Disinfection By-Product Formation in Drinking Water Treated with Chlorine Following UV Photolysis & UV/H_2O_2

by

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AUTHOR'S DECLARATION FOR ELECTRONIC SUBMISSION OF A THESIS

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ABSTRACT

As far back as the early 1900's when it was discovered that water could be a mode of transmitting diseases, chlorine was used to disinfect water. In the 1970's, the formation of disinfection by-products (DBPs) from the reaction of chlorine with natural organic matter was discovered. Since then there have been various studies on alternative disinfectants that could inactivate microorganisms and at the same time form less or no disinfection by-products.

More recently the ultraviolet (UV) irradiation has been used to both disinfect and remove organic contaminants in drinking water. Though the use of UV irradiation has been found to be very effective in the inactivation of microorganisms, it does not provide a residual effect to maintain the water's microbial quality in the distribution system. Due to this, a secondary disinfectant such as chlorine has to be used to achieve microbial stability, suggesting that the formation of chlorination disinfection by-products would still occur but perhaps in different quantities and with different chemical species.

In this research, the use of factorial experiments and single factor experiments were used to determine the effects of pH, alkalinity and UV-fluence (dose) on the formation of three classes of disinfection by-products; haloacetic acids (HAAs), haloacetonitriles (HANs) and trihalomethanes (THMs). These disinfection by-products were measured in water samples following post-UV chlorination and the UV treatment was either UV photolysis or UV/H_2O_2.

From the factorial experiment results, treatment of synthetic water with UV/H_2O_2, an advanced oxidation process (AOP), produced fewer post-UV chlorination disinfection by-products (PCDBPs) than UV photolysis. For chlorinated PCDBPs, the percentage difference between UV photolysis and UV/H_2O_2 was 55, 65 and 38% for total HAAs (HAA_9), total HANs (THANs) and total THMs (TTHMs) respectively. The percentage

difference between UV photolysis and UV/H_2O_2 for brominated PCDBPs was 41 and 42% for HAA_9 and TTHMs respectively.

Both the use of pH and alkalinity proved to be factors that were significant in affecting the yields of the PCDBPs studied. Increases in alkalinity were found to increase the formation of PCDBPs in the treatment of synthetic water with UV/H_2O_2. Alkalinity had the opposite effect for PCDBP formed under UV photolysis conditions. Increases in pH always decreased the formation of PCDBPs.

In the single factor experiments, haloacetic acid concentrations were unaffected as alkalinity was increased but dichloroacetonitrile and chloroform increased in concentration under treatment conditions of UV photolysis followed by chlorination. The UV/H_2O_2 treatment resulted in a decrease in concentration of the PCDBPs. In the pH studies, water samples were subjected only to the UV/H_2O_2 treatments and a reduction in concentration of PCDBPs occurred between pH 7 and 9.

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This thesis is dedicated to God almighty. Thank you for giving me the strength and courage to pull through. I couldn’t have done it without you

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LIST OF ABBREVIATIONS

%	Percent
AOP	Advanced oxidation process
Br_2AA	Dibromoacetic acid
Br_2ClAA	Dibromochloroacetic acid
Br_3AA	Tribromoacetic acid
BrAA	Bromoacetic acid
$BrCl_2AA$	Dichlorobromoacetic acid
BrClAA	Bromochloroacetic acid
$BrClCH_2$	Bromochloromethane
CH_2N_2	Diazomethane
$CHBr_3$	Bromoform
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloromethane
ClAA	Chloroacetic acid
Cl_2AA	Dichloroacetic acid
Cl_2AN	Dichloroacetonitrile
Cl_3AA	Trichloroacetic acid
DBP	Disinfection by-product
DPD	N,N-diethyl-*p*-phenylenediamine
ECD	Electron capture detector

GC	Gas chromatography
H^+	Hydrogen ion
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
HAA	Haloacetic acid
HAA_9	Total haloacetic acids (9 species)
I_3^-	Triiodide ion
IMAC	Interim maximum acceptable concentration
KI	Potassium iodide
KIO_3	Potassium iodate
MCL	Maximum contaminant limit
mg/L	Milligrams per litre
mJ/cm^2	Millijoules per centimetres squared
MNNG	1-methyl-3-nitro-1-nitrosoguanidine
MS	Mass spectrometer
MTBE	Methyl *tert* butyl ether
$Na_2B_4O_7 \bullet 10H_2O$	Sodium tetraborate decahydrate.
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
$OH^{\cdot}$	Hydroxyl radical
PCDBP	Post-UV chlorination disinfection by-product
pH	Negative logarithm of hydrogen ion concentration
pOH	Negative logarithm of hydroxyl ion concentration

THM	Trihalomethane
TTHMs	Total trihalomethanes
UFC	Uniform formation conditions
UV	Ultraviolet
USEPA	United States Environmental Protection Agency
μg/L	Micrograms per litre
WHO	World Health Organisation

CHAPTER 1

INTRODUCTION

1.1 Background

Ultraviolet (UV) irradiation has been investigated as a possible substitute for traditional chemical disinfection because chemical disinfectants such as chlorine, chloramines and chlorine dioxide produce by-products. There have been many research projects involved in the use of UV-based processes for disinfection purposes and advanced oxidation processes (AOPs). UV irradiation has proven to be effective in the inactivation of pathogenic microorganisms including *E coli* and *Cryptosporidium parvum* oocysts (Craik et al., 2001). Despite these advantages, the use of UV irradiation for water treatment plant has a draw back in that it does not maintain the water's microbial quality in the distribution system. Due to this, chemical disinfectants still have to be used as secondary disinfectants, however the concentrations used would not be as high as when they are used as primary disinfectants.

Apart from its use as a disinfectant, UV irradiation is also being used in the degradation of contaminants in water, such as methyl *tert* butyl ether (MTBE), trichloroethylene (TCE) and some taste and odour compounds. When combined with hydrogen peroxide, ozone or titanium dioxide the generation of the hydroxyl radical ($OH^{\bullet}$) is enhanced, which is the major oxidant at work in the degradation of contaminants. This type of process is called an advanced oxidation process (AOP).

According to Chang and Young (2000), AOPs have an advantage over conventional water treatment processes, such as aeration and granular activated carbon, in that the contaminant in question is degraded into other compounds possibly removing the contaminant from the environment and not just from the aqueous phase. Despite this, Karimi et al. (1997) noted that water quality parameters such as TOC and pH can inhibit the performance of AOPs. Carbonates and bicarbonates, found in high concentrations especially in groundwater, are also known to be scavengers of the OH radical.

Natural organic matter (NOM), a precursor of most disinfection by-products (DBPs), is known to react with chlorine to form trihalomethanes (THMs) and haloactetic acids (HAAs). According to Wiszniowski et al. (2002), humic acids constitute 90% of the composition of dissolved organic carbon and only 10-50% of this is removed via coagulation. The remaining humic acid may react with any form of chemical disinfectant used in the treatment of microorganisms. Degradation of NOM is also an area to which scientists are applying the technology of AOPs. Hand et al. (1995) and Symons and Worley (1995) have shown that certain AOPs can destroy DBP precursors possibly producing DBPs at levels below the maximum contaminant limit (MCL). The MCL set by USEPA in 2001 for TTHM and HAA_5 (consisting of ClAA, Cl_2AA, Cl_3AA, BrAA and Br_2AA) were 80 and 60μg/L respectively. In 1996, Health Canada set the interim maximum acceptable limit (IMAC) for TTHMs at 100μg/L and the provisional guideline values for Cl_2AN was set at 90μg/L by WHO in 1993.

1.2 Research Motivation

Water quality parameters such as pH and alkalinity have been found to have some effect on the degradation of organic compounds with UV irradiation, but there has not been much research that has focused on the effects of pH, alkalinity and UV-fluence on the breakdown of NOM and how, in turn, these affect the production of selected chlorination by-products. This is what brought about the extensive work and results that are described further in this thesis.

1.3 Objective and Scope

The first objective of this research was to determine how pH, alkalinity and UV-fluence affect the formation of trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) upon subsequent chlorination. It also involved determining, with the use of factorial experiments, interactions between these factors, and their effects on the formation of these post-UV disinfection by-products. Secondly, a comprehensive study involving single factor experiments on pH and alkalinity was carried out to observe the impacts of these factors on HAAs, HANs and THMs. While most of the experiments were performed using a model or "synthetic water", water from the post-filtration step of the Mannheim water treatment plant (MWTP) in Kitchener was also incorporated into the single factor experiments to verify the results in one natural water matrix.

1.4 Thesis Organization

Chapter 2 gives a comprehensive review of disinfection byproducts from pre- and post-UV chlorination including some developments concerning the analytical methods for determining the concentrations of these by-products. Chapter 3 describes the methods and materials used in this research. The results of the experiments are discussed in Chapters 4 and 5 while the conclusions based on the results are presented in Chapter 6 along with some recommendations.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter is a review of various known disinfection by-products (DBPs) formed while disinfecting water, particularly treatment of water using UV irradiation and UV-mediated technologies. This also considers the treatment of water using chlorine before UV irradiation and the use of chlorine as a secondary disinfectant.

2.2 Disinfection / Disinfectants

As described by Wallace et al. (2002), disinfection is the process of treating source water in drinking water treatment facilities by inactivating microorganisims. According to Eigener (1988), it is used in various fields of application with the aim of preventing the spread of infection and contamination.

There is a wide range of disinfectants used in water treatment. These include chlorine, chlorine dioxide, chloramines, ozone and ultraviolet irradiation. The most commonly used disinfectant for water treatment is chlorine. It has been in use as far back as the mid-19th century (Karlin, 1999), when Dr. John Snow established that water could be a mode of disease transmission. Chlorination is one of the most widely practised public health forms of disinfection in the developed world and according to Karlin (1999), it is credited with reducing cholera incidence by 90%, typhoid by 80% and amoebic dysentery by 50% in the United States.

2.2.1 UV Irradiation

UV disinfection has been applied in European drinking water treatment since the mid 1950's (Kruithof et al., 1992). This form of disinfection is being used in ground water treatment plants in Europe to destroy *E.coli*, and *Aeromonas* bacteria. It has also been in use for several years to treat domestic wastewater and house water in North America (Parrotta and Bekdash, 1998). The UV technology is regarded as safe, easy to use, and free of chemicals.

Parrotta and Bekdash (1998) mentioned that at a wavelength of approximately 254nm, two components of genetic material (deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)) absorb Ultraviolet light, and alter the nitrogenous heterocyclic components forming new bonds and rendering the microorganism unable to reproduce. In the electromagnetic spectrum, the UV light is situated between the X-ray and visible light as shown in Figure 2.1.

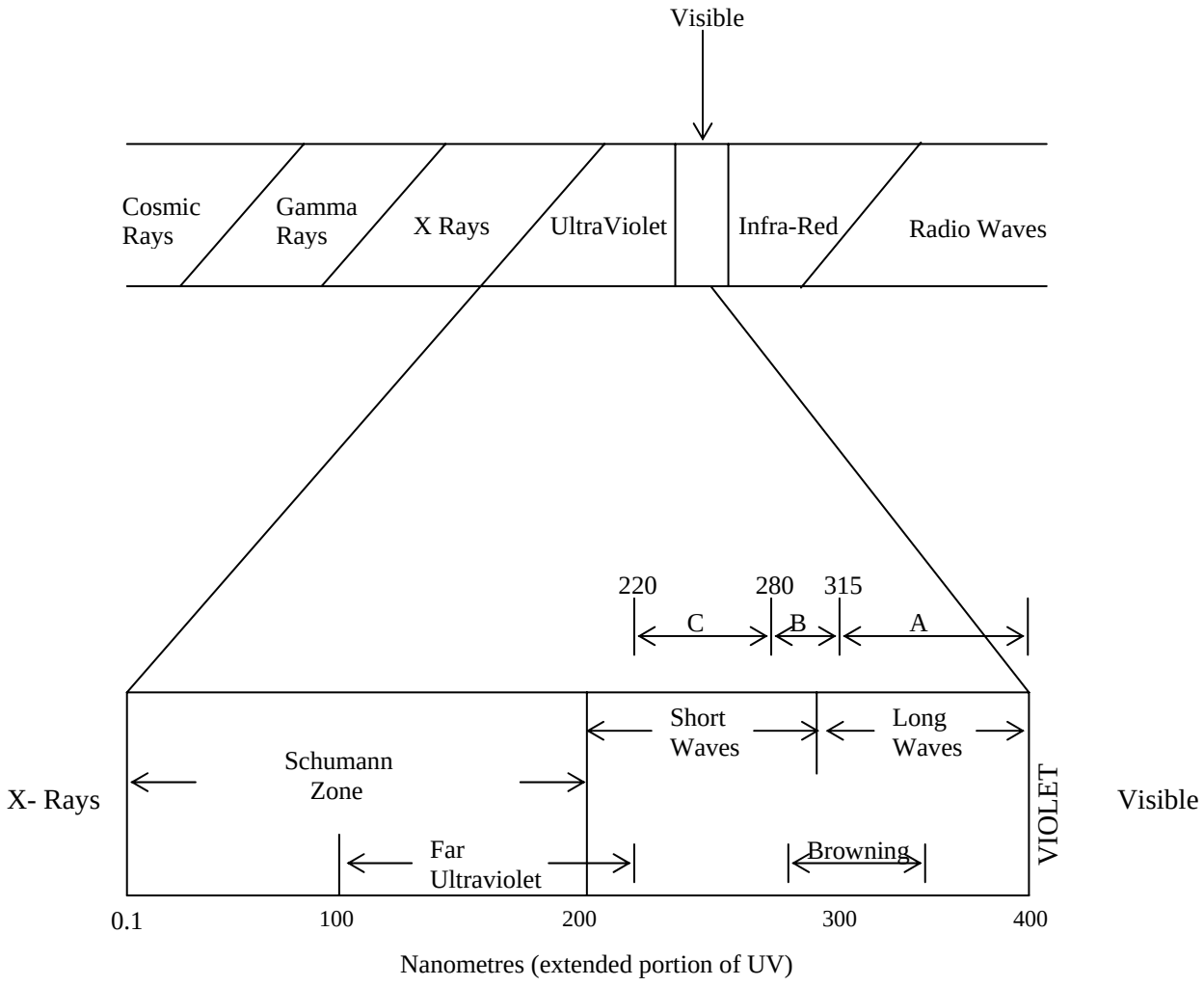

Figure 2.1 Range of the Electromagnetic Spectrum (Masschelein and Rice (2002)).

UV irradiation has been proved by Sundstrom et al. (1990), to destroy microorganisms and also decompose organic contaminants such as benzene. According to the authors, UV irradiation reduced benzene to half its concentration within 90min of irradiation. It is also known to transform dissolved organic carbon (DOC) into inorganic carbon, CO_2 and CO (Dahlen et al., 1996). UV irradiation also promoted the mineralization and fragmentation of natural organic matter (NOM) resulting in a decrease of the molecular size distribution

of NOM (Parkinson et al., 2001). The “C” band of the ultraviolet radiation is the most effective followed by bands “B” and “A” respectively. The range of the bands wavelengths given by Masschelein and Rice (2002) are:

UV-C 200nm-280nm,

UV-B 280nm-315nm and

UV-A 315nm-400nm

2.2.2 Pre-UV Chlorination

Water plants utilizing surface water sometimes use pre-chlorination to control biological growth in settling basins and filters, possibly increasing coagulation and disinfection efficiency (Parrott and Scott, 1980). According to Williams et al. (1996), pre-chlorination is used especially in the summer to control algal growth and filter fouling. Buffle et al. (2004) were able to determine that the use of chlorine along with ammonia in pre-chlorination before ozonation helps to reduce the formation of bromate. Oxenford (1995) also mentioned that chlorine may be used as an oxidant in transmission lines prior to entering a treatment facility for taste and odour control and to get a head start of disinfection apart from minimizing biological growth in the treatment plant. He further went on to say that chlorine has been effective in the control *zebra mussels* that affect transmission lines in the great lakes.

Despite these advantages, the use of chlorine prior to UV disinfection would cause the formation of DBPs and the concentration would depend on the source water. Golfinopoulos et al. (2003) studied the occurrence of different classes of DBPs such as

THMs in different treatment plants in Athens after pre-chlorination. They found that these DBPs did not occur in concentrations higher than the MCL set by the USEPA or WHO but Vajdic (1982) found that the discontinued use of pre-chlorination step in a Toronto treatment plant reduced the formation of THMs.

2.2.3 Post-UV Chlorination

In as much as the use of UV technology in disinfection has being proven to be effective, it does not maintain microbial stability in the distribution system. Despite this, it may still be a promising sole water treatment method for restaurants, rest areas, camps and schools that have short distribution systems (Parrotta and Bekdash, 1998). For treatment plants and distribution systems that serve a whole community, a secondary disinfectant that will provide a residual effect is needed. In most of the cases chlorine is used. Though more recently, chloramines have been used in distribution systems when it is more difficult to maintain free chlorine (Miller, 1993).

2.3 Advanced Oxidation Processes

Glaze and Kang (1990) defined advanced oxidation process (AOP) as ambient temperature processes that involve the generation of highly reactive radical intermediates, particularly the hydroxyl radical (others are hydrogen radical ($H^{\cdot}$) and electron e^{-}). In aqueous solutions, these radicals react with contaminants and at high doses oxidize them to carbon dioxide, water and salts. According to Table 2.1, the hydroxyl radical is the most powerful oxidizing species after fluorine; it is short lived and an extremely potent oxidizing agent (Legrini et al., 1993).

Table 2.1 Oxidation Potentials of Some Oxidants (Legrini et al., 1993)

Species	Oxidation Potential
Fluorine	3.03
Hydroxyl radical	2.80
Oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl peroxide	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

Peyton (1990) described the AOPs as a promising technology for the treatment of water especially those contaminated with organic chemicals because the chemicals used in the process decompose to harmless or beneficial by-products. According to Jeff and Bariach (1990) the use of AOPs as a water treatment technique, is a means of solving many problems created by soluble toxic water substances and organic chemicals found in ground water and wastewater leachate.

The commonly used oxidants in AOPs are hydrogen peroxide and ozone. These are used in conjunction with UV light or as dual oxidants i.e. UV/ H_2O_2, UV/O_3, UV/H_2O_2/O_3 or H_2O_2/O_3. Ollis et al. (1991) observed that though the use UV light or oxidant alone produces partial destruction of contaminants, only the simultaneous use of either light with an oxidant or of the dual oxidant (H_2O_2/O_3) yields complete mineralization of organics to carbon dioxide. These oxidants have advantages over each other, according

to Sundstrom et al. (1990) the advantage of hydrogen peroxide over ozone is that of storage, ease of mixing with water and costs that are less sensitive to scale of operation.

The use of semiconductors such as TiO_2 (Richardson et al. (1996) and Bolton (1990)) and electrons (Cooper et al., 1990) is also being investigated in advanced oxidation process. The TiO_2 particles in the anatase crystalline form were used by Bolton (1990) to bring about a complete mineralization of 2,4-dichlorophenol ($C_6H_4OCl_2$). This involved the reaction of the OH radical, produced from UV/TiO_2, to give hydrochloric acid, carbon dioxide and water as products. Hydrogen peroxide on the other hand uses UV light to cleave the O-O bond and generate the hydroxyl radical. The radical can then be scavenged by an organic compound to oxidize the organic, recombine with other hydroxyl species to reform hydrogen peroxide or initiate a radical chain degradation of the peroxide (Chang and Young, 2000).

Cooper et al. (1990) demonstrated the use of electrons in AOPs. This involves the irradiation of water with fast electrons generated either by ^{60}Co or electron accelerators.

The aqueous electron, $e^-_{aq,}$ reacts with other chemical compounds and contributes to their removal from the aqueous solutions.

Excessive use of hydrogen peroxide in AOPs can prove to be a disadvantage. Wang et al. (2000) observed that up to 0.01 % of the peroxide increased the destruction rate of humic acid, whereas a decrease occurred when the percentage was exceeded. The authors were also able to establish that an increase in concentration of carbonate/bicarbonate ions in water lowered the OH radical concentration possibly reducing the destruction rate of the organic. Even though the carbonate radical is also an oxidant, the potential is less than that of the OH radical.

2.4 Disinfection By-Products

Disinfection by-products are formed when certain disinfectants react with natural organic matter (NOM) in water (Wallace et al., 2002), and/or with organic contaminants (Chang and Young, 2000). So far, chlorination by–products are the most common types of by-products known to scientists. This is probably due to the fact that chlorine was the first type of chemical used in disinfection (Karlin, 1999). As discussed by Niewenhuijsen et al. (2000), chlorine reacts with natural organic compounds such as humic and fulvic acids, to form a wide range of unwanted halogenated organic compounds like trihalomethanes (THMs), haloacetic acids (HAAs), chlorophenols, chlorahydrates and haloacetonitriles (HANs).

Brominated DBPs are also formed especially in waters containing bromide ion. According to Clark et al. (2001) the presence and concentration of bromide ion affects

the overall formation of halogenated DBPs. In the year 2003, Richardson and Thruston conducted a study on the formation of DBPs from waters of high bromide levels treated with chlorine or chlorine dioxide. They found that elevated bromide concentration caused a significant shift in speciation of the DBPs from chlorinated to brominated DBPs. Basically, when waters containing bromide ion are chlorinated, the hypobromous acid (HOBr) is formed before the hypochlorous acid (HOCL). From Table 2.1 the oxidation potential of HOBr is higher than that of HOCl resulting in an initial reaction of HOBr with NOM and forming higher concentrations of brominated DBPs.

During a routine water quality characterisation carried out at the Ministry of Environment, Canada, two new DBPs were detected in treatment plants where chlorine was the primary disinfectant (Taguchi, 2001). They were tentatively identified as *1-aminoxy-1-bromobutan-2-ol* and *1-aminoxy-1-chlorobutan-2-ol*. To Taguchi's knowledge, these were the first aminoxy structures to be identified in treated drinking water. This shows that there is the possibility of the DBP formation of groups that are still unknown.

2.4.1 DBP Precursors

DBP precursors include both humic substances (a subset of natural organic matter) and organic contaminants found in surface and ground waters. Humic substances consists of humic acid, fulvic acid and humin (Manahan (1994), Corin et al. (1996)), while the organic contaminants are from materials such as gasoline (benzene (B), toluene (T)

xylenes (X)) or from leaks in halogenated solvent tanks e.g. perchloroethylene, trichloroethylene (Ollis et al., 1991).

Humic substances are an important class of complex agents that occur naturally. They are degradation-resistant materials formed during the decomposition of vegetation materials in soil, peat, and coal lignite or in any location where large quantities of vegetation have decayed. They have high molecular weight and are polyelectrolytic macromolecules (Manahan, 1994). According to Corin et al. (1996), they account for up to 90 % of dissolved organic carbon in surface waters. Humic acids are the fraction of humic substances that are not soluble in water under acidic conditions with pH less than 2 but soluble at a higher pH. Fulvic acid is the fraction that is soluble at all pH values while humin is the fraction that is insoluble at any pH value.

THMs are well known chlorination by-products. As reported by Gallard and Von Gunten (2002), *meta-dihydroxy* benzene (resorcinol), a phenolic structure identified in humic substances, have been considered as the main precursor of THMs from aquatic humic substances due to their high yield of THMs. Other structures such as phenolic compounds, β-diketones and some carboxylic acids that can be converted to ketoacids, such as citric acid, are also susceptible to form THMs in high yields. Methoxyl, phenolic and ketonic structural groups have been considered the most reactive groups to chlorine in natural organic matter.

2.4.2 UV/UV- Mediated By-Products

Disinfection with UV irradiation had been thought not to produce by-products of any kind (Wolf, 1990). However under some conditions the formation of by-products could be of significance. In the presence of nitrates or nitrites, elevated levels of mutagenic substances are formed from various amino acids on irradiation of water under neutral conditions (Mole, 1999).

In 1996, Corin and his colleagues showed that, aromatic hydroxy acids e.g. hydroxy benzoic acid and 3, 4-dihydoxy benzoic acid, were formed during UVC irradiation of aqueous NOM. This was in confirmation with the work done by Frimmel in 1998 when he observed that at elution times exceeding 32 min, new UV-absorbing fractions or factions with increased UV-absorbances in the irradiated samples are likely to contain low molecular organic acids. Corin et al. (1996) also observed non-volatile fatty acids (e.g. tetradecanoic (myristic) acid, hexadecanoic (palmitic) acid and octadecanoic (stearic) acid) as by-products after UV irradiation of humic waters. These probably originated from the degradation of lipids and tricylglycerols derived from algae and terrestrial plants. In 1996, Richardson and her colleagues identified *3-methyl-2,4-hexanedione* as a by-product of UV/TiO_2 treatment.

UV irradiation, including UV-mediated (e.g. UV/H_2O_2) have been found to degrade organic contaminants in water. In as much as this might be an advantage, by-products are also formed from these degradations and some are known to be present long after the contaminant have been oxidized. In the experiment performed by Chang and Young (2000) they found that the use of AOP in treating water contaminated with MTBE (methyl-tert-butyl ether) was successfully oxidized, but left a by-product tert-butyl formate (TBF). A significant amount of TBF was formed and it persisted beyond the time MTBE had been degraded.

Mole et al. (1999) noted from their experiment that the use of UV irradiation in the treatment of tetrachloroethene (PCE) contaminated waters has the potential to result in the formation of appreciable concentrations of dichloroacetic acid (Cl_2AA) and trichloroacetic acid (Cl_3AA). Further more, during the author's research experiment, they found that by-product of aldehydes and some unknown compounds tentatively identified as unsaturated amides (C_{16} and C_{18}) were formed on irradiation of Thames River sample containing about 40 mg/L of naturally occurring nitrate.

2.4.3 Pre-UV Chlorination By-Products

The use of chlorine has dramatically reduced the incident of waterborne diseases and also improved the quality of life. Unfortunately, an unwanted side effect is the formation of harmful by-products. Most of the by-products of the pre-UV chlorination are similar to those of chlorine treated waters, except that they may be in larger quantities. This is because in pre-chlorination, treatment with chlorine comes before physical treatments

(aeration, coagulation and filtration), possibly reacting with a greater portion of NOM and other chemicals that could have been reduced during aeration.

According to Lee et al. (2001), the most significant group of disinfection by-product formed during chlorination are the trihalomethanes (THMs). Aside from THMs, many other compounds comprising the chlorination by-products found in treated waters are haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloaldehyde, halopicrin, cyanogen chloride, halophenol and chloral hydrate.

In the study made by El-Dib and Ali (1995) on formation of THMs during the chlorination of raw Nile River water, it was found that the reaction rate of THMs progressively increased as the pH value of water was increased from 6 to 9. Also, they were able to find that THMs concentrations increased as the chlorine dose was increased; however THM formation was not found to be proportional to the applied chlorine dose.

2.4.4 Post-UV Chlorination By-Products

According to Kruithof (1992), post-UV chlorination causes a high mutagenic effect in the Ames test and produces highly brominated THMs in the presence of low bromide concentrations.

When chlorine was used as a secondary disinfectant, in an experiment performed by Richardson et al. (1996), following treatment with UV/TiO_2, several chlorinated and brominated DBPs were formed. Amongst them were some halomethanes and several

halonitriles. Most of the halogenated DBPs were the same as those observed when chlorine was used as the sole disinfectant but the number and concentration were lower. However a new compound tentatively identified as dihydro-4,5-dichloro-2-(3H) furanone was formed. In another set of experiments performed by Mole et al. (1999) THMs, trichloroacetic acid (Cl_3AA) and dichloroacetic acid (Cl_2AA) were determined as by-products in the chlorination of samples of Thames River following UV irradiation.

2.5 Identification of DBPs

Gas chromatography is a major analytical instrument in the determination of volatile DBPs. It utilizes a varying number of detectors depending on the type of compound to be quantified. Commonly used detectors are the mass spectrometer (MS), electron capture detector (ECD) and flame ionization detector (FID).

Gas chromatography is a quantitative and qualitative instrument that is sensitive and selective, depending on the type of detector employed. It is based upon the principle that when a mixture of volatile materials is transported by a carrier gas, it passes through a column containing an adsorbent solid phase or an absorbing liquid phase coated on a solid material. Each volatile component is then partitioned between the carrier gas and the solid or the liquid. The length of time required for the volatile component to move within the column is proportional to the degree to which it is retained by the non-gaseous state. Different components will emerge from the column at different times. These are measured by a detector in terms of their quantity and time they emerge. Usually a

recording of the response appears as peaks of different sizes depending upon the quantity of material producing the detector response (Manahan, 1994).

According to Nikolaou et al. (2002) four analytical methods have been used in the determination of volatile chlorinated DBPs in drinking water. These are based on the following techniques: liquid-liquid extraction-gas chromatography-electron capture detection (LLE-GC-ECD); liquid-liquid extraction-gas chromatography-mass spectrometry (LLE-GC-MS); purge and trap-gas chromatography-mass spectrometry (purge and trap-GC-MS); and headspace-gas chromatography-mass spectrometry (headspace-GC-MS).

DBPs may also be identified using low-resolution electron-impact (EI) mass spectrometry. This type of analysis is sufficient for regulated compounds that have been well characterised and whose spectra are in GC/EI-MS library database. Newly identified DBPs or unknown pollutants are often impossible to identify using GC/EI-MS alone as many of the compounds may not be present in any library database. When faced with this kind of issue, Richardson (1996) and her colleagues used a combination of mass spectrometry and infrared spectroscopy to aid in this process. An example of such a modified analytical approach is gas chromatography combined with fourier transform infrared spectroscopy (GC/FT-IR). High and low-resolution election impact mass spectrometry and low-resolution chemical ionization mass spectrometry can also be combined with gas chromatography, giving (GC/EI-MS) and (GC/CI-MS) respectively. Richardson noted that even these have limitations in that it was possible that extremely

polar compounds as well as thermally liable and higher molecular weight compounds could have escaped detection.

Zhang and Minear (2002), in their characterisation of high molecular weight DBPs, also mentioned that GC/MS is not amenable to identification of highly polar/hydrophilic/non-volatile derivatives and especially not amenable to identification of compounds with high molecular weight.

A new instrument used in the identification of DBPs is the high-field asymmetric waveform ion mobility spectrometry known as FAIMS; its principles of operation have been discussed by Guevremont and Purves (1999), Purves et al. (1998) and Ells et al. (1999).

Ells et al. (1999) described FAIMS as a new continuous flow technique for the separation of gas phase ions at an atmospheric pressure of 760 Torr and a room temperature of 298K. According to Purves and Guevremont (1999), it is an instrument that acts as an ion filter and can be set to continuously transmit one type of ion. Ells et al. (1999) also mentioned the fact that the application of FAIMS, using an electrospray-ionization (ESI) source and MS detection (ESI-FAIMS-MS) has potential for improving the detection of low m/z ions that are obscure in conventional ESI-MS by solvent and salt-related ions. The instrument has been described as a fast simple and sensitive method especially for the detection of HAA concentrations in source and treated water.

Ells et al. (1999) has also shown that FAIMS is a useful instrument in identifying polar and ionic compounds especially, HAAs, that tend to go undetected by GC/ECD or GC/MS except when methylated. According to Ells et al. (2000), FAIMS is capable of separating the haloacetic acids in gaseous solution. From their study, nine chlorinated and brominated haloacetic acids were selectively transmitted through FAIMS and detected by mass spectrometry at levels suitable for their direct monitoring in source and treated drinking water. Gabryelski et al. (2003) compared the use of ESI-FAIMS-MS with GC methods in the analysis of HAAs in drinking water and found FAIMS to be simple, faster to use, requiring no sample preparations or chromatographic separations and selective methods for the detection of HAAs.

2.6 By-Product Toxicity

Despite the fact that disinfection of diseases causing organisms is achievable, by-products occur with the use of disinfectants, some of which are known to be toxic. As mentioned by Chang and Young (2000), a disadvantage of any chemical or biological degradative treatment method, including AOPs, is their potential for forming by-products with higher toxicity than the original contaminant.

Since the pioneering work of Rook in 1974 (Garllard and Von Gunten, 2002), it has been known that the use of chlorine for disinfection purposes of drinking water leads to the formation of many by-products potentially harmful for human health. Ever since then there has been a pursuit to either find solutions to the eradication of such by-products from chlorine or seek alternative disinfectants.

Chlorination disinfection by-products in drinking water have received considerable interest because of their possible association with cancer, particularly bladder and rectal cancer (Nieuwenhuijsen et al., 2000). According to Karlin (1999), several of these by-products have the attribute of also causing unpleasant health outcomes in rodents, especially those bred specifically to be sensitive to these outcomes.

Several DBPs routinely found in drinking water have been reported by Nieuwenhuijsen et al. (2000), to cause reproductive and developmental toxicity in laboratory animals. For instance testicular damage in rats was caused by halogenated acetic acids and neutral tube and craniofacial defects with administration of dichloroacetic or trichloroacetic acids in rats. Chloroform has been found to cause liver tumors in female rats and renal tumors in male rats while chlorinated furanones has been found to cause DNA damage in rats (Komulainen, 2004).

In a laboratory study conducted by Richardson and Thruston (2003) to determine the contribution of humic acid isolated from the Sea of Galilee to DBPs, 2,3,5-tribromopyrrole was identified as a DBP. This compound was found to be 8 times,4.5 times, and 16 times more cytotoxic than dibromoacetic acid, 3-chloro-4-dichloromethyl)-5-hydroxy-2-[5H]-furanone [MX], and potassium bromate, respectively.The work done by Frimmel in 1998 showed that aquatic NOM samples irradiated with both UVA and UVB resulted in significant toxicity to *D. Magna.* This was in opposition to the work done by Parkinson et al. (2001) where no significant toxicity to *D.Carinata* was observed

in the acute immobilisation test for *HV MIEX samples (Concentrated NOM samples obtained from Hope Valley reservoir in South Australia) irradiated by UVA and UVB for 24 hrs. A number of factors such as pH of water, organism used, water sample could have been the cause of this outcome.

Parkinson et al. (2001) also found that UVC and UVC/H_2O_2 treated waters caused toxicity in acute immobilisation studies with *D.Carinata* and the mortality decreased when the metal chelating agent, DTPA, was added to the water sample. The authors therefore concluded that the toxicity of UVC and UVC/H_2O_2 could have been as a result of the presence of the copper ions found in the raw water. The copper ions should pose no harm to human health as long as copper levels are below the standard limit of 1.3 mg/L set by the US environmental protection agency.

Zhang and Minear (2002) mentioned that DBPs of molecular weights higher than 5000Da may not be associated with toxic risks. This was explained by the fact that for a chemical to produce adverse effect on humans, following exposure via drinking water, it must be absorbed into the body.

2.7 Summary

In the disinfection part of the treatment plant, the battle is not only in finding a suitable disinfectant that will inactivate any known microorganism but also one that will produce little or no by products. According to Miller (1993), the reduction of disinfection dosage will reduce DPB formation which will in turn increase the risk of microbial contaminants in finished waters. So there has to be a balance act between disinfection and DBPs formation.

According to Karlin (1999), some experts contend that a principal reason that alternate oxidants looks so attractive is that their by-products are poorly characterised. In other words, “we fear chlorine because we know so much about its by-products and trust alternates because we know so little” (Karlin 1999). The research discussed in this thesis was set to find more about the by-products of post UV/UV-mediated chlorination and how they are influenced by water parameters such as pH and alkalinity.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter outlines the materials and methods employed in the design of factorial, hierarchical and single factor experiments. It also explains the extraction methods used for disinfection by-products, THMs, HAAs & HANs and other analytical methods.

3.2 Materials

The synthetic water was the major medium employed in this research; it was prepared according to the concentration of the following compounds; magnesium chloride, calcium chloride, sodium nitrate, calcium sulphate, sodium bicarbonate, alginic acid and natural organic mater isolated from Suwannee River, Ohio. The synthetic water was modeled according to the post filtration stage of the Mannheim water treatment plant (MWTP) in Kitchener, Ontario. A detailed concentration of compounds making up the synthetic water is summarized in Table 3.1

Table 3.1 Synthetic Water Constituents (mg/L)

Ca^{2+}	Mg^{2+}	Na^{+}	$(CO_3)_{TOT}$	NO_3^-	Cl^-	SO_4^{2-}	NOM	TOC	Alginic Acid
29.10	9.99	36.20	90.00	3.00	40.00	55.00	2.56	4.00	5.32

A dilute solution of 6% sodium hypochlorite was used for the UFC tests and quenched with a stock solution of 8 g/L of sodium thiosulphite after 24 hours. Hydrogen peroxide (H_2O_2) was employed for advanced oxidation processes (AOPs). Potassium iodide, ammonium molybdate and sodium hydroxide, and a buffer solution of potassium hydrogen phthalate (pH 5) were used to determine initial and final concentrations of H_2O_2 before and after irradiation. Bovine liver (catalase) was used to quench the residual H_2O_2 concentration. Pentane was used in extracting THMs and HANs while MTBE was used as an extracting solvent for HAAs.

Standards for haloacetic acids, haloacetonitriles and trihalomethanes, diazald (N-methyl-N-nitroso-p-toluenesulfonamide) a diazomethane generating reagent, and pentane were purchased from Aldrich and Sigma Limited Canada located at 2149 Winston Park Drive, Oakville, Ontario. All other compounds used in the experiments were purchased from VWR International located at 2360 Argentia Road, Mississauga, Ontario.

3.3 Analytical Equipment/Apparatus

The Denver analytical balance was used in measuring all solid reagents. The negative logarithm of hydrogen ion (H^+) concentration, referred to as pH, was measured with the aid of a bench-top pH, direct ion-measurement meter model 420A and a combination pH electrode with temperature corrections purchased from Orion research Inc. Boston, USA. The instrument was standardized daily using a three point calibration of pH 4, 7 and 10 standard solutions obtained from VWR International.

The initial and final concentrations of hydrogen peroxide were determined using the UV-visible spectroscopy, Hewlett Packard 8453, at a wavelength of 351 nm. The 24 hr chlorine residual was analyzed according to N,N-diethyl-*p*-phenylenediamine (DPD) colorimetric methods (APHA-AWWA-WEF, 1995) with the aid of a DR/2000 spectrophotometer purchased from the HACH Company, Colorado, USA .

A 1 KW medium pressure lamp housed in the collimated beam apparatus shown in Figure 3.1 purchased from Calgon Carbon Corporation, Pittsburgh was used for irradiating all water samples. The value of fluence for the lamp was measured with the aid of a radiometer while the accuracy of the radiometer was checked using chemical actinometry.

Figure 3.1 Collimated Beam Apparatus (Calgon Carbon Corporation, Pittsburgh)

Two types of gas chromatography (GC) using the electron capture detector were used in the analysis of the disinfection by-products. The GCs were Hewlett Packard 5890 series III and the differences in the GCs are their column types and temperature settings. The

GCs are designated as GC I and GC II and their temperature settings are given in Appendix A.

3.4 Experimental Details

3.4.1 Factorial Experimental Design

A 2^3 factorial design was employed in this research to investigate the effects of pH alkalinity and UV-fluence in the formation of HAAs, HANs & THMs during chlorination of synthetic water samples following UV irradiation. The 2^3 factorial experiments resulted in 8 randomized runs and 4 randomized center points. For each of the factors, low, center and high points were chosen as illustrated in Tables 3.2 and 3.3 below. The various points were based on values occurring in natural waters while the centre points are midpoints between the low and high values. The centre point for pH was based on the midpoint of the hydroxyl ion concentration read as pH. Taking Run 1 as an instance, 300ml of the synthetic water (described in Table 3.1) were brought to a pH of 6 with no added alkalinity (but usually added in form of sodium bicarbonate) and irradiated at a UV-fluence of 1000 mJ/cm^2.

Table 3.2: A 2^3 Factorial Experiment

Run	pH	Add alkalinity (mg/L as $CaCO_{3)}$	UV-fluence (mJ/cm^2)
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9a	0	0	0
9b	0	0	0
9c	0	0	0
9d	0	0	0

Table 3.3 Various Points of the Factorial Experiment

Factors	Low Point (-1)	Midpoint (0)	High Point(+1)
pH	6	7.7	8
Add alkalinity (mg/L as $CaCO_3$)	0	100	200
UV-fluence (mJ/cm^2)	1000	3000	5000

3.4.2 Uniform Formation Conditions Test.

This test was performed according to the article written by Summers et al. (1996) and it was used assess the formation of HAAs, HANs and THMs. A stock solution of 1000 to 2000 mg/L was prepared from 6 % sodium hypochlorite. Water samples were chlorinated with 4 mg/l of the stock solution and the residual free chlorine was measured after 24 hrs ± 1. Both the water samples and the stock solution were brought to a pH of 8, with a buffer solution prepared from boric acid and sodium hydroxide, before chlorination. The residual chlorine was then quenched using100 μL of 8 g/L of sodium thiosulphate in 20 mL of water sample to prevent further post-UV chlorination disinfection by-product (PCDBP) formation. The (DPD) colorimetric method (APHA-AWWA-WEF, 1995) was used to determine the residual concentration of chlorine in the samples before it was quenched.

3.4.3 Preparation of Standards.

Calibration standards for the HAAs, HANs and THMs were obtained from Aldrich-Sigma Ltd. Varying concentrations of the standards were dispensed into 25 mL volumetric flasks and then filled to the mark with milli-Q ultra pure water. From each concentration, 20 mL of the sample was measured into 40 mL vials and a liquid-liquid extraction process was carried out for each of the DBPs as described in Section 3.5.4. The extracts were then analysed by the GC/ECD and used as the calibration curve. Three replicates were used per point and the range of R^2 obtained for the compounds was 0.92 - 0.98. These curves can be seen in Appendix A.

3.4.4 Liquid-Liquid Extraction of Disinfection By-Products

This section briefly describes the process involved in the extraction of the PCDBP, HAAs, HANs and THMs, the outline of each procedure may be found in Appendix A.

3.4.4.1 Diazomethane Generation

Diazomethane (CH_2N_2) is a gas at room temperature, liquefies at -23 ^oC and freezes at -145 ^oC. It is the most common methylating reagent for carboxylic and haloacetic acids, highly toxic and a carcinogen. It has been known to explode both as a gas and in solution (Aldrich-Sigma, 1993).

Diazomethane was generated in a MNNG diazomethane apparatus. The apparatus consists of two tubes. The inner tube holds the diazald and methanol while the outer tube holds MTBE. The whole setup was allowed to cool in ice for about 10 minutes before 600 μL of 5.82 N NaOH solution was added drop wise into the inner tube with a gas tight syringe. The apparatus was secured firmly before adding NaOH. The diazomethane gas

escapes through the hole located on the inner tube and it was collected in the MTBE in the outer tube. The reaction was allowed to go on for about 45 minutes until the MTBE turned yellow. The diazomethane in MTBE was then transferred into vials using flamed pasteur pipettes.

3.4.4.2 Haloacetic acids

The liquid-liquid extraction was carried out according to EPA method 552 with minor modifications. Oven baked sodium sulphate was added to 20 mL of the sample in a 40 mL vial. Concentrated sulphuric acid was also added to the water sample in the vial to maximize extraction of the HAAs. Methyl-*tert*-butyl was used as the extraction solvent while 2,3-dibromopropanoic acid and 2,3,5,6-tetrafluorobutanoic acid were used as internal and surrogate standards respectively. The solution was put in the shaker for seven minutes and then allowed to stand in room temperature for phase separation. The organic phase was pipette into test tubes and these were allowed to cool at 0 ^{o}C. Diazomethane was added to the cooled extracts to methylate the HAAs thereby facilitating the detection of the compounds by the GC/ECD. After adding diazomethane, the extracts were left to stand at 4 ^{o}C and room temperature for fifteen minutes each before washing the extracts with saturated sodium bicarbonate. Afterwards, and the organic phase was analysed by GC/ECD.

3.4.4.3 Haloacetonitriles & Trihalomethanes.

EPA method 551.1 with minor modifications was used to determine the concentration of THMs & HANs. Oven baked sodium sulphate was added to the 20 mL of the water sample in a 40 mL vial. The extract medium, pentane and the internal standard, 1,2-

dibromopropane were also added in to the 40 mL vial along with the water sample. The solution was put in the shaker for seven minutes and then left to stand in room temperature for phase separation. The organic phase was transferred into GC vials and analysed using GC/ECD.

3.4.5 Single Factor Experimental Design.

There were three factors that were considered significant in the factorial experiments, and out of these three factors, comprehensive studies on alkalinity and pH were carried out with the aid of single factor experiments. Alkalinity was varied from 0 to 250 mg/L as $CaCO_3$ with an interval of 50 mg/L as $CaCO_3$ while pH and UV-fluence were kept constant at 8 and 1000 mJ/cm^2 respectively. For pH studies, an add alkalinity of 0 mg/L as $CaCO_3$ and a UV-fluence of 1000 mJ/cm^2 was used while pH was varied from 5 to 9 with an interval of one pH unit.

Synthetic water, without bromide ion addition, treated with chlorine following UV photolysis and UV/H_2O_2 was used in the alkalinity studies. Water from the post-filtration step of the Mannheim water treatment plant was used for the pH studies and the treatment was solely the use of UV/H_2O_2 followed by chlorination. Two sets of pH studies were carried out on the water from the treatment plant, one without the addition of bromide ion and the other with the addition of 500 μg/L of bromide ion to study the formation of brominated DBPs.

3.4.5 Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) were employed with the use of hydrogen peroxide as the oxidant alongside UV irradiation. A dilute stock solution of 2000 mg/L

was prepared from the original concentration of 30 % hydrogen peroxide solution. For experiments involving AOPs, between 10 and 13 mg/L of the stock solution was added to 300 mL of the synthetic water before irradiation.

The concentration of hydrogen peroxide before and after irradiation was determined using the I_3^- method (commonly referred to as the Ghormely method) illustrated by Klassen et al. (1994). This involved the preparation of stock solution from potassium iodide, ammonium molybdate and sodium hydroxide, and a buffer solution of potassium hydrogen phthalate (pH 5). A 2.5 mL of the potassium iodide stock solution and the buffer solution were added into a 10 mL volumetric flask along with 1ml of the sample containing hydrogen peroxide. The solution was diluted up to 10 mL and the absorbance of the solution measured at 351 nm using the UV-vis spectrophotometer because the molar absorptivity of I_3^- is at its maximum at 351nm. The concentration of the peroxide was calculated according to Equation 3.1

$$[H_2O_2] = \frac{(A_1 - A_0)x10}{0.7776} \qquad \text{Equation 3.1}$$

Where

A_1 = final absorbance

A_0 = blank

The blank was a measurement of the absorbance of the 2.5 mL of the stock and buffer solutions diluted to 10ml in a volumetric flask. A concentration of 0.2 mg/L of Bovine liver (catalase) was used to quench the residual hydrogen peroxide as determined by Liu et al. (2003). Detailed addition of hydrogen peroxide can be seen in Appendix B.

3.4.6 Bromide Ion Concentration

Bromide ion in form of sodium bromide was added to synthetic water and water from the treatment plant in order to study the effect of pH and alkalinity on brominated DBPs. The bromide ion concentration used was 500 μg/L, concentrations below 500 μg/L could have been used this value was chosen in order to obtain measurable concentrations of DBPs especially BrAA as shown in Appendix C. At a concentration of 500 μg/L most brominated HAA compounds were at a maximum and measurable values of THMs also occurred at this point. For HANs, a separate experiment without the addition of bromide ion was performed so that the effect of pH and alkalinity on Cl_2AN could be studied.

3.5 Quality Control & Quality Assurance.

All measurements were carried out to a tolerance level of 2 % for pH and ± 0.02 mg/L as $CaCO_3$ for alkalinity. All amber glassware in which irradiated water was stored before chlorination was chlorine demand free as indicated in the article written by Summers et al (1996). Chlorination of sets of factorial and single factor experiments was carried out on the same day from the same solution of sodium hypochlorite to avoid varying concentration of chlorine in the samples. The GC/ECD was programmed to inject and analyse each sample three times to determine analytical precision. Sets of experiments were repeated whenever the variance of the center points of a particular set of factorial experiments was too large such that the PCDBP in question had no statistical significant factor. The variance was the calculated error for the analysis of variance. All experiments were randomised, including injection into the GC/ECD, to avoid bias and to ensure the error was normally distributed. Blanks and solvents were analysed with each set of samples to check for interferences in the solvent and water used in making up samples. It

was ensured that interferences were not higher that 1μg/L ± 0.02 otherwise; a new brand of solvent was used. Standards were also analysed with samples to check for the performance of the gas chromatograph and they were within the range of ±2 mg/L of the analysed concentration. The area of the internal standard was also used in checking for performance of the gas chromatography.

3.5.1 Radiometry/Chemical Actinometry

A 1KW medium pressure lamp was used for irradiation of water samples. An IL 1700 research radiometer with a SED 240 detector, capable of rejecting energy above a 320 nm wavelength, was used to determine the output of the lamp (International Lights, 1998). The chemical actinometer, KI/KIO_3, was used to verify the readings of the radiometer. This was carried out according to the protocol written by Bolton and Stefan (2003). The actinometer solution consisted of 9.96 g of potassium iodide (KI), 2.14 g of potassium iodate (KIO_3) and 0.381 g sodium tetraborate decahydrate ($Na_2B_4O_7 \bullet 10H_2O$) in 100 mL of water. The overall photochemical reaction is given in Equation 3.2:

$$8I^- + IO_3^- + 3H_2O + h\nu \longrightarrow 3I_3^- \quad 6OH^- \qquad \text{Equation 3.2}$$

5 mL of the actinometer solution in a 10 mL beaker was irradiated under a low pressure UV lamp for 2.5 minutes. The absorbance at a wavelength of 352 nm was measured. The sample was irradiated for up to 5 minutes at intervals of 0.5 minutes. The whole experiment was then repeated 4 times. For each experiment carried out the radiometer readings were recorded and then averaged. The output of the radiometer readings were then compared to that of the actinometry. Whenever the results differed by 10 %, it was recommended by Bolton and Stefan (2003) that the radiometer be sent back to the manufacturer for recalibration. The results of these experiments are given in Appendix D.

3.5.2 Hierarchical Experiment

Hierarchical experiments are usually conducted to diagnose sources of variability in manufacturing processes or in a laboratory method (Mason et al., 2003). In the current research, a hierarchical experiment was carried out by irradiating 4 samples prepared the same way using the center point conditions (pH =7.7, alkalinity =100 mg/L as $CaCO_3$, fluence = 100 mJ/cm^2). Each of the 4 irradiated samples were separated into five different vials and extracted making a total of twenty extracted samples. Each of the extracts was then injected five times into the GC/ECD for THMs analysis. For the analysis of HAAs, the samples were also prepared using the center point conditions except that five samples were irradiated, a total of twenty five samples were extracted, each of which was injected three times into the GC/ECD.

Analysis of variance was carried out to determine if the variations due to irradiation, extraction and the GC/ECD analysis steps of the hierarchical experiments were statistically significant. It was found that variations due to irradiation and extraction steps of the experiments were statistically significant but more variation was attributed to the extraction step based on relative comparison of the variance of each of the steps. In general the main source of error was due to the extraction step and this might have been due to evaporation of the compounds during extraction. The raw values of the THMs were quite large due to interference of chloroform in the extracting solvent. An extracting solvent with chloroform concentration less than 1 μg/L ± 0.02 was used for both the factorial and single factor experiments. Detailed data concerning the hierarchical experiment is shown in Appendix E.

CHAPTER 4

FACTORIAL EXPERIMENT RESULTS

4.1 Introduction

The preliminary studies carried out on post-UV chlorination disinfection by-products (PCDBPs), THMs, HANs & HAAs, were in the form of a full 2^3 (2x3) factorial experiment i.e. an experiment consisting of 3 factors of 2 levels each. Alkalinity (mg/L as $CaCO_3$), pH and UV-fluence (mJ/cm^2) were the main factors investigated. The factors and their levels are listed in Table 4.1.

Table 4.1 The 2^3 Factorial Experiment Levels

	Levels		
Factors	Low	Center	High
pH	6	7.7	8
Added alkalinity (mg/L as $CaCO_3$)	0	100	200
UV-fluence (mJ/cm^2)	1000	3000	5000

The high and low level values of pH and alkalinity used in the experiment were chosen to be within the range of values of naturally occurring waters while the centre points are midpoints between the low and high values. The centre point for pH was based on the midpoint of pOH read as pH. The values of alkalinity in Table 4.1 were concentrations that were added i.e. they do not include the value of alkalinity in the water used in the preparation of the synthetic which was 3.5 mg/L as $CaCO_3$. Though the value of UV-fluence is higher than that used in UV disinfection (~40 mJ/cm^2), the values chosen for

the experiment were representative of values that are typically applied in oxidative applications.

A set of factorial experiment consisted of eight runs, four center points and four control samples. Each of the synthetic water samples was irradiated with medium pressure ultraviolet light according to the various combinations of the levels in Table 4.2. The factorial runs are numbered from 1 to 8 while the center points are numbered from 9a to 9d.

There were four different sets of factorial experiment. UV photolysis or UV/H_2O_2 was used in the treatment of the first two sets of the factorial experiments. The same process was applied to the last two sets, except that 500 μg/L of bromide ion was added into synthetic water as sodium bromide (NaBr) prior to irradiation, in order to study the effect of the factors on the formation of brominated disinfection byproducts. The various set are illustrated in Table 4.3.

Table 4.2 Combination of Levels for the Factorial Experiment

Run	pH	Added alkalinity (mg/l as $CaCO_3$)	UV-fluence (mJ/cm^2)
1	6	0	1000
2	8	0	1000
3	6	200	1000
4	8	200	1000
5	6	0	5000
6	8	0	5000
7	6	200	5000
8	8	200	5000
9a	7.7	100	3000
9b	7.7	100	3000
9c	7.7	100	3000
9d	7.7	100	3000

Table 4.3 Description of Factorial Experiment Sets

Factorial Set	Description
UV Photolysis	Irradiation of samples with nothing added
UV/H_2O_2	Irradiation of samples, hydrogen peroxide added prior to irradiation
UV Photolysis (Br)	Irradiation of samples bromide ion added prior to irradiation
UV/H_2O_2 (Br)	Irradiation of samples, bromide ion and hydrogen peroxide added prior to irradiation

Following UV irradiation, each of the samples was chlorinated using 4 mg/L of sodium hypochlorite as described in Chapter 3. After 24 hours the free chlorine residual was quenched using sodium thiosulfate ($Na_2S_2O_3$), the samples were then extracted and analyzed by GC/ECD for disinfection by-products (haloacetic acids, haloacetonitriles and trihalomethanes).

The chromatography results were analyzed using Yates' algorithm as described by Box et al. (1978). Yates' algorithm is one of the analytical methods that can be used in obtaining effects and interactions of factors in factorial experiments. The effects of each factor and interaction obtained from the Yates' algorithm were used in computing the ANOVA table to determine factors that were statistically significant at 5 % significance level.

According to Mason et al. (2003) the effect of a factor is termed to mean the change in mean response of a factor as one move from low to high level of the factor while an interaction exists between two or more factors if the effect of each factor depends on the level of another factor. To determine the statistical significance of a factor or interaction, the four center points were used in error estimation which was used to determine F_{obs} by dividing the mean sum of squares (MS) by the error value. When $F_{obs} > F_{citical}$ the factor or interaction is considered statistically significant. The $F_{citical}$ used were values at 5 % significance level and are known values. According to Box et al. (1978), a positive sign on the effect of a factor or interaction can be interpreted to mean that the factor or interaction is increasing the yield of the particular PCDBP by the calculated amount of

the effect while a negative effect would imply that the yield of the PCDBP is being decreased.

4.2 Effect of UV Photolysis on Chlorinated PCDBPs

This section discusses the results of chlorinated disinfection by-products obtained during post-UV chlorination from factorial experiments obtained when synthetic water was irradiated under UV medium pressure lamp. After irradiation of the water samples 4 mg/L of sodium hypochlorite was added leaving a mean 24 hr free chlorine residual of 0.88 mg/L ± 0.02.

4.2.1 Haloacetic Acids

The haloacetic acid (HAA) species observed following the treatment of synthetic water with UV photolysis and chlorination were dichloroacetic acid (Cl_2AA) and trichloroacetic acid (Cl_3AA). Table 4.4 illustrates the concentration of Cl_2AA, Cl_3AA and the total amount of HAAs (HAA_9) for each factorial run, center point and control samples. The effect of each factor and interaction was calculated using the concentration of the HAAs in Table 4.4 using Yates' algorithm. Table 4.5 summarizes the results of the effects and interaction on these PCDBPs. For the analysis $F_{observed}$ was compared to an $F_{critical}$ of $F_{1,3,0.05}$. The numbers 1 and 3 correspond to the degrees of freedom obtained from the level of factorial experiment and number of center points respectively. The value 0.05 is the alpha (α) value at a 5% significance level

Table 4.4 Raw Data for Chlorinated Haloacetic Acids

Run	pH	Add alkalinity	UV-fluence	Cl_2 residual	HAAs (μg/L)		
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AA	Cl_3AA	HAA_9
1	6	0	1000	1.08	15.2	14.4	29.6
2	8	0	1000	1.00	13.4	13.2	26.5
3	6	200	1000	1.05	23.2	10.2	33.4
4	8	200	1000	1.23	10.4	13.5	23.9
5	6	0	5000	0.45	6.88	3.13	10.0
6	8	0	5000	0.76	5.05	2.19	7.24
7	6	200	5000	0.78	5.32	2.81	8.13
8	8	200	5000	0.74	4.78	3.17	7.95
9a	7.7	100	3000	0.79	7.31	5.55	12.9
9b	7.7	100	3000	0.75	7.07	6.76	13.8
9c	7.7	100	3000	0.99	9.89	8.76	18.7
9d	7.7	100	3000	0.92	7.70	5.52	13.2
			Variance		1.67	2.32	7.31
C1				1.77	17.5	21.6	39.0
C2				1.85	43.3	43.0	86.3
C3				1.97	15.6	19.2	34.9
C4				1.97	37.9	35.7	73.6
			Mean	1.89	28.6	29.9	58.4

Table 4.5 UV Photolysis: Effects of Factors and Interactions on the Formation of Dichloroacetic Acid and Trichloroacetic Acid

	Cl_2AA			Cl_3AA		
	Effect	F_{obs}	Significant	Effect	F_{obs}	Significant
Main Effects						
pH (P)	-4.24	21.6	Yes	+0.355	0.022	No
Alkalinity (A)	+0.794	0.757	No	-0.800	0.112	No
UV-fluence (F)	-10.0	120.8	Yes	-10.0	17.5	Yes
Interactions						
PxA	-2.39	6.87	No	+1.46	0.373	No
PxF	+3.06	11.2	Yes	-0.648	0.074	No
AxF	-1.71	3.52	No	+1.13	0.222	No
PxAxF	+3.04	11.1	Yes	-0.810	0.115	No

$F_{1,3,0.05} = 10.1$

Dichloroacetic acid had more significant factors than trichloroacetic acid. For Cl_2AA, UV-fluence and pH were found to be statistically significant while the significant interactions were pH and UV-fluence (PxF) and pH, alkalinity and UV-fluence (PxAxF). According to Box et al. (1978), when there is an interaction between two main factors, and it happens that both main factors and their interaction are statistically significant, the main factors cannot be interpreted separately but their effects have to be considered jointly. The joint effect of pH and UV-fluence (PxF) for Cl_2AA is illustrated in Figure 4.1. It can be observed from this figure that there is a decrease in the formation of Cl_2AA as pH was increased from 6 to 8 at both levels of UV-fluence, i.e. at 1000 and 5000 mJ/cm^2, but there is a greater reduction in Cl_2AA concentration when UV-fluence was increased from 1000 to 5000 mJ/cm^2 at both levels of pH.

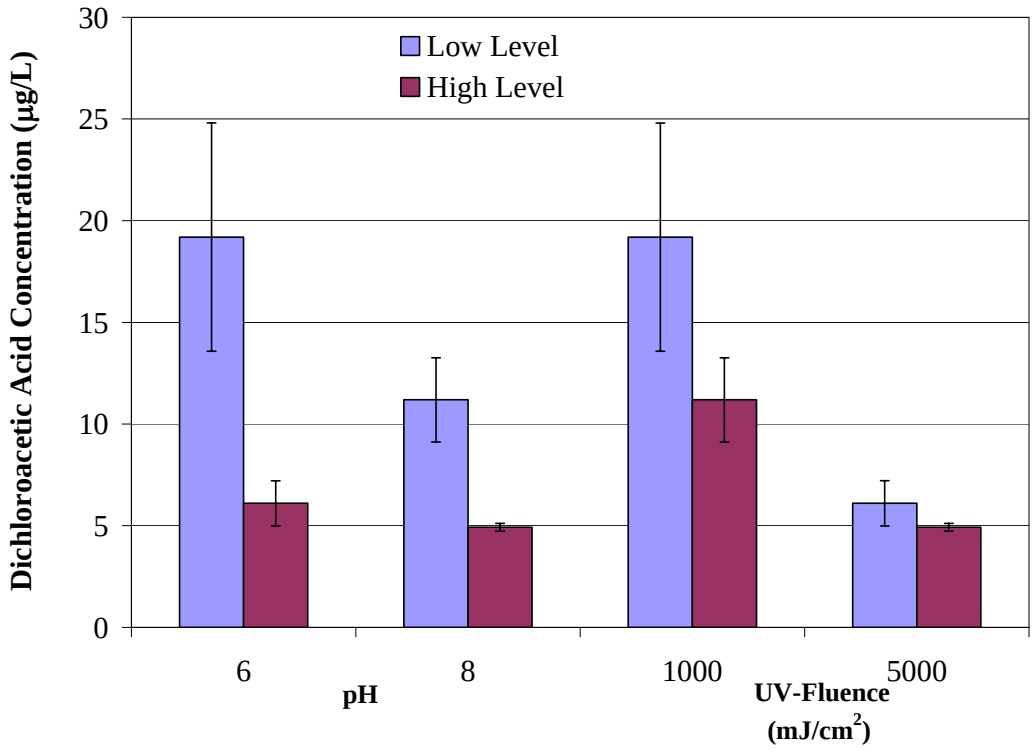

Figure 4.1 UV Photolysis: Joint Effect of pH and UV-Fluence on Dichloroacetic Acid Formation. (Error bars= standard deviation values)

Though the smallest amount of Cl_2AA occurred at pH 8 and at a UV-fluence of 5000 mJ/cm^2, the greatest percentage reduction occurred at pH 6 as UV-fluence was increased from 1000 to 5000 mJ/cm^2 and the concentration of Cl_2AA reduced from 19.19 µg/L to 6.1 µg/L. This is a 68 % reduction as opposed to a 58 % reduction that occurred at pH 8. The interaction, PxF, had a positive effect on the formation of Cl_2AA, indicating that an increase in both factors brought about an increase in the formation of Cl_2AA.

The error bars are indicated by the standard deviation of the values that make up the mean values of the interaction. The error bars for the low levels at pH 6 and 1000 mJ/cm^2 indicate that the values that make up the mean are at extremes of the mean. This is

expected as the mean values indicated by the columns in Figure 4.1 or figures in Figure 4.2 were influenced by the values of another factor. For instance the value 19.2 in Figure 4.2 are mean values of the data in the factorial experiment corresponding to pH 6 and UV-fluence of 1000 mJ/cm^2 influenced by alkalinity.

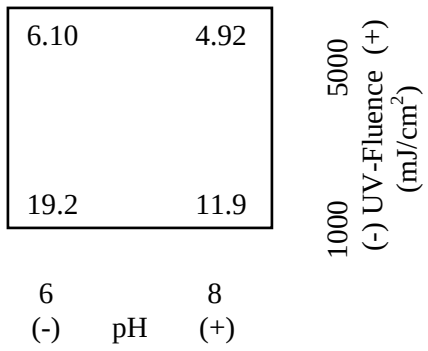

Figure 4.2 UV Photolysis: Interaction of pH and UV-Fluence on the Formation of Dichloroacetic Acid

Each side of the square in Figure 4.2 represents either pH or UV-fluence as indicated on the figure and each level of the factor is indicated with a negative sign representing the low level of the factor while the positive sign represents the high level. The value in each corner of the square represents the mean values obtained from the raw data of the factorial experiment made available in Appendix F. These values were obtained from mean values at various points of the factorial experiment. For instance the value 19.2 is the mean concentration of Cl_2AA at a pH of 6 and a UV-fluence of 1000 mJ/cm^2, this is averaged over the range of alkalinity, 0 and 200 mg/L as $CaCO_3$.

Alkalinity on its own was not statistically significant but since it was involved in the three factor interaction, PxAxF, this suggests that it still has an effect on the formation of Cl_2AA.

The only statistically significant factor in this set of experiments for the HAA species, trichloroacetic acid, was UV-fluence, the other factors were not found to be statistically significant as illustrated in Figure 4.3. The concentration of Cl_3AA was decreased by an approximate unit of 10.0 as UV-fluence was increased from 1000 mJ/cm^2 to 5000 mJ/cm^2.

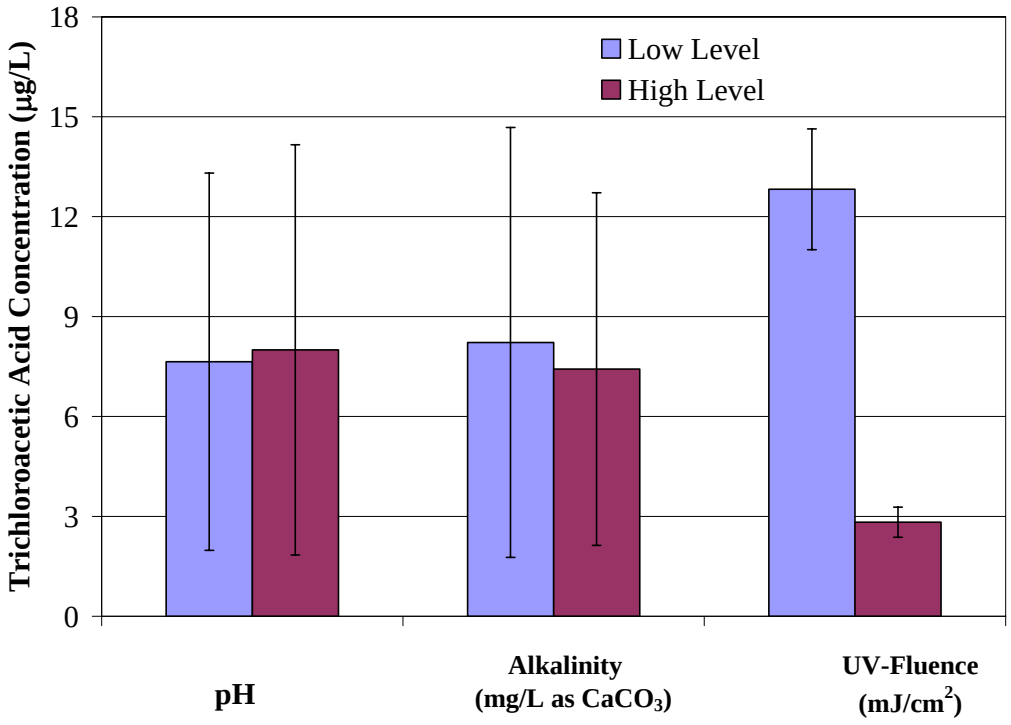

Figure 4.3 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Trichloroacetic Acid (Error bars= standard deviation values)

The error bars represent standard deviations calculated for each level of the factors. The standard deviation values for pH and alkalinity are higher than those of UV-fluence suggesting that there is an influence of a factor, in this case UV-fluence, on the standard deviation values.

4.2.2 Haloacetonitriles

Dichloroacetonitrile (Cl_2AN) was the only compound observed in the HANs group of disinfection by-products when synthetic water was treated with UV photolysis followed by chlorination. No main factors or interactions were found to be statistically significant for this compound, as illustrated in Figure 4.4. An increase in the concentration of Cl_2AN can be observed in this figure as both pH and alkalinity were increased from their lower to high levels. Concentration of each factorial run, center points and control samples for Cl_2AN is given in Appendix F.

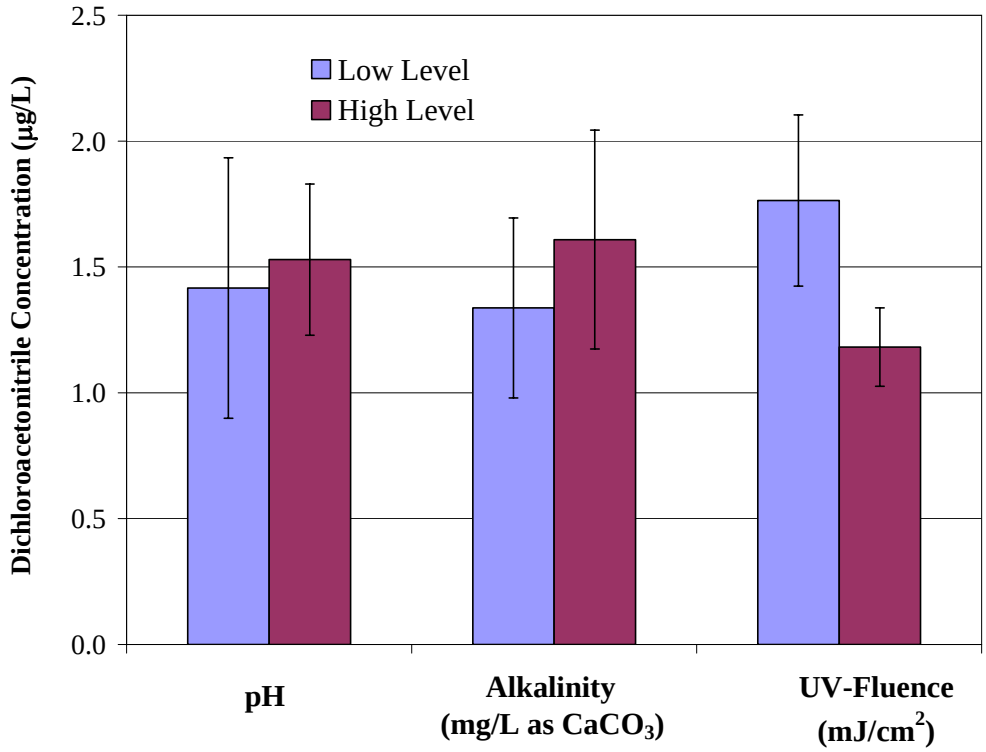

Figure 4.4 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Dichloroacetonitrile (Error bars= standard deviation values)

4.2.3 Trihalomethanes

Chloroform ($CHCl_3$) was the only compound of this group of DBP formed in this set of experiments. This was not unexpected as bromide ion was not added to the sample water. From Table 4.6, UV-fluence was significant with a corresponding effect of -42.1. This implies that as the UV-fluence was increased from 1000 mJ/cm^2 to 5000 mJ/cm^2, the formation of chloroform decreased by a unit of 42.1, a 62 % reduction. Figure 4.5 helps to illustrate the reduction in chloroform concentration as UV-fluence was increased. Concentration of each factorial run, center points and control samples for $CHCl_3$ is given in Appendix F.

Table 4.6 UV Photolysis: Effect of Factors and Interactions on Chloroform Formation

Source	Effect	F_{obs}	Significant
Main Effects			
pH (P)	-2.55	0.964	No
Alkalinity (A)	-5.32	4.21	No
UV-fluence (F)	-42.1	263	Yes
Interactions			
PxA	-0.894	0.119	No
PxF	-1.78	0.473	No
AxF	-1.31	0.254	No
PxAxF	+5.65	4.75	No

$F_{1, 3, 0.05} = 10.1$

The fact that the other factors, pH and alkalinity were not statistically significant does not mean they did not have some effect on the formation of chloroform but that their effect on chloroform cannot be confirmed beyond the significance level used in the variance analysis as illustrated in Figure 4.5. The high error bars for pH and alkalinity in Figure 4.5 shows that there is an influence of a factor on these values which in this case is UV-fluence.

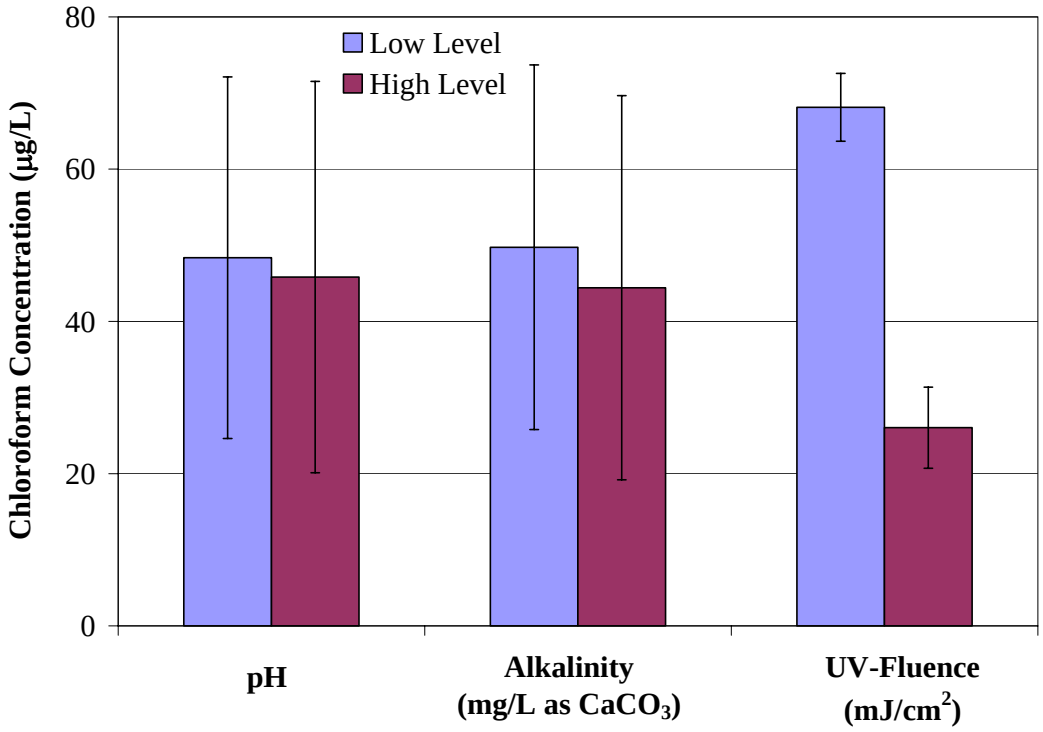

Figure 4.5 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Chloroform (Error bars= standard deviation values)

4.3 Effect of UV/H_2O_2 on Chlorinated PCDBPs

To provide treatment with an advanced oxidation process (AOP), hydrogen peroxide (H_2O_2) was added to the water sample to enhance the production of the OH radical. An mean concentration of 8.45 mg/L was added to each water sample before irradiation. All experimental runs were exposed to a UV-fluence of 1000, 3000 or 5000 mJ/cm^2 as low, center and high levels, respectively. These had a mean peroxide demand of 2.67, 5.59 and 7.53 mg/L ± 0.02, respectively.

Figure 4.6 shows the change in UV absorbance, measured at 351 nm, corresponding to the peroxide demand for each of the value of UV-fluence. The peroxide concentration

was measured according to the triiodide (I_3^-) method discussed in the article written by Klassen et al. (1994). This is explained in detail in Chapter 3. Detailed data concerning the addition and demand of hydrogen peroxide by each water sample are shown in Appendix B while the concentration of each factorial run, center points and control samples is given in Appendix F. Residual peroxide concentration was quenched with 0.2 mg/L of Bovine liver (catalase) as described by Liu et al. (2003). After irradiation of the water samples, 4 mg/L of sodium hypochlorite was added leaving a 24 hr free chlorine mean residual of 1.19 mg/L. The UV absorbance spectra for H_2O_2 after irradiation of the water sample are shown in Figure 4.6. The change in UV absorbance for NOM is usually obtained at 254 nm but this was not determined because it was beyond the scope of this thesis.

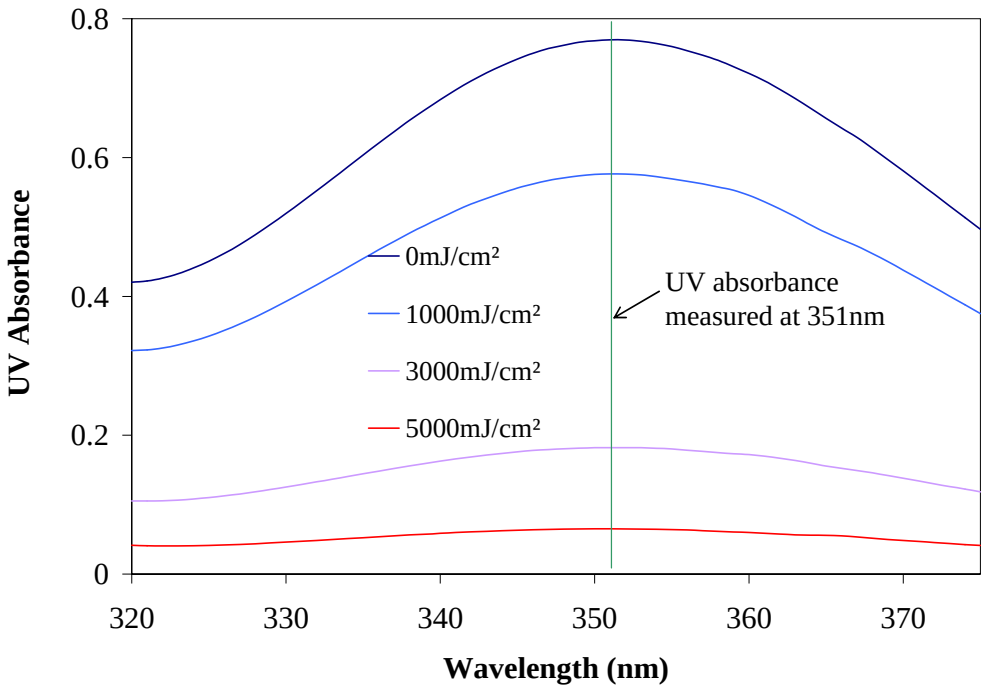

Figure 4.6 UV Absorbance Spectra Showing Varying Concentrations of Hydrogen Peroxide at Corresponding UV-Fluence.

4.3.1 Haloacetic Acids

In this set of experiment, dichloroacetic acid and trichloroacetic acids were the only HAAs species observed. The two-factor interaction, PxA, and the three-factor interaction, PxAxF, were found to be statistically significant for Cl_2AA, as shown in Table 4.7. The effect of the two factor interaction, PxA, for Cl_2AA is illustrated in Figures 4.7 and 4.8.

Table 4.7 UV/H_2O_2: Effects of Factors and Interactions on the Formation of Dichloroacetic Acid and Trichloroacetic Acid

	Cl_2AA			Cl_3AA		
	Effect	F_{obs}	Significant	Effect	F_{obs}	Significant
Main Effects						
pH (P)	+0.490	7.94	No	+0.297	1.26	No
Alkalinity (A)	+0.814	21.9	Yes	+1.28	23.2	Yes
UV-fluence (F)	-4.98	819	Yes	-4.50	287	Yes
Interactions						
PxA	-0.948	29.7	Yes	-0.220	0.689	No
PxF	+0.534	9.42	No	+0.576	4.72	No
AxF	-0.355	4.18	No	-0.713	7.21	No
PxAxF	+0.597	11.8	Yes	+0.021	0.006	No

$F_{1,3,0.05} = 10.1$

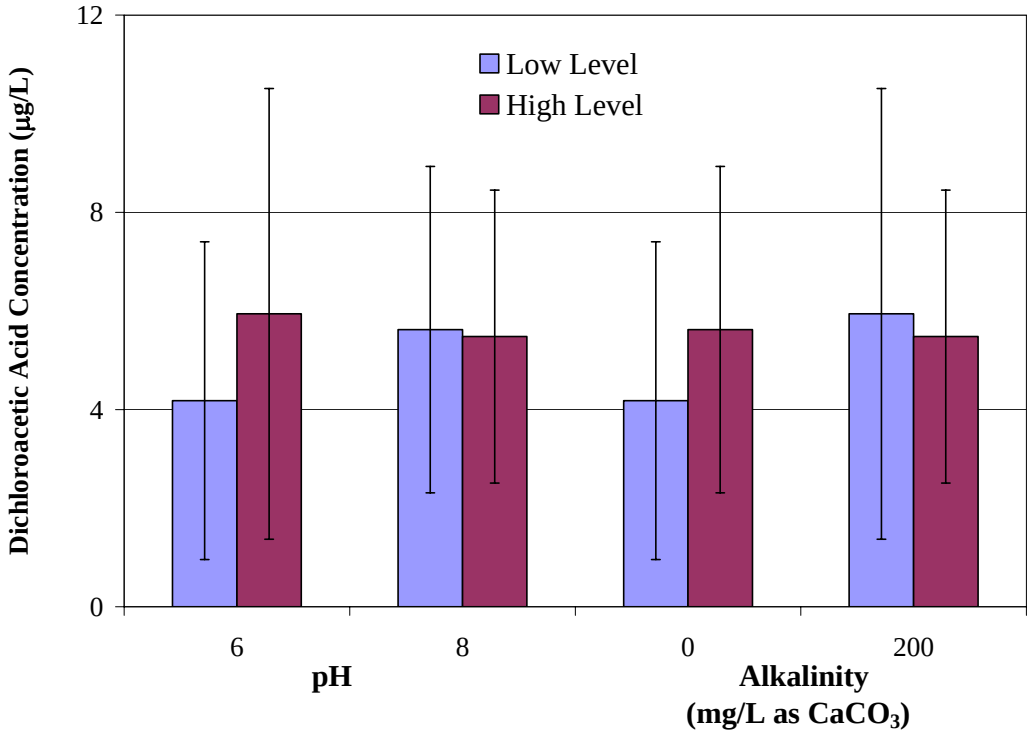

Figure 4.7 UV/H_2O_2: Joint Effect of the pH and Alkalinity on Dichloroacetic Acid Formation. (Error bars= standard deviation values)

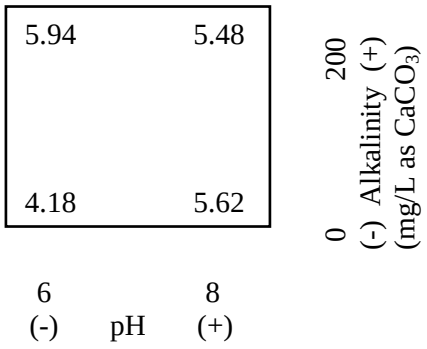

Figure 4.8 UV/H_2O_2: Interaction of pH and Alkalinity in the Formation of Dichloroacetic Acid

From Figures 4.7 and 4.8, as pH was increased from 6 to 8, an increase of 34 % occurred at 0 mg/L as $CaCO_3$ and a decrease of 7.7 % occurred at 200 mg/L as $CaCO_3$ of alkalinity. Also, as alkalinity was increased from 0 and 200 mg/L as $CaCO_3$, an increase of 42 % and a decrease of 7.7 % occurred at pH 6 and 8 respectively. An increase in Cl_2AA concentration was experienced at the low level of pH as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$. The same result was obtained at the low level of alkalinity as pH was increased from 6 to 8. On the other hand, a decrease occurred at the high levels of both factors as alkalinity and pH were increased from their low to high levels. This resulted in an overall reduction of Cl_2AA concentration, indicated by the negative effect -0.948 in Table 4.7. The effect of the three-factor interaction, PxAxF, correlated with an increase of 0.597 units in the formation of Cl_2AA.

The standard deviation values for pH and alkalinity, indicated by the error bars in Figure 4.7, are higher than those of UV-fluence because the effects of pH and alkalinity were averaged over the range of UV-fluence. Since the effect of UV-fluence on chloroform is larger than the other factors, the mean value of both pH and alkalinity calculated over UV-fluence resulted in large standard deviations for those factors.

Alkalinity and UV-fluence were both statistically significant factors for trichloroacetic acid. As alkalinity was increased from its low to high level, Cl_3AA increased in concentration by 45 % but decreased by 79 % when UV-fluence was increased from the low to high level. This is indicated by the positive and negative signs on the effects of alkalinity and UV-fluence in Table 4.7. The standard deviation values for pH and alkalinity in Figure 4.9 are higher than those of UV-fluence because the effects of pH and

alkalinity were averaged over the range of UV-fluence. Since the effect of UV-fluence on chloroform is larger than the other factors, the mean value of both pH and alkalinity calculated over UV-fluence resulted in large standard deviations for those factors.

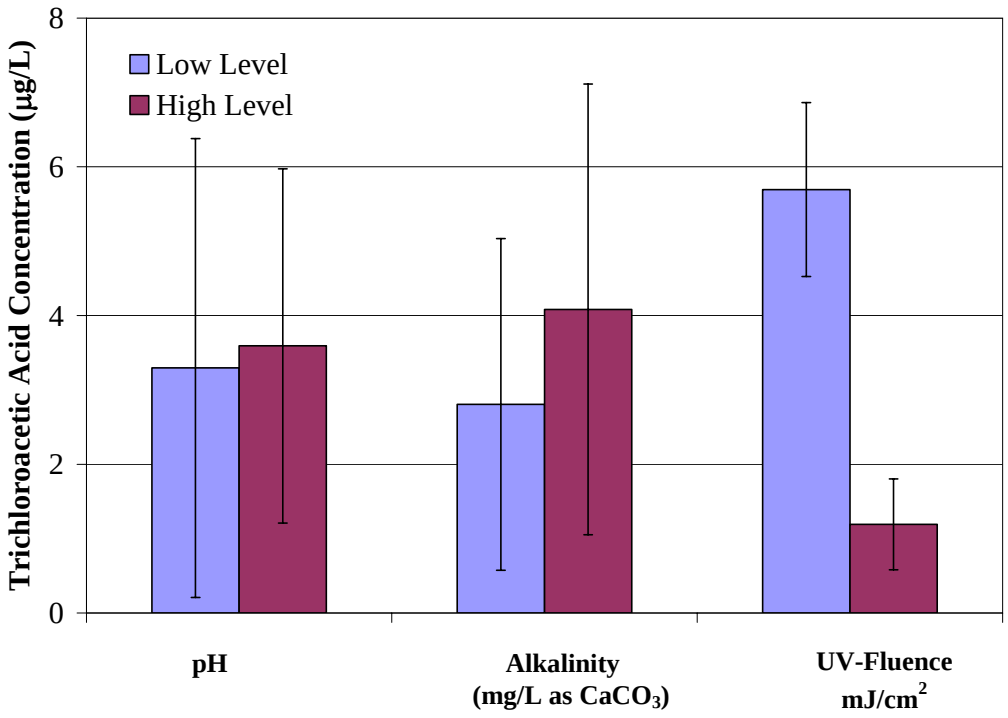

Figure 4.9 UV/ H_2O_2: Effect of pH, Alkalinity and UV-Fluence on the Formation of Trichloroacetic Acid (Error bars= standard deviation values)

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4.3.2 Haloacetonitriles

Dichloroacetonitrile was the only HAN Specie formed when synthetic water was treated with UV/H_2O_2 followed by chlorination. Alkalinity and UV-fluence were the main factors found to be statistically significant while the significant interactions were pH and UV-fluence (PxF) and the three-factor interaction, PxAxF. The effects of the factors and interaction for Cl_2AN formation is summarized in Table 4.8.

Table 4.8 UV/H_2O_2: Effect of Factors and Interactions on Cl_2AN Formation

	Effect	F_{obs}	Significant
Main Effects			
pH (P)	-0.044	6.78	No
Alkalinity (A)	+0.260	234	Yes
UV-fluence (F)	-0.326	368	Yes
Interactions			
PxA	+0.063	13	No
PxF	-0.160	89.0	Yes
AxF	+0.044	6.58	No
PxAxF	-0.390	527	Yes

$F_{1, 2, 0.05} = 18.5$

As explained in Section 4.1.1, the main factors cannot be explained independently when they are involved in an interaction. The interaction between the pH and UV-fluence is illustrated in Figures 4.10 and 4.11 below.

At pH 6 and 8 a decrease of 23 % and 60 % occurred respectively as UV-fluence was increased from 1000 mJ/cm^2 to 5000 mJ/cm^2. At 1000 mJ/cm^2 as pH was increased from 6 to 8, an increase of 17 % in the concentration of Cl_2AN occurred while a decrease of 40 % occurred at 5000 mJ/cm^2. Ultimately the greatest decrease occurred at a pH of 8 and a UV-fluence of 5000 mJ/cm^2. This is also indicated by the fact that the standard deviation at high pH and UV-fluence is smaller compared the other values in Figure 4.10 The interaction of pH and UV-fluence caused a decrease in the formation of Cl_2AN as both factors were increased from their low to high levels This is indicated by the negative sign associated with the effect of the interaction, PxF in Table 4.8. Alkalinity caused an increase in the formation of Cl_2AN but it was also involved in a three-factor interaction with pH and UV-fluence.

The three-factor interaction caused a decrease in the formation of Cl_2AN by a unit of 0.390.

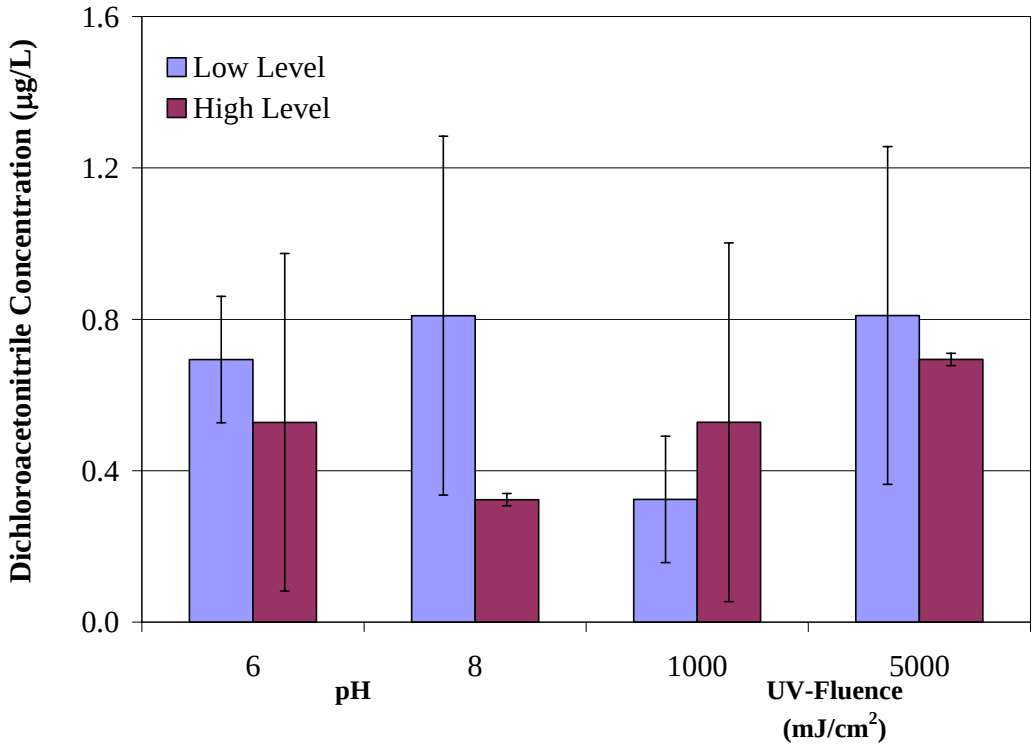

Figure 4.10 UV/H_2O_2: Joint Effect of pH and UV-Fluence on Dichloroacetonitrile Formation. (Error bars= standard deviation values)

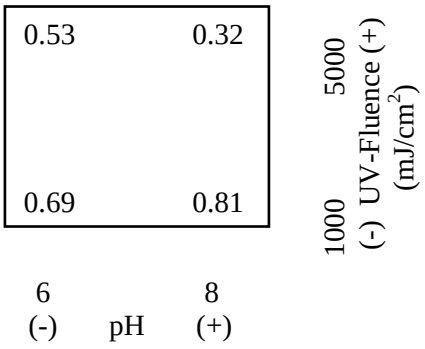

Figure 4.11 UV/H_2O_2: Interaction of pH and UV-Fluence in the Formation of Dichloroacetonitrile

4.3.3 Trihalomethanes

The effects of factors and interactions on the formation of chloroform when synthetic water was treated with UV/H_2O_2 followed by chlorine are illustrated in Table 4.9. In this experiment, UV-fluence was the only statistically significant factor with a F_{obs} of 21.2 which is greater than the $F_{critical}$ = 10.1 at 5 % significance level. This implies that UV-fluence caused a decrease in the formation of chloroform by 23.9 units as it was increased from 1000 to 5000 mJ/$cm^{2.}$ Alkalinity, pH were not statistically significant because their F_{obs} were lower than the $F_{critical}$. The effects of the three factors are illustrated in Figure 4.12.

Table 4.9 UV/H_2O_2: Effect of Factors and Interactions on Chloroform Formation

	Effect	F_{obs}	Significant
Main Effects			
pH (P)	-4.95	1.11	No
Alkalinity (A)	+3.70	0.620	No
UV-fluence (F)	-23.9	25.8	Yes
Interactions			
PxA	-2.55	0.294	No
PxF	+2.47	0.275	No
AxF	+2.57	0.298	No
PxAxF	-6.65	2.002	No
Error			

$F_{1, 3, 0.05}$ = 10.1

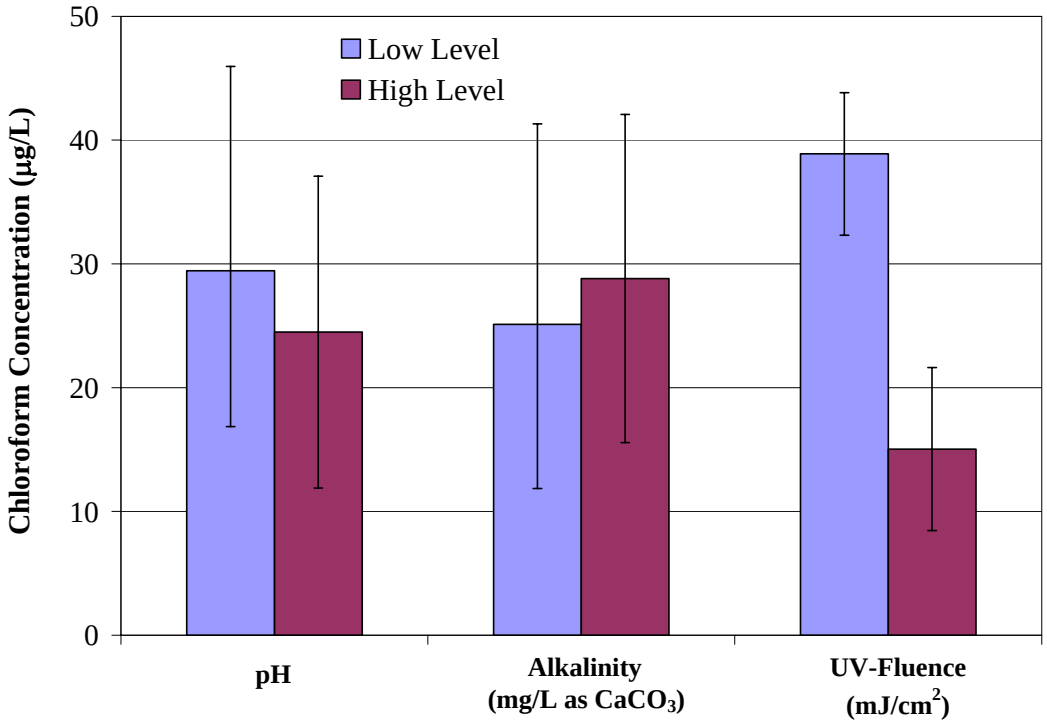

Figure 4.12 UV/H_2O_2: Effect of pH, Alkalinity and UV-Fluence on the Formation of Chloroform (Error bars= standard deviation values).

From Figure 4.12 the concentration of chloroform decreased by 61 %, and 17 %, respectively, as UV-fluence and pH were increased from their lower to high levels, while a 14 % increase in $CHCl_3$ concentration occurred as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$. The standard deviation values for pH and alkalinity are higher than those of UV-fluence because the effects of pH and alkalinity were averaged over the range of UV-fluence. Since the effect of UV-fluence on chloroform is larger than the other factors, the mean value of both pH and alkalinity calculated over UV-fluence resulted in large standard deviations for those factors.

4.4 Effect of UV Photolysis on Brominated PCDBPs

The term brominated post-UV chlorination DBPs (PCDBPs) in this section and other sections include the combination of bromine- and chlorine-containing PCDBP compounds (such as bromochloromethane) and PCDBPs containing only bromide ions (e.g. bromoform). In order to study the effect of UV photolysis, alkalinity and pH on brominated PCDBPs, 500 μg/L of bromide ion was added to synthetic water before irradiation, as described in Chapter 3 and Appendix C. After irradiation of the water samples 4 mg/L of sodium hypochlorite was added leaving a mean 24 hr free chlorine residual of 1.05 mg/L. The same experimental procedure that was applied in Section 4.1 was also applied in this set of experiments with the exception of the bromide ion addition. The following discussion focuses on THMs and HAAs because neither chlorinated nor brominated HANs were observed in this set of experiments. Concentrations of PCDBP measured in each factorial run, center points and control samples are given in Appendix F.

4.4.1 Haloacetic Acids

Out of the six brominated HAAs, only dichlorobromoacetic acid and bromochloroacetic acid had no statistically significant factors, the others are listed in Table 4.10 along with their significant factors.

Table 4.10 UV Photolysis: Effects of Factors and Interactions on the Formation of Statistically Significant Brominated Haloacetic Acids.

		Main Effects			Interactions			
		pH (P)	Alkalinity (A)	UV-fluence (F)	PxA	PxF	AxF	PxAxF
BrAA	Effect	-0.025	-0.093	-0.197	-0.043	-0.030	+0.069	+0.013
	F_{obs}	1.84	25.1	112	5.37	2.57	13.94	0.485
	Significant	No	Yes	Yes	No	No	Yes	No
Br_2ClAA	Effect	-0.143	-0.995	-6.10	-0.827	+0.009	+0.086	+0.805
	F_{obs}	0.298	14.5	544	10.0	0.001	0.108	9.48
	Significant	No	Yes	Yes	No	No	No	No
Br_2AA	Effect	-0.166	-0.930	-3.79	-0.135	+0.192	+0.448	+0.231
	F_{obs}	0.700	22.0	364	0.461	0.934	5.11	1.37
	Significant	No	Yes	Yes	No	No	No	No
Br_3AA	Effect	+0.092	-0.953	-4.55	-0.635	-0.120	+0.902	+0.822
	F_{obs}	0.182	19.6	447	8.72	0.311	17.6	14.6
	Significant	No	Yes	Yes	No	No	Yes	Yes

$F_{1,3,0.05} = 10.1$

The statistically significant factors for BrAA were alkalinity, UV-fluence and the two factor interaction, AxF. Since the two main factors that were significant also make up the two factor interaction, they would be explained jointly in Figures 4.13 and 4.14.

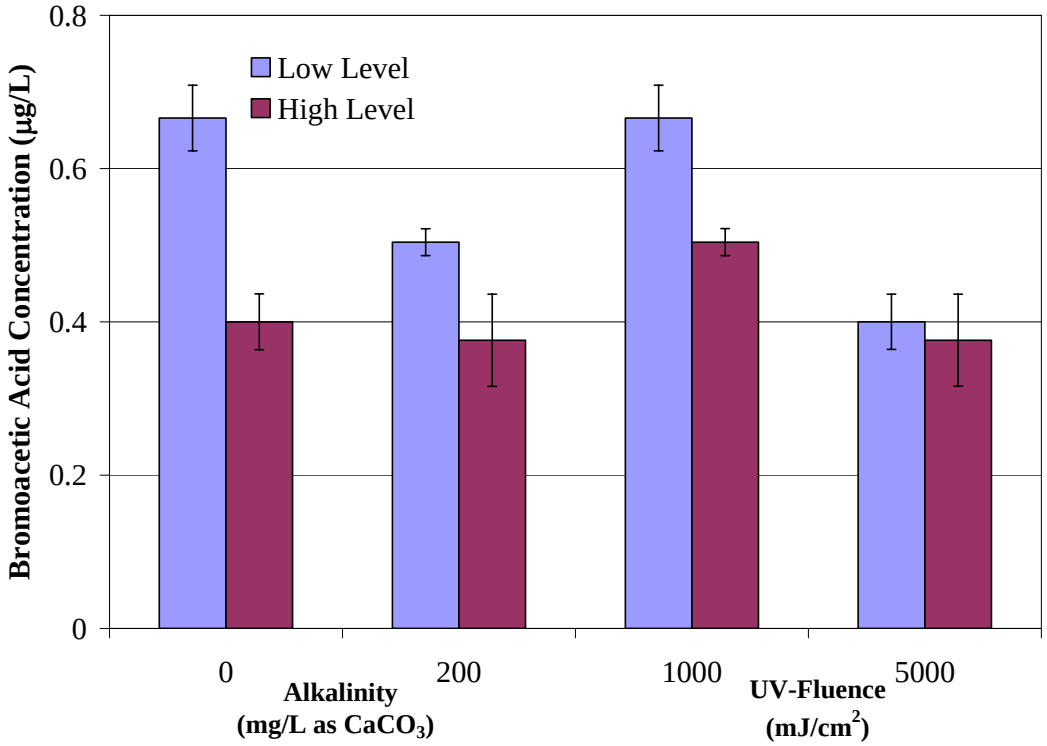

Figure 4.13 UV Photolysis: Joint Effect of Alkalinity and UV-Fluence on Bromoacetic Acid Formation (Error bars= standard deviation values)

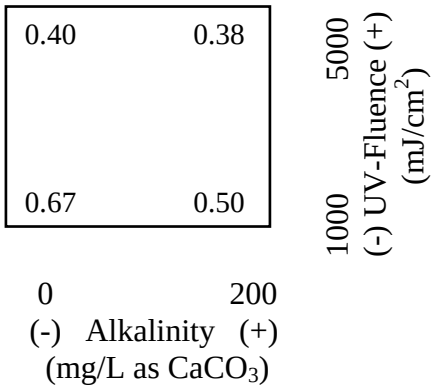

Figure 4.14 UV Photolysis: Interaction of Alkalinity and UV-Fluence in the Formation of Bromoacetic Acid.

Figures 4.13 and 4.14 illustrate the graphical and numerical illustration of the effect of AxF interaction on BrAA formation. At low and high levels of alkalinity, a decrease of 40 % and 24 % occurred as a result of increasing UV-fluence from 1000 to 5000 mJ/cm^2. As alkalinity was increased from 0 to 200 mg/L as $CaCO_3$, a 25 % decrease occurred at 1000 mJ/cm^2 of UV-fluence while a 5 % decrease occurred at 5000 mJ/cm^2 as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$. The effect of the AxF interaction caused a unit increase of 0.069 as both factors that make up the interaction were increased from their low to high levels.

For Br_2ClAA, alkalinity and UV-fluence were statistically significant and they had no interaction with any other factor. As alkalinity was increased from 0 to 200 mg/L as $CaCO_3$, the concentration of Br_2ClAA reduced by a unit of 0.995, a 19 % reduction. Also, as UV-fluence was increased from 1000 to 5000 mJ/cm^2, Br_2ClAA was reduced by a unit of 6.10, a 78 % reduction. The effects of the factors on Br_2ClAA are illustrated in Figure 4.15.

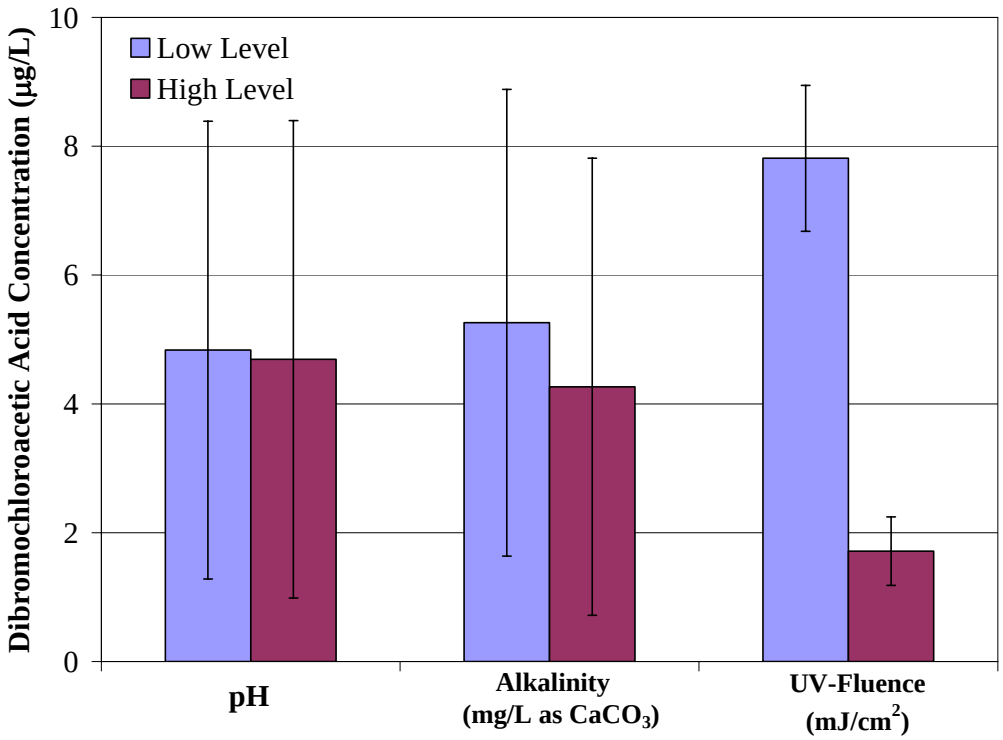

Figure 4.15 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Dibromochloroacetic Acid.

Like Br_2ClAA, dibromoacetic acid (Br_2AA) had no two-factor or three-factor interaction that was statistically significant. Alkalinity and UV-fluence were the only statistically significant factors. From Figure 4.16 it can be observed that both alkalinity and UV-fluence affected the formation of Br_2AA through a decrease in the concentration of 21 % and 64 % respectively as they were increased from their low to high levels. The standard deviation values for pH and alkalinity are higher than those of UV-fluence because the effects of pH and alkalinity were averaged over the range of UV-fluence. Since the effect of UV-fluence on dibromoacetic acid is larger than the other factors, a mean over UV-fluence resulted into large standard deviations

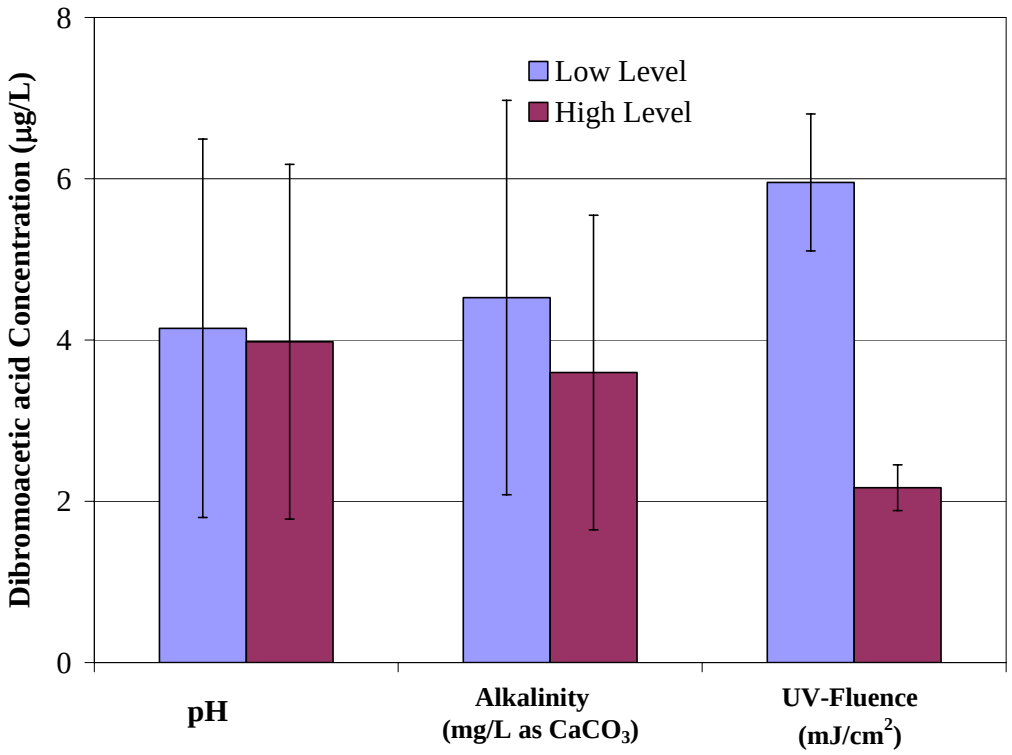

Figure 4.16 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Dibromoacetic Acid.

Unlike the other HAAs compounds, tribromoacetic acid (Br_3AA) had a statistically significant three factor interaction. The main factors, alkalinity and UV-fluence along with there interaction, AxF were also significant. The fact that pH was not statistically significant does not mean it did not have any effect on the formation of Br_3AA but this cannot be confirmed beyond the significance level used in variance analysis. Though as individual factors, the effects of alkalinity and UV-fluence reduced the formation of Br_3AA, the effect of the interaction of both factors, AxF, increased the formation of Br_3AA. From Figures 4.17 and 4.18, a decrease of 27 % and 3.5 % in the formation of Br_3AA occurred at low and high levels of UV-fluence respectively as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$.

This decrease is small compared to 79 % and 73 % decrease in formation of Br_3AA at low and high levels of alkalinity respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. Evidently the interaction was as a result of the sensitivity of the formation of Br_3AA to change in UV-fluence.

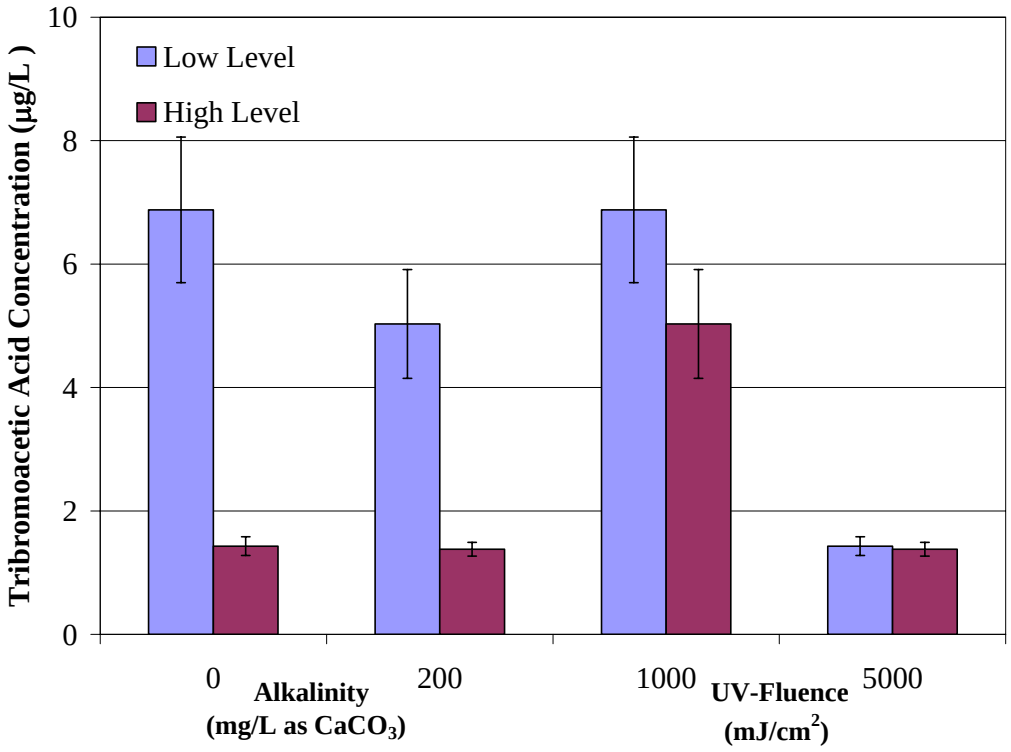

Figure 4.17 UV Photolysis: Joint Effect of Alkalinity and UV-Fluence on Tribromoacetic Acid Formation

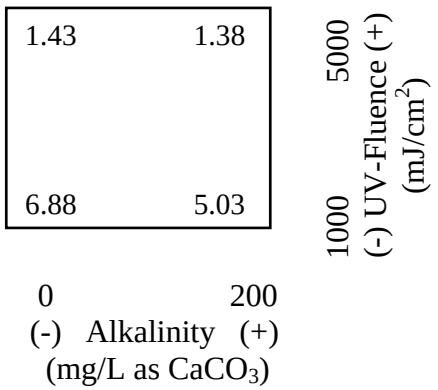

Figure 4.18 UV Photolysis: Interaction of Alkalinity and UV-Fluence in the Formation of Tribromoacetic Acid.

Dichloroacetic acid and trichloroacetic acids were also formed in this sets of experiments even though it was the study of brominated compounds that mandated the addition of bromide ion to synthetic water prior to irradiation. These two compounds were formed in smaller quantities than the UV photolysis experiment carried out without bromide ion addition. This was confirmed by Clark et al. (2001) who used factorial experiments to predict the formation of HAA compounds. The authors found that higher concentrations of bromide ion favored the formation of brominated compounds which form faster than their chlorinated counterparts.

Interestingly, the statistically significant factors for Cl_2AA and Cl_3AA formations were different from the ones explained in Section 4.1. This might have been as a result of introducing the bromide ion. The common significant factor in Section 4.1 and in this set of experiment was UV-fluence. From Table 4.11 it should be noted that although other factors were significant, the effect of UV-fluence was greater than the other factors and interactions.

Table 4.11 UV Photolysis: Effects of Factors and Interactions on the Formation of Cl_2AA and Cl_3AA Formed Along with Brominated Haloacetic Acids.

	Cl_2AA			Cl_3AA		
	Effect	F_{obs}	Significant	Effect	F_{obs}	Significant
Main Effects						
pH (P)	+0.082	1.94	No	+0.005	0.293	No
Alkalinity (A)	-0.267	20.5	Yes	-0.060	40.0	Yes
UV-fluence (F)	-1.42	580	Yes	-0.534	3171	Yes
Interactions						
PxA	-0.154	6.81	No	-0.066	48.2	Yes
PxF	-0.016	0.069	No	-0.005	0.301	No
AxF	+0.132	5.034	No	+0.047	24.8	Yes
PxAxF	+0.088	2.22	No	+0.052	30.5	Yes

$F_{1,3,0.05} = 10.1$

4.4.2 Trihalomethanes

Similar results were obtained when synthetic water was chlorinated following treatment with UV photolysis only except that brominated PCDBPs were present. As expected, the brominated PCDBPs were more in concentration than chloroform. This was also confirmed by Chang et al. (2001). Though chloroform was formed in reduced concentration, UV-fluence was still its only statistically significant factor as indicated in Table 4.12. This conformed to the results obtained when synthetic water was treated with chlorine following UV photolysis without the addition of bromide ion.

Table 4.12 UV Photolysis: Effects of Factors and Interactions on the Formation of Brominated THMs

		Main Effects			Interactions			
		pH (P)	Alkalinity (A)	UV-fluence (F)	PxA	PxF	AxF	PxAxF
$BrCl_2CH$	Effect	-1.10	0.120	16.0	-0.642	-0.409	0.284	0.123
	Fobs	0.362	0.004	76.6	0.124	0.050	0.024	0.005
	Significant	No	No	Yes	No	No	No	No
$ClCHBr_2$	Effect	-3.14	-0.729	-43.5	-2.82	-4.07	1.89	-4.03
	Fobs	0.222	0.012	42.8	0.180	0.375	0.081	0.367
	Significant	No	No	Yes	No	No	No	No
CHBr3	Effect	-5.27	-6.87	-23.1	-7.22	-5.45	6.79	-9.97
	Fobs	3.30	5.61	63.3	6.19	3.53	5.480	11.8
	Significant	No	No	Yes	No	No	No	No

$F_{1,2,0.05} = 18.5$

The three brominated THMs, dichlorobromomethane ($BrCl_2CH$), dibromochloromethane ($ClCHBr_2$) and bromoform ($CHBr_3$), had a common statistically significant factor, UV-fluence. This resulted in the reduction of the formation of $BrCl_2CH$, $ClCHBr_2$ and $CHBr_3$ by 72 %, 64 % and 30 % respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. The other factors and interactions were not statistically significant but their effects on the formation of brominated THMs are shown in Figure 4.19. Compared to UV-fluence, not much difference can be observed as pH and alkalinity were increased from their low to high level.

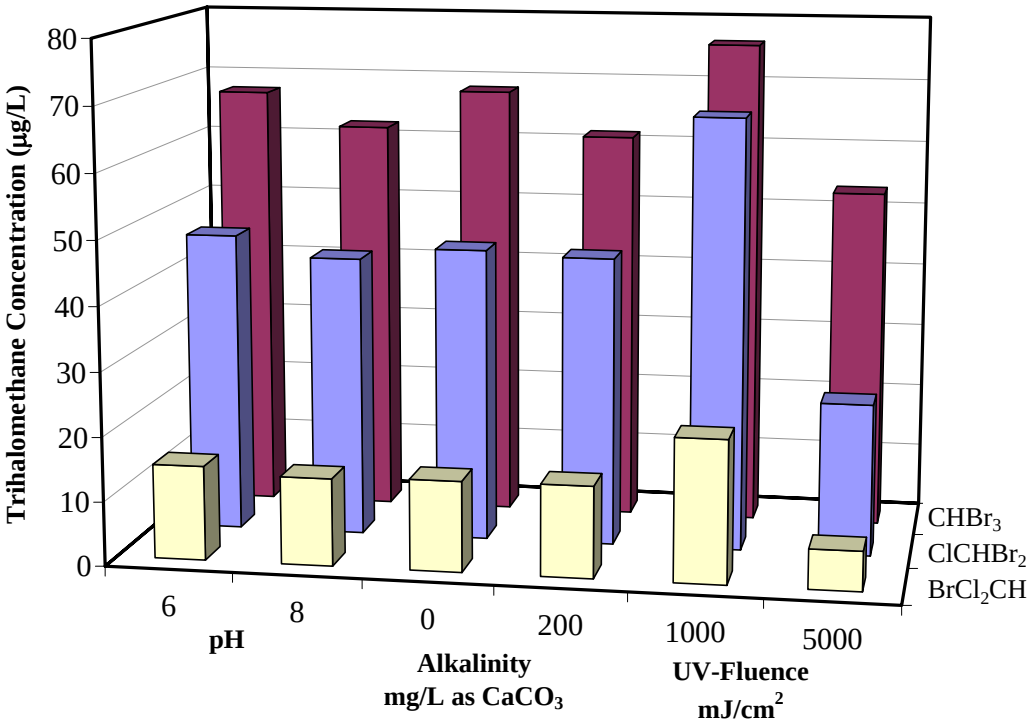

Figure 4.19 UV Photolysis: Effect of pH, Alkalinity and UV-Fluence on the Formation of Brominated THMs

4.5 Effect of UV/H_2O_2 on Brominated PCDBPs

To study the effect of UV/H_2O_2 on the formation of brominated PCDBPs, a mean concentration of 9.40 mg/L of hydrogen peroxide and 500 µg/L of bromide ion was added to the water sample prior to irradiation. All experimental runs were exposed to a UV-fluence of 1000, 3000 and 5000 mJ/cm^2; these had a mean peroxide demand of 2.77, 6.64 and 8.18 mg/L respectively. The peroxide concentration was measured according to the article written by Klassen et al. (1994) as explained in Chapter 3. Detailed data concerning the addition and demand of peroxide by each water sample are shown in

Appendix B while the concentration of each factorial run, center points and control samples is given Appendix F. Residual peroxide concentration was quenched with 0.2 mg/L of Bovine liver (catalase) as described by Liu et al. (2003). After irradiation of the water samples 4 mg/L of sodium hypochlorite was added leaving a mean 24 hr free chlorine residual of 0.61 mg/L. No haloacetonitrile compounds were observed in this set of experiments.

4.5.1 Haloacetic Acids

All six brominated HAAs had statistically significant factors and these are listed in Table 4.13. Bromoacetic acid (BrAA), bromochloroacetic acid (BrClAA) and dichlorobromo-acetic acid ($BrCl_2AA$) were produced in smaller quantities than the rest of the brominated post-UV chlorination disinfection by-products (PCDBPs).

Table 4.13 UV/H_2O_2: Effects of Factors and Interactions on Formation of Statistically Significant Brominated Haloacetic Acids.

		Main Effects			Interactions			
		pH (P)	Alkalinity (A)	UV-fluence(F)	PxA	PxF	AxF	PxAxF
BrAA	Effect	-0.065	-0.061	-0.266	-0.053	+0.010	+0.049	+0.039
	F_{obs}	31.2	27.6	521	20.4	0.723	18.0	11.1
	Significant	Yes	Yes	Yes	Yes	No	Yes	Yes
BrClAA	Effect	+0.201	-0.256	-1.68	+0.249	+0.103	+0.690	-0.405
	F_{obs}	2.32	3.78	163	3.59	0.606	27.4	9.45
	Significant	No	No	Yes	No	No	Yes	No
$BrCl_2AA$	Effect	-0.154	+0.325	-0.829	+0.073	+0.197	-0.227	+0.018
	F_{obs}	12.0	53.7	348	2.67	19.8	26.2	0.173
	Significant	Yes	Yes	Yes	No	Yes	Yes	No
Br_2ClAA	Effect	-0.043	+1.333	-4.07	+0.304	-0.083	-1.32	-0.430
	F_{obs}	0.045	44.0	408	2.29	0.172	43.4	4.57
	Significant	No	Yes	Yes	No	No	Yes	No
Br_2AA	Effect	-0.170	+0.171	-2.77	+0.056	+0.102	+0.033	+0.219
	F_{obs}	1.95	1.96	515	0.212	0.696	0.073	3.20
	Significant	No	No	Yes	No	No	No	No
Br_3AA	Effect	+0.432	+1.44	-3.29	+0.651	-0.408	-1.32	-0.269
	F_{obs}	9.59	106	554	21.7	8.54	88.9	3.71
	Significant	No	Yes	Yes	Yes	No	Yes	No

Bromoacetic acid had all factors and interactions statistically significant except for the interaction PxF. Since all the main factors for this compound are in interaction with other factors, their effects have been explained jointly in Figures 4.20 and 4.21.

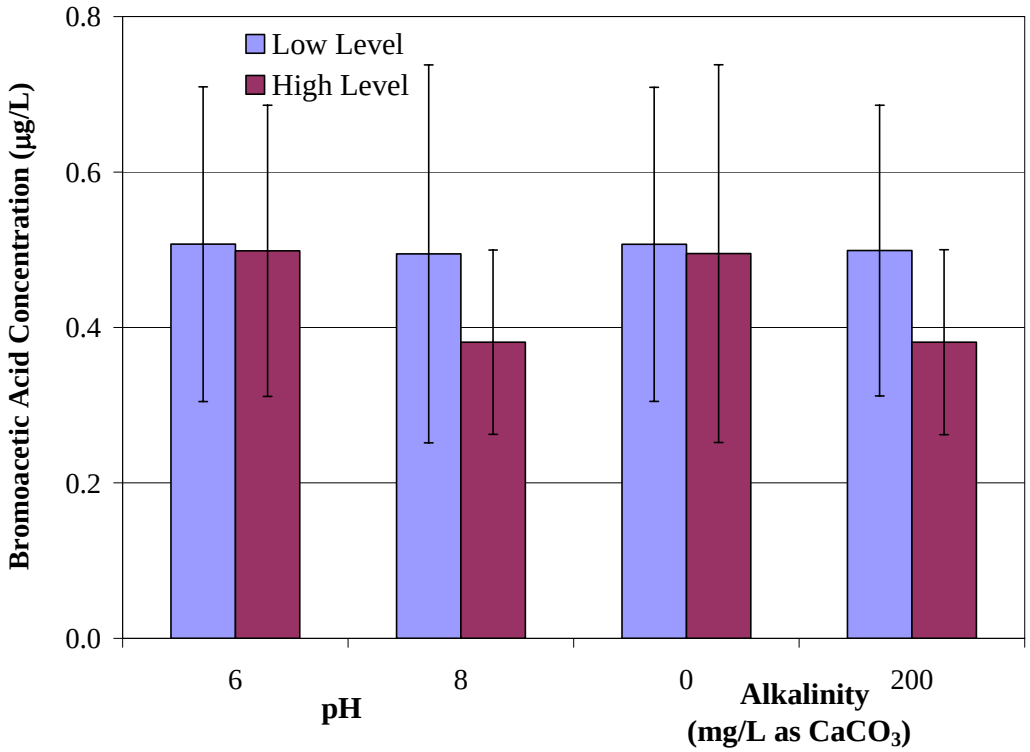

Figure 4.20 UV/H_2O_2: Joint Effect of pH and Alkalinity on Bromoacetic Acid Formation

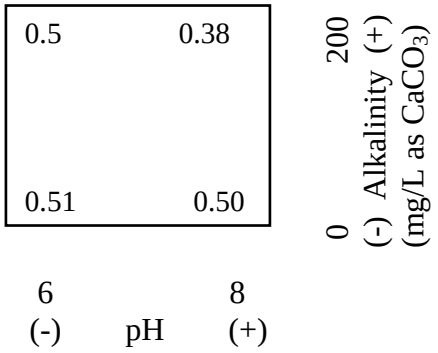

Figure 4.21 UV/H_2O_2: Interaction of pH and Alkalinity in the Formation of Bromoacetic Acid.

From Figures 4.20 and 4.21 the interaction between pH and alkalinity for BrAA took place as a result of change in alkalinity at pH 8 and change in pH at 200 mg/L as $CaCO_3$ of alkalinity. This resulted into a decrease of 24 % at pH 8 and an alkalinity of 200 mg/L as $CaCO_3$. Form Table 4.12 a reduction of 0.053 units in the formation of BrAA occurred when both factors pH and alkalinity are increased form their low to high levels.

The other significant interaction for BrAA was AxF illustrated in Figures 4.22 & 4.23 below. A 48 % and 40 % increase was observed at low and high levels of alkalinity respectively as UV-fluence was increased from 1000 mJ/cm^2 to 5000 mJ/cm^2.There was not much change at 5000 mJ/cm^2 as alkalinity was increased from its low to high level but a 17 % increase occurred at 1000 mJ/cm^2 as alkalinity was increased from its low to high level. This interaction was mainly due to change in UV-fluence from 1000 to 5000 mJ/cm^2 at both levels of alkalinity. The effect of the interaction, AxF, caused an increase in BrAA as alkalinity and UV-fluence were increased from their low to high levels shown by the negative effect in Table 4.12

The three factor interaction was also found significant and it had a positive effect implying that as all three factors were increased from their low to high levels the concentration of BrAA increased.

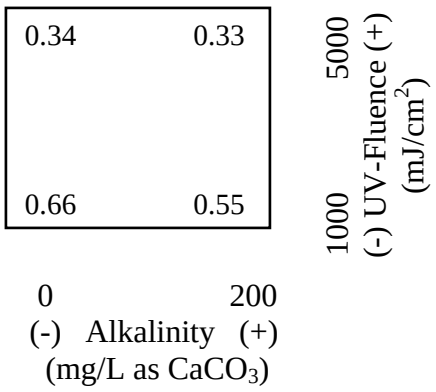

Figure 4.22 UV/H_2O_2: Interaction of Alkalinity and UV-Fluence in the Formation of Bromoacetic Acid

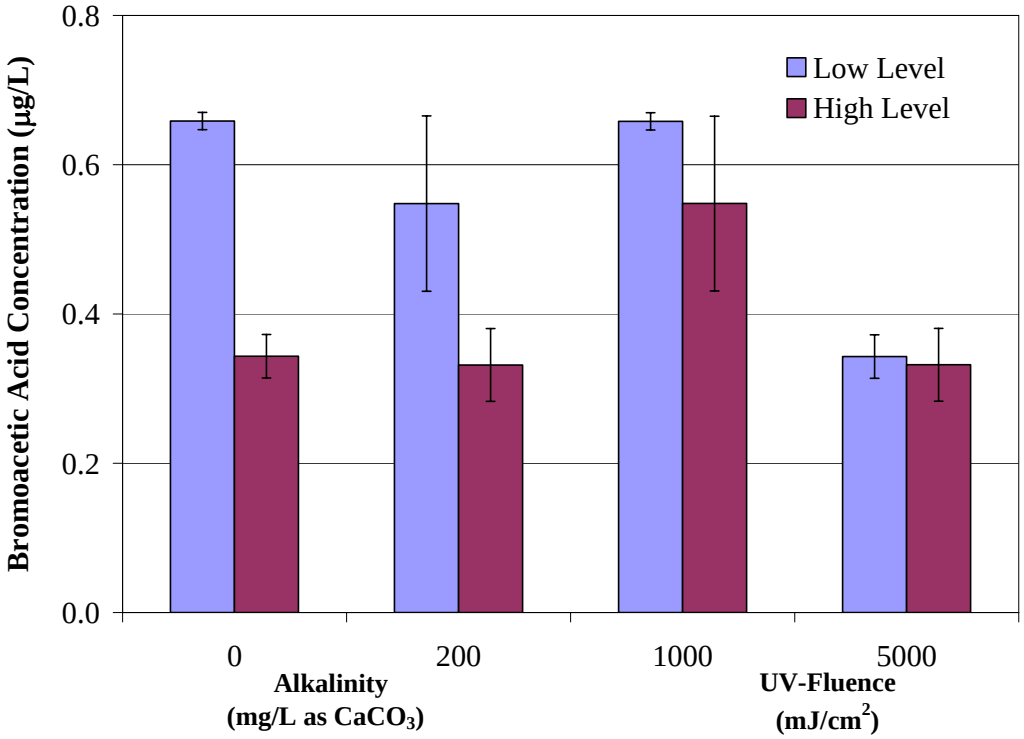

Figure 4.23 UV/H_2O_2: Joint Effect of Alkalinity and UV-Fluence on Bromoacetic Acid Formation

Bromochloroacetic had one statistically significant main factor, UV-fluence and one statistically significant interaction, AxF. From Figure 4.24, the interaction between UV-fluence and alkalinity in the formation of BrClAA occurred due to a greater change in UV-fluence from its low to high especially at 0 mg/L as $CaCO_3$ of alkalinity than other levels of alkalinity and UV-fluence. The interaction of alkalinity and UV-fluence caused an increase in the formation of BrClAA as both factors were increased from their low to high levels.

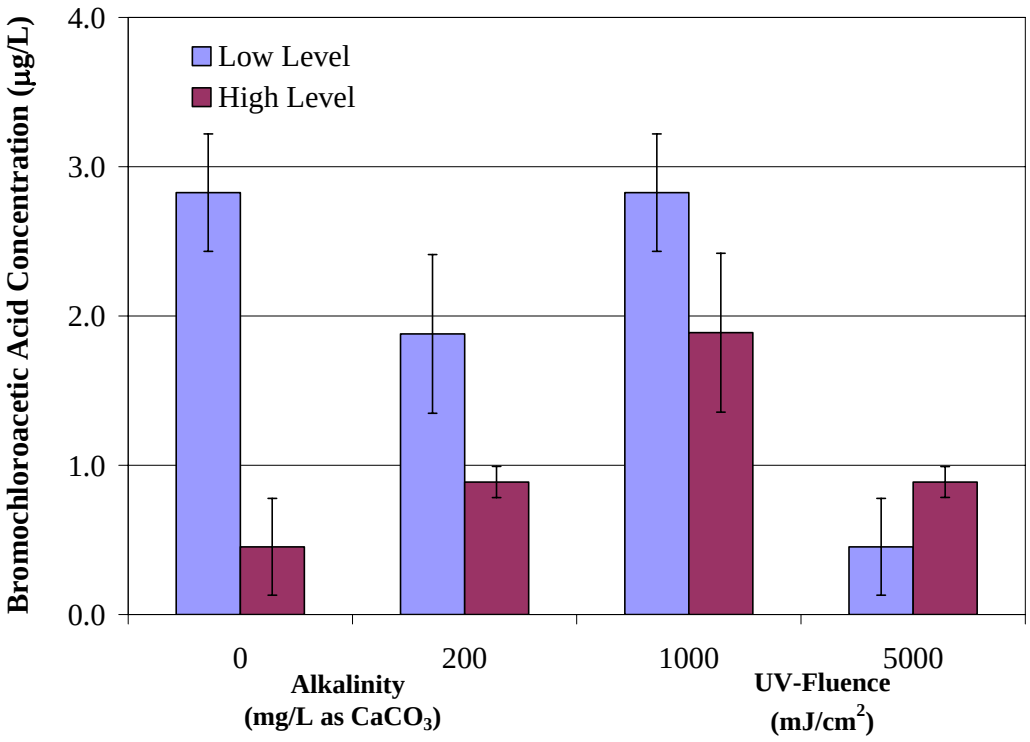

Figure 4.24 UV/H_2O_2: Joint Effect of Alkalinity and UV-Fluence on Bromochloroacetic Acid Formation

From Figure 4.25, at low and high levels of alkalinity 84 % and 51 % decrease in the formation of BrClAA occurred respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. At 1000 mJ/cm^2 of UV-fluence, a 97 % increase in the concentration of BrClAA occurred as alkalinity was increased form 0 to 250mg/L as $CaCO_3$ and a 35 % decrease at 5000 mJ/cm^2

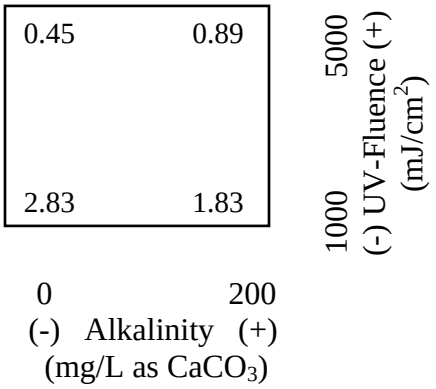

Figure 4.25 UV/H_2O_2: Interaction of Alkalinity and UV-Fluence in the Formation of Bromochloroacetic Acid

All main factors of dichlorobromoacetic acid ($BrCl_2AA$) were found to be statistically significant, while PxA and PxAxF were the only statistically insignificant interaction.

The percentage change that occurred at 1000 mJ/cm^2 as pH was increased from 6 to 8, was not as much as when UV-fluence was increased from 1000 to 5000 mJ/cm^2 at both levels of pH. This can be visualized in Figure 4.26. A decrease of 82 % and 70 % occurred at low and high levels of pH respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. On the other hand, a 19 % increase in the concentration of $BrCl_2AA$ occurred at the high level of UV-fluence while a 28 % decrease in concentration occurred at the low level of UV-fluence as pH was increased from 6 to 8.

The interaction of pH and UV-fluence, PxF, had a positive effect i.e. an increase in concentration occurred as the interacting factors moved from their low to high levels. From Figure 4.27 the greatest change in concentration of $BrCl_2AA$ for pH and UV-fluence occurred at 6 and 1000 mJ/cm^2 respectively. In other words the greatest changes at both factors occurred at the low levels. This is also indicated by the fact that their standard deviations are smaller than the other factors.

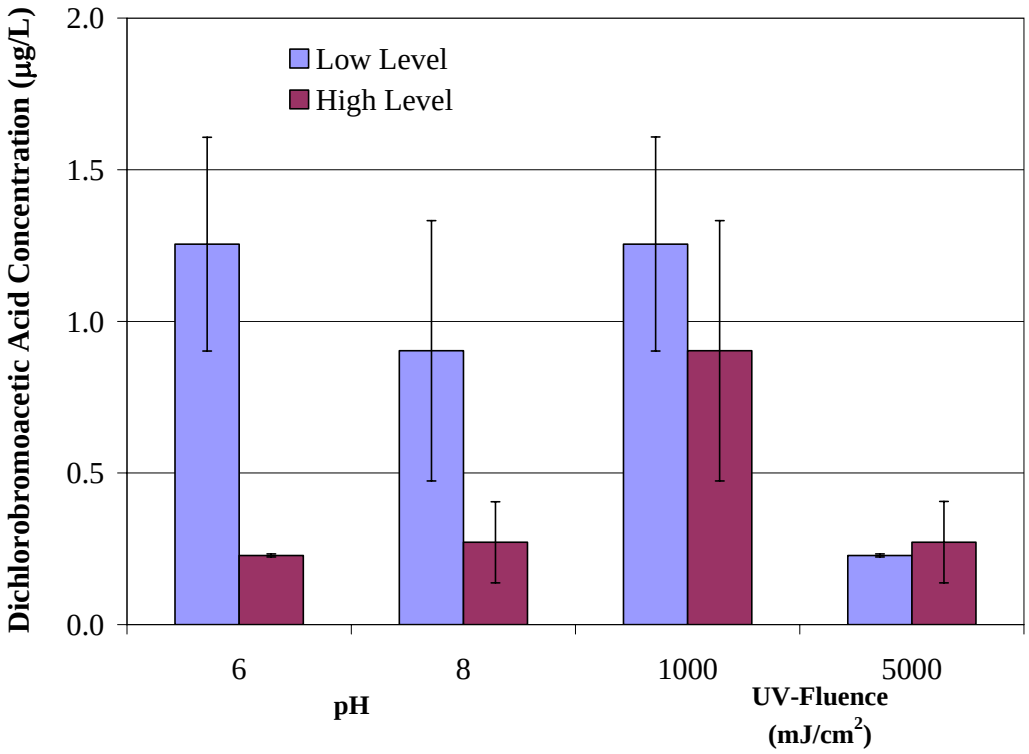

Figure 4.26 UV/H_2O_2: Joint Effect of pH and UV-Fluence on Dichlorobromoacetic Acid Formation.

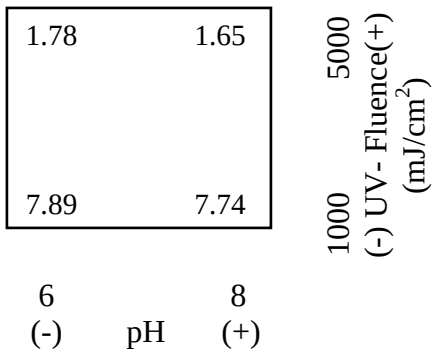

Figure 4.27 UV/H_2O_2: Interaction of pH and UV-Fluence in the Formation of Dichlorobromoacetic Acid

The interaction AxF on the formation of $BrCl_2AA$ is illustrated in Figures 4.28 and 4.29 below. From these figures, at both levels of UV-fluence an increase in the concentration of $BrCl_2AA$ occurred as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$, while a reduction of 75 % and 78 % in the concentration of $BrCl_2AA$ occurred at both low and high levels of alkalinity respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. The effect of the interaction, AxF being negative suggests that as both factors were increased from their low to high levels the concentration of $BrCl_2AA$ reduced.

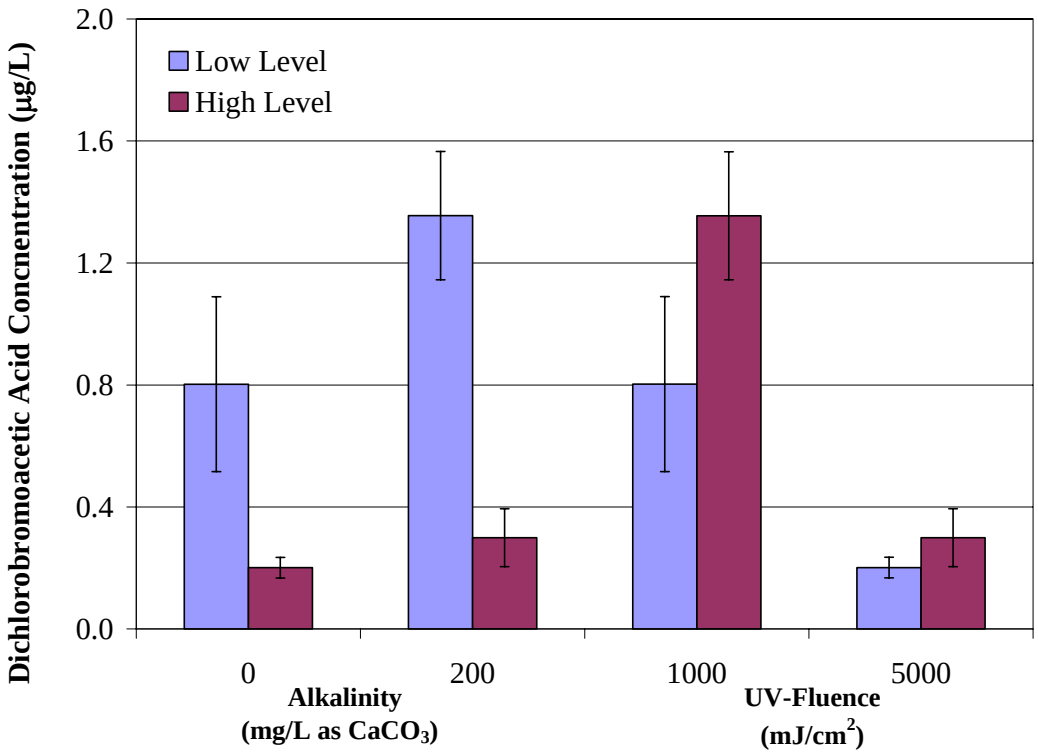

Figure 4.28 UV/H_2O_2: Joint Effect of Alkalinity and UV-Fluence on Dichlorobromoacetic Acid Formation.

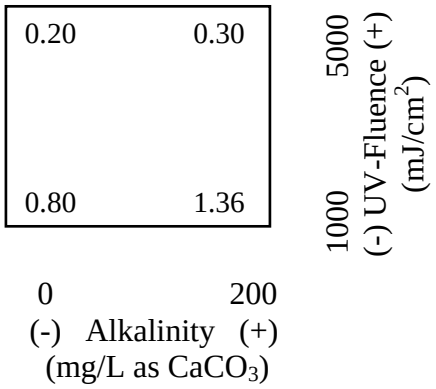

Figure 4.29 UV/H_2O_2: Interaction of Alkalinity and UV-Fluence in the Formation of Dichlorobromoacetic Acid

Alkalinity and UV-fluence and their interaction, AxF, were statistically significant for dibromochloroacetic acid. As always, the factors would be explained jointly as they were involved in an interaction. From Figures 4.30 and 4.31, at 5000 mJ/cm^2 there was no change in concentration of Br_2ClAA as alkalinity was increased from its low to high level but an increase of 63% occurred at 1000 mJ/cm^2 as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$. At both low and high levels of alkalinity an increase of 65% and 78% occurred respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. As both factors are increased from their low to high level, a 1.32 unit decrease in the concentration of Br_2ClAA occurred as indicated by the negative sign in Table 4.13. The error bars at 0 mg/L as $CaCO_3$ and 5000 mJ/cm^2 in Figure 4.30 are not shown because their standard deviations very small.

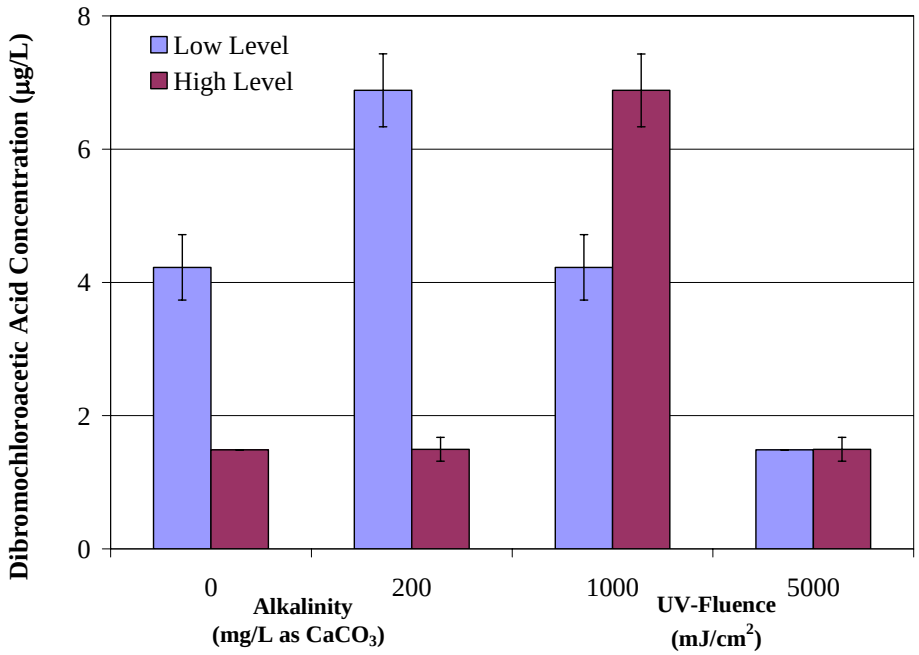

Figure 4.30 UV/H_2O_2: Joint Effect of Alkalinity and UV-Fluence on Dibromochloroacetic Acid Formation.

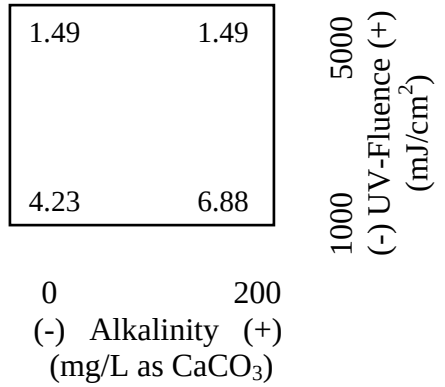

Figure 4.31 UV/H_2O_2: Interaction of Alkalinity and UV-Fluence in the Formation of Dibromochloroacetic Acid

UV-fluence was the only statistically significant factor of the HAA species dibromo-acetic acid (Br_2AA). From Table 4.13 it can be observed that as UV-fluence was increased from 1000 to 5000 mJ/cm^2, the concentration of Br_2AA decreased by a unit of 2.77, a decrease of 65 %. Alkalinity and pH were not statistically significant in the formation of Br_2AA as illustrated in Figure 4.32. Since the effect of UV-fluence on dibromoacetic acid is larger than the other factors, a mean of the effects of pH and alkalinity over UV-fluence resulted into a large standard deviation.

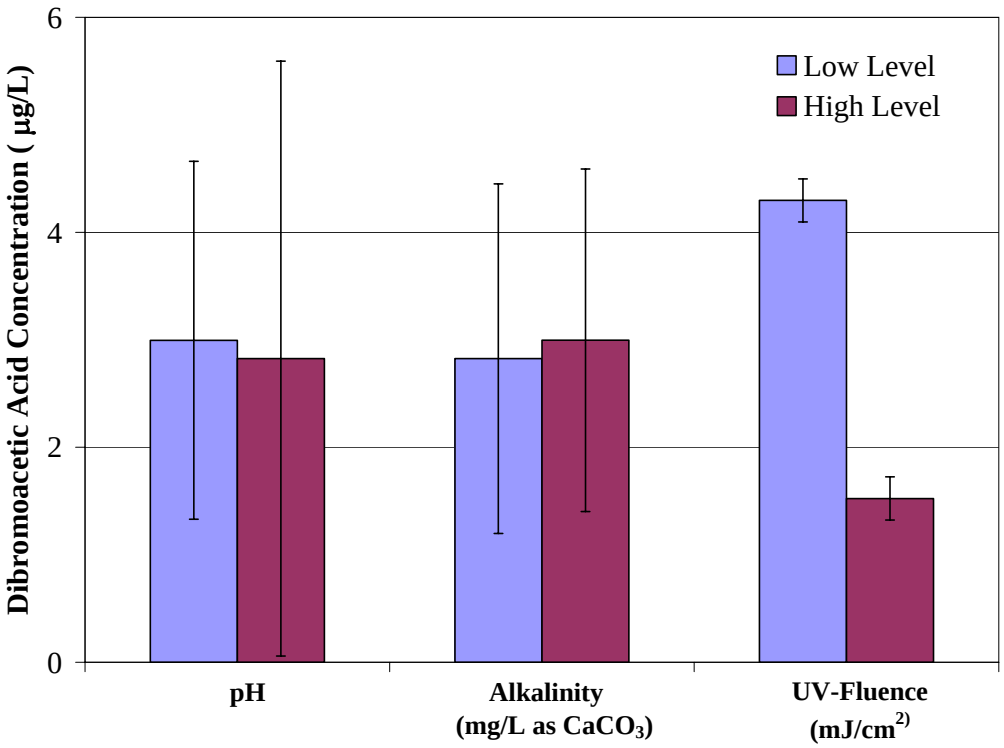

Figure 4.32 UV/H_2O_2: Effect of pH, Alkalinity and UV-Fluence on the Formation of Dibromoacetic Acid. (Error bars=standard deviations)

These two interactions, PxA and AxF, were found to be statistically significant for tribromoacetic acid (Br_3AA) along with main factors alkalinity and UV-fluence. Figures 4.33 and 4.34 illustrate the effect of PxA interaction on Br_3AA. At both low and high levels of pH an increase of 37 % and 55 % in the concentration of Br_3AA occurred as alkalinity was increased form 0 to 200mg/L as $CaCO_3$. At high level of alkalinity, an increase of 37 % in Br_3AA concentration occurred as pH was increased from 6 to 8 and a decrease of 10% occurred at low level alkalinity. The interaction had an effect of +0.651, implying that as both factors comprising the interaction were increased from there low to high levels; the concentration of Br_3AA was increased. The standard deviations on

Figure 4.33 are large indicating that the values used in obtaining the standard deviation are on the extreme sides of the mean.

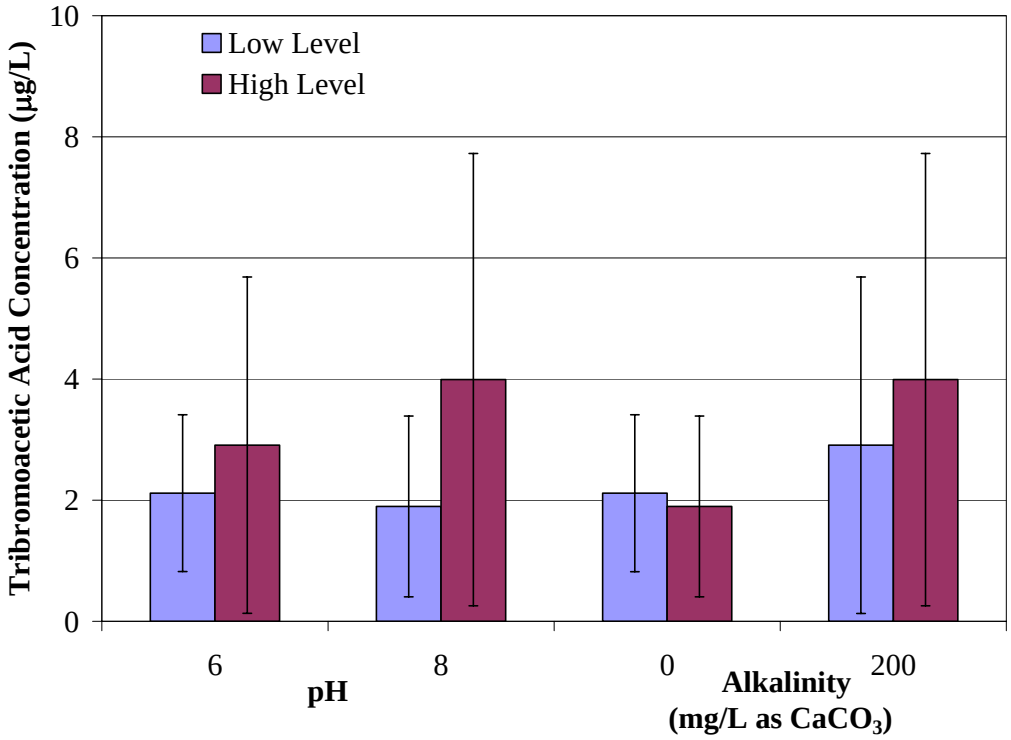

Figure 4.33 UV/H_2O_2: Joint Effect of pH and Alkalinity on Tribromoacetic Acid Formation.

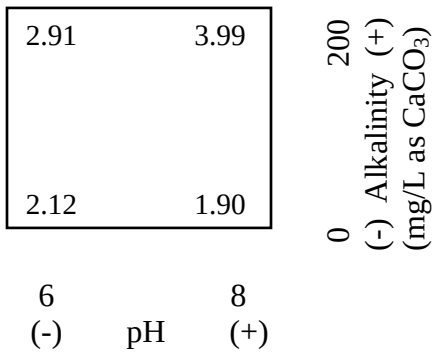

Figure 4.34 UV/H_2O_2**:** Interaction of pH and Alkalinity in the Formation of Tribromoacetic Acid.

The effect of the other interaction, AxF, on Br_3AA formation is illustrated in Figures 4.35 & 4.36 below. From these figures, a reduction of 66 % and 80 % in the concentration of Br_3AA occurred as UV-fluence was increased from 1000 to 5000 mJ/cm^2 at low and high levels of alkalinity respectively, while an increase of 92 % and 13 % in the concentration occurred as alkalinity was increased from 0 to 200 mg/L as $CaCO_3$ at both low and high levels of UV-fluence respectively. The interaction had an effect of -1.32, implying that as both factors comprising the interaction were increased from their low to high levels, Br_3AA experienced a reduction in concentration.

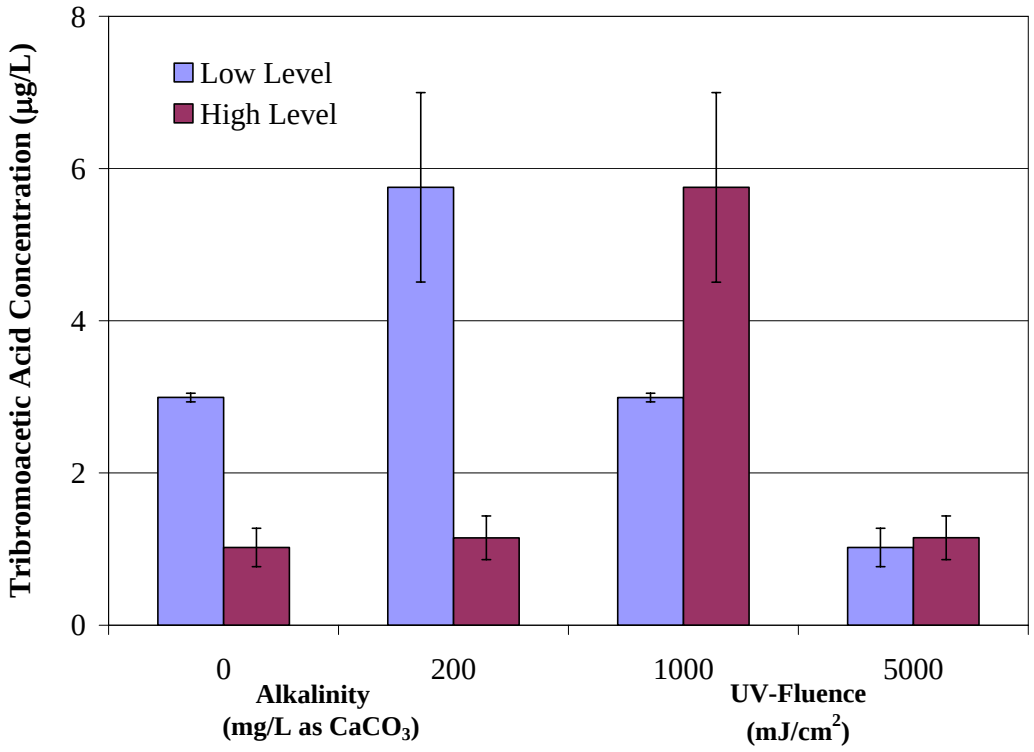

Figure 4.35 UV/H_2O_2: Joint Effect of Alkalinity and UV-Fluence on Tribromoacetic Acid Formation. (Error bars=standard deviations)

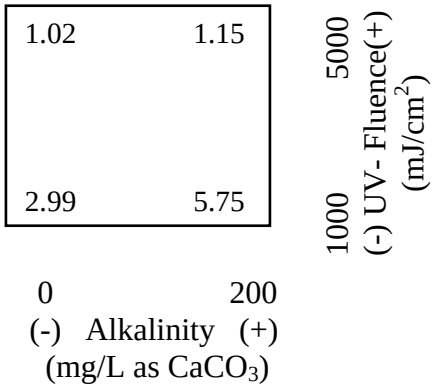

Figure 4.36 UV/H_2O_2: Interaction of Alkalinity and UV-Fluence in the Formation of Tribromoacetic Acid.

4.5.2 Trihalomethane

The effects of pH, alkalinity, UV-fluence and interactions on the formation of the brominated THMs are indicated in Table 4.14. Figure 4.37 also illustrates the effect of the pH alkalinity and UV-fluence on the brominated THMs. All the brominated THMs had UV-fluence as a statistically significant factor resulting into a reduction of 70 %, 61 % and 39 % for $BrCl_2CH$, $ClCHBr_2$ and $CHBr_3$ respectively as UV-fluence was increased from 1000 to 5000 mJ/cm^2. The factor pH was another statistically significant for $BrCl_2CH$. Increasing the pH value from 6 to 8 caused a decrease in concentration of $BrCl_2CH$ by 27 %. The other factors that were not statistical significant but they had some effect on the brominated THMs. Increase in pH resulted in deceases in the brominated THMs while increase in alkalinity caused an increase in the brominated THMs. The effects of these factors on brominated THMs are represented in Figure 4.37

Table 4.14 UV/H_2O_2: Effects of Factors and Interactions on the Formation of Brominated THMs

		Main Effects			**Interactions**			
		pH (P)	Alkalinity (A)	UV-fluence (F)	PxA	PxF	AxF	PxAxF
$BrCl_2CH$	Effect	-2.34	+2.03	-13.8	+0.165	+2.62	-0.427	+0.298
	Fobs	4.82	3.63	167	0.024	6.04	0.161	0.078
	Significant	No	No	Yes	No	No	No	No
$ClCHBr_2$	Effect	-13.0	+7.39	-36.8	-0.837	+11.1	-5.49	+6.47
	Fobs	22.9	7.43	184	0.095	16.9	4.10	5.69
	Significant	Yes	No	Yes	No	No	No	No
$CHBr_3$	Effect	-9.41	+15.9	-31.1	+1.20	+15.7	-7.84	-0.110
	Fobs	4.90	13.9	53.5	0.079	13.6	3.40	0.001
	Significant	No	No	Yes	No	No	No	No

$F_{1, 2, 0.05} = 18.5$

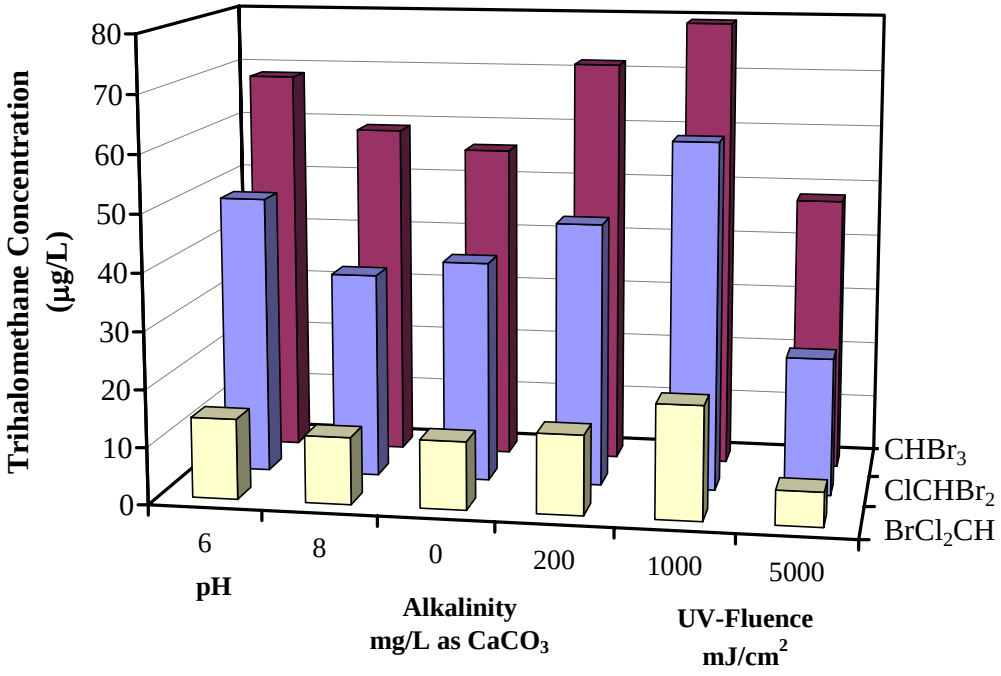

Figure 4.37 UV/H_2O_2: Effect of pH, Alkalinity and UV-Fluence on the Formation of Brominated THMs

4.6 Comparison of UV Photolysis and UV/H_2O_2

Two different treatment methods, UV Photolysis and UV/H_2O_2, were used in the factorial experiments to determine the effects of pH, alkalinity and UV-fluence in the formation of PCDBPs following chlorination. In this section these treatment methods were compared to determine the differences in their results.

The values of center points obtained in the factorial experiments of the total sum of PCDBPs i.e. HAA_9, THANs and TTHMs were used in the comparisons. Since the center points were carried out in triplicate or quadruplicate, a t-test was used to determine the differences in the means of the two treatments. A basis for comparison occurs because

the center points were subjected to the same experimental conditions and the synthetic water used in the experiments was produced with the same recipe given in Table 3.3. An F-test indicated in Table 4.15A below was used to determine the type of t-test to use.

Table 4.15A Variance Comparison of UV Photolysis and UV/H_2O_2 in Factorial Experiment.

Chlorinated	HAAs		HANs		THMs	
	UV photolysis	UV/H_2O_2	UV photolysis	UV/H_2O_2	UV photolysis	UV/H_2O_2
Mean	14.640	6.552	1.886	0.676	40.296	24.947
Variance	7.31	0.296	0.131	0.077	13.5	44.2
df	3	3	3	3	3	3
$F_{observed}$	24.7		1.7		3.28	
$F_{3,3,0.05}$	9.28		9.28		9.28	
Significant	Yes		No		No	
Brominated	HAAs				THMs	
	UV photolysis	UV/H_2O_2			UV photolysis	UV/H_2O_2
Mean	12.4	7.22			119	68.2
Variance	1.26	0.254			727	124
df	3	3			3	2
$F_{observed}$	4.96				5.88	
$F_{3,3,0.05}$	9.28					
$F_{3,2,0.05}$					19.16	
Significant	No				No	

Table 4.15B outlines the variables used to statistically compare the effects of UV photolysis and UV/H_2O_2 on the formation of PCDBPs. The columns denoted "chlorinated" and "brominated" refer to experimental sets for chlorinated and brominated PCDBPs discussed in previous sections. For the purposes of this analysis, the sum of brominated PCDBPs does not contain concentrations of their solely-chlorinated

counterparts even though they were formed alongside the brominated PCDBPs but in smaller quantities. “Difference in yield” is the difference between the mean PCDBP yields of both treatments while “*v*” is the number of independent observations used in the t-test calculation at 5% significance level.

The F-test conducted in Table 4.15A was used to determine if there was a significant difference in the variance of the treatment for the various groups of DBPs. The variance for chlorinated HAAs treated with both UV photolysis and UV/H_2O_2 were found to be statistically different therefore Equation 4.1 was used in determining if there was a difference between the treatments of UV photolysis and UV/H_2O_2. For other DBPs there were no significant differences in the variance for both treatments used therefore the sample variances were pooled and t_{obs} was calculated according to Equation 4.2.

$$(\bar{X}_1 - \bar{X}_2) \pm t_{\alpha/2}, v \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}$$ (Duever, 2003) Equation 4.1

Where $$v = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left[\left(\frac{s_1^2}{n_1}\right)^2 \frac{1}{n_1 - 1}\right] + \left[\left(\frac{s_2^2}{n_2}\right)^2 \frac{1}{n_2 - 1}\right]}$$

$$\bar{X}_1 - \bar{X}_2 \pm t_{\alpha/2}, v, S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}$$ (Duever, 2003) Equation 4.2

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

$$v = n_1 + n_2 - 2$$

Where $\bar{X}_1 - \bar{X}_2$ = difference in means of the treatments and n= number of observations.

A two-tailed t-test was performed to determine whether the difference in means of the PCDBPs for both treatments were statistically significant at 5 % significance level. A statistically significant difference exists between the means if $t_{obs} > t_{\alpha/2}$.

Table 4.15B Mean Comparison of UV Photolysis and UV/H_2O_2 in Factorial Experiments

	Chlorinated			Brominated	
	HAA_9	THANs	TTHMs	HAA_9	TTHMs
Difference in yield	8.09	1.21	15.3	5.13	51.2
df	3	6	6	6	5
t_{obs}	5.87	5.3	4.04	8.07	3.04
$t_{0.025,6}$		2.45	2.45	2.45	2.57
$t_{0.025,3}$	3.18				
Significantly different?	Yes	Yes	Yes	Yes	Yes

For all PCDBPs, both chlorinated and brominated, Table 4.11 shows that there is a statistically significant difference between experiments performed with UV photolysis and that of UV/H_2O_2. Since this is the case, mean values of the center points for each set of experiments can be compared graphically to determine which of the treatments gave a better reduction in PCDBPs.

Figures 4.38 and 4.39 show mean values of the center points for each PCDBP. The error bars indicate the standard deviation of the center points. Like the t-test, the center points used are the sum of all the compounds of a group of PCDBP that were observed in each set of experiments. A glance at these figures shows that the use of UV/H_2O_2 resulted in a greater reduction of PCDBPs than UV photolysis. For chlorinated PCDBPs, a percentage difference between UV photolysis and UV/H_2O_2 of 55, 65 and 38 % occurred with

HAA_9, THANs and TTHMs respectively, while for brominated PCDBPs a percentage difference of 41 % and 42 % occurred for HAA_9 and TTHMs respectively. This is not unusual as Beltran et al. (1996) in their study of the degradation of polynuclear aromatic hydrocarbons (PAH) in water found that UV/H_2O_2 enhanced the disappearance of PAH relative to UV photolysis.

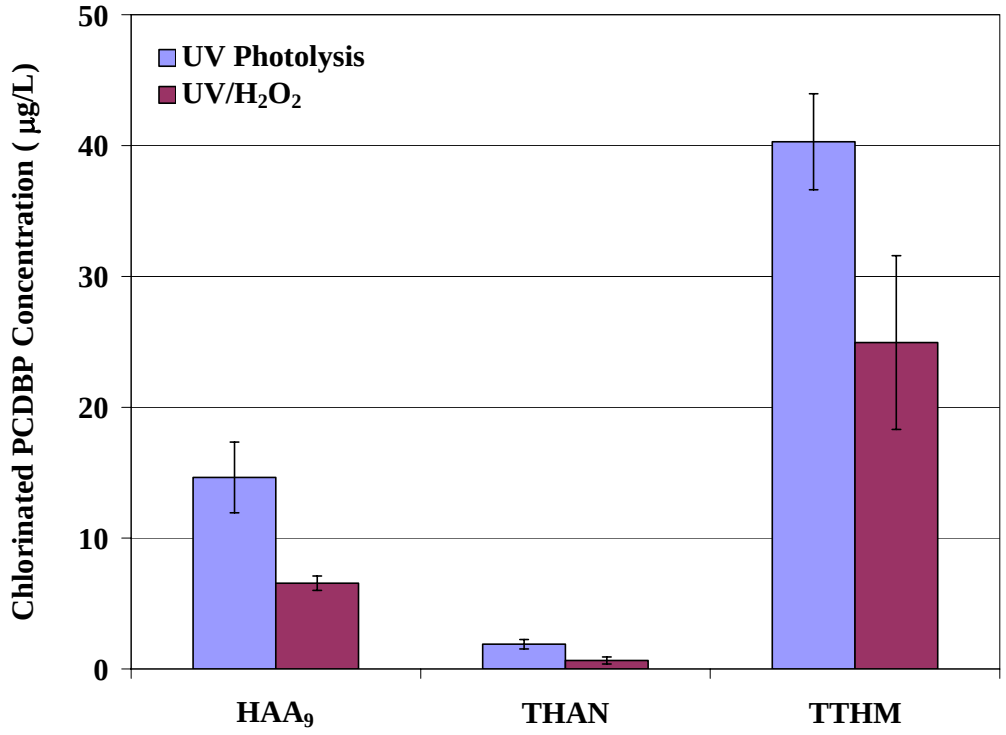

Figure 4.38 Comparisons of UV Photolysis and UV/H_2O_2 for Chlorinated PCDBPs (Error bars= standard deviations)

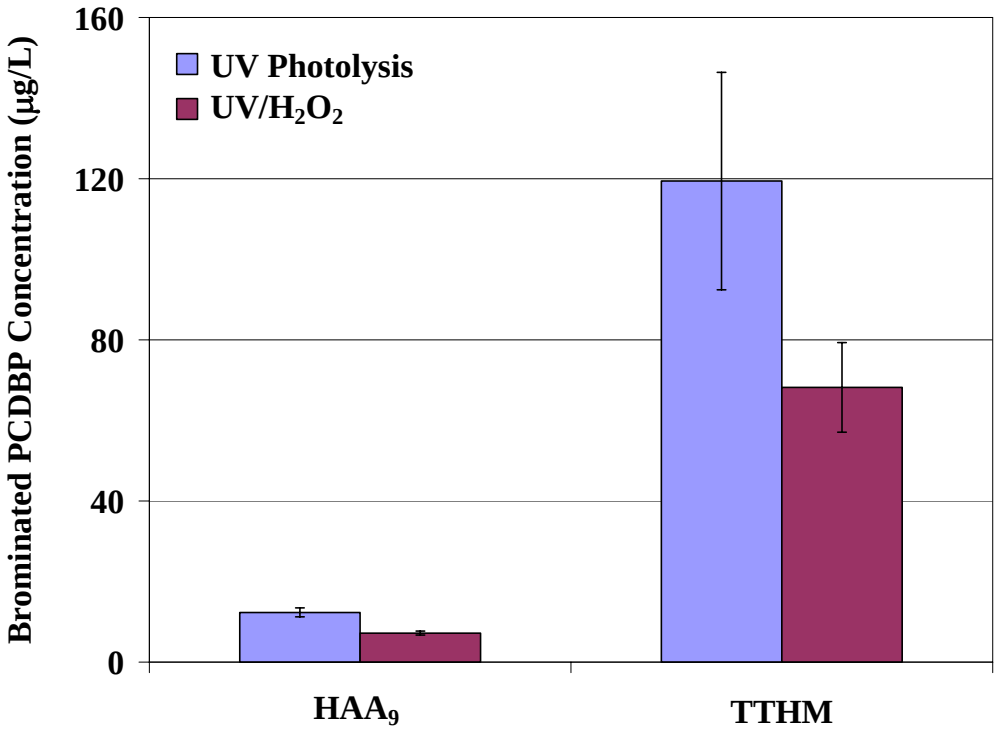

Figure 4.39 Comparisons of UV Photolysis and UV/H_2O_2 for Brominated PCDBPs

Table 4.16 is a comparison of significant factors of chlorinated PCDBPs for both UV photolysis and UV/H_2O_2 treatments followed by chlorination. The table also indicates the effects of the factors on PCDBPs.

Table 4.16 Comparison of Significant Factors of Chlorinated PCDBPs for UV Photolysis and UV/H_2O_2 (P=pH, A=Alkalinity and F=UV-Fluence).

		UV Photolysis		**UV/H_2O_2**	
PCDBP	**Compound**	Significant Factors	- or +	Significant Factors	- or +
THMs	$CHCl_3$	UV-fluence	-	UV-fluence	-
HAAs	Cl_2AA	pH	-	Alkalinity	+
		UV-fluence	-	UV-fluence	-
		PxF	-	PxA	-
		PxAxF	+	PxAxF	+
	Cl_3AA	UV-fluence	-	Alkalinity	+
				UV-fluence	-
HANs	Cl_2AN	None		Alkalinity	+
				UV-fluence	-
				PxF	-
				PxAxF	-

UV-fluence was statistically significant for all compounds of the PCDBPs studied and a reduction in these PCDBP always occurred whether the water sample was treated with either UV photolysis or UV/H_2O_2. The exception to this was for Cl_2AN, which had no statistically significant factor for treatment with UV photolysis. For both treatments, THMs had no other statistically significant factors than UV-fluence.

Of the HAAs species detected, Cl_2AA had the most significant factors. UV-fluence and the three factor interaction, PxAxF were common significant factors to both UV photolysis and UV/H_2O_2 for Cl_2AA. In both occasions, UV-fluence had a reducing effect while PxAxF had an increasing effect on the formation of Cl_2AA. Other significant

factors for Cl_2AA were alkalinity and pH. Alkalinity was significant in the UV/H_2O_2 treatment causing an increase in concentration while pH was significant in the treatment with UV photolysis causing a decrease in concentration. Dichloroacetic acid had two-factor interactions that were statistically significant with both treatments, PxF with UV photolysis and PxA with UV/H_2O_2. Both interactions brought about a reduction in the concentration of Cl_2AA. UV-fluence was a common significant factor to both treatments of UV photolysis and UV/H_2O_2 for Cl_3AA causing a decrease in its formation. Alkalinity was also a significant factor in the treatment with UV/H_2O_2, causing an increase in the formation of Cl_3AA.

There were no statistically significant factors for the HANs in the treatment of synthetic water with UV photolysis; it may be that the concentrations of Cl_2AN were too small for any factor to be significant. But in the treatment with UV/H_2O_2, alkalinity, UV-fluence, PxF, and PxAxF were statistically significant factors of Cl_2AN. All the significant factors in the treatment with UV/H_2O_2 caused a reduction in the formation of Cl_2AN with the exception of alkalinity which caused an increase in the formation of Cl_2AN. The comparison of significant factors of brominated PCDBPs for UV photolysis and UV/H_2O_2 are presented in Table 4.15. Relatively, more significant factors occurred with the UV/H_2O_2 treatment than with UV photolysis. UV-fluence was a statistically significant factor for most of the PCDBPs studied causing a reduction in their formation.

Table 4.17 Summary of Significant Factors of Brominated PCDBPs for UV Photolysis and UV/H_2O_2 (P=pH, A=Alkalinity and F=UV-Fluence)

		UV Photolysis		**UV/H_2O_2**	
PCDBP	**Compound**	Significant Factors	- or +	Significant Factors	- or +
THMs	$BrCl_2CH$	UV-fluence	-	UV-fluence	-
	$ClCHBr_2$	UV-fluence	-	UV-fluence	-
				pH	-
	$CHBr_3$	UV-fluence	-	UV-fluence	-
HAAs	BrAA	Alkalinity	-	pH	-
		UV-fluence	-	Alkalinity	-
		AxF	+	UV-fluence	-
				PxA	-
				AxF	+
				PxAxF	+
	BrClAA	None		UV-fluence	-
				AxF	+
	$BrCl_2AA$	None		pH	-
				Alkalinity	+
				UV-fluence	-
				PxF	+
				AxF	-
	Br_2ClAA	Alkalinity	-	Alkalinity	+
		UV-fluence	-	UV-fluence	-
		PxF	+	AxF	-
	Br_2AA	Alkalinity	-	UV-fluence	-
		UV-fluence	-		
	Br_3AA	Alkalinity	-	Alkalinity	+
		UV-fluence	-	UV-fluence	-
		AxF	+	AxF	-
		PxAxF	+		

When synthetic water was treated with UV photolysis, all brominated THM compounds had only one statistically significant factor, UV-fluence. The same case also occurred with the UV/H_2O_2 treatment except that $ClCHBr_2$ had an additional statistically

significant factor, pH. In general, all factors found to be statistically significant brominated THMs caused a reduction in their concentration whether synthetic water was treated with UV photolysis or UV/H_2O_2 followed by chlorination.

For BrAA, alkalinity, UV-fluence and AxF, were common statistically significant factors in both treatments with UV photolysis and UV/H_2O_2. PxA, PxAxF and pH were other statistically significant factors for BrAA in the treatment with UV/H_2O_2.

BrClAA had no statistically significant factors with the UV photolysis treatment but UV-fluence and AxF were found to be statistically significant factors with UV/H_2O_2. Though on its own alkalinity was not a significant factor in the treatment of synthetic water with UV/H_2O_2, its interaction with UV-fluence was found to increase the formation of BrClAA.

$BrCl_2AA$ also had no significant factor in the treatment of synthetic water with UV photolysis, but all the main factors pH, alkalinity and UV-fluence were statistically significant in the treatment with UV/H_2O_2. Of all these three factors, alkalinity was the only factor found to increase the formation of $BrCl_2AA$, suggesting a scavenging of the OH radical by the carbonate/bicarbonate ion with increase in alkalinity. Two interactions, PxA and AxF, also occurred in the treatment with UV/H_2O_2; they had negative and positive effects respectively on the formation of $BrCl_2AA$. In the treatment of synthetic water with UV Photolysis, alkalinity and UV-fluence were statistically significant for Br_2AA with both factors causing a reduction in concentration. However, no factor other than UV-fluence was statistically significant with the UV/H_2O_2 treatment.

Tribromoacetic acid (Br_3AA) had similar significant main factors for both UV photolysis and UV/H_2O_2 treatments, which are alkalinity and UV-fluence. In the treatment with UV photolysis, a negative effect occurred for alkalinity while a positive effect occurred for alkalinity with the UV/H_2O_2 treatment while the effect of UV-fluence caused a reduction in the formation of Br_3AA for both treatments. The two-factor interaction AxF was also significant for both treatments except that they had positive and negative effects for the UV photolysis and UV/H_2O_2 respectively. The three-factor interaction, PxAxF, was found significant for the UV photolysis but not for UV/H_2O_2.

Generally, for both chlorinated and brominated PCDBPs, wherever pH was found statistically significant, it caused a negative effect on the PCDBP i.e. a reduction in the concentration as pH was increased. This is in line with the findings of Senogles, et al. (2001) and Doong et al. (2001) who found that increase in pH favored the degradation of organic compounds treated with UV photolysis or UV/H_2O_2. In case of alkalinity, a negative effect always occurred with UV photolysis and a positive effect with UV/H_2O_2; however BrAA was an exception in this case. A negative effect for alkalinity suggests the production of carbonate radicals aiding the reduction of PCDBPs while a positive effect suggests a scavenging effect of the OH radical by the bicarbonate and carbonate ions.

Alkalinity does inhibit oxidation especially with AOPs. According to Beltran et al. (1993), the presence of bicarbonate ions had a negative effect on the degradation of atrazine due to their scavenging properties. But for UV photolysis it was observed by Beltran et al. (1993) and Wang et al. (2000) that bicarbonate and carbonate ions

(HCO_3^-/ CO_3^{2-}) did not affect the degradation of compounds they were studying. Some authors, Huang and Mabury (2000), Canonica and Tratnyek (2003) and Mazeller et al. (2002), have all written about the production of the carbonate radical ($CO_3^{\bullet-}$) during the scavenging of OH radical by carbonates and bicarbonates. Though this radical is less reactive and more selective than OH radical (SRP OH radical =2.01V at pH 12, SRP $CO_3^{\bullet-}$ =1.59V at pH 12), it reacts rapidly with electron rich compounds like NOM which is regarded as one of the major sinks of the carbonate radical in natural waters. With all this in view it seems reasonable that the effect of alkalinity in the treatment with UV photolysis could cause a reduction in PCDBPs through the generation of the carbonate radical which in turn helped in the degradation of precursors forming PCDBPs.

In general, the production of bicarbonate/carbonate ions in the UV/H_2O_2 treatment might have scavenged for OH radicals causing an increase in the formation of the PCDBPs as alkalinity was increased. There is also the possibility that carbonate radicals were formed in the UV photolysis treatment aiding in the decrease of the PCDBPs as alkalinity was increased. Also, there might not have been so much significant factors for THMs due to the large variation in the experiments. From the hierarchical experiment results in Appendix E, much variation was attributed to THMs than to the HAAs.

CHAPTER 5

SINGLE FACTOR EXPERIMENTS

5.1 Introduction

The factorial experiment factors, alkalinity and pH, were studied in greater detail with the use of single factor experiments. The single factor experiments involved varying the particular factor in question while keeping other factors constant at some target value. In order to determine more quantitatively how the factors, pH and alkalinity affected the PCDBPs, linear or log linear models were fitted to the data. The data were fitted to the models mainly to determine whether the effect of the factors decreased or increased PCDBP formation. The raw data for the single factor experiments are summarized in Appendix F. The following subsections discuss the results from these experiments.

5.2 Comprehensive Studies on Alkalinity

From the results of the factorial experiments, discussed in Chapter 4, it was noted that alkalinity was found to be significant in the analysis of several of the sets of the factorial experiments that were carried out. This created a motivation for an in depth study on alkalinity while keeping the values of pH and UV-fluence constant.

Synthetic water was used for the comprehensive studies on alkalinity with the same constituents listed in Table 3.3. Two sets of studies were carried out, one with synthetic water treated with UV photolysis and the other with UV/H_2O_2. Bromide ion was not added to the water prior to irradiation because the factorial experiments indicated that

chlorinated PCDBPs was expected to follow the same trend as their brominated counterparts. As described in Section 4.6, both brominated and chlorinated PCDBPs followed the same trend wherever alkalinity was statistically significant in treatment with either UV photolysis or UV/H_2O_2 followed by chlorination.

In the factorial experiments, two levels of alkalinity 0 and 200 mg/L as $CaCO_3$ were used while 100 mg/L as $CaCO_3$ was calculated as center point for analysis of variance. For the single factor experiments, alkalinity was varied from 0 to 250 mg/L as $CaCO_3$, with an interval of 50 mg/L as $CaCO_3$ in order to observe the trend of alkalinity between and beyond the range originally chosen for the factorial experiments. The other factors pH and UV-fluence were kept constant at 8 and 1000 mJ/cm^2, respectively. The pH value was chosen base on the mean pH value of the Mannheim treatment plant while 1000 mJ/cm^2 for UV-fluence was chosen based on the irradiation time (1 hr 20 min) which is shorter compared to those of the other UV-fluence values used in the factorial experiment.

5.2.1 Variation of Alkalinity with UV Photolysis

Alkalinity was varied from 0 to 250 mg/L as $CaCO_3$ with each experiment carried out in duplicate. After irradiation of the water samples, 4 mg/L of NaOCl was added to the water samples, as explained in Chapter 3, leaving a mean free chlorine residual of 1.69 mg/L ± 0.2 and a mean chlorine demand of 2.31 mg/L ± 0.2. After quenching the residual chlorine with sodium thiosulphate, the PCDBPs were extracted from the water samples and the extracts from the liquid-liquid extraction processes were analyzed in triplicate in the GC/ECD.

Haloacetic Acids

Dichloroacetic acid and trichloroacetic acid were the only HAA species formed in this set of experiment. The trend of these compounds as they vary with different levels of alkalinity when synthetic water was treated with UV photolysis followed by chlorination is shown in Figure 5.1. The error bars in the figure depict the standard deviation of various points on the curve.

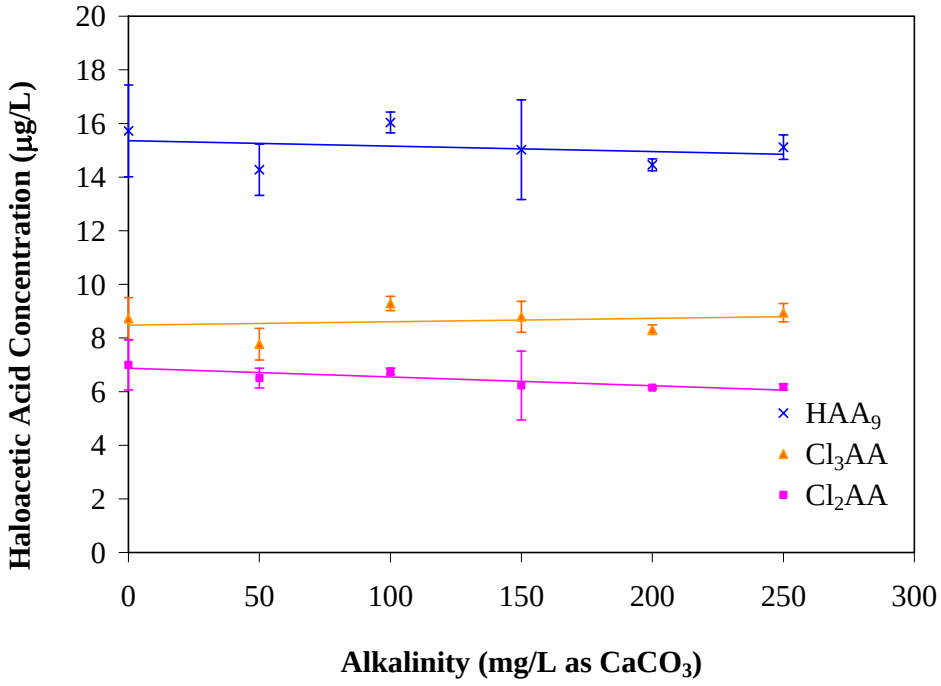

Figure 5.1 Effect of Alkalinity on HAAs When Treated with UV Photolysis Followed by Chlorination (pH 8, UV-Fluence 1000 mJ/cm^2, error bars= standard deviation).

A linear model applied to dichloroacetic acid (Cl_2AA) data was statistically significant at 5 % significance level with a coefficient of determination $R^2 = 0.77$. According to Duever (2003), the coefficient of determination is a ratio that indicates the percent of the variation that is explained by the model. The closer the coefficient is to 1, the more

adequately the model explains the data. The linear model applied to Cl_2AA seems to explain the data well, whereas this is the opposite for Cl_3AA and HAA_9, the total concentration of HAA species.

From the linear model applied to Cl_2AA, Cl_3AA and HAA_9, summarized in Table 5.1, one can tell that the slopes of the lines are very small. This suggests that there was little change associated with the yield of both compounds as alkalinity was varied from 0 to 250 mg/L as $CaCO_3$. Generally, as alkalinity was increased the formation of Cl_2AA decreased with a linear slope of 0.0033, Cl_3AA increased with a gentle slope of 0.0013 while HAA_9 decreased with a slope of 0.0020.

Trichloroacetic acid and the total concentration of HAA species (HAA_9) were not statistically significant at the 5 % significance level. This is also indicated by their *p*-values in Table 5.1. The probability value, also known as *p*-value, is the probability of obtaining a test statistic value more extreme than that obtained by chance if the null hypothesis is true (Tulley and Dubuc, 2002). The *p*-value is usually compared with the significance level of the test statistic and if the calculated *p*-value is less than the significant level, the result is said to be statistically significant. For the purposes of this research, the significance level used was 5% which can also be reported as a *p*-value =0.05. The use of p-values in this section was not only to determine the significance of the model applied to some data but mainly to indicate the closeness of the result to the significance level especially if the result was not statistically significant.

Table 5.1 Linear Models for Chlorinated HAAs Resulting from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV Photolysis

	Slope	Intercept	F_{obs}	$F_{1,4,0.05}$	R^2	*p*-value
Cl_2AA	-0.0033	6.87	13.4	7.71	0.77	0.023
Cl_3AA	+0.0013	8.48	0.18	7.71	0.04	< 0.25
HAA_9	-0.0020	15.4	0.32	7.71	0.07	< 0.25

Haloacetonitriles

Dichloroacetonitrile (Cl_2AN) was the only species of the HANs that was formed and it was formed in relatively low quantities than the HAAs and THMs. From Figure 5.2 and Table 5.2 it can be observed that the concentration of Cl_2AN increased with increase in alkalinity. This observation is confirmed by the positive slope of the linear model applied. In this case, as also with the haloacetic acids, the slope of the model was small implying that there was a small amount in the increase in concentration. The linear model applied to the data is insignificant at 5 % significance level but the appropriate p-value = 0.24. The linear model does not describe the Cl_2AN data adequately because the model was not statistically significant at 5 % significance level. This does not guarantee that as alkalinity is increased from 0 to 250 mg/L as $CaCO_3$ the concentration of Cl_2AN was not increased but that the linearity of the data cannot be confirmed from the available data. Figure 5.2 shows the linear trend applied to the data including the standard deviation at each point represented by the error bars.

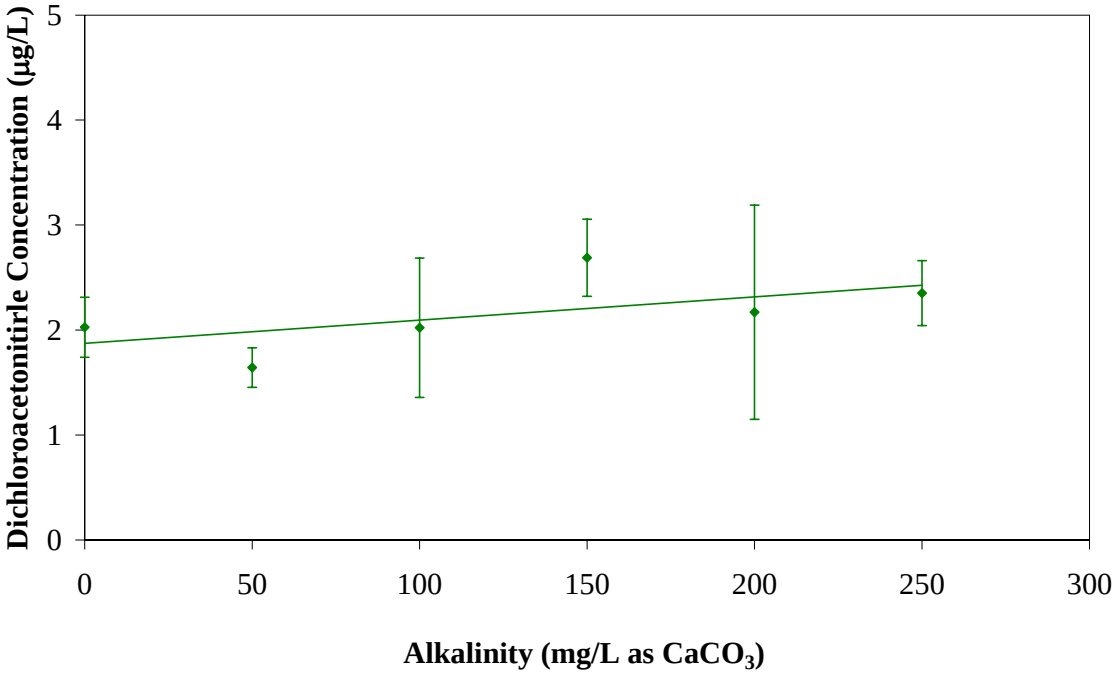

Figure 5.2 Effect of Alkalinity on Cl_2AN in Chlorination of Synthetic Water Following UV Photolysis (pH 8, UV-Fluence 1000 mJ/cm^2 Error bars = standard deviation).

Table 5.2 Statistical Analysis of Cl_2AN from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV Photolysis

Model: Concentration = 0.0022 x Alkalinity + 1.87

Source	df	SS	MS	F_{obs}	$F_{1,4,0.05}$	R^2	*p*-value
Regression	1	0.208	0.208	2.01	7.71	0.34	0.24
Error	4	0.413	0.103				
Total	5	0.602					

Trihalomethanes

For trihalomethanes, chloroform was the only compound formed. Figure 5.3 shows an increasing trend in the concentration of chloroform as alkalinity was increased from 0 to 250 mg/L as $CaCO_3$. This is confirmed by the positive slope of the linear model applied to the data illustrated in Table 5.3.

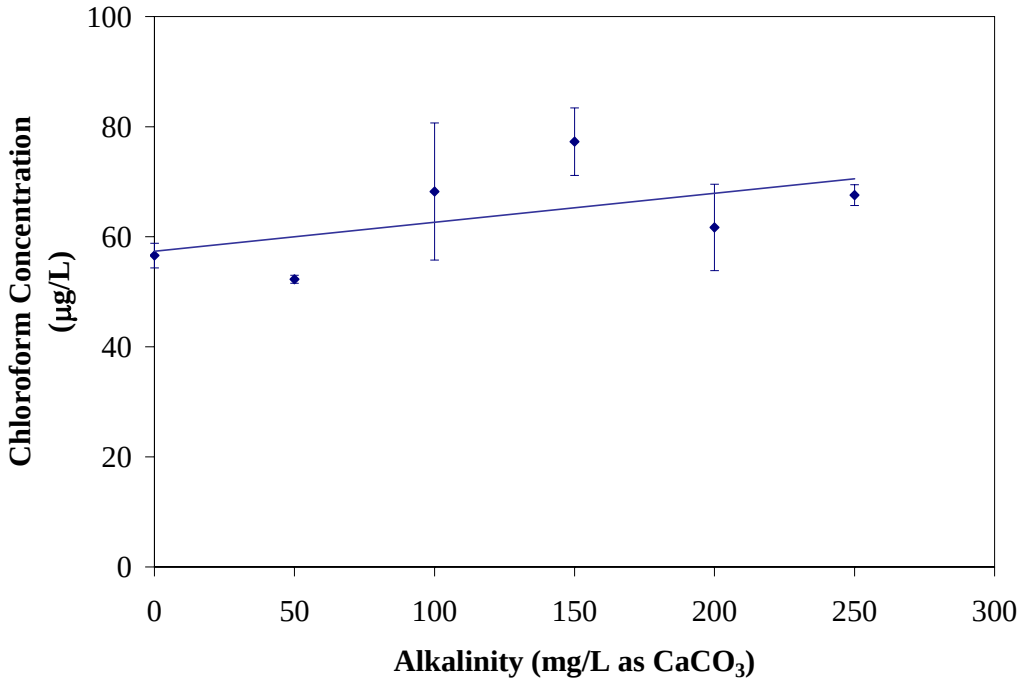

Figure 5.3 Effect of Alkalinity on $CHCl_3$ in the Chlorination of Synthetic Water Following UV Photolysis (pH 8, UV-fluence 1000 mJ/cm^2 error bars = standard deviation).

From Table 5.3 the linear model fitted to the data was not statistically significant at 5% significance level. The p-value for this model is slightly less than 0.25 i.e. $p < 0.25$. This does not guarantee that as alkalinity is increased from 0 to 250 mg/L as $CaCO_3$ the concentration of chloroform was not increased but that from the available data, the

linearity of the data cannot be confirmed. The insignificance of the model applied to the data may also be due to the scatter in the data, indicated especially at points 100, 150 and 200 mg/L as $CaCO_3$. At these points, the standard deviations indicated by the error bars were larger than those at the other alkalinity values. Though the data could not be fitted to a linear regression, a polynomial may fit but there is no literature backing that the relationship between chloroform concentration and alkalinity is in polynomial form.

Table 5.3 Statistical Analysis of Chloroform from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV Photolysis

Model: Concentration of $CHCl_3$ = 0.053 x Alkalinity + 57.4

Source	df	SS	MS	F_{obs}	$F_{1,4,0.05}$	R^2	*p*-value
Regression	1	121	121	1.72	7.71	0.31	$p<0.25$
Error	4	282	70.7				
Total	5	404					

5.2.2 Variation of Alkalinity with UV/H_2O_2

Synthetic water was also used in this set of experiments. It was treated in the same way as with UV photolysis except that a mean concentration of 11.7 mg/L ± 0.3 of hydrogen peroxide was added to each sample before irradiation. The mean hydrogen peroxide demand was 4.89 mg/L ± 0.3. After irradiation, 4 mg/L± 0.2 of NaOCl was added to each irradiated water sample. The mean chlorine demand was 2.20 mg/L± 0.2 leaving a 24 hr chlorine residual of 1.80 mg/L ± 0.2. Extracts from the liquid-liquid extraction procedure applied to the water samples were analyzed by GC/ECD for PCDBP concentrations.

Haloacetic Acids

Dichloroacetic and trichloroacetic acids were formed in about the same quantities. The negative slopes in Figure 5.4 and Table 5.4 show that there was a reduction in both concentrations as alkalinity was varied from 0 to 250 mg/L as $CaCO_3$. The linear models applied to both compounds in this case were not significant at 95 % and both have *p*-values less than 0.25. The error bars in the figure indicate standard deviations at the various alkalinity values

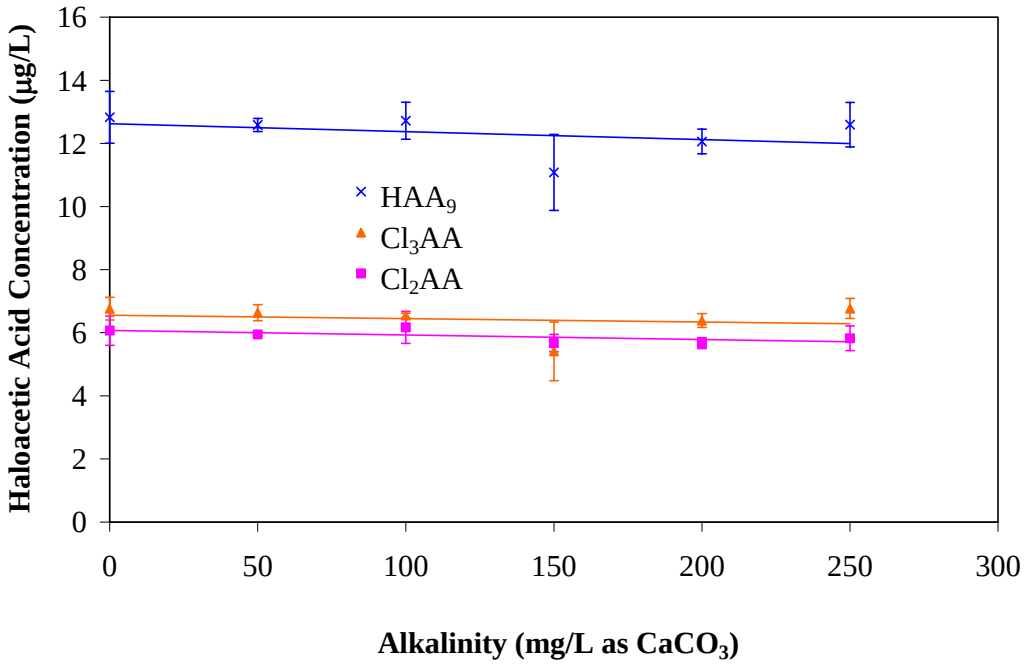

Figure 5.4 Effect of Alkalinity on Chlorinated HAAs in the Chlorination of Synthetic Water Following UV/H_2O_2 (pH 8, UV-fluence 1000 mJ/cm^2 error bars = standard deviation).

Table 5.4 Linear Models for Chlorinated HAAs Resulting from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV/ H_2O_2

	Slope	Intercept	F_{obs}	$F_{1,4,0.05}$	R^2	*p*-value
Cl_2AA	-0.0014	6.07	1.73	7.71	0.30	$p<0.25$
Cl_3AA	-0.0011	6.55	0.15	7.71	0.04	$p<0.25$
HAA_9	-0.0025	12.6	0.58	7.71	0.13	$p<0.25$

Haloacetonitriles

Applying a linear model to dichloroacetonitrile data revealed a possibly, very small reduction in concentration as alkalinity was increased. The linear model was found to be significant at a *p*-value of 0.18, but not at the 5 % significance level as can be seen in Table 5.5, where the $F_{observed}$ is less than the $F_{critical}$. The error bars representing the standard deviations at various points on the curve reveal a scatter in the data. The scatter is possibly due to low formation of in Cl_2AN.

Table 5.5 Statistical Analysis of Cl_2AN from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV/H_2O_2

Model: Concentration of Cl_2AN = -0.0017 x Alkalinity + 2.27

Source	df	SS	MS	$F_{observed}$	$F_{1,4,0.05}$	R^2
Regression	1	0.272	0.272	3.06	7.71	0.43
Error	4	0.356	0.089			
Total	5	0.628				

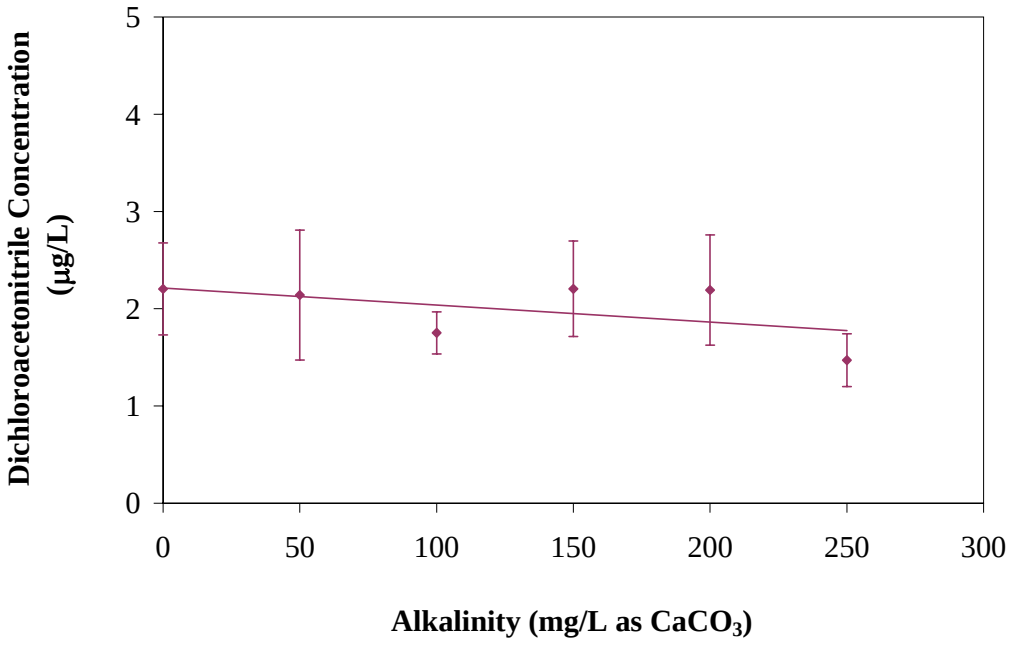

Figure 5.5 Effect of Alkalinity on Cl_2AN When in Chlorination of Synthetic Water Following UV/H_2O_2 (pH 8, UV-Fluence 1000 mJ/cm^2 error bars = standard deviation).

Trihalomethanes

The raw chloroform data, plotted in Figure 5.6, may be better fitted to a log model than a linear one; therefore the log concentration of the raw data was plotted against the alkalinity values giving a coefficient of determination of 0.82. This resulted in a statistically significant model at 5 % significance level with *p*-value = 0.014. The negative slope of the model in Table 5.6 shows that there was a reduction in the log concentration of chloroform as alkalinity was increase from 0 to 250 mg/L as $CaCO_3$.

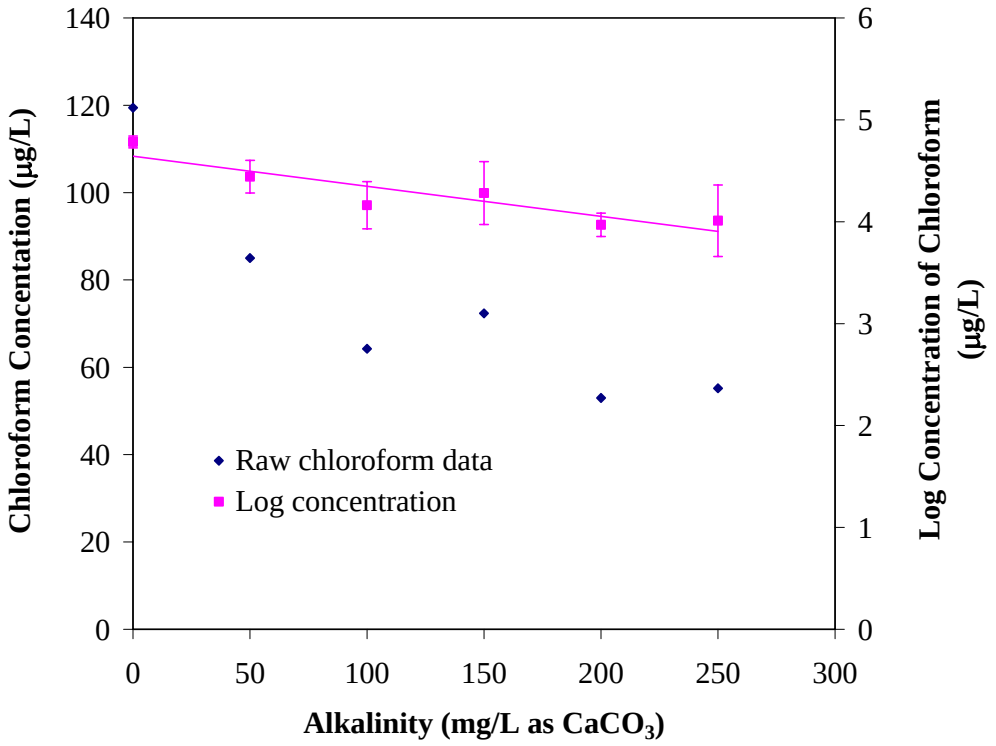

Figure 5.6 Effect of Alkalinity on $CHCl_3$ Concentration in Chlorination of Synthetic Water Following UV/H_2O_2 (pH 8, UV-Fluence 1000 mJ/cm^2 error bars = standard deviation)**.**

Table 5.6 Statistical Analysis of Chloroform Formation from Alkalinity Variation in Synthetic Water Treated with Chlorine Following UV/H_2O_2

Model: Log Concentration of Chloroform= -0.00295 x Alkalinity + 4.64

Source	df	SS	MS	$F_{observed}$	$F_{1,4,0.05}$	R^2	p-value
Regression	1	0.380	0.380	18.7	7.71	0.82	0.014
Error	4	0.081	0.020				
Total	5	0.462					

5.3 Comprehensive Studies on pH

One of the factors used in the 2^3 factorial experiments was pH and the two levels were 6 and 8. A pH of 7.7 was used as a center point, which is the midpoint for the hydroxyl ion concentration measured as pH. The factor pH was found to be statistically significant in the analysis of variance of the factorial experiment data, with pH increases during either UV photolysis or UV/H_2O_2 treatment causing a reduction in PCDBP concentrations.

Water from the post-filtration step of the Mannheim water treatment plant (MWTP) in Kitchener, Ontario, Canada was used in order to apply the results of the factorial experiment to a natural source. As explained in Chapter 3, the composition of the synthetic water was modeled according to the water from the post-filtration step of the MWTP; the only difference was the composition of natural organic matter of the source water for the treatment plant. Some water parameters of the post-filtration step of the MWTP as measured at the University of Waterloo are given in Table 5.7.

Table 5.7 Water Parameters of the Post-Filtration Step of the MWTP, Kitchener Ontario Analyzed at the University of Waterloo

Parameter	Concentration
Total Alkalinity	158 mg/L as $CaCO_3$
Total Hardness	256 mg/L as $CaCO_3$
pH	7.81
Bromide Ion	46 μg/L
TOC	4.4 mg/L

The water collected from the treatment plant was sampled from one post-filter point to avoid any form of variation. Also, the same batch of water from the treatment plant was used for the sets of experiments carried out to enable easy comparison and avoid day to day variation of the water composition.

There were two sets of experiments carried out with pH variation. The first set involved the use of water from the post–filtration step of the MWTP "as is", i.e. without the addition of bromide ion. Secondly, bromide ion was added to another set of samples in the form of sodium bromide in order to observe the effect of pH on brominated PCDBPs. The AOP, UV/H_2O_2, was used as the treatment process for both sets of experiments because the comparison made in Section 4.6 showed that a greater reduction of PCDBPs occurred with AOP than with UV photolysis. This was also confirmed by Senogles et al. (2001) and Doong et al. (2001).

UV-fluence was kept constant at 1000 mJ/cm^2 and there was no added alkalinity to that which was present in the water originally as shown in Table 5.7. The pH levels of 6 and 8 that were used in the factorial experiments were expanded in the pH comprehensive studies to involve varying the pH from 5 to 9 with an interval of one pH unit. The variation was achieved with the use of 0.1M H_2SO_4 and 0.1M NaOH to obtain an acidic or alkaline pH as the case may be.

5.3.1 Effect of pH on Chlorinated PCDBPs

The first set of pH experiments with water from the post-filtration step of the MWTP was carried out to study chlorinated PCDBPs (i.e. no bromide ion was added). Brominated PCDBPs were also formed but in smaller quantities than the chlorinated ones because the concentration of bromide ion in the water was approximately 46 μg/L ± 1.

A mean concentration of 13.0 mg/L± 0.2 of hydrogen peroxide was added to each water sample before irradiation and the mean peroxide demand was 4.85 mg/L ± 0.4. After irradiation, 12 mg/L ± 0.6 of NaOCl was added to each treated water sample. The mean chlorine demand was 6.27 mg/L ± 0.6. Extracts from the liquid-liquid extraction procedure applied to the water samples were then analyzed in the GC/ECD for PCDBP concentrations.

There was a higher chlorine demand for irradiated water from the MWTP than for synthetic water. This may be due to the composition of NOM in the source water for the MWTP. Considering the fact that the NOM used for the synthetic water was obtained from the Suwannee River, Ohio in the United States of America, the composition of the NOM from MWTP is likely to have been different from that of synthetic water. There may also have been differences in inorganic composition of the MWTP water relative to synthetic water even though the make-up of the synthetic water was based on historical mean concentrations of its major inorganic ions.

Haloacetic Acids

The compounds, Cl_2AA and Cl_3AA, were the only species of HAAs formed as pH was varied from 5 to 9 when the post-filtered water from the MWTP was treated with chlorine following UV/H_2O_2. The trend of the concentration of the HAA species, Cl_2AA and Cl_3AA are illustrated in Figure 5.7. It is obvious from the figure that there is a reduction in concentration for both compounds and the total HAA species as pH was increased from 5 to 9 during UV/H_2O_2. The error bars indicate the standard deviation at each point of the curve.

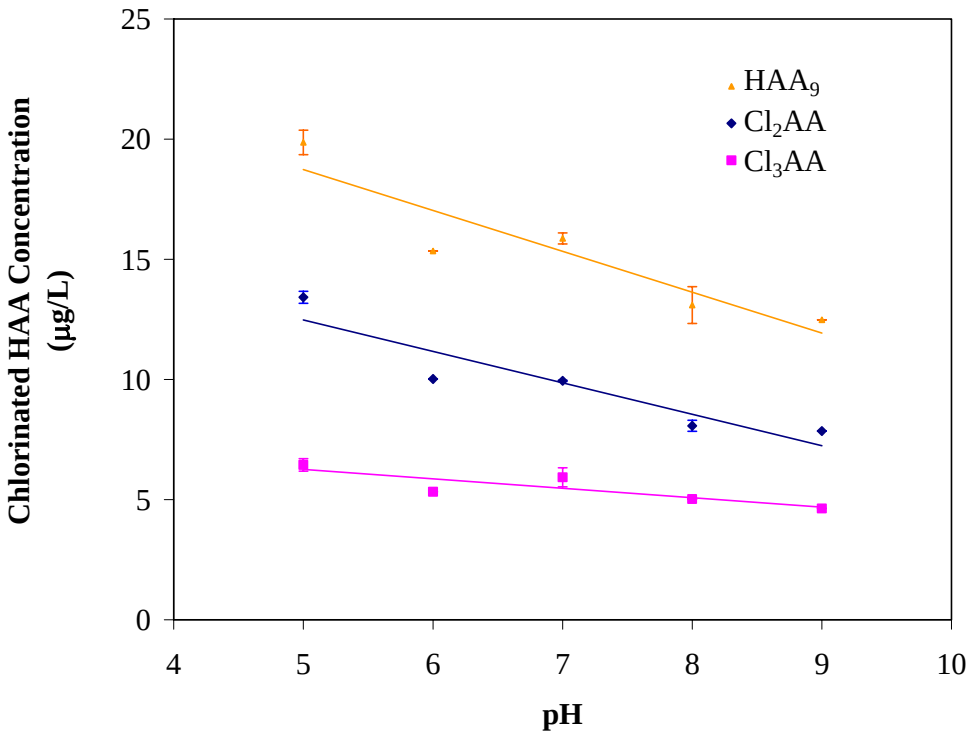

Figure 5.7 Effect of pH on Chlorinated HAAs in the Chlorination of Post-Filtered River Samples Following UV/H_2O_2 (UV-Fluence 1000 mJ/cm^2, Added Alkalinity 0 mg/L as $CaCO_3$ Error bars = standard deviation).

Applying a linear model to both of the compounds (Table 5.8) showed that the linear model for Cl_2AA was statistically significant at 5 % significance level with a coefficient of determination R^2 of 0.86. Although the linear model applied to Cl_3AA was not found to be statistically significant at the 5% significance level, it was significant at the 10 % significance level with a *p*-value = 0.064 and R^2 = 0.74. The total concentration of HAA species, HAA_9, was statistically significant at 5 % significance level with an R^2 of 0.85.

Table 5.8 Linear Models for Chlorinated HAAs Resulting from pH Variation in Post-Filtered River Samples Treated with Chlorine Following UV/ H_2O_2

	Slope	Intercept	F_{obs}	$F_{1,3,0.05}$	R^2	*p*-value
Cl_2AA	-1.83	22.7	18.2	10.1	0.86	0.023
Cl_3AA	-0.393	8.22	8.56	10.1	0.74	0.061
HAA_9	-1.70	27.2	17.4	10.1	0.85	0.025

Haloacetonitriles

Dichloroacetonitrile (Cl_2AN) was the only compound of the HANs that was formed with water from the post filtration step of the MWTP. The concentration of Cl_2AN was small relative to the concentrations of HAAs and THMs. The trend of this compound was also different from those of the HAAs. At pH 6, the concentration of Cl_2AN was higher than the other concentrations while a reduction in Cl_2AN concentration occurred between pH 6 and 9. It should be noted that the concentrations of Cl_2AN that were measured in this experiment were very low as so may be associated with a larger relative error. The higher value at pH 6 might be anomalous as there is no literature to indicate why it might be valid. Alternatively, a lower value at pH 5 could also be anomalous. Therefore in

consideration of both possibilities, a log linear model was fitted to the data from pH 6 to 9 and a linear model from pH 5 to 9, ignoring the concentration at pH 6 as shown in Figure 5.8. Although Table 5.9 indicates that the models fitted to the data were not significant at 5 % significance level, the negative slopes of the lines do show that a reduction occurred in the formation of Cl_2AN. The standard deviations represented by the error bars at pH 7 and 8 are higher than at other pH values, Extreme points of these error bars could still create a reduction in the linear trend applied to the data.

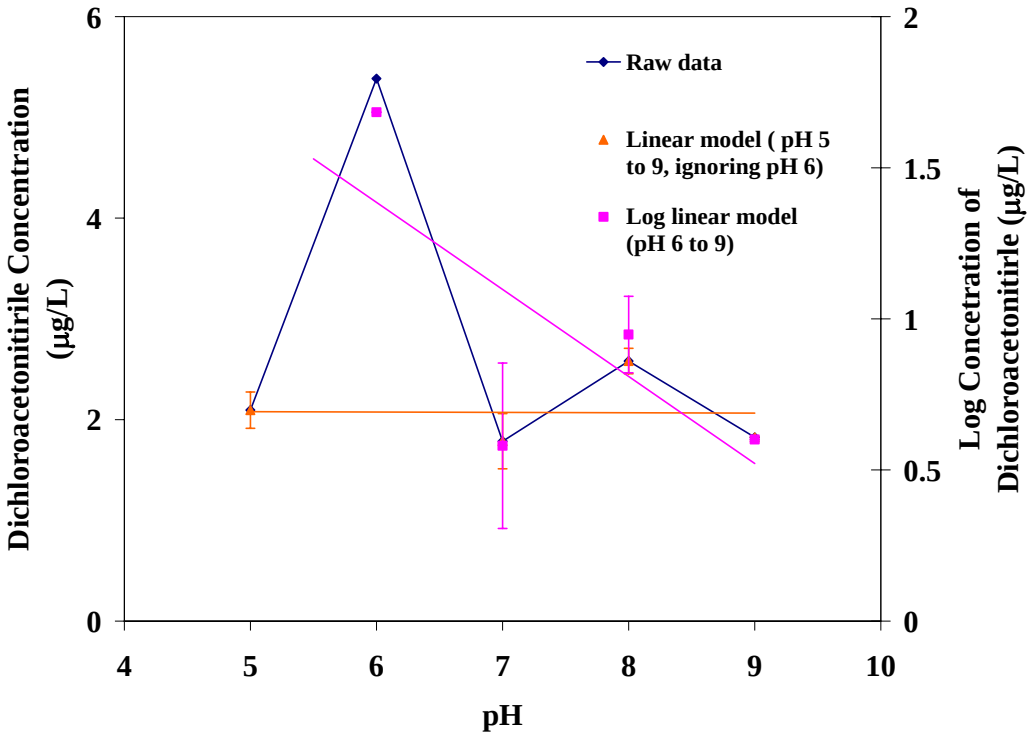

Figure 5.8 Effect of pH on Cl_2AN in the Chlorination of Post-filtered River samples Following UV/H_2O_2 (UV-Fluence 1000 mJ/cm^2, Added Alkalinity 0 mg/L as $CaCO_3$ Error bars = standard deviation,).

Table 5.9 Linear Models for Cl_2AN Resulting from pH Variation in Post-Filtered River Samples Treated with Chlorine Following UV/ H_2O_2

Cl_2AN	Slope	Intercept	F_{obs}	$F_{1,2,0.05}$	R^2	*p*-value
pH 6 to 9	-0.288	3.113	2.17	18.51	0.52	p<0.25
pH 5 to 9 (ignoring pH 6)	-0.0052	0.755	0.0055	7.71	0.003	p<0.25

Trihalomethanes

As with Cl_2AN, at pH 6, the concentration of $CHCl_3$ was also higher than the other concentrations while a reduction in the $CHCl_3$ concentration occurred between pH 6 and 9. This implies that a linear model would not be appropriate for the data. From Figure 5.9, a reduction is observed from pH 6 to 9, also from 5 to 9 (ignoring pH 6).

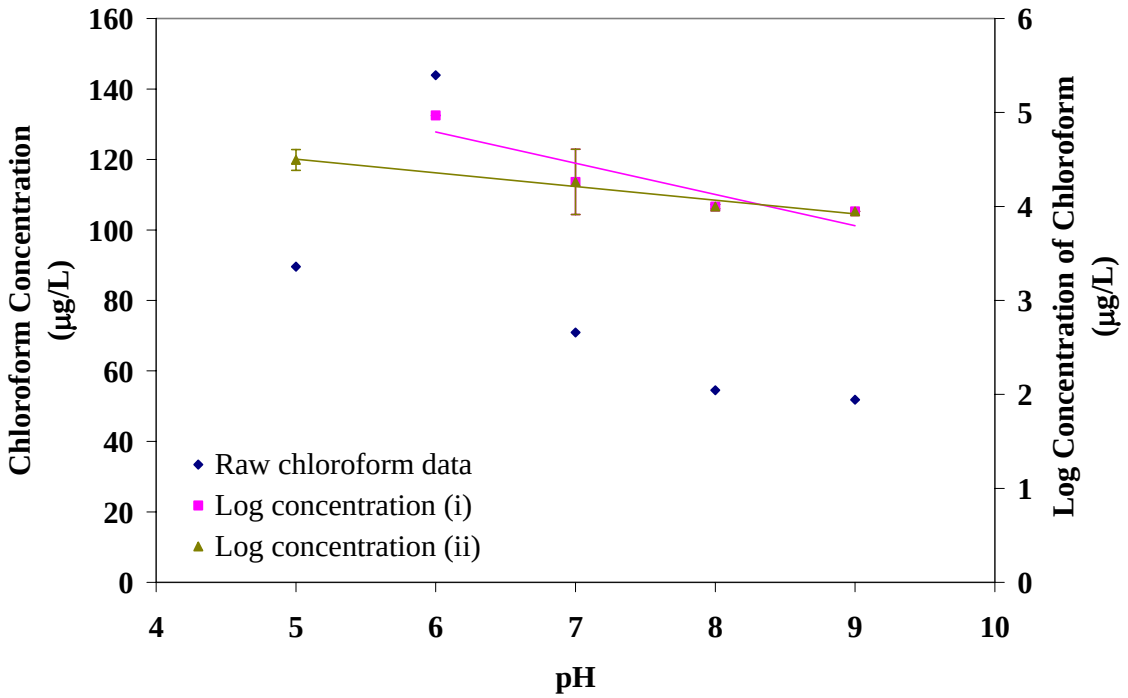

Figure 5.9 Effect of pH on $CHCl_3$ in the Chlorination of Post-Filtered River Samples Following UV/H_2O_2 (UV-Fluence 1000mJ/cm^2, Added Alkalinity 0 mg/L as $CaCO_3$ Error bars = standard deviation).

Applying linear models to the log concentration of $CHCl_3$ from pH 6 to 9 and pH 5 to 9 (ignoring pH 6) gave negative slopes as indicated in Table 5.10. This showed that the log concentration of $CHCl_3$ decreased linearly as pH was increased from 6 to 9. The coefficient of determination of the model applied to the log concentration of chloroform from pH 6 to 9 is 0.83. The model was not significant at 5% significance level but it was significant at 10% significance level with a p-value of 0.087. On the other hand, the linear model applied to the log concentration of $CHCl_3$ concentration from pH 5 to 9 (ignoring pH 6) was statistically significant at 5% significance level. The error bars applied to the curves in figure 5.9 represent standard deviations at various points on the log linear curves.

Table 5.10. Linear Models for $CHCl_3$ Resulting from pH Variation in Post-Filtered River Samples Treated with Chlorine Following UV/ H_2O_2

$CHCl_3$	Slope	Intercept	Fobs	$F_{1,2,0.05}$	R^2	*p*-value
pH 6 to 9	-0.333	6.79	10.01	18.51	0.83	0.087
pH 5 to 9 (ignoring pH 6)	-0.288	5.12	47.3	18.51	0.95	0.02

5.3.2 Effect of pH on Brominated PCDBPs

This set of experiment is similar to the one described in Section 5.3.1 except that 500 μg/L of sodium bromide was added to the water in order to enhance the production of the brominated PCDBPs. A mean concentration of 12.7 mg/L ± 0.3 of hydrogen peroxide was added to the water prior to irradiation resulting in a mean demand of 4.57 mg/L ± 0.6. Chlorinated HAAs & THMs were formed during this experiment and they followed

the same trends as in the experiments discussed in Section 5.3.1. No chlorinated or brominated HANs was observed in this set of experiments.

Haloacetic acids

All six brominated HAA species were observed in this experiment. From Figure 5.10, the compounds BrAA, BrClAA and Br_2AA followed the same trend, as pH was increased from 5 to 9 causing a reduction in the concentration of the compounds. The error bars indicated in the figure represents standard deviation. Table 5.11 shows that the linear model applied to all of these three compounds except for BrAA were statistically significant at the 5 % significance level. Bromoacetic acid on the other hand was significant at 10% significance level with a *p*-value = 0.068

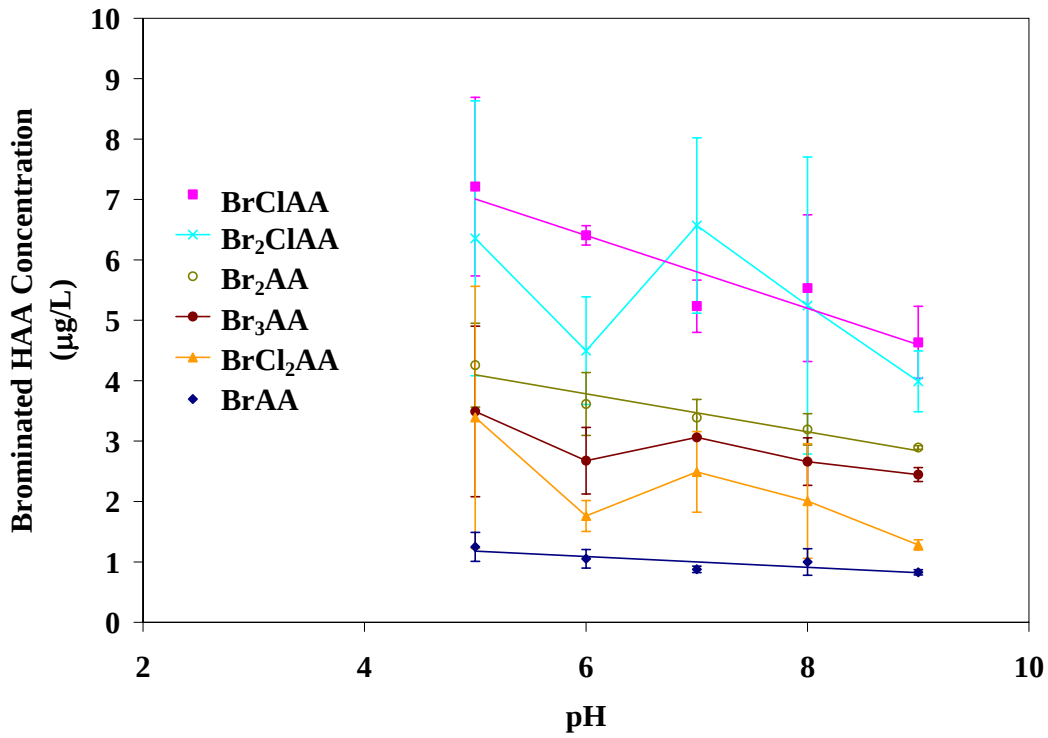

Figure 5.10 Effect of pH on Brominated HAAs in the Chlorination of Post-Filtered River Samples Following UV/H_2O_2 (UV-Fluence 1000 mJ/cm^2, Added Alkalinity 0 mg/L as $CaCO_3$ (Error bars =standard deviation)

Table 5.11 Linear Models Applied to Brominated HAAs Obtained from Chlorinating Post-Filtered River Samples Following UV/ H_2O_2.

Analysis including all data	Slope	Intercept	R^2	*p*-value	F_{obs}	$F_{1,3,0.05}$
BrAA	-0.089	1.624	0.73	0.065	8.13	10.1
BrClAA	-0.603	10.026	0.88	0.017	22.8	10.1
Br_2AA	-0.341	5.907	0.98	0.001	146	10.1
Analysis ignoring data at pH 6	Slope	Intercept	R^2	*p*-value	F_{obs}	$F_{1,2,0.05}$
$BrCl_2AA$	-0.515	6.03	0.99	0.006	154	18.5
Br_2ClAA	-0.575	9.71	0.69	0.17	4.36	18.5
Br_3AA	-0.268	4.86	0.98	0.008	126	18.5

A low concentration was observed at pH 6 for compounds Br_2ClAA, $BrCl_2AA$ and Br_3AA. This might have been due to the integration process of the GC/ECD for these compounds. Applying a linear model to the whole data would result in a low R^2 value and a statistically insignificant model at 5 % significance level. Since analytical error was strongly suspected to have influenced the results obtained at pH 6, a linear model was therefore applied to the data from pH 5 to 9, ignoring pH 6. The negative slopes of the linear models show that there was a reduction in these compounds from pH 5 to 9 (ignoring pH 6). The linear models applied from pH 5 to 9 (ignoring pH 6) for $BrCl_2AA$ and Br_3AA were statistically significant at 5 % significance level while that of Br_2ClAA was not found to be statistically insignificant at 5 % significance level with a *p*-value=0.17. This does not imply that the model applied to Br_2ClAA was not linear from pH 5 to 9, ignoring the data at pH 6, but due to the number of degrees of freedom, the reduction cannot be confirmed beyond the *p*-value given.

Trihalomethanes

The four trihalomethane compounds ($CHCl_3$, $BrCl_2CH$, $ClCHBr_2$ and $CHBr_3$) comprising the total concentration of the trihalomethanes (TTHMs) followed the same trend as observed in Figure 5.11. A low concentration was observed at pH 6 which is different from the chloroform trend shown in Figure 5.9 when bromide ion was not added to the water sample. The difference in trend might have been due to analytical error. Due to this, the experiments were repeated from pH 5 to 7. These points were the only points repeated as opposed to the whole experiments because from pH 7 to 9 in both Figures 5.9 and 5.11 a reduction was observed in the concentration of chloroform.

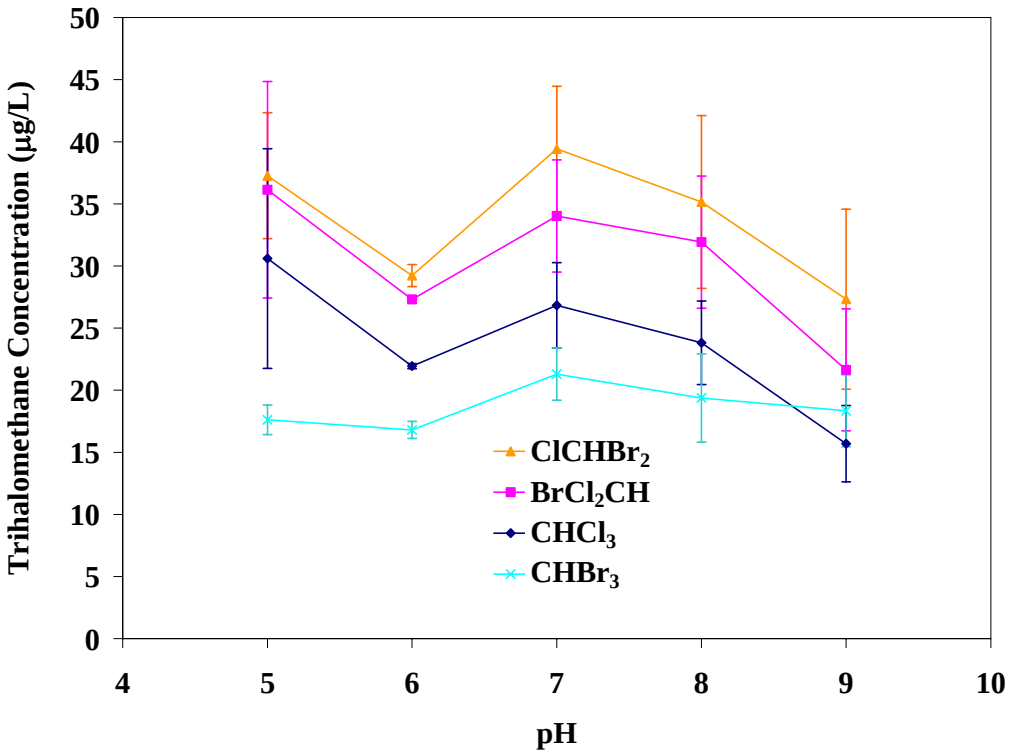

Figure 5.11 Effect of pH on THMs from Chlorination of Post-Filtered River Samples Following UV/H_2O_2 (UV-Fluence 1000 mJ/cm^2, Added Alkalinity 0 mg/L as $CaCO_3$ Error bars =standard deviation)

The same batch of water was used in the repetition of these experiments, to avoid any form of variation. The repeated experiments at pH 5 to 7 are shown in Figure 5.12. From this figure, similar or higher concentrations than those at pH 5 and 7 occurred at pH 6 for chloroform and other THM compounds, following the same trend as in Figure 5.9, suggesting that the data obtained at pH 6 in the initial experiment was anomalous.

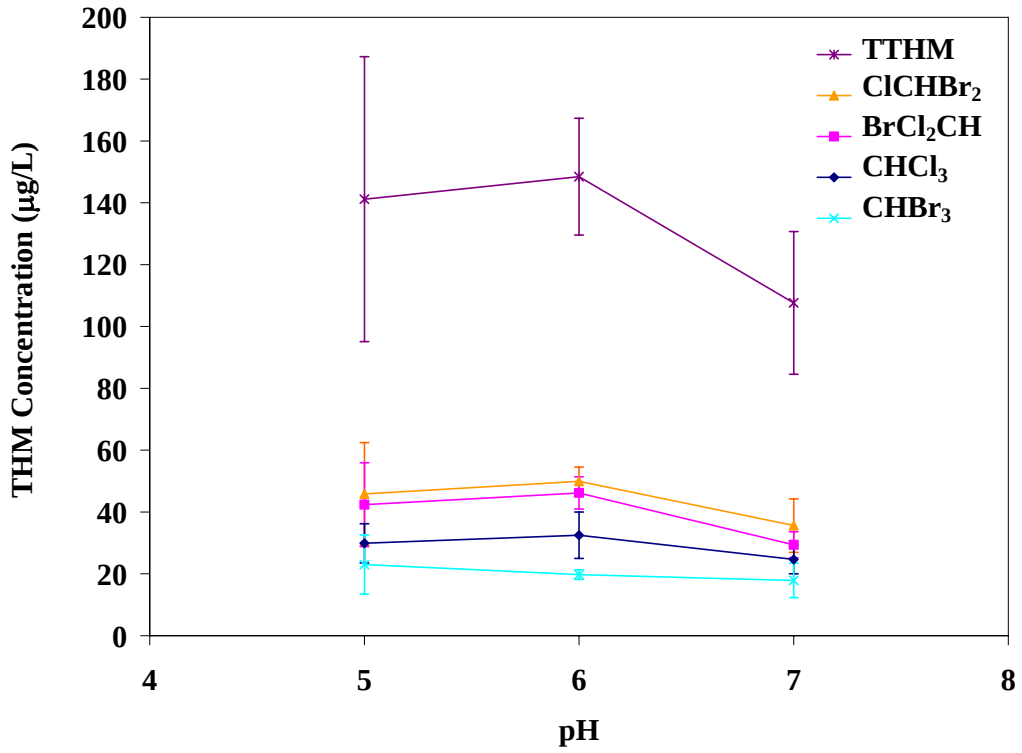

Figure 5.12 Repeat Experiments for pH 5, 6 and 7
(Error bars =standard deviation)

The data for pH 5 to 7 from Figures 5.11 and 5.12 were superimposed for comparison in Figure 5.13 which consists of chloroform and the total concentration of trihalomethanes (TTHMs) data. For chloroform, pH 5 and 7 coincide while there was an obvious difference in pH 6. For the TTHM data, there is a difference in pH 6 but the data for pH 5

did not coincide as much as it did for chloroform. Still, these results generally confirm the anomalous character of the data obtained initially at pH 6.

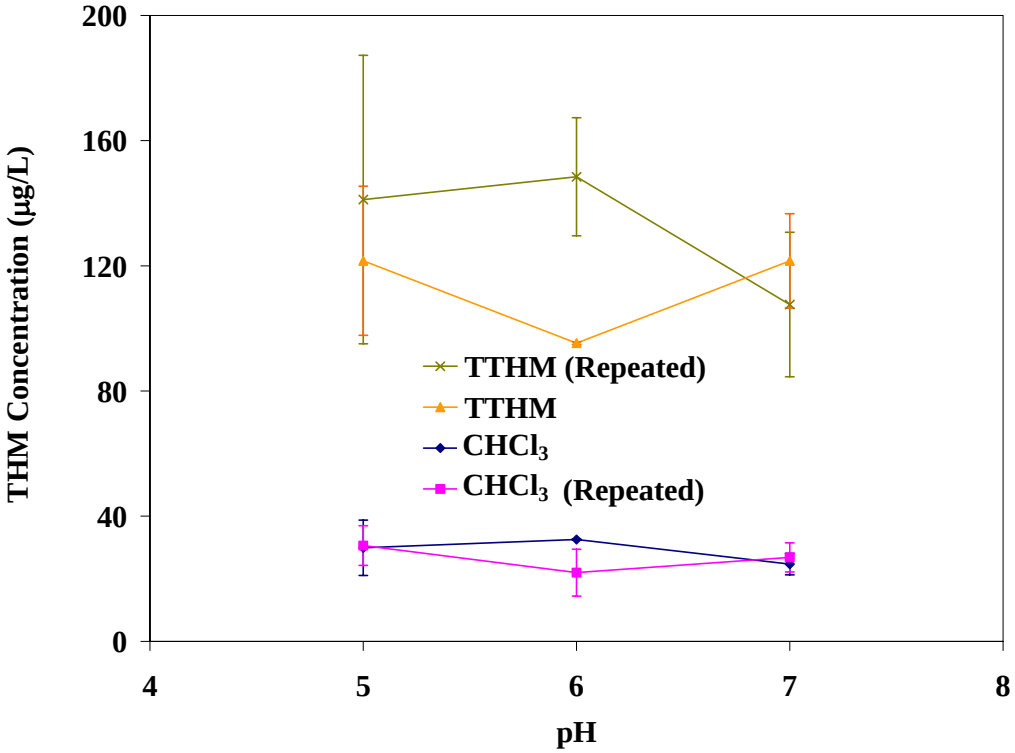

Figure 5.13 Comparison of Initial and Repeat Experiments for pH 5, 6 and 7 (Error bars =standard deviation)

In Table 5.12A, an F-test was used to determine whether differences existed between the variance of the initially performed experiments and the repeated ones. From the table, there were no significant differences in variance for the pH values except at pH 6.

A two-tailed student *t*-test in Table 5.12B was then used to determine the differences in the means of pH 5, 6 and 7 for the initially performed experiments and the repeated ones. The variances for pH 5 and 7 were pooled since the F-test confirmed that there were no statistically differences between the variances. The t_{obs} was therefore calculated according

to Equation 4.2. On the other hand, a statistical difference occurred between the variance at pH 6 for both repeated and initially performed experiments, therefore the t_{obs} was calculated according to Equation 4.1. For pH 5 and 7 the t_{obs} was less than 1 for both pH values, therefore it can be established that there are no differences between the means of pH 5 and 7 for the initial and repeated experiments. No difference was found for the means at pH 6 at 5 % significance level but it can be counted significant at 10% significance level and *p*-value = 0.062 This further confirms the possibility of an analytical problem at pH 6.

Table 5.12A Variance Comparison for Initial and Repeat Experiments for pH Studies

pH	5	5 (Repeat)	6	6 (Repeat)	7	7 (Repeat)
Mean(μg/L)	121.6	141.2	95.3	148.4	121.6	107.6
S^2	567.7	2123.5	0.2	355.9	227.6	533.1
F_{obs}	3.7		2078.7		2.3	
$F_{1,1,0.05}$	161.4		161.4		161.4	
Difference	No		Yes		No	

Table 5.12B Mean Comparison of Initial and Repeat Experiments for pH Studies

pH	5	5 (Repeat)	6	6 (Repeat)	7	7 (Repeat)
Mean(μg/L)	121.6	141.2	95.3	148.4	121.6	107.6
Difference in yield	19.6		53.2		13.9	
S_p^2/S^2	1346		0.2	355.9	380	
t_{obs}	0.015		3.983		0.037	
$t_{0.025,2}$	4.3		4.3		4.3	
Difference	No		No		No	

5.4 Summary of Comprehensive Studies

5.4.1 Alkalinity

For studies on alkalinity, a closer look at the Figures 5.1 and 5.4 for HAAs shows that there was little or no change in the concentration of HAAs as alkalinity was increased. The values of UV-fluence and pH were kept constant at 1000 mJ/cm^2 and 8 respectively for both treatments of UV photolysis and UV/H_2O_2 followed by chlorination.

Dichloroacetonitrile experienced an increase in concentration as alkalinity was increased when synthetic water was treated with chlorine following UV photolysis at a UV-fluence of 1000 mJ/cm^2 and a pH of 8. A decrease in concentration of Cl_2AN occurred with the UV/H_2O_2 treatment followed by chlorination while the values of UV-fluence and pH were kept constant at 1000 mJ/cm^2 and 8. Chloroform also had the same trend with UV photolysis and UV/H_2O_2 as with Cl_2AN i.e. an increase in concentration with UV photolysis and a decrease with UV/H_2O_2. As alkalinity was increased, both the bicarbonate and carbonate ions in the sample also increased. Since the OH radicals produced with UV photolysis is not as much as that of UV/H_2O_2, there is a possibility that bicarbonate and carbonate ions scavenged for the OH radicals, possibly reduced the amount of radicals left for oxidation of the NOM in the water sample in UV photolysis. This conformed to the experiments carried out by Beltran et al. (1993) in which bicarbonate ions scavenged for the OH radicals necessary for the degradation of atrazine. Since the addition of hydrogen peroxide to each water sample generates more OH radical than UV photolysis, alkalinity might not have had a significant scavenging effect on

Cl_2AN and $CHCl_3$. Also, the production of carbonate radicals, as studied by Mazeller et al. (2002), might have been formed possibly aiding in the reduction of these PCDBPs.

5.4.2 pH

All PCDBPs experienced a decrease in concentration especially between pH 7 and 9 as added alkalinity and UV-fluence were kept constant at 0 mg/L as $CaCO_3$ and 1000 mJ/cm^2 respectively. Some compounds experienced a high or low concentration at pH 6 creating a peak or valley in the trend of the PCDBPs in question at pH 6. The compounds Cl_2AA, Cl_3AA, BrAA, BrClAA, and Br_2AA experienced a linear reduction from 5 to 9 while the other PCDBPs had either a low or high concentration at pH 6. This created a difficulty in the application of a linear model from 5 to 9 for these compounds. The linear model was therefore applied from either pH 5 to 9 (ignoring pH 6) or pH 6 to 9. The reduction in PCDBPs as pH was increased conformed with the factorial experiment results in which a reduction occurred for all compounds that had pH has a statistically significant factor. The results also conformed to the findings of Zhao et al. (2004) who found that the degradation of pyridine with UV irradiation in the presence of TiO_2 suspensions is higher at pH > 7 than at acidic pHs between 5 and 7.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 General Conclusions

The main purpose of this research was to determine the effects of alkalinity, pH and UV-fluence on the formation of post-UV chlorination disinfection by-products (PCDBPs), HAAs, HANs and THMs. The studies involved a 2^3 factorial experiment with pH, alkalinity and UV-fluence as the main factors. A comprehensive study on alkalinity and pH was carried out with the aid of single factor experiments. These results were discussed in Chapters 4 and 5 and a few conclusions can be drawn.

The factorial experiments proved that the use of UV irradiation, and the AOP, UV/H_2O_2 can reduce PCDBPs through the degradation of their precursors. In all the various sets of factorial experiments, a reduction always occurred in the formation of the PCDBPs as UV-fluence was increased. Of the treatments studied UV photolysis and UV/H_2O_2, the AOP, UV/H_2O_2, proved to be the most effective in the degradation of the PCDBP precursors causing a reduction in concentration of the PCDBPs. In all the factorial experiments, the effect of UV-fluence was always greater than the other factors and interactions.

Dichloroacetonitrile (Cl_2AN) was the only HAN formed in the whole set of experiments. In the treatment of synthetic water with UV photolysis, Cl_2AN had no statistically significant main factor or interaction. Single factor experiments carried out at a pH of 9 consumed more hydrogen peroxide than the experiments carried out at other pH values. A greater reduction in PCDBP also occurred at pH 9 in the single factor experiments than at other pH values. Total concentration of chlorinated THMs and HAAs were less than the interim maximum acceptable concentration (IMAC) proposed by Environment Canada. However, a potential concern exists when brominated compounds are included in the total concentrations, especially for THMs, as the IMAC of 100 μg/L was exceeded at a UV-fluence of 1000mJ/cm^2 in the factorial experiments in which bromide ion was present.

6.1.2 Effect of Alkalinity on PCDBPs

In the factorial experiments, alkalinity was a statistically significant factor a number of times and was also in interaction with other factors. Neither the brominated or chlorinated THMs had alkalinity as a statistically significant factor, either as a main factor or in interaction with other factors, for both treatments of UV photolysis and UV/H_2O_2 followed by chlorination.

Alkalinity was found to be statistically significant for most HAA species in the factorial experiments. In the treatment of synthetic water with UV photolysis, alkalinity was not a statistically significant factor for chlorinated HAAs except in the three-factor interaction with pH and UV-fluence, PxAxF, for the compound Cl_2AA. The brominated HAAs, BrAA, Br_2ClAA, Br_2AA and Br_3AA, also had alkalinity as a statistically significant

factor, either as a main factor or in interaction with other factors in the UV photolysis treatment followed by chlorination. In this treatment, whenever alkalinity, as a main factor, was found significant, it always had a negative effect on the PCDBPs in question, thereby reducing the concentration of the PCDBPs. However, wherever alkalinity was in interaction with another factor, a positive effect existed; suggesting that the interaction of alkalinity with the other factors had an increasing effect on the formation of PCDBPs.

The UV/H_2O_2 treatment produced effects that were the opposite of those observed for UV photolysis for alkalinity changes in the factorial experiments. As a statistically significant factor, alkalinity caused an increase in the formation of both HAAs and HANs while its interaction with other factors caused a reduction in the concentration of PCDBPs. The exceptions to the above were for the compounds Cl_2AA, BrAA and BrClAA. The three-factor interaction, PxAxF, caused an increase in the formation of Cl_2AA while the two-factor interaction AxF had a positive effect on BrClAA. Alkalinity as a main factor reduced the concentration of BrAA, and the interactions AxF and PxAxF, causing an increase in the concentration of BrAA.

The single factor experiments involved varying alkalinity from 0 to 250 mg/L as $CaCO_3$. In this experiment, an increase in concentration occurred with all the PCDBPs when synthetic water was treated with UV photolysis followed by chlorination, except for Cl_2AA in which a decrease in concentration occurred. The significance of alkalinity to THM formation cannot be ruled out as the slope of the linear trend applied to the data was more than those of HAAs and HANs. Though an increase or decrease in PCDBPs

occurred in the single factor experiments as UV-fluence was held constant at 1000 mJ/cm^2, there was not a significant change in the concentration of HAAs and HANs as alkalinity was increased because the slopes of the linear trends fitted to the data were small. Treatment with UV/H_2O_2 brought about a reduction in concentration for all PCDBPs studied as alkalinity was increased.

6.1.3 Effect of pH on PCDBPs

In the factorial experiments, wherever pH was statistically significant, a reduction in mean PCDBPs occurred. In all the statistically significant three-factor interactions pH was involved in, an increase in the formation of PCDBPs also occurred except for Cl_2AN where treatment with UV/H_2O_2 brought about a decrease in concentration.. For both brominated and chlorinated compounds, significant two-factor interactions of pH with another factor caused a reduction in the PCDBPs except for the brominated HAAs, Br_2ClAA and $BrCl_2AA$, where the interaction PxF caused an increase in the formation of these PCDBPs.

A decrease in the concentration of PCDBPs occurred in single factor experiments as pH was varied from 6 to 8. Some compounds experienced a high or low concentration at pH 6 compared to other pH values. A linear trend was fitted to the HAA compounds, Cl_2AA, Cl_3AA, BrAA, BrClAA and Br_2AA, from pH 5 to 9 revealing a reduction in concentration in these compounds as pH was increased. The HAA compounds Br_2ClAA, $BrCl_2AA$, Br_3AA, Cl_2AN and the chlorinated and brominated THMs also experienced a reduction from pH 5 to 9 when the concentration at pH 6.

6.2 Recommendations

6.2.1 Water Treatment and PCDBP Analysis

From the results of this research, it is recommended that disinfection or advanced oxidation process be carried out at a pH greater than 7 since a reduction in PCDBPs occurred as pH was increased.

Alkalinity had little or no effect on HAA formation. Therefore the use of UV irradiation in the degradation of NOM could be carried out at a UV-fluence of 1000 mJ/cm^2 and at an alkaline pH for waters comprising mainly of HAA precursors. At 1000 mJ/cm^2 and an alkaline pH, the production of OH radicals is enhanced and less scavenging of the radicals by the bicarbonate and carbonate ions occurs. This can also be applied to THMs if the source water is low in bromide ion concentration.

During extraction of PCDBPs with pentane, analysis of the solvent should be made to ensure the solvent is free from the PCDBPs being analyzed to avoid any form of interference.

6.2.2 Further Research

The following are recommendations for further research:

- Other types of natural water such as soft water and lake water should be used in determining what effects pH, alkalinity and UV-fluence would have in the formation of PCDBPs from these sources.

- Different levels of UV-fluence should be investigated in order to determine if alkalinity and pH would have the same response as they did at 1000 mJ/cm^2 in the single factor experiments. It would also be worthwhile to determine if the factorial experiment results obtained between 1000 and 5000 mJ/cm^2 hold true for values of UV-fluence used in normal disinfection purposes.

- Since new PCDBPs are still being discovered, the use of FAIMS should be employed in the detection of new PCDBPs that may be associated with the use of UV photolysis and UV/H_2O_2 with or without the addition of a secondary disinfectant. .

- Further research should also be carried out to determine the effects of pH, alkalinity and UV-fluence in the DBPs associated with UV photolysis and UV/H_2O_2 without the addition of a secondary disinfectant, DBPs such as carboxylic acids and aldehydes. The effects of these factors on other PCDBPs, such as haloketones, should also be investigated.

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APPENDIX A: Determination of PCDBPs

Haloacetic Acid Determination

The method used in Extraction of HAA_9 from water samples is described below. This is in accordance with the Standard methods (APHA-AWWA-WEF, 1995) and EPA method 552 with minor modifications. The calibration curves were prepared with nominal concentrations of 0.5, 1, 5, 10, 20, 40, 80, 100, 120, 160, 200, 240 & 300µg/L and they are presented in figure C.1. This procedure also involves the generation of diazomethane a methylating agent. The calibration curves were plotted using internal standards, the axes are therefore in amount ratio and area ratio. These ratios are those of the nominal standards to that of the internal standard.

Haloacetic acid analysis
(Prepared by Rosanna Souza, 2000)

20 mL of sample
100µL of $Na_2S_2O_3$ 8 g/L (only if chlorine residual is expected)
6 g of oven dried Na_2SO_4
3 mL of conc. H_2SO_4
100 µL of 2,3-DBPA 10 mg/L
500µL of 2,3,5,6-TFBA 20 mg/L
5 mL of MTBE containing 100 µg/L of 1,2-DBP
⇓
Shake for 7 min
⇓
Let stand for 15 min for phase separation
⇓
Transfer exactly 3 mL of organic phase into a test tube
⇓
Cool extracts in freezer for 7 min
⇓
Add 300µL of CH_2N_2 (collected in 2.5 mL of MTBE)
⇓
Put samples in refrigerator at 4 °C for 15 min
Leave samples at room temperature for another 15 min
⇓
Wash extract with 2mL of saturated $NaHCO_3$
Transfer organic phase to a GC vial containing oven baked Na_2SO_4
⇓
GC/ECD

GC/ECD (GC II):

30 m x 0.25 mm x 0.25 µm film DB 1701 (or equivalent) capillary column with retention gap
2 µL injection, splitless 30s
Carrier gas: He 30 cm/s = 0.5 mL/min (at 37°C)
Makeup gas: N_2 23.1 mL/min
Injector 160°C; detector 300 °C
Oven: 37 °C (21 min) – 11 °C/min – 136 °C (3 min) – 20 °C/min – 236 °C (3 min)
Total run time: 41 min

Notes:
$HgCl_2$ can not be used as a preservative as it causes a large interference peak in the chromatogram.
Suitable quenching agents are NH_4Cl (35 mg in 20 mL vial) or NaS_2O_3 (100 µL of an 8 g/L solution).
NaN_3 as a preservative is also an option.
2,3-DBPA = 2,3-dibromopropionic acid
2,3,5,6-TFBA = 2,3,5,6-tetrafluorobenzoic acid
1,2-DBP = 1,2-dibromopropane

Diazomethane (CH_2N_2) Generation

1. Set up MNNG diazomethane generation apparatus on ice using a beaker filled with crushed ice and water.

2. Add 2.5mL of methyl- tertiary-butyl ether (MTBE) to outer tube of generator, cover with tin foil and place in ice bath.

3. Add ~1/2" of Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) to inner tube of generator using large end of Pasteur pipette.

4. Add ~0.5mL of methanol to cover Diazald by approximately 1/8" and secure cap and septum.

5. Place O-ring in glass joint, position inside tube firmly on top and secure clamp. Ensure that vapor exit hole is located on opposite side of clamp and rest clamp on spout of beaker. The seal **must** be very tight to ensure maximum CH_2N_2 generation and recovery.

6. Let cool on ice bath for 10 min.

7. Add 600 µL of 20% NaOH solution (100 g of NaOH in 500 mL of MilliQ H_2O) **dropwise** to inner tube with gas tight syringe (1drop/ 5secs). When NaOH is initially being added, there is a slight delay before the Diazald reacts violently so be sure to

add dropwise. Aim drops straight down into Diazald in bottom of inner tube avoiding tube surface and vapor exit hole. Leave syringe in place after all NaOH has been added – removal of the syringe will leave a hole in the septum from where CH_2N_2 may escape.

8. Allow CH_2N_2 to form for 30-45 min in ice bath. MTBE will become yellow when CH_2N_2 is formed.

9. Transfer CH_2N_2 in MTBE to 4mL vials using specially flamed Pasteur pipette and store vials in explosion-proof freezer (use within 2-4 weeks if possible).

10. Rinse inner tube several times with MilliQ H_2O.

11. Rinse inner and outer tube with methanol and MTBE until glassware is clean. Put glassware in oven at ~100C until dry.

12. Rinse NaOH syringe with MilliQ H_2O several times.

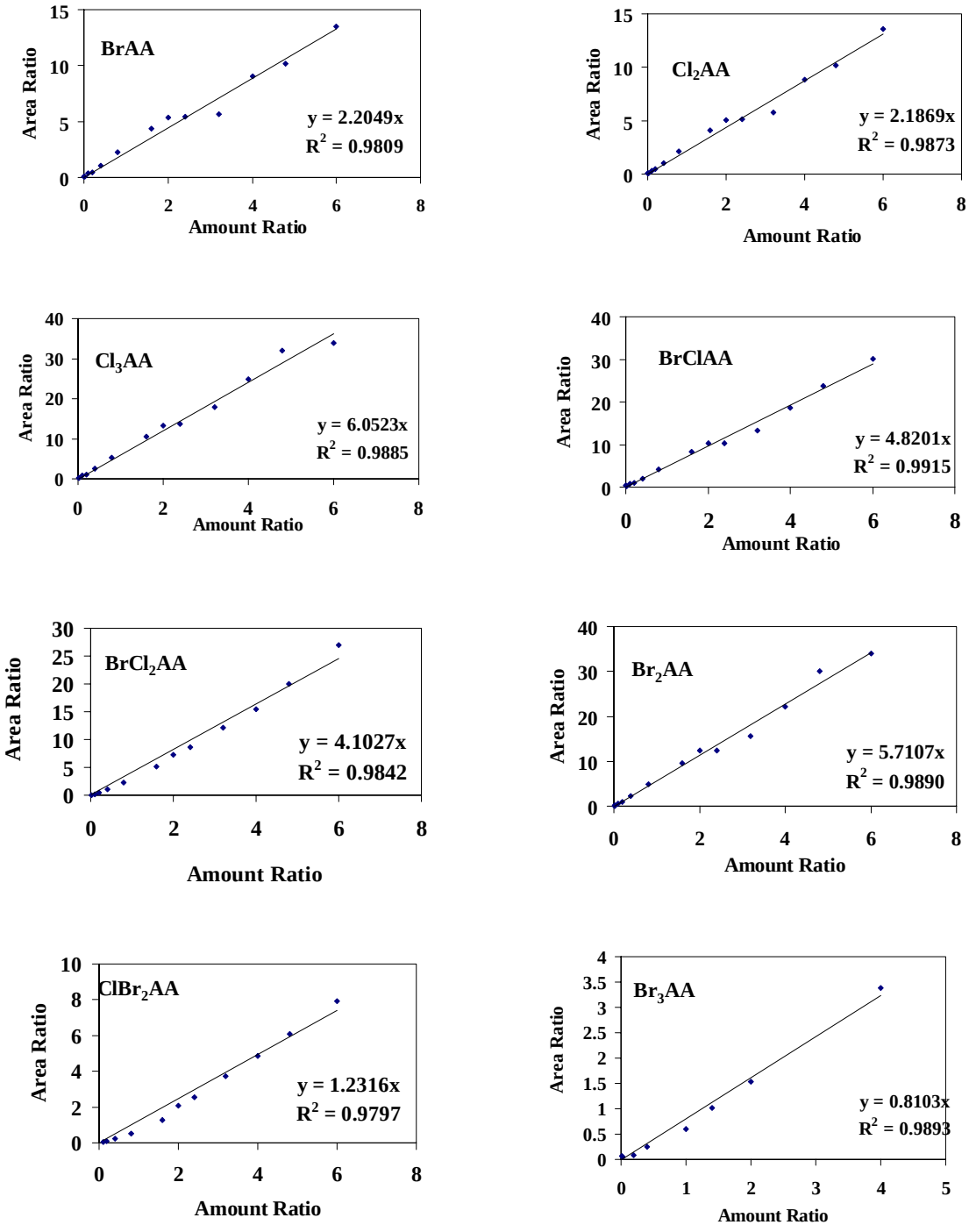

Figure A.1 HAAs Calibration Curves

THMs & HANs Determination

The THMs and HANs were determined according to method EPA 551.1 with minor modifications. Two sets of calibration curves were used, one for the factorial experiments and the other for single factor experiments. The GC/ECD had to be recalibrated due to changes in the GC response. The calibration curves are shown in figures C.2a and C.2b The process of extraction and analysis for these compounds is given below. The calibration curves were plotted using internal standards, the axes are therefore in amount ratio and area ratio. These ratios are those of the nominal standards to that of the internal standard.

THMs & HANs analysis
(Prepared by Rosanna Souza 2000)

20 mL of sample
100µL of $Na_2S_2O_3$ 8 g/L (only if chlorine residual is expected)
32.5 mg of $HgCl_2$ (only necessary if long term storage is expected)
5 g of oven dried Na_2SO_4
4mL of pentane containing 100 µg/L of 1,2-DBP (internal standard)
⇓
Shake for 7 min
⇓
Let stand 15 min for phase separation
⇓
Transfer organic layer to a GC vial containing oven dried Na_2SO_4
⇓
GC/ECD

GC/ECD (GC I):

30m x 0.32mm x 1µm film DB-5 (or equivalent) capillary column with retention gap
2µL injection split 1:43
Carrier gas: He
Makeup gas: P5
Injector 220 °C; detector 300 °C
Oven: 35 °C (5 min) – 10 °C/min - 70°C – 20 °C/min - 250°C (2.5 min)
Total run time: 20 min

Notes:
1,2-DBP = 1,2-dibromopropane

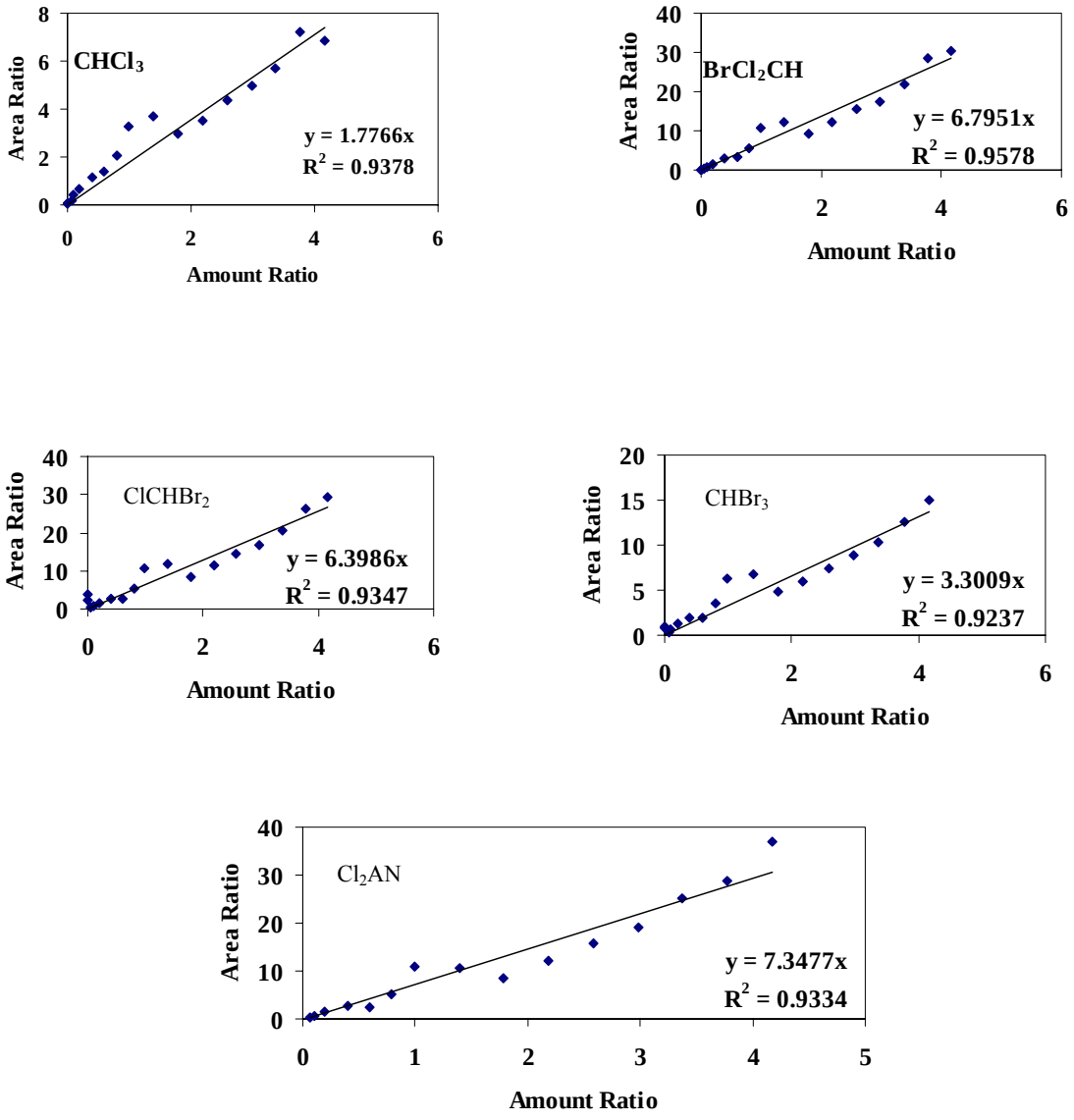

Figure A.2a Calibration Curves for THMs & Cl_2AN (Factorial Experiment)

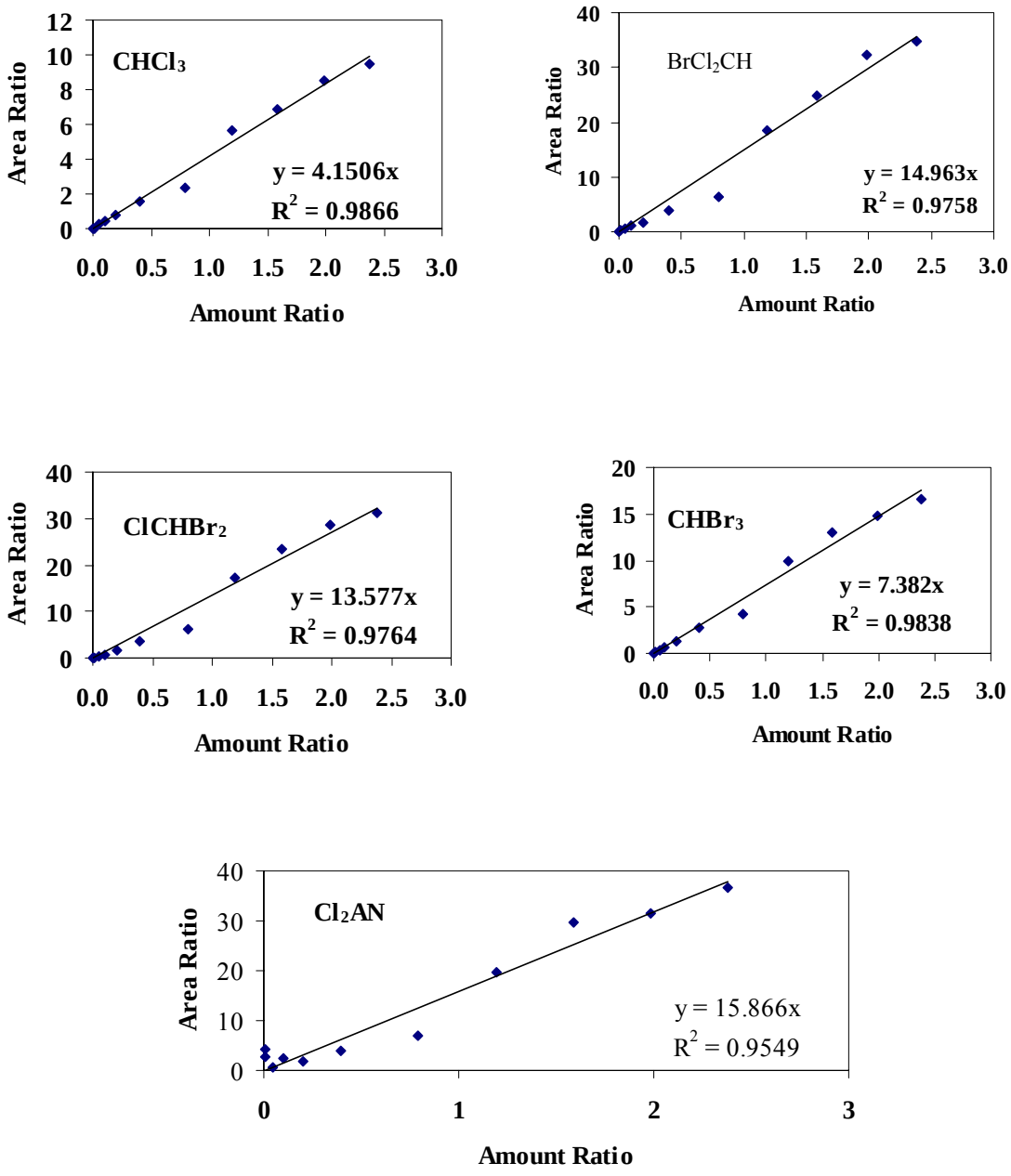

Figure A.2b Calibration Curves for THMs & Cl_2AN (Single Factor Experiment)

Appendix B: Hydrogen Peroxide Results

Table B.1 Factorial Experiments

	Initial concentration			Final concentration			
	Absorbance		H_2O_2 Conc.	Absorbance		H_2O_2 Conc.	H_2O_2 Demand
Run	A_o	Initial	mg/L	A_o	Final	mg/L	mg/L
1	0.0069	0.708	9.02	0.0069	0.451	5.72	3.30
2	0.0120	0.683	8.62	0.0120	0.481	6.03	2.59
3	0.0083	0.666	8.46	0.0083	0.482	6.09	2.37
4	0.0082	0.673	8.55	0.0082	0.486	6.15	2.40
5	0.0034	0.634	8.11	0.0065	0.063	0.730	7.39
6	0.0074	0.697	8.87	0.0123	0.081	0.883	7.99
7	0.0056	0.666	8.49	0.0072	0.103	1.24	7.25
8	0.0399	0.670	8.10	0.0399	0.087	0.609	7.49
9a	0.0120	0.636	8.02	0.0334	0.203	2.19	5.83
9b	0.0072	0.674	8.57	0.0069	0.226	2.82	5.76
9c	0.0114	0.671	8.49	0.0082	0.223	2.77	5.72
9d	0.0123	0.641	8.08	0.0083	0.244	3.03	5.05

Table B.2 Factorial Experiments (addition of Bromide ion)

	Initial concentration			Final concentration			
	Absorbance		H_2O_2 Conc	Absorbance		H_2O_2 Conc	H_2O_2 Demand
Run	Ao	Initial	mg/L	Ao	Final	mg/L	mg/L
1	0.0084	0.736	9.36	0.0084	0.542	6.86	2.50
2	0.0091	0.751	9.55	0.0066	0.538	6.84	2.71
3	0.0068	0.729	9.29	0.0068	0.527	6.70	2.60
4	0.0054	0.744	9.50	0.0054	0.487	6.20	3.30
5	0.0068	0.733	9.33	0.0121	0.140	1.65	7.69
6	0.0066	0.780	9.94	-0.0017	0.054	0.711	9.23
7	0.0044	0.726	9.28	0.0002	0.130	1.67	7.61
8*				0.0037	0.101	1.25	
9a	0.0061	0.756	9.65	0.0066	0.203	2.53	7.12
9b	0.0076	0.774	9.86	0.0068	0.257	3.22	6.64
9c	0.0084	0.727	9.24	0.0031	0.242	3.08	6.16
9d*	0.0054	0.662	8.45				

* Values for empty fields were missing.

Table B.3 Single Factor Experiments: Alkalinity Experiments

	Initial concentration			Final concentration			
	Initial Absorbance		H_2O_2 Conc	Final Absorbance		H_2O_2 Conc	H_2O_2 Demand
Run	Ao	$A_{Initial}$	mg/L	Ao	A_{Final}	mg/L	mg/L
0A	0.0017	0.922	11.8	0.0017	0.550	7.05	4.79
0B	0.0017	0.924	11.9	0.0017	0.538	6.90	4.96
50A	0.0077	0.921	11.7	0.0077	0.575	7.30	4.44
50B	0.0077	0.933	11.9	0.0077	0.569	7.22	4.67
100A	0.0017	0.895	11.5	0.0017	0.535	6.86	4.63
100B	0.0017	0.920	11.8	0.0017	0.529	6.78	5.03
150A	0.0077	0.951	12.1	0.0077	0.568	7.21	4.92
150B	0.0077	0.954	12.2	0.0077	0.575	7.30	4.87
200A	0.0045	0.905	11.6	0.0045	0.525	6.69	4.90
200B	0.0045	0.910	11.6	0.0045	0.509	6.49	5.149
250A	0.0017	0.907	11.6	0.0120	0.489	6.13	5.52
250B	0.0120	0.863	10.9	0.0120	0.485	6.09	4.860

Table B.4 Single Factor Experiments: pH Experiments with bromide addition

	Initial concentration			Final concentration			
	Initial Absorbance		H_2O_2 Conc	Final Absorbance		H_2O_2 Conc	H_2O_2 Demand
Run	Ao	$A_{Initial}$	mg/L	Ao	A_{Final}	mg/L	mg/L
5A	0.0093	1.01	12.9	0.0093	0.669	8.47	4.41
5B	0.0093	0.992	12.6	0.0093	0.692	8.78	3.86
6A	0.0159	0.983	12.4	0.0159	0.671	8.439	4.01
6B	0.0159	0.992	12.5	0.0159	0.631	7.91	4.64
7A	0.0093	0.973	12.4	0.0093	0.640	8.11	4.28
7B	0.0093	1.05	13.4	0.0093	0.656	8.31	5.05
8A	0.0093	1.0001	12.7	0.0093	0.641	8.12	4.63
8B	0.0093	0.979	12.5	0.0093	0.659	8.36	4.11
9A	0.0093	1.011	12.9	0.0093	0.573	7.25	5.63
9B	0.0093	0.976	12.4	0.0093	0.584	7.39	5.040

Table B.5 Single Factor Experiments: pH Experiments without Bromide addition

	Initial concentration			Final concentration			
	Initial Absorbance		H_2O_2 Conc	Final Absorbance		H_2O_2 Conc	H_2O_2 Demand
Run	Ao	$A_{Initial}$	mg/L	Ao	A_{Final}	mg/L	mg/L
5A	0.006	1.03	13.1	0.006	0.674	8.60	4.53
5B	0.006	1.02	13.0	0.006	0.649	8.27	4.73
6A	0.006	1.03	13.2	0.006	0.632	8.06	5.14
6B	0.006	1.02	13.0	0.006	0.687	8.76	4.25
7A	0.016	1.02	12.9	0.016	0.648	8.12	4.80
7B	0.016	1.01	12.8	0.016	0.637	7.99	4.77
8A	0.006	1.02	13.0	0.006	0.672	8.57	4.47
8B	0.006	1.03	13.1	0.006	0.662	8.45	4.68
9A	0.016	1.01	12.8	0.016	0.595	7.45	5.33
9B	0.016	1.02	12.9	0.016	0.568	7.10	5.76

Table B.6 Single Factor Experiments: pH Experiments

(Repeat experiments for bromide addition)

	Initial concentration			Final concentration			
	Initial Absorbance		H_2O_2 Conc	Final Absorbance		H_2O_2 Conc	H_2O_2 Demand
Run	A_o	$A_{Initial}$	mg/L	A_o	A_{Final}	mg/L	mg/L
5A	0.0097	0.911	11.6	0.0097	0.683	8.66	2.93
5B	0.0097	0.905	11.5	0.0097	0.690	8.75	2.77
6A	0.0097	0.844	10.7	0.0097	0.574	7.26	3.47
6B	0.0097	0.877	11.1	0.0097	0.601	7.61	3.54
7A	0.0097	0.857	10.9	0.0097	0.587	7.43	3.47
7B	0.0097	0.898	11.4	0.0097	0.598	7.56	3.87

APPENDIX C: Bromide Ion Concentration

A Bromide ion concentration of 500mg/L was added into the synthetic waster of waster from the post-filtration step of the MWTP. The results were based on the figures below as explained in Section 3.4.6

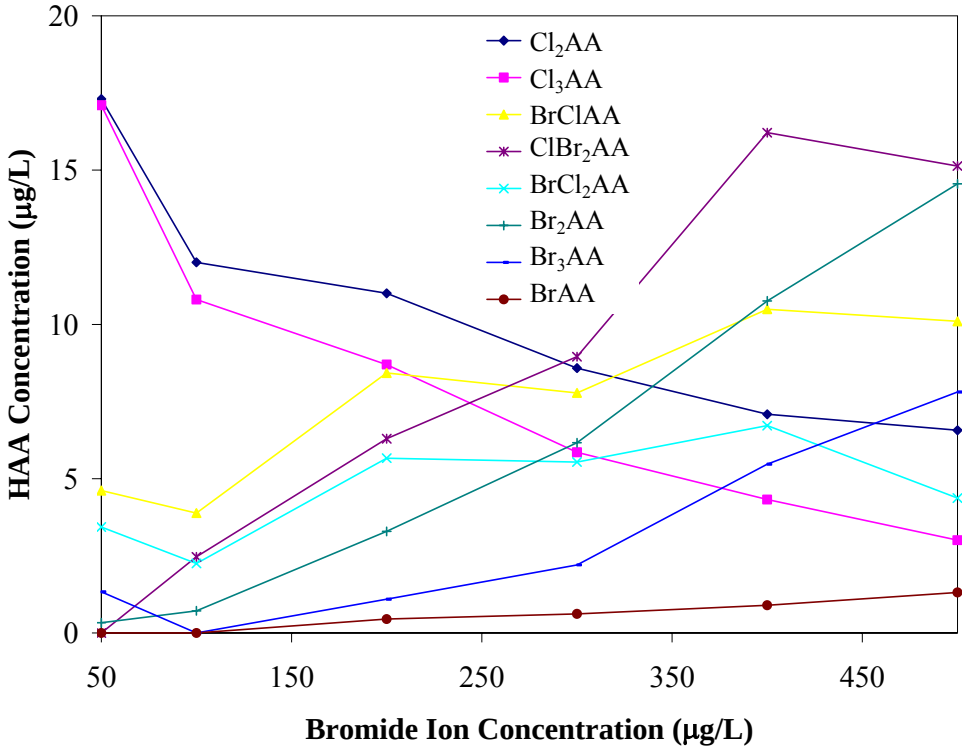

Figure C.1 Effect of Bromide Ion Variation on HAA Concentration

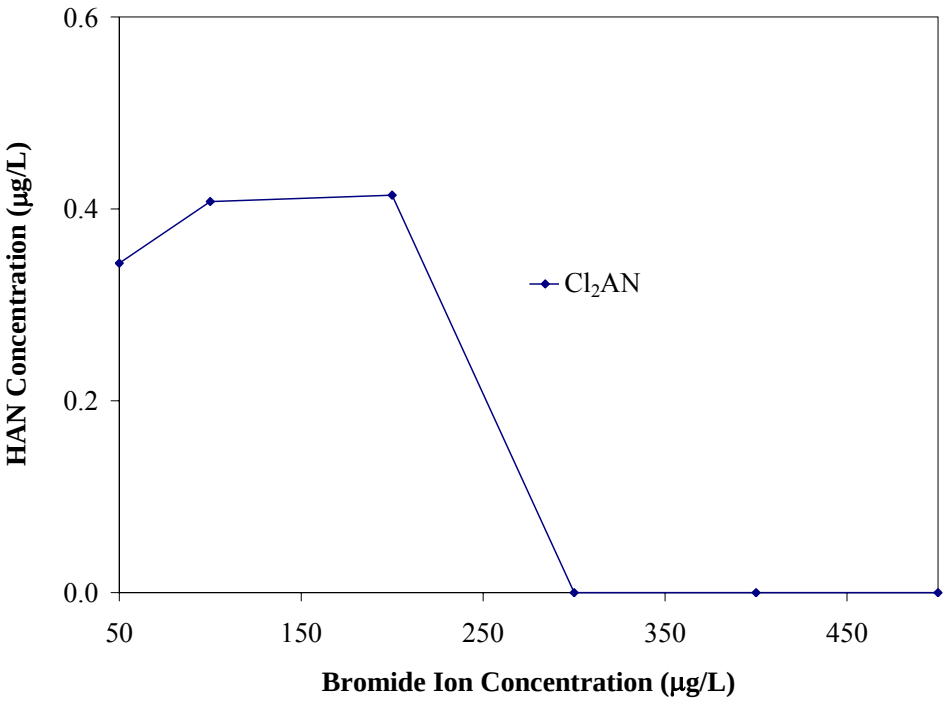

Figure C.2 Effect of Bromide Ion Variation on Cl_2AN Concentration

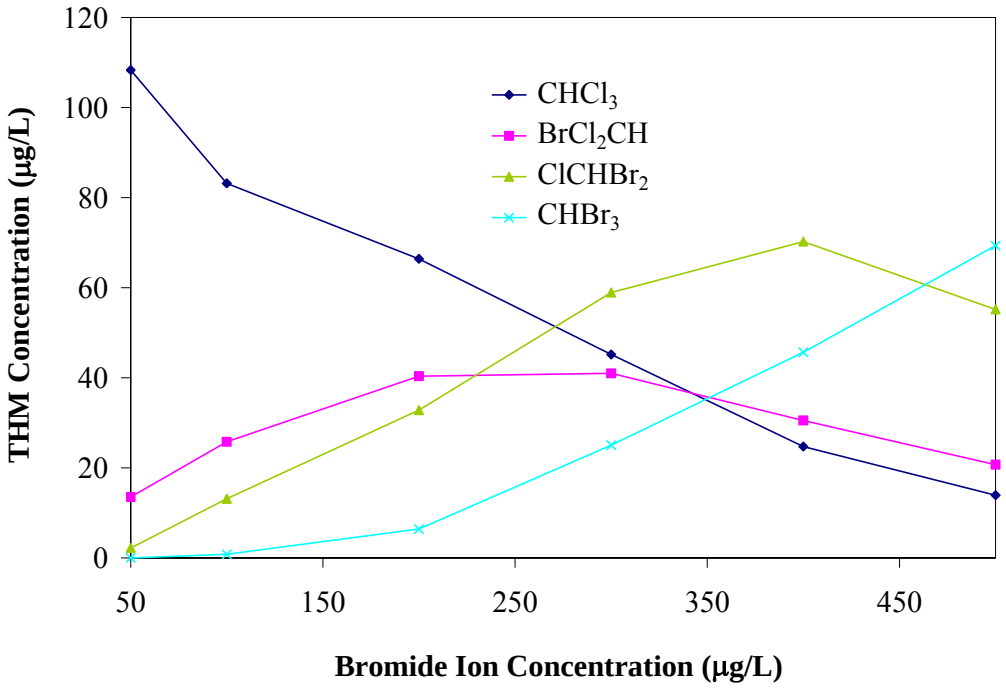

Figure C.3 Effect of Bromide Ion Variation on THM Concentration

APPENDIX D: Chemical Actinometry

The type of Actinometer used was the KI/KIO3 Solution. This was prepared according to the protocol written by Bolton and Stefan (2003), explained in chapter 3. Chemical Actinometry was carried out mainly to test the accuracy of the readings of the radiometer use in determining the output of the UV lamp. The radiometer has to be sent to the manufacturer for recalibration once the actinometry readings and that of radiometer deferred by 10%. The sample volume of the experiments was 5ml while the type of lamp used was a low pressure UV lamp. The tables below are a summary of the experiments carried out before and after the radiometer was sent out for recalibration.

Table D.1 Actinometry Experiments before Recalibration of Radiometer

Experiment No	$E_{Radiometer}$ (mW/cm^2)	$E_{Actinometry}$ (mW/cm^2)
1	0.169	0.206
2	0.173	0.205
3	0.183	0.220
4	0.183	0.220
Average	0.177	0.212
Standard Deviation	0.008	0.007

Table D.2 Actinometry Experiments after Recalibration of Radiometer

Experiment No	$E_{Radiometer}$ (mW/cm^2)	$E_{Actinometry}$ (mW/cm^2)
1	0.183	0.193
2	0.183	0.193
3	0.183	0.193
Average	0.183	0.193
Standard Deviation	0.0003	0.0005

From Table A.3 before the radiometer was recalibrated, the percentage difference between $E_{radiometer}$ and $E_{Actinometry}$ was 19.77% after recalibration the percentage difference was 5.5%.

APPENDIX E: Hierarchical Design

The Hierarchical experiment, also known as the nested design, was used to check for variations in the various steps of the experiments. Generally four samples drawn from synthetic water prepared in the same way were irradiated using the center point conditions shown in table 3.2. There were five samples of synthetic water prepared from the same batch of water, each of which were irradiated at 100mJ/cm^2 at pH of 7.7 and an alkalinity of 100mg/L as $CaCO_3$. After irradiation, five samples of 20ml were drawn from each of the five irradiated samples; these were used for extraction, making a total of twenty five extractions. From each of the extracts three or seven injections were analyzed for by the GC/ECD for HAAs and THMs respectively. The column "I" signifies the number of samples used in irradiation, column "E" indicates the number of samples used for extractions, column "A" indicates the number of injections made by the GC/ECD while $\sum Y_{IEA}$ indicates the raw data collected from the GC/ECD. The results are summarized below.

Table E.1 UV/H_2O_2: Hierarchical Experimental Results for HAAs

I	E	A	$\sum Y_{IEA}$
1	a	1	17.7
		2	17.2
		3	17.7
	b	1	18.6
		2	18.8
		3	19.4
	c	1	16.7
		2	17.4
		3	18.0
	d	1	19.2
		2	19.0
		3	19.3
	e	1	21.3
		2	20.6
		3	21.0
2	a	1	16.5
		2	16.5
		3	16.5
	b	1	15.4
		2	16.4
		3	16.1
	c	1	18.2
		2	18.4
		3	17.9
	d	1	17.6
		2	18.0
		3	17.9
	e	1	16.5
		2	16.5
		3	16.8
3	a	1	16.7
		2	16.2
		3	17.4
	b	1	18.5
		2	18.6
		3	18.4
	c	1	18.1
		2	18.3
		3	17.5

I	E	A	$\sum Y_{IEA}$
3	c	1	18.1
		2	18.3
		3	17.5
	d	1	16.8
		2	17.0
		3	16.3
	e	1	20.3
		2	20.3
		3	18.9
4	a	1	15.6
		2	16.3
		3	16.1
	b	1	16.0
		2	15.6
		3	15.8
	c	1	18.0
		2	17.6
		3	17.7
	d	1	15.5
		2	15.3
		3	15.6
	e	1	15.6
		2	15.4
		3	15.9
5	a	1	12.8
		2	13.0
		3	11.5
	b	1	17.8
		2	17.4
		3	17.9
	c	1	17.9
		2	17.8
		3	17.4
	d	1	16.5
		2	16.8
		3	16.9
	e	1	16.9
		2	15.9
		3	16.7

Table E.2 ANOVA Table for HAAs Hierarchical Experimental Results

					σ^2	σ
Source	df	SS	MS	F_{obs}	E(MS)	
Irradiation(I)	4	78.8	19.7	3.16	0.898	0.947
Extraction(E)	20	124	6.23	39.1	2.02	1.42
Analysis(A)	50	7.97	0.159		0.159	0.399
Total	74	211				

$F_{4,20} = 2.87$ $F_{distribution}$ is less than F_{obs} therefore there is significant variation btw irradiation.

$F_{20,50} = 1.78$ $F_{distribution}$ is less than F_{obs} therefore there is significant variation btw extraction.

From the table, the variation, E (MS) due to irradiation and analysis were less than one. But the variation due to irradiation is significant. There is a significant difference between sample extraction, $F_{obs} > F_{crit}$. The error associated with the various experimental steps shows that some error is involved in the GC/ECD analysis of the samples though that of the extraction is greater than it. This might have been due to evaporation of compounds during extraction.

Table E.3 UV/H_2O_2: Hierarchical Experimental Results for THMs

I	E	A	$\sum Y_{IEA}$
1	a	1	233
		2	247
		3	236
		4	245
		5	234
	b	1	314
		2	316
		3	306
		4	306
		5	291
	c	1	465
		2	470
		3	493
		4	504
		5	488
	d	1	305
		2	312
		3	310
		4	321
		5	320
	e	1	304
		2	311
		3	313
		4	324
		5	305

I	E	A	$\sum Y_{IEA}$
2	a	1	311
		2	319
		3	335
		4	301
		5	312
	b	1	323
		2	337
		3	356
		4	352
		5	324
	c	1	296
		2	297
		3	332
		4	360
		5	287
	d	1	371
		2	394
		3	387
		4	411
		5	387
	e	1	282
		2	288
		3	266
		4	267
		5	276

Table E. 3 cont'd UV/H_2O_2: Hierarchical Experimental Results for THMs

I	E	A	$\sum Y_{IEA}$
3	a	1	443
		2	443
		3	434
		4	436
		5	448
	b	1	485
		2	467
		3	477
		4	459
		5	459
	c	1	497
		2	521
		3	512
		4	522
		5	506
	d	1	374
		2	789
		3	808
		4	373
		5	383
	e	1	501
		2	521
		3	520
		4	510
		5	500

I	E	A	$\sum Y_{IEA}$
4	a	1	478
		2	290
		3	476
		4	276
		5	284
	b	1	464
		2	440
		3	678
		4	755
		5	432
	c	1	260
		2	266
		3	267
		4	269
		5	260
	d	1	303
		2	298
		3	318
		4	319
		5	322
	e	1	293
		2	454
		3	480
		4	278
		5	275

Table E .3 cont'd UV/H_2O_2: Hierarchical Experimental Results for THMs

I	E	A	$\sum Y_{IEA}$
5	a	1	383
		2	372
		3	195
		4	377
		5	195
	b	1	398
		2	428
		3	413
		4	406
		5	414
	c	1	581
		2	664
		3	320
		4	313
		5	306

I	E	A	$\sum Y_{IEA}$
5	c	1	581
		2	664
		3	320
		4	313
		5	306
	d	1	288
		2	294
		3	289
		4	287
		5	288
	e	1	255
		2	262
		3	262
		4	269
		5	262

Table E .4 ANOVA Table for THMs Hierarchical Experimental Results

					σ^2	σ
Source	df	SS	MS	F_{obs}	E(MS)	
Irradiation	4	499029	124757	4.99	3990	63.2
Extraction	24	599967	24998	5.51	4092	64.0
Analysis	124	562435	4535		4535	67.3
Total	152	1661432				

$F_{4,24} = 2.7$ $F_{distribution}$ is less than F_{obs} therefore there is significant variation btw irradiation.

$F_{24,124} =$ $F_{distribution}$ is less than F_{obs} therefore there is significant variation btw extraction

The raw values of the THMs are quite large because at time of experiment there was an interference of chloroform in the extracting solvent, elevating the concentration of chloroform. These also resulted in large values of E (MS). This was prevented in both factorial & single factor experiments by using an extracting solvent with chloroform concentration less than 1μg/L.

APPENDIX F: Factorial Experiment Results

Chlorinated DBPs Using UV Photolysis

Table F.1 HAAs Raw data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HAAs (μg/L)		
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AA	Cl_3AA	Total
1	6	0	1000	1.08	15.2	14.4	29.6
2	8	0	1000	1.00	13.4	13.2	26.5
3	6	200	1000	1.05	23.2	10.2	33.4
4	8	200	1000	1.23	10.4	13.5	23.9
5	6	0	5000	0.45	6.88	3.13	10
6	8	0	5000	0.76	5.05	2.19	7.24
7	6	200	5000	0.78	5.32	2.81	8.13
8	8	200	5000	0.74	4.78	3.16	7.95
9a	8	100	3000	0.79	7.31	5.55	12.9
9b	8	100	3000	0.75	7.07	6.76	13.8
9c	8	100	3000	0.99	9.89	8.76	18.7
9d	8	100	3000	0.92	7.7	5.52	13.2
			Variance		1.67	2.32	7.31
C1				1.77	17.5	21.6	39
C2				1.85	43.3	43	86.3
C3				1.97	15.6	19.2	34.9
C4				1.97	37.9	35.7	73.6
			Average	1.89	28.6	29.9	58.4

Table F.2a Yates' Algorithm for HAA_9

Run	HAA_9	[1]	[2]	[3]	Divisor	Effect	
1	29.6	56.1	113	147	8	18.3	Mean
2	26.5	57.3	33.3	-15.5	4	-3.88	P
3	33.4	17.3	-12.6	-0023	4	-0.006	A
4	23.9	16.1	-2.95	-3.74	4	-0.935	PA
5	10	-3.13	1.16	-80.1	4	-20	F
6	7.24	-9.46	-1.2	9.64	4	2.41	PF
7	8.13	-2.77	-6.33	-2.34	4	-0.585	AF
8	7.95	-0.179	2.59	8.92	4	2.23	PAF

Table F.2b ANOVA Table for Total HAA_9

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-3.883	30.2	1	30.2	4.12	No
Alkalinity	-0.006	0	1	0	0	No
UV-fluence	-20	802	1	802	110	Yes
Interactions						
PxA	-0.935	1.75	1	1.75	0.24	No
PxF	2.41	11.6	1	11.6	1.59	No
AxF	-0.6	0.69	1	0.69	0.09	No
PxAxF	2.23	9.95	1	9.95	1.36	No
Error			1	7.31		

$F_{1, 3, 0.05} = 10.1$

Table F.3a Yates' Algorithm for Cl_2AA

Run	Cl_2AA	[1]	[2]	[3]	Divisor	Effect	
1	15.2	28.6	62.2	84.2	8	10.5	Mean
2	13.4	33.6	22	-17	4	-4.2	P
3	23.2	11.9	-15	3.18	4	0.794	A
4	10.4	10.1	-2.36	-10	4	-2.93	PA
5	6.88	-1.9	5.01	-40.1	4	-10	F
6	5.05	-13	-1.83	12.2	4	3.06	PF
7	5.32	-1.8	-11	-6.85	4	-1.7	AF
8	4.78	-0.534	1.29	12.2	4	3.04	PAF

Table F.3b ANOVA Table for Cl_2AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-4.24	35.9	1	35.9	21.6	Yes
Alkalinity	0.794	1.26	1	1.26	0.76	No
UV-fluence	-10	201	1	201	121	Yes
Interactions						
PxA	-2.39	11.5	1	11.5	6.87	No
PxF	3.06	18.7	1	18.7	11.2	Yes
AxF	-1.71	5.86	1	5.86	3.52	No
PxAxF	3.04	18.5	1	18.5	11.1	Yes
Error			1	1.67		

$F_{1,3,0.05} = 10.1$

Table F.4a Yates' Algorithm for Cl_3AA

Run	Cl_3AA	[1]	[2]	[3]	Divisor	Effect	
1	14.4	27.6	51.3	62.6	8	7.82	Mean
2	13.2	23.7	11.3	1.42	4	0.355	P
3	10.2	5.32	2	-3.2	4	-0.8	A
4	13.5	5.97	-0.586	5.83	4	1.46	PA
5	3.13	-1.3	-3.85	-40	4	-10	F
6	2.19	3.27	0.65	-2.59	4	-0.648	PF
7	2.81	-0.941	4.54	4.5	4	1.13	AF
8	3.16	0.36	1.3	-3.24	4	-0.81	PAF

Table F.4b ANOVA Table for Cl_3AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.355	0.25	1	0.252	0.022	No
Alkalinity	-0.8	1.28	1	1.28	0.112	No
UV-fluence	-10	200	1	200	17.5	Yes
Interactions						
PxA	1.46	4.25	1	4.25	0.373	No
PxF	-0.648	0.84	1	0.839	0.074	No
AxF	1.13	2.54	1	2.54	0.222	No
PxAxF	-0.81	1.31	1	1.31	0.115	No
Error			1	11.4		$F_{1,3,0.05} = 10.1$

Table F.5 HANs Raw data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HANs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AN	Total
1	6	0	1000	1.08	1.33	1.33
2	8	0	1000	1.00	1.81	1.81
3	6	200	1000	1.05	2.15	2.15
4	8	200	1000	1.23	1.76	1.76
5	6	0	5000	0.45	0.95	0.95
6	8	0	5000	0.76	1.26	1.26
7	6	200	5000	0.78	1.24	1.24
8	8	200	5000	0.74	1.28	1.28
9a	8	100	3000	0.79	2.34	2.34
9b	8	100	3000	0.75	1.77	1.77
9c	8	100	3000	0.99	1.47	1.47
9d	8	100	3000	0.92	1.96	1.96
			Variance		0.13	0.13
C1				1.77	1.77	1.77
C2				1.85	0.99	0.99
C3				1.97	0.85	0.85
C4				1.97	1.12	1.12
			Average	1.89	1.18	1.18

Table F.6a Yates' Algorithm for THANs

Run	THANs	[1]	[2]	[3]	Divisor	Effect	
1	1.33	3.14	7.06	11.8	8	1.47	Mean
2	1.81	3.92	4.73	0.451	4	0.113	P
3	2.15	2.21	0.097	1.09	4	0.271	A
4	1.76	2.52	0.354	-1.15	4	-0.287	PA
5	0.949	0.489	0.777	-2.33	4	-0.582	F
6	1.26	-0.92	0.308	0.257	4	0.064	PF
7	1.24	0.311	-0.88	-0.469	4	-0.117	AF
8	1.28	0.043	-0.268	0.612	4	0.153	PAF

Table F.6b ANOVA Table for Total HANs

Source	Effect	S of S	df	MS	F	Significant
Main Effects						None
pH	0.113	0.025	1	0.025	0.193	
Alkalinity	0.271	0.147	1	0.147	1.12	
UV-fluence	-0.582	0.678	1	0.678	5.17	
Interactions						
PxA	-0.287	0.165	1	0.165	1.26	
PxF	0.064	0.008	1	0.008	0.063	
AxF	-0.117	0.027	1	0.027	0.209	
PxAxF	0.153	0.047	1	0.047	0.356	
Error			1	0.131		

$F_{1, 3, 0.05} = 10.1$

Table F.7 THMs Raw data

Run	**pH**	**Added alkalinity**	**UV-fluence**	**Cl_2 residual**	**THMs (μg/L)**	
		mg/l as $CaCO_3$	**mJ/cm^2**	**(mg/L)**	**$CHCL_3$**	**TTHMs**
1	6	0	1000	1.08	67.2	67.2
2	8	0	1000	1.00	73	73
3	6	200	1000	1.05	69.8	69.8
4	8	200	1000	1.23	62.5	62.5
5	6	0	5000	0.45	33.9	33.9
6	8	0	5000	0.76	24.8	24.8
7	6	200	5000	0.78	22.5	22.5
8	8	200	5000	0.74	22.9	22.9
9a	7.7	100	3000	0.79	43.1	43.1
9b	7.7	100	3000	0.75	38.3	38.3
9c	7.7	100	3000	0.99	36.1	36.1
9d	7.7	100	3000	0.92	43.6	43.6
			Variance	0.88	13.5	13.5
C1				1.77	99	99
C2				1.85	93.5	93.5
C3				1.97	84.1	84.1
C4				1.97	123	123
			Average	1.89	99.8	99.8

Table F.8a Yates' Algorithm for TTHMs

Run	TTHMs	[1]	[2]	[3]	Divisor	Effect	
1	67.2	140	273	377	8	47.1	Mean
2	73	132	104	-10.2	4	-2.55	P
3	69.8	58.7	-1.53	-21.3	4	-5.32	A
4	62.5	45.4	-8.67	-3.57	4	-0.894	PA
5	33.9	5.78	-8	-168	4	-42.1	F
6	24.8	-7.31	-13.3	-7.13	4	-1.78	PF
7	22.5	-9.09	-13.1	-5.23	4	-1.31	AF
8	22.9	0.429	9.52	22.6	4	5.65	PAF

Table F.8b ANOVA Table for Total TTHMs

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-2.55	13	1	13	0.96	No
Alkalinity	-5.32	56.6	1	56.6	4.21	No
UV-fluence	-42.1	3540	1	3540	263	Yes
Interactions						
PxA	-0.894	1.6	1	1.6	0.119	No
PxF	-1.78	6.36	1	6.36	0.473	No
AxF	-1.31	3.41	1	3.41	0.254	No
PxAxF	5.65	63.9	1	63.9	4.75	No
Error			1	13.5		

$F_{1, 3, 0.05} = 10.1$

Chlorinated DBPs Using UV/H_2O_2

Table F.9a HAAs Raw Data

Run	pH	Added alkalinity	Fluence	Cl_2 residual	HAAs (μg/L)		
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AA	Cl_3AA	Total
1	6	0	1000	1.19	6.46	4.72	11.2
2	8	0	1000	0.97	7.96	4.68	12.6
3	6	200	1000	1.13	9.17	6.95	16.1
4	8	200	1000	1.21	7.58	6.43	14.0
5	6	0	5000	0.03	1.9	0.373	2.27
6	8	0	5000	1.54	3.27	1.45	4.72
7	6	200	5000	1.28	2.71	1.14	3.85
8	8	200	5000	1.12	3.38	1.81	5.19
9a	7.7	100	3000	0.92	4.14	1.97	6.10
9b	7.7	100	3000	1.47	3.76	2.29	6.1
9c	7.7	100	3000	1.63	4.29	2.70	6.99
9d	7.7	100	3000	1.79	4.28	2.77	7.06
			Variance	1.19	0.060	0.141	0.296
C1					8.69	9.03	17.7
C2					8.57	8.78	17.4
C3					10.5	12.1	22.5
C4					11.3	12.7	24
				Average	9.76	10.6	20.3

Table F.10a Yates' Algorithm for HAA_9							
Run	HAA_9	[1]	[2]	[3]	Divisor	Effect	
1	11.2	23.8	53.9	70	8	8.75	Mean
2	12.6	30.1	16	3.15	4	0.787	P
3	16.1	6.99	-0.65	8.37	4	2.09	A
4	14	9.04	3.79	-4.67	4	-1.17	PA
5	2.27	1.46	6.32	-38	4	-9.48	F
6	4.72	-2.11	2.05	4.44	4	1.11	PF
7	3.85	2.45	-3.6	-4.3	4	-1.1	AF
8	5.19	1.35	-1.1	2.47	4	0.62	PAF

Table F.10b ANOVA Table for Total HAA_9

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.79	1.24	1	1.24	4.18	No
Alkalinity	2.09	8.76	1	8.76	29.6	Yes
UV-fluence	-9	180	1	180	607	Yes
Interactions						
PxA	-1.2	2.73	1	2.73	9.21	No
PxF	1.11	2.47	1	2.47	8.32	No
AxF	-1.1	2.28	1	2.28	7.69	No
PxAxF	0.62	0.76	1	0.76	2.57	No
Error			1	0.3		

$F_{1, 3, 0.05} = 10.1$

Table F.11a Yates' Algorithm for Cl_2AA

Run	Cl_2AA	[1]	[2]	[3]	Divisor	Effect	
1	6.46	14.4	31.2	42.4	8	5.3	Mean
2	7.96	16.8	11.3	1.96	4	0.49	P
3	9.17	5.17	-0.1	3.26	4	0.81	A
4	7.58	6.09	2.05	-3.8	4	-0.9	PA
5	1.9	1.5	2.34	-20	4	-5	F
6	3.27	-1.6	0.92	2.13	4	0.53	PF
7	2.71	1.37	-3.1	-1.4	4	-0.4	AF
8	3.38	0.67	-0.7	2.39	4	0.6	PAF

Table F.11b ANOVA Table for Cl_2AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.49	0.48	1	0.48	7.94	No
Alkalinity	0.81	1.33	1	1.33	21.9	Yes
UV-fluence	-5	49.6	1	49.6	820	Yes
Interactions						
PxA	-0.948	1.8	1	1.8	29.7	Yes
PxF	0.534	0.57	1	0.57	9.42	No
AxF	-0.355	0.25	1	0.25	4.18	No
PxAxF	0.597	0.71	1	0.71	11.8	Yes
Error			1	0.06		

$F_{1,3,0.05} = 10.1$

Table F.12a Yates' Algorithm for Cl_3AA

Run	Cl_3AA	[1]	[2]	[3]	Divisor	Effect	
1	4.72	9.4	22.8	27.5	8	3.44	Mean
2	4.68	13.4	4.77	1.19	4	0.297	P
3	6.95	1.82	-0.6	5.11	4	1.28	A
4	6.43	2.95	1.75	-0.879	4	-0.22	PA
5	0.37	-0.039	3.98	-18	4	-4.50	F
6	1.45	-0.52	1.13	2.30	4	0.576	PF
7	1.14	1.07	-0.481	-2.85	4	-0.713	AF
8	1.81	0.67	-0.398	0.082	4	0.021	PAF

Table F.12b ANOVA Table for Cl_3AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.3	0.18	1	0.18	1.25	No
Alkalinity	1.28	3.27	1	3.27	23.2	Yes
UV-fluence	-4.5	40.5	1	40.5	288	Yes
Interactions						
PxA	-0.2	0.1	1	0.1	0.69	No
PxF	0.58	0.66	1	0.66	4.72	No
AxF	-0.7	1.02	1	1.02	7.21	No
PxAxF	0.021	0.001	1	0.001	0.006	No
Error			1	0.14		

Table F.13 HANs Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HANs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AN	THANs
1	6	0	1000	1.19	0.812	0.812
2	8	0	1000	0.97	0.475	0.475
3	6	200	1000	1.13	0.575	0.575
4	8	200	1000	1.21	1.15	1.15
5	6	0	5000	0.03	0.213	0.213
6	8	0	5000	1.54	0.335	0.335
7	6	200	5000	1.28	0.843	0.843
8	8	200	5000	1.12	0.312	0.312
9a	8	100	3000	0.92	0.802	0.802
9b	8	100	3000	1.47	0.842	0.842
9c	8	100	3000	1.63	0.799	0.799
9d	8	100	3000	1.79	0.260	0.260
				Variance	0.001	0.001
				value of 9d not used		
C1				1.09	1.264	1.264
C2				1.16	0.796	0.796
C3				1.55	0.812	0.812
C4				1.71	0.632	0.632
			Average	1.378	0.876	0.876

Table F.14a Yates' Algorithm for THANs

Run	THANs	[1]	[2]	[3]	Divisor	Effect	
1	0.81	1.29	3.01	4.71	8	0.59	Mean
2	0.47	1.72	1.7	-0.2	4	0	P
3	0.58	0.55	0.23	1.04	4	0.26	A
4	1.14	1.16	-0.4	0.25	4	0.06	PA
5	0.21	-0.3	0.43	-1.3	4	-0.3	F
6	0.34	0.57	0.61	-0.6	4	-0.2	PF
7	0.84	0.12	0.91	0.17	4	0.04	AF
8	0.31	-0.5	-0.7	-1.6	4	-0.4	PAF

Table F. 14b ANOVA Table for THANs

SOURCE	EFFECT	S of S	DF	MS	F	Significant
Main Effects						
pH	-0.044	0.004	1	0.004	6.78	No
Alkalinity	0.260	0.135	1	0.135	234	Yes
Fluence	-0.326	0.212	1	0.212	368	Yes
Interactions						
PxA	0.063	0.008	1	0.008	13.9	No
PxF	-0.160	0.051	1	0.051	89	Yes
AxF	0.044	0.004	1	0.004	6.58	No
PxAxF	-0.390	0.304	1	0.304	527	Yes
Error			1	0.001		

$F_{1, 2, 0.05} = 18.51$

Table F.15 THMs Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	THMs (µg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	$CHCl_3$	TTHMs
1	6	0	1000	1.19	44.1	44.1
2	8	0	1000	0.97	32.6	32.6
3	6	200	1000	1.13	41.1	41.1
4	8	200	1000	1.21	37.8	37.8
5	6	0	5000	0.03	8.55	8.55
6	8	0	5000	1.54	15.3	15.3
7	6	200	5000	1.28	24	24
8	8	200	5000	1.12	12.3	12.3
9a	7.7	100	3000	0.92	24.2	24.2
9b	7.7	100	3000	1.47	26.3	26.3
9c	7.7	100	3000	1.63	32.7	32.7
9d	7.7	100	3000	1.79	16.6	16.6
			Variance		44.2	44.2
C1				1.09	102	102
C2				1.16	81.2	81.2
C3				1.55	66.5	66.5
C4				1.71	63.4	63.4
			Average	1.38	78.2	78.2

Table F.16a Yates' Algorithm for TTHMs

Run	Total	[1]	[2]	[3]	Divisor	Effect	
1	44.1	76.7	156	216	8	27	Mean
2	32.6	78.9	60.1	-19.8	4	-4.95	P
3	41.1	23.8	-14.8	14.8	4	3.7	A
4	37.8	36.3	-4.98	-10.2	4	-2.55	PA
5	8.55	-11.5	2.27	-95.5	4	-23.9	F
6	15.3	-3.3	12.5	9.86	4	2.47	PF
7	24	6.71	8.2	10.3	4	2.57	AF
8	12.3	-11.7	-18.4	-27.6	4	-6.65	PAF

Table F.16b ANOVA Table for TTHMs

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-4.95	49.1	1	49.1	1.11	No
Alkalinity	3.7	27.4	1	27.4	0.62	No
Fluence	-23.9	1140	1	1140	25.8	Yes
Interactions						
PxA	-2.55	13.2	1	13.2	0.294	No
PxF	2.47	12.1	1	12.1	0.275	No
AxF	2.57	13.2	1	13.2	0.298	No
PxAxF	-6.65	88.4	1	88.4	2	No
Error			1	44.2		

$F_{1, 3, 0.05} = 10.1$

Brominated DBPs Using UV Photolysis

Table F.17 HAA Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HAAs (μg/L)				
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	CL_2AA	Cl_3AA	BrAA	BrClAA	$BrCl_2AA$
1	6	0	1000	1.25	2.20	0.638	0.636	4.73	1.92
2	8	0	1000	1.18	2.54	0.766	0.696	4.98	2.40
3	6	200	1000	1.5	2.05	0.649	0.530	4.23	2.28
4	8	200	1000	1.55	1.90	0.541	0.478	4.35	1.40
5	6	0	5000	0.7	0.75	0.114	0.412	1.07	1.90
6	8	0	5000	0.5	0.88	0.128	0.387	0.879	2.18
7	6	200	5000	0.77	0.682	0.115	0.419	0.799	1.37
8	8	200	5000	0.83	0.683	0.101	0.333	0.951	1.52
9a	8	100	3000	0.96	0.951	0.169	0.402	2.29	2.87
9b	8	100	3000	1.02	0.749	0.158	0.364	2.20	1.85
9c	8	100	3000	1.18	0.838	0.140	0.406	2.30	2.15
9d	8	100	3000	1.13	0.870	0.167	0.354	1.68	1.96
			Variance		0.007	0.000	0.001	0.087	0.207
C1					2.41	0.97	0.59	5.45	2.62
C2					3.18	1.57	0.62	5.97	4
C3					3.99	1.71	0.66	6.39	3.36
C4					3.49	1.66	0.71	6.69	4.59
				Average	3.27	1.48	0.645	6.124	3.64

Table F.17 HAA Raw Data cont'd

Run	pH	Added alkalinity	Fluence	HAAs (μg/L)			
		mg/l as $CaCO_3$	mJ/cm^2	Br_2ClAA	Br_2AA	Br_3AA	Total
1	6	0	1000	7.61	6.64	6.05	30.4
2	8	0	1000	9.09	6.65	7.72	34.8
3	6	200	1000	8.16	5.63	5.65	29.2
4	8	200	1000	6.38	4.90	4.40	24.4
5	6	0	5000	2.22	2.45	1.54	10.4
6	8	0	5000	2.11	2.37	1.32	10.3
7	6	200	5000	1.34	1.87	1.30	7.89
8	8	200	5000	1.18	1.99	1.46	8.21
9a	8	100	3000	2.53	3.21	2.3	14.7
9b	8	100	3000	1.84	2.53	2.2	11.9
9c	8	100	3000	2.17	2.93	2.9	13.8
9d	8	100	3000	2.66	2.87	2.5	13.1
			Variance	0.137	0.079	0.093	1.44
				0.370	0.281	0.304	1.2
C1				14.0	7.99	7.81	41.90
C2				13.	7.19	5.97	41.7
C3				10.7	7.06	4.37	38.3
C4				15.8	8.26	7.48	48.7
			Average	1345	7.62	6.42	42.6

Table F.18a Cl_2AA Yates' Algorithm

Run	Cl_2AA	[1]	[2]	[3]	Divisor	Effect	
1	2.2	4.75	8.69	11.7	8	1.46	Mean
2	2.54	3.95	3	0.33	4	0.082	P
3	2.05	1.64	0.196	-1.1	4	-0.267	A
4	1.9	1.37	0.133	-0.616	4	-0.154	PA
5	0.751	0.340	-0.800	-5.69	4	-1.42	F
6	0.884	-0.144	-0.270	-0.062	4	0.016	PF
7	0.682	0.133	-0.484	0.530	4	0.132	AF
8	0.683	0.001	-0.132	0.352	4	0.088	PAF

Table F.18b ANOVA Table for Cl_2AA						
Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.082	0.014	1	0.014	1.94	No
Alkalinity	-0.267	0.143	1	0.143	20.5	Yes
UV-fluence	-1.42	4.05	1	4.05	581	Yes
Interactions						
PxA	-0.154	0.05	1	0.05	6.81	No
PxF	-0.016	0	1	0	0.07	No
AxF	0.132	0.035	1	0.035	5.03	No
PxAxF	0.088	0.015	1	0.015	2.22	No
Error			1	0.01		

$F_{1,3,0.05} = 10.1$

Table F.19a Cl_3AA Yates' Algorithm

Run	Cl_3AA	[1]	[2]	[3]	Divisor	Effect	
1	0.638	1.403	2.59	3.05	8	0.381	Mean
2	0.766	1.19	0.458	0.021	4	0.005	P
3	0.649	0.242	0.021	-0.240	4	-0.060	A
4	0.541	0.216	0.000	-0.263	4	-0.066	PA
5	0.114	0.128	-0.214	-2.13	4	-0.534	F
6	0.128	-0.108	-0.026	-0.021	4	-0.005	PF
7	0.115	0.013	-0.236	0.189	4	0.047	AF
8	0.101	-0.014	-0.027	0.209	4	0.052	PAF

Table F.19b ANOVA Table for Cl_3AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.005	0.000	1	0.000	0.293	No
Alkalinity	-0.060	0.007	1	0.007	40	Yes
UV-fluence	-0.534	0.569	1	0.569	3171	Yes
Interactions						
PxA	-0.066	0.009	1	0.009	48.2	Yes
PxF	-0.005	0.000	1	0.000	0.301	No
AxF	0.047	0.004	1	0.004	24.8	Yes
PxAxF	0.052	0.005	1	0.005	30.5	Yes
Error			1	0.000		

$F_{1,3,0.05} = 10.1$

Table F.20a BrAA Yates Algorithm

Run	BrAA	[1]	[2]	[3]	Divisor	Effect	
1	0.636	1.33	2.34	3.89	8	0.487	Mean
2	0.696	1.008	1.55	-0.101	4	-0.025	P
3	0.530	0.800	0.009	-0.372	4	-0.093	A
4	0.478	0.752	-0.110	-0.172	4	-0.043	PA
5	0.412	0.061	-0.324	-0.789	4	-0.197	F
6	0.387	-0.051	-0.048	-0.119	4	-0.030	PF
7	0.419	-0.025	-0.112	0.277	4	0.069	AF
8	0.333	-0.085	-0.060	0.052	4	0.013	PAF

Table F.20b ANOVA Table for BrAA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.025	0.001	1	0.001	1.84	No
Alkalinity	-0.093	0.017	1	0.017	25.08	Yes
UV-fluence	-0.197	0.078	1	0.078	112	Yes
Interactions						
PxA	-0.043	0.004	1	0.004	5.37	No
PxF	-0.030	0.002	1	0.002	2.57	No
AxF	0.069	0.010	1	0.010	13.9	Yes
PxAxF	0.013	0.000	1	0.000	0.485	No
Error			1	0.001		

$F_{1,3,0.05} = 10.1$

Table F.21a BrClAA Yates Algorithm

Run	BrClAA	[1]	[2]	[3]	Divisor	Effect	
1	4.730	9.708	18.287	21.986	8	2.748	Mean
2	4.978	8.579	3.699	0.335	4	0.084	P
3	4.227	1.950	0.375	-1.328	4	-0.332	A
4	4.353	1.750	-0.040	0.222	4	0.056	PA
5	1.071	0.248	-1.128	-14.588	4	-3.647	F
6	0.879	0.126	-0.200	-0.415	4	-0.104	PF
7	0.799	-0.192	-0.122	0.928	4	0.232	AF
8	0.951	0.152	0.344	0.466	4	0.117	PAF

Table F.21b ANOVA Table for BrClAA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.084	0.014	1	0.014	0.161	No
Alkalinity	-0.332	0.220	1	0.220	2.536	No
UV-fluence	-3.647	26.600	1	26.600	306.083	Yes
Interactions						
PxA	0.056	0.006	1	0.006	0.071	No
PxF	-0.104	0.021	1	0.021	0.247	No
AxF	0.232	0.108	1	0.108	1.239	No
PxAxF	0.117	0.027	1	0.027	0.313	No
Error			1	0.087		

$F_{1,3,0.05} = 10.13$

Table F.22a $BrCl_2AA$ Yates' Algorithm

Run	$BrCl_2AA$	[1]	[2]	[3]	Divisor	Effect	
1	1.92	4.32	8.01	15	8	1.87	Mean
2	2.4	3.68	6.97	0.013	4	0	P
3	2.28	4.08	-0.411	-1.8	4	-0.457	A
4	1.4	2.89	0.42	-1.49	4	-0.373	PA
5	1.9	0.47	-0.638	-1.03	4	-0.258	F
6	2.18	-0.884	-1.19	0.835	4	0.209	PF
7	1.37	0.279	-1.357	-0.553	4	-0.138	AF
8	1.52	0.145	-0.134	1.22	4	0.306	PAF

Table F.22b ANOVA Table for $BrCl_2AA$

SOURCE	EFFECT	S of S	df	MS	F	Significant
Main Effects						None
pH	0.003	0.000	1	0.000	0.000	
Alkalinity	-0.457	0.418	1	0.418	2.016	
UV-fluence	-0.258	0.133	1	0.133	0.640	
Interactions						
PxA	-0.373	0.278	1	0.278	1.34	
PxF	0.209	0.087	1	0.087	0.420	
AxF	-0.138	0.038	1	0.038	0.184	
PxAxF	0.306	0.187	1	0.187	0.902	
Error			1	0.207		

$F_{1,3,0.05} = 10.13$

Table F.23a Br_2ClAA Yates Algorithm

Run	Br_2ClAA	[1]	[2]	[3]	Divisor	Effect	
1	7.61	16.7	31.2	38.1	8	4.76	Mean
2	9.09	14.5	6.9	-0.570	4	-0.143	P
3	8.16	4.34	-0.304	-3.98	4	-0.995	A
4	6.38	2.52	-0.266	-3.31	4	-0.827	PA
5	2.224	1.48	-2.16	-24.4	4	-6.10	F
6	2.11	-1.78	-1.82	0.038	4	0.009	PF
7	1.34	-0.111	-3.26	0.344	4	0.086	AF
8	1.18	-0.155	-0.044	3.22	4	0.805	PAF

Table F.23b ANOVA Table for Br_2ClAA

SOURCE	EFFECT	S of S	df	MS	F	Significant
Main Effects						
pH	-0.143	0.041	1	0.041	0.298	No
Alkalinity	-0.995	1.98	1	1.980	14.5	Yes
UV-fluence	-6.1	74.4	1	74.4	544	Yes
Interactions						
PxA	-0.827	1.37	1	1.37	10.	No
PxF	0.009	0.000	1	0.000	0.001	No
AxF	0.086	0.015	1	0.015	0.108	No
PxAxF	0.805	1.3	1	1.3	9.48	No
Error			1	0.137		No

$F_{1,3,0.05} = 10.13$

Table F.24a Br_2AA Yates Algorithm

Run	Br_2AA	[1]	[2]	[3]	Divisor	Effect	
1	6.64	13.3	23.8	32.5	8	4.06	Mean
2	6.65	10.5	8.67	-0.664	4	-0.166	P
3	5.63	4.82	-0.716	-3.72	4	-0.93	A
4	4.90	3.86	0.052	-0.539	4	-0.135	PA
5	2.45	0.009	-2.76	-15.1	4	-3.79	F
6	2.37	-0.724	-0.964	0.767	4	0.192	PF
7	1.87	-0.071	-0.733	1.79	4	0.448	AF
8	1.99	0.123	0.194	0.928	4	0.232	PAF

Table F.24b ANOVA Table for Br_2AA

SOURCE	EFFECT	S of S	df	MS	F	Significant
Main Effects						
pH	-0.166	0.055	1	0.055	0.700	No
Alkalinity	-0.930	1.73	1	1.73	22	Yes
UV-fluence	-3.79	28.7	1	28.7	364	Yes
Interactions						
PxA	-0.135	0.036	1	0.036	0.461	No
PxF	0.192	0.074	1	0.074	0.934	No
AxF	0.448	0.402	1	0.402	5.11	No
PxAxF	0.232	0.108	1	0.108	1.37	No
Error			1	0.079		

$F_{1,3,0.05} = 10.13$

Table F.25a Br_3AA Yates' Algorithm

Run	Br_3AA	[1]	[2]	[3]	Divisor	Effect	
1	6.05	13.8	23.8	29.4	8	3.68	Mean
2	7.71	10.1	5.61	0.37	4	0.09	P
3	5.65	2.85	0.42	-3.8	4	-953	A
4	4.4	2.75	-0.1	-2.5	4	-0.6	PA
5	1.53	1.67	-3.7	-18	4	-4.6	F
6	1.32	-1.25	-0.1	-0.5	4	-0.1	PF
7	1.3	-0.215	-2.9	3.61	4	0.9	AF
8	1.46	0.159	0.37	3.29	4	0.82	PAF

Table F.25b ANOVA Table for Br_3AA

SOURCE	EFFECT	S of S	DF	MS	F	Significant
Main Effects						
pH	0.092	0.017	1	0.017	0.182	No
Alkalinity	-0.953	1.82	1	1.82	19.7	Yes
UV-fluence	-4.55	41.4	1	41.4	447	Yes
Interactions						
PxA	-0.635	0.807	1	0.807	8.72	No
PxF	-0.120	0.029	1	0.029	0.31	No
AxF	0.902	1.63	1	1.63	17.6	Yes
PxAxF	0.822	1.35	1	1.35	14.6	Yes
Error			1	0.093		$F_{1,3,0.05} = 10.13$

Table F.26a HAA_9 Yates' Algorithm							
Run	HAA_9	[1]	[2]	[3]	Divisor	Effect	
1	30.4	65.3	119	155	8	19.4	Mean
2	34.8	53.5	36.2	0.33	4	0.08	P
3	29.2	20.7	-0.41	-17	4	-4.24	A
4	24.4	15.5	0.735	-8.1	4	-2.03	PA
5	10.5	4.41	-12	-83	4	-20.6	F
6	10.3	-4.82	-5.22	1.14	4	0.29	PF
7	7.29	-0.2	-9.22	6.52	4	1.63	AF
8	8.21	0.92	1.11	10.3	4	2.58	PAF

Table F.26b ANOVA Table for HAA_9

SOURCE	EFFECT	S of S	df	MS	F	Significant
Main Effects						
pH	0.082	0.013	1	0.013	0.009	No
Alkalinity	-4.24	35.9	1	35.9	24.983	Yes
UV-Fluence	-20.6	852	1	852	592.917	Yes
Interactions						
PxA	-2.03	8.22	1	8.22	5.717	No
PxF	0.286	0.163	1	0.163	0.113	No
AxF	1.63	5.31	1	5.311	3.694	No
PxAxF	2.59	13.4	1	13.4	9.290	No
Error			1	1.44		

$F_{1,3,0.05} = 10.13$

Table F.27 THMs Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 Residual	THMs (μg/L)				
		mg/l as $CaCO_3$	mJ/cm^2	mg/L	$CHCl_3$	$BrCl_2CH$	$ClCHBr_2$	CHBr3	Total
1	6	0	1000	1.25	11.1	22.2	68.6	84.4	186
2	8	0	1000	1.18	9.96	22.2	68.3	81.8	182
3	6	200	1000	1.50	10.8	22.8	64.8	68	166
4	8	200	1000	1.55	9.49	21.3	66.9	70.9	169
5	6	0	5000	0.70	3.29	6.45	23.3	50	83
6	8	0	5000	0.50	2.17	5.46	22.9	56.5	87
7	6	200	5000	0.77	2.85	7.37	31.3	67.1	109
8	8	200	5000	0.83	2.2	5.35	17.2	39.2	64
9a	7.7	100	3000	0.96	3.97	10.3	40	77.7	132
9b	7.7	100	3000	1.02	2.54	5.88	24.9	50.1	83.4
9c	7.7	100	3000	1.18	3.65	10.2	38.4	76.8	129
9d	7.7	100	3000	1.13	5.12	11.9	47.4	84.3	149
			Variance	1.05	1.12	6.65	88.5	16.8	782
C1				1.65	10.7	22.9	74.6	83	191
C2				2.04	19	37.5	98	79.4	234
C3				2.06	25	44	110	84.6	264
C4				2.11	22.2	45.3	136	116	319
			Average	1.97	19.2	37.4	105	90.7	252

Table F.28a Yates' Algorithm for TTHMs

Run	TTHMs	[1]	[2]	[3]	Divisor	Effect	
1	186	369	704	1050	8	131	Mean
2	182	335	343	-42	4	-10.55	P
3	166	170	-1.56	-31.1	4	-7.8	A
4	169	173	-41	-42.4	4	-10.6	PA
5	83	-3.88	-34	-360	4	-90.2	F
6	87	2.32	2.56	-39.1	4	-10	PF
7	109	3.99	6.2	36.2	4	9.05	AF
8	64	-44.6	-48.6	-54.8	4	-13.7	PAF

Table F.28a ANOVA Table for TTHMs						
Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-11	223	1	223	0.285	No
Alkalinity	-7.8	121	1	121	0.154	No
UV-fluence	-90.2	16300	1	16300	20.8	Yes
Interactions						
PxA	-10.6	225	1	225	0.288	No
PxF	-9.77	191	1	191	0.244	No
AxF	9.05	164	1	164	0.209	No
PxAxF	-13.7	376	1	376	0.48	No
Error			1	782		

$F_{1, 3, 0.05} = 10.1$

Table F. 29a Yates' Algorithm for $CHCl_3$

Run	$CHCl_3$	[1]	[2]	[3]	Divisor	Effect	
1	11.1	21	41.3	51.8	8	6.48	Mean
2	9.96	20.3	10.5	-4.18	4	-1.05	P
3	10.8	5.46	-2.41	-1.17	4	-0.194	A
4	9.49	5.05	-1.78	0.294	4	0.073	PA
5	3.29	-1.1	-0.761	-30.8	4	-7.7	F
6	2.17	-1.3	-0.414	0.629	4	0.157	PF
7	2.85	-1.1	-0.185	0.347	4	0.087	AF
8	2.2	-0.65	0.48	0.663	4	0.166	PAF

Table F.29b ANOVA Table for $CHCl_3$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-1.05	2.19	1	2.19	1.95	No
Alkalinity	-0.294	0.17	1	0.17	0.15	No
UV-fluence	-7.7	119	1	119	106	Yes
Interactions						
PxA	0.073	0.01	1	0.01	0.01	No
PxF	0.157	0.05	1	0.05	0.04	No
AxF	0.087	0.02	1	0.02	0.01	No
PxAxF	0.166	0.05	1	0.05	0.05	No
Error			1	1.12		

$F_{1,3,0.05} = 10.1$

Table F.30a Yates' Algorithm for $BrCl_2CH$

Run	$BrCl_2CH$	[1]	[2]	[3]	Divisor	Effect	
1	22.2	44.4	88.5	113	8	14.1	Mean
2	22.2	44.1	24.6	-4.4	4	-1.1	P
3	22.8	11.9	-1.4	0.481	4	0.12	A
4	21.3	12.7	-3.01	-2.56	4	-0.6	PA
5	6.45	0.08	-0.328	-64.8	4	-16	F
6	5.46	-1.45	0.81	-1.64	4	-0.4	PF
7	7.37	-0.987	-1.53	1.14	4	0.28	AF
8	5.35	-2.03	-1.04	0.491	4	0.12	PAF

Table F.30b ANOVA Table for $BrCl_2CH$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-1.1	2.41	1	2.41	0.36	No
Alkalinity	0.12	0.03	1	0.03	0	No
UV-fluence	-16	509	1	509	76.6	Yes
Interactions						
PxA	-0.642	0.825	1	0.825	0.12	No
PxF	-0.409	0.335	1	0.335	0.05	No
AxF	0.284	0.161	1	0.161	0.02	No
PxAxF	0.124	0.03	1	0.03	0	No
Error			1	6.65		

$F_{1,3,0.05} = 10$

Table F.31a Yates' Algorithm for $ClCHBr_2$

Run	$ClCHBr_2$	[1]	[2]	[3]	Divisor	Effect	
1	68.6	137	269	363	8	45.4	Mean
2	68.3	132	94.6	-13	4	-3.1	P
3	64.8	46.2	1.87	-2.9	4	-0.7	A
4	66.9	48.5	-14	-11	4	-2.8	PA
5	23.3	-0.3	-5.2	-170	4	-44	F
6	22.9	2.14	2.32	-16	4	-4.1	PF
7	31.3	-0.4	2.41	7.56	4	1.89	AF
8	17.2	-14.1	-14	-16	4	-4.03	PAF

Table F.31b ANOVA Table for $ClCHBr_2$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-3.1	19.7	1	19.7	0.22	No
Alkalinity	-0.7	1.06	1	1.06	0.01	No
UV-fluence	-44	3790	1	3790	42.8	Yes
Interactions						
PxA	-2.8	15.9	1	15.9	0.18	No
PxF	-4.1	33.1	1	33.1	0.37	No
AxF	1.89	7.14	1	7.14	0.08	No
PxAxF	-4	32.4	1	32.4	0.37	No
Error			1	88.5		

$F_{1,3,0.05} = 10.1$

Table F.32a Yates' Algorithm for $CHBr_3$

Run	$CHBr_3$	[1]	[2]	[3]	Divisor	Effect	
1	84.4	166	305	518	8	64.8	Mean
2	81.8	139	213	-21	4	-5.3	P
3	68	107	0.35	-27	4	-6.9	A
4	70.9	106	-21	-29	4	-7.2	PA
5	50	-2.6	-27	-92	4	-23	F
6	56.5	2.93	-0.2	-22	4	-5.4	PF
7	67.1	6.47	5.51	27.2	4	6.79	AF
8	39.2	-28	-34	-40	4	-10	PAF

Table F.32b ANOVA Table for CHBr3

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-5.3	55.6	1	55.6	3.3	No
Alkalinity	-6.9	94.4	1	94.4	5.61	No
UV-fluence	-23	1060	1	1060	63.3	Yes
Interactions						
PxA	-7.2	104	1	104	6.19	No
PxF	-5.4	59.4	1	59.4	3.53	No
AxF	6.79	92.2	1	92.2	5.48	No
PxAxF	-10	199	1	199	11.8	No
Error			1	16.8		

$F_{1,2,0.05} = 18.5$

Brominated DBPs Using UV/H_2O_2

Table F.33 HAA Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 Residual	HAAs (μg/L)				
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	CL_2AA	Cl_3AA	BrAA	BrClAA	$BrCl_2AA$
1	6	0	1000	1.25	1.99	0.597	0.650	3.10	1.01
2	8	0	1000	1.18	1.76	0.490	0.667	2.55	0.6
3	6	200	1000	1.5	1.97	0.484	0.631	1.50	1.50
4	8	200	1000	1.55	1.39	0.438	0.465	2.26	1.21
5	6	0	5000	0.7	1.13	0.183	0.364	0.225	0.225
6	8	0	5000	0.5	0.846	0.158	0.323	0.683	0.177
7	6	200	5000	0.77	0.815	0.164	0.366	0.814	0.232
8	8	200	5000	0.83	0.780	0.213	0.297	0.962	0.366
9a	8	100	3000	0.96	0.855	0.195	0.437	1.13	0.175
9b	8	100	3000	1.02	0.981	0.223	0.408	1.190	0.268
9c	8	100	3000	1.18	1.01	0.250	0.420	1.38	0.327
9d	8	100	3000	1.13	1.35	0.257	0.399	1.54	0.249
			Variance		0.044	0.001	0.000	0.035	0.004
C1					2.09	0.832	0.470	2.86	2.72
C2					2.5	0.981	0.556	3.40	2.84
C3					2.85	1.2	0.660	3.35	2.98
C4					2.51	1.1	0.651	4.11	1.87
				Average	2.49	1.03	0.584	3.43	2.60

Table F.33 HAA Raw Data cont'd

Run	pH	Added alkalinity	UV-fluence	HAAs (μg/L)			
		mg/l as $CaCO_3$	mJ/cm^2	Br_2ClAA	Br_2AA	Br_3AA	Total
1	6	0	1000	4.57	4.28	3.03	19.2
2	8	0	1000	3.88	4.17	2.95	17.1
3	6	200	1000	6.5	4.58	4.87	22
4	8	200	1000	7.27	4.15	6.63	23.8
5	6	0	5000	1.48	1.59	1.2	6.4
6	8	0	5000	1.48	1.25	0.84	5.76
7	6	200	5000	1.62	1.52	0.94	6.48
8	8	200	5000	1.37	1.73	1.35	7.07
9a	8	100	3000	1.83	1.96	0.97	7.55
9b	8	100	3000	2.42	1.88	1.14	8.51
9c	8	100	3000	1.82	2.28	1.44	8.93
9d	8	100	3000	1.91	2.04	1.26	9.01
			Variance	0.08	0.03	0.04	0.45
C1				13.1	6.72	8.04	36.8
C2				11.8	7.06	7.32	36.4
C3				12.4	8.04	8.09	39.6
C4				9.12	7.62	9.12	36.1
			Average	11.6	7.36	8.14	37.2

Table F.34a Cl_2AA Yates' Algorithm

Run	Cl_2AA	[1]	[2]	[3]	Divisor	Effect	
1	1.99	3.75	7.11	10.72	8	1.34	Mean
2	1.76	3.36	3.57	-1.12	4	-0.280	P
3	1.97	1.97	-0.803	-0.772	4	-0.193	A
4	1.39	1.6	-0.317	-0.098	4	-0.024	PA
5	1.13	-0.229	-0.393	-3.54	4	-0.886	F
6	0.846	-0.574	-0.378	0.486	4	0.122	PF
7	0.815	-0.281	-0.344	0.015	4	0.004	AF
8	0.780	-0.035	0.246	0.591	4	0.148	PAF

Table F.34b ANOVA Table for Cl_2AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.28	0.157	1	0.157	3.52	No
Alkalinity	-0.193	0.074	1	0.074	1.67	No
UV-fluence	-0.886	1.57	1	1.57	35.3	Yes
Interactions						
PxA	-0.024	0.001	1	0.001	0.027	No
PxF	0.122	0.030	1	0.030	0.664	No
AxF	0.004	0.000	1	0.000	0.001	No
PxAxF	0.148	0.044	1	0.044	0.980	No
Error			1	0.044		

$F_{1,3,0.05} = 10.13$

Table F.35a Cl_3AA Yates Algorithm

Run	Cl_3AA	[1]	[2]	[3]	Divisor	Effect	
1	0.597	1.09	2.01	2.73	8	0.341	Mean
2	0.490	0.922	0.717	-0.129	4	-0.032	P
3	0.484	0.341	-0.153	-0.129	4	-0.032	A
4	0.438	0.376	0.024	0.135	4	0.034	PA
5	0.183	-0.107	-0.164	-1.29	4	-0.323	F
6	0.158	-0.046	0.036	0.177	4	0.044	PF
7	0.164	-0.025	0.061	0.200	4	0.050	AF
8	0.213	0.049	0.074	0.013	4	0.003	PAF

Table F.35b ANOVA Table for Cl_3AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.032	0.002	1	0.002	2.61	No
Alkalinity	-0.032	0.002	1	0.002	2.57	No
UV-fluence	-0.323	0.209	1	0.209	259	Yes
Interactions						
PxA	0.034	0.002	1	0.002	2.85	No
PxF	0.044	0.004	1	0.004	4.89	No
AxF	0.050	0.005	1	0.005	6.21	No
PxAxF	0.003	0.000	1	0.000	0.028	No
Error			1	0.001		$F_{1,3,0.05} = 10.1$

Table F.36a BrAA Yates' Algorithm

Run	BrAA	[1]	[2]	[3]	Divisor	Effect	
1	0.650	1.32	2.41	3.76	8	0.470	Mean
2	0.667	1.1	1.35	-0.26	4	-0.065	P
3	0.631	0.687	-0.15	-0.244	4	-0.061	A
4	0.465	0.663	-0.11	-0.21	4	-0.053	PA
5	0.364	0.016	-0.221	-1.063	4	-0.266	F
6	0.323	-0.166	-0.023	0.040	4	0.010	PF
7	0.366	-0.041	-0.183	0.198	4	0.049	AF
8	0.297	-0.069	-0.028	0.155	4	0.039	PAF

Table F.36b ANOVA Table for BrAA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.065	0.008	1	0.0084	31.2	Yes
Alkalinity	-0.061	0.007	1	0.0075	27.6	Yes
UV-fluence	-0.266	0.141	1	0.1412	521	Yes
Interactions						
PxA	-0.053	0.006	1	0.0055	20.4	Yes
PxF	0.010	0.000	1	0.0002	0.723	No
AxF	0.049	0.005	1	0.0049	18.04	Yes
PxAxF	0.039	0.003	1	0.0030	11.08	Yes
Error			1	0.0003		

$F_{1,3,0.05} = 10.1$

Table F.37a BrClAA Yates' Algorithm

Run	BrClAA	[1]	[2]	[3]	Divisor	Effect	
1	3.10	5.65	9.41	12.1	8	1.51	Mean
2	2.55	3.76	2.683	0.802	4	0.201	P
3	1.50	0.908	0.196	-1.02	4	-0.256	A
4	2.26	1.78	0.606	0.997	4	0.249	PA
5	0.225	-0.556	-1.89	-6.73	4	-1.68	F
6	0.683	0.752	0.87	0.410	4	0.103	PF
7	0.814	0.458	1.31	2.76	4	0.690	AF
8	0.962	0.148	-0.311	-1.62	4	-0.405	PAF

Table F.37b ANOVA Table for BrClAA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.201	0.080	1	0.080	2.32	No
Alkalinity	-0.256	0.131	1	0.131	3.78	No
UV-fluence	-1.68	5.66	1	5.66	163	Yes
Interactions						
PxA	0.249	0.124	1	0.124	3.59	No
PxF	0.103	0.021	1	0.021	0.606	No
AxF	0.690	0.952	1	0.952	27.4	Yes
PxAxF	-0.405	0.328	1	0.328	9.45	No
Error			1	0.035		

$F_{1,3,0.05} = 10.1$

Table F.38a $BrCl_2AA$ Yates' Algorithm

Run	$BrCl_2AA$	[1]	[2]	[3]	Divisor	Effect	
1	1.01	1.61	4.32	5.32	8	0.664	Mean
2	0.60	2.71	0.999	-0.617	4	-0.154	P
3	1.50	0.402	-0.703	1.30	4	0.325	A
4	1.21	0.598	0.087	0.290	4	0.073	PA
5	0.225	-0.406	1.11	-3.32	4	-0.829	F
6	0.177	-0.298	0.196	0.790	4	0.197	PF
7	0.232	-0.048	0.108	-0.910	4	-0.227	AF
8	0.366	0.134	0.182	0.074	4	0.018	PAF

Table F.38b ANOVA Table for $BrCl_2AA$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.154	0.048	1	0.048	12.0	Yes
Alkalinity	0.325	0.212	1	0.212	53.7	Yes
UV-fluence	-0.829	1.38	1	1.38	348	Yes
Interactions						
PxA	0.073	0.011	1	0.011	2.67	No
PxF	0.197	0.078	1	0.078	19.8	Yes
AxF	-0.227	0.103	1	0.103	26.2	Yes
PxAxF	0.018	0.001	1	0.001	0.173	No
Error			1	0.004		

$F_{1,3,0.05} = 10.1$

Table F.39a Br_2ClAA Yates' Algorithm

Run	Br_2ClAA	[1]	[2]	[3]	Divisor	Effect	
1	4.57	8.45	22.2	28.2	8	3.52	Mean
2	3.88	13.77	5.96	-0.171	4	-0.043	P
3	6.5	2.97	0.081	5.33	4	1.33	A
4	7.27	2.99	-0.252	1.22	4	0.304	PA
5	1.49	-0.693	5.31	-16.3	4	-4.07	F
6	1.49	0.774	0.019	-0.334	4	-0.083	PF
7	1.620	0.000	1.47	-5.3	4	-1.32	AF
8	1.37	-0.252	-0.252	-1.72	4	-0.430	PAF

Table F.39b ANOVA Table for Br_2ClAA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.043	0.004	1	0.004	0.045	No
Alkalinity	1.3343	3.56	1	3.56	44	Yes
UV-fluence	-4.07	330	1	33.0	408	Yes
Interactions						
PxA	0.304	0.185	1	0.185	2.29	No
PxF	-0.083	0.014	1	0.014	0.172	No
AxF	-1.32	3.50	1	3.50	43.4	Yes
PxAxF	-0.430	0.370	1	0.370	4.57	No
Error			1	0.081		

$F_{1,3,0.05} = 10.1$

Table F.40a Br_2AA Yates' Algorithm

Run	Br_2AA	[1]	[2]	[3]	Divisor	Effect	
1	4.28	8.46	17.2	23.3	8	2.91	Mean
2	4.17	8.73	6.1	-0.7	4	-0.2	P
3	4.58	2.84	-0.5	0.68	4	0.17	A
4	4.15	3.25	-0.1	0.23	4	0.06	PA
5	1.59	-0.1	0.28	-11	4	-2.8	F
6	1.25	-0.4	0.41	0.41	4	0.1	PF
7	1.52	-0.3	-0.3	0.13	4	0.03	AF
8	1.73	0.21	0.55	0.87	4	0.22	PAF

Table F.40b Br_2AA ANOVA Table						
Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.170	0.058	1	0.058	1.95	No
Alkalinity	0.171	0.059	1	0.059	1.96	
UV-fluence	-2.77	15.4	1	15.4	515	Yes
Interactions						
PxA	0.056	0.006	1	0.006	0.212	No
PxF	0.102	0.021	1	0.021	0.696	No
AxF	0.033	0.002	1	0.002	0.073	No
PxAxF	0.219	0.096	1	0.096	3.20	No
Error			1	0.030		

$F_{1,3,0.05} = 10.1$

Table F.41a Br_3AA Yates' Algorithm

Run	Br_3AA	[1]	[2]	[3]	Divisor	Effect	
1	3.03	5.98	17.5	21.8	8	2.73	Mean
2	2.95	11.5	4.34	1.73	4	0.43	P
3	4.87	2.04	1.68	5.77	4	1.44	A
4	6.63	2.3	0.05	2.6	4	0.65	PA
5	1.2	-0.1	5.52	-13	4	-3.3	F
6	0.84	1.76	0.25	-1.6	4	-0.4	PF
7	0.94	-0.4	1.84	-5.3	4	-1.3	AF
8	1.35	0.41	0.76	-1.1	4	-0.3	PAF

Table F.41b ANOVA Table for Br_3AA

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	0.432	0.374	1	0.374	9.59	No
Alkalinity	1.44	4.17	1	4.17	106	Yes
UV-fluence	-3.29	21.6	1	21.6	554	Yes
Interactions						
PxA	0.651	0.847	1	0.847	21.7	Yes
PxF	-0.408	0.333	1	0.333	8.54	No
AxF	-1.32	3.47	1	3.47	88.9	Yes
PxAxF	-0.269	0.145	1	0.145	3.711	No
Error			1	0.039		No

$F_{1,3,0.05} = 10.1$

Table F.42a HAA_9 Yates' Algorithm

Run	HAA_9	[1]	[2]	[3]	Divisor	Effect	
1	19.5	36.3	87.2	113	8	14.1	Mean
2	16.8	50.9	25.7	0	4	0	P
3	24	12.4	0.23	15.5	4	3.87	A
4	26.9	13.3	-0.3	6.26	4	1.56	PA
5	6.4	-2.7	14.6	-61	4	-15	F
6	6	2.98	0.88	-0.5	4	-0.1	PF
7	6.58	-0.4	5.72	-14	4	-3.4	AF
8	6.7	0.13	0.53	-5.2	4	-1.3	PAF

Table F.42b ANOVA Table for HAA_9

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-0.011	0.000	1	0.000	0.001	No
Alkalinity	3.87	29.9	1	29.9	67.9	Yes
Fluence	-15.4	472	1	472	1073	Yes
Interactions						
PxA	1.56	4.9	1	4.9	11.1	Yes
PxF	-0.126	0.032	1	0.032	0.073	No
AxF	-3.43	23.5	1	23.5	53.3	Yes
PxAxF	-1.3	3.37	1	3.37	7.65	No
Error			1	0.440		

$F_{1,3,0.05} = 10.1$

Table F.43 THMs Raw Data

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	THMs (μg/L)				
		mg/l as $CaCO_3$	mJ/cm^2	mg/L	$CHCl_3$	$BrCl_2CH$	$ClCHBr_2$	$CHBr_3$	Total
1	6	0	1000	0.68	8.74	21	62.8	80.6	173
2	8	0	1000	0.39	6.81	16.1	46	54.2	123
3	6	200	1000	0.33	9.52	23.5	82.9	103	219
4	8	200	1000	0.90	7.95	18.5	51.5	79.2	157
5	6	0	5000	0.45	4.21	5.3	26.8	41.5	77.8
6	8	0	5000	0.41	2.07	5.12	19.3	46.7	73.2
7	6	200	5000	0.58	2.67	6.44	23.1	48.5	80.6
8	8	200	5000	0.65	2.96	7.18	26.8	55.8	92.8
9a	7.7	100	3000	0.58	4.2	6.51	20.2	33.3	64.2
9b	7.7	100	3000	0.89	3.6	8.93	26.8	45.1	84.5
9c	7.7	100	3000	0.86	2.78	6.17	20.1	37.4	66.5
			Variance		0.51	2.27	14.7	36.1	123
C1				0.83	8.83	19.2	47.5	65.1	141
C2				0.84	6.27	13.8	40.5	44.5	105
C3				1.02	7.38	12.9	32.4	34.2	86.9
C4				0.59	6.07	10.7	27.7	31.9	76.4
			Average	0.82	7.14	14.1	37	43.9	102

Table F.44a Yates' Algorithm for TTHMs

Run	TTHMs	[1]	[2]	[3]	Divisor	Effect	
1	173	296	672	997	8	125	Mean
2	123	376	324	-100	4	-26	P
3	219	151	-110	102	4	25.6	A
4	157	173	7.55	4.88	4	1.22	PA
5	77.8	-50	80	-350	4	-87	F
6	73.2	-62	22.4	119	4	29.8	PF
7	80.6	-4.6	-12	-58	4	-14	AF
8	92.8	12.2	16.8	28.7	4	7.17	PAF

Table F.44b ANOVA Table for TTHMs

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-26	1360	1	1360	45.3	Yes
Alkalinity	25.6	1310	1	1310	43.7	No
UV-fluence	-87	15100	1	15100	504	Yes
Interactions						
PxA	1.22	2.98	1	2.98	0.1	No
PxF	29.8	1780	1	1780	59.4	No
AxF	-14	415	1	415	13.8	No
PxAxF	7.17	103	1	103	3.43	No
Error			1	30		

$F_{1, 2, 0.05} = 18.5$

Table F.45b Yates' Algorithm for $CHCl_3$

Run	$CHCl_3$	[1]	[2]	[3]	Divisor	Effect	
1	8.74	15.6	33	44.9	8	5.62	Mean
2	6.81	17.5	11.9	-5.3	4	-1.3	P
3	9.52	6.28	-3.5	1.26	4	0.32	A
4	7.95	5.62	-1.8	2.78	4	0.69	PA
5	4.21	-1.9	1.93	-21	4	-5.3	F
6	2.07	-1.6	-0.7	1.65	4	0.41	PF
7	2.67	-2.1	0.35	-2.6	4	-0.6	AF
8	2.96	0.29	2.43	2.07	4	0.52	PAF

Table F.45b ANOVA Table for $CHCl_3$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-1.3	3.57	1	3.57	7.05	No
Alkalinity	0.32	0.2	1	0.2	0.39	No
UV-fluence	-5.3	55.8	1	55.8	110	Yes
Interactions						
PxA	0.69	0.97	1	0.97	1.91	No
PxF	0.41	0.34	1	0.34	0.67	No
AxF	-0.6	0.84	1	0.84	1.66	No
PxAxF	0.52	0.54	1	0.54	1.06	No
Error			1	0.51		

$F_{1,2,0.05} = 18.5$

Table F.46a Yates' Algorithm for $BrCl_2CH$

Run	$BrCl_2CH$	[1]	[2]	[3]	Divisor	Effect	
1	21	37.1	79.1	103	8	12.9	Mean
2	16.1	42	24	-9	4	-2.3	P
3	23.5	10.4	-10	8.12	4	2.03	A
4	18.5	13.6	0.56	0.66	4	0.17	PA
5	5.3	-4.8	4.91	-55	4	-14	F
6	5.12	-5.1	3.2	10.5	4	2.62	PF
7	6.44	-0.2	-0.3	-1.7	4	-0.4	AF
8	7.18	0.74	0.93	1.19	4	0.3	PAF

Table F.46a ANOVA Table for $BrCl_2CH$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-2.3	10.9	1	10.9	4.82	No
Alkalinity	2.03	8.23	1	8.23	3.63	No
UV-fluence	-14	379	1	379	167	Yes
Interactions	0	0	0	0	0	
PxA	0.17	0.05	1	0.05	0.02	No
PxF	2.62	13.7	1	13.7	6.04	No
AxF	-0.4	0.36	1	0.36	0.16	No
PxAxF	0.3	0.18	1	0.18	0.08	No
Error			1	2.27		

$F_{1,2,0.05} = 18.5$

Table F.47a Yates' Algorithm for $ClCHBr_2$

Run	$ClCHBr_2$	[1]	[2]	[3]	Divisor	Effect	
1	62.8	109	243	339	8	42.4	Mean
2	46	134	96	-52	4	-13	P
3	82.9	46.1	-48	29.5	4	7.39	A
4	51.5	49.9	-3.7	-3.3	4	-0.8	PA
5	26.8	-17	25.7	-150	4	-37	F
6	19.3	-31	3.8	44.5	4	11.1	PF
7	23.1	-7.5	-15	-22	4	-5.5	AF
8	26.8	3.77	11.3	25.9	4	6.47	PAF

Table F.47b ANOVA Table for $ClCHBr_2$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-13	337	1	337	22.9	Yes
Alkalinity	7.39	109	1	109	7.43	No
UV-fluence	-37	2710	1	2710	184	Yes
Interactions						
PxA	-0.8	1.4	1	1.4	0.1	No
PxF	11.1	248	1	248	16.9	No
AxF	-5.5	60.2	1	60.2	4.1	No
PxAxF	6.47	83.6	1	83.6	5.69	No
Error			1	14.7		

$F_{1,2,0.05} = 18.5$

Table F.48a Yates' Algorithm for $CHBr_3$

Run	CHBr3	[1]	[2]	[3]	Divisor	Effect	
1	80.6	135	317	509	8	63.7	Mean
2	54.2	182	192	-38	4	-9	P
3	103	88.2	-50	63.4	4	15.9	A
4	79.2	104	12.5	4.79	4	1.2	PA
5	41.5	-26	47.4	-120	4	-31	F
6	46.7	-24	16	62.7	4	15.7	PF
7	48.5	5.19	2.62	-31	4	-7.8	AF
8	55.8	7.36	2.18	-0.4	4	-0.1	PAF

Table F.48b ANOVA Table for $CHBr_3$

Source	Effect	S of S	df	MS	F	Significant
Main Effects						
pH	-9	177	1	177	4.9	No
Alkalinity	15.9	503	1	503	13.9	No
UV-fluence	-31	1930	1	1930	53.5	Yes
Interactions						
PxA	1.2	2.87	1	2.87	0.08	No
PxF	15.7	492	1	492	13.6	No
AxF	-7.8	123	1	123	3.4	No
PxAxF	-0.1	0.02	1	0.02	0.001	No
Error			1	36.1		

$F_{1,2,0.05} = 18.5$

Appendix G: Single Factor Experiment Results

Alkalinity Experiments

Table G.1 UV Photolysis: Raw Data for HAAs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HAAs (μg/L)		
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AA	Cl_3AA	Total
1	8	0	1000	1.68	6.34	8.17	14.5
2	8	0	1000	1.58	7.65	9.28	16.9
3	8	50	1000	1.71	6.25	7.35	13.6
4	8	50	1000	1.74	6.77	8.19	15
5	8	100	1000	1.77	6.66	9.1	15.8
6	8	100	1000	1.81	6.83	9.48	16.3
7	8	150	1000	1.76	7.14	9.2	16.3
8	8	150	1000	1.77	5.32	8.38	13.7
9	8	200	1000	1.40	6.12	8.19	14.3
10	8	200	1000	1.92	6.18	8.44	14.6
11	8	250	1000	1.39	6.25	9.19	15.4
12	8	250	1000	1.76	6.09	8.7	14.8
C1				2.48	11.3	16.4	27.7
C2				2.68	10.4	14.5	25
C3				2.40	11	14	25.1
C4				2.60	8.72	13.2	21.9
			Average	2.54	10.4	14.6	24.9

Table G.2 UV/H_2O_2: Raw Data for HAAs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HAAs (μg/L)		
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AA	Cl_3AA	Total
1	8	0	1000	1.93	5.36	6.38	11.7
2	8	0	1000	1.86	6.02	6.89	12.9
3	8	50	1000	1.99	6.11	6.63	12.7
4	8	50	1000	1.79	6.18	6.27	12.5
5	8	100	1000	1.91	5.72	7	12.7
6	8	100	1000	1.96	6.43	7.11	13.5
7	8	150	1000	1.59	5.91	5.99	11.9
8	8	150	1000	1.68	5.52	4.68	10.2
9	8	200	1000	1.42	5.83	6.14	12
10	8	200	1000	1.73	6.07	6.45	12.5
11	8	250	1000	1.85	5.27	6.32	11.6
12	8	250	1000	1.91	5.82	6.77	12.6
C1				2.56	11.3	15.2	26.5
C2				2.50	9.05	13.1	22.2
C3				2.54	8.12	12.4	20.6
			Average	2.53	9.48	13.6	23.1

Table G.3 UV photolysis: Raw Data for HANs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HANs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl2AN	THANs
0A	8	0	1000	1.68	1.83	1.83
0B	8	0	1000	1.58	2.23	2.23
50A	8	50	1000	1.71	1.78	1.78
50B	8	50	1000	1.74	1.51	1.51
100A	8	100	1000	1.77	1.55	1.55
100B	8	100	1000	1.81	2.49	2.49
150A	8	150	1000	1.76	2.43	2.43
150B	8	150	1000	1.77	2.95	2.95
200A	8	200	1000	1.4	2.89	2.89
200B	8	200	1000	1.92	1.45	1.45
250A	8	250	1000	1.39	2.57	2.57
250B	8	250	1000	1.76	2.13	2.13
C1				2.48	1.47	1.47
C2				2.68	1.21	1.21
C3				2.40	2.09	2.09
C4				2.60	1.8	1.8
			Average	2.54	1.64	1.64

Table G.4 UV/H_2O_2: Raw Data for HANs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	HANs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	Cl_2AN	THANs
0A	8	0	1000	1.93	2.54	2.54
0B	8	0	1000	1.86	1.87	1.87
50A	8	50	1000	1.99	1.67	1.67
50B	8	50	1000	1.79	2.61	2.61
100A	8	100	1000	1.91	1.9	1.9
100B	8	100	1000	1.96	1.6	1.6
150A	8	150	1000	1.59	2.55	2.55
150B	8	150	1000	1.68	1.86	1.86
200A	8	200	1000	1.42	2.59	2.59
200B	8	200	1000	1.73	1.79	1.79
250A	8	250	1000	1.85	1.28	1.28
250B	8	250	1000	1.91	1.66	1.66
C1				2.56	1.59	1.59
C2				2.50	0.96	0.96
C3				2.54	0.97	0.97
			Average	2.53	1.17	1.17

Table G.5 UV photolysis: Raw Data for THMs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	THMs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	CHCL3	TTHMs
0A	8	0	1000	1.68	55	55
0B	8	0	1000	1.58	58.2	58.2
50A	8	50	1000	1.71	51.8	51.8
50B	8	50	1000	1.74	52.8	52.8
100A	8	100	1000	1.77	59.4	59.4
100B	8	100	1000	1.81	77	77
150A	8	150	1000	1.76	72.9	72.9
150B	8	150	1000	1.77	81.6	81.6
200A	8	200	1000	1.40	67.2	67.2
200B	8	200	1000	1.92	56.1	56.1
250A	8	250	1000	1.39	68.9	68.9
250B	8	250	1000	1.76	66.2	66.2
C1				2.48	144	144
C2				2.68	114	114
C3				2.40	126	126
C4				2.60	148	148
			Average	2.54	133	133

Table G.6 UV/H_2O_2 Treatment: Raw Data for THMs

Run	pH	Added alkalinity	UV-fluence	Cl_2 residual	THMs (μg/L)	
		mg/l as $CaCO_3$	mJ/cm^2	(mg/L)	$CHCl_3$	Total
0A	8	0	1000	1.93	114	114
0B	8	0	1000	1.86	124	124
50A	8	50	1000	1.99	75.4	75.4
50B	8	50	1000	1.79	94.6	94.6
100A	8	100	1000	1.91	74.7	74.7
100B	8	100	1000	1.96	53.8	53.8
150A	8	150	1000	1.59	87.9	87.9
150B	8	150	1000	1.68	56.8	56.8
200A	8	200	1000	1.42	57.3	57.3
200B	8	200	1000	1.73	48.7	48.7
250A	8	250	1000	1.85	41.8	41.8
250B	8	250	1000	1.91	68.6	68.6
C1				2.56	94.3	94.3
C2				2.50	83.4	83.4
C3				2.54	75.6	75.6

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Table G.7: Raw Data for HAAs (added alkalinity= 0mg/L as $CaCO_3$, UV-fluence=1000mJ/cm^2)

Run	pH			24 hr Cl_2 demand	HAAs (µg/L)			
	Before	**Adjusted**	**After**	**(mg/L)**	**CL_2AA**	**Cl_3AA**	**BrAA**	**BrClAA**
5A	7.53	5.02	7.13	6.00	13.6	6.63	0.29	2.13
5B	7.80	5.00	7.11	5.35	13.2	6.26	0.25	2.91
6A	7.80	6.03	8.03	6.50	10	5.33	0.23	1.79
7A	8.02	6.99	7.66	5.90	9.96	6.21	0.29	2.35
7B	8.02	6.99	above 7.5	5.90	9.92	5.65	0.23	2.02
8A	7.74	7.98	8.59	6.65	7.91	5.02	0.19	1.1
8B	7.70	8.02	8.45	6.65	8.23	5.03	0.27	2.18
9B	8.02	9.02	8.83	7.20	7.85	4.63	0.29	2.48
C1					6.1	4.56	0.2	1.33
C2					8.06	5.75	0.29	1.55
C3					9.24	7.9	0.26	2.27
C4					6.37	4.48	0.2	1.78
				Average	7.44	5.67	0.24	1.73

Table G.7: Raw Data for HAAs (added alkalinity= 0mg/L as $CaCO_3$, UV-fluence=1000mJ/cm^2) Cont'd

Run	pH			HAAs (µg/L)			
	Before	**Adjusted**	**After**	**$BrCl_2AA$**	**Br_2ClAA**	**Br_2AA**	**Total**
5A	7.53	5.02	7.13	1.38	1.02	0.25	25.3
5B	7.80	5.00	7.11	1.63	0.71	0.21	25.2
6A	7.80	6.03	8.03	0.85	1.11	0.24	19.6
7A	8.02	6.99	7.66	1.1	0.98	0.25	21.1
7B	8.02	6.99	above 7.5	1.26	0.91	0.28	20.3
8A	7.74	7.98	8.59	1.71	0.75	0.18	16.9
8B	7.70	8.02	8.45	0.5	1.01	0.22	17.4
9B	8.02	9.02	8.83	0.89	1.02	0.3	17.5
C1				0.997	9.16	0.19	22.5
C2				0.59	10.2	0.21	26.6
C3				1.81	0.74	0.29	22.5
C4				1.03	0.45	0.26	14.6
			Average	1.1	5.13	0.24	21.6

Table G.8: Raw Data for HAAs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2 Br^- = 500 μg/L)

Run	pH			24hr Cl_2 demand	HAAs (μg/L)			
	Before	Adjusted	After	(mg/L)	CL_2AA	Cl_3AA	BrAA	BrClAA
5A	7.76	4.96	7.13	6.65	8.67	2.56	1.42	8.26
5B	7.60	5.02	7.53	7.20	6.03	1.84	1.08	6.17
6A	8.19	6.04	8.06	7.05	5.93	1.67	1.16	6.29
6B	8.13	6.00	8.05	6.75	5.09	1.3	0.94	6.52
7A	7.71	6.94	7.94	6.85	5.14	1.23	0.91	5.54
7B	7.74	7.01	7.91	6.50	5.91	1.46	0.84	4.93
8A	7.65	8.01	8.48	7.20	4.21	1.41	0.84	4.67
8B	7.63	7.98	8.52	7.05	5.68	1.64	1.16	6.39
9A	7.70	9.02	8.82	7.60	3.77	1.13	0.8	4.21
9B	7.78	8.98	8.65	8.00	4.64	1.14	0.86	5.06
C1				3.8	4.779	1.288	0.771	4.752
C2				3.7	3.944	1.430	0.706	4.406
C3				3.4	4.151	1.354	0.813	4.480
C4				3.5	4.782	1.310	0.843	5.012
			Average	3.6	4.414	1.345	0.783	4.662

Table G.9: Raw Data for HAAs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2 Br^- = 500 μg/L) cont'd

Run	pH			HAAs (μg/L)				
	Before	Adjusted	After	$BrCl_2AA$	Br_2ClAA	Br_2AA	Br_3AA	Total
5A	7.76	4.96	7.13	4.93	7.97	4.75	4.49	43.0
5B	7.60	5.02	7.53	1.86	4.75	3.77	2.49	28
6A	8.19	6.04	8.06	1.94	3.87	3.98	2.29	27.1
6B	8.13	6.00	8.05	1.58	5.13	3.25	3.06	26.95
7A	7.71	6.94	7.94	2.02	5.54	3.18	3.06	26.6
7B	7.74	7.01	7.91	2.96	7.59	3.6	0	27.3
8A	7.65	8.01	8.48	2.68	6.98	3.01	2.94	26.7
8B	7.63	7.98	8.52	1.34	3.51	3.38	2.38	25.5
9A	7.70	9.02	8.82	1.22	4.34	2.91	2.37	20.8
9B	7.78	8.98	8.65	1.34	3.63	2.87	2.53	22.1
C1				1.23	6.72	3.65	2.47	25.7
C2				2.01	6.39	3.53	2.02	24.4
C3				1.97	8.97	3.44	2.53	27.7
C4				0.95	8.05	3.4	1.74	26.1
			Average	1.54	7.53	3.5	2.19	26

Table G.10: Raw Data for HANs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2)

Run	pH			24hr Cl_2	HANs (μg/L)
	Before	Adjusted	After	Demand(mg/L)	Cl_2AN
5A	7.53	5.02	7.13	6.00	2.36
5B	7.80	5.00	7.11	5.35	1.83
6A	7.80	6.03	8.03	6.50	5.39
7A	8.02	6.99	7.66	5.90	1.45
7B	8.02	6.99	above 7.5	5.90	2.13
8A	7.74	7.98	8.59	6.65	2.81
8B	7.70	8.02	8.45	6.65	2.35
9B	8.02	9.02	8.83	7.20	1.82
C1				2.30	1.82
C2				1.90	1.19
C3				2.70	1.19
C4				2.60	1.86
			Average	2.38	1.41

Table G.11: Raw Data for THMs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2)

Run	pH			24h Cl_2	THMs (µg/L)			
	Before	Adjusted	After	Demand(mg/L)	$CHCl_3$	$BrClCH_2$	$ClCHBr_2$	Total
5A	7.53	5.02	7.13	6.00	82.6	12.7	3.84	99.2
5B	7.80	5.00	7.11	5.35	96.6	13.8	4.09	114
6A	7.80	6.03	8.03	6.50	144	21.8	6.47	172
7A	8.02	6.99	7.66	5.90	53.8	9.39	3.08	66.3
7B	8.02	6.99	above 7.5	5.90	88	15.4	5.04	108
8A	7.74	7.98	8.59	6.65	53.6	9.51	3.21	66.4
8B	7.70	8.02	8.45	6.65	55.4	10.3	3.65	69.3
9B	8.02	9.02	8.83	7.20	51.8	10.8	4.38	67
C1				2.30	53.8	11.9	4.73	70.4
C2				1.90	51.4	9.84	7.19	68.4
C3				2.70	38.7	8.44	3.68	50.8
C4				2.60	64.5	14.9	5.73	85.1
			Average	2.38	51.5	11.1	5.53	68.1

Table G.12: Raw Data for THMs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2 Br^- = 500 µg/L)

Run	pH			24h Cl_2	THMs (µg/L)				
	Before	Adjusted	After	Demand(mg/L)	$CHCl_3$	$BrCl_2CH$	$ClCHBr_2$	$CHBr_3$	Total
5A	7.76	4.96	7.13	6.65	36.8	42.3	40.9	18.5	138
5B	7.60	5.02	7.53	7.20	24.3	30	33.7	16.8	105
6A	8.19	6.04	8.06	7.05	22.1	27.3	29.9	16.3	95.6
6B	8.13	6.00	8.05	6.75	21.8	27.3	28.6	17.3	95
7A	7.71	6.94	7.94	6.85	24.4	30.8	35.9	19.8	111
7B	7.74	7.01	7.91	6.50	29.3	37.2	43	22.8	132
8A	7.65	8.01	8.48	7.20	21.4	28.2	30.2	16.9	96.7
8B	7.63	7.98	8.52	7.05	26.2	35.7	40.1	21.9	124
9A	7.70	9.02	8.82	7.60	17.9	25.1	32.5	20.4	95.8
9B	7.78	8.98	8.65	8.00	13.5	18.2	22.2	16.3	70.2
C1				3.80	12.8	17.5	23.8	15	69.2
C2				3.70	13.5	18.7	27.4	16.4	76.1
C3				3.40	17.8	27.5	37	24.5	107
C4				3.50	15.7	24.5	34.2	20.9	95.2
			Average	3.60	15.7	23.6	32.9	19.2	86.8

Table G.13: Raw Data for Repeat pH points of THMs (added alkalinity= 0 mg/L as $CaCO_3$, UV-fluence=1000 mJ/cm^2 Br^- = 500 µg/L)

Run	pH			24h Cl_2	THMs (µg/L)				
	Before	Adjusted	After	Demand(mg/L)	$CHCl_3$	$BrCl_2CH$	$ClCHBr_2$	$CHBr_3$	TTHMs
5A	7.93	5.02	6.47	6.90	25.4	32.8	34.1	16.3	109
5B	8.02	5.00	6.58	6.80	34.4	52	57.6	29.8	174
6A	7.90	6.03	7.97	6.90	37.8	49.9	53.2	20.9	162
6B	8.05	5.99	7.89	6.40	27.2	42.5	46.7	18.7	135
7A	8.00	7.00	8.27	6.90	21.4	26.5	29.5	13.9	91.3
7B	7.98	7.01	8.29	6.80	28	32.4	41.7	21.9	124
C1				1.80	18.8	28.2	42.3	21.3	111
C2				4.40	23.7	31.2	41	24.7	121
			Average	3.10	23.7	31.2	41	23	116