The Formation and Control of Iodinated Trihalomethanes in Drinking Water Treatment

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THE FORMATION AND CONTROL OF IODINATED TRIHALOMETHANES IN DRINKING WATER TREATMENT

A Thesis
Presented to the Graduate School of Clemson University

In Partial Fulfillment of the Requirements for the Degree Master of Science Environmental Engineering and Science

by Darryl Bryce Jones August 2009

Accepted by:
Tanju Karanfil, Ph.D., P.E., BCEE, Committee Chair
David Freedman, Ph.D.
Cindy Lee, Ph.D.
ABSTRACT

Ever since toxic disinfection by-products (DBPs) were discovered in the 1970s, drinking water utilities have had to continue to develop treatment strategies to reduce the acute health risk from infectious pathogens in water, and at the same time limit the formation of disinfection by-products. The recent two stage (1998, 2006) D/DBP rule enacted by the Environmental Protection Agency (EPA) which sets limits of 80 µg/L for trihalomethanes (THMs) and 60 µg/L for haloacetic acids (HAAs) will likely put more pressure on utilities in the future to decrease their chlorine contact time and follow that with ammonia addition to form monochloramine because chloramination practices form fewer THMs and HAAs.

Generally, iodinated DBPs are the most toxic DBPs followed by the brominated and chlorinated DBPs. Because monochloramine practices favor the formation of iodinated DBPs, there are increasing concerns that utilities may be forming more toxic iodinated DBPs such as iodinated trihalomethanes (I-THMs).

The main objective of this research was to investigate I-THM formation and control during water treatment for a realistic Br⁻/I⁻ mass ratio of 10, at two representative bromide/iodide levels [(i) 200 µg/L and 20 µg/L, and (ii) 800 µg/L and 80 µg/L] encountered in source waters. Unfortunately, previous I-THM research often neglected this very important Br⁻/I⁻ ratio because iodide was often added in much higher concentrations than bromide. Specifically, this research project focused on three main sub-objectives: (i) to investigate and compare I-THM formation from preformed monochloramine and prechlorination followed by ammonia addition, (ii) to evaluate three
commonly used preoxidants in water treatment (potassium permanganate, chlorine dioxide, and hydrogen peroxide) for controlling I-THM formation, and (iii) to investigate the importance of bromide to iodide ratio in I-THM formation and speciation from preformed monochloramine and preoxidation.

The results showed that for preformed monochloramine, I-THM formation was more favorable in low-SUVA waters than high-SUVA waters. On the other hand, for prechlorination followed by ammonia addition, high-SUVA waters generally formed higher concentrations of I-THMs than low-SUVA waters. For preformed monochloramine, generally higher I-THM and THM formation was observed at lower pH. However, if the iodide concentration was high (≥80 µg/L), significant iodoform (CHI$_3$) formation was sometimes observed at higher pH. For prechlorination, it was shown that increases in Cl$_2$/DOC ratio and Cl$_2$/I$^-$ ratio decreased I-THM formation, but increased THM formation. Overall, significant differences in I-THM speciation for preformed monochloramine and prechlorination were observed.

The results for preoxidation showed that potassium permanganate and hydrogen peroxide were unsuccessful in reducing I-THM formation. Chlorine dioxide showed promising results for reducing I-THM formation for high iodide concentrations (≥80 µg/L) because iodoform (CHI$_3$) formation sometimes decreased with increasing preoxidation dose. In some cases, I-THM formation was enhanced from preoxidation.

Investigations into the importance of bromide to iodide ratio showed that I-THM yields and speciation formed from preformed monochloramine and preoxidants will depend significantly on bromide to iodide ratios and concentrations.
DEDICATION

To my parents, Bryce and Barbara

For all the advice, encouragement and support you have given me
ACKNOWLEDGMENTS

Special thanks to my research advisor, Dr. Tanju Karanfil, for his guidance, strong work ethic, and teachings about both life and research. I would also like to acknowledge Dr. David Freedman and Dr. Cindy Lee for devoting time to advise me on my personal and career goals, as well as serving on my research committee.

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Finally, I would like to thank my parents, Bryce and Barbara, and my sister Karen for their love and understanding when times were busy.
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LIST OF ABBREVIATIONS

AOP Advanced Oxidation Process
AWWA American Water Works Association
CT Credit Disinfectant Contact Time Credit
DBD N,N – diethyl – p – phnylenediamine
DBP Disinfection By-product
D/DBP Disinfection and Disinfection By-product Rule
DDW Distilled and De-ionized Water
DOC Dissolved Organic Carbon
DOM Dissolved Organic Matter
DWTP Drinking Water Treatment Plant
EPA Environmental Protection Agency
FAS Ferrous Ammonium Sulfate
GC Gas Chromatography
HAA Haloacetic Acid
HPLC High Performance Liquid Chromatography
HRP Horseradish Peroxidase
IC Ion Chromatography
ICR Information Collection Rule
I-THMs Iodinated Trihalomethanes
LGB Lissamine Green B
MCL Maximum Contaminant Level
MW Molecular Weight
MRL Minimum Reporting Level
MTBE Methyl-tert-butyl –ether
ND Not Detected
NOM Natural Organic Matter
SAR Structure Activity Relationship
SDWA Safe Drinking Water Act
SUVA Specific Ultraviolet Absorbance at 254 nm
THMs Brominated and Chlorinated Trihalomethanes
THM10 Molar sum of the 4 regulated THMs and 6 iodinated THMs
TOC Total Organic Carbon
TOX Total Organic Halide
TTHM Total Trihalomethane (the mass sum of the 4 regulated THMs)
UFC Uniform Formation Conditions
UHP Ultra High Purity
UTOX Unknown Total Organic Halide
UV Ultraviolet Light
WWTP Wastewater Treatment Plant
Disinfection of water supplies began in the early 1900s and has resulted in a significant decrease in typhoid fever and cholera in the United States (McGuire 2006). However, it was not until much later that the negative implications of disinfection were realized as harmful disinfection by-products (DBPs) were not discovered until the 1970s (Bryant et al. 1992). The formation of chloroform ($\text{CHCl}_3$) was reported in 1974 (Rook 1974, Bellar et al. 1974). In response to harmful water contaminants and DBPs, the U.S. government passed the Safe Drinking Water Act (SDWA) in 1974, and later in 1979, the U.S. government passed the Total Trihalomethane Rule (TTHM) (Roberson 2008). Since then, utilities have had to comply with two competing goals:

- Reduction of the acute health risk from infectious pathogens in water
- Reduction of the chronic health risk of disinfection by-products (DBPs).

These contradictory goals became more significant when the Enhanced Surface Water Treatment Rule (1989) and the two stage (1998, 2006) D/DBP rule were enacted by the Environmental Protection Agency (EPA) (Bryant et al. 1992, Roberson 2008). Currently, trihalomethanes (THMs) and haloacetic acids (HAAs) are the only organic disinfection by-products regulated at maximum contaminant levels (MCLs) of 80 $\mu$g/L and 60 $\mu$g/L, respectively. Bromate and chlorite are the only inorganic DBPs regulated, and their MCLs are 0.010 mg/L and 1.0 mg/L, respectively (EPA 1999).
Recently, many drinking water utilities, especially the largest utilities, have switched from chlorine to monochloramine disinfection to comply with THM and HAA regulatory limits because monochloramine forms much lower concentrations of these DBPs (Seidel et al. 2005, McGuire 2006). While analytical techniques have improved considerably since the 1970s and have allowed for the detection of over 500 recently discovered DBPs, total organic halide (TOX) formed from chlorination of natural organic matter (NOM) is still largely unknown, and the percentage of unknown total organic halide (UTOX) is much greater for monochloramine disinfection (Hua and Reckhow 2008a). The relative toxicity of this unknown fraction compared to the regulated DBPs has not been determined. Specifically, three categories of unregulated, emerging DBPs are being studied due to their recently discovered toxicity. These include iodinated DBPs, nitrogenous DBPs, and emerging carbonaceous DBPs (Richardson 2003, Karanfil et al. 2008). While increased chloramination practice at utilities reduces THM and HAA effluent concentrations, there is concern that small concentrations of very toxic emerging DBPs, especially the iodinated trihalomethanes (I-THMs) are formed when the concentrations of bromide and iodide are elevated in the source water (Hansson et al. 1987, Leitner et al. 1998, Bichsel and Von Gunten 2000a, Hua et al. 2004, Krasner et al. 2006, Richardson et al. 2008).

Even small concentrations of I-THMs are a concern because of their potent toxicity as compared to the regulated THMs which include only the chlorinated and brominated haloforms (Woo et al. 2002). Recent mammalian cell toxicity results demonstrated that one species of I-THMs, iodoform (CHI₃), was 60 times and 146 times
more cytotoxic than bromoform (CHBr$_3$) and chloroform (CHCl$_3$), respectively (Plewa and Wagner 2008). Additionally, when the cytotoxicity and genotoxicity of chlorinated, brominated, and iodinated versions of acetic acids, acetamides and haloforms were calculated separately, and when the representative compounds were combined into one of three subgroups (I-DBPs, Br-DBPs, Cl-DBPs), iodinated DBPs were far more toxic than the other halogenated DBPs (Richardson et al. 2007). Furthermore, since the likelihood of I-DBP formation increases during monochloramine addition due to the persistence of hypoiiodous acid (HOI) as an oxidant under these conditions, it is very likely that I-THMs track well with other toxic I-DBPs formed (Krasner et al. 2006, Richardson et al. 2008).

There have been a number of distribution studies that have detected I-THMs in drinking water (Hansson et al. 1987, Khiari et al. 1999, Richardson et al. 2003, Krasner et al. 2006, Richardson et al. 2008). Thomas and his colleagues (1980) characterized dichloriodomethane (CHCl$_2$I) as the fifth THM species (There are currently four regulated species of THM). Overall, CHCl$_2$I is the most commonly detected I-THM species followed by bromochloroiodomethane (CHBrClI) (Khiari et al. 1999, Krasner et al. 2006, Richardson et al. 2008). Brass and others (1977) detected CHCl$_2$I in 85 out of 111 U.S. water supplies that were surveyed.

On the other hand, when the concentration of iodide is high, and ammonia is added before chlorine or simultaneously with chlorine to form monochloramine, iodoform (CHI$_3$) is the dominant species (Hansson et al. 1987). Iodoform has a very low taste and odor threshold compared to the other THM species (Cancho et al. 2001). The
other three I-THM species (CHBr$_2$I, CHBrI$_2$, and CHClI$_2$), have been detected in other monitoring studies, but they are usually found less frequently.

While there have been laboratory studies that have explored I-THM formation from chlorine, ozone, chlorine dioxide, and monochloramine, the spiked concentrations of iodide in the tested waters were too high and unrealistic for predicting I-THM formation in drinking water plants. Furthermore, the bromide to iodide ratio (Br$^-$/I$^-$) was unrealistic. Since both bromine and iodine are found in source waters together, and they incorporate into THMs, it is important to understand their competition for substitution.

The Br$^-$/I$^-$ mass ratio is typically around 10 according to a bromide, iodide and occurrence study that investigated surface waters and groundwaters located inland and close to the sea (Richardson et al. 2008). Furthermore, a bromide and iodide occurrence study of South Carolina wastewater plant effluents conducted by Karanfil and others (2009) also suggests that the bromide to iodide ratio encountered in wastewater effluents is approximately 10. Previous I-THM research often neglected this very important ratio because iodide was in higher concentrations than bromide. This opposite higher iodide than bromide scenario is rarely encountered in practice.

Overall, the main objective of this thesis was to understand I-THM formation and control for the treatment of source waters with a realistic Br$^-$/I$^-$ mass ratio of 10, at two representative Br$^-$/I$^-$ levels [(i) 200 µg/L and 20 µg/L, (ii) 800 µg/L and 80 µg/L]. These two levels are considered a moderate and high level of bromide/iodide according to the occurrence study of Richardson and others (2008) in which bromide varied from 24 to 1120 µg/L and iodide varied from 0.4 to 104 µg/L in source waters. To further enhance
understanding and confirm the importance of investigating realistic bromide to iodide ratios, an additional Br/I level of 100 µg/L / 200 µg/L was also investigated. Through the testing of three different bromide and iodide levels, the effects of bromide and iodide concentration on I-THM formation and speciation were explored. Specifically, this research project focused on 3 main objectives:

**The first objective was to investigate and compare I-THM formation from preformed monochloramine and prechlorination followed by ammonia addition.** Chlorine may be added simultaneously with ammonia to form monochloramine (i.e. resembling preformed monochloramine) or utilities may practice a short free chlorine contact time prior to ammonia addition to achieve sufficient disinfection credit. It was important to explore a number of factors regarding I-THM formation which included (i) the effects of NOM characteristics, (ii) pH, (iii) chlorine contact time, and (iv) chlorine dose. The effects of treatment strategy and bromide and iodide concentration on I-THM speciation were also investigated.

**The second objective was to investigate the effects of three commonly used preoxidants (potassium permanganate, chlorine dioxide, and, hydrogen peroxide [w/o UV or O₃]) on I-THM formation.** Oxidants are commonly added to the process water usually at the beginning of a water treatment plant to remove color, taste, or odor, and also to aid coagulation and disinfection processes. A contact time of 20 minutes was tested, and the ability of the oxidants to convert iodide to iodate (thus preventing I-THM formation) or to alter the reactivity of NOM to increase or decrease I-THM formation was investigated.
The third objective was to investigate the importance of bromide to iodide ratio on I-THM formation and speciation. An opposite Br⁻/I⁻ ratio of 0.5 (100 µg/L bromide and 200 µg/L iodide) was compared with a more typical Br⁻/I⁻ ratio of 10 (800 µg/L bromide and 80 µg/L iodide). Comparisons of I-THM yields and speciation from these two contrasting bromide to iodide ratios provided more insight for understanding I-THM formation in practice and in laboratory research.
CHAPTER TWO
LITERATURE REVIEW

2.1 Emerging Disinfection By-products

Disinfection by-products (DBPs) are formed from the reactions of dissolved organic matter (DOM) with oxidants and disinfectants. The majority of DBPs are halogenated organics that are generally characterized as total organic halide (TOX) (Reckhow 2008). Even though more than 500 DBPs have been identified since the 1970s when DBPs were first discovered, only 11 organic and inorganic DBPs are currently regulated by the U.S. EPA (Karanfil et al. 2008). Fifty of the 500+ unregulated DBPs were selected as high priority because of their potential toxicity determined from structural activity relationship (SAR) analyses (Weinberg et al. 2002). The highest priority DBPs included haloacetonitriles, haloketones, haloacetyladdehydes, halogenated furanones, halonitromethanes, haloamides, and the halomethanes, especially the iodo-trihalomethanes. These high priority DBPs were measured seasonally at 12 U.S. full-scale treatment plants in a nationwide occurrence study conducted from 2000-2002 (Krasner et al. 2006). The plants that were selected used a variety of different oxidants and disinfectants which included chlorine, monochloramine, ozone, and chlorine dioxide. Furthermore, plants were selected that utilized source waters that contained higher total organic carbon (TOC) and bromide concentrations unlike a previous DBP survey in 1997-1998, the Information Collection Rule (ICR) (Krasner et al. 2006). The goal was to isolate conditions that would result in greater formation of emerging DBPs. It was discovered that many of the emerging DBPs including iodo-trihalomethanes (I-THMs)
were formed mostly from alternative oxidants and disinfectants as opposed to chlorine. This is a large concern as many utilities, especially the large ones (plants serving more than 100,000 people) have recently added or switched to chlorine dioxide as a primary oxidant and monochloramine as a secondary disinfectant (Figure 2.1). In fact, nowadays, monochloramine is practiced more frequently at very large utilities that treat surface waters (Figure 2.2). Overall, chlorine is still the dominant disinfectant used for groundwater treatment because there are lower risks of DBP formation due to low TOC levels (Figure 2.3).

Figure 2.1 Chlorine dioxide and chloramines as primary and secondary disinfectants in large utilities (adapted from McGuire 2006)
Figure 2.2 Secondary disinfection practices for utilities treating surface water (adapted from Seidel et al. 2005)

Figure 2.3 Secondary disinfection practices for utilities treating groundwater (adapted from Seidel et al. 2005)
Because many emerging DBPs are formed from monochloramine, a follow up study conducted by Richardson and others (2008) that focused only on monochloramine plants detected I-THMs, even though some of the source waters contained minimal concentrations of bromide and iodide.

Overall, the recent DBP occurrence studies suggest that utilities that are using alternative treatment strategies in order to comply with THM and HAA regulatory limits may be promoting the formation of more toxic DBPs such as iodinated trihalomethanes.

2.2 Iodinated DBP Toxicities

When the EPA prioritized all of the identified DBPs, the iodinated DBPs as a group were more toxic than the brominated or chlorinated DBPs due to the stronger leaving potential of the iodine atom (Richardson et al. 2007). Figure 2.4 shows that iodinated DBPs are more cytotoxic and genotoxic than brominated or chlorinated DBPs.

![Figure 2.4 Toxicity of halogenated disinfection by-products (Plewa et al. 2008)](image)
Additionally, mammalian cell toxicity results, completed in 2008, provided evidence for the toxicity of iodinated DBPs because iodoform ($\text{CHI}_3$) was 60 times and 146 times more cytotoxic than bromoform ($\text{CHBr}_3$) and chloroform ($\text{CHCl}_3$), two regulated THMs, respectively (Plewa and Wagner 2008). Furthermore, iodinated HAAs were considered more toxic than their brominated and chlorinated analogs because iodoacetic acid (IAA) was 3 times and 287 times more cytotoxic than bromoacetic acid and chloroacetic acid, respectively (Plewa et al. 2004). It should be noted that iodoacetic acid is considered by far the most genotoxic DBP to mammalian cells (Plewa et al. 2004). When the 6 I-THM species were analyzed individually, iodoform ($\text{CHI}_3$) was considered the most cytotoxic, and chlorodiodomethane ($\text{CHClI}_2$) was considered the most genotoxic I-THM species (Richardson et al. 2008). These toxicology results suggest that even though iodinated DBPs may be at much smaller concentrations than chlorinated or brominated DBPs, their higher toxicity warrants some consideration when exposure risks are determined.

2.3 Odor and Taste Problems

In addition to their toxicity, I-THMs have very low odor and taste thresholds (Cancho et al. 2001). This is a concern as even small concentrations will result in serious taste and odor complains by water consumers (Hansson et al. 1987). The odor thresholds of I-THMs are given in Table 2.1, and the threshold decreases with increasing iodine substitution (Boleda et al. 2007).
Table 2.1: Odor descriptors and threshold concentrations for iodinated THMs (Cancho et al. 2001)

<table>
<thead>
<tr>
<th>I-THM Species</th>
<th>Odor Descriptor</th>
<th>Odor Threshold [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₂I</td>
<td>sweet, syrup</td>
<td>8.9</td>
</tr>
<tr>
<td>CHBrClI</td>
<td>sweet, fresh grass, perfumed, alcoholic</td>
<td>8.4</td>
</tr>
<tr>
<td>CHBr₂I</td>
<td>sweet, solvent, perfumed, bitumen</td>
<td>6.4</td>
</tr>
<tr>
<td>CHClI₂</td>
<td>medicinal, sweet, solvent candy</td>
<td>0.2</td>
</tr>
<tr>
<td>CHBrI₂</td>
<td>medicinal, sweet, solvent, perfumed</td>
<td>0.2</td>
</tr>
<tr>
<td>CHI₃</td>
<td>medicinal, sweet, perfumed, gum</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Even small concentrations of I-THMs, especially iodoform (CHI₃), will result in medicinal and sweet smelling water. The odor threshold concentrations are a magnitude or two lower than concentrations for chloroform and bromoform which are 100 and 300 µg/L, respectively (Bruchet et al. 1989). Additionally, the taste threshold for iodoform was very low in one study because consumers described water containing iodoform at a concentration of 5 µg/L as tasting like plastic or medicine (Hansson et al. 1987).

It is fortunate that oxidants can suppress iodoform by oxidizing iodide to iodate, an inert, non-toxic form of iodine (Bichsel and Von Gunten 2000a). The applications of these oxidants in drinking water treatment will be discussed in the following sections.

2.4 Free Chlorine

Chlorine was first used as a disinfectant for drinking water in 1904 to aid filtration processes in the prevention of waterborne diseases such as typhoid and cholera (Bryant et al. 1992). Since then, it is has been the traditional method for achieving effective primary disinfection (CT credit) and for achieving sufficient disinfection residual in drinking water distribution (EPA 1999). When gaseous chlorine (Cl₂) or sodium hypochlorite
(NaOCl) is added to water, hypochlorous acid (HOCI) and hypochlorite ion (OCl^-) are the species formed, and the one that dominates depends on the pH. Aqueous chlorine acts as a biocide by violently scavenging electrons from microorganisms and NOM in order to return to its much more stable (-1) oxidation state (Bryant et al. 1992).

\[ \text{2.5 Breakpoint} \]

If ammonia is present in the water, chlorine will react with ammonia (NH}_3\text{) to form appreciable levels of monochloramine (NH}_2\text{Cl}) if the chlorine to nitrogen weight ratio is at least 3. Higher concentrations of chlorine up to a weight ratio of about 7.6 will form dichloramine (NHCl}_2\text{). Both monochloramine and dichloramine are collectively referred to as combined chlorine. Breakpoint is achieved when the chlorine/nitrogen ratio is sufficiently high that ammonia is completely oxidized, and the chlorine residual continues to increase with higher chlorine doses. This usually occurs between a weight ratio of 7 and 9. Only after a sufficient Cl}_2\text{/NH}_3\text{ ratio (breakpoint), will free chlorine be significant (Bryant et al. 1992).}

\[ \text{2.6 Monochloramine} \]

Sometimes chlorine doses below the breakpoint are desirable to form monochloramine. An advantage of monochloramine over free chlorine is a reduction in THM and HAA disinfection by-product formation. (Seidel et al. 2005, McGuire 2006). Because the chlorine atom is bound to a large ammonium group, monochloramine reacts with NOM differently and does not form THMs like free chlorine (Vikesland et al. 1998).
Monochloramine disinfection was practiced as long ago as 1916, but its popularity has fluctuated over the past 100 years because of the low availability and high cost of ammonia during World War II, and its weaker disinfecting capability as compared to chlorine (Bryant et al. 1992). But over the past 25 years, the advantages of monochloramine including its persistence as a secondary disinfectant and its inability to form high levels of THMs and HAAs, are outweighing its disadvantages, and monochloramine popularity has continued to increase (Seidel et al. 2005, McGuire 2006).

Monochloramine disinfection is practiced in four ways: (i) addition of preformed chloramine, (ii) concurrent addition of chlorine and ammonia, (iii) preammoniation, or (iv) prechlorination. Preformed monochloramine practice combines Cl₂ and NH₃ to form chloramines in a separate stream prior to addition to the main process stream. Full-scale applications of preformed monochloramine are very rare, and the simultaneous addition of both chlorine and ammonia at the same point in the plant (concurrent addition) is more common. In addition, ammonia and chlorine are often added at different points in the plant to achieve variable contact times in order (i) to increase disinfection effectiveness (prechlorination), or (ii) to decrease THM and HAA formation (preammoniation) (Bryant et al. 1992).

2.7 Prechlorination Followed by Ammonia Addition

An advantage of prechlorination followed by ammonia practices is the combination of a strong primary disinfectant (chlorine) followed by a fairly stable secondary disinfectant (monochloramine). The addition of chlorine at the beginning of the plant achieves sufficient microorganism kill levels, while the addition of ammonia
later in the treatment process consumes the free chlorine to form monochloramine, which prevents dangerous biological re-growth in distribution (Bryant et al. 1992).

On the other hand, if too much ammonia is added to form monochloramine, biological regrowth can be a major problem. Microbial mediated decomposition of ammonia (nitrification) may occur in distribution systems which can result in nitrite problems (partial nitrification), or losses in monochloramine residuals (Liu et al. 2005).

Another advantage for short prechlorination contact times prior to ammonia addition is fewer THMs and HAAs in the effluent compared to when free chlorine is used as the sole disinfectant (Bryant et al. 1992). Nevertheless, THM concentration may still increase in distribution from monochloramine practices, even after reactive free chlorine is quenched by ammonia addition prior to discharge. A pilot study demonstrated that for short contact times prior to ammonia addition, chlorine reacted with NOM to form large molecular weight intermediates, which degraded to chloroform in distribution (Speed et al. 1987). These findings suggest that shortening chlorination contact times does not always reduce DBP formation.

Even though chlorine forms THMs and HAAs, prechlorination offers many advantages which include oxidation of iron and manganese, control of tastes and odors, removal of color, and enhancement of coagulation and filtration processes. However, current DBP regulations have discouraged many utilities from using chlorine as a preoxidant, and so utilities have turned to other alternative preoxidants such as chlorine dioxide, hydrogen peroxide, and potassium permanganate (EPA 1999).
2.8 Preoxidants

2.8.1 Potassium Permanganate

Potassium permanganate (KMnO₄) has been used as an all purpose disinfectant as early as 1873. However, gradually chlorine replaced it as the most common all purpose biocide in the 1900s. Nowadays, KMnO₄ is used only as a disinfectant for specific applications such as human and veterinary medicine. Its niche in drinking water treatment has been chemical preoxidation to remove taste, odor, color, and dissolved iron and manganese (Bryant et al. 1992). Permanganate also prevents biological growth in the treatment plant by directly oxidizing cell material and destroying essential enzymes of bacteria, fungi, viruses, and algae (Weber and Posselt 1972).

Potassium permanganate is most known for its intense purple color, and the formation of a precipitate (MnO₂) after manganese is reduced from its (+7) oxidation state to its (+4) oxidation state. The MnO₂ precipitate has catalytic properties which often result in smaller doses of KMnO₄ required than expected, and it is often added before filters for this reason (O'Connell 1978). Furthermore, the precipitate exhibits an additional benefit for removing microorganisms during sedimentation through biological attachment to the MnO₂ colloidal surface (Cleasby et al. 1964, Posselt et al. 1967). The removal of the color and the dissolved/precipitated manganese is critical prior to distribution for prevention of pink, then later brown colored water, and for prevention of deposition of MnO₂ in consumer hot water heaters or dishwashers (Montgomery 1985).

The effectiveness of KMnO₄ as an oxidant is greater at higher pH because permanganate will react more aggressively with organic anions than neutral molecules.
(Bryant et al. 1992). On the other hand, its effectiveness as a biocide is enhanced at lower pH (<6) especially with regards to *E. coli* and *L. pneumophila* (Cleasby et al. 1964, Yahya et al., 1990). Phenol, iron, manganese, and algae are still sufficiently removed under slightly acidic conditions, so KMnO₄ is an ideal disinfectant/oxidant for source waters with low pH. The consumption of alkalinity from KMnO₄ and NOM reactions is often a concern for plants practicing alum coagulation which requires high alkalinity.

Finally, potassium permanganate will reduce THM formation levels if it replaces prechlorination as a preoxidant. Potassium permanganate will destroy THM precursors if a high dose is added (>10 mg/L), a long contact time is applied, and the pH of the water is sufficiently high (Singer et al. 1980, Ficek and Boll 1980, George et al. 1990).

2.8.2 Chlorine Dioxide

Because chlorine dioxide (ClO₂) can accomplish the benefits of raw water preoxidation without forming significant levels of THMs and HAAs, it is gaining more popularity as an alternative to chlorine in drinking water treatment (Gallagher et al. 1994, Gordon and Rosenblatt 1996). It was originally used as a bleaching agent as early as 1940 in the pulp and paper industry, and it is a yellowish colored gas (Bryant et al. 1992) that has a distinct odor resembling that of strong chlorine, kerosene, or cat urine (Hoehn 1993). Although the oxidation potential of chlorine dioxide is a little less than chlorine, it is still an effective oxidizer of iron and manganese, and an effective remover of color, taste and odor of source water (Malkov and Sadar 2007). Also, it is an effective killer of *Cryptosporidium* and *Giardia* at shorter contact times than chlorine (Finch et al. 1995).
Yet, there are a few disadvantages to chlorine dioxide systems. Firstly, chlorine
dioxide is often used as only a primary disinfectant because of its low stability,
undesirable taste, and obnoxious odor (Chen and Rest 1996). Secondly, it must always be
generated on-site due to its explosive properties. It is generated by the addition of
chlorine gas to sodium chlorite or the acidification of a sodium chlorite solution. Thirdly,
chlorine dioxide production systems and reactions with NOM form regulated inorganic
DBPs. Very fine tuning of generators and ClO₂ dosage limits are necessary to prevent the
formation of disinfection byproducts (Gallagher et al. 1994, Gordon and Rosenblatt
1996).

Chlorine dioxide reacts with NOM by a completely different mechanism than
chlorine partially because of the higher oxidation state of chlorine in ClO₂ (+4) than in
HOCl (+1). Unlike chlorine, chlorine dioxide does not react by breaking carbon-carbon
bonds, but reacts by a one electron transfer mechanism as it is reduced to form chlorite
(ClO₂⁻). Thus complete mineralization or chlorine substitution does not usually occur
from chlorine dioxide (Hoehn et al. 1996). Easily oxidized organic molecules such as
unsaturated compounds, alcohols, aldehydes, mercaptans, disubstituted organic sulfides,
and aliphatic amine react readily, but very few THMs and HAAs are formed (Noack and
Doerr 1977, Werdehoff and Singer 1987). An additional advantage of chlorine dioxide
preoxidation is a reduction in THM formation potential if ClO₂ is followed by chlorine
due to the alteration of NOM precursors (EPA 1999).

One of the biggest problems with chlorine dioxide is the formation of chlorite, a
regulated inorganic DBP. The reactions of chlorine dioxide with NOM and bromide or
the photodecomposition of chlorine dioxide form chlorite ($\text{ClO}_2^-$). Since chlorite is regulated at 1 mg/L, chlorine dioxide doses are pretty well restricted to 1 mg/L due to expected 70-100% conversion of chlorine dioxide to chlorite (Rav-Acha et al. 1984, Werdehoff and Singer 1987, Gordon et al. 1990). Once chlorite is formed, it can be further oxidized to chlorate, but chlorate is also considered a toxic DBP that might be regulated in the future (Hoehn 1993).

2.8.3 Hydrogen Peroxide

Even though the oxidation potential of hydrogen peroxide is greater than that of chlorine or chlorine dioxide, the rate of its reaction or decomposition in water treatment at ambient temperature is very slow, and so catalysis is often necessary. Transition metal salts, ultraviolet light (UV), or ozone ($\text{O}_3$) serve as catalysts during advanced oxidation processes (AOPs) (Eskicioglu et al. 2008). During these processes, very reactive hydroxyl radicals, formed from $\text{H}_2\text{O}_2$-accelerated-decomposition of ozone, break down NOM and toxic compounds (Hoigné and Bader 1978). The major applications of AOPs include (i) wastewater treatment with Fenton reagent (Neyens and Baeyens 2003), (ii) groundwater remediation of solvents such as TCE and PCE (Masten and Hoigné 1992, Aieta et al. 1988, Glaze and Kang, 1988), and (iii) removal of taste and odor compounds such as geosmin and 2-methylisoborneol (Pereira et al. 1996, Ferguson et al. 1990, Huck et al., 1995). Applications of AOPs in drinking water treatment have not been widespread because of their high cost and their inability to remove recalcitrant toxic compounds at the µg/L levels due to competitive reactions with mg/L of NOM (Glaze 1986).
AOPs that produce hydroxyl radicals will also convert hydrophobic humic acids of NOM into hydrophilic compounds (Sarathy and Mohseni 2009). Furthermore, these reactions will make compounds more biodegradable, and thus AOPs are often used as a pretreatment in biofiltration or wastewater applications (Jammes et al. 1994, Karpel Vel Leitner 1997, Eskicioglu et al. 2008).

O$_3$/H$_2$O$_2$ advanced oxidation processes have sometimes reduced THM formation due to the degradation of humic substances into lower molecular weight compounds, which are less reactive with chlorine (Duguet et al. 1985, Amy et al. 1986). But if bromide is present, the formation of HOBr, and small molecular weight THM precursors can result in significant THM yields (Dore et al. 1978, Graham et al. 1994). Bromate (BrO$_3^-$) can also be formed from AOPs, but its formation can be suppressed by applying higher H$_2$O$_2$/O$_3$ ratios which result in higher levels of hydroxyl radicals produced that consume O$_3$ (Kruithof et al. 1997, Miller 1993).

2.9 Control of I-THMs with Oxidants

While a substantial amount of research has been completed to examine the reactions of oxidants with NOM to reduce DBP formation, only limited studies have looked at the fate of bromide and iodide after preoxidation. Kumar and colleagues (1986) and Bichsel and Von Gunten (1999) have been pioneers in addressing the question for chlorine, chloramines, and ozone. These three oxidants will oxidize iodide (I$^-$) to hypoiiodous acid (HOI) in a fast reaction, but only ozone and chlorine will further oxidize HOI to iodate (IO$_3^-$). The HOI to IO$_3^-$ pathway is the most desirable because as far as we know iodinated THMs or other I-DBPs will only form from reactions between HOI and
NOM (Figure 2.5). As for bromide (Br\(^{-}\)), Cl\(_2\) (HOCl) can oxidize Br\(^{-}\) to Br\(_2\) (HOBr), but NH\(_2\)Cl is not strong enough to oxidize Br\(^{-}\) (Table 2.2).

Figure 2.5: Fate of iodine during oxidative water treatment processes (Bichsel and Von Gunten 1999)

<table>
<thead>
<tr>
<th>Oxidizing Agent</th>
<th>Reducing Agent</th>
<th>Redox Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>Cl(^{-})</td>
<td>1.49 V</td>
</tr>
<tr>
<td>OCl</td>
<td>Cl(^{-})</td>
<td>0.89 V</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>Br(^{-})</td>
<td>1.07 V</td>
</tr>
<tr>
<td>NH(_2)Cl</td>
<td>Cl(^{-})</td>
<td>0.75 V</td>
</tr>
<tr>
<td>I(_2)</td>
<td>I(^{-})</td>
<td>0.55 V</td>
</tr>
</tbody>
</table>

The formation of I-THMs are likely from monochloramine addition because the half life of HOI is longer than the HOI to I\(^{-}\) disproportionation reaction, which may take up to a year (Bichsel and von Gunten 2000b). On the other hand, the half life of HOI
during chlorination is on the order of minutes or hours (Figure 2.6). This correlates with
the necessary reaction times for HOI to react with NOM to form I-THMs, and so I-THM
formation during chlorination processes is also possible. In contrast, ozone suppresses I-
THM formation because HOI is oxidized to IO$_3^-$ in seconds (Von Gunten 2003).

![Figure 2.6: The half life of HOI during oxidation (Bichsel and von Gunten 1999)](image)

Reactions of potassium permanganate, chlorine dioxide, or hydrogen peroxide
with Br$^-$ and I$^-$ alone, or in combination with monochloramine have not been explored in
depth. Potassium permanganate (redox potential: 1.68V) is capable of oxidizing bromide
to bromine (HOBr in water) according to Lawani (1976).

$$MnO_4^- + 5Br^- + 8H^+ \rightarrow Mn^{2+} + 2.5Br_2 + 4H_2O$$

Since the oxidation potential of iodide is lower than bromide, permanganate will
similarly oxidize I$^-$ to HOI. The literature does not suggest whether or not the oxidation
of HOI to IO$_3^-$ by KMnO$_4$ is possible. As mentioned previously, this reaction is the
desired pathway to prevent I-THM formation.

A study by Li and others (1996) suggested that chlorine dioxide (redox potential:
0.8 V) was capable of oxidizing Br$^-$ to HOBr because the formation of bromoform
(CHBr$_3$) was observed. Furthermore, when chlorine dioxide was combined with
monochloramine to treat water with high concentrations of bromide, THM formation was
higher than from the two oxidants alone (Heller-Grossman 1999), which suggests that chlorine dioxide may oxidize NOM to form chloramination DBP precursors (Richardson et al. 1994, Agus et al. 2009).

The reaction of chlorine dioxide with iodide is a multi-step reaction mechanism which consists of two intermittent radical iodide species to ultimately form I₂ (HOI in water) and I₃⁻ (Fabian and Gordon 1997).

\[
\begin{align*}
\text{ClO}_2 + I^- & \rightarrow \text{ClO}_2^- + I^* \\
I^* + I^- & \rightarrow I_2^- \\
\text{ClO}_2 + I_2^- & \rightarrow \text{ClO}_2^- + I_2 \\
I_2 + I^- & \rightarrow I_3^-
\end{align*}
\]

Hua and Reckhow (2007b) agree that chlorine dioxide converts iodide to HOI, but does not convert HOI to IO₃⁻. They observed higher formation of I-THMs from chlorine dioxide than chlorine, and detected only trace amounts of IO₃⁻.

Information on hydrogen peroxide (redox potential: 1.78V) mediated oxidation of iodide is scarce, but there have been studies that have investigated hydrogen peroxide and bromide. Iodide and bromide redox reactions are similar except for differences in their redox potentials (Table 2), so details about bromide oxidation are important for understanding reactions with iodide. Von Gunten and Hoigne (1994) determined that H₂O₂ reacted with HOBr to form Br⁻.

\[
H_2O_2 + HOBr \rightarrow H^+ + Br^- + H_2O + O_2
\]

This suggests that even if Br⁻ is oxidized by chlorine (from NH₂Cl decomposition), the conversion of HOBr back to Br⁻ is very likely, and reactions of HOBr with NOM to form brominated THMs are minimized (Von Gunten and Oliveras...
On the other hand, if ammonia is present in the system at high concentrations due to the application of a lower chlorine to nitrogen ratio, \( \text{HOBr} \) will react with \( \text{NH}_3 \) to form bromamines (Haag et al. 1984), which have been suggested to be involved in THM formation (Luong et al. 1982).

Since the oxidation potential of the reaction of \( \Gamma^- \) to \( \text{I}_2 \) (HOI in water) is lower than the corresponding reaction of bromide, hydrogen peroxide may be strong enough to oxidize \( \Gamma^- \) to HOI. But it is more important to know if HOI is further oxidized to \( \text{IO}_3^- \), so that I-THM formation will be suppressed. For one or both reactions to occur, a catalyst that initiates \( \text{H}_2\text{O}_2 \) decomposition to reactive hydroxyl radical may be required.

Overall, it is possible that the addition of oxidants may actually enhance I-THM formation instead of suppressing it, much like monochloramine, if the \( \Gamma^- \) to HOI to \( \text{IO}_3^- \) pathway stalls at HOI as a product. If the half-life of HOI is sufficiently long, HOI will react with NOM to form I-THMs. The reactions of oxidants with NOM are also important because (i) NOM consumes oxidants such that HOI may not be significantly formed, and also (ii) NOM may be altered such that is more reactive/less reactive in I-THM formation.

2.10 Iodine and Bromine Chemistry

Iodide (\( \Gamma^- \)) and iodate (\( \text{IO}_3^- \)) are the most thermodynamically stable inorganic forms of iodine in water (Whitehead 1984, Moran et al. 2002). A significant amount of iodine is bound to organic matter as well. Plant litter, soil organic (humic) matter, and especially colloidal organic matter are likely carriers of iodine (Oktay et al. 2001, Anderson et al. 2002, Steinberg et al. 2008a). There are strong covalent carbon-iodine
bonds that are produced by electrophilic substitution of iodine into phenolic humic material (Warwick et al. 1993). In one study, as much as 85% of total iodine was bound up in the organic fraction (Oktay et al. 2001). The dominant isotope is $^{127}$I (close to 100%), but the levels of $^{129}$I in the environment (250kg) have more than doubled due to nuclear bomb testing and nuclear fuel reprocessing (Oktay et al. 2001). Natural sources of iodine to rivers include oceanic iodide delivered atmospherically and iodine weathered from rocks (Whitehead 1984). Saltwater intrusion of groundwaters near the coast may also result in elevated concentrations (Agus et al. 2009). Anthropogenic sources of iodine to surface water include agricultural runoff and municipal and industrial waste discharges (Whitehead 1984, Karanfil et al. 2009).

Bromide like iodide is naturally present in surface waters, and its concentration can also be elevated due to saltwater intrusion (Agus et al. 2009). The dominant form of bromine in aquatic systems is bromide ($\text{Br}^-$). Bromate ($\text{BrO}_3^-$) is not as common in natural systems because it requires a very strong oxidant such as ozone to convert bromide to bromate (Haag et al. 1984). Overall, bromide is much more stable than iodide because iodide undergoes various oxidation/reduction reactions and more biological transformations (Whitehead 1984, Steinberg et al. 2008b). Dissolved bromide, like iodide, also can originate from human activities. Applications of brine to extract oil from the ground have resulted in bromide concentrations in excess of 3 mg/L in groundwater (Richardson et al. 1999). Also, elevated concentrations of bromide have been observed in effluents of industrial or municipal wastewater discharges (Karanfil et al. 2009).
2.11 Br⁻/I⁻ Concentrations and Ratio

In a study of drinking water utilities in 23 cities in the United States and Canada conducted by Richardson and others (2008), the bromide concentration in the source waters varied between 24 and 1120 µg/L (median of 109 µg/L) and the iodide concentration varied between 0.4 and 104.2 µg/L (median of 10.3 µg/L).

In another general survey of United States, Canadian, and European rivers, the iodide concentration in one river was as high as 212 µg/L (Moran et al. 2002). On the other hand, the iodide concentration in ground waters is generally lower than rivers and varies between 0.01 and 20 µg/L, but can exceed 50 µg/L in ground waters near the coast due to salt water intrusion (Cancho et al. 2000).

Generally, when the concentration of bromide is high, it is expected that the concentration of iodide will also be high because both come from similar sources. In the study by Richardson and others (2008), the Br⁻/I⁻ mass ratio in source waters varied from 2.9 to 238 and the average was 13.3. This is much lower than the Br⁻/I⁻ ratio in sea water which is closer to 1000. (Agus et al. 2009). Such large variations in the bromide to iodide ratio in freshwater are due to salt water intrusion, various salt deposits containing different levels of bromide and iodide, anthropogenic influences, and the general instability of iodide as an aqueous species compared to bromide (Whitehead 1984, Steinberg et al. 2008b). There are two significant points to be made regarding bromide and iodide concentrations found in source waters by Richardson and others (2008): (i) bromide was always at a higher concentration than iodide, and (ii) the bromide and iodide ratio varied, but a representative Br⁻/I⁻ ratio for freshwater was roughly 10.
As mentioned previously, an occurrence study of 12 plants with “challenged” source waters was conducted (Krasner et al. 2006). While I-THM levels were typically lower than THMs, there was one plant that produced a high concentration of I-THMs as the sum of I-THMs was 81% of the mass concentration of THM4 or TTHM (Figure 2.7).

The concentration of bromide in the source water was 150 μg/L, and the plant simultaneously added chlorine and ammonia at the same location (thus closely simulating preformed monochloramine addition). As observed in Figure 2.7, CHCl₂I was the dominant species detected, and was at a higher concentration than any regulated THM species. Iodoacids which are even more toxic than I-THMs were also detected for the first time at this particular plant.

Figure 2.7 THM and I-THM formation from chloramination of a Br⁻/I⁻ challenged source water (Krasner et al. 2006)
The detection of I-THMs and HAAs from chloramination plants prompted a follow-up study of plants in 22 cities that used monochloramine disinfection (Richardson et al. 2008). The source waters had varying bromide and iodide concentrations as well as different prechlorination contact times prior to ammonia addition. It was unexpected that I-THM formation was observed at all six plants in which iodide in the source water was below 0.13 μg/L. These findings suggest that organic iodide may play a role in I-THM formation. Results from seven plants with short prechlorination contact times (<1 min) and two plants practicing only chlorination are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Disinfectant</th>
<th>TOC</th>
<th>Bromide</th>
<th>Iodide</th>
<th>Br/I</th>
<th>CHBrClI</th>
<th>CHCl₂I</th>
<th>Sum I-THM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH₂Cl</td>
<td>5.1</td>
<td>699</td>
<td>65</td>
<td>11</td>
<td>5.4</td>
<td>1.5</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>NH₂Cl</td>
<td>5.6</td>
<td>133</td>
<td>1.0</td>
<td>133</td>
<td>1.4</td>
<td>3.5</td>
<td>4.9</td>
</tr>
<tr>
<td>6</td>
<td>NH₂Cl</td>
<td>3.3</td>
<td>96</td>
<td>0.4</td>
<td>240</td>
<td>0.2</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>Cl₂</td>
<td>3.5</td>
<td>214</td>
<td>7.3</td>
<td>29</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>NH₂Cl</td>
<td>5.2</td>
<td>204</td>
<td>10.3</td>
<td>20</td>
<td>1.0</td>
<td>5.1</td>
<td>6.1</td>
</tr>
<tr>
<td>13</td>
<td>NH₂Cl</td>
<td>5.1</td>
<td>186</td>
<td>22.3</td>
<td>8</td>
<td>2.1</td>
<td>5.7</td>
<td>7.8</td>
</tr>
<tr>
<td>15</td>
<td>NH₂Cl</td>
<td>NR</td>
<td>107</td>
<td>ND</td>
<td>N/A</td>
<td>0.2</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>17</td>
<td>NH₂Cl</td>
<td>3.9</td>
<td>NR</td>
<td>22.4</td>
<td>N/A</td>
<td>3.5</td>
<td>0.6</td>
<td>4.1</td>
</tr>
<tr>
<td>19</td>
<td>Cl₂ (but natural ammonia present to form NH₂Cl)</td>
<td>5.0</td>
<td>300</td>
<td>104.2</td>
<td>3</td>
<td>0.7</td>
<td>1.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

While, the concentration of iodoacids are not presented, high concentrations of iodinated HAAs were also detected in plants with short chlorine contact time, and it is feasible that I-THMs can serve as strong indicators for the potential formation of very toxic iodinated HAAs.
Only CHCl$_2$I and CHBrClI were measured in the Richardson and other occurrence study (2008) because those were the two I-THM species most commonly observed in the previous occurrence study (Krasner et al. 2006). Furthermore, in a Barcelona distribution study, out of 37 samples analyzed, 33 had CHCl$_2$I, 27 had CHBrClI, and only three contained iodoform for a source water with a bromide concentration of 750 µg/L (Khiari et al. 1999). In addition, Brass and others (1975) reported CHCl$_2$I in 85/111 U.S. water supplies in a national organic monitoring survey. Cancho and his colleagues (2000) reported that CHCl$_2$I, CHBrClI and CHBr$_2$I were detected in a drinking water plant (source water Br$^-$: 700 µg/L, I$: 3 µg/L), while no I-THMs were detected in the distribution system. Richardson and others (2003) reported that only trace levels of CHBr$_2$I and CHCl$_2$I were detected after prechlorination of a source water (Br$: 2000$ µg/L, I$: 18$ µg/L), while I-THMs were usually formed more frequently from chlorine dioxide addition instead (Table 2.4).

**Table 2.4 I-THMs identified in the lab and in practice (adapted from Richardson et al. 2003)**

<table>
<thead>
<tr>
<th></th>
<th>Sampling 2 (May 99)</th>
<th>Sampling 3 (Sept 99)</th>
<th>Sampling 5 (July 00)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl$_2$ ClO$_2$ + NH$_2$Cl</td>
<td>Cl$_2$ ClO$_2$ + Cl$_2$</td>
<td>Cl$_2$ ClO$_2$ lab ClO$_2$</td>
</tr>
<tr>
<td>CHCl$_2$I</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHBrClI</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHBr$_2$I</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHCI$_2$I</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHClI$_2$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHBrI$_2$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CHI$_3$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Overall, iodoform was rarely formed in the previous studies. It is rarely detected unless the iodide concentration is high, and usually only when ammonia is added before chlorine (Hansson et al. 1987). In Australia, one large utility switched from chlorine to monochloramine in order to maintain a disinfectant residual in its very large water distribution system, but consumers immediately complained about a medicinal taste and odor. The culprit was iodoform. The concentration of bromide and iodide in the source water was 700 and 50 µg/L, respectively. The utility added ammonia 80 seconds before chlorine, and as a result, there was no free chlorine contact time. The iodoform issue was resolved by adding chlorine a few minutes before ammonia. Even though higher concentrations of bromoform were formed, iodoform levels were reduced below 1 µg/L.

2.13 Halide Competition

When source waters containing bromide and iodide are chlorinated, HOCl will react with bromide and iodide to form HOBr and HOI. As a result, there are three oxidants present (HOCl, HOBr, and HOI) that can substitute to form THMs or other unknown DBPs. Even though bromide and iodide are at much smaller concentrations than applied chlorine (µg/L vs. mg/L levels), bromide and iodide may outcompete chlorine due to their faster substitution rate kinetics (Gallard et al. 2003, Westerhoff et al. 2004). Overall, it is generally believed that HOCl is a better oxidizing agent, while HOBr and HOI are better substituting agents (Ichihashi et al. 1999, Gallard et al. 2003). HOBr substitution rate constants are 1-2 magnitudes higher than HOCl constants. Unlike chlorine, HOI can compete with HOBr because HOBr rate constants vary from as little as 5 to as much as 500 times those of HOI constants. But, HOI is at a disadvantage to begin
with during the chlorination of drinking water because bromide concentrations are always higher than iodide concentrations in source waters, and HOI can be oxidized to IO₃⁻ by HOCl (Richardson et al. 2008, Bichsel and von Gunten 1999).

### 2.14 pH Effects

#### 2.14.1 Halogenating Agents and Substitution

It is generally accepted that deprotonated acids are more reactive than the protonated analogs for substitution (Westerhoff et al. 2004). However, hypiodous acid (HOI) will dominate over hypoiodate (OI⁻) for a pH range of 6 to 9 because the pKₐ of HOI/OI⁻ is 10.6 (Bichsel and Von Gunten 2000b). The values for HOCl and HOBr are much lower. The pKₐ of HOCl/OCl⁻ is 7.5, while the pKₐ of HOBr/OBr⁻ is 8.8. Overall, chlorine speciation will be significant for a pH range of 6 to 9, but bromine and iodine speciation will likely be dominated by HOBr and HOI, respectively.

Westerhoff and others (2004) concluded that there was little variability in the second order rate constants for HOBr/OBr⁻ between pH 5 and 11. The researchers emphasized that the hydrogen dissociation of the halogenating agent and NOM was not significant over this pH range. Gallard and others (2003) concluded that in the pH range between 6 and 9, the reaction between HOBr and phenoxide ions dominated and not OBr⁻ and phenoxide ions.

In conclusion, since the pKₐ of aqueous iodine is greater than aqueous bromine, HOI dominates over OI⁻, and so OI⁻ is probably not a significant factor in I-THM formation for pH ranges of typical source waters.
2.14.2 Monochloramine Stability

Monochloramine (NH₂Cl) is fairly stable for pH ≥ 7.5, and thus the only strong oxidant present in a bromide/iodide system is HOI when NH₂Cl is added to water (Valentine et al. 1986, Bichsel and von Gunten 1999). Monochloramine is not strong enough of an oxidant to convert Br⁻ to HOBr, unlike free chlorine (Trofe et al. 1980, Valentine and Jafvert 1988). But when the pH is reduced to 6, and high concentrations of bromide are present, acid- and bromine-catalyzed reactions occur and result in additional oxidants and halogenating agents to the system (Karanfil et al. 2007). Reaction scheme one (shown below) is the formation of bromochloramine (NHBrCl), which results from Br⁻ reacting with protonated monochloramine (NH₃Cl⁺) (Trofe et al. 1980). Reaction scheme two (below) is increased acid-catalyzed hydrolysis of monochloramine to form HOCl (Valentine and Jafvert 1988). Then, free chlorine reacts with Br⁻ to form HOBr (Bousher et al. 1986). Then, HOBr can react with NH₂Cl to form NHBrCl (Gazda and Margerum 1994), or it can react with NOM to form DBPs (Chang et al. 2001).

**Reaction Scheme 1 (Karanfil et al. 2007)**

\[
\begin{align*}
\text{NH}_2\text{Cl} + H^+ & \rightarrow \text{NH}_3\text{Cl}^+ \\
\text{NH}_3\text{Cl}^+ + \text{Br}^- & \rightarrow \text{NH}_3\text{Br}^+ \\
\text{NH}_2\text{Cl} + \text{NH}_3\text{Br}^+ & \rightarrow \text{NHBrCl}
\end{align*}
\]

**Reaction Scheme 2 (Karanfil et al. 2007)**

\[
\begin{align*}
\text{H}_2\text{O} + \text{NH}_2\text{Cl} & \rightarrow \text{HOCl} + \text{NH}_3 \\
\text{HOCl} + \text{Br}^- & \rightarrow \text{HOBr} \\
\text{HOBr} + \text{NH}_2\text{Cl} & \rightarrow \text{NHBrCl}
\end{align*}
\]
Now that acid- and bromine-catalyzed decomposition of monochloramine has been discussed, it is important to understand how it relates to I-THM formation pathways. Overall, the consequence of monochloramine decomposition at pH 6 is the formation of HOCl, HOBr, and HOI that will all compete for THM precursors (Figure 2.8). The small concentration of HOCl formed from NH$_2$Cl decomposition may oxidize HOI to IO$_3^-$ and remove iodine as a competing halogenating agent (Bichsel and Von Gunten 1999). The reactivity of the three halogenating agents will result in the formation of both THMs and I-THMs for pH less than 7.5. Also, there may be reactions of monochloramine (NH$_2$Cl) and bromochloramine (NHBrCl) with NOM to form unknown DBPs (Hua and Reckhow 2008a, Luong et al. 1982).

I-THM formation pathways for pH greater than 7.5 are different because monochloramine will not decompose to chlorine at higher pH (Figure 2.9). HOBr will not be formed because HOCl is not present and NH$_2$Cl is incapable of oxidizing bromide to HOBr. The only oxidant in the system will be HOI as a result of reactions between I$^-$ and NH$_2$Cl. In addition, HOI will not be further oxidized to IO$_3^-$ by NH$_2$Cl (Bichsel and Von Gunten 1999), so I-THM formation will probably be favorable at higher pH due to the persistence of HOI. There will also be reactions of NH$_2$Cl with NOM to form unknown DBPs. The reactions of NHBrCl with NOM are not shown because the formation of bromochloramines is more likely at lower pH (Trofe et al. 1980, Gazda and Margerum 1994).
Figure 2.8 I-THM formation pathways from preformed NH₂Cl for pH <7.5

Figure 2.9 I-THM formation pathways from preformed NH₂Cl for pH >7.5
2.15.1 pH Effect

The substitution of iodide with NOM to form I-THMs is a base-catalyzed electrophilic substitution reaction where HOI is the electrophile. According to Bichsel and Gunten (2000), there are three steps in iodoform formation from proposed I-THM precursors which include aldehydes and ketones. These steps include the enolization step, the iodination step, and the hydrolysis step. At low pH, the first two steps, enolization and iodination are rate limiting, and thus HOI is much slower to react with NOM to form the tri-iodinated iodoform. At higher pH, the hydrolysis step is the rate limiting step, and thus HOI is swifter to react with NOM to form intermediates in the I-THM formation pathway (Hua and Reckow 2008a). Furthermore, as the pH is increased, the iodoform precursor, an enol is converted to its conjugate base, enolate, at a higher pH and because the enolate is negatively charged, and it is a much stronger nucleophile than the enol, it reacts more readily with the electrophile, HOI, to form iodoform or other I-THMs. (Bruice 2004).

So, when the pKₐ of HOI/OI⁻ and the alterations of NOM due to pH changes are considered, the most important factor in I-THM formation with changes in pH is most likely the deprotonation of the NOM. Furthermore, iodine is the most sensitive to electron donating or electron accepting substitutes on NOM components (Gallard et al. 2003). This suggests that the pH of the source water, as well as the functional groups and characteristics of the NOM will be very important for predicting I-THM formation.
2.15.2 NOM Effect

Natural organic matter (NOM) is a mixture of organic compounds that vary in size, structure, and polarity (Westerhoff et al. 2004, Hua and Reckhow 2007a). Generally, NOM can be characterized by its specific ultraviolet absorbance (SUVA$_{254}$/DOC), which indicates the aromaticity of the organic matter. Humic substances (high-SUVA) which are typically rich in aromatic carbon are considered the dominant THM precursors (Kitis et al. 2001). But other studies have suggested that low-SUVA components certainly play a role in DBP formation (Ates et al. 2007). High-SUVA NOM components are generally large hydrophobic compounds containing phenol-like structures with conjugated double bonds, while low-SUVA components are aliphatic compounds such as sugars and proteins (Jarusuthirah et al. 2002).

Recent studies suggest that low-SUVA NOM components may be significant precursors of I-THMs. Hua and Reckhow (2005, 2007a, 2008b) reported that bromine and iodine were more reactive with hydrophilic and low molecular weight (MW) fractions to form THMs and HAAs than their corresponding hydrophobic and high MW fractions. However, hydrophobic and high MW fractions produced more unknown total organic halides (UTOX) when reacting with bromine and iodine which suggests that high-SUVA components were very reactive, but they were forming brominated and iodinated compounds other than THMs.
2.16 1-THM Formation in the Laboratory

2.16.1 The Effect of Oxidant or Disinfectant

One of the first laboratory studies conducted to understand 1-THM formation from various oxidants was conducted by Bichsel and Von Gunten (2000a). The purpose of their investigation was to understand the fate of iodide from the application of ozone, chlorine, and monochloramine. They studied two different source waters, one from a lake and one from a river. The source water characteristics are provided in Table 2.5.

**Table 2.5: Water characteristics for Lake Zurich and the Seine River (Bichsel and Von Gunten 2000a)**

<table>
<thead>
<tr>
<th>Water Parameters</th>
<th>Lake</th>
<th>River</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>1.3 mg/L</td>
<td>3.5 mg/L</td>
</tr>
<tr>
<td>Br⁻</td>
<td>15 μg/L</td>
<td>30 μg/L</td>
</tr>
<tr>
<td>I⁻</td>
<td>not reported</td>
<td>not reported</td>
</tr>
<tr>
<td>SUVA</td>
<td>not reported</td>
<td>not reported</td>
</tr>
</tbody>
</table>

Since the ambient iodide was very low, the researchers added 50 μg/L of I⁻ to the source waters. The researchers summarized the differences between the oxidants in terms of formation of the organic and inorganic products (Table 2.6).
It is observed in Table 2.6 that I-THMs were never detected when ozone was applied, and the primary product was iodate. On the other hand, chlorine and chloramine formed iodoform and other I-THMs. More specifically, chloramine formed more iodoform, while chlorine formed the chlorinated, iodinated species. Brominated I-THMs were rarely observed because the ambient bromide (15 or 30 µg/L) was low compared to the concentration of chlorine (0.5 or 1.0 mg/L) and iodide (50 µg/L).

Chlorine kinetics studies demonstrated that while 90% of HOI was gone after 30 minutes, only 50% of the final iodate concentration was reached after 1 hour. I-THM formation was a little slower, as half of the final iodoform concentration was reached after two hours, and it took 10 hours for all I-THM reactions to be completed.

In summary, this study demonstrated that the iodate suppression pathway and the I-THM formation pathway were competitive when the iodide concentration was moderately high, and the chlorine dose was low. Furthermore, even though the Br⁻/I⁻ ratio was not realistic in this study, the results demonstrated that chlorination of waters with high iodide levels can form iodinated THMs.
2.16.2 Chlorination and High Iodide Levels

Hua and others (2006) investigated the effects of higher chlorine doses (5.0, 6.2 mg/L) on I-THM formation in waters with very high iodide concentrations (254, 1269, 3807 μg/L). The ambient concentrations of bromide in the low- and high-SUVA tested water were very low compared to the spiked iodide concentrations. The characteristics of the waters are presented in Table 2.7.

<table>
<thead>
<tr>
<th></th>
<th>Winnipeg</th>
<th>Tulsa</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>8.5 mg/L</td>
<td>5.1 mg/L</td>
</tr>
<tr>
<td>Br⁻</td>
<td>9 µg/L</td>
<td>63 µg/L</td>
</tr>
<tr>
<td>I⁻</td>
<td>not given</td>
<td>not given</td>
</tr>
<tr>
<td>SUVA</td>
<td>1.6 L/mg-m</td>
<td>3.1 L/mg-m</td>
</tr>
</tbody>
</table>

The two major findings from this study were (1) that dichloroiodomethane (CHCl₂I) was the dominant I-THM species during chlorination, and (2) CHCl₂I formation increased with small chlorine doses and then decreased with higher doses. The THM and I-THM speciation results are shown in Figure 2.10, and it is evident that CHCl₂I was dominant for all iodide levels, and iodoform (CHI₃) was not a dominant species until the concentration of iodide was very high (3807 μg/L). At this level, the concentrations of I-THMs were greater than the regulated THMs. Also, there was very minor formation of brominated I-THMs because the concentration of bromide and the Br⁻ /I⁻ ratio was too low.
Figure 2.10: Effect of iodide concentration on the formation and distribution of THMs and I-THMs: a) Winnipeg water b) Tulsa water (Hua et al. 2006)

The results from Hua et al. (2006) also suggested that the presence of chlorine enhanced I-THM formation, especially CHCl₂I, when the chlorine dose was small and the iodide concentration was sufficiently high (Figure 2.11a). As was previously discussed (Bichsel and von Gunten 2000), it was generally believed that chlorination minimized I-THM formation by favoring the oxidation of HOI to iodate. These results from Hua and others suggest that if the Cl₂/I⁻ ratio is sufficiently low, I-THM formation is favorable. However, this may not be true for total organic iodine (TOI) (Figure 2.11b).
Figure 2.11 Chlorine dose and the formation of iodinated DBPs (I$: 254 \mu g/L$)
(a) I-THMs (b) TOI, TOCl, TOBr, and IO$^-$ (Hua et al. 2006)

2.16.3 High Levels of Bromide and Iodide

In the previous two studies, the concentration of iodide was increased without increasing the concentration of bromide. As mentioned previously, bromide should be at least the concentration of iodide, and most often it is ten times greater. A much earlier study conducted by Bunn and others (1975) investigated the formation of four trihalomethanes with (1) high concentrations of bromide and iodide separately, and (2)
high concentrations of bromide and iodide together during chlorination. The results in Table 2.8 demonstrate that the addition of Cl\(^{-}\) and F\(^{-}\) had no effect on regulated THM formation as expected, while the addition of Br\(^{-}\) and I\(^{-}\) certainly affected THM speciation.

Table 2.8 THM formation from 7 mg/L HOCl and halide addition (Bunn et al. 1975)

<table>
<thead>
<tr>
<th>Halide Added</th>
<th>CHCl(_3) [µg/L]</th>
<th>CHBrCl(_2) [µg/L]</th>
<th>CHBr(_2)Cl [µg/L]</th>
<th>CHBr(_3) [µg/L]</th>
<th>Total [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>172</td>
<td>20</td>
<td>1</td>
<td>&lt;1</td>
<td>193</td>
</tr>
<tr>
<td>1 mg/L F(^{-})</td>
<td>158</td>
<td>17</td>
<td>1</td>
<td>&lt;1</td>
<td>176</td>
</tr>
<tr>
<td>1 mg/L Cl(^{-})</td>
<td>166</td>
<td>18</td>
<td>1</td>
<td>&lt;1</td>
<td>185</td>
</tr>
<tr>
<td>1 mg/L Br(^{-})</td>
<td>21</td>
<td>35</td>
<td>30</td>
<td>50</td>
<td>136</td>
</tr>
<tr>
<td>1 mg/L I(^{-})</td>
<td>67</td>
<td>15</td>
<td>1</td>
<td>&lt;1</td>
<td>83</td>
</tr>
</tbody>
</table>

As observed in Table 2.8, the addition of bromide shifted speciation towards the more brominated THMs, while the addition of iodide reduced THM formation due to the formation of CHCl\(_2\)I, CHClI\(_2\), and CHI\(_3\) (species not shown).

When excessively high bromide and iodide levels were added at the same time (5 mg/L, 5 mg/L), bromide did not outcompete iodide for substitution and form only brominated and chlorinated THMs because there was significant formation of I-THM species (Table 2.9). Overall when the bromide to iodide ratio was 1.0, CHBr\(_2\)I was the dominant species, while CHI\(_3\) (iodoform) was also significant.

Table 2.9 I-THMs formed from chlorination of water (5 mg/L Br\(^{-}\) and 5 mg/L I\(^{-}\)) (Bunn et al. 1975)

<table>
<thead>
<tr>
<th>I-THM Species</th>
<th>Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_2)I</td>
<td>&lt;MRL</td>
</tr>
<tr>
<td>CHClI(_2)</td>
<td>24</td>
</tr>
<tr>
<td>CHI(_3)</td>
<td>66</td>
</tr>
<tr>
<td>CHBr(_2)I</td>
<td>138</td>
</tr>
<tr>
<td>CHBrI(_2)</td>
<td>22</td>
</tr>
<tr>
<td>CHBrCl(_2)</td>
<td>&lt;MRL</td>
</tr>
</tbody>
</table>
2.16.4 Bromide and Iodide Ratio and Incorporation

The Br⁻/I⁻ ratio was changed significantly in another study in order to understand the competition between bromine and iodine for substitution into THMs (Gould et al. 1984). Bromine (η_{Br}) and iodine incorporation factors (η_{I}) were calculated. For a mixture of THMs, the general formula was CHCl_{η_{Cl}}Br_{η_{Br}}I_{η_{I}}, and for each species the sum of η_{Cl}, η_{Br}, and η_{I} added up to 3.0. Likewise, when the incorporation factors were calculated for the whole mixture, the average incorporation factors added up to 3.0. The experiment included chlorination of a model THM precursor, 2,4,6-hydroxyacetophenone (2,4,6-THA) for 4.5 hours with a very high chlorine concentration of 420 mg/L.

Table 2.10 Halogen incorporation factors for chlorination of 210 μM 2,4,6 THA (adapted from Gould et al. 1984)

<table>
<thead>
<tr>
<th>Br⁻ [mg/L]</th>
<th>I⁻ [mg/L]</th>
<th>Br⁻/I⁻</th>
<th>η_{Br}</th>
<th>η_{I}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>10.2</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>0.3</td>
<td>101.5</td>
<td>0.00</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>6.4</td>
<td>0.5</td>
<td>12.59</td>
<td>0.29</td>
<td>0.00</td>
</tr>
<tr>
<td>6.4</td>
<td>101.5</td>
<td>0.06</td>
<td>0.56</td>
<td>0.07</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Br⁻ [mg/L]</th>
<th>I⁻ [mg/L]</th>
<th>Br⁻/I⁻</th>
<th>η_{Br}</th>
<th>η_{I}</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.9</td>
<td>0.5</td>
<td>125.9</td>
<td>2.01</td>
<td>0.00</td>
</tr>
<tr>
<td>63.9</td>
<td>10.2</td>
<td>6.30</td>
<td>1.54</td>
<td>0.01</td>
</tr>
<tr>
<td>63.9</td>
<td>101.5</td>
<td>0.63</td>
<td>1.88</td>
<td>0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Br⁻ [mg/L]</th>
<th>I⁻ [mg/L]</th>
<th>Br⁻/I⁻</th>
<th>η_{Br}</th>
<th>η_{I}</th>
</tr>
</thead>
<tbody>
<tr>
<td>639.2</td>
<td>0.0</td>
<td>n/a</td>
<td>2.74</td>
<td>0.00</td>
</tr>
<tr>
<td>479.4</td>
<td>253.8</td>
<td>1.89</td>
<td>2.31</td>
<td>0.01</td>
</tr>
<tr>
<td>319.6</td>
<td>507.6</td>
<td>0.63</td>
<td>0.21</td>
<td>0.39</td>
</tr>
<tr>
<td>159.8</td>
<td>761.4</td>
<td>0.21</td>
<td>0.02</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0</td>
<td>1015.2</td>
<td>n/a</td>
<td>0</td>
<td>0.58</td>
</tr>
</tbody>
</table>

As observed in Table 2.10, as halide ion concentration was increased, their respective incorporation factor increased. In addition, iodine incorporation was only observed when the Br⁻/I⁻ ratio was very low, and usually only when it was below 1.0.
In summary, even though the chlorine contact time was very short (4.5 hours for all I-THMs to form), and the concentration of chlorine, bromide, and iodide were very high and unrealistic, the results demonstrated the dominance of bromine over iodine in THM substitution.

2.16.4 Chlorine to Nitrogen Ratio and Chloramine Dose

As mentioned previously, if there is a sufficient level of ammonia in the water, combined chlorine (chloramines) will form if the chlorine dose is too low to achieve breakpoint. If a utility intends to operate under monochloramine conditions instead of at breakpoint, it will aim for a Cl$_2$N ratio between 3 and 4 (Figure 2.12). A study by Leitner and others (1998) demonstrated that iodoform formation is an issue when the iodide concentration is high (260 µg/L) and the applied Cl$_2$/N weight ratio is within the range of 2-8 (Figure 2.13). Furthermore, these results suggest that the concentration of monochloramine is not as critical in I-THM formation because the concentration of applied NH$_2$Cl varied between 1.0 and 1.75 over the 2-8 Cl$_2$/N ratio range, and the levels of iodoform formed fluctuated around an average of 12 µg/L (Figures 2.12 and 2.13). In summary, iodoform will form if chloramine is present, and free chlorine is negligible.
Figure 2.12 Chlorine species formed from different Cl₂/N ratios (Leitner et al. 1998)

Figure 2.13 Cl₂/N ratio and iodoform formation (adapted from Leitner et al. 1998)
Another study evaluated the effect of Cl₂/N ratio for two different NH₂Cl target residuals, but at more realistic bromide and iodide concentrations. Khiari and colleagues (1999) tested a 3:1 versus a 5:1 Cl₂/N ratio. But because the concentration of bromide and iodide were much lower (Br⁻ =110 μg/L, I⁻ = 14 μg/L), the dominant I-THM species was not iodoform. The only two species detected consistently were CHCl₂I and CHBrClI (Figure 2.14). The major conclusions from this study were: (i) a large increase in monochloramine residual (0.5 mg/L to 4.0 mg/L) increased I-THM formation, (ii) and an increase in Cl₂/N ratio (3:1 to 5:1) resulted in negligible reductions in I-THM formation.

![Figure 2.14: The effect of Cl₂/N ratio and NH₂Cl residual on I-THM formation (adapted from Khiari et al. 1999)](chart)
Overall, the results of the studies by Leitner and others (1998) and Khiari and others (1999) suggest that Cl₂/N ratio is not critical in I-THM formation as long as breakpoint is not surpassed. Also, small differences in monochloramine dose (such as between 1 and 2 mg/L) will not have an appreciable impact on I-THM formation.

2.16.5 The Order of Chlorine and Ammonia Addition

Even though the Cl₂/N ratio is not critical in the formation of iodoform, the order of addition between chlorine and ammonia is very important. A laboratory study by Hansson and others (1987) demonstrated that iodoform formation occurs when ammonia is added prior to chlorine addition, while its formation is suppressed when Cl₂ followed by NH₃ addition is practiced. In the laboratory study, Australian raw water (ambient 700 μg/L Br⁻ and 50 μg/L I⁻) was supplemented with an additional 40 μg/L I⁻, and the water was chloraminated by adding NH₃ first followed by HOCl. Iodoform was formed in a concentration of 8 μg/L. On the other hand, when the Cl₂/NH₃ process was practiced, <1 μg/L of iodoform was formed; CHBr₂I and CHBrClI were detected; and bromoform (CHBr₃⁻) was a dominant species.

Overall, the conclusion from this research was that the order of addition of chlorine and ammonia was very important. The findings of this study resulted in an implementation of a pre-chlorination contact time of 80 seconds prior to ammonia addition for a challenged source water (high Br⁻, high I⁻). After the change, taste and odor problems due to iodoform were no longer an issue, and THM levels were reasonably low.
2.16.6 pH Effect for High Iodide Concentrations

Hua and Reckhow (2008a) investigated source waters spiked with an unrealistically high concentration of iodide (1900 µg/L). The bromide concentration was more typical of source waters (78 µg/L), and therefore the Br⁻/I⁻ ratio was very low, 0.04 µg/µg, compared to an expected value close to 10.

The results, shown in Figure 2.15, suggested that I-THM concentration increased with pH, while unknown total organic iodide (UTOI) decreased with higher pH. In terms of speciation, the formation of iodoform was more favorable at higher pH while formation of the mixed chlorinated/brominated species of I-THM was less favorable. However, overall, iodoform was always the dominant species regardless of pH.

![Figure 2.15 Effect of pH on I-THM formation (Hua and Reckhow 2008a)]
2.16.7 The Effect of Oxidant or Disinfectant on I-THM Speciation

While the work of Bichsel and von Gunten (2000a) was critical for a fundamental understanding of the general risk of I-THM formation during ozone, chlorine and monochloramine processes, the researchers did not address chlorine dioxide as an oxidant, and they did not report the concentrations of individual I-THMs for the different oxidant treatments. A follow up study by Hua and Reckhow (2007b) analyzed five treatment schemes that included chlorine dioxide, and they reported I-THM speciation differences among the different oxidant treatments (Figure 2.16).

Figure 2.16 The formation of I-THMs and iodate from oxidation and disinfection (Hua and Reckhow 2007b)

As seen in Figure 2.16, the dominant species formed from monochloramine was iodoform (CHI₃), while the dominant species from chlorine was CHCl₂I. In addition,
monochloramine formed the highest concentration of I-THMs, while ozone only formed trace amounts of CHCl₂I. Another interesting observation was that it was not necessary to add NH₂Cl after ClO₂ for I-THM formation to occur. It is important to note that in the distribution studies of Richardson and others (2003) many I-THM species were formed from ClO₂ followed by NH₂Cl, while only CHBr₂I was formed after ClO₂ alone. The source water investigated contained a much higher concentration of bromide than iodide (2000 µg/L versus 18 µg/L).

In contrast, in Hua and Reckhow’s study as shown in Figure 2.16, CHI₃, CHClI₂, and CHCl₂I were the species formed from chlorine dioxide addition. The formation of CHBr₂I was not reported. It is possible that this species was not formed because of the much lower bromide concentration (95 µg/L) that was tested.

Even though it is difficult to make conclusions for practical applications because of the very high level of iodide spiked (200 µg/L) and unrealistic Br⁻ to I⁻ ratio (95µg/L / 200µg/L = 0.48) analyzed in this study, Hua’s and Reckhow’s work still provided important insights for other iodinated DBP research.
While valuable information was obtained from the previous laboratory studies, some of the experiment conditions such as bromide and iodide concentration, and \( \text{Br}^\text{-}/\text{I}^- \) ratio were not typical of source waters. Sometimes iodide was in a concentration greater than bromide, which almost never occurs in source waters. Also, the experimental reaction times were too short for some slower forming I-THMs such as iodoform to completely form. In addition, sometimes the SUVA values of the waters were not reported, or only one source water was tested. This thesis will address some of the questions regarding I-THM formation from various oxidants under practical conditions for a high- and low-SUVA water. Through these findings, scientists and utilities may gain some insight as to some potential I-THM control strategies to keep the public safe from I-THMs and other iodinated DBPs.
CHAPTER THREE

RESEARCH OBJECTIVES AND APPROACH

The main objective of this research was to investigate I-THM formation and control during water treatment for a realistic Br⁻/I⁻ mass ratio of 10, at two representative bromide/iodide levels [(i) 200 µg/L and 20 µg/L, and (ii) 800 µg/L and 80 µg/L]. Unfortunately, previous I-THM research often neglected this very important ratio because iodide was often added in much higher concentrations than bromide. Specifically, this research project focused on three main sub-objectives:

1. **To investigate and compare I-THM formation from preformed monochloramine and prechlorination followed by ammonia addition.** To accomplish this goal, raw and treated water samples were collected from two South Carolina drinking water treatment plants. *Raw* was defined as water directly from the source, while *treated* was defined as water collected after primary treatment without chlorine addition (i.e. after coagulation/flocculation and sedimentation). The source waters of the two plants had different NOM characteristics due to various anthropogenic and natural inputs as a result of their location in South Carolina. The waters were dosed at uniform formation conditions (UFC). This meant a residual of approximately 2.0 mg/L NH₂Cl residual after 24 hours. For prechlorination, the waters were dosed to achieve 0.5 and 1.0 mg/L Cl₂ residual after 5 minutes or 20 minutes, and then chlorine and ammonia were then added to form monochloramine (NH₂Cl). For preformed
monochloramine treatments, NH₂Cl was prepared in a separate beaker and then was added to samples.

2. **To compare the effects of three commonly used preoxidants, potassium permanganate, chlorine dioxide, and hydrogen peroxide (w/o UV, O₂), on I-THM formation.** A contact time of 20 minutes was tested, and the abilities of the oxidants to convert iodide to iodate (thus preventing I-THM formation), or to alter the reactivity of NOM to enhance or diminish I-THM formation was investigated. I-THM formation was measured (i) after oxidation alone, (ii) after preformed monochloramine addition, and (iii) after preoxidation followed by preformed monochloramine addition. The doses of among the oxidants varied, and the concentrations were representative of typical doses applied in practice.

3. **To investigate the importance of bromide to iodide ratio on I-THM formation and speciation from preformed monochloramine and preoxidation.** An opposite Br⁻/I⁻ ratio of 0.5 (100 µg/L bromide and 200 µg/L iodide) was compared with a more typical Br⁻/I⁻ ratio of 10 (800 µg/L bromide and 80 µg/L iodide). Three factors were explored which included, (i) the effect of pH on I-THM formation, (ii) the effect of preoxidation with potassium permanganate or chlorine dioxide, and (iii) the effect of preoxidant addition alone.
CHAPTER FOUR  
MATERIALS AND METHODS

4.1 Drinking Water Treatment Plants and Collection Dates

Table 4.1-4.3 list the characteristics of the waters collected from the Hanahan drinking water treatment plant (Charleston, SC) and the SJWD drinking water plant (Lyman, SC) in May 2008, November 2008, and March 2009. The plants were selected because of their proximity to Clemson University, and because of their differences in their NOM characteristics due to different anthropogenic and natural influences as a result of their location in the state (inland vs. coastal). Three batches of water were collected to fulfill each of the three objectives. The water collected in May 2008 was used to investigate objective 1, or I-THM formation from prechlorination and preformed monochloramine addition. The second batch of water collected in November 2008 was used to investigate objective 2, or I-THM formation from preoxidation and preformed monochloramine addition. Finally, the third batch of water collected in March 2009, was used to investigate objective 3, or the effect of Br/I ratio on I-THM formation from preoxidation and chloramination. Preformed monochloramine was added to the 3 different batches to confirm that I-THM formation or speciation did not change significantly over time due to seasonal changes in NOM characteristics. It was determined that I-THM yields and the species formed in SJWD and Charleston raw water were similar for the three different batches (Figures A1-A4).
### Table 4.1 Characteristics of Charleston and SJWD waters (May, 2008)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Charleston Raw</th>
<th>Charleston Treated</th>
<th>SJWD Raw</th>
<th>SJWD Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>6.0</td>
<td>2.6</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>SUVA	extsubscript{254} (L/mg-m)</td>
<td>4.2</td>
<td>2.0</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>$\Gamma$ (µg/L)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Br$^-$ (µg/L)</td>
<td>100</td>
<td>100</td>
<td>28</td>
<td>28</td>
</tr>
</tbody>
</table>

### Table 4.2 Characteristics of Charleston and SJWD waters (November, 2008)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Charleston Raw</th>
<th>Charleston Treated</th>
<th>SJWD Raw</th>
<th>SJWD Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>6.4</td>
<td>2.5</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>SUVA	extsubscript{254} (L/mg-m)</td>
<td>3.8</td>
<td>2.0</td>
<td>2.6</td>
<td>1.9</td>
</tr>
<tr>
<td>$\Gamma$ (µg/L)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Br$^-$ (µg/L)</td>
<td>115</td>
<td>115</td>
<td>33</td>
<td>33</td>
</tr>
</tbody>
</table>

### Table 4.3 Characteristics of Charleston and SJWD waters (March, 2009)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Charleston Raw</th>
<th>Charleston Treated</th>
<th>SJWD Raw</th>
<th>SJWD Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>7.4</td>
<td>3.1</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>SUVA	extsubscript{254} (L/mg-m)</td>
<td>3.7</td>
<td>2.0</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>$\Gamma$ (µg/L)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Br$^-$ (µg/L)</td>
<td>78</td>
<td>78</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>
The formation of I-THMs from typical oxidant and disinfectant doses was evaluated in the laboratory. Three different bromide and iodide concentration levels were evaluated (200/20, 800/80, and 100/200 µg/L / µg/L). The waters were buffered with sodium bicarbonate (4mM), and suitable volumes of bromide and iodide stock solutions were spiked into the tested waters to achieve the target concentrations. The disinfection strategies applied during the UFC experiments were (i) preformed monochloramine addition, (ii) prechlorination (5 min or 20 min) followed by ammonia addition, and (iii) chlorine dioxide/hydrogen peroxide/potassium permanganate (20 min) followed by chloramination. The UFC doses for preformed monochloramine (NH₂Cl) varied with pH, and chlorine (Cl₂) doses for prechlorination varied for different contact times and Cl₂ residual levels. The concentrations are presented in Table A.1 for preformed NH₂Cl and Tables A.2 and A.3 for prechlorination. As a reminder, for prechlorination, chlorine was added first, and then Cl₂ and NH₃ (Cl₂/NH₃: 3.5 by weight) were then added to form a UFC NH₂Cl dose. The UFC monochloramine doses for the preoxidation experiments varied depending on the oxidant, and the dose and their determining factors will be discussed in Chapter 6.

Small volumes (<1 ml) of stock solutions were added to 65 mL reactors (no headspace) to produce the desired oxidant/disinfectant concentration. All oxidants and disinfectants were spiked using long needle glass syringes such that the oxidants/disinfectants were added to the bottom of the reactor and dispersed quickly. After spiking, reactors were stirred vigorously on magnetic stir plates. If a contact time
was required (i.e. during prechlorination, preoxidation), additional chemicals were spiked to the reactors after 5 or 20 minutes of contact time, and were mixed for an additional 5 minutes afterwards.

After oxidant/disinfectant addition, the 65 ml bottles were capped tightly without headspace to minimize DBP volatilization. The bottles subjected to the different treatment strategies were reacted for 24 hours at ambient room temperature. For each disinfection scenario, duplicate reactors were prepared. The concentration of monochloramine and pH were measured after 24 hours.

Ten milliliter representative samples from the 65 ml reactors were then quenched with a stoichiometric amount of sodium sulfite (Na₂SO₃, 8 mg/L) to destroy NH₂Cl and prevent further unintended reactions between monochloramine, bromide, iodide, and MTBE. Water samples were extracted immediately after quenching. Overall, the mass concentrations of I-THMs and THMs reported in figures are the average results for two independent bottles treated under the same conditions.

4.3 Analytical Methods

Many of the analytical methods described in this section have already been well established in Dr. Karanfil’s research group from the work of previous students (Ilke McAliley and Ying Hong) and some of them (i.e., bromide, iodide, and I-THM) were developed for this project by a group of researchers (Dr. Hocheol Song, Aysenur Saglam, Jia Hu, Jesse Addison, and the author of this thesis) in Dr. Karanfil’s group. Table 4.3 on the following page shows a summary of analytical methods used in this project.
Table 4.3 Analytical methods and minimum reporting levels

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Measurement Method</th>
<th>Equipment</th>
<th>Minimum Reporting Level or Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC(^{b})</td>
<td>(mg/L)</td>
<td>SM 5310B</td>
<td>TOC-V(_{\text{CHS}}), Shimadzu Corp., Japan</td>
<td>0.15</td>
</tr>
<tr>
<td>UV Absorbance(^{c})</td>
<td></td>
<td>SM 5910</td>
<td>DU 640, Beckman Inst. Inc., USA</td>
<td>±0.005(^{d})</td>
</tr>
<tr>
<td>pH</td>
<td>(µg/L)</td>
<td>SM 4500-H(^{+})</td>
<td>420A, Orion Corp., USA</td>
<td>±0.01(^{e})</td>
</tr>
<tr>
<td>(\text{Br})</td>
<td>(µg/L)</td>
<td>USEPA Method 300</td>
<td>ED 40, Dionex Corp., USA</td>
<td>(\text{Br}=10),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HPLC coupled with UV detection</td>
<td>Dionex HPLC</td>
<td>2</td>
</tr>
<tr>
<td>Residual Free/Combined Chlorine</td>
<td>(mg/L)</td>
<td>SM 4500-Cl(_{\text{F}})</td>
<td>NA</td>
<td>0.1-0.15 mg/L</td>
</tr>
<tr>
<td>ClO(_{2})</td>
<td>(mg/L)</td>
<td>LGB/HRP method,</td>
<td>DU 640, Beckman Inst. Inc., USA</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SM 4500-Cl(_{2})</td>
<td>HACH Test Kit</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{O}_2)</td>
<td>(mg/L)</td>
<td>Hach Hydrogen Peroxide Test Kit</td>
<td>HACH Test Kit</td>
<td>0.2</td>
</tr>
<tr>
<td>KMnO(_{4})</td>
<td>(mg/L)</td>
<td>SM 4500-KMnO(_{4})</td>
<td>DU 640, Beckman Inst. Inc., USA</td>
<td>0.5</td>
</tr>
<tr>
<td>THM and I-THM(^{f})</td>
<td>(µg/L)</td>
<td>USEPA Method 551.1</td>
<td>6890 GC-ECD, Agilent, USA</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^{a}\) As reported by the manufacturer. \(^{b}\) Reagent grade potassium hydrogen phthalate was used to prepare external standards. Precision ranged from 0.05 to 0.15 mg/L. \(^{c}\) Measured at wavelengths of 254 using a 1 cm cell. \(^{d}\) Photometric accuracy (absorbance units). \(^{e}\) Accuracy (pH units). \(^{f}\) Methyl-tert butyl ether (MtBE) solvent extraction and gas chromatography (GC) with electron capture detector (ECD) analysis. NA: Not applicable.
4.3.1 Total Organic Carbon

Total organic carbon (TOC) was measured using a Shimadzu TOC-VCHS high temperature combustion analyzer equipped with an auto-sampler. The samples were automatically purged by the analyzer for four minutes before analysis. TOC standards were prepared from 1000 mg/L stock solutions of potassium hydrogen phthalate, and calibration curves were produced for TOC ranging from 0.5-35 mg C/L.

4.3.2 UV Absorbance

UV absorbance was measured using a Cary 300 UV-Vis spectrophotometer (Varian). Samples were measured at wavelength 254 nm in quartz cuvettes. Distilled and Deionized (DDI) water was used as the blank. The blank was measured after several rinses with DDI.

4.3.3 pH

pH was measured using a SM 4500-H+ pH electrode with an Orion 420A pH meter (Orion Corp., USA). The pH meter and electrode were calibrated for every use using standard pH 4, pH 7 and pH 10 buffer solutions (VWR).
4.3.4 Bromide

Bromide was measured using a Dionex DX-600 ion chromatograph equipped with a suppressor. The eluent used in the ion chromatograph was 9 mM Na₂CO₃ and samples were separated using a Dionex HC9 column that was coupled with an AG-HC9 guard column. A 250 µL injection volume was used for drinking water samples being analyzed for bromide.

Calibration standards were prepared with NaBr (>99.9%, Sigma-Aldrich). A low range calibration curve was produced for bromide (5-400 µg/L).

4.3.5 Iodide

Iodide was measured using a method developed by Schwehr and Santschi (2003). The method involves ion chromatographic separation of a sample and measurement with high performance liquid chromatography (HPLC) and UV detection. A 100 µL sample was injected to a Dionex HPLC system (Ultimate 9000) equipped with Dionex AS-10 and AG-10 columns. The mobile phase consisting of DDW and 0.4 g/L NaOH was gradient fed with a flow rate of 1 mL/min. The detector was monitored at a wavelength of 226 nm.

Calibration standards were prepared through dilution of a certified 0.1 M iodide solution (Thermo Scientific) with DDW. A low range calibration curve was produced for iodide (2-200 µg/L).
THMs and I-THMs were measured using USEPA Method 551.1 with minor modifications. A 10 mL sample was extracted with 10 mL of methyl-tert-butyl-ether (MTBE, Sigma-Aldrich) followed by immediate addition of 3 grams of sodium sulfate (for salting out effect) and 1 g of cupric sulfate (for visual phase separation). The samples were then placed on a shaker table at 300 rpm for 30 minutes to dissolve the sodium and cupric sulfate completely. The MTBE extract was analyzed on an Agilent 6890 gas chromatograph (GC) equipped with a DB-1 (J&W Scientific 30m x 0.25mm x 0.001mm) column. I-THM species were purchased from Helix Biotech (Toronto, Canada). Stock solutions were prepared by adding 1 mL of MTBE to 1 µg of pure compound measured by a micro-balance. Calibration standards were then produced from further dilutions of the pure compounds. The GC temperature program used was 35 ºC for 22 minutes, 10 ºC /min to 125 ºC and hold for 1 min., 30 ºC /min to 300 ºC and hold for 4 min. A 2 µL injection volume was used in splitless mode. The make-up and carrier gases used were ultra-high purity (UHP) helium at 51.7 mL/min and UHP nitrogen at 51.4 mL/min. The total run time was 42 minutes. The injector temperature was set at 250 ºC. The detector temperature was set at 290 ºC.
4.5 Disinfectant and Oxidant Preparation and Measurement

4.5.1 Free Chlorine and Preformed Monochloramine

Chlorine stock solutions were prepared by a 100 times dilution of a sodium hypochlorite solution (5% available chlorine). Preformed monochloramine stock solutions were prepared by slowly adding (1 drop per second) a 50 ml known Cl₂ stock solution (pH 9) to a 50 ml solution of (NH₄)₂SO₄ (pH 8.5).

Chlorine and chloramines concentrations were measured using the N, N-diethyl-p-phenylenediamine (DPD) method (Standard Method 4500). Chlorine and chloramines samples were diluted based on their expected residual chlorine or chloramines concentration prior to measurement. The sample was then combined in a beaker with 5 mL of DPD indicator solution and 5 mL of phosphate buffer. After mixing, the sample was titrated using a ferrous ammonium sulfate (FAS) solution. For monochloramine measurements, a pinch of potassium iodide granules was added to the sample to release combined chlorine (monochloramine) to form free chlorine. The DPD solution was used as a color indicator, the phosphate buffer was used for pH control, and the FAS titrant was used for color removal. The DPD indicator solution and FAS solution were made according to the Standard Method 4500 Cl. A standard 1:5 dilution was made for both the FAS solution and the sample. Dilution by this method resulted in a recorded volume of titrant being the same value as the chlorine/chloramines concentration in the sample.
4.5.2 Potassium Permanganate (KMnO₄)

The potassium permanganate stock solution was prepared by dissolving crystals of KMnO₄ in 100 ml DDW water. A high level of analytical precision was essential as 30mg +/- 0.1mg of solid had to be added to the solution. The standard spectrophotometric method (4500-KMnO₄) was applied. In this method, the concentration of KMnO₄ is directly proportional to the absorbance at 525 nm, and so standards varying from 0.5 to 10 mg/L KMnO₄ were prepared. It was necessary to filter the sample with 0.2 µm filters prior to analysis to avoid interferences due to solid MnO₂.

4.5.3 Chlorine Dioxide (ClO₂)

Chlorine dioxide was produced in the lab following a procedure developed at the University of Toronto (Figure 4.1). Slow acidification of sodium chlorite solution with sulfuric acid produced chlorine dioxide and chlorine as a by-product.

![Figure 4.1 Chlorine dioxide lab-scale production setup (Design from Univ. of Toronto Environmental Engineering Laboratory)]
Undesirable chlorine was transformed into chlorine dioxide by passing the gas through another solution of sodium chlorite. The whole system was operated under a vacuum in the hood. The flow rate of sodium chlorite solution was monitored closely because flow rates that were too fast resulted in the cold chlorine dioxide reservoir turning red, which was an explosive hazard. The gas bottle was covered in foam as a precaution. If the production system was operating at its optimum, the chlorine dioxide solution was a yellow color, and progressively became a darker yellow as all the sodium chlorite in the reservoir on the left was reacted. The system was shut-down safely by first disconnecting the gas wash bottles farthest from the vacuum, and then disconnecting bottles carefully in tandem. The vacuum was not turned off until all bottles were disconnected.

The chlorine dioxide stock solution was kept in an amber glass bottle with no headspace in the refrigerator and was not stored for more than a month. The concentration of ClO$_2$ was determined using the Lissamine Green B (LGB) and Horseradish Peroxidase method (HRP) (U.S. EPA method 327). The horseradish peroxidase converted chlorite to chlorine dioxide, and chlorine dioxide oxidized the LGB dye and changed its red adsorption spectrum (Dattilio et al. 2005, Wu et al. 2007). A spectrophotometer was used to measure the absorbance difference between the reagent blank, a sparged and an unsparged sample. By this methodology, the concentration of chlorine dioxide and chlorite in the stock was determined. For the samples, the concentration of chlorine dioxide and chlorite was determined after 20 min and also after 24 hours. The measurement after 20 min was an unsparged sample, and thus was the sum
of both chlorine dioxide and chlorite. Chlorine dioxide and chlorite individual concentrations were only measured after 24 hours because 5 minutes of sparging time was required to determine the concentrations of both chlorine dioxide and chlorite.

While the LGB dye method was time consuming and required a number of chemicals, it was shown to be the most precise method with the least interference (Hofmann et al. 1998). Chlorophenol red, acid chrome violent k, and amaranth are other dyes that are commonly used. The DBD chlorine dioxide method with glycine as a chlorine masking agent is very common, but the DBD color change is not stable, even over minutes due to continued oxidation of DBD by the chlorite product (Gordon et al. 2000, Desai 2002). For this reason, the DBP method was only used as a confirmation for the results from the LGB method.

4.5.4 Hydrogen Peroxide (H$_2$O$_2$)

Hydrogen peroxide stock solutions were prepared from a dilution of a 30% solution of ACS grade hydrogen peroxide. The stock concentration of H$_2$O$_2$ was 400 mg/L. The concentration of hydrogen peroxide in the stock and the samples was measured using a Hach Test Kit (model HYP-1, Cat. No. 22917-00). All concentrations were confirmed using both a high range (1 drop = 1 mg/L H$_2$O$_2$), and low range (1 drop = 0.2 mg/L H$_2$O$_2$) measurement after appropriate dilutions. The procedure included the addition of 1 ml of ammonium molybdate and the addition of a sulfite packet to a 50 ml sample. The concentration of H$_2$O$_2$ was determined using a titration with sodium thiosulfate. All the necessary reactants were included with the kit.
Utilities that practice monochloramine often institute a short chlorine contact time prior to ammonia addition to achieve disinfection credit. The addition of ammonia later in the plant forms monochloramine as a secondary disinfectant. Sometimes, chlorine and ammonia are added simultaneously, which results in essentially a chlorine contact time of zero. These situations can be represented by preformed monochloramine addition in the laboratory.

In this chapter, objective one will be discussed. The factors important in THM and I-THM formation that will be addressed are the effects of NOM, pH, chlorine contact time and chlorine dose. Furthermore, bromine and iodine substitution as well as I-THM speciation from the two treatment strategies will be compared. All the experiments in this chapter utilized the waters collected in May of 2008 (Table 4.1), and only the two realistic bromide and iodide concentrations were investigated (200 µg/L and 20 µg/L, 800 µg/L and 80 µg/L) in this chapter.

5.1 The Effects of NOM

The premise of this section is to determine whether the characteristic of NOM (natural organic matter) represented as SUVA$_{254}$ (specific ultraviolet absorbance at 254 nm) may be partially responsible for differences in THM and I-THM formation from preformed monochloramine or prechlorination followed by ammonia addition. To accomplish this objective, Charleston raw and treated waters were diluted to equivalent
DOC concentrations as their respective SJWD waters. Dilution was necessary to ensure that two waters with the same DOC concentrations had different NOM characteristics. In this section, the results for the two raw waters are compared more frequently than the two treated waters because their SUVA$_{254}$ values and thus their NOM characteristics were likely to vary more between them than the two treated waters. The results for the treated waters are shown in Appendix B.

5.1.1 Treatment Strategy

The THM results for preformed monochloramine and for prechlorination followed by ammonia addition are presented in Figures 5.1 and 5.2, for SJWD and Charleston raw water, respectively. The UFC preformed monochloramine dose is provided in the figures, and the prechlorination doses to achieve a Cl$_2$ residual of 0.5 and 1.0 mg/L after 5 minutes are also shown. The first most noticeable observation is that, as expected, there was no THM formation from preformed monochloramine. On the other hand, for prechlorination followed by ammonia addition, THM concentrations increased with both (i) increasing chlorine dose (chlorine residual), and (ii) increasing bromide/iodide concentrations.

In terms of the effects of NOM characteristics, the high-SUVA water, Charleston raw water (SUVA$_{254}$: 4.2 L/mg-m) formed more THMs than the low-SUVA, SJWD water (SUVA$_{254}$: 2.5 L/mg-m) for the highest bromide/iodide level (800 µg/L / 80 µg/ L), while the effect of NOM was negligible at the lower bromide/iodide level (200 µg/L / 20 µg/ L). Overall, these results support previous research findings that high-SUVA NOM contains more THM precursors overall than low-SUVA NOM (Kitis et al. 2001).
Figure 5.1 THM formation in SJWD raw water from preformed monochloramine and prechlorination followed by ammonia addition

Figure 5.2 THM formation in diluted Charleston raw water from preformed monochloramine and prechlorination followed by ammonia addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.
As shown in Figure 5.3, I-THM formation in SJWD raw water followed a very different trend compared to THMs. For the (800 µg/L / 80 µg/L) bromide/iodide level, high levels of I-THMs were formed from preformed monochloramine, while I-THM formation was significantly reduced when prechlorination followed by ammonia was practiced. Reductions of approximately 60 and 90% were observed for prechlorination doses to achieve 5 minute Cl₂ residuals of 0.5 and 1.0 mg/L, respectively. But, prechlorination had little effect on I-THM concentrations for the (200 µg/L / 20 µg/L) bromide/iodide level.

In contrast, for the high-SUVA water, as shown in Figure 5.4, I-THM formation was often greater from prechlorination as compared to preformed monochloramine. This was unexpected because it is generally understood that prechlorination normally reduces I-THM formation through the oxidation of iodide to HOI and further to IO₃⁻ (Bichsel and Von Gunten 1999). It seems that high-SUVA waters, which contain NOM components more reactive with chlorine, will likely divert chlorine from oxidizing hypoiodous acid to iodate. Furthermore, preoxidation of the NOM by chlorine may break down the NOM to smaller molecular weight NOM components, and thus make it more susceptible for iodine substitution to form I-THMs (Hua and Reckhow 2007a).

Overall, these conflicting results due to differences in NOM reactivity with chlorine and iodine to form THMs and I-THMs suggest that prechlorination followed by ammonia or preformed monochloramine (simulating the simultaneous addition of chlorine and ammonia at the same point in the plant) will require a water specific approach to control the formation of both THMs and I-THMs.
Figure 5.3 I-THM formation in SJWD raw water from preformed monochloramine and prechlorination followed by ammonia addition

Figure 5.4 I-THM formation in diluted Charleston raw water from preformed monochloramine and prechlorination followed by ammonia addition

XXX/XX in the legends indicates the bromide/iodide concentrations ($\mu$g/L / $\mu$g/L).
Error bars indicate the concentration range obtained from two independent samples.
5.1.2 Preformed Monochloramine - Iodide/DOC Ratio

The results for I-THM formation from preformed monochloramine addition are presented in Figure 5.5 for both the raw and treated waters. Because the DOC concentrations were 1.7 mg/L for the raw waters and 1.2 mg/L for the treated waters, only the two raw waters are comparable, and the two treated waters are comparable. Overall, the low-SUVA waters (SJWD) consistently formed higher levels of I-THMs than the high-SUVA waters (Charleston). This was true for both bromide and iodide levels. It is important to point out that the differences in I-THM yields for the two treated waters cannot be explained solely by differences in their SUVA value because their values were very close (1.8 vs. 2.0 L/mg-m). However, because SJWD treated water is formed from primary treatment of low-SUVA source water, while Charleston treated water is derived from high-SUVA water, the NOM characteristics of the source water may partially explain the differences in I-THM formation between the treated waters.

It was also demonstrated in this study that I-THM yield increased with increasing I/DOC ratios. The results for the 4 waters are presented in Figure 5.6. It is evident that for an equivalent I/DOC ratio, iodine was more efficiently incorporated in low-SUVA waters to form I-THMs than high-SUVA waters. This supports previous research suggesting that bromine and iodine were more reactive with low-SUVA NOM to form I-THMs as compared to high-SUVA NOM (Hua and Reckhow 2007a). Furthermore, I-THM formation was more favorable when high-SUVA NOM components were removed during coagulation/flocculation and sedimentation as evident from higher I-THM yields in the treated waters as compared to the raw waters for an equivalent I/DOC.
Figure 5.5 I-THM formation from preformed monochloramine (UFC dose)

XXX/XX in the legend indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.

Figure 5.6 Importance of I⁻ on I-THM formation

*some values calculated from dilution studies
5.1.3 Prechlorination

As expected for prechlorination, higher THM yields were observed in Charleston water which contained high-SUVA NOM components. The THM results for 0.5 mg/L and 1.0 mg/L chlorine residual are presented in Figures 5.7 and 5.8. This was especially true for higher Cl2/DOC ratios and higher concentrations of bromide and iodide (Figure 5.8). The effect of NOM characteristics was negligible at the 200/20 level. Similarly, in Figure 5.9, higher I-THM formation was generally observed in the high-SUVA water than the low-SUVA water at the 800/80 level, and the effects of NOM were negligible at the 200/20 level. It appears that at lower Cl2/DOC ratios (Figure 5.9), the reactivity of NOM is an important factor in I-THM formation, while at higher Cl2/DOC ratios (Figure 5.10), the oxidation of HOI to IO3⁻ becomes a more important factor. The effect of NOM characteristics on I-THM formation at lower Cl2/DOC ratios may be explained as follows: High-SUVA NOM will react preferentially with chlorine and thus divert chlorine from further oxidization of HOI to IO3⁻. On the other hand, for a low-SUVA water, chlorine will be less reactive with NOM and will more likely oxidize HOI to IO3⁻, and thus reduce I-THM formation (Bichsel and Von Gunten 2000). The details of chlorine, iodine, and NOM reactivity from both prechlorination and preformed monochloramine will be discussed in the next section which covers pathway discussion.
Figure 5.7 THM formation in the raw waters from prechlorination (0.5 mg/L Cl₂ residual after 5 minutes) followed by ammonia addition

Figure 5.8 THM formation in the raw waters from prechlorination (1.0 mg/L Cl₂ residual after 5 minutes) followed by ammonia addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure 5.9 I-THM formation in the raw waters from prechlorination (0.5 mg/L Cl₂ residual after 5 minutes) followed by ammonia addition.

XX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
5.1.4 I-THM Formation Pathways

The pathways discussed in this section are conceptualizations based on the observations from this study and other previous research findings. No reaction intermediates were quantified nor was any kinetic work done.

For pH $\geq 7.5$, the dominant oxidant formed by monochloramine addition will be HOI. According to Figure 5.11, HOCl will not be a significant factor because monochloramine (NH$_2$Cl) will not significantly decompose to HOCl for $pH \geq 7.5$ (Karanfil et al. 2007). Furthermore, HOBr will not be a significant factor because HOCl for all intensive purposes is not present, and monochloramine is incapable of oxidizing Br$^-$ to HOBr (Trofe et al. 1980). Since hypoiodous acid (HOI) will not further be oxidized to iodate (IO$_3^-$) by monochloramine (Bichsel and Von Gunten 1999), HOI will be available to oxidize NOM and then subsequently form iodinated DBPs by two proposed pathways: (i) If the natural organic matter is composed primarily of low-SUVA components, then I-THMs and other low molecular weight iodinated DBPs will form. (ii) On the other hand, if the NOM is composed primarily of high-SUVA, high molecular weight compounds, then the formation of large molecular weight iodinated DBPs, also known as unknown total organic iodine (UTOI) will be more favorable.

If both high and low molecular weight NOM is present, the formation of UTOI will probably be more likely because Hua and Reckhow (2007a) demonstrated that iodine was very reactive with large molecular weight hydrophobic compounds to form UTOI, and the lower formation of I-THMs in Charleston versus SJWD raw water at equivalent I/DOC ratios supports this hypothesis. But, if the iodine/DOC ratio is very
high, both the formation of unknown iodinated DBPs, and I-THM formation will probably occur. This is supported by the observation that I-THM formation can still occur in Charleston raw water at very high I/DOC ratios (Figure 5.6).

Figure 5.11 Iodinated DBP formation pathways from preformed monochloramine

For prechlorination followed by ammonia addition the chemistry is a little more involved than the preformed monochloramine case due to chlorine's reactivity with NOM, bromide, and iodide. As shown in Figure 5.12, the proposed mechanisms for I-THM formation are divided up into NOM oxidation steps and substitution steps for simplicity. Overall, there are two fundamental differences from the preformed monochloramine case. The first difference is significant formation of HOBr from
chlorine, which does not occur from monochloramine addition (Bousher et al. 1986). Secondly, HOI can be further oxidized to IO$_3^-$ by chlorine unlike monochloramine (Bichsel and Von Gunten 1999). These two major differences result in HOBr, HOCl, and HOI being present and acting as important oxidants and substituting agents during prechlorination.

![Diagram of DBP formation pathways from prechlorination](image)

**Figure 5.12 DBP formation pathways from prechlorination**

To summarize the oxidation steps, chlorine will first oxidize NOM to form NOM$^X$, and similarly there might be some oxidation of NOM by HOI to form HOI*. Bromine or chlorine can then substitute into NOM$^X$ (NOM oxidized by chlorine) to form THMs, other DBPs, and other unknown total organic halides (UTOX). Or, HOI can
further oxidize NOM\textsuperscript{X} (NOM oxidized by chlorine) to form NOM\textsuperscript{XX}. HOBr, HOI, and 
HOCl can also substitute into NOM\textsuperscript{XX} to form I-THMs and other iodinated DBPs.

Overall, the oxidation of NOM by chlorine will be more important for high-
SUVA waters for I-THM formation to occur because oxidation of NOM will break up the 
large molecular weight NOM components to form smaller molecules such that very large 
HOI and HOBr can substitute to form I-THMs. On the other hand, for less chlorine 
reactive NOM components (low-SUVA), the oxidation of NOM will be less significant, 
and the oxidation of HOI to IO\textsubscript{3}\textsuperscript{-} will be the controlling factor. Overall, for both high and 
low-SUVA waters, the oxidation of NOM by HOI and subsequent substitution to form I-
THMs, iodinated DBPs, or UTOI will probably not be a large factor because (i) chlorine 
is more reactive as an oxidant than HOI, and (ii) HOI is being converted to iodate while 
NOM oxidation is occurring. In addition, the oxidation of NOM by chlorine will destroy 
large molecular weight UTOI precursors, and so UTOI formation will likely be 
minimized during prechlorination followed by ammonia addition. The formation of 
UTOI is more likely during preformed monochloramine. This supports the findings that 
monochloramine forms more UTOX than chlorine (Hua and Reckhow 2008a).
5.2 Preformed Monochloramine – The Effects of pH

Application of preformed monochloramine resembles the simultaneous addition of chlorine and ammonia in the plant after primary treatment which includes coagulation, flocculation, and sedimentation. Therefore, only the treated waters (water collected after primary treatment) will be discussed in this section. The results for the raw waters are still included in Appendix C because it is still valuable to consider the results for waters with higher DOC and also more hydrophobic NOM characteristics in order to gain a more complete understanding of I-THM formation.

Since the pH of waters may vary from 6-9 with an average of around 8, it is important to understand the effects of pH on preformed monochloramine stability and THM/I-THM formation. As mentioned previously, monochloramine stability increases with pH such that is fairly stable at pH 7.5 and 9, but the decomposition to chlorine and ammonia is considerable at pH 6 (Karanfil et al. 2007). The formation of additional oxidants such as HOCl and HOBr at lower pH may impact THM and I-THM formation.

5.2.1 THM and I-THM Formation

The results in Figures 5.13 and 5.14 of the two treated waters demonstrate that monochloramine decomposition to chlorine was occurring at pH 6 because small concentrations of THMs were formed. Furthermore, some bromide may have been oxidized to HOBr by chlorine at pH 6 because with increasing bromide, more THMs were formed. This supports the finding by Diehl and others (2000). It is also possible that some bromochloramine or other bromamine species may have been involved in bromine
substitution (Luong et al. 1982). Similar to the THMs, according to Figures 5.15 and 5.16, I-THM formation was observed at pH 6 in both waters, and yields increased with increasing bromide/iodide concentrations. It is fair to conclude that HOI was formed in the system, but it is unlikely that iodamines played a role because the formation of iodoamines was demonstrated to be unfavorable (Bichsel and Von Gunten 1999).

Overall with increasing pH, the formation of I-THMs tended to decrease. This was true except for the highest bromide and iodide level (800/80) in SJWD water (low-SUVA). The conflicting results for this higher bromide and iodide condition were due to three factors: (i) very high I/DOC ratios which favored iodoform (CHI$_3$) formation, (ii) low-SUVA NOM favoring the formation of I-THMs in SJWD water, and (iii) overall increased reactivity of NOM precursors and iodine for substitution at higher pH (Hua and Reckow 2008a, Bruice 2004, Bichsel and Von Gunten 2000a).
Figure 5.13 pH effect on THM formation in SJWD treated water from monochloramine addition

Figure 5.14 pH effect on THM formation in Charleston treated water from monochloramine addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure 5.15 pH effect on I-THM formation in SJWD treated water from monochloramine addition

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Figure 5.16 pH effect on I-THM formation in Charleston treated water from monochloramine addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
5.2.2 Bromine and Iodine Incorporation

In order to gain an understanding of the competition between bromine and iodine for substitution to form THMs and I-THMs, two incorporation factors were determined. Since, the most commonly used bromine incorporation factor (BIF) includes only the 4 regulated THMs, a new BIF or $\eta_{\text{Br}}$ was calculated which included the 3 I-THM species. Overall, there are 10 THM and I-THM species, and the molar sum of these species is referred to as THM10. The bromine incorporation factors ($\eta_{\text{Br}}$) and the iodine incorporation factors ($\eta_{\text{I}}$) were calculated from the molarity of individual I-THM and THM species and the molarity of THM10 as follows:

$$\eta_{\text{Br}} = \frac{([CHBrClI] + [CHBrI_2] + [CHClI_2,Br]) \times 1 + ([CHBr_3,I] + [CHBr_2,ClI]) \times 2 + [CHBr_3] \times 3}{\text{THM10}}$$

$$\eta_{\text{I}} = \frac{([CHClI_2,I] + [CHBrClI] + [CHBr_2I]) \times 1 + ([CHClI_2] + [CHBr_2I_2]) \times 2 + [CHI_3] \times 3}{\text{THM10}}$$

The formulas above indicate that both $\eta_{\text{Br}}$ and $\eta_{\text{I}}$ can vary from 0 to 3. If $\eta_{\text{Br}} = 3$ and $\eta_{\text{I}} = 0$, then the only species present is bromoform (CHBr$_3$). Conversely, if $\eta_{\text{Br}} = 0$ and $\eta_{\text{I}} = 3$, then the only species present is iodoform (CHI$_3$). But if both $\eta_{\text{Br}} = 0$ and $\eta_{\text{I}} = 0$, then the only species present is chloroform (CHCl$_3$). Overall, it is more likely that $\eta_{\text{Br}}$ and $\eta_{\text{I}}$ are somewhere between 0 and 3, which indicates that the THM species formed are a mix of mono, di, and tri brominated and iodinated species.
The bromine and iodine incorporation factors depended highly on pH as shown in Figures 5.17 and 5.18. With increasing pH, bromine incorporation/substitution decreased, while the opposite was true for iodine. For bromine, this was primarily due to monochloramine decomposition and formation of HOBr or bromochloramines that occurred at lower pH. On the other hand, iodine incorporation factors were higher with increasing pH because HOBr, a competing substituting agent was less of a factor, and deprotonated NOM precursors were probably more reactive with HOI, an electrophile, for iodine substitution (Bruice 2004). In addition, this supports the work by Bichsel and Von Gunten (2000a) when they concluded that iodination rate increased with pH from enhanced OH catalysis.
Figure 5.17 pH effect on incorporation factors for SJWD treated water (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).

ηBr in the legend represents the bromine incorporation factor.
ηI in the legend represents the iodine incorporation factor.

Figure 5.18 pH effect on incorporation factors for Charleston treated water (800/80)
5.2.3 I-THM and THM Speciation

Now that incorporation factors have been discussed, it is beneficial to discuss individual species because the toxicities of species may vary. It is important to track dichloroiodomethane (CHClI₂) and iodoform (CHI₃) because these are considered the most genotoxic and cytotoxic THM species, respectively. Because it is difficult to analysis all 10 THM species together, and the formation of I-THMs and THMs do not necessarily follow similar formation patterns as demonstrated in Section 5.1, I-THM and THM speciation are presented separately.

I-THM speciation results for a bromide and iodide concentrations of 200 µg/L and 20 µg/L (200/20) at pH 6, 7.5, and 9 are shown in Figures 5.19 and 5.20. At pH 6 and 7.5, I-THM speciation was comprised mostly of CHCl₂I and CHBrClI with a very small amount of iodoform (CHI₃). This supports the findings of distribution studies in which CHCl₂I and CHBrClI were the I-THM species that were commonly detected for source waters will lower bromide and iodide levels (Khiari et al. 1999, Krasner et al. 2006, Richardson et al. 2008).

According to Figures 5.21 and 5.22, when the concentrations of bromide and iodide were increased to 800 µg/L and 80 µg/L (800/80), CHBr₂I and CHBrI₂ became important species at pH 6. Furthermore, at a higher iodide level, iodoform became the dominant species at pH 7.5 and 9. This supports the occurrence studies of Hansson and others (1987) in which iodoform was formed when the concentration of iodide was at similar levels (50 µg/L). It is important to note that a small amount of CHClI₂ was observed at the 800/80 bromide/iodide level. The formation of both CHI₃ and CHClI₂ is
again significant because they are the most cytotoxic and genotoxic THM species (Richardson et al. 2008).

The small amounts of mixed bromo-, chloro-, iodinated THMs formed at pH 7.5 may be due to small amounts of monochloramine decomposition to chlorine. Minimal levels of THMs (<1 µg/L) were detected in Charleston treated water (Figure 5.14), which suggests that chlorine may have been present in small amounts. The formation of bromochloramine species may explain the formation of brominated I-THMs as bromamine species formed small levels of brominated THMs in previous studies (Luong et al. 1982).

The THM results for pH 6 are presented in Figures 5.23 and 5.24. The THM results for pH 7.5 and 9 are not shown because minimal formation occurred (<2 µg/L). Overall, speciation shifted from chlorinated THMs to brominated THMs as the bromide/iodide level was increased from 200/20 to 800/80 with bromoform being the dominant species at 800 µg/L and 80 µg/L. Analysis of the THM and I-THM results together suggest that brominated species dominated more in SJWD water, while the chlorinated species were more prevalent in Charleston water. This is probably due to two factors: There were (i) higher bromide/DOC ratios in SJWD water than Charleston water, and (ii) treated NOM from a low-SUVA source water was probably more reactive with bromine to form brominated THMs than the treated water from a high-SUVA source water.
Figure 5.19 pH effect on I-THM speciation for SJWD treated water (200/20)

Figure 5.20 pH effect on I-THM speciation for Charleston treated water (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the six I-THM species.
Figure 5.21 pH effect on I-THM speciation for SJWD treated water (800/80)

Figure 5.22 pH effect on I-THM speciation for Charleston treated water (800/80)

(XXX/XX) in the captions indicate the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legends are the six I-THM species.
XXX/XX on the x-axis indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the four regulated THM species.
Prechlorination prior to ammonia addition to form monochloramine in-situ is a very common practice because often a minimum chlorine contact time is required to achieve sufficient disinfection credit. Two contact times, 5 min and 20 min, were examined in this study. Also, two chlorine residuals, 0.5 mg/L and 1.0 mg/L, measured after the contact time were investigated. Since consistent chlorine residuals were chosen, the chlorine doses often varied between the waters tested (Table A.2). Results for both the raw and treated waters will both be presented to gain a more general understanding of the practical implications of prechlorination for I-THM and THM control. Although, some results will focus more on the treated waters because while raw waters are often sometimes chlorinated, they are rarely also chloraminated in practice. This is because the addition of coagulants and sedimentation of the raw water occurs prior to chlorine and ammonia addition to form monochloramine. Regardless of these circumstances, results for the raw water are included in Appendix D to further understanding.

5.3 Prechlorination – The Effects of Chlorine Dose and Contact Time

5.3.1 Prechlorination Contact Time

Because the half life of HOI in the presence of chlorine ranges from minutes to hours to days (Figure 2.6), it was important to determine if 5 or 20 minutes of chlorine contact time were adequate to reduce I-THM formation. Results in Figures 5.25 and 5.26 demonstrate that increasing contact time (CT) from 5 min to 20 min to achieve a chlorine residual of 0.5 mg/L decreased I-THM formation for bromide/iodide concentrations of (200 µg/L / 20 µg/L) and (800 µg/L / 80 µg/L). The effect was more noticeable for the
800/80 level. In contrast, in Figures 5.27 and 5.28, increasing chlorine CT to achieve a residual of 1.0 mg/L had a much smaller effect on I-THM yields. This suggests that there would be no apparent advantage to increasing chlorine contact time for higher chlorine residuals if I-THM minimization was the goal.

Furthermore, regulated THM concentrations increased with chlorine contact time for both chlorine residuals. The results for 1.0 mg/L Cl₂ residual are presented in Figures 5.29 and 5.30. It is important to note that for bromide levels in excess of 800 µg/L, longer prechlorination contact times may result in THM levels above the MCL of 80 µg/L.

Overall, these results suggest that 20 min to achieve a residual of 0.5 mg/L, or 5 min to achieve 1.0 mg/L residual will be the best options to reduce I-THM formation without resulting in excessive THM formation. It is also important to note that selection of specific chlorine doses and chlorine contact times will also need to consider the disinfection requirement (i.e. CT credit) for utilities. It is likely that shorter chlorine contact times will require higher chlorine doses, and alternatively longer chlorine contact times could achieve CT credit with a lower chlorine dose.
Figure 5.25 Effect of prechlorination contact time on I-THM formation in SJWD treated water for a chlorine residual of 0.5 mg/L

XXX/XX in the legends indicate the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.

Figure 5.26 Effect of prechlorination contact time on I-THM formation in Charleston treated water for a chlorine residual of 0.5 mg/L
Figure 5.27 Effect of prechlorination contact time on I-THM formation in SJWD treated water for a chlorine residual of 1.0 mg/L

Figure 5.28 Effect of prechlorination contact time on I-THM formation in Charleston treated water for a chlorine residual of 1.0 mg/L

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure 5.29 Effect of prechlorination contact time on THM formation in SJWD treated water for a chlorine residual of 1.0 mg/L

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.
5.3.2 Cl\textsubscript{2}/DOC and Cl\textsubscript{2}/I Ratio

Hua and colleagues (2006) suggested that the Cl\textsubscript{2}/DOC and Cl\textsubscript{2}/I ratio are important in controlling I-THM formation. To provide additional evidence for this finding, the results for the raw and treated water of SJWD and Charleston were combined to establish relationships between chlorine dose and I-THM and THM formation. The results for the four waters suggest that with increasing Cl\textsubscript{2}/DOC ratio, I-THM formation will decrease. This was true for a bromide and iodide concentration of 200 µg/L and 20 µg/L as shown in Figure 5.31, and it was especially true for the 800/80 level as shown in Figure 5.32. The effect was also independent of chlorine contact time (Figures D.7 and D.8). Part of the reason for decreasing I-THM formation may be partially attributed to DBP precursors preferentially forming the brominated and chlorinated regulated THMs as Cl\textsubscript{2}/DOC was increased. THM results are presented in Figures 5.33 and 5.34. Two important observations can be made from these plots. First, THM yields increased with Cl\textsubscript{2}/DOC ratio, and second, longer contact times resulted in higher THM yields.
Figure 5.31 I-THM formation from prechlorination of four waters for various Cl₂/DOC ratios (200/20)

Figure 5.32 I-THM formation from prechlorination of four waters for various Cl₂/DOC ratios (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure 5.33 THM formation from prechlorination of four waters for various Cl₂/DOC ratios (200/20)

Figure 5.34 THM formation from prechlorination of four waters for various Cl₂/DOC ratios (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
The opposing effects of Cl$_2$/DOC ratio on I-THM and THM formation were combined to establish a relationship between Cl$_2$/DOC and the I-THM/THM10 ratio. THM10 is the combined molar sum of the 4 regulated THM and the 6 iodinated THM species. The results for the 200/20 and 800/80 bromide and iodide levels are presented in Figures 5.35 and 5.36. For concentrations of 200 µg/L bromide and 20 µg/L iodide, Cl$_2$/DOC ratio and chlorine CT had no noticeable effect on I-THM/THM10 ratio. All values ranged from 0.05 to 0.2. On the other hand, results for concentration of 800 µg/L and 80 µg/L (Figure 5.36) demonstrate that increasing Cl$_2$/DOC ratios will generally result in lower I-THM/THM10 ratios. Furthermore, increasing chlorine contact time resulted in overall slightly lower I-THM/THM10 ratios. This may be due to the preferential formation of THMs as opposed to the formation of I-THMs for longer chlorine contact times (more time for Cl$_2$ to replace bromines or iodines that had already substituted to form I-THMs).

A decrease in I-THM formation from increasing prechlorination dose are very different from the results for preformed monochloramine because increasing NH$_2$Cl dose did not significantly decrease I-THM formation (Figures D.11 and D.12).

Much of the scatter in the previously discussed plots is partially due to combining the results for four waters with different DOC concentrations and NOM characteristics. All original plots are presented in Appendix D.
Figure 5.35 I-THM/THM10 as a function of Cl₂/DOC ratio (200/20)

Figure 5.36 I-THM/THM10 as a function of Cl₂/DOC ratio (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
In addition to the Cl₂/DOC ratio, the Cl₂/I⁻ ratio is also important in reducing I-THM formation through further oxidation of HOI to IO₃⁻ such that HOI is unable to react with NOM to form I-THMs. The reduction in I-THM yields with increasing Cl₂/I⁻ ratios is exemplified in Figure 5.37 below. The results for 20 min contact time are shown in Figure D.13. The relationship was clearer for 5 minutes of contact time than 20 minutes. This is probably due to (i) generally lower Cl₂/I⁻ ratios tested for the 5 minutes of contact time and (ii) also the possibility that the Cl₂/I⁻ oxidation reactions occurs on the order of minutes.

![Figure 5.37 I-THM yields in four waters as a function of Cl₂/I⁻ ratios for 5 minute contact time](image)

Error bars indicate the concentration range obtained from two independent samples.
Now that the practical implications of preformed monochloramine and prechlorination followed by ammonia addition have been discussed (I-THM/THM yields and ratio, $\text{Cl}_2/$DOC, $\text{Cl}_2/\Gamma$, $\Gamma/$DOC, and pH), it is valuable to compare bromide and iodide incorporation, and speciation for preformed monochloramine and prechlorination with 5 minute chlorine contact time for a typical pH encountering in practice (pH around 7.5).

The bromine and iodine incorporation factors indicate which halogenating agent will dominate in substitution. This is important because the iodinated DBPs as a group are more cytotoxic and genotoxic than brominated or chlorinated DBPs (Plewa et al. 2008). Furthermore, an analysis of specific DBPs is essential because recent toxicology tests have indicated that not all THM species exhibit the same toxicity. For example, CHClI$_2$ and CHI$_3$ are considered the most genotoxic and cytotoxic THM species, respectively (Richardson et al. 2008). Analysis of these parameters as a function of bromide and iodide concentration will aid in an understanding of when it may be advantageous to practice either prechlorination or preformed monochloramine.

5.4.1 Bromine and Iodine Incorporation

As a review, the bromine and iodine incorporation factors can vary from 0 to 3, and they indicate the average number of bromines or iodine that substitute. The bromine incorporation factors for SJWD treated water and Charleston treated are presented in Figures 5.38 and 5.39, respectively. For preformed monochloramine, bromine
incorporation is minimal, and even a four times increase in bromine concentration has no major effect on bromine incorporation. In contrast, during prechlorination, bromine incorporation is much more significant and increasing Br⁻/I⁻ concentrations increased bromine incorporation. Similarly, with increasing prechlorination dose, there was an increase in bromine incorporation for the highest bromide and iodide level (800 µg/L and 80 µg/L). This can be attributed to at higher chlorine doses, more NOM was oxidized which allowed bromine to substitute. The effect of dose was negligible for bromide and iodide concentrations of 200 µg/L and 20 µg/L.

In contrast to bromine incorporation, substantial iodine incorporation occurred during preformed monochloramine addition according to Figures 5.40 and 5.41. Also, increasing iodide concentration resulted in more iodine incorporation. On the other hand, during prechlorination, iodine incorporation was very minimal, and increasing iodide concentration by four times had a minimal effect on iodine incorporation. Overall, since bromide was also increased by four times, it was probably out-competing iodide during prechlorination.

The differences in bromine and iodine incorporation for preformed monochloramine and prechlorination can be explained by monochloramine and chlorine reactivity with these halide ions. This was briefly mentioned in Section 5.1. Very little bromine incorporation is observed from preformed monochloramine addition because monochloramine is incapable of oxidizing bromide to HOBr (Figure 5.11). The small amount of bromine incorporation may be due to a small amount of bromochloramine acting as a substituting agent, or a small amount of chlorine (derived from
monochloramine decomposition) oxidizing bromide to HOBr. On the other hand, bromine incorporation is very favorable during prechlorination because of the presence of chlorine which readily oxidizes bromide to HOBr (Figure 5.12).

Iodine incorporation factors are substantial for preformed monochloramine because NH$_2$Cl cannot further oxidize HOI to IO$_3^-$ (Figure 5.11). On the other hand, during prechlorination, chlorine further oxidizes hypoiodous acid to iodate (Figure 5.12), and consequently iodine incorporation factors are much smaller as compared to preformed monochloramine. Overall, bromine and iodine incorporation factors are important because it indicates whether brominated or iodinate DBPs will dominate. As a group, iodinated DBPs are more toxic. Because individual species have varying toxicities, I-THM and THM speciation for prechlorination and preformed monochloramine will now be discussed.
Figure 5.38 Bromine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (SJWD treated water)

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).

Figure 5.39 Bromine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (Charleston treated water)
Figure 5.40 Iodine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (SJWD treated water)

Figure 5.41 Iodine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (Charleston treated water)

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
5.4.2 I-THM and THM Speciation

For preformed monochloramine, CHCl\textsubscript{2}I, CHBrClI, and small concentrations of CHI\textsubscript{3} (iodoform) were important I-THM species for bromide and iodide concentrations of 200 µg/L and 20 µg/L (Figures 5.42 and 5.43). When the concentrations of bromide and iodide were increased by 4 times to the 800/80 level, I-THM speciation shifted to almost entirely iodoform will small levels of CHBrI\textsubscript{2} and CHClI\textsubscript{2} (Figures 5.44 and 5.45). On the other hand, for prechlorination, the dominant I-THM species were the 3 brominated I-THMs which included CHBrClI, CHBrI\textsubscript{2}, and CHBr\textsubscript{2}I for the 200/20 and 800/80 bromide and iodide levels. Generally, when the concentration of bromide was increased, CHBr\textsubscript{2}I emerged as a more dominant species overall, while CHBrI\textsubscript{2} was still an important species, but not a dominant species.

The speciation results for THMs for bromide and iodide concentration of 200/20 and 800/80 (µg/L / µg/L) are shown in Figures 5.46 through 5.49. Overall, increasing chlorine dose did not significantly affect THM speciation. The results were as expected because mixed chloro- and bromo- THMs dominted at the 200/20 level, while bromoform (CHBr\textsubscript{3}) dominated at the 800/80 level.

These results suggest that if the iodide concentration is greater than approximately 80 µg/L, five minutes of prechlorination will probably be adequate to reduce the formation of CHI\textsubscript{3} and CHClI\textsubscript{2}, the most toxic THM species. But if the concentration of iodide is high, the concentration of bromide will also be high, so the formation of brominated THMs and I-THMs may be a concern.
Figure 5.42 I-THM speciation for SJWD treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20)

Figure 5.43 I-THM speciation for Charleston treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the six I-THM species.
Figure 5.44 I-THM speciation for SJWD treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the six I-THM species.

Figure 5.45 I-THM speciation for Charleston treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80)
Figure 5.46 THM speciation for SJWD treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20)

Figure 5.47 THM speciation for Charleston treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the four regulated THM species.
Figure 5.48 THM speciation for SJWD treated water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the four regulated THM species.
CHAPTER SIX
PREOXIDANTS FOR I-THM CONTROL

This chapter will examine potassium permanganate (KMnO₄), chlorine dioxide (ClO₂), and hydrogen peroxide (H₂O₂) as preoxidants that can potentially reduce I-THM formation in raw waters. It is not well known if these oxidants will further oxidize HOI to IO₃⁻, and thus reduce I-THM formation. There is also the possibility that I-THM formation will be enhanced due to the oxidation or breakdown of NOM components thus making NOM more reactive for iodinated THM substitution. As mentioned in Chapter 5, enhanced I-THM formation was observed from prechlorination oxidation. I-THM formation from preoxidants alone (without monochloramine addition) may also occur due to the oxidation of I⁻ to HOI, and so this will also be investigated in this chapter. The concentrations of bromide and iodide that are investigated are (200 µg/L and 20 µg/L), and (800 µg/L and 80 µg/L) as in the previous chapter, but new batches of raw waters collected in November 2008 (Table 6.2) were used for these preoxidation experiments. Raw waters were selected because preoxidants are usually applied at the beginning of plants to remove color, taste, or odor, and also to aid in coagulation and disinfection.

6.1 Potassium Permanganate

6.1.1 The Effect of Preoxidation

Doses of 1.0 mg/L and 3.0 mg/L of KMnO₄ were added to SJWD and Charleston raw waters, and after 20 minutes of preoxidation, preformed monochloramine was added. In addition, preformed monochloramine without the prior addition of KMnO₄ was also
included for comparison. The results for SJWD and Charleston are shown in Figures 6.1 and 6.2. The results show that for both waters, I-THM formation was enhanced through potassium permanganate oxidation at both bromide and iodide levels. It appears that oxidation/alteration of the NOM was more of a factor than oxidation of iodide all the way to iodate. Previous research with permanganate preoxidation has shown that KMnO₄ may break down high-SUVA NOM to smaller molecular weight, low-SUVA NOM components (Chen and Valentine 2008). As mentioned in Chapter 5, iodine has been shown to be more reactive with low molecular weight NOM components to form I-THMs (Hua and Reckhow 2007a). A reduction in SUVA may partially explain the enhanced I-THM formation from permanganate preoxidation.

The results for the regulated THMs are shown in Figures 6.3 and 6.4. For SJWD raw water, it was interesting to observe small levels of THM formation from the permanganate followed by monochloramine treatment because no THMs were observed from preformed monochloramine addition alone. Also the concentration of THMs increased with permanganate dose. THMs were formed at small levels in Charleston raw water regardless of treatment. Analysis of the results for preoxidation alone did not form THMs (not shown), so it appears that the presence of both NH₂Cl and KMnO₄ were necessary for THM formation to occur. It should be noted that these levels are minimal compared to the THM concentrations formed from prechlorination.

The observed THM formation from the combined treatment may be due to the reaction of permanganate with monochloramine to form HOCl and subsequently HOBr. KMnO₄ has a higher redox potential than NH₂Cl (1.68 V vs. 0.75 V) and since KMnO₄
residuals were measurable after 20 minutes (Table F.1), it is quite possible that permanganate reacted with monochloramine and caused some decomposition to chlorine. Furthermore, results in Table F.1 in Appendix F supports this theory because higher monochloramine doses were necessary after preoxidation than without preoxidation to achieve approximately 2.0 mg/L NH₂Cl residual after 24 hours. This suggests that permanganate may have been accelerating monochloramine decomposition to chlorine. Since monochloramine was decomposing to chlorine, the formation of HOBr and bromochloramines may have occurred. This would offer an explanation for the brominated THMs formed in SJWD raw water.

Since I-THM formation was minimal in Charleston raw water, only incorporation and speciation for SJWD raw water will be discussed in the next two parts.
Figure 6.1 I-THM formation in SJWD raw water from monochloramine and permanganate preoxidation

Figure 6.2 I-THM formation in Charleston raw water from monochloramine and permanganate preoxidation

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure 6.3 THM formation in SJWD raw water from monochloramine and permanganate preoxidation

XXX/XX in the legends indicates the bromide/iodide concentrations (\(\mu g/L/\mu g/L\)). Error bars indicate the concentration range obtained from two independent samples.

Figure 6.4 THM formation in Charleston raw water from monochloramine and permanganate preoxidation
6.1.2 Incorporation and Speciation

Bromine and iodine incorporation factors are shown in Figures 6.5 and 6.6. Overall, iodine incorporation was much greater than bromine incorporation. Also, with increasing preoxidation dose prior to monochloramine addition, iodine incorporation decreased slightly and bromine incorporation increased slightly for bromide and iodide concentrations of 200 µg/L and 20 µg/L in SJWD raw water. The same was true for concentrations of 800 µg/L and 80 µg/L. An analysis of I-THM speciation in Figure 6.7 and 6.8 demonstrates that CHBr$_2$I increased and CHBrI$_2$ increased as a result of preoxidation. For bromide and iodide concentrations of 200 µg/L and 20 µg/L, CHCl$_2$I and CHBrClI increased with preoxidation dose, while iodoform (CHI$_3$) increased at the 800/80 level, and was always the dominant species. Preoxidation had no apparent effect on CHClI$_2$, and this suggests that permanganate will not prevent the formation of CHI$_3$ or CHClI$_2$, the most cytotoxic and genotoxic THM species, respectively.

The THM results for the 800/80 bromide/iodide level in Figure 6.9 demonstrate that bromoform (CHBr$_3$) was the dominant species with a small amount of CHBr$_2$Cl formed for preoxidation with 3.0 mg/L KMnO$_4$. Less than reportable THMs were observed in SJWD raw water at the 200/20 level. This suggests that when permanganate preoxidation is practiced, and the concentration of bromide is sufficiently high, the reactions between NH$_2$Cl and KMnO$_4$ may form chlorine and ultimately HOBr. It is important to note that permanganate addition without monochloramine did not form brominated THMs. The effect of permanganate addition alone will be discussed later in Section 6.4.
Figure 6.5 Incorporation factors for monochloramine and permanganate preoxidation of SJWD raw water (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).

ηBr in the legends represents the bromine incorporation factor.

ηI in the legends represents the iodine incorporation factor.
Figure 6.7 I-THM speciation for monochloramine and permanganate preoxidation of SJWD raw water (200/20)

Figure 6.8 I-THM speciation for monochloramine and permanganate preoxidation of SJWD raw water (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the six I-THM species.
While the results from this study still leave questions unanswered, the results did lead to some practical conclusions. For practical KMnO$_4$ doses, I-THM formation was enhanced from preoxidation for two representative Br$^-$/I$^-$ levels (200 µg/L / 20 µg/L) and (800 µg/L/ 80 µg/L). This suggests that the oxidation of HOI to IO$_3^-$ was a minor pathway, if it occurred. The mechanisms for enhanced I-THM formation are not well known, but a possible reduction in the SUVA of the NOM from preoxidation may be partially responsible.
6.2 Chlorine Dioxide

Previous research demonstrates that I-THM formation is possible from both chlorine dioxide addition alone and a combined chlorine dioxide/monochloramine treatment. The purpose of this section is to discuss I-THM results for the combined treatment strategy, while Section 6.4 will discuss I-THM formation from chlorine dioxide alone as well as the other oxidants.

The chlorine dioxide (ClO$_2$) doses tested were 0.5 mg/L and 1.0 mg/L for a contact time of 20 minutes prior to preformed monochloramine addition. It is important to realize that only doses of approximately 0.5 to 1.5 mg/l ClO$_2$ will be practical in drinking water treatment because of the expected 70% to 100% conversion of chlorine dioxide to chlorite, which is a regulated inorganic DBP (Gordon et al. 1990). Chlorite was formed from chlorine dioxide doses of 0.5 and 1.0 mg/L in this study, but it was always below the MCL of 1.0 mg/L (Table F3). Overall, preoxidation with ClO$_2$ did not seem to significantly affect the UFC monochloramine dose (Table F4).

6.2.1 The Effect of Preoxidation

The results in Figure 6.10 for SJWD raw water suggests that chlorine dioxide unlike potassium permanganate showed promise for reducing I-THM levels for high bromide and iodide concentrations (800 µg/L and 80 µg/L). On the other hand, for a lower bromide and iodide level (200/20), and thus a lower I/DOC ratio, the addition of chlorine dioxide as a preoxidant increased I-THM formation. This compliments the
results for prechlorination as discussed in Chapter 5 in which preoxidation enhanced I-THM formation under some circumstances.

Similar to the results of other oxidants, I-THM formation was minimal in Charleston raw water as shown in Figure 6.11. Preoxidation of Charleston raw water slightly increased I-THM formation for both bromide and iodide levels. This is consistent with the results for the 200/20 Br⁻/I⁻ level for SJWD water. This suggests that I⁻/DOC ratio may be a factor in I-THM formation chlorine dioxide preoxidation because Charleston had lower I⁻/DOC ratios overall due to its higher DOC concentration.

Overall, the formation of I-THMs from monochloramine even after preoxidation with chlorine dioxide supports the results of Hua and Reckhow (2007b) in which they concluded that further oxidation of iodide to iodate by chlorine dioxide was probably not significant because they detected iodate at very low levels in their study. They investigated only one dose of 1.5 mg/L, and so the mechanism of this observed reduction in I-THM formation with increasing chlorine dioxide doses for higher I⁻/DOC ratios is unknown at this time. In order to gain further understanding, the incorporation factors and speciation for SJWD raw water will be discussed in the next two parts because I-THM formation from Charleston raw water was minimal.
Figure 6.10 I-THM formation in SJWD raw water from preformed monochloramine and chlorine dioxide preoxidation

Figure 6.11 I-THM formation in Charleston raw water from preformed monochloramine and chlorine dioxide preoxidation

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
6.2.2 Incorporation and Speciation

For the lower bromide and iodide concentrations (200 µg/L and 20 µg/L) in SJWD raw water, bromine and iodine incorporation factors were relatively unchanged from preoxidation with ClO₂ (Figure 6.12). On the other hand, for the higher bromide/iodide level (800/80), iodine incorporation factors decreased significantly with the addition of chlorine dioxide as a preoxidant (Figure 6.13). In contrast, bromine incorporation increased from preoxidation, but the values were still lower than iodine incorporation. As mentioned in Chapter 5, switching from preformed monochloramine to prechlorination practices had a substantial effect on bromine incorporation. This indicates that one advantage of chlorine dioxide over chlorine is that small doses of chlorine dioxide can reduce iodine incorporation for waters with high concentrations of bromide and iodide without resulting in high concentrations of brominated THMs.

The I-/DOC and Br-/DOC ratio and the chlorine dioxide dose also have an impact on the I-THM species that are formed from preoxidation with chlorine dioxide followed by monochloramine. The results in Figure 6.14 for SJWD raw water demonstrate that I-THM speciation was relatively unchanged from preoxidation practices for bromide and iodide concentrations of 200 and 20 µg/L. On the other hand, Figure 6.15 demonstrates that for higher bromide and iodide concentration there was a substantial reduction in iodoform (CHI₃) formation when chlorine dioxide was added. Overall it appears that three species decreased, and they were the tri-iodinated and the di-iodinated species (CHI₃, CHClI₂, and CHBrI₂). The decrease of CHBrI₂ was less obvious. In contrast, the mono-iodinated species stayed the same or increased with increasing preoxidation dose.
Similar to KMnO$_4$ preoxidation, minimal THMs ($<3 \, \mu g/L$) were measured from ClO$_2$ preoxidation. CHBr$_2$Cl and CHBr$_3$ were the only species (Figure 6.16). This supports the findings of Heller-Grossman and others (1999) in which they observed higher THMs formation from a combined treatment than the sum of individual treatments of chlorine dioxide and monochloramine. They suggested that chlorine dioxide reacted with NOM to form THM precursors.

Overall, the results for preoxidation with chlorine dioxide were somewhat surprising because it reduced iodoform formation when higher doses were applied. According to Fabian and Gordon (1997), chlorine dioxide reacts with iodide to form an iodide radical species on its way to ultimately forming HOI. It may further oxidize iodide to iodate, but Hua and Reckhow (2007b) did not detect appreciable levels of iodate for a chlorine dioxide dose of 1.5 mg/L. In addition, chlorine dioxide is very different from chlorine because it reacts with NOM by a one electron transfer mechanism (Hoehn et al. 1996). Therefore, it is important to not disregard reactions of chlorine dioxide with NOM. These questions prompted additional experimentation regarding the effects of varying I$^-$/DOC ratios and ClO$_2$/DOC ratios that will be addressed in Chapter 7.
Figure 6.12 Bromine and iodine incorporation factors for monochloramine and chlorine dioxide preoxidation of SJWD raw water (200/20)

Incorporation Factor

- ηBr in the legend represents the bromine incorporation factor.
- ηI in the legend represents the iodine incorporation factor.

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).

Figure 6.13 Bromine and iodine incorporation factors for monochloramine and chlorine dioxide preoxidation of SJWD raw water (800/80)
Figure 6.14 I-THM speciation for monochloramine and chlorine dioxide preoxidation of SJWD raw water (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the six I-THM species.

Figure 6.15 I-THM speciation for monochloramine and chlorine dioxide preoxidation of SJWD raw water (800/80)
Figure 6.16 THM speciation for monochloramine and chlorine dioxide preoxidation of SJWD raw water (800/80)

(XXX/XX) in the caption indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the four regulated THM species.
6.3 Hydrogen Peroxide

In this section hydrogen peroxide (H$_2$O$_2$) will be investigated as a preoxidant to reduce I-THM formation. Two practical doses of 2.0 and 5.0 mg/L will be examined. The addition of a catalyst in combination with hydrogen peroxide was not tested, as the goal was to determine if hydrogen peroxide alone for 20 minutes of contact time prior to monochloramine addition could oxidize iodide all the way to iodate.

6.3.1 The Effect of Preoxidation

As demonstrated with SJWD and Charleston raw water in Figures 6.17 and 6.18, it seems that preoxidation with H$_2$O$_2$ will not be a viable option to significantly reduce I-THM formation because I-THM yields were similar or slightly greater when comparing the combined treatment process to preformed monochloramine. This suggests that hydrogen peroxide will not significantly oxidize iodide to iodate.

There were residual concentrations of hydrogen peroxide at the time of monochloramine addition (Table F.5), so this suggests that hydrogen peroxide had the opportunity to react with monochloramine, bromide, iodide, as well as NOM. These reactions are probably important because it was necessary to add very high concentrations of monochloramine after H$_2$O$_2$ preoxidation. The required NH$_2$Cl dose to achieve 2.0 mg/L NH$_2$Cl residual after 24 hours increased substantially when H$_2$O$_2$ dose was increased, and bromide/iodide concentration was increased (Table F.6). The required NH$_2$Cl dose was sometimes as high as 14.0 mg/L. To put it in perspective, the 24 hour UFC dose for preformed monochloramine without preoxidation ranged from 3.0 to 3.4
mg/L (depending on which raw water was investigated) and was relatively independent of bromide and iodide concentration.

Because monochloramine dose depended highly on the concentration of bromide and iodide present, this suggests that one or both of these anions played a significant role in hydrogen peroxide mediated monochloramine decomposition. This supports findings from other researchers suggesting that bromide acts as a catalyst to increase NH$_2$Cl decay rate through the decomposition of bromochloramine species (Vikesland et al. 2001).

The oxidation of Br$^-$ to HOBr by chlorine as a result of monochloramine decomposition is also important. Furthermore, H$_2$O$_2$ was demonstrated to react with HOBr to re-form Br$^-$ (Von Gunten and Hoigne 1994). As a result of these two reactions, there seems to be complex cyclical reactions that occur between bromide, monochloramine, and hydrogen peroxide. This may explain why impractical doses of monochloramine were required for high concentrations of bromide and iodide.

The remainder of this section will focus on the results for SJWD raw water because the formation of I-THMs was so minimal in Charleston water.
Figure 6.17 I-THM formation in SJWD raw water from monochloramine and hydrogen peroxide preoxidation

Figure 6.18 I-THM formation in Charleston raw water from monochloramine and hydrogen peroxide preoxidation

XXX/XX in the legends indicate the bromide/iodide concentrations ($\mu$g/L / $\mu$g/L).
Error bars indicate the concentration ranges obtained from two independent samples.
6.3.2 The Effect of pH and Preoxidation on Bromine Incorporation

Since it was hypothesized that hydrogen peroxide reacted with HOBr to re-form Br\(^-\), it was important to investigate if H\(_2\)O\(_2\) reduced bromine incorporation at pH 6 in which HOBr was shown to be a larger factor for THM and I-THM substitution (Section 5.2). A comparison of Figures 6.19 and 6.20 suggests that H\(_2\)O\(_2\) reduced bromine incorporation (\(\eta_{Br}\)) at pH 6 in SJWD raw water for high concentrations of bromide and iodide, whereas this was not observed at pH 7.5. The iodine incorporation factors (\(\eta_I\)) for pH 6 and 7.5 were relatively unchanged by hydrogen peroxide addition.

A closer analysis of I-THM speciation at pH 6 in Figure 6.21 shows that there was a reduction in CHBr\(_2\)I and CHBrI\(_2\) followed by an increase in CHBrClI when preformed monochloramine was supplemented with hydrogen peroxide. While on the other hand, according to Figure 6.22, hydrogen peroxide had minimal effects on speciation at pH 7.5.

The THM results for SJWD water in Figure 6.23 emphasize that hydrogen peroxide was likely converting HOBr to Br\(^-\) because bromoform formation was substantially reduced when hydrogen peroxide was used as a preoxidant at pH 6.

Overall, these results suggest that H\(_2\)O\(_2\) as a preoxidant prior to preformed NH\(_2\)Cl addition will not reduce I-THM formation. Hydrogen peroxide may reduce bromine incorporation for waters with high concentrations of bromide by reducing HOBr to Br\(^-\), but this is a minor issue compared to the impractical higher doses of NH\(_2\)Cl that will be required when using H\(_2\)O\(_2\) as a preoxidant. Catalysts such as higher temperatures, metals, or UV light may be necessary for hydrogen peroxide to be successful at reducing I-THM formation.
Figure 6.19 Incorporation factors for monochloramine and hydrogen peroxide preoxidation of SJWD raw water at pH 6 (800/80)

Figure 6.20 Incorporation factors for monochloramine and hydrogen peroxide preoxidation of SJWD raw water at pH 7.5 (800/80)

(XXX/XX) in the caption indicates the bromide/iodide concentrations (\(\mu\)g/L / \(\mu\)g/L).

\(\eta_{\text{Br}}\) in the legend represents the bromine incorporation factor.

\(\eta_{\text{I}}\) in the legend represents the iodine incorporation factor.
Figure 6.21 I-THM speciation for monochloramine and hydrogen peroxide preoxidation of SJWD raw water at pH 6 (800/80)

Figure 6.22 I-THM speciation for monochloramine and hydrogen peroxide preoxidation of SJWD raw water at pH 7.5 (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legend are the six I-THM species.
Figure 6.23 THM speciation for monochloramine and hydrogen peroxide preoxidation of SJWD raw water at pH 6 (800/80)

(XXX/XX) in the caption indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legend are the 4 regulated THM species.
6.4 Preoxidants Alone

6.4.1 Potassium Permanganate Dose Alone

It is important to examine if I-THM formation from potassium permanganate alone is possible. The results in Figure 6.24 show that iodoform is the only I-THM species formed from the addition of 3.0 mg/L KMnO₄. Iodoform was only observed for high bromide and iodide concentrations (800 µg/L and 80 µg/L). This confirms that KMnO₄ is capable of oxidizing iodide to HOI. These results suggest that if iodide is low, permanganate may react more readily with NOM instead of iodide. Overall, a much smaller formation of iodoform was observed as compared to from preformed monochloramine addition or the combined treatment. This suggests that the majority of iodoform is formed from monochloramine. Furthermore, enhanced I-THM formation from permanganate preoxidation prior to monochloramine addition is not due to the addition of another oxidant (KMnO₄) and its ability to oxidize I⁻ to HOI. It is more likely that KMnO₄ broke down high-SUVA NOM and altered the NOM such that it was more reactive for iodine substitution to form I-THMs from monochloramine addition. The oxidation of Br⁻ to HOBr by KMnO₄ (Lawani 1976) is probably not significant because no brominated THMs or I-THMs were observed from permanganate addition alone.

6.4.2 Hydrogen Peroxide Dose Alone

I-THM formation from hydrogen peroxide alone was also only observed for the highest bromide and iodide concentrations (800 µg/L and 80 µg/L) as shown in Figure 6.24. Iodoform (CHI₃) was the only I-THM or THM species detected which suggests that
H₂O₂ was capable of oxidizing I⁻ to HOI, but was not capable of oxidizing Br⁻ to HOBr. In fact, as mentioned previously, the reverse reaction is thermodynamically favorable (Von Gunten and Hoigne 1994).

Overall, much lower iodoform formation was observed from peroxide alone as compared to preformed monochloramine addition or the combined treatment. This demonstrates that monochloramine is the primary oxidant responsible for I-THM formation when hydrogen peroxide is used as a preoxidant.

6.4.3 Chlorine Dioxide Dose Alone

Similar to potassium permanganate, chlorine dioxide alone did not form bromoform (CHBr₃) at reportable levels. The chlorine dioxide dose and bromide concentrations must have been too low for CHBr₃ formation to occur because Li and others (1996) observed bromoform formation for 1-6 mg/L Br⁻ and 10 mg/L chlorine dioxide. It seems that for practical conditions, a combined chlorine dioxide, monochloramine treatment is required for bromoform formation.

The addition of chlorine dioxide also formed iodoform for bromide and iodide concentrations of 800 µg/L and 80 µg/L, but the concentrations formed were much less than the concentration formed from preformed monochloramine or the combined treatment. In addition, a small concentration of CHCl₂I was observed. It is important that other I-THMs were formed besides iodoform because the other two oxidants, potassium permanganate and hydrogen peroxide, only formed iodoform. The formation of iodoform and other I-THM species from chlorine dioxide is consistent with studies of Hua and Reckhow (2007b) in which CHI₃ was the dominant species for a ClO₂ dose of 1.5 mg/L.
with minor formations of CHCl₂I and CHClI₂ (Figure 2.16). In contrast, in this study CHCl₂I was formed at about the same levels as CHI₃. The much lower iodide concentration investigated (80 µg/L vs. 200 µg/L) may explain these differences. This suggests that I⁻/DOC or ClO₂⁻/I⁻ ratios are important for I-THM speciation. Overall, in both studies higher I-THM formation was observed from preformed monochloramine addition alone than chlorine dioxide addition alone. Since Hua and Reckhow (2007b) observed iodoform as the dominant species from chlorine dioxide addition, it was beneficial to perform additional experiments with a higher iodide concentration. The next chapter will compare I-THM speciation formed from preformed monochloramine and preoxidants for two different Br⁻/I⁻ ratios.

Figure 6.24 I-THM speciation for preoxidant addition in the absence of monochloramine to SJWD raw water (800/80)

XXX/XX in the caption indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legend are the six I-THM species.
The IMPORTANCE OF BROMIDE TO IODIDE RATIO

The premise of this chapter is to compare I-THM formation in the same water with contrasting bromide and iodide ratios. In the previous two chapters, the Br⁻/I⁻ ratio was kept constant at 10 (µg/L / µg/L), and the concentrations of bromide and iodide were increased proportionally. The two Br⁻/I⁻ levels tested were (200 µg/L / 20 µg/L) and (800 µg/L/ 80 µg/L). In this chapter, an opposite Br⁻/I⁻ ratio of 0.5 and bromide/iodide concentrations of 100 µg/L / 200 µg/L were tested. I-THM speciation formed from this higher iodide than bromide scenario was compared side-by-side with the more realistic higher bromide than iodide condition (800 µg/L and 80 µg/L) examined in the previous two chapters. The 100/200 Br⁻/I⁻ ratio was chosen because (i) the median concentration of bromide in source waters for an I-THM occurrence study was approximately 100 µg/L (Richardson et al. 2008), and (ii) in another survey of United States rivers, the concentration of iodide was a high as 212 µg/L (Moran et al. 2002). These experiments utilized new batches of Charleston and SJWD raw waters that were collected in March 2009 (Table 6.3).

7.1 pH and Br⁻/I⁻ Ratio

The results from Chapter 5 demonstrated that there was a pH effect with regards to I-THM yields and speciation. For lower bromide and iodide concentrations it was found that I-THM formation decreased with increasing pH. On the other hand, when the concentration of iodide was high, there was a slight increase in I-THM formation with
increasing pH primarily due to the formation of iodoform (CHI$_3$). In Figure 7.1, the results for SJWD raw water with bromide and iodide concentrations of 800 µg/L and 80 µg/L showed that there was no pH effect in regards to I-THM formation in terms of molar concentrations. But, when a higher concentration of iodide was added to the water, and the concentration of bromide was reduced, there was a substantial increasing pH effect due to the formation of iodoform at higher pH (Figure 7.2). Another important observation was that iodoform was the dominant species at all pH for bromide and iodide concentrations of 100 µg/L and 200 µg/L, respectively. Conversely, the brominated I-THMs dominated at pH 6 for bromide and iodide concentrations of 800 µg/L and 80 µg/L (Figure 7.1). Overall, higher I-THM concentrations were observed for the 100/200 scenario than the opposite 800/80 Br$^-$/I$^-$ condition. Similar trends were observed for Charleston raw water in Figures 7.3 and 7.4, but I-THM formation still decreased with pH when the concentration of iodide was increased from 80 to 200 µg/L. This was probably due to two main factors: overall lower I$^-$/DOC ratios in Charleston raw water due to its higher DOC concentration, and also lower formation of iodoform because Charleston is a high-SUVA water that probably contains more larger molecular weight aromatic NOM and fewer smaller molecular weight I-THM precursors.

The impact of Br$^-$/I$^-$ ratio on THM formation at pH 6 is shown in Figures 7.5 and 7.6. As expected, when the concentration of bromide was reduced from 800 to 100 µg/L, THM speciation shifted from brominated THMs to chlorinated THMs. Overall, THM concentrations were much lower for a lower bromide concentration.
Figure 7.1 pH Effect on I-THM speciation for SJWD raw water treated with 5.0 mg/L NH₂Cl (800/80)

Entries in the legends are the six I-THM species.

Figure 7.2 pH Effect on I-THM speciation for SJWD raw water treated with 5.0 mg/L NH₂Cl (100/200)

(XXX/XXX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Figure 7.3 pH effect on I-THM speciation for Charleston raw water treated with 5.0 mg/L NH$_2$Cl (800/80).

(XXX/XXX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legends are the six I-THM species.
Figure 7.5 Importance of Br⁻/I⁻ ratio for THM speciation in SJWD raw water treated with 5.0 mg/L NH₂Cl at pH 6

XXX/XXX on the x-axis indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the four regulated THM species.

Figure 7.6 Importance of Br⁻/I⁻ ratio for THM speciation in Charleston raw water treated with 5.0 mg/L NH₂Cl at pH 6
7.2 Preoxidation

7.2.1 Potassium Permanganate

The results for permanganate preoxidation of SJWD water are shown in Figures 7.7 and 7.8. I-THM formation still increased due to preoxidation regardless of the Br/I ratio or the bromide and iodide concentrations. I-THM concentrations were much higher, and this was mostly due to the formation of iodoform. In addition, the brominated I-THMs were less of a factor for lower concentrations of bromide than iodide (100/200). Another important observation was a slight increase in chlorodiiomethane (CHClI₂) formation when the concentration of iodide was increased from 80 to 200 µg/L. This was especially true for Charleston raw water in Figures 7.9 and 7.10. It is important to note that this higher concentration of iodide would almost never be encountered in practice, and this may be one reason why CHClI₂ has rarely been found in distribution studies.
Figure 7.7 I-THM speciation for a monochloramine dose of 5.0 mg/L and permanganate preoxidation of SJWD raw water (800/80)

Figure 7.8 I-THM speciation for a monochloramine dose of 5.0 mg/L and permanganate preoxidation of SJWD raw water (100/200)

(XXX/XXX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the six I-THM species.
Figure 7.9 I-THM speciation for a monochloramine dose of 5.0 mg/L and permanganate preoxidation of Charleston raw water (800/80)

Figure 7.10 I-THM speciation for a monochloramine dose of 5.0 mg/L and permanganate preoxidation of Charleston raw water (100/200)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legends are the six I-THM species.
7.2.2 Chlorine Dioxide

As mentioned in Chapter 6, preoxidation with chlorine dioxide substantially reduced the formation of iodoform (CHI$_3$) in SJWD raw water as compared to preformed monochloramine when the iodide concentration was 80 µg/L. This prompted a follow up study with the same iodide concentration and a higher iodide concentration added to new batches of water. A reduction in iodoform formation was still observed in Figure 7.11 for a new batch of SJWD water with bromide and iodide concentrations of 800 µg/L and 80 µg/L. Formation of the di-iodinated THM species was also reduced from preoxidation. As observed in Figure 7.12, when the concentration of iodide was increased to 200 µg/L, iodoform formation was still suppressed and to a greater extent with increasing ClO$_2$ dose. Formation of the di-iodinated THM species was also reduced from preoxidation.

Similar to the results in Chapter 6, I-THM formation increased due to preoxidation of Charleston raw water. The increase was primarily due to the formation of CHCl$_2$I (Figure 7.13 and 7.14). For chlorine dioxide doses of 0.5 and 1.0 mg/L, iodoform formation in Charleston raw water was not suppressed for bromide and iodide concentrations of 100 µg/L and 200 µg/L. This was a surprising finding because iodoform was reduced in SJWD raw water at the same iodide level. Because chlorine dioxide is probably more reactive with the NOM of Charleston water due to its higher SUVA and higher DOC concentration (lower ClO$_2$/DOC ratio), perhaps chlorine dioxide reacted with NOM instead of preventing iodoform formation.
Figure 7.11 I-THM speciation for a monochloramine dose of 5.0 mg/L and chlorine dioxide preoxidation of SJWD raw water (800/80)

Figure 7.12 I-THM speciation for a monochloramine dose of 5.0 mg/L and chlorine dioxide preoxidation of SJWD raw water (100/200)

(XXX/XXX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the six I-THM species.
Figure 7.13 I-THM speciation for a monochloramine dose of 5.0 mg/L and chlorine dioxide preoxidation of Charleston raw water (800/80)

(XXX/XXX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the six I-THM species.

Figure 7.14 I-THM speciation for a monochloramine dose of 5.0 mg/L and chlorine dioxide preoxidation of Charleston raw water (100/200)
5.3 Preoxidants Alone

Since I-THM formation from potassium permanganate and chlorine dioxide without monochloramine addition is also possible, higher iodide concentrations were added to SJWD raw water and Charleston raw water. The results were as expected because iodoform (CHI$_3$) formation increased for higher concentrations of iodide than bromide in SJWD raw water when 3 mg/L of potassium permanganate was added (Figure 7.15). Iodoform was not detected in Charleston raw water for either the 800/80 or 100/200 Br$^-$/I$^-$ ratios. This suggests that permanganate was more reactive with the NOM of Charleston water than iodide to form HOI, or the NOM was insufficiently oxidized by KMnO$_4$ for I-THM substitution to occur.

![Figure 7.15 Importance of Br$^-$/I$^-$ ratio on I-THM speciation from 3.0 mg/L permanganate addition to SJWD raw water](image)

(XXX/XXX) on the x-axis indicates the bromide/iodide concentrations ($\mu$g/L / $\mu$g/L). Entries in the legend are the six I-THM species.
The effect of Br⁻/I⁻ ratio and concentrations on I-THM formation was also investigated with chlorine dioxide. Similar to the results observed in Chapter 6, CHCl₂I and CHI₃ were the dominant species for SJWD water with 800 µg/L of bromide and 80 µg/L of iodide. But when the concentration of iodide was increased to 200 µg/L and bromide was reduced to 100 µg/L, iodoform became the dominant species (Figure 7.16). This matches the findings of Hua and Reckhow (2007b) in which iodoform was the dominant species formed from 1.5 mg/L ClO₂ (Figure 2.16). The Br⁻/I⁻ ratio was similar as the ambient bromide concentration in their source water was 95 µg/L, and 200 µg/L of iodide was added. Overall, I-THM speciation in Charleston raw water was similar to SJWD water, but I-THM formation was lower overall (Figure 7.17), and iodoform was never a dominant species.
Figure 7.16 Importance of Br⁻/I⁻ ratio on I-THM speciation from 1.0 mg/L chlorine dioxide addition to SJWD raw water.

XXX/XXX in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the six I-THM species.

Figure 7.17 Importance of Br⁻/I⁻ ratio on I-THM speciation from 1.0 mg/L chlorine dioxide addition to Charleston raw water.
CHAPTER EIGHT
CONCLUSIONS AND RECOMMENDATIONS

The important conclusions for each objective of this study were as follows:

Objective 1: Investigate and compare I-THM formation from preformed monochloramine and prechlorination followed by ammonia addition

- For preformed monochloramine, a high-SUVA water formed lower levels of I-THMs than a low-SUVA water for equivalent I/DOC ratios. Conversely, for prechlorination followed by ammonia addition, a high-SUVA water formed higher levels of I-THMs than a low-SUVA water for equivalent I/DOC ratios. Furthermore, prechlorination with a small chlorine dose and short contact time sometimes increased I-THM formation as compared to preformed monochloramine addition.

- For preformed monochloramine, generally higher I-THM and THM formation was observed at lower pH. However, if the iodide concentration was high (≥80 µg/L), significant iodoform (CHI$_3$) formation was sometimes observed at higher pH, and this resulted in greater I-THM formation at higher pH.

- Generally, a short chlorine contact time (CT) (i.e. 5 min) with a higher dose (1.0 mg/L Cl$_2$ residual), or a longer CT (i.e. 20 min) with a lower dose (0.5 mg/L Cl$_2$ residual) reduced I-THM formation without resulting in excessive THM formation.
- For increasing Cl\textsubscript{2}/DOC ratios, the I-THM/THM10 ratio decreased. Furthermore, the Cl\textsubscript{2}/I ratio was also significant because increasing Cl\textsubscript{2}/I ratios reduced I-THM formation.
- For preformed monochloramine, iodine incorporation dominated over bromine incorporation, while on the other hand, for prechlorination followed by ammonia addition, bromine incorporation dominated. This resulted in significant differences in I-THM speciation for the two treatment strategies.

**Objective 2:** Investigate the effects of three commonly used preoxidants (potassium permanganate, chlorine dioxide, and, hydrogen peroxide [w/o UV or O\textsubscript{3}]) on I-THM formation

- For potassium permanganate (KMnO\textsubscript{4}), I-THM formation was higher from preoxidation as compared to preformed monochloramine addition alone. Also, bromine incorporation increased slightly when preoxidation was practiced.
- For chlorine dioxide (ClO\textsubscript{2}), preoxidation decreased I-THM formation as compared to monochloramine addition alone when the I/DOC ratio was higher. On the other hand, when the I/DOC ratio was lower, chlorine dioxide enhanced I-THM formation.
- For hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), preoxidation exhibited no appreciable effect on I-THM formation. Very high and impractical doses of monochloramine were required, and the UFC dose increased with higher H\textsubscript{2}O\textsubscript{2} concentrations and higher bromide and iodide concentrations.
- I-THM formation was observed from all 3 oxidants alone, but I-THM concentrations were lower as compared to the amounts formed from preformed monochloramine addition or preoxidation followed by monochloramine addition.

**Objective 3: Investigate the importance of bromide to iodide ratio on I-THM formation and speciation**

- A minimal pH effect or a decrease in I-THM formation with increasing pH was observed when bromide was in a higher concentration than iodide (Br⁻/I⁻ = 10). Conversely, when the concentration of iodide was higher than bromide (Br⁻/I⁻ = 0.5), there was a substantial increase in iodoform formation with increasing pH.

- For higher concentrations of iodide than bromide, permanganate (KMnO₄) preoxidation increased I-THM formation as compared to preformed monochloramine addition as a result of a significant increase in iodoform formation with increasing preoxidation dose.

- For higher concentrations of iodide than bromide, I-THM formation in lower DOC, lower SUVA water was reduced from preoxidation with chlorine dioxide (ClO₂) as compared to preformed monochloramine addition alone. Conversely, preoxidation enhanced I-THM formation in higher DOC, higher SUVA water.

- Overall, higher iodide concentrations (200 µg/L) substantially increased iodoform formation and also increased CHClI₂ formation. This suggests that these species, considered the most cytotoxic and genotoxic, respectively, will be at significantly lower levels at lower iodide concentrations (<80 µg/L).
Some important observations regarding incorporation and speciation are as follows:

- At pH 7.5, CHCl\textsubscript{2}I and CHBrClI were the I-THM species observed at moderate bromide and iodide concentrations (200 µg/L and 20 µg/L) for preformed monochloramine and prechlorination followed by ammonia addition. At higher bromide and iodide concentrations (800 µg/L and 80 µg/L), CH\textsubscript{3}I (iodoform) was the dominant species formed from preformed monochloramine, while CHBr\textsubscript{2}I and CHBr\textsubscript{2}I were the most important I-THM species formed from prechlorination.

- At pH 6, preformed monochloramine formed mixed I-THM species for bromide and iodide concentrations of 800 and 80 µg/L. For bromide and iodide concentrations of 200 and 20 µg/L, CHCl\textsubscript{2}I and CHBrClI were dominant species.

- Increasing KMnO\textsubscript{4} preoxidation doses increased iodoform formation and the brominated I-THM species. Bromoform (CHBr\textsubscript{3}) also increased, but it was at much smaller concentrations.

- Overall, higher ClO\textsubscript{2} preoxidation doses usually reduced iodoform (CH\textsubscript{3}I) formation and increased CHCl\textsubscript{2}I formation.

- Preoxidation with hydrogen peroxide decreased bromine substitution into I-THMs and THMs at pH 6, but not at pH 7.5.

- Iodoform was possible from all three oxidants alone without the addition of monochloramine. Chlorine dioxide formed additional I-THM species.

- When chlorine dioxide was added without monochloramine, iodoform (CH\textsubscript{3}I) was a dominant species for higher I/DOC ratios, while dichloroiodomethane (CHCl\textsubscript{2}I) was a dominant species for lower I/DOC ratios.
Some recommendations for utilities to reduce I-THM formation are as follows:

- Generally, for the treatment of low DOC, low-SUVA waters with high concentrations of bromide and iodide (>800 and 80 µg/L), prechlorination followed by ammonia addition will be preferred. Conversely, if the source water is high DOC, high-SUVA, adding chlorine and ammonia at the same location will be preferable.

- Generally, if the iodide concentration is less than 20 µg/L, utilities adding chlorine and ammonia at the same point in the plant will probably form minimal levels of I-THMs.

- Prechlorination will decrease I-THM formation in most cases when the concentration of iodide is high (80 µg/L). Low or moderate chlorine doses (approximately less than 5.0 mg/L) should be applied because higher chlorine doses will form brominated and chlorinated THMs at higher concentrations.

- If the concentration of iodide is high (I/DOC ratio is high), increasing chlorine dioxide dose may reduce the formation of iodoform and di-iodinated I-THM species. Only chlorine dioxide doses ranging from 0 to 1.5 mg/L will be practical due to the 70%-100% conversion of chlorine dioxide to chlorite, a regulated DBP. Overall, the formation of THMs from chlorine dioxide preoxidation will be very minimal as compared to prechlorination.

- For lower bromide and iodide concentrations typically encountered in practice (≤ 200 µg/L and 20 µg/L), the dominant I-THM species formed will probably be CHCl₂I and CHBrClI.
Some recommendations for future research are as follows:

- It will be interesting to determine if the three oxidants in this study were capable of oxidizing iodide to iodate under typical drinking water treatment conditions. Iodate ($\text{IO}_3^-$) was measured in this study with ion chromatography, but the detection limit was too high to measure it at the low $\mu\text{g}/\text{L}$ scale. A method developed by Snyder and colleagues (2005), which utilizes an (LC/MS/MS) system can detect $\text{IO}_3^-$ concentrations at $\mu\text{g}/\text{L}$ levels.

- There was an NOM effect regarding the practices of prechlorination and preformed monochloramine. It would be interesting to investigate if there is an NOM effect regarding I-THM reduction or enhancement from preoxidation.

- An investigation into the use of some catalysts with hydrogen peroxide would be valuable. Since hydrogen peroxide had no appreciable effect on iodoform formation, perhaps the addition of UV light, transitional metal salts, or higher temperatures will increase $\text{H}_2\text{O}_2$ decomposition and form additional oxidants.

- The most promising preoxidant for I-THM control, ozone, was not investigated in this study because it is well known that ozone oxidizes iodide to iodate. The problems with ozone are that it is expensive, and the formation of bromate ($\text{BrO}_3^-$) is a large concern. To control I-THM formation in waters containing high concentrations of bromide and iodide, perhaps a combined $\text{H}_2\text{O}_2/\text{O}_3$ process would be beneficial because bromate formation might be suppressed by applying higher $\text{H}_2\text{O}_2/\text{O}_3$ ratios (Kruithof et al. 1997, Miller 1993).
• A future occurrence study focusing on plants utilizing waters with high concentrations of iodide that also practice chlorine dioxide preoxidation would be beneficial because chlorine dioxide demonstrated the most promising results in this study for reducing iodoform (CHI₃) formation.

• Laboratory research on I-THM formation from chlorine dioxide is still minimal (Hua and Reckhow 2007b, Richardson et al. 2003). There are additional factors that should be investigated such as ClO₂/DOC ratio and ClO₂/I⁻ ratio.

• Finally, it would be interesting to compare these I-THM results with iodinated HAA results. At least for the regulated THMs and HAAs, their mechanisms of formation are quite different. For example, THM formation from chlorination increases with pH, while HAA formation decreases. Since both groups of iodinated DBPs are toxic, it is important not to generalize based on the I-THM results alone. A laboratory study measuring both iodinated THMs and HAAs under the same conditions is still needed.
APPENDICES
Appendix A:

Supplementary Information for Chapter 4
Figure A1 I-THM formation from preformed monochloramine addition to SJWD raw water for three collection dates (800/80)

Figure A2 I-THM formation from preformed monochloramine addition to Charleston raw water for three collection dates (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Figure A3 I-THM speciation for SJWD raw water for three collection dates (800/80)

Figure A4 I-THM speciation for Charleston raw water for three collection dates (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the six I-THM species.
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</thead>
<tbody>
<tr>
<td></td>
<td>pH 6</td>
<td>pH 7.5</td>
<td>pH 9</td>
</tr>
<tr>
<td>SJWD raw water</td>
<td>3.6</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>SJWD treated water</td>
<td>3.2</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Charleston raw water</td>
<td>5.0</td>
<td>3.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Charleston treated water</td>
<td>4.0</td>
<td>2.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table A.2 Prechlorination doses for contact times and residuals at pH 7.5 (mg/L)

<table>
<thead>
<tr>
<th></th>
<th>5 Minute Contact Time</th>
<th></th>
<th>20 Minute Contact Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 mg/L Cl₂</td>
<td>1.0 mg/L Cl₂</td>
<td>0.5 mg/L Cl₂</td>
</tr>
<tr>
<td>SJWD raw water</td>
<td>1.1</td>
<td>1.8</td>
<td>1.25</td>
</tr>
<tr>
<td>SJWD treated water</td>
<td>0.95</td>
<td>1.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Charleston raw water</td>
<td>2.25</td>
<td>3.0</td>
<td>3.25</td>
</tr>
<tr>
<td>Charleston treated water</td>
<td>1.3</td>
<td>1.9</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table A.3 UFC monochloramine doses for prechlorination at pH 7.5 (mg/L)

<table>
<thead>
<tr>
<th></th>
<th>5 Minute Contact Time</th>
<th></th>
<th>20 Minute Contact Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 mg/L Cl₂</td>
<td>1.0 mg/L Cl₂</td>
<td>0.5 mg/L Cl₂</td>
</tr>
<tr>
<td>SJWD raw water</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>SJWD treated water</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Charleston raw water</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Charleston treated water</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Appendix B:

Supplementary Information for Section 5.1
B.1 THM formation in SJWD treated water from preformed monochloramine and prechlorination followed by ammonia addition

Figure B.2 THM formation in diluted Charleston treated water from preformed monochloramine and prechlorination followed by ammonia addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure B.3 I-THM formation in SJWD treated water from preformed monochloramine and prechlorination followed by ammonia addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.

Figure B.4 I-THM formation in diluted Charleston treated water from preformed monochloramine and prechlorination followed by ammonia addition
Figure B.5 THM formation in the treated waters from prechlorination (0.5 mg/L Cl$_2$ residual after 5 minutes) followed by ammonia addition.

Figure B.6 THM formation in the treated waters from prechlorination (1.0 mg/L Cl$_2$ residual after 5 minutes) followed by ammonia addition.

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).

Error bars indicate the concentration range obtained from two independent samples.
Figure B.7 I-THM formation in the treated waters from prechlorination (0.5 mg/L Cl$_2$ residual after 5 minutes) followed by ammonia addition. XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Appendix C:

Supplementary Information for Section 5.2
XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.
Figure C.3 pH effect on I-THM formation in SJWD raw water from monochloramine addition

Figure C.4 pH effect on I-THM formation in Charleston raw water from monochloramine addition

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.
Figure C.5 pH effect on incorporation factors for SJWD raw water (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).

ηBr in the legend represents the bromine incorporation factor.

ηI in the legend represents the iodine incorporation factor.

Figure C.6 pH effect on incorporation factors for Charleston raw water (800/80)
Figure C.7 pH effect on I-THM speciation for SJWD raw water (200/20)

Figure C.8 pH effect on I-THM speciation for Charleston raw water (200/20)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legends are the six I-THM species.
Figure C.9 pH effect on I-THM speciation for SJWD raw water (800/80)

Figure C.10 pH effect on I-THM speciation for Charleston raw water (800/80)

(XXX/XX) in the captions indicate the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legends are the six I-THM species.
XXX/XX on the x-axis indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legends are the four regulated THM species.
Appendix D:
Supplementary Information for Section 5.3
Figure D.1 Effect of prechlorination contact time on I-THM formation in SJWD raw water for a chlorine residual of 0.5 mg/L

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.

Figure D.2 Effect of prechlorination contact time on I-THM formation in Charleston raw water for a chlorine residual of 0.5 mg/L
Figure D.3 Effect of prechlorination contact time on I-THM formation in SJWD raw water for a chlorine residual of 1.0 mg/L

Figure D.4 Effect of prechlorination contact time on I-THM formation in Charleston raw water for a chlorine residual of 1.0 mg/L

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure D.5 Effect of prechlorination contact time on THM formation in SJWD raw water for a chlorine residual of 1.0 mg/L

[Diagram showing THM formation for SJWD raw water]

Table D.6 Effect of prechlorination contact time on THM formation in Charleston raw water for a chlorine residual of 1.0 mg/L

[Diagram showing THM formation for Charleston raw water]

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure D.7 Effect of chlorine contact time on I-THM formation from prechlorination of four waters for various Cl\textsubscript{2}/DOC ratios (200/20)

Figure D.8 Effect of chlorine contact time on I-THM formation from prechlorination of four waters at various Cl\textsubscript{2}/DOC ratios (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Error bars indicate the concentration range obtained from two independent samples.
Figure D.9 I-THM/THM10 as a function of Cl$_2$/DOC ratio for complete data set (200/20)

Figure D.10 I-THM/THM10 as a function of Cl$_2$/DOC ratio for complete data set (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Figure D.11 The effect of preformed monochloramine dose on I-THM formation in SJWD treated water at pH 7.5

Figure D.12 The effect of preformed monochloramine dose on I-THM formation in Charleston raw water at pH 7.5

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).
Error bars indicate the concentration range obtained from two independent samples.
Figure D.13 I-THM yields in four waters as a function of Cl₂/I⁻ ratios for 20 minute contact time
Error bars indicate the concentration range obtained from two independent samples.
Appendix E:

Supplementary Information for Section 5.4
Figure E.1 Bromine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (SJWD raw water)

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).

Figure E.2 Bromine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia (Charleston raw water)
Figure E.3 Iodine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia addition (SJWD raw water)

XXX/XX in the legends indicates the bromide/iodide concentrations (µg/L / µg/L).

Figure E.4 Iodine incorporation factors for preformed monochloramine and 5 minutes of prechlorination followed by ammonia addition (Charleston raw water)
Figure E.5 I-THM speciation for SJWD raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20) 

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legend are the six I-THM species.

Figure E.6 I-THM speciation for Charleston raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20)
Figure E.7 I-THM speciation for SJWD raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80)

Figure E.8 I-THM speciation for Charleston raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80)

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L). Entries in the legend are the six I-THM species.
Figure E.9 THM speciation for SJWD raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20).

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the four regulated THM species.

Figure E.10 THM speciation for Charleston raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (200/20).
Figure E.11 THM speciation for SJWD raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80).

(XXX/XX) in the captions indicates the bromide/iodide concentrations (µg/L / µg/L).
Entries in the legend are the four regulated THM species.

Figure E.12 THM speciation for Charleston raw water from preformed monochloramine and 5 minutes of prechlorination followed by ammonia (800/80).
Appendix F:
Supplementary Information for Chapter 6
### Table F.1 Potassium permanganate residuals after 20 min and 24 hours (mg/L)

<table>
<thead>
<tr>
<th>Dose</th>
<th>SJWD Raw</th>
<th></th>
<th>Charleston Raw</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min.</td>
<td>24 hrs.</td>
<td>20 min.</td>
<td>24 hrs.</td>
</tr>
<tr>
<td>1 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200/20</td>
<td>1.1</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>800/80</td>
<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>3 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200/20</td>
<td>2.5</td>
<td>1.6</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>800/80</td>
<td>2.4</td>
<td>1.4</td>
<td>1.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

### Table F.2 UFC monochloramine doses for potassium permanganate preoxidation experiments (mg/L)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>SJWD Raw</th>
<th>Charleston Raw</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>1 mg/L KMnO&lt;sub&gt;4&lt;/sub&gt;, NH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>3 mg/L KMnO&lt;sub&gt;4&lt;/sub&gt;, NH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>4.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

### Table F.3 Chlorine dioxide and chlorite residuals after 20 min and 24 hours (mg/L)

<table>
<thead>
<tr>
<th>ClO&lt;sub&gt;2&lt;/sub&gt; Dose</th>
<th>SJWD Raw</th>
<th></th>
<th>Charleston Raw</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min.</td>
<td>24 hrs.</td>
<td>20 min.</td>
<td>24 hrs.</td>
</tr>
<tr>
<td>0.5 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NM</td>
<td>0</td>
<td>NM</td>
<td>0</td>
</tr>
<tr>
<td>ClO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>NM</td>
<td>0.3</td>
<td>NM</td>
<td>0.3</td>
</tr>
<tr>
<td>Total</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>1.0 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NM</td>
<td>0.8</td>
<td>NM</td>
<td>0.6</td>
</tr>
<tr>
<td>ClO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>NM</td>
<td>0.8</td>
<td>NM</td>
<td>0.6</td>
</tr>
<tr>
<td>Total</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
</tr>
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</table>
Table F.4 UFC monochloramine doses for chlorine dioxide (mg/L)

<table>
<thead>
<tr>
<th>NH₂Cl</th>
<th>200/20</th>
<th>800/80</th>
<th>NH₂Cl Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SJWD Raw</td>
<td>Charleston Raw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₂Cl</td>
<td>200/20</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>0.5 mg/L ClO₂, NH₂Cl</td>
<td>200/20</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>1.0 mg/L ClO₂, NH₂Cl</td>
<td>200/20</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>3.3</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table F.5 Hydrogen peroxide residuals after 20 min and 24 hours (mg/L)

<table>
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<tr>
<th>Dose</th>
<th>SJWD Raw</th>
<th>Charleston Raw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min.</td>
<td>24 hrs.</td>
</tr>
<tr>
<td>2 mg/L</td>
<td>200/20</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>1.6</td>
</tr>
<tr>
<td>5 mg/L</td>
<td>200/20</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table F.6 UFC monochloramine doses for hydrogen peroxide (mg/L)

<table>
<thead>
<tr>
<th>NH₂Cl</th>
<th>200/20</th>
<th>800/80</th>
<th>NH₂Cl Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SJWD Raw</td>
<td>Charleston Raw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₂Cl</td>
<td>200/20</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>2 mg/L H₂O₂, NH₂Cl</td>
<td>200/20</td>
<td>6.0</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>9.0</td>
<td>4.0</td>
</tr>
<tr>
<td>5 mg/L H₂O₂, NH₂Cl</td>
<td>200/20</td>
<td>9.0</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>800/80</td>
<td>14.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>
REFERENCES


Reckhow, D. (2008) “Can treatment and occurrence research keep up with the CCL process? The case of DBPs (and PPCPs).” Research Committee Seminar on CCL3 VA section AWWA.


