ABSTRACT

THOM CHAIKET. Evaluation of Ozonation, Enhanced Coagulation, and Biofiltration for the Control of Disinfection by-Products in Drinking Water. (Under the Direction of DR. PHILIP C. SINGER)

Pilot-plant studies were conducted at the Indianapolis Water Company's White River Filtration Plant to assess the effectiveness of ozonation, enhanced coagulation, and biofiltration in controlling disinfection by-products in the filtered water. Nine experiments were conducted; operating variables included point of ozonation with respect to coagulation, pH of ozonation and coagulation, ozone dose and bromide conditions. Performance was assessed by monitoring pertinent water quality parameters and the reduction of trihalomethane (THM4) and haloacetic acid (HAA9) formation potentials under uniform formation conditions (UFC).

The results showed that White River water was not amenable to TOC removal by coagulation. Ozonation, biofiltration, and adjustment of pH did not enhance TOC removal efficiency. Nonetheless, a significant amount of THM4 and HAA9 precursors were removed, with overall removals as high as 66% and 81% respectively. Coagulation and ozonation were equally effective in removing precursors, and biofiltration was found to be more effective with ozonation placed after coagulation and settling. The relative reduction in DBP formation potentials tracked the relative reduction in UV absorbance; This parallel provided insights into the high DBP removal despite low TOC removal. From the regulatory standpoint, all operations were capable of producing filtered water that met Stage I requirements under UFC conditions. As for the effects of bromide on DBP speciation, bromo-substituted THMs and HAAs accounted for up to 90% and 50% in their respective classes when the water was spiked with 200 μg/L of bromide. Additional data analysis found significant correlation between the molar ratios $CHBrCl_2/CHCl_3$ and $BrCl_2AA/Cl_3AA$, and $CHBrCl_2/CHCl_3$ and $BrClAA/Cl_2AA$

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CHAPTER 1: INTRODUCTION

Disinfection of drinking water by chlorine produces a number of halogenated disinfection by-products (DBPs). Among these, trihalomethanes (THMs) and haloacetic acids (HAAs) are the dominant species found in finished water (Rook, 1976; Quimby, et al., 1980; Krasner, et al., 1989; Singer, et al., 1992). Members of these two classes of DBPs have been identified as possible human carcinogens (NCI, 1976; Regli, et al., 1992). Because of the health risks associated with them, the US Environmental Protection Agency (US EPA) began regulating the levels of these DBPs in finished drinking water from as early as 1979 (US EPA, 1979). The current regulated levels are given by Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule which establishes maximum contaminant levels (MCLs) for total trihalomethanes (THM4) and five of the haloacetic acids (HAA5) at 80 and 60 μg/L, respectively (US EPA, 1998).

A number of researchers (Bellar, et al., 1974; Rook, 1976; Stevens, et al., 1976; Christman et al., 1983) have shown that natural organic material (NOM), which is the major component of total organic carbon (TOC) in raw drinking water, is the principal precursor of DBPs. Kavanaugh (1978) and Babcock and Singer (1979) have shown coagulation to be an effective method of NOM removal. Based on these and other findings, EPA has required the implementation of enhanced coagulation—defined as modified coagulation to attain greater NOM removal—for the treatment of surface water (US EPA, 1998). Based on raw water alkalinity and TOC concentration, a utility must achieve a specific percent removal of NOM—using TOC as the surrogate—before the point of continuous disinfection. If a utility cannot achieve the necessary TOC removal by this method, it can meet the enhanced coagulation requirements by performing coagulation at a coagulant dose and pH such that an addition of 10 mg/L of alum results in a TOC

removal of 0.3 mg/L or less. This alternative method has been referred to as the "point of diminishing return" (PODR) criterion.

White et. al (1997) have shown that waters with a low TOC content and/or a low specific UV absorbance (SUVA) value are not amenable to TOC removal by coagulation. To increase NOM removal, ozonation and biofiltration have been suggested to aid coagulation (Semmens and Staples, 1986; Miltner, et al., 1992; LeCourt, et al., 1997). Ozone oxidizes NOM to form organic by-products that are biodegradable, and the biodegradability has been quantified using the parameter biodegradable dissolved organic carbon (BDOC) (Servais, et al., 1987; Joret et al., 1988). Speitel et al. (1993) and Krasner et al. (1993b) found that the BDOC content can be removed by biofiltration. Ozonation also provides microbial inactivation, thereby serving as an alternative primary disinfectant to chlorine. Hence, the combination of coagulation, ozonation and biofiltration can be an effective drinking water treatment scheme from a number of standpoints.

However, water treatment with ozone has some drawbacks. Ozone can produce its own set of DBPs, some of which are possible human carcinogens (Glaze, et al., 1989; Weinberg, et al., 1993). Specifically, when bromide is present in the water, bromate is produced (Haag and Hoigne, 1983; von Guten and Hoigne, 1992). Kurokawa et al. (1986) found bromate to cause the formation of renal tumors in rats. A second potential negative effect of ozonation is the increase in biodegradability of the oxidation by-products. There would be concerns of possible microbial regrowth in the distribution system in case biofiltration cannot effectively remove the BDOC content (Sontheimer, 1979; Janssens, et al., 1985; Speitel, et al., 1993; Krasner, et al., 1993b; LeCourt, et al., 1997).

There were two objectives to this study. The first objective was to evaluate the effectiveness of several pilot-scale treatment options involving enhanced coagulation, ozonation, and biofiltration of a raw drinking water containing a relatively low TOC concentration, high alkalinity, and a relatively low SUVA. The pilot operations were conducted at the Indianapolis

Water Company's White River Filtration Plant in Indianapolis, IN. The variables in the treatment train included the point of ozonation with respect to coagulation, ozone dose required for various disinfection objectives, and pH of coagulation and ozonation. With the increasing interest in bromo-substituted DBPs due to their potential carcinogenicity, the effects of bromide addition on DBP speciation were also investigated. The effectiveness of the treatment trains was assessed based on the removal of pertinent water quality parameters including turbidity, and TOC, DOC and BDOC content, and the control of DBP formation potential.

CHAPTER 2: LITERATURE REVIEW

2.1: Introduction

Historically, chlorine has been used to control microbial contaminants in drinking water. It is cost-effective, reliable, easily quantified, and produces a residual which contributes to additional disinfection in the distribution system. However, in chlorinating water containing natural organic material (NOM), disinfection by-products (DBPs), some of which have been proven to be health risks, are produced.

The objectives of this chapter are to review chlorination and subsequent DBP formation, and to elaborate on the chemistry of NOM, the primary DBP precursor, and treatment techniques used for its removal. These techniques include coagulation, ozonation, and biofiltration.

2.2: Chlorination and Disinfection by-Products (DBPs)

Chlorination is generally conducted using hypochlorous acid (HOCl) and hypochlorite (OCl^-). The overall reaction of chlorine with NOM can be summarized as

$$HOCl \text{ and } OCl^- + NOM \longrightarrow \text{Halogenated DBPs} \qquad (2.1)$$

Various studies have shown trihalomethanes (THMs) and haloacetic acids (HAAs) to be the two major classes of DBPs produced from chlorination (Krasner, 1989; Singer, 1994). In the absence of bromide, chloroform and di- and trichloro acetic acids are the dominant species in their respective DBP classes (Christman et al., 1983; Reckhow and Singer, 1984). Other classes of DBPs formed from chlorination include haloacetonitriles, haloketones, halopicrins, cyanogen halides, and haloaldehydes (Christman, et al., 1983; Coleman et al., 1984) . However, these identified species do not account for all of the halogenated DBPs produced from chlorination. Singer (1993) indicates that approximately 50% of the halogenated DBPS commonly found in chlorinated finished water have not been identified.

When bromide is present in the water, hypochlorous acid reacts with bromide to produce hypobromous acid (HOBr). Hypobromous acid is active and, together with HOCl, will react with NOM to produce mixed bromo-chloro substituted by-products. The extent of bromine substitution is dependent on the ratio of the bromide concentration to the applied HOCl dose. Generally, the higher the ratio, the larger the extent of bromine substitution (Singer, 1993).

Since the objectives of this project are focused on THM and HAA formation and control, the discussion in this report will be limited to these two classes of DBPs. The THM and HAA species produced from chlorination of water containing NOM and significant amounts of bromide are:

THMs:

- Chloroform ($CHCl_3$)
- Bromodichloromethane ($CHBrCl_2$)
- Dibromochloromethane ($CHBr_2Cl$)
- Bromoform ($CHBr_3$)

HAAs:

- Monochloroacetic acid (ClAA)
- Monobromoacetic acid (BrAA)
- Dichloroacetic acid (Cl_2AA)
- Dibromoacetic acid (Br_2AA)
- Trichloroacetic acid (Cl_3AA)
- Tribromoacetic acid (Br_3AA)
- Bromochloroacetic acid (BrClAA)
- Bromodichloroacetic acid ($BrCl_2AA$)
- Dibromochloroacetic acid (Br_2ClAA)

There are various factors governing the formation of DBPs including pH, contact time, temperature, NOM characteristics, chlorine dose, and bromide concentration. Except for the latter two factors which have already been addressed in the above section, the remaining factors are discussed briefly. The pH of chlorination affects HAA and THM formation differently. In the former DBP class, the formation of TCAA increases with decreasing pH while DCAA tends to be independent of pH (Reckhow and Singer, 1984; Shi, 1998). In addition, Cowman and Singer (1996) found the increase in formation of di- and trihalogenated HAAs containing

bromine to be greater than the increase in formation of their chlorine-substituted counterparts. As for THMs, studies have shown that THM formation tends to increase with increasing pH (Stevens, et al., 1976; Reckhow and Singer, 1984; Singer, et al., 1992; Shi, 1998). In terms of contact time, Reckhow and Singer (1984) found that both THMs and HAAs continue to form, though slower than the initial formation rate, as long as the DBP precursors are in contact with free chlorine. Increasing temperature increases reaction kinetics. Therefore, higher production of DBPs would be expected in the warmer seasons. NOM characteristics will be discussed in length later in this section.

There are various approaches to assess the formation of DBPs. Among these, are the formation potential (FP) test, simulated distribution system (SDS) test, and uniform formation conditions (UFC) test. Under FP test, waters are chlorinated using high dose and long incubation time, both of which do not represent the disinfection conditions in most treatment plants (Stevens, et al., 1976). As a result, the DBPs formed under this test are found at higher concentrations and tend to have greater degrees of chlorine substitution over bromine substitution than what would be expected under the "normal" disinfection conditions. Under SDS test conditions, waters are chlorinated under site-specific conditions of time, temperature, pH and chlorine dose or residual that reflect the conditions in the distribution system. In its 1978 study, the EPA initiated the use of the SDS test and found it to be effective in accurately representing DBP formation in distribution systems (Miller, et al., 1982). However, as noted by Summers et al. (1996), the site specific nature of the SDS test prevented comparison of DBP formations in different systems. In addressing this limitation, Summers developed the UFC test in which DBP formation is measured under constant conditions that are representative of the average conditions in US distribution systems. These average conditions are: incubation time—24±1 h, incubation temperature—20.0±1.0 °C, incubation pH—8.0±0.2, and free chlorine residual after 24 hours—1.0±0.4 mg/L.

2.3: Health Risks of DBPs

There have been numerous studies dating back to the mid-1970's which identified a number of DBPs as carcinogens and provided evidence for an association between cancer and consumption of chlorinated drinking water. Chloroform was identified as a carcinogen in 1976 (NCI, 1976). As Singer (1994) has cited in his review paper on THMs and other DBPs, di- and trichloroacetic acids have been identified as animal carcinogens. Furthermore, Regli et. al (1992) reported that dichloroacetic acid can potentially be more potent than any of the THMs.

Numerous epidemiological studies and animal bioassays have been conducted and showed that certain types of cancers are potentially linked to the consumption of chlorinated drinking water (Morris, et al., 1992; McGeehin et al., 1993; King and Marrett, 1996; Cantor et al., 1998). From their studies using rats and mice, Boorman et al. (1999) reported that chloroform caused renal cancer in rodents. Furthermore, they found that $CHBr_2Cl$ was associated with an increase in liver tumors in female mice and $CHBrCl_2$ caused a significant increase in colon cancer in rats. Lastly, $CHBr_3$ was cited to have caused a low incidence of colon tumors in female rats. As for the HAA species, Cl_2AA was found to produce liver tumors in mice and rats (Herren-Freund, et al., 1987; DeAngelo, et al., 1991; Daniel, et al. 1992; DeAngelo, et al., 1996). DeAngelo et al. (1997) also found that Cl_3AA causes liver tumors in mice but not rats.

Studies have shown THMs and HAAs can have adverse reproductive effects. Namely, Waller et al. (1998) associated a higher risk of miscarriage in pregnant women in their first trimester to the regular consumption of chlorinated drinking water containing more than 75μg/L of THMs. In terms of animal cancer bioassays, Linder et al. (in press) found that Cl_2AA caused testicular toxicity.

2.4: Aquatic Natural Organic Material (NOM)

Aquatic natural organic material (NOM) is a term used to collectively describe the various natural organic substances, both particulate and dissolved, found in aquatic systems.

Particulate NOM includes microbial biomass and organic colloids, and has a negative surface charge (Water Quality and Treatment, 1990). Dissolved NOM consists of organic material leached from terrestrial sources and products of biodegradation and microbial processes. Typically, more than 90% of NOM is dissolved in nature (Thurman, 1985).

Dissolved NOM is divided into two categories: hydrophobic and hydrophilic. The hydrophobic fraction, also referred to as humic substance, represents 30-90% of the total dissolved organic carbon in most waters, and is also believed to be responsible for the color in natural water (Edwards and Amirtharajah, 1985). Croué et al. (in press) indicate that humic substances derive from both microbial processes and plant decomposition, and the origin of the vegetation influences the chemical characteristics of NOM. Humic substances stemming from the latter source tend to have large amounts of aromatic carbon and are high in phenolic content. The opposite is true for humic substances derived from microbial processes. In addition to aromatic carbon and phenolic components, studies have shown humic substances, regardless of origin, to contain in varying degrees carboxyl groups, alcohol OH groups, methoxy groups, ketones, and aldehydes (Reckhow, et al., 1990). With the presence of these functional groups, it can be inferred that pH will have a strong effect on the behavior of humic substances. Specifically, when the pH of the water is increased, humic substances will be in their anionic form due to deprotonation of their phenolic and carboxylic functional groups (Edwards and Amirtharajah, 1985).

Humic substances can be further categorized into two classes: humic and fulvic acids. Humic acids contain a larger amount of aromatic carbon, specifically aromatic phenolic functional groups, which have been shown to be strongly associated with chlorine reactivity (Hanna, et al., 1991; Croué, et al., in press). Additionally, Reckhow et al. (1990) and Harrington et al. (1996) have shown that chlorine consumption and DBP formation are proportional to the aromatic carbon content of NOM. Fulvic acids, which make up the dominant fraction of humic substances, have a larger amount of carboxyl and heteroaliphatic carbon.

In terms of reactivity, humic substances are significant chlorine consumers. Humic acids consume greater amounts of chlorine and produce more THMs and HAAs (chloroform, and DCAA and TCAA, respectively) than fulvic acids (Reckhow, et al., 1990; Martin, 1995; Leenheer, 1996). In view of its reactivity with chlorine and its position as the most abundant fraction of NOM in many surface waters, humic substances are considered to be the major DBP precursors in most natural water (Croué, et al., in press).

"Non-humic" substances are classified under the hydrophilic fraction. From an analytical standpoint, the hydrophilic fraction is the NOM fraction that passes through an XAD-8 resin column operating under acidic conditions (Leenheer, 1981; Thurman and Malcolm, 1981). This fraction is thought to have larger amounts of carboxylic acids and carbohydrates, and also contributes to DBP formation, although to a lesser degree than the humic fraction (Amy et al., 1992).

2.4.1: Biodegradable Dissolved Organic Carbon (BDOC): Biodegradable Fraction of NOM

In addition to being DBP precursors, NOM can also serve as substrate for microorganisms present in distribution systems. In quantifying this biodegradable fraction, the measurements of biodegradable dissolved organic carbon (BDOC) have been used in a number of studies (Servais, et al., 1987; Joret et al., 1988). Methods for measuring BDOC can be categorized into two groups: biomass-based methods and DOC-based method (Huck, 1990). The methods from the first group are complex and time-consuming, and only approximate BDOC content from corresponding growth of microorganism. On the other hand, the DOC-based methods measure the change in DOC and, therefore, provides a direct measure of BDOC. In addition, they are relatively easier and quicker than their biomass-based counterparts.

Both attached and suspended biomass media can be used in DOC based-methods. However, with its long incubation time, the latter do not provide any advantage over biomass-based methods, from the standpoint of time. On the other hand, the incubation time for the attached biomass-based methods is generally brief and can be as short as five days. In their

study, Joret et al. (1988) utilized this approach and used biologically active sand (BAS) as media in an open system in which aeration was provided by means of pumping. They found biodegradation under such conditions was rapid, and BDOC could be reliably quantified after an incubation period of five days. Allgeier et al. (1998) modified Joret et al.'s approach and formatted it to be applicable for bench-scale closed systems. Their work resulted in a simplified and cost-effective method to assess BDOC content. A detailed description of Allgeier et al.'s approach is provided in Chapter 3.

2.5: Coagulation

Coagulation is an important process in drinking water treatment. It is an effective chemical process in which a coagulant is added to the water to promote the removal of turbidity (overall particulate materials including particulate NOM) and dissolved NOM by chemical destabilization (Babcock and Singer, 1979; Semmens and Field, 1980; Chadik and Amy, 1983; Reckhow and Singer, 1984; White et al., 1997). Given that NOM is responsible for causing color in water and, more importantly, to be the principal precursor of DBPs, it can be seen that the removal of NOM by coagulation is important from both health and aesthetic standpoints.

This section is dedicated to a discussion of two aspects of alum coagulation. First, two mechanisms of coagulation under typical operating conditions will be addressed. The mechanisms are adsorption-charge neutralization and enmeshment/sweep coagulation. The second topic to be discussed is the set of parameters that influence the chemistry of coagulation. These parameters include pH, temperature, and NOM characteristics. The first two parameters will be addressed in the "mechanisms" section, and NOM will be addressed separately.

2.5.1: Coagulation Mechanisms

With its low cost and effective performance, alum ($Al_2(SO_4)_3$-$14H_2O$) is the principal coagulant in drinking water treatment (Viessman and Hammer, 1993; Water Quality and Treatment, 1990). Its behavior in water is based on the aqueous chemistry of aluminum, Al(III). Upon addition to water, Al(III) participates in a series of hydrolysis reactions to produce a

number of monomeric and polymeric species. Baes and Mesmer (1976) identified these species to be: Al^{+3}, $AlOH^{+2}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-}$, $Al(OH)_3$ (amorphous), $Al_2(OH)_2^{+4}$, $Al_3(OH)_4^{+5}$, and $Al_{13}O_4(OH)_{24}^{+7}$. The latter three represent the multimeric and polymeric fraction. Van Benschoten and Edzwald (1990a) suggest the Al(III) species that are significant in coagulation include Al^{+3}, $AlOH^{+2}$, and $Al(OH)_4^{-}$. However, Hall and Packham (1965) and Dempsey et al. (1984) also included the three multimeric and polymeric species on the list of important species.

Because of Al(III) hydrolysis, pH has a major impact on Al(III) speciation. In considering the typical pH range of coagulation—from 5.0 to 8.0—the polymeric species are dominant in the pH range of 5 to 6.0. Above pH 6.0, $Al(OH)_3$ precipitates and, with the pH above 6.5, $Al(OH)_4^{-}$ becomes the predominant Al (III) species (Stumn and Morgan, 1996)

Coagulation of particulate materials achieved mainly under the mechanisms of adsorption-charge neutralization and enmeshment/sweep coagulation (Water Quality and Treatment, 1990; White, et al., 1997). The former mechanism is dominant when water is treated in the pH range of 5-6, where the polymeric Al(III) species dominate. These species bring about destabilization by adsorbing onto the particulate materials, neutralizing the negatively charged particle. Enmeshment/sweep coagulation for particulate removal dominates in the pH range of 6-8. In this region, Al(III) is least soluble and the precipitation of amorphous $Al(OH)_3$ is highly probable. During the precipitation period, particles become enmeshed in the precipitate.

Removal of dissolved NOM by coagulation is achieved via charge neutralization/precipitation and adsorption. The former combination of mechanisms occurs in the pH region where the polymeric Al(III) dominates. The highly positive polymeric Al(III) species neutralize the carboxylic and phenolic functional groups of the NOMs and form insoluble aluminum-humate precipitates. In the pH range where the formation of $Al(OH)_3$ is highly probable, removal of dissolved NOM occurs primary via sorption onto the metal hydroxide floc. The precipitates from both modes of coagulation can be removed by conventional sedimentation processes.

With kinetics considerations, it can be seen how temperature will affect Al(III) speciation. Using thermodynamic data for the pertinent hydrolysis reactions, White (1996) constructed a solubility diagram for Al(III) at 25 °C and 15 °C (not shown). The comparison of the two diagrams indicated that the decrease in temperature produced a shift in the solubility of Al(III) toward high pH value, as well as a decrease in the minimum solubility.

2.5.2: Effects of NOM Characteristics on Coagulation

There are a number of parameters which influences the effectiveness of coagulation. The impacts of pH and temperature have been addressed in the previous sections. In addition to these parameters, NOM characteristics should also be considered. In general, humic substances, or the hydrophobic fraction of NOM, are preferentially removed during coagulation (Hall and Packham, 1965; Babcock and Singer, 1979; Collins, et al., 1986; Croué, et al, 1997; White, et al., 1997). Within the humic fraction, studies have shown fulvic acids to be less readily removed by coagulation than humic acids (Hall and Packham, 1965; Babcock and Singer, 1979). A number of surrogates have been used to estimate the hydrophobic fraction of NOM. Among these, specific UV absorbance (SUVA), which is defined as the ratio of the UV absorbance at 254 nm to the DOC concentration, has been utililized successfully for this purpose in many studies (Edzwald, 1993; White, et al, 1997; Croué, et al, in press).

It should be noted also that the presence of NOM will affect the hydrolysis of Al(III). As an example, Lind and Hem (1975) found that organic solutes can drastically change the shape of the Al(III) solubility diagram, and therefore, altering the pH dependence of coagulation mechanisms.

2.6: Ozonation and Biofiltration

Ozone is a strong oxidant, and has been used extensively in water treatment to remove taste and odor (Anselme, et al., 1985; Jestin, et al., 1987b). With increasing frequency, ozonation has also been utilized as a disinfectant. In particular, a number of researchers have shown ozone to be very effective in inactivating Giardia and Cryptosporidium (Wickramanayake, et al., 1984;

Finch and Fairbairm, 1991; Labatiuk, et al., 1992). However, disinfection with ozone has been associated with a number of negative effects. Namely, ozone can produce its own set of DBPs, some of which are possible human carcinogens (Glaze, et al., 1989; Weinberg, et al., 1993). Specifically, when bromide is present in the water, bromate is produced (Haag and Hoigne, 1983; von Guten and Hoigne, 1992). A second negative effect of ozonation is the increase in biodegradability of the oxidation by-products, which has implications for possible microbial regrowth in the distribution system (Sontheimer, 1979; Janssens, et al., 1985; Speitel, et al., 1993; Krasner, et al., 1993; LeCourt, et al., 1997).

This section provides an elaboration of the points mentioned above. In addition, ozone chemistry and the coupling of ozonation with biofiltration—a treatment combination which utilizes the increase in biodegradability after ozonation—are discussed.

2.6.1: Ozone Chemistry with NOM and Bromide

A number of studies have been conducted to show how ozone changes NOM characteristics. Among these, the works of Collins et al. (1986), Edwards and Benjamin (1992a), and Paralkar and Edzwald (1996) have shown that ozonation partially oxidizes NOM to produce by-products with lower molecular weight, lower SUVA, and more hydrophilic characteristics than the parent NOM. Carlson (1997) has shown that ozone also increases the acidity of the NOM.

In terms of reactivity, ozone can react directly with NOM to produce DBPs, including aldehydes, carboxylic acids, organic peroxides, and ketoacids (Weinberg, et al., 1993; Singer, 1993). When bromide is present, ozone also reacts with the halogen in a series of radical chain reactions to produce hypobromous acid (HOBr) and bromate (BrO_3^-) (Haag and Hoigne, 1983). Therefore, it can be seen that NOM and bromide will compete for ozone. In water with low bromide content, the reaction of ozone with NOM will dominate (Shukiary, et al., 1994). It should be noted that the reaction of ozone with bromide is pH-dependent and, as mentioned earlier, HOBr is a main participant in the reactions producing brominated HAAs and THMs.

In addition to pH, there are a number of other factors which affect ozone consumption and disinfection. As reported by Hoigne (1988), ozone consumption increases when the pH and temperature are increased. Linking this pH dependence to by-product formation, brominated THM and HAA formation tends to dominate over bromate formation at lower pH values (Fielding and Hutchinson, 1995; Hickey, 1997). The temperature dependence is intuitive when considering its effects on reaction kinetics. Hoigne (1988) also indicated that ozone consumption increases with TOC and bromide concentrations.

As mentioned above, ozonation produces oxidation by-products that are more biodegradable than the parent NOM. Kim et al. (1995) has shown that, in some waters, the BDOC content can increase by 20% . Werner and Hambsch (1986) found a relationship between the increase in BDOC content and the applied ozone dose. Specifically, BDOC increased rapidly at ozone doses up to 1 mg O_3/ mg DOC and only by a small amount at an applied dose between 1 and 1.5 mg O_3/ mg DOC. There is some debate about the upper limit at which ozone no longer significantly influences biodegradability. Van der Kooij et al. (1989) suggested the upper limit was 2 mg O_3/ mg DOC. For the overall effect, Huck (1990) found a consistent increase in assimilable organic carbon (AOC) content—a parameter similar to BDOC—at an ozone dose of 0.5 mg O_3/ mg DOC.

2.6.2: Biofiltration

Various studies have been conducted to evaluate biofiltration following ozonation, for a number of reasons (Semmens and Staples, 1986; Huck et al., 1994, LeCourt et al., 1997; Paode, et al., 1997). As Hozalski and Bouwer (in press) point out, biofiltration is an inexpensive method that provides effective removal of biodegradable NOM, thus limiting potential microbial regrowth in the distribution system. In addition, the process has also been shown to be effective in removing TOC and micropollutants (Bouwer and Crowe, 1988; Symons, 1994; Hozalski et al., 1995). Furthermore, Siddiqui et al. (1994) demonstrated that biofiltration can also remove bromate.

A number of researchers have investigated the effects of various parameters on biofiltration. Carlson et al. (1994) found biofiltration to be temperature-dependent, and Coffey et al. (1997) have shown the process to be significantly impaired at temperatures below 10°C. In terms of operating parameters, empty bed contact time (EBCT) and backwashing operations affect the efficiency of biofiltration. Hozalski and Bouwer (in press) suggested effective removal of BDOC can be achieved in biofilters operating with rapid media filter EBCTs in the range of 2 to 20 minutes. Effective backwashing is an important component of biofiltration operations. That is, without backwashing, headloss will build up across the filter, decreasing the efficiency of operation. In terms of the selection of backwash water, studies have been conducted on both water and chlorinated water. Ahmad and Amirtharajah (1997) reported an increasing rate of headloss build up in successive filter runs when granular activated carbon (GAC) biofilters were backwashed with water only. For filters backwashed with chlorinated water, the researchers found decreasing rate of headloss development in successive runs and attributed the reduction to the loss of biomass. Miltner et al. (1995) found that backwashing with chlorinated water have similar effects on dual-media (anthracite and sand) biofilters. To stabilize the change in the rate of headloss development in successive runs, Ahmad and Amirtharajah (1997) suggested the use of air scour to assist backwashing. The application of air scouring was found to produce insignificant change in rate of headloss development and to lower the total headloss across the biofilters.

In terms of filter media, studies have indicated the performances of GAC and anthracite biofilters are comparable under pseudo-steady state conditions (Coffey, et al., 1995; Daniel and Teefy, 1995). In a critical review of these two and other similar studies, Hozalski and Bower (in press) reported GAC biofilters can outperform their anthracite counterparts under extreme conditions which include start-ups and low temperature operations.

CHAPTER 3: MATERIALS AND METHODS

3.1: Introduction

This study was conducted on a pilot plant scale. Given the complex nature of pilot plant studies, planning and experimental design were carefully addressed prior to the initiation of the project. This section presents the experimental plan and a description of the pilot plant used for this work. In addition, all analytical methods used in this study are also reviewed.

3.2: Experimental Plan

Water from the White River Treatment Plant of the Indianapolis (IN) Water Company was selected for this study for several reasons: it has a relatively low SUVA and a low bromide concentration, and it has been demonstrated to contain TOC that is not very amenable to coagulation (White et al, 1997).

Nine treatment simulations were evaluated in this study (see Table 3.1). All nine incorporated enhanced coagulation, ozonation, and biofiltration in the treatment train. In the first six runs, the order of treatment was ozonation, coagulation and sedimentation, and biofiltration. Within these pre-ozonation runs, treatment was examined at two ozonation/coagulation pH values (ambient pH—between 7.8 and 8.0—and pH 6.5), two ozone doses (for 0.5 log Giardia inactivation and 1.0 log Cryptosporidium inactivation), and two bromide conditions (ambient bromide levels—approximately 20 μg/L—and a 200 μg/L bromide spike). In the remaining three runs (ie. the intermediate-ozonation runs), ozonation was placed after coagulation and sedimentation. For these intermediate- ozonation experiments, the effects of ozone dose (for 0.5 log Giardia and 1.0 log Cryptosporidium inactivation) and bromide spike (200 μg/L) were investigated. The pilot plant was operated in each mode for three weeks, and it was assumed the operation was at steady state after the second week. The exception to this schedule was for the

modes in which bromide spiking was investigated. It was assumed that the bromide did not affect treatment efficiencies and, therefore, the pilot plant was operated in this mode for two weeks with the assumption that steady state was achieved after one week. During the last week of operation in each experiment, samples were taken on three consecutive days and analyzed for turbidity, TOC and dissolved organic carbon (DOC) concentrations, biodegradable organic carbon (BDOC) concentration, UV absorbance at 254 nm, and THM and HAA formation potential (see below).

Prior to pilot plant operations, preliminary bench-scale coagulation studies were conducted to determine the enhanced coagulation dosage requirements for the experiments to be conducted on the pilot scale. The bench scale studies began in July, 1998 and were completed in August 1998. Pilot plant operations were initiated in September, 1998 and were completed in April, 1999.

Table 3.1: Treatment Trains Evaluated.

Exp #	Description of Treatment Train
1	Pre-ozone dosed at ambient pH for 0.5 log Giardia inactivation, coagulated at ambient pH
2	Pre-ozone dosed at pH 6.5 for 0.5 log Giardia inactivation, coagulated at pH 6.5
3	Pre-ozone dosed at pH 6.5 for 1 log Cryptosporidium inactivation, coagulated at pH 6.5
4	Same as #3, with 200 μg/L bromide spike
5	Pre-ozone dosed at ambient pH for 1 log Cryptosporidium inactivation, coagulated at ambient pH
6	Same as #5, with 200 μg/L bromide spike
7	Enhanced coagulation at ambient pH, intermediate ozone dosed for 0.5 log Giardia inactivation at enhanced coagulation pH
8	Enhanced coagulation at ambient pH, intermediate ozone dosed for 1 log Cryptosporidium inactivation at enhanced coagulation pH
9	Same as #8, with 200 μg/L bromide spike

3.3: Pilot Plant Description

Malcolm Pirnie's (Indianapolis, IN) 2.0 gpm mobile pilot trailer was used in this study. The trailer was equipped with units to perform the following processes:

- Rapid mixing
- Flocculation
- Sedimentation
- Ozonation
- Biofiltration

Figure 3.1 is a schematic diagram of the Malcolm Pirnie pilot plant. Ozonation took place in one countercurrent contact column, followed by a four-chamber contact basin. There were two meters which displayed the ozone concentrations at the output line from the ozone generating unit and at the off-gas line from the ozone contact column. The coagulation apparatus included a rapid mixing unit, a flocculation basin, and a sedimentation tank. The rapid mixing unit consisted of a static mixer, with the coagulant (alum) feed point upstream of the mixer. There were three chambers in the flocculation basin, and the mixing energies in each chamber were tapered by variable speed mixers. After flocculation, the water entered the sedimentation tank through a perforated baffle wall. Sedimentation was enhanced by fitting the basin with tube settlers. The combined flocculation and sedimentation basins had an approximate hydraulic detention time of three hours. In terms of treatment order, ozone was applied to raw water upstream of the rapid mixing unit under the pre-ozonation mode of operation. Under intermediate-ozonation experiments, ozone was applied to the settled water.

Four 3-inch diameter filter columns were positioned downstream from the coagulation and ozonation units. They operated in parallel as biologically-active biofilters, each at a hydraulic loading of 3 gpm/sf, with an empty-bed contact time (EBCT) of approximately 5 minutes. Two biofilters were dual media anthracite and sand, and the remaining two were dual media granular activated carbon (GAC) and sand. The GAC was taken from another pilot plant operation and was fully exhausted with respect to its TOC adsorption capacity. The top media in each biofilter had a depth of 20 inches and an effective size of 1.1 mm; the sand had a depth of 10 inches and an effective size of 0.5 mm. For the experiments in which ozonation and coagulation were conducted at pH 6.5, the pH of one biofilter from each set was adjusted approximately 7.1 with caustic. Initially, the pH adjustment was made to a value of 8.0. However, the ability to increase the pH of biofilter operation was limited due to the potential $CaCO_3$ precipitation.

3.3.1: Pilot Plant Operations

The pilot plant was operated by Malcolm Pirnie engineers with the assistance of staff from the Indianapolis Water Company. For each day of operation, pertinent pilot plant operating data and treatment targets were recorded. These parameters included water temperature, pH of ozonation and coagulation, ozone dose, target and calculated CT (ozone concentration times time) values. Ozone dose was calculated to be the transferred ozone, which was the difference between the two measurements of ozone concentration mentioned earlier multiplied by the ratio of the air flow rate to water flow rate. The target CTs for Giardia inactivation at the ambient experimental temperatures were taken from the Guidance Manual for the Surface Water Treatment Rule (EPA, 1991); the target CTs for Cryptosporidium inactivation were assumed to be seven times the CTs for 1-log Giardia inactivation. The actual CTs were determined by first establishing the T10s for each stage of the 4-stage ozonation dissipation tank. To do so, a tracer study was conducted in which the dissolved ozone residuals in the effluent of the dissipation tank and each of the four stages were measured. It was assumed that the T10 for each stage was the product of the T10 of the tank and the ratio of the volume of the stage to the total tank volume. The actual CT for the particular stage was the product of the average dissolved ozone concentration and the T10 value of that stage. The sum from the four stages represented total CT. No CT credit was given to the countercurrent contact column. The results from the tracer study can be found in Appendix A.

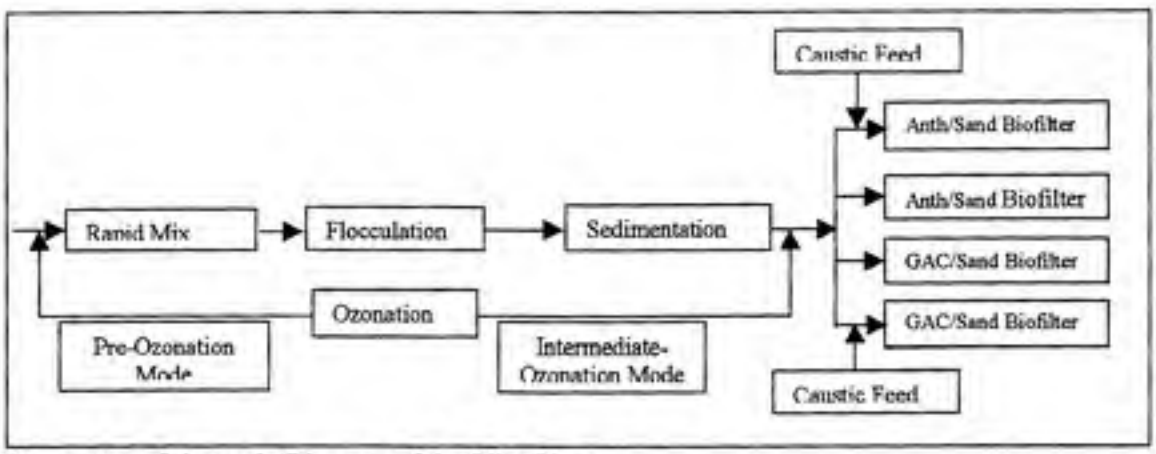

Figure 3.1. Schematic Diagram of the Pilot Plant.

3.4: Sample Collection and Handling

Water samples were collected from seven points off the pilot plant on three consecutive days in the middle of the third week of each pilot plant run. For the pre-ozonation experiments, the samples were: raw water, ozonated raw water, settled water, and 4 filtered waters. For the intermediate-ozonation experiments, the samples were: raw water, settled water, ozonated settled water, and 4 filtered waters. Samples were analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations, Ultraviolet (UV) absorbance at 254 nm, formation potentials of all four trihalomethanes and nine haloacetic acids under UFC test (UFC THM4 and UFC HAA9). UV absorbance at 272 nm was also measured before and after UFC chlorination (see below for description of analytical methods). Due to analytical constraints, samples for BDOC analysis were taken only on the first and the third day of sample collection. It was assumed that the average of the three days (two days in the case of BDOC) represented the steady-state water quality characteristics for that sampling location. All samples were collected by the Malcolm Pirnie team with assistance from Indianapolis Water Company personnel.

TOC/DOC samples were collected in 40-mL borosilicate amber glass vials with phenolic screw caps and Teflon-faced silicone rubber septa (Laboratory Supply Distributors Corp., Mt. Laurel, NJ). For the purpose of preservation, a drop of 2-N hydrochloric acid was added with a pasteur pipette to the TOC/DOC sample vial. Samples intended for BDOC measurements, UV absorbance analysis, THM4 formation potential, and HAA9 formation potential were collected in 500- and 1000-mL borosilicate amber bottles with Teflon-lined screw caps (Laboratory Supply Distributors Corp., Mt. Laurel, NJ). All samples were shipped in ice-chests packed with ice packs, and sent to the University of North Carolina at Chapel Hill (UNC) via overnight carrier. At UNC, the samples were refrigerated at 4°C until analysis. All samples were analyzed within one week of receipt.

3.5: Glassware Preparation

Glassware for sample collection and general laboratory use, excluding all volumetric pieces, was soaked in Alkonox detergent overnight, rinsed with tap water three times, and then rinsed with deionized organic free water (DOFW; Dracor Inc., Durham, NC) three times. The glassware was then immersed in a 10% nitric acid bath overnight, rinsed with tap water three times, rinsed with DOFW three times, and then oven-dried at 180°C. Volumetric glassware was prepared in the same manner as the general glassware except they were not oven-dried. Instead, they were rinsed with methanol (JT Baker, Phillipsburg, NJ) three times and air-dried. Glassware used for chlorine residual measurements and chlorination (see below) was prepared in the same manner as the general glassware with the additional step of soaking overnight in approximately 100 mg/L Cl_2 solution prepared from stock sodium hypochlorite (Aldrich Chemical, Milwaukee, WI) prior to rinsing with DOFW. All plastics (caps and septa) were soaked in tap water overnight, rinsed with DOFW three times, and then oven-dried at 80°C.

3.6: Analytical Methods

3.6.1: Ultraviolet (UV) Absorbance Measurements

The procedures for UV absorbance measurements were in accordance with Standard Method 5910 (Standard Methods, 1995). The samples were prepared by filtering through 0.45 μm Supor-450 membrane filters (Gelman Sciences, Ann Arbor, MI). The UV absorbance at 254 nm and 272 nm was measured using a U-2000 UV-Visible spectrophotometer (Hitachi Instruments, Danbury, CT). DOFW was used to zero the instrument. Measurements were made using a 1-cm quartz cell. The cell was rinsed once with DOFW and once with sample water prior to measurement.

3.6.2: Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) Measurements

TOC and DOC concentrations were measured with a Shimadzu 5000 Total Organic Carbon Analyzer which was equipped with an ASI 5000 auto-sampler (Shimadzu Corporation, Columbia, MD). Analysis for TOC and DOC content was conducted according to the procedures

dictated in Standard Method 5310B (Standard Methods, 1995), with one revision; 2-N hydrochloric acid rather than phosphoric acid was used to acidify the samples. This substitution was made because the Shimadzu analyzer is sensitive to excess phosphoric acid. For DOC analysis, the samples were first filtered through pre-rinsed 0.45 μm Supor-450 membrane filters (Gelman Sciences, Ann Arbor, MI).

Prior to sample measurement, the TOC analyzer was calibrated using four standard solutions (0, 2, 4, and 6 mg/L as C) prepared from dilutions of a 1000 mg/L organic carbon stock solution. The stock solution was made by dissolving the required amount of anhydrous potassium biphthalate, $C_8H_5KO_4$ (Nacalai Tesque, Kyoto, Japan) in DOFW. Ultra-high purity air was the carrier gas, and was supplied by Holox Company (Morrisville, NC).

During analysis, a set of standard solutions—same as those used for calibration—were included after each set of ten samples. This precautionary action to taken to monitor the possibility of sample degradation while the samples sat on the autosampler waiting to be analyzed. If the results from these check standards were not within ten percent of the original calibration solutions, these checkpoints were used instead to construct a new calibration curve. The TOC and DOC concentrations in subsequent samples were then determined using the new calibration curve. It was assumed the concentrations in all ten samples preceding the checkpoints could accurately determined using the original calibration curve.

3.6.3: Biodegradable Dissolved Organic Carbon (BDOC) Measurements

The procedures for BDOC analysis were based on the method outlined by Allgeier et al (1996). The pH of the samples was adjusted to approximately 8.0 using diluted sodium hydroxide solution or diluted hydrochloric acid solution, as appropriate. If the samples could not be analyzed immediately, they were acidified to pH 2.0 with concentrated hydrochloric acid, and refrigerated at 4°C. Because of analytical limitations, samples from only six of the seven locations in the pilot plant were conducted in duplicate.

Bioacclimatized sand was collected from the pilot plant and used as media in the BDOC analysis. Wide-mouth square French bottles with Teflon-lined caps (Krackeler Scientific Inc., Durham, NC) were used as BDOC reactors. The headspace volume to sample volume to sand weight proportion was 1.5mL:2.1mL:1g, with the weight of the wet sand being 65 $\pm$ 2 grams. The BDOC samples were shaken on an orbital shaker (Lab-line Instruments, Melrose Park, IL) at approximately 150 rpm. The incubation took place at room temperature, and lasted five days. The BDOC concentration of the water was calculated as the difference between the DOC concentration of the sample at the start of the analysis and the DOC concentration after the five-day incubation period.

3.6.4: Chlorination Under Uniform Formation Conditions (UFC)

The procedures for UFC chlorination were based on methods suggested by Summers, et. al. (1996). The samples were chlorinated at pH 8.0 $\pm$ 0.2 with sufficient chlorine to provide a free chlorine residual of 1.0 $\pm$ 0.4 mg/L Cl_2 after storage at 20 $\pm$ 1°C for 24 $\pm$ 1 hours. The stock chlorine solution was prepared by diluting 4-5% sodium hypochlorite solution. A stock chlorine solution was prepared by diluting approximately 5 mL of a 4-5% sodium hypochlorite solution (Aldrich Chemical, Milwaukee, WI) in 20 mL of DOFW. The actual concentration of the stock solution was determined by sodium thiosulfate titration in accordance with Standard Method 4500-Cl (Standard Methods, 1995). A volume of the stock solution was diluted to prepare a working chlorine solution in the range of 1000 to 1300 mg/L Cl_2. Borate was then added to buffer the solution at pH 8. As in the case of stock solution, the actual concentration of the working solution was determined by sodium thiosulfate titration in accordance with Standard Method 4500-Cl (Standard Methods, 1995).

Chlorination was conducted in 125-mL amber Boston round bottles with Teflon-lined screw caps (Laboratory Supply Distributor Inc., Mt. Laurel, NJ). The bottles were made chlorine demand-free as described above. The proper chlorine dose for a particular water sample was determined from a calibration curve developed from a preliminary chlorination experiment. In

this experiment, three samples of the test water were chlorinated at different doses under UFC conditions. After the 24-hour holding period at 20°C, the free chlorine residual in each sample was determined using a chlorine residual colorimeter (Hach Company, Loveland, CO). The results were then used to construct a calibration curve of chlorine dose against free chlorine residual, from which the requisite dose for the UFC chlorinations was determined.

Following the UFC chlorinations, each chlorinated sample was transferred to two 40-mL borosilicate vials with Teflon-lined top hat septa and screw caps for analysis of THM4 and HAA9. Both sets of vials contained approximately 60 mg of ammonium sulfate (Mallinckrodt, Paris, KY) which was used to quench residual chlorine. In the HAA9 vials, 20 μL of 10 μg/L sodium azide (Aldrich Chemical, Milwaukee, WI) was also added as a biocide if the samples were not analyzed within 24 hours. The quenched samples were refrigerated at 4°C until analysis. To ensure the criteria of the UFC test were met, temperature, pH, and free chlorine residual of the chlorinated samples were measured prior to quenching.

3.6.4.1: Trihalomethanes (THM4)

The samples were analyzed for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ using a liquid-liquid extraction procedure modified after Standard Method 6232 (Standard Methods, 1995). "THM Grade" Pentane (Burdick and Jackson, Muskegon, MI) was used as the organic solvent. Four mL of pentane containing approximately 40 μg/L of 1,2 dibromopropane (Sigma Chemical, Bellefonte, PA), which served as the internal standard that monitors repeatability of the injection, was added to 20 mL of each water sample. Approximately 6 grams of ACS grade granular sodium sulfate (Mallinckrodt, Paris, KY), previously baked at 400 °C for 24 hours, was then added to the sample vial. The vial was vortex-mixed for one minute and a period of 10 minutes was given to allow the aqueous and the organic layers to separate. A volume of the pentane layer was transferred with a pasteur pipette to 1.8 mL auto-sample vials and capped with aluminum TFE-faced seals.

A set of six THM calibration solutions (0, 5, 10, 25, 50, and 100 μg/L)was extracted in the same manner as the samples. These solutions were made from primary and secondary dilutions of EPA THM Calibration Standard cocktail (Supelco Inc., Bellefonte, PA) in DOFW. The dilutions were made by adding the proper volumes of the EPA Standard cocktail in impurity-free methanol (Burdick and Jackson, Muskegon, MI).

Sample extracts were analyzed on a Hewlett Packard model 5890A gas chromatograph (GC) with an electron capture detector (Hewlett-Packard Company, Cary, NC). The gas chromatographic conditions for THM analysis are summarized in Table 3.2. From the set of chromatograms of the calibration solutions, the retention times of the four THM species and the internal standard were determined. The peaks at these five retention times were marked and integrated to yield peak areas. A calibration curve of the relative peak area (defined as the ratio of the peak area of the THM species to the peak area of the internal standard) and THM concentration was then constructed for each of the four THM species. Using this procedure, the relative peak areas on the chromatograms of the samples were converted to their respective THM concentrations. If the difference between the internal standard peak area on the chromatogram of a sample and the average internal standard peak from the calibration curves was greater than 15%, then the sample was discarded due to unreliable injection. All THM analyses were conducted at room temperature.

During GC analysis, a 10 μg/L THM check standard solution was run after each set of ten samples. This sample was included to monitor the possibility of analyte degradation or loss of calibration while the samples sat on the autosampler waiting to be analyzed. If the check standard produced a result that was not within 15% of the corresponding calibration solutions, all samples subsequent to this point were considered unacceptable due to degradation, and were discarded.

Table 3.2. Gas Chromatographic Conditions for THM Analysis.

Column	
Type:	DB-1 column (Supelco, Bellefonte, PA)
Length:	30 m
Internal Diameter:	0.25 mm
Film Thickness:	1.0 μm
Temperature Sequence:	
10 min @ 35°C, increase to 50°C @ 5°C/min and hold for 1 min, increase to 250°C @ 10 °C/min and hold for 5 min: Total Run Time = 39.0 min	
Injector	
Injection Volume:	2 μL
Temperature:	180°C
Detector	
Type:	Electron capture
Temperature:	280°C
Gases	
Carrier Gas:	Helium (Holox, Morrisville, NC)
Carrier Flow:	1.5 mL/min @ 35°C
Makeup Gas:	Nitrogen (Holox, Morrisville, NC)

3.6.4.2: Haloacetic Acids (HAA9)

All nine halogenated acetic acid species were analyzed using a liquid-liquid extraction procedure based on Standard Method 6251B (Standard Methods, 1995) and EPA Method 552 (US EPA, 1990). The procedure consisted of three parts: diazomethane generation, extraction, and derivatization. Diazomethane was generated in an assemblage—consisting of two separable concentric glass tubes, o-ring seal, and clamp—placed in ice. The inner tube could be closed with a Teflon-lined screw cap, and had an outlet hole on its shaft to allow gas transfer into the outer tube when the two units were joined together. Approximately three mL of ultra-Resi grade methyl tertiary-butyl ether (MtBE) (JT Baker, Phillipsburg, NJ) was added to the outer tube. One mL of MtBE and one mL of carbitol (Aldrich Chemical, Milwaukee, WI) were added to the inner tube. Approximately 200 mg of diazald (Aldrich Chemical, Milwaukee, WI) was then added to the inner tube. With the screw cap intact on the inner tube, and both tubes securely clamped together, the contents of the inner tube were mixed carefully and not allowed to drip into the outer tube. Approximately 1.5 mL of 45% KOH (JT Baker, Phillipsburg, NJ) was added to the inner tube. Diazomethane was generated in gaseous form in the inner tube, escaped through the outlet

hole, and passed into the MtBE solvent in the outer tube. After 45 minutes of generation, the diazomethane solution was collected and refrigerated at 4°C until the derivatization procedure was performed. All glassware used in the diazomethane generation process was soaked in a 5 N NaOH bath for 24 hours to destroy unreacted diazald and residual diazomethane prior to the general cleaning procedures described above.

Prior to extraction, the samples were allowed to equilibrate to room temperature after removal from refrigeration. After equilibration, 20 mL of the sample was transferred into a 40-mL glass, open-top screw-top vial with a Teflon-lined top hat silicone septum. To the sample vial, 20 µL of 20 µg/mL of 2,3-dibromopropionic acid (prepared from 1 mg/mL in MtBE solution purchased from Supelco (Bellefonte, PA)) and 2 mL of concentrated sulfuric acid were added. The 2,3-dibromopropionic acid served as the surrogate which was used to monitor the efficiency of extraction and derivatization. Because of the temperature rise due to the addition of acid, the samples were allowed to re-equilibrate to room temperature. Four mL of ultra-Resi grade MtBE (JT Baker, Phillipsburg, NJ) containing approximately 40 µg/L of 1,2,3-trichloropropane (Aldrich Chemical, Milwaukee, WI), which served as the internal standard, followed by approximately 6 grams of sodium sulfate (Mallinckrodt, Paris, KY), previously baked at 400°C for 24 hours, were then added to the sample vial. The vial was vortex-mixed for one minute and a period of 10 minutes was given to allow the aqueous and organic layers to separate. The MtBE layer was transferred with a pasteur pipette to fill a 2-mL volumetric flask with screw-cap and Teflon-lined septum to the mark for derivatization.

Approximately 50 mg of anhydrous, powdered magnesium sulfate (Aldrich Chemical, Milwaukee, WI) was added to the 2-mL flask to minimize the effect of water on the derivatization process (Brophy, et. al., 1999). After allowing the drying agent to settle, 225 µL of diazomethane solution was added to the flask, and the flask was stored in the refrigerator for approximately 15 minutes. Again, the samples were allowed to equilibrate to room temperature

after refrigeration. Approximately 0.1 gram of silicic acid (JT Baker, Phillipsburg, NJ) was added to the sample to quench residual diazomethane. A volume of the supernatant portion of the derivatized sample was then transferred to 1.8 mL auto-sample vials and capped with aluminum TFE seals.

A set of six HAA9 calibration solutions (0, 1, 5, 10, 20, 40 μg/L) was extracted in the same manner as the samples. These solutions were made from primary and secondary dilutions of EPA HAA6 which consisted of ClAA, Cl_2AA, Cl_3AA, BrAA, BrClAA, Br_2AA Calibration Standard, and $BrCl_2AA$, Br_2ClAA, and Br_3AA cocktails (all purchased from Supelco Inc., Bellefonte, PA) in DOFW. The dilutions were made by adding the proper volumes of the EPA Standard cocktails in impurity-free methanol (Doe & Ingalls, Durham, NC).

Derivatized sample extracts were analyzed on a Hewlett Packard model 5890A GC with an electron capture detector (Hewlett-Packard Company, Cary, NC). The gas chromatographic conditions for HAA analysis are summarized in Table 3.3. From the set of chromatograms of the calibration solutions, the retention times of the nine HAA species, the internal standard, and the surrogate were determined. The peaks at these eleven retention times were then marked and integrated to yield peak areas. A calibration curve of the relative peak area (defined as the ratio of the peak area of the HAA species to the peak area of the internal standard) against the HAA concentration was then constructed for each of the nine HAA species. Using this procedure, the relative peak areas on the chromatograms were converted to their respective HAA concentrations. If the difference between the internal standard peak or the surrogate peak on the chromatogram of a sample and their respective average peaks from the calibration curves was greater than 15%, then the sample was discarded due to unreliable extraction and/or derivatization.

During GC analysis, a 10 μg/L HAA check standard solution was included after each set of ten samples. This precautionary action was taken to monitor the possibility of sample degradation while the samples sat on the autosampler waiting to be analyzed. If the check

standard produced a result that was not within 15% of the corresponding calibration solution, all samples subsequent to the checkpoint were considered unacceptable due to degradation, and were discarded.

Table 3.3. Gas Chromatographic Conditions for HAA Analysis.

Column	
Type:	DB-1 column (Supelco, Bellefonte, PA)
Length:	30 m
Internal Diameter:	0.25 mm
Film Thickness:	1.0 μm
Temperature Sequence:	
21 min @ 37°C, increase to 136°C @ 5°C/min and hold for 3 min, increase to 250°C @ 20°C/min and hold for 3 min: Total Run Time = 52.5 min	
Injector	
Injection Volume:	2 μL
Temperature:	180°C
Split Valve opened at:	0.5 min
Detector	
Type:	Electron capture
Temperature:	300°C
Gases	
Carrier Gas:	Helium (Holox, Morrisville, NC)
Carrier Flow:	1.5 mL/min @ 37°C
Makeup Gas:	Nitrogen (Holox, Morrisville, NC)

3.7: Quality Assurance and Control (Q/A and Q/C) Guidelines

To ensure the quality of sample handling and analysis, Q/A and Q/C measures were taken. In sample handling, preservatives were used to minimize sample degradation. As for analysis, sample duplicates were analyzed when laboratory capacities were not limited and check standards were used to monitor sample degradation. The specific Q/A and Q/C measures for each analysis were described in the previous section.

For all analyses involving calibration, calibration solutions were prepared fresh on the day of analysis. In the case of TOC analysis, a new stock solution was made approximately every three months. In the case of THM analysis, a comparison of calibration chromatograms from run to run was made to monitor the quality of the primary and secondary THM solutions. If there existed a consistent trend of changes, then the primary and secondary THM solutions were

discarded and a new set of solutions was prepared. Due to the relative instability of certain HAA species, the primary and secondary HAA solutions were made fresh for each analysis. In addition, new stock HAA solutions were used approximately every three months. Examples of certificates of analysis for the THM and HAA standards are attached in Appendix B, and illustrative calibration curves and GC chromatograms are presented in Appendices C and D, respectively.

Because they were more complex and sensitive, additional Q/A and Q/C measures were taken in the case of THM and HAA analyses. Travel blanks were used to monitor sample contamination during shipment. Travel blanks were DOFW solutions with added preservatives that were the same as those used in preserving THM and HAA samples, and these were analyzed along with the actual samples. Internal standards were used to monitor the injection repeatability of the GC. A surrogate, in the case of HAA analysis, was utilized to monitor the repeatibility of the derivatization process. For both analyses, spike tests were conducted occasionally to monitor the quality of the calibration solutions. In this test, pairs of duplicate samples were divided into two groups. The samples in one group were spiked with a known DBP concentration. The difference in concentration for each set of corresponding samples from the two group was calculated. If the difference was not within 20% of the known spike, then the calibration was considered unreliable and this was recorded for the particular analysis. In general, the spike tests produced results within the 20% criteria.

As for the data, statistical analyses were conducted for each water quality parameter. Namely, the average, standard deviation, and coefficient of variance were calculated based on the three-days (two days, in the case of BDOC) collection period. In general, the results were not accepted if the coefficient of variance was greater than 20% or if an apparent trend existed for the data to change with time.

CHAPTER 4: RESULTS AND DISCUSSION

4.1: Introduction

Prior to pilot-plant operations, preliminary bench-scale coagulation studies were conducted to determine the enhanced coagulation dosage requirements for the experiments to be conducted on the pilot scale. The bench-scale studies began in July, 1998 and were completed in August 1998. Pilot-plant operations were initiated in September, 1998 and were completed in April, 1999. The pilot plant was run in both pre-ozonation and intermediate ozonation modes, as described in Chapter 3.

This chapter consists of the results and discussion of the findings from these two parts of the study. In addition, qualitative comparisons of treatment trains and other relevant observations are presented.

4.2: Preliminary Coagulation Experiments

Indianapolis water has a relatively low TOC content (about 3.1 mg/L), high alkalinity (generally above 200 mg/L as $CaCO_3$), high hardness (approximately 300 mg/L as $CaCO_3$), and a relatively low SUVA (about 2.5 L/mg-m). Jar tests conducted on this water showed that the TOC in Indianapolis water was not amenable to removal by coagulation with alum, supporting the earlier findings of White et. al (1997). An illustrative TOC coagulation profile is shown in Figure 4.1. Pertinent data from all of the coagulation experiments can be found in Appendix E.

As can be seen in Figure 4.1, only 0.4 mg/L of TOC—corresponding to approximately 18%—of the initial TOC concentration was removed by coagulation and settling even at alum doses up to 40 mg/L. Furthermore, the results from coagulation experiments in which the pH of coagulation was adjusted to 6.5 prior to alum addition indicated similar TOC removal efficiency (not shown). With this low percent TOC removal and the observation that TOC removal was less

than the "point of diminishing return" criterion of 0.3 mg/L TOC/10 mg/L alum (US EPA, 1998), turbidity removal was used to determine the required alum dose. (Turbidity was measured on-site by Malcolm Pirnie personnel.) In most cases, the requisite alum dose based on turbity removal was in range of 25 to 30 mg/L.

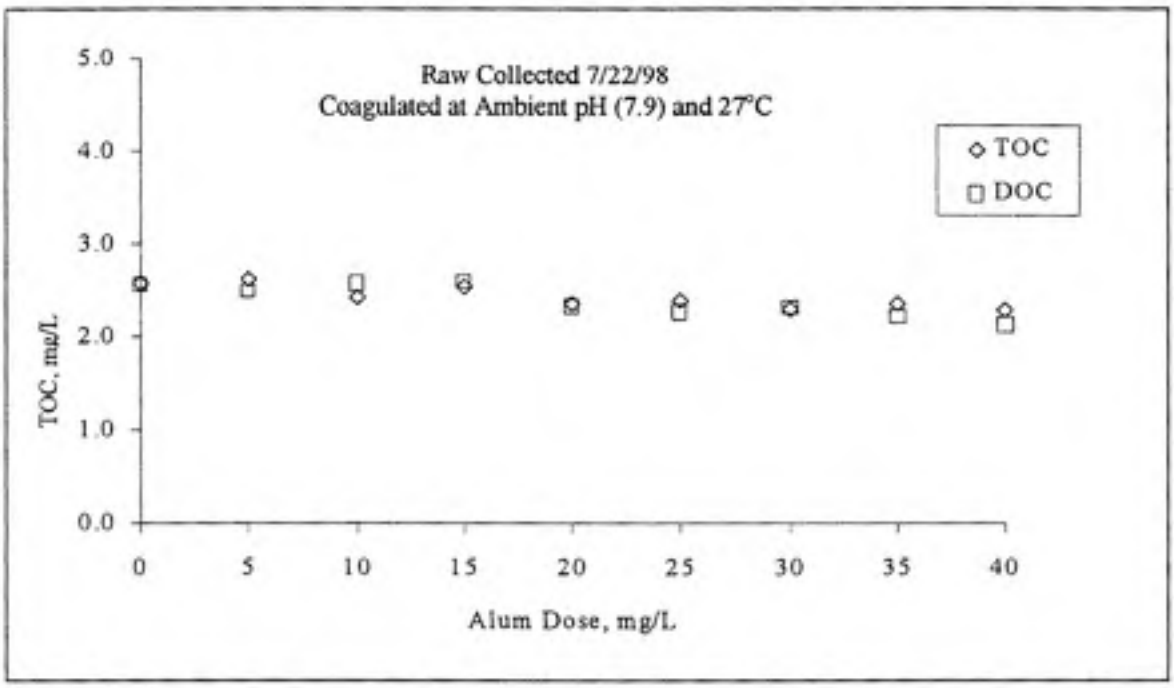

Figure 4.1. Illustrative Coagulation Results for TOC Removal.

4.3: Pilot Plant Operations

4.3.1: Pilot Plant Operation Overview

An illustrative summary of data obtained from a typical pilot plant operation is presented in Table 4.1. As noted in Chapter 3, samples were collected from seven stations of the pilot plant on three consecutive days in the third week of each pilot plant run. Filters 1 and 2 represent the GAC/sand filters and Filters 3 and 4 the anthracite/sand filters. Due to analytical constraints, samples for BDOC analysis were taken only on the first and third day of the sample collection period. It was assumed that the average of the three days (two days in the case of BDOC) represented the steady-state water quality characteristics for that sampling location. To validate

this assumption, the standard deviation and coefficient of variance were calculated for each parameter. Generally, the assumption of steady-state was considered valid if the coefficient of variance was below 20% and no trend for the data to change with time was apparent. In addition to the analytical data, the operating data and treatment targets of each pilot plant operation were also recorded. These parameters included ozone dose, target and calculated CT (ozone concentration times time) values, water temperature, and pH of ozonation and coagulation. The specific operating parameters for the nine pilot plant operations are presented in Table 4.2. It should be noted that there was no temperature control during treatment. However, the temperature difference between the raw and filtered waters was generally less than 2 °C. It also should be noted that the applied alum doses were generally higher than those estimated in the preliminary coagulation experiments. The increase is attributed to the seasonal variability in the water turbidity and temperature. Summaries from all nine pilot-plant operations can be found in Appendix F.

Table 4.1. Illustrative Summary of Experimental Data.

Experiment : 5 01/19/99-01/21/99

Operating Objectives: Pre-ozonate at ambient pH for 1 log Cryptosporidium, coagulate at ambient pH

Operating conditions	1/19/99	1/20/99	1/21/99
Ozone dose, mg/L	2.36	3.29	1.79
Target CT, mg-min/L	2.24	2.24	2.24
Calc CT, mg-min/L	2.01	2.17	1.74
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	45	45	41
pH of coagulation	7.2	7.1	7.1
pH of ozonation	7.8	7.6	7.6
Temp of raw water, °C	4	4	3
Avg Temp of effluent water, °C	5	6	6

Water Quality Characteristics

Turbidity, NTU	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	13.9	19.4	26.7	20.0	6.4	32%
Ozonated	13.5	18.1	24.4	18.7	5.5	29%
Settled	6.7	6.6	9.0	7.4	1.4	18%
Filter 1	0.26	0.34	1.9	0.83	0.91	110%
Filter 2	0.20	0.35	2.5	1.0	1.3	127%
Filter 3	0.56	0.85	2.0	1.1	0.8	68%
Filter 4	0.49	0.40	0.85	0.58	0.24	41%

Table 4.1. Cont'd

TOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	4.6	3.7	4.0	4.1	0.4	10%
Ozonated	5.0	4.3	4.9	4.7	0.4	9%
Settled	3.8	3.8	4.3	3.9	0.3	7%
Filter 1	2.9	2.8	3.1	2.9	0.2	7%
Filter 2	2.9	3.0	3.2	3.0	0.2	6%
Filter 3	2.9	3.0	3.3	3.1	0.2	6%
Filter 4	2.9	3.1	3.6	3.2	0.4	11%

DOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	3.9	3.6	4.1	3.9	0.2	5%
Ozonated	4.5	4.4	5.1	4.7	0.4	9%
Settled	3.7	3.8	4.4	4.0	0.4	10%
Filter 1	2.8	2.9	3.0	2.9	0.1	5%
Filter 2	2.8	3.0	3.2	3.0	0.2	6%
Filter 3	2.9	3.1	3.3	3.1	0.2	8%
Filter 4	2.9	3.3	3.6	3.2	0.4	11%

UV absorbance at 254 nm, cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.103	0.106	0.132	0.114	0.016	14%
Ozonated	0.060	0.061	0.077	0.066	0.010	14%
Settled	0.035	0.04	0.038	0.038	0.003	7%
Filter 1	0.031	0.037	0.035	0.034	0.003	9%
Filter 2	0.032	0.036	0.037	0.035	0.003	8%
Filter 3	0.035	0.036	0.036	0.036	0.001	2%
Filter 4	0.035	0.037	0.042	0.038	0.004	9%

UV absorbance at 272 nm, cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.083	0.085	0.109	0.092	0.014	16%
Ozonated	0.043	0.042	0.055	0.047	0.007	16%

BDOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	Q	N/A	1.2	1.2		
Ozonated	1.1	N/A	2.3	1.7	0.8	50%
Settled	1.2	N/A	1.7	1.4	0.3	24%
Filter 1	0.9	N/A	1.1	1.0	0.2	18%
Filter 2	1.0	N/A	1.3	1.1	0.2	18%
Filter 3	1.0	N/A	1.3	1.2	0.2	18%
Filter 4	1.1	N/A	1.6	1.4	0.4	26%

UFC THM4, µg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	130	139	167	145	19	13%
Ozonated	74	96	116	95	21	22%
Settled	70	51	60	60	9	16%
Filter 1	46	49	55	50	5	10%
Filter 2	48	43	48	47	3	6%
Filter 3	49	45	53	49	4	8%
Filter 4	49	46	54	50	4	8%

UFC HAA9 , µg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	106	110	139	118	18	15%
Ozonated	74	74	95	81	12	15%
Settled	37	42	58	46	11	24%
Filter 1	31	31	40	34	5	15%
Filter 2	29	34	43	35	7	20%
Filter 3	32	36	46	38	7	19%
Filter 4	35	35	45	38	6	15%

Δ UV272 , cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.033	0.028	0.035	0.032	0.004	11%
Ozonated	0.012	0	0	0.012	0.004	28%

Cl_2 consumed, mg/L-Cl_2	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	7.0	7.6	7.6	7.4	0.3	5%
Ozonated	6.8	7.1	7.4	7.1	0.3	4%

Note: N/A implies the sample was not analyzed for that particular parameter
Q implies the analytical data is questionable.

Table 4.2. Operating Parameters and Treatment Targets for the Nine Pilot-Plant Operations.

Exp #	Target CT, min-mg/L	Actual CT, min-mg/L	Ozone Dose, mg/L	Alum Dose, mg/L	pH of Ozonation	pH of Coagulation
1	0.08	0.14	1.1	42	8.0	7.8
2	0.12	0.40	0.7	29	6.5	6.5
3	2.24	2.56	2.8	23	6.3	6.4
4	2.24	2.80	2.4	21	6.3	6.5
5	2.24	1.98	2.5	44	7.7	7.1
6	2.24	2.32	3.0	37	7.4	7.8
7	0.23	0.73	0.8	26	7.9	7.7
8	3.36	4.27	2.6	30	7.9	7.6
9	3.36	3.01	2.3	30	8.1	7.8

The raw water quality characterics for the nine pilot-plant operations are presented in Table 4.3. The range of variability in the TOC and DOC concentrations from experiment to experiment was from 2.5 to 4.4 mg/L. Turbidity and temperature exhibited a wider range of variability. The ranges for the two parameters were 8.6 to 31.8 NTU and 3.7 to 20.5 °C, respectively. Because of these differences, direct quantitative comparisons among the different experiments was limited. As for variability within the three-day collection period, except for turbidity, the measured raw water quality parameters exhibited low standard deviations (not shown). Though not tabulated, the ambient bromide concentration in the raw water was on the order of 25 μg/L.

Table 4.3. Raw Water Quality Characteristics for the Nine Pilot-Plant Experiments.

Exp #	Temperature, °C	Turbidity, NTU	TOC, mg/L-C	DOC, mg/L-C	UV-254 Abs, cm^{-1}	SUVA, $Lmg^{-1}m^{-1}$
1	20.5	31.8	3.1	2.8	0.080	2.9
2	16.7	18.4	2.6	2.7	0.082	3.0
3	10.7	9.6	3.9	4.4	0.094	2.1
4	12.5	17.4	3.1	2.5	0.081	3.2
5	3.7	20	4.1	3.9	0.114	2.9
6	7.3	18.7	2.8	2.7	0.101	3.7
7	5.7	8.6	2.5	2.5	0.072	2.9
8	8.3	17.8	2.5	2.6	0.064	2.5
9	10.7	26.3	2.9	3.0	0.067	2.2

Note: UV-254 Absorbance of raw water in experiment 2 was estimated from UV272 vs UV254 Correlation.

4.3.2: Results from Pre-Ozonation Experiments

4.3.2.1: Turbidity Removal

The turbidity profiles for the six pre-ozonation experiments are shown in Figure 4.2. The average turbidity of the raw water ranged from 9.6 to 31.8 NTU (see Table 4.3). This variability was observed from experiment to experiment as well as during the sample collection period, as indicated by the large "error" bars in the figure. This type of fluctuation is common for 'run of the river' water with no upstream storage or equalization facilities.

The turbidity of the settled and filtered water ranged from 2.7 to 8.2 NTU and 0.17 to 2.7 NTU, respectively. (The filtered water quality shown in Figure 4.2 and subsequent Figures is the average from all four filters.) The high ends of these two ranges reflect difficulties encountered in operating the pilot plant. In terms of removal targets, the pilot plant was not able to reliably meet settled and filtered water turbidity goals of 2.0 and 0.1 NTU, respectively.

It should be noted that the only chemical added for coagulation was alum. It was decided in the study design that polymers or other coagulants were not to be used as aids for coagulation or filtration so as not to introduce another variable that could potentially affect DBP precursor removal. During winter months, operation of the pilot plant to achieve low settled and filtered water turbidities was especially challenging when limited to chemical treatment with alum. By comparison, the full-scale plant fed polymer to raw and settled water nearly 50% of the time in January, February, and March 1999.

The turbidity profiles of the four biofilters are illustrated in Figure 4.3. This figure shows the results from experiments 3 and 4, the experiments in which ozonation and coagulation were conducted at approximately pH 6.5, and the ozone dose was based on one log inactivation of Cryptosporidium. The influent pH to one GAC/sand column and one anthracite/sand column was adjusted to approximately 7.1, while the other pair was operated at the pH of coagulation. Under these operating conditions and given the

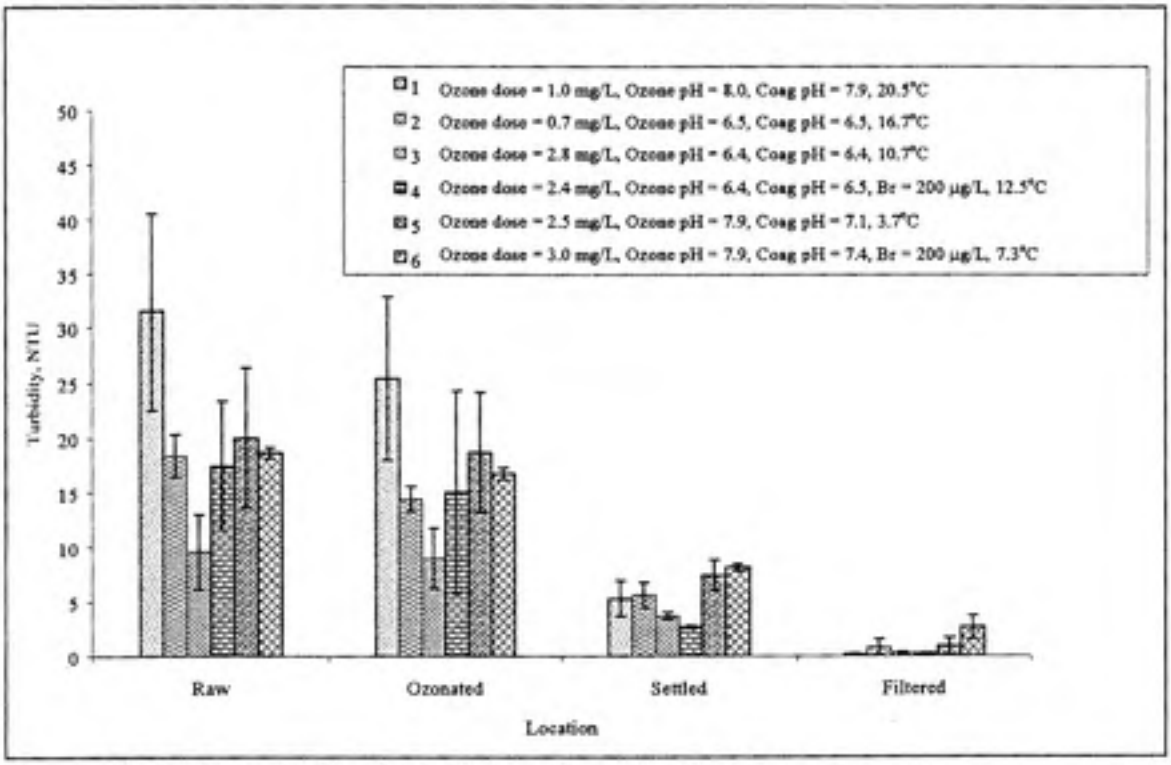

Figure 4.2. Turbidity Profiles for the Six Pre-Ozonation Experiments.

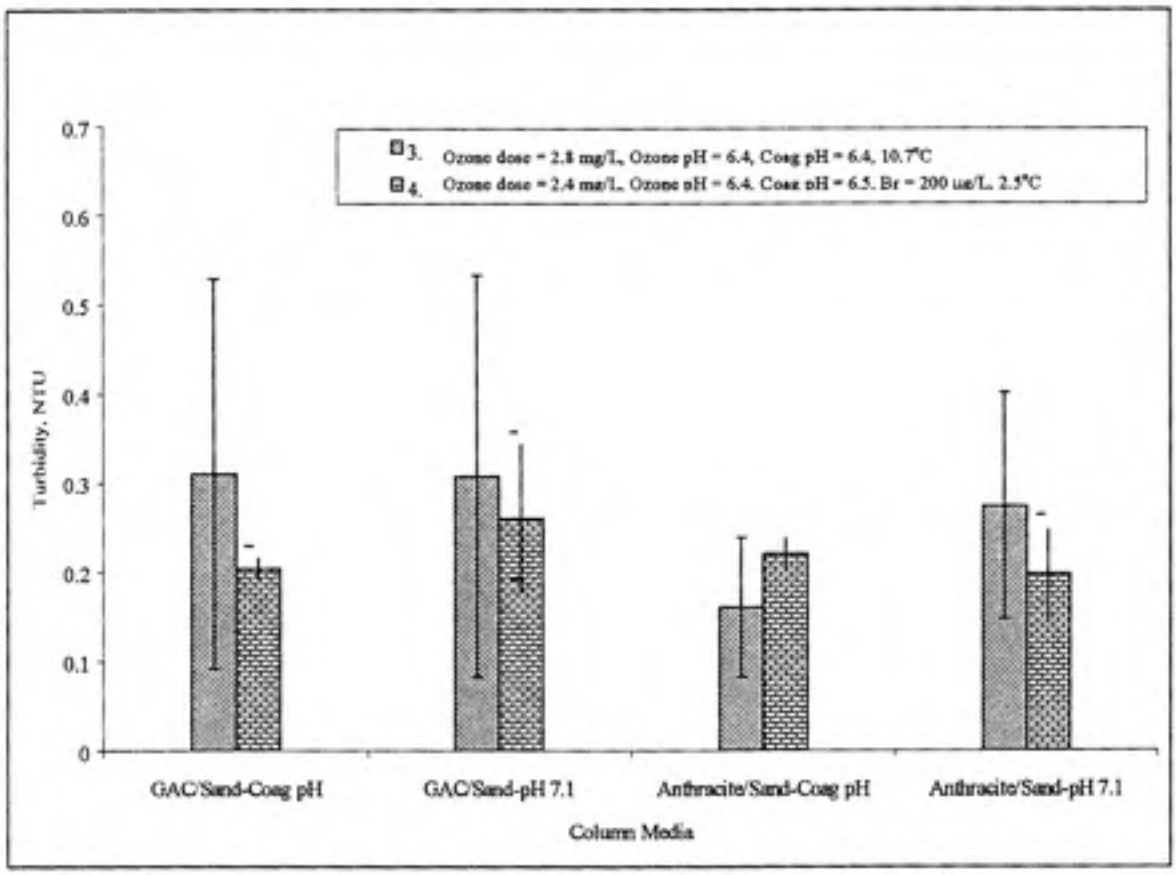

Figure 4.3. Comparison of Filtered Water Turbidity With Different Filter Media.

variability in effluent turbidity for the four columns, the two different types of filter media and the pH of filtration did not appear to significantly influence turbidity removal.

4.3.2.2: TOC and DOC Removal

TOC and DOC profiles for the pre-ozonation experiments are shown in Figures 4.4 and 4.5, respectively. In both cases, for all the experimental runs, the profiles show little change with treatment, suggesting that the raw water contains organic material that is not very amenable to coagulation. This observation is consistent with the jar test results, as well as the work of White, et. al (1997). The degree of TOC and DOC removal was approximately the same for all six experiments, indicating that TOC and DOC removal were not significantly affected by differences in ozone dose or pH of ozonation and coagulation.

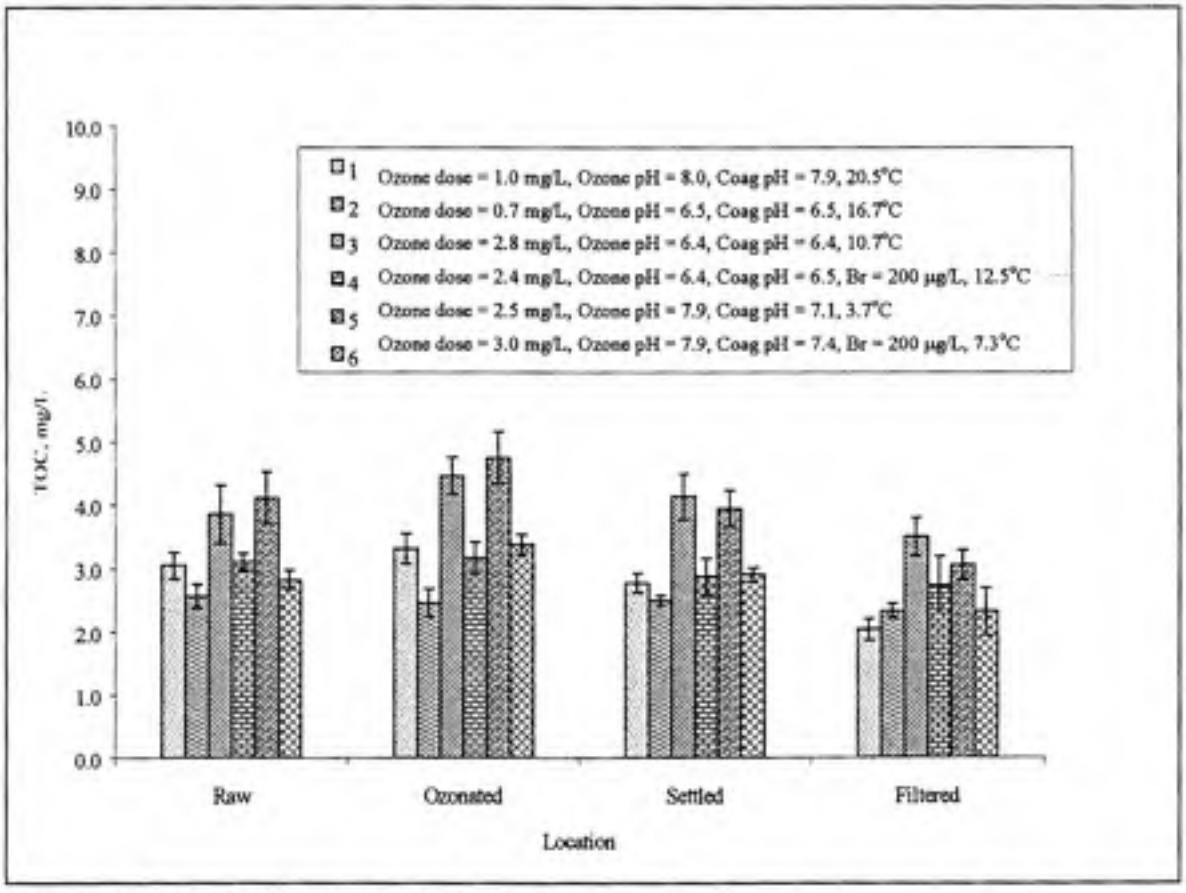

Figure 4.4. TOC Profiles for the Pre-Ozonation Experiments.

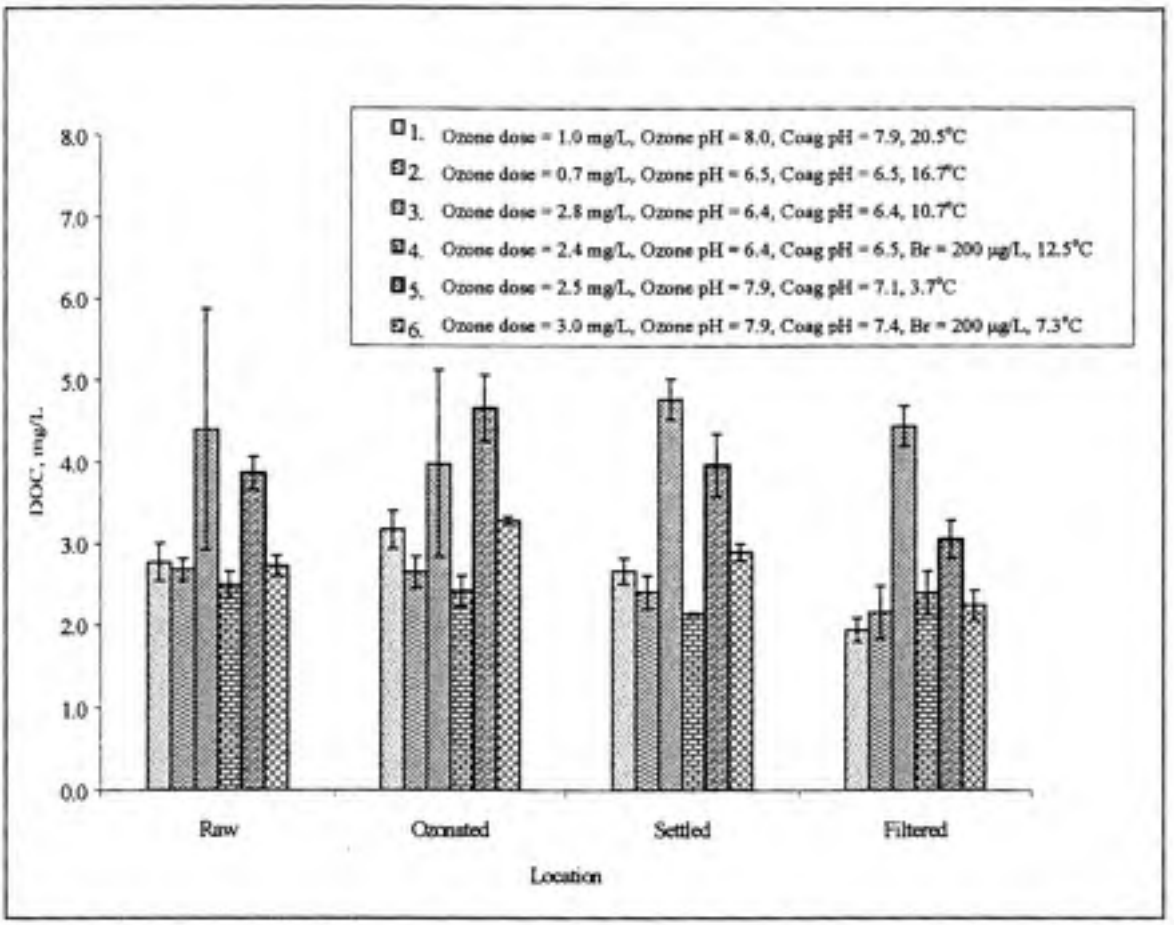

Figure 4.5. DOC Profiles for the Pre-Ozonation Experiments.

4.3.2.3: Reduction in UV-254 Absorbance

The profiles of UV absorbance at 254 nm (UV-254) for the pre-ozonation experiments are shown in Figure 4.6. The profiles show significant reduction across each treatment process, with an overall reduction of 42 to 69%. The greatest extent of reduction was observed in Experiments 3 to 6, in which the ozone doses were the highest. Within the treatment train, the highest reduction in UV absorbance occurred in the ozonation step, in which 16 to 61% of the initial UV absorbance in the raw water was eliminated. For coagulation/sedimentation and biofiltration, up to 24% and 7%, respectively, of the initial UV absorbance in the raw water was eliminated.

The reduction in UV absorbance can be used to explain the changes in organic content as a result of ozonation and coagulation. In accordance with the literature (Reckhow and Singer, 1984; Collins, et al., 1986; Edwards and Benjamin, 1992; Paralkar and Edzwald, 1996), it is believed that ozonation is responsible for cleavage of the aromatic carbon structures of NOM which are responsible for the UV absorbance at 254 nm. In the case of coagulation, the small amount of TOC that was removed was mostly hydrophobic and aromatic in nature (Hall and Packham, 1965; Babcock and Singer, 1979; Collins, et al., 1986; White, et al., 1997). Thus, the reduction in UV absorbance as a result of coagulation can be attributed to the physical removal of this NOM component.

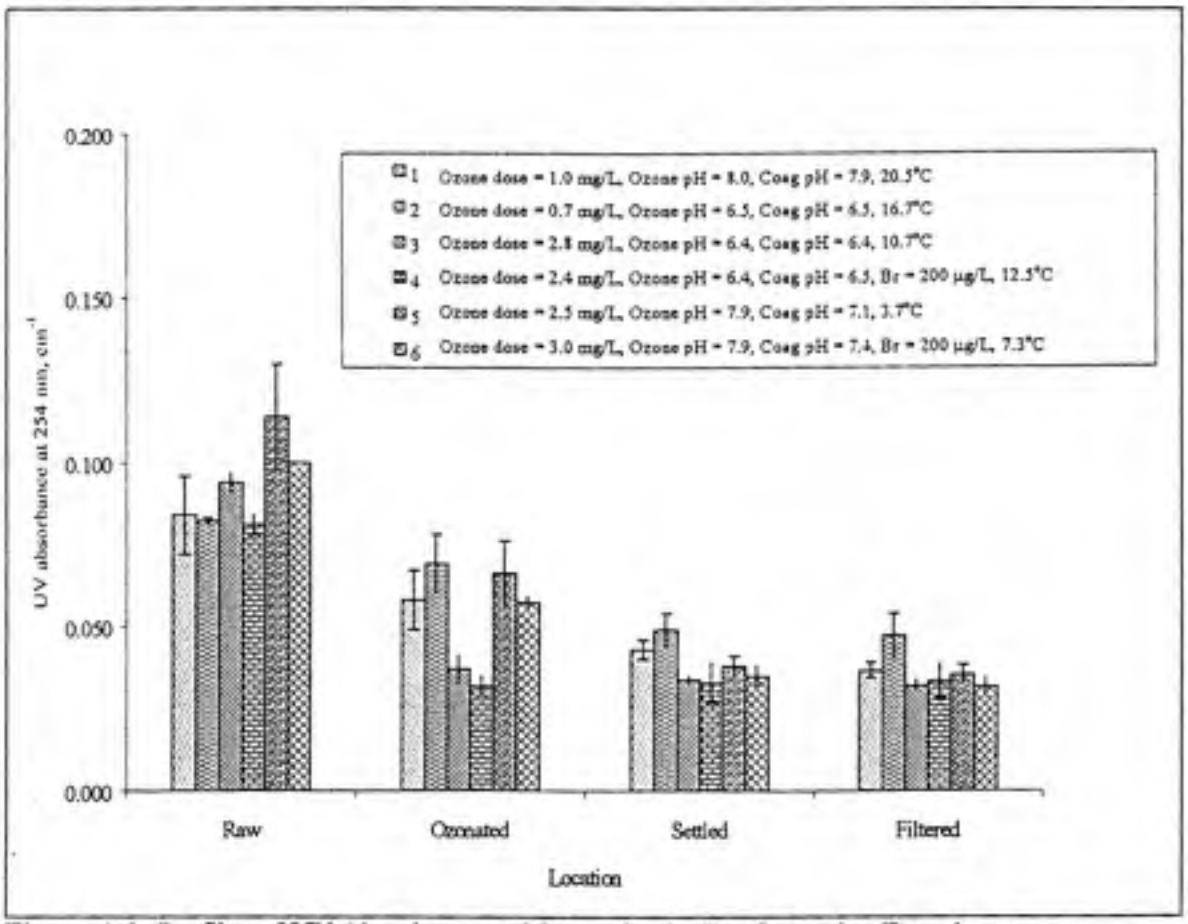

Figure 4.6. Profiles of UV Absorbance at 254 nm for the Pre-Ozonation Experiments.

4.3.2.4: BDOC Removal

The BDOC profiles for the pre-ozonation experiments are shown in Figure 4.7. The average BDOC concentration in the raw water ranged from 0.5 to 1 mg/L and represented

between 10 and 31% of the DOC content. This range is relatively high for a natural water, again perhaps because the raw water was a 'run of the river' supply with different types of seasonal inputs and variable amounts of detention time for biodegradation of background DOC to occur. Ozonation increased the BDOC level in the water by as much as 1.1 mg/L; the largest increases were observed in Experiments 5 and 6 in which high ozone doses were applied and ozonation was conducted at the higher ambient pH values. It was expected that the additional biodegradability due to ozonation could be removed by biofiltration. However, with no significant difference between the BDOC contents before and after filtration, biofiltration did not meet removal expectations.

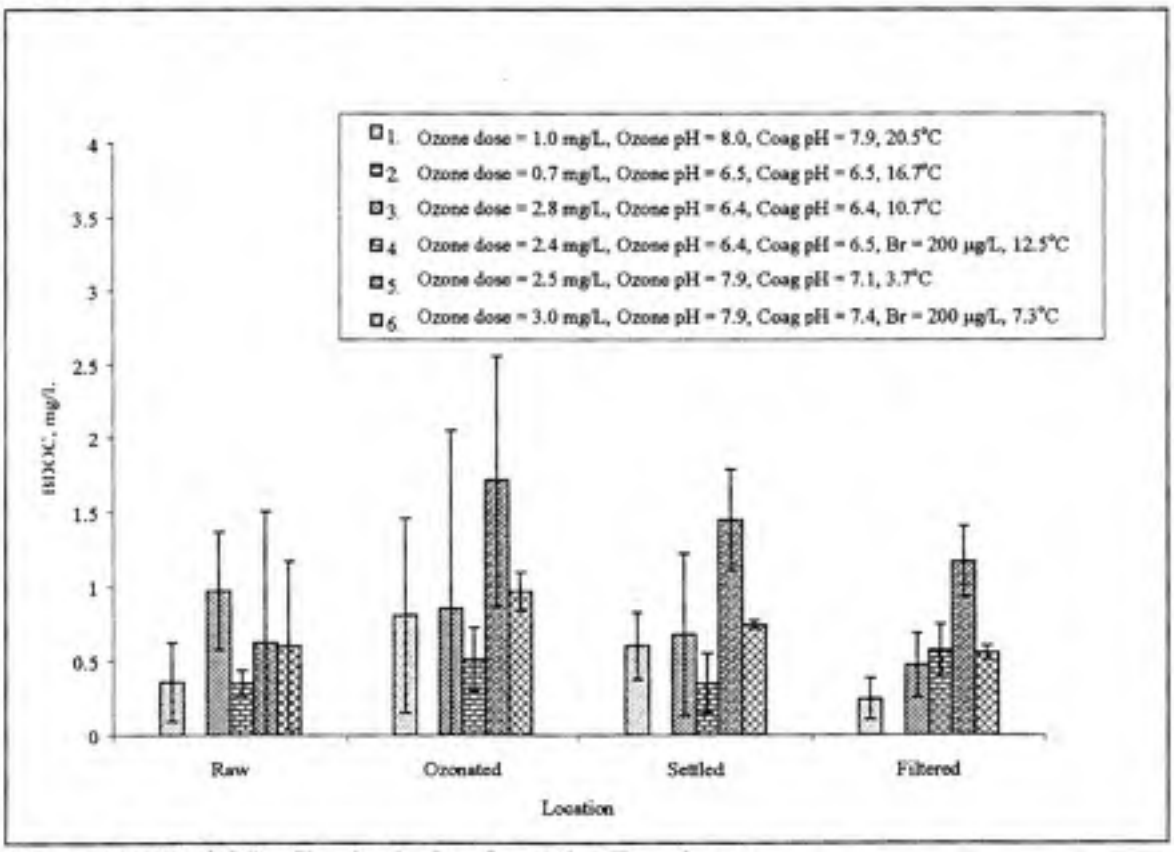

Figure 4.7. BDOC Profiles for the Pre-Ozonation Experiments.

The BDOC concentrations of the filter effluents from each of the four filters are shown in Figures 4.8 and 4.9. Figure 4.8 illustrates the results from the experiments in which ozonation

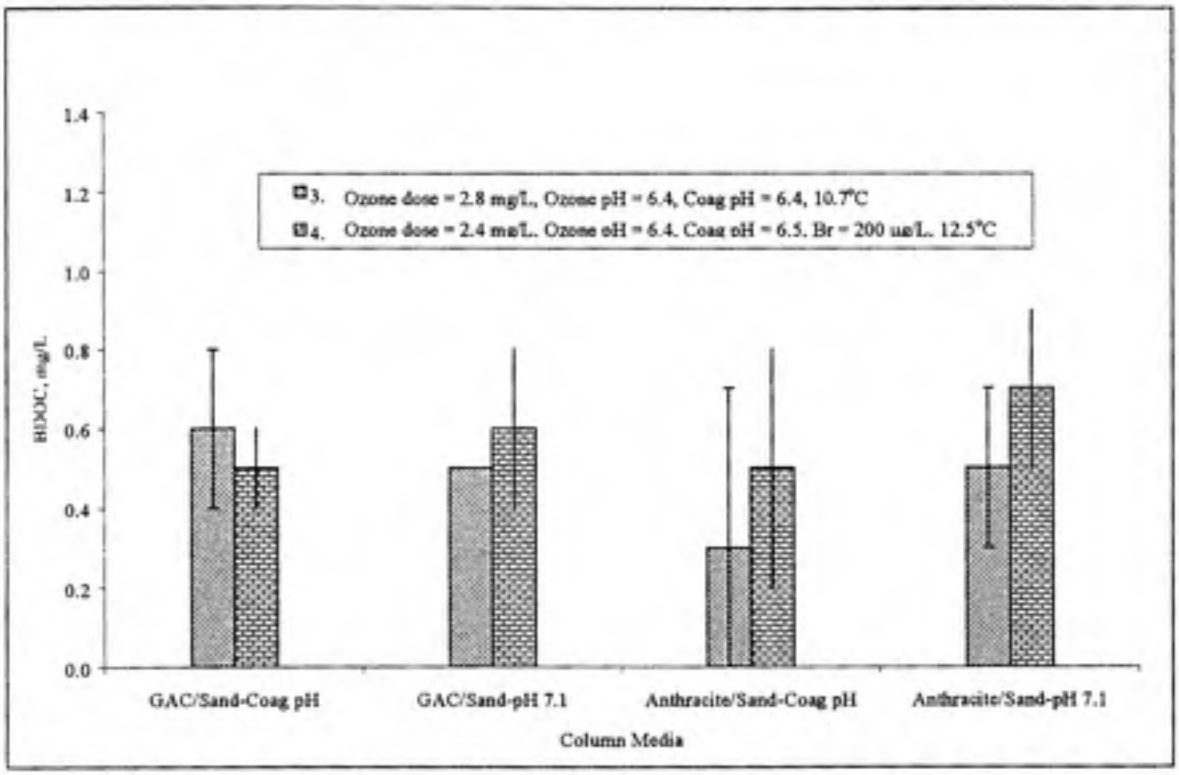

Figure 4.8. Comparison of BDOC in Filtered Water With Different Filter Media for Experiments in Which Ozonation and Coagulation were Conducted at pH 6.5.

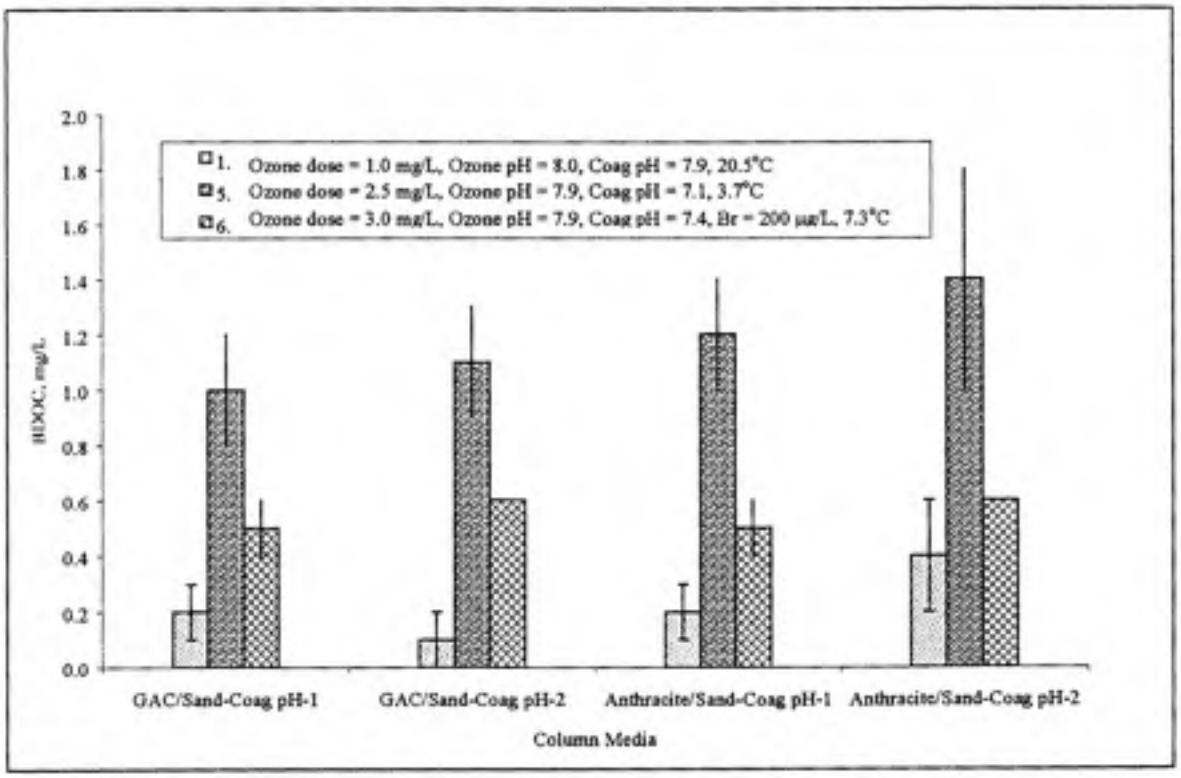

Figure 4.9. Comparison of BDOC in Filtered Water With Different Filter Media for Experiments in Which Ozonation and Coagulation were Conducted at Ambient pH.

and coagulation were conducted at approximately pH 6.5, and one column from each set of filters was pH-adjusted to approximately 7.1. Figure 4.9 shows the corresponding results for the experiments in which ozonation and coagulation were conducted at ambient pH with no adjustment to the pH of filtration. The BDOC content of the filtered water was in the range of 0.2 to 1.4 mg/L. With this amount of BDOC in the filtered water, there would be some concern regarding possible biofilm growth in the distribution system. It is unclear as to why the biofilters, in general, were not more effective in removing BDOC. A possible explanation could be the cold water temperature which has been shown to hinder biological activity (Carlson, et al., 1994; Coffey, et al., 1997). Another explanation could be the higher TOC of the raw water undergoing ozonation, particularly in Experiment 5.

Figures 4.7 to 4.9 show that there was a significant amount of variation in the measured BDOC values. In some cases, the standard deviation was as high as 0.2 mg/L, which was in the same range as the analytical uncertainty associated with the Shimadzu TOC analyzer. These discrepencies are attributed to the nature of the "simplified" BDOC analytical procedure (Allgeier, et. al, 1996), which is intensified in the case of waters with low BDOC content. Furthermore, these variations tend to obscure any differences that might exist between the different filter media and between the different pH's of filtration.

4.3.2.5: Removal of DBP Formation Potential

Trihalomethanes

The profiles for THM4 formation potential, as measured by the UFC test (see Chapter 3), for the pre-ozonation experiments are shown in Figure 4.10. Due to sample contamination, no THM analysis was conducted in Experiment 1. The average UFC THM4 concentrations in the raw water ranged from 115 to 180 μg/L, and the variability from experiment to experiment tracked the variability in TOC concentration to some degree. Overall, 51 to 66% of the THM4 precursor content of the raw water was removed. The highest removals occurred in the ozonation and coagulation stages, with each stage responsible for approximately 20% of the total removal.

The highest percentage removal of THM4 precursors occurred in Experiment 5, in which ozonation and coagulation were conducted at a pH of about 7.5, and the ozone application was targeted for 1 log Cryptosporidium inactivation. The average UFC THM4 concentrations in the filtered water ranged from 49 to 77 μg/L. Therefore, all treatment sequences were able to produce filtered water which satisfied the THM4 requirement for Stage 1 of the D/DBP Rule despite the poor overall removal of TOC. In addition, the quality of the settled water in most experiments also met the Stage 1 requirements.

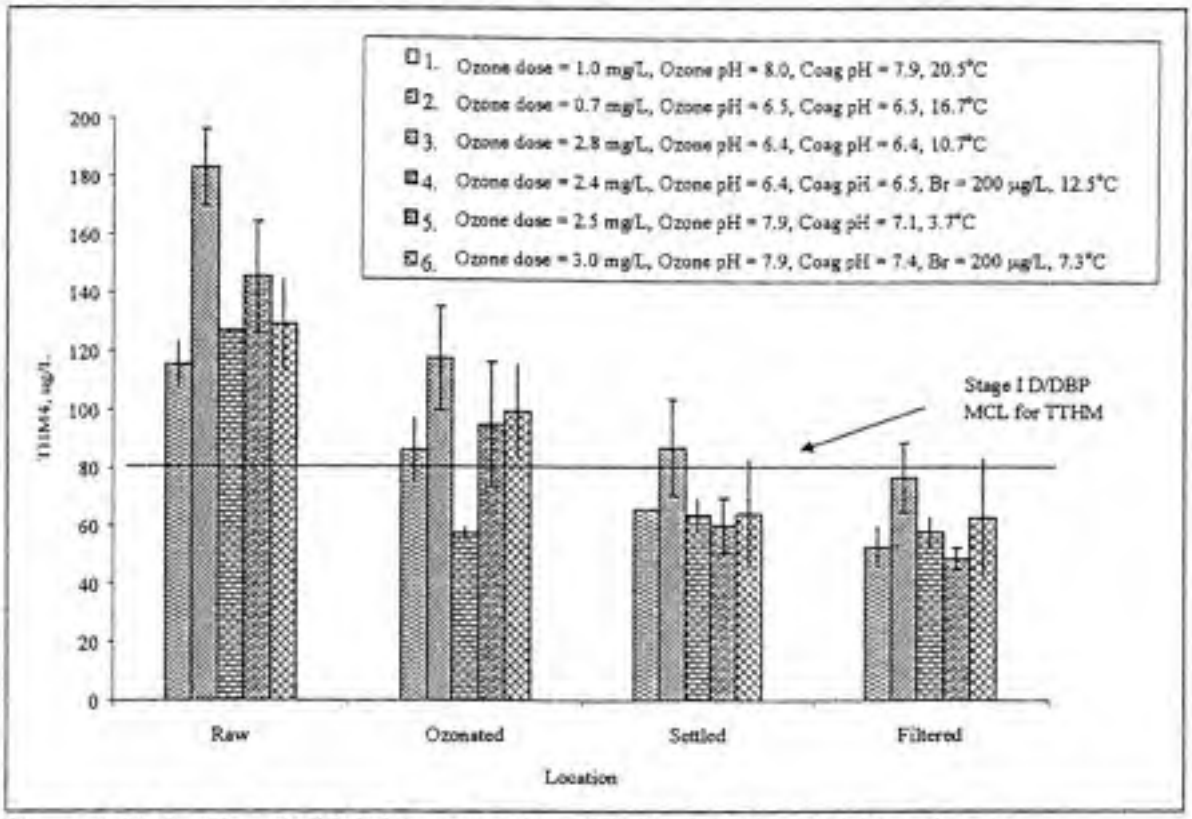

Figure 4.10. Profiles of THM4 Formation Potentials for Pre-Ozonation Experiments.

The effects of a 200 μg/L bromide spike on THM speciation in the raw and filtered water are shown in Figures 4.11A and 4.11B, respectively. In these figures, the number of top of the bar represents the UFC THM4 concentration for the particular experiment. In experiments where ozonation and coagulation were conducted at pH 6.5 (Experiments 3 and 4), $CHCl_3$ and $CHBrCl_2$ were the dominant species and represented approximately 84% and 15%, respectively, of the UFC THM4 in the raw water under ambient bromide conditions. With the bromide spike, the

relative presence of mixed bromo-chloro species became more significant, especially $CHBr_2Cl$. Specifically, the relative concentrations of $CHBrCl_2$ and $CHBr_2Cl$ increased to 30% and 31%, respectively. As for bromoform, its relative concentration increased from 1% to 6% after the bromide spike. In the case of filtered water, the shift towards bromo-substitution in THM speciation was more pronounced. Under ambient bromide conditions, the relative concentrations of $CHCl_3$, $CHBrCl_2$, and $CHBr_2Cl$ in the filtered water were approximately 68%, 23%, and 9%, respectively. With the bromide spike, the respective relative concentrations became 22%, 21%, and 38%. Furthermore, the relative concentration of bromoform rose to 19%.

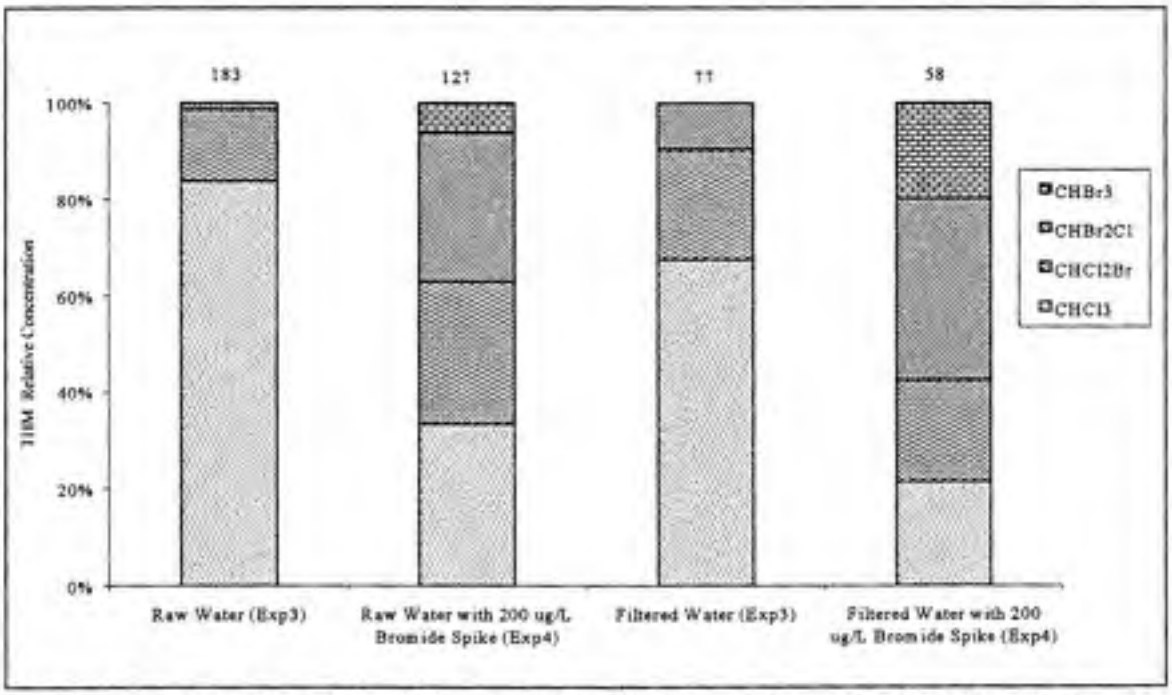

Figure 4.11A. THM Speciation in Raw and Filtered Water Before and After 200 μg/L Bromide Spike in Pre-Ozonation Experiments in Which Ozonation and Coagulation were Conducted at pH 6.5.

The bromide spike also affected THM speciation in the experiments where ozonation and coagulation were conducted at ambient pH (Experiments 5 and 6). Under ambient bromide conditions, the mixed bromo-chloro THMs represented 10% and 25% of the UFC THM4 in raw and filtered water, respectively. With the bromide spike, the respective quantities increased to 40 and 70%. The increases in relative bromoform concentration were similar to those in the previous set of experiments.

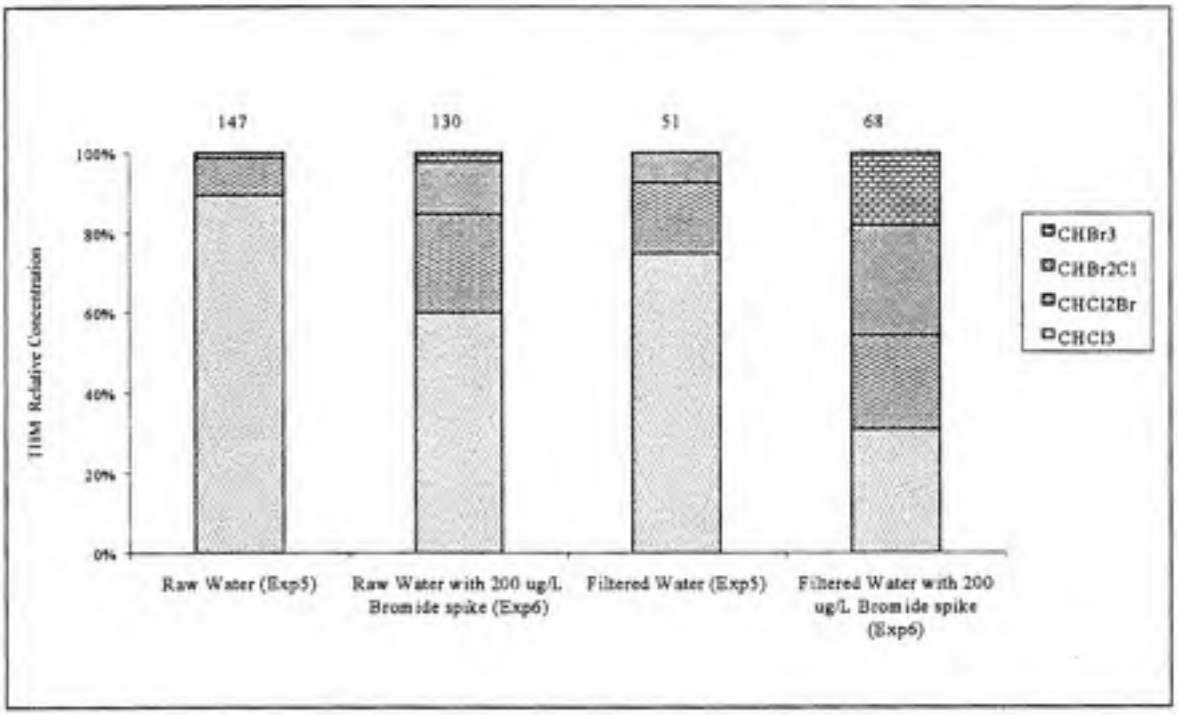

Figure 4.11B. THM Speciation in Raw and Filtered Water Before and After 200 μg/L Bromide Spike in Pre-Ozonation Experiments in Which Ozonation and Coagulation were Conducted at Ambient pH.

Haloacetic Acids

The profiles of HAA9 formation potential, as measured by the UFC test (see Chapter 3), for the pre-ozonation experiments are shown in Figure 4.12. Excluding Experiment 4, where the data were questionable, the average UFC HAA9 concentrations in the raw water ranged from 82 to 138 μg/L. The overall removal of HAA9 precursors ranged from 48% to 76%. The highest percentage removal of HAA9 precursors occurred in Experiment 1, in which ozonation and coagulation were conducted at a pH of about 7.5, and the ozone application was targeted for 0.5 log Giardia inactivation. The UFC HAA9 concentrations in the filtered water ranged from 21 to 42 μg/L. Therefore, all treatment sequences were able to produce filtered water which satisfied the HAA requirements of Stage 1 of the D/DBP Rule, despite the poor removal of TOC. As was the case for THM4, the quality of the settled water in four of the experiments also met the Stage 1 requirements for HAAs. . In terms of relative removal, ozonation and coagulation were

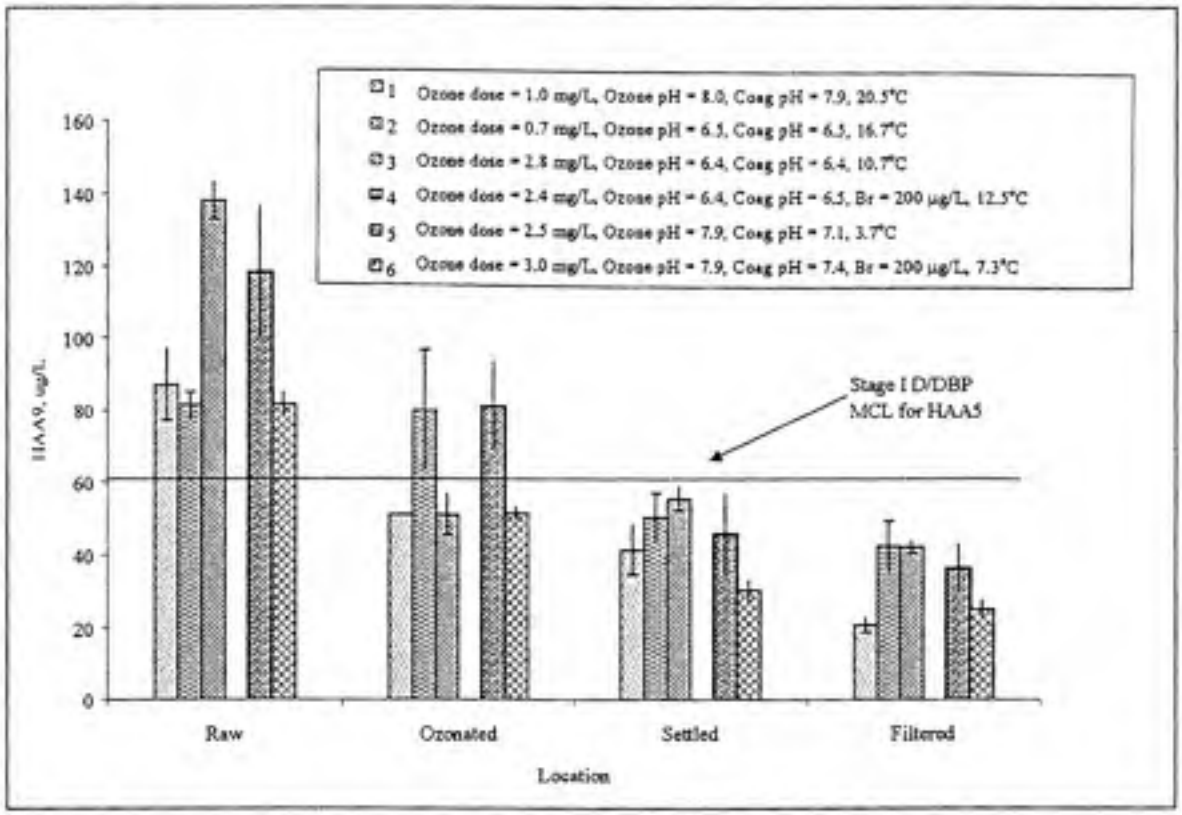

Figure 4.12. Profiles of HAA9 Formation Potentials for Pre-Ozonation Experiments.

responsible for reducing 41 to 63% and 0 to 36%, respectively, of the HAA9 formation potential in the raw water.

The effects of the 200 µg/L bromide spike on HAA speciation in raw and filtered water are shown in Figure 4.13. Under ambient bromide conditions, Cl_3AA and Cl_2AA were the dominant HAA species formed in the raw water following UFC chlorination. They accounted for approximately 93% of the HAA9 concentration, while the remaining fraction was made up of almost equally of $BrCl_2AA$ and BrClAA. With the bromide spike, the relative presence of mixed bromo-chloro species increased so that the sum of the relative concentrations of $BrCl_2AA$ and BrClAA increased to 26%. The same trend in speciation was also observed for the filtered water. Initially, the sum of $BrCl_2AA$ and BrClAA in the filtered water represented approximately 14% of the total HAA. With the bromide spike, the fraction representing the bromo-substituted species increased to 33%.

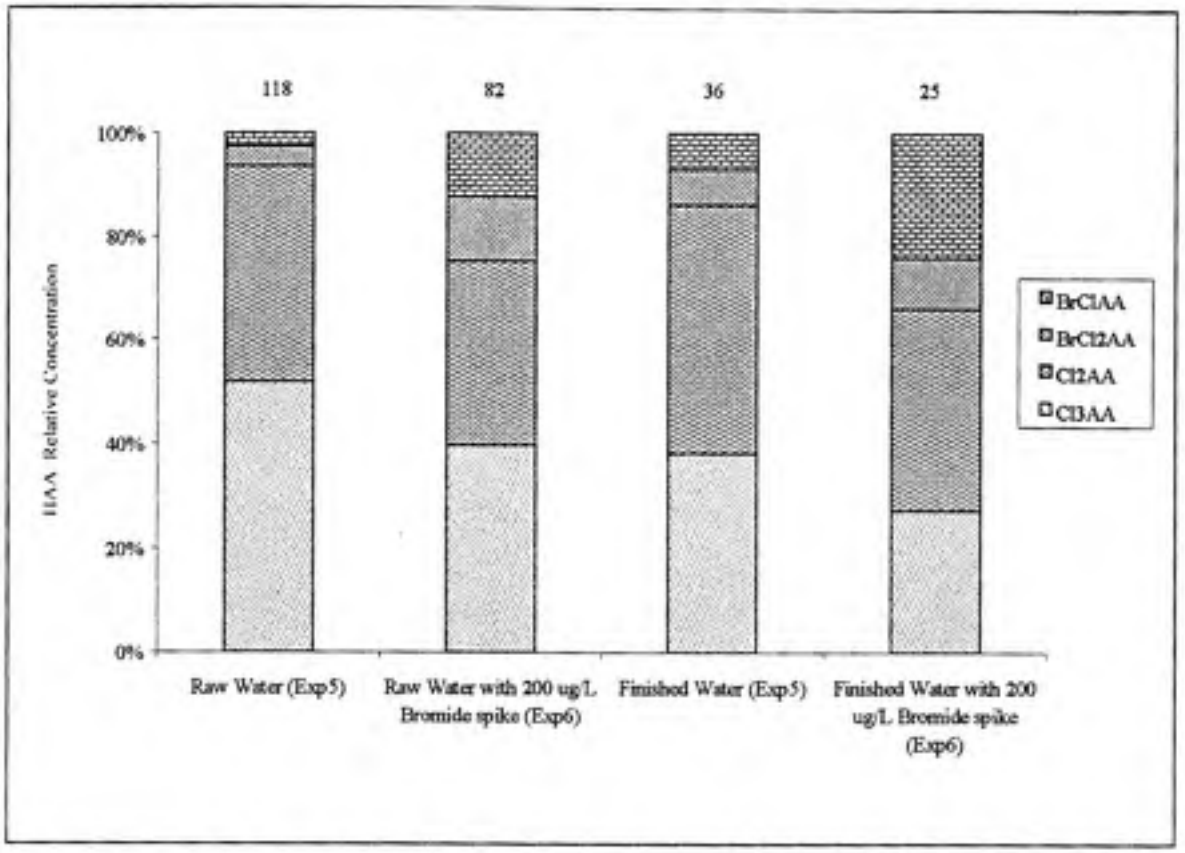

Figure 4.13. HAA Speciation in Raw and Filtered Water Before and After 200 µg/L Bromide Spike in Pre-Ozonation Experiments in Which Ozonation and Coagulation were Conducted at Ambient pH.

4.3.3: *Results from Intermediate-Ozonation Experiments*

4.3.3.1: Turbidity Removal

The turbidity profiles for the three intermediate-ozonation experiments are shown in Figure 4.14. Removal patterns similar to those observed in the pre-ozonation experiments were seen in these profiles. Appreciable variability existed from experiment to experiment as well as during the 3-day intensive sample collection period. The turbidity of the raw water ranged from 8.6 to 26.3 NTU (see Table 4.3), and the turbidity of the settled and filtered water were on the order of 6 to 10 NTU and 0.4 to 0.8 NTU, respectively. The overall removal ranged from 92 to 98%, with most of the removal occurring in the coagulation and settling step.

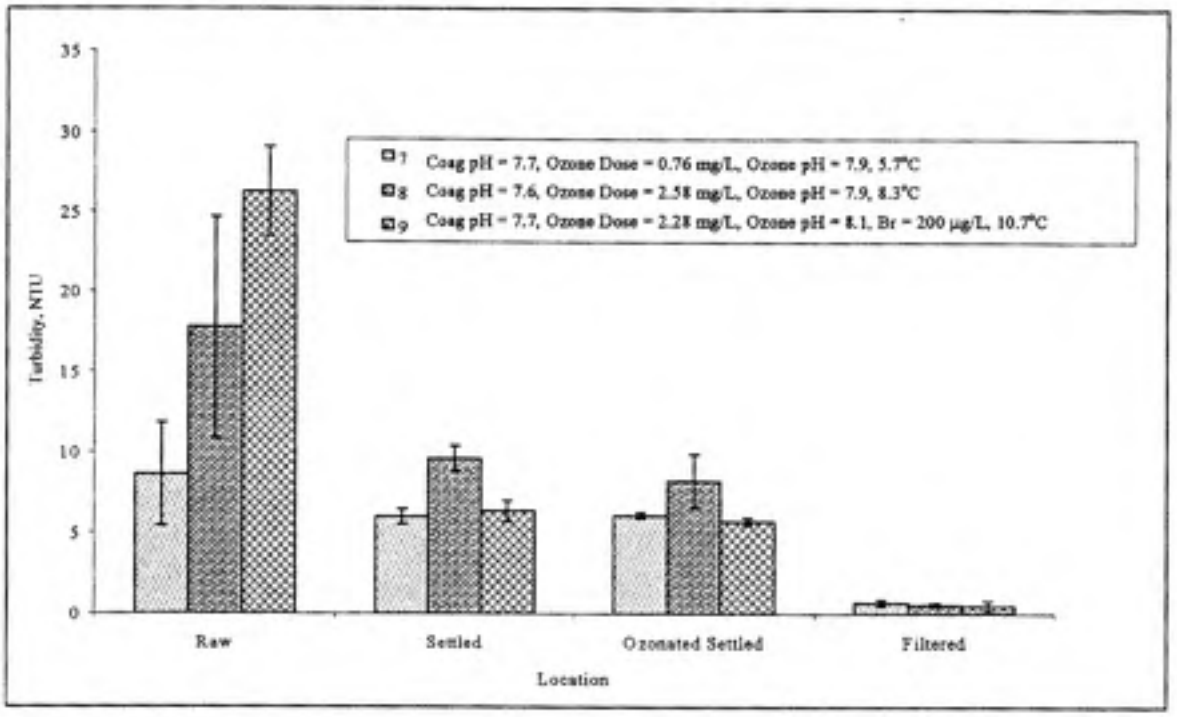

Figure 4.14. Turbidity Profiles for the Intermediate-Ozonation Experiments.

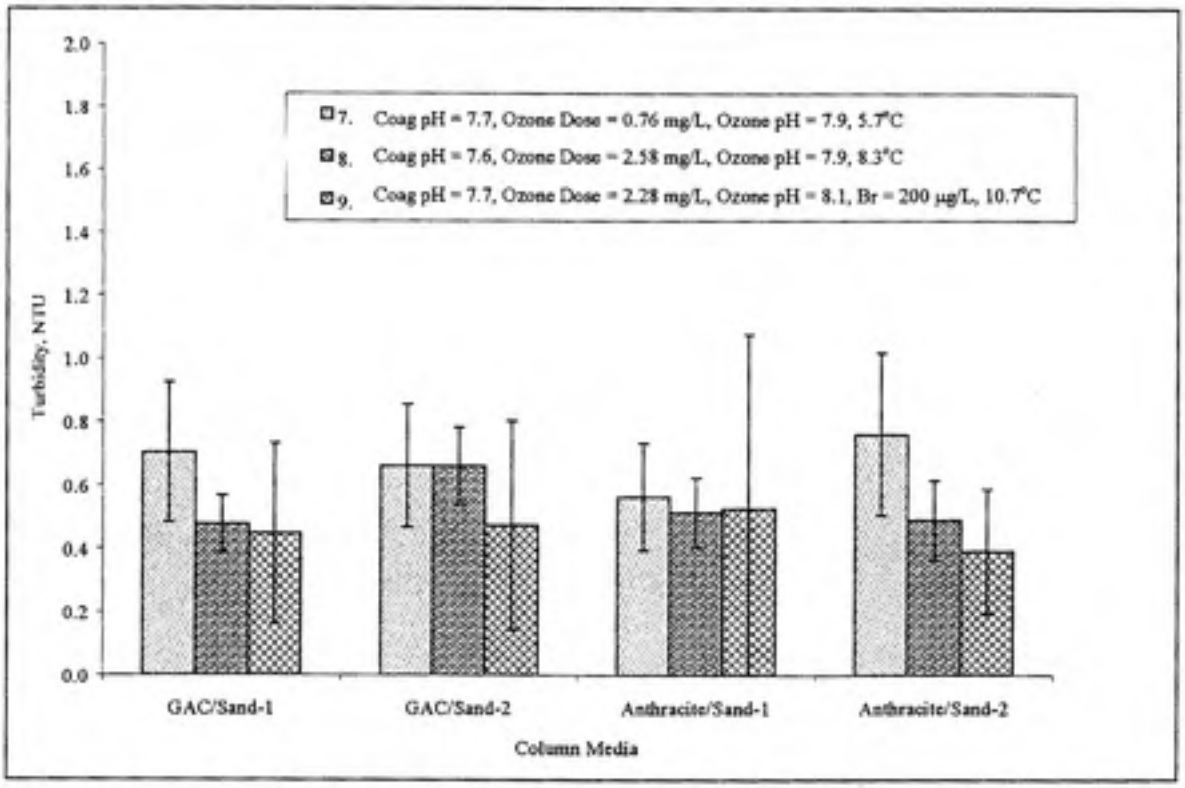

Figure 4,15. Comparison of Filtered Water Turbidity With Different Filter Media

The turbidity profiles of the four filters for the three intermediate-ozonation experiments are illustrated in Figure 4.15. Since all the experiments were conducted under the same pH, only the effects of filter media were examined. Given the similarity in effluent turbidity among the four columns for each of the three experiments, the two different types of filter media did not appear to significantly influence turbidity removal.

4.3.3.2: TOC and DOC Removal

TOC and DOC profiles for the intermediate-ozonation experiments are shown in Figures 4.16 and 4.17, respectively. The two sets of profiles exhibit similar trends to the corresponding profiles for the pre-ozonation experiments. There was little change in TOC and DOC concentrations with treatment, and the degree of removal was on the same order for all three experiments.

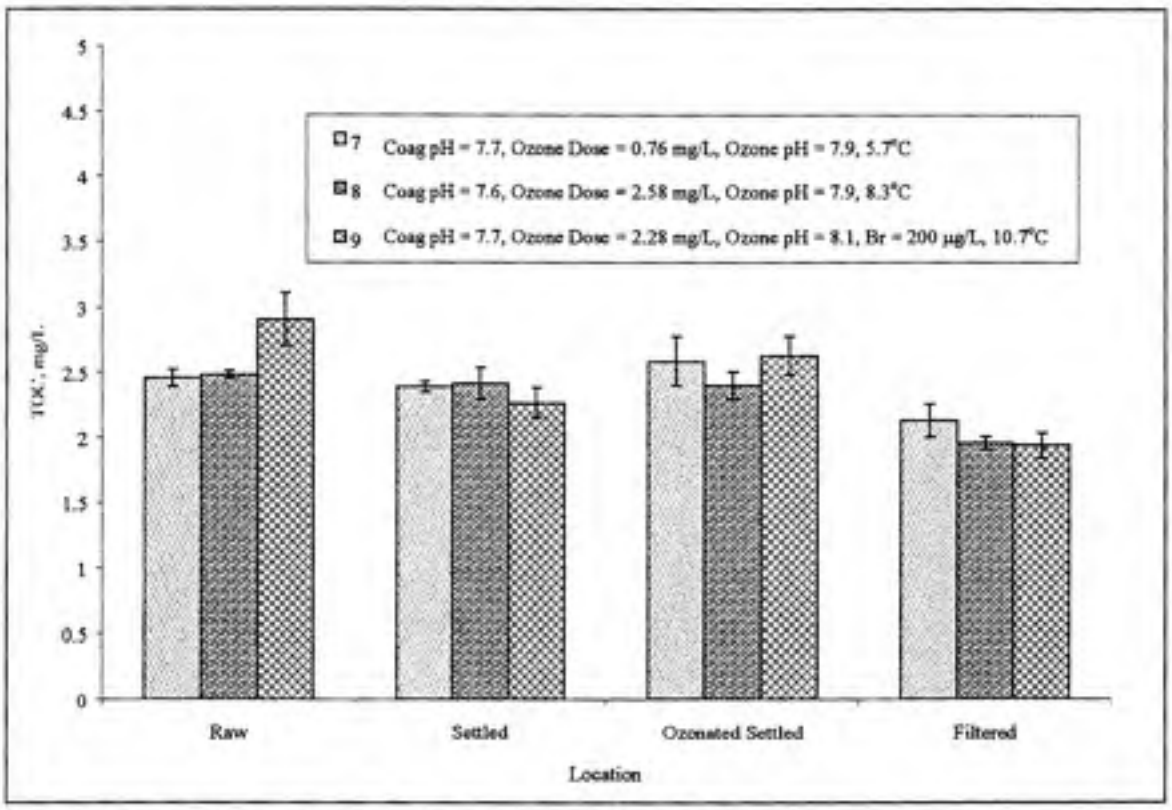

Figure 4.16. TOC Profiles for the Intermediate-Ozonation Experiments.

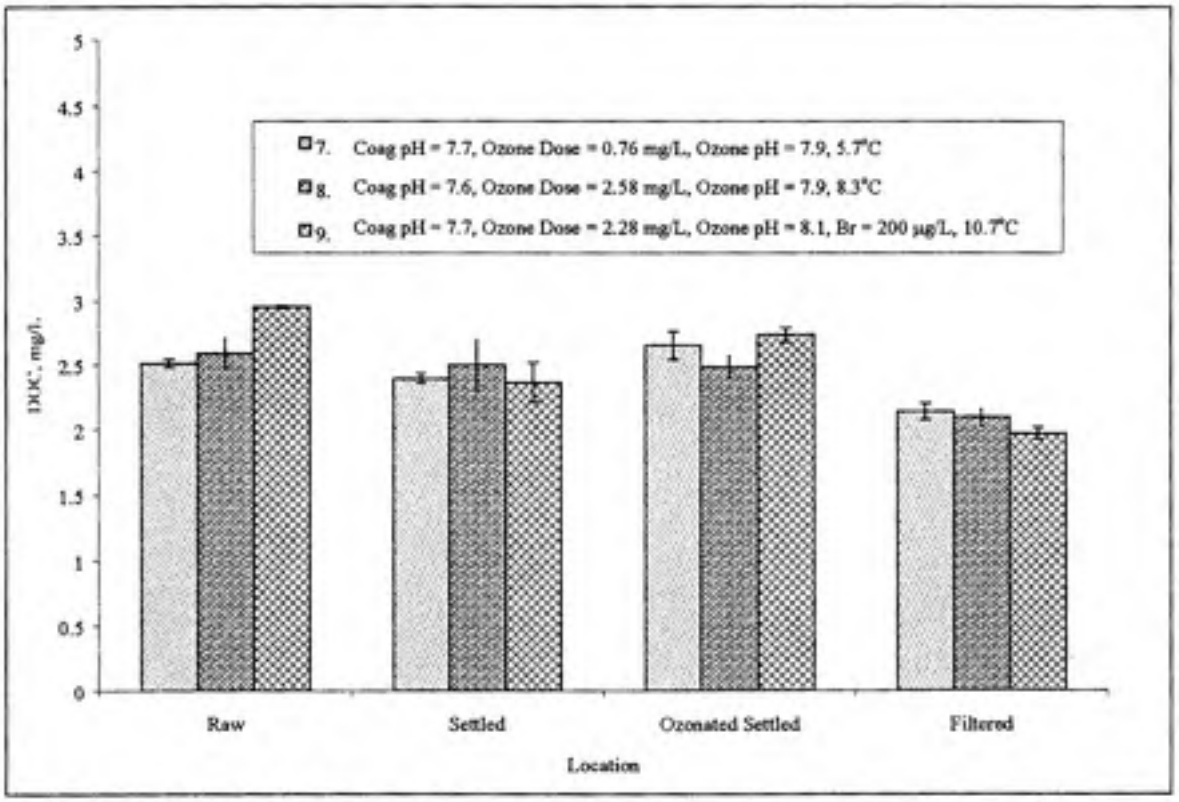

Figure 4.17. DOC Profiles for the Intermediate-Ozonation Experiments.

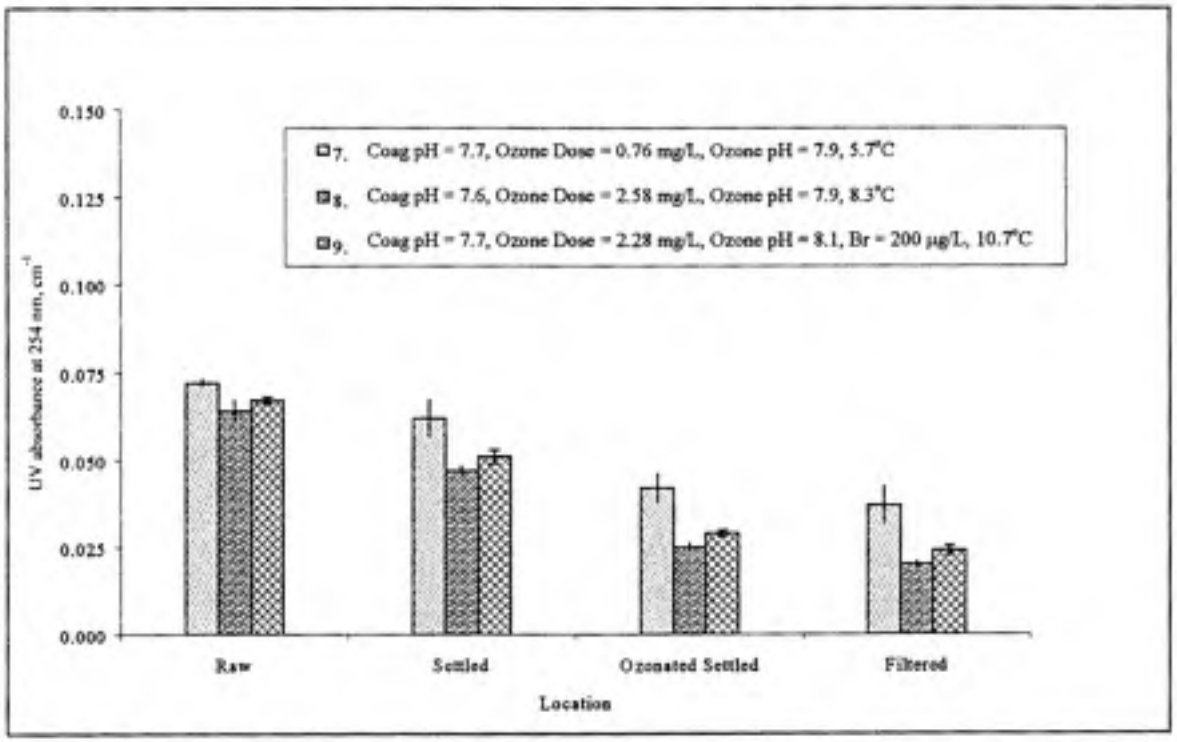

Figure 4.18. Profiles of UV Absorbance at 254 nm for the Intermediate-Ozonation Experiments.

4.3.3.3: Reduction in UV-254 Absorbance

The profiles of UV absorbance at 254 nm for the intermediate-ozonation experiments are shown in Figure 4.18. Significant reduction in UV absorbance was observed in each treatment step. The overall reduction ranged from 47 to 68%, with the highest reduction occurred in the ozonation step, ranging from 28 to 34%. As for coagulation/sedimentation and biofiltration, up to 27% and 7%, respectively, of the UV absorbance in the raw water were reduced. Lastly, in comparing these profiles with their pre-ozonation counterparts, there was no clear evidence to suggest a dependence of the reduction in UV absorbance on the position of ozonation with respect coagulation.

4.3.3.4: BDOC Removal

The BDOC profiles for the intermediate-ozonation experiments are shown in Figure 4.19. The BDOC content of the raw water ranged from 0.3 to 0.6 mg/L and represented between 8 to 20% of the DOC content. Unlike the pre-ozonation experiments, the trend in increased BDOC

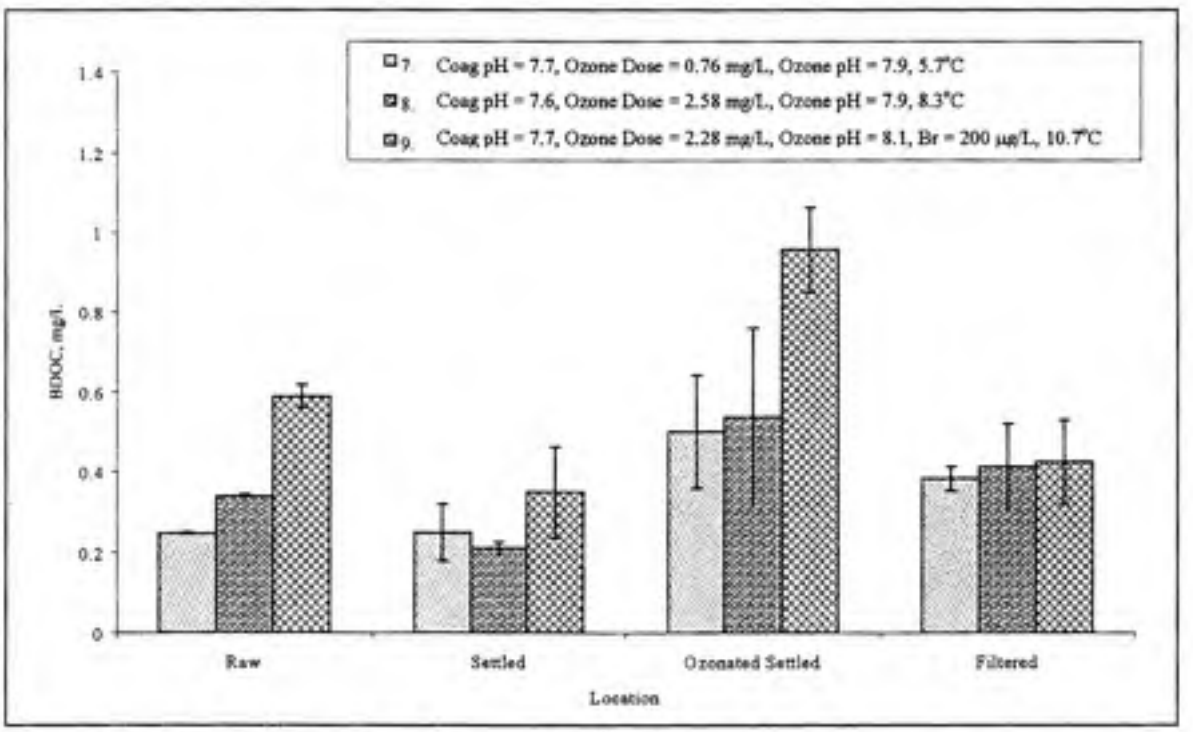

Figure 4.19. BDOC Profiles for the Intermediate-Ozonation Experiments.

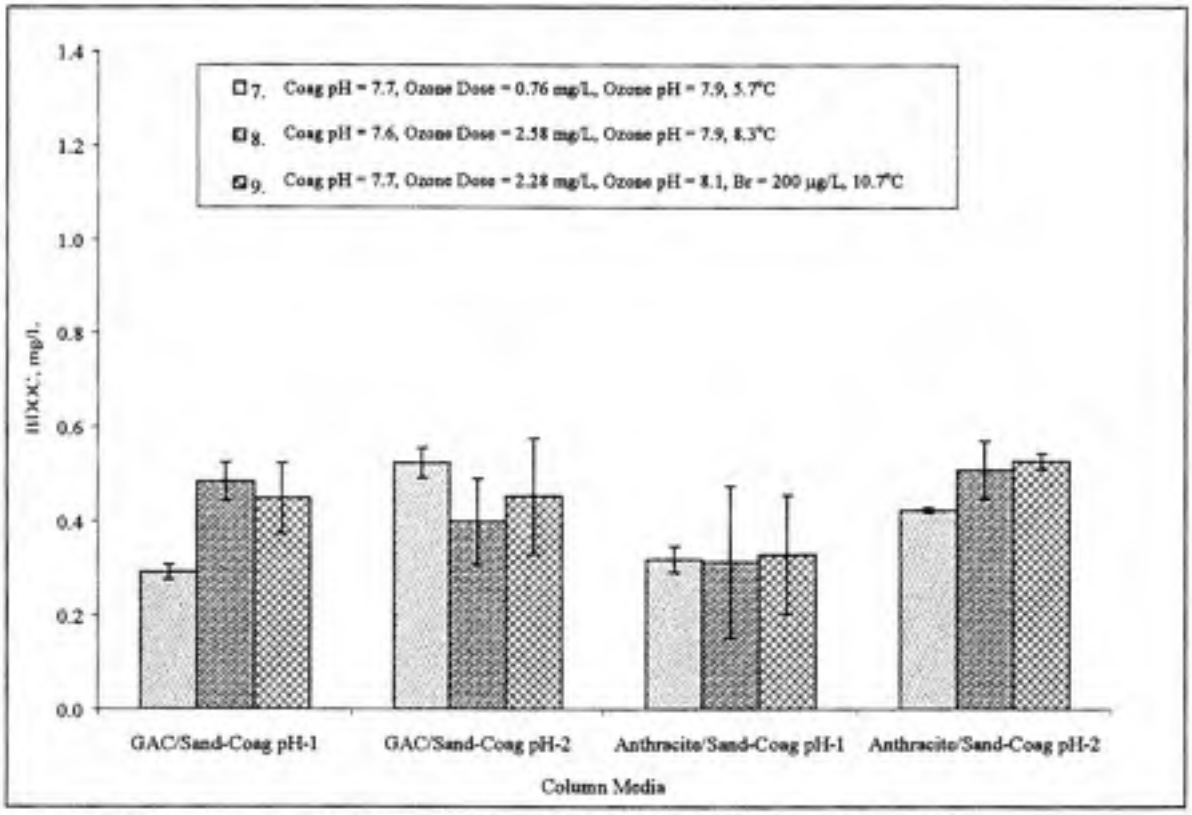

Figure 4.20. Comparison of BDOC in Filtered Water With Different Filter Media.

content due to ozonation was more consistent from experiment to experiment. Ozonation increased the BDOC level in the water by as much as 0.6 mg/L, which corresponded to a relative increase of 100 to 200%. After ozonation, a higher percentage of the DOC—20 to 37%—was found to be biodegradable.

The BDOC concentrations of the effluents from each of the four filters are shown in Figure 4.20. The BDOC content of the filtered water was on the order of 0.3 to 0.5 mg/L, which might be problematic with respect to biofilm growth in the distribution system. As to filter performance, BDOC removal was minimal in two of the three intermediate-ozonation experiments. The temperature of the water in those two runs was below 10°C (see Table 4.3). As mentioned earlier, biofiltration has been found to be significantly impaired below 10 °C (Coffey, et al., 1997). Therefore, no conclusive interpretation on the effects of column media on BDOC removal can be made.

4.3.3.5: Removal of DBP Formation Potential

Trihalomethanes

The profiles for UFC THM4 formation potentials for the intermediate-ozonation experiments are shown in Figure 4.21. The UFC THM4 concentrations in the raw water ranged from 100 to 140 μg/L, and their variability from experiment to experiment corresponded directly with the variability in TOC concentration. Overall, 47 to 58% of the THM4 precursors in the raw water was removed. The highest removal occurred in the ozonation and coagulation stages, with each stage responsible for approximately 20% removal. Additionally, up to 16% of the THM4 precursor were removed by biofiltration. From a regulatory standpoint, all treatment trains produced filtered water which complied with the THM4 requirements of Stage I of the D/DBP Rule.

The effects of a 200 μg/L bromide spike on THM speciation in the raw and filtered water are shown in Figure 4.22. Again, the number on top of the column represents the THM4 concentration for that particular experiment. The same trend in speciation observed for the pre-ozonation experiments was seen in the intermediate-ozonation experiments. Under ambient bromide conditions, the mixed bromo-chloro THM species accounted for approximately 20% and 35% of the THM4 concentrations in the raw and filtered water, respectively. With the bromide spike, the formation of these species, and bromoform, became more significant. For the case of raw water, $CHBr_2Cl$ and $CHBrCl_2$ each represented approximately 29% of the THM4 concentration, which was on the same order as the relative concentration of $CHCl_3$. Bromoform accounted for 10% and 29% of the THM4 concentration in the raw water and filtered water, respectively.

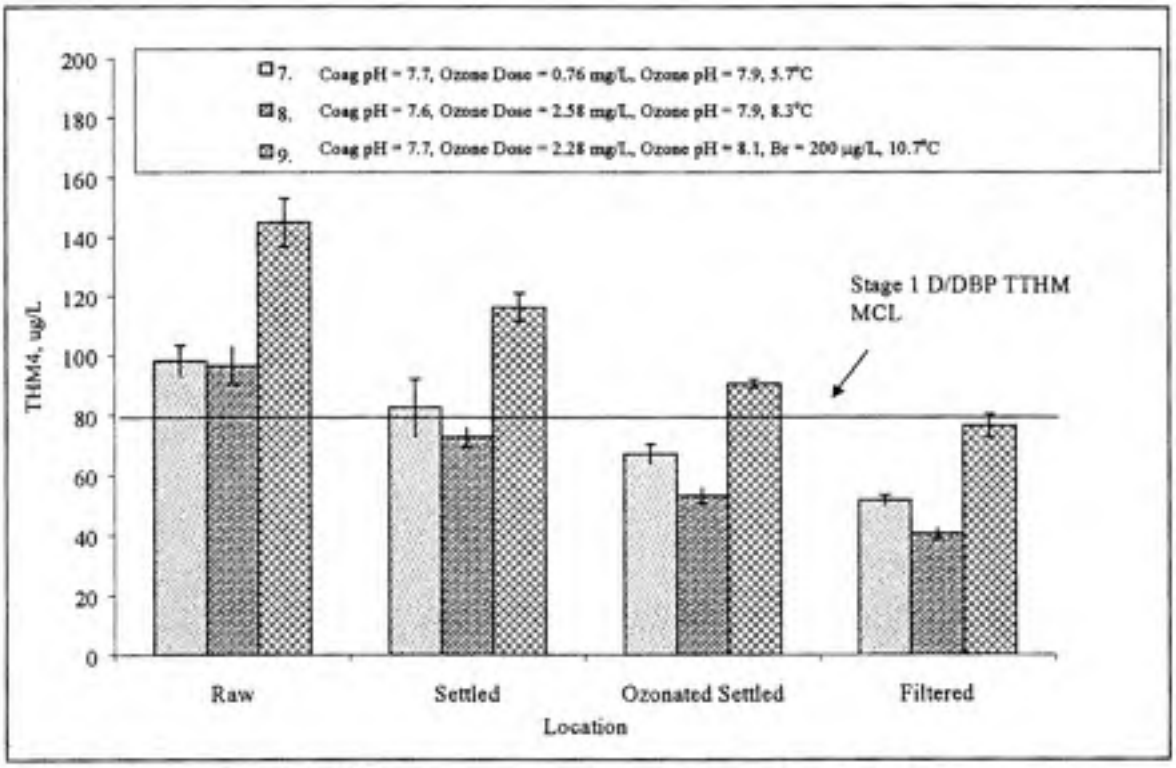

Figure 4.21. Profiles of THM4 Formation Potentials for Intermediate-Ozonation Experiments.

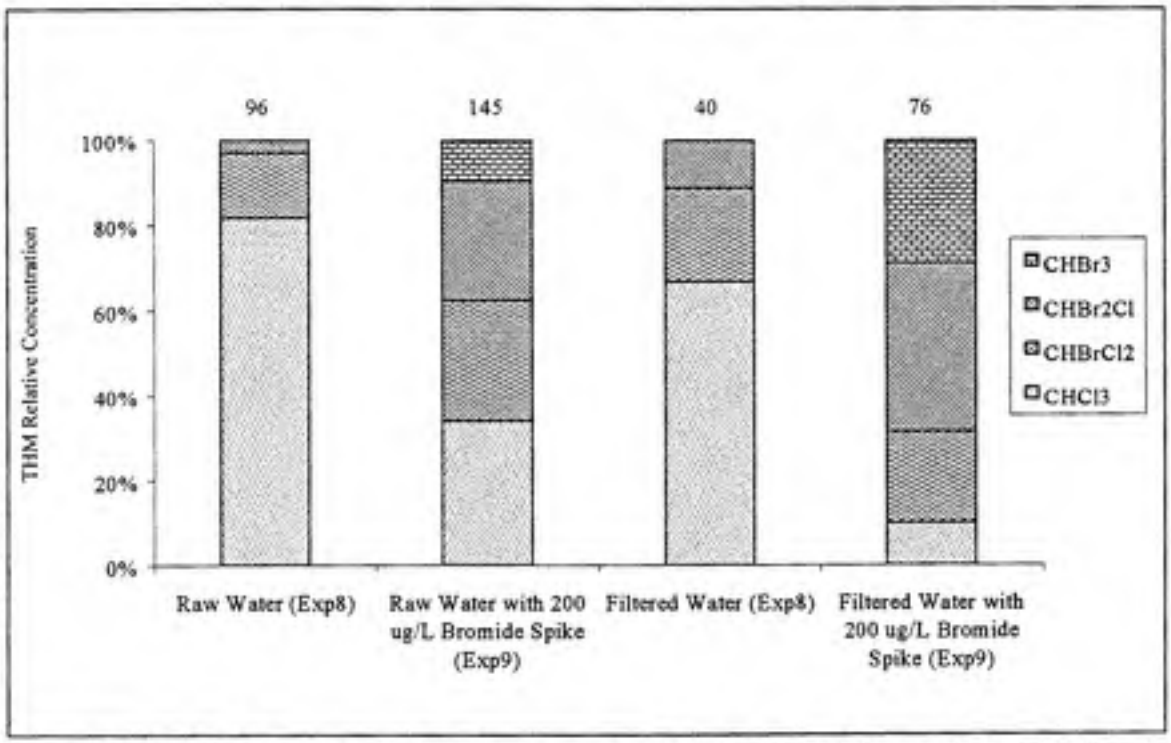

Figure 4.22. THM Speciation in Raw Water and Filtered Water Before and After 200 µg/L Bromide Spike for the Intermediate-Ozonation Experiments.

Haloacetic Acids

The profiles of the UFC HAA9 formation potentials for the intermediate-ozonation experiments are shown in Figure 4.23. It was observed that the average UFC HAA9 concentrations in the raw water were at a level below the requirements of Stage I of the D/DBP Rule. In addition, the UFC HAA9 concentration in the filtered water was on the order of 20 μg/L—about 10 μg/L below the Stage II requirement. In terms of overall performance, 60 to 81% of the HAA9 precursor in the raw water was removed. On average, coagulation, ozonation, and biofiltration were responsible for 23%, 27% and 21% removal, respectively.

The effects of the 200 μg/L bromide spike on HAA speciation are shown in Figure 4.24. Under ambient bromide condition, $BrCl_2AA$ and BrClAA accounted for approximately 20% of the total HAA concentration in both raw and filtered waters. With the bromide spike, the bromo-substituted fraction increased to 50%. In the raw water, this fraction included $BrCl_2AA$, BrClAA, Br_2ClAA, and Br_2AA, with the first two being the dominant bromo-substituted species. For filtered water with the bromide spike, BrClAA was the only bromo-substituted species detected at measurable levels.

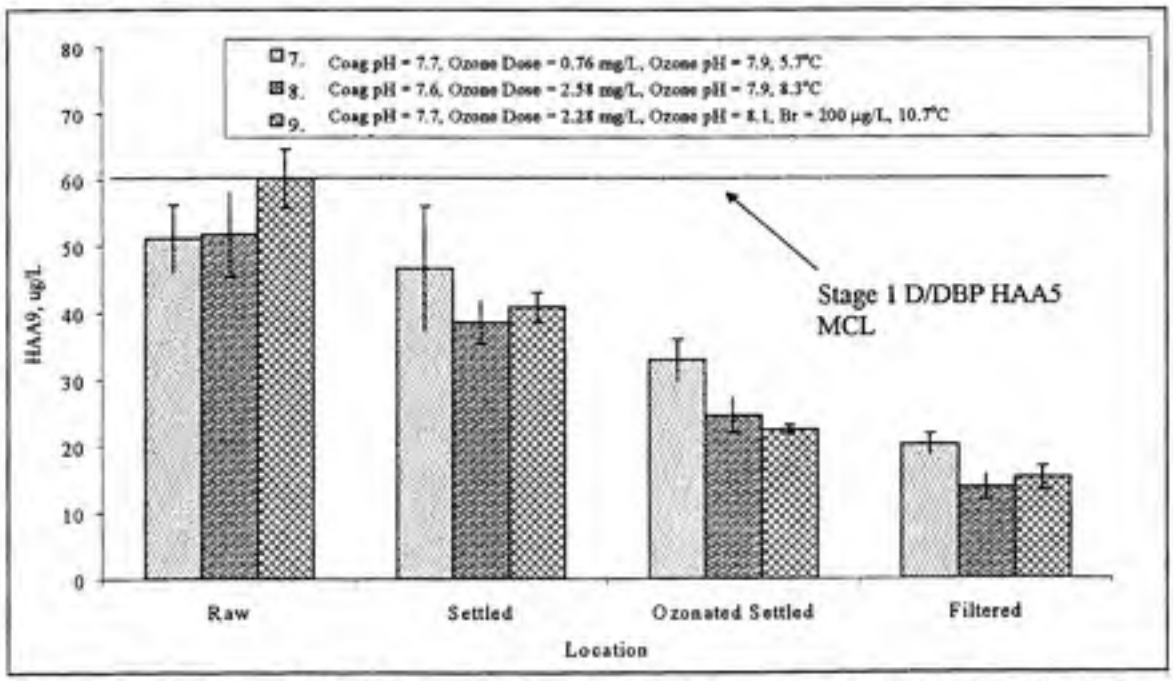

Figure 4.23. Profiles of HAA9 Formation Potentials for Intermediate-Ozonation Experiments.

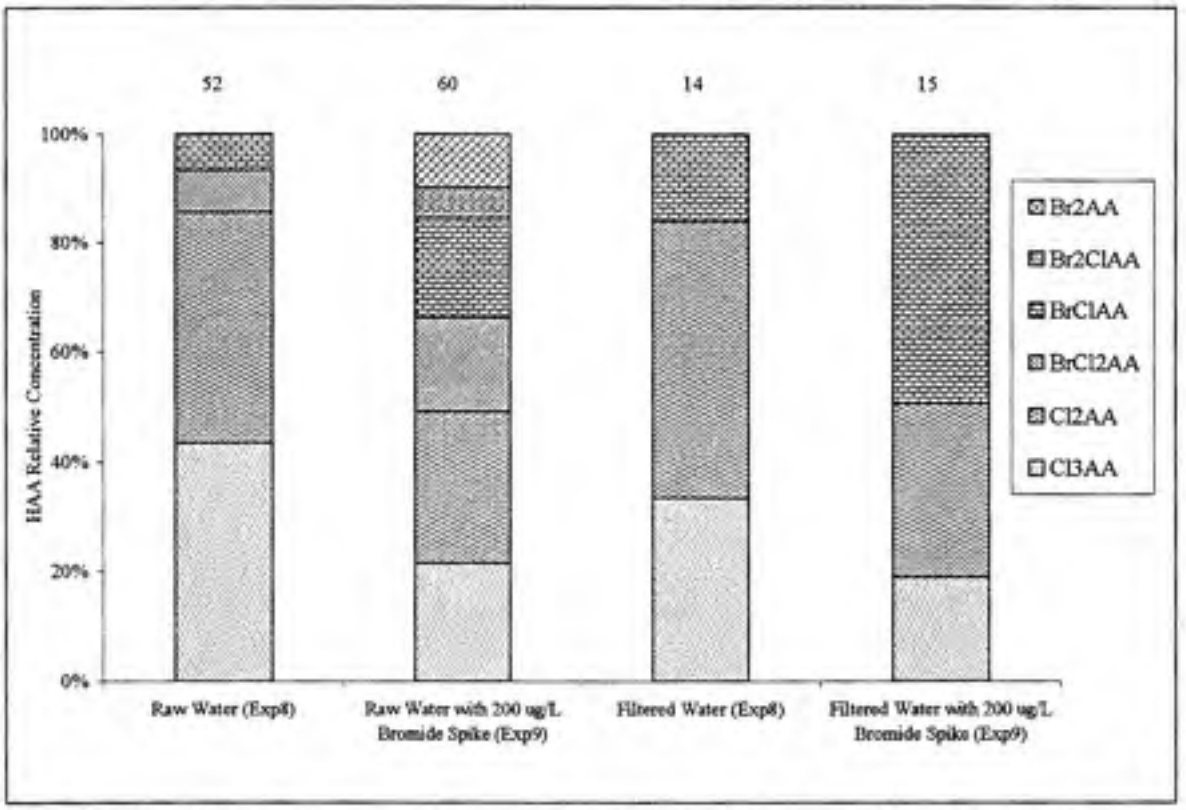

Figure 4.24. HAA Speciation in Raw and Filtered Water Before and After 200 μg/L Bromide Spike in the Intermediate-Ozonation Experiments.

4.4: Relationship Between DBP Formation Potential and UV Absorbance

The reduction in UV absorbance provides insights into the high reduction in THM4 and HAA9 formation potential observed, despite the low TOC removal. From visual inspection of the profiles of UV absorbance and UFC THM4 and UFC HAA9 concentrations (Figures 4.6, 4.10, and 4.12, in the case of pre-ozonation and Figures 4.18, 4.21, and 4.23 in the case of intermediate-ozonation), it can be seen that the reduction of both DBP formation potential tracks the reduction in UV absorbance to a significant degree. In fact, this behavior has been observed in previous studies, including Reckhow, et al. (1990). Quantitatively, as shown in Figures 4.25 and 4.26, linear relationships can be drawn between the relative reduction of THM4 and HAA9 formation potential and the relative reduction of UV absorbance. The respective R^2-values are both 0.75, which imply relatively strong statistical significance of both regression functions. In

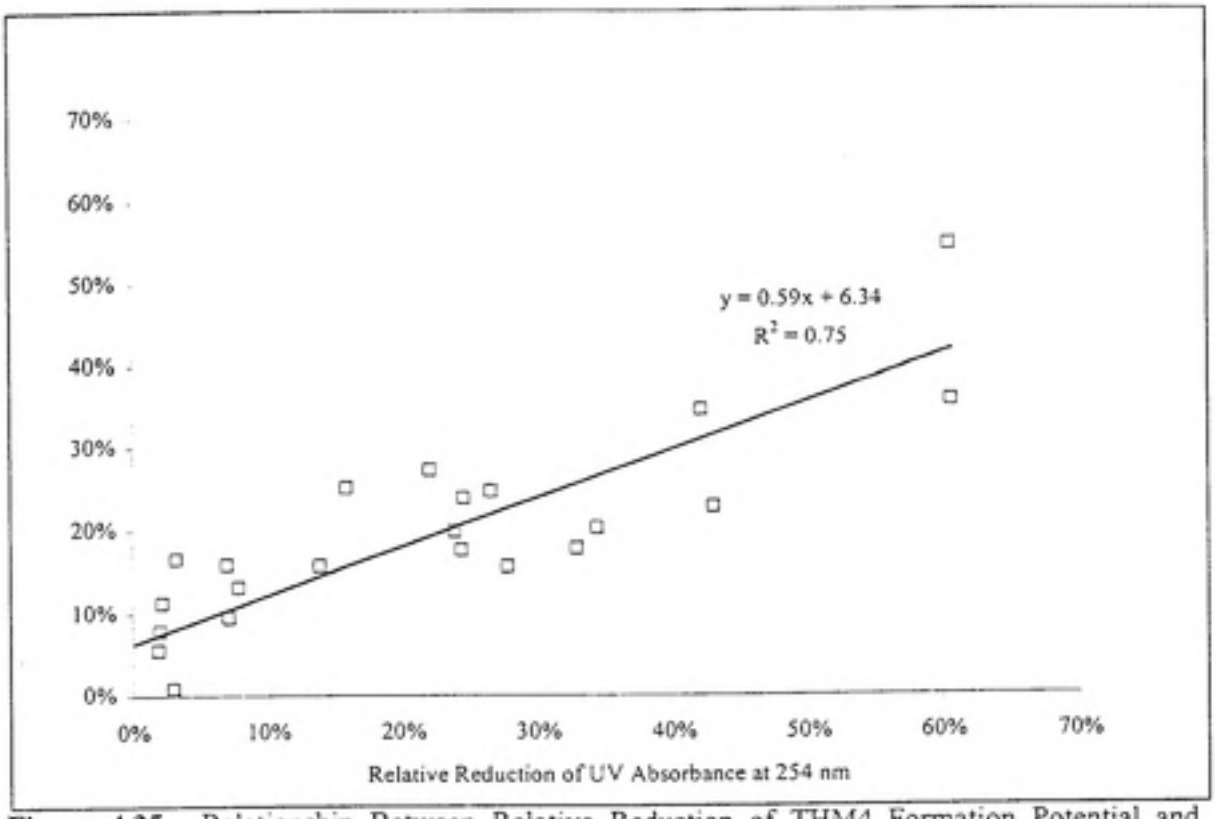

Figure 4.25. Relationship Between Relative Reduction of THM4 Formation Potential and Relative Reduction of UV Absorbance at 254 nm.

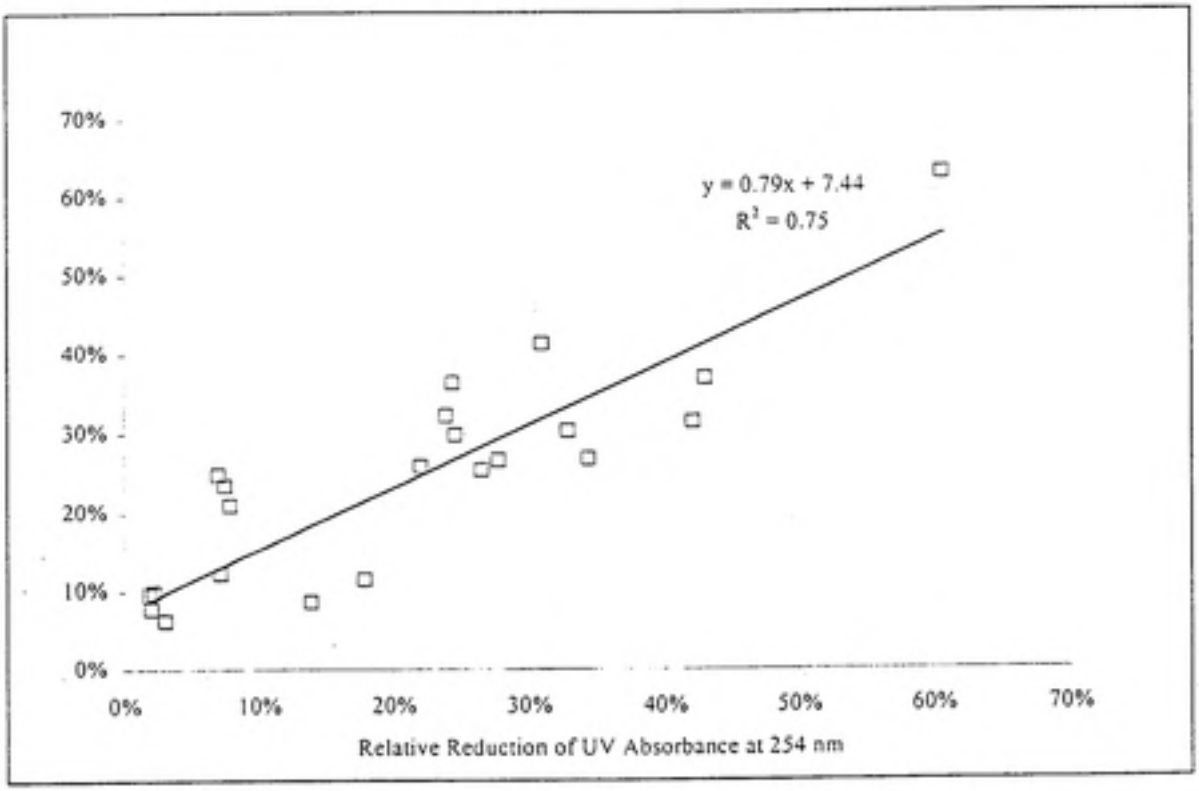

Figure 4.26. Relationship Between Relative Reduction of HAA9 Formation Potential and Relative Reduction of UV Absorbance at 254 nm.

comparing the slopes of the functions, it can be seen that a change of one percent reduction in UV absorbance corresponded to higher relative destruction/removal of HAA9 precursors than THM4 precursors. The effects of bromide concentration were found to have minimal effects on the pertinent statistical parameters (ie. slope and R^2-value) of the correlations (see Appendix H). .

It is believed that the reduction in the UV absorbance was brought about by both chemical and physical pathways. The former could occur during ozonation, in which alterations of organics brought about by the oxidation process—such as the cleavage of aromatic structures—produced by-products that were less likely to absorb UV light (see Section 4.3.2.3). With the reduced presence of aromatic carbon, it could be inferred that the altered NOM would be less reactive with chlorine and, therefore, less likely to contribute towards chlorinated DBP formation. As for the physical pathway, it is likely that the reductions in UV absorbance across the coagulation and biofiltration processes resulted from the physical (and biological) removal of the highly reactive fraction of NOM. Given that the scale of TOC concentrations are 1000 times that of DBP concentrations, it can be expected that a small removal of this active fraction of NOM can correspond to a significant change in DBP formation.

4.5: Summary of Pilot Plant Operations

Tables 4.4 and 4.5 summarize the relative and overall removal efficiencies, respectively, of the water quality parameters pertinent to DBP formation for the nine pilot plant operations. (Because minimal removals occurred during each treatment step, the relative removals of TOC and DOC were not tabulated in Table 4.4.) Reduction of DBP formation potential occurred to the greatest extent during the ozonation and coagulation steps. The relative removals of THM4 formation potential during ozonation and coagulation were as high as 55% and 27%, respectively. The respective maximum removals of HAA9 formation potential were 63% and 36%. As for biofiltration, significant reduction of the DBP formation potential during this step was found in two of the intermediate-ozonation experiments (Experiments 7 and 8). In these two experiments, the relative removal by biofiltration was on the same order as those in the two upstream treatment

steps. The reduction in UV absorbance was the highest as a result of ozonation and coagulation. The relative reduction the two treatment steps were as high as 61% and 27%, respectively.

Table 4.4. Summary of Relative Removal Efficiencies in the Treatment Steps for the Nine Pilot-Plant Operations

		%Removal		
Exp #	Treatment	UV-254 Absorbance	THM4*	HAA9*
1	Ozonation	31	N/A	41
	Coagulation	18	N/A	11
	Biofiltration	7	N/A	24
2	Ozonation	16	25	Q
	Coagulation	24	18	36
	Biofiltration	2	11	10
3	Ozonation	61	36	63
	Coagulation	3	17	-3
	Biofiltration	2	6	10
4	Ozonation	60	55	Q
	Coagulation	-1	-5	Q
	Biofiltration	-1	5	Q
5	Ozonation	42	35	32
	Coagulation	25	24	30
	Biofiltration	2	8	8
6	Ozonation	43	23	37
	Coagulation	22	27	26
	Biofiltration	3	1	6
7	Ozonation	28	16	27
	Coagulation	14	16	9
	Biofiltration	7	16	25
8	Ozonation	34	20	27
	Coagulation	27	13	25
	Biofiltration	8	25	21
9	Ozonation	33	18	30
	Coagulation	24	20	32
	Biofiltration	7	10	12

Note: N/A indicates analysis was not conducted on this parameter.
Q implies questionable data.
'*' indicates the DBPs were determined using the UFC test.
The (-) % indicates a slight increase in the measured parameter relative to the measurement at the sample point directly upstream.

In terms of overall removal, turbidity removal was higher than 90% in most cases. The removal of TOC and DOC ranged from 0 to 34%. Given the low initial TOC concentration, the 34% removal corresponded to a TOC removal of approximately 0.4 mg/L. Despite low TOC removal, significant amounts of DBP precursors were removed, as reflected by the high overall

reduction in UV absorbance (see Section 4.4). Based on UFC testing, the reduction in the formation potential of THM4 and HAA9 ranged from 47 to 66% and 48 to 81%, respectively.

Table 4.5. Summary of Overall Removal Efficiencies for the Nine Pilot-Plant Operations

	%Removal					
Exp #	Turbidity	TOC	DOC	UV-254 Absorbance	THM4*	HAA9*
1	99	9	30	56	N/A	76
2	95	9	19	42	54	48
3	97	9	0	66	58	70
4	99	12	4	59	54	Q
5	96	26	21	69	66	66
6	86	18	18	68	51	69
7	92	16	16	49	47	60
8	97	22	19	69	58	73
9	98	33	34	64	48	81

Note: N/A indicates analysis was not conducted on this parameter.
Q implies questionable data.
'*' indicates the DBPs were determined using the UFC test.

For reference, the summaries to the nine pilot-plant operations and the corresponding DBP speciations can be found in Appendices F and G, respectively.

4.6: Additional Findings

The UFC chlorination work yielded results that were interesting from a number of standpoints. As reported in previous sections, they provided insight into the formation potentials of THM4 and HAA9 in treated water, as well as their speciation due to the presence of bromide. This information is useful in terms of regulatory compliance and also from a health effects standpoint.

This section presents the results from additional analyses of the UFC chlorination data. The link between chlorine consumption and the change in UV absorbance at 272 nm is addressed with reference to the work of Korshin et al. (1997). Furthermore, various relationships between THM and HAA formation are discussed.

4.6.1: Correlation between the Change in UV Absorbance at 272 nm and DBP Production

An attempt was made to correlate the change in UV absorbance at 272 nm (ΔUV272) with chlorine consumption and THM4 and HAA9 formation. The basis of this investigation stemmed from the strong correlation between ΔUV272 and the production of total organic halide (TOX) due to chlorination, as reported by Korshin et al. (1997). Twenty-nine data points consisting of raw water samples and the next sample collected off the treatment step downstream were used. Data from the chlorinated filtered water samples from three pre-ozonation experiments were also included, but it was decided the data from the remaining filtered water samples would not be used because the change in UV absorbance in those cases were minimal (on the order of 0.001). In addition, HAA data from Experiment 4 were also not used because they were questionable

A plot of ΔUV272 against chlorine consumption was contructed, as shown in Figure 4.27. Regression analysis using Excel based on this set of data indicated a significant correlation between ΔUV272 and chlorine consumption (ΔCl_2). The resulting regression function is

$$\Delta UV272 = 0.0031\Delta Cl_2, \qquad R^2 = 0.41 \qquad (4.1)$$

where ΔUV272 [=] cm^{-1} and ΔCl_2 [=] mg/L-Cl_2

Using the t-test with $\alpha = 0.05$, the intercept was determined to be insignificant, and can be considered as zero.

Figure 4.28 illustrates the relationship between the formation of THM4 and HAA9 with ΔUV272. Regression analysis showed significant correlations for both parameters. The respective regression functions are

$$(UFC\ THM4) = 27(\Delta UV272) + 0.4, \qquad R^2 = 0.60 \qquad (4.2)$$

$$(UFC\ HAA9) = 17(\Delta UV272) + 0.2, \qquad R^2 = 0.64 \qquad (4.3)$$

where the units of the DBPs are μM. Regression was also conducted using mass concentrations of THM4 and HAA9 (not shown). The resulting regression functions did not fit any better than

Equations (4.2) and (4.3). In comparing these findings with other studies, the estimate of the slope in the THM4 correlation function was approximately half of the corresponding value reported by Korshin et al. (1997). The difference between the two estimators might be explained by the fact that in this study some of the data points were derived from ozonated water samples. As shown in this study and previous studies (Malley and co-workers, 1986; Rechkow, et al., 1986), ozonation contributes to the reduction in THM4 precursor concentrations.

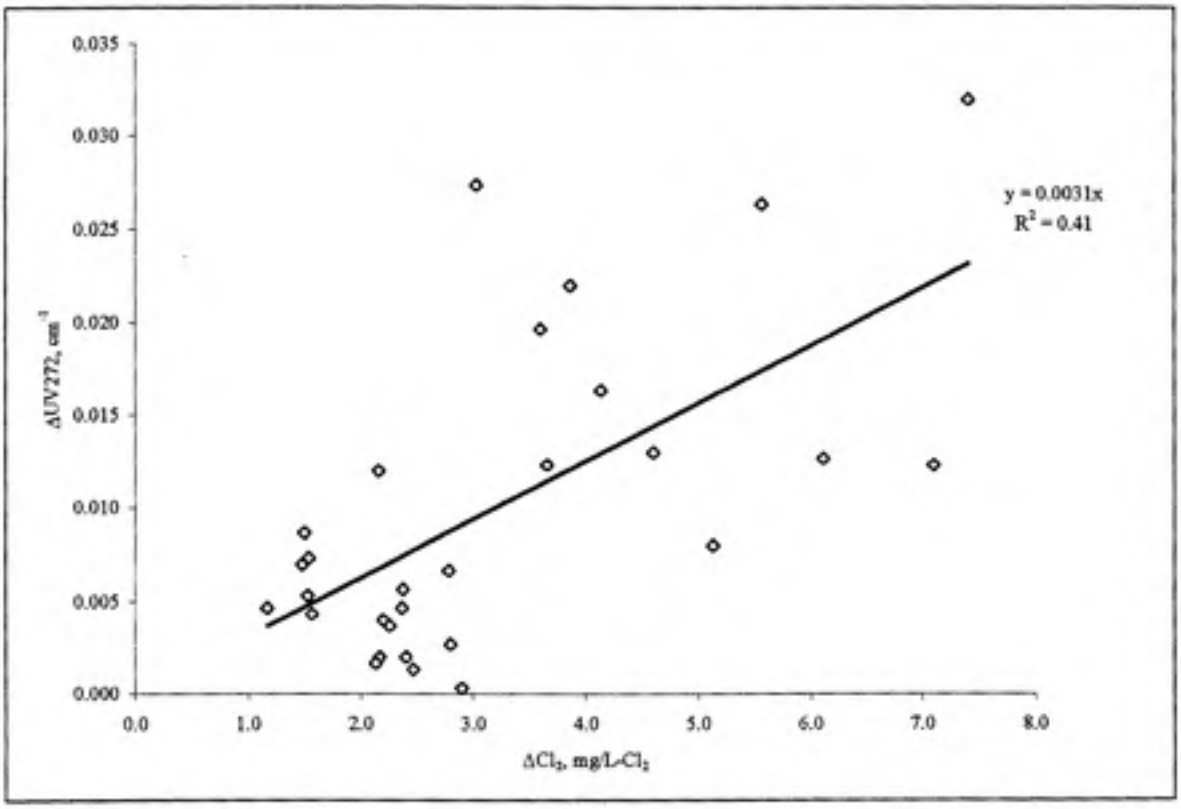

Figure 4.27. Relationship Between Change in UV Absorbance at 272 nm and Chlorine Consumption.

It should be noted that the regression of the sum of the two groups of DBPs—in both molar and mass units—against ΔUV272 resulted in a higher R^2-value. This finding is not surprising considering the sum of THM4 and HAA9 would be a better estimator of TOX than the individual DBP species.

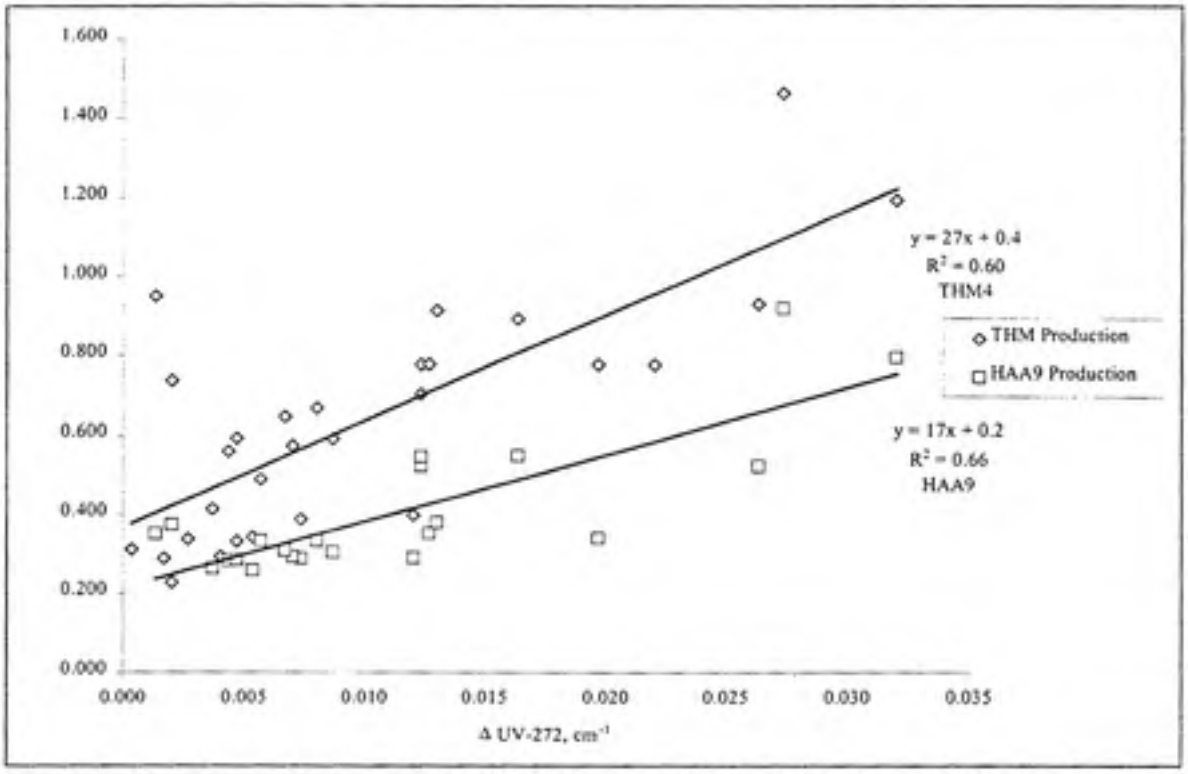

Figure 4.28. Relationship Between the Formations of THM4 and HAA9 and ΔUV272.

4.6.2: Comparison of THM4 and HAA9 Formation

Several relationships between THM4 and HAA9 were investigated. Figure 4.29 illustrates the mass relationship between THM4 and HAA9 formation. Regression analysis indicated a significant correlation between the two classes of DBPs. That is,

(HAA9 formation, μg/L) = 0.67(THM4 formation, μg/L) – 9.77, $R^2 = 0.63$ (4.4)

The slope in Equation (4.4) is considered significant by the t-test with $\alpha = 0.05$, and is on the same order as those found in other studies (Krasner, et al., 1989; Singer, et al., 1998). However, it should be noted that the regression functions from the referenced studies are not based on all nine haloacetic acids. Krasner et al. (1989) conducted regression analysis using the five regulated HAA species (excluding TBAA and the mixed bromo-chloro substituted species) while Singer et al. (1998) considered the five species and BrClAA. In addition, the differing pH of chlorination can explain the varying formation of THMs and HAAs.

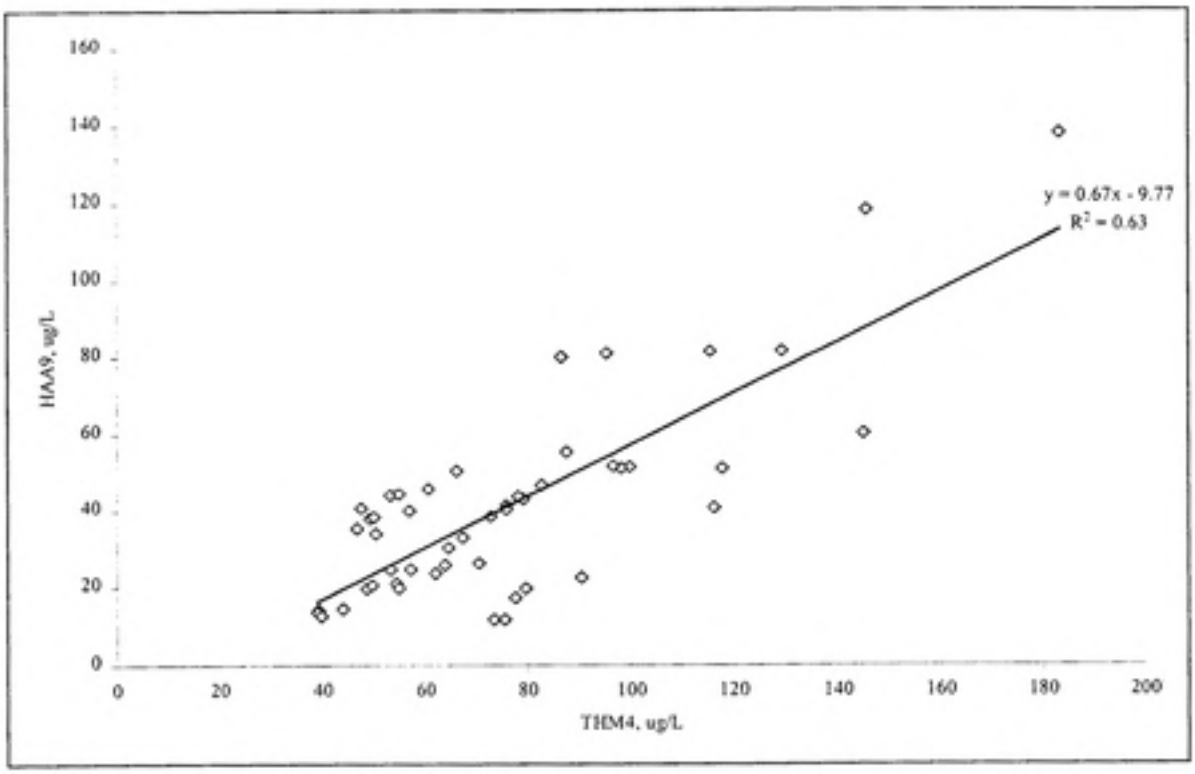

Figure 4.29. Relationship Between THM4 Formation and HAA9 Formation, on Mass Basis.

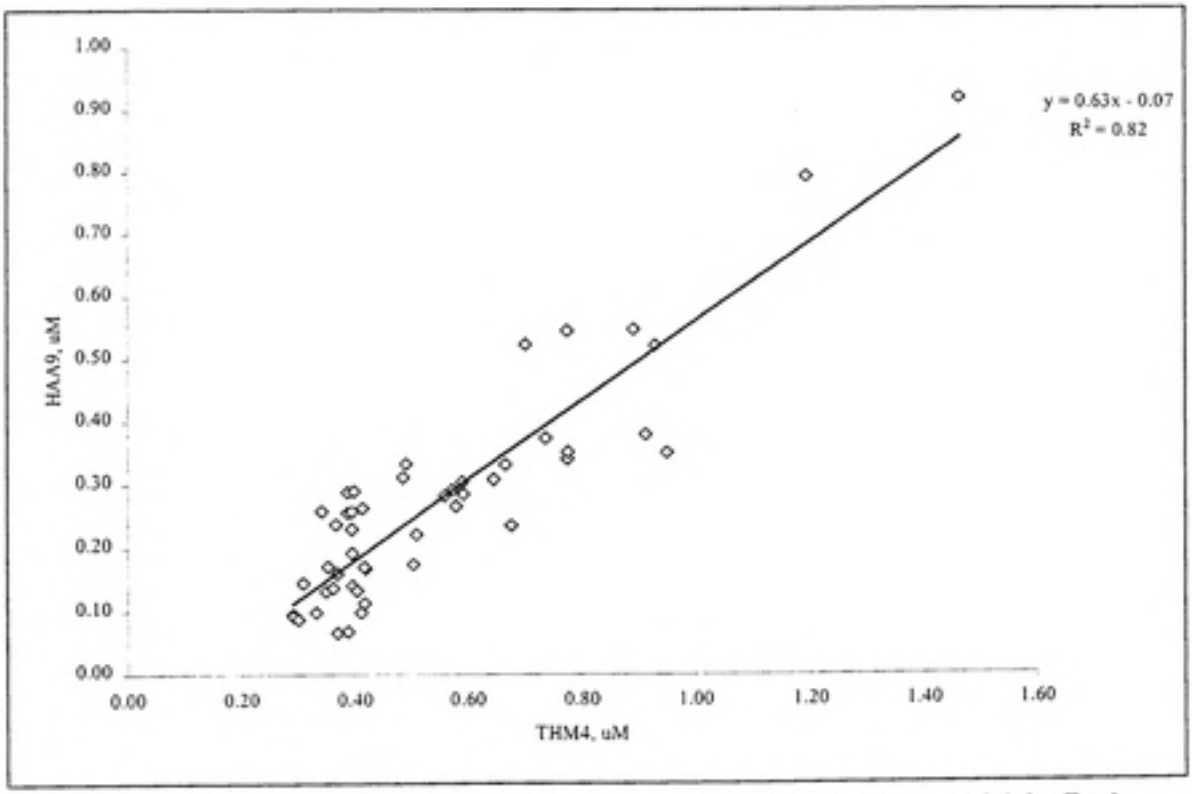

Figure 4.30. Relationship Between THM4 Formation and HAA9 Formation, on Molar Basis.

The molar relationship between THM4 and HAA9 formation is shown in Figure 4.30. In comparing the two figures, it is clear that, based on the data of this study, both the molar relationship and mass relationship between THM4 and HAA9 formation are similar, although the fit is better in the former case.

The relative degree of bromine substitution in the two DBP classes was also examined. Reckhow and Singer (1984) suggested that the formation of $CHCl_3$ and Cl_3AA might be derived from the reactions of chlorine and a common precursor. Assuming a common reaction pathway, for bromine reactions, too, it might be hypothesized that the relative degree of bromine substitution for these two classes of DBPs might also be similar. In testing this assumption in their probability model, Cowman and Singer (1995) found a relative similar distribution in the speciation of THMs and HAAs.

Figure 4.31 illustrates the relationship between the molar ratios $CHBrCl_2/CHCl_3$ and $BrCl_2AA/Cl_3AA$. Regression analysis indicated a positive correlation between the two ratios, with the regression function being:

$$(CHBrCl_2/CHCl_3) = 1.04\ (BrCl_2AA/Cl_3AA), \qquad R^2 = 0.71 \qquad (4.5)$$

A t-test using, $\alpha = 0.05$, indicated the intercept was insignificant, and can be inferred to be zero. Figure 4.32 illustrates the relationship between the molar ratios $CHBrCl_2/CHCl_3$ and $BrClAA/Cl_2AA$. Regression analysis indicated a positive correlation between the two ratios, and the regression function is

$$(CHBrCl_2/CHCl_3) = 1.2\ (BrCl_2AA/Cl_3AA), \qquad R^2 = 0.97 \qquad (4.6)$$

A t-test, using $\alpha = 0.05$, indicated insignificant intercept, and therefore zero assumption can be applied.

In both Equations 4.5 and 4.6, the slopes are significant and are close to one, thus supporting Reckhow and Singer's (1984) hypothesis on the similarity of the relative bromide speciation in THMs and both di- and trihaloacetic acids. From a prediction standpoint, the two models are extremely useful, considering the limited database for $BrCl_2AA$ and BrClAA.

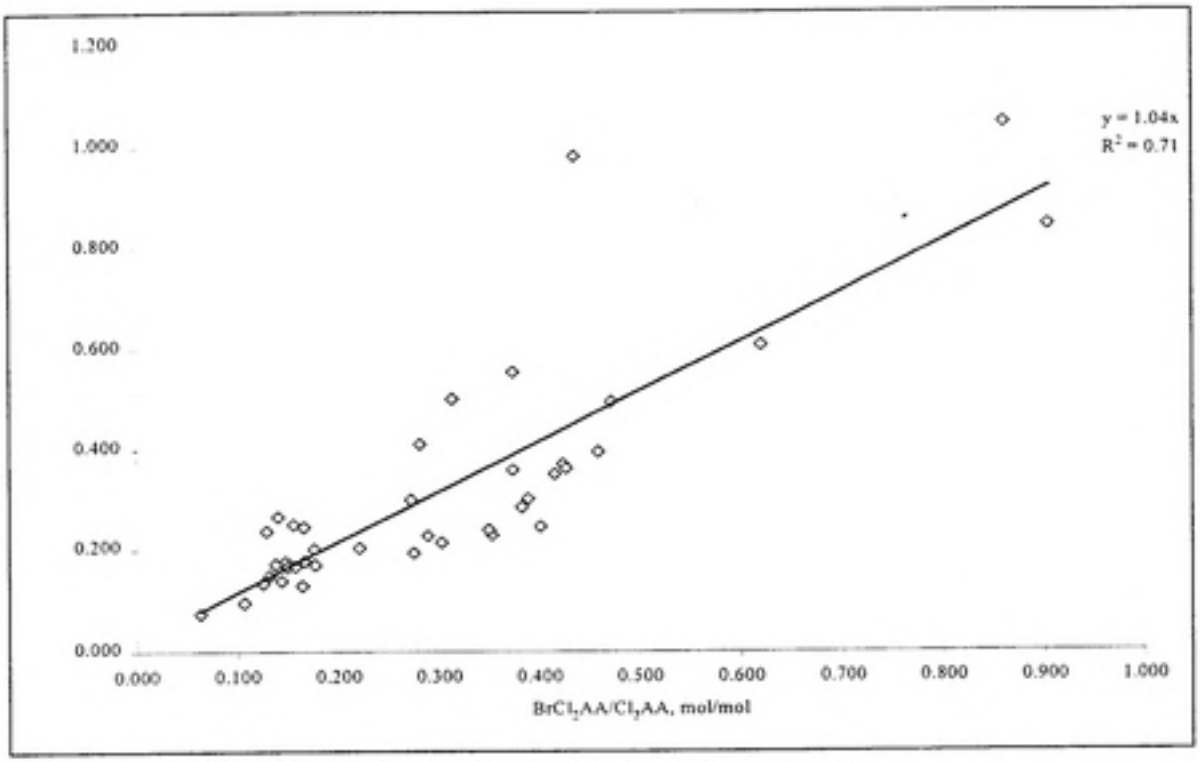

Figure 4.31. Relationship Between $CHBrCl_2/CHCl_3$ and $BrCl_2AA/Cl_3AA$.

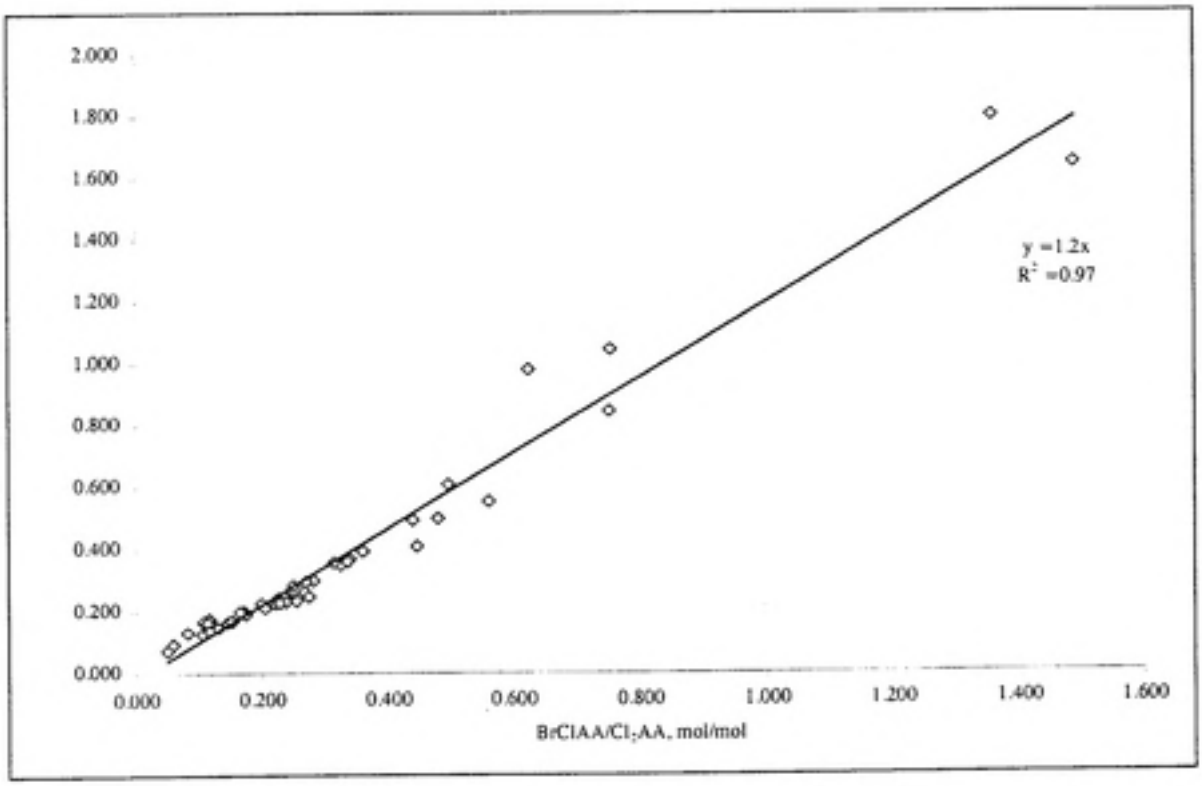

Figure 4.32. Relationship Between $CHBrCl_2/CHCl_3$ and $BrClAA/Cl_2AA$.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1: Introduction

Pilot-plant studies were conducted at the Indianapolis (IN) Water Company's (IWC) White River Filtration Plant to assess the effectiveness of ozonation, enhanced coagulation, and biofiltration in treating drinking water. Nine treatment trains were evaluated; operating variables included point of ozonation with respect to coagulation, pH of ozonation and coagulation, ozone doses targeted for Giardia and Cryptosporidium inactivation, and bromide concentration. This section highlights the major findings of this work and presents recommendations for future work.

5.2: Conclusions

The raw water from the White River was found not to be amenable to TOC removal by coagulation due to its relatively low TOC content and SUVA value. Removal varied from 0 to 34%, with the upper limit of the range corresponding to approximately 0.4 mg/L TOC removal. In comparing the different treatment trains, the difference in the degrees of TOC removal was minimal.

Despite low overall TOC removal, a significant amount of THM4 and HAA9 formation potential was reduced. Overall reductions were as high as 66% and 81% for the respective DBPclasses. For both pre- and intermediate-ozonation modes, coagulation and ozonation were equally effective in reducing THM4 and HAA9 formation potentials. In some intermediate-ozonation experiments, biofiltration was found to be equally effective—especially for the removal of HAA9 precursors—as the two upstream treatment steps. From a regulatory standpoint, all nine treatment trains yielded filtered water that produced THM4 and HAA9 concentrations (under uniform formation conditions) that met the requirements of Stage I of the D/DBP Rule.

The reduction in DBP formation potential paralleled the reduction in UV absorbance to a significant degree. In line with previous studies, it is believed that ozone initiated cleavage of aromatic carbon structures to produce smaller oxidation by-products that were less likely to absorb UV light and to contribute towards chlorinated DBP formation. The change in UV absorbance across the coagulation and biofiltration processes indicated chemical and physical removal of aromatic compounds which are believed to be the highly chlorine-reactive fraction of NOM. Given the difference in scale, the small removal of this fraction of NOM could produce a significant reduction in THM and HAA formation.

In addition to producing an overall reduction in UV absorbance of up to 50%, ozonation also affected the BDOC content of the water. The ozone application increased the BDOC concentration by as much as 200%, which corresponded to as much as a 1.1 mg/L increase.

In terms of DBP speciation, chloroform, and di- and trichloroacetic acids were the principal THM and HAA species produced from chlorination of the filtered water under ambient bromide conditions (~ 25 μg/L). With a 200 μg/L bromide spike, formation of the bromo-substituted THMs and HAAs under uniform formation conditions (UFC) was increased. The three bromo-substituted THM species contributed as much as 90% of the THM4 concentration in the filtered water. Bromochloro- and dibromochloroacetic acids constituted up to 50% of the total HAA concentration in the filtered water.

Based on the available DBP data, regression analysis indicated a significant linear relationship between the molar ratios $CHBrCl_2/CHCl_3$ and $BrCl_2AA/Cl_3AA$, and $CHBrCl_2/CHCl_3$ and $BrClAA/Cl_2AA$. In the former set of ratios, the slope and R^2-value are 1.04 and 0.71, respectively. The respective parameters for the latter set are 1.2 and 0.97. These findings suggest that the two bromo-chloro- substituted acetic acids can be estimated from THM4 and Cl_2AA and Cl_3AA.

5.3: Recommendations

Similar studies should be conducted on other waters with different types of TOC that might be more amenable to coagulation. In selecting candidates for such studies, run of the river waters with highly variable water quality should not be chosen. It is also recommended that the parallel between the reduction in UV absorbance and the removal of DBP precursors be investigated in future studies.

More studies should be done to further explore the relationship among the THM and HAA species. Data sets from other studies where THM4 and HAA9 data have been collected should be utilized to confirm the correlation between the molar ratios $CHBrCl_2/CHCl_3$ and $BrCl_2AA/Cl_3AA$, and $CHBrCl_2/CHCl_3$ and $BrClAA/Cl_2AA$ presented in this work, as well as to develop a correlation for the dibromo- and tribromo-substituted species. These studies will aid in the prediction of HAA9 concentrations in chlorinated waters where only data on HAA5—and BrClAA, in some cases—exist.

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Appendix A: Results from Tracer Studies

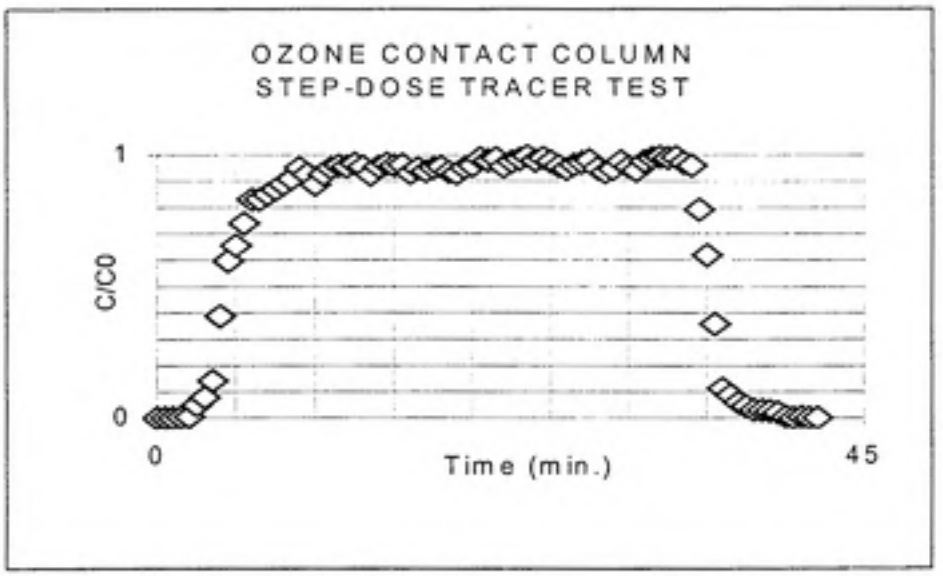

Figure A1. Tracer Study for the Ozone Contact Column. T_{10} = 3.17 minutes.

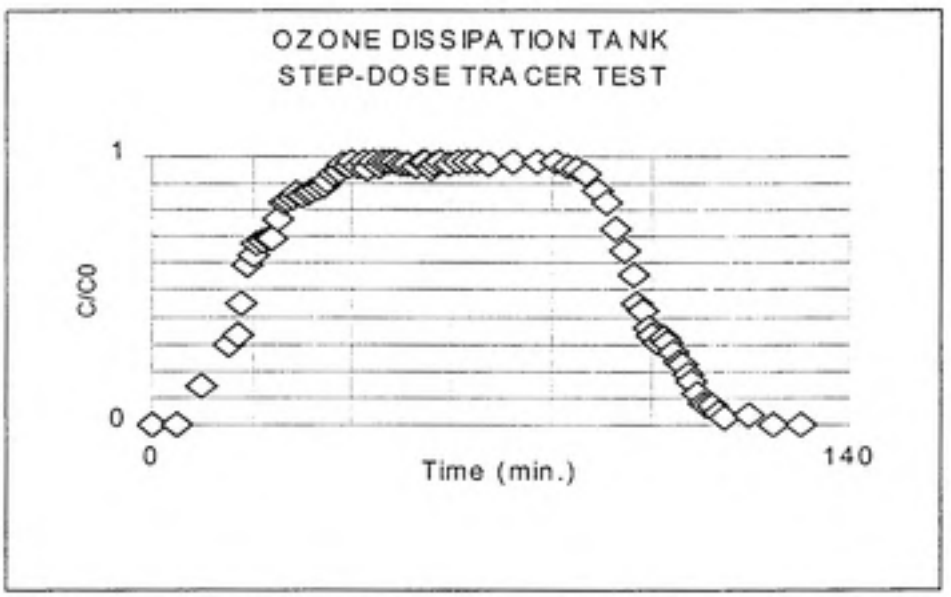

Figure A2: Tracer Study for the Ozone Dissipation Tank. T_{10} = 8.52 minutes.

Note: Tracer studies were conducted by Melissa Moran and Catherine Pallotta of Malcolm Pirnie, Inc. (Indianapolis, IN).

Appendix B: Examples of Certification of Analysis for Trihalomethane and Haloacetic Acids Standard

Certificate of Analysis

DESCRIPTION: EPA 552 Halogenated Acetic Acids Mix

CATALOG NO.: 48047 MFG DATE: Jul-1998

LOT NO.: LA-77547 EXPIRATION DATE: Jul-2001

SOLVENT: METHYL TERT-BUTYL ETHER

ANALYTE (1)	CAS NUMBER	PERCENT PURITY(2)	WEIGHT(3) CONCENTRATION	ANALYTICAL(4) CONCENTRATION		STD DEV	SUPELCO LOT NO
BROMOACETIC ACID	79-08-3	99.0	2001	2060	+/-	13.7	LA30827
BROMOCHLOROACETIC ACID	5589-96-8	98.0	1999	2051	+/-	23.1	LA70710
CHLOROACETIC ACID	79-11-8	99.0	2000	2047	+/-	14.5	LA34811
DIBROMOACETIC ACID	631-64-1	99.9	2000	2062	+/-	26.0	LA30828
DICHLOROACETIC ACID	79-43-6	99.0	2001	2068	+/-	20.7	LA30825
TRICHLOROACETIC ACID	76-03-9	96.3	2000	2088	+/-	27.1	LA30826

(1) Listed in alphabetical order.

(2) Determined by capillary GC-FID, unless otherwise noted.

(3) NIST traceable weights are used to verify balance calibration with the preparation of each lot. Concentration of analyte in solution is ug/ml +/- 0.5%, based upon balance and Class A volumetric glassware. Weights are corrected for analytes less than 98% pure.

(4) Determined by chromatographic analysis against an independently prepared reference lot. Mean of replicate injections. Analytical values are within +/- 10% of weight conc.; +/- 15% for gases.

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Quality Control Supervisor

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16823-0048 USA • Phone (814) 359-3441

Certificate of Analysis

DESCRIPTION: Trihalomethanes Calibration Mix

CATALOG NO.: 48140-U MFG DATE: Mar-1998

LOT NO.: LA-74632 EXPIRATION DATE: May-2000

SOLVENT: METHANOL

ANALYTE (1)	CAS NUMBER	PERCENT PURITY(2)	WEIGHT(3) CONCENTRATION	ANALYTICAL(4) CONCENTRATION	STD DEV	SUPELCO LOT NO
BROMODICHLOROMETHANE	75-27-4	96.7	2000	2025	+/- 66.6	LA47472
BROMOFORM	75-25-2	99.0	2000	1926	+/- 78.6	LA56679
CHLOROFORM	67-66-3	99.0	2000	1961	+/- 21.0	LA55584
DIBROMOCHLOROMETHANE	124-48-1	98.2	2000	1989	+/- 41.6	LA67079

(1) Listed in alphabetical order.

(2) Determined by capillary GC-FID, unless otherwise noted.

(3) NIST traceable weights are used to verify balance calibration with the preparation of each lot. Concentration of analyte in solution is ug/ml +/- 0.5%, based upon balance and Class A volumetric glassware. Weights are corrected for analytes less than 98% pure.

(4) Determined by chromatographic analysis against an independently prepared reference lot. Mean of replicate injections. Analytical values are within +/- 10% of weight conc.; +/- 15% for gases.

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Certificate of Analysis

SCRIPTION: Bromodichloroacetic acid

MFG. DATE: Aug 1998

CATALOG NO.: 442499 (1)

LOT NO.: LA-77665 EXP. DATE: Aug 2001

CAS NUMBER: 71133-14-7 MOLECULAR FORMULA: C2HO2CL2BR

PHYSICAL PROPERTIES	ASSAY	
Purity (2)	99.0%	(a)
Melting point	72.0 - 74.0 deg C	

(1) This product is packaged from R473870 Lot number LA55953.

(2) Determined by GC-FID unless otherwise noted.

(a) HPLC UV-220nm

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Certificate of Analysis

:CRIPTION: Tribromoacetic acid

MFG. DATE: Jan 1998

CATALOG NO.: 442819 (1)

LOT NO.: LA-73525

EXP. DATE: Jan 2001

CAS NUMBER: 75-96-7

MOLECULAR FORMULA: C2HBR3O2

MOLECULAR WEIGHT: 297

SYSICAL PROPERTIES	ASSAY	
FTIR	Matches: SUPELCO	Lib. No.: LA43788
rity (2)	92.00% (a)	
rity (2)	99.00%	
Purity (2)	99.00% (b)	
lting point	130.0 - 131.0 deg C	

(1) This product is packaged from R473420 Lot number LA43788.

(2) Determined by GC-FID unless otherwise noted.

[a] GC; detector ECD

[b] HPLC UV-210nm

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Certificate of Analysis

ICRIPTION: Chlorodibromoacetic acid

ATALOG NO.: 4-42519 (1) TEST DATE: Dec 1995

LOT NO.: LA-65440

CAS NUMBER: 5278-95-5 MOLECULAR FORMULA: C2HO2BR2CL

HYSICAL PROPERTIES	ASSAY	
Purity (2)	99.00%	(a)
urity (2)	99.00%	(b)
elting point	97.0 - 98.0 deg C	

(1) This product is packaged from R471875 Lot number LA54857.

(2) Determined by GC-FID unless otherwise noted.

(a) HPLC UV-220nm

(b) Complex mixture, purity cannot be accurately determined.

wood Doughty
Quality Control Supervisor

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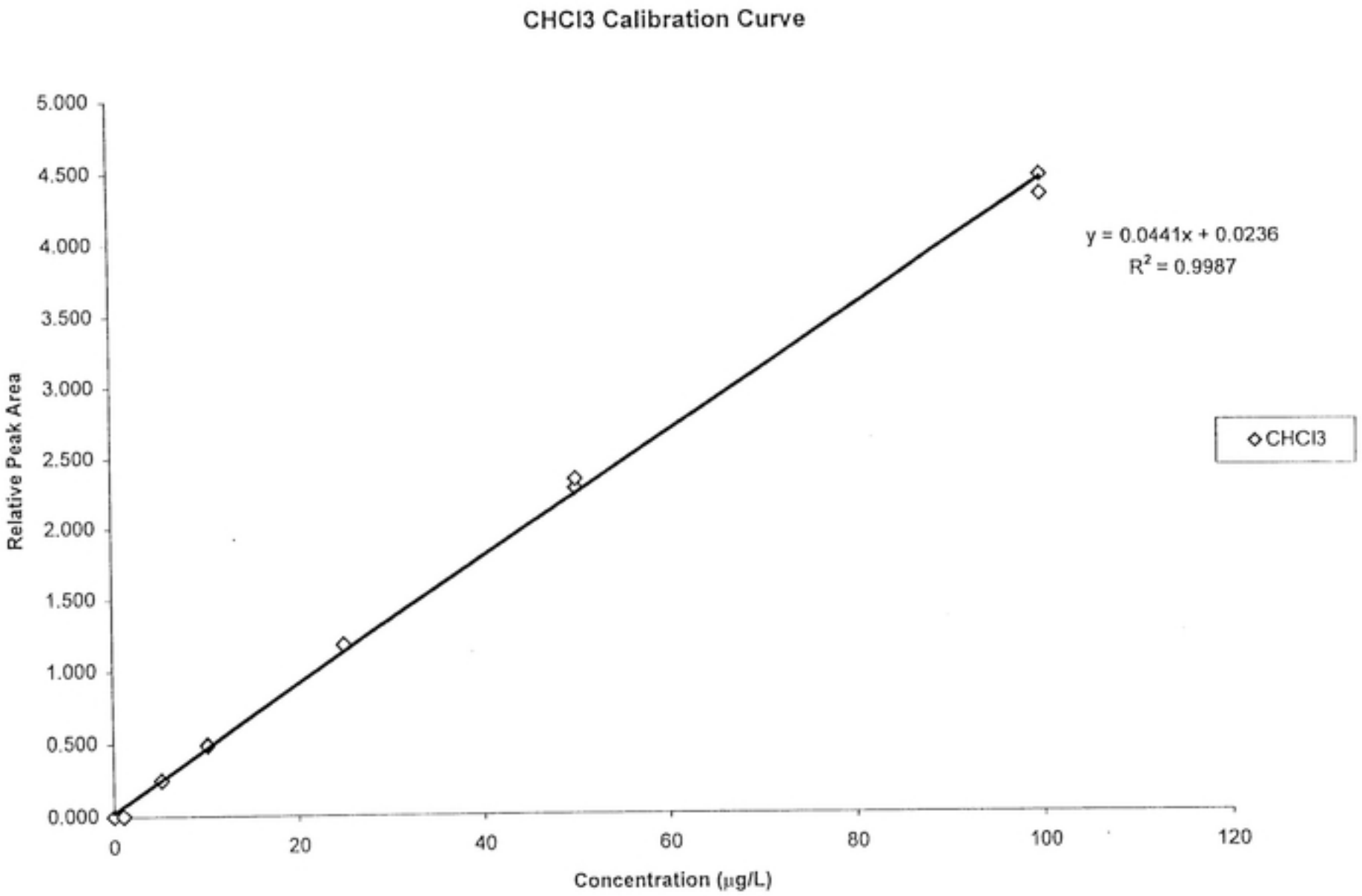
Appendix C: Examples of Calibration Curves from Analysis of Trihalomethanes and Haloacetic Acids


CHCl3 Calibration Curve
Relative Peak Area
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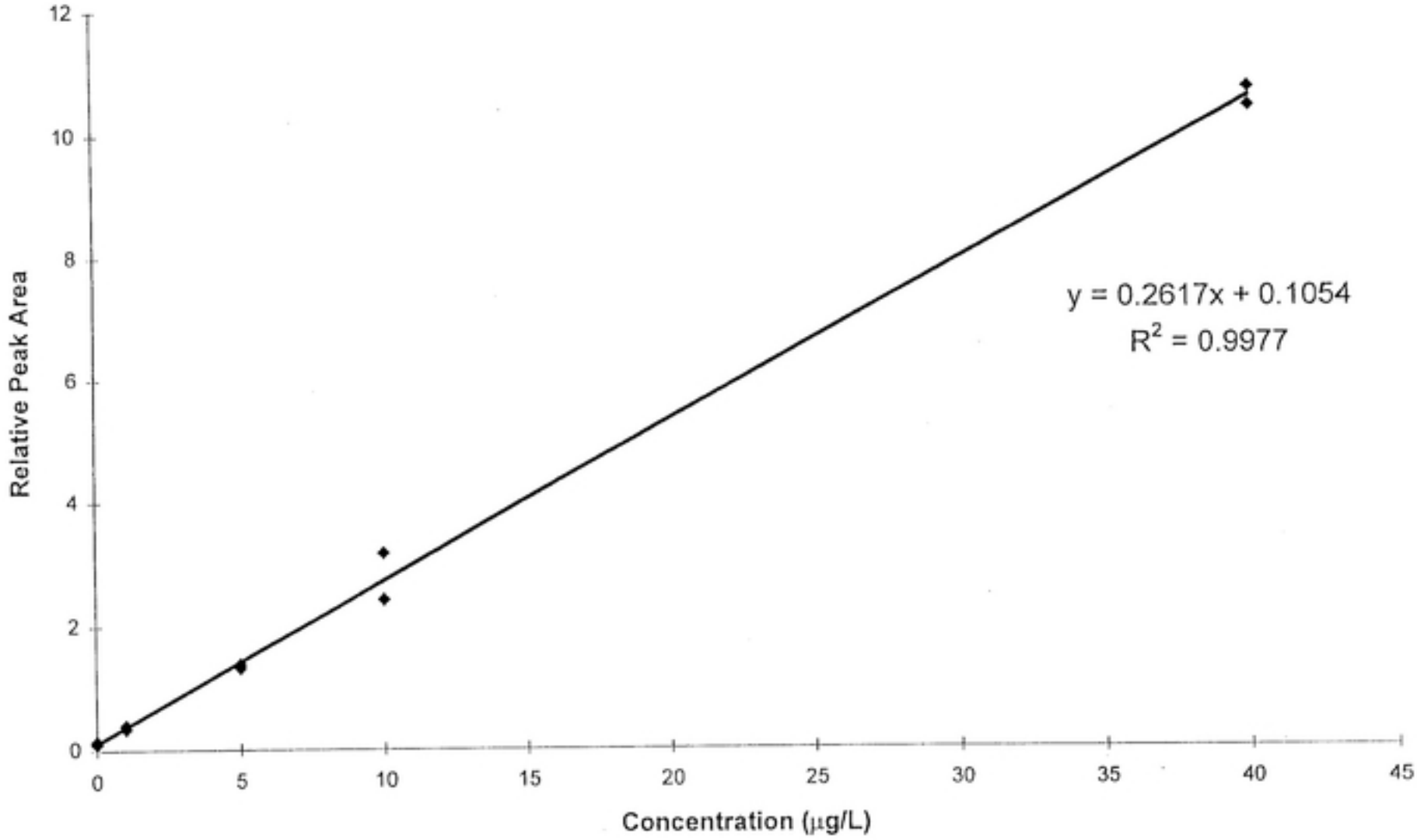
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
20
40
60
80
100
120
Concentration (µg/L)
y = 0.0441x + 0.0236
R² = 0.9987
◇CHCl3

TCAA Calibration Curve



Appendix D: Examples of Gas Chromatograms from the Analysis of Trihalomethanes and Haloacetic Acids

Area Percent Report

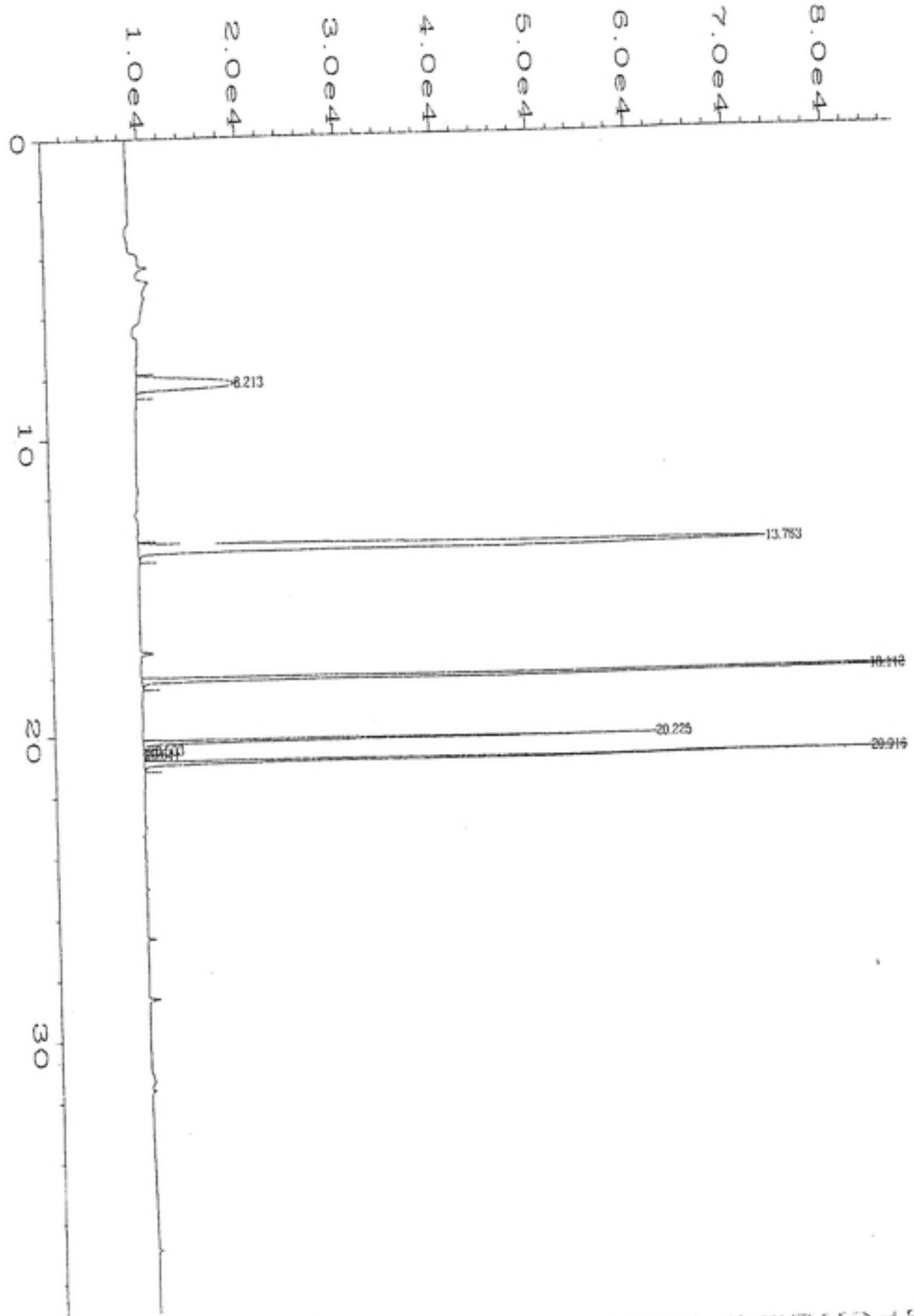
ata File Name : C:\HPCHEM\1\DATA\TC111298\008F0101.D
perator : TC
nstrument : ANALYZER1
ample Name : ~~BB~~ 50A
un Time Bar Code:
cquired on : 12 Nov 98 02:10 AM
eport Created on: 14 Nov 98 01:49 PM

Page Number : 1
Vial Number : 8
Injection Number : 1
Sequence Line : 1
Instrument Method: THMLU.MTH
Analysis Method : THMLU.MTH

ig. 1 in C:\HPCHEM\1\DATA\TC111298\008F0101.D

Pk#	Ret Time	Area	Height	Type	Width	Area %
1	8.213	208968	9977	BB	0.248	9.8192
2	13.763	779915	64333	BB	0.181	36.6474
3	18.112	656397	145180	BB	0.072	30.8435
4	20.225	185981	52698	BV	0.054	8.7391
5	20.503	1708	450	VB	0.050	0.0803
6	20.641	139	57	BB	0.033	0.0065
7	20.916	295047	88374	BB	0.051	13.8640

otal area = 2128155



C:\HPCHEM\1\DATA\TC1128&\08F0101.D

Data File Name : C:\HPCHEM\1\DATA\TC111298\012F0101.D
Operator : TC
Instrument : ANALYZER1
Sample Name : 258 10/20 R
Run Time Bar Code:
Acquired on : 12 Nov 98 05:11 AM
Report Created on: 14 Nov 98 01:59 PM
Sample Info : No biocide or quenching agent added-sample held with all other samples in the fridge.

Page Number : 1
Vial Number : 12
Injection Number : 1
Sequence Line : 1
Instrument Method: THMLU.MTH
Analysis Method : THMLU.MTH

Sig. 1 in C:\HPCHEM\1\DATA\TC111298\012F0101.D

Pk#	Ret Time	Area	Height	Type	Width	Area %
1	8.218	379010	17849	BB	0.253	33.6987
2	13.375	54553	4285	BV	0.158	4.8505
3	13.757	401759	33128	VB	0.199	35.7214
4	18.110	73360	17223	BB	0.067	6.5227
5	18.729	568	140	BB	0.055	0.0505
6	18.903	510	140	BV	0.052	0.0454
7	19.023	2349	556	VB	0.059	0.2089
8	19.208	920	257	BB	0.047	0.0818
9	19.555	120	49	BB	0.034	0.0106
10	19.865	2789	855	BB	0.047	0.2480
11	20.129	879	366	BV	0.035	0.0782
12	20.224	197303	55758	VV	0.054	17.5427
13	20.391	1221	330	VB	0.046	0.1085
14	20.542	82	35	BB	0.035	0.0073
15	20.651	548	103	BB	0.078	0.0488
16	20.935	8730	2107	BV	0.061	0.7762

Total area = 1124701

Area Percent Report

ata File Name : C:\HPCHEM\1\DATA\AM110798\013F0101.D
perator : AM
nstrument : ANALYZER1
ample Name : 50-A
un Time Bar Code:
cquired on : 05 Nov 98 04:31 PM
eport Created on: 15 Nov 98 05:47 PM

Page Number : 1
Vial Number : 13
Injection Number : 1
Sequence Line : 1
Instrument Method: HAA2.MTH
Analysis Method : HAA2TC.MTH

ig. 1 in C:\HPCHEM\1\DATA\AM110798\013F0101.D

Pk#	Ret Time	Area	Height	Type	Width	Area %
1	13.853	5793	168	BV	0.418	0.1586
2	20.330	31598	2019	BBA	0.232	0.8649
3	20.450	0	1035	Rsho	0.000	0.0000
4	27.659	0	21128	Fsho	0.000	0.0000
5	27.701	233584	35304	BBA	0.102	6.3937
6	27.945	0	427	Rsho	0.000	0.0000
7	28.066	0	197	Rsho	0.000	0.0000
8	28.633	199	50	BV	0.051	0.0054
9	28.834	238539	42660	PV	0.088	6.5293
10	33.059	698	158	BV	0.069	0.0191
11	33.275	38203	8303	PV	0.071	1.0457
12	33.529	438575	105653	VV	0.065	12.0046
13	33.694	0	424	Rsho	0.000	0.0000
14	33.834	593709	144702	VBA	0.065	16.2510
15	36.897	221	53	BV	0.066	0.0061
16	37.107	489410	130522	VV	0.059	13.3961
17	37.315	74576	20339	VV	0.056	2.0413
18	37.516	4069	682	VV	0.085	0.1114
19	37.618	2978	680	VV	0.063	0.0815
20	37.752	565465	156842	VV	0.057	15.4779
21	37.906	0	747	Rsho	0.000	0.0000
22	40.936	87162	33864	BV	0.043	2.3858
23	41.140	466471	131072	PV	0.056	12.7682
24	41.282	12518	1956	VBA	0.088	0.3427
25	44.534	91	29	PV	0.053	0.0025
26	44.652	0	4	Fsho	0.000	0.0000
27	44.762	369516	107251	PBA	0.054	10.1144

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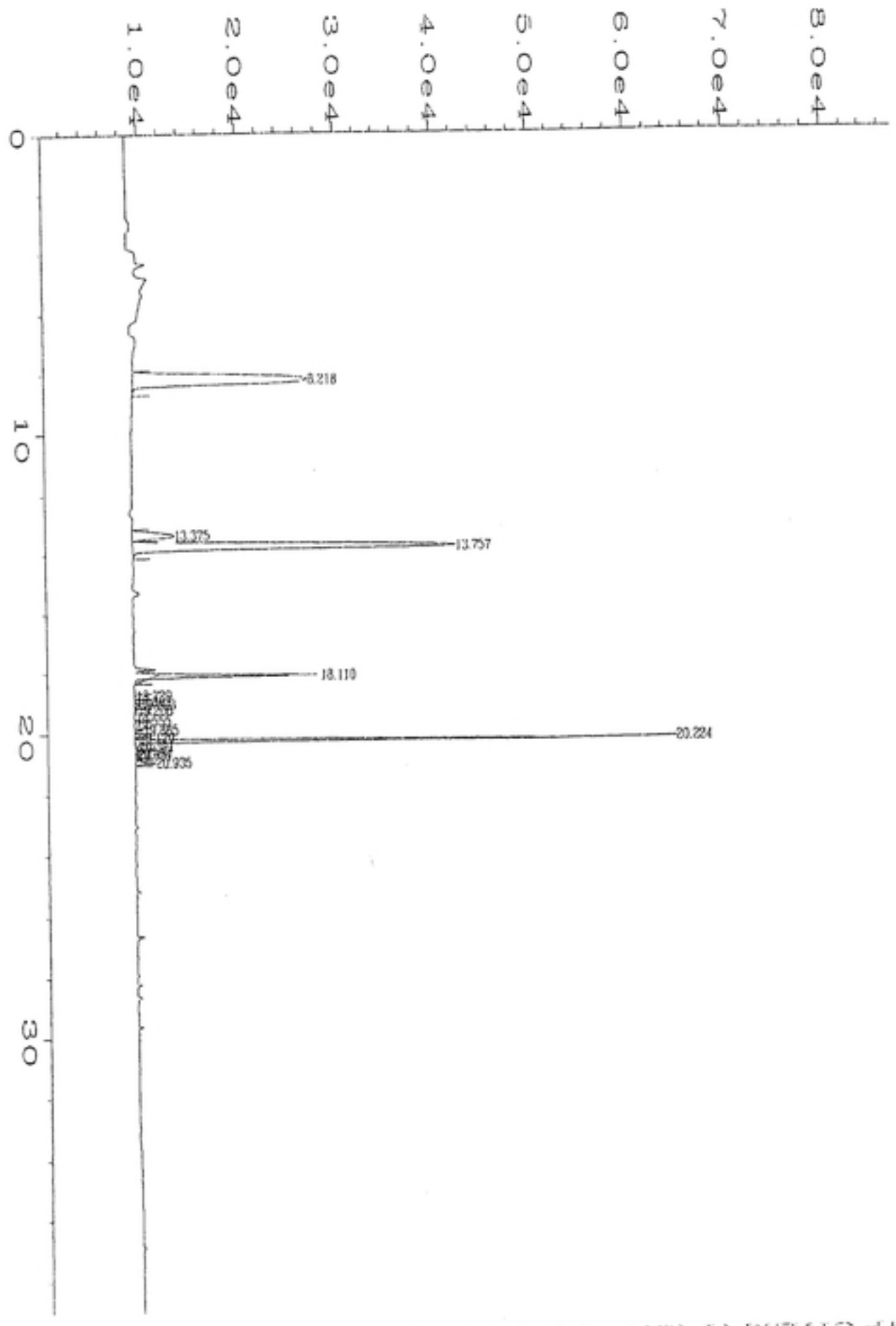
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18.110
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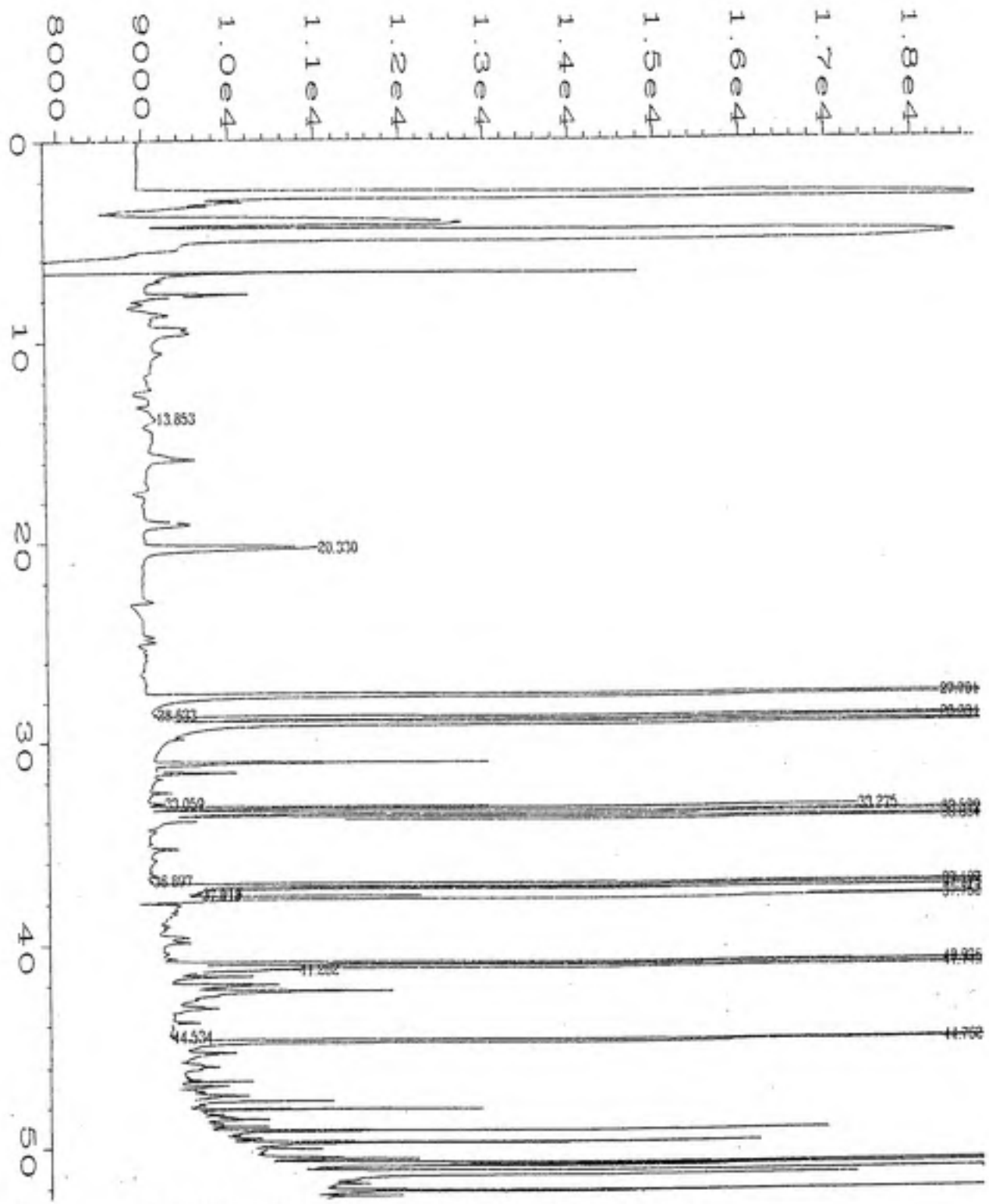
C:\HPCHEM\1\DATA\TC11289\012FO101.D



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cquired on : 05 Nov 98 04:31 PM
eport Created on: 15 Nov 98 05:46 PM

Page Number : 1
Vial Number : 13
Injection Number : 1
Sequence Line : 1
Instrument Method: HAA2.MTH
Analysis Method : HAA2TC.MTH

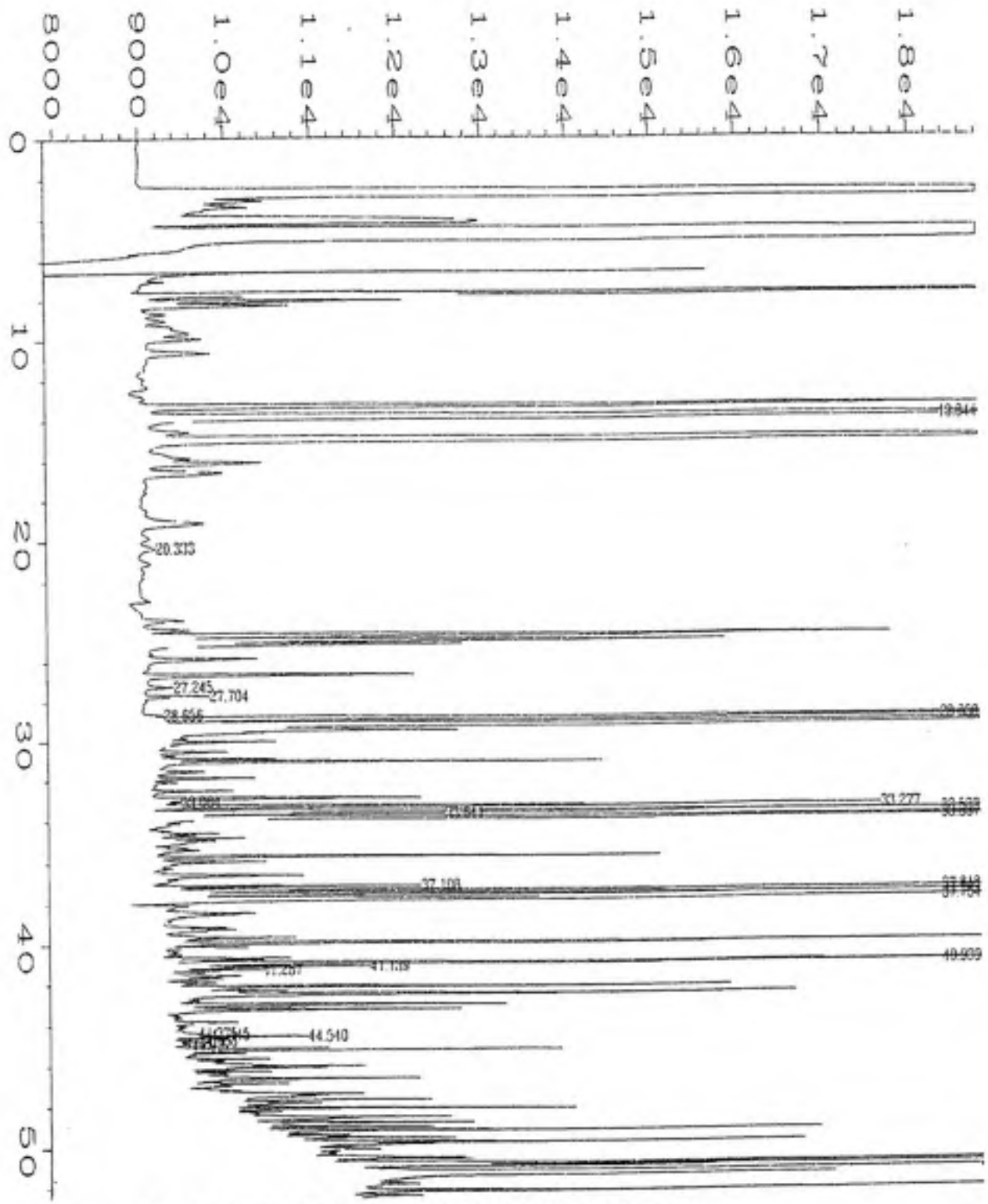
ata File Name : C:\HPCHEM\1\DATA\AM110798\015F0101.D
perator : AM
nstrument : ANALYZER1
mple Name : 10/26 R
un Time Bar Code:
quired on : 05 Nov 98 06:27 PM
eport Created on: 15 Nov 98 05:53 PM

Page Number : 1
Vial Number : 15
Injection Number : 1
Sequence Line : 1
Instrument Method: HAA2.MTH
Analysis Method : HAA2TC.MTH

ig. 1 in C:\HPCHEM\1\DATA\AM110798\015F0101.D

Pk#	Ret Time	Area	Height	Type	Width	Area %
1	13.844	249334	23930	BV	0.164	19.7068
2	14.095	0	158	Rsho	0.000	0.0000
3	20.333	2545	172	BBA	0.207	0.2012
4	27.245	191	155	BV	0.021	0.0151
5	27.704	4449	754	VV	0.093	0.3516
6	28.656	385	138	BV	0.054	0.0304
7	28.938	177079	31866	VV	0.087	13.9960
8	33.064	572	158	BV	0.059	0.0452
9	33.277	41264	8448	VV	0.075	3.2614
10	33.533	69581	17423	PV	0.062	5.4996
11	33.641	13784	3392	VV	0.060	1.0895
12	33.837	383414	94611	VBA	0.064	30.3043
13	37.108	12498	3171	PV	0.061	0.9879
14	37.297	0	13638	Fsho	0.000	0.0000
15	37.318	79534	22045	VV	0.055	6.2862
16	37.509	47077	11436	VV	0.063	3.7209
17	37.694	0	5529	Fsho	0.000	0.0000
18	37.754	101211	19498	VV	0.073	7.9995
19	37.849	0	2225	Rsho	0.000	0.0000
20	40.939	62322	25025	BV	0.043	4.9258
21	41.139	6671	1983	PV	0.054	0.5272
22	41.287	3240	951	PV	0.054	0.2561
23	44.375	528	185	BV	0.048	0.0417
24	44.445	1435	348	VV	0.062	0.1135
25	44.540	5745	1515	VV	0.059	0.4541
26	44.738	1070	270	PV	0.065	0.0845
27	44.829	354	117	VV	0.051	0.0280
28	44.937	932	193	VBA	0.070	0.0736

otal area = 1265215



Data File Name : C:\HPCHEM\1\DATA\AM110798\015F0101.D
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Instrument : ANALYZER1
Sample Name : 10/26 R
Auto Time Bar Code:
Acquired on : 05 Nov 98 06:27 PM
Report Created on: 15 Nov 98 05:52 PM

Page Number : 1
Vial Number : 15
Injection Number : 1
Sequence Line : 1
Instrument Method: HAA2.MTH
Analysis Method : HAA2TC.MTH

Appendix E: Summaries of Preliminary Coagulation Experiments

Table E1: Coagulation of Indianapolis raw water, collected on 7/22/98, T = 27 °C, conducted at ambient pH.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	7.9	14.9	2.5	2.6	0.090	0.071	3.46
1	0	7.9	14.9	2.6	2.6	0.094	0.073	3.62
2	5	7.8	13.7	2.6	2.5	0.094	0.073	3.76
3	10	7.8	12.7	2.4	2.6	0.090	0.070	3.46
4	15	7.7	7.1	2.5	2.6	0.090	0.070	3.46
5	20	7.6	2.9	2.4	2.3	0.086	0.068	3.74
6	25	7.6	2.4	2.4	2.3	0.083	0.065	3.61
7	30	7.6	2.1	2.3	2.3	0.082	0.064	3.57
8	35	7.6	2.3	2.4	2.2	0.081	0.063	3.68
9	40	7.6	2.7	2.3	2.1	0.077	0.060	3.67

Table E2: Coagulation of Indianapolis raw water, collected on 7/22/98, T = 27 °C, conducted at pH 6.5. The pH was adjusted with hydrochloric acid.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	6.6	16.5	2.4	2.6	0.092	0.072	3.54
1	5	6.6	16.4	2.4	2.5	0.086	0.067	3.44
2	10	6.6	11.1	2.4	2.2	0.081	0.063	3.68
3	15	6.6	5.4	2.4	2.1	0.077	0.059	3.67
4	20	6.6	2.4	2.3	2.1	0.073	0.055	3.48
5	25	6.6	1.7	2.1	2.1	0.068	0.052	3.24
6	30	6.5	1.4	2.2	2.2	0.068	0.051	3.09
7	35	6.7	1.8	2.1	2.1	0.064	0.049	3.09
8	40	6.7	0.74	2.0	2.1	0.063	0.047	3.00

Table E3: Coagulation of Indianapolis raw water, collected on 7/30/98, T = 25 °C, conducted at ambient pH.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	7.8	>200	2.6	2.6	0.110	0.088	4.23
1	0	7.8	34	2.6	2.5	0.110	0.088	4.40
2	5	7.7	13.5	2.4	2.6	0.108	0.087	4.15
3	10	7.7	6.6	2.5	2.6	0.104	0.083	4.00
4	15	7.6	3.7	2.4	2.3	0.096	0.076	4.17
5	20	7.6	2.6	2.4	2.3	0.085	0.069	3.70
6	25	7.6	1.9	2.3	2.3	0.081	0.062	3.52
7	30	7.5	1.5	2.4	2.2	0.078	0.058	3.54
8	35	7.4	1.6	2.3	2.1	0.075	0.056	3.57

Table E4: Coagulation of Indianapolis ozonated raw water, 0.53 mg /l ozone; CT = 0.5 mg*min/l, collected on 8/10/98, T = 26 °C, conducted at ambient pH.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	7.7	25.0	4.5	5.0	0.061	0.042	1.22
1	0	7.8	14.8	4.7	4.5	0.061	0.041	1.36
2	5	7.7	12.8	4.4	5.0	0.056	0.038	1.12
3	10	7.5	6.2	4.3	4.5	0.051	0.034	1.13
4	15	7.5	2.3	4.3	4.5	0.050	0.032	1.11
5	20	7.4	1.4	4.1	4.0	0.046	0.029	1.15
6	25	7.4	0.97	4.0	3.8	0.042	0.028	1.11
7	30	7.3	0.62	3.8	3.9	0.042	0.025	1.08
8	35	7.3	0.64	3.7	4.1	0.038	0.023	0.93

Table E5: Coagulation of Indianapolis ozonated raw water, 0.53 mg /l ozone; CT = 0.5 mg*min/l, collected on 8/10/98, T = 26 °C, conducted at pH 6.5. The pH was adjusted with hydrochloric acid.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
1	0	6.7	11.7	4.1	4.2	0.066	0.048	1.57
2	5	6.7	11.8	4.1	3.9	0.06	0.044	1.54
3	10	6.7	11.4	3.9	3.6	0.053	0.037	1.47
4	15	6.7	3.4	3.6	3.4	0.046	0.033	1.35
5	20	6.6	1.9	4.7	4.6	0.044	0.031	0.96
6	25	6.5	0.99	3.0	2.9	0.036	0.025	1.24
7	30	6.4	0.93	2.9	2.8	0.036	0.025	1.29
8	35	6.4	0.70	4.7	4.7	0.034	0.023	0.72

Table E6: Coagulation of Indianapolis ozonated raw water, 7.28 mg/l ozone; CT = 1.8 mg*min/l, collected on 8/18/98, T = 24 °C, alkalinity = 214 mg/l $CaCO_3$, conducted at ambient pH.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	7.9	10.8			0.041	0.034	
1	0	7.7	6.1			0.037	0.034	
2	5	7.9	4.2			0.029	0.032	
3	10	7.8	1.3			0.028	0.030	
4	15	7.8	1.0			0.026	0.028	
5	20	7.8	1.2			0.025	0.028	
6	25	7.7	1.2			0.022	0.026	

Table E7: Coagulation of Indianapolis ozonated raw water, 7.28 mg/l ozone; CT = 1.8 mg*min/l, collected on 8/18/98, T = 24 °C, alkalinity = 214 mg/l $CaCO_3$, conducted at pH 6.5. The pH was adjusted with hydrochloric acid.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
1	0	6.3	10.6			0.028	0.033	
2	5	6.6	7.3			0.028	0.029	
3	10	6.5	5.2			0.018	0.028	
4	15	6.7	2.4			0.017	0.025	
5	20	6.6	1.8			0.017	0.022	
6	25	6.6	1.1			0.013	0.021	
7	30	6.5	0.89			0.012	0.020	
8	35	6.3	0.64			0.011	0.018	

Note: Due to malfunctioning problem with TOC analyzer, TOC and DOC analyses were not conducted for this set of coagulation experiments.

Table E8: Coagulation of Indianapolis ozonated raw water, 0.22 mg /L ozone; CT = 0.98 mg*min/l, collected on 8/25/98, T = 26 °C, pH adjusted to 6.6-6.8 at IWC.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	6.6	12	3.0	3.2	0.048	0.038	1.50
1	0	6.8	7.3	2.9	3.2	0.049	0.038	1.53
2	5	6.8	6.1	2.8	3.0	0.043	0.033	1.43
3	10	6.8	3.1	2.6	2.7	0.040	0.030	1.48
4	15	6.8	0.87	2.5	2.6	0.032	0.026	1.23
5	20	6.8	0.50	2.6	2.5	0.034	0.025	1.36
6	25	6.8	0.59	2.3	2.6	0.033	0.024	1.27
7	30	6.5	0.48	2.3	2.4	0.034	0.025	1.42
8	35	6.7	0.41	2.2	2.4	0.031	0.025	1.29

Table E9: Coagulation of Indianapolis ozonated raw water, 0.22 mg /L ozone; CT = 0.15 mg*min/l, Collected on 8/31/98, T = 24 °C, pH adjusted to 6.6-6.8 at IWC.

Sample	Alum Dose	pH	Turbidity	TOC	DOC	UV 254	UV 272	SUVA
	mg/l		NTU	mg/l	mg/l	cm^{-1}	cm^{-1}	l/(mg*m)
raw water	-	6.7	33	3.0	2.9	0.054	0.045	1.86
1	0	6.9	12	2.9	3.1	0.058	0.045	1.87
2	5	6.9	5.5	2.9	3.0	0.050	0.042	1.67
3	10	6.9	2.2	2.7	2.8	0.042	0.034	1.50
4	15	6.8	0.83	2.4	2.4	0.038	0.030	1.58
5	20	6.8	0.98	2.4	2.4	0.040	.0.030	1.67
6	25	6.9	0.99	2.7	2.4	0.038	0.029	1.58

Appendix F: Summaries of Pilot Plant Operations

Experiment 1: 092998-100198 and 100698-100898

Operating Objectives: Pre-ozonate at ambient pH for 0.5 log Giardia, coagulate at ambient pH
Two sets of samples were collected for Experiment 1. The first set was collected from 092998 to 100198, and the second set was collected from 100698 to 100898. The purpose for collecting the samples twice was to determine whether the pilot plant is running at steady state after two weeks of operation.

Batch 1: 092998-100198

Operating conditions	9/29/98	9/30/98	10/1/98
Ozone dose, mg/L	0.98	1.12	0.91
Target CT, mg-min/L	0.08	0.08	0.08
Calculated CT, mg-min/L	0.15	0.28	0.23
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	40	41	41
pH of coagulation	7.9	7.9	8.0
pH of ozonation	7.9	8.0	8.1
Temp of raw water, °C	23.8	23.8	23.3
Ave Temp of effluent water, °C	23.3	23.3	23.3

Water Quality Characteristics

Turbidity, NTU	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	25.4	26.0	25.6	25.7	0.3	1%
Ozonated	20.1	22.5	22.8	21.8	1.5	7%
Settled	3.9	4.0	4.2	4.0	0.2	4%
Filter 1	0.13	0.15	0.13	0.14	0.01	8%
Filter 2	0.16	0.17	0.10	0.14	0.04	26%
Filter 3	0.15	0.16	0.11	0.14	0.03	19%
Filter 4	0.13	0.23	0.24	0.20	0.06	30%

TOC, mg/L	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	3.1	2.8	2.9	2.9	0.1	5%
Ozonated	3.2	2.9	3.3	3.2	0.2	6%
Settled	2.6	2.6	2.9	2.7	0.2	7%
Filter 1	2.0	2.0	1.8	1.9	0.1	6%
Filter 2	1.7	2.1	1.8	1.9	0.2	10%
Filter 3	2.1	2.3	2.0	2.1	0.2	8%
Filter 4	2.1	2.2	2.0	2.1	0.1	5%

DOC, mg/L	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	2.8	2.4	2.9	2.7	0.3	10%
Ozonated	3.1	3.0	3.2	3.1	0.1	4%
Settled	2.6	2.4	2.8	2.6	0.2	8%
Filter 1	2.0	1.9	1.7	1.9	0.2	9%
Filter 2	1.8	1.8	1.7	1.8	0.1	3%
Filter 3	2.0	2.0	1.9	2.0	0.1	3%
Filter 4	2.3	2.0	2.0	2.1	0.2	8%

UV absorbance at 254 nm, cm^{-1}	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	0.076	0.075	0.075	0.075	0.001	1%
Ozonated	0.053	0.051	0.048	0.051	0.003	5%
Settled	0.040	q	0.040	0.040	0.000	0%
Filter 1	0.030	0.036	0.029	0.032	0.004	12%
Filter 2	0.032	0.035	0.029	0.032	0.003	9%
Filter 3	0.038	0.042	0.035	0.038	0.004	9%
Filter 4	0.038	q	0.035	0.037	0.002	6%

Batch 1: 092998-100198

UV absorbance at 272 nm, cm^{-1}	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	0.063	0.063	0.062	0.063	0.001	1%
Ozonated	0.041	0.041	0.038	0.040	0.002	4%
Settled	0.031	q	0.031	0.031	0.000	0%
Filter 1	0.023	0.027	0.021	0.024	0.003	13%
Filter 2	0.023	0.027	0.022	0.024	0.003	11%
Filter 3	0.030	0.031	0.027	0.029	0.002	7%
Filter 4	0.026	q	0.025	0.026	0.001	3%

BDOC, mg/L	9/29/98	9/30/98	10/1/98	Average	Std Dev	CV
Raw	0.3	N/A	0.4	0.4	0.1	27%
Ozonated	1.8	N/A	0.6	1.2	0.8	67%
Settled	0.8	N/A	0.8	0.8	0.0	5%
Filter 1	0.1	N/A	0.2	0.1	0.1	74%
Filter 2	0.1	N/A	0.1	0.1	0.0	24%
Filter 3	0.3	N/A	0.3	0.3	0.0	9%
Filter 4	0.6	N/A	0.4	0.5	0.1	23%

Note: UFC THM4 and UFC HAA9 were not measured in Batch 1 of Experiment 1.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'q' indicates the data point is questionable.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment 1: 092998-100198 and 100698-100898

Operating Objectives: Pre-ozonate at ambient pH for 0.5 log Giardia, coagulate at ambient pH
Two sets of samples were collected for Experiment 1. The first set was collected from 092998 to 100198, and the second set was collected from 100698 to 100898. The purpose for collecting the samples twice was to determine whether the pilot plant is running at steady state after two weeks of operation.

Batch 2: 100698-100898

Operating conditions	10/6/98	10/7/98	10/8/98
Ozone dose, mg/L	1.33	0.9	1.13
Target CT, mg-min/L	0.08	0.08	0.08
Calculated CT, mg-min/L	0.16	0.13	0.13
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	44	38	45
pH of coagulation	7.7	7.9	7.8
pH of ozonation	8.0	8.1	8.0
Temp of raw water, °C	21.1	20.3	20
Ave Temp of effluent water, °C	21.9	20.6	20.6

Water Quality Characteristics

Turbidity, NTU	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	47.0	36.1	27.0	37.4	10.0	27%
Ozonated	32.0	37.1	18.0	29.0	9.9	34%
Settled	5.2	6.7	7.9	6.6	1.4	20%
Filter 1	0.15	0.23	0.18	0.19	0.04	22%
Filter 2	0.17	0.39	0.22	0.26	0.12	44%
Filter 3	0.11	0.17	0.13	0.14	0.03	22%
Filter 4	0.15	0.13	0.26	0.18	0.07	39%

TOC, mg/L	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	3.2	3.0	3.3	3.2	0.2	5%
Ozonated	3.4	3.4	3.7	3.5	0.2	5%
Settled	2.9	2.8	2.9	2.8	0.1	2%
Filter 1	2.1	2.1	1.4	1.9	0.4	24%
Filter 2	2.1	2.0	2.0	2.0	0.1	5%
Filter 3	2.2	2.2	2.1	2.2	0.1	4%
Filter 4	2.4	2.1	2.1	2.2	0.1	6%

DOC, mg/L	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	2.9	2.7	3.0	2.9	0.2	6%
Ozonated	3.3	2.9	3.5	3.3	0.3	9%
Settled	2.7	2.6	2.8	2.7	0.1	4%
Filter 1	2.1	1.9	1.3	1.8	0.4	21%
Filter 2	2.0	1.9	1.9	1.9	0.1	4%
Filter 3	2.2	2.0	2.1	2.1	0.1	4%
Filter 4	2.2	2.0	2.1	2.1	0.1	3%

UV absorbance at 254 nm, cm^{-1}	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	0.077	0.077	0.097	0.084	0.012	14%
Ozonated	0.052	0.055	0.068	0.058	0.009	15%
Settled	0.040	0.044	0.045	0.043	0.003	6%
Filter 1	0.031	0.037	0.035	0.034	0.003	9%
Filter 2	0.033	0.032	0.036	0.034	0.002	6%
Filter 3	0.040	0.038	0.040	0.039	0.001	3%
Filter 4	0.037	0.040	0.042	0.040	0.003	6%

Batch 2: 100698-100898

UV absorbance at 272 nm, cm^{-1}	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	0.065	0.065	0.084	0.071	0.011	15%
Ozonated	0.042	0.043	0.056	0.047	0.008	17%
Settled	0.033	0.037	0.038	0.036	0.003	7%
Filter 1	0.027	0.030	0.028	0.028	0.002	5%
Filter 2	0.026	0.026	0.032	0.028	0.003	12%
Filter 3	0.031	0.031	0.034	0.032	0.002	5%
Filter 4	0.032	0.033	0.032	0.032	0.001	2%

BDOC, mg/L	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	0.0	N/A	0.7	0.3	0.4	129%
Ozonated	0.5	N/A	0.4	0.4	0.1	14%
Settled	0.3	N/A	0.5	0.4	0.2	38%
Filter 1	0.4	N/A	0.3	0.3	0.0	11%
Filter 2	0.2	N/A	0.2	0.2	0.1	28%
Filter 3	0.2	N/A	0.1	0.1	0.0	37%
Filter 4	0.2	N/A	<0.1	N/A	N/A	N/A

UFC HAA9, µg/L	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	q	80	94	87	10	11%
Ozonated	51	51	51	51	0	0%
Settled	39	49	36	41	7	16%
Filter 1	20	22	19	20	2	8%
Filter 2	19	23	q	21	3	13%
Filter 3	22	22	17	20	3	14%
Filter 4	21	21	22	21	1	3%

Cl_2 consumed, mg/L-Cl_2	10/6/98	10/7/98	10/8/98	Average	Std Dev	CV
Raw	4.4	4.2	4.9	4.5	0.4	8%
Ozonated	3.2	3.4	3.5	3.3	0.2	5%
Settled	3.0	3.2	2.7	2.9	0.3	9%
Filter 1	1.3	1.4	1.4	1.4	0.0	3%
Filter 2	1.5	1.2	1.4	1.4	0.1	11%
Filter 3	1.3	1.4	1.4	1.4	0.0	3%
Filter 4	1.3	1.3	1.4	1.3	0.0	3%

Note: UFC THM4 samples were lost due to contamination.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'q' indicates the data point is questionable.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment 1: 092998-100198 and 100698-100898

Operating Objectives: Pre-ozonate at ambient pH for 0.5 log Giardia, coagulate at ambient pH

Two sets of samples were collected for Experiment 1. The first set was collected from 092998 to 100198, and the second set was collected from 100698 to 100898. The purpose for collecting the samples twice was to determine whether the pilot plant is running at steady state after two weeks of operation.

Experiment 1: 092998-100198 and 100698-100898

Two week Average

Water Quality Characteristics

Turbidity, NTU	Average	Std Dev	CV
Raw	31.5	9.0	29%
Ozonated	25.4	7.5	29%
Settled	5.3	1.6	31%
Filter 1	0.16	0.04	24%
Filter 2	0.20	0.10	50%
Filter 3	0.14	0.03	19%
Filter 4	0.19	0.06	31%

TOC, mg/L	Average	Std Dev	CV
Raw	3.1	0.2	7%
Ozonated	3.3	0.2	7%
Settled	2.8	0.1	5%
Filter 1	1.9	0.3	15%
Filter 2	1.9	0.1	8%
Filter 3	2.1	0.1	6%
Filter 4	2.1	0.1	6%

DOC, mg/L	Average	Std Dev	CV
Raw	2.8	0.2	8%
Ozonated	3.2	0.2	7%
Settled	2.7	0.2	6%
Filter 1	1.8	0.3	15%
Filter 2	1.9	0.1	6%
Filter 3	2.0	0.1	4%
Filter 4	2.1	0.1	6%

UV absorbance at 254 nm, cm^{-1}	Average	Std Dev	CV
Raw	0.080	0.009	11%
Ozonated	0.055	0.007	13%
Settled	0.042	0.002	6%
Filter 1	0.033	0.003	10%
Filter 2	0.033	0.002	8%
Filter 3	0.039	0.002	6%
Filter 4	0.038	0.003	7%

Experiment 1: 092998-100198 and 100698-100898

Water Quality Characteristics Two week average

UV absorbance at 272 nm, cm^{-1}	Average	Std Dev	CV
Raw	0.067	0.008	13%
Ozonated	0.044	0.006	15%
Settled	0.034	0.003	10%
Filter 1	0.026	0.003	13%
Filter 2	0.026	0.004	14%
Filter 3	0.031	0.002	7%
Filter 4	0.030	0.004	13%

BDOC, mg/L	Average	Std Dev	CV
Raw	0.4	0.3	74%
Ozonated	0.8	0.7	81%
Settled	0.6	0.2	37%
Filter 1	0.2	0.1	57%
Filter 2	0.1	0.1	67%
Filter 3	0.2	0.1	49%
Filter 4	0.4	0.2	54%

UFC HAA9, µg/L	Average	Std Dev	CV
Raw	87	10	11%
Ozonated	51	0	0%
Settled	41	7	16%
Filter 1	20	2	8%
Filter 2	21	3	13%
Filter 3	20	3	14%
Filter 4	21	1	3%

Experiment 2: 102698-102898

Operating Objectives: Pre-ozonate at pH 6.5 for 0.5 log Giardia, coagulate at pH 6.5

Operating conditions	10/26/98	10/27/98	10/28/98
Ozone dose, mg/L	0.95	0.64	0.59
Target CT, mg-min/L	0.12	0.12	0.12
Calculated CT, mg-min/L	0.16	0.5	0.53
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	26	30	30
pH of coagulation	6.5	6.5	6.5
pH of ozonation	6.5	6.5	6.5
Temp of raw water, °C	16	17	17
Ave Temp of effluent water, °C	17	19	18

Water Quality Characteristics

Turbidity, NTU	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	16.2	19.7	19.3	18.4	1.9	10%
Ozonated	14.9	15.2	13.1	14.4	1.1	8%
Settled	5.7	4.5	6.7	5.6	1.1	20%
Filter 1	0.51	0.8	1.3	0.86	0.37	43%
Filter 2	0.37	0.3	2.2	0.94	1.05	112%
Filter 3	0.32	0.4	1.7	0.82	0.80	97%
Filter 4	0.28	0.3	1.6	0.72	0.73	100%

TOC, mg/L	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	2.7	q	2.4	2.6	0.2	7%
Ozonated	2.4	2.3	2.7	2.5	0.2	9%
Settled	2.5	2.4	2.6	2.5	0.1	3%
Filter 1	2.4	2.4	2.1	2.3	0.2	8%
Filter 2	2.6	2.4	2.5	2.5	0.1	5%
Filter 3	2.3	2.3	2.2	2.3	0.0	2%
Filter 4	q	2.2	q	2.2	N/A	N/A

DOC, mg/L	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	q	2.8	2.6	2.7	0.1	5%
Ozonated	2.9	2.6	2.5	2.7	0.2	7%
Settled	2.2	2.5	2.5	2.4	0.2	9%
Filter 1	2.3	1.8	1.9	2.0	0.2	12%
Filter 2	2.5	2.0	2.4	2.3	0.3	13%
Filter 3	2.1	1.9	2.4	2.1	0.2	10%
Filter 4	2.7	2.2	1.6	2.2	0.5	25%

UV absorbance at 254 nm, cm^{-1}	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	0.082	0.082	0.083	0.082	0.001	1%
Ozonated	0.075	0.074	0.059	0.069	0.009	12%
Settled	0.055	0.044	0.050	0.049	0.005	11%
Filter 1	0.046	0.043	0.043	0.044	0.002	5%
Filter 2	0.045	0.040	0.058	0.048	0.009	19%
Filter 3	0.049	0.042	0.044	0.045	0.004	8%
Filter 4	0.051	0.040	0.065	0.052	0.012	24%

UV absorbance at 272 nm, cm^{-1}	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	0.067	0.067	0.068	0.067	0.001	1%
Ozonated	0.061	0.060	0.048	0.056	0.007	13%
Settled	0.044	0.035	0.040	0.040	0.005	11%
Filter 1	0.037	0.034	0.034	0.035	0.002	5%
Filter 2	0.036	0.032	0.047	0.038	0.008	20%
Filter 3	0.039	0.033	0.035	0.036	0.003	9%
Filter 4	0.041	0.032	0.053	0.042	0.011	25%

UFC THM4, µg/L	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	124	110	112	115	8	7%
Ozonated	84	98	77	86	11	12%
Settled	66	66	66	66	0	0%
Filter 1	45	49	48	47	2	4%
Filter 2	48	47	64	53	10	18%
Filter 3	61	58	51	57	5	9%
Filter 4	47	50	67	55	11	20%

UFC HAA9, µg/L	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	79	q	84	82	4	4%
Ozonated	97	79	64	80	17	21%
Settled	52	43	56	50	7	13%
Filter 1	44	35	43	41	5	12%
Filter 2	44	33	55	44	11	25%
Filter 3	47	33	40	40	7	18%
Filter 4	45	39	49	44	5	11%

Δ UV272 ,cm^{-1}	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	0.016	0.013	0.02	0.016	0.004	22%
Ozonated	0.015	0.013	0.009	0.012	0.003	25%
Settled	0.01	0.003	0.004	0.006	0.004	67%
Filter 1	0.006	0.005	0.005	0.005	0.001	11%
Filter 2	0.006	0.006	0.01	0.007	0.002	31%
Filter 3	0.006	0.004	0.001	0.004	0.003	69%
Filter 4	0.011	0.003	0.022	0.012	0.010	79%

Cl_2 consumed, mg/L-Cl_2	10/26/98	10/27/98	10/28/98	Average	Std Dev	CV
Raw	4.3	4.3	3.8	4.1	0.3	7%
Ozonated	3.9	3.9	3.3	3.7	0.3	9%
Settled	2.3	2.1	2.6	2.4	0.3	11%
Filter 1	1.5	1.6	1.4	1.5	0.1	7%
Filter 2	1.7	1.3	1.6	1.5	0.2	12%
Filter 3	2.2	2.3	2.4	2.3	0.1	5%
Filter 4	2.1	2.1	2.4	2.2	0.2	8%

Note: UV absorbance at 254 nm were determined from UV272-UV254 correlation.

SOOC samples were lost due to contamination.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'q' indicates the data point is unreliable.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment : 3 11/21/98-11/23/98

Operating Objectives: Pre-ozonate at pH 6.5 for 1 log Cryptosporidium, coagulate at pH 6.5

Operating conditions	11/21/98	11/22/98	11/23/98
Ozone dose, mg/L	2.81	2.80	2.80
Target CT, mg-min/L	2.24	2.24	2.24
Calculated CT, mg-min/L	2.59	2.55	2.55
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	23	23	23
pH of coagulation	6.3	6.4	6.4
pH of ozonation	6.3	6.4	6.3
Temp of raw water, °C	11	10	11
Ave Temp of effluent water, °C	11	12	13

Water Quality Parameters

Turbidity, NTU	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	13.5	7.4	7.9	9.6	3.4	35%
Ozonated	12.1	7.2	7.6	9.0	2.7	30%
Settled	4.1	3.6	3.5	3.7	0.3	8%
Filter 1	0.6	0.2	0.2	0.3	0.2	70%
Filter 2	0.6	0.2	0.1	0.3	0.2	73%
Filter 3	0.1	0.1	0.3	0.2	0.1	49%
Filter 4	0.4	0.2	0.3	0.3	0.1	46%

TOC, mg/L	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	3.3	4.2	4.1	3.9	0.5	12%
Ozonated	4.1	4.7	4.5	4.5	0.3	7%
Settled	3.8	4.5	4.1	4.1	0.4	9%
Filter 1	3.7	3.9	3.4	3.7	0.3	7%
Filter 2	3.5	3.9	3.1	3.5	0.4	12%
Filter 3	3.3	3.7	3.3	3.4	0.2	7%
Filter 4	3.6	3.5	3.0	3.4	0.3	9%

DOC, mg/L	36120.0	36121.0	36122.0	Average	Std Dev	CV
Raw	3.4	N/A	5.4	4.4	1.5	33%
Ozonated	3.2	N/A	4.8	4.0	1.1	29%
Settled	4.6	N/A	4.9	4.8	0.2	5%
Filter 1	4.6	N/A	4.3	4.4	0.1	3%
Filter 2	4.2	N/A	4.4	4.3	0.1	2%
Filter 3	4.9	N/A	4.3	4.6	0.4	9%
Filter 4	4.7	N/A	4.2	4.4	0.3	8%

UV absorbance at 254 nm, cm^{-1}	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	0.097	0.094	0.091	0.094	0.003	3%
Ozonated	0.035	0.041	0.034	0.037	0.004	10%
Settled	0.035	0.034	0.033	0.034	0.001	3%
Filter 1	0.029	0.033	0.031	0.031	0.002	6%
Filter 2	0.030	0.031	0.030	0.030	0.001	2%
Filter 3	0.034	N/A	0.033	0.034	0.001	2%
Filter 4	0.031	0.036	0.035	0.034	0.003	8%

UV absorbance at 272 nm, cm^{-1}	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	0.084	0.082	0.081	0.082	0.002	2%
Ozonated	0.028	0.032	0.027	0.029	0.003	9%
Settled	0.027	0.028	0.030	0.028	0.002	5%
Filter 1	0.025	0.027	0.029	0.027	0.002	7%
Filter 2	0.027	0.027	0.027	0.027	0.000	0%
Filter 3	0.028	N/A	0.029	0.029	0.001	2%
Filter 4	0.026	0.028	0.032	0.029	0.003	11%

BDOC, mg/L	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	1.2	N/A	0.7	0.9	0.4	38%
Ozonated	1.6	N/A	0.0	0.8	1.1	140%
Settled	1.0	N/A	0.3	0.6	0.5	78%
Filter 1	0.5	N/A	0.7	0.6	0.1	22%
Filter 2	0.5	N/A	0.4	0.5	0.0	6%
Filter 3	0.0	N/A	0.6	0.3	0.4	141%
Filter 4	0.3	N/A	0.6	0.5	0.2	47%

UFC THM4, µg/L	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	168	193	188	183	13	7%
Ozonated	109	138	106	118	18	15%
Settled	69	101	92	87	17	19%
Filter 1	75	92	60	76	16	21%
Filter 2	81	81	75	79	3	4%
Filter 3	72	85	70	76	8	11%
Filter 4	56	83	95	78	20	26%

UFC HAA9, µg/L	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	133	143	138	138	5	4%
Ozonated	46	57	50	51	6	11%
Settled	53	59	54	55	3	6%
Filter 1	40	40	44	41	2	6%
Filter 2	42	44	43	43	1	2%
Filter 3	39	40	43	40	2	6%
Filter 4	42	45	44	44	2	3%

Δ UV272 ,cm^{-1}	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	0.030	0.024	0.028	0.027	0.003	11%
Ozonated	0.002	0.001	0.001	0.001	0.001	43%
Settled	0	0.002	0.004	0.002	0.002	100%
Filter 1	0.003	0.004	0.006	0.004	0.002	35%
Filter 2	0.004	0.005	0.005	0.005	0.001	12%
Filter 3	0.004	N/A	0.01	0.007	0.004	61%
Filter 4	0.007	0.007	0.012	0.009	0.003	33%

Cl_2 consumed, mg/L-Cl_2	11/21/98	11/22/98	11/23/98	Average	Std Dev	CV
Raw	2.9	3.4	2.8	3.0	0.3	11%
Ozonated	2.5	2.5	2.4	2.5	0.1	2%
Settled	2.3	2.4	2.5	2.4	0.1	4%
Filter 1	1.8	1.7	1.2	1.6	0.3	21%
Filter 2	1.3	1.3	0.9	1.2	0.2	20%
Filter 3	1.7	1.3	1.4	1.5	0.2	16%
Filter 4	1.5	1.7	1.3	1.5	0.2	13%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

TOC and DOC data may be questionable due to possible contamination of phosphoric acid.

Experiment : 4 12/7/98-12/9/98

Operating Objectives: Spike with 200 ug/L Br, pre-ozonate at pH 6.5 for 1 log Cryptosporidium, coagulate at pH 6.5

Operating conditions	12/7/98	12/8/98	12/9/98
Ozone dose, mg/L	3.23	2.07	2.04
Target CT, mg-min/L	2.24	2.24	2.24
Calculated CT, mg-min/L	2.73	2.25	3.41
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	21	21	21
pH of coagulation	6.2	6.6	6.6
pH of ozonation	6.3	6.3	6.4
Temp of raw water, °C	13.5	13	11
Ave Temp of effluent water, °C	14	13	11

Water Quality Characteristics

Turbidity, NTU	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	24.1	15.3	12.9	17.4	5.9	34%
Ozonated	25.5	11.6	8.0	15.0	9.3	62%
Settled	2.8	2.5	2.8	2.7	0.2	6%
Filter 1	0.19	0.21	0.21	0.20	0.01	6%
Filter 2	0.33	0.17	0.28	0.26	0.08	31%
Filter 3	0.24	0.21	0.21	0.22	0.02	8%
Filter 4	0.23	0.14	0.22	0.20	0.05	25%

TOC, mg/L	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	3.2	3.0	3.1	3.1	0.1	4%
Ozonated	3.4	3.2	2.9	3.2	0.2	8%
Settled	2.6	3.1	2.9	2.9	0.3	10%
Filter 1	1.9	2.5	2.5	2.3	0.3	15%
Filter 2	2.9	2.7	2.7	2.8	0.1	3%
Filter 3	2.6	2.5	2.2	2.4	0.2	10%
Filter 4	4.6	2.3	3.5	3.5	1.1	32%

DOC, mg/L	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	2.4	N/A	2.6	2.5	0.2	7%
Ozonated	2.6	N/A	2.3	2.4	0.2	8%
Settled	2.2	N/A	2.1	2.1	0.0	1%
Filter 1	1.9	N/A	2.0	2.0	0.1	3%
Filter 2	2.9	N/A	2.1	2.5	0.5	21%
Filter 3	2.2	N/A	2.2	2.2	0.0	1%
Filter 4	3.3	N/A	2.6	2.9	0.5	16%

UV absorbance at 254 nm, cm^{-1}	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	0.079	0.079	0.085	0.081	0.003	4%
Ozonated	0.033	0.029	0.034	0.032	0.003	8%
Settled	0.028	0.031	0.039	0.033	0.006	17%
Filter 1	0.027	0.031	0.036	0.031	0.005	14%
Filter 2	0.043	0.030	0.035	0.036	0.007	18%
Filter 3	0.029	0.030	0.037	0.032	0.004	14%
Filter 4	0.038	0.030	0.037	0.035	0.004	12%

UV absorbance at 272 nm, cm^{-1}	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	0.067	0.066	0.073	0.069	0.004	6%
Ozonated	0.022	0.021	0.028	0.024	0.004	16%
Settled	0.023	0.025	0.032	0.027	0.005	18%
Filter 1	0.019	0.022	0.028	0.023	0.005	20%
Filter 2	0.031	0.022	0.029	0.027	0.005	17%
Filter 3	0.020	0.023	0.029	0.024	0.005	19%
Filter 4	0.027	0.024	0.030	0.027	0.003	11%

BDOC, mg/L	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	0.3	N/A	0.4	0.4	0.1	24%
Ozonated	0.7	N/A	0.5	0.6	0.1	20%
Settled	0.5	N/A	0.4	0.4	0.1	14%
Filter 1	0.5	N/A	0.6	0.5	0.1	13%
Filter 2	0.8	N/A	0.5	0.6	0.2	35%
Filter 3	0.7	N/A	0.6	0.7	0.1	11%
Filter 4	0.8	N/A	0.6	0.7	0.2	24%

UFC THM4, µg/L	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	q	q	127	127	N/A	N/A
Ozonated	59	56	q	58	2	4%
Settled	q	60	68	64	6	9%
Filter 1	50	47	45	47	3	5%
Filter 2	65	61	58	61	4	6%
Filter 3	59	63	49	57	7	13%
Filter 4	73	60	68	67	7	10%

UFC HAA9, µg/L	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	q	q	57	57	N/A	N/A
Ozonated	19	17	q	18	1	8%
Settled	q	20	16	18	3	16%
Filter 1	11	10	15	12	3	22%
Filter 2	15	11	12	13	2	16%
Filter 3	12	12	12	12	0	0%
Filter 4	15	15	12	14	2	12%

Δ UV272 , cm^{-1}	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	0.029	0.016	0.021	0.022	0.007	30%
Ozonated	0.001	0	0	0.000	0.001	173%
Settled	0.003	0.003	0.002	0.003	0.001	22%
Filter 1	0.001	0.001	0.004	0.002	0.002	87%
Filter 2	0.005	0.001	0.006	0.004	0.003	66%
Filter 3	0	0.001	0.004	0.002	0.002	125%
Filter 4	0.005	0.004	0.005	0.005	0.001	12%

Cl_2 consumed, mg/L-Cl_2	12/7/98	12/8/98	12/9/98	Average	Std Dev	CV
Raw	3.9	3.9	3.8	3.9	0.1	1%
Ozonated	2.8	2.7	3.2	2.9	0.3	9%
Settled	2.6	2.6	3.2	2.8	0.3	12%
Filter 1	2.2	2.3	2.0	2.2	0.2	7%
Filter 2	2.2	2.4	2.0	2.2	0.2	9%
Filter 3	2.2	2.1	2.1	2.1	0.1	3%
Filter 4	2.5	2.3	2.3	2.4	0.1	5%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

In experiments in which ozonation and coagulation were conducted at pH 6.5, Filters 2 and 4 were pH adjusted to approximately 7.5.

Experiment : 5 01/19/99-01/21/99

Operating Objectives: Pre-ozonate at ambient pH for 1 log Cryptosporidium, coagulate at ambient pH

Operating conditions	1/19/99	1/20/99	1/21/99
Ozone dose, mg/L	2.36	3.29	1.79
Target CT, mg-min/L	2.24	2.24	2.24
Calc CT, mg-min/L	2.01	2.17	1.74
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	45	45	41
pH of coagulation	7.2	7.1	7.1
pH of ozonation	7.8	7.6	7.6
Temp of raw water, °C	4	4	3
Avg Temp of effluent water, °C	5	6	6

Water Quality Characteristics

Turbidity, NTU	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	13.9	19.4	26.7	20.0	6.4	32%
Ozonated	13.5	18.1	24.4	18.7	5.5	29%
Settled	6.7	6.6	9.0	7.4	1.4	18%
Filter 1	0.26	0.34	1.9	0.83	0.91	110%
Filter 2	0.2	0.35	2.5	1.0	1.3	127%
Filter 3	0.56	0.85	2.0	1.1	0.8	68%
Filter 4	0.49	0.40	0.85	0.58	0.24	41%

TOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	4.6	3.7	4.0	4.1	0.4	10%
Ozonated	5.0	4.3	4.9	4.7	0.4	9%
Settled	3.8	3.8	4.3	3.9	0.3	7%
Filter 1	2.9	2.8	3.1	2.9	0.2	7%
Filter 2	2.9	3.0	3.2	3.0	0.2	6%
Filter 3	2.9	3.0	3.3	3.1	0.2	6%
Filter 4	2.9	3.1	3.6	3.2	0.4	11%

DOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	3.9	3.6	4.1	3.9	0.2	5%
Ozonated	4.5	4.4	5.1	4.7	0.4	9%
Settled	3.7	3.8	4.4	4.0	0.4	10%
Filter 1	2.8	2.9	3.0	2.9	0.1	5%
Filter 2	2.8	3.0	3.2	3.0	0.2	6%
Filter 3	2.9	3.1	3.3	3.1	0.2	8%
Filter 4	2.9	3.3	3.6	3.2	0.4	11%

UV absorbance at 254 nm, cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.103	0.106	0.132	0.114	0.016	14%
Ozonated	0.060	0.061	0.077	0.066	0.010	14%
Settled	0.035	0.04	0.038	0.038	0.003	7%
Filter 1	0.031	0.037	0.035	0.034	0.003	9%
Filter 2	0.032	0.036	0.037	0.035	0.003	8%
Filter 3	0.035	0.036	0.036	0.036	0.001	2%
Filter 4	0.035	0.037	0.042	0.038	0.004	9%

UV absorbance at 272 nm, cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.083	0.085	0.109	0.092	0.014	16%
Ozonated	0.043	0.042	0.055	0.047	0.007	16%

BDOC, mg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	q	N/A	1.2	1.2	N/A	N/A
Ozonated	1.1	N/A	2.3	1.7	0.8	50%
Settled	1.2	N/A	1.7	1.4	0.3	24%
Filter 1	0.9	N/A	1.1	1.0	0.2	18%
Filter 2	1.0	N/A	1.3	1.1	0.2	18%
Filter 3	1.0	N/A	1.3	1.2	0.2	18%
Filter 4	1.1	N/A	1.6	1.4	0.4	26%

UFC THM4, µg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	130	139	167	145	19	13%
Ozonated	74	96	116	95	21	22%
Settled	70	51	60	60	9	16%
Filter 1	46	49	55	50	5	10%
Filter 2	48	43	48	47	3	6%
Filter 3	49	45	53	49	4	8%
Filter 4	49	46	54	50	4	8%

UFC HAA9, µg/L	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	106	110	139	118	18	15%
Ozonated	74	74	95	81	12	15%
Settled	37	42	58	46	11	24%
Filter 1	31	31	40	34	5	15%
Filter 2	29	34	43	35	7	20%
Filter 3	32	36	46	38	7	19%
Filter 4	35	35	45	38	6	15%

Δ UV272, cm^{-1}	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	0.033	0.028	0.035	0.032	0.004	11%
Ozonated	0.012	0	0	0.012	0.004	28%

Cl_2 consumed, mg/L-Cl_2	1/19/99	1/20/99	1/21/99	Average	Std Dev	CV
Raw	7.0	7.6	7.6	7.4	0.3	5%
Ozonated	6.8	7.1	7.4	7.1	0.3	4%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

In experiments in which ozonation and coagulation were conducted at pH 6.5, Filters 2 and 4 were pH adjusted to approximately 7.5.

Experiment : 6 2/2/99-2/4/99

Operating Objectives: Spike with 200 ug/L Br, pre-ozonate at ambient pH for 1 log Cryptosporidium, coagulate at ambient pH

Operating conditions	2/2/99	2/3/99	2/4/99
Ozone dose, mg/L	2.67	3.27	3.16
Target CT, mg-min/L	2.24	2.24	2.24
Calculated CT, mg-min/L	1.9	2.83	2.24
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	34	53	23
pH of ozonation	7.8	7.9	7.8
pH of coagulation	7.4	7.3	7.4
Temp of raw water, °C	7	7	8
Avg Temp of treated water, °C	10.5	9	10

Water Quality Characteristics

Turbidity, NTU	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	19.2	18.6	18.2	18.7	0.5	3%
Ozonated	17.3	16.3	16.6	16.7	0.5	3%
Settled	7.8	8.4	8.3	8.2	0.3	4%
Filter 1	8.9	2.8	4.0	5.2	3.2	61%
Filter 2	1.7	1.8	2.1	1.9	0.2	11%
Filter 3	1.4	2.2	2.4	2.0	0.5	26%
Filter 4	1.3	1.4	2.2	1.6	0.5	31%

TOC, mg/L	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	3.0	2.8	2.7	2.8	0.1	5%
Ozonated	3.4	3.5	3.2	3.4	0.2	5%
ettled	2.9	2.8	3.0	2.9	0.1	4%
lter 1	N/A	1.9	2.1	2.0	0.2	8%
Filter 2	2.1	2.1	2.2	2.1	0.1	3%
Filter 3	2.2	2.1	2.4	2.2	0.1	6%
Filter 4	2.2	2.1	2.4	2.2	0.1	6%

DOC, mg/L	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	2.8	2.8	2.6	2.7	0.1	5%
Ozonated	3.3	3.3	3.2	3.3	0.1	2%
Settled	2.9	2.8	3.0	2.9	0.1	3%
Filter 1	2.6	2.0	2.2	2.2	0.3	14%
Filter 2	2.2	2.1	2.2	2.2	0.0	2%
Filter 3	2.4	2.1	2.4	2.3	0.2	7%
Filter 4	2.4	2.0	2.5	2.3	0.2	10%

UV absorbance at 254 nm, cm^{-1}	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	0.100	0.100	0.100	0.100	0.000	0%
Ozonated	0.058	0.055	0.058	0.057	0.002	3%
Settled	0.034	0.032	0.038	0.035	0.003	9%
Filter 1	0.032	0.03	0.034	0.032	0.002	6%
Filter 2	0.031	0.029	0.034	0.031	0.003	8%
Filter 3	0.031	0.030	0.037	0.033	0.004	12%
Filter 4	0.032	0.030	0.035	0.032	0.003	8%

UV absorbance at 272 nm, cm^{-1}	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	0.079	0.079	0.079	0.079	0.000	0%
Ozonated	0.039	0.038	0.04	0.039	0.001	3%

BDOC, mg/L	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	1.0	N/A	0.2	0.6	0.6	94%
Ozonated	0.9	N/A	1.1	1.0	0.1	13%
Settled	0.8	N/A	0.7	0.7	0.0	4%
Filter 1	0.4	N/A	0.5	0.5	0.1	18%
Filter 2	0.6	N/A	0.6	0.6	0.0	0%
Filter 3	0.6	N/A	0.5	0.5	0.1	13%
Filter 4	0.6	N/A	0.6	0.6	0.0	5%

UFC THM4, µg/L	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	116	126	146	129	15	12%
Ozonated	83	101	115	100	16	16%
Settled	48	60	85	64	19	29%
Filter 1	Q	47	76	62	21	33%
Filter 2	48	42	81	57	21	37%
Filter 3	44	66	81	64	18	29%
Filter 4	52	67	92	70	20	28%

UFC HAA9, µg/L	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	78	83	84	82	3	4%
Ozonated	49	53	52	51	2	3%
Settled	29	29	33	30	3	9%
Filter 1	23	23	25	24	1	5%
Filter 2	23	23	27	25	2	10%
Filter 3	25	25	28	26	2	6%
Filter 4	26	23	30	26	4	15%

Δ UV272, cm^{-1}	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	0.026	0.027	0.026	0.026	0.001	2%
Ozonated	0.008	0	0	0.008	0.000	0%

Cl_2 consumed, mg/L-Cl_2	2/2/99	2/3/99	2/4/99	Average	Std Dev	CV
Raw	5.6	5.5	5.6	5.6	0.1	1%
Ozonated	5.1	4.9	5.4	5.1	0.3	5%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment : 7 2/22/99-2/25/99

Operating Objectives: Enhanced coagulation at ambient pH, post-ozone dose for 0.5 log Giardia inactivation at enhanced coagulation pH

Operating conditions	2/22/99	2/23/99	2/25/99
Ozone dose, mg/L	0.73	0.73	0.82
Target CT, mg-min/L	0.23	0.23	0.23
Calculated CT, mg-min/L	0.28	1.46	0.44
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	30	24	24
pH of coagulation	7.8	7.7	7.6
pH of ozonation	8.0	7.8	7.9
Temp of raw water, °C	6	5.5	5.5
Avg Temp of effluent water, °C	7	7	7

Water Quality Characteristics

Turbidity, NTU	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	12.3	7.3	6.3	8.6	3.2	37%
Settled	6.39	6.1	5.5	6.0	0.5	8%
Ozonated Settled	q	5.9	6.2	6.1	0.2	3%
Filter 1	0.46	0.89	0.76	0.70	0.22	31%
Filter 2	0.49	0.87	0.62	0.66	0.19	29%
Filter 3	0.40	0.55	0.74	0.56	0.17	30%
Filter 4	0.48	0.98	0.82	0.76	0.26	34%

TOC, mg/L	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	2.5	2.4	2.5	2.5	0.1	3%
Settled	2.4	2.4	2.4	2.4	0.0	2%
Ozonated Settled	2.8	2.6	2.4	2.6	0.2	7%
Filter 1	2.2	2.1	2.1	2.1	0.1	3%
Filter 2	2.4	2.0	2.0	2.1	0.2	10%
Filter 3	q	2.1	2.0	2.1	0.1	4%
Filter 4	2.4	2.1	2.1	2.2	0.2	7%

DOC, mg/L	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	q	2.5	2.5	2.5	0.0	1%
Settled	2.4	2.4	2.4	2.4	0.0	2%
Ozonated Settled	2.7	2.7	2.5	2.6	0.1	4%
Filter 1	2.1	2.0	2.2	2.1	0.1	3%
Filter 2	2.2	2.1	2.0	2.1	0.1	4%
Filter 3	q	2.2	2.1	2.1	0.0	2%
Filter 4	2.2	2.2	2.1	2.2	0.1	3%

UV absorbance at 254 nm, cm^{-1}	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	0.073	0.072	0.071	0.072	0.001	1%
Settled	0.068	0.060	0.058	0.062	0.005	9%
Ozonated Settled	0.047	0.039	0.040	0.042	0.004	10%
Filter 1	0.045	0.035	0.035	0.038	0.006	15%
Filter 2	0.045	0.035	0.035	0.038	0.006	15%
Filter 3	0.035	0.035	0.035	0.035	0.000	0%
Filter 4	0.047	0.030	0.034	0.037	0.009	24%
Filtered				0.037	0.005	14%

UV absorbance at 272 nm, cm^{-1}	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	0.068	0.060	0.060	0.063	0.005	7%
Ozonated	0.036	0.033	0.039	0.036	0.003	8%

BDOC, mg/L	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	0.3	N/A	0.3	0.3	0.0	13%
Settled	0.2	N/A	0.3	0.3	0.1	28%
Ozonated Settled	0.6	N/A	0.4	0.5	0.1	28%
Filter 1	0.3	N/A	0.3	0.3	0.0	6%
Filter 2	0.5	N/A	0.5	0.5	0.0	6%
Filter 3	0.3	N/A	0.3	0.3	0.0	9%
Filter 4	0.4	N/A	0.4	0.4	0.0	2%

UFC THM4, µg/L	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	100	102	92	98	5	5%
Settled	72	84	91	83	9	11%
Ozonated Settled	71	65	66	67	3	5%
Filter 1	Q	49	48	48	0	1%
Filter 2	47	53	49	49	3	6%
Filter 3	56	54	52	54	2	3%
Filter 4	56	53	55	55	1	2%

UFC HAA9, µg/L	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	50	53	50	51	2	3%
Settled	46	47	47	47	1	1%
Ozonated Settled	36	31	32	33	3	8%
Filter 1	22	20	18	20	2	10%
Filter 2	19	19	23	21	2	11%
Filter 3	22	20	20	21	1	5%
Filter 4	22	19	18	20	2	11%

Δ UV272 , cm^{-1}	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	0.023	0.018	0.018	0.020	0.003	15%
Ozonated	0.006	0.007	0.007	0.007	0.001	9%

Cl_2 consumed, mg/L-Cl_2	2/22/99	2/23/99	2/25/99	Average	Std Dev	CV
Raw	3.7	3.6	3.5	3.6	0.1	3%
Ozonated	2.9	2.7	2.7	2.8	0.1	4%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment : 8 3/16/99-3/18/99

Operating Objectives: Enhanced coagulation at ambient pH, post-ozone dose for 1.0 log Cryptosporidium inactivation at enhanced coagulation pH

Operating conditions	3/16/99	3/17/99	3/18/99
Ozone dose, mg/L	2.64	3.20	1.89
Target CT, mg-min/L	3.36	3.36	3.36
Calculated CT, mg-min/L	4.77	4.34	3.69
Alum Dose, mg/L-$Al_2(SO_4)_3 \cdot 14H_2O$	30	30	30
pH of coagulation	7.6	7.6	7.6
pH of ozonation	8.0	7.8	7.9
Temp of raw water, °C	7	9	9
Avg Temp of effluent water, °C	9	11	11

Water Quality Characteristics

Turbidity, NTU	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	10.5	18.5	24.3	17.8	6.9	39%
Settled	9.1	10.5	9.1	9.6	0.8	8%
Ozonated Settled	6.9	7.6	10.1	8.2	1.7	20%
Filter 1	0.56	0.49	0.38	0.5	0.1	19%
Filter 2	0.72	0.52	0.74	0.7	0.1	18%
Filter 3	0.43	0.47	0.64	0.5	0.1	22%
Filter 4	0.62	0.37	0.48	0.5	0.1	26%

TOC, mg/L	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	2.5	2.5	2.5	2.5	0.0	1%
[illegible]ttled	2.4	2.3	2.5	2.4	0.1	5%
[illegible]onated Settled	2.4	2.5	2.3	2.4	0.1	4%
Filter 1	1.9	1.9	1.9	1.9	0.0	2%
Filter 2	1.9	1.9	2.0	1.9	0.1	3%
Filter 3	2.0	2.1	2.0	2.0	0.1	3%
Filter 4	1.9	2.0	2.0	2.0	0.1	3%

DOC, mg/L	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	2.4	2.7	2.7	2.6	0.1	5%
Settled	2.6	2.7	2.3	2.5	0.2	8%
Ozonated Settled	2.6	2.4	2.5	2.5	0.1	4%
Filter 1	2.2	2.0	1.9	2.1	0.1	6%
Filter 2	2.1	2.0	2.0	2.1	0.1	2%
Filter 3	2.1	2.2	2.2	2.1	0.0	1%
Filter 4	2.2	2.1	2.0	2.1	0.1	3%

UV absorbance at 254 nm, cm^{-1}	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	0.063	0.062	0.068	0.064	0.003	5%
Settled	0.047	0.046	0.047	0.047	0.001	1%
Ozonated Settled	q	0.024	0.025	0.025	0.001	3%
Filter 1	0.020	0.020	0.021	0.020	0.001	3%
Filter 2	0.020	0.020	0.021	0.020	0.001	3%
Filter 3	0.020	0.020	0.020	0.020	0.000	0%
Filter 4	0.019	0.020	0.020	0.020	0.001	3%

UV absorbance at 272 nm, cm^{-1}	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	0.052	0.052	0.054	0.053	0.001	2%

BDOC, mg/L	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	0.3	N/A	0.3	0.3	0.0	1%
Settled	0.2	N/A	0.2	0.2	0.0	7%
Ozonated Settled	0.4	N/A	0.7	0.5	0.2	41%
Filter 1	0.5	N/A	0.5	0.5	0.0	8%
Filter 2	0.3	N/A	0.5	0.4	0.1	23%
Filter 3	0.2	N/A	0.4	0.3	0.2	51%
Filter 4	0.6	N/A	0.5	0.5	0.1	12%

UFC THM4, µg/L	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	90	97	103	96	6	7%
Settled	70	71	76	73	3	4%
Ozonated Settled	q	51	55	53	3	5%
Filter 1	40	38	39	39	1	3%
Filter 2	38	39	40	39	1	2%
Filter 3	39	40	39	40	0	1%
Filter 4	40	42	49	44	5	11%
Filtered				40	2	4%

UFC HAA9, µg/L	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	49	50	56	52	3	7%
Settled	37	38	41	39	2	6%
Ozonated Settled	25	26	23	25	2	6%
Filter 1	14	14	14	14	0	2%
Filter 2	13	14	14	14	0	2%
Filter 3	14	10	14	13	2	19%
Filter 4	15	14	15	15	0	2%
Filtered				14	1	6%

Δ UV272 , cm^{-1}	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	0.013	0.013	0.012	0.013	0.001	5%

Cl_2 consumed, mg/L-Cl_2	3/16/99	3/17/99	3/18/99	Average	Std Dev	CV
Raw	6.1	6.1	6.1	6.1	0.0	0%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Experiment : 9 3/29/99-3/31/99

Operating Objectives: 200 ug/L Bromide Spike, Enhanced coagulation at ambient pH, post-ozone dose for 1.0 log Cryptosporidium inactivation

Operating conditions	3/29/99	3/30/99	3/31/99
Ozone dose, mg/L	1.87	2.51	2.45
Target CT, mg-min/L	3.36	3.36	3.36
Calculated CT, mg-min/L	2.57	2.75	3.70
Alum Dose, mg/L-$Al_2(SO_4)_3$-$14H_2O$	30	30	30
pH of coagulation	7.8	7.8	7.8
pH of ozonation	7.9	8.4	8.0
Temp of raw water, °C	11.5	11.5	9
Avg Temp of effluent water, °C	13.5	14	9

Water Quality Characteristics

Turbidity, NTU	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	23.4	29	26.4	26.3	2.8	11%
Settled	5.7	6.3	7.0	6.3	0.7	10%
Ozonated Settled	5.9	q	5.5	5.7	0.2	4%
Filter 1	0.15	0.72	0.47	0.4	0.3	64%
Filter 2	0.20	0.84	0.38	0.5	0.3	70%
Filter 3	0.13	1.15	0.30	0.5	0.5	104%
Filter 4	0.21	0.60	0.36	0.4	0.2	50%

TOC, mg/L	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	2.7	2.9	3.1	2.9	0.2	7%
Settled	2.2	2.2	2.4	2.3	0.1	5%
Ozonated Settled	2.5	2.7	2.7	2.6	0.1	6%
Filter 1	1.8	1.7	1.9	1.8	0.1	4%
Filter 2	1.8	1.8	2.0	1.9	0.1	5%
Filter 3	1.9	2.1	2.2	2.1	0.1	6%
Filter 4	1.9	2.0	2.1	2.0	0.1	6%

DOC, mg/L	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	3.0	3.0	2.9	3.0	0.0	0%
Settled	2.4	2.2	2.5	2.4	0.2	6%
Ozonated Settled	2.7	2.8	2.7	2.7	0.1	2%
Filter 1	1.9	1.9	1.8	1.9	0.0	2%
Filter 2	1.9	2.0	1.9	1.9	0.0	1%
Filter 3	2.0	2.1	2.0	2.0	0.1	3%
Filter 4	2.0	2.1	2.1	2.1	0.1	3%

UV absorbance at 254 nm, cm^{-1}	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	0.066	0.068	0.067	0.067	0.001	1%
Settled	0.05	0.053	0.051	0.051	0.002	3%
Ozonated Settled	0.029	Q	0.028	0.029	0.001	2%
Filter 1	0.027	0.024	0.024	0.025	0.002	7%
Filter 2	0.025	0.025	0.023	0.024	0.001	5%
Filter 3	0.024	0.025	0.023	0.024	0.001	4%
Filter 4	0.024	0.024	0.023	0.024	0.001	2%

UV absorbance at 272 nm, cm^{-1}	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	0.052	0.054	0.056	0.054	0.002	4%

BDOC, mg/L	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	0.6	N/A	0.6	0.6	0.0	5%
Settled	0.4	N/A	0.4	0.4	0.0	0%
Ozonated Settled	0.9	N/A	1.0	1.0	0.1	7%
Filter 1	0.5	N/A	0.4	0.4	0.1	17%
Filter 2	0.4	N/A	0.5	0.5	0.1	27%
Filter 3	0.2	N/A	0.4	0.3	0.1	38%
Filter 4	0.5	N/A	0.5	0.5	0.0	3%

UFC THM4, µg/L	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	135	151	149	145	8	6%
Settled	122	114	113	116	5	4%
Ozonated Settled	89	Q	91	90	1	2%
Filter 1	76	72	72	73	2	3%
Filter 2	79	72	75	75	4	5%
Filter 3	81	76	76	77	3	4%
Filter 4	87	74	77	79	6	8%

UFC HAA9, µg/L	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	64	55	61	60	4	7%
Settled	39	43	41	41	2	5%
Ozonated Settled	23	Q	22	23	1	3%
Filter 1	11	12	13	12	1	7%
Filter 2	14	11	11	12	2	16%
Filter 3	19	16	17	17	1	7%
Filter 4	19	17	23	20	3	16%

Δ UV272 ,cm^{-1}	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	0.011	0.013	0.015	0.013	0.002	15%

Cl_2 consumed, mg/L-Cl_2	3/29/99	3/30/99	3/31/99	Average	Std Dev	CV
Raw	4.6	4.6	4.6	4.6	0.0	0%

Note: 'q' indicates the data point is questionable.

'N/A' is used when the parameter is not applicable due to lack of data or unreliable data.

Due to broken samples during shipment S, and F1-F4 UFC samples from 4/1/99 were used for the respective 3/30/99 samples.

'UFC' indicates chlorination under uniform formation condition (pH =8.0, Temp = 20 °C, Free Chlorine Residual = 1.0 mg/L-Cl_2)

Filters 1 and 2 are GAC/sand filters; Filters 3 and 4 are anthracite/sand filters.

Appendix G: Summaries of Trihalomethane and Haloacetic Acid Formation Under Uniform Formation Conditions (UFC) for Pilot-Plant Operations

Experiment 2
Experiment Date: 10/26 to 10/28

		Concentration (µg/L)				
		$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	10/26	93	25	5	<1	124
	10/27	83	23	4	<1	110
	10/28	84	24	4	<1	112
	Avg.	86	24	5		115
	Std Dev.	6	1	1		8
	CV	7%	5%	16%		7%
Ozonated	10/26	61	19	4	<1	84
	10/27	71	22	5	<1	98
	10/28	51	19	7	<1	77
	Avg.	66	21	5		86
	Std Dev.	7	2	1		11
	CV	10%	11%	21%		13%
Settled	10/26	42	18	6	<1	66
	10/27	41	17	8	<1	66
	10/28	43	17	5	<1	66
	Avg.	42	17	6		66
	Std Dev.	1	0	2		0
	CV	3%	0%	26%		0%
F1	10/26	25	14	6	<1	45
	10/27	27	15	7	<1	49
	10/28	28	14	6	<1	48
	Avg.	27	14	6		47
	Std Dev.	1	0	1		2
	CV	5%	2%	15%		4%
F2	10/26	28	15	6	<1	48
	10/27	28	14	5	<1	47
	10/28	40	18	6	<1	64
	Avg.	31	16	6		53
	Std Dev.	8	2	1		9
	CV	25%	14%	16%		18%
F3	10/26	36	17	6	<1	61
	10/27	34	16	8	<1	58
	10/28	30	15	6	<1	51
	Avg.	34	16	7		57
	Std Dev.	4	1	1		5
	CV	12%	7%	16%		9%
F4	10/26	28	14	5	<1	47
	10/27	28	15	7	<1	50
	10/28	41	19	7	<1	67
	Avg.	32	16	6		55
	Std Dev.	7	2	1		11
	CV	23%	15%	24%		20%

	Average THM Concentration, µg/L				
Location	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	86	24	5	<1	115
Ozonated	66	21	5	<1	86
Settled	42	17	6	<1	66
F1	27	14	6	<1	47
F2	31	16	6	<1	53
F3	34	16	7	<1	57
F4	32	16	6	<1	55

Experiment 3
Experiment Date: 11/21 to 11/23

		Concentration (µg/L)				
		$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	11/21	141	25	2	<1	168
	11/22	163	28	2	<1	193
	11/23	157	28	3	<1	188
	Avg.	154	27	2		183
	Std Dev.	11	2	0		13
	CV	7%	8%	16%		7%
Ozonated	11/21	79	23	8	<1	109
	11/22	104	26	8	<1	138
	11/23	75	22	9	<1	106
	Avg.	91	24	8		118
	Std Dev.	18	2	0		18
	CV	20%	9%	1%		15%
Settled	11/21	48	17	4	<1	69
	11/22	73	21	7	<1	101
	11/23	66	20	7	<1	92
	Avg.	69	20	7		87
	Std Dev.	5	1	0		16
	CV	7%	4%	1%		19%
F1	11/21	50	18	7	<1	75
	11/22	57	23	11	<1	92
	11/23	38	15	7	<1	60
	Avg.	48	19	8		76
	Std Dev.	10	4	3		16
	CV	20%	21%	30%		21%
F2	11/21	55	18	8	<1	81
	11/22	54	19	8	<1	81
	11/23	50	17	8	<1	75
	Avg.	53	18	8		79
	Std Dev.	3	1	0		3
	CV	5%	4%	3%		4%
F3	11/21	50	16	5	<1	72
	11/22	61	17	7	<1	85
	11/23	48	16	7	<1	70
	Avg.	53	17	6		76
	Std Dev.	7	1	1		8
	CV	14%	4%	13%		11%
F4	11/21	38	14	4	<1	56
	11/22	57	19	7	<1	83
	11/23	67	20	8	<1	95
	Avg.	54	18	6		78
	Std Dev.	15	3	2		20
	CV	27%	17%	34%		25%

Average THM Concentration, µg/L					
Location	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	154	27	2	<1	183
Ozonated	91	24	8	<1	118
Settled	69	20	7	<1	87
F1	48	19	8	<1	76
F2	53	18	8	<1	79
F3	53	17	6	<1	76
F4	54	18	6	<1	78

Experiment 4
Experiment Date: 12/7 to 12/9

		Concentration (µg/L)				
		$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	12/7	q				
	12/8	q				
	12/9	42	38	39	8	127
	Avg.	42	38	39	8	127
	Std Dev.					
	CV					
Ozonated	12/7	17	16	20	5	59
	12/8	11	13	22	9	56
	12/9	q				
	Avg.	14	15	21	7	57
	Std Dev.	4	2	1	2	2
	CV	29%	14%	7%	33%	4%
Settled	12/7	q				
	12/8	17	15	22	7	60
	12/9	14	16	25	12	68
	Avg.	15	16	24	9	64
	Std Dev.	2	1	3	4	6
	CV	11%	8%	11%	38%	9%
F1	12/7	9	10	20	11	50
	12/8	9	10	19	8	47
	12/9	8	9	19	9	45
	Avg.	9	10	19	9	47
	Std Dev.	1	1	1	1	3
	CV	8%	8%	3%	14%	6%
F2	12/7	15	14	24	12	65
	12/8	12	13	23	13	61
	12/9	10	11	23	14	58
	Avg.	12	13	24	13	61
	Std Dev.	3	1	0	1	3
	CV	22%	10%	2%	9%	5%
F3	12/7	14	13	22	11	59
	12/8	17	13	22	11	63
	12/9	10	9	21	10	49
	Avg.	13	12	22	10	57
	Std Dev.	3	2	1	1	7
	CV	25%	17%	4%	8%	12%
F4	12/7	20	18	24	10	73
	12/8	14	13	22	12	60
	12/9	13	12	25	18	68
	Avg.	16	14	24	13	67
	Std Dev.	4	3	1	4	6
	CV	26%	23%	6%	30%	9%

Note: 'q' indicates the data point is unreliable.

	Average THM Concentration, µg/L				
Location	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	42	38	39	8	127
Ozonated	14	15	21	7	57
Settled	15	16	24	9	64
F1	9	10	19	9	47
F2	12	13	24	13	61
F3	13	12	22	10	57
F4	16	14	24	13	67

Experiment 5
Experiment Date: 1/19 to 1/23

		Concentration (ug/L)				
		CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	1/19	111	18	3	<1	130
	1/20	127	13	2	<1	139
	1/21	158	10	1	<1	167
	Avg.	132	13	2	<1	145
	Std Dev.	24	4	1	0	19
	CV	18%	29%	61%	0%	13%
Ozonated	1/19	58	12	4	<1	74
	1/20	84	11	3	<1	96
	1/21	107	10	2	<1	116
	Avg.	83	11	3	<1	95
	Std Dev.	24	1	1	0	21
	CV	29%	12%	48%	0%	22%
Settled	1/19	53	13	5	<1	70
	1/20	42	8	3	<1	51
	1/21	53	7	2	<1	60
	Avg.	49	9	3	<1	60
	Std Dev.	6	3	2	0	9
	CV	12%	34%	59%	0%	16%
F1	1/19	30	11	6	<1	46
	1/20	38	9	4	<1	49
	1/21	46	8	3	<1	55
	Avg.	38	9	4	<1	50
	Std Dev.	8	1	2	0	5
	CV	21%	14%	40%	0%	10%
F2	1/19	32	11	6	<1	48
	1/20	33	8	3	<1	43
	1/21	41	7	2	<1	48
	Avg.	35	9	4	<1	47
	Std Dev.	5	2	2	0	3
	CV	13%	22%	52%	0%	6%
F3	1/19	33	11	6	<1	49
	1/20	35	8	3	<1	45
	1/21	45	7	2	<1	53
	Avg.	38	9	4	0	49
	Std Dev.	7	2	2	0	4
	CV	17%	21%	50%	0%	8%
F4	1/19	34	11	6	<1	49
	1/20	36	8	3	<1	46
	1/21	46	7	2	<1	54
	Avg.	39	9	4	0	50
	Std Dev.	7	2	2	0	4
	CV	17%	21%	48%	0%	8%

Average THM Concentration, µg/L					
Location	CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	132	13	2	<1	145
Ozonated	83	11	3	<1	95
Settled	49	9	3	<1	60
F1	38	9	4	<1	50
F2	35	9	4	<1	47
F3	38	9	4	0	49
F4	39	9	4	0	50

Experiment 6
Experiment Date: 2/2 to 2/4

		Concentration (ug/L)				
		CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	2/2	96	16	3	<1	116
	2/3	75	35	15	1	126
	2/4	63	45	32	6	146
	Avg.	78	32	17	3	129
	Std Dev.	17	14	14	4	15
	CV	21%	45%	85%	118%	12%
Ozonated	2/2	65	14	5	<1	83
	2/3	50	27	20	3	101
	2/4	35	33	36	12	115
	Avg.	50	25	21	7	100
	Std Dev.	15	10	15	6	16
	CV	30%	39%	74%	79%	16%
Settled	2/2	34	10	5	<1	48
	2/3	22	17	17	4	60
	2/4	19	23	30	12	85
	Avg.	25	17	17	8	64
	Std Dev.	8	7	13	6	19
	CV	33%	39%	73%	73%	29%
F1	2/2			Lost		
	2/3	12	13	17	6	47
	2/4	12	19	30	16	76
	Avg.	12	16	23	11	62
	Std Dev.	0	4	9	7	21
	CV	1%	25%	40%	68%	33%
F2	2/2	31	11	6	<1	48
	2/3	27	10	6	<1	42
	2/4	14	20	31	16	81
	Avg.	24	14	14	16	57
	Std Dev.	9	6	15		21
	CV	39%	42%	102%		37%
F3	2/2	29	10	6	<1	44
	2/3	21	18	20	6	66
	2/4	14	20	30	16	81
	Avg.	22	16	19	11	64
	Std Dev.	7	5	12	7	18
	CV	34%	33%	66%	60%	29%
F4	2/2	36	11	6	<1	52
	2/3	23	19	20	6	67
	2/4	19	24	33	16	92
	Avg.	26	18	19	11	70
	Std Dev.	9	7	13	7	20
	CV	34%	37%	69%	59%	28%

Note: 'q' indicates the data point is unreliable.

Average THM Concentration, µg/L					
Location	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	TTHM
Raw	78	32	17	3	129
Ozonated	50	25	21	7	100
Settled	25	17	17	8	64
F1	12	16	23	11	62
F2	24	14	14	16	57
F3	22	16	19	11	64
F4	26	18	19	11	70

Experiment 7
Experiment Date: 2/22 to 2/24

		Concentration (ug/L)				
		CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	2/22	81	16	4	<1	100
	2/23	82	16	4	<1	102
	2/24	73	16	4	<1	92
	Avg.	79	16	4	<1	98
	Std Dev.	5	0	0		5
	CV	7%	2%	5%		5%
Settled	2/22	56	13	4	<1	72
	2/23	65	15	4	<1	84
	2/24	70	17	5	<1	91
	Avg.	64	15	4	<1	83
	Std Dev.	7	2	1		9
	CV	11%	12%	15%		11%
Ozonated	2/22	50	14	7	<1	71
	2/23	47	12	6	<1	65
	2/24	45	13	7	<1	66
	Avg.	48	13	6	<1	67
	Std Dev.	3	1	1		3
	CV	6%	6%	8%		5%
F1	2/22			Lost		
	2/23	30	11	7	<1	49
	2/24	29	11	7	<1	48
	Avg.	30	11	7	<1	48
	Std Dev.	1	0	0		0
	CV	3%	1%	4%		1%
F2	2/22	31	10	6	<1	47
	2/23	33	12	7	<1	53
	2/24	30	11	7	<1	49
	Avg.	32	11	7	<1	49
	Std Dev.	2	1	1		3
	CV	6%	8%	14%		6%
F3	2/22	36	12	7	<1	56
	2/23	35	11	7	<1	54
	2/24	33	12	7	<1	52
	Avg.	35	12	7	<1	54
	Std Dev.	2	0	0		2
	CV	5%	3%	5%		3%
F4	2/22	38	12	6	<1	56
	2/23	35	11	7	<1	53
	2/24	35	12	7	<1	55
	Avg.	36	12	7	<1	55
	Std Dev.	2	0	1		1
	CV	5%	3%	8%		2%

Summary	Concentration (ug/L)				
	CHCl3	CHCl2Br	CHBr2Cl	CHBr3	TTHM
Raw	79	16	4	<1	98
Settled	64	15	4	<1	83
Ozonated Settled	48	13	6	<1	67
F1	30	11	7	<1	48
F2	32	11	7	<1	49
F3	35	12	7	<1	54
F4	36	12	7	<1	55

Experiment 8
Experiment Date: 3/16 to 3/18

		Concentration (ug/L)				
		CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	3/16	73	15	3	<1	90
	3/17	79	16	3	<1	97
	3/18	88	14	2	<1	103
	Avg.	80	15	3	<1	96
	Std Dev.	7	1	1		6
	CV	9%	6%	21%		7%
Settled	3/16	56	13	3	<1	70
	3/17	55	14	4	<1	71
	3/18	62	13	3	<1	76
	Avg.	58	13	3	<1	73
	Std Dev.	4	0	1		3
	CV	7%	3%	17%		4%
Ozonated	3/16			9		
	3/17	38	10	4	<1	51
	3/18	42	10	4	<1	55
	Avg.	54	13	4	<1	69
	Std Dev.	24	5	1		28
	CV	44%	38%	18%		40%
F1	3/16	27	9	5	<1	40
	3/17	24	9	5	<1	38
	3/18	26	9	4	<1	39
	Avg.	26	9	5	<1	39
	Std Dev.	1	0	0		1
	CV	5%	2%	5%		3%
F2	3/16	25	9	5	<1	38
	3/17	25	9	5	<1	39
	3/18	27	9	4	<1	40
	Avg.	26	9	5	<1	39
	Std Dev.	1	0	0		1
	CV	5%	1%	8%		2%
F3	3/16	27	9	4	<1	39
	3/17	27	9	5	<1	40
	3/18	28	9	4	<1	39
	Avg.	27	9	4	<1	40
	Std Dev.	0	0	0		0
	CV	2%	3%	8%		1%
F4	3/16	27	9	4	<1	40
	3/17	28	9	5	<1	42
	3/18	35	11	4	<1	49
	Avg.	30	10	5	<1	44
	Std Dev.	4	1	0		5
	CV	14%	12%	8%		11%

Summary	Concentration (ug/L)				
	CHCl3	CHCl2Br	CHBr2Cl	CHBr3	TTHM
Raw	80	15	3	<1	96
Settled	58	13	3	<1	73
Ozonated Settled	54	13	4	<1	69
F1	26	9	5	<1	39
F2	26	9	5	<1	39
F3	27	9	4	<1	40

Experiment 9
Experiment Date: 3/29 to 3/31

		Concentration (ug/L)				
		CHCl3	CHBrCl2	CHBr2Cl	CHBr3	TTHM
Raw	3/29	43	39	40	14	135
	3/30	52	43	41	15	151
	3/31	54	42	40	13	149
	Avg.	49	41	40	14	145
	Std Dev.	6	2	1	1	8
	CV	12%	5%	2%	6%	6%
Settled	3/29	26	32	42	22	122
	3/30	29	31	37	16	114
	3/31	25	30	39	19	113
	Avg.	27	31	39	19	116
	Std Dev.	2	1	3	3	5
	CV	8%	3%	6%	16%	4%
Ozonated	3/29	14	22	33	20	89
	3/30			9		
	3/31	18	24	34	16	91
	Avg.	16	23	33	18	90
	Std Dev.	2	1	0	2	1
	CV	16%	6%	0%	14%	2%
F1	3/29	5	13	30	28	76
	3/30	7	16	29	21	72
	3/31	6	14	29	24	72
	Avg.	6	14	29	24	73
	Std Dev.	1	1	1	4	2
	CV	22%	10%	3%	15%	3%
F2	3/29	7	16	32	24	79
	3/30	6	14	29	23	72
	3/31	8	17	29	20	75
	Avg.	7	16	30	23	75
	Std Dev.	1	1	1	2	4
	CV	16%	9%	5%	9%	5%
F3	3/29	8	17	32	23	81
	3/30	10	18	29	19	76
	3/31	10	18	29	18	76
	Avg.	9	18	30	20	77
	Std Dev.	1	0	1	3	3
	CV	8%	2%	5%	13%	4%
F4	3/29	8	18	35	26	87
	3/30	9	17	29	19	74
	3/31	9	18	30	20	77
	Avg.	9	18	31	22	79
	Std Dev.	1	0	3	4	6
	CV	7%	3%	10%	18%	8%

Summary	Concentration (ug/L)				
	CHCl3	CHCl2Br	CHBr2Cl	CHBr3	TTHM
Raw	49	41	40	14	145
Settled	27	31	39	19	116
Ozonated Settled	16	23	33	18	90
F1	6	14	29	24	73
F2	7	16	30	23	75
F3	9	18	30	20	77
F4	9	18	31	22	79

HAA Data for Experiment 1: 100698-100898

Sample	Concentrations of HAA species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
10-8-R	5	1	36	6	2	38	5	<1	<1	94
10-7-R	4	2	30	6	2	30	6	<1	<1	80
10-6-R					q					q
Average	4	2	33	6	2	34	6	<1	<1	87
St. Dev.	0	0	5	0	0	5	1			11
RSD	4%	5%	14%	2%	1%	16%	12%			1
10-8-O	3	1	23	5	1	15	3	<1	<1	51
10-7-O	4	1	21	6	2	14	3	<1	<1	51
10-6-O	4	1	21	6	2	13	3	<1	<1	51
Average	4	1	22	5	2	14	3	<1	<1	51
St. Dev.	0	0	1	0	0	1	0			3
RSD	8%	18%	4%	9%	22%	7%	7%			1
10-8-S	3	1	13	5	2	8	4	<1	<1	36
10-7-S	3	1	19	5	2	14	4	<1	<1	49
10-6-S	3	1	15	5	2	10	4	<1	<1	39
Average	3	1	15	5	2	11	4	<1	<1	41
St. Dev.	0	0	3	0	0	3	0			7
RSD	7%	9%	19%	7%	14%	30%	10%			1
10-8-F1	q	q	7	4	2	4	1	<1	<1	19
10-7-F1	3	1	7	4	2	3	1	<1	<1	22
10-6-F1	3	1	6	4	3	3	1	<1	<1	20
Average	3	1	7	4	2	3	1	<1	<1	20
St. Dev.	3	1	1	0	0	1	0			6
RSD	61%	81%	10%	3%	11%	20%	14%			2
10-8-F2					q					q
10-7-F2	3	1	7	4	2	4	1	<1	<1	23
10-6-F2	2	1	6	4	2	3	1	<1	<1	19
Average	2	1	6	4	2	3	1	1.11	<1	21
St. Dev.	1	0	3	2	1	1	0			9
RSD	91%	45%	73%	48%	29%	55%	17%			4
10-8-F3	1	1	6	3	2	3	1	<1	<1	17
10-7-F3	2	1	7	4	2	3	1	<1	<1	21
10-6-F3	3	1	7	4	2	3	1	<1	<1	22
Average	2	1	7	4	2	3	1	<1	<1	20
St. Dev.	1	0	1	1	0	0	0			3
RSD	40%	34%	10%	13%	16%	10%	3%			1
10-8-F4	3	1	7	4	2	4	1	<1	<1	21
10-7-F4	2	1	7	4	2	3	1	<1	<1	20
10-6-F4	2	1	6	4	2	3	2	<1	<1	20
Average	2	1	7	4	2	3	1	<1	<1	21
St. Dev.	0	0	0	0	0	0	0			2
RSD	15%	27%	5%	3%	9%	8%	10%			1

Note: 'q' indicates the data point is questionable.

Average Species Concentration

Sample	Concentrations of HAA species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	4	2	33	6	2	34	6	<1	<1	87
Ozonated	4	1	22	5	2	14	3	<1	<1	51
Settled	3	1	15	5	2	11	4	<1	<1	41
Filter 1	3	1	7	4	2	3	1	<1	<1	20
Filter 2	2	1	6	4	2	3	1	1	<1	21
Filter 3	2	1	7	4	2	3	1	<1	<1	20
Filter 4	2	1	7	4	2	3	1	<1	<1	21

HAA Data for Experiment 2: 101698-102898

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
	3	<1	28	7	<1	36	10	<1	<1	84
					q					q
	4	<1	31	7	<1	29	8	<1	<1	79
	4	<1	30	7	<1	33	9	<1	<1	82
	1		2	0		5	2			3
	16%		8%	3%		15%	19%			4%
	3	<1	29	6	<1	34	11	<1	<1	84
	3	<1	28	7	<1	31	10	<1	<1	79
	3	<1	28	7	<1	45	14	<1	<1	97
	3	<1	26	7	<1	33	12	<1	<1	80
	0		4	0		11	2			17
	15%		17%	6%		32%	17%			21%
	2	<1	17	6	<1	21	10	<1	<1	56
	2	<1	15	6	2	13	6	<1	<1	43
	2	<1	17	6	<1	18	9	<1	<1	52
	2	<1	16	6	2	17	8	<1	<1	50
	0		1	0		4	2			7
	5%		7%	3%		23%	21%			13%
	2	<1	12	6	2	14	8	<1	<1	43
	1	<1	11	6	2	10	6	<1	<1	35
	2	<1	12	6	2	15	8	<1	<1	44
	1	<1	12	6	2	13	7	<1	<1	41
	0		0	0	0	3	1			5
	30%		3%	3%	14%	22%	20%			12%
	2	<1	17	7	<1	21	9	<1	<1	55
	2	<1	11	5	2	8	5	<1	<1	33
	1	<1	13	6	2	15	8	<1	<1	44
	2	<1	13	6	2	13	7	<1	<1	44
	0		3	1	0	6	2			11
	14%		24%	10%	19%	42%	28%			25%
	2	<1	12	5	2	12	7	<1	<1	40
	2	<1	12	5	2	8	4	<1	<1	33
	2	<1	15	6	<1	16	8	<1	<1	47
	2	<1	13	6	2	12	6	<1	<1	40
	0		1	0	0	4	2			7
	10%		12%	7%	16%	36%	30%			18%
	2	<1	16	6	2	15	8	<1	<1	49
	2	<1	12	6	2	11	7	<1	<1	39
	2	<1	13	6	<1	16	8	<1	<1	45
	2	<1	13	6	2	14	7	<1	<1	44
	0		2	0	0	3	1			5
	13%		15%	6%	5%	18%	9%			11%

Note: 'q' indicates the data point is questionable.

Average Species Concentration

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	4	<1	30	7	<1	33	9	<1	<1	82
Ozonated	3	<1	26	7	<1	33	12	<1	<1	80
Settled	2	<1	16	6	2	17	8	<1	<1	50
Filter 1	1	<1	12	6	2	13	7	<1	<1	41
Filter 2	2	<1	13	6	2	15	7	<1	<1	44
Filter 3	2	<1	13	6	2	12	6	<1	<1	40
Filter 4	2	<1	13	6	2	14	7	<1	<1	44

HAA Data for Experiment 3: 112198-112498

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	BrIAA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
11-21-R	6	<1	46	7	<1	61	13	<1	<1	133
11-22-R	6	<1	47	7	<1	70	14	<1	<1	143
11-24-R	6	<1	44	6	<1	68	14	<1	<1	138
Average	6	<1	46	6	<1	66	14	<1	<1	138
St. Dev.	0		1	0		4	1			5
RSD	1%		3%	3%		7%	7%			4%
11-21-O	3	<1	20	5	2	13	4	<1	<1	46
11-22-O	4	<1	25	5	2	16	5	<1	<1	57
11-23-O	3	<1	21	5	2	14	5	<1	<1	50
Average	3	<1	22	5	2	14	5	<1	<1	51
St. Dev.	1		3	0	0	2	0			5
RSD	18%		13%	4%	3%	11%	7%			10%
11-21-S	3	<1	19	6	2	16	7	<1	<1	53
11-22-S	4	<1	24	6	1	18	6	<1	<1	59
11-23-S	3	<1	21	6	1	17	6	<1	<1	54
Average	3	<1	21	6	1	17	6	<1	<1	55
St. Dev.	0		2	0	0	1	1			3
RSD	14%		11%	1%	11%	6%	12%			5%
11-21-F1	<1	<1	17	5	2	11	5	<1	<1	40
11-22-F1	2	<1	16	5	2	10	4	<1	<1	40
11-23-F1	3	<1	15	5	2	12	7	<1	<1	44
Average	3	<1	16	5	2	11	5	<1	<1	41
St. Dev.	0		1	0	0	1	2			3
RSD	2%		5%	2%	10%	10%	30%			6%
11-21-F2	0	<1	17	5	2	12	6	<1	<1	42
11-22-F2	3	<1	17	5	2	11	6	<1	<1	44
11-24-F2	3	<1	16	5	2	11	5	<1	<1	43
Average	2	<1	17	5	2	11	6	<1	<1	43
St. Dev.	2		0	0	0	0	0			1
RSD	89%		2%	0%	6%	4%	4%			3%
11-21-F3	<1	<1	16	5	2	11	5	<1	<1	39
11-22-F3	<1	<1	18	5	2	10	5	<1	<1	40
11-24-F3	3	<1	16	5	2	12	5	<1	<1	43
Average	3	<1	17	5	2	11	5	<1	<1	40
St. Dev.			1	0	0	1	0			2
RSD			7%	1%	1%	6%	6%			5%
11-21-F4	<1	<1	16	5	2	13	6	<1	<1	42
11-22-F4	3	<1	18	5	2	13	5	<1	<1	45
11-23-F4	3	<1	18	5	2	10	5	<1	<1	44
Average	3	<1	17	5	2	12	5	<1	<1	44
St. Dev.	0		1	0	0	2	1			2
RSD	7%		8%	3%	13%	13%	13%			4%

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	BrIAA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	6	<1	46	6	<1	66	14	<1	<1	138
Ozonated	3	<1	22	5	2	14	5	<1	<1	51
Settled	3	<1	21	6	1	17	6	<1	<1	55
Filter 1	3	<1	16	5	2	11	5	<1	<1	41
Filter 2	2	<1	17	5	2	11	6	<1	<1	43
Filter 3	3	<1	17	5	2	11	5	<1	<1	40
Filter 4	3	<1	17	5	2	12	5	<1	<1	44

HAA Data for Experiment 4: 120798-120998

Sample	Concentrations of HAA Species, µg/L									
	MCAA	MBAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA	THAA
					q					q
					q					q
	<1	<1	15	13	7	11	8	2	<1	57
	<1	<1	15	13	7	11	8	2	<1	57
	<1	<1	6	5	3	3	2	<1	<1	19
	<1	2	3	5	5	<1	2	<1	<1	17
					q					q
	<1	2	5	5	4	3	2	<1	<1	18
			1.75	0.15	1.32		0.17			1
			38%	3%	30%		10%			7%
					q					q
	<1	<1	5	6	4	2	3	<1	<1	20
	<1	<1	4	5	5	2	<1	<1	<1	16
	<1	<1	5	6	5	2	3	<1	<1	18
			0.38	0.43	0.32	0.40				3
			8%	8%	7%	19%				15%
	<1	<1	2	4	4	<1	<1	<1	<1	11
	<1	<1	2	4	4	<1	<1	<1	<1	10
	<1	<1	2	5	5	<1	2	2	<1	15
	<1	<1	2	4	4	<1	2	2	<1	12
			0.17	0.30	0.28					2
			5%	7%	6%					20%
	<1	<1	3	5	5	2	<1	<1	<1	15
	<1	<1	3	4	5	<1	<1	<1	<1	11
	<1	<1	2	5	5	<1	<1	<1	<1	12
	<1	<1	3	4	5	2	<1	<1	<1	13
			0.51	0.41	0.31					2
			19%	9%	6%					14%
	<1	<1	3	5	5	<1	<1	<1	<1	12
	<1	<1	3	4	5	<1	<1	<1	<1	12
	<1	<1	2	4	4	<1	2	<1	<1	12
	<1	<1	3	4	5	<1	2	<1	<1	12
			0.66	0.22	0.24					0
			26%	5%	5%					0%
	<1	<1	4	4	4	2	<1	<1	<1	15
	<1	<1	3	5	5	2	<1	<1	<1	15
	<1	<1	2	4	6	<1	<1	<1	<1	12
	<1	<1	3	4	5	2	<1	<1	<1	14
			1.04	0.30	0.89	0.29				2
			31%	7%	19%	13%				13%

Note: 'q' indicates the data point is unreliable.

Sample	Average Concentrations of HAA Species, µg/L									
	MCAA	MBAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA	THAA
Raw	<1	<1	15	13	7	11	8	2	<1	57
Ozonated	<1	2	5	5	4	3	2	<1	<1	18
Settled	<1	<1	5	6	5	2	3	<1	<1	18
Filter 1	<1	<1	2	4	4	<1	2	2	<1	12
Filter 2	<1	<1	3	4	5	2	<1	<1	<1	13
Filter 3	<1	<1	3	4	5	<1	2	<1	<1	12
Filter 4	<1	<1	3	4	5	2	<1	<1	<1	14

HAA Data for Experiment 4: 120798-120998

1. THAA are all very low for this run. The following issues were investigated to determine the cause for the low results:
   a. The surrogate peaks are consistent for all samples. Therefore, contamination is not likely the cause.
   b. The internal standard peaks are also consistent.
   c. Dechlorination was added before MgSO4 in samples from 12/7 and 12/8. However, there was no overall difference between samples from these two dates and the samples from 12/9 at the respective sampling locations.
   d. 12/9-O, 12/9-S, 12/7-F4 have negligible F.R. However, THAA in these species are not different from the those samples collected at the same locations.

HAA Data for Experiment 5: 011999-012199

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
[illegible]	<1	<1	41	4	<1	54	7	<1	<1	106
[illegible]	<1	<1	47	3	<1	55	5	<1	<1	110
[illegible]	<1	<1	60	2	<1	75	2	<1	<1	139
[illegible]	<1	<1	49	3	<1	61	5	<1	<1	118
St. Dev.			10	1		11	2			18
RSD			20%	41%		18%	54%			15%
[illegible]	<1	<1	31	4	<1	32	7	<1	<1	74
[illegible]	<1	<1	35	2	<1	33	3	<1	<1	74
[illegible]	<1	<1	45	2	<1	45	3	<1	<1	95
[illegible]	<1	<1	37	3	<1	37	5	<1	<1	81
St. Dev.			7	1		7	2			12
RSD			20%	44%		20%	47%			15%
[illegible]	<1	<1	20	3	<1	12	2	<1	<1	37
[illegible]	<1	<1	21	2	<1	17	3	<1	<1	42
[illegible]	<1	<1	28	2	<1	25	3	<1	<1	58
[illegible]	<1	<1	23	2	<1	18	3	<1	<1	46
St. Dev.			4	1		7	0			11
RSD			19%	21%		36%	15%			23%
[illegible]	<1	<1	15	3	<1	10	3	<1	<1	31
[illegible]	<1	<1	15	2	<1	12	2	<1	<1	31
[illegible]	<1	<1	20	2	<1	16	2	<1	<1	40
[illegible]	<1	<1	17	3	<1	13	2	<1	<1	34
St. Dev.			3	1		3	1			5
RSD			16%	29%		24%	38%			14%
[illegible]	<1	<1	13	3	<1	10	3	<1	<1	29
[illegible]	<1	<1	16	2	<1	13	2	<1	<1	34
[illegible]	<1	<1	20	2	<1	19	2	<1	<1	43
[illegible]	<1	<1	17	2	<1	14	3	<1	<1	35
St. Dev.			3	1		4	0			7
RSD			21%	28%		32%	12%			20%
[illegible]	<1	<1	15	3	<1	11	3	<1	<1	32
[illegible]	<1	<1	17	2	<1	14	2	<1	<1	36
[illegible]	<1	<1	22	2	<1	20	2	<1	<1	46
[illegible]	<1	<1	18	2	<1	15	3	<1	<1	38
St. Dev.			4	1		5	0			8
RSD			20%	27%		32%	10%			20%
[illegible]	<1	<1	16	4	<1	11	3	<1	<1	35
[illegible]	<1	<1	17	2	<1	13	2	<1	<1	35
[illegible]	<1	<1	22	2	<1	19	2	<1	<1	45
[illegible]	<1	<1	18	3	<1	14	2	<1	<1	38
St. Dev.			3	1		4	1			6
RSD			17%	46%		28%	21%			15%

Note: 'q' indicates the data point is questionable.

Sample	Concentrations of HAA Species , µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	<1	<1	49	3	<1	61	5	<1	<1	118
Ozonated	<1	<1	37	3	<1	37	5	<1	<1	81
Settled	<1	<1	23	2	<1	18	3	<1	<1	46
Filter 1	<1	<1	17	3	<1	13	2	<1	<1	34
Filter 2	<1	<1	17	2	<1	14	3	<1	<1	35
Filter 3	<1	<1	18	2	<1	15	3	<1	<1	38
Filter 4	<1	<1	18	3	<1	14	2	<1	<1	38

HAA Data for Experiment 6: 020299-020499

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
	<1	<1	32	4	<1	37	5	<1	<1	78
	<1	<1	28	10	2	32	11	<1	<1	83
	<1	<1	24	14	5	24	13	3	<1	84
	<1	<1	28	10	3	31	10	3	<1	82
			4	5	2	7	4			3
			13%	54%	59%	21%	46%			4%
	<1	<1	24	4	<1	19	3	<1	<1	49
	<1	<1	20	8	3	14	6	<1	<1	53
	<1	<1	16	11	6	9	7	3	<1	52
	<1	<1	20	8	4	14	6	3	<1	51
			4	4	2	5	2			2
			20%	47%	47%	34%	29%			3%
	<1	<1	14	3	<1	10	2	<1	<1	29
	<1	<1	10	6	3	6	4	<1	<1	29
	<1	<1	9	8	5	4	4	2	<1	33
	<1	<1	11	6	4	7	3	2	<1	30
			2	3	2	3	1			3
			22%	48%	42%	44%	33%			9%
	<1	<1	9	3	<1	8	2	<1	<1	23
	<1	<1	6	6	3	4	3	1	<1	23
	<1	<1	5	7	5	3	2	2	<1	25
	<1	<1	7	5	4	5	2	2	<1	24
			2	2	2	3	0	1		1
			31%	37%	40%	51%	20%	31%		5%
	<1	<1	11	3	<1	8	1	<1	<1	23
	<1	<1	10	3	<1	8	2	<1	<1	23
	<1	<1	6	7	6	4	2	2	<1	27
	<1	<1	9	4	6	7	2	2	<1	25
			3	2		3	0			2
			29%	55%		39%	26%			10%
	<1	<1	11	3	<1	9	3	<1	<1	25
	<1	<1	7	6	3	4	2	2	<1	25
	<1	<1	6	7	6	4	3	2	<1	28
	<1	<1	8	6	5	6	2	2	<1	26
			2	2	2	3	0	0		2
			30%	35%	39%	51%	18%	8%		6%
	<1	<1	12	3	<1	9	2	<1	<1	26
	<1	<1	8	5	3	4	2	<1	<1	23
	<1	<1	8	8	6	4	3	2	<1	30
	<1	<1	9	5	4	6	2	2	<1	26
			3	2	2	3	1			4
			28%	43%	42%	45%	32%			15%

Note: 'q' indicates the data point is unreliable.

Sample	Average Concentrations of HAA Species , µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	<1	<1	28	10	3	31	10	3	<1	82
Ozonated	<1	<1	20	8	4	14	6	3	<1	51
Settled	<1	<1	11	6	4	7	3	2	<1	30
Filter 1	<1	<1	7	5	4	5	2	2	<1	24
Filter 2	<1	<1	9	4	6	7	2	2	<1	25
Filter 3	<1	<1	8	6	5	6	2	2	<1	26
Filter 4	<1	<1	9	5	4	6	2	2	<1	26

HAA Data for Experiment 7: 022199-02599
(samples not collected on 022499)

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
	<1	<1	21	4	<1	22	3	<1	<1	50
	<1	<1	22	4	<1	23	4	<1	<1	53
	<1	<1	22	4	<1	20	3	<1	<1	50
	<1	<1	22	4	<1	22	4	<1	<1	51
			1	0		1	0			2
			2%	8%		6%	7%			3%
	<1	<1	19	4	<1	20	3	<1	<1	46
	<1	<1	19	4	<1	20	4	<1	<1	47
	<1	<1	20	4	<1	19	3	<1	<1	47
	<1	<1	19	4	<1	20	3	<1	<1	46
			0	0		1	0			0
			2%	5%		3%	5%			1%
	<1	<1	16	3	<1	13	3	<1	<1	36
	<1	<1	15	3	<1	10	2	<1	<1	31
	<1	<1	15	3	<1	11	3	<1	<1	32
	<1	<1	16	3	<1	12	3	<1	<1	33
			1	0		1	0			3
			5%	3%		13%	14%			8%
	<1	<1	10	3	<1	7	1	<1	<1	22
	<1	<1	9	3	<1	6	1	<1	<1	20
	<1	<1	8	3	<1	5	1	<1	<1	18
	<1	<1	9	3	<1	6	1	<1	<1	20
			1	0		1	0			2
			9%	5%		13%	14%			10%
	<1	<1	9	4	<1	6	1	<1	<1	19
	<1	<1	9	4	<1	6	1	<1	<1	19
	<1	<1	11	3	<1	7	2	<1	<1	23
	<1	<1	10	4	<1	6	1	<1	<1	21
			1	0		1	0			2
			12%	4%		15%	29%			11%
	<1	<1	11	3	<1	6	2	<1	<1	22
	<1	<1	10	4	<1	6	1	<1	<1	20
	<1	<1	10	3	<1	6	1	<1	<1	20
	<1	<1	10	3	<1	6	1	<1	<1	21
			1	0		0	0			1
			8%	7%		3%	24%			5%
	<1	<1	11	4	<1	7	1	<1	<1	22
	<1	<1	9	3	<1	6	1	<1	<1	19
	<1	<1	9	3	<1	5	1	<1	<1	18
	<1	<1	10	3	<1	6	1	<1	<1	20
			1	0		1	0			2
			11%	7%		12%	19%			11%

Note: 'q' indicates the data point is unreliable.

Sample	Average Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	<1	<1	22	4	<1	22	4	<1	<1	51
Settled	<1	<1	19	4	<1	20	3	<1	<1	46
Ozonated	<1	<1	16	3	<1	12	3	<1	<1	33
Filter 1	<1	<1	9	3	<1	6	1	<1	<1	20
Filter 2	<1	<1	10	4	<1	6	1	<1	<1	21
Filter 3	<1	<1	10	3	<1	6	1	<1	<1	21
Filter 4	<1	<1	10	3	<1	6	1	<1	<1	20

HAA Data for Experiment 8: 031699-031899

Sample	Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
	2	<1	19	3	<1	20	4	<1	<1	49
	2	<1	21	3	<1	21	4	<1	<1	50
	2	<1	23	3	<1	24	4	<1	<1	56
	2	<1	21	3	<1	22	4	<1	<1	52
	0		2	0		2	0			3
	4%		8%	5%		9%	1%			7%
	<1	<1	16	3	<1	15	3	<1	<1	37
	2	<1	15	3	<1	15	3	<1	<1	38
	2	<1	16	3	<1	17	3	<1	<1	41
	2	<1	16	3	<1	15	3	<1	<1	39
	0		0	0		1	0			2
	10%		3%	5%		7%	7%			6%
	1	0	11	2	<1	8	2	<1	<1	25
	2	1	18	3	<1	9	3	<1	<1	26
	1	0	10	2	<1	7	2	<1	<1	23
	<1	<1	13	3	<1	8	2	<1	<1	25
			4	1		0	1			2
			33%	20%		5%	35%			6%
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	14
			0	0		0				0
			5%	3%		2%				2%
	<1	<1	7	2	<1	5	<1	<1	<1	13
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	14
			0	0		0				0
			2%	5%		3%				2%
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	1	<1	<1	<1	10
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	4	<1	<1	<1	13
			0	0		2				2
			4%	3%		57%				19%
	<1	<1	7	2	<1	5	<1	<1	<1	15
	<1	<1	7	2	<1	5	<1	<1	<1	14
	<1	<1	7	2	<1	5	<1	<1	<1	15
	<1	<1	7	2	<1	5	<1	<1	<1	15
			0	0		0				0
			3%	5%		2%				2%

Note: 'q' indicates the data point is unreliable.

Sample	Average Concentrations of HAA Species, µg/L									HAA9
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	
Raw	2	<1	21	3	<1	22	4	<1	<1	52
Settled	2	<1	16	3	<1	15	3	<1	<1	39
Ozonated	<1	<1	13	3	<1	8	2	<1	<1	25
Filter 1	<1	<1	7	2	<1	5	<1	<1	<1	14
Filter 2	<1	<1	7	2	<1	5	<1	<1	<1	14
Filter 3	<1	<1	7	2	<1	4	<1	<1	<1	13
Filter 4	<1	<1	7	2	<1	5	<1	<1	<1	15

HAA Data for Experiment 9: 032999-033199

Sample	Concentrations of HAA Species, µg/L									
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	HAA9
[illegible]	<1	1	15	11	5	14	13	5	<1	64
[illegible]	<1	1	17	11	6	12	8	2	<1	55
[illegible]	2	1	17	11	6	12	9	3	<1	61
[illegible]	2	1	16	11	6	13	10	3	<1	60
[illegible]		0	1	0	0	1	3	2		4
[illegible]		38%	7%	1%	7%	10%	30%	46%		7%
[illegible]	<1	1	8	9	7	5	6	3	<1	39
[illegible]	<1	1	10	9	6	7	7	3	<1	43
[illegible]	<1	1	8	9	7	5	6	4	<1	41
[illegible]	<1	1	9	9	7	6	6	4	<1	41
[illegible]		0	1	0	1	1	1	0		2
[illegible]		18%	9%	3%	8%	16%	11%	5%		5%
[illegible]	<1	<1	5	6	5	2	3	2	<1	23
[illegible]					q					q
[illegible]	<1	<1	6	5	5	3	2	1	<1	22
[illegible]	<1	<1	6	6	5	2	3	2	<1	23
[illegible]			0	0	0	0	0	0		1
[illegible]			5%	4%	8%	6%	11%	11%		5%
[illegible]	<1	<1	2	3	5	1	<1	<1	<1	11
[illegible]	<1	<1	2	4	5	1	<1	<1	<1	12
[illegible]	<1	<1	3	4	5	1	<1	<1	<1	13
[illegible]	<1	<1	2	4	5	1	<1	<1	<1	12
[illegible]			1	0	0	0				1
[illegible]			22%	10%	8%	28%				7%
[illegible]	<1	<1	2	4	5	1	1	<1	<1	14
[illegible]	<1	<1	2	3	5	1	<1	<1	<1	11
[illegible]	<1	<1	2	3	5	1	<1	<1	<1	11
[illegible]	<1	<1	2	4	5	1	1	<1	<1	12
[illegible]			0	0	0	0				2
[illegible]			21%	13%	5%	18%				16%
[illegible]	<1	<1	3	5	6	2	1	1	<1	19
[illegible]	<1	<1	3	5	5	2	1	<1	<1	16
[illegible]	<1	<1	3	5	5	2	1	1	<1	17
[illegible]	<1	<1	3	5	5	2	1	1	<1	17
[illegible]			0	0	1	0	0	0		1
[illegible]			25%	4%	11%	7%	25%	8%		7%
[illegible]	<1	<1	3	5	6	3	1	<1	<1	19
[illegible]	<1	<1	4	5	5	2	1	<1	<1	17
[illegible]	<1	<1	5	6	7	4	1	<1	<1	23
[illegible]	<1	<1	4	5	6	3	1	<1	<1	20
[illegible]			1	1	1	1	0			3
[illegible]			22%	14%	14%	33%	15%			16%

Note: 'q' indicates the data point is unreliable.

Sample	Average Concentrations of HAA Species, µg/L									
	ClAA	BrAA	Cl2AA	BrClAA	Br2AA	Cl3AA	BrCl2AA	Br2ClAA	Br3AA	HAA9
Raw	2	1	16	11	6	13	10	3	<1	60
Settled	<1	1	9	9	7	6	6	4	<1	41
Ozonated	<1	<1	6	6	5	2	3	2	<1	23
Filter 1	<1	<1	2	4	5	1	<1	<1	<1	12
Filter 2	<1	<1	2	4	5	1	1	<1	<1	12
Filter 3	<1	<1	3	5	5	2	1	1	<1	17
Filter 4	<1	<1	4	5	6	3	1	<1	<1	20

Appendix H: Additional Plots on the Relationship Between the Relative Reduction of DBP Formation Potential and the Relative Reduction in UV Absorbance at 254 nm

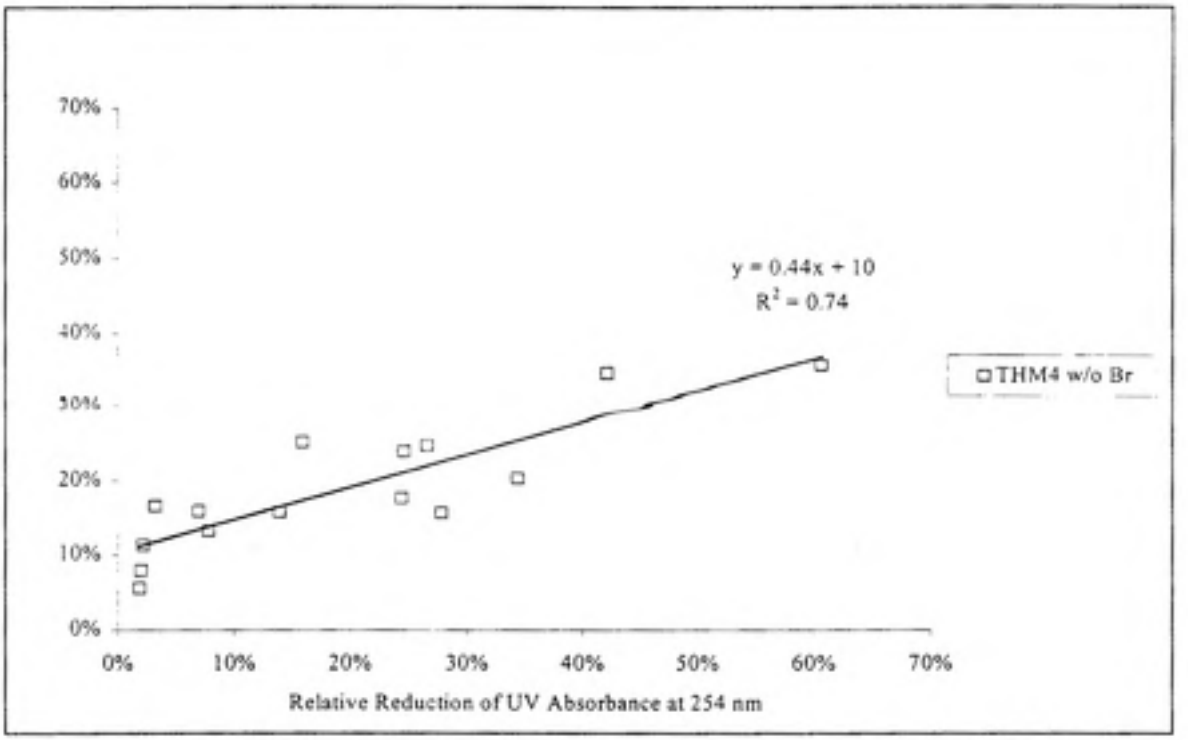

Figure H1: Relationship Between Relative Reduction of THM4 Formation Potential and Relative Reduction of UV Absorbance at 254 nm, using Data from Experiments With No Bromide Spike.

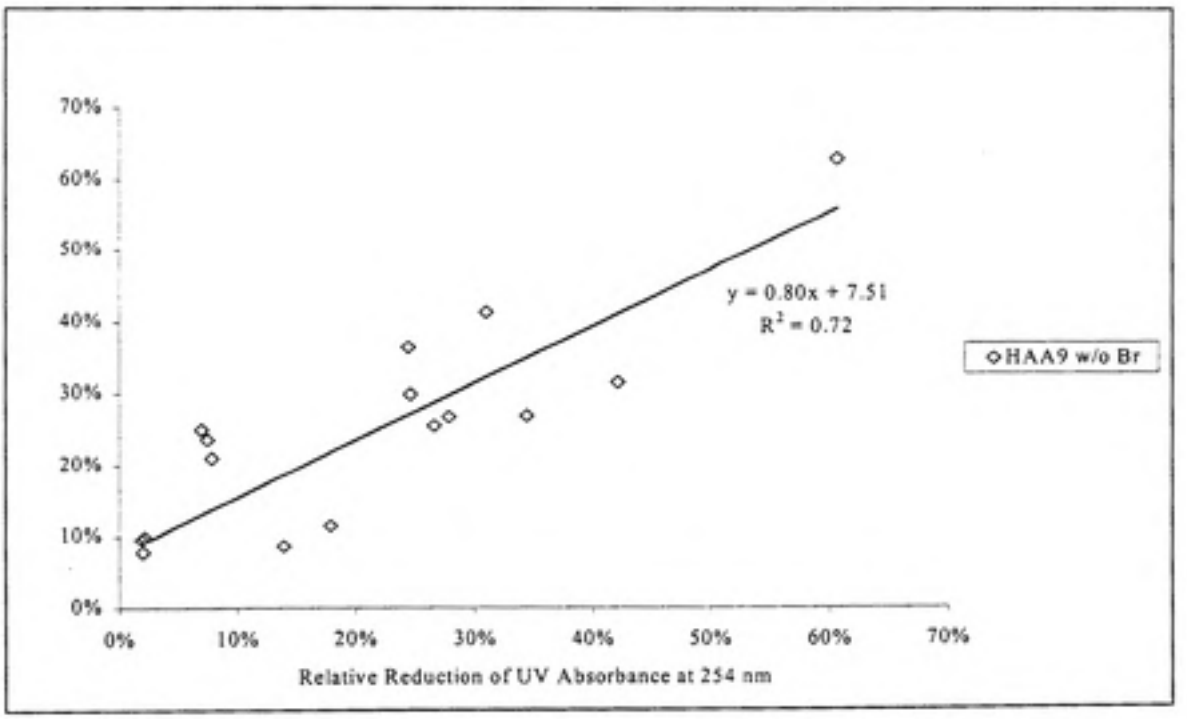

Figure H2: Relationship Between Relative Reduction of HAA9 Formation Potential and Relative Reduction of UV Absorbance at 254 nm, using Data from Experiments With No Bromide Spike.