THE EFFECT OF PREDISINFECTION WITH CHLORINE DIOXIDE ON THE FORMATION OF HALOACETIC ACIDS AND TRIHALOMETHANES IN A DRINKING WATER SUPPLY

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(ABSTRACT)

In an effort to maintain compliance with current and future United States Environmental Protection Agency regulations governing haloacetic acids (HAAs) and trihalomethanes (THMs), the Blacksburg, Christiansburg, VPI (BCVPI) Water Authority in Radford, Virginia elected to eliminate prechlorination and replace it with preoxidation using chlorine dioxide (ClO_2). Prior to full-scale application at the BCVPI Water Treatment Plant, jar testing was done to determine the effects of ClO_2 on the formation of HAAs and THMs.

Jar testing results showed a significant reduction in THM formation potential when 2.0 mg/L ClO_2 was applied to raw water and chlorination was delayed. Chlorine dioxide doses less than 2.0 mg/L were statistically insignificant in the reduction of THM formation potentials below samples that were prechlorinated according to the BCVPI Water Treatment Plant's current practice. Likewise, ClO_2 did not alter HAA formation potentials in such a way that statistical differences could be detected between ClO_2 pretreatment and prechlorination, even at a dose of 2.0 mg/L ClO_2.

The two inorganic byproducts of ClO_2, chlorite and chlorate, were also measured following jar tests. Chlorite concentrations increased with an increased ClO_2 dose, but remained below 1.0 mg/L. Chlorate was formed in all jar-test samples.

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CHAPTER 1.

INTRODUCTION

In the early 1900s, the United States drinking water industry drastically reduced the number of fatal waterborne disease outbreaks when it began chlorinating drinking water. Some ninety years later, the United States Environmental Protection Agency imposed stringent regulations governing chlorination of drinking water supplies because this same chemical, which had saved so many lives, produced suspected carcinogens in the presence of naturally occurring organic matter (Letterman 1999).

Two groups of these potential carcinogens are trihalomethanes (THMs) and haloacetic acids (HAAs). Both form when chlorine reacts with natural organic matter in raw water. Chlorine dioxide (ClO_2) is an alternative to chlorine because it is an oxidizing agent rather than a chlorinating agent, and therefore, will not form chlorinated disinfection byproudcts such as HAAs and THMs under typical water treatment conditions (Aieta and Berg 1986). Consequently, many drinking water utilities add ClO_2 to their raw water and delay chlorination until later in the treatment process in efforts to comply with existing state and federal THM regulations. Effective January 1, 2002, the Disinfectant/Disinfection Byproducts Rule (*Federal Register* 1998) will become effective, and the THM maximum contaminant level (MCL) will be reduced from 0.10 mg/L to 0.080 mg/L. In addition, a new MCL for HAAs (0.060 mg/L) will be imposed.

The study described in this thesis was conducted at the Blacksburg, Christiansburg, VPI (BCVPI) Water Authority's water treatment plant (WTP), which is located in Radford, Virginia, approximately twelve miles from the Virginia Tech campus. The Authority provides drinking water to two towns and the university at an average rate of 7 million gallons per day. The raw-water source is the New River, and the intake is located several miles from the WTP. The treatment process includes prechlorination, coagulation, flocculation, sedimentation, filtration and post chlorination.

Since 1979, THM levels in treated water at the BCVPI WTP have routinely been below the existing MCL. The available data, however, show that some changes in the existing treatment practices will be required to ensure that the HAA MCL is consistently met. So, the Authority plans to evaluate the effectiveness of adding ClO_2 as a preoxidant

instead of chlorine to the raw water, which is pumped to the treatment plant from the New River. Chlorination will be delayed until after coagulation and flocculation have bound much of the natural organic matter in floc.

Chlorine dioxide use in conjunction with delayed chlorination is widely documented and accepted as an effective practice for reducing THM concentrations in finished water, but less information is available on the success of such practices for reducing HAAs. Because HAAs were the BCVPI Authority's major concern and because of the apparent gap in available research on the topic, a critical objective of this research was to provide insight into the role ClO_2 might play in reducing HAA formation.

The research project described in this thesis was a laboratory-scale study that preceded a full-scale evaluation of ClO_2 as a preoxidant. The objectives were to:

- Evaluate the extent to which ClO_2 preoxidation of raw water and delayed chlorination can reduce the HAA and THM formation potentials of New River water under treatment conditions similar to those in the full-scale WTP.
- Determine the levels of the two inorganic ClO_2 byproducts, chlorite and chlorate, in water treated in jar tests.

CHAPTER 2.

LITERATURE REVIEW

Chlorine Dioxide General Properties and Chemistry

Chlorine dioxide (ClO_2) is a greenish-yellow gas that exists as a free radical. Solutions are also greenish-yellow and have an odor similar to chlorine. In air, the odor can be detected at concentrations as low as 0.3 ppm. Other chemical characteristics are shown in Table 2-1.

Table 2-1: Chlorine Dioxide General Properties (Material Safety Data Sheet for Chlorine Dioxide and Gordon 2001)

Chemical Formula	ClO_2
Molecular Weight	67.5 g/mol
Liquid Specific Gravity (0°C)	1.64
Melting Point	-59°C (-75°F)
Boiling Point	11°C (52°F)
Vapor Pressure (20°C)	760 mm Hg
Solubility in Water (20°C)	0.8 g/100 g
Vapor Density in Air (Air = 1)	2.3
Ignition Temperature	130°C (266°F)
$\Delta G°$ (25°C)	2.95 kcal/mol
$\Delta H°$ (25°C)	25 kcal/mol
$\Delta S°$ (25°C)	43.9 eu (aq)
Partition Coefficient (35°C)	21.5

ClO_2 does not hydrolyze in water but exists as a dissolved gas at temperatures above 11°C. Solutions are extremely volatile and must be kept in closed containers (White 1999). When exposed to ultraviolet light, ClO_2 in solution will photolytically decompose to chlorate ion (ClO_3^-). Hence, solutions must also be stored in the dark to avoid a decrease in solution strength and the undesirable formation of ClO_3^- (Gordon et al. 1972).

ClO_2 remains stable and does not ionize in solution between pH 2 and 10. In high pH waters, however, ClO_2 will disproportionate to chlorite ion (ClO_2^-) and ClO_3^- according to the following reaction (Gallagher et al. 1994 citing Rosenblatt 1978):

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \qquad [1]$$

ClO_2 is explosive at 5.8 psi (40 kPa) above atmospheric pressure and therefore, it can neither be stored nor compressed and must be generated on-site when it is used at water treatment facilities. At concentrations greater than 10 g/L in solution, explosive vapor pressures exist, but this feature is not a great concern to water utility personnel because ClO_2 is generally used at dosages between 0.1 to 5 mg/L (Aieta and Berg 1986).

Chlorine Dioxide Reactions

Chlorine dioxide oxidizes organic matter; it does not chlorinate it. Chlorine, on the other hand, reacts by oxidation and electrophilic substitution (Aieta and Berg 1986). Chlorine dioxide behaves as a selective oxidant through a one-electron transfer, as follows (USEPA 1999):

$$ClO_{2(aq)} + e^- \rightarrow ClO_2^- \qquad [2]$$

During oxidation reactions, with organic matter, 50 to 70 percent of the ClO_2 dose will be converted to ClO_2^- and the remainder will be converted to ClO_3^- and chloride ion (USEPA 1999).

Another potential source of ClO_2^- in drinking water treated with ClO_2 is unreacted sodium chlorite ($NaClO_2$) that passes through the ClO_2 generator. This problem is eliminated if the solid $NaClO_2$: gaseous chlorine system produced by CDG Technology, Inc. is used. Chlorate can also be present in stock sodium chlorate ($NaClO_3$) solutions and, in fact, a certain percentage of $NaClO_3$ impurity is allowed. Usually, the amount is much less than one percent. Chlorate can also form during ClO_2 generation. In this reaction, an unstable, unsymmetrical intermediate (chlorine oxide) is formed, (reaction [3]).

$$Cl_2 + ClO_2^- \rightarrow \{Cl_2O_2\} + Cl^- \qquad [3]$$

When both reactants are present in high concentration, the intermediate readily forms ClO_2 by either of the two following reactions:

$$2\{Cl_2O_2\} \rightarrow 2ClO_2 + Cl_2 \qquad [4]$$

$$\{Cl_2O_2\} + ClO_2^- \rightarrow 2ClO_2 + Cl^- \qquad [5]$$

In generators that function with low initial reactant concentrations, or when excess chlorine is present, the intermediate will form chlorate according to reactions [6] and [7] (Gates 1998; Gordon 2001; USEPA 1999).

$$\{Cl_2O_2\} + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+ \quad [6]$$

$$\{Cl_2O_2\} + HOCl \rightarrow ClO_3^- + Cl_2 + H^+ \quad [7]$$

Chlorate ion can also be formed from the photolytic decay of ClO_2. The problem with ClO_3^- formation is that, unlike ClO_2^-, once formed, it cannot be removed from the water (White 1999). Plants that practice softening must also take precautions when using ClO_2 because under alkaline conditions, ClO_2 will form ClO_2^- and ClO_3^- (USEPA 1999).

Chlorine Dioxide Generation

ClO_2 can be generated by several different methods, but the most common processes utilize a 25 percent $NaClO_2$ solution that is reacted with either an aqueous or gaseous chlorine source (Aieta and Berg 1986). The various methods are described below in greater detail.

Acid: Chlorite Solution

This is an older technique for generating ClO_2 that involves acidifying the $NaClO_2$ solution by addition of either sulfuric or hydrochloric acid. The common reactions for the use of sulfuric acid are (White 1999):

$$4NaClO_2 + 2H_2SO_4 \rightarrow 2Na_2SO_4 + 2ClO_2 + HCl + HClO_3 + H_2O \quad [8]$$

and/or

$$10NaClO_2 + 5H_2SO_4 \rightarrow 5Na_2SO_4 + 8ClO_2 + 2HCl + 4H_2O \quad [9]$$

Hydrochloric acid is preferred over sulfuric acid because it produces a higher ClO_2 yield. The reaction is as follows (White 1999):

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + H_2O \quad [10]$$

These methods are seldom used in water treatment, primarily because the ClO_2 yields are low. For instance, in reaction [10], only four moles of ClO_2 are produced for every five moles of $NaClO_2$, so the maximum conversion is only 80 percent (White 1999).

Chlorine Solution: Chlorite Solution

This technique for the production of ClO_2 utilizes aqueous chlorine (reaction [11]) (Gordon 2001).

$$2ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + OH^- \quad [11]$$

Early ClO_2 generators added 200-300 percent more aqueous chlorine than the stoichiometric requirement so that yields would be improved. This problem was minimized in later systems by lowering the solution pH to favor hypochlorous acid and molecular chlorine. A problem with generators based on this technique is that ClO_3^- may be produced (Aieta and Berg 1986).

An additional drawback to the use of aqueous chlorine solution for the generation of ClO_2 is that the reaction rate is slower than in generators based on most other methods, with the exception of the acid method previously described. The production rate for this system is approximately 1000 pounds per day (lb/day) (USEPA 1999).

Though not commonly used in the United States, another aqueous chlorine design is the French Loop. Chlorine gas is added to a recycling loop of water until the solution is saturated. The solution is then reacted with liquid $NaClO_2$ to form ClO_2 (USEPA 1999).

Gaseous Chlorine: Liquid or Solid Chlorite Systems

Some generators produce ClO_2 by reacting liquid $NaClO_2$ with gaseous chlorine. These gaseous chlorine generators produce ClO_2 at rates of 5–120,000 lb/day. In this system, described by reaction [12], $NaClO_2$ reacts under a vacuum with gaseous chlorine.

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \quad [12]$$

The reaction occurs rapidly and at a neutral pH. High ClO_2 yields, 95–99 percent can be achieved with less than 2 percent excess chlorine present in solution (USEPA 1999).

A recent innovation in ClO_2 generation technology is a proprietary system produced by CDG Technology, Inc. (Bethlehem, PA) that reacts humidified, diluted chlorine gas with solid $NaClO_2$ in cartridge form. The result is a high-purity ClO_2 gas that is added directly to the water (White 1999).

Emerging Technologies

One recently developed technology generates ClO_2 from a 25 percent $NaClO_2$ solution that is recycled through an electrolyte cell (USEPA 1999). Chlorine dioxide production by electrolytic means is limited, however, and these systems at present are suitable only for small systems.

Another generation method involves the use of $NaClO_3$. This procedure has long been used by the pulp and paper industry but has only recently been made available to drinking water plants (USEPA 1999; Gordon 2001). This system uses excessive amounts of hydrogen peroxide and sulfuric acid according to the following reaction:

$$2ClO_3^- + H_2SO_4 + H_2O_2 \rightarrow 2ClO_2 + O_2 + SO_4^{2-} + 2H_2O \qquad [13]$$

Problems with this method may inhibit its eventual success in the drinking water industry. For example, the perchlorate ion, which is a human-health hazard, can form under acidic conditions and can also be present in the commercial $NaClO_3$ solution (Gordon 2001). In addition, the procedure generates a waste stream containing hydrogen peroxide and sulfuric acid that poses a disposal problem for water utilities.

Chlorine Dioxide as a Disinfectant

Chlorine dioxide is a powerful disinfectant. In fact, most research has determined that it is either more effective or equal to chlorine on a mass-dose basis (Rittman 1997). In regards to bacterial inactivation, Trakhtman (1949) determined that ClO_2 doses of 1 mg/L to 5 mg/L were sufficient to kill *Escherichia coli* and *Bacillus anthracoides* in turbid waters. Bedulivich et al. (1954) showed that ClO_2 was equal to or better than chlorine in effectiveness against *Salmonella typhosa* and *S. paratyphi*. Similar studies have shown ClO_2 to be an effective disinfectant against other bacteria of concern, including *Eberthella typhosa*, *Shigella dysenteriae*, *S. paratyphi B*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* (Ridenour 1949).

As well as being an effective bactericide, ClO_2 has also been shown to be effective for inactivation of many viruses. Various researchers have proven its effectiveness against *Poliovirus* 1 and *Coxsackie virus A9* (USEPA 1999 citing Ridenour and Ingols 1946, Cronier et al. 1978, and Scarpino 1979). When compared to chlorine at

higher than neutral pH, ClO_2 is a stronger disinfectant against *Echovirus* 7, *Coxsackie virus B3*, and *Sendaivirus* (Smith and McVey 1973).

Of great concern to water utilities today are the pathogenic protozoa *Giardia lamblia, Giardia muris, and Cryptosporidium parvum.* Researchers have found that *Giardia* cysts and *Cryptosporidium* oocysts are largely resistant to free chlorine, UV irradiation, and chloramines (Korich et al. 1990; Lorenzo-Lorenzo et al. 1993; Ransome et al. 1993). Hofmann et al. (1997) showed a 3-log *Giardia* inactivation after a 60-minute contact time with ClO_2 at dosages between 1.5 mg/L and 2 mg/L. Lykins et al. (1991) showed that ClO_2 is also a strong disinfectant against *Cryptosporidium* oocysts.

Chlorine Dioxide Byproducts and Regulations

As noted earlier, the two inorganic byproducts of ClO_2 are ClO_2^- and ClO_3^-. No maximum contaminant level (MCL) currently exists for ClO_3^-, but the MCL for ClO_2^- is 1.0 mg/L and the maximum contaminant level goal (MCLG) is 0.8 mg/L. Chlorite ion in water leaving the treatment plant must be monitored daily and monthly samples must be collected for analysis from three places in the distribution system (one near the first customer, one at a point approximately equal to the average hydraulic residence time in the system, and the third at a distant point in the distribution system). Compliance is based on the average concentration (*Federal Register 1998*).

Certain studies have indicated that ClO_2^- produces hemolytic anemia (Condie 1986). Condie (1986), citing Bercz et al. (1982), described hematological effects found in monkeys that were given both ClO_2^- and ClO_3^- in increasing dosages. The current ClO_2^- MCL was based on the results of a two-generation study of rats that was sponsored by the Chemical Manufacturers Association (Gates 1998).

Chlorine dioxide residuals in drinking water are also regulated by the USEPA (*Federal Register* 1998). The maximum residual disinfectant level (MRDL) for ClO_2 in water leaving the treatment plant is 0.8 mg/L.

Various impact studies have been performed with ClO_2 and laboratory animals. Chlorine dioxide was found to have adverse health effects, including decreased serum T_4 levels, hematological anemia, increased plasma cholesterol, and decreased plasma thyroid hormones (Condie 1986). Condie (1986) also expressed concern over the formation of

iodinated organics from the reaction of residual ClO_2 in drinking water and iodine present in bodily fluids, such as saliva and gastric juices. These iodinated organics may behave as thyroid antagonists, or thyromimetic agents.

Chlorine dioxide may also form other byproducts in addition to ClO_2^- and ClO_3^-. In reactions with humic and fulvic acids, ClO_2 can produce quinones, hydroquinones, aldehydes, and carboxylic acids (Rav-Acha 1984). Chlorinated byproducts, however, are formed in only part per trillion levels because ClO_2 oxidizes rather than chlorinates organic matter (Richardson 1998).

Chlorine Dioxide Usage during Water Treatment

According to the 1995 Community Water Systems Survey conducted by the USEPA, 14.2 percent of surface water treatment systems servicing a population of 50,001-100,000 are using ClO_2 as a predisinfectant compared to 47.5 percent using chlorine, 15.5 percent using chloramines, and 5.4 percent using ozone (USEPA 1997). No systems servicing less than 1000 reported using ClO_2. Of the groundwater systems, the only service population that reported using ClO_2 as a predisinfectant was the one servicing 50,001-100,000 and their ClO_2 usage only comprised 3.1 percent compared to other oxidant usage.

Many of the water utilities that use ClO_2 have reported receiving numerous odor complaints from customers. Customers describe the odors as kerosene-like and cat-urine-like. The source of these odors was unknown for many years, but utilities suspected ClO_2 as the cause. Complaints occurred only when the ClO_2 feed was on, but no odors were detected at the plants themselves. Hoehn et al. (1990) substantiated the utilities' claims that the odors were associated with ClO_2 use. They found that ClO_2 was being regenerated at a few tenths of a mg/L in the distribution system between the plant and the customers' households. Ellenberger et al. (1998) found ClO_2 concentrations ranging from 0.03 mg/L to 0.17 mg/L at the homes of customers who complained of kerosene or cat-urine odors.

Once regenerated, the ClO_2 would react with organic compounds in the air to form the kerosene- and cat-urine-like odors. A common source of the air-phase organic compounds is new carpeting. To prevent these odors from forming, ClO_2 reformation

must be prevented either by ClO_2^- removal at the treatment plant or substitution of chloramines for free chlorine as the residual disinfectant in the distribution system (Hoehn et al. 1990).

Ironically, many water utilities have installed ClO_2 because it provides effective control for some types of tastes and odors. Because ClO_2 does not chlorinate organic material, the formation of odorous chlorinated phenolic compounds is avoided (Gallagher et al. 1994).

Another use for ClO_2 is manganese and iron oxidation. Both are nuisances in that they will stain laundry and plumbing fixtures. Chlorine dioxide can quickly oxidize both manganous ion and ferrous ion in source waters (White 1972; Knocke et al. 1990).

Chlorine Dioxide Reactions with Natural Organic Matter

Chlorine forms disinfection byproducts (DBPs) by chlorination of natural organic matter (NOM) in the source water. The NOM itself is a heterogeneous assortment of species derived from a variety of sources, including terrestrial plants, algae, bacteria, and macrophytes. Characterizing NOM and its propensity to form DBPs has been a challenge for researchers. For example, humic substances derived from microbes often contain considerable nitrogen but little aromatic carbon and phenolic groups, while humic substances derived from higher plants have just the opposite (Croue et al. 1999).

The amount of NOM in water is normally expressed as dissolved organic carbon (DOC) and particulate organic carbon (POC). The sum of these is the total organic carbon (TOC) (Letterman 1999). In most natural waters, humic substances comprise the majority of NOM and, therefore, are the most important DBP precursors (Letterman 1999; Croue et al. 1999). Disinfection byproduct concentrations increase with an increased amount of precursor material in the water. These precursor substances are anionic polyelectrolytes with a range of molecular weights. Their carboxyl and phenolic groups give them their negative charge. They contain aromatic as well as aliphatic components (Letterman 1999).

Humic substances in water are usually classified as either fulvic acids or humic acids. Humic acids precipitate when a water sample is acidified to pH 2.0, while fulvic acids remain soluble (Pomes et al. 1999). Several researchers have found humic acids to

react more readily with chlorine than fulvic acids (Reckhow et al. 1990; Oliver and Thurman 1983). The DBP formation potential is also greater for humic acids. In chlorination studies conducted by Reckhow et al. (1990), chlorine was reacted at neutral pH with fulvic and humic acids. The sum of the dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) yields was larger than the chloroform yield. Croue et al. (1999) citing Croue (1987) conducted a similar study with water adjusted to pH 7.5 and found, as did Reckhow et al. (1990), that the DCAA and TCAA yields surpassed the chloroform yield. In a later study, Croue et al. (1999) found higher concentrations of haloacetic acids (HAAs) than trihalomethanes (THMs) and attributed the difference to the fact that hydrophobic acids (humic substances) are removed by conventional treatment practices, leaving the hydrophilic acids (nonhumic substances) to react with free chlorine to form DBPs. Thus, the hydrophilic acids may in fact be the main DBP precursors at treatment plants where chlorine is added only at the end of the treatment process. Croue et al. (1999) stated that most research has concentrated on the difference between DBP formation with fulvic and humic acids, but more work needs to be done to understand the differences between hydrophobic and hydrophilic acids in the formation of DBPs.

Because there is no currently accepted parameter for identifying DBP precursors, a parameter called specific ultraviolet absorbance (SUVA) is used to forecast DBP formation potentials (Croue et al. 1999). This value is the ratio of UV absorbance to DOC concentration (Letterman 1999). Croue et al. (1999) noted that some waters with comparable SUVA values have shown very different chlorine demands and DBP formation potentials.

Trihalomethanes and Haloacetic Acids

THMs and HAAs comprise the first and second most prevalent halogenated DBPs found in drinking water, respectively. Both are regulated by the USEPA because of the human health risks associated with exposure to them. Toxicology studies have found many of these compounds to be carcinogenic in laboratory animals. Some have also caused adverse reproductive or developmental effects. Four THMs and nine HAAs comprise the majority of the halogenated DBPs found in chlorinated drinking water, but

the EPA only regulates five HAAs (*Federal Register* 1998). The MCL of 0.080 mg/L for TTHMs is the running quarterly average of the sum of the four THMs (chloroform, bromodichloromethane, chlorodibromomethane, and chloroform). Likewise, the MCL of 0.060 mg/L for HAA5 is the running quarterly average of the sum of the mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acid (*Federal Register* 1998). No MCL has been proposed for the remaining four HAAs. This set of regulations is part of the Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) Rule.

Also covered under the Stage 1 D/DBP Rule are the MRDLs for ClO_2, chlorine, and chloramine and the MCLs for ClO_2^- and bromate (*Federal Register* 1998). The proposed Stage 2 D/DBP Rule may reduce the TTHM MCL to 0.040 mg/L and the HAA5 MCL to 0.030 mg/L (Arora et al. 1997). A summary of the regulations is provided in Table 2-2.

Table 2-2: Trihalomethanes and Haloacetic Acids (*Federal Register* 1998 and Chem Service 2000)

Group	Compound	Formula	MCLG, mg/L	MCL, mg/L
Total Trihalomethanes (TTHMs)	Chloroform	$CHCl_3$	*	0.080 (annual average)
	Bromodichloromethane	$CHCl_2Br$	0	
	Dibromochloromethane	$CHClBr_2$	0.06	
	Bromoform	$CHBr_3$	0	
Haloacetic Acids (HAA5)	Monochloroacetic Acid	$CH_2ClCOOH$	---	0.060 (annual average)
	Dichloroacetic Acid	$CHCl_2COOH$	0	
	Trichloroacetic Acid	CCl_3COOH	0.3	
	Monobromoacetic Acid	$CH_2BrCOOH$	---	
	Dibromoacetic Acid	$CHBr_2COOH$	---	
Remaining Haloacetic Acids	Bromochloroacetic Acid	$CHBrClCOOH$	N/A	N/A
	Bromodichloroacetic Acid	$CBrCl_2COOH$		
	Chlorodibromoacetic Acid	$CBr_2ClCOOH$		
	Tribromoacetic Acid	CBr_3COOH		

--- = no MCLG established; * = originally set to 0, but removed by order of the U.S. Court of Appeals for the District of Columbia Circuit (*Federal Register* 2000)

Compliance with the MCL for TTHMs and HAA5 requires that samples be collected quarterly. Large distribution systems should monitor at four locations throughout their system. One of the locations should be their maximum residence time location (MRTL). Medium-size utilities are required to sample only at the distribution-system MRTL.

Small utilities are required to collect only one sample a year at the MRTL during the warmest time of the year (Williams et al. 2000; Chen and Weisel 1998). The assumption inherent in these requirements is that THM and HAA concentrations will be the greatest at the MRTL because it represents the maximum time possible for reactions to occur. This assumption appears to hold for THMs.

A yearlong study in England found a 40-60 percent increase in THMs with increasing distance from the water treatment plant, even though the chlorine residual steadily decreased with distance (Chen and Weisel 1998 citing Brett and Calverley 1979). Others have corroborated these results (Williams et al. 2000; Letterman 1999). This relationship, however, may not exist for HAAs. Williams et al. (2000) monitored HAA5 levels at the MRTL in the Newport News, Virginia distribution system during several summers and found either low or undetectable levels of HAA5. Other local utilities have experienced similar results. The researchers were able to link the degradation of DCAA to bacteria found in the biofilm (Williams et al. 2000).

Chen and Weisel (1998) also found that DCAA concentrations decreased with increased residence time along the distribution system. The decrease was more dramatic in warmer seasons, possibly as a result of increased microbial activity during periods when water temperatures were warmer. The TCAA concentrations also declined but by a smaller amount.

Effect of Water Quality on DBP Formation

The propensity of a humic substance to form DBPs is complicated and varies not only with the properties of the humic substance itself, but also with water quality parameters such as pH, temperature, and bromide concentration. Chlorine residual concentration is also a key player (Croue et al. 1999). In general, THM formation increases with increasing pH (Letterman 1999; AWWA 1982). On the other hand, HAA formation decreases with increasing pH (Letterman 1999).

In terms of temperature effects, both THM and HAA formation increase with increasing temperature (Letterman 1999; AWWA 1982; Dojlido et al. 1999; Arora et al. 1997). Conversely, elevated temperatures may also speed the biological degradation of HAAs (Letterman 1999; Williams et al. 2000).

Another parameter that has a positive effect on HAA and THM formation is bromide ion. In chlorinated waters, bromide is oxidized by chlorine to hypobromous acid, which ultimately forms brominated DBPs (Letterman 1999).

Finally, high chlorine doses will form greater concentrations of DBPs as long as the water is not limited by the amount of precursor material. This is why shifting the chlorination point to later in the treatment process may decrease DBP formation. There is less precursor material for the chlorine to react with after coagulation and flocculation have occurred (Letterman 1999). As for ClO_2, increasing doses have been shown to have the opposite effect as chlorine. Treated-water THM and HAA concentrations decrease following treatment with ClO_2 at doses above 1.5 mg/L (Griese 1991).

Chlorine Dioxide, Haloacetic Acids and Trihalomethanes

One of the most common reasons utilities switch to ClO_2 is for DBP control. Dietrich et al. (1992) found that 65 percent of 32 plants surveyed were using ClO_2 precisely for that reason. As stated earlier, ClO_2 disinfection differs from chlorine disinfection in that ClO_2 does not chlorinate organic material. It oxidizes it, thereby avoiding the formation of THMs and HAAs.

Some studies have linked ClO_2 to the formation of THMs and HAAs. For instance, Chang et al. (2000) found that HAAs and THMs were formed when 15-30 mg/L ClO_2 was reacted with vanillic, *p*-hydroxybenzoic, and humic acids. The DBPs increased with an increasing ClO_2 dose. Gordon (2001) and Masschelein (1979) dispute research results such as these saying the formation of DBPs from ClO_2 is most likely the result of chlorine and/or ClO_2^- contamination in the ClO_2 solution itself. In fact, other studies have shown that ClO_2 will not react to form THMs and HAAs. For example, the Los Angeles Department of Water and Power (LADWP) evaluated the use of ClO_2 to control algal growth in an open reservoir that provides finished water. The LADWP had been using chlorine to control the algae problem, but THMs and HAAs were being formed. Chlorine dioxide for the study was generated by reacting liquid $NaClO_2$ (25 percent solution) with chlorine gas under vacuum. The ClO_2 solution was applied to the reservoir at chosen times during select summer and fall evenings at dosages ranging between 0.8 to 1.5 mg/L as ClO_2. Both THM and HAA levels decreased during treatment with ClO_2,

and the levels rose once chlorination was resumed. Chlorite ion and ClO_3^- levels were below 1 mg/L in the distribution system and did not cause concern. The trials showed that ClO_2 could effectively control the algae problem without producing THMs and HAAs (Stolarik and Liu 2000).

The Evansville, Indiana Water and Sewer Utility evaluated the ability ClO_2 addition for reducing THM formation in a 100 gpm (gallons per minute) pilot plant study. As part of the study, ClO_2 was used as a predisinfectant. Samples were collected monthly during the one year study and following collection, were incubated at pH 8 with a free chlorine residual for three days before analysis. The THM levels in the plant's effluent were 60 percent less when ClO_2 was used than when pre- and post chlorination were practiced. Neither disinfectant altered the TOC concentration (Lykins and Griese 1986). In a later study, Griese (1991) found that incrementally increasing the ClO_2 dose led to further reductions in THM and HAA concentrations. Increasing the ClO_2 dose from 2 mg/L to 5 mg/L resulted in a 48 percent reduction in THMs. The HAA concentrations decreased when ClO_2 concentrations were increased to levels greater than 3 mg/L (Griese 1991).

Li et al. (1996) also studied the formation of THMs in waters treated with ClO_2. Bromide-free water that was treated with up to 20 mg/L ClO_2 and 2.0 mg/L humic acid was free of THMs. However, bromoform was found in water containing bromide ion and humic acids when it was treated with ClO_2. The bromoform concentration increased with increasing ClO_2 dose and increased bromide ion content. The authors speculated that bromoform formed when either ClO_2 or ClO_2^- oxidized bromide ion to form hydrobromous acid, which in turn, reacted with humic acid (Li et al. 1996). Experiments were also performed with combination solutions of ClO_2 and chlorine. Chloroform was the only THM detected in bromide-free water. If the ClO_2-to-chlorine ratio (w/w) was increased to 3, chloroform formation was reduced by 90 percent.

In one final example, ClO_2 was evaluated as a predisinfectant in a 30 gpm pilot plant for possible use at a direct filtration plant (Hulsey et al. 2000). Chlorine dioxide dosages were 0.2 mg/L, 0.5 mg/L and 1.0 mg/L. The addition point was varied to determine the impacts on DBP formation and other parameters. Simulated distribution system tests were set up by adjusting samples from the full scale plant and the pilot plant

to pH 7.8 and measuring pH, chlorine residual, THMs and HAAs at 1, 24, 48, and 168 hours after chlorination. It was necessary to add chlorine to the pilot plant samples to produce a residual of 2.5 mg/L. Chlorine dioxide residuals and ClO_2^- concentrations in samples taken from the pilot plant were also determined. The five HAAs that are included in the MCL plus bromochloroacetic acid were analyzed. The TTHM and HAA6 concentrations were reduced 23 percent and 4 percent, respectively, when the ClO_2 dose was 0.2 mg/L, 32 percent and 43 percent, respectively, when the dose was 0.5 mg/L, and 23 percent and 33 percent, respectively, when the dose was 1.0 mg/L. Chlorite ion concentrations in filtered water after treatment with ClO_2 at 0.2, 0.5, and 1.0 mg/L were, respectively, 0.24 mg/L, 0.55 mg/L, and 0.83 mg/L, all less than the current 1.0 mg/L MCL. Increased ClO_2 doses may have had a more beneficial effect on DBP formation, but ClO_2^- formation is a concern and a constraint on the amount of ClO_2 that can be used unless some means are provided to remove it (Hulsey et al. 2000).

CHAPTER 3.

METHODS AND MATERIALS

Materials

All glassware was purchased from Fisher Scientific (Atlanta, GA) and cleaned by soaking it in a chromic acid cleaning solution for eight hours, rinsing it three times with Nanopure® water, and allowing it to air-dry. Plasticware was cleaned with water containing a detergent, Sparkleen®, then rinsed thoroughly with Nanopure® water and allowed to air-dry.

All chemicals were purchased from Fisher Scientific unless indicated otherwise. The standards used for trihalomethane (THM) and haloacetic acid (HAA) calibrations were purchased from Chem Service, Inc. (West Chester, PA). The THM standards were a mixture of four compounds (chloroform (CASRN 67-66-3), dichlorobromomethane (CASRN 75-27-4), chlorodibromomethane (CASRN 124-48-1), and bromoform (CASRN 75-25-2)) and the HAA standards were a mixture of nine HAAs and a surrogate, 2,3-dibromopropionic acid (CASRN 600-05-5). The nine HAAs in the standard included: mono- (CASRN 79-11-8), di- (CASRN 79-43-6), and trichloroacetic acid (CASRN 76-03-9); mono- (CASRN 79-08-3), di- (CASRN 631-64-1), and tribromoacetic acid (CASRN 75-96-7); and three acetic acid isomers containing both chlorine and bromine, (bromochloroacetic acid (CASRN 5589-96-8), bromodichloroacetic acid (CASRN 71133-14-7), and chlorodibromoacetic acid (CASRN 5278-95-5)). An internal standard, 1,2,3-trichloropropane (CASRN 96-18-4), was also purchased from Chem Service, Inc. Haloacetic acid methyl derivatives were purchased from Fisher Scientific to check the HAA extraction and analysis procedure.

The stock chlorine solution was prepared by bubbling high purity chlorine gas into a solution of 1.5 L of Nanopure® and 4 g NaOH. The chlorine gas feed was turned off once the solution reached pH 7. When not in use, the stock solution was refrigerated in the dark at 4°C.

The chlorine dioxide (ClO_2) stock solution was generated by passing 4 percent chlorine gas through a solid sodium chlorite ($NaClO_2$) reactor cartridge according to

instructions provided by CDG Technology, Inc. (Bethlehem, PA), the provider of the ClO_2 generator. When not in use, the stock solution was refrigerated in an opaque, glass container at 4°C. Prior to each use, the absorbance of the ClO_2 solution was determined with a Beckman (Fullerton, CA) spectrophotometer (DU® 640) set to 360 nm. The absorbance was inserted into the Beer's Law equation to obtain a concentration in moles/L ClO_2 as follows:

$$a=\varepsilon bc$$

Where: a = absorbance, nm
ε = ClO_2 extinction coefficient, 1225 $M^{-1}cm^{-1}$
b = cuvette path length, cm
c = ClO_2 concentration, moles/L

Jar Test Procedure

All samples generated in this study were obtained from bench-scale jar tests performed at the Blacksburg, Christiansburg, VPI Water Authority's Water Treatment Plant (WTP) in Radford, Virginia. The jar test procedure was an adaptation of a protocol developed specifically for the Authority in a memorandum from Dr. George Budd, Andrea Hargette, and Paul Hargette of Black & Veatch Corporation and dated June 9, 1999. The jar test procedures mimic, as best possible, the full-scale plant conditions and are summarized in Table 3-1 below:

Table 3-1: Jar Test Conditions at the Blacksburg, Christiansburg, VPI WTP

Process Step	Mixing Speed (rpm)	Duration (min)
Raw Water Travel Time	10	15
Rapid Mix	100	2
Flocculation – Stage 1	20	16
Flocculation – Stage 2	10	16
Flocculation – Stage 3	5	3
Sedimentation	0	8

The travel-time step was not part of the jar test procedure developed by Black & Veatch, but it was added to the protocol to simulate raw-water travel time from the New River intake to the WTP. This was an important addition to the protocol because future treatment modifications at the WTP included pretreatment of raw water with ClO_2. The

ClO_2 contact time in the transmission main to the WTP was estimated to be approximately 15 minutes.

Initially, only three samples were treated during the jar tests, but eventually, four additional jars were included in the protocol. Coagulant was added to all jars prior to rapid mix. The coagulant was polyaluminum chloride (DelPAC 2500, Delta Chemical Company; Baltimore, MD), which was the same coagulant being used at the WTP. The applied dosages were the same as that being added at the WTP on the day jar testing was performed. Samples that were prechlorinated were treated with chlorine along with the coagulant immediately before rapid mixing began. Samples that were post chlorinated were treated with chlorine after stage 2 flocculation. A description of the treatments applied to each of the samples is show in Table 3-2.

Table 3-2: Treatments Applied During Jar Tests

Jar Number	Jar Treatment	Description of Jar Treatment Process
Jar 1	Predisinfection with Chlorine – Simulated Current WTP Conditions Jar 1	2.0 mg/L chlorine added with coagulant prior to rapid mix; no post chlorination
Jar 2	Post chlorination – Simulated Delayed Chlorination	No predisinfection; 2.0 mg/L post chlorination
Jar 3	Preoxidation with ClO_2	2.0 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
Jar 4	Preoxidation with ClO_2	1.0 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
Jar 5	Preoxidation with ClO_2	0.5 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
Jar 6	Blank	0.5-1.0 mg/L ClO_2 pretreatment of Nanopure® water; 2.0 mg/L post chlorination
Jar 7	No disinfection	No pre- or post treatment with either ClO_2 or chlorine

With the exception of Jar 6 (Blank), water used in the jar tests was taken from the intake pipe immediately before the start of the test. The water in Jar 6 was Nanopure®. All jars

containing ClO_2 were covered in aluminum foil to minimize the photolytic decomposition of the oxidant. Water temperatures were recorded prior to the start of the testing, and the pH of each treated sample was measured at the conclusion of the testing.

Total chlorine residuals in water samples treated with chlorine but not ClO_2 were determined according to Section 4500-Cl D in *Standard Methods for the Examination of Water and Wastewater* (1998). The titration was performed at the treatment plant with a Wallace & Tiernan A-790 titrator (Vineland, NJ). Samples that had been treated with ClO_2 during the jar tests were analyzed for residual chlorine, ClO_2 and chlorite ion (ClO_2^-) with a Bailey-Fischer & Porter amperometric titrator according to Method 4500-E ClO_2 in *Standard Methods for the Examination of Water and Wastewater* (1998). After the titrations were completed, samples for additional analyses were collected from each jar. The sampling protocol is described later.

Additional raw water characteristics; including turbidity, alkalinity, pH, temperature, and hardness; were recorded from the operator logbook at the WTP. These measurements were the most recent ones obtained by the plant's operators.

Chlorite Ion and Chlorate Ion Analyses

Samples to be analyzed for ClO_2^- and chlorate ion (ClO_3^-) analysis were collected directly from the jars and purged with nitrogen gas for 10 minutes to remove any residual ClO_2. Aliquots of the purged sample were placed in amber, 40-mL glass vials with Teflon-lined screw caps, and preserved by addition of ethylenediamine solution at a concentration of 50 mg/L. The sampling and analysis procedures were those prescribed in USEPA Method 300.1 (USEPA 2000). Samples were stored at 4°C for up to 14 days before being analyzed.

Chlorite ion and ClO_3^- concentrations in the preserved samples were determined with a Dionex 300 ion chromatograph equipped with a conductivity detector and AS40 Automated Sampler. The columns used for ion separation included a Dionex AG9-HC, 4 mm anion guard column and a Dionex AS9-HC, 4 mm anion separator column. The anion suppressor, which was also purchased from Dionex, was an ASRS-I, 4 mm device.

TOC Analyses

Samples for total organic carbon (TOC) analysis were collected from the jars and placed in amber, 40-mL glass vials with Teflon-lined screw caps. They were preserved by addition of phosphoric acid to pH 2 and refrigerated at 4°C until analyzed. Prior to analysis, the samples were purged with oxygen to remove carbon dioxide. The analyses were performed within 30 days of collection with a Sievers (Boulder, CO) Portable TOC Analyzer 800 with an autosampler.

Haloacetic Acid and Trihalomethane Simulated Distribution System Potential Analyses

After chlorine analyses were completed, settled water samples were collected from each of the jars and placed in either a 500 mL or 1000 mL volumetric flask. Chlorine was then added to the flask to increase the concentration to a specific level. For example, if the settled water chlorine concentration was 1.5 mg/L, as determined by amperometric titration, 2.5 mg/L of chlorine would be needed to increase the concentration to 4.0 mg/L. Ultimately, the goal was to ensure that the chlorine residual after three days storage would be between 1.5 mg/L and 2.0 mg/L. Samples were also buffered to pH 7 by addition of a 1M phosphate buffer so that the pH would remain constant during the three-day incubation period. The buffer was prepared by adding 68.1 g KH_2PO_4 and 11.7 g NaOH to reagent-grade water and diluting to a 500 mL volume. One mL of buffer was added to 1-L samples, and 0.5 mL was added to 500 mL samples. The sample solution was then brought up to volume by addition of the settled water.

After the addition of phosphate buffer and chlorine, the sample water was added to either 60-mL clear-glass vials wrapped in aluminum foil with Teflon-lined screw caps for HAA analysis or 40-mL amber glass vials with Teflon-lined screw caps for THM analysis. Other aliquots of the samples were placed in120-mL plastic containers for chlorine residual analysis at the end of the incubation period. Vials containing the samples to be analyzed for THM analysis were airtight and headspace-free. Samples were returned to the Virginia Tech Environmental Engineering Laboratory and stored in the dark for three days at ambient (21-24°C) temperature.

After three days, residual chlorine concentrations in the 120-mL samples were determined by amperometric titration according to section 4500-Cl D. of *Standard Methods* (1998) with a Fischer Scientific CL Titrimeter 397.

Samples containing chlorine at levels between 1.5 mg/L and 2.0 mg/L or as close as possible to this range were selected for analysis, dechlorinated according to their specific EPA method (552.2 for HAA samples and 502.2 for THM samples), and refrigerated at 4°C until the analyses could be performed.

Total Trihalomethane Analysis Procedure

Total THM analyses were performed according to USEPA Method 502.2 (USEPA 1995). The method offers several capillary column choices, and Column 3, which is a J&W Scientific DB-624 (30 m long x 0.53 mm ID, 3 µm film thickness), was chosen. The analytical instrument was a Tremetrics (Austin, TX) 9001 gas chromatograph (GC) with a Tracer (Austin, TX) 1000 Hall detector, Tekmar (Cincinnati, OH) 3000 Purge and Trap Concentrator, and Tekmar 2016 Purge and Trap autosampler. The trap purchased for the research was a Supelco (Bellefonte, PA) VOCARB 300 Purge Trap K.

Because this method does not recommend a GC temperature program for elution of THMs through a DB-624 column, one was established through experimentation. The temperature program that gave the best results was an initial temperature of 45°C held for 3 minutes, ramped to 200°C at 11°C/min, and then stopped at 200°C.

Haloacetic Acid Analysis Procedure

The HAA analyses were performed according the EPA Method 552.2 (USEPA 1995) with a Hewlett Packard 5890 GC equipped with an electron capture detector and Hewlett Packard autosampler. The capillary column was a Supelco SPB-1701 column (30 m long x 0.25 mm ID, 0.25 µm film thickness).

Statistical Calculations

Statistical analyses were conducted using the NCSS 97 software package (Hintze 1997). The Kruskal-Wallis nonparameteric analysis of variance test was used to

determine if the medians of the various data sets were statistically different. If they were statistically different, a Kruskal-Wallis multiple comparison test was performed to elucidate the differences. An alpha value (σ) of 0.05 was selected for all the analyses.

CHAPTER 4.

RESULTS

Effects of Chlorine Dioxide on Trihalomethane Formation

Figure 4-1 is a box plot showing total trihalomethane (TTHM) concentrations formed during jar testing and the subsequent holding period. The solid line within each box is the median value, the dashed line is the mean, and the upper and lower boundaries are the 10^{th} and 90^{th} percentile values. The error bars above and below the boxes represent the 5^{th} and 95^{th} percentiles, while solid circles indicate outliers. Treatment that water in each jar received is abbreviated on the x-axis, and Table 4-1 provides descriptions of each abbreviation. The dashed line on Figure 4-1 corresponds to the maximum contaminant level (MCL) for TTHMs of 0.080 mg/L.

Kruskal-Wallis multiple comparison z-value tests showed that the THM levels that developed in water pretreated with 2.0 mg/L ClO_2 (2.0 CD) and in the blank were significantly lower than THMs that developed in waters that were (1) pretreated with chlorine (Pre-chl), (2) treated with neither oxidant, either pre- or post treatment (No Dis), and (3) treated by post chlorination only (No Pre-chl). Furthermore, THM concentrations that developed in water pretreated with 2.0 mg/L ClO_2 were significantly lower when compared to those in water pretreated with 0.5 mg/L ClO_2 (0.5 CD) but not with 1.0 mg/L (1.0 CD). Finally, THM levels that developed in water pretreated with 2.0 mg/L ClO_2 were not significantly greater than those that formed in the blank, even though they appear to be greater from examination of Figure 4-1.

An additional Kruskal-Wallis multiple comparison z-value test was performed on the ClO_2 samples to determine whether ClO_2 dose affected the final TTHM levels. Trihalomethanes that developed in water pretreated with ClO_2 were compared to those that developed in water when chlorination was delayed until after flocculation (No Pre-chl). No prechlorination was considered the zero dose when the statistical test was performed. It was selected as the basis of the comparison because the treatment those samples received was most similar to treatment the samples treated with ClO_2 received (i.e., no prechlorination but with post chlorination). In this case, the median THM level in samples pretreated with 2.0 mg/L ClO_2 was statistically different from the median

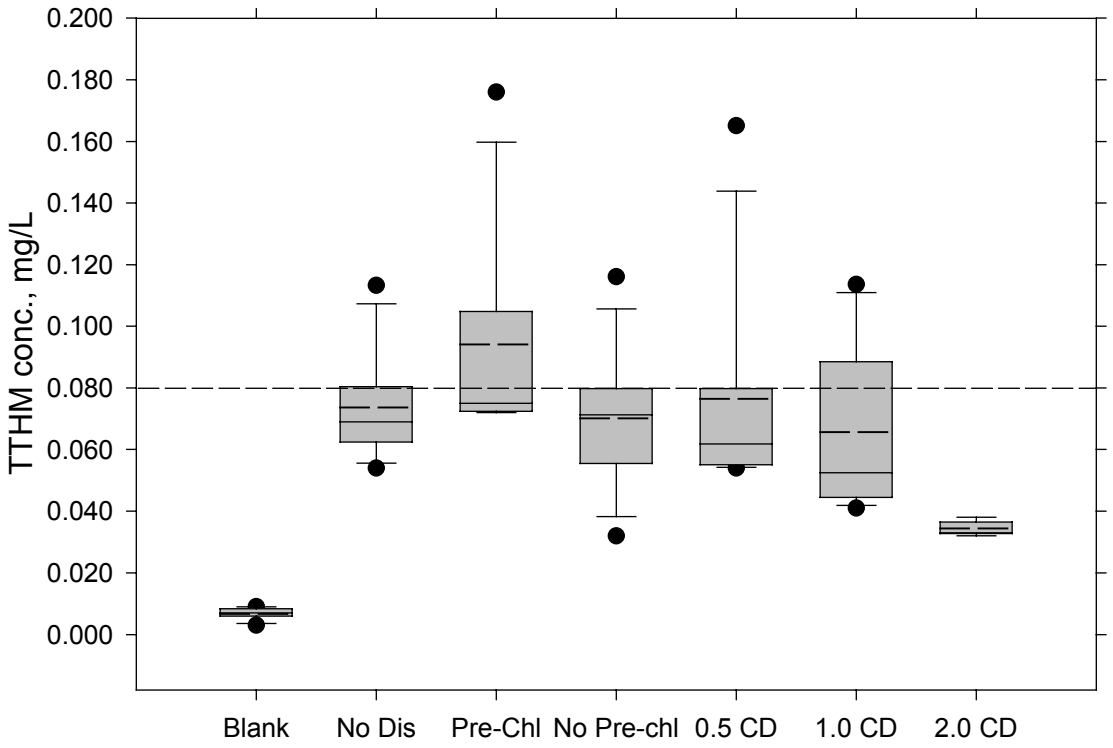


Figure 4-1: Total trihalomethanes generated at the Blacksburg, Christiansburg, VPI Water Treatment Plant

Table 4-1: Description of jar testing protocol and graph abbreviations

Abbreviation	Jar Description	Details of Jar Test Procedure
Pre-chl	Predisinfection with Chlorine – Simulated Current WTP Conditions	2.0 mg/L chlorine added with coagulant prior to rapid mix; no post chlorination
No Pre-chl	Post chlorination – Simulated Delayed Chlorination	No predisinfection; 2.0 mg/L post chlorination
0.5 CD	Predisinfection with ClO_2	0.5 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
1.0 CD	Predisinfection with ClO_2	1.0 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
2.0 CD	Predisinfection with ClO_2	2.0 mg/L ClO_2 pretreatment; 2.0 mg/L post chlorination
Blank	Blank	0.5-1.0 mg/L ClO_2 pretreatment in Nanopure® water; 2.0 mg/L post chlorination
No Dis	No disinfection	No pre- or post treatment with either ClO_2 or chlorine

THM level in samples pretreated with both 0.5 mg/L ClO_2 and1.0 mg/L ClO_2, and in those that were not prechlorinated. No other differences were apparent from the statistical analyses.

Figure 4-2 is a plot of the percent reductions in the TTHMs concentrations that developed in five samples treated by the various treatment scenarios relative to the TTHM concentrations in samples that were prechlorinated as part of the jar-test procedure. A positive value indicates that the TTHM concentration in a sample treated by a protocol that did not include prechlorination was less than the TTHM concentration in a prechlorinated sample treated on the same day. As can be seen in Figure 4-2, TTHM concentrations in samples not treated with either chlorine or ClO_2 (No Dis) were highly variable and at times, no differences between that treatment and prechlorination were evident. When samples were not prechlorinated, the percent reduction in TTHMs relative to the prechlorinated-sample TTHMs ranged from no reduction to 55 percent. The TTHMs in samples treated with 0.5 mg/L ClO_2 were from 6 to 26 percent lower than those in the pretreated samples. Similarly, TTHMs in samples treated with 1.0 mg/L and 2.0 mg/L ClO_2 were from 1 to 50 percent and 47 to 59 percent less, respectively, than in the prechlorinated sample.

Figure 4-3 is a plot of only the fall and winter TTHM concentrations. When only the fall and winter TTHM concentrations are plotted, the data seem to indicate a trend of lower TTHMs with an increased ClO_2 dose. However, Kruskal-Wallis multiple comparison z-value tests performed on the data showed that none of the ClO_2 treatments were statistically different from one another. The median TTHM concentrations in water pretreated with 0.5 mg/L ClO_2 and in water that was not prechlorinated were the only samples that differed statistically from those in the blank. The median TTHM concentration in water pretreated with 1.0 mg/L ClO_2 was statistically different from the median TTHM concentration in the prechlorinated sample. Finally, the median TTHM concentrations in water pretreated with 2.0 mg/L ClO_2 differed statistically from the median TTHM value in samples that were not prechlorinated and those to which no oxidant was added during the jar tests.

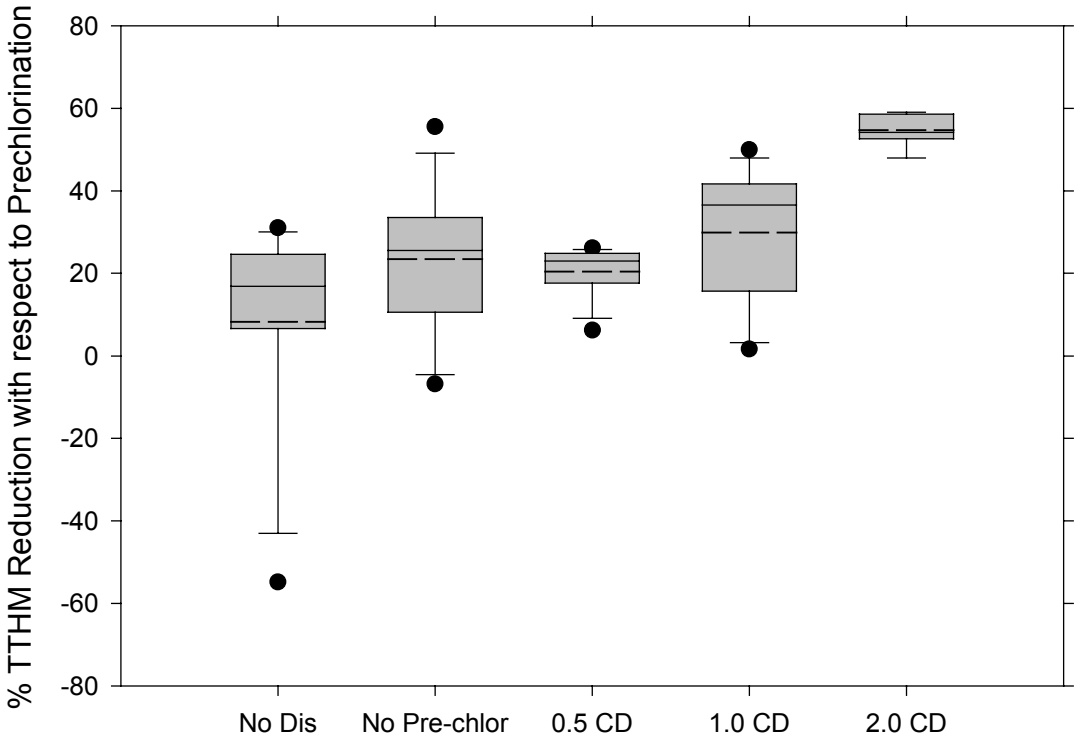


Figure 4-2: Percent Reduction in TTHM concentrations as compared to predisinfection with chlorine

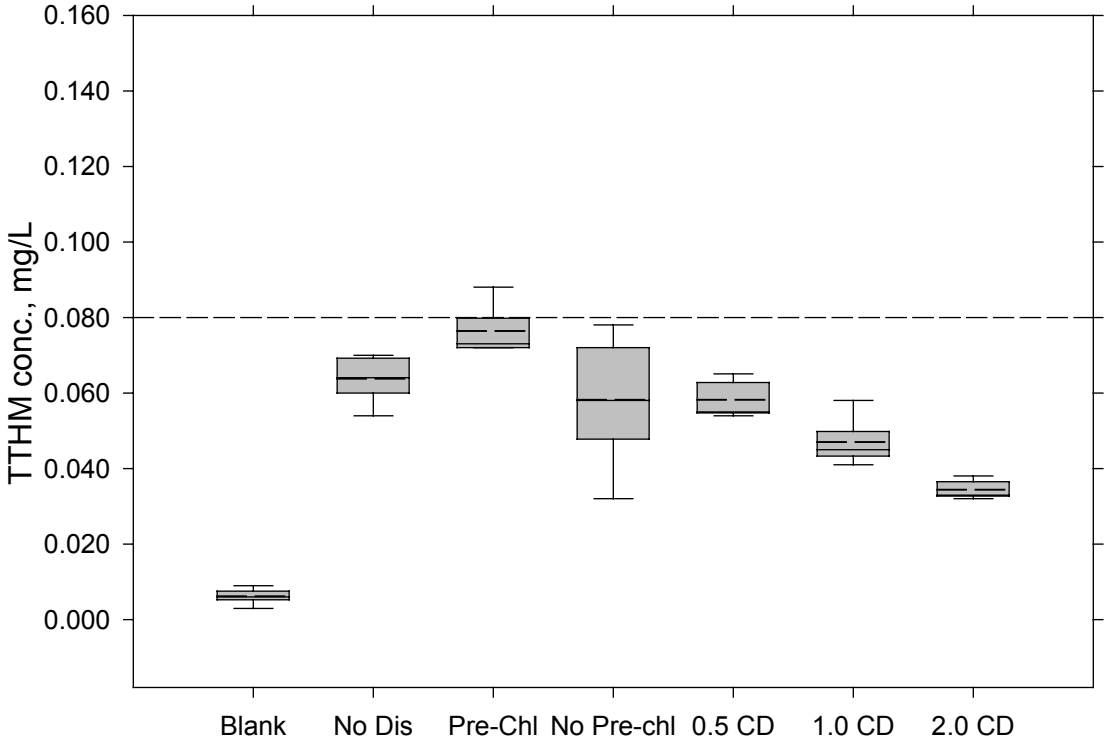


Figure 4-3: Fall and winter (October-March) TTHM concentrations

Figure 4-4 shows the relative amounts of chloroform and bromodichloromethane comprising the TTHM concentration on March 24, 2001. The results are typical of data obtained on other dates. Bromoform and chlorodibromomethane were not detected in samples collected on this date, and in all others samples, they were insignificant compared to the other THM species. The relative amounts of chloroform and bromodichloromethane in each sample did not seem to be related in any way to the various treatments applied during the jar tests.

Effects of Chlorine Dioxide on Haloacetic Acid Formation

Figure 4-5 is a box plot showing the concentrations of the five haloacetic acids (HAAs) (mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids) in samples treated according to the same protocols as previously presented. The dashed line indicates the MCL for HAA5, which is 0.060 mg/L. As can be seen, the results were much more variable than the TTHM results in Figure 4-1, and none of the treatments reduced the median HAA5 to levels below the MCL. Kruskal-Wallis multiple comparison z-value tests showed that the only significantly different medians were between the blank and all the other sample treatments except the 2.0 mg/L ClO_2 pretreatment.

A Kruskal-Wallis multiple comparison z-value test was also performed to examine the dependence of ClO_2 dose on HAA5 formation. No prechlorination was considered to be the zero dose when the statistical test was performed because of its similarity in treatment processes. As was true in the analysis of the THM data, the median of samples that were not pretreated with chlorine was selected as the basis of the comparison because the treatment those samples received was most similar to treatment the samples treated with ClO_2 received (i.e., no prechlorination but with post chlorination). The analysis found that all medians were statistically equal, and therefore, there were no significant differences between any of the HAA5 concentrations regardless of the treatment the samples received.

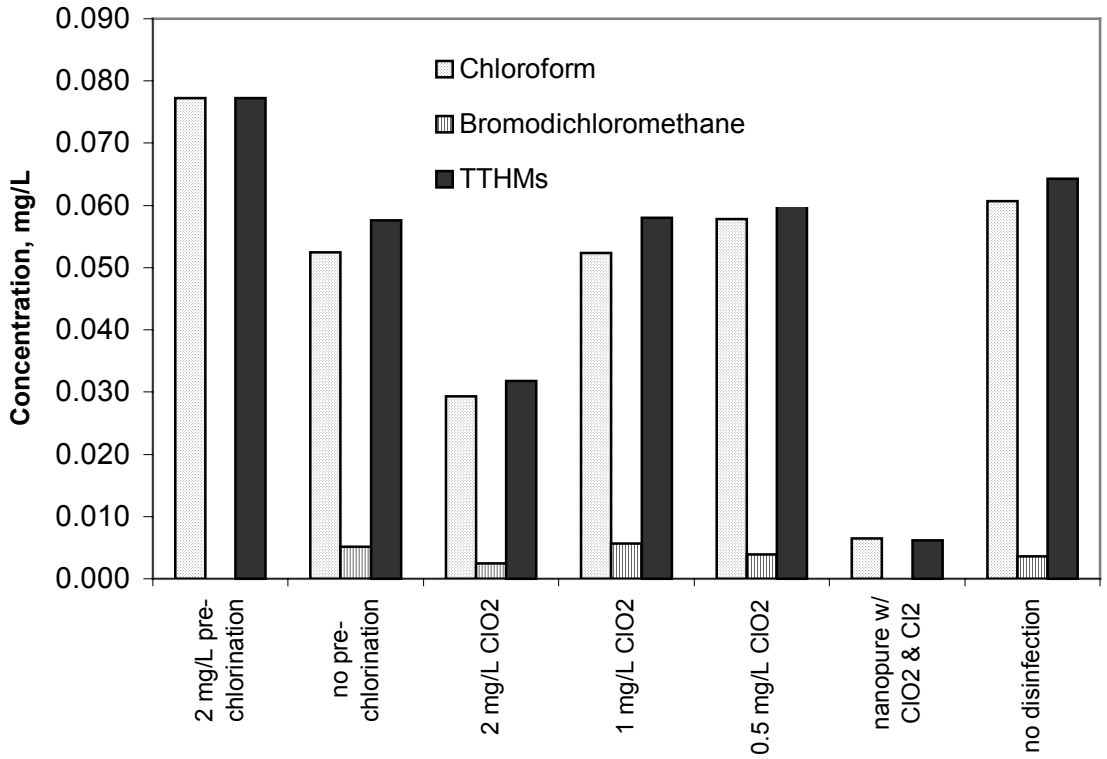


Figure 4-4: Typical distribution of TTHM compounds. These results are from jar testing on 3/24/2001.

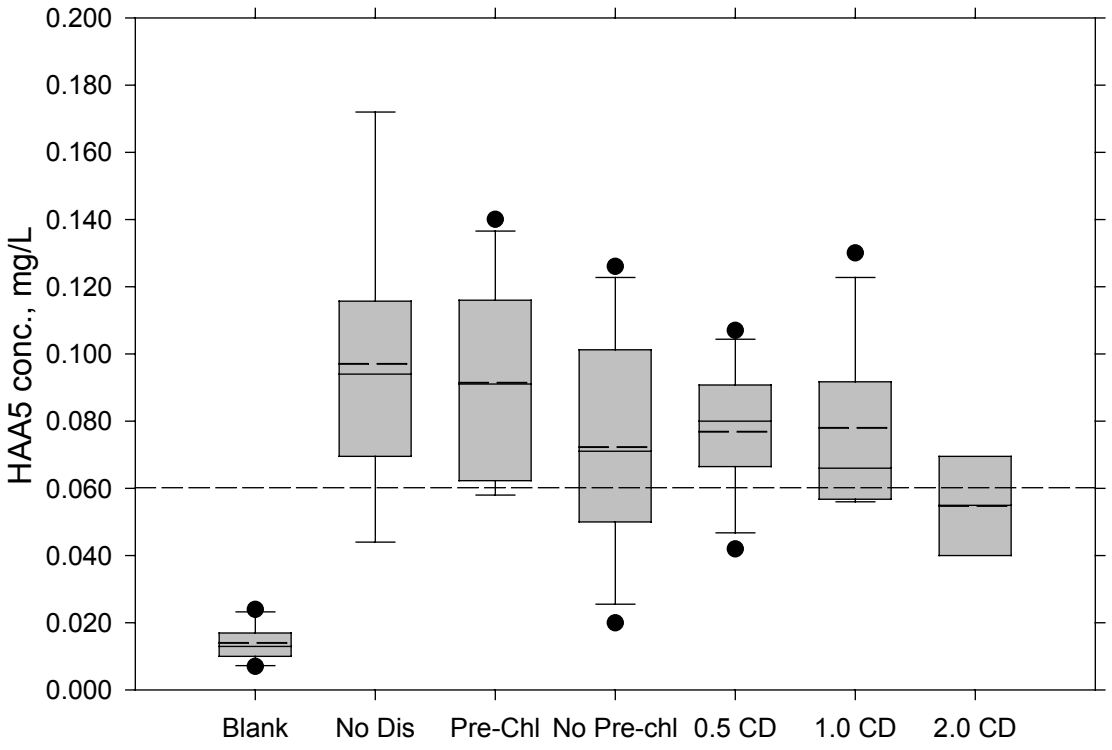


Figure 4-5: HAA5 concentrations from jar testing at the Blacksburg, Christiansburg, VPI Water Treatment Plant

Figure 4-6 is a plot of the percent reductions in HAA5 concentration that developed in the five samples that were treated by the various treatment scenarios relative to the HAA concentrations in samples that were prechlorinated as part of the jar-test procedure. When neither chlorine nor ClO_2 was added, the reductions relative to the prechlorinated sample ranged from zero to 24 percent. When samples were not prechlorinated, the percent reduction in HAA5 concentrations relative to the prechlorinated-sample HAA5 levels ranged from zero to 22 percent (with the exception of the 73 percent outlier). The HAA5 concentrations in samples treated with 0.5 mg/L ClO_2, 1.0 mg/L ClO_2, and 2.0 mg/L ClO_2 were from zero to 34 percent, zero to 35 percent, and 9 to 42 percent less, respectively, than in the prechlorinated sample.

Figure 4-7 is a box plot of the fall and winter HAA5 concentrations. The median concentrations are still close to the MCL. Recall from Figure 4-3 that the fall and winter TTHM concentrations were distributed below the MCL.

Though the USEPA only requires monitoring of the five HAAs just discussed, all nine acids were analyzed in this study. Figure 4-8 is a plot of all nine HAAs as functions of the treatment the water received. Once again, other than the blank, there were no statistical differences in median concentrations associated with the various treatments. The plot of HAA9 concentrations is very similar to that of HAA5 concentrations (Figure 4-5) because two compounds, TCAA and DCAA, made up a majority of the total HAA concentration. This fact is well illustrated by Figure 4-9 that depicts the percentage of the HAA5 concentrations that is accounted for by DCAA and TCAA.

Total Organic Carbon Concentrations in Treated Water

Figure 4-10 is a plot of seasonal variations in TOC remaining after treatment by the various treatment scenarios. As can be seen, the concentrations varied little throughout the entire study period. Additionally, other than the blank, TOC concentrations remaining after each of the treatments were not statistically different from one another (Figure 4-11).

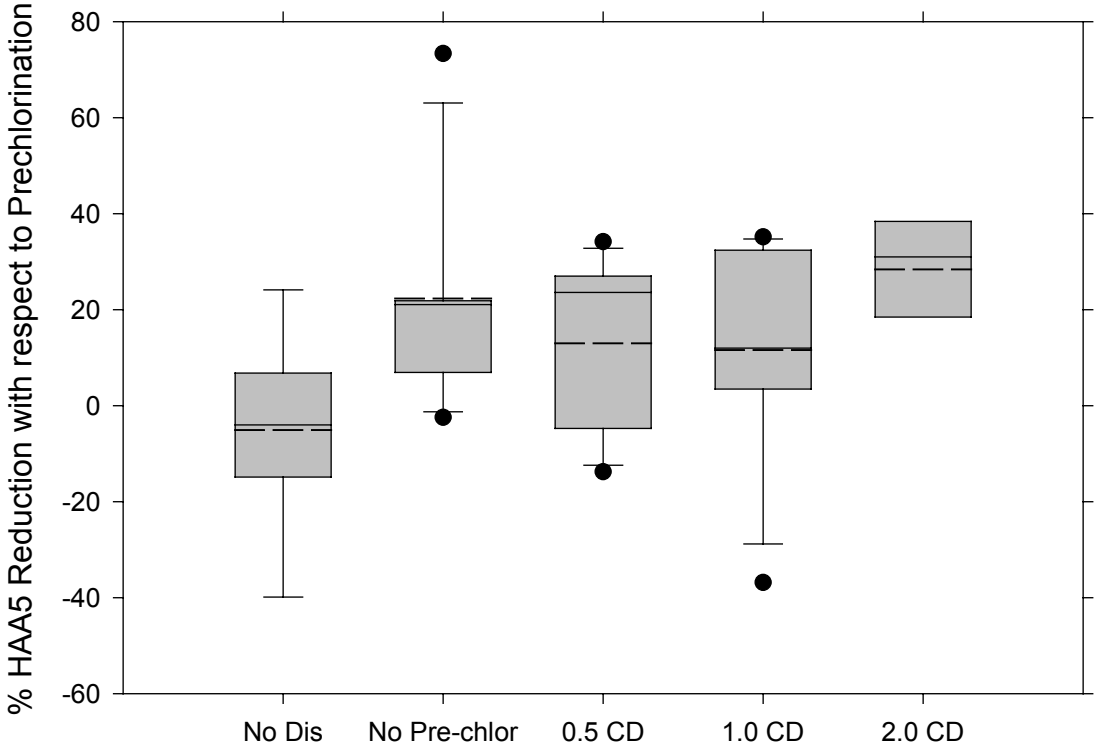


Figure 4-6: Percent reduction in HAA5 concentration as compared to predisinfection with chlorine

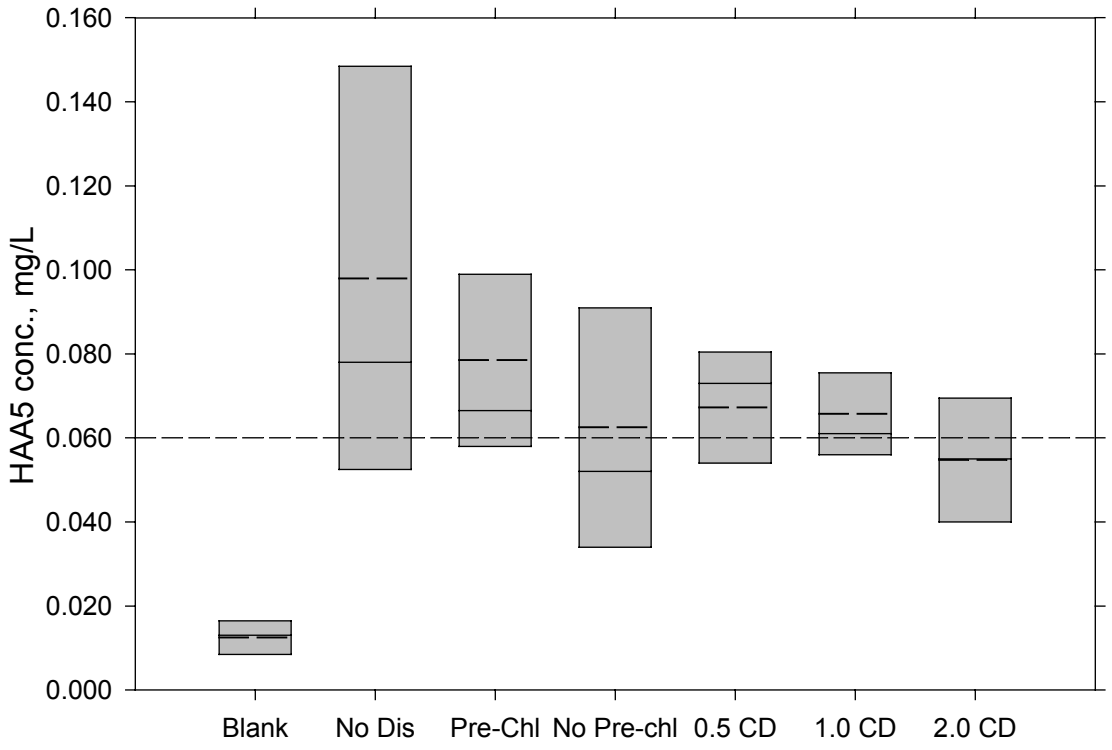


Figure 4-7: Fall and winter (October-March) HAA5 concentrations

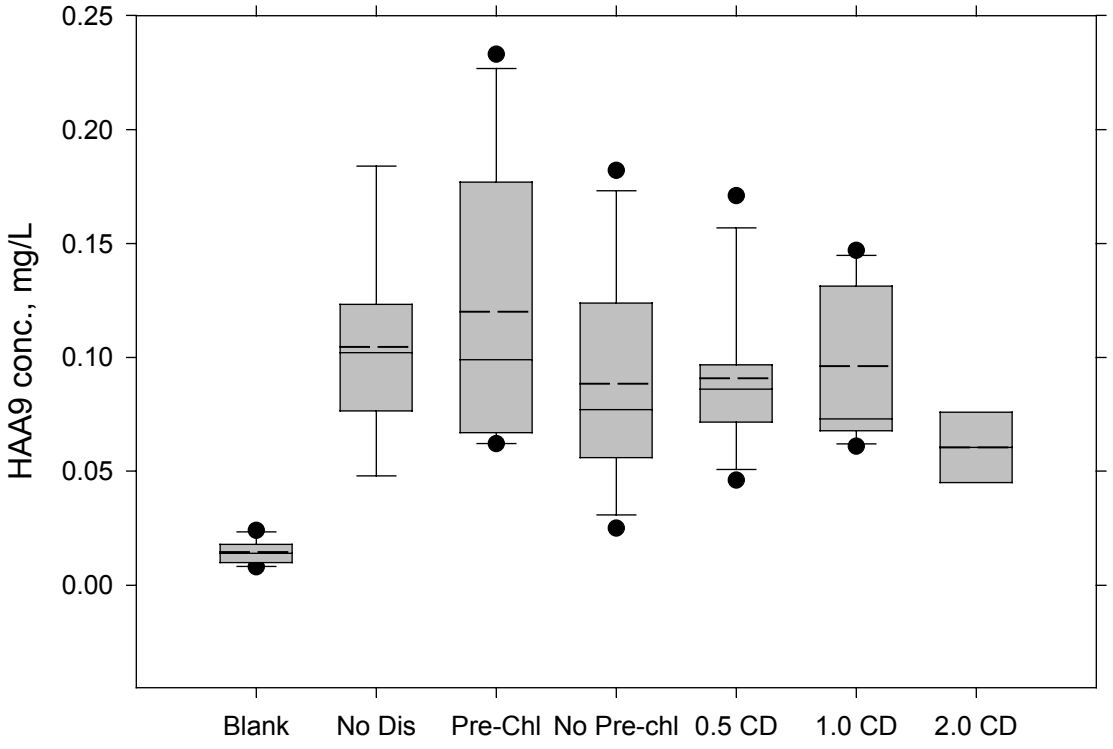


Figure 4-8: HAA9 Concentrations

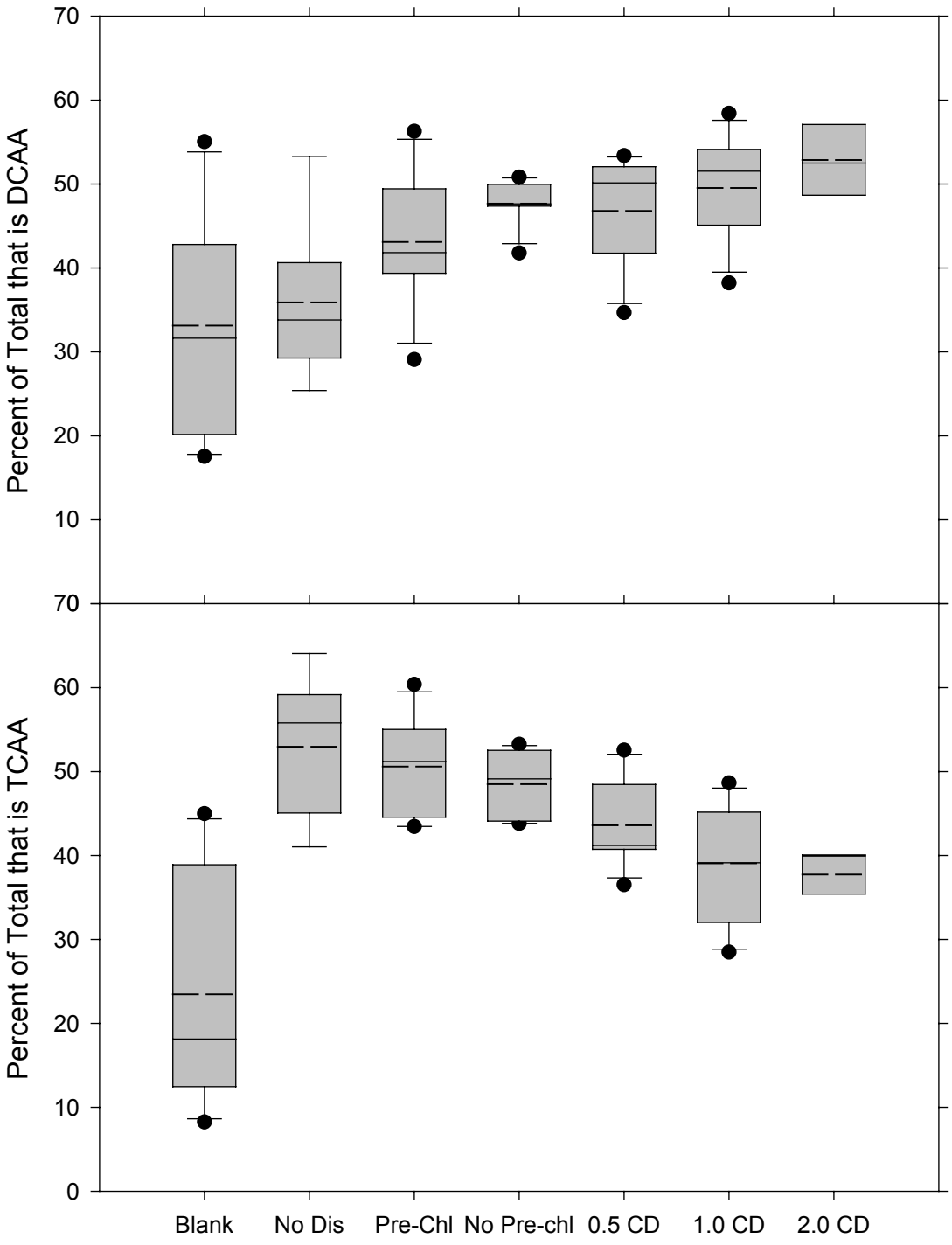


Figure 4-9: Percentage of total HAA5 comprised of DCAA and TCAA (percentages refer to actual concentrations shown in Figure 4-5).

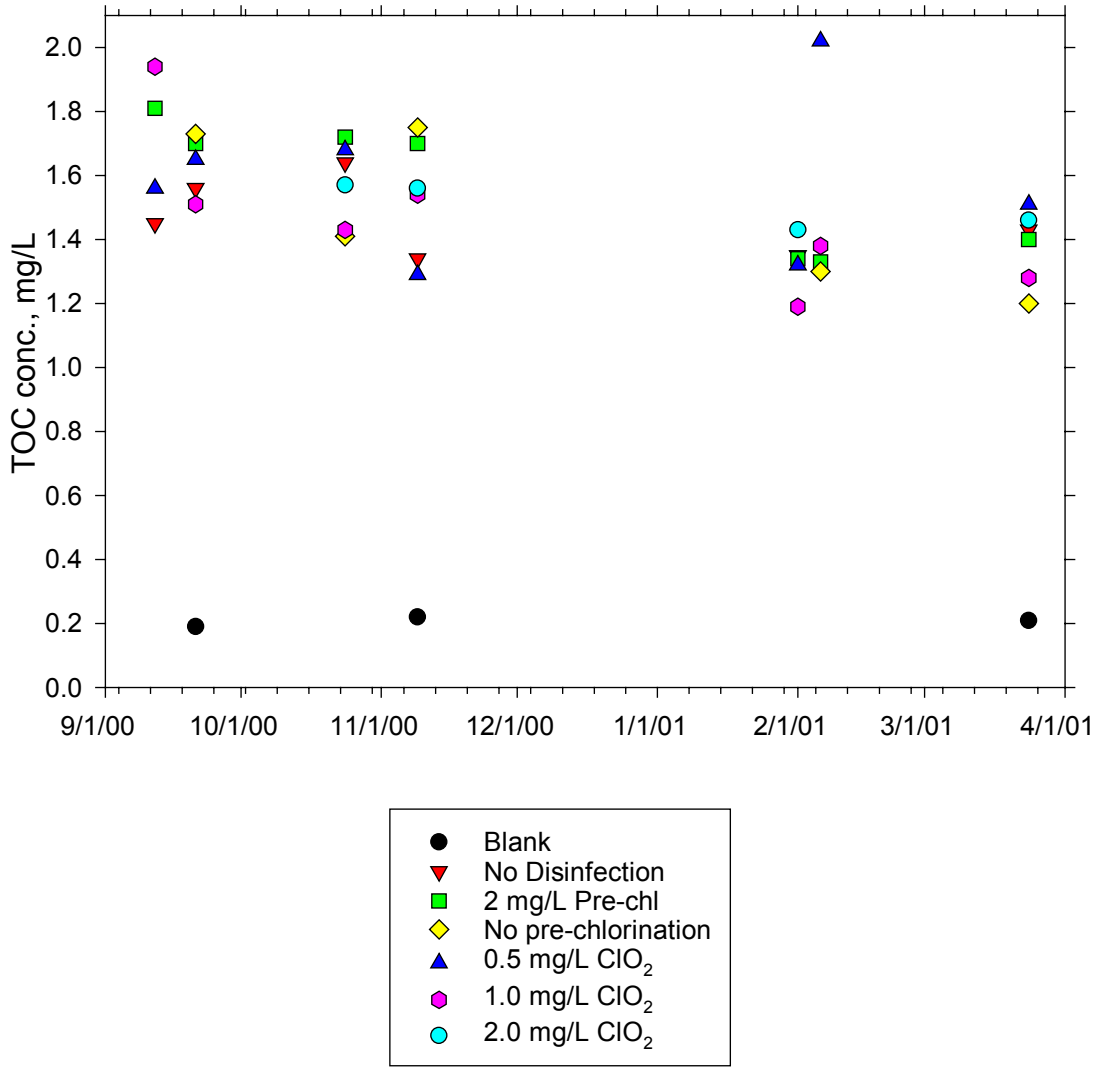


Figure 4-10: Seasonal variations in TOC measured in each jar at the conclusion of jar testing

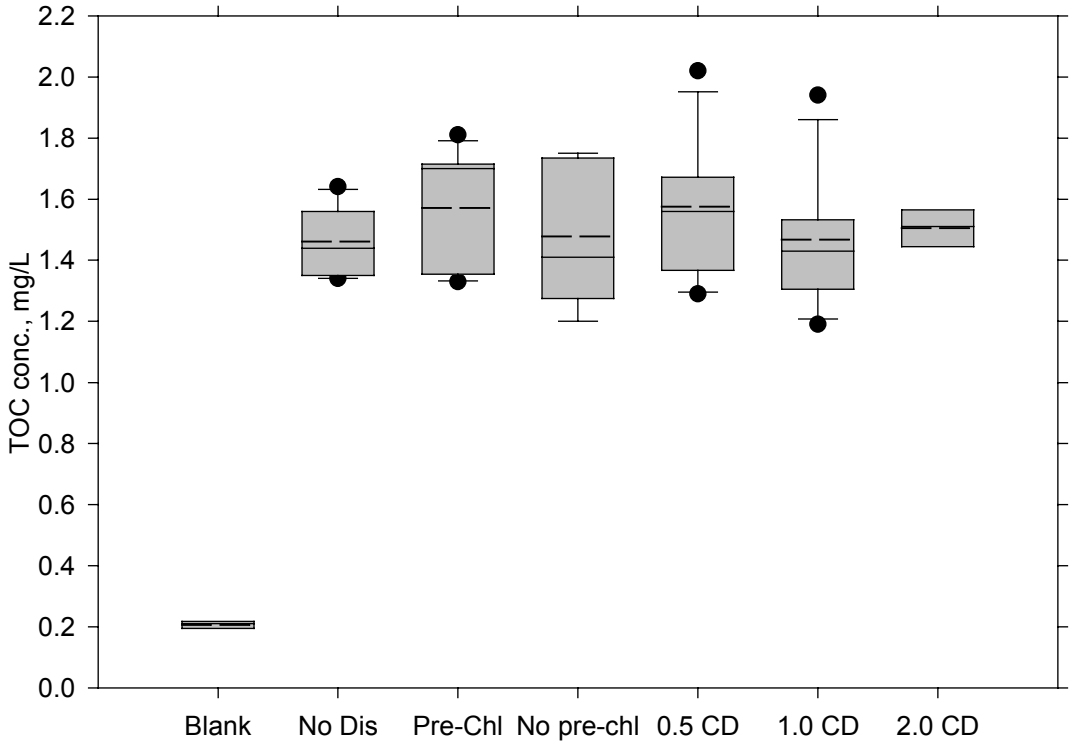
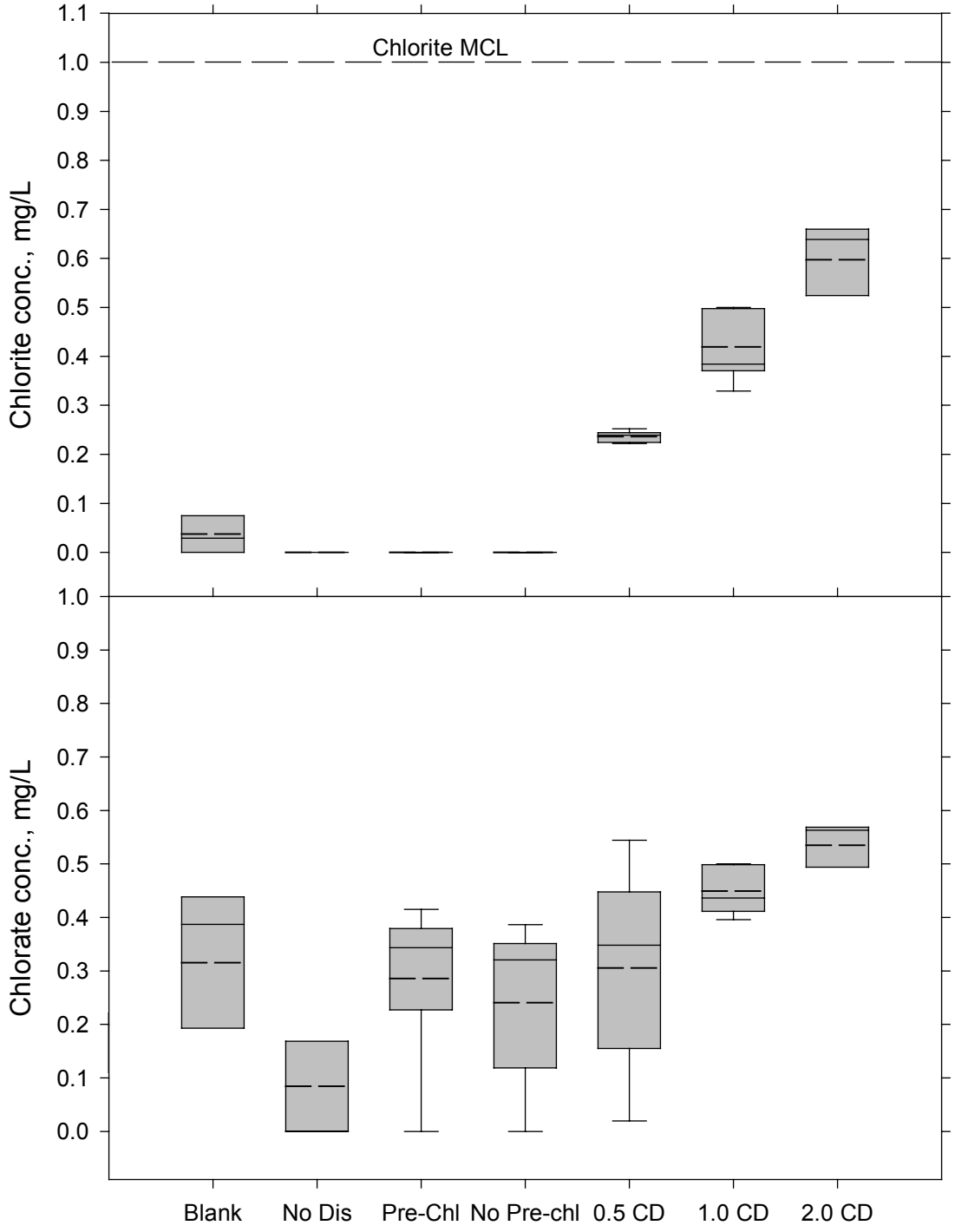


Figure 4-11: Concentration of TOC measured in each jar at conclusion of jar testing

Chlorite and Chlorate Results

Figure 4-12a shows the concentrations of ClO_2^- and ClO_3^- measured in each jar at the conclusion of jar testing. As expected, no ClO_2^- was formed in the absence of ClO_2 and the ClO_2^- concentration increased with increasing amounts of added ClO_2. Concentrations of ClO_2^- in samples treated with 0.5 mg/L ClO_2 ranged from 0.22 to 0.25 mg/L. Concentrations in samples treated with 1.0 mg/L ClO_2 were between 0.33 and 0.50 mg/L ClO_2^-, while those in samples treated with 2.0 mg/L ClO_2 ranged from 0.49 to 0.67 mg/L.

Figure 4-12b is a box plot of ClO_3^-. Chlorate formation is one of the byproducts of ClO_2 treatment and, as expected, it was present in samples at increasing concentrations as the ClO_2 dose increased. Unexpectedly, ClO_3^- also was found in samples that had not been treated with ClO_2.



Figures 4-12a (Chlorite) and 4-12b (Chlorate): Chlorite and chlorate concentrations measured at the conclusion of jar testing

CHAPTER 5.

DISCUSSION

An important factor influencing DBP formation is the type of water treatment process the source water is subjected to and the type of oxidant that is used. Various studies, including those undertaken by Stolarik and Liu (2000), Lykins and Griese (1986), Li et al. (1996), and Hulsey et al. (2000), have shown that ClO_2 will not form THMs or HAAs. Therefore, the expectation during this project was that samples of New River water that were treated with ClO_2 would produce fewer THMs and HAAs than samples that were prechlorinated and not treated with ClO_2. The expectations were not entirely met for THMs and were never met for HAA5. Statistical differences in TTHMs in prechlorinated samples and those treated with ClO_2 were not evident until the ClO_2 dose was increased to 2.0 mg/L. Griese (1991) and Hulsey et al. (2000) found that increased doses of ClO_2 lead to increasing reductions in THM formation. Hulsey et al. (2000) recorded THM reductions with ClO_2 doses as low as 0.2 mg/L. Griese (1991) saw approximately 60 percent reduction in THM concentrations when 1.0-1.5 mg/L of ClO_2 was applied as compared to prechlorinated samples. During this project, the three-day THM formation potentials after 2.0 mg/L ClO_2 treatment were from 47 percent and 59 percent lower than in samples prechlorinated instead of being dosed with ClO_2 (Figure 4-2). While no statistical differences were found between THMs in samples treated with 0.5 mg/L and 1.0 mg/L ClO_2, it should not be assumed that treatment at these dosages provided no benefits. Statistically significant differences may have become apparent had more jar tests been conducted.

This study also examined differences in THM and HAA formation in samples treated with ClO_2 and those in which chlorination was delayed until after flocculation and those to which neither chlorine nor ClO_2 was added during treatment. The addition of no oxidant is not a viable water-treatment alternative, but it was considered as a basis of comparison to HAAs and THMs that formed following the other treatments. As before, the only treatment that produced statistically different results was the 2.0 mg/L ClO_2 pretreatment (Figure 4-1). Because the THM concentrations were lower after treatment

with 2.0 mg/L ClO_2 than they were in water treated with no preoxidant this indicates that ClO_2 effectively oxidized organic material, leaving less in the water to react with chlorine when it was added later.

Unfortunately, ClO_2 pretreatment failed to reduce HAAs to levels that were statistically different than those produced by any of the other treatments except the blank, which was coagulated, flocculated and settled Nanopure® water to which 0.5 mg/L to 1.0 mg/L ClO_2 had been added as a preoxidant and 2.0 mg/L chlorine had been added as a post disinfectant (Figure 4-5). Increasing the ClO_2 dose incrementally from 0.5 mg/L to 1.0 mg/L to 2.0 mg/L did not reduce HAA concentrations to statistically different levels. In fact, the only statistically significant differences were those between HAAs that formed following the different treatments and those in the blank. Overall, the effects of ClO_2 on HAA5 results were inconclusive. In contrast, previous studies of ClO_2 impacts on HAA formation by others (Hulsey et al. 2000, Stolarik and Liu 2000, and Griese 1991) showed reductions in HAA concentrations following ClO_2 application to the water. Though, Griese (1991) only saw reductions when he increased the ClO_2 dose to 3 mg/L.

Many WTP operators are reluctant to use high doses of ClO_2 because of ClO_2^- production (chlorate is seldom, if ever, an issue). Chlorite ion concentrations in samples treated with ClO_2 were lower than expected, and none approached the 1.0 mg/L MCL (Figure 4-12a). The ranges of ClO_2^- concentrations in water following treatment with 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L were, respectively, 0.22 to 0.25 mg/L, 0.33 to 0.50 mg/L, and 0.49 to 0.67 mg/L, all of which are lower than or equal to the expected levels of from 50 percent to 70 percent of the ClO_2 dose (USEPA 1999). While the presence of ClO_2^- and ClO_3^- in samples treated with ClO_2 was expected, the appearance of ClO_3^- in other samples was not expected (Figure 4-12b). Chlorate ion can also form by reactions between ClO_2^- and chlorine and, therefore, that reaction may account for a fraction of the ClO_3^- in ClO_2-treated samples. Chlorate concentrations did increase with increasing additions of ClO_2, but it was found also in samples that had not been treated with ClO_2.

Gordon (Personal communication, July 20, 2001) attributed the unexpected appearance of ClO_3^- in samples that were not treated with ClO_2 (Figure 4-12b) to contamination of the stock chlorine solution that was used during this study and said that

it was a consequence of the preparation method. Apparently, chlorinating a 0.067 M NaOH solution until the pH is reduced to pH 7.0 assures development of ClO_3^-.

CHAPTER 6.

SUMMARY AND CONCLUSIONS

Summary

- The 3-day THM formation potentials in water pretreated with 2.0 mg/L ClO_2 were from 47 percent to 59 percent lower than those in water pretreated with chlorine (Figure 4-2). Lower ClO_2 dosages were statistically insignificant.
- The 3-day HAA5 formation potentials were not significantly reduced by ClO_2 pretreatment at any level (Figure 4-5).
- Chlorite concentrations in all samples were below the MCL of 1.0 mg/L (Figure 4-12a).
- Chlorate formed in all samples (Figure 4-12b), but some ClO_3^-, including that found in samples not treated with ClO_2, was present possibly as a result of the chlorine solution used in the jar tests.

Prompted by HAA and THM concentrations near the current MCLs, the Blacksburg, Christiansburg, VPI (BCVPI) WTP approved this project to evaluate the use of ClO_2 as an alternative preoxidant to chlorine. In many cases, ClO_2 is a viable alternative because unlike chlorine, it does not react with NOM to form DBPs (Aieta and Berg 1986). Therefore, the BCVPI Water Authority's hope was that replacing chlorine with ClO_2 as a preoxidant would aid in meeting the upcoming HAA5 MCL.

Chlorine dioxide preoxidation would be a good alternative to prechlorination for THM control at the WTP but only at doses higher than 1.0 mg/L. Statistically significant reductions in the 3-day THM formation potential did not occur until 2.0 mg/L ClO_2 was applied. At 2.0 mg/L ClO_2, neither the current MCL of 0.080 mg/L nor the anticipated Stage 2 D/DBP Rule MCL of 0.040 mg/L was exceeded. The three-day THM formation potentials of all prechlorinated samples, however, exceeded 0.040 mg/L (Table 6-1), which is the anticipated Stage 2 D/DBP Rule MCL.

Neither the Stage 1 nor the anticipated Stage 2 HAA5 MCLs were achieved by ClO_2 pretreatment during this study and, in fact, provided no apparent advantage over the current treatment practice (prechlorination) at the BCVPI Water Authority's WTP (Table

6-1). While ClO_2 pretreatment has been found to be beneficial in other locations, its future benefits for HAA control at the BCVPI WTP is in doubt. Even at the Stage 1 MCL, HAA5 concentrations were out of compliance 50 percent of the time when jars were treated with 2.0 mg/L ClO_2. Further jar testing would be beneficial to determine if increasing the ClO_2 above 3 mg/L, as was done by Griese (1991), would provide better results. Of course, at higher doses, ClO_2^- formation may present a problem, but there is some leeway as the samples from jar testing in this study never exceeded ClO_2^- concentrations of 0.67 mg/L. One additional concern when using increased ClO_2 doses is that the WTP must monitor ClO_2 concentrations leaving the plant, and the concentration cannot exceed the MRDL of 0.8 mg/L.

Conclusions

Preoxidation with ClO_2 reduced THM concentrations when the ClO_2 dose approached 2 mg/L. It produced fewer THMs than the BCVPI Water Authority's current practice of prechlorination. However, the ClO_2 doses did not alter HAA5 concentrations in such a way that statistical differences could be detected between ClO_2 pretreatment and prechlorination. Preoxidation with ClO_2 may provide other benefits, such as improved coagulation and manganese oxidation, though these effects were not investigated during this study. Finally, ClO_2^- formation is not a concern when from 0.5 mg/L to 2.0 mg/L ClO_2 is added to the New River source water.

Table 6-1: Summary of the number of times each treatment option was below the current and proposed MCLs

	Number of Times DBP Concentration was Below EPA MCLs					
MCL	No Disinfection[1]	Prechlorination[2]	No Prechlorination[3]	0.5 mg/L ClO_2[4]	1.0 mg/L ClO_2[4]	2.0 mg/L ClO_2[4]
0.080 mg/L TTHM	5/7	5/8	6/8	6/8	6/8	5/5
0.060 mg/L HAA5	1/5	2/7	3/7	1/7	3/7	2/4
0.040 mg/L TTHM	0/7	0/8	1/8	0/8	0/8	5/5
0.030 mg/L HAA5	0/5	0/7	1/7	0/7	0/7	0/4

1: No pre- or post oxidant added

2: Prechlorination with 2 mg/L chlorine; no post chlorination

3: Post chlorination only

4: Preoxidation with ClO_2; post chlorination

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APPENDIX A

Trihalomethane Results from Jar Testing

Table A-1: TTHM Results from August 10, 2000

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2.0 mg/L pre-chlorination	0.170	0.006	0.000	0.000	0.176
Jar 2	no pre-chlorination	0.108	0.007	0.000	0.000	0.116
Jar 3	1 mg/L ClO_2	0.099	0.006	0.000	0.000	0.105
Jar 4	0.5 mg/L ClO_2	0.160	0.005	0.000	0.000	0.165
Raw Water	Raw Water	0.228	0.010	0.000	0.000	0.238

Table A-2: TTHM Results from September 12, 2000

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1*-0.05	2 mg/L pre-chlorination	0.078	0.012	0.008	0.008	0.098
Jar 1	2 mg/L pre-chlorination	0.067	0.006	0.000	0.000	0.073
Jar 2	no pre-chlorination	0.064	0.008	0.001	0.000	0.073
Jar 2 (d)	no pre-chlorination	0.060	0.006	0.000	0.000	0.066
Jar 3	1 mg/L ClO_2	0.063	0.009	0.001	0.000	0.072
Jar 4	0.5 mg/L ClO_2	0.053	0.009	0.000	0.000	0.062
Jar 5	nanopure w/ ClO_2 & Cl_2	0.008	0.000	0.000	0.000	0.009
Jar 6	no disinfection	0.105	0.006	0.002	0.000	0.113

* = sample + 0.05 mg/L Standard (d) = duplicate sample collected in different vial

Table A-3: TTHM Results from September 21, 2000

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1*-0.05	2 mg/L pre-chlorination	0.092	0.012	0.000	0.002	0.103
Jar 1	2 mg/L pre-chlorination	0.115	0.006	0.000	0.000	0.122
Jar 2	no pre-chlorination	0.075	0.007	0.000	0.000	0.082
Jar 2 (d)	no pre-chlorination	0.080	0.009	0.000	0.000	0.089
Jar 3	1 mg/L ClO_2	0.106	0.008	0.000	0.000	0.113
Jar 4	0.5 mg/L ClO_2	0.087	0.008	0.000	0.000	0.095
Jar 5	nanopure w/ ClO_2 & Cl_2	0.007	0.000	0.000	0.000	0.007
Jar 5*-0.05	nanopure w/ ClO_2 & Cl_2	0.010	0.004	0.001	0.005	0.014
Jar 6	no disinfection	0.080	0.004	0.000	0.000	0.084

* = sample + 0.05 mg/L Standard (d) = duplicate sample collected in different vial

Table A-4: TTHM Results from October 24, 2000

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2 mg/L pre-chlorination	0.075	0.006	0.002	0.003	0.088
Jar 1*	2 mg/L pre-chlorination	0.069	0.001	0.000	0.000	0.070
Jar 2	no pre-chlorination	0.063	0.006	0.001	0.000	0.070
Jar 3	2 mg/L ClO_2	0.031	0.005	0.001	0.000	0.036
Jar 4	1 mg/L ClO_2	0.038	0.005	0.001	0.000	0.044
Jar 4 d.	1 mg/L ClO_2	0.038	0.006	0.001	0.000	0.045
Jar 5	0.5 mg/L ClO_2	0.057	0.007	0.000	0.000	0.065
Jar 6	nanopure w/ ClO_2 & Cl_2	0.006	0.000	0.000	0.000	0.006
Jar 7	no disinfection	0.063	0.007	0.000	0.000	0.070

* = sample + 0.05 mg/L Standard d = duplicate collected in separate vial

Table A-5: TTHM Results from November 9, 2000

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2 mg/L pre-chlorination	0.067	0.006	0.000	0.000	0.073
Jar 1*	2 mg/L pre-chlorination	0.068	0.007	0.000	0.000	0.075
Jar 2	no pre-chlorination	0.071	0.007	0.000	0.000	0.078
Jar 3	2 mg/L ClO_2	0.034	0.005	0.000	0.000	0.038
Jar 4	1 mg/L ClO_2	0.040	0.006	0.000	0.000	0.045
Jar 4 d.	1 mg/L ClO_2	0.041	0.006	0.000	0.000	0.047
Jar 5	0.5 mg/L ClO_2	0.049	0.006	0.000	0.000	0.055
Jar 6	nanopure w/ ClO_2 & Cl_2	0.003	0.000	0.000	0.000	0.003
Jar 7	no disinfection	0.048	0.006	0.000	0.000	0.054

* = sample + 0.05 mg/L Standard (already subtracted out) d = duplicate collected in separate vial

Table A-6: TTHM Results from February 1, 2001

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2 mg/L pre-chlorination	0.064	0.006	0.002	0.000	0.072
Jar 1*-0.02	2 mg/L pre-chlorination	0.070	0.005	0.003	0.000	0.078
Jar 2	no pre-chlorination	0.046	0.006	0.000	0.000	0.053
Jar 3	2 mg/L ClO_2	0.027	0.005	0.001	0.000	0.033
Jar 4	1 mg/L ClO_2	0.034	0.006	0.001	0.000	0.041
Jar 4 (d)	1 mg/L ClO_2	0.035	0.006	0.001	0.004	0.045
Jar 5	0.5 mg/L ClO_2	0.041	0.008	0.001	0.004	0.054
Jar 6	nanopure w/ ClO_2 & Cl_2	0.007	0.002	0.000	0.000	0.009
Jar 7	no disinfection	0.055	0.007	0.000	0.000	0.062

* = sample + 0.02 mg/L Standard d = duplicate collected in separate vial

Table A-7: TTHM Results from February 6, 2001

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2 mg/L pre-chlorination	0.064	0.007	0.000	0.000	0.072
Jar 1*-0.02	2 mg/L pre-chlorination	0.065	0.005	0.000	0.001	0.071
Jar 2	no pre-chlorination	0.027	0.004	0.000	0.000	0.032
Jar 3	2 mg/L ClO_2	0.027	0.005	0.001	0.000	0.033
Jar 4	1 mg/L ClO_2	0.040	0.006	0.001	0.000	0.047
Jar 4 (d)	1 mg/L ClO_2	0.040	0.007	0.001	0.000	0.047
Jar 5	0.5 mg/L ClO_2	0.048	0.007	0.001	0.000	0.055
Jar 6	nanopure w/ ClO_2 & Cl_2	0.004	0.002	0.000	0.000	0.007
Jar 7	no disinfection	0.061	0.007	0.001	0.000	0.069

* = sample + 0.02 mg/L Standard d = duplicate collected in separate vial

Table A-8: TTHM Results from March 24, 2001

		Concentration, mg/L				
Jar Number	**Description**	**Chloroform**	**Bromodichloromethane**	**Chlorodibromomethane**	**Bromoform**	**TTHMS**
Jar 1	2 mg/L pre-chlorination	0.077	0.000	0.000	0.000	0.077
Jar 1*	2 mg/L pre-chlorination	0.059	0.003	0.000	0.000	0.061
Jar 2	no pre-chlorination	0.052	0.005	0.000	0.000	0.058
Jar 3	2 mg/L ClO_2	0.029	0.003	0.000	0.000	0.032
Jar 4	1 mg/L ClO_2	0.052	0.006	0.000	0.000	0.058
Jar 4 (d)	1 mg/L ClO_2	0.062	0.004	0.000	0.000	0.066
Jar 5	0.5 mg/L ClO_2	0.058	0.004	0.000	0.000	0.062
Jar 6	nanopure w/ ClO_2 & Cl_2	0.006	0.000	0.000	0.000	0.006
Jar 7	no disinfection	0.061	0.004	0.000	0.000	0.064

* = sample - 0.02 mg/L Standard d = duplicate collected in separate vial

APPENDIX B

Haloacetic Acid Results from Jar Testing

Table B-1: HAA Results from August 10, 2000

		Concentration, mg/L										
Jar Number	**Description**	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	HAA 5	HAA 9
Jar 1	2.0 mg/L pre-chlorination	0.008	0.005	0.061	0.067	0.007	0.013	0.000	0.000	0.074	0.140	0.233
Jar 2	no pre-chlorination	0.006	0.001	0.056	0.048	0.004	0.006	0.000	0.000	0.063	0.110	0.182
Jar 3	1 mg/L ClO_2	0.005	0.002	0.050	0.037	0.007	0.006	0.000	0.000	0.041	0.094	0.147
Jar 4	0.5 mg/L ClO_2	0.005	0.001	0.057	0.044	0.007	0.005	0.000	0.000	0.052	0.107	0.171
Raw water*	Raw Water	0.005	0.000	0.073	0.072	0.003	0.007	0.000	0.000	0.030	0.150	0.189

*no coagulant added

Table B-2: HAA Results from September 12, 2000

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA5**	**HAA9**
Jar 1	2 mg/L pre-chlorination	0.003	0.002	0.047	0.040	0.007	0.003	0.000	0.000	0.000	0.091	0.102
Jar 2	no pre-chlorination	0.003	0.002	0.034	0.031	0.004	0.002	0.000	0.000	0.000	0.071	0.077
Jar 3	1 mg/L ClO_2	0.006	0.004	0.032	0.017	0.005	0.002	0.000	0.000	0.000	0.059	0.066
Jar 4	0.5 mg/L ClO_2	0.004	0.004	0.032	0.028	0.005	0.003	0.000	0.000	0.000	0.068	0.076
Jar 5	nanopure w/ ClO_2 & Cl_2	0.006	0.011	0.005	0.002	0.000	0.000	0.000	0.000	0.000	0.024	0.024
Jar 6	no disinfection	0.004	0.005	0.025	0.040	0.002	0.003	0.024	0.000	0.000	0.097	0.103

Table B-3: HAA Results from September 21, 2000

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA5**	**HAA9**
Jar 1	2 mg/L pre-chlorination	0.003	0.000	0.039	0.053	0.002	0.001	0.000	0.000	0.000	0.095	0.099
Jar 2	no pre-chlorination	0.003	0.001	0.038	0.033	0.003	0.003	0.000	0.000	0.000	0.075	0.081
Jar 3	1 mg/L ClO_2	0.004	0.000	0.067	0.059	0.004	0.002	0.000	0.000	0.000	0.130	0.136
Jar 4	0.5 mg/L ClO_2	0.003	0.000	0.049	0.041	0.003	0.003	0.000	0.000	0.000	0.094	0.100
Jar 5	nanopure w/ ClO_2 & Cl_2	0.004	0.003	0.002	0.001	0.000	0.000	0.000	0.000	0.000	0.010	0.010
Jar 6	no disinfection	0.004	0.003	0.034	0.053	0.004	0.004	0.000	0.000	0.000	0.094	0.102

Table B-4: HAA Results from October 24, 2000

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA 5**	**HAA 9**
Jar 1	2 mg/L pre-chlorination	0.000	0.000	0.048	0.074	0.001	0.026	0.001	0.026	0.026	0.123	0.202
Jar 2	no pre-chlorination	0.006	0.000	0.053	0.067	0.006	0.006	0.000	0.000	0.000	0.126	0.138
Jar 3	2 mg/L ClO_2	0.007	0.001	0.035	0.029	0.003	0.004	0.000	0.000	0.000	0.071	0.078
Jar 4	1 mg/L ClO_2	0.009	0.000	0.049	0.026	0.026	0.006	0.000	0.000	0.000	0.085	0.117
Jar 4 d.	1 mg/L ClO_2	0.007	0.000	0.033	0.033	0.007	0.004	0.000	0.000	0.000	0.073	0.085
Jar 5	0.5 mg/L ClO_2	0.007	0.000	0.041	0.033	0.002	0.004	0.000	0.000	0.000	0.081	0.087
Jar 6	nanopure w/ ClO_2 & Cl_2	0.007	0.000	0.007	0.002	0.001	0.000	0.000	0.000	0.000	0.017	0.018
Jar 7	no disinfection	0.009	0.001	0.053	0.110	0.004	0.008	0.000	0.000	0.000	0.172	0.184

Table B-5: HAA Results from February 1, 2001

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA 5**	**HAA 9**
Jar 1	2 mg/L pre-chlorination	0.000	0.000	0.032	0.025	0.003	0.002	0.000	0.000	0.000	0.058	0.063
Jar 2	no pre-chlorination	0.000	0.000	0.027	0.029	0.003	0.003	0.000	0.000	0.000	0.056	0.062
Jar 3	2 mg/L ClO_2	0.000	0.000	0.023	0.015	0.003	0.001	0.000	0.000	0.000	0.038	0.043
Jar 4	1 mg/L ClO_2	0.009	0.000	0.026	0.021	0.003	0.002	0.000	0.000	0.000	0.056	0.061
Jar 5	0.5 mg/L ClO_2	0.005	0.000	0.021	0.015	0.003	0.001	0.000	0.000	0.000	0.042	0.046
Jar 6	nanopure w/ ClO_2 & Cl_2	0.000	0.000	0.004	0.003	0.001	0.000	0.000	0.000	0.000	0.007	0.008
Jar 7	no disinfection	0.000	0.000	0.023	0.020	0.003	0.002	0.000	0.000	0.000	0.044	0.048

Table B-6: HAA Results from February 6, 2001

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA 5**	**HAA 9**
Jar 1	2 mg/L pre-chlorination	0.015	0.000	0.022	0.038	0.004	0.000	0.000	0.000	0.000	0.075	0.079
Jar 2	no pre-chlorination	0.000	0.000	0.010	0.011	0.003	0.001	0.000	0.000	0.000	0.020	0.025
Jar 3	2 mg/L ClO_2	0.009	0.000	0.032	0.027	0.006	0.000	0.000	0.000	0.000	0.068	0.074
Jar 4	1 mg/L ClO_2	0.012	0.000	0.025	0.029	0.006	0.002	0.000	0.000	0.000	0.066	0.073
Jar 5	0.5 mg/L ClO_2	0.010	0.000	0.028	0.042	0.003	0.002	0.000	0.000	0.000	0.080	0.086
Jar 6	nanopure w/ ClO_2 & Cl_2	0.008	0.000	0.004	0.004	0.002	0.000	0.000	0.000	0.000	0.016	0.017
Jar 7	no disinfection	0.007	0.000	0.026	0.045	0.006	0.002	0.000	0.000	0.000	0.078	0.086

Table B-7: HAA Results from March 24, 2001

		Concentration, mg/L										
Jar Number	**Description**	**MCAA**	**MBAA**	**DCAA**	**TCAA**	**BCAA**	**BDCAA**	**DBAA**	**CDBAA**	**TBAA**	**HAA 5**	**HAA 9**
Jar 1	2 mg/L pre-chlorination	0.003	0.000	0.024	0.030	0.002	0.002	0.000	0.000	0.000	0.058	0.062
Jar 2	no pre-chlorination	0.001	0.000	0.023	0.023	0.005	0.002	0.000	0.000	0.000	0.048	0.054
Jar 3	2 mg/L ClO_2	0.005	0.000	0.023	0.013	0.003	0.001	0.000	0.000	0.000	0.042	0.047
Jar 4	1 mg/L ClO_2	0.003	0.000	0.025	0.027	0.015	0.002	0.000	0.000	0.000	0.056	0.073
Jar 5	0.5 mg/L ClO_2	0.006	0.000	0.027	0.033	0.001	0.002	0.000	0.000	0.000	0.066	0.070
Jar 6	nanopure w/ ClO_2 & Cl_2	0.003	0.000	0.004	0.004	0.000	0.000	0.000	0.000	0.000	0.010	0.011
Jar 7	no disinfection	Not Reported										

APPENDIX C

Chlorite Results from Jar Testing

Table C-1: Chlorite Results, mg/L

	Jar Description						
Jar Test Date	**Nanopure**	**No Disinfection**	**2 mg/L Pre-chlor**	**No Pre-chlor**	**0.5 mg/L ClO_2**	**1.0 mg/L ClO_2**	**2.0 mg/L ClO_2**
8/10/2000	---	---	0	0	0.242	0.497	---
9/12/00	---	---	---	---	---	---	---
9/21/2000	0.091	0	0	0	0.239	0.500	---
10/24/2000	---	---	---	---	---	---	---
11/9/2000	---	---	---	---	---	---	---
2/1/2001	0	0	0	0	0.225	0.384	0.667
2/6/2001	0.059	0	0	0	0.252	0.385	0.639
3/24/2001	0	0	0	0	0.222	0.329	0.486
"---" denotes no results reported							
Average	0.037	0	0	0	0.236	0.419	0.597
Median	0.029	0	0	0	0.239	0.385	0.639

APPENDIX D

Chlorate Results from Jar Testing

Table D-1: Chlorate Results, mg/L

	Jar Description						
Jar Test Date	**Nanopure**	**No Disinfection**	**2 mg/L Pre-chlor**	**No Pre-chlor**	**0.5 mg/L ClO_2**	**1.0 mg/L ClO_2**	**2.0 mg/L ClO_2**
8/10/2000	---	---	0	0	0.2	0.5	---
9/12/00	---	---	---	---	---	---	---
9/21/2000	0.386	0	0.303	0.321	0.020	0.396	---
10/24/2000	---	---	---	---	---	---	---
11/9/2000	---	---	---	---	---	---	---
2/1/2001	0	0.337	0.343	0.339	0.348	0.437	0.563
2/6/2001	0.388	0	0.415	0.387	0.416	0.498	0.570
3/24/2001	0.488	0	0.367	0.159	0.545	0.417	0.471

"---" denotes no results reported

Average	0.316	0.084	0.286	0.241	0.306	0.449	0.535
Median	0.387	0	0.343	0.321	0.348	0.437	0.563

APPENDIX E

Total Organic Carbon Results from Jar Testing

Table E-1: TOC Results, mg/L

	Jar Description						
Jar Test Date	**Nanopure**	**No Disinfection**	**2 mg/L Pre-chlor**	**No Pre-chlor**	**0.5 mg/L ClO_2**	**1.0 mg/L ClO_2**	**2.0 mg/L ClO_2**
8/10/2000	---	---	---	---	---	---	---
9/12/2000	---	1.45	1.81	---	1.56	1.94	---
9/21/2000	0.19	1.56	1.70	1.73	1.65	1.51	---
10/24/2000	---	1.64	1.72	1.41	1.68	1.43	1.57
11/9/2000	0.22	1.34	1.70	1.75	1.29	1.54	1.56
2/1/2001	3.64	1.35	1.34	2.81	1.32	1.19	1.43
2/6/2001	1.43	2.89	1.33	1.30	2.02	1.38	3.17
3/24/2001	0.21	1.43	1.40	1.20	1.51	1.28	1.46
Average	1.14	1.67	1.57	1.70	1.58	1.47	1.84
Median	0.22	1.45	1.70	1.57	1.56	1.43	1.56

"---" denotes no results reported

APPENDIX F

Raw water Quality Measurements

Table F-1: Water Quality parameters of untreated New River water and coagulant dose applied on day of jar tests

Jar Test Date	Temperature, deg F	Alkalinity, mg/L	Turbidity, NTU	Hardness, mg/L	pH	Coagulant Dose, mg/L
8/10/2000	78	52	7.9	56	7.6	26
9/12/2000	78	50	3.7	54	7.4	45
9/21/2000	76	52	2.0	55	7.3	24
10/24/2000	68	56	1.8	60	8.3	18
11/9/2000	66	55	2.6	60	7.4	18
2/1/2001	48	46	4.0	52	7.4	25
2/6/2001	45	50	2.5	54	8.2	25
3/24/2001	50	45	5.6	46	7.3	36
Average	64	51	3.8	55	7.6	27
Median	67	51	3.2	55	7.4	25

APPENDIX G

Statistical Analyses of THMs and HAAs

Table G-1: Statistical Output for TTHMs

Analysis of Variance Report

Page/Date/Time	1 7/22/2001 2:13:30 PM
Database	D:\tthm kruskal wallis.S0
Response	THMs

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: Treatment	6	3.673418E-02	6.122364E-03	8.37	0.000004*	0.999813
S(A)	44	3.216684E-02	7.310645E-04			
Total (Adjusted)	50	6.890102E-02				
Total	51					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks

Hypotheses

Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	6	30.79535	0.000028	Reject Ho
Corrected for Ties	6	30.8079	0.000028	Reject Ho

Number Sets of Ties	9
Multiplicity Factor	54

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0.5	8	237.00	29.63	0.7511	0.0618
1	8	210.50	26.31	0.0648	0.0525
2	5	54.50	10.90	-2.3915	0.033
nanopure	7	28.00	4.00	-4.2154	0.007
no_disin	7	223.50	31.93	1.1360	0.069
no_pre_chlor	8	246.50	30.81	0.9972	0.0713
pre_chlor	8	326.00	40.75	3.0563	0.07505

Table G-1 continued

Analysis of Variance Report

Page/Date/Time 2 7/22/2001 2:13:30 PM
Database D:\tthm kruskal wallis.S0
Response THMs

Kruskal-Wallis Multiple-Comparison Z-Value Test

THMs	0.5	1	2	nanopure	no_disin
0.5	0.0000	0.4457	2.2099	3.3312	0.2995
1	0.4457	0.0000	1.8190	2.9006	0.7301
2	2.2099	1.8190	0.0000	0.7928	2.4163
nanopure	3.3312	2.9006	0.7928	0.0000	3.5154
no_disin	0.2995	0.7301	2.4163	3.5154	0.0000
no_pre_chlor	0.1598	0.6055	2.3500	3.4856	0.1451
pre_chlor	1.4970	1.9427	3.5229	4.7775	1.1468

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Kruskal-Wallis Multiple-Comparison Z-Value Test

THMs	no_pre_chlor	pre_chlor
0.5	0.1598	1.4970
1	0.6055	1.9427
2	2.3500	3.5229
nanopure	3.4856	4.7775
no_disin	0.1451	1.1468
no_pre_chlor	0.0000	1.3372
pre_chlor	1.3372	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Table G-2: Statistical Output for Fall and Winter TTHMs

Analysis of Variance Report

Page/Date/Time 1 7/22/2001 5:10:42 PM
Database C:\Program Files\NCSS97\Report\partialthms.S0
Response C2

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: C1	6	1.593937E-02	2.656562E-03	38.99	0.000000*	1.000000
S(A)	28	0.0019076	6.812857E-05			
Total (Adjusted)	34	1.784697E-02				
Total	35					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks

Hypotheses

Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	6	27.55619	0.000114	Reject Ho
Corrected for Ties	6	27.59097	0.000112	Reject Ho

Number Sets of Ties	9
Multiplicity Factor	54

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0.5 CD	5	106.00	21.20	0.7542	0.055
1.0 CD	5	75.50	15.10	-0.6835	0.045
2.0 CD	5	44.50	8.90	-2.1449	0.033
No Pre-chlor	5	106.50	21.30	0.7778	0.058
nano	5	15.00	3.00	-3.5355	0.006
no dis	5	121.50	24.30	1.4849	0.064
pre chlor	5	161.00	32.20	3.3470	0.073

Table G-2 continued

Analysis of Variance Report

Page/Date/Time 2 7/22/2001 5:10:42 PM
Database C:\Program Files\NCSS97\Report\partialthms.S0
Response C2

Kruskal-Wallis Multiple-Comparison Z-Value Test

C2	0.5 CD	1.0 CD	2.0 CD	No Pre-chlor	nano
0.5 CD	0.0000	0.9418	1.8991	0.0154	2.8101
1.0 CD	0.9418	0.0000	0.9573	0.9573	1.8682
2.0 CD	1.8991	0.9573	0.0000	1.9146	0.9110
No Pre-chlor	0.0154	0.9573	1.9146	0.0000	2.8255
nano	2.8101	1.8682	0.9110	2.8255	0.0000
no dis	0.4786	1.4205	2.3778	0.4632	3.2887
pre chlor	1.6984	2.6403	3.5975	1.6830	4.5085

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Kruskal-Wallis Multiple-Comparison Z-Value Test

C2	no dis	pre chlor
0.5 CD	0.4786	1.6984
1.0 CD	1.4205	2.6403
2.0 CD	2.3778	3.5975
No Pre-chlor	0.4632	1.6830
nano	3.2887	4.5085
no dis	0.0000	1.2198
pre chlor	1.2198	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Table G-3: Statistical Output for ClO_2 dose comparisons of TTHMs

Analysis of Variance Report

Page/Date/Time	1 7/22/2001 5:26:34 PM
Database	C:\Program Files\NCSS97\Report\DoseTTHM.S0
Response	TTHM

Tests of Assumptions Section

Assumption	Test Value	Prob Level	Decision (0.05)
Skewness Normality of Residuals	3.2775	0.001047	Reject
Kurtosis Normality of Residuals	2.4811	0.013098	Reject
Omnibus Normality of Residuals	16.8979	0.000214	Reject
Modified-Levene Equal-Variance Test	0.8161	0.497141	Accept

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: C1	3	5.950875E-03	1.983625E-03	2.46	0.086164	0.541585
S(A)	25	2.016106E-02	8.064426E-04			
Total (Adjusted)	28	2.611194E-02				
Total	29					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks

Hypotheses

Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	3	10.85285	0.012549	Reject Ho
Corrected for Ties	3	10.86355	0.012487	Reject Ho

Number Sets of Ties	4
Multiplicity Factor	24

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0	8	145.00	18.13	1.2199	0.0713
0.5	8	147.00	18.38	1.3175	0.0618
1	8	123.50	15.44	0.1708	0.0525
2	5	19.50	3.90	-3.2043	0.033

Table G-3 continued

Analysis of Variance Report

Page/Date/Time 2 7/22/2001 5:26:34 PM
Database C:\Program Files\NCSS97\Report\DoseTTHM.S0
Response TTHM

Kruskal-Wallis Multiple-Comparison Z-Value Test

TTHM	0	0.5	1	2
0	0.0000	0.0588	0.6316	2.9319
0.5	0.0588	0.0000	0.6903	2.9835
1	0.6316	0.6903	0.0000	2.3780
2	2.9319	2.9835	2.3780	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 2.6383

Table G-4: Statistical Output for HAA5

Analysis of Variance Report

Page/Date/Time	1 7/22/2001 5:37:15 PM
Database	C:\Program Files\NCSS97\Report\HAA5stats.S0
Response	HAA5

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: C1	6	2.741776E-02	4.569627E-03	5.34	0.000498*	0.987044
S(A)	36	3.078275E-02	8.550764E-04			
Total (Adjusted)	42	5.820051E-02				
Total	43					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks

Hypotheses

Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	6	18.99519	0.004172	Reject Ho
Corrected for Ties	6	19.01673	0.004135	Reject Ho

Number Sets of Ties	9
Multiplicity Factor	90

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0.5 CD	7	177.50	25.36	0.7731	0.08
1.0 CD	7	169.50	24.21	0.5099	0.066
2.0 CD	4	62.50	15.63	-1.0662	0.055
nano	6	22.00	3.67	-3.8555	0.013
no dis	5	150.00	30.00	1.5155	0.094
no prechl	7	159.00	22.71	0.1645	0.071
prechl	7	205.50	29.36	1.6942	0.091

Table G-4 continued

Analysis of Variance Report

Page/Date/Time 2 7/22/2001 5:37:15 PM
Database C:\Program Files\NCSS97\Report\HAA5stats.S0
Response HAA5

Kruskal-Wallis Multiple-Comparison Z-Value Test

HAA5	0.5 CD	1.0 CD	2.0 CD	nano	no dis
0.5 CD	0.0000	0.1704	1.2373	3.1067	0.6318
1.0 CD	0.1704	0.0000	1.0920	2.9430	0.7874
2.0 CD	1.2373	1.0920	0.0000	1.4762	1.7076
nano	3.1067	2.9430	1.4762	0.0000	3.4653
no dis	0.6318	0.7874	1.7076	3.4653	0.0000
no prechl	0.3940	0.2236	0.9013	2.7282	0.9915
prechl	0.5963	0.7667	1.7458	3.6796	0.0875

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Kruskal-Wallis Multiple-Comparison Z-Value Test

HAA5	no prechl	prechl
0.5 CD	0.3940	0.5963
1.0 CD	0.2236	0.7667
2.0 CD	0.9013	1.7458
nano	2.7282	3.6796
no dis	0.9915	0.0875
no prechl	0.0000	0.9903
prechl	0.9903	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Table G-5: Statistical Output for Fall and Winter HAA5

Analysis of Variance Report

Page/Date/Time	1 7/22/2001 5:00:38 PM
Database	C:\Program Files\NCSS97\Report\HAA5.S0
Response	C2

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: C1	6	2.741776E-02	4.569627E-03	5.34	0.000498*	0.987044
S(A)	36	3.078275E-02	8.550764E-04			
Total (Adjusted)	42	5.820051E-02				
Total	43					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks

Hypotheses

Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	6	18.99519	0.004172	Reject Ho
Corrected for Ties	6	19.01673	0.004135	Reject Ho

Number Sets of Ties	9
Multiplicity Factor	90

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0.5 CD	7	177.50	25.36	0.7731	0.08
1.0 CD	7	169.50	24.21	0.5099	0.066
2.0 CD	4	62.50	15.63	-1.0662	0.055
nano	6	22.00	3.67	-3.8555	0.013
no dis	5	150.00	30.00	1.5155	0.094
no pre chl	7	159.00	22.71	0.1645	0.071
pre chl	7	205.50	29.36	1.6942	0.091

Table G-5 continued

Analysis of Variance Report

Page/Date/Time 2 7/22/2001 5:00:38 PM
Database C:\Program Files\NCSS97\Report\HAA5.S0
Response C2

Kruskal-Wallis Multiple-Comparison Z-Value Test

C2	0.5 CD	1.0 CD	2.0 CD	nano	no dis
0.5 CD	0.0000	0.1704	1.2373	3.1067	0.6318
1.0 CD	0.1704	0.0000	1.0920	2.9430	0.7874
2.0 CD	1.2373	1.0920	0.0000	1.4762	1.7076
nano	3.1067	2.9430	1.4762	0.0000	3.4653
no dis	0.6318	0.7874	1.7076	3.4653	0.0000
no pre chl	0.3940	0.2236	0.9013	2.7282	0.9915
pre chl	0.5963	0.7667	1.7458	3.6796	0.0875

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Kruskal-Wallis Multiple-Comparison Z-Value Test

C2	no pre chl	pre chl
0.5 CD	0.3940	0.5963
1.0 CD	0.2236	0.7667
2.0 CD	0.9013	1.7458
nano	2.7282	3.6796
no dis	0.9915	0.0875
no pre chl	0.0000	0.9903
pre chl	0.9903	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 3.0381

Table G-6: Statistical Output for ClO_2 dose comparisons of HAA5

Analysis of Variance Report

Page/Date/Time 1 7/22/2001 5:18:25 PM
Database
Response C2

Tests of Assumptions Section

Assumption	Test Value	Prob Level	Decision (0.05)
Skewness Normality of Residuals	0.8994	0.368431	Accept
Kurtosis Normality of Residuals	0.3500	0.726338	Accept
Omnibus Normality of Residuals	0.9315	0.627680	Accept
Modified-Levene Equal-Variance Test	0.6041	0.619619	Accept

Analysis of Variance Table

Source Term	DF	Sum of Squares	Mean Square	F-Ratio	Prob Level	Power (Alpha=0.05)
A: C1	3	1.604724E-03	5.349081E-04	0.71	0.559112	0.173852
S(A)	21	1.591104E-02	7.576683E-04			
Total (Adjusted)	24	1.751576E-02				
Total	25					

* Term significant at alpha = 0.05

Kruskal-Wallis One-Way ANOVA on Ranks
Hypotheses
Ho: All medians are equal.
Ha: At least two medians are different.

Test Results

Method	DF	Chi-Square (H)	Prob Level	Decision(0.05)
Not Corrected for Ties	3	2.330604	0.506683	Accept Ho
Corrected for Ties	3	2.3387	0.505148	Accept Ho

Number Sets of Ties	6
Multiplicity Factor	54

Group Detail

Group	Count	Sum of Ranks	Mean Rank	Z-Value	Median
0	7	90.50	12.93	-0.0303	0.071
0.5	7	104.00	14.86	0.7868	0.08
1	7	98.00	14.00	0.4237	0.066
2	4	32.50	8.13	-1.4454	0.055

Table G-6 continued

Analysis of Variance Report
Page/Date/Time 2 7/22/2001 5:18:25 PM
Database
Response C2

Kruskal-Wallis Multiple-Comparison Z-Value Test

C2	0	0.5	1	2
0	0.0000	0.4911	0.2728	1.0431
0.5	0.4911	0.0000	0.2183	1.4619
1	0.2728	0.2183	0.0000	1.2758
2	1.0431	1.4619	1.2758	0.0000

Regular Test: Medians significantly different if z-value > 1.9600
Bonferroni Test: Medians significantly different if z-value > 2.6383

VITA

Charissa Larine Harris was born on February 27, 1975. She received a Bachelor of Arts in Environmental Sciences from the University of Virginia, Charlottesville, Virginia in 1997. She then worked for two years at an engineering firm before returning to school to begin a Master of Science in Environmental Engineering. She completed her graduate work at Virginia Polytechnic Institute and State University, Blacksburg, Virginia in 2001.