ABSTRACT

VANESSA RANHADA PINTO JORGE PEREIRA. Use of a Chloraminated Drinking Water System to Develop Accurate Predictive Patterns of Exposure to Disinfection-By-Products by Consumers. (under the direction of Dr. HOWARD S. WEINBERG)

In an attempt to provide more accurate exposure levels to disinfection by-products (DBPs) in drinking water by consumers, the levels of trihalomethanes (THMs), haloacetic acids (HAAs), and total organic halogen (TOX) were measured and correlated between the point of entry (POE) from an ozone-chloramination plant and those measured throughout the distribution system (DS).

Samples collected every four hours during five consecutive days showed that temporal variability in the DBP levels at the POE can be expected. However, this variability appeared to be dampened in the distribution system with the average levels of DBPs measured over an extended period very similar at all sample points. A single grab sample collected from a representative DS point would therefore be a good indication of DBP exposure to consumers of that drinking water.

This study will demonstrate how a monitoring program was evolved that provides for a reasonable exposure level of DBPs to consumers of drinking water using a minimum number of sampling points and events in a chloraminated distribution system.

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ACKNOWLEDGEMENTS

First and foremost, I would like to thank Dr. Howard S. Weinberg for his invaluable and continuous guidance and encouragement. I am also deeply grateful to Dr. Phillip C. Singer for his expertise. This research benefited enormously from his input. I am also in debt to Dr. Michael D. Aitken for being a reader of this thesis and for providing important academic guidance during these last two years.

I would also like to thank Carrie Delcomyn, Frederique Blin and Daniel Radiloff for their help in sample analyses, Larry McMillan for clarifications about water treatment processes and Martesa Webb for helping with sample collection, Dr. David Savitz and Christina Makarushka for their valuable input in this research, and my laboratory research group and office mates for their support and friendship during these years.

Financial support from the American Water Works Association Research Foundation, project 2579, is gratefully acknowledged.

As for my dear family and portuguese friends "muito obrigado, o vosso amor permitiu-me ultrapassar todos os obstáculos durante estes dois anos".

I. OBJECTIVES

This study is part of a five-year project being conducted by a team specializing in epidemiology, water chemistry and engineering, statistics, and obstetrics to determine whether the occurrence of spontaneous abortion might be related to the presence of disinfection by-products (DBPs) in drinking water.

Previous epidemiological studies found positive correlations between the presence of DBPs in drinking water and spontaneous abortion. However, these studies used gross estimates of exposure, not considering the DBP spatial and temporal variability, and therefore have a serious risk of misclassification of exposure associated.

The objectives of this aspect of the study are to provide approaches to accurately assess exposure to DBPs in drinking water, measured in terms of trihalomethane (THM), haloacetic acid (HAA), and total organic halogen (TOX) concentrations.

To meet these objectives, this study focused on an intensive evaluation of the DBP concentrations in the finished water and distribution system at a water treatment plant using chloramination for final disinfection. Sample collection approaches were studied including the development of a sampling strategy to determine the most representative distribution system locations from which samples should be collected to accurately predict the exposure to DBPs by consumers.

II. BACKGROUND

II.A. Disinfection of Drinking Water

Disinfection of drinking water using free chlorine and chloramines is widely used and has saved millions of lives from waterborne diseases.

II.A.1. Disinfection using Free Chlorine

Chlorine can be used in water treatment as an oxidizing agent (mainly used for taste, odor and color control and oxidation of iron and manganese of groundwater supplies) and as a disinfectant (for inactivation of microorganisms). The advantages of its use include the easy production, control, storage, transport and application, low cost, and having a very broad range of effectiveness including the aesthetic quality control, removal of iron, manganese and hydrogen sulfide, sterilization of mains and storage tanks, restoration and preservation of pipe capacity and maintenance of a persistent stable residual in the distribution system.

The disinfection of drinking water using chlorine can be achieved by applying it as a compressed gas under pressure or in liquid solutions (sodium hypochlorite or calcium hypochlorite).

The condensation of molecular chlorine gas into a liquid can be achieved when the gas is subject to pressures in excess of its vapor pressure with the release of heat and a decrease in specific volume of about 450 fold (Haas, 1990). It can be used as a gas ($Cl_{2(g)}$) generated after supplying the thermal energy necessary to the vaporization of liquid chlorine under pressure.

The hydrolysis of chlorine gas in water occurs according to the following reaction:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad K_h=4\times10^{-4}\,(mol/L)^2 \qquad [II.1]$$

Hypochlorous acid is a relatively weak acid that will tend to dissociate in water forming hydrogen and hypochlorite ions:

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad pKa=7.5 \qquad [II.2]$$

In waters of pH between 6.5 and 8.5 we can expect both species to be present to some degree. The degree of disinfection obtained will depend greatly on pH as the disinfection efficiency of HOCl is much higher than OCl^- (Maier et al., 2000).

If hypochlorite salts are used to disinfect the water, the following reactions occur:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- \qquad [II.3]$$

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca^{2+} + 2OH^- \qquad [II.4]$$

The hypochlorous acid will then follow the dissociation reaction described in [II.2].

II.A.2. Disinfection using Combined Chlorine

In the presence of ammonia, water chlorination will lead to the formation of chloramines (monochloramine, dichloramine or trichloramine), with the rates of reaction and product formation dependent on pH, relative concentration of NH_4^+ and HOCl, contact time and temperature.

The breakpoint curve consists in a representation of chemical relationships formed when chlorine is added to water that contains ammonia.

Theoretically, at chlorine to ammonia weight ratios less than 5:1 and pH values between 7 and 8, common conditions applied during drinking water chloramination, monochloramine (NH_2Cl) will be the predominant form in the water [II.5].

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O \qquad [II.5]$$

At larger chlorine to ammonia ratios and lower pH values, the NH_2Cl concentrations decrease with an increase in the dichloramine ($NHCl_2$) concentrations [I.6]. The rate of this reaction will be much slower than the monochloramine formation reaction and will increase with the pH decrease.

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \qquad [II.6]$$

If the pH were kept between 7 and 8 and the chlorine: ammonia weight ratios increased to approximately 15:1, trichloramine would be formed [II.7].

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 \text{ (trichloramine)} + H_2O \qquad [II.7]$$

The breakpoint phenomenon occurs when chlorine is applied in sufficient doses (chlorine to ammonia molar ratios higher than 1.5 or weight ratios higher than 7.5) to meet the ammonia demand in water and leaving a free chlorine residual [II.8]. In practice the chlorine to ammonia molar ratio tends to be closer to 2 to 1 (10 to 1 by weight).

$$2NH_3 + 3HOCl \rightleftharpoons N_2 \text{ (gas)} + 3H^+ + 3Cl^- + 3H_2O \qquad [II.8]$$

In order to achieve drinking water disinfection, monochloramine is formed preferentially at the treatment plant by controlling the chlorine:ammonia ratio to a value generally less than 5:1 on a weight basis (approximately 1:1 on a molar basis). The chloramine residuals desired to achieve efficient disinfection performances range from 1 to 5 mg/L as Cl_2 (Valentine et al., 1998).

Monochloramine disproportionation can occur by hydrolysis of monochloramine (described in equation [II.5]) or by general acid catalysis (described in equation [II.9]) if the concentration of proton donors increases (Symons et al., 1998).

$$NH_2Cl + NH_2Cl + H^+ \rightleftharpoons NHCl_2 + NH_3 + H^+ \qquad [II.9]$$

Valentine and Jafvert (1988) found that the carbonate system can increase the rate of acid-catalyzed disproportionation at typical concentrations and pH values of drinking water.

The formation of bromamines and bromochloramines has also been described in the literature when chloramination is used as a disinfectant of waters containing bromide (Symons et al., 1998). According to these authors, the speciation of bromamines is, as for chloramines, a function of pH and ammonia to bromine ratio. Bromamines form faster than chloramines but their contribution to disinfection is thought to be minimal after 24 to 48 hours in the distribution system because they are short-lived. Their reactivity to form DBPs is not well documented yet even though little formation of THMs is expected to occur from dibromamine (Sugam and Helz, 1980).

Valentine (1986) suggested the possibility of an important contribution of bromochloramine to DBP production in bromide containing waters due to the high reactivity of its bromine atom.

The definition of the terms free chlorine, combined chlorine, and chlorine residual are presented in the following expressions (Stumm and Morgan, 1996) with the terms in parentheses being normally negligible:

$$\text{Free chlorine} = (2[Cl_2]) + [HOCl] + [OCl^-] \qquad [II.10]$$

$$\text{Combined chlorine} = [NH_2Cl] + 2[NHCl_2] + (3[NCl_3]) \qquad [II.11]$$

$$\text{Total Chlorine residual} = \text{free and combined chlorine} \qquad [II.12]$$

II.A.3. Microbiocidal Efficacy of Free Chlorine and Chloramines

Chlorine is a strong oxidizing agent that when added to the water as a gas forms a mixture of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). At 20°C and pH values lower than 7.5, HOCl will be the predominant form having a higher germicidal effect.

Monochloramine provides a stable residual in the distribution system but is a weaker disinfectant than free chlorine as shown by the relative values of Ct for various target microorganisms in Table 1. The Ct value (C×t) is indicative of the disinfectant effectiveness with C being the disinfectant concentration while t is the time required to achieve a certain level of inactivation. An example of some Ct values comparing the microbiocidal efficiency (for bacteria, virus and parasites) reported by different authors is presented in the following table (Maier et al., 2000).

Table 1: Comparison of the microbiocidal efficiency of free chlorine with combined chlorine at 5°C and pH values ranging from 6 to 9 (99% inactivation)[1]

Organism	Ct for free chlorine (mg/L×min)	Ct for chloramines (mg/L×min)
Bacteria - *E. coli*	0.04	113
Virus - Polio 1	1.7	1420
Protozoa - *G. muris*	250	1400

The Chick-Watson first-order kinetics model is normally assumed for explaining microbial inactivation [II.13],

$$\frac{N_t}{N_o} = e^{-kC^n t} \qquad \text{[II.13]}$$

[1] Adapted from Maier, 2000

where N_o is the number of organisms at time zero, N_t the number of organisms at time t, k the inactivation rate, C the disinfectant concentration, n an empirical constant and t the time. However this assumption is not usually met in practice. Retardant and multihit inactivation curves are expected to be obtained instead due to the presence of heterogeneous populations (with different susceptibilities of microbes) and to diffusion limitations of the disinfectants in reaching targets respectively.

II.A.4. Factors that Influence Microbial Inactivation by Free Chlorine and Monochloramines

Microbial inactivation is site and system specific being influenced by a variety of factors depending on the microbial and water characteristics. The following biological, chemical and physical factors have been summarized from different disinfection studies (Sobsey, 1989):

- ***Microbe characteristics***

Even though disinfection resistance within the same group or specie of organism is expected to differ, the following order of resistance is reported: vegetative bacteria < viruses < bacterial spores < acid-fast bacteria < protozoan cysts < spores and eggs. The physiological state, antecedent growth conditions, prior disinfectant exposure and injury caused by environmental agents and the methods used to determine viability are also important factors to consider.

• ***Type of disinfectant***

For a specific microbial species, free chlorine (strong oxidant) will generally be more efficient than chloramines (weak oxidant). The chemistry of action by these agents differs.

• ***Water quality***

Characteristics of water that influence disinfection include turbidity, dissolved organic matter, reduced inorganic constituents, pH, and temperature. Increased resistance to disinfection by free and combined chlorine of several different organisms is expected to occur as suspended solids can protect microbes from disinfection and/or consume disinfectant. Dissolved organic matter and reduced inorganic compounds can react with free chlorine with a consequent reduction of the disinfectant concentration available for reaction with the microorganisms. Microbial inactivation using free chlorine is more efficient at low pH (pH<7.5) where hypochlorous acid predominates. Microbial inactivation using monochloramine is also pH dependent with higher degree of inactivation being obtained at pH 6-7. An increase in temperature will generally lead to higher inactivation rates.

II.A.5. Mechanisms of Microbial Inactivation by Free Chlorine and Chloramines

The mechanisms for both disinfectants are not totally elucidated. According to Stewart and Olson (1996), bacterial inactivation by chlorine occurs as a result of alteration to the outer cellular membrane permeability with leakage of critical cell components, interference with cell-associated membrane functions (e.g. phosphorylation of high energy compounds), impairment of enzyme and protein function as a result of irreversible binding of the sulfyhydryl groups and nucleic acid denaturation.

Inactivation of viruses by chlorine is obtained by interaction with capsid proteins or nucleic acid with the site of action depending on the disinfectant concentration and the type of virus (Thurman and Gerba, 1988). Chloramine inactivation of microorganisms is mainly obtained by irreversible denaturation of proteins (Stewart and Olson, 1996). Monochloramine disinfection of bacteria is obtained by the oxidation of sulfydryl-containing enzymes and reactions with the nucleic acid while inactivation of viruses by monochloramines is obtained by interaction with capsid proteins or nucleic acid (Maier et al., 2000). The mechanisms of parasites' inactivation by chlorine and chloramines are still uncertain.

II.A.6. Other Disinfectants used in Drinking Water

Chlorine dioxide (ClO_2) is a strong oxidizing agent and disinfectant but it does not hydrolyze in water existing as a dissolved gas. It can be generated by reaction of chlorine gas with sodium chlorite according to the following expression:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad [II.14]$$

According to Sobsey (1989) chlorine dioxide is as, or more, effective in inactivating bacteria and viruses in water than chlorine and certainly a much more powerful disinfectant than chloramines. The microbial inactivation occurs by denaturation of the sulfyhydryl groups contained in proteins, inhibition of protein synthesis, denaturation of nucleic acid and impairment of permeability control (Maier et al., 2000).

Ozone is a very strong oxidant and disinfectant but highly volatile and reactive and therefore it does not produce a stable and persistent disinfectant residual. It is a much more powerful disinfectant than chlorine and chloramines (Maier et al., 2000).

The bacterial inactivation seems to occur by the same mechanisms described for chlorine while virus inactivation may occur by breakup of the capsid proteins into subunits, resulting in release of the RNA, which may then be damaged (Maier et al., 2000). Synergistic effects can occur when ozone and chloramines or ozone and chlorine are used.

UV is a very strong disinfectant that reacts primarily with nucleic acids causing pyrimidine dimers and other alterations (Maier et al., 2000). However it does not provide a disinfectant residual. Low pressure mercury lamps (with low intensity; monochromatic light at 254 nm) or medium pressure mercury lamps (higher intensity; polychromatic light at 220-280 nm) can be used.

The use of a mixture of oxidants (free chlorine, chlorine dioxide, hydrogen peroxide, ozone and other short lived oxidants) was compared with free chlorine and a higher reduction of *Cryptosporidium parvum* oocysts and *Clostridium perfringens* spores were obtained by this mixture (Venczel et al., 1997).

II.B. Disinfection By-Products

In the mid-1970s, the by-products resulting of the reaction of chlorine with the natural organic matter present in the water were discovered (Rook, 1974 and Beller et al., 1974).

II.B.1. Natural Organic Matter

The major part of the organic matter present in natural waters consists of decay-resistant molecules derived from the initial microbiological decay of plants. In the latter process, the organic molecules are broken by oxidation with the consequent formation of molecules with carboxylic groups at the point where the new molecule was separated from its original structure (Benjamin, 2002).

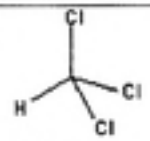
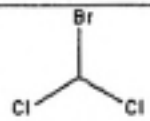
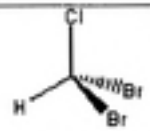
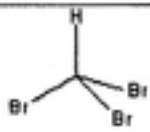
Even though carboxylic groups are considered to be the predominant groups attached to the natural organic matter (NOM), a variety of other functional groups can be also found in these complex molecules.

The presence of these molecules in water can lead to problems in the treatment plants such as the presence of color, the decrease in the adsorption capacity of activated carbon beds, exertion of chlorine and other oxidant demands, the transport of organic and inorganic pollutants through the treatment facility, and the formation of disinfection by-products (DBPs) during disinfection (Haas, 1990). The humic content of the NOM with its higher aromatic carbon content is expected to lead to a higher DBP production than the non-humic materials (Singer, 1999).

II.B.2. Disinfection By-Products Properties

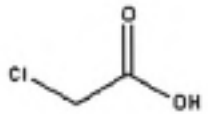
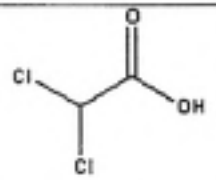
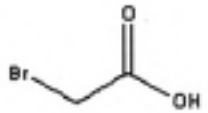
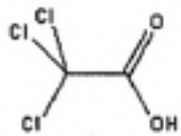
The trihalomethanes (THMs) and haloacetic acids (HAAs) constitute the majority of the identified DBPs found in drinking water. The chemical characteristics of THMs and HAAs are presented in Table 2 and 3.

Table 2: Properties of THMs [2]

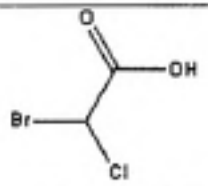
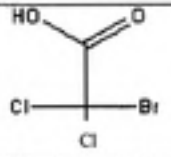
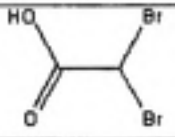
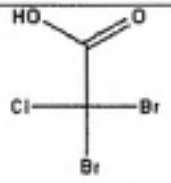
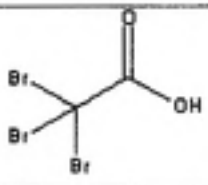
Name	Molecular formula	Chemical Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Log P (octanol-water)
Trichloromethane or Chloroform	$CHCl_3$		119.4	-63.7	61.7	1.97
Bromodichloromethane	$CHBrCl_2$		163.8	-57.1	90.1	2.00
Dibromochloromethane	$CHBr_2Cl$		208.3	-20	120.0	2.16
Tribromomethane or Bromoform	$CHBr_3$		252.7	8.3	149.5	2.40

[2] Adapted from www.chemfinder.com

Table 3: Properties of HAAs [2]

Name (abbreviation)	Molecular formula	Chemical Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Log P (octanol-water)	pKa
Chloroacetic acid (ClAA)	$C_2H_3ClO_2$		94.5	61-62	188	0.22	2.87
Dichloroacetic Acid (Cl_2AA)	$C_2H_2Cl_2O_2$		128.9	9.7	194	0.92	1.26
Bromoacetic acid (BrAA)	$C_2H_3BrO_2$		138.9	49	206	0.41	2.89
Trichloroacetic acid (Cl_3AA)	$C_2HCl_3O_2$		163.4	57	196	1.33	0.512

[2] Adapted from www.chemfinder.com and http://www.hbg.psu.edu

Name (abbreviation)	Molecular formula	Chemical Structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Log P (octanol-water)	pKa
Bromochloroacetic acid (BrClAA)	$C_2H_2BrClO_2$		173.4	25	215	Nav	Nav
Bromodichloroacetic acid ($BrCl_2AA$)	$C_2HBrCl_2O_2$		207.8	78-80	Nav	Nav	Nav
Dibromoacetic acid (Br_2AA)	$C_2H_2Br_2O_2$		217.8	39-41	128-130	Nav	Nav
Dibromochloroacetic acid (Br_2ClAA)	$C_2HBr_2ClO_2$		252.3	108-110	Nav	Nav	Nav
Tribromoacetic acid (Br_3AA)	$C_2HBr_3O_2$		296.7	130-133	245	Nav	Nav

Nav – not available

[1] Adapted from www.chemfinder.com and http://www.hbg.psu.edu

II.B.3. Mechanism of Disinfection By-Products Formation

The formation of THMs, HAAs as well as other halogenated DBPs (with the total organic halide (TOX) representing all the halogenated DBPs formed) occurs when chlorine is added to water that contains NOM. The presence of bromide in source waters will generate bromine substituted forms of these DBPs (Figure 1).

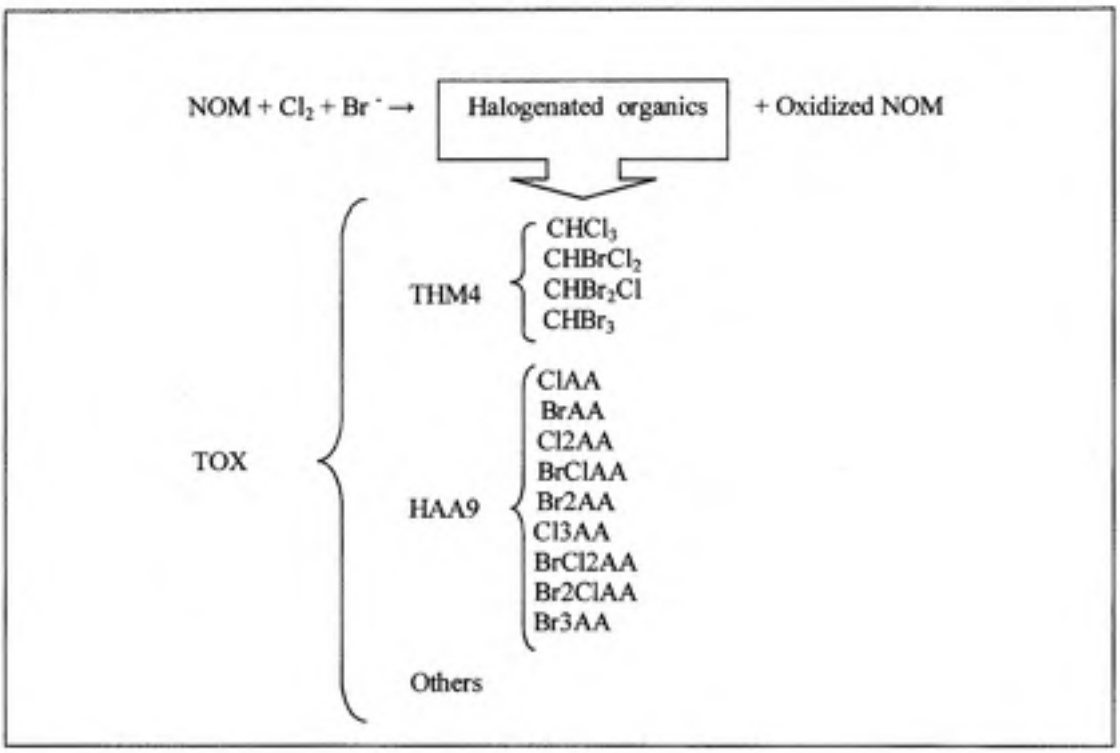


Figure1: THM and HAA formation

Even though the mechanisms of DBP formation have been studied by several investigators (e.g. Rook, 1977 and Reckhow and Singer, 1985) they are still not totally elucidated. Rook (1977) suggested the haloform reaction to describe the mechanisms of THM formation from fulvic acids involving a base-catalyzed series of halogenation and hydrolysis reactions.

Reckhow and Singer (1985) studied the chloroform, trichloroacetic acid and dichloroacetic acid mechanisms of formation from fulvic acids and suggested β-diketone moieties to be THM and HAA precursors formed by oxidation of fulvic acids. According to Singer (2001), the kinetics of HAA formation is faster than the THM formation. This fact is expected to influence DBP speciation in the distribution system.

II.B.4. Health Effects

Several toxicological and epidemiological studies have been trying to establish a relation between the presence of DBPs in water and human health. These include the study of several cancers (e.g. colon, bladder, and liver), and adverse reproductive outcomes such as low birth weight, preterm delivery, spontaneous abortion, still-birth, and birth defects including problems in the central nervous system, cardiac defects, oral cleft, respiratory and neural tube defects (Boorman et al., 1999 and Nieuwenhuijsen et al., 2000).

Even though these associations have been found in some of the toxicological studies conducted on laboratory animals, the doses administered have been very high and mostly given by gavage and therefore the human exposure extrapolation from these studies must be carefully done.

As for the epidemiological studies conducted, a crude methodology used to access exposure can lead to some scepticism in the results. Nevertheless, the serious health effects suggested by the studies thus urge for the development of accurate predictive patterns of human exposure to DBPs in drinking water.

II.B.4.a. Literature Review on Spontaneous Abortion Exposure Assessment

Several studies have recently been conducted showing a relationship between the presence of halogenated disinfection by-products (DBPs) in tap water and spontaneous abortion (e.g. Savitz et al., 1995 and Waller et al., 1998). Spontaneous abortion, a pregnancy lost prior to the completion of twenty weeks gestation, is important to study as it accounts for approximately ten percent of the identified pregnancies losses and is thought to be the cause of several unidentified pregnancies losses. Although causes of spontaneous abortion are still not clearly identified, strong associations were established among women with a history of a previous spontaneous abortion and advanced maternal ages (Kallen, 1988, Kline et al., 1989). Other associations established with cigarette smoking (Ness et al., 1999), caffeine (Fenster et al., 1998), occupational chemical exposure (Lindbohm et al, 1984), stressfull and physically demanding work (Eskenazi et al, 1994) and drinking water (e.g. Waller et al., 1998 and Swan et al., 1998) are still considered speculative.

The first epidemiologic study that tried to establish a relation between the presence of DBPs in drinking water and spontaneous abortion was conducted by Ashengrau and other investigators in 1989 and found that women served by surface water were 2.2 times more likely to experience a spontaneous abortion than women that drank water from a groundwater source. The comparison between the effects of drinking tap or bottled water in the spontaneous abortion rates were studied by Zierler (1992) who found higher spontaneous abortion rates among the tap water consumers. In 1998, a group of investigators found a positive relation between the consumption of six or more glasses of cold tap water and spontaneous abortion (Swan et al., 1998). Waller et al. (1998) then found a positive association between spontaneous abortion and consumption of five or more glasses of cold tap water per day containing at least 75 µg/L of TTHMs. An additional correlation was established with women consuming five or more glasses of cold tap water per day containing at least 18 µg/L of bromodichloromethane.

One of the limitations of all of these studies is an inadequate assessment of the DBP concentrations to which the consumers were exposed as several of the exposure levels assumed were based on a single retrospective measurement.

II.B.5. Regulatory Requirements

The health risks that have been associated with the presence of DBPs in drinking water constituted the driving force for the development of regulations for the control of THMs and HAAs in drinking water. In the USA, the maximum contaminant level (MCL) of 100 μg/L was established for total trihalomethanes (TTHMs) in 1979 (USEPA, 1979), and applied to systems serving more than 10,000 consumers. Compliance is achieved if the running annual averages of quarterly samples taken in selected locations in the distribution system is below the maximum contaminant level (MCL). This value has recently been tightened (USEPA, 1998) by the Stage I DBP Rule effective January 2002 and applicable to all systems using disinfection. The new MCL for TTHMs will then be 80 μg/L (USEPA, 1998) and a new MCL is established for the sum of five of the nine HAAs (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid) at 60 μg/L.

The maintenance of a minimum chlorine residual of 0.2 mg/L entering the distribution system and a measurable residual throughout the system was regulated in the Surface Water Treatment Rule (USEPA, 1996) to provide consumers protection from microbial contamination.

II.B.6. DBP Production by Different Disinfectants

Zhang et al. (2000) compared the DBPs formed from chlorination and chloramination finding that chlorination produced the largest amounts of organic halogenated DBPs while the use of chloramination greatly reduced the organic halogenated DBPs compared with chlorination. The substitution of free chlorine with chloramines for disinfection has therefore been made by utilities concerned with elevated levels of disinfection by-products.

The most characterized by-products of reactions between ClO_2 and NOM are the inorganic reduction products chlorite and chlorate (Pelizzetti et al., 1994).

Even though the use of ozone was found to decrease the halogenated DBP precursors associated with chlorination, it produces other DBPs such as aldehydes, aldoacids, ketoacids and carboxylic acids due to the reaction of ozone with the humic substances while brominated organics and inorganic bromate will form in bromide containing raw waters (Weinberg and Glaze, 1996).

The use of ozone prior to terminal chlorination or chloramination was found by several authors to decrease the TOX formation potential (Kuhn and Sander, 1979, Yamada et al., 1983 and Reckhow, 1984). According to Reckhow (1984) the use of ozone will lead to a shift in the TOX speciation from $CHCl_3$ and Cl_3AA towards Cl_2AA. The author also found that alum coagulation would lead to a decrease in the organic halogen precursors in the range 50 and 90% with optimal removal in the pH range 5 to 5.5. However, the use of pre-ozonation was found to deteriorate the alum ability to remove the precursors.

The DBPs associated with the use of UV and mixtures of oxidants are still uncertain.

II.B.7. Factors that Influence DBP Exposure Levels

Several factors can influence the level of human exposure to DBPs in drinking water including raw water characteristics, the processes used for the water treatment, the distribution system, storage facilities characteristics and integrity, and consumer water usage (Singer, 2001).

II.B.7.a. Raw Water Characteristics

The concentration and properties of the NOM in the raw water have an important influence on DBP formation; waters with higher concentrations of NOM are expected to be associated with higher levels of DBPs (Singer, 1999), while the hydrophobic organic carbon content of the NOM is expected to be the major DBP precursor groups (Singer, 1999; Chang et al., 2001). The aromatic carbon content of the organic constituents in water as determined by specific ultraviolet absorbance (SUVA: UV absorbance of water at 254 nm per water dissolved organic carbon (DOC) concentration × 100) has been shown to be a good surrogate of DBP production (Barrett et al., 2000).

The bromide concentration of the water influences the DBP character with an increase in bromide to chlorine ratio leading to an increase in bromine incorporation into the DBPs (Singer, 1999).

The temperature of the water influences the amount and rate of DBP formation represented by higher THM and HAA concentrations obtained during the warmer months of the year (Singer, 1999).

II.B.7.b. Water Treatment

According to Singer (1999), the pH levels maintained throughout the treatment process influences the DBP formation. At higher pH values the THM formation has been shown to increase while trihaloacetic acid formation decreases (the dihaloacetic acid formation is apparently not influenced by pH).

The removal or transformation of NOM prior to disinfection will decrease DBP formation. The removal can be achieved during the treatment process by coagulation, granular activated carbon adsorption, membrane filtration or biological degradation while transformation can be obtained by the use of oxidants such as ozone or an advanced oxidation process (Barrett et al., 2000).

The concentration of DBPs will depend on the disinfectant, the dose used, and contact time.

The treatment objective to limit DBP formation should therefore be to add the minimum amount of a final disinfectant that would still allow control of the microbiological quality of distributed water, using the minimum contact time possible, following a treatment process that will maximize the NOM removal.

For example, in a conventional treatment process (Figure 2) using chloramination as final disinfection, the addition of chlorine and ammonia (preformed chloramine) as shown in Figure 2a would lead to lower THM and HAA production, than when chlorine and ammonia are added separately as shown in Figure 2b. Under both treatment processes the chlorination DBP levels generated in the treatment plant are expected to remain fairly constant in the distribution system in the absence of a free chlorine residual.

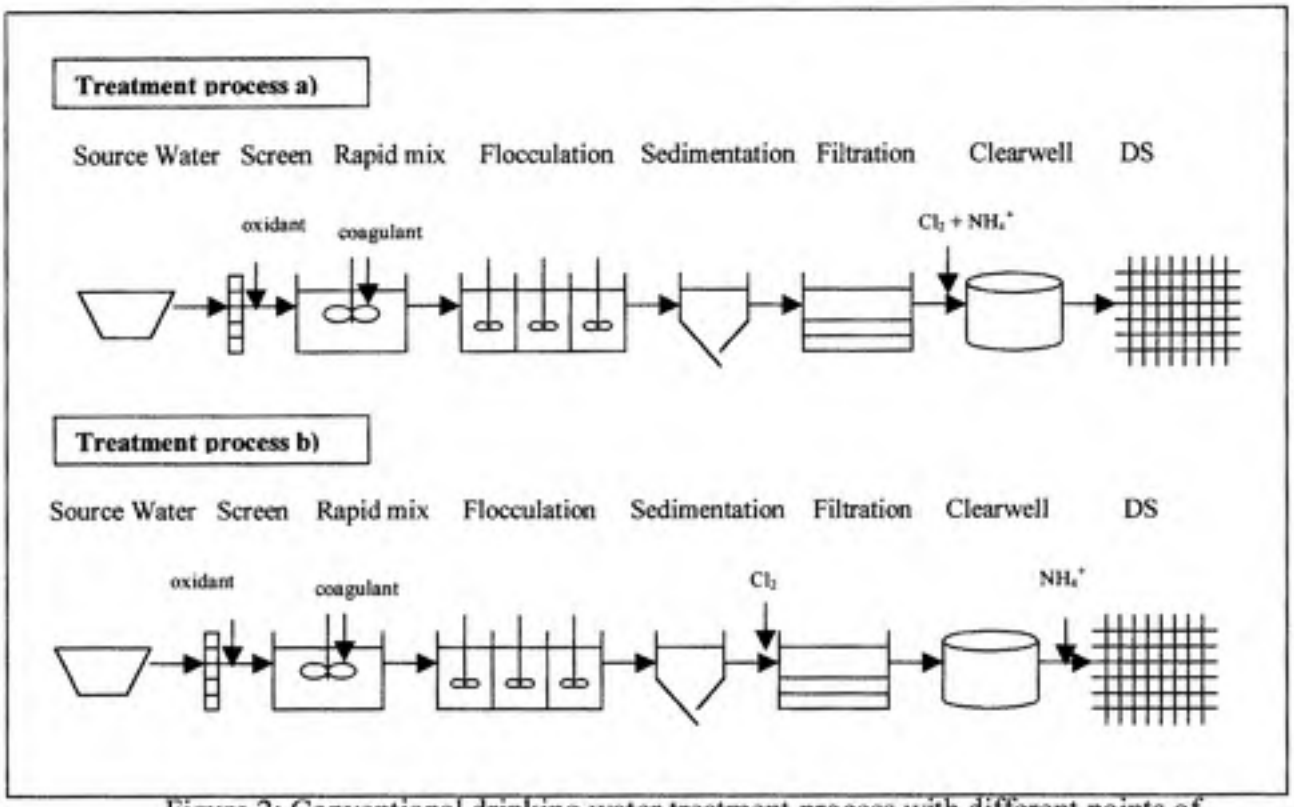


Figure 2: Conventional drinking water treatment process with different points of addition of final disinfectants

II.B.7.c. Distribution System

Maintaining an adequate disinfection residual throughout the distribution system is necessary in order to protect costumers from waterborne disease. However, as stated earlier, the maintenance of this residual will lead to DBP formation in the presence of precursor materials. DBP formation in the distribution system is dependent on the type of disinfectant used.

Free chlorine generates THMs and HAAs much faster and at higher levels than chloramines. With a free chlorine residual, THMs and HAAs will continue to form in the distribution system as long as the precursor materials remain (Singer, 2001).

When monochloramine is used, once ammonia is added and free chlorine is removed, the rate of THM and HAA formation is much slower and hence, the levels in the distribution system should stay close to the levels leaving the plant, unless the chloramine disproportionates back to free chlorine (equation II.5).

Chlorine decay in distribution systems is expected to occur due to reactions with the organic matter and other materials present in the water. Losses also result from reactions of chlorine with the pipe wall related materials (such as biofilms and coating leading to corrosion) (Vasconcelos et al., 1996). Laboratory studies have shown that significantly higher chlorine consumption is obtained from the corrosion of ferrous pipe materials than from biofilm reactions (Vasconcelos et al., 1996). In these studies the rate of reaction of chlorine at the pipe wall was found to be inversely related to the pipe diameter and limited by the rate of mass transfer of chlorine to the wall. Even though raising the pH of the treated water may prevent corrosion it may lead to the increase in THM production.

The contact time in the distribution system will be a very important factor in characterizing human exposure especially when free chlorine is used as disinfectant since DBP formation will continue to occur (Singer, 2001). The residence time varies depending on the water demand, design of the network, storage capacity in the system and operation of the storage tanks. Even when chloraminated water is used, the residence time can also be important. In a study conducted by Chen and Weisel (1998) the concentration of some DBPs (haloacetonitriles, haloketones, chloropicrin, and haloacetic acids) were found to decrease with increased residence time, while in a distribution system the THM levels increased.

The kinetics of DBP formation is also expected to influence the DBP speciation with time (diurnal and seasonal DBP variation) and space (variation of DBP levels in different distribution system locations). Therefore, the faster kinetics of HAA formation will lead to a large part of HAA formation potential being achieved in the treatment plant rather than in the distribution system.

The opposite might be true for THM formation due to the lower kinetic rates associated with these by products (Singer, 2001). Fifty percent or more of the total THM production can occur in the distribution systems (Mays, 2000).

According to Singer (2001), even though it has been shown that the chlorine demand, calculated by subtracting the chlorine residual (measured at the sampling point) from the chlorine dosage applied in the treatment plant, can be a good predictor of TTHM exposure, this extrapolation must be carefully done as the raw water characteristics (for example the presence in the water of chlorine demanding impurities) and the pipe materials such as unlined cast iron pipes can alter this relation.

The stagnation of water in dead end mains and storage facilities with excess volumes and long residence times will be responsible for the deterioration of water quality in terms of loss of disinfectant residual in the water and DBP production (Vasconcelos et al., 1996).

The rate of loss of disinfectant residual is a function of time and rate of disinfectant decay affected by microbiological activity, temperature, nitrification, exposure to UV light as well as amount and type of disinfectant (Mays, 2000). The decay in storage facilities will mainly occur by reactions with the bulk liquid as opposed to wall effects.

The following factors related to storage facilities are expected to increase the DBP formation (Mays, 2000):

- long contact time;
- the use of rechlorination;
- tanks material (steel storage tanks may be subjected to very high temperatures);
- increase of pH due to leaching of hydroxides and carbonates from the concrete surfaces.

All these considerations imply that significant temporal and spatial variations in DBP concentrations and therefore in exposure are expected to occur especially when free chlorine is used as a disinfectant.

II.B.7.c.i. DBP Formation under Simulated Distribution System Conditions

The evolution of studies that simulate the distribution system conditions are important in order to predict the distribution system variability and to minimize the amount of sample analyses. By submitting disinfected water to laboratory conditions that try to mimic the distribution system conditions, these studies estimate the expected DBP variations in the distribution system.

Rossman et al. (2001) conducted a study that proved that bottle incubation studies can be useful for estimating the kinetics of THM and HAA growth in distribution systems. The authors compared the levels of THMs and six of the HAAs formed in chlorinated water circulated in an unlined ductile iron pipe with the same water kept under the same pH and temperature in glass bottles. The results obtained show that even though a higher THM production was found in the pipe experiment this increase was not significant, and that the total HAA formation under the two experiments were similar, even though in the pipe experiment more dichloroacetic acid and less trichloroacetic acid were produced than in the bottle experiment with time.

III. EXPERIMENTAL PROCEDURES AND METHODS

III.A. Experimental Procedures

III.A.1. Description of the Study Project

A five-year project is now being conducted by a team specializing in epidemiology, water chemistry and engineering, statistics, and obstetrics with a common objective of corroborating or disputing the hypothesis that the occurrence of spontaneous abortion might be related to the presence of DBPs in drinking water. In order to achieve this objective, three utilities with different levels and distribution of DBPs are being studied monitoring the pregnancy of a minimum of 950 women (at less than 12 weeks' gestation). All the women enrolled are expected to complete an interview to assess their water use and provide information on potential confounders.

In support of the epidemiological study, the research presented here has the objective of providing an approach to accurately assess exposure of these subjects to DBPs in these systems measured in terms of trihalomethane (THM), haloacetic acid (HAA) and total organic halogen (TOX) concentrations.

To meet these objectives, this study focused on an intensive evaluation of the DBP concentrations in the water at the water treatment plant and distribution system at one of the three utilities. Sample collection approaches were studied including a sampling strategy to determine the best distribution system locations at which samples should be collected.

III.A.1.a. Description of the Treatment Plant

The treatment plant treats surface water using conventional surface water treatment processes consisting of coagulation, flocculation, sedimentation and filtration (Figure 3). Ozone is used as a pretreatment-oxidant, chlorine is used as the primary disinfectant, and chloramination is employed for final (secondary) disinfection. The water's relatively high total organic carbon (5-8 mg/L) and low bromide (20-30 µg/L) concentrations subjected to a two-stage chlorination suggested that the system served by this treatment plant could be representative of a high level of exposure to chlorinated DBPs.

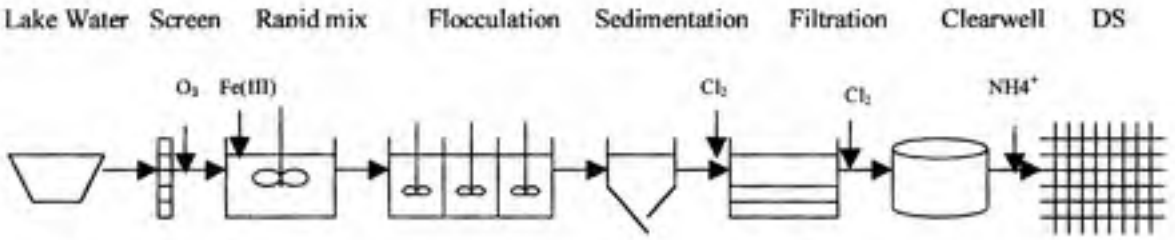


Figure 3: Treatment process employed in the study-system

Pre-ozonation, coagulation and filtration using granular activated carbon (GAC) are expected to play an important role in the DBP precursor removal. Pre-ozonation can serve the dual purpose of enhancing subsequent coagulation as well as oxidizing THM and HAA precursor molecules.

The use of ferric chloride as coagulant at pH values lower than six is expected to greatly enhance the TOC removal prior to GAC filtration (Nowack et al., 1999).

Using chloramination, the total trihalomethane (TTHM) and total haloacetic acid (THAA) concentrations are expected to remain fairly constant throughout the distribution system even though their concentrations leaving the plant may be relatively high due to a period of contact between chlorine and the water prior to the ammonia addition.

If this hypothesis is correct, then analysis of a small amount of samples at representative points in the distribution system should reliably reflect the levels of DBPs to which all consumers of the distributed water are exposed.

At this particular plant, during March each year, the treatment plant uses free chlorine in the distribution system instead of chloramines to disinfect the water. During this period one might, therefore, expect the DBP concentrations to be higher as well as more variable throughout the distribution system. The change in disinfectant is used for obtaining a more effective cleaning of the mains and attack of biofilms that might have become resistant to the disinfection with chloramines. Obtaining exposure data during this period would require a more comprehensive monitoring process.

III.A.1.b. Distribution System Description

The distribution system studied serves a population of approximately three hundred thousand consumers. In order to monitor the water quality that consumers would be exposed to, samples were collected during this study period from taps in fire stations and community centers located throughout the distribution system.

ArcView GIS Version 3.2 was used to overlap the maps of streets and pipes in the distribution system and to locate geographically the water treatment plant, the storage tanks, the distribution system locations used for sampling experiments and the subjects enrolled in the study. It is a very useful visualization tool to use in exposure characterization studies as it simplifies decisions allowing the users to solve the problems faster.

Figure 4 presents the distribution system sampling locations (water treatment plant, fire stations, and community centers) as well as the approximate location of the four pressure zones[3] (PZ) identified according to their overflow water level, and the ten storage tanks.

[3] Pressure Zone – Area of the distribution system served from a specific reservoir or pumping station

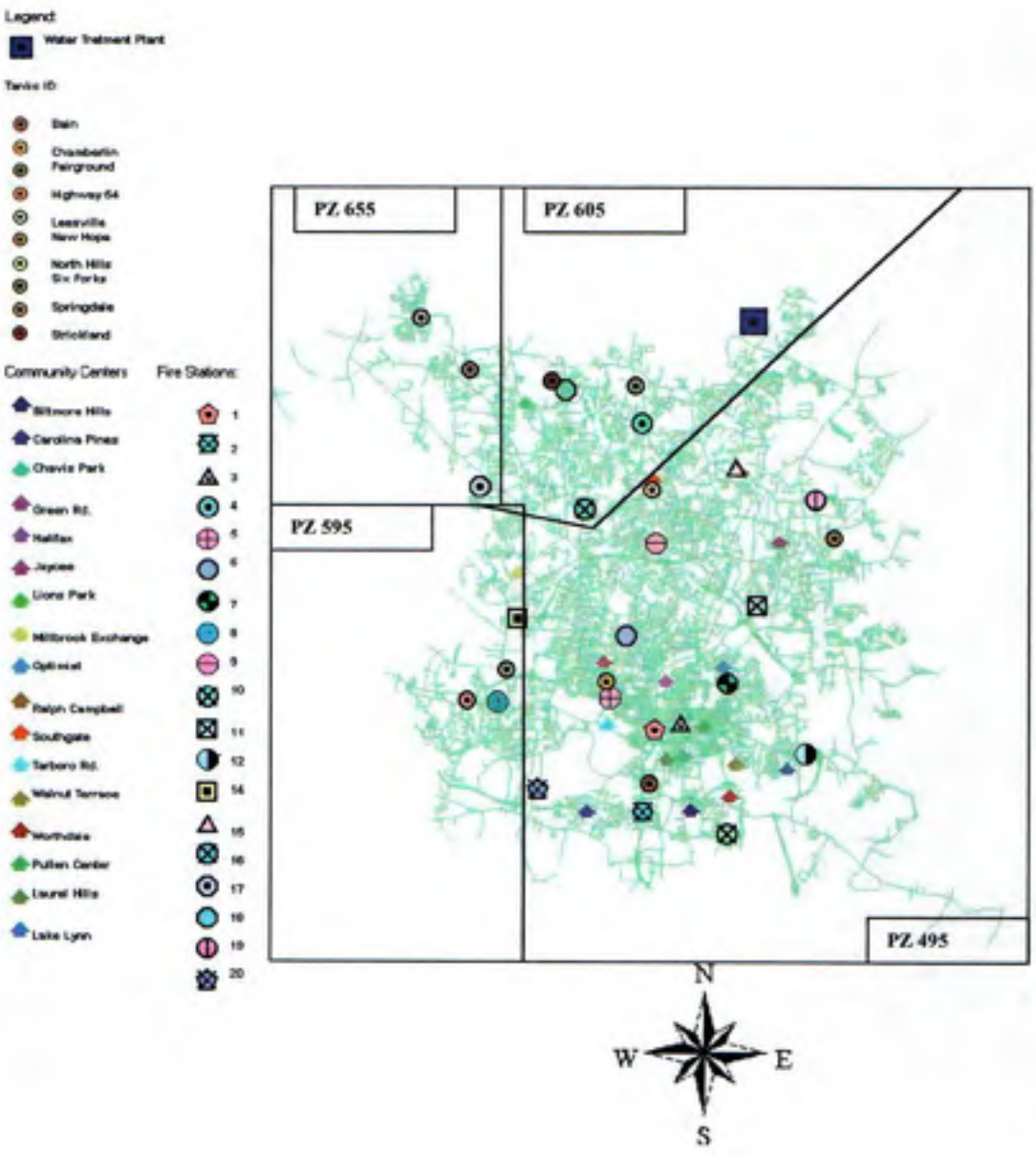


Figure 4: Distribution System Map

The hydraulic retention times (HRTs) from the treatment plant to the sampling locations used in the distribution system (fire stations, community centers, and wastewater treatment plant) presented in Table 4 were determined by fluoride tracer studies conducted in 1996 and 1998 by the water treatment plant (Zhang, 2001).

Table 4: Estimated hydraulic retention time in sampling locations

Sampling location	Station ID	Estimated HRT (h)
Fire Station	1	29.9
	2	21.8
	3	51.5
	4	33.2
	5	28.2
	6	394
	7	34.7
	8	34.3
	9	27.7
	10	45.5
	11	8.3
	12	19.1
	14	19.7
	15	14.2
	16	11.8
	17	11.4
	18	60.8
	19	9.3
	20	133
Community Centers	Biltmore Hills	97
	Carolina Pines	>270
	Chavis Park	98
	Green Rd	23
	Halifax	>486
	Jaycee	70
	Lions Park	36
	Millbrook Exchange	40
	Optimist	52
	Ralph Campbell	43
	Southgate	75
	Tarboro Rd.	18
	Walnut Terrace	51
	Worthdale	>540
	Pullen Center	41
	Laurel Hills	>540
	Lake Lynn	102
WWTP		103

The sampling points with higher estimated retention times are probably located in dead end mains of the system and therefore the DBP concentrations monitored at these points are expected to be high.

The distribution system studied can be divided in four pressure zones named according to their overflow water level as 495, 595, 605 and 655. Pumping stations connect the pressure zones between them.

The distribution system contains ten storage tanks used to equalize the pumping requirements and the operating pressures and to provide water in case of emergencies (e.g. fire fighting and pumping outages). Table 5 presents the information concerning the storage tanks present in the different pressure zones (Travaglia, 2000). The use of the storage facilities is expected to contribute to loss of disinfectant residual and formation of DBPs.

Table 5: Storage tank locations, storage and overflow volumes

Tank ID	Pressure Zone	Storage Volume (MG)	Overflow Level (ft)	Minimum Level (ft)
Plant Clearwell	605	12	400	396
Six Forks		1	605	596
Strickland		1	605	595
Springdale	655	0.5	643	625
Leesville		0.5	655	630
Highway 54	595	1	600	576
Fairground		1	595	583
Chamberlin	495	5	495	470
Bain Clearwell		8	252	246
New Hope		2	495	477
North Hills		8	497	470

III.A.2. Holding Time Study: Effects of Chloramination on THM and HAA Levels over Time

The study-utility was selected for the exposure characterization based on the assumption that the levels of THMs and HAAs would remain constant in the chloraminated distribution system. To verify this assumption, in July 2000, chloraminated water was collected at the water treatment plant (point of entry to the distribution system) into a series of vials designated for THM and HAA analysis and transported back to the university laboratory.

The samples were then transferred to an incubator with a programmed temperature of 22°C simulating the temperature conditions of the distribution system pipes, and removed daily over 13 days from the incubator, quenched of residual disinfectant and transferred to a refrigerator (with a temperature of about 4°C) where they were kept until analyzed. Samples for THM and HAA analysis were taken every day from the incubator.

The sample identification was made according to the dates used to simulate the distribution system retention times (for example a sample ID of 1 was given to a sample kept in the incubator for one day while sample 0 was the sample that was not put in the incubator, being immediately quenched and transferred to the refrigerator).

Even though the incubator was programmed to a temperature of 22°C, its temperature varied during the experimental period between 23.7 and 28.3°C. As the distribution system temperature is also expected to vary, these changes in temperature are believed to be insignificant.

A replicate sample was treated the same way as the initial sample but was collected after all the other samples to access any possible change in water quality during sample collection.

III.A.3. DBP Variability at the Point of Entry to the Distribution System

An intensive sampling program was conducted at the water treatment plant POE in order to assess the short-term variability in the concentration of DBPs entering the distribution system. Tap water samples were collected for THM, HAA and TOX analysis from the water treatment plant (from the finished water tap of the main laboratory) every four hours during five consecutive days (October 10 to October 15, 2000), quenched and refrigerated at the water treatment plant until all the samples were collected, and then shipped back overnight to the university laboratory in a cooler at 4-10°C. Upon receipt the samples were refrigerated immediately at 4°C until analyzed.

The sample identification was made according to the dates and times of sample collection.

III.A.4. Temporal and Spatial Variability in DBP Levels

In order to determine the short-term temporal and spatial variability in the DBP levels, three experiments were conducted in which sampling was performed at the point of entry to the distribution system and at one or two location(s) within the distribution system. The three experiments were conducted at different times in the year. The first two were conducted in January and February of 2001, while the third was conducted in August of 2001. Seasonal variability was therefore also observed.

Point of entry samples were collected at the water treatment plant (from the finished water tap of the main laboratory) every six hours over four consecutive days and at the selected distribution system locations during each of the three different sampling events. The samples were refrigerated at these locations until all the samples were collected, and then shipped back overnight to the university laboratory in a cooler at 4-10°C. Upon receipt the samples were refrigerated immediately where they were kept at 4°C until analyzed.

Table 6 summarizes the information of the sampling events, including the dates in which sampling occurred at each location used to characterize the temporal and spatial variability in the DBP levels.

Table 6: Dates and sampling locations used to characterize the temporal and spatial variability in the DBP levels

Sampling Event	Dates of sample collection at the WTP	Identification given to DS location sampled	Dates of sample collection at the DS	Estimated HRT at DS location sampled (h)
I	Jan 30 to Feb 4, 2001	DS I	Feb 5 to Feb 9, 2001	103
II	Feb 15 to Feb 19, 2001	DS II	Feb 16 to Feb 21, 2001	~24*
III	Aug 13 to Aug 17,2001	DS III-A	Aug 13 to Aug 17,2001	19.7
III		DS III-B	Aug 13 to Aug 17,2001	~24*

* Approximate HRT assumed at distribution location sampled, due to the nearest fire station or community center estimated HRT

DSI and DSIII-A locations correspond to the wastewater treatment plant and fire station 14, respectively. As for the other locations sampled (DSII and DSIII-B), since the samples were taken from distribution system locations other than the fire stations and community centers, for which the HRT was estimated based on an earlier tracer study conducted (Zhang, 2001), the HRT of the locations sampled was considered to be approximately the HRT estimated for the nearest fire station.

Figure 5 presents the distribution system boundaries with the water treatment plant and the locations of the distribution system sample sites chosen due to their easy access over a 24-hour day and willingness of someone to collect samples.

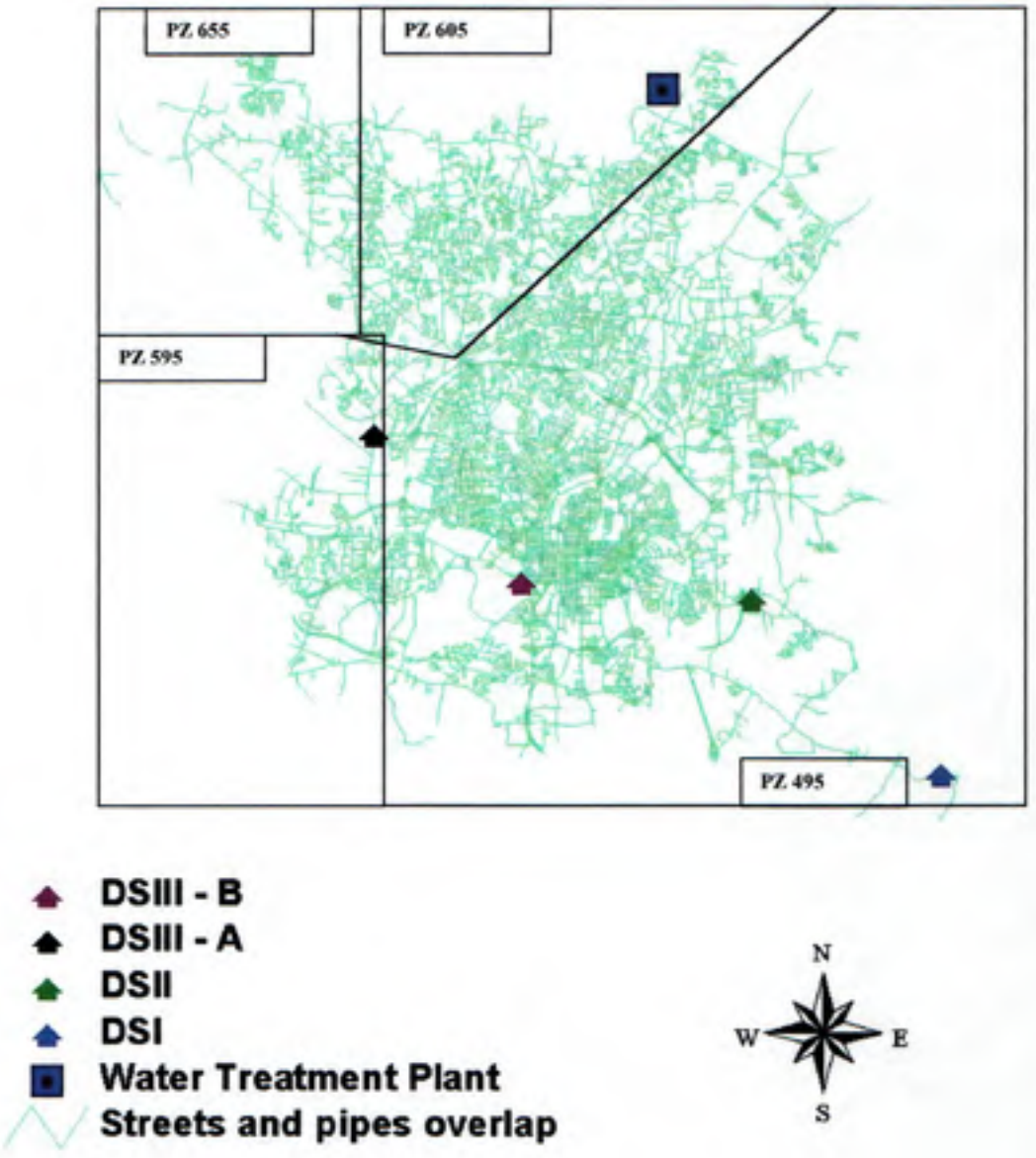


Figure 5: Location of the water treatment plant relative to the four distribution system locations sampled (DSI, DSII, DSIII-A and DSIII-B) in the three sampling events

III.A.5. Water Quality Modeling

EPANET version 2.0, a water distribution system modeling package developed by the U.S Environmental Protection Agency's Water Supply and Water Resources Division, was used for the simulation of the THM levels, assumed as conservative constituents, in the chloraminated distribution system water.

Pitometer Associates using their software WaterMax, developed the hydraulic network model of the distribution system for the utility studied in 1992, to help the public utility with planning analyses such as the location of new storage tanks and pumps. The model developed was highly skeletonized as it includes only 360 miles of pipes with a diameter equal to or greater than twelve inches, of the approximate 1100 miles of pipes in the distribution system (Travaglia, 2000). The model was updated in 1997 to include the increase in demand and pipes with a diameter equal to or greater than twelve inches added to the distribution system between 1992 and 1997, increasing the overall number of pipe segments in the model to 700. The network model was converted from the WaterMax format to a format compatible with EPANET by Travaglia (2000). Travaglia also updated the flow, demand patterns, volume of storage tanks and pumping schedules of the model.

The model was used to make predictions of the TTHM levels in the distribution system and these were then compared to the field data collected over different times of the year at three locations (DSI, DSII and DSIII-A). Due to the use of chloramination for final disinfection, the TTHM levels leaving the plant were modeled in the system as being nonreactive constituents. The field concentrations measured at the point of entry from the treatment plant were used as input data to the model. At the distribution system location modeled, an initial THM concentration was also used as input to the model based on the concentrations measured at this location. The model was run for 12 days at DSI and 8 days at DSII and DSIII-A.

Table 7 summarizes the THM sample collection periods used as input to the model.

Table 7: THM sample collection period used as input for EPANET simulations

DS Location Simulated	Dates of THM data collection used as input at WTP	Dates of THM data collection used as initial THM data input at DS location	Data predicted at DS location
DSI	Feb 1 (9h) to Feb 4 (21h)	Average DS data*	Feb 6 (6h) to Feb 9 (24h)
DSII	Feb 16 (6h) to Feb19 (12h)	Feb 16 (6h)	Feb 17 (6h) to Feb 20 (12h)
DSIII-A	Aug 13 (18h) to Aug 17 (18h)	Aug 13 (18h)	Aug 14 (18h) to Aug 17 (12h)

* As no samples were collected on Feb 1 at DSI, an average of the values measured at this location from Feb 6 (6h) to Feb 9 (24h) was used as initial THM level

III.A.6. Weekly Exposure to DBPs

In order to provide a measure of exposure to consumers from DBPs in their tap water, a single grab sample for THM, HAA and TOX analysis was collected each week from April to August 2001 from a representative point in the distribution system (DSIII-A). This location is presented in Figure 5 (of section III.A.4.) and was considered as a representative point of the distribution system exposure levels after the study of the spatial variations in DBP levels in the distribution system (described in section III.A.4.) was conducted.

After collection the samples were transported back to the university laboratory in a cooler at 4-10°C. Upon receipt the samples were refrigerated immediately where they were kept at 4°C until analyzed.

III.A.7. DBP Exposure During Period of Free Chlorine

During one month per year, the treatment plant uses free chlorine instead of chloramination in the distribution system in order to clean the mains and attack the biofilms that might have become resistant to the disinfection using chloramination.

During this period, as the DBP concentrations were expected to be higher and to vary in the distribution system with increasing residence times, weekly samples were collected at the water treatment plant and from several different locations in the distribution system in order to assess exposure (Figure 6). These locations included 8 fire stations (FS) and one community center (CC). The ten distribution system locations were chosen in order to represent different ages of water situated in the four pressure zones of the system:

- PZ655 (FS17);
- PZ605 (WTP, FS18 and FS16);
- PZ595 (FS8);
- PZ495 (FS15, FS12, FS5, FS6 and CC2).

A higher number of samples were collected at PZ495 due to the higher number of study subjects located in this area. On the second week of sample collection, samples were collected by mistake from FS9 instead of FS18. This FS is therefore also represented in the Figure 6. The addresses of the subjects enrolled in the project were also located in the distribution system map using ArcView so that if the DBP concentrations were found to vary spatially during this month their exposure would be assessed based on their location rather than an average obtained from all the sampling locations.

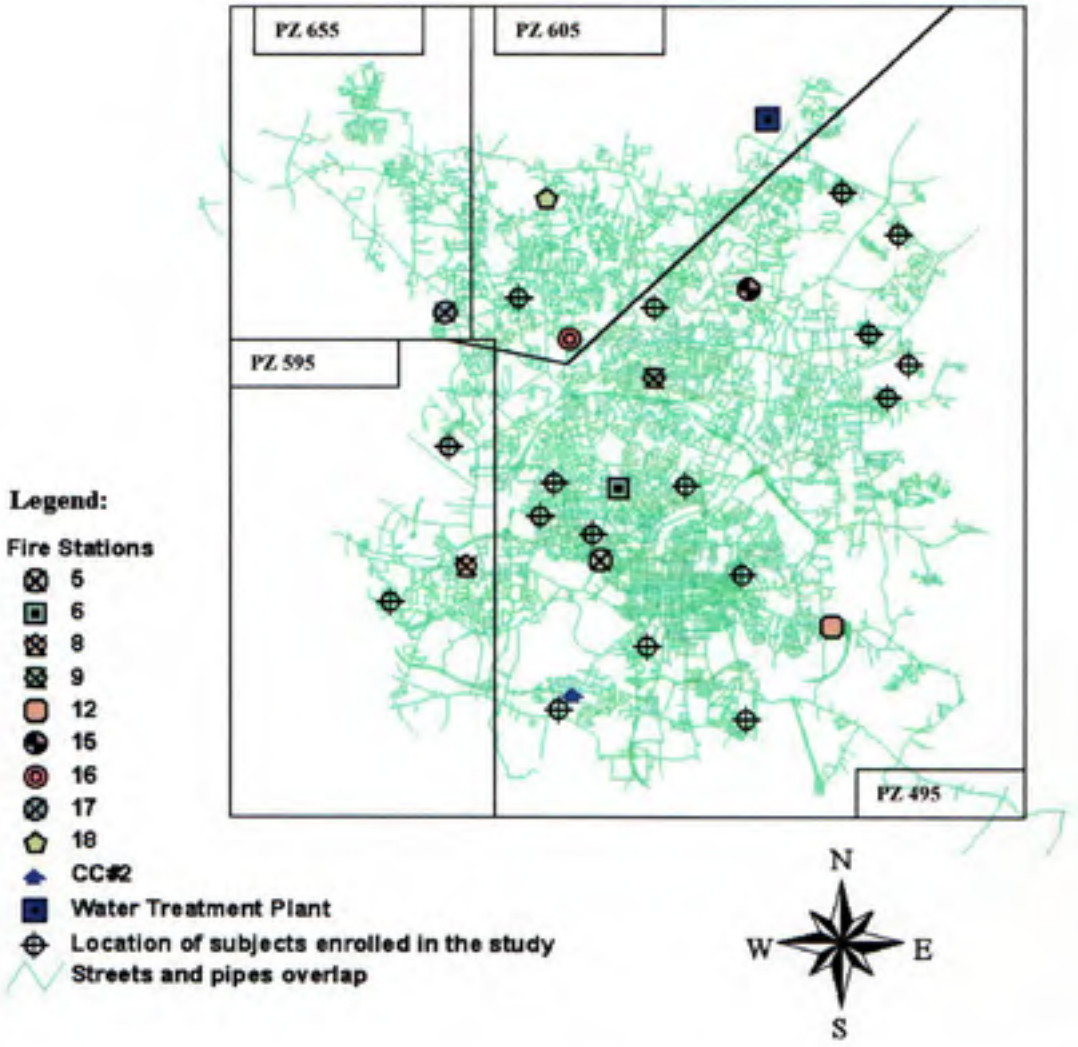


Figure 6: ArcView map with the 10 DS sampling points chosen, the water treatment and the localization of the subjects enrolled in the study

The estimated hydraulic retention times (Zhang, 2001) of the locations sampled are presented in Table 8.

Table 8: Retention times at the sampling points

DS sampling location	Rt (h)
WTP	0
FS # 17	11
FS # 16	12
FS # 15	14
FS # 12	19
FS # 9	28
FS # 5	28
FS # 8	34
FS # 18	61
FS # 6	394
CC # 2	>270

Every week, 10 locations of the distribution system, were sampled and the samples were transported back to the university laboratory in a cooler at 4-10°C. Upon receipt the samples were refrigerated immediately where they were kept at 4°C until analyzed.

III.A.8. Analysis of Possible Confounding Factors in Exposure Characterization

When studies of exposure characterization are conducted it is important to consider certain confounding factors that might affect the DBP concentrations in the water being ingested and therefore lead to assigning incorrect levels of exposure. The effect of possible confounding factors such as time of sample collection, boiling and refrigerating water, and point of use filter devices were studied (i.e. consumption of water other than directly from the tap) in a distribution system different than the one described in section III.A.1.b. that uses chlorine as final disinfectant.

In order to understand the effect that the time of sample collection may have on the THM levels that consumers are exposed to, the comparison between the THM levels obtained in samples collected in a chlorinated system in the early morning (at 6h) and in the evening (at 18h) was made.

To understand the effect of boiling and refrigerating water, 3 tap water samples were collected at the same time; one was immediately transferred to a vial containing the appropriate quenching agent, one was boiled, cooled over night and then transferred in the morning to the vial for THM analysis and the other refrigerated over night and then transferred in the morning to the vial for THM analysis.

The effect of using a point of use filter was studied by comparing the THM and HAA removals obtained by five different filters: four activated carbon filters and one reverse osmosis filter. The removals obtained when the filter was installed were also compared in two of the activated carbon filters to the removals obtained after more than half of the filter capacity was used (approximately 60gal).

III.B. Experimental Methods

III.B.1. Sample Collection

The DBP levels that consumers were exposed to, during the period of this study, were determined by samples collected for THM, HAA and TOX analysis. The sample collection procedure and a compositing technique developed to minimize the number of samples analyzed are presented in the following sections.

III.B.1.a. Sample Collection Procedure

Before collecting the samples, the predetermined preservatives (see standard operating procedure for each set of analytes) are placed in the empty vials. In the case of HAAs, 4 mg sodium azide is also present in each 40 mL vial as a biocide. During sample collection the sample bottles are not rinsed or overfilled.

The vials as well as the bags holding them should be labeled immediately after or before collection with the date and time of collection.

The samples are collected with the vial held at an angle and the water allowed to run slowly down the side of the sample vial to prevent the sample aeration. The sample is then filled to the rim and the bottle then capped with the shiny, teflon-faced side of the septum towards the water. Inverting the vial three times allows the mixing of the water with the preservatives. If an air bubble is present the cap is removed after mixing, a few more drops of sample added and then the vial recapped. This procedure should be repeated until there are no air bubbles present in the sample.

Travel and field blanks accompany the samples. The field blanks are opened at the site of sample collection while the samples are being collected. The travel blanks are not opened but simply accompany samples during shipment and handling.

After collection the samples are kept in a refrigerator and analyzed as soon as possible.

III.B.1.b. Development of a Compositing Technique

With the objective of simplifying the sampling procedure to assess the water DBP concentrations, a user friendly, time saving and efficient compositing technique was developed.

The THM and HAA samples were composited in head-space free teflon bags, while the TOX samples were composited by pulling up fixed-volume aliquots into the adsorption module channels.

This technique involved compositing several samples collected at different times at a specific location and comparing the DBP analysis of that composite sample with the average DBP concentrations obtained from all the individual samples collected at those times.

III.B.2. Analytical Methods

III.B.2.a. Trihalomethanes

The method used for the THM analysis and evolved from the EPA Method 551.1 (1995), employs a micro-extraction technique (liquid-liquid extraction) for the isolation of chloroform, bromodichloromethane, chlorodibromomethane, and bromoform from water and subsequently analyzed by gas chromatography using an electron capture detector (GC/ECD).

The THM extraction used 4 mL of pentane with internal standard (1,2-dibromopropane) and 6 g of sodium sulfate to 20 mL of aqueous sample. After vortexing for one minute, the supernatant pentane extract was analyzed by GC/ECD. Figure 7 presents a summary of the steps involved in the THM analysis. The standard operating procedure developed for the THM analyses is presented in Appendix A.

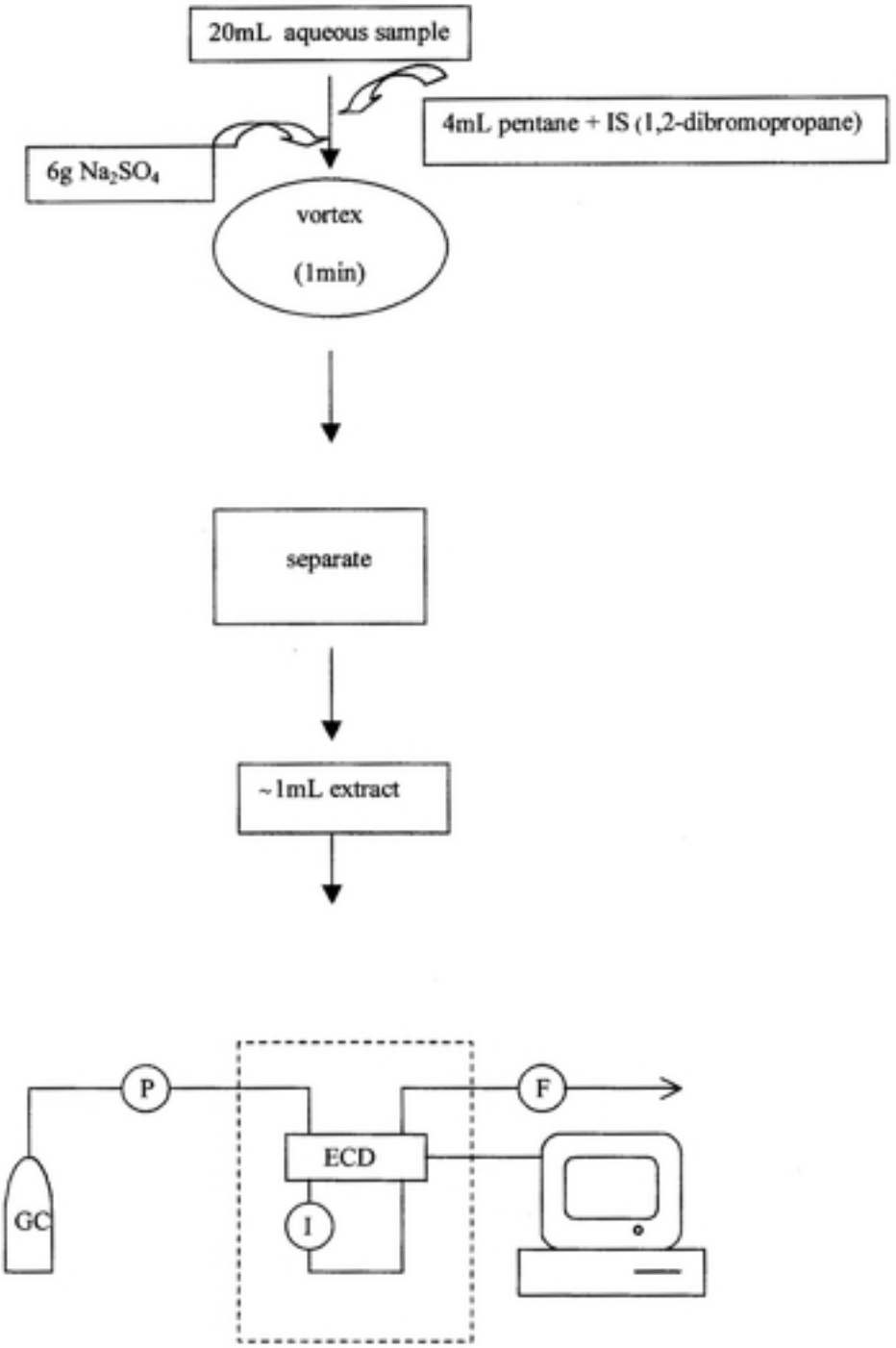


Figure 7: Summary of THM analysis procedure

III.B.2.b. Haloacetic Acids

The method used in the HAA extractions was developed by Brophy (1999) adapted from EPA method 552.2 (U.S. EPA 1995b) and Standard Method 6251B (Standard Methods 1995) and involves liquid-liquid extraction of the protonated acids from water using methyl tert-butyl ether (MtBE) as organic solvent, methylation of the acids using diazomethane, and subsequent analysis of the methyl esters by gas chromatography. Figure 8 presents a summary of the steps involved in the HAA analysis while a complete presentation of the method is presented in Appendix B.

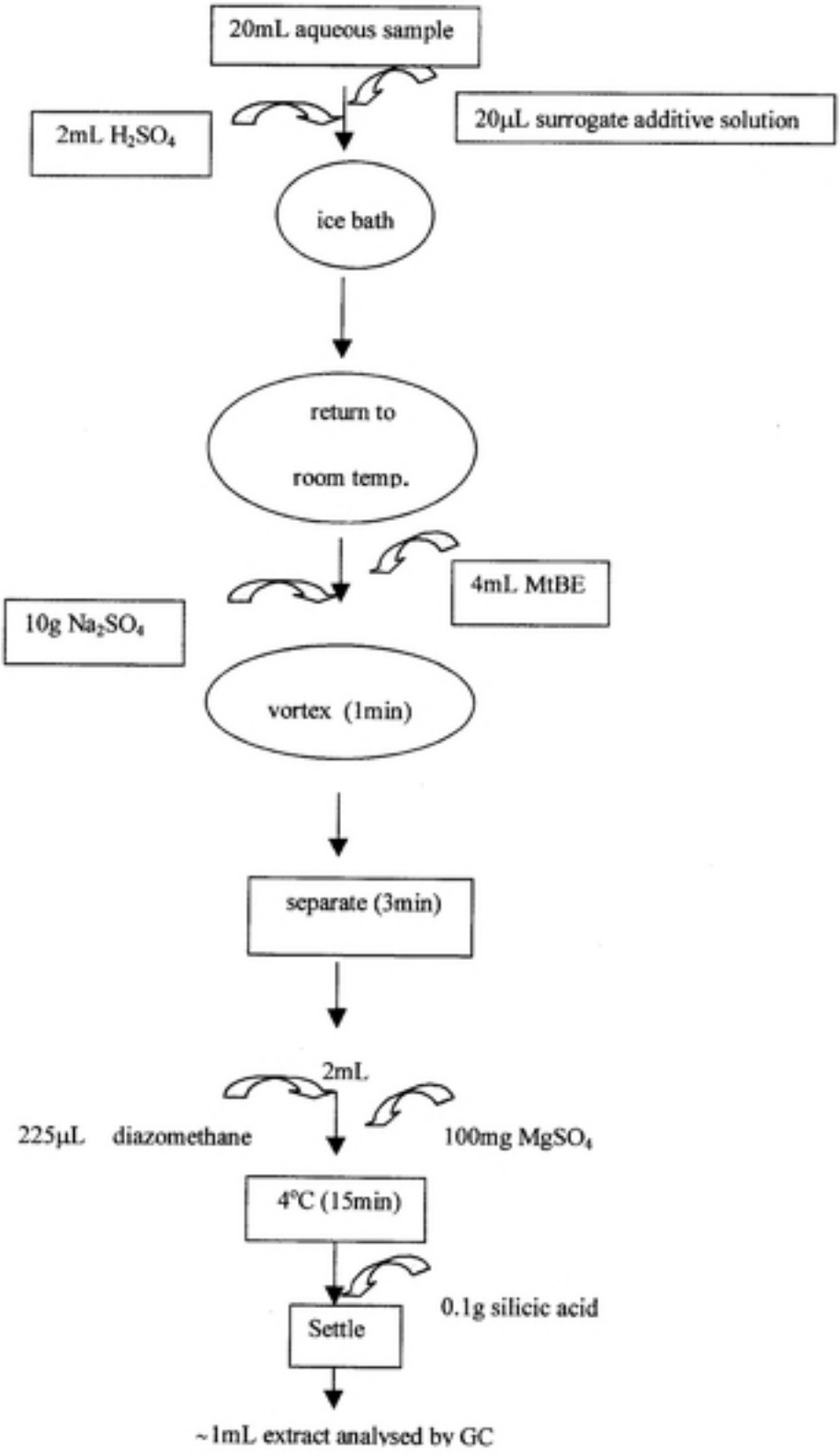


Figure 8: Summary of HAA analysis procedure

III.B.2.d. Total Organic Bromide

After several authors (e.g. Plewa et al., 1999 and Richard, 1995) suggested that the brominated species are more toxic than the chlorinated ones, Echigo et al. (2000) proposed a method to differentiate between the total organic chlorinated compounds (TOCl) and the total organic brominated compounds (TOBr). This difference can not be done using a conventional TOX measurement as the coulometric titration cell is insensitive to the difference between the two ions. The authors (Echigo et al., 2000) therefore proposed an analytical method that collects the HBr and HCl in the off-gas from the TOX analyzer in water instead of being titrated in the coulometric cell and analysis of the ions using ion chromatography. Figure 10 presents a summary of the steps involved in the TOBr analysis while the standard operating procedure developed for this analysis is presented in Appendix D.

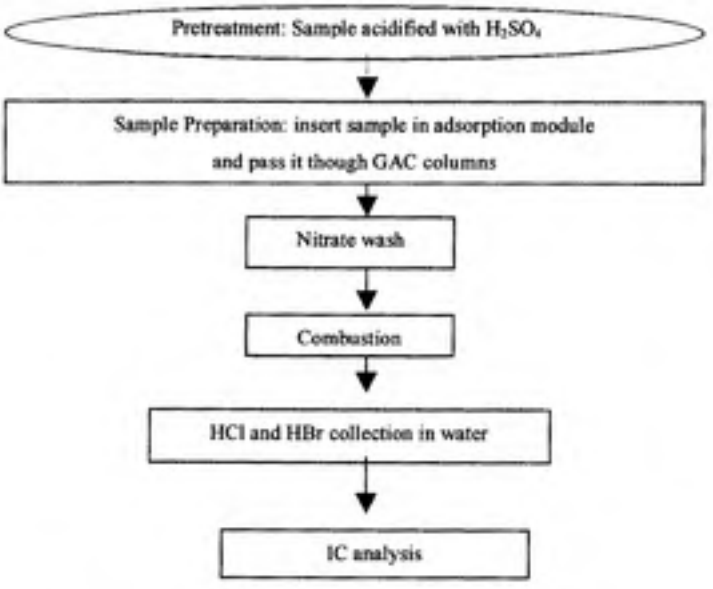


Figure 10: Summary of TOBr analysis procedure

III.B.2.c. Total Organic Halide

TOX analysis will allow the determination of the total halogenated DBPs. This determination is important as, due to the complexity and diversity of NOM, a significant part of these compounds remain unidentified (Echigo et al., 2000). Figure 9 presents a summary of the steps involved in the TOX analysis while the standard operating procedure developed for this analysis is presented in Appendix C.

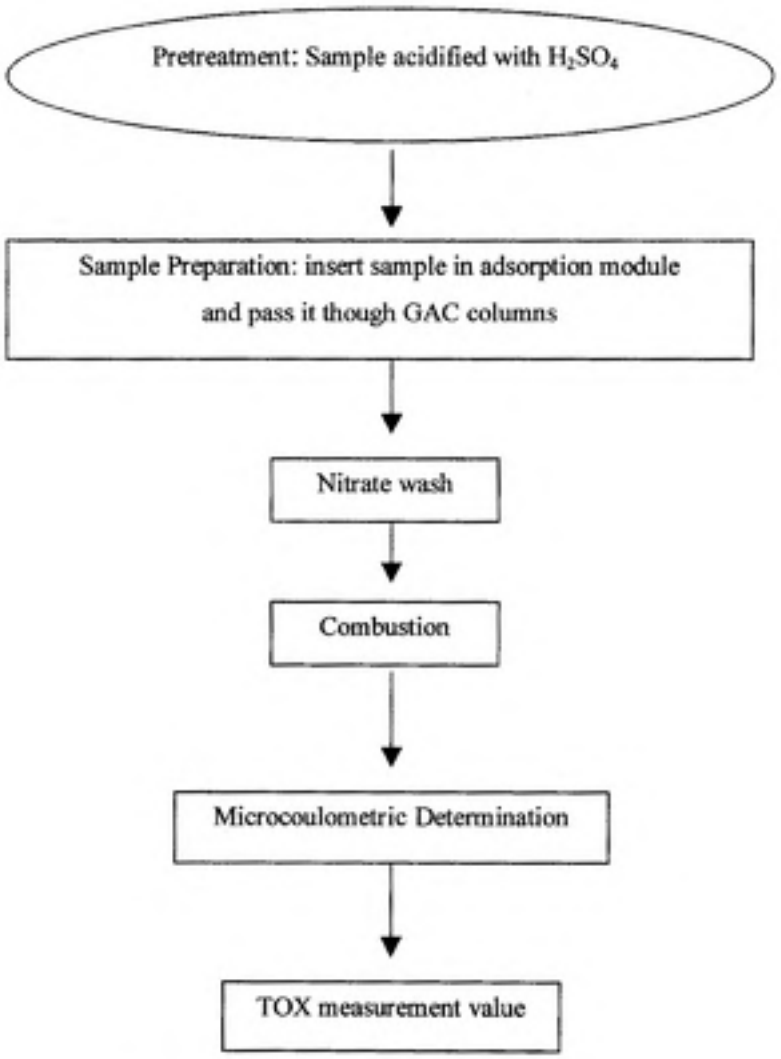


Figure 9: Summary of TOX analysis procedure

III.B.2.c. Free and Total Chlorine

The analysis of free and total chlorine was made using a colorimeter test kit (Hach Chemical, Loveland CO). The samples' analysis using this kit is very simple and quick involving the following steps: zero the colorimeter using a sample blank (laboratory grade water), insert reacted sample into the instrument's cell holder, and read the results in concentration units. It is very important to rinse the cell between analyses to ensure the measurement accuracy. The operating procedure followed to use the Hach Kit for the analysis of free and total chlorine is presented in Appendix E.

IV. RESULTS AND DISCUSSION

IV.A. Effects of Chloramination on THM and HAA Levels

IV.A.1. Bottle Storage Test

With the objective of determining whether chloramination contributes to the continuing formation of THM and HAA during distribution of drinking water, DBP levels were measured in chloraminated water collected from the point of entry, in July 2000, and held over 13 days at 22°C.

The variability in THM levels resulting from the continued exposure of the treatment plant finished water to chloramine is illustrated in Figure 11.

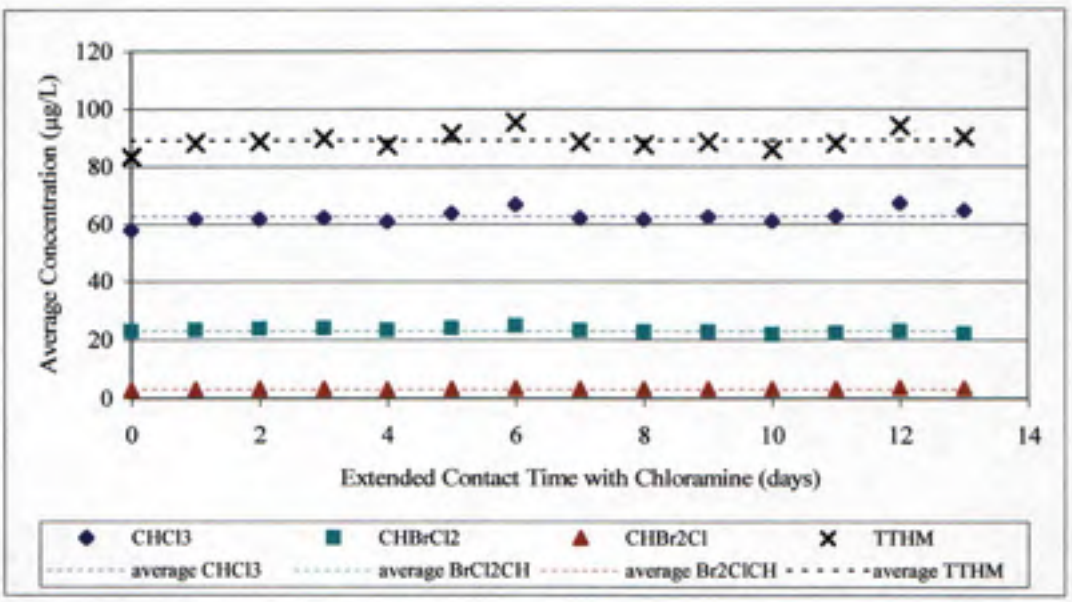


Figure 11: THM concentrations as a function of extended contact time with chloramine

THM and HAA extractions were performed on two different days for the analysis of samples 0 to 6 (0 to 6 days at 22°C) and samples 7 to 13 (7 to 13 days at 22°C). Tables F1 and F2 in Appendix F present the concentrations obtained for the THM and HAA samples, respectively. Sample 6 duplicate failed quality control and is therefore excluded from the table.

With a coefficient of variation of less than 8% over the thirteen days of continued exposure to chloramines, it is apparent that the concentrations of the individual THM species as well as the total THM (TTHM) species remained fairly constant. This suggests that the removal of the chlorine by reaction with ammonia to form chloramines stops the formation of THMs. The high levels present in the finished water were most likely formed in the treatment plant during the period of free chlorine contact prior to the addition of ammonia.

Figure 12 shows that the concentrations of the individual HAA species as well as the total HAA species detected (THAA) remained fairly constant over 8 days (with coefficients of variation of less than 11%). The results obtained in days 5, 6 and 9 to 13 are not shown as they failed the quality control evaluation due to chromatography detection problems with the chloroacetic acid and bromodichloroacetic acid methyl ester peaks.

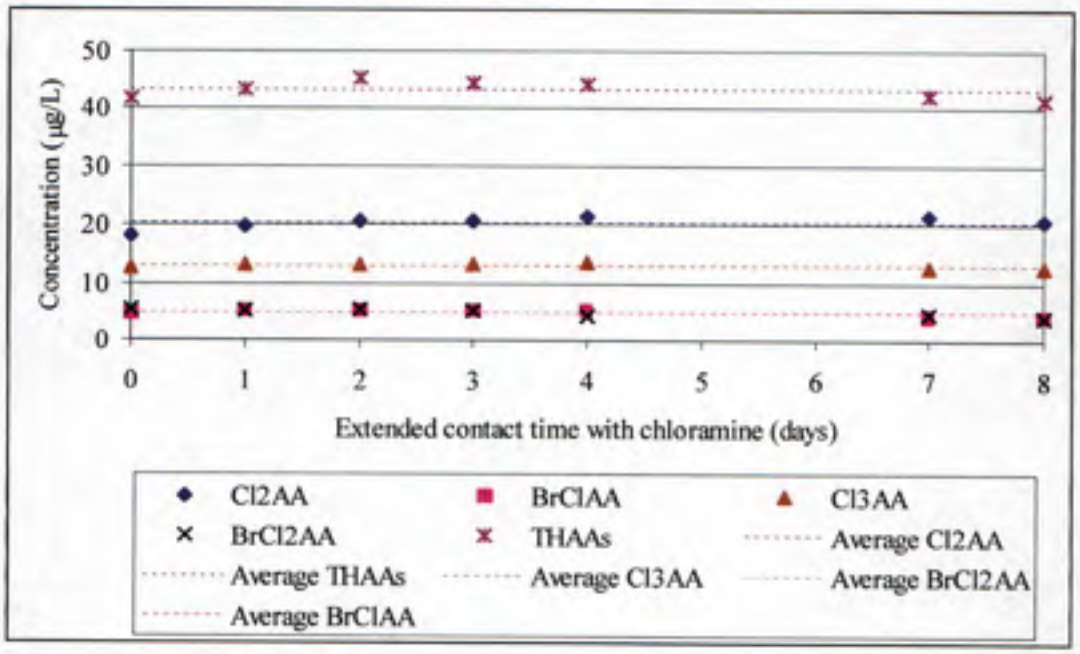


Figure 12: HAA concentrations as a function of extended contact time with chloramine

The results obtained in this study corroborate the hypothesis that a chloramine residual does not change the THM and HAA concentrations or speciation once formed, at least under bottle storage conditions.

IV.A.2. Field Monitoring Tests

TTHM data generated by the treatment plant during the year 2000 for point of entry (POE) and six distribution system locations (fire stations) are presented in Figure 13, and confirm the conclusions drawn from our controlled experiments (having coefficients of variation lower than 10%). Even though the levels of TTHMs varied with time of year, the measured values on any sampling date tended to be constant throughout the distribution system during a single sampling event.

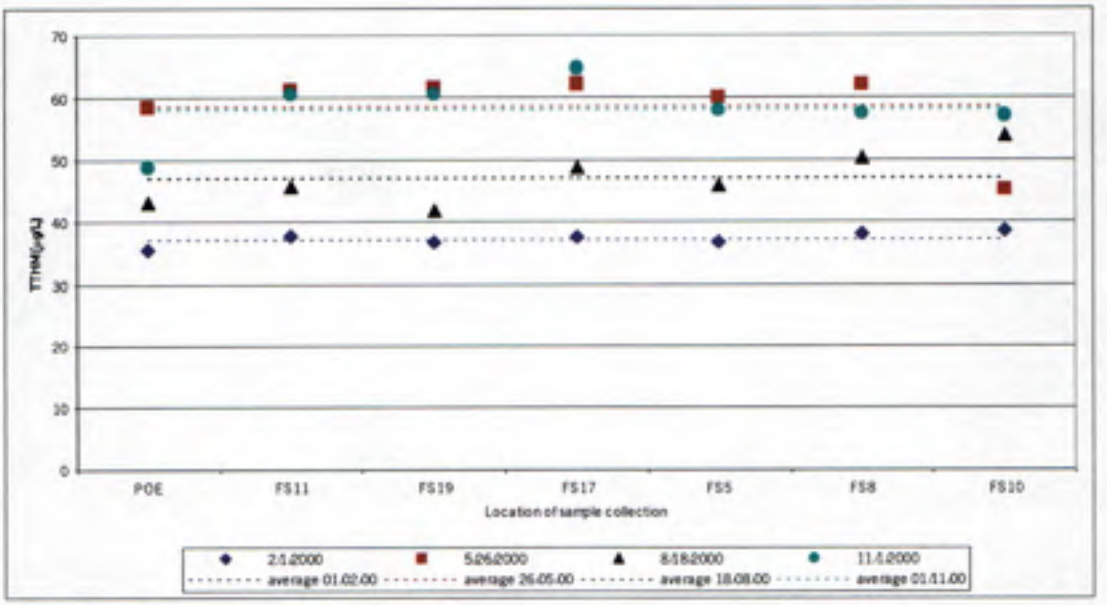


Figure 13: Concentrations of total trihalomethanes measured in the distribution system during the year 2000

These results suggested that the concentration of THMs and HAAs in tap water from any point in the distribution system might be obtained from analysis of a single representative point in the system. However, this assumes that no major fluctuations in the levels of DBPs entering the system occur over the period during which the measured level is used.

In order to determine if this hypothesis could be used in practice, temporal and spatial variability in the chloraminated finished and distributed water was examined.

IV.B. DBP Variability at the Point of Entry to the Distribution System (Temporal Effects)

In the intensive sampling program conducted at the water treatment plant, tap water samples were collected for THM, HAA and TOX analysis from the finished water tap of the main laboratory every four hours during five consecutive days (October 10 to October 15, 2000).

The THM concentrations of the individual species as well as the total of the detected species are presented in Figure 14.

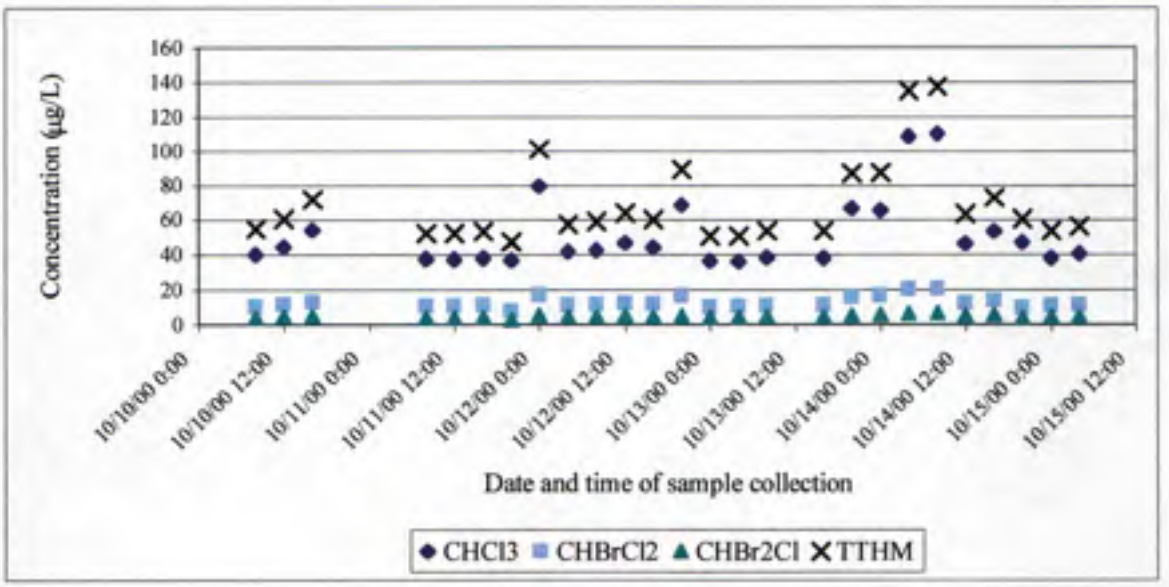


Figure 14: THM variability at the point of entry to the distribution system

Figure 14 shows the dramatic variation in the THM concentrations leaving the treatment plant with very high values occurring during the night periods (exception being the 14th of October with the highest TTHM value obtained at 8 AM).

Due to the large set of samples extracted, one vial from a pair of duplicate samples (10/14/00 4:00) was extracted at the beginning of the batch while its duplicate was extracted at the end of the batch to determine if any significant THM losses occurred while standing. The 3% coefficient of variation obtained between the two samples show that no significant losses occurred.

The only analysis made by the water treatment plant during the study period was for THM on the 13th October at 10AM (result: TTHM=64.3 µg/L). The average TTHM obtained in this study at 8AM on the same day was 53.6 µg/L.

Tables F3, F4, and F5 in Appendix F present the concentrations obtained for the THM, HAA, and TOX samples, respectively.

A summary of the TTHM, THAA and TOX concentrations obtained at the point of entry to the distribution system is presented in Figure 15 and Table 9.

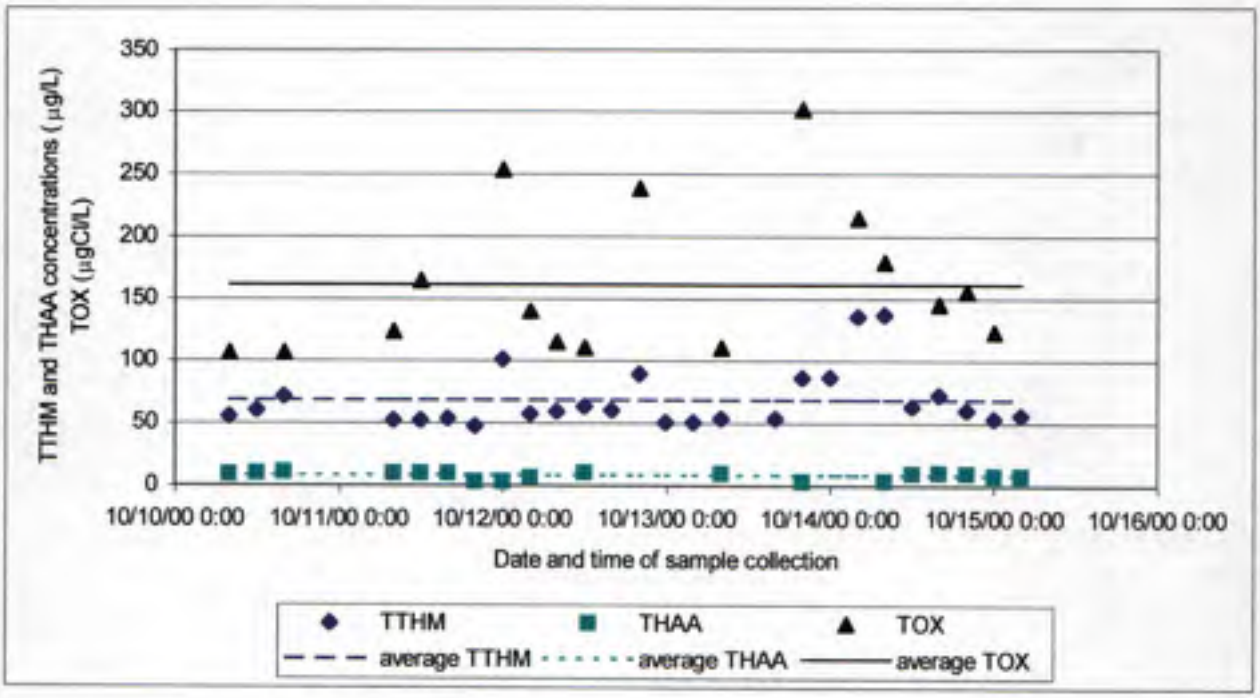


Figure 15: TTHM, THAA and TOX variability at the point of entry to the distribution system

Table 9: TTHM, THAA and TOX variability at the point of entry to the distribution system

Date and time of sample collection	TTHM (µg/L)	THAA (µg/L)	TOX (µgCl/L)
10/10/00 8:00	54.9	8.2	106
10/10/00 12:00	60.3	9.5	Nav
10/10/00 16:00	71.6	10.5	106
10/11/00 8:00	52.2	9.7	123
10/11/00 12:00	52.1	9.8	164
10/11/00 16:00	53.3	9.5	Nav
10/11/00 20:00	47.3	3.1	Nav
10/12/00 0:00	101	3.0	253
10/12/00 4:00	57.2	6.0	140
10/12/00 8:00	58.9	Nav	115
10/12/00 12:00	63.5	10.3	111
10/12/00 16:00	60.1	Nav	Nav
10/12/00 20:00	89.4	Nav	238
10/13/00 0:00	50.7	Nav	Nav
10/13/00 4:00	50.7	Nav	Nav
10/13/00 8:00	53.6	9.8	111
10/13/00 16:00	53.5	Nav	Nav
10/13/00 20:00	86.9	2.6	302
10/14/00 4:00	135	Nav	215
10/14/00 0:00	87.3	Nav	Nav
10/14/00 8:00	137	3.4	180
10/14/00 12:00	63.5	9.7	Nav
10/14/00 16:00	72.6	9.9	146
10/14/00 20:00	60.4	9.7	156
10/15/00 0:00	53.4	7.1	123
10/15/00 4:00	56.1	7.4	Nav
Average (µg/L)	68.6	7.7	162
Stdev (µg/L)	24.3	2.9	60.0
CV (%)	35.5	37.0	37.1
Max (µg/L)	137	10.5	302
Min (µg/L)	47.3	2.6	106

Nav – Not available

From the results shown above and the coefficients of variation obtained (35% for the THM samples, and 37% for the HAA and TOX samples), it is apparent that a single grab sample at the point of entry to the system cannot reliably be used for providing DBP exposure levels to consumers of the distributed water.

Possible explanations for the fluctuations could be inconsistency with the manner in which chloramination is carried out, variable flow rates or hydraulic retention times at the water treatment plant. Since ammonia is added manually by the treatment plant operator, it is possible that at certain times during the day a free chlorine residual is carried through the plant to the point of entry to the distribution system.

The unknown halide (OX) content, presented in Table 10, was calculated by subtracting the TTHM and THAA concentrations obtained (measured in terms of the chloride concentration) from the TOX concentrations.

When studying chloramination under controlled conditions, Zhang and other authors (2000) found a higher percentage of unknown halide (85%) than was shown in this study (average 58%). However, Singer and Chang (1989) reported that in surface waters that had undergone conventional treatment at near-neutral pH, the TTHMs comprised approximately 26% of the TOX concentration.

Table 10: Calculation of the Unknown Organic halide (OX) concentration

Date and time of sample collection	TTHM (µg Cl/L)	THAA (µg Cl/L)	TOX (µg Cl/L)	Unknown OX (µgCl/L)	Unknown OX/TOX (%)
10/10/00 8:00	44.8	4.5	106.3	57.0	54
10/10/00 16:00	58.8	5.9	106.3	41.5	39
10/11/00 8:00	42.4	5.5	123.1	75.1	61
10/11/00 12:00	42.3	5.5	164.4	116.5	71
10/12/00 0:00	82.3	1.6	252.9	168.9	67
10/12/00 4:00	46.6	2.6	139.9	90.7	65
10/12/00 12:00	51.8	5.2	110.9	53.9	49
10/13/00 8:00	43.4	5.5	110.7	61.8	56
10/13/00 20:00	71.8	1.4	301.7	228.4	76
10/14/00 8:00	115.0	1.9	179.7	62.9	35
10/14/00 16:00	59.3	5.5	145.5	80.7	55
10/14/00 20:00	50.1	5.5	155.8	100.3	64
10/15/00 0:00	43.2	3.8	123.2	76.1	62
Average (µg/L)	58	4	155	93	58
Stdev (µg/L)	21	2	60	52	12
CV (%)	37	41	38	56	20
Max (µg/L)	115	6	302	228	76
Min (µg/L)	42	1	106	42	35

IV.B.1. Development of a Compositing Technique

The samples collected in this experiment were also used to develop a compositing technique. The good recoveries obtained when the result of the composited sample was divided by the average of the individual sample results are shown in Table 11. Duplicate samples were analyzed using the THM and HAA methods.

Table 11: Recoveries obtained using a composite method

Analyte	Number of samples composited	Average value	Composite value	Recoveries obtained
THMs	12	61.4 µg/L 62.7 µg/L	55.7 µg/L 61.7 µg/L	91% 99%
HAAs	12	7.4 µg/L 7.3 µg/L	6.7µg/L 6.7µg/L	90% 92%
TOX	5	127 µgCl/L	165 µgCl/L	130%

Table F3b in appendix F presents the THM results obtained in the two duplicate composite samples (A and B) created using ten milliliters of the samples identified in Table F3 as A and B. Table F4b in appendix F presents the HAA results obtained in the two duplicate composite samples (A and B) created using ten milliliters of the samples identified in Table F4 as A and B. Table F5 in Appendix F presents the TOX results obtained in a composite sample (A) created using ten milliliters of the samples identified as A.

IV.C. Temporal and Spatial Variability in DBP Levels

In order to determine if the variation in the DBP levels leaving the plant would also occur within the distribution system, three different experiments were conducted in which sampling was performed at the point of entry to the distribution system and at four different locations within the distribution system. These locations are representative of the two pressure zones where most of the subjects enrolled in the study are expected to reside. Analysis of seasonal variability was possible since the three experiments were conducted during different times of the year; the first two were conducted in January and February while the third was conducted in August. In the third experiment, samples were collected at the point of entry to the distribution system and at two distribution system locations (DSIII-A and DSIII-B).

In the three sampling events, conducted on three different occasions, tap water samples were collected at the treatment plant (WTP) and at different distribution system locations depicted in Figure 5 (which shows the boundaries of distributed city water) every six hours over 4 days.

◆ *Distribution System Location I*

Tap water samples were collected for THM analysis every six hours at the point of entry to the distribution system (water treatment plant) and five days later at the waste water treatment plant (DSI) with an estimated hydraulic retention time of approximately five days in an attempt to capture the effect of spatial effects on a plug of water leaving the treatment plant. Figure 16 compares the TTHM values from the point of entry at the water treatment plant (from Jan 30 to Feb 4 of 2001) with the distribution system sample point DSI (from Feb 5 to Feb 9 of 2001).

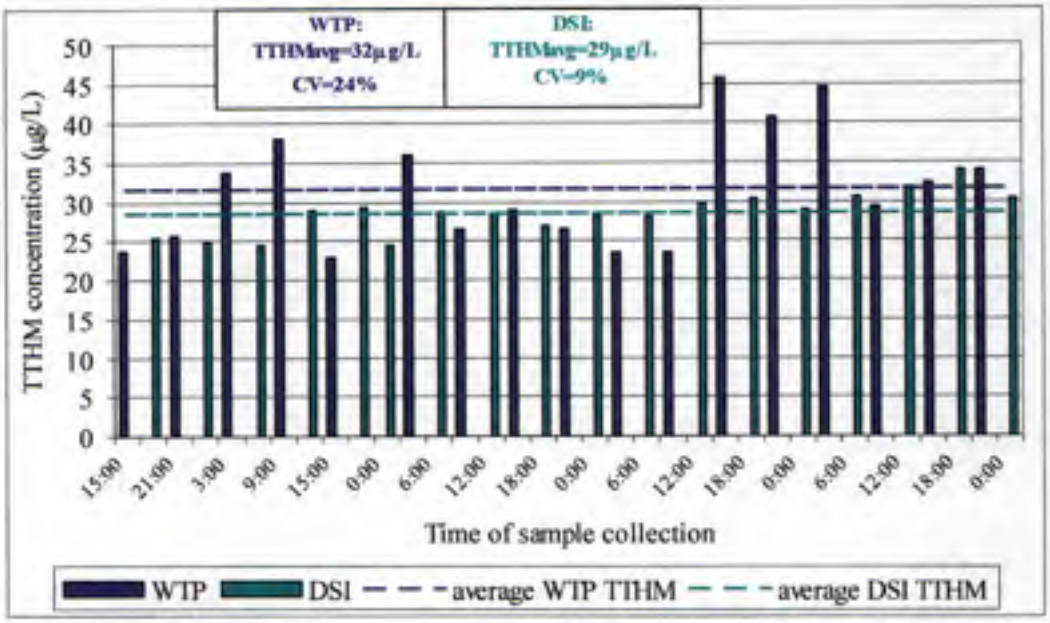


Figure 16: Comparison of total trihalomethane concentrations leaving the treatment plant (WTP) and in the distribution system (DSI)

The results obtained show that the variation in the TTHM levels leaving the treatment plant (with a coefficient of variation of 24%) is dampened in the distribution system (with a coefficient of variation of only 9%). The average TTHM concentration obtained for the WTP samples (32µg/L) was very similar to the average value obtained in the DS samples (29µg/L).

The fluctuations in the TTHM levels at the point of entry to the distribution system observed in October 2000 (Figure 14) were again observed in this experiment with the extreme values being once more obtained during the night periods (of the three highest values obtained in this experiment at the water treatment plant, two of them occurred at night: 21h and 3h).

Tables F6 and F7 from Appendix F present the THM concentrations obtained for the samples collected at the treatment plant and DSI, respectively.

Distribution System Location II

Tap water samples were collected for THM, HAA and TOX analysis every six hours at the treatment plant and one day later at a DS location (DSII) with a hydraulic retention time of approximately one day. Figure 17 compares the TTHM values from the point of entry to the distribution system (collected between Feb 15 to Feb 19 of 2001) with the distribution system sample point DSII (collected between Feb 16 to Feb 20 of 2001).

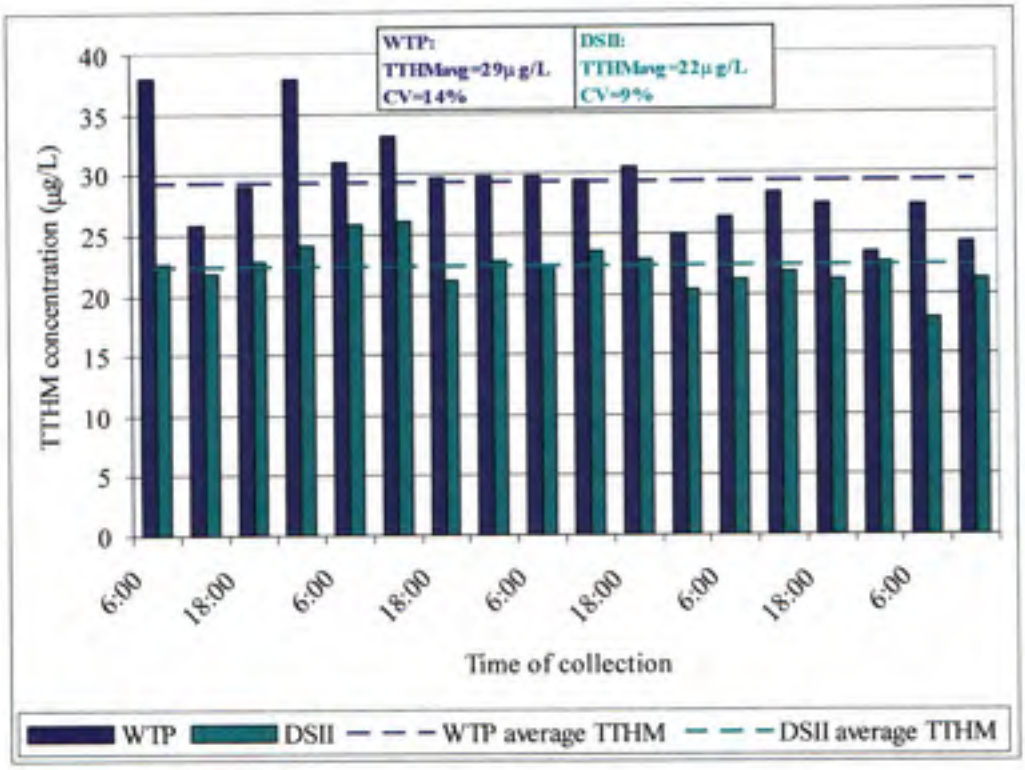


Figure 17: Comparison of total trihalomethane concentrations leaving the treatment plant (WTP) and in the distribution system (DSII)

The results obtained show that the variation in the TTHM levels leaving the treatment plant (with a coefficient of variation of 14%) is dampened in the distribution system (with a coefficient of variation of 9%).

However, the average TTHM concentration obtained for the WTP samples (29μg/L) was higher than the average values obtained in the DSII samples (22μg/L). The THM levels at the WTP contributing the widest disparity were again obtained during the night periods.

The four HAA and TOX samples collected each day at the different time periods were composited into a single sample in the university laboratory (according to the procedure described in session IV.B.1.) to simplify the analysis. Duplicate samples were similarly prepared.

Table 12 presents the average of the THM concentrations measured each day at the treatment plant and in the distribution system location as well as the daily composite HAA and TOX concentrations. TOX samples were not collected at the point of entry to the distribution system.

Table 12: Daily average TTHM and THAA concentrations measured at the treatment plant (WTP) and at DSII

	WTP		DSII				
Date	THAA (μg/L)	TTHM (μg/L)	THAA (μg/L)	TTHM (μg/L)	TOX (μg Cl/L)	Unknown OX (μg Cl/L)	Unknown OX/TOX (%)
15-Feb	28	31	Nav	Nav	Nav	Nav	Nav
16-Feb	29	32	27	23	274	241	88
17-Feb	33	30	26	24	257	224	87
18-Feb	35	27	32	23	241	206	85
19-Feb	26	25	29	21	239	206	86
20-Feb	Nav	Nav	29	20	240	209	87
21-Feb	Nav	Nav	29	20	Nav	Nav	Nav
Average	30	29	29	22	250	217	87
Stdev	4	3	2	2	15	15	1
CV (%)	12	11	7	8	6	7	1

Nav – Not Available

The THAA daily coefficients of variation obtained in the DSII samples are low because the daily values are composited, which will eliminate variability. The coefficients of variation for TTHMs and THAA were marginally higher at the treatment plant than in DSII. The TOX temporal variation of the composites obtained over 5 days at DSII is small.

The higher levels of THAA compared to TTHMs has been noticed by other authors examining chloraminated systems (Zhang et al., 2000).

The average percent of unknown halide obtained in this experiment (87%), was higher than in the temporal study at the point of entry to the distribution system (58%) and than the values reported by Singer and Chang in 1989 (with TTHM comprising approximately 26% of the TOX concentration). However, the value obtained was similar to the percentage of unknown halide reported under controlled conditions (85%) by Zhang et al. (2000).

Tables F8 and F9 in Appendix F present the concentrations obtained for the individual THM and composited HAA samples at the treatment plant and distribution system location sampled.

◆ *Distribution System Locations III*

Tap water samples were collected for THM analysis approximately every six hours at the treatment plant and for THM and TOX analysis at two distribution system locations (DSIII – A and DSIII - B) each with estimated hydraulic retention times of approximately one day. This experiment took place during the warm water month of August. Figure 18 presents the TTHM and TOX levels obtained in the distribution system location sampled (DSIII-A) while Figure 19 shows the comparison between the TTHM concentrations obtained at the point of entry to the distribution system and the levels at DSIII- A and DSIII-B. The TTHM and TOX results seem to follow the same trends.

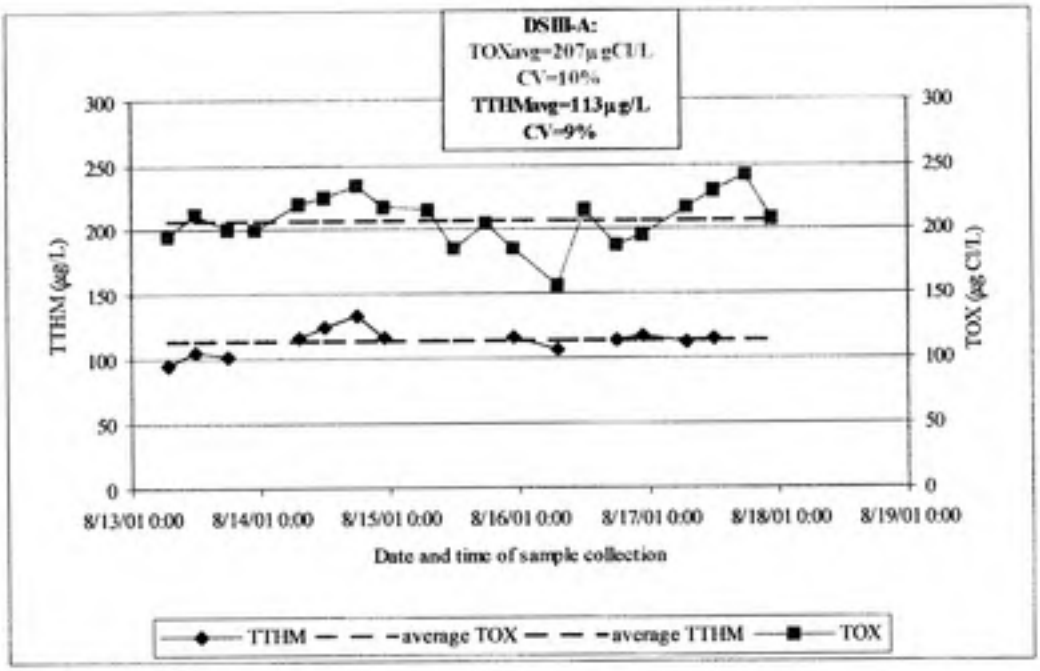


Figure 18: TTHM and TOX at DSIII – A

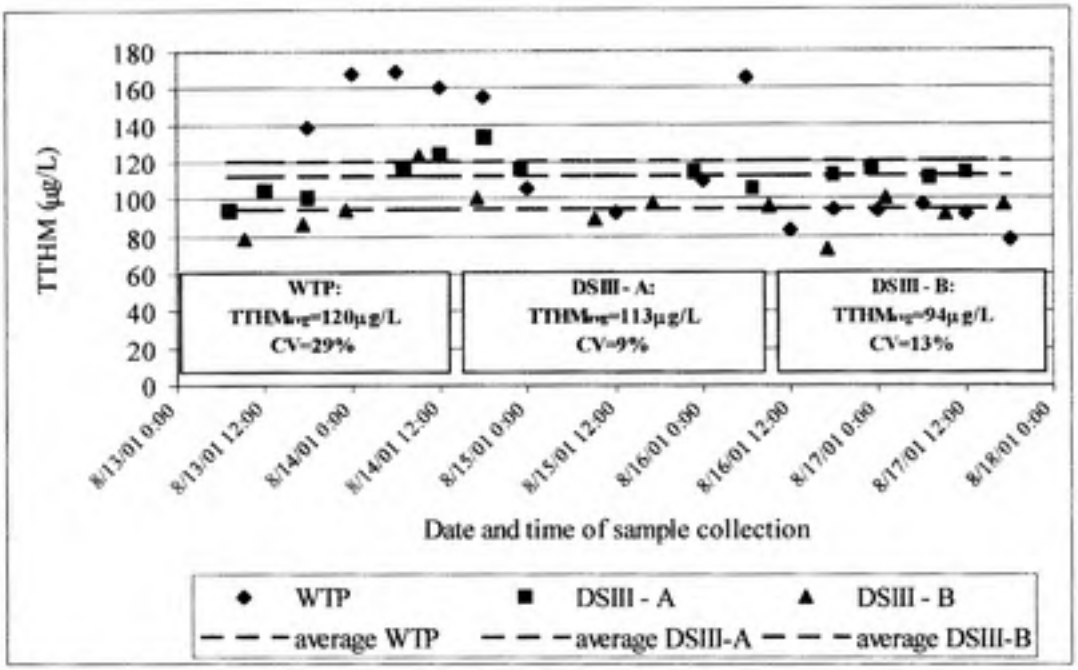


Figure 19: Comparison between the TTHM concentrations obtained at the water treatment plant (WTP) and two distribution system points (DSIII-A and DSIII-B)

The results show that the variation in the TTHM levels leaving the treatment plant (with a coefficient of variation of 29%) is again dampened in the two distribution system locations sampled (with coefficients of variation of 9 and 13%). The average of the THM levels obtained at the water treatment plant (120 μg/L) was higher than the average THM levels obtained in the distribution system at DSIII-A (113 μg/L) and DSIII-B (94 μg/L).

Seasonal variation was observed, with much higher average concentrations obtained in the treatment plant and distribution system during this August sampling compared to the results obtained in February.

Table F10 of Appendix F presents the THM results obtained in the treatment plant whereas Table F11 presents the THM and TOX results obtained at DSIII-A and Table F12 presents the THM results obtained at DSIII – B.

The three sets of data suggest that sampling at any point in the distribution system would be a more accurate way of characterizing DBP exposure than sampling at the point of entry to the system. Collection of a grab sample in the distribution system could then be an accurate way of characterizing exposure providing that no major changes in water quality or treatment operations occur in the treatment plant. Collecting a grab sample from the point of entry at the treatment plant would not be an accurate way for assigning exposure since the DBP levels there were found to be very variable. On the other hand, with a smaller coefficient of variation in the distribution system, a grab sample collected in the distribution system at any time during the day in a particular week would provide a reliable measure of such exposure to consumers of the distributed water for that week, assuming that there are no abnormal pockets in the distribution system where aged water might appear different in DBP quality compared to the rest of the system.

IV.D. WATER QUALITY MODELING

◆ *Distribution System Location I*

Figure 20 presents a comparison between the experimental (observed) and model (computed) results obtained when the model was run using the variable TTHM concentrations leaving the treatment plant from February 1 2001 at 9:00 to February 4 2001 at 21:00 (these concentrations are presented in Table 13). This input was used to predict the results obtained in DSI (which corresponds to node 6619 in the model) from February 6 at 6:00 to February 9 at 24:00 (these concentrations are presented in Table 13). An initial concentration equal to the average of the THM levels measured at DSI (28.6 μg/L) was used as initial concentration at this location.

Table 13: TTHM data used as input for simulations at DSI

WTP		DSI	
Sample ID	TTHM (μg/L)	Sample ID	TTHM (μg/L)
2/01/01 9:00	38.0	2/06/01 6:00	24.5
2/01/01 15:00	23.0	2/06/01 12:00	28.9
2/01/01 21:00 *	32.3	2/06/01 18:00	29.3
2/02/01 3:00	36.0	2/06/01 24:00	24.6
2/02/01 9:00	26.4	2/07/01 6:00	28.7
2/02/01 15:00	29.0	2/07/01 12:00	28.5
2/02/01 21:00	26.5	2/07/01 18:00	26.9
2/03/01 3:00	23.6	2/07/01 24:00	28.3
2/03/01 9:00	23.6	2/08/01 6:00	28.2
2/03/01 15:00	45.8	2/08/01 12:00	29.7
2/03/01 21:00	40.7	2/08/01 18:00	30.4
2/04/01 3:00	44.6	2/08/01 24:00	29.0
2/04/01 9:00	29.3	2/09/01 6:00	30.6
2/04/01 15:00	32.4	2/09/01 12:00	31.8
2/04/01 21:00	34.1	2/09/01 18:00	34.1
Nap	Nap	2/09/01 24:00	30.4

Nap – Not applicable; * average was assumed as no measured value for 2/01/01 21:00

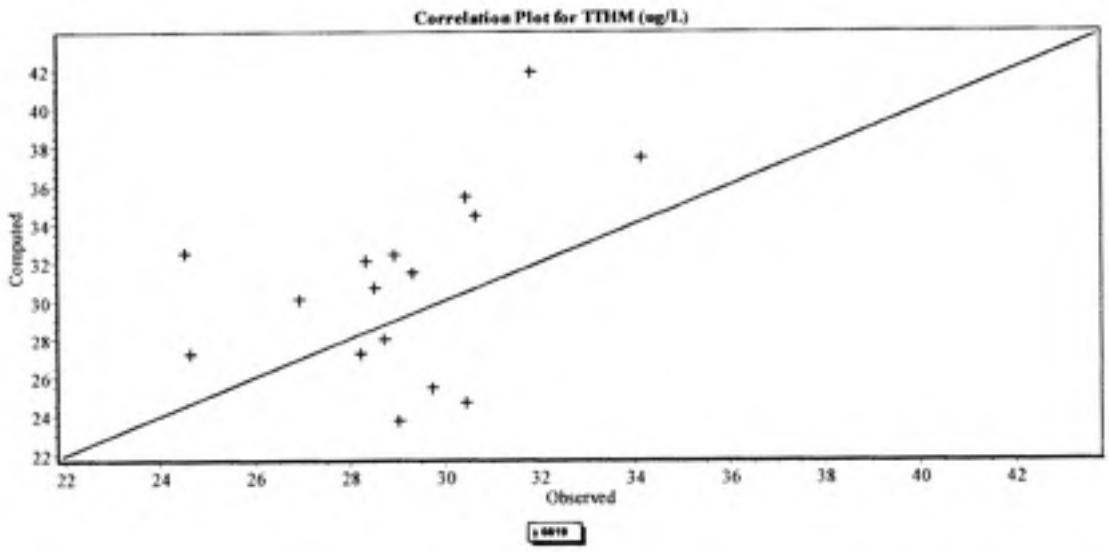


Figure 20: Comparison between the experimental (observed) and the model (computed) TTHM concentrations obtained in DSI for February 6 to 9 of 2001

The average of the experimental results considered (29.0 μg/L) was very close to the average of the computed results (30.1 μg/L).

- ***Distribution System Location II***

Figure 21 presents a comparison between the experimental (observed) and model (computed) results obtained when the model was run using the variable signal concentrations leaving the treatment plant (Table 14) in the second sampling event. An initial concentration of 22.6 μg/L was considered in DSII (node 6623 of the distribution system) and after the model was run, the results were compared with the fourteen experimental results obtained in DSII presented in Table 14.

Table 14: TTHM data used as input for simulations at DSII

WTP		DSII	
Sample ID	TTHM (µg/L)	Sample ID	TTHM (µg/L)
2/16/01 6:00	30.9	2/17/01 6:00	25.8
2/16/01 12:00	33.1	2/17/01 12:30	26.1
2/16/01 18:00	29.6	2/17/01 18:00	21.1
2/16/01 24:00	29.7	2/17/01 24:00	22.7
2/17/01 6:00	29.8	2/18/01 6:00	22.4
2/17/01 12:00	29.4	2/18/01 14:15	23.6
2/17/01 18:00	30.4	2/18/01 18:15	22.9
2/18/2001 0:00	24.8	2/19/01 00:00	20.3
2/18/2001 6:00	26.3	2/19/01 6:00	21.2
2/18/01 12:00	28.3	2/19/01 14:00	21.8
2/18/01 18:00	27.4	2/19/01 18:00	21.1
2/19/2001 0:00	23.3	2/19/01 24:00	22.6
2/19/2001 6:00	27.3	2/20/01 6:00	17.9
2/19/01 12:00	24.1	2/20/01 12:00	21.1

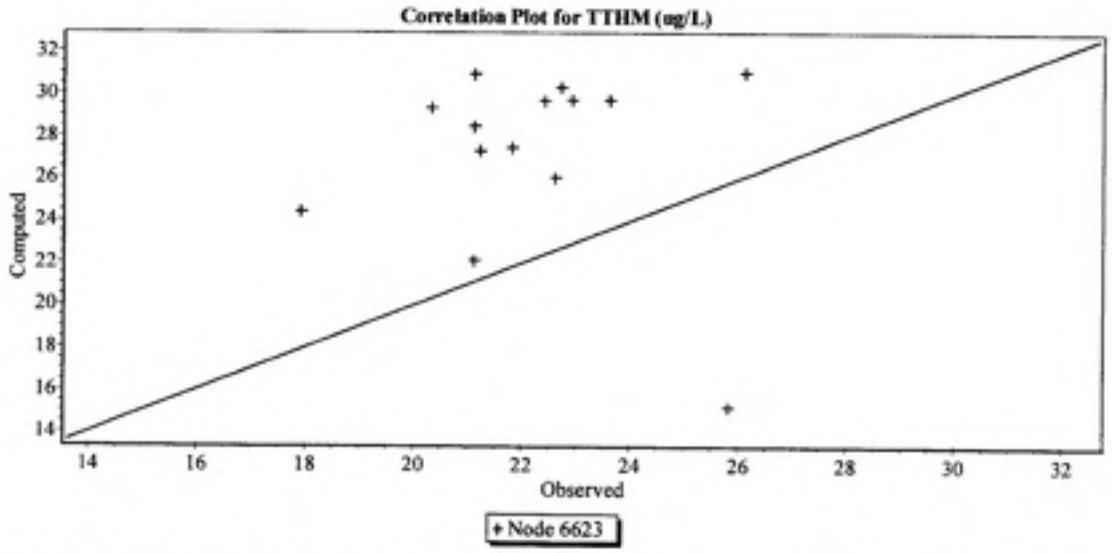


Figure 21: Comparison between the experimental (observed) and the model (computed) TTHM results obtained in DSII for February 17 to 20 of 2001

With the exception of the first experimental value (25.8 µg/L after 24h) the concentrations modeled overestimated the experimental results and the model agreement was poor. The average of the experimental results considered was 22.2 µg/L while the average of the computed results was 27.3 µg/L.

◆ *Distribution System Location III-A*

Figure 22 compares the experimental and model results obtained in DSIII-A when the model was run using the variable TTHM concentrations leaving the treatment plant (Table 15) in the third sampling event. An initial concentration of 101µg/L was considered in DSIII-A (node 3507 of the distribution system) and after the model was run the results were compared with the eight experimental results obtained at DSIII-A (Table 15).

Table 15: TTHM data used as input for simulations at DSIII-A

WTP		DSIII-A	
Sample ID	TTHM (µg/L)	Sample ID	TTHM (µg/L)
8/13/01 18:00	139	8/14/01 18:00	133
8/14/01 0:00	168	8/14/01 23:00	116
8/14/01 6:00	169	Nap	Nap
8/14/01 12:00	160	Nap	Nap
8/14/01 18:00	155	Nap	Nap
8/15/01 0:00	106	Nap	Nap
8/15/01 6:00 *	120	Nap	Nap
8/15/01 12:00	92.5	Nap	Nap
8/15/01 18:00 *	120	Nap	Nap
8/16/01 0:00	109	8/15/01 23:00	115
8/16/01 6:00	166	8/16/01 7:00	106
8/16/01 12:00	83.1	Nap	Nap
8/16/01 18:00	94.5	8/16/01 18:00	113
8/17/01 0:00	93.0	8/16/01 23:00	116
8/17/01 6:00	96.8	8/17/01 7:00	111
8/17/01 12:00	91.6	8/17/01 12:00	114
8/17/01 18:00	78.4	Nap	Nap

Nap – Not applicable; * average was assumed as no measured value for 8/15/01 at 6:00 and 18:00

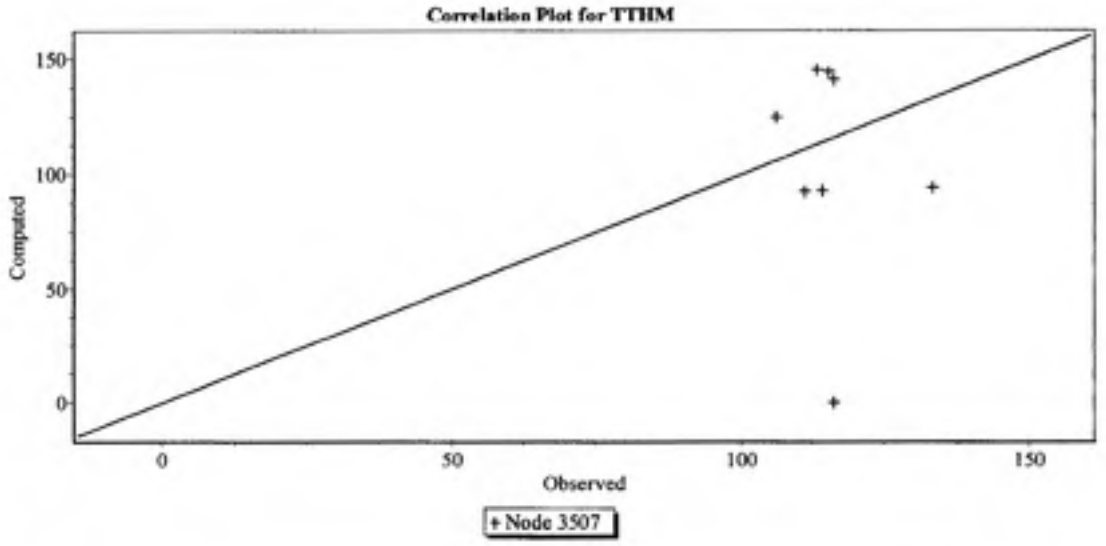


Figure 22: Comparison between the experimental (observed) and the model (computed) TTHM results obtained in DSIII-A for August 14 to 17 of 2001

The average of the experimental results considered (115.5μg/L) was 10% higher than the average of the computed results (104.7μg/L).

The cause of the apparent disagreement between the measured and predicted data in the three distribution system locations is that the model used for this system was only approximate and needs a proper hydraulic calibration.

IV.E. Weekly Exposure to DBP

As the spatial variations in DBP levels in the distribution system were found to be minimal provided there are no major changes in water quality or treatment operations at the plant, grab THM, HAA and TOX samples were taken each week from a representative point in the distribution system (DSIII-A) to provide a measure of exposure of consumers to DBPs in their tap water for that week.

The THM results obtained, presented in Figure 23, show an increase in the TTHM concentrations and variability in the summer months (especially in July and August) as compared to cooler months of April and May. The relative distribution of each of the individual THM species appears to vary in relation to the season. Chloroform contribution to the TTHM seems to increase in the summer months whereas the proportion of the other two detectable THM species (bromodichloromethane and dibromochloromethane) towards the TTHM concentrations seems to decrease (Figure 24).

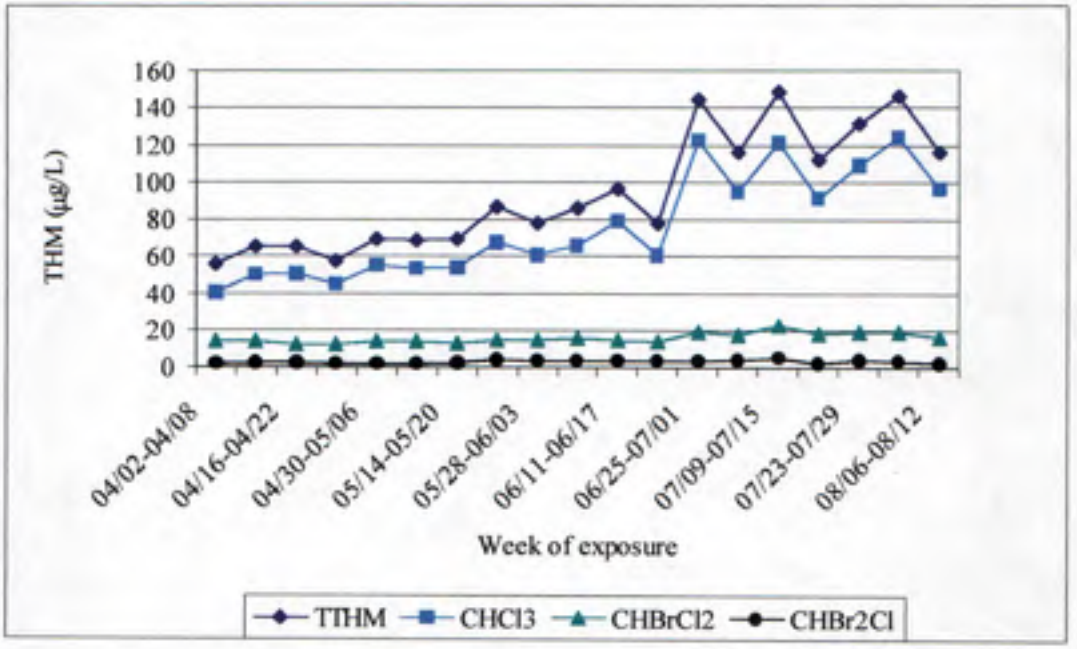


Figure 23: THM results of weekly samples collected at DSIII-A

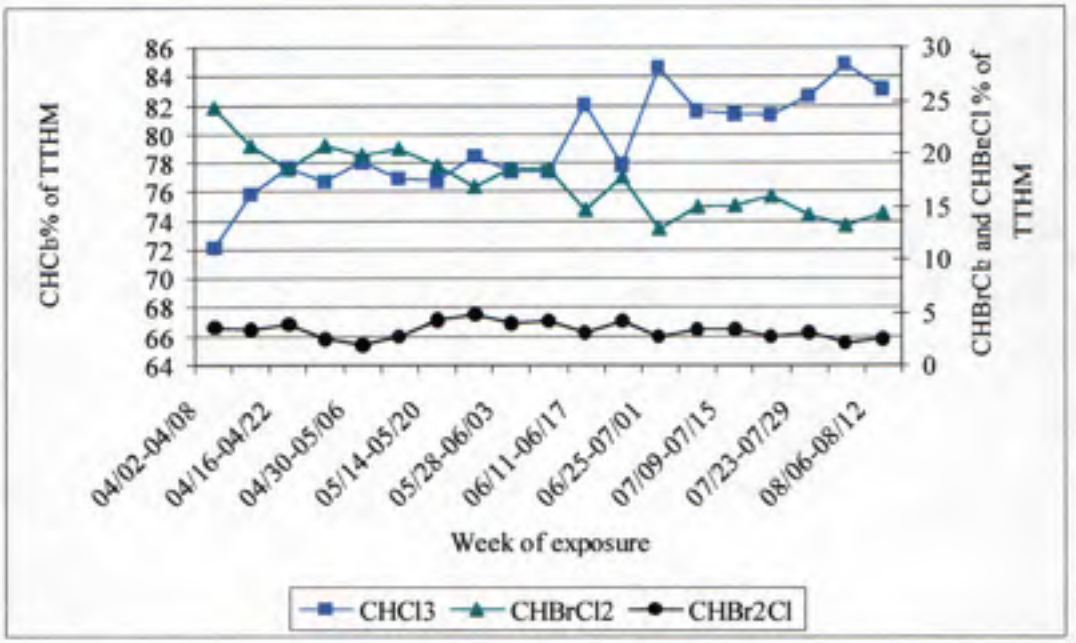


Figure 24: Relative proportion of individual THM species contribution to TTHM at DSIII-A

To determine whether the difference between the mean values obtained from April 6 to June 8 and June 13 to August 10 is significant, a t test was conducted assuming that the two groups have similar variance. The results obtained show that the means of the relative distribution of chloroform and bromodichloromethane obtained from April 6 to June 8 are significantly different than the means obtained from June 13 to August 10 at the 1% significance level. However, the mean of the relative distribution of dibromochloromethane obtained from April 6 to June 8 is not significantly different than the mean obtained from June 13 to August 10.

Figure 25 shows the comparative trends of THM, HAA and TOX during the same period.

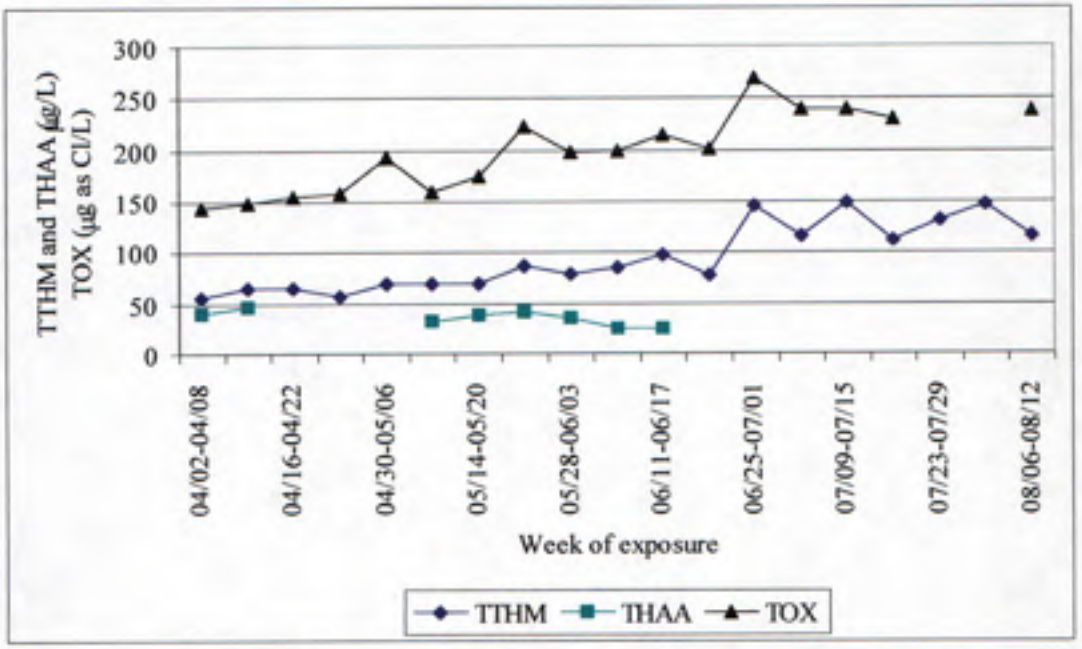


Figure 25: TTHM, THAA and TOX results of weekly samples collected in DSIII-A

Figure 26 shows that reasonable correlation can be detected in the TTHM and TOX results obtained from April 6 to August 10 of 2001 (r^2=0.8354), with the slope obtained significantly different from zero at the 1% level. However this result should be carefully interpreted as the two parameters used in the linear regression analysis have a common term (Singer and Chang, 1989).

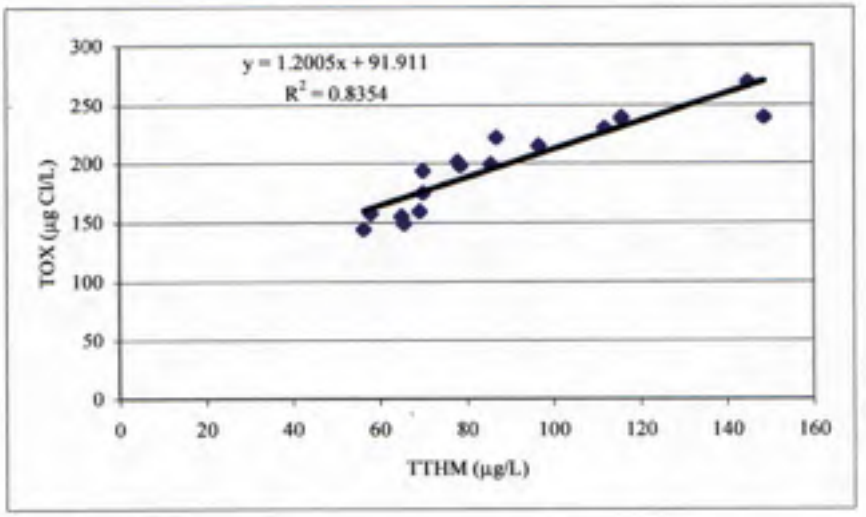


Figure 26: Correlation between the TOX and THM concentrations obtained weekly

The TTHM concentrations obtained in the sixteen weekly samples collected between the 6th of April and the 10th of August accounted for between 30 and 46 percent of the TOX.

The limited amount of HAA data is insufficient to permit extensive correlations with the other DBP parameters to be tested. The THAA concentrations obtained in the eight weekly samples collected between the 6th of April and the 13th of June accounted for between 6 to 16 percent of the TOX.

IV.F. DBP Exposure in a Free Chlorine System

During March of 2001 (March 1 to March 28), as the treatment plant used free chlorine instead of chloramination in the distribution system, samples were collected at the point of entry to the distribution system and at nine distribution system locations situated in the four pressure zones of the system each week (Figure 6).

Figure 27 presents the comparison between the TTHM and free chlorine residuals obtained each week.

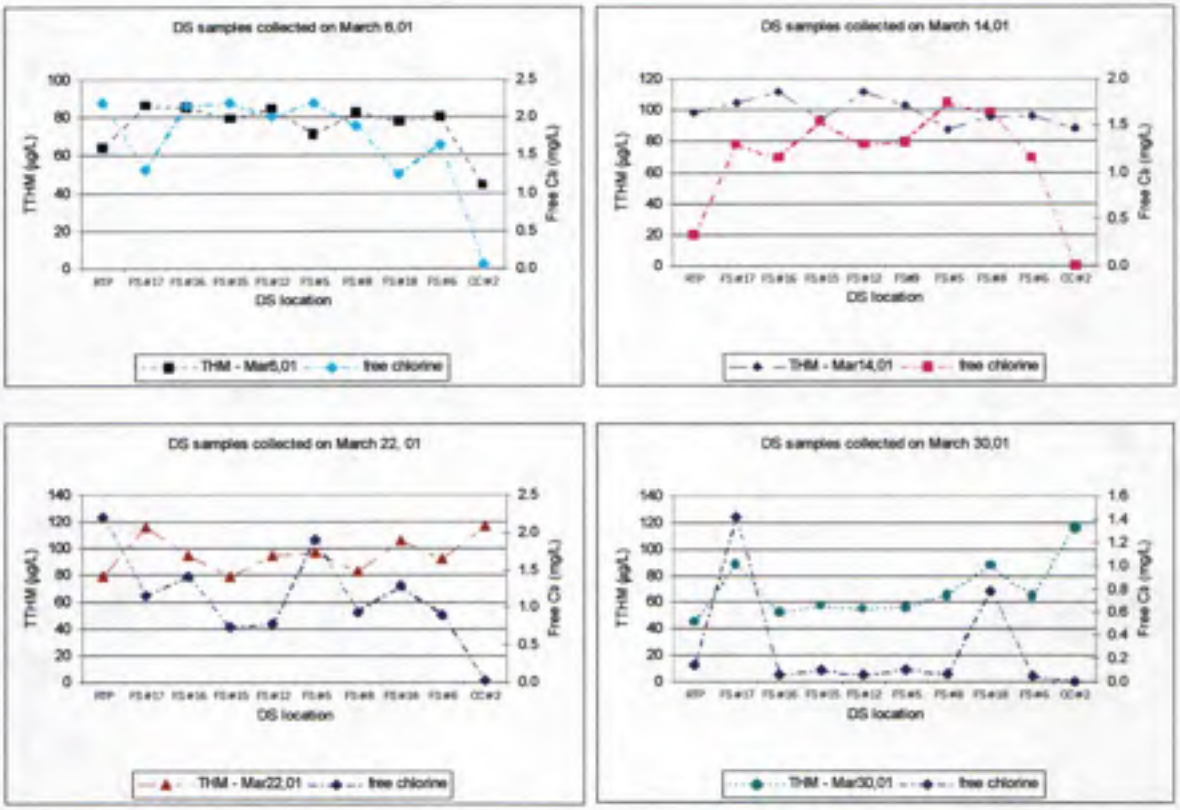


Figure 27: Comparison between the TTHM and free chlorine residuals results obtained in each week

On the last sampling event (Mar30, 01) the low free chlorine residuals obtained are indicative that the treatment plant had already converted back to using chloramination as final disinfectant (March 29, 01). The low values of free chlorine obtained throughout the four weeks in CC2 suggest the possibilities that during the four weeks the water samples collected were still of chloraminated water or that the free chlorine had reacted or dissipated. These hypotheses are corroborated by the very high residence times estimated to be associated with this location (>270h).

The free chlorine value obtained in the second week at the treatment plant is very low compared to what we would expect to obtain in chlorinated water and suggests perhaps a temporary low dosage or experimental error in the reported measurement. In the distributed chlorinated water, a decrease in the chlorine residual might reflect an increase in chlorine demand that in turn generated increased THM formation. This correlation could be observed in many of the locations during the first two weeks.

From the results presented in Figure 27, it seems that the low chlorine residuals obtained in the location CC2 are due to reaction or dissipation of chlorine since in the third and fourth week the free chlorine values are still low but the TTHM values are increasing probably as a result of the use of free chlorine as final disinfectant.

Table 16 presents the average TTHM and THAA results obtained in each location sampled during the four weeks.

Table 16: TTHM and THAA results during period of chlorination

		Mar6, 01		Mar14, 01		Mar22, 01		Mar30, 01	
DS Location	Rt (h)	TTHM (µg/L)	THAA (µg/L)	TTHM (µg/L)	THAA (µg/L)	TTHM (µg/L)	THAA (µg/L)	TTHM (µg/L)	THAA (µg/L)
RTP	0	63.5	32.1	97.9	45.0	79.0	49.6	44.7	38.8
FS # 17	11.4	85.7	53.1	105	40.2	116	72.3	88.4	66.2
FS # 16	11.8	85.4	38.0	111	51.0	94.7	59.7	52.4	50.0
FS # 15	14.2	78.9	37.6	93.8	40.4	79.0	45.8	56.7	50.6
FS # 12	19.1	84.2	41.7	111	46.3	94.1	60.1	54.5	44.8
FS#9	27.7	Nav	Nav	103	44.5	Nav	Nav	Nav	Nav
FS # 5	28.2	71.6	34.1	87.1	33.3	97.3	52.1	56.5	45.4
FS # 8	34.3	82.6	42.5	95.4	44.8	83.2	47.4	65.8	50.4
FS # 18	60.8	77.9	43.3	Nav	Nav	106	63.1	86.9	61.2
FS # 6	394	80.0	55.4	95.7	44.5	92.1	55.2	64.7	51.7
CC # 2	>270	43.8	37.7	88.2	47.8	116	70.4	117	60.0
Average		75.3	41.6	98.9	43.8	95.8	57.6	68.7	51.9
Stdev		13.0	7.6	8.6	4.9	13.8	9.2	22.1	8.4
CV(%)		17.3	18.3	8.7	11.1	14.3	16.0	32.2	16.1
Average w/out CC2		78.9	40.9	100	40.4	93.6	52.4	63.4	49.7
CV w/out CC2 (%)		9.2	18.9	8.2	11.4	13.3	15.2	23.8	16.3

Nav – Not Available

Even though much higher DBP levels were obtained during this month due to the chlorine addition, as opposed to the month before when chloramination was used (in February the average results obtained varied between 20 to 30µg/L), the spatial variation in the distribution system wasn't as variable as one would expect in a chlorinated system the exception being the variation obtained in CC2 where due to the high residence times the older water appeared to contain residual chloramine during the first two weeks of this survey.

Figure 28 presents the comparison between the TTHM and HAA results obtained in each week. The trends of TTHM and THAA levels seem to be highly correlated, throughout the system.

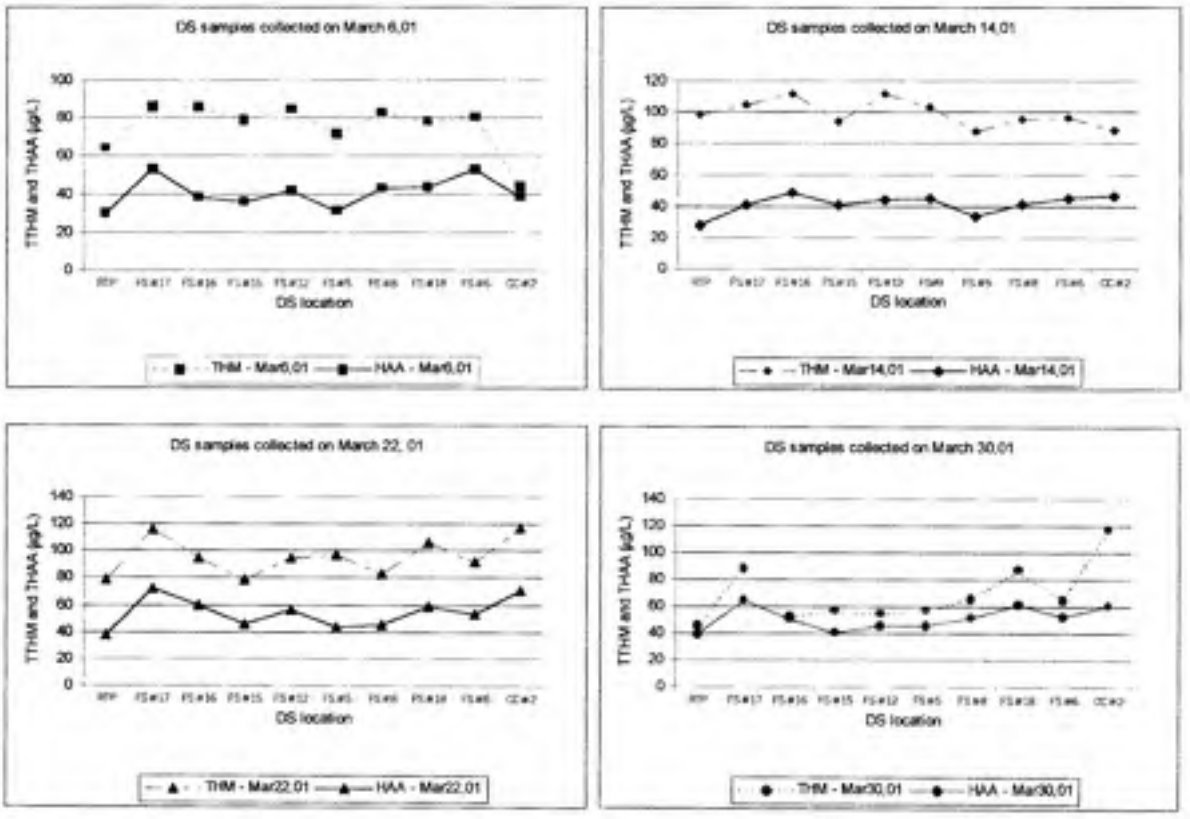


Figure 28: Comparison between the TTHM and THAA results obtained in each week

The lower differences obtained between the TTHM and THAA results in the final week when the system had returned to chloramination as reflected in the lower THM levels are indicative of the higher HAA formation kinetics of reaction as compared to THM. With the free chlorine carried through a part of the plant prior to the addition of ammonia the HAA formation mainly occurs primarily in the treatment plant whereas the slower rate of THM formation prevents its maximum formation potential being achieved prior to the addition of ammonia. As expected these lower differences are not obtained in fourth week at the point CC2 because the older water at this location would have been exposed to free chlorine.

Figure 29 presents the comparison between the TOX and the TTHM and THAA results obtained in each week.

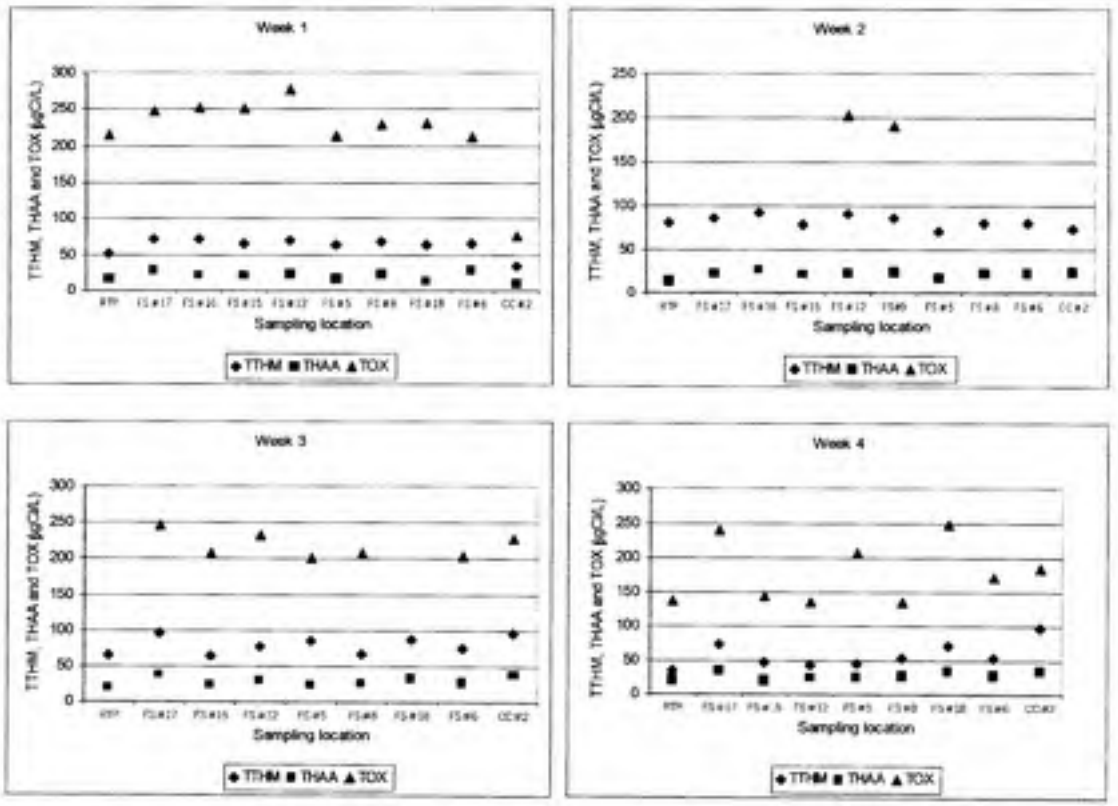


Figure 29: Comparison between the TOX and the TTHM and THAA results obtained in each week

Low coefficients of variation were obtained in the TOX samples in the first week if CC2 is not considered ($CV_{w/out\ CC2}$=9% while $CV_{w/CC2}$= 25%), in the second week where just two samples were analyzed due to experimental errors (CV=4%), and in the third week ($CV_{w/out\ CC2}$=8% and $CV_{w/CC2}$= 8%). In the fourth week there was variation in the results obtained ($CV_{w/out\ CC2}$=27% and $CV_{w/CC2}$= 25%). Higher coefficients of variation were also found in the fourth week in the THM and HAA samples when some points may have still be in contact with a free chlorine residual while others were chloraminated.

The trends of TOX also seem to be correlated with the TTHM and THAA levels, throughout the system.

A two-way analysis of variance was used to test at the 0.05 level of significance whether the differences among the TTHM levels obtained for the different sample locations are significant, and also whether the differences among the TTHM levels in the different weeks are significant. The results show that the differences among the TTHM levels obtained for the different sample locations are not significant, whereas the differences among the TTHM levels in the different weeks are significant at the 0.05 significance level.

Table F13 in Appendix F presents the location, date, and time of sample collection and free chlorine measurements made immediately after sample collection using a Hach colorimeter kit.

Tables F14 and F15 in Appendix F present the concentrations obtained for the THM and HAA samples, respectively, during the period of chlorination.

The TOX results, the unknown organic halide (OX) content calculated based on the TOX, THM and HAA concentrations obtained and the percentage of unknown halide are presented on Table F16 in Appendix F.

IV.F.I. Comparison of DBP Formation in a Chlorinated and Chloraminated System

The average of the TTHM, THAA and TOX results obtained in the third and fourth week of this study (conducted in March of 2001) at six locations (WTP, FS17, FS16, FS15, FS12 and FS5) were used to compare the relative contributions of TTHM and THAA to TOX (presented as chloride) in the chlorinated system with the chloraminated system. These results are presented in Figure 30 and Table F17 of Appendix F. The other locations sampled during these weeks were not used in this comparison as in the fourth week, even though the THM levels decrease, due to their higher estimated retention times they could still be subject to chlorinated water.

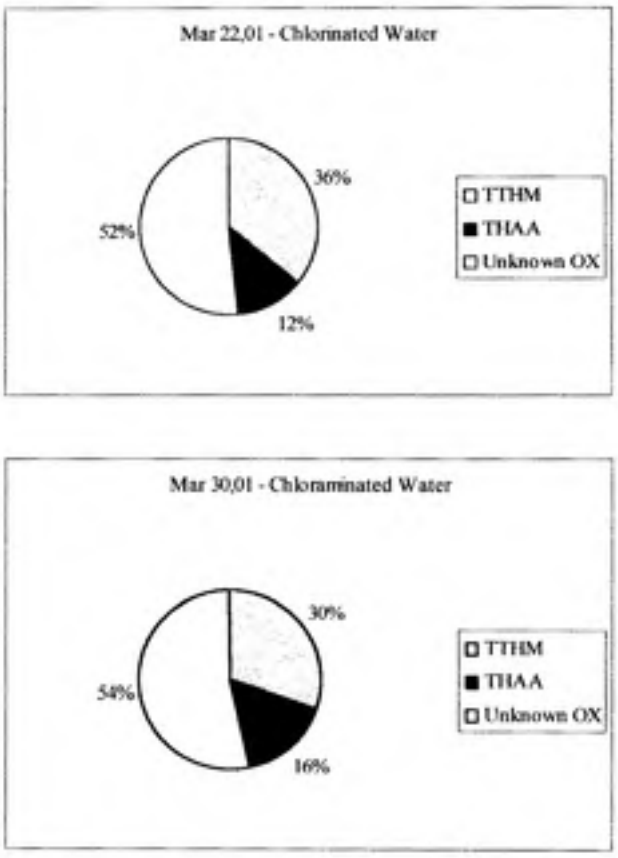


Figure 30: Comparison between the TTHM, THAA and unknown OX levels in chlorinated and chloraminated waters

Although the levels of TTHM and TOX are lower in the chloraminated system, Figure 30 shows that the relative proportions of TTHM, THAA, and OX in terms of chlorine do not seem to be significantly different in this particular sampling event.

Figure 31 compares the TTHM and THAA levels in the point of entry to the distribution system when chlorine and chloramines are used to as final disinfectant.

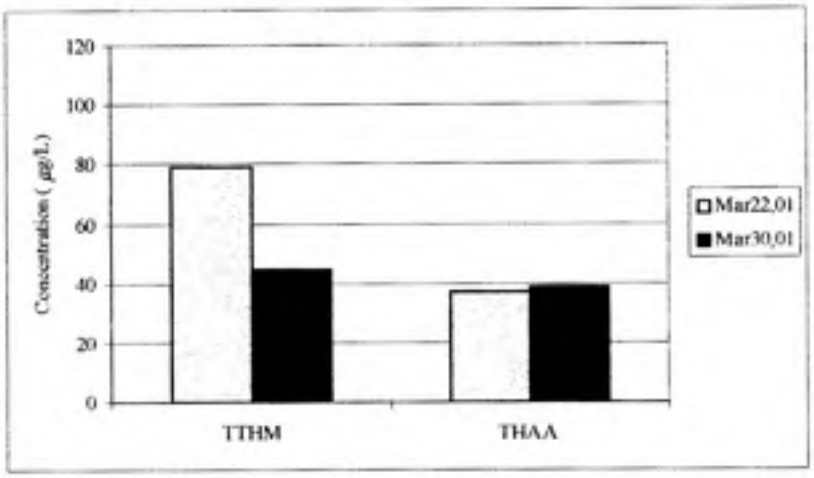


Figure 31: Comparison between the TTHM and THAA levels in the point of entry to the distribution system when chlorine (Mar 22, 01) and chloramines (Mar 30, 01) are used to as final disinfectant

The results show that the HAA formation under chlorination is similar to the HAA formation under chloramination whereas the THM formation under chlorination is much higher than under chloramination. These results might be explained because the HAA formation occurs mainly at the treatment plant due to their faster kinetics, whereas THM form both in the treatment plant and distribution system.

IV.G. ANALYSIS OF POSSIBLE CONFOUNDING FACTORS IN EXPOSURE CHARACTERIZATION

IV.G.1. Effect of Time of Sample Collection

Samples were collected in a chlorinated system early in the morning (at 6h; sample ID: D) and in the evening (18h; sample ID: A). The comparison between the results obtained (presented in Table F18 of Appendix F) showed that the early morning samples had approximately 20% higher THM levels than samples taken in the evening.

IV.G.2. Effect of Boiling or Refrigerating Water

In the same experiment (presented in Table F18 of Appendix F) water samples were also collected in order to understand the effect of boiling (B) and refrigerating water (C). Boiling water was found to remove approximately 97% of the TTHMs concentrations whereas refrigerating water (at approximately 4°C) in an open container will have a low effect in the TTHMs removal of approximately 8%.

IV.G.3. Effect of Using a Point of Use Filter

A filter study conducted showed that different THM and HAA removals can be expected depending on the filter characteristics and the age of the filter. Table 17 show the efficiency of THM and HAA removals obtained with five different filters, four used activated carbon (Brita Ultra Model FF-100, 1999; PUR Ultimate, 1999; Teledyne Water Pik, 1997; and Brita Pitcher 1998), while the fifth employed reverse osmosis at a local grocery. T1 corresponds to sample collections when the filter was installed while T2 corresponds to sample collections after more than half of the filter capacity was used (approximately 60 gal).

The THM and HAA levels measured in this experiment using filters installed in three different locations are presented in Tables F19 and F20 of Appendix F.

Table 17: Efficiency of TTHM and THAA removal by point of use filters

	TTHM		THAA	
	T1	T2	T1	T2
Brita Ultra	100%	75%	94%	51%
PUR Ultimate	100%	100%	100%	88%
Teledyne Water Pik	99%	Nav	78%	78%
Brita Pitcher	93%	Nav	68%	Nav
Reverse Osmosis	Nav	48%	Nav	100%

Nav – Not available; T1 sample collection when the filter was installed; T2 - sample collection after more than half of the filter capacity was used

From these preliminary results it can be observed that the levels of THMs and HAAs in filtered water differ significantly from the source tap water. In order to assign accurate DBP exposure data to consumers, it is therefore essential to determine if a significant amount of drinking water consumption originates from this type of point of use treatment.

V. CONCLUSIONS

This study involved an intensive evaluation of the DBP concentrations in the finished water and distribution system of a water treatment plant using chloramination for final disinfection. Due to the challenges associated with the capture of temporal and spatial variability of DBP levels that consumers are exposed to, the development of this type of study is essential for the accomplishment of an accurate exposure characterization in drinking water.

With the objective of simplifying the sampling procedure to assess DBP levels resulting from temporal variability in the chloraminated drinking water, a time-saving and efficient compositing technique was developed. Good recoveries were obtained with this technique for THM (91 to 99% recovery obtained in twelve samples composited), HAA (90 to 92% recovery obtained in twelve samples composited) and TOX (130% recovery obtained in five samples composited).

The effects of chloramination on THM and HAA levels were studied to validate the hypothesis that provided no major changes occurred in the water treatment plant operations and source water quality, the levels of THMs and HAAs would remain fairly constant in the distribution system. The results obtained after submitting chloraminated water to laboratory conditions simulating the distribution system corroborated the hypothesis that a chloramine residual does not change the THM and HAA concentrations or speciation, at least under controlled conditions. Furthermore, analysis of the total THM data generated by the treatment plant during the year 2000 for the point of entry to the distribution system and six distribution system locations confirmed the conclusions drawn from the controlled experiments. Hence, even though the levels of total THMs varied with time of year, the measured values on any sampling date tended to be reasonably constant throughout the distribution system during a single sampling period.

These results suggested that the level of DBPs consumed from any point in the distribution system might be obtained from analysis of a single point in the system, assuming no major fluctuations in the levels of DBPs entering the system occurred. In order to verify this hypothesis an intensive sampling program was carried out on five consecutive days at 4-hour intervals at the treatment plant in order to assess the variability of the DBPs entering the distribution system. From the coefficients of variation obtained (35% for the THM samples, and 37% for the HAA and TOX samples), it is apparent that a single grab sample at the point of entry to the system would not be representative of the concentrations in the system to which consumers are exposed. This finding cautions the use of point of entry samples to characterize exposure even though such values were often used in past epidemiological studies conducted to characterize exposure. The underlying causes of the fluctuations appear to be related to plant operations.

In order to determine if the variation in the DBP levels leaving the plant would also occur in the distribution system, three different experiments were conducted in which sampling was performed at the point of entry to the distribution system and in different locations within the distribution system. The results suggest that sampling at a point in the distribution system would be a more accurate way of characterizing DBP exposure than sampling at the point of entry to the system. Similarly, collection of a weekly grab sample in the distribution system could be an accurate way of characterizing exposure providing that no major changes in water quality or treatment operations occur in the treatment plant. The analysis of these weekly grab samples showed an increase in the TTHM concentrations and variability in the summer months (of July and August with an average value of 128μg/L and a coefficient of variation of 16%) as compared to cooler months of April and May (with an average value of 68.8μg/L and a coefficient of variation of 10%). This is also reflected by similar trends in TOX. These seasonal differences need to be considered in the exposure characterization as, for example, two neighbor subjects enrolled in a study in different seasons, will have very different levels of exposure to disinfection-by-products.

The relative distribution of chloroform and bromodichloromethane appears to vary in relation to the season; as chloroform contribution to the TTHM seems to increase in the summer months while bromodichloromethane contribution towards the TTHM concentrations seems to decrease. In the study of DBP correlations with spontaneous abortion for which this research was developed, such seasonal variation would be significant when considering the short period of exposure (approximately 20 weeks) for which the correlation would be relevant.

During one month per year when the treatment plant disinfects the water using free chlorine instead of chloramination, the DBP levels were monitored rigorously since they were expected to be higher and vary in the distribution system. Even though higher DBP concentrations were obtained during this time, the spatial variation in the distribution system wasn't as variable as one might otherwise expect in a chlorinated system. The exceptions are those locations with high residence times where an older chloramines residual would still be carried during the early weeks of chlorination and vice versa at the end of the month. The trends of TTHM, THAA and TOX seemed to correlate throughout the system.

The comparison between the use of chlorine and chloramines as final disinfectant shows that in chloraminated water, lower differences between the TTHM and THAA concentrations can be expected. In spite of the difference in DBP levels between the chlorinated and chloraminated system, the amount of unidentified organic halogen (OX) remains similar (approximately 50%).

The use of ArcView to visualize geographically the information of the system studied was very useful, simplifying the decision process.

The use of EPANET for the simulation of the DBP variation in the distribution system studied showed disagreement between the measured and predicted data in the three distribution system locations modeled probably because the network model used is highly skeletonized and is not properly hydraulically calibrated.

Finally, when studies of exposure characterization are conducted it is important to consider certain confounding factors, such as time of sample collection, whether water is cold or boiled, and filter use, all of which will affect the DBP levels in the water. Some cursory examination of these factors revealed a significant diversion from the DBP levels measured in cold tap water. Each of these should therefore be examined in more detail in future studies.

In summary, this study successfully demonstrated the ability to obtain accurate DBP exposure to consumers of chloraminated drinking water by collecting and measuring DBPs in a single week grab sample from a representative point in the distribution system.

The results of this study will thus serve the epidemiological community in the future human exposure studies related to drinking water quality.

VI. RECOMMENDATIONS FOR EXPOSURE ASSESSMENT STUDIES

The suggestions described in this chapter should be considered in future studies involving drinking water exposure characterization.

Conduct studies to capture the variability in water quality at the point of entry to the distribution system as well as in different locations in the distribution system. When the exposure to DBPs is being characterized, the study of systems using chloramination as final disinfectant will probably simplify the sampling strategy and exposure characterization due to a lower temporal and spatial variability expected throughout the system.

A questionnaire is usually given to the subjects enrolled in these studies. Include in the questionnaire a section of water consumption where all the possible confounding factors (such as the amount of water consumed, time of consumption, use of filters, boiling or refrigerating water before use) are considered.

In order to fully characterize exposure to DBPs, exposure by other routes should also be considered such as inhalation and dermal absorption caused for example by bathing and washing dishes and clothes.

If available, use the tracer studies conducted in the system to understand it better and locate any locations where the water quality might be poorer and variable.

Use geographic information systems to locate the subjects enrolled in the system and the sampling locations used, in order to better characterize their exposure when there is variability in the distribution system water quality.

Work in close contact with the water treatment plant utility personnel so that if major changes in treatment occur or any problems that might influence the DBP concentrations in the water surface, they are communicated fast enough to allow the capture of these variations in the distribution system through additional sampling.

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Appendix A – THM Standard Operation Procedure

A.1. Material and Reagents

The following materials and reagents are needed to perform the THM analysis:

- Gas Chromatograph (HP 5890 series) equipped with a HP7673 series injector and auto sampler, a capillary column (DB-1) and electron capture detector (μECD);
- Gas cylinders (one with helium (carrier gas) and another with nitrogen (make-up detector gas), both UHP 99.999% pure);
- Vortex mixer;
- Dispenser bottle (capacity: 1L);
- Spatulas;
- Glass vials with screw-top caps and PFTE-lined septa (capacity: 40mL);
- Volumetric flasks (capacity: 100mL) with glass stoppers;
- Measuring cylinder (capacity: 25mL);
- Micropipettes (adjustable volume: 10.0-60.0μL and 50.0-250.0μL);
- Glass capillaries for above micropipettes;
- Pasteur pipettes;
- Glass beaker;
- Autosampler vials with crimp caps and Teflon septa (capacity: 2mL);
- Crimper;

- Laboratory grade water (Dracor high purity water system);
- Tap water samples;
- THM standard mix (Supelco – catalog number 48140-U; concentration: 2000µg/L; 1mL);
- Pentane for THM analysis (Burdick & Jackson – High Purity Solvent ; 1 Liter);
- Methanol THM grade (Sigma-Aldrich; 235mL);
- THM internal standard: 1,2-dibromopropane (Ultra Scientific– catalog number RHH-050; 1g; 97% purity);
- Sodium sulfate (Na_2SO_4; Mallinckrodt Analytical Reagent; granular; 2.5Kg).

All the glassware used was acid washed in order to keep it free of any potential contamination. This procedure includes washing the glassware with Alconox powder detergent, rinsing it with tap water and deionized, organic-free reagent water and then soak in a 10% ACS-Grade HNO_3 bath overnight. Rinse thoroughly with tap water and then at least three times with deionized, organic-free reagent water. Rinse glassware three times with methanol and dry it in an 180°C oven for at least 24 hours. For the caps and septa, set the oven temperature at 80°C. The volumetric glassware should ***not*** be placed in the oven but be left inverted in the hood to dry.

A.2. Sample collection

The sample bottles should contain sodium sulfite (Mallinckrodt Analytical Reagent; granular; 500g; add 1mg to the 40mL THM vials) as dechlorination agent.

Do not rinse sample bottles before collection and do not overfill the sample bottles.

Label the vials and the bags with the date and time of collection.

Collect the samples with the vial held at an angle and let the water run slowly down the side of the sample vial to prevent the sample aeration. Fill the sample to the rim then cap the bottle with the shiny, teflon-faced side of the septum towards the water. Invert the vial 3 times to mix the water with the dechlorination agents. If an air bubble is present remove the cap after mixing and add a few drops more of sample and recap the vial. Repeat this procedure until there are no air bubbles present in the sample.

After collection keep the vials in a refrigerator at 4°C up to a maximum holding time of 14 days.

A.3. Method

A.3.1. Solvent Analysis

Use pentane as extracting solvent. It is hydrophobic and liophilic and therefore the addition of this solvent to water will generate two layers with the organic compounds migrating to the solvent according to their partition coefficients. Using the octanol-water partition coefficient as a surrogate for organic phase-water partition behavior of the analytes we can conclude that they are very soluble in the organic layer due to their high partition coefficients (P_{CHCl_3}=93.3molL^{-1}octanol/(molL^{-1}water); P_{CHBrCl_2}=100molL^{-1} octanol/(molL^{-1}water); P_{CHBr_2Cl}=144.5molL^{-1}octanol/(molL^{-1}water); P_{CHBr_3}=251.2molL^{-1} octanol/(molL^{-1}water)) (http\\www.chemfinder.com).

This analysis of the solvent blank should be performed prior to extraction to ensure that the solvent used and the instrument are free from contamination. If the instrument is contaminated, the temperature of the column should be increased to 250°C during approximately 20min.

The internal standard (IS) 1,2-dibromopropane should be used in order to perform an internal standard calibration due to the assumption that this chemical is unlikely to be found in any sample analyzed with the gas chromatographic method employed, thus not interfering with the separation of the individual target THM species.

The IS addition to the solvent should provide a concentration of approximately 50μg/L in the total volume needed for adding 4mL of this extracting solvent to each sample.

Before adding the solvent with IS to the samples this mixture should also be analyzed by gas chromatography.

A.3.2. Liquid- Liquid Extraction

The trihalomethane calibration standard mixture with 2000μg/L of each of the four THM species should be used to prepare primary (100 μg/L) and secondary (10 μg/L) dilutions.

Different volumes of these dilutions should then be added to 100mL of laboratory grade water (LGW) in order to prepare a calibration curve for each of the analytes with concentrations that would allow their determination. Different concentration ranges should be used according to the sample location and the season as in the colder months of the year we can expect the THMs concentrations to be lower.

When preparing the calibration curve dilutions, each volumetric flask should filled to the neck with LGW and the volumes of standard solutions needed to prepare the different concentrations should be added below the LGW surface to minimize evaporation. The volumetric flask should then be filled to the mark with LGW. This step should be performed rapidly to minimize evaporation that would result in the loss of the analytes and with extreme precision in order to generate accurate calibration curves.

Use a measuring cylinder to transfer 20mL of sample to the 40mL vial where the sample is initially kept. The cylinder measurements of the calibration curve samples should be performed from the lowest (LGW with 0μg/L) to the highest concentration to minimize errors due to contamination from one sample to the next in the calibration curve. Before each measurement the cylinder should be rinsed with LGW and then with sample. A second cylinder should be used for the sample measurements.

Add 4mL of pentane containing internal standard and placed in a dispenser bottle to 20mL of sample making sure that no gas bubbles are present in the dispenser tube.

The addition of a salt (6g of Na_2SO_4) is used in order to increase the rate of THM transfer to the solvent by increasing the ionic strength of water. The salt must be completely dissolved and, therefore, immediately after the addition the vials must be shaken vigorously and then mixed for one minute using the vortex mixer. The upper layer (1mL) is then transferred to the autosampler vial using a Pasteur pipette taking care to prevent water and any non-dissolved Na_2SO_4 particles being transferred. A new pipette should be used for each sample and the autosampler vials rinsed with sample before being filled to half of its capacity. The autosampler vials are then placed on a gas chromatograph for analysis of samples. In case the immediate GC analysis is not possible the extracts should be kept in the freezer and analyzed as soon as possible.

The GC should be programmed in order to follow the steps described below. Before injecting the sample the 10μL GC syringe should be rinsed three times with solvent in order to clean the syringe and ensure that no air bubbles are present and then be rinsed three times with sample before pulling up the sample for injection.

2μL of the liquid sample should be injected rapidly through a septum into the injection port set to a temperature of 150°C. As this temperature is higher than the boiling point of the least volatile component of the sample it promotes an instantaneous volatilization of the sample.

The injection port is set to a splitless mode in order for the all the sample to be injected. As the major part of the sample is solvent, comprising only about 1% of the target analytes, a septum purge line allows a large portion of this solvent to be purged away (half a minute after the injection; with a flow of 66.4mL/min) to a carbon column, after the all the target analytes have moved onto the chromatographic column transported by the carrier gas.

The inert carrier gas (helium UHP, 99.999% pure) flows through a mid-polarity capillary column (DB-1), 30m long with an internal diameter of 250μm, and a film thickness of 0.1μm which is used to separate the target analytes. The small diameter leads to a slow flow rate of 1.1mL/min.

The column is housed in an oven where the temperature can be programmed to accomplish the best resolution of the analytes of interest. The analytes with the higher boiling points spend more time in the stationary phase and elute at larger retention times than their lower boiling point counterparts. The starting temperature (35°C) is equal to the temperature of the lower boiling point component (pentane). After ten minutes, the temperature starts to increase at a rate of 5°C/min until it reaches a temperature of 50°C which is held for 1minute. Then the temperature is increased to 250°C at a rate of 10°C/min which is maintained for 5 minutes. The four analytes resolve well from each other using this combination of parameters due to their distinctly different boiling points (Tb_{CHCl_3} =61.1°C; Tb_{CHBrCl_2} =90°C; Tb_{CHBr_2Cl} =120°C; Tb_{CHBr_3} =149.1°C) (source:http\\www.chemfinder.com).

The different analytes can then be automatically detected as they emerge from the column by an electron capture detector. To prevent sample condensation in the detector, its temperature must be increased to 300°C.

However, at this high temperature the viscosity of the gas will also increase and therefore a make up gas to the detector is provided to maintain a high gas velocity. The makeup gas used can be nitrogen and the combined flow achieved is 60mL/min.

A.3.3. Data Analysis

The internal standard (IS) peak can be easily identified using the calibration curve points due to the relatively constant values of height and area associated with this peak independently of the sample concentration increase that will be obtained in the calibration curve. Its retention time is also identified by comparing the pentane chromatogram with the pentane plus IS chromatogram.

The detector response for each of the four THM species will increase in the calibration chromatograms as the concentration increases. Their identification is done based on their boiling points: (Tb_{CHCl_3} =61.1°C; Tb_{CHBrCl_2} =90°C; Tb_{CHBr_2Cl} =120°C; Tb_{CHBr_3} =149.1°C) and therefore they will elute in the following order: chloroform, bromodichloromethane, chlorodibromomethane and bromoform.

Based on their molecular weights (Mr_{CHCl_3}=119.4; Mr_{CHBrCl_2}=163.8; Mr_{CHBr_2Cl}=208.3; Mr_{CHBr_3}=252.7) their elution order is the same if we consider that the heavier compounds will take more time to leave the column.

The retention time and area information from the chromatograms can be used to calculate the retention times and areas of the four components relative to the retention time and area of internal standard (relative retention time and relative peak area). The mean ($\bar{x}$), absolute standard deviation (std) and coefficient of variation (CV) of the collective internal standard responses should also be calculated using the following equations:

$$\bar{x} = \frac{\sum_{i=1}^{N} xi}{N} \qquad [A.1]$$

$$std = \sqrt{\frac{\sum_{i=1}^{N} \left(xi - \bar{x}\right)^2}{N - 1}} \qquad [A.2]$$

$$CV = \frac{std}{\bar{x}} \times 100 \qquad [A.3]$$

IS responses contributing to a collective CV higher than 10% should be removed from consideration and the chromatogram flagged for quality control failure.

To ensure the validity of the data obtained a calibration check should be performed every 10 samples by running again a point of the calibration curve and samples spiked with known THM concentrations should be analyzed and compared to the non-spiked samples.

Appendix B – HAA Standard Operation Procedure

Source: Brophy, 1999

1. Apparatus:

a) Sample containers and extraction vials: 40-mL screw-cap vials with TFE-lined silicone septa. Clean vials by washing with Alconox powder detergent, then soaking in a 10% ACS-Grade HNO_3 bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with deionized, organic-free reagent water. Dry glassware in a 180°C oven for at least 24 hours. Repeat same procedure for caps and septa. For the caps and septa, set the oven temperature at 80°C.

b) Microsyringes: 5, 10, 25 µL.

c) Micropipettors: 10-60 µL, 50-250 µL.

d) Syringe: 5-mL glass, gastight syringe with 18 gauge stainless steel needle.

e) Volumetric flasks: 2, 5, 10, 100 mL. Clean flasks by washing with detergent, then soaking in a 10% HNO_3 bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with deionized, organic-free reagent water. Finally, rinse three times with HPLC-Grade methanol, then invert to air-dry on dioxin-free paper in a ventilation hood.

f) Vortex Mixer: Thermolyne Type 16700 Mixer-MaxiMix I, or equivalent.

g) Standard Storage Vials: 5-mL, amber glass with TFE-faced silicone septa. See part *1a* for cleaning procedures.

h) Transfer pipets: 14.6- and 23-cm disposable glass pasteur pipettes.

i) Gas Chromatograph: HP-5890 Series II

1) Column: Type: DB1 fused silica capillary (J&W Scientific, Folsom, CA).
Length: 30 m.
Internal Diameter: 0.25 mm.
Film Thickness: 1 µm.

2) Temperature Program: Initial Temp: 37°C. Hold for 21 minutes.
Ramp to 136°C at 5°C/min. Hold for 3 minutes.
Ramp to 250°C at 20°C/min. Hold for 3 minutes.
Run-Time: 52.5 minutes.

3) Injector: Injection Volume: 2 µL.
Temperature: 180°C.
Split Valve opened at 0.5 min.

4) Detector: Type: Electron Capture.
Temperature: 280-300°C.

5) Carrier Gas: Helium (99.999+% purity).
Flow Rate: 1-1.5 mL/min at 37°C.

6) Make-Up Gas: Nitrogen (99.999+% purity).
Flow Rate: 40-60 mL/min.

j) Salt scoop, small glass funnel, and 15 mL beaker: Stainless steel spatula for scooping sodium sulfate; funnel and beaker for measurement and transfer of salt.

k) Pipeting Dispensers: Adjustable 5- and 2-mL sizes with TFE transfer lines that can be mounted onto suppliers' reagent bottles. These are to be used for dispensing MtBE and H_2SO_4, respectively.

l) Diazomethane Generator: Use millimole-size generator with "o"-ring joint (Aldrich or equivalent). See part *1a* for initial cleaning procedures. Immediately after use, soak entire apparatus in 5N NaOH for at least 30 minutes, to quench any unreacted Diazald. Rinse thoroughly with tap water, then soak in 10% HNO_3 bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with deionized, organic-free reagent water. Dry glassware in a 180°C oven for at least 24 hours.

m) Volumetric and graduated pipettes: Two 1-mL volumetric pipettes, and one 5-mL graduated pipette. See part *1e* for cleaning procedures.

n) Graduated cylinder: 25-mL. See part *1e* for cleaning procedure.

o) Teflon tape: 1/2- and 1-inch.

2. Reagents

a) Extraction solvent: 99+% MtBE. Ultra-Resi Analyzed (Baker) or equivalent.

b) Sodium sulfate: Granular, ACS grade. Heat at 400°C overnight in a shallow, porcelain dish covered with aluminum foil. Store in a glass-stoppered bottle.

c) Methanol (for rinsing glassware): HPLC grade or equivalent.

d) Reagents for diazomethane generation:

1) Sodium hydroxide bath, 5N: Dissolve 200g of ACS low-carbonate grade pellets in 1 L tap water.

2) Di(ethylene glycol) ethyl ether (Carbitol)-Aldrich

3) N-methyl-n-nitroso-p-toluene sulfonamide (Diazald)-Aldrich

4) Potassium hydroxide, KOH: 45% (w/w) solution-Aldrich

e) Silicic acid: n-Hydrate powder.-Baker

f) Sulfuric acid, H_2SO_4: Concentrated, ACS grade.

g) Drying agent: 99+% purity magnesium sulfate, $MgSO_4$. Anhydrous powder.-Aldrich

h) Haloacetic acid standard stock solutions (Supelco): ClAA, BrAA, Cl_2AA, Cl_3AA, BrClAA, and Br_2AA were purchased in a multicomponent stock solution with a concentration of 2 mg/mL of each component in MtBE. $BrCl_2AA$, $ClBr_2AA$, and Br_3AA were purchased as neat standards, from which stock solutions were prepared in MtBE. Stock solutions can be stored in the freezer in amber vials, sealed with teflon tape, for up to 3 months.

i) Multicomponent, haloacetic acid additive solutions: Prepare a primary and a secondary dilution from the haloacetic acid stock solutions. When preparing these dilutions, choose concentrations which will allow 20-50 µL or less of each stock solution to be added to 100 mL of reagent water when preparing the calibration standards. Additive solutions should be prepared on the day of analysis.

j) Haloester standard stock solutions (Supelco): ClAA, BrAA, Cl_2AA, Cl_3AA, BrClAA, and Br_2AA methyl esters were purchased in a multicomponent stock solution with a concentration of 1 mg/mL of each component in MtBE. $BrCl_2AA$, $ClBr_2AA$, and Br_3AA methyl esters were purchased as neat standards, from which stock solutions were prepared in MtBE. Stock solutions can be stored in the freezer in amber vials from 1g, sealed with teflon tape, for up to 3 months.

k) Multicomponent, haloester additive solution: Prepare a primary dilution using the methyl esters stock solutions. This solution will be used to prepare one sample containing ester standards, to be run on the gas chromatograph along with samples.

l) Internal standard (Aldrich): 1,2,3-trichloropropane , 99+% purity.

m) Internal standard stock solution: Weigh 25 mg of standard in 5-mL MtBE. This will yield a stock solution with a concentration of 5 mg/mL. This stock solution can be stored in the refrigerator at 4°C and used for up to six months.

n) Surrogate (Supelco): 2,3-dibromopropionic acid, 99+% purity. Stock solution purchased at a concentration of 1 mg/mL in MtBE.

o) Surrogate additive solution: Prepare a solution by filling a 5-mL volumetric flask to the neck with MtBE. Add 100 µL of surrogate stock solution, then top to the line with MtBE. Cap and invert to mix. This will yield a surrogate additive solution with a concentration of 20 µg/mL.

p) Surrogate ester stock solution: Methyl-2,3-dibromopropionate, 98+% purity. Stock solution purchased at a concentration of 1mg/mL in MtBE.

q) Surrogate ester additive solution: Prepare a solution by filling a 5-mL volumetric flask to the neck with MtBE. Add 100 µL of surrogate ester stock solution, then top to the line with MtBE. Cap and invert to mix. This will yield a surrogate additive solution with a concentration of 20 µg/mL.

r) Reagent water: Deionized, organic-free.

3. Procedure

a) Sample Collection, Preservation, and Storage

Samples should be collected in clear-glass 40-mL vials with screw-top caps and PFTE-lined septa. Prior to collection, add approximately 25 mg of crystalline ammonium sulfate ($(NH_4)_2SO_4$) and 10 mg/L sodium azide (NaN_3) to each collection vial in which you do not expect the residual free chlorine to exceed 5mg/L as Cl_2. Chloramine residuals may require a different quenching agent. Fill the sample bottle to the rim, then cap the bottle with the shiny, Teflon-faced side of the septum towards the water. Invert the bottle 2-3 times to mix the water with the preservatives. If an air bubble is present, remove the cap after mixing and add a few drops more of the sample and recap the bottle. Repeat this procedure until there are no air bubbles present in the sample.

Samples should be stored on ice immediately after collection, then placed in a refrigerator and stored at 4°C until the time of analysis. Samples should be analyzed as soon as possible after collection, with a maximum holding time of 14 days at 4°C.

Once derivatized, sample extracts should be analyzed on the gas chromatograph as soon as possible. The extracts may be stored in the freezer at –11°C, but for no more than 14 days.

b) Preparation of diazomethane:

Process should be carried out in a ventilation hood.

Set up diazomethane generation apparatus on ice. Add 3 mL of MtBE to the outside tube of the generator. Assemble to parts of generator together, with o-ring seal, and clamp. Make sure that the vapor outlet hole of the inner tube is facing upwards, so the reactants will not leak into the outside tube of the generator. Check for leaks in generator before adding reagents to inner tube of generator.

Add 1 mL of MtBE, then 1 mL of Carbitol to the inside tube of generator. Add approximately 200 mg of Diazald to the inside tube of the generator. Close the screw-cap with TFE-lined septum and mix the contents of the inner tube gently. Make sure that none of the contents of the inner tube leaks out into the outer tube of the generator. Place reactor in ice bath for 10 minutes.

Keeping reactor in ice bath, add 1.5 mL of 45% KOH dropwise to the inner tube of the generator with a gas-tight syringe through the septum. Be careful not to allow pressure build-up in the inner tube.

Allow diazomethane to form on ice for 30-45 minutes. Every five minutes, mix contents of apparatus gently.

Remove reactor from ice bath. Wipe off any excess water from outside of generator. Remove inner jacket of the reactor and place it in a 5 N NaOH bath. Transfer diazomethane from the outer tube of generator to a 40-mL vial with TFE-lined septum. Store diazomethane in an explosion-proof freezer until ready to be used. For safety reasons, this solution should be used within 24 hours.

Soak all glassware used to generate diazomethane in a 5N NaOH bath for at least 30 minutes, to destroy any unreacted Diazald.

c) Preparation of Calibration Standards

Prepare standards in 100 mL of deionized, organic-free water.

Prepare aqueous calibration standards by injecting measured amounts of the appropriate multicomponent haloacetic acid additive solution into reagent water. Fill 100-mL volumetric flasks to the neck with reagent water. Add the appropriate amount of haloacetic acid additive solution, then fill to the line with reagent water. Prepare five different concentrations ranging from 1 µg/L to 50 µg/L, along with a sample of blank reagent water. Apportion 20-mL aliquots, using a graduated cylinder, of each calibration standard, in duplicate, into 40-mL glass, screw-top vials with TFE-lined silicone septa. Extract and derivatize these standards along with samples , according to procedure outlined below.

If many samples are being analyzed, prepare a calibration point to be run after every ten samples. Choose a concentration that is expected to be within the range of unknown samples.

Prepare one sample using the multicomponent, methyl ester additive solution. This standard should be prepared directly in MtBE, at a concentration within the range of expected concentrations for samples being analyzed.

d) Microextraction:

Extraction and derivatization process should be carried out in a ventilation hood.

Remove samples from storage and allow them to equilibrate to room temperature. Transfer 20 mL from each sample container into a 40-mL glass, screw-top vial a with TFE-lined silicone septum.

Add 20 µL of the surrogate additive solution to each sample and mix contents gently. If adding spikes of known haloacetic acid concentrations to samples, do so at this time.

Add 2.0 mL of concentrated H_2SO_4 to each vial. Cool in an ice bath, then allow samples to return to room temperature. Add 10 g baked Na_2SO_4, then 4.0 mL MtBE. Immediately cap vial and shake briefly to break up any salt clumps.

Vortex each vial for 1 minute, then stand vials upright and allow the two phases to separate for at least 3 minutes.

e) Derivatization and Quenching

Transfer 2 mL of the top ether layer of each sample to a 2 mL volumetric flask. Add approximately 100 mg of anhydrous, powdered $MgSO_4$ to each sample. Cap and invert once to mix. Allow excess $MgSO_4$ to settle to bottom of flask.

Add 225 µL of cold diazomethane/MtBE solution to each sample. Cap sample and invert once to mix. Hold samples in an explosion-proof refrigerator at 4°C for 15 minutes, then place extracts in hood for another 15 minutes, until they reach room temperature. A persistent, if faint, yellow color should remain in each extract. This indicates that enough diazomethane was present in the extract to drive the esterification reaction.

Add approximately 0.1 g of silicic acid to each sample, to quench excess diazomethane. Let excess silicic acid settle to bottom of flask.

Transfer each extract to an autosampler vial for GC analysis. Be sure not to transfer any silicic acid to autosampler vials; silicic acid could clog the needle of the autosampler syringe. Store samples in freezer at -15 °C until shortly before analysis. Allow extracts to warm to room temperature before analyzing on the gas chromatograph.

Appendix C: TOX Standard Operating Procedure

1. SYSTEM DESCRIPTION

1.1. Adsorption Module

Model: AD-2000 Adsorption Module

Model n°: 890-161

Serial n°: 99292009

1.2. Organic Halide Analyzer

Model: DX-2000 Organic Halide Analyzer

Model n°: 890-162

Serial n°: 99292009

1.3. Software

AOX/TOX by column – Copyright 1993-1996 Rosemount Dohrmann Div. - Version 2.10

2. REAGENTS

Appendix C.I. provides the information of the reagents used including the grade, concentrations used, how to prepare, holding time and the location where they are stored.

3. SAMPLE COLLECTION AND DECHLORINATION

Samples for TOX analysis should be collected in amber bottles (with volume capacity of 125 or 250mL) that contain sodium sulfite (Na_2SO_3; Mallinckrodt Analytical Reagent; granular; 500g). 80µL of a 40mg/mL solution of Na_2SO_3 should be added to the 125mL bottles (160µL to 250mL bottles).

Before collecting samples, the sample tap should be opened and allowed to run to waste for 2-3 minutes. The flow should then be reduced, the bottle placed at a slant and the water allowed to run down the side.

When the bottle is almost full, cap the bottle with the teflon side of the liner facing inwards. Invert the bottle to mix and then open the cap and completely fill so that no air bobbles remain. Invert to confirm absence of air.

After collection, samples should be kept in a refrigerator at 4°C until analysis, which should take place within 14 days of collection.

4. SAMPLE PRE-TREATMENT

Before the analysis 25 drops of concentrated sulfuric acid (A.C.S. Plus) should be added to the 125mL samples (50 drops to 250mL bottles) after they achieve room temperature.

5. SAMPLE PREPARATION - ADSOPTION

The amount of sample, rate of adsorption to the carbon columns, channel fill rate and use of sample prime, can be adjusted in the control panel using the arrow keys after selecting the channel in use and pressing the keys "sample" and "menu".

Program used for sample channels (1-4):
Sample volume: 50mL
Adsorption rate: 3mL/min.
Fill rate: Fast (66mL/min)
Sample prime: YES
Priming volume: 5mL

Program used in the nitrate channel:
Sample volume: 2mL
Adsorption rate: 1mL/min.

Before commencing ensure that the previous user has rinsed the channels with DIW. This information should be written in the TOX logbook.

To load the samples in the channels, choose one of the channels (1-4) keys, press the "Start/Stop" key, connect the sample to the channel using one of the fill tubes (Figure C1 a)) and then press "OK".

After desired volume of sample is in the channel, the screen will display the message "connect columns (then press OK)". Aqueous samples are then passed through two carbon columns connected in series at a flow rate that permits complete adsorption of the organic halogens.

Disconnect the fill tube, connect two GAC columns (after punching holes in both ends of each column) in series using a connector (Figure C1 b)) and press the "OK" key.

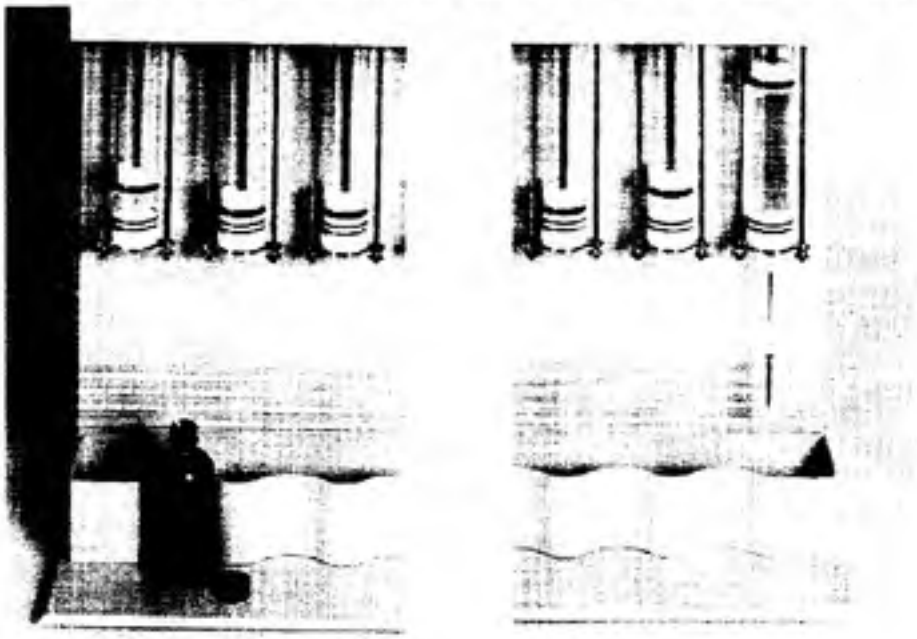

Figure C1: Adsorption module; a) Sample loading connection; b) Column connection

After the passage of each sample, fill the channel with DIW through the fill tubes and discharge to waste in order to clean it.

The sample columns are then rinsed with a nitrate solution (see section 2. for preparation) in order to remove residual chloride ions. This solution should be present in the last channel of the adsorption module. When there is not enough nitrate wash solution in the channel the screen will display "insufficient NO_3 solution". Press "OK" after attaching the fill tube connecting the channel to the bottle with the nitrate solution. This and the preparation of the first nitrate blank (prepared in one single column) can be done while the adsorption is taking place.

Connect the GAC columns to the nitrate channel, press the "nitrate" channel key followed by the "start/stop" key, and then the "OK" key.

When the run is complete disconnect the columns from the adsorption module and transfer the samples to the DX2000 organic halide analyzer.

At least two nitrate blanks (prepared in one single column) should be analyzed in each run in the beginning and in the end of the adsorption process. The total number of nitrate blanks should depend on the number of samples prepared as in each run in the DX2000 organic halide analyzer, that corresponds to the analyzes of 14 rack positions (enough to run six samples and two nitrate blanks), a nitrate blank should be analyzed in the beginning and in the end of the run.

6. Instrument Preparation

Before commencing ensure that the gas supply (of oxygen for the combustion and Helium used as carrier gas) is enough. Never use the instrument without checking that the pressure of both gases is higher that 500psi.

Use laboratory coat and gloves during all the procedure and laboratory goggles whenever handling acids.

Figure C2 presents the titration cell parts.

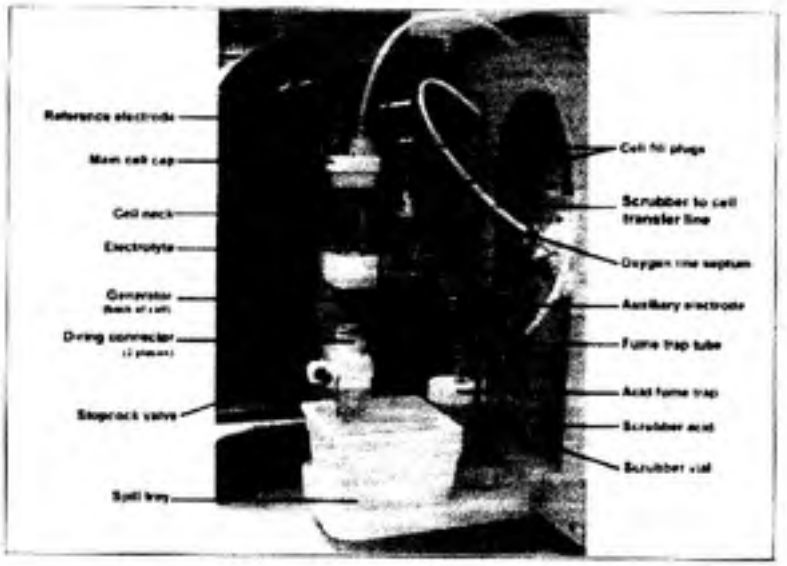

Figure C2: Titration cell parts

Before beginning each analysis the following maintenance steps must be followed.

6.1. Scrubber vial

When the instrument is not working the scrubber should always be disconnected from the combustion tube.

To change the acid in the scrubber vial dilute the sulfuric acid by transferring it form the scrubber vial to a one liter beaker filed with tap water. In the sink, open the tap water allowing it to run with reduced flow and carefully empty the beaker contents.

Fill the scrubber vial half way to the marked line with fresh 80% sulfuric acid.

6.2. Spill tray and Acid fume trap

Change the soda in the spill tray after making sure that the acid is neutralized. If acid is still present in the tray use more sodium bicarbonate to neutralize it, empty the tray into aluminum foil and empty the contents in the garbage. Before throwing it in the garbage be sure that no acetic acid smell can be detected, keeping it in the hood until this condition is meet.

After rinsing the tray with tap water and drying it, fill it to about 1/3 with sodium bicarbonate to neutralize cell electrolyte.

Empty the acid fume trap contents in the sink, rinse it with DIW and insert sodium bicarbonate (soda ash) to about 1/4 full and DIW to about 1/2 full as shown in Figure C3.

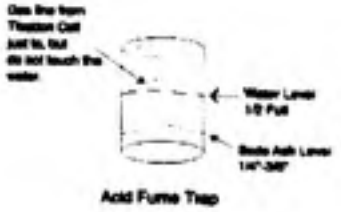

Figure C3: Acid fume trap

6.3. Coulometric Cell

Change acid in the cell. Remove the cell fill plugs, open the stopcock valve to remove the acid from the cell to the spill tray, close the valve and fill the cell until the cell neck with fresh 70% acetic acid.

Check if the reference electrode (figure C4) has bubbles.

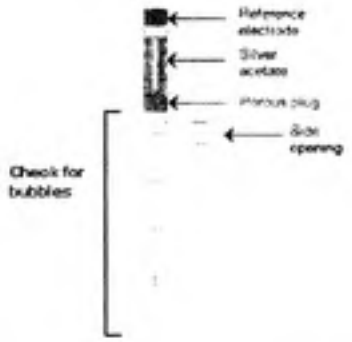

Figure C4: Reference electrode

Do not remove the metal reference electrode from the reference electrode assembly. Problems in obtaining a stable baseline are likely to occur if the metal reference electrode is moved as it connects to the silver acetate reagent.

If there are bubbles present in the reference electrode, remove it from the cell and ***take it to a hood with a moving window that will protect you from a possible spill.*** Remove the side-opening plug and insert a syringe filled with 70% acetic acid in the side opening. With the part of the reference electrode that contains silver acetate facing down, slowly inject the acid from the syringe to the electrode. Repeat this procedure three times making sure that all the bubbles are removed by moving the electrode.

Be careful when doing this step as the syringe can suddenly detach from the side opening and release acetic acid.

7. DX2000 Settings

To start the analysis in the computer choose the icon "AOX/TOX by column" and press OK.

7.1. Gas and Temperature Settings

In the "System Setup" menu bar click "open" and turn the system to a "Ready" position that will turn on the gas flow and increase the furnace temperature to 850°C from its standby temperature of 550 °C. When the temperature reaches the desired ready mode temperature a light in the temperature control panel indicator will be on.

Connect the scrubber vial to the combustion tube and close the injection port lid. In the front panel check that the gases flow reaches the marked position. If it is necessary to verify the gases flow-rates, attach a bubble meter to the inlet gas tubes and adjust the flow rates of each gas separately, to the desired flow of 200mL/min, using the rotameter knobs in the front panel.

A total flow of 400mL/min can then be verified by measuring the flow coming out of the line that connects the scrubber to the cell.

7.2. Baseline monitor

Select in the "System Checks" menu the "baseline monitor" option and wait for about 15 minutes until the baseline is stable. The voltage reading should be higher than 250V. If the voltage reading is lower than 250V, flush the cell with fresh acetic acid or use the NaCl solution (200ng/µl) to make injections in the cell until the desired voltage value is obtained.

In the "System Setup" menu bar click "open" and turn the cell to the "ON" position. In the "System Checks" menu choose again the "baseline monitor" option and wait until the baseline is stable. If you wish to see the current instead of the voltage reading, select in the "options" menu the "graph mode" option of your choice. Both current and voltage will always be displayed in the bottom of the computer screen.

7.3. Cell Check

To verify if the cell is working properly inject a known amount (e.g. 5µl) of a NaCl solution (200ng/µl) and check the recovery obtained.

In the "System Checks" menu choose the "cell check" option fill the "run info" menu with the information of the solution injected. Before pressing the "start" key have the syringe ready for the injection. Press "start", wait for a message saying "inject to cell then press ok", take the white cell fill plug (Figure C2) from main cell cap, inject the desired volume into the titration cell and press "ok".

If the recovery obtained is between 90-110% the cell is working properly.

7.4. Clean Boat

Before starting to analyze samples, the boat has to be cleaned by choosing the "clean boat" option in the "System Checks" menu.

7.5. Combustion Check

To verify the furnace performance, inject a known amount (e.g. 5µl) of a trichlorophenol standard solution (500ng/µl) into the boat and check the recovery obtained.

After removing the plastic bottoms of a carbon column, open the injection port lid and use the ejector tool to insert the GAC into the boat. ***Be careful to not touch the boat with the tool, as the boat is extremely fragile.***

In the "System Checks" menu choose the "combustion check" option fill the "run info" menu with the information of the solution injected. Before pressing the "start" key have the syringe ready for the injection. Press "start", wait for a message saying "inject to boat then press ok", inject the desired volume through the septum and press "ok".

If the recovery obtained is between 90-110% the combustion is being effective.

Looking to the carbon condition in the boat after being combusted (should be white) should also give an indication of whether the combustion was efficiently done and if there are any leaks in the system. Regular checks of the carbon condition must therefore be done while samples are being analyzed.

7.6. Autosampler Preparation

Under the "Run" menu select "auto injector" and then "setup information". Identify, in the sample information window, the samples put in each of the rack positions. For each sample there will be a top and bottom column that should be given the same "sample ID" and under the "Column" box be specified whether they correspond to a top or bottom column. Pressing the "rack summary" key will allow the review of the run setups.

A nitrate blank should be analyzed in the first and last positions of the rack. In these samples, under the column box specify the nitrate columns as "top only".

After removing the plastic covers from the top and bottom of each column, insert the columns in the correct rack positions with the top of each column facing the bottom of the rack to minimize sample losses.

After saving the setup press "OK" to exit the sample information window and in the auto injector run results window press "start run".

Analyzing a nitrate blank as the sample in a batch of the rack allows the determination of whether the system is ready for another run. If a negative value is obtained the instrument should be stabilized again before the next batch of samples is analyzed.

When all the samples have been analyzed, disconnect the scrubber from the combustion tube and the red septa from the scrubber vial, in the "System Setup" menu bar click "open" and turn the system to the "Standby" position, vacuum the boat and clean it with DIW, and clean the autoinjector ports.

7.7. TOX measurements

To see the results obtained click in the "results" menu and select "system log". Copy the results obtained and paste them into a new file. Every 6-month period save the system log file with other name and delete the contents of the log file.

The following expressions can be used to determine the samples concentration (in μgCl/L) and the breakthrough percentage (that should be lower than 10%). An average of the nitrate blank values should be used as blank in the expressions bellow.

$$Final\ result(\mu Cl/L) = \frac{(top + bottom) - 2 \times blank}{Adsorption\ Volume} \quad [C.1]$$

$$Breakthrough(\%) = \frac{(bottom - blank) \times 100}{(top + bottom - 2 \times blank)} \quad [C.2]$$

8. Quality Assurance/Quality Control

8.1. Cell and combustion check recoveries

In order to ensure the validity of the data collected, it is extremely important to perform a cell check and combustion check before each analysis. If the recoveries obtained range between 90-110% the system is being effective in the determination of the total organic halide content of the samples.

8.2. Haloacetic acids and trihalomethanes recoveries

Standard haloacetic acid (HAA) and thrihalomethane (THM) solutions were analyzed using the absorption module and the organic halide analyzer (DX-2000) to measure their TOX content and therefore access the percent recoveries obtained with this instrument (Table CI). The cell check recovery obtained was 107% and the combustion check recovery obtained was 96%.

Table CI: Percent recoveries obtained in the analyzes of standard concentrations prepared of the HAA and THM individual species ([std]).

	Sample ID	[std] (μg/L)	[std] (μg as Cl/L)	Final result (μg Cl/L)	Recovery (%)
HAA	chloroacetic acid	100	38	35	93
	dichloroacetic acid	100	55	71	129
	trichloroacetic acid	100	65	75	115
	dibromoacetic acid	100	33	41	125
	bromochloroacetic acid	100	41	47	115
	bromoacetic acid	100	26	35	138
	bromodichloroacetic acid	100	51	35	69
	tribromoacetic acid	100	36	26	73
	chlorodibromoacetic acid	100	42	46	110
THM	chloroform	100	89	60	68
	bromochloromethane	100	65	43	66
	dibromochloromethane	100	51	34	66
	bromoform	100	42	29	68

The conversion of μg/L to μg as Cl/L is based on the molecular weight of the compound and in the Cl and Br content as shown in the following expression.

$$[std](\mu gasCl/L) = [std](\mu g/L) \times \frac{Mr(Cl)}{Mr(compound)} + [std](\mu g/L) \times \frac{Mr(Br)}{Mr(compound)} \times \frac{Mr(Cl)}{Mr(Br)} \quad [C.3]$$

In order to identify if the low recoveries obtained in the THM standard solutions were due to weak adsorption into the carbon columns, a direct injection of bromoform was made in the boat. The percent recovery obtained was 69.9% indicating that the low percent recoveries obtained are not explainable by a weak adsorption onto the carbon columns.

8.3. Holding time study

A large amount of chloraminated drinking water was collected on the 27th of August to determine the amount of acid that should be added to the samples, the samples holding time, and whether the sulfuric acid should be added immediately to the samples (when they are received in the laboratory) or just before analysis.

The addition of 25 drops of ACS PLUS sulfuric acid to the samples dropped the pH from 6.8 to 1.1 and was found to be the maximum amount of acid to add to the 125mL bottles without sample spillage.

Table CII summarizes the experimental procedure followed to determine the samples holding time and whether the sulfuric acid should be added immediately to the samples or just before analysis.

Table CII: Sample ID and experimental procedure followed

Sample	Experiment
0	add acid and analyze immediately (Aug28,00)
14a	add acid immediately (Aug28,00); analyse 14 days later (Sep11,00)
14b	add acid before analysis (Sep11,00)
29a	add acid immediately (Aug28,00); analyse 28 days later (Sep26,00)
29b	add acid before analysis (Sep26,00)

Figure C5 presents the results obtained in function of the time of sample storage and acid addition.

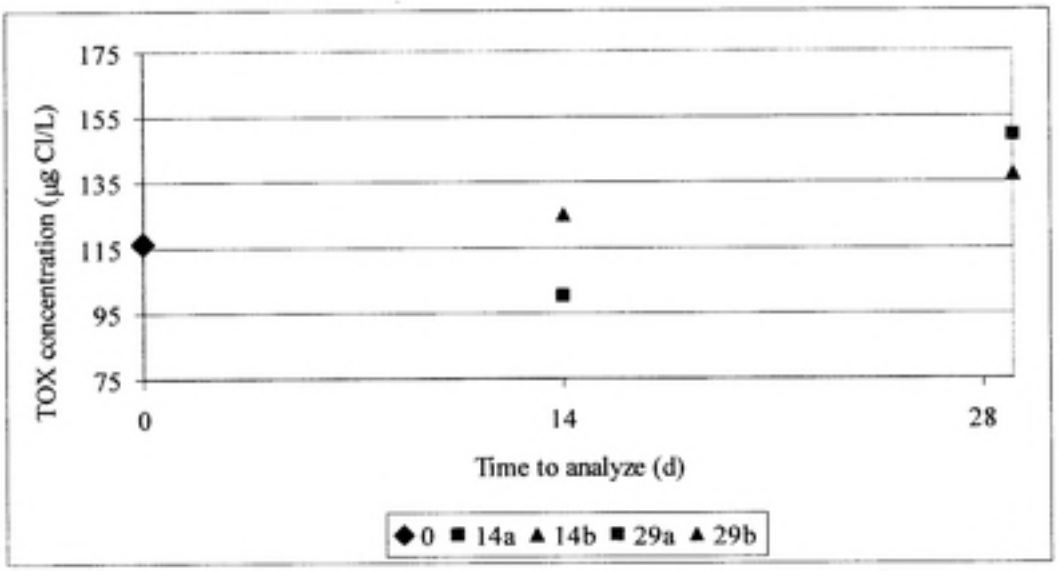

Figure C5: TOX concentrations obtained in this experiment

From the results obtained we can conclude that by adding the acid to the samples prior to the analyzes a TOX concentration closer to the immediate analysis value is obtained and that by keeping the samples in the refrigerator 29 days we can expect an increase in the TOX concentration of about 18%.

Appendix C.I. – Reagents used in TOX analysis

Table CIII – Reagents for TOX analysis

Reagent	Grade	Preparation	Concentration	Usage	Storage	Holding time
Laboratory Grade Water (LGW)	N/A	N/A	N/A	Preparing solutions Fill the acid fume trap Clean AD channels Clean column connectors Clean TOX boat	N/A	N/A
Acetic Acid	Reagent grade	Add 7 parts acetic acid to 3 parts LGW	70%	Cell electrolyte	Room 129 acid cabinet	One week
Sulfuric Acid	Reagent grade	Add 8 parts acetic acid to 2 parts LGW	80%	Scrubber solution	Room 103 acid cabinet	One week
Potassium nitrate	Reagent grade	Weigh 8.2g potassium nitrate into 1L volumetric flask. Dilute to the mark with LGW.	5,000mgNO_3/L in water	Nitrate wash solution	Room 103	
Sodium Chloride	Reagent grade	**Stock solution:** weigh 1.650g NaCl into a 100mL volumetric flask. Dilute to the mark with LGW. Pipette 2mL of stock solution into a 100mL volumetric flask. Dilute to the mark with LGW.	200ngCl/µL in DIW	Cell check standard	Room 103	
2,4,6-Trichlorophenol	Reagent grade	**Stock solution:** weigh 1.856 2,4,6-Trichlorophenol into a 100mL volumetric flask. Dilute to the mark with methanol. Pipette 5mL of stock solution into a 100mL volumetric flask. Dilute to the mark with methanol.	500ngCl/µL in methanol	Combustion check standard	Room 129 cabinet at room temperature	
Sodium bicarbonate				Spill tray Acid fume trap	Room 103	
He	UHP			Carrier gas	Room 103	
O_2	UHP			Combustion	Room 103	

Appendix D: TOBr Standard Operating Procedure

1. SYSTEM DESCRIPTION

Figure D1 presents a description of the method and the components involved.

1.1. Adsorption Module

Model: AD-2000 Adsorption Module

Model n°: 890-161

Serial n°: 99292009

1.2. Organic Halide Analyzer

Model: DX-2000 Organic Halide Analyzer

Model n°: 890-162

Serial n°: 99292009

1.3. DX-2000 Software

AOX/TOX by column – Copyright 1993-1996 Rosemount Dohrmann Div. - Version 2.10

1.4. Ion Chromatograph

Dionex Ion chromatography system equipped with an eluent degas module, a LCM-3 conductivity detector, an ASM-3 Automated sampler and a GPM-2 gradient pump coupled to a RS232 Advanced computed interface

1.5. IC Software

Dionex - PeakNet software - version 4.30 - Copyright 1992

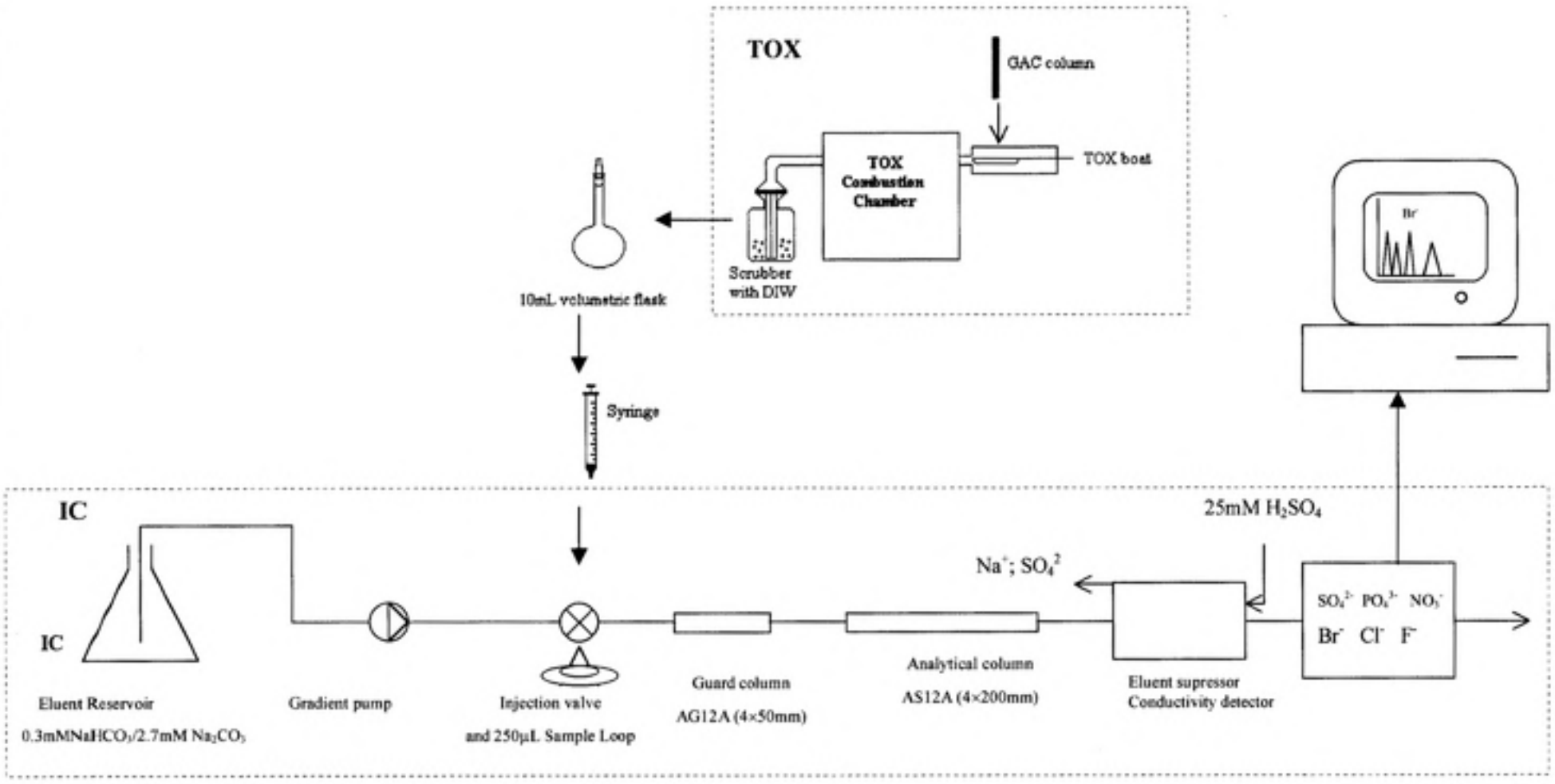

Figure D1: Flow chart with major components of the TOBr method

2. Reagents

Appendix D.I. provides the information of the reagents used including the grade, concentrations used, how to prepare, holding time and the location where they are stored.

3. Sample collection and dechlorination

Samples for TOBr analysis should be collected in the same amber bottles used for TOX collection (with volume capacity of 125 or 250mL) that contain sodium sulfite (Na_2SO_3). 80µL of a 40mg/mL solution of Na_2SO_3 should be added to the 125mL bottles (160µL to 250mL bottles).

Before collecting samples, the sample tap should be opened and allowed to run to waste for 2-3 minutes. The flow should then be reduced, the bottle placed at a slant and the water allowed to run down the side. When the bottle is almost full, cap the bottle with the teflon side of the liner facing inwards. Invert the bottle to mix and then open the cap and completely fill so that no air bobbles remain. Invert to confirm absence of air.

After collection, samples should be kept in a refrigerator at 4°C until analysis, which should take place within 14 days of collection.

4. Sample pre-treatment

Before the analysis 25 drops of concentrated sulfuric acid (A.C.S. Plus) should be added to the 125mL samples (50 drops to 250mL bottles) after they achieve room temperature. In case the TOX and TOBr analysis are not performed in the same day, the sample left should be transferred to a lower volume container so that is kept airspace free in the refrigerator until analysis.

5. Sample preparation - Adsoption

The amount of sample, rate of adsorption to the carbon columns, channel fill rate and use of sample prime, can be adjusted in the control panel using the arrow keys after selecting the channel in use and pressing the keys "sample" and "menu".

Program used for sample channels (1-4):

Sample volume: 25mL

Adsorption rate: 3mL/min.

Fill rate: Fast (66mL/min)

Sample prime: YES

Priming volume: 5mL

Program used in the nitrate channel:

Sample volume: 2mL

Adsorption rate: 1mL/min.

Before commencing ensure that the previous user has rinsed the channels with DIW. This information should be written in the TOX/TOBr logbook.

To load the samples in the channels, choose one of the channels (1-4) keys, press the "Start/Stop" key, connect the sample to the channel using one of the fill tubes (Figure D2 a)) and then press "OK". After desired volume of sample is in the channel, the screen will display the message "connect columns (then press OK)". Aqueous samples are then passed through two carbon columns connected in series at a flow rate that permits complete adsorption of the organic halogens.

Disconnect the fill tube, connect two GAC columns (after punching holes in both ends of each column) in series using a connector (Figure D2 b)) and press the "OK" key.

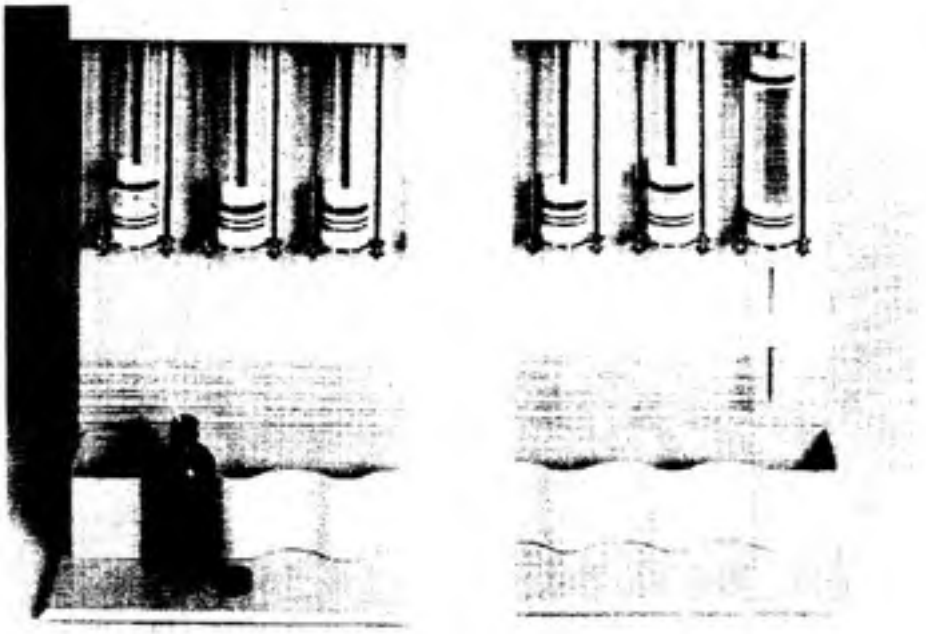

Figure D2: Adsorption module; a) Sample loading connection; b) Column connection

After the passage of each sample, fill the channel with DIW through the fill tubes and discharge to waste in order to clean it.

The sample columns are then rinsed with a nitrate solution (see section 2. for preparation) in order to remove residual chloride ions. This solution should be present in the last channel of the adsorption module. When there is not enough nitrate wash solution in the channel the screen will display "insufficient NO_3 solution". Press "OK" after attaching the fill tube connecting the channel to the bottle with the nitrate solution. This and the preparation of the first nitrate blank (prepared in one single column) can be done while the adsorption is taking place.

Connect the GAC columns to the nitrate channel, press the "nitrate" channel key followed by the "start/stop" key, and then the "OK" key.

When the run is complete disconnect the columns from the adsorption module and transfer the samples to the DX2000 organic halide analyzer.

6. TOX INSTRUMENT PREPARATION

Before commencing ensure that the gas supply (of oxygen for the combustion and Helium used as carrier gas) is enough. Never use the instrument without checking that the pressure of both gases is higher that 500psi.

Insert a filter in the carrier gas line.

Use laboratory coat and gloves during all the procedure and laboratory goggles whenever handling acids.

Figure D3 presents the titration cell parts.

Even though the coulometric cell will not be used while running the TOBr samples the maintenance steps described bellow must be followed in order to maintain the instrument with a stable baseline which is necessary to be able to run samples.

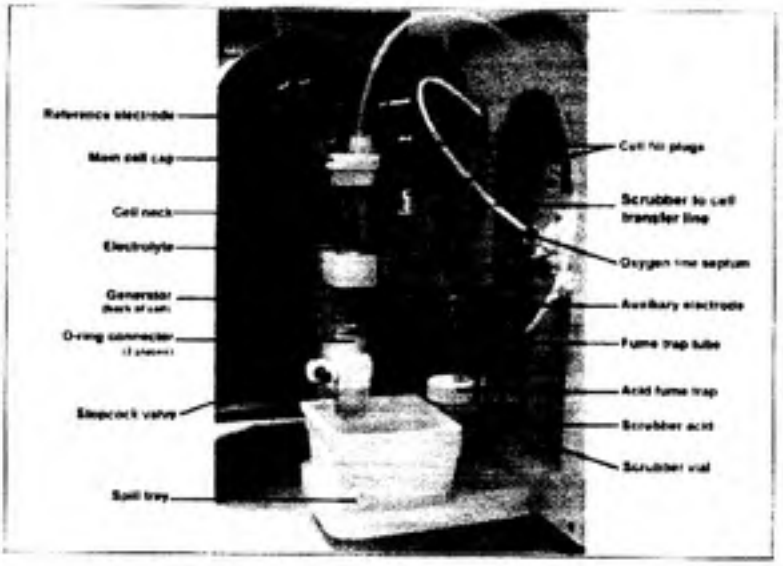

Figure D3- Titration cell parts

Before beginning each analysis the following maintenance steps must be followed.

6.1. Scrubber vial

When the instrument is not working the scrubber should always be disconnected from the combustion tube.

To change the acid in the scrubber vial dilute the sulfuric acid by transferring it form the scrubber vial to a one liter beaker filed with tap water. In the sink, open the tap water allowing it to run with reduced flow and carefully empty the beaker contents.
Fill the scrubber vial half way to the marked line with fresh 80% sulfuric acid.

6.2. Spill tray and Acid fume trap

Change the soda in the spill tray after making sure that the acid is neutralized. If acid is still present in the tray use more sodium bicarbonate to neutralize it, empty the tray into aluminum foil and empty the contents in the garbage. Before throwing it in the garbage be sure that no acetic acid smell can be detected, keeping it in the hood until this condition is meet.
After rinsing the tray with tap water and drying it, fill it to about 1/3 with sodium bicarbonate to neutralize cell electrolyte.

Empty the acid fume trap contents in the sink, rinse it with DIW and insert sodium bicarbonate (soda ash) to about 1/4 full and DIW to about 1/2 full as shown in FigureD4.

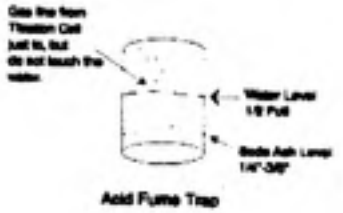

Figure D4: Acid fume trap

6.3. Coulometric Cell

Change acid in the cell. Remove the cell fill plugs, open the stopcock valve to remove the acid from the cell to the spill tray, close the valve and fill the cell until the cell neck with fresh 70% acetic acid.

7. DX2000 SETTINGS

To start the analysis in the computer choose the icon "AOX/TOX by column" and press OK.

7.1. Gas and Temperature Settings

In the "System Setup" menu bar click "open" and turn the system to a "Ready" position that will turn on the gas flow and increase the furnace temperature to 850°C from its standby temperature of 550 °C. When the temperature reaches the desired ready mode temperature a light in the temperature control panel indicator will be on.

Connect the scrubber vial to the combustion tube and close the injection port lid. In the front panel check that the gases flow reaches the marked position. If it is necessary to verify the gases flow-rates, attach a bubble meter to the inlet gas tubes and adjust the flow rates of each gas separately, to the desired flow of 200mL/min, using the rotameter knobs in the front panel.

A total flow of 400mL/min can then be verified by measuring the flow coming out of the line that connects the scrubber to the cell.

7.2. Baseline monitor

Select in the "System Checks" menu the "baseline monitor" option and wait for about 15 minutes until the baseline is stable. The voltage reading should be higher than 250V. If the voltage reading is lower than 250V, flush the cell with fresh acetic acid or use the NaCl solution (200ng/µl) to make injections in the cell until the desired voltage value is obtained.

In the "System Setup" menu bar click "open" and turn the cell to the "ON" position. In the "System Checks" menu choose again the "baseline monitor" option and wait until the baseline is stable. If you wish to see the current instead of the voltage reading, select in the "options" menu the "graph mode" option of your choice. Both current and voltage will always be displayed in the bottom of the computer screen.

7.4. Clean Boat

Before starting to analyze samples, the boat has to be cleaned by choosing the "clean boat" option in the "System Checks" menu.

7.5. Combustion Check

To verify the furnace performance, inject a known amount (e.g. 5µl) of a trichlorophenol standard solution (500ng/µl) into the boat and check the recovery obtained.

After removing the plastic bottoms of a carbon column, open the injection port lid and use the ejector tool to insert the GAC into the boat. ***Be careful to not touch the boat with the tool, as the boat is extremely fragile.***

In the "System Checks" menu choose the "combustion check" option fill the "run info" menu with the information of the solution injected. Before pressing the "start" key have the syringe ready for the injection. Press "start", wait for a message saying "inject to boat then press ok", inject the desired volume through the septum and press "ok".

If the recovery obtained is between 90-110% the combustion is being effective.

Looking to the carbon condition in the boat after being combusted (should be white) should also give an indication of whether the combustion was efficiently done and if there are any leaks in the system.

Regular checks of the carbon condition must therefore be done while samples are being analyzed.

7.6. Manual Injection

As after the run some time is needed for disconnecting the scrubber with LGW from the combustion tube, manual injections should be used instead of using the autosampler. Under the "Run" menu select "manual". There is no need to identify the samples as the coulometric cell is not going to be used. Press start run and when the message " Inject to boat and then press OK" is displayed in the screen, disconnect the srubber vial with sulfuric acid from the combustion tube and connect a scrubber vial containing LGW up to the mark. Cover the connection between the scrubber vial and the combustion tube with heating tape. After removing the plastic covers from the top and bottom of each column, insert the columns in the boat and press "OK" in the screen. When combustion step finishes, and the boat is coming back to the cooling position, disconnect the scrubber vial from the combustion tube. Empty the scrubber vial contents into a 10mL volumetric flask and flush the gas inner tube with LGW up to the mark. The sample is then transferred to a 3mL syringe that will inject it's contents in the IC.

A sample blank (25mL LGW that passed through all this procedure) should be the first sample to be analyzed.

When all the samples have been analyzed, disconnect the scrubber from the combustion tube, in the "System Setup" menu bar click "open" and turn the system to the "Standby" position, vacuum the boat and clean it with DIW.

8. Ion Chromatography

Follow the Dionex Ion Chromatographic operating procedure to stabilize the IC and manually inject the samples. This method uses a 250μL sample loop, an AG12A (4×50mm) guard column and an AS12A (4×200mm) analytical column. The reagents used are presented in Appendix D.I.

8.1. System Stabilization

1. Remove the plugs at the end of the waste regenerant solution, and mobile phase (mp) lines located in the sink.
2. Open the main valve of the UHP Helium gas tank.

Change the tank when the pressure is about 500psi

3. Switch on Autosampler.
4. Switch on Conductivity Detector (square blue button).
5. Turn the conductivity cell to OFF.
6. Turn on pump in the back.
7. Make sure all modules are in LOCAL position.
8. Switch on Eluant Degas Module. Set pressure at 5psi by turning the black knob accordingly.
9. Flip the corresponding mp bottle switch to an on position (color coordinated). Switch on eluent degas module. Flip the corresponding switch to mp to SPARGE. Loosen the cap on reservoir bottle. Open up the sparge port on bottle by removing plug. Then attach the corresponding sparge line. Listen for a bubbling noise. Let it degas for 30 min if it is a new mp or for 10 min for an old mp.
10. Remove corresponding sparge line, plug up sparge port, switch from sparge to PRESSURIZE, and immediately tighten the mp cap.
11. Double check pressure is at 5psi.

12. On the gradient pump, set the right reservoir to the proper percent. For example, only using the 2.7mM Na_2CO_3/0.3mM $NaHCO_3$ mp, would involve pressing "%", "4" and then "1" "0" "0", so the pump would be drawing 100% from mp 4. Make sure that other reservoirs are set at 0%. In addition set the flow rate to 1.2mL/min.

13. Prime the pump: Attach the 10ml syringe to the white knob/port on the gradient pump. Turn the stick towards the syringe so that it is point towards you. Push START so that the mobile phase will run. The syringe will fill slowly with mp, you can aid it by gently pulling the syringe back. Stop at approximately 6mL, push STOP, and turn stick back to original position. Disconnect syringe and empty contents to waste in the sink. Repeat this procedure once more, including throwing the contents to waste. Finally, repeat this procedure but DO NOT throw the contents to waste. Keep the syringe attached to the white knob/port on the gradient pump and loosen the black knob on the cylindrical pump heads by turning it to the left. Turn the stick towards you and slowly push the contents of the syringe into the pump. Any air bubbles should be pushed out and the line should be dripping mp (in the waste volumetric between the UV Detector and Gradient Pump) as you push in the contents of the syringe. With about 1mL left, tighten the black knob and turn the stick back to the original position. Waste rest of contents to sink.

14. Press START to start the mp flow, tighten the regenerant cap and start the regenerant solution (25mM H2SO4).

MAKE SURE that all modules are in a LOCAL position.

15. Let the system equilibrate to a stable pressure. If the pressure starts to rise dramatically toward the limit, something is probably in a line, creating a "blockage". ***Make sure the two lines in the sink are dripping.***

16. Once pressure stabilizes (can use log book as reference depending on column/loop/etc.), turn the conductivity cell ON. Let system stabilize again while monitoring pressures.

8.2. Load a Sample

1. Load a method: Press "Start", "Programs", "Dionex", "PeakNet", "PeakNet Main Menu", "MetACI";
2. Make the appropriate changes and save the method;
3. Return to the main menu and press "RunACI" and load the method ("load method") saved;
4. For manual Injections press "% 5 0" (valve 5 off), then "run" and "hold" rapidly (the valve will change from the inject to the load position), then "% 5 1" (valve 5 on), inject ~1mL of sample, press "run" and "hold" rapidly (the valve will change from the load to the inject position);
5. In the computer select "run", "start", write the name of the sample and press "OK".

A calibration curve should be prepared with concentrations in the range expected of the samples. A calibration curve obtained for bromide is presented in Figure D5.

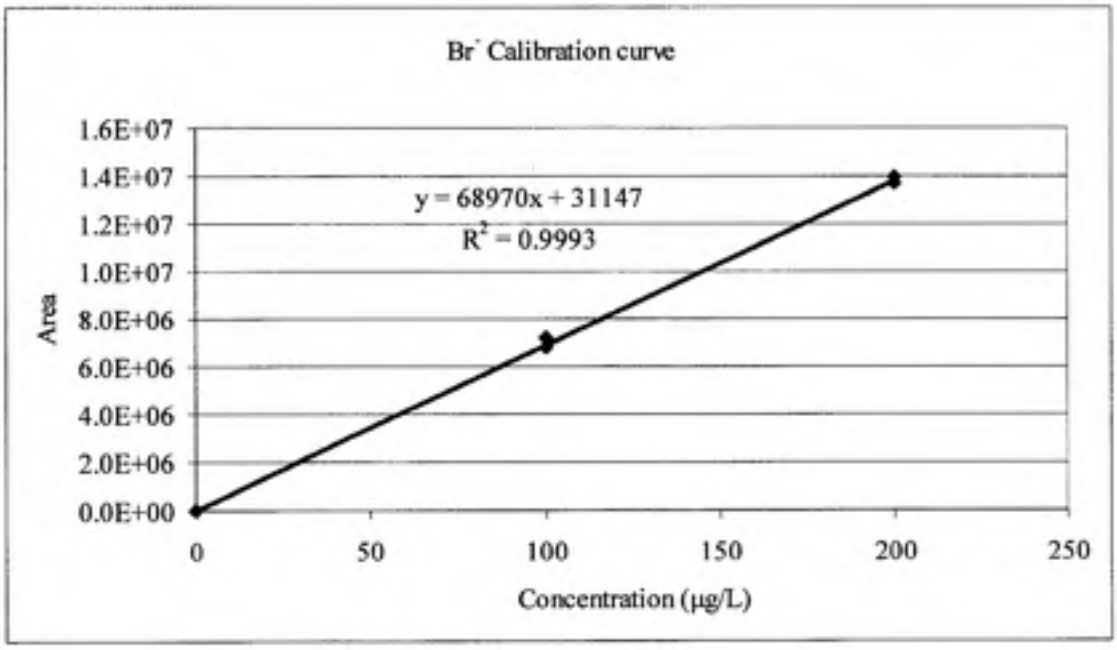

Figure D5: Bromide calibration curve

8.3. IC Shutdown Procedure

1. Pump and detector should be in "local".
2. Turn off "CELL" on detector.
3. "STOP" flow on the pump.
4. Relieve pressure from the regenerant guage.
5. Loosen cap on regenerant bottle.
6. Loosen cap on reservoir bottle.
7. Connect sparge line(s) to reservoir bottles.
8. Switch to "SPARGE".
9. Relieve pressure of main guage.
10. Main switch to "OFF".
11. Disconnect sparge line(s) and plug reservoir bottle.
12. Turn off corresponding reservoir numbered switch.
13. Switch to "PRESSURIZE".
14. Tighten cap(s) on reservoir bottles.
15. Close off the helium gas cylinder.
16. Plug the regenerant lines located in the back of the sink.
17. Turn off monitor only.
18. Turn off blue power switch located above detector panel (the detector and pump will shut off).
19. Turn off ALS with a switch located in the back of the unit (in case it was used).

9. Quality Assurance/Quality Control

9.1. Combustion check recoveries

In order to ensure the validity of the data collected, it is extremely important to perform a combustion check in the TOX before each analysis. If the TOX recoveries obtained range between 90-110% the system is being effective in combusting the organic halides.

9.2. Haloacetic acids recoveries

Table D1 presents the recoveries obtained when direct injections of 100µL of a standard solution with a concentration of 100µg/L of Br_2AA and $ClBr_2AA$ in LGW were made in the boat.

Table D1: HAA recoveries obtained without using the adsorption module

	[Theoretical] (µg Br/L)	Br^- % Recovery
Br_2AA	39	73
	88	77
$ClBr_2AA$	63	78
	101	75

When the adsorption of 25mL of sample ([Br_2AA]=100µg/L) into granular activated carbon was used using the procedure in sections 5 and 7.6, 77% recovery was obtained (as Br^-) as the average of two aqueous samples analyzed in this way. In this experiment after checking the Br_2AA standard recovery by TOX (107% recovery), the effects of acidification of samples, use of heating tape around the end of the combustion tube, and gas flow rates (Qg) were studied. The results shown in Figure D6 are averages of replicate samples.

From the results obtained we can conclude that the best recoveries are obtained when the samples are acidified, heating tape is used and using a carrier and combustion gas flow rates of 200mL/min.

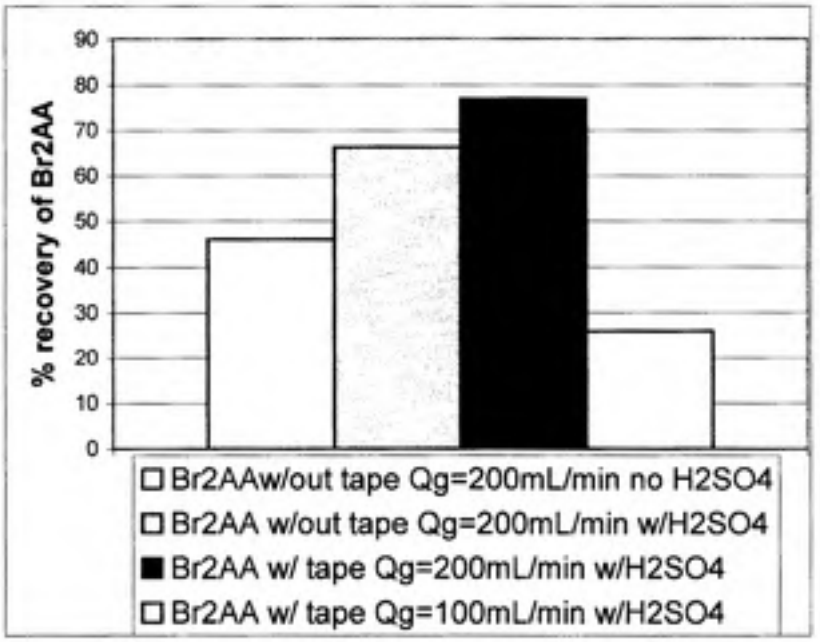

Figure D6: Comparison of different conditions used in the TOBr method

9.2.1. Recovery Calculation

Example of the concentration that can be expected after 25mL of a 100µg/L standard solution of Br_2AA ([Br_2AA] (µg/L)) was passed through two GAC columns, combusted and diluted into a final volume of 10mL:

$$[Br_2AA](\mu gBr/L) = \frac{[Br_2AA](\mu g/L) \times Mr(Br) \times 2}{Mr(Br_2AA)} \times 2.5 = \frac{100 \times 160}{218} \times 2.5 = 183$$

being Mr the molecular weight of Br_2AA.

9.3. Spike recoveries

In each batch of samples a replicate should be run with the collected scrubber sample spiked with bromide at a level equal to the concentration determined in the unspiked sample.

Appendix D.I. – Reagents used in TOX analysis

Reagent	Grade	Preparation	Concentration	Usage	Storage	Holding time
Laboratory Grade Water (LGW)	N/A	N/A	N/A	Preparing solutions Fill the acid fume trap Clean AD channels Clean column connectors Clean TOX boat	N/A	N/A
Acetic Acid	Reagent grade	Add 7 parts acetic acid to 3 parts LGW	70%	Cell electrolyte	Room 129 acid cabinet	One week
Sulfuric Acid	Reagent grade	Add 8 parts acetic acid to 2 parts LGW	80%	Scrubber solution	Room 103 acid cabinet	One week
Potassium nitrate	Reagent grade	Weigh 8.2g potassium nitrate into 1L volumetric flask. Dilute to the mark with LGW.	5,000mgNO_3/L in water	Nitrate wash solution	Room 103	
Sodium Chloride	Reagent grade	**Stock solution:** weigh 1.650g NaCl into a 100mL volumetric flask. Dilute to the mark with LGW. Pipette 2mL of stock solution into a 100mL volumetric flask. Dilute to the mark with LGW.	200ngCl/µL in DIW	Cell check standard	Room 103	
2,4,6-Trichlorophenol	Reagent grade	**Stock solution:** weigh 1.856 2,4,6-Trichlorophenol into a 100mL volumetric flask. Dilute to the mark with methanol. Pipette 5mL of stock solution into a 100mL volumetric flask. Dilute to the mark with methanol.	500ngCl/µL in methanol	Combustion check standard	Room 129 cabinet at room temperature	
Sodium bicarbonate				Spill tray Acid fume trap	Room 103	
He	UHP			Carrier gas	Room 103	
O_2	UHP			Combustion	Room 103	

Appendix D.I. – Reagents used in IC analysis

Reagent	Grade	Preparation	Concentration	Usage	Storage	Holding time
Laboratory Grade Water (LGW)	N/A	N/A	N/A	Preparing solutions Dilutions	N/A	N/A
Sulfuric Acid	Reagent grade	Add 5.6mL sulfuric acid to 4 L of LGW	25mM	Regenerant solution	Room 103 acid cabinet	1mo
Na_2CO_3	Reagent grade	Weigh 0.5723g into 2L of LGW	2.7mM	Mobile Phase	Room 108	1mo
$NaHCO_3$	Reagent grade	Weigh 0.0504g into 2L of LGW	0.3mM	Mobile Phase	Room 108	1mo
NaCl	Analytical Reagent	Weigh 0.1648g into 100mL of LGW	1g/L	Calibration Curve Standard	Room 108	6mo
NaBr	Analytical Reagent	Weigh 0.1288g into 100mL of LGW	1g/L	Calibration Curve Standard	Room 108	6mo
He	UHP			Carrier gas	Room 103	N/A

Appendix E – Free and Total Chlorine Determination

Hach Kit Instructions

Before putting the sample into the 10mL bottle or test tube, rinse them 3 times with LGW and then with sample

1. Free Chlorine

The instrument should be in the low range (2 decimal places).

1) Pour LGW up to the line on the 10-mL bottle.
2) Place the bottle in the holder of the instrument and cap.
3) Press zero.
4) Empty LGW from bottle and pour in sample.
5) Place 1 packet of free chlorine powder in the 10-mL bottle and mix for 20 sec.
6) Allow solution to stand for 1 minute.
7) After 1 min, put the bottle in the holder, cap, and press read.

2. For Total Chlorine

The instrument will be in the high range (1 decimal place).

1) Pour sample up to the line on the 10-mL bottle.
2) Place 2 packets of total chlorine powder in the bottle and mix for 20 sec.
3) Allow solution to stand for 3 minutes.
4) While waiting place the black insert into the holder of the instrument.
5) Pour LGW into one of the test tubes.
6) Place the tube into the holder, cap, and press zero.
7) Pour out the LGW.
8) After 3 min, pour some sample into the test tube.
9) Place the tube in the holder, cap, and press read.

3. *To change instrument from one function to another:*

1) Press zero and read buttons simultaneously.
2) After 1 sec take your finger off the zero button.
3) Leave finger on read button until screen reads "LO" or "HI" (depending on the function you are changing to).

Appendix F – Tables from Results Chapter

Table F1: THM concentrations in chloraminated drinking water held over 13 days

	Concentration (µg/L)				
Holding time (d)	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
0	59.7	23.3	3.0	<1	86.0
0	55.9	22.4	2.6	<1	80.9
1	61.4	23.6	3.1	<1	88.0
1	62.4	23.1	3.1	<1	88.6
2	64.7	24.5	3.4	<1	92.5
2	58.8	23.2	3.0	<1	85.0
3	63.3	24.7	3.4	<1	91.4
3	61.2	23.5	3.3	<1	88.0
4	60.1	23.3	3.1	<1	86.5
4	61.6	23.4	3.2	<1	88.2
5	63.8	24.0	3.4	<1	91.2
5	63.8	24.1	3.4	<1	91.4
6	66.8	24.9	3.6	<1	95.3
7	64.1	24.1	3.6	<1	91.8
7	59.7	22.3	3.1	<1	85.1
8	62.6	23.1	3.3	<1	89.0
8	60.3	22.5	3.2	<1	86.1
9	63.0	23.1	3.4	<1	89.5
9	61.8	22.6	3.2	<1	87.6
10	60.7	22.0	3.2	<1	85.9
10	60.9	21.8	3.2	<1	85.9
11	62.7	22.3	3.3	<1	88.3
11	62.6	22.1	3.3	<1	87.9
12	69.8	23.8	3.9	<1	97.5
12	64.7	22.1	3.4	<1	90.2
13	63.4	22.0	3.4	<1	88.8
13	66.1	22.2	3.4	<1	91.7
Average (µg/L)	62.4	23.1	3.3	<1	88.8
Std	2.7	0.9	0.2	Nap	3.4
CV (%)	4.4	3.9	7.1	Nap	3.8

Nap – Not applicable

Table F2: HAA concentrations in chloraminated drinking water held over 8 days

	Concentration (µg/L)									
sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
0	<2	<2	18.2	4.9	13.0	<2	5.4	<2	<2	41.4
0	<2	<2	18.1	4.6	12.6	<2	Nav	<2	<2	42.2
1	<2	<2	19.7	5.2	13.2	<2	5.1	<2	<2	43.2
1	<2	<2	19.9	5.2	13.1	<2	5.6	<2	<2	43.8
2	<2	<2	20.5	5.2	13.2	<2	5.2	<2	<2	44.2
2	<2	<2	20.6	5.4	13.1	2.0	5.5	<2	<2	46.6
3	<2	<2	20.8	5.1	13.2	<2	5.1	<2	<2	44.3
3	<2	<2	20.3	5.3	13.1	<2	Nav	<2	<2	44.5
4	<2	<2	21.2	5.3	13.3	<2	4.3	<2	<2	44.2
4	<2	<2	21.3	5.4	13.4	<2	4.3	<2	<2	44.4
7	<2	<2	21.1	4.2	12.5	<2	Nav	<2	<2	41.1
7	<2	<2	21.6	4.5	12.7	<2	4.7	<2	<2	43.5
8	<2	<2	19.8	4.0	12.3	<2	4.1	<2	<2	40.1
8	<2	<2	21.3	4.4	12.8	<2	4.1	<2	<2	42.6
Average (µg/L)	<2	<2	20.3	4.9	13.0	<2	4.9	<2	<2	43.3
Stdev	Nap	Nap	1.1	0.5	0.3	Nap	0.6	Nap	Nap	1.7
CV (%)	Nap	Nap	5.4	9.5	2.6	Nap	11.9	Nap	Nap	3.9

Nap - Not applicable; Nav - Not available

Table F3: THM variability at the point of entry to the distribution system

Date and Time of Sample Collection	Concentration (µg/L)				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
10/10/00 8:00	40.3	10.7	4.1	<2	55.1
10/10/00 8:00	40.1	10.6	4.0	<2	54.7
10/10/00 12:00	44.0	11.7	4.3	<2	59.9
10/10/00 12:00	44.5	11.7	4.4	<2	60.6
10/10/00 16:00	51.7	12.5	4.6	<2	68.8
10/10/00 16:00	55.9	13.6	4.8	<2	74.3
10/11/00 8:00 B	38.0	11.2	3.8	<2	53.0
10/11/00 8:00 A	36.9	10.7	3.7	<2	51.4
10/11/00 12:00 B	38.0	11.1	3.9	<2	53.0
10/11/00 12:00 A	36.4	11.0	3.9	<2	51.3
10/11/00 16:00 B	36.7	11.0	3.9	<2	51.6
10/11/00 16:00 A	39.3	11.5	4.1	<2	55.0
10/11/00 20:00 B	36.7	7.9	2.8	<2	47.3
10/12/00 0:00 B	77.5	16.5	5.0	<2	99.0
10/12/00 0:00 A	81.4	17.0	5.2	<2	104
10/12/00 4:00 B	40.8	11.2	4.4	<2	56.5
10/12/00 4:00 A	42.2	11.3	4.5	<2	58.0
10/12/00 8:00 B	44.1	12.0	4.7	<2	60.8
10/12/00 8:00 A	40.8	11.6	4.6	<2	57.0
10/12/00 12:00 B	46.3	12.5	4.9	<2	63.6
10/12/00 12:00 A	46.3	12.4	4.7	<2	63.4
10/12/00 16:00 B	43.9	11.8	4.5	<2	60.2
10/12/00 16:00 A	43.5	11.9	4.5	<2	60.0
10/12/00 20:00 B	69.6	16.9	5.0	<2	91.4
10/12/00 20:00 A	66.6	16.0	4.7	<2	87.3
10/13/00 0:00 B	35.5	10.0	4.1	<2	49.6
10/13/00 0:00 A	37.1	10.6	4.2	<2	51.8
10/13/00 4:00 B	36.3	10.5	4.3	<2	51.2
10/13/00 4:00 A	35.8	10.3	4.3	<2	50.3
10/13/00 8:00	38.6	10.9	4.5	<2	54.0
10/13/00 8:00	37.9	10.9	4.4	<2	53.2
10/13/00 16:00	37.7	10.9	4.4	<2	53.0
10/13/00 16:00	38.0	11.3	4.6	<2	53.9
10/13/00 20:00	66.2	15.7	4.8	<2	86.6
10/13/00 20:00	66.4	16.0	4.9	<2	87.3
10/14/00 4:00	106	19.9	6.4	<2	133
10/14/00 4:00	111	20.4	6.5	<2	138
10/14/00 0:00	65.1	16.5	5.7	<2	87.3
10/14/00 8:00	113	20.7	6.6	<2	140
10/14/00 8:00	108	20.6	6.6	<2	135
10/14/00 12:00	46.0	12.5	5.0	<2	63.5
10/14/00 16:00	53.8	13.6	5.5	<2	72.9
10/14/00 16:00	52.9	13.8	5.6	<2	72.2
10/14/00 20:00	47.0	9.7	3.7	<2	60.4
10/15/00 0:00	37.8	10.9	4.5	<2	53.2
10/15/00 0:00	38.2	10.9	4.6	<2	53.6
10/15/00 4:00	39.3	11.0	4.6	<2	54.9
10/15/00 4:00	41.3	11.3	4.7	<2	57.4
Average (µg/L)	51.5	12.8	4.7	<2	68.9
Max (µg/L)	113	20.7	6.6	Nap	140
Min (µg/L)	35.5	7.9	2.8	Nap	47.3

Nap - Not applicable; two composite samples were created using samples identified as A and B

Table F3b: THM levels in composite samples created using samples A and B from table F3

	Concentration (µg/L)				
Sample	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
Composite A	45.1	12.0	4.4	<2	61.5
Composite A	45.2	12.2	4.6	<2	61.9
Composite B	40.0	10.9	4.1	<2	55.0
Composite B	41.3	11.0	4.1	<2	56.4

Table F4: HAA variability at the point of entry to the distribution system

Sample ID	Concentration (µg/L)									
	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
10/10/00 8:00	<2	<2	4.5	<2	<2	<2	2.6	<2	<2	7.1
10/10/00 8:00	<2	<2	4.7	<2	2.1	<2	2.5	<2	<2	9.3
10/10/00 12:00	<2	<2	4.8	<2	2.0	<2	2.6	<2	<2	9.4
10/10/00 12:00	<2	<2	4.8	<2	2.0	<2	2.6	<2	<2	9.4
10/10/00 16:00	<2	<2	5.8	<2	2.3	<2	2.3	<2	<2	10.4
10/10/00 16:00	<2	<2	5.7	<2	2.3	<2	2.6	<2	<2	10.6
10/11/00 8:00 A	<2	<2	4.6	<2	2.7	<2	2.0	<2	<2	9.3
10/11/00 8:00 B	<2	<2	4.5	<2	2.7	<2	2.8	<2	<2	10
10/11/00 12:00 A	<2	<2	4.7	<2	2.5	<2	2.6	<2	<2	9.8
10/11/00 12:00 B	<2	<2	4.7	<2	2.5	<2	2.6	<2	<2	9.8
10/11/00 16:00 A	<2	<2	4.9	<2	2.4	<2	2.6	<2	<2	9.9
10/11/00 16:00 B	<2	<2	4.6	<2	2.4	<2	2.2	<2	<2	9.2
10/11/00 20:00 A	<2	<2	3.3	<2	<2	<2	<2	<2	<2	3.3
10/11/00 20:00 B	<2	<2	2.9	<2	<2	<2	<2	<2	<2	2.9
10/12/00 0:00 A	<2	<2	3.0	<2	<2	<2	<2	<2	<2	3.0
10/12/00 0:00 B	<2	<2	3.0	<2	<2	<2	<2	<2	<2	3.0
10/12/00 4:00 A	<2	<2	4.6	<2	<2	<2	2.4	<2	<2	7.0
10/12/00 4:00 B	<2	<2	4.9	<2	<2	<2	<2	<2	<2	4.9
10/12/00 12:00	<2	<2	5.8	<2	2.3	<2	2.8	2.4	<2	13.3
10/12/00 12:00	<2	<2	5.2	<2	2.2	<2	<3	<2	<2	7.4
10/13/00 8:00	<2	<2	4.9	<2	2.1	<2	2.8	<2	<2	9.8
10/13/00 8:00	<2	<2	5.0	<2	2.1	<2	2.7	<2	<2	9.8
10/13/00 20:00	<2	<2	2.5	<2	<2	<2	<2	<2	<2	2.5
10/13/00 20:00	<2	<2	2.6	<2	<2	<2	<2	<2	<2	2.6
10/14/00 8:00 A	<2	<2	3.1	<2	<2	<2	<2	<2	<2	3.1
10/14/00 8:00 B	<2	<2	3.7	<2	<2	<2	<2	<2	<2	3.7
10/14/00 12:00 A	<2	<2	5.0	<2	2.0	<2	2.5	<2	<2	9.5
10/14/00 12:00 B	<2	<2	5.2	<2	2.1	<2	2.6	<2	<2	9.9
10/14/00 16:00 A	<2	<2	5.5	<2	2.0	<2	2.4	<2	<2	9.9
10/14/00 16:00 B	<2	<2	5.4	<2	2.0	<2	2.4	<2	<2	9.8
10/14/00 20:00 A	<2	<2	5.2	<2	2.0	<2	2.6	<2	<2	9.8
10/14/00 20:00 B	<2	<2	5.1	<2	2.0	<2	2.6	<2	<2	9.7
10/15/00 0:00 A	<2	<2	4.6	<2	<2	<2	2.5	<2	<2	7.1
10/15/00 0:00 B	<2	<2	4.6	<2	<2	<2	2.5	<2	<2	7.1
10/15/00 4:00 A	<2	<2	4.7	<2	<2	<2	2.6	<2	<2	7.3
10/15/00 4:00 B	<2	<2	4.8	<2	<2	<2	2.7	<2	<2	7.5
Average (µg/L)	<2	<2	4.5	<2	2.2	<2	2.5	2.4	<2	7.7
Max (µg/L)	Nap	Nap	5.8	Nap	2.7	Nap	2.8	2.4	Nap	13.3
Min (µg/L)	Nap	Nap	2.5	Nap	<2	Nap	<2	<2	Nap	2.5

Nap - Not applicable; two composite samples were created using samples identified as A and B

Table F4b: HAA levels in composite samples created using samples A and B from table F4

	Concentration (µg/L)									
Sample ID	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_3AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
Composite A	<2	<2	4.4	<2	<2	<2	2.3	<2	<2	6.7
Composite B	<2	<2	4.3	<2	<2	<2	2.3	<2	<2	6.7

Table F5: TOX variability at the point of entry to the distribution system

	Top Column (µg Cl)	Bottom Column (µg Cl)	Final result (µg Cl/L)	Breakthrough (%)
10/10/00 8:00 A	4.83	0.834	106	12.4
10/10/00 16:00	4.885	0.777	106	11.3
10/11/00 8:00 A	5.648	0.853	123	11.0
10/11/00 12:00	7.5	1.066	164	10.9
10/12/00 0:00	10.144	2.848	253	21.1
10/12/00 4:00	5.957	1.387	140	17.3
10/12/00 8:00 A	4.832	1.274	115	19.1
10/12/00 12:00	4.426	1.466	111	23.3
10/12/00 20:00	9.249	2.991	238	23.7
10/13/00 8:00 A	4.861	1.023	111	15.3
10/13/00 20:00	14.313	1.118	302	6.3
10/14/00 4:00	9.277	1.802	215	15.2
10/14/00 8:00 A	8.282	1.052	180	9.8
10/14/00 16:00	6.803	0.821	145	8.9
10/14/00 20:00	6.136	2.003	156	23.5
10/15/00 0:00	5.206	1.301	123	18.3
Composite A	7.336	1.269	165	13.3

A – a composite sample was created using the samples identified as A

Table F6: THM concentrations at the point of entry to the distribution system (temporal and spatial variability study during January and February 2001)

	Coacentration (µg/L)				
Date and time	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
1/30/01 9AM	15.3	6.2	2.0	<2	23.5
1/30/01 9AM	16.9	6.3	2.1	<2	25.3
1/30/01 3PM	14.4	5.6	<2	<2	22.0
1/30/01 3PM	14.8	5.6	2.0	<2	22.3
1/30/01 9PM	15.8	6.0	2.3	<2	24.2
1/30/01 9PM	16.4	5.9	2.3	<2	24.6
1/31/01 3AM	10.8	6.0	2.3	<2	19.0
1/31/01 3AM	11.3	5.8	2.1	<2	19.3
1/31/01 9AM	12.5	5.5	2.0	<2	20.0
1/31/01 9AM	14.4	5.3	<2	<2	21.6
1/31/01 3PM	15.2	5.9	2.2	<2	23.3
1/31/01 3PM	16.1	5.9	2.2	<2	24.1
1/31/01 9PM	16.7	6.6	2.5	<2	25.8
1/31/01 9PM	16.7	6.4	2.5	<2	25.6
2/01/01 3AM	22.8	7.5	3.6	<2	33.9
2/01/01 3AM	22.6	7.6	3.6	<2	33.9
2/01/01 9AM	25.4	9.3	4.2	<2	38.9
2/01/01 9AM	24.2	8.8	4.1	<2	37.1
2/01/01 3PM	13.7	6.7	2.4	<2	22.9
2/01/01 3PM	14.1	6.6	2.4	<2	23.0
2/02/01 3AM	24.2	8.8	4.6	<2	37.7
2/02/01 3AM	21.5	8.3	4.5	<2	34.4
2/02/01 9AM	15.6	7.4	3.5	<2	26.4
2/02/01 9AM	16.1	6.8	3.5	<2	26.4
2/02/01 3PM	17.8	7.6	3.1	<2	28.5
2/02/01 3PM	18.3	7.9	3.2	<2	29.5
2/02/01 9PM	13.8	5.9	2.6	<2	22.4
2/02/01 9PM	14.4	6.3	2.8	<2	23.6
2/03/01 3AM	14.0	6.2	2.9	<2	23.1
2/03/01 3AM	14.3	6.7	3.1	<2	24.1
2/03/01 9AM	15.0	6.0	2.8	<2	23.8
2/03/01 9AM	14.6	6.0	2.8	<2	23.3
2/03/01 3PM	32.0	9.7	5.5	<2	47.1
2/03/01 3PM	30.0	9.3	5.2	<2	44.5
2/03/01 9PM	26.2	8.3	4.5	<2	39.1
2/03/01 9PM	28.1	9.3	4.8	<2	42.3
2/04/01 3AM	28.1	9.3	4.8	<2	42.3
2/04/01 3AM	30.1	9.1	5.1	<2	44.4
2/04/01 3PM	20.5	7.9	3.9	<2	32.4
2/04/01 3PM	19.9	7.2	4.1	<2	31.2
2/04/01 9PM	21.6	8.1	4.0	<2	33.7
2/04/01 9PM	28.8	10.9	<2	<2	40.5

Table F7: THM concentrations in DSI samples (temporal and spatial variability study during February 2001)

	Concentration (µg/L)				
Date and time	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
2/05/01 24:00	14.4	7.4	3.1	<2	25.0
2/5/2001 18:00	14.6	7.0	3.2	<2	24.8
2/5/2001 18:00	15.1	8.0	3.3	<2	26.4
2/06/01 6:00	13.9	6.8	3.1	<2	23.8
2/06/01 6:00	14.6	7.4	3.2	<2	25.2
2/06/01 12:00	17.4	7.6	3.5	<2	28.5
2/06/01 12:00	17.1	8.6	3.5	<2	29.3
2/06/01 18:00	18.3	8.1	4.1	<2	30.6
2/06/01 18:00	16.9	7.7	3.6	<2	28.1
2/06/01 24:00	14.9	7.2	3.1	<2	25.3
2/06/01 24:00	13.9	7.0	3.1	<2	23.9
2/07/01 6:00	17.1	8.3	3.6	<2	28.9
2/07/01 6:00	17.2	7.7	3.6	<2	28.5
2/07/01 12:00	16.6	7.7	4.0	<2	28.3
2/07/01 12:00	16.6	8.3	3.7	<2	28.7
2/07/01 18:00	14.7	7.9	3.7	<2	26.4
2/07/01 18:00	16.2	7.5	3.6	<2	27.3
2/07/01 24:00	17.0	8.5	3.6	<2	29.0
2/07/01 24:00	16.4	7.5	3.5	<2	27.5
2/08/01 6:00	16.7	8.6	3.6	<2	28.8
2/08/01 6:00	15.8	8.1	3.6	<2	27.5
2/08/01 12:00	17.3	8.4	3.8	<2	29.5
2/08/01 12:00	17.9	8.2	3.8	<2	29.9
2/08/01 18:00	18.1	8.2	3.8	<2	30.1
2/08/01 18:00	18.5	8.5	3.8	<2	30.8
2/08/01 24:00	17.3	8.8	3.7	<2	29.8
2/08/01 24:00	16.0	8.5	3.7	<2	28.2
2/09/01 6:00	18.1	8.4	3.8	<2	30.3
2/09/01 6:00	18.3	8.6	3.9	<2	30.8
2/09/01 12:00	19.3	8.2	3.9	<2	31.5
2/09/01 12:00	20.1	8.2	3.9	<2	32.2
2/09/01 18:00	20.6	8.9	4.3	<2	33.7
2/09/01 18:00	21.3	8.9	4.2	<2	34.5
2/09/01 24:00	18.2	8.5	3.8	<2	30.4
2/09/01 24:00	18.2	8.4	3.8	<2	30.5

Table F8: THM samples concentration at the point of entry to the distribution system (collected between Feb 15 and Feb 19) and in DSII (collected between Feb 16 and Feb 20) - temporal and spatial variability study during February 2001

Time of collection	WTP concentrations (µg/L)					DSII concentrations (µg/L)				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
6:00	22.1	11.9	3.5	<2	37.6	14.6	7.9	<2	<2	22.6
6:00	23.1	11.7	3.5	<2	38.3	Nav	Nav	Nav	Nav	Nav
12:00	14.5	7.9	2.6	<2	25.0	13.7	7.4	<2	<2	21.1
12:00	15.1	8.5	3.0	<2	26.7	14.4	8.2	<2	<2	22.5
18:00	16.2	9.0	3.1	<2	28.4	14.8	8.1	<2	<2	22.9
18:00	17.1	9.3	3.1	<2	29.6	14.9	7.6	<2	<2	22.5
0:00	22.0	10.5	3.3	<2	35.8	14.8	7.6	<2	<2	22.4
0:00	24.6	11.8	3.6	<2	40.0	17.1	8.6	<2	<2	25.7
6:00	18.0	9.6	3.4	<2	30.9	17.4	8.4	<2	<2	25.8
12:00	20.8	10.4	3.4	<2	34.6	17.9	9.2	<2	<2	27.1
12:00	18.5	9.8	3.3	<2	31.5	16.9	8.2	<2	<2	25.1
18:00	16.8	9.0	3.1	<2	28.9	12.5	7.8	<2	<2	20.3
18:00	18.3	9.0	3.0	<2	30.3	14.0	7.9	<2	<2	21.9
0:00	17.7	9.5	3.1	<2	30.4	15.1	7.6	<2	<2	22.7
0:00	16.6	9.3	3.2	<2	29.1	Nav	Nav	Nav	Nav	Nav
6:00	17.8	9.2	3.0	<2	30.0	15.5	7.3	<2	<2	22.8
6:00	17.5	9.1	3.0	<2	29.6	14.4	7.5	<2	<2	21.9
12:00	16.7	9.0	3.1	<2	28.8	15.6	8.0	<2	<2	23.6
12:00	17.7	9.2	3.1	<2	30.0	Nav	Nav	Nav	Nav	Nav
18:00	18.2	9.4	3.4	<2	31.0	15.0	8.2	<2	<2	23.2
18:00	17.9	9.0	3.0	<2	29.9	14.7	7.8	<2	<2	22.5
0:00	14.5	7.4	2.5	<2	24.5	13.0	7.2	<2	<2	20.3
0:00	14.3	8.0	2.9	<2	25.2	Nav	Nav	Nav	Nav	Nav
6:00	14.5	8.2	2.8	<2	25.5	12.7	6.9	<2	<2	19.7
6:00	15.8	8.3	2.8	<2	27.0	14.8	7.9	<2	<2	22.7
12:00	16.4	8.7	3.1	<2	28.2	13.9	7.9	<2	<2	21.8
12:00	16.7	8.7	3.0	<2	28.4	Nav	Nav	Nav	Nav	Nav
18:00	16.3	8.3	3.0	<2	27.6	13.4	7.7	<2	<2	21.1
18:00	15.9	8.4	2.9	<2	27.2	Nav	Nav	Nav	Nav	Nav
0:00	13.5	7.9	2.7	<2	24.1	16.3	7.6	<2	<2	23.9
0:00	11.8	7.9	2.9	<2	22.6	13.8	7.5	<2	<2	21.3
6:00	15.4	8.5	3.4	<2	27.3	11.2	6.7	<2	<2	17.9
6:00	15.2	8.6	3.5	<2	27.3	Nav	Nav	Nav	Nav	Nav
12:00	14.0	7.3	2.6	<2	24.0	13.1	7.3	<2	<2	20.4
12:00	13.4	8.0	2.9	<2	24.3	14.3	7.5	<2	<2	21.8

Nav – Not available

Table F9: HAA concentrations in daily composited samples at the point of entry to the distribution system and in the distribution system (DSII)

	Sample	Concentration (µg/L)									
		ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
WTP	15-Feb	<2	<2	9.2	3.8	5.0	2.1	7.0	<2	<2	27.1
	15-Feb	<2	<2	8.4	4.7	6.9	2.1	6.2	<2	<2	28.4
	16-Feb	<2	<2	9.7	5.1	6.6	2.1	6.3	<2	<2	29.8
	16-Feb	<2	<2	9.4	3.8	5.3	2.1	8.2	<2	<2	28.9
	17-Feb	2.4	<2	10.5	5.5	7.3	2.1	7.5	<2	<2	35.2
	17-Feb	<2	<2	9.9	5.1	6.8	2.1	7.5	<2	<2	31.4
	18-Feb	<2	<2	8.2	5.3	7.2	2.0	6.0	<2	<2	28.7
	19-Feb	<2	<2	8.4	3.8	4.6	2.1	6.7	<2	<2	25.6
	19-Feb	<2	<2	8.8	4.0	4.6	2.1	7.3	<2	<2	26.8
	travel blank	<2	<2	<2	<2	<2	<2	<2	<2	<2	NA
DSII	16-Feb	<2	<2	8.6	3.7	4.7	2.1	7.6	<2	<2	26.7
	16-Feb	<2	<2	8.2	4.0	4.5	2.1	7.5	<2	<2	26.3
	17-Feb	<2	<2	8.2	3.7	4.7	2.0	7.7	<2	<2	26.4
	18-Feb	<2	<2	9.5	5.5	7.5	2.1	7.5	<2	<2	32.1
	19-Feb	<2	<2	9.8	3.7	5.2	2.1	9.2	<2	<2	30.1
	19-Feb	<2	<2	9.3	3.8	5.2	2.1	8.2	<2	<2	28.6
	20-Feb	<2	<2	9.1	5.3	6.8	2.1	8.1	<2	<2	31.3
	20-Feb	<2	<2	8.0	3.8	4.5	2.0	7.9	<2	<2	26.1
	21-Feb	2.2	<2	8.9	3.7	4.4	2.1	7.9	<2	<2	29.2
	travel blank	<2	<2	<2	<2	2.3	<2	<2	<2	<2	2.3

Table F10: THM results obtained at the treatment plant (temporal and spatial variability study during August 2001)

Date and time of Sample collection	Concentration (µg/L)				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
8/13/01 18:00	115.0	20.7	3.1	<1	139
8/14/01 0:00	139.0	23.9	4.9	<1	168
8/14/01 6:00	141.0	23.1	4.6	<1	169
8/14/01 12:00	132.0	23.3	4.7	<1	160
8/14/01 18:00	128.0	22.3	4.6	<1	155
8/15/01 0:00	85.1	16.2	4.5	<1	106
8/15/01 12:00	73.9	14.5	4.1	<1	92.5
8/16/01 0:00	89.4	16.0	4.0	<1	109
8/16/01 6:00	140.0	21.2	4.6	<1	166
8/16/01 12:00	65.3	13.9	3.9	<1	83.1
8/16/01 18:00	74.9	15.5	4.1	<1	94.5
8/17/01 0:00	74.7	14.4	3.9	<1	93.0
8/17/01 6:00	78.6	14.3	3.9	<1	96.8
8/17/01 12:00	73.7	14.1	3.8	<1	91.6
8/17/01 18:00	62.8	12.1	3.5	<1	78.4
Average	98.2	17.7	4.1	<1	120
Stdev	30.25	4.16	0.50	Nap	34.6
CV (%)	30.8	23.5	12.0	Nap	28.9
Maximum	141	23.9	4.9	Nap	169
Minimum	62.8	12.1	3.1	Nap	78.4

Nap - Not applicable

Table F11: THM and TOX results at the distribution system (DSIII-A) (temporal and spatial variability study during August 2001)

Date and time of sample collection	Concentration (µg/L)					TOX
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	(µg Cl /L)
8/13/01 7:00	75.6	16.3	2.7	<1	94.6	195
8/13/01 12:00	84.4	17.3	2.6	<1	104	212
8/13/01 18:00	81.5	16.9	2.6	<1	101	201
8/13/01 23:00	Nav	Nav	Nav	Nav	Nav	199
8/14/01 7:00	95.3	16.2	4.0	<1	116	220
8/14/01 12:00	103	17.2	4.2	<1	124	226
8/14/01 18:00	111	18.0	4.3	<1	133	233
8/14/01 23:00	94.9	16.8	4.2	<1	116	218
8/15/01 7:00	Nav	Nav	Nav	Nav	Nav	216
8/15/01 12:00	Nav	Nav	Nav	Nav	Nav	185
8/15/01 18:00	Nav	Nav	Nav	Nav	Nav	204
8/15/01 23:00	92.9	17.7	4.4	<1	115	184
8/16/01 7:00	84.8	16.7	4.2	<1	106	156
8/16/01 12:00	Nav	Nav	Nav	Nav	Nav	215
8/16/01 18:00	91.2	17.6	4.3	<1	113	186
8/16/01 23:00	94.2	17.7	4.3	<1	116	196
8/17/01 7:00	91.3	16.0	4.1	<1	111	216
8/17/01 12:00	93.7	16.3	4.1	<1	114	230
8/17/01 18:00	Nav	Nav	Nav	Nav	Nav	241
8/17/01 23:00	Nav	Nav	Nav	Nav	Nav	208
Average	84.0	16.0	3.8	<1	113	207
Stdev	16.8	2.2	0.7	Nap	9.9	20.1
CV (%)	20	14	18	Nap	9	10
Maximum	111	18.0	4.4	Nap	133	241
Minimum	49.8	9.7	2.5	Nap	94.6	156

Nap - Not applicable; Nav - Not available

Table F12: THM results at the distribution system (DSIII-B)

	Concentration (µg/L)				
Date and Time of sample collection	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
8/13/01 9:20	62.0	14.5	2.5	<1	79.0
8/13/01 17:10	69.5	15.4	2.1	<1	87.0
8/13/01 23:10	76.0	15.7	2.5	<1	94.2
8/14/01 9:10	101	18.2	4.4	<1	124
8/14/01 17:10	81.0	15.7	4.0	<1	101
8/15/01 9:15	70.6	14.0	4.2	<1	88.8
8/15/01 17:10	77.6	15.9	4.2	<1	97.7
8/16/01 9:10	77.9	14.2	3.8	<1	95.9
8/16/01 17:10	58.5	11.3	3.3	<1	73.1
8/17/01 1:00	81.4	14.5	4.0	<1	99.9
8/17/01 9:15	74.9	13.4	3.7	<1	92.0
8/17/01 17:15	79.4	13.9	3.8	<1	97.1
Average (µg/L)	75.8	14.7	3.5	<1	94.1
Stdev (µg/L)	10.7	1.68	0.77	Nap	12.5
CV(%)	14.2	11.4	21.7	Nap	13.3
Max (µg/L)	101	18.2	4.4	Nap	123
Min (µg/L)	58.5	11.3	2.1	Nap	73.1

Nap - Not applicable

Table F13: Sample collection information during period of chlorination

Mar 6,01			Mar 14,01			Mar 22,01			Mar 30,01		
Time	Location	Free chlorine (mg/L)	Time	Location	Free chlorine (mg/L)	Time	Location	Free chlorine (mg/L)	Time	Location	Free chlorine (mg/L)
10:30	WTP	2.2	10:30	WTP	0.32	10:07	WTP	2.2	10:40	WTP	0.14
11:00	FS15	2.2	11:45	FS15	1.54	10:35	FS15	0.74	11:15	FS15	0.1
11:30	FS6	1.64	12:05	FS9	1.33	11:00	FS6	0.9	11:50	FS5	0.11
11:45	FS5	2.19	12:30	FS6	1.15	11:30	FS12	0.79	12:10	FS6	0.05
12:15	FS12	2.02	12:50	FS5	1.74	12:00	CC2	0.03	12:40	FS12	0.06
12:45	CC2	0.06	14:00	FS12	1.29	12:45	FS8	0.93	13:00	CC2	0.00
13:20	FS8	1.89	14:35	CC2	0.00	13:26	FS17	1.16	13:30	FS8	0.07
13:45	FS17	1.3	15:35	FS8	1.63	14:02	FS5	1.91	14:00	FS17	1.42
14:10	FS16	2.15	16:00	FS17	1.29	14:26	FS16	1.41	14:20	FS16	0.06
14:30	FS18	1.25	16:15	FS16	1.15	14:46	FS18	1.28	14:40	FS18	0.78

Table F14: Levels of THMs at various points in the distribution system during the period of chlorination

	Mar6,01					Mar14,01					Mar22,01					Mar30,01				
	Concentration (µg/L)																			
Location	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
WTP	44.2	15.1	3.2	<2	62.4	74.5	18.0	5.1	<2	97.6	58.0	20.5	2.5	<2	81.0	26.9	15.5	2.2	<2	44.5
WTP	45.3	15.9	3.3	<2	64.6	75.8	18.9	3.5	<2	98.2	54.9	19.7	2.3	<2	76.9	27.1	15.6	2.2	<2	44.9
FS # 17	63.6	19.4	3.2	<2	86.1	80.7	19.3	5.7	<2	106	92.5	24.1	4.1	<2	121	63.6	22.8	3.4	<2	89.8
FS # 17	63.2	18.9	3.2	<2	85.3	79.4	18.5	5.5	<2	103	85.9	22.3	3.8	<2	112	61.0	22.6	3.4	<2	87.0
FS # 16	68.2	17.6	2.9	<2	88.6	81.3	20.7	6.1	<2	108	67.8	23.5	2.4	<2	93.7	33.2	17.0	2.6	<2	52.8
FS # 16	62.0	17.2	3.0	<2	82.2	86.1	22.2	6.6	<2	115	70.0	23.3	2.4	<2	95.7	32.3	17.0	2.6	<2	51.9
FS # 15	58.7	16.3	3.3	<2	78.3	71.2	19.1	3.3	<2	93.6	52.4	22.4	2.7	<2	77.5	37.3	17.8	2.9	<2	58.0
FS # 15	59.8	16.5	3.3	<2	79.5	72.4	18.5	3.1	<2	94.0	54.2	23.4	2.9	<2	80.5	35.3	17.3	2.7	<2	55.3
FS # 12	62.1	18.7	3.0	<2	83.8	85.7	20.8	6.8	<2	113	67.9	23.4	2.8	<2	94.1	34.2	17.5	2.5	<2	54.2
FS # 12	62.8	18.6	3.1	<2	84.5	82.3	20.6	6.3	<2	109	67.8	23.6	2.8	<2	94.2	34.9	17.5	2.6	<2	54.9
FS # 5	57.6	15.5	3.0	<2	76.2	79.3	19.4	3.5	<2	102	77.5	22.9	2.6	<2	103	35.4	18.2	2.6	<2	56.3
FS # 5	49.1	14.9	3.0	<2	67.1	81.3	19.4	3.4	<2	104	66.7	22.2	2.7	<2	91.5	36.1	17.9	2.7	<2	56.7
FS # 8	63.6	18.0	3.3	<2	84.9	64.7	17.3	2.9	<2	84.9	56.6	22.9	2.8	<2	82.3	42.2	20.1	2.9	<2	65.2
FS # 8	59.6	17.3	3.2	<2	80.2	68.7	17.7	3.0	<2	89.4	59.0	22.2	2.8	<2	84.1	43.0	20.3	3.0	<2	66.3
FS # 18	55.4	17.8	3.2	<2	76.5	75.2	18.5	4.9	<2	98.6	81.1	20.4	5.3	<2	107	58.8	23.9	3.4	<2	86.1
FS # 18	58.6	17.2	3.5	<2	79.3	70.5	18.4	3.2	<2	92.2	79.2	21.2	5.3	<2	106	59.8	24.4	3.5	<2	87.6
FS # 6	58.2	18.6	3.0	<2	79.9	73.7	20.1	4.0	<2	97.7	67.1	23.3	3.0	<2	93.4	41.6	18.9	2.7	<2	63.2
FS # 6	58.3	18.5	3.2	<2	80.0	70.3	19.6	3.9	<2	93.8	63.6	23.9	3.2	<2	90.7	43.3	20.0	2.9	<2	66.2
CC # 2	27.1	10.8	4.8	<2	42.7	68.1	16.6	5.8	<2	90.5	90.1	19.4	5.8	<2	115	90.7	21.2	5.5	<2	117
CC # 2	28.7	11.4	4.8	<2	44.9	64.6	15.8	5.5	<2	85.8	91.7	19.9	6.0	<2	118	89.7	21.1	5.5	<2	116

Table F15: Levels of HAAs at various points in the distribution system during the period of chlorination

Date	Location	Average Concentration (μg/L)									
		ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
Mar6,01	WTP	2.8	<2	7.4	3.5	3.9	<2	9.6	<2	4.3	30.0
	FS#17	3.3	<2	21.3	3.5	10.6	<2	11.3	<2	3.1	53.1
	FS#16	2.0	<2	16.9	3.2	7.0	<2	8.9	<2	<2	38.0
	FS#15	<2	<2	15.1	3.8	7.5	<2	8.1	<2	2.8	35.8
	FS#12	2.3	<2	18.9	3.4	8.9	<2	9.3	<2	<2	41.7
	FS#5	<2	<2	11.8	3.7	6.3	<2	9.5	<2	<2	31.3
	FS#8	<2	<2	16.7	3.7	9.6	<2	10.7	<2	3.5	42.5
	FS#18	3.7	<2	17.0	3.9	10.4	<2	8.3	<2	<2	43.3
	FS#6	1.7	<2	18.1	4.5	10.3	2.4	11.5	2.0	4.8	52.3
	CC#2	5.4	<2	11.5	3.7	5.5	<2	11.7	<2	<2	37.7
Mar14,01	WTP	<2	<2	10.7	3.1	4.3	<2	8.4	<2	2.1	27.6
	FS#17	<2	<2	16.2	4.0	9.6	<2	10.3	<2	<2	40.2
	FS#16	3.4	<2	21.7	3.8	8.7	2.0	11.3	<2	<2	48.1
	FS#15	2.2	<2	15.8	3.8	6.9	<2	9.0	<2	3.8	40.4
	FS#12	<2	<2	18.1	4.0	8.6	<2	10.4	<2	2.6	43.7
	FS#9	<2	<2	19.9	4.4	9.3	<2	9.2	<2	3.4	44.5
	FS#5	2.0	<2	10.7	3.5	5.8	<2	8.6	<2	3.6	33.3
	FS#8	3.2	<2	12.6	5.3	8.2	3.0	11.3	2.0	<2	41.4
	FS#6	2.3	<2	18.1	3.6	8.5	<2	9.5	<2	2.5	44.5
	CC#2	2.1	<2	19.2	3.7	11.5	<2	7.6	<2	2.8	45.8
Mar22,01	WTP	2.0	<2	17.0	4.2	8.1	2.4	8.3	3.9	5.3	37.2
	FS#17	6.6	<2	22.0	4.9	14.7	2.2	11.3	8.5	2.2	72.3
	FS#16	2.3	<2	19.1	4.8	14.0	2.2	10.1	3.2	4.0	59.7
	FS#15	2.0	<2	10.7	4.3	9.8	2.2	8.4	2.9	6.4	45.8
	FS#12	2.7	<2	17.8	4.7	13.7	2.2	10.5	3.6	3.9	56.2
	FS#5	3.4	<2	13.2	4.1	11.0	2.1	8.5	2.5	<2	43.5
	FS#8	2.1	<2	14.3	4.6	12.2	2.1	9.4	2.4	<2	45.0
	FS#18	3.5	<2	21.6	4.9	15.8	2.0	11.6	2.6	<2	59.2
	FS#6	3.1	<2	15.9	4.8	13.5	2.3	10.5	2.9	<2	52.9
	CC#2	2.9	<2	23.7	4.4	17.1	2.0	7.5	6.7	8.7	70.4
Mar30,01	WTP	<2	<2	10.7	4.4	10.7	2.3	8.9	2.4	3.3	38.8
	FS#17	5.3	<2	17.8	5.6	21.4	2.3	10.6	2.4	<2	64.2
	FS#16	3.2	<2	12.3	4.9	11.8	2.3	9.8	2.6	3.1	50.0
	FS#15	<2	<2	12.6	5.0	11.6	2.5	8.7	2.4	4.7	40.4
	FS#12	3.5	<2	11.9	4.6	11.2	2.1	8.5	2.5	3.3	44.8
	FS#5	4.0	<2	13.6	4.9	13.3	2.1	7.3	2.7	<2	45.4
	FS#8	2.3	<2	15.8	5.3	15.9	<2	10.2	2.0	<2	50.4
	FS#18	2.6	<2	19.4	5.7	21.1	<2	11.4	2.3	<2	62.5
	FS#6	2.1	<2	16.1	5.3	15.4	2.2	10.1	2.2	3.0	51.7
	CC#2	<2	<2	12.8	3.1	27.2	<2	10.9	2.5	3.5	60.0

Table F16: Calculation of the unknown halide from the THM, HAA and TOX results

		Concentration (µg Cl/L)				
Date	Location	TTHM	THAA	TOX	Unknown OX	Unknown OX/TOX (%)
Mar6,01	WTP	51.6	15.0	215	148	69.0
	FS # 17	70.5	28.2	247	149	60.1
	FS # 16	70.8	20.5	253	161	63.9
	FS # 15	65.1	19.3	250	166	66.3
	FS # 12	69.3	22.8	276	184	66.7
	FS # 5	63.0	17.0	214	134	62.6
	FS # 8	68.0	23.1	229	138	60.2
	FS # 18	63.9	11.7	231	155	67.2
	FS # 6	65.6	27.3	211	118	56.0
	CC # 2	34.5	9.7	75.8	31.6	41.7
Mar14,01	WTP	81.1	14.7	Nav	Nav	Nav
	FS # 17	86.4	22.1	Nav	Nav	Nav
	FS # 16	91.7	25.9	Nav	Nav	Nav
	FS # 15	77.8	21.1	Nav	Nav	Nav
	FS # 12	91.6	23.5	202	87.2	43.1
	FS#9	85.9	24.1	191	80.8	42.4
	FS # 5	70.4	17.2	Nav	Nav	Nav
	FS # 8	79.0	21.7	Nav	Nav	Nav
	FS # 6	79.0	23.6	Nav	Nav	Nav
	CC # 2	72.5	24.8	Nav	Nav	Nav
Mar22,01	WTP	64.6	18.9	Nav	Nav	Nav
	FS # 17	96.6	37.0	245	112	45.5
	FS # 16	77.8	31.1	Nav	Nav	Nav
	FS # 15	63.8	23.0	207	120	58.1
	FS # 12	77.1	29.5	231	125	53.9
	FS # 5	85.3	22.9	201	92.7	46.1
	FS # 8	67.6	24.3	206	115	55.5
	FS # 18	87.6	32.1	Nav	Nav	Nav
	FS # 6	75.1	27.9	204	101	49.5
	CC # 2	96.7	36.5	228	94.4	41.5
Mar30,01	WTP	35.2	20.7	136	79.6	58.7
	FS # 17	72.0	34.8	240	133	55.4
	FS # 16	41.6	25.6	141	73.7	52.3
	FS # 15	45.2	20.2	143	77.6	54.3
	FS # 12	43.4	23.2	135	68.6	50.7
	FS # 5	44.7	24.2	207	138	66.7
	FS # 8	52.6	27.7	134	53.4	39.9
	FS # 18	70.3	33.8	247	143	57.9
	FS # 6	51.9	28.0	171	91.4	53.3
	CC # 2	96.9	33.9	184	53.2	28.9

Nav – Not available

Table F17: Comparison between the TTHM, THAA and unknown OX levels in chlorinated (March 22) and chloraminated waters (March 30)

		Concentration (µg Cl/L)				
Date	Location	TTHM	THAA	TOX	Unknown OX	Unknown OX/TOX (%)
Mar22,01	WTP	64.6	18.9	NA	NA	NA
	FS # 17	96.6	37.0	245	112	45.5
	FS # 16	77.8	31.1	NA	NA	NA
	FS # 15	63.8	23.0	207	120	58.1
	FS # 12	77.1	29.5	231	125	53.9
	FS # 5	85.3	22.9	201	92.7	46.1
average		77.5	27.1	221	112	50.9
stdev		12.5	6.7	20.7	14.1	6.1
CV(%)		16.1	24.6	9.4	12.6	12.0
Mar30,01	WTP	35.2	20.7	136	79.6	58.7
	FS # 17	72.0	34.8	240	133	55.4
	FS # 16	41.6	25.6	141	73.7	52.3
	FS # 15	45.2	20.2	143	77.6	54.3
	FS # 12	43.4	23.2	135	68.6	50.7
	FS # 5	44.7	24.2	207	138	66.7
average		47.0	24.8	144	83.3	50.0
stdev		12.8	4.9	72.4	42.5	17.6
CV(%)		27.1	19.6	50.1	51.0	35.1

Table F18: Effect of time of collection, boiling and refrigerating water on THM levels in tap water

Sample ID	Average Concentration (µg/L)			
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	TTHM
WTP	25.0	9.0	1.6	35.6
D	53.1	16.2	3.0	72.4
D	54.9	16.9	3.1	75.0
C	41.2	12.6	2.3	56.2
C	40.6	12.6	2.2	55.4
B	1.8	Nav	Nav	1.8
B	1.8	Nav	Nav	1.8
A	47.1	15.1	2.8	65.0
A	40.3	13.3	2.5	56.1

Nav – Not available; A – sample collected in the evening; B – sample boiled; C – sample refrigerated; D – sample collected in the morning

Table F19: Effect of point of use filters in THM levels

		Concentration (µg/L)				
	Sample identification	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
Location 1	T1 Unfiltered	137	14.5	1.5	<1	153
	T1 Unfiltered	137	15.5	1.6	<1	155
	T1 Brita Ultra	<1	<1	<1	<1	Nap
	T1 Brita Ultra	<1	<1	<1	<1	Nap
	T1 Brita Pitcher	10.1	1.1	<1	<1	11.2
	T1 Brita Pitcher	10.3	1.1	<1	<1	11.4
	T2 Unfiltered	135	18.0	2.1	<1	155
	T2 Unfiltered	120	15.2	1.2	<1	136
	T2 Brita Ultra	34.2	1.3	<1	<1	35.4
	T2 Brita Ultra	34.9	1.3	<1	<1	36.2
Location 2	T1 Unfiltered	155	16.0	1.6	<1	172
	T1 Unfiltered	148	15.9	1.7	<1	166
	T1 PUR Ultimate	<1	<1	<1	<1	Nap
	T1 PUR Ultimate	<1	<1	<1	<1	Nap
	T1 Teledyne Water Pik	<1	<1	<1	<1	Nap
	T1 Teledyne Water Pik	1.2	<1	<1	<1	1.2
	T2 Unfiltered	176	17.3	1.7	<1	195
	T2 Unfiltered	171	17.5	1.8	<1	190
	T2 PUR Ultimate	<1	<1	<1	<1	Nap
	T2 PUR Ultimate	<1	<1	<1	<1	Nap
	T2 Teledyne Water Pik	<1	<1	<1	<1	Nap
	T2 Teledyne Water Pik	<1	<1	<1	<1	Nap
Location 3	T2 Unfiltered	99.0	14.4	1.3	<1	115
	T2 Unfiltered	101	14.4	1.3	<1	116
	T2 Reverse Osmosis	60.8	<1	<1	<1	60.8
	T2 Reverse Osmosis	59.7	<1	<1	<1	59.7

Nap – Not applicable; T1 – sample collection when filter was installed; T2 – sample collection after more than half of the filter capacity was used

Table F20: Effect of point of use filters in HAA levels

		Concentration (µg/L)									
	Sample identification	ClAA	BrAA	Cl_2AA	BrClAA	Cl_3AA	Br_2AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	THAA
Location 2	T1 Unfiltered	4.0	<2	17.9	<2	20.4	<2	2.2	<2	<2	44.4
	T1 Unfiltered	<2	<2	17.6	<2	20.0	<2	6.2	<2	<2	43.9
	T1 PUR Ultimate	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	T1 PUR Ultimate	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	T1 Teledyne Water Pik	<2	<2	9.5	<2	<2	<2	<2	<2	<2	9.5
	T1 Teledyne Water Pik	<2	<2	9.8	<2	<2	<2	<2	<2	<2	9.8
	T2 Unfiltered	<2	<2	16.9	<2	17.3	<2	4.5	<2	<2	38.7
	T2 Unfiltered	<2	<2	17.0	<2	17.5	<2	4.5	<2	<2	39.0
	T2 PUR Ultimate	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	T2 PUR Ultimate	2.2	<2	2.2	<2	<2	<2	<2	<2	<2	4.4
	T2 Teledyne Water Pik	<2	<2	8.7	<2	<2	<2	<2	<2	<2	8.7
	T2 Teledyne Water Pik	<2	<2	8.4	<2	<2	<2	<2	<2	<2	8.4
Location 1	T1 Unfiltered	2.4	<2	18.6	<2	22.0	<2	5.4	<2	<2	48.3
	T1 Unfiltered	<2	<2	17.3	<2	20.1	<2	5.7	<2	<2	43.2
	T1 Brita Ultra	2.7	<2	<2	<2	<2	<2	<2	<2	<2	2.7
	T1 Brita Ultra	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	T1 Brita Pitcher	<2	<2	4.4	<2	4.5	<2	<2	<2	<2	8.9
	T1 Brita Pitcher	<2	<2	10.0	<2	10.4	<2	<2	<2	<2	20.4
	T2 Unfiltered	2.3	<2	17.6	<2	20.7	<2	<2	<2	<2	40.6
	T2 Unfiltered	2.2	<2	18.0	<2	21.0	<2	4.2	<2	<2	45.3
	T2 Brita Ultra	3.7	<2	10.4	<2	8.0	<2	<2	<2	<2	22.2
	T2 Brita Ultra	<2	<2	11.4	<2	8.3	<2	<2	<2	<2	19.7
Location 3	T2 Unfiltered	2.0	<2	14.1	<2	15.4	<2	3.6	<2	<2	35.2
	T2 Unfiltered	2.4	<2	15.4	<2	16.9	<2	5.0	<2	<2	39.7
	T2 Reverse Osmosis	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	T2 Reverse Osmosis	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2

T1 – sample collection when filter was installed; T2 – sample collection after more than half of the filter capacity was used