ABSTRACT

The objective of this study was to investigate the effect of bromide ion concentration on the distribution of haloacetic acid (HAA) species resulting from chlorination, ozonation and chloramination of waters containing humic substances. HAAs are by-products of drinking water disinfection, and laboratory animal studies have suggested that these compounds are associated with carcinogenicity, developmental toxicity and reproductive toxicity. The potential risk to human health posed by HAAs and the varying toxicological significance of HAA species necessitate an understanding of the factors that affect HAA formation and speciation. In this study, waters were analyzed for all nine of the HAA species containing bromine and chlorine. Standards for bromodichloroacetic acid and dibromochloroacetic acid were not commercially available but were synthesized at the University of North Carolina and the University of Massachusetts.

Aquatic humic substances were obtained by XAD-8 extraction from raw waters at Myrtle Beach, SC and Palm Beach County, FL. Model waters were prepared containing 4 mg/L total organic carbon, 2 mM inorganic carbon, and ten bromide concentrations ranging from 0-25 µM (0-2 mg/L). Samples were chlorinated at pH 8 and pH 6 with and without pre-ozonation. Additional samples were chloraminated at pH 8 with and without pre-ozonation. Chlorinated and chloraminated samples were incubated at 20°C for 24 hours in the dark, after which time oxidant residuals were measured and quenched. The samples were extracted into ether, derivatized with diazomethane, then analyzed for the nine HAAs on a gas chromatograph with electron capture detector.

Bromide ion concentration was an important factor in HAA speciation in chlorinated waters. Bromo-chloro species (bromochloroacetic acid, bromodichloroacetic acid and dibromochloroacetic acid) were readily formed from chlorination of bromide-containing waters, and they constituted at least 10% of the total HAAs in waters containing as little as 1.2 µM Br^- (0.1 mg/L). Distribution of the HAAs among mono-, di-, and trihalogenated species appeared to be independent of bromide ion concentration. In addition, bromide ion appeared to have similar effects on HAA speciation in both waters studied. Lowering the pH of chlorination from pH 8 to pH 6 enhanced the formation of several species; however, HAA speciation was little affected. Pre-ozonation appeared to enhance bromine incorporation into the HAAs produced from subsequent chlorination.

Total HAA formation in chloraminated waters was decreased approximately 90% compared to total HAA formation in chlorinated waters. Dichloroacetic acid was the principal species formed in chloraminated waters. Chloramination of bromide-containing waters resulted in some formation of brominated species, principally bromoacetic acid, dibromoacetic acid and bromochloroacetic acid; little formation of trihalogenated species was observed from chloramination, both in the presence and absence of bromide ion. Pre-ozonation followed by chloramination enhanced total HAA formation compared to chloramination alone; however, total HAA formation was still decreased by approximately 90% compared to chlorination.

The results suggest that the bromo-chloro HAAs, whose occurrence in finished drinking waters is presently not known, are readily formed during chlorination of bromide-containing waters. Chloramination and pre-ozonation followed by chloramination appear to be effective means of controlling HAA formation. In addition, the effect of bromide ion on HAA speciation may be independent of the source of humic substances.

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List of Abbreviations

BCAA	bromochloroacetic acid
BrClAA	bromochloroacetic acid
$BrCl_2AA$	bromodichloroacetic acid
Br_2ClAA	dibromochloroacetic acid
CV	coefficient of variation
DBAA	dibromoacetic acid
DBCAA	dibromochloroacetic acid
DBPs	disinfection by-products
DCAA	dichloroacetic acid
DCBAA	dichlorobromoacetic acid
DOBr	dissolved organic bromide
DOC	dissolved organic carbon
DPD	N,N-diethyl-1,4-phenylenediamine
EI	electron impact
GC	gas chromatograph
HAAs	haloacetic acids
MBAA	bromoacetic acid
MCAA	chloroacetic acid
MCL	maximum contaminant level
MDL	method detection limit
MS	mass spectrometer
MtBE	methyl tertiary-butyl ether
NOM	natural organic material
RA	relative area
RR_t	relative retention time
TBAA	tribromoacetic acid
TCAA	trichloroacetic acid

THAAs	total haloacetic acids
THMs	trihalomethanes
TOC	total organic carbon
TOX	total organic halogen
USEPA	U.S. Environmental Protection Agency

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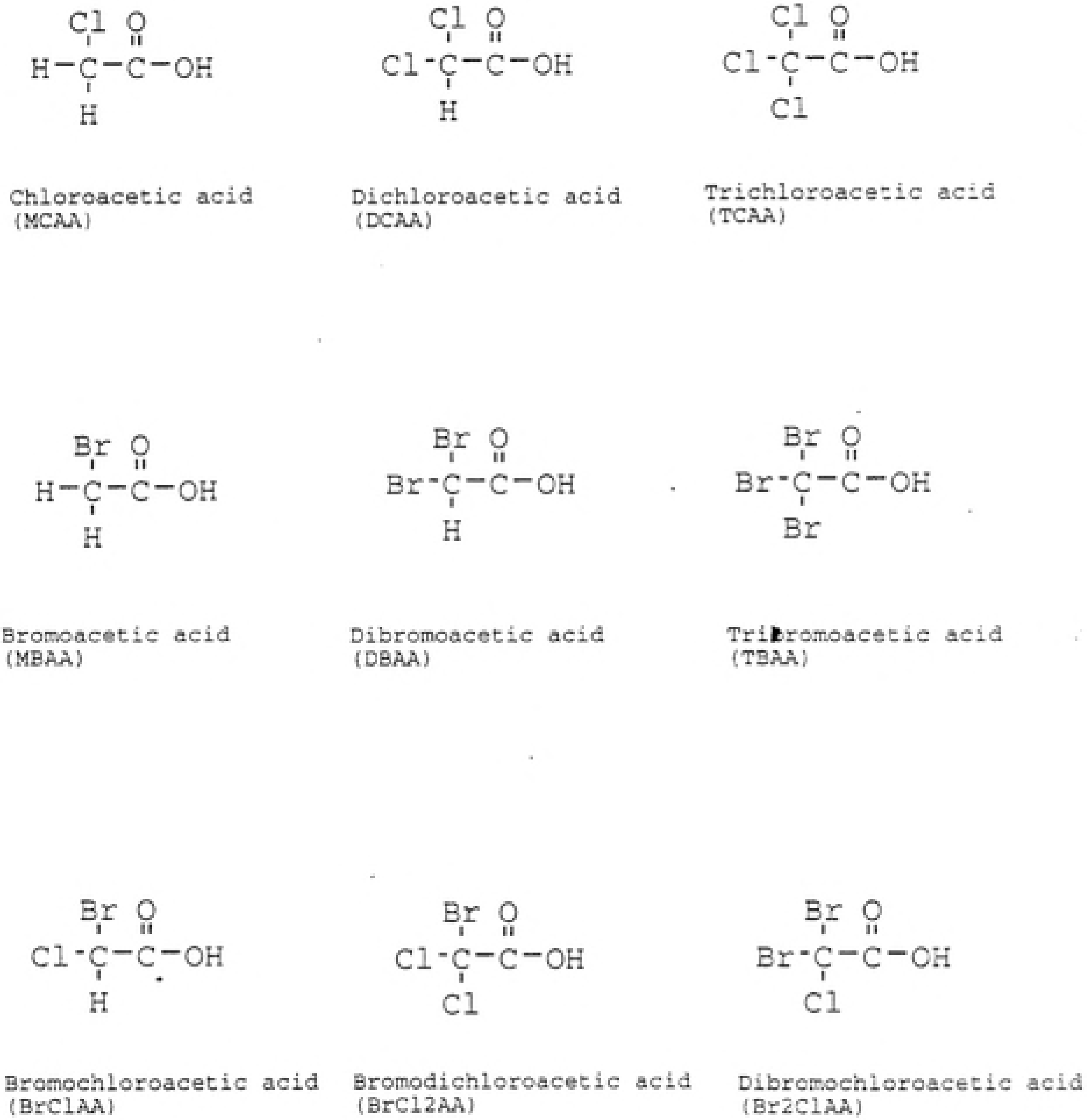
Chapter 1
Introduction

The presence of halogenated disinfection by-products (DBPs) in drinking water became a concern in the early 1970s when chloroform was identified in New Orleans finished drinking water. This discovery prompted the U.S. Environmental Protection Agency (USEPA) to conduct the National Organics Reconnaissance Survey of raw waters and finished drinking waters for the purpose of identifying and quantifying halogenated organic compounds present in the waters. This study included eighty water treatment facilities chosen to represent a variety of source water qualities and water treatment practices, and the results of the study indicated a widespread occurrence of halogenated organics in finished drinking water (1).

Disinfection by-products are thought to be formed primarily by reaction of the chemical disinfectant (chlorine, chloramine, ozone, etc.) with natural organic material (NOM), of which humic substances are the principal component. Much of the initial research on DBPs focused on the trihalomethanes (THMs); however, several other groups of DBPs have been identified and are presently of significant interest including the haloacetic acids (HAAs), haloacetonitriles, haloketones, halopicrins, cyanogen halides, chloral hydrate, and bromate. Some of the factors that affect the formation of DBPs are disinfectant type, dose and residual; temperature, pH, reaction time, nature and concentration of total organic carbon (TOC), and bromide ion concentration.

There are nine species of haloacetic acids containing chlorine and bromine. These species are the subject of the present research and are shown in Figure 1.1. The toxicological properties of these compounds are not well understood, but they are of concern to public health because of suspected carcinogenicity, as well as developmental, reproductive, and hepatic toxicity. Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) have been studied more extensively than the other HAAs, and they have been identified as major halogenated species both in laboratory chlorinations of aquatic humic materials (2-4) and in chlorinated drinking water (5-6). Brominated HAAs, primarily bromoacetic acid (MBAA) and dibromoacetic acid (DBAA), have been identified in waters containing high concentrations of bromide (6). Only minimal study has been conducted on the HAA species containing both chlorine and bromine (mixed species) due to the unavailability of commercial standards. At the time of this research, standards for bromodichloroacetic acid ($BrCl_2AA$) and dibromochloroacetic acid (Br_2ClAA) were not commercially available but had been synthesized at the University of North Carolina and the University of Massachusetts; bromochloroacetic acid (BrClAA) had recently become commercially available prior to initiation of this work.

Haloacetic acids in drinking water are presently not regulated, but it is expected that they will be included in the Disinfectants/Disinfection By-Products Rule to be proposed by the USEPA in 1994. A maximum contaminant level (MCL) of 60 µg/L "total" HAAs (THAAs) has been proposed. This figure includes only five of the HAAs: chloroacetic acid (MCAA), DCAA, TCAA, MBAA and DBAA.



Chloroacetic acid (MCAA)

Dichloroacetic acid (DCAA)

Trichloroacetic acid (TCAA)

Bromoacetic acid (MBAA)

Dibromoacetic acid (DBAA)

Tribromoacetic acid (TBAA)

Bromochloroacetic acid (BrClAA)

Bromodichloroacetic acid (BrCl2AA)

Dibromochloroacetic acid (Br2ClAA)

Figure 1.1. Chemical structures of the haloacetic acids

It is well known that naturally occurring bromide in raw waters is readily incorporated into HAAs in the form of organically bound bromine during water chlorination. Drinking water sources containing high bromide concentrations are typically found in coastal areas where seawater intrusion may be occurring. A recent nationwide survey of bromide concentrations in U.S. drinking water sources estimated that the mean occurrence level of bromide is 62 µg/L with an overall observed range of <5-429 µg/L (7).

Ozonation and chloramination are alternative disinfection strategies to chlorination, and these treatment techniques are used by a number of water utilities in the U.S. There is presently great interest in both ozonation and chloramination as methods for controlling chlorination by-product formation, as well as concern regarding their respective by-products. Ozone is an efficient disinfectant; however, ozone residuals do not persist in drinking water. Ozonated waters are commonly treated with chlorine or chloramine as a secondary disinfectant to maintain a residual in the distribution system.

The purpose of the present study is primarily to investigate the effect of bromide ion concentration on speciation of the haloacetic acids. It is reasonable to expect, and health effects studies have suggested, that individual HAA species are of varying toxicological significance. From this consideration it is evident that in order to accurately assess risk to human health it is not sufficient to know the occurrence of a few selected species, or even the total concentration of HAA species, but rather it is important to know the occurrence levels of each individual species. For this reason it is important to understand the factors affecting the distribution of HAAs among individual species. The inclusion of all nine of the HAA species in this study provides a more complete view of HAA speciation than many of the previous studies, which have focused primarily on only five of the HAAs.

Haloacetic acid speciation was investigated during chlorination, ozonation and chloramination of model waters prepared from extracted aquatic humic substances. Chlorinations were conducted at both pH 8 and pH 6, and all ozonations were followed by either chlorination or chloramination. Secondary goals of the study include comparison of the effect of these different chemical treatment techniques on quantitative formation of each of the nine haloacetic acids, and comparison of two different sources of natural organic material with respect to HAA formation and speciation.

Chapter 2
Literature Review

Chlorination of drinking water is known to produce both halogenated and non-halogenated products, and only a fraction of these chlorination products have been identified and characterized. In 1980 Christman et al. (3) identified several chlorinated and non-chlorinated organic acids as products of chlorination of aquatic humic substances at pH 12, and these researchers noted that DCAA and TCAA were particularly abundant. These results were confirmed by additional chlorination studies of aquatic humic substances both at pH 12 and at neutral pH (2,4). In 1983 Uden and Miller (5) identified DCAA and TCAA in tap water at levels similar to that of chloroform (30-160 µg/L). A nation-wide survey of the occurrence of disinfection by-products in U.S. finished drinking waters estimated the median concentration of "total" haloacetic acid species to be 19 µg/L (6). This estimate is the sum of only five of the HAA species: MCAA, DCAA, TCAA, MBAA and DBAA.

Health effects

The health effects of haloacetic acids are not well understood, and much of what is known is based on studies of laboratory animals exposed to high concentrations (on the order of g/L) of individual compounds. The chlorinated acetic acids have been studied the most; limited study of MBAA and DBAA in relation to reproductive and developmental toxicity has recently begun (8).

Both DCAA and TCAA have been shown to induce hepatic tumors in mice (9-11). Both compounds are also associated with hepatic toxicity in mice and rats, and DCAA appears to cause more severe effects than TCAA (10,12). Larson and Bull (13) observed that DCAA is metabolized to a greater extent than TCAA in rats and mice, and it is expected that the toxicity and carcinogenicity of DCAA result from biologically reactive metabolites of this compound.

Haloacetic acids have also been associated with developmental and reproductive toxicity. DCAA and TCAA have both been shown to induce adverse developmental effects in rats, principally cardiovascular malformations (14,15). In addition, reproductive toxicity in male rats and dogs has been observed for DCAA (16).

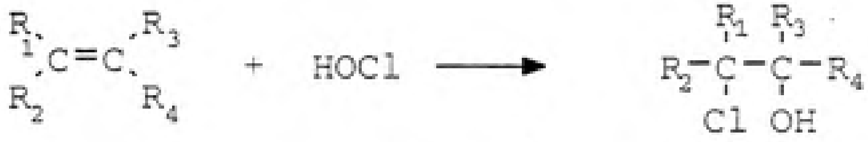
Aqueous chemistry of chlorine and bromine

It is thought that the majority of halogenated disinfection by-product formation results from reactions between halogens and humic substances in drinking water. The chemical structure of aquatic humic substances has not been elucidated (and it is expected that structure may vary from one source to the next), but chemical degradation studies have suggested the presence of aromatic rings, hydroxyl groups, methoxyl groups, carboxyl groups, phenolic groups, ketones and aldehydes.

Aqueous chlorine (HOCl) reacts with organic compounds through electrophilic and oxidative mechanisms. In aqueous solution an equilibrium is established between HOCl and OCl^-, with HOCl being the more reactive of the two species:

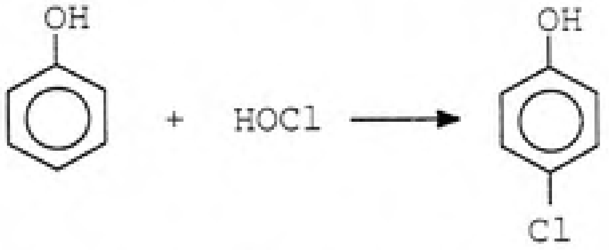
$$HOCl \rightleftharpoons H^+ + OCl^- \quad pK_a = 7.6 \text{ @ } 15\text{-}20^\circ C$$

Chlorine is known to electrophilically add to double bonds:



This reaction is facilitated by electron-donating substituents.

Chlorine is also known to participate in electrophilic aromatic substitution, as in the chlorination of phenol:



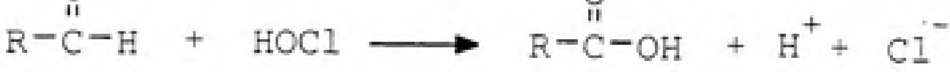
The aromatic ring is activated by substituents such as -OH, -OCH$_3$ and -NR$_2$ which can donate electron density to the ring, stabilizing intermediates. It is believed that activated aromatic groups in humic substances are particularly important disinfection by-product precursors (17).

In addition, HOCl and OCl$^-$ are strong oxidants. Their oxidation potentials are:

$HOCl + H^+ + 2e^- \text{----->} Cl^- + H_2O \quad E_0 = +1.49$ volts

$OCl^- + 2H^+ + 2e^- \text{----->} Cl^- + H_2O \quad E_0 = +1.71$ volts

HOCl can react with organic compounds simply as an oxidant, without addition of halogen. An example of such a reaction is the oxidation of an aldehyde to a carboxylic acid:



$$R-\overset{O}{\overset{\|}{C}}-H + HOCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + H^+ + Cl^-$$

In addition, chlorine is capable of oxidatively cleaving ring structures.

Hypochlorous acid oxidizes bromide ion to hypobromous acid. This is clearly thermodynamically favorable upon inspection of the oxidation potentials:

	E_0 (volts)
$HOCl + H^+ + 2e^- \longrightarrow Cl^- + H_2O$	+1.49
$Br^- + H_2O \longrightarrow HOBr + H^+ + 2e^-$	-1.33
$HOCl + Br^- \longrightarrow HOBr + Cl^-$	+0.16

This has been shown to be a rapid reaction at 25°C, with a rate expression of the form $d[HOBr]/dt = k[HOCl][Br^-]$ and a second-order rate constant $k=2.95\times10^3\ M^{-1}sec^{-1}$ (18).

The reactions of HOBr are similar in mechanism to those of HOCl and include addition to double bonds, electrophilic aromatic substitution and oxidation. Like HOCl, an equilibrium is established between hypobromous acid and hypobromite ion in aqueous solution:

$$HOBr \rightleftharpoons H^+ + OBr^- \qquad pK_a = 8.7 \text{ @ } 15\text{-}20°C$$

Again HOBr is the more reactive of the two species.

Some researchers (19-21) have suggested that bromine and chlorine species that are more electrophilic than HOCl and HOBr are responsible for much of the aqueous halogenation of organic compounds other than highly activated compounds. The electrophilic species that have been proposed include BrCl, Br_2, Cl_2, H_2OBr^+, H_2OCl^+ and Cl_2O. In studying the aqueous chlorination and bromination of p-xylene, Voudrias et al. (20) observed that halogenation was catalyzed by H^+, Cl^-, and Br^-. They observed the following order of reactivity with p-xylene:

$BrCl > Cl_2 - Cl_2O > Br_2 > HOBr > HOCl$

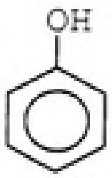
In addition, they suggested that H_2OBr^+ may be even more reactive than BrCl. Even though the concentrations of these more electrophilic species are very small at near-neutral pH, it has been suggested that they may still be important species because of their high reactivity. Theoretical calculations for the halogenation of aromatic compounds at pH 6 suggested that BrCl is the most important brominating species even though its concentration is five orders of magnitude less than that of HOBr (21). These calculations predicted the importance of halogenating species to be in the order:

$BrCl > H_2OBr^+ > Cl_2 > Cl_2O > HOBr$

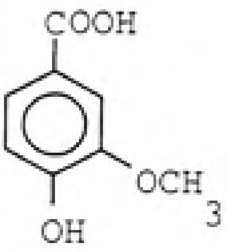
These more electrophilic halogenating agents are favored by low pH, and it has been observed that total organic halogen (TOX) formation from chlorination of humic substances tends to increase with decreasing pH (17,22).

Mechanisms of HAA formation

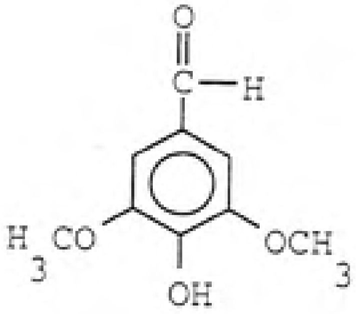
The chemical pathways by which haloacetic acids are formed during chlorination of raw waters are not well understood. Uncertainty in the chemical structure of humic substances makes elucidation of the reaction mechanisms particularly difficult. Much of the research in this area has involved chlorination of model compounds with structural characteristics believed to be similar to those of humic substances. Since activated aromatic compounds tend to be highly reactive with chlorine, and activated aromatic groups are known to be present in humic substances, it is expected that such groups may be precursors of disinfection by-products when drinking water is chlorinated. In a study of the chlorination of fulvic acids and humic acids, Reckhow et al. (17) observed greater yields of TOX, $CHCl_3$, TCAA and DCAA from the humic acid fraction of natural organic material; compared to the fulvic acid fraction, the humic acids had greater aromaticity, greater phenolic content, greater UV_{254} absorbance (an indicator of unsaturation), and less carboxyl content. In a study of model compounds chlorinated at pH 7, Reckhow and Singer (22) observed relatively high yields of TCAA from the following compounds:



phenol

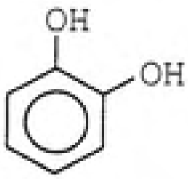


vanillic acid

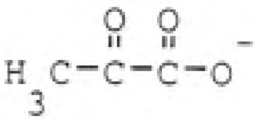


syringealdehyde

In addition, the following two compounds showed lesser, but significant, yields of TCAA:



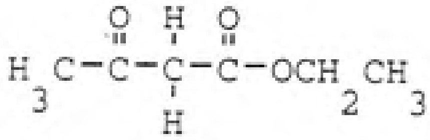
1,2-dihydroxybenzene



$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O^-$$

pyruvate

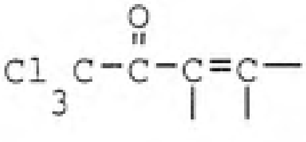
Chlorination of each of these five compounds at pH 7 produced DCAA as well, but in much smaller amounts. Among these model compounds the ratio of TCAA/DCAA ranged from 14-20. A β-ketoester of the form:



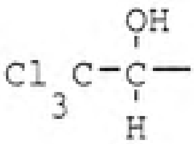
$\mathrm{H_3C{-}C({=}O){-}CH_2{-}C({=}O){-}OCH_2CH_3}$

was identified as producing high yields of DCAA, with a ratio of DCAA/TCAA ≈ 450. Possible reaction pathways were proposed for the formation of DCAA and TCAA from β-diketones and from pyruvate; these pathways are shown in Figure 2.1.

De Leer et al. (23) have observed the formation of some chlorinated compounds containing a trichloromethyl group from the chlorination of terrestrial humic substances at conditions of low chlorine dose. The identified compounds were of the form:



$\mathrm{Cl_3C{-}C({=}O){-}C{=}C{-}}$



$\mathrm{Cl_3C{-}CH(OH){-}}$

It has been suggested that such compounds may be intermediates in the formation of TCAA and $CHCl_3$ (17).

Factors affecting HAA formation

Factors that are known to have an effect on haloacetic acid formation in chlorinated waters include chlorine dose, pH of

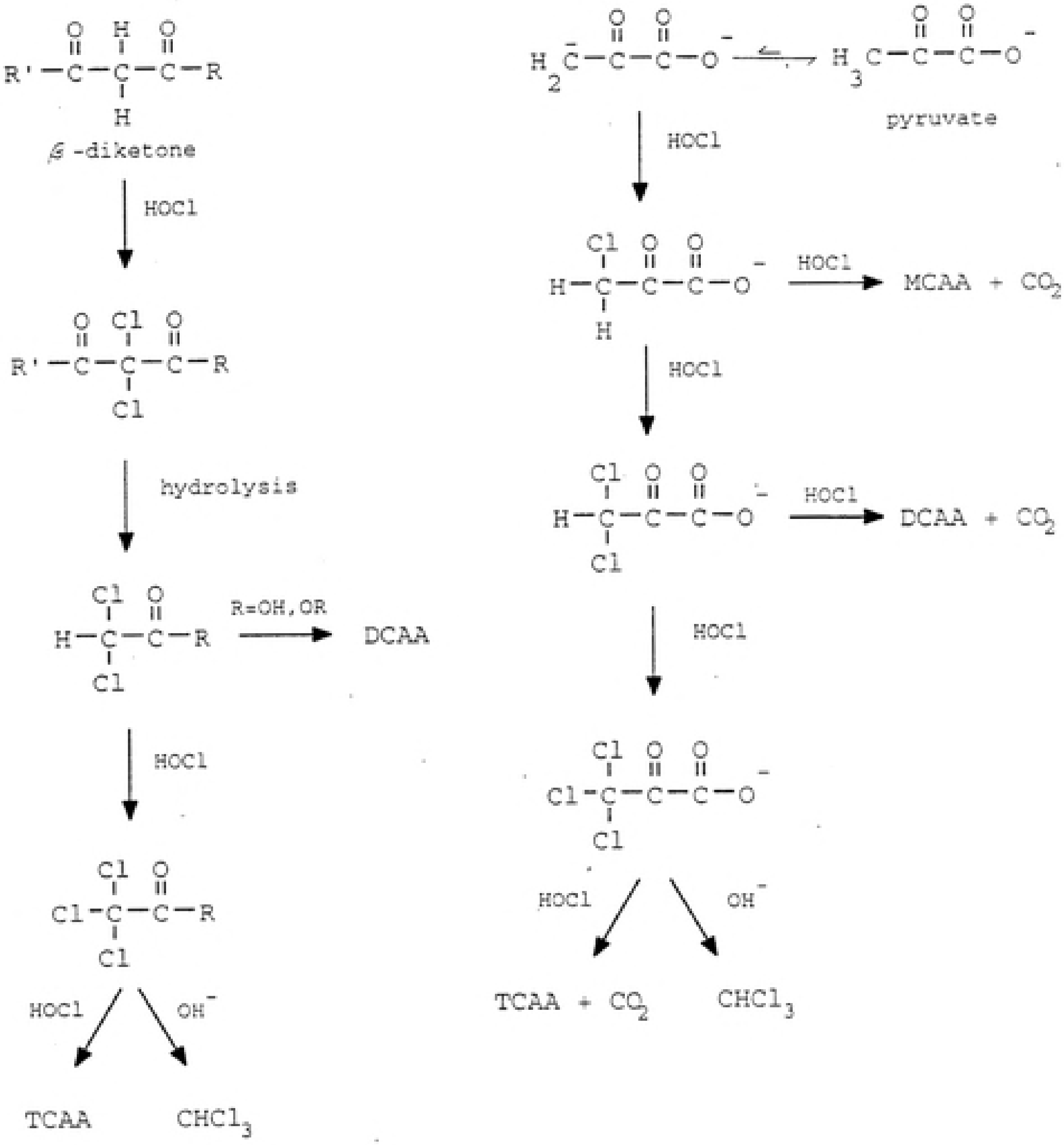


Figure 2.1. Proposed pathways of HAA formation (from Reckhow and Singer (22))

chlorination, reaction time, TOC concentration, bromide ion concentration, and temperature. Much of what is presently known is based on studies involving only MCAA, DCAA, TCAA, MBAA and DBAA. Little is known about how these factors affect formation of the bromo-chloro species because of the unavailability of analytical standards for these compounds.

Miller and Uden (24) investigated the influence of chlorine dose on DCAA and TCAA formation from soil fulvic acids, and they observed that the formation of these compounds was enhanced by high chlorine doses. In addition, TCAA appeared to be more greatly affected by the ratio of NaOCl to organic carbon (C) than did DCAA. Relative formation of DCAA compared to TCAA was dependent on chlorine dose. At a low chlorine dose (mg NaOCl/mg C = 0.5), the formation of DCAA was greater than that of TCAA; but at higher chlorine doses (NaOCl/C $\geq$ 1), TCAA was formed in excess of DCAA. At very high chlorine doses (NaOCl/C > 5), a fairly constant ratio of TCAA/DCAA = 3 was observed.

Studying the formation of HAAs from chlorination of commercial humic acid in the presence of bromide ion, Pourmoghaddas et al. (25) observed that a high chlorine dose slightly increased TCAA and BrClAA formation, greatly increased $BrCl_2AA$ and Br_2ClAA formation, and did not significantly affect DCAA formation. Conversely, DBAA and tribromoacetic acid (TBAA) were enhanced by a lower chlorine dose.

A general trend of increasing HAA formation with decreasing pH has been observed for several of the HAA species. Studies of DCAA and TCAA by Miller and Uden (24) and Reckhow and Singer (22) suggest that although such an overall trend is observable, the behavior of these species as a function of pH is both non-linear and complex. In chlorinated waters containing bromide ion in the pH range 5-9.4, Pourmoghaddas et al. (25) observed that the formation of TCAA, BrClAA, $BrCl_2AA$, Br_2ClAA and TBAA was clearly enhanced at low pH. pH appeared to have less, if any, effect on DCAA, MBAA and DBAA formation.

Formation of the haloacetic acids generally increases with increasing reaction time. DCAA and TCAA have been shown to exhibit rapid initial formation during the first few minutes of chlorination (24,26). Doré et al. (26) and Zhu and Reckhow (27) have observed continued, slow formation of these compounds even after 6 days of reaction. Pourmoghaddas et al. (25) did observe a slight decrease in TBAA concentration at 168 hours relative to 48 hours; this is likely due to the instability of this compound.

Competition between chlorine and bromine in halogenation reactions with humic substances

Several researchers have observed that bromine appears to be more reactive than chlorine in substitution reactions with organics during chlorination of model compounds and humic substances in the presence of bromide ion (20,21,28,29). Bromine is expected to be more reactive than chlorine in addition and substitution reactions because it is a more polarizable molecule. Rook et al. (28) observed a molar ratio of chlorine to bromine incorporation into THMs of Cl/Br = 5.5 with a molar ratio of (added chlorine)/Br^- equivalent to 40. Voudrias et al. (21) observed that the chlorination of p-xylene in the presence of Br^-

produced much greater amounts of bromo-p-xylene than chloro-p-xylene even though the concentration of HOCl was 3-5x greater than that of Br^-. In addition, Sweetman et al. (30) observed greater formation of brominated products from treatment of phenol with HOCl + Br^- than from treatment with Br^--free HOBr alone. It was suggested that some HOBr participates in oxidation reactions with production of Br^-, and this Br^- can be reoxidized to HOBr when HOCl is present. Based on studies of resorcinol reacted with equimolar HOCl and HOBr, Rook et al. (28) concluded that chlorine was being preferentially consumed in oxidation reactions and bromine in electrophilic substitution reactions.

Several researchers have studied the effect of bromide ion concentration on THM formation and speciation in chlorinated waters (29,31-34). These studies have identified bromide concentration and TOC concentration as important factors in THM speciation. In general, as bromide ion concentration increases, chloroform formation decreases, bromoform increases, and the mixed species (bromodichloromethane and dibromochloromethane) pass through a maximum value. This is shown graphically in Figure 2.2. Additionally, several studies have shown that the μM concentration of total THMs increases with increasing bromide concentration (29,31,34); however, Cooper et al. (33) did not observe a dependence of total THM formation on bromide ion concentration. Luong et al. (32) demonstrated that decreasing TOC concentration shifts speciation to more brominated THMs. This study also showed that decreasing the chlorine dose from 8 to 2 mg/L (TOC=2.5 mg/L) resulted in decreased total THM formation but did not significantly change the distribution of

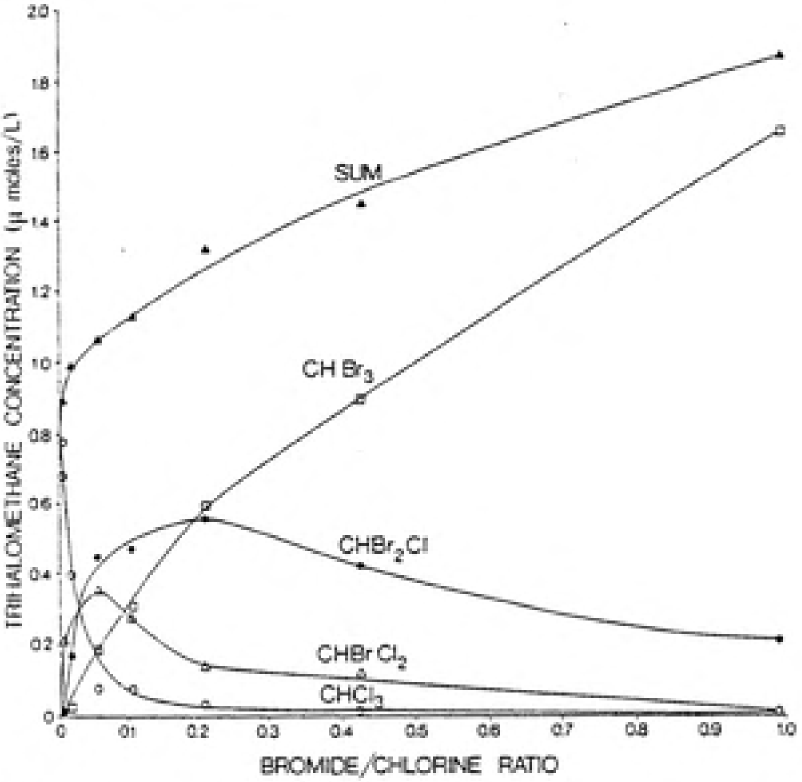


Figure 2.2. Speciation of THMs as a function of bromide/chlorine (mg/mg) ratio. 2.5 mg/L fulvic acid, 25 mg/L chlorine, pH 7, 20°C, 24 hours reaction time (from Oliver (34)).

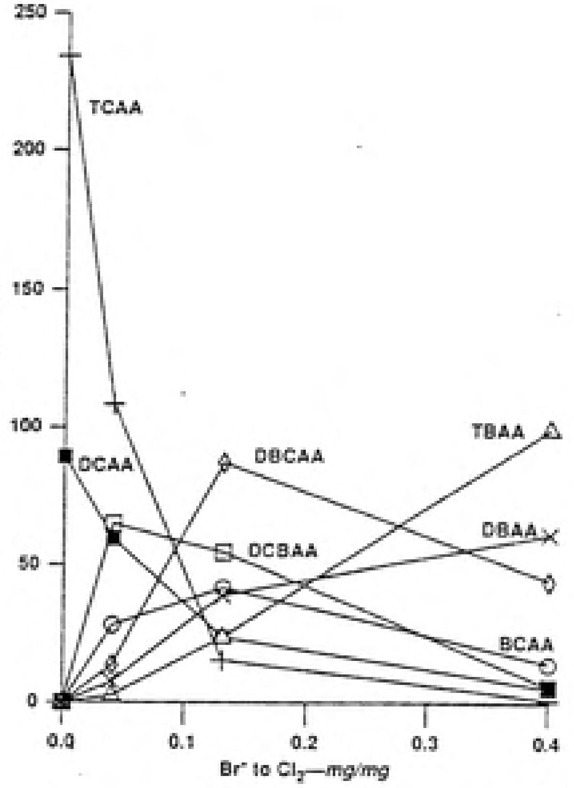


Figure 2.3. Speciation of HAAs as a function of bromide/chlorine (mg/mg) ratio. 2.83 mg/L humic acid, 11.5 mg/L chlorine, pH 7, 25°C, 168 hours reaction time (from Pourmoghaddas et al. (25)).

species.

Pourmoghaddas et al. (25) have shown that behavior of the HAA species with respect to bromide concentration appears to be similar in some ways to that of the THMs. With increasing bromide concentration, the formation of DCAA and TCAA decreased, MBAA, DBAA and TBAA increased, and BrClAA, $BrCl_2AA$ and Br_2ClAA passed through a maximum value (Figure 2.3). It appears that at low bromide/chlorine ratios (<0.05 on a mg/mg basis), the principal species formed, in decreasing order of significance, were TCAA, DCAA, $BrCl_2AA$, BrClAA, Br_2ClAA, DBAA and TBAA. At the highest bromide concentration studied (4.5 mg/L), HAA formation was in the order:

TBAA > DBAA > Br_2ClAA > BrClAA > $BrCl_2AA$, DCAA > TCAA.

Aqueous chemistry of chloramines

Chloramination is an alternative disinfection strategy to chlorination which is known to produce lower levels of HAAs, THMs and TOX. In typical water treatment practice, chloramines are formed by reacting hypochlorous acid (free chlorine) with ammonia. Reaction of free chlorine with organic nitrogen that may be present in natural waters produces organic chloramines. Bromamines can be formed analogously by reaction of hypobromous acid with nitrogenous compounds.

The chloramine species of principal interest in water disinfection is monochloramine (NH_2Cl). Compared to free chlorine, monochloramine is a weaker oxidant, a weaker disinfectant, and it is less reactive with organic compounds. Monochloramine is formed by reaction of equimolar amounts of free chlorine and ammonia:

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O \qquad K_{eq} = 1.5\times10^{11} \qquad (35)$$

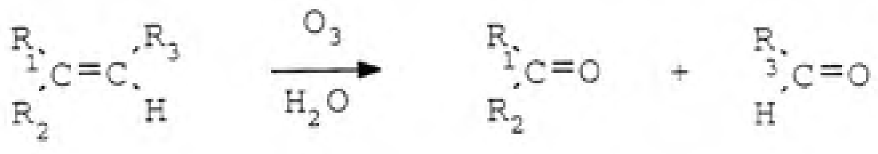
The second-order rate constant for the forward reaction is $k=4.2\times10^6\ M^{-1}sec^{-1}$ at 25°C (36). The reverse reaction, hydrolysis of monochloramine to free chlorine and ammonia, occurs with a first order rate constant of $2.1\times10^{-5}\ sec^{-1}$ at 25°C (36). When excess free chlorine is present, di- and trichloramine species ($NHCl_2$, NCl_3) can be formed as well. The formation of monochloramine is favored by high pH and molar ratios of $HOCl:NH_3 \leq 1:1$.

The mechanisms of reactions between chloramines and aquatic humic substances are not well understood. It has been suggested that in many of the reactions producing chlorinated by-products the active chlorinating species may be the small concentrations of free chlorine that are in equilibrium with monochloramine (37).

Aqueous chemistry of ozone

Ozone is a strong oxidant, and it is highly reactive with natural organic material in water. Ozone is also known to decompose autocatalytically in aqueous solution, and a pathway for the decomposition has been described by Staehelin and Hoigné (38). The decomposition of ozone is intitiated by hydroxide ion, and molecular ozone is thus less stable at elevated pH. An important product of ozone decomposition is the hydroxyl radical ($^{\cdot}OH$), which propagates the radical chain decomposition of ozone. Radical scavengers such as carbonate and bicarbonate help to stabilize molecular ozone. Hydroxyl radicals are also oxidant species and generally react with organic compounds more rapidly and less selectively than ozone.

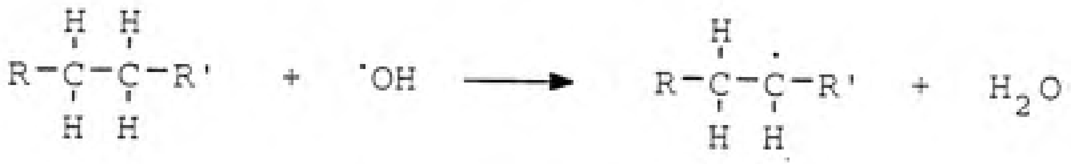
Ketones, aldehydes and carboxylic acids are common products of the ozonation of organic compounds. Ozone tends to be highly reactive with double bonds, and an example is the ozonolysis of an alkene:



$$R_1R_2C{=}C(R_3)H \xrightarrow[H_2O]{O_3} R_1R_2C{=}O + R_3HC{=}O$$

Ozone is known to be reactive with aromatic compounds and is capable of cleaving aromatic rings. Electron-donating substituents such as $-OH$ and $-OCH_3$ activate aromatic rings toward ozonation reactions as well as chlorination reactions. When an aromatic compound contains side chains, these substituents are often more readily oxidized by ozone than is the aromatic nucleus due to the high stability of the aromatic π system.

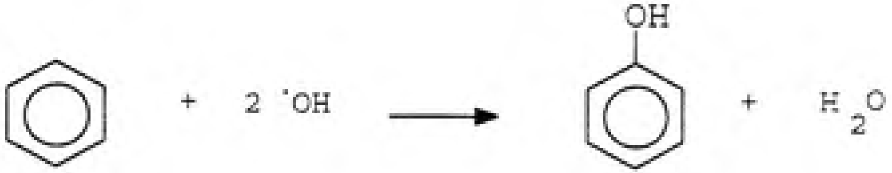
The hydroxyl radical is also reactive with organic compounds. A common reaction of the hydroxyl radical with saturated organic compounds is hydrogen abstraction, resulting in a radical:



$$R-CH_2-CH_2-R' + {}^{\cdot}OH \longrightarrow R-CH_2-\dot{C}H-R' + H_2O$$

The resulting radicals are often highly reactive and unstable.

Another common reaction of ${}^{\cdot}OH$ is addition to aromatic compounds:



With regard to formation of chlorinated disinfection by-products, Reckhow et al. (39) and Legube et al. (40) have suggested that molecular ozone may tend to react with sites on humic substances that are also highly reactive towards chlorine, whereas hydroxyl radicals may tend to react with sites that are less reactive with chlorine. Both groups of researchers have observed that UV absorbance at 270nm (an indication of unsaturation) of aquatic fulvic acids is lowered by ozonation, and the magnitude of this decrease is greater when ozonation is carried out in the presence of bicarbonate. They reason that ozone is destroying aromaticity, and that molecular ozone is more efficient at destroying aromaticity than is the hydroxyl radical.

Ozone-bromide reactions

Ozone oxidizes bromide ion to hypobromite according to the reaction:

$$O_3 + Br^- \text{----->} O_2 + OBr^-$$

Haruta and Takeyama (41) and Haag and Hoigné (42) have studied the kinetics of this reaction and have found it to be first-order in Br^- and O_3. Haag and Hoigné (42) have evaluated the rate constant to be $k=160\pm20\ M^{-1}sec^{-1}$ at 20°C. In the presence of excess ozone, hypobromite is oxidized to bromate:

$2O_3 + OBr^- \text{----->} 2O_2 + BrO_3^-$ $k=100\pm20\ M^{-1}sec^{-1}$ at 20°C

This reaction is favored by conditions of high pH because HOBr is much less reactive with ozone than is OBr^-. It is thus expected that ozonation of bromide-containing waters at low pH will result in significant organic bromination, whereas at high pH, bromide is more likely to be converted to bromate if there is sufficient ozone present. Haag and Hoigné (42) have also suggested a reaction by which hypobromite is reduced by ozone to bromide ion:

$O_3 + OBr^- \text{----->} 2O_2 + Br^-$ $k=330\pm60\ M^{-1}sec^{-1}$ at 20°C

Bromide is again available for oxidation to $HOBr/OBr^-$ by ozone or by subsequent chlorination.

Bromide can also act as a hydroxyl radical scavenger according to the reaction:

$^{\cdot}OH + Br^- \text{----->} HOBr^{\cdot-}$

This is a rapid reaction with a rate constant $k=1.1x10^{10}\ M^{-1}sec^{-1}$ at 20°C (43). Hypobromite and hypobromous acid will also react rapidly with hydroxyl radicals:

$^{\cdot}OH + BrO^- \text{----->} OH^- + BrO^{\cdot}$ $k=4.2x10^9\ M^{-1}sec^{-1}$ at 20°C

$^{\cdot}OH + HOBr \text{----->} BrO^{\cdot} + H_2O$ $k=2.0x10^9\ M^{-1}sec^{-1}$ at 20°C

The rate constants for Br^-, HOBr and BrO^- reacting with hydroxyl radicals are approximately 1-4 orders of magnitude greater than the rate constants for the reactions of carbonate and bicarbonate with hydroxyl radicals:

$^{\cdot}OH + CO_3^{-2} \text{----->} OH^- + CO_3^{\cdot-}$ $k=3.9x10^8\ M^{-1}sec^{-1}$ at 20°C

$^{\cdot}OH + HCO_3^- \text{----->} H_2O + CO_3^{\cdot-}$ $k=8.5x10^6\ M^{-1}sec^{-1}$ at 20°C

Bicarbonate has been well studied as a radical scavenger in ozonation reactions. The rate constants suggest that for sufficiently high concentrations of bromide, bromide ion may be an important radical scavenger in ozonation reactions.

Ozonation and disinfection by-product formation

Because of the concern about halogenated disinfection by-products, there has been much interest in using ozone as a primary disinfectant. Ozone residuals do not persist in drinking water, however, and a secondary disinfectant such as chlorine or monochloramine is subsequently applied to maintain a residual in the distribution system. It is therefore important to understand how ozonation affects subsequent formation of halogenated disinfection by-products from chlorination and chloramination, and this has been the subject of several studies. Another important issue is the potential formation of brominated disinfection by-products from ozonation of bromide-containing waters. The suspected health effects of several brominated disinfection by-products has caused this issue to be of serious concern.

The formation of chlorinated disinfection by-products in pre-ozonated, chlorinated waters appears to be complex and influenced by ozone dose, inorganic carbon concentration and pH of chlorination. The most common results that have been reported regarding the formation of DCAA and TCAA following pre-ozonation have been observations that DCAA formation is often enhanced or not affected by pre-ozonation, while TCAA formation is often decreased by pre-ozonation under typical water treatment conditions (26,27,39).

Reckhow et al. (39) have demonstrated that the impact of pre-ozonation on subsequent HAA formation is influenced by the pH of chlorination. For example, DCAA formation was enhanced by pre-ozonation when chlorinations were performed at neutral and high pH values; but it was decreased by pre-ozonation when chlorinations were performed at low pH (pH<4). Similar trends were observed for TCAA and $CHCl_3$.

The impact of ozone on HAA formation is also influenced by ozone dose and bicarbonate concentration. In pre-ozonated waters, the formation of DCAA and TCAA generally decreases with increasing ozone dose (39,40). The same trend has been observed for $CHCl_3$ and TOX formation in pre-ozonated, chlorinated waters (26,39). In addition, pre-ozonation in the presence of bicarbonate ion appears to decrease DCAA, TCAA and $CHCl_3$ formation compared to pre-ozonation in the absence of bicarbonate ion (26,39,40).

The mechanisms by which pre-ozonation enhances or decreases HAA formation in chlorinated waters is not well understood, and individual species may be affected differently. It appears that the influence of pre-ozonation on subsequent HAA formation is complex and will be highly dependent on water quality and water treatment conditions.

Zhu and Reckhow (27) recently studied the behavior of DCAA and TCAA formation during ozonation and post-chloramination of aquatic humic substances in the presence of 1 mM bicarbonate. The formation of both compounds was decreased in pre-ozonated waters compared to waters receiving chloramine alone. For both types of treatment conditions, DCAA and TCAA were observed at concentrations less than 10 µg/L (TOC = 4.1 mg/L).

An important concern with ozonation is the formation of brominated by-products. Rook et al. (28) noticed early on in the study of THMs that pre-ozonation shifted THM speciation toward the more highly brominated species in chlorinated waters, and he suggested that some of the active sites on THM precursors may become partially brominated during ozonation. Glaze et al. (44) have observed that dissolved organic bromide (DOBr) formation during ozonation is favored by high bromide concentrations, low pH and low alkalinity. Specific disinfection by-products that have been observed to be formed from ozonation alone include MBAA, DBAA, $CHBr_3$ and BrO_3^- (26,40,42,44,45).

Siddiqui and Amy (45) studied the effects of pH and ozone dose on DBAA formation from ozonation of raw waters. They observed that over the pH range 6-8.5, DBAA formation was enhanced by lower pH of ozonation, and DBAA formation increased with increasing ozone dose up to a dose of 4 mg O_3:1 mg dissolved organic carbon (DOC); at higher ozone doses DBAA formation declined. Haag and Hoigné (42) observed a similar effect of ozone dose on bromoform formation, showing that $CHBr_3$ formation was maximum at moderate ozone doses. Siddiqui and Amy (45) also observed that bromoform formation was dependent on DOC concentration, with a peak formation within the range of 2-9 mg/L DOC. They suggest that decline in $CHBr_3$ formation at high DOC concentrations may be the result of ozone-DOC reactions competing with ozone-bromide reactions.

Chapter 3
Materials and Methods

The study was designed to investigate the influence of bromide ion concentration on HAA speciation and the impact of various chemical treatment techniques on the speciation. All experiments were conducted on model waters containing aquatic humic substances extracted from raw drinking water sources in Myrtle Beach, SC and Palm Beach County, FL. Waters were prepared at ten bromide concentrations, ranging from 0-25 µM (0-2 mg/L). Bromide concentrations were chosen to be representative of low, moderate and high concentrations typically encountered in water treatment. Concentrations at the high end of the range (1, 1.5, and 2.0 mg/L Br^-) are extreme values, but these concentrations do sometimes occur in natural waters. Experimental waters were subjected to the following chemical treatments: chlorination (pH 8 and pH 6), chloramination (pH 8), pre-ozonation (pH 7) followed by chlorination, and pre-ozonation (pH 7) followed by chloramination. Samples were analyzed for all nine of the HAA species by gas chromatography. An outline of the experimental design is given in Figure 3.1.

Preparation of glassware

Glassware for general laboratory use was soaked in Alconox detergent overnight, rinsed with tap water, soaked in 10% nitric acid overnight, soaked in distilled, deionized water, then oven-dried at 85°C. Glassware used in measurement of chlorine and chloramine residuals was subsequently made chlorine demand-free by soaking in a chlorine solution (approximately 1000 mg/L as

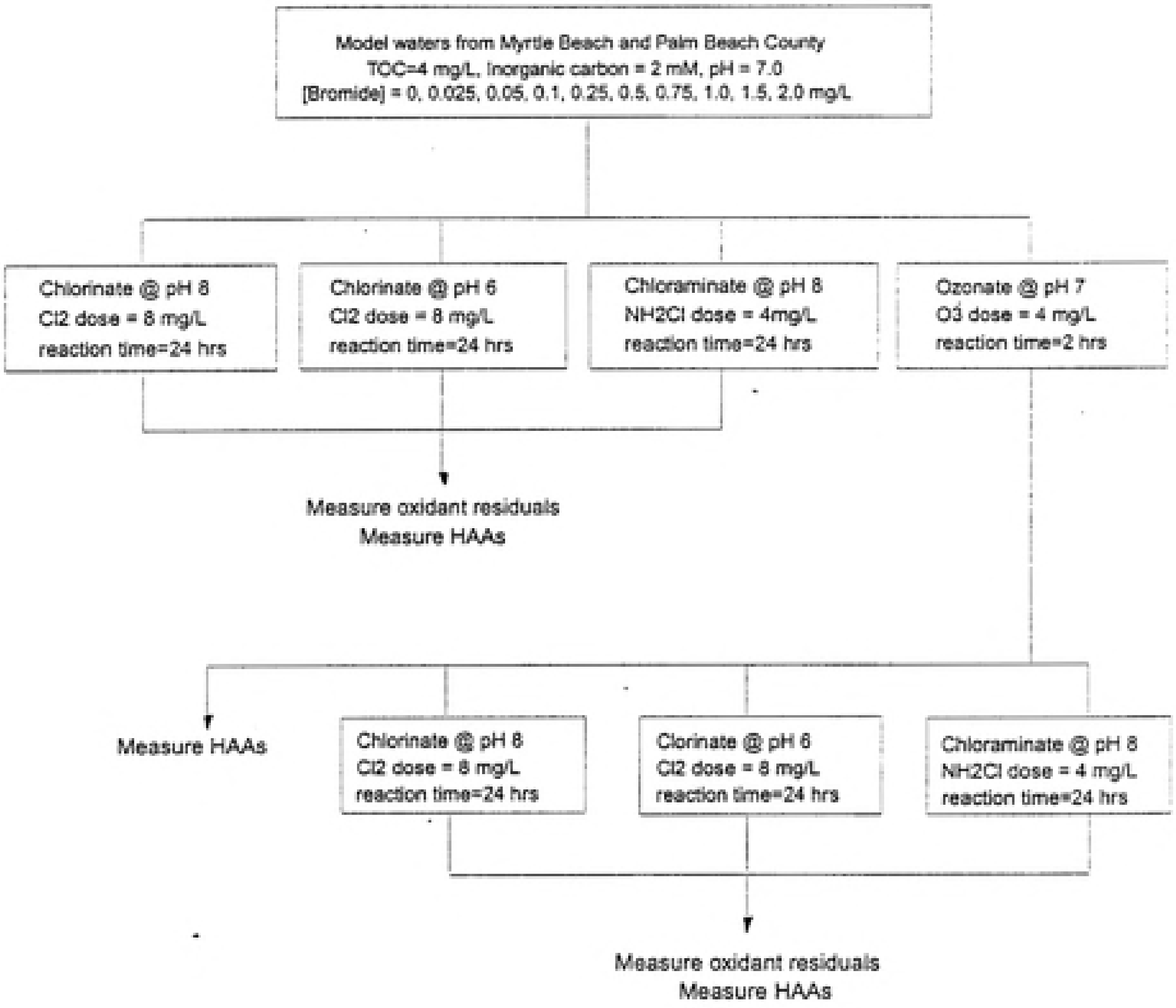


Figure 3.1. Experimental design

Cl_2) for at least 1 hr, then rinsing it well with deionized, chlorine demand-free water (Dracor Inc., Durham, NC).

Glass bottles in which ozonations, chlorinations and chloraminations were performed were soaked in detergent overnight, rinsed with tap water, soaked in 10% nitric acid overnight, rinsed with distilled, deionized water, soaked in a chlorine solution (at least 10 mg/L as Cl_2) overnight, rinsed well with deionized, chlorine demand-free water, then oven-dried at 85°C.

All 40-ml vials used for sample collection, storage and extraction were soaked in detergent overnight, rinsed with tap water, soaked in a chromic acid solution overnight, soaked in distilled, deionized water, and oven-dried at 85°C. All plastics (caps, septa, etc.) were soaked in detergent overnight, soaked in distilled, deionized water, then oven-dried at 52°C.

Isolation of humic substances

Humic substances were collected from raw water at the Myrtle Beach, SC and Palm Beach County, FL drinking water utilities. The drinking water source at Myrtle Beach is the Intracoastal Waterway, and the source at Palm Beach is the Floridan Aquifer. The hydrophobic fraction of the natural organic material was isolated by adsorption onto Amberlite XAD-8 resin (Rohm & Haas) using the method described by Thurman and Malcolm (46). Prior to sending the resin to the water utilities, it was cleaned by Soxhlet extraction. The resin was rinsed with 0.1 N NaOH for 5 days then Soxhlet-extracted with methanol (24 hrs), diethyl ether (24 hrs), acetonitrile (24 hrs) and methanol (24 hrs). Clean resin was stored in methanol until the time of its use.

Clean XAD-8 resin was packed into a glass column in a total volume of 3 L of resin, and the column was shipped to the water utility. Raw water fed to the column first passed through a 1.0 µm honeycomb filter for removal of particulates, and this influent stream was then acidified to pH 2 with 1.0 N HCl prior to entering the column. At the Myrtle Beach utility filtered, acidified raw water was fed to the column at a rate of 100 ml/min for a period of approximately 120 hrs. Based on measurements of the total organic carbon concentration of influent and effluent streams it was estimated that a total of approximately 8940 mg of TOC was adsorbed onto the resin. At the Palm Beach County utility filtered, acidified raw water was fed to the column at a rate of 100 ml/min for approximately 163 hrs. The total amount of TOC adsorbed was estimated to be approximately 5300 mg.

After the desired amount of natural organic material had been extracted, the column was shipped back to UNC for elution. The column was initially rinsed in a downflow mode with 3 L (one bed volume) of deionized, organic-free water, primarily for the removal of chloride. In the case of Myrtle Beach humic substances, the column was then back-eluted with a total volume of 14.5 L of 0.1 N NaOH at a rate of 100 ml/min. The first 6.5 L of eluate were collected in 500 ml fractions (a total of 13 fractions). The following 8 L of eluate were discarded. After measuring the TOC concentration of each fraction, fractions #4-9 were combined, passed through an AG-MP-50 cation exchange resin (Bio-Rad Laboratories, Richmond, CA) for the removal of sodium ions, and then stored at 5°C for experimental use. Fractions

#1-3 and #10-13 were discarded. The concentration of the stored solution of humic substances was approximately 1170 mg/L TOC. In the case of Palm Beach humic substances, the column was back-eluted with a total volume of 20 L of 0.1 N NaOH at a rate of 100 ml/min. The first 10 L of eluate were collected in 500 ml fractions. After measuring the TOC of each fraction, fractions #5-10 were combined, passed through a cation exchange resin, and stored at 5°C for further use. The resulting concentration of this solution was approximately 900 mg/L TOC.

Preparation of model waters

Model waters were prepared in the laboratory by diluting the concentrated humic materials into deionized, organic-free Dracor water at a final concentration of 4 mg/L TOC. In order to ensure that the humic substances dissolved completely, the concentrated humic extract was initially added to Dracor water adjusted to pH 10.5 with 10 N NaOH. A specified amount of 1 M $NaHCO_3$ ("Baker Analyzed", J.T. Baker Inc., Phillipsburg, NJ) was then added to the solution resulting in an inorganic carbon concentration of 2 mM. The pH of this solution was then lowered to pH 7 with concentrated H_2SO_4. This original solution was prepared at a concentration of approximately 5 mg/L TOC. The TOC concentration of the solution was measured with a Model 700 TOC analyzer (O.I. Corporation, College Station, TX). Portions of this solution were then diluted with appropriate amounts of laboratory water and 1 M $NaHCO_3$ to result in model waters with the following characteristics:

Water to be pre-ozonated	Water to be chlorinated or chloraminated only
TOC = 4.65 mg/L	TOC = 4.00 mg/L
Inorganic C = 2 mM	Inorganic C = 2 mM
pH = 7.2	pH = 7.0

Water intended for ozonation was prepared at 4.65 mg/L TOC to account for a subsequent 15% dilution with an ozone solution during batch ozonation. This water was also prepared at pH 7.2 to compensate for the lowering of pH by 0.2 units upon addition of an ozone stock solution at pH 3. The TOC concentrations of the model waters were measured, and these waters were stored in cubitainers at 5°C until use (not more than 3 days).

Ozonation procedure

All ozonations were performed in batch with an applied ozone dose of 4 mg/L (a 1:1 ratio of O_3 dose (mg/L):TOC (mg/L)).

Ozone stock solutions were prepared at concentrations of 20-30 mg/L of dissolved ozone. Ozone was generated from oxygen with a Sander's Model 200 ozone generator and bubbled into 2 L of deionized, organic-free water adjusted to pH 3 with 1 M H_2SO_4; the solution was maintained on ice during preparation. Dissolved ozone concentrations of 20-30 mg/L were achieved after 2-3 hours of ozonation. The final concentration of this stock solution was determined directly by measurement of UV absorbance at a wavelength of 258 nm in a Cary 219 spectrophotometer (Varian Associates, Inc., Palo Alto, CA) using a 1 cm cell.

Ozone concentrations were calculated from

$$[O_3]\ (\text{mg/L}) = \frac{\text{Abs}_{258} \times 48000\ \text{mg}\ O_3/\text{mol}\ O_3}{\varepsilon \times \ell}$$

where

ε = extinction coefficient for liquid phase ozone at λ=258nm = 2950 L/(mol*cm) (47)

ℓ = path length = 1 cm

This stock solution was used immediately.

Prior to ozonation, sodium bromide (EM Science, Cherry Hill, NJ) was added to model waters containing 4.65 mg/L TOC to prepare ten different samples ranging in bromide concentration from 0-25 µM (0-2 mg/L). Batch ozonations were performed in clear glass bottles in a total volume of 310 ml by adding appropriate amounts of ozone stock solution to a stirred sample of the model waters. The bottles were then stoppered headspace free and stored at room temperature for 2 hours. It was verified by the indigo method (47) that no measurable ozone residual persisted after 2 hours.

Chlorination and chloramination procedures

Model waters for chlorination and chloramination studies were prepared containing 0-25 µM bromide. Series of samples were chlorinated at pH 6.0 and pH 8.0, and chloraminated at pH 8.0. Pre-ozonated waters were subjected to the same chemical treatments.

Chlorine solutions were prepared by diluting 4-6% sodium hypochlorite (Fisher Scientific, Fair Lawn, NJ) into deionized, chlorine demand-free water at a final concentration of

750-1000 mg/L as Cl_2. Stock concentrations were determined by the iodometric method (Standard Method #4500-Cl B) (47). This solution was prepared fresh on the day of use and was stored at room temperature in an amber bottle during use.

Chloraminations were performed by treating samples with preformed monochloramine. In the preparation of monochloramine, equal volumes of ammonium sulfate (EM Science, Gibbstown, NJ) and chlorine solutions adjusted to pH 9 (with NaOH or H_2SO_4) were added sequentially to a well mixed Ehrlenmeyer flask on ice in a concentration ratio of 4 mg/L as Cl_2 : 1 mg/L as N. The resulting solution had at least 96% conversion of free chlorine to monochloramine, and no residual free chlorine persisted; this was determined by the DPD ferrous titrimetric method (Standard Method #4500-Cl F) (47). The concentration of monochloramine in these solutions ranged from 500-700 mg/L as Cl_2. The solution pH was between 10-11, and the solution was stable over 24 hours. Monochloramine was prepared fresh on the day of use and was stored in an Ehrlenmeyer flask covered with aluminum foil during use.

Model waters were previously prepared with 4 mg/L of TOC, at pH 7.0 and with an inorganic carbon concentration of 2 mM. Prior to treatment, samples were buffered at pH 8.0 with 0.05 M Na_2HPO_4 (Mallinckrodt Specialty Chemicals Co., Paris, KY) and at pH 6.0 with 0.05 M NaH_2PO_4 (EM Science). Waters were then divided into series of ten 350 ml samples, and sodium bromide was added to each series of samples to produce waters containing 0-25 μM bromide. The pHs of pre-ozonated waters were measured, and these samples were then individually buffered at pH 8.0 and pH 6.0 with

0.05 M phosphate.

All chlorinations and chloraminations were performed in 300 ml chlorine demand-free clear glass bottles. Samples were brought to room temperature prior to treatment. All chlorinated samples received a chlorine dose of 8 mg/L as Cl_2 and all chloraminated samples received a monochloramine dose of 4 mg/L as Cl_2. These doses were chosen to ensure that a residual was maintained in all samples over a 24 hour reaction period. Pre-ozonated samples were treated approximately 2 hours after ozonation in the same BOD bottles in which ozonations had been performed. The appropriate amount of chlorine or monochloramine was added to each well-stirred sample, and samples were stoppered headspace-free after approximately 30 seconds of mixing. Sample dilution by addition of chlorine or monochloramine solutions was less than 1.2%. Samples were then stored in the dark at 20°C for 24 hours. Samples that had not been pre-ozonated were treated in the same manner as the pre-ozonated samples.

Sample collection and storage

Samples to be analyzed for HAA formation resulting from ozonation alone were collected in duplicate 2 hours following ozonation. Samples were collected headspace-free in 40-ml glass vials with polypropylene screw caps and teflon-lined septa. Each vial contained 150 mg of ammonium sulfate to be consistent with chlorinated samples, in which addition of ammonium sulfate was required to quench free chlorine. Samples were stored at 5°C for no more than 4 days prior to HAA analysis.

Chlorinated and chloraminated samples were collected in duplicate 24 hours following treatment in the same manner described above. At the time of sample collection, chlorinated samples were analyzed for free chlorine and free bromine residuals, and chloraminated samples were analyzed for monochloramine and free bromine residuals by the DPD ferrous titrimetric method (47). Free bromine residuals were distinguished from free chlorine residuals by adding glycine, which selectively quenches free chlorine, to the sample prior to DPD analysis. Analysis of a second sample by the DPD method, without addition of glycine, provided the sum of free chlorine and free bromine residuals. Samples for HAA analysis were stored at 5°C for no more than 4 days.

Analysis of haloacetic acids

Samples were analyzed for HAAs by a modification of the method of McGuire et al. (48). A detailed description of the procedure is given in Appendix A. In general, 20-ml aliquots of acidified, salt-containing samples were extracted with 5 ml methyl t-butyl ether (MtBE). The ether layer was separated, derivatized with diazomethane, and samples were then analyzed on an HP-5890 Series II gas chromatograph with electron capture detector (Hewlett-Packard, San Fernando, CA).

Standards

High purity analytical standards for MCAA, DCAA, TCAA, MBAA, DBAA and BrClAA were obtained as a 2 g/L mixture in MtBE from Supelco (Bellefonte, PA); TBAA, dibromopropane and 2,3-dibromopropionic acid were obtained from Aldrich Chemical

Co. (Milwaukee, WI). BrCl$_2$AA and Br$_2$ClAA were not commercially available. BrCl$_2$AA was synthesized at the University of North Carolina, and Br$_2$ClAA was synthesized at the University of Massachusetts.

Bromodichloroacetic acid

BrCl$_2$AA was synthesized in the laboratory of Dr. Avram Gold at the University of North Carolina (Chapel Hill, NC), following the method of Zimmer et al. (49). The identity of this compound was verified by mass spectral analysis of the methyl ester on a Saturn II GC/MS (Varian Chromatography Systems, Walnut Creek, CA). A 5 mg/L sample of the synthesized compound was prepared in MtBE and derivatized with diazomethane. The sample was injected into the GC/MS and passed through a DB-5 column (J&W Scientific, Folsom, CA) for gas chromatographic separation. The column was 30 m in length, with a 0.25 mm inner diameter (ID) and a 0.25 µm film thickness. The temperature program was:

37°C --------------> 136°C --------------> 236°C
3 min   5°C/min   3 min   20°C/min   3 min

injector temperature = 157°C, flow rate = 1 ml/min,
injection volume = 2 µl

The mass spectrum of the sample was obtained by electron impact (EI) with an ion trap detector. Instrument settings and data analysis were controlled by Saturn Revision C software interfaced with the instrument. The ionizing potential was 70 eV, the ion trap manifold temperature was 220°C, the mass scan range was 40-300 amu, and the scan rate was 1 scan per second.

The EI mass spectrum of the BrCl$_2$AA peak is shown in Appendix B. The mass spectrum obtained agrees well with that previously reported by Xie et al. (50).

After verifying the identity of the BrCl$_2$AA, it was necessary to estimate its purity in order to use it as a quantitative standard. Based on the synthesis method, it was expected that impurities, if present, were most likely to be other HAA species. Samples of 500 µg/L BrCl$_2$AA in MtBE were derivatized with diazomethane then analyzed on an HP-5890 Series II gas chromatograph with electron capture detector. Column specifications and temperature conditions were:

Column: DB1701 (J&W Scientific), 30 m length, 0.25 mm ID,
0.25 µm film thickness

40°C --------> 66°C --------> 150°C --------> 210°C
2 min 2°C/min 6°C/min 2 min 20°C/min 3 min

injector temperature = 157°C, detector temperature = 300°C
flow rate = 1 ml/min, injection volume = 2 µl

Three minor peaks in addition to the dominant BrCl$_2$AA methyl ester peak were present. Based on relative retention times these three peaks were identified, in order of significance, as the methyl esters of DCAA, BrClAA, and DBAA. The concentrations of these impurities were determined by running a series of calibration samples along with the BrCl$_2$AA sample. Details of these calculations are presented in Appendix C. The purity of BrCl$_2$AA was estimated to be 97%.

Dibromochloroacetic acid

Br$_2$ClAA was synthesized by Dr. Yuefeng Xie at the University of Massachusetts (Amherst, MA). The synthesis of this compound was based on the method of Zimmer et al. (49), with the modifications detailed by Xie et al. (50). The electron impact and positive-ion chemical ionization (PCI) mass spectra of this compound were previously reported by Xie et al. (50).

The purity of Br_2ClAA was assessed in a manner similar to that reported for $BrCl_2AA$. Small amounts of impurities were identified, in order of significance, as TBAA, BrClAA and DBAA. The purity was estimated to be 91% (Appendix C).

Storage and stability of HAA standards

The Supelco HAA mixture containing 2 g/L each of MCAA, DCAA, TCAA, MBAA, DBAA and BrClAA in MtBE received from Supelco was stored at -15°C until the day of use. Standards of TBAA, $BrCl_2AA$ and Br_2ClAA were prepared individually in MtBE at concentrations in the range 0.5-10 g/L and stored at -15°C until use.

A criterion was developed to determine how long these primary stock solutions could be stored without losing their integrity. The criterion was based on tracking the slopes of the calibration curves for each individual HAA species. It was decided that a given stock solution could be used until the slope of the calibration curve decreased by more than 10% from its original value (i.e., slope from the date of first use of the fresh standard). Based on this criterion it was determined that the Supelco mixture was stable for up to 3 months (less than 10% decay of each species), and that TBAA, $BrCl_2AA$ and Br_2ClAA were each stable for only 2 weeks.

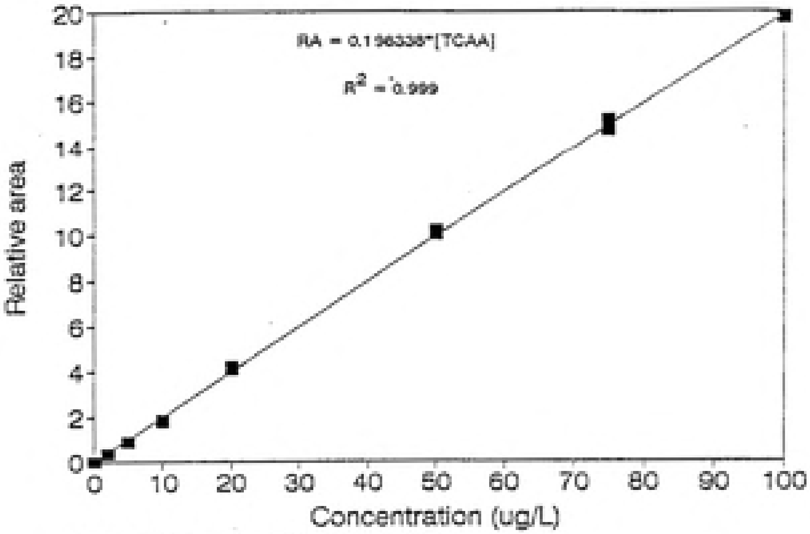
Calibration curves

HAA concentrations in the chlorinated, chloraminated and ozonated samples were calculated from calibration curves generated from standards. On the day of sample extraction two standard solutions were prepared in methanol. Solution I was a dilution of the 2 g/L Supelco mixture of the more stable HAAs, to a concentration of 0.1 g/L of each HAA. Solution II contained 0.1 g/L each of the less stable HAAs (TBAA, $BrCl_2AA$ and Br_2ClAA). These solutions were used to prepare two independent calibration curves. Each solution was diluted into deionized, organic-free water in various concentrations to produce a series of calibration samples (usually 8-10 points) ranging in individual HAA concentrations from 0-150 µg/L. These standards were extracted and analyzed at the same time as experimental samples.

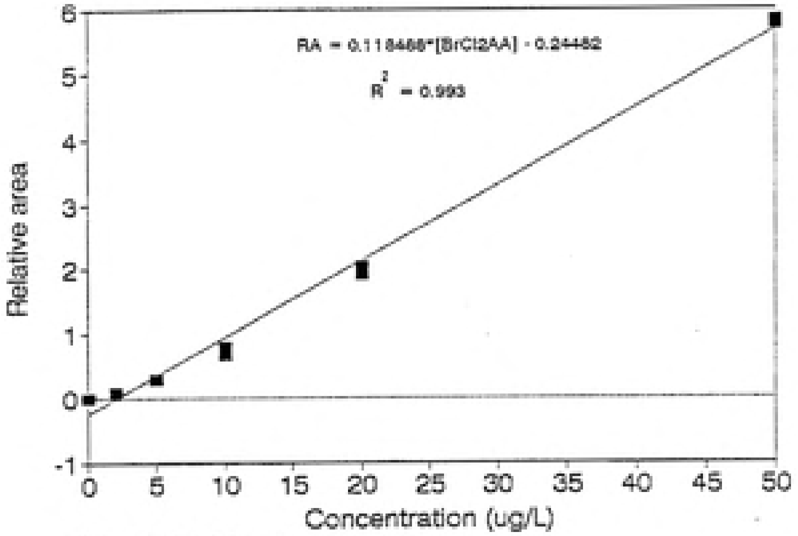
The more stable HAAs generally gave linear responses over the range of concentrations of interest in this study. The calibration curves for TBAA, $BrCl_2AA$ and Br_2ClAA were not linear over the entire range of concentrations. This was accounted for by estimating one linear calibration curve in the range 0-50 µg/L and another linear calibration curve in the range 50-150 µg/L. Typical calibration curves for TCAA and $BrCl_2AA$ are shown in Figure 3.2; representative calibration curves of each of the nine HAA species are presented in Appendix D.

Gas chromatographic analysis

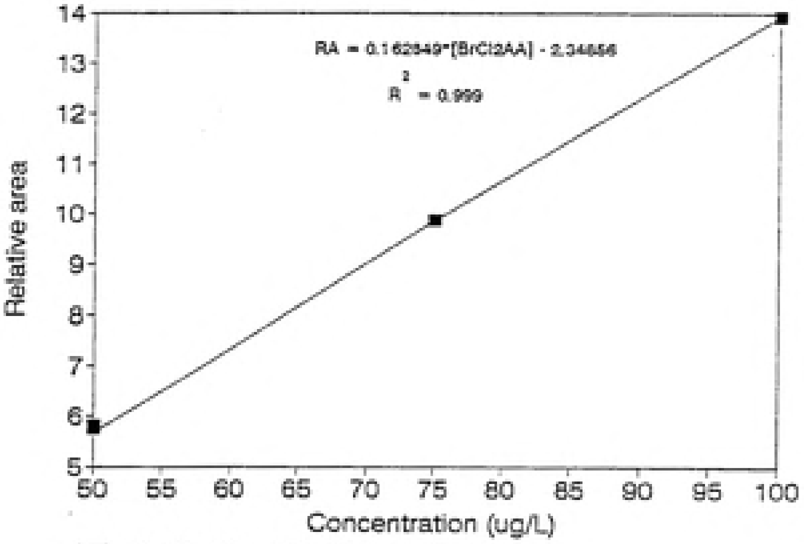
All samples were analyzed on an HP-5890 Series II gas chromatograph with electron capture detector. GC sample analysis generally began as soon as sample preparation was completed.



(a) TCAA, 0-100 μg/L



(b) $BrCl_2AA$, 0-50 μg/L



(c) $BrCl_2AA$, 50-100 μg/L

Figure 3.2. Haloacetic acid calibration curves

However, when storage was required, samples were stored at -15°C for not more than 2 days in 2-ml glass autovials with aluminum crimp caps and PTFE teflon-lined butyl rubber septa.

Preliminary chromatography indicated that TCAA and BrClAA co-eluted and could not be resolved using the temperature program previously reported by McGuire et al. (48) with DB-5 columns of 30 m and 60 m lengths, 0.25 mm ID and 0.25 µm film thickness. This may have been due in part to the age of the columns used.

Good separation of each of the nine HAA species was achieved by using a DB-1701 column, which is more polar than the DB-5 column, and a modification of a temperature program previously reported by Pourmoghaddas (51). Column specifications and GC conditions were:

Column: DB1701 (J&W Scientific), 30 m length, 0.25 mm ID,
0.25 µm film thickness

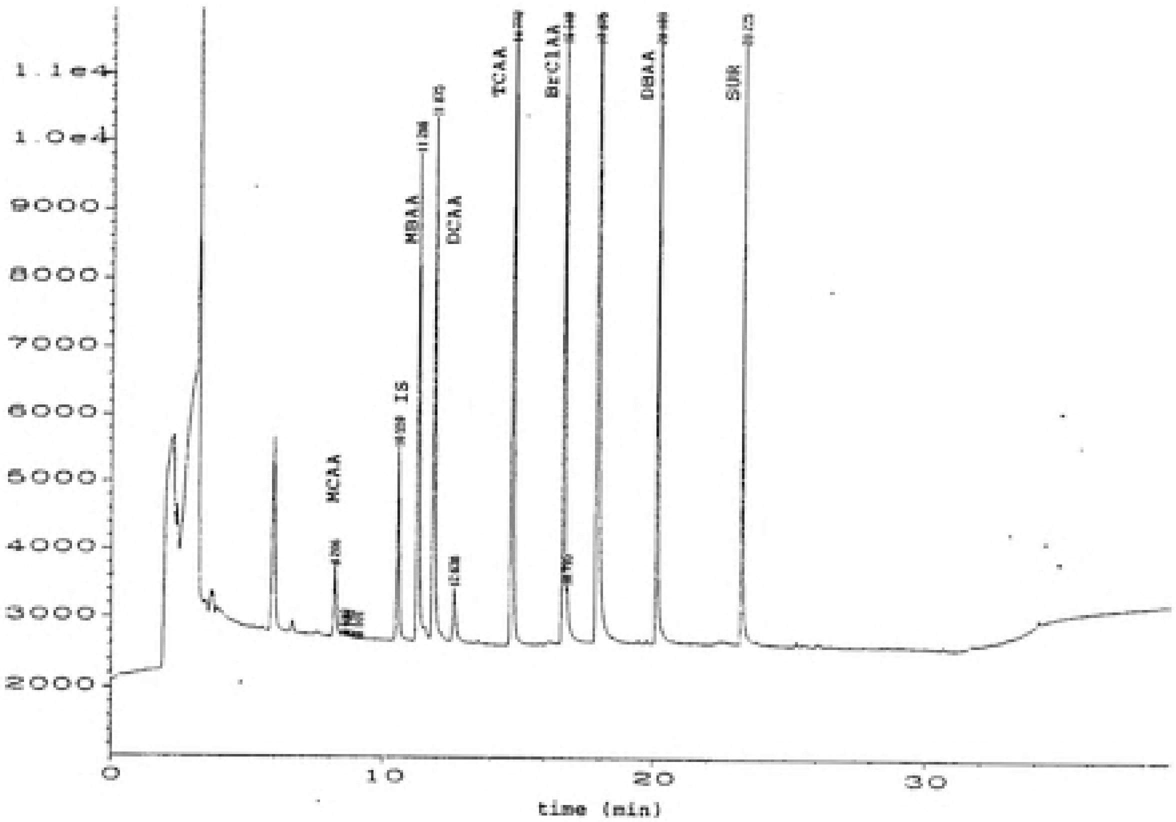
Temperature program:

40°C --------> 66°C --------> 150°C --------> 210°C
2 min 2°C/min 6°C/min 2 min 20°C/min 3 min

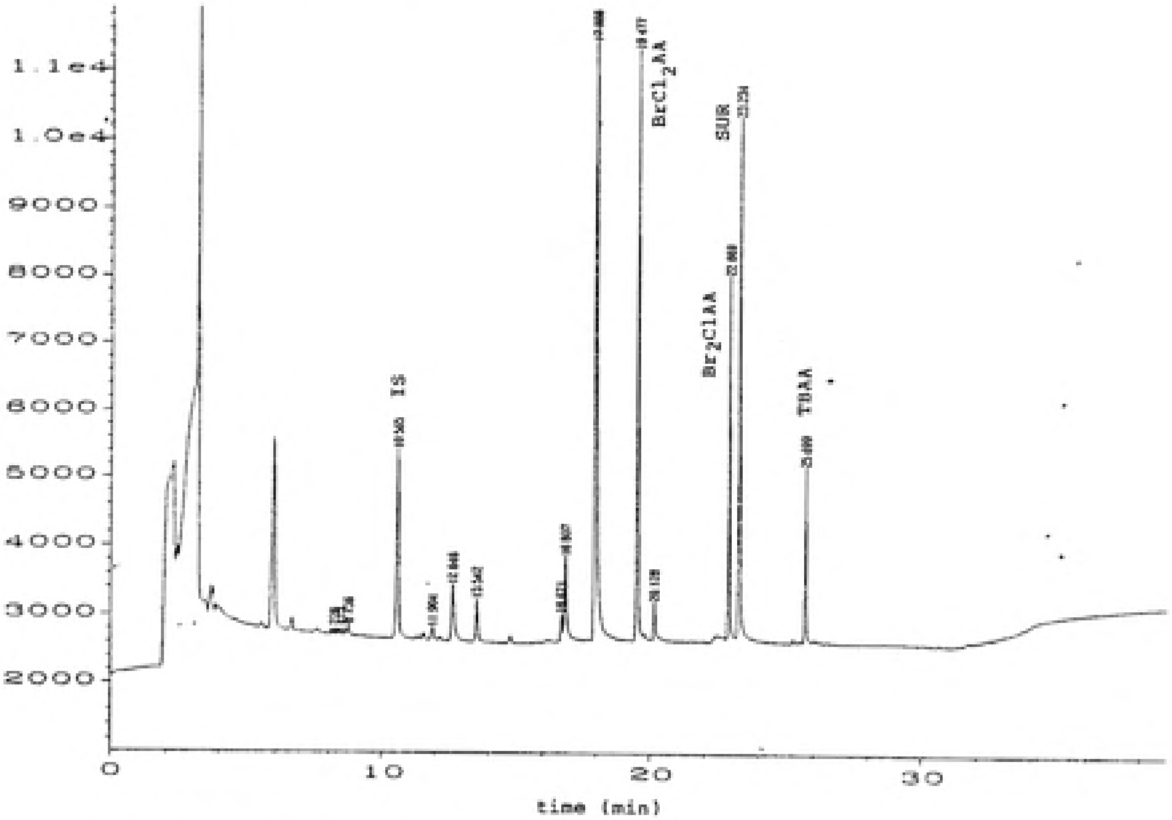
injector temperature = 157°C, detector temperature = 300°C
flow rate = 1 ml/min, injection volume = 2 µl

Representative chromatograms of calibration samples are shown in Figure 3.3, and a chromatogram of an experimental sample is shown in Figure 3.4.

GC information was collected and organized by HPCHEM Station software which prepared a report for each sample. The report consisted of a chromatogram and a data sheet containing retention time, integrated area, height, type, width, and % of total peak area for each peak.



(a) 20 µg/L standard I



(b) 20 µg/L standard II

Figure 3.3. Chromatograms of HAA standards

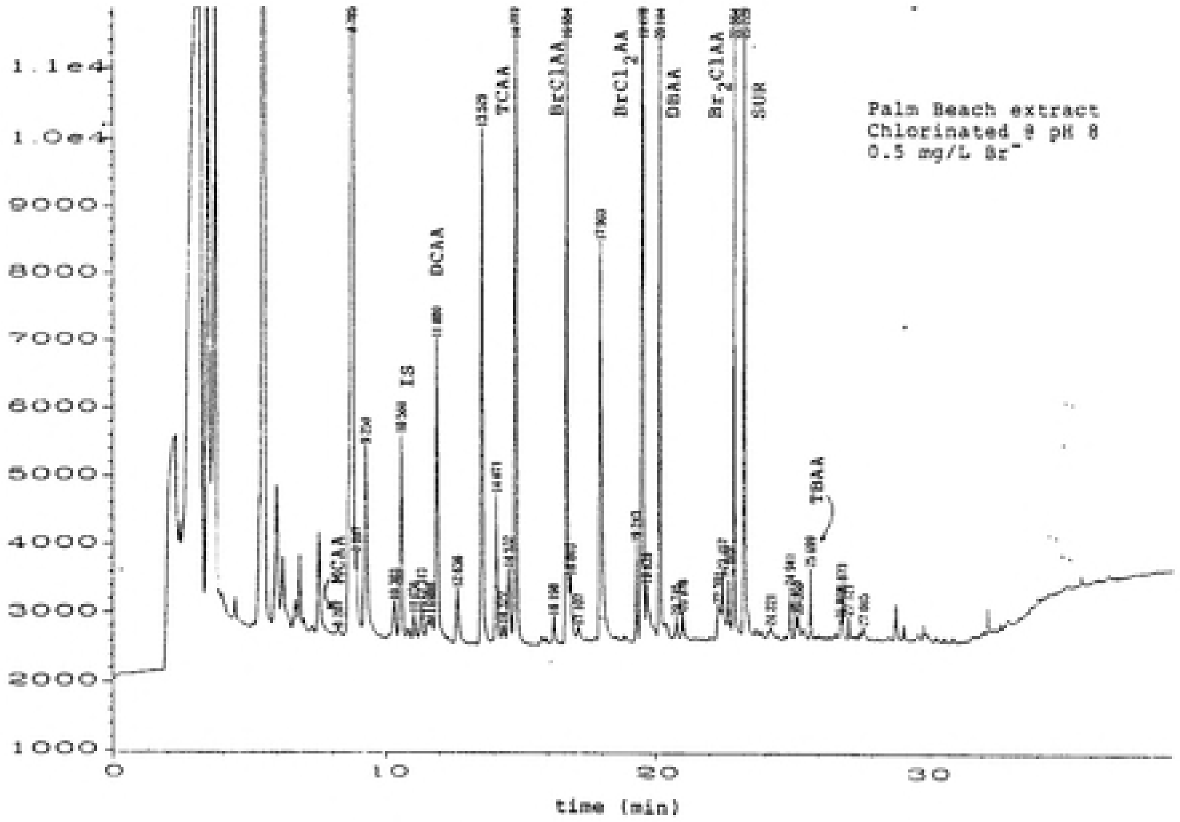


Figure 3.4. Chromatogram of a chlorinated Palm Beach sample

Data analysis

Retention time and peak area for each HAA species present in calibration and experimental samples were entered into a QUATTRO PRO spreadsheet software program. All data analysis calculations and graphing were performed in this spreadsheet.

All samples contained an internal standard (dibromopropane) and a surrogate recovery standard (2,3-dibromopropionic acid) at uniform concentration in each sample. All HAA retention times and peak areas were converted to relative retention times (RR_t) and relative areas (RA) with respect to the internal standard (IS). Individual HAA species were identified by their relative retention times. The relative retention time of each of the HAA species is given in Appendix A.

The relative area of the surrogate recovery standard gave an indication of the consistency of the analysis procedure from sample to sample. Good agreement between surrogate relative areas of calibration samples and those of experimental samples suggested that extraction of HAAs from deionized, organic-free water was similar to extraction from the model water matrix, and thus the method of calibration appeared to be valid for these model waters.

All samples were analyzed in duplicate, and concentrations were determined by comparison of relative peak areas to the relative peak areas of the calibration standards. The average of the two duplicates became the reported value for a sample.

Method detection limits

Method detection limits (MDLs) were calculated based on the guidelines described by McGuire et al. (48). Seven replicate standards were prepared in deionized, organic-free water at concentrations of 1 µg/L (MCAA, DCAA, TCAA, MBAA, DBAA, BrClAA) or 2 µg/L (TBAA, $BrCl_2AA$, Br_2ClAA). These samples were carried through the entire method of HAA analysis. The MDL for each species was calculated from:

$$MDL = t * s$$

where

t = student t value for 6 degrees of freedom and a 99% confidence interval = 3.143

s = standard deviation of the 7 replicates

The method detection limits are shown in Table 3A.

Table 3A. Method detection limits of HAA species

Species	MDL (µg/L)
MCAA	0.91
DCAA	0.59
TCAA	0.29
MBAA	0.40
DBAA	0.29
TBAA	3.01
BrClAA	0.48
$BrCl_2AA$	2.24
Br_2ClAA	2.18

The derivation of these values is given in Appendix E.

Statistical treatment of results

The results that will be presented were obtained from four primary experiments, each of which contained several series of samples:

<u>Experiment 1</u>:
Myrtle Beach extract chlorinated at pH 8
Myrtle Beach extract chlorinated at pH 6
Myrtle Beach extract pre-ozonated, chlorinated at pH 8
Myrtle Beach extract pre-ozonated, chlorinated at pH 6

<u>Experiment 2</u>:
Myrtle Beach extract chloraminated at pH 8
Myrtle Beach extract pre-ozonated, chloraminated at pH 8
Myrtle Beach extract ozonated

<u>Experiment 3</u>:
Palm Beach extract chlorinated at pH 8
Palm Beach extract chlorinated at pH 6
Palm Beach extract pre-ozonated, chlorinated at pH 8
Palm Beach extract pre-ozonated, chlorinated at pH 6

<u>Experiment 4</u>:
Palm Beach extract chloraminated at pH 8
Palm Beach extract pre-ozonated, chloraminated at pH 8
Palm Beach extract ozonated

Series of samples within each experiment were treated and analyzed at the same time to minimize experimental error.

Experiment 1 was repeated to assess the reproducibility of the results. The duplicate experiments showed the same effects of bromide ion concentration, pH of chlorination, and pre-ozonation on HAA speciation and formation. In addition, there was good agreement between measured concentrations of individual species. An average coefficient of variation (CV) is reported for each of the HAA species in Table 3B. The coefficient of variation is defined as:

CV = (sample standard deviation)/(sample mean)*100%

It is an indication of the uncertainty in the data. For each of the HAA species, two sets of data were available for forty different experimental conditions. The reported coefficient of variation is an average for these forty conditions.

Table 3B. Coefficients of variation for HAA measurements from different experiments.

HAA	CV (%)
MCAA	5.1
DCAA	6.2
TCAA	9.1
MBAA	9.1
DBAA	11.1
TBAA	20.9
BrClAA	9.3
$BrCl_2AA$	16.2
Br_2ClAA	7.8

It was expected that the variability in measurements of HAA concentration within an experimental group would be less than the variability among data generated at different times. The variability among data within an experimental group was estimated by chlorinating five identical samples containing 6 μM Br^- (a mid-range concentration to get appreciable formation of each of the nine HAA species); each sample was then analyzed in triplicate. The mean values of each of the five samples were compared, and the coefficients of variation are reported for each of the HAA species in Table 3C. All data are reported in Appendix F.

The results were not subjected to a rigorous statistical analysis. The calculated coefficients of variation were used as guidelines for interpreting whether or not observed differences were beyond the range of data variability.

Table 3C. Coefficients of variation for HAA measurements from the same experiment.

HAA	CV (%)
MCAA	1.5
DCAA	1.9
TCAA	1.2
MBAA	6.5
DBAA	2.9
TBAA	2.2
BrClAA	1.4
$BrCl_2AA$	1.2
Br_2ClAA	1.3

Chapter 4
Results and Discussion

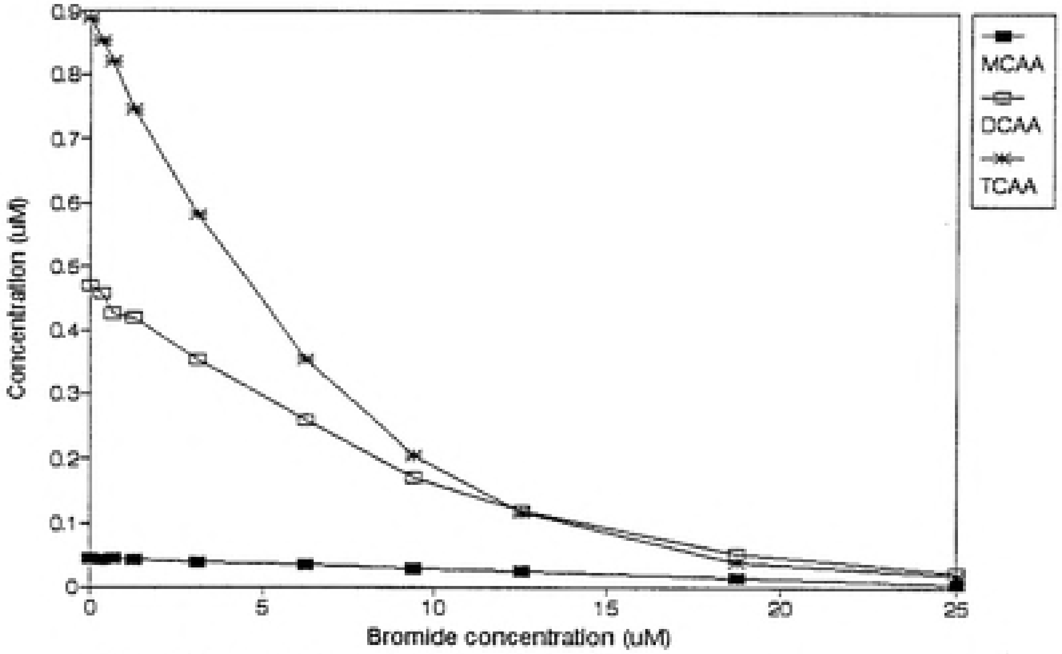
The results that will be presented assess the effects of bromide ion concentration, pH of chlorination, ozonation, and chloramination on haloacetic acid speciation and formation. All of the data that will be presented graphically in this chapter is reported numerically in Appendix F.

Patterns of HAA speciation in extracts chlorinated at pH 8

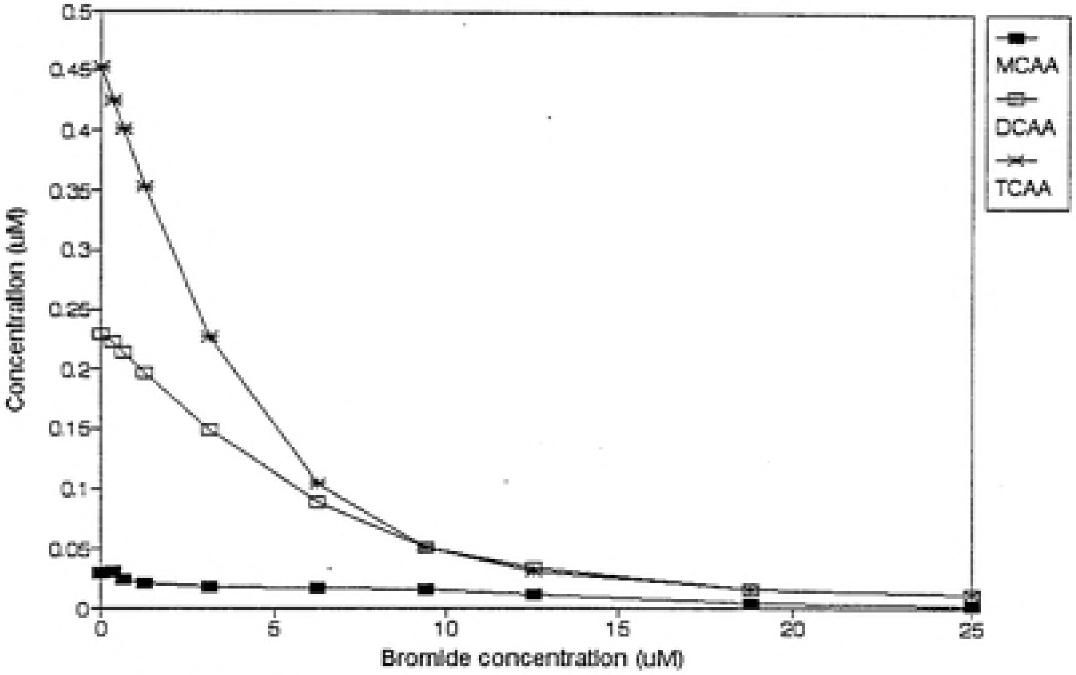
Formation of individual species

Increasing bromide concentration from 0-25 µM (0-2 mg/L) gradually shifted HAA speciation from the chlorinated species to the mixed bromo-chloro species to the brominated species during chlorination of the humic extracts at pH 8. The patterns of formation of individual species as functions of bromide ion concentration are shown in Figures 4.1-4.3. The two waters show similar patterns of HAA speciation.

The mixed bromo-chloro species are particularly interesting because the formation of each of these species exhibits a peak at a specific bromide concentration. It is likely that the bromide concentrations at which each of the species peak are dependent on TOC concentration and chlorine dose. The regions of bromide concentrations at which the species peak under the conditions of the present study are given in Table 4A. In both waters BrClAA and $BrCl_2AA$, each of which contain 1 mole Br per mole HAA, reach their maximum concentration in approximately the same region of bromide concentration; Br_2ClAA, which contains 2 moles Br per

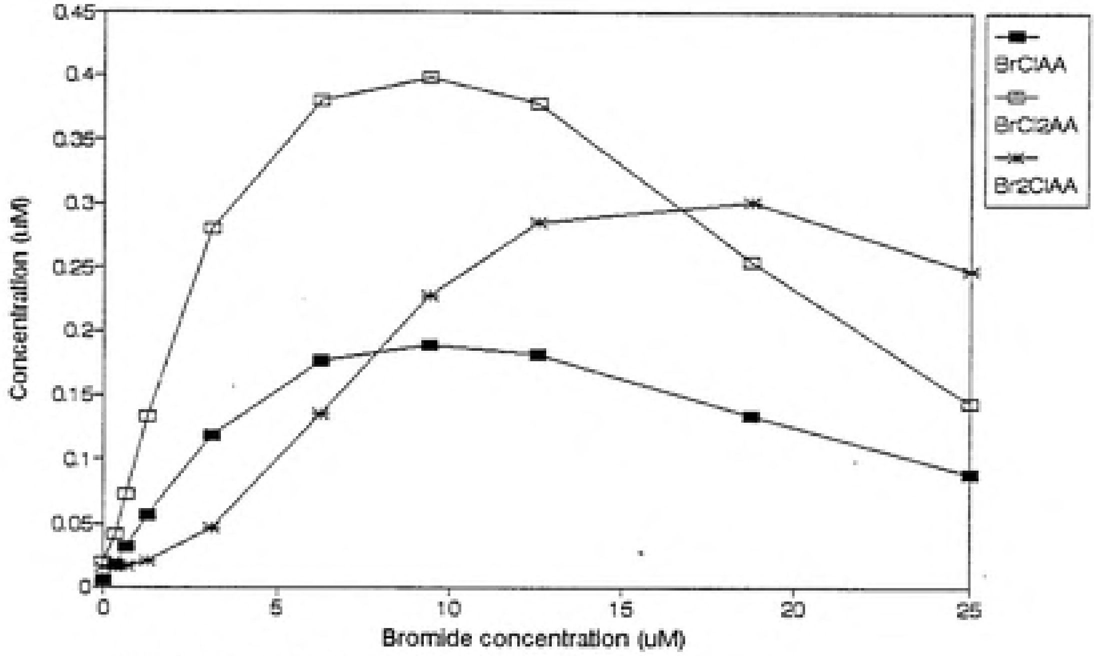


(a) Myrtle Beach extract

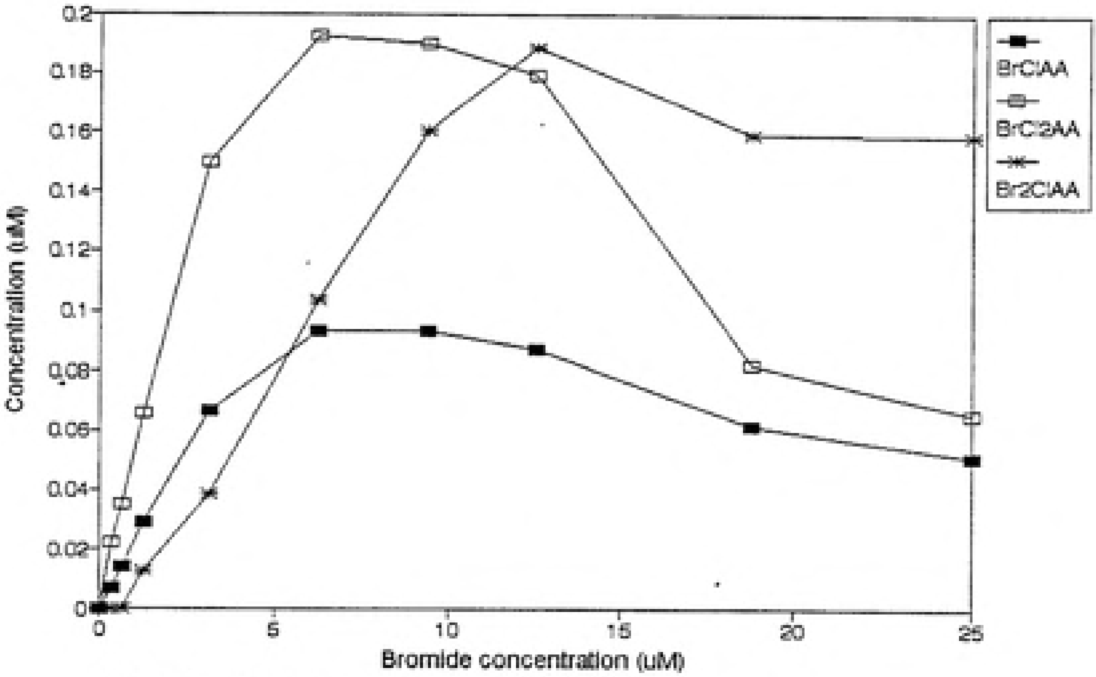


(b) Palm Beach extract

Figure 4.1. Formation of chlorinated HAAs as a function of bromide concentration during chlorination at pH 8.

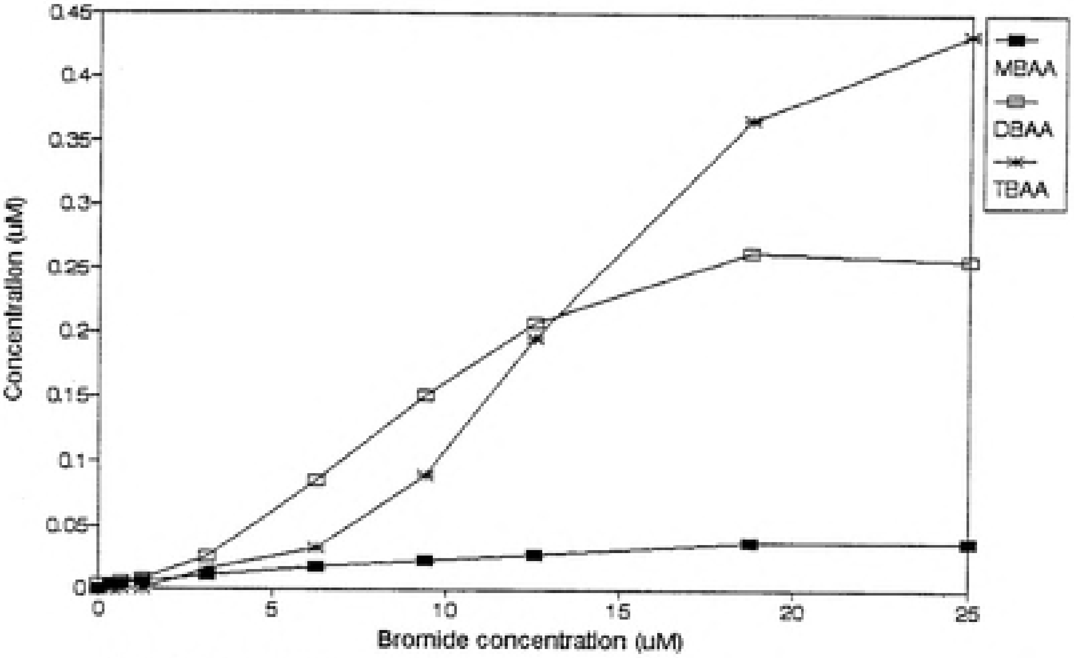


(a) Myrtle Beach extract

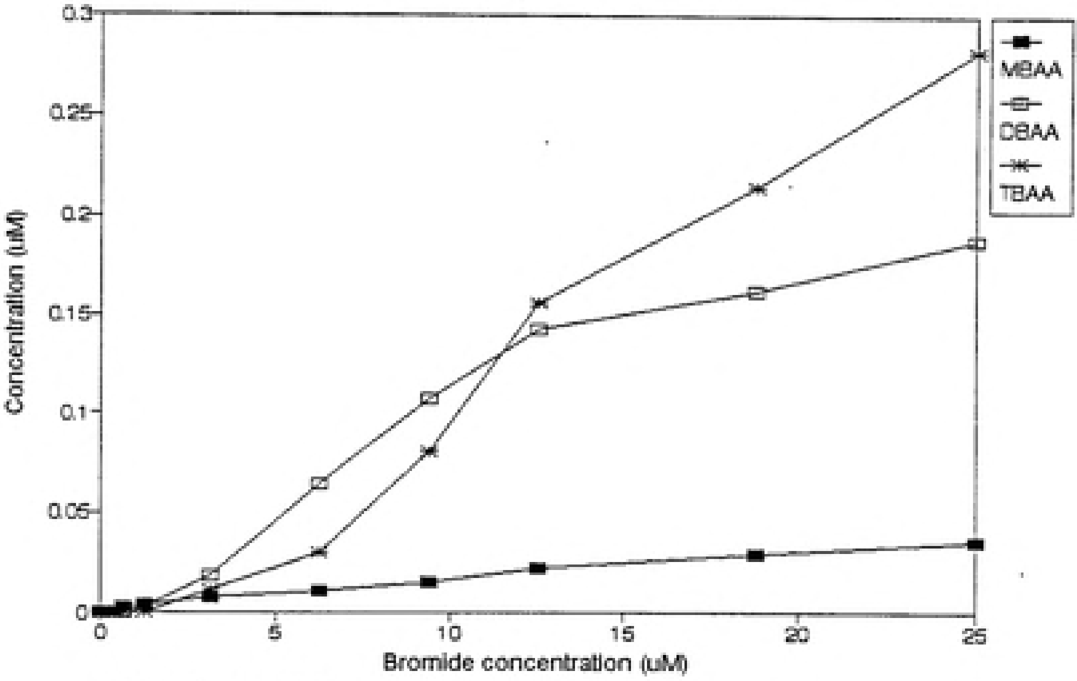


(b) Palm Beach extract

Figure 4.2. Formation of bromo-chloro HAAs as a function of bromide concentration during chlorination at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.3. Formation of brominated HAAs as a function of bromide concentration during chlorination at pH 8.

mole HAA, peaks at a bromide concentration approximately two times greater.

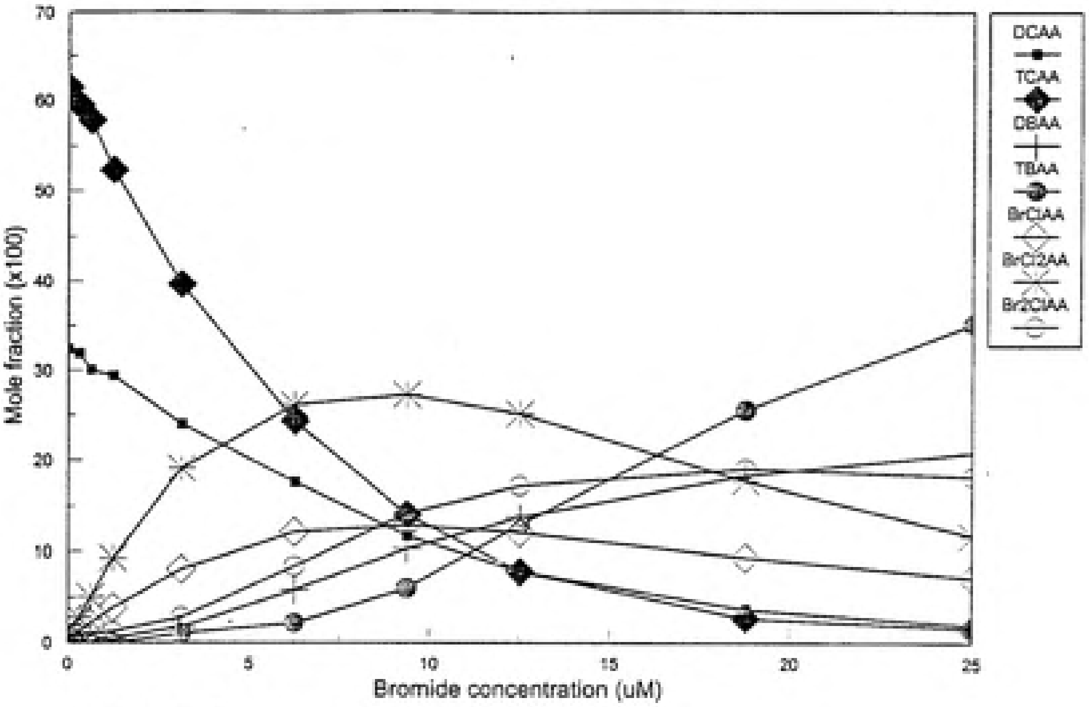
Table 4A. Bromide concentrations of peak formation of mixed bromo-chloro species during chlorination at pH 8.

Sample	Species	$[Br^-]$ at peak (μM)
Myrtle Beach	BrClAA $BrCl_2AA$ Br_2ClAA	9 9 19
Palm Beach	BrClAA $BrCl_2AA$ Br_2ClAA	7 8 13

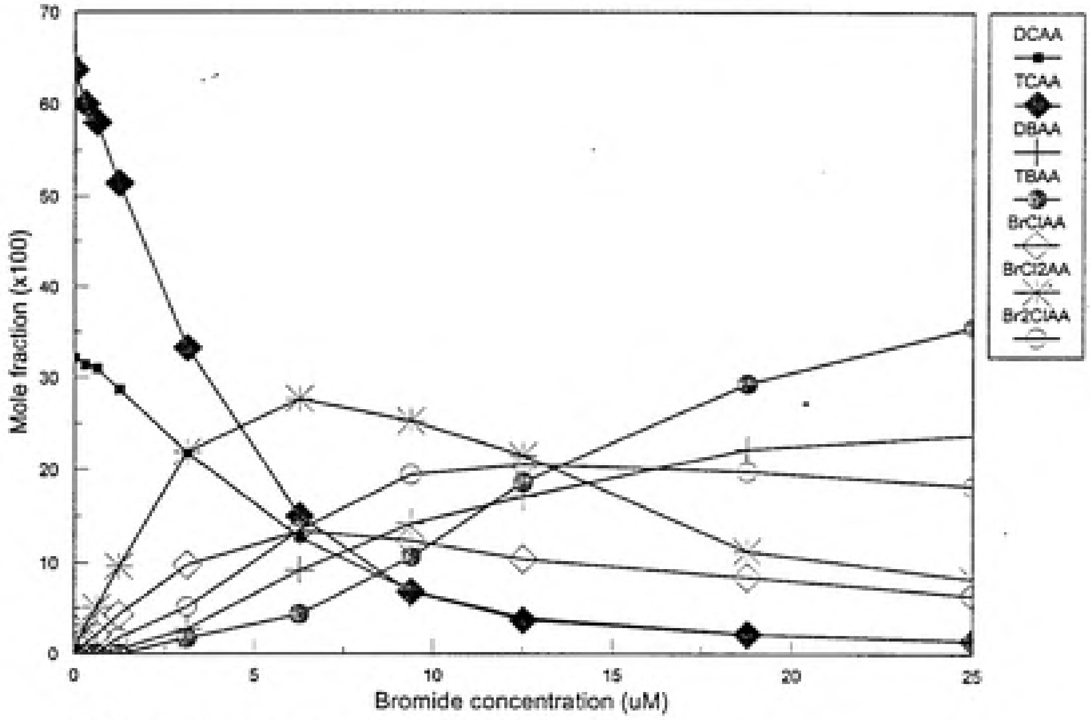
Distribution of individual species

Distribution diagrams of the HAA species are presented in Figure 4.4, where individual HAA species are plotted as mole fractions of the total molar HAA concentration. There is a striking similarity between the distribution of species in both waters. The principal species formed at bromide concentrations less than 5 μM is TCAA, between 5 and 13 μM Br^- the dominant species is $BrCl_2AA$, and at bromide concentrations greater than 16 μM the principal species is TBAA. It is evident from Figure 4.4 that the bromo-chloro species, which have not been well studied, may constitute a significant fraction (at least 10%) of the total haloacetic acids (THAAs) in waters containing as little as 1 μM bromide; $BrCl_2AA$ is particularly abundant. At fairly low bromide concentrations (< 3 μM) speciation is generally in the order:

TCAA > DCAA > $BrCl_2AA$ > BrClAA > Br_2ClAA > DBAA > TBAA.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.4. Distribution of individual HAA species in extracts chlorinated at pH 8.

At the high end of the bromide range studied (>20 µM) speciation is in a nearly opposite order:

TBAA > DBAA > Br_2ClAA > $BrCl_2AA$ > BrClAA > DCAA, TCAA.

MCAA and MBAA, which are not included in these diagrams, individually constituted less than 5% of the total molar concentration of HAAs in all cases.

The observed patterns of HAA speciation are qualitatively similar to results reported by Pourmoghaddas et al. (25) for the chlorination of humic acid in the presence of bromide, shown previously in Figure 2.3. The speciation may be influenced by TOC concentration and chlorine dose.

Total HAA formation

The distribution of HAA species in the two extracts appears similar even though absolute amounts of HAAs formed from Myrtle Beach extract are consistently greater than the amounts formed from Palm Beach extract. Total µM HAA formation over the full range of bromide concentrations studied is shown in Figure 4.5. THAA formation from Myrtle Beach extract is approximately 2X greater than that from Palm Beach extracts despite the same initial TOC concentration (4 mg/L). THAA formation appears to be fairly constant over the range of bromide concentrations studied.

Total formation of chlorinated, bromo-chloro and brominated species

The sum of the chlorinated, bromo-chloro and brominated species as a function of bromide concentration is shown in Figure 4.6. It is clear that the chlorinated species are the principal species formed at low bromide concentrations, the

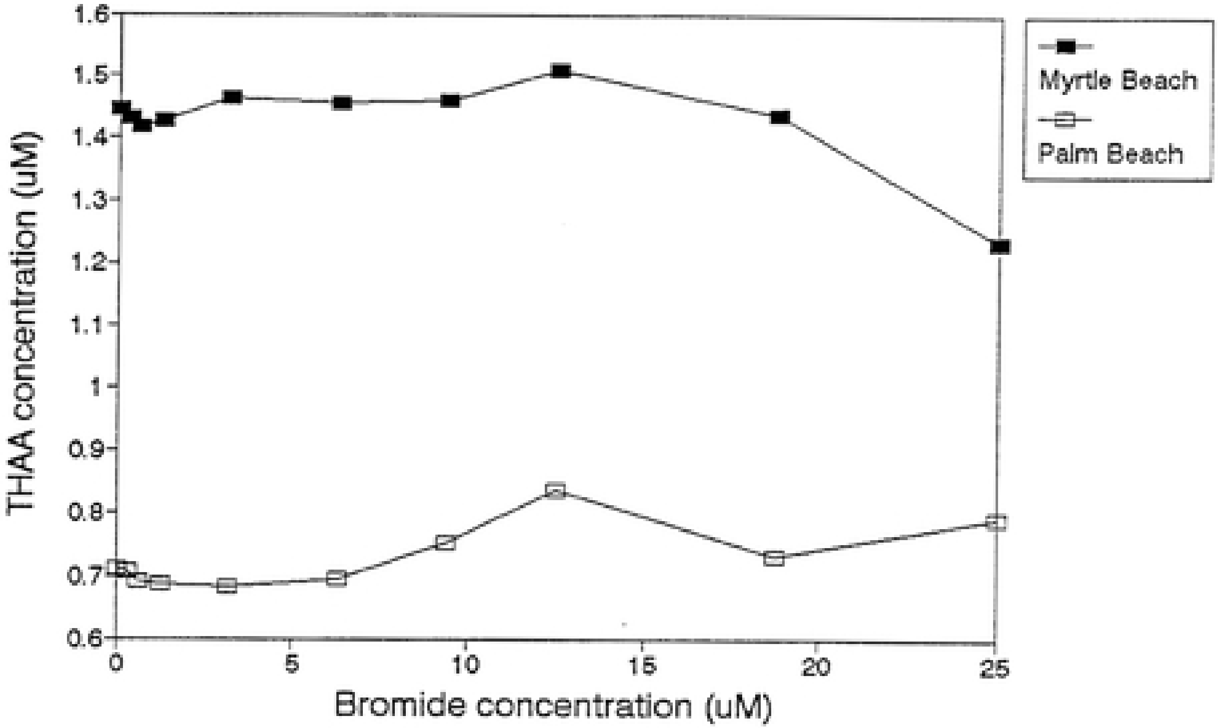
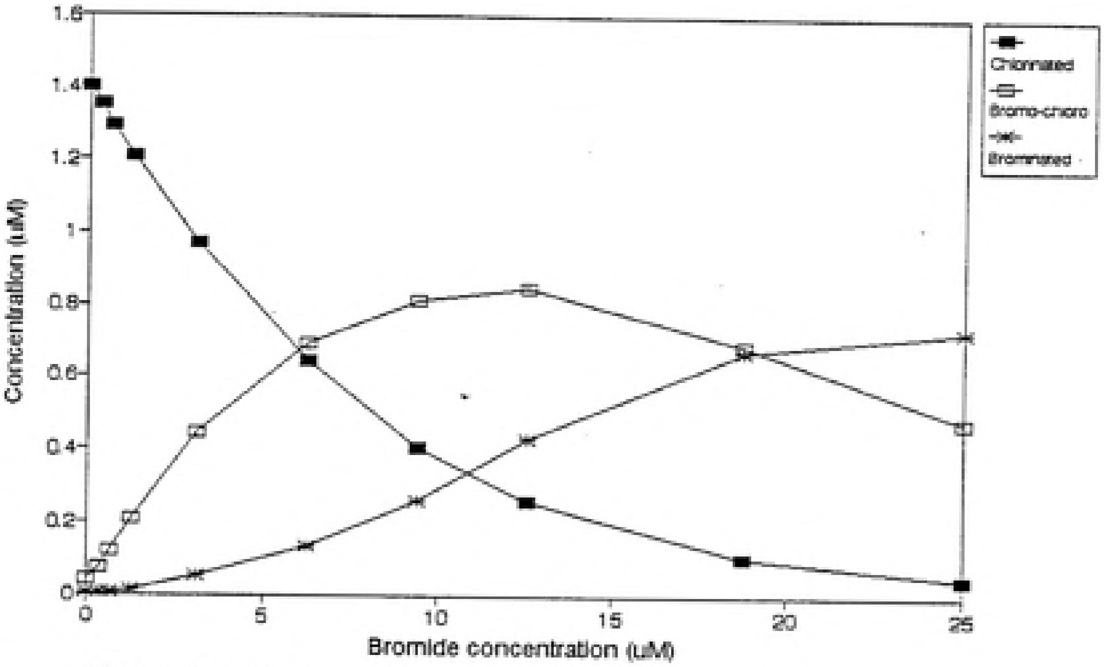
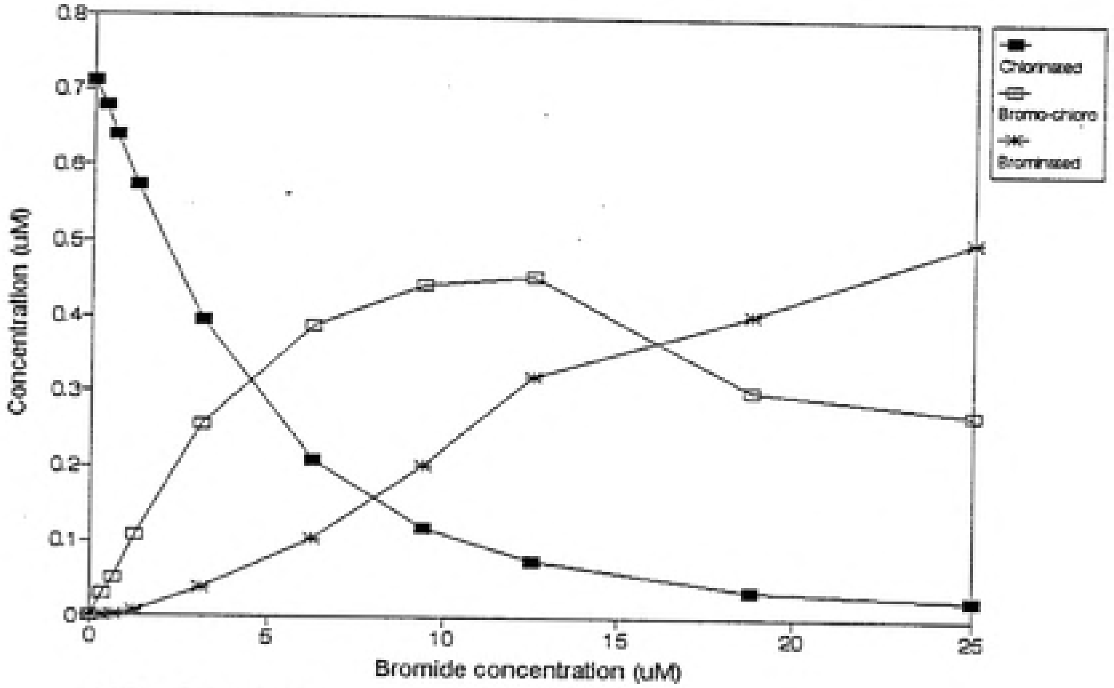


Figure 4.5. Total HAA formation in extracts chlorinated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.6. Sum of chlorinated, bromo-chloro, and brominated HAA species in extracts chlorinated at pH 8.

bromo-chloro species dominate mid-range among the bromide concentrations studied, and the brominated species predominate at the high end of the bromide range. The principal species formed can be grouped into the ranges of bromide concentrations given in Table 4B.

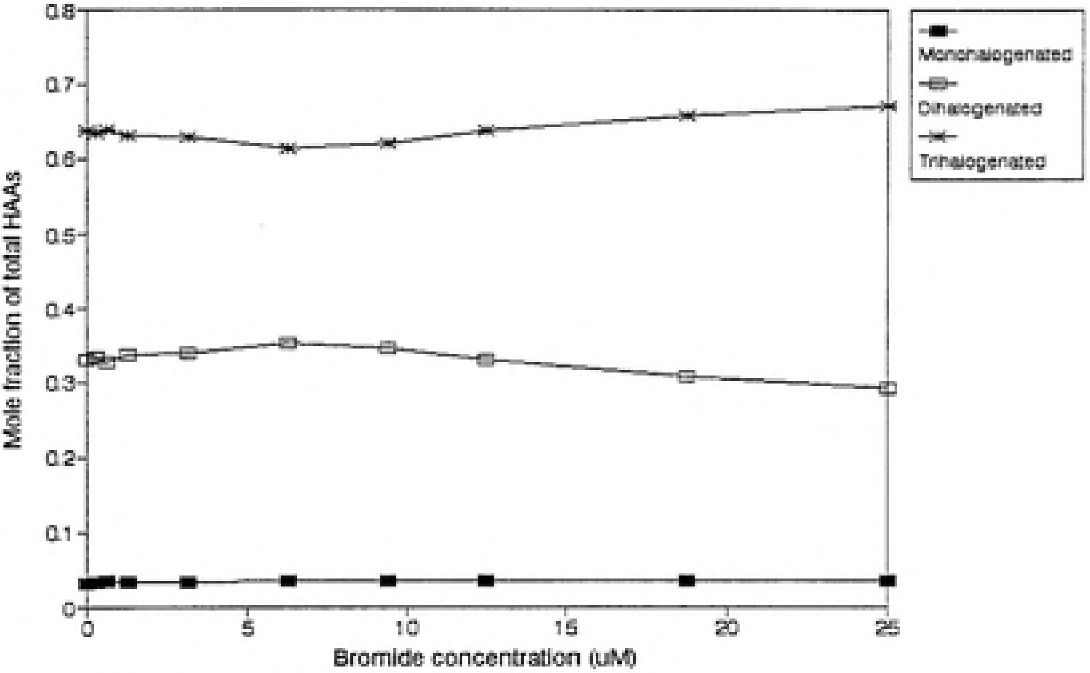
Table 4B. Bromide ranges of principal species formed in extracts chlorinated at pH 8.

Sample	Species	$[Br^-]$ (µM)
Myrtle Beach	Chlorinated Bromo-chloro Brominated	0 - 6 6 - 19 > 19
Palm Beach	Chlorinated Bromo-chloro Brominated	0 - 4 4 - 16 > 16

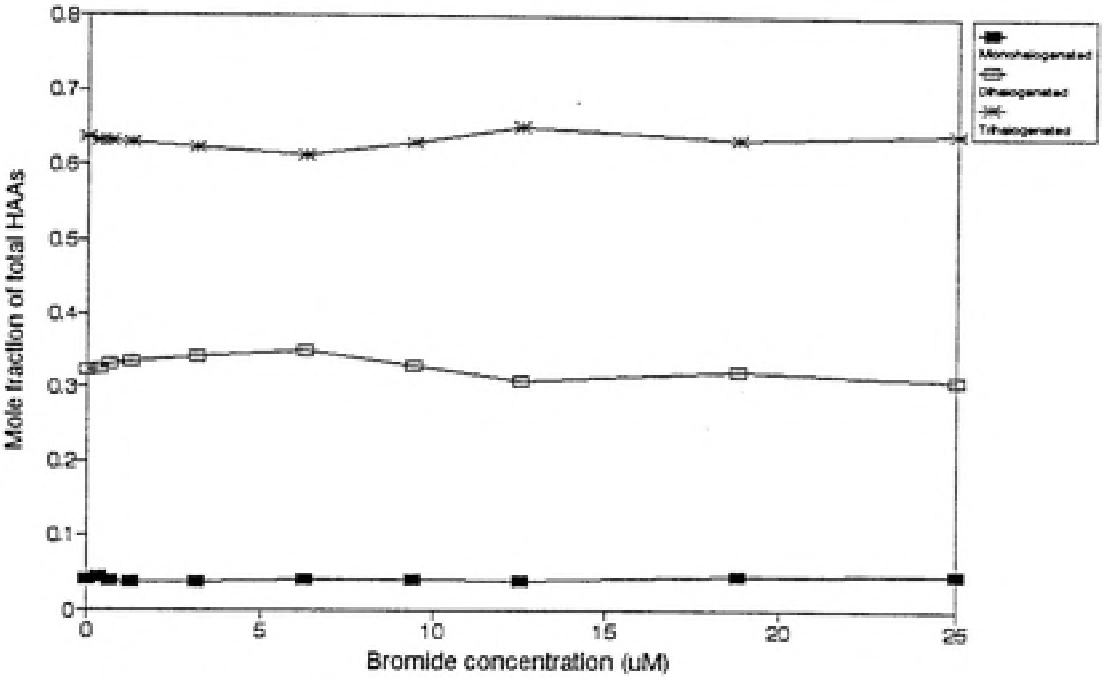
Distribution of HAAs among mono-, di-, and trihalogenated species

HAA speciation was also analyzed by grouping the HAAs into mono-, di-, and trihalogenated species. This was done because it is likely that each of the monohalogenated species (MCAA and MBAA) are formed through similar chemical pathways, and likewise for the dihalogenated species (DCAA, DBAA and BrClAA) and the trihalogenated species (TCAA, TBAA, $BrCl_2AA$ and Br_2ClAA). In addition, the pathways of formation of the mono-, di-, and trihalogenated species may be related to one another.

In both waters the trihalogenated species constituted the greatest mole fraction of the total HAAs (61-67%), the dihalogenated species made up 30-36% of the total, and the monohalogenated species constituted 3-5% of the total (Figure 4.7). The fraction of the total HAAs present as mono-, di-, or trihalogenated species appeared to be fairly constant



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.7. Distribution of HAAs into mono-, di-, and trihalogenated species in extracts chlorinated at pH 8.

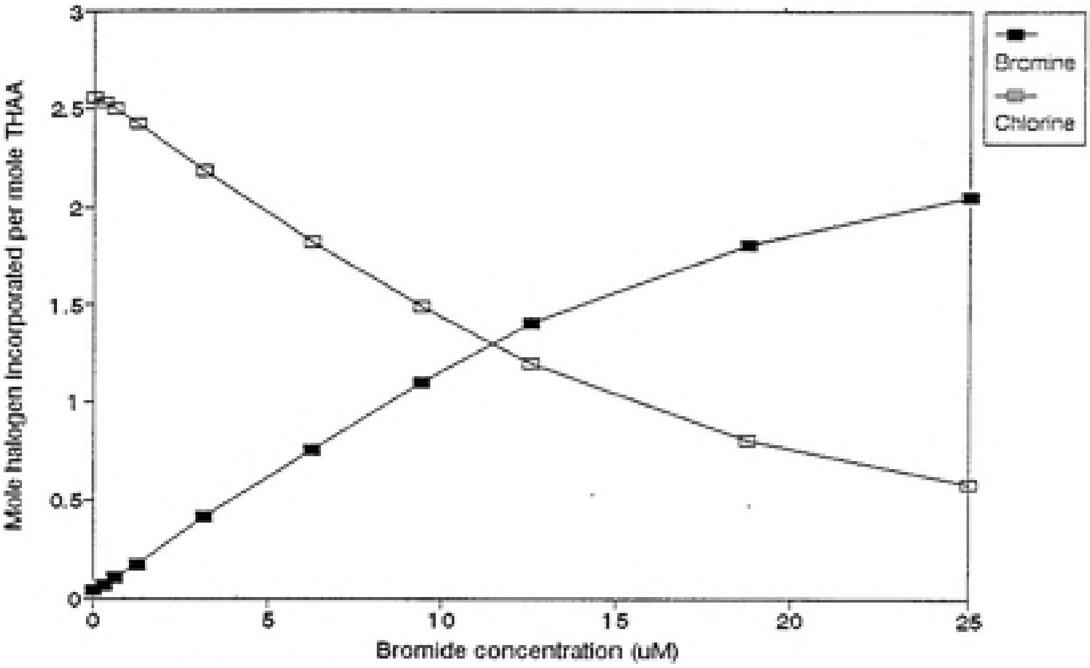
over the range of bromide concentrations studied. The two extracts showed strikingly similar distributions despite their differences in absolute THAA formation.

In waters chlorinated at pH 8 in the absence of bromide, relative formation of TCAA compared to DCAA on a weight basis (μg TCAA/μg DCAA) was approximately 2.4:1 (mg Cl_2/mg TOC = 2). This is similar to previous results reported by Miller and Uden (24) of a weight ratio of TCAA/DCAA=2.25 at a chlorine to carbon weight ratio of 2. Miller and Uden showed that relative formation of TCAA and DCAA is dependent on chlorine dose, with the more highly halogenated species being favored by high chlorine dose. These observations suggest that these two compounds may proceed through common dihalogenated intermediates that can either be oxidized or hydrolyzed to DCAA or further chlorinated to form TCAA. This idea is similar to the mechanisms proposed by Reckhow and Singer (22) which were shown previously in Figure 2.1.

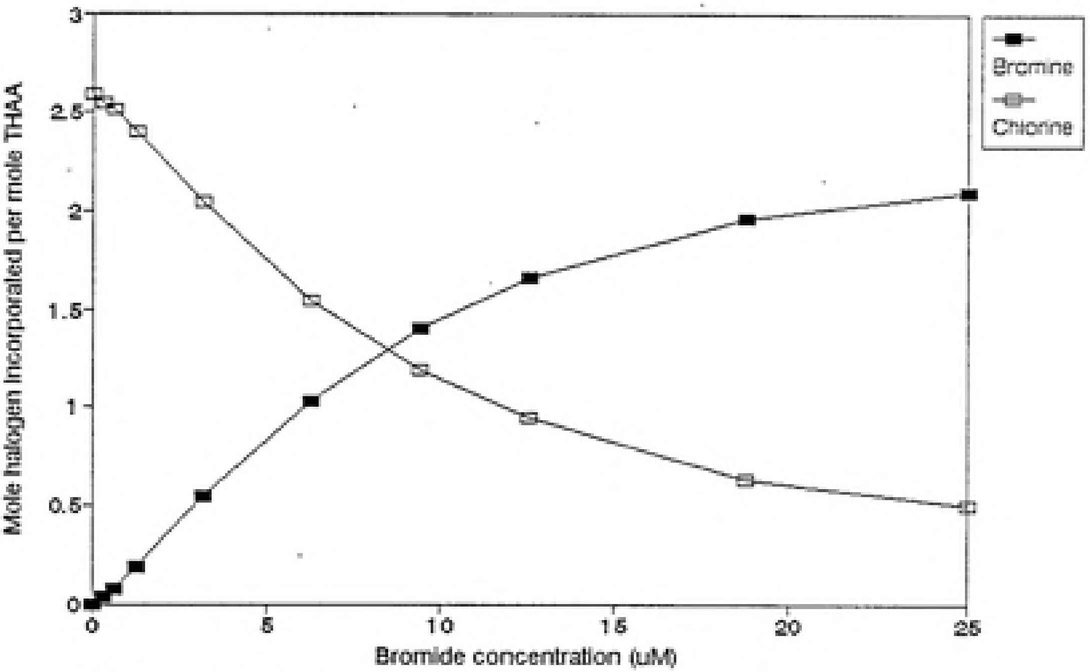
In the present study, the effect of chlorine dose was not investigated; however, it is likely that chlorine dose would affect the distribution of the HAAs among the mono-, di-, and trihalogenated species in this system. Bromide ion concentration, however, did not appear to affect this distribution.

Bromine and chlorine incorporation

Total bromine and chlorine incorporation into the HAAs is plotted in Figure 4.8 as μmoles bromine (or μmoles chlorine) incorporated per μmole of total HAAs produced as a function of



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.8. Bromine and chlorine incorporation into HAAs in extracts chlorinated at pH 8.

bromide concentration. The data was adjusted in this manner to account for variations in the THAA concentration at different conditions. The results suggest that bromine is more reactive than chlorine in substitution and addition reactions that form HAAs. In Myrtle Beach extract bromine incorporation is equivalent to chlorine incorporation at approximately 12 μM Br^-, corresponding to a ratio of Br^- to initial applied HOCl of 0.11 mole Br^-/mole HOCl. Bromine and chlorine incorporation in Palm Beach extract are equivalent at approximately 8 μM Br^-, corresponding to 0.07 mole Br^-/mole HOCl.

It is interesting to notice in Figure 4.8 that the points at which bromine and chlorine incorporation are equivalent represent a composition of approximately 1.3 μmoles halogen per μmole THAA. This means that the average halogen composition of a mole of HAA at this point is approximately 1.3 moles Br and 1.3 moles Cl, or 2.6 moles total halogen. In the absence of bromide, the average composition of 1 mole HAA is approximately 2.6 moles chlorine (total halogen). It appears that although more highly brominated species are being formed as bromide concentration increases, the average total halogen content remains fairly constant. This is also expressed by the observed uniform partitioning of HAA species into mono-, di-, and trihalogenated species. Considering the distribution to average approximately 65% trihalogenated, 33% dihalogenated and 3% monohalogenated, average halogen composition is:

$$0.65*(3 \text{ moles X}) + 0.33*(2 \text{ moles X}) + 0.03*(1 \text{ mole X}) =$$
$$= 2.64 \text{ moles halogen per mole HAA}$$

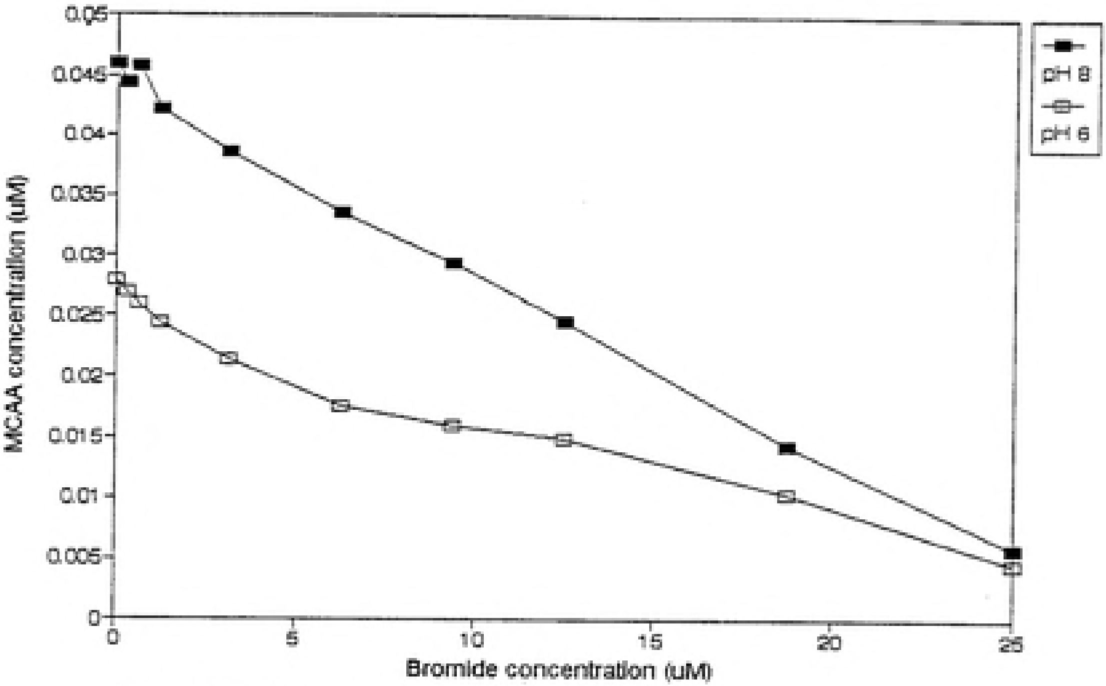
Effect of pH on HAA formation and speciation in chlorinated waters

Formation of individual species

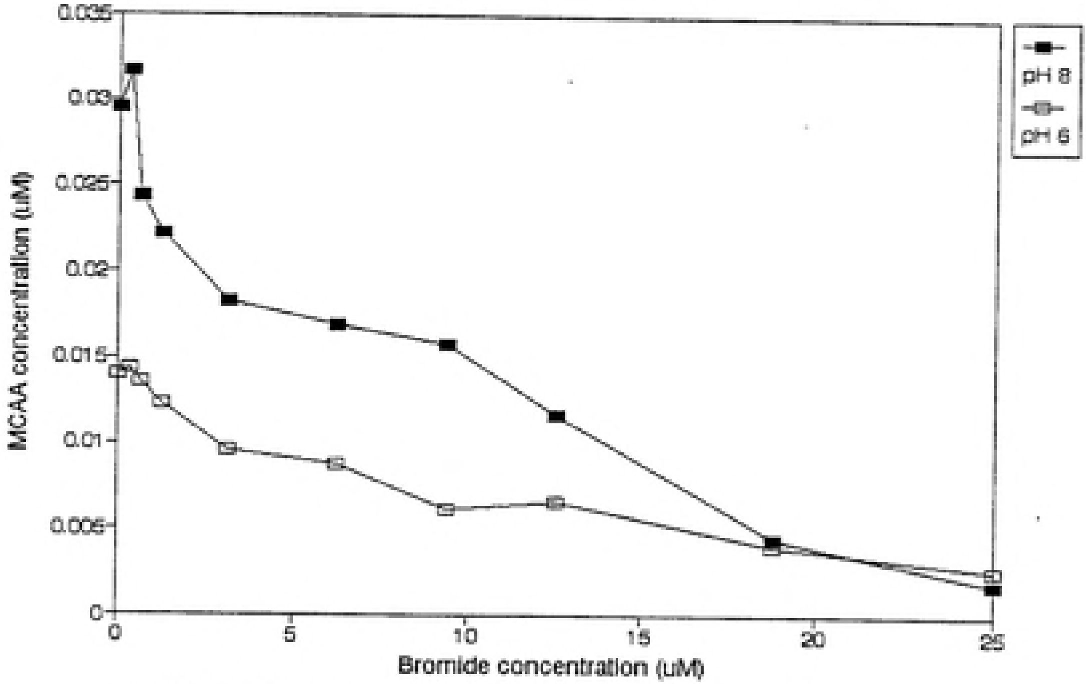
The effect of pH on HAA formation was investigated by chlorinating waters buffered at pH 6 and pH 8. Individual HAA species responded differently to variation in the pH of chlorination, and for some species the effect of pH appeared to be affected by bromide concentration. The influence of pH is shown graphically in Figures 4.9-4.17. One thing that is immediately clear is that the two extracts show strikingly similar behavior. The formation of several species was enhanced by lowering the pH from 8 to 6, most notably DBAA, BrClAA, $BrCl_2AA$ and Br_2ClAA. In general, the di- and trihalogenated species containing bromine appeared to be more greatly affected by pH than their chlorinated counterparts, DCAA and TCAA. In both waters MCAA formation was clearly decreased on the order of 30-50% by lowering the pH to 6, while MBAA formation appeared to be little affected. The behavior of DCAA with respect to chlorination pH appeared to depend on bromide concentration. In both waters DCAA formation appeared to be little affected by pH at low bromide concentrations (less than 3 µM); however, in the range 6-19 µM Br^-, DCAA formation appeared to be enhanced at pH 6 by approximately 20-40%.

Total HAA formation

Compared to pH 8, chlorination at pH 6 increased total µM HAA formation in Myrtle Beach samples over the full range of bromide concentration by 7-60 %. In Palm Beach samples

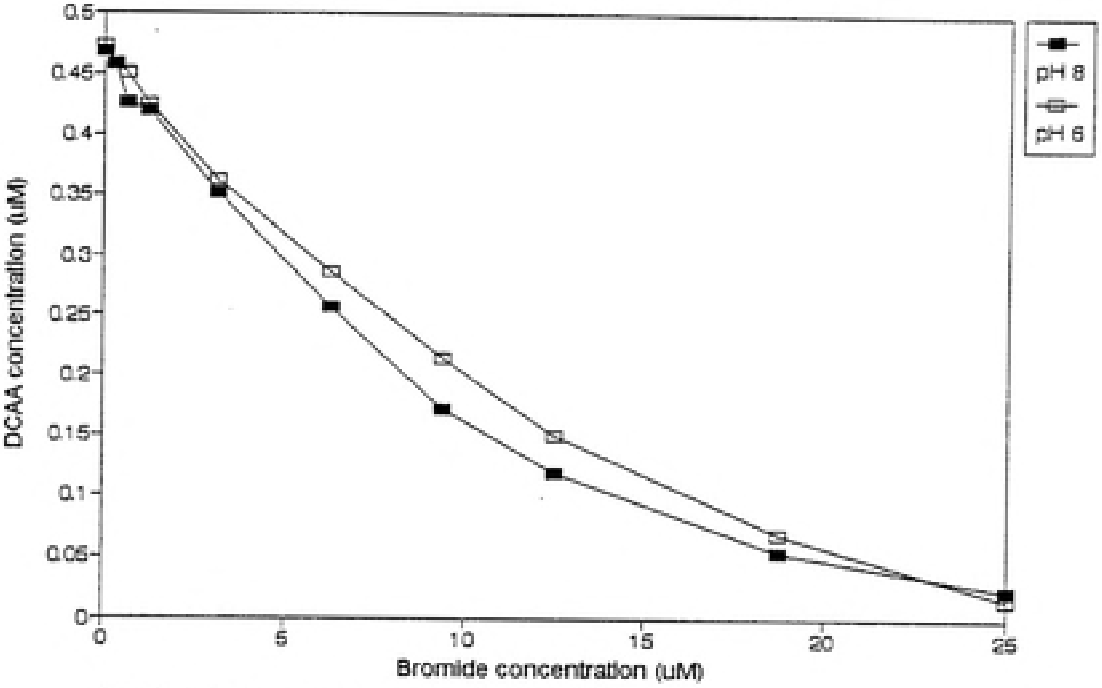


(a) Myrtle Beach extract

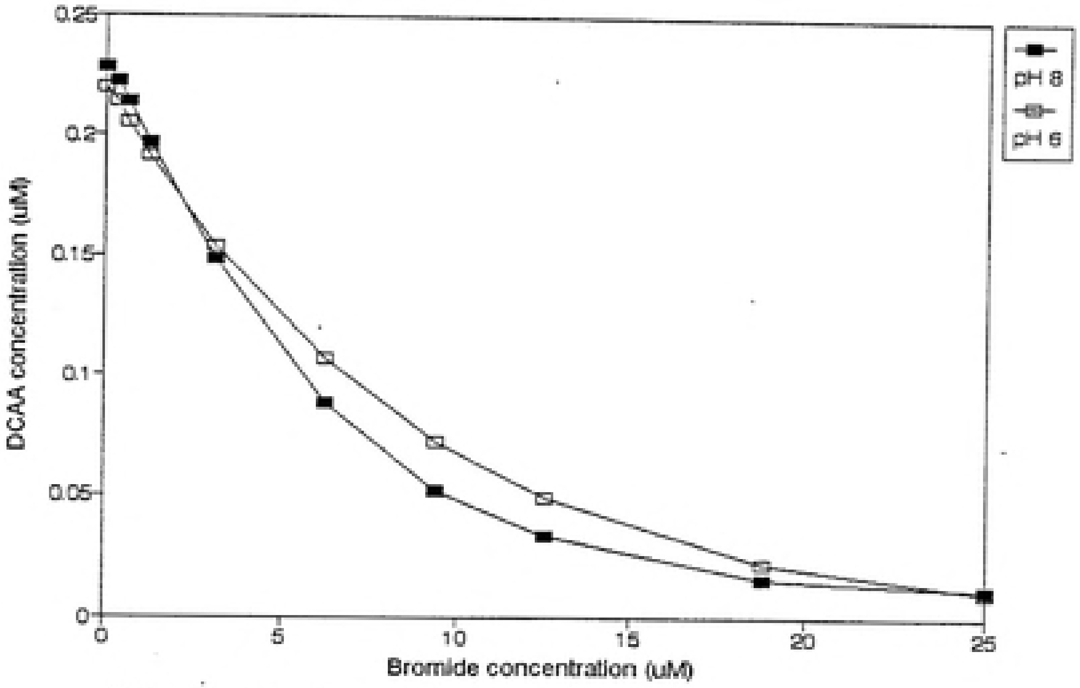


(b) Palm Beach extract

Figure 4.9. Influence of pH on MCAA formation in chlorinated extracts.

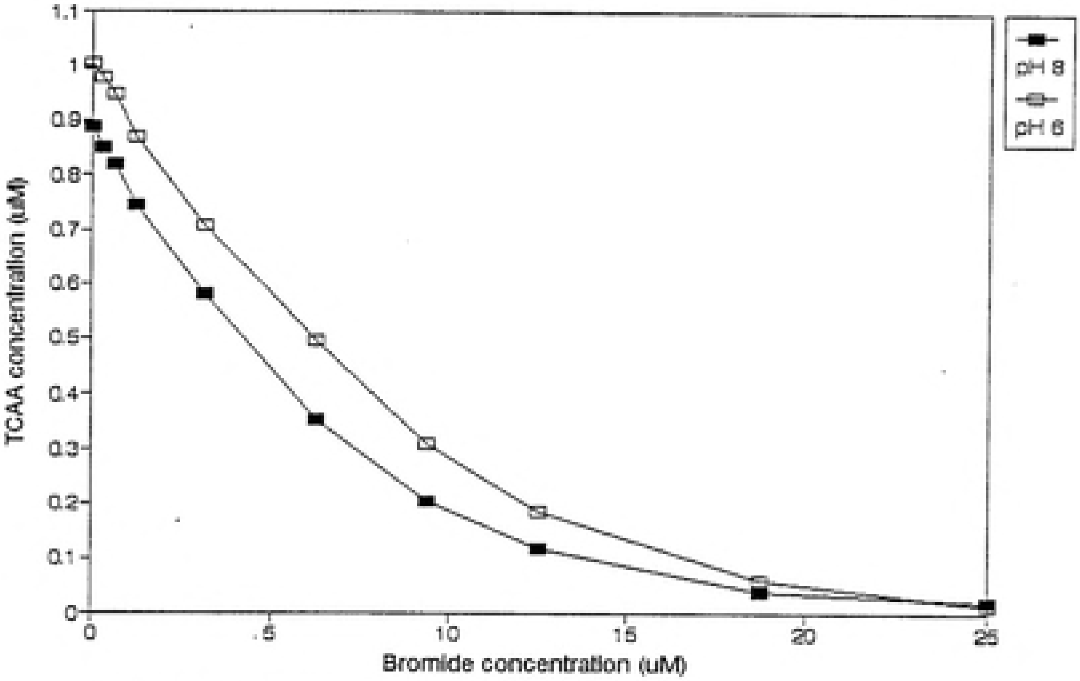


(a) Myrtle Beach extract

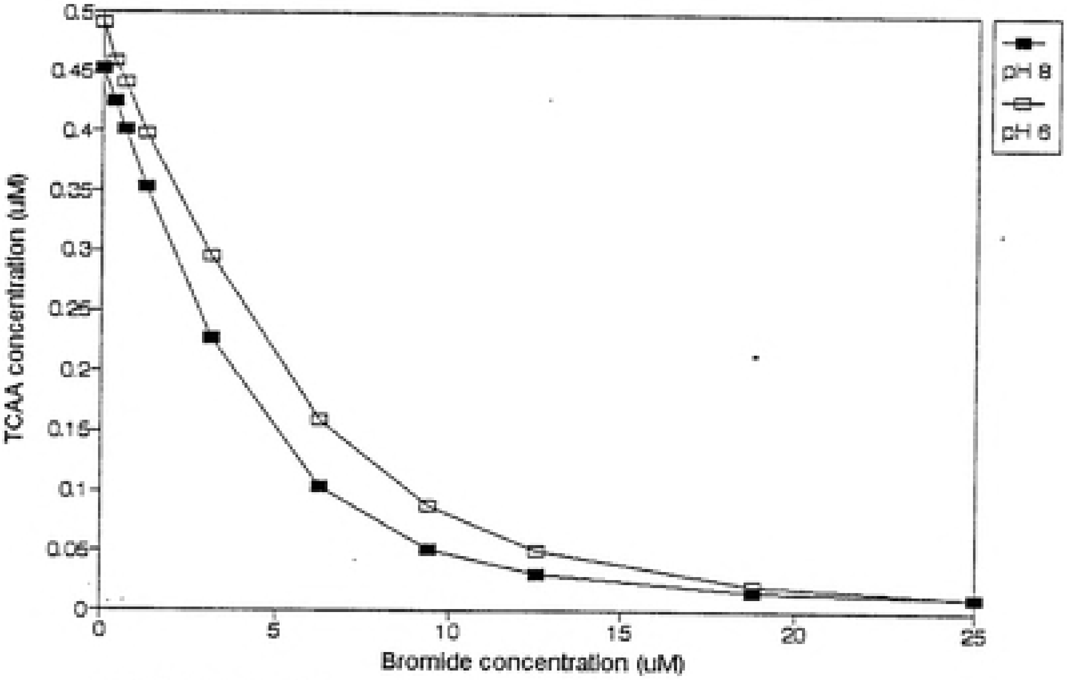


(b) Palm Beach extract

Figure 4.10. Influence of pH on DCAA formation in chlorinated extracts.

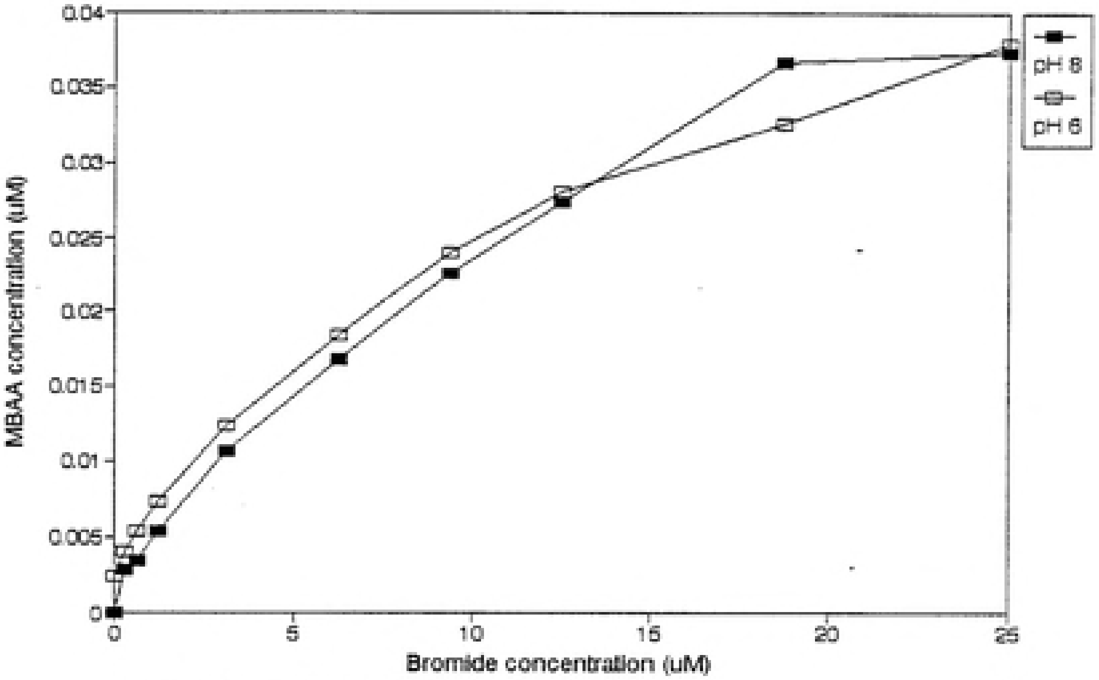


(a) Myrtle Beach extract

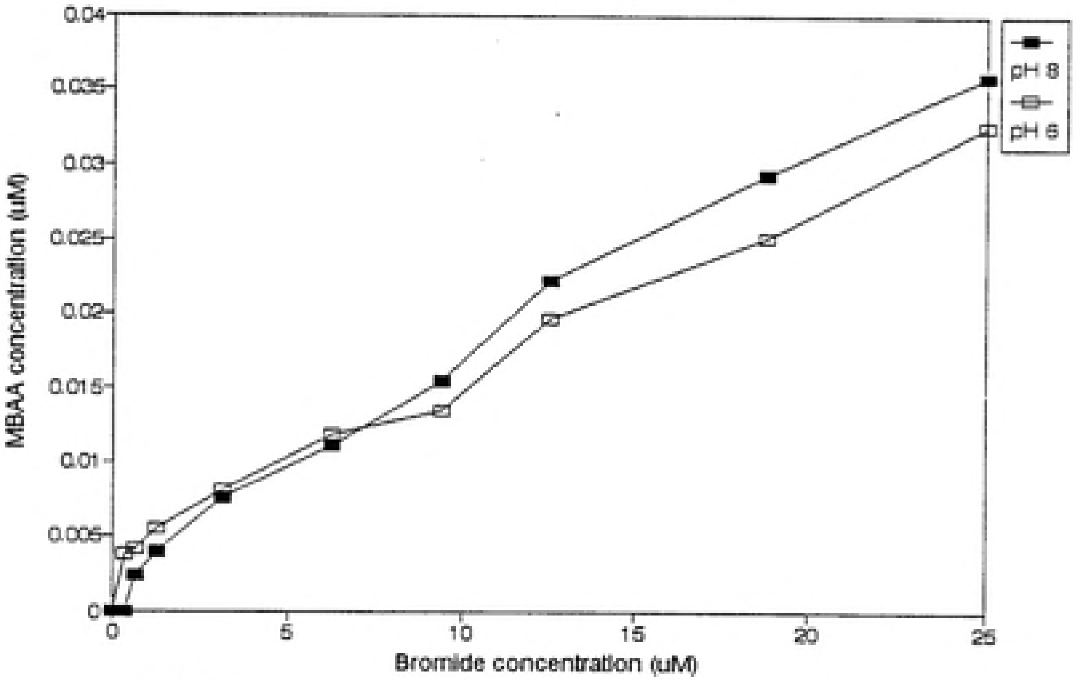


(b) Palm Beach extract

Figure 4.11. Influence of pH on TCAA formation in chlorinated extracts.

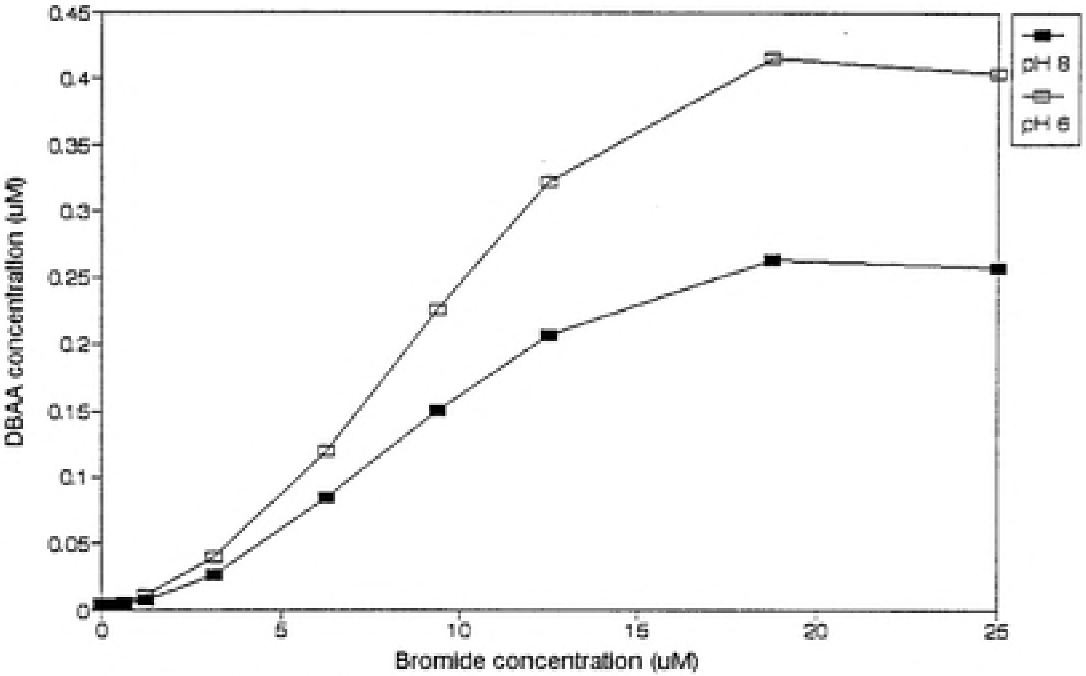


(a) Myrtle Beach extract

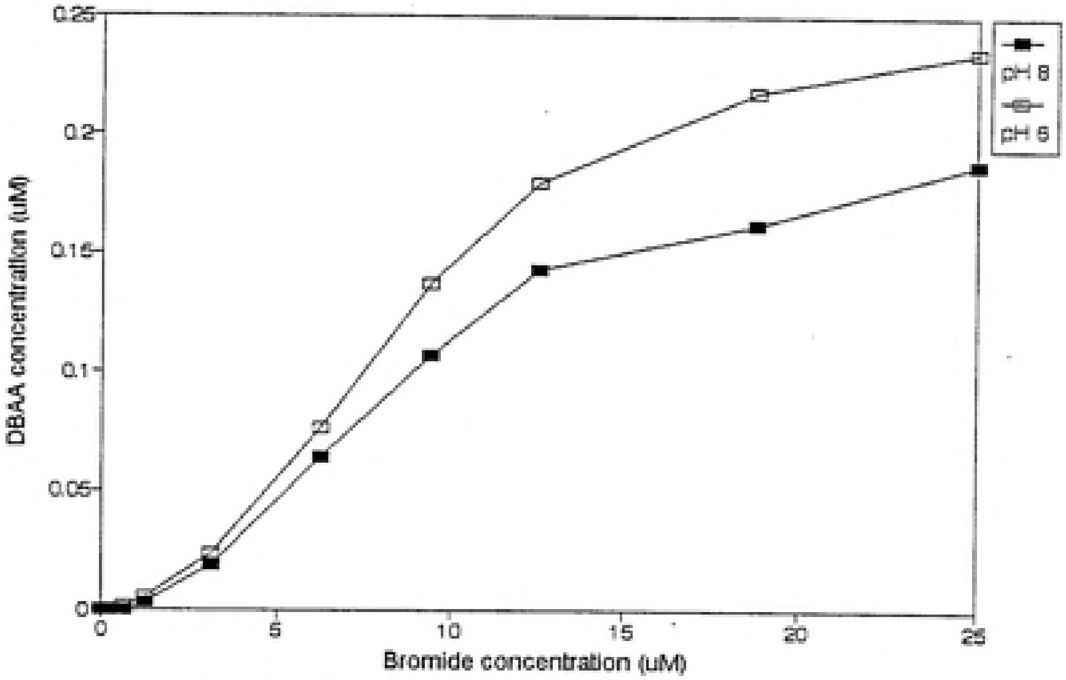


(b) Palm Beach extract

Figure 4.12. Influence of pH on MBAA formation in chlorinated extracts.

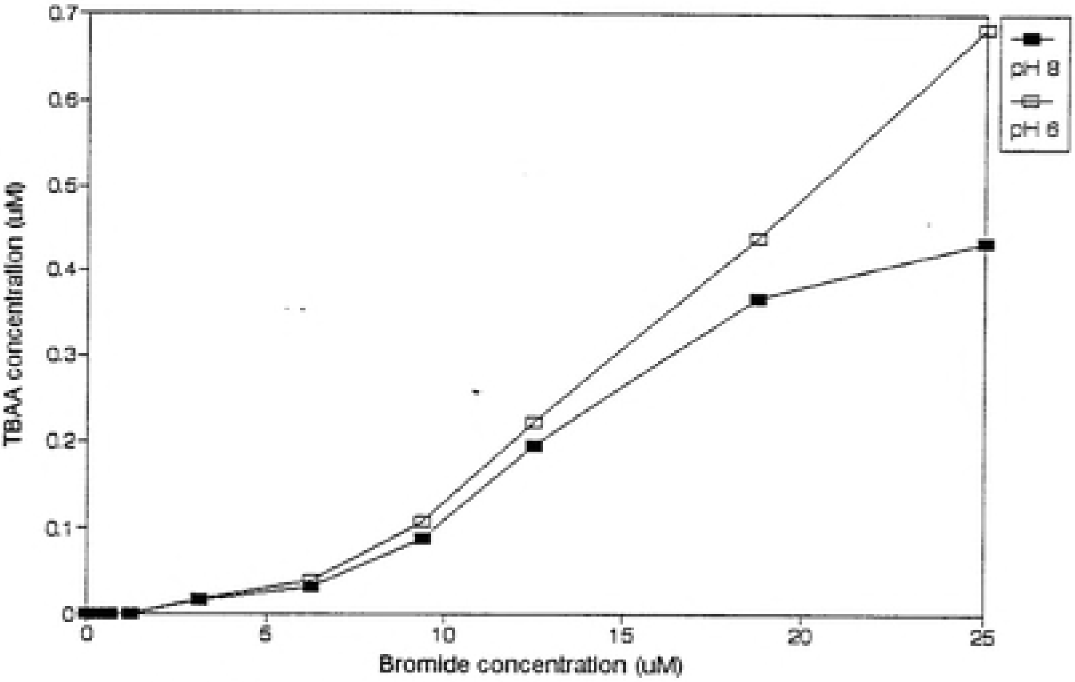


(a) Myrtle Beach extract

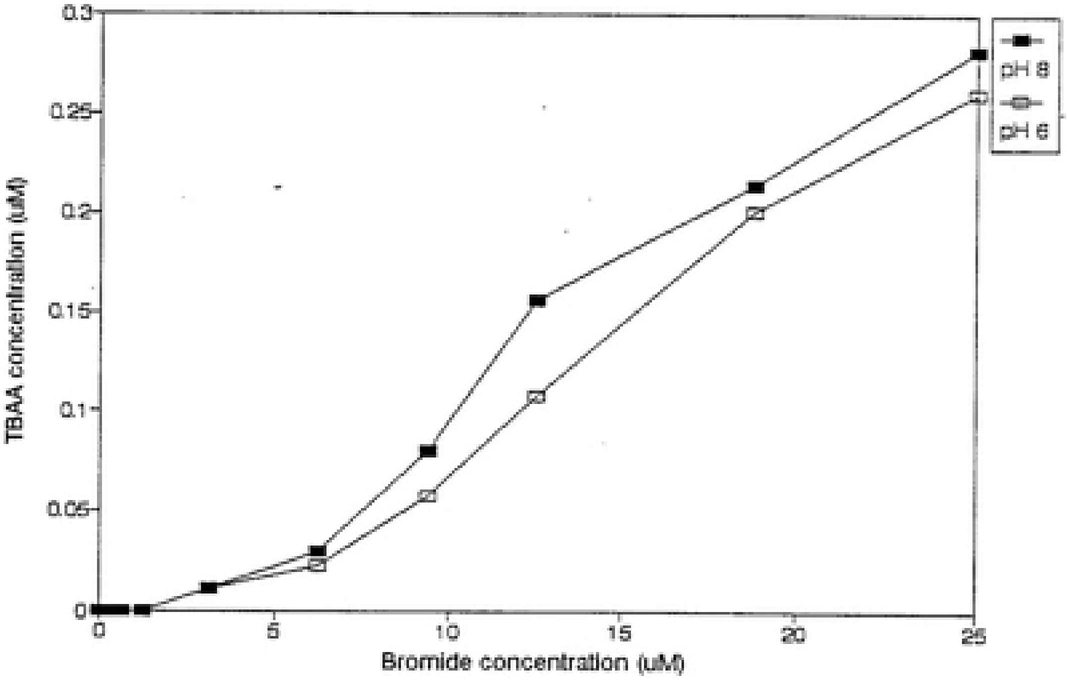


(b) Palm Beach extract

Figure 4.13. Influence of pH on DBAA formation in chlorinated extracts.

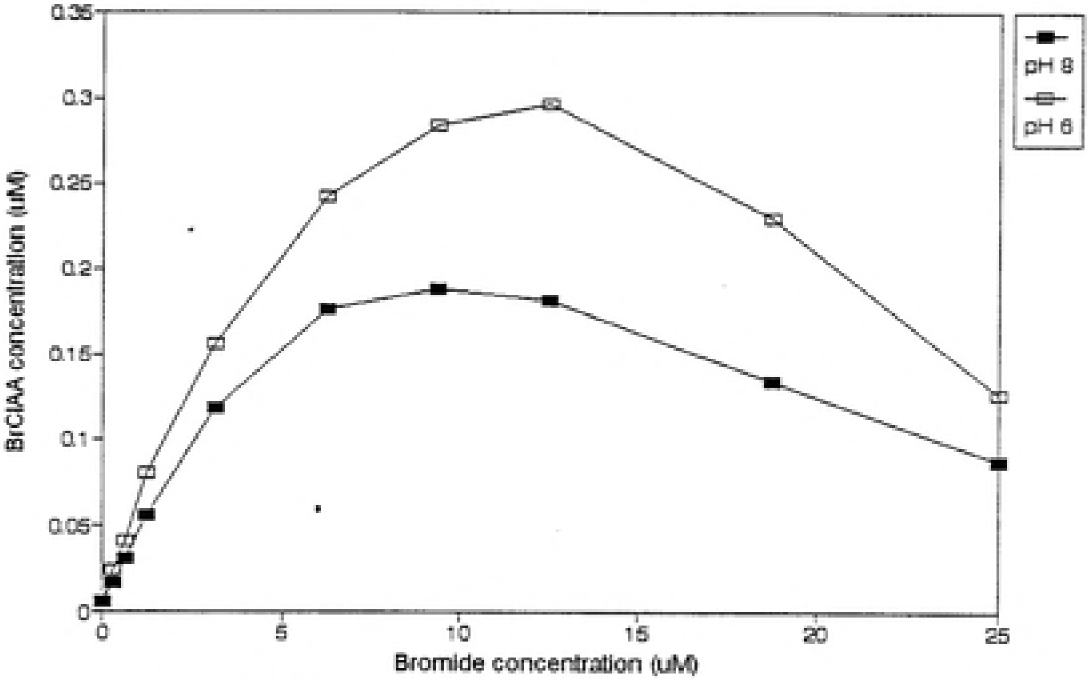


(a) Myrtle Beach extract

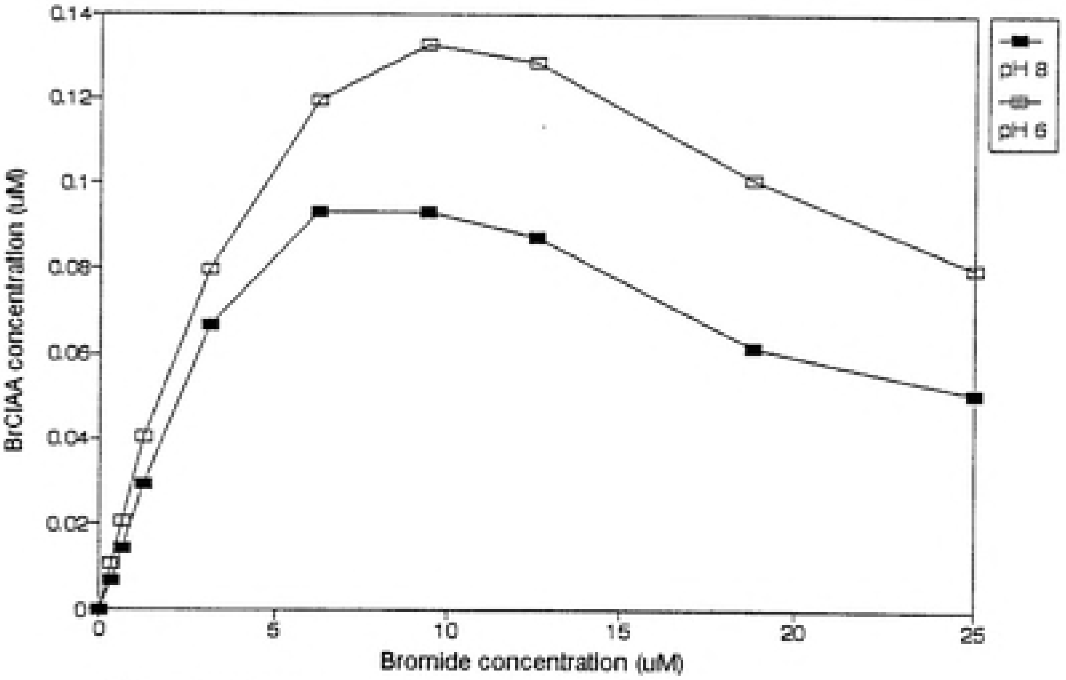


(b) Palm Beach extract

Figure 4.14. Influence of pH on TBAA formation in chlorinated extracts.

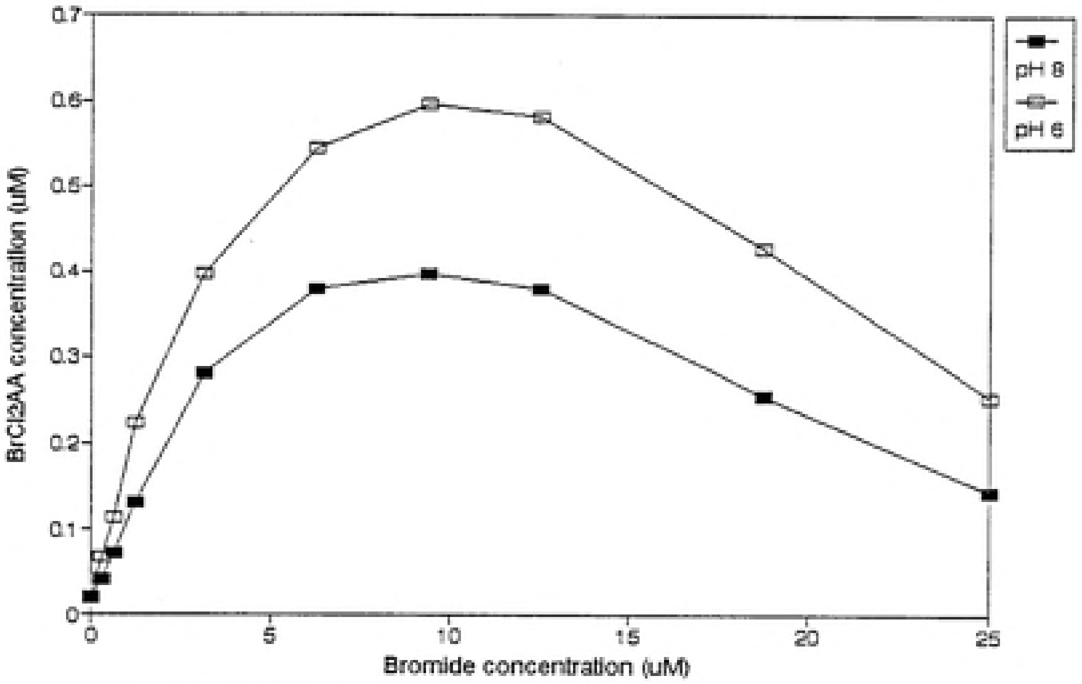


(a) Myrtle Beach extract

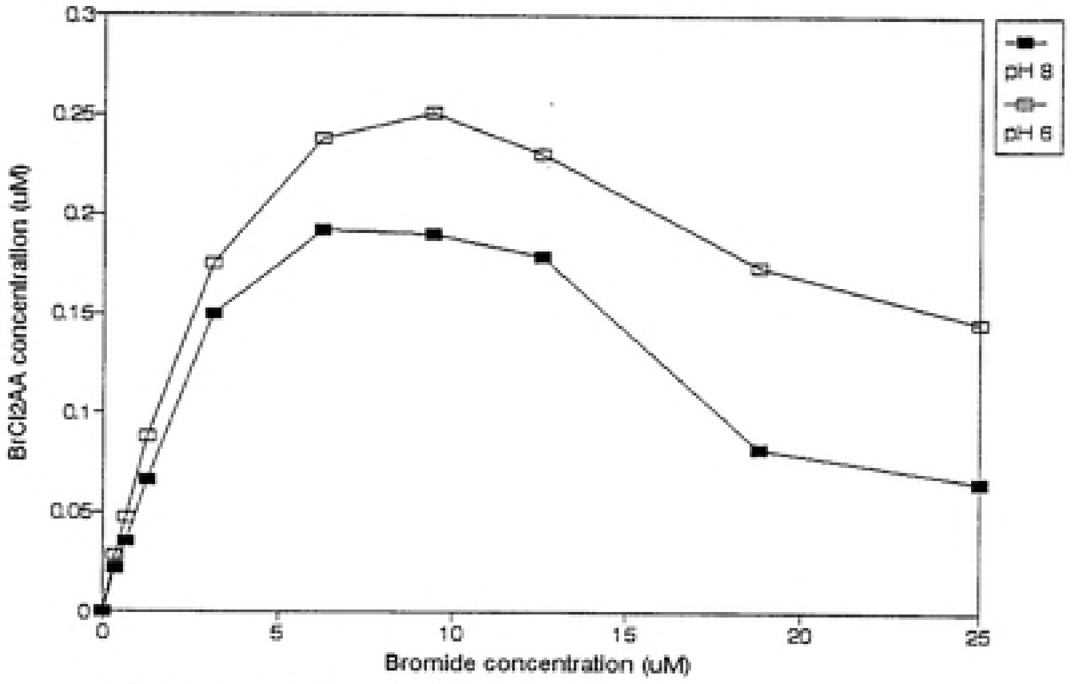


(b) Palm Beach extract

Figure 4.15. Influence of pH on BrClAA formation in chlorinated extracts.

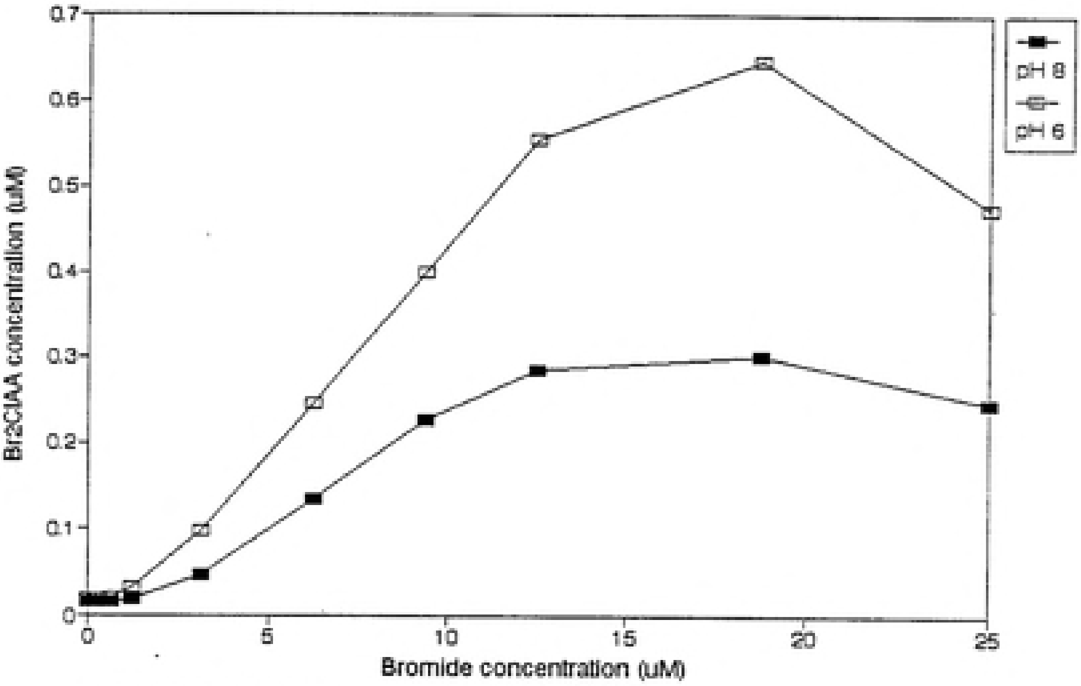


(a) Myrtle Beach extract

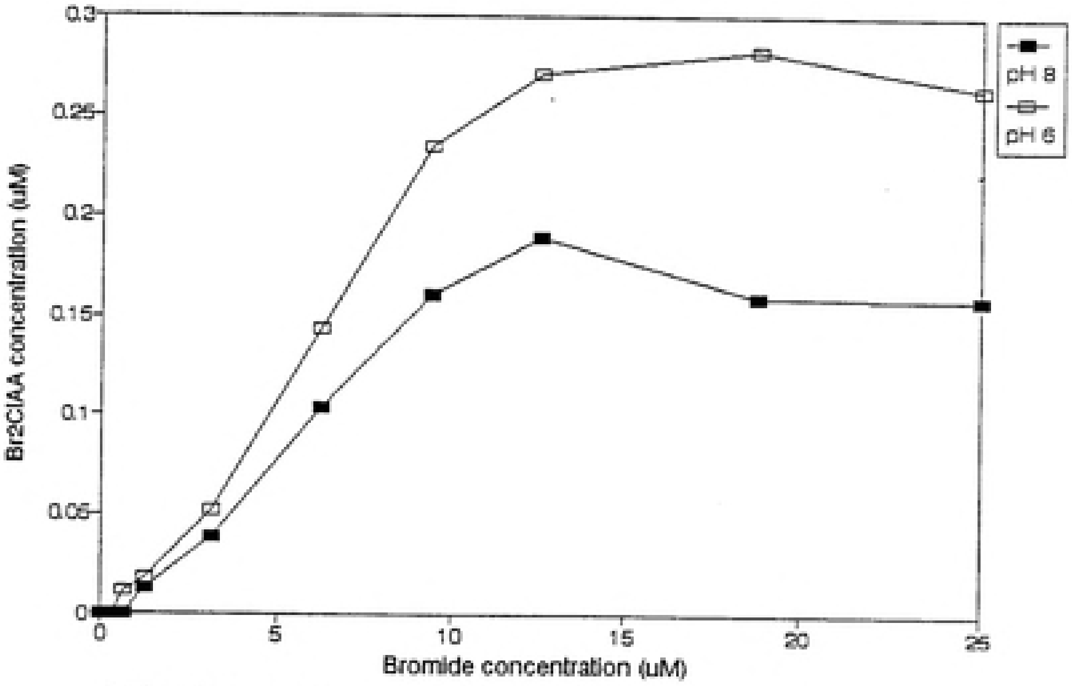


(b) Palm Beach extract

Figure 4.16. Influence of pH on $BrCl_2AA$ formation in chlorinated extracts.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.17. Influence of pH on Br_2ClAA formation in chlorinated extracts.

containing more than 0.3 μM Br^-, increases in THAA formation were observed on the order of 8-40%. THAA formation at pH 6 and pH 8 is shown in Figure 4.18. In both waters chlorinated at pH 6, there is a significant increase in THAA concentration with increasing bromide concentration up to 12 μM Br^-.

Distribution of individual species

The distribution of individual HAA species was not dramatically affected by lowering the pH of chlorination from pH 8 to pH 6; however, a few differences were noticeable. Br_2ClAA formation was greatly increased by lowering the pH of chlorination, and in both waters this species constituted a larger fraction of the total HAAs at pH 6 than at pH 8. In Palm Beach extracts, in regions of bromide concentration greater than 12 μM, a smaller fraction of the total HAAs was present as TBAA at pH 6 compared to pH 8, and a greater fraction of the total was present as $BrCl_2AA$. Distribution diagrams showing each of the individual HAA species at pH 6 are presented in Figure 4.19.

Total formation of chlorinated, bromo-chloro and brominated species

A comparison of the sums of chlorinated, bromo-chloro and brominated species formed at pH 6 and pH 8 reflects the increase in the formation of bromo-chloro species at pH 6. The results from chlorinations at pH 6 are shown in Figure 4.20, and this figure may be compared to Figure 4.6 for chlorinations at pH 8. In both waters the range of bromide concentrations over which the bromo-chloro species were the principal species formed was greater at pH 6 compared to pH 8. A comparison of the bromide

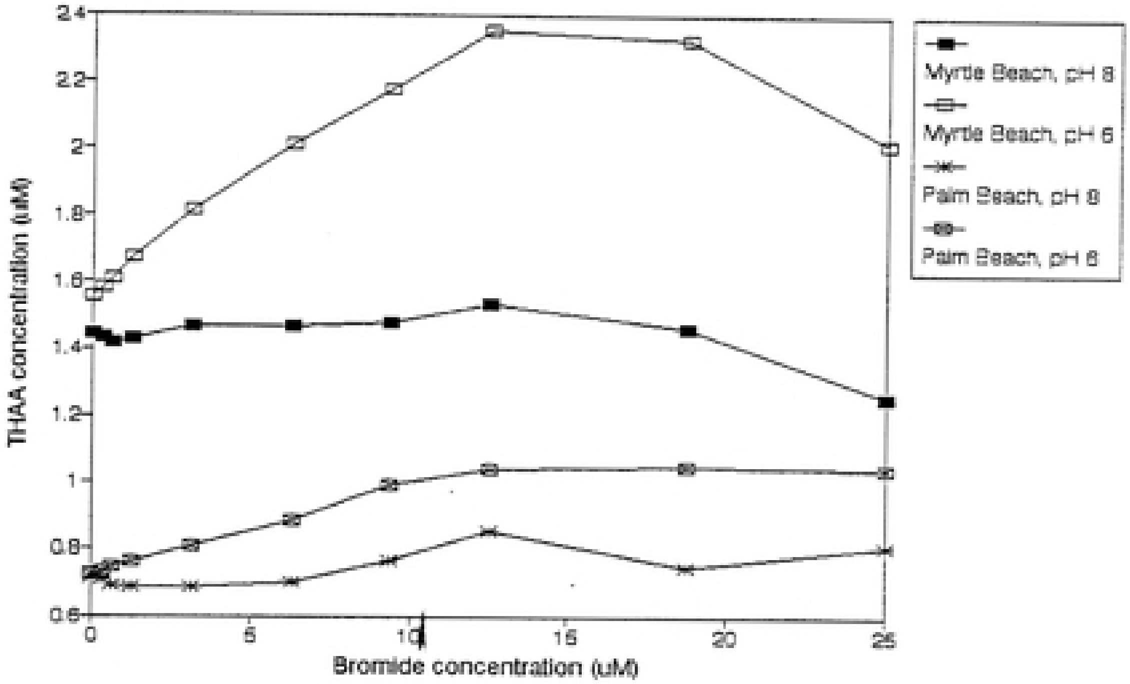
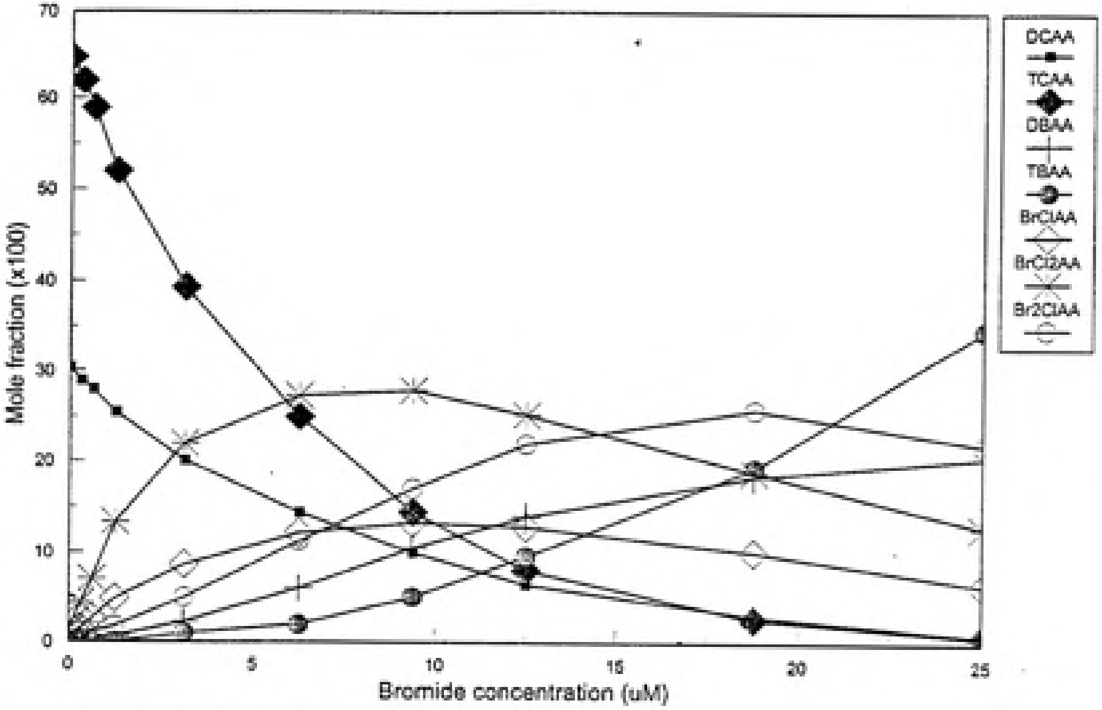
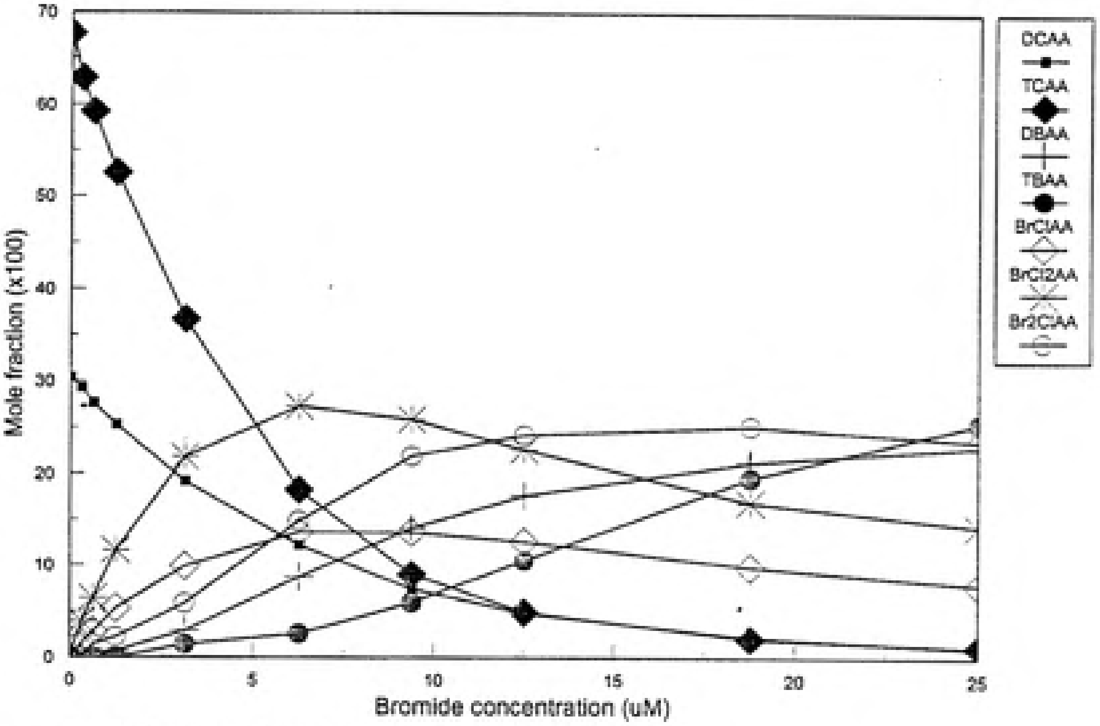


Figure 4.18. Influence of pH on total HAA formation in chlorinated extracts.

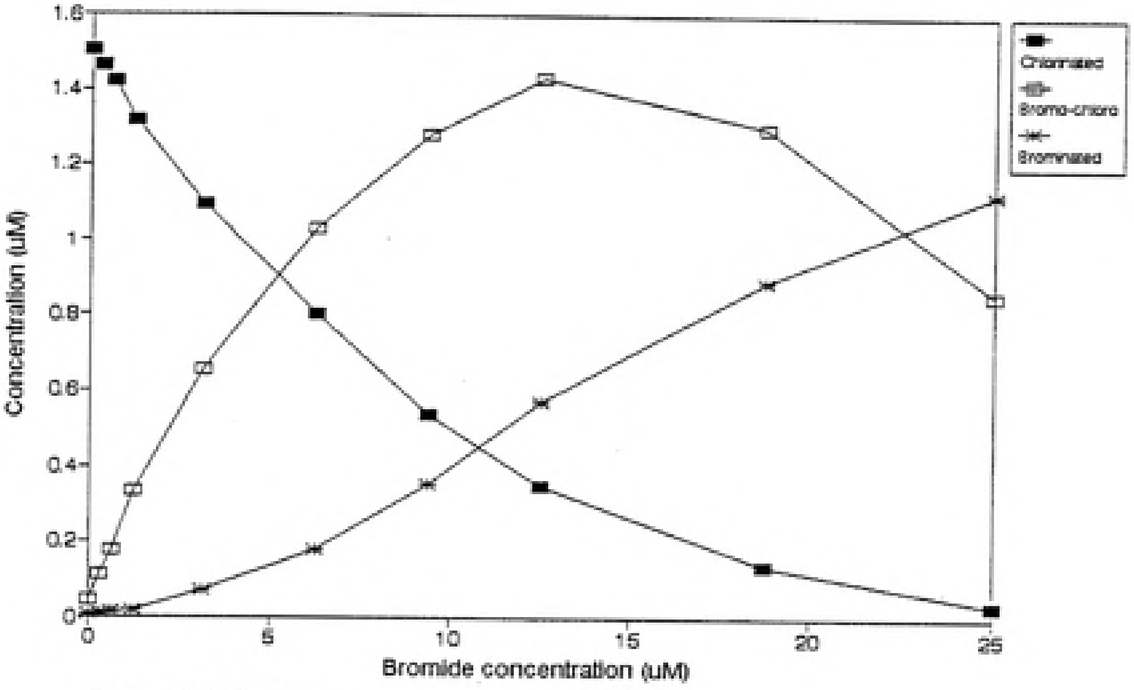


(a) Myrtle Beach extract

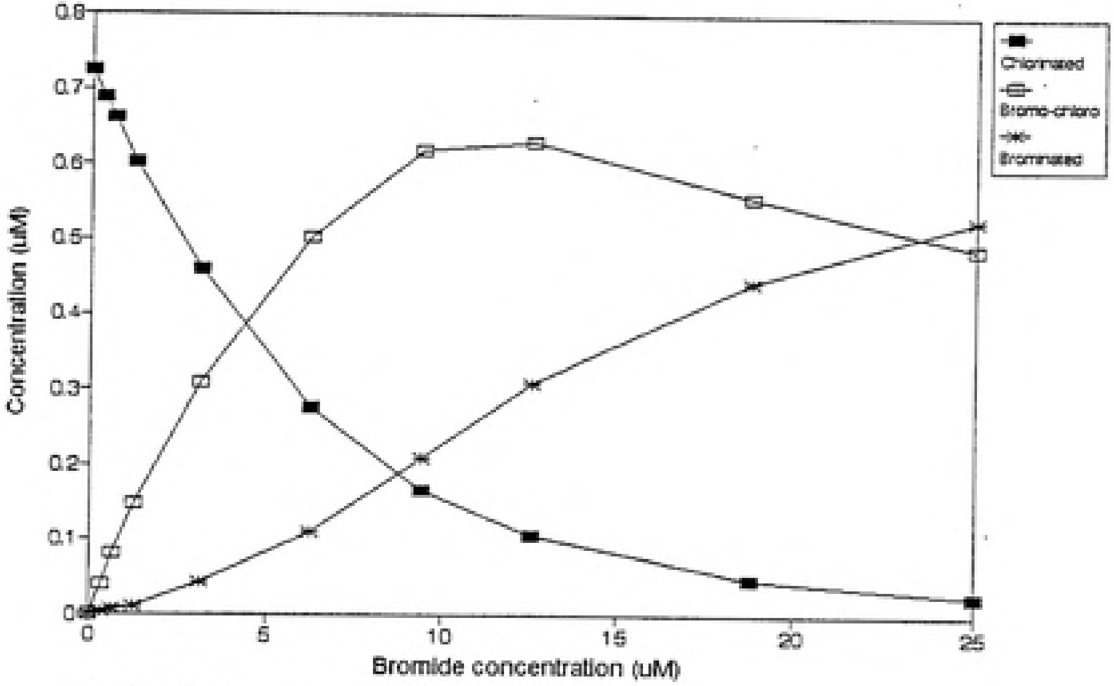


(b) Palm Beach extract

Figure 4.19. Distribution of individual HAA species in extracts chlorinated at pH 6.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.20. Sum of chlorinated, bromo-chloro, and brominated HAA species in extracts chlorinated at pH 6.

ranges of principal species formed at pH 6 and pH 8 is given in Table 4C.

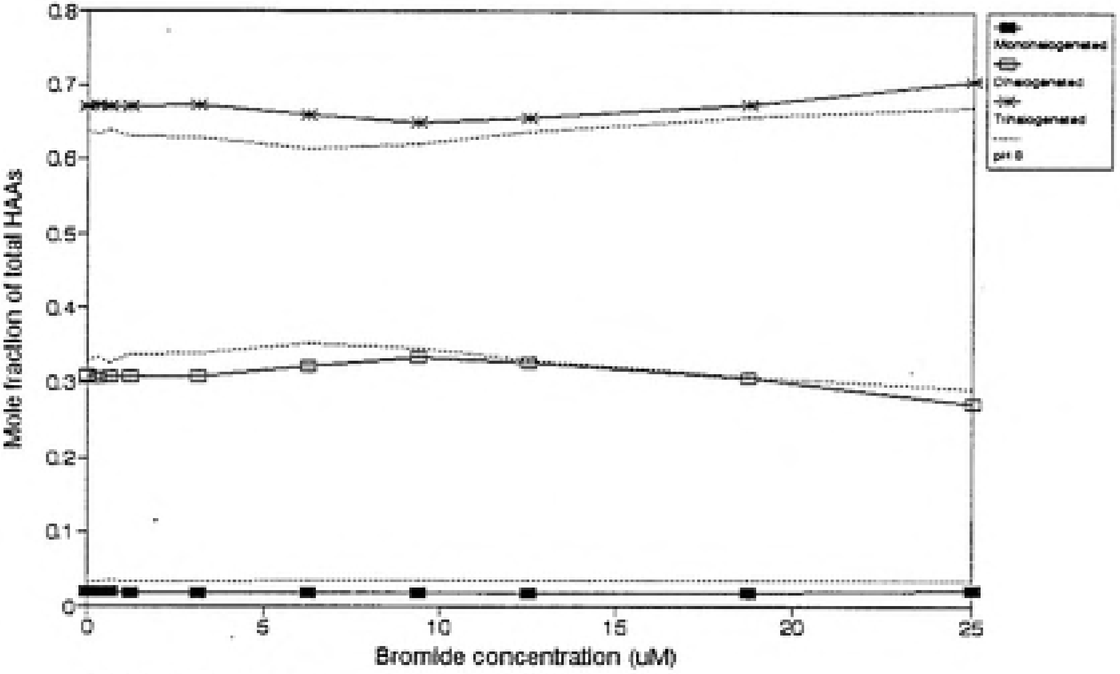
Table 4C. Influence of pH on bromide ranges of principal species formed in chlorinated extracts.

Sample	Species	pH 6 [Br-] (μM)	pH 8 [Br-] (μM)
Myrtle Beach	Chlorinated Bromo-chloro Brominated	0-6 6-22 >22	0-6 6-19 >19
Palm Beach	Chlorinated Bromo-chloro Brominated	0-4 4-22 >22	0-4 4-16 >16

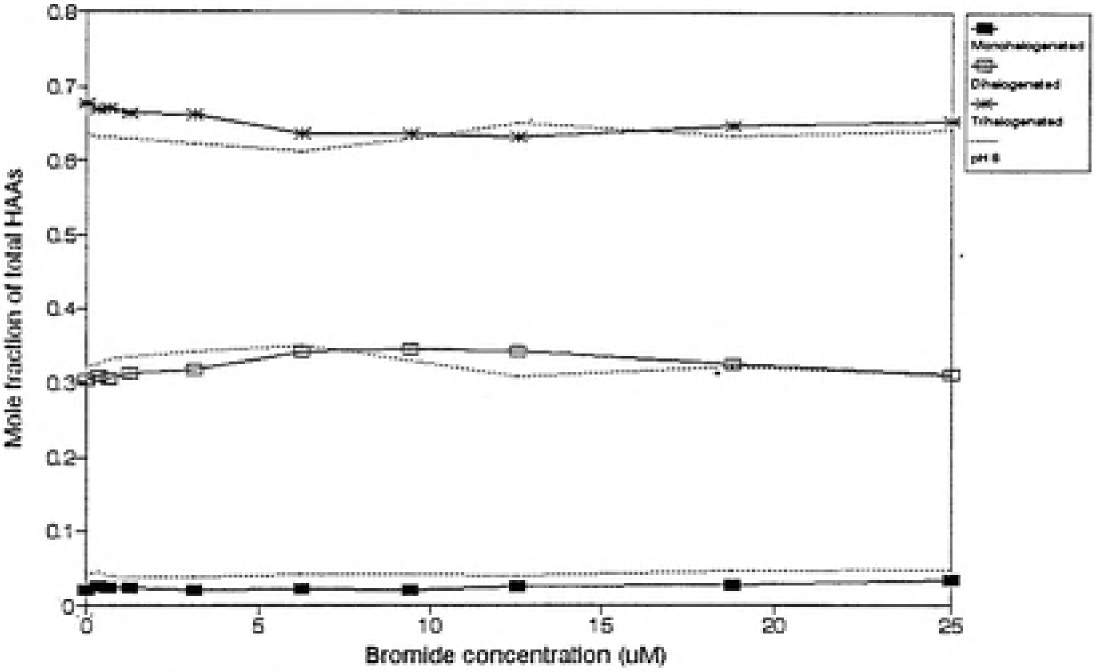
Distribution of HAAs among mono-, di-, and trihalogenated species

Distribution of the HAAs into mono-, di-, and trihalogenated species at pH 6 is shown in Figure 4.21. The distributions are similar to those observed at pH 8. Speciation among mono-, di-, and trihalogenated species again appears to be independent of bromide concentration. The two extracts show nearly identical behavior, and mole fractional distribution among mono-, di-, and trihalogenated species at pH 6 is similar to that at pH 8: at pH 6, the trihalogenated species constitute 62-70% of the total HAAs, the dihalogenated species comprise 28-35% of the total, and the monohalogenated species make up 1.8-3.5% of the total.

Based on previous observations by Miller and Uden (24) and Reckhow and Singer (22) that the ratio of TCAA/DCAA tends to increase with decreasing pH, one might expect to see increased speciation of the HAAs into trihalogenated species and decreased speciation into the dihalogenated species at a lower pH of chlorination. The results presented in Figure 4.21 may suggest



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.21. Distribution of HAAs into mono-, di-, and trihalogenated species in extracts chlorinated at pH 6.

such an effect; however, it appears that the range of pH studied was not sufficiently large for the results to either support or contradict this idea.

Bromine and chlorine incorporation

Bromine and chlorine incorporation into the HAAs is compared for chlorinations at pH 6 and pH 8 in Figure 4.22. It appears that changing the pH of chlorination from 8 to 6 had little effect on bromine and chlorine incorporation per mole of THAA in both Myrtle Beach and Palm Beach extracts.

Formation of brominated HAAs from ozonation alone

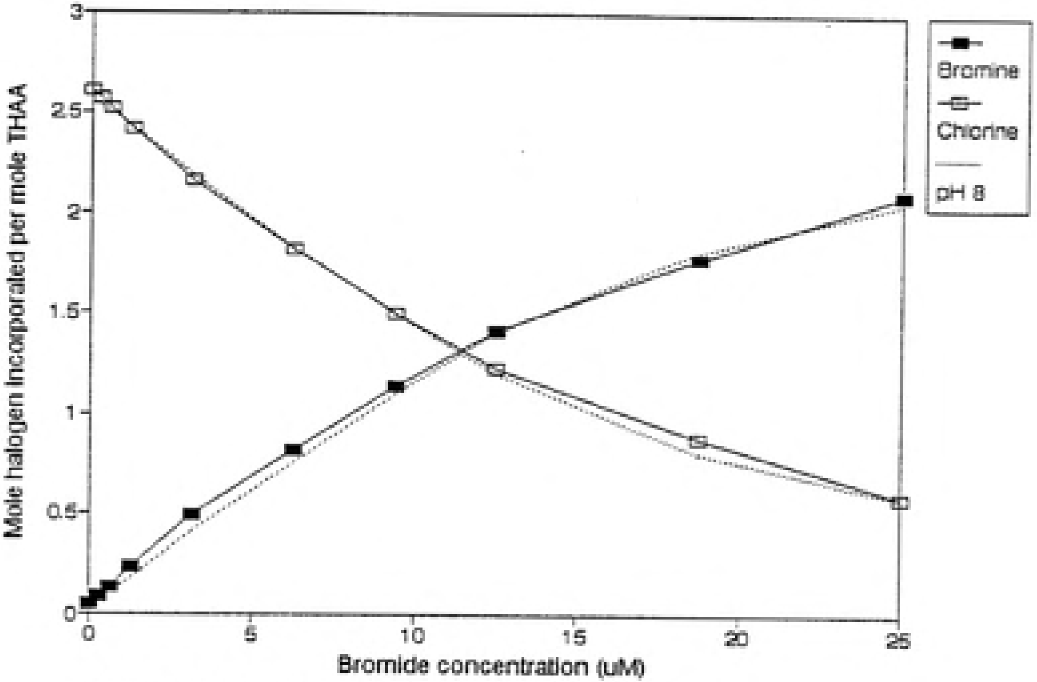
In both waters batch ozonation of 4 mg/L TOC at a dose of 1 mg O_3 : 1 mg TOC resulted in little formation of brominated HAAs. MBAA and DBAA were detected in samples containing 12-25 µM Br^- at concentrations less than 0.016 µM (3.4 µg/L).

Effect of pre-ozonation on HAA formation and speciation in chlorinated waters

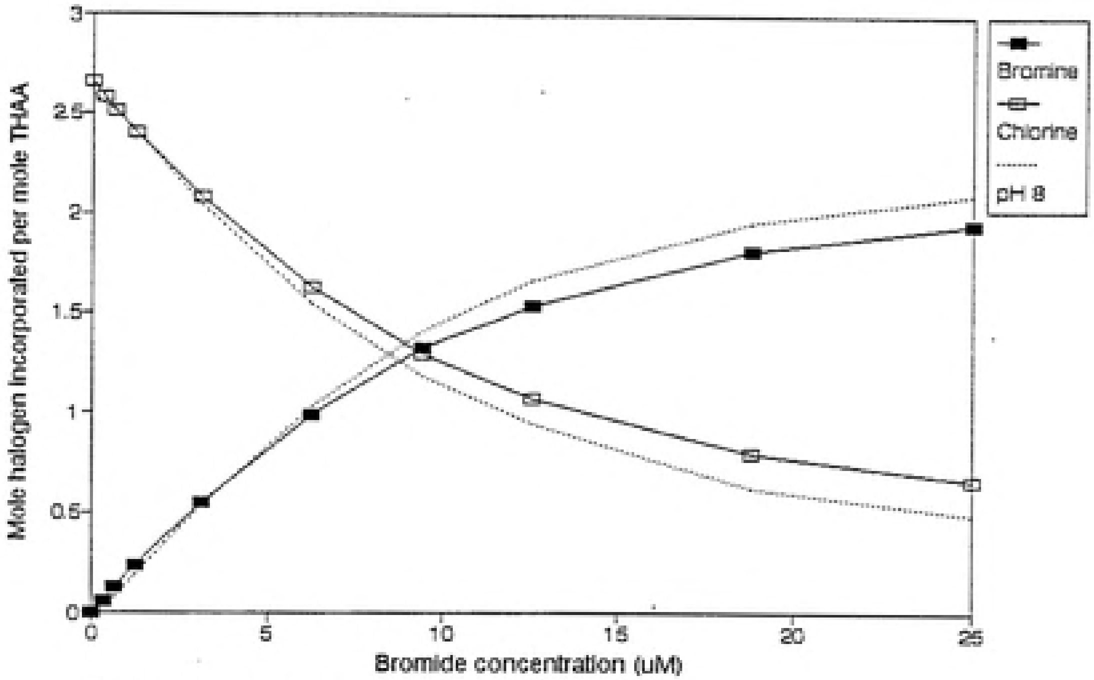
Formation of individual species

The effect of ozone on subsequent formation of HAAs from post-chlorination was investigated by preparing ozonated, post-chlorinated samples along with samples that received chlorine alone. The effects of pre-ozonation on individual HAA formation in samples chlorinated at pH 8 are shown in Figures 4.23-4.31. Figures for samples chlorinated at pH 6 are contained in Appendix G.

In samples chlorinated at pH 8, pre-ozonation generally

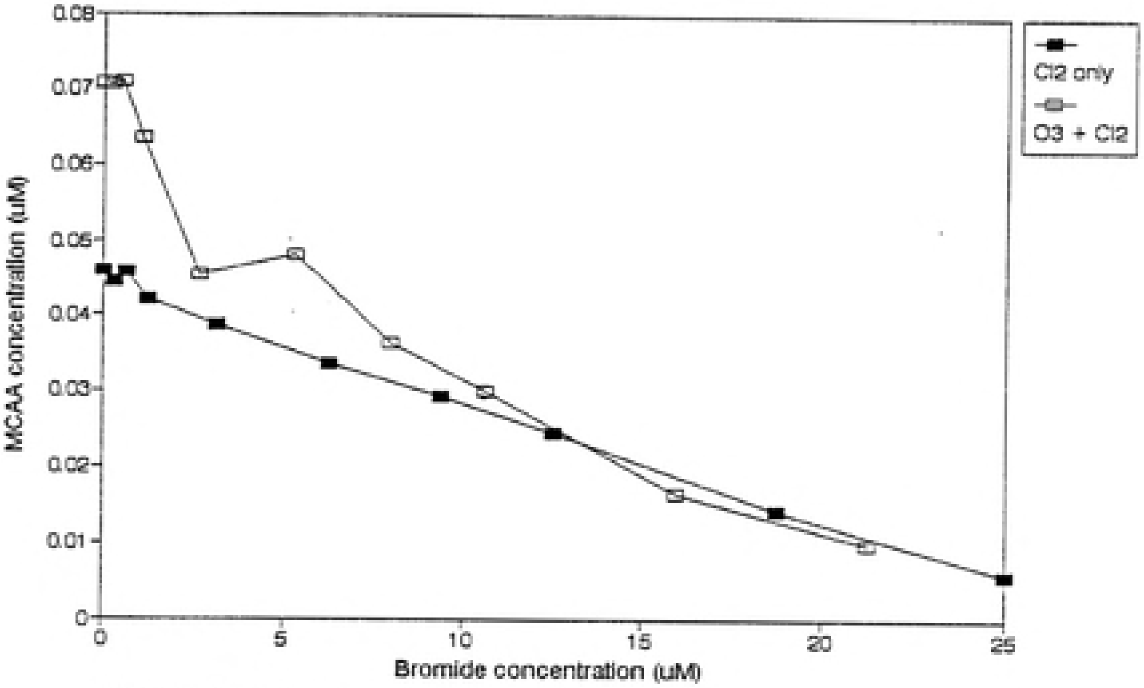


(a) Myrtle Beach extract

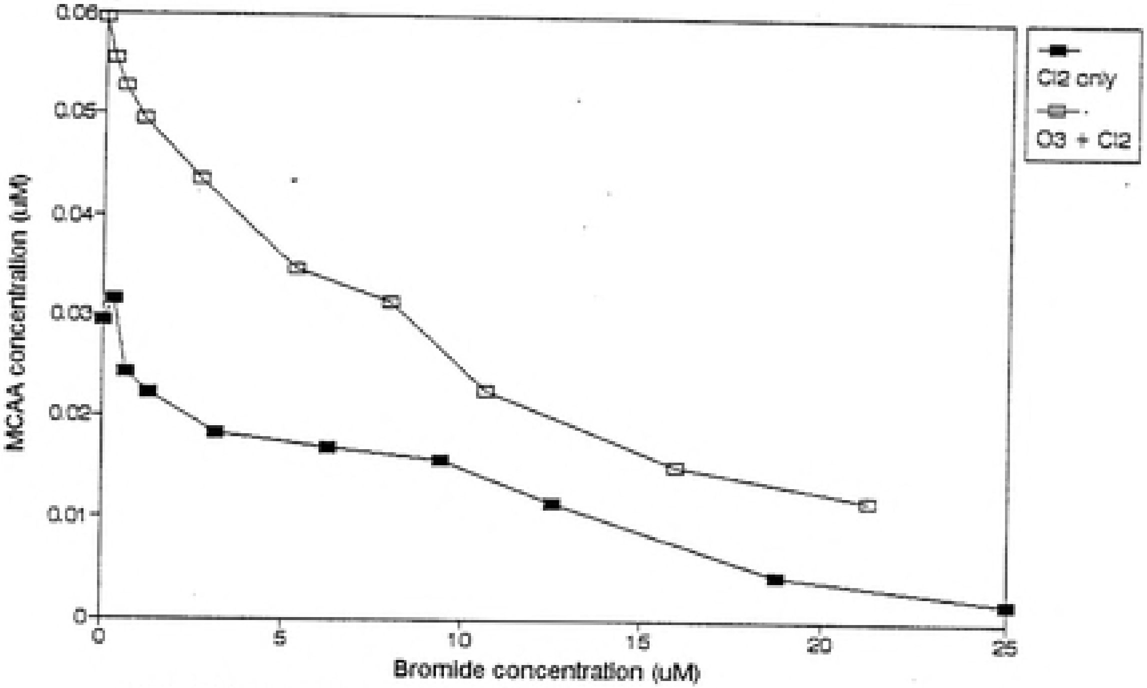


(b) Palm Beach extract

Figure 4.22. Bromine and chlorine incorporation into HAAs in extracts chlorinated at pH 6.

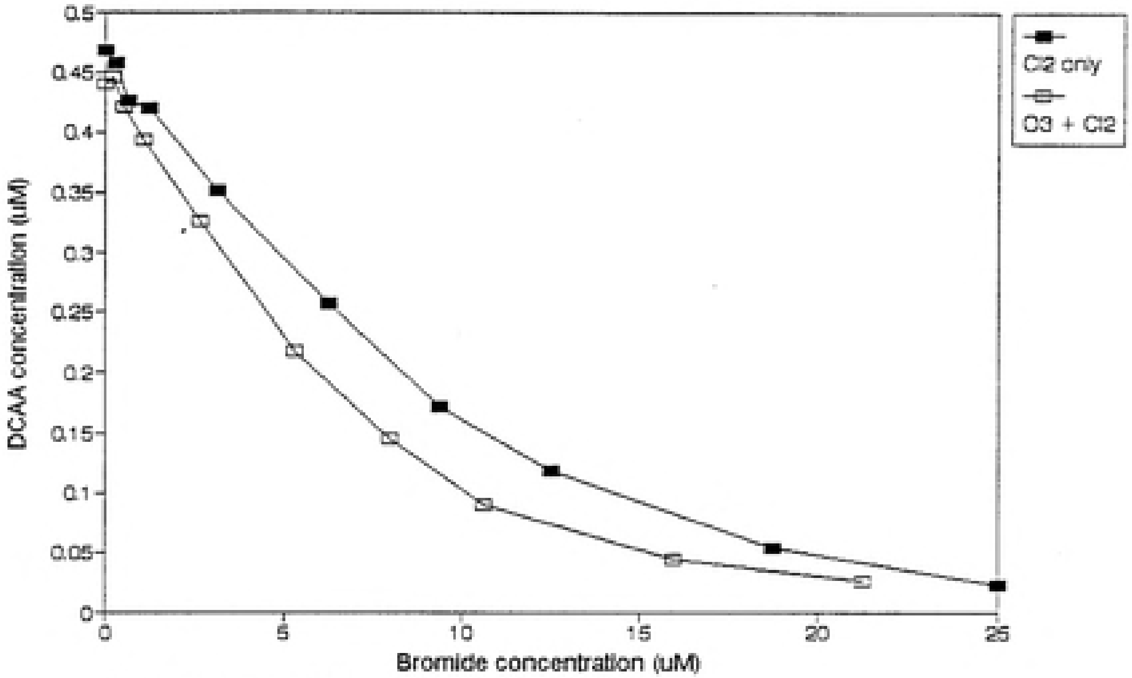


(a) Myrtle Beach extract

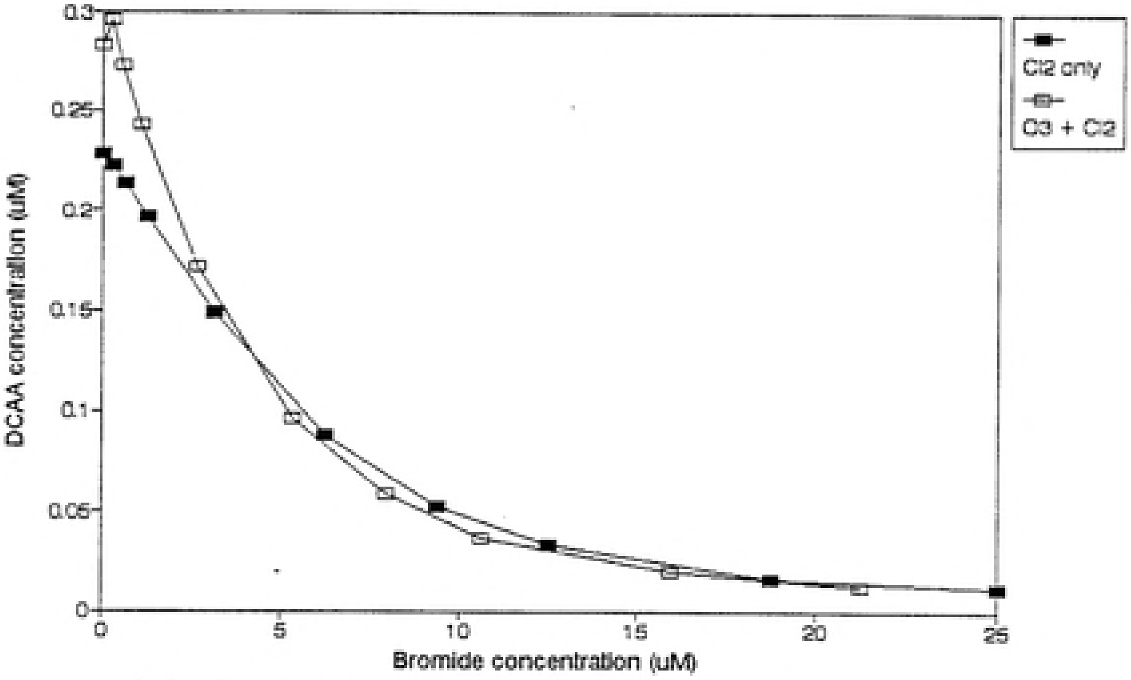


(b) Palm Beach extract

Figure 4.23. Influence of ozone on MCAA formation in extracts chlorinated at pH 8.

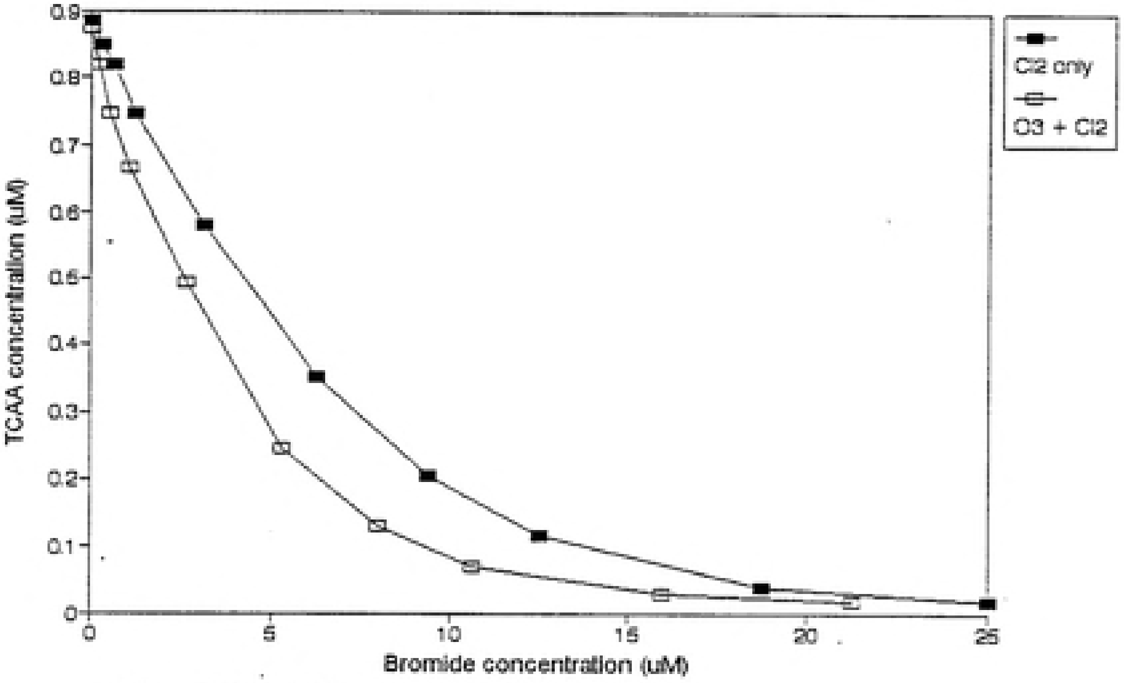


(a) Myrtle Beach extract

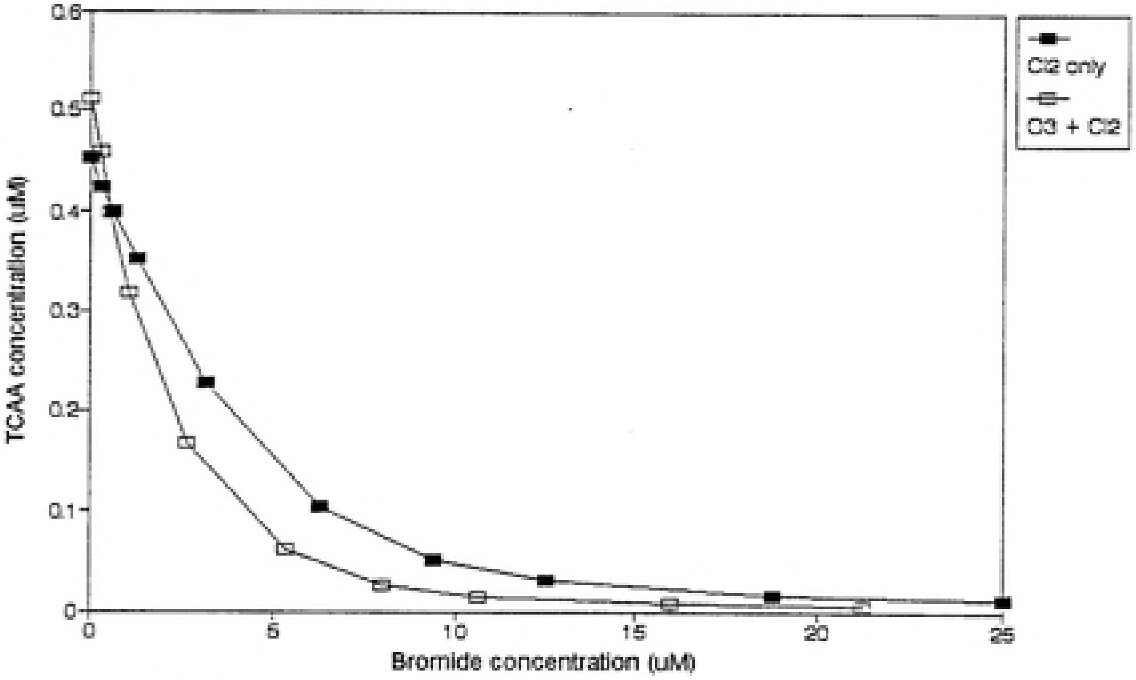


(b) Palm Beach extract

Figure 4.24. Influence of ozone on DCAA formation in extracts chlorinated at pH 8.

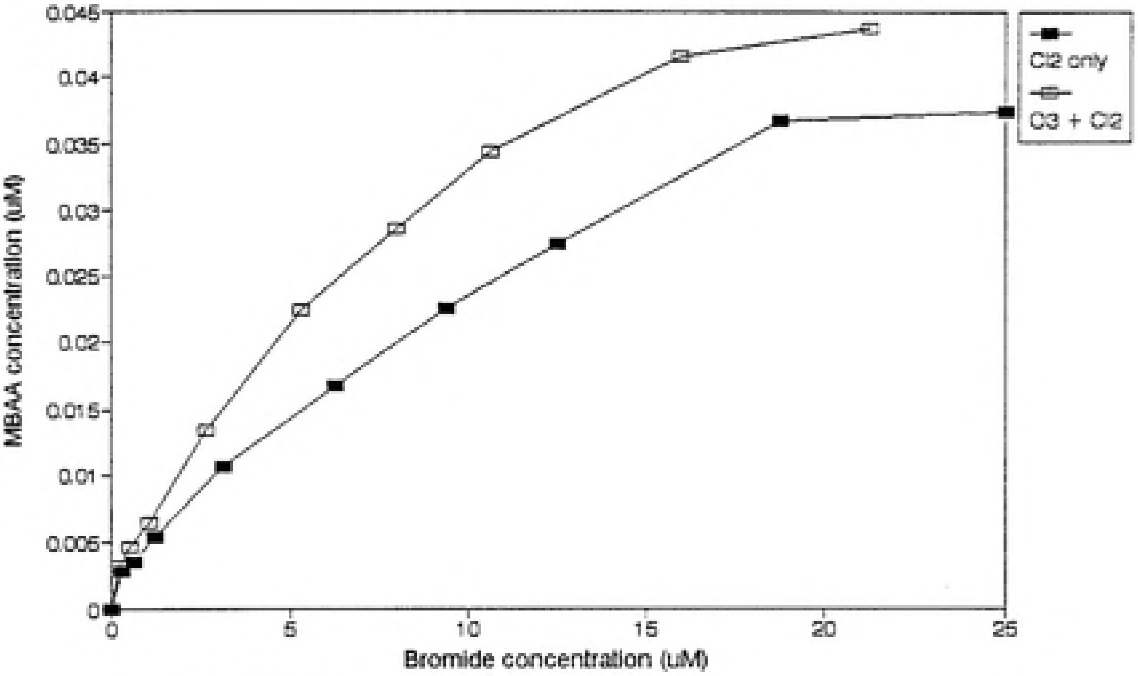


(a) Myrtle Beach extract

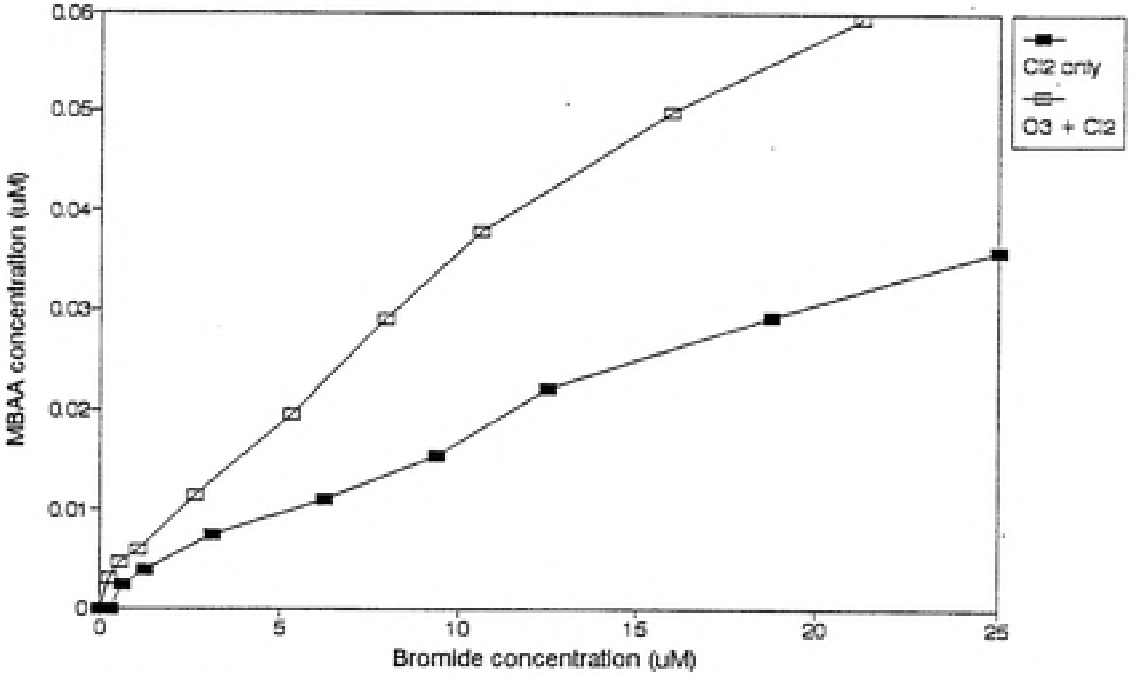


(b) Palm Beach extract

Figure 4.25. Influence of ozone on TCAA formation in extracts chlorinated at pH 8.

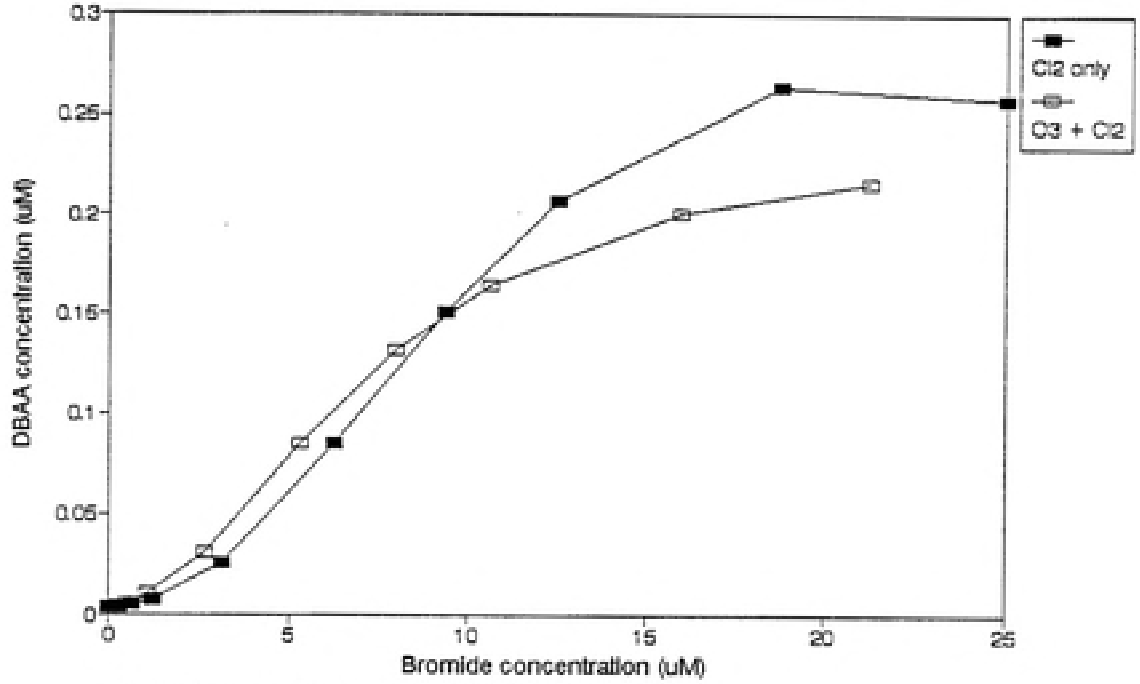


(a) Myrtle Beach extract

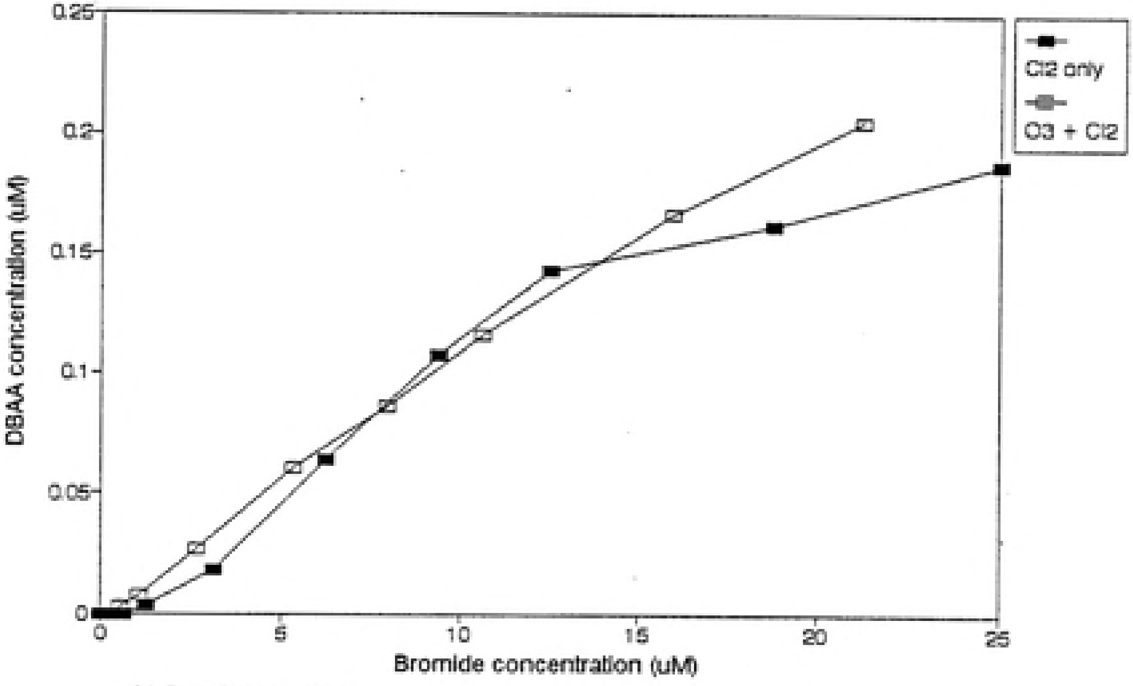


(b) Palm Beach extract

Figure 4.26. Influence of ozone on MBAA formation in extracts chlorinated at pH 8.

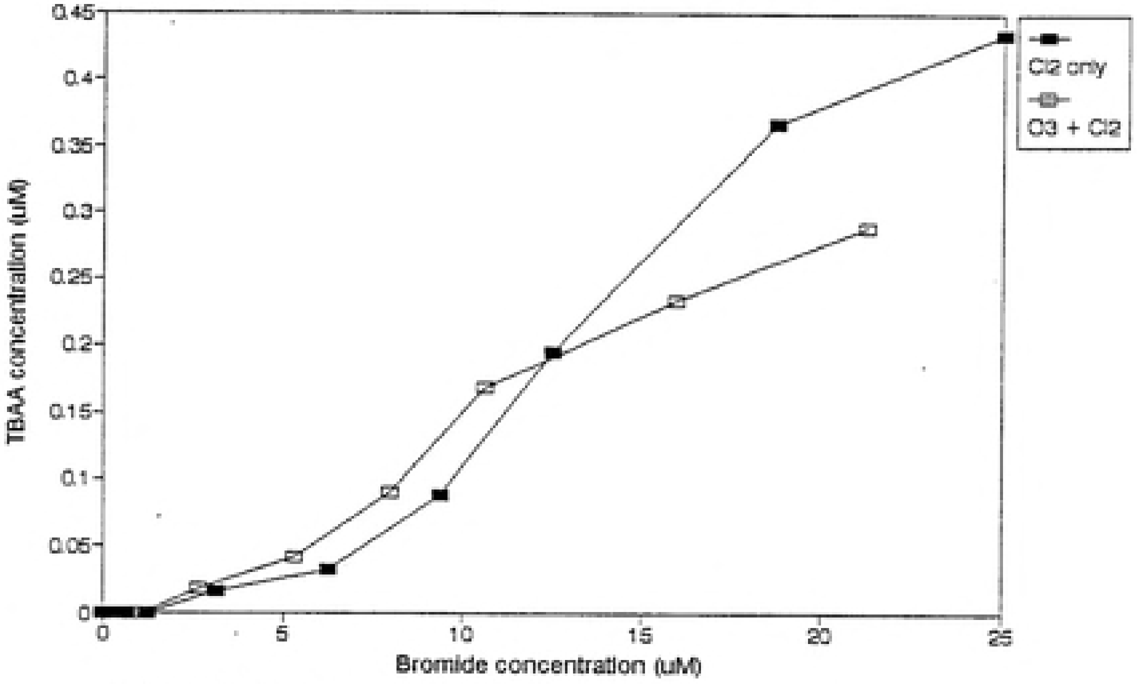


(a) Myrtle Beach extract

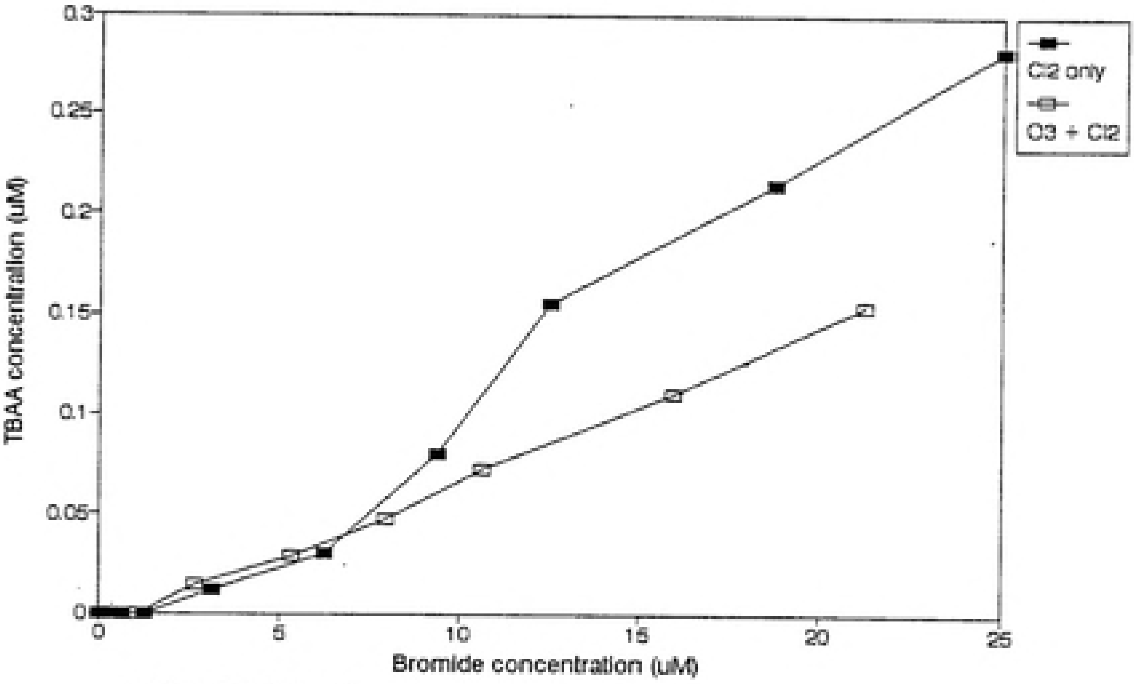


(b) Palm Beach extract

Figure 4.27. Influence of ozone on DBAA formation in extracts chlorinated at pH 8.

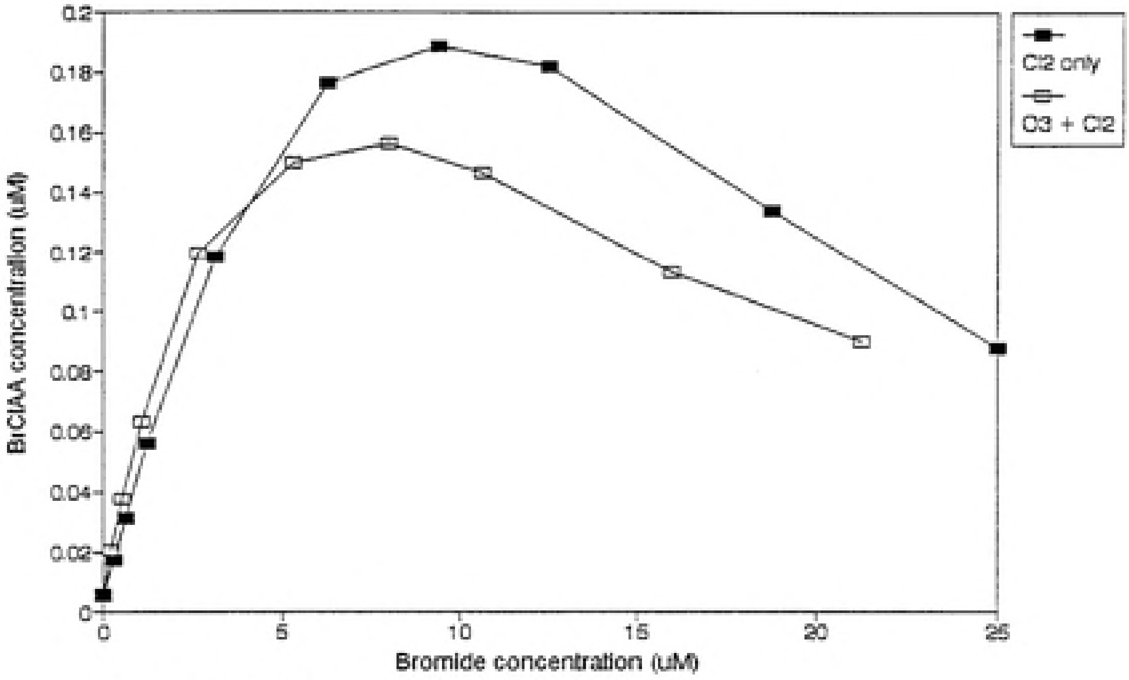


(a) Myrtle Beach extract

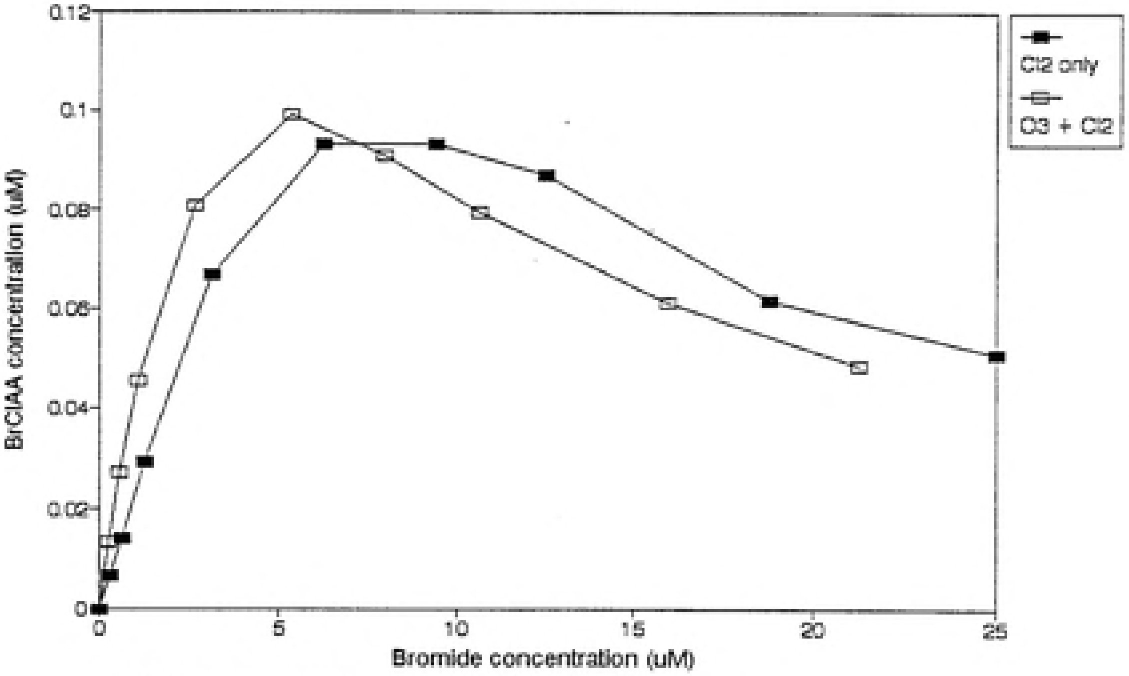


(b) Palm Beach extract

Figure 4.28. Influence of ozone on TBAA formation in extracts chlorinated at pH 8.

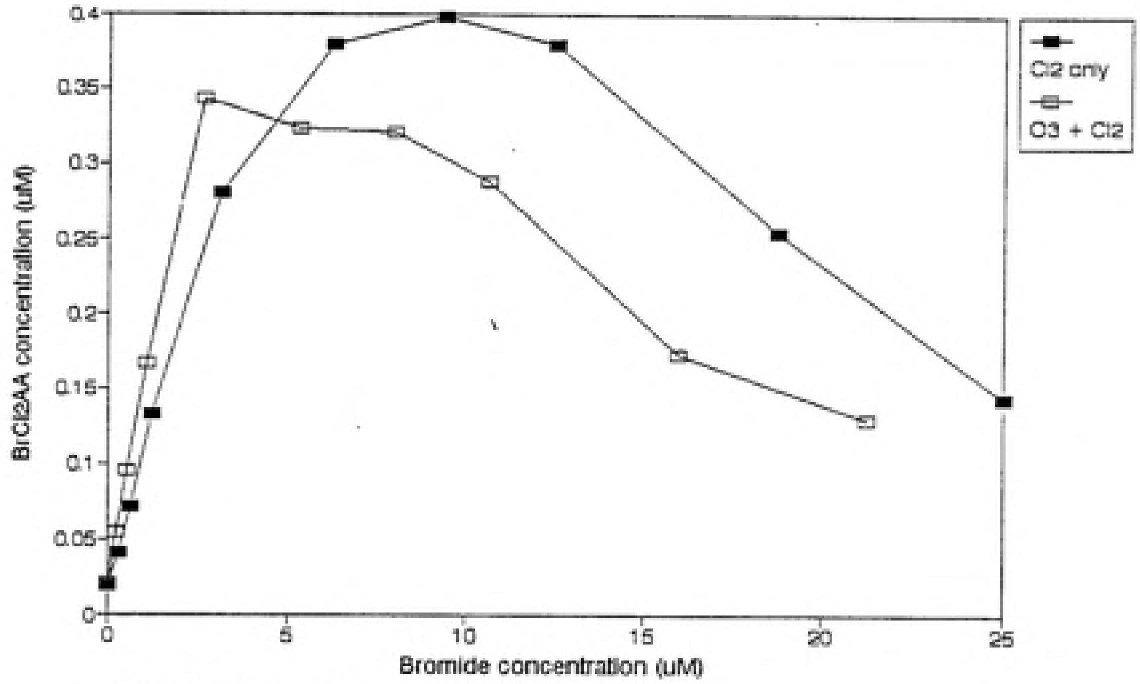


(a) Myrtle Beach extract

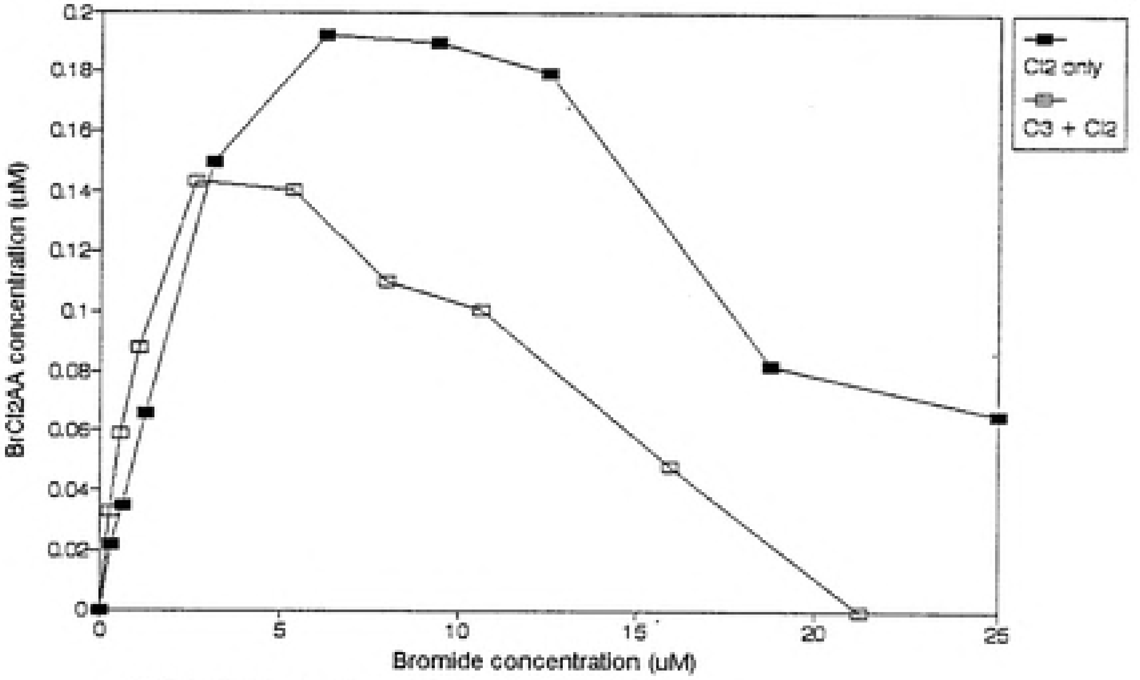


(b) Palm Beach extract

Figure 4.29. Influence of ozone on BrClAA formation in extracts chlorinated at pH 8.

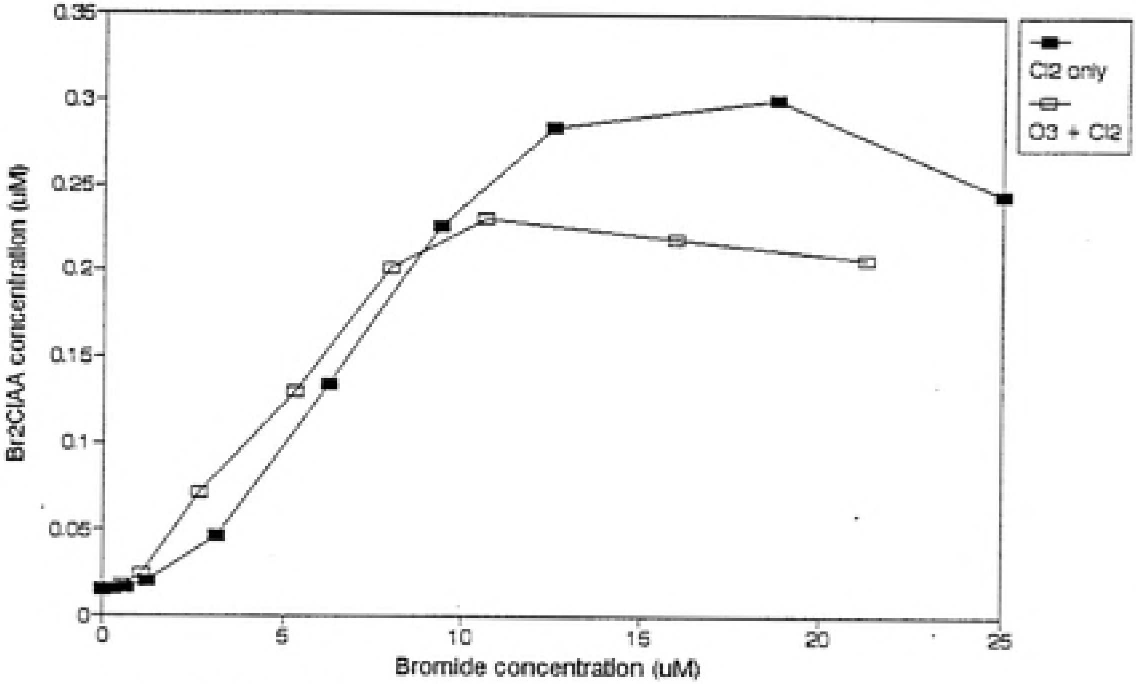


(a) Myrtle Beach extract

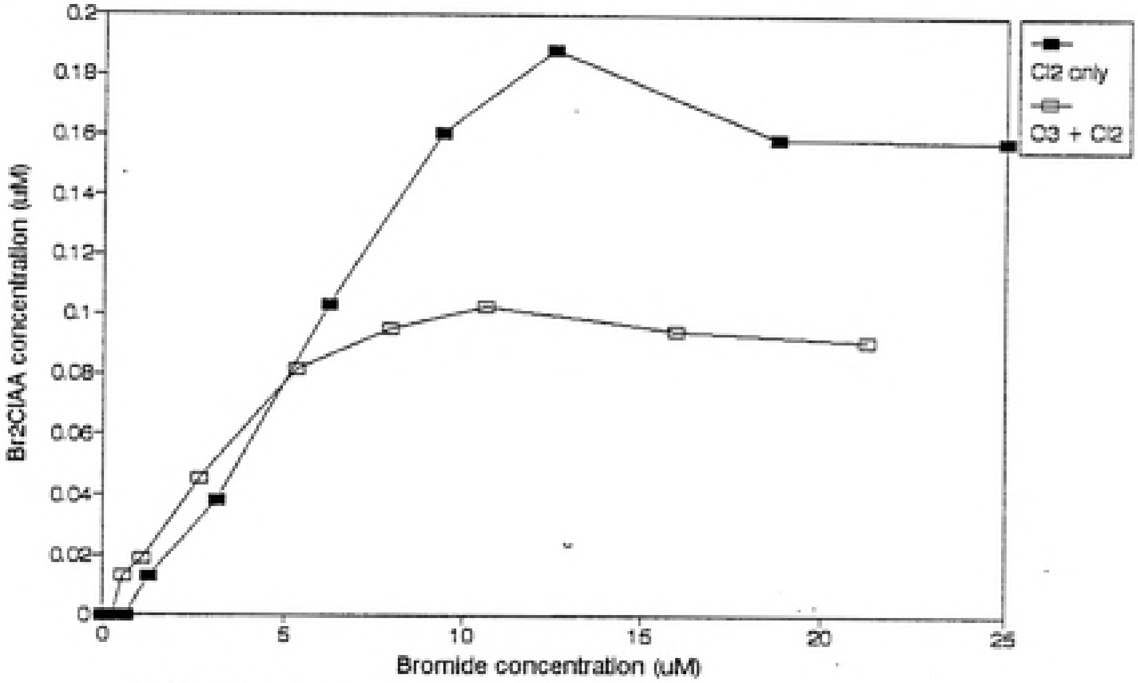


(b) Palm Beach extract

Figure 4.30. Influence of ozone on $BrCl_2AA$ formation in extracts chlorinated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.31. Influence of ozone on Br_2ClAA formation in extracts chlorinated at pH 8.

enhanced MCAA and MBAA formation. Similar results were obtained at pH 6, except in the case of MCAA formation in Myrtle Beach samples, which appeared to be little affected by pre-ozonation at pH 6.

In Myrtle Beach extracts pre-ozonation lowered DCAA and TCAA formation in all cases, and the magnitude of the decrease appeared to increase with increasing bromide concentration. For example, at pH 8 DCAA and TCAA decreases were on the order of 2-13% for bromide concentrations less than 1.25 µM, but at bromide concentrations greater than 5 µM the reductions were on the order of 25-60%. DCAA and TCAA behavior in Palm Beach samples was more complex. At pH 8 the formation of both species was enhanced at bromide concentrations less than 0.3 µM (29% for DCAA, 10% for TCAA), but was decreased by pre-ozonation at higher bromide concentrations. The pH of chlorination further affected the behavior of these two species. At pH 6 DCAA formation was enhanced by pre-ozonation at both low and high bromide concentrations (15-30%), and TCAA formation was decreased over the full range of bromide concentrations (25-75%).

In both waters the mixed bromo-chloro species again exhibited a pattern of formation that peaked in the range of bromide concentrations studied. Pre-ozonation appeared to shift the maximum formation of each of these species to slightly lower bromide concentrations.

In general, the effect of pre-ozonation on the formation of brominated and bromo-chloro species (excluding MBAA) appeared to depend on bromide concentration. The results suggest that pre-ozonation generally enhanced the formation of these species to some degree at low and moderate bromide concentrations (less than 6 µM Br^-), and tended to significantly decrease the formation of these species at very high bromide concentrations (greater than 12.5 µM Br^-). These results were consistent in samples chlorinated both at pH 8 and pH 6. There were a few exceptions to these general patterns, most notably that DBAA formation was enhanced to a small extent by pre-ozonation of Palm Beach extracts containing both low and high concentrations of bromide at pH 8 and pH 6, and BrClAA formation was enhanced over all bromide concentrations in Palm Beach extracts chlorinated at pH 6.

A possible explanation for the observation that the effect of pre-ozonation on the formation of bromine-containing HAAs depends on initial bromide concentration may come from an examination of the potential role of bromide ion as a hydroxyl radical scavenger. It is well known that ozone oxidizes Br^- to HOBr, and it is likely that the observed enhancement in bromine-containing HAAs by pre-ozonation of low bromide waters is a result of partial bromination of HAA precursors during pre-ozonation. However, other factors must be involved in the ozonation of high bromide waters since it was observed that pre-ozonation decreased the formation of bromine-containing HAAs in such waters.

Bicarbonate ion has been well-studied as a hydroxyl radical scavenger. Several studies (26,39,40) have shown that DCAA and TCAA formation in chlorinated waters is decreased by pre-ozonation in the presence of bicarbonate ion relative to pre-ozonation in the absence of bicarbonate, and it has been suggested that molecular ozone is more effective at destroying HAA precursors than is the hydroxyl radical.

The large rate constant for reaction of Br^- with the hydroxyl radical ($k=1.1x10^{10}\ M^{-1}sec^{-1}$ at 20°C compared to $k=8.5x10^{6}\ M^{-1}sec^{-1}$ at 20°C for the reaction between HCO_3^- and $^{\cdot}OH$) suggests that bromide may be an important radical scavenger. Potential radical scavengers in the model waters of this study include bicarbonate ion, bromide ion and the natural organic material. Relative rates of hydroxyl radical scavenging were calculated as $k_i[S_i]$, where k_i=rate constant of reaction between scavenger and $^{\cdot}OH$ and S_i=concentration of scavenger. The equilibrium concentration of HCO_3^- at pH 7 was determined to be 1.61 mM (from a total inorganic carbon concentration of 2 mM). The remaining inorganic carbon was present primarily as H_2CO_3, which does not contribute to $^{\cdot}OH$ scavenging. The rate constant for reaction of natural organic material with $^{\cdot}OH$ ($k=3.8x10^{4}\ L(mg\ DOC)^{-1}sec^{-1}$) was obtained from Haag and Yao (52). Relative scavenging by natural organic material and bicarbonate ion is given by:

$$k_{NOM}[NOM] = (3.8x10^{4}\ L(mg\ DOC)^{-1}sec^{-1})*(4\ mg/L\ TOC)$$
$$k_{NOM}[NOM] = 152,000\ sec^{-1}$$

$$k_{HCO3-}[HCO_3^-] = (8.5x10^{6}\ M^{-1}sec^{-1})*(1.61x10^{-3}\ M)$$
$$k_{HCO3-}[HCO_3^-] = 13,685\ sec^{-1}$$

Scavenging by bromide ion was calculated from $k_{Br-}[Br^-] = (1.1x10^{10}\ M^{-1}sec^{-1})[Br^-]$. The relative rates of scavenging by bromide are given at 5 µM increments of bromide concentration in Table 4D.

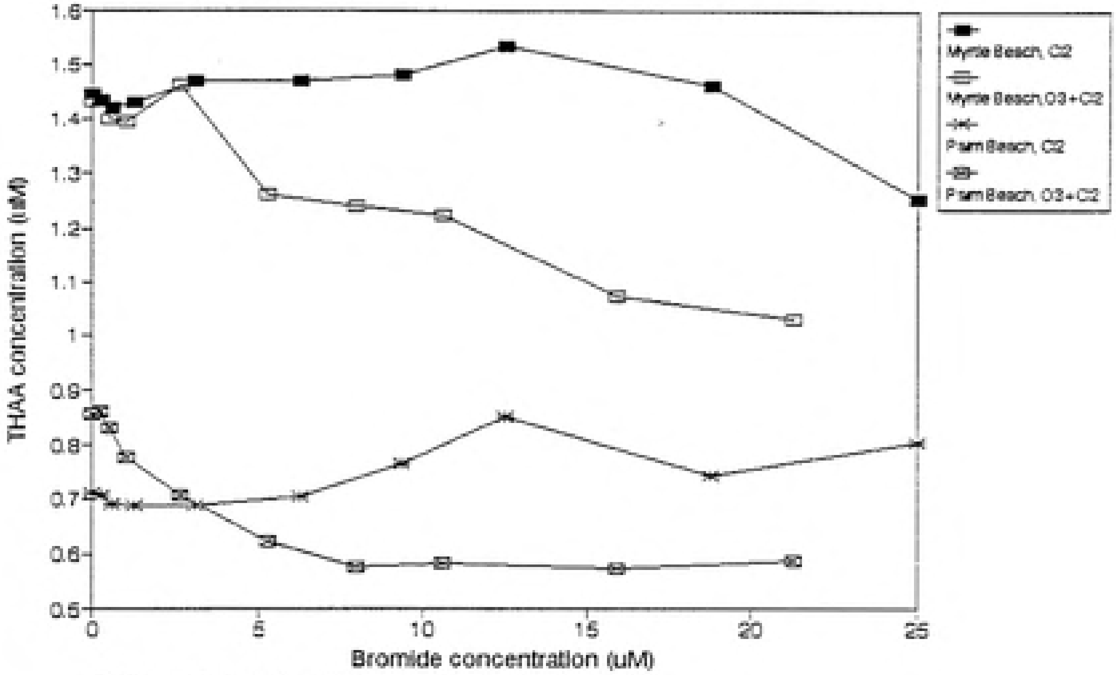
Table 4D. Relative rates of hydroxyl radical scavenging by bromide ion at various bromide concentrations.

$[Br^-]$ (μM)	$k_{Br^-}.[Br^-]$ (sec^{-1})
1	11,000
5	55,000
10	110,000
15	165,000
20	220,000
25	275,000

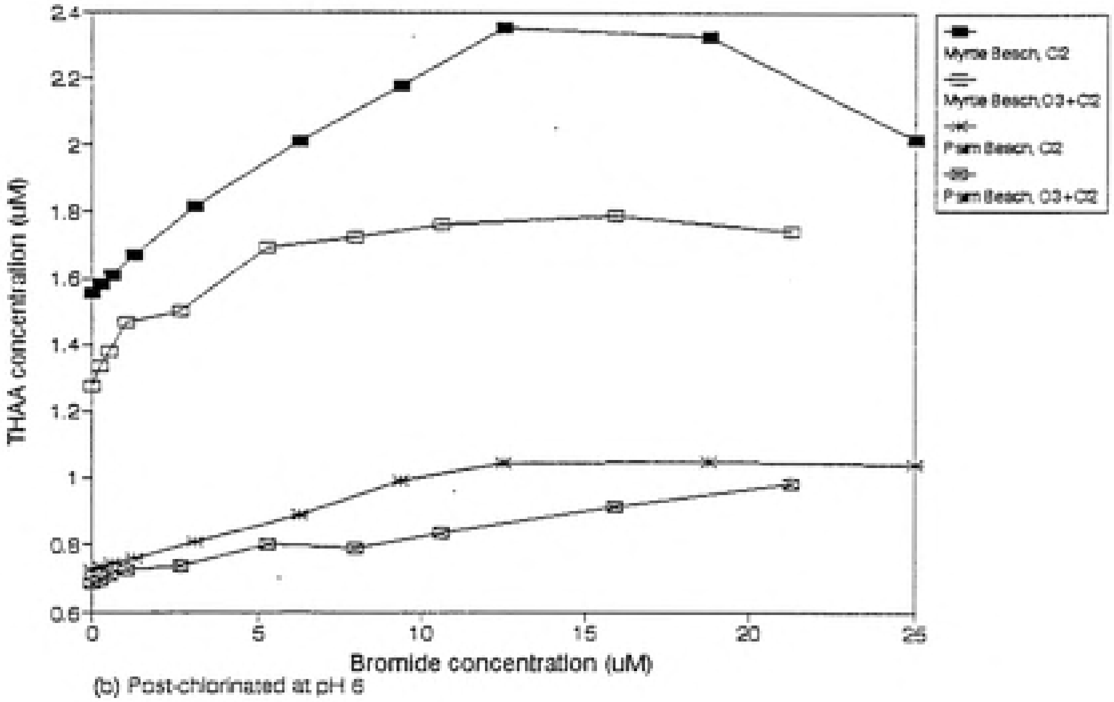
The relative rates suggest that hydroxyl radical scavenging by bromide ion is competitive with scavenging by NOM and HCO_3^-, and bromide ion appears to be the principal radical scavenger at bromide concentrations greater than 15 μM. This may explain the observation that pre-ozonation decreased the formation of bromine-containing HAAs (as well as DCAA and TCAA) in high bromide waters if molecular ozone is indeed more efficient at destroying HAA precursors than is the hydroxyl radical, as has been suggested by Reckhow et al. (39) and Legube et al. (40).

Total HAA formation

Total haloacetic acid formation in pre-ozonated waters is compared to waters treated with chlorine alone in Figure 4.32. The effect of pre-ozonation on subsequent total HAA formation from chlorination at pH 8 appears to depend on bromide concentration. In Myrtle Beach extracts containing less than 3 μM Br^-, pre-ozonation does not appear to affect total HAA formation; and in Palm Beach extracts containing less than 3 μM Br^-, pre-ozonation appears to enhance total HAA formation compared to treatment with chlorine alone. In waters containing



(a) Post-chlorinated at pH 8



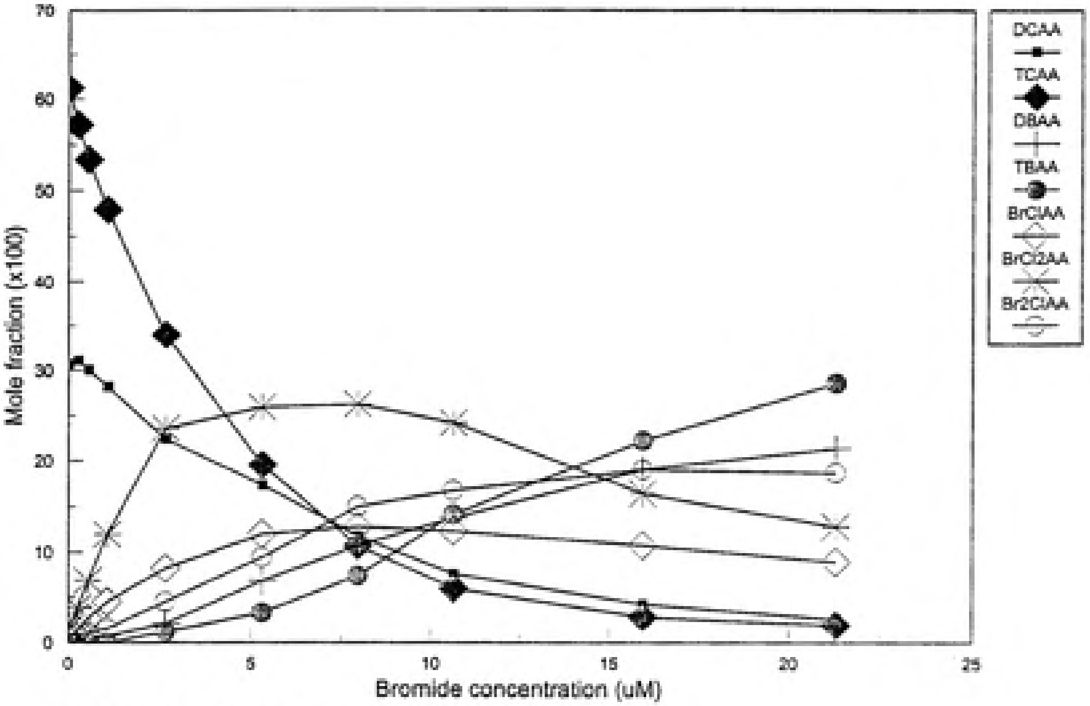
(b) Post-chlorinated at pH 6

Figure 4.32. Effect of pre-ozonation on total HAA formation in chlorinated extracts.

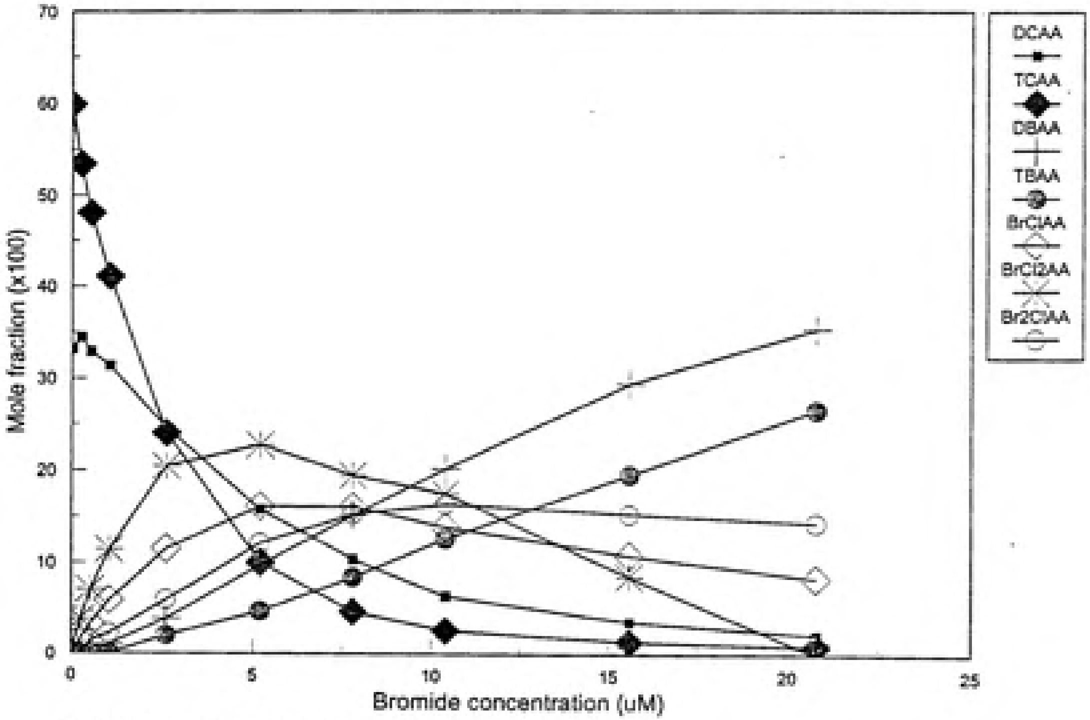
higher concentrations of bromide, however, total HAA formation is significantly decreased by pre-ozonation. In both waters chlorinated at pH 6, pre-ozonation appears to decrease total HAA formation relative to treatment with chlorine alone over the entire range of bromide concentrations studied.

Distribution of individual species

Distribution of the HAAs into individual species in pre-ozonated, chlorinated (pH 8) waters is shown in Figure 4.33. In comparison to waters treated with chlorine alone (see Figure 4.4), each of the HAAs containing bromine (excluding MBAA) appears to constitute a slightly larger fraction of the total HAAs in pre-ozonated waters at low bromide concentrations (<5 μM). At high bromide concentrations, speciation of the HAAs in pre-ozonated Myrtle Beach extracts is similar to the speciation observed in unozonated Myrtle Beach extracts; however, in Palm Beach extracts containing high concentrations of bromide, DBAA becomes the principal species in pre-ozonated waters in contrast to TBAA being the principal species in unozonated waters. In addition, TCAA appears to constitute a significantly smaller fraction of the total HAAs in both pre-ozonated extracts compared to unozonated extracts. Similar results were observed when post-chlorination was performed at pH 6. Distributions resulting from pre-ozonation followed by chlorination at pH 6 are given in Appendix H.



(a) Myrtle Beach extract



(b) Palm Beach extract

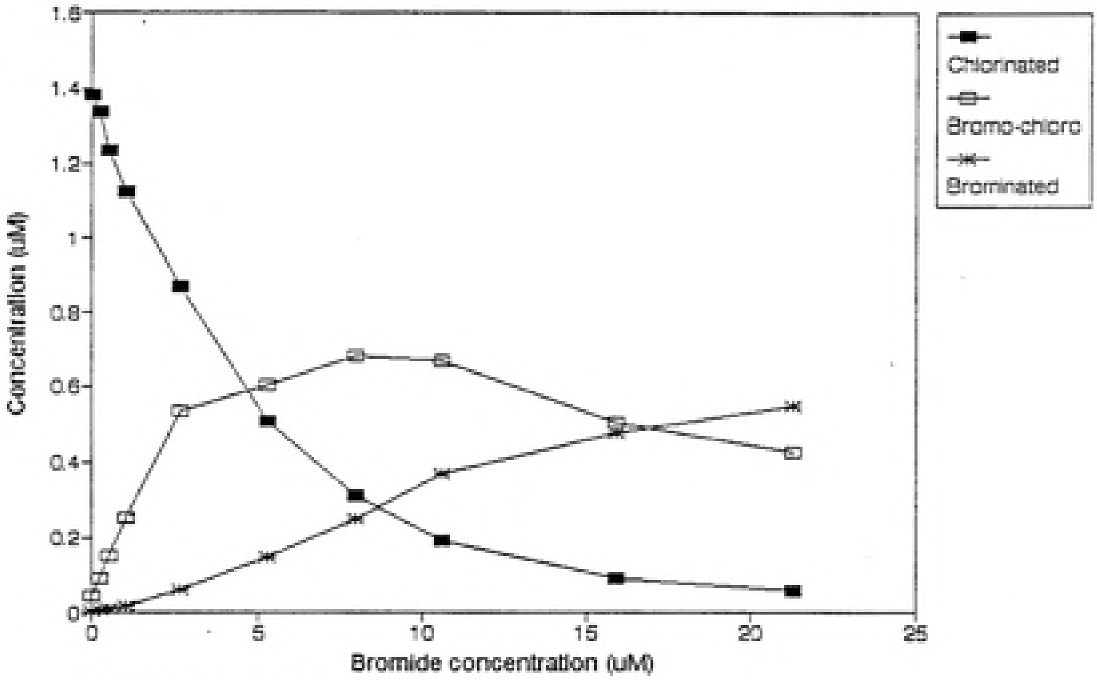
Figure 4.33. Distribution of individual HAA species in pre-ozonated extracts chlorinated at pH 8.

Total formation of chlorinated, bromo-chloro and brominated species

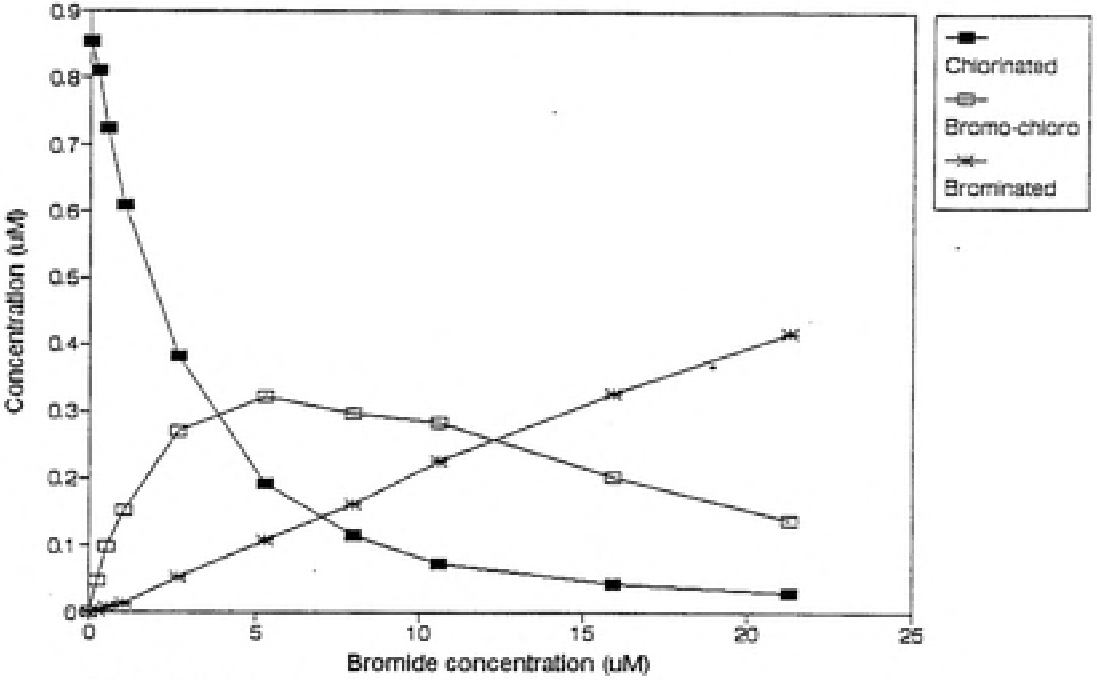
Total formation of chlorinated, bromo-chloro and brominated HAAs was investigated in pre-ozonated samples, and the results are shown in Figures 4.34 and 4.35. Comparison of these figures to Figures 4.6 and 4.20, respectively, suggests that species containing bromine become the principal species at lower bromide concentrations in pre-ozonated extracts compared to extracts that received chlorine alone. A comparison of the ranges of bromide concentrations over which each of these groups of species dominates in pre-ozonated and unozonated extracts is given in Table 4E.

Table 4E. Influence of pre-ozonation on bromide ranges of principal species formed in chlorinated extracts.

Sample	Species	pre-ozonated [Br^-] (μM)	unozonated [Br^-] (μM)
Myrtle Beach pH 8	Chlorinated Bromo-chloro Brominated	0-5 5-16 >16	0-6 6-19 >19
Myrtle Beach pH 6	Chlorinated Bromo-chloro Brominated	0-3 3-21 not observed	0-6 6-22 >22
Palm Beach pH 8	Chlorinated Bromo-chloro Brominated	0-4 4-12 >12	0-4 4-16 >16
Palm Beach pH 6	Chlorinated Bromo-chloro Brominated	0-3 3-16 >16	0-4 4-22 >22

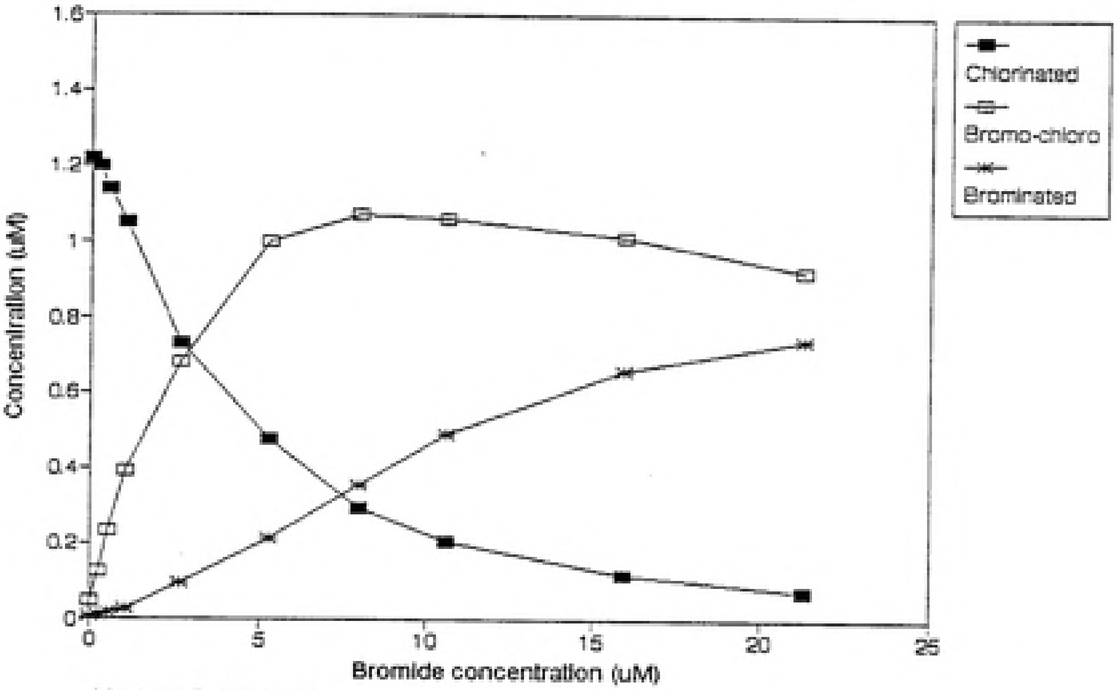


(a) Myrte Beach extract

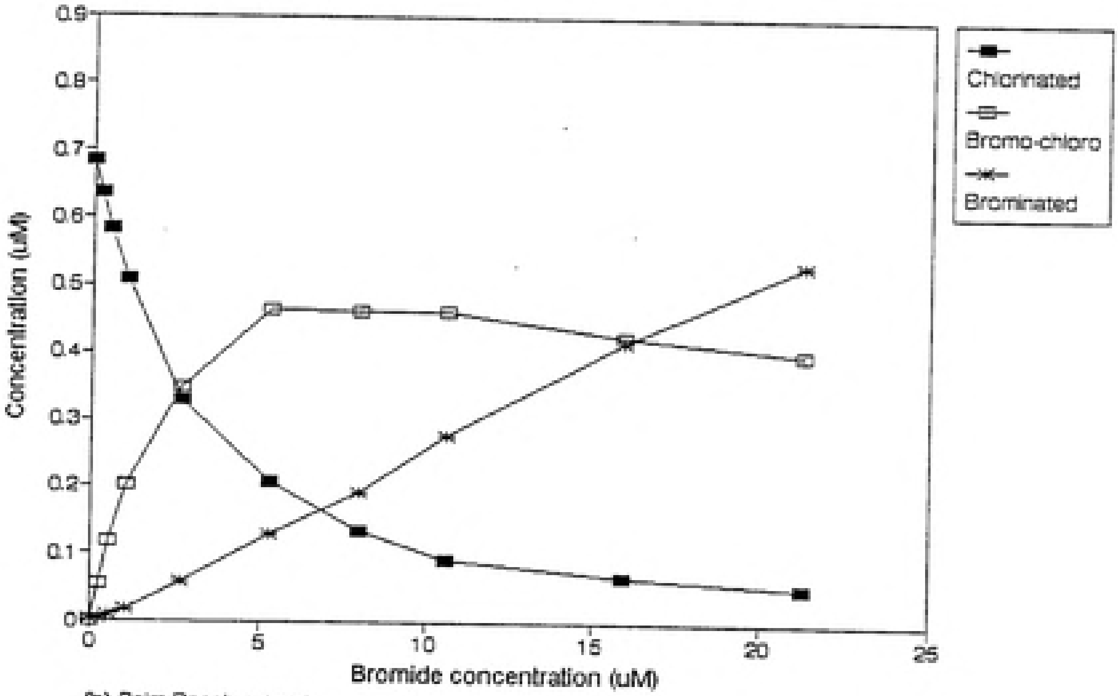


(b) Palm Beach extract

Figure 4.34. Sum of chlorinated, bromo-chloro, and brominated HAA species in pre-ozonated extracts chlorinated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

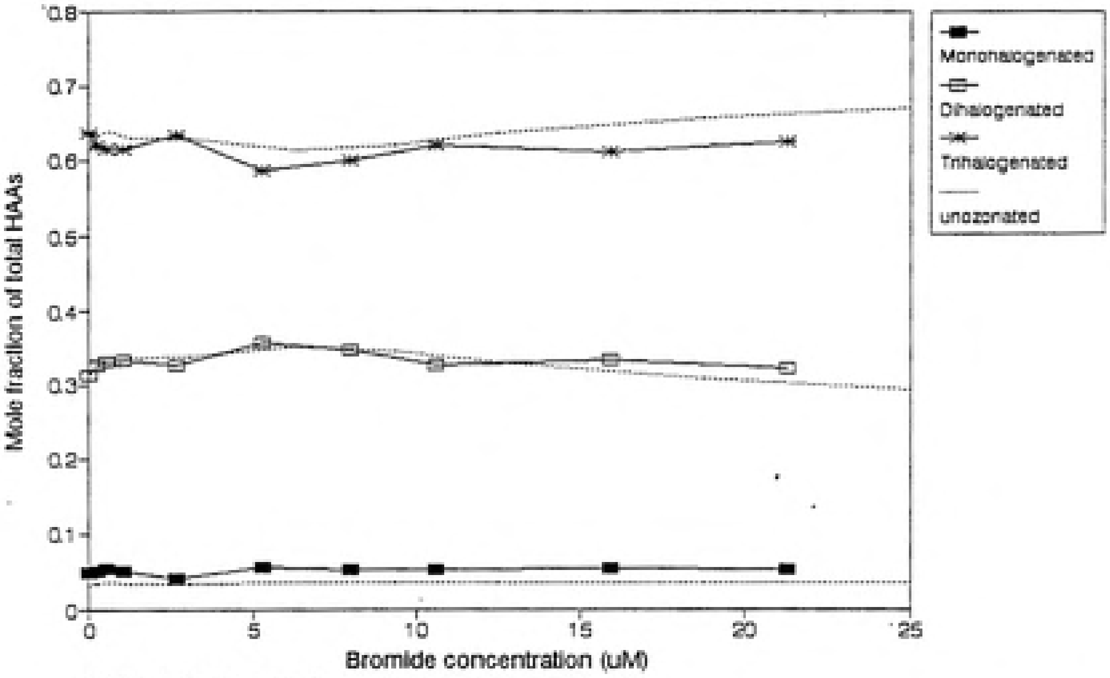
Figure 4.35. Sum of chlorinated, bromo-chloro, and brominated HAA species in pre-ozonated extracts chlorinated at pH 6.

Distribution of HAAs among mono-, di-, and trihalogenated species

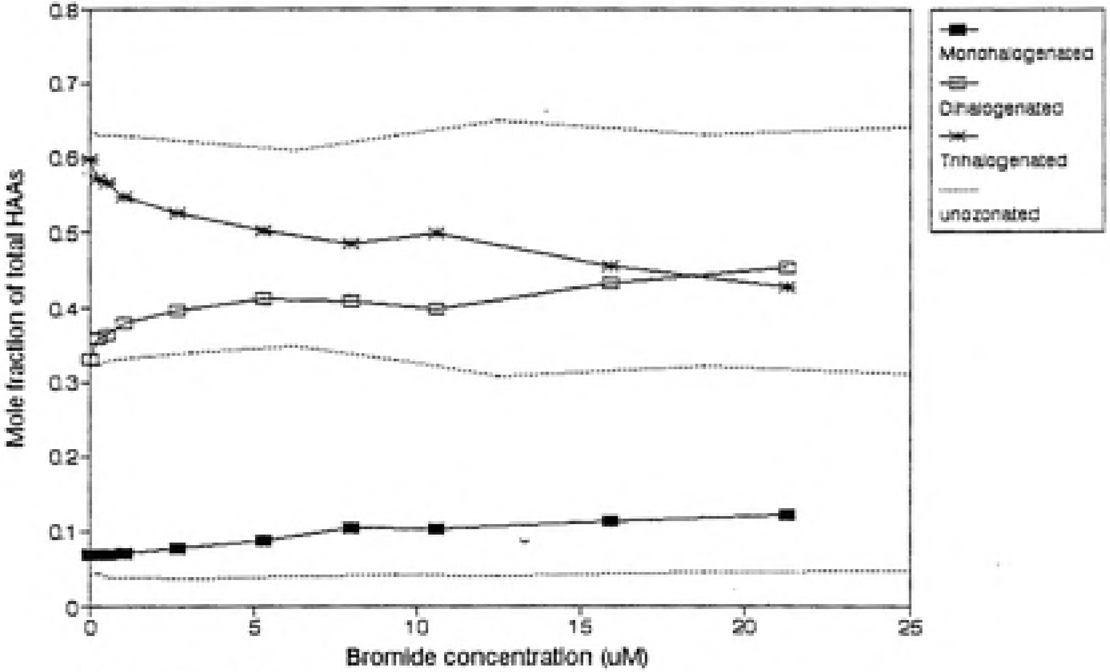
Distributions of the HAAs into mono-, di-, and trihalogenated species in pre-ozonated extracts are shown in Figures 4.36 and 4.37. In Myrtle Beach extracts, pre-ozonation does not appear to significantly affect this speciation. In addition, the speciation again appears to be independent of bromide concentration. In Palm Beach extracts, however, pre-ozonation appears to decrease speciation into the trihalogenated species and to increase speciation into the dihalogenated species. In addition, Figure 4.36 suggests that distribution of the HAAs among mono-, di-, and trihalogenated species in pre-ozonated Palm Beach extracts chlorinated at pH 8 may be influenced by bromide ion concentration.

Bromine and chlorine incorporation

Bromine and chlorine incorporation were evaluated by plotting µmoles bromine (or µmoles chlorine) incorporated per µmole of total HAAs. Figures 4.38 and 4.39 indicate that pre-ozonation enhances bromine incorporation per µmole THAA at bromide concentrations less than 20 µM in Myrtle Beach extracts and less than 10-15 µM in Palm Beach extracts. This is consistent with the observations that pre-ozonation tended to increase the distribution of HAAs into the bromine-containing species. The effect of ozone at higher bromide concentrations is less clear. Rook et al. (28) have observed that pre-ozonation tends to shift THM speciation toward the more highly brominated species, and it appears that pre-ozonation has a similar effect on HAA speciation. It is likely that HAA precursors become

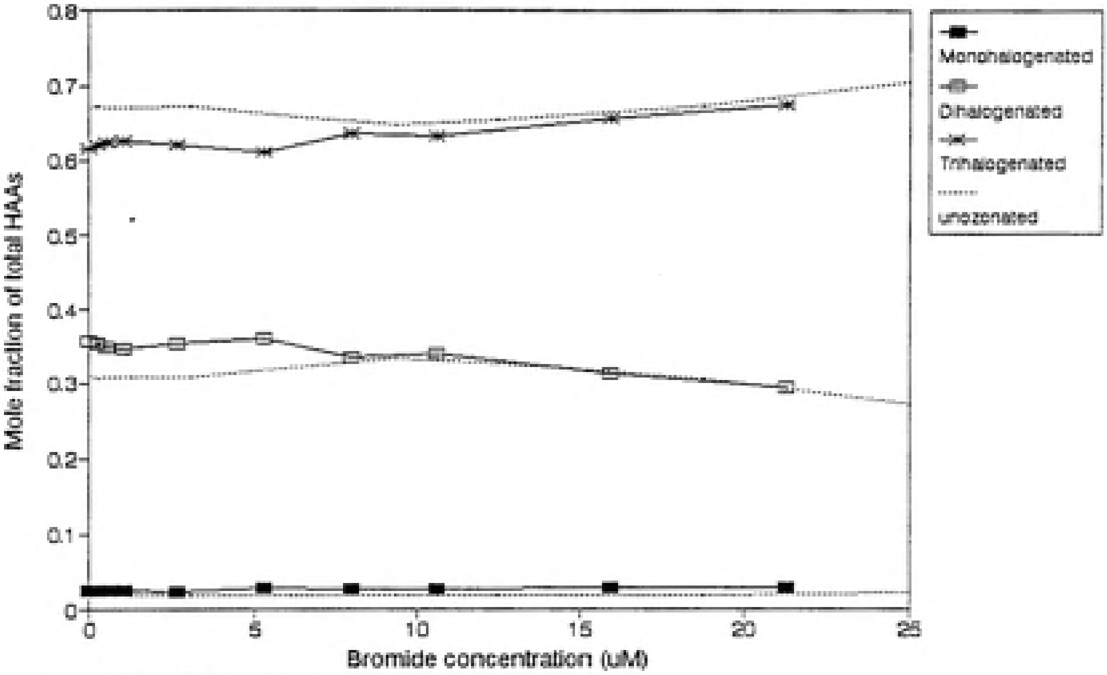


(a) Myrtle Beach extract

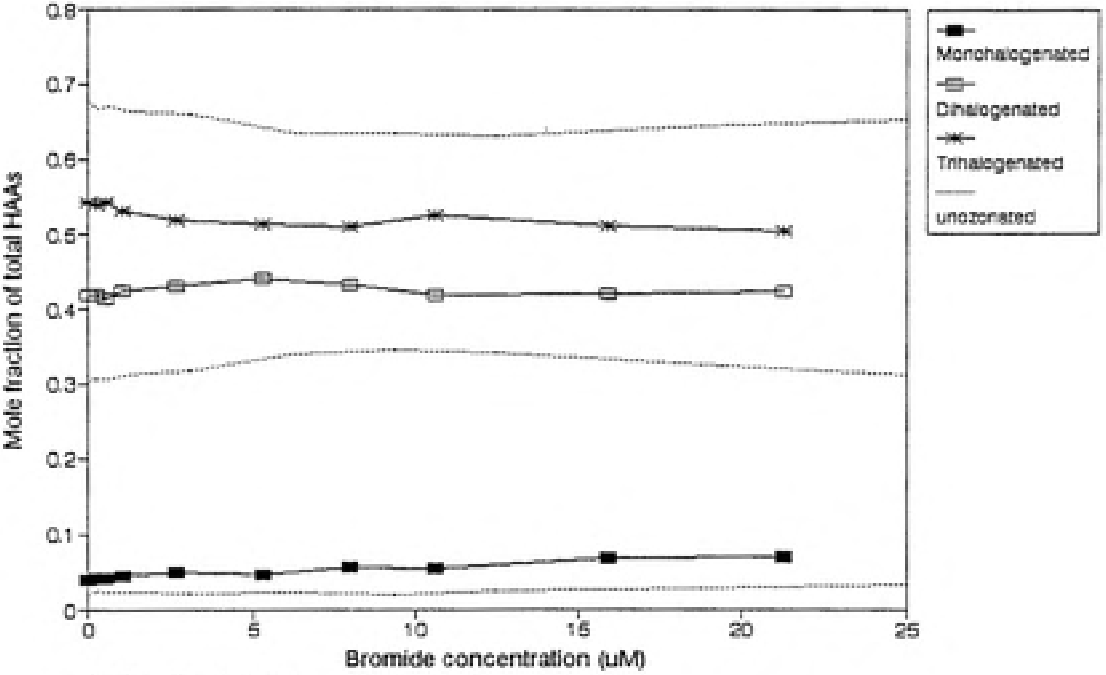


(b) Palm Beach extract

Figure 4.36. Distribution of HAAs into mono-, di-, and trihalogenated species in pre-ozonated extracts chlorinated at pH 8.

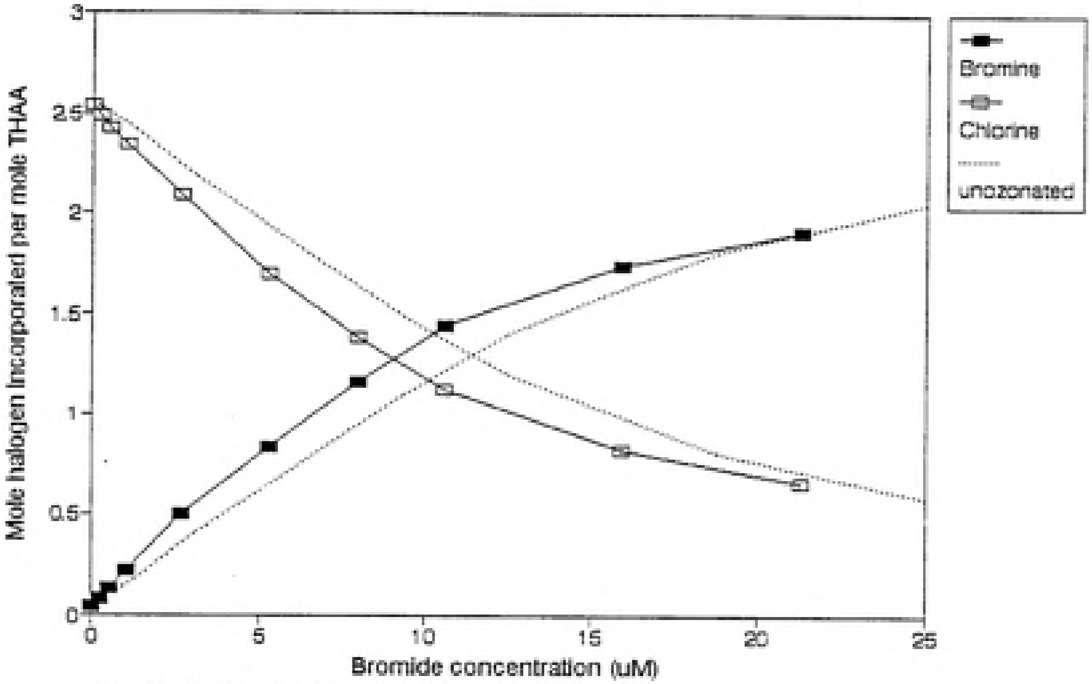


(a) Myrtle Beach extract

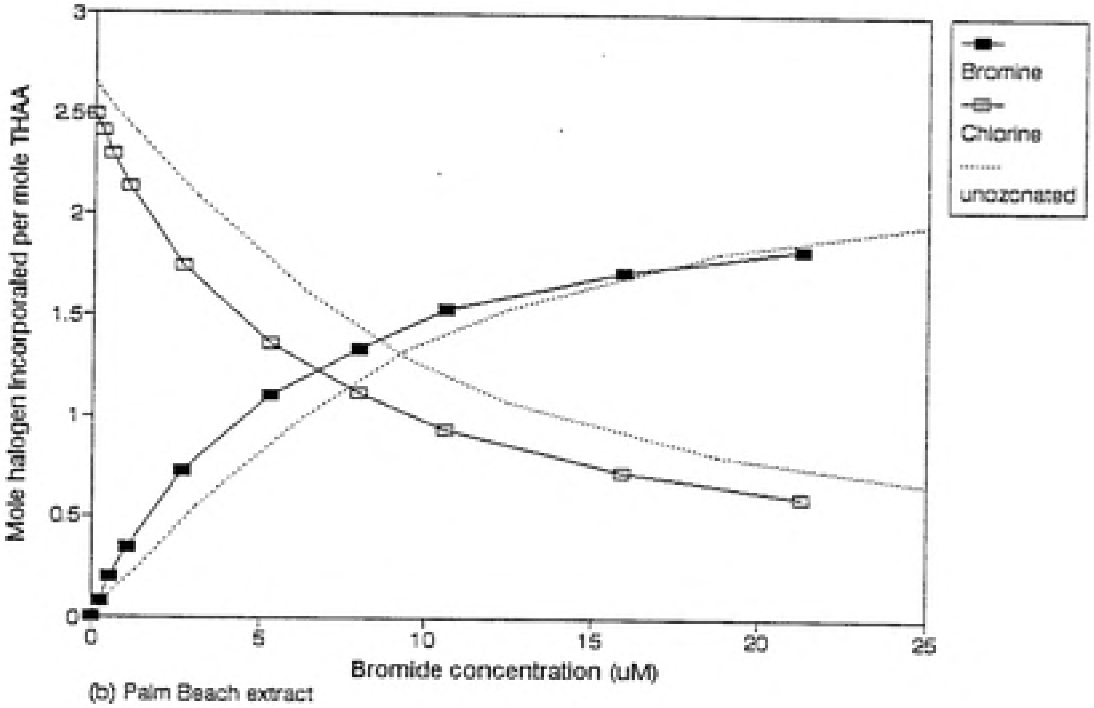


(b) Palm Beach extract

Figure 4.37. Distribution of HAAs into mono-, di-, and trihalogenated species in pre-ozonated extracts chlorinated at pH 6.

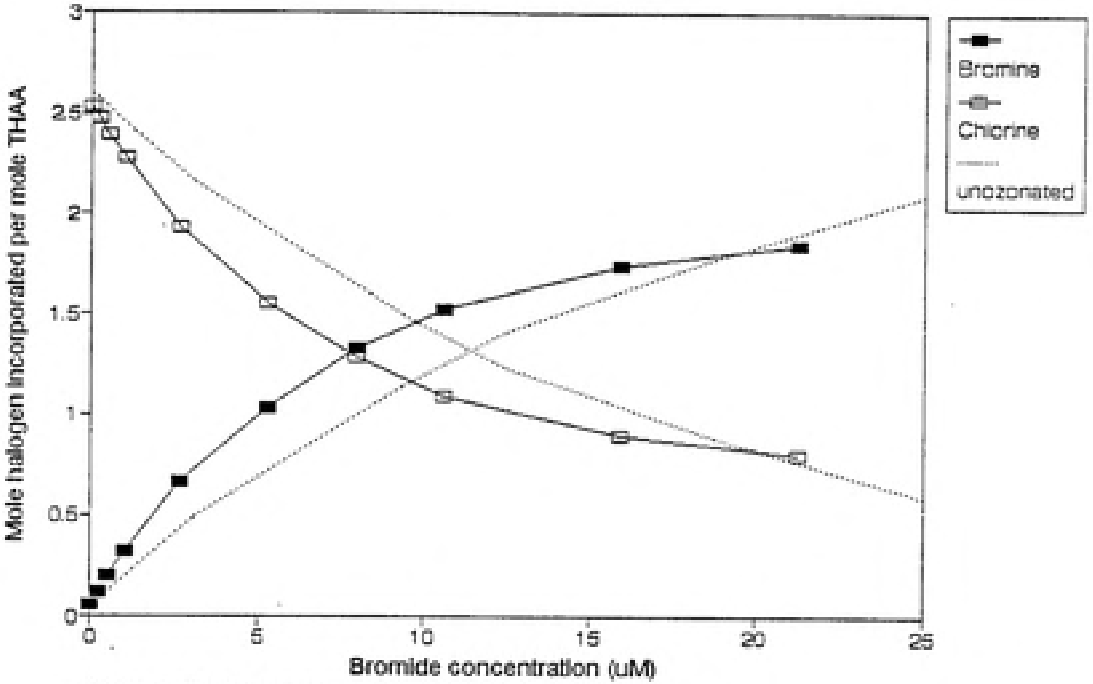


(a) Myrtle Beach extract

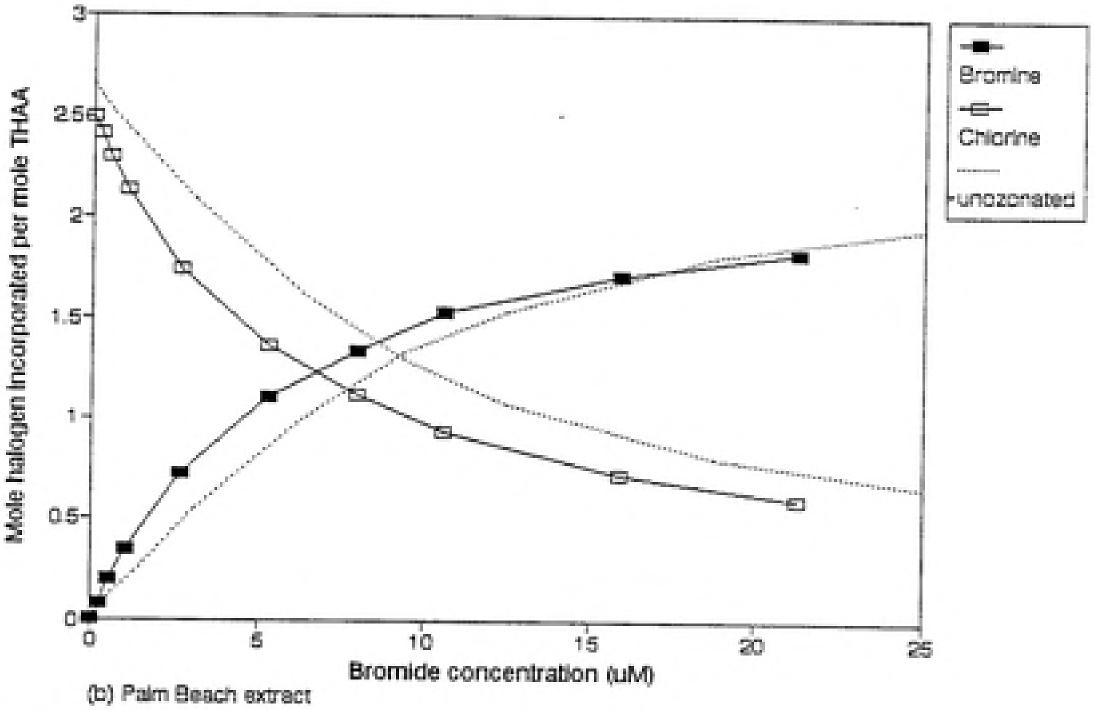


(b) Palm Beach extract

Figure 4.38. Bromine and chlorine incorporation into HAAs in pre-ozonated extracts chlorinated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.39. Bromine and chlorine incorporation into HAAs in pre-ozonated extracts chlorinated at pH 6.

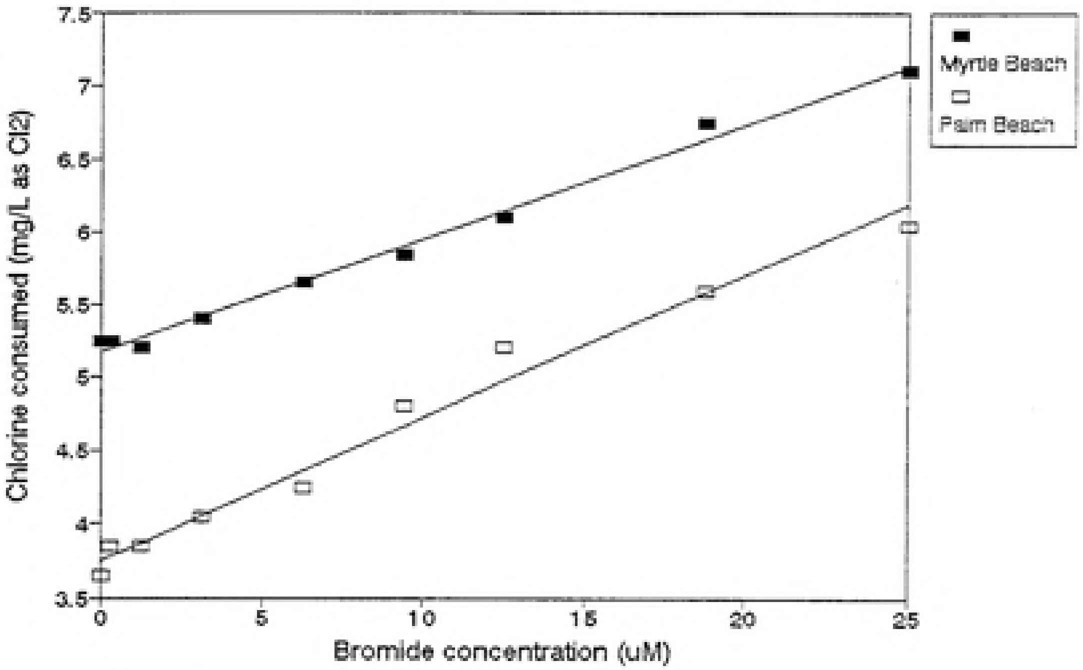
partially brominated during ozonation.

Pre-ozonation appeared to have little effect on the total halogen content of the HAAs. In waters treated with chlorine alone, each mole of total HAAs consistently contained approximately 2.6 moles of total halogen. In pre-ozonated Myrtle Beach extracts, each mole of total HAAs again contained approximately 2.6 moles of total halogen. In pre-ozonated Palm Beach extracts, there was approximately 2.5 moles of total halogen incorporated per mole of total HAAs; this slightly lower value resulted from the observed decrease in speciation into trihalogenated species and increase in speciation into dihalogenated species.

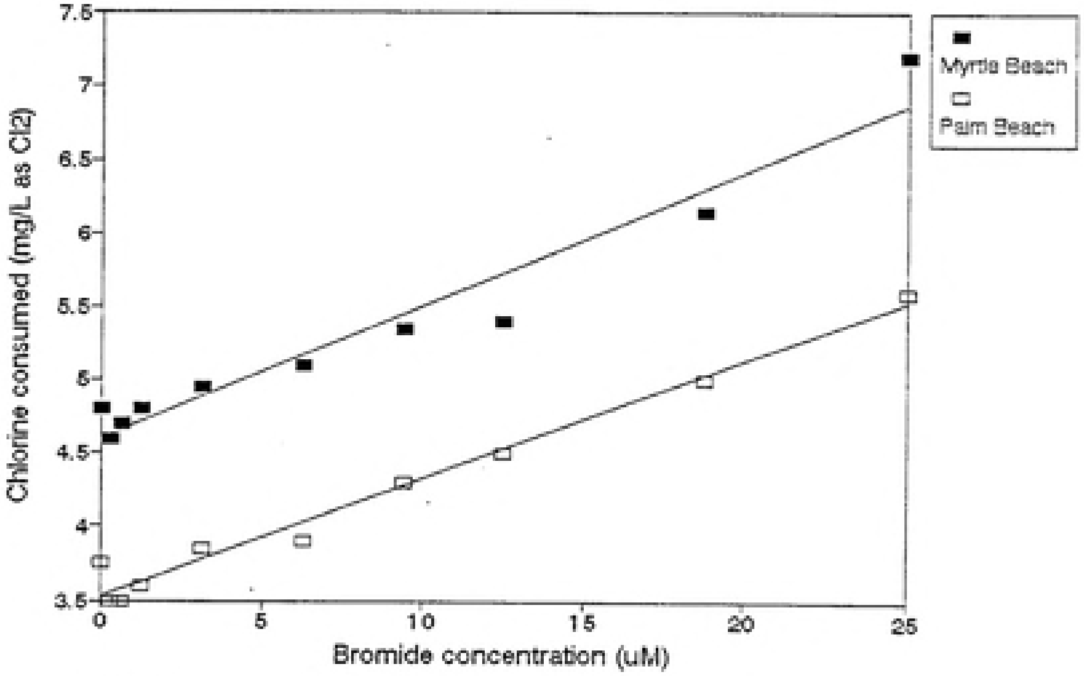
Effect of bromide ion concentration on chlorine consumption

In several chlorinated waters there was an observed trend of increased chlorine consumption with increasing bromide ion concentration. Bromide ion exerts a chlorine demand through the reaction: $HOCl + Br^- \text{----->} HOBr + Cl^-$. Sweetman et al. (30) have suggested that Br^- may be "recycled" through oxidation reactions. HOBr can participate in oxidation reactions that do not involve incorporation of Br into organics. Br^- is a product of such reactions. Br^- can then be reoxidized to HOBr by HOCl, and thus 1 mole of Br^- can potentially consume more than 1 mole of HOCl.

In waters chlorinated both at pH 8 and pH 6, there appeared to be a linear increase in chlorine consumption with increasing bromide ion concentration. This is shown in Figure 4.40. Chlorine consumption in pre-ozonated, chlorinated extracts is



(a) pH 8



(b) pH 6

Figure 4.40. Effect of bromide ion on chlorine consumption in chlorinated extracts.

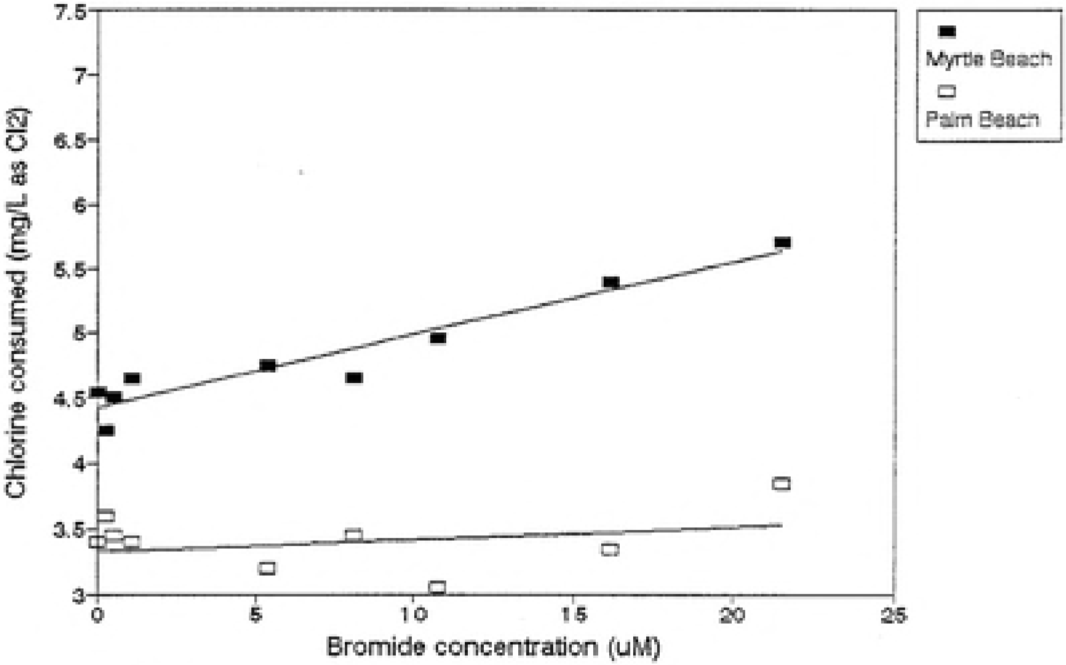
shown in Figure 4.41. In pre-ozonated Myrtle Beach extract, chlorine consumption again appeared to increase with increasing bromide concentration; however, bromide ion appeared to have little effect on chlorine consumption in pre-ozonated Palm Beach extract.

HAA formation and speciation in extracts chloraminated at pH 8

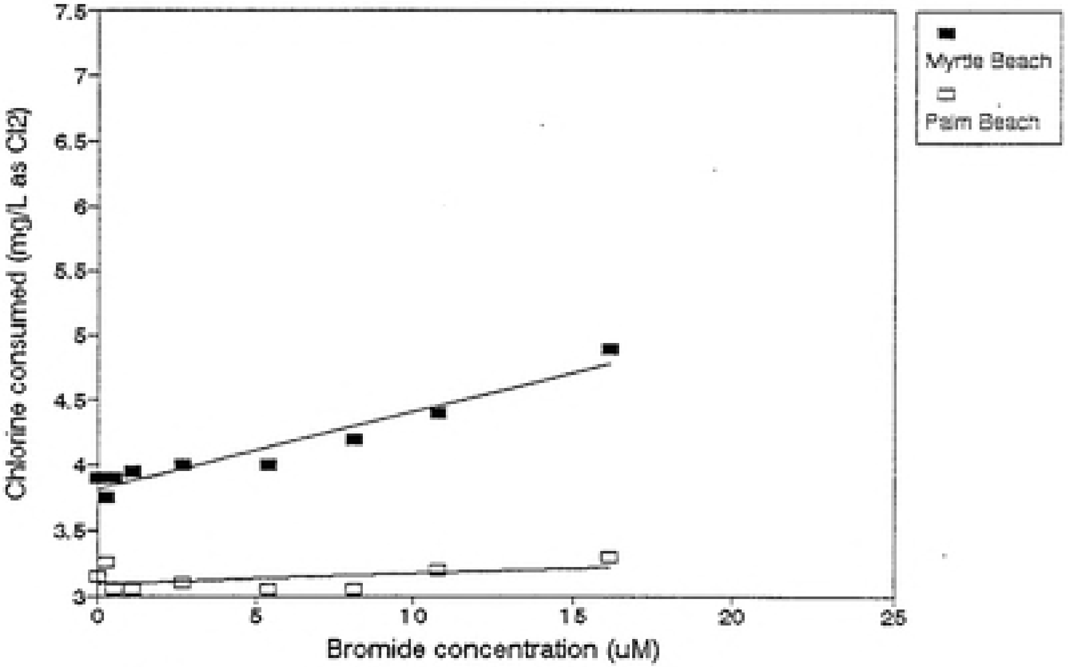
Formation and distribution of individual species

Compared to chlorination, chloramination of Myrtle Beach and Palm Beach extracts at pH 8 showed a dramatic decrease in total µM HAA formation, on the order of 88-95%. DCAA was the principal species formed from chloramination, but observed concentrations did not exceed 0.070 µM (9 µg/L). Chloramination did produce some of the brominated species, principally MBAA, DBAA, and BrClAA. The highest observed concentrations of each of these species were 0.024 µM MBAA (3.3 µg/L), 0.023 µM DBAA (5 µg/L), and 0.020 µM BrClAA (3.4 µg/L). In contrast to its behavior in chlorinated extracts, BrClAA formation did not exhibit a peak in the range 0-25 µM Br^- during chloramination. Distribution diagrams of the HAA species formed in chloraminated Myrtle Beach and Palm Beach extracts are shown in Figure 4.42.

The trihalogenated HAA species are not shown in Figure 4.42 because the formation of these species was greatly suppressed by chloramination. TCAA formation was below the detection limit of 0.0018 µM (0.29 µg/L) in all chloraminated samples. Br_2ClAA and TBAA were quantifiable only in samples containing greater than 12.5 µM Br^- and at concentrations below 0.01 µM (2 µg/L). $BrCl_2AA$

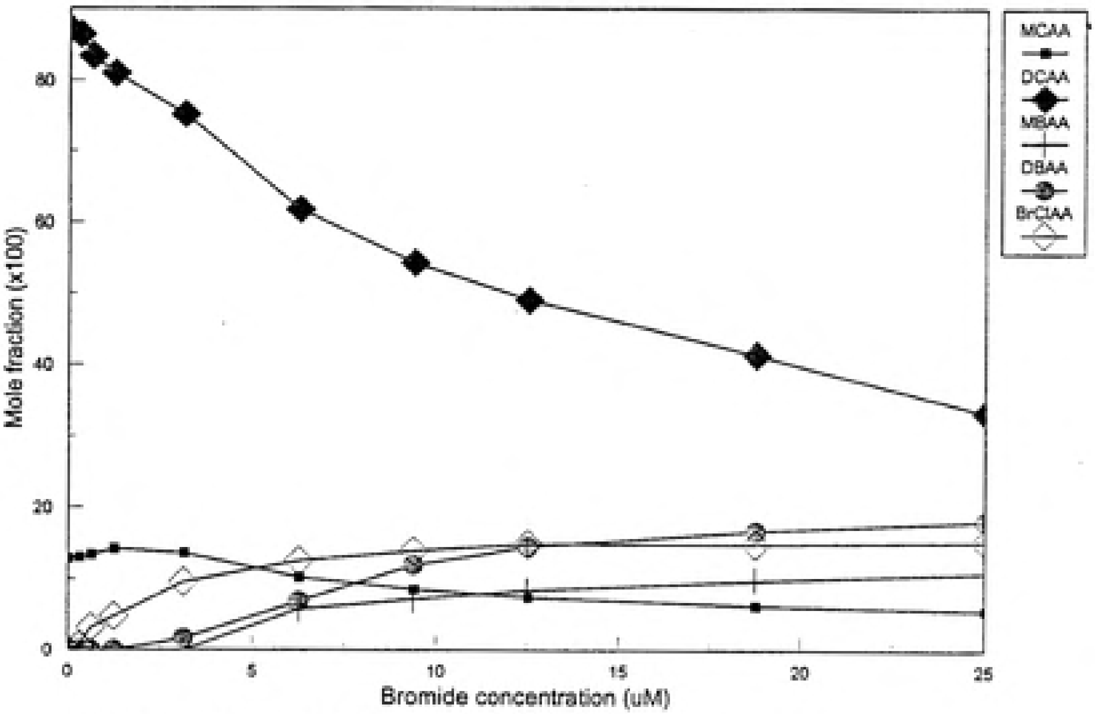


(a) pH 8

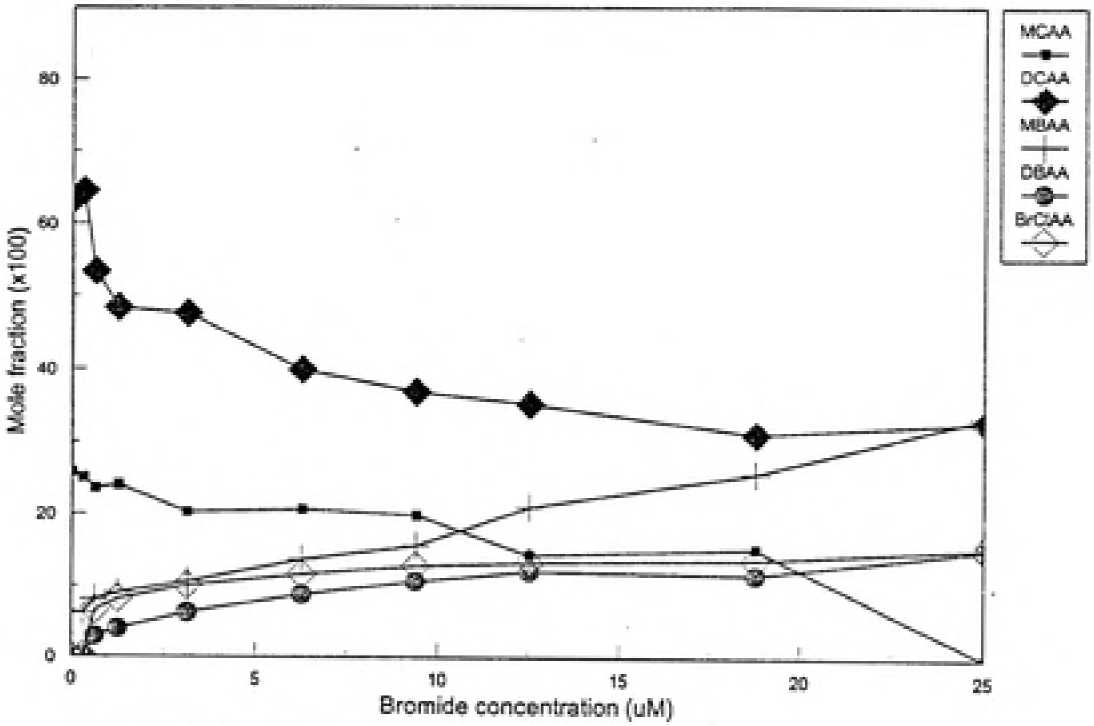


(b) pH 6

Figure 4.41. Effect of bromide ion on chlorine consumption in pre-ozonated, chlorinated extracts.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.42. Distribution of individual HAA species in extracts chloraminated at pH 8.

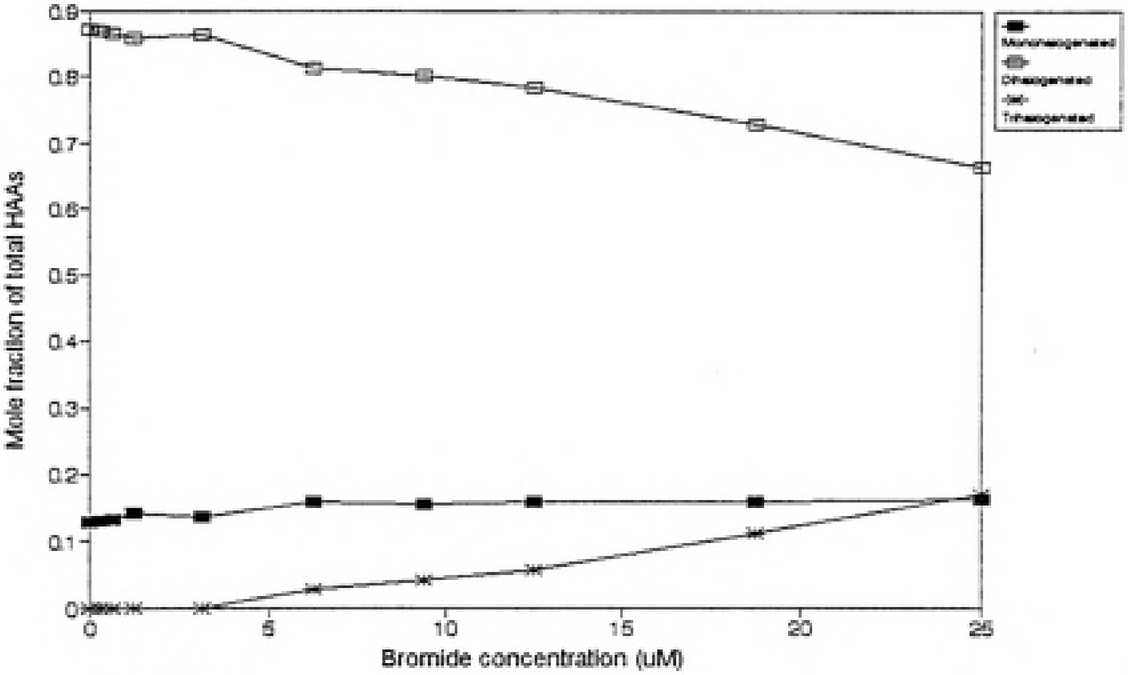
was also detected only at concentrations below 0.01 µM (2.3 µg/L).

Distribution of HAAs among mono-, di-, and trihalogenated species

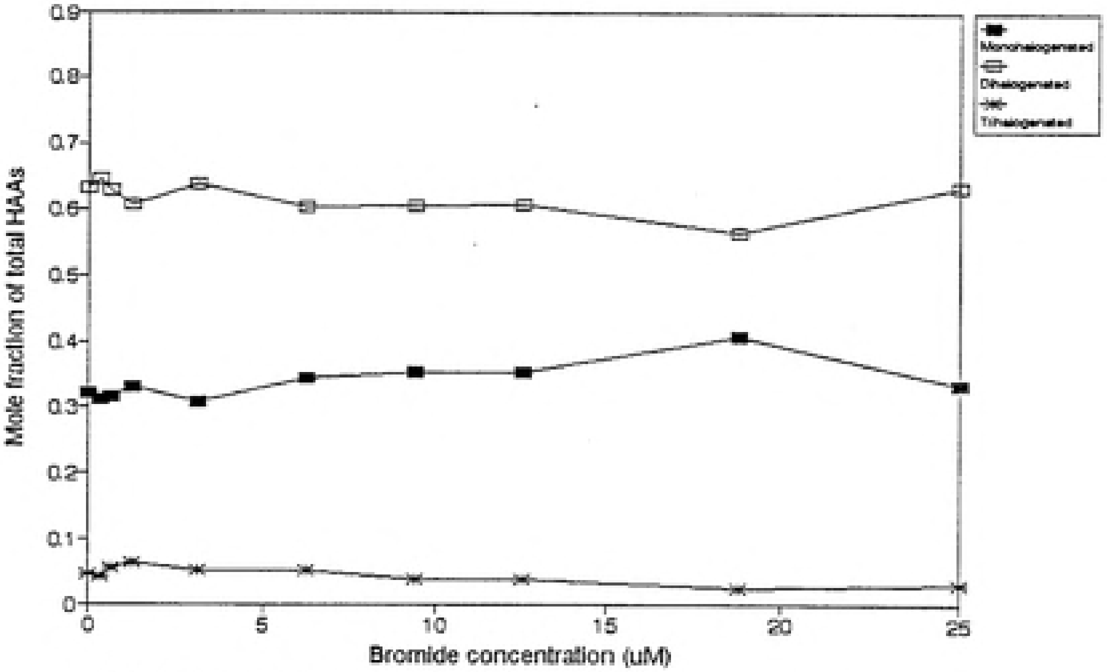
Distribution of the HAAs among the mono-, di-, and trihalogenated species is shown in Figure 4.43. The distribution of species during chloramination differed greatly from the distributions observed from chlorination. It is apparent that in the chloraminated extracts the trihalogenated species accounted for less than 17% of the total HAAs in Myrtle Beach extracts and less than 7% of the total in Palm Beach extracts. This is in contrast to the observation that the trihalogenated species constituted approximately 65% of the total HAAs in chlorinated waters. In the chloraminated waters, the dihalogenated species (primarily DCAA) accounted for the greatest fraction of the total HAAs (66-87% in Myrtle Beach extracts and 57-65% in Palm Beach extracts). Formation of the monohalogenated species was also observed, and they accounted for 13-16% of the total HAAs in Myrtle Beach extracts and 31-41% of the total in Palm Beach extracts.

Bromine and chlorine incorporation

Total bromine and chlorine incorporation into the HAAs in chloraminated waters is shown in Figure 4.44. Although bromine incorporation increases with increasing bromide concentration, total chlorine incorporation into the HAAs is greater that total bromine incorporation over the entire range of bromide concentrations studied.

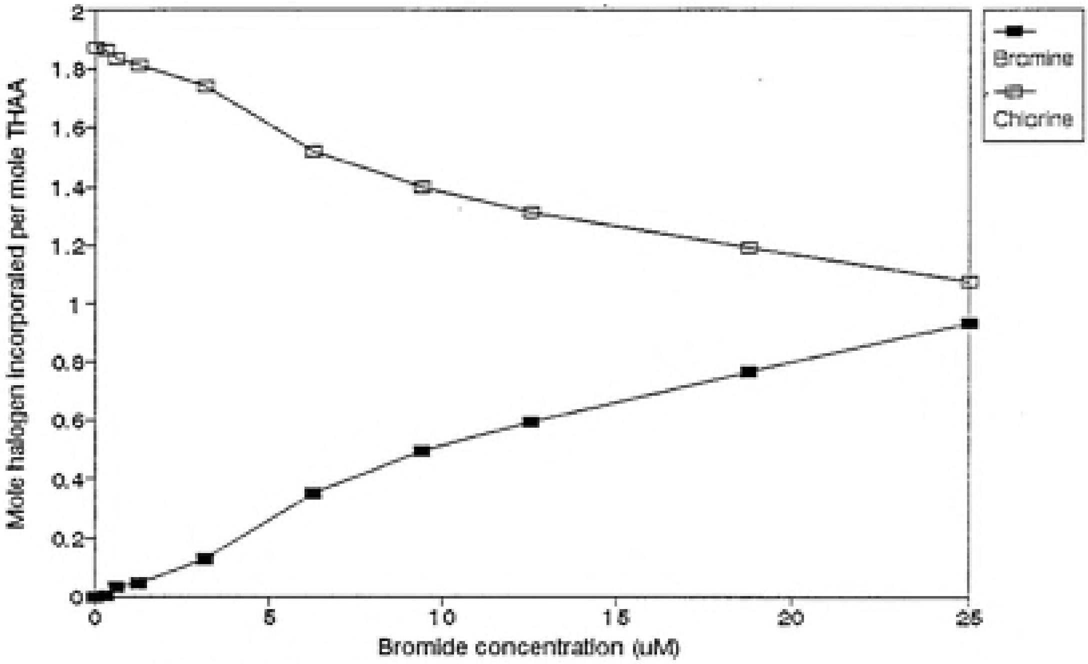


(a) Myrtle Beach extract

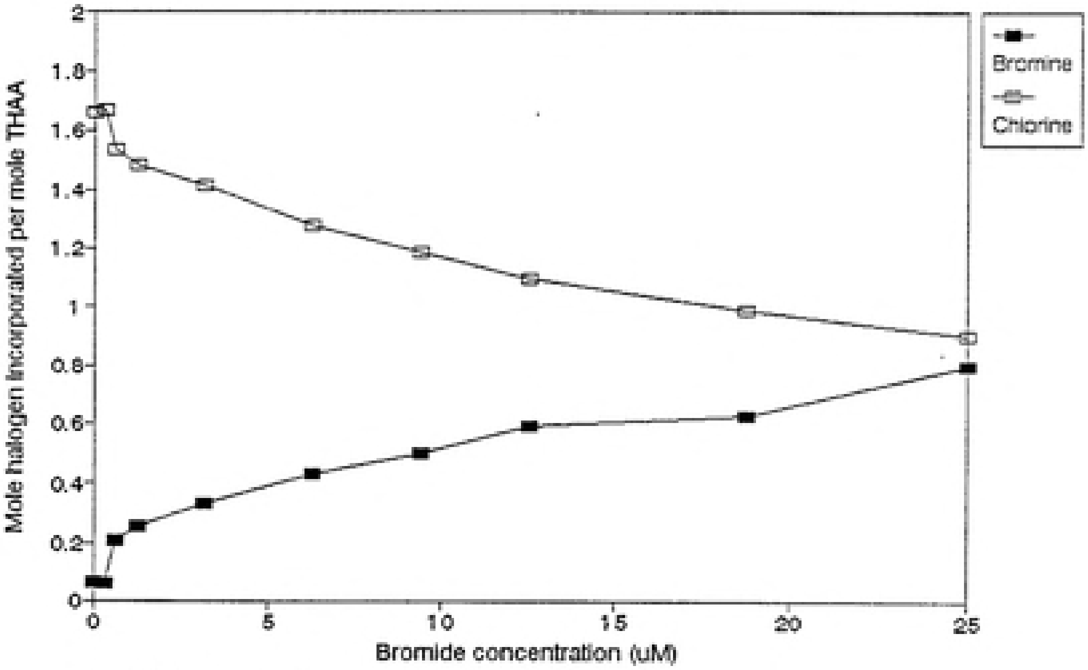


(b) Palm Beach extract

Figure 4.43. Distribution of HAAs into mono-, di-, and trihalogenated species in extracts chloraminated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.44. Bromine and chlorine incorporation into HAAs in extracts chloraminated at pH 8.

In contrast to chlorinated waters in which each mole of total HAAs contained approximately 2.6 moles of total halogen, the HAAs produced from chloramination contained approximately 1.7-1.9 moles of total halogen per mole of total HAAs in the range of bromide concentrations studied. This is a reflection of the observation that chlorination favored formation of the tri- and dihalogenated species, while chloramination favored formation of the di- and monohalogenated species.

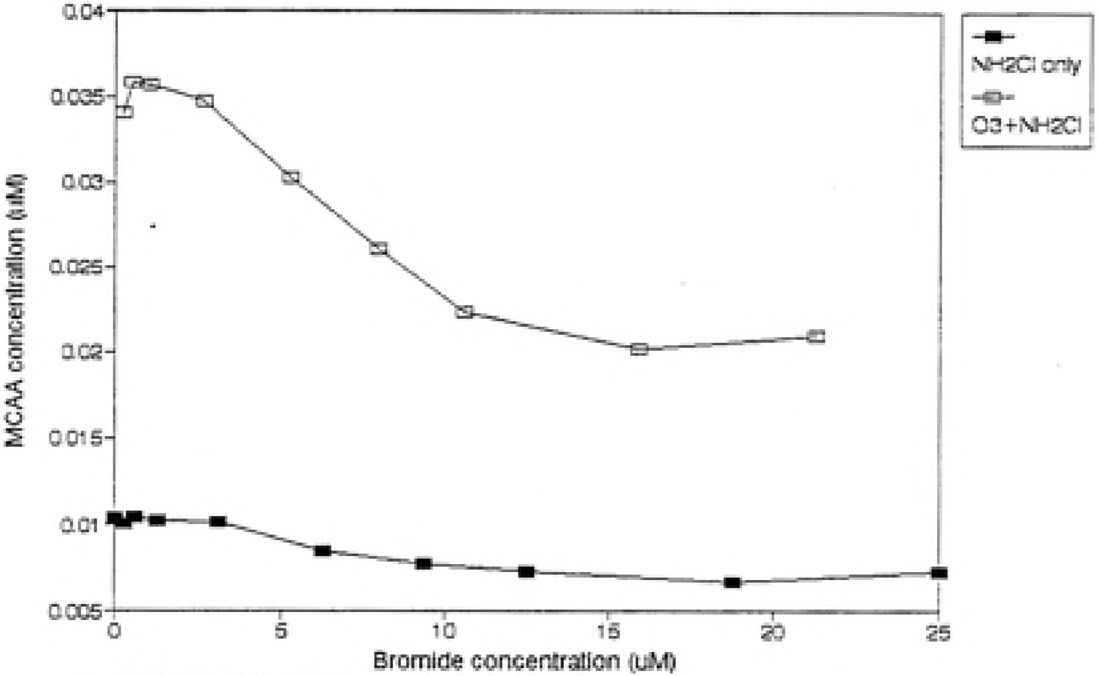
Influence of pre-ozonation on HAA formation and speciation in chloraminated waters

Formation of individual species

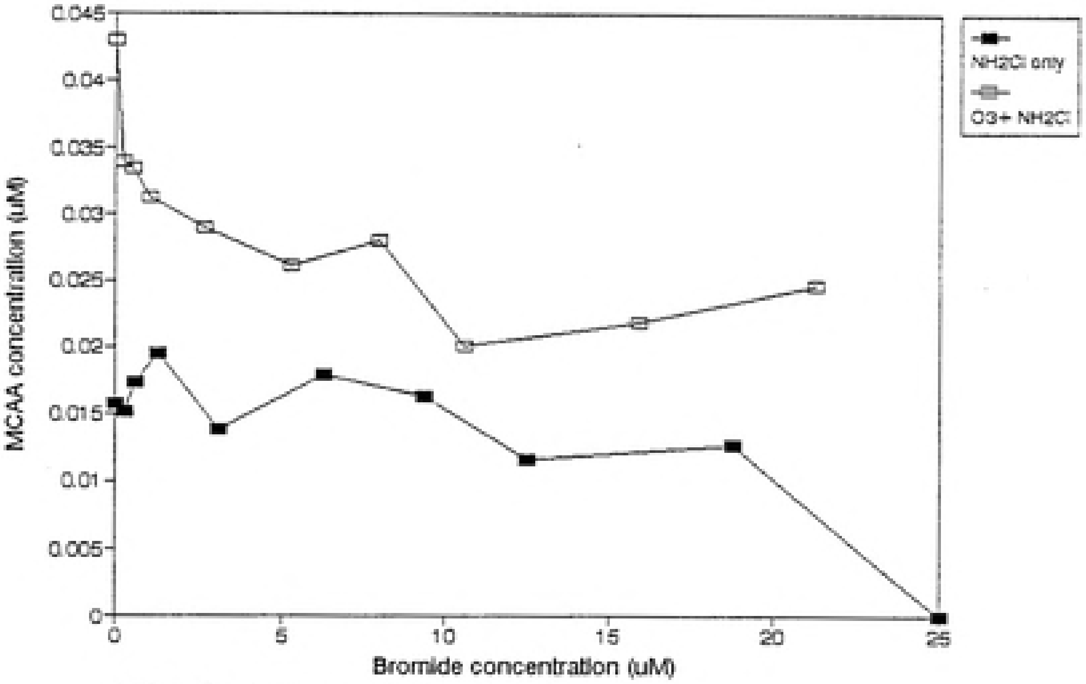
In both Myrtle Beach and Palm Beach waters, pre-ozonation enhanced the formation of MCAA and DCAA. MBAA formation was enhanced by pre-ozonation at high bromide concentrations (>9 µM) in both waters, and DBAA formation was enhanced in Palm Beach samples containing more than 9 µM Br^-; DBAA formation appeared to be unaffected by pre-ozonation in Myrtle Beach samples. These results are shown in Figures 4.45-4.48. It is important to note that although pre-ozonation enhanced the formation of some species, the absolute concentrations of individual species did not exceed 0.1 µM (13 µg/L) in any chloraminated samples.

Total HAA formation

Total HAA formation was enhanced by pre-ozonation in both waters compared to chloramination alone. The effect of pre-ozonation on THAA formation in chloraminated waters is shown in Figure 4.49. Total HAA formation in pre-ozonated, chloraminated

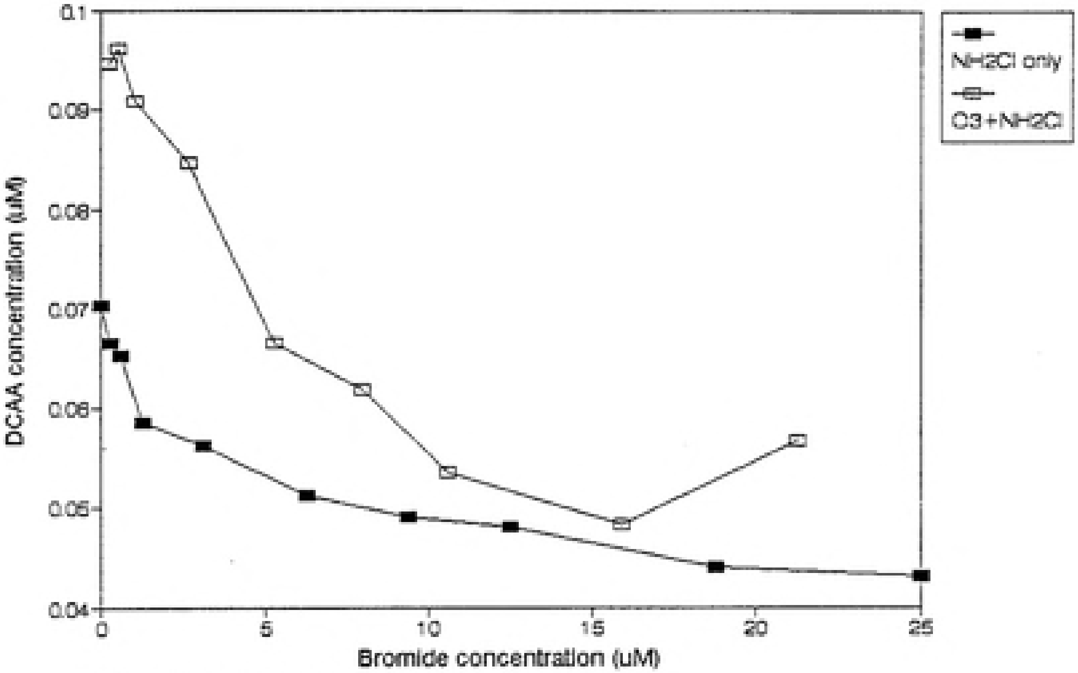


(a) Myrtle Beach extract

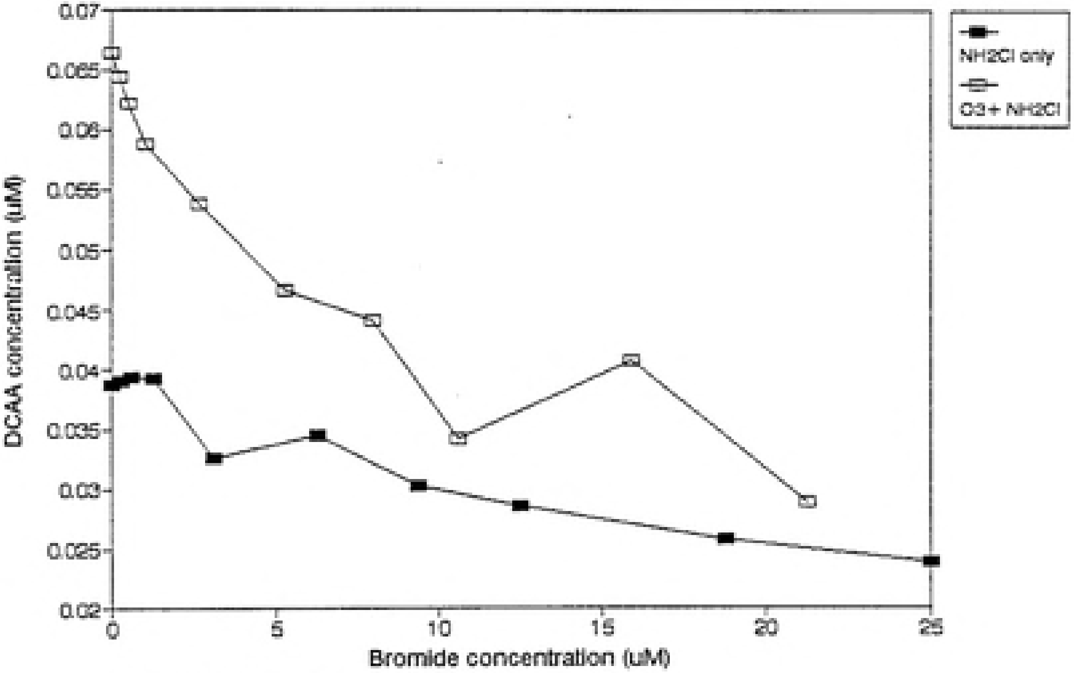


(b) Palm Beach extract

Figure 4.45. Influence of ozone on MCAA formation in extracts chloraminated at pH 8.

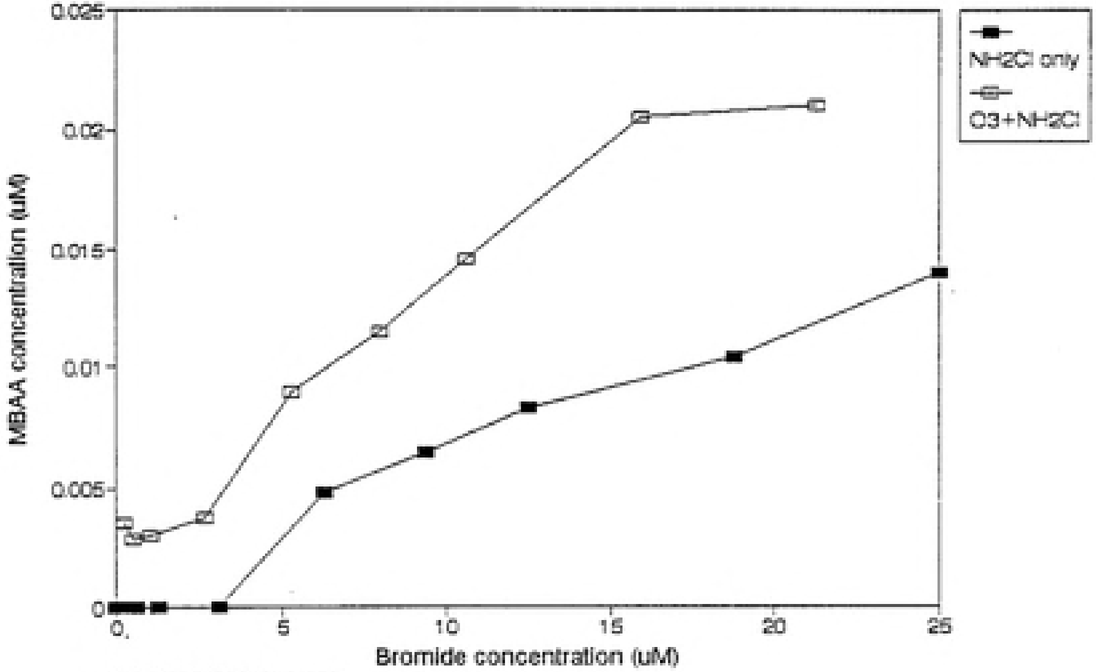


(a) Myrtle Beach extract

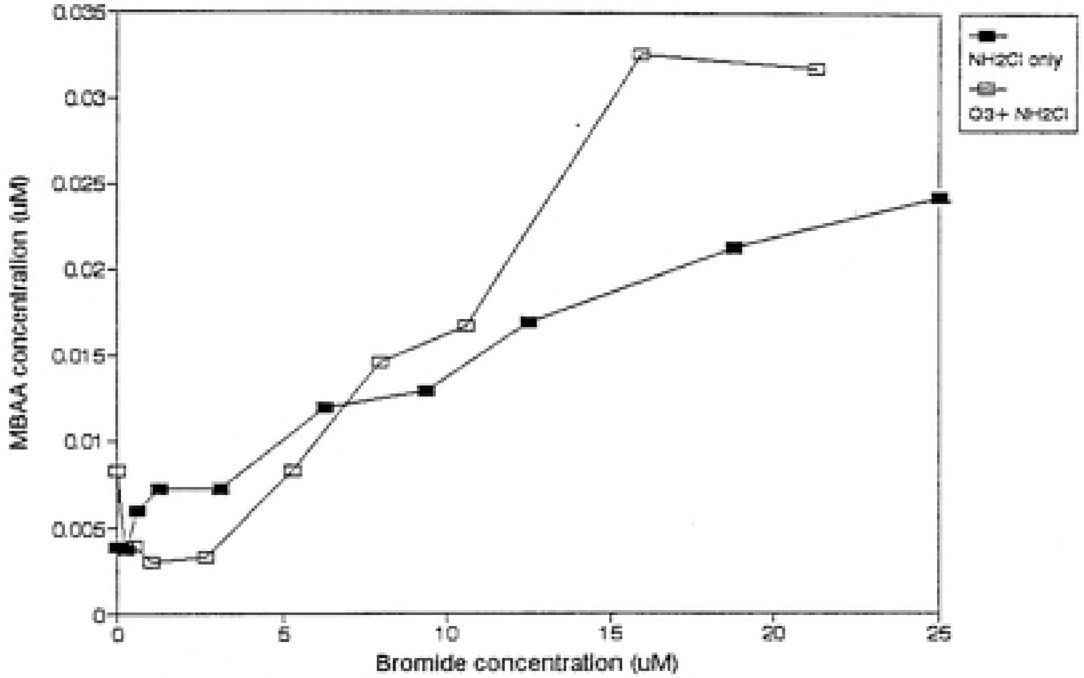


(b) Palm Beach extract

Figure 4.46. Influence of ozone on DCAA formation in extracts chloraminated at pH 8.

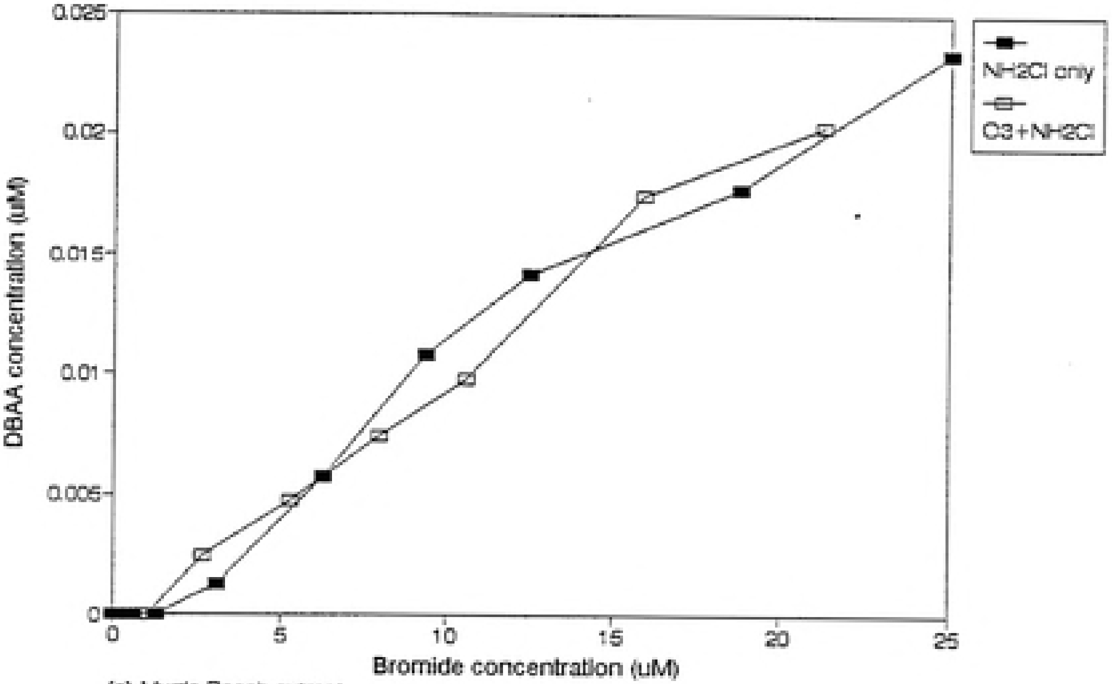


(a) Myrtle Beach extract

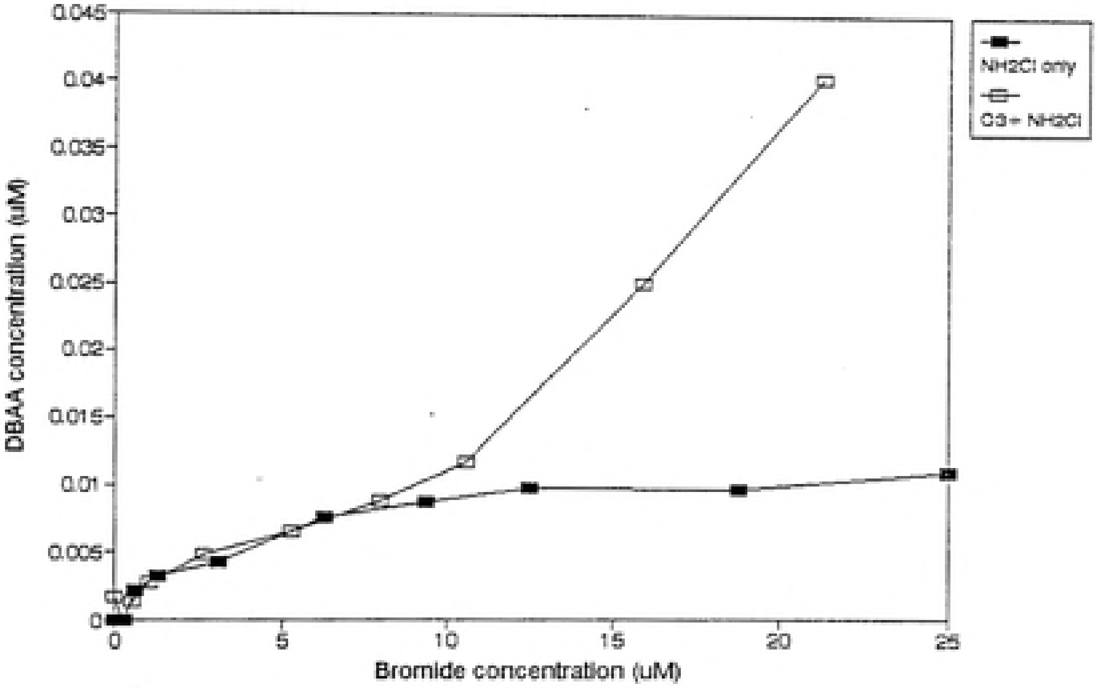


(b) Palm Beach extract

Figure 4.47. Influence of ozone on MBAA formation in extracts chloraminated at pH 8.

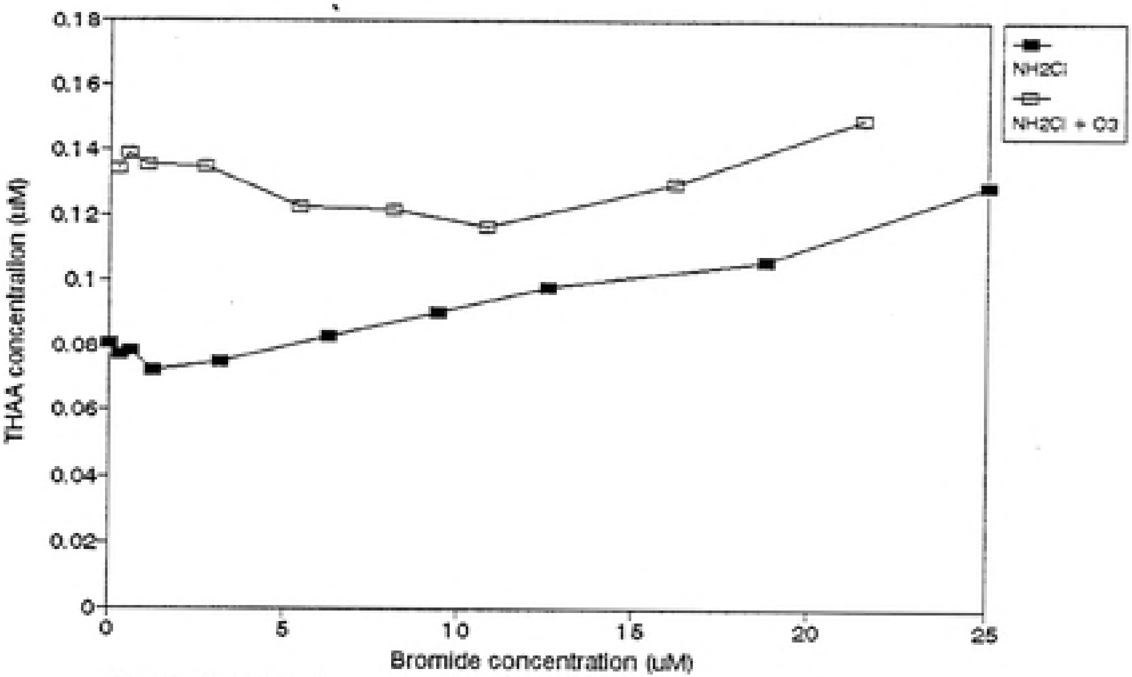


(a) Myrtle Beach extract

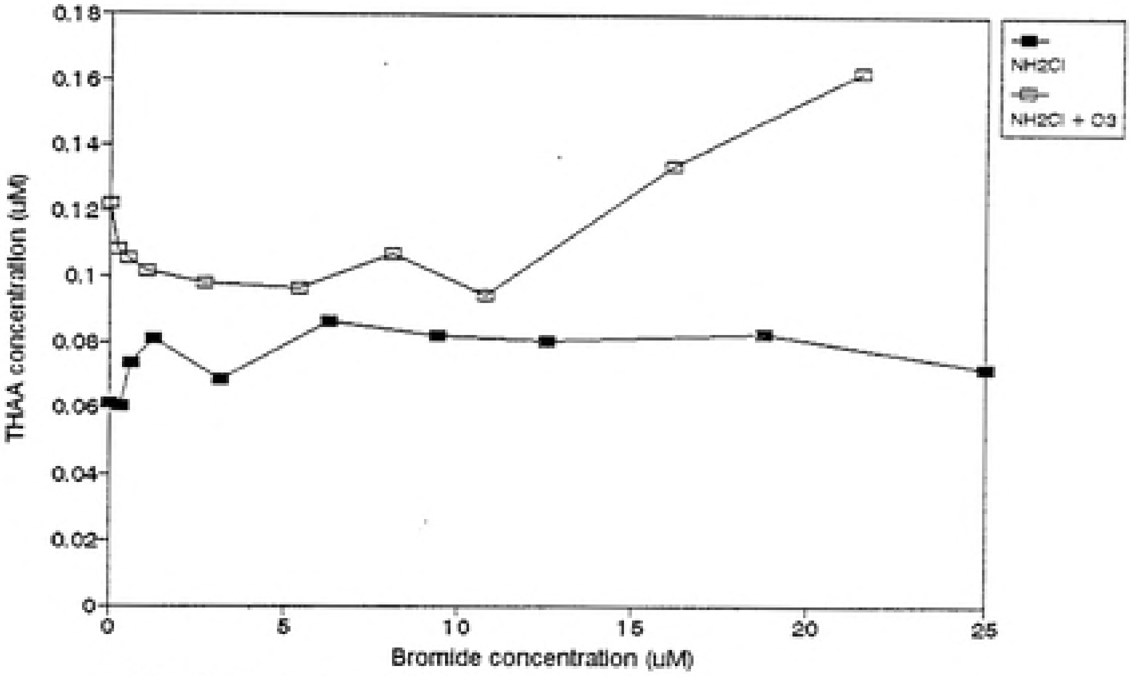


(b) Palm Beach extract

Figure 4.48. Influence of ozone on DBAA formation in extracts chloraminated at pH 8.



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.49. Influence of pre-ozonation on total HAA formation in chloraminated extracts.

waters was still decreased by approximately 90% compared to THAA formation in chlorinated waters.

Distribution of individual species

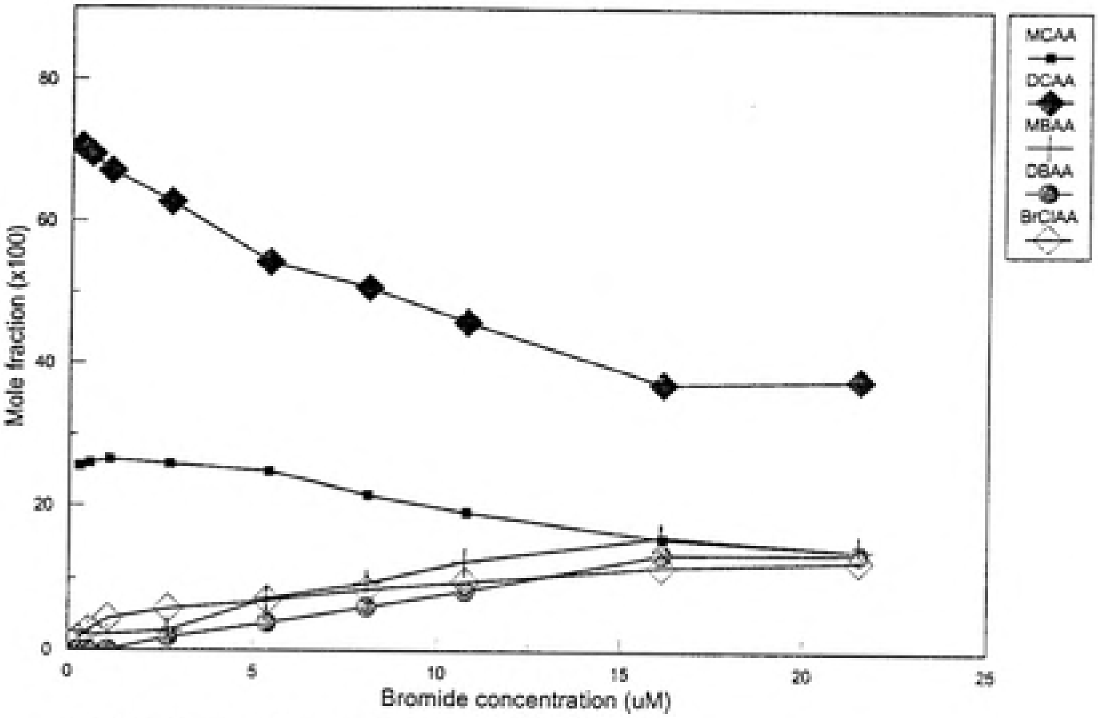
Distributions of individual HAA species in ozonated, post-chloraminated waters are shown in Figure 4.50. Again, DCAA was the principal species formed in nearly all cases. MCAA constituted a more significant fraction of the total HAAs in pre-ozonated samples compared to samples that received chloramine alone (see Figure 4.42). Palm Beach extracts appeared to be more susceptible than Myrtle Beach extracts to formation of brominated HAAs, and MBAA and DBAA individually constituted approximately 20-25% of the total HAAs in Palm Beach samples containing high concentrations of bromide (>15 µM).

Distribution of HAAs among mono-, di-, and trihalogenated species

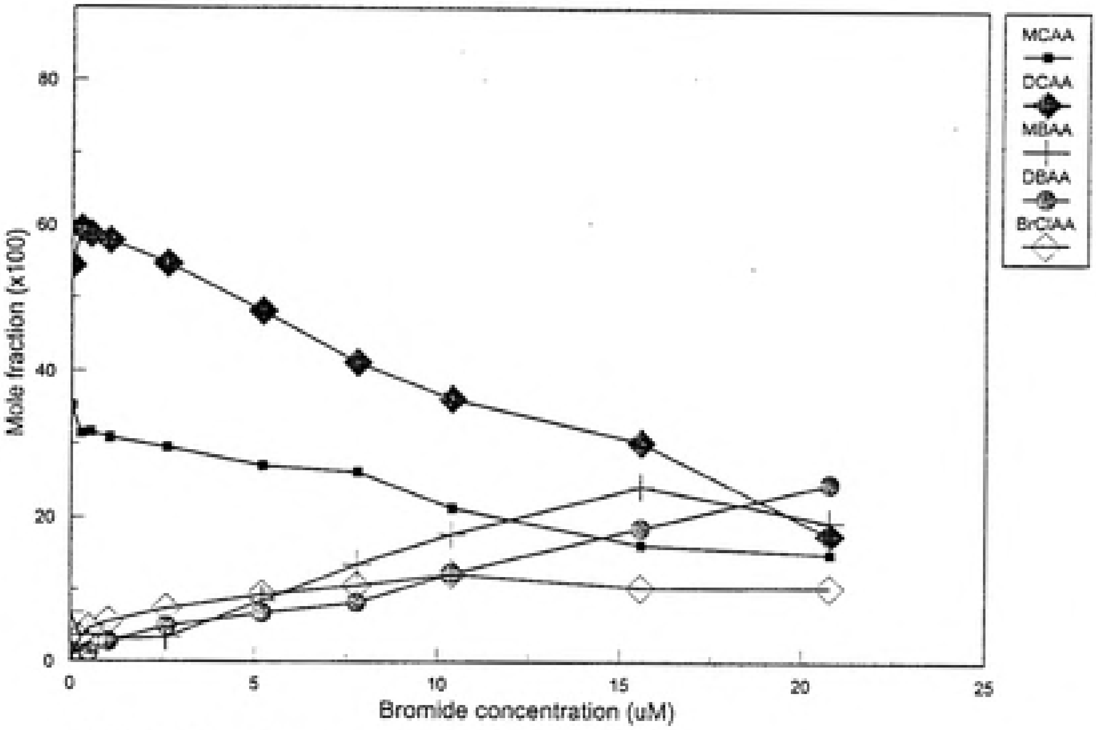
Speciation into dihalogenated and monohalogenated species remained fairly constant over the range of bromide concentrations studied. In Myrtle Beach extracts, pre-ozonation appeared to increase the significance of the contribution of monohalogenated species to total HAAs; however, in Palm Beach extracts, pre-ozonation did not have a pronounced effect on this speciation. Speciation of the HAAs into mono, di and trihalogenated species is shown in Figure 4.51.

Bromine and chlorine incorporation

The two extracts exhibited differing behavior in terms of bromine and chlorine incorporation. In plotting bromine and

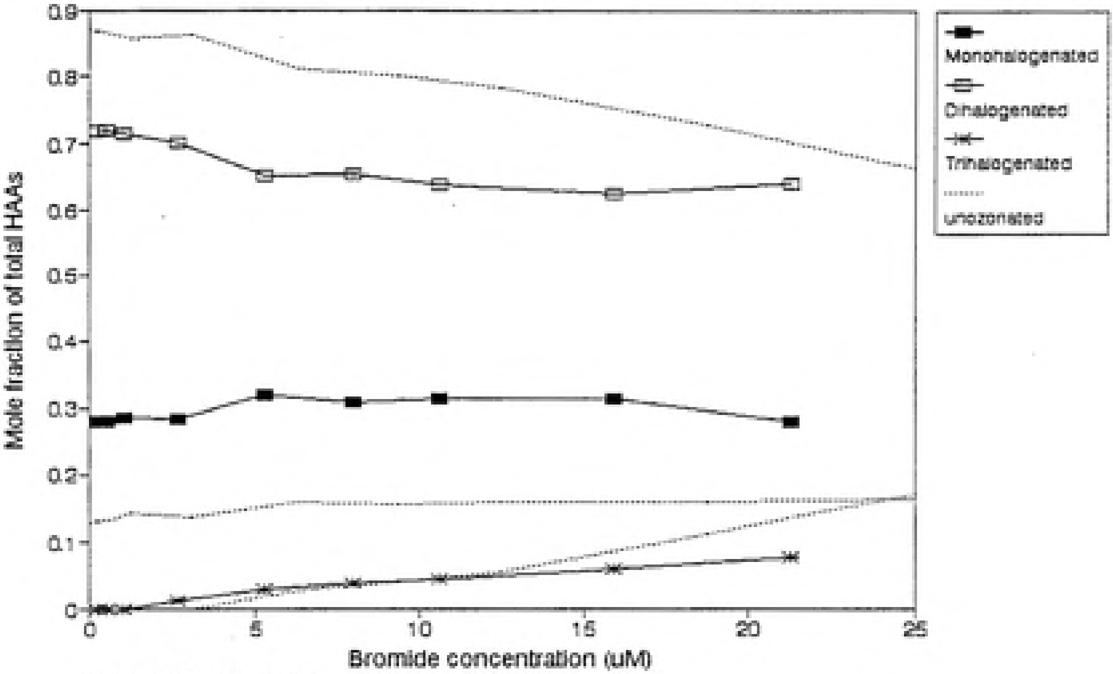


(a) Myrtle Beach extract

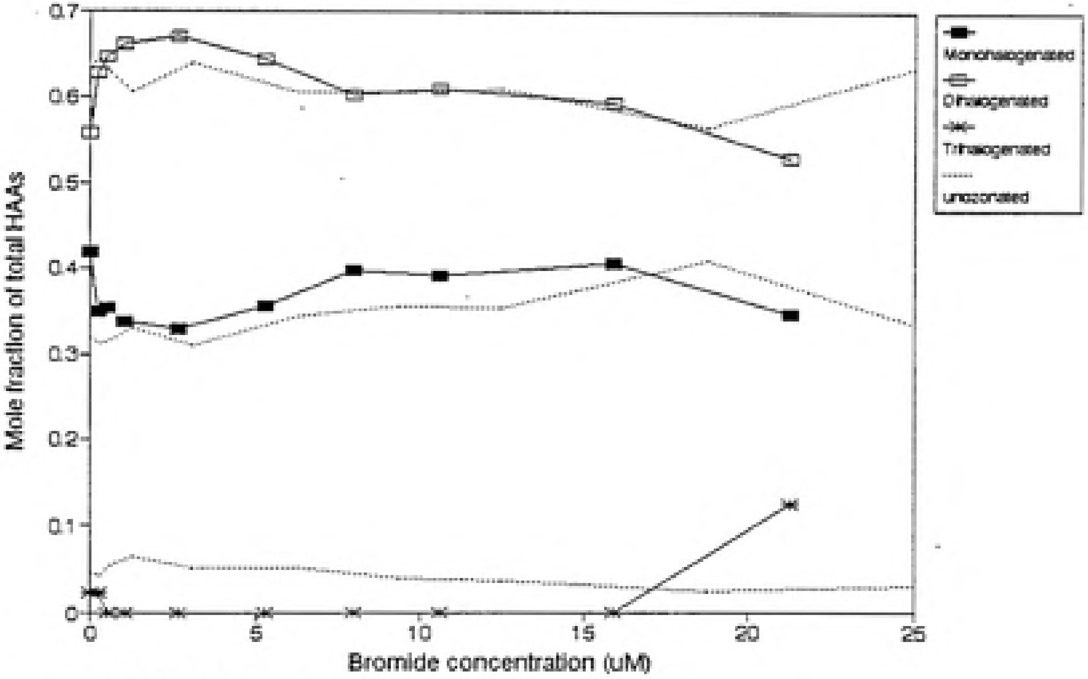


(b) Palm Beach extract

Figure 4.50. Distribution of individual HAA species in pre-ozonated extracts chloraminated at pH 8.



(a) Myrtle Beach extract



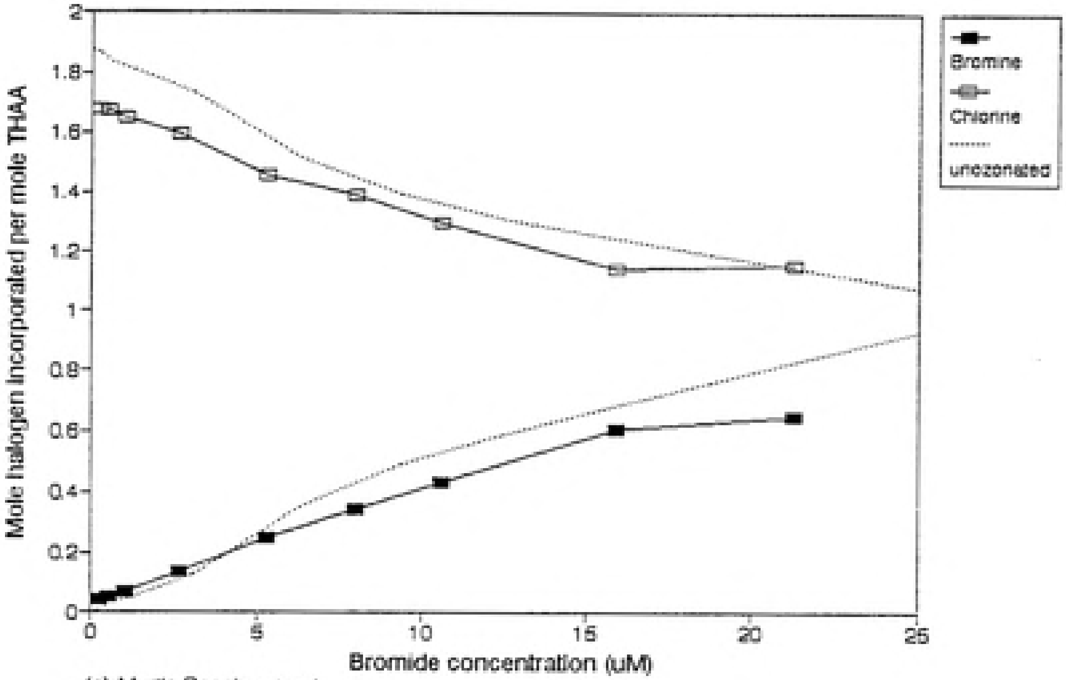
(b) Palm Beach extract

Figure 4.51. Distribution of HAAs into mono-, di-, and trihalogenated species in pre-ozonated extracts chloraminated at pH 8.

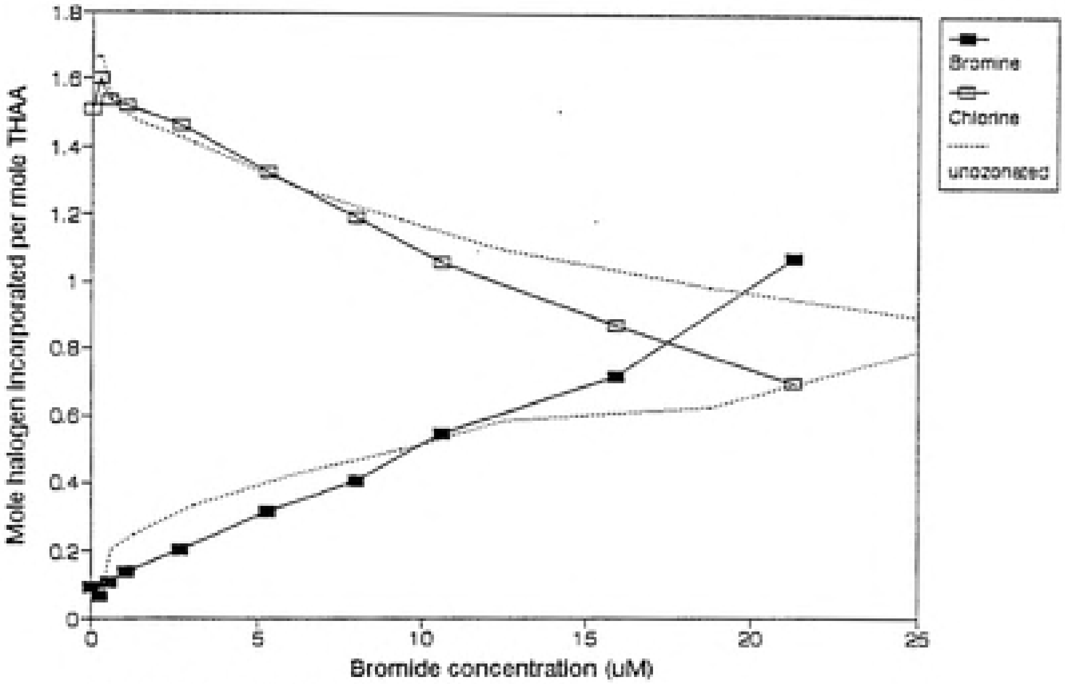
chlorine incorporation normalized for total µM HAA formation (Figure 4.52), pre-ozonation appears to enhance bromine incorporation into HAAs in Palm Beach extracts containing high concentrations of bromide (>12.5 µM). On the other hand, bromine incorporation into the HAAs in chloraminated Myrtle Beach extracts does not appear to be affected much by pre-ozonation.

Implications of the work

Haloacetic acids in drinking water are currently not regulated; however, there is concern about their risk to human health, and a maximum contaminant level (MCL) for "total" HAAs is expected to be part of the Disinfectants/Disinfection By-products Rule to be proposed by the USEPA this year. The expected MCL for "total" HAAs is 60 µg/L, and this figure includes only five of the HAA species: MCAA, DCAA, TCAA, MBAA and DBAA. An important question at the outset of this research was whether other HAA species, particularly the three bromo-chloro species, may be important species formed in chlorinated waters. The occurrence of bromo-chloro species in finished drinking waters is presently not known primarily because chemical standards for $BrCl_2AA$ and Br_2ClAA are not commercially available, and a standard for BrClAA has become available only recently. The results of this study suggest that the bromo-chloro species, particularly $BrCl_2AA$, may be a concern in chlorinated waters containing both low and high concentrations of bromide. The health effects of the bromo-chloro HAAS are presently not known, and the findings suggest that health effects studies of these compounds should be



(a) Myrtle Beach extract



(b) Palm Beach extract

Figure 4.52. Bromine and chlorine incorporation into HAAs in pre-ozonated extracts chloraminated at pH 8.

conducted.

Analysis of finished drinking water samples from the Metropolitan Water District of Southern California supported these laboratory findings. The source water at this plant contained 2.75 µM Br^- (0.22 mg/L) and 3.32 mg/L TOC, and the water was treated both with chlorine and chloramines. The sum of the nine HAA species in the finished water was 52.6 µg/L. The five HAAs currently being considered for regulation accounted for only 54% of this total on a weight basis, while the three bromochloro species accounted for 46% of the total HAAs. These results are shown in Table 4F.

Table 4F. HAA concentrations and distributions in finished drinking water from the Metropolitan Water District of Southern California

Analyte	Conc (µg/L)	Mole fraction of total HAAs
MCAA	1.17	0.04
DCAA	7.02	0.19
TCAA	5.07	0.11
MBAA	1.78	0.04
DBAA	9.18	0.14
TBAA	BDL	0
BrClAA	10.8	0.21
BrCl2AA	12.2	0.20
Br2ClAA	5.37	0.07
Total HAAs	52.6	

Although disinfection by-product regulations are currently based on concentrations by weight, this may be a misleading approach since different compounds have different weights. In Table 4F the distributions of species measured in the finished drinking water samples are also given in terms of mole fractions of the total HAAs. The bromo-chloro species constitute nearly 50% of the total HAAs on a molar basis.

The present study suggests that pre-ozonation followed by chlorination is not likely to be an effective means of controlling HAA formation in waters typically encountered in practice (containing less than 3 μM Br^-). Chloramination and pre-ozonation followed by chloramination clearly appear to be favorable methods for minimizing HAA formation (total HAA decreases of approximately 90% were observed relative to chlorinated waters).

This research suggests that different waters may behave similarly with respect to HAA speciation as a function of bromide concentration. This work, along with further study of the effects of total organic carbon concentration and chlorine dose on the distribution of HAAs may provide a framework for mathematically modeling HAA speciation in chlorinated waters.

The present work may also provide insights into the chemical pathways by which HAAs are formed, suggesting that each of the trihalogenated species are formed through the same pathways, each of the dihalogenated species are formed through the same pathways, and each of the monohalogenated species are formed through the same pathways. Further investigations of the effects of chlorine dose and pH of chlorination may help to elucidate the relationships between the mono-, di-, and trihalogenated species.

Chapter 5
Conclusions and Recommendations

Conclusions

The primary goal of this study was to assess haloacetic acid speciation resulting from chlorination, ozonation and chloramination of bromide-containing waters. Secondary goals included assessing the effects of the pH of chlorination and the method of chemical treatment on quantitative formation of each of the nine HAA species, as well as investigating the influence of the source of natural organic material on HAA formation and speciation.

The results of this study indicate that bromide ion concentration is an important factor in HAA speciation in chlorinated waters, with high bromide concentrations favoring formation of the more highly brominated species. The three bromo-chloro species are readily formed during chlorination of bromide-containing waters, and it appears that $BrCl_2AA$ will be the most abundant of the bromo-chloro species formed in waters typically encountered in practice (containing less than 12 µM Br^-). Significant formation of the bromo-chloro species may be observed even in waters containing low concentrations of bromide; in this study these species constituted at least 10% of the total HAAs in waters containing as little as 1.2 µM Br^-.

Distribution of the haloacetic acids among mono-, di-, and trihalogenated species during chlorination of humic substances appears to be independent of bromide ion concentration. Each of the trihalogenated species may be formed through similar chemical pathways, and likewise for the mono- and dihalogenated species.

Under the conditions of this study, the distribution of species in chlorinated waters was approximately 65% trihalogenated species, 33% dihalogenated species, and 2% monohalogenated species. This partitioning was similar in waters chlorinated at pH 8 and in waters chlorinated at pH 6. The average halogen composition of the HAAs in chlorinated waters was approximately 2.6 moles of halogen per mole of total HAAs.

Changing the pH of chlorination from pH 8 to pH 6 enhances the formation of several HAA species, most notably DBAA, BrClAA, $BrCl_2AA$, and Br_2ClAA. Distribution of the HAAs among individual species is altered only slightly, however, by this change in pH. In addition, bromine incorporation into the HAAs does not appear to be significantly affected by lowering the pH of chlorination from pH 8 to pH 6.

Under the conditions of this study, ozonation alone resulted in little formation of brominated HAAs; however, pre-ozonation enhanced bromine incorporation into the HAAs produced by subsequent chlorination compared to chlorination alone. In this study pre-ozonation followed by chlorination at pH 8 was not an effective means of controlling HAA formation in waters containing less than 3 µM Br^-.

Total HAA formation is dramatically decreased (~90% in this study) in chloraminated waters compared to chlorinated waters, both in the presence and absence of bromide ion. DCAA is the principal species formed in chloraminated waters. Chloramination of bromide-containing waters results in some formation of species containing bromine, primarily MBAA, DBAA and BrClAA; however, little formation of trihalogenated species is observed from chloramination both in the presence and absence of bromide. The average halogen composition of the HAAs in chloraminated waters is approximately 1.7-1.9 moles of halogen per mole of total HAAs.

Pre-ozonation followed by chloramination enhances total HAA formation compared to chloramination alone; however, total HAA formation from pre-ozonation followed by chloramination is decreased by approximately 90% compared to total HAA formation from chlorination.

Although the two sources of natural organic material produce different amounts of total HAAs, they show similar behavior with respect to HAA speciation, both in terms of distributions among individual species and distributions among mono-, di-, and trihalogenated species. The effect of bromide ion on HAA speciation may be independent of the source of natural organic material.

Recommendations for future research

Based on the findings that the bromo-chloro HAAs may be important species formed in chlorinated drinking waters, it is recommended that the health effects of these compounds should be investigated. In addition, the nationwide occurrence of these compounds in finished drinking waters needs to be assessed.

In the present study, all experiments were conducted at a single TOC concentration and a single chlorine dose. It is expected that the ratios of Br^-/TOC and Br^-/HOCl will influence HAA speciation. Thus the effects of variations in TOC concentration and chlorine dose on HAA speciation in bromide-containing waters should be investigated.

Some striking similarities in HAA speciation were observed between the chlorinated Myrtle Beach and Palm Beach extracts, both in terms of distributions of individual species as functions of bromide ion concentration and in terms of distributions of species among mono-, di-, and trihalogenated species. These are exciting findings; however, a greater number of humic substances need to be investigated to ascertain whether these distributions are independent of the source of NOM. Identification of effects that are consistent from one water to the next will provide a better understanding of haloacetic acids.

In this study it was observed that bromide ion concentration did not affect the distribution of the HAAs among the mono-, di-, and trihalogenated species in chlorinated waters even though the distributions of individual species formed in low-bromide waters were quite different from those in high-bromide waters. It is expected that the monohalogenated species are formed through the same chemical pathways, and likewise for the di- and trihalogenated species. Previous studies have suggested that pH and chlorine dose affect relative formation of DCAA and TCAA. Studying the effect of these two factors on HAA speciation in bromide-containing waters may help to provide an understanding of whether the pathways through which the mono-, di-, and trihalogenated species are formed are related to each other.

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Appendix A

Analysis of Haloacetic Acids

A modification of the method of McGuire et al. (48)

HAAs measured: MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BrClAA, $BrCl_2AA$, Br_2ClAA

Internal standard: 1,2-dibromopropane

Surrogate recovery standard: 2,3-dibromopropionic acid

Sources and purities of analytical standards:

MCAA, DCAA, TCAA,
MBAA, DBAA, BrClAA: Supelco "Haloacetic Acids Mix 552", lots# LA36722 & LA36723, solution containing 2 g/L of each HAA in MtBE, 97+% purity.

TBAA: Aldrich, lot# AX 06928PW, crystalline solid, 99% purity.

$BrCl_2AA$: Synthesized at UNC-CH, crystalline solid, estimated 97% purity (see Appendix C).

Br_2ClAA: Synthesized at University of Massachusetts, crystalline solid, estimated 91% purity (see Appendix C).

1,2-dibromopropane: Aldrich, lot# 02614TT, liquid, 97% purity.

2,3-dibromopropionic acid: Aldrich, lot# AY 11025LX, crystalline solid, 99% purity.

Prepare stock solutions of HAA standards:

> Gravimetrically prepare 1-10 g/L solutions of TBAA, $BrCl_2AA$ and Br_2ClAA in 2 ml MtBE. Store at -15°C for no longer than 2 weeks. Store 2 g/L Supelco mixture at -15°C for no longer than 3 months.

Prepare stock solutions of surrogate and internal standard:

> Gravimetrically prepare 5-15 g/L solutions in 10 ml methanol. Store at -15°C.

Prepare HAA calibration solution I by diluting 2 g/L Supelco mixture to 0.1 g/L in 2 ml methanol.

Prepare HAA calibration solution II by diluting TBAA, $BrCl_2AA$ and Br_2ClAA stock solutions to 0.1 g/L in 2 ml methanol.

Prepare dilution of surrogate at 0.02 g/l in 10 ml methanol.

Prepare MtBE extraction solvent with 35 µg/L internal standard.

Preparation of diazomethane:

- -- set up MNNG Diazomethane-generation apparatus on ice
- -- set up 5 N NaOH bath
- -- add 5 ml clean MtBE to outer tube of generator
- -- add small amount (<150 mg) 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) to inner tube of generator (caution: MNNG is a potent mutagen)
- -- clamp generator, close screw cap top with teflon-lined septa, let cool on ice for 15 min.
- -- add 1 ml 5 N NaOH drop-wise to inner tube with gas tight syringe (be careful of pressure build up)
- -- allow diazomethane to form for 30-45 min. (on ice)
- -- puncture septa with syringe to release pressure
- -- transfer diazomethane to 40 ml vial on ice, store in explosion-proof freezer, preferrably not longer than 1 day
- -- place all diazomethane glassware and MNNG spatula in 5 N NaOH bath for 30 min. (to destroy any unreacted MNNG)

Preparation of calibration standards:

- -- prepare standards in 100 ml deionized, organic-free water
- -- add appropriate amount of HAA calibration solution to water to prepare a series of 8-10 standards ranging in concentration from 0-150 µg/L. Prepare two separate series of standards- one from HAA calibration solution I and the other from solution II
- -- measure 20 ml of standard in a graduated cylinder, transfer to a 40 ml vial (prepare in duplicate or triplicate)
- -- add 20 µl 0.02 g/L surrogate to each vial
- -- place vials in refrigerator for at least 15 min.

Preparation of samples:

- -- measure out 20 ml sample, transfer to 40 ml vial
- -- add 20 µl 0.02 g/L surrogate to each vial
- -- place vials in refrigerator for at least 15 min.

Extraction:

- -- add 1 ml concentrated H_2SO_4 to each vial
- -- add 5 ml MtBE (containing internal standard) to each vial
- -- add 6 g sodium sulfate (previously baked at 500°C for 24 hrs) to each vial
- -- vortex each vial 1 min.

Appendix A, cont.

Derivatization:

For each sample:
- -- transfer 2 ml of the ether layer to a 2 ml volumetric flask
- -- place volumetric flasks on ice
- -- add 175 µl cold diazomethane to each volumetric flask
- -- allow diazomethane to react for 30 min. (on ice)
- -- add a few crystals of silica gel (previously activated by heating at 180°C for 24 hrs) to quench excess diazomethane
- -- if volumetric flasks have to be reused, rinse with methanol, acetone, methanol

Transfer samples to autovials.

Quench left-over diazomethane reagent with glacial acetic acid.

Analyze on HP-5890 Series II gas chromatograph with electron capture detector.

Column: DB1701 (J&W Scientific), 30 m length, 0.25 mm ID, 0.25 µm film thickness

Temperature program:

40°C --------> 66°C --------> 150°C --------> 210°C
2 min 2°C/min 6°C/min 2 min 20°C/min 3 min

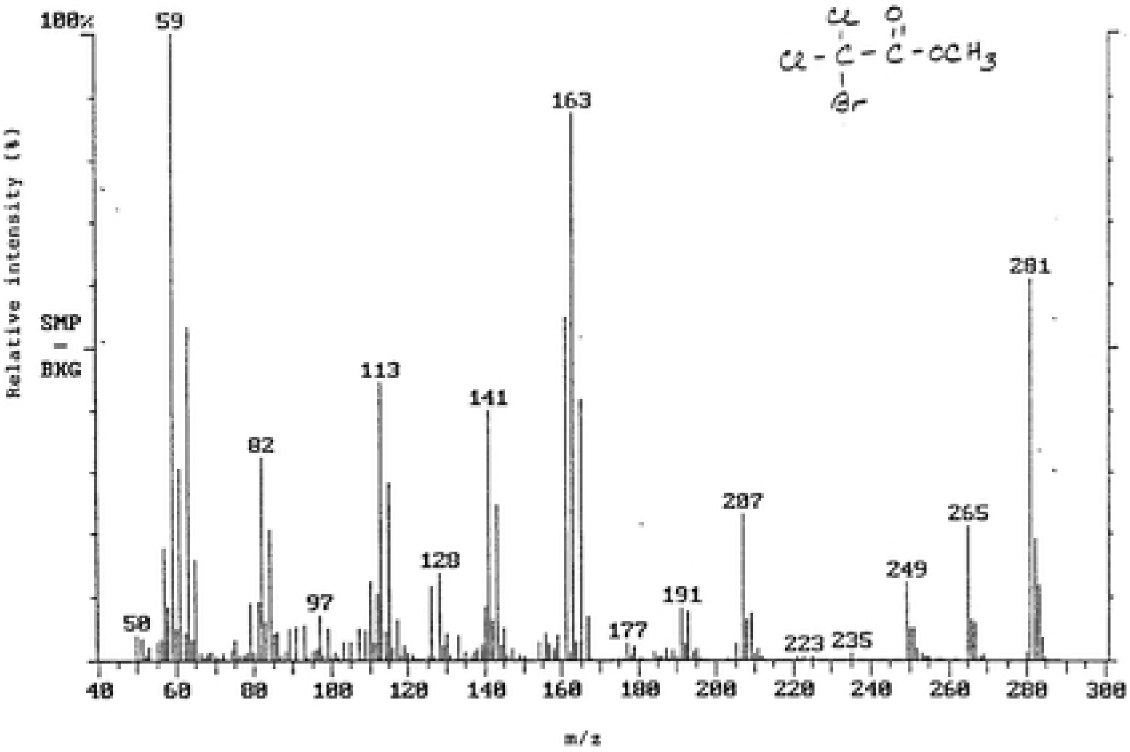
injector temperature = 157°C, detector temperature = 300°C
flow rate = 1 ml/min, injection volume = 2 µl

Relative retention times:

	$\underline{RR_t}$
MCAA	0.776
DCAA	1.125
TCAA	1.399
MBAA	1.068
DBAA	1.905
TBAA	2.432
BrClAA	1.577
$BrCl_2AA$	1.844
Br_2ClAA	2.165

Appendix B

Mass Spectrum of Synthesized Bromodichloroacetic Acid Methyl Ester



Appendix C

Purity of Bromodichloroacetic Acid and Dibromochloroacetic Acid

Bromo-dichloroacetic acid

Prepare 500 µg/L BrCl$_2$AA in MtBE, methylate, analyze on GC.

Prepare 0, 50, 100 µg/L HAA standards in MtBE, methylate, analyze.

This analysis was initially performed on 1/31/93, then repeated on 2/26/93.

RA = relative area

Calibration curve equations:

For sample #1 (1/31/93):

[DCAA] = RA/0.026218
[BrClAA] = RA/0.03498
[DBAA] = RA/0.034268

For sample #2 (2/26/93):

[DCAA] = RA/0.018918
[BrClAA] = RA/0.032308
[DBAA] = RA/0.025696

Impurities in 500 µg/L BrCl$_2$AA samples

	DCAA	BrClAA	DBAA
Relative area			
Sample 1	0.388	0	0.0299
Sample 2	0.168	0.193	0.0445
Conc. (µg/L)			
Sample 1	14.80	0.00	0.87
Sample 2	8.88	5.97	1.73
Avg. conc.	11.84	2.99	1.30
% impurity in 500 µg/L sample	2.37	0.60	0.26

Total % impurities = 3.23

Dibromo-chloroacetic acid

Prepare 1000 µg/L Br$_2$ClAA in MtBE, methylate, analyze on GC

Prepare 0, 100, 250 µg/L HAA standards in MtBE, methylate, analyze on GC.

Appendix C, cont.

This analysis was initially performed on 7/7/93, then repeated on 7/11/93.

Calibration curve equations:

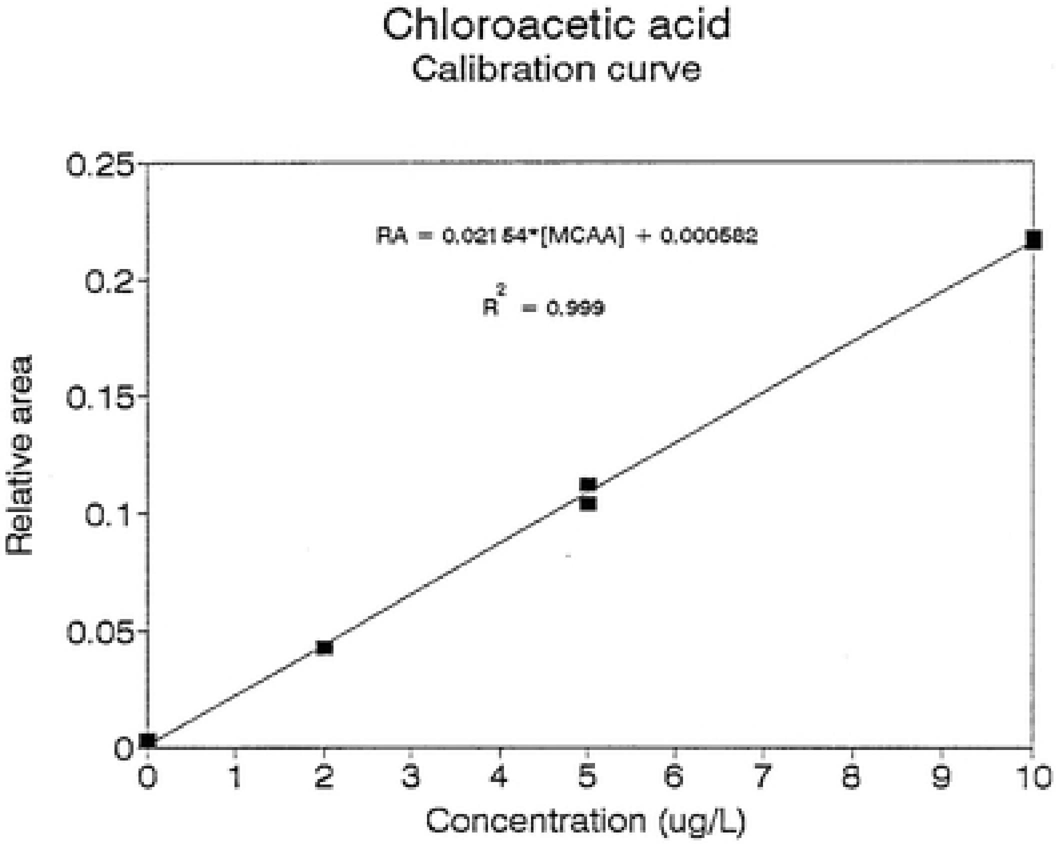
For samples #1-2 (7/7/93):	For samples #3-4 (7/11/93):
[TBAA] = RA/0.008582	[TBAA] = RA/0.007701
[BrClAA] = RA/0.048143	[BrClAA] = RA/0.047689
[DBAA] = RA/0.055081	[DBAA] = RA/0.052245

Impurities in 1000 µg/L Br_2ClAA samples

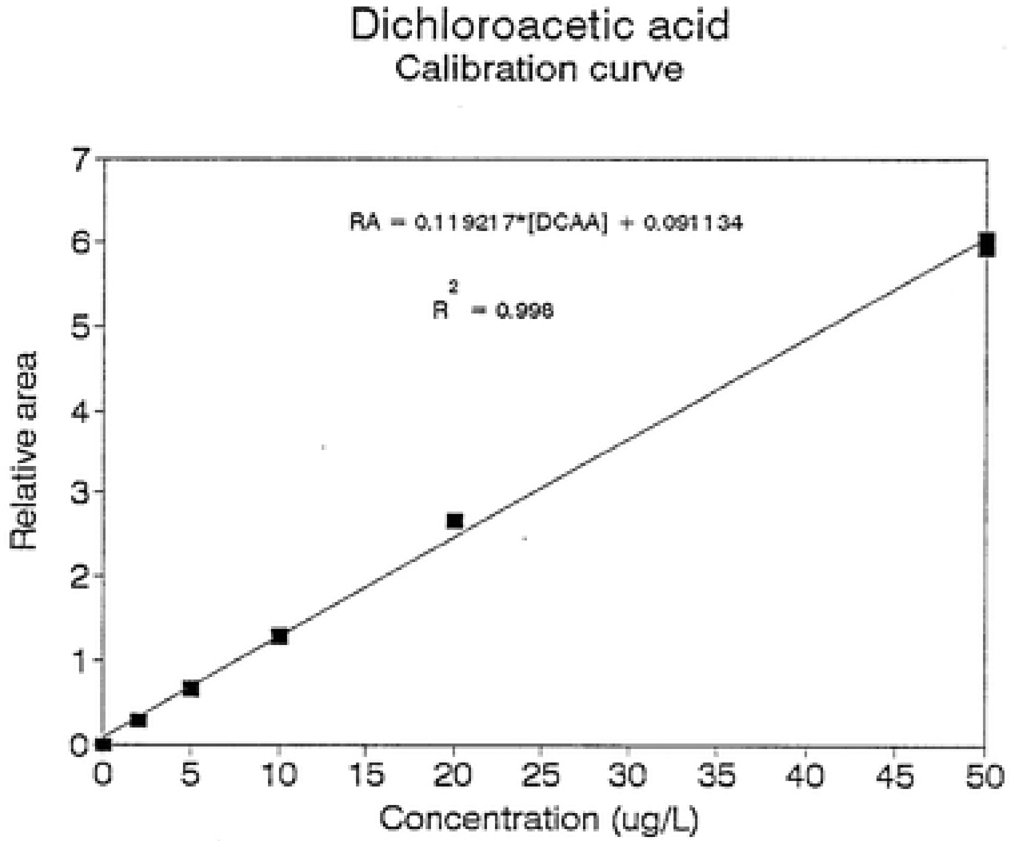
	TBAA	BrClAA	DBAA
Relative area			
Sample 1	0.563	1.061	0.110
2	0.559	1.254	0.123
3	0.411	1.397	0.124
4	0.410	1.498	0.137
Conc. (µg/L)			
Sample 1	65.6	22.0	2.00
2	65.1	26.1	2.23
3	53.4	29.3	2.37
4	53.2	31.4	2.62
Avg. conc.	59.3	27.2	2.31
% impurity in 1000 µg/L sample	5.93	2.72	0.23

Total % impurities = 8.88

Appendix D
HAA Calibration Curves

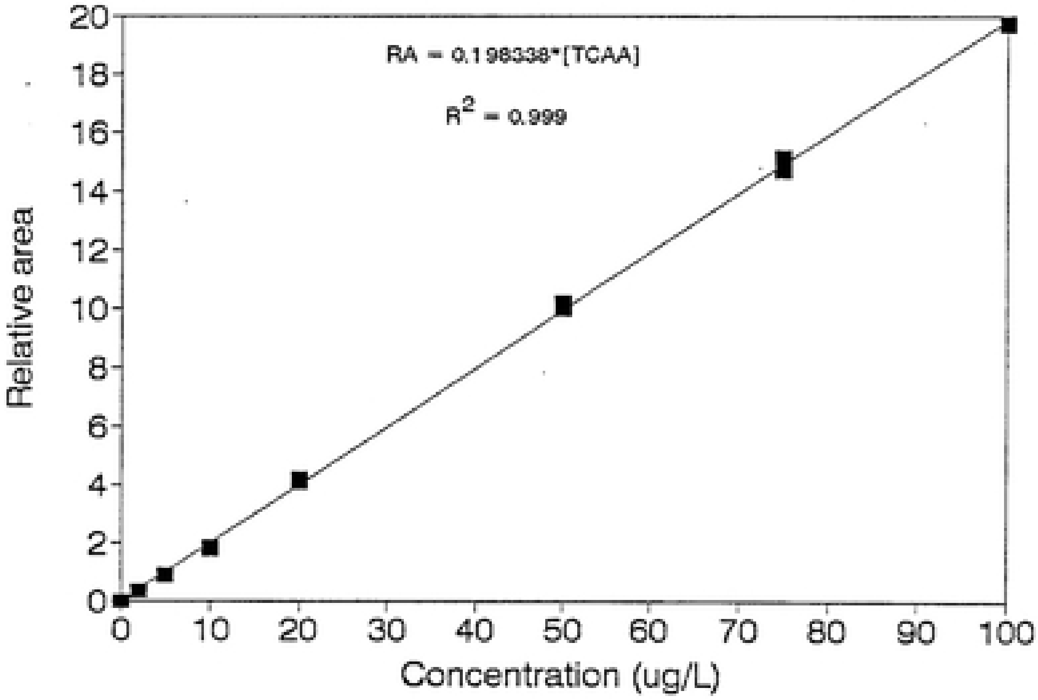


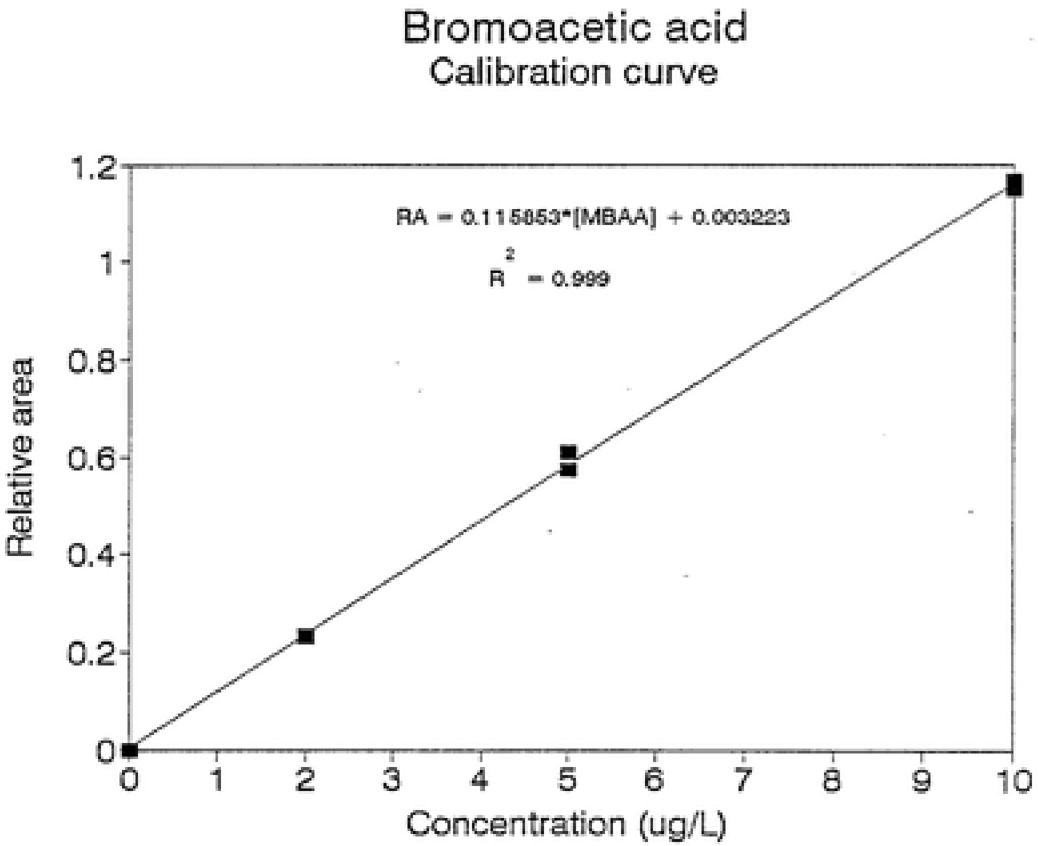
Appendix D, cont.

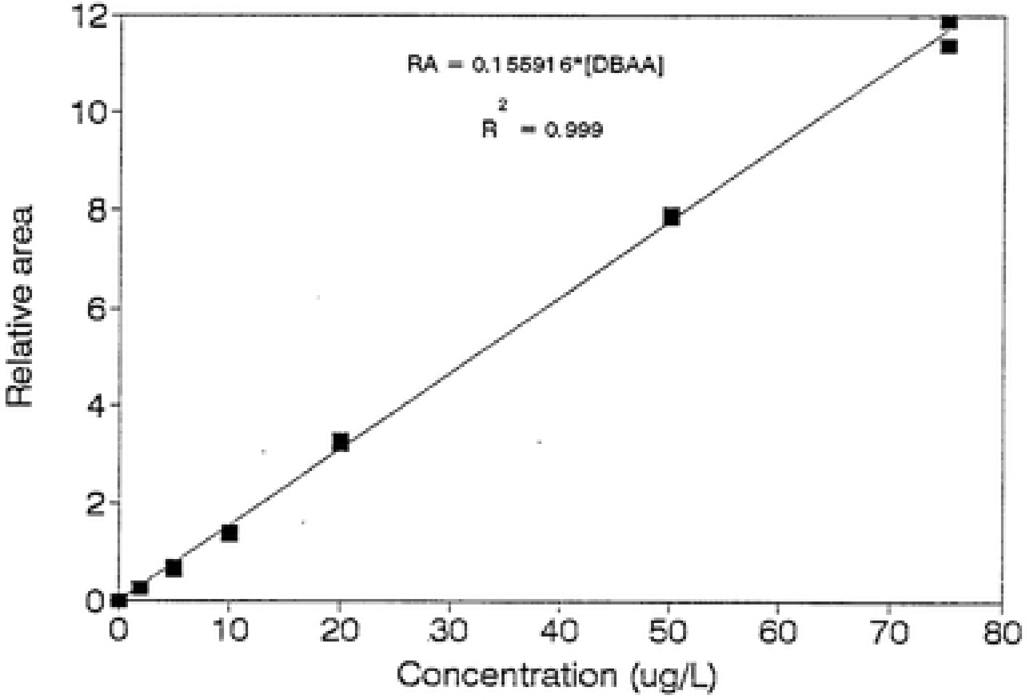

Dichloroacetic acid
Calibration curve

Appendix D, cont.

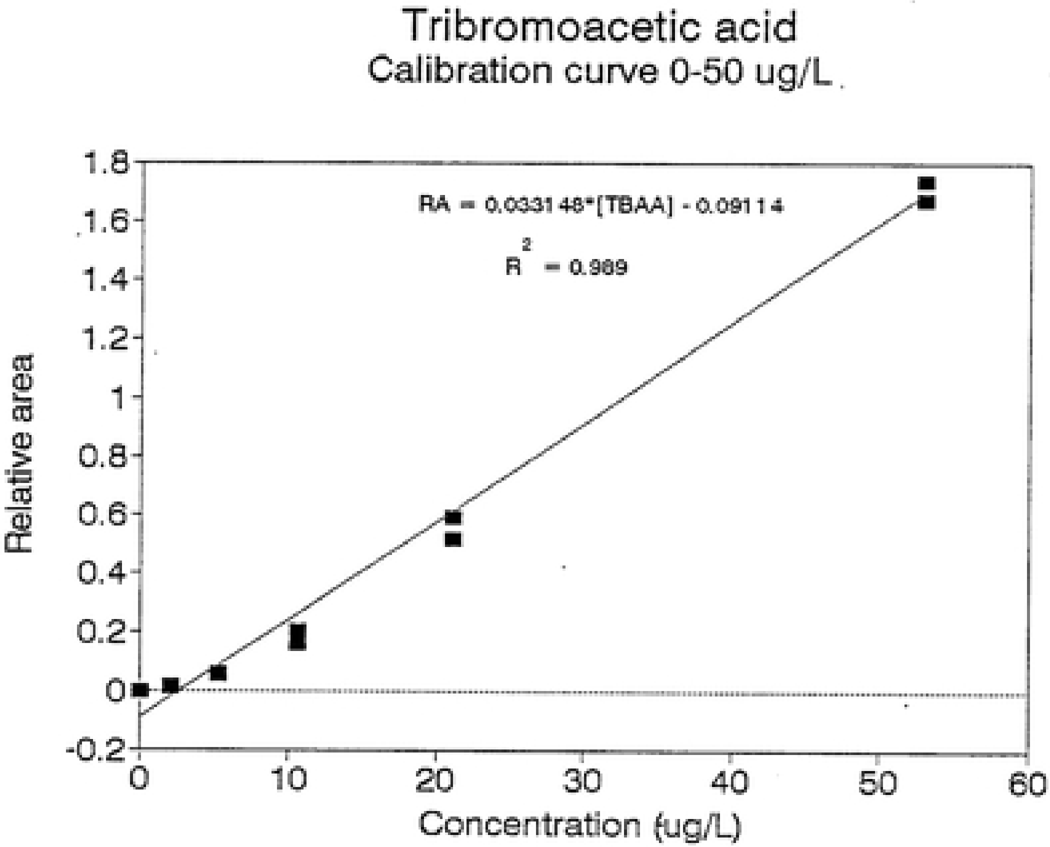
Trichloroacetic acid
Calibration curve

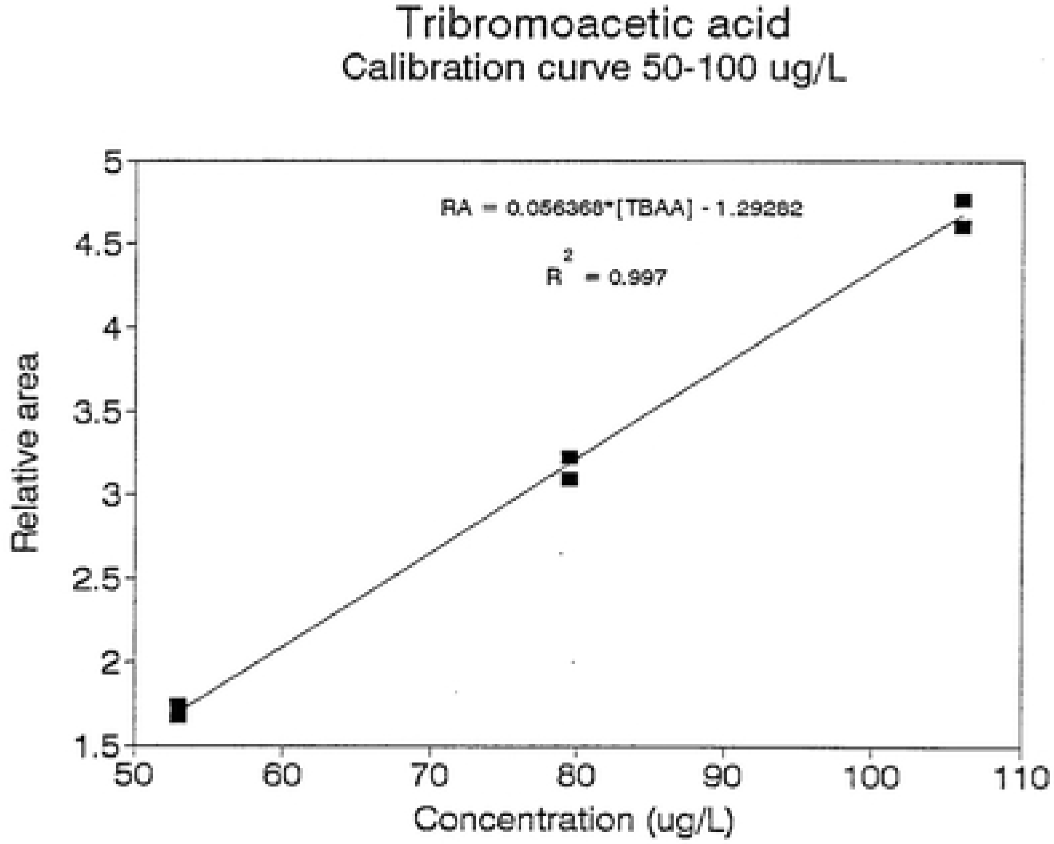



Bromoacetic acid
Calibration curve
RA = 0.115853*[MBAA] + 0.003223
R 2 = 0.999
Relative area
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
Concentration (ug/L)

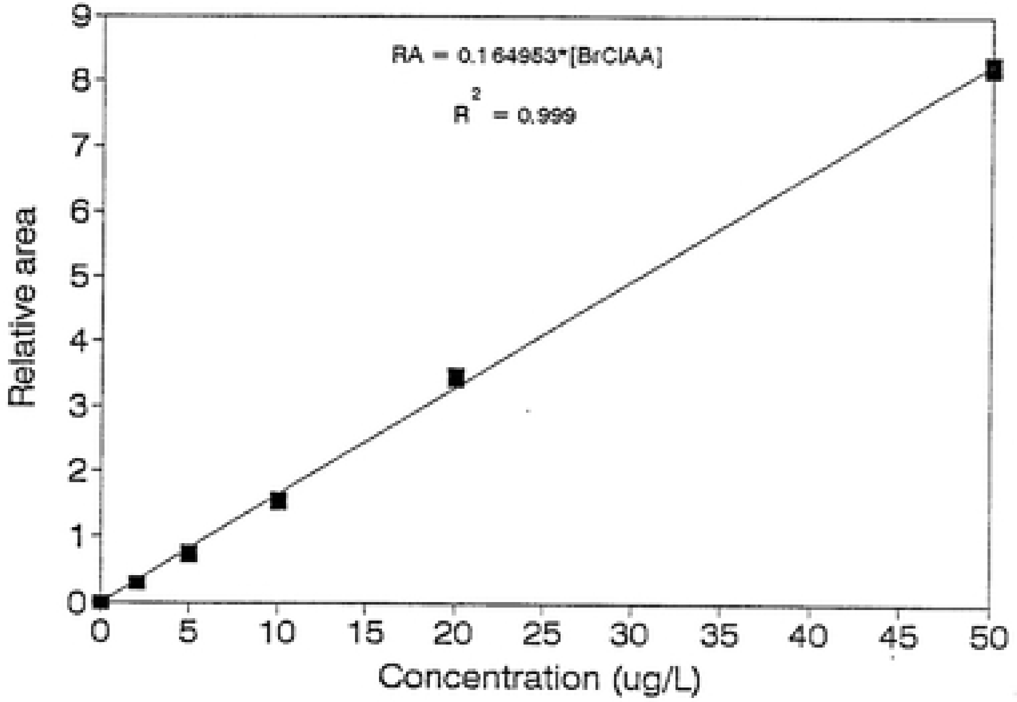


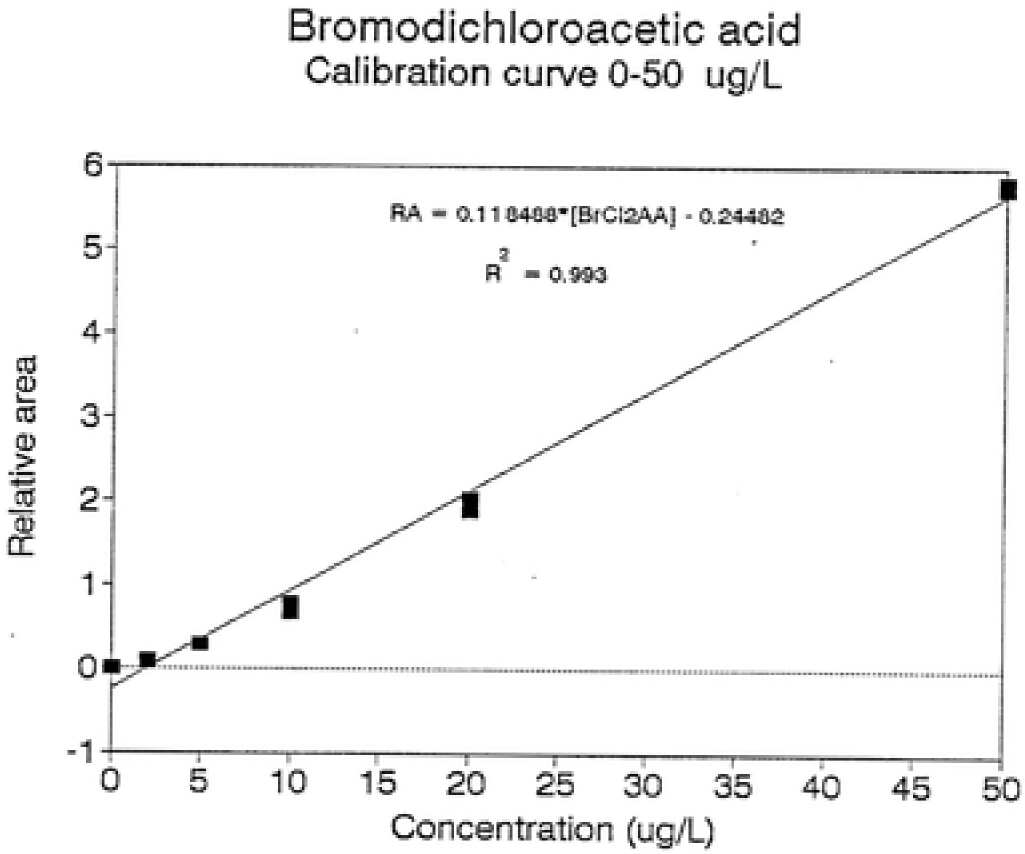
Dibromoacetic acid
Calibration curve

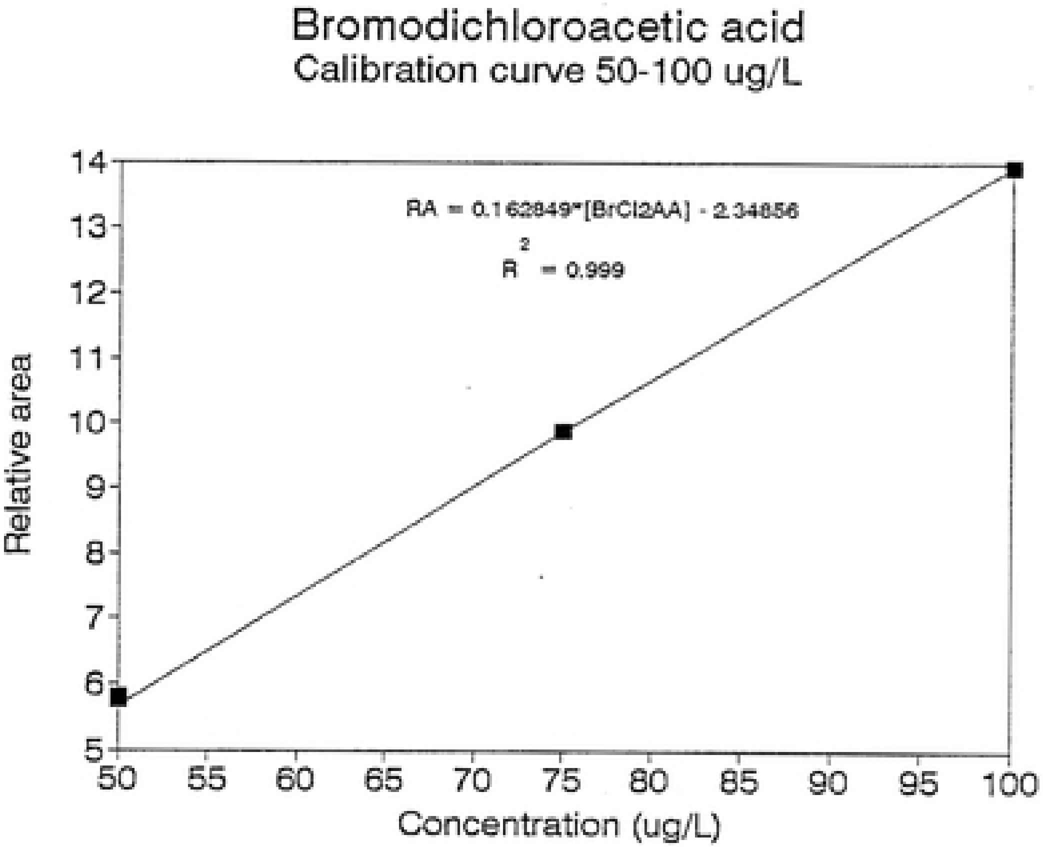

Tribromoacetic acid
Calibration curve 0-50 ug/L
RA = 0.033148*[TBAA] - 0.09114
R^2 = 0.989
Relative area
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
Concentration (ug/L)


Tribromoacetic acid
Calibration curve 50-100 ug/L
RA = 0.056368*[TBAA] - 1.29282
R^2 = 0.997
Relative area
1.5
2
2.5
3
3.5
4
4.5
5
50
60
70
80
90
100
110
Concentration (ug/L)

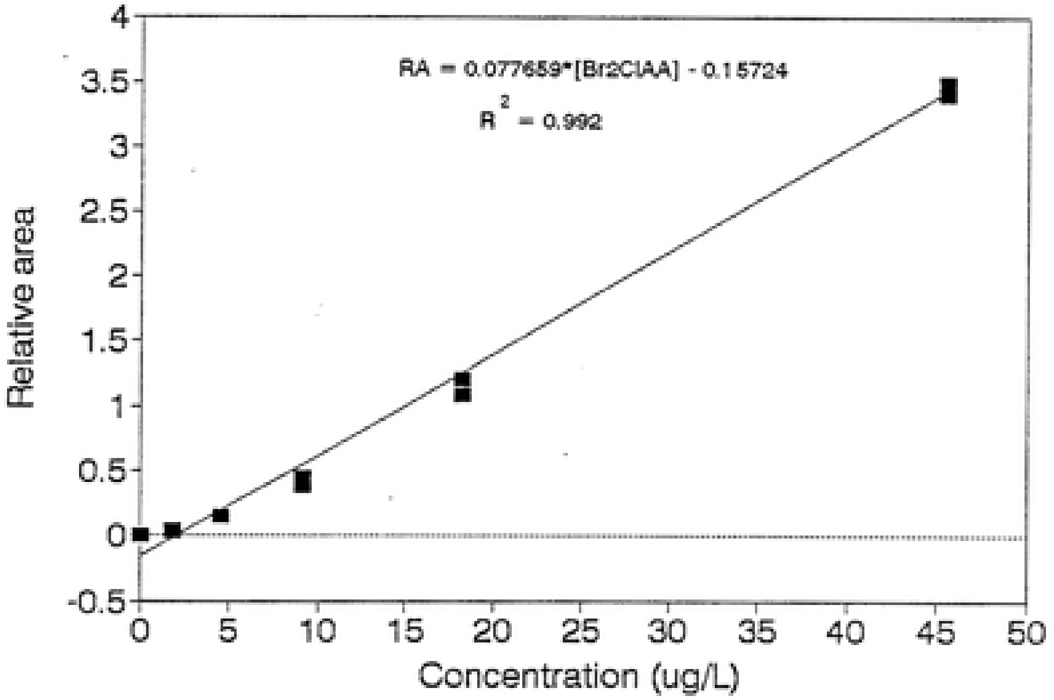
Appendix D. cont.


Bromo-chloroacetic acid
Calibration curve


Bromodichloroacetic acid
Calibration curve 0-50 ug/L
RA = 0.118468*[BrCl2AA] - 0.24482
R2 = 0.993
Relative area
6
5
4
3
2
1
0
-1
0
5
10
15
20
25
30
35
40
45
50
Concentration (ug/L)


Bromodichloroacetic acid
Calibration curve 50-100 ug/L
RA = 0.162849*[BrCl2AA] - 2.34856
R^2 = 0.999
Relative area
14
13
12
11
10
9
8
7
6
5
50
55
60
65
70
75
80
85
90
95
100
Concentration (ug/L)

Appendix D, cont.

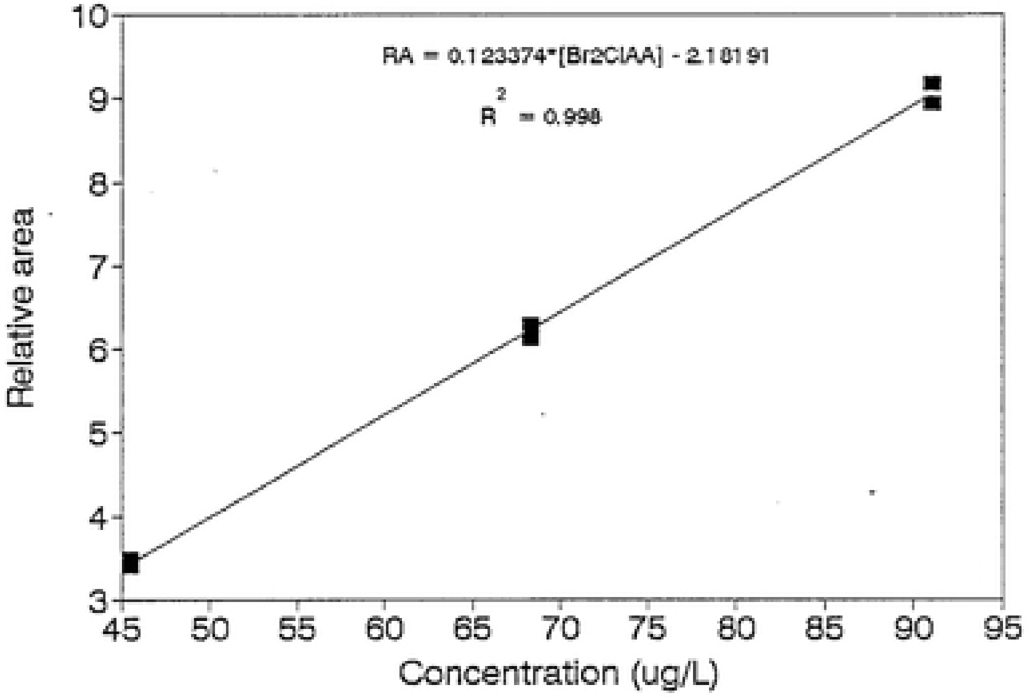


Dibromochloroacetic acid
Calibration curve 0-50 ug/L

Appendix D, cont.

Dibromochloroacetic acid

Calibration curve 50-100 ug/L



Appendix E
Method Detection Limits for HAAs

Run 7 replicate samples at 1-5x the expected MDL
-- 1 µg/L for MCAA, DCAA, TCAA, MBAA, DBAA, BrClAA
-- 2 µg/L for TBAA, BrCl$_2$AA, Br$_2$ClAA

Calculate standard deviation (s) of the relative areas of the 7 replicates

MDL (relative area) = 3.143 * s

Convert to MDL (µg/L) by substituting relative area into calibration curve equations

Calibration curves:

[MCAA] = RA/0.01204 (2/19/93)
[DCAA] = RA/0.099518 (2/19/93)
[TCAA] = RA/0.181776 (2/19/93)
[MBAA] = RA/0.08501 (2/19/93)
[DBAA] = RA/0.18935 (2/19/93)
[TBAA] = (RA+0.09114)/0.033148 (9/14/93)
[BrClAA] = RA/0.110144 (2/19/93)
[BrCl2AA] = (RA+0.24482)/0.118488 (9/14/93)
[Br2ClAA] = (RA+0.15724)/0.077659 (9/14/93)

Replicate samples:

	HAA area	IS area	RA		HAA area	IS area	RA
MCAA	171	13043	0.0131	TCAA	1611	13043	0.1235
2/19/93	217	12191	0.0178	2/19/93	1476	12191	0.1211
	191	11962	0.0160		1345	11962	0.1124
	157	13201	0.0111		1799	13201	0.1363
	147	11664	0.0126		1673	11664	0.1434
	195	9824	0.0198		1571	9824	0.1599
	206	10561	0.0195		1563	10561	0.1480
DCAA	1426	13043	0.1093	MBAA	923	13043	0.0708
2/19/93	1355	12191	0.1111	2/19/93	924	12191	0.0758
	1330	11962	0.1112		936	11962	0.0782
	1481	13201	0.1122		980	13201	0.0742
	1579	11664	0.1354		931	11664	0.0798
	1502	9824	0.1529		963	9824	0.0980
	1527	10561	0.1446		1015	10561	0.0961

Appendix E, cont.

	HAA area	IS area	RA
DBAA	1380	13043	0.1058
2/19/93	1327	12191	0.1089
	1252	11962	0.1047
	1725	13201	0.1307
	1495	11664	0.1282
	1417	9824	0.1442
	1537	10561	0.1455
TBAA	205	14833	0.0138
9/14/93	169	14988	0.0113
	312	15473	0.0202
	233	15214	0.0153
	243	14952	0.0162
	205	14811	0.0138
	236	15014	0.0157
BrClAA	1278	13043	0.0980
2/19/93	1272	12191	0.1043
	1248	11962	0.1043
	1621	13201	0.1228
	1467	11664	0.1258
	1365	9824	0.1389
	1455	10561	0.1378

	HAA area	IS area	RA
$BrCl_2AA$	1246	14833	0.0840
9/14/93	1026	14988	0.0685
	1161	15473	0.0750
	1289	15214	0.0847
	1285	14952	0.0859
	1133	14811	0.0765
	1280	15014	0.0853
Br_2ClAA	613	14833	0.0413
9/14/93	506	14988	0.0338
	603	15473	0.0390
	658	15214	0.0432
	676	14952	0.0452
	579	14811	0.0391
	657	15014	0.0438

Calculation of MDLs:

	s	3.143*s	MDL (µg/L)
MCAA	0.00349	0.01098	0.91
DCAA	0.01855	0.05830	0.59
TCAA	0.01682	0.05286	0.29
MBAA	0.01079	0.03392	0.40
DBAA	0.01763	0.05541	0.29
TBAA	0.00275	0.00864	3.01
BrClAA	0.01675	0.05264	0.48
$BrCl_2AA$	0.00671	0.02110	2.24
Br_2ClAA	0.00386	0.01214	2.18

Appendix F
Numerical Data of Haloacetic Acid Results

This appendix contains numerical data and calculations of the results presented in Chapter 4. Data is reported in terms of μg/L concentrations, μM concentrations, and mole fractions of the total HAAs. Calculations regarding the sums of chlorinated, bromo-chloro and brominated species, distribution of the HAAs into mono-, di-, and trihalogenated species, and bromine and chlorine incorporation are given as well.

Samples are named by a system that gives the following information: source of NOM, pH of chlorination, type of chemical treatment, and concentration of bromide. Some examples of the labelling system are given below:

MB8CL0Br = Myrtle Beach extract chlorinated at pH 8, 0 mg/L Br^-

MB6OCL2.0Br = Myrtle Beach extract, ozonated, post-chlorinated at pH 8, 2.0 mg/L Br^-

PB8CN0.5Br = Palm Beach extract chloraminated at pH 8, 0.5 mg/L Br^-

PB8OCN0Br = Palm Beach extract, ozonated, post-chloraminated at pH 8, 0 mg/L Br^-

PBO 0.025Br = Palm Beach extract treated with ozone alone, 0.025 mg/L Br^-

Appendix F, cont.

	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
8/23	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB8OCL0Br	6.69	56.6	143	0	0.78	0
MB8OCL0.025Br	6.68	57.5	134	0.45	0.9	0
MB8OCL0.05Br	6.7	54.2	122	0.64	1.3	0
MB8OCL0.1Br	6	50.6	109	0.9	2.34	0
MB8OCL0.25Br	4.29	42	80.7	1.86	6.8	5.25
MB8OCL0.5Br	4.55	27.9	39.9	3.11	18.5	12.4
MB8OCL0.75Br	3.42	18.6	21.4	3.98	28.6	26.8
MB8OCL1.0Br	2.83	11.6	11.6	4.78	35.7	50
MB8OCL1.5Br	1.57	5.78	4.87	5.77	43.7	69.4
MB8OCL2.0Br	0.94	3.41	3.18	6.08	47.1	85.7
8/23						
MB8CL0Br	4.34	60.4	145	0	0.82	0
MB8CL0.025Br	4.19	58.9	139	0.4	0.85	0
MB8CL0.05Br	4.32	54.9	134	0.48	1.07	0
MB8CL0.1Br	3.98	54	122	0.75	1.66	0
MB8CL0.25Br	3.64	45.4	95	1.48	5.7	4.63
MB8CL0.5Br	3.17	33	57.8	2.33	18.5	9.55
MB8CL0.75Br	2.77	22.1	33.5	3.13	32.8	26.2
MB8CL1.0Br	2.32	15.2	19.2	3.82	45.1	57.9
MB8CL1.5Br	1.36	6.91	6.39	5.1	57.4	109
MB8CL2.0Br	0.56	3.04	3.18	5.19	56.1	129
8/23						
MB6OCL0Br	2.69	57.2	122	0.39	0.78	0
MB6OCL0.025Br	2.69	56.2	120	0.7	0.98	0
MB6OCL0.05Br	2.61	53.8	113	0.97	1.59	0
MB6OCL0.1Br	2.59	50.6	103	1.37	3.2	0
MB6OCL0.25Br	1.76	37	69.4	2.39	12.5	5.58
MB6OCL0.5Br	2	28.9	38.3	3.48	29.9	15.3
MB6OCL0.75Br	1.57	19.5	20.8	4.06	42.3	38.9
MB6OCL1.0Br	1.44	15.4	12	4.33	54.9	62.4
MB6OCL1.5Br	1.21	8.95	5.96	5.28	63.4	98
MB6OCL2.0Br	0.88	5.32	4.12	5.83	65.1	119
8/23						
MB6CL0Br	2.63	60.9	164	0.33	0.86	0
MB6CL0.025Br	2.54	59	160	0.56	0.99	0
MB6CL0.05Br	2.45	58.1	155	0.75	1.26	0
MB6CL0.1Br	2.3	54.8	142	1.02	2.48	0
MB6CL0.25Br	2.02	46.7	116	1.72	8.79	5.24
MB6CL0.5Br	1.66	36.9	81.2	2.56	26.1	11.7
MB6CL0.75Br	1.51	27.6	50.5	3.33	49.2	31.9
MB6CL1.0Br	1.41	19.2	30.4	3.9	70.2	66
MB6CL1.5Br	0.98	8.77	9.77	4.53	90.7	130
MB6CL2.0Br	0.44	2.04	2.2	5.28	88	203

Appendix F, cont.

	ug/L	ug/L	ug/L	ug/L
8/23	BrClAA	BrCl2AA	Br2ClAA	THAA
MB8OCL0Br	1	4.45	3.74	216.26
MB8OCL0.025Br	3.54	11.5	3.86	218.43
MB8OCL0.05Br	6.54	19.9	4.44	215.72
MB8OCL0.1Br	10.9	34.6	6.21	220.55
MB8OCL0.25Br	20.7	71.3	18.2	251.1
MB8OCL0.5Br	26	67.3	32.7	232.36
MB8OCL0.75Br	27.1	66.7	50.9	247.5
MB8OCL1.0Br	25.4	59.8	58.4	260.11
MB8OCL1.5Br	19.6	35.9	55.5	242.09
MB8OCL2.0Br	15.6	26.9	52.4	241.31
8/23				
MB8CL0Br	0.93	3.98	3.92	219.39
MB8CL0.025Br	2.95	8.47	3.93	218.69
MB8CL0.05Br	5.42	14.9	4.16	219.25
MB8CL0.1Br	9.67	27.5	5.05	224.61
MB8CL0.25Br	20.5	58.3	11.7	246.35
MB8CL0.5Br	30.6	79	33.9	267.85
MB8CL0.75Br	32.7	82.7	57.3	293.2
MB8CL1.0Br	31.5	78.8	71.8	325.64
MB8CL1.5Br	23.2	52.8	75.9	338.06
MB8CL2.0Br	15.2	29.9	62.2	304.37
8/23				
MB6OCL0Br	1.28	4.89	4.17	193.4
MB6OCL0.025Br	5.38	15.6	4.64	206.19
MB6OCL0.05Br	10.2	30.9	6.28	219.35
MB6OCL0.1Br	17.6	51.8	10.3	240.46
MB6OCL0.25Br	32.7	74.7	33.1	269.13
MB6OCL0.5Br	43.3	94.9	74.1	330.18
MB6OCL0.75Br	40.3	91.5	101	359.93
MB6OCL1.0Br	39.6	79.5	114	383.57
MB6OCL1.5Br	34.7	67.5	123	408
MB6OCL2.0Br	30.1	63.8	112	406.15
8/23				
MB6CL0Br	0.98	4.35	4.49	238.54
MB6CL0.025Br	4.12	14.1	4.73	246.04
MB6CL0.05Br	7.14	23.5	5.22	253.42
MB6CL0.1Br	14	46.4	8.1	271.1
MB6CL0.25Br	27.1	82.5	24.8	314.87
MB6CL0.5Br	42	113	62.2	377.32
MB6CL0.75Br	49.2	124	101	438.24
MB6CL1.0Br	51.4	121	140	503.51
MB6CL1.5Br	39.8	88.9	163	536.45
MB6CL2.0Br	22	52.6	120	495.56

APPENDIX F, cont.

8/23	uM MCAA	uM DCAA	uM TCAA	uM MBAA	uM DBAA	uM TBAA
MB8OCL0Br	0.071	0.439	0.875	0.000	0.004	0.000
MB8OCL0.025Br	0.071	0.446	0.820	0.003	0.004	0.000
MB8OCL0.05Br	0.071	0.420	0.747	0.005	0.006	0.000
MB8OCL0.1Br	0.064	0.393	0.667	0.006	0.011	0.000
MB8OCL0.25Br	0.045	0.326	0.494	0.013	0.031	0.018
MB8OCL0.5Br	0.048	0.216	0.244	0.022	0.085	0.042
MB8OCL0.75Br	0.036	0.144	0.131	0.029	0.131	0.090
MB8OCL1.0Br	0.030	0.090	0.071	0.034	0.164	0.169
MB8OCL1.5Br	0.017	0.045	0.030	0.042	0.201	0.234
MB8OCL2.0Br	0.010	0.026	0.019	0.044	0.216	0.289
8/23						
MB8CL0Br	0.046	0.469	0.888	0.000	0.004	0.000
MB8CL0.025Br	0.044	0.457	0.851	0.003	0.004	0.000
MB8CL0.05Br	0.046	0.426	0.820	0.003	0.005	0.000
MB8CL0.1Br	0.042	0.419	0.747	0.005	0.008	0.000
MB8CL0.25Br	0.039	0.352	0.582	0.011	0.026	0.016
MB8CL0.5Br	0.034	0.256	0.354	0.017	0.085	0.032
MB8CL0.75Br	0.029	0.171	0.205	0.023	0.151	0.088
MB8CL1.0Br	0.025	0.118	0.118	0.028	0.207	0.195
MB8CL1.5Br	0.014	0.054	0.039	0.037	0.264	0.367
MB8CL2.0Br	0.006	0.024	0.019	0.037	0.258	0.435
8/23						
MB6OCL0Br	0.028	0.444	0.747	0.003	0.004	0.000
MB6OCL0.025Br	0.028	0.436	0.735	0.005	0.004	0.000
MB6OCL0.05Br	0.028	0.417	0.692	0.007	0.007	0.000
MB6OCL0.1Br	0.027	0.393	0.631	0.010	0.015	0.000
MB6OCL0.25Br	0.019	0.287	0.425	0.017	0.057	0.019
MB6OCL0.5Br	0.021	0.224	0.234	0.025	0.137	0.052
MB6OCL0.75Br	0.017	0.151	0.127	0.029	0.194	0.131
MB6OCL1.0Br	0.015	0.119	0.073	0.031	0.252	0.210
MB6OCL1.5Br	0.013	0.069	0.036	0.038	0.291	0.330
MB6OCL2.0Br	0.009	0.041	0.025	0.042	0.299	0.401
8/23						
MB6CL0Br	0.028	0.472	1.004	0.002	0.004	0.000
MB6CL0.025Br	0.027	0.458	0.979	0.004	0.005	0.000
MB6CL0.05Br	0.026	0.451	0.949	0.005	0.006	0.000
MB6CL0.1Br	0.024	0.425	0.869	0.007	0.011	0.000
MB6CL0.25Br	0.021	0.362	0.710	0.012	0.040	0.018
MB6CL0.5Br	0.018	0.286	0.497	0.018	0.120	0.039
MB6CL0.75Br	0.016	0.214	0.309	0.024	0.226	0.108
MB6CL1.0Br	0.015	0.149	0.186	0.028	0.322	0.222
MB6CL1.5Br	0.010	0.068	0.060	0.033	0.416	0.438
MB6CL2.0Br	0.005	0.016	0.013	0.038	0.404	0.684

APPENDIX F, cont.

	uM	uM	uM	uM
8/23	BrClAA	BrCl2AA	Br2ClAA	THAA
MB8OCL0Br	0.006	0.021	0.015	1.431
MB8OCL0.025Br	0.020	0.055	0.015	1.436
MB8OCL0.05Br	0.038	0.096	0.018	1.400
MB8OCL0.1Br	0.063	0.167	0.025	1.395
MB8OCL0.25Br	0.119	0.343	0.072	1.462
MB8OCL0.5Br	0.150	0.324	0.130	1.261
MB8OCL0.75Br	0.156	0.321	0.202	1.241
MB8OCL1.0Br	0.147	0.288	0.232	1.224
MB8OCL1.5Br	0.113	0.173	0.220	1.073
MB8OCL2.0Br	0.090	0.129	0.208	1.032
8/23				
MB8CL0Br	0.005	0.019	0.016	1.446
MB8CL0.025Br	0.017	0.041	0.016	1.432
MB8CL0.05Br	0.031	0.072	0.016	1.420
MB8CL0.1Br	0.056	0.132	0.020	1.429
MB8CL0.25Br	0.118	0.281	0.046	1.470
MB8CL0.5Br	0.177	0.380	0.134	1.468
MB8CL0.75Br	0.189	0.398	0.227	1.481
MB8CL1.0Br	0.182	0.379	0.285	1.535
MB8CL1.5Br	0.134	0.254	0.301	1.464
MB8CL2.0Br	0.088	0.144	0.247	1.257
8/23				
MB6OCL0Br	0.007	0.024	0.017	1.273
MB6OCL0.025Br	0.031	0.075	0.018	1.333
MB6OCL0.05Br	0.059	0.149	0.025	1.383
MB6OCL0.1Br	0.102	0.249	0.041	1.467
MB6OCL0.25Br	0.189	0.359	0.131	1.503
MB6OCL0.5Br	0.250	0.457	0.294	1.694
MB6OCL0.75Br	0.232	0.440	0.400	1.723
MB6OCL1.0Br	0.228	0.383	0.452	1.765
MB6OCL1.5Br	0.200	0.325	0.488	1.791
MB6OCL2.0Br	0.174	0.307	0.444	1.742
8/23				
MB6CL0Br	0.006	0.021	0.018	1.555
MB6CL0.025Br	0.024	0.068	0.019	1.583
MB6CL0.05Br	0.041	0.113	0.021	1.612
MB6CL0.1Br	0.081	0.223	0.032	1.674
MB6CL0.25Br	0.156	0.397	0.098	1.816
MB6CL0.5Br	0.242	0.544	0.247	2.011
MB6CL0.75Br	0.284	0.597	0.400	2.178
MB6CL1.0Br	0.297	0.582	0.555	2.357
MB6CL1.5Br	0.230	0.428	0.646	2.329
MB6CL2.0Br	0.127	0.253	0.476	2.016

APPENDIX F, cont.

	Mole fraction Xi (x100)					
8/23	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB8OCL0Br	4.95	30.69	61.18	0.00	0.25	0.00
MB8OCL0.025Br	4.93	31.07	57.14	0.23	0.29	0.00
MB8OCL0.05Br	5.07	30.04	53.35	0.33	0.43	0.00
MB8OCL0.1Br	4.56	28.15	47.85	0.46	0.77	0.00
MB8OCL0.25Br	3.11	22.28	33.79	0.92	2.14	1.21
MB8OCL0.5Br	3.82	17.16	19.36	1.77	6.73	3.31
MB8OCL0.75Br	2.92	11.63	10.56	2.31	10.58	7.28
MB8OCL1.0Br	2.45	7.35	5.80	2.81	13.40	13.77
MB8OCL1.5Br	1.55	4.18	2.78	3.87	18.70	21.79
MB8OCL2.0Br	0.96	2.56	1.89	4.24	20.96	27.99
8/23						
MB8CL0Br	3.18	32.40	61.39	0.00	0.26	0.00
MB8CL0.025Br	3.10	31.90	59.41	0.20	0.27	0.00
MB8CL0.05Br	3.22	30.00	57.78	0.24	0.35	0.00
MB8CL0.1Br	2.95	29.31	52.26	0.38	0.53	0.00
MB8CL0.25Br	2.62	23.96	39.56	0.72	1.78	1.06
MB8CL0.5Br	2.29	17.43	24.10	1.14	5.78	2.19
MB8CL0.75Br	1.98	11.58	13.85	1.52	10.17	5.96
MB8CL1.0Br	1.60	7.68	7.66	1.79	13.49	12.71
MB8CL1.5Br	0.98	3.66	2.67	2.51	18.01	25.10
MB8CL2.0Br	0.47	1.88	1.55	2.97	20.49	34.59
8/23						
MB6OCL0Br	2.24	34.86	58.67	0.22	0.28	0.00
MB6OCL0.025Br	2.14	32.70	55.10	0.38	0.34	0.00
MB6OCL0.05Br	2.00	30.17	50.00	0.50	0.53	0.00
MB6OCL0.1Br	1.87	26.76	42.99	0.67	1.00	0.00
MB6OCL0.25Br	1.24	19.09	28.26	1.14	3.82	1.25
MB6OCL0.5Br	1.25	13.24	13.84	1.48	8.10	3.04
MB6OCL0.75Br	0.96	8.78	7.39	1.70	11.27	7.61
MB6OCL1.0Br	0.86	6.77	4.16	1.77	14.28	11.92
MB6OCL1.5Br	0.72	3.88	2.04	2.12	16.26	18.44
MB6OCL2.0Br	0.53	2.37	1.45	2.41	17.15	23.02
8/23						
MB6CL0Br	1.79	30.38	64.56	0.15	0.25	0.00
MB6CL0.025Br	1.70	28.91	61.87	0.25	0.29	0.00
MB6CL0.05Br	1.61	27.97	58.87	0.34	0.36	0.00
MB6CL0.1Br	1.45	25.40	51.94	0.44	0.68	0.00
MB6CL0.25Br	1.18	19.95	39.11	0.68	2.22	0.97
MB6CL0.5Br	0.87	14.23	24.72	0.92	5.96	1.96
MB6CL0.75Br	0.73	9.83	14.20	1.10	10.37	4.94
MB6CL1.0Br	0.63	6.32	7.90	1.19	13.68	9.44
MB6CL1.5Br	0.45	2.92	2.57	1.40	17.88	18.81
MB6CL2.0Br	0.23	0.79	0.67	1.89	20.04	33.94

Appendix F, cont.

	Mole fraction Xi (x100)		
8/23	BrClAA	BrCl2AA	Br2ClAA
MB8OCL0Br	0.40	1.50	1.04
MB8OCL0.025Br	1.42	3.86	1.07
MB8OCL0.05Br	2.69	6.84	1.26
MB8OCL0.1Br	4.51	11.94	1.77
MB8OCL0.25Br	8.17	23.46	4.93
MB8OCL0.5Br	11.89	25.67	10.28
MB8OCL0.75Br	12.60	25.87	16.26
MB8OCL1.0Br	11.97	23.52	18.92
MB8OCL1.5Br	10.54	16.10	20.50
MB8OCL2.0Br	8.72	12.54	20.13
8/23			
MB8CL0Br	0.37	1.32	1.07
MB8CL0.025Br	1.19	2.85	1.09
MB8CL0.05Br	2.20	5.05	1.16
MB8CL0.1Br	3.90	9.26	1.40
MB8CL0.25Br	8.05	19.09	3.16
MB8CL0.5Br	12.02	25.89	9.15
MB8CL0.75Br	12.74	26.87	15.34
MB8CL1.0Br	11.84	24.70	18.54
MB8CL1.5Br	9.14	17.36	20.56
MB8CL2.0Br	6.98	11.45	19.62
8/23			
MB6OCL0Br	0.58	1.85	1.30
MB6OCL0.025Br	2.33	5.63	1.38
MB6OCL0.05Br	4.25	10.75	1.80
MB6OCL0.1Br	6.92	17.00	2.78
MB6OCL0.25Br	12.55	23.91	8.73
MB6OCL0.5Br	14.75	26.96	17.34
MB6OCL0.75Br	13.49	25.56	23.24
MB6OCL1.0Br	12.95	21.68	25.61
MB6OCL1.5Br	11.18	18.14	27.23
MB6OCL2.0Br	9.97	17.62	25.48
8/23			
MB6CL0Br	0.36	1.35	1.14
MB6CL0.025Br	1.50	4.29	1.18
MB6CL0.05Br	2.56	7.02	1.28
MB6CL0.1Br	4.83	13.34	1.92
MB6CL0.25Br	8.61	21.86	5.41
MB6CL0.5Br	12.05	27.04	12.26
MB6CL0.75Br	13.03	27.40	18.39
MB6CL1.0Br	12.58	24.71	23.55
MB6CL1.5Br	9.86	18.37	27.74
MB6CL2.0Br	6.30	12.56	23.60

APPENDIX F, cont.

Bromine and chlorine incorporation

Bromine incorporation		Chlorine incorporation		
uM	per uM THAA	uM	per uM THAA	
				8/23
0.0640	0.0447	3.6387	2.5429	MB8OCL0Br
0.1179	0.0821	3.5703	2.4870	MB8OCL0.025Br
0.1852	0.1323	3.3993	2.4282	MB8OCL0.05Br
0.3066	0.2198	3.2710	2.3455	MB8OCL0.1Br
0.7357	0.5032	3.0570	2.0906	MB8OCL0.25Br
1.0508	0.8330	2.1412	1.6974	MB8OCL0.5Br
1.4431	1.1630	1.7179	1.3844	MB8OCL0.75Br
1.7651	1.4425	1.3766	1.1250	MB8OCL1.0Br
1.8704	1.7428	0.8744	0.8147	MB8OCL1.5Br
1.9777	1.9165	0.6779	0.6569	MB8OCL2.0Br
				8/23
0.0631	0.0437	3.7053	2.5624	MB8CL0Br
0.0996	0.0696	3.6252	2.5309	MB8CL0.025Br
0.1492	0.1051	3.5497	2.5001	MB8CL0.05Br
0.2488	0.1741	3.4611	2.4219	MB8CL0.1Br
0.6014	0.4091	3.2134	2.1861	MB8CL0.25Br
1.1087	0.7550	2.6784	1.8240	MB8CL0.5Br
1.6296	1.1003	2.1992	1.4849	MB8CL0.75Br
2.1573	1.4051	1.8378	1.1970	MB8CL1.0Br
2.6556	1.8145	1.1819	0.8075	MB8CL1.5Br
2.5816	2.0540	0.7335	0.5836	MB8CL2.0Br
				8/23
0.0739	0.0581	3.2276	2.5355	MB6OCL0Br
0.1569	0.1177	3.3039	2.4783	MB6OCL0.025Br
0.2789	0.2016	3.3188	2.3989	MB6OCL0.05Br
0.4717	0.3216	3.3451	2.2807	MB6OCL0.1Br
0.9990	0.6645	2.9061	1.9332	MB6OCL0.25Br
1.7483	1.0321	2.6299	1.5525	MB6OCL0.5Br
2.2846	1.3259	2.2147	1.2854	MB6OCL0.75Br
2.6811	1.5193	1.9201	1.0881	MB6OCL1.0Br
3.1113	1.7374	1.5986	0.8927	MB6OCL1.5Br
3.2117	1.8432	1.3992	0.8030	MB6OCL2.0Br
				8/23
0.0725	0.0466	4.0500	2.6045	MB6CL0Br
0.1422	0.0899	4.0590	2.5641	MB6CL0.025Br
0.2126	0.1319	4.0621	2.5204	MB6CL0.05Br
0.3984	0.2380	4.0420	2.4150	MB6CL0.1Br
0.8961	0.4935	3.9251	2.1615	MB6CL0.25Br
1.6556	0.8232	3.6578	1.8187	MB6CL0.5Br
2.4797	1.1387	3.2494	1.4922	MB6CL0.75Br
3.3289	1.4126	2.8872	1.2252	MB6CL1.0Br
4.1297	1.7732	2.0573	0.8833	MB6CL1.5Br
4.2301	2.0983	1.1856	0.5881	MB6CL2.0Br

APPENDIX F, cont.

Sum of chlorinated, bromo-chloro and brominated HAA species (uM)

Distribution of HAAs into mono, di and trihalogenated species

Sample				Mole fraction of THAAs		
8/23	Cl2	Br-Cl	Br2	monohal	dihal	trihal
MB8OCL0Br	1.385	0.042	0.004	0.0495	0.3134	0.6371
MB8OCL0.025Br	1.337	0.091	0.007	0.0515	0.3278	0.6206
MB8OCL0.05Br	1.238	0.151	0.011	0.0540	0.3316	0.6145
MB8OCL0.1Br	1.123	0.254	0.017	0.0502	0.3343	0.6155
MB8OCL0.25Br	0.865	0.535	0.062	0.0402	0.3258	0.6339
MB8OCL0.5Br	0.509	0.603	0.149	0.0559	0.3578	0.5863
MB8OCL0.75Br	0.312	0.679	0.250	0.0523	0.3481	0.5996
MB8OCL1.0Br	0.191	0.666	0.367	0.0526	0.3272	0.6201
MB8OCL1.5Br	0.091	0.506	0.476	0.0542	0.3341	0.6117
MB8OCL2.0Br	0.056	0.427	0.549	0.0521	0.3224	0.6255
8/23						
MB8CL0Br	1.402	0.040	0.004	0.0318	0.3304	0.6379
MB8CL0.025Br	1.352	0.073	0.007	0.0330	0.3336	0.6334
MB8CL0.05Br	1.292	0.119	0.008	0.0346	0.3255	0.6399
MB8CL0.1Br	1.208	0.208	0.013	0.0333	0.3375	0.6292
MB8CL0.25Br	0.972	0.445	0.052	0.0335	0.3379	0.6287
MB8CL0.5Br	0.643	0.691	0.134	0.0343	0.3524	0.6133
MB8CL0.75Br	0.406	0.814	0.261	0.0350	0.3448	0.6202
MB8CL1.0Br	0.260	0.846	0.430	0.0339	0.3300	0.6361
MB8CL1.5Br	0.107	0.689	0.668	0.0349	0.3081	0.6569
MB8CL2.0Br	0.049	0.478	0.730	0.0344	0.2935	0.6721
8/23						
MB6OCL0Br	1.219	0.047	0.006	0.0246	0.3572	0.6182
MB6OCL0.025Br	1.199	0.125	0.010	0.0251	0.3537	0.6212
MB6OCL0.05Br	1.137	0.232	0.014	0.0250	0.3495	0.6255
MB6OCL0.1Br	1.051	0.392	0.025	0.0254	0.3469	0.6277
MB6OCL0.25Br	0.731	0.679	0.093	0.0238	0.3546	0.6216
MB6OCL0.5Br	0.480	1.000	0.214	0.0273	0.3608	0.6119
MB6OCL0.75Br	0.295	1.073	0.355	0.0266	0.3354	0.6379
MB6OCL1.0Br	0.208	1.063	0.494	0.0263	0.3400	0.6337
MB6OCL1.5Br	0.119	1.013	0.659	0.0284	0.3131	0.6585
MB6OCL2.0Br	0.076	0.925	0.742	0.0294	0.2949	0.6757
8/23						
MB6CL0Br	1.504	0.044	0.006	0.0194	0.3100	0.6706
MB6CL0.025Br	1.464	0.110	0.009	0.0195	0.3070	0.6734
MB6CL0.05Br	1.426	0.175	0.011	0.0194	0.3088	0.6717
MB6CL0.1Br	1.319	0.336	0.019	0.0189	0.3091	0.6720
MB6CL0.25Br	1.094	0.652	0.070	0.0186	0.3078	0.6736
MB6CL0.5Br	0.801	1.033	0.178	0.0179	0.3224	0.6597
MB6CL0.75Br	0.539	1.281	0.357	0.0184	0.3324	0.6492
MB6CL1.0Br	0.350	1.434	0.573	0.0182	0.3258	0.6560
MB6CL1.5Br	0.138	1.304	0.887	0.0185	0.3066	0.6749
MB6CL2.0Br	0.034	0.856	1.126	0.0212	0.2712	0.7076

Appendix F, cont.

ug/L concentrations of HAAs

	ug/L MCAA	ug/L DCAA	ug/L TCAA	ug/L MBAA	ug/L DBAA	ug/L TBAA
7/12						
MB8OCL0Br	5.8	55.9	129	0.33	0	0
MB8OCL0.025Br	5.98	56.7	122	0.48	0	0
MB8OCL0.05Br	5.65	57.1	116	0.64	0	0
MB8OCL0.1Br	5.74	53.4	103	0.86	0.76	0
MB8OCL0.25Br	4.84	41.5	70.2	1.62	5.48	0
MB8OCL0.5Br	4.5	25.1	28.7	3.5	15.8	9.02
MB8OCL0.75Br	3.42	14.3	11.7	4.78	25.4	23.9
MB8OCL1.0Br	2.6	9.3	5.15	5.69	32.2	44.4
MB8OCL1.5Br	1.53	4.35	1.2	7.58	40.1	62.6
MB8OCL2.0Br	1.01	3.14	0.7	7.71	49.4	80.5
7/12						
MB8CL0Br	4.29	64.5	147	0	0	0
MB8CL0.025Br	4.11	64.9	143	0.41	0	0
MB8CL0.05Br	4.2	64.1	140	0.56	0	0
MB8CL0.1Br	3.98	60.6	130	0.7	0.1	0
MB8CL0.25Br	3.65	50.6	101	1.3	3.7	0
MB8CL0.5Br	3.2	36.5	60	2.1	16	3.94
MB8CL0.75Br	2.66	24.3	32.3	2.84	30.2	18.1
MB8CL1.0Br	2.36	15.8	17.8	3.61	42.3	48.5
MB8CL1.5Br	0.94	6.02	4.19	4.56	52.6	91.1
MB8CL2.0Br	0.56	2.92	1.08	5.84	59.8	118
7/12						
MB8OCN0Br	0.2	5.95	0	0	0	0
MB8OCN0.025Br	3.22	12.2	0	0.49	0	0
MB8OCN0.05Br	3.39	12.4	0	0.4	0	0
MB8OCN0.1Br	3.37	11.7	0	0.42	0	0
MB8OCN0.25Br	3.28	10.9	0	0.52	0.53	0
MB8OCN0.5Br	2.86	8.59	0	1.24	1.04	0
MB8OCN0.75Br	2.47	7.97	0	1.59	1.62	0
MB8OCN1.0Br	2.11	6.91	0	2.02	2.13	0
MB8OCN1.5Br	1.91	6.24	0	2.86	3.81	0
MB8OCN2.0Br	1.98	7.31	0	2.92	4.43	0.71
7/12						
MB8CN0Br	0.98	9.07	0	0	0	0
MB8CN0.025Br	0.95	8.59	0	0	0	0
MB8CN0.05Br	0.99	8.42	0	0	0	0
MB8CN0.1Br	0.97	7.55	0	0	0	0
MB8CN0.25Br	0.96	7.25	0	0	0.27	0
MB8CN0.5Br	0.8	6.61	0	0.67	1.25	0
MB8CN0.75Br	0.73	6.33	0	0.9	2.35	0
MB8CN1.0Br	0.69	6.2	0	1.15	3.1	0
MB8CN1.5Br	0.63	5.67	0	1.44	3.86	0.91
MB8CN2.0Br	0.69	5.55	0	1.94	5.1	2.01

Appendix F, cont.

ug/L concentrations of HAAs

	ug/L BrClAA	ug/L BrCl2AA	ug/L Br2ClAA	ug/L THAA
7/12				
MB8OCL0Br	0.33	1.14	0.55	193.05
MB8OCL0.025Br	2.66	8.51	0.63	196.96
MB8OCL0.05Br	5.41	18.9	1.29	204.99
MB8OCL0.1Br	9.61	33.8	3.37	210.54
MB8OCL0.25Br	18	58.5	16	216.14
MB8OCL0.5Br	23.1	60.6	38.1	208.42
MB8OCL0.75Br	23.9	54.9	50.4	212.7
MB8OCL1.0Br	22.1	47.9	54.7	224.04
MB8OCL1.5Br	17.7	25.8	52.4	213.26
MB8OCL2.0Br	16.3	22	53.7	234.46
7/12				
MB8CL0Br	0.17	0.57	0.61	217.14
MB8CL0.025Br	2.05	4.98	0.62	220.07
MB8CL0.05Br	4.65	12.2	0.9	226.61
MB8CL0.1Br	8.38	23.5	1.62	228.88
MB8CL0.25Br	19.3	54.5	8.24	242.29
MB8CL0.5Br	29.8	73.1	34.4	259.04
MB8CL0.75Br	32.1	73.7	56.6	272.8
MB8CL1.0Br	31.2	71	72.8	305.37
MB8CL1.5Br	22.2	52.8	75.1	309.51
MB8CL2.0Br	16.2	26.6	65	296
7/12				THAA
MB8OCN0Br	0	0	0	6.15
MB8OCN0.025Br	0.36	0	0	16.27
MB8OCN0.05Br	0.66	0	0	16.85
MB8OCN0.1Br	1.04	0	0	16.53
MB8OCN0.25Br	1.36	0.35	0	16.94
MB8OCN0.5Br	1.49	0.74	0	15.96
MB8OCN0.75Br	1.8	0.97	0	16.42
MB8OCN1.0Br	1.95	1.11	0	16.23
MB8OCN1.5Br	2.64	1.64	0	19.1
MB8OCN2.0Br	3.26	1.96	0	22.57
7/12				
MB8CN0Br	0	0	0	10.05
MB8CN0.025Br	0.08	0	0	9.62
MB8CN0.05Br	0.43	0	0	9.84
MB8CN0.1Br	0.6	0	0	9.12
MB8CN0.25Br	1.24	0	0	9.72
MB8CN0.5Br	1.8	0.49	0	11.62
MB8CN0.75Br	2.18	0.8	0	13.29
MB8CN1.0Br	2.53	1.04	0.17	14.88
MB8CN1.5Br	2.73	1.56	0.33	17.13
MB8CN2.0Br	3.4	2.26	1.16	22.11

APPENDIX F, cont.

uM concentrations of HAAs

	uM MCAA	uM DCAA	uM TCAA	uM MBAA	uM DBAA	uM TBAA
7/12						
MB8OCL0Br	0.061	0.434	0.790	0.002	0.000	0.000
MB8OCL0.025Br	0.063	0.440	0.747	0.003	0.000	0.000
MB8OCL0.05Br	0.060	0.443	0.710	0.005	0.000	0.000
MB8OCL0.1Br	0.061	0.414	0.631	0.006	0.003	0.000
MB8OCL0.25Br	0.051	0.322	0.430	0.012	0.025	0.000
MB8OCL0.5Br	0.048	0.195	0.176	0.025	0.073	0.030
MB8OCL0.75Br	0.036	0.111	0.072	0.034	0.117	0.081
MB8OCL1.0Br	0.028	0.072	0.032	0.041	0.148	0.150
MB8OCL1.5Br	0.016	0.034	0.007	0.055	0.184	0.211
MB8OCL2.0Br	0.011	0.024	0.004	0.056	0.227	0.271
7/12						
MB8CL0Br	0.045	0.500	0.900	0.000	0.000	0.000
MB8CL0.025Br	0.044	0.503	0.875	0.003	0.000	0.000
MB8CL0.05Br	0.044	0.497	0.857	0.004	0.000	0.000
MB8CL0.1Br	0.042	0.470	0.796	0.005	0.000	0.000
MB8CL0.25Br	0.039	0.393	0.618	0.009	0.017	0.000
MB8CL0.5Br	0.034	0.283	0.367	0.015	0.073	0.013
MB8CL0.75Br	0.028	0.189	0.198	0.020	0.139	0.061
MB8CL1.0Br	0.025	0.123	0.109	0.026	0.194	0.163
MB8CL1.5Br	0.010	0.047	0.026	0.033	0.242	0.307
MB8CL2.0Br	0.006	0.023	0.007	0.042	0.275	0.398
7/12						
MB8OCN0Br	0.002	0.046	0.000	0.000	0.000	0.000
MB8OCN0.025Br	0.034	0.095	0.000	0.004	0.000	0.000
MB8OCN0.05Br	0.036	0.096	0.000	0.003	0.000	0.000
MB8OCN0.1Br	0.036	0.091	0.000	0.003	0.000	0.000
MB8OCN0.25Br	0.035	0.085	0.000	0.004	0.002	0.000
MB8OCN0.5Br	0.030	0.067	0.000	0.009	0.005	0.000
MB8OCN0.75Br	0.026	0.062	0.000	0.011	0.007	0.000
MB8OCN1.0Br	0.022	0.054	0.000	0.015	0.010	0.000
MB8OCN1.5Br	0.020	0.048	0.000	0.021	0.017	0.000
MB8OCN2.0Br	0.021	0.057	0.000	0.021	0.020	0.002
7/12						
MB8CN0Br	0.010	0.070	0.000	0.000	0.000	0.000
MB8CN0.025Br	0.010	0.067	0.000	0.000	0.000	0.000
MB8CN0.05Br	0.010	0.065	0.000	0.000	0.000	0.000
MB8CN0.1Br	0.010	0.059	0.000	0.000	0.000	0.000
MB8CN0.25Br	0.010	0.056	0.000	0.000	0.001	0.000
MB8CN0.5Br	0.008	0.051	0.000	0.005	0.006	0.000
MB8CN0.75Br	0.008	0.049	0.000	0.006	0.011	0.000
MB8CN1.0Br	0.007	0.048	0.000	0.008	0.014	0.000
MB8CN1.5Br	0.007	0.044	0.000	0.010	0.018	0.003
MB8CN2.0Br	0.007	0.043	0.000	0.014	0.023	0.007

Appendix F, cont.

uM concentrations of HAAs

	uM BrClAA	uM BrCl2AA	uM Br2ClAA	uM THAA
7/12				
MB8OCL0Br	0.002	0.005	0.002	1.297
MB8OCL0.025Br	0.015	0.041	0.002	1.312
MB8OCL0.05Br	0.031	0.091	0.005	1.345
MB8OCL0.1Br	0.055	0.163	0.013	1.347
MB8OCL0.25Br	0.104	0.282	0.063	1.289
MB8OCL0.5Br	0.133	0.292	0.151	1.122
MB8OCL0.75Br	0.138	0.264	0.200	1.052
MB8OCL1.0Br	0.127	0.231	0.217	1.045
MB8OCL1.5Br	0.102	0.124	0.208	0.941
MB8OCL2.0Br	0.094	0.106	0.213	1.006
7/12				
MB8CL0Br	0.001	0.003	0.002	1.452
MB8CL0.025Br	0.012	0.024	0.002	1.464
MB8CL0.05Br	0.027	0.059	0.004	1.492
MB8CL0.1Br	0.048	0.113	0.006	1.481
MB8CL0.25Br	0.111	0.262	0.033	1.482
MB8CL0.5Br	0.172	0.352	0.136	1.446
MB8CL0.75Br	0.185	0.355	0.224	1.399
MB8CL1.0Br	0.180	0.342	0.289	1.450
MB8CL1.5Br	0.128	0.254	0.298	1.344
MB8CL2.0Br	0.093	0.128	0.258	1.229
7/12				
MB8OCN0Br	0.000	0.000	0.000	0.048
MB8OCN0.025Br	0.002	0.000	0.000	0.134
MB8OCN0.05Br	0.004	0.000	0.000	0.139
MB8OCN0.1Br	0.006	0.000	0.000	0.135
MB8OCN0.25Br	0.008	0.002	0.000	0.135
MB8OCN0.5Br	0.009	0.004	0.000	0.123
MB8OCN0.75Br	0.010	0.005	0.000	0.122
MB8OCN1.0Br	0.011	0.005	0.000	0.117
MB8OCN1.5Br	0.015	0.008	0.000	0.130
MB8OCN2.0Br	0.019	0.009	0.000	0.150
7/12				
MB8CN0Br	0.000	0.000	0.000	0.081
MB8CN0.025Br	0.000	0.000	0.000	0.077
MB8CN0.05Br	0.002	0.000	0.000	0.078
MB8CN0.1Br	0.003	0.000	0.000	0.072
MB8CN0.25Br	0.007	0.000	0.000	0.075
MB8CN0.5Br	0.010	0.002	0.000	0.083
MB8CN0.75Br	0.013	0.004	0.000	0.091
MB8CN1.0Br	0.015	0.005	0.001	0.098
MB8CN1.5Br	0.016	0.008	0.001	0.106
MB8CN2.0Br	0.020	0.011	0.005	0.130

Appendix F, cont.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)					
	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
7/12						
MB8OCL0Br	4.74	33.44	60.90	0.18	0.00	0.00
MB8OCL0.025Br	4.82	33.52	56.91	0.26	0.00	0.00
MB8OCL0.05Br	4.45	32.94	52.81	0.34	0.00	0.00
MB8OCL0.1Br	4.51	30.76	46.82	0.46	0.26	0.00
MB8OCL0.25Br	3.98	24.99	33.35	0.91	1.95	0.00
MB8OCL0.5Br	4.25	17.35	15.66	2.25	6.46	2.71
MB8OCL0.75Br	3.44	10.54	6.81	3.27	11.08	7.66
MB8OCL1.0Br	2.64	6.91	3.02	3.92	14.15	14.33
MB8OCL1.5Br	1.72	3.59	0.78	5.80	19.57	22.42
MB8OCL2.0Br	1.06	2.42	0.43	5.52	22.55	26.98
7/12						
MB8CL0Br	3.13	34.47	61.98	0.00	0.00	0.00
MB8CL0.025Br	2.97	34.40	59.81	0.20	0.00	0.00
MB8CL0.05Br	2.98	33.33	57.45	0.27	0.00	0.00
MB8CL0.1Br	2.84	31.73	53.72	0.34	0.03	0.00
MB8CL0.25Br	2.61	26.49	41.72	0.63	1.15	0.00
MB8CL0.5Br	2.34	19.58	25.40	1.05	5.08	0.92
MB8CL0.75Br	2.01	13.48	14.14	1.46	9.91	4.36
MB8CL1.0Br	1.72	8.45	7.51	1.79	13.39	11.27
MB8CL1.5Br	0.74	3.48	1.91	2.44	17.98	22.85
MB8CL2.0Br	0.48	1.84	0.54	3.42	22.35	32.37
7/12						
MB8OCN0Br	4.39	95.61	0.00	0.00	0.00	0.00
MB8OCN0.025Br	25.38	70.45	0.00	2.63	0.00	0.00
MB8OCN0.05Br	25.86	69.32	0.00	2.08	0.00	0.00
MB8OCN0.1Br	26.34	67.00	0.00	2.23	0.00	0.00
MB8OCN0.25Br	25.72	62.64	0.00	2.77	1.80	0.00
MB8OCN0.5Br	24.66	54.28	0.00	7.27	3.89	0.00
MB8OCN0.75Br	21.45	50.71	0.00	9.39	6.10	0.00
MB8OCN1.0Br	19.12	45.87	0.00	12.44	8.37	0.00
MB8OCN1.5Br	15.58	37.28	0.00	15.86	13.47	0.00
MB8OCN2.0Br	14.01	37.89	0.00	14.05	13.59	1.60
7/12						
MB8CN0Br	12.85	87.15	0.00	0.00	0.00	0.00
MB8CN0.025Br	13.04	86.37	0.00	0.00	0.00	0.00
MB8CN0.05Br	13.39	83.44	0.00	0.00	0.00	0.00
MB8CN0.1Br	14.20	81.01	0.00	0.00	0.00	0.00
MB8CN0.25Br	13.59	75.19	0.00	0.00	1.66	0.00
MB8CN0.5Br	10.20	61.74	0.00	5.81	6.91	0.00
MB8CN0.75Br	8.54	54.24	0.00	7.16	11.92	0.00
MB8CN1.0Br	7.44	48.99	0.00	8.43	14.50	0.00
MB8CN1.5Br	6.27	41.35	0.00	9.75	16.66	2.88
MB8CN2.0Br	5.64	33.22	0.00	10.78	18.07	5.23

Appendix F, cont.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)		
	BrClAA	BrCl2AA	Br2ClAA
7/12			
MB8OCL0Br	0.15	0.42	0.17
MB8OCL0.025Br	1.17	3.12	0.19
MB8OCL0.05Br	2.32	6.76	0.38
MB8OCL0.1Br	4.12	12.08	0.99
MB8OCL0.25Br	8.06	21.85	4.92
MB8OCL0.5Br	11.88	25.99	13.46
MB8OCL0.75Br	13.10	25.11	18.99
MB8OCL1.0Br	12.21	22.07	20.76
MB8OCL1.5Br	10.85	13.19	22.08
MB8OCL2.0Br	9.35	10.53	21.17
7/12			
MB8CL0Br	0.07	0.19	0.17
MB8CL0.025Br	0.81	1.64	0.17
MB8CL0.05Br	1.80	3.94	0.24
MB8CL0.1Br	3.26	7.63	0.43
MB8CL0.25Br	7.51	17.70	2.20
MB8CL0.5Br	11.89	24.32	9.43
MB8CL0.75Br	13.24	25.36	16.04
MB8CL1.0Br	12.41	23.56	19.90
MB8CL1.5Br	9.53	18.91	22.16
MB8CL2.0Br	7.61	10.42	20.97
7/12			
MB8OCN0Br	0.00	0.00	0.00
MB8OCN0.025Br	1.55	0.00	0.00
MB8OCN0.05Br	2.74	0.00	0.00
MB8OCN0.1Br	4.43	0.00	0.00
MB8OCN0.25Br	5.81	1.25	0.00
MB8OCN0.5Br	7.00	2.90	0.00
MB8OCN0.75Br	8.52	3.83	0.00
MB8OCN1.0Br	9.63	4.57	0.00
MB8OCN1.5Br	11.73	6.08	0.00
MB8OCN2.0Br	12.57	6.30	0.00
7/12			
MB8CN0Br	0.00	0.00	0.00
MB8CN0.025Br	0.60	0.00	0.00
MB8CN0.05Br	3.17	0.00	0.00
MB8CN0.1Br	4.79	0.00	0.00
MB8CN0.25Br	9.56	0.00	0.00
MB8CN0.5Br	12.50	2.84	0.00
MB8CN0.75Br	13.89	4.25	0.00
MB8CN1.0Br	14.86	5.10	0.69
MB8CN1.5Br	14.80	7.06	1.23
MB8CN2.0Br	15.13	8.39	3.55

APPENDIX F, cont.

Bromine incorporation		Chlorine incorporation		
uM	per uM THAA	uM	per uM THAA	
0.0000	0.0000	0.0944	1.9561	MB8OCN0Br
0.0056	0.0417	0.2255	1.6783	MB8OCN0.025Br
0.0067	0.0482	0.2321	1.6724	MB8OCN0.05Br
0.0090	0.0666	0.2232	1.6477	MB8OCN0.1Br
0.0181	0.1344	0.2151	1.5931	MB8OCN0.25Br
0.0306	0.2495	0.1793	1.4602	MB8OCN0.5Br
0.0414	0.3394	0.1695	1.3905	MB8OCN0.75Br
0.0507	0.4338	0.1515	1.2963	MB8OCN1.0Br
0.0787	0.6061	0.1481	1.1403	MB8OCN1.5Br
0.0971	0.6489	0.1721	1.1496	MB8OCN2.0Br
				7/12
0.0000	0.0000	0.1511	1.8715	MB8CN0Br
0.0005	0.0060	0.1438	1.8637	MB8CN0.025Br
0.0025	0.0317	0.1436	1.8344	MB8CN0.05Br
0.0035	0.0479	0.1309	1.8101	MB8CN0.1Br
0.0096	0.1288	0.1298	1.7353	MB8CN0.25Br
0.0290	0.3497	0.1261	1.5186	MB8CN0.5Br
0.0445	0.4914	0.1262	1.3942	MB8CN0.75Br
0.0577	0.5876	0.1288	1.3116	MB8CN1.0Br
0.0809	0.7604	0.1267	1.1912	MB8CN1.5Br
0.1208	0.9321	0.1394	1.0754	MB8CN2.0Br

APPENDIX F, cont.

Mole fraction of mono, di, trihalogenated species

	mono	di	tri	uM Br-
MB8OCN0Br	0.044	0.956	0.000	0.00
MB8OCN0.025Br	0.280	0.720	0.000	0.27
MB8OCN0.05Br	0.279	0.721	0.000	0.54
MB8OCN0.1Br	0.286	0.714	0.000	1.08
MB8OCN0.25Br	0.285	0.703	0.012	2.69
MB8OCN0.5Br	0.319	0.652	0.029	5.38
MB8OCN0.75Br	0.308	0.653	0.038	8.08
MB8OCN1.0Br	0.316	0.639	0.046	10.77
MB8OCN1.5Br	0.314	0.625	0.061	16.14
MB8OCN2.0Br	0.281	0.640	0.079	21.50
7/12	mono	di	tri	uM Br-
MB8CN0Br	0.129	0.871	0.000	0
MB8CN0.025Br	0.130	0.870	0.000	0.31
MB8CN0.05Br	0.134	0.866	0.000	0.63
MB8CN0.1Br	0.142	0.858	0.000	1.25
MB8CN0.25Br	0.136	0.864	0.000	3.13
MB8CN0.5Br	0.160	0.812	0.028	6.26
MB8CN0.75Br	0.157	0.801	0.043	9.39
MB8CN1.0Br	0.159	0.783	0.058	12.52
MB8CN1.5Br	0.160	0.728	0.112	18.77
MB8CN2.0Br	0.164	0.664	0.172	25

Appendix F, cont.

ug/L concentrations of HAA species

	ug/L MCAA	ug/L DCAA	ug/L TCAA	ug/L MBAA	ug/L DBAA	ug/L TBAA
7/21						
MB6OCL0Br	2.57	63.4	126	0.37	0	0
MB6OCL0.025Br	2.42	61	124	0.59	0.21	0
MB6OCL0.05Br	2.39	58	112	0.81	0.55	0
MB6OCL0.1Br	2.29	53.9	101	1.24	2.17	0
MB6OCL0.25Br	1.97	41.2	66.9	2.12	9.69	3.3
MB6OCL0.5Br	1.65	28.7	31.6	3.19	27.2	10.4
MB6OCL0.75Br	1.55	19.3	14.6	3.78	40.8	24.4
MB6OCL1.0Br	1.26	13.4	6.95	4.06	44.5	38.4
MB6OCL1.5Br	1.03	6.7	2.7	4.9	47.8	61.6
MB6OCL2.0Br	0.82	4.48	1.53	5.69	50.3	76.7
7/21						
MB6CL0Br	2.55	62.4	164	0	0	0
MB6CL0.025Br	2.39	61.6	157	0.44	0.22	0
MB6CL0.05Br	2.34	60.5	153	0.67	0.43	0
MB6CL0.1Br	2.16	56.9	141	0.83	1.3	0
MB6CL0.25Br	1.95	49	115	1.43	6.31	2.95
MB6CL0.5Br	1.37	36.3	75.1	2.1	22.9	8.22
MB6CL0.75Br	1.33	26.4	45.4	2.78	43	20.8
MB6CL1.0Br	1.2	18.8	25.2	3.24	60.6	42.2
MB6CL1.5Br	0.7	8.52	7.26	3.58	77.7	91.7
MB6CL2.0Br	0.67	4.51	3.22	4.36	83.8	143

APPENDIX F, cont.

ug/L concentrations of HAA species

	ug/L BrClAA	ug/L BrCl2AA	ug/L Br2ClAA	ug/L THAA
7/21				
MB6OCL0Br	0.71	2.84	2	197.89
MB6OCL0.025Br	4.37	11.5	2.36	206.45
MB6OCL0.05Br	8.06	20.6	3.4	205.81
MB6OCL0.1Br	16.7	40.3	8.1	225.7
MB6OCL0.25Br	30.1	65.7	30.3	251.28
MB6OCL0.5Br	39.4	73.8	66.5	282.44
MB6OCL0.75Br	40.2	65.7	89.3	299.63
MB6OCL1.0Br	34.1	51.7	91.9	286.27
MB6OCL1.5Br	25.1	35	84.5	269.33
MB6OCL2.0Br	20.7	27.5	75.9	263.62
7/21				
MB6CL0Br	0.41	2.3	2.32	233.98
MB6CL0.025Br	2.94	9.23	2.46	236.28
MB6CL0.05Br	5.49	16.7	2.97	242.1
MB6CL0.1Br	11	33.2	5.13	251.52
MB6CL0.25Br	23.6	65.4	18.7	284.34
MB6CL0.5Br	37.1	94.3	57.1	334.49
MB6CL0.75Br	44.1	100	93.7	377.51
MB6CL1.0Br	42.3	92.1	123	408.64
MB6CL1.5Br	32.5	63.7	142	427.66
MB6CL2.0Br	24.9	48.9	136	449.36

APPENDIX F, cont.

uM concentrations of HAA species

7/21	uM MCAA	uM DCAA	uM TCAA	uM MBAA	uM DBAA	uM TBAA
MB6OCL0Br	0.027	0.492	0.771	0.003	0.000	0.000
MB6OCL0.025Br	0.026	0.473	0.759	0.004	0.001	0.000
MB6OCL0.05Br	0.025	0.450	0.686	0.006	0.003	0.000
MB6OCL0.1Br	0.024	0.418	0.618	0.009	0.010	0.000
MB6OCL0.25Br	0.021	0.320	0.410	0.015	0.044	0.011
MB6OCL0.5Br	0.017	0.223	0.193	0.023	0.125	0.035
MB6OCL0.75Br	0.016	0.150	0.089	0.027	0.187	0.082
MB6OCL1.0Br	0.013	0.104	0.043	0.029	0.204	0.129
MB6OCL1.5Br	0.011	0.052	0.017	0.035	0.219	0.208
MB6OCL2.0Br	0.009	0.035	0.009	0.041	0.231	0.259
7/21						
MB6CL0Br	0.027	0.484	1.004	0.000	0.000	0.000
MB6CL0.025Br	0.025	0.478	0.961	0.003	0.001	0.000
MB6CL0.05Br	0.025	0.469	0.937	0.005	0.002	0.000
MB6CL0.1Br	0.023	0.441	0.863	0.006	0.006	0.000
MB6CL0.25Br	0.021	0.380	0.704	0.010	0.029	0.010
MB6CL0.5Br	0.015	0.282	0.460	0.015	0.105	0.028
MB6CL0.75Br	0.014	0.205	0.278	0.020	0.197	0.070
MB6CL1.0Br	0.013	0.146	0.154	0.023	0.278	0.142
MB6CL1.5Br	0.007	0.066	0.044	0.026	0.357	0.309
MB6CL2.0Br	0.007	0.035	0.020	0.031	0.385	0.482

Appendix F, cont.

uM concentrations of HAA species

7/21	uM BrClAA	uM BrCl2AA	uM Br2ClAA	uM THAA
MB6OCL0Br	0.004	0.014	0.008	1.319
MB6OCL0.025Br	0.025	0.055	0.009	1.353
MB6OCL0.05Br	0.046	0.099	0.013	1.328
MB6OCL0.1Br	0.096	0.194	0.032	1.402
MB6OCL0.25Br	0.174	0.316	0.120	1.431
MB6OCL0.5Br	0.227	0.355	0.264	1.463
MB6OCL0.75Br	0.232	0.316	0.354	1.454
MB6OCL1.0Br	0.197	0.249	0.364	1.333
MB6OCL1.5Br	0.145	0.168	0.335	1.190
MB6OCL2.0Br	0.119	0.132	0.301	1.136
7/21				
MB6CL0Br	0.002	0.011	0.009	1.538
MB6CL0.025Br	0.017	0.044	0.010	1.540
MB6CL0.05Br	0.032	0.080	0.012	1.561
MB6CL0.1Br	0.063	0.160	0.020	1.583
MB6CL0.25Br	0.136	0.315	0.074	1.679
MB6CL0.5Br	0.214	0.454	0.226	1.798
MB6CL0.75Br	0.254	0.481	0.371	1.891
MB6CL1.0Br	0.244	0.443	0.488	1.931
MB6CL1.5Br	0.187	0.307	0.563	1.867
MB6CL2.0Br	0.144	0.235	0.539	1.878

Appendix F, cont.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)					
7/21	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB6OCL0Br	2.06	37.30	58.49	0.20	0.00	0.00
MB6OCL0.025Br	1.89	34.97	56.10	0.31	0.07	0.00
MB6OCL0.05Br	1.90	33.87	51.62	0.44	0.19	0.00
MB6OCL0.1Br	1.73	29.83	44.10	0.64	0.71	0.00
MB6OCL0.25Br	1.46	22.34	28.62	1.07	3.11	0.78
MB6OCL0.5Br	1.19	15.22	13.23	1.57	8.54	2.40
MB6OCL0.75Br	1.13	10.29	6.15	1.87	12.88	5.65
MB6OCL1.0Br	1.00	7.80	3.19	2.19	15.33	9.71
MB6OCL1.5Br	0.92	4.37	1.39	2.96	18.44	17.45
MB6OCL2.0Br	0.76	3.06	0.82	3.61	20.33	22.76
7/21						
MB6CL0Br	1.76	31.48	65.29	0.00	0.00	0.00
MB6CL0.025Br	1.64	31.04	62.43	0.21	0.07	0.00
MB6CL0.05Br	1.59	30.06	59.99	0.31	0.13	0.00
MB6CL0.1Br	1.44	27.89	54.53	0.38	0.38	0.00
MB6CL0.25Br	1.23	22.64	41.93	0.61	1.73	0.59
MB6CL0.5Br	0.81	15.66	25.57	0.84	5.85	1.54
MB6CL0.75Br	0.74	10.83	14.69	1.06	10.44	3.71
MB6CL1.0Br	0.66	7.55	7.99	1.21	14.41	7.36
MB6CL1.5Br	0.40	3.54	2.38	1.38	19.11	16.56
MB6CL2.0Br	0.38	1.86	1.05	1.67	20.49	25.66

APPENDIX F, cont.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)		
7/21	BrClAA	BrCl2AA	Br2ClAA
MB6OCL0Br	0.31	1.04	0.60
MB6OCL0.025Br	1.86	4.09	0.69
MB6OCL0.05Br	3.50	7.46	1.01
MB6OCL0.1Br	6.87	13.83	2.29
MB6OCL0.25Br	12.14	22.10	8.40
MB6OCL0.5Br	15.54	24.28	18.03
MB6OCL0.75Br	15.94	21.74	24.34
MB6OCL1.0Br	14.76	18.67	27.34
MB6OCL1.5Br	12.17	14.15	28.15
MB6OCL2.0Br	10.51	11.65	26.49
7/21			
MB6CL0Br	0.15	0.72	0.60
MB6CL0.025Br	1.10	2.88	0.63
MB6CL0.05Br	2.03	5.15	0.75
MB6CL0.1Br	4.01	10.09	1.28
MB6CL0.25Br	8.11	18.74	4.42
MB6CL0.5Br	11.90	25.24	12.59
MB6CL0.75Br	13.45	25.44	19.64
MB6CL1.0Br	12.63	22.95	25.25
MB6CL1.5Br	10.04	16.42	30.16
MB6CL2.0Br	7.65	12.53	28.71

APPENDIX F cont.
ug/L concentration of HAAs in ozonated samples

7/7	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB8O 0Br	0	0	0	0	0	0
MB8O 0.025Br	0	0	0	0	0	0
MB8O 0.05Br	0	0	0	0	0	0
MB8O 0.1Br	0	0	0	0	0	0
MB8O 0.25Br	0	0	0	0	0	0
MB8O 0.5Br	0	0	0	0	0	0
MB8O 0.75Br	0	0	0	0	0	0
MB8O 1.0Br	0	0	0.17	0.34	0	0
MB8O 1.5Br	0	0	0	0.39	0.24	0
MB8O 2.0Br	0	0	0.17	0.59	0.49	0

7/7	BrClAA	BrCl2AA	Br2ClAA
MB8O 0Br	0	0	0
MB8O 0.025Br	0	0	0
MB8O 0.05Br	0	0	0
MB8O 0.1Br	0	0	0
MB8O 0.25Br	0	0	0
MB8O 0.5Br	0	0	0
MB8O 0.75Br	0	0	0
MB8O 1.0Br	0	0	0
MB8O 1.5Br	0	0	0
MB8O 2.0Br	0	0	0

APPENDIX F, cont.

uM concentration of HAAs in ozonated samples

7/7	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB8O 0Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.025Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.05Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.1Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.25Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.5Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 0.75Br	0.000	0.000	0.000	0.000	0.000	0.000
MB8O 1.0Br	0.000	0.000	0.001	0.002	0.000	0.000
MB8O 1.5Br	0.000	0.000	0.000	0.003	0.001	0.000
MB8O 2.0Br	0.000	0.000	0.001	0.004	0.002	0.000

7/7	BrClAA	BrCl2AA	Br2ClAA	THAA
MB8O 0Br	0.000	0.000	0.000	0.000
MB8O 0.025Br	0.000	0.000	0.000	0.000
MB8O 0.05Br	0.000	0.000	0.000	0.000
MB8O 0.1Br	0.000	0.000	0.000	0.000
MB8O 0.25Br	0.000	0.000	0.000	0.000
MB8O 0.5Br	0.000	0.000	0.000	0.000
MB8O 0.75Br	0.000	0.000	0.000	0.000
MB8O 1.0Br	0.000	0.000	0.000	0.003
MB8O 1.5Br	0.000	0.000	0.000	0.004
MB8O 2.0Br	0.000	0.000	0.000	0.008

Appendix F, cont.

Mole fractions of HAA species in ozonated samples

7/7	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
MB8O 0Br						
MB8O 0.025Br						
MB8O 0.05Br						
MB8O 0.1Br						
MB8O 0.25Br						
MB8O 0.5Br						
MB8O 0.75Br						
MB8O 1.0Br	0.00	0.00	29.83	70.17	0.00	0.00
MB8O 1.5Br	0.00	0.00	0.00	71.82	28.18	0.00
MB8O 2.0Br	0.00	0.00	13.81	56.35	29.85	0.00

7/7	BrClAA	BrCl2AA	Br2ClAA
MB8O 0Br			
MB8O 0.025Br			
MB8O 0.05Br			
MB8O 0.1Br			
MB8O 0.25Br			
MB8O 0.5Br			
MB8O 0.75Br			
MB8O 1.0Br	0.00	0.00	0.00
MB8O 1.5Br	0.00	0.00	0.00
MB8O 2.0Br	0.00	0.00	0.00

Appendix F, cont.

ug/L concentrations of HAAs

9/14	ug/L MCAA	ug/L DCAA	ug/L TCAA	ug/L MBAA	ug/L DBAA	ug/L TBAA
PB8OCL0Br	5.63	36.5	83.6	0	0	0
PB8OCL0.025Br	5.25	38.2	75	0.42	0	0
PB8OCL0.05Br	4.98	35.2	65.2	0.64	0.61	0
PB8OCL0.1Br	4.68	31.3	52	0.82	1.62	0
PB8OCL0.25Br	4.12	22.2	27.5	1.58	5.86	4.1
PB8OCL0.5Br	3.29	12.5	10.1	2.72	13.1	8.59
PB8OCL0.75Br	2.98	7.58	4.3	4.04	18.7	14.2
PB8OCL1.0Br	2.14	4.71	2.4	5.26	25.3	21.5
PB8OCL1.5Br	1.44	2.58	1.24	6.94	36.3	32.8
PB8OCL2.0Br	1.12	1.6	0.85	8.27	44.8	45.8
9/14						
PB8CL0Br	2.79	29.5	74	0	0	0
PB8CL0.025Br	2.99	28.7	69.4	0	0	0
PB8CL0.05Br	2.3	27.6	65.5	0.34	0	0
PB8CL0.1Br	2.1	25.4	57.7	0.55	0.66	0
PB8CL0.25Br	1.73	19.2	37.2	1.04	4.06	3.44
PB8CL0.5Br	1.6	11.4	17	1.54	13.9	8.95
PB8CL0.75Br	1.49	6.73	8.4	2.14	23.3	23.8
PB8CL1.0Br	1.1	4.31	5.05	3.08	31.1	46.2
PB8CL1.5Br	0.42	2.06	2.57	4.07	35.3	63.7
PB8CL2.0Br	0.18	1.49	1.84	4.99	40.9	83.7
9/14						
PB6OCL0Br	2.3	37	60.9	0.4	0	0
PB6OCL0.025Br	2.42	34.7	55.9	0.56	0	0
PB6OCL0.05Br	2.24	32.1	50.8	0.86	0.57	0
PB6OCL0.1Br	2.28	29.2	42.1	1.24	1.7	0
PB6OCL0.25Br	2.14	21	23.3	1.99	6.81	3.75
PB6OCL0.5Br	1.8	15.9	10.4	2.57	17.6	8.88
PB6OCL0.75Br	1.61	11.3	4.95	3.98	24.1	16
PB6OCL1.0Br	1.27	7.99	3.11	4.69	33.5	26.8
PB6OCL1.5Br	1.09	5.85	1.76	7.15	48	44
PB6OCL2.0Br	0.95	4.48	1.19	8.36	60.2	58.2
9/14						
PB6CL0Br	1.32	28.4	80.2	0	0	0
PB6CL0.025Br	1.36	27.6	75.1	0.53	0	0
PB6CL0.05Br	1.28	26.5	72.1	0.57	0.33	0
PB6CL0.1Br	1.16	24.7	65.1	0.76	1.17	0
PB6CL0.25Br	0.91	19.9	48.3	1.12	5.08	3.4
PB6CL0.5Br	0.83	13.8	26.1	1.64	16.6	6.71
PB6CL0.75Br	0.58	9.3	14.3	1.87	29.9	17.2
PB6CL1.0Br	0.62	6.31	8.21	2.73	39.2	31.9
PB6CL1.5Br	0.38	2.88	3.45	3.49	47.5	59.6
PB6CL2.0Br	0.25	1.36	1.91	4.52	51.1	77.3

Appendix F, cont.

ug/L concentrations of HAAs

	ug/L	ug/L	ug/L	ug/L
9/14	BrClAA	BrCl2AA	Br2ClAA	THAA
PB8OCL0Br	0	0	0	125.73
PB8OCL0.025Br	2.31	6.8	0	127.98
PB8OCL0.05Br	4.71	12.2	3.3	126.84
PB8OCL0.1Br	7.88	18.3	4.77	121.37
PB8OCL0.25Br	14	29.8	11.6	120.76
PB8OCL0.5Br	17.2	29.1	20.6	117.2
PB8OCL0.75Br	15.8	22.9	24	114.5
PB8OCL1.0Br	13.8	20.9	26	122.01
PB8OCL1.5Br	10.6	10	23.9	125.8
PB8OCL2.0Br	8.41	0	23.1	133.95
9/14				
PB8CL0Br	0	0	0	106.29
PB8CL0.025Br	1.2	4.58	0	106.87
PB8CL0.05Br	2.46	7.3	0	105.5
PB8CL0.1Br	5.08	13.7	3.27	108.46
PB8CL0.25Br	11.6	31.1	9.74	119.11
PB8CL0.5Br	16.2	40	26.1	136.69
PB8CL0.75Br	16.2	39.5	40.5	162.06
PB8CL1.0Br	15.1	37.3	47.6	190.84
PB8CL1.5Br	10.7	17.1	40.2	176.12
PB8CL2.0Br	8.84	13.6	40	195.54
9/14				
PB6OCL0Br	0	0	0	100.6
PB6OCL0.025Br	3.82	6.99	0	104.39
PB6OCL0.05Br	7.43	12.6	3.54	110.14
PB6OCL0.1Br	12.8	21.2	6.47	116.99
PB6OCL0.25Br	21.2	32.3	17.7	130.19
PB6OCL0.5Br	25.6	34.5	38.1	155.35
PB6OCL0.75Br	24.8	28.6	45.9	161.24
PB6OCL1.0Br	23.2	25.6	52.1	178.26
PB6OCL1.5Br	20.4	21.2	52.2	201.65
PB6OCL2.0Br	18.5	19	51.4	222.28
9/14				
PB6CL0Br	0	0	0	109.92
PB6CL0.025Br	1.89	5.96	0	112.44
PB6CL0.05Br	3.59	9.88	2.93	117.18
PB6CL0.1Br	7	18.3	4.63	122.82
PB6CL0.25Br	13.8	36.5	13.1	142.11
PB6CL0.5Br	20.7	49.6	36.2	172.18
PB6CL0.75Br	23	52.2	59.1	207.45
PB6CL1.0Br	22.3	48	68.4	227.67
PB6CL1.5Br	17.5	36.1	71.3	242.2
PB6CL2.0Br	13.9	30.3	66.4	247.04

Appendix F, cont.

uM concentrations of HAAs

9/14	uM MCAA	uM DCAA	uM TCAA	uM MBAA	uM DBAA	uM TBAA
PB8OCL0Br	0.060	0.283	0.512	0.000	0.000	0.000
PB8OCL0.025Br	0.056	0.296	0.459	0.003	0.000	0.000
PB8OCL0.05Br	0.053	0.273	0.399	0.005	0.003	0.000
PB8OCL0.1Br	0.050	0.243	0.318	0.006	0.007	0.000
PB8OCL0.25Br	0.044	0.172	0.168	0.011	0.027	0.014
PB8OCL0.5Br	0.035	0.097	0.062	0.020	0.060	0.029
PB8OCL0.75Br	0.032	0.059	0.026	0.029	0.086	0.048
PB8OCL1.0Br	0.023	0.037	0.015	0.038	0.116	0.072
PB8OCL1.5Br	0.015	0.020	0.008	0.050	0.167	0.111
PB8OCL2.0Br	0.012	0.012	0.005	0.060	0.206	0.154
9/14						
PB8CL0Br	0.030	0.229	0.453	0.000	0.000	0.000
PB8CL0.025Br	0.032	0.223	0.425	0.000	0.000	0.000
PB8CL0.05Br	0.024	0.214	0.401	0.002	0.000	0.000
PB8CL0.1Br	0.022	0.197	0.353	0.004	0.003	0.000
PB8CL0.25Br	0.018	0.149	0.228	0.007	0.019	0.012
PB8CL0.5Br	0.017	0.088	0.104	0.011	0.064	0.030
PB8CL0.75Br	0.016	0.052	0.051	0.015	0.107	0.080
PB8CL1.0Br	0.012	0.033	0.031	0.022	0.143	0.156
PB8CL1.5Br	0.004	0.016	0.016	0.029	0.162	0.215
PB8CL2.0Br	0.002	0.012	0.011	0.036	0.188	0.282
9/14						
PB6OCL0Br	0.024	0.287	0.373	0.003	0.000	0.000
PB6OCL0.025Br	0.026	0.269	0.342	0.004	0.000	0.000
PB6OCL0.05Br	0.024	0.249	0.311	0.006	0.003	0.000
PB6OCL0.1Br	0.024	0.227	0.258	0.009	0.008	0.000
PB6OCL0.25Br	0.023	0.163	0.143	0.014	0.031	0.013
PB6OCL0.5Br	0.019	0.123	0.064	0.019	0.081	0.030
PB6OCL0.75Br	0.017	0.088	0.030	0.029	0.111	0.054
PB6OCL1.0Br	0.013	0.062	0.019	0.034	0.154	0.090
PB6OCL1.5Br	0.012	0.045	0.011	0.051	0.220	0.148
PB6OCL2.0Br	0.010	0.035	0.007	0.060	0.276	0.196
9/14						
PB6CL0Br	0.014	0.220	0.491	0.000	0.000	0.000
PB6CL0.025Br	0.014	0.214	0.460	0.004	0.000	0.000
PB6CL0.05Br	0.014	0.206	0.441	0.004	0.002	0.000
PB6CL0.1Br	0.012	0.192	0.399	0.005	0.005	0.000
PB6CL0.25Br	0.010	0.154	0.296	0.008	0.023	0.011
PB6CL0.5Br	0.009	0.107	0.160	0.012	0.076	0.023
PB6CL0.75Br	0.006	0.072	0.088	0.013	0.137	0.058
PB6CL1.0Br	0.007	0.049	0.050	0.020	0.180	0.108
PB6CL1.5Br	0.004	0.022	0.021	0.025	0.218	0.201
PB6CL2.0Br	0.003	0.011	0.012	0.033	0.235	0.261

APPENDIX F. cont.

uM concentrations of HAAs

	uM	uM	uM	uM
9/14	BrClAA	BrCl2AA	Br2ClAA	THAA
PB8OCL0Br	0.000	0.000	0.000	0.855
PB8OCL0.025Br	0.013	0.033	0.000	0.860
PB8OCL0.05Br	0.027	0.059	0.013	0.831
PB8OCL0.1Br	0.045	0.088	0.019	0.776
PB8OCL0.25Br	0.081	0.143	0.046	0.706
PB8OCL0.5Br	0.099	0.140	0.082	0.623
PB8OCL0.75Br	0.091	0.110	0.095	0.576
PB8OCL1.0Br	0.080	0.101	0.103	0.584
PB8OCL1.5Br	0.061	0.048	0.095	0.574
PB8OCL2.0Br	0.049	0.000	0.092	0.589
9/14				
PB8CL0Br	0.000	0.000	0.000	0.711
PB8CL0.025Br	0.007	0.022	0.000	0.708
PB8CL0.05Br	0.014	0.035	0.000	0.691
PB8CL0.1Br	0.029	0.066	0.013	0.688
PB8CL0.25Br	0.067	0.150	0.039	0.688
PB8CL0.5Br	0.093	0.192	0.103	0.704
PB8CL0.75Br	0.093	0.190	0.161	0.766
PB8CL1.0Br	0.087	0.179	0.189	0.852
PB8CL1.5Br	0.062	0.082	0.159	0.746
PB8CL2.0Br	0.051	0.065	0.159	0.806
9/14				
PB6OCL0Br	0.000	0.000	0.000	0.687
PB6OCL0.025Br	0.022	0.034	0.000	0.697
PB6OCL0.05Br	0.043	0.061	0.014	0.710
PB6OCL0.1Br	0.074	0.102	0.026	0.727
PB6OCL0.25Br	0.122	0.155	0.070	0.734
PB6OCL0.5Br	0.148	0.166	0.151	0.800
PB6OCL0.75Br	0.143	0.138	0.182	0.791
PB6OCL1.0Br	0.134	0.123	0.207	0.836
PB6OCL1.5Br	0.118	0.102	0.207	0.914
PB6OCL2.0Br	0.107	0.091	0.204	0.987
9/14				
PB6CL0Br	0.000	0.000	0.000	0.725
PB6CL0.025Br	0.011	0.029	0.000	0.732
PB6CL0.05Br	0.021	0.048	0.012	0.746
PB6CL0.1Br	0.040	0.088	0.018	0.760
PB6CL0.25Br	0.080	0.176	0.052	0.810
PB6CL0.5Br	0.119	0.239	0.144	0.888
PB6CL0.75Br	0.133	0.251	0.234	0.993
PB6CL1.0Br	0.129	0.231	0.271	1.044
PB6CL1.5Br	0.101	0.174	0.283	1.049
PB6CL2.0Br	0.080	0.146	0.263	1.042

Appendix F, cont.

Mole fractions of individual HAAs

	Mole fraction Xi (x100)					
9/14	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
PB8OCL0Br	6.98	33.14	59.89	0.00	0.00	0.00
PB8OCL0.025Br	6.46	34.45	53.38	0.35	0.00	0.00
PB8OCL0.05Br	6.34	32.85	48.01	0.55	0.34	0.00
PB8OCL0.1Br	6.38	31.27	41.00	0.76	0.96	0.00
PB8OCL0.25Br	6.17	24.38	23.83	1.61	3.81	1.96
PB8OCL0.5Br	5.59	15.56	9.92	3.14	9.65	4.65
PB8OCL0.75Br	5.48	10.21	4.57	5.05	14.91	8.31
PB8OCL1.0Br	3.88	6.26	2.52	6.49	19.90	12.42
PB8OCL1.5Br	2.66	3.49	1.32	8.70	29.03	19.26
PB8OCL2.0Br	2.01	2.11	0.88	10.11	34.91	26.20
9/14						
PB8CL0Br	4.15	32.17	63.68	0.00	0.00	0.00
PB8CL0.025Br	4.47	31.44	60.00	0.00	0.00	0.00
PB8CL0.05Br	3.52	30.98	58.01	0.35	0.00	0.00
PB8CL0.1Br	3.23	28.65	51.36	0.58	0.44	0.00
PB8CL0.25Br	2.66	21.65	33.10	1.09	2.71	1.69
PB8CL0.5Br	2.41	12.56	14.78	1.58	9.07	4.29
PB8CL0.75Br	2.06	6.82	6.71	2.01	13.96	10.47
PB8CL1.0Br	1.37	3.92	3.63	2.60	16.76	18.28
PB8CL1.5Br	0.60	2.14	2.11	3.93	21.74	28.79
PB8CL2.0Br	0.24	1.43	1.40	4.46	23.31	35.02
9/14						
PB6OCL0Br	3.54	41.78	54.26	0.42	0.00	0.00
PB6OCL0.025Br	3.68	38.64	49.12	0.58	0.00	0.00
PB6OCL0.05Br	3.34	35.07	43.80	0.87	0.37	0.00
PB6OCL0.1Br	3.32	31.18	35.47	1.23	1.07	0.00
PB6OCL0.25Br	3.09	22.19	19.42	1.95	4.26	1.72
PB6OCL0.5Br	2.38	15.42	7.96	2.31	10.10	3.74
PB6OCL0.75Br	2.16	11.08	3.83	3.62	13.99	6.82
PB6OCL1.0Br	1.61	7.42	2.28	4.04	18.40	10.81
PB6OCL1.5Br	1.26	4.96	1.18	5.63	24.10	16.22
PB6OCL2.0Br	1.02	3.52	0.74	6.10	28.01	19.88
9/14						
PB6CL0Br	1.93	30.38	67.69	0.00	0.00	0.00
PB6CL0.025Br	1.97	29.26	62.84	0.52	0.00	0.00
PB6CL0.05Br	1.82	27.56	59.17	0.55	0.20	0.00
PB6CL0.1Br	1.62	25.21	52.43	0.72	0.71	0.00
PB6CL0.25Br	1.19	19.07	36.52	1.00	2.88	1.42
PB6CL0.5Br	0.99	12.06	18.00	1.33	8.58	2.55
PB6CL0.75Br	0.62	7.27	8.82	1.36	13.83	5.84
PB6CL1.0Br	0.63	4.69	4.82	1.88	17.24	10.30
PB6CL1.5Br	0.38	2.13	2.01	2.40	20.79	19.15
PB6CL2.0Br	0.25	1.01	1.12	3.12	22.52	25.01

APPENDIX F, cont.

Mole fractions of individual HAAs

	Mole fraction Xi (x100)		
9/14	BrClAA	BrCl2AA	Br2ClAA
PB8OCL0Br	0.00	0.00	0.00
PB8OCL0.025Br	1.55	3.80	0.00
PB8OCL0.05Br	3.27	7.06	1.57
PB8OCL0.1Br	5.85	11.34	2.44
PB8OCL0.25Br	11.43	20.30	6.51
PB8OCL0.5Br	15.92	22.47	13.10
PB8OCL0.75Br	15.82	19.13	16.52
PB8OCL1.0Br	13.64	17.23	17.66
PB8OCL1.5Br	10.65	8.38	16.51
PB8OCL2.0Br	8.23	0.00	15.54
9/14			
PB8CL0Br	0.00	0.00	0.00
PB8CL0.025Br	0.98	3.11	0.00
PB8CL0.05Br	2.05	5.08	0.00
PB8CL0.1Br	4.26	9.59	1.89
PB8CL0.25Br	9.73	21.76	5.61
PB8CL0.5Br	13.28	27.35	14.70
PB8CL0.75Br	12.20	24.81	20.96
PB8CL1.0Br	10.22	21.07	22.15
PB8CL1.5Br	8.28	11.04	21.37
PB8CL2.0Br	6.33	8.12	19.68
9/14			
PB6OCL0Br	0.00	0.00	0.00
PB6OCL0.025Br	3.16	4.83	0.00
PB6OCL0.05Br	6.04	8.54	1.98
PB6OCL0.1Br	10.16	14.04	3.53
PB6OCL0.25Br	16.65	21.17	9.56
PB6OCL0.5Br	18.46	20.75	18.88
PB6OCL0.75Br	18.09	17.40	23.01
PB6OCL1.0Br	16.01	14.74	24.71
PB6OCL1.5Br	12.87	11.16	22.63
PB6OCL2.0Br	10.82	9.27	20.65
9/14			
PB6CL0Br	0.00	0.00	0.00
PB6CL0.025Br	1.49	3.92	0.00
PB6CL0.05Br	2.78	6.37	1.56
PB6CL0.1Br	5.31	11.59	2.41
PB6CL0.25Br	9.83	21.69	6.41
PB6CL0.5Br	13.45	26.88	16.16
PB6CL0.75Br	13.37	25.30	23.60
PB6CL1.0Br	12.33	22.13	25.98
PB6CL1.5Br	9.62	16.56	26.95
PB6CL2.0Br	7.70	14.00	25.27

Appendix F, cont.

	Bromine incorporation into HAAs		Chlorine incorporation into HAAs	
9/14	uM	per uM THAA	uM	per uM THAA
PB8OCL0Br	0.0000	0.0000	2.1613	2.5291
PB8OCL0.025Br	0.0491	0.0571	2.1045	2.4466
PB8OCL0.05Br	0.1223	0.1471	1.9540	2.3505
PB8OCL0.1Br	0.1921	0.2474	1.7307	2.2289
PB8OCL0.25Br	0.4228	0.5985	1.3067	1.8496
PB8OCL0.5Br	0.6293	1.0098	0.8752	1.4043
PB8OCL0.75Br	0.7360	1.2779	0.6348	1.1022
PB8OCL1.0Br	0.8739	1.4973	0.5236	0.8972
PB8OCL1.5Br	1.0137	1.7659	0.3302	0.5752
PB8OCL2.0Br	1.1657	1.9785	0.1924	0.3265
9/14				
PB8CL0Br	0.0000	0.0000	1.8463	2.5953
PB8CL0.025Br	0.0290	0.0409	1.8025	2.5455
PB8CL0.05Br	0.0518	0.0749	1.7400	2.5173
PB8CL0.1Br	0.1312	0.1908	1.6502	2.3995
PB8CL0.25Br	0.3734	0.5427	1.4043	2.0413
PB8CL0.5Br	0.7221	1.0258	1.0879	1.5455
PB8CL0.75Br	1.0747	1.4028	0.9086	1.1861
PB8CL1.0Br	1.4189	1.6654	0.8061	0.9461
PB8CL1.5Br	1.4603	1.9585	0.4693	0.6294
PB8CL2.0Br	1.6914	2.0997	0.3993	0.4957
9/14				
PB6OCL0Br	0.0029	0.0042	1.7169	2.4988
PB6OCL0.025Br	0.0597	0.0857	1.6800	2.4112
PB6OCL0.05Br	0.1430	0.2014	1.6329	2.2996
PB6OCL0.1Br	0.2517	0.3464	1.5539	2.1385
PB6OCL0.25Br	0.5328	0.7256	1.2797	1.7427
PB6OCL0.5Br	0.8857	1.1070	1.0875	1.3593
PB6OCL0.75Br	1.0564	1.3356	0.8836	1.1172
PB6OCL1.0Br	1.2825	1.5342	0.7813	0.9346
PB6OCL1.5Br	1.5707	1.7176	0.6633	0.7253
PB6OCL2.0Br	1.8071	1.8314	0.5948	0.6028
9/14				
PB6CL0Br	0.0000	0.0000	1.9275	2.6577
PB6CL0.025Br	0.0434	0.0593	1.8902	2.5833
PB6CL0.05Br	0.0986	0.1322	1.8763	2.5151
PB6CL0.1Br	0.1814	0.2386	1.8260	2.4024
PB6CL0.25Br	0.4482	0.5535	1.6883	2.0850
PB6CL0.5Br	0.8772	0.9880	1.4425	1.6247
PB6CL0.75Br	1.3144	1.3240	1.2824	1.2918
PB6CL1.0Br	1.6041	1.5369	1.1170	1.0702
PB6CL1.5Br	1.9039	1.8151	0.8431	0.8038
PB6CL2.0Br	2.0358	1.9541	0.6939	0.6660

APPENDIX F, cont.

Sum of chlorinated, brominated, mixed species
concentration (uM)

Cl2	Br2	Mixed	9/14
0.8546	0.0000	0.0000	PB8OCL0Br
0.8111	0.0030	0.0460	PB8OCL0.025Br
0.7249	0.0074	0.0990	PB8OCL0.05Br
0.6107	0.0133	0.1524	PB8OCL0.1Br
0.3842	0.0521	0.2702	PB8OCL0.25Br
0.1936	0.1087	0.3209	PB8OCL0.5Br
0.1167	0.1628	0.2965	PB8OCL0.75Br
0.0739	0.2265	0.2833	PB8OCL1.0Br
0.0429	0.3272	0.2040	PB8OCL1.5Br
0.0295	0.4196	0.1401	PB8OCL2.0Br
			9/14
0.7114	0.0000	0.0000	PB8CL0Br
0.6792	0.0000	0.0290	PB8CL0.025Br
0.6395	0.0024	0.0493	PB8CL0.05Br
0.5725	0.0070	0.1082	PB8CL0.1Br
0.3950	0.0377	0.2552	PB8CL0.25Br
0.2095	0.1051	0.3894	PB8CL0.5Br
0.1194	0.2026	0.4441	PB8CL0.75Br
0.0760	0.3207	0.4553	PB8CL1.0Br
0.0362	0.4061	0.3034	PB8CL1.5Br
0.0247	0.5058	0.2750	PB8CL2.0Br
			9/14
0.6842	0.0029	0.0000	PB6OCL0Br
0.6370	0.0040	0.0557	PB6OCL0.025Br
0.5837	0.0088	0.1175	PB6OCL0.05Br
0.5084	0.0167	0.2015	PB6OCL0.1Br
0.3282	0.0582	0.3479	PB6OCL0.25Br
0.2061	0.1292	0.4647	PB6OCL0.5Br
0.1350	0.1932	0.4627	PB6OCL0.75Br
0.0945	0.2779	0.4636	PB6OCL1.0Br
0.0677	0.4202	0.4266	PB6OCL1.5Br
0.0521	0.5327	0.4019	PB6OCL2.0Br
			9/14
0.7253	0.0000	0.0000	PB6CL0Br
0.6883	0.0038	0.0396	PB6CL0.025Br
0.6605	0.0056	0.0799	PB6CL0.05Br
0.6024	0.0108	0.1468	PB6CL0.1Br
0.4597	0.0428	0.3072	PB6CL0.25Br
0.2756	0.1106	0.5016	PB6CL0.5Br
0.1658	0.2087	0.6182	PB6CL0.75Br
0.1058	0.3072	0.6308	PB6CL1.0Br
0.0475	0.4441	0.5573	PB6CL1.5Br
0.0249	0.5277	0.4892	PB6CL2.0Br

APPENDIX F, cont.

	Mole fractions of mono, di and trihalogenated species		
9/14	monohal	dihal	trihal
PB8OCL0Br	0.0698	0.3314	0.5989
PB8OCL0.025Br	0.0681	0.3600	0.5718
PB8OCL0.05Br	0.0690	0.3645	0.5665
PB8OCL0.1Br	0.0714	0.3808	0.5477
PB8OCL0.25Br	0.0778	0.3962	0.5260
PB8OCL0.5Br	0.0873	0.4113	0.5014
PB8OCL0.75Br	0.1053	0.4094	0.4853
PB8OCL1.0Br	0.1037	0.3980	0.4983
PB8OCL1.5Br	0.1136	0.4317	0.4547
PB8OCL2.0Br	0.1212	0.4525	0.4263
9/14			
PB8CL0Br	0.0415	0.3217	0.6368
PB8CL0.025Br	0.0447	0.3242	0.6311
PB8CL0.05Br	0.0388	0.3303	0.6309
PB8CL0.1Br	0.0381	0.3336	0.6284
PB8CL0.25Br	0.0375	0.3409	0.6216
PB8CL0.5Br	0.0398	0.3491	0.6111
PB8CL0.75Br	0.0407	0.3298	0.6295
PB8CL1.0Br	0.0397	0.3091	0.6512
PB8CL1.5Br	0.0453	0.3216	0.6331
PB8CL2.0Br	0.0470	0.3108	0.6423
9/14			
PB6OCL0Br	0.0396	0.4178	0.5426
PB6OCL0.025Br	0.0426	0.4180	0.5394
PB6OCL0.05Br	0.0421	0.4148	0.5431
PB6OCL0.1Br	0.0455	0.4241	0.5304
PB6OCL0.25Br	0.0504	0.4310	0.5187
PB6OCL0.5Br	0.0469	0.4398	0.5133
PB6OCL0.75Br	0.0578	0.4316	0.5106
PB6OCL1.0Br	0.0565	0.4182	0.5253
PB6OCL1.5Br	0.0689	0.4193	0.5118
PB6OCL2.0Br	0.0712	0.4235	0.5053
9/14			
PB6CL0Br	0.0193	0.3038	0.6769
PB6CL0.025Br	0.0249	0.3075	0.6676
PB6CL0.05Br	0.0237	0.3054	0.6710
PB6CL0.1Br	0.0234	0.3123	0.6643
PB6CL0.25Br	0.0219	0.3178	0.6604
PB6CL0.5Br	0.0232	0.3409	0.6359
PB6CL0.75Br	0.0197	0.3446	0.6356
PB6CL1.0Br	0.0251	0.3426	0.6323
PB6CL1.5Br	0.0278	0.3255	0.6467
PB6CL2.0Br	0.0338	0.3123	0.6539

Appendix F, cont

ug/L concentrations of HAAs

9/30	ug/L MCAA	ug/L DCAA	ug/L TCAA	ug/L MBAA	ug/L DBAA	ug/L TBAA
PB8OCN0Br	4.06	8.56	0.45	1.15	0.37	0
PB8OCN0.025Br	3.21	8.3	0.4	0.54	0	0
PB8OCN0.05Br	3.16	8.01	0	0.56	0.29	0
PB8OCN0.1Br	2.96	7.58	0	0.42	0.61	0
PB8OCN0.25Br	2.74	6.93	0	0.46	1.06	0
PB8OCN0.5Br	2.47	6.01	0	1.15	1.43	0
PB8OCN0.75Br	2.65	5.69	0	2.02	1.93	0
PB8OCN1.0Br	1.9	4.41	0	2.33	2.55	0
PB8OCN1.5Br	2.07	5.25	0	4.54	5.46	0
PB8OCN2.0Br	2.33	3.72	0.79	4.42	8.78	4.53
9/30						
PB8CN0Br	1.49	4.99	0.46	0.54	0	0
PB8CN0.025Br	1.43	5.03	0.42	0.52	0	0
PB8CN0.05Br	1.64	5.07	0.67	0.83	0.47	0
PB8CN0.1Br	1.84	5.06	0.85	1.01	0.71	0
PB8CN0.25Br	1.31	4.2	0.58	1.01	0.94	0
PB8CN0.5Br	1.69	4.45	0.73	1.65	1.66	0
PB8CN0.75Br	1.54	3.9	0.53	1.79	1.91	0
PB8CN1.0Br	1.1	3.68	0.49	2.36	2.14	0
PB8CN1.5Br	1.2	3.33	0.34	2.96	2.11	0
PB8CN2.0Br	0	3.07	0.36	3.38	2.4	0
9/30						
PBO 0Br	0	0	0	0	0	0
PBO 0.025Br	0	0	0	0	0	0
PBO 0.05Br	0	0	0	0	0	0
PBO 0.1Br	0	0	0	0	0	0
PBO 0.25Br	0	0	0	0	0.34	0
PBO 0.5Br	0	0	0	0.41	0.26	0
PBO 0.75Br	0	0	0	0.47	0.5	0
PBO 1.0Br	0	0	0	0.58	1.02	0
PBO 1.5Br	0	0	0	0.94	3.41	0
PBO 2.0Br	0	0	0	0.83	3.28	0

Appendix F, cont.

ug/L concentrations of HAAs

	ug/L	ug/L	ug/L	ug/L
9/30	BrClAA	BrCl2AA	Br2ClAA	THAA
PB8OCN0Br	0	0	0	14.59
PB8OCN0.025Br	0.6	0	0	13.05
PB8OCN0.05Br	0.84	0	0	12.86
PB8OCN0.1Br	0.98	0	0	12.55
PB8OCN0.25Br	1.26	0	0	12.45
PB8OCN0.5Br	1.57	0	0	12.63
PB8OCN0.75Br	1.98	0	0	14.27
PB8OCN1.0Br	2.01	0	0	13.2
PB8OCN1.5Br	2.42	0	0	19.74
PB8OCN2.0Br	2.97	0	0	27.54
9/30				
PB8CN0Br	0	0	0	7.48
PB8CN0.025Br	0	0	0	7.4
PB8CN0.05Br	0.84	0	0	9.52
PB8CN0.1Br	1.15	0	0	10.62
PB8CN0.25Br	1.19	0	0	9.23
PB8CN0.5Br	1.75	0	0	11.93
PB8CN0.75Br	1.83	0	0	11.5
PB8CN1.0Br	1.88	0	0	11.65
PB8CN1.5Br	1.98	0	0	11.92
PB8CN2.0Br	1.94	0	0	11.15
9/30				
PBO 0Br	0	0	0	0
PBO 0.025Br	0	0	0	0
PBO 0.05Br	0	0	0	0
PBO 0.1Br	0	0	0	0
PBO 0.25Br	0	0	0	0.34
PBO 0.5Br	0	0	0	0.67
PBO 0.75Br	0	0	0	0.97
PBO 1.0Br	0	0	0	1.6
PBO 1.5Br	0	0	0	4.35
PBO 2.0Br	0	0	0	4.11

APPENDIX F, cont.

uM concentrations of HAAs

	uM MCAA	uM DCAA	uM TCAA	uM MBAA	uM DBAA	uM TBAA
9/30						
PB8OCN0Br	0.043	0.066	0.003	0.006	0.002	0.000
PB8OCN0.025Br	0.034	0.064	0.002	0.004	0.000	0.000
PB8OCN0.05Br	0.033	0.062	0.000	0.004	0.001	0.000
PB8OCN0.1Br	0.031	0.059	0.000	0.003	0.003	0.000
PB8OCN0.25Br	0.029	0.054	0.000	0.003	0.005	0.000
PB8OCN0.5Br	0.026	0.047	0.000	0.008	0.007	0.000
PB8OCN0.75Br	0.028	0.044	0.000	0.015	0.009	0.000
PB8OCN1.0Br	0.020	0.034	0.000	0.017	0.012	0.000
PB8OCN1.5Br	0.022	0.041	0.000	0.033	0.025	0.000
PB8OCN2.0Br	0.025	0.029	0.005	0.032	0.040	0.015
9/30						
PB8CN0Br	0.016	0.039	0.003	0.004	0.000	0.000
PB8CN0.025Br	0.015	0.039	0.003	0.004	0.000	0.000
PB8CN0.05Br	0.017	0.039	0.004	0.006	0.002	0.000
PB8CN0.1Br	0.019	0.039	0.005	0.007	0.003	0.000
PB8CN0.25Br	0.014	0.033	0.004	0.007	0.004	0.000
PB8CN0.5Br	0.018	0.035	0.004	0.012	0.008	0.000
PB8CN0.75Br	0.016	0.030	0.003	0.013	0.009	0.000
PB8CN1.0Br	0.012	0.029	0.003	0.017	0.010	0.000
PB8CN1.5Br	0.013	0.026	0.002	0.021	0.010	0.000
PB8CN2.0Br	0.000	0.024	0.002	0.024	0.011	0.000
9/30						
PBO 0Br	0.000	0.000	0.000	0.000	0.000	0.000
PBO 0.025Br	0.000	0.000	0.000	0.000	0.000	0.000
PBO 0.05Br	0.000	0.000	0.000	0.000	0.000	0.000
PBO 0.1Br	0.000	0.000	0.000	0.000	0.000	0.000
PBO 0.25Br	0.000	0.000	0.000	0.000	0.002	0.000
PBO 0.5Br	0.000	0.000	0.000	0.003	0.001	0.000
PBO 0.75Br	0.000	0.000	0.000	0.003	0.002	0.000
PBO 1.0Br	0.000	0.000	0.000	0.004	0.005	0.000
PBO 1.5Br	0.000	0.000	0.000	0.007	0.016	0.000
PBO 2.0Br	0.000	0.000	0.000	0.006	0.015	0.000

Appendix F, cont.

uM concentrations of HAAs

9/30	uM BrClAA	uM BrCl2AA	uM Br2ClAA	uM THAA
PB8OCN0Br	0.000	0.000	0.000	0.122
PB8OCN0.025Br	0.003	0.000	0.000	0.108
PB8OCN0.05Br	0.005	0.000	0.000	0.106
PB8OCN0.1Br	0.006	0.000	0.000	0.102
PB8OCN0.25Br	0.007	0.000	0.000	0.098
PB8OCN0.5Br	0.009	0.000	0.000	0.097
PB8OCN0.75Br	0.011	0.000	0.000	0.107
PB8OCN1.0Br	0.012	0.000	0.000	0.094
PB8OCN1.5Br	0.014	0.000	0.000	0.134
PB8OCN2.0Br	0.017	0.000	0.000	0.163
9/30				
PB8CN0Br	0.000	0.000	0.000	0.061
PB8CN0.025Br	0.000	0.000	0.000	0.060
PB8CN0.05Br	0.005	0.000	0.000	0.074
PB8CN0.1Br	0.007	0.000	0.000	0.081
PB8CN0.25Br	0.007	0.000	0.000	0.068
PB8CN0.5Br	0.010	0.000	0.000	0.086
PB8CN0.75Br	0.011	0.000	0.000	0.082
PB8CN1.0Br	0.011	0.000	0.000	0.081
PB8CN1.5Br	0.011	0.000	0.000	0.083
PB8CN2.0Br	0.011	0.000	0.000	0.073
9/30				
PBO 0Br	0.000	0.000	0.000	0.000
PBO 0.025Br	0.000	0.000	0.000	0.000
PBO 0.05Br	0.000	0.000	0.000	0.000
PBO 0.1Br	0.000	0.000	0.000	0.000
PBO 0.25Br	0.000	0.000	0.000	0.002
PBO 0.5Br	0.000	0.000	0.000	0.004
PBO 0.75Br	0.000	0.000	0.000	0.006
PBO 1.0Br	0.000	0.000	0.000	0.009
PBO 1.5Br	0.000	0.000	0.000	0.022
PBO 2.0Br	0.000	0.000	0.000	0.021

Appendix F, cont.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)					
9/30	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA
PB8OCN0Br	35.20	54.38	2.26	6.78	1.39	0.00
PB8OCN0.025Br	31.42	59.52	2.26	3.59	0.00	0.00
PB8OCN0.05Br	31.62	58.73	0.00	3.81	1.26	0.00
PB8OCN0.1Br	30.84	57.87	0.00	2.98	2.76	0.00
PB8OCN0.25Br	29.54	54.74	0.00	3.37	4.96	0.00
PB8OCN0.5Br	27.05	48.23	0.00	8.56	6.79	0.00
PB8OCN0.75Br	26.22	41.24	0.00	13.59	8.28	0.00
PB8OCN1.0Br	21.31	36.24	0.00	17.77	12.40	0.00
PB8OCN1.5Br	16.31	30.31	0.00	24.33	18.66	0.00
PB8OCN2.0Br	15.14	17.72	2.97	19.53	24.75	9.37
9/30						
PB8CN0Br	25.78	63.26	4.60	6.35	0.00	0.00
PB8CN0.025Br	25.03	64.52	4.25	6.19	0.00	0.00
PB8CN0.05Br	23.54	53.31	5.56	8.10	2.92	0.00
PB8CN0.1Br	24.02	48.40	6.42	8.97	4.02	0.00
PB8CN0.25Br	20.26	47.60	5.19	10.62	6.30	0.00
PB8CN0.5Br	20.69	39.92	5.17	13.74	8.81	0.00
PB8CN0.75Br	19.88	36.89	3.96	15.71	10.69	0.00
PB8CN1.0Br	14.40	35.31	3.71	21.01	12.15	0.00
PB8CN1.5Br	15.30	31.11	2.51	25.66	11.67	0.00
PB8CN2.0Br	0.00	32.82	3.04	33.53	15.19	0.00
9/30						
PBO 0Br						
PBO 0.025Br						
PBO 0.05Br						
PBO 0.1Br						
PBO 0.25Br	0.00	0.00	0.00	0.00	100.00	0.00
PBO 0.5Br	0.00	0.00	0.00	71.20	28.80	0.00
PBO 0.75Br	0.00	0.00	0.00	59.58	40.42	0.00
PBO 1.0Br	0.00	0.00	0.00	47.14	52.86	0.00
PBO 1.5Br	0.00	0.00	0.00	30.18	69.82	0.00
PBO 2.0Br	0.00	0.00	0.00	28.41	71.59	0.00

APPENDIX F, CONT.

Mole fractions of individual HAA species

	Mole fraction Xi (x100)		
9/30	BrClAA	BrCl2AA	Br2ClAA
PB8OCN0Br	0.00	0.00	0.00
PB8OCN0.025Br	3.20	0.00	0.00
PB8OCN0.05Br	4.58	0.00	0.00
PB8OCN0.1Br	5.56	0.00	0.00
PB8OCN0.25Br	7.40	0.00	0.00
PB8OCN0.5Br	9.37	0.00	0.00
PB8OCN0.75Br	10.67	0.00	0.00
PB8OCN1.0Br	12.28	0.00	0.00
PB8OCN1.5Br	10.39	0.00	0.00
PB8OCN2.0Br	10.52	0.00	0.00
9/30			
PB8CN0Br	0.00	0.00	0.00
PB8CN0.025Br	0.00	0.00	0.00
PB8CN0.05Br	6.57	0.00	0.00
PB8CN0.1Br	8.18	0.00	0.00
PB8CN0.25Br	10.03	0.00	0.00
PB8CN0.5Br	11.67	0.00	0.00
PB8CN0.75Br	12.87	0.00	0.00
PB8CN1.0Br	13.41	0.00	0.00
PB8CN1.5Br	13.75	0.00	0.00
PB8CN2.0Br	15.42	0.00	0.00
9/30			
PBO 0Br			
PBO 0.025Br			
PBO 0.05Br			
PBO 0.1Br			
PBO 0.25Br	0.00	0.00	0.00
PBO 0.5Br	0.00	0.00	0.00
PBO 0.75Br	0.00	0.00	0.00
PBO 1.0Br	0.00	0.00	0.00
PBO 1.5Br	0.00	0.00	0.00
PBO 2.0Br	0.00	0.00	0.00

Appendix F, cont.

	Bromine incorporation		Chlorine incorporation	
9/30	uM	per uM THAA	uM	per uM THAA
PB8OCN0Br	0.0117	0.0956	0.1841	1.5072
PB8OCN0.025Br	0.0073	0.0679	0.1736	1.6046
PB8OCN0.05Br	0.0115	0.1091	0.1626	1.5366
PB8OCN0.1Br	0.0143	0.1405	0.1546	1.5213
PB8OCN0.25Br	0.0203	0.2068	0.1438	1.4641
PB8OCN0.5Br	0.0305	0.3151	0.1285	1.3287
PB8OCN0.75Br	0.0437	0.4082	0.1278	1.1938
PB8OCN1.0Br	0.0518	0.5485	0.1001	1.0607
PB8OCN1.5Br	0.0968	0.7203	0.1173	0.8733
PB8OCN2.0Br	0.1754	1.0766	0.1140	0.7000
9/30				
PB8CN0Br	0.0039	0.0635	0.1016	1.6611
PB8CN0.025Br	0.0037	0.0619	0.1009	1.6684
PB8CN0.05Br	0.0151	0.2052	0.1132	1.5341
PB8CN0.1Br	0.0204	0.2518	0.1202	1.4825
PB8CN0.25Br	0.0228	0.3326	0.0966	1.4104
PB8CN0.5Br	0.0372	0.4304	0.1104	1.2771
PB8CN0.75Br	0.0410	0.4997	0.0971	1.1840
PB8CN1.0Br	0.0475	0.5873	0.0886	1.0956
PB8CN1.5Br	0.0521	0.6275	0.0820	0.9879
PB8CN2.0Br	0.0576	0.7933	0.0654	0.9018
9/30				
PBO 0Br	0.0000		0.0000	
PBO 0.025Br	0.0000		0.0000	
PBO 0.05Br	0.0000		0.0000	
PBO 0.1Br	0.0000		0.0000	
PBO 0.25Br	0.0031		0.0000	
PBO 0.5Br	0.0053		0.0000	
PBO 0.75Br	0.0080		0.0000	
PBO 1.0Br	0.0135		0.0000	
PBO 1.5Br	0.0381		0.0000	
PBO 2.0Br	0.0361		0.0000	

Appendix F, cont.

Mole fraction of mono, di and trihalogenated species

9/30	monohal	dihal	trihal
PB8OCN0Br	0.4198	0.5577	0.0226
PB8OCN0.025Br	0.3501	0.6272	0.0226
PB8OCN0.05Br	0.3543	0.6457	0.0000
PB8OCN0.1Br	0.3381	0.6619	0.0000
PB8OCN0.25Br	0.3291	0.6709	0.0000
PB8OCN0.5Br	0.3561	0.6439	0.0000
PB8OCN0.75Br	0.3980	0.6020	0.0000
PB8OCN1.0Br	0.3908	0.6092	0.0000
PB8OCN1.5Br	0.4064	0.5936	0.0000
PB8OCN2.0Br	0.3468	0.5298	0.1234
9/30	monohal	dihal	trihal
PB8CN0Br	0.3213	0.6326	0.0460
PB8CN0.025Br	0.3122	0.6452	0.0425
PB8CN0.05Br	0.3163	0.6281	0.0556
PB8CN0.1Br	0.3299	0.6060	0.0642
PB8CN0.25Br	0.3088	0.6393	0.0519
PB8CN0.5Br	0.3443	0.6041	0.0517
PB8CN0.75Br	0.3559	0.6045	0.0396
PB8CN1.0Br	0.3542	0.6087	0.0371
PB8CN1.5Br	0.4096	0.5653	0.0251
PB8CN2.0Br	0.3353	0.6343	0.0304
9/30			
PBO 0Br			
PBO 0.025Br			
PBO 0.05Br			
PBO 0.1Br			
PBO 0.25Br	0.0000	1.0000	0.0000
PBO 0.5Br	0.7120	0.2880	0.0000
PBO 0.75Br	0.5958	0.4042	0.0000
PBO 1.0Br	0.4714	0.5286	0.0000
PBO 1.5Br	0.3018	0.6982	0.0000
PBO 2.0Br	0.2841	0.7159	0.0000

Appendix F, cont

HAA data from repeated chlorinations
for the purpose of assessing reproducibility of results
October 28, 1993

Chlorinated Palm Beach extracts containing 0.5 mg/L Br-

Sample #	MCAA ug/L	DCAA ug/L	TCAA ug/L	MBAA ug/L	DBAA ug/L	TBAA ug/L
1 A	1.579	10.414	15.171	1.508	13.715	7.539
1 B	1.602	10.532	15.56	1.468	14.177	7.778
1 C	1.59	10.487	15.431	1.391	13.951	7.848
2 A	1.603	10.01	14.899	1.444	13.607	7.616
2 B	1.602	10.606	15.549	1.36	12.692	7.386
2 C	1.578	10.153	14.896	1.169	12.366	7.172
3 A	1.481	9.959	14.801	1.506	13.476	7.849
3 B	1.579	10.196	15.089	1.471	12.896	7.773
3 C	1.597	10.244	14.843	1.393	13.038	7.484
4 A	1.52	10.044	14.592	1.389	12.017	7.135
4 B	1.641	10.331	15.398	1.439	13.03	7.719
4 C	1.609	10.344	15.432	1.146	14.155	7.963
5 A	1.492	9.904	14.937	1.134	12.566	7.289
5 B	1.558	9.993	15.103	1.329	13.532	7.413
5 C	1.607	10.191	15.371	1.337	13.619	7.423

APPENDIX F, cont.

Sample #	BrClAA ug/L	BrCl2AA ug/L	Br2ClAA ug/L
1 A	14.054	36.944	20.405
1 B	14.357	38.421	21.231
1 C	14.231	38.042	20.977
2 A	13.781	37.239	20.716
2 B	14.099	36.705	20.052
2 C	13.68	35.965	19.76
3 A	13.723	37.296	20.863
3 B	13.975	37.718	20.994
3 C	13.664	36.085	19.878
4 A	13.403	35.042	19.145
4 B	14.139	37.872	20.852
4 C	14.3	38.803	21.542
5 A	13.561	36.759	20.601
5 B	13.771	37.519	20.884
5 C	13.917	37.616	21.048

APPENDIX F cont

Chlorine and chloramine consumption as a function of bromide

mg/L as Cl2

	Myrtle Beach Chlorinated, pH 8			Myrtle Beach Chlorinated, pH 6		
[Br-] mg/L	Total oxidant Residual	HOBr Residual	Chlorine consumed	Total oxidant	HOBr	Chlorine consumed
0	2.8	0.05	5.25	3.3	0.1	4.8
0.31	2.8	0.05	5.25	3.5	0.1	4.6
0.63	1.9	0.05	6.15	3.4	0.1	4.7
1.25	2.85	0.05	5.2	3.3	0.1	4.8
3.13	2.65	0.05	5.4	3.2	0.15	4.95
6.26	2.4	0.05	5.65	3	0.1	5.1
9.39	2.2	0.05	5.85	2.75	0.1	5.35
12.52	1.95	0.05	6.1	2.7	0.1	5.4
18.77	1.35	0.1	6.75	2	0.15	6.15
25	1.15	0.25	7.1	1.2	0.4	7.2

	Palm Beach Chlorinated, pH 8			Palm Beach Chlorinated, pH 6		
[Br-] mg/L	Total oxidant	HOBr	Chlorine consumed	Total oxidant	HOBr	Chlorine consumed
0	4.4	0.05	3.65	4.4	0.15	3.75
0.31	4.2	0.05	3.85	4.6	0.1	3.5
0.63	4.3	0.05	3.75	4.6	0.1	3.5
1.25	4.2	0.05	3.85	4.5	0.1	3.6
3.13	4	0.05	4.05	4.25	0.1	3.85
6.26	3.8	0.05	4.25	4.2	0.1	3.9
9.39	3.3	0.1	4.8	3.85	0.15	4.3
12.52	2.95	0.15	5.2	3.7	0.2	4.5
18.77	2.75	0.35	5.6	3.4	0.4	5
25	2.6	0.65	6.05	3.1	0.7	5.6

APPENDIX F, cont.

Myrtle Beach
Ozonated, chlorinated, pH 8

[Br-] mg/L	Total oxidant residual	HOBr residual	Chlorine consumed
0	3.5	0.05	4.55
0.27	3.8	0.05	4.25
0.54	3.55	0.05	4.5
1.08	3.4	0.05	4.65
2.69	2.9	0.05	5.15
5.38	3.3	0.05	4.75
8.08	3.4	0.05	4.65
10.77	3.1	0.05	4.95
16.14	2.7	0.1	5.4
21.5	2.65	0.35	5.7

Myrtle Beach
Ozonated, chlorinated, pH 6

Total oxidant	HOBr	Chlorine consumed
4.2	0.1	3.9
4.4	0.15	3.75
4.2	0.1	3.9
4.2	0.15	3.95
4.15	0.15	4
4.15	0.15	4
3.95	0.15	4.2
3.8	0.2	4.4
3.4	0.3	4.9
2.2	0.4	6.2

Palm Beach
Ozonated, chlorinated, pH 8

[Br-] mg/L	Total oxidant	HOBr	Chlorine consumed
0	4.7	0.1	3.4
0.27	4.45	0.05	3.6
0.54	4.65	0.1	3.45
1.08	4.65	0.05	3.4
2.69	4.9	0.05	3.15
5.38	4.9	0.1	3.2
8.08	4.7	0.15	3.45
10.77	5.2	0.25	3.05
16.14	5.1	0.45	3.35
21.5	4.85	0.7	3.85

Palm Beach
Ozonated, chlorinated, pH 6

Total oxidant	HOBr	Chlorine consumed
4.95	0.1	3.15
4.9	0.15	3.25
5.1	0.15	3.05
5.1	0.15	3.05
5.05	0.15	3.1
5.1	0.15	3.05
5.2	0.25	3.05
5.2	0.4	3.2
5.3	0.6	3.3
5.3	0.85	3.55

APPENDIX F, cont.

Myrtle Beach
Chloraminated, pH 8

[Br-] mg/L	Chloramine residual	Chloramine consumed
0	3.65	0.35
0.31	3.45	0.55
0.63	3.55	0.45
1.25	3.45	0.55
3.13	3.45	0.55
6.26	3.4	0.6
9.39	3.6	0.4
12.52	3.55	0.45
18.77	3.55	0.45
25	3.55	0.45

Myrtle Beach
Ozonated, chloraminated, pH 8

[Br-] mg/L	chloramine residual	Chloramine consumed
0	2.3	1.7
0.27	3	1
0.54	3.25	0.75
1.08	3.2	0.8
2.69	3.1	0.9
5.38	3.2	0.8
8.08	3.15	0.85
10.77	3.25	0.75
16.14	3.4	0.6
21.5	3.15	0.85

Palm Beach
Chloraminated, pH 8

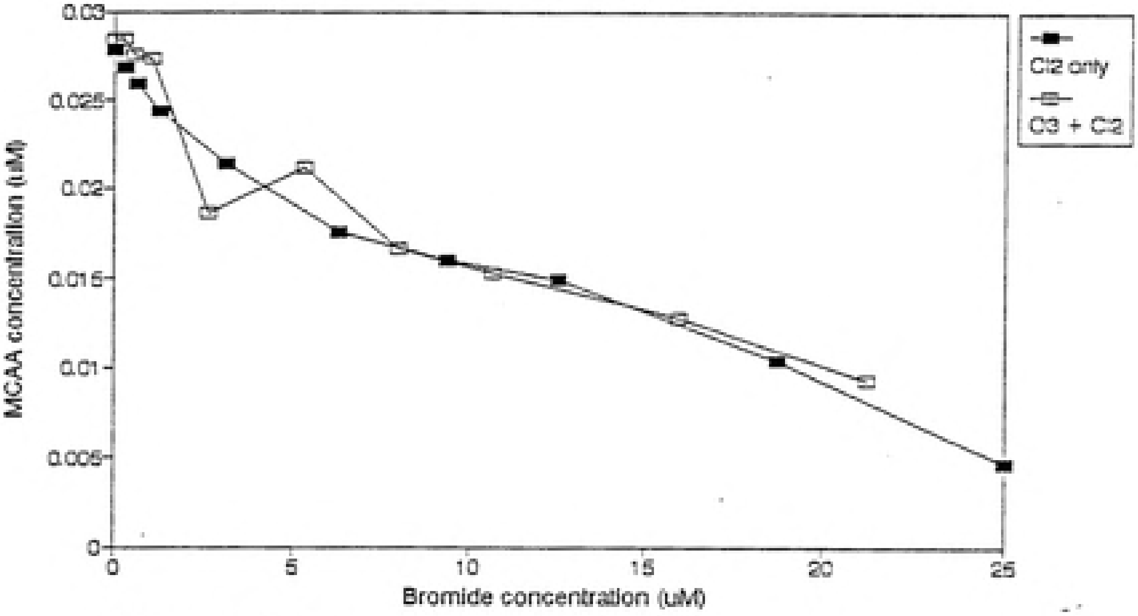
[Br-] mg/L	Chloramine residual	Chloramine consumed
0	3.9	0.1
0.31	3.6	0.4
0.63	3.75	0.25
1.25	3.4	0.6
3.13	3.45	0.55
6.26	3.5	0.5
9.39	3.5	0.5
12.52	3.7	0.3
18.77	3.7	0.3
25	3.8	0.2

Palm Beach
Ozonated, chloraminated, pH 8

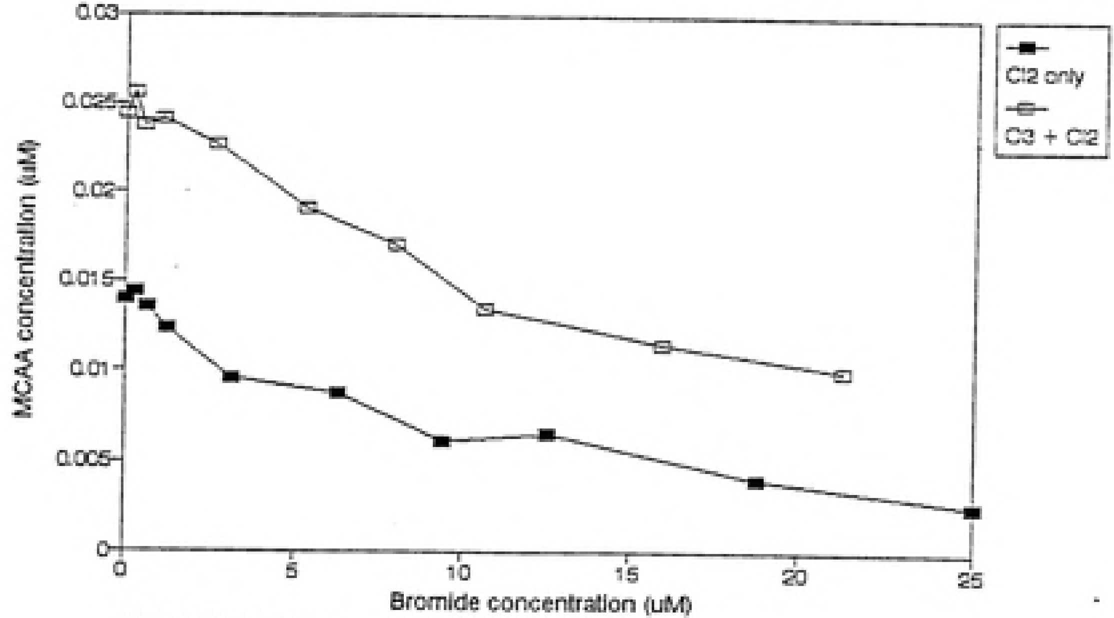
[Br-] mg/L	chloramine residual	Chloramine consumed
0	3.5	0.5
0.27	3.5	0.5
0.54	3.3	0.7
1.08	3.3	0.7
2.69	3.3	0.7
5.38	3.25	0.75
8.08	3.3	0.7
10.77	3.3	0.7
16.14	3.3	0.7
21.5	3.3	0.7

Appendix G
Effects of pre-ozonation on HAA formation in extracts chlorinated at pH 6

Influence of ozone on MCAA formation in chlorinated extracts, pH 6



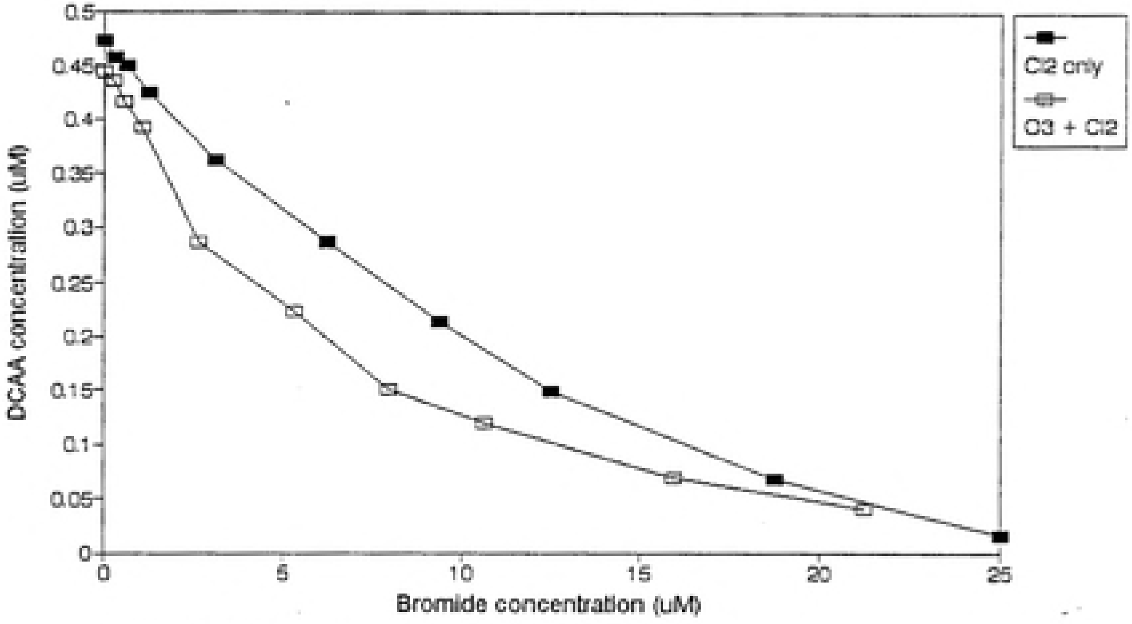
(a) Myrte Beach extract



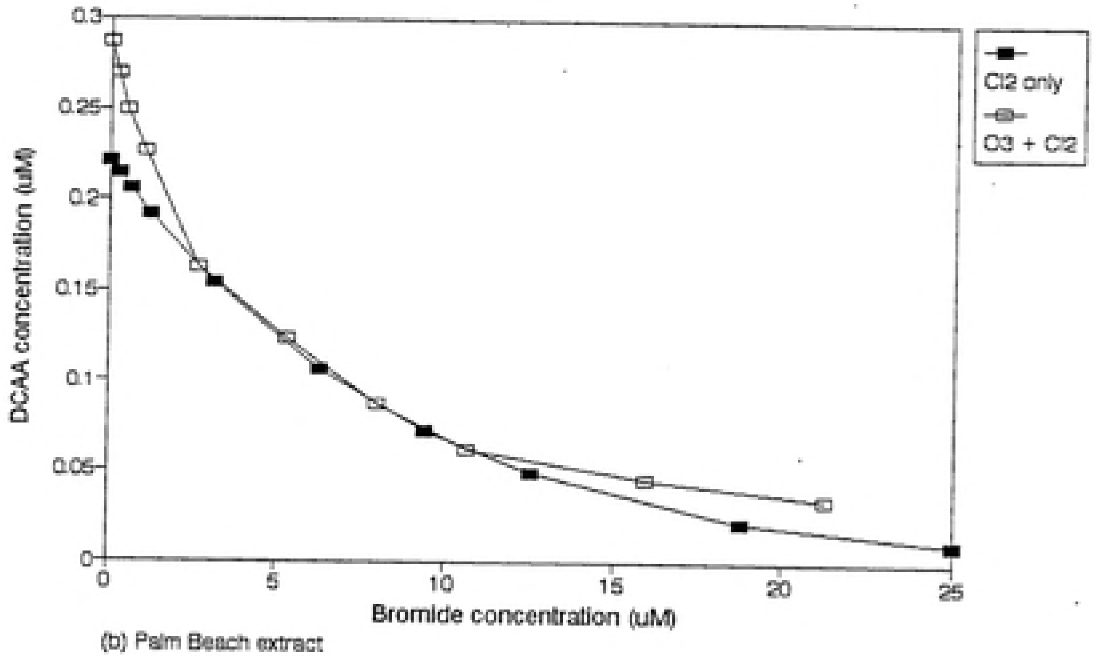
(b) Palm Beach extract

APPENDIX G, cont.

Influence of ozone on DCAA formation in chlorinated extracts, pH 6



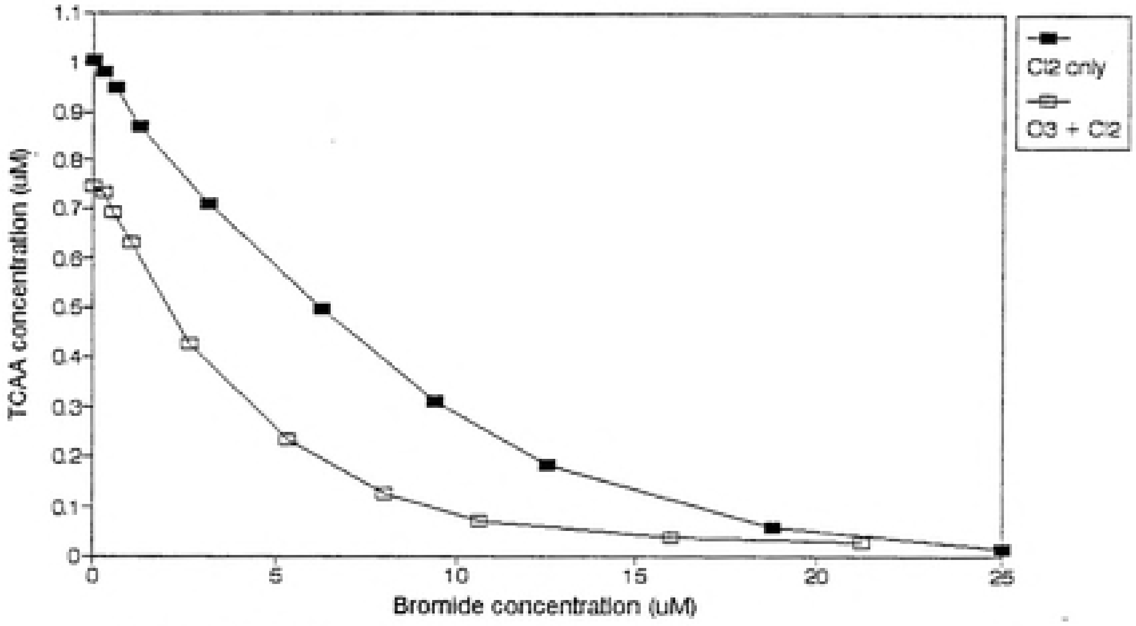
(a) Myrtle Beach extract



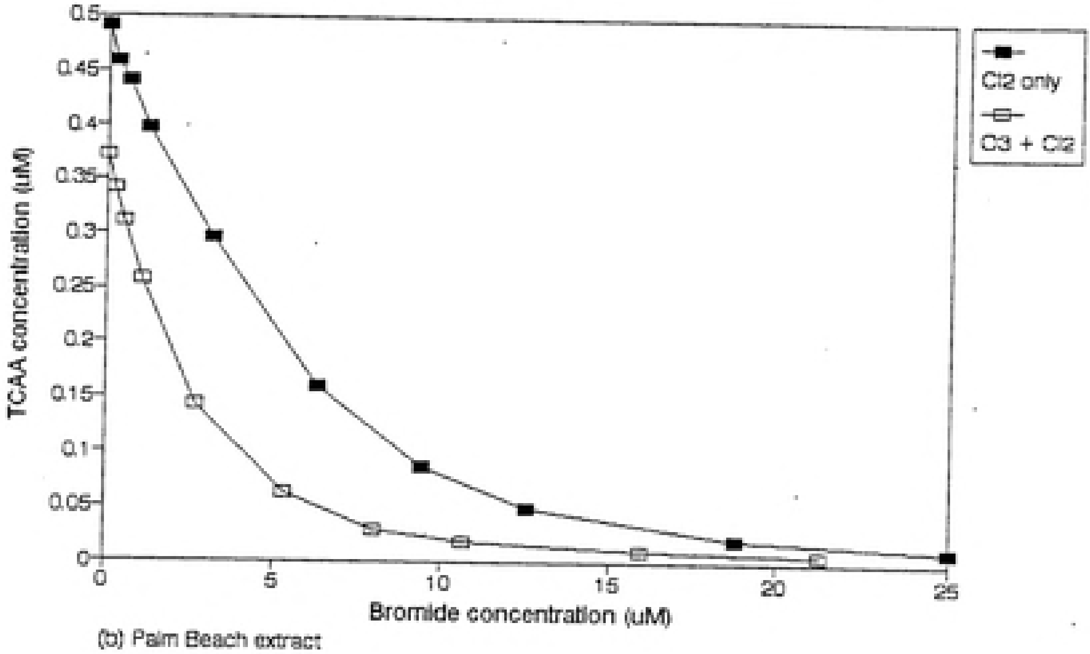
(b) Palm Beach extract

APPENDIX G, Cont.

Influence of ozone on TCAA formation in chlorinated extracts, pH 6



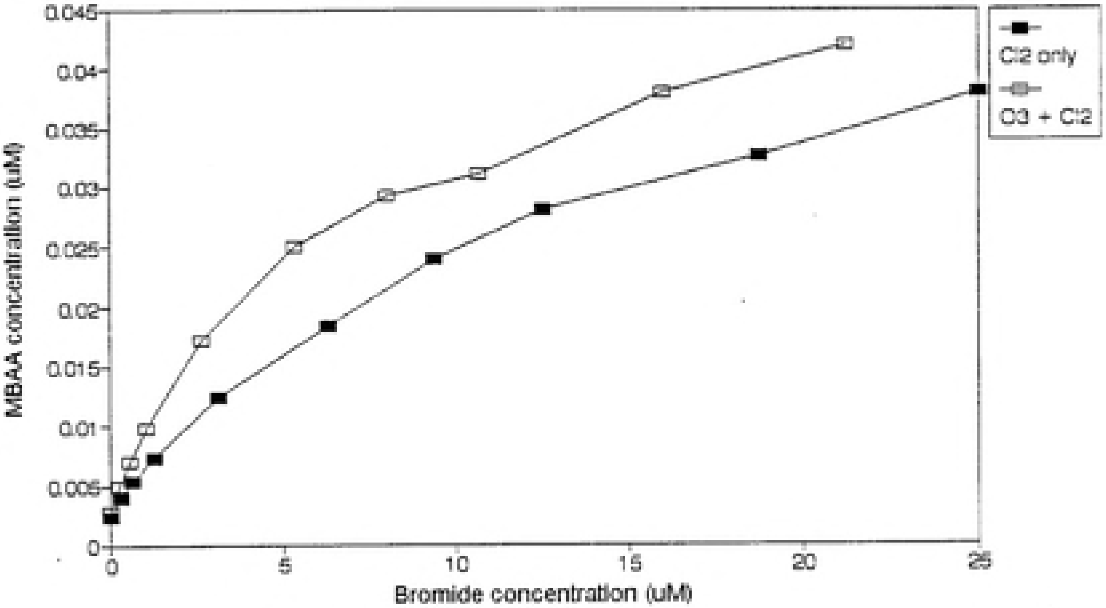
(a) Myrtle Beach extract



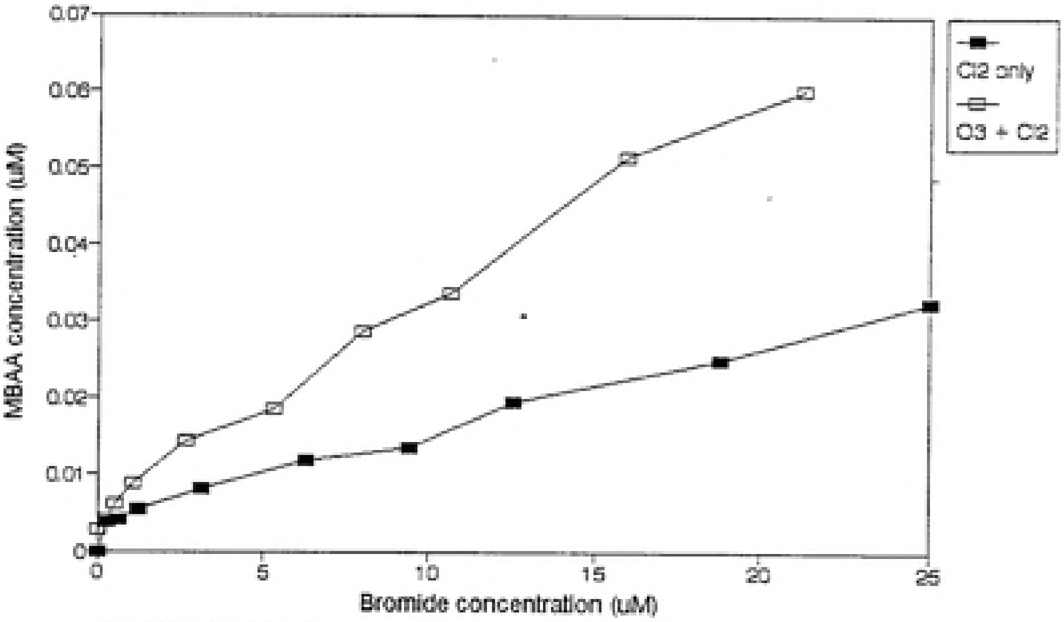
(b) Palm Beach extract

Appendix G, cont.

Influence of ozone on MBAA formation in chlorinated extracts, pH 6



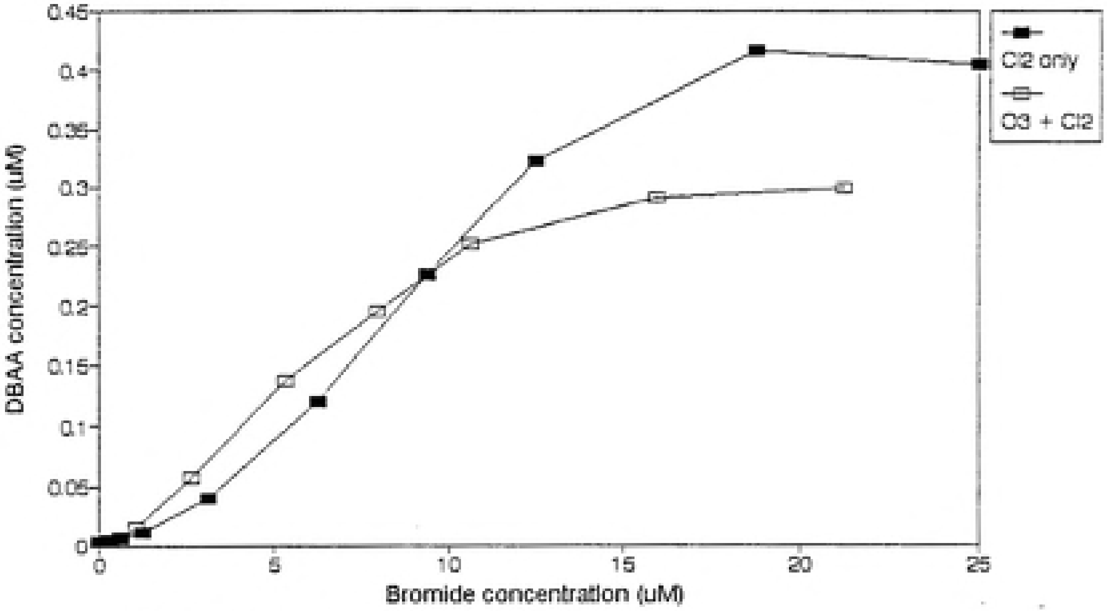
(a) Myrtle Beach extract



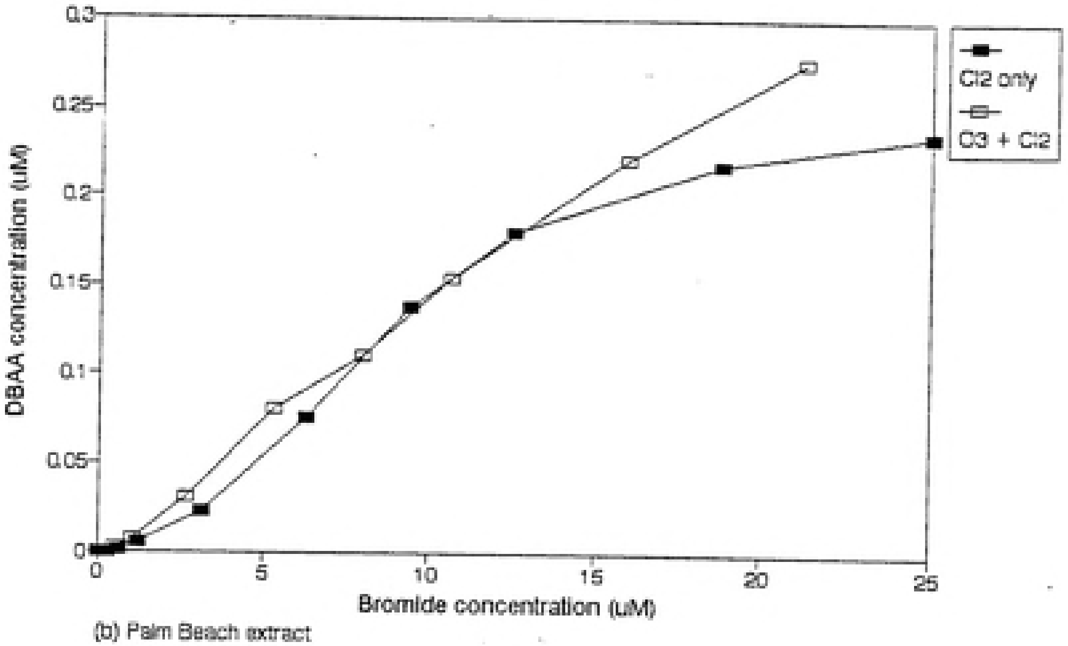
(b) Palm Beach extract

APPENDIX G, cont.

Influence of ozone on DBAA formation in chlorinated extracts, pH 6



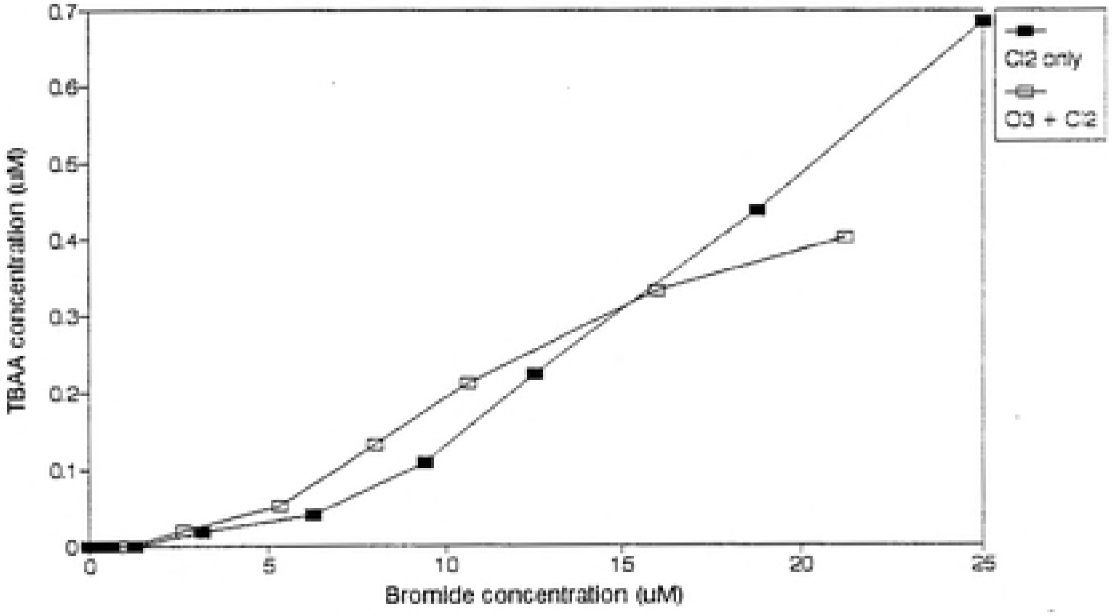
(a) Myrtle Beach extract



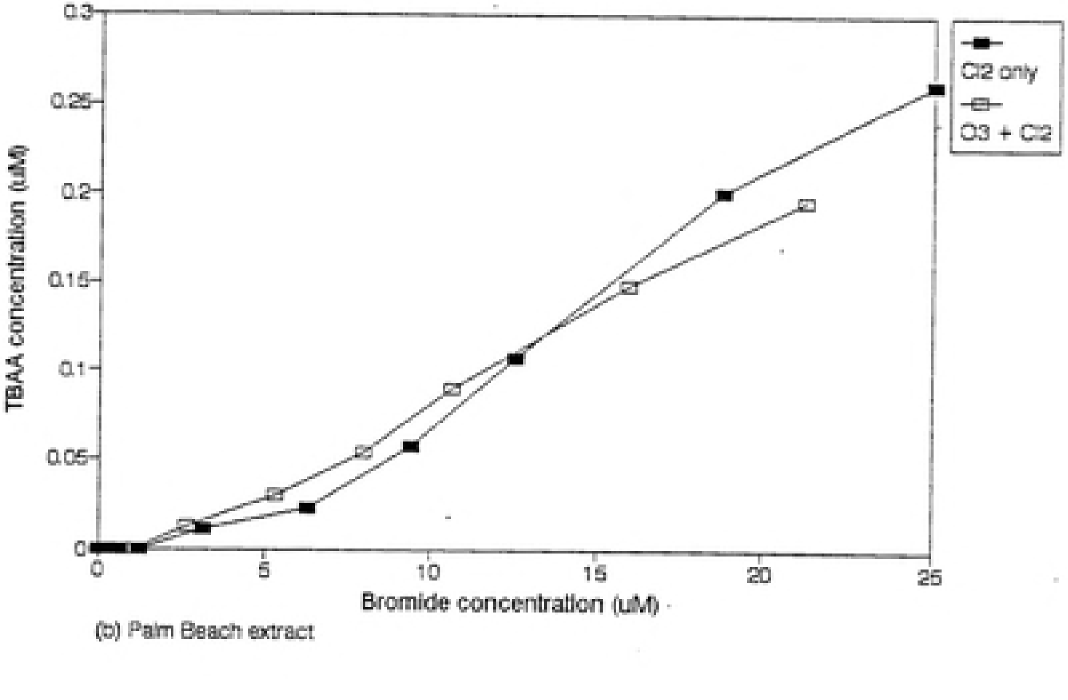
(b) Palm Beach extract

APPENDIX G, cont.

Influence of ozone on TBAA formation
in chlorinated extracts, pH 6



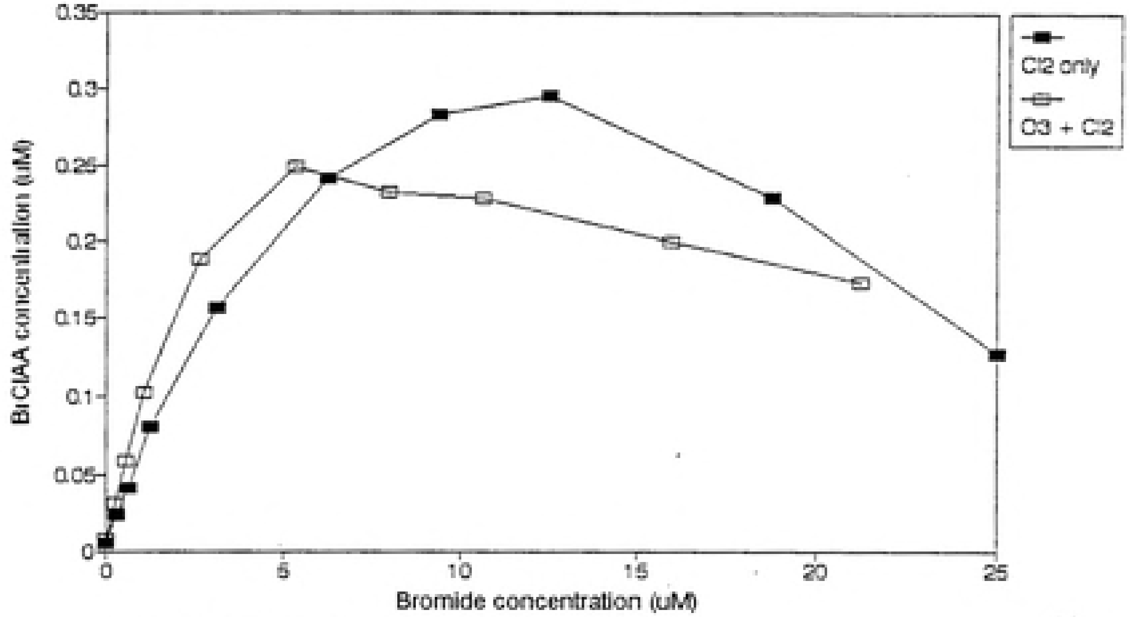
(a) Myrtle Beach extract



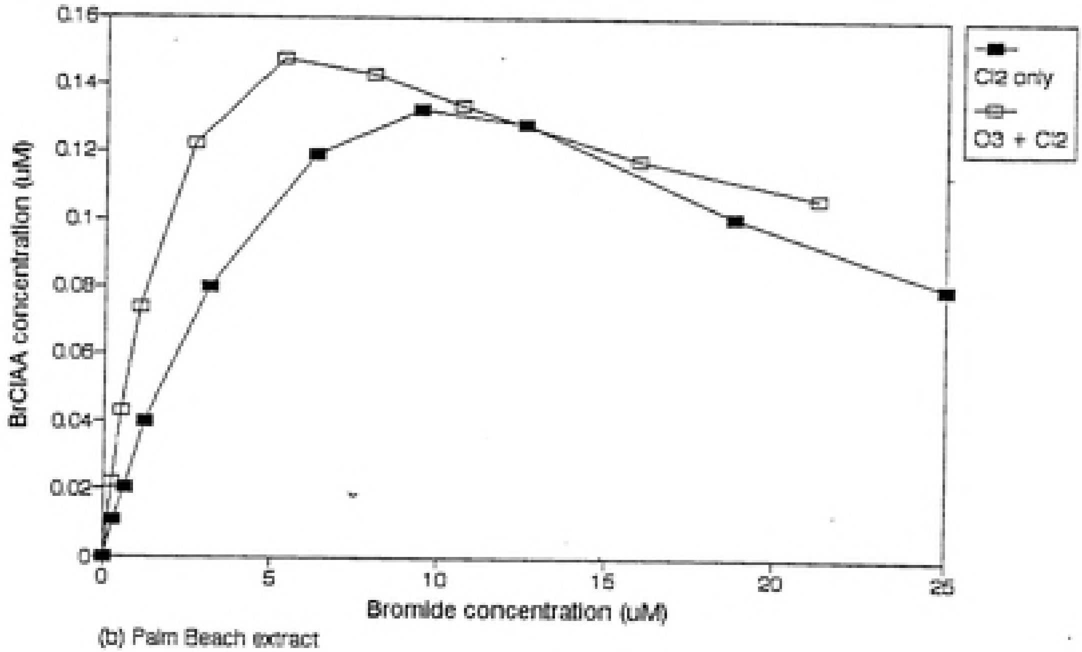
(b) Palm Beach extract

Appendix G, cont.

Influence of ozone on BrClAA formation in chlorinated extracts, pH 6



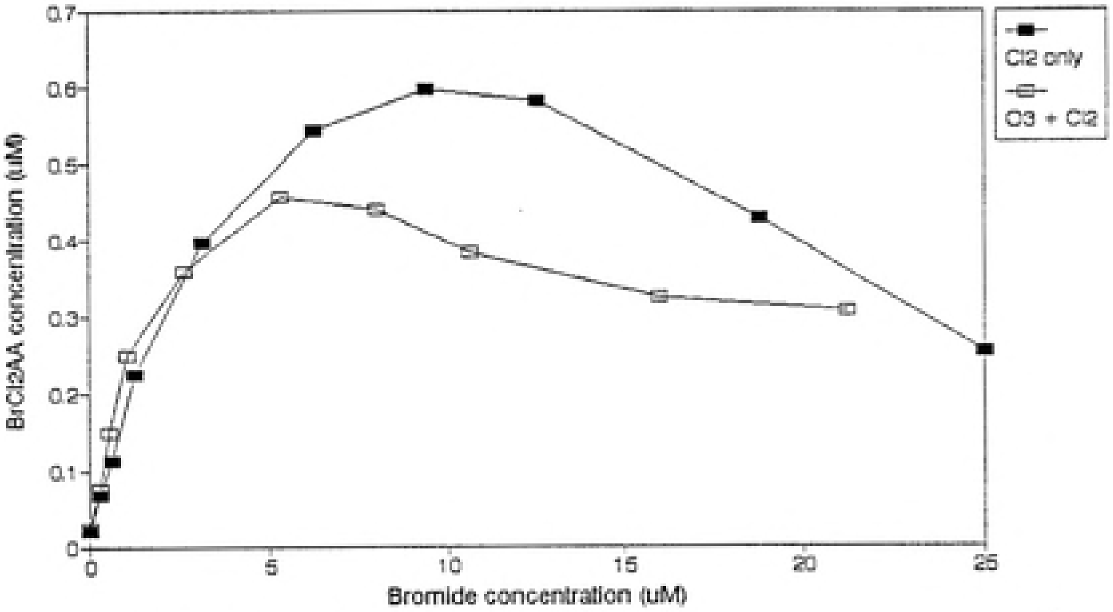
(a) Myrtle Beach extract



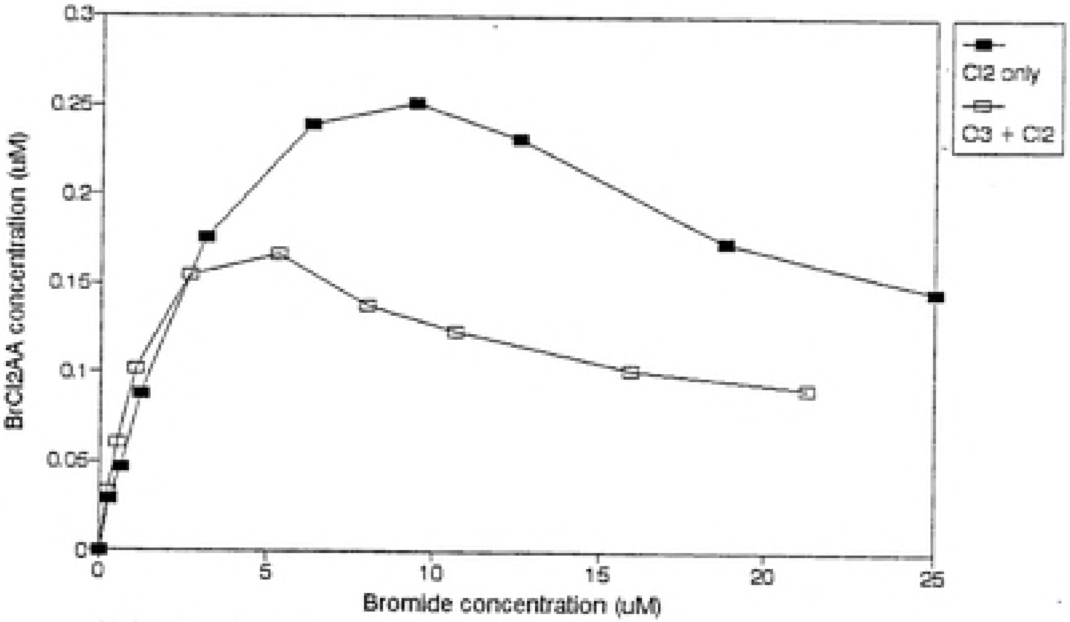
(b) Palm Beach extract

APPENDIX G, cont.

Influence of ozone on BrCl2AA formation in chlorinated extracts, pH 6



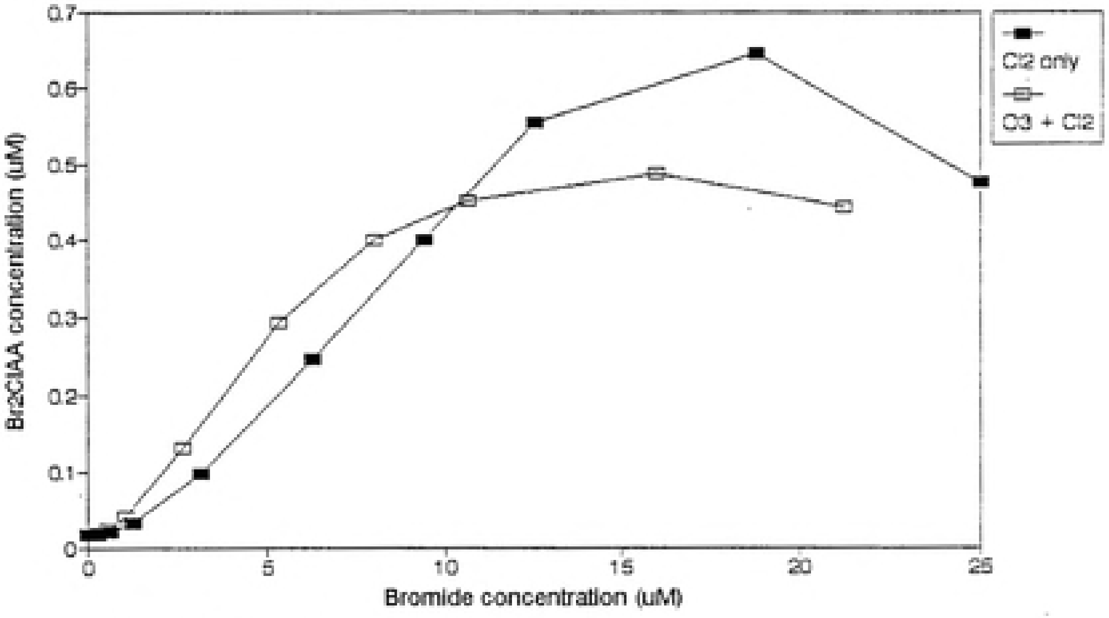
(a) Myrtle Beach extract



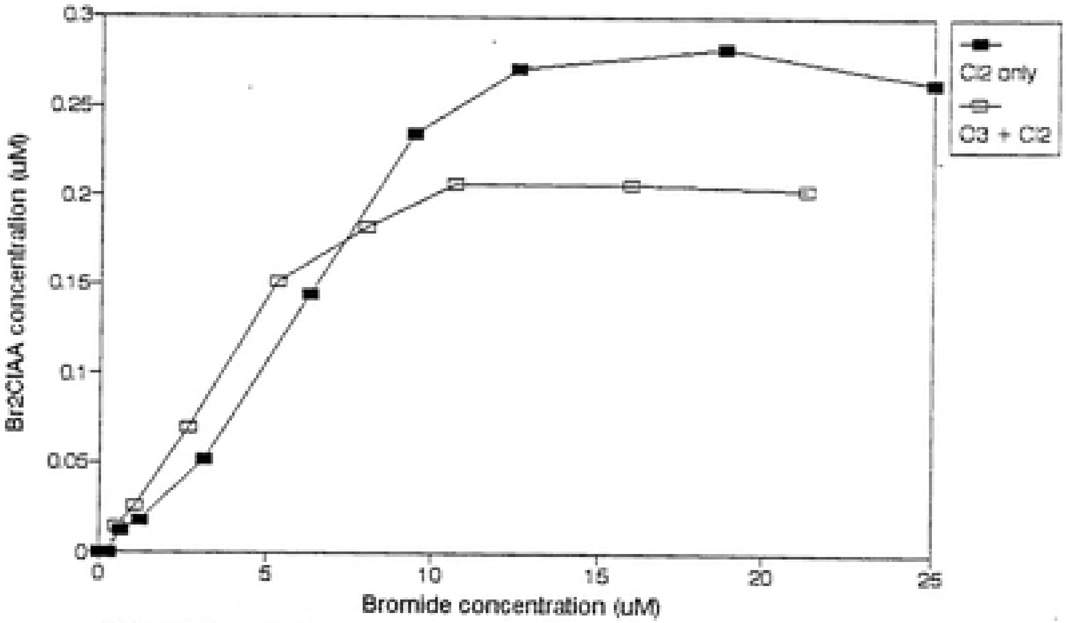
(b) Palm Beach extract

Appendix G, cont.

Influence of ozone on Br2ClAA formation
in chlorinated extracts, pH 6



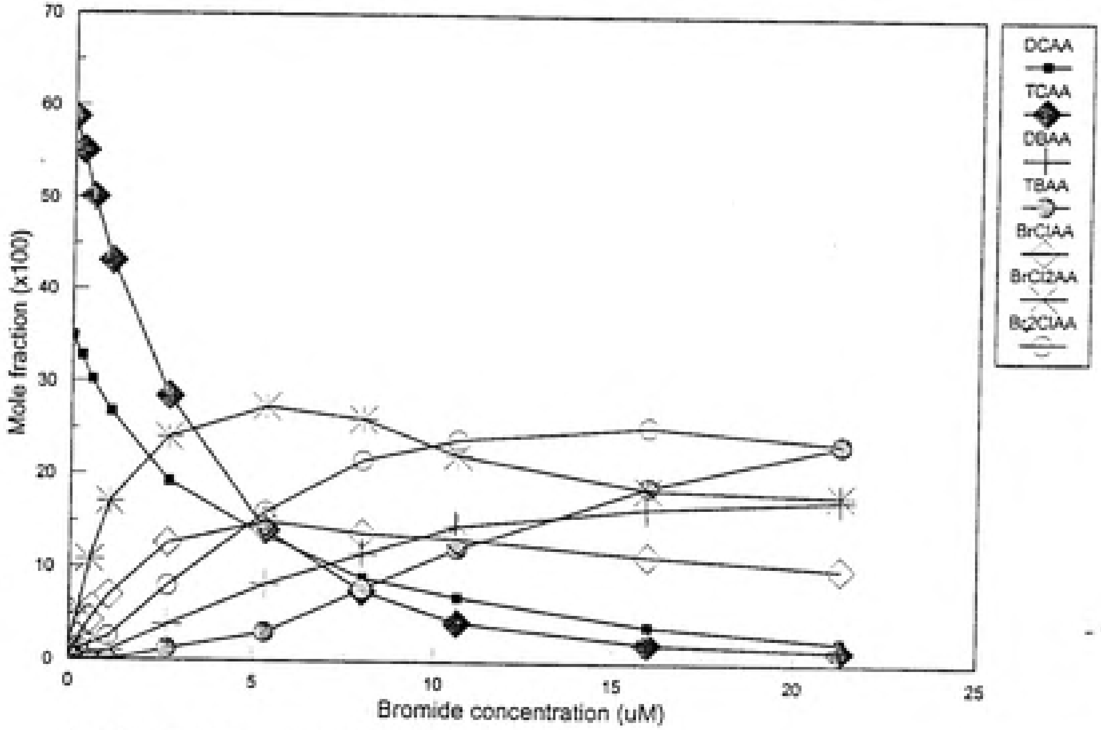
(a) Myrtle Beach extract



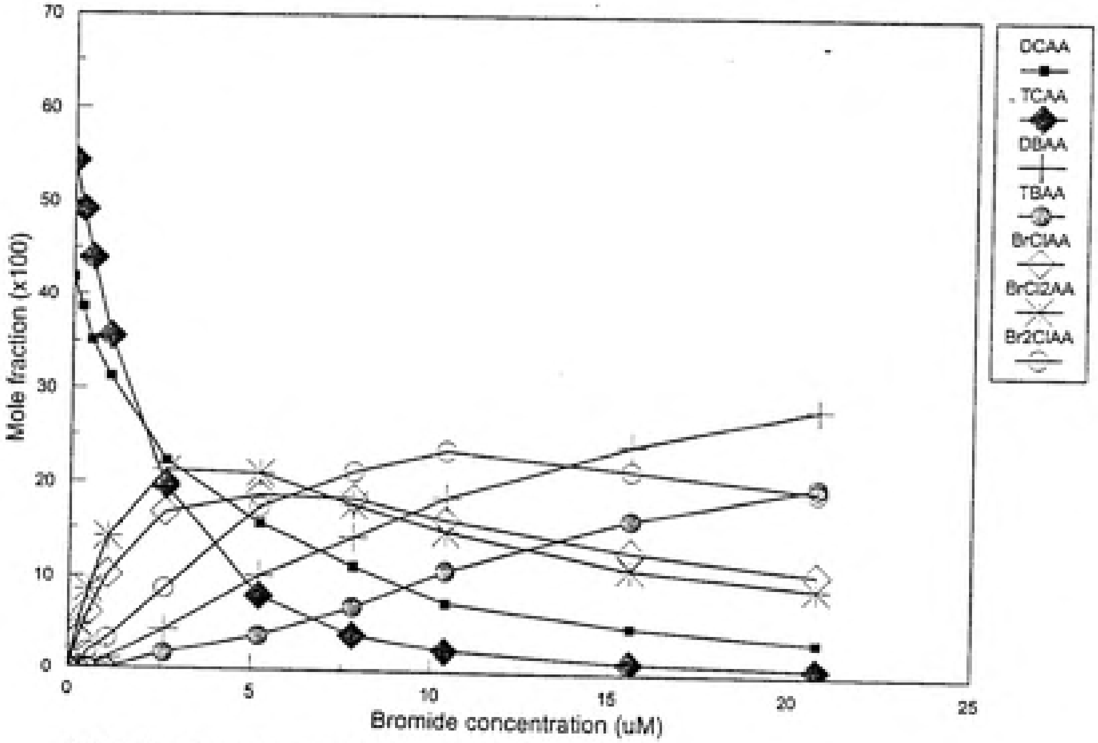
(b) Palm Beach extract

APPENDIX H

Distribution of individual HAA species in ozonated, chlorinated extracts, pH 6



(a) Myrtle Beach extract



(b) Palm Beach extract