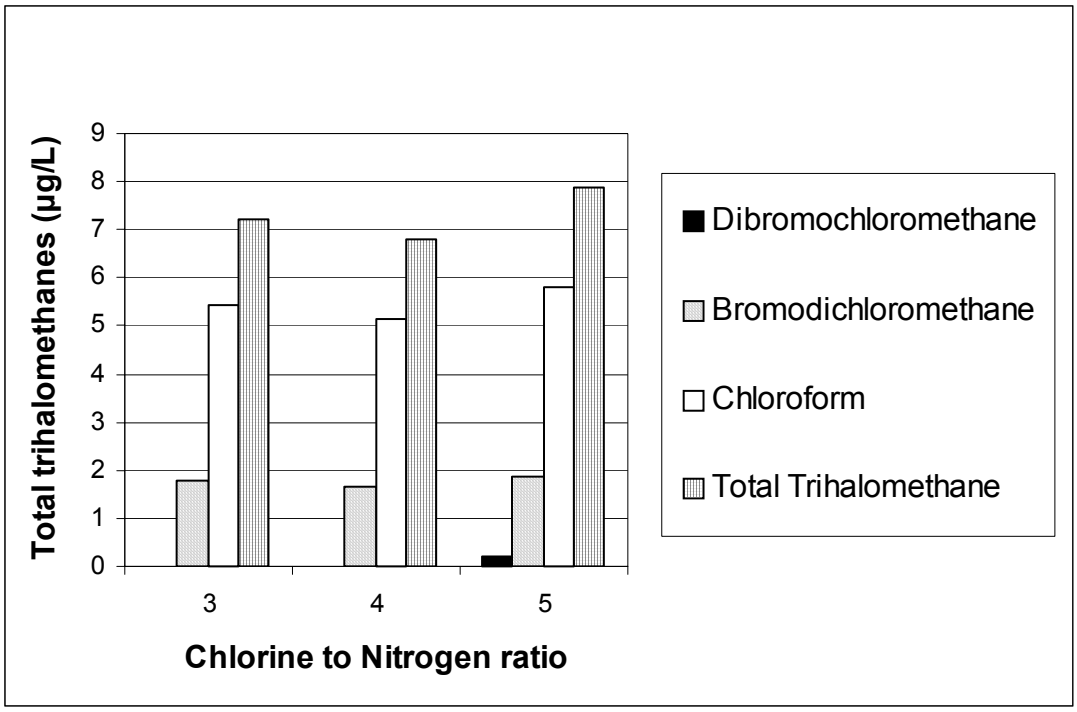

Figure 12: Feb. 2003-THM distribution versus chlorine to ammonia ratio with 3 hour period of free chlorine at t= 24 hours.

decrease could be explained by the malfunctions experienced by the GC-MS during the time period when the February 2003 set of data was being run.

4.5 Summary of Results

Chlorine is a much stronger disinfectant than chloramines. The Worcester Water Filtration Plant receives CT credit for the contact time of free chlorine in the clearwells. To receive the same CT credit, a higher dosage of chloramines would be needed or alternatively the plant would need to increase the ozone dose or contact time as ozone is also used as a primary disinfectant. Changing to a disinfectant that would not provide equivalent CT credit is important to consider before switching from chlorine to chloramines.

At the present time, the Worcester Water Filtration Plant is meeting the regulations for trihalomethane concentrations. The Stage I D/DBP regulation (current regulation regarding TTHM limits in drinking water) sets a MCL for TTHMs at 80 μg/L. The range of TTHMs found in the Worcester distribution system during a water analysis on March 14, 2001 varied from 16 μg/L to 45 μg/L. The quarterly average of TTHMs at this time was 32.2 μg/L and the running average was 42.2 μg/L. The Stage II D/DBP rule is expected in 2003, and it is anticipated that this rule will require that the 80 μg/L MCL be met according to a location running annual average, rather than a distribution-wide average.

The treatment plant meets the Stage I D/DBP limits and will most likely meet the Stage II D/DBP requirements. However, if future regulations become more stringent or the water supply degrades, the plant could consider a change to their disinfection practices to reduce THM formation. If the filtration plant was to switch to chloramination at a ratio of 3:1 (with a free chlorine period of 6 hours), they could expect approximately a 38% decrease in total trihalomethane formation. This decrease is based on the data from December 2001 and April 2002 for a 54 hour residence time. In these experiments, a reduction of TTHMs from 21.6 - 23.9 μg/L to 13.2 – 15.5 μg/L was found. Based on current plant levels of approximately 40 μg/L, switching to chloramines would reduce the TTHMs formed to about 25 μg/L.

5.0 Conclusions and Recommendations

This research examined using chloramines instead of free chlorine to reduce trihalomethane formation at the Worcester Water Filtration Plant. Residence time, pH, temperature, chlorine to nitrogen ratio and free chlorine period were varied.

5.1 Conclusions

The results of this research have shown that TTHM formation is affected by a number of variables, and that THM levels can be decreased by using chloramines instead of free chlorine. Specific conclusions based on the December 2001 and April 2002 data are as follows:

- pH significantly affected TTHM formation. Using a 6 hour free chlorine contact time followed by 24 hours of chloramination at a chlorine to nitrogen ratio of 3:1, TTHM levels ranged from 5.4 µg/L at a pH 6.0 to 41.1 µg/L at a pH 9.2.
- For the chloramination samples, the residence time from 6 to 54 hours did not significantly affect THM concentrations. The chloramination samples (preceeded by 6 hours of free chlorine contact time) had a peak TTHM concentration of approximately 15 µg/L after a 30 or 54 hour residence time.
- When ammonia was added after 6 hours, most of the TTHMs were formed during the period of free chlorine (approximately 14 µg/L formed in the first six hours, out of a total of 15 µg/L).
- Samples that were disinfected with just free chlorine produced approximately 23 µg/L TTHMs compared to 14 µg/L for chloramination samples at near neutral pH and with a 54 hour residence time.

- Chlorine to nitrogen ratios between 3:1 and 7:1 were all effective at reducing TTHM formation potential, compared to disinfection with free chlorine.
- The Worcester Water Filtration Plant could expect a 38% reduction in TTHM formed if they switched to chloramines using a chlorine to nitrogen ratio of 3:1 and maintaining a free chlorine period of 6 hours. This would give the plant reduced TTHM levels as well as giving the Worcester Water Filtration Plant the same amount of CT credit.

5.2 Future Work

With the regulations that the U.S. EPA has enacted and plans to enact, the Worcester Water Filtration Plant is within the MCLs for trihalomethane concentrations. If regulations become stricter or if the raw water quality degrades, more research should be conducted examining trihalomethane reductions achieved by using chloramination. Specifically, research should be conducted on the water supply during other seasons, such as the summer. Next, additional experiments should be completed to optimize the chloramination ratio. Lastly, an analysis on the primary disinfection systems in the treatment plant should be done to see if the free chlorine reaction period can be reduced.

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Appendix A – Trihalomethane Data

Table 14: December 2001 and April 2002 experiment design plan

Sample number	Chlorine to Nitrogen ratio	Target pH	Time (hr)
1	0	7.5	18
2	0	7.5	30
3	0	7.5	54
4	2	7.5	18
5	2	7.5	30
6	2	7.5	54
7	3	7.5	18
8	3	7.5	30
9	3	7.5	54
10	5	7.5	18
11	5	7.5	30
12	5	7.5	54
13	7	7.5	18
14	7	7.5	30
15	7	7.5	54
16	0	6	30
17	3	6	30
18	5	6	30
19	0	10	30
20	3	10	30
21	5	10	30
22	0	7.5	6

December 2001:

- Water temperature = 7ºC
- TOC = 2.97 mg/L
- DOC = 2.72 mg/L
- Chlorine dosed at time zero = 2.6 mg/L
- Free chlorine residual at 6 hours = 1.9 mg/L

April 2002

- Water temperature = 9ºC
- Chlorine dosed at time zero = 2.2 mg/L
- Free chlorine residual at 6 hours = 1.5 mg/L

Table 15: December 2001 results

Sample #	Vial #	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl_2$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.04	18	0	13.96	3.37	0.23	17.56
1	2	7.5	7.04	18	0	13.95	3.28	0.23	17.46
2	1	7.5	7.64	30	0	12.74	3.16	0.19	16.09
2	2	7.5	7.64	30	0	12.42	2.83	0.26	15.51
3	1	7.5	6.81	54	0	19.24	4.40	0.29	23.93
3	2	7.5	6.81	54	0	4864.87*	1402.34*	210.05*	6477.26*
4	1	7.5	7.09	18	2	17.53	3.69	0.29	21.51
4	2	7.5	7.09	18	2	16.28	3.71	0.23	20.22
5	1	7.5	6.78	30	2	12.08	2.99	0.24	15.31
5	2	7.5	6.78	30	2	13.25	3.34	0.22	16.81
6	1	7.5	6.87	54	2	13.38	3.38	0.23	16.99
6	2	7.5	6.87	54	2	10.38	3.31	0.21	13.90
7	1	7.5	6.96	18	3	11.70	2.55	0.21	14.46
7	2	7.5	6.96	18	3	11.02	2.31	0.17	13.50
8	1	7.5	6.81	30	3	13.19	2.89	0.16	16.24
8	2	7.5	6.81	30	3	12.49	2.90	0.15	15.54
9	1	7.5	6.72	54	3	12.27	3.00	0.15	15.42
9	2	7.5	6.72	54	3	11.64	2.84	0.17	14.65
10	1	7.5	6.97	18	5	13.91	3.19	0.36	17.46
10	2	7.5	6.97	18	5	8.76	1.68	0.02	10.46
11	1	7.5	6.76	30	5	14.41	3.39	0.26	18.06
11	2	7.5	6.76	30	5	14.83	3.49	0.26	18.58
12	1	7.5	6.84	54	5	11.18	3.17	0.24	14.59
12	2	7.5	6.84	54	5	10.92	3.13	0.20	14.25
13	1	7.5	6.93	18	7	12.84	3.07	0.19	16.10
13	2	7.5	6.93	18	7	12.70	3.01	0.22	15.93
14	1	7.5	6.87	30	7	14.11	3.45	0.28	17.84
14	2	7.5	6.87	30	7	14.22	3.25	0.23	17.70
15	1	7.5	6.74	54	7	11.96	2.94	0.11	15.01
15	2	7.5	6.74	54	7	10.50	2.80	0.10	13.40
16	1	6	6.39	30	0	11.44	1.96	0.02	13.42
16	2	6	6.39	30	0	11.46	2.15	-0.03	13.58
17	1	6	6.46	30	3	9.09	1.70	-0.08	10.71
17	2	6	6.46	30	3	8.92	1.59	-0.09	10.42
18	1	6	6.73	30	5	8.90	1.62	-0.08	10.44
18	2	6	6.73	30	5	8.96	1.60	-0.12	10.44
19	1	10	9.49	30	0	47.76	6.61	0.79	55.16
19	2	10	9.49	30	0	52.28	7.19	0.83	60.30
20	1	10	9.19	30	3	34.96	5.04	0.54	40.54
20	2	10	9.19	30	3	36.15	5.01	0.49	41.65
21	1	10	9.40	30	5	36.97	5.14	0.49	42.60
21	2	10	9.40	30	5	34.52	4.63	0.53	39.68
22	1	7.5	7.26	6	0	11.59	2.34	0.14	14.07
22	2	7.5	7.26	6	0	11.62	2.38	0.10	14.10

*data disregarded

Table 16: December 2001 average results

Sample #	Vial #	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl_2$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.04	18	0	13.96	3.33	0.23	17.51
2	1	7.5	7.64	30	0	12.58	3.00	0.23	15.80
3	1	7.5	6.81	54	0	19.24	4.40	0.29	23.93
4	1	7.5	7.09	18	2	16.91	3.70	0.26	20.87
5	1	7.5	6.78	30	2	12.67	3.17	0.23	16.06
6	1	7.5	6.87	54	2	11.88	3.35	0.22	15.45
7	1	7.5	6.96	18	3	11.36	2.43	0.19	13.98
8	1	7.5	6.81	30	3	12.84	2.90	0.16	15.89
9	1	7.5	6.72	54	3	11.96	2.92	0.16	15.04
10	1	7.5	6.97	18	5	11.34	2.44	0.19	13.96
11	1	7.5	6.76	30	5	14.62	3.44	0.26	18.32
12	1	7.5	6.84	54	5	11.05	3.15	0.22	14.42
13	1	7.5	6.93	18	7	12.77	3.04	0.21	16.02
14	1	7.5	6.87	30	7	14.17	3.35	0.26	17.77
15	1	7.5	6.74	54	7	11.23	2.87	0.11	14.21
16	1	6	6.39	30	0	11.45	2.06	-0.01	13.50
17	1	6	6.46	30	3	9.01	1.65	-0.09	10.57
18	1	6	6.73	30	5	8.93	1.61	-0.10	10.44
19	1	10	9.49	30	0	50.02	6.90	0.81	57.73
20	1	10	9.19	30	3	35.56	5.03	0.52	41.10
21	1	10	9.40	30	5	35.75	4.89	0.51	41.14
22	1	7.5	7.26	6	0	11.61	2.36	0.12	14.09

Table 17: April 2002 results

Sample number	Vial number	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.13	18	0	12.60	3.70	0.84	17.14
1	2	7.5	7.13	18	0	11.84	3.67	0.79	16.30
2	1	7.5	7.06	30	0	18.15	4.61	0.95	23.71
2	2	7.5	7.06	30	0	10.22	2.31	0.58	13.11
3	1	7.5	7.7	54	0	16.49	5.09	0.97	22.55
3	2	7.5	7.7	54	0	14.83	4.98	0.88	20.69
4	1	7.5	7.18	18	2	9.18	3.60	0.80	13.58
4	2	7.5	7.18	18	2	9.10	3.10	0.83	13.03
5	1	7.5	6.94	30	2	6.12	1.80	0.44	8.36
5	2	7.5	6.94	30	2	10.83	3.78	0.91	15.52
6	1	7.5	7.54	54	2	9.30	3.64	0.74	13.68
6	2	7.5	7.54	54	2	8.75	3.51	0.73	12.99
7	1	7.5	7.22	18	3	9.37	3.28	0.77	13.42
7	2	7.5	7.22	18	3	10.72	3.46	0.89	15.07
8	1	7.5	6.82	30	3	10.30	3.52	0.87	14.69
8	2	7.5	6.82	30	3	10.58	3.39	0.80	14.77
9	1	7.5	6.77	54	3	8.65	3.41	0.77	12.83
9	2	7.5	6.77	54	3	9.20	3.54	0.78	13.52
10	1	7.5	7.63	18	5	10.66	3.34	0.80	14.80
10	2	7.5	7.63	18	5	10.62	3.47	0.92	15.01
11	1	7.5	7.37	30	5	7.54	2.15	0.62	10.31
11	2	7.5	7.37	30	5	9.48	3.26	0.77	13.51
12	1	7.5	6.76	54	5	9.34	3.59	0.75	13.68
12	2	7.5	6.76	54	5	9.45	3.58	0.76	13.79
13	1	7.5	6.81	18	7	*	*	*	*
13	2	7.5	6.81	18	7	10.27	3.57	0.81	14.65
14	1	7.5	6.84	30	7	12.51	4.07	0.90	17.48
14	2	7.5	6.84	30	7	11.07	3.84	0.92	15.83
15	1	7.5	7.26	54	7	10.96	3.82	0.84	15.62
15	2	7.5	7.26	54	7	9.46	3.37	0.74	13.57
16	1	6	6.21	30	0	7.78	1.84	0.56	10.18
16	2	6	6.21	30	0	5.35	1.53	0.42	7.30
17	1	6	6.02	30	3	2.41	0.60	0.20	3.21
17	2	6	6.02	30	3	5.84	1.35	0.40	7.59
18	1	6	6.08	30	5	3.05	0.55	0.18	3.78
18	2	6	6.08	30	5	5.69	1.28	0.41	7.38
19	1	10	9.64	30	0	55.36	6.53	1.28	63.17
19	2	10	9.64	30	0	62.57	7.27	1.30	71.14
20	1	10	9.43	30	3	23.47	2.34	0.46	26.27
20	2	10	9.42	30	3	35.79	3.40	0.55	39.74
21	1	10	9.78	30	5	31.20	3.00	0.59	34.79
21	2	10	9.78	30	5	887.17*	97.60*	12.33*	997.10*
22	1	7.5	7.5	6	0	10.73	3.06	0.72	14.51
22	2	7.5	7.5	6	0	8.83	2.81	0.74	12.38

Table 18: April 2002 average results

Sample number	Vial number	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.13	18	0	12.22	3.69	0.82	16.72
2	1	7.5	7.06	30	0	14.19	3.46	0.77	18.41
3	1	7.5	7.70	54	0	15.66	5.04	0.93	21.62
4	1	7.5	7.18	18	2	9.14	3.35	0.82	13.31
5	1	7.5	6.94	30	2	8.48	2.79	0.68	11.94
6	1	7.5	7.54	54	2	9.03	3.58	0.74	13.34
7	1	7.5	7.22	18	3	10.05	3.37	0.83	14.25
8	1	7.5	6.82	30	3	10.44	3.46	0.84	14.73
9	1	7.5	6.77	54	3	8.93	3.48	0.78	13.18
10	1	7.5	7.63	18	5	10.64	3.41	0.86	14.91
11	1	7.5	7.37	30	5	8.51	2.71	0.70	11.91
12	1	7.5	6.76	54	5	9.40	3.59	0.76	13.74
13	1	7.5	6.81	18	7	10.27	3.57	0.81	14.65
14	1	7.5	7.43	30	7	11.79	3.96	0.91	16.66
15	1	7.5	7.26	54	7	10.21	3.60	0.79	14.60
16	1	6	6.21	30	0	6.57	1.69	0.49	8.74
17	1	6	6.02	30	3	4.13	0.98	0.30	5.40
18	1	6	6.08	30	5	4.37	0.92	0.30	5.58
19	1	10	9.64	30	0	58.97	6.90	1.29	67.16
20	1	10	9.42	30	3	29.63	2.87	0.51	33.01
21	1	10	9.78	30	5	31.20	3.00	0.59	34.79
22	1	7.5	7.50	6	0	9.78	2.94	0.73	13.45

Table 19: February 2003 experiment design plan

Sample number	Chlorine to Nitrogen ratio	Target pH	Time (hr)	Ammonia added at
1	3	7.5	6	0 hour
2	3	7.5	12	0 hour
3	3	7.5	24	0 hour
4	4	7.5	6	0 hour
5	4	7.5	12	0 hour
6	4	7.5	24	0 hour
7	5	7.5	6	0 hour
8	5	7.5	12	0 hour
9	5	7.5	24	0 hour
10	3	7.5	6	3 hour
11	3	7.5	12	3 hour
12	3	7.5	24	3 hour
13	4	7.5	6	3 hour
14	4	7.5	12	3 hour
15	4	7.5	24	3 hour
16	5	7.5	6	3 hour
17	5	7.5	12	3 hour
18	5	7.5	24	3 hour
19	0	7.5	3	
20	4	7.5	12	6 hour
21	4	7.5	24	6 hour
22	0	7.5	6	

February 2003

- Water temperature = 5ºC
- TOC = 3.20 mg/L
- DOC = 3.04 mg/L
- Chlorine dosed at time zero = 2.75 mg/L
- Free chlorine residual at 6 hours = 1.7 mg/L

Table 20: February 2003 results

Sample Number	Vial Number	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.37	6	3	3.10	1.12		4.22
1	2	7.5	7.37	6	3	3.60	1.25		4.85
2	1	7.5	7.19	12	3	4.25	1.65		5.90
2	2	7.5	7.19	12	3	4.45	1.79		6.24
3	1	7.5	7.08	24	3	2.18	0.22		2.40
3	2	7.5	7.08	24	3	3.48	1.24		4.72
4	1	7.5	7.19	6	4	3.52	1.28		4.80
4	2	7.5	7.19	6	4	3.92	1.44		5.36
5	1	7.5	7.29	12	4	4.02	1.41		5.43
5	2	7.5	7.29	12	4	3.10	1.10		4.20
6	1	7.5	7.35	24	4	4.50	1.29	0.74	6.53
6	2	7.5	7.35	24	4	1.32	0.11		1.43
7	1	7.5	7.12	6	5	1.61			1.61
7	2	7.5	7.12	6	5	3.71	1.46		5.17
8	1	7.5	7.14	12	5	3.98	1.38		5.36
8	2	7.5	7.14	12	5	3.63	1.28		4.91
9	1	7.5	7.33	24	5	6.08	1.39		7.47
9	2	7.5	7.33	24	5	3.53	1.24		4.77
10	1	7.5	6.97	6	3	5.31	2.19		7.50
10	2	7.5	6.97	6	3	4.66	2.11	0.12	6.89
11	1	7.5	7.11	12	3	4.91	2.07	0.11	7.09
11	2	7.5	7.11	12	3	6.43	2.72		9.15
12	1	7.5	7.15	24	3	3.37	0.92		4.29
12	2	7.5	7.15	24	3	7.47	2.64		10.11
13	1	7.5	7.16	6	4	4.95	1.19		6.14
13	2	7.5	7.16	6	4	7.99	2.81		10.80
14	1	7.5	7.44	12	4	5.46	2.49		7.95
14	2	7.5	7.44	12	4	5.62	2.65		8.27
15	1	7.5	7.28	24	4	7.45	2.90		10.35
15	2	7.5	7.28	24	4	2.81	0.44		3.25
16	1	7.5	7.23	6	5	5.89	2.68		8.57
16	2	7.5	7.23	6	5	5.95	2.69		8.64
17	1	7.5	7.19	12	5	5.51	2.38		7.89
17	2	7.5	7.19	12	5	6.23	2.80		9.03
18	1	7.5	7.31	24	5	5.96	2.44		8.40
18	2	7.5	7.31	24	5	5.69	1.28	0.41	7.38
19	1	7.5	7.4	3	0	4.93	2.05		6.98
19	2	7.5	7.4	3	0	5.33	2.20		7.53
20	1	7.5	7.21	12	4	6.08	2.76		8.84
20	2	7.5	7.21	12	4	4.88	2.21	0.12	7.21
21	1	7.5	7.18	24	4	6.98	2.58		9.56
21	2	7.5	7.18	24	4	7.47	3.04		10.51
22	1	7.5	7.57	6	0	5.60	2.44	0.20	8.24
22	2	7.5	7.57	6	0	6.80	2.93		9.73

Table 21: February 2003 average results

Sample number	Vial number	Target pH	Actual pH	Time (hr)	Cl_2:N ratio	$CHCl_3$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_2Cl$ (µg/L)	TTHM (µg/L)
1	1	7.5	7.37	6	3	3.35	1.19	0	4.54
2	1	7.5	7.19	12	3	4.35	1.72	0	6.07
3	1	7.5	7.08	24	3	2.83	0.73	0	3.56
4	1	7.5	7.19	6	4	3.72	1.36	0	5.08
5	1	7.5	7.29	12	4	3.56	1.26	0	4.82
6	1	7.5	7.35	24	4	2.91	0.70	0.37	3.98
7	1	7.5	7.12	6	5	2.66	0.73	0	3.39
8	1	7.5	7.14	12	5	3.81	1.33	0	5.14
9	1	7.5	7.33	24	5	4.81	1.32	0	6.12
10	1	7.5	6.97	6	3	4.99	2.15	0.06	7.20
11	1	7.5	7.11	12	3	5.67	2.40	0.06	8.12
12	1	7.5	7.15	24	3	5.42	1.78	0	7.20
13	1	7.5	7.16	6	4	6.47	2.00	0	8.47
14	1	7.5	7.44	12	4	5.54	2.57	0	8.11
15	1	7.5	7.28	24	4	5.13	1.67	0	6.80
16	1	7.5	7.23	6	5	5.92	2.69	0	8.61
17	1	7.5	7.19	12	5	5.87	2.59	0	8.46
18	1	7.5	7.31	24	5	5.83	1.86	0.21	7.89
19	1	7.5	7.4	3	0	5.13	2.13	0	7.26
20	1	7.5	7.21	12	4	5.48	2.49	0.06	8.03
21	1	7.5	7.18	24	4	7.23	2.81	0	10.04
22	1	7.5	7.57	6	0	6.20	2.69	0.10	8.99